

Decision Support Tools for Environmentally Conscious Chemical Process Design

by

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Abstract

The environment has emerged as an important determinant of the performance of the modern chemical industry. Process engineering in the 21st century needs to evolve to include environmental issues as part of the design objectives, rather than as constraints on operations.

A frequently cited objection to the use of quantitative indicators of environmental performance in product and process design is that the underlying data are too uncertain for the numbers to have any real meaning. This thesis demonstrates that explicit incorporation of uncertainties allows bounds to be established on the confidence of decisions made on the basis of uncertain indicators. The examples provided show that large uncertainties in indicators used to assess environmental performance do not necessarily imply uncertainty in decision-making.

A series of computer-aided decision making tools have been developed to decrease the barriers to the use of environmental valuation functions in routine design activities. These tools include: uncertainty propagation of relative performance measures, a spreadsheet-based fate, transport and exposure model for chemicals, an information content chart for assessing the quality of uncertain indicators, a screening procedure to identify the most important structural and parametric uncertainties in multimedia exposure models, a process by product input-output life cycle assessment method to generate correlated distributions of unit environmental indicators, an extension of the deterministic equivalent modeling method for the generation of spreadsheet based polynomial chaos expansion metamodels of process flowsheet models, and a database for managing uncertain parameters used in environmental valuation models.

Case studies are presented to help the reader in learning the use of the tools. The tools are also applied to an analysis of the U.S. toxics release inventory, in which confidence bounds are developed for the trends in impacts and the contributions of industrial sectors and specific chemical compounds to overall potential impact.

Although the tools were developed bearing in mind the need for methods to evaluate the environmental performance of chemical process design alternatives, the ideas can be applied to any decision context in which there are significant uncertainties in the parameters of the objective function.

Thesis Supervisor: Gregory J. McRae
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I was fortunate to graduate from high school at the same time that Mr. Eduardo Grado was assistant director of admissions at MIT. Eddie was instrumental in opening the doors of MIT to qualified students from south of the border. Had it not been for Eddie's recruitment trip to Mexico in the fall of 1986, I would have never entertained the idea of travelling abroad for my college education.

I first heard about MIT from Dr. José Miguel Gonzalez Santaló for whom I worked in the afternoons during my junior year in High School. Pepe also helped me to discover my interest in environmental studies. I remember a conversation we had in which I told him I wanted to study engineering but were not sure about which branch to pursue. Pepe told me that engineers solve problems, so I should think about which problems I would be most interested in solving. The choice of environmental engineering became evident after that conversation.

Prof. Dave Marks and Prof. Greg McRae gave me vast freedom and their full support to define and pursue my own thesis project as a graduate student at MIT. I recall talking with Dave two years after my graduation from the Environmental Engineering Science undergraduate program at MIT. I told him I wanted to pursue a Ph.D. in pollution prevention and asked him whether there were any faculty members at MIT with whom I could work towards that goal. I wanted to learn how to design cleaner processes from the start, instead of adding pollution control technology to processes after they were built. His response was something along the lines of "Come over and we'll figure it out once you are here". I followed his advice, came back to MIT in the fall of 1994, and Dave provided me with a home at the Parsons lab and financial support for two years while I learned enough process engineering to be able to talk intelligently with chemical engineers. When I met Greg and told him about my research interest he gave a warm and enthusiastic welcome to his research group. Ever since, whenever I had doubts about the relevance of my research Greg would give me a big confidence boost with his interest and enthusiasm for my work.

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Table of Contents

CHAPTER 1 INTRODUCTION.....	29
1.1 THESIS STATEMENT.....	29
1.2 STRUCTURE OF THESIS	30
1.3 SUMMARY OF CONTRIBUTIONS	35
1.4 READING GUIDE.....	36
CHAPTER 2 ENVIRONMENTALLY CONSCIOUS CHEMICAL PROCESS DESIGN.....	39
2.1 CHALLENGES FOR CHEMICAL PROCESS DESIGN IN THE 21 ST CENTURY	39
2.2 THE DESIGN PROCESS	42
2.3 FRAMING OF THE DESIGN PROBLEM WITH THE ENVIRONMENT AS AN OBJECTIVE	45
2.4 APPROACHES TO THE GENERATION OF ENVIRONMENTALLY SUPERIOR DESIGN ALTERNATIVES	49
2.4.1 <i>Use of documented pollution prevention solutions as a source of design alternatives</i>	51
2.4.2 <i>Design by case study</i>	51
2.4.3 <i>Hierarchical design approaches and other methods of structured thinking</i>	51
2.4.4 <i>Pinch analysis and other targeting techniques</i>	52
2.4.5 <i>Mathematical programming</i>	55
2.4.6 <i>Expert systems and other Artificial Intelligence approaches</i>	56
2.5 ANALYSIS OF DESIGN ALTERNATIVES	57
2.6 APPROACHES TO THE EVALUATION OF DESIGN ALTERNATIVES.....	59
2.6.1 <i>Environmental concerns as constraints on economic optimization</i>	60
2.6.2 <i>Environmental concerns as objectives</i>	61
Minimization of emissions of pollutants of concern.....	62
Minimization of mass of waste generated	62
Minimization of contributions to specific environmental problems	63
Minimization of overall indicators of environmental impact.....	65
Industrial perspective	66
2.6.3 <i>Trading off environmental objectives against other design objectives</i>	66
2.7 THE ROLE OF SENSITIVITY ANALYSIS	69
2.8 RESEARCH NEEDS	70
Generation of alternatives.....	71
Analysis of alternatives	71
Evaluation of alternatives	72
Sensitivity analysis	72
2.9 CONCLUSIONS	72
2.10 LITERATURE CITED	73
CHAPTER 3 VALUATION MODELS.....	85

3.1	INTRODUCTION	85
3.2	ECONOMIC VALUATION MODELS	88
3.2.1	<i>The total annualized profit economic valuation model</i>	89
3.2.2	<i>Capital charge factor models</i>	92
Annuity formula	93	
Douglas Model	93	
3.2.3	<i>Installed equipment cost annualization factor model</i>	95
3.2.4	<i>Uncertainties in economic valuation models</i>	98
Uncertainties in prices	99	
Uncertainties in equipment cost	101	
Uncertainties in installation cost factors	103	
Uncertainties in annualization factors	106	
Summary	116	
3.2.5	<i>The impact of widely used heuristics on the resolution of the operating vs. capital cost tradeoff</i> ...	116
Example: Sizing a heat exchanger	120	
3.3	ENVIRONMENTAL VALUATION MODELS	125
3.3.1	<i>Introduction</i>	125
3.3.2	<i>Uncertainties in environmental valuation models</i>	127
Uncertainties in the estimation of environmental exchanges	129	
Uncertainties in characterization factors	130	
Uncertainties in weighting factors	131	
Default environmental valuation factors used in this work	137	
Summary	139	
3.4	CONCLUSIONS	139
3.5	NOMENCLATURE	140
3.6	LITERATURE CITED	141
CHAPTER 4 DECISION MAKING UNDER UNCERTAINTY		145
4.1	INTRODUCTION	145
4.2	UNCERTAINTIES IN PROCESS DESIGN	145
4.3	APPROACHES TO DECISION MAKING UNDER UNCERTAINTY	148
4.4	DECREASING DECISION UNCERTAINTY BY PRESERVING CORRELATION STRUCTURE	150
4.5	CONFIDENCE LIMITS ON THE OPTIMUM VALUES OF DECISION VARIABLES	156
4.6	UTILITY FUNCTIONS	157
4.6.1	<i>Introduction</i>	157
4.6.2	<i>Single-attribute utility functions</i>	158
4.6.3	<i>Multiple-attribute utility functions</i>	163
4.7	EXAMPLES	166
4.7.1	<i>Choosing the operating set point for a solvent recovery system</i>	166

Introduction	166
Analysis	167
Results	170
4.7.2 <i>Sizing a heat exchanger</i>	176
Introduction	176
Analysis	177
Results	185
4.8 CONCLUSION	191
4.9 LITERATURE CITED	191
CHAPTER 5 SENSITIVITY ANALYSIS	193
5.1 INTRODUCTION	193
5.2 IDENTIFICATION OF IMPROVEMENT OPPORTUNITIES	193
5.3 UNCERTAINTY ANALYSIS	195
5.3.1 <i>Introduction</i>	195
5.3.2 <i>Variance contribution methods</i>	196
5.3.3 <i>Correlation methods</i>	197
5.4 EXAMPLE: RETROFIT OF A SOLVENT RECOVERY SYSTEM	201
5.4.1 <i>Original process</i>	201
5.4.2 <i>Process with heat exchanger</i>	203
Sensitivity analysis results	204
Uncertainty analysis results	205
5.4.3 <i>Process with steam stripping column</i>	209
Introduction	209
Analysis	210
Results	219
5.5 LITERATURE CITED	222
CHAPTER 6 EVALUATION OF THE ENVIRONMENTAL IMPACT OF TOXIC RELEASES	223
6.1 INTRODUCTION	223
6.2 TOXICITY INDICATORS	224
6.2.1 <i>Introduction</i>	224
6.2.2 <i>Uncertainties in toxicity indicators</i>	226
6.3 SPREADSHEET-BASED MODEL FOR THE GENERATION OF TOXICITY INDICATORS UNDER UNCERTAINTY	232
6.3.1 <i>Multi-media fate and transport model</i>	233
Model structure	234
Compartment properties	237
Intermedia transport equations	240
Solution method	247
Parametric uncertainties	249

6.3.2	<i>Human exposure model</i>	255
	Exposure pathways and exposure media contact rates	255
	Environmental media concentrations	258
	Concentrations of chemicals in irrigated soil	259
	Concentration of chemicals in aboveground crops.....	260
	Concentration in root crops	273
	Farm animal intake doses	276
	Fish bioconcentration models.....	276
	Milk biotransfer models	278
	Beef biotransfer models.....	281
	Egg biotransfer model	283
	Concentration of chemicals in tap water.....	286
	Concentration of chemicals in bathroom air.....	286
6.3.3	<i>Toxicity endpoints</i>	287
	Cancer effects.....	287
	Chronic non-cancer effects.....	288
	Aggregation of cancer and non-cancer impacts.....	290
6.3.4	<i>Chemical-specific input data requirements</i>	291
6.3.5	<i>Modeling results</i>	295
	Human exposure potentials	295
	Human toxicity potentials.....	297
6.4	MANAGEMENT OF UNCERTAINTY IN TOXICITY IMPACT INDICATORS	301
6.4.1	<i>Ranking of model uncertainties through the analysis of relative indicator distributions</i>	301
	Method	301
	Results.....	303
	Discussion	305
6.4.2	<i>Assessment of the information content of indicators</i>	305
	Illustrative examples.....	307
	Comparison to other indicators of information content.....	309
	Applications	311
6.5	CASE STUDY: APPLICATION OF THE HUMAN TOXICITY POTENTIAL INDICATOR TO THE TOXIC RELEASE INVENTORY	317
6.5.1	<i>Introduction</i>	317
6.5.2	<i>Analysis</i>	319
	Environmental releases.....	319
	Fate, transport, and exposure modeling.....	320
	Sources of Information.....	320
	Uncertainty propagation.....	320
	Choice of uncertain outputs.....	320
6.5.3	<i>Results</i>	321

Year-to-year comparisons	321
Chemical comparisons.....	324
A risk-based assessment of the 33/50 Program	327
Industrial sector comparisons	330
6.5.4 Discussion	333
Comparison with other results based on chronic toxicity indicators.....	334
Case study conclusions.....	348
6.6 LITERATURE CITED	349
CHAPTER 7 PROCESS BY PRODUCT INPUT-OUTPUT LIFE CYCLE ASSESSMENT.....	355
7.1 INTRODUCTION	355
7.1.1 Life cycle assessment.....	356
7.1.2 Input-output analysis.....	357
7.2 ILLUSTRATIVE EXAMPLE	359
7.3 THE PIO-LCA METHOD	360
7.3.1 Input data	360
7.3.2 The inventory analysis stage of PIO-LCA.....	369
7.3.3 The impact analysis stage of PIO-LCA.....	377
7.3.4 The improvement analysis stage of PIO-LCA.....	381
7.4 ILLUSTRATIVE APPLICATIONS	383
7.4.1 Obtaining a life-cycle inventory and life-cycle environmental indicators for chlorine production. .	383
7.4.2 Identifying the main drivers for environmental impact in chlorine production.	383
7.4.3 Obtaining unit indicators for process design evaluation.	384
7.4.4 Comparing three processes for manufacturing chlorine.....	386
7.4.5 Impact of changing input suppliers.	389
7.4.6 Comparison between chlorine production in the United States and Western Europe	391
7.5 UNCERTAINTY PROPAGATION.....	393
7.5.1 Introduction.....	393
7.5.2 Sensitivity analysis	397
Analysis of contributions to the environmental impact indicator	397
Analysis of contributions to uncertainty.....	401
7.5.3 Implementation in practice: Generation of correlated unit impact distributions.....	407
7.6 DISCUSSION.....	408
7.6.1 Computational cost of refining the analysis.....	408
7.6.2 Relationship to linear programming formulations.....	409
Derivation of LP formulation from PIO-LCA matrices and vectors.....	409
Comparison with other LP formulations	411
7.6.3 Specifying appropriate market shares.....	412
7.7 CONCLUSIONS	413

7.8	APPENDIX: VECTOR AND MATRIX GLOSSARY	415
7.9	LITERATURE CITED	383
CHAPTER 8 UNCERTAINTY PROPAGATION STRATEGIES.....		419
8.1	INTRODUCTION.....	419
8.2	DEVELOPMENT OF SPREADSHEET METAMODELS FOR STOCHASTIC OPTIMIZATION OF FLOWSHEET MODELS	420
8.2.1	<i>Introduction to the deterministic equivalent modeling method.....</i>	<i>420</i>
8.2.2	<i>Extension to generate models that respond to decision variables as well as to uncertain inputs</i>	<i>424</i>
8.2.3	<i>Example: generating DEMM metamodels for the solvent recovery case study</i>	<i>426</i>
8.3	GENERATION OF MULTIVARIATE DISTRIBUTIONS TO INTERFACE PROCESS MODELS WITH VALUE MODELS ..	431
8.3.1	<i>Introduction.....</i>	<i>431</i>
8.3.2	<i>Preserving correlation structure through direct use of Monte Carlo results.....</i>	<i>432</i>
8.3.3	<i>Preserving correlation structure through the use of copula multivariate distributions.....</i>	<i>433</i>
	Example.....	435
8.4	CONCLUSION	440
8.5	LITERATURE CITED	441
CHAPTER 9 KNOWLEDGE REPRESENTATION AND DATA MANAGEMENT STRATEGIES.....		443
9.1	INTRODUCTION.....	443
9.2	DATA CHARACTERISTICS	443
9.3	SYSTEM REQUIREMENTS.....	446
9.4	ENVEvalTool: A TOOL FOR MANAGING ENVIRONMENTAL EVALUATION INFORMATION	447
9.4.1	<i>Data model.....</i>	<i>447</i>
9.4.2	<i>Sources of data.....</i>	<i>452</i>
9.4.3	<i>System functions.....</i>	<i>457</i>
	Generation of toxicity indicator distributions.....	457
	Generation of input data for the PIO-LCA method	457
	Other functions.....	458
9.5	SUGGESTED IMPLEMENTATION WITHIN ORGANIZATIONS.....	458
9.6	SOURCES OF INFORMATION CITED	461
CHAPTER 10 RECOMMENDATIONS FOR FUTURE WORK.....		465
10.1	ENVIRONMENTALLY CONSCIOUS GENERATION OF DESIGN ALTERNATIVES	465
10.2	ENVIRONMENTALLY CONSCIOUS PROCESS SIMULATION	465
10.3	INTEGRATION OF PROCESS SIMULATION WITH ENVIRONMENTAL VALUATION MODELS.....	466
10.4	ENVIRONMENTAL VALUATION METHODS	466
10.5	ECONOMIC VALUATION METHODS	466
10.6	UNCERTAINTY PROPAGATION AND UNCERTAINTY ANALYSIS	467
10.7	KNOWLEDGE MANAGEMENT STRATEGIES.....	467

10.8 CASE STUDIES.....	468
CHAPTER 11 CONCLUSIONS.....	469
APPENDIX A SOLVENT RECOVERY SYSTEM DESIGN CASE STUDY.....	471
A.1 PROBLEM STATEMENT.....	471
A.2 PROCESS MODELS.....	474
A.3 VALUATION MODELS.....	475
A.4 ASSESSMENT OF UNCERTAINTIES.....	477
<i>A.4.1 Uncertainty in process model parameters.....</i>	<i>477</i>
NTRL parameters.....	477
Heat transfer coefficient.....	479
Overall tray efficiency.....	480
<i>A.4.2 External uncertainties.....</i>	<i>481</i>
Uncertainties in prices over the life of the project.....	482
Uncertainty in regulatory environment.....	482
<i>A.4.3 Valuation model uncertainties.....</i>	<i>483</i>
A.5 LITERATURE CITED.....	487
APPENDIX B ENVEALTOOL DATABASE DOCUMENTATION.....	489
B.1 DATA TABLE STRUCTURES AND RELATIONSHIPS.....	489
B.2 QUERIES AND VISUAL BASIC CODE USED TO EXPORT DATA TO THE HUMAN EXPOSURE MODEL.....	532
<i>B.2.1 Overview.....</i>	<i>532</i>
Software required.....	532
Execution sequence.....	532
<i>B.2.2 Visual Basic code implemented within the Access database.....</i>	<i>534</i>
<i>B.2.3 Queries and auxiliary tables.....</i>	<i>536</i>
<i>B.2.4 Visual Basic code implemented within the Excel workbook.....</i>	<i>539</i>
B.3 QUERIES AND VISUAL BASIC CODE USED TO EXPORT DATA TO THE PIO-LCA MODEL.....	541
<i>B.3.1 Overview.....</i>	<i>541</i>
Software required.....	541
Execution sequence.....	541
<i>B.3.2 Visual Basic code implemented within the Access database.....</i>	<i>542</i>
<i>B.3.3 Queries, forms, and auxiliary tables.....</i>	<i>545</i>
<i>B.3.4 Visual Basic code implemented within the Excel workbook.....</i>	<i>563</i>
APPENDIX C PIO-LCA METHOD SPREADSHEET IMPLEMENTATION.....	575
C.1 INPUT REQUIREMENTS.....	575
C.2 VISUAL BASIC CODE.....	579

List of Figures

FIGURE 1-1: STRUCTURE OF THESIS. PART I: THE DESIGN PROCESS	31
FIGURE 1-2: STRUCTURE OF THESIS. PART II: ENVIRONMENTAL EVALUATION TOOLS	33
FIGURE 2-1: U.S. CHEMICAL INDUSTRY ENVIRONMENTAL EXPENDITURES IN PERSPECTIVE (1999 DATA).....	40
FIGURE 2-2: THE DESIGN PROCESS.....	43
FIGURE 2-3: EVOLUTION IN THE FRAMING OF THE CHEMICAL PROCESS SYNTHESIS PROBLEM.	47
FIGURE 2-4: MATERIAL FLOWS IN A CHEMICAL PROCESS	50
FIGURE 3-1: ELEMENTS OF AN ECONOMIC VALUATION MODEL.....	89
FIGURE 3-2: HISTORICAL DATA AND FUTURE UNCERTAINTY FOR METHYLENE CHLORIDE PRICES	101
FIGURE 3-3: HISTORICAL DATA AND FUTURE UNCERTAINTY FOR NATURAL GAS PRICES	101
FIGURE 3-4: CORRELATIONS FOR THE ESTIMATION OF PURCHASED EQUIPMENT COST OF FLOATING-HEAD SHELL AND TUBE HEAT EXCHANGERS	102
FIGURE 3-5: GUTHRIE'S INSTALLATION FACTORS FOR HEAT EXCHANGERS	105
FIGURE 3-6: MARGINAL CONTRIBUTIONS TO INSTALLED EQUIPMENT COST WITH RESPECT TO PURCHASED EQUIPMENT COST FOR HEAT EXCHANGERS (BASED ON GUTHRIE'S DATA).....	105
FIGURE 3-7: ANNUALIZATION FACTOR PROBABILITY DENSITY DISTRIBUTIONS (DOUGLAS MODEL).....	110
FIGURE 3-8: PROBABILITY DENSITY DISTRIBUTIONS FOR INSTALLED EQUIPMENT COST ANNUALIZATION FACTORS CALCULATED USING THE DOUGLAS MODEL FOR THREE DIFFERENT DESIGN SCENARIOS, USING A DISCOUNT RATE OF 15%.....	113
FIGURE 3-9: INSTALLED EQUIPMENT COST ANNUALIZATION FACTOR DISTRIBUTIONS OBTAINED FROM THE ECONOMIC EVALUATION ASSUMPTIONS OF VARIOUS PROCESS DESIGN BOOKS.	114
FIGURE 3-10: RESULTS OF THE ENERGY AND WASTE REDUCTION CONTESTS AT DOW CHEMICAL (LOUISIANA DIVISION).....	117
FIGURE 3-11: HEAT EXCHANGER SIZING EXAMPLE FLOWSHEET	121
FIGURE 3-12: EQUIPMENT COST CORRELATIONS USED IN THE HEAT EXCHANGER SIZING EXAMPLE.....	123
FIGURE 3-13: COMPONENTS OF AN ENVIRONMENTAL VALUATION MODEL	127
FIGURE 3-14: COMPARISON OF RELATIVE WEIGHTING FACTORS FOR VARIOUS ENVIRONMENTAL IMPACT CATEGORIES ACROSS FOUR ENVIRONMENTAL VALUATION METHODS.	135
FIGURE 4-1: AVAILABILITY OF INFORMATION, DESIGN FREEDOM, AND PORTION OF PROCESS PERFORMANCE FIXED BY DESIGN DECISIONS AS A FUNCTION OF THE PROCESS DEVELOPMENT STAGE	146
FIGURE 4-2: DISTRIBUTIONS OF ABSOLUTE VALUATIONS FOR THE ILLUSTRATIVE EXAMPLE	152
FIGURE 4-3: SCATTER PLOT OF VALUATIONS FOR THE ILLUSTRATIVE EXAMPLE, UNDER THE ASSUMPTION OF INDEPENDENCE BETWEEN VALUATION DISTRIBUTIONS	152
FIGURE 4-4: SCATTER PLOT OF ACTUAL VALUATIONS FOR THE ILLUSTRATIVE EXAMPLE	153
FIGURE 4-5: RELATIVE VALUATIONS FOR THE ALTERNATIVES IN THE ILLUSTRATIVE EXAMPLE	154
FIGURE 4-6: EXAMPLE OF DECISION-MAKING CYCLE FOR PROCESS DESIGN BASED ON TWO OBJECTIVES.....	156

FIGURE 4-7: INDIFFERENCE CURVES FOR A TWO ATTRIBUTE UTILITY FUNCTION OVER RELATIVE COST AND RELATIVE ENVIRONMENTAL IMPACT WITH $\alpha=0.1$	164
FIGURE 4-8: ZERO-UTILITY INDIFFERENCE CURVES FOR THE ATTRIBUTES RELATIVE COST AND RELATIVE ENVIRONMENTAL IMPACT BASED ON THE PROPOSED LOGARITHMIC UTILITY FUNCTION.....	165
FIGURE 4-9: FLOWSHEET FOR THE CONCENTRATION SET POINT SELECTION EXAMPLE.....	167
FIGURE 4-10: STEAM CONSUMPTION AS A FUNCTION OF EFFLUENT CONCENTRATION SET POINT FOR THE SET POINT SELECTION EXAMPLE.....	168
FIGURE 4-11: JOINT PROBABILITY DENSITY DISTRIBUTION OF THE UNIT ENVIRONMENTAL INDICATORS FOR STEAM AND METHYLENE CHLORIDE DISCHARGES.....	170
FIGURE 4-12: VARIABLE COSTS AS A FUNCTION OF EFFLUENT CONCENTRATION SET POINT	171
FIGURE 4-13: ENVIRONMENTAL IMPACT INDICATOR DISTRIBUTIONS FOR THE CONCENTRATION SET POINT SELECTION EXAMPLE.....	172
FIGURE 4-14: RELATIVE ENVIRONMENTAL IMPACT DISTRIBUTIONS WITH RESPECT TO A 100 PPM BASE CASE FOR THE CONCENTRATION SET POINT SELECTION EXAMPLE	172
FIGURE 4-15: RELATIVE ENVIRONMENTAL IMPACT DISTRIBUTIONS VS. RELATIVE VARIABLE COST (100 PPM BASE CASE) FOR THE CONCENTRATION SET POINT SELECTION EXAMPLE.....	173
FIGURE 4-16: RELATIVE ENVIRONMENTAL IMPACT DISTRIBUTIONS WITH RESPECT TO A 25 PPM BASE CASE FOR THE CONCENTRATION SET POINT SELECTION EXAMPLE	174
FIGURE 4-17: PROBABILITY DENSITY PLOT FOR THE ENVIRONMENTAL IMPACT INDICATOR OF THE 18 PPM ALTERNATIVE RELATIVE TO THE 25 PPM ALTERNATIVE.....	175
FIGURE 4-18: FLOWSHEET FOR THE HEAT EXCHANGER SIZING EXAMPLE	176
FIGURE 4-19: PROBABILITY DISTRIBUTIONS USED IN THE TAC ECONOMIC VALUATION FUNCTION FOR THE HEAT EXCHANGER SIZING EXAMPLE	181
FIGURE 4-20: PROBABILITY DISTRIBUTIONS USED IN THE ENVIRONMENTAL VALUATION FUNCTION FOR THE HEAT EXCHANGER SIZING	183
FIGURE 4-21: TOTAL ANNUALIZED COST DISTRIBUTIONS FOR THE HEAT EXCHANGER SIZING EXAMPLE.....	186
FIGURE 4-22: RELATIVE TOTAL ANNUALIZED COST DISTRIBUTIONS FOR THE HEAT EXCHANGER SIZING EXAMPLE ...	187
FIGURE 4-23: PROBABILITY DENSITY PLOT FOR THE TAC OF THE 2900 FT ² ALTERNATIVE RELATIVE TO THE 3500 FT ² BASE CASE ALTERNATIVE	187
FIGURE 4-24: ENVIRONMENTAL IMPACT INDICATOR DISTRIBUTIONS FOR THE HEAT EXCHANGER SIZING EXAMPLE..	188
FIGURE 4-25: RELATIVE ENVIRONMENTAL IMPACT DISTRIBUTIONS FOR THE HEAT EXCHANGER SIZING EXAMPLE....	189
FIGURE 4-26: RELATIVE ENVIRONMENTAL IMPACT VS. RELATIVE TOTAL ANNUALIZED COST FOR A SUBSET OF THE ALTERNATIVES CONSIDERED IN THE HEAT EXCHANGER SIZING EXAMPLE	190
FIGURE 5-1: SCATTER PLOT OF 1000 PAIRS (X ₁ , Y) FROM THE MODEL DEFINED IN EQ (5-10).....	198
FIGURE 5-2: FLOWSHEET FOR THE CONCENTRATION SET POINT SELECTION EXAMPLE.....	202
FIGURE 5-3: DISTRIBUTIONS FOR THE CONTRIBUTION OF PROCESS INPUTS AND PROCESS OUTPUTS TO THE ENVIRONMENTAL IMPACT INDICATOR FOR TWO DIFFERENT EFFLUENT CONCENTRATION SET POINTS.....	202

FIGURE 5-4: FLOWSHEET FOR THE HEAT EXCHANGER SIZING EXAMPLE	204
FIGURE 5-5: DISTRIBUTIONS FOR THE CONTRIBUTION OF PROCESS INPUTS AND PROCESS OUTPUTS TO (A) TOTAL ANNUALIZED COST, AND (B) ENVIRONMENTAL IMPACT INDICATOR FOR THE 3500 FT ² HEAT EXCHANGER ALTERNATIVE.....	205
FIGURE 5-6: UNCERTAIN FACTOR CONTRIBUTIONS TO THE UNCERTAINTY IN TOTAL ANNUALIZED COST FOR THREE DIFFERENT CHOICES OF HEAT EXCHANGER SIZE	206
FIGURE 5-7: UNCERTAIN FACTOR CONTRIBUTIONS TO THE UNCERTAINTY IN ENVIRONMENTAL IMPACT VALUATIONS FOR THREE DIFFERENT HEAT EXCHANGER SIZE CHOICES	207
FIGURE 5-8: UNCERTAIN FACTOR CONTRIBUTIONS TO THE UNCERTAINTY IN RELATIVE TOTAL ANNUALIZED COST FOR TWO DIFFERENT CHOICES OF HEAT EXCHANGER SIZE (BASE CASE ALTERNATIVE HAS A 3,500 FT ² HEAT EXCHANGER).....	208
FIGURE 5-9: UNCERTAIN PARAMETER CONTRIBUTIONS TO THE UNCERTAINTY EN RELATIVE ENVIRONMENTAL IMPACT VALUATIONS FOR TWO DIFFERENT CHOICES OF HEAT EXCHANGER SIZE (BASE CASE ALTERNATIVE HAS A 3,500 FT ² HEAT EXCHANGER).....	209
FIGURE 5-10: FLOWSHEET FOR THE STRIPPING COLUMN RETROFIT EXAMPLE	210
FIGURE 5-11: RELATIVE NPC DISTRIBUTIONS FOR TWO STRIPPING COLUMN DESIGNS RELATIVE TO THE ECONOMICALLY OPTIMUM DESIGN	220
FIGURE 5-12: RELATIVE ENVIRONMENTAL IMPACT DISTRIBUTIONS FOR TWO STRIPPING COLUMN DESIGNS RELATIVE TO THE ECONOMICALLY OPTIMUM DESIGN	220
FIGURE 5-13: PROBABILITY DENSITY PLOTS OF DISCOUNTED CASH FLOW FOR THE ORIGINAL AND THE RETROFITTED SOLVENT RECOVERY PROCESSES	221
FIGURE 5-14: PROBABILITY DENSITY PLOT FOR THE RELATIVE ENVIRONMENTAL IMPACT OF THE RETROFITTED SOLVENT RECOVERY PROCESS RELATIVE TO THE ORIGINAL PROCESS.....	221
FIGURE 6-1: CORRELATION BETWEEN HOFSTETTER DALYs AND EDF TEP CANCER INDICATORS (AIR EMISSIONS)	228
FIGURE 6-2: CORRELATION BETWEEN HOFSTETTER DALYs AND EDF TEP CANCER INDICATORS (WATER DISCHARGES).....	229
FIGURE 6-3: LINKAGE OF EMISSIONS TO HUMAN DOSE THROUGH A COMBINED MULTIMEDIA FATE, TRANSPORT, AND EXPOSURE MODEL	232
FIGURE 6-4: COMPARISON BETWEEN THE CONTINUOUS AND INTERMITTENT RAIN APPROACHES TO ESTIMATING RAIN DISSOLUTION TRANSPORT RATES (PERSISTENCE OF EMISSIONS OF TRI SUBSTANCES TO AIR).....	244
FIGURE 6-5: SENSITIVITY OF THE FATE AND TRANSPORT MODEL TO THE EXCLUSION OF THE RAIN DISSOLUTION MECHANISM (PERSISTENCE OF EMISSIONS OF TRI SUBSTANCES TO AIR).	245
FIGURE 6-6: COMPARISON BETWEEN TWO METHODS OF ESTIMATING IRRIGATED SOIL CONCENTRATIONS (1000 KG/HR DISCHARGES TO WATER OF TRI CHEMICALS INTO A 10 MILLION KM ² LANDSCAPE).....	260
FIGURE 6-7: RELATIONSHIP BETWEEN THE PLANT-SOIL BIOCONCENTRATION FACTOR AND OCTANOL-WATER PARTITION COEFFICIENT.	264

FIGURE 6-8: RELATIONSHIP BETWEEN THE STEM CONCENTRATION FACTOR AND THE OCTANOL-WATER PARTITION COEFFICIENT.....	264
FIGURE 6-9: RELATIONSHIP BETWEEN THE TRANSPIRATION STREAM CONCENTRATION FACTOR AND THE OCTANOL-WATER PARTITION COEFFICIENT	265
FIGURE 6-10: FIT OF THE OPTIMIZED BRIGGS ET AL. PLANT-SOIL BIOCONCENTRATION FACTOR TO THE EXPERIMENTAL DATA OF TRAVIS AND ARMS.	266
FIGURE 6-11: FIT OF THE OPTIMIZED BRIGGS ET AL. STEM CONCENTRATION FACTOR MODEL TO THE EXPERIMENTAL DATA OF BRIGGS ET AL.....	266
FIGURE 6-12: RELATIONSHIP BETWEEN LEAF AIR CONDUCTANCE AND THE OCTANOL-AIR PARTITION COEFFICIENT .	270
FIGURE 6-13: COMPARISON BETWEEN TWO METHODS FOR ESTIMATING CHEMICAL CONCENTRATIONS IN ABOVE-GROUND CROPS	273
FIGURE 6-14: ROOT-SOIL WATER BIOCONCENTRATION MODELS.....	275
FIGURE 6-15: ROOT-DRY SOIL BIOCONCENTRATION MODELS.	275
FIGURE 6-16: COMPARISON OF FISH BIOCONCENTRATION FACTOR CORRELATIONS WITH EXPERIMENTAL DATA	277
FIGURE 6-17: COMPARISON OF MILK BIOTRANSFER FACTOR MODELS WITH EXPERIMENTAL DATA.....	280
FIGURE 6-18: COMPARISON OF BEEF BIOTRANSFER CORRELATIONS WITH EXPERIMENTAL DATA	282
FIGURE 6-19: CORRELATION BETWEEN BEEF AND MILK BIOTRANSFER FACTORS.....	283
FIGURE 6-20: CORRELATION BETWEEN POULTRY AND CATTLE FAT-DIET BIOACCUMULATION FACTORS.....	284
FIGURE 6-21: COMPARISON OF CHICKEN EGG BIOTRANSFER FACTOR CORRELATION WITH EXPERIMENTAL DATA	286
FIGURE 6-22: CORRELATION BETWEEN TLV VALUES AND CHRONIC NON-CANCER HEALTH EFFECTS RISK ASSESSMENT VALUES.	293
FIGURE 6-23: DISTRIBUTION OF GEOMETRIC MEANS FOR THE EXPOSURE INDICATOR OF 1,318 CHEMICALS INCLUDED IN THE WMPT DATABASE.....	296
FIGURE 6-24: DISTRIBUTION OF UNCERTAINTY FACTORS FOR THE EXPOSURE INDICATOR OF 1,318 CHEMICALS INCLUDED IN THE WMPT DATABASE.....	297
FIGURE 6-25: DISTRIBUTION OF CANCER RISK INDICATORS FOR EMISSIONS TO AIR OF 263 SUBSTANCES WITH REPORTED TRI EMISSIONS IN 1988-1997 AND SOME INFORMATION REGARDING CARCINOGENICITY.	298
FIGURE 6-26: DISTRIBUTION OF CHRONIC TOXICITY INDICATORS (EXPRESSED AS CANCER RISK EQUIVALENTS) FOR EMISSIONS TO AIR OF 505 SUBSTANCES WITH REPORTED TRI EMISSIONS IN 1988-1997.	299
FIGURE 6-27: DISTRIBUTION OF UNCERTAINTIES IN CANCER RISK INDICATORS FOR EMISSIONS TO AIR OF 263 SUBSTANCES WITH REPORTED TRI EMISSIONS IN 1988-1997 AND SOME INFORMATION REGARDING CARCINOGENICITY.....	300
FIGURE 6-28: DISTRIBUTION OF UNCERTAINTIES IN CHRONIC RISK INDICATORS FOR EMISSIONS TO AIR OF 505 SUBSTANCES WITH REPORTED TRI EMISSIONS IN 1988-1997	300
FIGURE 6-29: INFORMATION CONTENT CHART FOR EXAMPLE 1	308
FIGURE 6-30: INFORMATION CONTENT CHART FOR EXAMPLE 2	309

FIGURE 6-31: NON-CANCER INHALATION ROUTE RISK ASSESSMENT FACTOR -- INFORMATION CONTENT CHART FOR TRI CHEMICALS WITH REPORTED EMISSIONS IN THE PERIOD 1988-1997	312
FIGURE 6-32: HUMAN HEALTH CONCERN SCORING ALGORITHM USED IN EPA'S WASTE MINIMIZATION PRIORITIZATION TOOL	313
FIGURE 6-33: INFORMATION CONTENT CHART FOR THE WMPT CASE STUDY (SET OF 363 CHEMICALS WITH TOXICITY DATA IN THE WMPT DATABASE)	314
FIGURE 6-34: INFORMATION CONTENT CHART FOR THE HUMAN EXPOSURE INDICATOR (SET OF 1318 CHEMICALS IN THE WMPT DATABASE)	315
FIGURE 6-35: INFORMATION CONTENT CHART FOR THE TRI INDICATORS CASE STUDY (SET OF 505 CHEMICALS WITH REPORTED EMISSIONS TO AIR IN 1987-1997)	316
FIGURE 6-36: INFORMATION CONTENT CHART FOR THE USE OF HTP (CANCER) TO RANK CHEMICALS IN THE TRI (SET OF 263 CHEMICALS WITH CANCER INFORMATION)	316
FIGURE 6-37: TRI 1988-1995. COMBINED AIR EMISSIONS, WATER DISCHARGES, AND WASTEWATER TREATMENT PLANT TRANSFERS: (A) AGGREGATED BY MASS, (B) COMBINED CANCER AND NON-CANCER CHRONIC EFFECTS HEALTH RISK INDICATOR, (C) CHRONIC RISK INDICATOR RELATIVE TO 1988.	322
FIGURE 6-38: TRI 1988-1995. CHRONIC HEALTH RISK INDICATOR FROM COMBINED AIR EMISSIONS, WATER DISCHARGES, AND WASTEWATER TREATMENT PLANT TRANSFERS, RELATIVE TO 1995	323
FIGURE 6-39: INDIVIDUAL CHEMICAL CONTRIBUTIONS TO (A) TOTAL REPORTED QUANTITIES, AND (B) COMBINED CANCER AND NON-CANCER CHRONIC TOXICITY INDICATOR (TRI CHEMICALS WITH MORE THAN 10 MILLION POUNDS OF REPORTED RELEASES IN 1997)	325
FIGURE 6-40: INDIVIDUAL CHEMICAL CONTRIBUTIONS TO (A) COMBINED CANCER AND NON-CANCER CHRONIC TOXICITY INDICATOR, AND (B) TOTAL REPORTED QUANTITIES (TRI CHEMICALS WITH MORE THAN A 5% CHANCE OF CONTRIBUTING AT LEAST 1/100 OF THE TOTAL CHRONIC HEALTH RISK)	326
FIGURE 6-41: REPORTED TRI RELEASES AND TRANSFERS OF 33/50 PROGRAM CHEMICALS, 1988-1997	328
FIGURE 6-42: CHRONIC TOXICITY RISK FROM REPORTED TRI RELEASES AND TRANSFERS OF 33/50 PROGRAM CHEMICALS, 1988-1997 (RELATIVE TO 1988)	328
FIGURE 6-43: 33/50 PROGRAM CHEMICAL CONTRIBUTIONS TO (A) CHRONIC TOXICITY RISK, AND (B) TOTAL QUANTITY RELEASED, (1988 TRI)	331
FIGURE 6-44: INDUSTRY CONTRIBUTIONS TO (A) TOTAL MASS AND (B) TOTAL CHRONIC HEALTH INDICATOR (1997 REPORTED TRI AIR EMISSIONS, WATER DISCHARGES, AND TRANSFERS TO WASTEWATER TREATMENT PLANTS)	332
FIGURE 6-45: UNIT CANCER RISK INDICATORS FOR COMPOUNDS IN THE POLYCYCLIC AROMATIC COMPOUNDS (PAC) CHEMICAL GROUP	333
FIGURE 6-46: COMPARISON BETWEEN EDF CANCER TOXIC EQUIVALENT POTENTIALS AND DISTRIBUTIONS FOR THE CONTRIBUTION TO THE TOTAL CANCER RISK INDICATOR (TOP 50 CHEMICALS WITH REPORTED 1997 RELEASES OR TRANSFERS TO AIR, SURFACE WATER, AND WASTEWATER TREATMENT PLANTS, SORTED BY EDF CANCER SCORE).	336

FIGURE 6-47: COMPARISON BETWEEN EDF CANCER TOXIC EQUIVALENT POTENTIALS AND DISTRIBUTIONS FOR THE CONTRIBUTION TO THE TOTAL CANCER RISK INDICATOR (TOP 50 CHEMICALS WITH REPORTED 1997 RELEASES OR TRANSFERS TO AIR, SURFACE WATER, AND WASTEWATER TREATMENT PLANTS, SORTED BY MEDIAN CONTRIBUTION TO CANCER RISK).....	337
FIGURE 6-48: COMPARISON BETWEEN EDF NON-CANCER TOXIC EQUIVALENT POTENTIALS AND DISTRIBUTIONS FOR THE CONTRIBUTION TO THE TOTAL NON-CANCER CHRONIC TOXICITY INDICATOR (TOP 50 CHEMICALS WITH REPORTED 1997 RELEASES OR TRANSFERS TO AIR, SURFACE WATER, AND WASTEWATER TREATMENT PLANTS, SORTED BY EDF NON-CANCER SCORE).....	338
FIGURE 6-49: COMPARISON BETWEEN EDF NON-CANCER TOXIC EQUIVALENT POTENTIALS AND DISTRIBUTIONS FOR THE CONTRIBUTION TO THE TOTAL NON-CANCER CHRONIC TOXICITY INDICATOR (TOP 50 CHEMICALS WITH REPORTED 1997 RELEASES OR TRANSFERS TO AIR, SURFACE WATER, AND WASTEWATER TREATMENT PLANTS, SORTED BY MEDIAN CONTRIBUTION TO NON-CANCER TOXICITY INDICATOR).....	339
FIGURE 6-50: PLOT OF CONTRIBUTION TO CANCER RISK INDICATOR VS. EDF CANCER TOXIC EQUIVALENT POTENTIAL SCORE (ALL TRI RECOGNIZED OR SUSPECTED CARCINOGENS WITH REPORTED 1997 RELEASES OR TRANSFERS TO AIR, WATER, AND WASTEWATER TREATMENT PLANTS).....	341
FIGURE 6-51: PLOT OF CONTRIBUTION TO NON-CANCER CHRONIC TOXICITY INDICATOR VS. EDF NON-CANCER TOXIC EQUIVALENT POTENTIAL SCORE (ALL TRI CHEMICALS WITH REPORTED 1997 RELEASES OR TRANSFERS TO AIR, WATER, AND WASTEWATER TREATMENT PLANTS).....	342
FIGURE 6-52: COMPARISON BETWEEN OPPTEIM SCORES AND CONTRIBUTION TO COMBINED CHRONIC TOXICITY INDICATOR (TOP 50 TRI CHEMICALS WITH 1997 REPORTED EMISSIONS TO AIR, SORTED BY OPPTEIM SCORE).....	345
FIGURE 6-53: COMPARISON BETWEEN OPPTEIM SCORES AND CONTRIBUTION TO COMBINED CHRONIC TOXICITY INDICATOR (TOP 50 TRI CHEMICALS WITH 1997 REPORTED EMISSIONS TO AIR, SORTED BY MEDIAN CONTRIBUTION TO TOXICITY INDICATOR).....	346
FIGURE 6-54: PLOT OF CONTRIBUTION TO COMBINED CHRONIC TOXICITY INDICATOR VS. OPPTEIM SCORE (ALL TRI CHEMICALS WITH REPORTED 1997 EMISSIONS TO AIR).....	347
FIGURE 6-55: CORRELATION BETWEEN OPPTEIM SCORES AND POUNDS EMITTED WEIGHTED BY TOXICITY (TRI CHEMICALS WITH REPORTED 1997 STACK OR FUGITIVE AIR EMISSIONS).....	348
FIGURE 7-1: PROCESS TREE REPRESENTATION OF CHLORINE PRODUCTION IN THE LCA SOFTWARE SIMAPRO.....	357
FIGURE 7-2: PROCESS AND PRODUCT CHAINS INVOLVED IN THE PRODUCTION OF CHLORINE.....	358
FIGURE 7-3: TWO ALTERNATIVE APPROACHES FOR LISTING EMISSIONS OF COMBUSTION PRODUCTS ASSOCIATED WITH THE COAL-FIRED POWER PLANT PROCESS.....	365
FIGURE 7-4: CORRESPONDENCE BETWEEN PRODUCT-PROCESS FLOW DIAGRAMS AND INPUT-OUTPUT MATRICES.....	370
FIGURE 7-5: ENVIRONMENTAL EXCHANGE CONTRIBUTIONS TO THE ENVIRONMENTAL IMPACT INDICATOR OF CHLORINE PRODUCTION FOR THREE CHLOR-ALKALI PROCESSES.....	388
FIGURE 7-6: PROCESS THROUGHPUT CONTRIBUTIONS TO THE ENVIRONMENTAL IMPACT INDICATOR FOR CHLORINE PRODUCTION FOR THREE CHLOR-ALKALI PROCESSES.....	388

FIGURE 7-7: COMPARISON BETWEEN THE U.S. NATIONAL GRID AND A GAS-FIRED COGENERATION PLANT AS SOURCES OF ELECTRICITY FOR CHLORINE PRODUCTION USING THE MEMBRANE CELL PROCESS.....	391
FIGURE 7-8: COMPARISON OF THE ENVIRONMENTAL IMPACT OF CHLORINE PRODUCTION IN UNITED STATES VS. WESTERN EUROPE	393
FIGURE 7-9: UNCERTAINTY DISTRIBUTIONS FOR THE OVERALL ENVIRONMENTAL INDICATOR FOR CHLORINE PRODUCTION OBTAINED FROM MONTE CARLO SIMULATION OF THE PIO-LCA MODEL.....	395
FIGURE 7-10: COMPARISON OF THREE CHLOR-ALKALI PROCESSES USING ABSOLUTE ENVIRONMENTAL IMPACT INDICATORS.....	396
FIGURE 7-11: COMPARISON OF THREE CHLOR-ALKALI PROCESSES USING RELATIVE ENVIRONMENTAL IMPACT INDICATORS.....	397
FIGURE 7-12: DISTRIBUTIONS FOR PROCESS CONTRIBUTIONS TO THE ENVIRONMENTAL IMPACT INDICATOR OF CHLORINE PRODUCTION.....	399
FIGURE 7-13: DISTRIBUTIONS FOR EMISSION CONTRIBUTIONS TO THE ENVIRONMENTAL IMPACT INDICATOR OF CHLORINE PRODUCTION.....	400
FIGURE 7-14: DISTRIBUTIONS FOR ENVIRONMENTAL PROBLEM CATEGORY CONTRIBUTIONS TO THE ENVIRONMENTAL IMPACT INDICATOR OF CHLORINE PRODUCTION.....	401
FIGURE 7-15: RANK CORRELATION COEFFICIENTS FOR THE UNCERTAINTY IN THE ABSOLUTE VALUE OF THE OVERALL ENVIRONMENTAL EVALUATION INDICATOR FOR CHLORINE PRODUCTION.....	403
FIGURE 7-16: RANK CORRELATION COEFFICIENTS FOR THE UNCERTAINTY IN THE RATIO OF THE LIFE-CYCLE UNIT ENVIRONMENTAL INDICATOR OF THE DIAPHRAGM CELL PROCESS TO THAT OF THE MEMBRANE CELL PROCESS	404
FIGURE 7-17: RANK CORRELATION COEFFICIENTS FOR THE UNCERTAINTY IN THE RATIO OF THE LIFE-CYCLE UNIT ENVIRONMENTAL INDICATOR OF THE MEMBRANE CELL PROCESS TO THAT OF THE MERCURY CELL PROCESS...	405
FIGURE 7-18: RANK CORRELATION COEFFICIENTS FOR THE UNCERTAINTY IN THE CONTRIBUTION OF EMISSIONS OF MERCURY TO AIR TO THE OVERALL ENVIRONMENTAL IMPACT INDICATOR OF CHLORINE PRODUCTION	406
FIGURE 7-19: RANK CORRELATION COEFFICIENTS FOR THE UNCERTAINTY IN THE CONTRIBUTION OF THE HUMAN CHRONIC TOXICITY POTENTIAL (NON-CANCER) CATEGORY TO THE OVERALL ENVIRONMENTAL IMPACT INDICATOR OF CHLORINE PRODUCTION	407
FIGURE 7-20: IMPACT OF PRODUCT MARKET SHARE SPECIFICATIONS ON THE ENVIRONMENTAL IMPACT VALUATION OF CHLORINE PRODUCTION.....	413
FIGURE 8-1: DEMM FLOW DIAGRAM (COLLOCATION APPROACH)	423
FIGURE 8-2: EXPLICIT ACCESS TO A MODEL RESPONSE SURFACE THROUGH THE MONTE CARLO METHOD	425
FIGURE 8-3: USE OF DEMMUCOM TO GENERATE PCE METAMODELS OF PROCESS FLOWSHEET MODELS	426
FIGURE 8-4: HEAT EXCHANGER SIZING EXAMPLE PROCESS FLOWSHEET.....	427
FIGURE 8-5: INDEX OF AGREEMENT VS. ORDER OF APPROXIMATION USED TO BUILD THE PCE MODEL	428
FIGURE 8-6: DETAIL VIEW OF THE INDEX OF AGREEMENT VS. LEVEL OF APPROXIMATION CHART	429
FIGURE 8-7: NUMBER OF MODEL RUNS NEEDED TO BUILD AND EVALUATE THE GOODNESS OF FIT OF THE PCE MODEL	429

FIGURE 8-8: VARIANCE CONTRIBUTION ANALYSIS	430
FIGURE 8-9: EXAMPLE OF @RISK REPRESENTATION OF A MULTIVARIATE NORMAL COPULA DISTRIBUTION.....	435
FIGURE 8-10: SCATTER PLOT OF 2000 (STEAM, METHYLENE CHLORIDE DISCHARGE) UNIT ENVIRONMENTAL INDICATOR PAIRS OBTAINED FROM MONTE CARLO SIMULATION OF A PIO-LCA MODEL.....	436
FIGURE 8-11: CONTOUR PLOT OF THE EMPIRICAL JOINT PROBABILITY DENSITY OF STEAM AND METHYLENE CHLORIDE DISCHARGE UNIT ENVIRONMENTAL INDICATORS	437
FIGURE 8-12: 3-DIMENSIONAL PLOT OF THE EMPIRICAL JOINT DENSITY OF THE UNIT INDICATORS OF STEAM AND METHYLENE CHLORIDE.....	437
FIGURE 8-13: CONTOUR PLOT OF THE BIVARIATE NORMAL COPULA DISTRIBUTION FOR STEAM AND METHYLENE CHLORIDE DISCHARGES ESTIMATED FROM PARAMETER FITTING OF MONTE CARLO RESULTS	438
FIGURE 8-14: 3-DIMENSIONAL PLOT OF THE BIVARIATE NORMAL COPULA DISTRIBUTION OF THE UNIT INDICATORS OF STEAM AND METHYLENE CHLORIDE	438
FIGURE 8-15: CONTOUR PLOT OF THE BIVARIATE NORMAL DISTRIBUTION FOR STEAM AND METHYLENE CHLORIDE DISCHARGES UNIT ENVIRONMENTAL INDICATORS OBTAINED UNDER THE ASSUMPTION THAT THE UNIT INDICATORS ARE INDEPENDENT FROM EACH OTHER.	439
FIGURE 8-16: 3-DIMENSIONAL PLOT OF THE JOINT DISTRIBUTION OF THE UNIT INDICATORS OF STEAM AND METHYLENE CHLORIDE, OBTAINED UNDER THE ASSUMPTION OF INDEPENDENCE AMONG THE UNIT INDICATOR DISTRIBUTIONS.	439
FIGURE 8-17: COMPUTATIONAL ADVANTAGES OF USING THE TOOLS DESCRIBED IN THIS CHAPTER IN THE ENVIRONMENTAL EVALUATION OF PROCESS FLOWSHEETS UNDER UNCERTAINTY	440
FIGURE 9-1: PROBABILITY DISTRIBUTIONS FOR THE VALUE OF THE HENRY'S LAW CONSTANT FOR 1,4- DICHLOROBENZENE	445
FIGURE 9-2: COMPARISON OF PROBABILITY DISTRIBUTIONS FOR THE CANCER ORAL POTENCY FACTOR OF BENZENE	446
FIGURE 9-3: ENVEvalTOOL DATA MODEL (INPUT-OUTPUT DATA AND ECONOMIC INFORMATION).....	448
FIGURE 9-4: ENVEvalTOOL DATA MODEL (CHEMICAL PROPERTIES AND VALUATION FACTORS).....	449
FIGURE 9-5: SCATTER PLOT OF PHYSPROP DATABASE EXPERIMENTAL HENRY'S LAW CONSTANT VALUES VS. EXPERIMENTAL VALUES FROM STAUDINGER ET AL.	456
FIGURE 9-6: SCATTER PLOT OF HENRY'S LAW CONSTANT VALUES ESTIMATED USING THE HENRYWINB BOND CONTRIBUTION METHOD VS. EXPERIMENTAL VALUES FROM THREE DIFFERENT SOURCES.....	456
FIGURE 9-7: INFORMATION FLOW DIAGRAM FOR THE IMPLEMENTATION OF THE AN ENVIRONMENTAL EVALUATION KNOWLEDGE MANAGEMENT SYSTEM WITHIN A PRIVATE ORGANIZATION	460
FIGURE A-1: FLOWSHEET FOR THE METHYLENE CHLORIDE RECOVERY SYSTEM.....	472
FIGURE A-2: TRADEOFFS IN THE OPERATION OF THE METHYLENE CHLORIDE RECOVERY SYSTEM.....	473
FIGURE A-3: COMPARISON OF EXPERIMENTAL DATA TO INFINITE DILUTION COEFFICIENTS CALCULATED USING THE PARAMETERS STORED IN THE ASPEN PLUS DATA BANKS	477

FIGURE A-4: MONTE CARLO SIMULATION RESULTS FOR THE METHYLENE CHLORIDE INFINITE DILUTION ACTIVITY COEFFICIENT IN WATER CALCULATED USING THE NRTL MODEL AND THE JOINT DISTRIBUTION OF PARAMETERS GIVEN BY EQ (A-7)	479
FIGURE A-5: O'CONNELL'S CORRELATION FOR OVERALL TRAY EFFICIENCY	481
FIGURE A-6: DISTRIBUTIONS FOR FUTURE EFFLUENT CONCENTRATION STANDARDS	483
FIGURE A-7: ENVIRONMENTAL EXCHANGE CONTRIBUTIONS TO THE ENVIRONMENTAL IMPACT INDICATOR OF METHYLENE CHLORIDE RELEASES	485
FIGURE A-8: IMPACT CATEGORY CONTRIBUTIONS TO THE ENVIRONMENTAL IMPACT INDICATOR FOR METHYLENE CHLORIDE DISCHARGES	486
FIGURE A-9: ENVIRONMENTAL EXCHANGE CONTRIBUTIONS TO THE ENVIRONMENTAL IMPACT INDICATOR OF STEAM (WITH NATURAL GAS USED AS BOILER FUEL)	486
FIGURE A-10: IMPACT CATEGORY CONTRIBUTIONS TO THE ENVIRONMENTAL IMPACT INDICATOR FOR STEAM (WITH NATURAL GAS USED AS BOILER FUEL)	487
FIGURE B-1: LAYOUT OF THE CHEMICAL PROPERTIES DATA ENTRY OF THE FATE, TRANSPORT AND EXPOSURE SPREADSHEET MODEL	533
FIGURE C-1: LAYOUT OF SHEET1 IN THE PIO-LCA WORKBOOK	576
FIGURE C-2: LAYOUT OF SHEET2 IN THE PIO-LCA WORKBOOK	577
FIGURE C-3: LAYOUT OF SHEET3 IN THE PIO-LCA WORKBOOK	577
FIGURE C-4: LAYOUT OF SHEET4 IN THE PIO-LCA WORKBOOK	578

List of Tables

TABLE 2-1: WASTE GENERATION IN DIFFERENT SEGMENTS OF THE CHEMICAL INDUSTRY	40
TABLE 2-2: APPROACHES TO ENVIRONMENTAL ISSUES IN CHEMICAL PROCESS DESIGN BOOKS.	41
TABLE 2-3: PROCESS SYNTHESIS TASKS AND REFERENCES TO EXAMPLES OF THEIR APPLICATION TO WASTE MINIMIZATION PROBLEMS USING THE MATHEMATICAL PROGRAMMING APPROACH.....	55
TABLE 2-4: TOXICITY-BASED INDICATORS FOR THE EVALUATION OF ENVIRONMENTAL RELEASES	65
TABLE 2-5: ENVIRONMENTAL INDICATORS USED FOR PROCESS EVALUATION IN THE CHEMICAL INDUSTRY	67
TABLE 3-1: COMPARISON OF APPROACHES TO THE ESTIMATION OF INSTALLATION COST FACTORS.....	104
TABLE 3-2: PARAMETRIC UNCERTAINTIES IN THE CAPITAL COST ESTIMATION MODEL OF DOUGLAS.....	107
TABLE 3-3: PARAMETRIC UNCERTAINTIES IN THE TOTAL PRODUCT COST MODEL.....	108
TABLE 3-4: UNCERTAIN FACTORS IN THE CAPITAL CHARGE FACTOR MODEL.....	109
TABLE 3-5: IMPACT OF PARAMETRIC UNCERTAINTY ON ANNUALIZATION FACTORS	110
TABLE 3-6: CHANGES MADE TO THE PARAMETERS IN THE DOUGLAS ANNUALIZATION FACTOR MODEL FOR THE PURPOSE OF DERIVING AN ANNUALIZATION FACTOR APPROPRIATE FOR SIZING EQUIPMENT.....	112
TABLE 3-7: EFFECT OF INDIRECT COST FACTOR ASSUMPTIONS ON THE ANNUALIZATION FACTORS OBTAINED FROM THE DOUGLAS MODEL	113
TABLE 3-8: INSTALLED EQUIPMENT COST ANNUALIZATION FACTOR MODEL ASSUMPTIONS AND RESULTS FOR VARIOUS PROCESS DESIGN TEXTBOOKS.	115
TABLE 3-9: VALUES OF THE ANNUALIZATION FACTOR USED IN THE HEAT EXCHANGER SIZING EXAMPLE	122
TABLE 3-10: RESULTS FOR THE HEAT EXCHANGER SIZING EXAMPLE.....	124
TABLE 3-11: WIDELY USED ENVIRONMENTAL IMPACT METRICS FOR SPECIFIC ENVIRONMENTAL PROBLEMS	128
TABLE 3-12: TYPICAL UNCERTAINTIES IN AIR POLLUTANT EMISSION FACTORS	130
TABLE 3-13: EXAMPLES OF THE UNCERTAINTIES IN CHARACTERIZATION FACTORS	131
TABLE 3-14: ENVIRONMENTAL PROBLEM WEIGHTING FACTORS USED IN FOUR DIFFERENT ENVIRONMENTAL VALUATION MODELS	134
TABLE 3-15: IMPLIED TRADEOFFS IN THE ECO-INDICATOR'99 MODEL.....	137
TABLE 3-16: ENVIRONMENTAL VALUATION FACTORS USED IN THIS THESIS	138
TABLE 4-1: DATA FOR THE ILLUSTRATIVE EXAMPLE	151
TABLE 4-2: EXAMPLES OF THE APPLICATION OF THE SINGLE ATTRIBUTE LOGARITHMIC UTILITY FUNCTION OVER DISTRIBUTIONS OF RELATIVE MEASURES OF PERFORMANCE (RATIO INDICATORS).....	162
TABLE 4-3: EXPECTED UTILITY MINIMIZATION RESULTS FOR THE CONCENTRATION SET POINT SELECTION EXAMPLE.....	175
TABLE 4-4: UNCERTAINTY DISTRIBUTIONS USED TO BUILD THE SPREADSHEET-BASED PROCESS METAMODEL.....	179
TABLE 5-1: UNCERTAINTY ANALYSIS RESULTS FOR THE EXAMPLE WITH CORRELATED UNCERTAIN INPUTS.....	201
TABLE 5-2: STRUCTURE OF DEMM METAMODELS USED TO PROPAGATE UNCERTAINTY IN THE STRIPPING COLUMN RETROFIT EXAMPLE.....	212
TABLE 5-3: UNCERTAINTY DISTRIBUTIONS USED TO BUILD THE SPREADSHEET-BASED PROCESS METAMODEL.....	213

TABLE 5-4: UNCERTAINTY DISTRIBUTIONS USED IN THE ECONOMIC VALUATION MODEL	216
TABLE 5-5: STOCHASTIC OPTIMIZATION RESULTS FOR THE RETROFIT EXAMPLE.....	219
TABLE 6-1: HIERARCHY OF TOXICITY INDICATORS, BASED ON THE RISK ASSESSMENT PARADIGM	225
TABLE 6-2: TOXICITY INDICATORS AVAILABLE IN THE OPEN LITERATURE	227
TABLE 6-3: UNCERTAINTY FACTORS FOR CANCER INDICATORS BASED ON CORRELATIONS AMONG INDICATOR SYSTEMS	230
TABLE 6-4: UNCERTAINTY FACTORS FOR NON-CANCER INDICATORS BASED ON CORRELATIONS AMONG INDICATOR SYSTEMS.....	230
TABLE 6-5: UNCERTAINTY FACTORS FOR CHRONIC TOXICITY INDICATORS (COMBINED CANCER AND NON-CANCER) BASED ON CORRELATIONS AMONG INDICATOR SYSTEMS	230
TABLE 6-6: COMPARTMENTS INCLUDED IN THE MULTI-MEDIA FATE AND TRANSPORT MODEL	234
TABLE 6-7: CHEMICAL TRANSPORT AND TRANSFORMATION PROCESSES INCLUDED IN THE FATE AND TRANSPORT MODEL.....	236
TABLE 6-8: PURE PHASE FUGACITY CAPACITY DEFINITIONS	238
TABLE 6-9: BULK COMPARTMENT FUGACITY CAPACITY DEFINITIONS	238
TABLE 6-10: ADJUSTMENTS TO Z VALUES REQUIRED FOR CHEMICALS WITH NEGLIGIBLE VAPOR PRESSURE.....	239
TABLE 6-11: ADVECTION D VALUE DEFINITIONS	239
TABLE 6-12 : DEGRADATION D VALUE DEFINITIONS.....	239
TABLE 6-13: INTERMEDIA TRANSPORT D VALUE DEFINITIONS	240
TABLE 6-14: MASS TRANSFER COEFFICIENT DEFINITIONS	242
TABLE 6-15: DISTRIBUTIONS FOR THE PARAMETERS DESCRIBING THE LOWER ATMOSPHERE COMPARTMENT	250
TABLE 6-16: DISTRIBUTIONS FOR THE PARAMETERS DESCRIBING THE SURFACE WATER COMPARTMENT	251
TABLE 6-17: DISTRIBUTIONS FOR THE PARAMETERS DESCRIBING THE SOIL COMPARTMENTS.....	252
TABLE 6-18: DISTRIBUTIONS FOR THE PARAMETERS DESCRIBING THE SEDIMENTS COMPARTMENT.....	252
TABLE 6-19: DISTRIBUTIONS FOR THE PARAMETERS DESCRIBING THE TERRESTRIAL VEGETATION COMPARTMENT ..	253
TABLE 6-20: DISTRIBUTIONS FOR THE PARAMETERS USED TO CALCULATE TRANSPORT RATES	254
TABLE 6-21: EXPOSURE MEDIA CONTACT RATE EXPRESSIONS.....	256
TABLE 6-22: DISTRIBUTIONS FOR THE PARAMETERS IN THE EXPOSURE MEDIA CONTACT RATE EXPRESSIONS	256
TABLE 6-23: EXPOSURE PATHWAYS IN THE EXPOSURE MODEL.....	257
TABLE 6-24: ENVIRONMENTAL MEDIA CONCENTRATIONS USED IN THE HUMAN EXPOSURE MODEL	258
TABLE 6-25: PURE PHASE VOLUME FRACTIONS IN PLANT LEAVES	261
TABLE 6-26: PLANT-SOIL BIOCONCENTRATION FACTOR MODEL PARAMETERS.....	263
TABLE 6-27: LITERATURE VALUES FOR THE PARAMETERS IN THE TRAPP AND MATTHIES AERIAL PLANT PARTS BIOACCUMULATION MODEL.....	268
TABLE 6-28: LITERATURE VALUES FOR THE PARAMETERS IN THE LEAF CONDUCTANCE MODEL.....	269
TABLE 6-29: PARAMETER VALUES USED IN THE ABOVE-GROUND CROPS BIOCONCENTRATION MODEL.....	272
TABLE 6-30: FARM ANIMAL EXPOSURE MEDIA CONTACT RATES.....	276

TABLE 6-31: VALUES FOR THE PARAMETERS USED IN THE BATHROOM AIR CONCENTRATION MODEL	287
TABLE 6-32: SAFETY FACTORS APPLIED TO NON-CANCER TOXICITY DATA FOR THE DERIVATION OF REFERENCE DOSES	290
TABLE 6-33: EXPRESSIONS USED TO PROVIDE ESTIMATES FOR REQUIRED CHEMICAL-SPECIFIC PARAMETERS WITH MISSING DATA	292
TABLE 6-34: DATA ELEMENTS USED TO DERIVE PROBABILITY DISTRIBUTIONS FOR NON-CANCER CHRONIC TOXICITY REFERENCE CONCENTRATIONS (TRI CHEMICALS WITH EMISSIONS TO AIR, DISCHARGES TO WATER, OR TRANSFERS TO WASTEWATER TREATMENT PLANTS IN 1988-1997)	294
TABLE 6-35: STRUCTURAL UNCERTAINTIES IN THE COMBINED MULTIMEDIA EXPOSURE MODEL	302
TABLE 6-36: SENSITIVITY RESULTS FOR STRUCTURAL UNCERTAINTIES.....	304
TABLE 6-37: SENSITIVITY ANALYSIS RESULTS (TOP 20 PARAMETRIC UNCERTAINTIES)	305
TABLE 6-38: SENSITIVITY RESULTS FOR EXPOSURE PATHWAYS	306
TABLE 6-39: HERTWICH'S RESOLUTION METRIC RESULTS FOR EXAMPLES 1 AND 2.	310
TABLE 6-40: LIST OF CHEMICALS IN THE 33/50 PROGRAM, COMPARED WITH LISTS CREATED ON THE BASIS OF CHEMICAL CONTRIBUTIONS TO RISK FROM 1988 AND 1997 TRI RELEASES.....	329
TABLE 6-41: AVAILABILITY OF INDICATORS TO SCORE 1997 REPORTED TRI RELEASES	334
TABLE 6-42: DEFAULT TOXICITY DISTRIBUTIONS USED.....	335
TABLE 7-1: USE AND MAKE MATRICES FOR THE CHLORINE LCA EXAMPLE.....	361
TABLE 7-2: ENVIRONMENTAL EXCHANGES MATRIX FOR THE CHLORINE LCA EXAMPLE.....	364
TABLE 7-3: MARKET SHARE MATRIX FOR THE CHLORINE LCA EXAMPLE	366
TABLE 7-4: PRICE AND DEMAND VECTORS FOR THE CHLORINE LCA EXAMPLE	367
TABLE 7-5: ALLOCATION MATRIX FOR THE CHLORINE LCA EXAMPLE.....	368
TABLE 7-6: PROCESS BY PRODUCT THROUGHPUT MATRIX FOR THE CHLORINE LCA EXAMPLE	369
TABLE 7-7: PRODUCT-BY-PRODUCT DIRECT REQUIREMENTS MATRIX FOR THE CHLORINE LCA EXAMPLE	371
TABLE 7-8: PRODUCT-BY-PRODUCT TOTAL REQUIREMENTS MATRIX FOR THE CHLORINE LCA EXAMPLE	372
TABLE 7-9: VECTORS OF PRODUCT REQUIREMENTS AND EQUIVALENT PRODUCTION REQUIREMENTS FOR THE CHLORINE LCA EXAMPLE	373
TABLE 7-10: THROUGHPUT REQUIREMENTS VECTORS FOR THE CHLORINE LCA EXAMPLE	374
TABLE 7-11: LIFE CYCLE ENVIRONMENTAL EXCHANGES INVENTORY AND MATRICES OF PROCESS CONTRIBUTIONS TO THE INVENTORY FOR THE CHLORINE LCA EXAMPLE.....	375
TABLE 7-12: CHARACTERIZATION AND VALUATION FACTORS USED IN THE CHLORINE LCA EXAMPLE.....	378
TABLE 7-13: LIFE-CYCLE IMPACT VALUATION FOR THE CHLORINE LCA EXAMPLE, SHOWING ENVIRONMENTAL EXCHANGE AND IMPACT CATEGORY CONTRIBUTIONS	380
TABLE 7-14: LIFE-CYCLE IMPACT VALUATION FOR THE CHLORINE LCA EXAMPLE, SHOWING PROCESS AND IMPACT CATEGORY CONTRIBUTIONS	381
TABLE 7-15: ENVIRONMENTAL INDICATORS PER UNIT OF PRODUCT FOR THE CHLORINE LCA EXAMPLE.....	384

TABLE 7-16: ENVIRONMENTAL IMPACT VALUATIONS PER UNIT OF ENVIRONMENTAL EXCHANGE FOR THE CHLORINE LCA EXAMPLE	385
TABLE 7-17: ENVIRONMENTAL INDICATORS PER UNIT OF PROCESS THROUGHPUT FOR THE CHLORINE LCA EXAMPLE (DIRECT AND INDIRECT IMPACTS)	386
TABLE 7-18: ENVIRONMENTAL INDICATORS PER UNIT OF PROCESS THROUGHPUT FOR THE CHLORINE LCA EXAMPLE (DIRECT IMPACTS ONLY).....	387
TABLE 7-19: TECHNICAL COEFFICIENT MATRICES FOR THE CHLORINE LCA EXAMPLE, INCORPORATING A COGENERATION PROCESS INTO THE PROCESS NETWORK.....	390
TABLE 7-20: MARKET SHARE MATRIX FOR THE PRODUCTION OF CHLORINE UNDER CA. 1990 WESTERN EUROPEAN CONDITIONS	392
TABLE 7-21: LINEAR PROGRAMMING RESULTS FOR THE CHLORINE LCA EXAMPLE	411
TABLE 9-1: LISTING OF RECORDS IN THE DISTRIBUTIONS TABLE OF THE ENVVALTOOL DATABASE	451
TABLE 9-2: CORRELATIONS AMONG PROBABILITY DISTRIBUTIONS FOR IMPACT CATEGORY VALUATION FACTORS DERIVED FROM THE EPS METHOD.....	452
TABLE 9-3: SOURCES OF DATA FOR PHYSICAL PROPERTIES USED IN EXPOSURE MODELING	453
TABLE 9-4: SOURCES OF DATA FOR FACTORS CHARACTERIZING THE CONTRIBUTIONS OF CHEMICALS TO SPECIFIC ENVIRONMENTAL PROBLEMS.....	453
TABLE 9-5: RANK ORDER OF SOURCES OF HENRY'S LAW CONSTANT DATA USED IN THE ENVVALTOOL DATABASE	455
TABLE A-1: INPUT DATA FOR THE METHYLENE CHLORIDE RECOVERY OPTIMIZATION PROBLEM	472
TABLE A-2: UNIT OPERATION MODELS USED.....	474
TABLE A-3: NOMINAL VALUES FOR THE PARAMETERS IN THE NRTL MODEL	475
TABLE A-4: NRTL PARAMETER DATA SETS STORED IN THE ASPEN PLUS DATA BANKS	475
TABLE A-5: PRODUCTS AND PROCESSES IN THE PIO-LCA MODEL USED FOR THE ENVIRONMENTAL EVALUATION OF THE ALTERNATIVES IN THE SOLVENT RECOVERY EXAMPLE	476
TABLE A-6: OVERALL HEAT TRANSFER COEFFICIENTS FOR HEAT EXCHANGERS TRANSFERRING HEAT BETWEEN TWO AQUEOUS STREAMS	480
TABLE A-7: METHYLENE CHLORIDE EFFLUENT CONCENTRATION LIMITS FOR SEVERAL U.S. JURISDICTIONS.....	482
TABLE A-8: MARGINAL DISTRIBUTIONS FOR THE UNIT ENVIRONMENTAL IMPACT OF KEY INPUTS AND OUTPUTS IN THE SOLVENT RECOVERY CASE STUDY	484
TABLE A-9: RANK CORRELATION MATRIX OBTAINED FOR THE SOLVENT RECOVERY CASE STUDY UNIT ENVIRONMENTAL INDICATORS	484

Chapter 1 Introduction

1.1 Thesis Statement

This thesis focuses on the development of systematic procedures for incorporating knowledge and concerns about environmental impacts into the design of chemical processes, recognizing and managing the uncertainties associated with the evaluation of potential environmental impacts. This dissertation aims to tackle the challenge of linking traditional process design (modeling within the plant), with environmental assessment (modeling of the interactions of a chemical process with the environment), while recognizing the diversity of value judgements regarding the environment (building value models).

Several benefits can be expected from an explicit incorporation of environmental objectives in chemical process design:

- Lower environmental impacts from new and retrofitted processes as compared with processes designed only with environmental compliance in mind.
- Anticipation and avoidance of future regulations that could impact a process, since new regulations are typically introduced years after knowledge regarding environmental hazards first becomes available.
- Discovery of design alternatives with superior economic performance, since superior environmental performance is often associated with materials and energy efficiency. Typically a designer will consider a very narrow set of alternatives within the possible universe of design alternatives. Procedures that identify design features leading to environmental problems, in conjunction with procedures that identify the major contributors to process costs, should be useful in focusing the attention of process designers on a richer set of design alternatives.
- Improved allocation of environmental protection resources within an organization that operates chemical processes.
- Improved relations with the communities that implicitly or explicitly give a corporation the license to build and operate chemical processes, since the major concerns of outside

stakeholders can be incorporated into the environmental value models used to evaluate designs.

The research problem examined here is a special case of the more general problem of designing a system when the designer is uncertain about (but not indifferent to) the tradeoffs among conflicting objectives, and about how to measure the extent to which an objective is met. The procedures developed in this project should be applicable in many other multi-criteria design settings.

1.2 Structure of Thesis

The thesis is organized into two parts. The first part (Chapters 2 to 5) concentrates on the design process itself. Figure 1-1 shows a flow diagram for the activities in the design process. Given a problem statement, design teams will generate alternatives, analyze them (perhaps through the use of process models), and evaluate their merit. Several iterations will be undertaken (inner loop) until no further opportunities to improve the design are perceived within the current problem framing. The term problem framing is used here to refer to the set of explicit or implicit decisions that set the scope for the design effort. Sensitivity analysis can be used to assess the impact of these decisions, and refine them if necessary (outer loop). A proposed design will emerge from this process once the design team is satisfied that no further significant improvement opportunities are available to them within the time framework allocated to the project.

Chapter 2 reviews the literature on design procedures for chemical processes that explicitly consider environmental issues. The organizational framework for the review is the design process itself, as shown in Figure 1-1.

Chapter 3 highlights the role of design as a tradeoff resolution exercise. The chapter discusses how designers use economic valuation models for guidance in the resolution of the tradeoffs inherent to process design. Every design implies a set of material and energy flows, as well as a set of processing equipment specifications. Economic value models map this information into widely understood metrics (revenues, operating costs, and capital costs) and summarize them into indicators that can be used to rank alternatives (e.g. net present value, internal rate of return, or total annualized cost). The chapter discusses how the widely used

economic value models introduce a bias against capital expenditures in the conceptual phase of process design, which in turn leads to material use, energy consumption, and waste generation rates that are in excess of those that would be economically optimum. This finding is consistent with published accounts of the abundance of overlooked energy conservation and waste reduction projects with rates of return in excess of 100%/year. The second half of the chapter introduces environmental valuation models. Environmental valuation models are a necessary requirement for incorporating environmental concerns as design objectives. These models map the information on equipment and material and energy flows implied by a design into environmental impact metrics. An environmental problem oriented framework is advocated for the structuring of environmental value models. The framework recognizes explicitly that value judgments are needed to generate an indicator of overall environmental performance. Conceptually, there is no difference between economic and environmental value functions. The main distinction comes from differences in data availability and precision.

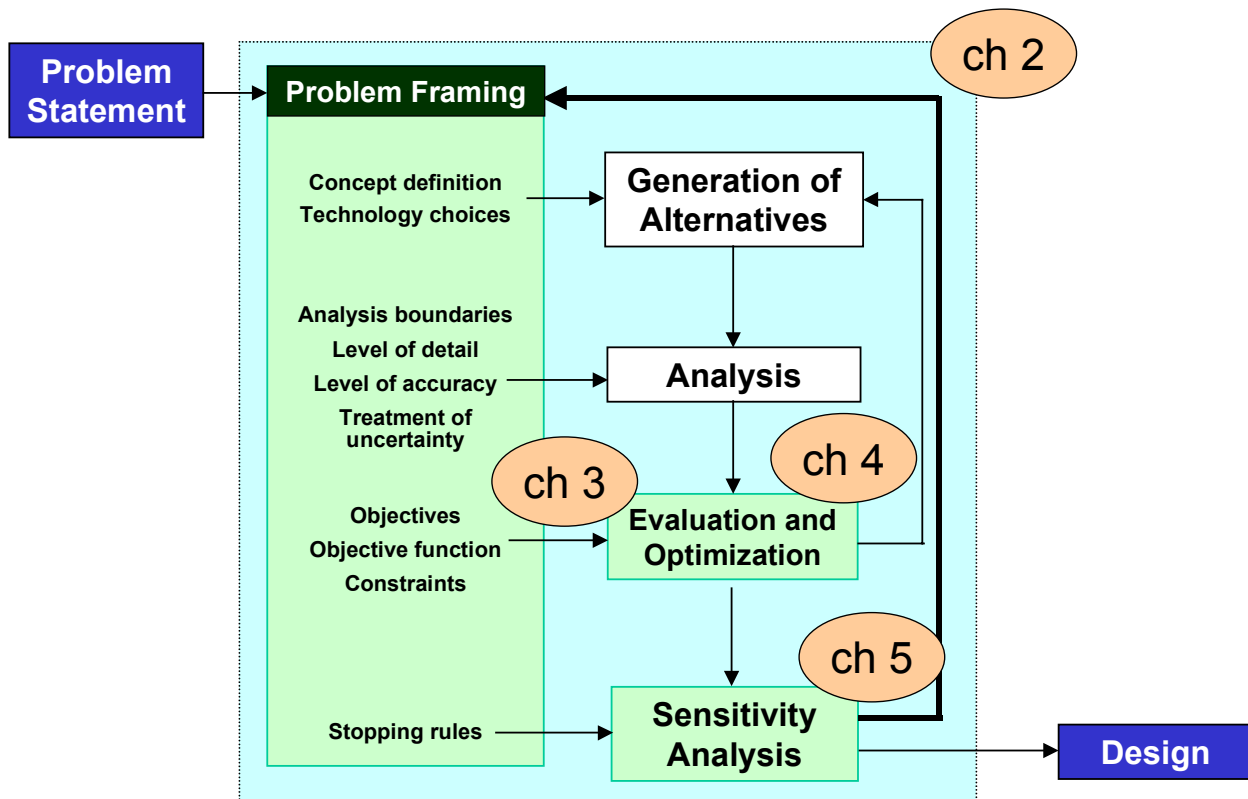


Figure 1-1: Structure of Thesis. Part I: The Design Process

Given the uncertainties inherent to the data used in environmental valuation models, **Chapter 4** discusses decision making under uncertainty in the context of process design. After reviewing the types of uncertainty present in process design, the chapter shows that even if there is significant uncertainty associated with the absolute value of a design metric, there might be considerable less uncertainty in the selection of a superior design among various alternatives based on that metric. The reason is the potential for a high degree of correlation among distributions for the performance metrics of competing alternatives. It follows that the key to the successful use of environmental value models in process design is to structure the models and the decision procedures in a way that preserves the underlying correlation structure. The procedures described in this chapter enable the designer to select superior designs and to assess the confidence with which a design can be judged to be superior to other alternatives. In some cases, the uncertainties in a valuation function will not permit the distinction among competing design alternatives, based upon the criteria the valuation function is trying to measure. This is also a useful result, since it tells the designer that other criteria should be used to distinguish among alternatives.

Chapter 5 describes two important types of sensitivity analysis. The first type of analysis is used to identify the features of a design that have the largest contribution to its performance. This analysis consists of propagating the uncertainty in the relative contribution of individual design features to the overall measure of performance of a design. This type of analysis is very useful for establishing promising directions in the generation of new alternatives. The second type of sensitivity analysis examines the contribution of model uncertainties and value function uncertainties to the uncertainty in the discrimination between two competing alternatives. This type of sensitivity analysis provides guidance for allocating resources to collect the data that would be most helpful to decision making. A key conclusion obtained in this chapter is that even though an environmental valuation model might contain hundreds of uncertain factors, only a few of them are typically significant contributors to design choice uncertainty. Generous uncertainty bounds may be placed on uncertain data elements at a first iteration, followed by careful examination of the minority of factors that turn out to be important in decision-making.

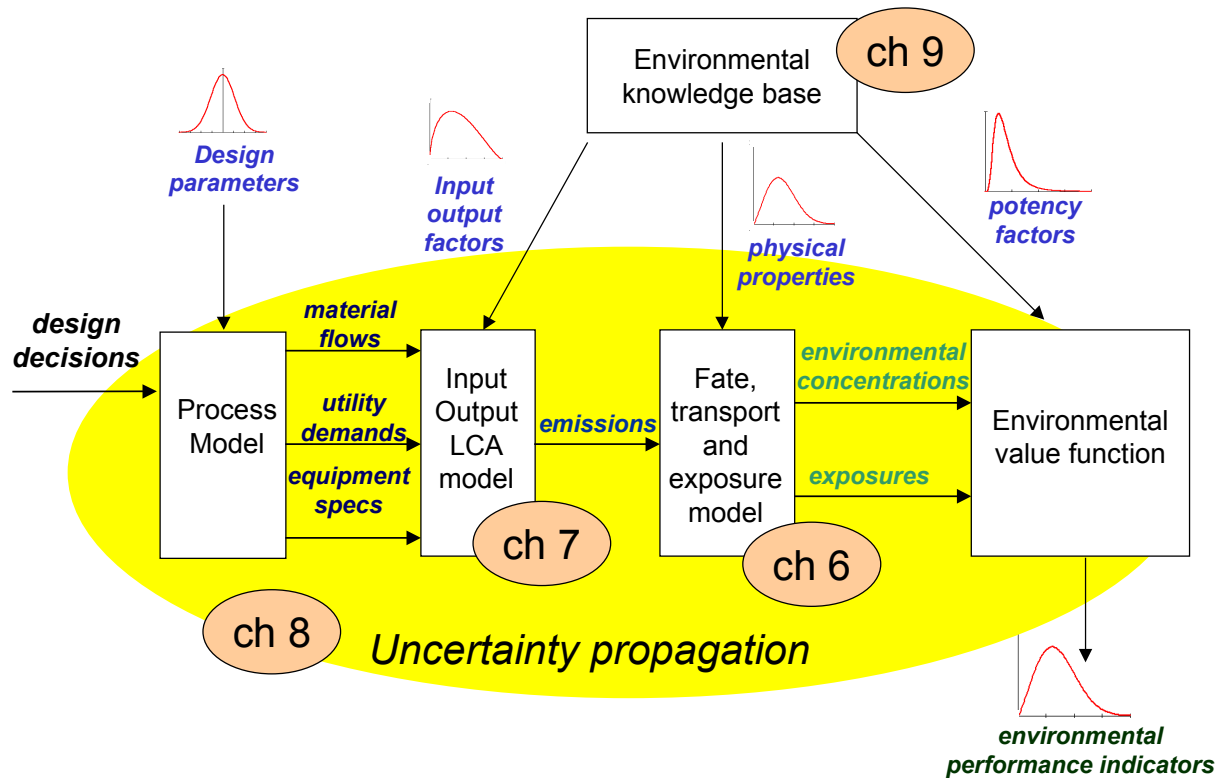


Figure 1-2: Structure of Thesis. Part II: Environmental Evaluation Tools

The second part of thesis (chapters 6 to 9) describes the set of computer-aided tools used to compute uncertainty distributions for the environmental impact valuation indicator of process design alternatives. The computation of environmental indicators corresponding to a set of design decisions requires several modeling steps. First, a process model is used to compute mass and energy balances, as well as basic equipment design specifications. This information then needs to be translated into a vector of environmental interventions (e.g. air emissions) associated with each process input and output. For the case of raw materials and services, emissions should include estimates of the emissions associated with upstream processes (life-cycle view). Information about emissions can then be converted into estimates of environmental concentrations and estimates of exposure through the use of multimedia fate, transport and exposure models. Finally, indicators for the contribution of each chemical to each environmental problem of interested can be computed. Aggregation of individual environmental impact category scores into a final indicator is done using weighting factors derived from the preferences of decision-makers or organizations.

Chapter 6 argues that the evaluation of the potential environmental impact of toxic releases should be given high priority within the environmental evaluation of chemical process designs. The chemical industry is responsible (directly or indirectly) for a large fraction of the releases of toxic chemicals to the environment. In addition, the public is more concerned about toxic releases from chemical plants than about other environmental impacts the chemical industry might cause. Available indicators of toxicity potential are reviewed, and it is argued that most of them are inadequate for use in the procedures described in chapters 4 and 5 because they either include too few chemicals, or do not provide information regarding the uncertainty in the indicators. It is widely accepted that risk due to exposure to toxic chemicals is proportional to exposure and toxicity. A spreadsheet-based model of chemical fate, transport and exposure that allows propagation of uncertainties while preserving correlation structure was developed as part of this dissertation. The model is needed to relate emissions to impacts. The human exposure model includes improved models for bioaccumulation through the terrestrial food chain (the most widely used models currently in use have the potential for grossly overestimating terrestrial food chain bioconcentration of chemicals with high octanol-water and octanol-air partition coefficients, since these models are not constrained by mass balances). The fate, transport and exposure models are applied to a data set of 1300 chemicals to identify the model and parametric uncertainties that have the largest impact on the distribution of relative exposures. This analysis provides a roadmap for advancing research in exposure modeling. The chapter also describes the development of a tool for assessing the information content of indicators. This tool is applied to the assessment of the information content of the indicators in EPA's Waste Minimization Prioritization Tool (WMPT). The WMPT assigns toxicity, persistence and bioaccumulation scores to chemicals based on a fence line approach, in which chemicals receive a discrete score of 1, 2 or 3 on each criterion. The EPA adopts this approach in order to be able to combine data of different levels of quality. The example shows that the fence line procedure dilutes the quality of the data to the lowest common denominator, resulting in an indicator with significantly less information content than the one developed in this work using the same underlying data. The chapter closes with a comprehensive assessment of the potential environmental impact of the releases to the environment reported in the Toxics Release Inventory.

Chapter 7 develops the process-by-product input-output life cycle assessment methodology (PIO-LCA) as a way to manage uncertain life-cycle assessment data in a way that enables the generation of uncertain life-cycle impact indicators without sacrificing correlation structure. Life-cycle assessment tools are needed in the context of environmental evaluation of chemical processes in order to take into account the impacts generated by the upstream processes that provide the inputs used by a design. A key feature of the procedure is the transparent and consistent treatment of multiproduct processes and products produced in multiple processes through economic allocation rules.

Chapter 8 shows how economic and environmental valuation models with uncertain parameters can be integrated with the flowsheet models that are the main tool used by chemical process designers today. The deterministic equivalent modeling method (DEMM) is used to generate spreadsheet-based polynomial chaos expansion metamodels of the process flowsheet models. The metamodels capture the impact of uncertainties in physical parameters on process performance, which can be combined with spreadsheet-based economic and environmental valuation models. The resulting combined model can be used for stochastic optimization and sensitivity analysis, enabling the designer to identify the parameters (physical, economic, or environmental) that have the largest impact on the ranking of competing alternatives.

Chapter 9 discusses needs and strategies for managing the available knowledge that is relevant to environmental valuation models. It describes the data model, data sources, and system functions of the database application developed in this project. The chapter closes with recommendations for implementing systems of this kind within organizations, as well as recommendations to public generators and providers of environmental evaluation data (governmental and academic organizations).

1.3 Summary of Contributions

The following list contains the major contributions made to enable designers to include environmental concerns as an explicit objective in their designs.

- Explicit use of uncertainty propagation and uncertainty analysis as a means to cope with partial information regarding environmental impacts.

- Propagation of the uncertainty in relative performance measures as a way to manage the decision uncertainty introduced by large uncertainties in valuation model parameters.
- Development of a method for the propagation of uncertainties in life-cycle impact assessment while preserving correlation structure.
- Analysis of the uncertainties in toxicity indicators.
- Development of an information content tool to rate sets of uncertain indicators in terms of their usefulness to rank alternatives with confidence.
- Development of a tool to identify key parametric and structural uncertainties in models used to derive environmental indicators.
- Refinement of existing models used to assess human exposure to pollutants.
- Extension of the deterministic equivalent modeling method to the generation of polynomial chaos expansion representations of process flowsheet models that are suitable for stochastic optimization
- Demonstration of the application of multivariate copula distributions to derive a compact representation of the results of Monte Carlo simulations involving hundreds or thousands of uncertain parameters while preserving most of the information regarding correlations among the output variables of interest.
- Development of an environmental knowledge management tool to organize uncertain data needed as input to environmental evaluation models.
- Demonstration of the application of the tools developed in this project through well documented case studies.

1.4 Reading guide

The author hopes that this thesis will be of value to present and future chemical process designers who might not be experts on decision analysis or environmental science. In writing this thesis an effort was made to strike a balance the need to reach an expert audience without boring them with background details, and the need to reach a wider audience without

overwhelming them with technical jargon. The following reading list attempts to compensate for any shortcomings in attaining the second goal:

- *Making hard decisions: an introduction to decision analysis*, by Robert T. Clemen (Duxbury Press, 1996 2nd ed.) gives an excellent overview to decision analysis, including many examples. A new version of this book with the title *Making hard decisions with Decision Tools Suite* (Duxbury Press, 2000) contains step-by-step instructions at the end of each chapter for the use of Palisade Corporation's Decision Tools Suite to solve the examples in the text. The Decision Tools Suite was used extensively for uncertainty propagation and uncertainty analysis in this thesis.
- *Uncertainty: A Guide to Dealing with Uncertainty in Quantitative Risk and Policy Analysis*, by M. Granger Morgan and Max Henrion (Cambridge University Press, 1990) is an excellent summary of all aspects related to the incorporation of uncertainty into models of physical and social systems.
- *Environmental Assessment of Products* by Wenzel, Hauschild, and Alting (Chapman & Hall, 1997) provides a very good overview of life cycle assessment and methods to estimate the contributions of chemicals to various environmental impacts
- *Multimedia environmental models: the fugacity approach* by Donald Mackay (Lewis publishers, 1991) provides an excellent overview of multimedia environmental modeling by the creator of the methodology.

Most of the tools developed in this work can be applied outside of the field of chemical engineering. For interested readers who do not have a background in chemical engineering, an introductory chemical process design book such as *Conceptual Design of Chemical Process* by James Douglas (McGraw-Hill, 1988) or *Analysis, Synthesis, and Design of Chemical Processes* by Turton, Bailie, Whiting, and Shaeiwitz (Prentice Hall PTR, 1988) should be sufficient as a source of context-specific information.

Chapter 2 Environmentally Conscious Chemical Process Design¹

con·scious \ 'kän-chəs\ *adj.* [L. conscius, fr. com- with + scire to know] 7. done or acting with critical awareness 8 **a**: likely to notice, consider, or appraise **b**: being concerned or interested **c**: marked by strong feelings or notions.

Webster's Ninth New College dictionary

2.1 Challenges for chemical process design in the 21st century

Chemical manufacturers face many challenges, including global competition and regulatory demands for more benign products and production processes. Environmental issues also determine how society perceives the chemical industry. Images of dangerous pollution, reinforced by data on the generation of hazardous pollutants [1,2] have continued to drive public perception, which in turn has put pressure on governments and regulatory agencies to tighten environmental regulations. Industry has responded to these concerns by developing programs (such as Responsible Care) that establish goals for environmental health, safety, and product stewardship [3]. More than 4,000 companies or facilities around the world have embraced the ISO 14001 environmental management system standard. The standard requires senior management to adopt an environmental policy document that demonstrates commitment to compliance with national laws and regulations, continual improvement, and pollution prevention [4]. While the goals are certainly appropriate, the real problem and opportunity is how to translate them into action.

The enormity of the challenge can be seen in Table 2-1. Even just using material economy as a measure of waste generation there are wide variations across the chemical industry and obviously many opportunities for improvement. Typically the most common way to reduce pollutant emissions has been to add control technology to bring the process into compliance with discharge standards. One consequence of this approach has been the allocation of large amounts of capital to the installation and operation of environmental control equipment (Figure 2-1).

¹ Reprinted, with permission, from J.A. Cano-Ruiz and G.J. McRae, *Annual Review of Energy and the Environment*, Volume 23:499-536. ©1998 by Annual Reviews www.AnnualReviews.org.

While there is a clear need to improve economic and environmental performance there is unfortunately very little operational guidance about how to do much better. For example, consider the list of reference texts shown in Table 2-2. These books, which are currently used in teaching chemical process design, contain little or no mention of environmental issues, the process of decision making involving tradeoffs, or the larger context of the design process itself. At present much of the needed information is scattered throughout the literature. The focus of this review paper is to identify the issues, information sources and approaches to process design that have the potential to lead to improvements in both economic performance and environmental quality.

Table 2-1: *Waste generation in different segments of the chemical industry*²

Industry segment	Product tonnage	Waste generation (kg byproducts/kg product)
Oil Refining	10^6 - 10^8	~0.1
Bulk Chemicals	10^4 - 10^6	<1-5
Fine Chemicals	10^2 - 10^4	5-50
Pharmaceuticals	10^1 - 10^3	25-100+

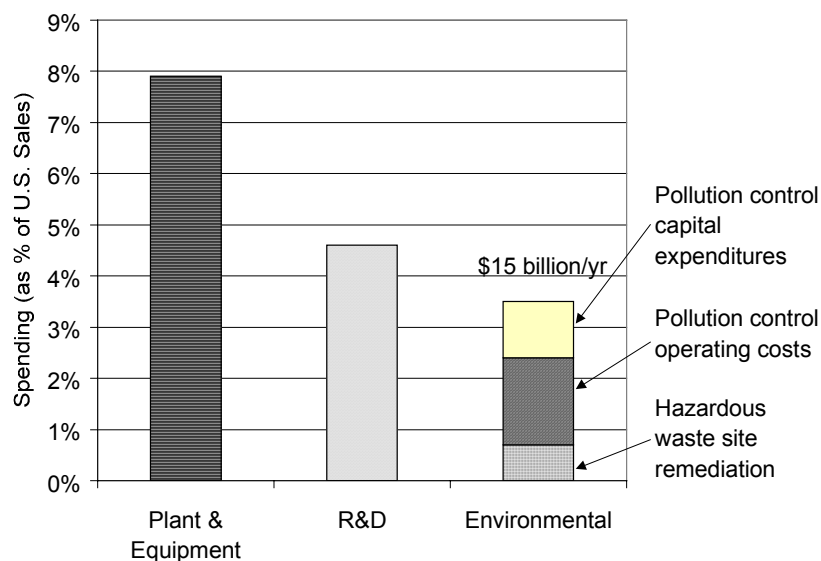


Figure 2-1: *U.S. Chemical Industry environmental expenditures in perspective (1999 data)*³

² Obtained from references [5,6]

³ Data from reference [7]

Table 2-2: Approaches to environmental issues in chemical process design books.

Reference	Treatment of environmental issues
Valle-Riestra: Project Evaluation in the Chemical Processing Industries [8]	States that "the initiative to participate effectively in the struggle to preserve the integrity of the environment must ultimately originate with each engineer's inner conviction, not with externally imposed regulations", but only uses economic criteria for evaluating designs.
Ulrich: A Guide to Chemical Engineering Process Design and Economics [9]	Includes costing data for waste treatment facilities. Otherwise no mention of environmental issues.
Wells & Rose: The Art of Chemical Process Design [10]	Advises the designer to be aware of the environmental constraints that are applicable at the project location.
Douglas: Conceptual Design of Chemical Processes [11]	1-page section stresses the importance of including the cost of meeting environmental constraints in process cost estimates.
Edgar & Himmelblau: Optimization of Chemical Processes [12]	Optimization is restricted to economic objective functions.
Baasel: Preliminary Chemical Engineering Plant Design [13]	43-page chapter on "Pollution and its Abatement" includes a discussion of the issues involved in determining appropriate standards. No methodologies are given for evaluating the environmental merit of a design
Hartmann & Kaplick: Analysis and Synthesis of Chemical Process Systems [14]	Introduction says that "(processes) must scarcely pollute the environment", but methodologies to prevent pollution are not discussed.
Peters & Timmerhaus: Plant Design and Economics for Chemical Engineers, 4 th ed. [15]	Contains a 16-page section on the challenges posed by environmental regulations and on "end-of-pipe" treatment technologies.
Smith: Chemical Process Design [16]	States that "chemical processes will in the future need to be designed as part of an industrial development which retains the capacity of ecosystems to support industrial activity and life." Includes a chapter on waste minimization and a chapter on effluent treatment. Includes many ideas and examples for decreasing waste generation, but does not include environmental evaluation methodologies.
Ludwig: Applied Process Design for Chemical and Petrochemical Plants [17]	Environmental issues are not mentioned.
Woods: Process Design and Engineering Practice [18]	The single reference to environmental issues says that "the equipment must fit into the environment safely."
Perry's Chemical Engineer's Handbook, 7 th ed. [19]	111-page chapter on waste management has an 8-page section on pollution prevention.
Biegler, Grossmann & Westerberg: Systematic Methods of Chemical Process Design [20]	Paragraph on environmental issues states that "environmental concerns involve satisfying the very large number of regulations the government imposes on the operation of a process."
Turton <i>et al.</i>: Analysis, Synthesis, and Design of Chemical Processes [21]	Includes data on waste treatment and disposal costs. Adds an "environmental control block" to the generic block flow process diagram. Advocates pollution prevention over "end-of-pipe" treatment alternatives. Includes 19-page chapter on "Health, Safety, and the Environment". Mentions the pollution prevention hierarchy and life-cycle analysis, but does not give specific guidance, methodologies or examples.

2.2 The design process

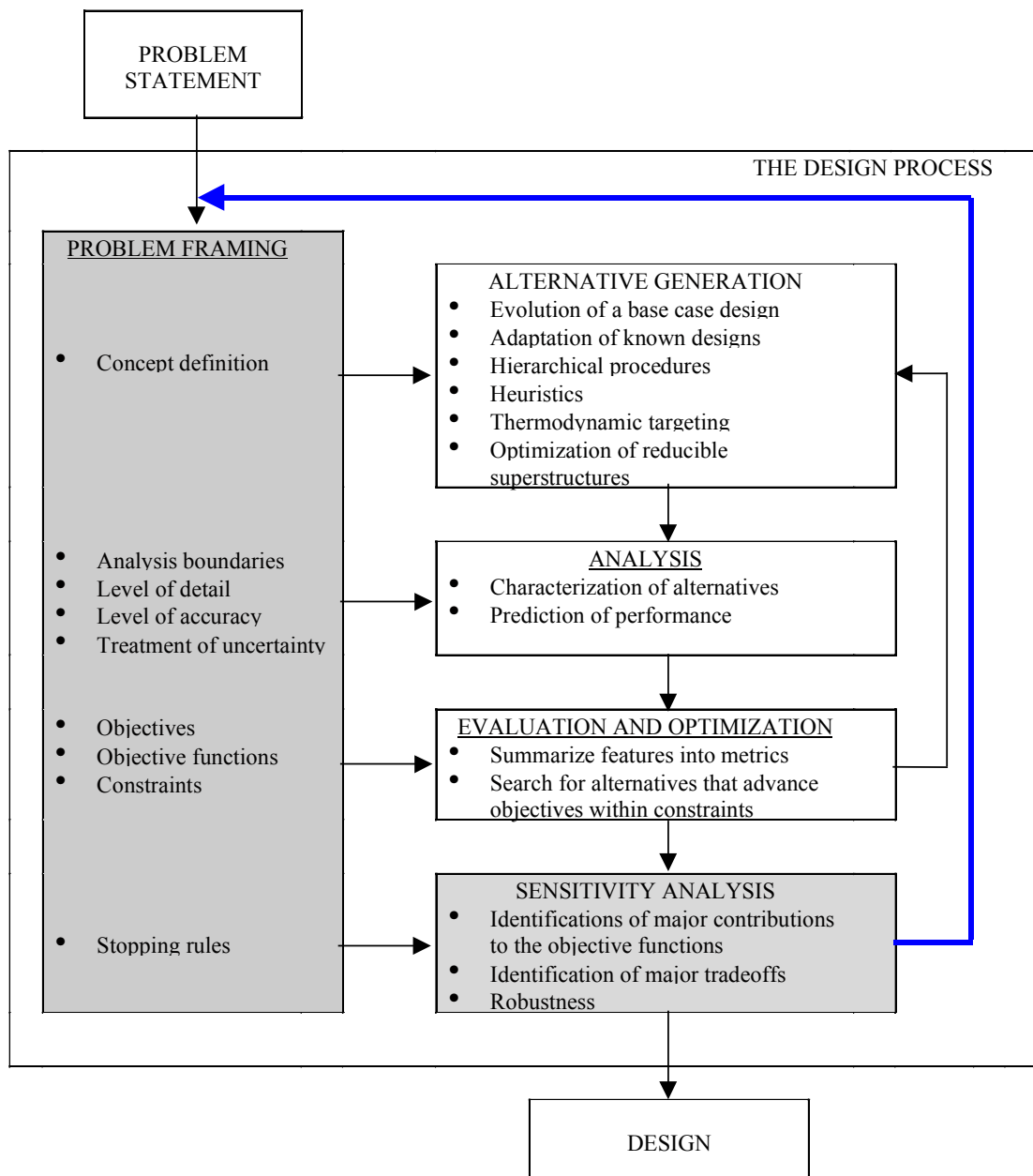
Design is a complex activity [22]. It involves accepting as input an abstract description of the desires of an organization and delivering a detailed description of a concrete product, process or system that will satisfy those desires. The activity is well characterized as a decision process, involving many decision-makers and multiple levels of detail. Figure 2-2 gives a flow diagram of the design activity. The design cycle is composed of all the discrete steps shown in the figure. Similar diagrams have been proposed elsewhere (e.g. [20,23]).

Design starts with problem framing. Its critical importance in determining the outcome of the design process is often overlooked. Design problems are rarely fully specified. Along the path from receiving a problem statement to delivering a completed design, design teams make decisions about concept definition, scope of analysis, design objectives, constraints, evaluation criteria, and stopping rules. Often framing decisions are made implicitly, by following available precedent. In a recent paper [24], Sargent recognizes the role of problem framing by distinguishing between performance models (those used in the analysis stage of the cycle), and valuation models (those used for alternative evaluation).

Once the design problem has been properly specified, the next step is the *generation of alternatives*. There are many different methods for generating chemical process design alternatives, including the application of existing design concepts and the generation of new ones from first principles. Since the time available to complete a design project is often very limited, there is a tradeoff between the number of alternatives that are explored and the level of detail with which they can be analyzed. *Systematic alternative generation* tools attempt to reduce the severity of this tradeoff, by allowing a large number of alternatives to be generated and evaluated simultaneously.

After alternatives have been generated, the next step is the *analysis of alternatives*. In this step, engineering analysis (usually starting with mass and energy balances) is applied to each alternative generated to make predictions about the expected performance of the system. The result of this step might be a list of the inputs and outputs of the process, including the flow rate, composition, pressure, temperature and physical state of all material streams in the process, as well as the energy consumption rate from various sources. Other useful information concerns

the stocks of materials in the process, as well as other information related to the sizing of the equipment units.



Given a problem statement, the design work flows according to this diagram. Each box in the diagram corresponds to a section of this chapter in which approaches to the incorporation of environmental objectives to each step of the design cycle are discussed. Items highlighted are often not recognized explicitly as elements of chemical process design

Figure 2-2: The design process.

The analysis step will produce a large number of information elements for each alternative analyzed. In the *evaluation* step, this information is summarized into indicators of performance that can be used to assess whether the requirements specified during the objective formulation step have been met, and the extent to which the design objectives have been advanced. These indicators typically include economic indicators, such as capital investment required and operating cost, but should also include indicators of safety and environmental performance. The evaluation step ends with a ranking of alternatives according to their overall level of attractiveness.

Process design is iterative. Before returning to the beginning of the design cycle, a designer must examine the results obtained at the evaluation stage to identify opportunities for improvement. This can be done at the sensitivity analysis stage. If the design team concludes that there are no significant remaining opportunities for improvement, then the work stops. Otherwise, an additional iteration on the design cycle is undertaken. Iterations might involve generating additional alternatives, or modifying the framing of the problem (for example, by deciding to carry out more detailed analysis). There is a strong interaction between alternative generation, analysis, and evaluation, as depicted in Figure 2-2 by the inner feedback loop connecting these three activities.

The various sections of this chapter organize the relevant literature in terms of the steps of the design cycle. When a particular design procedure contains elements relevant to more than one step of the design cycle, we have chosen to mention it only once, in the first relevant section of the review. Papers have been selected for their relevance to the design of chemical processes when avoiding environmental damage is one of the objectives of the design. Although this review focuses on process design, we must acknowledge that it is not worth investing considerable effort in designing an environmentally benign process for the manufacture of an environmentally hazardous chemical for which the intended use is dissipative (e.g. the well known cases of tetraethyl lead and CFCs). A relatively recent American Chemical Society symposium-based book is a good pointer to the literature on the environmentally conscious design of chemical products [25].

2.3 Framing of the design problem with the environment as an objective

A design problem may be represented by the mathematical program:

$$\begin{aligned} & \text{Max} && P(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta}) \\ & && \mathbf{d}, \mathbf{z} \\ \text{s.t.} &&& \mathbf{h}(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta}) = \mathbf{0} &&& \text{(Problem DP)} \\ &&& \mathbf{g}(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta}) \leq \mathbf{b} \\ &&& \mathbf{d} \in \mathbf{D}, \mathbf{z} \in \mathbf{Z} \end{aligned}$$

where \mathbf{d} , \mathbf{z} are the vectors of design and control variables, respectively, $\boldsymbol{\theta}$ is the vector of uncertain parameters, $\mathbf{h}(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta})$ is the vector of equations defining the model of the process, $P(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta})$ is the objective function (which might be a function of multiple objectives), $\mathbf{g}(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta})$ is the vector of equations defining the constraints on the process, \mathbf{b} is the vector of parameters giving the upper bound of the constraint equations, and \mathbf{D} and \mathbf{Z} are the domains over which the design and control variables are defined.

Solving problem DP is only one of the activities involved in the design process. Prior to deciding on the values of the \mathbf{d} variables (which can be done by a computer given enough power and appropriate algorithms), the designer must make decisions regarding the choice of design objectives (i.e. what objective functions to use and what constraints to include), the set of design alternatives to consider (i.e. the choice of decision variables to include and their domain, as well as the logical constraints relating the variables), and the scope and degree of accuracy of the model representing the problem (i.e. the functional form of the system equations). The set of all decisions made in the formulation of the optimization problem is what we call “problem framing”. The design process involves a series of iterations in which a different version of problem DP is solved until either (a) the designer is satisfied with the design or (b) the time allocated to the design problem has been exhausted. Analysis carried out at each iteration around the cycle gives the designer information that can be used in the formulation of the next version of the design problem.

Figure 2-3 shows our view of the evolution of the framing of chemical process design problems over the last 40 years. Initially, chemical process design was limited to the design of the core reaction and separation processes. In response to the 1970s energy crisis, the domain of

chemical process design was increased to include the interaction of the core process with the utility systems. Methods for heat and power integration were developed and applied to industrial problems, and today most chemical process design books include at least one chapter on heat integration or heat exchange network design. As the cost of complying with environmental regulations increased, chemical process designers became aware of the need to take waste generation into account in their work. Academia was slower to internalize this need, and often ignored the generation of waste in the formulation of process synthesis problems. A typical example of this is a version of the second process diagram in Figure 2-3, published in a 1985 review paper of mathematical programming approaches to process synthesis [26]. In that diagram, there are not outputs from the system other than the desired products.

The third panel of Figure 2-3 summarizes four emerging trends in the evolution of problem framing with respect to the consideration of environmental impacts:

- 1) Inclusion of the waste treatment infrastructure in the analysis boundaries Blau [27] estimated that up to 50% of the capital for new processes is devoted to handling wastes. As a result, industry is incorporating waste handling in the scope of process synthesis activities, and making efforts to design processes that can use existing waste processing infrastructure, avoiding the need to invest in new treatment facilities.
- 2) Materials integration The success of energy integration techniques in reducing operating and capital costs [28] raised the question of whether similar savings can be achieved through materials integration. The potential savings might be overlooked if the boundaries of analysis are drawn too tightly during problem framing. Mizsey [29] has suggested that process design should include efforts to identify potential matches between wastes (material sources) and raw material requirements (material sinks) across processes and plants within a company. El-Halwagi and other researchers are developing materials integration techniques as a cost-effective way of reducing pollutant emissions [30].

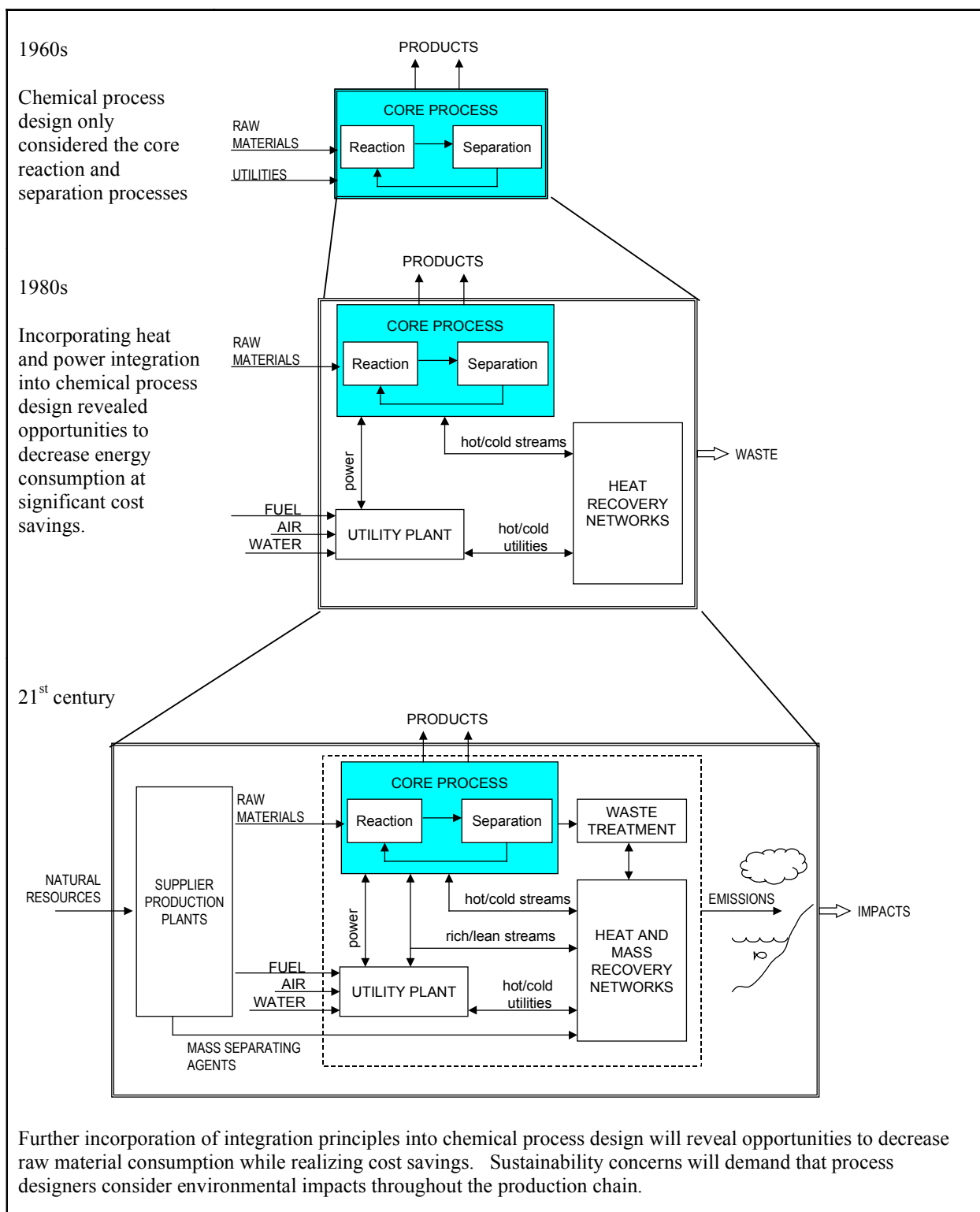


Figure 2-3: Evolution in the framing of the chemical process synthesis problem.

- 3) Life cycle analysis Life-cycle analysis (also referred to as life-cycle assessment) is a framework for considering the environmental impacts associated with every stage in the life cycle of a product, from raw materials production to final disposal. The consequences of ignoring impacts over the entire life-cycle can be illustrated by an example taken from the chemical engineering literature: In one of the first attempts to integrate environmental objectives in the design of chemical processes, Grossmann and coworkers considered the problem of synthesizing industrial chemical complexes with the two basic objectives of maximizing net present value and minimizing the toxicity of the material flows in the system [31]. The configuration they found when minimizing toxicity was one in which the production of all intermediates was carried out by suppliers. Even though the flows of toxic materials decreases within the limits of the complex under this design, the overall environmental impact could increase, if the production processes of the suppliers are more polluting than those considered by the designers of the chemical complex, or if the supplier plants were located in more sensitive areas. Academia has recently applied life-cycle thinking to chemical process synthesis problems [32-36], and there is growing interest in its use in industry, particularly in Europe. Bretz & Fankhauser [37] have published an account of the routine use of life cycle assessment as part of chemical process design at Ciba Specialty Chemicals. The company developed a specialized computer system for integrating life-cycle inventory data for more than 4,700 raw materials and 1,700 products.
- 4) Shift in emphasis from effluent concentrations to environmental impacts Most environmental regulations are written in terms of effluent concentration standards. Smith and Delaby [38] have noted that regulations in terms of concentrations do not give a real account of the actual emissions. Furthermore, design problems framed as “minimize cost subject to not exceeding allowable concentration limits” can result in solutions where dilution of waste streams is used to meet the standard without changing the amount of pollutants released to the environment [39]. Limiting effluent concentrations is only a means to achieve the end objective of improving environmental quality [40]. Sharratt & Kiperstok have recently coupled environmental receptor models to the mass exchange network synthesis problem in order to pose the environmental constraint as an environmental quality standard, instead of as an effluent concentration standard [41,42]. Industry has also applied this idea: Amoco used

exposure to benzene in the vicinity of its Yorktown refinery (determined through environmental modeling) as a criterion to rank pollution prevention projects [43,44].

2.4 Approaches to the generation of environmentally superior design alternatives

The design of chemical processes with lower environmental impact starts with an understanding of the sources of emissions and waste in chemical processes. Figure 2-4 (adapted from [45]) is an abstraction of a chemical process, in which raw materials are processed into desired products. Byproducts might be generated, either as a result of the desired reaction stoichiometry, or as the consequence of undesired secondary reactions (selectivity losses). Unwanted byproducts might also be generated in the separation system (e.g. by polymerization reactions in distillation column reboilers). Purge streams are necessary to prevent the accumulation of trace components in recycle streams, unless these components can exit the process in the product or byproduct streams. Other materials introduced to the process include reaction agents (e.g. catalysts, solvents, diluents, heat carriers) and separation agents (e.g. solvents, adsorbents, entrainers), which contribute to waste generation since they degrade with time and may exit the process with the purge or byproduct streams. Leaks (known in the literature as “fugitive emissions”) might occur anywhere in the system. In addition, emissions are produced in the systems that provide utilities to the process.

The term “zero-avoidable pollution” or ZAP has been coined to refer to the byproduct waste generated in processes in which all raw materials, reaction agents, and separation agents are recycled with 100% efficiency [46]. It is worth noting that ZAP designs are not necessarily designs with minimum environmental impact. There are two reasons for this: first, separation and recycling require energy, and there are emissions associated with the supply of energy to a process (e.g. emissions from fuel combustion); second, the quantity and composition of byproduct waste generated in a ZAP design can be changed by changing the reaction path or by changing the design of the reactor network. Examples of alternative “green” synthesis pathways to a large number of chemicals have been reported [47,48].

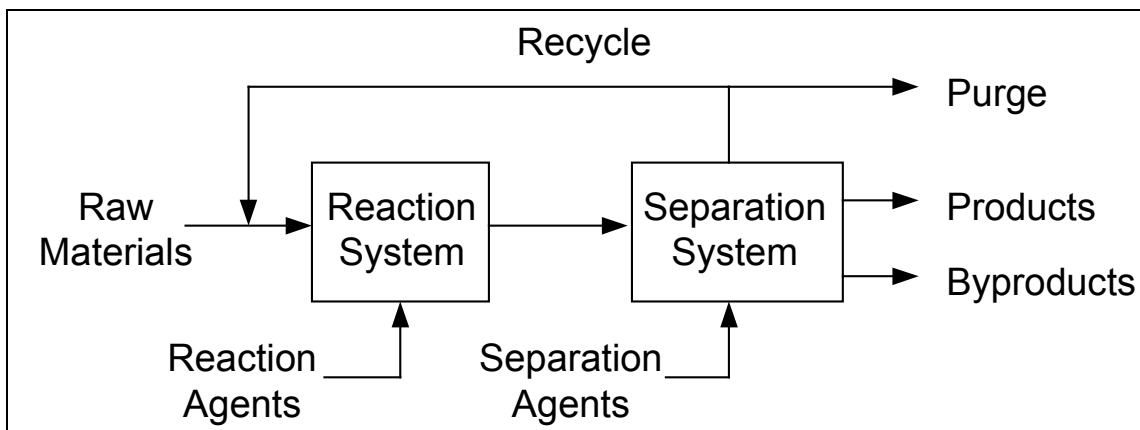


Figure 2-4: Material flows in a chemical process

The goal of environmentally conscious alternative generation is to produce designs that:

- have high economic potential
- have high conversion of raw materials into desired products,
- use energy efficiently, and
- avoid the release of hazardous substances to the environment.

The key to the discovery of such designs is process integration (energy integration, materials integration, and processing task integration). Pollution from a chemical process can be viewed as the consequence of using the environment as a sink for unwanted byproducts and unrecovered materials. Using nonrenewable resources as a source of raw materials for a process raises issues of sustainability. These observations imply that design alternatives that increase the use of process units and streams as material sources and sinks might have lower environmental impact. There are well-established energy integration techniques that reduce consumption of utilities by using process streams as sources and sinks of heat [28]. The use of processing task integration in reactive distillation processes has been shown to reduce costs, energy use, and emissions [49,50].

Framing of the problem influences the range of alternatives that may be considered, through the decisions made during concept definition. A narrow concept definition might fix prematurely the process chemistry, or limit the type of unit operations considered (e.g. it might restrict the design team to use conventional, well-proven technologies).

Reviews of methodologies to generate design alternatives with pollution prevention as an objective have been given by Manousiathakis & Allen [51], Rossiter & Kumana [52], and Spriggs [22,53]. The classification of approaches that follows is partly based on the discussion presented in these references.

2.4.1 Use of documented pollution prevention solutions as a source of design alternatives

Ideas for reducing waste generation in chemical processes have been published in professional journals [54-63]. These ideas range from general questions intended to elicit ideas to very specific process and equipment changes. Two particularly comprehensive collections of ideas have been assembled by Nelson [64], and Smith & Petela [65-70]. Englehardt compiled a list of references to pollution prevention technologies and classified them according to their placement in the pollution prevention hierarchy and the function of the industrial hazardous materials involved [71]. Government agencies compile and publish ideas for preventing pollution in specific industry sectors from time to time (e.g. [72-75]). Electronic databases have been created to enable designers to search for solutions that are most relevant to their applications [76,77].

2.4.2 Design by case study

Under this approach, process models are used to simulate the performance of an existing process or a base case design. The design team next thinks of process modifications that might improve system performance. The process model is modified to incorporate the proposed changes, and simulations are carried out to check whether the desired performance improvements are realized in the model. With the availability of process simulators (e.g. Aspen Plus), this approach to process design has become widespread. Examples of applications to pollution prevention are given in [78-88]. Process modifications explored by this technique are usually incremental in nature.

2.4.3 Hierarchical design approaches and other methods of structured thinking

Douglas [89] applied his hierarchical process synthesis procedure to the problem of identifying potential pollution problems and identifying process alternatives that can be used to

eliminate these problems. The recommendations obtained by his procedure are fairly general (e.g. “change the chemistry”, “change the solvent”, “look for a different separation system”) and serve as a starting point for the search of design alternatives. The procedure has been used to classify process improvements reported in the literature according to the sources of waste and the waste minimization techniques applied [90]. Rossiter and coworkers built upon the procedure by adding more key questions at each decision level, and used it to generate attractive alternatives for reducing waste generation and emissions from the fluid catalytic cracking unit at Amoco’s Yorktown, VA, refinery [91]. More recently, Douglas expanded his set of synthesis rules for the design of separation system flowsheets for mixtures of vapors, organic liquids, aqueous liquids, and solids [92]. The rules acknowledge explicitly the generation of waste streams and provide some guidance for addressing the pollution problems arising from these streams.

2.4.4 Pinch analysis and other targeting techniques

Pinch technology (birefly described below) was first developed as a tool for reducing the capital and energy costs of a processing plant through the design of heat exchanger networks. It is most often used to design the heat recovery network of a process, once the core reaction and separation processes have been defined. Pinch technology recognizes that the majority of chemical processes contain heat sources (hot process streams that need to be cooled) and sinks (cold streams that need to be heated). Instead of using utilities (e.g. steam, cooling water) to bring all process streams to their desired temperatures, pinch technology exploits the heat sources and sinks in the process before using utilities, thus reducing the operating cost of a design. A key feature of the pinch design method is that minimum utility consumption targets and approximate capital costs of the associated heat exchanger network can be established prior to the development of a design. Another key feature is its use of diagrams to identify integration opportunities within a process, a plant, or a total site. A review of the state of the art in pinch analysis up to 1994 is given in [28]. Buehner and Rossiter have reviewed the application of pinch analysis to waste minimization problems [93]. Reducing energy consumption in a plant can be translated into reduced flue gas emissions (for a given fuel and combustion technology type), since less fuel needs to be burned [94]. BASF reported the results of an energy efficiency campaign undertaken at their Ludwigshafen plant in the early 1980s [95]. Their efforts resulted

in significant reductions in the generation of CO₂, SO₂, NO_x, CO, ash, and wastewater, despite increased production levels.

Minimizing energy consumption might not always result in minimizing the environmental impact of utility systems. Smith and Delaby argue that the established methods to target the minimum energy consumption for a given process do not necessarily give insights about the emissions of combustion products associated with supplying the heat and power needed by the process [38]. They argue that considering global emissions (emissions generated by fuel combustion on-site at furnaces, boilers, and gas turbines and off site at power generation plants) gives a broader view of the pollution problem and is the view that should be universally adopted.

Many separation processes are driven by heat inputs (e.g. distillation, evaporation) or by heat removal (condensation, crystallization). When such processes are used to recover materials from waste streams, thermal pinch analysis can be used to minimize the cost and emissions associated with the separation. Smith & Delaby have given examples where energy savings are achieved by integrating materials recovery and waste treatment units with the rest of the process [94]. Richburg & El-Halwagi developed a short-cut method for the cost-optimal design of condensation networks for the recovery of volatile organic compounds from air, based on pinch analysis concepts [96].

El-Halwagi & Manousiathakis exploited the analogy between mass and heat transfer to develop the concept of mass exchange network synthesis, based on the pinch method for heat exchanger network synthesis [97]. They developed tools analogous to those used in thermal pinch analysis (composition interval diagram, composite curves, grid diagram) and applied them to a sample problem. A mass exchanger can be any direct-contact countercurrent mass transfer operation, such as absorption, adsorption, liquid-liquid extraction, ion exchange, leaching, and stripping [30]. As applied to pollution prevention, the goal of mass exchange networks is to transfer species that are potential pollutants in effluent streams to streams in which they might have positive value [50]. The idea of matching material sources and sinks has been further elaborated by El-Halwagi and coworkers in the concept of waste-interception networks [98]. The main goal of these networks is to provide selective interception and rerouting of undesirable

species that would otherwise exit a process to those parts of the process that can act as sinks for these species.

Wang & Smith have developed a pinch design methodology for wastewater minimization, using the more general mass exchange network framework as a basis [99,100]. Processes that use water are represented as limiting water profiles in a concentration versus mass load diagram, which is analogous to the temperature versus enthalpy diagram used in the design of heat exchanger networks. The limiting water profile for a process represents the minimum amount of water with the highest possible concentration of contaminants that would be able to perform the task required in that process, and is not necessarily the actual water profile that will be used in the final design. Pinch analysis techniques are then used to establish targets for minimum freshwater use (enabling reuse of water in processes that tolerate higher contaminant concentrations) and to design networks consistent with those targets. The methodology includes the possibility of water regeneration (treatment) and recycling, and can be used in problems that involve multiple contaminants. An extension has been developed that makes the methodology applicable to batch processes [101]. The same framework was used to develop a methodology for the design of distributed effluent treatment systems that seeks to minimize the cost of achieving specified concentrations in the wastewater effluent of a site by segregating wastewater streams, combining them when economies of scale are attainable, and matching streams to treatment processes [102]. Analysis at Linnhoff March have developed a similar methodology, trademarked WaterPinch [103]. This method plots water sources and demands in a purity versus water mass flow rate diagram. Composite curves are developed for the sources and the demands, and the pinch point is located. Freshwater and wastewater targets can be read directly from the diagram, once the composite curves have been brought together at the pinch point. Pinch analysis techniques have been applied to industrial wastewater minimization problems [104-106].

Researchers have developed other targeting approaches for minimizing waste generation in the core reaction and separation processes. Flower and coworkers have developed tools for establishing mass-efficiency targets for reaction and separation systems [107,108]. By using the concept of the attainable region for reactors and the assumption of sharp splits for separators, they develop lower bounds on the mass of waste byproducts that can be obtained for a given reaction scheme. Ahmad & Barton presented a methodology for the automatic targeting of

maximum feasible solvent recovery from streams with an arbitrary number of components by batch distillation [109].

2.4.5 Mathematical programming

The mathematical programming approach to process synthesis optimizes a reducible superstructure to find the best combination of process units that achieve the design task. Manousiathakis & Allen reviewed several process synthesis concepts and outlined their importance for waste minimization [51]. Table 2-3 summarizes their task definitions and gives examples of the application of mathematical programming to waste minimization under each task.

Table 2-3: Process synthesis tasks and references to examples of their application to waste minimization problems using the mathematical programming approach.

Task	Task Definition [51]	Examples
Material Synthesis	Given a set of desirable properties, identify a material that possesses these properties.	[36,110-113]
Reaction Path Synthesis	Identify a reaction path that employs substances from a set of permissible chemicals to yield a desired product (meeting economic, thermodynamic and kinetic constraints).	[112,114-116]
Reactor Network Synthesis	Given a reaction mechanism identify a network of reactors in which these reactions transform raw materials to products at optimum venture cost.	[117]
Separator Network Synthesis	Given a set of multicomponent feed streams, identify a network of separators that can yield a set of desired product streams at a minimum venture cost.	[118-123]
Recycle/Reuse Network Synthesis	Given a set of multicomponent waste streams, identify a network of separators that allows the recycle of these waste streams (meeting quality specifications) at minimum venture cost.	[98]
Heat Exchanger Network Synthesis	Given a set of hot and a set of cold streams identify a network of heat exchanger units that can transfer heat from the hot to the cold streams at minimum venture cost.	[124]
Mass Exchanger Network Synthesis	Given a set of rich streams and a set of lean streams, synthesize a network of mass exchange units that can transfer certain species from the rich streams to the lean streams at minimum venture cost.	[39,97,119,125-132]
Total Flowsheet Synthesis	Given a reaction path that transforms new materials to desired products identify a network of process units that accomplishes the transformation at minimum venture cost.	[32,80,133,134]

There are a large number of published mathematical programming formulations of the problem of synthesizing recycle/reuse networks for waste reduction. Although direct contact mass exchangers are used in the majority of these formulations [39,97,119,125-131,135-137], other unit operations have also been used, including condensers [118,121-123], and pressure-driven membrane units [119,120,138]. The scope of applications include: single [39,118,119,121,123,125-129,137,138] or multiple [122,131] transferable pollutants; linear [39,119,125,126,129,131,137], convex [127], or general nonlinear [128] equilibrium functions; fixed [118,121-123,125-129,131,138] or variable (within bounds) [39,120,130,137] recovery targets; physical [39,118-123,125,126,130,131,135,137,138] or chemically reactive [127,128] separations; inclusion of mass separating agent regeneration unit operations in the network [126], and inclusion of flexibility constraints [137].

A common feature in these formulations is the use of cost minimization as the objective function in the optimization. Earlier formulations used a two-stage optimization procedure [39,118,125-129,131]. First, operating cost minimization is used to establish minimum utility consumption targets. This is followed by the solution of a mixed integer linear programming transshipment problem to design a network with the minimum number of units that meets the minimum operating cost targets. More recent formulations use a total cost minimization approach, which include capital costs in the objective function [120-122,129,130,138]. Both types of objective functions include only the cost side of the profit equation. As the value of recovered materials is not included, opportunities to improve the economic performance of these networks by increasing material recovery beyond targets specified in the framing of the optimization problem might be overlooked.

2.4.6 Expert systems and other Artificial Intelligence approaches

Huang and colleagues have listed features of the problem of generating waste minimization alternatives that make knowledge-based expert systems and fuzzy logic attractive tools for designers [132,139]:

- Incorporating environmental objectives into process design requires knowledge from many disciplines; thus the task is knowledge-intensive.

- The generation of waste minimization options is heavily dependent on experience. Quantitative descriptions of the processes generating waste are often not available; hence, qualitative information needs to be incorporated in the analysis.
- The available information pertaining to the environmental impact of a process is often uncertain, imprecise, incomplete, and qualitative in the design stage.
- A large number of regulations and strategies for pollution prevention might be expressed as rules.

One of the major barriers to process integration is the perception that highly integrated processes are very difficult to control. Huang & Fan have addressed this problem by developing a hybrid intelligent design system that improves the controllability of heat and mass exchanger networks by choosing stream matches that improve an index of controllability while keeping the operating cost of the network at its minimum [136]. Their system combines pinch analysis for the generation of targets with an expert system, fuzzy logic, and neural networks to assign stream matches.

Computer-assisted systems for the rapid generation of alternative synthesis paths to a desired chemical are available (e.g. SYNGEN, LHASA). Their use to support pollution prevention initiatives has been explored by government agencies [140] and as teaching aides [141].

The EnviroCAD system has been developed at the New Jersey Institute of Technology as an extension of BioDesigner, a program for the design and evaluation of integrated biochemical processes [142]. The system takes as input data a set of waste streams and recommends alternatives for waste recovery and recycling, treatment and disposal based on three knowledge bases. An expert system for generating feasible treatment trains for waste streams has also been embedded in the Process_Assesor module of the BatchDesign_Kit under development at MIT [46,143,144]. The expert system is based on heuristic rules containing knowledge of regulations and treatment technologies.

2.5 Analysis of design alternatives

The function of the analysis step is to generate the information elements needed to evaluate the merit of a design. A challenge for designers interested in incorporating

environmental considerations into their work is that many of the information elements needed to evaluate the environmental impact of a proposed design alternative are not normally generated in the analysis stage when economic performance is the only design objective. Consider the case of fugitive emissions. Fugitive emissions are losses of process fluids through leaks in equipment. Although these losses are strongly influenced by equipment choices and operating procedures, decisions made at the conceptual design stage (e.g. temperature, pressure and flow rate of recycle streams) are also important contributing factors. Fugitive emissions are usually too small to impact the process mass and energy balances (typically 500-1500 g/Mg of product) [50], but in some plants it has been estimated that fugitive emissions are responsible for 70-90% of the environmental releases of hazardous substances [145]. Since the value of the materials lost through fugitive emissions can be neglected in the economic evaluation of a process, no effort is made during process design to estimate the magnitude of fugitive emission losses. However, such estimates might be very important in determining the environmental merit of competing design alternatives. Another example is that of selectivity losses in reactors. From an economic perspective, all that is needed during the analysis stage is an estimate of the amount of raw materials converted to unwanted byproducts, and an estimate of the resources needed to separate the unwanted byproducts from the desired product. Estimation of the amounts of individual byproducts is usually not required. However, two processes with the same selectivity to the desired product might have very different environmental impact, depending on the composition of the unwanted byproduct stream. Thus, the set of chemical species considered in the analysis might have to be expanded beyond the set used when economic performance is the only evaluation criterion.

Not all mass and energy balances that are relevant for estimating the pollutant emissions from a process are included in the standard flowsheets used during process design. For example, although energy consumption is typically quantified, the emissions associated with the generation of electricity or steam of various grades typically are not. In addition, environmental concentrations of released pollutants might be necessary for a proper evaluation of the potential environmental impact of a design. In this case, the material balances used to evaluate the process need to be expanded to include the fate and transport of environmentally sensitive species.

It has been noted [142,146] that commercial process simulators are still very deficient in predicting chemical species concentrations in dilute process effluent or waste streams. Unit

operation models for innovative separation technologies (e.g. membrane separations) and waste treatment equipment are not included in commercial process simulators, and are therefore usually not included in conceptual process designs. Farag and colleagues described the structure of models of pollution control and waste treatment processes they developed using the Aspen Plus simulator [147]. They noted that a challenge in the development of these models is that they often involve the handling of types of materials that are not well characterized.

2.6 Approaches to the evaluation of design alternatives

The central question in process evaluation within an environmentally conscious design framework is how to evaluate design alternatives from an environmental perspective. A related question is how to balance environmental objectives with other design objectives.

Problem framing has a direct impact on this step of the design cycle. When the problem is framed, decisions are made with respect to objectives that the design should advance, and in particular, about the objective functions that will be used to translate the data produced during the analysis step into aggregate metrics that can be used to optimize and rank design alternatives.

A quantitative evaluation of a process flowsheet involves summarizing the information generated during the analysis stage of design into a few metrics that can be used to optimize and rank design alternatives. An example of a metric used for economic evaluation is the net present value [15]. It allows a design team to summarize into a single number information regarding production and consumption of materials and utilities, as well as design specifications for equipment. The additional information needed is unit prices for materials and utilities, correlations that relate equipment design specifications to their installed cost, and the discount rate used by the firm to make tradeoffs between capital spent in the present and future cash flows.

In contrast to the calculation of net present value, where all the additional information needed to summarize flowsheet information into a single metric can be obtained from company databases, market data, or vendors, no such information is available to chemical process designers to allow the computation of an overall widely-accepted index of environmental performance. There are three main reasons for this:

- 1) Relevant properties of chemicals (e.g. toxicity, environmental degradation constants) are not readily available in the tools commonly used by chemical engineers (process simulators, chemical process design handbooks). The properties have not been measured for a large number of chemicals, and the measurements that have been made frequently show wide ranges of variation. Although structure-activity relationship tools exist for estimating the toxicity of chemicals for which biological assays are not available [148], the accuracy of their predictions needs much improvement.
- 2) With the exception of environmental problems that are global in nature (e.g. ozone layer depletion and greenhouse gas concentration increases), location-specific knowledge is needed to estimate potential environmental impacts. This is particularly challenging when trying to estimate the environmental impact of the production of inputs obtained from external suppliers.
- 3) People differ in the importance they assign to various environmental impacts. This is not a matter of disagreement about facts, but of differences in values.

2.6.1 Environmental concerns as constraints on economic optimization

The most common approach to incorporate environmental considerations in chemical process design has been to treat them as constraints: upper limits are set for pollutant flows or concentrations in waste streams (based on regulatory requirements), and designs that satisfy these constraints are evaluated in terms of economic indicators, such as net present value [80], annualized profit [134,149], payback period [53], operating margin [79,115], total annualized cost [35,36,96,100,102,118-122,125,130,135,137,138,150-153], or operating cost [39,51,96-98,122,126-128,131,139]. The search for economically attractive waste minimization design alternatives is advanced by including the cost of waste treatment and disposal in the economic objective function [79-81,89]. The costs associated with the retirement of process equipment and site restoration at the end of the useful life of a process have usually not been included in the analysis.

Surprisingly, the value of products, byproducts and recovered materials is often not included in the objective function, as the majority of authors have chosen to use cost minimization as their economic objective. Depending on how the optimization problem is

framed, this might lead to overlooking opportunities to increase the profitability of a design by recovering materials from waste streams beyond the level required by compliance.

The main problem with incorporating environmental considerations as constraints on the flow or concentration of chemical species in particular waste streams is that the proposed solutions might not address the underlying environmental concern. This is illustrated by the examples given in a couple of papers addressing the synthesis of membrane separation networks for waste reduction [119,138]. The proposed networks split an aqueous waste stream into two streams, one of which has a pollutant concentration that is low enough to meet the specified discharge limits. However, neither the fate nor the treatment cost of the concentrated stream are considered in the solution.

A variation of this approach is to optimize for economic performance while setting environmental objectives in terms of environmental quality standards in a particular receptor (e.g. a water body or the airshed in an urban area) [41,42]. Although this approach presents opportunities to achieve the desired level of environmental protection at lower social cost, it poses challenges to individual firms, since their allowable emissions or discharges would be affected by those of other firms sharing the same receptor.

2.6.2 Environmental concerns as objectives

Instead of treating environmental considerations as constraints, designers can choose to treat them as an objective to be balanced against other objectives in the design [31-33,35,36,46,86,117,124,134,149,153,154]. This requires establishing environmental performance measures. Several authors [155-157] have noted that the lack of metrics to support objective environmental assessments is one of the main barriers to developing effective pollution prevention and design for the environment approaches. Linninger and coworkers have pointed out that the lack of a general binding value system for environmental impact assessment makes it very difficult to evaluate the environmental impact of a design [144]. Given the diversity of prevailing views regarding the environment, such a binding value system might never become available.

MINIMIZATION OF EMISSIONS OF POLLUTANTS OF CONCERN

In cases where the emission of a single pollutant is the most important environmental concern affecting a design, the mass of pollutant released to the environment can be used as an indicator of environmental impact. Such an approach has been used to study the tradeoff between control cost and emissions of nitrogen oxides from a power plant [158] and a refinery [151]. Some authors have chosen to use carbon dioxide emissions as a measure of flue gas emissions from power generation [38], or associated with utilities used in chemical production [81].

When more than one chemical is a source of environmental concern, environmental evaluation becomes more complicated. One approach is to use the release inventory directly as a set of indicators. This might be an acceptable solution when only a few pollutants are involved. As an example, Chang & Hwang use emissions of CO_x, SO_x, and NO_x as three independent environmental objectives to be minimized in the design of utility systems for chemical plants [124]. The approach becomes unmanageable when upstream emissions are considered, as it is done in life-cycle analysis. It is not uncommon for life-cycle inventories to contain releases and discharges of dozens of different species. In such cases it is clearly necessary to summarize the information into a small number of indicators that can be used to optimize and rank alternatives.

MINIMIZATION OF MASS OF WASTE GENERATED

It has been argued that mass is the only consistent and universal basis for aggregating waste streams [83]. Indeed, indicators based on the mass of waste generated are the ones most commonly used in the chemical engineering literature. Examples of indicators used are: the total mass of waste generated [109,117,134,149,159], the mass of waste generated per unit mass of product [5,6,82,83,86-88,160-162], and the mass of waste generated as a percentage of the total mass of outputs from a process [163].

If waste minimization is understood as reducing the mass of waste generated in the production of a product, the mass-based indices used in the references cited above are suitable indicators for the objective of minimizing waste. However, it should be kept in mind that waste minimization is a means, not an end. The goal is improved environmental quality [164]. In seeking to avoid value judgements regarding the relative environmental impact of different

chemicals, some authors go to the extreme of including inert substances (such as nitrogen in flue gases) in the computation of the mass of waste generated [159]. Clearly, chemical process designers should not be indifferent between the emission of 1 lb. of N₂ and the emission of the same amount of a highly toxic chemical.

Recognizing that not all substances in a waste stream raise the same level of concern with respect to their environmental impact, some authors compute total mass of waste in special categories of concern [46,161,165,166]. Some common categories include: regulated hazardous waste, volatile organic compounds, and substances included in regulatory lists, such as the Toxic Release Inventory in the United States. In the system used at Polaroid Corporation, all materials used or generated by the company are placed in one of five categories, according to their potential hazard [167]. The total mass of materials used (in the case of the two most sensitive categories) or contained in waste streams (in the case of the other three categories) is reported separately for each category.

Although the approach mentioned above is a step in the right direction, it still falls short of what is needed to incorporate environmental considerations into the evaluation of a design. The reason is that the contribution of a unit mass emission to a particular environmental impact might vary by orders of magnitude among the chemicals included even in narrowly defined categories. The alternative is to shift the focus from emissions to impacts.

MINIMIZATION OF CONTRIBUTIONS TO SPECIFIC ENVIRONMENTAL PROBLEMS

In the problem-oriented approach, the relative contributions of different chemical species to identified environmental problems are used to obtain a weighted sum of the masses of chemicals emitted. The resulting figure can be interpreted as the mass emissions of a single reference substance that would have the same contribution to an environmental problem of concern as the particular mix of emissions being analyzed. For example, emissions of different greenhouse gases may be aggregated into an index by multiplying the emissions of each gas by its global warming potential relative to CO₂ [168].

The first attempts to apply the problem oriented approach in the development of environmental indicators for the evaluation of chemical processes focused on toxicity. Grossmann and coworkers multiplied the material flows in a chemical process by the inverse of

the LD₅₀ of each material, and added the resulting figures to obtain a toxicity index [31]. In a study of the structure of the petrochemical industry that would minimize the toxicity of organic pollutant emissions, Fathi-Afshar & Yang [154] divided material flows by their threshold limit values (TLVs are upper limits to the concentration of pollutants in air in the work environment recommended by the American Conference of Governmental Industrial Hygienists [169]), and multiplied them by their vapor pressure (they assumed that fugitive emissions are proportional to vapor pressure). TLVs were also used by Horvath and coworkers as the basis for an index of toxic emissions [170].

Literally dozens of different ranking and scoring schemes have been proposed to evaluate chemicals based on measures of toxicity or measures of toxicity and exposure [171]. These systems differ in the scoring criteria used, the endpoints used to score each criterion, the algorithm used to aggregate individual scores into an overall score, and the procedures used to score chemicals with missing data. The hierarchy of indicators proposed by Jia and coworkers (see Table 2-4) gives an example of the different levels of sophistication that can be used to evaluate the potential toxic impacts of a design. The fourth type of index is based on the PEC/PNEC (Predicted Environmental Concentration / Predicted No Effect Concentration) concept used for risk characterization [172], and has been characterized as the most consistent with an environmental science approach [173]. Cave & Edwards have recently applied an index of this type to compare the environmental hazard of six alternative routes to the production of methyl methacrylate, based on the total inventory of chemicals present in the corresponding plants [174]. Variations of these indices that take into account bioaccumulation in the food chain have been developed [175,176]. A further level of sophistication is embedded in the Human Toxicity Potential index developed by Hertwich and coworkers [177]. In addition to toxicity, persistence, and environmental mobility, this index takes into account the relationship between environmental concentrations and chemical doses received through different exposure routes.

Toxicity is not the only environmental concern relevant to chemical process design. Other relevant environmental problems to which a chemical process might contribute include ozone layer depletion, climate modification, acid precipitation, and photochemical smog formation. Stefanis and coworkers [32,33,35,36,112,153] and Kniel and collaborators [34] have applied such problem-oriented indices to the design of chemical processes.

Table 2-4: Toxicity-based indicators for the evaluation of environmental releases

Aspects Considered	Example
Mass	$Q_{1m} = \sum_c E_{c,m}$ <p>Q_{1m} is a toxicity-based environmental indicator for chemical releases to medium m. $E_{c,m}$ is the mass of chemical c released to medium m</p>
Mass + Toxicity	$Q_{2m} = \sum_c \frac{E_{c,m}}{C_{c,m}}$ <p>$C_{c,m}$ is the toxicity-based reference concentration of chemical c in medium m. Examples include the threshold limit value (TLV), lethal concentration fifty (LC₅₀), and the predicted no effect concentration (PNEC). Other measures of toxicity that can be used instead of reference concentrations include reference doses and cancer potency factors.</p>
Mass + Toxicity + Persistence	$Q_{3m} = \sum_c \frac{E_{c,m} \tau_{c,m}}{C_{c,m}}$ <p>$\tau_{c,m}$ is the persistence of chemical c in medium m, and depends on the rate of the chemical loss by advection, reaction and transfer to other media</p>
Mass + Toxicity + Persistence + Environmental Mobility	$Q_{4m} = \sum_c \frac{\left(\sum_j E_{c,j} F_{c,j,m} \right) \tau_{c,m}}{C_{c,m}}$ <p>$F_{c,j,m}$ is the intermedia mobility fraction of chemical c from medium j to medium m. The values of $\tau_{c,m}$ and $F_{c,j,m}$ are context specific. Estimating these values requires either the use of a multimedia mass balance model or a broad database of chemical fate observations.</p>

Note: this table has been adapted from a table shown in reference [178]

MINIMIZATION OF OVERALL INDICATORS OF ENVIRONMENTAL IMPACT

Efforts have been made to develop an overall index of environmental impact for use in the quantitative evaluation of chemical process flowsheets [84,85,179,180]. Chemical process designers willing to use such indices must keep in mind that these indices are meaningless without input from the users about their values regarding the environment. The Eco-indicator 95 is an example of an environmental indicator developed for product design applications where the method developers have been very explicit about the value judgements used to weight contributions to different environmental damages [181]. The method developers are also explicit about the decisions they made to include or exclude environmental problem categories in their indicator (for example, they decided to exclude local toxic impacts, since their focus was on environmental effects on an European scale). The weighting factors used in the Eco-indicator 95

are developed in two stages. First, individual problem oriented indicators are normalized by the indicators corresponding to the emissions inventory of Europe. In the second stage, normalized scores are multiplied by reduction factors. The reduction factor for a particular problem is defined as the factor by which the current European emissions would have to be reduced so that the resulting impact would not exceed “1 death per million people per year”, or a “5% ecosystem impairment”. The method developers are explicit in expressing their value judgement that 1 death per million people per year is equivalent to a 5% ecosystem impairment. Users who do not share that value judgement would need to develop their own reduction factors for each problem.

INDUSTRIAL PERSPECTIVE

Examples of environmental indicators being used to evaluate processes in the chemical industry are given in Table 2-5. DeSimone & Popoff have published a book with accounts of the approaches used by a wide variety of firms to measure their environmental performance [182].

2.6.3 Trading off environmental objectives against other design objectives

The selection and refinement of a final design is a multiobjective decision problem, where economic, environmental, and safety concerns might be in conflict [45]. As explained above, “the environmental objective” is in itself a collection of many objectives, where improving one objective might not be possible without worsening another. For example, decreasing solvent emissions by increased separations and recycling might lead to increased emissions of combustion gases from energy generation.

The first step in the analysis of a decision problem with multiple objectives is the identification of the set of non-dominated alternatives, also known as the Pareto set [46]. A dominated alternative is one that is inferior to another feasible alternative in the set with respect to all attributes under consideration. This means that for each dominated alternative there is at least one “win-win” alternative that can be attained without sacrificing achievement in any of the design objectives. The set of alternatives that remains after all the dominated alternatives have been removed is the set of non-dominated alternatives. Techniques for identifying the set of non-dominated alternatives include the “ ϵ -constraint technique” and the “weighting method

approach”. Both of these techniques have been applied to process design problems with economic and environmental objectives [31,32,35,36,117,134,149,153,154]. For simple problems involving discrete alternatives and only two objectives, the set of non-dominated alternatives may be identified by inspection [151].

Table 2-5: Environmental indicators used for process evaluation in the chemical industry

Company	Environmental index used	Comments
Roche [160]	Total mass of waste (before end-of-pipe treatment) per unit mass of end product	
3M [163]	Total mass of waste as a fraction of the total mass of outputs of a process (including products, byproducts and wastes)	
Polaroid [167]	Total mass of chemical use or waste in each of five categories per standard unit or product	All chemicals in raw materials and waste are assigned to one of the five categories, based on relative hazard.
Rohm and Hass [183]	Weighted sum of waste stream masses, per unit mass of product	Weighting factors are the product of a toxicity score (based on its NFPA health hazard rating) and a “mode of delivery to the environment” score (based on whether the waste stream is directly discharged, treated before release, or recycled or reused).
Imperial Chemical Industries [184]	Equivalent emissions of reference substance for ten environmental impact categories	Potency factors for each category are developed based on published studies and standards.
Ciba Specialty Chemicals [37]	Eco-Indicator 95 [181] and Swiss Eco-scarcity method [185]	The toxicity of most chemicals is not considered in either indicator. The Eco-scarcity method is based on national emission targets established by the Swiss government.

The selection of the “best compromise” alternative from the set of non-dominated alternatives requires input about the values and preferences of the people responsible for making the decision. Thus, design teams working on a problem with multiple objectives are faced with the need to apply multiattribute decision making techniques [186,187] in which most process engineers are not trained. Some authors attempt to avoid the elicitation of values by normalizing the objectives (so that their values for all alternatives are in the range 0-1), and then

computing a norm [31,84,154]. This does not remove the need to evaluate tradeoffs, it merely makes it more difficult to do so by eliminating relevant information.

Multiobjective goal programming is a technique that has also been used to solve chemical process design problems without specifying weighting factors to tradeoff objectives against one another [46,124]. The procedure involves stating goals for each objective of the design, ranking the objectives in order of importance, and then choosing the alternative that minimizes lexicographically the vector of deviations from the aspiration levels. With this procedure, the decision-maker makes tradeoffs implicitly by specifying the aspiration levels. In addition, it is likely that the tradeoffs will not be consistent across projects, since the aspiration levels will be case specific. A further problem with this technique lies in its use of lexicographical minimization, since the technique does not attempt to strike a balance among conflicting objectives. A marginal improvement in a highly ranked goal, no matter how small, is always preferred to improvements in goals ranked below it, no matter how large. An example of this is given by a lexicographic pollution prevention index that has been used to rank pollution prevention alternatives [76,77]. In this index, the classification of the solution according to the pollution prevention hierarchy is given priority over all other considerations. As a result, the most expensive, inefficient, and difficult to implement source reduction alternative is ranked higher than the most profitable, effective, and easy to implement recycling option.

Weighted sums of dimensionless scores are commonly used to make decisions involving multiple criteria. In the analytical hierarchy process, the criteria are organized in a hierarchy, where higher level scores are weighted sums of lower level scores [188]. Tradeoffs made using these methods will not be consistent across projects, since the attribute values used in the normalization are case specific. Applications of these techniques to pollution prevention projects have been published [43,189,190].

A different reaction to the valuation problem is to dismiss it as a “social science” problem outside of the field of process engineering, but this gives no assistance to design engineers facing the challenge of making a decision. Our perspective on this issue is that even though it might be difficult to establish precise levels for the tradeoffs that decision makers are prepared to make, it is always possible to place bounds on them. Sensitivity analysis (discussed in the next section) can then be used to determine whether there is a need to undertake more thorough elicitation of

preferences. Ideally, many of these questions would be addressed at the corporate or division level, allowing management to give design teams uniform guidance regarding the tradeoffs that the company is prepared to make among the different objectives.

2.7 *The role of sensitivity analysis*

The main goal of sensitivity analysis is to determine whether the best alternative identified advances the design objectives sufficiently, given current levels of uncertainty, to make further search unnecessary. Framing of the design problem should specify the criteria to be used to determine whether the gains from additional analysis are worth the additional time required. With respect to environmental objectives, the design team needs to be able to identify those aspects of the design that are driving the environmental impact. It is also necessary to understand the tradeoffs associated with the modification of the aspects of the design driving the impacts.

Ciric and collaborators have noted that costs associated with waste treatment and disposal are difficult to estimate, since direct costs (e.g. landfill fees) are rapidly increasing and indirect costs (e.g. liability, paperwork) are significant but hard to quantify [134,149]. This observation motivated them to develop a procedure for determining the sensitivity of the maximum net profits of a chemical process to changes in the waste treatment cost. In this procedure, the concave portions of the solution set of the multiobjective problem that maximizes profits and minimizes waste are mapped into the solutions of the original profit maximization problem for different values of the waste treatment cost.

There are very few examples of the application of sensitivity analysis to published mathematical programming formulations of waste minimization [119,122,138]. Two of these examples examine only the impact of adding additional structural constraints for the network of separation units [122,138], while the other one analyzed the sensitivity of the optimal network to equipment cost [119]. Sensitivity analysis on variables fixed at the problem framing stage (e.g. recovery or concentration targets) has not been reported.

Many aspects of the evaluation of a chemical process design with respect to its environmental performance are subject to considerable uncertainty. Diwekar has examined the impact of uncertainties associated with technical factors alone (e.g. equipment performance,

emission rates) in the economic and environmental performance of a power plant design [158]. Proponents of environmental impact assessment indices [170,178] have noted the need for quantifying the uncertainties in environmental indices and in any rankings that might result from these indices, but work in this area is still in its infancy.

In order to improve the environmental performance of a design, it is necessary to understand what are the features of a design that are the main drivers of its environmental impact. Thus, the calculation of an environmental index is not very useful unless the results can be presented in a way that allows the design team to set priorities for further design work. Unfortunately, most of the work reported in the literature has not addressed this problem. Tools analogous to the cost diagrams introduced by Douglas & Woodcock for the screening of designs (based on economic objectives) [191] could be very useful in this regard. Hilaly & Sikdar [82,83] recommend the calculation of pollution indices (a measure of the mass of waste produced per unit mass of product) for a complete flowsheet as well as for individual process streams. In their procedure, the units associated with process streams with high pollution indices are then targeted for waste minimization. Heinzle & Hungerbühler use a mass loss index (MLI) to allocate all mass flows leaving a process to their cause. Causes of mass inefficiencies include stoichiometric formation of byproducts in desired reactions, incomplete conversion, selectivity losses, purification losses, impurities contained in substrates, and losses of solvents, catalysts and other auxiliary materials not recycled with 100% efficiency. By weighting individual streams by their cost or by a relative measure of environmental impact, those causes of mass inefficiency with the greatest cost or potential ecological impact can be identified. The design team would focus their attention on reducing those sources of inefficiency in the next iteration.

2.8 Research needs

In December of 1992, the Center for Waste Reduction of the American Institute of Chemical Engineers, the U.S. Environmental Protection Agency and the U.S. Department of Energy sponsored a workshop to identify requirements for improving process simulation and design tools with respect to the incorporation of environmental considerations in the simulation and design of chemical processes [192,193]. Most of the needs identified during that workshop are still present today. The following list combines the subset of the needs identified in that

workshop that we find most relevant (marked with an asterisk) with some additional needs we identified during the preparation of this review.

GENERATION OF ALTERNATIVES

- Increase the integration of process chemistry into the generation of design alternatives
- Develop tools to identify new reaction pathways and catalysts *
- Extend alternative generation methods to include non-conventional unit operations *
- Develop methods that allow the rapid identification of opportunities to integrate processes
- Develop methods to recognize opportunities to match waste streams with feed streams, and to prescribe the operations needed to transform a waste stream into a usable feed stream.

ANALYSIS OF ALTERNATIVES

- Predict generation of undesired byproducts *
- Improve prediction of reaction rates *
- Predict fugitive emissions and emissions from nonroutine operations (e.g. startup) *
- Improve characterization of non-equilibrium phenomena *
- Include waste-treatment unit operations in process simulators
- Increase the ability of process simulators to track dilute species *
- Improve stochastic modeling and optimization *
- Link process and environmental models *
- Build databases of properties relevant to environmental characterization of processes and link them to process simulators
- Include information about uncertainties in databases
- Create databases with typical mass and energy balances (including trace components of environmental significance) for widely used raw materials in the chemical industry, to facilitate the characterization of upstream processes.

- Develop guidelines to match the level of detail used in process models with the accuracy needed to make decisions

EVALUATION OF ALTERNATIVES

- Develop accounting rules to allocate environmental impacts to specific processes and products in complex plants
- Develop environmental impact indices that are able to combine data of different quality while preserving their information content
- Develop screening indicators
- Develop frameworks that facilitate the elicitation of preferences needed as input to multiobjective optimization

SENSITIVITY ANALYSIS

- Incorporate sensitivity analysis as a standard element in papers and books related to chemical process design
- Develop indicator frameworks that allow rapid identification of the features of a design that drive its environmental impact.

2.9 Conclusions

Environmental issues are emerging as one of the major driving forces for change in the chemical industry. This chapter has presented a review of the issues, methodologies and future needs for integrating environmental concerns into the design and operation of chemical manufacturing facilities. While there are clearly many needs perhaps one of the most overriding opportunities is for a change in attitudes. A view of product and process design that sees environment as an objective and not just as a constraint on operations can lead to the discovery of design alternatives with improved environmental and economic performance. An adoption of environmentally conscious design ideas in academic curricula is perhaps the most significant leverage point for moving the practice of chemical process design in this direction.

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Chapter 3 Valuation Models

“Since experience indicates that only a small number of ideas will ever have a payout, we see that evaluation is one of the most significant components of any design methodology”.

James M. Douglas

3.1 Introduction

Design problems are always underdefined. There are a large number of choices a designer can make in the design of a process. The choices include process chemistry, type of unit operations, flowsheet topology (i.e. how the different unit operations are interconnected), equipment selection and sizing, stream flow rates, temperatures and pressures, materials of construction, process control strategies, etc. Douglas states that it is often possible to generate 10^4 to 10^9 alternative processes for even a single-product plant [1]. According to Biegler, Grossmann and Westerberg, it is not uncommon for the number of design alternatives for a chemical process (based on the discrete decisions alone) to number 10^{15} [2]. It can be expected that among this vast number of process alternatives, some alternatives will be much better than others.

A key step needed to convert an ill-posed design problem into a well-posed problem is to define the goals of the design. Some of these goals will be objectives, while others will be constraints. The difference between an objective and a constraint is that designers aim to maximize or minimize objectives (e.g. maximize profit, minimize environmental impact), while they only strive to meet constraints (e.g. meet government regulations, fit process within available land area). It is common to find some degree of conflict among goals. In such cases, the designer must decide how to resolve the tradeoffs among conflicting objectives. A very common tradeoff is the one between minimizing capital investment and minimizing operating costs. It is almost always possible to decrease operating costs by increasing investment in equipment. Whether or not the additional investment is justified depends on, among other factors, the return that a firm can expect to earn in alternative investments.

The role of the evaluation step of the design cycle is to map design decisions into quantitative indicators that enable the design team to assess the degree to which various design

alternatives advance the goals of a design problem. This is done through valuation models (also known as “objective functions”). While process models map design decisions into material flows and utility consumption rates, value models map physical information into measures of performance. These measures of performance are then used to rank alternatives and to gain insights about the most promising directions for evolving the design.

A sense of the importance of careful consideration of valuation models can be gained from the following quote from Ralph L. Keeney’s book “Value-focused thinking” [3]:

“In many complex decision situations, the consequences are significant, meaning in the hundreds of millions of dollars or involving potential fatalities or large-scale environmental degradation. The only reason for an interest in such problems is because some consequences may be much better than others, and some alternatives may be much better than others. And yet the amount of time devoted to careful study of the appropriate values is minuscule relative to the time used to address other aspects of the decision situation. The “objective function” may be chosen in an hour with very little thought, while several person-years of effort and millions of dollars may be used to model the relationships between the alternatives and the consequences and to gather information about the relationships. Since values are the entire reason for caring about the problem, it would seem reasonable to use a portion of those resources to structure, quantify, and understand the relevant values. Such an effort should be used to build a value model.”

While chemical engineers devote considerable effort to building and validating process models, relatively little effort is spent developing and validating the valuation models used to assess the performance of their proposed designs. I will show later in this chapter that one of the byproducts of the lack of attention paid to valuation models is a significant bias against capital expenditures that results in investment in processing equipment that is below the economic optimum.

This chapter argues that the use of appropriate value models is fundamental to enable designers to identify superior alternatives. In particular, incorporation of environmental concerns as additional objectives, rather than as constraints, should enable designers to develop process alternatives with superior environmental *and economic* performance. There are several reasons for this:

- a) Environmental regulations are constantly evolving. What is permissible today might not be permissible in the future. Treating environmental concerns as objectives rather than

constraints will result in designs that are less likely to require expensive retrofits as environmental regulations are tightened.

- b) Some of the reasons that contribute to environmental impacts also contribute to increase costs. For example, material that escapes a process plant as a pollutant can not be sold as a product. Instead, additional resources must be used to treat the material to decrease its hazard. Similarly, excessive use of utilities leads to pollution from the plants that provide the utilities. It is to be expected that there will be a correlation between energy and material efficiency on one hand, and environmental performance on the other hand.
- c) The existence of a vast number of alternatives for any design problem means that design teams will only have time to explore a limited subset of the set of all possible alternatives. It is unlikely that they will find the best design on the first trial. Using a richer valuation model to score the alternatives allows designers to identify the features of a design that contribute (or detract) the most to several dimensions of performance. If design teams have this information, they should be able to brainstorm more productively in subsequent iterations around the design cycle.

This chapter is organized into two major sections. The first section discusses economic valuation models, while the second one focuses on environmental valuation models. The section on economic valuation models takes an in-depth look at the economic objective functions commonly used at the conceptual stage of process design. A detailed derivation of the annualized profit economic potential model is shown, followed by a thorough discussion of the uncertainties in the model. The section closes with a discussion of the biases inherent to the model, showing that these biases result not only in equipment that is too small relative to the economic optimum, but also in excessive generation of pollutants. The section on environmental valuation models builds upon the discussion on economic models to make the argument that the two types of models are conceptually similar, with the major distinction due to differences in data availability and user familiarity. The two main approaches to the construction of environmental valuation models are shown, with references to various valuation systems. Uncertainties are discussed, with particular emphasis on the uncertainties in weighting factors.

3.2 *Economic Valuation Models*

The most common valuation models in use have monetary units. This is natural, since a principal objective for building a process is to make a profit. Figure 3-1 shows the structure of a typical economic valuation model. The first step in the evaluation procedure is to map design decisions into flow rates and process equipment specifications through the use of process models. The flow rates can then be converted into recurring cash streams (e.g. revenues and operating costs) by multiplying them by unit prices. Process equipment specifications can be translated into purchased equipment costs through the use of cost correlations or equipment fabrication cost models. At the conceptual design stage, all other capital costs are estimated as a function of the purchased equipment cost. Additional recurring cash streams (e.g. operating labor and maintenance costs) are also a function of the equipment specifications. The last step of the analysis is the combination of capital costs and recurring cash streams into a single measure of economic performance. Recurring cash streams occurring in future periods can be discounted and added to the capital cost to obtain a net present value (NPV), or the capital costs can be annualized and added to the recurring cash streams to obtain a total annualized profit (TAP). A frequently used metric is the total annualized cost (TAC), in which the revenue streams are excluded from the analysis. Using TAC as an economic objective is only justified if all the design alternatives produce the same amounts of products. A third option is to calculate the internal rate of return of the investment (IRR). The IRR is defined as the discount rate that would make the NPV equal to zero.

A key element in any economic value model of chemical process designs is the set of coefficients used to combine revenues, operating costs and equipment costs into a single number, since these coefficients ultimately determine how the operating cost vs. capital cost tradeoff is resolved. These coefficients are examined in detail in the following sections, using annualized economic value models as the framework. Section 3.2.1 introduces the total annualized profit (TAP) economic valuation model. The discussion of economic valuation models is built around the TAP metric instead of around the NPV metric because it is more commonly used at the conceptual stage of design. The conclusions of this section do not change if NPV is used instead of TAP as the economic valuation function. The annualization factor (AF) is introduced as the key parameter used to compare installed equipment costs and raw material and utility costs on the same basis. There are two major components to the annualization factor. The first

component is used to annualize capital investments necessary for the construction of a process. The key parameter used to quantify this component is the capital charge factor (CCF). In section 3.2.2, two capital charge factor models are described. The second component in the annualization factor accounts for fixed recurrent costs arising from the equipment, such as maintenance, local taxes and insurance. A full AF model including both components is described in section 3.2.3. Section 3.2.4 discusses the uncertainties associated with the various parameters in the TAP model. Finally, section 3.2.5 makes the argument that the economic valuation procedures advocated by the process design textbooks are biased against capital investment. The impact of this bias is explored through an example.

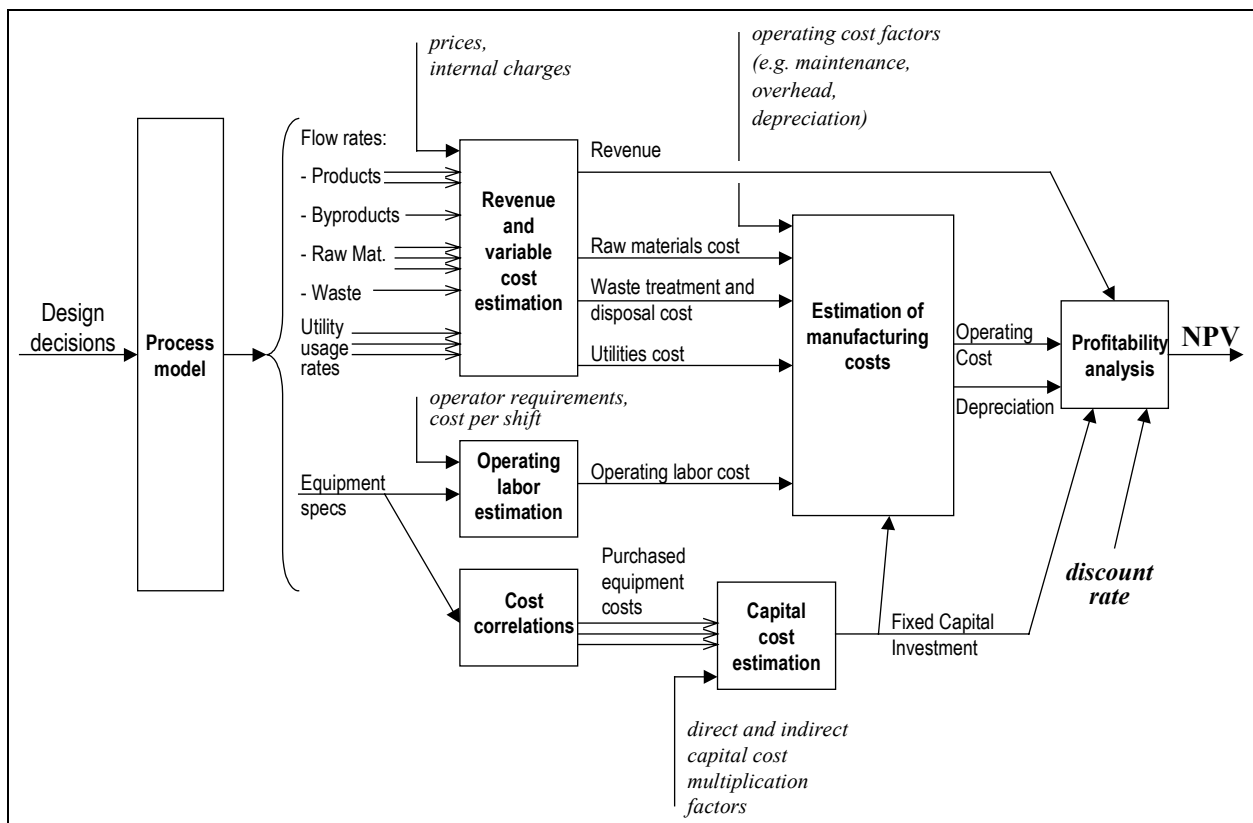


Figure 3-1: Elements of an economic valuation model

3.2.1 The total annualized profit economic valuation model

Process models usually yield the following information:

- Rates of products, byproducts, wastes, and raw materials (from the mass balance)
- Utility usage rates (from the energy balance)

- Size data for major equipment units (from the performance equations used to model each unit operation)

The first two sets of information can be translated into economic potentials for the process through the use of prices [1]:

$$\begin{aligned} EP_1 &= \text{Revenue} - \text{Raw Material Costs} \\ &= \sum F_{prod} P_{prod} - \sum F_{raw mat} P_{raw mat} \end{aligned} \quad (3-1)$$

$$\begin{aligned} EP_2 &= EP_1 - \text{Waste Treatment and Disposal Costs} - \text{Utility Costs} \\ &= EP_1 - \sum F_{waste} P_{waste} - \sum F_{util} P_{util} \end{aligned} \quad (3-2)$$

These economic potentials are upper limits for the gross margin of the process. The gross margin is defined by:

$$\text{Gross Margin} = \text{Revenue} - \text{Variable Costs} \quad (3-3)$$

The main difference between gross margin and the economic potential EP_2 given above is that the former includes other variable costs (such as labor) which can not be easily estimated directly from the mass and energy balances.

The conversion of equipment sizes into capital cost typically takes place according to the following steps:

1. Equipment cost correlations are used to estimate *purchased equipment cost* (C_p).
2. Purchased equipment costs are multiplied by a series of factors to account for (i) direct material and labor used for installation, (ii) indirect installation costs, and (iii) contingencies and fees, to obtain an estimate of the *total installed equipment cost*, also known as *onsite cost*, *inside battery limits cost*, or *total module cost* (C_{TM}).
3. An additional factor is sometimes used to account for necessary investments in auxiliary facilities, such as utility and waste treatment plants. The total cost obtained is known as the *Fixed Capital Investment (FCI)* or *Grassroots Cost* (C_{GR}).

When this procedure for estimating capital costs is used, the only direct information used is major equipment costs, which typically represent 20 to 40 percent of the fixed capital investment. The rest of the capital costs are assumed to increase in direct proportion to the cost of equipment. Although this procedure yields fixed capital costs that are within 30% of the actual fixed capital cost, it has the effect of overestimating the marginal capital cost increase due

to changes in equipment. Processes designed through the optimization of an objective function that uses purchased cost correlations and cost factors to estimate fixed capital investment costs are likely to have equipment that is too small relative to the true optimum, since the impact of each additional dollar invested in process equipment is overestimated. A more detailed discussion of this observation is given in section 3.2.5.

Under the annualized costs economic valuation model, the economic objective function to be maximized at the conceptual stage of design is

$$EP_3 = EP_2 - AF \times C_{TM} \quad (3-4)$$

where AF is the installed equipment cost annualization factor and C_{TM} is the total installed equipment cost (see discussion above). Various process design textbooks differ in their recommendations with respect to appropriate values of the AF . For example, Smith [4] obtains the AF using the formula:

$$AF = \frac{i(1+i)^N}{(1+i)^N - 1} \quad (3-5)$$

where i is the applicable annual discount rate (or interest rate), and N is the number of years over which the capital cost is annualized. With $i = 15\%$, and $N = 11$ years⁴, the formula above yields $AF = 0.191 \text{ yr}^{-1}$. In his chemical process design book [5], Ulrich recommends using an AF between 0.15 and 0.20 yr^{-1} .

Douglas calculates AF using the expression [1]:

$$AF = 0.191 + 2.42CCF \quad (3-6)$$

where the capital charge factor (CCF) is calculated according to the formula:

$$CCF = \frac{\left[\frac{1}{n} [(1+i)^n - 1] + 0.295i - \frac{\tau}{N} \right] (1+i)^N - 0.225i + \frac{\tau}{N}}{1.3(1-\tau)[(1+i)^N - 1]} \quad (3-7)$$

In the expression above, n is the length of the period of construction (years), N is the number of years of operation, i is the discount rate, and τ is the tax rate. With $i = 15\%$, $n = 4$ years, $N = 11$ years, and $\tau = 48\%$ (the tax rate used by Douglas in his book), the CCF is calculated as 0.358 yr^{-1} . With the assumptions stated above, the Douglas method yields $AF = 1.05 \text{ yr}^{-1}$

⁴ The choice of $i=15\%$ and $N=11$ years is made for consistency with Douglas [1]

(Douglas uses a value of 1 yr^{-1} throughout his textbook). Using the current tax rate of 34% yields $CCF=0.298 \text{ yr}^{-1}$ and $AF = 0.91 \text{ yr}^{-1}$. There is a rather large discrepancy (more than a factor of 4 difference) in AF values among the different sources. Sources of the discrepancy include:

- The Douglas method includes an annual charge for maintenance, local taxes and insurance. This is the first term on the right hand side of eq (3-6).
- The Douglas method assumes offsite costs equal to 45% of onsite costs for plant expansions; the annualization factor used by Smith does not consider offsite costs
- The Douglas method assumes that the installed equipment cost does not include contingencies and fees, so it adds them to the annualized capital cost. It also adds a factor for working capital and startup capital. These factors together with the offsite cost factor account for the coefficient preceding CCF in eq (3-6).
- Douglas' CCF formula considers taxes, depreciation, recovery of working capital and the salvage value of the equipment at the end of the project.
- The Douglas method assumes a long period of construction ($n = 4$). If construction is assumed to take place in one year ($n = 1$), the CCF drops to 0.287, resulting in an AF of 0.887.

The large discrepancy in annualization factors justifies a closer examination of how the annualization factor is derived. Design teams should invest the time required to verify that the assumptions made in deriving the annualization factors they use to evaluate the tradeoff between equipment costs and operating costs are appropriate for their design problem. In the next two subsections derivations of expressions for the capital charge factor and the annualization factor are presented, based on cost ratios frequently quoted in process design books.

3.2.2 Capital charge factor models

The capital charge factor (CCF) is defined here as the factor by which the total capital investment (TCI) should be multiplied, so that the ratio of the modified capital cost to the annual variable cost is the same as the ratio of the relative contributions of fixed capital cost and

variable cost to the net present value (NPV) economic performance metric. In other words, if NPV is given by

$$NPV = -a_0 TCI + a_1 \sum F_{prod} P_{prod} - a_2 \sum F_{rawmat} P_{rawmat} - \dots \quad (3-8)$$

then the CCF is given by the ratio a_0/a_2 .

ANNUITY FORMULA

The simplest CCF model is the annuity formula:

$$CCF = \frac{i(1+i)^N}{(1+i)^N - 1} \quad (3-9)$$

where i is the discount rate (per year) and N is the project life (years).

This model is appropriate when taxes, working capital and salvage value credits to net present value can be neglected. Otherwise, more sophisticated models are needed.

DOUGLAS MODEL

In this subsection a detailed derivation of the Douglas CCF model (eq (3-7)) is presented. The presentation given here differs from that by Douglas in that all of the input variables used in the derivation are preserved in symbolic form, while Douglas substitutes numeric values throughout his derivation. Deriving the model in symbolic form enables the carrying out of sensitivity and uncertainty analysis on the final CCF model as a function of uncertainties in the key ratios used to derive it. A nomenclature has been added to end of this chapter to help the reader to follow the derivation.

The Douglas CCF model is built on the following assumptions:

- Fixed capital investments (FCI) are distributed uniformly over a period of n years
- Annual operating cash flows are constant over a project life of N years following start-up
- Straight-line depreciation is used
- Depreciation allowances are excluded from total product cost (TPC)

- Working capital (WC) and start-up cost (SC) are added to the FCI to obtain the total capital investment (TCI)
- Working capital and part of the equipment cost (the salvage value, SV) are recovered at the end of the project
- The present value is calculated with respect to the year in which process operations start

With these assumptions, the net present value is the sum of the following three components:

a) Initial investment:

$$- \text{Present Value of Fixed Capital Investment} - \text{Working Cap.} - \text{Startup Cost} = - (FCI) \left\{ \left(\frac{1}{n} \right) \left[\frac{(1+i)^n - 1}{i} \right] + \frac{WC}{FCI} + \frac{SC}{FCI} \right\} \quad (3-10)$$

b) Present value of cash flow from operations (net of taxes):

$$\left[(1-\tau)(\text{Revenue} - TPC) + \tau(\text{Depreciation}) \right] \left[\frac{1 - (1+i)^{-N}}{i} \right] = \left[(1-\tau)(\text{Revenue} - TPC) + \tau \left(\frac{FCI}{N} \right) \right] \left[\frac{1 - (1+i)^{-N}}{i} \right] \quad (3-11)$$

c) Recovery of working capital and salvage value at the end of the project, discounted to present value:

$$(\text{Working Cap.} + \text{Salvage Value}) \left[\frac{1}{(1+i)^N} \right] = (FCI) \left(\frac{WC}{FCI} + \frac{SV}{FCI} \right) \left[\frac{1}{(1+i)^N} \right] \quad (3-12)$$

Adding the three terms yields

$$NPV = \left\{ (1-\tau) \left[\frac{1 - (1+i)^{-N}}{i} \right] \right\} (\text{Revenue} - TPC) - \left\{ \left(\frac{1}{n} \right) \left[\frac{(1+i)^n - 1}{i} \right] + \frac{WC}{FCI} \left[1 - \frac{1}{(1+i)^N} \right] + \frac{SC}{FCI} - \left(\frac{\tau}{N} \right) \left[\frac{1 - (1+i)^{-N}}{i} \right] - \frac{SV}{FCI} \left[\frac{1}{(1+i)^N} \right] \right\} (FCI) \quad (3-13)$$

or, in terms of the TCI :

$$NPV = \left\{ (1-\tau) \left[\frac{1 - (1+i)^{-N}}{i} \right] \right\} (\text{Revenue} - TPC) - \left\{ \left(\frac{1}{n} \right) \left[\frac{(1+i)^n - 1}{i} \right] + \frac{WC}{FCI} \left[1 - \frac{1}{(1+i)^N} \right] + \frac{SC}{FCI} - \left(\frac{\tau}{N} \right) \left[\frac{1 - (1+i)^{-N}}{i} \right] - \frac{SV}{FCI} \left[\frac{1}{(1+i)^N} \right] \right\} \left(\frac{FCI}{TCI} \right) (TCI) \quad (3-14)$$

where the ratio of TCI to FCI is given by

$$\frac{TCI}{FCI} = 1 + \frac{WC}{FCI} + \frac{SC}{FCI} \quad (3-15)$$

According to the definition, the CCF is given by the ratio of the TCI coefficient to the (*Revenue-TPC*) coefficient in eq (3-14):

$$CCF = \frac{\left\{ \left(\frac{1}{n} \right) \left[\frac{(1+i)^n - 1}{i} \right] + \frac{WC}{FCI} \left[1 - \frac{1}{(1+i)^N} \right] + \frac{SC}{FCI} - \left(\frac{\tau}{N} \right) \left[\frac{1 - (1+i)^{-N}}{i} \right] - \frac{SV}{FCI} \left[\frac{1}{(1+i)^N} \right] \right\}}{\left(\frac{TCI}{FCI} \right) \left\{ (1-\tau) \left[\frac{1 - (1+i)^{-N}}{i} \right] \right\}} \quad (3-16)$$

$$= \frac{\left\{ \left(\frac{1}{n} \right) [(1+i)^n - 1] + i \left(\frac{SC}{FCI} + \frac{WC}{FCI} \right) - \frac{\tau}{N} \right\} (1+i)^N - i \left(\frac{WC}{FCI} + \frac{SV}{FCI} \right) + \left(\frac{\tau}{N} \right)}{\left(1 + \frac{WC}{FCI} + \frac{SC}{FCI} \right) (1-\tau) [(1+i)^N - 1]}$$

The final model is a function of 7 parameters: i , n , N , τ , (WC/FCI) , (SC/FCI) , and (SV/FCI) ⁵. With $n = 1$, and no taxes, depreciation, working capital, startup costs or salvage value, eq (3-16) reduces to eq (3-9).

The procedure used by Douglas to derive the CCF can be implemented on a spreadsheet to compute CCF for other cases, such as those with non-uniform schedules for investment, process throughput, or depreciation.

3.2.3 Installed equipment cost annualization factor model

Part of the total product cost consists of factors that are commonly assumed to be proportional to the capital investment. Examples of these factors are maintenance, local taxes, and insurance. These kinds of costs need to be included in the analysis of the operating cost vs. installed equipment capital cost tradeoff. This is the origin of the term in eq (3-6) that does not depend on the capital charge factor.

According to Douglas, the total product cost (TPC) is the sum of the following components:

⁵ The definition of these symbols is given in the nomenclature (section 3.5)

- I. Manufacturing cost is the sum of direct production costs, fixed charges, and plant overhead
- A. Direct production costs
1. Raw materials (obtained from flow rates of feed streams in the mass balance)
 2. Utilities (estimated from the energy balance)
 3. Maintenance and repairs: about 2-10% of FCI
 4. Operating supplies: about 10-20% of cost for maintenance and repairs
 5. Operating labor: estimated as \$100,000 (in 1988 dollars) times the number of shift positions (the number of shift-positions needs to be estimated from an examination of the flowsheet)
 6. Direct supervision and clerical labor: about 10-25% of operating labor
 7. Laboratory charges: about 10-20% of operating labor
 8. Patents and royalties: about 0-6% of total product cost
- B. Fixed Charges equal the sum of local taxes and insurance (depreciation is treated separately)
1. Local taxes: about 1-4% of FCI
 2. Insurance: about 0.4-1% of FCI
- C. Plant Overhead (*OVHD*): about 50-70% of the cost of operating labor, supervision, and maintenance
- II. General expenses: Sales, administration, research and engineering (*SARE*) costs are about 2.5% of the sales revenue for chemical intermediates, although they might be higher for finished products sold directly to consumers.

Adding all the components yields the following expression:

$$\begin{aligned}
 TPC = & \text{RawMat.} + \text{Util.} + \frac{\text{Maint.}}{\text{FCI}} \left(1 + \text{OVHD} + \frac{\text{Op.Supp.}}{\text{Maint.}} \right) \text{FCI} + \\
 & \left(1 + \frac{\text{Superv.}}{\text{Op.Labor}} + \frac{\text{Lab}}{\text{Op.Labor}} \right) (1 + \text{OVHD}) \text{Op.Labor} + \frac{\text{Royalties}}{\text{TPC}} \text{TPC} + \frac{\text{Tax \& Ins.}}{\text{FCI}} \text{FCI} + \frac{\text{SARE}}{\text{Rev.}} \text{Rev}
 \end{aligned} \tag{3-17}$$

or, after factoring the terms that depend on TPC:

$$TPC = \frac{\text{RawMat.} + \text{Util.} + \left[\frac{\text{Maint.}}{\text{FCI}} \left(1 + \text{OVHD} + \frac{\text{Op.Supp.}}{\text{Maint.}} \right) + \frac{\text{Tax \& Ins.}}{\text{FCI}} \right] \text{FCI} + \left(1 + \frac{\text{Superv.}}{\text{Op.Labor}} + \frac{\text{Lab}}{\text{Op.Labor}} \right) (1 + \text{OVHD}) \text{Op.Labor} + \frac{\text{SARE}}{\text{Rev.}} \text{Rev}}{1 - \frac{\text{Royalties}}{\text{TPC}}} \tag{3-18}$$

The TAP metric is defined by:

$$TAP = (Revenue - TPC) - CCF \times TCI \quad (3-19)$$

Substituting eq. (3-18) into eq (3-19) yields

$$TAP = \left\{ \frac{\left(1 - \frac{Royalties}{TPC} + \frac{SARE}{Rev.}\right) Rev. - RawMat. - Util - \left(1 + \frac{Superv.}{Op.Labor} + \frac{Lab}{Op.Labor}\right) (1 + OVHD) Op.Labor}{1 - \frac{Royalties}{TPC}} \right\} - \left\{ CCF + \frac{\left[\frac{Maint.}{FCI} \left(1 + OVHD + \frac{Op.Supp.}{Maint.}\right) + \frac{Tax \& Ins.}{FCI} \right] \frac{FCI}{TCI}}{1 - \frac{Royalties}{TPC}} \right\} TCI \quad (3-20)$$

Equation (3-20) has two bracketed terms. The first term includes the contributions of product revenue, raw materials, utilities, and operating labor. The second term includes an annual charge from the initial capital investment (given by the CCF factor) plus charges due to recurrent costs arising from equipment cost (maintenance, local taxes, and insurance).

The expression for the annualization factor is derived from equations (3-4) and (3-20). Defining the installed equipment cost annualization factor (AF) as the factor by which the installed equipment costs (C_{TM}) should be multiplied so that the ratio of the corrected equipment cost to the raw material cost is the same as the ratio of the TCI coefficient to the raw material costs coefficient in eq (3-20) yields the following expression:

$$AF = \left\{ \left(1 - \frac{Royalties}{TPC}\right) CCF + \left(\frac{Maint.}{FCI} \left(1 + OVHD + \frac{Op.Supp.}{Maint.}\right) + \frac{Tax \& Ins.}{FCI} \right) \frac{FCI}{TCI} \right\} \frac{TCI}{C_{TM}} \quad (3-21)$$

The only remaining step is to relate the total capital investment to installed equipment cost (i.e. to derive an expression for the TCI/C_{TM} ratio). Douglas breaks down fixed capital investment into the following components:

A. Direct costs

1. Onsite costs or ISBL (inside of battery limits) costs are obtained as the sum of the product of the purchased cost of each piece of equipment times an equipment-specific bare module factor
2. Offsite costs or OSBL (outside of battery limits) costs refer to auxiliary facilities (e.g. steam plant, cooling towers) and buildings. Douglas distinguishes between two cases:
 - a) Expansion of existing facility: 40 to 50% of onsite costs

b) Construction of a grass-roots plant or a major plant expansion: up to 200 or 400% of the onsite costs

B. Indirect costs

1. Owner's costs include engineering, supervision and construction expenses; however, the bare module factors used to estimate onsite costs already include engineering and construction. Douglas uses a factor of $5\% \times \text{Direct costs}$
2. Contingencies and fees. Douglas assumes that the sum of contingencies and fees equals about 20% of the direct costs
 - a) Contingency: about 5-20% of FCI
 - b) Contractor's fee: about 1.5-5% of FCI

Adding the components listed above yields

$$FCI = C_{TM} \left(1 + \frac{\text{Offsite}}{\text{Onsite}} \right) \left(1 + \frac{\text{Owner's}}{\text{Direct}} + \frac{\text{Cont \& Fee}}{\text{Direct}} \right) \quad (3-22)$$

Combining eqs (3-15), (3-21) and (3-22) yields the expression used by Douglas to calculate the installed equipment cost annualization factor:

$$AF = \left(1 + \frac{\text{Owner's}}{\text{Direct}} + \frac{\text{Cont \& Fee}}{\text{Direct}} \right) \left(1 + \frac{\text{Offsite}}{\text{Onsite}} \right) \left[\frac{\text{Maint.}}{FCI} \left(1 + \text{OVHD} + \frac{\text{Op.Supp.}}{\text{Maint}} \right) + \frac{\text{Tax \& Ins.}}{FCI} \right] + \left(1 + \frac{\text{WC}}{FCI} + \frac{\text{SC}}{FCI} \right) \left(1 + \frac{\text{Owner's}}{\text{Direct}} + \frac{\text{Cont \& Fee}}{\text{Direct}} \right) \left(1 + \frac{\text{Offsite}}{\text{Onsite}} \right) \left(1 - \frac{\text{Royalties}}{\text{TPC}} \right) CCF \quad (3-23)$$

This is the expression used to compare the tradeoff between a marginal increase in variable costs (e.g. raw materials, utilities) and a marginal increase in installed equipment cost. If the product of the annualization factor times an incremental installed equipment cost is less than the annual raw material and/or utility savings obtained as a result of the additional investment, then the investment is profitable. The AF depends on the parameters of the CCF model, as well on the values of the 8 additional cost ratios used in eq. (3-23).

3.2.4 Uncertainties in economic valuation models

This section examines the uncertainties in the economic valuation model

$$EP_3 = \sum F_{prod} P_{prod} - \sum F_{rawmat} P_{rawmat} - \sum F_{util} P_{util} - \sum F_{waste} P_{waste} - AF \times C_{TM} \quad (3-24)$$

The focus is on the uncertainties that depend only on the valuation model, that is, uncertainties that will affect the value of the economic potential metric even when the predictions of the process models are assumed to be 100% accurate. Under this assumption, the uncertainty in the first four terms on the right-hand side of eq. (3-24) depends exclusively on the uncertainty in prices. There are three sources of uncertainty for the last term in eq. (3-24):

- a) Uncertainties in the models used to estimate purchased equipment costs from equipment sizes and specifications
- b) Uncertainties in the derivation of installed equipment costs from purchased equipment costs
- c) Uncertainties in the parameters in the annualization factor model.

Each of these sources of uncertainty is examined in detail in the following subsections.

UNCERTAINTIES IN PRICES

Even though current prices for all products, raw materials, utilities, and waste treatment and disposal services might be known precisely at the time of a conceptual design evaluation, the average prices⁶ throughout the life of the project are uncertain. Discounted cash flow average prices throughout the life of the project can be calculated using the following expression:

$$P^{av} = \frac{\sum_{k=n}^{N+n} P_k (1+i)^{-k}}{\sum_{k=n}^{N+n} (1+i)^{-k}} \quad (3-25)$$

where P_k is the price k years into the future, n is the number of years into the future when the process will start operations, N is the number of years the process will operate, and i is the discount rate. As the discount rate increases, the weight of prices farther into the future decreases, resulting in less uncertain discounted cash flow average prices.

In this work, future prices are estimated using a Markov-type model, where the price in year $k+1$ is related to the price in year k by the price volatility multiplier f_p ⁷:

$$P_{k+1} = f_p P_k \quad (3-26)$$

⁶ The term *average prices* is used here to mean *discounted cash flow average prices*. Today's prices are more relevant to the average price as evaluated today than prices 10 years from now.

⁷ f_p is a random variable.

This method is the same as the one commonly used to model the uncertainty in stock prices in the financial literature [6]. Historical data can be used to estimate f_p distributions for each price of interest by following this procedure:

1. Convert all prices to real prices (i.e. correct prices for inflation)
2. Calculate the ratio of the real price in year j to the real price in year $j+1$
3. Compute the logarithmic mean and geometric standard deviation of all price ratios in the sample
4. Model f_p as independent identically distributed (i.i.d.) lognormal distributions with median value equal to the logarithmic mean of the price ratios and uncertainty factor equal to the square of the geometric standard deviations⁸.

In the absence of historical data (for example, for prices for a new product), the marketing department can be asked to estimate subjective distributions for f_p .

The results of the procedure are illustrated in Figure 3-2 (methylene chloride prices) and Figure 3-3 (natural gas prices). Historical data were obtained from the journal *Chemical Marketing Reporter* and from the U.S. Energy Information Agency, respectively. The U.S. producer price index (average for all commodities) was used to correct prices for inflation. A value of 1 was chosen for n , while a triangular distribution with parameters minimum = 9.5, maximum = 16.5, and most likely value = 10 was chosen for N (see Table 3-4). The graphs show historical data as well as 68% and 95% confidence intervals for prices up to year 2016. Each graph also shows a sample price trajectory calculated by the Markov price model. The central value and 95% confidence intervals for the year 2001 discounted cash flow average price are provided as well. The resulting uncertainty factor calculated for both average prices was close to 1.5.

⁸ The uncertainty factor is defined here as the factor by which the median or central value should be multiplied or divided to yield the 95% confidence interval around the central value.

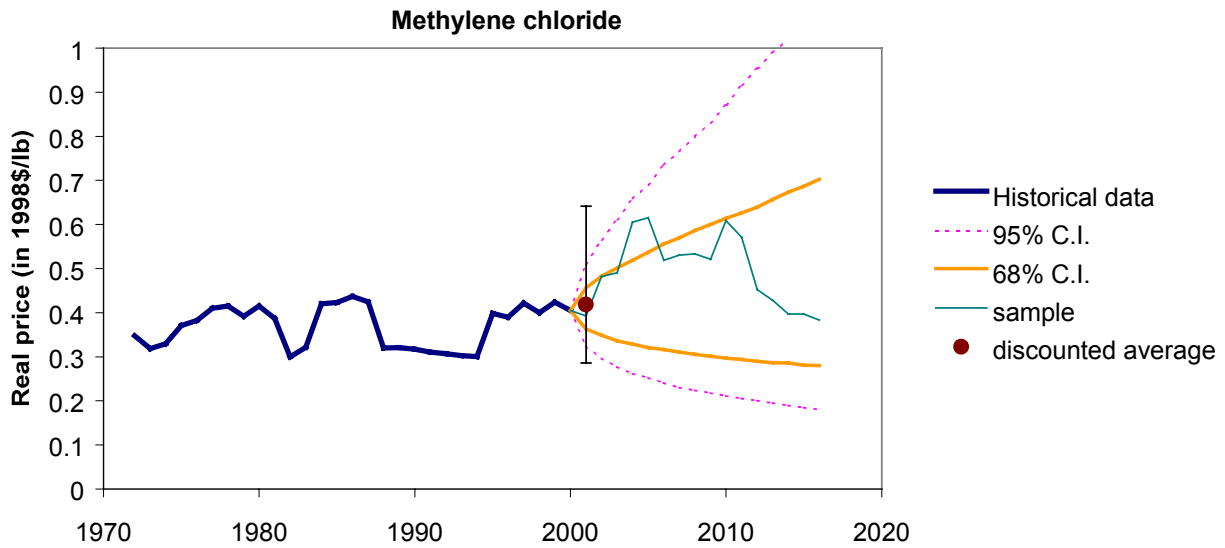


Figure 3-2: Historical data and future uncertainty for methylene chloride prices

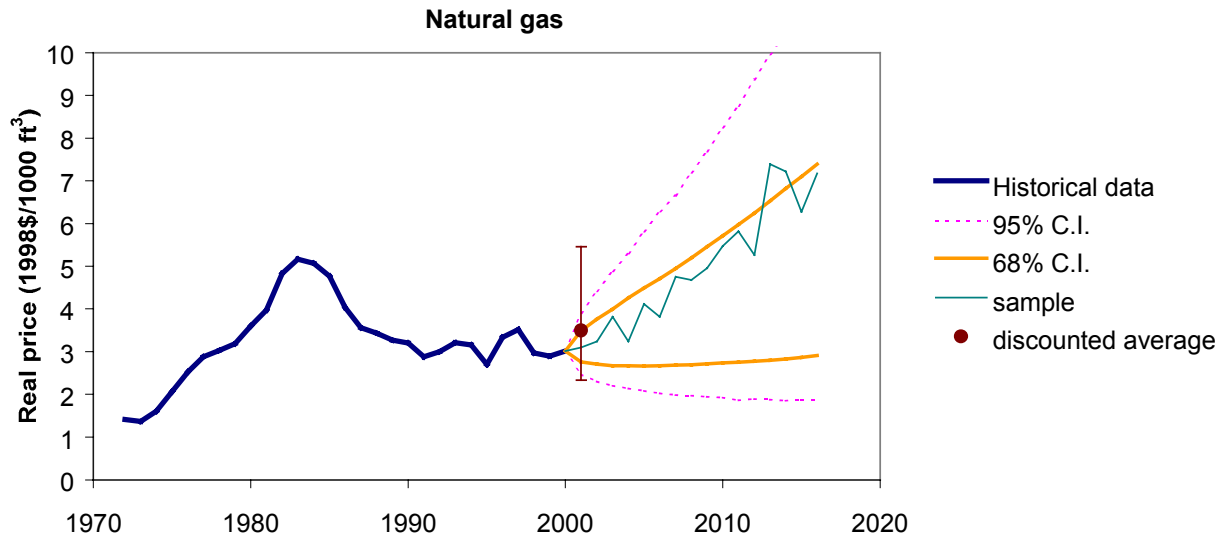


Figure 3-3: Historical data and future uncertainty for natural gas prices

UNCERTAINTIES IN EQUIPMENT COST

The uncertainty in purchased equipment cost correlations is illustrated here through an example. Figure 3-4 shows a comparison among heat exchanger purchased equipment cost correlations obtained from six different sources [1,7-11]. Cost data from the various sources was brought to the same basis by using the 1996 (mid year) value of the Marshall & Swift Equipment

Cost Index (M&S=1037) [11]. Even for such a common piece of equipment as a heat exchanger, there is roughly a factor of 3 difference between the low and high estimates obtained from the chart (this translates into an uncertainty factor of 1.7 around the central estimate). In the charts presented in his book [12], Guthrie placed uncertainty bounds around the central estimates. For the heat exchanger case, the uncertainty bounds are given by the central estimate plus or minus 33% (the uncertainty bounds are also shown in Douglas' book, where a few of Guthrie's charts are reproduced). The author assumes that Guthrie used 68% confidence intervals. If this is indeed the case, then the data used by Guthrie have an uncertainty factor of 1.8 around the central estimate, which is consistent with the range values shown in Figure 3-4.

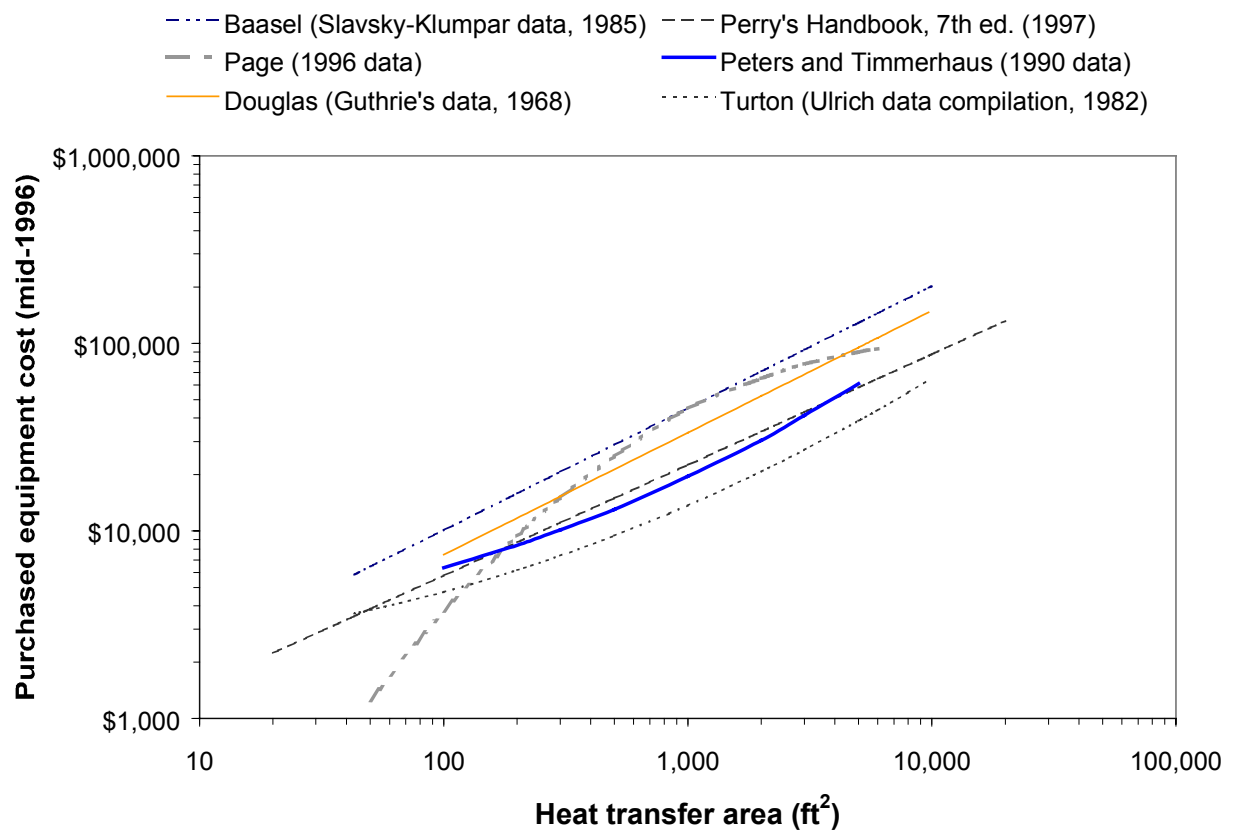


Figure 3-4: Correlations for the estimation of purchased equipment cost of floating-head shell and tube heat exchangers

UNCERTAINTIES IN INSTALLATION COST FACTORS

At the conceptual stage of design, installed equipment costs are usually derived by multiplying purchased equipment costs by installation cost factors. These factors account for all the expenses needed to install a new equipment unit, including labor, piping, insulation, paint, instrumentation, shipping, engineering, supervision, etc., and are also known as *bare module factors*. A general expression for the installation cost factor, f_{BM} , may be written as:

$$f_{BM} = B_1 + B_2 F_M F_P \quad (3-27)$$

where F_M and F_P are correction factors for material of construction and design pressure, respectively. For each piece of equipment, the installed equipment cost is calculated by the relationship

$$C_{BM} = f_{BM} C_p \quad (3-28)$$

where C_p is the purchased cost for a carbon-steel unit designed to operate at atmospheric pressure, and C_{BM} is the installed cost (or bare module cost) of the specified unit. Total installed equipment cost C_{TM} is obtained by adding the bare module costs for the various pieces of equipment in the design:

$$C_{TM} = \sum C_{BM} \quad (3-29)$$

Various design books differ in the way they obtain installation cost factors, as illustrated in Table 3-1. The surprising level of agreement among the factors for heat exchangers shown in the third column of the table is not the result of different authors arriving independently to the same figures, but rather a consequence of the fact that, with the exception of the Aspen simulator, all of the sources cited rely directly or indirectly on the work published by K.M. Guthrie more than 25 years ago [12,13].

Although the installation factors shown in Table 3-1 are independent of equipment size, this is not what was shown in Guthrie's original work. Figure 3-5 compares Guthrie's "norm" bare module factors for heat exchangers with bare module factors calculated using the charts in Guthrie's book as a function of base equipment cost. The difference between the two size-dependent curves shown is the inclusion or exclusion of engineering man-hours in the bare module cost. Personal computers and design software available today that was not available in 1970 should have significantly reduced this cost component. The chart demonstrates that relying on norm modular factors (the factors quoted in all the design books) might result in significant

errors in the estimate of the contribution of a particular unit to fixed capital investment. This translates into suboptimal sizing of individual units. In general, the use of size-independent installation factor biases the designer in the direction of specifying units that are too small relative to the optimum. This can be more clearly seen in Figure 3-6, where the marginal contribution to total installed equipment cost with respect to purchased equipment cost is shown for heat exchangers. Assuming a constant installation cost factor increases the total installed cost of heat exchangers by \$3.14 to \$3.39 (depending on whether single or multiple installation modular factors are used) for each \$1.00 increase in equipment cost. However, using the more rigorous size-dependent factor results in significantly lower contributions, even for the smallest equipment sizes.

Table 3-1: Comparison of approaches to the estimation of installation cost factors

Author	Approach	Example for Heat Exchangers
Smith [4] Douglas [1]	$B_1 = 0$ $B_2 = f(\text{equipment type only})$	$B_2 = 3.5$
Turton et al. [11] Ulrich [5]	$B_1 \neq B_2$ both factors are a function of equipment type only	$B_1 = 1.8$; $B_2 = 1.50$ (Fixed tube sheet or U-Tube type)
Biegler et al. [2]	$B_2 = 1.0$ $B_1 = f(\text{equipment type, total equipment cost})$ There are 5 values depending on the total purchased cost of all units within each equipment type	$B_1 = 2.29$ ($\Sigma C_p < \$200K$) = 2.18 ($\$200K < \Sigma C_p < \$400K$) = 2.14 ($\$400K < \Sigma C_p < \$600K$) = 2.12 ($\$600K < \Sigma C_p < \$800K$) = 2.09 ($\$800K < \Sigma C_p < \$1,000K$) C_p above are given in 1968 prices
Baasel [7]	$B_1 = 0$ $B_2 = f(\text{equipment type, number of units installed})$	$B_1 = 3.39$ (single unit) $B_1 = 3.29$ (2 to 6 units) $B_1 = 3.18$ (6 to 12 units) $B_1 = 3.14$ (12 to 18 units) $B_1 = 3.12$ (18 to 24 units) $B_1 = 3.09$ (24 to 30 units)
Aspen Plus process simulator (release 9) ^a	$B_1 \neq B_2$ both factors are a function of equipment type only	$B_1 \cong 1.91$ $B_2 \cong 1.90$

a) The factor model in Aspen Plus gives material factors (in \$ material/\$ purchased equipment cost) and labor factors (in man-hours/1979 material cost). The values of B_1 and B_2 in the table were calculated by multiplying the labor factors by estimated 1979 hourly wages.

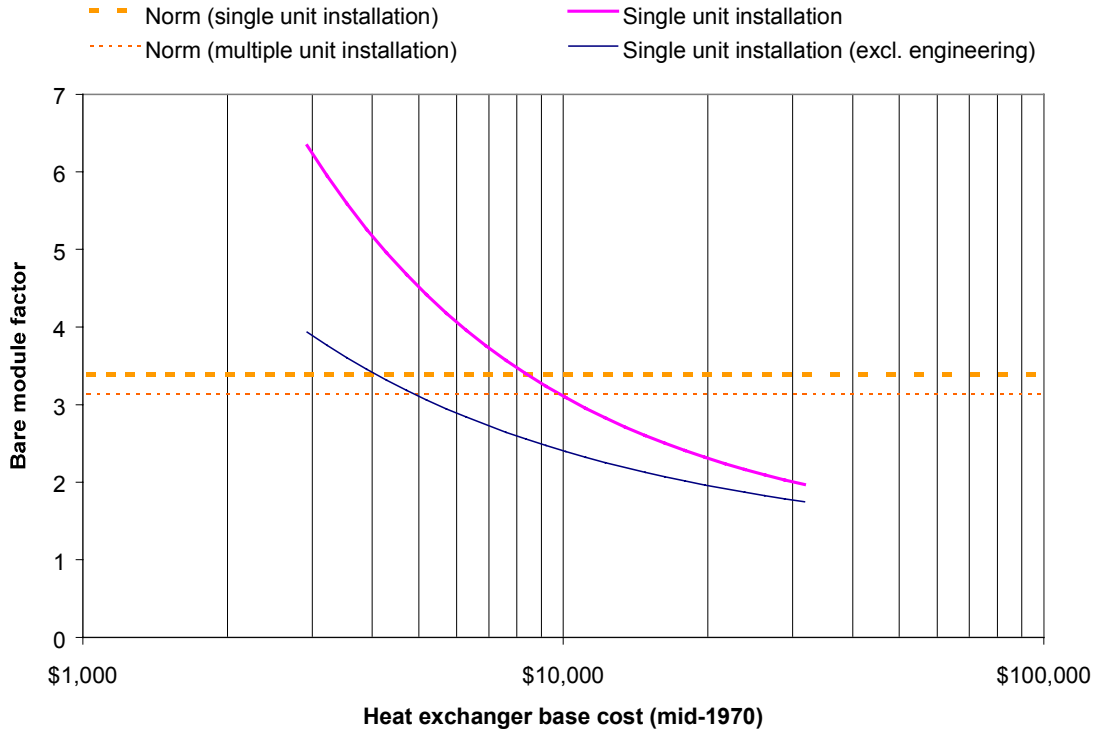


Figure 3-5: Guthrie's installation factors for heat exchangers

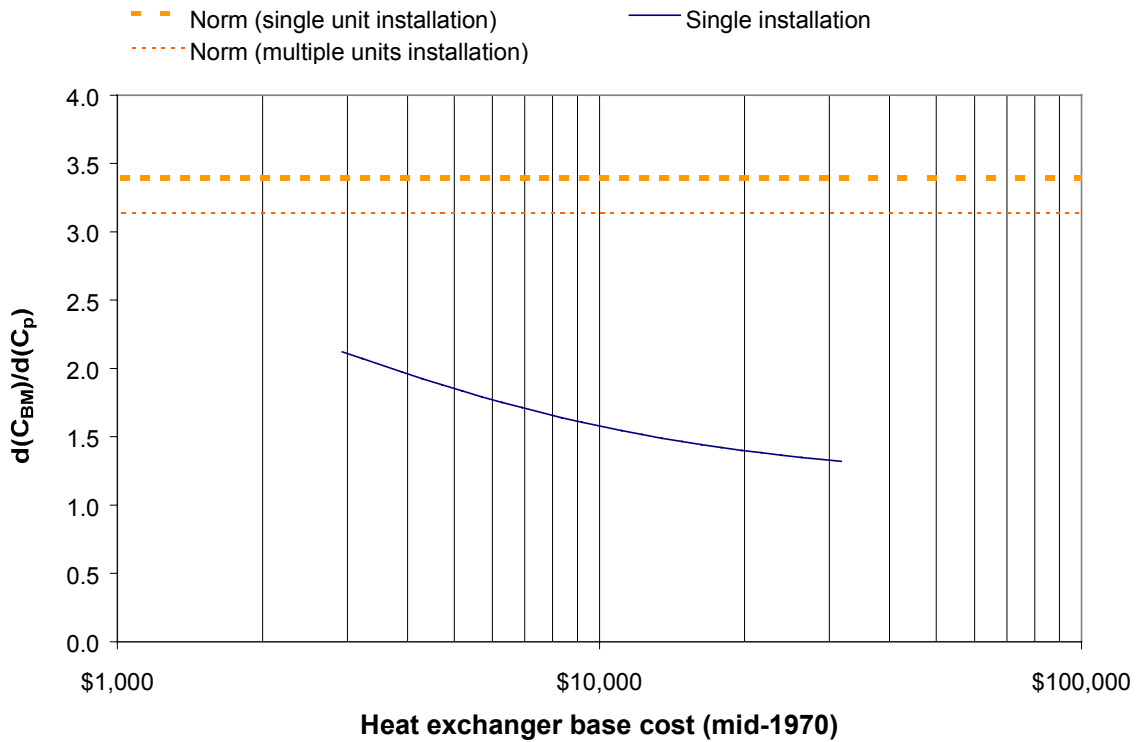


Figure 3-6: Marginal contributions to installed equipment cost with respect to purchased equipment cost for heat exchangers (based on Guthrie's data)

UNCERTAINTIES IN ANNUALIZATION FACTORS

Parametric Uncertainties

As illustrated in section 3.2.1, there is a large discrepancy in recommended values of the annualization factor among various process design textbooks. A close examination of the assumptions used to derive the annualization factor in any of the textbooks shows that there are also significant uncertainties in the annualization factor model parameters. The factors used to derive total capital investment and annual charges (e.g. from maintenance and insurance) are not precisely known and are likely to vary from project to project. In addition, it is difficult to predict the actual project life, so the number of years of operation is a very important uncertain factor.

To illustrate the uncertainty inherent in annualization factors, information used by Douglas in the derivation of the annualization factor value he uses has been transformed into probability distributions for the various factors. For most factors, a triangular probability distribution was used, with the range given by the minimum and maximum values cited by Douglas, and the most likely value given by the particular value chosen by Douglas when he carried out his calculations. When the most likely value chosen by Douglas would not be the same as the mean of a triangular distribution built as described above, a beta distribution was used instead. The parameters of the distribution were chosen such that the shape of the distribution was close to triangular and its mean was the same as the value used by Douglas. Uniform distributions were used when Douglas cited a range of values but did not choose a most likely value. A summary of the distributions used in the total product cost and total capital investment models is given in Table 3-2 through Table 3-4.

A Monte Carlo simulation of a more detailed spreadsheet version of the annualization factor model discussed in section 3.2.3 yielded the results shown in Table 3-5 for six different combinations of discount rate and tax law assumptions. The table shows that annualization factors increase as the discount rate increases. They also increase when the tax rate increases and when less generous depreciation schedules are allowed. Plots of four of the distributions are shown in Figure 3-7. Not surprisingly, the annualization factor is very sensitive to the choice of discount rate, as evidenced by the widening of the distributions for the case where the design team is uncertain about the appropriate value of the discount rate.

Table 3-2: Parametric uncertainties in the capital cost estimation model of Douglas

Capital cost component	Distribution for cost factor	Mean value
I. Fixed capital investment (FCI)		
A. Direct costs		
<u>Onsite costs</u> or ISBL (inside of battery limits) are obtained as the sum of the product of the purchased cost of each piece of equipment times an equipment-specific bare module factor: 50-60% of FCI		
<u>Offsite costs</u> or OSBL (outside of battery limits), refer to auxiliary facilities (e.g. steam plant, cooling towers) and buildings. Douglas distinguishes between two cases:		
a) Expansion of existing facility: 40 to 50% of onsite costs	$\frac{\text{Offsite}}{\text{Onsite}} = T(40\%, 45\%, 50\%)^a$	45%
b) Construction of a grass-roots plant or a major plant expansion: up to 200 or 400% of the onsite costs	$\frac{\text{Offsite}}{\text{Onsite}} = U(200\%, 400\%)^b$	300%
B. Indirect costs		
<u>Owner's costs</u> include engineering, supervision and construction expenses: 5 to 15% of direct costs; however, the bare module factors used to estimate onsite costs already include engineering and construction.	$\frac{\text{Owner's}}{\text{Direct}} = T(2.5\%, 5\%, 7.5\%)$ <i>(estimated using one half of the range of engineering and supervision)</i>	5%
<u>Contingencies and fees.</u> Douglas assumes that the sum of contingencies and fees equals about 20% of the direct costs		
a) Contingency: about 5-20% of FCI	$\frac{\text{Cont.}}{\text{Direct}} = T(5\%, 13.25\%, 20\%)$ <i>The most likely value is chosen so that mean of the sum of contingency and fee corresponds to 20% of the direct costs</i>	16.75%
b) Contractor's fee: about 1.5-5% of FCI	$\frac{\text{Fee.}}{\text{Direct}} = U(1.5\%, 5\%)$	3.25%
II. Working capital: about 10-20% of the TCI	$\frac{\text{WC}}{\text{TCI}} = T(10\%, 15\%, 20\%)$	15%
III. Start-up costs: about 8-10% of FCI	$\frac{\text{SC}}{\text{FCI}} = \beta(8\%, 10.3\%, 10\%, 10.4\%)^c$ <i>The mode and the maximum value were chosen so that the mean value corresponds to the value used by Douglas without extending the range too much beyond the range cited.</i>	10%
Accuracy factor: Probable accuracy of a study estimate (factored estimate) is up to $\pm 25\%$	$\frac{\text{TCI}}{\text{TCI}_{nom}} = T(75\%, 100\%, 125\%)$	100%

a) A T(a,b,c) distribution is a triangular distribution with parameters a=minimum value, b=most likely value, c=maximum value.

b) A U(a,b) distribution is a uniform distribution with parameters a=minimum value, b=maximum value.

c) A $\beta(a,b,c,d)$ distribution is a beta distribution with parameters a=minimum value, b=mode, c=mean, d=maximum

Table 3-3: Parametric uncertainties in the total product cost model

Total product cost component	Distribution for cost factor	Mean value
I. Manufacturing cost		
A. Direct production costs		
1. Raw materials		
2. Utilities		
3. Maintenance and repairs: about 2-10% of FCI	$\frac{Maint}{Onsite} = \frac{Maint}{FCI} \div \frac{Onsite}{FCI}$ $= \frac{\beta(2\%,3\%,4\%,10\%)}{U(50\%,60\%)}$	$\frac{4\%}{55\%}$
4. Operating supplies: about 10-20% of cost for maintenance and repairs	$\frac{Op.Sup.}{Maint.} = T(10\%,15\%,20\%)$	15%
5. Operating labor		
6. Direct supervision and clerical labor: about 10-25% of operating labor	$\frac{Superv.}{Op.Labor} = \beta(10\%,21\%,20\%,25\%)$	20%
7. Laboratory charges: about 10-20% of operating labor	$\frac{Lab}{Op.Labor} = T(10\%,15\%,20\%)$	15%
8. Patents and royalties: about 0-6% of total product cost	$\frac{Royalties}{TPC} = T(0\%,3\%,6\%)$	3%
B. Fixed Charges		
Local taxes: about 1-4% of FCI		
Insurance: about 0.4-1% of FCI	$\frac{Tax \& Ins.}{FCI} = \beta(1.4\%,2.9\%,3\%,5\%)$	3%
C. Plant Overhead: about 50-70% of the cost of operating labor, supervision, and maintenance	$OVHD = T(50\%,60\%,70\%)$	60%
II. General expenses: Administrative costs are about 2-5% of total product cost	$\frac{SARE}{Rev} = \beta(2.0\%,2.1\%,2.5\%,5\%)$	2.5%

Table 3-4: Uncertain factors in the capital charge factor model

Factor in CCF calculation	Distribution for CCF factor	Mean value																			
<u>Tax rate:</u> Douglas uses 48%, but comments that the rate has been changed and is likely to change again in the future; the current tax rate is 34%	<u>Base case:</u> Fixed at $\tau = 48\%$	48%																			
	<u>Current tax law case:</u> 34% for the first year. For subsequent years $\tau_j = \tau_{j-1} + \Delta\tau$ where ($\Delta\tau$) is modeled as a discrete distribution with the following values and probabilities ^a : <table border="1" style="margin-left: 20px;"> <thead> <tr> <th>$\Delta\tau$</th> <th>P($\Delta\tau$)</th> </tr> </thead> <tbody> <tr><td>-8%</td><td>0.01</td></tr> <tr><td>-4%</td><td>0.02</td></tr> <tr><td>-2%</td><td>0.04</td></tr> <tr><td>-1%</td><td>0.08</td></tr> <tr><td>0%</td><td>0.70</td></tr> <tr><td>+1%</td><td>0.08</td></tr> <tr><td>+2%</td><td>0.04</td></tr> <tr><td>+4%</td><td>0.02</td></tr> <tr><td>+8%</td><td>0.01</td></tr> </tbody> </table>	$\Delta\tau$	P($\Delta\tau$)	-8%	0.01	-4%	0.02	-2%	0.04	-1%	0.08	0%	0.70	+1%	0.08	+2%	0.04	+4%	0.02	+8%	0.01
$\Delta\tau$	P($\Delta\tau$)																				
-8%	0.01																				
-4%	0.02																				
-2%	0.04																				
-1%	0.08																				
0%	0.70																				
+1%	0.08																				
+2%	0.04																				
+4%	0.02																				
+8%	0.01																				
<u>Depreciation allowance:</u> Douglas uses 0.1(FCI) which corresponds to straight-line depreciation with 10-yr lifetime, but most corporations take advantage of the modified accelerated cost recovery system (MACRS) depreciation schedule allowed by current tax law.	<u>Base case:</u> Fixed at 10%/yr for first 10 years, zero thereafter)	10%/yr																			
	<u>Current tax law case:</u> MACRS method for 9.5 years class life	<table border="1" style="margin-left: 20px;"> <thead> <tr> <th>Yr</th> <th>%/yr</th> </tr> </thead> <tbody> <tr><td>1</td><td>20.00</td></tr> <tr><td>2</td><td>32.00</td></tr> <tr><td>3</td><td>19.20</td></tr> <tr><td>4</td><td>11.52</td></tr> <tr><td>5</td><td>11.52</td></tr> <tr><td>6</td><td>5.76</td></tr> <tr><td>7</td><td>0</td></tr> </tbody> </table>	Yr	%/yr	1	20.00	2	32.00	3	19.20	4	11.52	5	11.52	6	5.76	7	0			
Yr	%/yr																				
1	20.00																				
2	32.00																				
3	19.20																				
4	11.52																				
5	11.52																				
6	5.76																				
7	0																				
<u>Service life:</u> Douglas states that for petroleum processes a 16-yr life is often assumed, while for chemical plants an 11-yr life is often taken.	$N = T(9.5,10,16.5)$	12																			
<u>Period of construction:</u> Douglas uses 4 years	Fixed at 4 yers	4																			
<u>Fraction of capital investment made during first year of construction:</u> 10-15% of FCI; Douglas uses 10%	T(10%,10%,15%)	11.67%																			
<u>Fraction of capital investment made during second and third years of construction:</u> 35-40% of FCI each year; Douglas uses 40%	two i.i.d. T(35%,40%,40%) distributions	38.33%																			
<u>Revenues and variable costs during first three years of operation as a fraction of the nominal value.</u> Douglas states that experience indicates that the production rate increases from 60 to 90 to 95% during the first, second, and third years of operation, respectively.	Fixed at 60% for year 1,	60%																			
	90% for year 2,	90%																			
	and 95% for year 3.	95%																			
<u>Discount rate.</u> Douglas states that a value of $i = 0.15$ is the smallest value he would ever consider for a new project, and that a value of 0.20 is more realistic to add a margin of safety. For a high-risk project he might use $i=0.33$	<u>Base case:</u> Fixed at 20%/yr	20%																			
	<u>Value judgment uncertainty case:</u> $i=\beta(15\%,17\%,20\%,33\%)$	20%																			

a) The probability distribution is loosely based on changes in U.S. corporate tax rates in the period 1929-1991 [10]

Table 3-5: Impact of parametric uncertainty on annualization factors

		Depreciation and taxes	
		Douglas base case	Current tax laws case
Discount rate	$i = 15\%$	median = 1.05 yr ⁻¹ UF = 1.26	median = 0.87 yr ⁻¹ UF = 1.26
	$i = 20\%$	median = 1.38 yr ⁻¹ UF = 1.25	median = 1.12 yr ⁻¹ UF = 1.25
	Uncertain: $i = \beta(15\%, 17\%, 20\%, 33\%)$	median = 1.37 yr ⁻¹ UF = 1.52	median = 1.11 yr ⁻¹ UF = 1.49

Note: UF = Uncertainty factor, defined such that the 95% confidence interval is given by (median/UF, median×UF)

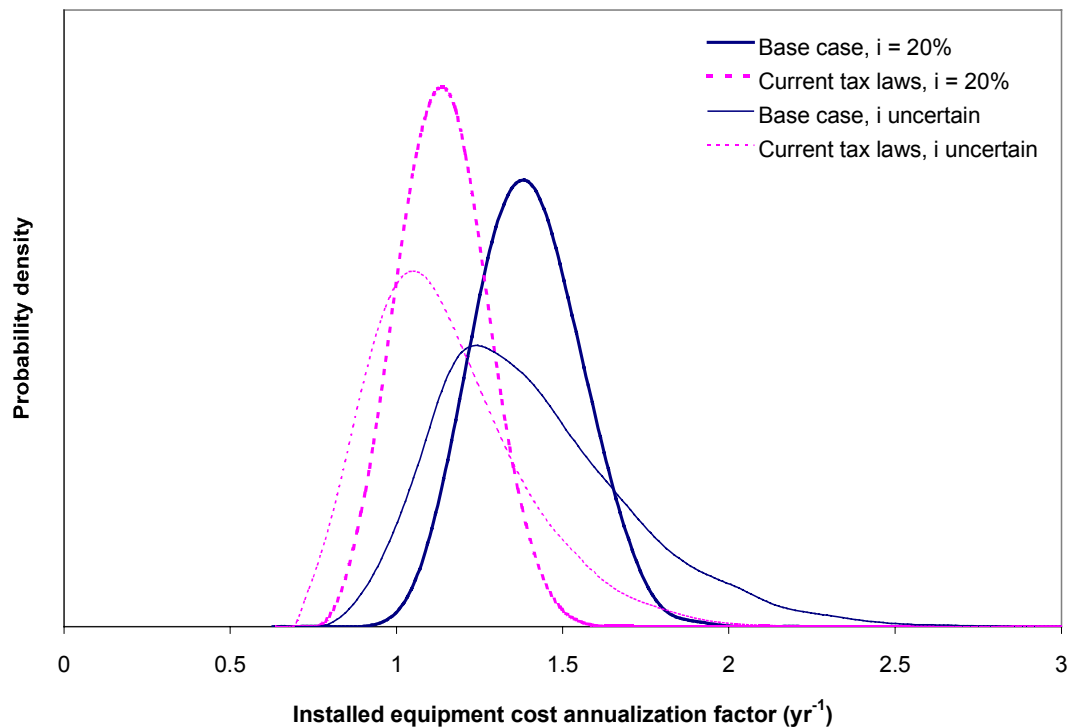


Figure 3-7: Annualization factor probability density distributions (Douglas model)

Structural uncertainties

This section examines the impact of various structural uncertainties on the installed equipment cost annualization factor. The first structural uncertainty analyzed is the type of indirect costs included in the estimation of fixed capital investment. Douglas considers two types of projects: (i) expansion of an existing facility, and (ii) construction of a grassroots plant (see Table 3-2). Peters and Timmerhaus consider an additional type of project, which lies somewhere in between the two types of projects considered by Douglas: construction of a new plant at an existing site [10].

Even though the factored capital cost estimation method yields acceptable predictions of total capital cost at the conceptual stage of design, it is not obvious that annualization factors built using the full set of cost factors are appropriate for the purpose of sizing equipment. For example, the optimum number of trays for a distillation column should not be a function of whether the column is being added to an existing plant or erected as part of a new plant at a new site. For this reason annualization factors are computed here for an additional type of project, referred to as an “equipment sizing project”. Table 3-6 shows the modifications made to the parameters in the Douglas annualization factor model in the calculation of equipment sizing annualization factors. In choosing which factors to set to zero, consideration was given to whether a particular cost item could be expected to increase proportionally with equipment cost as the size of a particular piece of equipment (e.g. a distillation column) was increased. As previously discussed, one would not expect offsite costs to increase (for the case of distillation columns and heat exchangers they should actually decrease, as consumption of utilities decreases). Unanticipated costs (accounted for by the contingency/FCI factor) should not change. The amount of working capital would not be expected to change significantly, since the bulk of the material stored in the plant is located in storage tanks, and not in processing equipment. The amount of royalties paid should remain constant, so the royalties/TPC factor is set to zero as well. An additional adjustment made for the calculation of the equipment sizing annualization factors was to change the reference cost for the maintenance cost and salvage value factors. Installed equipment costs are used as reference cost instead of fixed capital investment, using the distribution of FCI to C_{TM} ratios in the facility expansion case to carry out the conversion. This is done based on the assumption that the real cost driver for maintenance cost is installed equipment cost and not fixed capital investment. Keeping FCI as the cost driver would have resulted in an underestimation of maintenance cost as FCI decreases when many of the cost ratios are set to zero.

Table 3-6: Changes made to the parameters in the Douglas annualization factor model for the purpose of deriving an annualization factor appropriate for sizing equipment

Factors	Change
Offsite/Onsite	} Set to zero
Owner's cost/Direct cost	
Contingency/FCI	
Working capital/TCI	
Start-up capital/FCI	
Royalties/TPC	
Overhead Rate	
SARE/Revenue	
Fraction of capital investment made in first, second, and third years of construction (all investments are assumed to be made in the last year of construction)	
Maintenance factor	Changed from $\beta(2\%,3\%,4\%,10\%) \times \text{FCI}$ to $\beta(3.46\%,5.74\%,7.26\%,16.4\%) \times C_{\text{TM}}$ (since maintenance is assumed to be proportional to installed equipment cost and FCI decreases significantly after many fixed cost factors are set to zero).
Salvage value	Changed from 3% of FCI to 5.5% of Installed equipment cost

The difference between the three design scenarios are shown in Table 3-7 and Figure 3-8, for the base case Douglas model with straight-line depreciation, a tax rate of 48%, and a discount rate of 15%. There is more than a factor of 6 difference in installed equipment cost annualization factors between the equipment sizing scenario and the grassroots plant scenario. This means that an additional dollar invested in equipment would have to generate six times as much savings in raw materials or utilities costs to be considered worthwhile if grassroots scenario annualization factors are used to evaluate alternative designs, as compared to the case of using equipment sizing scenario annualization factors. As discussed above, the optimum size of a piece of processing equipment should be independent of whether it is being retrofitted to an existing process or installed in a new site. Economic valuation models based on the grassroots plant scenario may be appropriate for assessing the economic viability of an entire project, but should not be used within an optimization framework to set equipment sizes.

Table 3-7: Effect of indirect cost factor assumptions on the annualization factors obtained from the Douglas model

Case	AF (central value, in yr ⁻¹)	Uncertainty factor
Grassroots plant	2.66	1.43
Plant expansion	1.05	1.26
Equipment sizing	0.41	1.26

Notes: $i = 15\%$, $\tau = 48\%$, and straight-line depreciation; cost factor distributions are given in Table 3-2 through Table 3-4 (base case distributions).

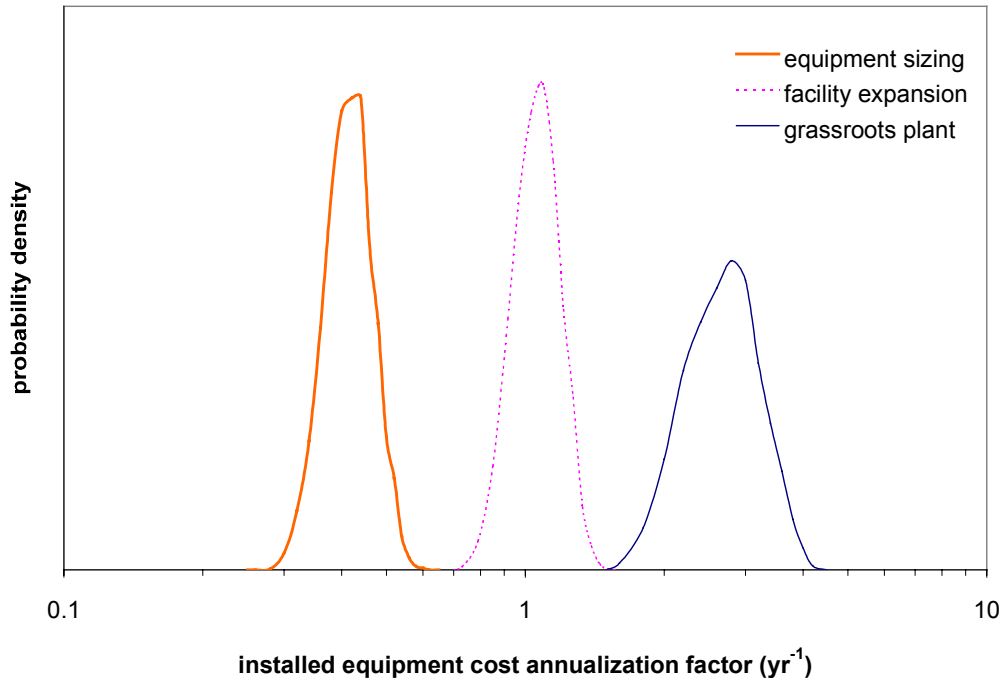


Figure 3-8: Probability density distributions for installed equipment cost annualization factors calculated using the Douglas model for three different design scenarios, using a discount rate of 15%

The second structural uncertainty examined in the section is the set of assumptions used to build the cost model. Douglas-type annualization factor models were developed based on information contained in several process design textbooks. Table 3-8 lists the major assumptions made in each of the cases examined. A discount rate of 15% was used in all cases. The parameters obtained for the distributions of the installed equipment cost annualization factor are listed in the last two rows of the table. Distributions for a subset of these cases (those corresponding to the facility expansion design scenario) are shown in Figure 3-9. There is about a factor of four difference between the low end of the lowest distribution and the high end of the highest distribution. Even if facility expansion annualization factors are used to evaluate

alternative process designs instead of more appropriate equipment sizing annualization factors, Figure 3-9 shows that the rule of thumb $AF = 1 \text{ yr}^{-1}$ shifts the operating cost vs. capital cost tradeoff too much in the direction of avoiding capital expenditures.

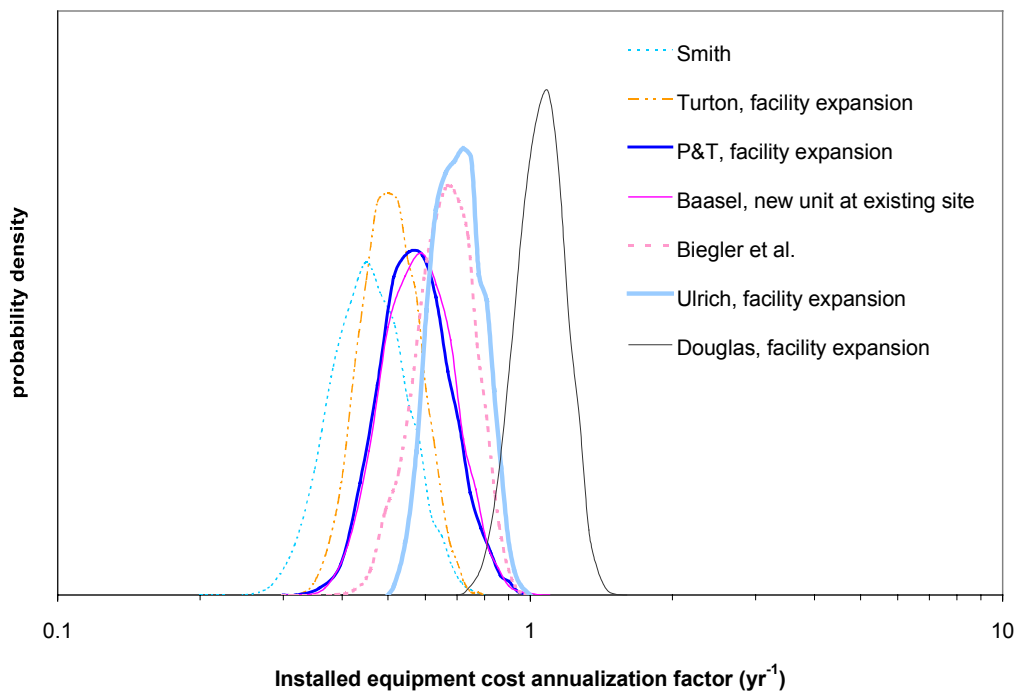


Figure 3-9: Installed equipment cost annualization factor distributions obtained from the economic evaluation assumptions of various process design books.

This exercise has shown that there are significant uncertainties in the value of the annualization factor that is appropriate for use in conceptual design stage economic objective functions, even when designers have no uncertainty regarding the appropriate value of the discount rate to be used in the economic analysis. It is important to emphasize that this finding also applies when the net present value economic valuation model is used, since the total annualized profits economic valuation metric is proportional to net present value. Using the definition of the capital charge factor, and assuming that all capital investments are made in the first year of the project, TAP and NPV are related through the expression

$$NPV = -TCI + \frac{Revenue - TPC}{CCF} = \frac{TAP}{CCF} \quad (3-30)$$

Table 3-8: Installed equipment cost annualization factor model assumptions and results for various process design textbooks.

	Douglas [1]		Smith [4]	Turton et al. [11]		Biegler et al. [2]	Peters and Timmerhaus [10]			Baasel [7] ^a		Ulrich [5]	
	Facility expansion	Grass-roots		Facility expansion	Grass-roots		Facility expansion	New unit existing site	Grass-roots	New unit existing site	Grass-roots	Facility expansion	Grass-roots
<i>Maint/FCI</i>	2-10%		6%	2-10%		4-6%	2-6%			2.5-8.6%		2-10%	
<i>Op.Sup./Maint</i>	10-20%		n/c ^b	10-20%		40%	10-20%			15-20%		10-20%	
<i>OVHD</i>	50-70%		n/c	50-70%		20%	50-70%			n/c		50-70%	
<i>Tax&Ins./FCI</i>	1.4-5%		n/c	1.4-5%		3%	1.4-5%			2-3%		1.4%-3%	
<i>Offsite</i>	40-50%	200-400%	25-67%	0%	27-43%	40%	12-29%	12-32%	21-45%	10-26%	45-56%	0%	23-37%
<i>Onsite</i>													
<i>Cont&Fee/FCI</i>	6.5-25%		n/c	15%		15%	5-13%			9%		13%	10%
<i>FCI accuracy</i>	25%		30%	-20% to +30%		25-40%	-20% to +40%			14%		-20% to +30%	
<i>WC/FCI</i>	10-20%		15%	15%-20%		18%	10-20%			13-26%		10-20%	
<i>SC/FCI</i>	8-10%		n/c	n/c		n/c	8-10%			8-10%		n/c	
<i>Depreciation</i>	Straight line		n/c	MACRS schedule		MACRS	MACRS schedule			ACRS schedule		Straight line	
<i>Service Life</i>	10-16 years		5-10 years	10-15 years		9-15 yr	9-13 years			7-11 years		10 years	
<i>Tax rate</i>	48%		n/c	30%		34%	34%			34%		50%	
<i>SV/FCI</i>	3%		n/c	n/c		n/c	0-10%			n/c		n/c	
<i>Period of construction</i>	4 years		1 year	2 years		1 year	1 year			2-3 years		3 years	
<i>AF (central value, yr⁻¹)</i>	1.05	2.66	0.46	0.52	0.67	0.66	0.57	0.59	0.67	0.58	0.76	0.70	0.91
<i>AF (uncertainty factor)</i>	1.26	1.43	1.44	1.32	1.32	1.32	1.40	1.39	1.40	1.40	1.40	1.28	1.27

a) Parameters not provided in the main body of the text were derived from examples.

b) n/c = not considered

SUMMARY

The following uncertainties in the annualized profit economic evaluation model have been identified and characterized:

- Prices (uncertainty factor ~ 1.5 , might be much higher for new products, waste disposal services)
- Purchased equipment cost (uncertainty factor ~ 1.7)
- Installation cost factor (uncertainty factor \sim up to 1.5, depending on equipment size)
- Annualization factor (uncertainty factor ~ 1.4 if the discount rate is known)

Chapter 4 discusses approaches to decision making and flowsheet optimization in the presence of significant uncertainties in valuation models or objective functions. The following section focuses on the impact of the biases (systematic errors) identified in the annualized profit valuation model.

3.2.5 The impact of widely used heuristics on the resolution of the operating vs. capital cost tradeoff

"Hey, there is a \$100 bill on the floor over there!"

"That can't possibly be a real \$100 bill. If it were, some one would have already picked it up."

Opening quote in *"Preventing Industrial Pollution at its Source: A Final Report of the Michigan Source Reduction Initiative"*

This section discusses how the widely used economic value models used in the conceptual phase of process design introduce biases against capital expenditures, which in turn lead to material use, energy consumption, and waste generation rates that are in excess of those that would be economically optimum. This finding is consistent with published accounts of the abundance of overlooked energy conservation and waste reduction projects with rates of return in excess of 100%/year. For example, Figure 3-10 shows selected results from the energy and waste reduction contest at the Louisiana division of the Dow Chemical Company [14].

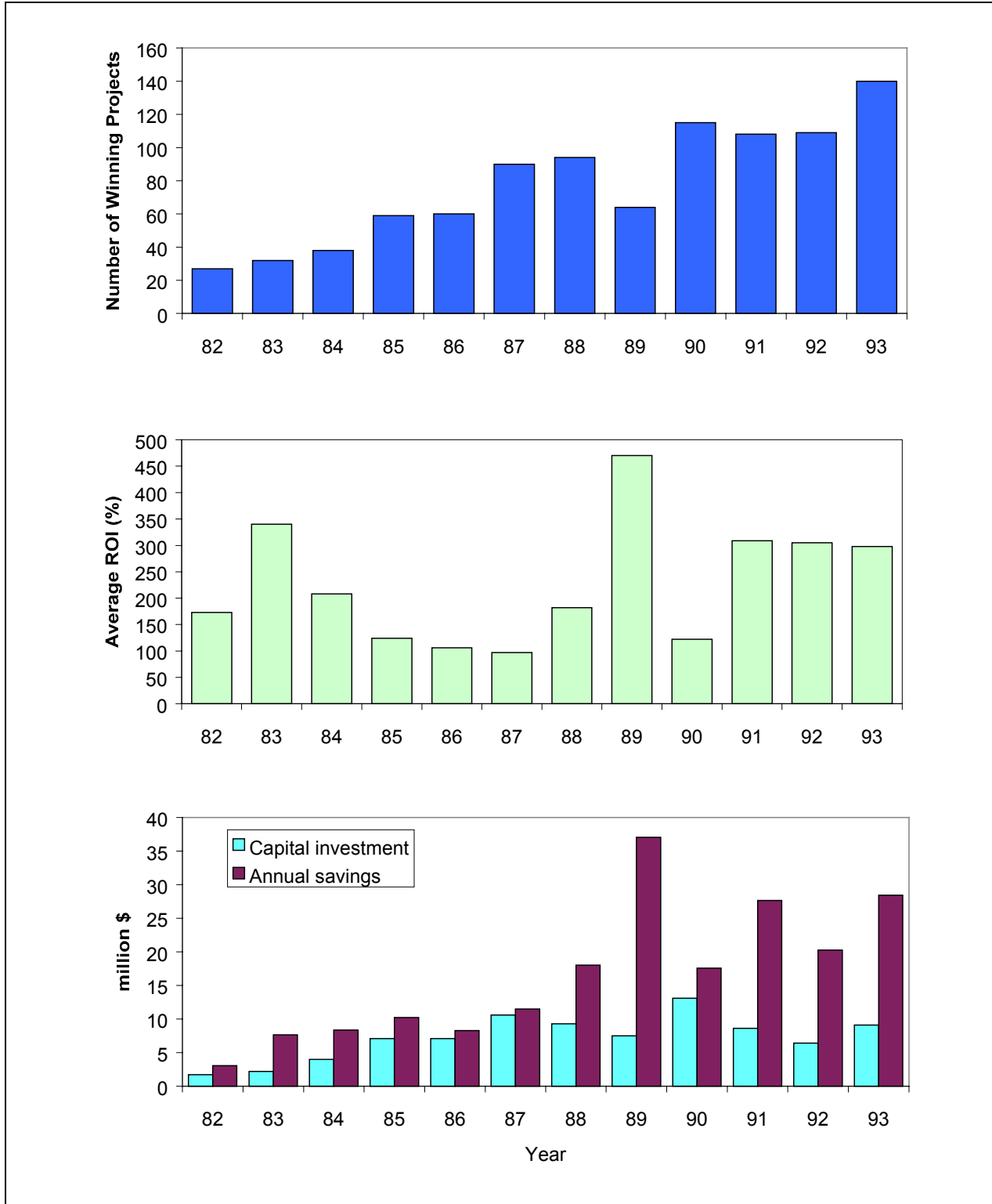


Figure 3-10: Results of the Energy and Waste Reduction Contests at Dow Chemical (Louisiana Division)

It is remarkable that after 12 years of having the contest, the number of winning projects continued to increase, when one would have expected that as time went by it would have become more difficult to find profitable opportunities to save energy and reduce waste. The average return on investment for all projects was greater than 100% in each of the 12 years for which data was provided, and it was as high as 450% in 1989. A recent account of a similar effort at the Midland site [15] reported a 180% annual return on \$3 million invested in projects to reduce toxic waste generation and emissions. These projects have such high rates of return that they would be worth pursuing even if there were no environmental benefits associated to them. Amazingly, by the own admission of the Dow managers involved in the Midland project, the investment opportunities would not have been identified in the absence of a pollution prevention objective. A question that comes to mind after reading these accounts is: why is there such an abundance of suboptimal processes?

The author proposes two answers to this question. The first one was already briefly discussed at the beginning of this chapter, namely, that there is such a vast number of design alternatives associated to any process design problem that it is highly unlikely that designers will have examined the most profitable ones before the time available for analysis is exhausted. The second one, which is examined in detail here, is that widely used economic valuation models and procedures introduce biases against profitable capital investments.

Consider again the economic potential valuation model, eq (3-24). Assume that the design team is trying to size the equipment for a design alternative. As the equipment sizes vary, the flows of materials and utilities are likely to vary as well. The direction and magnitude of the variations would be predicted by the process model. Variations in flow rates impact the economic potential of the process through the first four terms on the right hand side of eq (3-24). Increasing the size of the equipment also impacts the economic potential directly by increasing the capital cost and the annual maintenance, local tax and insurance charges, which are captured by the last term in eq (3-24). An increase in equipment size is profitable if the marginal increase in economic potential from the terms varying with flow rates is larger than the marginal increase in annualized capital costs. For example, increasing the number of trays in a distillation column would decrease the amount of utilities needed to effect the desired separation, thus increasing the economic potential through a reduction in the magnitude of the utility cost term. But increasing the number of trays would increase the cost of acquiring, installing, and maintaining the column.

At some point the additional annualized costs associated with increasing the number of trays would be larger than the utility savings. The optimum number of trays would then be given by the number at which the incremental utility savings are just balanced by the incremental annualized cost.

The marginal utility savings are given by:

$$\frac{\partial(\sum F_{util} P_{util})}{\partial n_t} = P_{HU} \frac{\partial \dot{Q}_H}{\partial n_t} + P_{CU} \frac{\partial \dot{Q}_C}{\partial n_t} \quad (3-31)$$

while the marginal increase in annualized column costs is given by:

$$\frac{\partial(AF \sum f_{BM} C_p)}{\partial n_t} = AF \frac{\partial C_{BM}}{\partial C_p} \frac{\partial C_p}{\partial n_t} \quad (3-32)$$

Assume that we have available a perfect process model that allows us to predict precisely the marginal changes in utility consumption rates in the distillation column with respect to the number of trays. Assume further that we have company data that allows us to estimate precisely the change in purchased column cost with respect to the number of trays. In that case, the point at which the two marginal changes are equal depends entirely on the utility prices (P_{HU} and P_{CU}), the marginal change in bare module cost with respect to purchased cost ($\partial C_{BM}/\partial C_p$), and the annualization factor (AF). As these last two factors increase, adding a tray becomes less desirable. Current economic evaluation models introduce the following biases:

- The use of installation factors that are independent of size overestimates the magnitude of ($\partial C_{BM}/\partial C_p$), as was shown in Figure 3-6 for the case of heat exchangers. This source might be responsible for a factor-of-two overestimation in marginal annualized capital costs.
- Depending on the annualization factor model used, there might be many capital cost factors considered that are independent of the sizing decision. The most obvious example is the (offsite/onsite) capital cost factor that accounts for auxiliary facilities. Instead of allocating the capital cost of utility and waste treatment plants to the utility and waste streams that make the building of these plants necessary, the offsite/onsite capital cost factor allocates them to the equipment that could reduce the need for such plants. In this case, not only the magnitude, but even the sign of the predicted marginal change is wrong! Based on the distributions shown in Figure 3-8, it may be estimated that current procedures overestimate the magnitude of AF by a factor of 2 to 8.

- Current design methods encourage designers to apply generous contingency factors and high discount rates as a way to respond to uncertainties. Both adjustments result in increasing the magnitude of the annualization factor, introducing further biases against capital investments. Consider a project where the major source of uncertainty is product price. The process will be designed using well-known technology. Increasing the discount rate and contingency factors in the economic potential model used to size equipment will result in heat exchangers and distillation columns that are too small relative to the optimum resolution of the well-known tradeoff between equipment size and utilities cost. A high discount rate might be appropriate for managers evaluating the decision of whether or not to go ahead with the entire project, but the sizing of conventional equipment should be done according to annualization factors that accurately reflect marginal costs and a firm's opportunity cost of capital. Rather than imposing large discount rates, managers should use uncertainty analysis to generate a distribution of net present values for the project using the firm's opportunity cost of capital. This approach would result in an appropriate resolution of the capital vs. operating cost tradeoff without the loss of any information regarding risk (a more thorough discussion on approaches to decision making with uncertainties in valuation models is given in Chapter 40).

EXAMPLE: SIZING A HEAT EXCHANGER

The points made in the preceding paragraphs are illustrated here through an example. Consider the solvent recovery flowsheet shown in Figure 3-11 (details on the case study from which the flowsheet was extracted are given in Appendix A). Assume that this flowsheet is part of a new process being built in an undeveloped site (grassroots project). Assume further that the product made by the parent process is a new pharmaceutical product. Because of uncertainties in the demand for the product and its price, management has instructed the design team to use a 25% discount rate to evaluate the project. We are currently interested in determining the optimum size for the heat exchanger used to preheat the feed to the solvent recovery system.

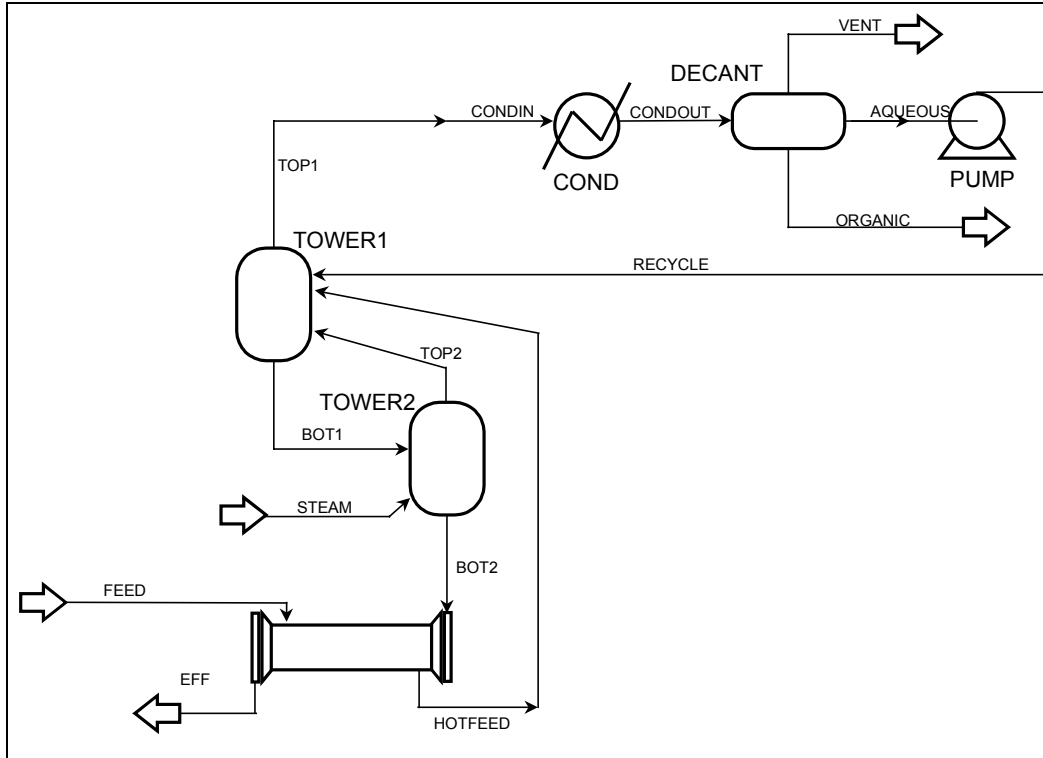


Figure 3-11: Heat exchanger sizing example flowsheet

An Aspen Plus process model is used to predict the steam input rates required to comply with a specification of 2 parts per million (ppm) methylene chloride in the effluent. In this example it is assumed that there are no uncertainties in physical properties. Uncertainties in the economic valuation model parameters are also ignored here, with the exception of structural uncertainties that contribute to the bias against capital investment (a separate heat exchanger sizing example that takes into account uncertainties in physical properties and valuation model parameters is given in section 4.7.2). The optimum size of the heat exchanger is found directly by the simulator as the solution to the following optimization problem:

$$\begin{aligned} \underset{Area, F_{steam}}{\text{Min}} \quad & AF \times f_{BM} \times C_p (Area) + P_{steam} F_{steam} \\ \text{s.t.} \quad & C_{CH_2Cl_2, eff} \leq 2 \text{ ppm} \end{aligned}$$

The key tradeoff in the optimization is the capital cost of the heat exchanger vs. the cost of steam required to achieve the effluent concentration specification. As the area of the heat exchanger increases, more heat is transferred from the effluent stream to the feed stream, decreasing the steam requirement in the flash drums. The objective function used for the

optimization captures this tradeoff. For the sake of simplicity in the illustration, cooling water costs associated to the condenser and electricity costs associated to the pump are omitted from the objective function. These costs are small compared to the cost of steam and move in the same direction as steam costs when the area of the heat exchanger is varied. The annualization factor is found through the procedure outlined in section 3.2.3. In this example information in the book by Peters and Timmerhaus [10] is used to derive the annualization factors. Three design contexts are examined: new plant at new site (grassroots design), expansion of an existing facility, and equipment sizing. As explained earlier, equipment sizing annualization factors should always be used to size equipment, regardless of design context. The point of solving the optimization problem with annualization factors derived from other sets of assumptions is to illustrate the magnitude of the bias against capital investment resulting from applying such economic valuation rules. For each design context two AF values are calculated: one for a discount rate of 25% and another one for a discount rate of 15%, assuming that the latter rate is the opportunity cost of capital of the firm. This results in six different values for the AF , summarized in Table 3-9.

Table 3-9: Values of the annualization factor used in the heat exchanger sizing example

Discount rate	design context		
	GR: grassroots design	FE: facility expansion	ES: equipment sizing
25%	0.91 (1.4)	0.78 (1.4)	0.50 (1.2)
15%	0.67 (1.4)	0.57 (1.4)	0.38 (1.2)

Note: the values in parenthesis are the uncertainty factors around the central estimate.

The cost correlation in Perry's handbook [8] is used to obtain the purchased heat exchanger cost as a function of heat transfer area. Two approaches to estimating the installation factor f_{BM} are used. First, a value of 3.39 independent of size is used, as recommended by most design books (see Table 3-1). In the second approach, size-dependent installation factors were derived from the charts provided by Guthrie [12]⁹. The resulting curves for purchased and installed equipment costs are shown in Figure 3-12.

⁹ Engineering cost was excluded from the calculation. It is assumed that the number of person-hours required to design a heat exchanger has decreased considerably since the time of publication of Guthrie's book due to the current availability of personal computers and design software.

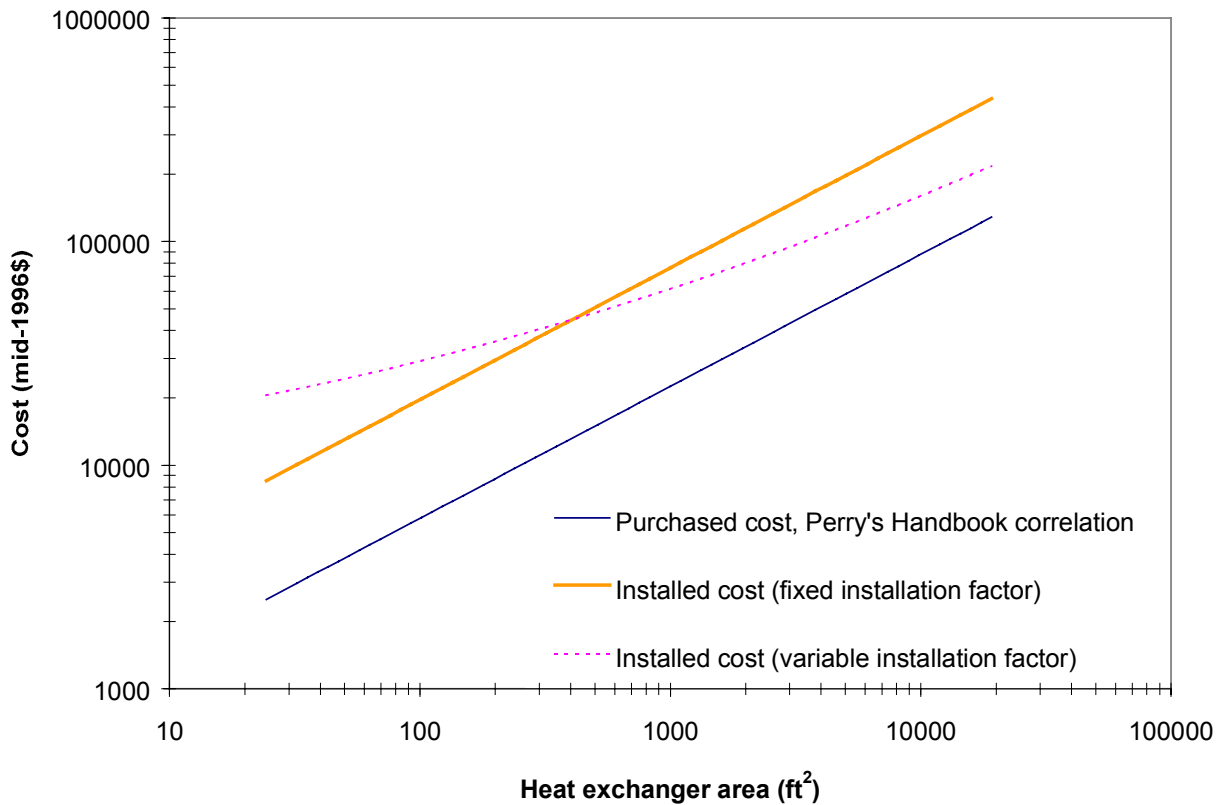


Figure 3-12: Equipment cost correlations used in the heat exchanger sizing example

The combination of 6 values for the annualization factor and two approaches to estimating the installation cost factor yield 12 separate cases. The assumptions for each case, as well as the optimization results, are shown in Table 3-10. Case 1 corresponds to my interpretation of the recommendations by design textbooks and what would result from using the economic valuation model embedded in earlier versions of the Aspen process simulator (the current version does no longer include economic evaluation). I do not know whether this is what is practiced in industry at the conceptual design stage. Case 12 corresponds to what I believe would be the correct value model to use for the purpose of sizing equipment. The optimum heat transfer area recommended by the recommended approach is more than 3 times larger than the heat exchanger area obtained using the rules of thumb given in design textbooks. The last three columns of the table give the incremental investment, annual operating cost savings, and internal rates of return on the incremental investment of the optimum design values obtained for each set of economic valuation parameters compared to the base case. With an internal rate of return of 60%, the incremental investment of \$42,000 needed to install a 3,500 ft² heat exchanger instead

of a 960 ft² one would be paid back in less than two years. An additional benefit is obtained if environmental concerns are part of the design objective, since steam use is reduced by 1,400 lb./hr. This translates into a 14% reduction in emissions from the boiler used to raise the steam.

In conclusion, this example has demonstrated how current economic evaluation practices (use of high discount rates, use of factored capital cost estimates, use of size-independent installation cost factors) might bias designers against profitable capital investments. This bias against capital investment can be reasonably expected to result in higher use of utilities and higher waste generation rates. Careful consideration of economic valuation models used to size equipment at the conceptual stage of design can thus be expected to lead to designs that are more profitable and have lower environmental impact.

Table 3-10: Results for the heat exchanger sizing example

Case	Basis for AF^a	i	AF	f_{BM}	Area (ft ²)	Steam use (lb/hr)	Installed cost ^b	Annual op. cost (\$/yr) ^c	Incre- mental invest- ment ^d	Annual savings (\$/yr) ^e	IRROII ^f
1	GR	25%	0.91	fixed	962	11110	\$63,581	266,463			
2	FE	25%	0.78	fixed	1044	10973	\$65,531	263,551	\$1,950	2,911	148%
3	ES	25%	0.50	fixed	1585	10340	\$76,776	250,406	\$13,194	16,056	119%
4	GR	15%	0.67	fixed	1245	10701	\$69,997	257,853	\$6,416	8,610	132%
5	FE	15%	0.57	fixed	1397	10549	\$73,132	254,756	\$9,551	11,707	120%
6	ES	15%	0.38	fixed	1904	10186	\$82,487	247,616	\$18,906	18,847	96%
7	GR	25%	0.91	variable	1780	10260	\$80,329	249,037	\$16,748	17,426	101%
8	FE	25%	0.78	variable	2037	10117	\$84,724	246,322	\$21,143	20,141	92%
9	ES	25%	0.50	variable	2921	9788	\$98,038	240,513	\$34,456	25,950	70%
10	GR	15%	0.67	variable	2284	9990	\$88,693	243,919	\$25,112	22,544	86%
11	FE	15%	0.57	variable	2630	9878	\$93,909	242,035	\$30,327	24,428	76%
12	ES	15%	0.38	variable	3490	9664	\$105,566	238,667	\$41,984	27,795	60%

a) GR = grassroots (new plant at new site), FE = facility expansion, ES = equipment sizing

b) The installed cost is calculated using size-dependent installation cost factors

c) Includes charges for maintenance, maintenance supplies, maintenance overhead, local taxes and insurance

d) Installed cost (case i) – Installed cost (case 1)

e) Annual operating cost (case i) – Annual operating cost (case 1)

f) IRROII: Internal rate of return on incremental investment. Calculated assuming (conservatively) a 5-year service life.

3.3 Environmental valuation models

3.3.1 Introduction

Treating environmental concerns as an objective in process design requires the use of a quantitative measure of performance that provides the designer with information about the effects of design decisions on potential environmental impacts. An environmental valuation model is the means through which environmental concerns may influence the tradeoffs made by a designer.

As in the case of economic valuation models, the role of environmental valuation models is to summarize information about material flows, utility usage rates, and equipment design specifications into a small set of performance metrics. These performance metrics can then be used to rank alternative designs.

There is no universally accepted measure of environmental performance. One of the reasons for this is that people differ in the importance they assign to different types of environmental impacts. While science and engineering can be used to estimate the potential contribution of a particular design to specific environmental problems, the relative importance assigned to different environmental impacts is something that must be done by decision-makers based on their own values regarding the environment.

There is a growing literature on methods for environmental impact assessment [16-21]. Although these methods have been mostly developed to aid designers of consumer products, the principle on which the methods are based can be applied to process design problems. There are two major approaches to environmental evaluation that can be distinguished on the basis of the stage of the analysis at which societal values with respect to the environment are incorporated. In the first approach, government goals and regulations are used directly to weigh emissions of different substances. One example is the Swiss eco-points system, which is based on the Swiss government assessment of the sustainable level of Swiss emissions of various substances [22]. The Swiss eco-points environmental valuation model is given by:

$$Indicator = 10^{12} \times \sum_i \left(\frac{1}{Fc_i} \times \frac{F_i}{Fc_i} \right) \times \Delta F_i \quad (3-33)$$

where F_{c_i} is the sustainable emission of substance i in Switzerland (according to the policy objectives of the Swiss government), F_i is the level of emissions of substance i in the year used as reference for the computation of the weighting factors, and ΔF_i is the level of emissions attributable to the product or process under consideration. Another example is the “critical volumes” method, where emissions to air are weighted by the inverse of an air concentration standard (usually a standard for workplace exposure) and emissions to water are weighted by the inverse of a drinking water concentration standard [23,24]. In this way, masses of various pollutants are expressed as volumes of contaminated air or contaminated water.

The second approach to environmental valuation is known as the problem-oriented approach. Under this approach, scientific considerations are treated separately from societal considerations. The problem-oriented approach proceeds according to the following steps:

1. Design decisions are used to generate an inventory of emissions of potentially harmful substances. A life-cycle perspective is used to create the inventory. This means, in the case of process evaluation, that not only the direct emissions of the process are considered, but also the emissions by upstream processes that supply raw materials and utilities.
2. Environmental science is used to translate the emissions inventory into marginal contributions to the driving force behind various types of environmental problems. For some environmental problems there are widely accepted indicators for weighting the contribution of different substances to the driving force for that problem (e.g. global warming potentials and ozone depletion potentials, see Table 3-11). Consensus has not yet been achieved on measures of the contribution to the driving force for other problems (e.g. ecotoxicity).
3. A weighting method is used to summarize the contributions to the various environmental problems into a single indicator of environmental performance. Procedures used to derive the weighting factors include contingent monetary valuation of impacts [16,21], use of political targets [20], and elicitation of preferences from expert panels [19].

The sequence of steps is illustrated by the example in Figure 3-13. Even though the structure of the environmental valuation model is linear, environmental impacts are not necessarily assumed to be linear functions of the emissions. For example, many of the characterization factors in use are derived from perturbations around highly nonlinear models. What the linear structure of model implies is that the contribution of a particular process to

environmental impacts is small enough relative to the contribution from all human activities that the marginal change in impacts can be approximated by a linear function.

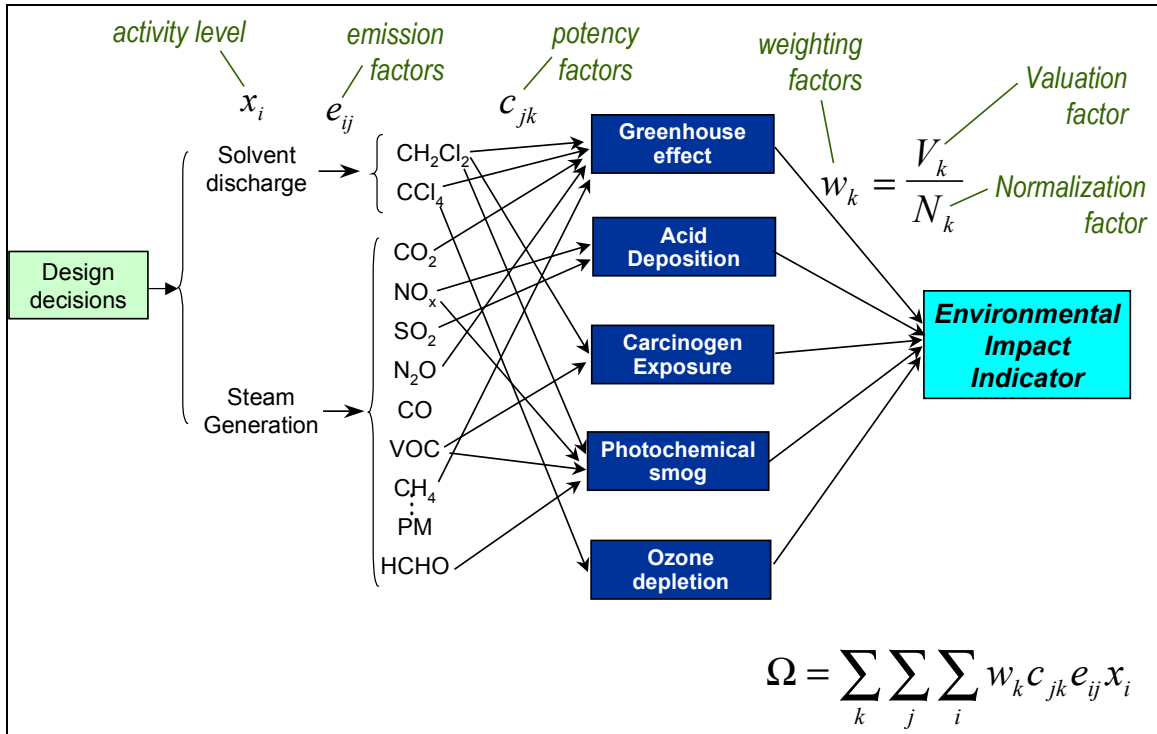


Figure 3-13: Components of an environmental valuation model¹⁰

3.3.2 Uncertainties in environmental valuation models

There are several sources of uncertainty in environmental valuation models. First, there are uncertainties in the estimation of the magnitude of environmental exchanges resulting from a given activity (e.g. what pollutants and in what amounts will be emitted to provide 1 kWh of electricity to a process?). Then there is scientific uncertainty about the magnitude of the marginal contribution to specific environmental problems due a marginal increase in specific environmental exchanges. Finally, there is valuation uncertainty about the relative importance assigned to marginal contributions to specific environmental problems. Each of these sources of uncertainty are discussed in the following subsections.

¹⁰ The following subscripts are used in the figure: i is used for activities, j for environmental exchanges (e.g. emissions of a particular substance), and k for environmental impact categories (e.g. ozone depletion).

Table 3-11: Widely used environmental impact metrics for specific environmental problems

Environmental Problem	Characterization factor	Characterization factor definition	Sources of characterization factors	Comments
Climate change	Global warming potential (GWP)	$GWP_i = \frac{\int_0^T a_i m_i(t) dt}{\int_0^T a_{CO_2} m_{CO_2}(t) dt}$ <p>where a_i is the radiative forcing due to a unit increase in atmospheric concentration of gas i, $m_i(t)$ is the time-decaying atmospheric abundance of a pulse of injected gas, and T is the time horizon.</p>	Intergovernmental Panel on Climate Change [25]	A time horizon of 100 years is usually chosen. CO ₂ is the reference substance. The GWP is then expressed as kg of CO ₂ equivalents per kg of substance.
Stratospheric ozone depletion	Ozone depletion potential (ODP)	$ODP_i = \frac{\int_0^T \delta[O_3]_i(t) dt}{\int_0^T \delta[O_3]_{CFC-11}(t) dt}$ <p>where $\delta[O_3]_i(t)$ is the calculated time-decaying depletion in global column average ozone concentration due to a unit pulse emission of substance i, and T is the time-horizon for the calculation</p>	World Meteorological Organization [26]	$T=\infty$ is usually chosen. A two-dimensional model of the atmosphere is used for the calculations. The ODP is expressed as kg of CFC-11 equivalents per kg of substance
Photochemical smog	Photochemical Oxidants Creation Potential (POCP)	$POCP_i = \frac{\int_0^T \delta[O_3]_i(t) dt}{\int_0^T \delta[O_3]_{Ethylene}(t) dt}$ <p>where $\delta[O_3]_i(t)$ is the calculated change in ozone concentration due to a marginal change in emissions of substance i, and T is the time-horizon for the calculation</p>	Various researchers [27-32]	T is usually 4 to 5 days. A trajectory photochemical model is normally used. The most widely used POCP values are based on a trajectory from Germany to Ireland. The POCP is expressed as kg of ethylene equivalents per kg of substance
Acid deposition	Acidification Potential (AP)	$AP_i = \frac{n_i / MW_i}{n_{SO_2} / MW_{SO_2}}$ <p>where n_i is the number of hydrogen ions released per mole of substance i emitted, and MW_i is the molecular weight of substance i.</p>	[17,33,34]	The AP is expressed as kg of SO ₂ equivalents per kg of substance. If the geographical location of the emissions is known, a more sophisticated acidification potential can be used, based on marginal changes in the area of ecosystems impacted per marginal change in emissions (see ref. [34])

UNCERTAINTIES IN THE ESTIMATION OF ENVIRONMENTAL EXCHANGES.

The most common environmental exchanges considered in environmental valuation models are pollutant emissions. Three types of emissions are important with respect to process design. The first type is direct emissions from the process. The second type is direct emissions from upstream processes located in the same site that supply raw materials or utilities for the process. Finally, upstream emissions taking place in other locations might have significant environmental impact contributions (for example, emissions at electricity generating plants). Direct emissions from the process are not known with certainty before the process is built, and might be subject to significant estimation uncertainties, specially if the pollutants are not expected to have a major influence in the overall mass balance. Direct emissions from upstream processes located in the same plant may be measured or estimated. Measured emissions might be subject to statistical variation. Additional sources of uncertainty for offsite emissions include accessibility to data, allocation rules, and comprehensiveness of the analysis. A method designed to manage these sources of uncertainty is presented in Chapter 7.

The range of uncertainties in emission factors is illustrated in Table 3-12. At the conceptual stage of design it might be difficult to estimate emissions of compounds that do not affect significantly the mass and energy balances, since these compounds are not likely to be included in process models. Depending on their environmental mobility, persistence, and toxicity, however, these compounds might account for a significant fraction of the impact from a process. The author recommends that designers estimate the order of magnitude of the emissions and then use the methods discussed in Chapter 5 to determine whether it is important to obtain more accurate estimates. A typical order of magnitude for fugitive emissions for volatile organic chemicals is 1/1000 of the stream flows in a process [35].

Table 3-12: Typical uncertainties in air pollutant emission factors

Pollutant	Measurement method	UF (directly measured)	UF (extrapolated)	Type of emission source	Reference
CO ₂	Analysis of fuel carbon	1.02	1.4	Combustion processes	[16]
SO ₂	Analysis of fuel sulphur content	1.1	3	Uncontrolled combustion processes	Estimate, this work
CO	Continuously monitored	2.2	4	Large incineration plants	[16]
CO	Random sampling	1.2	4	Car fleet	[16]
CH ₄	Gradient method or collection in hoods	2.2	9	Diffuse emissions from landfills	[16]
PAC	Random sampling, gas or liquid chromatography	4	16	Power and heat generation	[16]
Metals	Random sampling of particles	4	16	Combustion processes where the metals are trace elements	[16]
Specific organic compounds	Organic vapor analyzer readings	3	10+	Fugitive emissions	Estimate, based on data in [35]

UNCERTAINTIES IN CHARACTERIZATION FACTORS

Characterization factors are used to translate environmental exchanges into contributions to specific environmental problems. Characterization factors are also known as classification factors [18], or equivalency factors [16,20], and are commonly expressed in units of equivalent kg of a reference substance per kg of substance of interest. The Eco-indicator'99 method uses the term “damage factors” to refer to characterization factors expressed in units of physical damages per kg of substance of interest [19]. Uncertainties in characterization factors come mainly from scientific uncertainties, although value judgment uncertainties also play a role through the choice of reference scenarios and time horizons. Table 3-13 provides a few examples of uncertainties in characterization factors. Uncertainty factors derived from information given by the source of each factor are indicated (in parenthesis) when available. The table shows examples of variations in characterization factors due to evolving knowledge and models (the GWP for methane and the POCP for ethanol), due to differences in reference scenarios (the ODP for HFC-141b), and differences among authors (PM₁₀). Typical uncertainty factors are in the

range 2 to 25. Uncertainty factors for other endpoints (such as toxic effects) might be an order of magnitude higher, as discussed in Chapter 6.

Table 3-13: Examples of the uncertainties in characterization factors

Environmental Problem	Characterization factor endpoint (units)	Example substance	Scenario	Characterization factor value (UF)	Ref.	Comments
Climate Change	Contribution to radiative forcing (kg CO ₂ equivalent/kg)	CH ₄	T = 100 yrs	11	[36]	1992 estimate
				24.5	[37]	1994 estimate
				21 (1.8)	[25]	1995 estimate
Ozone depletion	Contribution to depletion of stratospheric ozone concentrations (kg CFC-11 equivalent/kg)	HCFC-141b	T = ∞	0.10	[38]	
			T = 500 yrs	0.11		
			T = 100 yrs	0.13		
			T = 20 yrs	0.33		
			T = 5 yrs	0.54		
Photochemical Smog	Contribution to increase in tropospheric ozone concentrations (kg Ethylene equivalent/kg)	Ethanol	T = 5 days (Austria to Ireland trajectory)	0.399	[28]	
				0.386	[27]	
				0.446 (1.23)	[31]	
			Average of 11 European trajectory scenarios	0.268 (2)	[30]	
Respiratory effects	Premature mortality ^a (YOLL/kg)	PM ₁₀	Global average	4.2×10 ⁻⁴ (9)	[16]	
			European average	7.6×10 ⁻⁴ (19)	[19]	

a) YOLL = Years of life lost

UNCERTAINTIES IN WEIGHTING FACTORS

The final step in the environmental valuation model shown in Figure 3-13 is the aggregation of the various environmental problem category scores into an overall environmental indicator. This requires the use of weighting factors. The weighting factors should reflect the tradeoffs a decision-maker is willing to make among marginal increases in the indicators for the various environmental problems. There are three main approaches used to derive the weighting factors:

- (a) Monetary methods Under this approach estimates are made of the physical impacts resulting from an increase in the score for each environmental problem (e.g. the number of skin cancer cases resulting from a 1% decrease in stratospheric ozone concentration). Contingent valuation methods are then used to place a monetary value on each type of physical impact. The sum of the product of the marginal physical impacts times the monetary value per impact is then used as the weighting factor for the environmental problem score. The resulting overall environmental indicator has monetary units. Environmental valuation models using this approach include the Swedish EPS system [16] and the explicit life cycle assessment method (XLCA) [21]. Monetized environmental impacts should not be added directly to total annual profit to obtain an overall indicator of performance for a process, unless it is clear that the corporation carrying out the project is willing to tradeoff a dollar of private cost for a dollar of social cost¹¹.
- (b) Political targets This method computes the score for each environmental problem indicator that would result if environmental exchanges for a particular region in a reference year met the goals set by a government. The inverse of the score for each problem becomes the weighting factor. The resulting overall environmental indicator can be interpreted as the contribution of a particular process to the total allowable impact. An example of this approach is the EDIP method, which uses Danish political targets to derive the weighting factors [20]. Implicit in this method is the strong assumption that governments arrive to political targets for each environmental problem using the same procedures to balance costs and benefits.
- (c) Multicriteria assessment methods In this approach the weights are derived from the opinion of a panel of experts.. A typical procedure is to compute the scores resulting from a known pattern of environmental exchanges (e.g. the annual emissions of an entire region) and to ask the panel what percent increase in the score for environmental problem X would be deemed equally undesirable as a 10% increase in the score for environmental problem Y. The resulting indicator has arbitrary units (e.g. “eco-points” in the case of the Eco-Indicator’99 method [19]). The resulting weighting factors can be strongly dependent on the way the

¹¹ Most corporations would probably even resist trading off one dollar of social cost for a *cent* of private cost.

questions to the experts are framed (see discussion about the weights in the Eco-Indicator'99 method below)

Table 3-14 compares the weighting factors assigned to several environmental problem category scores by four different environmental valuation models. Due to the lack of consensus on indicators to measure contributions to human toxicity and ecotoxicity, the table gives the weighting factors assigned by each model to a unit emission of a representative chemical within each category. Since the overall indicator units used by the different methods are different across models, entries in the table can not be directly compared. However, ratios of the entries in one column can be compared to ratios of the same entries in other columns, since all the valuation models are linear. One such comparison is shown in Figure 3-14 where selected valuation factors from Table 3-14 have been normalized by dividing them by the valuation factor for the photochemical smog impact category. The value for most ratios spans two orders of magnitude or less. Notable exceptions are the eutrophication : photochemical smog valuation factor ratio (3 orders of magnitude) and the mercury ecotoxicity : photochemical smog valuation factor ratio (4 orders of magnitude). The benzene cancer impact : photochemical smog valuation ratio is remarkably stable. It is clear from the chart that the Eco-Indicator'99 method places a much higher relative valuation on ecosystem impacts than the other methods listed.

There are significant differences in some of the weighting factors used by the different models. Take for example CFC-11. It contributes to both global warming and ozone depletion. It has an ODP of 1 (by definition) and a GWP₁₀₀ in the range 540 to 2100 [25]. In the EDIP method, the contribution of CFC-11 to ozone depletion is considered to be between 360 and 1140 times as serious as its contribution to global warming, while in the Eco-Indicator'99 method the contribution to ozone depletion is only between 2 and 10 times as serious as the contribution to global warming. In the EPS method both contributions are comparable. Another interesting comparison is given by the weighting factors used for the toxic effects of lead and benzene. In both the XLCA and EPS systems, a unit emission of lead to air is considered to be at least three orders of magnitude more harmful than a unit emission of benzene to air. Both emissions are comparable in importance in the EDIP method, while the toxic impact of lead on humans is neglected in the Eco-Indicator'99 method. In view of the data in Figure 3-14, it is reasonable to assign an uncertainty factor of 10 to most of the weighting factors used in

environmental valuation models. Higher uncertainty factors (30-100) would be appropriate for the valuation factors for ecosystem impact categories.

Table 3-14: Environmental problem weighting factors used in four different environmental valuation models

Impact category	Indicator units	EDIP ^b EnvPts/unit	Eco-Indicator'99 ^a			XLCA US\$/unit	EPS Eur/unit
			Hierarch. EcoPts/unit	Egalitarian EcoPts/unit	Individ. EcoPts/unit		
HUMAN HEALTH IMPACTS							
Global Warming	kg CO2 equiv.	0.00015	0.0055	0.0041	0.013	0.014	0.11
Ozone Depletion	kg CFC-11 equiv.	114	27	20	57	n/c ^c	99
Photochemical smog	kg Ethylene equiv.	0.06	0.055	0.041	0.13	5	1.8
Primary particles	kg PM10 equiv.	n/c	9.7	7.3	18	12.6	37
Secondary particles	kg SO2 equiv.	n/c	1.4	1.0	2.6	12.6	4.3
Human toxicity (cancer)							
Benzene to air	kg Benzene	0.06	0.065	0.048	0.11	1.9	1.9
Human toxicity (non-cancer)							
Hg to air	kg Hg	2.7	n/c	n/c	n/c	1900	48
Pb to air	kg Pb	0.032	n/c	n/c	n/c	4400	2910
ECOSYSTEM IMPACTS							
Eutrophication	kg NO2 equiv	0.0067	0.45	0.56	0.32	n/c	0.018
Acidification	kg SO2 equiv.	0.010	0.081	0.10	0.058	0.38	0.017
Ecotoxicity							
Malathion to soil	kg Malathion	n/c	0.0022	0.0027	0.0015	n/c	0.015
Hg to air	kg Hg	0.022	65	81	2.5	n/c	12
RESOURCE DEPLETION							
		ResPts/unit					
Copper	kg Cu	0.016	0.87	1.2	49	n/c	208
Crude oil	kg Crude oil	3.9E-05	0.14	0.11	0	n/c	0.51

- a) The Eco-Indicator'99 method provides weighting factors for three different world-views. The world-views are labeled "Hierarchist", "Egalitarian", and "Individualist".
- b) In the EDIP method, environmental impacts and resource impacts are scored separately. No weighting factor is provided to aggregate environmental impact points and resource points into a single overall score.
- c) n/c = not considered; the substance or impact category receives a valuation of zero.

In investing resources to pursue environmental quality beyond the level required by laws and regulations, corporations should verify that the weighting factors they assign to each of the environmental problems are consistent with their values and the values of their stakeholders. Although precise weighting factors might be impossible to obtain, it should not be difficult to obtain ranges for the weighting factors based on tradeoffs that the corporation and its stakeholders know they would be willing to consider. The decision-making procedures introduced in the next chapter allow designers to identify superior alternatives even in the presence of uncertainties in valuation model coefficients.

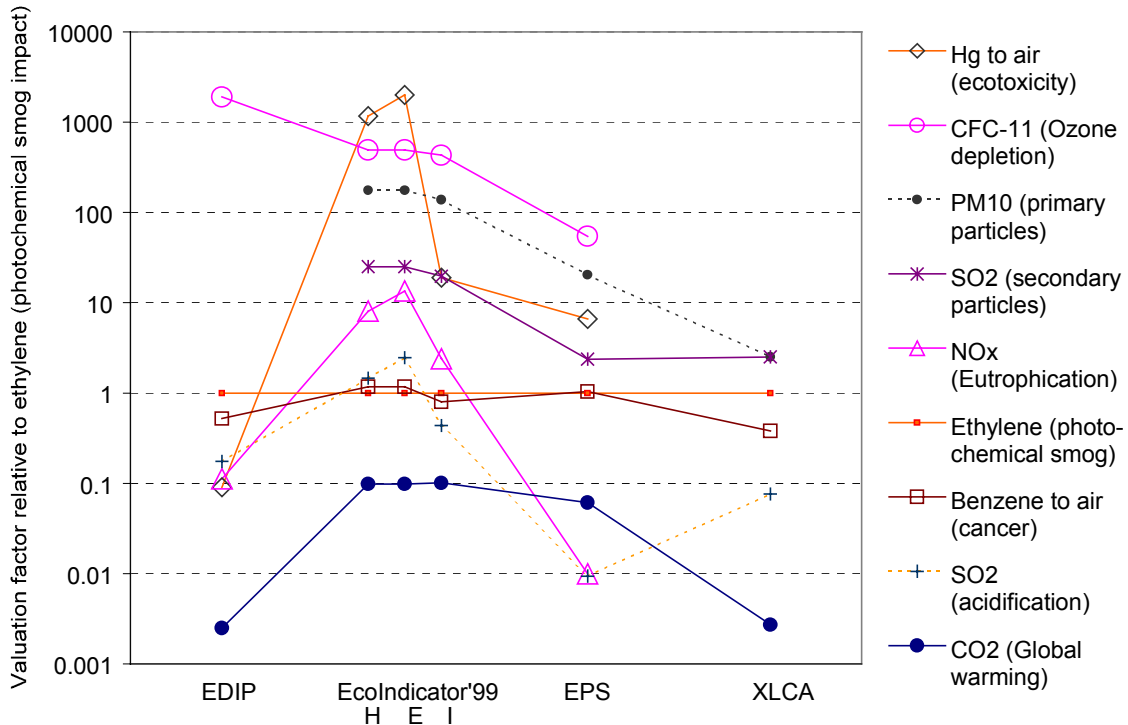


Figure 3-14: Comparison of relative weighting factors for various environmental impact categories across four environmental valuation methods.

It is very important to check that the tradeoffs implied by the chosen weights are consistent with tradeoffs the decision-makers know they would be willing to make. To illustrate this point, a brief discussion of the weighting method used by a widely used environmental evaluation method is presented next. The developers of the Eco-Indicator'99 method used a panel procedure to derive the weights they use to combine scores for impacts on human health, ecosystems, and resources. Human health impacts combine mortality and morbidity effects using disability-adjusted life-years lost (DALYs) as a metric¹², ecosystem quality impacts are measured in terms of potentially disappeared fraction of vascular plant species per m² per year (PDFm²yr)¹³, and depletion of nonrenewable resources is measured in terms of the excess energy

¹² The DALY indicator measures the total amount of ill health, due to disability and premature death, attributable to specific diseases and injuries. For example, a death occurring at age 30 instead of age 82 (the reference life expectancy for the model) is assigned 52 DALYs. Years lived with disabilities receive scores lower or equal than 1 DALY/year. For example, 10 years lived with paraplegia are assigned a score of 5 to 7 DALYs, while 10 years living with arthritis may receive a score of 1.2 to 2.4 DALYs.

¹³ The two following situations would receive the same score: (a) complete elimination of all plant species from a 100 m² plot for 10 years, (b) elimination of 1% of plant species from a 100 km² region for a year. Both situations

that would be required to produce the resource sometime in the future when the total amount extracted by mankind equals 5 times the amount extracted up to 1990 (in MJ). In the panel procedure, the method developers asked panel members to rank the relative importance of the contributions of 1990 European emissions and land-use patterns to each of the three categories. Developers classified respondents into three types of worldviews regarding the environment (Hierarchists, Egalitarians, and Individualists) and used their responses to develop weighting factors for each of the impact categories and worldviews.

According to the Eco-indicator'99 method, subscribers to each of the worldviews should be willing to make the tradeoffs shown in Table 3-15¹⁴. It would be acceptable, for example, to clear forests in order to supply the world's need for fuels from agriculture, as long as the annual yield per m² was higher than the tradeoff value shown in the last column of the table¹⁵. Individualists should be willing to tradeoff a year of life expectancy today for 50,000 MJ of energy in the distant future. At current electricity prices (the most expensive form of energy) and assuming no discounting, this would place a value of about \$1,500 per year of life saved. This is in sharp contrast with the description of the individualist perspective given in the Eco-indicator'99 methodology report. According to the report, individualists have a short-term rather than a long-term perspective, and give more importance to the needs of present generations over the needs of future generations. Implied valuations for a year of life saved under the other two perspectives range from \$17,000 to \$32,000, which are consistent with the low end of the range used in methods based on willingness to pay. This example indicates that the method of value elicitation used in the Eco-indicator'99 method resulted in a gross overestimation of the weighting factor for the resource impact category, at least with respect to the individualist perspective. The author suspects that the reason for this is that members of the panel were not asked what tradeoffs they would be willing to consider, but rather to rank the damage categories in decreasing order of importance, with some information about the current level of impacts in Europe as background.

would be assigned a score of 1000 PDFm²yr. The models used in the Eco-indicator'99 method assume that damages to ecosystems are reversible over a sufficiently long time scale.

¹⁴The tradeoffs were calculated by first computing how many eco-points are assigned to 1 MJ of excess energy, 1 DALY, and 1 PDFm²yr for each of the three perspectives. The figures were then divided by each other, since the method assumes that 1 ecopoint due to human health impacts is valued as much as 1 ecopoint due to resource depletion or 1 ecopoint due to decreasing ecosystem quality.

Table 3-15: Implied tradeoffs in the Eco-indicator'99 model

Perspective	Resources- Human Health tradeoff (MJ/DALY)	Ecosystem Quality- Human Health tradeoff (PDFm2yr/DALY)	Resources- Ecosystem Quality tradeoff (MJ/PDFm2yr)
Egalitarian	576,531	198,980	2.897
Hierarchist	1,095,890	333,904	3.282
Individualist	49,517	1,190,506	0.042

Note: to put this figures in perspective, 1991 per capita energy consumption in Europe was 193,000 MJ while 1991 cropland use per capita was 2,700 m² [39]; there were 0.11 DALYs lost per capita in established market economies in 1990 [40].

DEFAULT ENVIRONMENTAL VALUATION FACTORS USED IN THIS WORK

Table 3-16 lists the valuation factors used for the case studies in this thesis. The valuation factors were chosen so that they would be consistent with the EPS and XLCA methods. Values for the weighting factor used for the ecotoxicity categories were chosen so that the valuation of 1 kg of mercury (released to either air, water, or soil) in terms of its aquatic or terrestrial ecotoxicity would be approximately equal to one half the value used in the EPS method¹⁶. Valuation factors for the eutrophication and acid deposition categories were increased based largely on Figure 3-14, which shows that the EPS method is the only one that gives a higher weighting to a GWP unit than to both an EP and an AP unit. In building Table 3-16, the author attempted to span the range of uncertainties in weighting factors observed in environmental valuation methods in current use. The author does not recommend, however, that designers apply these weighting factors directly without checking first that implied tradeoffs are consistent with the values of their corporations.

¹⁵ Production of rapeseed oil in Europe currently yields about 3.5 MJ/m²yr [16]

¹⁶ The assumption is that half of the valuation comes from impacts on aquatic organisms and half from impacts to terrestrial organisms

Table 3-16: Environmental valuation factors used in this thesis

Impact category	Indicator (units)	Valuation factor (\$/unit)	Uncertainty factor	Characterization factor sources used
Global warming	GWP (kg CO ₂ equivalent)	0.03	10	IPCC [25,36,37] EPS method [16]
Ozone depletion	ODP (kg CFC-11 equivalent)	100	10	WMO [17,26,38]
Photochemical smog	POCP (kg ethylene equivalent)	2	10	Derwent et al. [27-31]
Particulate matter impacts (including secondary aerosols)	(kg PM ₁₀ equivalent)	40	10	Derived from EPS method [16]
Human toxicity (cancer)	(DALYs)	85000	4	Eco-Indicator'99 [19] Derived from EDF [41] ^a Derived from MPCA [42] ^b EPS method [16] Chapter 6 of this thesis
Human toxicity (non-cancer effects, excludes impacts from ozone and particulates)	(DALYs)	85000	4	Eco-Indicator'99 [19] EPS method [16] derived from EDF [41] ^c derived from CML/RIVM [43] ^d derived from MPCA [42] ^c Chapter 6 of this thesis
Acidification	AP (kg SO ₂ equivalent)	0.8	10	H ⁺ Stoichiometry [34] EPS method [16]
Eutrophication	EuP _{water} (kg N-tot equivalent)	0.8	50	EPS method [16] CML/NOVEM/RIVM [17]
Aquatic ecotoxicity	AETP (kg 1,4-dichlorobenzene to water equivalent)	0.0001	100	CML/RIVM [43]
Terrestrial ecotoxicity	TETP (kg 1,4-dichlorobenzene to industrial soil equivalent)	0.0000003	100	CML/RIVM [43]

a) The conversion factors 1 TEP_{cancer, air} (kg benzene to air equivalent) = 7.5×10^{-6} DALY_s, and 1 TEP_{cancer, water} (kg benzene to water equivalent) = 3.9×10^{-5} DALY_s were used.

b) The conversion factor 1 MPCA unit (dimensionless) = 3.0×10^{-18} DALY_s/kg was used, for substances for which the MPCA score was based on cancer endpoints

c) The conversion factors 1 TEP_{noncancer, air} (kg toluene to air equivalent) = 1.3×10^{-9} DALY_s, and 1 TEP_{noncancer, water} (kg toluene to water equivalent) = 3.3×10^{-9} DALY_s were used.

d) The conversion factor 1 HTP unit (kg 1,4-dichlorobenzene equivalent to air) = 6.5×10^{-10} DALY_s was used, for substances for which the HTP score was based on human non-cancer endpoints

e) The conversion factor 1 MPCA unit (dimensionless) = 3.0×10^{-18} DALY_s/kg was used, for substances for which the MPCA score was based on human non-cancer endpoints

See Chapter 6 for a discussion on the uncertainties associated with extrapolating characterization factors across various methods.

SUMMARY

The following uncertainties in problem-oriented environmental valuation models have been identified and characterized:

- Environmental exchange (emission) factors (uncertainty factor ~ 1.02 to 20)
- Characterization factors (uncertainty factor ~ 2 to 25 for most impacts, 100+ for toxicity indicators)
- Weighting factors (uncertainty factor ~ 4-10 for human health related categories, 10-100 for ecosystem impacts)

As expected, these uncertainties are much larger than the uncertainties in the economic valuation model discussed in the previous subsection. However, large uncertainties do not imply lack of information. Chapter 4 shows how the decision problem may be structured in a way that enables designers to identify superior alternatives even in the presence of these large uncertainties.

3.4 Conclusions

This chapter makes two important points:

- Careful consideration of the valuation models used to compare design alternatives is necessary for the identification of superior alternatives. Economic valuation models frequently used at the conceptual stage of process design bias designers against profitable capital investments. This bias is likely to result in energy use and waste generation rates that are higher than those that would be economically optimum, leading to excessive environmental impact.
- There are no conceptual differences between economic and environmental valuation models. Both types of valuation models include uncertain parameters and subjective value judgments. The main differences are the availability of data (e.g. prices are more readily available than environmental problem potency factors), the size of the uncertainties, and the familiarity of decision-makers with making value choices (e.g. choosing discounting factors vs. choosing weighting factors for environmental problem driving force indicators). Tools developed in

this work aim to decrease the barriers to incorporating environmental objectives in process design by addressing each of these three differences.

3.5 Nomenclature

AETP	Aquatic ecotoxicity potential (kg 1,4-dichlorobenzene to water equivalent)
AF	Annualization factor (year ⁻¹)
AP	Acidification potential (kg SO ₂ equivalent)
C _p	Purchased cost of a piece of equipment constructed of carbon steel and designed to operate at atmospheric pressure (\$)
CCF	Capital charge factor (year ⁻¹)
C _{TM}	Total installed equipment cost, also known as onsite cost (\$)
DALYs	Disability-adjusted life years lost (person-years)
EP ₁	First screening level economic potential (Revenue from products minus raw materials cost, \$/yr)
EP ₂	Second screening level economic potential (EP ₁ minus waste treatment and disposal and utility costs, \$/yr)
EP ₃	Third screening level economic potential (EP ₂ minus annualized equipment cost, \$/yr)
EuP	Eutrophication Potential (kg N-tot equivalent)
F _{prod}	Flow rate of product from a process (lb/yr)
F _{raw mat}	Flow rate of raw material fed to a process (lb/yr)
F _{waste}	Flow rate of waste stream (lb/yr)
F _{util}	Utility use rate (e.g. kWh/yr)
f _{BM}	Installation factor, also known as bare module factor (\$/\$)
f _p	Price volatility multiplier
FCI	Fixed capital investment (\$)
GWP	Global warming potential (kg CO ₂ equivalent)
i	discount rate (%/yr)
IRR	Internal Rate of Return (%/yr)
n	length of period of construction (years)
N	process service life (years)
NPV	Net Present Value (\$)
ODP	Ozone depletion potential (kg CFC-11 equivalent)
OVHD	Plant overhead rate (\$/\$)
P _{prod}	Product price (\$/lb)
P _{raw mat}	Raw material price (\$/lb)
P _{waste}	Waste treatment and disposal cost (\$/lb)
P _{util}	Utility price (e.g. \$/kWh)
PM ₁₀	Particulate matter less than 10 microns in diameter
POCP	Photochemical oxidants creation potential (kg ethylene equivalent)
SARE	Sales, administration, research, and engineering expenses (\$/yr)
SC	Startup Cost (\$)
SV	Salvage Value (\$)
TAC	Total Annualized Cost (\$/yr)
TAP	Total Annualized Profit (\$/yr)
TETP	Terrestrial ecotoxicity potential (kg 1,4-dichlorobenzene to industrial soil equivalent)
TPC	Total Product Cost (\$/yr)
WC	Working Capital (\$)
τ	Tax rate (%)

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Chapter 4 Decision Making under Uncertainty

4.1 Introduction

Uncertainty is always present in models of real systems. There is uncertainty about the model structure, uncertainty about the values of model parameters, uncertainty in forecasting external conditions, and uncertainty about decision-maker preferences regarding various aspects of process performance. This chapter addresses the problem of making decisions when there is considerable uncertainty in the valuation functions used to assess system performance. Although the techniques in this chapter can be applied to any decision problem in which the decision-maker is uncertain about the valuation of alternatives, they are particularly relevant to the incorporation of environmental issues as design objectives. The chapter starts with a brief review of uncertainties in process design and the approaches used to address them. The chapter continues with the description of a procedure to reduce decision uncertainty by preserving the correlation among the distributions of performance indicators obtained for competing alternatives. An extension of the procedure that allows placing uncertainty bounds on the optimum values of decision variables is presented next. A brief discussion of utility theory is used to introduce utility functions that may be used to embed the decision uncertainty reducing procedure proposed here into mathematical programming formulations. Two examples are given at the end of the chapter to illustrate the application of the ideas introduced herein.

4.2 Uncertainties in process design

Process design proceeds in several stages, starting from basic research and development, followed by process synthesis, conceptual design, and finally, by detailed design. As a process moves from the initial research stage to construction and operation, the amount of information available increases. There is considerable uncertainty at the early stages of the design process. Unfortunately, it is at these early design stages that the majority of the process costs and environmental impacts become fixed by decisions made on the basis of uncertain information [1,2], since as the design process advances the freedom available to designers to change the design is reduced. These trends are shown in Figure 4-1.

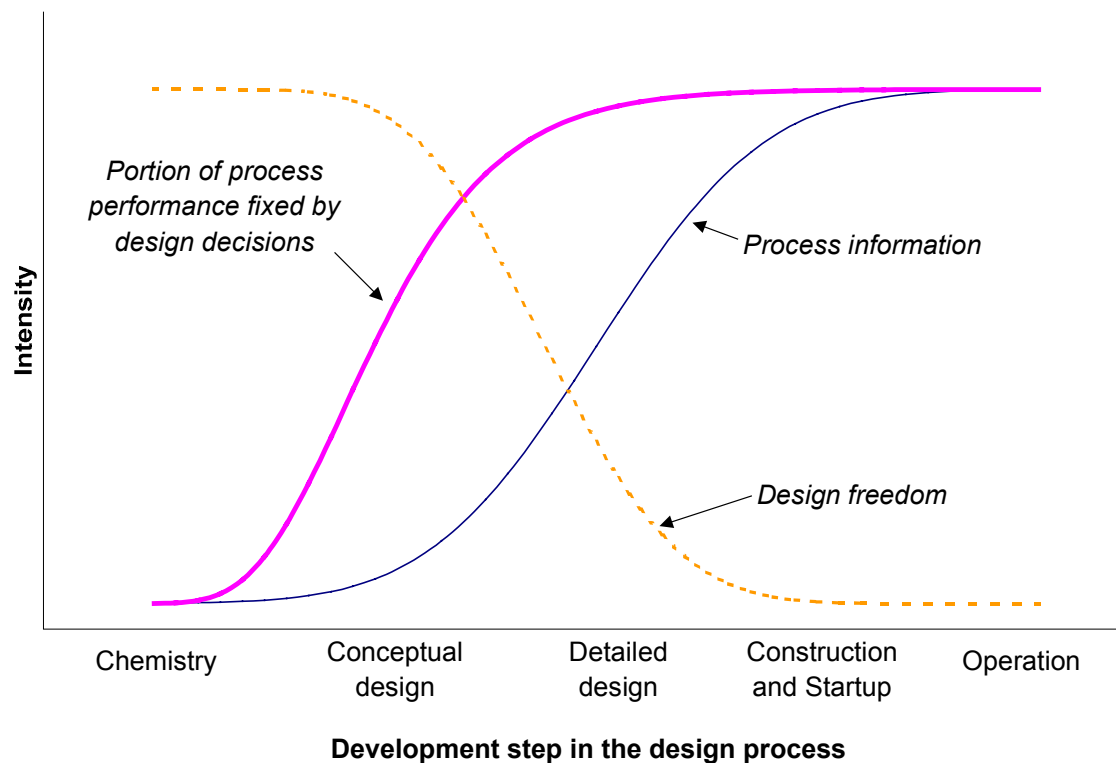


Figure 4-1: Availability of information, design freedom, and portion of process performance fixed by design decisions as a function of the process development stage

There are many uncertainties that are important in the design of a process. The following categories have been proposed for the classification of uncertainties related to process design [3]:

- a) Model-inherent uncertainty includes uncertainty about parameters for which a single true value exists, but the value is not precisely known at design time. It includes kinetic constants, physical properties, and transport parameters. Information regarding this type of uncertainty is usually obtained from experimental data.
- b) Process-inherent uncertainty refers to uncertainty in fluctuating parameters, such as stream flow rates and temperatures. Information regarding this type of uncertainty is usually obtained from plant measurements. Two cases can be distinguished here. In the first case, the values of the parameters fluctuate, but the range and frequency of variations are well known. In the second case, the values of the parameters are anticipated to fluctuate, but the range and frequency of variations are not precisely known at the time of the design effort. In the first case, there is variability rather than

uncertainty. All the values in the parameter distribution are true, in the sense that all the values will be experienced by the process once it is built. The appropriate way to deal with this type of uncertainties is to compute a distribution-weighted average of the valuation models over the range of variability. Process control systems may be included in the design to reduce variability. The second case is a combination of variability and uncertainty. In this case, the parameters of the variation distribution themselves are uncertain. Not all of the possible values in the variation distribution will be realized once the process is built. For example, it might be anticipated that a flow rate to a process will vary in a way that can be described by a normal distribution with coefficient of variation (i.e. the standard deviation divided by the mean) equal to 10%. However, there is uncertainty about what the true value for the mean of the flow rate distribution will be once the design is built, perhaps due to uncertainty in product demand. In this case, the mean of the distribution would itself be described a subjective probability distribution.

- c) External uncertainty includes uncertainty about factors external to the process, such as market conditions (product demand, raw material prices) and ecosystem sensitivity to process emissions. The uncertainties in valuation model parameters discussed in Chapter 3 would be included in this uncertainty class.

In addition to the *parametric* uncertainties mentioned above (uncertainties about the value of a parameter used in a model), there are also *structural* uncertainties, which are uncertainties about the models themselves. Not all models describe the world with the same accuracy. Simplified (short-cut) models are frequently used at the early stages of design. Engineers are constantly trying to strike a balance between model accuracy and the availability of information. A very detailed model of a reactor might be available, but it might not offer significant improvement as a decision support tool over a simpler model if most of the model parameters are known with very little precision.

The academic process design community often represents design problems as mathematical programs of the following form:

$$\begin{aligned} & \text{Max} && V(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta}) \\ & && \mathbf{d}, \mathbf{z} \\ \text{s.t.} & && \mathbf{h}(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta}) = \mathbf{0} \\ & && \mathbf{g}(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta}) \leq \mathbf{b} \\ & && \mathbf{d} \in \mathbf{D}, \mathbf{z} \in \mathbf{Z} \end{aligned} \quad (\text{Problem DP1})$$

where \mathbf{d} , \mathbf{z} are the vectors of design and control variables, respectively, $\boldsymbol{\theta}$ is the vector of uncertain parameters, $\mathbf{h}(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta})$ is the vector of equations defining the model of the process, $V(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta})$ is the objective function (which may be a function of multiple objectives), $\mathbf{g}(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta})$ is the vector of equations defining the constraints on the process, \mathbf{b} is the vector of parameters giving the upper bound of the constraint equations, and \mathbf{D} and \mathbf{Z} are the domains over which the design and control variables are defined.

In the above representation, parametric uncertainty is uncertainty about the values of the parameters in vector $\boldsymbol{\theta}$, while structural uncertainty is uncertainty about the functional form of the functions $V(\bullet)$, $\mathbf{h}(\bullet)$, and $\mathbf{g}(\bullet)$. Parametric uncertainty can be conveniently represented by probability distributions over the range of values that may be assumed by the parameters. There is no equally convenient way of representing structural uncertainty within a mathematical framework. An approach that has been suggested is to embed multiple models into a larger metamodel with each submodel being assigned a certain degree of belief [4]. In this way, the structural uncertainty is transformed into a discrete parametric uncertainty.

4.3 Approaches to decision making under uncertainty

Uncertainty in most engineering models used at the conceptual stage of process design is frequently ignored. This is unfortunate, since it can be shown that if we have any knowledge of the uncertainty then the expected value of including uncertainty in the analysis is never negative (neglecting the extra effort involved in the analysis) [5]. Due to increases in computing power and advances in the development of uncertainty propagation techniques, the amount of effort needed to incorporate uncertainty analysis into the design process decreases every year.

A common approach to design under uncertainty is the use of heuristics. These include the use of contingency factors, high discount rates, and overdesign factors. These heuristics are

designed to decrease the downside risk of project. If a project can be shown to be profitable despite the use of all of these adjustments, then designers feel confident that there is a very small chance that the project will turn out to be unprofitable. The previous chapter showed how some of these rules of thumb might lead to biases against profitable investment.

The preferred approach to dealing with uncertainty is to incorporate it explicitly in the analysis. The book by Morgan and Henrion [5] provides an excellent guide to dealing with uncertainty in quantitative analysis. Pistikopoulos [3] reviews several research developments for incorporating uncertainty in mathematical optimization models of chemical processes. Tatang [6] developed the deterministic equivalent modeling method to reduce the barriers to performing uncertainty analysis of engineering systems by significantly reducing computational cost (relative to Monte Carlo simulation).

Direct incorporation of uncertainty allows designers to search for designs that maximize the expected value of a measure of performance of their choice. For designs with several goals, chance constrained formulations can be used to maximize the expected value of an objective subject to satisfying prescribed goals with a probability equal or higher than a value specified by the designers [7]. In mathematical terms, the chance-constrained optimization problem is given by:

$$\begin{aligned}
 & \text{Max}_{\mathbf{d}, \mathbf{z}} && E[V(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta})] \\
 & \text{s.t.} && \mathbf{h}(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta}) = \mathbf{0} && \text{(Problem DP2)} \\
 & && \mathbf{P}[g(\mathbf{d}, \mathbf{z}, \boldsymbol{\theta}) \geq \mathbf{b}] \leq \boldsymbol{\alpha} \\
 & && \mathbf{d} \in \mathbf{D}, \mathbf{z} \in \mathbf{Z}
 \end{aligned}$$

where $E[\bullet]$ is the expected value operator, $P[g(\bullet) \geq b]$ is the probability that the function $g(\bullet)$ has a value equal or greater than constant b , and $\boldsymbol{\alpha}$ is the vector of acceptable probabilities of exceeding the vector of constant values \mathbf{b} .

While these approaches are well suited for goals that are measured in tangible units, they are not as useful when the goals are more difficult to measure. In particular, it is not obvious that maximizing the expected value of an environmental impact indicator that may be uncertain to more than an order of magnitude would help designers to identify the least damaging alternative. An alternative approach is introduced in the following section.

4.4 Decreasing decision uncertainty by preserving correlation structure

This section focuses on the problem of discriminating among competing alternatives when there are significant uncertainties in the valuation models used to assess their merit. One of the conclusions reached in Chapter 3 was that there are significant uncertainties in the valuation models used to assess the performance of alternative process designs. The uncertainties are rather large in the case of environmental valuation models. Even though the uncertainties were not as large for the case of economic valuation models, they were still significant.

The presence of large uncertainties in environmental valuation functions creates a dilemma for designers interested in improving environmental performance. On one hand, ignoring uncertainties and ranking designs based on a nominal environmental performance score leads to results that are at best difficult to justify. On the other hand, including uncertainties would appear to make it difficult to make decisions, since the noise in indicator scores might be much larger than the difference in scores among the various alternatives. Fortunately, there is a way out of this dilemma. The key to the solution is that uncertain scores may be highly correlated, and thus uncertainties in scores might not always imply uncertainty in distinguishing among alternatives.

A small example is used to illustrate the difference between uncertainty in valuation functions and the uncertainty in ranking alternatives based on uncertain value functions. Consider two alternatives, A and B. Both alternatives differ with respect to the levels of two attributes. It is assumed that the levels of the attributes are known with certainty. An additive value function is used to evaluate the two alternatives. The function used is

$$V_i = c_1L_{1,i} + c_2L_{2,i} \quad (4-1)$$

where V_i is the valuation assigned to alternative i (assume that V is a measure of performance we are interested in maximizing), $L_{j,i}$ is the level of attribute j in alternative i , and c_j is the valuation coefficient for a unit of attribute j . Even though we are certain about the levels of the attributes in both alternatives, we are uncertain about the values of the valuation coefficients (this is similar to being uncertain about prices in economic value functions or about unit environmental

indicators in environmental value functions). The attribute levels and valuation coefficient distributions used for this example are shown in Table 4-1.

Table 4-1: Data for the illustrative example

	Attribute level (Alternative A) $L_{i,A}$	Attribute level (Alternative B) $L_{i,B}$	Valuation coefficient c_i
Attribute 1	4	3.7	LogN(2,5)
Attribute 2	0.1	0.05	LogN(8,10)

Note: $\text{logN}(a,b)$ is used to represent a lognormal distribution with central value a and uncertainty factor b . The uncertainty factor is equal to the square of the geometric standard deviation.

As a consequence of the uncertainty in the valuation coefficients, the valuations for alternative A (V_A) and alternative B (V_B) are uncertain. Monte Carlo simulation was used to propagate the uncertainty in the valuations. The results are shown in Figure 4-2. The box plots in the figure mark the median valuation as well as the 5th, 25th, 75th, and 95th percentile valuations. At first glance, it appears that it would not be possible to distinguish between the two alternatives with a reasonable degree of confidence, since the distributions for their valuations overlap so much. However, an examination of the attribute values in Table 4-1 shows that this must be mistaken conclusion. The level of each of the attributes is higher for alternative A than for alternative B, so alternative A must be better than alternative B regardless of the uncertainty in the valuation coefficients, as long as the sign of the coefficients is always positive.

Judging decision uncertainty by the overlap in the distributions of the valuation of each alternative presupposes that these distributions are independent of each other, when they may be in fact highly correlated. For example, Figure 4-3 shows a scatter plot of the results of a Monte Carlo simulation of the valuation of alternatives A and B assuming that the distributions shown in Figure 4-2 are independent. This plot is very different from a plot of the results of the original simulation, shown in Figure 4-4. As expected, in no instance Alternative B receives a higher valuation than Alternative A (all of the scatter points are below the 1:1 diagonal line in the figure). It follows that the distributions shown in Figure 4-2 are not independent, but in fact are highly correlated. The reason is that in the states of the world in which a valuation parameter c_j is high, it is high for both alternatives. Despite the order of magnitude uncertainty in the absolute level of the valuations, there is no decision uncertainty whatsoever about the relative ranking of

the alternatives. As long as the alternatives in a decision problem share at least one attribute, one can expect that there will be correlations among the valuations for the various alternatives.

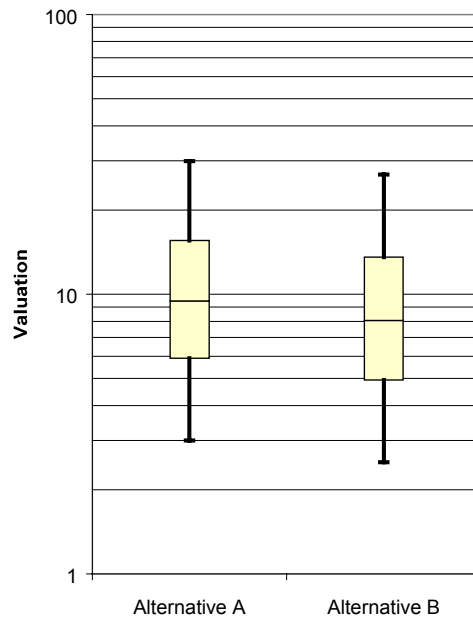


Figure 4-2: Distributions of absolute valuations for the illustrative example

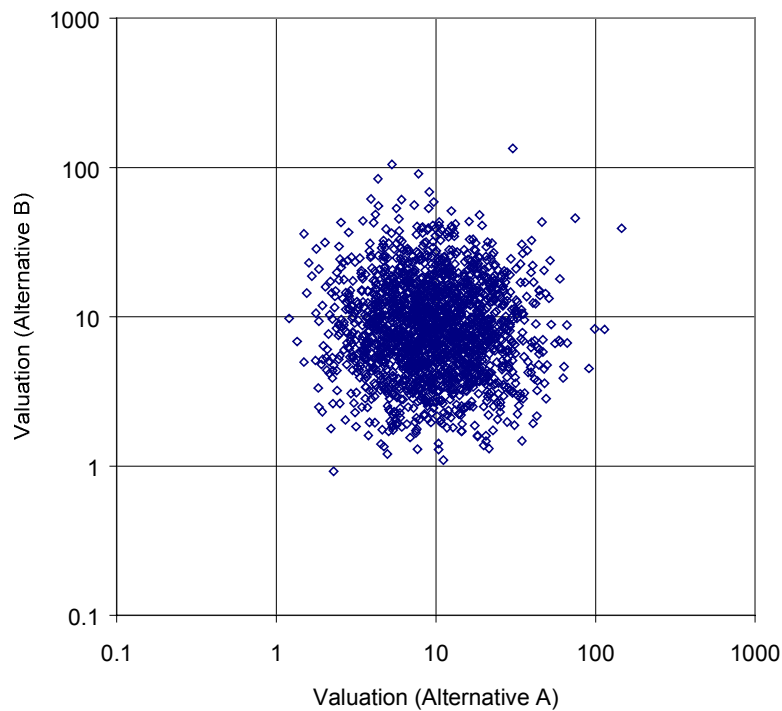


Figure 4-3: Scatter plot of valuations for the illustrative example, under the assumption of independence between valuation distributions

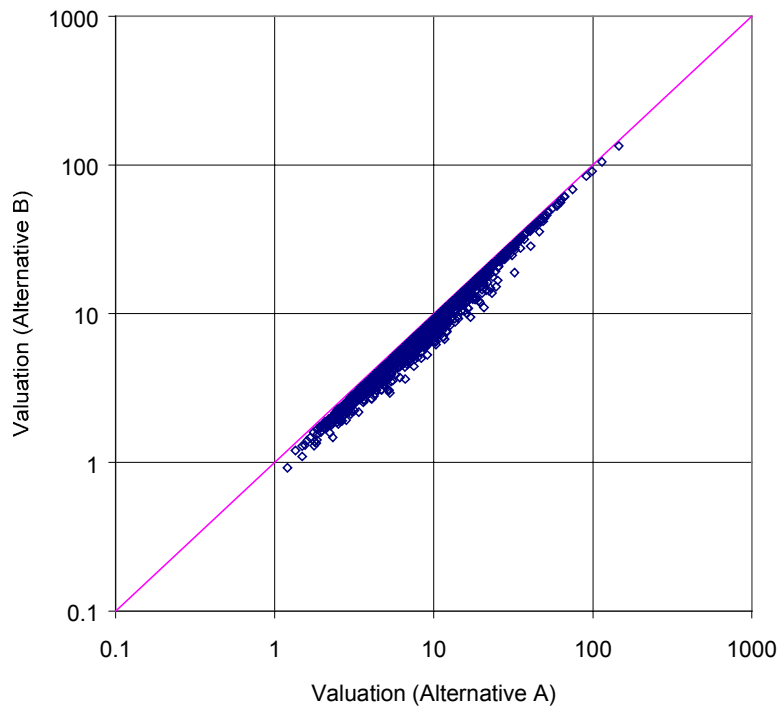


Figure 4-4: Scatter plot of actual valuations for the illustrative example

What this example indicates is that whenever there are significant uncertainties in valuation functions, it is more useful to look at relative measures of performance rather than absolute levels of performance.

To illustrate this point, the uncertainty in the relative measures $V_A - V_B$ and V_A/V_B was propagated. The first relative measure is the difference in valuations between two alternatives (referred to from here on as the delta indicator), while the second relative measure is the ratio of the valuations of two alternatives (referred to as the ratio indicator).

The results are shown in Figure 4-5. The box plots for both indicators tell the decision-maker that he or she may be at least 95% confident that Alternative A is superior to Alternative B since, in the case of delta indicator, the 5th percentile value is greater than zero, and in the case of the ratio indicator, the 5th percentile value is greater than one. The delta indicator might be useful to decision-makers when the valuation function is measured in tangible units (e.g. \$). In such cases, the distribution of differences can be used to make statements such as “one can be $x\%$ confident that alternative y is z units better (or worse) than the reference alternative”. If the decision-maker is not used to thinking in terms of the valuation function units (e.g.

environmental impact measured in “eco-points”), then the distribution of delta indicators is not likely to provide much information. In such cases the distribution of a ratio indicator is much more useful, since it enables the user to make statements of the type “one can be $x\%$ confident that alternative y has at most $z\%$ of the impact of the reference alternative”. Decision-makers who are not used to thinking in terms of eco-points might not have any trouble ranking alternatives based on their relative environmental impact expressed as a ratio.

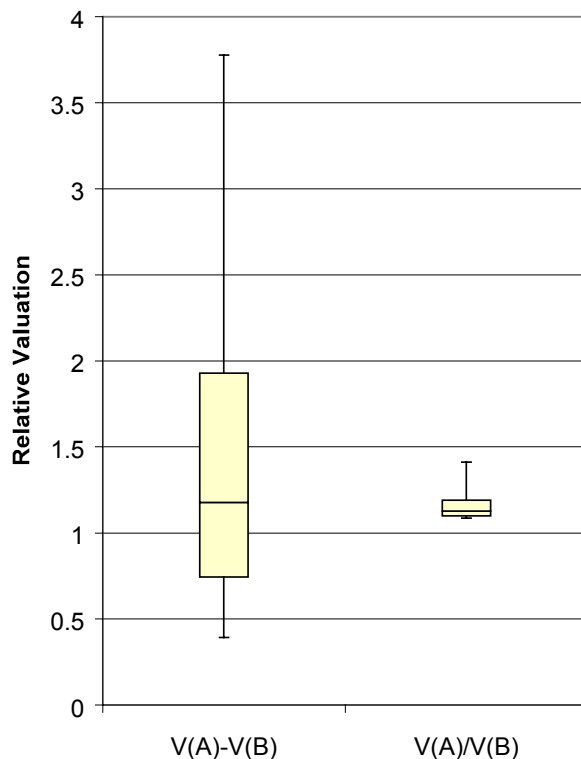


Figure 4-5: Relative valuations for the alternatives in the illustrative example

Referring again to Figure 4-5, the statement can be made that Alternative A is between 0.4 and 3.8 units better than Alternative B (90% confidence level). This might or might not be very informative, depending on how tangible the units of valuation are. Alternatively, the statement that Alternative A has between 1.08 and 1.4 times the value of Alternative B can also be made (again, at the 90% confidence level). This is a more tangible statement to most people. These figures are consistent with the attribute levels shown in Table 4-1, as they must be. When c_1 is much larger than c_2 , then the relative valuation will be given by the ratio of the values of attribute 1 in Alternatives A and B ($4/3.7 = 1.08$). When c_2 is much larger than c_1 then the

relative valuation is given by the ratio of the values of attribute 2 ($0.1/0.05 = 2$). Thus in this simple example one should be 100% confident that Alternative A has between 1.08 and 2 times the value of Alternative B, regardless of the distribution of the coefficients c_1 , and c_2 .

This simple example has shown how important it is to consider the correlation among the valuation distributions for various alternatives as a way to reduce decision uncertainty in the presence of significant valuation uncertainties. Further illustrations of the power of the technique are provided by the two examples at the end of this chapter. The following decision algorithm may be used to choose the best design among a discrete set of alternatives:

1. *Choose one of the alternatives as the base case alternative.* The lack of an “official” base case should not be an impediment to implementing this procedure. Any alternative may be used as a base case.
2. *Use uncertainty propagation techniques to obtain distributions of relative valuations for each alternative with respect to the base case.* Monte Carlo simulation has been used for most of the examples in this thesis. When Monte Carlo simulation is infeasible due to the amount of time needed to run a model (e.g. when the time needed to converge a process flow sheet model is greater than a few seconds), other techniques are needed. A review of such techniques is provided in Chapter 8.
3. *Select the most promising alternative, based on the relative valuation distributions, and designate it as the new base case.* For problems involving a few discrete alternatives and two objectives (e.g. economics and environmental performance), the most promising alternative may be selected by inspection of a graphical representation of the relative distributions (e.g. see Figure 4-26 in the example at the end of this chapter). Otherwise, stochastic optimization techniques based on utility functions are needed. These techniques are discussed in section 4.6.
4. *If no alternative with a significant probability of being superior to the current base case was found in step 3, exit the loop. Otherwise, go back to step 2.* After the best alternative is chosen the sensitivity analysis techniques discussed in Chapter 5 may be used to gain insights about the features of the design that most influence its performance. Such information can be used to generate new alternatives.

Figure 4-6 provides a graphical representation of the information flows involved in the propagation of the uncertainty in two relative measures of performance (discounted cash flow and environmental impact).

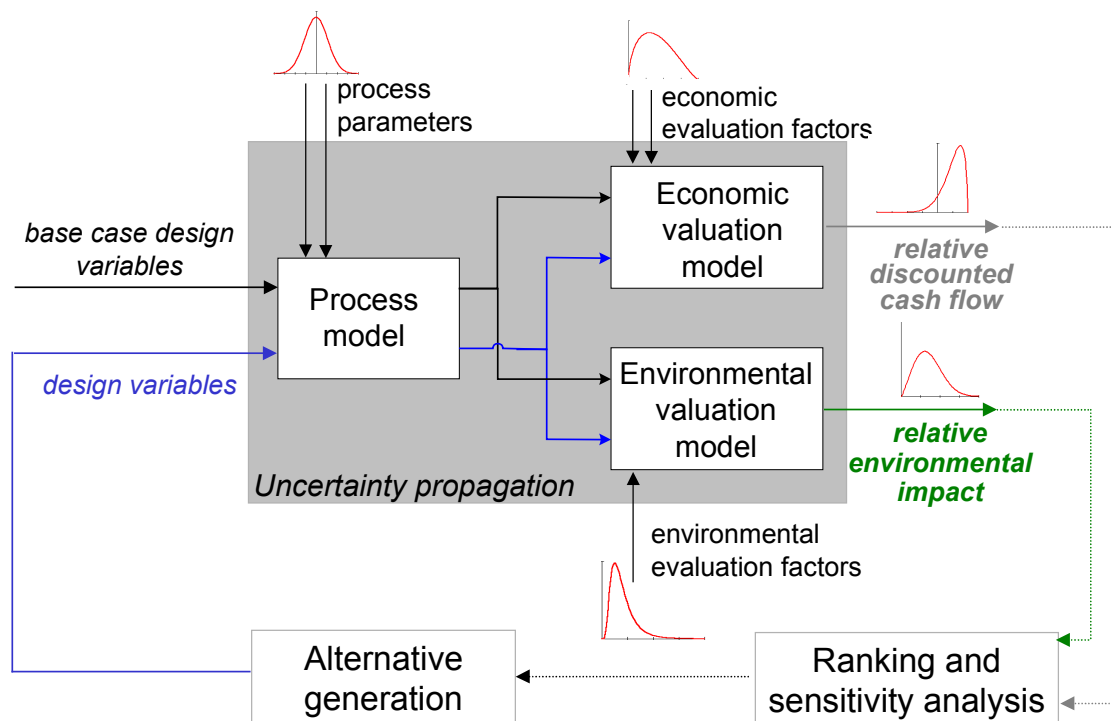


Figure 4-6: Example of decision-making cycle for process design based on two objectives

4.5 Confidence limits on the optimum values of decision variables

The procedure described in the previous section can be used to select the most promising alternative from a set in the presence of large uncertainties. Determining the optimum value of a decision variable under uncertainty is not very meaningful without a confidence interval around the optimum value. Some design variables might be optimal within a small range, while others may vary over a wide range without causing significant changes in expected performance.

Distributions of the relative valuation of alternatives with respect to a chosen base case may be used to establish confidence limits around the optimum values of the decision variables. The procedure is outlined here and illustrated in the examples at the end of this chapter:

1. Choose the design with the decision variables set at their optimum level as the base case design, following the algorithm described in the previous section.

2. Select a set of alternative designs. When more than one decision variable is involved, the alternative designs may be selected by varying the values of the decision variables using design-of-experiments techniques.
3. Select a desired confidence interval (for example, the 68% confidence interval corresponding to 1 standard deviation in normal distributions)
4. Propagate uncertainties in relative measures of performance. Test whether the hypothesis “Alternative i is better than the base alternative” can be rejected with confidence level equal to the desired confidence interval. If the hypothesis can be rejected, then alternative i would fall outside the desired confidence interval around the optimum, otherwise alternative i should be included in the confidence interval. For delta indicators, one is interested in the probability that the value of the delta indicator is lower than zero for objective functions one is interested in minimizing (e.g. cost, environmental impact) or higher than zero for functions one is interested in maximizing (e.g. profits). If the probability is higher than the confidence of interest, then the hypothesis can be rejected. For ratio indicators the same criteria apply, but the reference point is one instead of zero.
5. Add new alternatives and repeat step 4 until the desired level of resolution in the confidence interval is obtained.

4.6 Utility functions

“If a process change can reduce emissions by 40% while increasing costs by less than 5% we would implement it”

Experienced process designer at Dow Chemical

4.6.1 Introduction

While graphs of relative measures of performance such as the ones introduced in section 4.4 might be sufficient as decision-making aides in cases with a relative small set of discrete alternatives, it is desirable to have available utility functions for use by stochastic optimization algorithms. A utility function would allow a designer to use a computer and optimization algorithms to carry out the search for the most promising alternative, without requiring the

designer to spend considerable amounts of time examining graphs of relative performance distributions. This is particularly useful if a superstructure model of the process is available that encodes multiple flowsheet configurations. The graphical tools introduced earlier in this chapter could always be used at the end of the analysis to check whether the new base case identified by the computer is indeed preferable to the current base case, given a designer's attitude to risk and his or her willingness to make tradeoffs among competing objectives.

The approach to utility functions taken here is pragmatic. They are used mainly as devices to enable computer-based searches of promising alternatives. The utility functions introduced in this chapter most likely do not capture all the nuances of attitudes towards risk and towards tradeoffs among multiple objectives that designers might exhibit.

The usefulness of utility functions arises from the definition of utility in utility theory [8]. According to utility theory, if an appropriate utility is assigned to each possible consequence and the expected utility of each alternative is calculated, then the best alternative is the one with the highest expected utility. Utility functions can then be used within stochastic optimization algorithms, with the maximization of expected utility as the objective function of the optimization. The main difficulty lies in the determination of the appropriate utilities.

Utility theory can be applied to problems with a single attribute or to problems with multiple attributes. The main purpose of the application of utility theory to problems with a single attribute is to properly take into account decision-makers attitudes towards risk. Multiple attribute utility functions are useful both in situations where there is uncertainty (thus combining a decision-maker's attitudes towards risk with his or her attitudes towards tradeoffs), and in situations without uncertainty (in this case the role of the utility function is to capture decision-maker attitudes towards tradeoffs by collapsing a vector of attributes into a single scalar measure of preference).

4.6.2 Single-attribute utility functions

There is a wide body of evidence that most decision-makers are not indifferent among acts with the same expected payoff but different payoff probability distributions. For example, consider the following four alternatives [8]:

Alternative 1: earn \$100,000 for sure

Alternative 2: earn \$200,000 or \$0, each with probability 0.50

Alternative 3: earn \$1,000,000 with probability 0.1, or \$0 with probability 0.90

Alternative 4: earn \$200,000 with probability 0.9 or lose \$800,000 with probability 0.1

For each of the four alternatives, the expected amount earned is exactly \$100,000. Using expected earnings as the criterion for selecting among alternatives would yield the prediction that decision-makers should be indifferent among the alternatives listed above. However, most people are not indifferent among the four alternatives, since their risk profiles are quite different. The assessment of utilities for a single attribute typically proceeds along the following procedure:

1. Set up a scale by arbitrarily assigning utility values to two possible values of the uncertain attribute (the symbol x is used to refer to a particular value taken by the attribute). Usually a utility value of zero is assigned to the least preferred possible value of the attribute (x^o) and a utility of one to the most preferred possible value (x^*). Using the notation $u(x)$ to refer to the utility of attribute value x , the choice above would give $u(x^o) = 0$ and $u(x^*) = 1$.
2. For each other possible attribute value, assess a probability p such that the decision maker is indifferent between an alternative that yields the value of interest and a second alternative that has a p chance of yielding the most preferred value and a complementary $1-p$ chance of yielding the least preferred value. Then, because the expected utility of both alternatives must be the same under utility theory, the utility of outcome x is given by the relation

$$u(x) = p u(x^*) + (1-p) u(x^o) = p \times 1 + p \times 0 = p \quad (4-2)$$

In problems with a few possible (discrete) consequences, the direct assessment technique may be appropriate. For problems with a large number of possible consequences it is more useful to define a utility function and set the value of its parameters through the assessment of the utilities of a few discrete points. For more details the reader is referred to the work of Keeney and Raiffa [8] and to the introductory book on decision analysis by Clemen [9].

The assessment of utility functions over attributes with which the decision-maker has no familiarity (e.g. eco-points) can be extremely difficult. To address this problem, and to take full advantage of the information embedded in relative measures of performance, it is proposed that relative measures of performance be used as the basis for utility functions when the attribute units are not very tangible. Such utility functions must satisfy the requirement

$$E[u(x^A|B \text{ as base case})] = -E[u(x^B|A \text{ as base case})] \quad (4-3)$$

where the notation $E[u(x^A|B \text{ as base case})]$ stands for the expected value of the utility of alternative A with respect to the attribute x measured relative to alternative B. This condition is needed to guarantee that if alternative A is preferred to alternative B when the evaluation is made using B as the base case alternative, alternative A will still be preferred to alternative B if the evaluation is made using A as the base case alternative. This condition places strict restrictions on the form that utility functions may take, and in particular, it restricts the type of risk attitudes that may be encoded. This is the main disadvantage to the use of relative measures of performance. For problems where there are large uncertainties (especially if these uncertainties are related to the valuation models), it is a small price to pay in exchange for reducing decision uncertainty.

A simple utility function that satisfies eq (4-3) for relative measures of performance based on ratios is the logarithmic function

$$u\left(\frac{x^i}{x^{bc}}\right) = -\ln\left(\frac{x^i}{x^{bc}}\right) \quad (4-4)$$

The negative sign in eq (4-4) implies that lower values of attribute x are preferred (for example, when x is a measure of environmental impact). When higher values of attribute x are preferred, then the negative sign should be dropped. Eq (4-4) is only applicable to attributes that can not change sign (for example, it could be use to compare relative cost, but not relative profit). Decision-makers who accept eq (4-4) as a utility function should be indifferent between a base case design and an alternative that has an equal probability of having twice or half the impact of the base case design.

Table 4-2 shows the results of the application of the utility function given by eq (4-4) to four different distributions of relative performance. For each example, four views of the distribution are shown: density plots (using a linear or a logarithmic scale for the relative measure of performance) and box plots, showing the 5th, 25th, 50th, 75th, and 95th percentiles of the distributions (using a linear or a logarithmic scale). The certainty equivalent relative performance for each distribution is shown as a thick line. In the case of examples (i) and (iii), a decision-maker whose attitude towards risk was well represented by eq (4-4) would be indifferent between the base case design and a design with relative performance (e.g. relative

environmental impact) described by the distributions shown in the corresponding row of the table. In the case of example (ii), the designer would prefer the base case design, but would be indifferent between the alternative design and a design guaranteed to have twice the environmental impact of the base case design. Finally, the designer would prefer the design alternative with relative performance distribution as shown in example (iv), and would be indifferent between that alternative and an alternative guaranteed to have half of the environmental impact of the base case design.

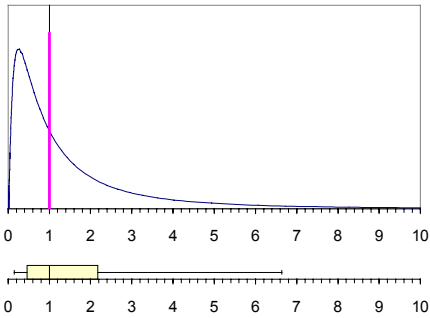
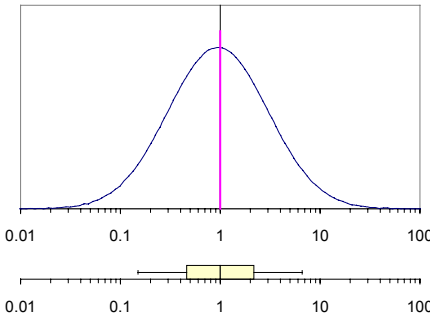
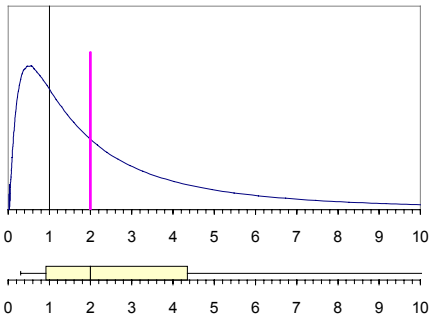
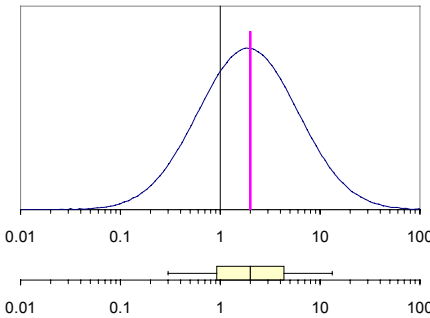
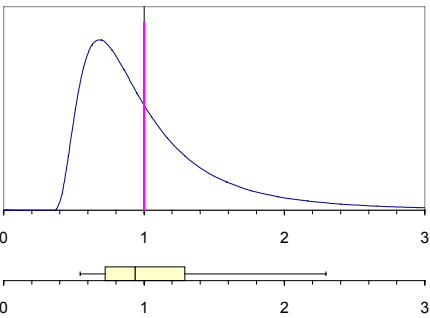
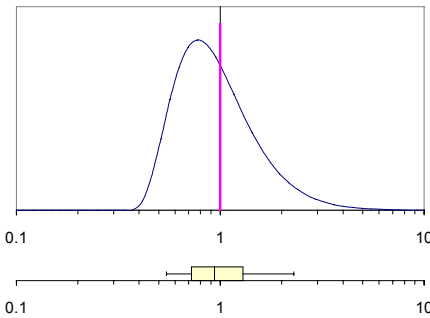
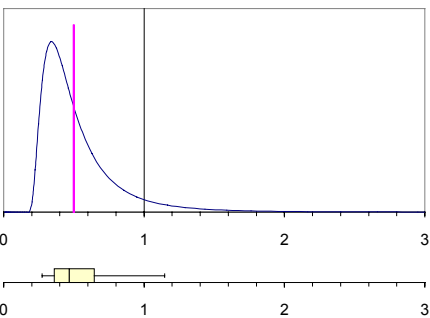
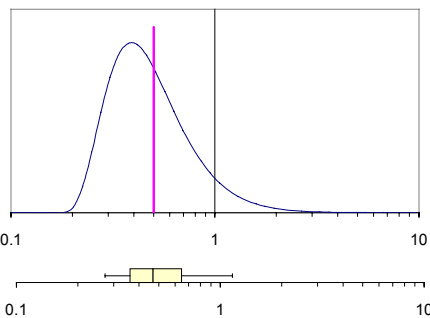
For designers for whom the tradeoffs implied by eq (4-4) would not be acceptable, alternative utility functions satisfying eq (4-3) may be tried. In particular, the family of utility functions given by

$$u\left(\frac{x^i}{x^{bc}}\right) = -\text{sign}\left[\ln\left(\frac{x^i}{x^{bc}}\right)\right] \times \left|\ln\left(\frac{x^i}{x^{bc}}\right)\right|^m \quad (4-5)$$

may be used to vary the weight given to extreme values¹⁷ by varying the value of the parameter m (m is restricted to positive values). When m is less than one, less weight is given to extreme values. A value of $m=1$ yields eq (4-4), while a value of m larger than one increases the emphasis given to extreme values.

¹⁷ Here the phrase “extreme values” is used to refer to values that are relatively distant from 1.0 on a logarithmic scale.

Table 4-2: Examples of the application of the single attribute logarithmic utility function over distributions of relative measures of performance (ratio indicators)

No.	Linear scale	Log scale	CE ^a Relative performance
i			1
ii			2
iii			1
iv			0.5

Note: (a) CE = certainty equivalent. The certainty equivalent relative performance is defined as the constant relative performance having a utility equal to the expected utility over the distribution of relative performance. In the case of the logarithmic utility function given by (4-4) it is given by $\exp\{-E[u(x^i/x^{bc})]\}$.

4.6.3 Multiple-attribute utility functions

In principle, the direct assessment procedure outlined for single-attribute utilities could also be used to assess utilities over multiple attributes. This is practical if there are only a few consequences over the vector of attributes \mathbf{x} (e.g. the discrete set of N alternatives given by $\mathbf{x}^1, \mathbf{x}^2, \dots, \mathbf{x}^N$), where N is a small number. In the direct assessment procedure, the utility values for two of these alternatives would be assigned directly. The rest of the utility values would be obtained by asking the decision-maker to express preferences involving the outcome represented by the set of attribute values \mathbf{x}^i and lotteries involving the sets of attribute values for which utilities were assigned directly. In practice, this is rarely done. Instead, single-attribute utility functions are first assessed over each of the attributes and then, after checking the validity of certain assumptions, a multiattribute utility function of the type

$$u(\mathbf{x}) = f(u_1(x_1), u_2(x_2), \dots) \quad (4-6)$$

is postulated. A commonly used function is the multilinear utility function, which in the case of two attributes is given by:

$$u(x_1, x_2) = k_1 u_1(x_1) + k_2 u_2(x_2) + k_{12} u_1(x_1) u_2(x_2) \quad (4-7)$$

The three constants in eq (4-7) are assessed by asking the decision maker to express his or her preferences over three sets of lotteries involving different combinations of attribute outcomes. A detailed procedure is provided in Keeney and Raiffa's book [8].

Most designers would probably have a difficult time expressing their preferences over lotteries involving tradeoffs between absolute measures of economic and environmental performance. On the other hand, designers are used to thinking of tradeoffs involving intangible objectives in terms such as those used in the opening quote of this section. For this reason, the following two-attribute utility function is proposed:

$$u\left(\frac{\mathbf{x}^i}{\mathbf{x}^{bc}}\right) = -(1-\alpha)\ln\left(\frac{x_1^i}{x_1^{bc}}\right) - \alpha\ln\left(\frac{x_2^i}{x_2^{bc}}\right) \quad (4-8)$$

where the weighting factor α may take values between zero and one. For the examples used in this thesis, the attributes x_1 = total annualized cost (TAC) and x_2 = environmental impact indicator (Ω) are used. Choosing an α value of 0.5 would give equal importance to reducing relative cost and reducing relative environmental impact. There is empirical evidence that private

companies do not assign equal weight to environmental and economic performance [10], so lower values of α would be typically chosen.

A contour plot of eq (4-8) is shown in Figure 4-7 for the case $\alpha=0.1$. Designers for whom eq (4-8) $\alpha=0.1$ is a good representation of their willingness to make tradeoffs between cost and environmental impact would be indifferent among design alternatives lying on the same utility curve in Figure 4-7. They should also be willing to switch from the base case alternative to any design lying on a utility curve higher than zero. In particular, one can see that the two-attribute utility function shown in Figure 4-7 is consistent with the statement quoted at the beginning of this section. An alternative with 5% more cost than the base case alternative but 60% of the impact (40% across-the-board reduction in emissions) needs to have a utility equal or higher than zero in order to be preferred. The impact of the value of the weighting factor α on the shape of the zero utility indifference curve is shown in Figure 4-8. This chart may be used by design teams to find the α -value that is consistent with their willingness to make tradeoffs between relative cost and relative environmental impact. For example, designers for whom the value $\alpha=0.05$ is appropriate would not be willing to make the tradeoff mentioned in the opening quote of this section, since the alternative with 1.05% relative cost and 60% relative impact is now located above the zero utility indifference curve.

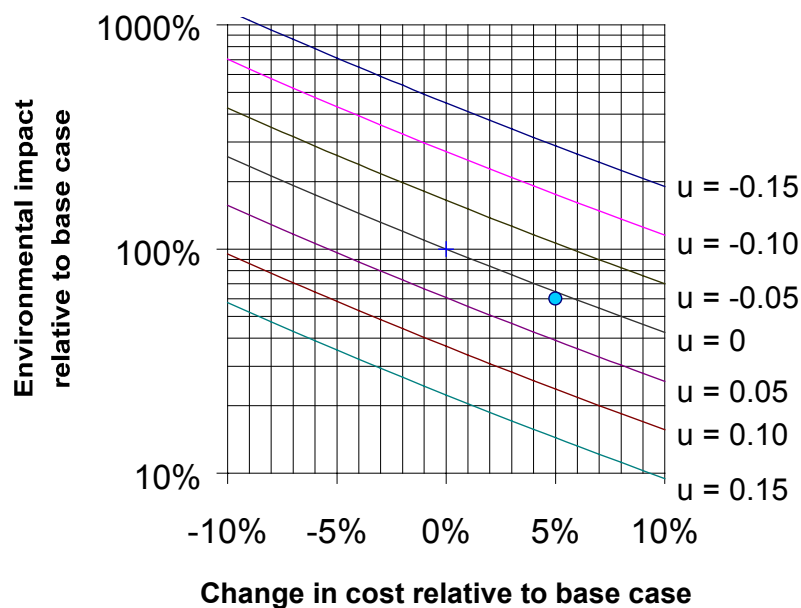


Figure 4-7: Indifference curves for a two attribute utility function over relative cost and relative environmental impact with $\alpha=0.1$

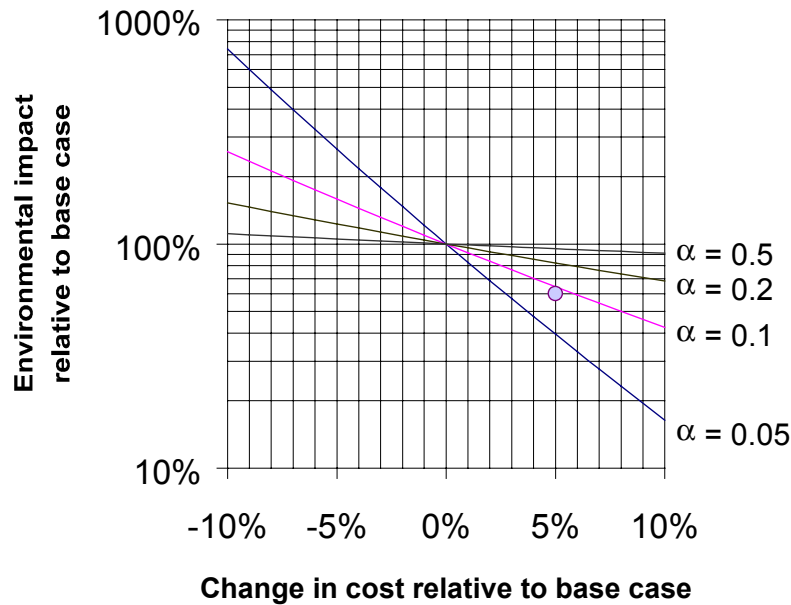


Figure 4-8: Zero-utility indifference curves for the attributes relative cost and relative environmental impact based on the proposed logarithmic utility function.

Given the high level of uncertainty in measures of environmental performance, the author believes that the utility functions proposed in this chapter are satisfactory for incorporation in stochastic programming formulations, particularly at the conceptual stage of design. Even if the utility functions do not capture fully designer attitudes towards risk and their willingness to make tradeoffs among competing objectives, they include enough flexibility to serve as a good first approximation to the preference structure of a decision-maker. One way to verify that the design alternative found by the computer through maximization of expected utility is indeed superior to the design alternative that maximizes expected economic performance is to propagate the uncertainties in relative cost and relative environmental impact of the maximum expected utility alternative with respect to the minimum expected cost alternative. Designers could then examine plots of these distributions and check whether they would be willing to make the tradeoffs made by the computer.

4.7 Examples

4.7.1 Choosing the operating set point for a solvent recovery system

INTRODUCTION

The solvent recovery system configuration shown in Figure 4-9 was used for this example. The function of the system is to recover methylene chloride solvent from the feed stream into the recycle stream. The amounts of solvent not recovered are discharged to the sewer system with the effluent stream. A feed stream containing 1.4% weight fraction methylene chloride in water is fed to the process. The flow rate of the feed stream is 100,000 lb./hr and its temperature 95°F. 200 psia steam is used to strip methylene chloride from water in the two flash drums labeled TOWER1 and TOWER2. The mixture of water and solvent vapors recovered from the top of TOWER1 is fed to a condenser. Upon condensation at 75°F, two liquid phases are formed. The aqueous phase is returned to the TOWER1 vessel, while the solvent-rich phase is recycled to the upstream process, thus decreasing the need for purchasing fresh solvent. Steam inputs are regulated by a concentration controller. The task in this example is to find the optimum concentration set point for the controller. A motivation for doing this might be to negotiate a discharge permit with the local authorities. Details on the case study used as a basis for this example are given in Appendix A.

The key tradeoff in this system involves steam input and solvent losses. As the amount of steam fed to the system increases, more methylene chloride is recovered overhead, and less is lost as discharge to the sewer. From an economic perspective, the tradeoff is one between the cost of supplying steam and the cost of purchasing make-up methylene chloride to replace the amounts lost with the wastewater discharge. There are also tradeoffs from an environmental impact perspective. The key tradeoff is that between the impact of the discharged solvent (including the impact of producing the make-up methylene chloride required to replace what is lost), and the impact of supplying steam (including the impact of producing and burning the fuel used in the steam boiler).

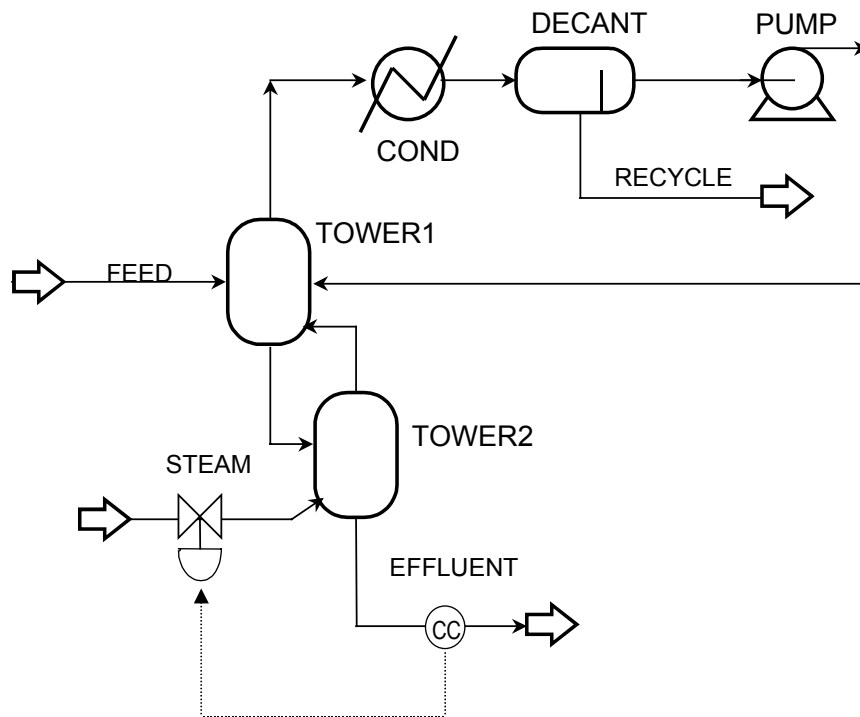


Figure 4-9: Flowsheet for the concentration set point selection example

For this example it is assumed that the process is already operating. Further assumptions made are that the system performance is known, and that the amount of steam required to meet a given effluent concentration standard is given by the curve shown in Figure 4-10¹⁸.

ANALYSIS

Sources of Uncertainty

Because of the assumptions given in the introduction, the only uncertainties in this example are the ones associated with the evaluation of environmental performance. Future prices are uncertain, but the set point could be changed in the future to respond to changes in prices. The concern in this example is to find the optimum concentration set point given today's conditions. A different set point could be chosen tomorrow if conditions changed. Uncertainties associated with evaluating environmental performance include uncertainties in emission factors, input-output technical coefficients¹⁹, environmental problem contribution characterization factors

¹⁸ The curve was obtained from a model of the system implemented on the Aspen Plus process simulator.

¹⁹ Used to generate the life-cycle emissions inventories according to the PIO-LCA method, see Chapter 7.

for individual chemicals, fate and transport properties of chemicals, human exposure model parameters, and environmental problem valuation factors.

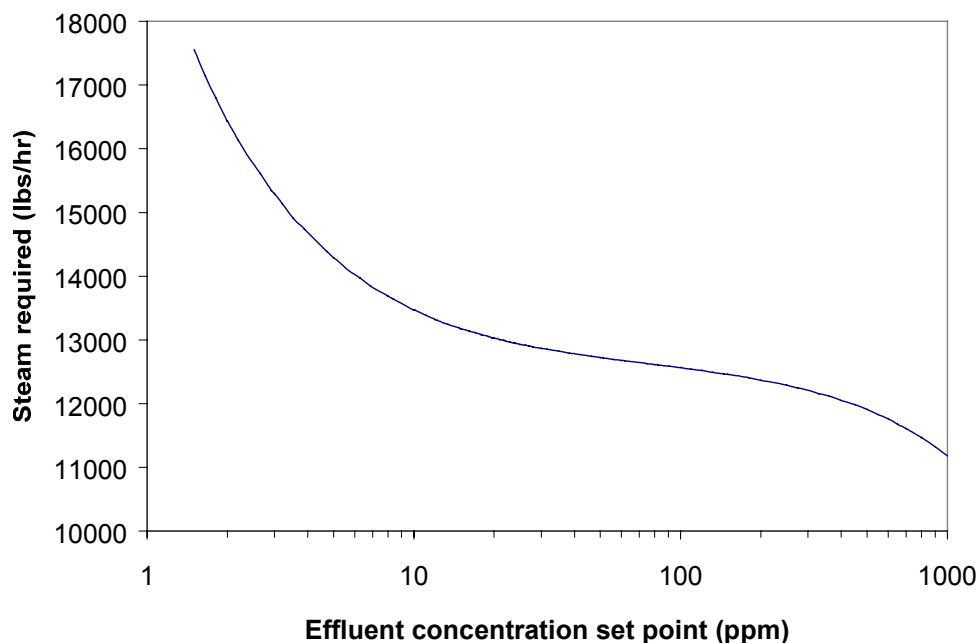


Figure 4-10: Steam consumption as a function of effluent concentration set point for the set point selection example

Process Model

A model of the process shown in Figure 4-9 was developed using the Aspen Plus process simulator. A design specification was used to vary the steam input rate (F_{steam} , in lb./hr) to meet specified methylene chloride concentrations in the effluent. The mass flow of methylene chloride in the effluent stream ($F_{CH_2Cl_2}$, in lb./hr) was passed along with the steam input rate to the valuation models. For this exercise it was assumed that the model predictions matched exactly the observed process performance.

Economic Valuation Model

The key economic tradeoff is the one between utility costs (mostly due to steam use) and the costs associated with purchasing make-up methylene chloride to replace what is lost with the effluent. The variable cost²⁰ for this system is given by:

$$Cost = F_{steam} P_{steam} + F_{CH_2Cl_2} P_{CH_2Cl_2} \quad (4-9)$$

It was assumed that current prices for steam and methylene chloride are, respectively, \$2.9/1000 lbs. and \$0.40/lb.

Environmental Valuation Model

It would be interesting to know what the environmentally optimum concentration set point would be, since this information might be of help in anticipating or negotiating effluent concentration standards for this process. The environmental impact of the system is evaluated using the expression:

$$\Omega = F_{steam} \Omega_{steam} + F_{CH_2Cl_2} \Omega_{CH_2Cl_2} \quad (4-10)$$

where Ω_i are unit environmental impact indicators. Using the methods explained in Chapters 6 and 7, the following distributions were obtained for the marginal environmental impact valuations of 1 lb. of 200 psia steam and 1 lb. of methylene chloride released to the sewer system²¹:

$$\log_{10} \Omega_{steam} = -3.38 + 4.07 \times \text{Beta}(\alpha_1 = 5.19, \alpha_2 = 12.19) \quad (4-11)$$

$$\log_{10} \Omega_{CH_2Cl_2} = -1.44 + \text{Gamma}(\alpha = 7.21, \beta = 0.17) \quad (4-12)$$

The distributions are correlated with a rank correlation coefficient of 0.66. The copula method²² was used to generate the joint distribution shown in Figure 4-11. Note the wide range spanned by the distribution (about 2 orders of magnitude in each direction)²³.

²⁰ There are additional costs from electricity consumption by the pump and cooling water use at the condenser, but since these costs are much lower than the steam and make-up solvent costs they have been omitted from the presentation.

²¹ The marginal environmental impact valuations are given in units of ELU (environmental load units) per pound. An ELU is defined as a dollar of social cost calculated according to the contingent valuation method, using the weighting factors given in Table 3-16.

²² See section 7.5.3

²³ See Figure 4-20 for probability density plots of the marginal distributions.

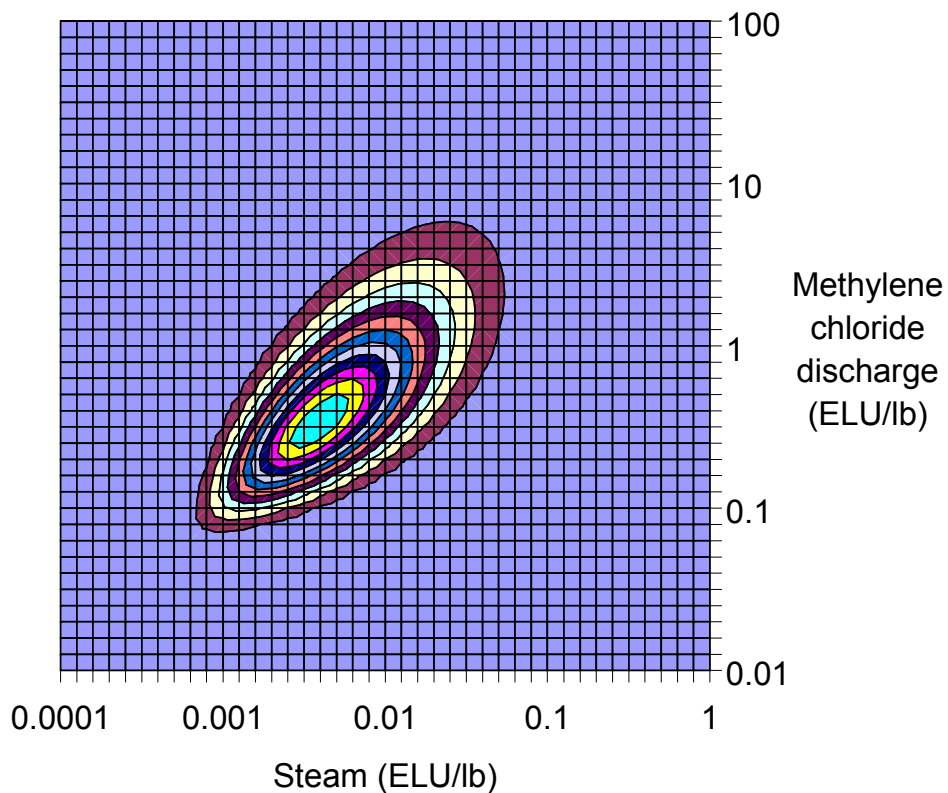


Figure 4-11: Joint probability density distribution of the unit environmental indicators for steam and methylene chloride discharges

RESULTS

Set point selection based on economic considerations

Given the assumption that the system performance is well known, it is straightforward to determine the economically optimum set point. All the information needed is the price of the make-up solvent and the cost of the utilities used by the system. Using a solvent cost of \$0.40/lb methylene chloride and a steam cost of \$2.9/1000 lbs. one finds that the economically-optimum set point is 25 ppm (see Figure 4-12), which yields a variable cost of \$38.7/hr (or \$310,000/yr assuming 8000 hrs of operation per year).

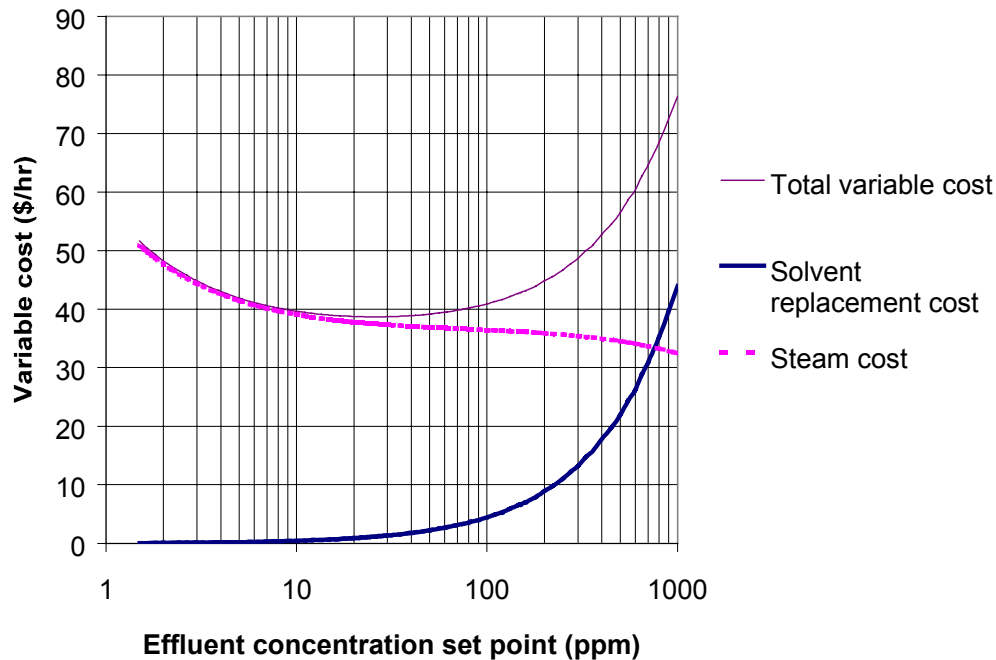


Figure 4-12: Variable costs as a function of effluent concentration set point

Set point selection based on graphical analysis of environmental impact distributions

Figure 4-13 shows the simulated distributions for the environmental impact indicator of several different effluent concentration set points. The chart shows the median valuation as well as the 5th, 25th, 75th, and 95th percentiles of each distribution.

It would be difficult to distinguish among the alternatives with confidence on the basis of the results shown in Figure 4-13, given the overlaps among the various distributions. A very different picture is obtained when the ratio of the environmental valuation for each set point to the environmental valuation of a reference set point is used as a basis for the decision. Figure 4-14 shows the results when a set point of 100 ppm is used as a base case. It is now clear than set points above 100 ppm or below 10 ppm are more likely to be considered to have more serious environmental impacts than the base case. On the other hand, set points in the range 15-80 ppm have an even or better chance of having lower environmental impact.

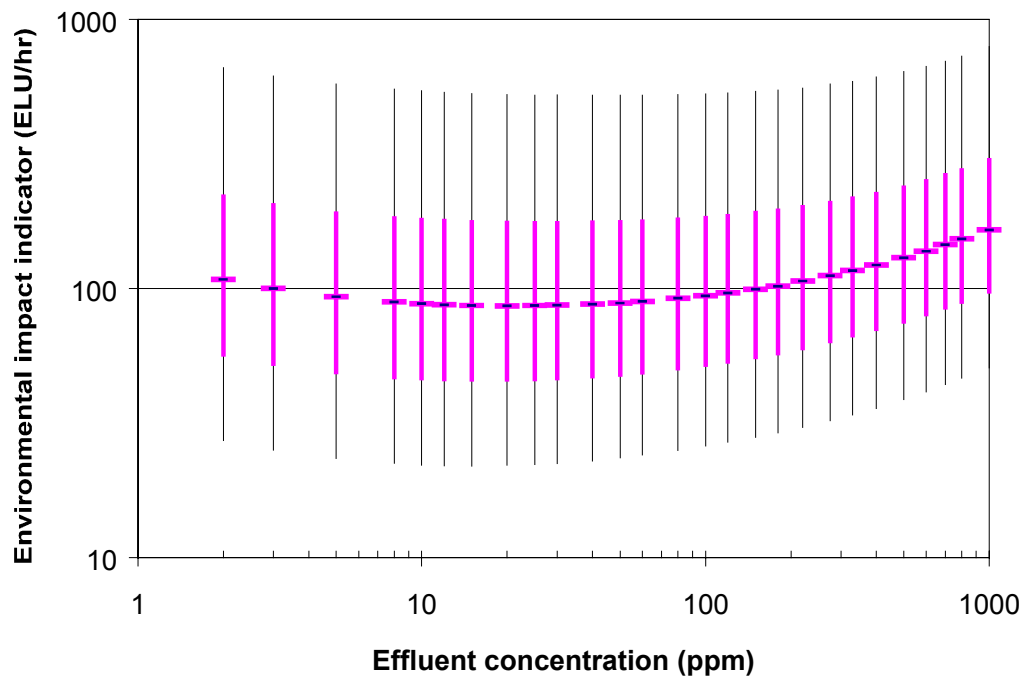


Figure 4-13: Environmental impact indicator distributions for the concentration set point selection example

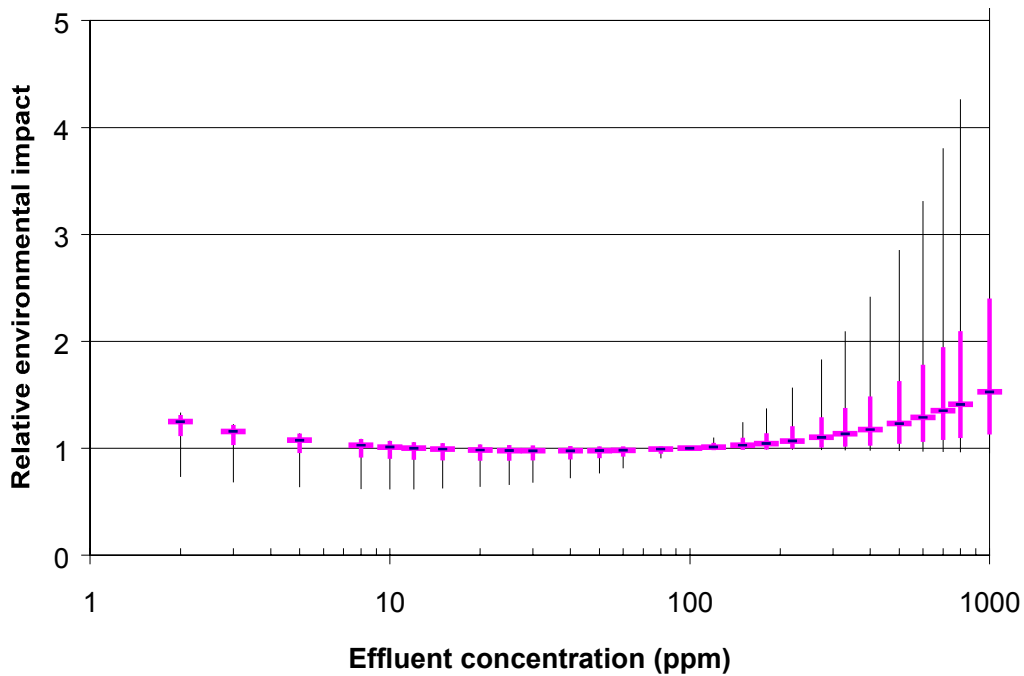


Figure 4-14: Relative environmental impact distributions with respect to a 100 ppm base case for the concentration set point selection example

A plot of relative environmental impact distributions vs. relative variable cost (taking the 100 ppm set point as base case) is shown in Figure 4-15. This plot shows that the minimum cost alternative (setting the concentration set point at 25 ppm) has a reasonable chance of having better environmental performance than the 100 ppm base case. Based on this observation, the 25 ppm alternative is chosen as the new base case and carry out an additional Monte Carlo simulation.

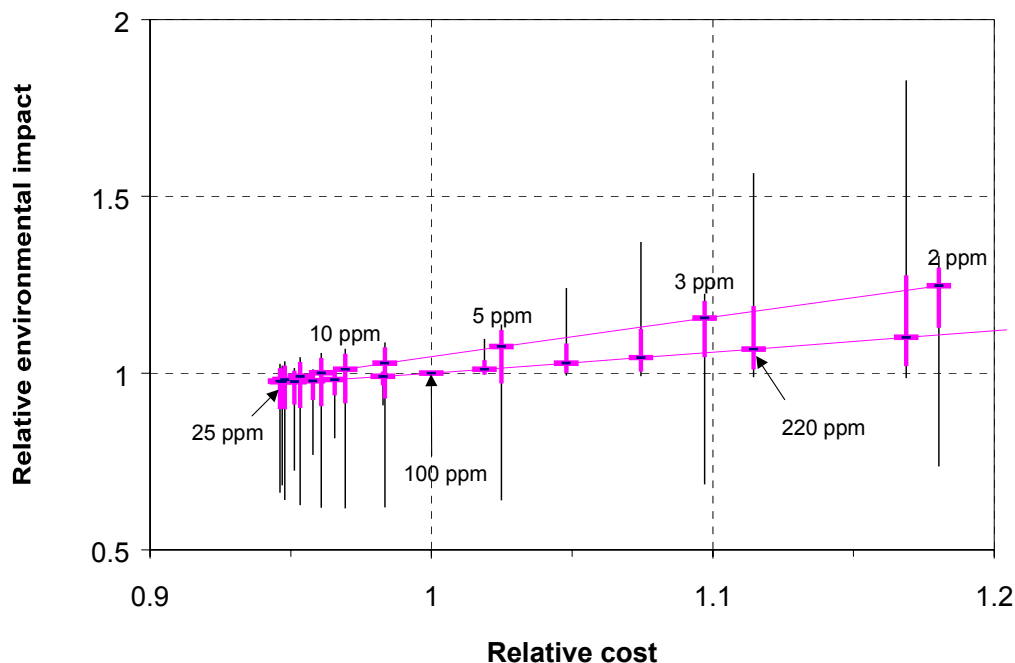


Figure 4-15: Relative environmental impact distributions vs. relative variable cost (100 ppm base case) for the concentration set point selection example²⁴

The results of the simulation are shown in Figure 4-16. The majority of the alternatives now have more than a 50% chance of having more environmental impact than the 25 ppm alternative chosen as the new base case. In particular, once can be 95% confident that tightening the effluent concentration standard to 2 ppm would result in worsening the environmental impact. Alternatives in the range 15 ppm to 180 ppm have more than a 25% chance of having lower environmental impact than the 25 ppm alternative, but the magnitude of the improvement is very small (especially compared to the magnitude of the potential worsening for the higher

²⁴ A line connecting the median points of the distribution was added to help the reader to follow the trends in relative impact and relative cost as the effluent concentration set point varies from 2 to 300 ppm.

concentration set points). Based on this analysis the conclusion is reached that in this particular example choosing the set point that minimizes variable costs is consistent with minimizing environmental impact. If one accepts the 25 ppm alternative as a plausible environmentally optimum choice, then a 75% confidence interval of 15 ppm to 180 ppm would be obtained based on the procedure described in section 4.5.

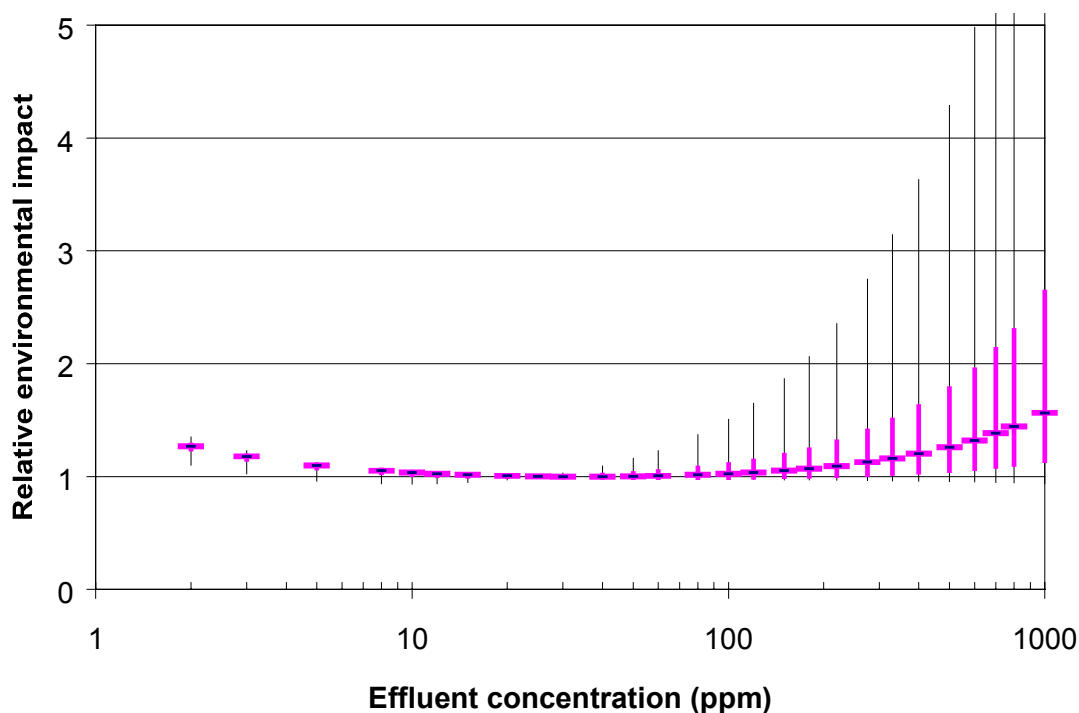


Figure 4-16: Relative environmental impact distributions with respect to a 25 ppm base case for the concentration set point selection example

Set point selection by expected utility minimization

Table 4-3 shows stochastic optimization results obtained using the utility function introduced in section 4.6. The optimization problem was solved twice, first using the 100 ppm alternative as the base case, and then using the economic optimum (25 ppm) alternative as the base case. As shown in Table 4-3, the optimization results were sensitive to the value of α ($\alpha=0$ corresponds to single criterion economic optimization, while $\alpha=1$ corresponds to single criterion environmental impact minimization), but not to the choice of base case.

Table 4-3: Expected utility minimization results for the concentration set point selection example

α	Base case = 100 ppm		Base case = 25 ppm	
	Optimum set point	Expected utility	Optimum set point	Expected utility
0	25	0.0553	25	0
0.05	25	0.0566	25	0
0.1	25	0.0579	25	0
0.2	24	0.0608	24	0.00003
0.5	23	0.0687	23	0.0003
1	21	0.0828	21	0.0013

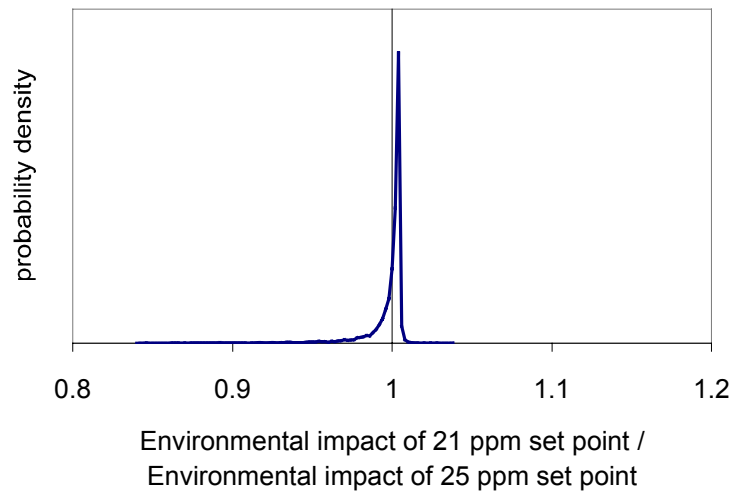


Figure 4-17: Probability density plot for the environmental impact indicator of the 18 ppm alternative relative to the 25 ppm alternative

The probability density plot for the environmental impact indicator of the 21 ppm concentration set point alternative relative to the 25 ppm alternative is shown in Figure 4-17. As Table 4-3 indicates, the utility function $U = -\ln(\text{Relative Environmental Impact})$ transforms the density plot shown in Figure 4-17 into an expected utility of 0.0013. This means that a decision-maker concerned only with environmental performance and having risk attitudes consistent with the logarithmic utility function would be indifferent between: (a) switching from the 25 ppm base case to the 21 ppm alternative, and (b) switching from the 25 ppm base case to an alternative guaranteed to have 99.87% of the environmental impact of the 25 ppm alternative²⁵. The utility function thus gives a slightly higher weight to the relative long tail below a relative

²⁵ $-\ln(0.9987) = 0.0013$

impact of 1 than to the bulk of the density which is concentrated at a position slightly larger than 1. Given the minor relative environmental benefit that could be expected from switching to the 21 ppm alternative, it is decided to keep the 25 ppm alternative as the optimum set point, which is the same result that had been obtained through the graphical method.

4.7.2 Sizing a heat exchanger

INTRODUCTION

This example is a follow-up to the heat exchanger sizing problem presented in section 3.2.5. The design scenario is the same as the one discussed in that section. The question of interest is finding the optimum size for a heat exchanger that will be used to preheat the feed to the solvent recovery process shown in Figure 4-18. Details on the case study used as a basis for this example are given in Appendix A. As in chapter 3, it is assumed that the process is required to comply with a concentration limit of 2 ppm methylene chloride in the effluent²⁶.

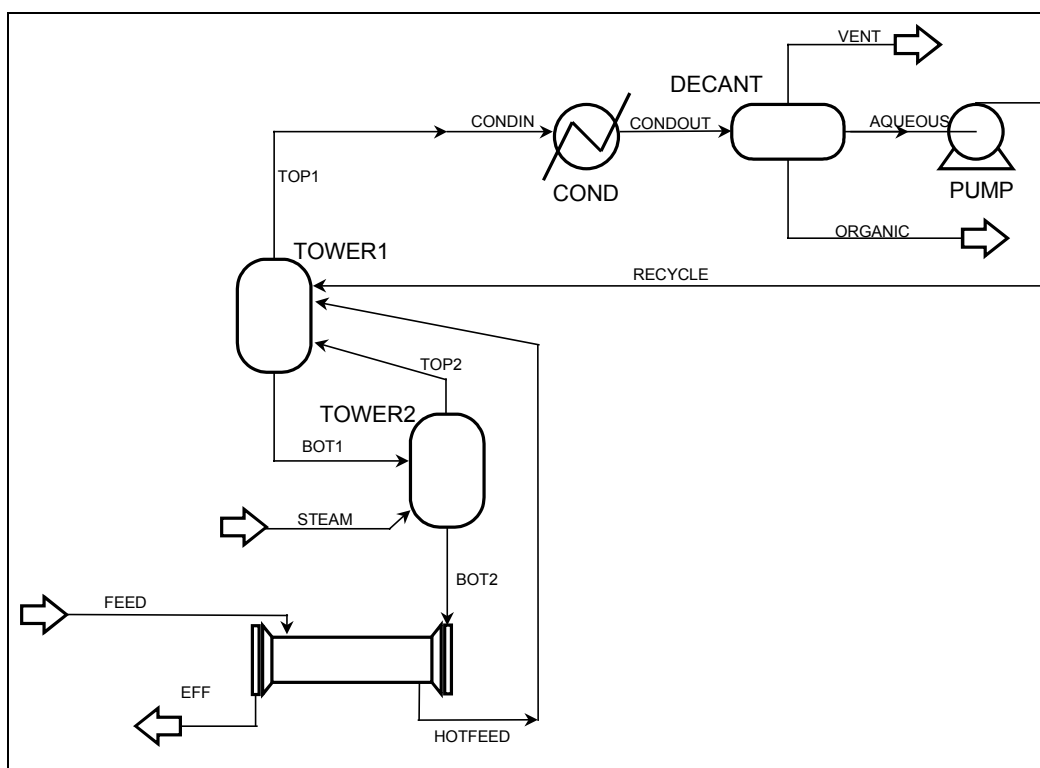


Figure 4-18: Flowsheet for the heat exchanger sizing example

²⁶ This assumption implies that local regulators have not yet been enlightened by the results of the previous example.

ANALYSIS

Sources of Uncertainty

The following sources of uncertainty are considered:

- a) Model-inherent uncertainties. Uncertainties in the overall heat transfer coefficient and in the vapor-liquid and liquid-liquid equilibria of mixtures of water and methylene chloride are considered.
- b) Process-inherent uncertainties. Variability (rather than uncertainty²⁷) in feed temperature and concentration is considered. Feed flow is assumed to be constant (for example, through a flow controller and a storage tank upstream from the process).
- c) Valuation model uncertainties. For the economic valuation model, uncertainties in prices, equipment cost, and annualization factors²⁸ are considered. Uncertainties in the environmental valuation model include uncertainties in emission factors, input-output technical coefficients, characterization factors, fate and transport properties of chemicals, human exposure model parameters, and environmental problem valuation factors²⁹.

Process Model

A model of the process shown in Figure 4-18 was developed using the Aspen Plus simulator. Uncertainty analysis of this model was carried out using the deterministic equivalent modeling method (DEMM, see section 8.2). DEMM was used to develop a spreadsheet-based metamodel of the Aspen plus model. The metamodel takes two types of inputs: uncertain inputs and decision variable values. The uncertain inputs used in the metamodel were: thermodynamic binary interaction parameters for the activity coefficient model of the methylene chloride-water system, overall heat transfer coefficient for the heat exchanger, feed temperature, and feed concentration. The decision variables were the logarithm of the effluent concentration set point

²⁷ Recall the distinction between uncertainty and variability made in section 4.2.

²⁸ The uncertainty in the annualization factor arises from uncertainties in many parameters (see section 3.2.4).

²⁹ See the following sections for further discussion on environmental value model uncertainties: 3.3.2 (general discussion and discussion of uncertainties in valuation factors); 6.4 (uncertainties in the human exposure model); 7.5 (uncertainties in the PIO-LCA model).

and the logarithm of the heat exchanger area³⁰. Uncertain outputs calculated by the metamodel included: steam use rate, condenser duty, and methylene chloride discharge rate. Steam use and condenser duty were modeled using a full fourth order approximation with second-, third-, and fourth-order cross terms, while the effluent discharge was modeled using a fourth order approximation without cross terms. Table 4-4 summarizes the uncertainty distributions used in the process model. Details on the derivation of these distributions can be found in Appendix A (section A.4).

Economic Valuation Mode

The key economic tradeoff is the one between operating cost (mostly due to steam use) and the costs associated with the exchanger (including capital cost and annual charges due to maintenance, taxes and insurance)³¹. A total annualized cost (TAC) economic valuation model was used to take these tradeoffs into account:

$$TAC = F_{steam} P_{steam} + F_{cw} (\dot{Q}_{cond}) P_{cw} + F_{CH_2Cl_2} P_{CH_2Cl_2} + AF \times f_{BM} C_p (Area_{HX}) \quad (4-13)$$

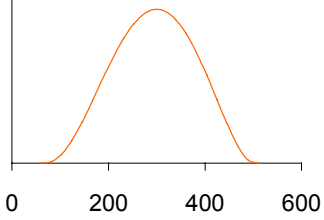
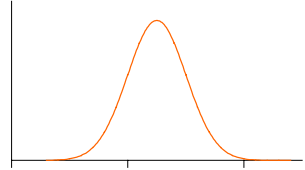
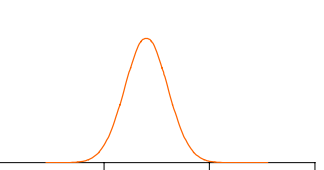
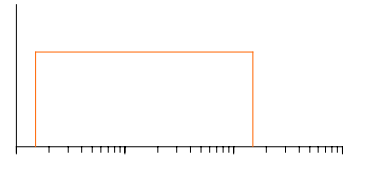
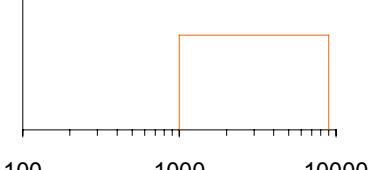
For a given choice of heat exchanger area, the spreadsheet process metamodel will generate distributions for the annual steam consumption (F_{steam}), condenser cooling duty (\dot{Q}_{cond}), and methylene chloride discharges in the effluent ($F_{CH_2Cl_2}$) as a function of the uncertain process model parameters. The cooling water use (F_{cw}) is calculated as a function of the condenser duty assuming an allowable water temperature rise of 30°F. Distributions for the discounted-cash flow average prices (P_i) for steam and methylene chloride were estimated using the procedure described in section 3.2.4, while the price of cooling water was assumed to be constant. The following distributions were used:

200 psia steam:	$\$0.0029/\text{lb} \times \text{LogNormal}(\text{median}=1.027, UF=1.124)$
Cooling water:	$\$0.12/\text{m}^3$ (fixed)
Methylene chloride:	$\$0.40/\text{lb} \times \text{LogNormal}(\text{median}=1.005, UF=1.122)$

³⁰ It was found that the output variables of interest were easier to describe in terms of polynomials of $\log(C_{sp})$ and $\log(\text{Area})$ than in terms of polynomials of C_{sp} and Area . Using logarithms enables one to use lower order approximations to obtain an accurate model as compared to using untransformed variables.

³¹ See section 3.2 for a discussion on the operating cost vs. capital cost tradeoff.

Table 4-4: Uncertainty distributions used to build the spreadsheet-based process metamodel

Input variable	Distribution	Probability density plot
Binary interaction parameters in the NRTL model	$\begin{bmatrix} A_{ij} \\ A_{ji} \\ \alpha_{ij} \end{bmatrix} = \begin{bmatrix} -7.7458 \\ 8.8375 \\ 0.16294 \end{bmatrix} + \begin{bmatrix} -3.1260 & 0 & 0 \\ -1.7359 & 1.7264 & 0 \\ 0.008333 & 0.007525 & -0.01496 \end{bmatrix} \begin{bmatrix} \xi_a \\ \xi_b \\ \xi_c \end{bmatrix}$ $B_{ij} = 978.01 - 279.64A_{ij}$ <p>where ξ_a, ξ_b, and ξ_c are independent unit normal random variables.</p>	
Overall heat transfer coefficient	$U = 70 \frac{BTU}{\circ F \cdot ft^2 \cdot hr} + 430 \frac{BTU}{\circ F \cdot ft^2 \cdot hr} \times \text{Beta}(\alpha_1 = 3.14, \alpha_2 = 2.86)$	 <p>Overall heat transfer coefficient (BTU °F⁻¹ hr⁻¹ ft⁻²)</p>
Feed temperature	$T_{feed} = \text{Normal}(\mu = 95^\circ F, \sigma = 5^\circ F)$	 <p>Feed temperature (°F)</p>
Feed concentration	$C_{feed} = \text{Normal}(\mu = 1.4 \text{ wt}\%, \sigma = 0.2 \text{ wt}\%)$	 <p>Feed concentration (wt%)</p>
Concentration set point	$C_{sp} = 15 \text{ ppm} \times 10^{\text{Uniform}(-1,1)}$	 <p>Effluent concentration set point</p>
Heat exchanger area	$\text{Area}_{HX} = 3000 \text{ ft}^2 \times 3^{\text{Uniform}(-1,1)}$	 <p>Heat exchanger area (ft²)</p>

The cost correlation in Perry's handbook [11] was used to estimate the purchased equipment cost of the heat exchanger, with a correction factor designed to take into account the uncertainty in the cost correlation³²:

$$C_p(\text{Area}_{HX}) = \$21,700 \times \left(\frac{\text{Area}_{HX}}{1000 \text{ ft}^2} \right)^{0.59} \times \text{LogNormal}(\text{median} = 1, UF = 1.65) \quad (4-14)$$

A size-dependent installation cost factor was used, following the advice given in section 3.2.5. The following equation was derived based on data published in Guthrie's cost estimation book [12]:

$$\log_{10} f_{BM} = 1.5134 - 0.4974 \times \log_{10}(\text{Area}_{HX}/1 \text{ ft}^2) + 0.0641 \times [\log_{10}(\text{Area}_{HX}/1 \text{ ft}^2)]^2 \quad (4-15)$$

Finally, the distribution for the equipment-sizing annualization factor (AF) derived from data in the book by Peters & Timmerhaus was used (assuming a discount rate of 15% and a uniform distribution for the period of operation, ranging from 9 to 13 years). The uncertainty in the annualization factor was modeled using a lognormal distribution with median value 0.38 yr⁻¹ and an uncertainty factor of 1.2 (see Table 3-9 and related text). Probability density plots of the four probability distributions used in the economic valuation model are shown in Figure 4-19.

Environmental Valuation Model

As the size of the heat exchanger increases and steam consumption decreases, one would expect environmental impact to decrease due to lower fuel production and combustion requirements. An initial response to sizing a heat exchanger based on environmental criteria might then be to make it as large as feasible. There are limits to this strategy, however. As the heat exchanger area increases, the marginal amount of energy saved per incremental area decreases. At some point, the incremental energy needed to build a very large exchanger (starting with the energy needed to produce the steel sheet) will be larger than the incremental energy savings. Therefore one can expect that for very large heat exchangers the environmental impact of manufacturing the exchanger will be greater than the avoided environmental impact from raising steam.

³² The uncertainty factor was estimated using the charts published in [12]. This uncertainty factor is also consistent with the range of equipment costs obtained from several different cost correlations (see Figure 3-4)

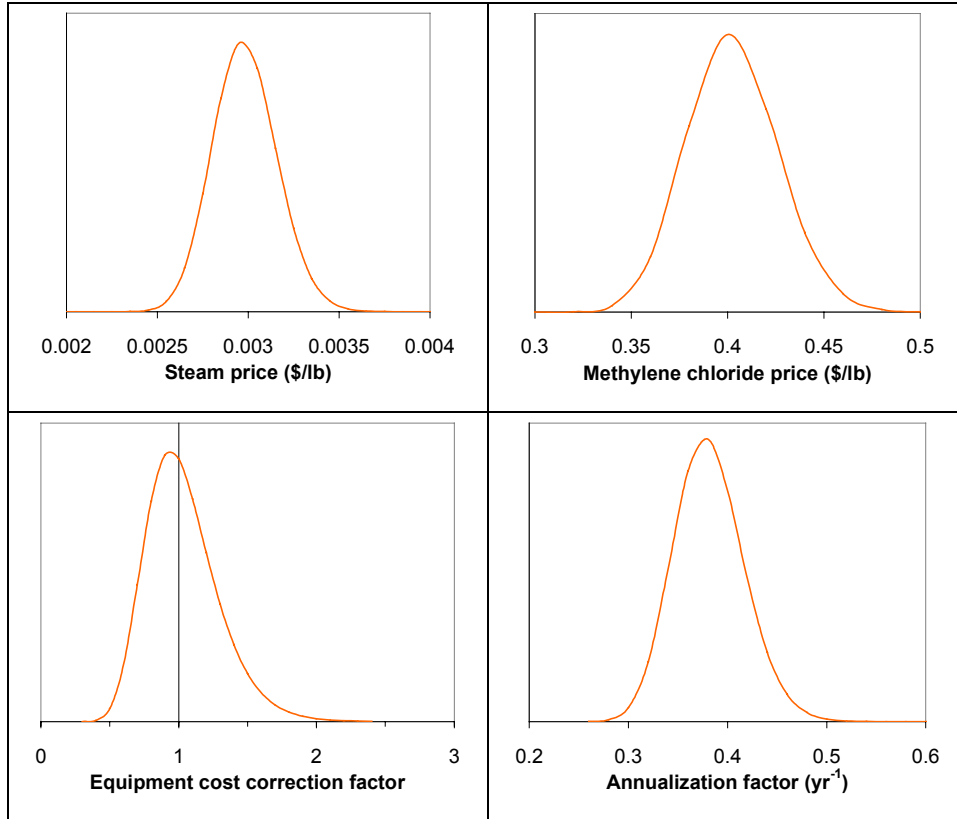


Figure 4-19: Probability distributions used in the TAC economic valuation function for the heat exchanger sizing example

For this exercise, it is assumed the most of the environmental impact of building the exchanger is due to the production of the steel sheet used in its construction. Under this assumption, the environmental valuation function used for this example is given by

$$\Omega = F_{steam} \Omega_{steam} + F_{cw} (\dot{Q}_{cond}) \Omega_{cw} + F_{CH_2Cl_2} \Omega_{CH_2Cl_2} + \frac{W_{HX} (Area_{HX}) \Omega_{steel}}{N} \quad (4-16)$$

where Ω is an annualized environmental impact indicator (in environmental load units/yr.)³³, the Ω_i are unit environmental impact indicators (calculated using the PIO-LCA method, as described in section 7.3.4), N is the number of years the process will be in operation (assumed uncertain and represented by a discrete uniform distribution with range 9 to 13 years), and W_{HX} is the weight of the heat exchanger calculated as a function of its area. Modeling the shell of the exchanger as a cylinder, W_{HX} is estimated as:

³³ An “environmental load unit” or ELU is a dollar of social cost calculated using the environmental problem valuation factors given in Table 3-16.

$$W_{HX} = \left(\pi DL + 2\pi \left(\frac{D}{2} \right)^2 \right) h_{shell} \rho_{steel} + Area_{HX} h_{tubes} \rho_{steel} \quad (4-17)$$

where D , L and h_{shell} are, respectively, the shell diameter, length, and thickness, h_{tubes} is the thickness of the tubes, and ρ_{steel} is the density of steel. The shell is assumed to have a thickness of $3/8$ in. [13], and a length of 16 ft [14]. The shell diameter is calculated as a function of the heat exchanger area by the expression [14]:

$$D = (3 \text{ ft}) \sqrt{\frac{Area_{HX}}{1100 \text{ ft}^2}} \quad (4-18)$$

A steel density of 0.2833 lb/in^3 (7.85 g/cm^3) is assumed. It is further assumed that $3/4$ in. outside diameter tubes are used. The tube wall thickness at this stage of the design is uncertain in the range 0.034-0.134 in. (0.9-3.4 mm) [11]. This uncertainty is represented by a beta distribution with parameters $\alpha_1=1.65$ and $\alpha_2=3.27$.

The copula method (see section 7.5.3) was used to generate a joint distribution of the unit environmental indicators for steam (in ELU/lb. 200 psia steam), cooling water (in ELU/m³), methylene chloride discharges (in ELU/lb.), and steel sheet (in ELU/lb.). The marginal distributions used are:

$$\log_{10} \Omega_{steam} = -3.38 + 4.07 \times \text{Beta}(\alpha_1 = 5.19, \alpha_2 = 12.19) \quad (4-19)$$

$$\log_{10} \Omega_{cw} = \text{Normal}(\mu = -1.64, \sigma = 0.47) \quad (4-20)$$

$$\log_{10} \Omega_{CH_2Cl_2} = -1.44 + \text{Gamma}(\alpha = 7.21, \beta = 0.17) \quad (4-21)$$

$$\log_{10} \Omega_{steel} = -1.27 + \text{Erlang}(m = 6, \beta = 0.20) \quad (4-22)$$

The joint distribution of unit environmental indicators is generated by combining the marginal distributions listed above with the following rank correlation matrix:

	Ω_{steam}	Ω_{cw}	$\Omega_{CH_2Cl_2}$	Ω_{steel}
Ω_{steam}	1	0.68	0.66	0.62
Ω_{cw}	0.68	1	0.68	0.80
$\Omega_{CH_2Cl_2}$	0.66	0.68	1	0.66
Ω_{steel}	0.62	0.80	0.66	1

Probability density plots for all of the distributions used in the environmental valuation function (eq (4-16)) are shown in Figure 4-20. Note the wide range (between 2 and 3 orders of magnitude) spanned by the distributions for unit environmental impacts.

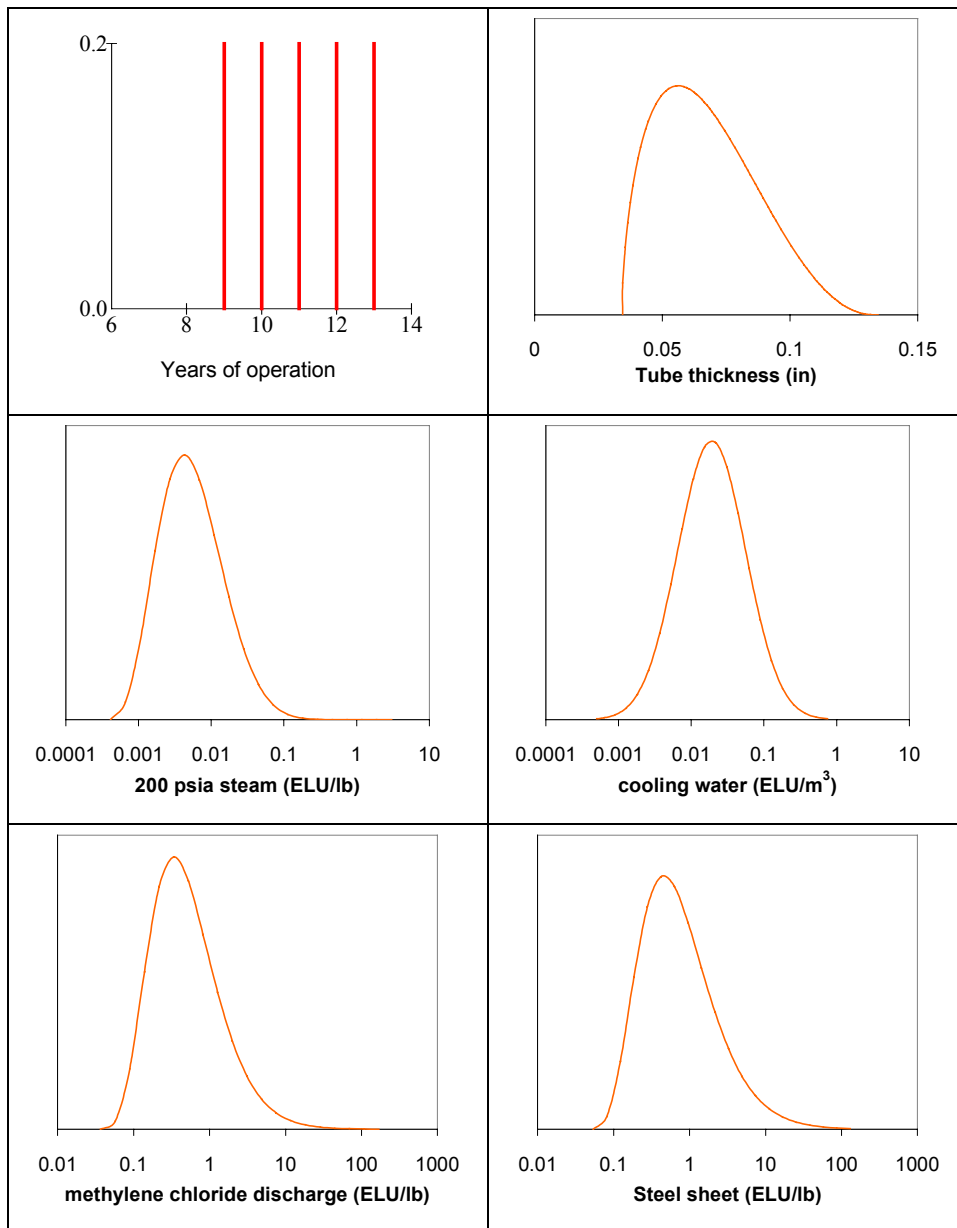


Figure 4-20: Probability distributions used in the environmental valuation function for the heat exchanger sizing

Propagation of Uncertainty

In order to preserve the correlations among the valuation distributions for the various design alternatives, both valuation models were incorporated in the spreadsheet containing the process metamodel. Process-inherent uncertainties are addressed by integrating over the

different realizations of the uncertainty in feed flow and concentration³⁴. For example, the average TAC for each realization of the model-inherent (\mathbf{x}_m) and valuation model uncertainties (\mathbf{x}_v) and each value of the decision variable $Area_{HX}$ is calculated as:

$$TAC_{ave}(\mathbf{x}_m, \mathbf{x}_v, Area_{HX}) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} TAC(\mathbf{x}_m, \mathbf{x}_v, T_{feed}, C_{feed}, Area_{HX}) f(T_{feed}) f(C_{feed}) dT_{feed} dC_{feed} \quad (4-23)$$

where $f(T_{feed})$ and $f(C_{feed})$ are the probability density functions for the feed temperature and the feed methylene chloride concentration, respectively.

Nested Monte Carlo simulations are avoided through the use of the Gaussian quadrature method to perform the integration [15]:

$$TAC_{ave}(\mathbf{x}_m, \mathbf{x}_v, Area_{HX}) \cong \sum_{i=1}^N \sum_{j=1}^N TAC(\mathbf{x}_m, \mathbf{x}_v, T_{feed,i}, C_{feed,j}, Area_{HX}) w_{ij} \quad (4-24)$$

For each realization the model-inherent and valuation model uncertainties, the TAC model is evaluated N^2 times for different discrete values of T_{feed} and C_{feed} . The matrix below shows the values used and the weights (w_{ij}) assigned to each combination of values (3 quadrature points per process variable were used)³⁵:

		C_{feed}		
		1.05wt%	1.40 wt%	1.75 wt%
T_{feed}	86.3 °F	0.027778	0.111111	0.027778
	95.0 °F	0.111111	0.444444	0.111111
	103.7 °F	0.027778	0.111111	0.027778

The same procedure is used to calculate average environmental impact indicators as a function of the decision and uncertain variables.

Distributions for the following indicators are calculated through Monte Carlo Simulation:

- $TAC_{ave}(Area_{HX})$
- $\Omega_{ave}(Area_{HX})$

³⁴ See the discussion in section 4.2, under the heading Process-inherent uncertainty.

³⁵ The weight values were obtained from the tables in reference [15]. Tables of weight values can also be found in [16,17].

- $\frac{TAC_{ave}(Area_{HX})}{TAC_{ave}(3500\text{ft}^2)}$
- $\frac{\Omega_{ave}(Area_{HX})}{\Omega_{ave}(3500\text{ft}^2)}$

A heat exchanger area of 3500 ft² was chosen as the base case design, based on the results of the example in section 3.2.5. It is crucial that the same realization of the uncertain process and valuation parameters be used for the evaluation of the numerator and denominator in the relative measures of performance in order to preserve the correlation among the valuations for the alternatives and the base case design. Propagation of uncertainties was carried out using Microsoft Excel (version 97 SR-1) with the @Risk add-on (version 3.5, Palisade Corporation) on a personal computer with a Pentium II processor.

RESULTS

Sizing according to economic criteria

Figure 4-21 shows the distributions for the total annualized cost (TAC) of several different heat exchanger size alternatives obtained by propagating uncertainties through the process and economic valuation models. The plot shows the median value as well as the 5th, 25th, 75th, and 95th percentile values. Due mostly to the uncertainty in the thermodynamic parameters (see Chapter 5 for a full sensitivity analysis), there is considerable uncertainty in the amount of steam required to meet the effluent concentration set point. This translates directly into uncertainty in annual steam costs, and thus in total annualized cost. An examination of Figure 4-21 would suggest that there is very little difference in economic performance for heat exchanger sizes in the range 1000 to 8000 ft². Faced with this information, designers would be inclined to specify the lowest heat exchanger size (1000 ft²), since it has the lowest capital cost. This conclusion would be wrong, as demonstrated in Figure 4-22, where the uncertainty in the ratio of the TAC of each alternative to the TAC of the 3500 ft² base case alternative is shown. The high degree of correlation in TAC among the various alternatives allows one to say with more than 85% confidence that the 3500 ft² alternative is cheaper than the 1000 ft² alternative. One might be uncertain about what the actual TAC will be, but one knows that the 1000 ft² alternative will cost between 1.8% less and 12.3% more than the 3500 ft² alternative (90%

confidence interval), depending on how the uncertainties are resolved. It can also be said with more than 75% confidence that sizes lower than 1800 ft² or larger than 3700 ft² would be more costly than the base case alternative. Accepting the base case alternative as the economic optimum, the statement above defines the 75% confidence interval around the optimum. Expected TAC minimization would have yielded 2900 ft² as the optimum size for the heat exchanger, but would not have given any information regarding the confidence interval around the optimum. As Figure 4-23 shows, the 2900 ft² alternative is indeed better on average than the 3500 ft² alternative, but the difference is very small (within 1% in most cases). Designers interested in such small differences could carry out an additional Monte Carlo simulation choosing 2900 ft² as the new base case to refine the confidence interval around the economic optimum.

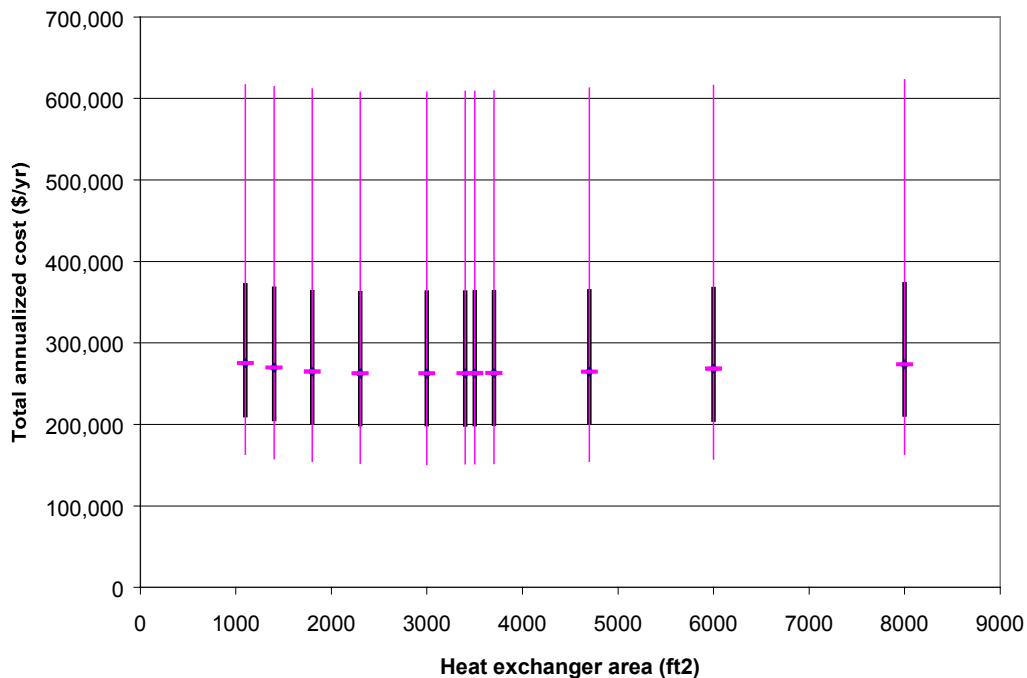


Figure 4-21: Total annualized cost distributions for the heat exchanger sizing example

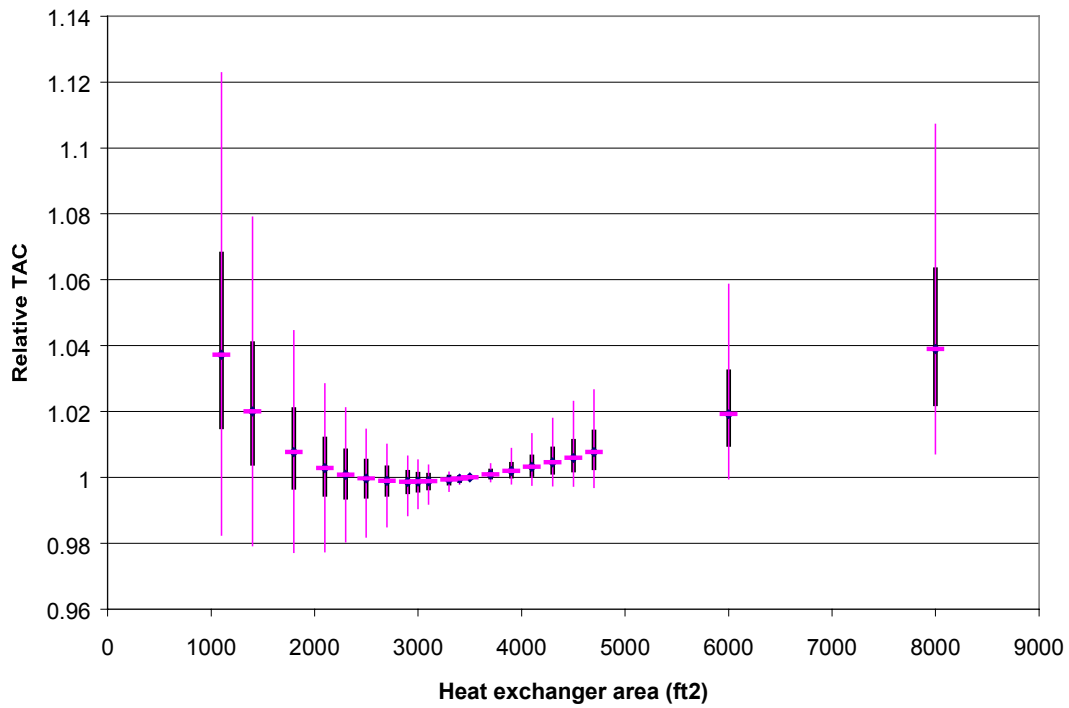


Figure 4-22: Relative total annualized cost distributions for the heat exchanger sizing example

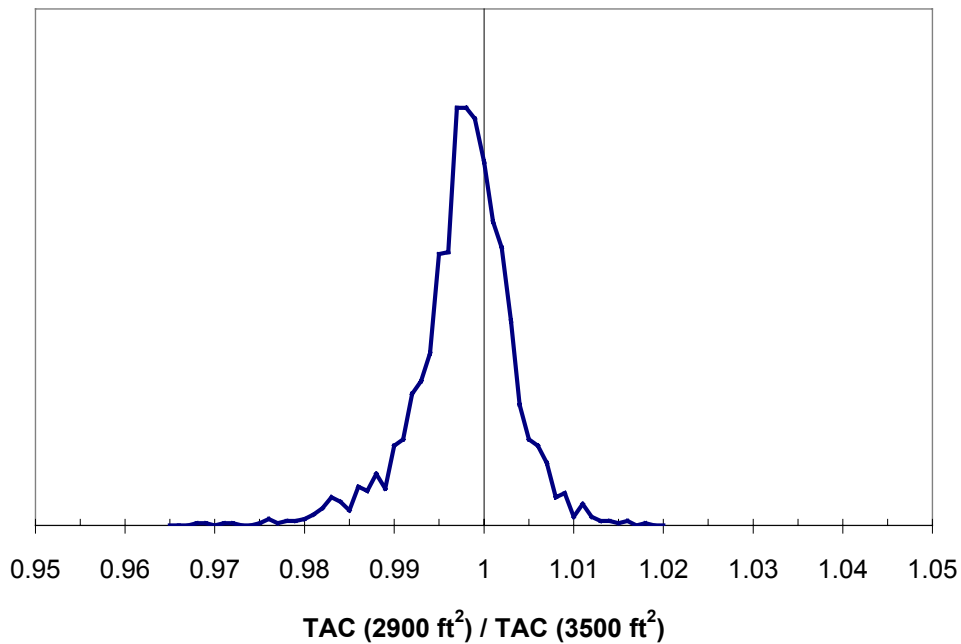


Figure 4-23: Probability density plot for the TAC of the 2900 ft² alternative relative to the 3500 ft² base case alternative

Sizing according to environmental impact criteria

Propagating the uncertainty in the absolute indicator of environmental performance yields very little information, as shown in Figure 4-24. The 90% confidence interval around the median indicator for each of the alternatives spans more than one order of magnitude (note that the scale for the y-axis in this figure is logarithmic, while the scale for the y-axis in Figure 4-21 was linear). A plot of the distribution of the ratio of the environmental indicator for each alternative to the environmental indicator for the base case alternative (3500 ft²) yields much more information, as shown in Figure 4-25. One can be more than 75% confident that decreasing the heat exchanger size to 3000 ft² or below will cause more environmental impact, while there is more than a 75% chance that increasing the size of the exchanger would improve environmental performance.

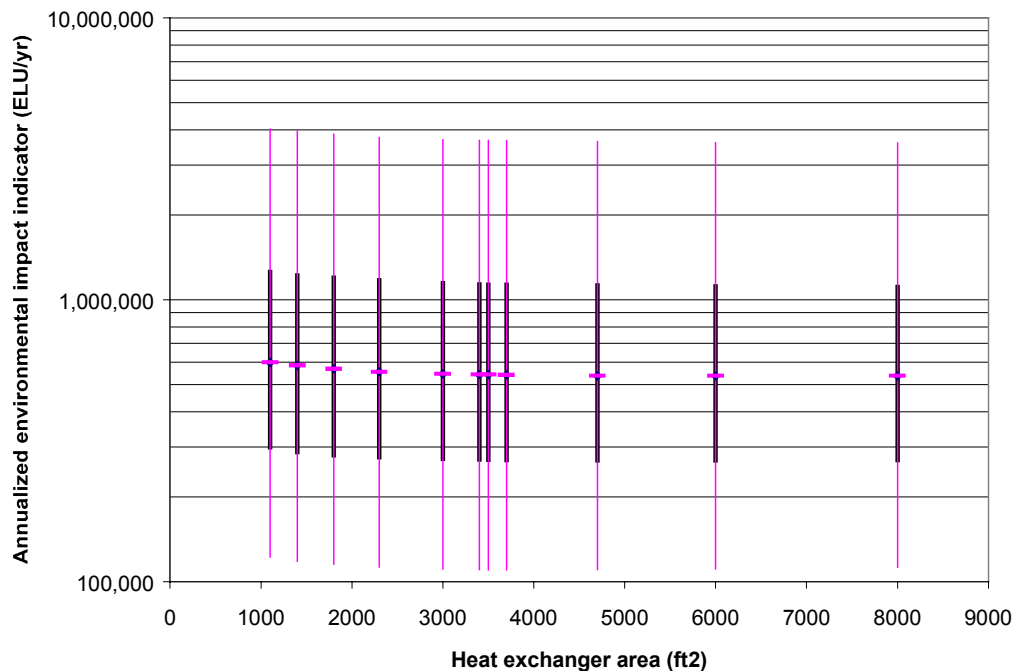


Figure 4-24: Environmental impact indicator distributions for the heat exchanger sizing example

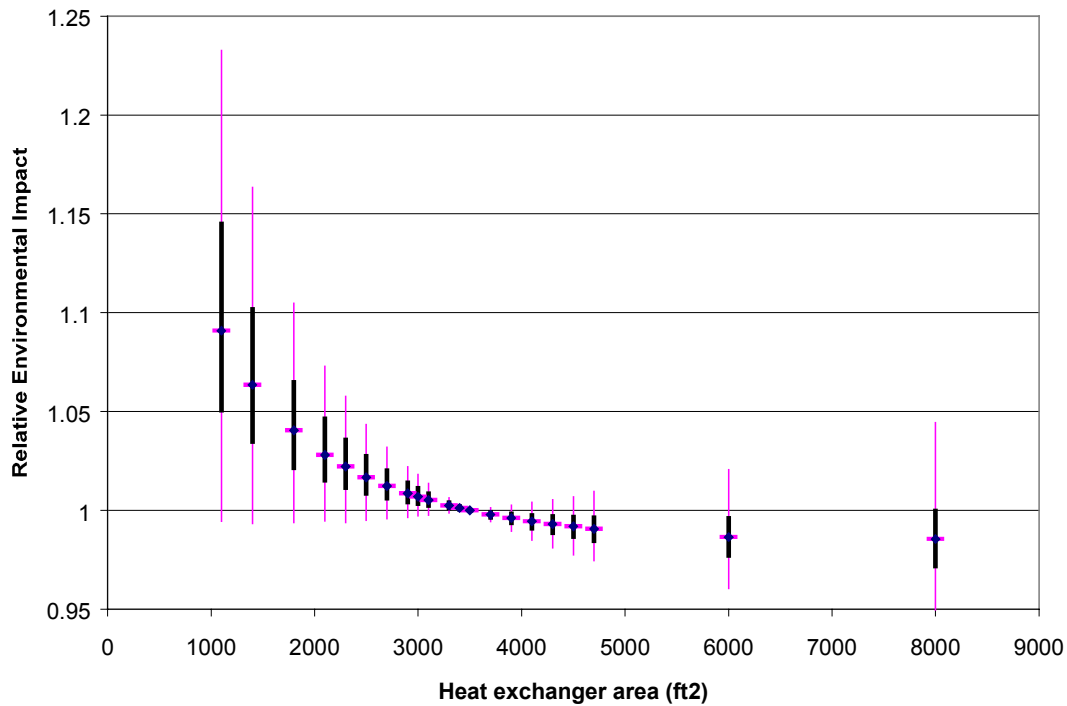


Figure 4-25: Relative environmental impact distributions for the heat exchanger sizing example

Sizing according to a compromise between economic and environmental impact criteria

Figure 4-26 shows a plot of the distribution of relative environmental impact vs. the distribution of relative TAC for a subset of the alternatives considered. Based on this diagram, one can see that the 2500 ft² alternative is an inferior alternative, since even though it has only an approximately even chance of having lower cost, it has more than a 90% chance of having worse environmental impact. The alternatives with areas of 2900 and 3100 ft² have more than an even chance of having lower annualized costs than the base alternative. Of these two, the 3100 ft² has the best distribution of relative impact, although its probability of exceeding the environmental impact of the base case alternative is more than 90%. Alternatives with sizes in the range 3400 ft² to 3700 ft² can barely be distinguished from one another. The 4500 ft² alternative has an 85% chance of having lower impact, but it also has an 85% chance of having higher cost. In this case, a tradeoff exists, and it is up to the design team to decide whether the additional expense is justified. Using the utility function introduced in section 4.6.3 with $\alpha=0.1$ yields a negative utility for the switch from the 3500 ft² to the 4500 ft² alternative. In other words, since

$$E\left[-(1-\alpha)\ln\left(\frac{TAC^{4500}}{TAC^{3500}}\right)-\alpha\ln\left(\frac{\Omega^{4500}}{\Omega^{3500}}\right)\right] < 0 \quad (4-25)$$

it may be concluded that the base alternative (the 3500 ft² alternative) would be preferred to the 4500 ft² alternative by designers whose willingness to make tradeoffs between relative measures of economic and environmental performance is well characterized by eq (4-8) with an α value of 0.1.

The maximum utility relative to the 3500 ft² base case among the alternatives considered is obtained for a heat exchanger size of 3100 ft². Giving equal weight to both criteria (that is, choosing $\alpha=0.5$), shifts the optimum size to 4100 ft². It is doubtful that a private company would every use higher α values. This indicates that the exchanger size that had been obtained in Chapter 3 without considering uncertainty is in fact close to optimal. Consideration of uncertainties would allow a designer to be quite confident about the decision, despite the considerable uncertainties faced at the conceptual stage of design.

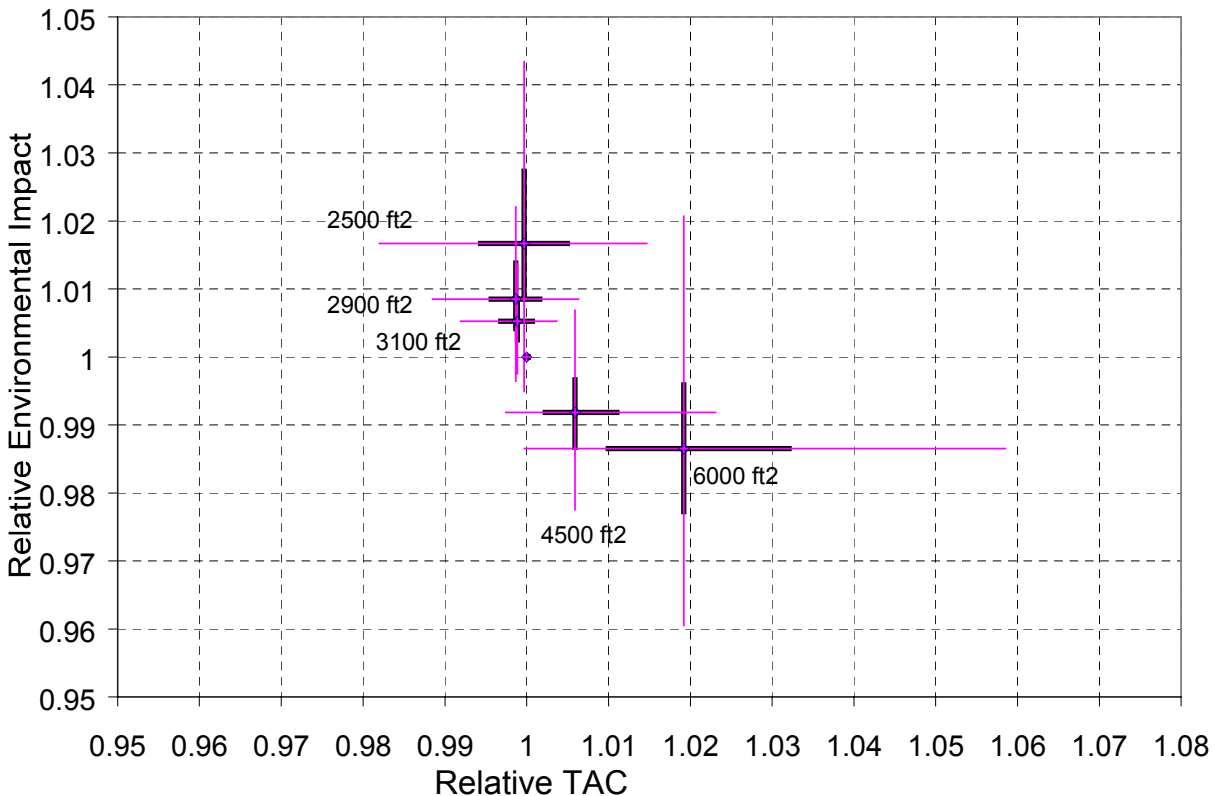


Figure 4-26: Relative environmental impact vs. relative total annualized cost for a subset of the alternatives considered in the heat exchanger sizing example

4.8 Conclusion

The key contribution made in this chapter is the idea of using relative measures of performance as a means to decrease the uncertainty in decision-making in the presence of large uncertainties in system and valuation models. The method works particularly well when parameters with large uncertainties have a strong influence in the absolute measures of performance of the alternatives one is interested in comparing.

4.9 Literature Cited

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Chapter 5 Sensitivity Analysis

5.1 Introduction

The previous chapter solved the problem of discriminating among design alternatives in the presence of large uncertainties. Finding the best alternative in a set is only one element of the design cycle. As reviewed in Chapter 2, design is an iterative activity. Design teams usually undertake several iterations in the design cycle. Before returning to the beginning of the design cycle, the results obtained at the evaluation stage must be examined to identify improvement opportunities. Having identified the process features that contribute the most to the different indicators used in its evaluation, design teams can use the alternative generation tools at their disposal to address the critical design features. At this stage it is also important to prioritize data collection efforts, so that resources are invested in obtaining the information that will contribute the most to reducing uncertainty in the key design decisions.

5.2 Identification of improvement opportunities

In order to improve the environmental performance of a design, it is necessary to identify the features of the design that are the main drivers of its environmental impact. Thus, the calculation of an environmental valuation metric is not very useful unless the results can be presented in a way that allows the design team to set priorities for further design work. Examples of sensitivity analysis tools used to identify pollution prevention opportunities in process design include the mass loss index (MLI) developed by Heinzle & Hungerbühler [1] and the mass-based pollution index developed by Hilaly & Sikdar as part of their waste reduction algorithm (WAR) [2,3].

In the MLI procedure, the mass of all non-product streams leaving a process are allocated to their cause. Causes of mass inefficiencies include stoichiometric formation of byproducts in desired reactions, incomplete conversion, selectivity losses, purification losses, impurities contained in substrates, and losses of solvents, catalysts and other auxiliary materials not recycled with 100% efficiency. By weighting individual streams by their cost or by a relative measure of environmental impact, those causes of mass inefficiency with the greatest cost or

potential ecological impact can be identified. The design team would focus their attention on reducing those sources of inefficiency in the next iteration.

In the WAR algorithm, pollution indices (measures of the mass of pollutants released per mass of product produced) are calculated for the whole process and for individual streams. Unit operations directly upstream from high pollution index streams are targeted for modification. In their papers, Hilaly & Sikdar are reluctant to include environmental impact metrics as a weighting factor in their mass-based indices. Specifically, they do not recommend including toxicity because “the toxicity of a compound cannot be quantified in terms of a unique numeric value” [3]. Although toxicity indicators are indeed uncertain, this does not mean that they do not contain information or that they can not be used for sensitivity analysis. In this subsection an approach is presented to increase the information content of sensitivity analysis using uncertain indicators.

Despite the large uncertainty in the absolute value of the overall environmental impact indicator for a design, the uncertainty in the contribution of individual design features to the overall indicator might be significantly lower. The reason for this is that in most situations the uncertainty in the indicator for the whole is highly correlated with the uncertainty in the indicator for the most important parts. Following the correlation-structure preservation principles introduced in section 4.4, it is recommended that sensitivity analysis be performed through the propagation of uncertainty in contribution ratios.

Consider an environmental valuation model written in terms of the process inputs (e.g. raw materials, utilities) and non-product outputs (e.g. waste streams):

$$\Omega = \sum_{i \in \text{Inputs}} \Omega_i \dot{I}_i + \sum_{j \in \text{Outputs}} \Omega_j \dot{O}_j \quad (5-1)$$

where \dot{I}_i is consumption rate of input i , \dot{O}_j is generation rate of input j , the Ω_i and Ω_j are the environmental impact indicators per unit of input and per unit of output, respectively, and Ω is the indicator for the whole process.

As seen in the examples of Chapter 4, the uncertainty in an indicator such as the one given in eq (5-1) may span more than an order of magnitude. Sensitivity analysis would be performed by propagation of the uncertainty in the ratios

$$f_{\text{impact},i} = \frac{\Omega_i \dot{I}_i}{\sum_{i \in \text{Inputs}} \Omega_i \dot{I}_i + \sum_{j \in \text{Outputs}} \Omega_j \dot{O}_j} \quad (5-2)$$

and

$$f_{\text{impact},j} = \frac{\Omega_j \dot{O}_j}{\sum_{i \in \text{Inputs}} \Omega_i \dot{I}_i + \sum_{j \in \text{Outputs}} \Omega_j \dot{O}_j} \quad (5-3)$$

where the same random variable realizations used to compute the numerator are used in the corresponding expression of the denominator. Examples of distributions for the above quantities obtained through Monte Carlo simulation are shown in the examples at the end of this section.

The procedure here is quite general and can be applied to any valuation model with uncertain parameters. As was shown in section 3.2.4 there are significant uncertainties associated with the economic valuation models used at the conceptual stage of design. It could even be applied to Hilaly & Sikdar's pollution indices, since even mass-based indicators will be uncertain at the conceptual design stage due to uncertainties in process model parameters.

5.3 Uncertainty analysis

5.3.1 Introduction

The term *uncertainty analysis* has been defined as the collection of methods used for comparing the importance of the input uncertainties in terms of their relative contributions to uncertainty in the outputs [4]. The related term *uncertainty propagation* is given to the collection of methods used to calculate the uncertainty in the model outputs induced by the uncertainties in its inputs. All of the techniques introduced thus far in Chapter 4 and section 5.2 are instances of uncertainty propagation. This section describes the use of uncertainty analysis techniques in the context of environmentally conscious chemical process design.

It is extremely useful to be able to identify the input parameter distributions that are responsible for most of the uncertainty in an output variable of interest. Having identified those parameters, resources could be invested to reduce their uncertainty (e.g. by performing experiments, or by making more careful valuation assessments), thereby reducing the uncertainty in the quantities on the basis of which decisions must be made (these include the relative measures of performance introduced in Chapter 4).

5.3.2 Variance contribution methods

In the case of an output variable that is the sum of normally distributed random variables, an exact determination of the contribution of the variance of each input variable to the variance of the output variable can be made analytically. Consider the following model:

$$y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 \quad (5-4)$$

where the x_i are normally distributed random variables with mean μ_i and standard deviation σ_i , and the a_i are model constants.

Under the assumptions stated above, the uncertainty in the output variable y is given by a normal distribution with parameters

$$\mu_y = a_0 + a_1\mu_1 + a_2\mu_2 + a_3\mu_3 \quad (5-5)$$

and

$$\sigma_y = \sqrt{a_1^2\sigma_1^2 + a_2^2\sigma_2^2 + a_3^2\sigma_3^2 + 2a_1a_2\sigma_{12} + 2a_1a_3\sigma_{13} + 2a_2a_3\sigma_{23}} \quad (5-6)$$

where σ_{ij} is the covariance between x_i and x_j .

In the case that x_1 , x_2 , and x_3 are mutually independent, their covariances are all equal to zero. In that case, the attribution of variance contributions is straightforward:

$$f_{\text{var},i} = \frac{a_i^2\sigma_i^2}{\sigma_y^2} \quad (5-7)$$

where $f_{\text{var},i}$ is the fraction of the variance contributed by variable x_i .

In the case of correlated variables, the allocation of the covariance term contributions to the variance contribution of each variable is split (somewhat arbitrarily) according to the contribution of the variance terms [5]. For example, the variance contribution attributed to variable x_1 would be:

$$f_{\text{var},1} = \frac{a_1^2\sigma_1^2 + \frac{2a_1a_2\sigma_{12}}{a_1^2\sigma_1^2 + a_2^2\sigma_2^2} + \frac{2a_1a_3\sigma_{13}}{a_1^2\sigma_1^2 + a_3^2\sigma_3^2}}{\sigma_y^2} \quad (5-8)$$

A similar derivation can be obtained for the case of models where the output variable is the product of powers of lognormally distributed input variables.

For other combinations of model structure and probability distributions, analytical expressions for the variance contribution are not as easy to obtain. One way to circumvent this

difficulty is to use the deterministic equivalent modeling method (DEMM). DEMM uses orthogonal polynomial chaos expansions (i.e. series expansions written in terms of polynomials of random variables) to approximate the distribution of an output variable [6,7]. A principal advantage of the method is that the variance contribution of each input variable can be directly estimated using the coefficients of the expansion. A disadvantage of the method from the perspective of this thesis is that its current implementation is not compatible with spreadsheet models that have hundreds of uncertain inputs, such as the environmental valuation models presented in section 6.3 and Chapter 7³⁶. For this reason, this section focuses on uncertainty analysis techniques that can be applied to the outputs of Monte Carlo simulations involving a large number of inputs.

5.3.3 Correlation methods

Correlation measures are used to evaluate the degree of association between pairs of random variables. By tradition, a measure of correlation between the variables X and Y must fulfill the following requirements [8]:

1. The correlation measure should take only values between -1 and $+1$
2. If the larger values of X tend to be observed at the same time that the large values of Y are observed, then the measure of correlation should be positive and close to $+1$ if the tendency is strong.
3. If larger values of X tend to be observed when small values of Y are observed, then the measure of correlation should be negative and close to -1 if the tendency is strong.
4. If values of X and Y are independent (i.e. if their variations are random with respect to one another) the measure of correlation should be close to 0 .

The most commonly used measure of correlation is Pearson's product moment correlation coefficient, also known as the linear correlation coefficient:

³⁶ The method is used for other purposes in this work (i.e. to generate polynomial chaos expansion models of flowsheet process models, as discussed in section 8.2).

$$r = \frac{\sum_{i=1}^n (X_i - \bar{X})(Y_i - \bar{Y})}{\left[\sum_{i=1}^n (X_i - \bar{X})^2 \sum_{i=1}^n (Y_i - \bar{Y})^2 \right]^{1/2}} \quad (5-9)$$

If the outputs of a Monte Carlo simulation are available in an electronic spreadsheet, then the Excel function CORREL(array1,array2) can be used to calculate r .

The Pearson correlation coefficient is a measure of the strength of the *linear* association between X and Y . A value of close to $r=0$ does not necessarily imply that two random variables are independent, but rather that their association, if one exists, is not linear.

Consider, for example, the model given by

$$y = 10^{x_1} + x_2 \quad (5-10)$$

where x_1 and x_2 are two independent random variables with parameters $(\mu_1=1, \sigma_1=2)$ and $(\mu_1=1, \sigma_1=0.1)^{37}$. The results of a Monte Carlo simulation of eq (5-10) with 1,000 iterations are shown in Figure 5-1. It is obvious from this chart (note the logarithmic y-axis) that most of the uncertainty in the value of y comes from the uncertainty in the value of x_1 . The degree of linear association is very weak, however, with a Pearson correlation coefficient of 0.236.

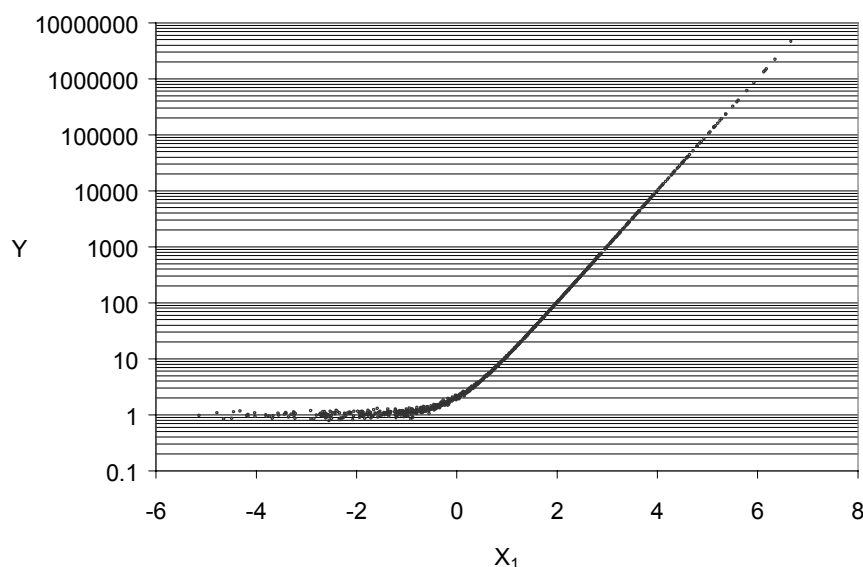


Figure 5-1: Scatter plot of 1000 pairs (X_1, Y) from the model defined in eq (5-10)

³⁷ This functional form appears frequently in environmental valuation models, since many parameters are typically described by lognormal distributions

A more robust measure of the degree of association between two random variables is the Spearman rank correlation coefficient (ρ), which is the Pearson product moment correlation coefficient applied to the sample ranks instead of being applied to the sample values [9]:

$$\rho = \frac{\sum_{i=1}^n \left(\text{rank}(x_i) - \frac{n+1}{2} \right) \left(\text{rank}(y_i) - \frac{n+1}{2} \right)}{\frac{n(n+1)(n-1)}{12}} \quad (5-11)$$

The rank correlation coefficient is a good indicator of dependence when the relationship between factors is monotonically increasing (positive coefficients) or decreasing (negative coefficients). In the example above, the rank correlation coefficient calculated between y and x_1 was 0.994. The rank correlation coefficient will still fail to detect strong associations that are not monotonic (e.g. $y = x^2$ when x is a normally distributed random variable with mean equal to zero)³⁸. In Microsoft Excel, the calculation of rank correlation coefficients is done in two steps. First, arrays of ranks are created by using the function `rank(cell ref, array ref)`. This is followed by the application of the `correl` function as explained before. The @Risk Monte Carlo simulation add-on for Excel³⁹ has the option of calculating rank correlation coefficients between each of the outputs and each of the inputs used in a simulation.

The Spearman rank correlation coefficient can be used as a test statistic to test for independence between two random variables. When the sample size (n) is large (as in Monte Carlo simulation), the p th quantile of ρ is given approximately by [8]:

$$w_p = \frac{\Phi^{-1}(p)}{\sqrt{n-1}} \quad (5-12)$$

where $\Phi^{-1}(p)$ is the inverse of the standard normal distribution evaluated at p ⁴⁰.

The property above can be used to test for independence between two random variables. For a two-tailed test, the hypotheses take the following form [8]:

³⁸ This is not anticipated to be a problem in environmental valuation models, as they consist mostly of sums of products of positive random variables.

³⁹ Palisade corporation, www.palisade.com

⁴⁰ For example, $\Phi^{-1}(0.9725) = 1.96$

H_0 : The X_i and Y_i are mutually independent

H_1 : Either (a) there is a tendency for the larger values of X to be paired with the larger values of Y , or (b) there is a tendency for the smaller values of X to be paired with the larger values of Y .

H_0 is rejected at the level α (e.g. at $\alpha=0.05$ corresponding to 95% confidence) if the absolute value of ρ is greater than the value of w_p given by eq (5-12) evaluated at $p = 1 - \alpha/2$. (e.g. evaluated at $p = 0.975$). For a Monte Carlo simulation with 2000 iterations, the absolute value of the correlation coefficient would have to be lower than $1.96/(2000-1)^{0.5} = 0.0438$ for the independence hypothesis to be accepted with more than 95% confidence. In spreadsheet models with hundreds of uncertain parameters, such as those employed in this work, the test above provides with a useful tool to screen out parameters that do not materially contribute to the uncertainty in a decision. In situations where the model size gets close to limitations in hardware or time available for analysis, this screening tool allows the analyst to remove uncertainty distributions that are unimportant.

Care must be taken with the interpretation of rank correlation coefficients for the case of correlated input variables. There can be situations where two input variables are strongly correlated, with one of them contributing strongly to the uncertainty in the output variable, while the other has only marginal importance. The rank correlation coefficient uncertainty analysis method will give large values of Pearson's ρ for both input variables.

As an example, consider the model given in eq. (5-4) with the following parameters:

<i>Variable</i>	a_i	μ_i	covariance matrix		
			x_1	x_2	x_3
x_1	1	0	x_1 100	x_2 0	x_3 8
x_2	1	0	x_2 0	x_2 10	x_3 0
x_3	1	0	x_3 8	x_3 0	x_3 1

Uncertainty analysis results are given in Table 5-1. The contribution of the variance in variable x_3 to the variance in y is negligible (less than 1%), and yet the value of its rank correlation coefficient is high, due to the high degree of correlation between x_1 and x_3 .

Table 5-1: Uncertainty analysis results for the example with correlated uncertain inputs

<i>Variable</i>	<i>Variance contribution</i>	<i>Spearman rank correlation coefficient</i>
x_1	91.2%	+0.95
x_2	7.9%	+0.26
x_3	0.9%	+0.78

Partial correlation and step-wise regression methods can be used to filter out inputs that do not have large contributions to the output uncertainty but are strongly correlated with inputs that do have significant contributions [8,9]. The step-wise linear regression method is available in @Risk. A partial rank correlation method is not yet available in that package.

5.4 Example: Retrofit of a solvent recovery system

5.4.1 Original process

This example is a continuation of the example introduced in section 4.7.1. The process flowsheet from that section is reproduced here as Figure 5-2. The problem originally posed was the identification of the best concentration set point for the operation of the process. Sensitivity analysis is applied in this section to two set point candidates: the economically optimum concentration set point, found in section 4.7.1 to be 25 ppm, and a 2 ppm limit that the local environmental permitting authorities have set for the process effluent.

It had been found in section 4.7.1 that, despite the large uncertainty in the environmental impact indicator (more than an order of magnitude, see Figure 4-13), it was possible to conclude with more than 95% confidence that operating the process at the lower concentration limit would have more serious environmental consequences than operating it at the economically optimum set point.

The results of the sensitivity analysis performed on both alternatives is shown in Figure 5-3. Despite the large uncertainties in the unit environmental indicators used in the example, there is virtually no uncertainty in the conclusion that at either set point the overwhelming majority of the environmental impacts are due to steam generation and not to the release of small quantities of methylene chloride. For the 25 ppm case, the 90% confidence interval for the contribution of steam to the total environmental impact indicator is given by the range 92.1 to

99.9%, while the 90% confidence interval for the steam contribution in the 2 ppm case is 99.1% to 99.9%.

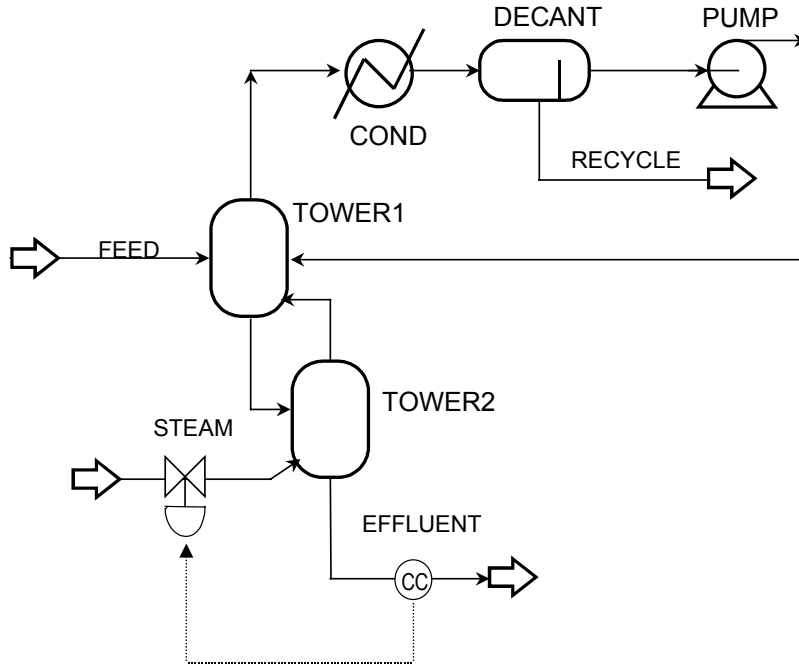


Figure 5-2: Flowsheet for the concentration set point selection example

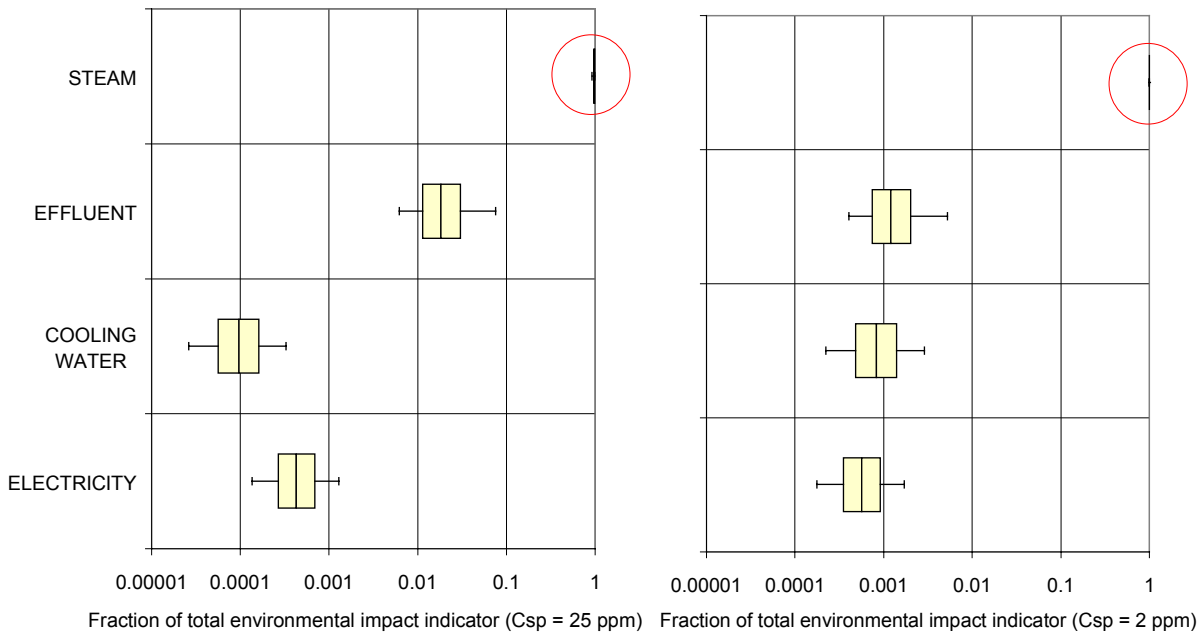


Figure 5-3: Distributions for the contribution of process inputs and process outputs to the environmental impact indicator for two different effluent concentration set points.

These results aid in the interpretation of the relative impact distributions shown in Figure 4-16. At low effluent concentration set points, most of the impact of both the reference and the alternative operation policies is contributed by steam. Thus in the expression

$$\frac{\Omega^{alt}}{\Omega^{bc}} = \frac{F_{steam}^{alt} \Omega_{steam} + F_{CH_2Cl_2}^{alt} \Omega_{CH_2Cl_2} + \dots}{F_{steam}^{bc} \Omega_{steam} + F_{CH_2Cl_2}^{bc} \Omega_{CH_2Cl_2} + \dots} \quad (5-13)$$

the first term in both the numerator and the denominator tends to dominate, and the environmental impact ratio is mostly the ratio of steam consumption of the alternative operation policy to the base case operation policy, yielding relatively narrow distributions for the relative impact indicator. As the concentration set point is increased, the relative importance of the second term in the numerator increases, and thus one obtains relatively broad distributions, as shown on the right hand side of Figure 4-16. It is clear from the sensitivity analysis that the main source of environmental impact is related to the raising of steam. These results can be used to negotiate with regulators an increase in the effluent concentration limit from 2 ppm to 25 ppm in exchange for making an investment to reduce steam consumption (for example, by installing a heat exchanger). The examples in sections 3.2.5 and 4.7.2 showed that the installation of a heat exchanger not only would reduce environmental impact but would also decrease overall costs.

5.4.2 Process with heat exchanger

In this example sensitivity and uncertainty analysis are applied to the example previously described in section 4.7.2. The flowsheet for that example is reproduced here as Figure 5-4⁴¹. The problem posed was the determination of the optimum size for a heat exchanger to be retrofitted to the solvent recovery process. Uncertainties in the example included physical uncertainties (thermodynamic parameters and heat transfer coefficient), economic valuation factors, and environmental valuation factors. The 90% confidence interval for total annualized cost (TAC) spanned a factor of roughly 3, while the uncertainty in the environmental impact indicator was an order of magnitude higher.

⁴¹ The reader should refer back to section 4.7.2 for details regarding the problem statement, process model, valuation models, and uncertainties.

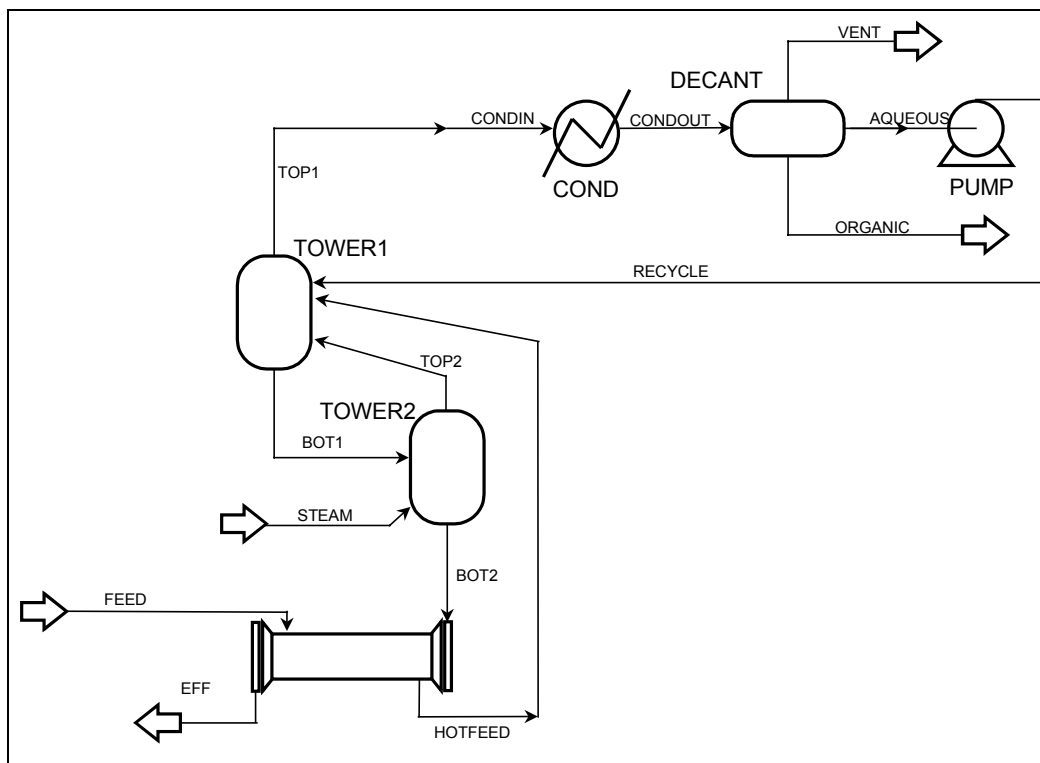


Figure 5-4: Flowsheet for the heat exchanger sizing example

SENSITIVITY ANALYSIS RESULTS

Figure 5-5 shows distributions for the contributions of steam consumption, cooling water use, heat exchanger procurement, and methylene chloride losses to the total annualized cost and environmental impact indicator valuation models used for this example. Despite the uncertainty it is clear that the largest contribution to both measures comes from steam consumption. Process designers should look for further ideas to decrease the amount of energy required to effect the recovery. One such idea (the use of a stripping column instead of two flash drums) is examined in the last example of this section.

It is interesting to note that the ranking of contributions with respect to the economic objective is not the same as the one with respect to the environmental objective. The impact of building the heat exchanger (estimated from the impact of all the processes involved in the manufacture of the required amount of steel sheet, starting with the extraction of fuels and raw materials) is minor compared to the environmental impact of the process input and output streams. From an economic perspective, however, the annualized cost of purchasing, installing, and maintaining the heat exchanger has a significant contribution to overall costs. In section

4.7.2 it was determined that a heat exchanger with an area of 2,900 ft² would minimize expected annualized cost. It was also found that environmental impact was likely to decrease as heat exchanger size increased.

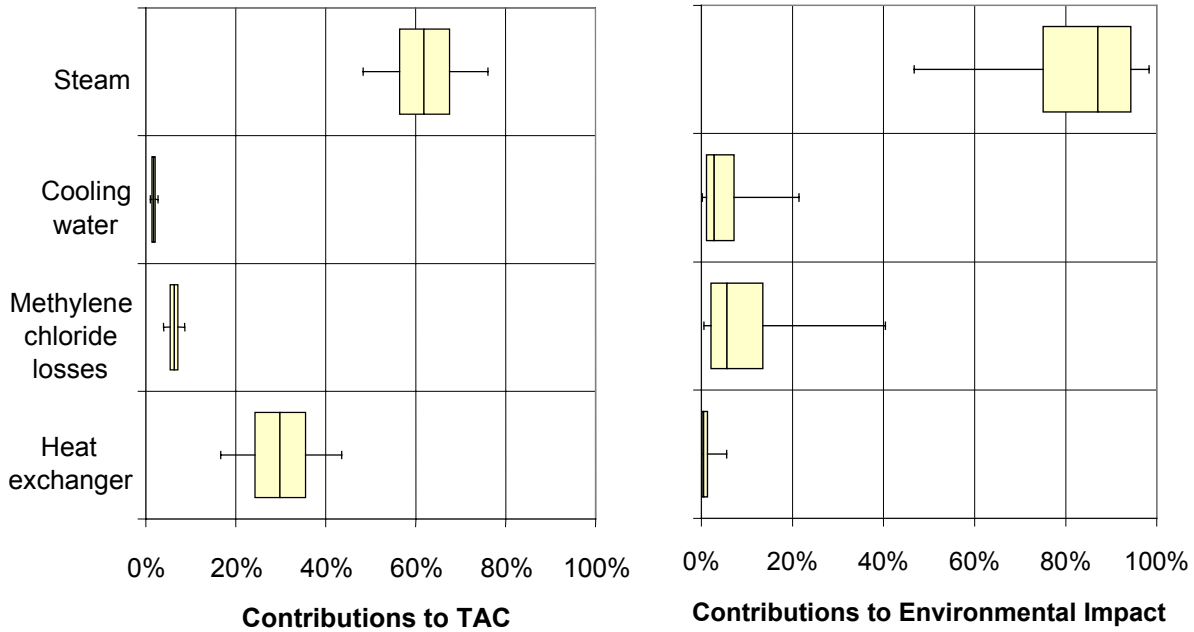


Figure 5-5: Distributions for the contribution of process inputs and process outputs to (a) total annualized cost, and (b) environmental impact indicator for the 3500 ft² heat exchanger alternative

UNCERTAINTY ANALYSIS RESULTS

The results of uncertainty propagation on absolute and relative measures of performance for this example were presented in section 4.7.2. In particular, a box plot of relative environmental impact distributions vs. relative TAC distributions taking a heat exchanger size of 3,500 ft² as the base case alternative was presented in Figure 4-26. On the basis of that plot, two alternatives (in addition to the base case alternative) are chosen for uncertainty analysis in this section. The choices selected are the 2,900 ft² alternative (i.e. the alternative with minimum expected TAC) and the 6,000 ft² alternative (which has more than a 75% chance of having less impact than the base case alternative, but also a non-negligible change of having higher impact).

Rank correlation coefficient plots for the absolute measures of performance are given in Figure 5-6 (TAC) and Figure 5-7 (environmental impact indicator). As these results were obtained by performing a Monte Carlo simulation with 2,000 points, the rank correlation

coefficient absolute value ($|\rho|$) below which lack of correlation of an uncertain input with the uncertain output of interest could be established (95% confidence) is calculated as 0.044 through the use of eq (5-12). The range of rank correlation coefficient values not considered significant is shown between the two dashed lines in the figures.

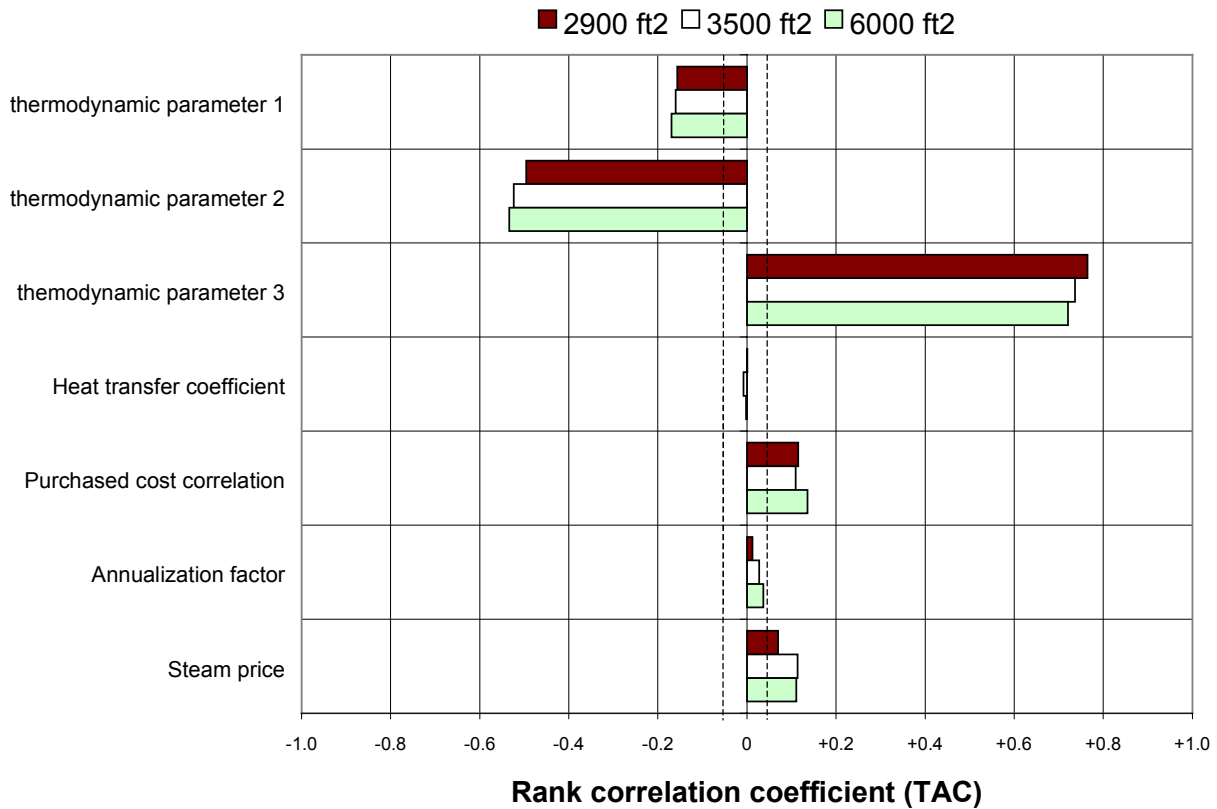


Figure 5-6: Uncertain factor contributions to the uncertainty in total annualized cost for three different choices of heat exchanger size

In the case of total annual cost, the largest contribution to uncertainty comes from the uncertainty in the parameters used to describe the vapor-liquid and liquid-liquid equilibria of the system water-methylene chloride. In particular, the infinite dilution activity coefficient for methylene chloride in water is a key factor in determining the amount of steam required to meet the 2 ppm effluent concentration specification. The uncertainty in the heat transfer coefficient is found to have a negligible effect on the uncertainty in TAC.

For the case of environmental impact valuation, Figure 5-7 shows that the uncertainty in the unit environmental impact for steam generation has by far the greatest contribution to uncertainty, followed by the uncertainty in thermodynamic parameters.

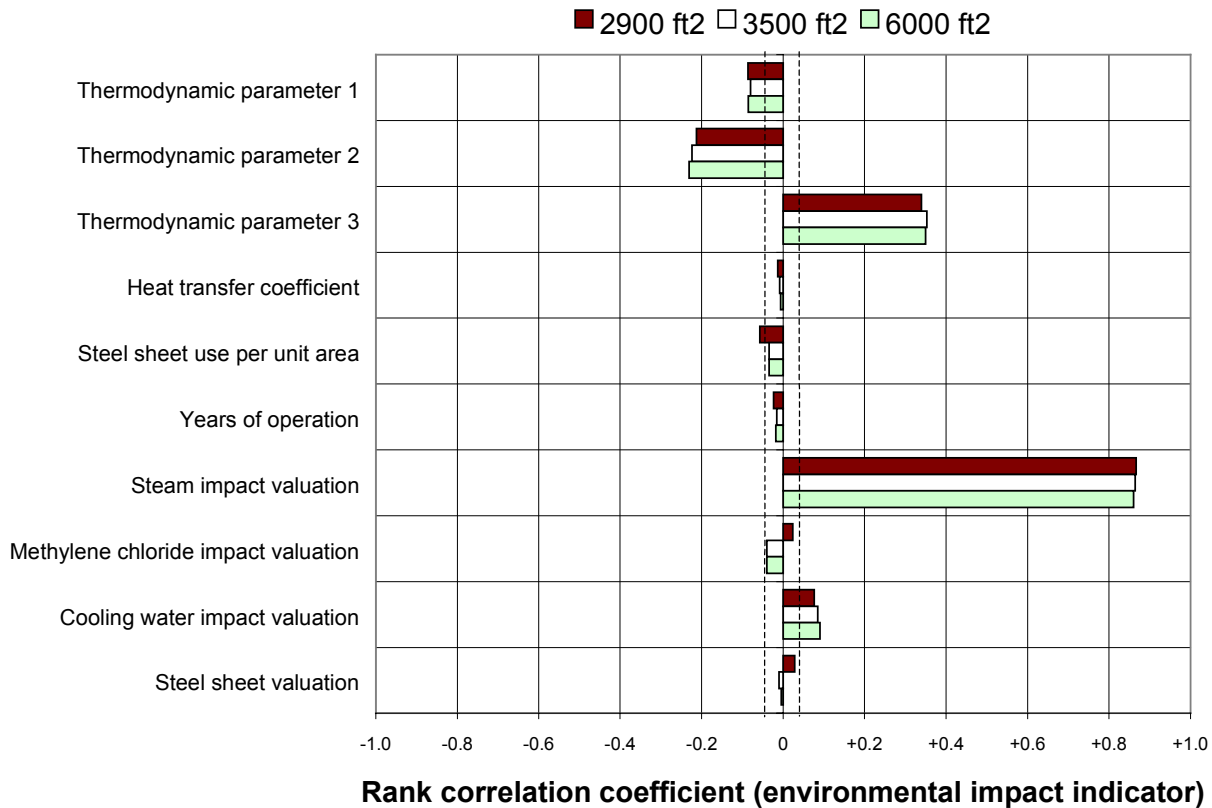


Figure 5-7: Uncertain factor contributions to the uncertainty in environmental impact valuations for three different heat exchanger size choices

The more relevant results regarding uncertainty in the selection among various alternatives are the rank correlation coefficient charts for relative measures of performance shown in Figure 5-8 (relative TAC) and Figure 5-9 (relative environmental impact). These figures show that the relative ranking of input uncertainties in terms of their contribution to the uncertainty in the performance measure indicators are not necessarily the same than that based on contributions to the uncertainty in the selection among competing alternatives.

With respect to the sizing of the heat exchanger based on economic considerations, Figure 5-8 shows that the uncertainty in thermodynamic parameters is still very important.

However other factors that did not contribute much to the uncertainty in TAC now show up as having very important contributions to relative TAC (i.e. the uncertainty in the equipment cost correlation and the uncertainty in the heat transfer coefficient). In the case of sizing based on environmental considerations, Figure 5-9 shows that thermodynamic parameter uncertainty is more important than the uncertainty in the unit environmental impact valuation for steam. As in the case of sizing according to economic considerations, the uncertainty in the heat transfer coefficient becomes important. These observations are consistent with engineering intuition, which tells us that the key factors determining whether the additional investment in heat exchanger area is justified given the incremental energy savings should be important to the decision.

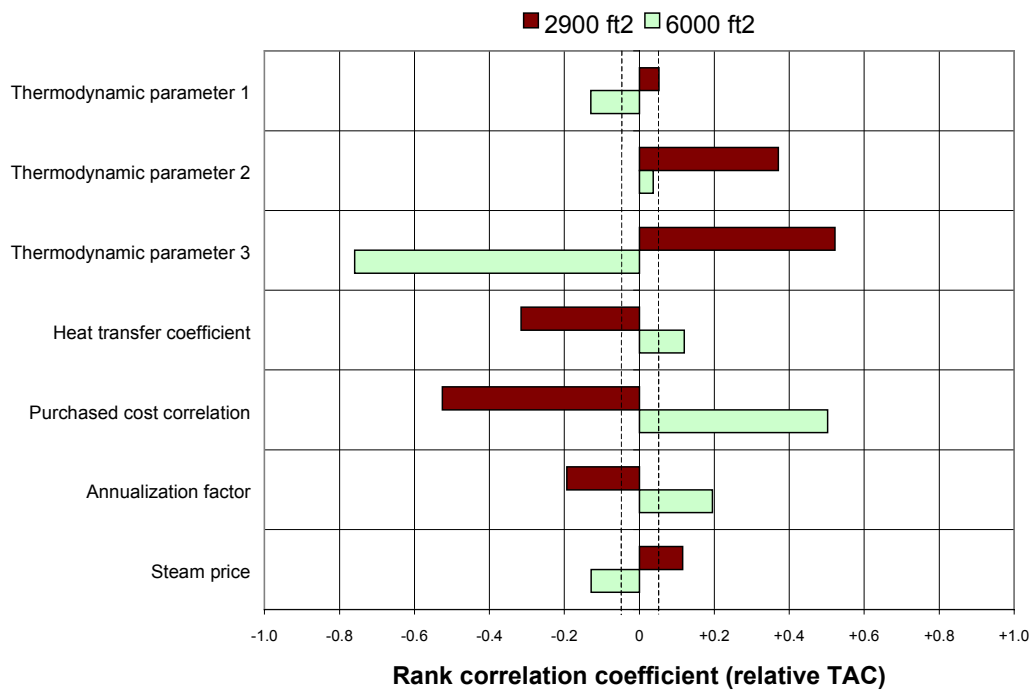


Figure 5-8: Uncertain factor contributions to the uncertainty in relative total annualized cost for two different choices of heat exchanger size (base case alternative has a 3,500 ft² heat exchanger)

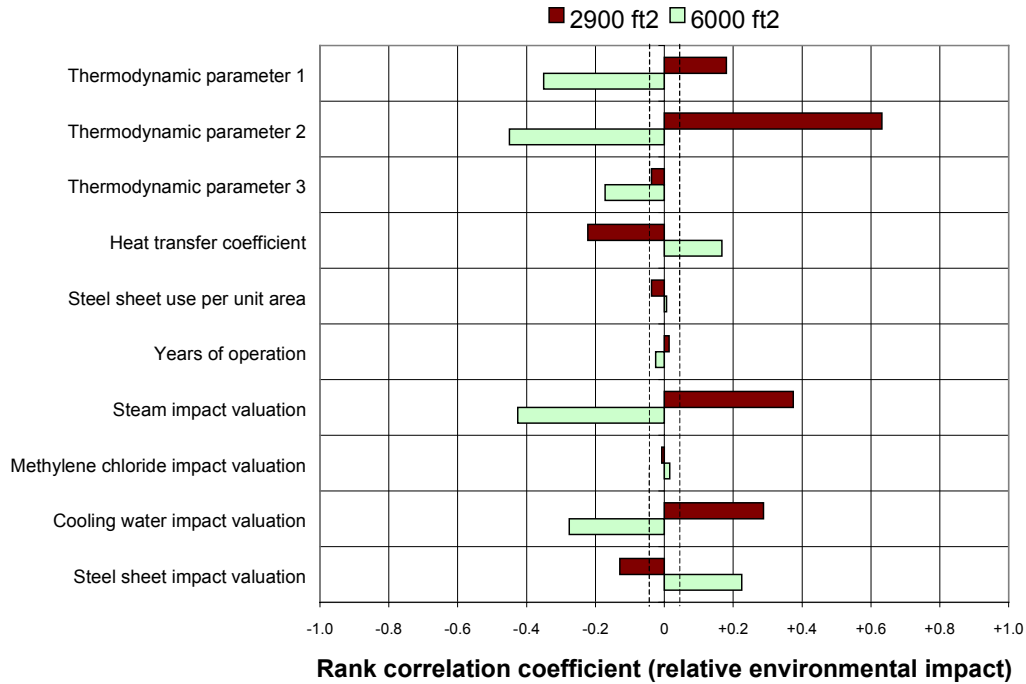


Figure 5-9: Uncertain parameter contributions to the uncertainty in relative environmental impact valuations for two different choices of heat exchanger size (base case alternative has a 3,500 ft² heat exchanger)

5.4.3 Process with steam stripping column

INTRODUCTION

Motivated by the sensitivity analysis performed in the previous example, this example considers an additional retrofit option to the installation of a heat exchanger: the replacement of the two flash drum vessels of the original process by a steam stripping column. The proposed flowsheet configuration is shown in Figure 5-10.

The tasks in the new design problem are the sizing of the heat exchanger and the design of the stripping column. There are three decision variables describing the column: the number of trays, its diameter, and the spacing between trays. As the number of trays increases, the separation efficiency increases. However, there are decreasing returns to scale, since the addition of a tray to a short column has a greater relative impact on separation efficiency than the addition of a tray to a tall column. Column diameter and tray spacing are important for proper operation of the column. A column with diameter that is too narrow has a higher chance of

flooding. When flooding occurs, liquid bypasses the tray contact area, resulting in failure of the column to achieve the desired separation.

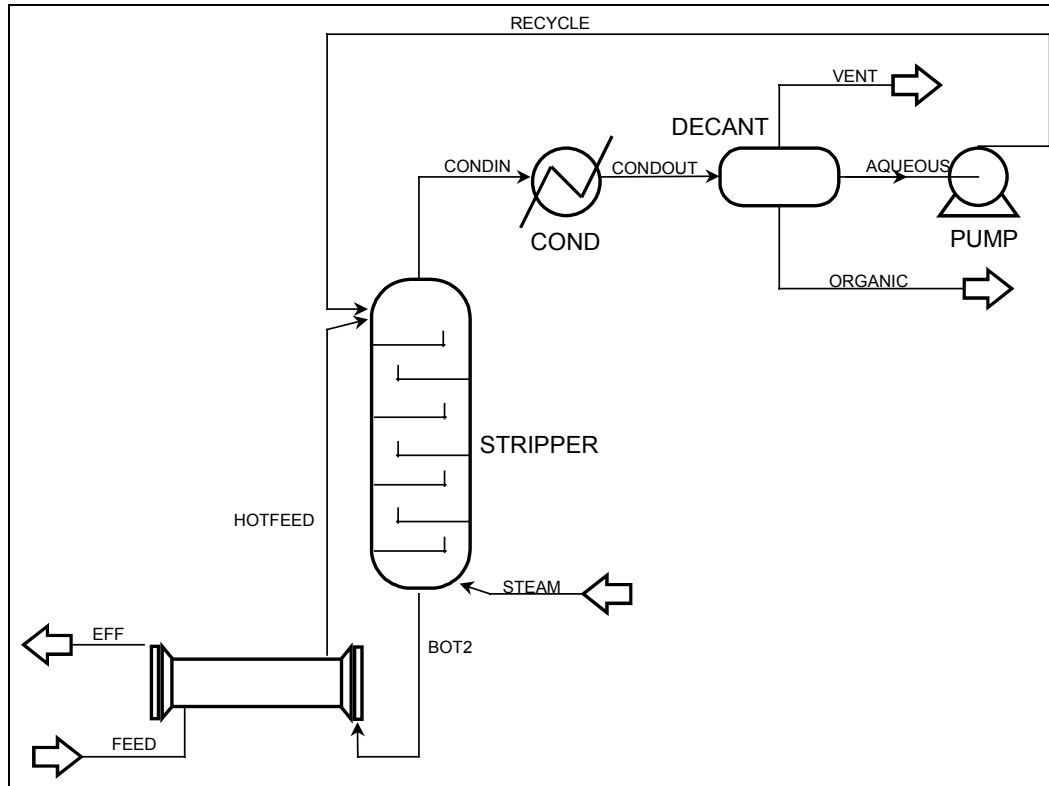


Figure 5-10: Flowsheet for the stripping column retrofit example

ANALYSIS

Sources of Uncertainty

The following sources of uncertainty are considered:

- a) Model-inherent uncertainties. Uncertainties in the overall heat transfer coefficient, in the column efficiency, and in the vapor-liquid and liquid-liquid equilibria of mixtures of water and methylene chloride are considered.
- b) Process-inherent uncertainties. Uncertainty (rather than variability) in feed flow and temperature is considered. Feed concentration is assumed to be the concentration of a saturated aqueous solution of methylene chloride in water at the feed temperature.

- c) External uncertainties. There is uncertainty about the future values of the permissible concentration of methylene chloride in the sewer discharge.
- d) Valuation model uncertainties. For the economic valuation model, uncertainties in future prices, equipment cost, and annualization factors⁴² are considered. Uncertainties in the environmental valuation model include uncertainties in emission factors, input-output technical coefficients, characterization factors, fate and transport properties of chemicals, human exposure model parameters, and environmental problem valuation factors⁴³.

Process Model

A model of the process shown in Figure 5-10 was developed using the Aspen plus simulator. Uncertainty propagation of this model was carried out using the deterministic equivalent modeling method (DEMM, see section 8.2). DEMM was used to develop two spreadsheet-based metamodel of the Aspen plus model. In model 1, the steam rate was set at the rate that minimized operating cost, which was assumed to be only a function of steam cost and methylene chloride replacement cost⁴⁴. In model 2, the steam rate was set at the rate necessary to meet a prescribed effluent concentration standard. The final spreadsheet model was a combination of both metamodels. Metamodel 1 was the default model used, unless the resulting effluent concentration was higher than the concentration standard encountered in a particular Monte Carlo iteration, in which case steam rate was set according to metamodel 2.

Table 5-2 lists the inputs used to build the two metamodels, as well as the uncertain outputs and the polynomial chaos expansion level of approximation used to model each output.

The uncertainty in column efficiency was modeled outside the DEMM representation of the Aspen model. For a given specification of the number of trays made by the designer, an equivalent theoretical number of trays is computed during the Monte Carlo simulation by

⁴² The uncertainty in the annualization factor arises from uncertainties in many parameters (see section 3.2.4).

⁴³ See the following sections for further discussion on environmental value model uncertainties: 3.3.2 (general discussion and discussion of uncertainties in valuation factors); 6.4 (uncertainties in the human exposure model); 7.5 (uncertainties in the PIO-LCA model).

⁴⁴ Under this assumption, the optimum steam rate is only a function of process uncertainties and the ratio of the prices of methylene chloride and steam. Knowledge of the actual prices is not necessary to find the optimum steam rate.

multiplying the specified physical number of trays by the uncertain column efficiency. The calculated theoretical number of trays is then used as an input to the metamodel.

Table 5-2: Structure of DEMM metamodels used to propagate uncertainty in the stripping column retrofit example

Model	Uncertain inputs	Decision variables	Uncertain outputs	PCE level of approximation
Model 1:	Feed flow rate	Area	Steam consumption rate	5 th + bilinear
Min	Feed temperature	$\ln N^a$	Condenser duty	5 th + bilinear
OpCost	NRTL parameters (3)	$\ln(P_{\text{steam}}/P_{\text{MeCl}_2})$	$\log_{10}(\text{Effluent concentration})$	4 th
	Heat transfer coefficient		$\log_{10}(\text{MeCl}_2 \text{ discharge rate})$	4 th
			Column flooding diameter at 24 in. tray spacing	5 th + bilinear
Model 2:	Feed flow rate	Area	Steam consumption rate	6 th + 3 rd order
Meet C_{sp}	Feed temperature	$\ln N^a$	Condenser duty	cross terms
	NRTL parameters (3)	Concentration set	MeCl_2 discharge rate	+ bilinear
	Heat transfer coefficient	point	Column flooding diameter at 24 in. tray spacing	(for all outputs)

a) $\ln N$ stands for the natural logarithm of the theoretical number of column stages. The collocation points calculated by DEMM were modified so that each collocation point used for $\ln N$ corresponded to an integer value of N .

Table 5-3 shows the distributions used to build the spreadsheet metamodel. It was assumed in this example that, as a result of the uncertainty analysis in the previous example, the design team spent resources in improving its estimate of the overall heat transfer coefficient. The new distribution is compared with the old distribution on the density plots in the second row of the table.

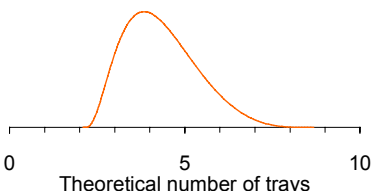
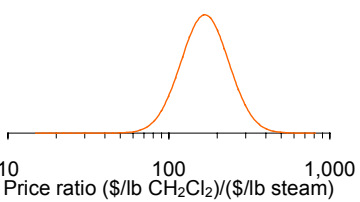
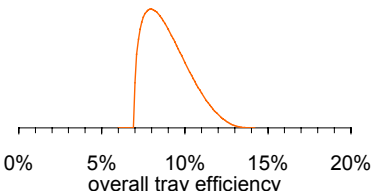
Economic Valuation Model

The key economic tradeoff is the one between operating cost (mostly due to steam use) and the costs associated with the exchanger and the stripping column (including capital cost and annual charges due to maintenance, taxes and insurance)⁴⁵. Because it was assumed in this example that effluent concentration standards could tighten from year to year, a net present cost (NPC) economic valuation model was used instead of the total annualized cost model used elsewhere in this thesis:

⁴⁵ See section 3.2 for a discussion on the operating cost vs. capital cost tradeoff.

Table 5-3: Uncertainty distributions used to build the spreadsheet-based process metamodel

Input variable	Distribution	Probability density plot
Binary interaction parameters in the NRTL model	$\begin{bmatrix} A_{ij} \\ A_{ji} \\ \alpha_{ij} \end{bmatrix} = \begin{bmatrix} -7.7458 \\ 8.8375 \\ 0.16294 \end{bmatrix} + \begin{bmatrix} -3.1260 & 0 & 0 \\ -1.7359 & 1.7264 & 0 \\ 0.008333 & 0.007525 & -0.01496 \end{bmatrix} \begin{bmatrix} \xi_a \\ \xi_b \\ \xi_c \end{bmatrix}$ $B_{ij} = 978.01 - 279.64 A_{ij}$ <p>where ξ_a, ξ_b, and ξ_c are independent unit normal random variables.</p>	
Overall heat transfer coefficient	$U = Normal\left(\mu = 225 \frac{BTU}{\circ F \cdot ft^2 \cdot hr}, \sigma = 50 \frac{BTU}{\circ F \cdot ft^2 \cdot hr}\right)$	
Feed temperature	$T_{feed} = Normal(\mu = 95^\circ F, \sigma = 5^\circ F)$	
Feed flow rate	$F_{feed} = Normal\left(\mu = 10^5 \frac{lb}{hr}, \sigma = 10^4 \frac{lb}{hr}\right)$	
Heat exchanger area	$Area_{HX} = Uniform(2000 ft^2, 5000 ft^2)$	
Concentration set point	$C_{sp} = 1 ppm \times 10^{Uniform(-2,1)}$	

Input variable	Distribution	Probability density plot
Number of theoretical trays	$\ln N = 0.78 + 2.13 \times \text{Beta}(\alpha_1 = 3.54, \alpha_2 = 3.70)$	
Methylene chloride to steam price ratio	$\frac{P_{CH_2Cl_2}}{P_{steam}} = \exp\{\text{Normal}(5.12, 0.34)\}$	
Overall tray efficiency	$\eta_{tray} = 0.07 + 0.07 \times \text{Beta}(\alpha_1 = 1.429, \alpha_2 = 3.571)$	

$$NPC = FCI + \sum_{k=1}^N \frac{F_{steam,k} P_{steam,k} + F_{cw} (\dot{Q}_{cond,k}) P_{cw} + F_{CH_2Cl_2,k} P_{CH_2Cl_2,k} + FCI \times \left(\frac{Maint}{FCI} \right) \left(1 + \frac{OpSup}{Maint} \right)}{(1+i)^k} (1 - \tau_k) + \tau_k f_{dep,k} FCI \quad (5-14)$$

where the parameter symbols used are the same as those used in the economic valuation models section (section 3.2). Depreciation factors ($f_{dep,k}$) are taken from the table of values for the MACRS method for a 9.5 year class life (see Table 3-4). The fixed capital investment (FCI) is given by:

$$FCI = \left[f_{BM,HX} C_{p,HX} (Area) + f_{BM,shell} C_{p,shell} (N_{trays}, D_{shell}, h_{trays}) + f_{BM,trays} C_{p,trays} (N_{trays}, D_{shell}) \right] \left(\frac{FCI}{C_{TM}} \right) \quad (5-15)$$

where the symbols not previously defined in Chapter 3 are N_{trays} (number of trays), D_{shell} (column diameter), h_{trays} (spacing between trays), and (FCI/C_{TM}) which is a factor used to calculate the contribution to FCI that can be directly attributed to the total installed equipment cost (C_{TM} , given by the sum of the terms inside the square brackets).

The purchased cost ($C_{p,i}$) and installation cost factor (f_{BM}) correlations used were those published in the process design textbook by Turton et al. [10]⁴⁶

For a given specification of heat exchanger area, and each realization of the random variables theoretical number of trays, feed flow, feed temperature, and year-to-year prices and effluent standards, the spreadsheet process metamodel will calculate the steam consumption (F_{steam}), condenser cooling duty (\dot{Q}_{cond}), and methylene chloride effluent discharge ($F_{CH_2Cl_2}$) corresponding to each year of operation. The model will also calculate the flooding diameter at $h_{trays} = 24$ inches. The annual cooling water use (F_{cw}) is calculated as a function of the condenser duty assuming an allowable water temperature rise of 30°F. It was assumed that the process would operate for 10 years. A discount rate of $i=15\%$ was used in the estimation of net present cost.

Year-to-year trajectories for methylene chloride prices, steam prices, tax rates, and effluent concentration standards were calculated using Markov-type models (see Figure 3-2 for confidence intervals and a sample trajectory of the future prices of methylene chloride calculated through this method). The price of cooling water was assumed to remain constant at \$0.12/m³. The uncertainty distributions used for the parameters in the economic valuation model are summarized in Table 5-4.

Environmental Valuation Model

The environmental valuation model was the same one used in section 4.7.2, augmented with terms to account for the environmental impact of fabricating the column⁴⁷:

$$\Omega = F_{steam} \Omega_{steam} + F_{cw} (\dot{Q}_{cond}) \Omega_{cw} + F_{CH_2Cl_2} \Omega_{CH_2Cl_2} + \frac{[W_{HX}(Area_{HX}) + W_{Shell}(D_{shell}, N_{trays}, h_{trays}) + N_{trays} W_{tray}(D_{shell})] \Omega_{steel}}{N} \quad (5-16)$$

⁴⁶ As the installation factors published in the textbook by Turton et al. (and in all other design textbooks) are size-independent installation factors, it must be recognized that the economic valuation function will introduce a bias against capital investment (see section 3.2.5). In a real design setting, designers should use plant data or knowledge bases such as the ICARUS process evaluator to estimate size-dependent installation cost factors.

⁴⁷ As in the case of the heat exchanger, the assumption is made that most of the impact comes from the fabrication of the steel sheet used to construct the column.

Table 5-4: Uncertainty distributions used in the economic valuation model

Input variable	Distribution	Probability density plot
Effluent concentration standard	$C_0 = 2 \text{ ppm}$ $C_k = C_{k-1} \times [1 - 0.5 \times \text{Bernoulli}(0.2)]$ (i.e. every year there is a 20% probability that the previous year standard will be halved)	
Fixed capital investment factor (equipment sizing projects)	$\left(\frac{FCI}{C_{BM}}\right) = 1.18 \times [0.80 + 0.5 \times \text{Beta}(\alpha_1 = 2.4, \alpha_2 = 3.6)]$	
Maintenance factor	$\left(\frac{\text{Maint}}{FCI}\right) = \text{Triangular}(a = 0.02, b = 0.06, c = 0.10)$	
Methylene chloride prices	$P_{CH_2Cl_2,0} = \$0.40 / lb$ $P_{CH_2Cl_2,k} = P_{CH_2Cl_2,k-1} \times \exp\{\text{Normal}[\ln(1.005), \ln(1.096)]\}$	
Operating supplies factor	$\left(\frac{Op.Sup.}{\text{Maint}}\right) = \text{Triangular}(a = 0.10, b = 0.15, c = 0.20)$	
Steam prices	$P_{\text{Steam},0} = \$0.0029 / lb$ $P_{\text{Steam},k} = P_{\text{Steam},k-1} \times \exp\{\text{Normal}[\ln(1.037), \ln(1.127)]\}$	
Tax rate	$\tau_0 = 0.34$ $\tau_k = \tau_{k-1} + \Delta\tau$ where $\Delta\tau$ is a discrete random variable with values and probabilities given in Table 3-4	

The heat exchanger weight (W_{HX}) is calculated according to eq (4-17). The weight of the column shell is given by:

$$W_{Shell} = \left(\pi D_{shell} H_{shell} + \frac{\pi}{4} D_{shell}^2 \right) h_{shell} \rho_{steel} \quad (5-17)$$

where the shell height (H_{shell}) is calculated as:

$$H_{Shell} = 15 \text{ ft} + N_{trays} h_{trays} \quad (5-18)$$

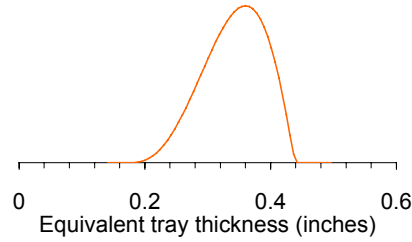
and the shell thickness may take 3 discrete sizes, depending on shell diameter: 0.4 in for $D_{shell} < 3.5$ ft, 0.47 in for $3.5 \text{ ft} < D_{shell} < 5$ ft, and 0.53 in for $D_{shell} > 5$ ft [10].

The weight of an individual tray (W_{tray}) is estimated using the expression

$$W_{tray} = \frac{\pi}{4} D_{shell}^2 h_{plate} \rho_{steel} \quad (5-19)$$

where h_{plate} is the equivalent thickness of a tray. This quantity is assumed uncertain, and is described by the following beta distribution:

$$h_{plate} = 0.125 \text{ in} + 0.25 \text{ in} \times \text{Beta}(\alpha_1 = 3.8, \alpha_2 = 2.2)$$



The rest of the uncertainties in the environmental valuation model (the unit environmental impact indicators and the heat exchanger tube thickness) are the same as those used in section 4.7.2.

Technical constraints

The following technical constraints were imposed on the design:

- The height:diameter aspect ratio of the column was restricted to be equal or lower than 30 [11]
- The maximum acceptable probability of flooding was set at 0.5%. Data from the Aspen plus simulator was used to derive a correlation for flooding diameter as a function of tray spacing and the flooding diameter at 24 inches of tray separation:

$$D_{flood,h} = \left(\frac{24in}{h_{trays}} \right)^{0.35} D_{flood,24in} \quad (5-20)$$

- The maximum acceptable frequency of violations of the concentration standard was set at 1%.
- Columns diameters were restricted to the range 2.5 ft to 6 ft
- The number of actual trays was restricted to the range 29 to 71 so that the theoretical number of trays would be restricted to the range 2 to 10.

Objective function

Designs were selected to maximize expected utility over relative net present cost and relative environmental impact, using eq (4-8) for the utility function.. The initial base case design had a heat exchanger area of 3,500 ft², 50 plates, a column diameter of 4 ft, and 9 inches of spacing between trays.

Optimization procedure

Stochastic optimization was used to identify the best values for the decision variables. The genetic algorithm RiskOptimizer for Excel⁴⁸ was used to solve the following optimization problem:

$$\begin{aligned} & \underset{Area, N_{trays}, D_{shell}, h_{trays}}{Max} \quad E \left[- (1 - \alpha) \ln \left(\frac{NPC}{NPC^{bc}} \right) - \alpha \ln \left(\frac{\Omega}{\Omega^{bc}} \right) \right] \\ & s.t. \quad P(D_{shell} \leq D_{flood,h}) \leq 0.005 \\ & \quad \quad P(C_{eff} \geq C_{std}) \leq 0.01 \\ & \quad \quad \frac{H_{shell}}{D_{shell}} \leq 30 \\ & \quad \quad 2000 \text{ ft}^2 \leq Area \leq 5000 \text{ ft}^2 \\ & \quad \quad 2.5 \text{ ft} \leq D_{shell} \leq 6 \text{ ft} \\ & \quad \quad h_{trays} (in) \in \{9, 12, 15, 18, 21, 24\} \\ & \quad \quad N_{trays} \in \{29, 30, 31, \dots, 71\} \end{aligned} \quad (P5-1)$$

⁴⁸ Palisade Corporation, www.palisade.com

RESULTS

Problem P5-1 was solved three times for three different values of the utility function parameter α : $\alpha=0$ (relative cost minimization), $\alpha=1$ (relative environmental impact minimization), and $\alpha=0.1$ (compromise between relative cost minimization and relative environmental impact minimization, giving more weight to the economic criterion). The results are summarized in Table 5-5.

Both the heat exchanger area and the tray spacing optimal values are at corner points. This means that the range of areas used to derive the metamodel was too narrow. The range should be expanded in a subsequent iteration.

Table 5-5: Stochastic optimization results for the retrofit example

	$\alpha=0$	$\alpha=0.1$	$\alpha=1$
Area (ft ²)	5000	5000	5000
Number of trays	36	42	60
Shell diameter (ft)	3.81	3.81	3.65
Tray spacing (in)	9	9	9

Following the recommendation given at the end of section 4.6.3, uncertainty propagation is performed on the relative performance metrics of the $\alpha=0.1$ and $\alpha=1$ designs using the economically optimum design ($\alpha=0$) as the base case. The results are shown in Figure 5-11 (relative cost) and Figure 5-12 (relative environmental impact). While it is clear that the 60 tray column will have lower environmental impact than the 36 tray column most of the time, it is also clear that it will be more expensive. On the other hand, the 42 tray column has a cost that is almost indistinguishable from that of the 36 tray column, but its environmental performance is clearly superior. Based on these observations, it appears that the expected utility minimization procedure with $\alpha=0.1$ was successful in finding a win-win alternative.

The performance of the design obtained after two iterations of the design cycle is quite impressive when compared to the original process (i.e. the design used for the example in section 5.4.1). Not only would net present cost decrease, but the uncertainty in net present cost would decrease as well (Figure 5-13). With respect to environmental performance, it is uncertain whether environmental impacts were decreased by a factor of five or by a factor of ten (Figure

5-14), but it is very clear that a substantial improvement was achieved, *despite order of magnitude uncertainties in the indicators used to measure environmental performance.*

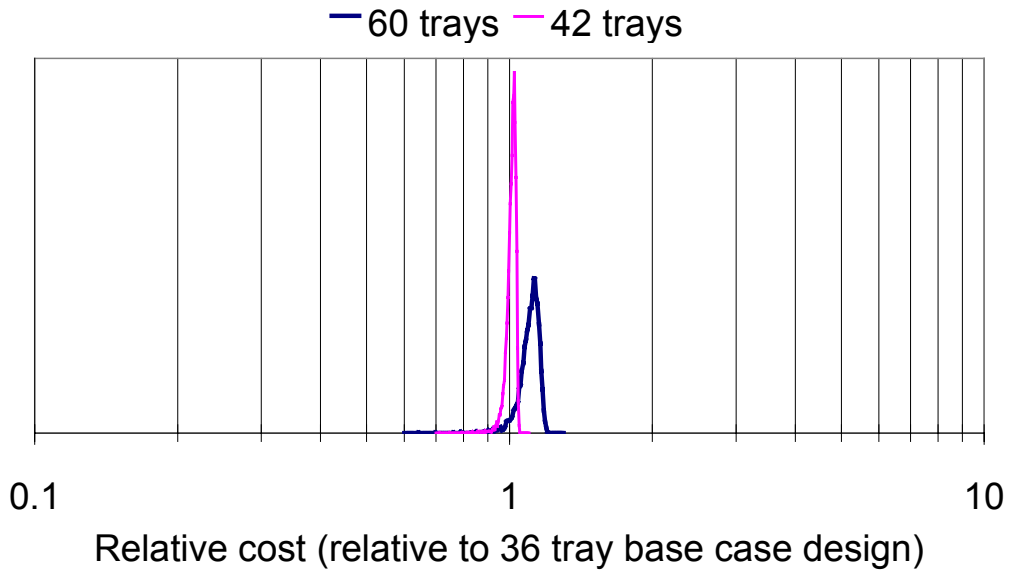


Figure 5-11: Relative NPC distributions for two stripping column designs relative to the economically optimum design

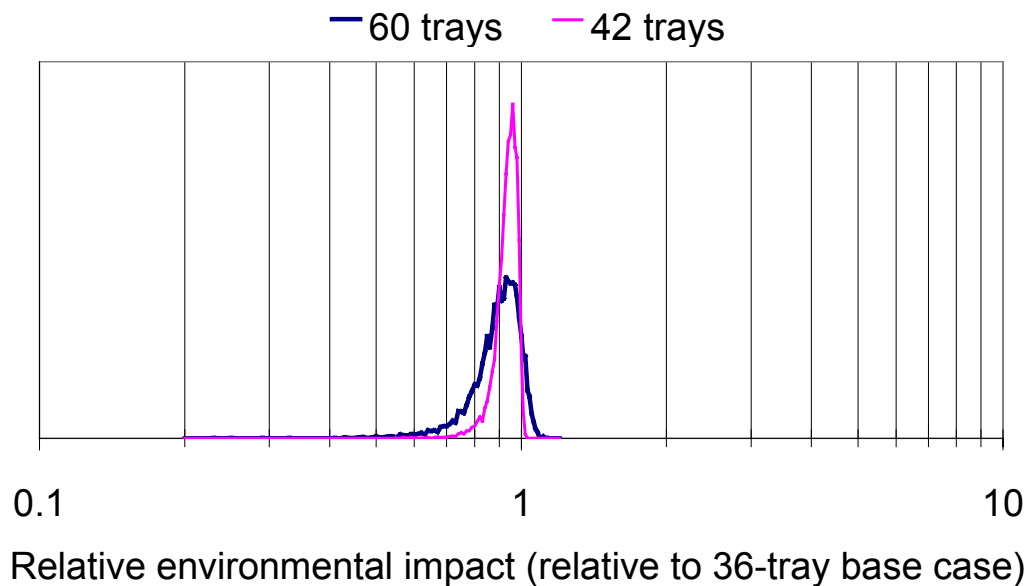


Figure 5-12: Relative environmental impact distributions for two stripping column designs relative to the economically optimum design

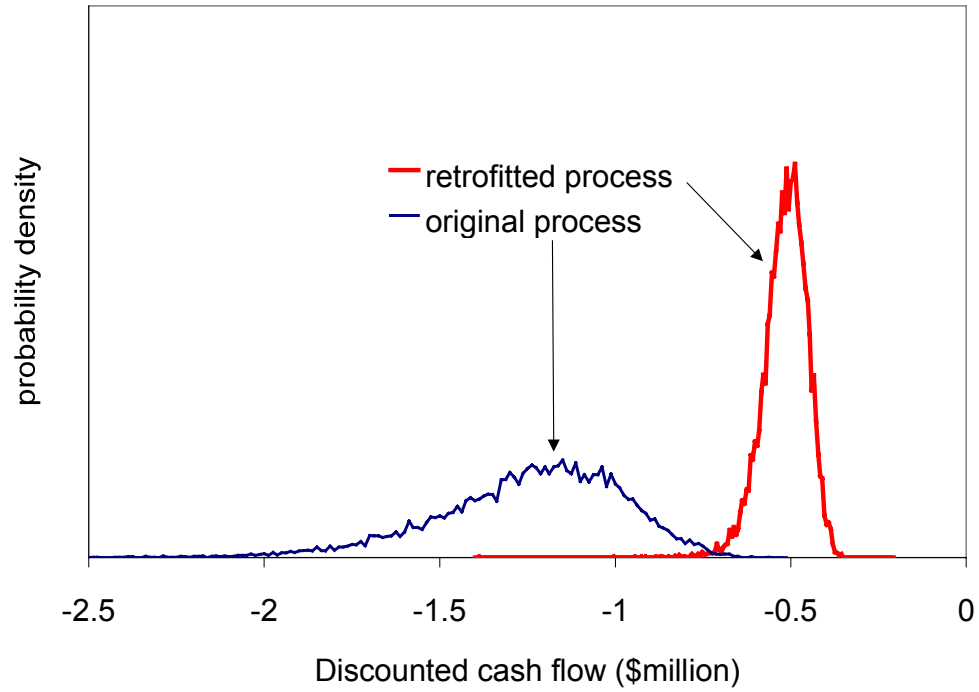


Figure 5-13: Probability density plots of discounted cash flow for the original and the retrofitted solvent recovery processes

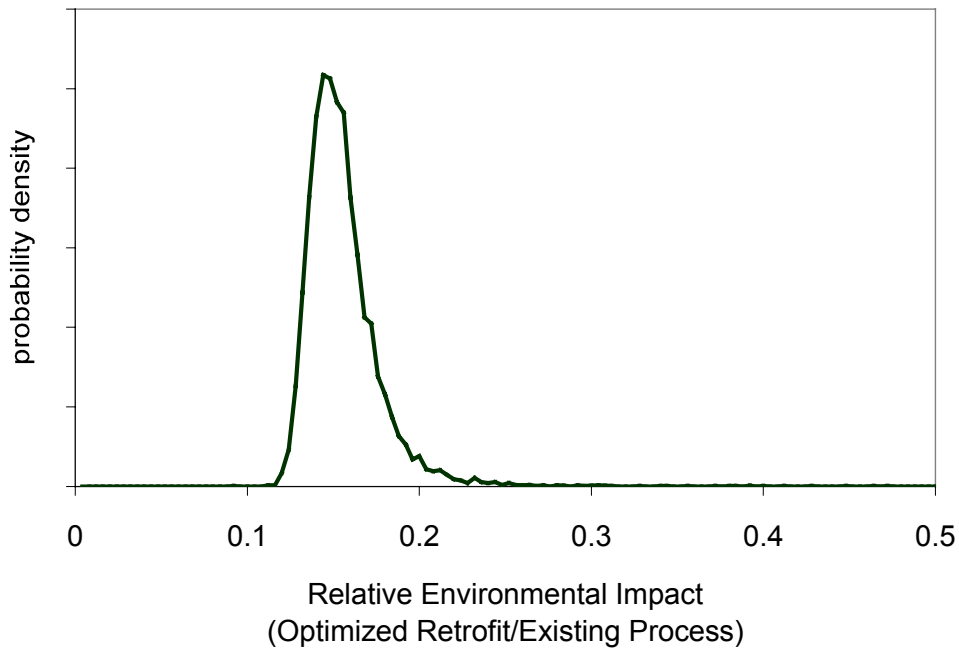


Figure 5-14: Probability density plot for the relative environmental impact of the retrofitted solvent recovery process relative to the original process

5.5 Literature cited

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Chapter 6 Evaluation of the Environmental Impact of Toxic Releases

6.1 Introduction

The evaluation of the potential environmental impact of toxic releases should be given high priority within the environmental evaluation of chemical process designs. A reason for this is that the chemical industry is responsible (directly or indirectly) for a large fraction of the releases of toxic chemicals to the environment. In addition, the public is more concerned about toxic releases from chemical plants than about other environmental impacts the chemical industry might cause.

Unfortunately, our knowledge about the potential environmental impacts of chemicals in the environment is incomplete and imprecise. Nevertheless, information does exist which can be used to support efforts to improve the environmental performance of products and processes. The purpose of this section is to provide designers with tools to assess the potential environmental impact of toxic chemical releases, recognizing and managing the many uncertainties involved.

The chapter is organized as follows:

- Section 6.2 introduces the concept of toxicity indicators. Eight different indicator systems available for process design are reviewed. An estimate of the uncertainty in toxicity indicators is made by examining correlations among the indicator values for chemicals common to several of the indicator sets.
- Section 6.3 describes the multi-media fate, transport, and human exposure model used in this dissertation to obtain probability distributions of human toxicity potential (HTP) indicators for a large number of chemicals. Special emphasis is placed on the derivation of the equations used in the exposure component of the model.
- Section 6.4 introduces two new tools for the management of uncertainty in environmental indicators. A sensitivity analysis tool is used to identify important parametric and structural uncertainties in the fate, transport, and exposure model. The quality of indicator sets is assessed through an information content graphical tool.

- Section 6.5 demonstrates the power of the tools introduced in earlier sections by undertaking an uncertainty analysis of the potential impact of the releases reported in the U.S. Toxics Release Inventory during the last 10 years. The case study demonstrates how present knowledge is sufficient to identify with confidence priorities for action and priorities for focused research.

6.2 Toxicity indicators

6.2.1 Introduction

Emission inventories typically include dozens of different substances. In some decision contexts the emissions inventories are sufficient to identify the option with lower potential impact. This can be done when one option has equal or higher emissions of every single substance in the inventory than another option to which it is being compared. Unfortunately, these decision contexts are rare. More often there are tradeoffs, in which one option has higher emissions of one substance but lower emissions of another one. In such cases it is necessary to summarize the vectors of emissions into a few scalar measures of performance that can be used to rank alternatives.

There are many types of toxic effects associated with chemicals in the environment. Many indicators can be developed, depending on which safeguard subjects (e.g. humans, aquatic organisms, fish-eating predators, etc.) and which endpoints are considered. Guinée and Heijungs [1] distinguish two approaches to the development of toxicity indicators: (i) develop separate indicators for each toxic effect, and (ii) base indicators on the environmental concentration or exposure dose at which the first observable adverse effect occurs. Human toxicity indicators are frequently developed for two types of effects: (a) cancer risk, for which no threshold concentration or dose is presumed to exist, and (b) non-cancer effects, for which a safe concentration or dose (the “no effect level”) is assumed to exist. Indicators for non-cancer effects are based on the concentration or dose at which the first observable adverse effect occurs. This implicitly assumes that all observable adverse effects are equally undesirable.

Indicators need to be consistent with the risk assessment paradigm, where risk depends on both toxicity and exposure. Literally dozens of different toxicity indicators or scoring systems have been proposed. The hierarchy shown in Table 6-1 (based on the work of Jia and

coworkers [2] and Hertwich and collaborators [3]) is useful for examining how closely a proposed indicator adheres to the risk assessment paradigm. In order of increasing sophistication, indicators use (a) toxicity alone, (b) toxicity and persistence, (c) toxicity, persistence, and environmental mobility, or (d) toxicity and exposure through several exposure pathways. Bioaccumulation is frequently used as a surrogate for exposure. Its use assumes that ingestion of plant and animal products is the predominant exposure route.

Table 6-1: Hierarchy of toxicity indicators, based on the risk assessment paradigm

Aspects Considered	Equation	Examples
Toxicity	$I_{1,m} = \sum_c \frac{E_{c,m}}{Q_{c,m}}$	[4,5]
Toxicity + Persistence	$I_{2,m} = \sum_c \frac{E_{c,m} \tau_{c,m}}{Q_{c,m}}$	[6]
Toxicity + Persistence + Bioaccumulation	$I_{3,m} = \sum_c \frac{E_{c,m} \tau_{c,m} B_c}{Q_{c,m}}$	[7]
Toxicity + Persistence + Environmental Mobility	$I_{4,m} = \sum_c \frac{(\sum_j E_{c,j} C_{c,j,m})}{Q_{c,m}}$	[2,8]
Toxicity + Persistence + Environmental Mobility + Bioaccumulation	$I_{5,m} = \sum_c \frac{(\sum_j E_{c,j} C_{c,j,m}) B_c}{Q_{c,m}}$	[9]
Toxicity + Persistence + Environmental Mobility + Exposure pathways	$I_6 = \sum_c \frac{(\sum_k E_{c,j} K_{c,j,k})}{Q_{c,k}}$	[3,10]

Notes: $I_{i,m}$ = toxicity potential indicator of sophistication level i applicable to environmental medium m ; $E_{c,m}$ = Emission of chemical c to medium m ; $Q_{c,k}$ = Toxic potency of chemical c through exposure route k ; $\tau_{c,m}$ = persistence of chemical c in medium m ; $C_{c,j,m}$ = Predicted concentration of chemical c in medium m as a result of a unit emission to medium j ; B_c = bioaccumulation factor for chemical c ; $K_{c,j,k}$ = predicted exposure to chemical c through exposure route k resulting from a unit emission to medium j .

Table 6-2 lists features of eight toxicity indicators available in the open literature. With the exception of the CMU-ET index [5], all of the indicators in the table include measures of exposure. As the table shows, indicator values are available for only a small number of chemicals. For comparison, the United States produce or import close to 3,000 chemicals (excluding polymers and inorganic chemicals) at rates of more than 1 million pounds per year [11], and there are more than 60,000 chemicals reported to be in commercial use [12]. The indicators with the largest number of scored chemicals in the table (WMPT, CMU-ET) are also

the ones that follow the risk assessment paradigm least closely. It is worth noting the effect of including potential doses in the range of values taken by the indicators. The CMU-ET index, which only includes toxicity, has a significantly lower range of indicator values, despite having the largest number of values of any of the indicator sets.

6.2.2 Uncertainties in toxicity indicators

Most of the sources of environmental indicators do not provide information about the uncertainty in individual indicator values. Hofstetter [13] provides a squared geometric standard deviation (σ_g^2) for each of his cancer indicators (the squared geometric standard deviation is the number by which the nominal value should be divided and multiplied to generate the 95% confidence interval for the indicator⁴⁹). The value of σ_g^2 ranges from 5 to 240. A similar range of σ_g^2 was calculated for the exposure component of the TEP cancer and non-cancer indicators [14]. Although these are large uncertainties, they are significantly lower than the dispersion in nominal indicator values. The typical squared geometric standard deviation for the set of indicator values of a system that takes into account exposure and toxicity ranges from 10^5 to 10^6 .

There are several sources of uncertainty in toxicity indicators. These include parametric uncertainties (e.g. toxic potency factors, physical properties of chemicals, environmental transport parameters), structural uncertainties (e.g. choice of models used to estimate exposure), and value-judgment uncertainties (e.g. risk level used to estimate acceptable carcinogen dose to compare cancer and non-cancer impacts on the same scale).

One way to estimate the total amount of uncertainty contained in these indicators is to examine plots of indicator values obtained from different sources that use similar methods. For example, Figure 6-1 shows a plot of Hofstetter cancer indicator values vs. EDF TEP cancer indicator values for emissions to air of 1 kg of each substance belonging to both indicator sets. The solid line in the figure is the best fit to the equation

$$(\text{Hofstetter cancer indicator}) = k(\text{EDF TEP indicator}) \quad (6-1)$$

⁴⁹ Throughout this work the term *uncertainty factor* has been used to refer to the square of the geometric standard deviation.

Table 6-2: Toxicity indicators available in the open literature

Indicator	Units	Release media	Multi-media model	Exposure routes	Toxicity endpoints	# of chemicals	# of TRI chemicals with 1997 releases	Uncertainty	Range
TEP Cancer [15]	kg benzene eq./kg	air water	CalTox	air, water, leaf crops, root crops, beef, milk, eggs, fish, soil, dermal	Cancer risk	129	106	σ_g^2 of exposure ranges from 5 to >120 [14] (uncertainties in toxicity not considered)	13 orders of magnitude $\sigma_g^2 \approx 40,000$
TEP Noncancer [15]	kg toluene eq./kg	air water			No effect dose	245	211		14 orders of magnitude $\sigma_g^2 \approx 100,000$
HTP [10]	kg 1,4-dichloro benzene to air eq/kg	air water ag soil ind soil	USES	air, water, leaf crops, root crops, beef, milk, fish, soil	No effect dose, 1 in 10,000 cancer risk dose	85	67	not considered	17 orders of magnitude $\sigma_g^2 \approx 50,000$
Cancer DALYs [13,16]	Disability-adjusted life-years lost/kg	air water	EUSES	air, water, leaf crops, root crops, beef, milk, fish, soil	Cancer risk	55	47	σ_g^2 ranges from 5 to 240; typical value is 30	10 orders of magnitude $\sigma_g^2 \approx 35,000$
MPCA index [17]	dimensionless (score proportional to risk)	air	Mackay	air, water, leaf crops, fish, soil	No effect dose, 1 in 100,000 cancer risk dose	163	116	not considered	18 orders of magnitude $\sigma_g^2 \approx 1,400,000$
EDIP ht [18]	person-yr/kg (magnitude of person-yr allowance based on Danish political targets for year 2000)	air water soil	Ad-hoc (persistence treated qualitatively)	air, leaf crops, beef, milk, fish, soil	No effect dose, 1 in 1,000,000 cancer risk dose	93	68	not considered	22 orders of magnitude $\sigma_g^2 \approx 300,000$
WMPT [9]	logarithmic scale with discrete values from 4 to 9 (1 point difference ~ 100-fold difference in risk)	any	Mackay	exposure estimated as persistence \times fish bioaccumulation factor	No effect dose, 3 in 1,000 cancer risk dose	368	177	not considered; minimum σ_g^2 of 10-100 due to discretization;	10 orders of magnitude $\sigma_g^2 \approx 48,000$
CMU-ET [5]	kg H2SO4 eq/kg	any	none	exposure is not a factor	TLV concentration (based on occupational exposure)	570	208	not considered	7 orders of magnitude $\sigma_g^2 \approx 670$

Note: There were 493 chemicals or chemical groups with reported releases to air, water or wastewater treatment plants in the 1997 Toxics Release Inventory (TRI). Of these, 235 are listed by the EDF as recognized or suspected carcinogens.

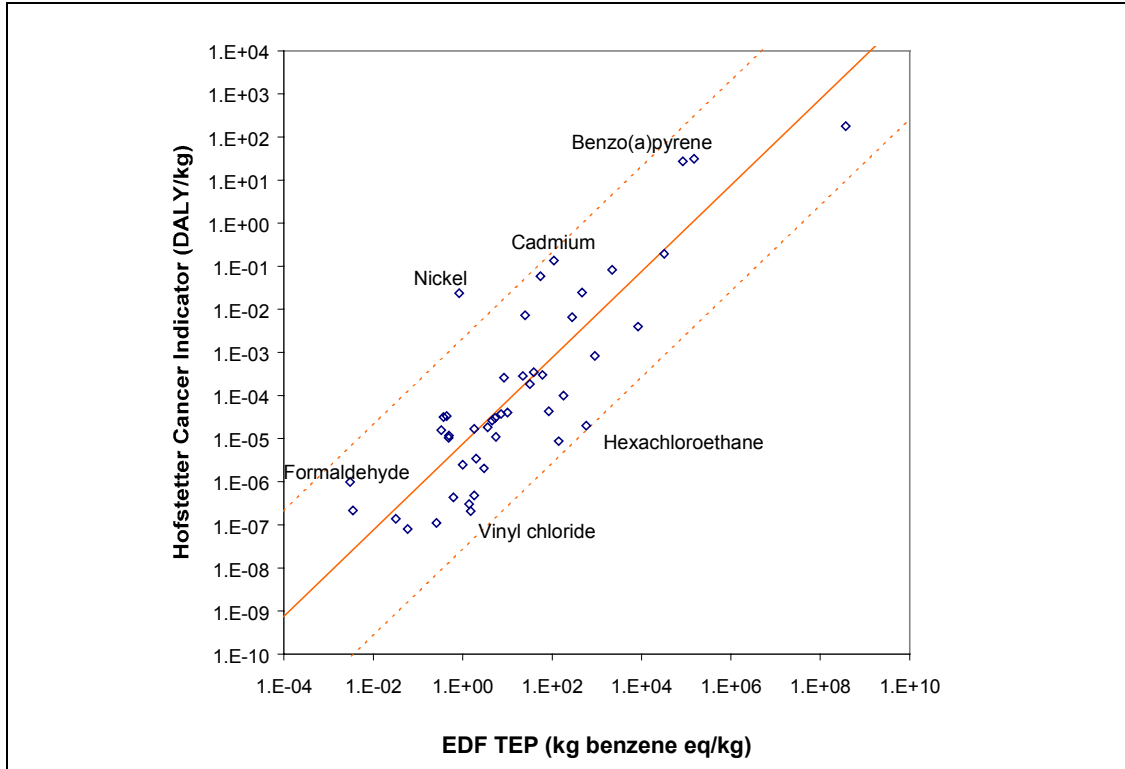


Figure 6-1: Correlation between Hofstetter DALYs and EDF TEP cancer indicators (air emissions)

The two dashed lines shown are plots of the relations

$$(Hofstetter\ cancer\ indicator) = (k \times UF)(EDF\ TEP\ cancer\ indicator) \quad (6-2)$$

and

$$(Hofstetter\ cancer\ indicator) = (k \div UF)(EDF\ TEP\ cancer\ indicator) \quad (6-3)$$

where k is an indicator unit conversion constant and UF is the uncertainty factor in the correlation, given by the equation

$$UF = \left[GSD \left(\frac{Hofstetter\ cancer\ indicator}{EDF\ TEP\ cancer\ indicator} \right) \right]^2 \quad (6-4)$$

where $GSD(\bullet)$ is the geometric standard deviation operator. For the comparison shown in Figure 6-1, k has a value of 7.5×10^{-6} , while UF takes a value of 280. This means that one could estimate a missing value of the Hofstetter cancer indicator for air emissions by multiplying the corresponding value from the EDF TEP indicator system by 7.5×10^{-6} . One would expect the estimated value to be accurate within a factor of 280 (95% confidence interval). Although the uncertainty factor is quite large, it is small compared to the 10 order-of-magnitude range of

indicator values. Thus there is reasonably good agreement between the two indicator sets with regard to air emission unit indicators.

The agreement is not as good for the case of unit indicators for discharges to water (Figure 6-2). In this case, the uncertainty factor takes a value of 4,800 (more than an order of magnitude higher than in the case of air emissions). Summaries of uncertainty factors for correlations among the indicator systems cited in Table 6-2 are shown in Table 6-3 (cancer indicators), Table 6-4 (non-cancer effects indicators), and Table 6-5 (combined cancer and non-cancer toxicity indicators). Also shown in the tables are the uncertainty factors for the correlation between air emissions and water discharges unit indicators within the same indicator system. The intermedia uncertainty factors are low (ranging from 40 to 230) for those systems that use multimedia partitioning models to calculate concentrations in exposure media. The intermedia uncertainty factor for the EDIP method is quite high (53,000). This indicates that the semi-quantitative procedure used to estimate exposures in the EDIP method gives quite different results than procedures based on rigorous multimedia fate and transport models.

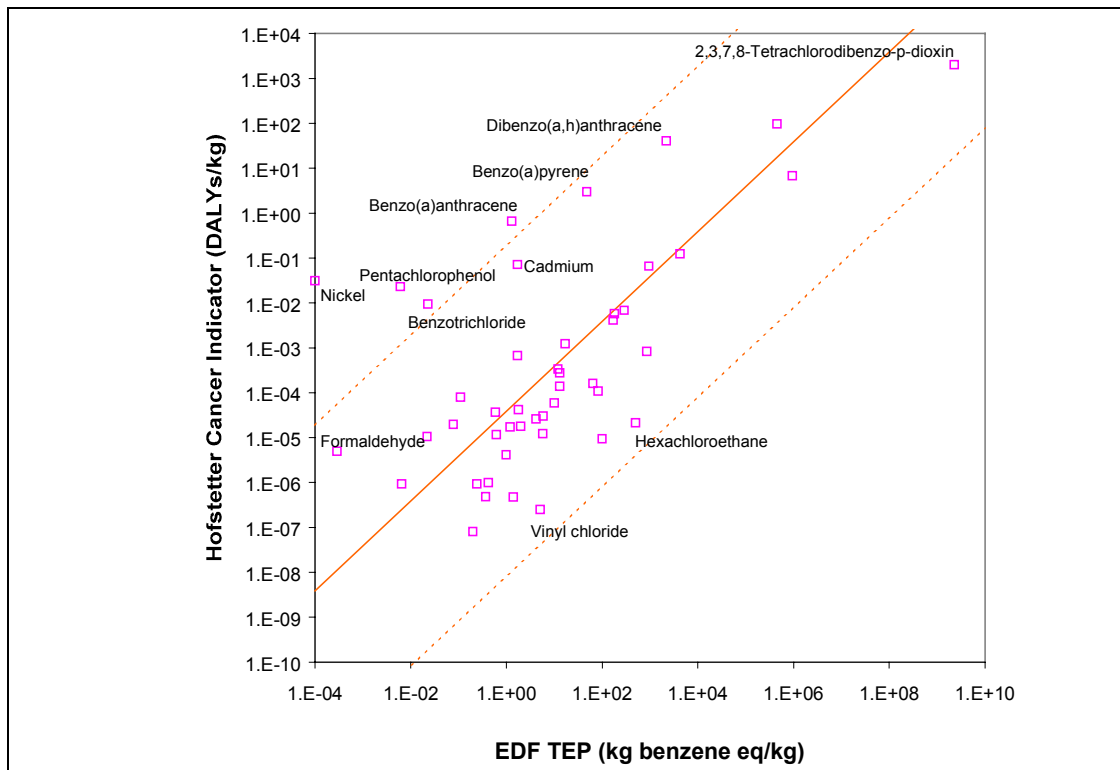


Figure 6-2: Correlation between Hofstetter DALYs and EDF TEP cancer indicators (water discharges)

Table 6-3: Uncertainty factors for cancer indicators based on correlations among indicator systems

	MPCA (Cancer)	TEP Cancer (air)	Cancer DALYs (air)	TEP Cancer (water)	Cancer DALYs (water)
MPCA (Cancer)	1 (N=55)	800 (N=49)	280 (N = 33)		
TEP Cancer (air)	800 (N=49)	1 (N=129)	270 (N=46)	210 (N=121)	
Cancer DALYs (air)	280 (N = 33)	270 (N=46)	1 (N=55)		40 (N=54)
TEP Cancer (water)		210 (N=121)		1 (N=129)	4,800 (N=45)
Cancer DALYs (water)			40 (N=54)	4,800 (N=45)	1 (N=55)

Table 6-4: Uncertainty factors for non-cancer indicators based on correlations among indicator systems

	MPCA (NonCancer)	TEP NonCancer (air)	HTP air)	TEP NonCancer (water)	HTP (water)
MPCA (NonCancer)	1 (N=108)	6,700 (N=71)	50,000 (N=20)		
TEP NonCancer (air)	6,700 (N=71)	1 (N=245)	1,800 (N=50)	150 (N=243)	
HTP (air)	50,000 (N=20)	1,800 (N=50)	1 (N=76)		230 (N=76)
TEP NonCancer (water)		150 (N=243)		1 (N=245)	63,000 (N=50)
HTP (water)			230 (N=76)	63,000 (N=50)	1 (N=76)

Table 6-5: Uncertainty factors for chronic toxicity indicators (combined cancer and non-cancer) based on correlations among indicator systems

	MPCA (human)	HTP (air)	EDIP ht (air)	WMPT (human)	EDIP ht (water)	HTP (water)
MPCA (human)	1 (N=108)	26,000 (N=44)	820,000 (N=38)	80,000 (N=76)		
HTP (air)	26,000 (N=44)	1 (N=84)	1,800 (N=36)	9,300 (N=50)		190 (N=84)
EDIP ht (air)	820,000 (N=38)	1,800 (N=36)	1 (N=92)	7,600 (N=28)	53,000 (N=93)	
WMPT (human)	80,000 (N=76)	9,300 (N=50)	7,600 (N=28)	1 (N=368)	34,000 (N=28)	27,000 (N=50)
EDIP ht (water)			53,000 (N=93)	34,000 (N=28)	1 (N=93)	23,000 (N=36)
HTP (water)		190 (N=84)		27,000 (N=50)	23,000 (N=36)	1 (N=84)

It can be concluded from the uncertainty factor tables that typical uncertainties in cancer indicators range from 2 to 3 orders of magnitude, while uncertainties for non-cancer effects

indicators range from 3 to 6 orders of magnitude. The larger uncertainties associated with non-cancer effects are most likely due to disagreements in the concentration or dose level considered to be safe, as well as to disagreements in the first observable effect that is considered adverse. The EDF TEP and MPCA indicators rely on United States risk assessment databases, while the HTP and EDIP systems rely on European databases. Later in the chapter (section 6.3.5) estimates are shown of the uncertainty in toxicity factors derived from the propagation of physical property and toxic potency probability distributions through a multimedia fate, transport and exposure model.

6.3 Spreadsheet-based model for the generation of toxicity indicators under uncertainty

This section describes the multi-media fate, transport, and human exposure model used in this work to obtain indicators of the potential toxic impacts of chemical releases on humans through chronic exposure. The information flows in the model are summarized in Figure 6-3.

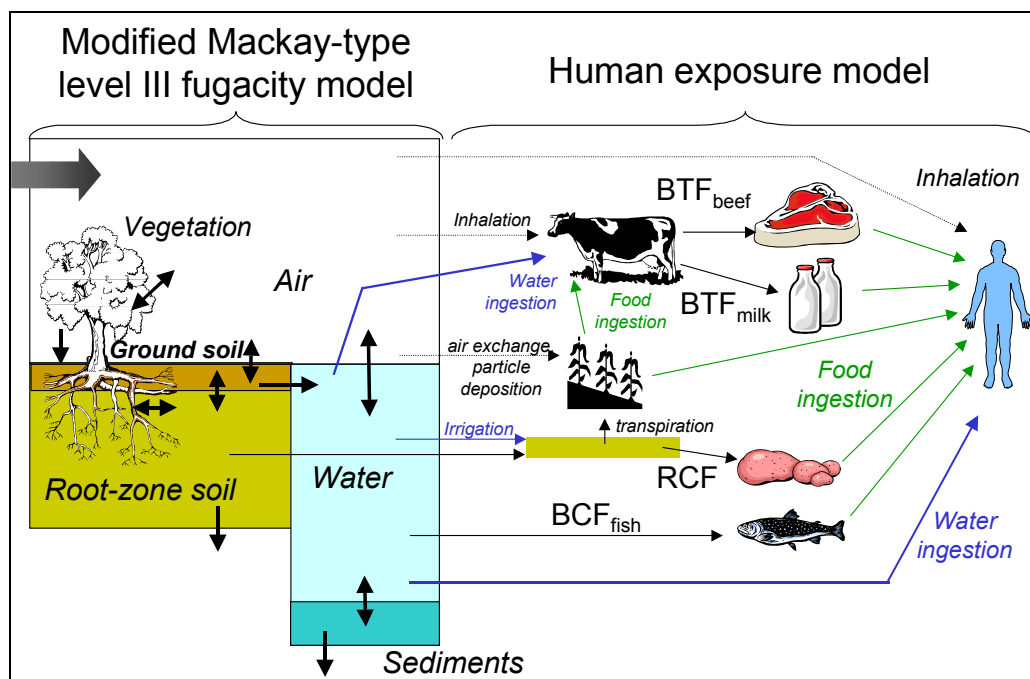


Figure 6-3: Linkage of emissions to human dose through a combined multimedia fate, transport, and exposure model

When a chemical substance is emitted to the environment, it will undergo transport and transformation processes. As a result of these processes, substance concentrations within the various environmental compartments will build up until the rate of the degradation processes becomes equal to the emission rate. People might be exposed to chemicals in the environment through a variety of pathways, including the inhalation of ambient air, and the ingestion of water and various food products. Depending on the properties of a specific chemical, the terrestrial or aquatic food chains might act to increase the concentration of the chemical in the fatty tissues of the organisms placed higher in the food chain. Once a substance enters an exposed subject through any of the pathways mentioned above, it might damage one or more target organs. The risk posed by a chemical to an organism is then not only a function of the inherent toxicity of the

chemical, but also of the likelihood that the chemical will be taken in by the target organism before it is degraded. There is an enormous range of lifetimes for chemicals in the environment. Many substances will be quickly decomposed through physical or biological processes, while others might persist in the environment for many years.

This section is organized as follows: the first subsection describes the model used to link emissions to environmental concentrations. With the exception of a few modifications that are discussed in detail, the model is largely a combination of Mackay's EQC model [19,20] and the CalTox model [21]. Tables are used throughout subsection 6.3.1 to provide all the necessary details of the model structure, equations, and parameter distributions in a concise manner. Subsection 6.3.2 provides a more detailed derivation of the exposure model. In the course of this project it was found that many of the correlations used widely today to estimate concentrations in food products have the potential to grossly exaggerate human exposure. A couple of the equations used by practitioners do not even adhere to mass balance constraints. This situation is remedied by the derivation of new correlations that give reasonable fits to the available experimental data while obeying fundamental physical principles.

Subsection 6.3.3 provides a brief overview of the toxicity endpoints commonly used in risk assessment and gives the equations used to combine measures of exposure and toxicity into toxicity indicators. Minimum data requirements and strategies to handle missing data are provided in subsection 6.3.4. The combined fate, transport, and exposure model was applied to a large data set, propagating uncertainties in model and chemical-specific parameters to generate uncertainty distributions for the human toxicity indicator of more than 500 chemicals. A summary of the results is given in subsection 6.3.5.

6.3.1 Multi-media fate and transport model

The multi-media fate and transport model used in this work is an adaptation of Mackay's level III fugacity model [19,20]. The model has been implemented on a Microsoft Excel spreadsheet so that all the chemical-specific calculations are made in one row of the spreadsheet. This allows simultaneous processing of thousands of chemicals in the same file. In addition, simultaneous calculation of exposure for the complete set of chemicals of interest allows preservation of correlation structure when propagating uncertainties through Monte Carlo

sampling. The spreadsheet structure enables the use of a single set of values for uncertain parameters common to all the chemicals (e.g. landscape parameters) within each iteration.

MODEL STRUCTURE

The model calculates how a chemical released to air, water or soil partitions among six compartments: lower atmosphere, surface water, sediments, ground soil, root-zone soil, and vegetation. Each compartment is modeled as a combination of two or more pure phases, as shown in Table 6-6. Thermodynamic equilibrium is assumed within each compartment. There are three differences in compartment structure between the model used in this work and the standard level III Mackay model:

- The aquatic biota phase is excluded from the surface water compartment, since its presence does not affect the mass balances even for the chemicals with the highest bioconcentration factors.
- Mackay's soil compartment has been split into two compartments, following the example set in the CalTox multimedia exposure model [21].
- A terrestrial vegetation compartment has been added. Inclusion of a terrestrial vegetation compartment in a Mackay-type model has been shown to have potentially significant effects on air and soil concentrations, depending on chemical properties [22].

Table 6-6: Compartments included in the multi-media fate and transport model

Compartment	Phases	Notes
Lower atmosphere	Air Aerosol particles	
Surface water	Water Suspended particles	Mackay's formulation includes an aquatic biota phase within the surface water compartment
Sediments	Water Sediment particles	
Ground-surface soil	Soil particles Water Air	Mackay's model includes a single soil compartment
Root-zone soil	Soil particles Water Air	
Terrestrial vegetation	Tissue lipids Tissue water Tissue air Soil layer	Mackay's model does not include a terrestrial vegetation compartment

Table 6-7 lists the contaminant transport and transformation processes included in the fate and transport model. All of the mechanisms included in Mackay's standard model have been incorporated to the model described here. Additional processes are needed to link the root-zone soil and terrestrial vegetation compartments. Most of these mechanisms were taken or adapted from the CalTox model. The impact of decisions made regarding model structure on human exposure is examined in detail in section 6.4.1.

The model equations are written in terms of fugacities (unit: Pa), fugacity capacities (units: mol/m³·Pa) and "D values" (units: mol/Pa·hr).

The fugacity property was defined by G.N. Lewis in 1901 as a convenient tool to define thermodynamic equilibrium for engineering applications [23]. In ideal gas mixtures the fugacity of a component is equal to its partial pressure. In general, the fugacity of a component i in a mixture, f_i , is defined using the chemical potential as

$$\mu_i = RT \ln f_i + \lambda_i(T) \quad (6-5)$$

where μ_i is the chemical potential and $\lambda_i(T)$ is the chemical potential of the pure component i in an ideal gas state at temperature T and pressure 1 bar or 1 atm., depending on the convention being used. The fugacity is thus a function of temperature, pressure, and composition. The multimedia partitioning model assumes that chemicals are present in the different environmental media in dilute enough quantities that their fugacities are only a function of temperature and of the concentration of the chemical of interest. It is also assumed that at equilibrium (the state at which the fugacity of a chemical in all compartments is the same), concentrations in the different compartments can be related through equilibrium constants (independent of composition).

The concentration $C_{i,j}$ of a chemical i in medium j is related to its fugacity $f_{i,j}$ through the fugacity capacity $Z_{i,j}$:

$$C_{i,j} = f_{i,j} Z_{i,j} \quad (6-6)$$

Table 6-7: Chemical transport and transformation processes included in the fate and transport model

Compartment	Gains	Losses
Lower atmosphere	emissions diffusion from surface water diffusion from ground-surface soil stomatal air exchange with plants* diffusion from plant leaves*	diffusion to surface water diffusion to ground-surface soil washout by rain particle deposition stomatal air exchange with plants* diffusion to plant leaves* gas-phase degradation advection
Surface water	discharges diffusion from air particle deposition from air washout by rain from air diffusion from sediments sediment resuspension soil solution runoff soil erosion	diffusion to air diffusion to sediments sediment deposition liquid-phase degradation advection
Sediments	diffusion from surface water sediment deposition	diffusion to surface water sediment resuspension degradation sediment burial
Ground-surface soil	releases diffusion from air particle deposition from air washout by rain from air diffusion from root-zone soil leaf loss and senescence*	diffusion to air soil solution runoff soil erosion diffusion to root-zone soil water advection to root-zone soil* degradation
Root-zone soil	diffusion from ground-surface soil water advection from ground-surface soil* phloem flow from plants*	diffusion to ground-surface soil root-uptake by plants* degradation* ground water leaching*
Terrestrial vegetation	particle deposition from air* stomatal air exchange* diffusion from air* particle deposition from air* root-uptake from root-zone soil*	stomatal air exchange diffusion to air* leaf loss and senescence (advection of plant matter to ground-soil)* phloem flow to root-zone soil*

Note: Processes marked with an asterisk* are not part of Mackay's EQC model.

For the air medium, Z_{air}^{50} is obtained from the ideal gas law as $Z_{\text{air}} = 1/RT$.

The model solves a set of 6 simultaneous algebraic equations (one equation per compartment):

⁵⁰ The subscript i for the chemical is dropped from the notation in the rest of this chapter for convenience, since all equations involve a single chemical species.

$$E_j + \sum_{k \neq j} f_k D_{kj} = \left(\sum_{k \neq j} D_{jk} + D_{A,j} + D_{R,j} \right) f_j \quad (6-7)$$

where E_j is the rate of emissions into compartment j (mol/hr), D_{jk} is the D value for transport from compartment j to compartment k , $D_{A,j}$ is the D value for advective transport from medium j to areas outside the model domain, and $D_{R,j}$ is the D value for degradation in medium j . All D values have units of mol/Pa·hr. Advective D values for the atmosphere and surface water compartments may be set to zero (closed model, appropriate for global modeling) or to rates based on the average residence time of air and water inside the modeling region (open model, appropriate for regional modeling). Advective D values are used to account for sediment burial and groundwater leaching regardless of whether the model is run as an open or closed system.

COMPARTMENT PROPERTIES

The fugacity capacity definitions for all the pure phases in the model are given in Table 6-8. The bulk fugacity capacity for a compartment is the sum of the fugacity capacity for each phase in the compartment multiplied by the volume fraction that the phase occupies. Bulk fugacity capacities used in this work are shown in Table 6-9.

For substances with negligible vapor pressure the Henry's law constant might be zero, which leads to an infinite fugacity capacity for the water phase. The approach taken by Mackay and others is to use a different equilibrium criterion as the calculation basis for substances of this type⁵¹. Defining Z_{water} as 1.0 for all chemicals with negligible vapor pressure introduces the equivalence equilibrium criterion Q , with units of mol/m³, to be used in place of fugacity (this is equivalent to the use of activities instead of fugacities when dealing with solutions in chemical engineering). Table 6-10 shows the adjustments made to the Z value expressions in the case of chemicals with negligible vapor pressure.

⁵¹ Mackay calls chemicals with negligible Henry's law constants "Type 2" chemicals, while chemicals modeled with the fugacity equilibrium criterion are "Type 1" chemicals".

Table 6-8: Pure phase fugacity capacity definitions

Phase	Z	Definition
Air	Z_{air}	$\frac{1}{RT}$
Water	Z_{water}	$\frac{1}{H}$
Soil particles	Z_{sp}	$\frac{\rho_{sp}}{1,000} K_{Ds} Z_{water}$ (If K_{Ds} not available, estimated as $K_{Ds} = \phi_{sp} K_{oc}$)
Sediment particles	Z_{dp}	$\frac{\rho_{dp}}{1,000} K_{Dd} Z_{water}$ (If K_{Dd} not available, estimated as $K_{Dd} = \phi_{dp} K_{oc}$)
Suspended particles	Z_{wp}	$\frac{\rho_{wp}}{1,000} K_{Dw} Z_{water}$ (If K_{Dw} not available, estimated as $K_{Dw} = \phi_{wp} K_{oc}$)
Aerosol particles	Z_{ap}	$\left(\frac{c\theta}{v_q}\right) \frac{1}{P_L^{vap}} Z_{air}$
Vegetation lipids	Z_{pl}	$K_{ow}^m Z_{water}$

Notes: R = gas constant (8.314 J/mol·K); T = absolute temperature (K), H = Henry's law constant (Pa·m³/mol); ρ_i = solid particle density (kg/m³); K_{Di} = solids-water partition coefficient (L/kg); ϕ_i = mass fraction of organic carbon in phase i (g/g); K_{oc} = organic carbon partition coefficient (if not available estimated as $\log K_{oc} = \log K_{ow} - b + N(0,0.36)$); $c\theta$ = constant in aerosol particle fugacity model (Pa); v_q = volume fraction aerosol particles in air (m³/m³); P_L^{vap} = vapor pressure of liquid (Pa): for solids P_L^{vap} is estimated as $P_L^{vap} = P^{vap} \exp\{6.79(1-T_m/T)\}$, where P^{vap} is the solid vapor pressure (Pa), and T_m is the melting point (K); K_{ow} is the octanol-water partition coefficient (dimensionless); m = constant in the vegetation lipids fugacity model.

Table 6-9: Bulk compartment fugacity capacity definitions

Compartment	Z	Definition
Lower atmosphere	Z_a	$(1 - v_q)Z_{air} + v_q Z_{ap}$
Surface water	Z_w	$(1 - v_{wp,w})Z_{water} + v_{wp,w}Z_{wp}$
Sediments	Z_d	$(1 - v_{dp,d})Z_{water} + v_{dp,d}Z_{dp}$
Ground soil	Z_g	$v_{a,g}Z_{air} + v_{w,g}Z_{water} + (1 - v_{a,g} - v_{w,g})Z_{sp}$
Root zone soil	Z_{rz}	$v_{a,rz}Z_{air} + v_{w,rz}Z_{water} + (1 - v_{a,rz} - v_{w,rz})Z_{sp}$
Ground vegetation	Z_p	$v_{a,p}Z_{air} + v_{w,p}Z_{water} + v_{L,p}Z_{pl} + v_{sp,p}Z_{sp}$

Notes: v_{ij} is the volume fraction of pure phase i in compartment j; all other terms are defined in Table 6-8.

Table 6-10: Adjustments to Z values required for chemicals with negligible vapor pressure.

Phase or compartment	Z	Adjustments to definitions for type II chemicals
Water	Z_{water}	1
Air	Z_{air}	H
Aerosol particles	Z_{ap}	K_{qw} (if K_{qw} not available, estimated as $K_{qw} = Z_{sp}$)
Terrestrial vegetation	Z_p	$\frac{SCF_{metals}}{TSCF_{metals}} \frac{\rho_p}{1,000} Z_{water} + v_{sp,p} Z_{sp}$ (only for metals)

Notes: K_{qw} : aerosol-water partition coefficient (m^3/m^3); SCF = stem concentration factor (kg fresh mass/L), TSCF = transpiration stream concentration factor; all other terms defined in Table 6-8 or Table 6-9.

The expressions for computing the advection and degradation D values are given in Table 6-11 and Table 6-12, respectively. Note that pure phase Z values are used for the lower atmosphere and surface water degradation D value definitions, while bulk phase Z values are used for the sediments, ground soil, and root zone soil compartments.

Table 6-11: Advection D value definitions

Compartment	D_A	Definition
Lower atmosphere	$D_{A,a}$	$G_{air} Z_a$
Surface water	$D_{A,w}$	$G_{water} Z_w$
Sediments	$D_{A,d}$	$U_{burial} A_w Z_d$
Ground soil	n/a	
Root zone soil	$D_{A,rz}$	$U_{recharge} A_g Z_{water}$
Vegetation	n/a	

Notes: G_i = Advective flow out of medium i (m^3/hr); U_{burial} = sediment burial rate ($m^3/m^2 \cdot h$); A_w = Horizontal area of the model domain occupied by water (m^2); A_g = Horizontal area of the domain occupied by land (m^2); $U_{recharge}$ = ground water recharge rate ($m^3/m^2 \cdot h$).

Table 6-12 : Degradation D value definitions

Compartment	D_R	Definition
Lower atmosphere	$D_{R,a}$	$k_a V_a Z_{air}$
Surface water	$D_{R,w}$	$k_w V_w Z_{water}$
Sediments	$D_{R,d}$	$k_d V_d Z_d$
Ground soil	$D_{R,g}$	$k_s V_g Z_g$
Root zone soil	$D_{R,rz}$	$k_s V_{rz} Z_{rz}$
Vegetation	$D_{R,p}$	Neglected

Notes: k_i = first order degradation decay constant in medium i (hr^{-1}); k_i is related to the degradation half life t_i through $k_i = \ln(2)/t_i$.

INTERMEDIA TRANSPORT EQUATIONS

Table 6-13 lists the expressions used to calculate the intermedia transport D values used in the model. The definitions for the mass transfer coefficients in Table 6-13 (the U values) are given in Table 6-14. Most of the equations were taken from Mackay's EQC model or from the CalTox model. The exceptions are discussed in the following paragraphs.

Table 6-13: Intermedia transport D value definitions

From	To	Mechanism	D	Expression	Source
Lower atmosphere	Surface water	Diffusion	$D_{aw,dif}$	$\frac{A_w}{\frac{1}{U_1 Z_{air}} + \frac{1}{U_2 Z_{water}}}$	Mackay
Lower atmosphere	Surface water	Rain dissolution	$D_{aw,r}$	$A_w \min \left(U_3 Z_{water}, \frac{h_a}{t_{rain}} Z_a \right)$	This work
Lower atmosphere	Surface water	Particle deposition	$D_{aw,dep}$	$A_g [U_3 Q + U_q] y_q Z_{ap}$	Mackay
Lower atmosphere	Surface water	All	D_{aw}	$D_{aw,dif} + D_{aw,r} + D_{aw,dep}$	Mackay
Surface water	Lower atmosphere	Diffusion	D_{wa}	$D_{aw,dif}$	Mackay
Lower atmosphere	Ground-surface soil	Diffusion	$D_{ag,dif}$	$\frac{A_g}{\frac{1}{U_5 Z_{air}} + \frac{1}{U_6 Z_{water}} + \frac{1}{U_7 Z_{air}}}$	Mackay
Lower atmosphere	Ground-surface soil	Rain dissolution	$D_{ag,r}$	$A_g \min \left(U_3 Z_{water}, \frac{h_a}{t_{rain}} Z_a \right)$	This work
Lower atmosphere	Ground-surface soil	Particle deposition	$D_{ag,dep}$	$A_g U_{23} Z_{ap}$	This work
Lower atmosphere	Ground-surface soil	All	D_{ag}	$D_{ag,dif} + D_{ag,r} + D_{ag,dep}$	Mackay
Ground-surface soil	Lower atmosphere	Diffusion	D_{ga}	$D_{ag,dif}$	Mackay
Surface water	Sediments	Diffusion	$D_{wd,dif}$	$A_w U_8 Z_{water}$	Mackay
Surface water	Sediments	Deposition	$D_{wd,dep}$	$A_w U_9 Z_{wp}$	Mackay
Surface water	Sediments	All	D_{wd}	$D_{wd,dif} + D_{wd,dep}$	Mackay
Sediments	Surface water	Resuspension	$D_{dw,res}$	$A_w U_{10} Z_{dp}$	Mackay
Sediments	Surface water	All	D_{dw}	$D_{wd,dif} + D_{dw,res}$	Mackay
Ground-surface soil	Surface water	Soil water runoff	$D_{gw,run}$	$A_g U_{11} Z_{water}$	Mackay
Ground-surface soil	Surface water	Erosion	$D_{gw,e}$	$A_g U_{12} Z_{sp}$	Mackay

From	To	Mechanism	D	Expression	Source
Ground-surface soil	Surface water	All	D_{gw}	$D_{gw,run} + D_{gw,e}$	Mackay
Ground-surface soil	Root-zone soil	Diffusion	$D_{g,rz,dif}$	$\frac{A_g}{\frac{1}{U_5 Z_{air} + U_6 Z_{water}} + \frac{1}{U_{13} Z_{air} + U_{14} Z_{water}}}$	CalTox
Ground-surface soil	Root-zone soil	Water advection	$D_{g,rz,adv}$	$A_g U_{15} Z_{water}$	CalTox
Ground-surface soil	Root-zone soil	All	$D_{g,rz}$	$D_{g,rz,dif} + D_{g,rz,adv}$	CalTox
Root-zone soil	Ground-surface soil	Diffusion	$D_{rz,g}$	$D_{g,rz,dif}$	CalTox
Root-zone soil	Terrestrial vegetation	Root uptake	$D_{rz,p}$	$A_g U_{16} Z_{water} TSCF$	This work
Terrestrial vegetation	Root-zone soil	Phloem flow	$D_{p,rz}$	$A_g U_{17} Z_{phl}$	CalTox
Terrestrial vegetation	Ground soil	Leaf loss and senescence	D_{pg}	$A_g U_{18} Z_p$	CalTox
Lower atmosphere	Terrestrial vegetation	Particle deposition	$D_{ap,dep}$	$A_g U_{19} Z_{ap}$	CalTox
Lower atmosphere	Terrestrial vegetation	Stomatal air exchange	$D_{ap,stom}$	$A_g LAI U_{20} Z_{air}$	CalTox
Lower atmosphere	Terrestrial vegetation	Diffusion	$D_{ap,dif}$	$\frac{A_g \times LAI}{\frac{1}{U_{21} Z_{air} + U_{22} Z_{water}} + \frac{1}{U_7 Z_{air}}}$	CalTox
Lower atmosphere	Terrestrial vegetation	All	D_{ap}	$D_{ap,dep} + D_{ap,stom} + D_{ap,dif}$	CalTox
Terrestrial vegetation	Lower atmosphere	All	D_{pa}	$D_{ap,stom} + D_{ap,dif}$	This work

Notes: U_i = Mass transport coefficient (m/hr), defined in Table 6-14; h_a = height of the lower atmosphere compartment (m); t_{rain} = average duration of interval between rainfall events (hr); Z_{phl} = fugacity capacity of phloem liquid = $f_{w,phl} Z_{water}$, where $f_{w,phl}$ is the volume fraction of water in the phloem liquid; LAI = leaf area index (m^2 leaves/ m^2 ground).

Table 6-14: Mass transfer coefficient definitions

U	Description	Expression	Source of Expression
U ₁	Air side, air-water MTC (m/hr)	Model parameter	
U ₂	Water side, air-water MTC (m/hr)	Model parameter	
U ₃	Rain rate (m ³ /m ² ·hr)	Model parameter	
U ₄	Aerosol wet and dry deposition	$(U_3Q + U_q)v_q$	Mackay
U ₅	Ground-soil:air phase diffusion MTC	$D_{Ag,eff}/(h_g/2)$ where $D_{Ag,eff} = v_{a,g}^{10/3}/(v_{a,g} + v_{w,g})^2]D_A$	Mackay CalTox
U ₆	Ground soil:water phase diffusion MTC	$D_{Wg,eff}/(h_g/2)$ where $D_{Wg,eff} = v_{w,g}^{10/3}/(v_{a,g} + v_{w,g})^2]D_W$	Mackay CalTox
U ₇	Air side, air-ground MTC	D_A/δ_{ag}	CalTox
U ₈	Sediment-water MTC	$\frac{1}{\delta_{wd}/D_W + (d_d/2)/D_{wd,eff}}$ where $D_{wd,eff} = v_{w,d}^{4/3}D_W$	CalTox
U ₉	Sediment deposition (m ³ /m ² ·hr)	Model parameter	
U ₁₀	Sediment resuspension	$f_{resusp}U_9$	Mackay
U ₁₁	Soil-water runoff	$f_{runoff}U_3$	Mackay
U ₁₂	Soil-solids runoff (erosion rate)	$U_{11}v_{ss,runoff}$	Mackay
U ₁₃	Root zone-soil:air phase diffusion MTC	$D_{Arz,eff}/(h_{rz}/2)$ where $D_{Arz,eff} = v_{a,rz}^{10/3}/(v_{a,rz} + v_{w,rz})^2]D_A$	Mackay CalTox
U ₁₄	Root zone soil:water phase diffusion MTC	$D_{Wtz,eff}/(h_g/2)$ where $D_{Wtz,eff} = v_{w,tz}^{10/3}/(v_{a,tz} + v_{w,tz})^2]D_W$	Mackay CalTox
U ₁₅	Recharge rate	$f_{recharge}U_3$	CalTox
U ₁₆	Transpiration rate	$(U_3 - U_{11} - U_{15}) \times \min(1.0, 0.43m^2/kg \times bio_{inv})$	This work
U ₁₇	Phloem flow rate	$f_{phl}U_{16}$	CalTox
U ₁₈	Leaf loss and senescence	d_p/τ_p	CalTox
U ₁₉	Aerosol deposition on plants	$U_q f_{int} v_q$	CalTox
U ₂₀	Stomata conductance	$(D_A/D_{wv-A})U_{wv-stom}$	CalTox
U ₂₁	Plant soil layer:air phase diffusion MTC	$D_{Ag,eff}/(\delta_{slyr}/2)$	CalTox
U ₂₂	Plant soil layer:water phase diffusion MTC	$D_{Wg,eff}/(\delta_{slyr}/2)$	CalTox
U ₂₃	Aerosol deposition on ground soil	$(U_3Q + (1 - f_{int})U_q)v_q$	This work

Notes: Q = particle scavenging ratio by rain (m³/m³); U_q = Aerosol dry deposition velocity (m/hr); $D_{Ai,eff}$ = effective diffusion coefficient in air phase of compartment i (m²/hr); h_i = depth or compartment i (m); D_A = diffusion coefficient in air (m²/hr); $D_{Wi,eff}$ = effective diffusion coefficient in water phase of compartment i (m²/hr); D_W = diffusion coefficient in water (m²/hr); δ_{ij} = thickness of boundary layer between compartments i and j (m); f_{resusp} = ratio of sediment resuspension rate to sediment deposition rate (dimensionless); f_{runoff} = ratio of runoff to precipitation (dimensionless); $v_{ss,runoff}$ = volume fraction of suspended solids in runoff water (m³/m³); bio_{inv} = terrestrial vegetation dry mass inventory (kg/m²); f_{phl} = ratio of phloem flow to transpiration rate (dimensionless); τ_p = effective lifetime of above-ground biomass (hrs); f_{int} = fraction of particles deposited over land area by dry deposition intercepted by plants (dimensionless); D_{wv-A} = diffusion coefficient for water vapor in air (m²/h); $U_{wv-stom}$ = conductance of water vapor through stomata (m/hr); δ_{slyr} = thickness of soil layer on plant surfaces (m).

Rain dissolution

The equations for transport from air to water or soil by rain dissolution used in Mackay's model are:

$$D_{aw,r} = U_3 A_w Z_{water} \quad (6-8)$$

and

$$D_{ag,r} = U_3 A_g Z_{water} \quad (6-9)$$

These equations in effect assume that rain takes place continuously. For compounds with low Henry's law constants the resulting persistence in air can be much less than an hour (for sulfuric acid, the model calculates a persistence of about 20 seconds, which is obviously too low). The solution adopted here is to set a ceiling on the rain dissolution transfer rate based on the frequency of rain events. The values of $D_{rw,max}$ and $D_{rs,max}$ are calculated by setting the minimum residence time due to rain dissolution to be equal to the average interval between rain events (t_{rain}):

$$D_{aw,r(max)} = \frac{V_{air} Z_a}{t_{rain}} \frac{A_w}{A_w + A_g} = \frac{h_a}{t_{rain}} A_w \quad (6-10)$$

and

$$D_{ag,r(max)} = \frac{V_{air} Z_a}{t_{rain}} \frac{A_g}{A_w + A_g} = \frac{h_a}{t_{rain}} A_g \quad (6-11)$$

The rain dissolution transport equations used are then:

$$D_{aw,r} = A_w \min \left(U_3 Z_{water}, \frac{h_a}{t_{rain}} Z_a \right) \quad (6-12)$$

and

$$D_{ag,r} = A_g \min \left(U_3 Z_{water}, \frac{h_a}{t_{rain}} Z_a \right) \quad (6-13)$$

as shown in Table 6-13.

A comparison between the two cases is shown in Figure 6-4, where the atmospheric persistence of emissions to air of the substances listed in the United States toxic release inventory (TRI) [24] is calculated according to both methods. Assuming continuous rain can lead to gross underestimates of atmospheric persistence for substances with very low Henry's law constants (an extreme example is phosphoric acid, for which the difference between the two

approaches is seven orders of magnitude). A similar observation was made by Hertwich in his doctoral dissertation with respect to the rain dissolution and wet deposition equations in the CalTox model [14]. The approach taken by Hertwich was to remove rain from the model. Figure 6-5 compares the approach used in this work to that taken by Hertwich. For a handful of substances in the TRI neglecting the rain dissolution mechanism leads to a moderate overestimation of persistence in air.

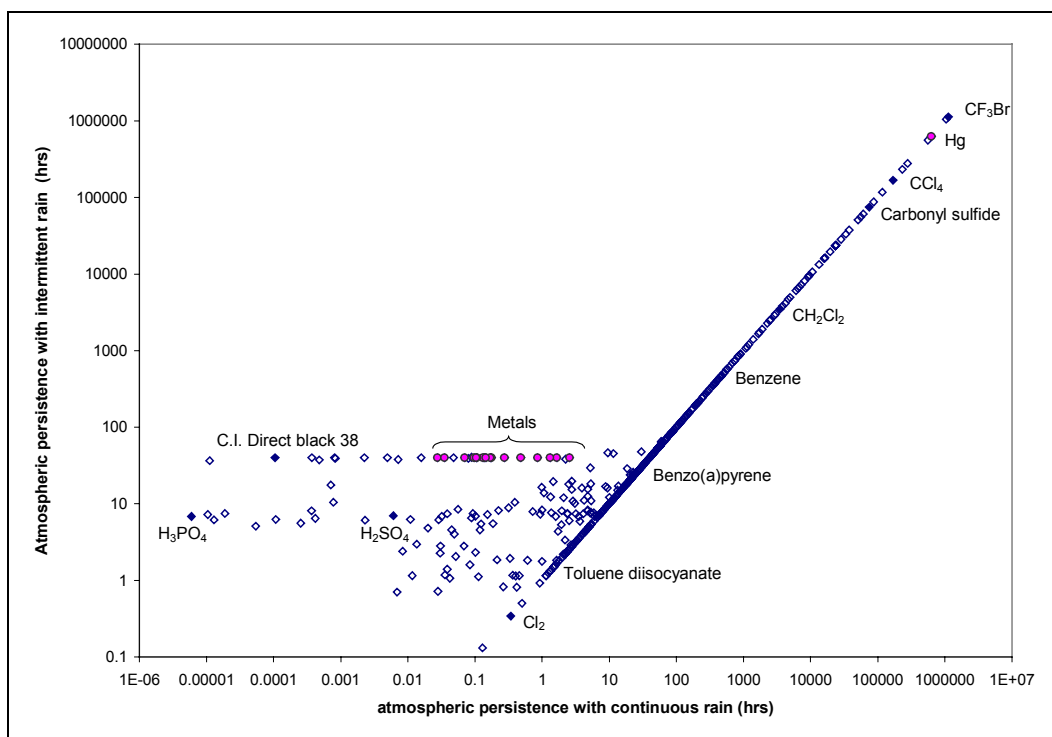


Figure 6-4: Comparison between the continuous and intermittent rain approaches to estimating rain dissolution transport rates (persistence of emissions of TRI substances to air).

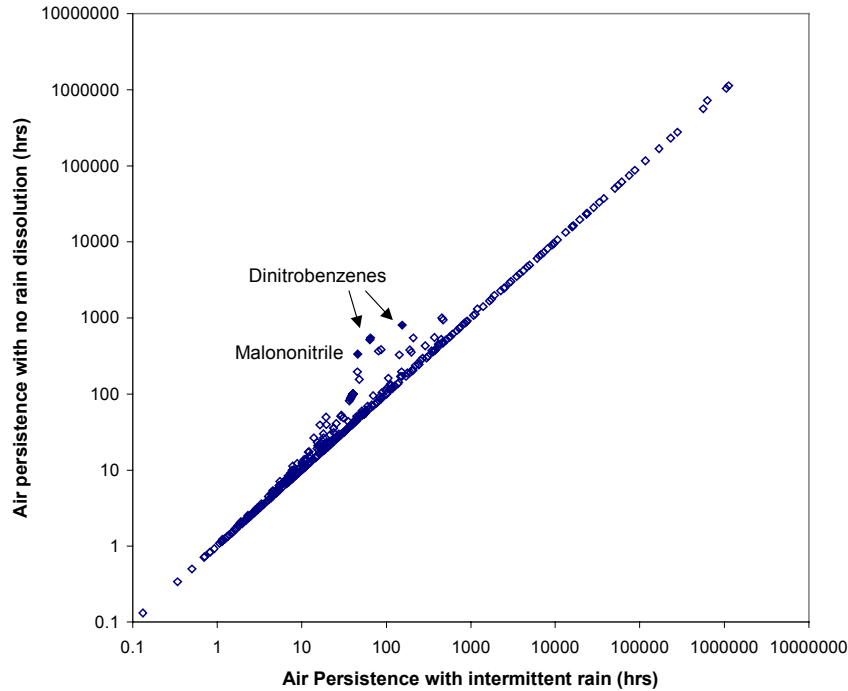


Figure 6-5: Sensitivity of the fate and transport model to the exclusion of the rain dissolution mechanism (persistence of emissions of TRI substances to air).

Particle deposition

Particles deposit through two mechanisms: dry deposition and scavenging by rain. For deposition to surface water, the particle deposition mass transfer coefficient is given by:

$$U_4 = (U_3Q + U_q)v_q \quad (6-14)$$

For deposition to land there are two types of surfaces available for deposition (ground-surface soil and terrestrial vegetation), and the combined particle deposition mass transfer coefficient should be allocated between the two. It is assumed that particles scavenged by rain do not adhere to plants and are deposited directly to ground soil. For particles deposited from air by dry deposition an interception factor (f_{int}) is used, calculated according to the equation used in the CalTox model:

$$f_{int} = 1 - \exp(-2.8 \text{ m}^2/\text{kg} \times bio_{inv}) \quad (6-15)$$

Under these assumptions, the mass transfer coefficients for particle deposition to ground-surface soil and terrestrial vegetation are given, respectively, by:

$$U_{23} = (U_3Q + (1-f_{int})U_q)v_q \quad (6-16)$$

and

$$U_{19} = U_q f_{int} v_q \quad (6-17)$$

with the sum of U_{23} and U_{19} being equal to U_4 .

Root uptake

In the CalTox model, the transfer of contaminants from root-zone soil to plants through root uptake (transpiration) is estimated as

$$D_{rz,p} = A_g U_{transpire} Z_{water} \quad (6-18)$$

where $U_{transpire}$ is calculated as a fraction of the balance between rain (U_3), runoff (U_{11}) and groundwater recharge (U_{15}):

$$U_{transpire} = (U_3 - U_{11} - U_{15}) f_{transpire} \quad (6-19)$$

where $f_{transpire}$ is the fraction of the evapotranspiration water flux from soil that is due to transpiration. CalTox models $f_{transpire}$ as a function of the vegetation density:

$$f_{transpire} = 0.43 \text{ m}^2/\text{kg} \times bio_{inv} \quad (6-20)$$

Two modifications were made to the CalTox equations. First, $f_{transpire}$ is constrained to be less or equal than 1.0:

$$U_{16} = (U_3 - U_{11} - U_{15}) \times \min(1.0, 0.43 \text{ m}^2/\text{kg} \times bio_{inv}) \quad (6-21)$$

The second modification made is to adjust the flux in eq (6-18) to take into account the transpiration stream concentration factor ($TSCF$):

$$D_{rz,p} = A_g U_{transpire} Z_{water} TSCF \quad (6-22)$$

The $TSCF$ is defined as the ratio of the concentration of a chemical in the transpiration stream to that in soil water, and is dependent upon lipophilicity (see section 6.3.2 for details)

Atmosphere-vegetation exchange

The transfer of chemicals from air to plants is the sum of three contributions: stomatal gas exchange, diffusion through leaves, and particle deposition:

$$Flux_{ap} = D_{ap} f_a = (D_{ap, stom} + D_{ap, dif} + D_{ap, dep}) f_a \quad (6-23)$$

The CalTox model sets $D_{pa} = D_{ap}$. This assumes that the rate of particle deposition on to leaf surfaces is balanced by the removal of these particles by wind. If further assumes that particles achieve thermodynamic equilibrium with leaves before their removal. This assumption is dropped here, and particle resuspension from leaves is neglected. This leads to

$$Flux_{pa} = D_{paf_a} = (D_{ap, stom} + D_{ap, dif})f_p \quad (6-24)$$

SOLUTION METHOD

Chemical fugacities in each of the six environmental compartments in the model are found by solving the following system of equations:

$$E_a - D_{T,af_a} + D_{waf_w} + D_{gaf_g} + D_{paf_p} = 0 \quad (6-25)$$

$$E_w + D_{awf_a} - D_{T,wf_w} + D_{gwf_g} + D_{dwf_d} = 0 \quad (6-26)$$

$$E_g + D_{agf_a} - D_{T,gf_g} + D_{rzgf_{rz}} + D_{pgf_p} = 0 \quad (6-27)$$

$$+ D_{grzf_g} - D_{T,rzf_{rz}} + D_{przf_p} = 0 \quad (6-28)$$

$$+ D_{wdf_w} - D_{T,df_d} = 0 \quad (6-29)$$

$$+ D_{apf_a} + D_{rzpf_{rz}} - D_{T,pf_p} = 0 \quad (6-30)$$

where the $D_{T,i}$ terms are the total losses from compartment i , including reaction, advection and transfer to other compartments, as shown in eqs (6-31) to (6-36) below:

$$D_{T,a} = D_{aw} + D_{ag} + D_{ap} + D_{R,a} + D_{A,a} \quad (6-31)$$

$$D_{T,w} = D_{wa} + D_{wd} + D_{R,w} + D_{A,w} \quad (6-32)$$

$$D_{T,g} = D_{ga} + D_{gw} + D_{grz} + D_{R,g} \quad (6-33)$$

$$D_{T,rz} = D_{rzg} + D_{rzp} + D_{R,rz} + D_{A,rz} \quad (6-34)$$

$$D_{T,d} = D_{dw} + D_{R,d} + D_{A,d} \quad (6-35)$$

$$D_{T,p} = D_{pa} + D_{pg} + D_{prz} \quad (6-36)$$

The solution to the system of equations (6-25) to (6-30) is given by:

$$f_{rz} = \frac{\frac{D_{ap}D_{prz}}{D_{T,p}}(b_2 + a_3b_3) + D_{grz}b_3}{D_{T,rz} - D_{grz}a_5 - \frac{D_{prz}}{D_{T,p}}(D_{ap}(a_3a_5 + a_4) + D_{rzp})} \quad (6-37)$$

$$f_g = b_3 + a_5f_{rz} \quad (6-38)$$

$$f_a = b_2 + a_3f_g + a_4f_{rz} \quad (6-39)$$

$$f_w = b_1 + a_1f_a + a_2f_g \quad (6-40)$$

$$f_d = \frac{D_{wd}}{D_{T,w}}f_w \quad (6-41)$$

$$f_p = \frac{D_{ap}f_a + D_{rzp}f_{rz}}{D_{T,p}} \quad (6-42)$$

where:

$$d_1 = D_{T,w} - \frac{D_{wd}D_{dw}}{D_{T,d}} \quad (6-43)$$

$$a_1 = \frac{D_{aw}}{d_1} \quad (6-44)$$

$$a_2 = \frac{D_{gw}}{d_1} \quad (6-45)$$

$$b_1 = \frac{E_w}{d_1} \quad (6-46)$$

$$d_2 = D_{T,a} - \frac{D_{ap}D_{pa}}{D_{T,p}} - D_{wa}a_1 \quad (6-47)$$

$$a_3 = \frac{D_{wa}a_2 + D_{ga}}{d_2} \quad (6-48)$$

$$a_4 = \frac{D_{rzp}D_{pa}}{D_{T,p}d_2} \quad (6-49)$$

$$b_2 = \frac{E_a + D_{wa}b_1}{d_2} \quad (6-50)$$

$$d_3 = D_{T,g} - D_{ag}a_3 - \frac{D_{ap}D_{pg}}{D_{T,p}}a_3 \quad (6-51)$$

$$b_3 = \frac{E_g + \left(D_{ag} + \frac{D_{pg}D_{ap}}{D_{T,p}} \right) b_2}{d_3} \quad (6-52)$$

$$a_5 = \frac{D_{ag}a_4 + \frac{D_{pg}}{D_{T,p}}(D_{ap}a_4 + D_{rzp}) + D_{rzg}}{d_3} \quad (6-53)$$

PARAMETRIC UNCERTAINTIES

The tables in this chapter contain the parameter distributions used in the implementation of the multimedia fate and transport model. Lognormal distributions have been used for all of the parameters. In this work, lognormal distributions are characterized by two parameters: the central value⁵² ($X_{(50)}$), and the uncertainty factor (UF). The lognormal density function is related to these two parameters by:

$$f(x) = \frac{1}{x \sqrt{2\pi \left(\frac{\ln UF}{2}\right)^2}} \exp\left(-\frac{(\ln x - \ln X_{(50)})^2}{2 \left(\frac{\ln UF}{2}\right)^2}\right) \quad (6-54)$$

The 95% confidence interval for a random variable described by a lognormal distribution with parameters $X_{(50)}$ and UF is the given by $(X_{(50)} \div UF, MLV_{(50)} \times UF)$ ⁵³. The moments of the lognormal distribution are given by:

$$Mean = X_{(50)} \exp\left(\frac{(\ln \sqrt{UF})^2}{2}\right) \quad (6-55)$$

and

$$Variance = X_{(50)}^2 \exp\left(\left(\ln \sqrt{UF}\right)^2\right) \left[\exp\left(\left(\ln \sqrt{UF}\right)^2\right) - 1\right] \quad (6-56)$$

The UF is also equal to the geometric standard deviation squared (σ_g^2). Finally, the UF is related to the coefficient of variation, CV , by

$$UF = \left(\exp\left\{\sqrt{\ln(1 + CV^2)}\right\}\right)^2 \quad (6-57)$$

where CV is defined as the ratio of the standard deviation to the mean of the distribution. The CalTox model uses the mean value and the CV to parametrize lognormal distributions [25,26]. Although mathematically equivalent, the $(X_{(50)}, UF)$ parametrization is preferred to the (mean value, CV) parametrization, since the former can easily be translated into confidence intervals. $X_{(50)}$ and UF values presented in the tables in this section that list the CalTox model as their

⁵² The central value is defined as the median of the distribution. The median is also the 50th percentile value, meaning that 50% of the values in the distribution will be below this value.

⁵³ The shorthand notation $x \sim \text{LogN}(a,b)$ is used throughout this thesis to describe random variables that are lognormally distributed with parameters $X_{(50)}=a$ and $UF=b$.

source were obtained by applying eqs (6-55) and (6-57) to the parameters used by the CalTox model.

Equations for parameters used in Table 6-8 through Table 6-14 that are calculated as a function of other parameters are also shown in the tables below.

Table 6-15: Distributions for the parameters describing the lower atmosphere compartment

Symbol	Parameter Name	Central value	Source of central value	Uncertainty factor	Source of UF
A	Model domain area	$10 \times 10^{12} \text{ m}^2$	This work	n/a	calculation basis
h_a	Atmospheric mixing height	1000 m	[20]	2.45	This work ^a
U_{wind}	Yearly average wind speed	1.44 m/s	[25]	3.4	[25]
t_{rain}	Interval between rain events	72 hrs	This work (subjective)	2.0	This work (subjective)
v_q	Volume fraction of aerosols in atmosphere	10×10^{-11}	[20]	3.2	[25]
T	Annual mean temperature	288 K	[27]	1.05	This work (subjective)
$c\theta$	aerosol fugacity correlation constant	$3.57 \times 10^{10} (v_q)^{0.4}$	estimated from data in [27]		
V_a	Air compartment volume	$A \cdot h_a$	[20]		
t_a	Air compartment advection residence time ^b	$\frac{\sqrt{A}}{0.23 \times U_{\text{wind}}}$	[27]		
G_a	Advective flow out of air compartment	$\frac{V_a}{t_a}$	[20]		

a) An UF of $6^{0.5}$ was chosen so that the maximum value of h_a (arbitrarily defined as the 0.99997 fractile of the lognormal distribution) would not exceed 6000 m (the global average value).

b) Used when the model is run as an open system. If the model is run as a closed system $t_a = \infty$.

Table 6-16: Distributions for the parameters describing the surface water compartment

Symbol	Parameter Name	Central value	Source of central value	Uncertainty factor	Source of UF
f_{water}	Fraction of landscape surface occupied by surface water	0.10	[20]	2.65	This work ^a
h_w	Surface water mixed depth	20 m	[20]	2.24	This work ^b
ρ_{water}	Water density	1000 kg/m ³	[20]	–	Well known parameter
t_{water}	Advective residence time ^c	1000 hrs	[20]		
$v_{\text{wp,w}}$	Volume fraction of suspended sediments in surface water	5×10^{-6}	[20]	5.3	[25]
ϕ_{wp}	Organic carbon content of suspended sediment particles	20% by volume	[20]	1.1	This work ^d
ρ_{wp}	Suspended sediment particle density	1500 kg/m ³	[20]	1.1	[25]
A_w	Area occupied by surface water	$A \cdot f_{\text{water}}$	[20]		
V_w	Surface water compartment volume	$A_w \cdot h_w$	[20]		
G_w	Advective flow out of surface water compartment	$\frac{V_w}{t_w}$	[20]		

- a) An UF of $7^{0.5}$ was chosen so that the maximum value of f_{water} (arbitrarily defined as the 0.99997 fractile of the lognormal distribution) would not exceed 70% (the global average value).
- b) An UF of $5^{0.5}$ was chosen so that the maximum value of h_w (arbitrarily defined as the 0.99997 fractile of the lognormal distribution) would not exceed 100 m (the global average value for the oceans).
- c) Used when the model is run as an open system. If the model is run as a closed system = ∞ .
- d) An UF of $(1.2)^{0.5}$ was chosen so that the maximum value of ϕ_{wp} (arbitrarily defined as the 0.99997 fractile of the lognormal distribution) would not exceed 25% (the maximum value cited by Mackay).

Table 6-17: Distributions for the parameters describing the soil compartments

Symbol	Parameter Name	Central value	Source of central value	Uncertainty factor	Source of UF
h_g	Ground surface soil depth	0.007 m	[25]	5.29	[25]
h_{rz}	Root-zone soil depth	0.80 m	[25]	2.53	[25]
ϕ_{sp}	Organic carbon content of soil particles	2.0% by volume	[20]	2.0	This work ^a
ρ_{sp}	Soil particle density	2400 kg/m ³	[20]	1.1	[25]
$v_{a,g}$	Volume fraction of air in ground surface soil	0.24	[25]	1.6	[25]
$v_{w,g}$	Volume fraction of water in ground surface soil	0.13	[25]	1.8	[25]
$v_{a,rz}$	Volume fraction of air in root-zone soil	0.21	[25]	1.8	[25]
$v_{w,rz}$	Volume fraction of water in root-zone soil	0.12	[25]	1.8	[25]
b	Contant in the organic carbon partitioning model	0.35	This work, based on data in [20,27]	1.05	This work, based on data in [20,27]
A_g	Area occupied by soil	$A_g \cdot (1 - f_{water})$	[20]		
V_g	Volume of the ground surface soil compartment	$A_g \cdot h_g$	[27]		
V_{rz}	Volume of the root-zone soil compartment	$A_g \cdot h_{rz}$	[27]		

- a) An UF of $(4)^{0.5}$ was chosen so that the maximum value of f_{oc} (arbitrarily defined as the 0.99997 fractile of the lognormal distribution) would not exceed 8% (the maximum value cited by Mackay).

Table 6-18: Distributions for the parameters describing the sediments compartment

Symbol	Parameter Name	Central value	Source of central value	Uncertainty factor	Source of UF
h_d	Depth of sediments	0.05 m	[20]	5.3	[25]
ϕ_{dp}	Organic carbon content of sediment particles	4.0% by volume	[20]	2.5	This work ^a
ρ_{dp}	Sediment particle density	2400 kg/m ³	[20]	1.1	[25]
$v_{s,d}$	Volume fraction of solids in sediments	0.2	[20]	2.0	This work ^b
V_d	Volume of the sediments compartment	$A_w \cdot h_d$	[20]		

- a) An UF of $(0.25/0.04)^{0.5}$ was chosen so that the maximum value of ϕ_{dp} (arbitrarily defined as the 0.99997 fractile of the lognormal distribution) would not exceed 25% (the maximum value cited by Mackay)
- b) An UF of $(4)^{0.5}$ was chosen so that the maximum value of $v_{s,d}$ (arbitrarily defined as the 0.99997 fractile of the lognormal distribution) would not exceed 80% (the maximum value cited by Mackay).

Table 6-19: Distributions for the parameters describing the terrestrial vegetation compartment

Symbol	Parameter Name	Central value	Source of central value	Uncertainty factor	Source of UF
h_p	Equivalent depth of terrestrial vegetation compartment	0.01 m	[28]	5.6	[25]
f_{dm}	Terrestrial vegetation dry matter fraction	20%, by weight	[25]	2.2	[25]
f_{above}	Fraction of terrestrial vegetation dry mass above ground	0.50	[29]	–	not assessed
ρ_p	Terrestrial vegetation fresh mass density	810 kg/m ³	[25]	1.5	[25]
$V_{a,p}$	Volume fraction of air in terrestrial vegetation tissues	0.20	Table 6-29	–	uncertainty in UF_Kpa dominates
$V_{w,p}$	Volume fraction of water in terrestrial vegetation tissues	0.64	Table 6-29	–	uncertainty in UF_Kpa dominates
$V_{L,p}$	Volume fraction of lipids in terrestrial vegetation tissues	0.012	Table 6-29	–	uncertainty in UF_Kpa dominates
m	Exponent of K_{ow} in the equation $Z_{pl} = K_{ow}^m Z_{water}$	0.89	Table 6-29	1.13	Table 6-29
UF_Kpa	Uncertainty factor associated with the leaf-air partition coefficient correlation ^a	100	[30]	n/a	
δ_{slyr}	Thickness of soil layer on vegetation surfaces	5×10 ⁻⁶ m	[29]	–	not assessed
$f_{w,phl}$	Volume fraction of water in phloem sap	0.90	[26]	–	not assessed
τ_p	Effective lifetime of above-ground biomass tissues	4320 hrs	[29]	–	not assessed
SCF _{metals}	Default stem concentration factor for metals	120 L/kg fresh plant	[18]	–	not assessed
V_p	Volume of terrestrial vegetation compartment	$A_g \cdot h_p$	[28]		
bio _{inv}	Terrestrial vegetation dry mass inventory	$\frac{d_p \rho_p f_{dm}}{f_{above}}$	[26]		
LAI	Leaf area index	$5.6 \frac{m^2}{kg} bio_{inv}$	[26]		
$V_{sp,v}$	Volume fraction of soil particles on vegetation surfaces	$\frac{\delta_{slyr} LAI \times A_g}{V_p}$	This work		
TSCF _{metals}	Default transpiration stream concentration factor for metals	TSCF _{max}	This work (assumed)		

a) In the spreadsheet model, a correction factor modeled as LogN(1,100) is used to account for the uncertainty in the estimation of vegetation-air partition coefficients.

Table 6-20: Distributions for the parameters used to calculate transport rates

Symbol	Parameter Name	Central value	Source of central value	Uncertainty factor	Source of UF
U_1	Air side, air-water MTC	5 m/hr	[20]	–	not assessed
U_2	Water side, air-water MTC	0.022 m/hr	This work, based on data in [20,27]	1.5	This work, based on data in [20,27]
U_3	Rain rate	0.474 m/yr	[20]	2.8	[25]
U_9	Sediment deposition rate	5×10^{-7} m ³ /m ² /hr	[20]	3.0	This work (subjective)
Q	Aerosol rain scavenging ratio	2×10^5	[20]	10	
U_q	Aerosol dry deposition velocity	10 m/h	[20]	8.8	[25]
D_A	Diffusion coefficient in air	0.02 m ² /hr	[20]	3.2	This work, based on data in [27]
D_W	Diffusion coefficient in water	2×10^{-6} m ² /hr	[20]	3.2	This work, based on data in [27]
δ_{ag}	Thickness of air-soil boundary layer	0.005 m	[25]	1.49	[25]
δ_{wd}	Thickness of water-sediments boundary layer	0.02 m	[20]	–	not assessed
f_{resusp}	ratio of sediment resuspension rate to sediment deposition rate	0.40	[28]	1.25	This work, based on data in [28]
f_{runoff}	ratio of runoff to precipitation rates	0.50	[20]	1.37	[25]
$f_{recharge}$	ratio of ground water recharge to precipitation rates	0.006	[27]	2.0	This work (subjective)
f_{phl}	ratio of phloem flow to transpiration rate	0.1	[29]	–	not assessed
D_{wv-A}	diffusion coefficient for water vapor in air	0.086 m ² /hr	[29]	–	not assessed
$U_{wv-stom}$	conductance of water vapor through stomata	376 m/day	[29]	–	not assessed
$V_{ss,runoff}$	Runoff solids volume fraction	2×10^{-4}	[20]	2.0	This work (subjective)

6.3.2 Human exposure model

The exposure model links modeled environmental concentrations to human exposure. Two intake routes are considered: ingestion and inhalation. A third route (dermal exposure) is included in the CalTox model, but not used here. Sensitivity analysis carried out on a large set of chemicals (see Section 6.4.1) showed that this route had a negligible contribution to total human exposure for emissions to air and water. It was therefore omitted from the final model. The total human exposure is the sum of the product of exposure media contact rates (R_i) times exposure media concentrations (C_i):

$$\boxed{Exposure = \sum_i R_i C_i} \quad (6-58)$$

EXPOSURE PATHWAYS AND EXPOSURE MEDIA CONTACT RATES

There are 9 exposure media in the model: air, bathroom air, tap water, fish, aboveground crops, root crops, beef, milk, and eggs. Concentrations and contact rates with these media are used to derive indicators of human exposure via the inhalation and oral routes. These indicators are given by:

$$\boxed{Dose_{inh} = \frac{R_{bath\ air} C_{bath\ air} + R_{air} C_{air}}{(\sum E_j)/A}} \quad (6-59)$$

and

$$\boxed{Dose_{oral} = \frac{R_{tapwater} C_{tapwater} + R_{leafcrops} C_L + R_{rootcrops} C_{rootcrops} + R_{fish} C_{fish} + R_{milk} C_{milk} + R_{beef} C_{beef} + R_{eggs} C_{eggs}}{(\sum E_j)/A}} \quad (6-60)$$

where the doses calculated by the model are normalized by the ratio of emissions to landscape area. The final dose indicators have therefore units of [(mg/kg/day)/(kg/km²/day)].

The expressions used to calculate the exposure media contact rates (the R_i in eqs (6-59) and (6-60)) are listed in Table 6-21. Table 6-22 shows the distributions for the parameters in the exposure media contact rate expressions used. The model estimates exposure media concentrations on the basis of environmental media concentrations calculated by the fate and transport model. The estimation of five auxiliary quantities is also required: concentrations in irrigated ground surface and root-zone soils, and daily intakes by dairy cattle, beef cattle, and

hens. There are a total of 35 exposure pathways linking environmental media concentrations to human intake. These pathways are summarized in Table 6-23.

Table 6-21: Exposure media contact rate expressions

Exposure medium	Type of contact	Contact rate expression	Contact rate units
Bathroom air	inhalation	$ET_{\text{bath}} \times BR_{\text{active}}$	$\text{m}^3/\text{kg}/\text{day}$
Air	inhalation	$ET_{\text{resting}} \times BR_{\text{resting}} + (24 - ET_{\text{bath}} - ET_{\text{resting}}) \times BR_{\text{active}}$	$\text{m}^3/\text{kg}/\text{day}$
Tap water	ingestion	$IR_{\text{tap water}}$	$\text{m}^3/\text{kg}/\text{day}$
Aboveground crops	ingestion	$IR_{\text{grain}} + IR_{f/v} f_{\text{above}}$	$\text{kg}/\text{kg}/\text{day}$
Root crops	ingestion	$IR_{f/v} (1 - f_{\text{above}})$	$\text{kg}/\text{kg}/\text{day}$
Fish	ingestion	IR_{fish}	$\text{kg}/\text{kg}/\text{day}$
Milk	ingestion	IR_{milk}	$\text{kg}/\text{kg}/\text{day}$
Beef	ingestion	IR_{beef}	$\text{kg}/\text{kg}/\text{day}$
Eggs	ingestion	IR_{eggs}	$\text{kg}/\text{kg}/\text{day}$

Table 6-22: Distributions for the parameters in the exposure media contact rate expressions

Symbol	Parameter name	Central value	Uncertainty factor
ET_{bath}	Exposure time in shower or bath	0.23 hrs/day	3
BR_{active}	Active breathing rate	0.0182 $\text{m}^3/\text{kg}/\text{hr}$	1.8
BR_{resting}	Resting breathing rate	0.0063 $\text{m}^3/\text{kg}/\text{hr}$	1.5
ET_{resting}	Exposure time, resting	8 hrs/day	1.1
$IR_{\text{tap water}}$	Tap water ingestion rate	0.022 L/kg/day	1.5
IR_{grain}	Grain ingestion rate	0.0036 kg/kg/day	1.5
$IR_{f/v}$	Fruits and vegetables ingestion rate	0.0048 kg/kg/day	1.5
f_{above}	Fraction of ingested fruit and vegetables that are aboveground crops	0.47	1.2
IR_{fish}	Fish ingestion rate	0.00027 kg/kg/day	2.2
IR_{milk}	Milk ingestion rate	0.0064 kg/kg/day	1.5
IR_{beef}	Beef ingestion rate	0.0029 kg/kg/day	1.5
IR_{eggs}	Eggs ingestion rate	0.00044 kg/kg/day	1.8

Note: Parameter values and uncertainty factors taken from [26].

Table 6-23: Exposure pathways in the exposure model

Environmental medium	Intermediate pathway steps		Exposure medium	Intake Route		
Air (gas and aerosols)				→ Inhalation		
			→ Aboveground crops	→ Ingestion		
	→ Inhalation by dairy cattle		→ Milk	→ Ingestion		
	→ Inhalation by beef cattle		→ Beef	→ Ingestion		
	→ Inhalation by hens		→ Eggs	→ Ingestion		
Ground soil				→ Aboveground crops		
	→ Ingestion by dairy cattle		→ Milk	→ Ingestion		
	→ Ingestion by beef cattle		→ Beef	→ Ingestion		
	→ Ingestion by hens		→ Eggs	→ Ingestion		
	→ Above-ground crops	→ Ingestion by dairy cattle		→ Milk	→ Ingestion	
		→ Ingestion by beef cattle		→ Beef	→ Ingestion	
		→ Ingestion by hens		→ Eggs	→ Ingestion	
Root zone soil				→ Root crops		
				→ Aboveground crops		
	→ Above-ground crops	→ Ingestion by dairy cattle		→ Milk	→ Ingestion	
		→ Ingestion by beef cattle		→ Beef	→ Ingestion	
		→ Ingestion by hens		→ Eggs	→ Ingestion	
Surface water (dissolved phase)				→ Tap water		
				→ Bathroom air		
Surface water (dissolved and suspended particle phases)				→ Fish		
	→ Ingestion by dairy cattle		→ Milk	→ Ingestion		
	→ Ingestion by beef cattle		→ Beef	→ Ingestion		
	→ Ingestion by hens		→ Eggs	→ Ingestion		
	→ Irrigated ground soil				→ Aboveground crops	
		→ Ingestion by dairy cattle		→ Milk	→ Ingestion	
		→ Ingestion by beef cattle		→ Beef	→ Ingestion	
		→ Ingestion by hens		→ Eggs	→ Ingestion	
		→ Above-ground crops	→ Ingestion by dairy cattle		→ Milk	→ Ingestion
			→ Ingestion by beef cattle		→ Beef	→ Ingestion
			→ Ingestion by hens		→ Eggs	→ Ingestion
	→ Irrigated root-zone soil				→ Root crops	
					→ Aboveground crops	
		→ Above-ground crops	→ Ingestion by dairy cattle		→ Milk	→ Ingestion
			→ Ingestion by beef cattle		→ Beef	→ Ingestion
			→ Ingestion by hens		→ Eggs	→ Ingestion

The rest of this subsection is organized as follows: the equations used to compute environmental media concentrations are given first. This is followed by a description of the equations used to estimate chemical concentrations in irrigated soil. Crop concentration models are discussed next, starting with models for the estimation of concentrations in above-ground plant parts, followed by a discussion of the models used to estimate concentrations in roots. The equation and parameters used to estimate intake of chemicals by farm animals is given after the section on concentrations in crops. Animal bioaccumulation models are discussed next, starting with the well known fish bioconcentration models and proceeding to biotransfer models for the estimation of concentrations in beef, milk, and eggs. New correlations are proposed to overcome a major flaw in models currently in use, namely that they do not obey mass balance constraints and might have animals excreting chemicals in amounts larger than they take in. The subsection closes with the expressions used to estimate chemical concentrations in tap water and bathroom air.

ENVIRONMENTAL MEDIA CONCENTRATIONS

Concentrations of chemicals in environmental media are derived directly from the fugacities calculated by the multimedia fate and transport model. The symbols, units, and expressions for the environmental media concentrations used in the exposure model are listed in Table 6-24.

Table 6-24: Environmental media concentrations used in the human exposure model

Medium	Phase	Symbol	Concentration Units	Equation
air	vapor	C_a^v	mg/(m ³ air)	$Z_{air} f_a \times \left(10^6 \frac{mg}{kg}\right)$
	particles	C_a^{part}	mg/(m ³ air)	$v_q Z_{ap} f_a \times \left(10^6 \frac{mg}{kg}\right)$
ground surface soil	bulk	C_{gs}	mg/(kg dry soil)	$\left(Z_{sp} + \frac{v_{w,s}}{v_{s,s}} Z_{water} \right) \frac{f_{g(irr)}}{\rho_{sp}} \times \left(10^6 \frac{mg}{kg}\right)$
root zone soil	pore water	C_{sw}	mg/(L water)	$Z_{water} f_{rz(irr)} \times \left(10^6 \frac{mg}{kg}\right) \times \left(10^{-3} \frac{m^3}{L}\right)$
surface water	liquid	C_w^l	mg/(L water)	$Z_{water} f_w \times \left(10^6 \frac{mg}{kg}\right) \times \left(10^{-3} \frac{m^3}{L}\right)$
	suspended particles	C_w^{ss}	mg/(L water)	$v_{s,w} Z_{wp} f_w \times \left(10^6 \frac{mg}{kg}\right) \times \left(10^{-3} \frac{m^3}{L}\right)$

Note: $f_{g(irr)}$ and $f_{rz(irr)}$ are the fugacities of irrigated ground surface soil and irrigated root-zone soil, respectively.

CONCENTRATIONS OF CHEMICALS IN IRRIGATED SOIL

Concentrations in irrigated soil are estimated using the fugacities calculated by the fate and transport model. The following equations are used:

$$f_{g(irr)} = \frac{E_g + D_{ag} f_a + D_{rzg} f_{rz} + D_{pg} f_p + U_{irr} A_g Z_w f_w}{D_{Rg} + D_{ga} + D_{g\,rz,diff} + (D_{gw} + D_{g\,rz,inf}) \left(\frac{U_3 + U_{irr}}{U_3} \right)} \quad (6-61)$$

and

$$f_{rz(irr)} = \frac{D_{prz} f_p + \left[D_{g\,rz,diff} + D_{g\,rz,inf} \left(\frac{U_3 + U_{irr}}{U_3} \right) \right] f_{g(irr)}}{D_{Rrz} + D_{rzp} + D_{rzg} + D_{Arz} \left(\frac{U_3 + U_{irr}}{U_3} \right)} \quad (6-62)$$

where U_{irr} is the irrigation rate, in units of $\text{m}^3/\text{m}^2 \cdot \text{hr}$, and $f_{g(irr)}$ and $f_{rz(irr)}$ are the fugacities in irrigated ground surface soil and irrigated root zone soil, respectively (the rest of the symbols are defined in section 6.3.1). When there is no irrigation ($U_{irr} = 0$), $f_{g(irr)}$ and $f_{rz(irr)}$ become equal to f_g and f_{rz} , respectively. A value of U_{irr} equal to $0.876 \text{ m}^3/\text{m}^2 \cdot \text{hr}$ is used.

This approach is very different from the one used in the CalTox model. In CalTox, soil water concentrations are estimated by adding the soil water concentration calculated by the fate and transport model to the product of the surface water concentration and an arbitrary factor called “fraction of chemical concentration in irrigation water retained in soil water”, which is assumed to be equal for all chemicals (the default value is $f_{irr} = 0.25$). This procedure leads to the following equations for irrigated soil fugacities:

$$f_{g(irr)} = f_g + f_{irr} f_w \quad (6-63)$$

and

$$f_{rz(irr)} = f_{rz} + f_{irr} f_w \quad (6-64)$$

The results of the two approaches are compared in Figure 6-6 for the case of water releases of the compounds in the toxic release inventory. The CalTox approach results in much higher irrigated soil concentrations for volatile compounds and for compounds with very large soil-water partition coefficients.

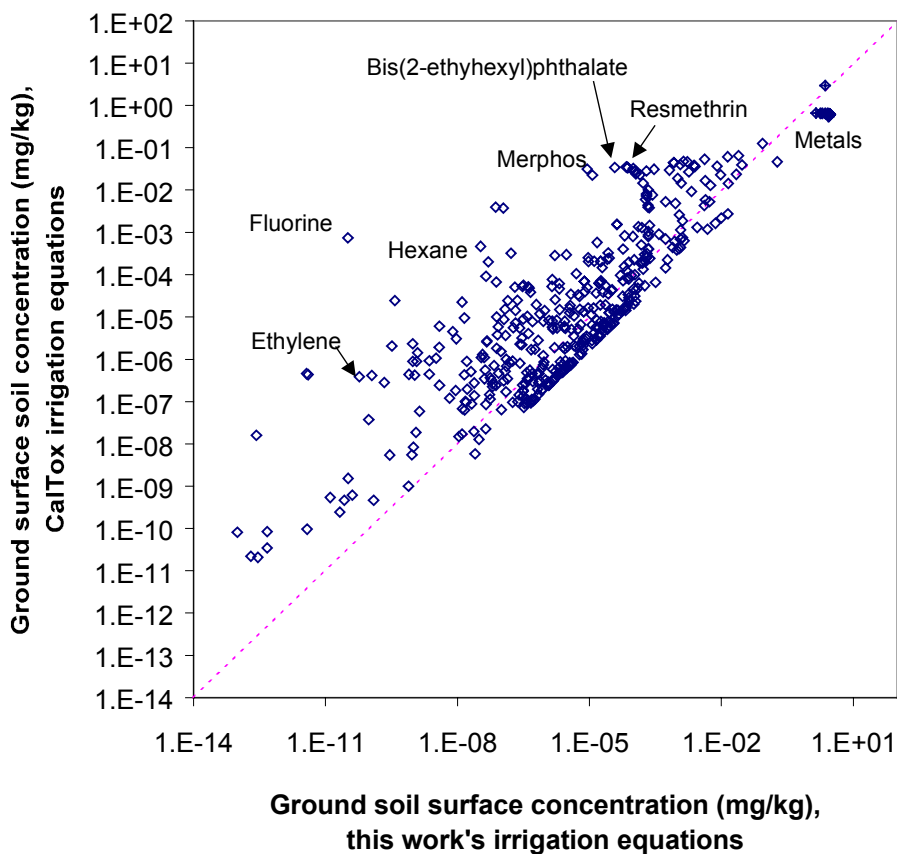


Figure 6-6: Comparison between two methods of estimating irrigated soil concentrations (1000 kg/hr discharges to water of TRI chemicals into a 10 million km² landscape)

CONCENTRATION OF CHEMICALS IN ABOVEGROUND CROPS

Three types of models are presented here: (i) bioconcentration in plant leaves of chemicals taken up from air, (ii) bioconcentration in plant leaves and stems of chemicals taken up from soil, and (iii) models combining the previous two mechanisms plus aerosol deposition and rain splash. The first two types of models are discussed because they contain building blocks for the third model. The section shows that for many chemicals it is necessary to take into account the kinetics of chemical uptake. Commonly used thermodynamic equilibrium models can lead to gross overestimation (many orders of magnitude) of chemical concentrations in plants.

Plant leaves-air bioconcentration model

The most common approach to model the bioconcentration of organic compounds in above ground vegetation is to assume that plant leaves are in thermodynamic equilibrium with the surrounding air [17,31]:

$$BCF_{leaves(dry)/air} = \frac{\rho_A}{\rho_D} K_{L/A} = \frac{\rho_A}{\rho_D} \left[v_A + \frac{RT}{H} (v_W + v_C K_{C/W} + v_G K_{ow}) \right] \quad (6-65)$$

where $BCF_{leaves(dry)/air}$ is the plant leaves-air bioconcentration factor in (mg/kg dry mass)/(mg/kg air), ρ_A is the density of air (kg/m^3), ρ_D is the dry weight content per volume of fresh leaves (kg/m^3), $K_{L/A}$ is the leaf-air partition coefficient (dimensionless), v_i are volume fractions in the leaf (with the subscripts A , W , C , G corresponding to air, water, cuticle, and glycerol lipids, respectively), and $K_{C/W}$ is the cuticle-water partition coefficient (dimensionless).

The last two terms in eq (6-65) may be grouped into a single term that depends on K_{ow} :

$$v_C K_{C/W} + v_G K_{ow} \approx v_{L,p} K_{ow}^m \quad (6-66)$$

where $v_{L,p}$ is the volume fraction of lipids in the plant and m is a correction factor for differences between plant lipids and octanol [32].

Substitution of eq (6-66) into eq (6-65) yields

$$BCF_{leaves(dry)/air} = \frac{\rho_A}{\rho_D} K_{L/A} = \frac{\rho_A}{\rho_D} \left[v_A + \frac{RT}{H} (v_W + v_{L,p} K_{ow}^m) \right] \quad (6-67)$$

Table 6-25 summarizes values of v_A , v_W , $v_{L,p}$, and m found in the literature.

Table 6-25: Pure phase volume fractions in plant leaves

Reference	v_A	v_W	$v_{L,p}$	m
Riederer [31]	0.30	0.645	0.007	1
Hope [33]	0.40	0.40	0.01	1
Paterson [34]	0.19	0.70	0.05	1
Trapp and Matthies [32]		0.80	0.02	0.75-0.97
Paterson [35]	0.24	0.727	0.03	1

It has been noted that for large values of the product $(RT/H)K_{ow}$, the time needed to reach equilibrium may exceed the life of the leaf [34], and thus it can be expected that eq (6-67) would tend to overestimate contaminant concentration in plants when the kinetics of uptake are comparable to the kinetics for leaf growth.

Above-ground plant parts-soil bioconcentration models

Two models are widely used for the plant-soil bioconcentration factor. The first model is the Travis and Arms correlation [36]:

$$BCF_{plant(dry)/soil} = 38.7(K_{ow})^{-0.58} \quad (6-68)$$

where $BCF_{plant(dry)/soil}$ has units of (mg/kg dry plant)/(mg/kg dry soil).

The bioconcentration factor may be expressed in units of (mg/kg fresh plant)/(mg/kg dry soil) by multiplying by the plant dry matter fraction, f_{DM} (with units of kg dry plant/kg fresh plant):

$$BCF_{plant(fresh)/soil} = f_{DM} BCF_{plant(dry)/soil} \quad (6-69)$$

McKone assumes $f_{DM} = 0.20$ to yield [33]:

$$BCF_{plant(fresh)/soil} = 7.7(K_{ow})^{-0.58} \quad (6-70)$$

The second widely used model is the stem concentration factor model proposed by Briggs et al. [37]:

$$SCF = K_{stem/xylem} TSCF \quad (6-71)$$

where SCF is the stem concentration factor [(mg/kg fresh plant)/(mg/L soil solution)], $K_{stem/xylem}$ is the stem-xylem stream partition coefficient [(mg/kg fresh plant)/(mg/L transpired water)], and $TSCF$ is the transpiration stream concentration factor [in units of (mg/L transpired water)/(mg/L soil solution)]. $K_{stem/xylem}$ is related to K_{ow} by:

$$K_{stem/xylem} = \frac{1}{\rho_{plant}} (v_{w,p} + v_{L,p} (K_{ow})^m) \quad (6-72)$$

The $TSCF$ is modeled using a Gaussian curve:

$$TSCF = TSCF_{max} \exp[-(\log K_{ow} - a)^2 / b] \quad (6-73)$$

Table 6-26 summarizes parameter values found in the literature for equations (6-69)–(6-73).

Table 6-26: Plant-soil bioconcentration factor model parameters

Reference	$v_{w,p}$	$v_{l,p}$	m	$TSCF_{max}$	a	b	f_{DM}
Briggs et al. [37]	0.82	0.0089	0.95	0.784	1.78	2.44	
Hsu et al. [38]				0.7	3.07	2.78	
Table 6-25	0.4-0.8	0.007-0.5	0.75-1.00				
McKone [33]							0.20
Optimized, with data from [36-39]	0.64	0.012	0.89	0.9*	1.78*	4.83	0.28

* Parameter value at lower allowed bound

The two models are compared in Figure 6-7 and Figure 6-8 below. Bioconcentration factors expressed in terms of the concentration in dry soil can be converted to bioconcentration factors expressed in terms of the concentration in soil solution using the soil-water distribution coefficient (K_D), with units of (mg/kg soil particles)/(mg/L water):

$$K_D = f_{oc} \times 0.41 K_{ow} \quad (6-74)$$

where f_{oc} is the organic carbon weight fraction of the soil. CalTox uses a value of 0.3% for f_{oc} , while Mackay uses a value of 2%. The two bioconcentration factors are related by:

$$SCF = \frac{C_{soil}}{C_{soil\ water}} BCF_{plant(fresh)/soil} = \left(K_D + \frac{v_{w,s}}{v_{s,s} \rho_{sp}} \right) BCF_{plant(fresh)/soil} \quad (6-75)$$

where $v_{w,s}$ is the volume fraction of water in soil, $v_{s,s}$ is the volume fraction of solid particles in soil, and ρ_{sp} is the solid particle density (kg/L). Typical values are $v_{w,s} = 0.3$, $v_{s,s} = 0.5$, and $\rho_{sp} = 2.65$ kg/L.

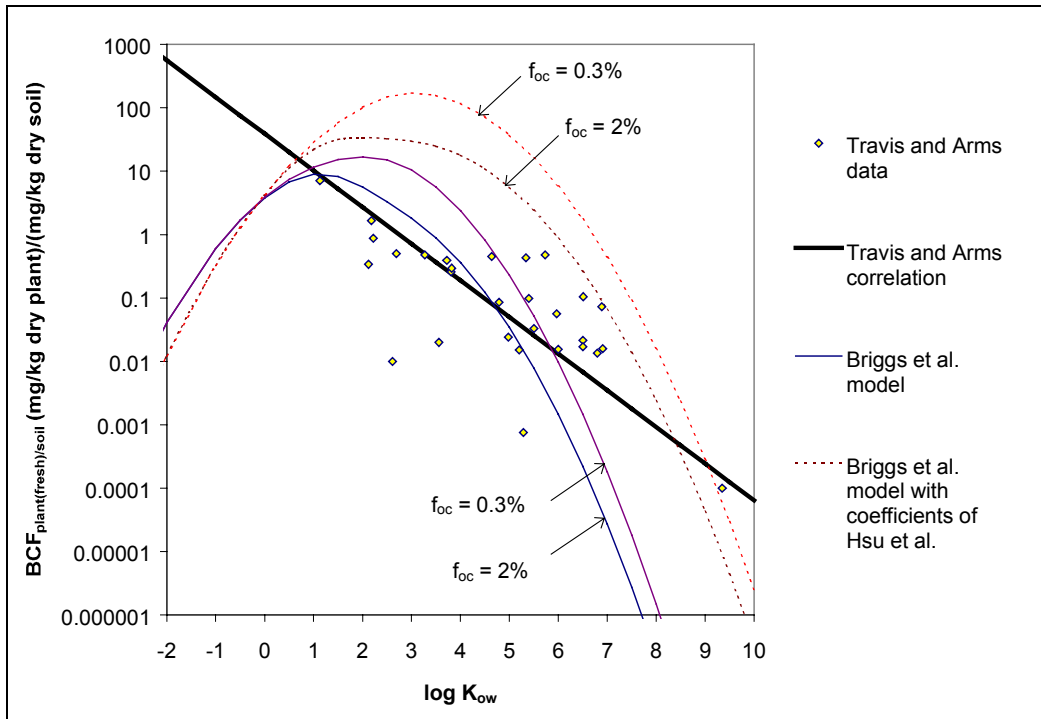


Figure 6-7: Relationship between the plant-soil bioconcentration factor and octanol-water partition coefficient.

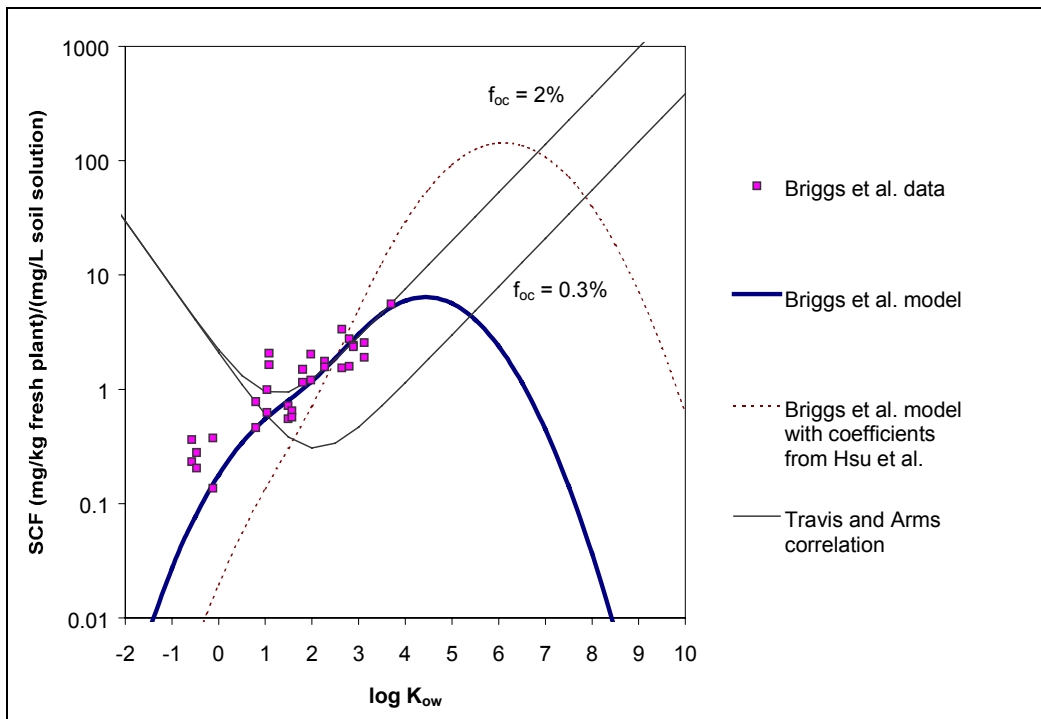


Figure 6-8: Relationship between the stem concentration factor and the octanol-water partition coefficient

The Travis and Arms correlation fits the data of Travis and Arms better than the Briggs et al. model with either the constants of Briggs et al. or those of Hsu et al. On the other hand, there is a very poor fit between the Travis and Arms correlation to the data of Briggs et al. at low values of K_{ow} . Estimating a new set of constants for the model of Briggs et al. yields acceptable agreement with all the experimental data, as shown in Figure 6-9, Figure 6-10, and Figure 6-11.

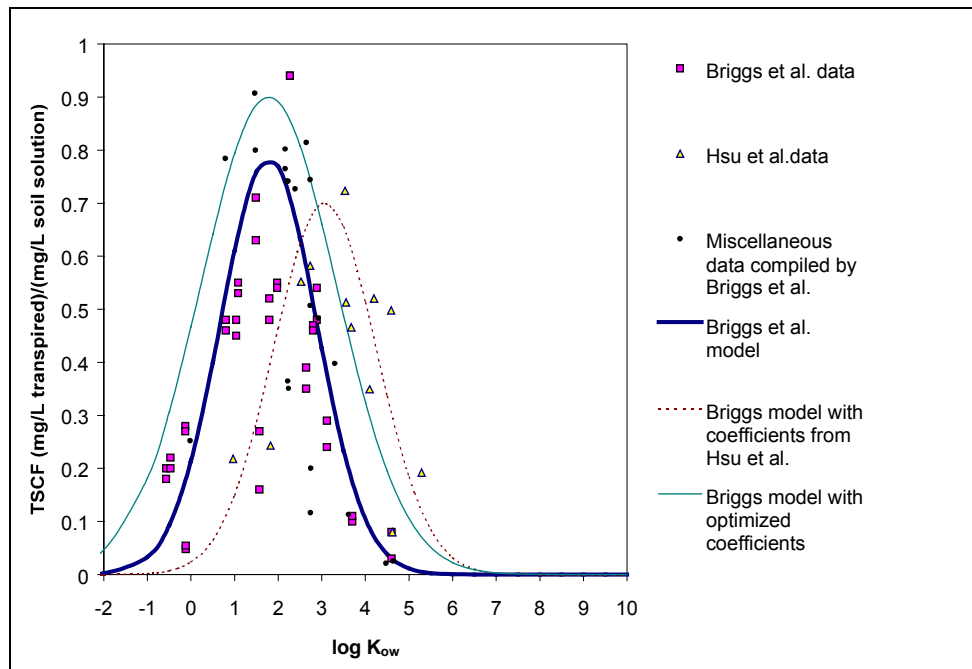


Figure 6-9: Relationship between the transpiration stream concentration factor and the octanol-water partition coefficient

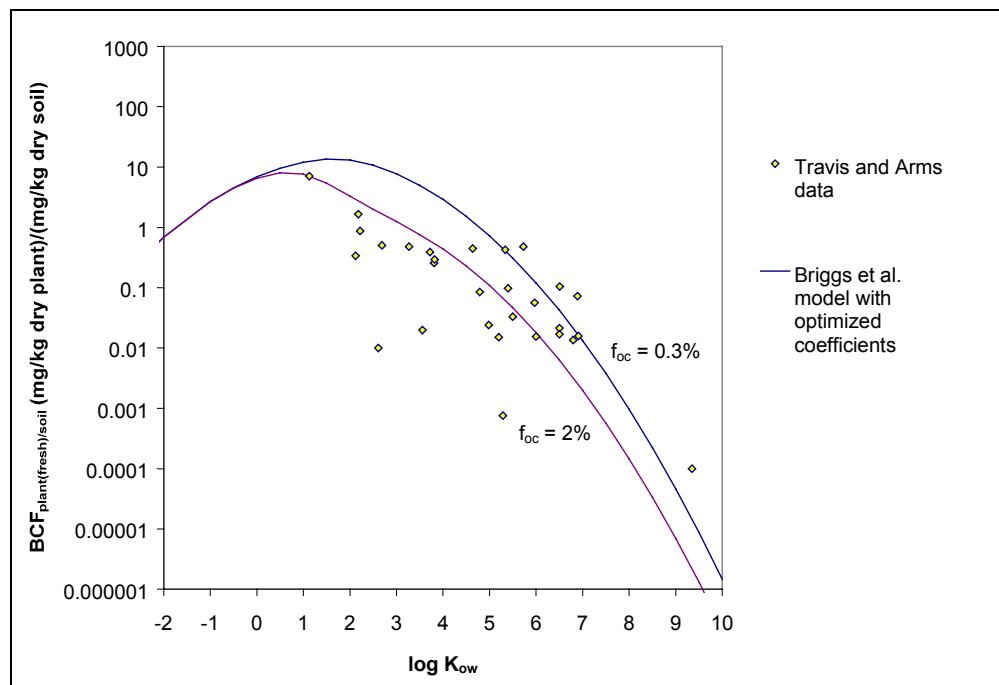


Figure 6-10: Fit of the optimized Briggs et al. plant-soil bioconcentration factor to the experimental data of Travis and Arms.

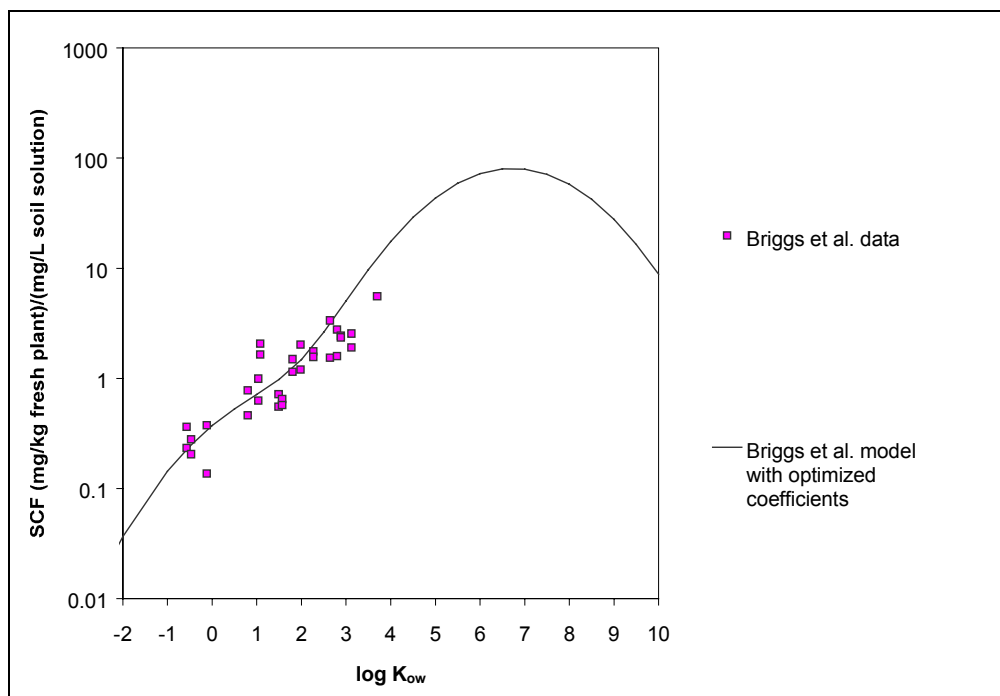


Figure 6-11: Fit of the optimized Briggs et al. stem concentration factor model to the experimental data of Briggs et al.

Models combining several uptake mechanisms

In the CalTox model, the concentration of organic chemicals in above-ground plant parts is the sum of four contributions:

- a) leaf-air exchange
- b) aerosol deposition
- c) uptake from soil through roots
- d) rain splash

The expression used in CalTox is:

$$C_{plants} = K_{pa}^v C_a^v + K_{pa}^{part} C_a^{part} + K_{ps} C_{rs} + K_{ps}^{rain} C_{gs} \quad (6-76)$$

where C_{plants} is the concentration in plants (mg/kg fresh mass), C_{rs} is the concentration in root soil (mg/kg dry soil), K_{ps} is given by $BCF_{plant(fresh)/soil}$ in eq (6-70), and K_{ps}^{rain} is a constant independent of chemical properties. The first two transfer coefficients have the following definitions:

$$K_{pa}^v = \frac{1}{\rho_F} K_{L/A} \quad (6-77)$$

$$K_{pa}^{part} = \frac{v_{dep}}{M_{plants} k_{ws}} \quad (6-78)$$

where ρ_F is the plant fresh mass density, v_{dep} is the particle deposition velocity (m/d), M_{plants} is the average inventory of plants per unit area (kg fresh mass/m²), k_{ws} is a first order rate constant for the removal of chemicals from vegetation surfaces as a result of weathering and senescence (day⁻¹).

By analogy with eq (6-78), K_{ps}^{rain} may be written as:

$$K_{ps}^{rain} = \frac{F_{soil}^{splash}}{M_{plants} k_{ws}} \quad (6-79)$$

where F_{soil}^{splash} is the flux of splashed soil to plants, given in units of (kg dry soil/m²/day).

Examination of the above expressions shows that while the rain splash and particle deposition mechanisms take plant growth into account, the air-leaf exchange mechanism assumes thermodynamic equilibrium, and thus may lead to an overestimation of contaminant concentrations in plants.

Trapp and Matthies proposed a model that combines uptake from soil and air with growth dilution and metabolism [32]:

$$C_L = \frac{1}{\rho_F} \frac{(Q/V_L)TSCF \cdot C_{sw} + g_T(A_L/V_L)C_a^v}{\frac{g_T(A_L/V_L)}{K_{L/A}} + k_e + k_g} \quad (6-80)$$

where C_L is the concentration in plant leaves (mg/kg fresh weight), (Q/V_L) is the ratio of transpiration (m^3/day) to leaf volume (m^3), C_{sw} is the contaminant concentration in soil water (mg/m^3), g_T is the leaf overall air-exchange conductance (m/day), (A_L/V_L) is the ratio of leaf area (m^2) to leaf volume (equal to the inverse of one half of the leaf average thickness, in m), k_e is a first-order elimination decay constant ($1/\text{day}$), and k_g is a first order plant growth constant ($1/\text{day}$). Possible decay mechanisms include metabolism and photodegradation. For the case of negligible soil uptake and air-exchange kinetics that are much faster than degradation and plant growth, eq (6-80) reduces to:

$$C_L = \frac{K_{L/A}C_a^v}{\rho_F} \quad (6-81)$$

which is the expression used in the CalTox model for the air (vapor phase) contribution to contaminant concentration in plants.

Typical values for the constants in eq (6-80) are given in Table 6-27.

Table 6-27: Literature values for the parameters in the Trapp and Matthies aerial plant parts bioaccumulation model

Parameter	Value	References
Q/V_L	$0.8 - 1.8 \text{ day}^{-1}$	[32]
	$4.6 - 13 \text{ day}^{-1}$	[35]
A_L/V_L	$850 - 2500 \text{ m}^{-1}$	[32]
	670 m^{-1}	[31]
	2800 m^{-1}	[35]
k_g	0.05 day^{-1}	[32]
	0.024 day^{-1}	[35]
	$0.01 - 0.10 \text{ day}^{-1}$	[40]
ρ_F	$715 \text{ kg}/\text{m}^3$	[31]
	$500 \text{ kg}/\text{m}^3$	[32]
	$890 \text{ kg}/\text{m}^3$	[34]

Values of g_T and k_e are properties specific to each chemical substance. The overall conductance can be written as the sum of a boundary layer resistance in series with two resistances in parallel: a cuticle resistance and a resistance for uptake through the stomata:

$$\frac{1}{g_T} = \frac{1}{g_{air,bl}} + \frac{1}{g_C + g_S} \quad (6-82)$$

The cuticle resistance is the product of the cuticle mass transfer coefficient times the cuticle-air partition coefficient, which is proportional to the octanol-air partition coefficient, as discussed at the beginning of this section. Thus, g_T can be related to $K_{O/A}$ through the expression:

$$\frac{1}{g_T} = \frac{1}{g_{air,bl}} + \frac{1}{k_{m,C}K_{O/A} + g_S} \quad (6-83)$$

Table 6-28 summarizes parameter values found in the literature.

Table 6-28: Literature values for the parameters in the leaf conductance model

Parameter	Value	References
$g_{air,bl}$ (m/s)	0.0003	[35]
	$0.01 \times (18/MW)^{0.5}$	[31]
	0.005	[32]
	0.003 (assuming $V/L = 1000 \text{ m}^{-1}$)	[34]
g_S (m/s)	$0.001 \times (18/MW)^{0.5}$	[31]
	0.0001 – 0.001	[32]
$k_{m,C}$ (m/s)	1.1×10^{-10} (assuming $V/L = 1000 \text{ m}^{-1}$)	[34]

The fitted model shown in Figure 6-12 has the following parameter values: $g_S = 0.0001$ m/s, $g_{air,bl} = 0.005$ m/s, $k_{m,C} = 1.3 \times 10^{-11}$ m/s; the confidence interval was generated by multiplying the values predicted by eq (6-83) by a lognormal distribution with central value 1 and an uncertainty factor of 3.2.

A derivation similar to the one used by Trapp and Matthies is used in the following paragraphs to derive a plant bioconcentration model that incorporates the four mechanisms used in the CalTox model. The main advantage of the model proposed here is that it avoids unrealistic overestimation of bioconcentration for chemicals with large values of $K_{O/A}$.

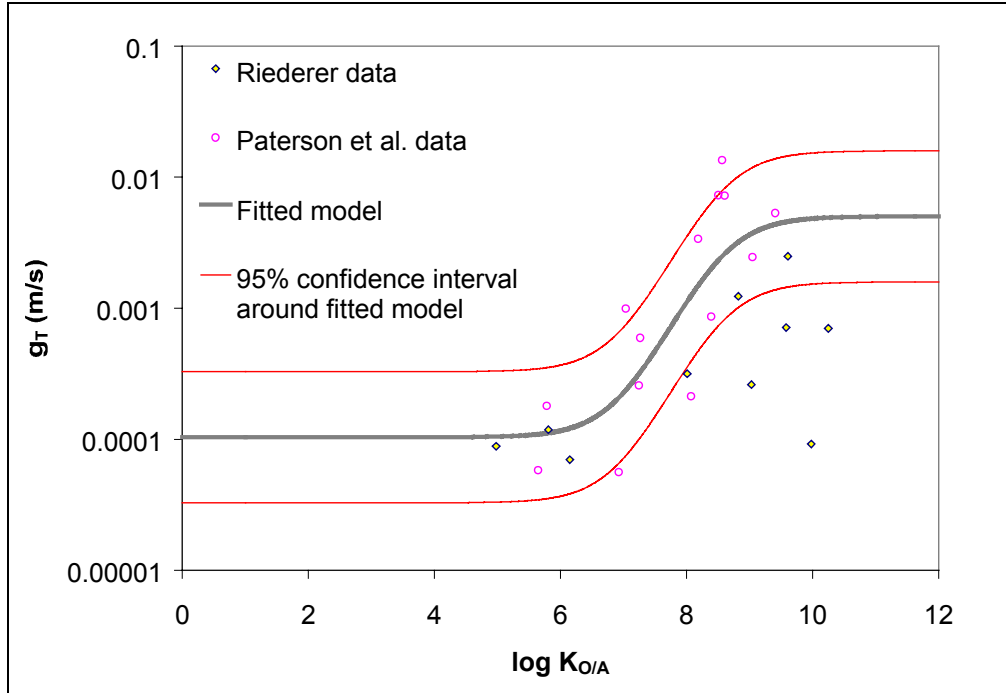


Figure 6-12: Relationship between leaf air conductance and the octanol-air partition coefficient

The mass balance in the aboveground parts of the plant is given by:

change of chemical mass in aerial plant parts =

$$\begin{aligned}
 & \text{gaseous flux from/to air } (N_A) + \text{flux from soil via xylem } (N_{Xy}) \\
 & - \text{flux to soil via phloem } (N_{Ph}) + \text{flux from particle deposition } (N_{dep}) \\
 & + \text{flux from rain splash } (N_{rain}) - \text{decay } (R_E)
 \end{aligned} \tag{6-84}$$

Expressed in mathematical terms, the mass balance becomes:

$$\begin{aligned}
 \frac{d(\rho_L V_L C_L)}{dt} = & A_L g_T \left(C_a^v - \frac{\rho_L C_L^{tissue}}{K_{L/A}} \right) + Q_{Xy} \cdot TSCF \cdot C_{sw} - Q_{Ph} \frac{C_L^{tissue}}{K_{stem/phloem}} \\
 & + v_{dep} \frac{A_L}{LAI} C_a^{part} + F_{soil}^{splash} \frac{A_L}{LAI} C_{soil} - k_e \rho_L V_L C_L
 \end{aligned} \tag{6-85}$$

where C_L^{tissue} is the contaminant concentration in plant tissue (mg/kg fresh plant), C_L^{dep} is the amount of contaminant deposited on plant surfaces (mg/kg fresh plant), Q_{Xy} is the upward flow of xylem sap (m^3/day), Q_{Ph} is the downward flow of phloem sap (m^3/day), $K_{stem/phloem}$ is the plant-phloem sap partition coefficient (L/kg fresh plant), LAI is the leaf-area index (m^2 leaves/ m^2 ground surface), and the other terms have been defined previously.

Assuming constant leaf density, the left-hand side of eq (6-85) may be expanded as

$$\frac{d(\rho_L V_L C_L)}{dt} = \rho_L V_L \frac{dC_L}{dt} + \rho_L C_L \frac{dV_L}{dt} \quad (6-86)$$

During the vegetative phase, the growth can be approximated by an exponential function [32], with a first order growth constant k_g :

$$\frac{dV_L}{dt} = k_g V_L \quad (6-87)$$

Substitution into eq (6-85) yields

$$\begin{aligned} \rho_L \frac{dC_L}{dt} = & \frac{A_L g_T}{V_L} \left(C_a^v - \frac{\rho_L C_L^{tissue}}{K_{L/A}} \right) + \frac{Q_{xy}}{V_L} \cdot TSCF \cdot C_{sw} - \frac{Q_{Ph}}{V_L} \frac{C_L^{tissue}}{K_{stem/phloem}} \\ & + \frac{v_{dep}}{LAI} \frac{A_L}{V_L} C_a^{part} + \frac{F_{soil}^{splash}}{LAI} \frac{A_L}{V_L} C_{soil} - k_e \rho_L C_L - k_g \rho_L C_L \end{aligned} \quad (6-88)$$

The leaf concentration (C_L) is the sum of the concentration in plant tissue (C_L^{tissue}) and the contribution from solid deposits on plant surfaces (C_L^{dep}). Assuming that deposits do not interact with plant tissue, eq (6-88) can be separated into

$$\begin{aligned} \rho_L \frac{dC_L}{dt} = & \frac{A_L g_T}{V_L} \left(C_a^v - \frac{\rho_L C_L^{tissue}}{K_{L/A}} \right) + \frac{Q_{xy}}{V_L} \cdot TSCF \cdot C_{sw} - \frac{Q_{Ph}}{V_L} \frac{C_L^{tissue}}{K_{stem/phloem}} \\ & - (k_e^{tissue} + k_g) \rho_L C_L^{tissue} \end{aligned} \quad (6-89)$$

and

$$\rho_L \frac{dC_L^{dep}}{dt} = \frac{v_{dep}}{LAI} \frac{A_L}{V_L} C_a^{part} + \frac{F_{soil}^{splash}}{LAI} \frac{A_L}{V_L} C_{soil} - (k_e^{dep} + k_g) \rho_L C_L^{dep} \quad (6-90)$$

At steady state,

$$C_L^{tissue} = \frac{1}{\rho_L} \frac{\frac{A_L g_T}{V_L} C_a^v + \frac{Q_{xy}}{V_L} \cdot TSCF \cdot C_{sw}}{\frac{A_L g_T}{V_L K_{L/A}} + \frac{Q_{Ph}}{\rho_L V_L K_{stem/phloem}} + k_e^{tissue} + k_g} \quad (6-91)$$

and

$$C_L^{dep} = \frac{\frac{v_{dep}}{LAI} \frac{A_L}{V_L} C_a^{part} + \frac{F_{soil}^{splash}}{LAI} \frac{A_L}{V_L} C_{soil}}{k_e^{dep} + k_g} \quad (6-92)$$

where the product $LAI(V_L/A_L)\rho_L$ is equal to the plant fresh mass inventory per unit area (M_{plants}) used in eqs (6-78) and (6-78). In the case where leaf-air exchange kinetics dominate over all other processes, eq (6-91) reduces to eq (6-81). Similarly, for the case where movement of chemicals by transpiration is the fastest process, eq (6-91) reduces to the Briggs model (eq (6-71)), provided that the product $K_{stem/phloem}(Q_{Ph}/Q_{Xy})$ is equal to $K_{stem/xylem}$.

The final form of the above-ground crops bioconcentration model used in this work is

$$C_L = \frac{1}{\rho_L} \frac{(A_L/V_L)g_T C_a^v + (Q_{Xy}/V_L) \cdot TSCF \cdot C_{sw}}{(A_L/V_L)g_T + \frac{Q_{Xy}}{\rho_L K_{stem/xylem}}} + \frac{\frac{v_{dep} C_a^{part}}{M_{plants}} + \frac{F_{soil}^{splash} C_{soil}}{M_{plants}}}{k_e^{dep} + k_g} \quad (6-93)$$

The list of parameter values for eq (6-88) is shown in Table 6-29.

Table 6-29: Parameter values used in the above-ground crops bioconcentration model

Parameter	Values	Reference
A_L/V_L	1400 m ⁻¹ , $\sigma_g^2 = 2.0$	Table 6-27
g_T	Eq (6-83) with the following parameter values: $g_{air,bl} = 0.005$ m/s $k_{m,C} = 1.3 \times 10^{-11}$ m/s $g_s = 0.0001$ m/s $\sigma_g^2 = 3.2$	
Q_{Xy}/V_L	3 d ⁻¹ , $\sigma_g^2 = 4.0$	Table 6-27
TSCF	Eq (6-73) with the following parameter values: $TSCF_{max} = 0.9$ $a = 1.78$ $b = 4.83$	Table 6-26
v_{dep}	190 m/d, $\sigma_g^2 = 9.0$	[20,40]
F_{soil}^{splash}	0.0003 kg soil/m ² /day	[33]
M_{plants}	3 kg(fresh mass)/m ² , $\sigma_g^2 = 3.0$	[40]
k_g	0.035 d ⁻¹ , $\sigma_g^2 = 3.0$	Table 6-27
k_e^{tissue}, k_e^{dep}	0	
ρ_L	814 kg/m ³ , $\sigma_g^2 = 1.5$	
$K_{L/A}$	Eq (6-68) with the following parameter values: $v_A = 0.20$ $v_W = 0.64$ $v_O = 0.012$	
$K_{stem/xylem}$	Eq (6-72) with the following parameter values: $\rho_L = 814$ kg/m ³ , $\sigma_g^2 = 1.5$ $v_{w,p} = 0.64$ $v_{L,p} = 0.012$ $m = 0.89$, $\sigma_g^2 = 1.13$	Table 6-26

The impact of using eq (6-76) vs. using eq (6-96) on the estimation of human exposure to TRI chemicals emitted to air is shown in Figure 6-13⁵⁴. Clearly, using an equilibrium model instead of a kinetic model to estimate concentrations in plant tissues can lead to very large overestimation errors for some chemicals.

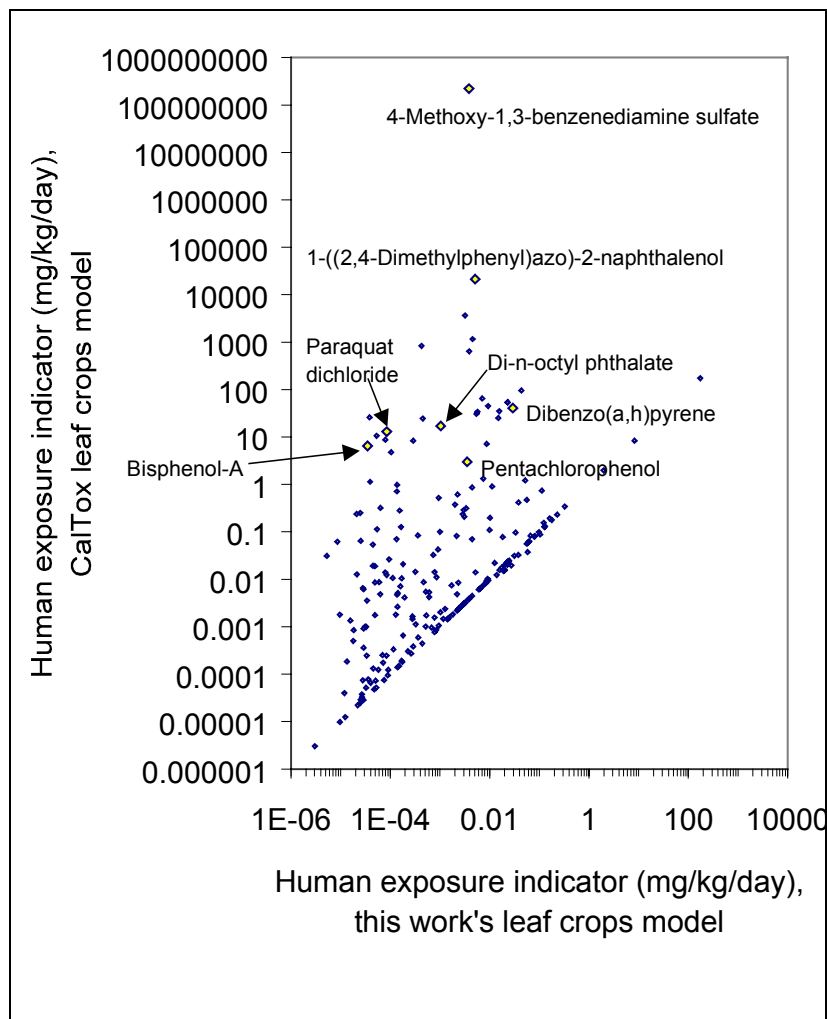


Figure 6-13: Comparison between two methods for estimating chemical concentrations in above-ground crops

CONCENTRATION IN ROOT CROPS

The concentration of a chemical in root crops is calculated using the equation

⁵⁴ Emissions to air of 1000 kg/hr of each chemical into a 100,000 km² landscape were used for the dose-based comparisons in this section.

$$\boxed{C_{root\ crops} = RCF \times C_{sw}} \quad (6-94)$$

where $C_{root\ crops}$ has units of mg/(kg fresh root), and RCF is the roots-soil solution bioconcentration factor, with units of (mg/kg root)/(mg/L soil solution).

There are two widely used root-soil bioconcentration models for organic chemicals. The one used in CalTox is based on the vegetation bioconcentration model of Travis and Arms (eq (6-70)). McKone multiplies the coefficient in eq (6-70) by a factor of 35 to extrapolate from above-ground plant parts to roots [26,33]:

$$BCF_{roots/soil} = 270(K_{ow})^{-0.58} \quad (6-95)$$

where $BCF_{roots/soil}$ is the roots-dry soil bioconcentration factor, with units of (mg/kg root)/(mg/kg dry soil).

This model can be converted from a dry-soil basis to a soil-water basis by use of the soil-water distribution coefficient:

$$RCF = \frac{C_{soil}}{C_{soil\ water}} BCF_{roots/soil} = \left(K_D + \frac{v_{w,s}}{v_{s,s} \rho_{sp}} \right) BCF_{roots/soil} \quad (6-96)$$

The Uniform System for the Evaluation of Substances [41] uses the model of Briggs *et al.* [39]:

$$\boxed{RCF = 0.82 + 0.03K_{ow}^{0.77}} \quad (6-97)$$

Figure 6-14 shows a comparison between the two RCF models. The analogous chart for $BCF_{roots/soil}$ is shown in Figure 6-15. Since K_D is estimated as a function of the organic carbon fraction (f_{oc}), the basis conversion factor shown in equation (6-96) is a function of f_{oc} . The two curves shown on each figure span the organic carbon fraction range of 0.3% to 2%. Given the close agreement between the available experimental data and Briggs model, this is the model incorporated into the exposure model used in this work.

A RCF of 120 (L/kg roots) is used as a default for metals and metal compounds [18].

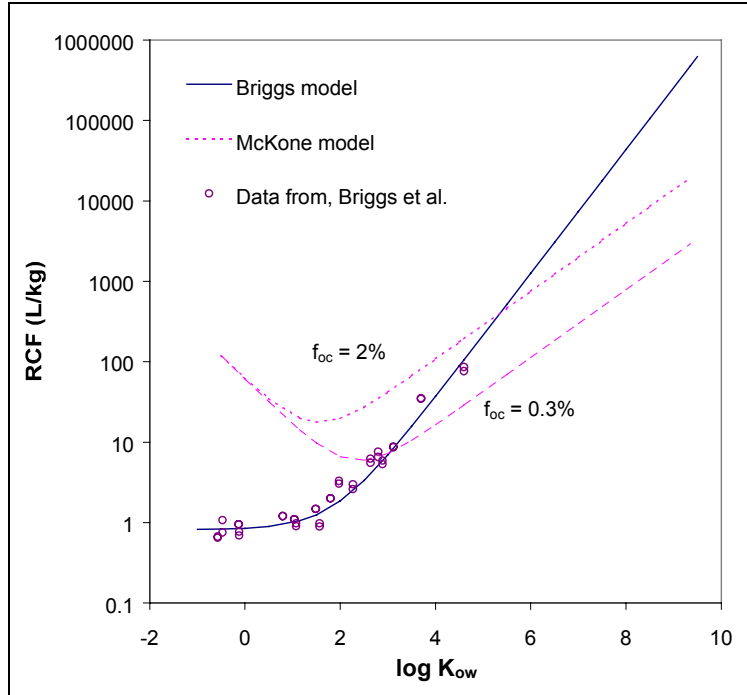


Figure 6-14: Root-soil water bioconcentration models.

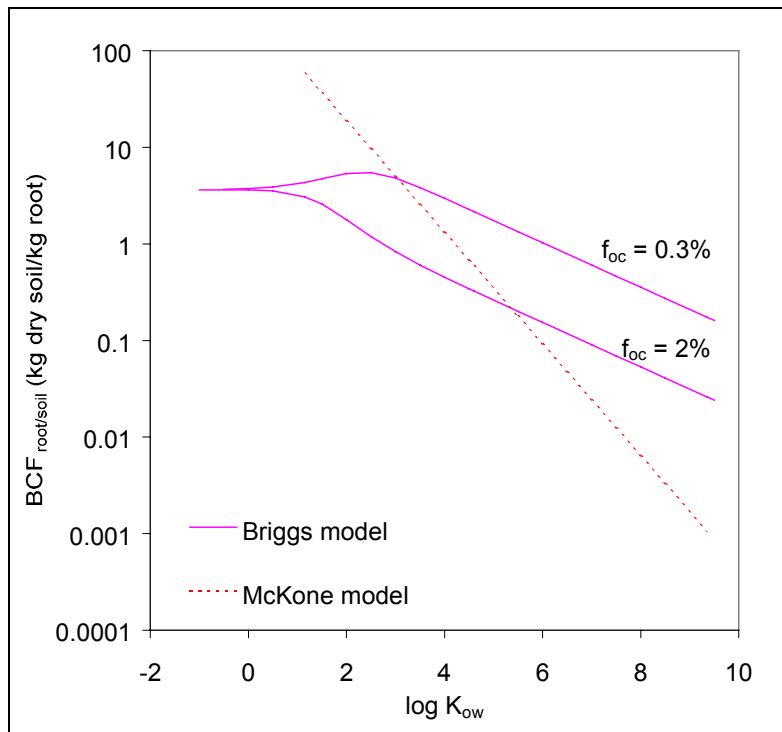


Figure 6-15: Root-dry soil bioconcentration models.

FARM ANIMAL INTAKE DOSES

The farm animal exposure model is similar to the one used by CalTox [21]. Farm animals are assumed to be exposed to chemicals in the environment through four intake routes: inhalation of air (vapor and particles), ingestion of water, ingestion of feed (aboveground crops), and ingestion of soil. The equation used is:

$$\boxed{Intake = Inh(C_a^v + C_a^{part}) + I_w(C_w^l + C_w^{ss})(1 - f_{w-gw}) + I_{feed}C_L + I_{soil}C_{gs}} \quad (6-98)$$

where $Intake_i$ is the daily intake of a chemical by a farm animal (beef cattle, dairy cattle, or hens) with units of mg/day, Inh is the animal inhalation rate (m^3/day), I_w is the water ingestion rate (L/day), I_{feed} is the animal feed ingestion rate (kg/day), I_{soil} is the soil ingestion rate (kg/day), C_L is the concentration in aboveground crops (mg/kg), and f_{w-gw} is the fraction of water needs supplied by groundwater. The distributions for the inhalation and ingestion parameters used in this work are listed in Table 6-30. The distribution used for f_{w-gw} is lognormal with central value 0.80 and $\sigma_g^2 = 1.2$ [26].

Table 6-30: Farm animal exposure media contact rates

Parameter (Units)	Dairy cattle	Beef cattle	Hens
Inh (m^3/day)	117; $\sigma_g^2 = 1.8$	same as dairy cattle	2.11; $\sigma_g^2 = 1.8$
I_w (L/day)	34; $\sigma_g^2 = 1.5$	same as dairy cattle	0.084; $\sigma_g^2 = 1.2$
I_{feed} (kg/day)	83; $\sigma_g^2 = 1.5$	56; $\sigma_g^2 = 2.2$	0.120; $\sigma_g^2 = 1.1$
I_{soil} (kg/day)	0.33; $\sigma_g^2 = 3.5$	same as dairy cattle	9.2×10^{-6} ; $\sigma_g^2 = 5.3$

Note: Parameter distributions were obtained from [26]. The table shows the central value and the squared geometric standard deviation of lognormal distributions.

FISH BIOCONCENTRATION MODELS

The most widely used [1,17,26,41-45] fish bioconcentration model is one proposed by Mackay [46]:

$$\log BCF = \log K_{ow} - 1.32; n = 44, r^2 = 0.95; se = 0.25 \quad (6-99)$$

where BCF is the ratio of the volumetric concentration of an organic chemical in fish to that in water. Mackay's model was derived from a data set with a minimum $\log K_{ow}$ of 1.35 and a maximum $\log K_{ow}$ of 6.0.

Experimental data shows that for chemicals with $\log K_{ow}$ greater than 6, the fish bioconcentration factor tends to level off or decrease, rather than increase [47]. For example,

Figure 6-16 shows data retrieved from the Syracuse Research Corporation ISIS BCF file by the U.S. Environmental Protection Agency [48]. The data clearly indicates that Mackay's model should not be used beyond the range of $\log K_{ow}$ values used to derive it. It has been shown that, even in the absence of metabolic transformation, the bioconcentration factor depends only on partitioning between fish lipids and water if the rate of elimination of chemicals from the fish through fecal excretion is small compared to the rate of transport of chemicals across the gills [49]. Assuming transport across the gills depends on diffusion across an aqueous and a lipid layer in series, it can be shown that for sufficiently high values of K_{ow} , transport across the aqueous layer will become the rate limiting process, leading to a leveling off or even a decrease in BCF at the high end of the K_{ow} scale.

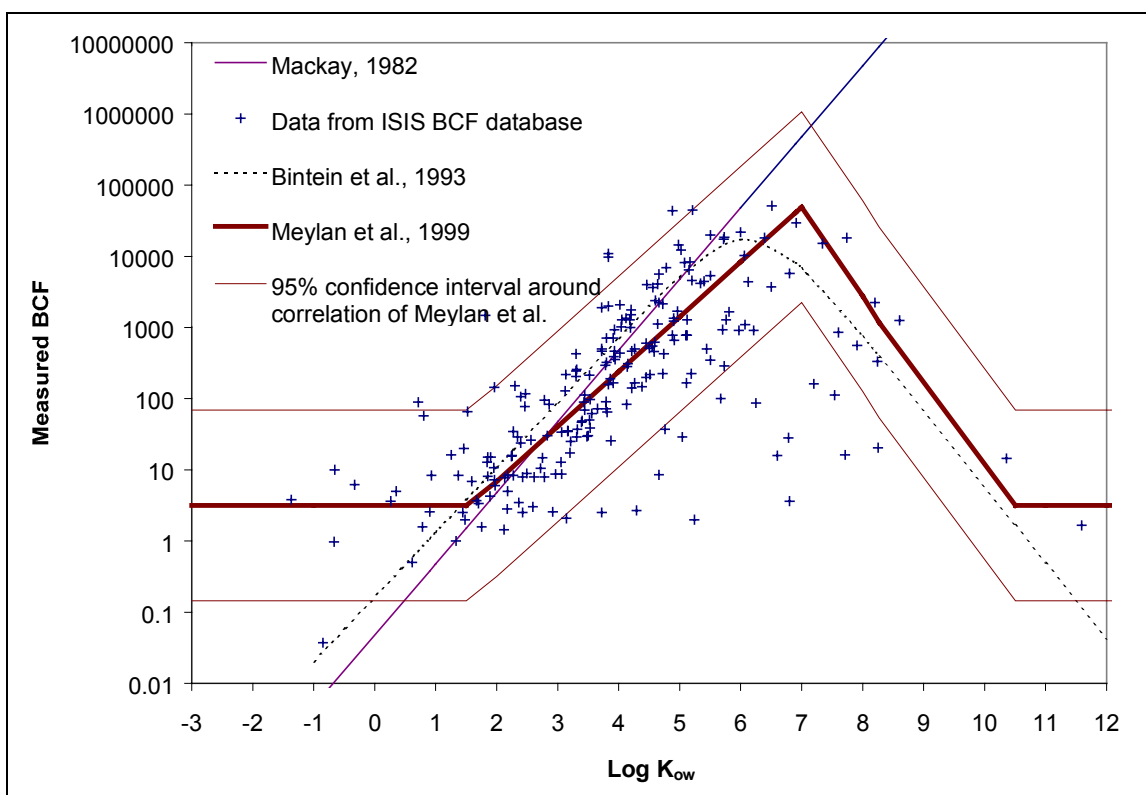


Figure 6-16: Comparison of fish bioconcentration factor correlations with experimental data

Among three alternative models designed to account for the decrease in BCF at high $\log K_{ow}$ values [50-52], the one developed by Bintein et al. [52] was judged to be of superior predictive ability when the models were tested against a database of BCF values recorded for 227 chemicals [53]:

$$\log BCF = 0.91 \log K_{ow} - 1.975 \log(K_{ow}/1.47 \times 10^6 + 1) - 0.786; \quad (6-100)$$

$$n=154, r = 0.95, se=0.347$$

A recent paper [54] describes a fish BCF estimation method based on statistical analysis of 694 chemicals. For nonionic compounds, the BCF is estimated according to the following relation:

$$\log BCF = \max(\min(0.77 \log K_{ow} - 0.70 + \sum F_i, -1.37 \log K_{ow} + 14.4 + \sum F_i), 0.5); \quad (6-101)$$

$$n = 610, r^2 = 0.73, se = 0.67$$

where F_i are correction factors derived from a compound's chemical structure. Meylan and coworkers found that eq (6-101) gave a better agreement between predicted and observed values than eq (6-100) when applied to the full data set of 610 compounds.

The following equation is used in the spreadsheet exposure model when experimental BCF values are not available⁵⁵:

$$\log BCF = \max(\min(0.77 \log K_{ow} - 0.70, -1.37 \log K_{ow} + 14.4), 0.5) + N(0, 0.67) \quad (6-102)$$

Eqs (6-100) and (6-102) are also shown in Figure 6-16. Note that for some compounds measured BCF are significantly lower than those predicted by eq (6-102). This is most likely due to metabolism. Biotransformation acts to decrease the equilibrium level of a labile chemical relative to that of a persistent chemical with the same hydrophobicity [55]. In the absence of information regarding biotransformation rates, the predictions of eq (6-102) may be considered estimates of the upper limit of the BCF .

MILK BIOTRANSFER MODELS

The most widely used [1,26,40,41,56] milk bioconcentration model is the biotransfer factor model of Travis and Arms [36]:

$$\log BTF_m = -8.10 + \log K_{ow}; n = 28, r^2 = 0.55, se = 0.80 \quad (6-103)$$

The milk biotransfer factor (BTF_m) is defined as the ratio of the contaminant concentration in milk (C_m , in mg/kg) to the lactating cow's daily contaminant intake ($Intake_{lc}$, in mg/day). This model has been criticized both for the high spread of the measured factors around

⁵⁵ The notation $N(a,b)$ is used throughout this thesis to represent a normally distributed random variable with mean value a and standard deviation b .

the predicted value [57,58], and for the fact that it predicts biotransfer factors for compounds with $\log K_{ow}$ values above 6.5 that would have the cow excreting more contaminant than it ingests [58].

A maximum value of BTF_m can be calculated on the basis that the amount of contaminant excreted in the milk must be less or equal to the amount taken in by the cow:

$$Q_m C_m \leq Intake_{lc} \quad (6-104)$$

where Q_m is the daily milk production rate (in kg/day). Use of the definition $BTF_m = C_m / Intake_{lc}$ yields:

$$BTF_m \leq \frac{1}{Q_m} \quad (6-105)$$

A typical value of Q_m is 17 kg/day [59]. Thus the maximum value of $\log BTF_m$ may be estimated as $-\log(17) = -1.2$.

McLachlan developed a model of the fractional absorption of contaminants in lactating cows [58], based on data for persistent hydrophobic contaminants:

$$f_{abs,lc} = \frac{1}{1.283 + 2.785 \times 10^{-8} K_{ow}} \quad (6-106)$$

Combining the absorption model with the mass balance constraint gives:

$$BTF_m = \frac{f_{abs,lc}}{Q_m} \quad (6-107)$$

This model predicts a constant milk biotransfer factor for $\log K_{ow}$ values lower than about 6. For compounds at the high end of the hydrophobicity scale, the model predicts milk biotransfer factors to be inversely proportional to K_{ow} .

Based on eq (6-107), McLachlan argues that the milk biotransfer factor should be independent of K_{ow} over a broad range. This is, however, inconsistent with the experimental data shown in Figure 6-17 [36,57,60]. Fractional absorption sets only an upper limit on the biotransfer factor to milk. The fate of absorbed contaminants includes excretion with milk, excretion with urine, storage in fat tissue, and metabolic degradation. It is very likely that the ratio of the fraction of absorbed contaminant excreted with milk to the fraction of absorbed contaminant excreted with urine is proportional to K_{ow} . This would explain why the data appears to indicate an upper limit for BTF_m that increases with K_{ow} for $\log K_{ow}$ values lower than 6. The

spread of the data below the maximum limit would be explained by metabolic degradation, which can not be predicted on the basis of $\log K_{ow}$ alone. Dowdy et al. have developed a model that predicts BTF_m based on the molecular connectivity index [57] with functional group correction factors for polar compounds. The standard error of the model they propose is lower than that for models based on K_{ow} . They believe their model is better able to account for variations in metabolism. It must be noted, however, that their model also violates the mass balance constraint for sufficiently large molecules.

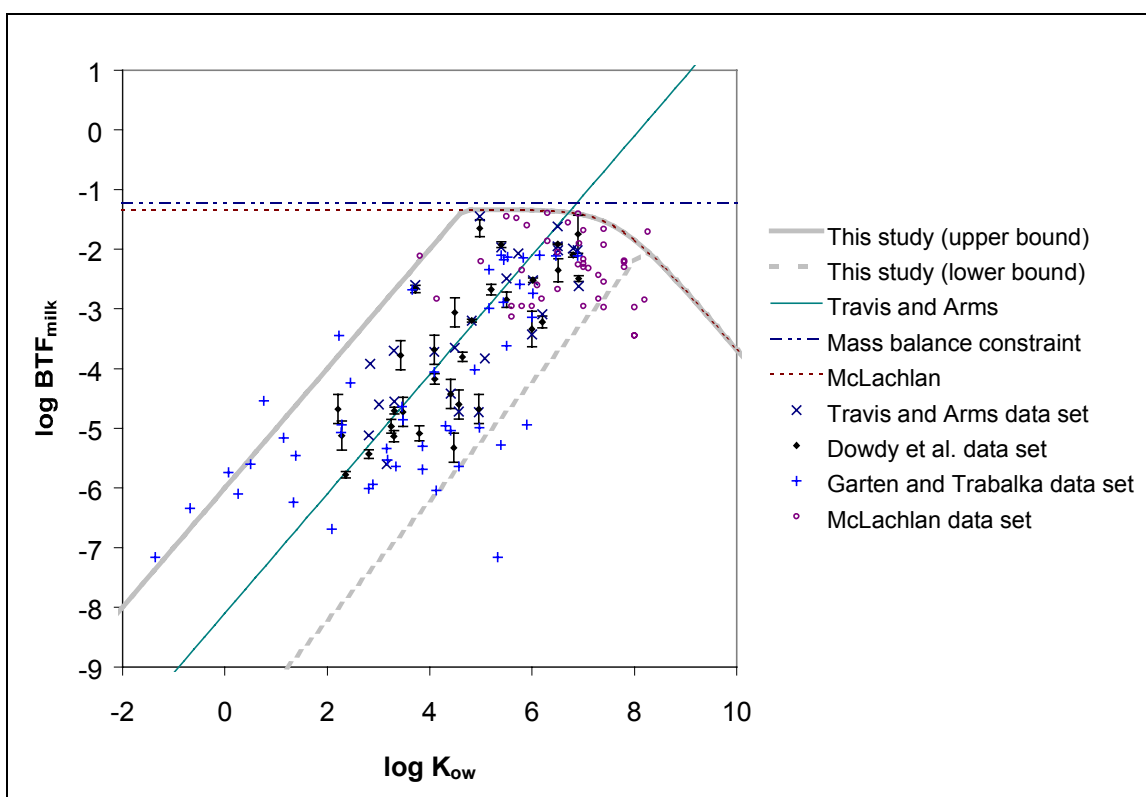


Figure 6-17: Comparison of milk biotransfer factor models with experimental data

A new model for BTF_m valid for compounds with negligible metabolic degradation in the cow is proposed here. The model can be used in risk assessment as a valid upper bound in the absence of experimental BTF_m values:

$$\log BTF_m = \min(\log K_{ow} - 6, \log f_{abs} - \log Q_m) \quad (6-108)$$

where f_{abs} is calculated according to eq (6-106). The model is shown in Figure 6-17. The uncertainty in the correlation is modeled using a uniform distribution for the intercept in eq (6-108):

$$\log BTF_m = \min(\log K_{ow} - U(6.0, 10.2), \log f_{abs} - \log Q_m) \quad (6-109)$$

For metals, a default value of -4.0 is used for $\log BTF_m$ when experimental values are not available.

BEEF BIOTRANSFER MODELS

As with the case of milk biotransfer models, the most widely used beef biotransfer model is the one proposed by Travis and Arms [36]:

$$\log BTF_b = -7.6 + \log K_{ow}; n = 36, r^2 = 0.65, se = 0.97 \quad (6-110)$$

The beef biotransfer factor (BTF_b) is defined as the ratio of a contaminant concentration in beef (C_b mg/kg) to the beef cow's daily intake ($Intake_{bc}$, in mg/day). Assuming a constant exposure to contaminants throughout the life of the cow, a maximum value for BTF_b can be calculated using the mass balance constraint:

$$C_b M_b \leq Intake_{bc} T_{bc} \quad (6-111)$$

where M_b is the mass of beef obtained from the cow (kg), and T_{bc} is the average age at which beef cattle are sacrificed. Substituting eq (6-111) into the definition of BTF_b yields:

$$BTF_b \leq \frac{T_{bc}}{M_b} \quad (6-112)$$

The ratio M_b/T_{bc} can be estimated from livestock inventory and beef production statistics as 0.33 kg/day. Thus an upper limit for $\log BTF_b$ is $-\log(0.33) = 0.48$, which is clearly an overestimate, since chemicals stored in beef fat would also be stored in other fat tissue. The Travis and Arms correlation violates even this conservative upper limit for values of $\log K_{ow}$ higher than about 8.1 (Figure 6-18).

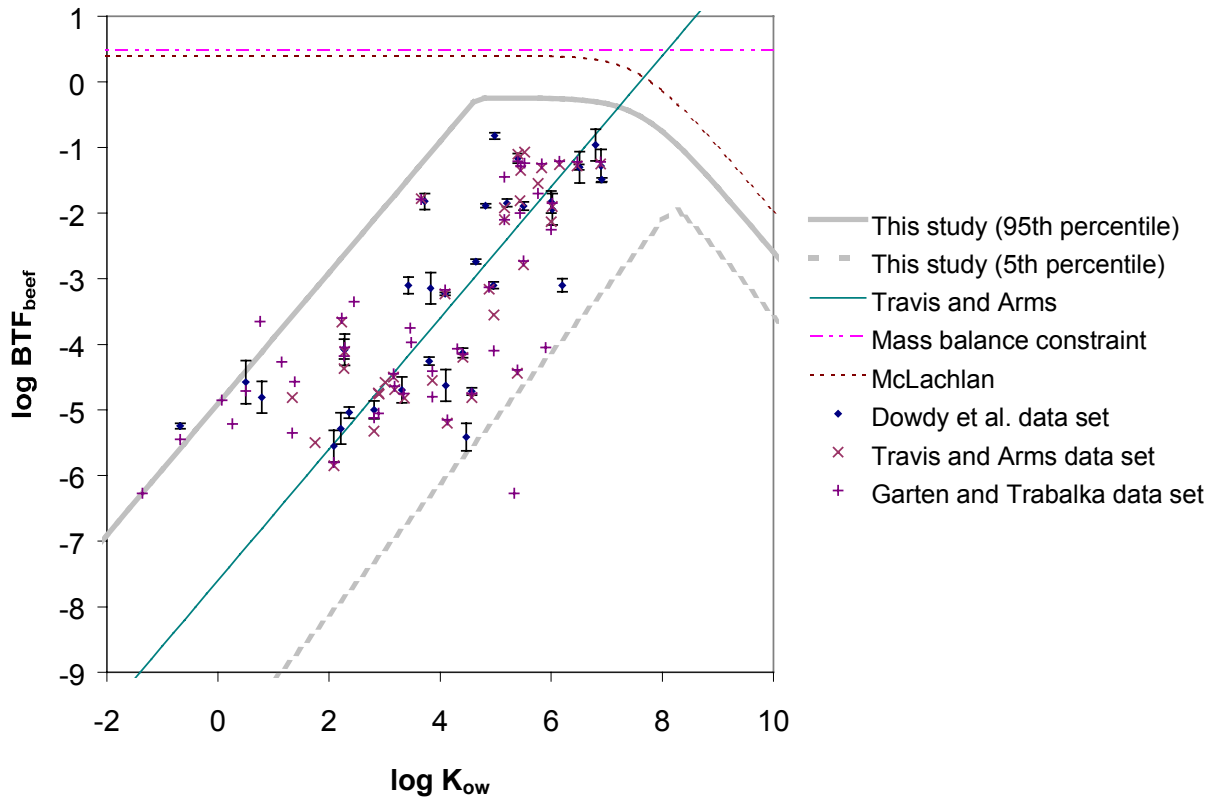


Figure 6-18: Comparison of beef biotransfer correlations with experimental data

McLachlan recommends dividing the total amount of contaminant absorbed during the life of a cow by its weight to estimate concentrations in the meat of nonlactating cattle. For nonlactating cattle, the absorption factor is given by

$$f_{abs,bc} = \frac{1}{1.200 + 2.785 \times 10^{-8} K_{ow}} \tag{6-113}$$

Combining the absorption model with the mass balance constraint gives:

$$BTF_b = \frac{f_{abs,bc} T_{bc}}{M_b} \tag{6-114}$$

There is a stronger correlation between BTF_b and BTF_m than between either of BTF_b or BTF_m with $\log K_{ow}$, as can be seen in Figure 6-19. A geometric mean regression of the data shown in the figure [36,57,61,62] yields

$$\log BTF_b = (1.16 \pm 0.05) \log BTF_m + 1.14 \pm 0.20; n = 50, r = 0.94 \quad (6-115)$$

Constraining the slope in eq (6-115) to be 1.0 yields

$$\log BTF_b = \log BTF_m + 0.59 + N(0, 0.50) \quad (6-116)$$

The use of equation (6-116) in risk assessment is recommended to estimate an upper limit for $\log BTF_b$, where BTF_m is either measured or estimated according to eq (6-108).

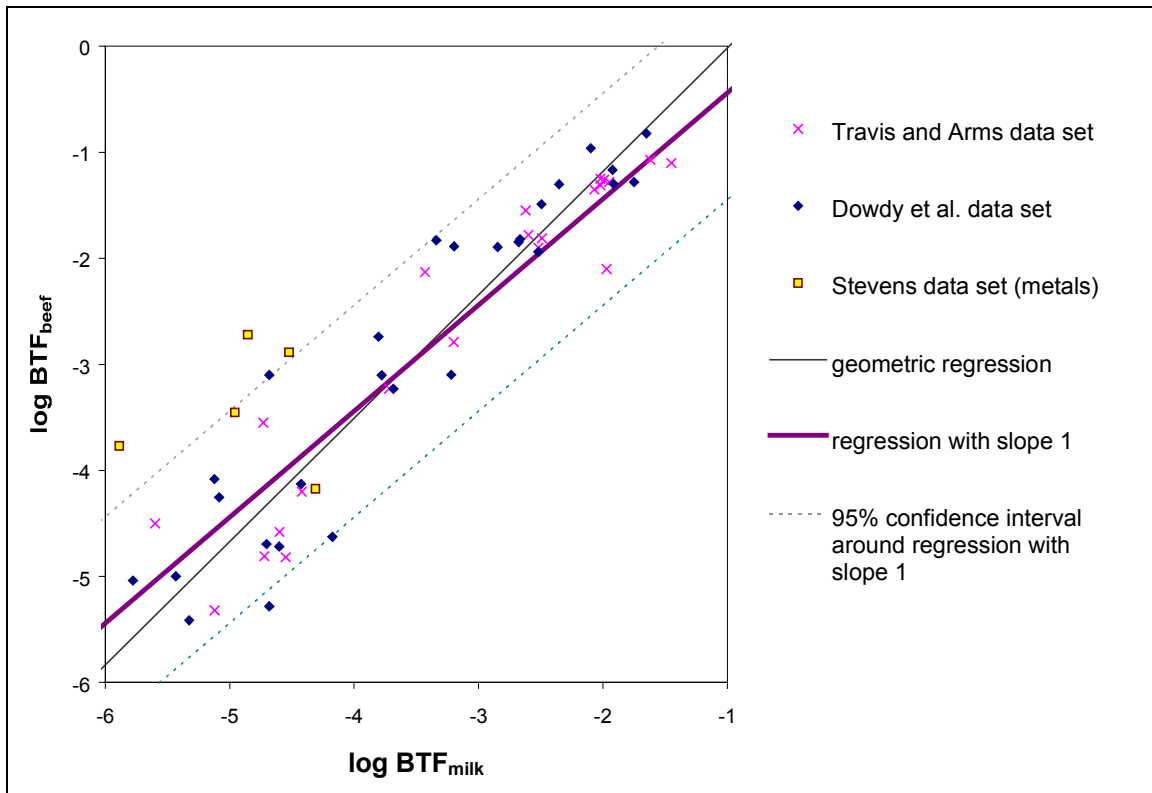


Figure 6-19: Correlation between beef and milk biotransfer factors

EGG BIOTRANSFER MODEL

There is no widely used model for the biotransfer of contaminants to chicken eggs. A model is derived here using the biotransfer model for milk and data for the fat/diet bioaccumulation factor in cows and poultry [60].

Figure 6-20 shows a plot of $BAF_{poultry}$ vs. BAF_{cow} . Both factors are given in units of (mg/kg animal fat)/(mg/kg dry feed). Geometric mean regression yields:

$$\log BAF_{poultry} = (0.93 \pm 0.10) \log BAF_{cow} + 0.82 \pm 0.21; n = 20, r = 0.89 \quad (6-117)$$

Since a slope of 1.0 is included in the confidence interval, a linear relationship between $BAF_{poultry}$ and BAF_{cow} may be assumed. Constraining the slope in eq (6-117) to be 1.0 and refitting the data yields

$$\log BAF_{poultry} = \log BAF_{cow} + 0.75 + N(0, 0.55) \quad (6-118)$$

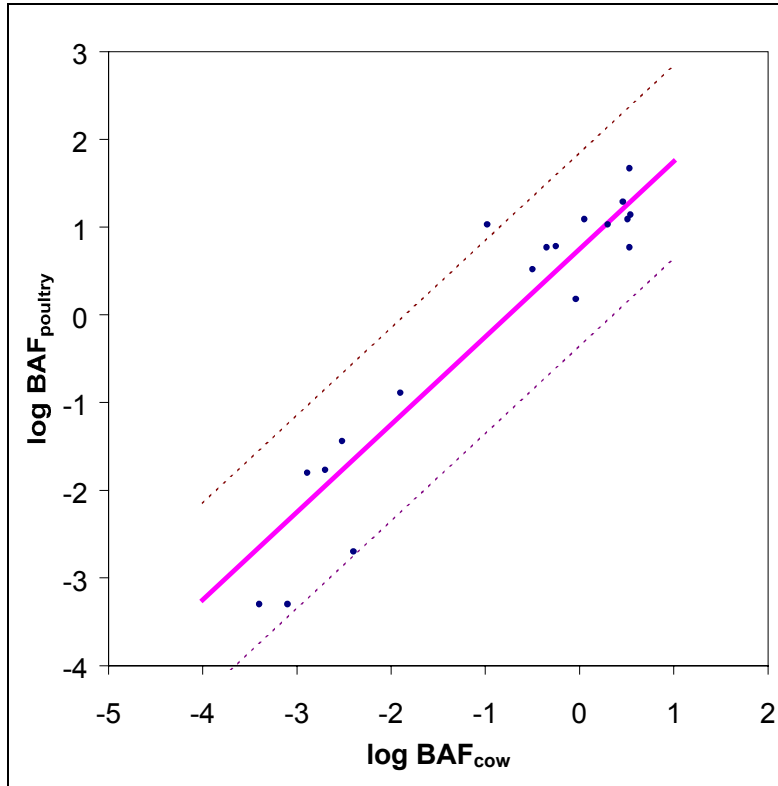


Figure 6-20: Correlation between poultry and cattle fat-diet bioaccumulation factors

The poultry fat/diet bioaccumulation factor is related to the eggs biotransfer factor through the relation

$$BTF_e = \frac{C_e}{Intake_h} = \frac{f_e C_{fat,e}}{Q_{feed,h} C_{feed}} = \frac{f_e}{Q_{feed,h}} BAF_{poultry} \quad (6-119)$$

where C_e is the concentration of contaminant in eggs (mg/kg), $Intake_h$ is the egg-laying hen daily contaminant intake rate (mg/day), f_e is the weight fraction of fat in eggs, $C_{fat,e}$ is the contaminant concentration in egg fat (mg/kg), $Q_{feed,h}$ is the food ingestion rate of hens (kg dry feed/day), and C_{feed} is the contaminant concentration in the feed (mg/kg dry feed).

Similarly, the milk biotransfer factor may be related to the cattle fat/diet bioaccumulation factor through the relation

$$BAF_{cow} = \frac{C_{fat,m}}{C_{feed}} = \frac{C_m/f_m}{Intake_{lc}/Q_{feed,lc}} = \frac{Q_{feed,lc}}{f_m} BTF_m \quad (6-120)$$

where $C_{fat,m}$ is the contaminant concentration in milk fat, f_m is the weight fraction of fat in milk, and $Q_{feed,lc}$ is the food ingestion rate of lactating cows (kg dry feed/day).

Combining equations (6-119) and (6-120) gives the following relationship between BTF_m and BTF_e :

$$BTF_e = \frac{f_e}{f_m} \frac{Q_{feed,lc}}{Q_{feed,h}} \frac{BAF_{poultry}}{BAF_{cow}} BTF_m \quad (6-121)$$

Typical values for the fat contents and feed rates above are: $f_e = 11\%$ [63], $f_m = 3.7\%$ [36,64], $Q_{feed,h} = 0.100$ kg/day [65], and $Q_{feed,lc} = 16$ kg/day [36,57].

Substituting these values and eq (6-118) into eq (6-121) yields:

$$\log BTF_e = \log BTF_m + 3.4 + N(0, 0.55) \quad (6-122)$$

The mass balance constraint for biotransfer to eggs is given by:

$$Q_e C_e \leq Intake_h \quad (6-123)$$

or

$$\log BTF_e \leq -\log Q_e \quad (6-124)$$

where Q_e is the daily egg production rate (kg/day) for a single hen. A typical value of $Q_e = 0.040$ kg/day is obtained by multiplying an annual egg production rate of 256 eggs/365 days [66] by an average egg weight of 0.058 kg [63]. As shown in Figure 6-21, eq (6-122) may violate the mass balance constraint.

The use of the following model, combining eqs (6-122) and (6-124), is recommended:

$$\log BTF_e = \min(\log BTF_m + 3.4 + N(0, 0.55), -\log Q_e) \quad (6-125)$$

where BTF_m is either measured or estimated using eq (6-108). The model is compared to experimental data in Figure 6-21. $BAF_{poultry}$ values in the data set published by Garten and Trabalka [60] were converted to BTF_e values using eq (6-119).

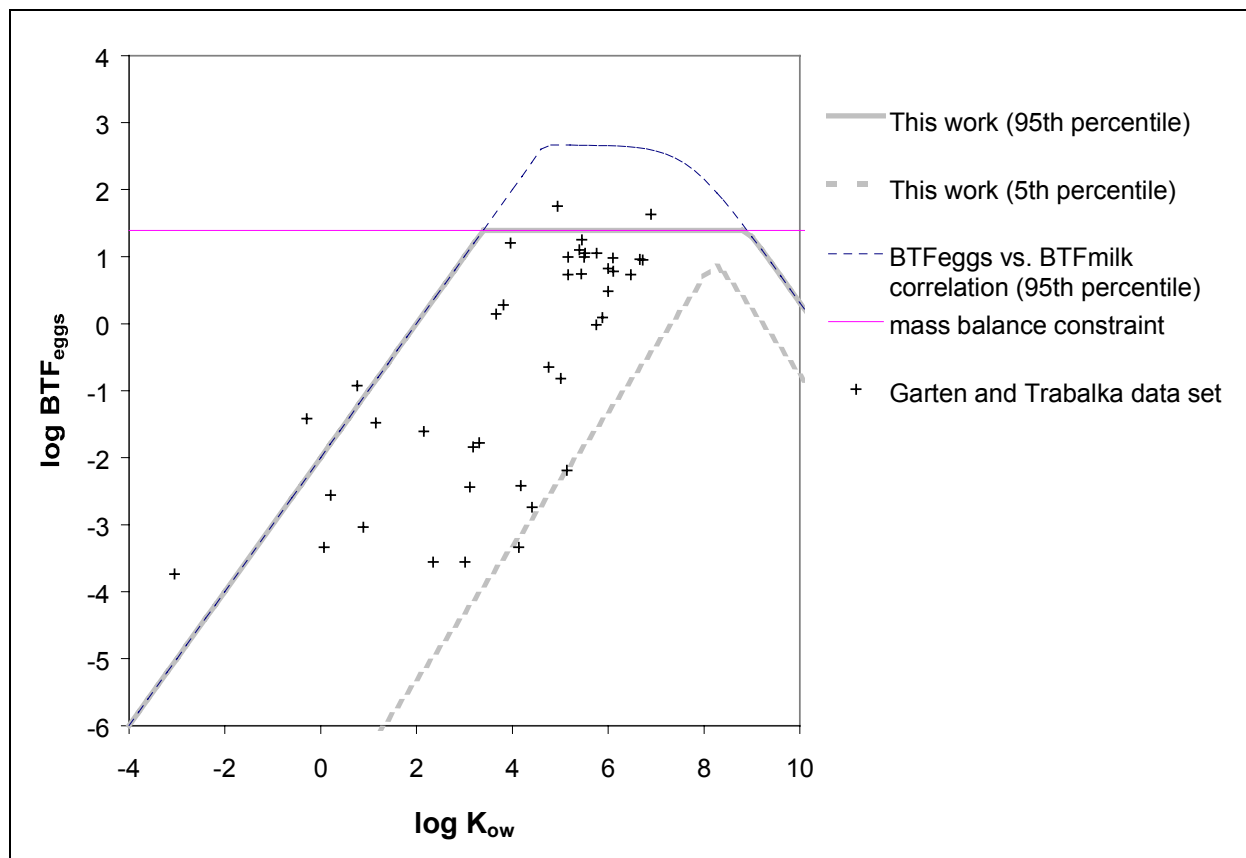


Figure 6-21: Comparison of chicken egg biotransfer factor correlation with experimental data

CONCENTRATION OF CHEMICALS IN TAP WATER

It is assumed that tap water is free of suspended particles. It is also assumed that the concentration of contaminants in ground water is zero. With these assumptions, the concentration of chemicals in tap water is given by:

$$C_{tap\ water} = (1 - f_{w-gw}) C_w^l \quad (6-126)$$

CONCENTRATION OF CHEMICALS IN BATHROOM AIR

Exposure to volatile chemicals transferred from tap water to air while showering might be significant relative to other exposure routes. The concentration in bathroom air ($C_{bath\ air}$) is estimated according to the method used in the CalTox model:

$$C_{\text{bath air}} = \left[0.6 \times \frac{3 \times 10^6 \left(\frac{\text{m}^2}{\text{s}} \right)^{-2/3}}{\frac{2.5}{D_w^{2/3}} + \left(\frac{RT}{H} \right) \frac{1}{D_a^{2/3}}} \right] \times \frac{W_{\text{bath}} C_{\text{tap water}}}{VR_{\text{bath}}} \quad (6-127)$$

where W_{bath} is the water use rate for showering/bathing (L/hr), VR_{bath} is the bathroom ventilation rate (m^3/hr), and the term enclosed in square brackets is a dimensionless mass transfer efficiency from water to air in the bathroom. Parameter values are given in Table 6-31.

Table 6-31: Values for the parameters used in the bathroom air concentration model

Symbol	Parameter name	Central value	Uncertainty factor
$f_{\text{w-gw}}$	Fraction of water needs supplied by groundwater	0.8	1.2
W_{bath}	Water use rate for showering/bathing	7.4 L/min	2.2
VR_{bath}	Bathroom ventilation rate	0.93 m^3/min	2.2

Note: Central values and uncertainty factors have been derived from data in [26].

6.3.3 Toxicity endpoints

Two types of toxic effect endpoints are usually considered in risk assessment: (i) cancer effects, and (ii) other chronic non-cancer effects.

CANCER EFFECTS

The risk associated with the exposure to cancer-causing agents is evaluated using either cancer potency factors (also known as cancer slope factors), or concentration-based unit risk factors. The lifetime probability of developing cancer is estimated by the equation:

$$P(\text{Cancer}) = \text{CSF} \times \text{Dose} \quad (6-128)$$

or

$$P(\text{Cancer}) = \text{UR} \times \text{Concentration} \quad (6-129)$$

where CSF is the cancer slope factor (usually expressed in units of $(\text{mg}/\text{kg}/\text{day})^{-1}$) and UR is the unit risk factor, which has inverse concentration units. Since unit risk factors are usually used to compute cancer risks for the inhalation route, the concentration used in the expression above is the concentration of the chemical in air. Unit risks can be converted to cancer slope factors

using exposure media contact rates. For example, the equivalence between inhalation unit risks and inhalation cancer slope factors is given by:

$$P(\text{Cancer}) = UR_{inh} \times C_a = CSF_{inh} \times (BR \times C_a) \quad (6-130)$$

where BR is the average breathing rate in units of $\text{m}^3/\text{kg}/\text{day}$ ⁵⁶. Thus

$$CSF_{inh} = \frac{UR_{inh}}{BR} \quad (6-131)$$

The lifetime cancer probability estimate assumes exposure to the same dose or concentration throughout the life span of the exposed individuals. An explicit assumption in the risk assessment paradigm for cancer-causing agents is that there is no safe level of exposure. As the dose or concentration decreases, there is a corresponding decrease in cancer risk, but the risk does not vanish unless the exposure drops to zero.

The cancer human toxicity potential (HTP) indicator calculated by the spreadsheet model is the sum of the cancer risk from the inhalation route and the cancer risk from the ingestion route. The risk for each route is computed by multiplying the appropriate modeled dose [in $(\text{mg}/\text{kg}/\text{day})/(\text{kg}/\text{km}^2/\text{day})$] by the cancer slope factor for that particular route [in units of $(\text{mg}/\text{kg}/\text{day})^{-1}$]:

$$HTP_{cancer} = CSF_{inh} \times Dose_{inh} + CSF_{oral} \times Dose_{oral} \quad (6-132)$$

where the inhalation and oral doses ($Dose_{inh}$ and $Dose_{oral}$, respectively) are calculated according to eqs (6-59) and (6-60). If a slope factor is only available for one of the routes, it is assumed that it can be applied to both routes. An exception is made when there is information available indicating that the substance does not pose health risks through the route for which toxicity potency factors are not available (e.g. inhalation potency factors are not extrapolated to estimate oral potency factors for asbestos and sulfuric acid).

CHRONIC NON-CANCER EFFECTS

For non-cancer health effects it is assumed that there are safe levels of chronic exposure below which no noticeable toxic effects will take place. The estimates for these safe-levels are known as reference concentrations (RfC) and reference doses (RfD) in the American literature.

⁵⁶ The standard assumption used is $BR = (20 \text{ m}^3/\text{day})/(70 \text{ kg}) = 0.286 \text{ m}^3/\text{kg}/\text{day}$

The nomenclature used in Europe is predicted no-effect concentrations (PNEC) and acceptable or tolerable daily intakes (ADI/TDI). These safe-levels are determined from observations of the lowest dose or concentration at which the first adverse effect occurs either in people or in experimental animals, or the highest dose at which there are no observable effects.

An implicit assumption made when comparing chemicals on the basis of their non-cancer assessment factors is that all toxic effects are equally undesirable. An alternative would be to calculate a separate assessment factor for each chronic toxic effect of concern, but due to the large number of potential end-points, the large number of chemicals in use, and the paucity of toxicity data, this option has not been pursued by the risk assessment community.

The metric used to characterize the risk from exposure to chemicals causing non-cancer effects is the hazard quotient (HQ), which compares the daily exposure to a chemical to the reference value at which no adverse effects are expected in even the most sensitive individuals of a population:

$$HQ = \frac{Dose}{RfD} \quad (6-133)$$

or

$$HQ = \frac{Concentration}{RfC} \quad (6-134)$$

Most of the risk assessment data is derived from animal studies, although for a few chemicals the available epidemiological data is sufficient to establish risk assessment factors based on direct observations of toxic impacts in humans. A series of safety factors are typically used to estimate human reference doses on the basis of animal reference doses. For example, the U.S. EPA uses the safety factors listed in Table 6-32 [67]. The cumulative nature of the safety factors means that a toxicological LOAEL obtained from a short-term animal study would be divided by a factor of in the range 1,000 to 10,000 in order to derive a human reference dose.

Table 6-32: Safety factors applied to non-cancer toxicity data for the derivation of reference doses

Type of uncertainty	Safety factor used
Uncertainty in the extrapolation from valid experimental results in studies using prolonged exposure to average healthy humans	10
Additional uncertainty in extrapolating from valid results of long-term studies on experimental animals when results of studies of human exposure are not available or are inadequate.	10
Additional uncertainty in extrapolating from less than chronic results on experimental animals when there are no useful long-term human data	10
Additional uncertainty in deriving an RfD from a lowest observable adverse effect level (LOAEL), instead of a no observable adverse effect level (NOAEL)	10
Modifying factor (MF) used to account for scientific uncertainties of the study and data base not explicitly treated above; e.g., the completeness of the overall data base and the number of species tested. The default value for the MF is 1.	1 to 10

The non-cancer HTP indicator is calculated by the spreadsheet model as the sum of the hazard quotient from the inhalation route and the hazard quotient from the ingestion route:

$$HTP_{noncancer} = \frac{Dose_{inh}}{RfD_{inh}} + \frac{Dose_{oral}}{RfD_{oral}} \quad (6-135)$$

where the inhalation reference dose (RfD_{oral}) is related to the reference concentration through an expression analogous to eq (6-131):

$$\frac{1}{RfD_{inh}} = \frac{1}{RfC} \times \frac{1}{BR} \quad (6-136)$$

If a reference dose is only available for one of the routes, it is assumed that it can be applied to both routes, unless there is information available indicating that the chemical poses no chronic non-cancer risks through the route for which a reference dose is not available.

AGGREGATION OF CANCER AND NON-CANCER IMPACTS

A combined chronic health indicator is computed as the weighed sum of the cancer risk indicator and the non-cancer effects indicator:

$$HTP = HTP_{cancer} + w \cdot HTP_{non-cancer} \quad (6-137)$$

where the weighing factor w is the probability of cancer that is considered equivalent to exposure to a non-carcinogen at the reference dose. Values of w in the environmental evaluation literature

range from 10^{-6} to 10^{-3} [9,17,18,68,69]. Uncertainty in the parameter w is therefore modeled by a lognormal distribution with central value 10^{-5} and an uncertainty factor of 100^{57} .

6.3.4 Chemical-specific input data requirements

In addition to toxicological cancer slope factors and reference doses, the multimedia fate, transport, and exposure model accepts chemical-specific data for the following parameters: Henry's law constant (H), vapor pressure (P^{vap}), solubility (Solub), molecular weight (MW), solid particles-water distribution coefficients in soil (K_{Ds}), sediments (K_{Dd}), and suspended sediments (K_{Dw}), melting point (T_{m}), aerosol-water partition coefficient (K_{qw}), octanol-water partition coefficient (K_{ow}), fish bioconcentration factor (BCF), degradation half-life in air (t_{a}), degradation half-life in water (t_{w}), aerobic degradation half-life (t_{aerobic}), hydrolysis half-life ($t_{\text{hydrolysis}}$), degradation half-life in soil (t_{s}), and degradation half-life in sediments (t_{sed}). Data gaps in required parameters are overcome using the default expressions shown in Table 6-33.

The environmental information management system EnvEvalTool developed in this work (see Chapter 9) was used to store toxicological and fate and transport data for chemicals. As described in section 9.4.2, a hierarchy of data sources was established for each type of data element, with less uncertain data sources ranked higher than sources with more uncertainty. An uncertainty distribution was assigned to each data element. When uncertainty distributions were not given in the original data source, lognormal distributions were assigned to them. The central value used was the nominal value published in the source consulted, while the uncertainty factor of the distribution was derived from correlations between data from the source of interest and data from the highest-quality sources for that type of data element.

Following the data quality ranking hierarchy, when no high-quality data was available for a required data element, estimates were obtained based on lower-preference quantitative, semi-quantitative or even qualitative information by generating correlations between lower-preference data and high-preference data.

⁵⁷ The uncertainty factor is defined here as the factor by which the central value should be multiplied and divided to yield the 95% confidence interval for the value of a lognormally-distributed random variable

Table 6-33: Expressions used to provide estimates for required chemical-specific parameters with missing data

Symbol	Expression used when parameter value is not available		
	“Type 1” chemicals	“Type 2” chemicals	Metals
H	1. $\frac{P_{vap}}{Solub/MW}$ 2. $\frac{P_{vap}^L}{\text{LogN}(15 \frac{mol}{m^3}, 1.4 \times 10^5)}$ 3. $\text{LogN}(0.46 \frac{Pa \cdot m^3}{mol}, 1.7 \times 10^6)$		0
K _{Ds}		$\phi_{sp}K_{oc}$	$\text{LogN}(1000, 525)$
K _{Dd}		$\phi_{dp}K_{oc}$	K _{Ds}
K _{Dw}		$\phi_{wp}K_{oc}$	K _{Ds}
P _L ^{vap}	1. P^{vap} (if $T \geq T_m$) $P^{vap} \exp\left\{6.79\left(1 - \frac{T_m}{T}\right)\right\}$ (if $T < T_m$) 2. $H \times \text{LogN}(15 \frac{mol}{m^3}, 1.4 \times 10^5)$		Not used
K _{qw}	Not used		Z _{sp}
K _{ow}		N(2.2, 2.0)	Not used
BCF		Eq (6-102)	$\text{LogN}(100, 2)$
t _a		$\text{LogN}(39 \text{ hrs}, 460)$	∞
t _w	1. $\text{Min}(t_{aerobic}, t_{hydrolysis})$ 2. $\text{Min}(\text{LogN}(500 \text{ hrs}, 11.4), t_{hydrolysis})$ 3. $\text{LogN}(500 \text{ hrs}, 11.4)$		∞
t _s		t _w	∞
t _{sed}		4 × t _s	∞

Notes: Most of the distributions listed in this table are based on data for TRI chemicals with 1997 reported emissions; the distribution for K_{Ds,metals} is based on data in [18]; the distribution for BCF_{metals} is derived from data in [70]; other expressions are taken from [9,27].

As an illustration, Table 6-34 shows the hierarchy used to assign distributions for the non-cancer inhalation reference concentration. The twelfth row of the table shows that occupational exposure threshold limit value factors were used to estimate reference concentrations for 76 of the chemicals with TRI emissions in the period of interest. A correction factor of 1/750 is used to estimate RfCs from TLVs, with an uncertainty factor 85. The source of these correction and uncertainty factors is shown in Figure 6-22, where risk assessment non-

cancer chronic inhalation factors are plotted against the ACGIH TLVs. The correction factor (CF) was given by the solution to the following optimization problem:

$$\begin{aligned} & \underset{CF}{\text{Min}} UF \\ & \text{s.t.} \quad \log_{10}(\sqrt{UF}) = \text{StdDev}(RfC - TLV \times CF) \\ & \quad \quad \quad CF > 0 \end{aligned} \tag{P6-1}$$

where $\text{StdDev}(\bullet)$ is the standard deviation operator, and UF stands for the uncertainty factor.

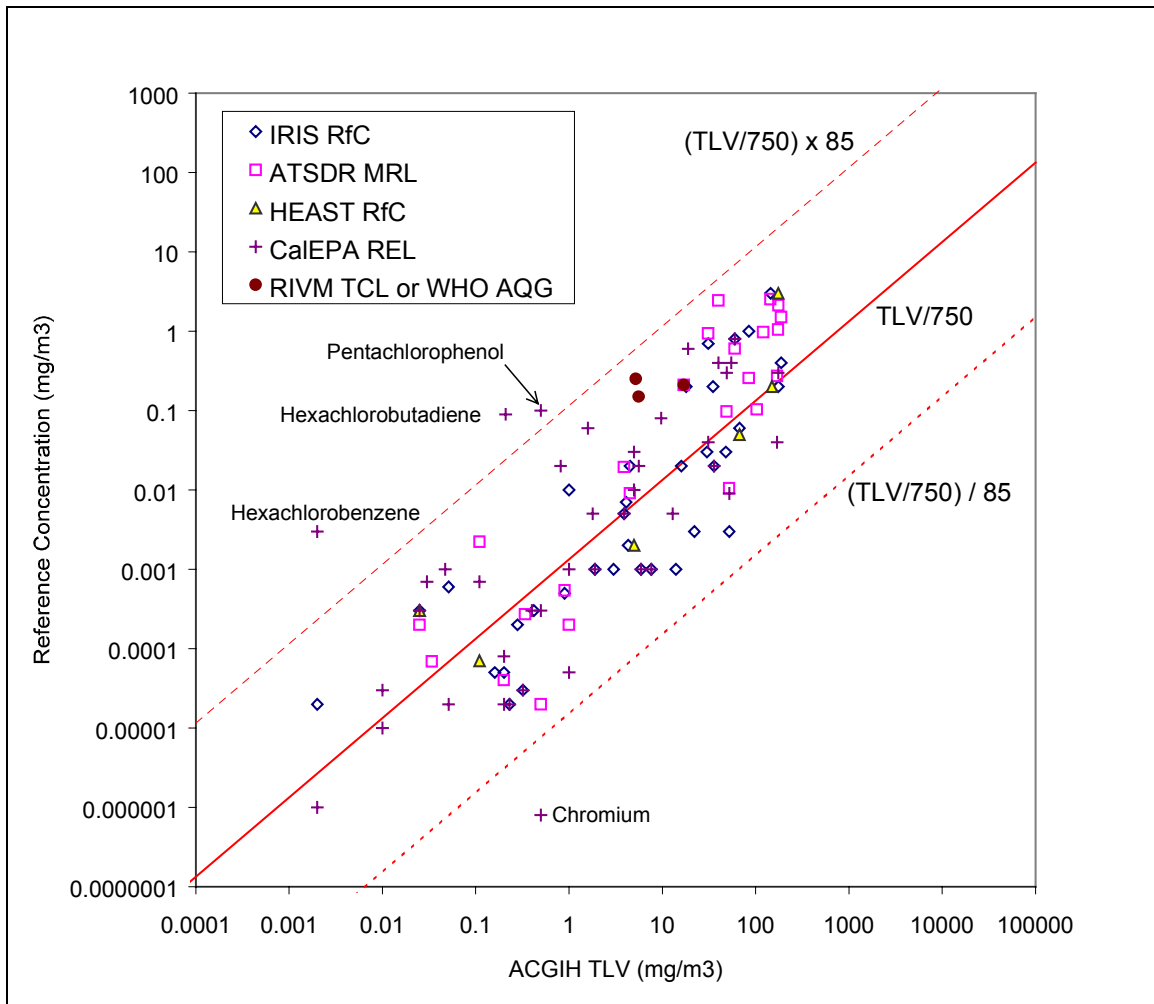


Figure 6-22: Correlation between TLV values and chronic non-cancer health effects risk assessment values.

Table 6-34: Data elements used to derive probability distributions for non-cancer chronic toxicity reference concentrations (TRI chemicals with emissions to air, discharges to water, or transfers to wastewater treatment plants in 1988-1997)

Type of Data	Data Element	Units	Source	Year	Number available	Number used	Median value	Uncertainty factor
Quantitative inhalation data	RfC	mg/m ³	This work	2000	18	18	Distribution developed on the basis of conflicting information	
	IRIS RfC	mg/m ³	[71]	2000	55	45	RfC	(SF×MF) ^{0.5} or 14
	ATSDR MRL	mg/m ³	[72]	2000	33	17	MRL	14
	CalEPA REL	µg/m ³	[73]	2000	129	63	1000×REL	14
	IRIS/HEAST RfC	mg/m ³	[74]	1999	18	9	RfC	14
	OPPTEIM RfC	mg/m ³	[75]	1999	89	16	RfC	(SF×MF) ^{0.5} or 14
	CalEPA REL	µg/m ³	[74]	1997	100	1	1000×REL	14
	EPA RfC	mg/m ³	[7]	1997	68	3	RfC	14
	EPA HWIR RfC	mg/m ³	[74]	1995	2	2	RfC	14
	EDF-CalEPA REL	µg/m ³	[74]	1994	2	2	1000×REL	14
	CAPCOA REL	µg/m ³	[74]	1992	7	6	1000×REL	14
Quantitative inh. data used with extrapolation	ACGIH TLV	mg/m ³	[76]	1997	219	76	TLV/750	85
	ACGIH LC ₅₀	mg/m ³	[77]	1991	72	1	LC ₅₀ /(150,000)	150
	NIOSH LC ₅₀	mg/m ³	[77]	1995	104	11	LC ₅₀ /(180,000)	200
Quantitative oral data	RfD	mg/kg/day	This work	2000	13	1	Distribution developed on the basis of conflicting information	
	IRIS RfD	mg/kg/day	[71]	2000	174	68	RfD×70/20	(SF×MF) ^{0.5} or 20
	IRIS/HEAST RfD	mg/kg/day	[74]	1999	216	9	RfD×70/20	20
	OPPTEIM RfD	mg/kg/day	[75]	1999	257	22	RfD×70/20	(SF×MF) ^{0.5} or 20
	OPP RfD	mg/kg/day	[74]	1997	29	8	RfD×70/20	20
Quantitative oral data used with extrapolation	CML RfD est from NOAEL	mg/kg/day	[10]	1996	4	1	RfD×70/20	60
	ACGIH LD ₅₀	mg/kg	[77]	1991	95	1	LD ₅₀ /(22,000)×70/20	140
	NIOSH LD ₅₀	mg/kg	[77]	1995	161	8	LD ₅₀ /(21,000)×70/20	200
Semi-quantitative	CERCLA RQ	lbs	[9]	1994	47	4	RQ/(45,400)×70/20	210
	CERCLA RQ	lbs	[7]	1994	64	2	RQ/(45,400)×70/20	210
Qualitative	HSAT Rank	1,2 or 3	[9]	1998	5	2	1→0.006; 2→0.005; 3→0.0006	400
	HSAT Rank	1,2 or 3	[7]	1997	314	48	1→0.006; 2→0.005; 3→0.0006	400
	HSAT Category Rank	1,2 or 3	[7]	1997	267	1	1→0.006; 2→0.005; 3→0.0006	400
	TSCA Triage	L, M or H	[78]	1994	257	12	L→0.018; M→0.007; H→0.003	480
No Data						33	0.005	800

Notes: “Source” is the reference from which the values were extracted (includes secondary sources); Year is the year of publication of the original database; “Median value” shows the formula used to convert data elements into median RfC values; SF and MF, are respectively, the uncertainty (safety) factor and the modifying factor used in the IRIS and HEAST databases.

In a few cases, credible sources had widely different values for the same data element. In such cases, distributions for the data element that were wide enough to include all credible estimates were developed and placed at the top of the hierarchy. For instance, the first row of Table 6-34 shows that there were 18 chemicals for which equally credible sources of reference concentrations differed by a factor larger than the default uncertainty factor of 14 assigned to the distributions. An example is chromium, for which the HEAST database gives a RfC of 0.0001 mg/m³ and for which CalEPA's OEHHA has assigned a REL of 0.0008 µg/m³ (8×10^{-7} mg/m³). For this case study a lognormal distribution with central value 9×10^{-6} mg/m³ and uncertainty factor 125 was used to span both distributions.

6.3.5 Modeling results

HUMAN EXPOSURE POTENTIALS

The combined fate, transport and exposure model was ran with data for a set of 1,318 chemicals were obtained from EPA's 1998 Waste Minimization Prioritization Tool Spreadsheet Document [9]. The purpose of the exercise was to examine the uncertainty associated with the estimation of chemical exposure. Figure 6-23 shows the distribution of geometric mean values for the exposure indicator associated with emissions to air and discharges to surface water. The figure also shows where in the distribution the values for three common chemicals fall. There is a 4 to 5 order-of-magnitude difference in exposure potential between phenol and carbon tetrachloride. This means that between 10,000 and 100,000 more pounds of phenol would have to be released to the environment as pounds of carbon tetrachloride for people to be exposed to equal quantities of both pollutants.

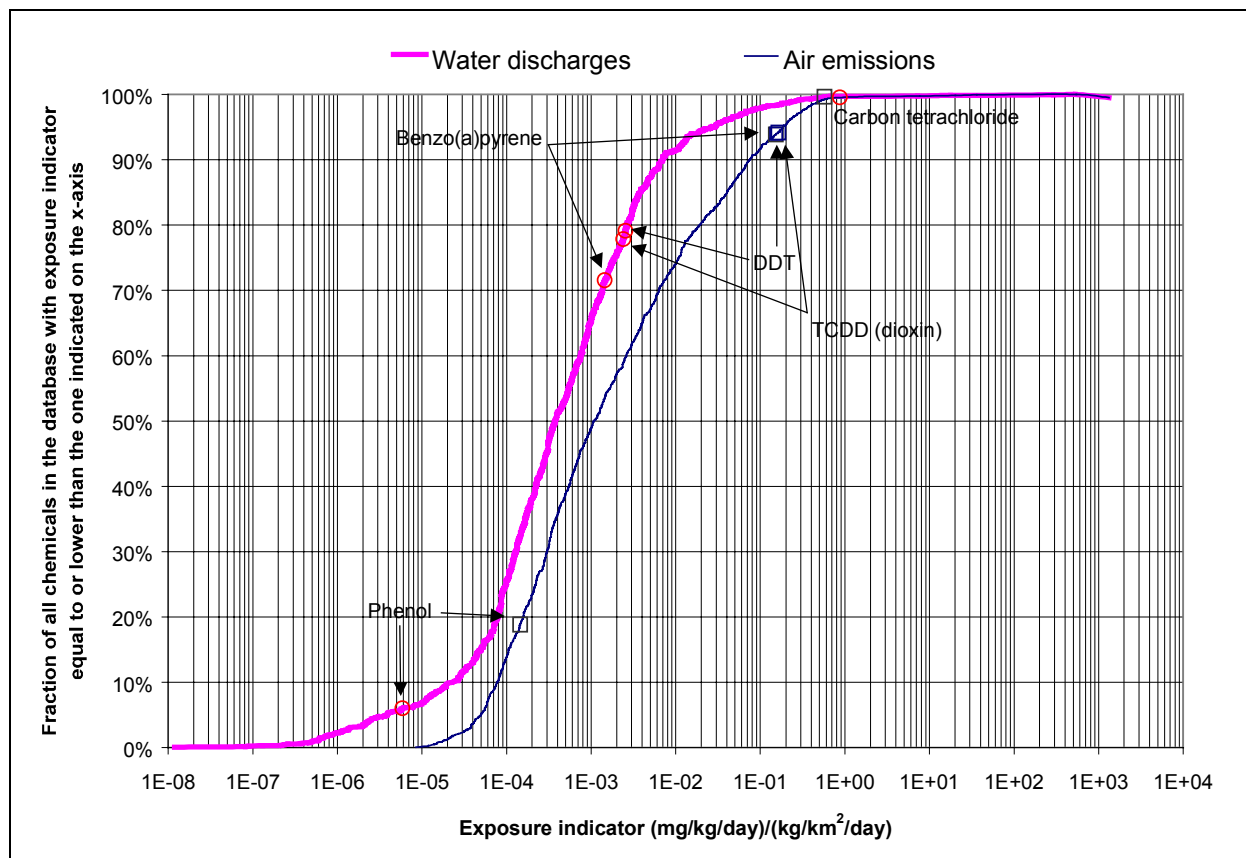


Figure 6-23: Distribution of geometric means for the exposure indicator of 1,318 chemicals included in the WMPT database

Figure 6-24 shows the distribution for uncertainty factors in the same sample of chemicals. Uncertainty factors were calculated from the Monte Carlo simulation results as the square of the geometric standard deviation of an indicator's value. Most of the uncertainty factors are in the range 4 to 200 (exposure from emissions to air), or in the range 10 to 100 (discharges to surface water).

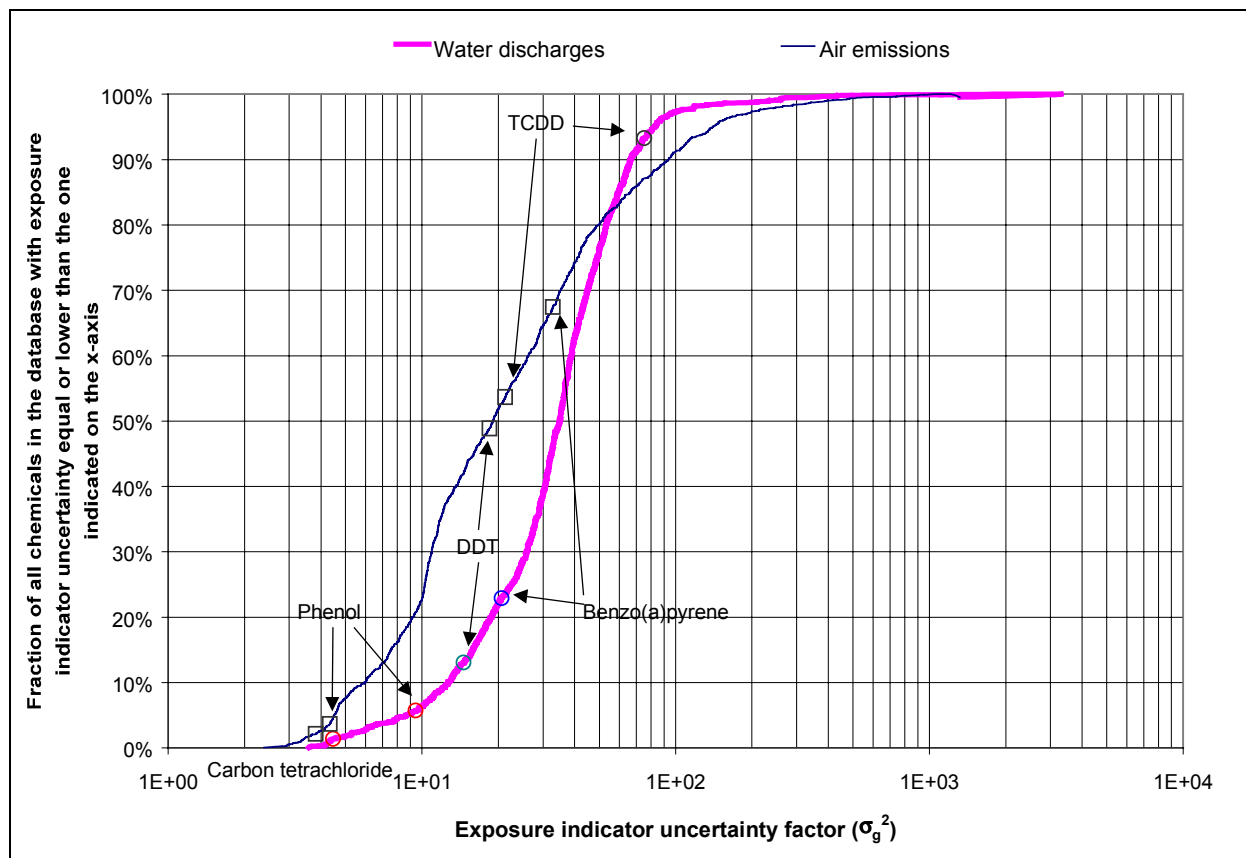


Figure 6-24: Distribution of uncertainty factors for the exposure indicator of 1,318 chemicals included in the WMPT database

HUMAN TOXICITY POTENTIALS

In a second exercise, distributions for human toxicity potentials (HTP, see eqs (6-132), (6-135), and (6-137)) were obtained for all of the chemicals in the U.S. toxics release inventory with any reported emissions in the period 1988-1997⁵⁸. As shown in Figure 6-25, the cancer indicator geometric means span a range of about 8 orders of magnitude. This means that the emission of one gram of a substance at the high end of the distribution of about one hundred million times as likely to cause cancer than the emission of a gram of a substance at the low end of the spectrum. In other words, it would be necessary to emit 100 metric tons of a substance at the low end of the distribution to generate a cancer risk that is approximately equal to that imposed by the emission of a gram of a substance from the high end of the distribution. A

⁵⁸ These distributions were obtained as part of the case study described in section 6.5.

similar plot is shown in Figure 6-26, this time for the case of a chronic health indicator that combines cancer and non-cancer impacts. This distribution is even broader, spanning a range of more than 10 orders of magnitude.

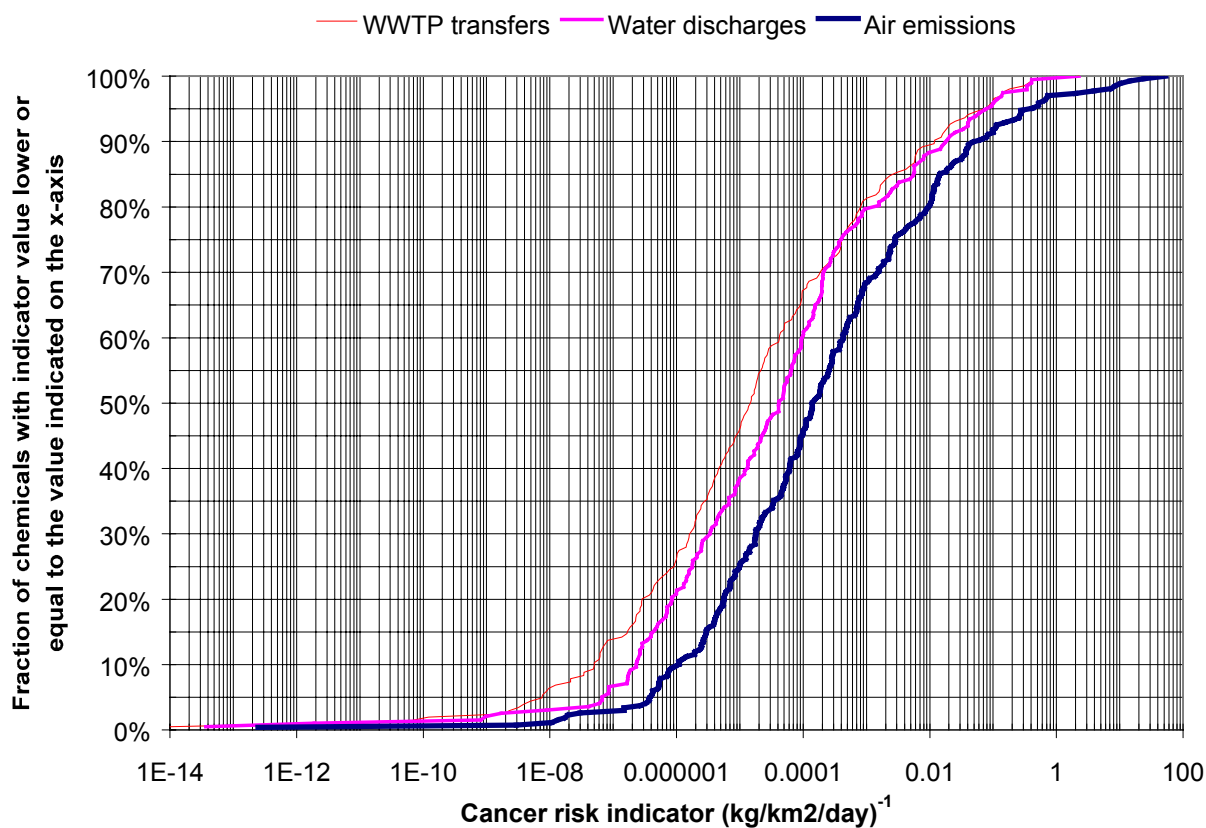


Figure 6-25: Distribution of cancer risk indicators for emissions to air of 263 substances with reported TRI emissions in 1988-1997 and some information regarding carcinogenicity.

The median uncertainty factor for cancer risk indicators is about 30, with 80% of the cancer risk indicators having uncertainty factors lower or equal than 100 (Figure 6-27). The range of uncertainty factors obtained here is consistent with the estimates in the range 5 to 240 made by Hofstetter (see section 6.2.2). It is also somewhat lower than the 2 to 3 orders of magnitude uncertainty that had been estimated on the basis of correlations among different indicator sets. Not surprisingly, the uncertainty factors associated with the combined cancer and non-cancer indicators are larger, as shown in Figure 6-28. In this case half of the chemicals have uncertainty factors larger than 100. These values are much lower, however, than the 3 to 5

orders of magnitude range that had been estimated on the basis of correlations among different indicator sets. Given the fact that the parametric uncertainties included in the model (both for landscape properties and chemical-specific properties) were quite generous, the poor agreement in indicator values among the various indicator sets presented in section 6.2.2 must be due to differences in model structure.

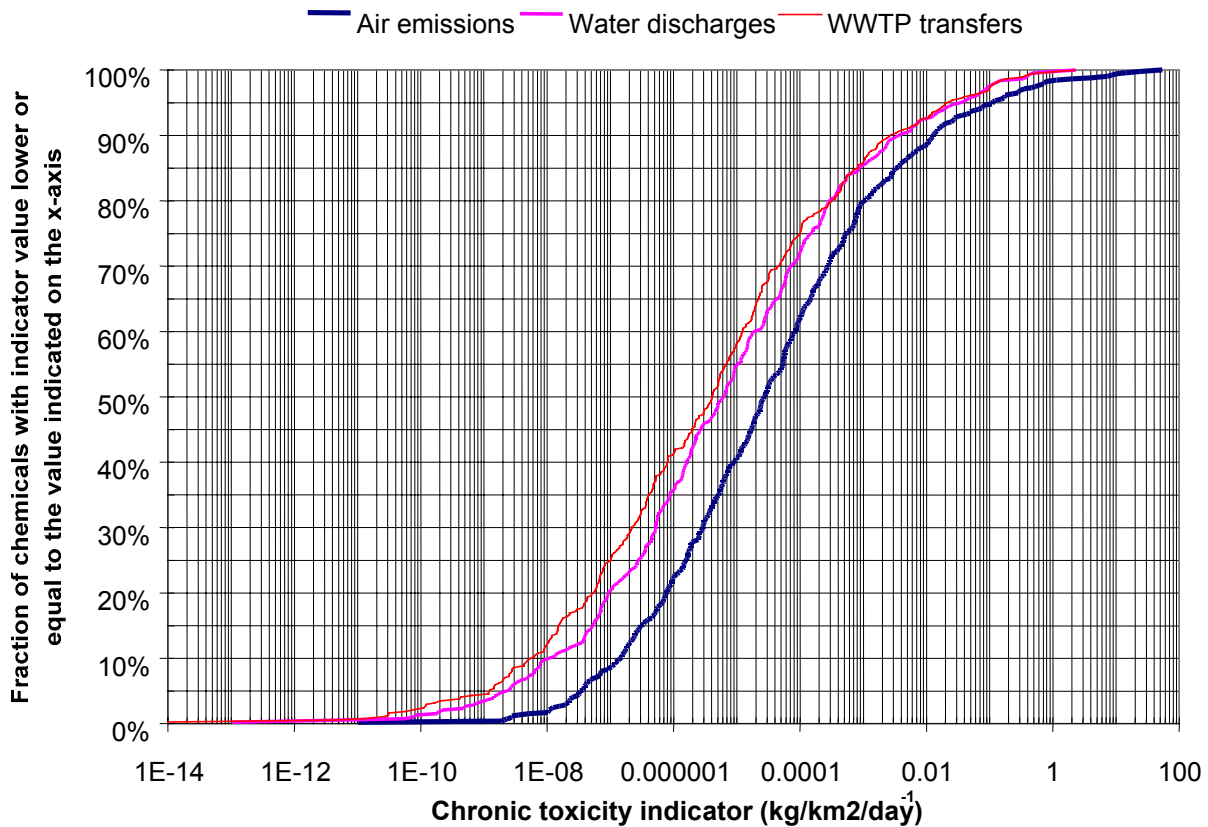


Figure 6-26: Distribution of chronic toxicity indicators (expressed as cancer risk equivalents) for emissions to air of 505 substances with reported TRI emissions in 1988-1997.

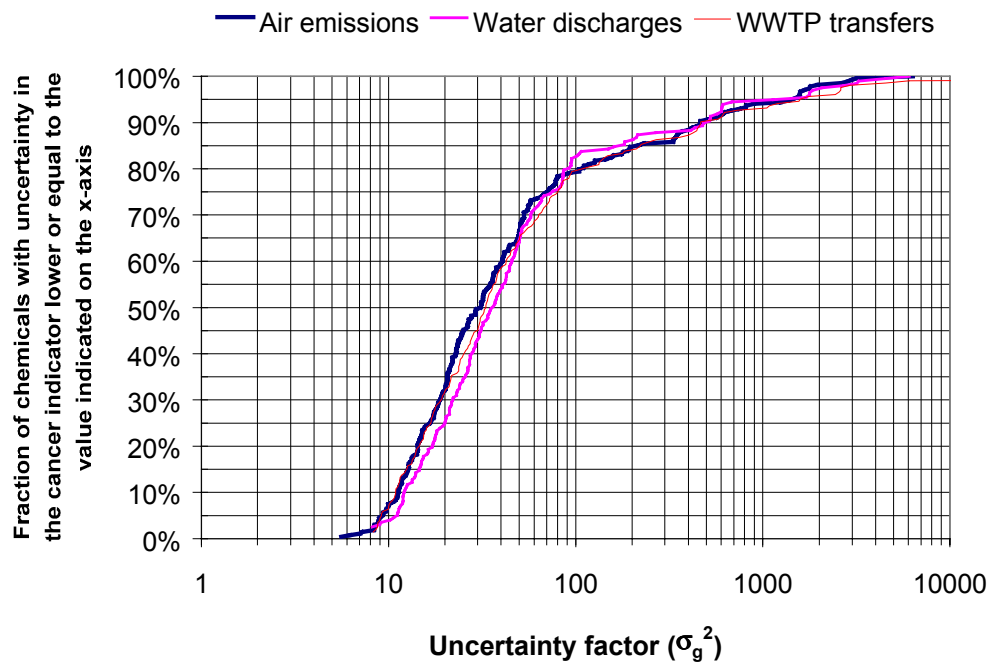


Figure 6-27: Distribution of uncertainties in cancer risk indicators for emissions to air of 263 substances with reported TRI emissions in 1988-1997 and some information regarding carcinogenicity.

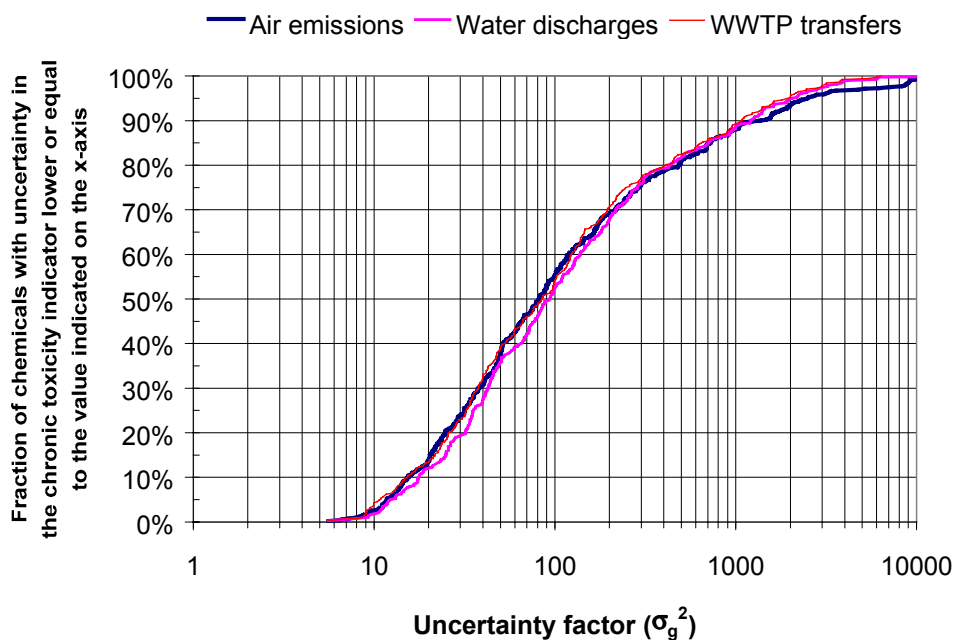


Figure 6-28: Distribution of uncertainties in chronic risk indicators for emissions to air of 505 substances with reported TRI emissions in 1988-1997

6.4 Management of uncertainty in toxicity impact indicators

6.4.1 Ranking of model uncertainties through the analysis of relative indicator distributions

Considerable effort was spent in section 6.3 to check whether assumptions made to model different environmental processes were sound. With so many possible choices and uncertain parameters, it would be very useful to have tools that enable the modeler to distinguish between those choices that are important and those that are inconsequential.

There are a large number of structural and parametric uncertainties in the model. The structural uncertainties are summarized in Table 6-35. In addition to chemical-specific uncertain parameters, there are 80 uncertain parameters in the combined multimedia exposure model (see the tables in section 6.3 for the parameter names and their distributions). The various structural and parametric uncertainties vary in their contribution to the uncertainty in human doses. Some of the uncertainties have a significant impact, while others have practically no effect.

METHOD

Properties of the distribution of relative doses are used to assess and rank model uncertainties. The relative dose of a chemical i computed by the model when parameter or structural uncertainty j is varied relative to the dose of the same chemical under base case (bc) conditions is given by:

$$RD_{i,j} = \frac{Dose_{i,j}}{Dose_{i,bc}} \quad (6-138)$$

For a set of chemicals, two properties of the distribution of $RD_{i,j}$ values can be used to assess the impact of uncertainties:

- (a) The **geometric mean** of the $RD_{i,j}$ values is used to assess whether uncertainty j introduces systematic biases in the calculated doses.
- (b) The **geometric standard deviation** shows whether uncertainty j changes the ranking of the chemicals in the set with respect to the computed dose.

Table 6-35: Structural uncertainties in the combined multimedia exposure model

Model	Num	Modeling choice	Mackay EQC [20]	CalTox [14]	This work
Fate and transport	1	Include aquatic biota subcompartment in surface water compartment?	Yes	No	No
	2	Number of soil layers	1	3	2
	3	Include terrestrial vegetation compartment?	No	Yes	Yes
	4	Include aerosol particle resuspension from soil?	No	Yes	No
	5	Include aerosol particle resuspension from plant surfaces?	n/a	Yes	No
	6	Include soil layer in the calculation of terrestrial vegetation bulk fugacities?	n/a	No	Yes
	7	Include aerosol particle layer in the calculation of terrestrial vegetation bulk fugacities?	n/a	Yes	No
	8	Include air advection out of control volume?	Yes	No	No
	9	Include water advection out of control volume?	Yes	No	No
	10	Basis for degradation rates in lower atmosphere compartment	?	Bulk comp.	Air phase
	11	Basis for degradation rates in surface water compartment	?	Bulk comp.	Water phase
	12	Basis for degradation rates in ground soil compartment	?	Water phase	Bulk comp.
	13	Basis for degradation rates in root zone soil compartment	n/a	Water phase	Bulk comp.
	14	Basis for degradation rates in sediments compartment	?	Water phase	Bulk comp.
	15	Type of rain dissolution equations used	Continuous	No rain	Intermittent
	16	Include TSCF correction to root uptake transport rate?	n/a	No	Yes
Exposure	17	Type of irrigation model	n/a	Fraction retained	Mass balance
	18	Type of leaf crops bioconcentration model	n/a	Equilibrium	Kinetic
	29	Root crops bioconcentration model used	n/a	McKone	Briggs et al.
	20	Milk biotransfer model used	n/a	Travis et al.	This work's
	21	Beef biotransfer model used	n/a	Travis et al.	This work's
	22	Eggs biotransfer model used	n/a	CalTox	This work's

Suppose we were uncertain about the landscape area used as a basis for the calculations. Increasing the landscape area by a factor of 10 while leaving emissions and all other parameters unchanged would decrease the dose of all chemicals by a factor of 10, since the concentrations in all environmental media would decrease by a factor of 10 (for a closed system). In this case, the geometric mean of the $RD_{i,(10x \text{ landscape area})}$ distribution would be 0.10, while the geometric

standard deviation would be exactly 1.0. This means that the ranking of chemicals with respect to dose is unchanged by the arbitrary choice of landscape area.

Data for a set of 1,318 chemicals were obtained from EPA's 1998 Waste Minimization Prioritization Tool Spreadsheet Document [9] were used for the analysis presented in this section. According to the EPA's documentation, this data set includes chemicals in commerce with the potential to adversely impact human or ecological health. The combined multimedia fate, transport and exposure model was used to estimate human doses resulting from releases of 1000 kg/hr to either air or water in a 100,000 km² landscape. The doses obtained with all the uncertain parameters set at their central values and all the modeling choices resolved as described in section 6.3 were used as base case doses in the sensitivity analysis. Uncertain parameters were sampled at the 5th and 95th percentiles of their distributions, while structural uncertainties were examined by switching the choice made in this work to the alternative choice⁵⁹.

RESULTS

Table 6-36 shows sensitivity analysis results for the structural uncertainties. The table is sorted in descending order of maximum geometric standard deviation. The structural uncertainty with the largest impact is the choice of aboveground crops bioconcentration model. Other structural uncertainties associated with the exposure model turn out to be very significant, including the choice of irrigation, milk biotransfer, and beef biotransfer models. Structural uncertainties with little consequence include: whether aquatic biota is considered in the calculation of bulk surface water fugacities, whether aerosol particles are resuspended from soil or plant surfaces, whether a soil layer is included in the calculation of bulk plant fugacities, and whether the TSCF correction is implemented for the uptake of chemicals from root zone soil by terrestrial vegetation.

Sensitivity analysis results for a subset of the parametric uncertainties are shown in Table 6-37. Only results for the top 20 parameters ranked in order of descending maximum geometric standard deviation are shown. The columns for the logarithmic mean metric show the ratio of

the maximum logarithmic mean to the minimum logarithmic mean. The impact of the parametric uncertainties is small compared to the impact of the modeling uncertainties. The most important parametric uncertainties are associated with aerosol particles, suspended sediments, the aboveground crops bioconcentration model, and with the parameter that specifies what fraction of water needs are satisfied by groundwater sources.

Table 6-36: Sensitivity results for structural uncertainties

Name	Model	Air emissions		Water discharges	
		GSD	LogMean	GSD	LogMean
Type of leaf crops bioconcentration model	Exposure	92.005	71.582	2.328	1.374
Type of milk biotransfer model	Exposure	7.713	1.117	7.520	1.799
Type of irrigation model	Exposure	1.142	1.040	6.240	3.841
Type of beef biotransfer model	Exposure	4.837	1.392	6.030	1.723
Basis for degradation rates in ground soil	Fate and Transport	3.269	2.073	4.365	2.069
Number of soil layers	Fate and Transport	1.456	1.023	2.893	0.780
Type of rain dissolution equations	Fate and Transport	2.691	0.678	1.000	1.000
Type of root crops bioconcentration model	Exposure	2.467	1.339	1.372	1.042
Basis for degradation rates in air	Fate and Transport	2.372	0.710	1.031	0.996
Include air advection?	Fate and Transport	2.366	0.764	2.228	0.824
Include water advection?	Fate and Transport	1.256	0.953	1.970	0.539
Include plants compartment?	Fate and Transport	1.817	1.028	1.338	1.046
Basis for degradation rates in root zone soil	Fate and Transport	1.577	1.234	1.111	1.039
Type of eggs biotransfer model	Exposure	1.123	1.012	1.397	1.077
Basis for degradation rates in sediments	Fate and Transport	1.011	1.001	1.233	1.148
Basis for degradation rates in water	Fate and Transport	1.000	1.000	1.182	0.922
Include aerosol layer in plants compartment?	Fate and Transport	1.049	0.995	1.029	0.997
Include TSCF correction to root uptake by terrestrial vegetation?	Fate and Transport	1.016	0.996	1.005	0.999
Include aerosol particle resuspension from leaf surfaces?	Fate and Transport	1.004	1.000	1.000	1.000
Include soil layer in plants compartment?	Fate and Transport	1.004	1.001	1.000	1.000
Include aquatic biota subcompartment in water compartment?	Fate and Transport	1.000	1.000	1.002	1.001
Include aerosol resuspension from ground soil?	Fate and Transport	1.001	1.000	1.000	1.000

⁵⁹ All the structural uncertainties are binary choices, with the exception of the number of soil layers. The 3-layer soil option was not implemented in the spreadsheet model, so the alternative choice used in the sensitivity analysis is 1 soil layer.

Table 6-37: Sensitivity analysis results (top 20 parametric uncertainties)

Symbol	UF	Ref	Model	Air Emissions		Water Discharges	
				Max(GSD _{5th} , GSD _{95th})	max(LogMean _{5th} , LogMean _{95th})	Max(GSD _{5th} , GSD _{95th})	max(LogMean _{5th} , LogMean _{95th})
					min(LogMean _{5th} , LogMean _{95th})		min(LogMean _{5th} , LogMean _{95th})
U _q	8.8	Table 6-20	Fate and transport	1.628	1.909	1.111	1.029
v _{wp,w}	5.3	Table 6-16	Fate and transport	1.001	1.000	1.470	1.338
f _{w-gw}	1.2	Table 6-31	Exposure	1.029	1.020	1.422	1.600
Q	10	Table 6-20	Fate and transport	1.400	1.210	1.049	1.007
M _{plants}	3.0	Table 6-29	Exposure	1.390	1.582	1.216	1.163
k _g	3.0	Table 6-29	Exposure	1.390	1.582	1.216	1.163
U ₉	3.0	Table 6-20	Fate and transport	1.086	1.023	1.388	1.628
v _q	3.2	Table 6-15	Fate and transport	1.346	1.328	1.053	1.015
h _p	5.6	Table 6-19	Fate and transport	1.333	1.157	1.077	1.023
h _g	5.29	Table 6-17	Fate and transport	1.198	1.161	1.310	1.202
h _w	2.24	Table 6-15	Fate and transport	1.054	1.041	1.295	2.268
m	1.13	Table 6-29	Exposure	1.295	1.266	1.098	1.044
h _a	2.45	Table 6-15	Fate and transport	1.280	2.766	1.192	1.178
F _{soil} ^{splash}	3.3	Table 6-29	Exposure	1.112	1.076	1.275	1.192
IR _{fish}	2.2	Table 6-22	Exposure	1.049	1.026	1.255	1.815
f _{water}	2.65	Table 6-15	Fate and transport	1.108	1.053	1.230	4.036
U ₃	2.8	Table 6-20	Fate and transport	1.192	1.051	1.060	1.024
D _A	3.2	Table 6-20	Fate and transport	1.185	1.026	1.011	1.001
h _{rz}	2.53	Table 6-17	Fate and transport	1.179	1.129	1.003	1.003

DISCUSSION

The procedure used here can also be used to identify exposure pathways that do not contribute significantly to the exposure indicator. This allows simplifying the model without eliminating important pathways. A structural sensitivity analysis with the WMPT chemical data set was carried out turning off one exposure pathway at a time. The results are shown in Table 6-38. The table shows that the egg ingestion and bathroom air inhalation pathways are not important and could be safely removed from the model.

6.4.2 Assessment of the information content of indicators

A set of indicators provides information if it allows a decision-maker to discriminate among alternatives. By definition, the assessment of the information content of indicators requires the specification of the decision context in which they will be applied. Since it is impossible to know *a priori* all the decision contexts in which environmental indicators will be applied, an arbitrary decision context is specified for the purpose of information content

assessment. The decision context is the discrimination among emissions of different substances, assuming the amounts emitted are the same (e.g. one is trying to decide whether a 1 kg emission of substance A is worse than the emission of 1 kg of substance B).

Table 6-38: Sensitivity results for exposure pathways

Sensitivity tested	Air emissions		Water discharges	
	GSD	LogMean	GSD	LogMean
Include air inhalation route?	4.992	0.446	3.008	0.752
Include irrigation of agricultural soil?	1.074	0.999	4.022	0.771
Include rainsplash to leaf crops?	1.075	0.969	3.986	0.785
Include plant ingestion route?	2.216	0.644	3.835	0.806
Include fish ingestion route?	1.237	0.973	3.511	0.326
Include aerosol deposition to leaf crops?	3.099	0.560	1.099	0.989
Include uptake from air by leaf crops?	2.515	0.556	1.180	0.949
Include water ingestion route?	1.042	0.985	2.026	0.642
Include uptake from soil by leaf crops?	1.613	1.340	1.037	1.001
Include beef ingestion route?	1.322	0.768	1.181	0.911
Include suspended particles in water ingested by farm animals?	1.000	1.000	1.297	0.929
Include milk ingestion route?	1.233	0.821	1.105	0.943
Include roots ingestion route?	1.202	0.939	1.027	0.995
Include bathroom air inhalation route?	1.000	1.000	1.022	0.992
Include egg ingestion route?	1.019	0.980	1.017	0.990

In the absence of information about the properties of the substances, one would expect to be wrong 50% of the time in making a statement such as “emitting 1 kg of substance A is worse than emitting 1 kg of substance B.” That is, without information one would not expect to be more accurate in making pair-wise comparisons as someone who makes the comparisons by flipping a coin. On the other hand, if a toxicity indicator was available that gave a higher (more damaging) score to A than to B, the confidence in the ranking would be a function of the difference in indicator scores and the uncertainty associated with the indicator score for each substance. Confidence in the ranking would increase as the difference in scores increased, but would decrease as the uncertainties in the individual indicators increased.

A graphical tool is proposed to assess the information content of indicators. This chart is referred to as an *information content chart*. The chart plots the descending cumulative fraction of the total pair-wise comparisons among members of a set that can be resolved at different confidence levels when an indicator is applied to rank the members of the set. The domain of the

x-axis goes from 50% (e.g. coin-flipping) to 100% (absolute confidence). The domain of the y-axis goes from 0 to 1. As the information content of an indicator increases, the curve in the chart shifts towards the upper right-hand side of the chart. This is illustrated next with a couple of examples.

ILLUSTRATIVE EXAMPLES

Example 1

Suppose we have 101 objects in a set. We have an indicator that assigns the scores 0,1,2,...100 to the different members of the set. If there were no uncertainty in the indicator, we would be able to rank any two objects selected from the set with 100% confidence, since no two objects have the same score. Assume instead that there is uncertainty, and that each indicator value is normally distributed with a mean value equal to the nominal score and a standard deviation equal to 1 (Case 1), 10 (Case 2), 20 (Case 3), or 50 (Case 4). The distribution for the difference between two normal random variables may be used to calculate the confidence with which two objects can be ranked:

$$Confidence_{jk} = F_N \left(\frac{|\mu_j - \mu_k|}{\sqrt{\sigma_j^2 + \sigma_k^2}} \right) \quad (6-139)$$

where $F_N(\bullet)$ is the standard normal distribution function, μ_i is the mean value of the indicator score for object i (the nominal value in this example), and σ_i is the standard deviation of the indicator score for object i (ranging from 1 to 50 in the example, depending on the case). In a more general case, where the uncertainty in the indicators is described by an arbitrary distribution function, the confidence is given by simulation:

$$Confidence_{jk} = \text{Max}\{100\% - \text{Perc}(Ind_j - Ind_k, 0), \text{Perc}(Ind_j - Ind_k, 0)\} \quad (6-140)$$

where $\text{Perc}(Ind_j - Ind_k, 0)$ is the percentile of the distribution of the difference in indicator scores of objects j and k that corresponds to a value of zero.

The information content chart for this example is shown in Figure 6-29. When the standard deviation of the indicator equals 1, one can be 95% confident in the ranking of the vast majority of pairs of objects drawn from the set. The exceptions are pairs that differ by 1 or 2 indicator score points. As the standard deviation of the scores increases, the fraction of pair-wise

comparisons that can be made with 95% confidence drops from 0.952 (case 1) to 0.59 (case 2), 0.30 (case 3) or 0 (case 4). This shows that as the uncertainty in an indicator increases, its information content decreases.

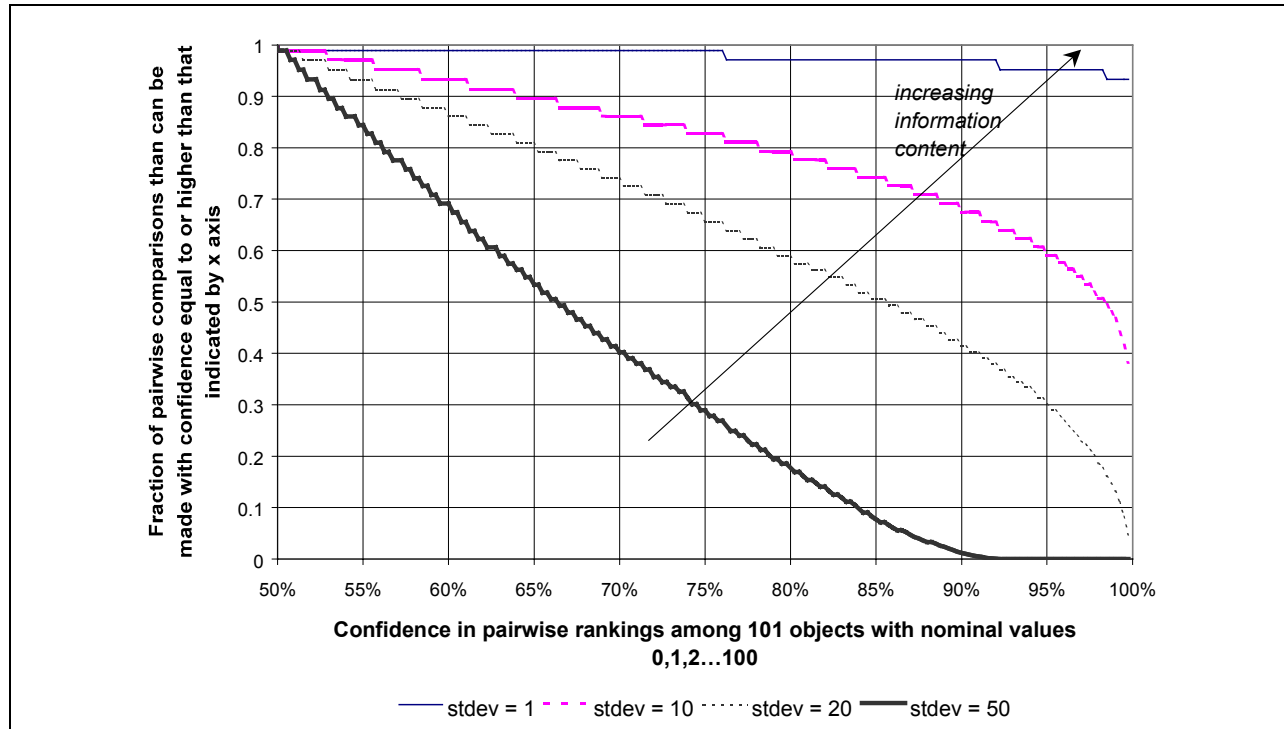


Figure 6-29: Information content chart for example 1

Example 2

Suppose we have two indicators available to rank the objects from the previous example. One of the indicators has a low standard deviation (assume every object's indicator has a standard deviation of 5), but it is only available for half of the objects in the set. The second indicator has a high standard deviation (assume a standard deviation of 50), but is available for all the objects in the set (this is the indicator used as Case 4 in the previous example). Figure 6-30 shows the information content chart for this example. Since the high-quality indicator is only available for half the objects in the set, it can only be applied in 25% of all possible pairwise comparisons among members of the set. For those cases in which it can be applied, the resolution is quite high. Almost 20% of the pair-wise comparisons (i.e., 80% of the comparisons that can be made on the basis of that indicator) can be made with 95% confidence. The low-quality indicator can be applied to all members of the set, so all possible pair-wise comparisons

can be made with more than 50% confidence. However, no comparisons can be made with 95% confidence. It is not necessary to choose between these two alternatives: using both indicators⁶⁰ gives a significant information content gain, as shown by the dashed curve in Figure 6-30.

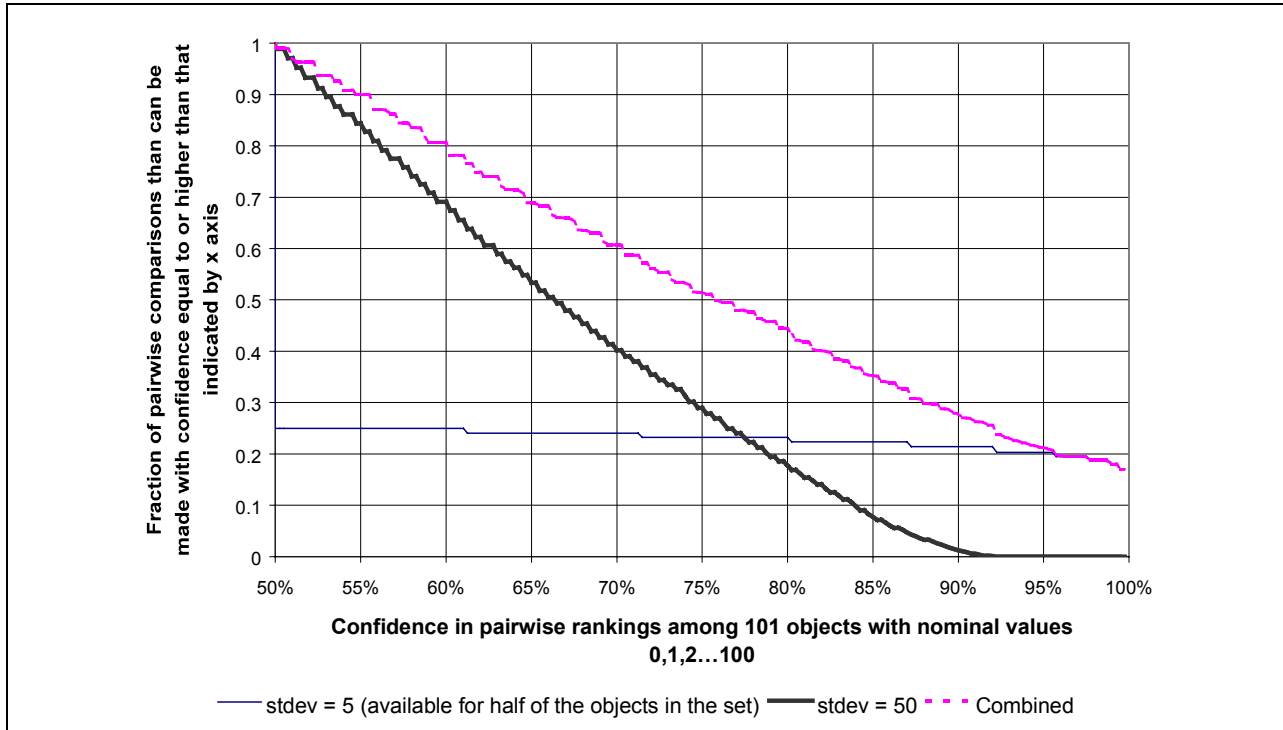


Figure 6-30: Information content chart for example 2

COMPARISON TO OTHER INDICATORS OF INFORMATION CONTENT

In a similar context to the one addressed in the chapter, Hertwich [14] proposed a *resolution metric* that measures how many times the indicator distribution for an object can be fitted into the indicator distribution for all objects, minus one. Hertwich’s definition is based on lognormal distributions:

$$Resolution_j = \frac{LMD_{set} - LMD_{object}}{LMD_{object}} \tag{6-141}$$

where *LMD* is a logarithmic measure of dispersion (e.g. the geometric standard deviation or the logarithm of the ratio of the 95th percentile value to the 5th percentile value).

⁶⁰ The high quality indicators are used for the objects for which it is available and the low quality indicators for the

Adapting Hertwich's definition to the examples in this section, the difference between the 95th and 5th percentile values is used as the measure of dispersion. Monte Carlo simulation was used to find the 5th and 95th percentiles⁶¹. The results are shown in Table 6-39. As the uncertainty in an indicator increases, Hertwich's resolution metric decreases. However, it is difficult to get a feeling for the differences in discrimination power among indicators based on the resolution metric alone. Several misleading conclusions could be derived from the resolution metric when applied to the examples in this section:

- It would appear that Case 1 is at least an order of magnitude more informative than Case 2, in example 1. The information content chart shows that there is at most a doubling in the comparisons that can be made with high confidence from Case 2 to Case 1.
- It is clear from the information content chart that combining indicators in example 2 is significantly more informative than using the high-quality indicator alone. This same conclusion is difficult to reach on the basis of resolution values.

The author believes that the information content chart proposed here is superior in its ability to inform decision-makers about the discrimination power of alternative indicators.

Table 6-39: Hertwich's resolution metric results for examples 1 and 2.

Example	Case	Resolution
Example 1	Case 1 ($\sigma = 1$)	26.9
	Case 2 ($\sigma = 10$)	1.97
	Case 3 ($\sigma = 20$)	0.76
	Case 4 ($\sigma = 50$)	0.14
Example 2	High quality	4.65 for half of the objects; 0 for the other half
	Low quality	0.14 for all objects
	Combination	5.20 for half of the objects; -0.38 for the other half

rest of the objects.

⁶¹ In the absence of uncertainty, the dispersion would be 90, i.e. the difference between the 95th and 5th percentiles of a uniform distribution from 0 to 100; with uncertainty the dispersion increases, since many of the objects are able to take values outside of the original range.

APPLICATIONS

Assessment of the information content of low quality data elements

Information content charts were used in the process of building the database of chemical properties used in the work (see section 9.4 for a description of the database). As an example, the information content chart for the data elements used to estimate non-cancer reference concentrations (RfC) for the inhalation exposure route is presented here. A summary of the information sources used to generate RfC distributions was presented in Table 6-34⁶². The corresponding information content chart is shown in Figure 6-31. The decision context used to build this chart was the comparison of TRI chemicals with reported releases in the period 1988-1997 on the basis of RfC values alone. Even though including semi-quantitative and qualitative data increases the number of chemicals that can be evaluated from 388 to 457, very little information is added, since the uncertainty factors associated with these data sources are comparable to the uncertainty factor of the prior distribution used when no information is available. On the other hand, the figure shows that information is added when TLVs and LC₅₀'s are used to estimate missing assessment values. Using these sources of information increases the fraction of pair-wise comparisons that can be resolved with 95% confidence from 0.12 to 0.16. There is an even larger information gain associated with allowing extrapolation from oral risk assessment values. Allowing this extrapolation increases the fraction of pair-wise comparisons that can be resolved with more than 95% confidence to 0.25.

Based on the information content chart it can be concluded that it is worthwhile to incorporate TLVs and LC₅₀s to the database, while there is no much benefit in compiling the semi-quantitative and qualitative data elements shown in the last 6 rows of the table.

⁶² The reader is encouraged to refer back to Table 6-34 (page 294) when following the discussion presented in this paragraph.

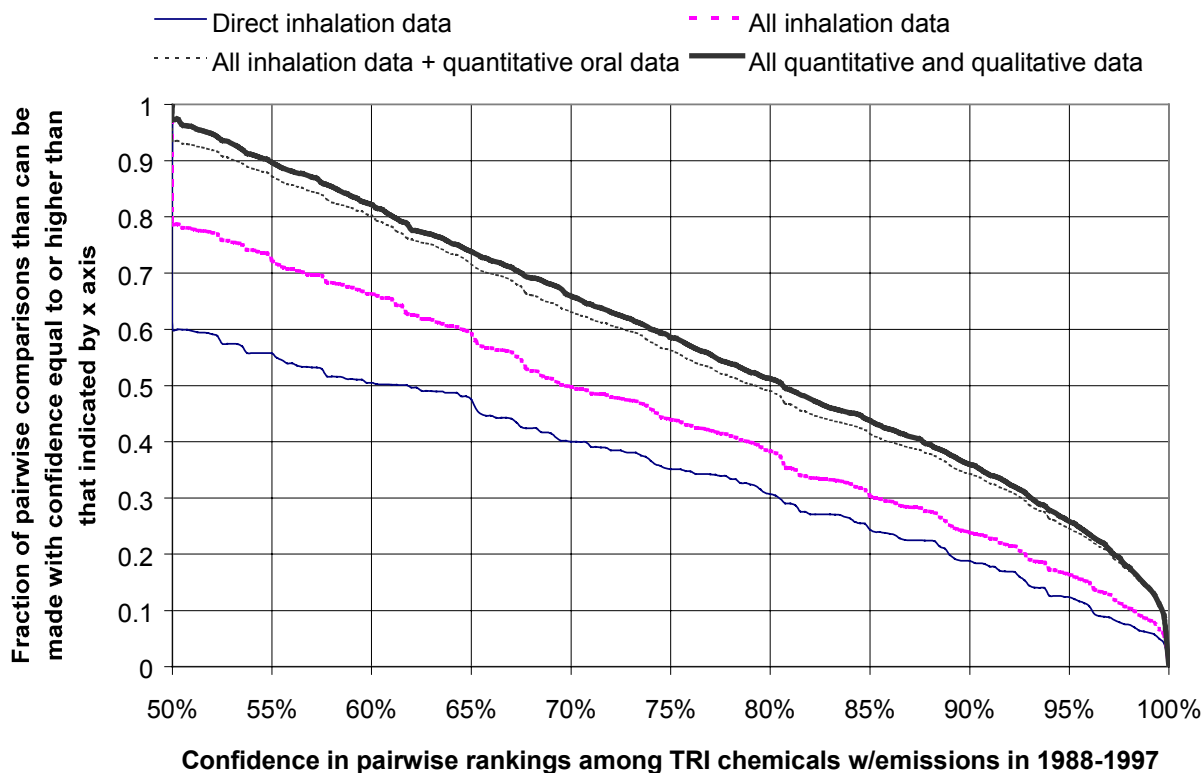


Figure 6-31: Non-cancer inhalation route risk assessment factor -- information content chart for TRI chemicals with reported emissions in the period 1988-1997

Comparing approaches to dealing with heterogeneous data

The Office of Solid Waste and the Office of Pollution Prevention and Toxics of the U.S. Environmental Protection Agency have developed a screening tool called the Waste Minimization Prioritization Tool (WMPT) [7,9]. The tool was designed to help stakeholders to prioritize source reduction and recycling activities based on human health and ecological risk.

One of the goals of the developers of the WMPT was to derive scores for the largest possible number of chemicals. In order to do this, data of different levels of quality had to be used. The EPA adopted a fence line approach to develop their scores. Each data element used in the scoring algorithm was assigned a value of 1 (low concern), 2 (medium concern) or 3 (high concern) using fence lines (i.e. border values) defined for each data source. For most high-quality data, a factor of 100 difference separated the fence line values. The scoring algorithm used to derive the human health concern score is shown in Figure 6-32.

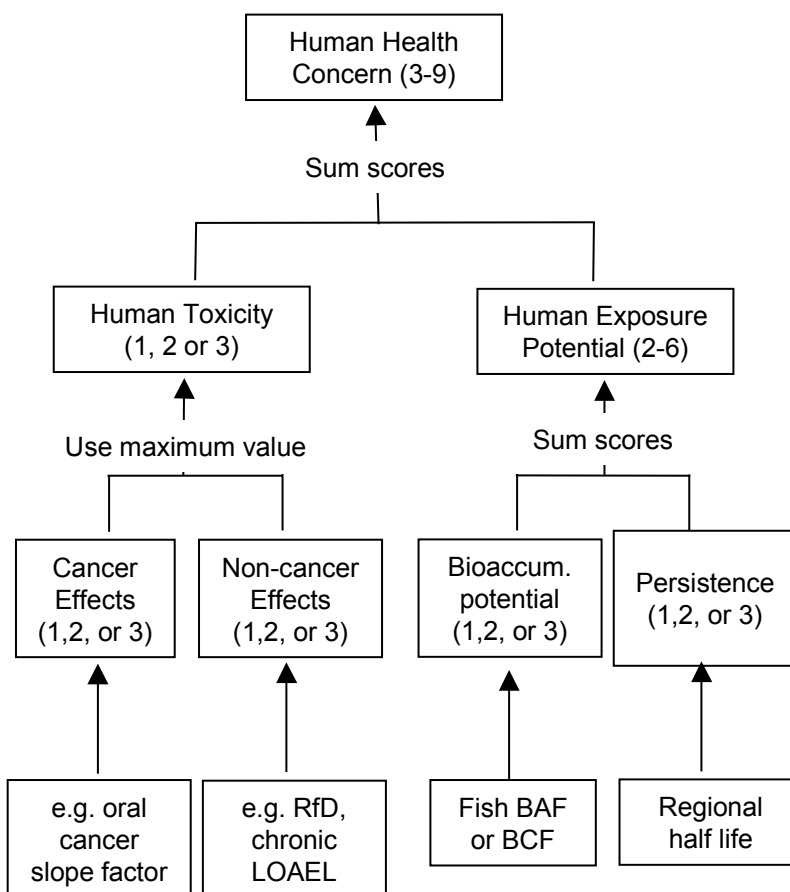


Figure 6-32: Human health concern scoring algorithm used in EPA's waste minimization prioritization tool

A problem with the fence line approach is that it reduces the quality of the data to the lowest common denominator. For instance, the highest quality data source used to estimate cancer toxicity is the cancer slope factor (CSF) extracted from the IRIS database. In the fence line approach, any IRIS CSF in the range 0.046 to 4.6 mg/kg/day is assigned a value of 2, resulting in a loss of information, since many CSFs are known to better precision than a factor-of-100 uncertainty.

An alternative approach, which is the one used in this work, is to estimate uncertainty factors for all levels of the data hierarchy, as was illustrated in Table 6-34 for the case of the non-cancer inhalation risk assessment factor. Uncertainties can then be propagated through the fate, transport and exposure model to estimate human exposure potential and combined with the probability distributions for the toxic potency factors to arrive at a distribution of human toxicity potentials (HTP).

The information content tool was used to compare both approaches. In deriving the information content plot for the WMPT scores, a standard deviation of 0.95 was assumed for the uncertainty in the final discrete score (this is equivalent to assuming that each of three additive factors has an uncertainty characterized by a standard deviation of 0.55)⁶³.

The information content plot for this comparison is shown in Figure 6-33. The step changes in the plot for the WMPT indicator are a consequence of the discrete scale used. Only 15% of all possible pairwise comparisons can be resolved with more than 90% confidence using the WMPT indicator (a score difference of 3 points is required). On the other hand, 45% of all possible pairwise comparisons can be resolved with more than 90% confidence through the propagation of uncertainties in the HTP model.

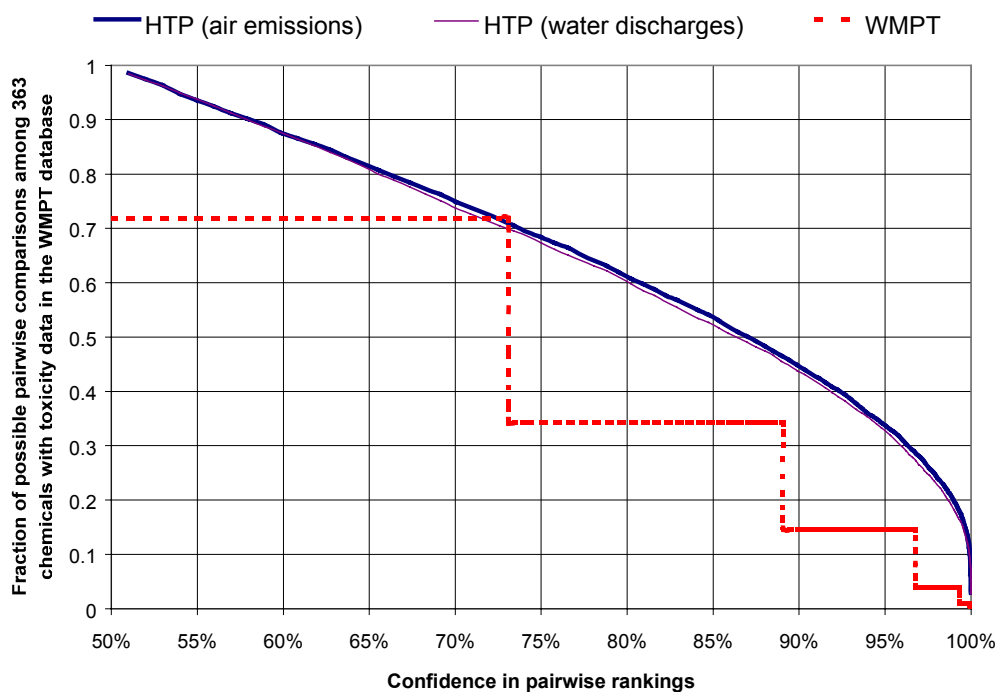


Figure 6-33: Information content chart for the WMPT case study (set of 363 chemicals with toxicity data in the WMPT database)

⁶³ The factor of 0.95 was derived by examining distributions of HTP values for chemicals within each WMPT human health concern discrete score. The geometric standard deviations of the distributions corresponded to WMPT standard deviations in the range 0.56 to 1.26.

Evaluating the quality of an environmental indicator

In this section information content charts are provided for the simulation results presented in section 6.3.5. Information content charts are presented for (i) human exposure potential indicators calculated for the set of 1318 chemicals in the WMPT database (Figure 6-34), (ii) human toxicity potential indicators (non-cancer and combined cancer and non-cancer) for the set of 505 chemicals with reported releases in the TRI in the period 1988-1997) (Figure 6-35), and (iii) human toxicity potential indicators for the subset of TRI chemicals with emissions for which some type of information regarding carcinogenicity is available (Figure 6-36).

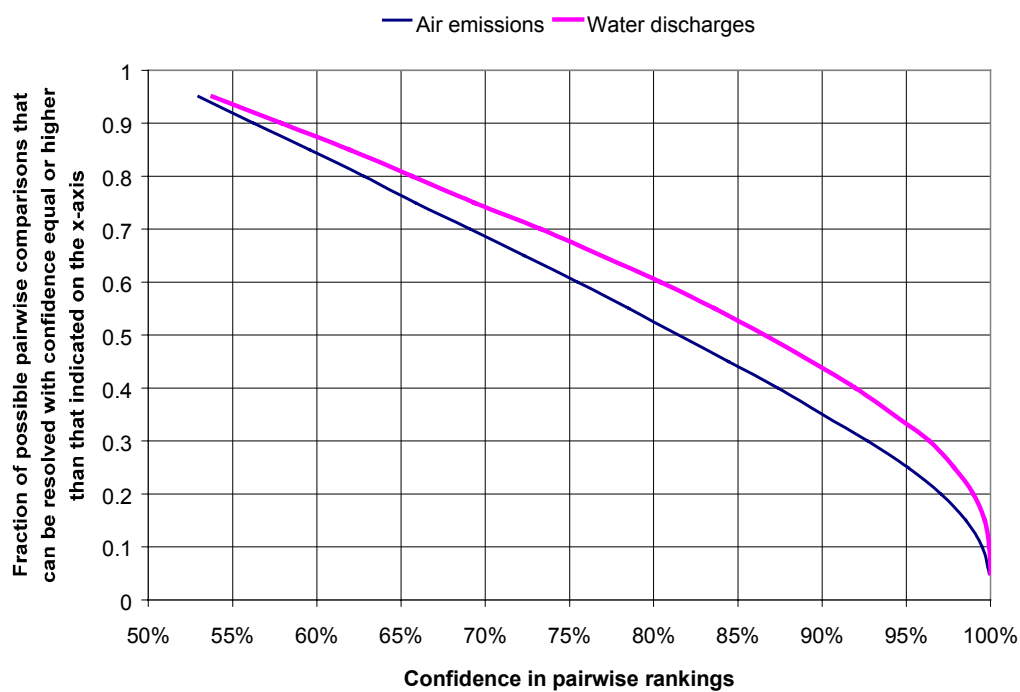


Figure 6-34: Information content chart for the human exposure indicator (set of 1318 chemicals in the WMPT database)

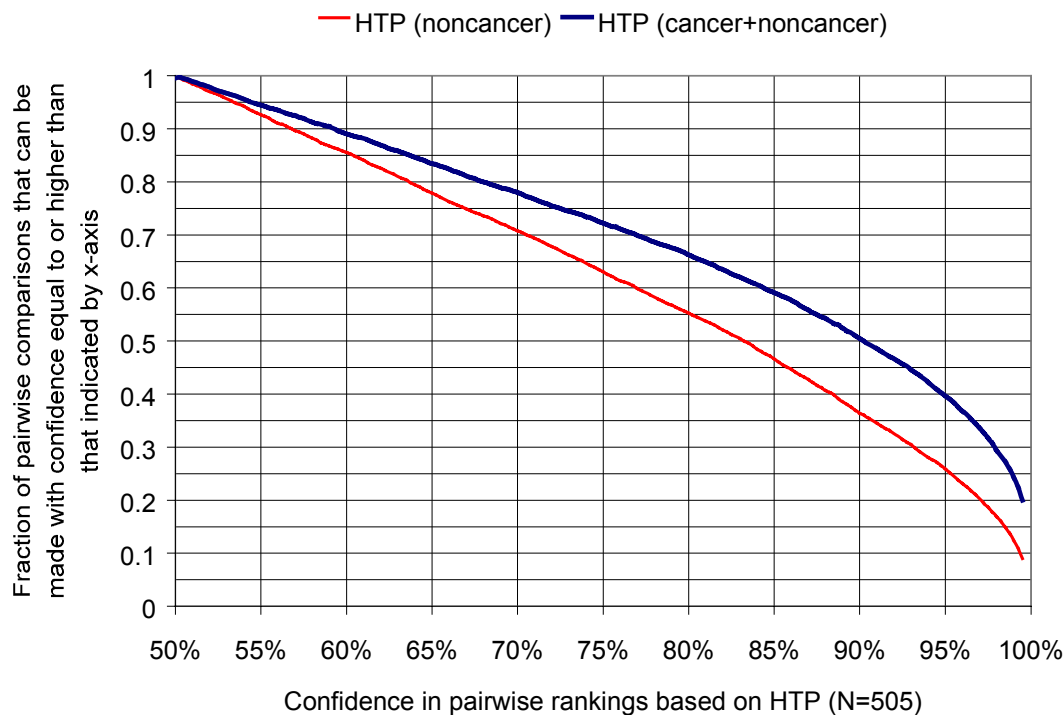


Figure 6-35: Information content chart for the TRI indicators case study (set of 505 chemicals with reported emissions to air in 1987-1997)

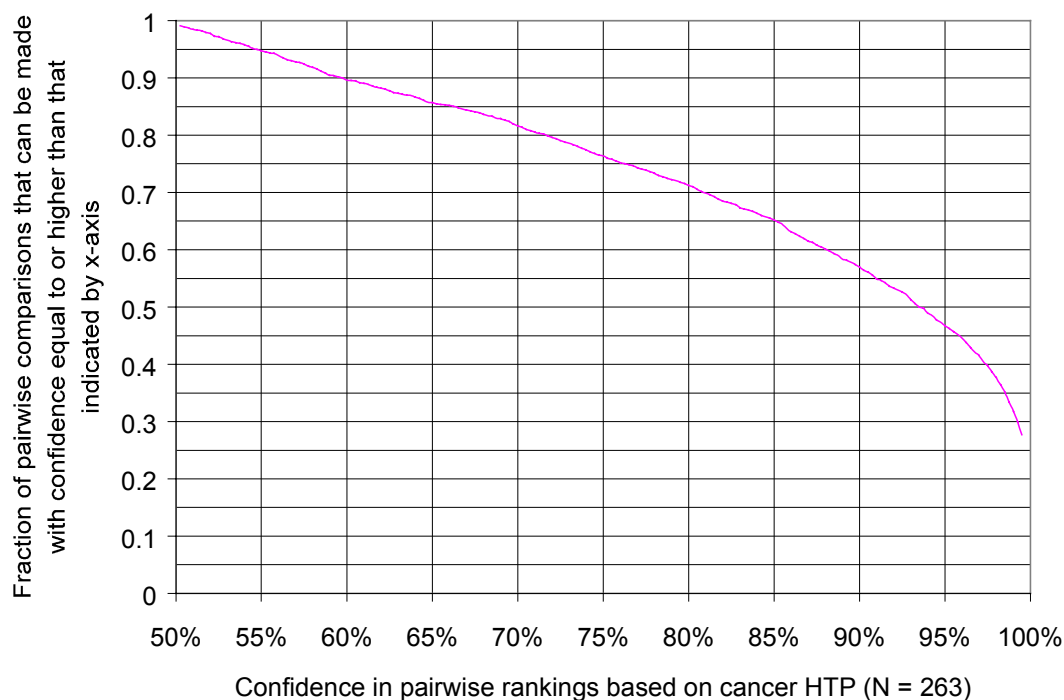


Figure 6-36: Information content chart for the use of HTP (cancer) to rank chemicals in the TRI (set of 263 chemicals with cancer information)

Despite the significant uncertainties involved in the calculation of exposure potentials and HTPs, the information content charts show that the information content of the indicators is reasonably high. More than 70% of pairwise comparisons can be resolved with 68% confidence or higher in all indicators. At the 95% confidence level, between 25% and 33% of chemical comparisons can be resolved on the basis of human exposure indicators, while 40% of all possible comparisons in the TRI set can be resolved on the basis of the combined cancer and non-cancer effects HTP indicator. Figure 6-35 also shows that there is a higher information content in a combined cancer and non-cancer effects indicator than in an indicator that only considers non-cancer effects, despite the rather large uncertainty used for the tolerable risk level factor used to bring both types of effects to the same scale (see eq (6-137)).

6.5 Case Study: Application of the human toxicity potential indicator to the Toxic Release Inventory

6.5.1 Introduction

Industries and governments around the world are making considerable efforts to compile data regarding releases of toxic chemicals to the environment. These efforts were initiated by the enactment of the Emergency Planning and Community Right-to-Know Act (EPCRA) in the United States in 1986. The EPCRA mandates manufacturing firms to report their releases of toxic chemicals annually. The information is collected and made available to the public by the U.S. Environmental Protection Agency (EPA). The universe of chemicals required to be reported has grown from an initial list of about 370 to more than 600. Starting with the reporting year 1998 (data for which will be published later this year), the universe of facilities required to report to the TRI was expanded to include metal mining, coal mining, coal and oil fired electric utilities, waste treatment and disposal facilities, solvent recovery services, and wholesale distributors of petroleum and chemicals.

The TRI has become a powerful tool for pollution prevention. The compilation and publication of lists of prominent toxic chemical releasers has prompted a large number of firms to make commitments to reduce their releases of TRI chemicals. There is some concern, however, that since these lists are compiled on the basis of the total mass of chemicals released, firms might be emphasizing the reduction of high-volume releases that might not pose much risk

to human health over the elimination of lower volume releases of the most toxic and persistent chemicals [2,5,8].

Indicators of human health risk from the release of toxic chemicals of increasing sophistication have been proposed. Horvath and coworkers used the inverse of the ACGIH occupational exposure threshold limit value (TLV) as a toxicity weighting factor to aggregate TRI data [5]. Their choice of inverse TLV as an indicator was mainly dictated by the availability of TLV values for a large fraction of the chemicals in the TRI. Hertwich and collaborators introduced a human toxicity-equivalent-potential indicator (TEP) that incorporates not only toxicity but also exposure through various pathways, including ingestion of plant and animal products [14]. The cancer and chronic non-cancer indicators for air emissions and water discharges developed by Hertwich et al. are being used by the Environmental Defense Fund (EDF) to rank facilities, industrial sectors, and chemical releases in their Scorecard web site [79].

There are two main barriers to the use of health impact indicators in pollution prevention:

- 1) None of the proposed indicators has scores for the complete set of chemicals of interest to regulators, producers, and concerned citizens.
- 2) While mass is not a good measure of risk, it has the advantage of being a tangible and objective measure. Although there are uncertainties associated with the measurement or estimation of emissions, there is no uncertainty in the meaning of the unit of measurement. There is no disagreement on the meaning of a kilogram. On the other hand, health risk impact indicators are necessarily uncertain quantities, even if the amounts emitted are exactly known. The uncertainty arises from uncertainties in the models that link emissions to potential doses, from uncertainties in physical properties, and from uncertainty in the toxicity endpoint values, which are usually extrapolated from animal data. A firm showing up as the top polluter in a list compiled on the basis of health risk impact indicators could argue its way down the list by challenging the data and methods used to derive the scores.

The EPA has been working in the development of environmental indicators for the TRI at least since 1991. They have recently released an inhalation risk indicator for use in scoring air releases only [68]. All other relevant exposure routes are not addressed by this indicator. While the agency is understandably reluctant to publish indicators that can be challenged due to

uncertainties in models or data, delay in including all relevant exposure routes means that these routes will not be considered when setting priorities for reducing risk.

This case study shows how uncertainty in models and data does not necessarily translate into uncertainty in decisions to reduce potential health impacts. Explicit incorporation of uncertainties is used to overcome the two barriers mentioned above. Lower quality data can be incorporated into the analysis, allowing chemicals with lower data availability to be scored (the score being more uncertain as less high quality data is available). The results of the analysis are not as easy to challenge, since disagreements about data are transformed into uncertainty distributions for the data element for which there is disagreement. Results that are robust in the presence of these uncertainties would not change depending on how the disagreement was ultimately resolved. Important results that are sensitive to particular uncertainties provide guidance to authorities and industries for the allocation of resources to reduce those uncertainties. Although the focus of this case study is on TRI releases, the methods discussed here are applicable to any decision problem where there is uncertainty in the indicator used to assess performance.

6.5.2 Analysis

ENVIRONMENTAL RELEASES

The following releases reported in the Toxic Release Inventory in the period 1988-1997 are considered: (i) total air emissions (stack emissions and fugitive emissions), (ii) surface water discharges, and (iii) transfers to publicly-owned wastewater treatment plants (POTWs). Wastewater treatment plant biodegradation and partitioning data are used to translate POTW transfers into emissions to air, discharges to surface water and releases to land (it is assumed that sludge from POTWs is applied to land). Other releases and transfers were not included in the calculations, since the judgement was made that releases to landfills and underground injection wells have a very small chance of reaching environmental media of concern.

FATE, TRANSPORT, AND EXPOSURE MODELING

Long-term human exposure to chemicals is modeled using the multimedia fate and transport model described in section 6.3.1 and the human exposure model described in section 6.3.2.

SOURCES OF INFORMATION

The environmental information management system EnvEvalTool developed in this work (see Chapter 9) was used to extract data and uncertainty distributions for physical properties and toxicity factors for the TRI chemicals with releases in the 1988-1997 period. The hierarchy contained in the EnvEvalTool was augmented for this case study by placing at the bottom of the hierarchy a prior distribution based on the distribution of that data element among the TRI chemicals in the database for which the element was available. This was done to ensure that the model could be run for all chemicals, even when data for a necessary physical property was missing.

UNCERTAINTY PROPAGATION

Monte Carlo simulations were performed using the @Risk add-on for Microsoft Excel (Palisade Corporation) on a personal computer with a Pentium-II processor, using 10,000 iterations per simulation.

CHOICE OF UNCERTAIN OUTPUTS

Two types of uncertain outputs were specified: (a) absolute values of health impact indicators, and (b) relative values of health impact indicators with respect to a benchmark. As shown in the results section, the second type of uncertain output is more useful for making comparisons and setting priorities. The reason is that a good choice of benchmark reduces decision uncertainties by taking advantage of the correlations among the distributions of absolute indicator values (see section 4.4 for a detailed discussion).

6.5.3 Results

YEAR-TO-YEAR COMPARISONS

There has been a significant decrease in the total mass of TRI chemicals released to the environment since the baseline year of 1988 (Figure 6-37, top chart). The total of air emissions, water releases, and transfers to wastewater treatment plants in 1997 was less than half of that in 1988, despite the substantial increase in the number of chemicals subject to reporting that took place in 1995. The human chronic toxicity indicator developed in this thesis was applied to the inventory to test whether a corresponding decrease in risk took place in the same period. The distributions for the indicator (Figure 6-37, middle chart) suggest that there is no significant difference in risk among the different reporting years, since the uncertainty (almost 2-orders of magnitude for the 90% confidence interval) is much larger than the difference in median values. However, this interpretation of the distributions does not take into account the fact that the distributions are highly correlated. A much better indication of progress is given by the distributions for the relative health risk indicator with respect to a reference year, as shown in the bottom chart of Figure 6-37, where 1988 is used as a reference year. Several interesting observations can be derived from the chart:

- Even though reported releases and transfers decreased by about 13% from 1988 to 1989, there is a 25% probability that the releases and transfers reported for 1989 had a higher impact than those reported in 1988;
- Despite the two orders of magnitude uncertainty in the health risk indicator, it can be said with confidence that reported releases and transfers in each year of the period 1990-1994 had lower potential health impacts than those of the benchmark year 1988.

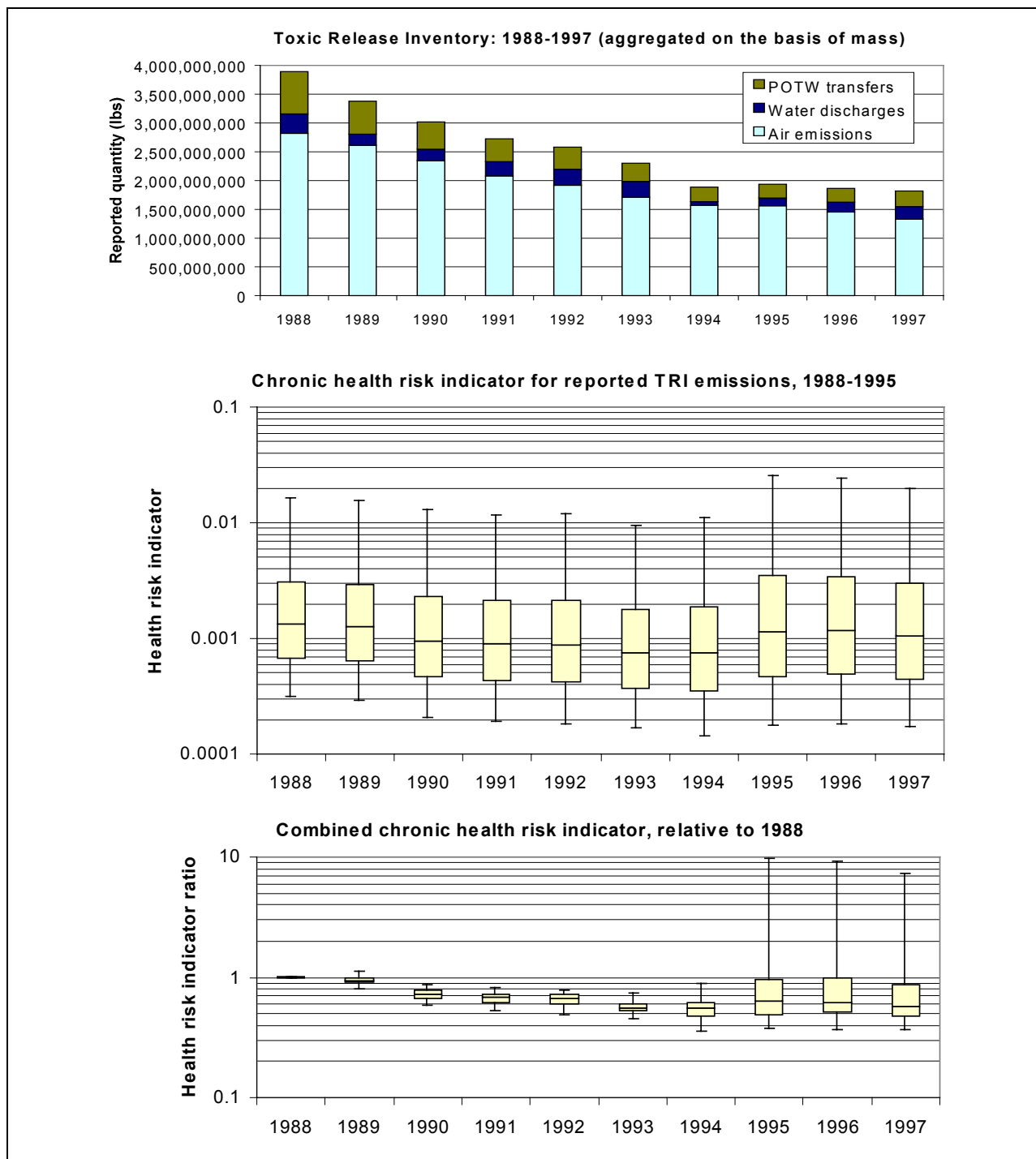


Figure 6-37: TRI 1988-1995. Combined air emissions, water discharges, and wastewater treatment plant transfers: (a) aggregated by mass, (b) combined cancer and non-cancer chronic effects health risk indicator, (c) chronic risk indicator relative to 1988.⁶⁴

⁶⁴ The Box plots show the median value and the 5th, 25th, 50th and 95th percentiles of the distributions.

- Even though the total mass of reported releases and transfers for 1997 was the lowest on record, their potential impact could be as much as eight times higher than the impact of the releases and transfers reported for 1988. The reason for this is the 1995 expansion of the set of chemicals required to be reported. Since there is no data for releases and transfers of the newly added chemicals for reporting years prior to 1995, the health risk indicators computed for 1988-1994 implicitly assume that emissions for these chemicals were equal to zero. This is extremely unlikely. If, in contrast, a qualitative change in the relative distributions from 1994 to 1995 had not been observed, it would have meant that the expansion in the chemical list was not justified from the point of view of chronic health risks.

Changing the reference year to 1995 yields the relative impact distributions shown in Figure 6-38. Even though the total mass of releases decreased from 1995 to 1997, one can only be about 65% confident that the risk posed by the 1997 reported releases and transfers was lower than those from 1995.

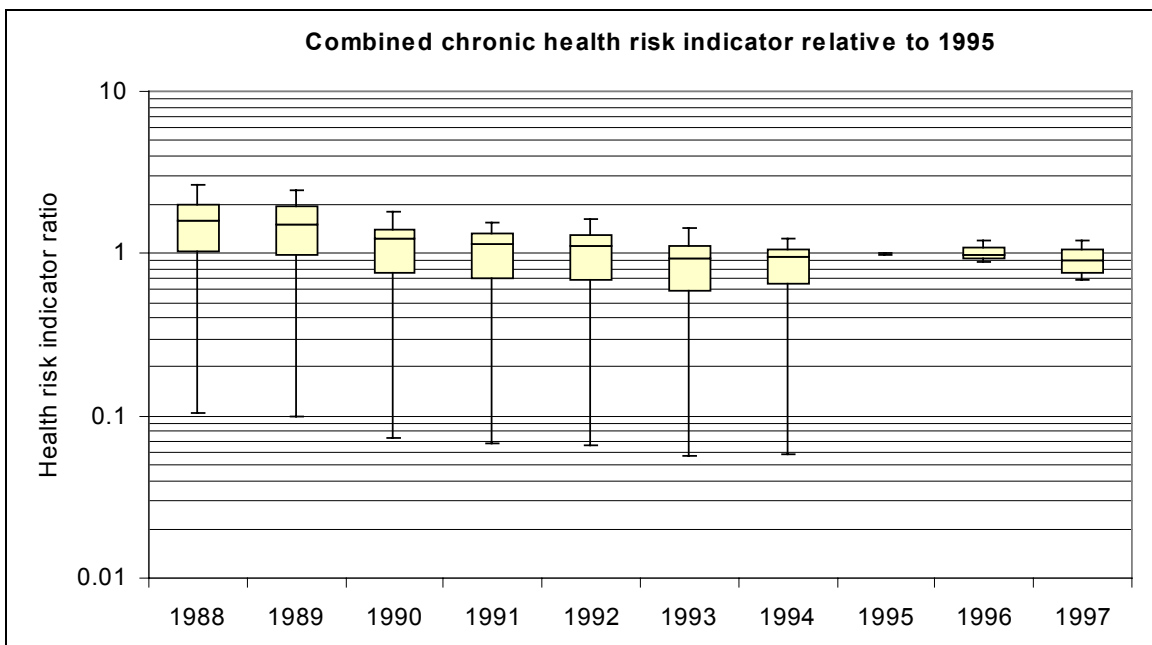


Figure 6-38: TRI 1988-1995. Chronic health risk indicator from combined air emissions, water discharges, and wastewater treatment plant transfers, relative to 1995

CHEMICAL COMPARISONS

In order to identify the TRI chemicals with the largest contributions to potential health impacts, distributions for the relative contribution of each chemical to the combined cancer and chronic non-cancer toxicity score were generated (this is another example of the application of the sensitivity analysis techniques introduced in section 5.2). Key results are shown in Figure 6-39 and Figure 6-40. Figure 6-39 shows the total quantities released and the contribution to risk from the TRI chemicals with 1997 releases larger than 10 million pounds. Methanol, nitrate compounds, and ammonia contribute, respectively, 16%, 12%, and 10% of the combined mass of TRI reported releases to air, water, and wastewater treatment plants in 1997. However, none of these chemicals has a significant probability of contributing to even 0.1% of the total chronic toxicity risk posed by the 1997 reported releases. As Figure 6-40 shows, the chemicals contributing most of the risk account for a very small fraction of the total mass of reported releases.

There were 425 chemicals or chemical categories with reported emissions to air, discharges to surface water, or transfers to wastewater treatment plants in the 1997 TRI. Only 21 of these chemicals or chemical groups have a 5% or greater probability of accounting for more than 1% of the total risk. These substances contributed less than 5% of the total mass of 1997 reported releases to air, water, and wastewater treatment plants.

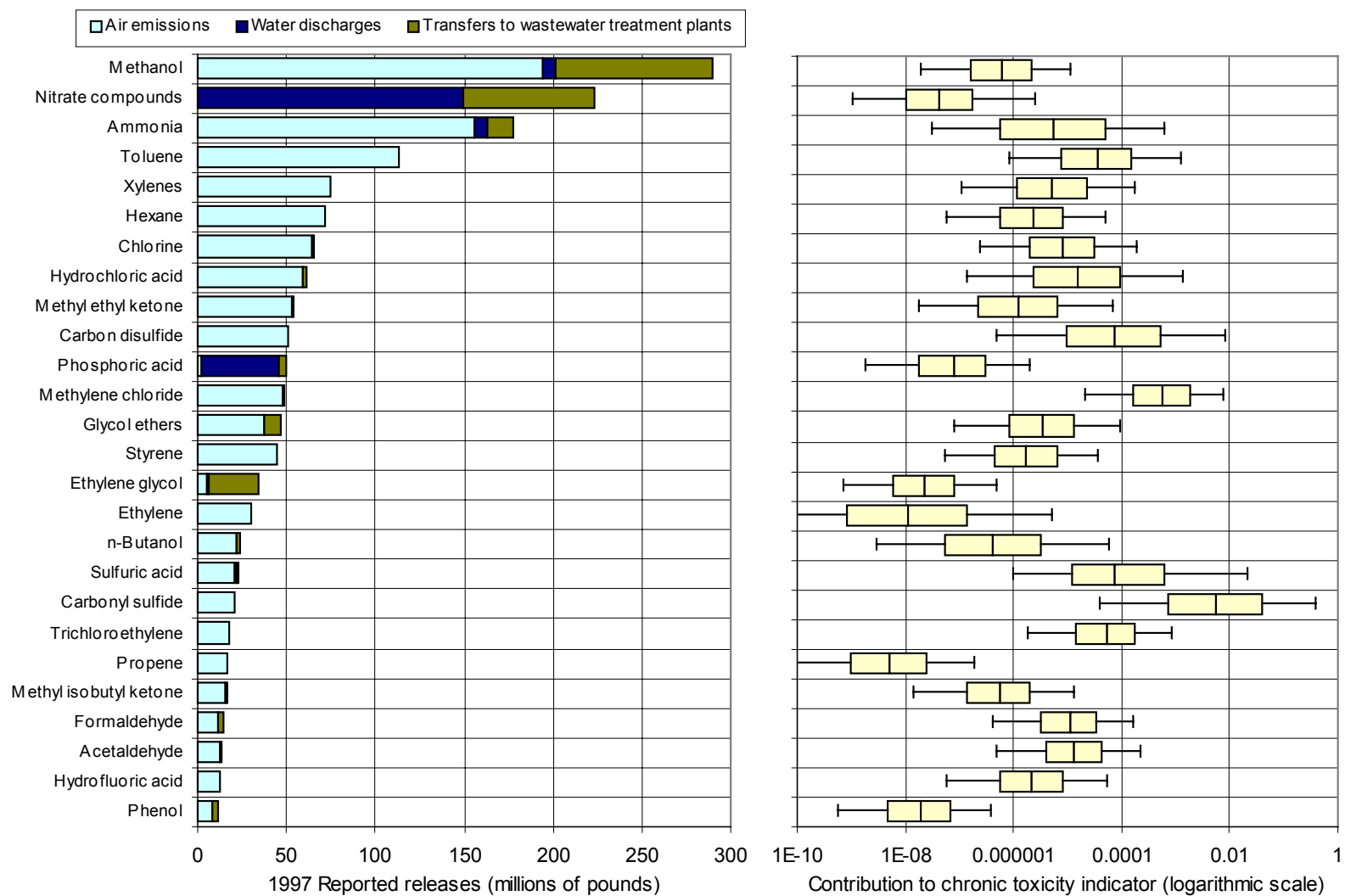


Figure 6-39: Individual chemical contributions to (a) total reported quantities, and (b) combined cancer and non-cancer chronic toxicity indicator (TRI chemicals with more than 10 million pounds of reported releases in 1997)

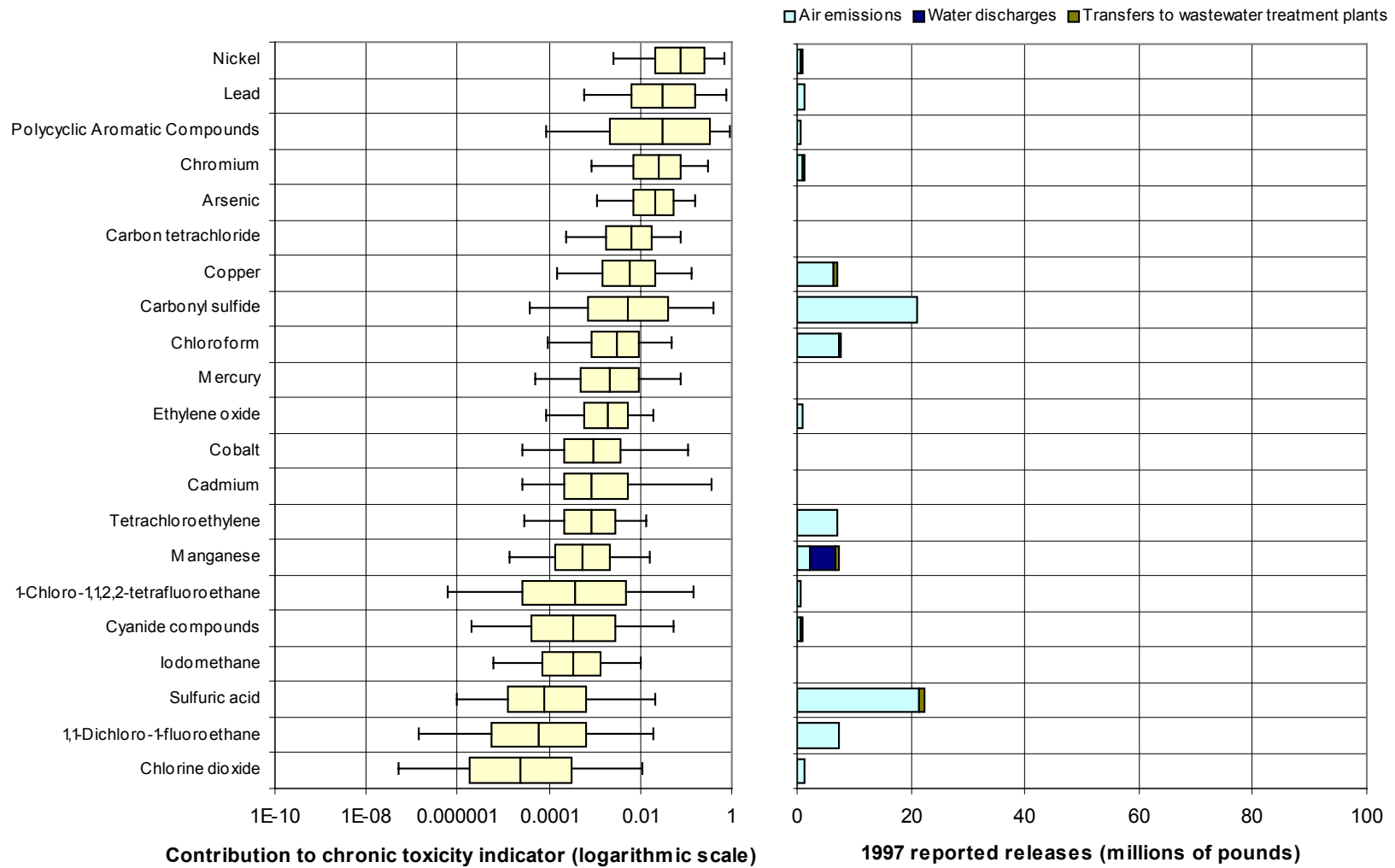


Figure 6-40: Individual chemical contributions to (a) combined cancer and non-cancer chronic toxicity indicator, and (b) total reported quantities (TRI chemicals with more than a 5% chance of contributing at least 1/100 of the total chronic health risk)

A RISK-BASED ASSESSMENT OF THE 33/50 PROGRAM

In 1991 the EPA launched the “33/50 program”, a voluntary initiative which received its name from its goals of reducing emissions and transfers of 17 high-priority chemicals by 33% in 1992 and by 50% in 1995 using reported 1988 data as a baseline [80]. Companies were invited to participate in the program by setting their own goals and schedules to meet them. The program met its goals ahead of schedule, as shown in Figure 6-41, and is highly regarded as an example of alternatives to traditional command and control regulations. The health risk indicator was applied to the releases and transfers shown in the figure to test whether a reduction in risk commensurate with the reduction in mass could be discerned. The result is shown in Figure 6-42. By 1995, the most likely reduction in risk achieved relative to the 1988 baseline was 55%, although there is a 5% probability that the achieved risk reduction was less than 32%. Contrary to the steady decrease in mass of chemicals released, it appears that not much progress was achieved between 1991 and 1992, or between 1995 and 1996. The reason for the discrepancy is that the chemicals that contribute the most to risk are not the chemicals released in the highest quantity. This can be seen in Figure 6-43, where individual chemical contributions to risk and mass are displayed for 1988. By completely eliminating releases of toluene, xylenes, methyl ethyl ketone, and methyl isobutyl ketone while leaving other releases unchanged, it would have been possible to meet the program goals with a 57% reduction in mass without making hardly a dent in risk. Fortunately, this was not the case, as emissions for each of the 17 chemicals have been reduced.

Two key findings of EPA’s final analysis of the 33/50 program [80] are that

- Facilities reported more source reduction activity (pollution prevention) for 33/50 chemicals than for other TRI chemicals and this activity covered a greater percentage of production-related waste for 33/50 chemicals than for other TRI chemicals, and
- Reductions continued at a higher rate for 33/50 chemicals than for other TRI chemicals in the year after the 33/50 Program ended.

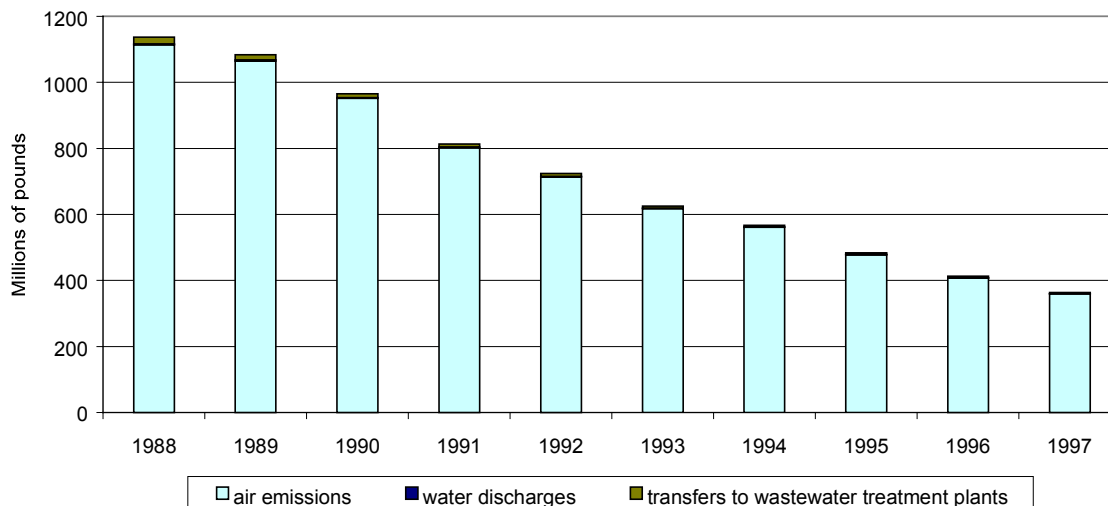


Figure 6-41: Reported TRI releases and transfers of 33/50 Program Chemicals, 1988-1997

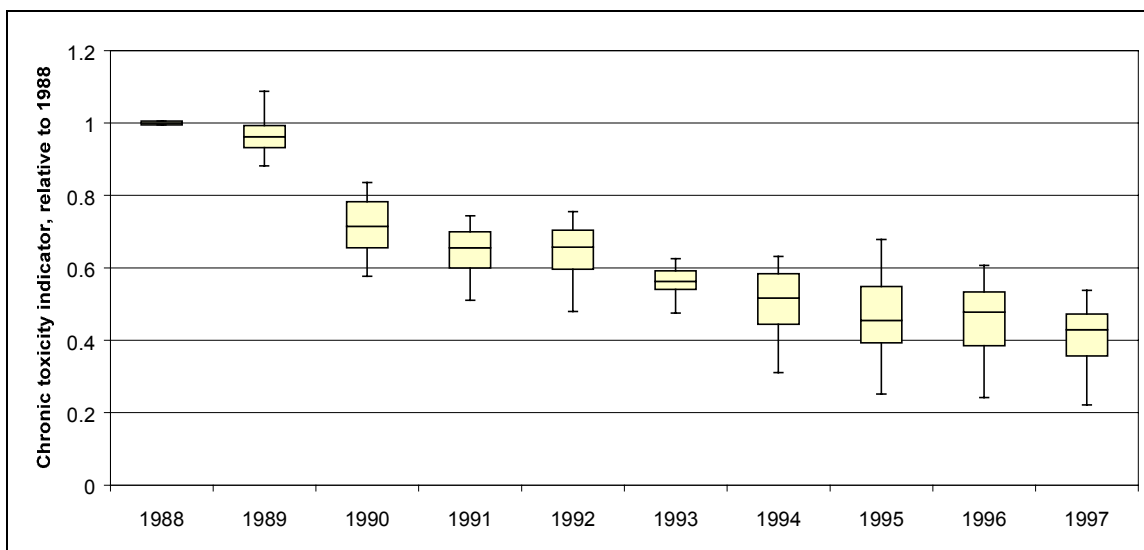


Figure 6-42: Chronic toxicity risk from reported TRI releases and transfers of 33/50 Program Chemicals, 1988-1997 (relative to 1988)

These findings highlight the importance of assembling lists of high priority pollutants based on the environmental goals one is trying to achieve. The sensitivity tools used in this case study were applied to the 1988 and 1997 TRI to identify those chemicals that should have been included in the 33/50 program, had the only selection criteria been reducing chronic health risks. A similar exercise was carried out to identify the chemicals that should be included in the next version of the program. Two selection criteria were used. First, the chemical or chemical group needed to have a 5% or higher probability of contributing at least 1% of the total chronic toxicity

score for the year evaluated. Second, the chemical needed to have a 5% or lower probability of contributing less than 1 in 1,000,000 to the total chronic toxicity score (this screen was used to eliminate chemicals for which the score was too uncertain)⁶⁵. The results are shown in Table 6-40. The most important omission from the original list appears to be arsenic and arsenic compounds (see Figure 6-40).

Table 6-40: List of chemicals in the 33/50 Program, compared with lists created on the basis of chemical contributions to risk from 1988 and 1997 TRI releases

Original 33/50 Chemicals	Chemicals selected based on contribution to risk from 1988 reported releases	Chemicals selected based on contribution to risk from 1997 reported releases
Carbon tetrachloride Chloroform Tetrachloroethylene Dichloromethane 1,1,1-Trichloroethane <i>Benzene</i> <i>Trichloroethylene</i> <i>Toluene</i> <i>Xylenes</i> <i>Methyl ethyl ketone</i> <i>Methyl isobutyl ketone</i>	Carbon tetrachloride Chloroform Tetrachloroethylene Dichloromethane 1,1,1-Trichloroethane Carbonyl sulfide Ethylene oxide 1,2-Dichloroethane Methyl chloride Methyl bromide Polybrominated biphenyls	Carbon tetrachloride Chloroform Tetrachloroethylene Carbonyl sulfide Ethylene oxide Polycyclic aromatic compounds Methyl iodide
Cadmium and compounds Chromium and compounds Lead and compounds Mercury and compounds Nickel and compounds Cyanide compounds	Cadmium and compounds Chromium and compounds Lead and compounds Mercury and compounds Nickel and compounds Cyanide compounds <u>Arsenic and compounds</u> Copper and compounds Cobalt and compounds Barium and compounds	Cadmium and compounds Chromium and compounds Lead and compounds Mercury and compounds Nickel and compounds Cyanide compounds Arsenic and compounds Copper and compounds Cobalt and compounds Manganese and compounds Sulfuric acid (air emissions)

Notes: The median contribution to risk from underlined chemicals is higher than 1%; chemicals in *italics* are not included in subsequent lists; chemicals in **boldface** do not appear in the original list of 33/50 chemicals; reporting of releases of polycyclic aromatic compounds was not required before 1995; 3 chemicals (1-Chloro-1,1,2,2-tetrafluoroethane, 1,1-dichloro-2-fluoroethane, and chlorine dioxide) were not included in the 1997 list due to the 5th percentile 1-in-a-million contribution filter, but their 95th percentile contribution exceeds 1% -- further research into their toxicity is needed to narrow the uncertainty.

⁶⁵ The list of chemicals meeting the first screen but failing the second one could be used to direct resources to the reduction of the uncertainties. One would expect producers of those chemicals to be among the first parties interested in carrying out the analysis to determine whether the true risk is more likely to be towards the higher or the lower end of the distribution.

INDUSTRIAL SECTOR COMPARISONS

Another example of the low correspondence between mass and risk is given by comparing TRI releases across industrial sectors. The left hand chart in Figure 6-44 compares industrial sectors on the basis of total reported mass of TRI chemicals released in 1997. Releases were aggregated into industrial sectors using the first 2 digits of the standard industry classification code (SIC code) reported by each facility in their TRI submission forms for 1997. The sector with the largest mass of chemicals released or transferred was Chemicals (SIC code 28), followed by Paper (SIC code 26) and Primary Metals (SIC code 33). The chart on the right hand side of Figure 6-44 tells a different story. Even though the Primary Metals sector account for only 11% of the mass of TRI chemicals released in 1997, it is responsible for 14 to 67% of the total chronic health risk posed by TRI releases. The food sector is fourth in mass rankings, with about 7% of reported TRI releases, but accounts for at most 0.7% of the health risk. In contrast, the textile sector, which contributed 1.3% of the mass, was responsible for up to 11% of the chronic health risk.

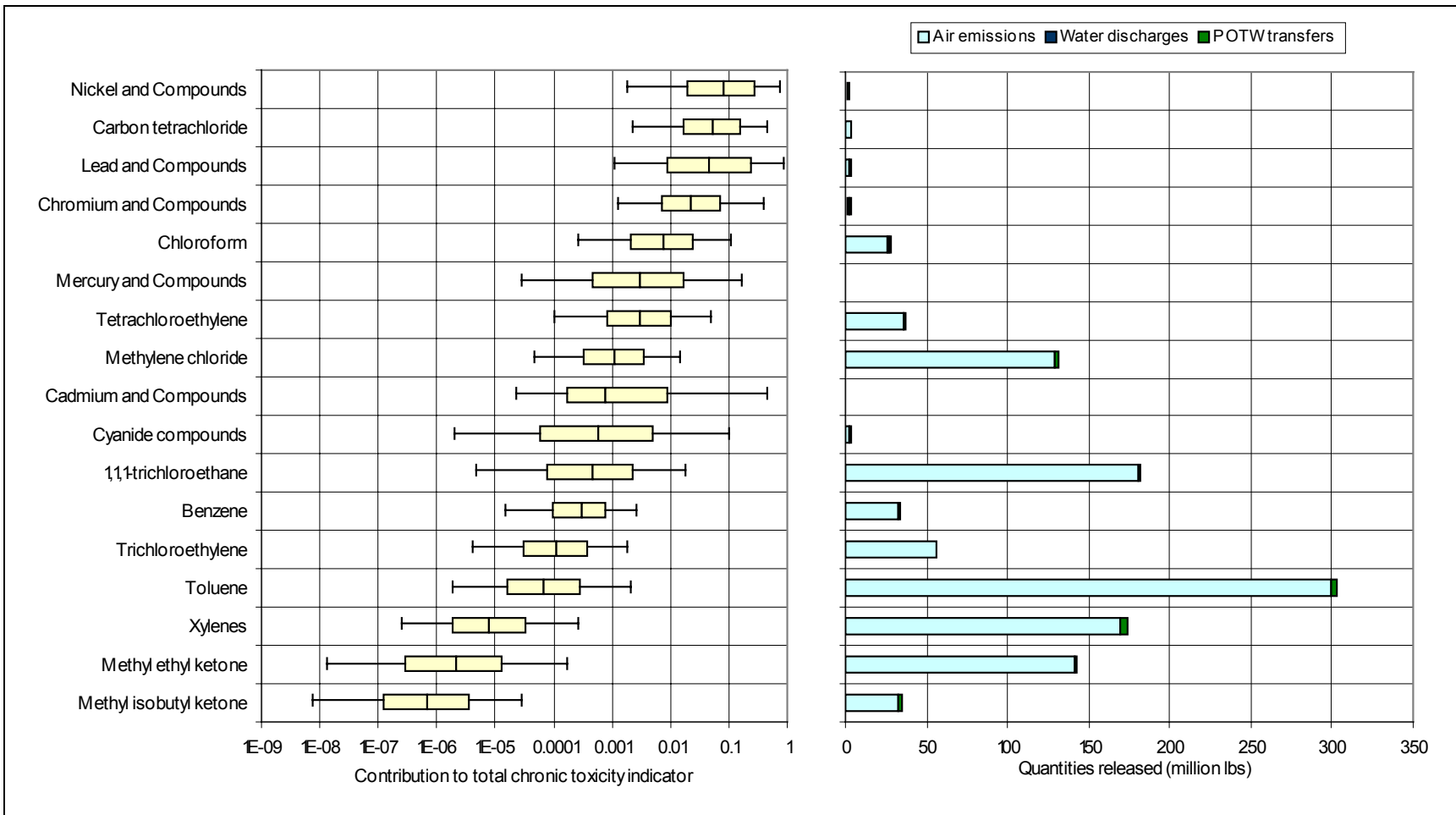


Figure 6-43: 33/50 Program chemical contributions to (a) chronic toxicity risk, and (b) total quantity released, (1988 TRI)

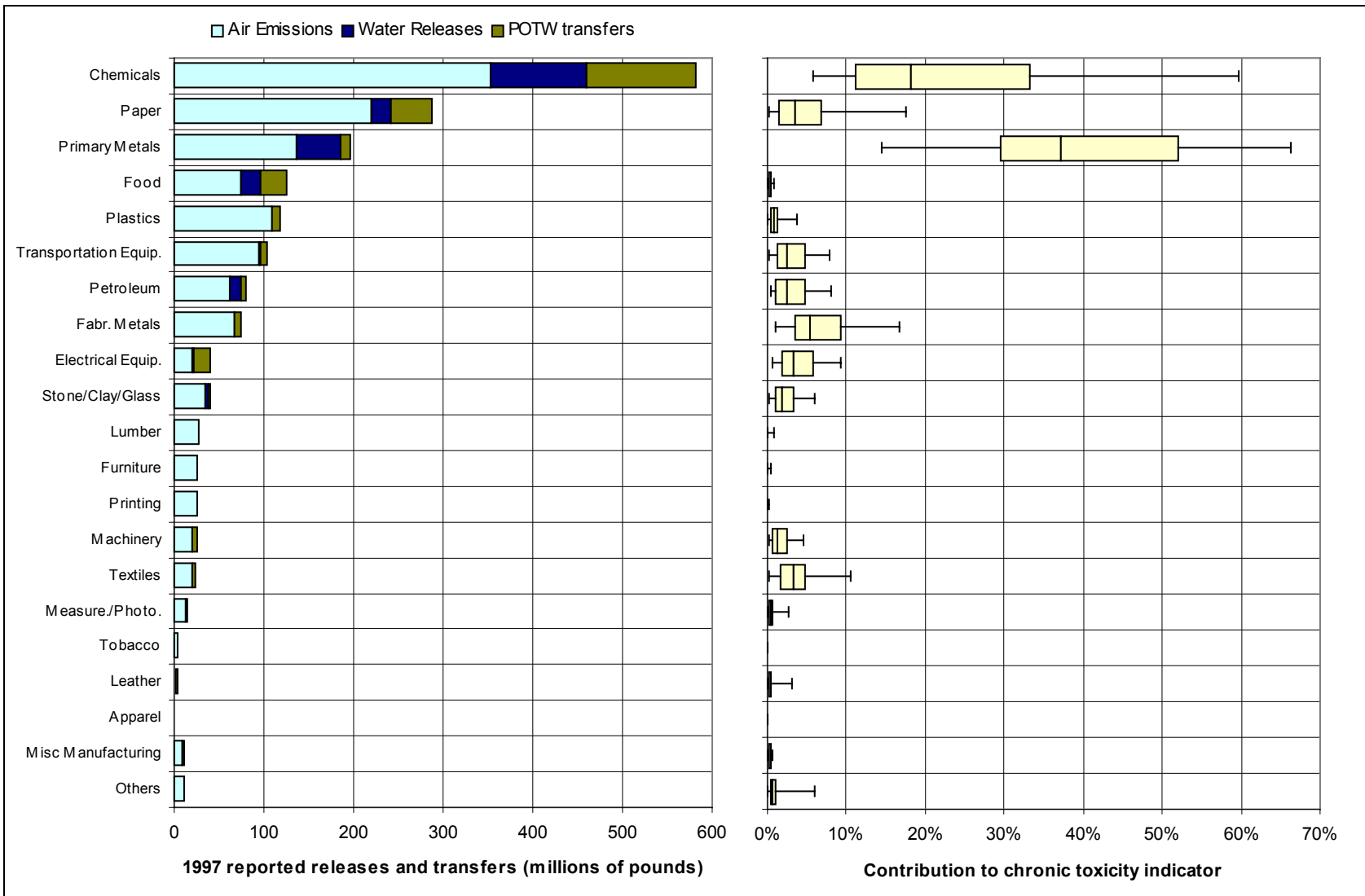


Figure 6-44: Industry contributions to (a) total mass and (b) total chronic health indicator (1997 reported TRI air emissions, water discharges, and transfers to wastewater treatment plants)

6.5.4 Discussion

A large fraction of the uncertainty in the ratio of potential chronic impact from reported TRI emissions in 1997 to the one for 1988 is due to the uncertainty in the contribution of polycyclic aromatic compounds. The EPA defines the polycyclic aromatic compounds group category as a set of including 19 specific chemicals [24]. The 19 compounds differ not only in toxicity, but also (and more widely) in fate and transport properties. Figure 6-45 shows the median value and the 50% and 90% confidence intervals for the unit cancer risk indicator for the 19 compounds in the PACs group. The large confidence interval for dibenzo(a,e)fluoranthene is due to physical property data gaps in the database. The distribution for the unit risk indicator for the group was obtained by sampling from each of the 19 distributions with equal probability. The result is that even though the 90% confidence interval for each PAC typically spans 2.5 to 3 orders of magnitude, the 90% confidence interval for the group indicator spans 5 orders of magnitude. Individual reporting of releases of each of the 19 compounds would be needed to decrease the uncertainty in the potential health risk posed by emissions from chemicals belonging to this category.

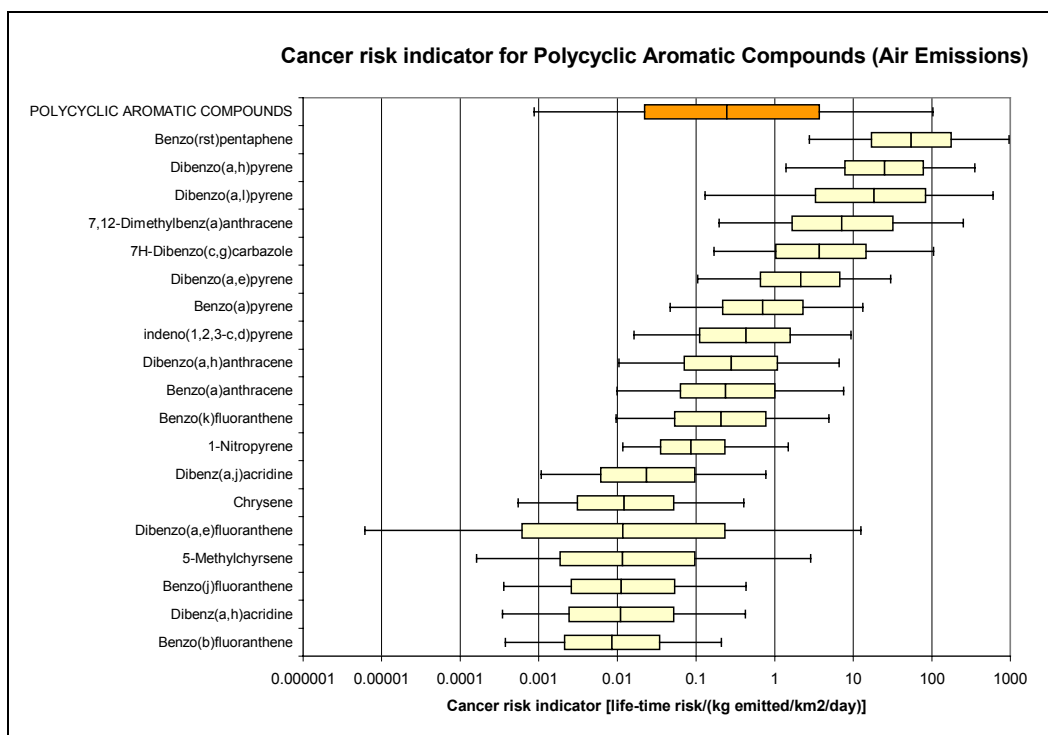


Figure 6-45: Unit cancer risk indicators for compounds in the Polycyclic Aromatic Compounds (PAC) chemical group.

COMPARISON WITH OTHER RESULTS BASED ON CHRONIC TOXICITY INDICATORS

This section compares the results obtained with the method described here to two other methods that are being used to rank TRI emissions from a risk-based perspective: (a) the Toxic Equivalent Potentials method used in the Environmental Defense Fund *Scorecard* web site (EDF TEP), and (b) the Environmental Indicators Model distributed in CD-ROM by EPA's Office of Pollution Prevention and Toxics (OPPTEIM). As Table 6-41 shows, using the probabilistic approach to estimating missing data elements resulted in a significant expansion of the set of chemicals or chemical groups with a risk score.

Table 6-41: Availability of indicators to score 1997 reported TRI releases

Toxicity endpoint	TRI chemicals with 1997 emissions and available indicators		
	EDF TEP	OPPTEIM	This work
Cancer	95 (45% of recognized or suspected carcinogens)		213 (100% of recognized or suspected carcinogens)
Non-cancer	193 (47%)		412 (100%)
Combined		315 (76%)	412 (100%)

EDF toxic equivalent potentials

The toxic equivalent potential scores used by the Environmental Defense Fund are calculated using similar procedures to the ones used to derive cancer and non-cancer chronic toxicity indicators in this work. The major differences are:

- The EDF uses the CalTox multimedia partitioning and exposure model. While the model used here shares many of the features of the CalTox model, there are some significant differences with respect to the calculation of concentrations in food, as discussed in section 6.3.2.
- The model used in this work does not consider the dermal contact exposure route.
- When degradation rates for a chemical in a particular medium are not available, the EDF sets the degradation rate to zero. The approach taken in this work was to assign an uncertainty distribution equal to the distribution of degradation rates among all the chemicals in the data set for which the rate is available.
- When high-quality toxicity assessment values are not available for at least one exposure route for a particular endpoint (either cancer or non-cancer), the EDF does not calculate a toxic equivalent potential for that endpoint. This effectively sets the toxic equivalent

potential to zero. In this dissertation lower-quality toxicity data were used instead to estimate uncertainty distributions with uncertainty factors derived from the correlation scatter between the lower-quality data set and higher quality data sets, as illustrated in Figure 6-22. When no toxicity data were available, the prior distributions in Table 6-42 were used.

Table 6-42: Default toxicity distributions used

Endpoint	Distribution for toxicity factor	Number of Chemicals
Non-cancer reference dose, mg/kg/day	Lognormal(0.005,800)	33
Cancer slope factor, (mg/kg/day) ⁻¹ (EDF recognized carcinogens)	Lognormal(0.84,1300)	2
Cancer slope factor, (mg/kg/day) ⁻¹ (EDF suspected carcinogens)	Lognormal(0.15,1300)	11

Notes: The first parameter in the distribution is the median value; the second parameter is the uncertainty factor (the quantity by which the median value should be multiplied or divided to generate the 95% confidence interval).

Figure 6-46 and Figure 6-47 compare EDF TEP cancer scores and relative contributions to the cancer risk indicator developed in this work for the top 50 chemicals ranked, respectively, by their EDF TEP score and their calculated median contribution to cancer risk. The scores and contributions are based on reported 1997 air emissions and water discharges. Figure 6-48 and Figure 6-49 show analogous information for non-cancer chronic effects.

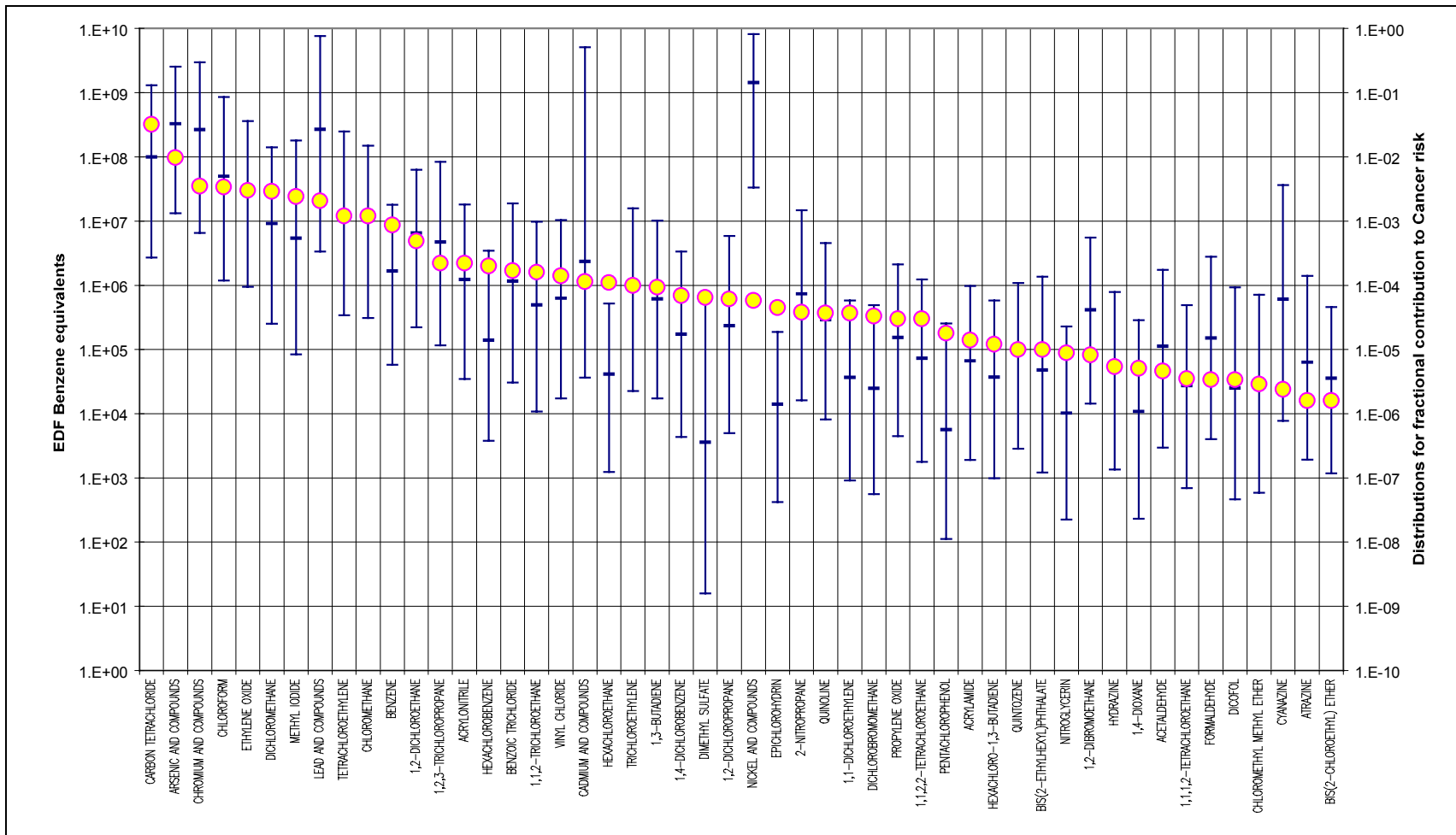


Figure 6-46: Comparison between EDF cancer toxic equivalent potentials and distributions for the contribution to the total cancer risk indicator (top 50 chemicals with reported 1997 releases or transfers to air, surface water, and wastewater treatment plants, sorted by EDF cancer score).

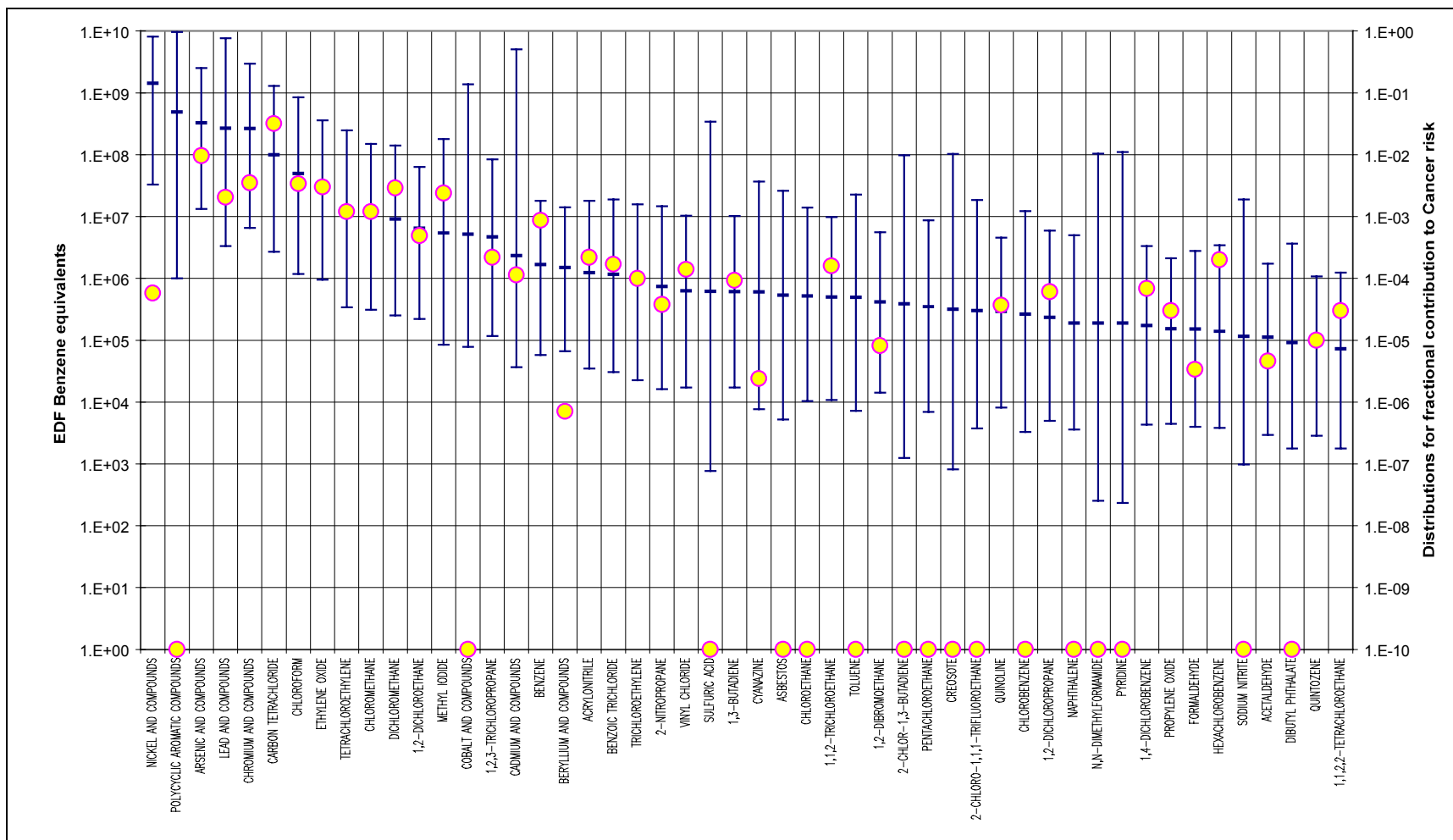


Figure 6-47: Comparison between EDF cancer toxic equivalent potentials and distributions for the contribution to the total cancer risk indicator (top 50 chemicals with reported 1997 releases or transfers to air, surface water, and wastewater treatment plants, sorted by median contribution to cancer risk).

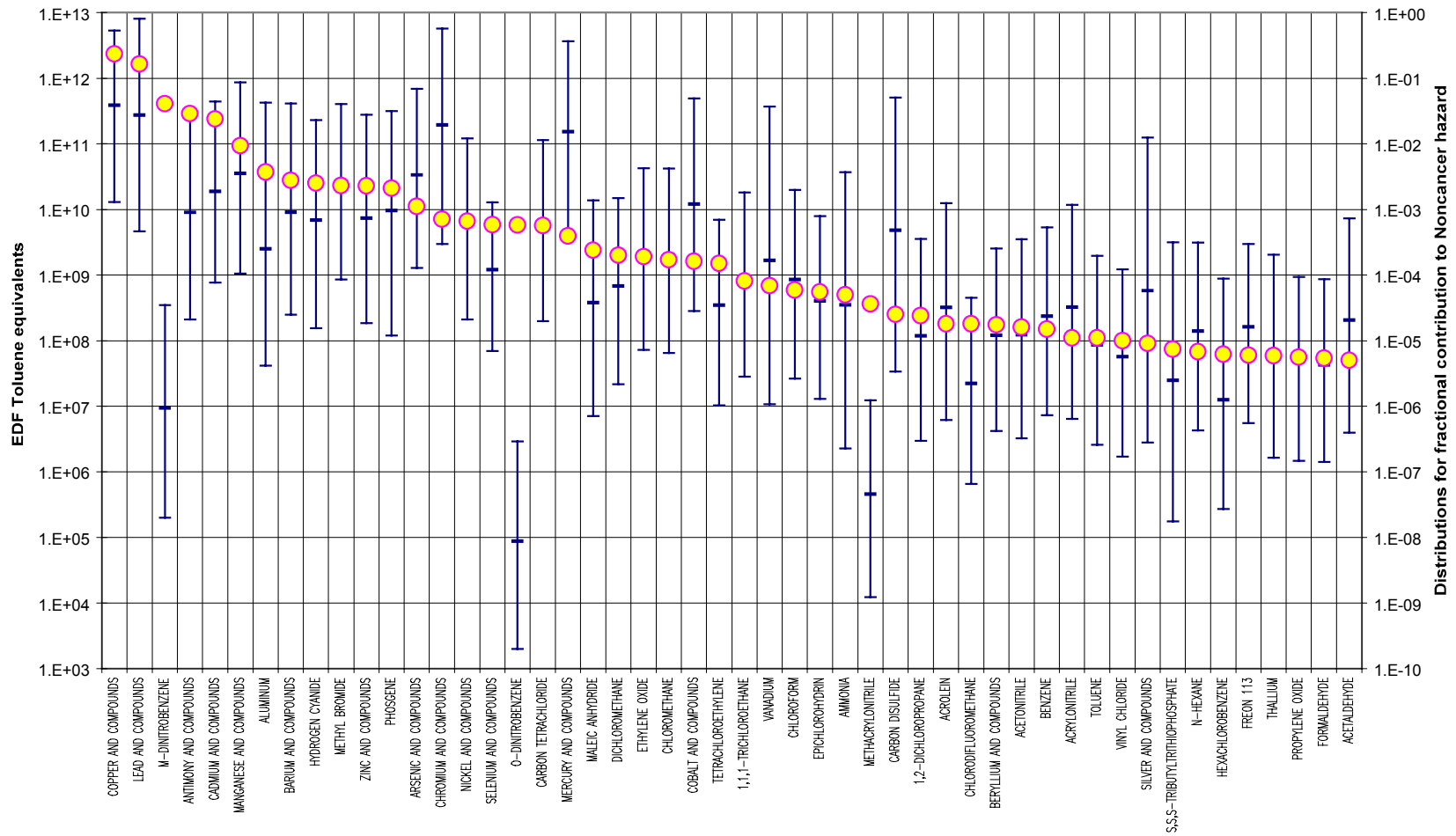


Figure 6-48: Comparison between EDF non-cancer toxic equivalent potentials and distributions for the contribution to the total non-cancer chronic toxicity indicator (top 50 chemicals with reported 1997 releases or transfers to air, surface water, and wastewater treatment plants, sorted by EDF non-cancer score).

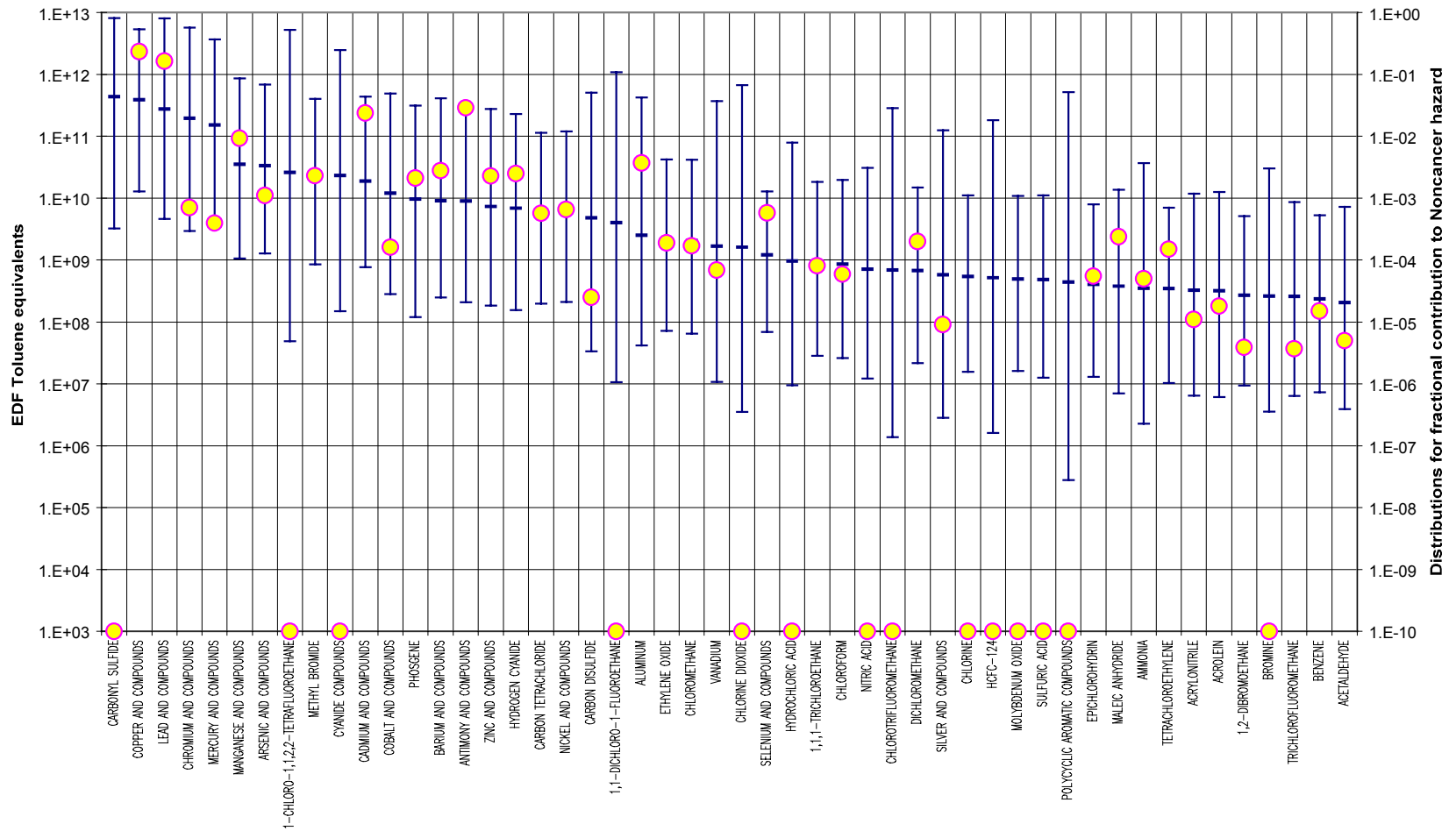


Figure 6-49: Comparison between EDF non-cancer toxic equivalent potentials and distributions for the contribution to the total non-cancer chronic toxicity indicator (top 50 chemicals with reported 1997 releases or transfers to air, surface water, and wastewater treatment plants, sorted by median contribution to non-cancer toxicity indicator).

There is general agreement between the results obtained here and the scores published in *Scorecard*. As Figure 6-50 shows, only 5 out of 88 compounds for which *Scorecard* has cancer scores fall outside the calculated 90% confidence intervals. Similarly, only 12 of 179 chemicals for which *Scorecard* has non-cancer scores are outside the 90% confidence intervals (Figure 6-51). The major differences can be traced to the way in which data gaps are handled. It appears that *Scorecard* overestimates the contribution of several substances (e.g. nitrobenzenes and methacrylonitrile in Figure 6-48) due to the assumption of infinite degradation lifetimes for substances with missing data. Similarly, nickel's contribution to cancer appears to be underestimated in *Scorecard* due to nonconsideration of nickel's cancer potency when ingested. The contributions of several important compounds are ignored in *Scorecard* due to lack of high-quality data (e.g. polycyclic aromatic compounds in Figure 6-47 and carbonyl sulfide in Figure 6-49). Other than differences in the treatment of missing high-quality data, the main difference between the results published in *Scorecard* and those shown here is that the EDF results could be considered as one out of the thousands of iterations used to generate the distributions shown here. The method developed in this work allows one to make statements about the confidence with which two chemicals, industrial sectors, facilities, or reporting years can be ranked with respect to one another. In the absence of correlations between indicator scores, the analysis suggests that differences in EDF scores of less than two orders of magnitude are not significant. Smaller differences (as the difference in score between two reporting years) could be significant only if the distributions for the scores were highly correlated. Propagation of the uncertainty in the ratio of the indicator scores would be required to determine how significant those differences are.

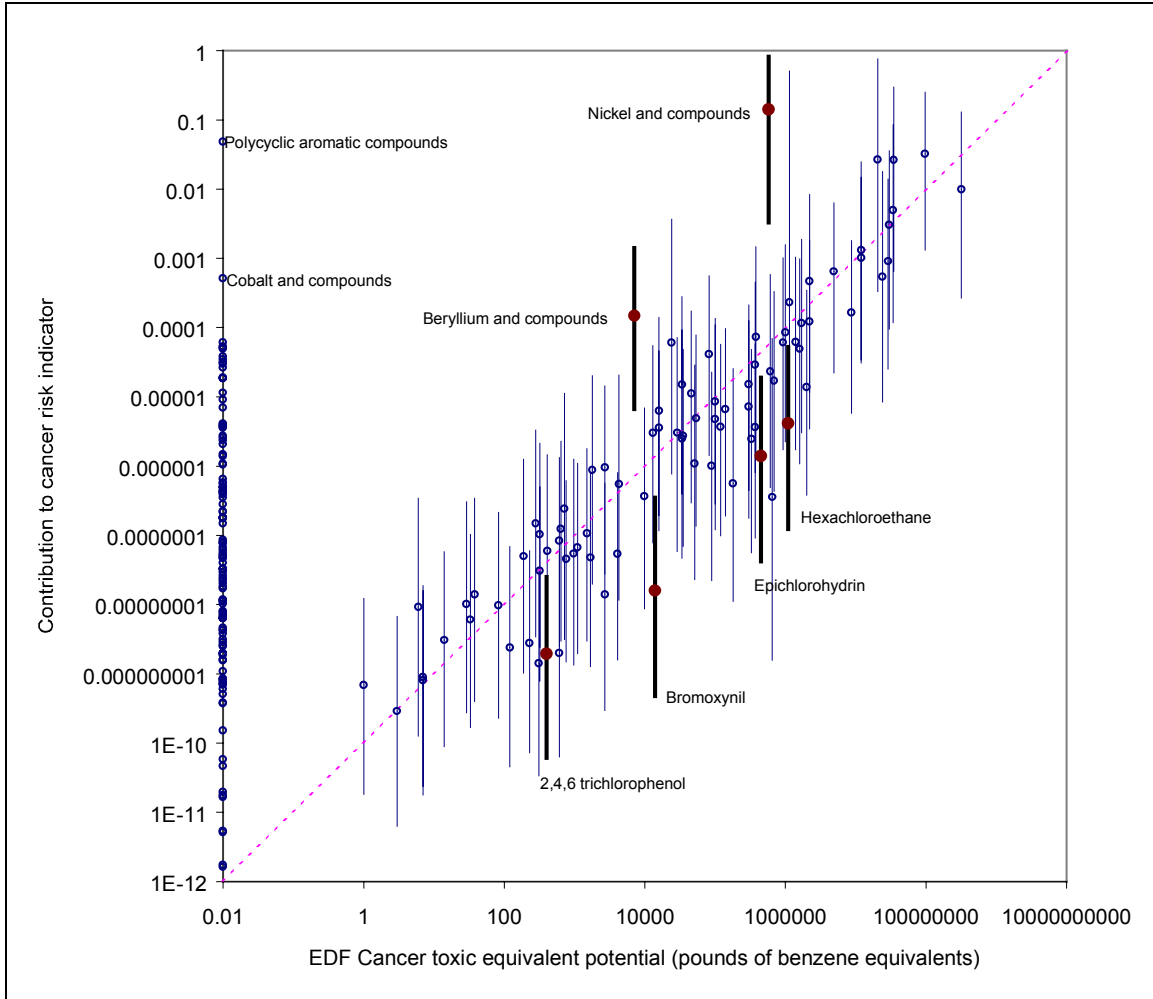


Figure 6-50: Plot of contribution to cancer risk indicator vs. EDF cancer toxic equivalent potential score (all TRI recognized or suspected carcinogens with reported 1997 releases or transfers to air, water, and wastewater treatment plants)

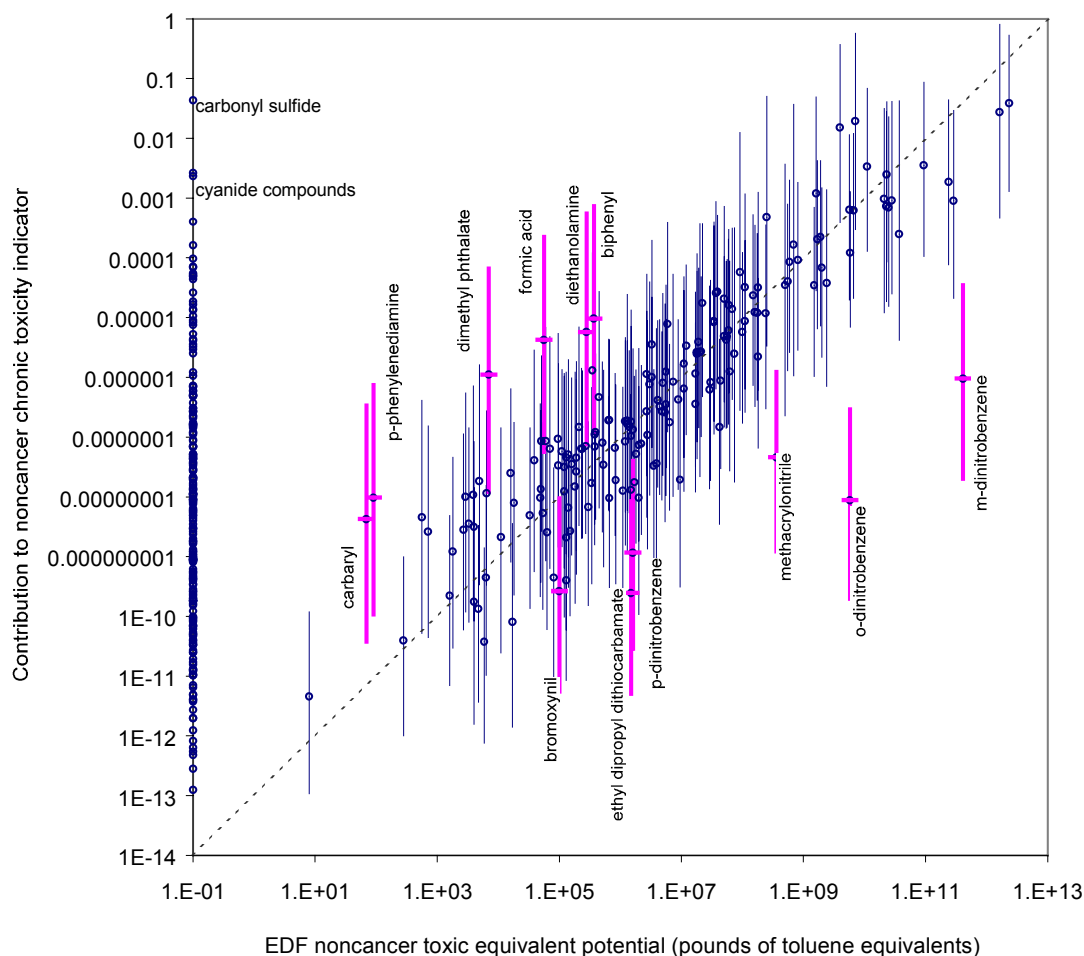


Figure 6-51: Plot of contribution to non-cancer chronic toxicity indicator vs. EDF non-cancer toxic equivalent potential score (all TRI chemicals with reported 1997 releases or transfers to air, water, and wastewater treatment plants)

OPPT Environmental Indicators Model

EPA's Office of Pollution Prevention and Toxics has developed an indicator model (OPPTEIM) for ranking TRI emissions [68]. The full model has been operationalized for air emissions only, and consists of four components:

- the quantity of pollutant emitted
- an adjustment for toxicity
- an adjustment for exposure potential
- an adjustment to reflect the size of the potentially exposed population

In contrast with the fate and transport model used in this work (in which pollutant concentrations are assumed to be well mixed within each of the environmental compartments of the fate and transport model), the OPPTEIM calculates air concentrations in the vicinity of each emission source. The OPPTEIM uses a Gaussian plume model to calculate pollutant concentrations in the center of each 1 km by 1 km grid cell in a 21 km by 21 km area surrounding a facility with emissions. Exposure potentials are calculated for each cell by multiplying the estimated pollutant concentration by an adult's breathing rate. Exposure potentials are multiplied by the population in each grid cell to yield the final exposure indicator. The OPPTEIM gives higher weighting to toxic emissions taking place in highly populated areas, while the fate and transport model used in this dissertation does not differentiate among emissions on the basis of their geographic location.

Other major differences between the EPA approach and the approach used in this work are: (i) in calculating air concentrations, the OPPTEIM takes into account air degradation rates only, while the model described in section 6.3.1 considers additional processes (such as particle deposition, rain dissolution, and dry deposition to surfaces), (ii) the exposure model described in section 6.3.2 considers the ingestion route in addition to the inhalation route. For many chemicals the ingestion route is the dominant long-term exposure route, even if they are emitted to air only.

Figure 6-52 and Figure 6-53 compare OPPTEIM scores and contributions to the combined chronic toxicity indicator calculated in this work for the top 50 chemicals ranked, respectively, by their OPPTEIM score and their median calculated contribution to chronic toxicity. The scores and contributions are based on reported 1997 air emissions only. There is less correspondence between the measure developed in this thesis and the OPPTEIM scores than between the combined health risk indicator and EDF's toxic equivalent potentials. This can be seen more clearly by comparing Figure 6-54 with Figure 6-50, or with Figure 6-51. The OPPTEIM tends to give lower scores relative to this work for substances with long environmental persistence and substances for which the main contribution to risk comes from the ingestion route. The model tends to give higher scores for substances that are quickly removed from the atmosphere by dry or wet deposition processes. This is not surprising, given the differences in the calculation of the exposure potentials. By restricting their calculations to a 441 km² area surrounding each facility, the OPPTEIM effectively gives equal exposure weight to

substances with atmospheric lifetimes higher than about a day, whether the lifetime is 2 days or 5 years. By ignoring the ingestion route, the OPPTEIM model does not give higher weighting to chemicals that bioaccumulate through food chains. The OPPTEIM is more appropriate for ranking exposures to people who live near an emission source (local impacts), while the risk indicator used in this dissertation is more appropriate for ranking risks to the general population (regional or global impacts). The indicator used in this work is particularly more relevant regarding cancer risk, since there is no exposure threshold for cancer effects. As distance from an emission source increases, the concentration of a persistent and volatile carcinogen decreases due to dilution, but the size of the exposed population increases.

Figure 6-55 shows that the exposure potential and population size adjustments have a very marginal impact in the OPPTEIM scores aggregated at the national level. 96.65% of the variation in the indicator can be explained by the product of mass released times toxicity via the inhalation route. As discussed above, the reason is that the potential exposure calculations are not affected by bioaccumulation and persistence (except for substances with degradation half lives shorter than a day).

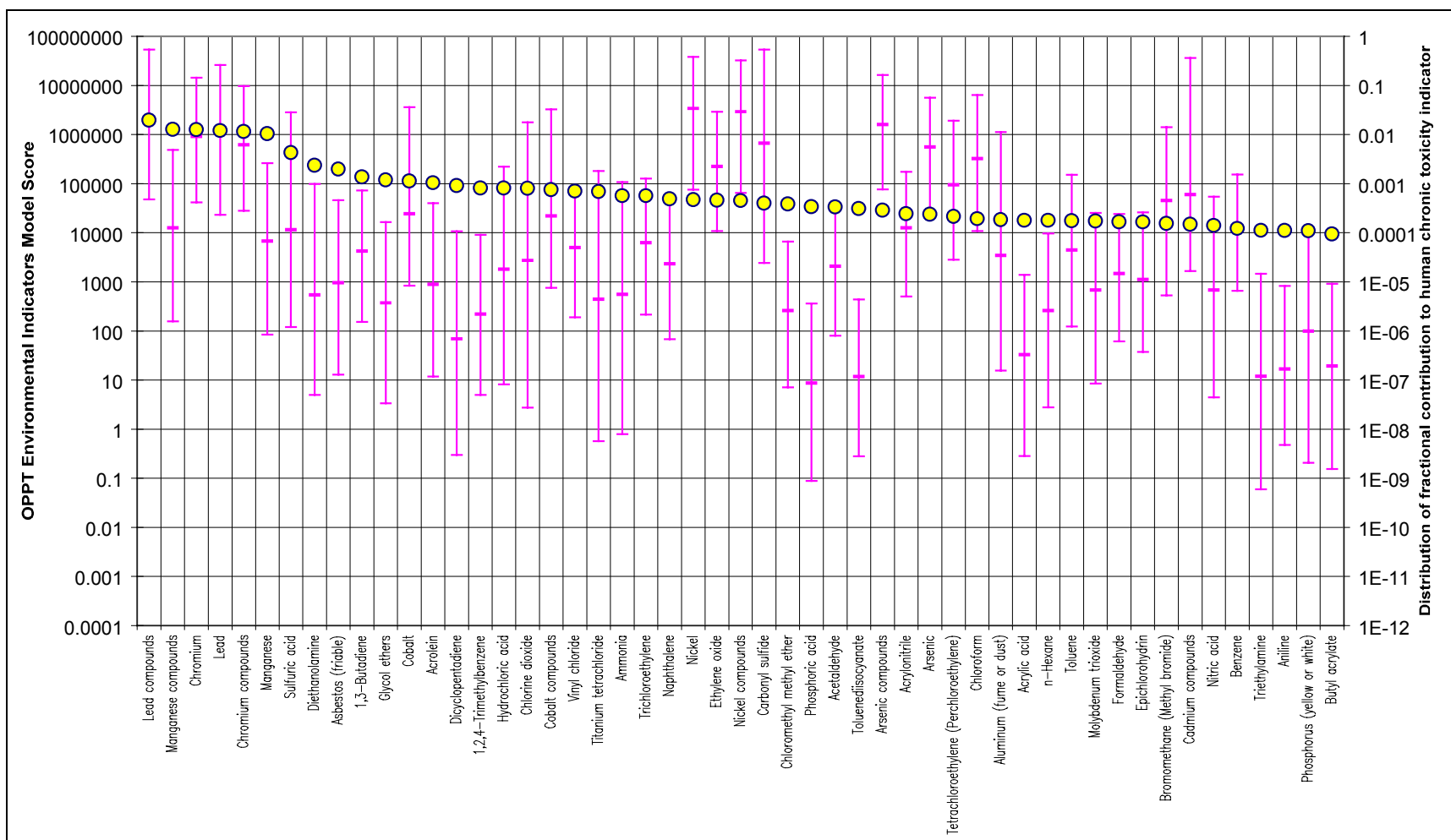


Figure 6-52: Comparison between OPPT EIM scores and contribution to combined chronic toxicity indicator (Top 50 TRI chemicals with 1997 reported emissions to air, sorted by OPPT EIM score)

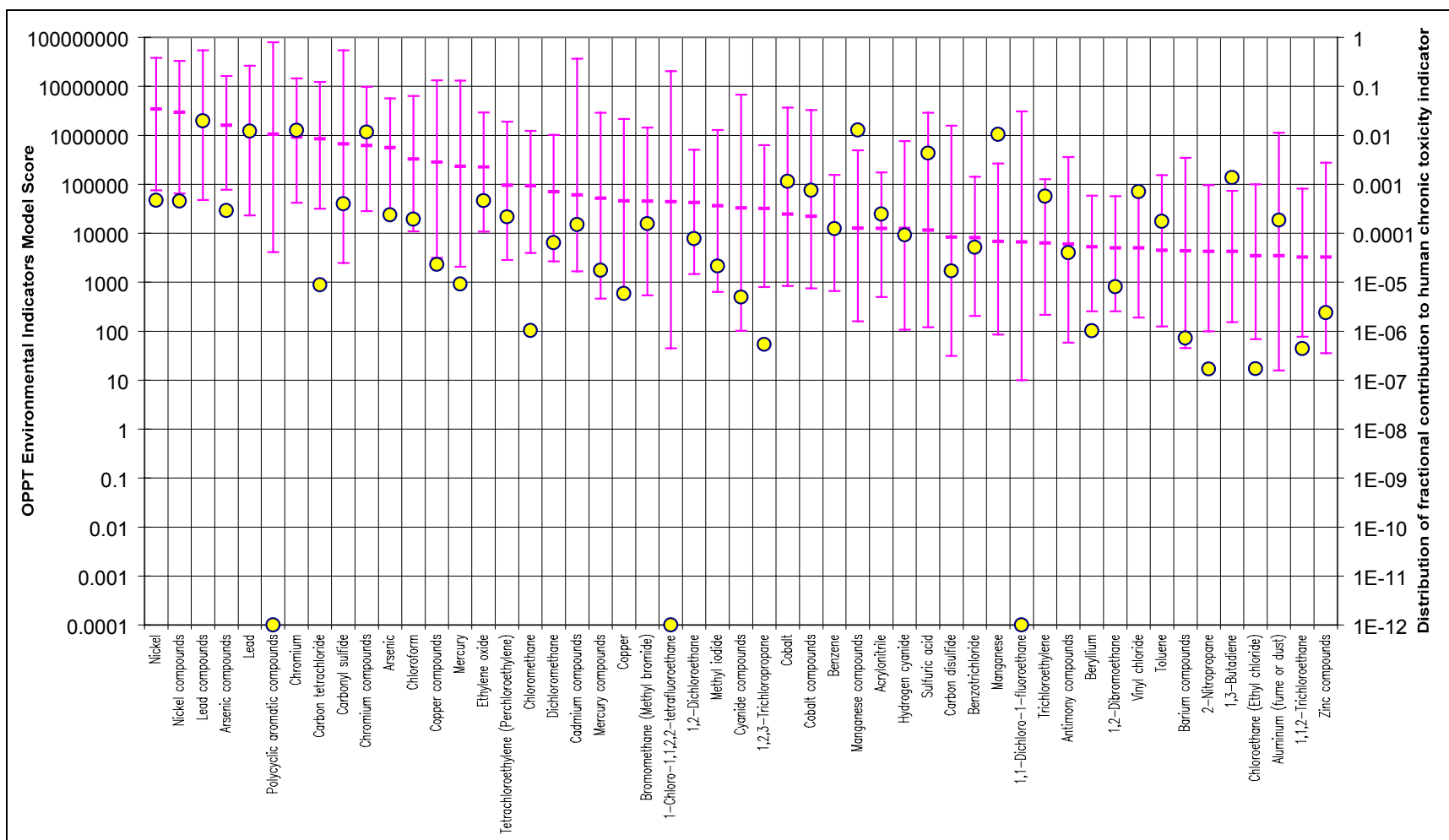


Figure 6-53: Comparison between OPPTEIM scores and contribution to combined chronic toxicity indicator (Top 50 TRI chemicals with 1997 reported emissions to air, sorted by median contribution to toxicity indicator)

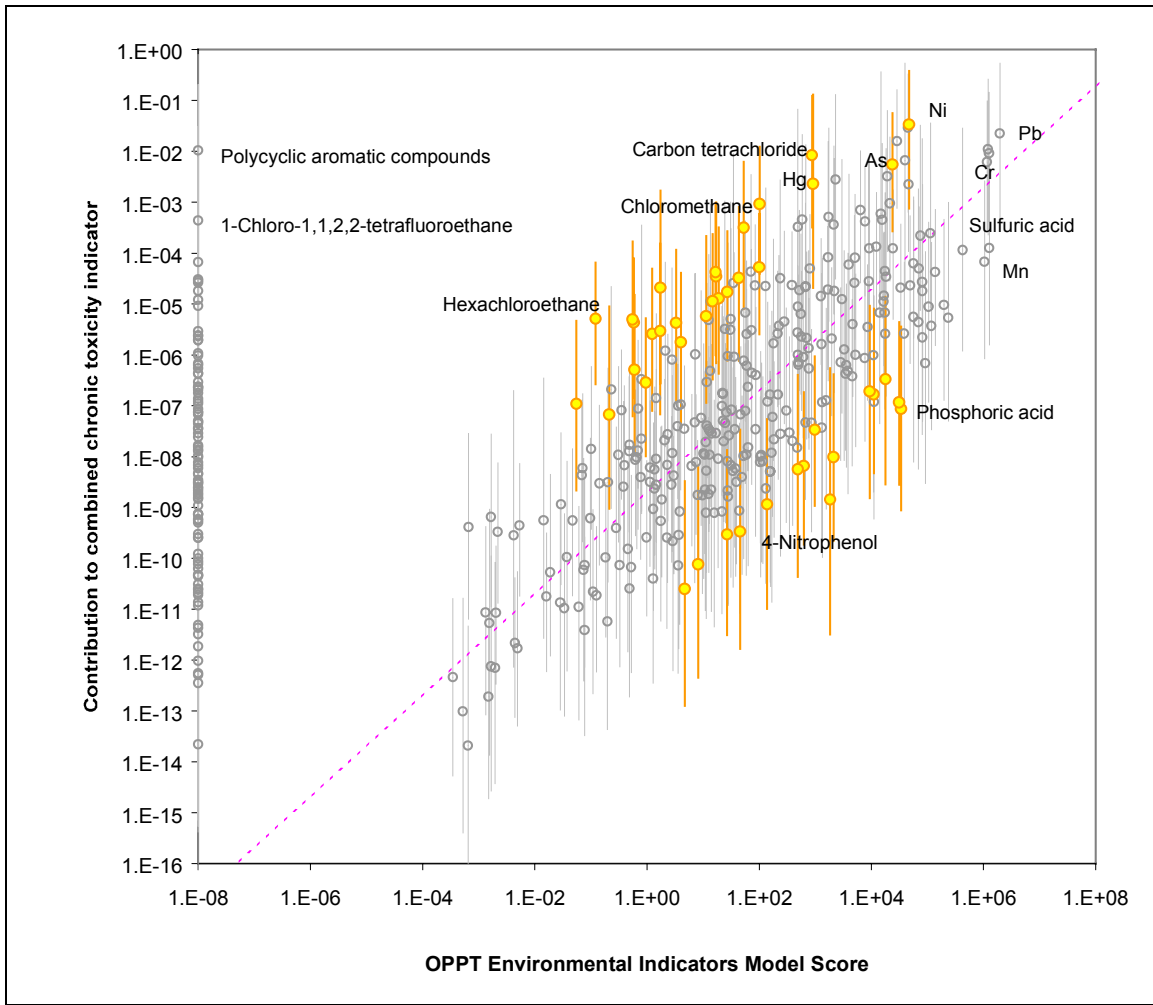


Figure 6-54: Plot of contribution to combined chronic toxicity indicator vs. OPTEIM score (all TRI chemicals with reported 1997 emissions to air)

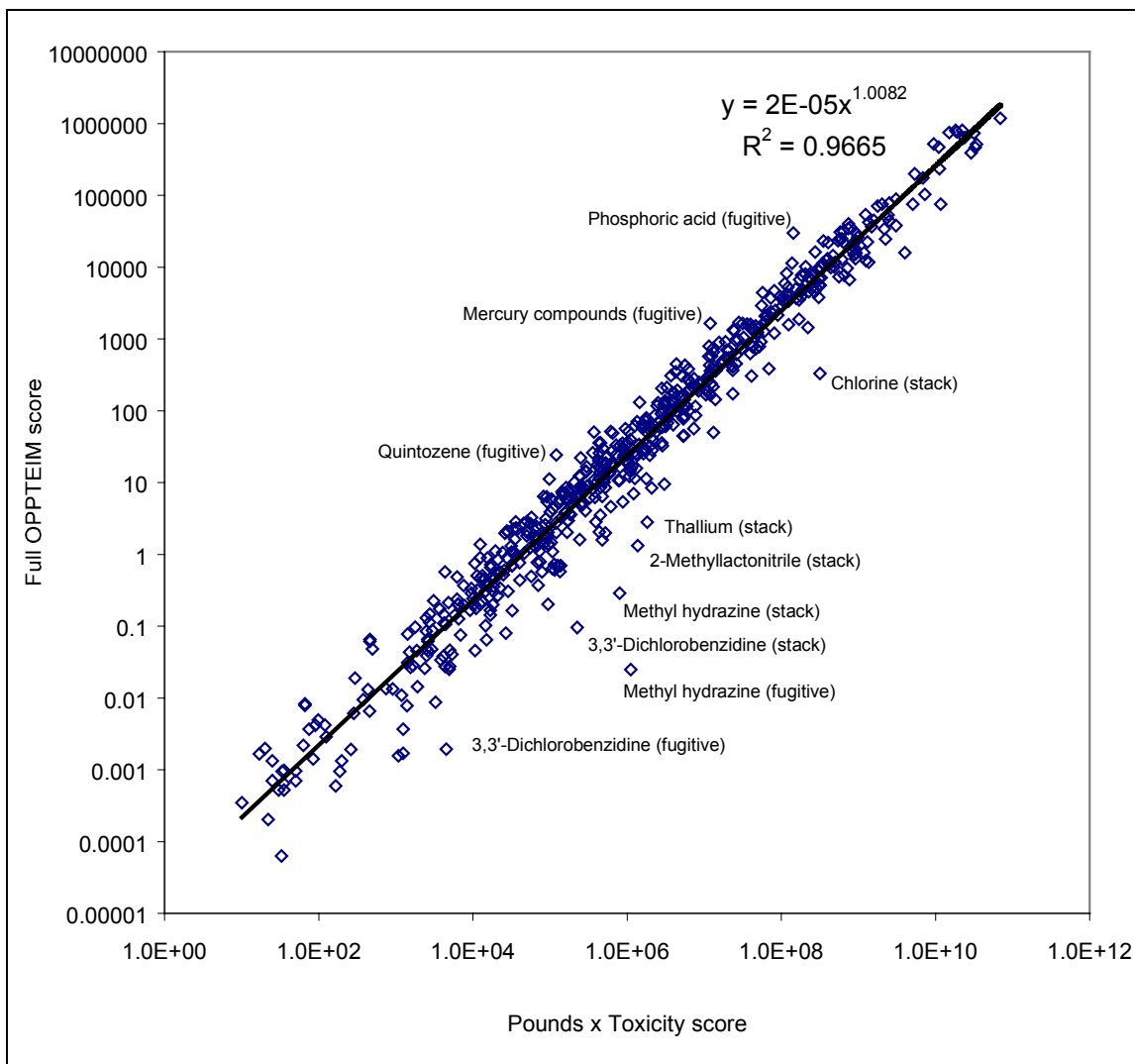


Figure 6-55: Correlation between OPPTTEIM scores and pounds emitted weighted by toxicity (TRI chemicals with reported 1997 stack or fugitive air emissions).

CASE STUDY CONCLUSIONS

Uncertainty propagation allows combination of information of different qualities without diluting the information content of the highest quality data. This example shows that uncertainties in indicators used to assess environmental performance do not necessarily imply uncertainty in decision-making. In particular, the analysis presented here shows two types of decisions that can be made:

- Identify priority pollutants that account for a majority of potential impacts
- Allocate resources to reduce key uncertainties

There are hundreds of chemicals with reported emissions in the toxics release inventory, but only a few of them have more than a 5% chance of contributing at least 1% of the total impact. There are also hundreds of data elements for which information of the highest quality is not available. However, there are only a few data elements that have the potential to affect the list of priority chemicals.

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Chapter 7 Process by Product Input-Output Life Cycle Assessment

7.1 Introduction

The incorporation of environmental issues as a design objective is limited in practice by the availability of environmental impact indicators appropriate for making quantitative tradeoffs. In contrast, designers have easy access to managerial cost accounting data that provide them with unit costs for the raw materials, utilities, and waste treatment services that might be part of their design. The availability of these unit costs allows designers to compare the economic performance of alternative designs, and to optimize their performance by resolving tradeoffs in the direction that maximizes profitability. If unit environmental indicators for raw materials, utilities, waste treatment services, and environmental releases were available, designers could compare alternative designs and resolve tradeoffs in the direction that minimizes potential environmental impact. A combination of economic and environmental objectives could then be used to identify superior design alternatives. The process-by-product input-output life cycle assessment (PIO-LCA) method developed in this chapter provides systematic procedures for generating unit environmental impact indicators in a transparent manner. In addition to providing indicator values, the procedure provides data that allow the user to interpret the results and to identify the factors that drive the indicator values. The method can be easily implemented on a spreadsheet. The resulting spreadsheet models can be rapidly updated when new information becomes available.

The remainder of the introductory section gives a brief overview of life-cycle assessment and input-output analysis. Section 7.2 introduces the example used throughout the rest of the chapter to illustrate the application of the PIO-LCA method. The method is developed in section 7.3, where data requirements are provided, followed by the derivation of the equations needed to generate and interpret environmental impact indicators. Section 7.4 demonstrates the versatility of the method by providing several illustrative applications of the matrices and vectors that can be generated with the method. Section 7.5 discusses the propagation of uncertainties in the input-output model. Finally, a comparison between the PIO-LCA method and a linear programming

formulation that uses the same underlying data is presented in the discussion section, showing how both approaches complement each other. A spreadsheet-based tool designed to automate the calculations presented in the chapter is presented in Appendix C.

7.1.1 Life cycle assessment

Engineers should consider not only the environmental impacts directly generated in the processes they design, but also take into account the environmental impacts associated with the provision of the products and services they specify as inputs to their processes. Failure to incorporate upstream impacts would lead to designs where as much production as possible is outsourced to suppliers, since emissions would then be placed outside of the boundary of analysis [1]. Life-cycle assessment (LCA) is a process used to evaluate the burdens placed on the environment by the production of a product or the provision of a service. The procedure attempts to take into account the use of resources and the generation of pollution at every stage of the supply, use, and disposal chains, from the initial extraction of raw materials until the point at which all residuals are returned to the environment [2].

The main stages in LCA are scope definition, inventory analysis, impact analysis, and improvement analysis. By far the most developed component of LCA is the inventory analysis stage. This is a very time consuming step for which specialized software and databases have been developed [3]. A problem with these databases is that the life cycle inventory for a product (e.g. electricity) is often provided without showing the contributions of each of the processes that contribute to the inventory. It is therefore very difficult, if not impossible, to update the inventories to reflect technological changes in one or more of the upstream processes. A second problem is that most product and process level LCA software represents production of a product as a process tree, when a network representation is often closer to reality. For example, Figure 7-1 shows the process tree for the production of chlorine in the Netherlands generated using SimaPro 4.0 and its processes database [3]. The emissions stored in the database for the processes that supply rock salt and electricity include emissions from upstream processes. An alternative representation is shown in Figure 7-2, where products and processes associated with the production of chlorine in the United States are shown as a network. Note that the three inputs to the chlor-alkali processes (brine, electricity, and thermal energy from gas-fired boilers) are connected (either directly or indirectly) to many processes in common, for example the coal-

fired power plant. If the emissions inventory for power generation in coal-fired power plants included trace metal emissions from coal combustion, then all three inputs would inherit a fraction of these emissions.

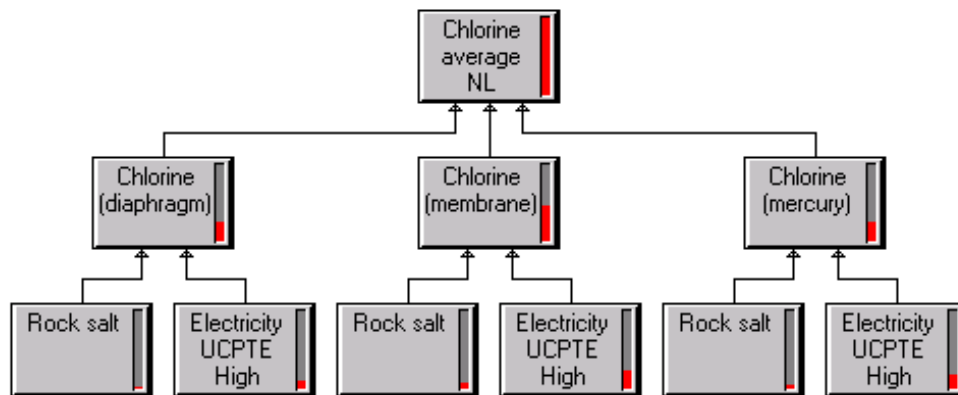


Figure 7-1: Process tree representation of chlorine production in the LCA software SimaPro

There are several important distinctions between the tree and network representations:

- 1) The network representation allows feedback loops, where the outputs of a process can be used by the processes that supply its inputs. For example, in Figure 7-2 natural gas is used as an input by the gas-fired power plants to generate electricity. Electricity is in turn used as an input for the production of natural gas.
- 2) The network representation shows the relationships among products produced in multiproduct processes.
- 3) The network representation shows more clearly instances of an input common to many processes.

The ability of a network representation to show more relationships than a tree representation also makes it appear to be more complicated to analyze, particularly due to the possible presence of feedback loops. Input-output analysis is used here to overcome this difficulty.

7.1.2 Input-output analysis

Input-output analysis techniques pioneered by Wassily Leontief [4] can be used to analyze complex production networks. A key assumption is that the network of interactions can

be appropriately described by linear relationships. For example, if 3.2 kWh of electricity were needed to produce 1 kg of chlorine, then 3200 kWh of electricity would be required to produce 1000 kg of chlorine. The majority of input-output models use data at the national or regional levels, with interactions among industries and commodities expressed in monetary terms. The methods can also be used at the enterprise level with interactions among processes and products expressed in physical units [5].

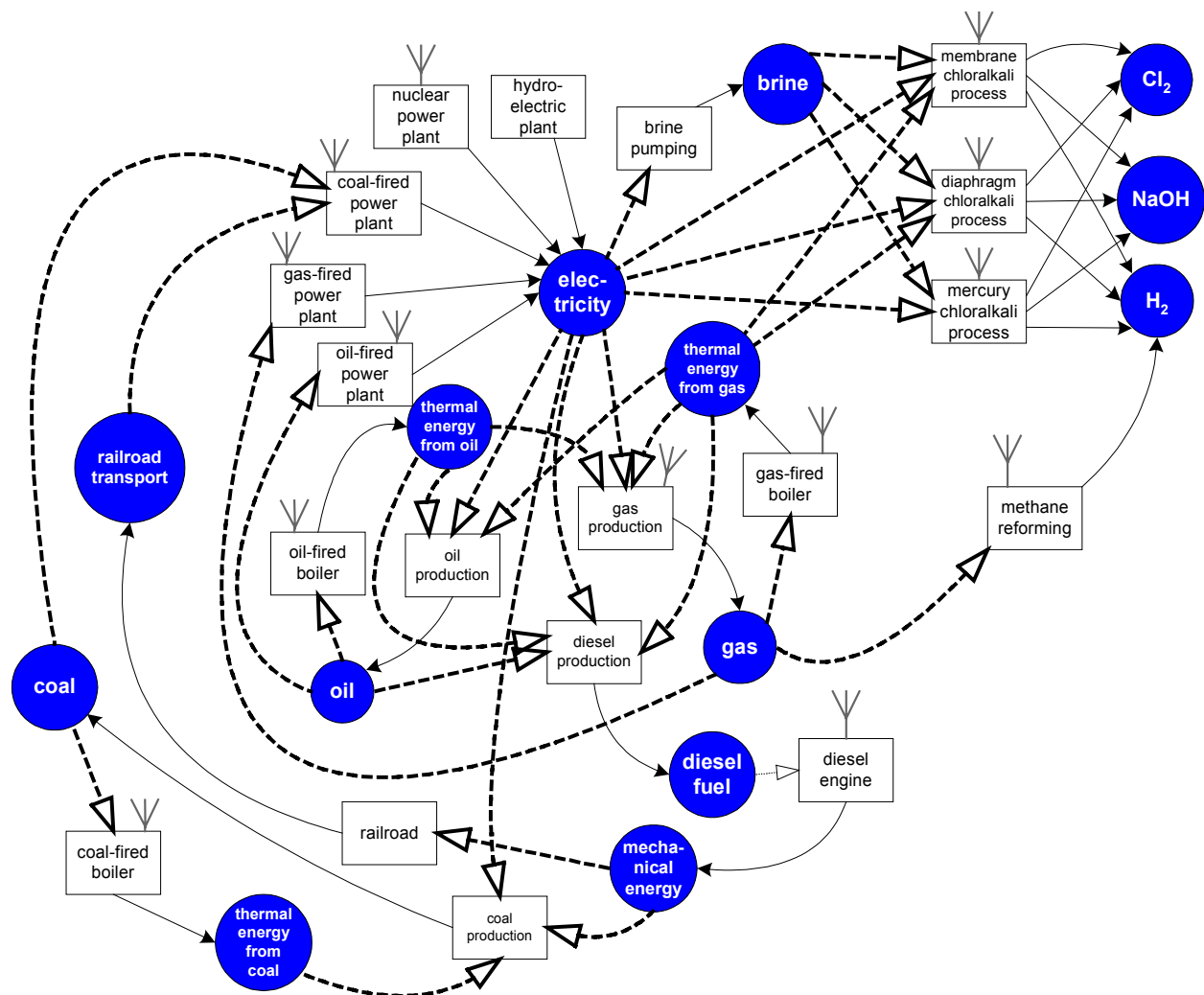


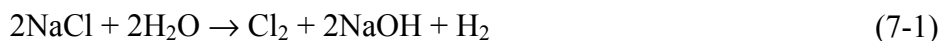
Figure 7-2: Process and product chains involved in the production of chlorine

The economic input-output approach to analyze environmental burdens as a result of economic activity was first studied by Leontief [6]. Detailed descriptions of various input-output models that incorporate environmental concerns have been provided by Miller [7]. By taking advantage of the more recent availability of data, the Green Design Initiative group at Carnegie Mellon University [8-10] has developed the methodology of economic input-output environmental life cycle assessment (EIO-LCA). This chapter builds on the methodology of EIO-LCA to allow for analysis at a deeper level of detail (process level), and to include impact and improvement analysis. The process level input-output life cycle assessment (PIO-LCA) methodology presented in this work provides systematic procedures for addressing multiproduct processes and products produced in multiple processes. It also provides a framework for organizing and managing LCA data in a way that allows designers to trace impacts to the processes that originate them and that allows rapid updating of life cycle inventories when emission factors for an underlying process are updated.

7.2 Illustrative example

A life-cycle impact assessment of chlorine production (from cradle to gate) is used as an example throughout this chapter to illustrate how the methodology is applied. Tables with intermediate results are provided so that this chapter may serve as a tutorial for analysts interested in learning the method. The method relies heavily on matrix algebra, which facilitates computer implementation but might be a source of confusion to the reader. A glossary of matrices and vectors is provided in the appendix (section 7.8). Readers are encouraged to refer frequently to the glossary and the tables as they follow the derivations in the next section. Even though the literature, government statistics, and specialized databases were consulted to obtain data for the example [3,11-17], the sources used might not be the most recent or most relevant. The purpose of this chapter is to introduce the tool and show its application, and not the presentation of particular analysis results for management or policy decisions.

There are three major processes currently in use for the production of chlorine. All three processes are based on the electrolysis of an aqueous solution of sodium chloride [11]:



The evolution of chlorine takes place in the anode of the electrolytic cell:



while the nature of the reaction at the cathode depends on the specific process. The three processes are the mercury cell process, the diaphragm cell process, and the membrane cell process. In the mercury cell process, sodium amalgam is produced at the cathode. The amalgam is reacted with water in a separate reactor to produce hydrogen gas and caustic soda solution. Mercury is recycled to the electrolytic cell. In the diaphragm cell process, the anode is separated from the cathode by a permeable asbestos-based diaphragm. Sodium hydroxide and hydrogen gas are produced directly at the cathode. Steam is used to evaporate water from the caustic solution recovered from the cathode. In the membrane cell process, a cation-permeable ion-exchange membrane separates the anode and the cathode. Only sodium ions and some water pass through the membrane. As in the case of the diaphragm cell process, sodium hydroxide and hydrogen gas are produced in the cathode. The caustic solution leaves the membrane cell at a relatively high concentration, and thus less steam is required to concentrate the solution to commercial specifications. The major difference in operating cost among the three processes is due to the consumption of energy as electricity and steam. In building the process network it was assumed that natural gas is the fuel used to generate the steam used in the membrane cell and diaphragm cell processes. For the sake of simplicity (and because of limited data), the processes supplying electrolytic cell materials have been omitted from the analysis.

7.3 *The PIO-LCA method*

7.3.1 Input data

Two *product-by-process* matrices represent the technologies: A “use matrix” (**B**) and a “make matrix” (**C**). Columns in each matrix correspond to individual processes, while rows correspond to products (product inputs in the use matrix, product outputs in the make matrix). The word “product” in this context refers to any product or service of economic value. Both matrices have the same dimensions, but they do not need to be square matrices. The only structural requirement is that each product with nonzero entries in the corresponding row of the use matrix must be produced by at least one process, and thus must have a nonzero entry in the corresponding row of the make matrix. An entry B_{ij} in the use matrix gives the number of units of product i that are used as input by one unit of throughput of process j . An entry C_{ij} in the

make matrix gives the number of units of product *i* that are produced as output by one unit of throughput of process *j*. The use and make matrices for the example are shown in Table 7-1⁶⁶. The second to fourth columns of the use and make matrices contain, respectively, the input and output information for the three alternative processes for producing chlorine through electrolysis.

Table 7-1: Use and make matrices for the chlorine LCA example

		PROCESS																					
		Brine pumping	Chloralkali production (diaphragm cell process)	Chloralkali production (membrane cell process)	Chloralkali production (mercury cell process)	Coal furnace	Coal production	Coal-fired power plant	Diesel engine	Diesel fuel production	Gas-fired power plant	Hydroelectric plant	Industrial gas furnace	Methane reforming	Natural gas production	Nuclear power plant	Oil furnace	Oil production	Oil-fired power plant	Railroad transport	Utility gas furnace		
PRODUCT INPUTS		B = f use matrix																					
Chlorine	kg																						
Coal	kg					1																	
Diesel fuel	kg								0.02														
Electricity	MJ	0.36	10.8	11	11.7		0.05			0.14				1.4	0.12			0.14					
Hydrogen	kg																						
Mechanical energy from diesel engines	MJ						2.53																
Natural gas	kg												19.5	2							0.27		
Oil	kg									1													
Railroad transport	kg-km					467											23.2						
Salt from brine	kg		1.65	1.65	1.65																		
Sodium hydroxide	kg																						
Thermal energy from coal furnace	MJ						0.01	10.2															
Thermal energy from industrial gas furnace	MJ		9	1.35						1.84				31.9	1.27			0.53					
Thermal energy from oil furnace	MJ									0.55					0.03			0.06	9.73				
Thermal energy from utility gas furnace	MJ										10.2												
PRODUCT OUTPUTS		C = f make matrix																					
Chlorine	kg		1	1	1																		
Coal	kg					1																	
Diesel fuel	kg									1													
Electricity	MJ							3.6			3.6	3.6									3.6		
Hydrogen	kg		0.03	0.03	0.03				1														
Mechanical energy from diesel engines	MJ													1									
Natural gas	kg														1								
Oil	kg																						
Railroad transport	kg-km																				1000		
Salt from brine	kg	1																					
Sodium hydroxide	kg		1.12	1.12	1.12																		
Thermal energy from coal furnace	MJ					29.6																	
Thermal energy from industrial gas furnace	MJ												1055										
Thermal energy from oil furnace	MJ															1055							
Thermal energy from utility gas furnace	MJ																					1055	

Processes with a single output have only one non-zero entry in the corresponding column of the make matrix. For example, the “coal production process” listed in column 6 of the matrices has a single output, and thus a single nonzero entry in the make matrix. The coefficient

⁶⁶ The four first tables in this chapter (Table 7-1 through Table 7-4) were generated automatically in Microsoft Excel using the EnvEvalTool described in section 9.4. Details are given in section B.3 in Appendix B.

of 1 in the matrix means that this process has been defined on the basis of the production of 1 kg of coal, since the unit of measurement used for the product “coal” is the kilogram.

Multi-product processes may have several nonzero entries in the corresponding column of the make matrix. In the example, all three chlor-alkali processes produce three products with commercial value: chlorine, sodium hydroxide, and hydrogen. Note that the entries in the make matrix give the meaning of a unit of throughput for each process. The results of the methodology are not sensitive to the basis chosen to define a unit of process throughput, as long as the units used to measure inputs and outputs of each product are consistent across all processes. Processes could be defined on the basis of a unit of product output, on the basis of annual production, or on any other basis that is convenient or consistent with existing sources of data. For example, the references consulted to obtain technical coefficients for the electricity generation processes give inputs, outputs and emissions on the basis of 1 kWh of electricity generated [12]. Since the unit for the electricity “product” in the tables is MJ, the corresponding entries in the make table were set to 3.6, using the unit conversion 1 kWh = 3.6 MJ. Similarly, a conversion factor of 1 million BTU = 1055 MJ was used to generate the entries for the most of the fossil fuel combustion processes⁶⁷, since the source consulted uses a million BTU of thermal energy as the basis for listing emissions.

Data regarding environmental exchanges are organized into a matrix of direct environmental exchanges (**E**). The columns of **E** correspond to the processes, listed in the same order as in matrices **B** and **C**, while its rows correspond to environmental exchanges. An entry E_{kj} gives the number of units of environmental exchange k arising from one unit of throughput of process j . For example, the entry in the fifth column and seventh row of Table 7-2 states that the coal furnace process generates 2.7 kg of carbon dioxide per kg of coal burned. Environmental exchanges include pollutant releases to the different environmental media, and may also include depletion of natural resources or any other externality of interest to the analyst. Mass and energy balances could be closed around each process if enough “product” and “environmental exchange” inputs and outputs were considered, but the applicability of the method does not require inclusion of all the inputs and outputs needed to close mass balances. As an example, consider the last column in Table 7-1 and Table 7-2. The “utility gas furnace” process uses a

⁶⁷ The exception is the coal furnace process, which is defined on the basis of 1 kg coal burned.

commercial input of 19.5 kg of natural gas (matrix **B**) to generate 1055 MJ of thermal energy as steam (matrix **C**). It also generates at least 54.4 kg of pollutants (sum of the entries in the last column of matrix **E**). Most of the difference between the mass of outputs and the mass of inputs can be attributed to the consumption of oxygen from the air used in combustion. However, since air is not a commercial input, there is no corresponding row for air in matrices **B** and **C**. There is also no row for oxygen depletion in matrix **E**, since the reservoir of oxygen in the atmosphere is not being disturbed significantly by human activities⁶⁸.

The analyst has the freedom to structure the use and make matrices in any manner that is consistent with the available data. In the example, data were available for the emission of combustion products from furnaces burning different types of fuels. Thermal power plant emissions were estimated by specifying thermal energy as an input for the power generation processes. When this modeling approach is adopted, there is no need to list combustion emissions in the power generation columns of matrix **E**, since combustion emissions are already taken into account by the specification of the output of a furnace process as an input to the corresponding power generation process. An alternative approach that could be taken is to list the emissions directly under the power generation processes, and replacing the specification of thermal energy as an input with the specification of the appropriate fuel input. The difference between the two approaches is shown schematically in Figure 7-3.

The existence of multiproduct processes and products that can be produced by different technologies makes it necessary to establish accounting rules to allocate or attribute process throughputs to product demands (since a one to one correspondence between products and processes would not exist in these cases). Allocation is necessary to avoid double counting. Suppose a design uses chlorine as an input, but it does not require any sodium hydroxide. It would not be reasonable to charge chlorine with the responsibility for all of the impacts resulting from the operation of the chlor-alkali processes. Clearly, consumers of sodium hydroxide share some of the responsibility for causing the chlor-alkali processes to be operated.

⁶⁸ The conversion of oxygen into carbon dioxide is a cause for concern, but this concern is properly taken into account by including a row for carbon dioxide emissions in matrix **E**

Table 7-2: Environmental exchanges matrix for the chlorine LCA example

EXCHANGE TYPE	EXCHANGE	UNITS	Brine pumping	Chloralkali production (diaphragm cell process)	Chloralkali production (membrane cell process)	Chloralkali production (mercury cell process)	Coal furnace	Coal production	Coal-fired power plant	Diesel engine	Diesel fuel production	Gas-fired power plant	Hydroelectric plant	Industrial gas furnace	Methane reforming	Natural gas production	Nuclear power plant	Oil furnace	Oil production	Oil-fired power plant	Railroad transport	Utility gas furnace
Air	2,3,7,8-Tetrachlorodibenzo-p-dioxin	kg					1E-11											1E-11				
Air	Ammonia	kg	9E-07	9E-07	9E-07																	
Air	Arsenic	kg					2E-07							1E-07				5E-06				1E-07
Air	Asbestos	kg			2E-08																	
Air	Barium	kg	1E-07	1E-07	1E-07									1E-06				9E-09				1E-06
Air	Cadmium	kg					2E-08											1E-06				
Air	Carbon dioxide	kg					2.7															
Air	Carbon monoxide	kg					0.002			0.076				54.4	5.5	0.21	6E-05	88.1				54.4
Air	Carbon tetrachloride	kg	5E-06	5E-06	5E-06					3E-04				0.016				0.018				0.018
Air	Chlorine	kg	0.004	0.004	0.004																	
Air	Cobalt	kg					5E-08							5E-08						2E-05		5E-08
Air	Cyanide	kg					1E-06															
Air	Dichlorodifluoromethane	kg	6E-06	6E-06	6E-06																	
Air	Hydrazine	kg	3E-09	3E-09	3E-09																	
Air	Hydrochloric acid	kg	1E-07	1E-07	1E-07		6E-04															
Air	Hydrogen sulfide	kg																				
Air	Isophorone	kg					3E-07															
Air	Lead	kg					2E-07															
Air	Mercury	kg			4E-06		4E-08							1E-07				5E-06				1E-07
Air	Methane	kg					3E-05							0.001				4E-07				
Air	Nickel	kg					1E-07							2E-06				1E-03				1E-04
Air	NOx (as NO2)	kg					0.005			0.001				0.063			0.002	0.14				0.024
Air	PM10	kg					0.008							0.003				0.044				0.001
Air	Sulfur dioxide	kg					0.017			1E-04				3E-04				0.6				3E-04
Air	Sulfuric acid	kg	4E-08	4E-08	4E-08																	
Air	Total Suspended Particles	kg								1E-04												
Water	Barium	kg	2E-07	2E-07	2E-07																	
Water	Chlorine	kg	1E-06	1E-06	1E-06																	
Water	Hydrochloric acid	kg	3E-07	3E-07	3E-07																	
Water	Mercury	kg					1E-07															
Water	Sulfuric acid	kg	2E-09	2E-09	2E-09				9E-04			5E-06		5E-04				0.001		1E-05		

E = [Environmental exchanges matrix]

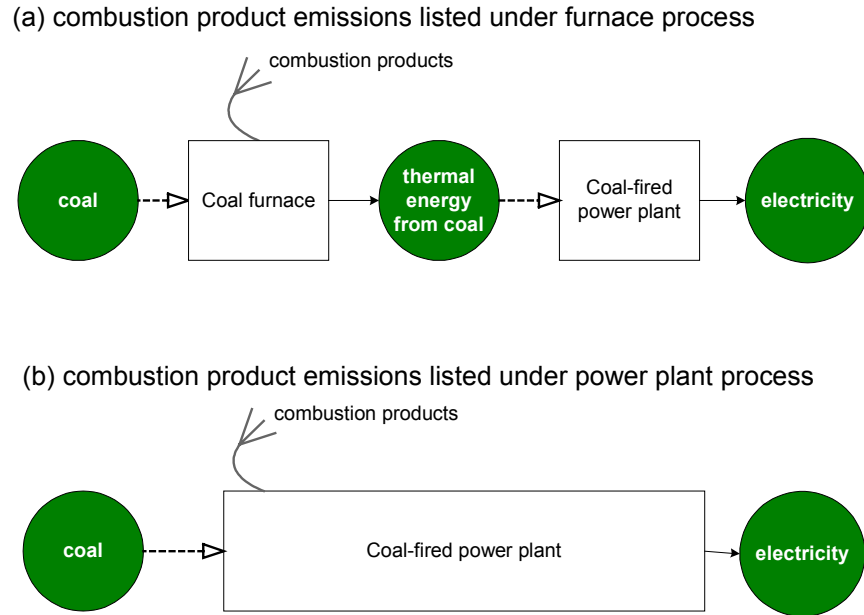


Figure 7-3: Two alternative approaches for listing emissions of combustion products associated with the coal-fired power plant process

Two sets of data are needed as inputs to the two allocation rules used in the PIO-LCA method. The first is information about the proportions (as a fraction of total demand) in which different processes are used to supply the demand for a product that can be made by different processes. This information is organized into a “market share” matrix (**F**). An entry F_{ji} gives the fraction of the demand for product i that is fulfilled by the outputs of process j . Table 7-3 shows the market share matrix for the example⁶⁹. The market shares correspond to production in the United States in the period 1980-1990. There are four products that are made by more than one process, namely electricity (column 6), and the products of the chlor-alkali processes (columns 1, 5, and 11). Electricity is generated by five different types of power plants, and the corresponding entries in **F** give the proportion in which each type of power plant contributes the supply of electricity to the United States national grid.

⁶⁹ Note the switching of rows and columns in matrix **F** compared to matrices **B**, **C**, and **E**. The reason for the switch is that the matrices are meant to be read by columns. The market share fractions shown on the table are relative to the total of all processes contributing to the output of the product shown in the table.

Table 7-3: Market share matrix for the chlorine LCA example

PROCESS	Chlorine	Coal	Diesel fuel	Electricity	Hydrogen	Mechanical energy from diesel engines	Natural gas	Oil	Railroad transport	Salt from brine	Sodium hydroxide	Thermal energy from coal furnace	Thermal energy from industrial gas furnace	Thermal energy from oil furnace	Thermal energy from utility gas furnace
Brine pumping										100%					
Chloralkali production (diaphragm cell process)	78%				8%						78%				
Chloralkali production (membrane cell process)	6%				1%						6%				
Chloralkali production (mercury cell process)	16%				2%						16%				
Coal furnace												100%			
Coal production		100%													
Coal-fired power plant				57%											
Diesel engine						100%									
Diesel fuel production			100%												
Gas-fired power plant				9%											
Hydroelectric plant				11%											
Industrial gas furnace													100%		
Methane reforming					90%										
Natural gas production							100%								
Nuclear power plant				20%											
Oil furnace														100%	
Oil production								100%							
Oil-fired power plant				3%											
Railroad transport									100%						
Utility gas furnace															100%

The second set of data needed is price information, organized in a product price vector (**p**). Prices are used to carry out throughput allocations of multiproduct processes on the basis of value. The reason for doing this is that product values (masses × price) are more representative of the driving force for the continuing operation of a process than product masses [18]. Some analysts prefer to carry out allocations on the basis of mass. This can easily be done in the PIO-LCA method by simply setting the same price per unit mass for all the products.

The only prices needed are the prices of products produced in multiproduct processes, since prices for products produced in single product processes do not affect the calculations. This is the reason why some of the entries in vector **p** shown in Table 7-4 have the default value 999 (any nonzero value can be used; the reason a nonzero value is needed is to prevent division by zero in eq (7-3) below).

Prices are used together with the make matrix in the first allocation accounting rule to build an “allocation matrix” (**G**). The entries in **G** are given by:

$$G_{ji} = \begin{cases} \frac{P_i}{\sum_{i'} C_{i'j} P_{i'}} & \forall C_{ij} \neq 0 \\ 0 & \forall C_{ij} = 0 \end{cases} \quad (7-3)$$

where the subscripts i and i' correspond to the product and the subscript j to the process.

Table 7-4: Price and demand vectors for the chlorine LCA example

PRODUCT	p = price vector	d = demand vector
Chlorine	0.21 \$/kg	1000 kg
Coal	999 \$/kg	0 kg
Diesel fuel	999 \$/kg	0 kg
Electricity	999 \$/MJ	0 MJ
Hydrogen	0.8 \$/kg	0 kg
Mechanical energy from diesel engines	999 \$/MJ	0 MJ
Natural gas	999 \$/kg	0 kg
Oil	999 \$/kg	0 kg
Railroad transport	999 \$/kg-km	0 kg-km
Salt from brine	999 \$/kg	0 kg
Sodium hydroxide	0.24 \$/kg	0 kg
Thermal energy from coal furnace	999 \$/MJ	0 MJ
Thermal energy from industrial gas furnace	999 \$/MJ	0 MJ
Thermal energy from oil furnace	999 \$/MJ	0 MJ
Thermal energy from utility gas furnace	999 \$/MJ	0 MJ

Note: The value 999 is used as a default value in the price vector when the price information is not needed (i.e. when the product is not made in multiproduct processes)

The value G_{ji} gives the amount of throughput of process j (as defined by the corresponding column in matrix \mathbf{C} – one unit of throughput makes the amounts of products shown in that column) that is attributable to one unit of the product i made in that process. Note that for single product processes the entry G_{ji} is given by $1/C_{ij}$. The allocation matrix for the example is given in Table 7-5. Note that in addition to allocating process throughputs to the individual products made in a multiproduct process, the allocation matrix also carries out basis conversions. Consider the power generation processes. The basis for these processes is that a unit of throughput generates 3.6 MJ of electricity. It follows that a product demand of 1 MJ of electricity from a power generation process would require a throughput of $1 \text{ MJ} \div 3.6 \text{ MJ} = 0.278$ power generation throughput units.

Table 7-5: Allocation matrix for the chlorine LCA example

	Chlorine (per kg)	Coal (per kg)	Diesel fuel (per kg)	Electricity (per MJ)	Hydrogen (per kg)	Mechanical energy from diesel engines (per MJ)	Natural gas (per kg)	Oil (per kg)	Railroad transport (per kg-km)	Salt from brine (per kg)	Sodium hydroxide (per kg)	Thermal energy from coal furnace (per MJ)	Thermal energy from industrial gas furnace (per MJ)	Thermal energy from oil furnace (per MJ)	Thermal energy from utility gas furnace (per MJ)
G = [Allocation matrix]															
Brine pumping										1					
Chloralkali production (diaphragm cell process)	0.419				1.596						0.479				
Chloralkali production (membrane cell process)	0.419				1.596						0.479				
Chloralkali production (mercury cell process)	0.419				1.596						0.479				
Coal furnace												0.034			
Coal production		1													
Coal-fired power plant				0.278											
Diesel engine						1									
Diesel fuel production			1												
Gas-fired power plant				0.278											
Hydroelectric plant				0.278											
Industrial gas furnace													9E-04		
Methane reforming					1										
Natural gas production							1								
Nuclear power plant				0.278											
Oil furnace														9E-04	
Oil production								1							
Oil-fired power plant				0.278											
Railroad transport									0.001						
Utility gas furnace															9E-04

The second allocation rule distributes the demand for a product among the different processes that produce it on the basis of market share. The allocation matrix is combined with the market share matrix to give a *process-by-product* throughput matrix (**D**), where each element of **D** is given by:

$$D_{ji} = F_{ji} \cdot G_{ji} \tag{7-4}$$

The entry D_{ji} gives the amount of throughput of process j that is attributable to the demand for one unit of product i at the current prices and prevailing process supply mix. Table 7-6 gives matrix **D** for the chlorine production example. Column 4 shows that a demand of 1 MJ of electricity is being charged with 0.159 units of throughput from the coal-fired plant process, 0.007 oil-fired plant throughput units, 0.025 gas-fired plant throughput units, 0.056 nuclear plant throughput units, and 0.030 hydroelectric plant throughput units. Since each throughput unit from a power plant has been defined to generate 3.6 MJ of electricity, it can easily be checked that together the throughputs from the 5 processes listed above do indeed generate 1.00 MJ of electricity.

Table 7-6: Process by product throughput matrix for the chlorine LCA example

$$D_{ji} = F_{ji} G_{ji}$$

	Chlorine (per kg)	Coal (per kg)	Diesel fuel (per kg)	Electricity (per MJ)	Hydrogen (per kg)	Mechanical energy from diesel engines (per MJ)	Natural gas (per kg)	Oil (per kg)	Railroad transport (per kg-km)	Salt from brine (per kg)	Sodium hydroxide (per kg)	Thermal energy from coal furnace (per MJ)	Thermal energy from industrial gas furnace (per MJ)	Thermal energy from oil furnace (per MJ)	Thermal energy from utility gas furnace (per MJ)
D = Process by product throughput matrix															
Brine pumping	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0
Chloralkali production (diaphragm cell process)	0.327	0	0	0	0.125	0	0	0	0	0	0.374	0	0	0	0
Chloralkali production (membrane cell process)	0.025	0	0	0	0.01	0	0	0	0	0	0.029	0	0	0	0
Chloralkali production (mercury cell process)	0.067	0	0	0	0.026	0	0	0	0	0	0.077	0	0	0	0
Coal furnace	0	0	0	0	0	0	0	0	0	0	0.034	0	0	0	0
Coal production	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
Coal-fired power plant	0	0	0	0.159	0	0	0	0	0	0	0	0	0	0	0
Diesel engine	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
Diesel fuel production	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
Gas-fired power plant	0	0	0	0.025	0	0	0	0	0	0	0	0	0	0	0
Hydroelectric plant	0	0	0	0.03	0	0	0	0	0	0	0	0	0	0	0
Industrial gas furnace	0	0	0	0	0	0	0	0	0	0	0	9E-04	0	0	0
Methane reforming	0	0	0	0	0.9	0	0	0	0	0	0	0	0	0	0
Natural gas production	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
Nuclear power plant	0	0	0	0.056	0	0	0	0	0	0	0	0	0	0	0
Oil furnace	0	0	0	0	0	0	0	0	0	0	0	0	9E-04	0	0
Oil production	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
Oil-fired power plant	0	0	0	0.007	0	0	0	0	0	0	0	0	0	0	0
Railroad transport	0	0	0	0	0	0	0	0	0.001	0	0	0	0	0	0
Utility gas furnace	0	0	0	0	0	0	0	0	0	0	0	0	0	0	9E-04

Summarizing, the data required to generate life-cycle environmental intervention inventories using the PIO-LCA method consists of technical descriptions of each process (in the corresponding columns of **B**, **C**, and **E**), and statistical/economic information regarding prices and market shares in the vector **p** and the matrix **F**. The relationship between the matrices **B**, **C**, and **E** and the process-product diagram is shown in Figure 7-4, using the mercury cell process as an example.

7.3.2 The inventory analysis stage of PIO-LCA

Once the data has been organized as described in the previous section, it is very easy to obtain life-cycle environmental exchanges associated with any vector of product output demands **d**, following standard input-output analysis techniques.

The vector of direct product production requirements arising from the demand vector **d** is given by

$$q_{direct} = (I + BD)d \tag{7-5}$$

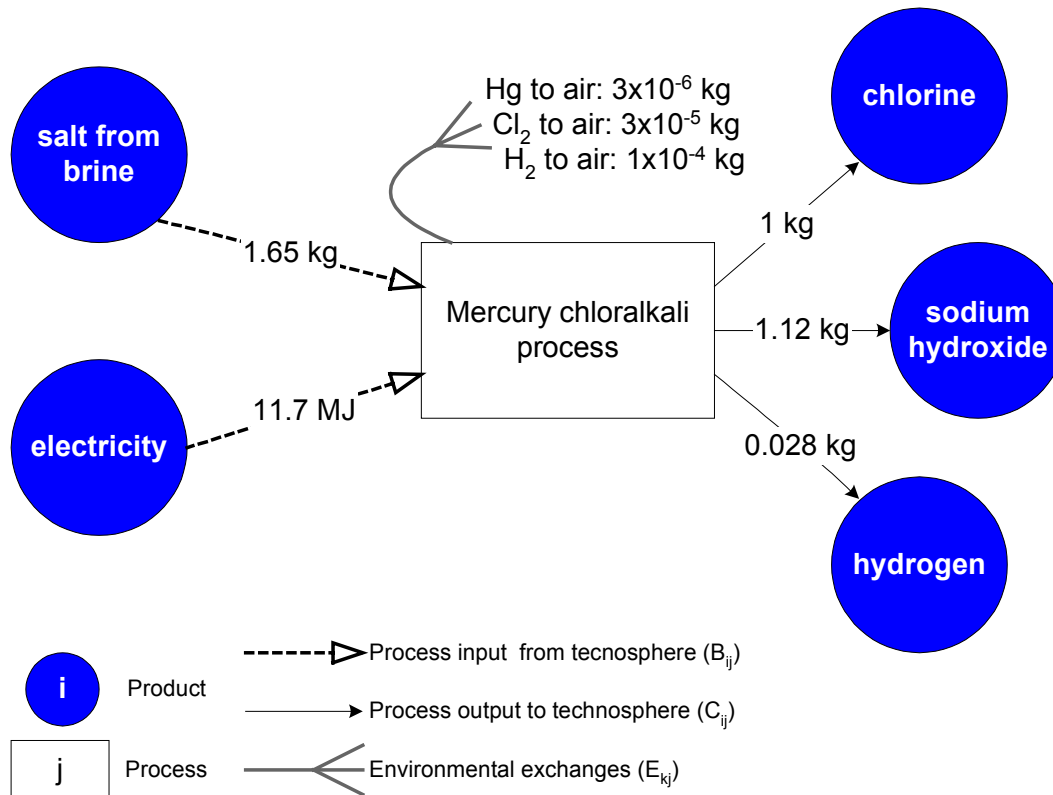


Figure 7-4: Correspondence between product-process flow diagrams and input-output matrices

where \mathbf{I} is the identity matrix, and the matrix product $\mathbf{BD} = \mathbf{A}_{\text{prod}}$ is the *product-by-product* direct requirements matrix. Table 7-7 shows matrix \mathbf{A}_{prod} for the example. Column 4 shows that the production of 1 MJ of electricity requires the provision of 1.631 MJ of thermal energy from coal-fired furnaces, 0.068 MJ from oil-fired furnaces, and 0.259 MJ from gas-fired utility furnaces. Column 1 shows that the production of 1 kg of chlorine is being charged with the production of 0.7 kg of salt and the generation of 4.6 MJ of electricity. These requirements are much lower than the requirements shown in the use matrix, which states that to produce 1 kg of chlorine, 1.85 kg of salt and between 10.8 and 11.7 MJ of electricity are required, depending on the process. The reason is that these processes also produce 1.12 kg of sodium hydroxide and 0.028 kg of hydrogen per kg of chlorine produced, and matrix \mathbf{A}_{prod} allocates the input requirements among all three of the chlor-alkali process outputs. Multiplying column 1 by 1 kg, column 11 by 1.12 kg, column 5 by 0.028 kg, and then adding the three vectors obtained, yields the actual amounts of physical inputs required.

Table 7-7: Product-by-product direct requirements matrix for the chlorine LCA example

$A_{prod} = BD$	Chlorine (per kg)	Coal (per kg)	Diesel fuel (per kg)	Electricity (per MJ)	Hydrogen (per kg)	Mechanical energy from diesel engines (per MJ)	Natural gas (per kg)	Oil (per kg)	Railroad transport (per kg-km)	Salt from brine (per kg)	Sodium hydroxide (per kg)	Thermal energy from coal furnace (per MJ)	Thermal energy from industrial gas furnace (per MJ)	Thermal energy from oil furnace (per MJ)	Thermal energy from utility gas furnace (per MJ)	
Chlorine (kg)																
Coal (kg)												0.034				
Diesel fuel (kg)						0.024										
Electricity (MJ)	4.591	0.052	0.144		3.009		0.124	0.142		0.36	5.246					
Hydrogen (kg)																
Mechanical energy from diesel engines (MJ)		2.53							3E-04							
Natural gas (kg)					1.8									0.018	0.018	
Oil (kg)			1												0.022	
Railroad transport (kg-km)												15.8				
Salt from brine (kg)	0.691				0.263						0.79					
Sodium hydroxide (kg)																
Thermal energy from coal furnace (MJ)		0.01	1.631													
Thermal energy from industrial gas furnace (MJ)	2.975	1.839	29.84		1.271	0.53					3.4					
Thermal energy from oil furnace (MJ)		0.545	0.068		0.027	0.064										
Thermal energy from utility gas furnace (MJ)			0.259													

The vector of total product requirements (including direct and indirect product requirements) is given by

$$q = (I + A_{prod} + A_{prod} A_{prod} + A_{prod} A_{prod} A_{prod} + \dots)d = (I - A_{prod})^{-1} d \tag{7-6}$$

where the matrix $(I - A_{prod})^{-1}$ is the *product-by-product* total requirements matrix. The terms in the sum can be interpreted as follows: Id is simply the amount of products demanded; $A_{prod}d$ gives the amounts of products (raw materials) used directly in the production of the products demanded; $A_{prod}A_{prod}d$ gives the amount of products required to produce the raw materials used by processes that manufacture the products demanded, etc. This principle has been applied before to process-based life cycle analysis. Boustead [19] suggests that the analyst should iterate on the calculation of requirements until no noticeable change is detected. This is in fact the calculation procedure given by the series $Id + A_{prod}d + A_{prod} A_{prod}d + A_{prod} A_{prod} A_{prod}d + \dots$

The product-by-product total requirements matrix for the example is given in Table 7-8. Note that now chlorine production (column 1) requires the production of coal, oil, diesel, and natural gas, as well as the supply of transportation services. The diagonal elements of matrix A_{prod} give an indication of the importance of feedback loops. Products for which the diagonal element has a value of 1 do not participate in feedback loops. Products that are part of feedback

loops have a diagonal value higher than 1. For example, the diagonal element for natural gas has a value of 1.025 in Table 7-8. This means that 0.025 kg of natural gas are consumed directly or indirectly by the processes needed to produce 1 kg of natural gas. The corresponding vectors of direct and total product requirements associated with the production of 1000 kg of chlorine are shown in Table 7-9.

Table 7-8: Product-by-product total requirements matrix for the chlorine LCA example

$(I - A_{prod})^{-1}$	Product by product total requirements matrix															
	Chlorine (per kg)	Coal (per kg)	Diesel fuel (per kg)	Electricity (per MJ)	Hydrogen (per kg)	Mechanical energy from diesel engines (per MJ)	Natural gas (per kg)	Oil (per kg)	Railroad transport (per kg-km)	Salt from brine (per kg)	Sodium hydroxide (per kg)	Thermal energy from coal furnace (per MJ)	Thermal energy from industrial gas furnace (per MJ)	Thermal energy from oil furnace (per MJ)	Thermal energy from utility gas furnace (per MJ)	
Chlorine (kg)	1															
Coal (kg)	0.269	1.004	0.016	0.055	0.189	4E-04	0.007	0.008	1E-07	0.02	0.307	0.034	1E-04	2E-04	1E-04	
Diesel fuel (kg)	0.017	0.061	1.001	0.004	0.012	0.024	4E-04	5E-04	6E-06	0.001	0.02	0.002	8E-06	1E-05	8E-06	
Electricity (MJ)	4.869	0.07	0.295	1.005	3.419	0.007	0.128	0.144	2E-06	0.362	5.565	0.002	0.002	0.003	0.002	
Hydrogen (kg)					1											
Mechanical energy from diesel engines (MJ)	0.714	2.541	0.043	0.147	0.501	1.001	0.019	0.021	3E-04	0.053	0.816	0.09	3E-04	5E-04	3E-04	
Natural gas (kg)	0.081	0.003	0.046	0.005	2.426	0.001	1.025	0.011	3E-07	0.002	0.093	1E-04	0.019	2E-04	0.019	
Oil (kg)	0.025	0.062	1.015	0.005	0.019	0.024	0.001	1.002	7E-06	0.002	0.028	0.002	2E-05	0.022	2E-05	
Railroad transport (kg-km)	125.5	1.967	7.603	25.91	88.14	0.182	3.292	3.716	1	9.326	143.5	15.87	0.061	0.082	0.061	
Salt from brine (kg)	0.691				0.263					1	0.79					
Sodium hydroxide (kg)											1					
Thermal energy from coal furnace (MJ)	7.946	0.125	0.481	1.64	5.579	0.012	0.208	0.235	3E-06	0.59	9.081	1.004	0.004	0.005	0.004	
Thermal energy from industrial gas furnace (MJ)	3.123	0.149	2.438	0.016	32.96	0.059	1.304	0.546	2E-05	0.006	3.569	0.005	1.024	0.012	0.024	
Thermal energy from oil furnace (MJ)	0.342	0.042	0.632	0.07	0.304	0.015	0.037	0.074	4E-06	0.025	0.391	0.001	7E-04	1.002	7E-04	
Thermal energy from utility gas furnace (MJ)	1.262	0.018	0.076	0.26	0.886	0.002	0.033	0.037	5E-07	0.094	1.442	6E-04	6E-04	8E-04	1.001	

As described in the previous section, environmental exchanges are associated with process throughputs rather than with products. The total product requirement vector can be translated into a total process throughput requirements vector by pre-multiplying with matrix **D**:

$$x = Dq = D(I - A_{prod})^{-1} d \tag{7-7}$$

The matrix $D(I - A_{prod})^{-1}$ is the *process-by-product* total requirements matrix. A direct process throughput requirements vector x_{direct} can be obtained by pre-multiplying the demand vector **d** by matrix **D**. The direct throughput requirements vectors gives the amount of process activity directly associated with the provision of the products specified in the demand vector. The total throughput requirements vectors gives the amount of process activity associated with the provision not only of the products specified in the demand vector, but also with the provision of all the necessary raw materials. The vectors of direct and indirect process throughput

requirements for the example are shown in Table 7-10. The vector $\mathbf{x}_{\text{direct}}$ has nonzero entries only for those processes whose outputs include products in the demand vector \mathbf{d} , while the vector \mathbf{x} has nonzero entries for all the processes needed to produce the products in vector \mathbf{d} , including those processes that supply raw materials. Vectors of throughput requirements need to be read side by side with matrix \mathbf{C} (e.g. Table 7-1), since matrix \mathbf{C} gives the definition a unit of throughput for each process.

Table 7-9: Vectors of product requirements and equivalent production requirements for the chlorine LCA example

	$\mathbf{q}_{\text{direct}} =$ direct product requirements vector	$\mathbf{q} =$ total product requirements vector	$\mathbf{C}\mathbf{x}_{\text{direct}} =$ equivalent direct production vector	$\mathbf{C}\mathbf{x} =$ equivalent total production vector
Chlorine (kg)	1000	1000	419	419
Coal (kg)		269		269
Diesel fuel (kg)		17		17
Electricity (MJ)	4591	4869		4865
Hydrogen (kg)			12	12
Mechanical energy from diesel engines (MJ)		714		714
Natural gas (kg)		81		81
Oil (kg)		25		25
Railroad transport (kg-km)		125546		125546
Salt from brine (kg)	691	691		691
Sodium hydroxide (kg)			469	469
Thermal energy from coal furnace (MJ)		7946		7946
Thermal energy from industrial gas furnace (MJ)	2975	3123		3123
Thermal energy from oil furnace (MJ)		342		342
Thermal energy from utility gas furnace (MJ)		1262		1262

Further insight into the role of allocation is obtained by pre-multiplying the throughput requirements vectors by matrix \mathbf{C} (as shown in the last two columns of Table 7-9). If there were no multiproduct processes in the model, or if products were demanded in the same proportion in which they are produced in multiproduct processes, then $\mathbf{C}\mathbf{x}_{\text{direct}}$ would be equal to the demand vector \mathbf{d} . In the example, vector \mathbf{d} has a single entry, namely the demand for 1000 kg chlorine. The process throughputs in vector $\mathbf{x}_{\text{direct}}$ result in the production of 419 kg chlorine, 469 kg sodium hydroxide, and 12 kg of hydrogen. This can be interpreted as follows: at the market prices used in the example, the demand for 1000 kg of chlorine is considered equivalent (in terms of its contribution to the generation of environmental impacts) to the demand for 419 kg Cl_2 , 469 kg NaOH , and 12 kg H_2 . Note that at the product prices given in Table 7-4, 1000 kg of

chlorine would be valued at \$210, which is the same as the combined value of the products listed in vector Cx_{direct} .

Table 7-10: Throughput requirements vectors for the chlorine LCA example

	$x_{direct} = Dd =$ vector of direct process throughput requirements	$x = Dq =$ vector of total process throughput requirements	
Brine pumping		691	$Dia(x)$
Chloralkali production (diaphragm cell process)	327	327	
Chloralkali production (membrane cell process)	25	25	
Chloralkali production (mercury cell process)	67	67	
Coal furnace		269	
Coal production		269	
Coal-fired power plant		775	
Diesel engine		714	
Diesel fuel production		17	
Gas-fired power plant		123	
Hydroelectric plant		147	
Industrial gas furnace		3	
Methane reforming			
Natural gas production		81	
Nuclear power plant		272	
Oil furnace		0.3	
Oil production		25	
Oil-fired power plant		34	
Railroad transport		126	
Utility gas furnace		1.2	

Once the total process throughput vector has been obtained, the vector of life cycle environmental exchanges can be computed using the environmental intervention matrix:

$$e = Ex = ED(I - A_{prod})^{-1} d \tag{7-8}$$

Table 7-11 shows the environmental exchanges inventory obtained for the chlorine production example. The vector e shown in Table 7-11 is similar in structure to emission inventories for chlorine published in emission inventory databases. Presented in this form, the inventory does not provide the user with information about which processes contribute to the resulting emissions.

Table 7-11: Life cycle environmental exchanges inventory and matrices of process contributions to the inventory for the chlorine LCA example

$e = Ex$ life cycle environmental exchanges inventory vector	E Dia(x) = iDirect Process Contributions																			
	Brine pumping	Chloralkali production (diaphragm cell process)	Chloralkali production (membrane cell process)	Chloralkali production (mercury cell process)	Coal furnace	Coal production	Coal-fired power plant	Diesel engine	Diesel fuel production	Gas-fired power plant	Hydroelectric plant	Industrial gas furnace	Methane reforming	Natural gas production	Nuclear power plant	Oil furnace	Oil production	Oil-fired power plant	Railroad transport	Utility gas furnace
Air: 2,3,7,8-Tetrachlorodibenzo-p-dioxin (kg)	3.50E-09				3E-09										4E-12					
Air: Ammonia (kg)	3.77E-04	3E-04	2E-05	6E-05																
Air: Arsenic (kg)	5.19E-05				5E-05							3E-07			1E-06					1E-07
Air: Asbestos (kg)	5.03E-07		5E-07																	
Air: Barium (kg)	4.65E-05	3E-05	3E-06	7E-06								3E-06			3E-09					1E-06
Air: Cadmium (kg)	6.63E-06				6E-06										5E-07					
Air: Carbon dioxide (kg)	1.05E+03				725.5		54.24					161		17.02	0.016	28.57				65.05
Air: Carbon monoxide (kg)	9.07E-01				0.618		0.214					0.047			0.006					0.022
Air: Carbon tetrachloride (kg)	2.09E-03	0.002	1E-04	3E-04																
Air: Chlorine (kg)	1.68E+00	1.307	0.101	0.268																
Air: Cobalt (kg)	1.91E-05				1E-05							2E-07			7E-06					6E-08
Air: Cyanide (kg)	3.04E-04				3E-04															
Air: Dichlorodifluoromethane (kg)	2.51E-03	0.002	2E-04	4E-04																
Air: Hydrazine (kg)	1.26E-06	1E-06	8E-08	2E-07																
Air: Hydrochloric acid (kg)	1.48E-01	3E-05	3E-06	7E-06	0.148									0.022	4E-05					
Air: Hydrogen sulfide (kg)	2.19E-02																			
Air: Isophorone (kg)	6.99E-05				7E-05															
Air: Lead (kg)	5.33E-05				5E-05							4E-07			2E-06					1E-07
Air: Mercury (kg)	2.78E-04			3E-04	1E-05										1E-07					
Air: Methane (kg)	2.04E+00				0.007							0.004	2.026		3E-04					2E-04
Air: Nickel (kg)	1.39E-04				3E-05							5E-06			1E-04					2E-06
Air: NOx (as NO2) (kg)	2.98E+00				1.344		0.928					0.187		0.449	0.045					0.029
Air: PM10 (kg)	2.09E+00				2.069							0.009			0.014					0.001
Air: Sulfur dioxide (kg)	5.08E+00				4.622		0.1					9E-04		0.163	0.195					3E-04
Air: Sulfuric acid (kg)	1.68E-05	1E-05	1E-06	3E-06																
Air: Total Suspended Particles (kg)	1.20E-01						0.071							0.049						
Water: Barium (kg)	8.38E-05	7E-05	5E-06	1E-05																
Water: Chlorine (kg)	4.19E-04	3E-04	3E-05	7E-05																
Water: Hydrochloric acid (kg)	1.26E-04	1E-04	8E-06	2E-05																
Water: Mercury (kg)	6.70E-06			7E-06																
Water: Sulfuric acid (kg)	7.00E-01	7E-07	5E-08	1E-07		0.698		6E-04	0.001						3E-04		4E-04			

$E(i-DBI)^{-1}x = i$ Total (direct + indirect) process contributions																																																																																																																																																																																																																																																																																																																																																																																							
	2E-10	3E-09	2E-10	6E-10	4E-09	1E-11	4E-09	4E-12	4E-12	2E-12	5E-12	7E-12	4E-12	3E-12	4E-12	2E-13	2E-12	3E-21	3E-04	2E-05	6E-05	4E-23	4E-20	3E-23	1E-23	3E-06	4E-05	3E-06	9E-06	5E-05	3E-07	5E-05	1E-07	1E-07	2E-07	4E-07	1E-07	9E-25	8E-25	9E-25	7E-08	4E-05	3E-06	7E-06	5E-08	5E-08	4E-08	1E-06	3E-07	5E-06	4E-07	1E-06	6E-06	4E-08	6E-06	2E-08	2E-08	5E-09	1E-08	2E-08	5E-07	7E-09	4E-07	1E-09	5E-09	45.31	846.4	55.01	150.1	786.7	58.39	786.4	58.34	4.1	72.22	178.8	24.93	0.016	29.03	1.52	27.92	2.761	72.22	0.044	0.708	0.052	0.146	0.837	0.208	0.836	0.216	0.002	0.023	0.05	0.003	0.006	9E-04	0.006	0.01	0.023	2E-20	0.002	1E-04	3E-04	2E-22	2E-19	2E-22	7E-23	1E-17	1.307	0.101	0.268	2E-19	2E-16	2E-19	5E-20	1E-17	1.307	0.101	0.268	2E-19	2E-16	2E-19	5E-20	1E-06	1E-05	1E-06	3E-06	1E-05	3E-07	1E-05	2E-07	2E-07	9E-08	2E-07	9E-08	7E-06	5E-08	7E-06	1E-08	9E-08	2E-05	2E-04	2E-05	5E-05	3E-04	1E-06	3E-04	3E-07	3E-07	2E-07	5E-07	6E-07	7E-08	2E-07	7E-08	1E-08	2E-07	2E-23	9E-24	1E-06	8E-08	2E-07	1E-25	1E-22	1E-25	4E-26	9E-27	0.008	0.114	0.009	0.025	0.148	6E-04	0.148	2E-04	2E-04	9E-05	2E-04	3E-04	0.02	6E-04	0.001	2E-04	2E-04	2E-04	2E-04	0.006	4E-06	5E-05	4E-06	1E-05	7E-05	3E-07	7E-05	7E-08	7E-08	4E-08	1E-07	1E-07	1E-07	2E-06	5E-08	1E-08	1E-08	3E-09	4E-08	3E-06	4E-05	3E-06	9E-06	5E-05	3E-07	5E-05	1E-07	1E-07	2E-07	5E-07	2E-08	2E-08	1E-07	8E-09	1E-07	7E-10	7E-09	0.032	1.878	0.054	0.106	0.029	0.021	0.029	0.02	0.02	0.598	1.483	2.076	0.002	0.007	0.002	9E-04	0.598	7E-06	1E-04	6E-07	9E-05	2E-07	2E-06	0.144	2.335	0.17	4.476	2.287	0.899	2.286	0.935	0.007	0.032	0.196	0.013	0.449	0.046	0.003	0.045	0.044	0.032	0.107	1.614	0.126	0.355	2.079	0.009	2.078	0.003	0.003	0.003	0.012	0.005	0.005	0.015	0.002	0.014	1E-04	0.003	0.261	3.911	0.306	0.864	4.749	0.122	4.748	0.111	0.011	0.004	0.01	0.012	0.163	0.196	0.005	0.188	0.005	0.004	1E-22	1E-05	1E-06	3E-06	2E-24	2E-21	2E-24	5E-25	1E-25	0.006	0.093	0.007	0.02	0.072	0.068	0.072	0.071	1E-04	7E-05	2E-04	3E-04	0.049	3E-05	9E-05	3E-05	0.003	7E-05	6E-22	7E-05	5E-06	1E-05	8E-24	9E-21	8E-24	3E-24	3E-21	3E-04	3E-05	7E-05	4E-23	4E-20	4E-23	1E-23	3E-24	9E-22	1E-04	8E-06	2E-05	1E-23	1E-20	1E-23	4E-24	9E-25	4E-22	7E-06	2E-23	1E-20	0.036	0.539	0.042	0.119	0.003	0.003	0.7	8E-04	8E-04	0.001	0.003	0.002	5E-04	5E-04	8E-04	4E-05

Two auxiliary matrices are helpful for understanding the sources of the total exchanges contained in vector e . A matrix of direct process contributions to the environmental exchanges inventory vector is generated by multiplying matrix E by the diagonal matrix $Diag(x)$ obtained by constructing a square matrix with zero entries in all of its off-diagonal elements and with each diagonal entry set equal to the corresponding entry in vector x . The $Diag(x)$ matrix for the

example is shown next to vector \mathbf{x} in Table 7-10. The $\mathbf{E Diag(x)}$ matrix decomposes the life cycle emissions inventory into the contributions to the inventory made by each process. This matrix is useful for tracing the environmental exchanges back to processes that generated them. For example, the $\mathbf{E Diag(x)}$ matrix in Table 7-11 shows that 725 kg out of the 1050 kg of carbon dioxide emissions attributed to the provision of 1000 kg of chlorine take place in coal furnaces. Note that the columns of matrix $\mathbf{E Diag(x)}$ can be added back to obtain vector \mathbf{e} .

The second matrix useful for interpretation gives the direct and indirect process contributions to the environmental exchanges vector. This matrix is given by the formula

$$\mathbf{E(I-DB)^{-1} Diag(x)} \quad (7-9)$$

where the matrix $(\mathbf{I-DB})^{-1}$ is the *process-by-process* total requirements matrix. This matrix shows not only the environmental exchanges resulting directly from operating each process to the extent required to supply the products in vector \mathbf{d} , but also the exchanges generated in the operation of all the processes needed to supply inputs to the process in each column. The bottom half of Table 7-11 shows that when indirect exchanges are included, the contribution of the coal-fired power plants to the carbon dioxide emissions inventory rises from 725 kg (direct emissions) to 787 kg (which includes the direct emissions plus all of the indirect emissions associated with the production and delivery of the fuel used by the power plants). Note that, in contrast with the case of the $\mathbf{E Diag(x)}$ matrix, the columns of $\mathbf{E(I-DB)^{-1} Diag(x)}$ can not be added to generate the environmental exchanges inventory⁷⁰.

This section has shown how life-cycle emission inventories can be generated as needed based on direct process emissions data. This provides a more transparent way to store and update emissions inventory data. It also provides a transparent mechanism to trace environmental exchanges back to the processes that generate them, which is very valuable for data quality control. As better information is obtained for any of the processes in the system, the matrix multiplication's would take care of updating the life-cycle inventories associated with any of the products in the system.

⁷⁰ For example, adding carbon dioxide emissions over all the columns yields 3200 kg. The reason for the discrepancy is that emissions taking place in one process are reported under many different processes (they are reported in the originating process plus all the downstream processes that use its outputs).

7.3.3 The impact analysis stage of PIO-LCA

It is common practice in life-cycle assessment to assume linear models at the impact assessment stage. This does not mean necessarily that environmental impacts are assumed to increase linearly with environmental exchanges over the whole range of possible exchanges (from zero to the world-wide level of exchanges), but rather that the contributions due to the process or product of interest to the designer are small enough compared to the total world output that the marginal increase in environmental impacts can be considered linear. Impact assessment usually proceeds in two steps. In the first step, environmental indices for individual impact categories are computed by multiplying each environmental intervention by a potency factor and adding the results within each impact category⁷¹. For example, to evaluate the contribution of a vector of emissions to the greenhouse effect impact category, the amounts of each substance emitted are multiplied by their global warming potentials (GWP) relative to that of CO₂.

A potency factor matrix \mathbf{H} can be defined so that each entry H_{kl} corresponds to the potency factor (or characterization or equivalency factor, as they are also known) for intervention k in terms of the unit of measure for impact category l . Table 7-12 shows the \mathbf{H} matrix used in the example. Sources for the characterization factors used are given in Table 3-16. Human toxicity potentials were calculated using the models described in section 6.3. As seen in Table 7-12, potency factors within any impact category might vary over many orders of magnitude.

The vector of impact category environmental indicators $\boldsymbol{\psi}$ is obtained by multiplying the transpose of matrix \mathbf{H} with the life-cycle inventory \mathbf{e} :

$$\boldsymbol{\psi} = \mathbf{H}^T \mathbf{e} = \mathbf{H}^T \mathbf{E} \mathbf{x} = \mathbf{H}^T \mathbf{E} \mathbf{D} (\mathbf{I} - \mathbf{A}_{\text{prod}})^{-1} \mathbf{d} \quad (7-10)$$

The vector has an entry for each environmental impact category.

The second step in the impact assessment stage is the evaluation step, where the individual impact category indicators are aggregated into an overall index of environmental impact Ω , by using weighting factors based on the preferences of the organization for which the analysis is being conducted. A vector of valuation factors \mathbf{w} can be defined, where each element w_k is the weight given to impact category k . Social cost based on willingness to pay was chosen here as an indicator, but any other valuation method (e.g. eco-points) can be used. The vector of

⁷¹ See section 3.3 for further discussion on environmental valuation methods.

valuation factors used in the example is also shown at the bottom of Table 7-12⁷². There is no unique correct value for these valuation factors, since they depend on the willingness of the decision-maker to make tradeoffs between different impact categories. The valuation factors are appropriate if they are consistent with the choices an organization is willing to make for setting priorities among environmental problems.

Table 7-12: Characterization and valuation factors used in the chlorine LCA example

EXCHANGE TYPE	ENVIRONMENTAL EXCHANGE	UNITS	ENVIRONMENTAL IMPACT CATEGORY							
			Global warming potential (100 year horizon) kg CO2 equivalent/kg	Ozone depletion potential kg CFC-11 equivalent/kg	Human toxicity potential (cancer) DALYs/kg	Human toxicity potential (noncancer) DALYs/kg	Respiratory effects kg PM10 equivalent/kg	Photo-chemical oxidants creation potential kg Ethylene equivalent/kg	Acidification potential kg SO2 equivalent/kg	Eutrophication potential kg NO2 to air equivalent/kg
H = [Characterization factor matrix]										
Air	2,3,7,8-Tetrachlorodibenzo-p-dioxin	kg			1.83E+03	1.22E+02				
Air	Ammonia	kg	-1.66E+01			1.31E-08		1.03E-01		
Air	Arsenic	kg			3.70E-02	8.55E-04			1.88E+00	2.71E+00
Air	Asbestos	kg			1.09E-03					
Air	Barium	kg				2.95E-05				
Air	Cadmium	kg			1.48E-01	6.34E-04				
Air	Carbon dioxide	kg	1.00E+00							
Air	Carbon monoxide	kg	3.00E+00			5.90E-08			1.80E-02	
Air	Carbon tetrachloride	kg	-1.52E+03	1.11E+00	1.45E-02	2.43E-04				
Air	Chlorine	kg				2.79E-07				
Air	Cobalt	kg			2.37E-02	5.45E-04				
Air	Cyanide	kg				4.21E-04				
Air	Dichlorodifluoromethane	kg	6.66E+03	9.80E-01		4.74E-07				
Air	Hydrazine	kg			5.22E-03	1.26E-05				
Air	Hydrochloric acid	kg	-1.53E+01			1.90E-07	9.50E-02		8.80E-01	
Air	Hydrogen sulfide	kg	-3.47E+01			2.78E-06	2.31E-01		1.88E+00	
Air	Isophorone	kg			2.29E-09	4.57E-11				
Air	Lead	kg			3.79E-03	9.28E-04				
Air	Mercury	kg				1.11E-01				
Air	Methane	kg	2.10E+01					6.00E-03		
Air	Nickel	kg			3.14E-02	2.43E-05				
Air	NOx (as NO2)	kg	4.00E+01			3.49E-06	7.63E-02	1.17E-01	7.00E-01	1.00E+00
Air	PM10	kg	-8.30E+00				1.00E+00			
Air	Sulfur dioxide	kg	-2.33E+01			4.21E-09	1.54E-01	4.80E-02	1.00E+00	
Air	Sulfuric acid	kg	-1.52E+01		1.45E-06	3.39E-07	1.00E-01		6.50E-01	
Air	Total Suspended Particles	kg	-8.30E+00				1.00E+00			
Water	Barium	kg				2.62E-05				
Water	Chlorine	kg				1.74E-06				
Water	Hydrochloric acid	kg				3.75E-08				
Water	Mercury	kg				8.74E-02				
Water	Sulfuric acid	kg			3.03E-13	1.37E-12				
Valuation factor	\$		3.00E-02	1.00E+02	85000	85000	40	2	0.8	0.8

If a vector w is available, the overall indicator can be calculated by:

$$\Omega = w^T \psi = w^T H^T e = w^T H^T E x = w^T H^T E D (I - A_{prod})^{-1} d \tag{7-11}$$

⁷² See section 3.3 for a discussion of valuation factors.

It is useful to have information about the contributions of each process or environmental intervention to the impact category and overall indicator scores. This aids the designer in understanding the sources of impacts and in setting priorities for checking the quality of the input data. The following matrix operations can be used to obtain such information (see Table 7-13 and Table 7-14 for results from the illustrative example):

- Diag(e) H: Matrix of contributions of environmental exchanges to impact category scores.
- Diag(e)H Diag(w): Matrix of contributions of environmental exchanges and impact categories to overall valuation.
- Diag(e)Hw: Vector of contributions of environmental exchanges to overall valuation.
- Diag(x) E^TH: Matrix of contributions of process throughputs to impact category scores.
- Diag(x) E^TH Diag(w): Matrix of contributions of process throughputs and impact categories to overall valuation.
- Diag(x) E^THw: Vector of contributions of process throughputs to overall valuation.
- Diag(w) H^TEx = Diag(w) H^Te: Vector of contributions of impact category scores to overall scores.
- $\psi = H^T e = H^T Ex$: Vector of impact category scores.
- $\Omega = w^T H^T e = w^T H^T Ex$: Overall valuation (scalar).

Table 7-13 and Table 7-14 show that the largest contribution to the overall indicator comes from the respiratory effects impact category, followed by the global warming category. Table 7-13 shows that the majority of the impacts are attributed to four substances: carbon dioxide (global warming impact), nitrogen oxides, sulfur dioxide, and particulate matter (mostly due to respiratory impacts). Mercury emissions (a salient source of concern in chlorine production) account for less than 2% of the total valuation. In terms of process contributions to the overall impact indicator, Table 7-14 shows that the majority of the impacts (80%) are due to combustion product emissions from coal furnaces. This shows the importance of the life cycle

Table 7-14: Life-cycle impact valuation for the chlorine LCA example, showing process and impact category contributions

	Diag(x) E ^T H								Diag(x) E ^T H Diag(w)								life-cycle environmental impact valuation (\$)	% contribution
	Impact Category Indicators								Impact Category Valuations									
	Global warming potential (100 year horizon) (kg CO2 equivalent/kg)	Ozone depletion potential (kg CFC-11 equivalent/kg)	Human toxicity potential (cancer) (DALYs/kg)	Human toxicity potential (noncancer) (DALYs/kg)	Respiratory effects (kg PM10 equivalent/kg)	Photo-chemical oxidants creation potential (kg Ethylene equivalent/kg)	Acidification potential (kg SO2 equivalent/kg)	Eutrophication potential (kg NO2 to air equivalent/kg)	Global warming potential (100 year horizon) (\$)	Ozone depletion potential (\$)	Human toxicity potential (cancer) (\$)	Human toxicity potential (noncancer) (\$)	Respiratory effects (\$)	Photo-chemical oxidants creation potential (\$)	Acidification potential (\$)	Eutrophication potential (\$)		
Brine pumping	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0%
Chloralkali production (diaphragm cell process)	10.56	0.004	2E-05	8E-07	3E-05	0	6E-04	8E-04	0.317	0.373	2.017	0.065	0.001	0	5E-04	6E-04	2.8	1.5%
Chloralkali production (membrane cell process)	0.812	3E-04	2E-06	6E-08	3E-06	0	5E-05	6E-05	0.024	0.029	0.155	0.005	1E-04	0	4E-05	5E-05	0.2	0.1%
Chloralkali production (mercury cell process)	2.166	8E-04	5E-06	3E-05	7E-06	0	1E-04	2E-04	0.065	0.076	0.414	2.594	3E-04	0	1E-04	1E-04	3.1	1.8%
Coal furnace	654.2	0	1E-05	7E-06	2.897	0.39	5.693	1.344	19.63	0	0.912	0.558	115.9	0.78	4.554	1.075	143.4	79.7%
Coal production	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0%
Coal-fired power plant	0	0	2E-13	1E-12	0	0	0	0	0	0	2E-08	8E-08	0	0	0	0	0.0	0.0%
Diesel engine	89.07	0	0	3E-06	0.158	0.117	0.749	0.928	2.672	0	0	0.277	6.301	0.234	0.599	0.742	10.8	6.0%
Diesel fuel production	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0%
Gas-fired power plant	0	0	2E-16	8E-16	0	0	0	0	0	0	2E-11	7E-11	0	0	0	0	0.0	0.0%
Hydroelectric plant	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0%
Industrial gas furnace	168.7	0	2E-07	7E-07	0.023	0.023	0.132	0.187	5.06	0	0.014	0.056	0.932	0.046	0.106	0.15	6.4	3.5%
Methane reforming	1E-13	0	0	0	0	0	0	0	4E-15	0	0	0	0	0	0	0	0.0	0.0%
Natural gas production	58.8	0	0	6E-08	0.005	0.012	0.041	0	1.764	0	0	0.005	0.202	0.024	0.033	0	2.0	1.1%
Nuclear power plant	13.75	0	0	2E-06	0.108	0.06	0.477	0.449	0.413	0	0	0.133	4.331	0.12	0.382	0.359	5.7	3.2%
Oil furnace	25.76	0	3E-06	2E-07	0.048	0.015	0.226	0.045	0.773	0	0.285	0.016	1.907	0.029	0.181	0.036	3.2	1.8%
Oil production	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0%
Oil-fired power plant	0	0	1E-16	5E-16	0	0	0	0	0	0	9E-12	4E-11	0	0	0	0	0.0	0.0%
Railroad transport	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0%
Utility gas furnace	66.25	0	7E-08	1E-07	0.004	0.004	0.02	0.029	1.987	0	0.006	0.009	0.142	0.008	0.016	0.023	2.2	1.2%

	$\Psi^T = (H^T E x)^T$	$(Diag(w) H^T E x)^T$	$\Omega = w^T H^T E x$
	Transpose of the vector of impact category indicators	Transpose of the vector of impact category valuations	
System Total	[1090 0.005 4E-05 4E-05 3.242 0.62 7.34 2.982]	[32.7 0.478 3.803 3.718 129.7 1.241 5.872 2.386]	179.9
% contribution		[18% 0% 2% 2% 72% 1% 3% 1%]	

7.3.4 The improvement analysis stage of PIO-LCA

In the context of process design, it is desirable to have available a set of unit indicators that can be used by designers to evaluate the tradeoffs associated with changing the mix of inputs and outputs of a process. Examples include deciding how to make tradeoffs between alternative raw materials or between increasing the efficiency with which a material is used and the amount of energy needed to increase material recovery.

Obtaining environmental indicator scores for each input to a process is only the first part of the analysis. Designers need to know what factors drive the score for each input, in order to identify improvement opportunities. Knowledge of the factors with the greatest contribution to the scores can also be used by those responsible for maintaining the information to set priorities when working to improve the quality of the data.

Matrix operations are also the starting point for sensitivity analysis. The necessary vectors and matrices are introduced in this subsection. Their application is illustrated in section 7.4.

The vector of indicators for the impact of each unit of environmental intervention is given by:

$$\mathbf{\Omega}_e = \mathbf{H}\mathbf{w} \quad (7-12)$$

Similarly, the vector of indicators corresponding to the direct impact of each unit of process throughput is given by:

$$\mathbf{\Omega}_{\text{direct}} = \mathbf{E}^T \mathbf{H}\mathbf{w} \quad (7-13)$$

while the vector of indicators corresponding to the total impact of each unit of process throughput is calculated using the expression:

$$\mathbf{\Omega}_x = (\mathbf{I} - \mathbf{DB})^{-1} \mathbf{E}^T \mathbf{H}\mathbf{w} \quad (7-14)$$

Finally, the vector of indicators for the impact of one unit of product is given by:

$$\mathbf{\Omega}_d = (\mathbf{I} - \mathbf{A}_{\text{prod}})^{-1} \mathbf{D}^T \mathbf{E}^T \mathbf{H}\mathbf{w} \quad (7-15)$$

Indicators can also be obtained at the impact category level. The matrix of indicators for the impact of each unit of environmental exchange within each impact problem category is matrix \mathbf{H} (by definition). The matrix of indicators for the direct impact of each unit of process throughput within each impact category is given by:

$$\mathbf{\Psi}_{\text{direct}} = \mathbf{E}^T \mathbf{H} \quad (7-16)$$

Similarly, the matrix of indicators for the total impact of each unit of process throughput within each impact category is given by:

$$\mathbf{\Psi}_x = (\mathbf{I} - \mathbf{DB})^{-1} \mathbf{E}^T \mathbf{H} \quad (7-17)$$

Finally, the matrix of indicators for the impact of each unit of product is given by:

$$\mathbf{\Psi}_d = (\mathbf{I} - \mathbf{A}_{\text{prod}})^{-1} \mathbf{D}^T \mathbf{E}^T \mathbf{H} \quad (7-18)$$

Examples of these matrices are given as needed in the next section.

7.4 Illustrative Applications

7.4.1 Obtaining a life-cycle inventory and life-cycle environmental indicators for chlorine production.

Given the input data in matrices **B**, **C**, **E**, **F** and **H**, and in vectors **p** and **w**, the next step would be to specify vector **d**. A basis of one metric ton of chlorine is chosen, and thus the only nonzero entry of vector **d** is the entry corresponding to the product “chlorine (kg)”, which is given a value of 1000. The environmental exchanges inventory is given by the vector $\mathbf{e} = \mathbf{ED}(\mathbf{I} - \mathbf{A}_c)^{-1}\mathbf{d}$ (Table 7-11), where matrices **D**, and **A_c** have been obtained as described in the Input Data section. The vector of life-cycle environmental indicators for each impact category in matrix **H** is given by $\boldsymbol{\psi} = \mathbf{H}^T\mathbf{e}$ (Table 7-13 or Table 7-14, bottom left). The overall indicator is computed using $\Omega = \mathbf{w}^T\boldsymbol{\psi}$ (Table 7-13 or Table 7-14, bottom right). A social cost of \$180/ton of chlorine is computed from the data used in the example. This turns out to be of the same order of magnitude as the selling price of chlorine (\$210/ton, as shown in Table 7-4). Since the potency and valuation factors used are typical of the factors used by regulatory agencies when they estimate the costs and benefits of environmental regulations, one could treat the ratio of the social cost to the price (or private cost) of chlorine as an indicator of the likelihood that this raw material (or the associated upstream processes) could face additional regulations in the future. Companies that strive to minimize the estimated social cost of their designs are less likely to be faced with the need to undertake expensive retrofits to respond to changes in the regulatory environment during the life of the process.

7.4.2 Identifying the main drivers for environmental impact in chlorine production.

The vector $\mathbf{Diag}(\mathbf{x})\mathbf{E}^T\mathbf{H}\mathbf{w}$ is used to identify the processes that contribute the most to the overall valuation. Table 7-14 shows that the largest contribution comes from coal combustion in furnaces (80%). The most important environmental exchanges can be identified using matrix $\mathbf{Diag}(\mathbf{e})\mathbf{H}\mathbf{w}$. The results in Table 7-13 show that the most important exchanges are emissions of SO₂, NO_x, CO₂, and PM₁₀. The $\mathbf{E}\mathbf{Diag}(\mathbf{x})$ matrix (top of Table 7-11) can be used to trace exchanges back to the processes that generate them. The data in Table 7-11 shows that 91% of the sulfur dioxide emissions, 45% of the nitrogen dioxide emissions, 69% of the carbon dioxide

emissions, and 99.2% of the particulate patter emissions originate in coal furnaces. With respect to mercury, only 4% of the emissions come from power plants and combustion processes, with the mercury cell process accounting for 96% of the emissions.

Table 7-15: Environmental indicators per unit of product for the chlorine LCA example

	Global warming potential (100 year horizon) (kg CO2 equivalent/kg)	Ozone depletion potential (kg CFC-11 equivalent/kg)	Human toxicity potential (cancer) (DALYs/kg)	Human toxicity potential (noncancer) (DALYs/kg)	Respiratory effects (kg PM10 equivalent/kg)	Photo-chemical oxidants creation potential (kg Ethylene equivalent/kg)	Acidification potential (kg SO2 equivalent/kg)	Eutrophication potential (kg NO2 to air equivalent/kg)	Global warming potential (100 year horizon) (\$)	Ozone depletion potential (\$)	Human toxicity potential (cancer) (\$)	Human toxicity potential (noncancer) (\$)	Respiratory effects (\$)	Photo-chemical oxidants creation potential (\$)	Acidification potential (\$)	Eutrophication potential (\$)	Overall valuation (\$)
Chlorine (per kg)	1.09	5E-06	4E-08	4E-08	0.003	6E-04	0.007	0.003	0.33	5E-04	0.004	0.004	0.13	0.001	0.006	0.002	0.18
Coal (per kg)	0.342	2E-23	6E-10	1E-08	6E-04	4E-04	0.003	0.003	0.01	2E-21	5E-05	0.001	0.025	9E-04	0.002	0.003	0.0417
Diesel fuel (per kg)	0.263	2E-22	7E-09	2E-09	3E-04	9E-05	1E-03	4E-04	0.008	2E-20	6E-04	1E-04	0.012	2E-04	8E-04	3E-04	0.0219
Electricity (per MJ)	0.18	4E-22	3E-09	2E-09	7E-04	1E-04	0.001	6E-04	0.005	4E-20	2E-04	2E-04	0.027	2E-04	0.001	5E-04	0.0343
Hydrogen (per kg)	9.096	2E-06	2E-08	3E-08	0.003	0.001	0.008	0.004	0.273	2E-04	0.002	0.002	0.106	0.002	0.006	0.003	0.40
Mechanical energy from diesel engines (per MJ)	0.131	8E-25	2E-10	5E-09	2E-04	2E-04	0.001	0.001	0.004	8E-23	1E-05	4E-04	0.009	3E-04	9E-04	0.001	0.0157
Natural gas (per kg)	0.838	9E-23	7E-10	1E-09	2E-04	2E-04	8E-04	2E-04	0.025	9E-21	6E-05	1E-04	0.006	4E-04	6E-04	1E-04	0.0329
Oil (per kg)	0.067	9E-23	1E-09	5E-10	1E-04	3E-05	3E-04	1E-04	0.002	9E-21	9E-05	4E-05	0.004	5E-05	2E-04	1E-04	0.0069
Railroad transport (per kg-km)	4E-05	-0	4E-14	1E-12	6E-08	4E-08	3E-07	4E-07	1E-06	-0	4E-09	1E-07	2E-06	9E-08	2E-07	3E-07	4.2E-06
Salt from brine (per kg)	0.065	1E-22	1E-09	9E-10	2E-04	4E-05	5E-04	2E-04	0.002	1E-20	9E-05	7E-05	0.01	9E-05	4E-04	2E-04	0.012
Sodium hydroxide (per kg)	1.246	5E-06	5E-08	5E-08	0.004	7E-04	0.008	0.003	0.037	5E-04	0.004	0.004	0.148	0.001	0.007	0.003	0.21
Thermal energy from coal furnace (per MJ)	0.094	-0	1E-09	1E-09	4E-04	6E-05	8E-04	3E-04	0.003	-0	1E-04	1E-04	0.015	1E-04	7E-04	2E-04	0.0195
Thermal energy from industrial gas furnace (per MJ)	0.07	9E-24	7E-11	2E-10	1E-05	1E-05	6E-05	6E-05	0.002	9E-22	6E-06	2E-05	4E-04	2E-05	5E-05	5E-05	0.0026
Thermal energy from oil furnace (per MJ)	0.077	2E-24	1E-08	5E-10	1E-04	4E-05	7E-04	1E-04	0.002	2E-22	8E-04	5E-05	0.006	9E-05	5E-04	1E-04	0.0096
Thermal energy from utility gas furnace (per MJ)	0.068	5E-22	7E-11	1E-10	6E-06	6E-06	3E-05	3E-05	0.002	5E-20	6E-06	9E-06	2E-04	1E-05	2E-05	2E-05	0.0023

7.4.3 Obtaining unit indicators for process design evaluation.

Suppose a designer is working on the retrofit of an existing process that uses chlorine as a raw material. Several process changes have been proposed to reduce chlorine emissions, and the designer is interested in analyzing the overall improvement in environmental performance. The proposed process changes differ in their effectiveness in reducing emissions, as well as in the type and amounts of utilities they consume. It would be therefore useful to the designer to have a unit indicator for the overall environmental impact of chlorine production, chlorine emissions, and key utilities, such as electricity and thermal energy (used for raising steam). These unit indicators could then be used in the same way as prices are used to evaluate the overall improvement in operating cost from retrofit alternatives designed to reduce cost. All of the required unit indicators are included in the vectors Ω_d and Ω_e shown respectively, in Table 7-15, and Table 7-16. The impact of chlorine production is valued at \$0.18/kg (first row in the last

column of Table 7-15), while chlorine emissions are valued at \$0.024/kg (tenth row in the last column of Table 7-16). This means that most of the environmental benefit obtained from decreasing chlorine emissions would be due to decreasing the demand for chlorine to replace what is lost, rather than from the impact of the chlorine emissions themselves. With respect to utilities, electricity is valued at \$0.034/MJ (or about 12 cents per kWh), and thermal energy from gas furnaces at \$0.0026/MJ (Table 7-15, rows 4 and 13). The valuation for the impact of thermal energy supply would increase to \$0.0195/MJ if coal were used as fuel (Table 7-15, row 12).

Table 7-16: Environmental impact valuations per unit of environmental exchange for the chlorine LCA example

	Global warming potential (100 year horizon) (\$)	Ozone depletion potential (\$)	Human toxicity potential (cancer) (\$)	Human toxicity potential (noncancer) (\$)	Respiratory effects (\$)	Photo-chemical oxidants creation potential (\$)	Acidification potential (\$)	Eutrophication potential (\$)	Overall valuation (\$)
H Diag(w)									
Matrix of impact category valuations per unit of environmental exchange									
Air: 2,3,7,8-Tetrachlorodibenzo-p-dioxin (per kg)	0	0	2E+08	1E+07	0	0	0	0	1.7E+08
Air: Ammonia (per kg)	-0.498	0	0	0.001	4.12	0	1.504	2.168	7.3
Air: Arsenic (per kg)	0	0	3141	72.67	0	0	0	0	3214
Air: Asbestos (per kg)	0	0	92.36	0	0	0	0	0	92
Air: Barium (per kg)	0	0	0	2.508	0	0	0	0	2.5
Air: Cadmium (per kg)	0	0	12565	53.86	0	0	0	0	12619
Air: Carbon dioxide (per kg)	0.03	0	0	0	0	0	0	0	0.030
Air: Carbon monoxide (per kg)	0.09	0	0	0.005	0	0.036	0	0	0.13
Air: Carbon tetrachloride (per kg)	-45.66	110.5	1234	20.63	0	0	0	0	1320
Air: Chlorine (per kg)	0	0	0	0.024	0	0	0	0	0.024
Air: Cobalt (per kg)	0	0	2017	46.3	0	0	0	0	2063
Air: Cyanide (per kg)	0	0	0	35.8	0	0	0	0	35.8
Air: Dichlorodifluoromethane (per kg)	199.7	98	0	0.04	0	0	0	0	298
Air: Hydrazine (per kg)	0	0	443.5	1.072	0	0	0	0	445
Air: Hydrochloric acid (per kg)	-0.459	0	0	0.016	3.8	0	0.704	0	4.1
Air: Hydrogen sulfide (per kg)	-1.042	0	0	0.236	9.224	0	1.504	0	9.9
Air: Isophorone (per kg)	0	0	2E-04	4E-06	0	0	0	0	0.00020
Air: Lead (per kg)	0	0	322.3	78.84	0	0	0	0	401
Air: Mercury (per kg)	0	0	0	9438	0	0	0	0	9438
Air: Methane (per kg)	0.63	0	0	0	0	0.012	0	0	0.64
Air: Nickel (per kg)	0	0	2666	2.065	0	0	0	0	2668
Air: NOx (as NO2) (per kg)	1.2	0	0	0.297	3.052	0.233	0.56	0.8	6.1
Air: PM10 (per kg)	-0.249	0	0	0	40	0	0	0	40
Air: Sulfur dioxide (per kg)	-0.699	0	0	4E-04	6.156	0.096	0.8	0	6.4
Air: Sulfuric acid (per kg)	-0.457	0	0.123	0.029	4.02	0	0.52	0	4.2
Air: Total Suspended Particles (per kg)	-0.249	0	0	0	40	0	0	0	40
Water: Barium (per kg)	0	0	0	2.229	0	0	0	0	2.2
Water: Chlorine (per kg)	0	0	0	0.148	0	0	0	0	0.15
Water: Hydrochloric acid (per kg)	0	0	0	0.003	0	0	0	0	0.0032
Water: Mercury (per kg)	0	0	0	7426	0	0	0	0	7426
Water: Sulfuric acid (per kg)	0	0	3E-08	1E-07	0	0	0	0	1.4E-07

$\Omega_e = Hw$
vector of environmental impact valuations per unit of environmental exchange

7.4.4 Comparing three processes for manufacturing chlorine.

Two approaches are illustrated. The first one is based on the use of the sensitivity matrices and vectors. Since the three chlor-alkali processes have been defined using the same throughput basis (the corresponding columns in the **C** matrix are identical), vector Ω_x can be used to compare the processes from a life-cycle perspective (including direct and indirect contributions). Table 7-17 (rows 2 to 4) shows that the mercury cell process has at least 10% more impact than either of the other two processes, while the membrane cell process is slightly better than the diaphragm cell process. The differences among the three processes are much more pronounced when only the direct process impacts given by vector $\Omega_{x\text{direct}}$ are considered (Table 7-18). This shows that most of the impact associated with the diaphragm and membrane cell processes arises from the processes energy inputs. It also means that while impacts in the area directly adjacent to a chlor-alkali facility will be significantly higher for a process using the mercury-cell process, the difference in overall long term impact over a larger geographic scale would not be very different.

Table 7-17: Environmental indicators per unit of process throughput for the chlorine LCA example (direct and indirect impacts)

Unit Impact Environmental Impact Indicators and Valuations	Global warming potential (100 year horizon) (kg CO2 equivalent/kg)	Ozone depletion potential (kg CFC-11 equivalent/kg)	Human toxicity potential (cancer) (DALYs/kg)	Human toxicity potential (noncancer) (DALYs/kg)	Respiratory effects (kg PM10 equivalent/kg)	Photo-chemical oxidants creation potential (kg Ethylene equivalent/kg)	Acidification potential (kg SO2 equivalent/kg)	Eutrophication potential (kg NO2 to air equivalent/kg)	Global warming potential (100 year horizon) (\$)	Ozone depletion potential (\$)	Human toxicity potential (cancer) (\$)	Human toxicity potential (noncancer) (\$)	Respiratory effects (\$)	Photo-chemical oxidants creation potential (\$)	Acidification potential (\$)	Eutrophication potential (\$)	Overall valuation (\$)
Brine pumping	0.065	5E-23	1E-09	9E-10	2E-04	4E-05	5E-04	2E-04	0.002	5E-21	9E-05	7E-05	0.01	9E-05	4E-04	2E-04	0.012
Chloralkali production (diaphragm cell process)	2.705	1E-05	1E-07	3E-08	0.008	0.001	0.017	0.007	0.081	0.001	0.009	0.003	0.306	0.003	0.014	0.006	0.42
Chloralkali production (membrane cell process)	2.21	1E-05	1E-07	3E-08	0.008	0.001	0.017	0.007	0.066	0.001	0.009	0.003	0.308	0.003	0.014	0.005	0.41
Chloralkali production (mercury cell process)	2.242	1E-05	1E-07	5E-07	0.008	0.001	0.018	0.007	0.067	0.001	0.009	0.041	0.326	0.003	0.015	0.006	0.47
Coal furnace	2.793	2E-24	4E-08	4E-08	0.011	0.002	0.024	0.009	0.084	2E-22	0.003	0.003	0.457	0.004	0.019	0.007	0.58
Coal production	0.342	-0	6E-10	1E-08	6E-04	4E-04	0.003	0.003	0.01	-0	5E-05	0.001	0.025	9E-04	0.002	0.003	0.042
Coal-fired power plant	0.968	6E-22	1E-08	1E-08	0.004	7E-04	0.008	0.003	0.029	6E-20	0.001	0.001	0.158	0.001	0.007	0.002	0.20
Diesel engine	0.131	6E-25	2E-10	5E-09	2E-04	2E-04	0.001	0.001	0.004	6E-23	1E-05	4E-04	0.009	3E-04	9E-04	0.001	0.016
Diesel fuel production	0.263	9E-24	7E-09	2E-09	3E-04	9E-05	1E-03	4E-04	0.008	9E-22	6E-04	1E-04	0.012	2E-04	3E-04	0.001	0.022
Gas-fired power plant	0.697	-0	7E-10	1E-09	6E-05	6E-05	3E-04	3E-04	0.021	-0	6E-05	9E-05	0.002	1E-04	3E-04	2E-04	0.024
Hydroelectric plant	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Industrial gas furnace	73.32	-0	7E-08	2E-07	0.011	0.011	0.06	0.066	2.2	-0	0.006	0.021	0.441	0.022	0.048	0.053	2.8
Methane reforming	9.645	-0	8E-09	1E-08	0.002	9E-04	0.005	0.003	0.289	-0	6E-04	0.001	0.063	0.002	0.004	0.002	0.36
Natural gas production	0.838	-0	7E-10	1E-09	2E-04	2E-04	8E-04	2E-04	0.025	-0	6E-05	1E-04	0.006	4E-04	6E-04	1E-04	0.033
Nuclear power plant	0.051	0	0	6E-09	4E-04	2E-04	0.002	0.002	0.002	0	0	5E-04	0.016	4E-04	0.001	0.001	0.021
Oil furnace	80.99	1E-22	1E-05	6E-07	0.15	0.046	0.705	0.143	2.43	1E-20	0.88	0.049	5.982	0.092	0.564	0.114	10
Oil production	0.067	-0	1E-09	5E-10	1E-04	3E-05	3E-04	1E-04	0.002	-0	9E-05	4E-05	0.004	5E-05	2E-04	1E-04	0.0069
Oil-fired power plant	0.747	-0	1E-07	5E-09	0.001	4E-04	0.006	0.001	0.022	-0	0.008	5E-04	0.055	8E-04	0.005	0.001	0.093
Railroad transport	0.035	-0	4E-11	1E-09	6E-05	4E-05	3E-04	4E-04	0.001	-0	4E-06	1E-04	0.002	9E-05	2E-04	3E-04	0.0042
Utility gas furnace	71.75	-0	7E-08	1E-07	0.006	0.007	0.032	0.027	2.152	-0	0.006	0.01	0.245	0.013	0.026	0.022	2.47

$$\Psi_x = (I - BD)^{-1} E^T H$$

Matrix of total (direct + indirect) environmental impact indicators per unit of process throughput

$$\Psi_x \text{ Diag}(w)$$

Matrix of total (direct + indirect) impact category valuations per unit of process throughput

$$\Omega_x = \Psi_x w$$

vector of total (direct + indirect) environmental impact valuations per unit of process throughput

Table 7-18: Environmental indicators per unit of process throughput for the chlorine LCA example (direct impacts only)

	Global warming potential (100 year horizon) (kg CO2 equivalent/kg)	Ozone depletion potential (kg CFC-11 equivalent/kg)	Human toxicity potential (cancer) (DALYs/kg)	Human toxicity potential (noncancer) (DALYs/kg)	Respiratory effects (kg PM10 equivalent/kg)	Photo-chemical oxidants creation potential (kg Ethylene equivalent/kg)	Acidification potential (kg SO2 equivalent/kg)	Eutrophication potential (kg NO2 to air equivalent/kg)	Global warming potential (100 year horizon) (\$)	Ozone depletion potential (\$)	Human toxicity potential (cancer) (\$)	Human toxicity potential (noncancer) (\$)	Respiratory effects (\$)	Photo-chemical oxidants creation potential (\$)	Acidification potential (\$)	Eutrophication potential (\$)	Overall valuation (\$)
Brine pumping	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Chloralkali production (diaphragm cell process)	0.032	1E-05	7E-08	2E-09	1E-07	0	2E-06	2E-06	1E-03	0.001	0.006	2E-04	4E-06	0	1E-06	2E-06	0.0085
Chloralkali production (membrane cell process)	0.032	1E-05	7E-08	2E-09	1E-07	0	2E-06	2E-06	1E-03	0.001	0.006	2E-04	4E-06	0	1E-06	2E-06	0.0085
Chloralkali production (mercury cell process)	0.032	1E-05	7E-08	5E-07	1E-07	0	2E-06	2E-06	1E-03	0.001	0.006	0.039	4E-06	0	1E-06	2E-06	0.0470
Coal furnace	2.434	0	4E-08	2E-08	0.011	0.001	0.021	0.005	0.073	0	0.003	0.002	0.431	0.003	0.017	0.004	0.53
Coal production	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Coal-fired power plant	0	0	3E-16	1E-15	0	0	0	0	0	0	2E-11	1E-10	0	0	0	0	1.28E-10
Diesel engine	0.125	0	0	5E-09	2E-04	2E-04	0.001	0.001	0.004	0	0	4E-04	0.009	3E-04	8E-04	0.001	0.0152
Diesel fuel production	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Gas-fired power plant	0	0	2E-18	7E-18	0	0	0	0	0	0	1E-13	6E-13	0	0	0	0	7.13E-13
Hydroelectric plant	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Industrial gas furnace	56.98	0	6E-08	2E-07	0.008	0.008	0.045	0.063	1.709	0	0.005	0.019	0.315	0.015	0.036	0.051	2.15
Methane reforming	5.5	0	0	0	0	0	0	0	0.165	0	0	0	0	0	0	0	0.165
Natural gas production	0.726	0	0	8E-10	6E-05	2E-04	5E-04	0	0.022	0	0	6E-05	0.002	3E-04	4E-04	0	0.025
Nuclear power plant	0.051	0	0	6E-09	4E-04	2E-04	0.002	0.002	0.002	0	0	5E-04	0.016	4E-04	0.001	0.001	0.021
Oil furnace	79.43	0	1E-05	6E-07	0.147	0.045	0.698	0.14	2.383	0	0.878	0.048	5.881	0.091	0.558	0.112	9.95
Oil production	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Oil-fired power plant	0	0	3E-18	1E-17	0	0	0	0	0	0	3E-13	1E-12	0	0	0	0	1.6E-12
Railroad transport	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Utility gas furnace	55.4	0	6E-08	9E-08	0.003	0.003	0.017	0.024	1.662	0	0.005	0.007	0.119	0.006	0.014	0.019	1.8

$$\Psi_{xdirect} = (I-BD)^{-1}E^T H$$

Matrix of direct environmental impact indicators per unit of process throughput

$$\Psi_{xdirect} \text{ Diag}(w)$$

Matrix of direct impact category valuations per unit of process throughput

$\Omega_{xdirect} = \Psi_{xdirect} W$
vector of direct environmental impact valuations per unit of process throughput

The second approach to comparing the processes is based on changing the market share matrix and repeating the analysis in parts (a) and (b) three times. In each iteration, the process of interest is given a 100% market share in the production of chlorine. This procedure allows the analyst to take full advantage of the information provided by the contribution matrices. Key results are shown in Figure 7-5 (chemical contributions) and Figure 7-6 (process contributions).

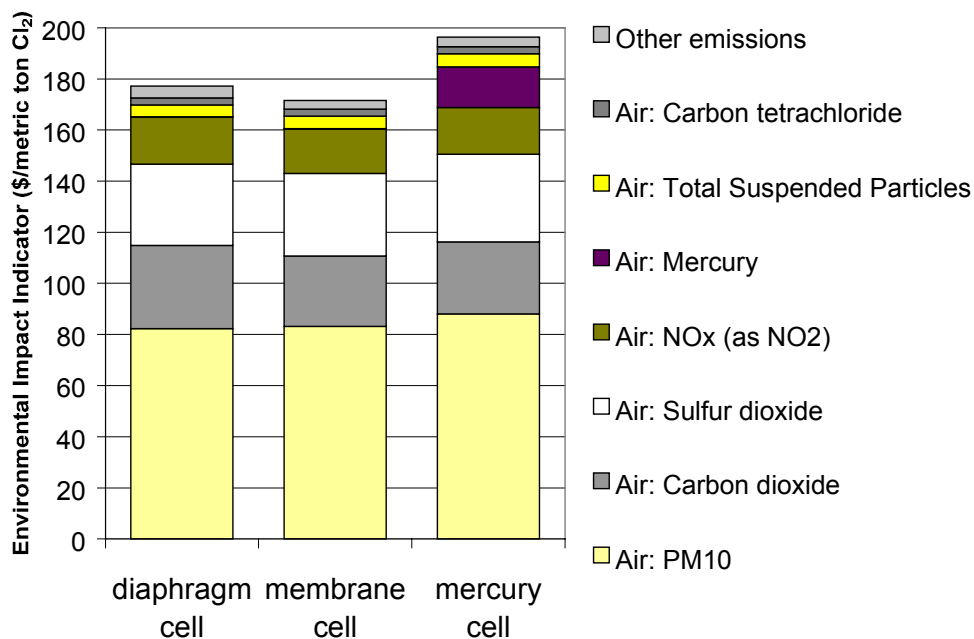


Figure 7-5: Environmental exchange contributions to the environmental impact indicator of chlorine production for three chlor-alkali processes

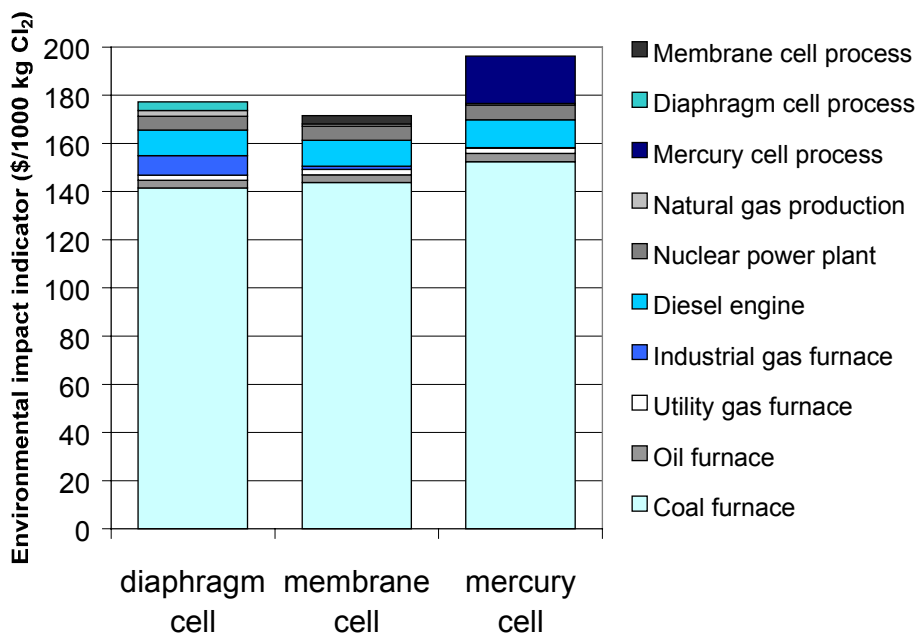


Figure 7-6: Process throughput contributions to the environmental impact indicator for chlorine production for three chlor-alkali processes

7.4.5 Impact of changing input suppliers.

The case of using an alternative source of electricity other than electricity from the national grid is examined next. In particular, the environmental impact indicator for chlorine production using the membrane cell and electricity supplied by the national grid is compared with the indicator for chlorine production also using the membrane cell, but using electricity from an on-site natural gas-fired cogeneration plant. Table 7-19 shows the changes made to the use and make matrices to incorporate a new process (the cogeneration plant) and two new products (electricity from cogeneration and thermal energy from cogeneration). It is assumed that only the chlor-alkali processes obtain electricity and steam from the cogeneration plant. All other processes in the network continue to consume electricity from the national grid. The fuel consumption per kWh of electricity from the cogeneration plant is assumed to be the same as that for a gas-fired power plant, but the industrial gas furnace is used rather than the utility gas furnace as the source of thermal energy. It is not necessary to fill out the entries for the cogeneration process in the environmental exchanges matrix, since the combustion product emissions of the industrial gas furnace are inherited by the cogeneration process through the specification of thermal energy as an input. An alternative approach would have been to enter natural gas as an input to the cogeneration process (instead of thermal energy) and to enter emission factors for the cogeneration process in the environmental exchanges matrix. An electricity price of \$0.06/kWh (\$0.0167/MJ) and steam price of \$0.0032/MJ are used in vector \mathbf{p} for the purposes of allocating cogeneration plant throughput to the two products electricity and steam (thermal energy). The results are shown in Figure 6. The social cost of chlorine production decreases by about a factor of 4 when the cogeneration plant is used as a source of the electricity and steam in the chlor-alkali processes.

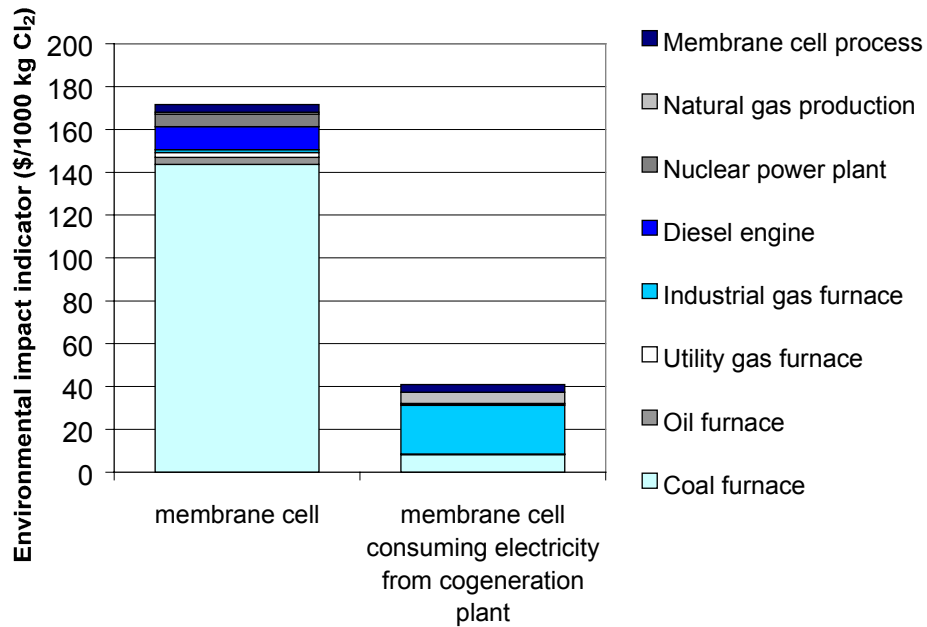


Figure 7-7: Comparison between the U.S. national grid and a gas-fired cogeneration plant as sources of electricity for chlorine production using the membrane cell process

7.4.6 Comparison between chlorine production in the United States and Western Europe

The mercury cell process is used to a larger extent in Europe than it is in the United States. It is estimated that in 1994, 64% of European chlorine was produced via the mercury cell process, while the diaphragm and membrane cell processes accounted for, respectively, 24% and 11% of total production [20]. The production mix for electricity is also different from the one in the United States, with lower contribution from coal power plants and higher contributions from nuclear, hydroelectric, and oil-fired plants. An estimate for the market shares in the UCPTE power network (Western Europe including the British Isles) is: 25.2% coal, 10.7% oil, 7.4% natural gas, 40.3% nuclear, and 16.4% hydro [21]. A comparison between chlorine production in the two regions can be obtained by changing the market share matrix F (Table 7-20) and repeating the analysis undertaken in subsections 7.4.1 and 7.4.2. Figure 7-8 shows the results of this exercise. Despite the higher contribution of the mercury cell process to chlorine production in Europe, the overall indicator for European production is 36% lower than the one for U.S. production, due mainly to the lower contribution of coal-fired power plants to electricity generation in Europe. Note that increasing either the toxicity potency factor for mercury or the

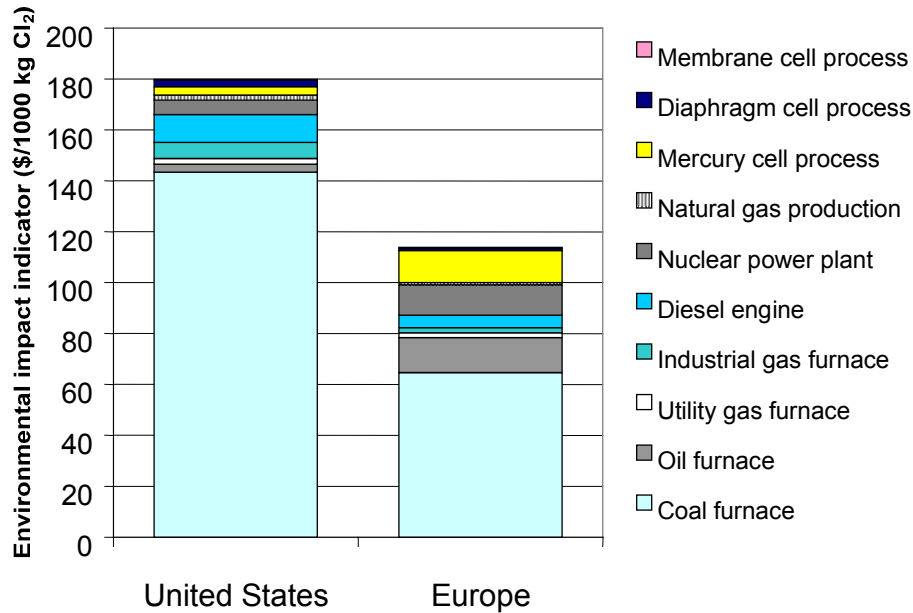


Figure 7-8: Comparison of the environmental impact of chlorine production in United States vs. Western Europe

7.5 Uncertainty propagation

7.5.1 Introduction

A legitimate question that may be raised after examining the results of the PIO-LCA environmental valuation method applied to the life cycle assessment of chlorine production is how much confidence can one place in the conclusions of the analysis. After all, there are many uncertainties involved in the estimation of the data used as input to the method⁷³.

The underlying data of the model is given by:

- process descriptions: **B**, **C**, and **E** matrices
- economic data: **p** vector, **F** matrix
- environmental assessment data: **H** matrix
- subjective valuation data: **w** vector

⁷³ In fact, 625 uncertain parameters were used in the PIO-LCA model of chlorine production, including 458 uncertain factors in the multimedia fate, transfer and human exposure model (see section 6.3) used to generate the characterization factors for the cancer and non-cancer chronic toxicity impact categories.

One of the advantages of organizing LCA data in the manner proposed in this chapter is to facilitate updating. For example, if new emissions data for the generation of electricity in coal-fired power plants became available it would not be necessary to reenter the emissions data for every process that uses electricity. The PIO-LCA method matrix multiplications would take care of propagating the change in emissions through the different processes that use electricity directly or indirectly. This property also allows the propagation of uncertainties in technical coefficients (i.e. use, make, and environmental exchange factors) and valuation data while preserving correlation structure. For example, when the emission of a particular trace substance in coal combustion is sampled at a high value in an iteration of a Monte Carlo simulation, that one high value would be used in the computation of all unit indicators that inherit that emission in that particular iteration. In this way, samples of correlated unit indicators may be drawn from the PIO-LCA model for use in environmental valuation functions.

Uncertainty propagation can be conveniently carried out in spreadsheet software with uncertainty analysis add-ons by substituting distribution functions for nominal values in the cells that contain the inputs to the model. In a reasonably sized model the maintenance and documentation of the distributions used becomes an important part of the task. One of the key functions of the EnvEvalTool introduced in section 9.4 is the generation of fully documented input matrices and vectors for the Excel spreadsheet implementation of the PIO-LCA model, including the appropriate uncertainty distribution functions.

The reader might recall that in section 7.3.3 a social cost of \$180 was estimated for the valuation of the environmental impacts associated with the production of 1000 kg of chlorine. Uncertainty analysis performed on the model shows that there is more than one order of magnitude uncertainty in this estimate, as shown in Figure 7-9.

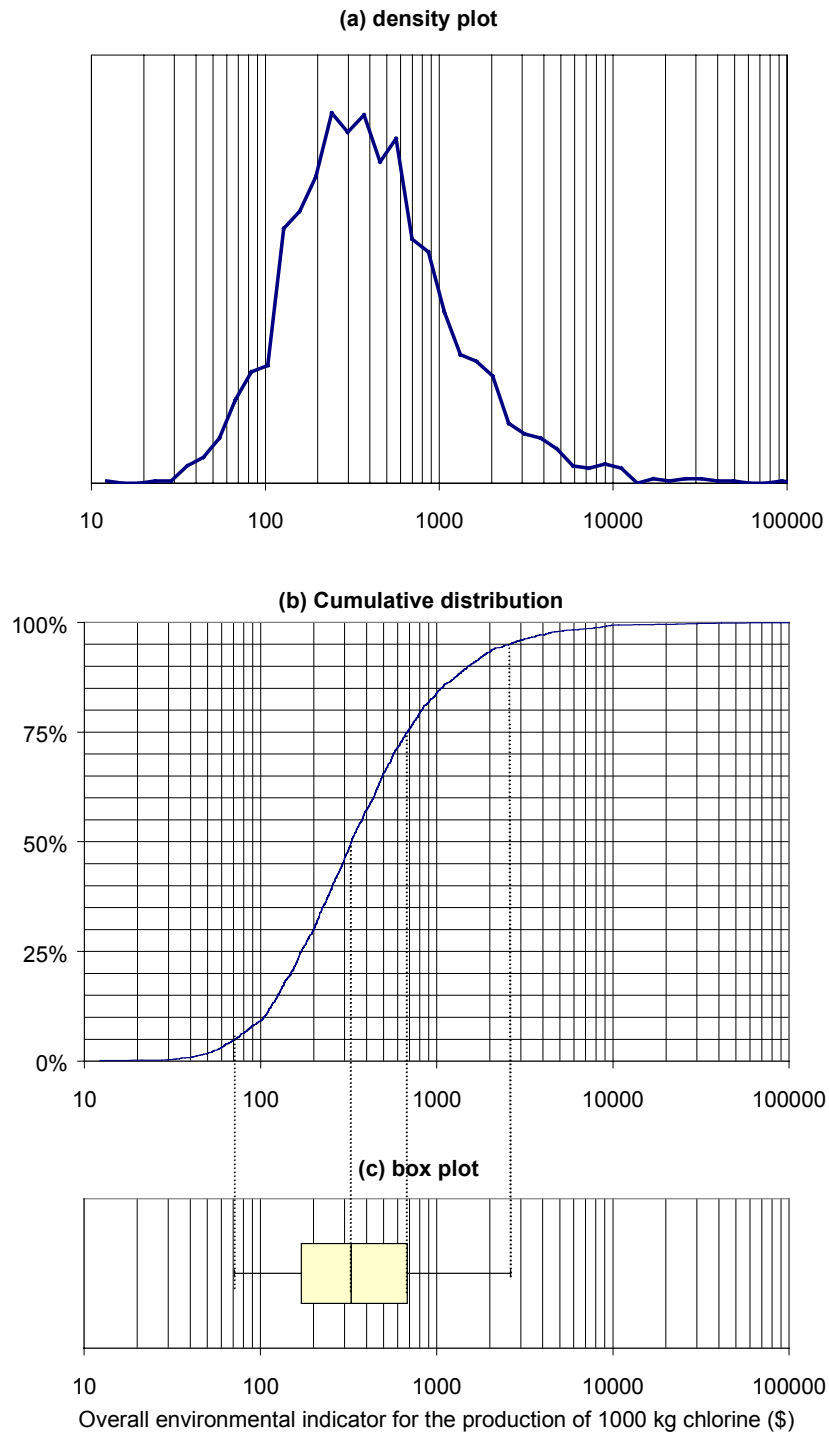


Figure 7-9: Uncertainty distributions for the overall environmental indicator for chlorine production obtained from Monte Carlo simulation of the PIO-LCA model

A comparison between the three chlor-alkali processes in the process network had shown that the mercury cell route was between 10 and 15% more damaging than the other two routes.

Propagation of uncertainties in the unit environmental indicators for the three processes (i.e. on the three elements of the Ω_x vector corresponding to the chlor-alkali processes) was carried out to test whether this conclusion was robust in the presence of uncertainty. A first look at the distributions obtained (Figure 7-10) suggests that the differences are not significant. This would be a mistaken conclusion. As explained in section 4.4, judgements about the ranking of two alternatives characterized by uncertain valuation functions should take into account correlations among the measures of performance for the two alternatives. Using the output file from the Monte Carlo simulation performed on the PIO-LCA model it is possible to derive ratios of the unit impact indicator for one chloralkali process against the indicator for another process. Those distributions are shown in Figure 7-11. Although there is a 70% chance that the diaphragm process has higher impact than the membrane process⁷⁴, the difference between the two processes is vary small. On the other hand, it can be concluded that the mercury cell process is significantly more damaging to the environment than the other two. The probability that the impacts of the mercury cell process receive a higher valuation than the impacts of the diaphragm cell and membrane cell processes are, respectively, 82% and 92%. There is also more than a 15% probability that the mercury cell process is at least twice as damaging than the other two⁷⁵.

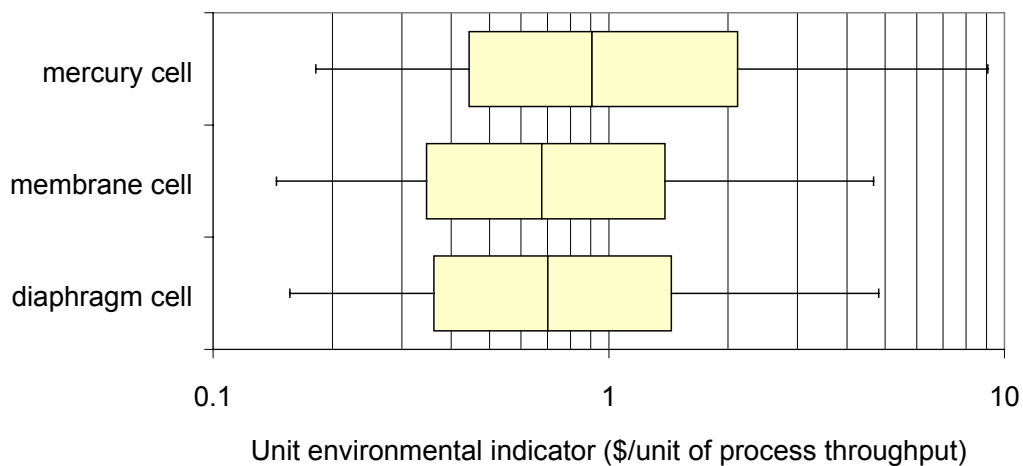


Figure 7-10: Comparison of three chlor-alkali processes using absolute environmental impact indicators

⁷⁴ 70% of the ratios of the environmental impact indicator of the diaphragm process to the indicator for the membrane process derived from the Monte Carlo simulation output file had values higher than 1. This means that in 70% of the cases the impact of the diaphragm process received a higher valuation.

⁷⁵ In more than 15% of the Monte Carlo iterations the impact ratios of the membrane cell process and the diaphragm cell process to the mercury cell process were lower than 0.5

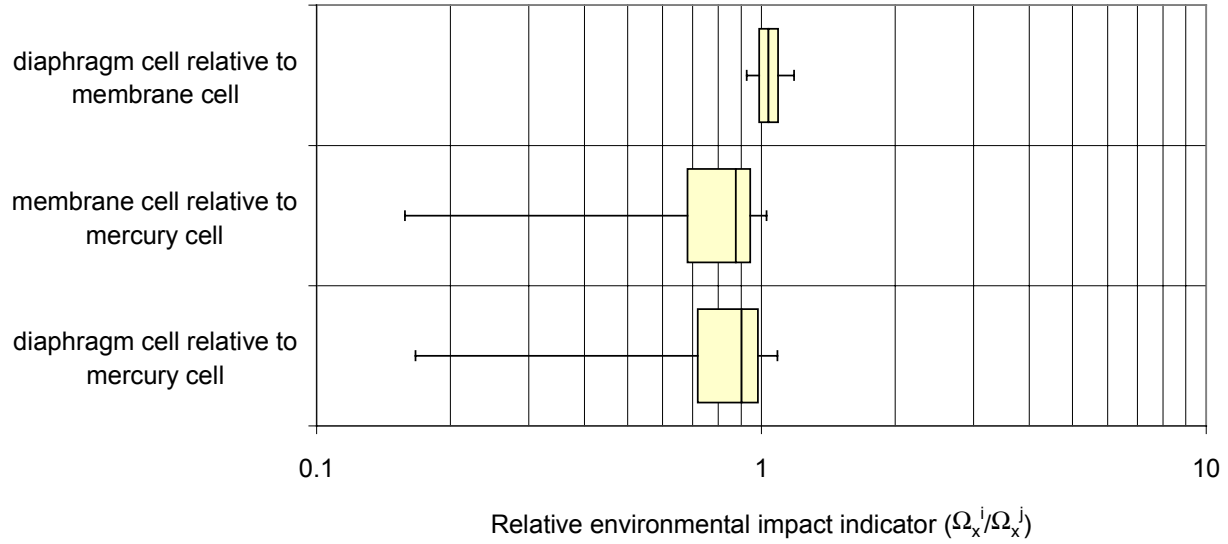


Figure 7-11: Comparison of three chlor-alkali processes using relative environmental impact indicators

This example has shown the power of the PIO-LCA method in decreasing decision uncertainty by preserving correlation structure in the presence of a large number of uncertainties. In fact, the confidence in the relative ranking of the three processes was increased in this example through the use of uncertainty analysis in a model that preserves correlation information. Additional information can be gained through the use of sensitivity analysis, discussed next.

7.5.2 Sensitivity analysis

ANALYSIS OF CONTRIBUTIONS TO THE ENVIRONMENTAL IMPACT INDICATOR

In terms of fractions of the overall indicator, the contributions of each process i , environmental exchange j , and impact category k can be calculated as follows:

$$f_{\text{proc},i} = (\mathbf{E}^T \mathbf{H} \mathbf{w})_i x_i / \Omega \quad (7-19)$$

$$f_{\text{ex},j} = (\mathbf{H} \mathbf{w})_j e_j / \Omega \quad (7-20)$$

$$f_{\text{cat},k} = w_k \psi_k / \Omega \quad (7-21)$$

Propagation of the uncertainty in the contributions above can be used to distinguish those factors that are important from those who do not even have a small chance of being important. It typically turns out that even when there are dozens of substances in a life-cycle emissions inventory, only a few of them have at least a 5% chance of accounting for more than 1% of the total score for a given activity. This suggests that at the beginning of the analysis, only order of magnitude estimates for direct emissions and characterization factors are needed. After a first pass, those factors that can not be neglected can be investigated more carefully.

The nominal contributions of each process and environmental exchange are shown in the last column of Table 7-14 and Table 7-13, respectively. The nominal contributions of each environmental problem category are shown in the last row of either table. By specifying the elements of the vectors just cited as uncertain outputs of the Monte Carlo simulation, it is possible to generate distributions for the contributions. Process contributions to the chlorine environmental impact valuation are shown in Figure 7-12. The reader might recall that in the discussion in section 7.3.3 it was said that the contribution of the chloralkali processes to the total impact valuation was minor (less than 4% of total). Figure 7-12 shows that this is true in many states of the world, but it also shows that in some states of the world⁷⁶ the contribution of the mercury cell process can be quite significant. The conclusion that the bulk of the impact is contributed by the combustion of coal in power plants to provide electricity for the processes is unchanged.

Distributions for the contributions of individual chemical emissions to the life-cycle environmental impact indicator of chlorine are shown in Figure 7-13. The figure confirms the observation made in section 7.3.3 that emissions of the combustion products carbon dioxide, sulfur dioxide, nitrogen oxides, and particulate matter account for the bulk of the impact. The figure also shows that although the nominal contribution of mercury emissions was minor (less than 2%), it can be significant depending on how uncertainties are resolved. An interesting point raised by Figure 7-13 is that in 10% of the iterations the effects of sulfur dioxide were valued to be beneficial. This happened when the valuation factor for global warming was sampled at a high end of the distribution and the valuation factor for respiratory effects of particulate matter

⁷⁶ The phrase “state of the world” refers to a particular combination of realizations of the random variables in the model.

was sampled at a low end of the distribution. Sulfate aerosols reflect sunlight and thus have a negative contribution to radiative forcing [22]. Unfortunately they are also quite damaging to human health, so in most of the model iterations the total impact of sulfur dioxide is judged to be adverse.

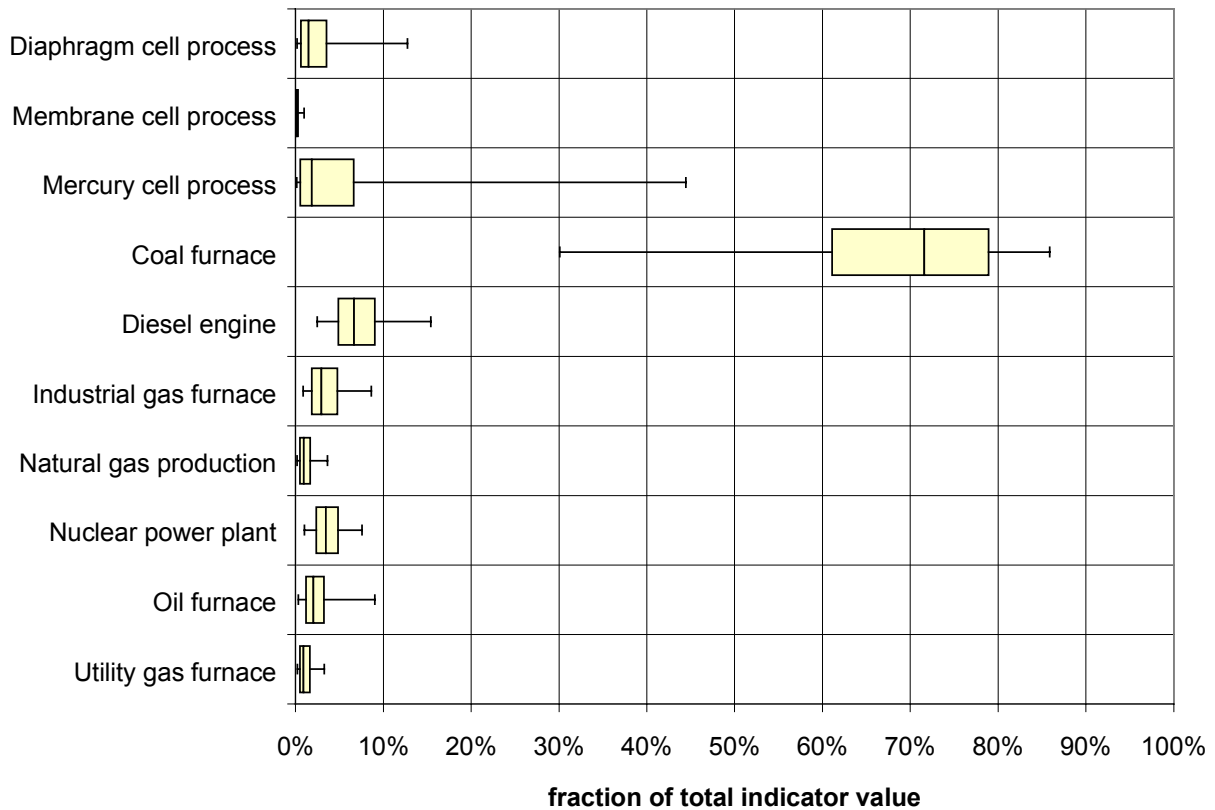


Figure 7-12: Distributions for process contributions to the environmental impact indicator of chlorine production

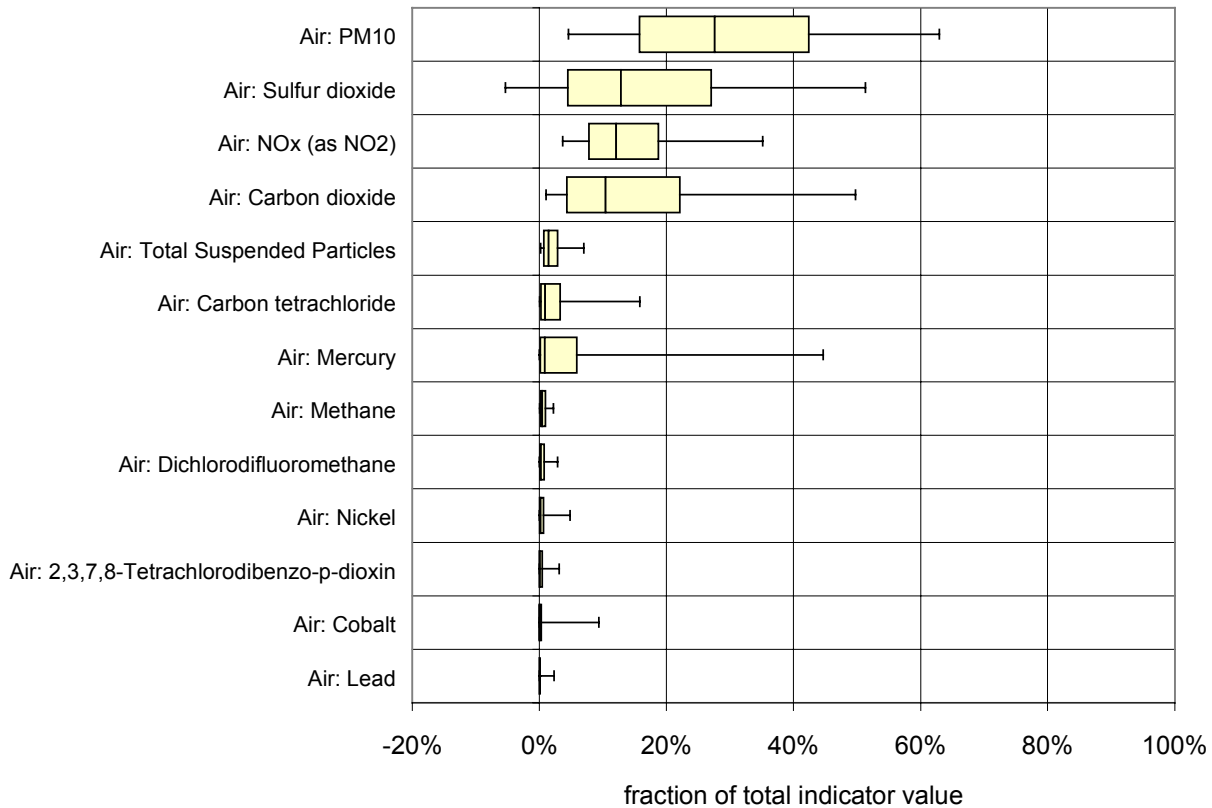


Figure 7-13: Distributions for emission contributions to the environmental impact indicator of chlorine production

Figure 7-14 shows distributions for the contributions of each environmental impact category considered in the example to the total impact valuation of chlorine production. The figure confirms the observation made in section 7.3.3 that the largest contribution comes from the respiratory effects of particulate matter category, followed by the global warming category. Two problem categories with relatively low nominal contributions to the total valuation (human cancer toxicity potential and human non-cancer toxicity potential, each with a nominal contribution of about 2%) have the potential for accounting for a large fraction of the total impact valuation. In particular, the human non-cancer toxicity potential category contributes to more than half of the impact in 10% of the Monte Carlo simulation iterations. In contrast, ozone depletion and photochemical smog creation have virtually no significant chance of having a significant contribution to the total valuation of the environmental impacts associated with chlorine production.

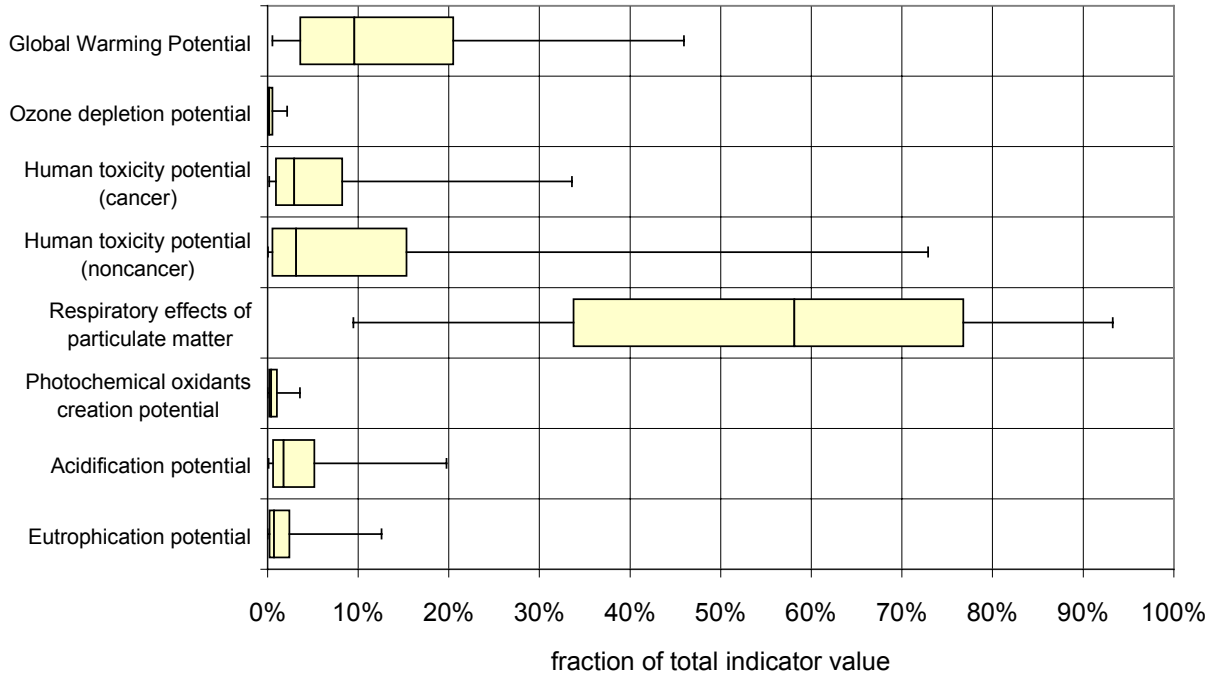


Figure 7-14: Distributions for environmental problem category contributions to the environmental impact indicator of chlorine production

ANALYSIS OF CONTRIBUTIONS TO UNCERTAINTY

Although the preceding examples confirmed many of the initial observations regarding significant contributions to the overall environmental impact indicator, they also raised some interesting questions regarding the potentially important contributions from sources not identified previously. The next step of the analysis is the identification of those parameters in the environmental valuation model that contribute the most to various uncertainties. Uncertainties considered include uncertainty in overall valuations, uncertainty in the ranking between two alternatives, and uncertainties in the contributions of various sources to the overall environmental indicator.

Identification of the factors that drive the uncertainty in the various model outputs of interest can be done using the output data generated during Monte Carlo simulation. Spearman rank correlation coefficients are computed between the outputs of interest and each of the uncertain inputs to the model. Those factors for which the absolute value of their rank

correlation coefficients with respect to the score of interest are closest to one would be targeted for more careful assessment of their probability distributions.

The Spearman rank correlation coefficient r_s between two sampled quantities, x and y , is given by:

$$r_s = \frac{\sum_{i=1}^n \left(\text{rank}(x_i) - \frac{n+1}{2} \right) \left(\text{rank}(y_i) - \frac{n+1}{2} \right)}{\frac{n(n+1)(n-1)}{12}} \quad (7-22)$$

This is a more robust measure of correlation than the linear correlation coefficient, and is a good indicator of dependence when the relationship between factors is monotonically increasing (positive coefficients) or decreasing (negative coefficients)⁷⁷.

As an example, Figure 7-15 shows the rank correlation coefficients between the uncertainty in the overall environmental impact indicator for chlorine production (shown in Figure 7-9) and the uncertainties in the model with which it is most strongly correlated. Valuation factor uncertainties dominate, with the top-ranked uncertainties being the uncertainties in the valuation factors for the respiratory effects, human toxicity potential, and global warming categories. Another significant parametric uncertainty is the uncertainty associated with the *tolerable risk level* parameter used to place cancer slope factors and non-cancer reference doses on the same scale (see eq (6-137)). Several correlated characterization factors for the contributions of several inorganic species to the formation of fine particulate matter follow in importance⁷⁸. The valuation factors for two impact categories that had been shown in Figure 7-14 to be unimportant turn out to be somewhat correlated with the overall impact valuation. The reason for this apparently paradoxical result is that the valuation factors for the ozone depletion and photochemical oxidant creation categories are correlated with all three of the valuation factors with the largest contributions to impact. Their correlation with the overall

⁷⁷ See section 5.3 for a more detailed discussion of Spearman rank correlation coefficients.

⁷⁸ The EPS method literature was used to derive distributions for the characterization factors of inorganics within the “respiratory effects from particulate matter” impact category [23]. In the EPS method the contribution of most inorganics to mortality and morbidity through the particulate matter pathway is estimated with reference to the contribution of sulfur dioxide. As a result, the uncertainty in the characterization factors for most inorganics (expressed as PM₁₀ equivalents) is a combination of the uncertainty in the SO₂ characterization factor and the uncertainty in the equivalence factor used to relate a specific inorganic compound to SO₂. The characterization factors could be decoupled by switching from PM₁₀ to SO₂ as the reference substance for the respiratory effects category.

value of the indicator is mostly a consequence of the drawing of correlated samples in the simulation⁷⁹

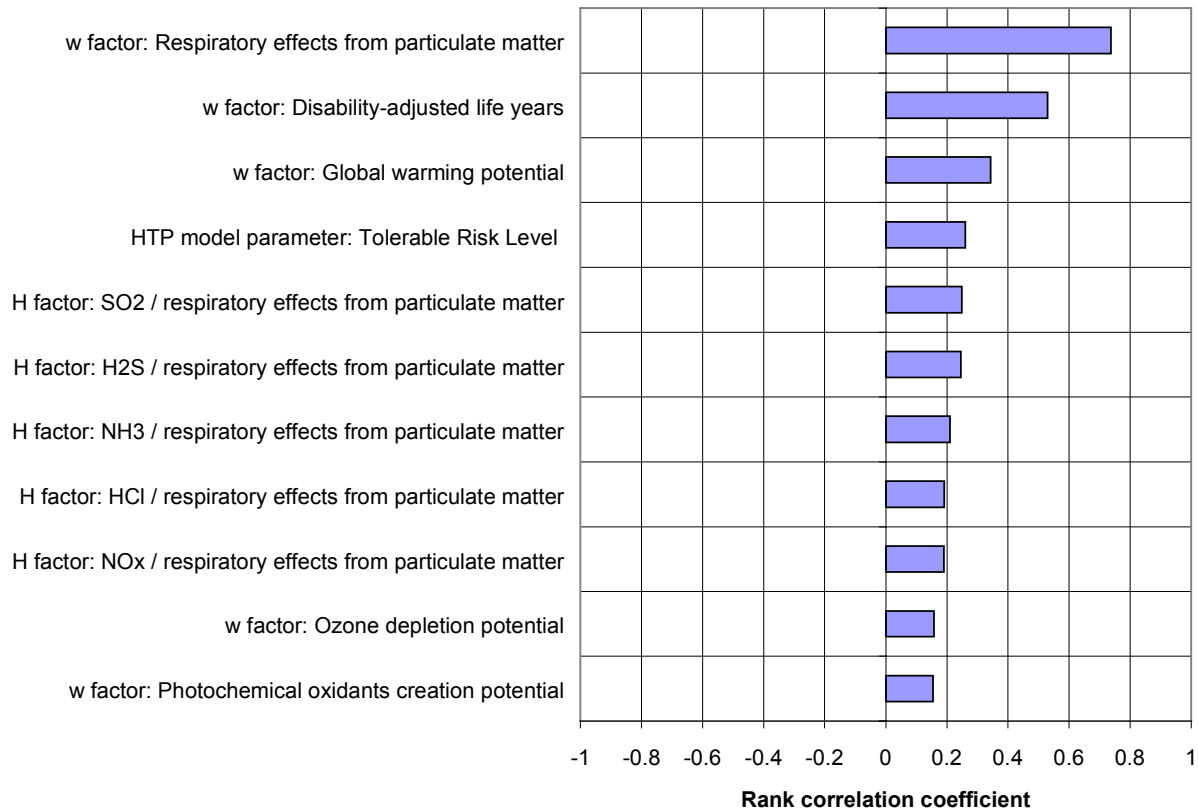


Figure 7-15: Rank correlation coefficients for the uncertainty in the absolute value of the overall environmental evaluation indicator for chlorine production

The next uncertainty examined is the uncertainty in the relative environmental indicator of chlorine production using the diaphragm cell process relative to that using the membrane cell process (the top distribution in Figure 7-11). The relative importance of valuation factor contributions is much lower in this case. The top uncertainties are now the uncertainties in the electricity consumption rate for both processes. Drawing a value for electricity consumption in the membrane cell process from the high end of its distribution tends to make the membrane cell process appear more damaging relative to the diaphragm cell process (the converse also applies). A major difference between the two processes is that the diaphragm cell process requires

⁷⁹ The storage of correlation coefficients in the EnvEvalTool database used as a source of the data for the chlorine example is discussed in section 9.4.1. That section also contains a table showing the correlation coefficients among environmental valuation factors used in this work (Table 9-2).

significantly more steam (thermal energy from the industrial gas furnace) than the membrane cell (see Table 7-1). The most significant contribution to the environmental impact of generating steam in gas fired boilers comes from carbon dioxide's contribution to the greenhouse effect. Because of this, the impact of chlorine production through the diaphragm process tends to be penalized when the valuation for the global warming impact is sampled from the high end of its distribution. The relatively high correlation of the environmental impact ratio with the valuation factor for the ozone depletion category is a byproduct of the correlation between the global warming and ozone depletion valuation factor distributions⁸⁰. Sampling from the high end of the respiratory effects valuation factor distribution tends to decrease the value of the environmental impact ratio, by decreasing the relative importance of the industrial gas furnace emissions as compared to the emissions from the coal furnaces used to generate electricity.

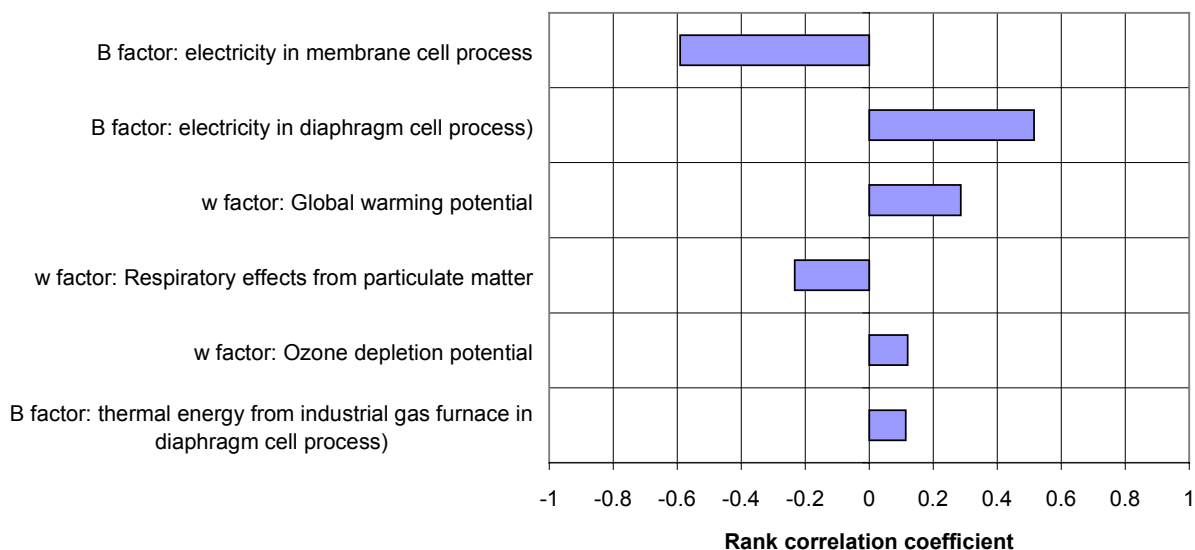


Figure 7-16: Rank correlation coefficients for the uncertainty in the ratio of the life-cycle unit environmental indicator of the diaphragm cell process to that of the membrane cell process

The analysis carried out for the uncertainty in the ratio of environmental impacts of chlorine production using the membrane cell process relative to the mercury cell process is shown in Figure 7-17. Uncertainties in several fate, transport, and toxicological properties of mercury are shown to be highly correlated with the environmental impact ratio. The main route

⁸⁰ The reader is referred again to Table 9-2.

for taking mercury out of the landscape in the multimedia fate and transport model used in this work is sediment burial. This loss mechanism is more effective when mercury partitions into particles (soil-water partition coefficient), when the particles deposit rapidly, and when a larger fraction of the landscape is covered by water. This explains why the last three factors in the figure are positively correlated with the impact ratio membrane cell process / mercury cell process. In contrast, increasing mercury emissions (E factor), increasing its toxicity ($1/RfC$), or increasing mercury's volatility (Henry's law constant) has the effect of increasing the potential for toxic effects from mercury (toxicity potential = exposure \times toxicity).

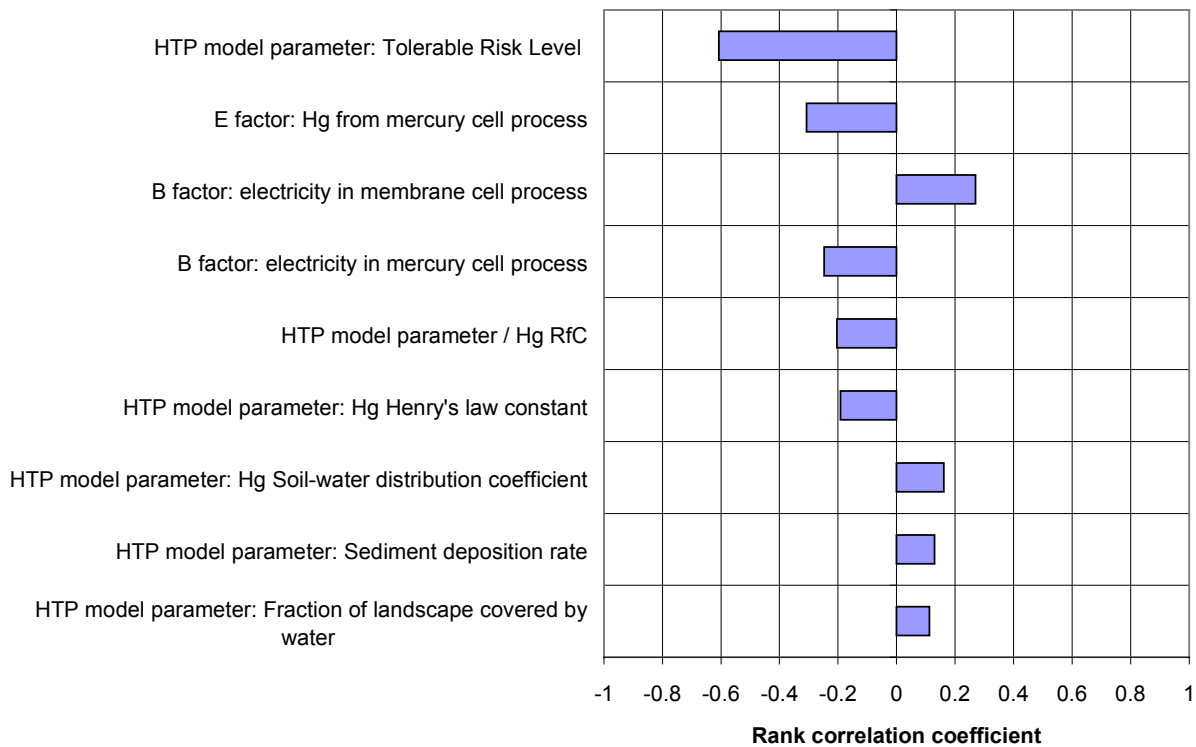


Figure 7-17: Rank correlation coefficients for the uncertainty in the ratio of the life-cycle unit environmental indicator of the membrane cell process to that of the mercury cell process

Not surprisingly, many of the same factors that contribute to make the mercury cell process less attractive than the membrane cell process also contribute to the uncertainty in the contribution of mercury emissions to the overall environmental impact indicator for chlorine production (recall the long tail of the distribution for this contribution shown in Figure 7-13). The rank correlation coefficients are shown in Figure 7-18. The negative coefficients for the

rank correlation with the respiratory effect factors for hydrogen chloride and ammonia are due to their contribution (and to the contribution of the factor for SO_2 , with which they are strongly correlated) to the denominator in eq (7-20).

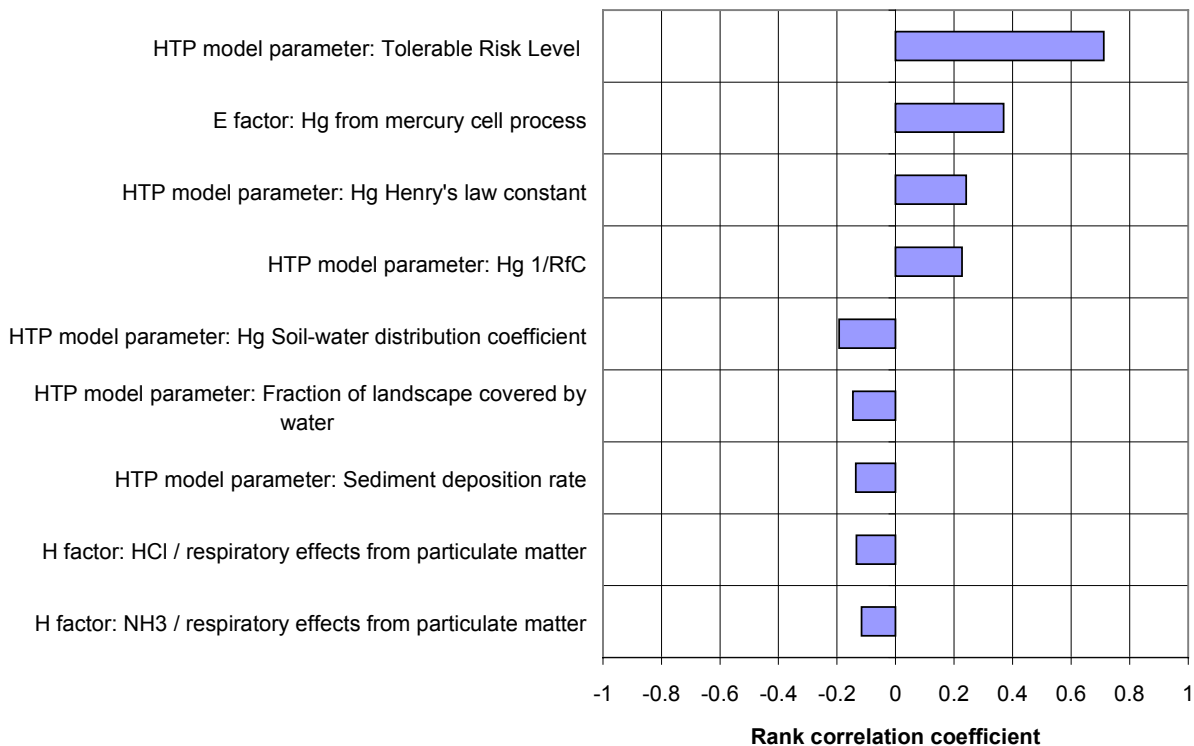


Figure 7-18: Rank correlation coefficients for the uncertainty in the contribution of emissions of mercury to air to the overall environmental impact indicator of chlorine production

Finally, Figure 7-19 analyzes the uncertainty in the contribution of the non-cancer toxic effects on humans impact category to the overall evaluation, which was shown in Figure 7-14 to have the potential to be a significant contributor. In addition to the factors that contribute to increasing the toxic impact valuation for mercury, the toxicity of nitrogen oxides turns out to be an important factor as well. The overwhelming source of uncertainty, however, is the uncertainty in the tolerable risk level subjective assessment parameter.

In summary, the analysis of contributions to uncertainty carried out in this section has identified no more than a couple dozen uncertainties (out of more than 600 used in the model) as uncertainties to which attention should be paid in order to decrease environmental valuation uncertainty and uncertainty in the ranking of alternative processes. The next logical step for this example would be to make a more careful assessment of the willingness of the decision makers

to make tradeoffs between cancer and non-cancer effects (it should be possible to cut down the uncertainty factor from 100 to maybe 10). After that, a compilation of the most recent data on the fate of mercury emissions in the environment should provide the largest opportunity for reducing uncertainty.

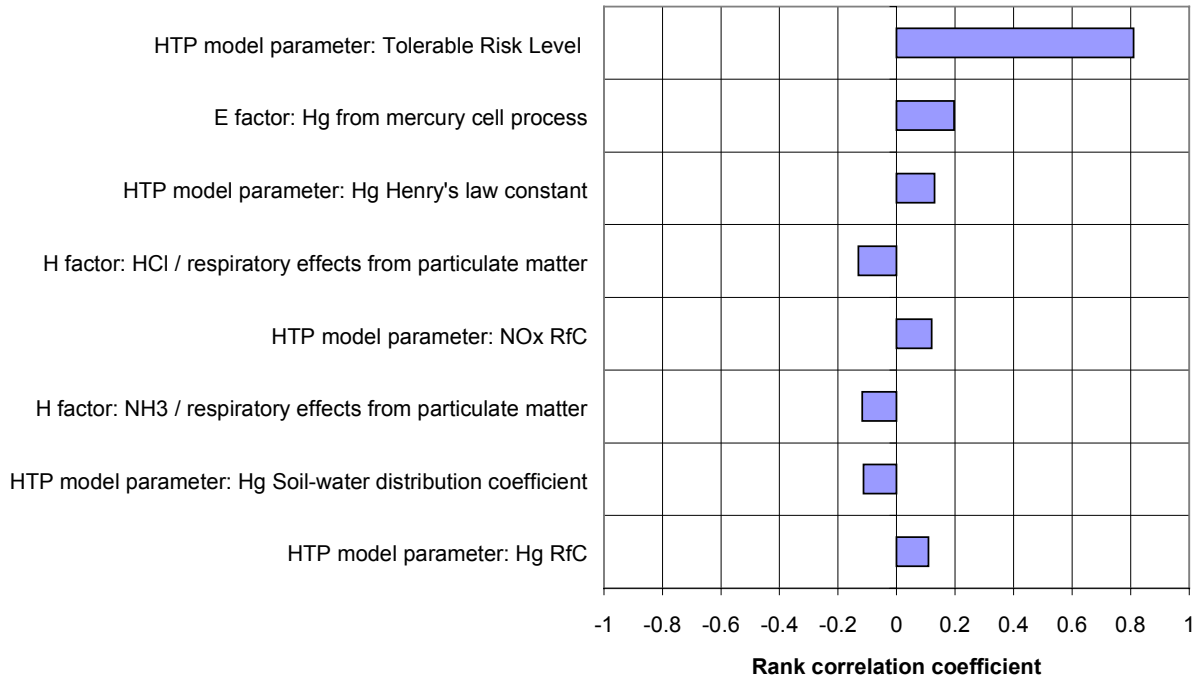


Figure 7-19: Rank correlation coefficients for the uncertainty in the contribution of the human chronic toxicity potential (non-cancer) category to the overall environmental impact indicator of chlorine production

7.5.3 Implementation in practice: Generation of correlated unit impact distributions

It is probably not practical for designers to embed the full PIO-LCA model⁸¹ in the valuation models used to assess and rank alternatives. Fortunately, the problem can be separated in a way that preserves the underlying correlation structure.

Eq (7-11) gives the full expression for calculating the overall environmental impact indicator associated with a vector of final demands.

⁸¹ This is especially true if a full multimedia exposure model is used concurrently to generate some of the characterization factors.

$$\Omega = \mathbf{w}^T \boldsymbol{\psi} = \mathbf{w}^T \mathbf{H}^T \mathbf{e} = \mathbf{w}^T \mathbf{H}^T \mathbf{E} \mathbf{x} = \mathbf{w}^T \mathbf{H}^T \mathbf{E} \mathbf{D} (\mathbf{I} - \mathbf{A}_{\text{prod}})^{-1} \mathbf{d} \quad (7-11)$$

The vector of unit environmental indicators $\boldsymbol{\Omega}_d$ can be generated independently of any design:

$$\boldsymbol{\Omega}_d = \mathbf{w}^T \mathbf{H}^T \mathbf{E} \mathbf{D} (\mathbf{I} - \mathbf{A}_{\text{prod}})^{-1} \quad (7-15)$$

Therefore, if a joint probability distribution of the unit environmental indicators in vector $\boldsymbol{\Omega}_d$ could be generated that preserved the correlation structure of the full PIO-LCA model, then the uncertainty in the overall environmental impact indicator would be obtained by propagating the uncertainty in the model

$$\Omega = \boldsymbol{\Omega}_d \mathbf{d} \quad (7-23)$$

where the vector \mathbf{d} could be the uncertain output of a process model. The main advantage of accomplishing this would be to decrease dramatically the number of distribution functions in the environmental valuation model, from the hundreds typically present in a combined PIO-LCA + Human Toxicity Potentials model to a handful of correlated unit indicator distributions.

In this work, the multivariate normal copula distribution [24] has been used to summarize the results of Monte Carlo simulations into joint probability distributions of unit environmental indicators. Details on the procedure are provided in section 8.3.

7.6 Discussion

7.6.1 Computational cost of refining the analysis

As shown by the illustrative applications, the PIO-LCA method allows LCA users to refine the analysis by incorporating new data elements as they become available. This is done by adding columns and rows to the data input matrices and vectors (\mathbf{B} , \mathbf{C} , \mathbf{E} , \mathbf{F} , \mathbf{H} , \mathbf{p} , and \mathbf{w}), or by filling zero entries in the existing matrices. As the problem becomes more complex, the matrices may grow in size or become less sparse, but the number of matrices used in the analysis does not change. The contribution and sensitivity matrices allow the analyst to determine whether the addition of a particular product, process, or environmental exchange changes the results significantly. Details of a Visual Basic implementation of the method in Microsoft Excel spreadsheets are given in Appendix C. The tool was used to generate automatically all the output matrices shown in this chapter.

7.6.2 Relationship to linear programming formulations

DERIVATION OF LP FORMULATION FROM PIO-LCA MATRICES AND VECTORS

The data required by the PIO-LCA methodology can be used as input to the following optimization problem:

$$\begin{aligned}
 \text{Min}_{\mathbf{x}} \quad & \mathbf{w}^T \mathbf{H}^T \mathbf{E} \mathbf{x} \\
 \text{s.t.} \quad & (\mathbf{C} - \mathbf{B}) \mathbf{x} \geq \mathbf{d} \\
 & \mathbf{x} \geq \mathbf{0} \\
 & \mathbf{C} \text{Diag}(\mathbf{x}) \geq \text{Diag}(\mathbf{C}\mathbf{x}) \mathbf{F}_{\min}^T
 \end{aligned} \tag{LP1}$$

where the matrix \mathbf{F}_{\min} can be used to place constraints on process throughputs. Specifying $\mathbf{F}_{\min} = \mathbf{F}$ forces processes to operate in such a way that products that can be supplied by more than one process are produced by the different processes in the proportions specified in the market share matrix \mathbf{F} . Unit indicators for each product would be given by the reduced costs on the demand constraints [25].

The linear programming (LP) formulation is useful for identifying changes in prevailing process market shares that would decrease the overall environmental impact indicator. To illustrate the use of the LP formulation and to compare it with the results of the allocation method, problem (LP1) is solved three times for the chlorine production example: (i) setting $(F_{\min})_{ji} = F_{ji}$ for the products chlorine and electricity (i.e. current market shares), (ii) chlorine process market share constraint removed, and (iii) setting $\mathbf{F}_{\min} = \mathbf{0}$ (no market share constraints). In case (i) there is no flexibility for switching among chlor-alkali or electricity processes. As shown in Table 7-21, the entries in the vector of process throughputs obtained using the LP formulation have higher values than the entries in the corresponding vector obtained using the matrix inversion method on the example. The reason is that the matrix inversion method incorporates allocation rules, so that the process throughputs (and the associated environmental impact scores) that would be obtained with the LP formulation are divided among the three products chlorine, sodium hydroxide and hydrogen. Note that the product $(\mathbf{C}-\mathbf{B})\mathbf{x}$ has three nonzero entries (one for each coproduct), while the demand vector \mathbf{d} has only an entry for chlorine. The unit indicator for chlorine would also be higher under the LP formulation than

under the PIO-LCA formulation, since the demand constraints for sodium hydroxide and hydrogen are non-binding. In effect, the LP formulation allocates all of the impacts of a multiproduct process to the product for which demand is equal to production rate (the product for which the demand is a binding constraint).

Case (ii) represents the problem of choosing the best process for manufacturing chlorine. The solution to the LP problem uses 1000 throughput units of the membrane process, with no throughput from either the mercury or the diaphragm processes. The total impact indicator is 5% lower than in case (i).

In case (iii) the LP formulation is allowed to choose among the different electricity processes as well as from the different chlor-alkali processes. Not surprisingly, electricity is only generated at hydroelectric plants, since the **E** matrix does not include any nonzero entries for that process. The total impact indicator is now 97% lower than in case (i). This is consistent with earlier results that showed that a large portion of the life-cycle environmental impact of chlorine manufacturing is due to the processes involved in electricity generation.

Table 7-21: Linear programming results for the chlorine LCA example

PIO-LCA solution	LP solution			
	F _{min} = F for electricity, F _{min} = 0 for all other products F _{min} = 0			
	Process throughputs: x			
PROCESSES				
Brine pumping	691.3	1650.0	1650.0	1650.0
Chloralkali production (diaphragm cell process)	326.8	780.0	0.0	0.0
Chloralkali production (membrane cell process)	25.1	60.0	1000.0	1000.0
Chloralkali production (mercury cell process)	67.0	160.0	0.0	0.0
Coal furnace	268.7	641.3	643.0	0.0
Coal production	268.7	641.3	643.0	0.0
Coal-fired power plant	775.0	1849.8	1854.6	0.0
Diesel engine	713.6	1703.2	1707.7	0.0
Diesel fuel production	17.1	40.9	41.0	0.0
Gas-fired power plant	123.1	293.8	294.5	0.0
Hydroelectric plant	147.4	355.1	356.0	3221.4
Industrial gas furnace	3.0	7.1	1.5	1.3
Methane reforming	0.0	0.0	0.0	0.0
Natural gas production	81.0	193.4	84.7	25.6
Nuclear power plant	271.9	648.9	650.6	0.0
Oil furnace	0.3	0.8	0.8	0.0
Oil production	24.7	58.9	59.0	0.0
Oil-fired power plant	33.8	80.7	80.9	0.0
Railroad transport	125.5	299.6	300.4	0.0
Utility gas furnace	1.2	2.9	2.9	0.0
PRODUCTS				
	Net production: (C-B)x			
Chlorine (kg)	419	1000	1000	1000
Coal (kg)	0	0	0	0
Diesel fuel (kg)	0	0	0	0
Electricity (MJ)	0	0	0	0
Hydrogen (kg)	12	28	28	28
Mechanical energy from diesel engines (MJ)	0	0	0	0
Natural gas (kg)	0	0	0	0
Oil (kg)	0	0	0	0
Railroad transport (kg-km)	0	0	0	0
Salt from brine (kg)	0	0	0	0
Sodium hydroxide (kg)	469	1120	1120	1120
Thermal energy from coal furnace (MJ)	0	0	0	0
Thermal energy from industrial gas furnace (MJ)	0	0	0	0
Thermal energy from oil furnace (MJ)	0	0	0	0
Thermal energy from utility gas furnace (MJ)	0	0	0	0
	Overall indicator: w^TH^TEx			
Total for all process throughputs	\$ 180	\$ 429	\$ 409	\$ 12

COMPARISON WITH OTHER LP FORMULATIONS

Rudd and coworkers [26] built a linear programming model of the petrochemical industry. The model includes 297 chemical processes and 203 products. The constraints of the model are given by:

$$\begin{aligned}
 F_i + \sum_{j=1}^M a_{ij} X_j &\geq D_i \\
 F_i &\leq S_i \\
 X_j &\leq B_j \\
 F_i, X_j &\geq 0
 \end{aligned}
 \tag{LP2}$$

Given an objective function, the model seeks the best combination of values for the process operation levels X_j and feedstock purchases F_i such that the product demands D_i are satisfied within the specified process capacity limits B_j and feedstock supply availabilities S_i . Fathi-Afshar and Yang [27] applied this model to the problem of identifying the petrochemical industry structure with the lowest production cost and lowest gross toxicity. Emissions of a particular toxic substance from the chemical processes in the network were assumed to be proportional to the total production requirements for that chemical and to its vapor pressure. The inverse of the ACGIH threshold limit value (TLV) was used as a toxicity potency factor. Sensitivity analysis was used to rank chemicals with respect to the total contribution (direct plus indirect) of a unit mass of chemical final demand to the overall toxicity indicator score, by obtaining the reduced cost of the demand constraints when the objective function is to minimize the overall toxicity indicator score.

In the present formulation, the coefficients a_{ij} are divided among the make and use matrices, with the positive coefficients being incorporated into the make matrix and the negative coefficients into the use matrix (as positive numbers). Product demands are incorporated into the product demand vector, and feedstock purchases from exogenous sources are not permitted (this is equivalent to setting $S_i = 0$ in Rudd's model), since in life cycle assessment one is interested in accounting for the environmental impacts associated the entire process and product network, including the production of feedstocks. Process throughput constraints may be placed in the formulation introduced here either indirectly using the F_{\min} matrix (particularly for the case of process throughputs outside of the decision-maker's control) or directly by using vectors of process throughput upper and lower bounds.

7.6.3 Specifying appropriate market shares

In the example presented here, the market shares of different power plants in the generation of electricity consumed by the chlor-alkali processes have a very significant impact on the calculated social cost of chlorine production. The question arises of what the appropriate market shares are that should be used for evaluating the impact of marginal increases in the demand for electricity. More generally, the relevant question is what rules should be used to specify market shares to appropriately reflect changes in environmental exchanges due to marginal increases in the demand for products and services. The shares of the different primary

energy sources in the planned capacity additions (1998-2007) to the United States power grid are 88.7% natural gas, 4.9% coal, 2.8% petroleum, 1.5% hydro, 0% nuclear, and 2.2% waste heat [28]. With respect to chlor-alkali production, it is likely that the majority of capacity additions will take place using the membrane cell process. Assuming a 100% capacity expansion market share for the membrane cell process and using the capacity expansion market shares listed above for the electricity generation processes, yield a much lower indicator for chlorine production (Figure 7-20). This example shows that the choice of basis for market shares can make a substantial difference in the analysis. It is suggested that capacity expansion market shares be used for products with increasing annual production. For products with stable or decreasing annual production it appears more appropriate to use average market shares, since demand for a product with decreasing production would tend to support continued operation of existing plants.

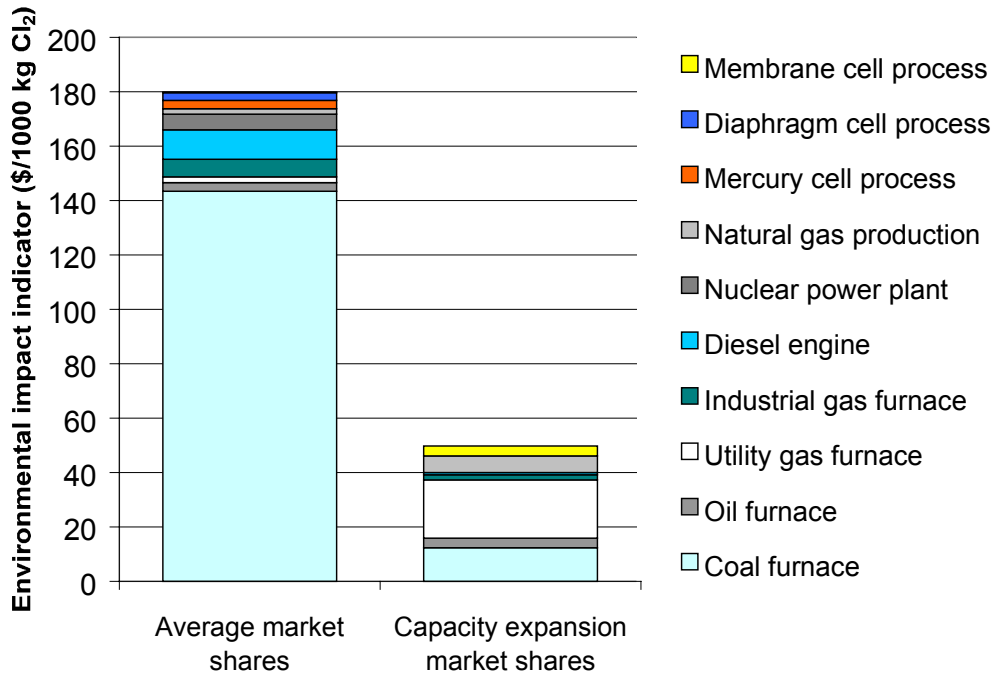


Figure 7-20: Impact of product market share specifications on the environmental impact valuation of chlorine production

7.7 Conclusions

The PIO-LCA method is a powerful tool for estimating environmental impact indicators for products and services. It allows designers not only to produce emission inventories and environmental impact scores, but also to trace environmental exchanges and contributions to the

indicators back to the processes that generate them. It also provides a flexible mechanism for storing environmental exchange data in a way that allows easy updating when new information becomes available. The allocation rules used by PIO-LCA are explicit and are directly related to the cause for processes to operate. A major benefit of the method is its ability to preserve correlations in unit environmental indicators for different products, processes, and environmental exchanges. As described in Chapter 4, preserving correlation structure is key to reducing decision uncertainty in the presence of large uncertainties in valuation models. The matrix manipulations shown in this chapter have been used to develop a PIO-LCA macro add-on to Microsoft Excel⁸². Other software tools have been developed to link the PIO-LCA method with the environmental information management system described in Chapter 9⁸³.

⁸² See Appendix C

⁸³ For a description of the tools, see Appendix B

7.8 Appendix: Vector and matrix glossary

Matrix or vector	Description	Rows	Columns	Example size
$A_{\text{prod}} = \mathbf{BD}$	Product-by-product direct requirements matrix	Products	Products	15 by 15
$A_{\text{proc}} = \mathbf{DB}$	Process-by-process direct requirements matrix	Processes	Processes	20 by 20
\mathbf{B}	Use matrix	Products	Processes	15 by 20
\mathbf{C}	Make matrix	Products	Processes	15 by 20
\mathbf{D}	Process-by-product throughput matrix	Processes	Products	20 by 15
\mathbf{d}	Demand vector	Products		15 by 1
$\text{Diag}(\mathbf{e}) \mathbf{H}$	Matrix of contributions of environmental exchanges to impact category scores	Exchanges	Impact categories	31 by 8
$\text{Diag}(\mathbf{e}) \mathbf{H} \text{Diag}(\mathbf{w})$	Matrix of contributions of environmental exchanges and impact categories to overall valuation	Exchanges	Impact categories	31 by 8
$\text{Diag}(\mathbf{e}) \mathbf{H}\mathbf{w}$	Vector of contributions of environmental exchanges to overall valuation	Exchanges		31 by 1
$\text{Diag}(\mathbf{x}) \mathbf{E}^T \mathbf{H}$	Vector of contributions of process throughputs to impact category scores	Processes	Impact categories	20 by 8
$\text{Diag}(\mathbf{x}) \mathbf{E}^T \mathbf{H} \text{Diag}(\mathbf{w})$	Matrix of contributions of process throughputs and impact categories to overall valuation	Processes	Impact categories	20 by 8
$\text{Diag}(\mathbf{x}) \mathbf{E}^T \mathbf{H}\mathbf{w}$	Vector of contributions of process throughputs to overall valuation	Processes		20 by 1
$\text{Diag}(\mathbf{w}) \mathbf{H}^T \mathbf{E}\mathbf{x}$	Vector of contributions of impact category scores to overall scores	Impact categories		8 by 1
\mathbf{E}	Environmental exchanges matrix	Exchanges	Processes	31 by 20
$\mathbf{E} \text{Diag}(\mathbf{x})$	Matrix of direct process contributions to the total environmental exchanges vector	Exchanges	Processes	31 by 20
$\mathbf{E}(\mathbf{I} - \mathbf{DB})^{-1} \text{Diag}(\mathbf{x})$	Matrix of direct plus indirect process contributions to the total environmental exchanges vector	Exchanges	Processes	31 by 20
$\mathbf{e} = \mathbf{E}\mathbf{x}$	Total environmental exchanges vector (known as the life cycle inventory in LCA)	Exchanges		31 by 1
\mathbf{F}	Market share matrix	Processes	Products	20 by 15
\mathbf{G}	Allocation matrix	Processes	Products	20 by 15
\mathbf{H}	Potency factors matrix	Exchanges	Impact categories	31 by 8
$(\mathbf{I} - \mathbf{DB})^{-1}$	Process-by-process total requirements matrix	Processes	Processes	20 by 20
$(\mathbf{I} - \mathbf{A}_{\text{prod}})^{-1}$	Product-by-product total requirements matrix	Products	Products	15 by 15
\mathbf{p}	Product price vector	Products		15 by 1

Matrix or vector	Description	Rows	Columns	Example size
$\mathbf{q} = (\mathbf{I} - \mathbf{A}_{\text{prod}})^{-1} \mathbf{d}$	Total product requirements vector	Products		15 by 1
$\mathbf{q}_{\text{direct}} = (\mathbf{I} + \mathbf{A}_{\text{prod}}) \mathbf{d}$	Direct product requirements vector	Products		15 by 1
$\mathbf{x} = \mathbf{D} \mathbf{q}$	Total process throughput requirements vector	Processes		20 by 1
$\mathbf{x}_{\text{direct}} = \mathbf{D} \mathbf{d}$	Direct process throughput requirements vector	Processes		20 by 1
\mathbf{w}	Valuation vector	Impact categories		8 by 1
$\Omega = \mathbf{w}^T \boldsymbol{\Psi}$	Overall valuation (scalar)			1 by 1
$\Omega_{\mathbf{d}} = (\mathbf{I} - \mathbf{A}_{\text{prod}})^{-1} \mathbf{D}^T \mathbf{E}^T \mathbf{H} \mathbf{w}$	Vector of overall impact indicators per unit of product	Products		15 by 1
$\Omega_{\mathbf{e}} = \mathbf{H} \mathbf{w}$	Vector of overall impact indicators per unit of environmental exchange	Exchanges		31 by 1
$\Omega_{\mathbf{x}} = (\mathbf{I} - \mathbf{D} \mathbf{B})^{-1} \mathbf{E}^T \mathbf{H} \mathbf{w}$	Vector of overall total (direct + indirect) impact indicators per unit of process throughput	Processes		20 by 1
$\Omega_{\mathbf{x}_{\text{direct}}} = \mathbf{E}^T \mathbf{H} \mathbf{w}$	Vector of overall direct impact indicators per unit of process throughput	Processes		20 by 1
$\Omega_{\mathbf{x}} = (\mathbf{I} - \mathbf{D} \mathbf{B})^{-1} \mathbf{E}^T \mathbf{H} \mathbf{w}$	Vector of overall total (direct + indirect) impact indicators per unit of process throughput	Processes		20 by 1
$\boldsymbol{\Psi} = \mathbf{H}^T \mathbf{e}$	Vector of environmental impact category indicators	Impact categories		8 by 1
$\boldsymbol{\Psi}_{\mathbf{d}} = (\mathbf{I} - \mathbf{A}_{\mathbf{c}})^{-1} \mathbf{D}^T \mathbf{E}^T \mathbf{H}$	Matrix of impact category indicators per unit of product	Products	Impact categories	15 by 8
$\boldsymbol{\Psi}_{\mathbf{x}_{\text{direct}}} = \mathbf{E}^T \mathbf{H}$	Matrix of direct impact category indicators per unit of process throughput	Processes	Impact categories	20 by 8
$\boldsymbol{\Psi}_{\mathbf{x}} = (\mathbf{I} - \mathbf{D} \mathbf{B})^{-1} \mathbf{E}^T \mathbf{H}$	Matrix of total (direct + indirect) impact category indicators per unit of process throughput	Processes	Impact categories	20 by 8

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Chapter 8 **Uncertainty propagation strategies**

8.1 Introduction

Most chemical processes built today are designed using process flowsheet models. Several companies license user-friendly software that enables designers to create a working process flowsheet model after a few hours of work.

One unintended consequence of the availability of these packages is that inexperienced engineers tend to place too much faith on the simulation results, without realizing that these results might be subject to considerable uncertainties. The most popular packages include large physical property data banks, and it is tempting to rely on these without first validating model predictions. Experienced designers know better, and in order to minimize the risk of designing a process that does not work as planned, they tend to add overdesign factors (also known as safety factors) to compensate for the uncertainty.

In recent years reports of the application of uncertainty propagation to process models have emerged from the academic community. In one of the earliest examples, researchers at Carnegie Mellon University added Monte Carlo simulation capabilities to the public version of the Aspen process simulator [1]. The tool was applied to the simulation of an integrated coal gasification combined cycle electricity generation system [2,3] in a contract for the U.S. Department of Energy. The researchers reported that it took in the order of 12 hours to run 100 Monte Carlo iterations on their model.

The impact of uncertainties in thermodynamic parameters on process designs has been studied through the propagation of uncertainties in unit operation model using Monte Carlo simulation [4,5]. A study of the design of a liquefied natural gas (LNG) plant through Monte Carlo simulation of a specially designed flowsheet program included stochastic optimization (i.e. decision variable optimization considering uncertainty) [6]. Several days of computer time were needed to converge to the optimum level of the decision variables.

Monte Carlo simulation has also been applied to differential-algebraic equation dynamic simulators [7,8]. In addition, several approaches to the consideration of uncertainty in mathematical programming representations of process design problems have been developed [9-11], but their application remains the domain of a small group of experts.

The author believes that process design will continue to be based on flowsheet simulators for the foreseeable future. These simulators offer many advantages to designers, including graphical interfaces and extensive libraries of unit operation models and physical property data. The propagation of parameter uncertainties through these models is not something done routinely in industry today, mainly because of the amount of time needed to run the models. This chapter explores procedures for reducing the amount of time required to carry out uncertainty propagation and uncertainty analysis in process models.

Even with the rapid advances in hardware and software, uncertainty propagation of flowsheet models through Monte Carlo simulation is not yet practical for most industrial-strength problems due to the amount of time needed to run the model hundreds of times. The goal of this chapter is to reduce the barriers to uncertainty propagation and uncertainty analysis of process models taking environmental concerns into consideration. This is done through the use of two tools: (a) the generation of spreadsheet process metamodels through the use of the deterministic equivalent modeling method (DEMM), and (b) the generation of multivariate unit environmental indicators that preserve most of the correlation information of a full PIO-LCA environmental evaluation model.

8.2 Development of spreadsheet metamodels for stochastic optimization of flowsheet models

8.2.1 Introduction to the deterministic equivalent modeling method

Our research group at MIT has accumulated considerable experience in the application of the deterministic equivalent modeling method (DEMM) for the uncertainty analysis of models of complex systems [12-16]. An excellent description of the method is provided in Cheng Wang's dissertation [15], to which the reader is referred for more background and details than the short summary given here.

The centerpiece of the method is the approximation of a random variable that is itself a function of other random variables by a polynomial chaos expansion (i.e. a truncated infinite series written in terms of orthogonal polynomials of random variables). In contrast to many other methods, the collocation approach of the DEMM method can be applied to models of the *black box* type (i.e. models for which the model equations are not available to the analyst). Flowsheet models are a prime example of models used as black box models, where designers are rarely aware of every single equation used by the flowsheeting software to build a model.

The polynomials used as a basis for the expansion are chosen depending on the probability distribution family to which the random variables used as model inputs belong. For example, consider a model whose output Y depends on random variables X_1 and X_2 :

$$Y = g(X_1, X_2) \quad (8-1)$$

Assume, without loss of generality, that X_1 and X_2 are normally distributed random variables. Because the input variables are normally distributed, each of them can be represented by a two-term polynomial of a unit normal random variable:

$$x_1 = a_1 + b_1\xi_1 \quad (8-2)$$

$$x_2 = a_2 + b_2\xi_2 \quad (8-3)$$

In the expressions above, the coefficients of the expansion correspond to the first two moments of the distribution (i.e. a_i is the mean of X_i and b_i its standard deviation). ξ_1 and ξ_2 are unit normal random variables with zero mean and unit standard deviation.

Since the input random variables were represented by polynomials in ξ_1 and ξ_2 , the polynomial chaos expansion of Y is made in terms of polynomials of the random variables ξ_1 and ξ_2 :

$$y = \sum_{j=1}^N y_j H_j(\xi_1, \xi_2) \quad (8-4)$$

where the H_j are a special class of orthogonal polynomials known as *Hermite polynomials*. Assume we are interested in developing a second order polynomial approximation. In that case, the expansion will have six terms:

$$H_1(\xi_1, \xi_2) = 1 \quad (8-5)$$

$$H_2(\xi_1, \xi_2) = \xi_1 \quad (8-6)$$

$$H_3(\xi_1, \xi_2) = \xi_2 \quad (8-7)$$

$$H_4(\xi_1, \xi_2) = \xi_1^2 - 1 \quad (8-8)$$

$$H_5(\xi_1, \xi_2) = \xi_1 \xi_2 \quad (8-9)$$

$$H_6(\xi_1, \xi_2) = \xi_2^2 - 1 \quad (8-10)$$

To generate the approximation to the original response $y = g(x_1, x_2)$, the model is solved six times for six pairs of different values (ξ_1, ξ_2) . These pairs of values are known as *collocation points* in the method, and are constructed from the zeros of the next order Hermite polynomial. In this case, the collocation points are:

$$(0,0) \qquad (1.732,0) \qquad (0,1.732)$$

$$(1.732,1.732) \qquad (-1.732,0) \qquad (0,-1.732)$$

The coefficients of the expansion (i.e. the y_j) are found by solving the system of equations

$$g(a_1 + 0 \cdot b_1, a_2 + 0 \cdot b_2) = \sum_{j=1}^6 y_j H_j(0,0) \quad (8-11)$$

$$g(a_1 + 1.732 \cdot b_1, a_2 + 0 \cdot b_2) = \sum_{j=1}^6 y_j H_j(1.732,0) \quad (8-12)$$

$$g(a_1 + 0 \cdot b_1, a_2 + 1.732 \cdot b_2) = \sum_{j=1}^6 y_j H_j(0,1.732) \quad (8-13)$$

$$g(a_1 + 1.732 \cdot b_1, a_2 + 1.732 \cdot b_2) = \sum_{j=1}^6 y_j H_j(1.732,1.732) \quad (8-14)$$

$$g(a_1 - 1.732 \cdot b_1, a_2 + 0 \cdot b_2) = \sum_{j=1}^6 y_j H_j(-1.732,0) \quad (8-15)$$

$$g(a_1 + 0 \cdot b_1, a_2 - 1.732 \cdot b_2) = \sum_{j=1}^6 y_j H_j(0,-1.732) \quad (8-16)$$

Six model runs are needed to obtain the terms on the left hand side of eqs (8-11)-(8-16).

The goodness of fit of the model is evaluated by solving the model at the collocation points for the next order of expansion approximation, and comparing the model response with the predictions of eq (8-4) with $N=6$ and the y_j values given by the solution to eqs (8-11)-(8-16). Figure 8-1 [15] shows a flow diagram for the implementation of the collocation approach of DEMM to black box models. Dr. Menner Tatang has developed a computer program (known as

demmucom) that carries out all the calculations and determinations shown in the diagram [14]. It is up to the user to make judgment calls with respect to which uncertain inputs should be included in the model, and with respect to whether the model has acceptable error and/or acceptable dimensionality.

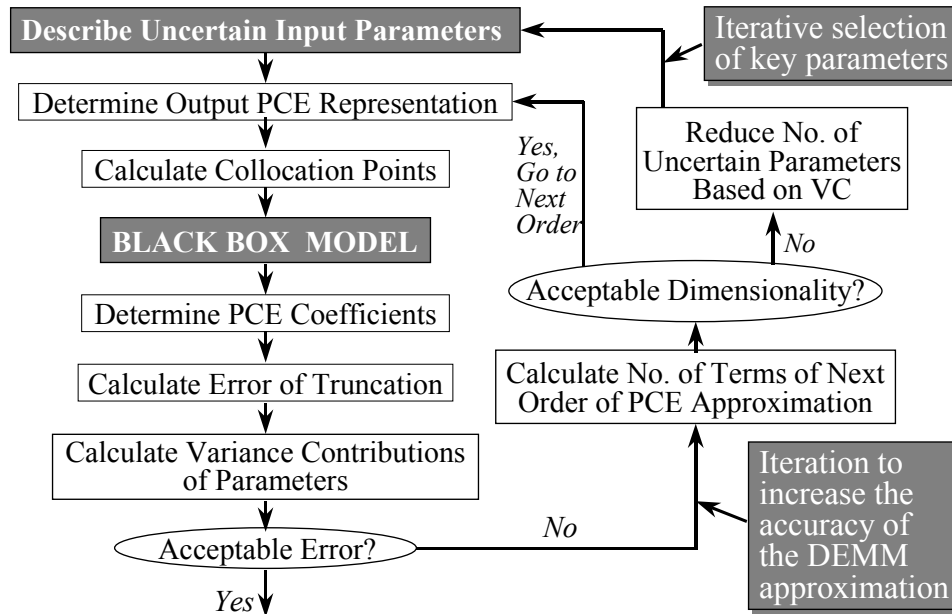


Figure 8-1: DEMM flow diagram (collocation approach)⁸⁴

If the uncertain response of interest is smooth and regular with respect to each of the uncertain inputs, then a highly accurate polynomial representation of the original model can be produced with a small number of model runs. Full probability distributions for the output variables of interest can be recovered by running a Monte Carlo simulation on the polynomial chaos expansion model. Even though a Monte Carlo simulation is still involved, there are large computational advantages to running a Monte Carlo simulation on a model that only takes a fraction of a second to calculate when compared to running a Monte Carlo simulation on a model that might take several minutes (or even hours) to converge. An additional advantage of the method is that variance contribution analysis (i.e. the attribution of contributions to variance in the output to each of the uncertain inputs) can be made directly by arithmetic manipulations of the coefficients in the expansion.

⁸⁴ Reproduced from reference [15]

8.2.2 Extension to generate models that respond to decision variables as well as to uncertain inputs

In some aspects, the deterministic equivalent modeling method may be seen as a member of a class of uncertainty propagation methods known as *response surface methods* [17]. The difference between Monte Carlo simulation and response surface methods may be explained using the diagram shown in Figure 8-2 [15] for a model that depends on two uncertain parameters. In Monte Carlo simulation, random values of the parameters x and y are drawn with probability proportional to that of the probability density function of x and y , respectively. The model $g(x,y)$ is evaluated for each pair of values (x,y) drawn by the Monte Carlo sampling routine. The solution to the model at each point is stored. As the number of samples drawn increases, the histogram of model responses approximates the probability density function of the random variable z . As the number of samples increases to infinity, the entirety of the response surface over the domain of the parameter distributions will be sampled. In response surface methods, the model $g(x,y)$ is evaluated at a small number of (x,y) points. A response surface is then fit through those points. The model is run at a new set of points and the predictions of the response surface approximation are compared with the model response. If the errors are small, the original model is set aside, and Monte Carlo simulation is carried out on the response surface model instead of on the original model to obtain an estimate of the probability density function of the output variable z .

There are three key issues related to response surface modeling [17]:

- Selection of the small discrete set of input variable values to run the model
- Screening the uncertain inputs to identify which ones need to be modeled as uncertain inputs
- Selection of a functional form for the response surface

The DEMM approach provides specific answers to the first and third issues. It also provides valuable information to help the user in resolving the second issue through the iterative parameter selection loop shown in Figure 8-1. In particular, *the collocation approach criterion for the selection of input variable sets strives to obtain a model that is most accurate in the high probability region of input parameter space.*

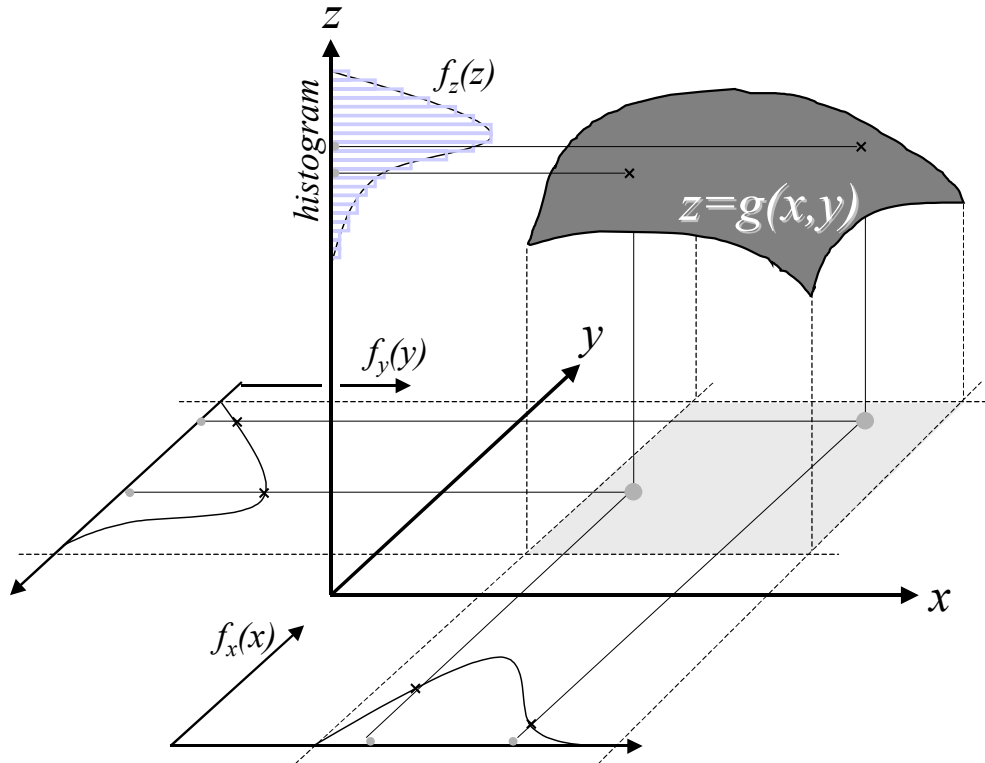


Figure 8-2: Explicit access to a model response surface through the Monte Carlo method⁸⁵

In this thesis, DEMM has been used as a response surface method to generate polynomial representations of flowsheet models that respond to changes in uncertain parameters *as well as to changes in decision variables*. The polynomial model is then implemented on spreadsheet software (Microsoft Excel) where it can be combined with spreadsheet-based economic and environmental impact valuation models. During Monte Carlo simulation, decision variable values are held constant while uncertain input parameters vary according to their specified probability distributions. In the approach taken in this work, decision variables are represented by uniform distributions over their allowed domains, so that DEMM will attempt to generate a response surface polynomial chaos expansion (PCE) metamodel that is equally accurate over the entire decision variable domain. The approach is schematically shown in Figure 8-3.

⁸⁵ Reproduced from reference [15]

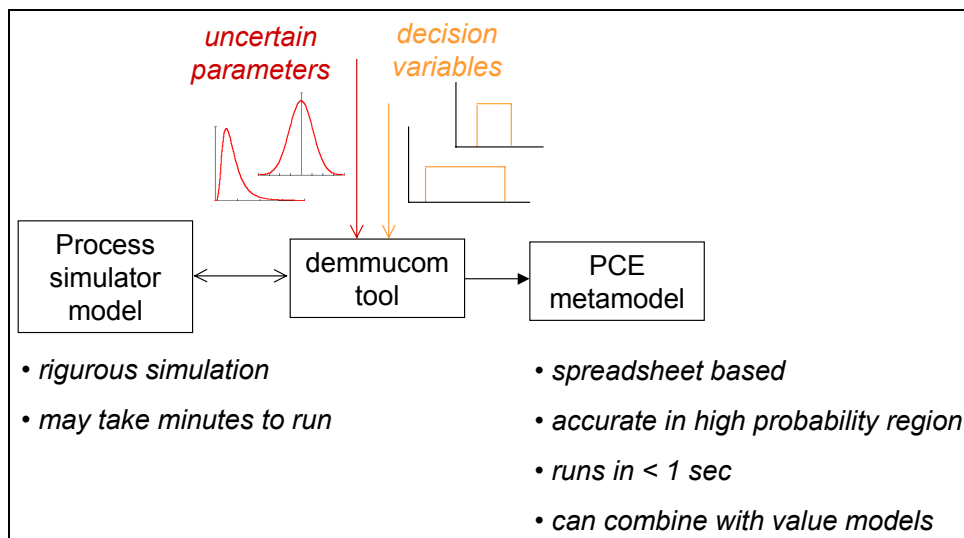


Figure 8-3: Use of demmucom to generate PCE metamodels of process flowsheet models

An additional advantage of using DEMM to generate a response surface model is that the variance contribution calculations of DEMM can be used as a type of global sensitivity analysis to rank decision variables with respect to their impact on changing the values of the output variables of interest⁸⁶. The use of DEMM to generate process flowsheet metamodels is illustrated next with an example

8.2.3 Example: generating DEMM metamodels for the solvent recovery case study

This section provides some details on the generation of the heat exchanger retrofit metamodel used for the examples in sections 4.7.2 and 5.4.2. The flowsheet for the process is reproduced here as Figure 8-4.

A model that responded to eight variables was built. Six of the variables (feed temperature, feed concentration, thermodynamic parameters ξ_a , ξ_b , ξ_c , and overall heat transfer coefficient) can be characterized as parametric uncertainties. The other two variables (heat exchanger area and effluent concentration set point) were decision variables. See Table 4-4 for descriptions and density plots of the probability distributions used.

A metamodel with 8 uncertain output variables was generated [steam use (Steam), condenser duty (Q), effluent concentration (Ceff), methylene chloride discharge in stream EFF

(inEff), methylene chloride flow in stream AQUEOUS (inAq), methylene chloride flow in stream VENT (inVent), methylene chloride flow in stream RECYCLE (inRecy), and effluent stream temperature (Teff)]. Only three of these (steam use, condenser duty, and methylene chloride discharge) were used as inputs to the valuation models in the examples.

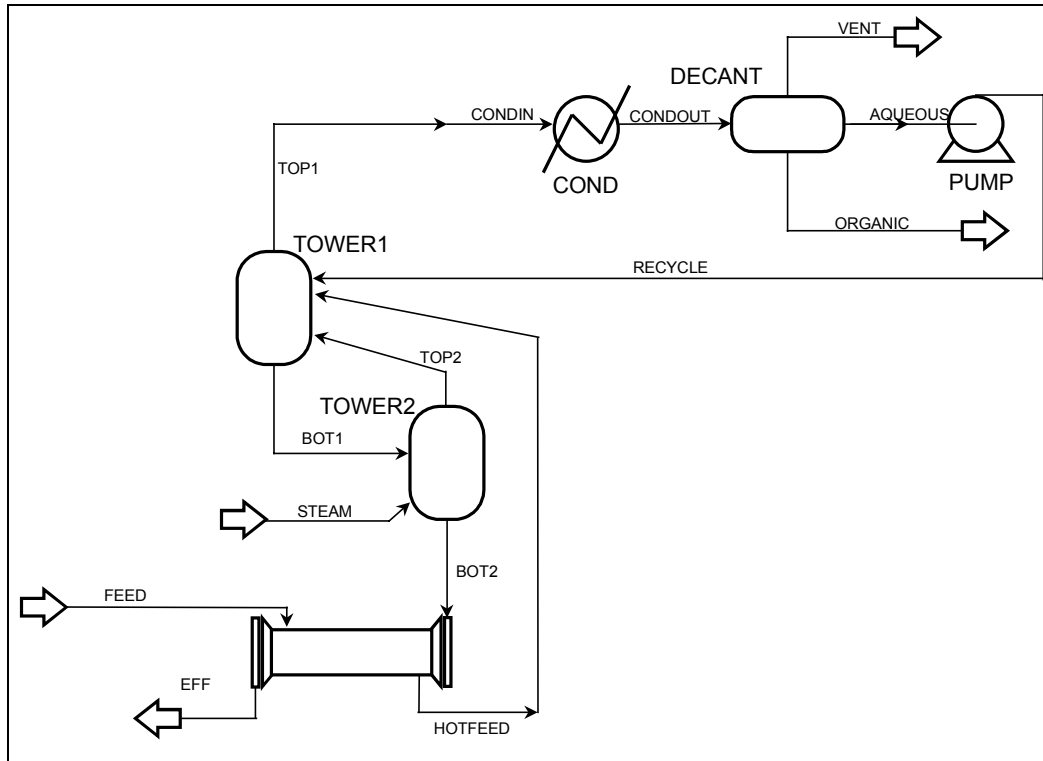


Figure 8-4: Heat exchanger sizing example process flowsheet

Plots of metamodel performance vs. order of approximation used are shown in Figure 8-5 and Figure 8-6 (detail view). A rather stringent criterion of 99.9% index of agreement was arbitrarily chosen as a stop criterion for adding additional terms to the approximation. A 4th order PCE expansion without cross terms achieved indices of agreement higher than 99.0% for all outputs of interest. Achieving 99.9% agreement for all the variables required the use of a full 4th order PCE with all the possible combinations of 2nd, 3rd, and 4th order cross terms. Although the cost of increasing the order approximation increases only linearly with the order of approximation when no cross terms are included in the model, the cost increases much more rapidly as higher order cross terms are added. As Figure 8-7 shows, the 4th order model without

⁸⁶ The variance contribution analysis is carried out treating the decision variables as additional uncertain parameters.

cross terms required only 74 flowsheet evaluations (33 for obtaining coefficients and 41 for error checking)⁸⁷. In contrast, the full 4th order model with all possible cross terms required a total of 1004 flowsheet evaluations (498 for obtaining coefficients and 506 for model error determination).

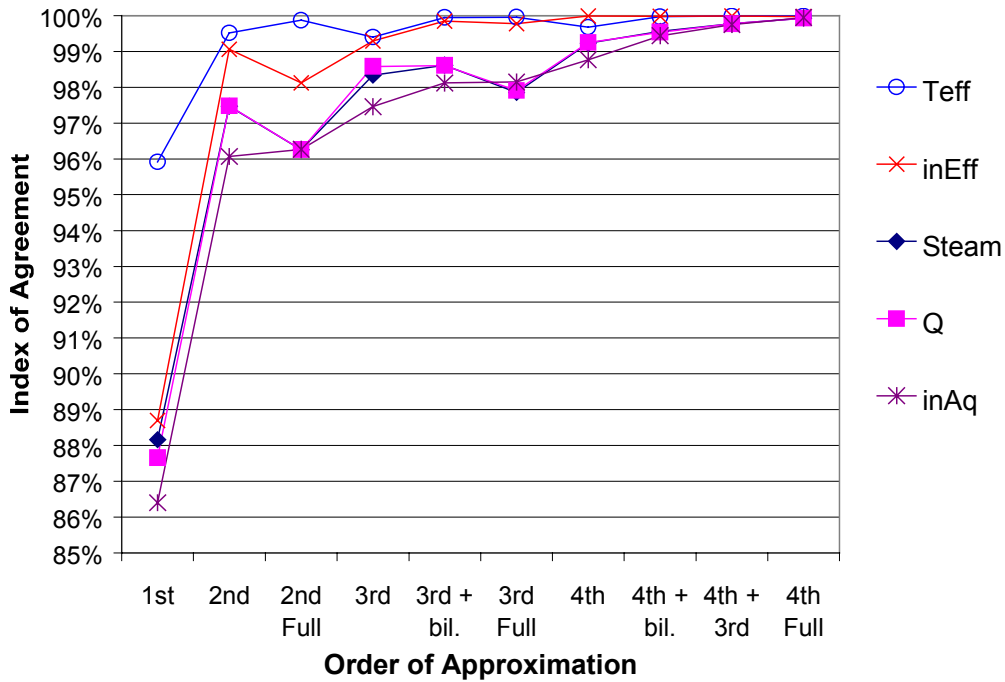


Figure 8-5: Index of agreement vs. order of approximation used to build the PCE model

⁸⁷ Of these, the 33 model evaluations needed for obtaining the coefficients were already available, since they were the ones used to calculate the error of truncation in the 3rd order model.

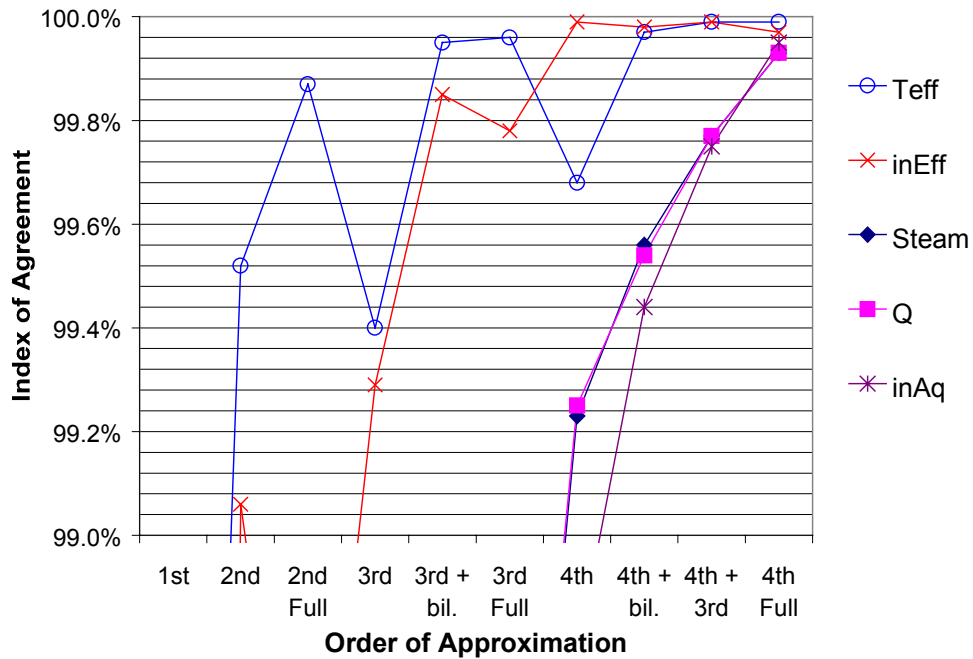


Figure 8-6: Detail view of the index of agreement vs. level of approximation chart

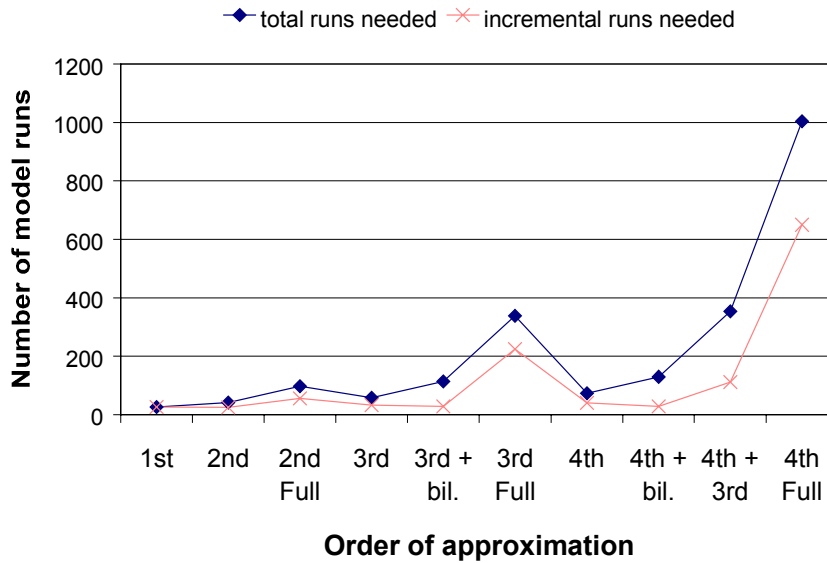


Figure 8-7: Number of model runs needed to build and evaluate the goodness of fit of the PCE model

Variance contribution results obtained under the assumption that the distributions specified for the decision variables were parametric uncertainties are shown in Figure 8-8. Decision variables account for a large fraction of the uncertainty in process outputs. Of the

parametric uncertainties, thermodynamic uncertainty is the most important in terms of the contribution to the uncertainty in steam use. This is in agreement with the uncertainty analysis carried out in section 5.4.2, in which it was found that the third thermodynamic parameter (thermoc) was the physical parameter with the largest contribution to uncertainties in annualized cost and environmental impact valuation. This chart also suggests that feed variability could have been dropped from the model, in order to decrease the number of cross terms required to achieve 99.9% index of agreement.

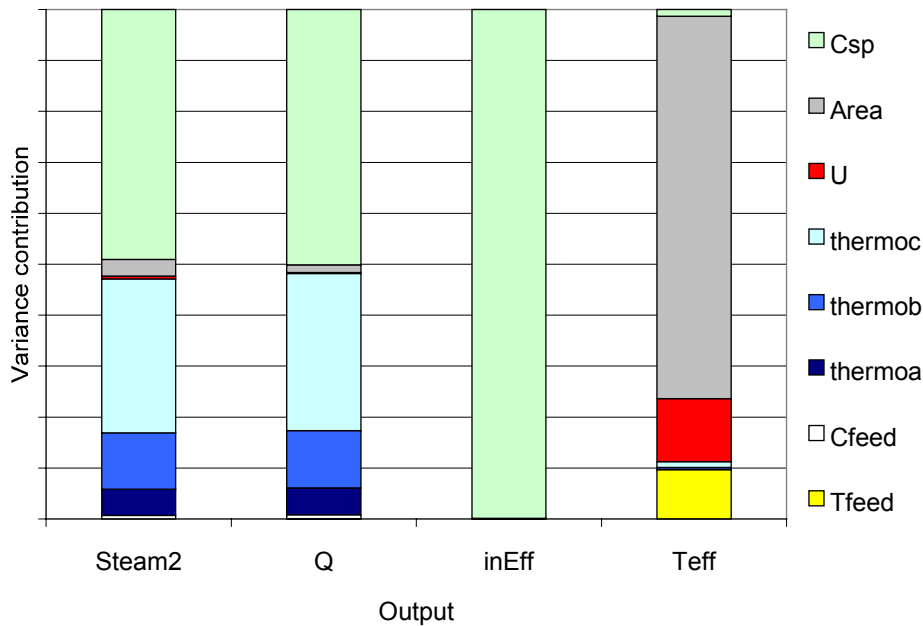


Figure 8-8: Variance contribution analysis

Even at 1004 model runs the cost of building the PCE model is lower than the cost of running Monte Carlo simulations on the Aspen flowsheet model, since a Metamodel valid over a wide range of effluent concentration set points and heat exchanger sizes was obtained with a number of flowsheet calls that is comparable to the number of simulations that would have been required to obtain output distributions for a *single* combination of concentration set point and heat exchanger area.

8.3 Generation of multivariate distributions to interface process models with value models

8.3.1 Introduction

From the point of view of a designer, all that is needed to incorporate environmental issues as an objective in process design is the availability of unit indicators. These indicators could then be applied to the input and output rates predicted by a design to produce an overall impact indicator (this is analogous to the use of prices to calculate operating cost as an economic performance indicator). A major difference between these indicators and prices is that the environmental indicators can be expected to have significant uncertainties associated to them. Neglecting to consider these uncertainties would undermine the effort by casting doubts on the significance of the results.

The PIO-LCA environmental valuation models introduced in Chapter 7 typically have hundreds of uncertain inputs. This is particularly true when the PIO-LCA model is linked to a fate, transport, and exposure model for the calculation of some of the characterization factors (e.g. human toxicity potentials). From the point of view of a designer, it is not practical to propagate hundreds of uncertainties through a large spreadsheet model every time a new design alternative is considered.

In section 7.5.3 it was shown that the PIO-LCA method could be used to propagate uncertainties in unit environmental impacts, independently of the input and output levels associated with any particular design. This suggests that the propagation of uncertainties in unit environmental impacts be done once, and its results used to obtain distributions for environmental impact indicators once the input and output levels of different designs have been specified.

Distribution fitting software (e.g. BestFit⁸⁸) can be used to fit a probability distribution to the results of a Monte Carlo simulation. Current software is able to test dozens of different distributions and fit distribution parameters to data sets containing hundreds of points within a couple of minutes. The availability of these tools suggests that a convenient way to generate the required unit impact distributions would be to obtain them through the fitting of Monte Carlo

⁸⁸ Palisade Corporation (www.palisade.com)

simulation data. The distributions obtained ($\sim 10^0$ to 10^1 distributions) could then be used instead of the original PIO-LCA model ($\sim 10^3 - 10^4$ distributions) to provide unit environmental valuations for process models.

A major weakness of the approach suggested above is that significant information might be lost in the translation of Monte Carlo results into distribution functions, even if the distribution functions fit the data perfectly. The reason for this is that the use of independently fitted distribution functions assumes that there are no correlations among the various modeled indicators, when the correlations might in fact be quite significant.

In Chapter 4 it was demonstrated that a key to avoid the overestimation of decision uncertainty is to preserve the correlations among the scores for different alternatives. Since different unit environmental impact indicators share many uncertain parameters in common (e.g. the valuation factor used to weigh global warming potentials), it is to be expected that unit environmental impact indicators will be correlated as well.

8.3.2 Preserving correlation structure through direct use of Monte Carlo results

One way to address the problem of information loss is to use the results of the Monte Carlo simulation directly. This would be done as follows:

1. Assign a sequential number to each iteration result from the Monte Carlo simulation, $i = 1, 2, 3, \dots, N$, where N is the number of iterations used in the simulation.
2. Arrange the iteration results in matrix form, where each row of the matrix corresponds to an iteration of the original simulation, and each column to a simulation output of interest. Using the example of unit environmental indicators as the simulated outputs of interest, the value of the unit environmental indicator for raw material j in iteration i would be given by Ω_{ij} .
3. At each iteration of the Monte Carlo simulation of a process model, draw a sample from the set $\{1, 2, 3, \dots, N\}$ with probability $1/N$. Use the value drawn as a lookup index to the matrix defined in the step above. Unit impact indicators should be read simultaneously from the row with index equal to the value drawn and used within the same iteration of the Monte Carlo simulation.

The method described above has the main advantage of preserving all the information regarding correlations among unit indicators contained in the results of the simulation of the PIO-LCA model. It has the disadvantage that the information about distribution densities and correlations among unit indicators is not accessible in explicit form. Its implementation on a spreadsheet model requires the allocation of several thousand cells to store the results of the original simulation. An alternative approach that yields a more compact representation is described next.

8.3.3 Preserving correlation structure through the use of copula multivariate distributions

Copula multivariate distributions represent joint distributions of random variables as a function of the marginal distributions. In mathematical symbols, the joint probability density $f(x_1, x_2, \dots, x_n)$ can be written in copula form as:

$$f(x_1, x_2, \dots, x_n) = f_1(x_1) \times \dots \times f_n(x_n) c[F_1(x_1), \dots, F_n(x_n)] \quad (8-17)$$

where $f_i(x_i)$ is the marginal probability density function (pdf) for random variable X_i , $F_i(x_i)$ is the corresponding cumulative distribution function (CDF), and the function $c[F_1(x_1), \dots, F_n(x_n)]$ is called the copula density. According to Sklar's Theorem (1959), any joint distribution can be written in copula form [18]. Portions of the information that follows has been obtained from the excellent introduction to copulas for decision analysis provided by Clemen and Reilly [18].

Although there are many copula families [19,20], the multivariate normal copula is used exclusively in this work, mostly for practical reasons, the most important one being the ease with which they can be simulated in the @Risk Monte Carlo simulation package. Like other copula families, the multivariate normal copula allows the specification of any distribution family for the marginal distributions. Its name is derived from the fact that it encodes dependence through pair-wise correlation coefficients in the same way that the multivariate normal distribution uses product-moment correlations to encode dependence among its marginal normal distributions.

The multivariate normal copula density function is given by

$$f(x_1, x_2, \dots, x_n) = f_1(x_1) \times \dots \times f_n(x_n) \times \exp\left\{-\mathbf{y}^T (\mathbf{R}^{-1} - \mathbf{I}) \mathbf{y} / 2\right\} / |\mathbf{R}|^{1/2} \quad (8-18)$$

where \mathbf{R} is matrix of product-moment correlation coefficients, \mathbf{I} is the identity matrix, and the elements of vector \mathbf{y} are defined as:

$$y_i = \Phi^{-1}[F_i(x_i)] \quad (8-19)$$

where Φ^{-1} is standard normal inverse transformation.

The elements r_{ij} of the \mathbf{R} matrix are obtained from the Spearman rank correlation coefficient (ρ_{ij}) between random variables X_i and X_j ⁸⁹:

$$r_{ij} = 2 \sin\left(\frac{\pi\rho_{ij}}{6}\right) \quad (8-20)$$

Simulating from a copula multivariate distribution is a straightforward task: The first step is to generate a vector (y_1, y_2, \dots, y_n) from a multivariate-normal process with correlation matrix \mathbf{R} . One way to accomplish this is to find a lower triangular matrix \mathbf{U} such that $\mathbf{U}\mathbf{U}^T = \mathbf{R}$. The vector \mathbf{y} would then be given by

$$\mathbf{y} = \mathbf{U}\boldsymbol{\xi} \quad (8-21)$$

where $\boldsymbol{\xi}$ is a vector of i.i.d. unit normal random variables [21] (i.e. independent normal random variables with $\mu=0$ and $\sigma=1$).

The second step of the procedure is to calculate the standard normal cumulative distribution function $\Phi(y_i)$ for each of the correlated standard unit random variables. Finally, the inverse marginal distribution functions are used to calculate the values of the random variables corresponding to the correlated unit normal random variables. The vector of random variable values thus obtained comes from a process that has the specified marginal distributions as well as the required rank correlation coefficients.

Distribution fitting and simulation from the distribution are even more straightforward if the package @Risk is used to carry out Monte Carlo simulations. For distribution fitting, the results of a Monte Carlo simulation would be used as input to a program such as BestFit to obtain the marginal distributions. The matrix of rank correlation coefficients would be obtained from the simulation output data by generating vector of ranks using the Excel function `rank(cell,array)` and computation of the person product-moment correlation between two arrays of ranks, using the Excel function `correl(rankarray1, rankarray2)`.

For simulation, the @Risk function

⁸⁹ For a discussion of rank correlation coefficients, see section 5.3.3.

$$=RiskCorrmat(\text{matrix cell range, position}) + \text{distribution function} \tag{8-22}$$

would be used, where matrix cell range specifies a range within the spreadsheet where the rank correlation coefficients are stored, position is the position of the variable of interest in the correlation matrix, and distribution function is any of the probability distributions available in @Risk.

As an example, the Excel and @Risk formulas needed to represent the uncertainty in the unit environmental impacts used in the example in section 4.7.2 are shown in Figure 8-9.

	A	B	C	D	E	F	G
1	Unit environmental indicators:		Steam	Cooling water	Methylene chloride	Steel sheet	
2	Steam	=RiskCorrmat(C2:F5,1)+RiskBeta(5.19,12.19))*4.07-3.38	1	0.68	0.66	0.62	
3	Cooling water	=RiskCorrmat(C2:F5,2)+RiskNormal(1.64,0.47)	0.68	1	0.68	0.8	
4	Methylene chloride	=RiskCorrmat(C2:F5,3)+RiskGamma(7.21,0.17))-1.44	0.68	0.68	1	0.66	
5	Steel sheet	=RiskCorrmat(C2:F5,4)+RiskErlang(6,0.2))-1.27	0.62	0.8	0.66	1	
6							
7							
8							
9							
10							

Figure 8-9: Example of @Risk representation of a multivariate normal copula distribution

The copula method has the advantage that it can provide a compact representation of the results of a Monte Carlo simulation. A further advantage is that the correlations among variables are shown explicitly. One of the disadvantages of the method is that it is only an approximation to the distribution underlying the Monte Carlo simulation used to fit its parameters.

EXAMPLE

Figure 8-10 shows a scatter plot of a 2000 iteration Monte Carlo simulation performed on the PIO-LCA model used to derive the unit environmental indicators for steam and methylene chloride discharges (see section A.4.3 for details). It is clear from the figure that high values of the unit indicator for steam tend to be associated with high values of the unit indicator for methylene chloride. Their rank correlation coefficient is 0.66. An empirical distribution obtained from these points is shown in Figure 8-11 in the form of a contour plot. A 3-dimensional view of the empirical distribution is presented in Figure 8-12. The height of each vertex in the surface plot was obtained by counting the number of scatter points located in a square with dimension equal to 1/3 or a log unit centered on the x-y coordinate of the vertex.

A contour plot and a 3-dimensional surface plot of the corresponding bivariate normal copula distribution are shown, respectively, in Figure 8-13 and Figure 8-14. The plots were obtained by evaluating eq (8-18) at 0.1 log unit intervals, using the marginal density functions $f_i(x_i)$ fitted to the data (shown in the top row of Figure A-8 in Appendix A). Comparing these plots with the empirical contour plot and the empirical surface plot it can be concluded that the bivariate copula distribution is a reasonably good approximation to the results of the Monte Carlo simulation. The goodness of the fit allows using only 6 cells in a spreadsheet to represent the uncertainty (2 cells for the @Risk expressions for the marginal distributions, and 4 cells for the correlation matrix), instead of 4000 cells to store the results of the Monte Carlo simulation.

For comparison, Figure 8-15 and Figure 8-16 show, respectively, the contour plot and the surface plot that would be obtained if it had been assumed that the marginal probability densities were independent from each other. It is clear that ignoring the correlation would have resulted in a significant loss of information.

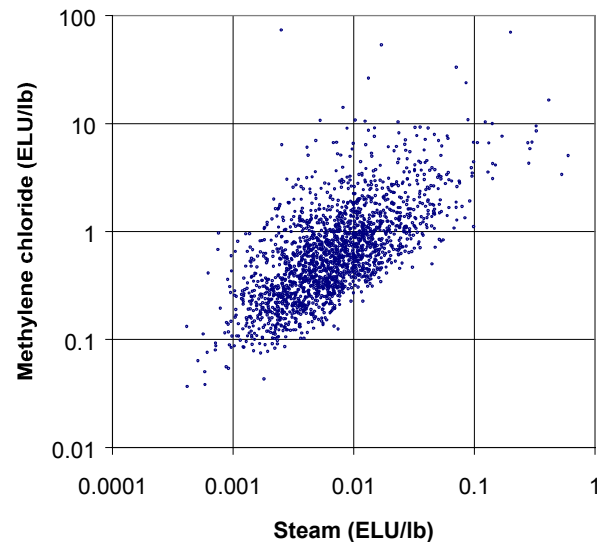


Figure 8-10: Scatter plot of 2000 (steam, methylene chloride discharge) unit environmental indicator pairs obtained from Monte Carlo simulation of a PIO-LCA model

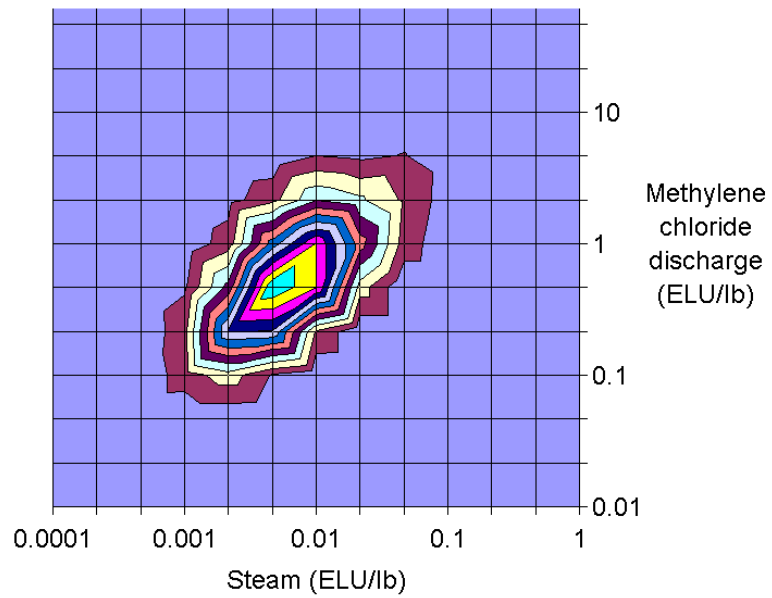


Figure 8-11: Contour plot of the empirical joint probability density of steam and methylene chloride discharge unit environmental indicators

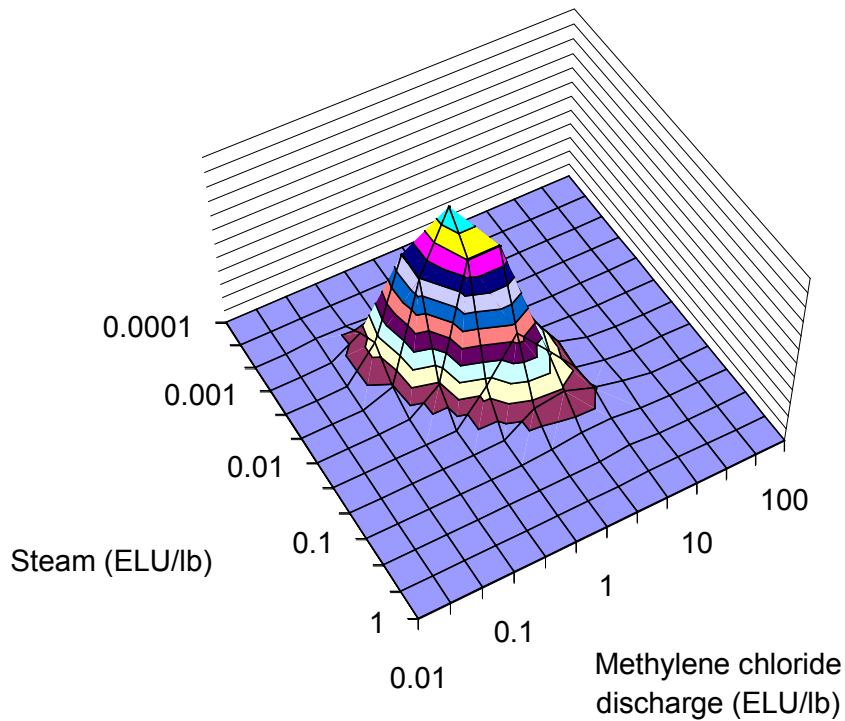


Figure 8-12: 3-dimensional plot of the empirical joint density of the unit indicators of steam and methylene chloride

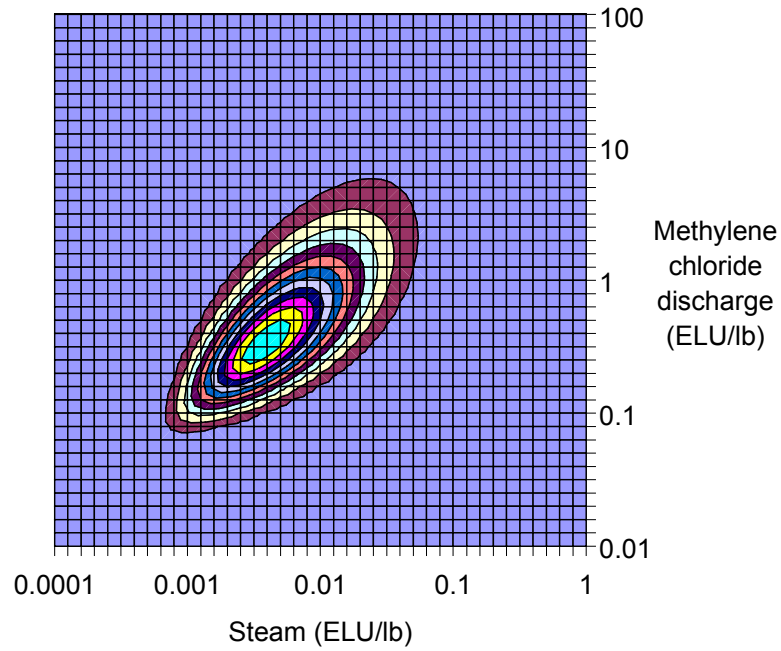


Figure 8-13: Contour plot of the bivariate normal copula distribution for steam and methylene chloride discharges estimated from parameter fitting of Monte Carlo results

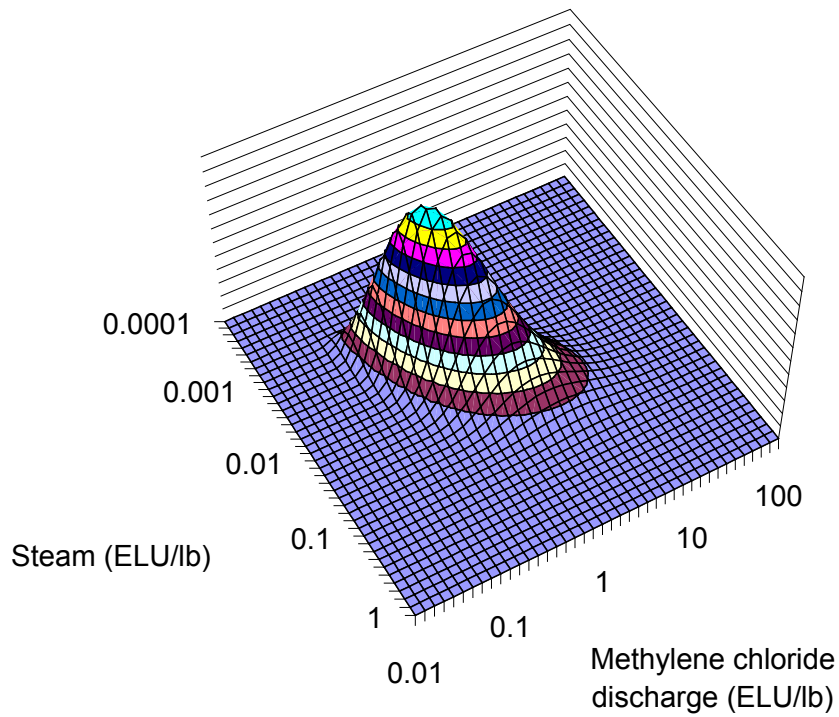


Figure 8-14: 3-dimensional plot of the bivariate normal copula distribution of the unit indicators of steam and methylene chloride

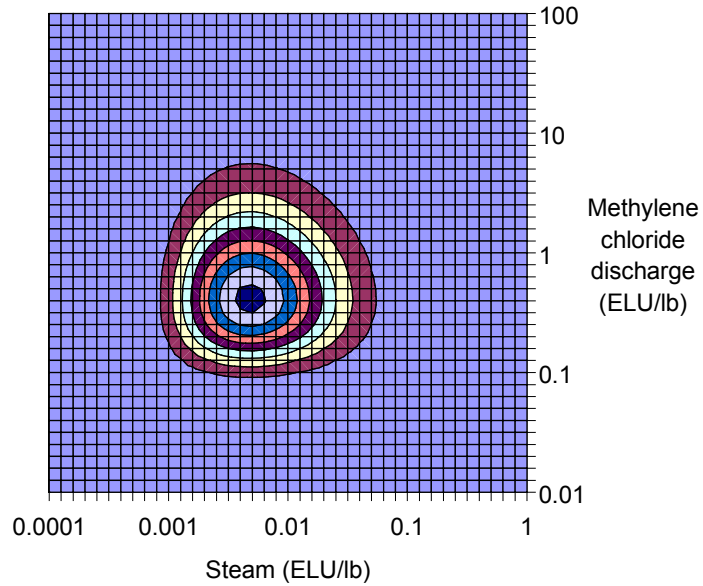


Figure 8-15: Contour plot of the bivariate normal distribution for steam and methylene chloride discharges unit environmental indicators obtained under the assumption that the unit indicators are independent from each other.

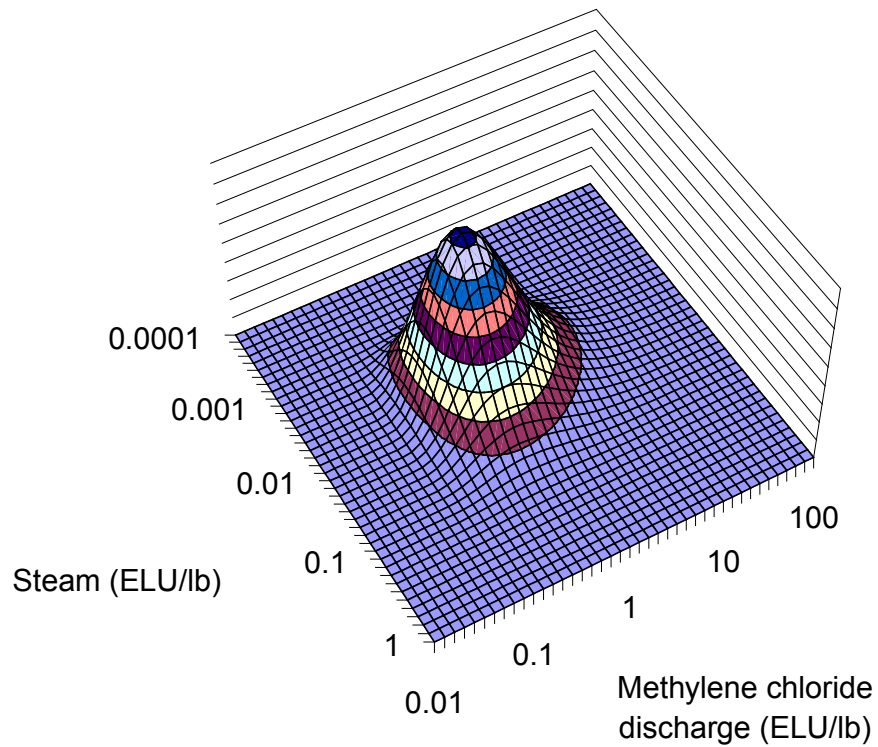


Figure 8-16: 3-dimensional plot of the joint distribution of the unit indicators of steam and methylene chloride, obtained under the assumption of independence among the unit indicator distributions.

8.4 Conclusion

Figure 8-17 summarizes the computational advantages of using the tools described in this chapter. PIO-LCA models contain hundreds of uncertain parameters, but are rapidly computed, since they are linear models. Their demand on CPU time is modest, but require substantial memory and/or storage capacity. Flowsheet models, in contrast, might take several minutes to converge but typically contain only a few uncertain parameters of importance. Combining both models produces a combined model with the worst characteristics of both. It contains hundreds of uncertain parameters and might take several minutes to converge. The tools described in this chapter address both weaknesses. Multivariate copula distributions are used to generate joint distributions of unit environmental indicators while preserving their correlation structure, thus dramatically decreasing the number of uncertain parameters that must be propagated. DEMM metamodels might take several dozen to several hundred flowsheet model runs to build, but once built they can be rapidly executed. The availability of a rapidly executable model with a low number of uncertain parameters greatly expands the universe of process design problems upon which stochastic optimization can be performed.

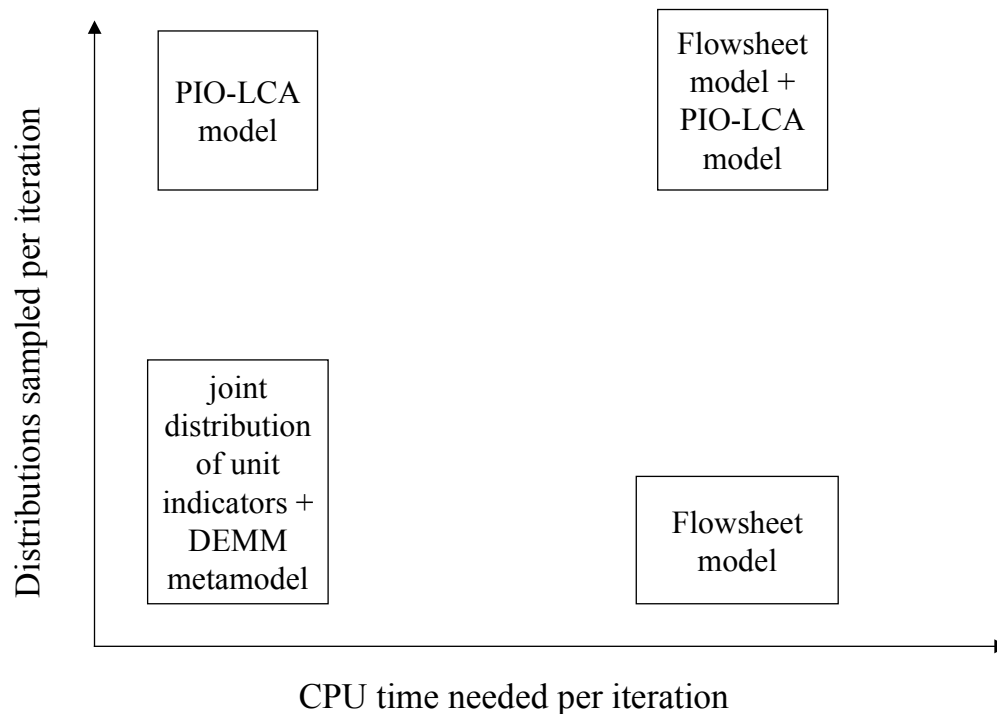


Figure 8-17: Computational advantages of using the tools described in this chapter in the environmental evaluation of process flowsheets under uncertainty

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Chapter 9 Knowledge representation and data management strategies

9.1 Introduction

There are two major differences between factors used in economic valuation models (e.g. prices) and factors used in environmental impact valuation models (e.g. toxicity factors). The former are fairly certain and relatively easy to obtain in the context of process design (e.g. by making a call to the purchasing department), while the latter are quite uncertain and not as widely available. An additional complication arises from the need to take into account impacts taking place in upstream processes (life cycle perspective). Private costs are usually fully internalized in prices, so it is not necessary to know details about the economic performance of upstream processes to obtain an indicator of life cycle economic performance. The indicator is the price itself. No such convenience exists with respect to the estimation of environmental impacts, therefore it becomes necessary to study a whole network including upstream processes in order to obtain estimates of life-cycle environmental impact. A method for analyzing these process networks was introduced in Chapter 7 (the process input-output life cycle assessment method, or PIO-LCA method). With the software tool described in Appendix C, the major barrier to the implementation of the PIO-LCA method is not the computation of the matrix operations, but rather the collection and maintenance of the data distributions used by the model.

These features of environmental valuation data make the use of an environmental knowledge management system a necessity for implementation in practice. Such a system is described in this chapter. Before proceeding to the description of the data model and system functions, some thoughts are provided regarding the characteristics of the data and the functions that the system needs to provide.

9.2 Data characteristics

Significant amounts of knowledge regarding the interaction of chemicals with the environment have been generated during the last few decades. As interest in environmental issues continues to grow, governments and corporations are devoting more resources to environmental research and to the testing of chemicals. Unfortunately, data are still lacking for a

large number of chemicals of commercial importance. The highest quality (least uncertain) data are available for only a relatively small set of chemicals. For larger sets of chemicals information is available, but its quality is lower. There is a tradeoff between data quality and data quantity. If we restrict ourselves to the use of high quality data only, we ignore a lot of existing knowledge. However, if we use low quality data we run the risk of diluting the information content of high quality data. An example of the latter is the Waste Minimization Prioritization Tool (WMPT) developed by the U.S. Environmental Protection Agency [1]. In the development of the WMPT the EPA adopted a fence line approach to allow the incorporation of semi-quantitative and even qualitative data in the ranking of chemicals according to their toxicity and potential for exposure. As a result, all the data used were converted into discrete scores of 1 (low concern), 2 (medium concern), and 3 (high concern). For properties measured in tangible units, a 1 point difference in this scale corresponded to a factor of about 100. This effectively diluted the information known to better than a factor of 100 to the lowest common denominator (see the example in section 6.4.2 for an information content analysis).

The approach taken here is to use and propagate probability distributions as a means to combine data of different qualities without diluting the information content of the high quality data. Two examples of the variability in data quality are provided here for environmentally relevant properties of chemicals. The first example concerns the Henry's law constant for the chemical 1,4-dichlorobenzene. 5 sources of data are compared in Figure 9-1: (i) the critical review of Henry's law constants by Staudinger and Roberts [2], (ii) Syracuse Research Corporation's physical properties database [3], (iii) an estimate based on the ratio of experimental vapor pressure and solubility data, (iv) a group contribution method (HENRYWING), and (v) a bond contribution method (HENRYWINB)⁹⁰. Although the central estimates given by the five methods are quite close, there are clear differences in the reliability of each source, with highest priority given to the critical selection of studies by Staudinger and Roberts and lowest priority given to the property estimation methods.

⁹⁰ Both methods are included in the HENRYWIN software published by the Syracuse Research Corporation.

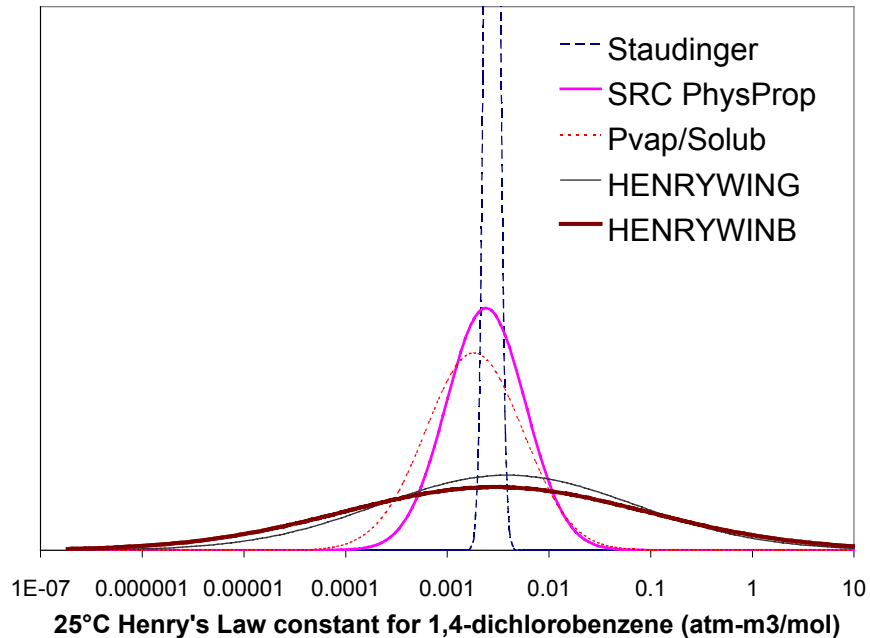


Figure 9-1: Probability distributions for the value of the Henry's law constant for 1,4-dichlorobenzene

The second example compares data for the oral cancer potency factor for benzene (Figure 9-2). The highest quality data available is a recent update to the entry for benzene in the IRIS database [4]. The cancer potency factor cited in the IRIS database was derived from human data (occupational exposure). At a lower level in the data hierarchy one finds potency factors derived from animal studies (CPDB mouse, CPDB rat, and RQPOT) [5]. The distribution assigned to the factor used by the California environmental protection agency (CalEPA) has an intermediate uncertainty range [6]. In this example there is more variability in central estimates than in the Henry's law constant example. The graph shows, however, that all the lower quality distributions include the high probability region of the IRIS cancer potency factor distribution within their high probability domains. Had a value for benzene not been available in the IRIS database, it would have reasonable to use a distribution based on rodent data. The confidence in the valuation of the impacts of benzene would necessarily have been lower than the one that can be obtained by using the IRIS database factor, but higher than the one that would be obtained if the only information available had been qualitative evidence indicating that benzene was a possible human carcinogen.

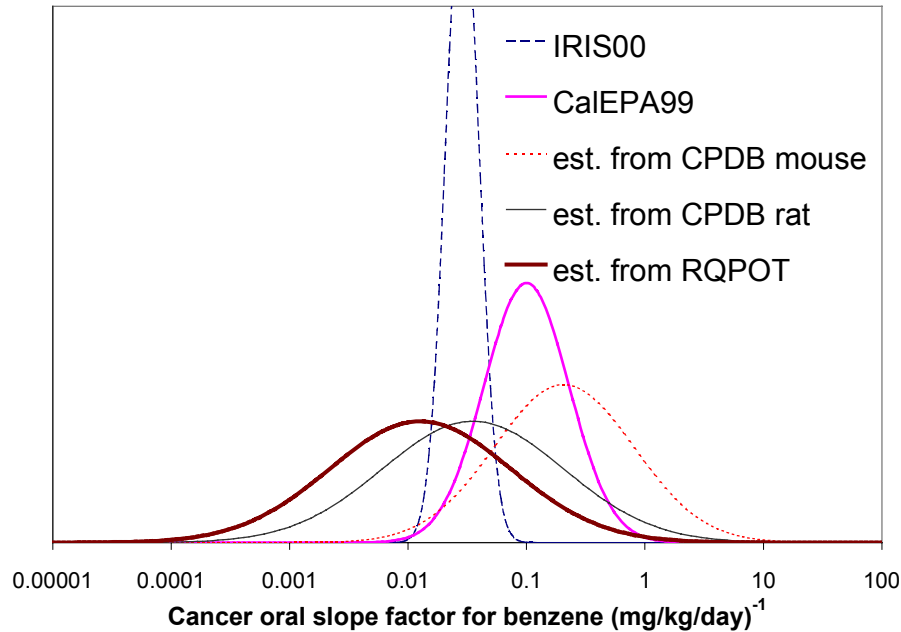


Figure 9-2: Comparison of probability distributions for the cancer oral potency factor of benzene

9.3 System requirements

An environmental evaluation information management system must be able to perform the following functions:

- Store probability distributions for various factors stored within the system. Examples given throughout this work have shown that it is not uncommon to have order-of-magnitude uncertainties surrounding factors used in environmental assessment.
- Allow users to rank sources of information so that the highest-quality sources will be accessed preferentially when retrieving data for environmental valuation models.
- Allow users to efficiently generate fully documented environmental valuation models on which uncertainty analysis (e.g. Monte Carlo simulation) can be performed. Users should be able to trace factors with large contributions to valuations (or to the uncertainty in valuations) back to the source of data and distributions used.
- Enable periodic updates of the data without losing older data. It is important to keep older data to check for consistency when various sources differ significantly.

It is also desirable that the system be able to interact with commonly available software packages. This facilitates the import of data from electronic sources (e.g. the internet and commercially-available CD-ROMs). An environmental knowledge management tool satisfying these requirements was developed for this dissertation and is described in the following section.

9.4 *EnvEvalTool: a tool for managing environmental evaluation information*

This section describes the environmental information management tool developed as part of this dissertation. The EnvEvalTool (short for “Environmental Evaluation Tool”) was developed taking advantage of widely used software. Microsoft Access was used for the database component of the tool, while Microsoft Excel was used as the modeling platform (the fate and transport model discussed in section 6.3 and the process input-output life cycle assessment model introduced in Chapter 7 were both implemented on Excel). The representation of uncertainty within the tool was designed to take full advantage of the availability of Monte Carlo simulation add-ons for Excel. The software package @Risk⁹¹ was used in this work, but the data model should be compatible with competing products with only minor modifications.

Key features of the tool and its implementation are discussed in this section. Details including table structures, SQL statements for queries, and listings of the Visual Basic code used to implement system functions are given in Appendix B.

9.4.1 Data model

The structure of the data model used in the EnvEvalTool is shown in Figure 9-3 and Figure 9-4. Figure 9-3 shows the tables in the data model that are used to manage the input-output and economic information required by the PIO-LCA method⁹², while Figure 9-4 shows the part of the data model that is used to manage chemical property and environmental problem valuation information. Relationships between tables are shown as lines connecting the appropriate fields. One-to-many relationships are noted by a 1 on the “one” side of the relationship and an ∞ on the “many” side.

⁹¹ Palisade Corporation (www.palisade.com)

⁹² See section 7.3.1 for a description of the required input data.

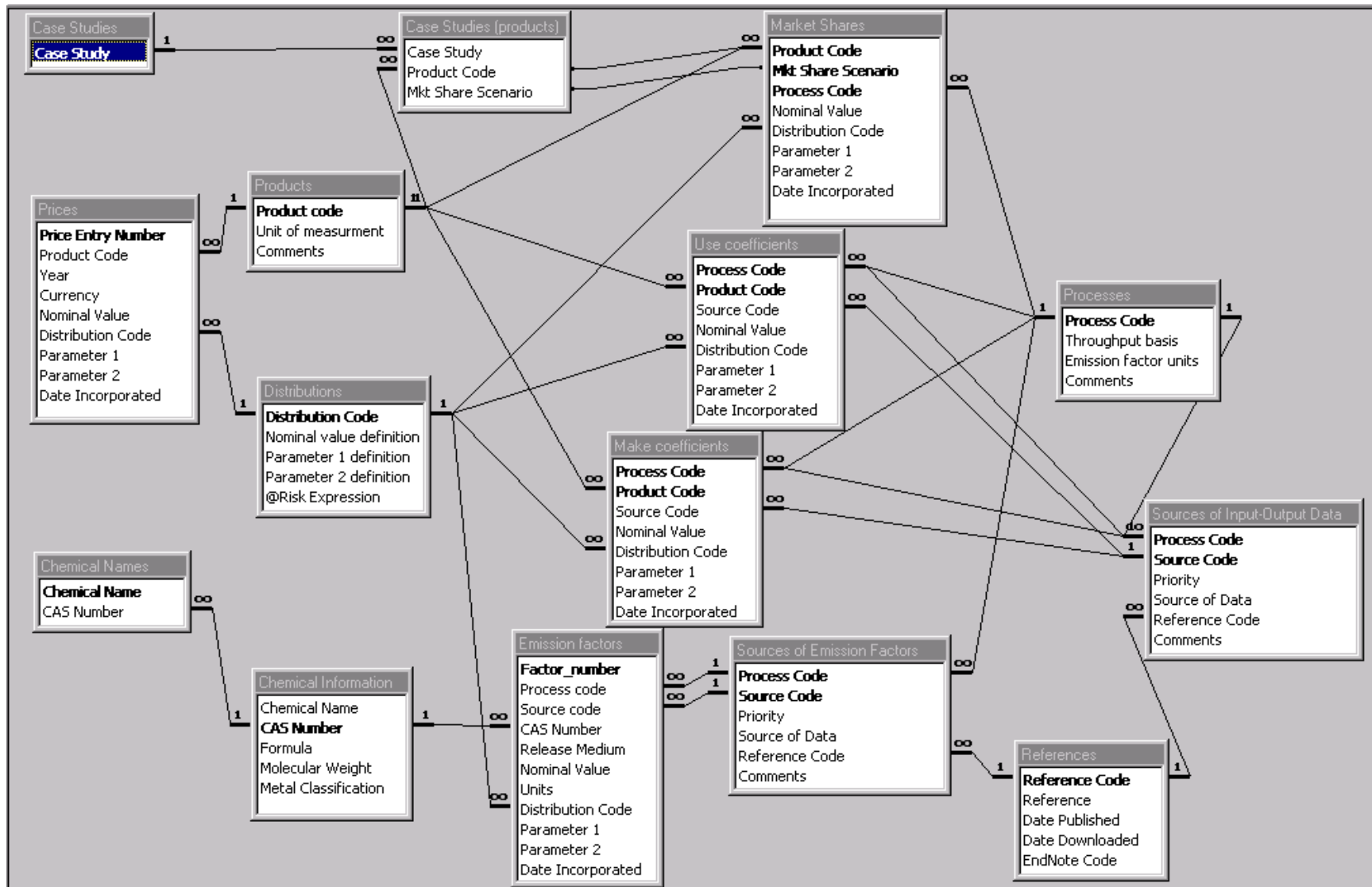


Figure 9-3: EnvEvalTool data model (input-output data and economic information)

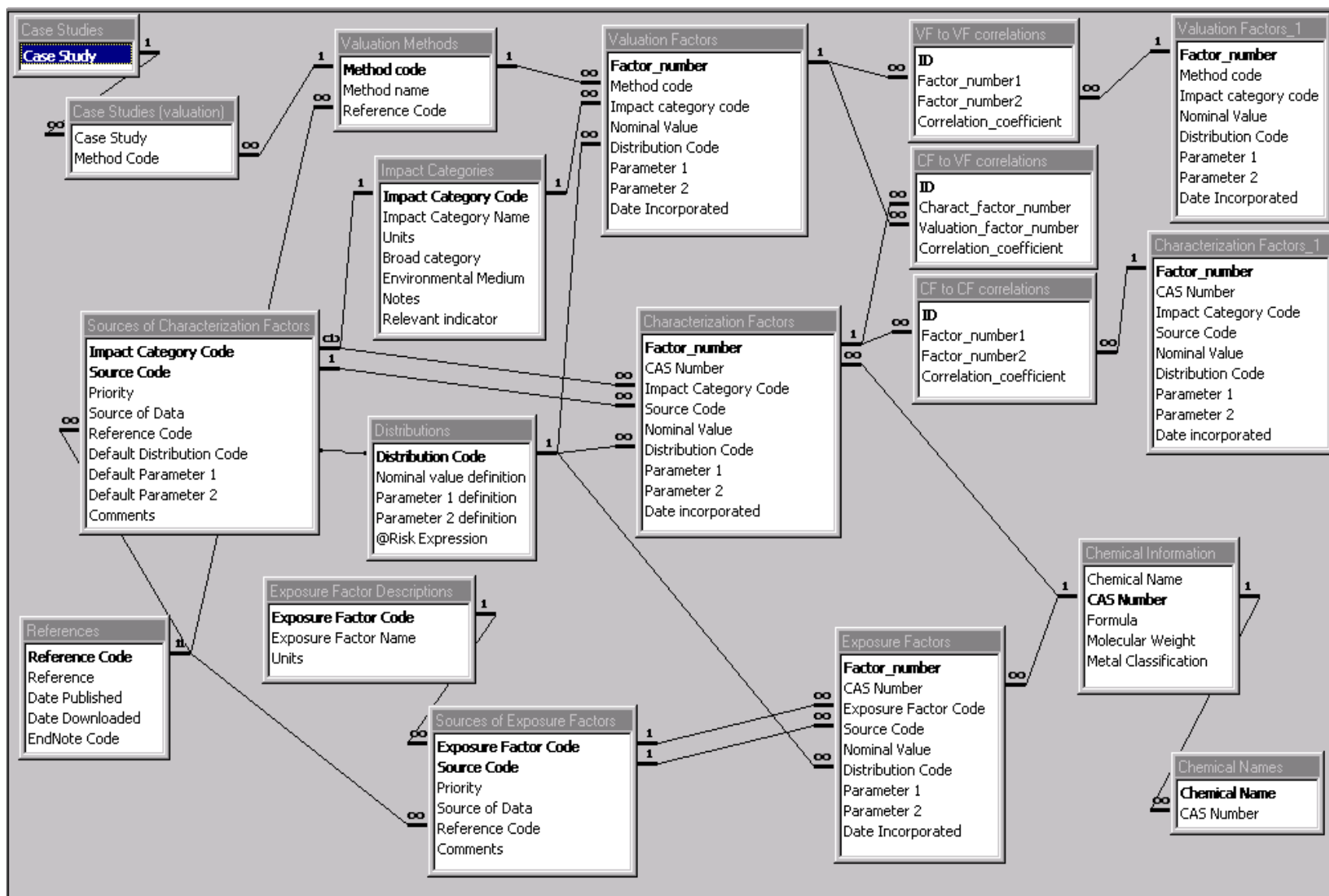


Figure 9-4: EnvEvalTool data model (chemical properties and valuation factors)

The tables used to store numeric information use the same data model to store information about uncertainty distributions. The Distributions table is used to store probability distribution definitions. In the current implementation, distributions with up to 3 parameters may be specified. The field @Risk Expression is used to provide the definition of each distribution function, and is given by the Excel formula that should multiply the nominal value to generate the desired distribution. Table 9-1 gives the list of distribution functions currently contained in the database. The last five rows of the table show the distributions used in the database to represent the uncertainty in the emission factors published by the EPA in the AP-42 series [7]⁹³. If it were decided that a lognormal distribution with uncertainty factor⁹⁴ of 10 overestimates the uncertainty emission factors with an AP-42 rating of E, a new distribution function definition could be entered in the @Risk Expression field of the Distributions table without having to modify every single record in the Emission factors table containing an E-rated emission factor. Every factor with a value “EPA_E” in its Distribution code field would then inherit the new distribution. This is just one illustration of the advantages of storing environmental evaluation data in a carefully considered data model.

A second feature common to most of the tables that store quantitative information is the use of a data source code to link to tables giving details about the source used to obtain a particular factor. All of the tables used to store source details are also linked to a table of bibliographic or electronic references (the References table). Important data contained in the References table included the download date for information obtained from electronic sources. The four tables used to manage data sources (Sources of Input-Output Data, Sources of Emission Factors, Sources of Characterization Factors, and Sources of Exposure Factors) include a Priority field used to store the order of preference in which data distributions should be used. The queries used to access the data then give preference to a high priority data element over a low priority data element when both elements are available for the same factor.

Chemicals in the database are uniquely identified through their chemical abstract service number (CAS Number). When a chemical has not been assigned a CAS number, the

⁹³ The EPA assigns five qualitative ratings to the emission factors in the AP-42 series, going from a rating of “A” (Excellent) to “E” (poor).

⁹⁴ Throughout this thesis the term “uncertainty factor” is used to refer to the square of the geometric standard deviation of the lognormal distribution.

CAS Number field is used to store a provisional code assigned by the user. A table of chemical synonyms (the Chemical Names table) is provided to facilitate the retrieval of CAS numbers when the user does not know the CAS number for a particular chemical of interest.

Table 9-1: Listing of records in the Distributions table of the EnvEvalTool database

Distribution Code	Nominal value definition	Parameter 1 definition	Parameter 2 definition	@Risk Expression
Binomial	High value	Low value	prob(low value)	$(1-(1-[\text{Parameter 1}]/[\text{Nominal Value}]) * \text{RiskBinomial}(1, [\text{Parameter 2}])))$
Lognormal	geometric mean	square of geometric standard deviation		$\text{exp}(\text{RiskNormal}(0, \ln([\text{Parameter 1}]/2)))$
Lognormal2	arithmetic mean	geometric mean / arithmetic mean	square of geometric standard deviation	$\text{exp}(\text{RiskNormal}(\ln([\text{Parameter 1}]), \ln([\text{Parameter 2}])/2))$
Missing Normal	nominal value arithmetic mean	two times the relative standard deviation		$(\text{RiskNormal}(1, [\text{Parameter 1}]/2))$
Normal2	arithmetic mean	two times the standard deviation		$(\text{RiskNormal}(1, (\text{abs}([\text{Parameter 1}] / [\text{Nominal Value}]))/2))$
Triangular	most likely value	Minimum / most likely value	Maximum / most likely value	$(\text{RiskTriang}([\text{Parameter 1}], 1, [\text{Parameter 2}])))$
Uniform	nominal value	Minimum / nominal value	Maximum / nominal value	$(\text{RiskUniform}([\text{Parameter 1}], [\text{Parameter 2}])))$
EPA_A	central value			$\text{exp}(\text{RiskNormal}(0, \ln(1.15)/2))$
EPA_B	central value			$\text{exp}(\text{RiskNormal}(0, \ln(1.3)/2))$
EPA_C	central value			$\text{exp}(\text{RiskNormal}(0, \ln(1.7)/2))$
EPA_D	central value			$\text{exp}(\text{RiskNormal}(0, \ln(3.0)/2))$
EPA_E	central value			$\text{exp}(\text{RiskNormal}(0, \ln(10)/2))$

As discussed in Chapter 4, preservation of correlation structure is key to reducing decision uncertainty when there are large uncertainties associated with valuation models. The EnvEvalTool provides a mechanism for storing correlation information, in the form of Spearman rank correlation coefficients⁹⁵. Three tables are used to store correlation coefficients, as shown in the top right portion of Figure 9-4. The current implementation allows storage of correlations among characterization factors, among valuation factors, and between characterization and valuation factors. As an example, the information provided in the documentation for the EPS environmental valuation method [8] was used to derive probability distributions for the valuation factors of several environmental problem categories⁹⁶ (Table 9-2). Examination of the results of

⁹⁵ See sections 5.3 and 8.3 for more discussion on rank correlation coefficients.

⁹⁶ See section 3.3 for a discussion of uncertainties in environmental problem category valuation factors.

the Monte Carlo simulation revealed a high degree of correlation among several factors. This is not surprising, since ultimately all the valuations in the EPS method depend on the valuations assigned to several endpoint effects, such a lost year of life expectancy or a year living with severe nuisance. When the valuation given to one of the endpoints (e.g. the value of a year of life expectancy lost) is sampled at the high end of its distribution, one would expect that the valuation factors derived from impact categories for which that endpoint is an important contributor [e.g. toxicity (DALYs) and health effects from particulate matter (PM10 effects)] would tend to take values at the high of their distributions as well.

Table 9-2: Correlations among probability distributions for impact category valuation factors derived from the EPS method.

	Global warming potential (GWP)	Ozone depletion potential (ODP)	Respiratory effects from particulate matter (PM effects)	Photochemical oxidants creation potential (POCP)	Disability-adjusted life years lost due to exposure to toxic substances (DALYs)	Eutrophication potential (EP)	Aquatic ecotoxicity potential (AETP)	Terrestrial ecotoxicity potential (TETP)
GWP	1	0.38	0.22	0.15	0.39			
ODP	0.38	1	0.13	0.15	0.24			
PM effects	0.22	0.13	1	0.17	0.53			
POCP	0.15	0.15	0.17	1	0.30			
DALYs	0.39	0.24	0.53	0.30	1			
EP						1	0.22	0.26
AETP						0.22	1	0.18
TETP						0.26	0.18	1

9.4.2 Sources of data

A wide variety of sources were consulted to obtain the data stored in the EnvEvalTool database. Sources included government agencies, commercial publishers, environmental advocacy groups, and academic research groups. The database currently stores more than 60,000 factors distributed among approximately 6,000 chemicals. Table 9-3 lists the codes and descriptions of the exposure modeling factors stored in the database, as well as the data sources relied upon for each factor. A similar listing is given in Table 9-4 for the case of environmental impact category characterization factors.

Table 9-3: Sources of data for physical properties used in exposure modeling

Exposure factor code	Exposure factor description	Sources of data
Tm	Melting point	[1,3,9]
Pvap	Vapor pressure at ~25 degC	[1,3,9,10]
Solub	Water solubility at ~25 degC	[3,9-11]
K Henry	Henry's law constant at ~25 degC	[1-3,9-12]
Log Kow	Base 10 logarithm of the Octanol-water partition coefficient	[1,3,9-11,13]
logKds	Soil-liquid partition coefficient	[10-12,14,15]
BCF	Bioconcentration factor	[1,10,11,13,16]
t_air	Half life in air	[1,3,10,11,17-19]
t_aerobic	Aerobic degradation half life	[1,10,13]
t_hydrolysis	Hydrolysis half life	[1,10,13]
t_water	Half life in surface water	[1,10,11,17,19]
t_soil	Half life in soil	[1,10,17,19]
t_sed	Half life in sediments	[1,10,17,19]
WWTP_to_air WWTP_to_water WWTP_to_sludge	Fraction of chemical entering a wastewater treatment plant that volatilizes to air, remains in water effluent, or partitions to sludge	[11]

Table 9-4: Sources of data for factors characterizing the contributions of chemicals to specific environmental problems

Impact category code	Impact category name	Sources of data
GWP100	Global Warming Potential over 100-year period	[8,20-25]
ODP	Ozone Depletion Potential	[23,26,27]
PM10 Effects	Health effects from particulate matter	[8,28]
Respiratory DALYs	Disability-adjusted life years lost due to respiratory effects	[29]
POCP	Photochemical Ozone Creation Potential	[8,27,28,30-34]
Cancer DALYs	Disability-adjusted life years lost due to chemical carcinogens	[1,8,29,35-38]
Cancer UR inh	Cancer concentration-in-air-based unit risk factor: Life-time cancer unit risk from inhalation of air containing 1 microgram/m3 of substance	[1,4,6,10,11,36,39,40]
Cancer CSF oral	Oral Cancer Slope factor	[1,4-6,10,11,13,36,40]
Cancer CSF	Cancer slope factor (based on weight-of-evidence)	[1,4,13,35,41-43]
NonCancer DALYs	Disability-adjusted life years lost due to chronic non-cancer effects from chemicals	[1,8,35-38,44]
NonCancer invRfC inh	Non-cancer chronic concentration-in-air-based toxicity factor	[1,4,10,11,13,35,40,44-47]
NonCancer invRfD oral	Non-cancer chronic oral dose-based toxicity factor	[1,4,10,11,13,40,44,46]
NonCancer invRfD	Non-cancer chronic dose-based toxicity factor	[1,13,48]
HTP	Human Toxicity Potential (cancer and non-cancer combined)	[1,28,37,44,49]
Occupational invTLV	Threshold Limit Value air concentration	[45]
AP	Acidification Potential	[8,28,50]
AAP	Aqueous Acidity Potential	[25]
EP	Eutrophication potential	[8,27]
N-nutri	Nitrogen nutrification potential	[8]
AETP (ag soil)	Aquatic Ecotoxicity Potential	[44]
ECA	Ecotoxicological classification factor for aquatic ecosystems	[1,25,27,51]
TETP	Terrestrial Ecotoxicity Potential	[44]

Unfortunately, most sources of data only provide nominal values without making quantitative statements on the uncertainties surrounding their data. In the few cases where the original source cited an uncertainty range or a coefficient of variation, the information provided was used to derive probability distributions. For the rest of the data, uncertainty distributions were derived on the basis of the scatter of plots of factor values from the source of interest against factors for the subset of chemicals available also in the source judged to be of highest quality. The procedure is illustrated here for the case of the Henry's law constant⁹⁷. Table 9-5 shows a summary of the Henry's law constant records stored in the EnvEvalTool database. With the exception of the review by Staudinger and Roberts [2], none of the sources consulted provided uncertainty factors for their reported values. Out of a total of 1785 chemicals with at least one Henry's law constant record in the database, only 198 had values and uncertainty factors published in Staudinger's review paper. Figure 9-5 shows an example of the procedure used to estimate uncertainty factors for the rest of the data sets. The figure shows a scatter plot of Henry's law constant values obtained from the PhysProp database (measured values) vs. the central estimated published by Staudinger. The uncertainty factor was computed according to the formula:

$$\log_{10}(\sqrt{UF}) = StdDev(\log_{10} K_{H,Staudinger} - \log_{10} K_{H,Phys Prop}) \quad (9-1)$$

The dashed lines on the plot correspond to the curves $K_H = K_{H,Staudinger} \times UF$ and $K_H = K_{H,Staudinger} \div UF$. A second example is shown in Figure 9-6 where experimental results from three different data sets are compared against the predictions of the HENRYWINB property estimation method. Not surprisingly, the uncertainty factors around estimated data are much higher than those associated with experimental data. Even though the uncertainty surrounding estimated values is large (several orders of magnitude), the distributions still convey significant information, since the range of possible values for the Henry's law constant for all the chemicals in the database⁹⁸ is much larger, spanning more than ten orders of magnitude.

⁹⁷ A similar example is provided in section 6.3.4 for the case of non-cancer chronic toxicity characterization factors.

⁹⁸ This would be the prior distribution for the Henry's law constant in the absence of any information

Table 9-5: Rank order of sources of Henry's law constant data used in the EnvEvalTool database

Rank	Source Code	Source of Data	Ref	Number available	Number used ^a	UF used ^b	comments
1	HgStudy	U.S. EPA	[12]	1	1	6	assumed
2	Staudinger	J. Staudinger and P.V. Roberts (Stanford U.)	[2]	198	198		provided in ref [2]
3	SRC PhysProp exp www	Syracuse Research Corporation	[3]	18	11	6	assumed
4	EPA96	U.S. Environmental Protection Agency (measured data)	[10]	199	104	6	regression vs. Staudinger
5	SRC PhysProp	Syracuse Research Corporation	[1]	494	367	6	regression vs. Staudinger
6	LIVECHEM	U.S. EPA	[10]	5	1	10	assumed (too few for regression)
7	Pvap/Solub	Any source of experimental solubility and Pvp data		197	52	10	assumed
8	HENRYWING	HENRYWIN Group Method Prediction (Syracuse Research Corporation)	[1]	663	384	325	regression vs. PhysProp K Henry
9	EPATRI99	U.S. EPA	[11]	347	129	975	assumed worst case (HENRYWIN Bond method used)
10	HENRYWINB	HENRYWIN Bond Method Prediction (Syracuse Research Corporation)	[1]	1296	382	975	regression vs. PhysProp K Henry
11	SRC PhysProp est www	Syracuse Research Corporation	[3]	18	7	975	assumed
12	ChemFinder	ChemProp Pro estimation functions in CambrideSoft's ChemFinder	[9]	1027	137	15000	regression vs. PhysProp K Henry
13	CHEMEST	GSC Corporation	[10]	40	12	20000	regression vs. PhysProp K Henry

a) Number used: number of chemicals for which the data source is the highest-rank available

b) UF: uncertainty factor. Lognormal distributions with geometric standard deviation equal to the square root of the uncertainty factor were used to represent the uncertainty in the data

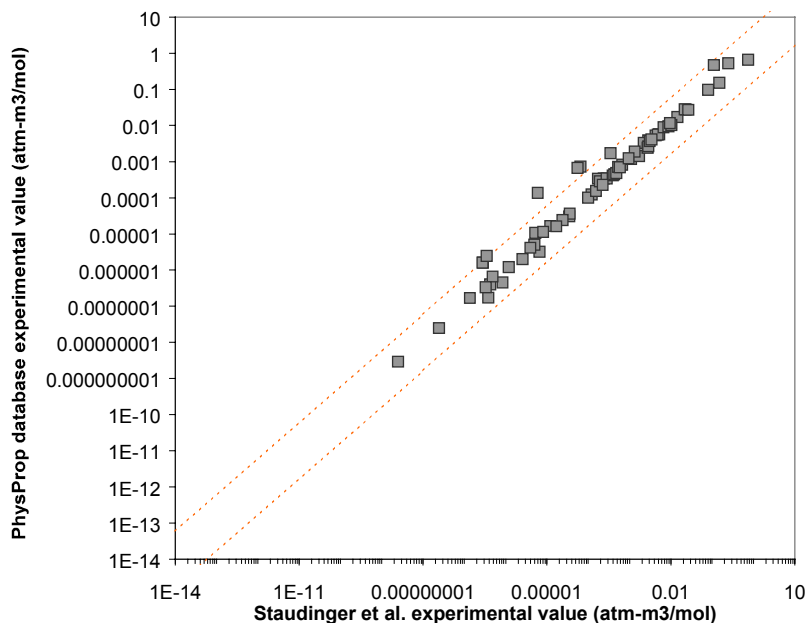


Figure 9-5: Scatter plot of PhysProp database experimental Henry's law constant values vs. experimental values from Staudinger et al.

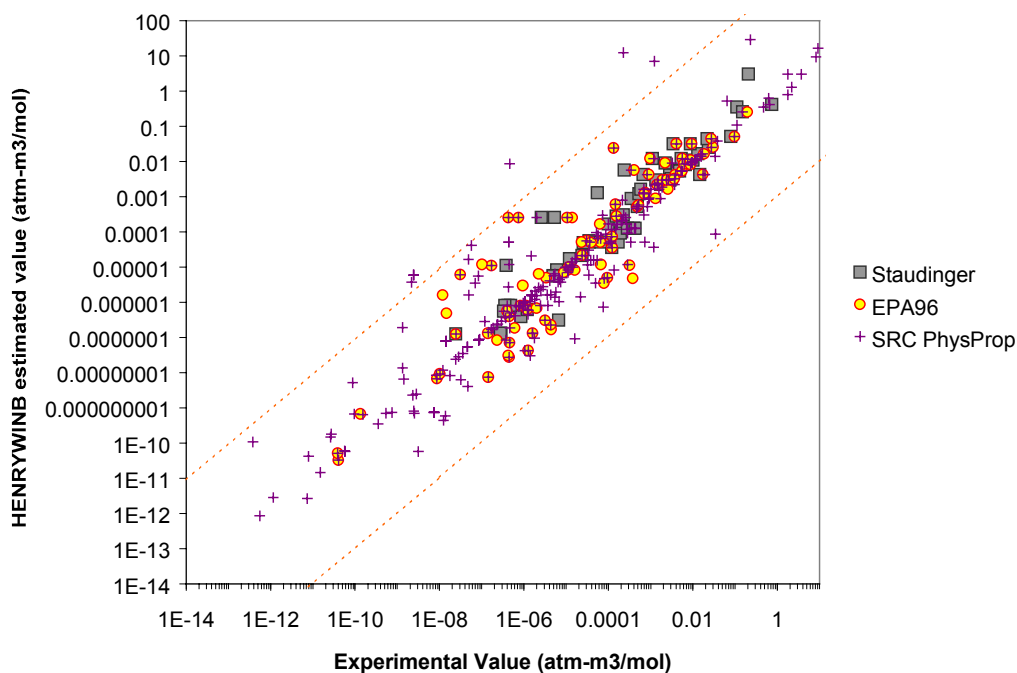


Figure 9-6: Scatter plot of Henry's law constant values estimated using the HENRYWINB bond contribution method vs. experimental values from three different sources

9.4.3 System functions

Two main functions have been implemented in the EnvEvalTool through combinations of macros and Visual Basic code. The functions are briefly described in the following paragraphs. Details are provided in sections B.2 and B.3 in the Appendix.

GENERATION OF TOXICITY INDICATOR DISTRIBUTIONS

Given a list of chemicals (identified by their CAS Numbers), an EnvEvalTool macro can export uncertainty distributions for all the required physical property and toxicity parameters to the spreadsheet-based human exposure model. The model can then be used to generate distributions of toxicity indicators that take into account not only toxicity, but also the likelihood of long term exposure to chemicals released to air, water, or soil. This function was used to generate the spreadsheets used to carry out the analysis of the Toxic Release Inventory case study in section 6.5. It was also used to generate the cancer and non-cancer chronic toxicity characterization factors used in the chlorine life cycle analysis example in Chapter 7, and in the generation of unit environmental impact indicators for the solvent recovery case study examples in chapters 4, 5, and 8. The macros take advantage of the information stored in the database to produce a fully documented spreadsheet model, in which every cell containing a probability distribution has a comment citing the source of the distribution. The author has found this feature to be very valuable in sensitivity analysis: whenever a factor was identified to be an important contributor to either overall valuations or to uncertainty in valuations, it was possible to quickly identify the data source used to obtain the distribution. The database would then be searched to check whether the factor used in the simulation was consistent with distributions for the same factor obtained from other sources.

GENERATION OF INPUT DATA FOR THE PIO-LCA METHOD

Given a list of products or processes of interest, a specification of market share scenarios, and a choice of environmental valuation method, an EnvEvalTool macro can create all the input data spreadsheets for the PIO-LCA method. The program builds a set of products and processes recursively, until there are no products in the set for which a process that produces them is not

included in the set⁹⁹. It then retrieves all the distributions for the emissions from processes in the set and for the characterization factors corresponding to the chemicals emitted and the impact categories included in the valuation method chosen. As in the case of the macro that feeds the human exposure model, all the cells that contain probability distributions in the resulting Excel spreadsheets will contain a comment specifying the source of data used.

OTHER FUNCTIONS

The time spent creating the data model and importing data for it from publicly available sources more than paid off in time saved in analysis later on. The relational structure of the database allows a wide variety of queries to be made. For example, all the tables in this chapter were generated using queries within the database (including the automatic placement of references at the end of this chapter through the use of the EndNote code field in the References table¹⁰⁰).

9.5 Suggested implementation within organizations

Environmental evaluation knowledge management systems such as the EnvEvalTool described in this chapter have a very important role to play in manufacturing organizations. Such systems can be used to overcome two of the major barriers to incorporating environmental performance as an explicit objective of product and process design, namely (i) the lack of readily accessible data regarding the environmental impact of various products, services, and emissions, and (ii) the reluctance to use available indicators due to the lack of confidence in their numeric values.

With regard to the first issue, it is certainly possible for an organization with even modest resources allocated to environmental management to compile most of the publicly available data regarding environmentally relevant properties of chemicals. After all, a single graduate student (the author) working over a period of about 4 months was able to compile a database with most of the publicly available information on characterization and exposure factors. Recent efforts

⁹⁹ Depending on how complete the input-output data stored in the Use Factors and Make Factors tables are, there may be instances of products for which no process that makes them is stored in the database. A query has been built to identify such products (see query QIO Products Used but not Made in section B.3.3).

¹⁰⁰ EndNote (ISI Research Soft, www.endnote.com) is a software package used to organize and retrieve bibliographic information.

undertaken by the Environmental Defense Fund and by the U.S. Environmental Protection Agency to post data in the internet have reduced the cost of accessing such information. Most organizations already have managerial cost databases with most of the input-output coefficients needed for the PIO-LCA method. A majority of them should also have decent emission factors for the processes they operate, since they are required by law to compile annual inventories of toxic releases. The area with the most difficulty in accessing data is perhaps the input-output coefficients and emission factors for upstream processes operated by organizations independent of the organization carrying out the analysis. Universities and consulting firms, however, are filling some of those gaps in an effort to provide data for life-cycle assessment software.

The second barrier has been uniquely addressed in this work through the use of uncertainty analysis. Application of environmental indicators is no longer an exercise based on faith, but one in which analysts can place confidence bounds on the conclusions derived from the environmental valuation models. With rapid advances in hardware and software, the computational cost of carrying out Monte Carlo simulations drops month by month. Existing software (e.g. @Risk) is sold with parallel calculation versions that allow the management of simulations on multiple CPUs over a network. Most organizations have dozens of personal computers with CPUs that are idle a significant portion of the time. Monte Carlo simulations of PIO-LCA and human exposure and toxicity models with more than 2000 uncertain parameters have been routinely carried out as part of this dissertation.

Figure 9-7 shows an information flow diagram for the management of environmental evaluation knowledge and its subsequent application to product and process design. A group within an organization would be charged with the responsibility of maintaining the environmental knowledge base for the organization. This knowledge base would be interfaced with the managerial cost accounting systems and with the environmental reporting system for the acquisition of input-output data and emission factor data for processes operated by the organization. Links to outside organizations (e.g. government agencies and academic institutions) would enable periodic updating of chemical-specific physical properties and environmental problem characterization factors. Establishment of standard protocols could make this updating automatic. Finally, top decision-makers within the organization would be consulted to set the valuation factors used by the organization, as well as the appropriate weighting factors to be used when examining tradeoffs between relative economic and

environmental performance (e.g. the α value in the utility function introduced in section 4.6.3). Uncertainty or lack of agreement in arriving at valuation and weighting factors would not be an impediment to their consideration in decision making using the methods developed in this work. Sensitivity analysis on important projects would help the managers of the knowledge base to set priorities for reducing the uncertainty in the most important parameters.

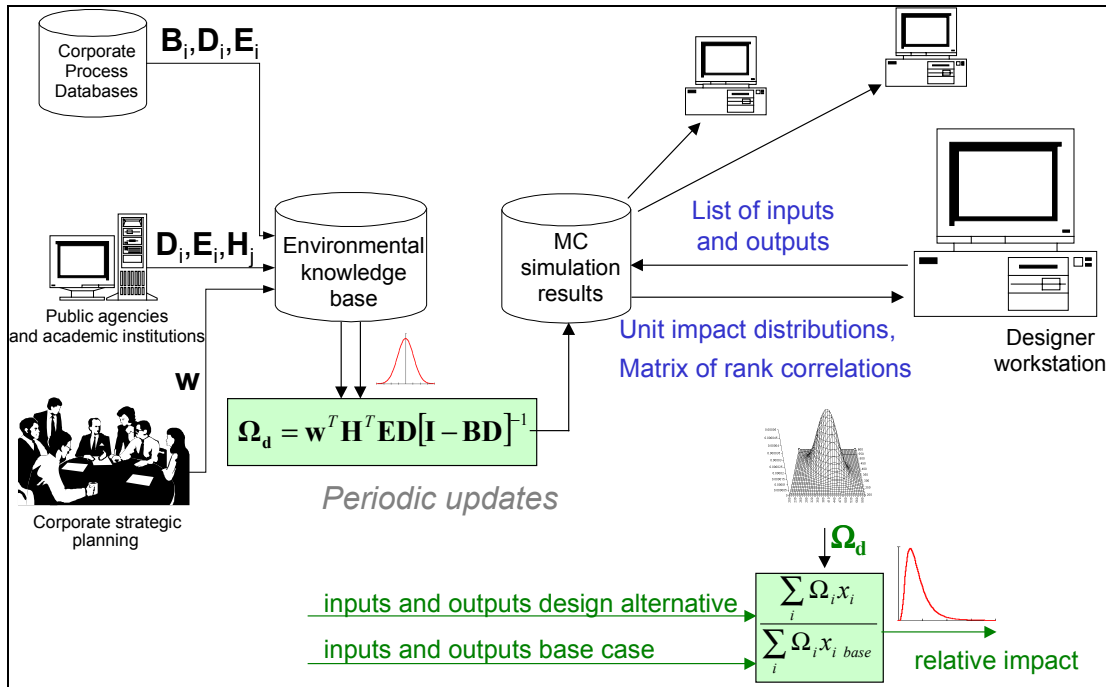


Figure 9-7: Information flow diagram for the implementation of the an environmental evaluation knowledge management system within a private organization

Designers would interact with the system by providing it with a list of the raw materials, services, and emissions that they expect will be part of their design. A PIO-LCA model would then be built on demand and run to generate a set of correlated unit environmental impact indicators. Designers would then be able to use these unit environmental impact indicator distributions to generate distributions for the relative environmental impact of alternative designs relative to a base case alternative using the procedures described in Chapter 4.

Governments and the academic community can greatly contribute to decreasing the barriers faced by corporations by publishing data electronically in standardized formats. Uncertainty factors should be provided with every data element published. Advances in hardware and software have resulted in a situation where we are more limited by the availability

of distribution functions for input data than by the cost or time required to carry out uncertainty analysis.

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Chapter 10 Recommendations for future work

Many opportunities to further the goal of enabling chemical process designers to incorporate environmental considerations as part of the design objectives were identified in the course of this project. This chapter provides a summary of promising leads.

10.1 Environmentally conscious generation of design alternatives

While this thesis focused on the decision support tools, many opportunities remain to develop tools that facilitate the generation of alternatives that are likely to have lower environmental impact. Research ideas include:

- Increase the integration of process chemistry into the generation of design alternatives
- Develop tools to identify new reaction pathways and catalysts
- Extend alternative generation methods to include non-conventional unit operations
- Develop methods that allow the rapid identification of opportunities to integrate processes
- Develop methods to recognize opportunities to match waste streams with feed streams, and to prescribe the operations needed to transform a waste stream into a usable feed stream.

10.2 Environmentally conscious process simulation

The decision support tools developed in this project relied on existing capabilities of process simulators for the generation of input-output process information. Not all of the process information needed to assess environmental performance is routinely available from process simulators, however. Capabilities that would provide more of the needed information include:

- Predict generation of undesired byproducts
- Improve prediction of reaction rates
- Predict fugitive emissions and emissions from nonroutine operations (e.g. startup)

- Include waste-treatment unit operations in process simulators
- Increase the ability of process simulators to track dilute species

10.3 Integration of process simulation with environmental valuation models

The following is a list of ideas for integrating physical models (e.g. process flowsheet models) with environmental valuation models:

- Further the development of the EnvEvalTool to include a field in the Chemical Information table with the internal code used to identify individual chemical species in process simulators. Modify process simulator graphic interfaces so that important environmental information for chemicals is displayed when a new chemical is added to a model.
- Compile databases with typical mass and energy balances (including trace components of environmental significance) for widely used raw materials in the chemical industry, to facilitate the characterization of upstream processes.

10.4 Environmental valuation methods

The examples in Chapter 5 showed that the uncertainty in weighting factors assigned to different environmental impact category indicators can be the largest source of decision uncertainty in the comparison of alternative designs. It is necessary to develop robust weighting factor assessment methods with consistency checks, to verify that the predictions of the model are consistent with the tradeoffs a decision maker would be willing to make.

10.5 Economic valuation methods

The analysis in section 3.2.5 suggested that designers might be routinely designing equipment that is too small relative to the economic optimum. This hypothesis needs to be either confirmed or disproved through collaboration with industrial partners. Economic models used at the conceptual design stage should be examined to extract the actual or implied value of the annualization factor used to resolve operating cost – capital cost tradeoffs. One of the sources of bias identified was the use of size-independent installation cost factors. Company data or data from knowledge bases (such as the Icarus knowledge base) could be used to derive equations for

size-dependent installation cost factors. These equations should then be submitted to Chemical Engineering handbooks for publication,

10.6 Uncertainty propagation and uncertainty analysis

The following are ideas for increasing the range of uncertainty propagation and uncertainty analysis tools available to process designers:

- Apply partial rank correlation coefficients for uncertainty analysis in models with correlated input variables
- Carry out an analysis of the amount of information lost when the copula method is applied. Develop or apply statistical tests to evaluate the goodness of fit of a multivariate copula distribution. Many different copula families are available. If satisfactory goodness of fit tests can be made available, then software such as TopRank could be extended to fit multivariate distributions
- Develop versions of the deterministically equivalent modeling method that are compatible with Excel and the Decision Tools Suite.
- Develop, through case studies, specific guidance for designers interested in using DEMM to create spreadsheet metamodels of flowsheet models. Issues to address include: guidance on the selection of an acceptable index of agreement, examples of responses for which the approach does not work, typical transformations that can be used to decrease the number of terms needed to achieve good approximations, effect of increasing the order of approximation vs. effect of including higher order cross terms, etc.

10.7 Knowledge management strategies

The value of a tool such as the EnvEvalTool developed for this work will increase dramatically as the number of people using the tool increases. Some ideas to achieve this include:

- Launching an international effort (perhaps within the ISO framework) to develop data representation and storage standards for the uncertain parameters and properties of chemicals needed as input to environmental valuation models.

- Defining standards for the exchange of environmental valuation data through the internet
- A major effort should be made by publishers of environmental assessment data to include quantitative uncertainty estimates with the nominal values they publish.

10.8 Case studies

- The use of the tools needs to be demonstrated in an industrial setting with practicing process designers.
- More case studies are needed for use in chemical engineering education.

Chapter 11 Conclusions

1. Environmental issues are emerging as one of the major driving forces for change in the chemical industry. A view of product and process design that sees environment as an objective and not just as a constraint on operations can lead to the discovery of design alternatives with improved environmental and economic performance. An adoption of environmentally conscious design ideas in academic curricula is perhaps the most significant leverage point for moving the practice of chemical process design in this direction.
2. A frequently cited objection to the use of quantitative indicators of environmental performance is that the underlying data are too uncertain for the numbers to have any meaning. This thesis demonstrated that explicit incorporation of uncertainties allows bounds to be established on the confidence of decisions made on the basis of uncertain indicators. The examples provided showed that large uncertainties in indicators used to assess environmental performance do not necessarily imply uncertainty in decision-making.
3. There are no major conceptual differences between environmental and economic evaluation models. Both types of models contain uncertain parameters and rely on value judgements. The models differ in the magnitude of the uncertainties, the accessibility of data, and in the familiarity of users with making the required value judgements.
4. Application of the tools in this thesis should allow designers to anticipate future regulations on the processes they design, since knowledge about potential environmental impacts is typically available years before the relevant regulations become enacted. The tools can also be used to negotiate multimedia pollution prevention strategies with stakeholders who do not necessarily share the same values regarding the environment with the company responsible for the operation of the processes.
5. Current availability of hardware and software is such that the main barrier to propagating uncertainties in large spreadsheet-based models has shifted from computer resources and analysis time to the availability of probability distributions for the relevant parameters. A

database and uncertainty estimation procedures were developed in this thesis to address this bottleneck.

6. Proper environmental assessment of products and processes requires a life cycle perspective. Unfortunately, most life-cycle emission inventories today do not allow users to trace specific emissions back to the first process that originated them. In addition, the data are difficult to maintain as new information becomes available. Structuring the life-cycle assessment problem around input-output matrices overcomes these difficulties.
7. The uncertainty and contributions to uncertainty in absolute measures of performance might be quite different from the uncertainty and contributions to uncertainty in relative measures of performance used to rank two alternatives. The use of relative measures of performance allows the comparison to be made taking full account of correlations between absolute measures that arise from uncertain parameters common to both alternatives.
8. While the size of problems for which uncertainty propagation can be undertaken through Monte Carlo simulation continues to increase as computer speeds rise and their costs drop, many process models used by designers today are too expensive for traditional Monte Carlo simulation. In the case of models with smooth and regular output responses to changes in uncertain input or manipulated variables, it is possible to build inexpensive spreadsheet-based metamodels through the deterministic equivalent modeling method with a small number of runs of the expensive flowsheet model. The application of this technique greatly expands the universe of flowsheet models for which uncertainty propagation can be routinely made.
9. The formal framework and methods described in this thesis allow the incorporation of sophisticated evaluation criteria in routine design activities, even in the presence of substantial uncertainty. The ideas presented here are quite general and can be applied to any decision problem with significant uncertainties in the objective function parameters.

The key conclusion of this thesis is that uncertainty is not the same as ignorance. In the ever more competitive business environment of the 21st century, corporations that ignore existing knowledge regarding the potential impact of their activities do so at their own peril.

Appendix A Solvent recovery system design case study

A.1 Problem statement

A manufacturing process produces a waste stream consisting of 1.4 weight percent methylene chloride (CH_2Cl_2) dissolved in water. A steam stripping process is used to recover most of the methylene chloride before discharging the processed stream into the sewer. The current configuration of the process used to effect the recovery is shown in Figure A-1. The feed stream is fed to the first tower, where vapor generated as a result of the injection of steam into the second tower strips methylene chloride from the incoming feed stream. The aqueous stream is then directed to the second tower, where the steam injected strips additional solvent. The mixture of water and methylene chloride vapor generated in the second tower and enriched in the first tower is collected from the top of the first tower and condensed. Upon condensation the liquid splits into a methylene-chloride-rich stream and a water-rich stream. A decanter separates these two phases. The solvent-rich phase is recycled back to the manufacturing process, while the aqueous stream is joined with the feed to the solvent recovery process. The effluent leaving the second tower is discharged to the sewer system. At the time the system was built, government standards set a concentration limit of one hundred parts per million (100 ppm) methylene chloride by weight (i.e. 100 mg/L) in the discharged effluent. The company operating this process has recently learned that the local sewer authority is planning to tighten the standard, possibly to a level as low as 2 ppm. Table A-1 provides key process conditions and process specifications.

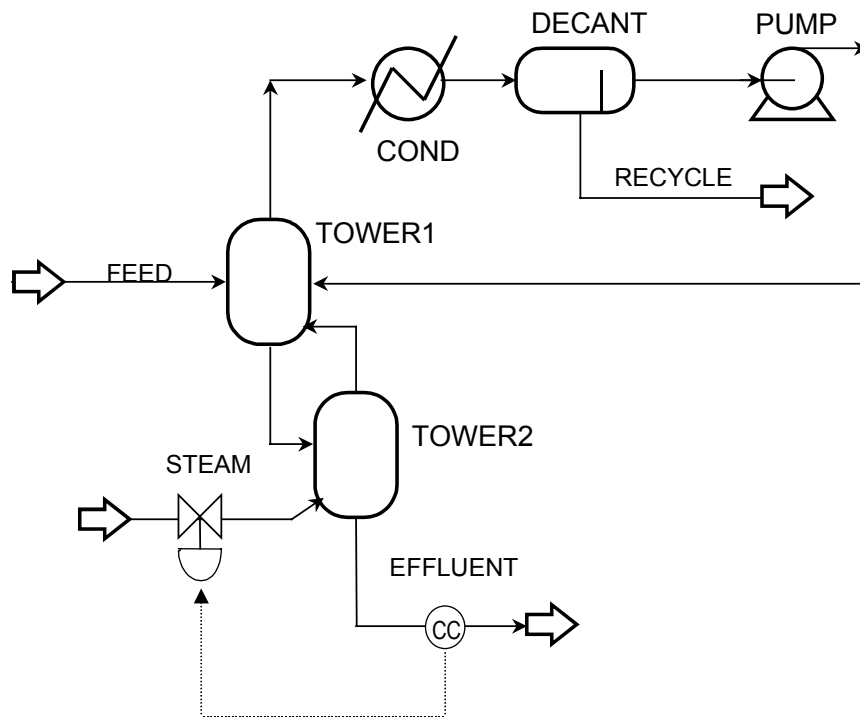


Figure A-1: Flowsheet for the methylene chloride recovery system

Table A-1: Input data for the methylene chloride recovery optimization problem

Streams:		
FEED	Mass Flow:	100,000
	lb./hr.	
	Temperature:	95 °F
	Pressure:	24.7 psi
	CH ₂ Cl ₂ mass fraction:	1.4%
STEAM	Saturated, 200 psi	
Equipment:		
TOWER1	Pressure:	18.70 psi
	Heat duty:	0
TOWER2	Pressure:	19.70 psi
	Heat duty:	0
COND	Pressure:	14.70 psi
	Temperature:	75 °F
DECANT	Pressure:	14.70 psi
	Heat duty:	0
PUMP	ΔPressure:	+5.00 psi

The key tradeoff in this system involves steam input and solvent losses. As the amount of steam fed to the system increases, more methylene chloride is recovered overhead, and less is lost as discharge to the sewer, thereby reducing its concentration (Figure A-2). From an economic perspective, the tradeoff is one between the cost of supplying steam and the cost of purchasing make-up methylene chloride to replace the amounts lost with the wastewater discharge (or the cost of the fines assessed if effluent standards are violated). There are also tradeoffs from an environmental impact perspective. The key tradeoff is that between the impact of the discharged solvent (including the impact of producing the methylene chloride required to replace what is lost), and the impact of supplying steam (including the impact of producing and burning the fuel used in the steam boiler).

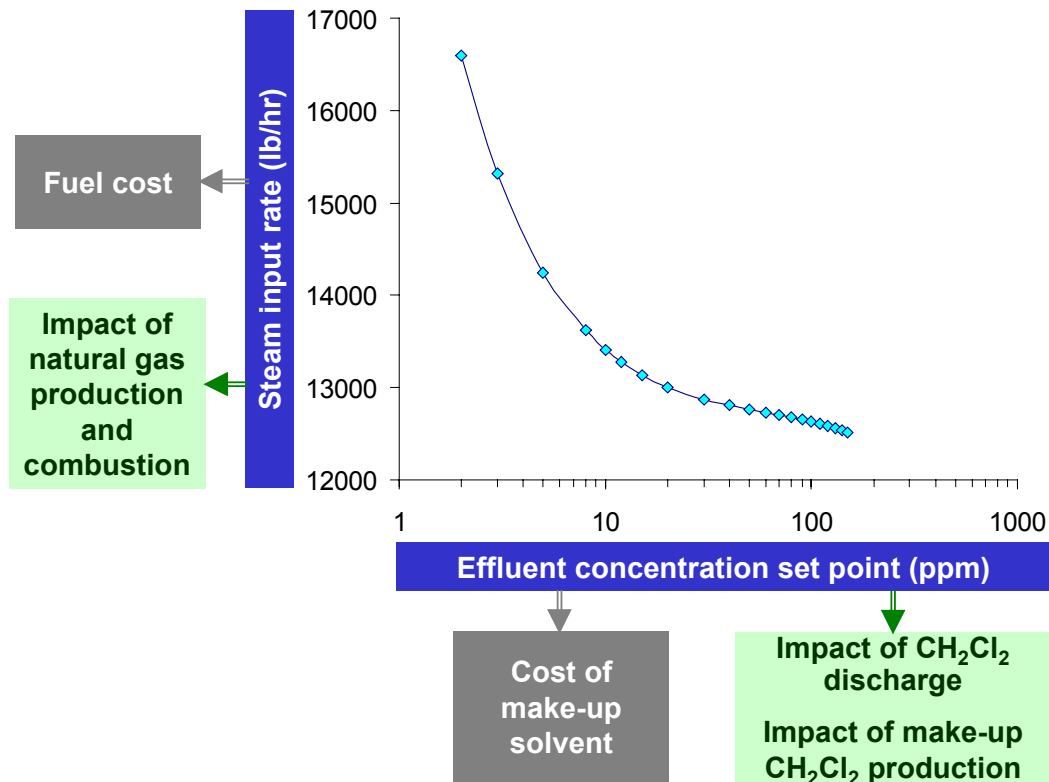


Figure A-2: Tradeoffs in the operation of the methylene chloride recovery system

A.2 Process models

Models of the process shown in Figure A-1 and of two alternative process configurations were built using version 10.0 of the Aspen Plus process simulator¹⁰¹. The two alternative process configurations included a heat exchanger to preheat the feed using the effluent stream. In addition, the second process alternative replaced the two flash drums (TOWER1 and TOWER2) by a stripping column with a variable number of theoretical stages. The Aspen Plus models used to simulate each unit operation are listed in Table A-2.

Table A-2: Unit operation models used

BLOCK ID	MODEL	DESIGN SPECS
TOWER1	FLASH2	Pressure, Heat Duty (Adiabatic)
TOWER2	FLASH2	Pressure, Heat Duty (Adiabatic)
COND	HEATER	Pressure, Temperature
DECANT	FLASH3	Pressure, Heat Duty (Adiabatic)
PUMP	PUMP	Δ Pressure
HX	HEATX	Area
STRIPPER	RADFRAC	Number of stages

The simulation involved two components: water and methylene chloride. Physical properties for both compounds were obtained from the pure components data bank in Aspen Plus. The thermodynamic model used for the vapor phase was the Redlich-Kwong equation of state. Liquid mixing properties were calculated using the NRTL model. The model is given by:

$$\ln \gamma_1(x_1, T) = (1 - x_1)^2 \left(\tau_{21}(T) \left(\frac{G_{21}(T)}{x_1 + (1 - x_1)G_{21}(T)} \right)^2 + \tau_{12}(T) \frac{G_{12}(T)}{((1 - x_1) + x_1 G_{12}(T))^2} \right) \quad (\text{A-1})$$

$$\ln \gamma_2(x_1, T) = x_1^2 \left(\tau_{12}(T) \left(\frac{G_{12}(T)}{(1 - x_1) + x_1 G_{12}(T)} \right)^2 + \tau_{21}(T) \frac{G_{21}(T)}{(x_1 + (1 - x_1)G_{21}(T))^2} \right) \quad (\text{A-2})$$

where:

$$G_{ij}(T) = \exp(-\alpha_{ij} \tau_{ij}(T)) \quad (\text{A-3})$$

$$\tau_{ij}(T) = A_{ij} + \frac{B_{ij}}{T} \quad (\text{A-4})$$

$$\alpha_{12} = \alpha_{21} \quad (\text{A-5})$$

Five parameters are needed to calculate the activity coefficients, namely A_{ij} , A_{ji} , B_{ij} , B_{ji} and α_{ij} . In the examples in sections 4.7.1 and 5.4.1 it was assumed that the process performance curves

were well known. Those curves were generated using the NRTL parameter values listed in Table A-3. In reality, there is quite a bit of uncertainty about the proper values for these parameters, as evidenced by the four sets of values stored in the Aspen Plus data banks (Table A-4). These uncertainties are examined in more detail in section A.4.

Table A-3: Nominal values for the parameters in the NRTL model

Parameter	Value
A_{ij}	-7.7458
A_{ji}	8.8375
B_{ij}	3144 K
B_{ji}	-1493.31 K
$\alpha_{ij} = \alpha_{ji}$	0.163

Table A-4: NRTL parameter data sets stored in the Aspen Plus data banks

Data bank	VLE-IG	VLE-RK	VLE-HOC	LLE-ASPEN
A_{ij}	0	0.0	0.0	-4.464
A_{ji}	0	0.0	0.0	6.6853
$B_{ij}(K)$	941.4288	940.1598	945.0139	2269.2642
$B_{ji}(K)$	1483.8632	1487.481	1488.0809	-839.8907
$\alpha_{ij} = \alpha_{ji}$	0.30	.30	.30	.20

A.3 Valuation models

The economic valuation models used in the examples are described in the introduction to each example. Depending on the decision context, any of the following three valuation models were used: Operating Cost, Total Annualized Cost, or Net Present Value.

The PIO-LCA method was used to obtain unit life cycle environmental impact valuations for steam, methylene chloride discharges, electricity, cooling water, and steel sheet. The process-product system used was a superset of the one used in the chlorine LCA example (Chapter 7). The system used had 30 products, 35 processes, 114 environmental exchanges, and 10 impact categories. The list of products and processes in the network is given in Table A-5

¹⁰¹ Aspen Technology, Inc., Cambridge, Mass., www.aspentech.com

Table A-5: Products and processes in the PIO-LCA model used for the environmental evaluation of the alternatives in the solvent recovery example

Products and services		Processes	
Chlorine	Salt from brine	Brine pumping	Methane reforming
Coal	Sinter pellets	Chloralkali production (diaphragm cell process)	Methanol production
Coke	Sodium hydroxide	Chloralkali production (membrane cell process)	Methyl chloride production
Cooling water	Steam (200 psia)	Chloralkali production (mercury cell process)	Methylene chloride discharge
Diesel fuel	Steel	Coal furnace	Methylene chloride production
Electricity	Steel sheet	Coal production	Natural gas production
Hydrogen	Thermal energy from coal furnace	Coal-fired power plant	Nuclear power plant
Hydrogen chloride	Thermal energy from industrial gas furnace	Coke production	Oil furnace
Iron	Thermal energy from oil furnace	Cooling water	Oil production
Iron ore	Thermal energy from utility gas furnace	Diesel engine	Oil-fired power plant
Limestone		Diesel fuel production	Oxygen production
Mechanical energy from diesel engines		Gas-fired power plant	Railroad transport
Methanol		Hydroelectric plant	Sinter pellet production
Methyl chloride		Hydrogen chloride production	Steam generation (200 psia)
Methylene chloride		Industrial gas furnace	Steel production
Methylene chloride discharge		Iron ore mining	Steel sheet production
Natural gas		Iron production	Utility gas furnace
Oil		Limestone production	
Oxygen			
Railroad transport			

Impact category valuation factors, as well as the sources of data used to download characterization factors for these impact categories into the EnvEvalTool are listed in Table 3-16. Human toxicity indicators were calculated using the multimedia fate, transport, and exposure model described in section 6.3. Indicators expressed in units of [equivalent lifetime cancer risk/(kg/km²/day)] were multiplied by a factor of 0.03 to estimate DALYs/kg, according to the following expression:

$$1 \text{ HTP unit} = \frac{\frac{1 \text{ cancer case}}{\text{person} \cdot 70 \text{ yr}}}{\frac{\text{kg}}{\text{km}^2 \text{ day}}} \times \frac{15 \text{ DALYs}}{\text{cancer case}} \times \frac{50 \text{ people}}{\text{km}^2} \times \frac{1 \text{ yr}}{365 \text{ days}} = 0.03 \frac{\text{DALYs}}{\text{kg}} \quad (\text{A-6})$$

where 70 years is the average life expectancy, 15 DALYs is the average number of years of life expectancy lost per cancer case, and 50 people/km² is roughly the population density of the continental United States.

A.4 Assessment of uncertainties

A.4.1 Uncertainty in process model parameters

NRTL PARAMETERS

Figure A-3 displays a comparison of experimental data with predictions of the infinite dilution activity coefficient of methylene chloride in water made with two thermodynamic models (NRTL or UNIQUAC) using parameter sets stored in the Aspen Plus databank. The chart demonstrates that the uncertainty is quite significant.

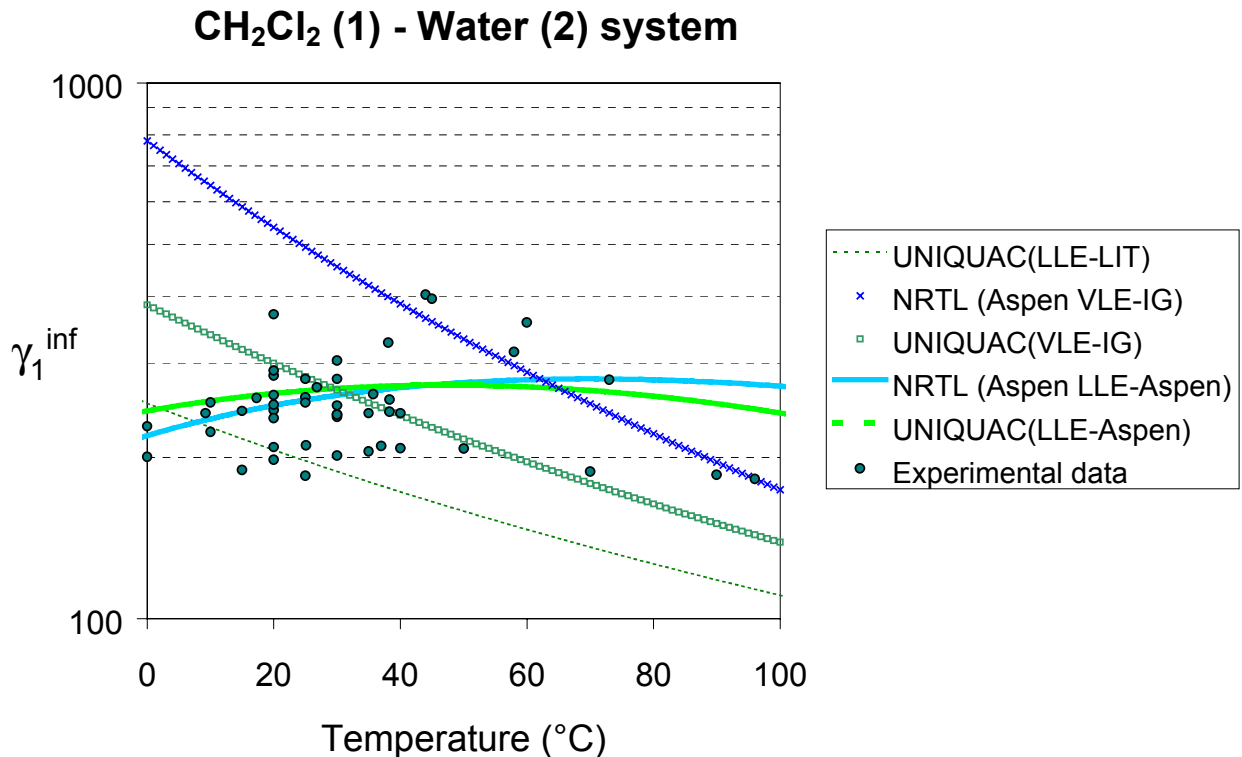


Figure A-3: Comparison of experimental data to infinite dilution coefficients calculated using the parameters stored in the Aspen Plus data banks

In order to estimate uncertainty distributions for the parameters on the basis of the available data, the maximum likelihood estimate maximization method for systems with unknown general covariance was used [1]. The method not only provides the user with point estimates of the parameters, but also with a covariance matrix obtained from the Hessian of the

maximum likelihood estimator function. All VLE and LLE data for the methylene chloride-water system identified through an intensive literature search were incorporated into the estimation procedure [2-18]. It was found during optimization that the values of the parameter pairs (A_{12}, B_{12}) and (A_{21}, B_{21}) were very tightly correlated. This observation allowed the uncertainty in the thermodynamic model to be represented as a function of three i.i.d unit normal random variables:

$$\begin{bmatrix} A_{ij} \\ A_{ji} \\ \alpha_{ij} \end{bmatrix} = \begin{bmatrix} -7.7458 \\ 8.8375 \\ 0.16294 \end{bmatrix} + \begin{bmatrix} -3.1260 & 0 & 0 \\ -1.7359 & 1.7264 & 0 \\ 0.008333 & 0.007525 & -0.01496 \end{bmatrix} \begin{bmatrix} \xi_a \\ \xi_b \\ \xi_c \end{bmatrix} \quad (\text{A-7})$$

$$B_{ij} = 978.01 - 279.64A_{ij}$$

Propagation of the above parameter uncertainties in the NRTL model yields the distribution for methylene chloride infinite dilution activity coefficients as a function of temperature shown in Figure A-4. Not surprisingly, the model is most accurate in the temperature range for which the most data are available. Unfortunately, there is quite a bit of uncertainty at the temperature in which the steam stripping process operates ($\sim 100^\circ\text{C}$).

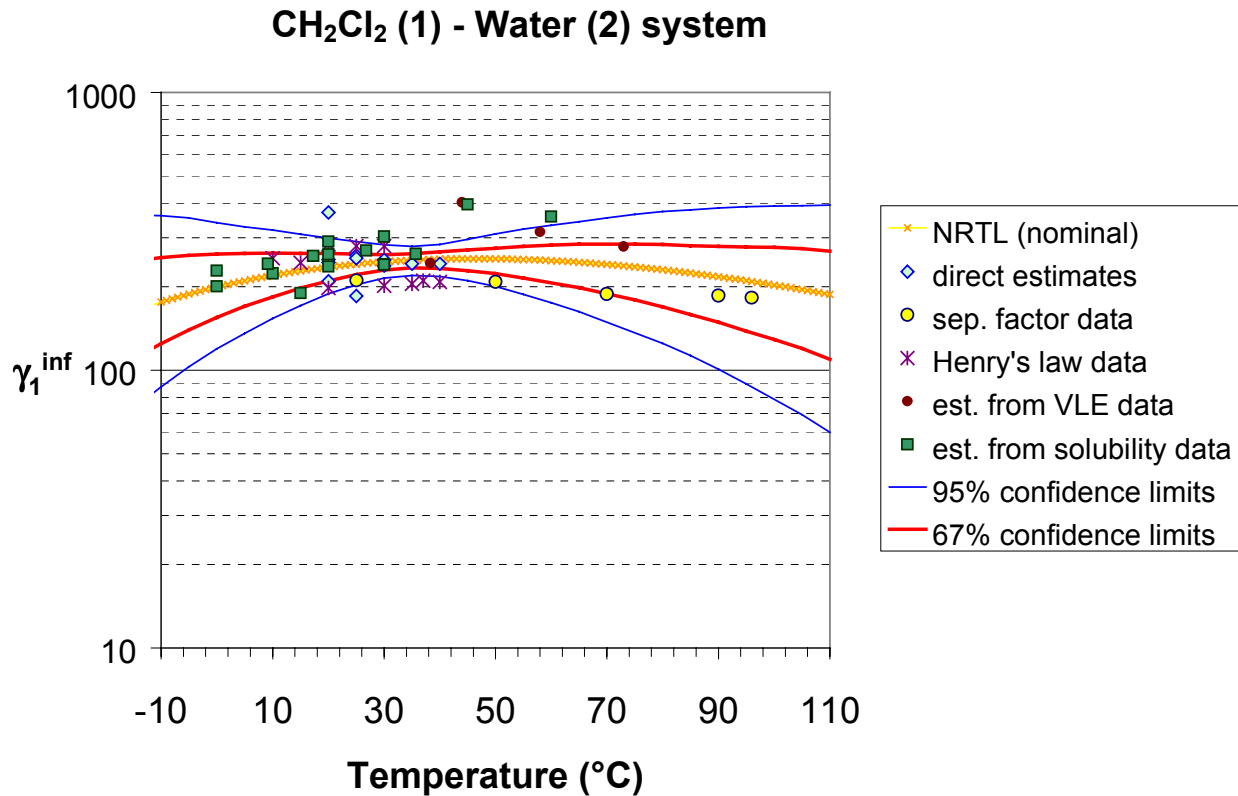


Figure A-4: Monte Carlo simulation results for the methylene chloride infinite dilution activity coefficient in water calculated using the NRTL model and the joint distribution of parameters given by eq (A-7)

HEAT TRANSFER COEFFICIENT

The installation of a heat exchanger between the effluent and the feed is considered as a potential retrofit alternative. The effluent stream is essentially pure water, while the feed stream is about 98% water by mass. Hence, heat transfer coefficients between two aqueous streams are needed. Design books were consulted for typical values of the overall heat transfer coefficient, yielding the values listed in Table A-6: Based on those values, a subjective beta distribution with parameters (min=70 Btu^oF⁻¹ft⁻²hr⁻¹, max=500 Btu^oF⁻¹ft⁻²hr⁻¹, $\alpha_1=3.14$, and $\alpha_2=2.86$) was assigned to the heat transfer coefficient. A plot of this distribution is shown in Table 4-4.

Table A-6: Overall heat transfer coefficients for heat exchangers transferring heat between two aqueous streams

Shell side	Tube side	Design U Btu/(°F ft ² hr)	Source
Deminerlized water	Water	300-500	[19]: Table 10-10
Jacket water	Water	230-300	
Water	Water	200-250	
Cooling tower water	Cooling tower water	70	[20]: Table A.7-2
Cooling tower water	Boiler water	100	
Boiler water	Boiler water	167	
Water	Water	250-500	[21]: Table15.6
Water	Liquid	150	[22]: Table 9.11

OVERALL TRAY EFFICIENCY

For simulation (column rating in ASPEN PLUS) either the Murphree efficiency or the vapor efficiency need to be specified. Calculation of these efficiencies can only be done with detailed design data. At this stage of the design, the only practical measure of efficiency is the overall efficiency. Given an actual number of trays, the uncertain overall efficiency is used to calculate the corresponding theoretical number of trays, which in turn is used to estimate the system performance.

The O'Connell correlation [23] was used to estimate the overall column efficiency, as recommended by Douglas [20] and Kister [24]. The data for the original paper were fitted to a cubic equation that relates the logarithm of O'Connell's independent variable group to the logarithm of the overall tray efficiency.

O'Connell's independent variable group (which involves the Henry's law constant, system pressure and liquid viscosity) may be rewritten as:

$$\frac{HP}{\mu} = \frac{1}{\gamma_1(x_1, T) P_1^{vap}(T) M_L} \frac{\rho_L P}{\mu_L} = \frac{\rho_L P}{\gamma_1(x_1, T) P_1^{vap}(T) M_L \mu_L} = \frac{\rho_L}{K_1(T, P) M_L \mu_L} \quad (\text{A-8})$$

where K_1 is the equilibrium ratio of methylene chloride (the ratio of the vapor mole fraction to the liquid mole fraction).

Although the system pressure (P), methylene chloride vapor pressure (P_1^{vap}), average liquid viscosity (μ_L), average liquid molecular weight (M_L), and average liquid mass density (ρ_L)

are quite well determined, the activity coefficient is not (recall Figure A-4), and thus the overall column efficiency is a strong function of one of the uncertain inputs.

In addition, O'Connell's correlation is not perfect. The uncertainty in the prediction was modeled by multiplying the prediction of the correlation by a correction factor, whose logarithm is assumed to be normally distributed with mean 0 and standard deviation 0.20.

Figure A-5 shows the correlation used, the experimental data upon which the correlation is based, and the 67% and 95% confidence limits on the overall column efficiency that are obtained using the assumed distribution function for the correlation error.

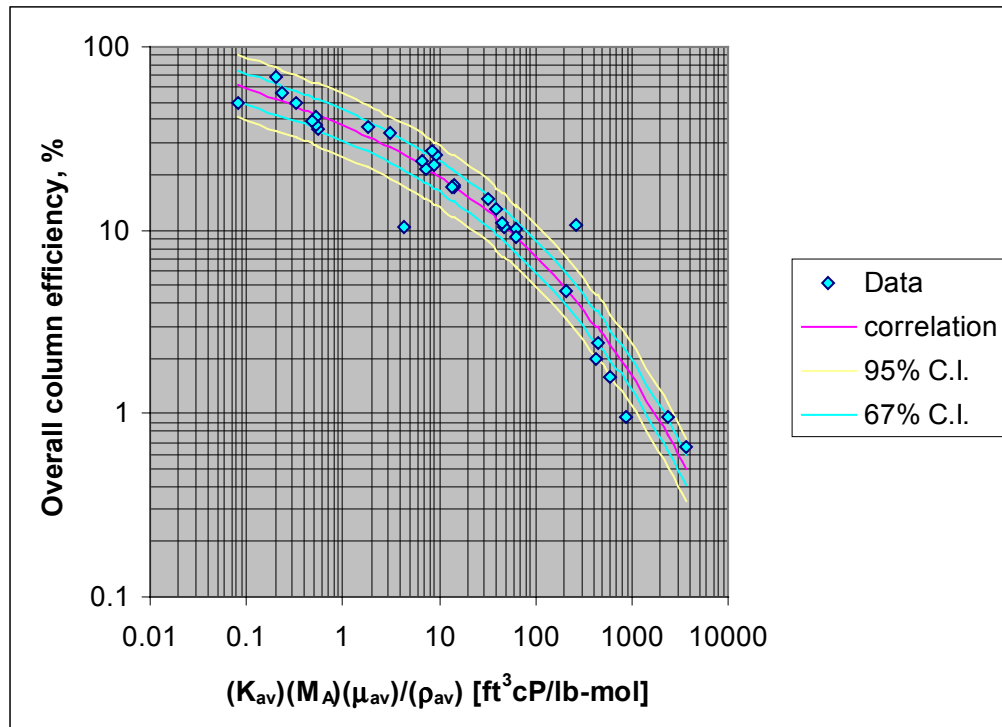


Figure A-5: O'Connell's correlation for overall tray efficiency

For the stochastic optimization exercise in section 5.4.3, the overall tray efficiency was modeled as a subjective beta distribution with minimum=7%, maximum=14%, most likely value 8% and mean 9%. A plot of the distribution is shown in Table 5-3.

A.4.2 External uncertainties

UNCERTAINTIES IN PRICES OVER THE LIFE OF THE PROJECT

Uncertainties in future prices of methylene chloride and steam (assumed to be proportional to the price of natural gas) were simulated using the Markov process described in section 3.2.4. The ranges in future prices simulated by this method are shown in Figure 3-2 and Figure 3-3.

UNCERTAINTY IN REGULATORY ENVIRONMENT

Methylene chloride is considered a toxic pollutant and its discharges to sewers and water streams are regulated by federal and local authorities. Table A-7 gives a sample of methylene chloride effluent concentration limits placed by different authorities.

Table A-7: Methylene chloride effluent concentration limits for several U.S. jurisdictions

Source of limit	Concentration limit (ppm)	Comments
Federal: 40 CFR part 414.100 (Organic chemicals, plastics, and synthetic fibers industries)	0.040 (maximum monthly average) 0.089 (maximum for any one day)	Direct discharge point sources that use end-of-pipe biological treatment
Federal: 40 CFR part 414.101 (Organic chemicals, plastics, and synthetic fibers industries)	0.036 (maximum monthly average) 0.170 (maximum for any one day)	Direct discharge point sources that do not use end-of-pipe biological treatment
Federal: 40 CFR part 414.111 (Organic chemicals, plastics, and synthetic fibers industries)	0.036 (maximum monthly average) 0.170 (maximum for any one day)	Indirect discharge point sources
Federal: 40 CFR part 433 (Metal finishing point source category)	2.13 (maximum for any 1 day)	The limit applies to "total toxic organics" (TTO), which includes methylene chloride
East Bay Municipal Utility District (Berkeley, CA)	0.50	Applies to total identifiable chlorinated hydrocarbons in sewer discharges
City of Cookeville, TN	2.2	Based on 24-hour composite samples; applies to industrial wastewater discharges to the sewer
City of Rochester, MN	1.00	Applies to discharges of wastewater to the sewer
Massachusetts Water Resources Authority (360 CMR part 10.000)	1.00	Applies to discharges of wastewater to the sewer.

For the case study it is assumed that the current limit is 2.0 ppm, but it is also assumed that the limit might be tightened in the future. In any year, the limit may be unchanged or halved. The probability of tightening is assumed to be 20% in each year. Figure A-6 shows the distribution of concentration standards resulting from this Markov process. Although there is at least a 5% probability that the standard will stay at the current level for the next 10 years (the

assumed service life of the equipment), there is also at least a 5% probability that the standard could tighten to as much as 0.06 ppm.

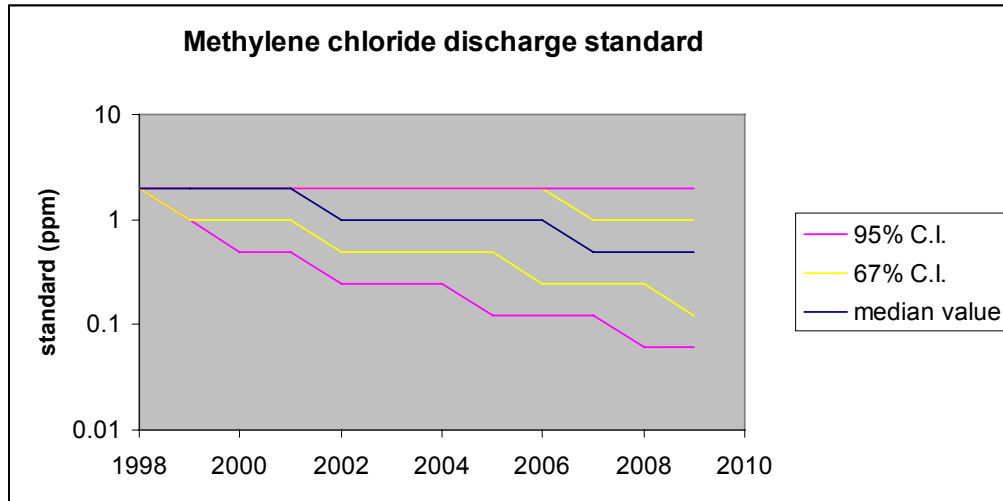


Figure A-6: Distributions for future effluent concentration standards

A.4.3 Valuation model uncertainties

The uncertainties in economic valuation model parameters are discussed in section 3.2.4. This section will focus exclusively in the uncertainties in unit indicators derived from the combined PIO-LCA and multimedia fate, transport and exposure models.

A multivariate normal copula distribution was fit to the results of a Monte Carlo simulation of the full PIO-LCA + Multimedia exposure model. The marginal distributions obtained through the use of the software package BestFit¹⁰² are displayed in Table A-8. The corresponding matrix of rank correlations, obtained through the method described in section 8.3.3, is given in Table A-9.

¹⁰² Palisade corporation, www.palisade.com

Table A-8: Marginal distributions for the unit environmental impact of key inputs and outputs in the solvent recovery case study

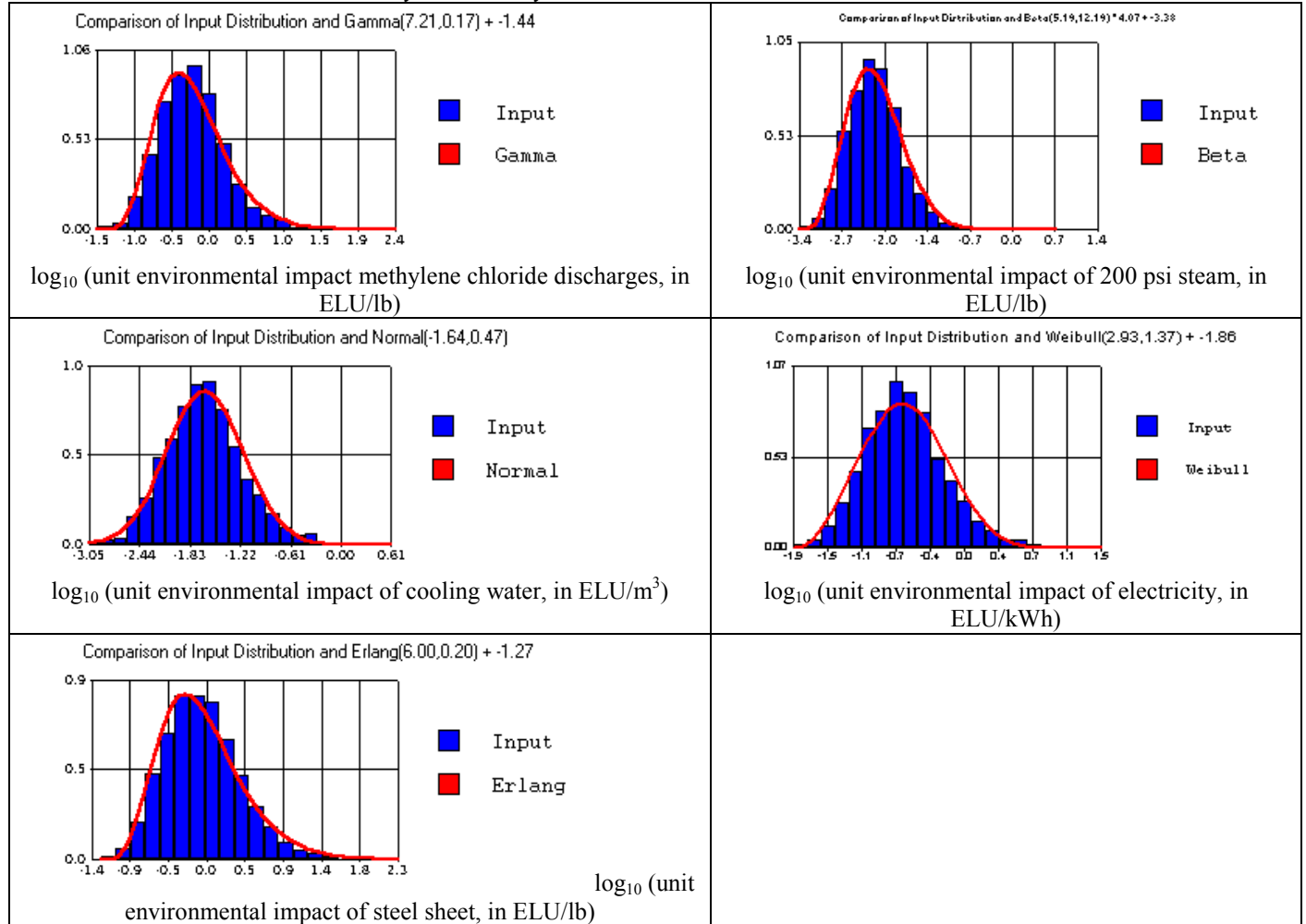


Table A-9: Rank correlation matrix obtained for the solvent recovery case study unit environmental indicators

	Cooling water (per m3)	Electricity (per kWh)	CH2Cl2 discharge (per lb)	Steam (per lb)	Steel sheet (per lb)
Cooling water (per m3)	1	0.938961	0.675747	0.677726	0.801129
Electricity (per kWh)	0.938961	1	0.721461	0.717245	0.849475
CH2Cl2 discharge (per lb)	0.675747	0.721461	1	0.661496	0.662199
Steam (per lb)	0.677726	0.717245	0.661496	1	0.624209
Steel sheet (per lb)	0.801129	0.849475	0.662199	0.624209	1

Contribution sensitivity analysis (see section 7.5.2) was carried out as a check on the quality on the results. The results obtained confirm one’s intuition that the toxic effects of methylene chloride (Figure A-7 and Figure A-8) should be the main drivers of the environmental

impact of methylene chloride discharges. In the case of steam, Figure A-9 and Figure A-10 show that the main contribution comes from the global warming potential of carbon dioxide. The contribution of nitrogen oxides comes second, but mostly due to their contribution to the formation of nitrate particles, rather than because of their contribution to photochemical smog. If decision makers felt that the smog contribution should be comparable or higher than the particle effects contribution, then this analysis would suggest to them to access the EnvEvalTool database and update the characterization factors for nitrogen oxides or the magnitude of the weighting factor assigned to the photochemical oxidants creation potential (PCOP) indicator.

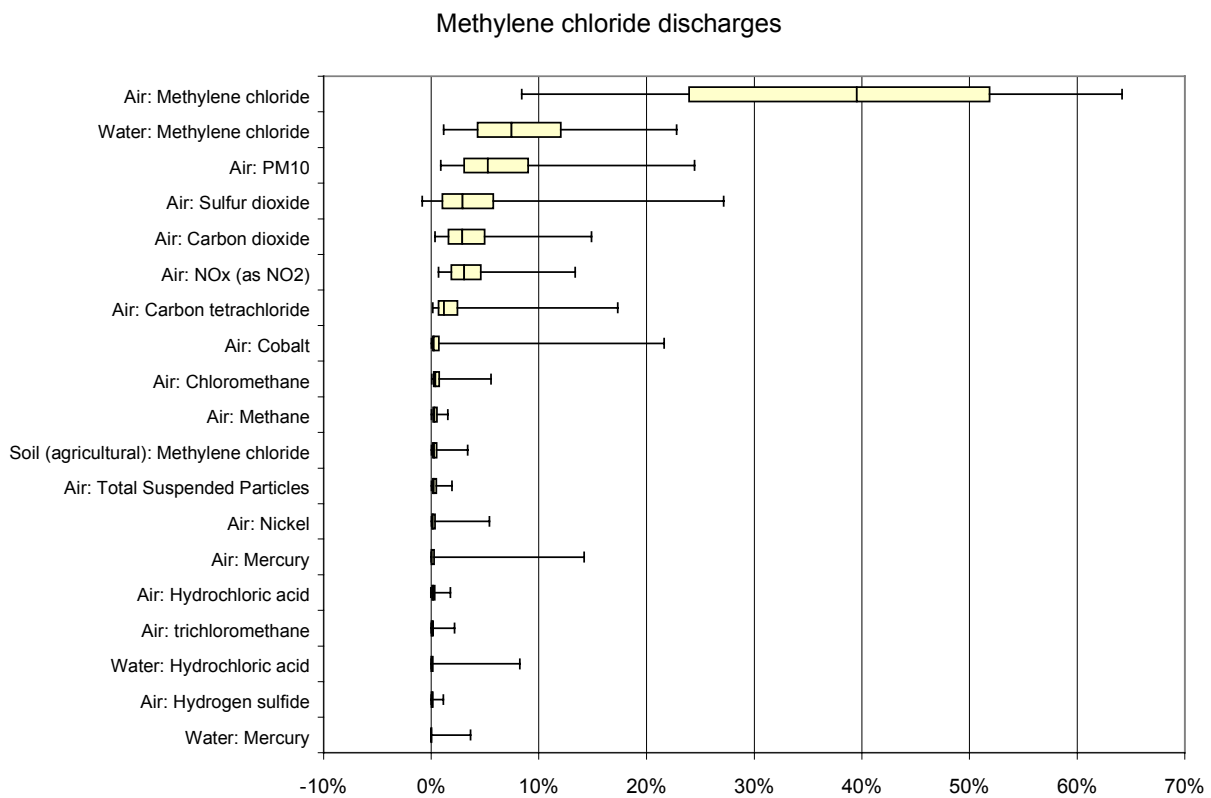


Figure A-7: Environmental exchange contributions to the environmental impact indicator of methylene chloride releases

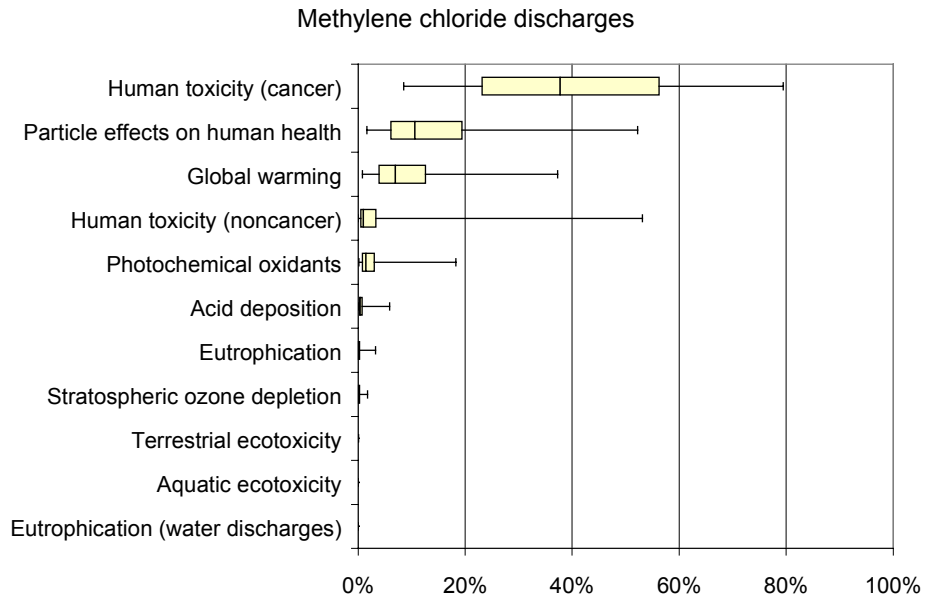


Figure A-8: Impact category contributions to the environmental impact indicator for methylene chloride discharges

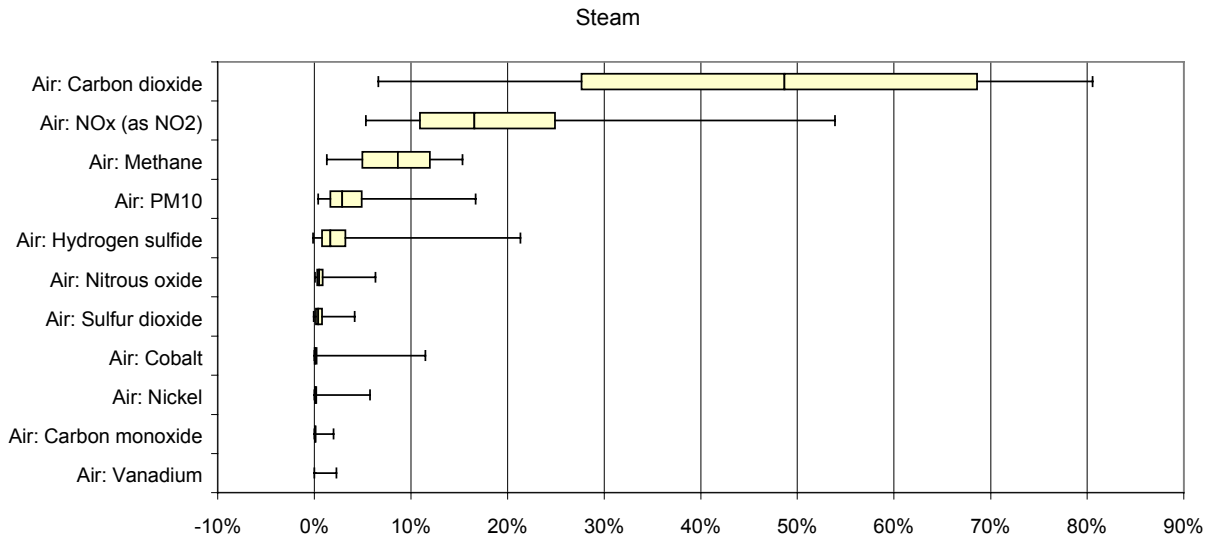


Figure A-9: Environmental exchange contributions to the environmental impact indicator of steam (with natural gas used as boiler fuel)

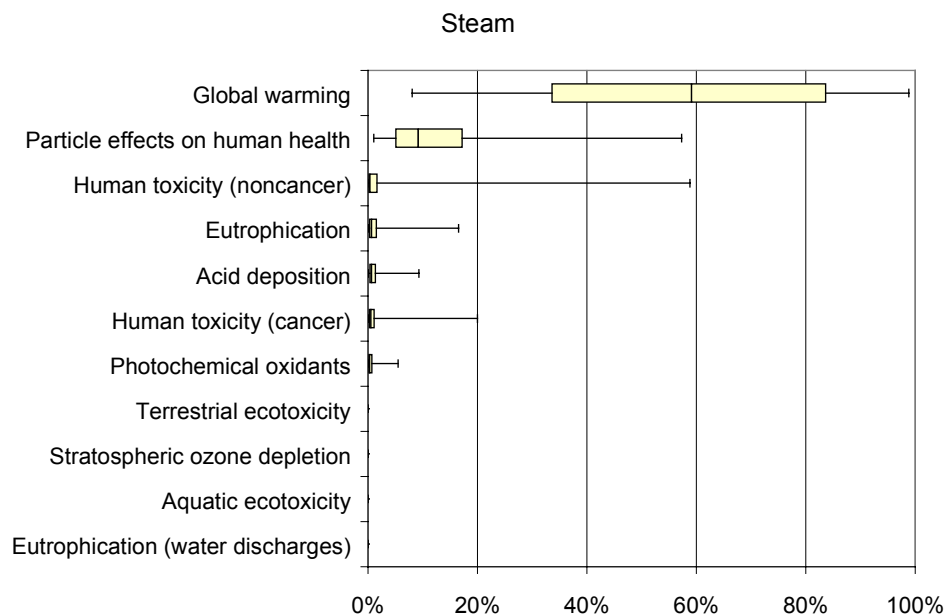


Figure A-10: Impact category contributions to the environmental impact indicator for steam (with natural gas used as boiler fuel)

A.5 Literature cited

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Appendix B EnvEvalTool database documentation

B.1 Data Table Structures and Relationships

A summary of the data model used in the EnvEvalTool database was presented in Figure 9-3 and Figure 9-4. Details on the tables and their relationships are presented in this section. The following list gives the page number in which detailed information for each table appears in this Appendix:

Case Studies, 490
Case Studies (products), 491
Case Studies (valuation), 492
CF to CF correlations, 493
CF to VF correlations, 494
Characterization Factors, 495
Chemical Information, 497
Chemical Names, 499
Distributions, 500
Emission factors, 502
Exposure Factor Descriptions, 504
Exposure Factors, 505
Impact Categories, 507
Make coefficients, 508
Market Shares, 510
Prices, 512
Processes, 513
Products, 515
References, 517
Sources of Characterization Factors, 519
Sources of Emission Factors, 521
Sources of Exposure Factors, 522
Sources of Input-Output Data, 524
Use coefficients, 526
Valuation Factors, 528
Valuation Methods, 530
VF to VF correlations, 531

Table: Case Studies

Properties

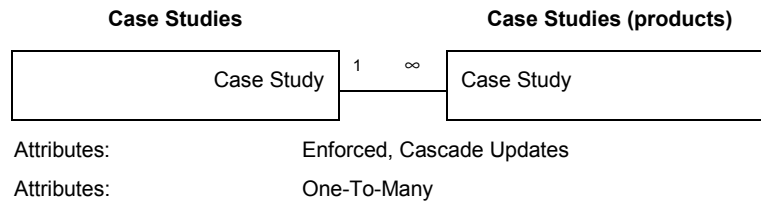
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Columns

Name	Type	Size
Case Study	Text	50

Relationships

Case Studies - Case Studies (products)



Case Studies - Case Studies (valuation)

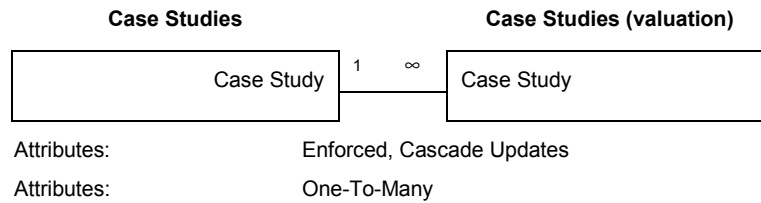


Table Indexes

Name	Number of Fields
PrimaryKey	1
Fields:	Case Study, Ascending

Table: Case Studies (products)

Properties

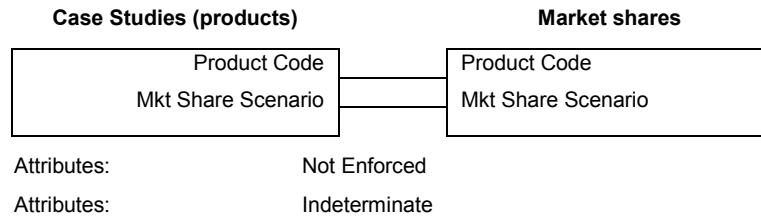
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Columns

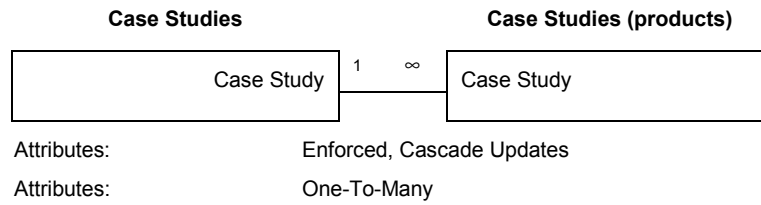
Name	Type	Size
Case Study	Text	50
Product Code	Text	50
Mkt Share Scenario	Text	50

Relationships

Case Studies (products) - Market Shares



Case Studies - Case Studies (products)



Products - Case Studies

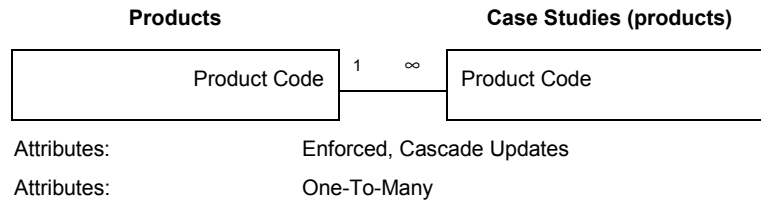


Table Indexes

Name	Number of Fields
Case Study	1
Fields:	Case Study, Ascending

Table: Case Studies (valuation)

Properties

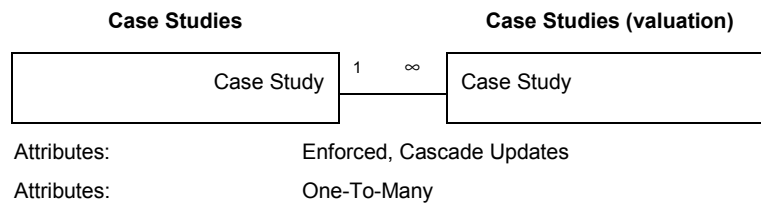
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Columns

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Method Code	Text	50

Relationships

Case Studies - Case Studies (valuation)



Valuation Methods - Case Studies (valuation)

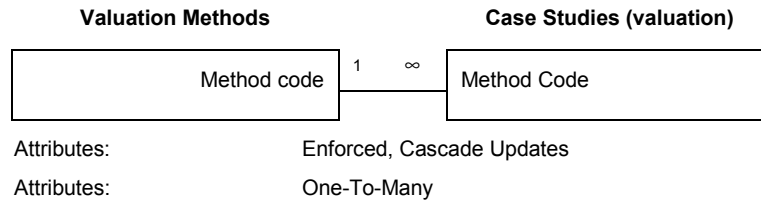


Table Indexes

Name	Number of Fields
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Fields:	Method Code, Ascending

Table: CF to CF correlations

Properties

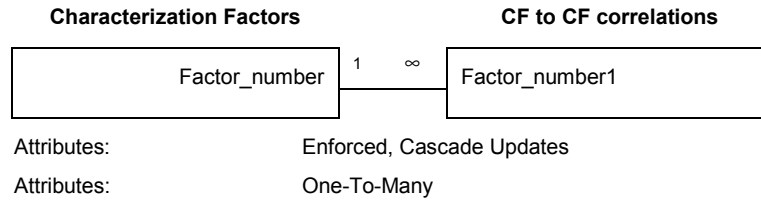
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 RecordCount: 208

Columns

Name	Type	Size
ID	Number (Long)	4
Factor_number1	Number (Long)	4
Factor_number2	Number (Long)	4
Correlation_coefficient	Number (Double)	8

Relationships

Characterization Factors - CF to CF correlations



Characterization Factors - CF to CF correlations_1

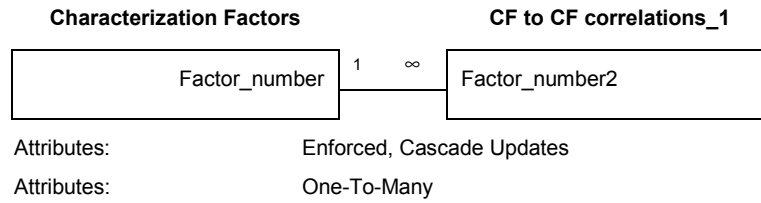


Table Indexes

Name	Number of Fields
Factor numbers	2
Fields:	Factor_number1, Ascending
PrimaryKey	1
Fields:	ID, Ascending

Table: CF to VF correlations

Properties

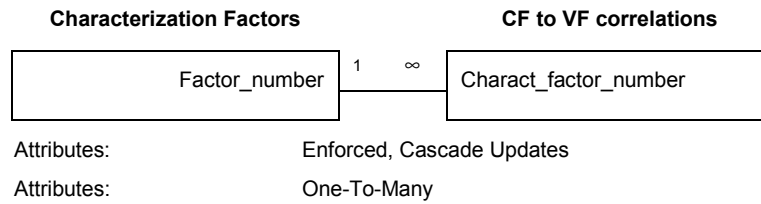
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RecordCount:	97		

Columns

Name	Type	Size
ID	Number (Long)	4
Charact_factor_number	Number (Long)	4
Valuation_factor_number	Number (Long)	4
Correlation_coefficient	Number (Double)	8

Relationships

Characterization Factors - CF to VF correlations



Valuation Factors - CF to VF correlations

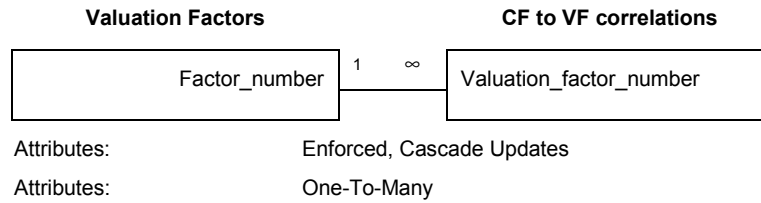


Table Indexes

Name	Number of Fields
Factor numbers	2
Fields:	Charact_factor_number, Ascending Valuation_factor_number, Ascending
PrimaryKey	1
Fields:	ID, Ascending

Table: Characterization Factors

Properties

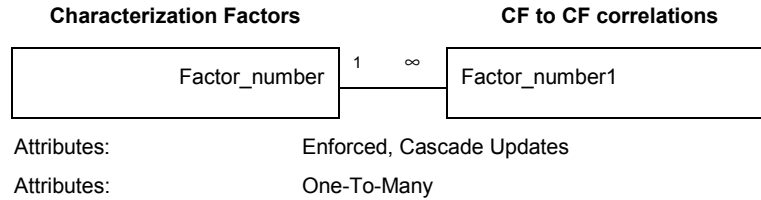
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 RecordCount: 24206

Columns

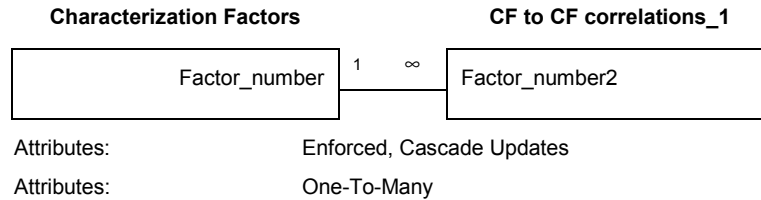
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Impact Category Code	Text	255
Source Code	Text	255
Nominal Value	Number (Double)	8
Distribution Code	Text	255
Parameter 1	Number (Double)	8
Parameter 2	Number (Double)	8
Date incorporated	Date/Time	8

Relationships

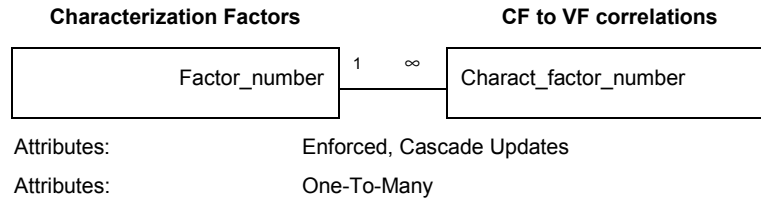
Characterization Factors - CF to CF correlations



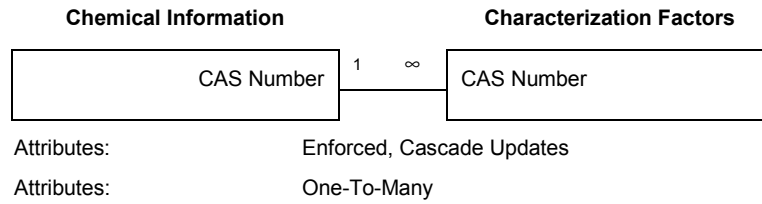
Characterization Factors - CF to CF correlations_1



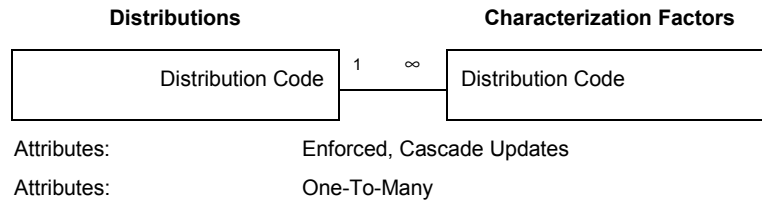
Characterization Factors - CF to VF correlations



Chemical Information - Characterization Factors



Distributions - Characterization Factors



Sources of Characterization Factors - Characterization Factors

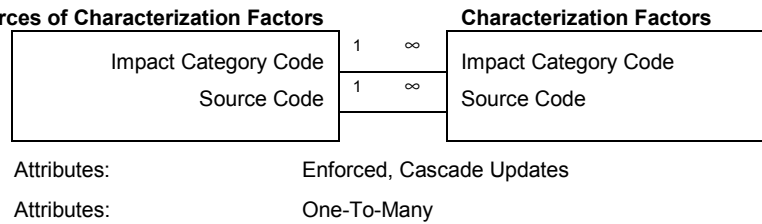


Table Indexes

Name	Number of Fields
PrimaryKey	1
Fields:	Factor_number, Ascending
Sources of Characterization	2
Fields:	Impact Category Code, Ascending
	Source Code, Ascending

Table: Chemical Information

Properties

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Molecular Weight	Number (Double)	8
Metal Classification	Text	3

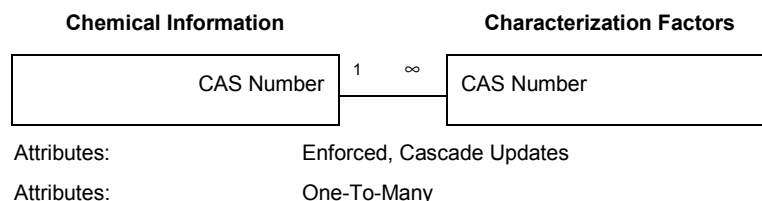
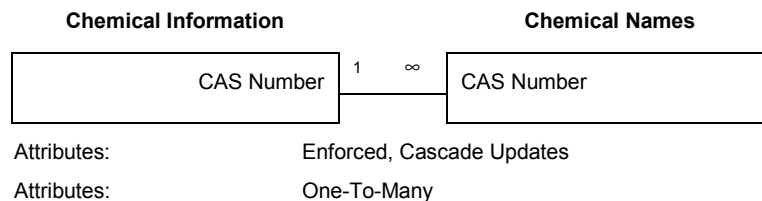
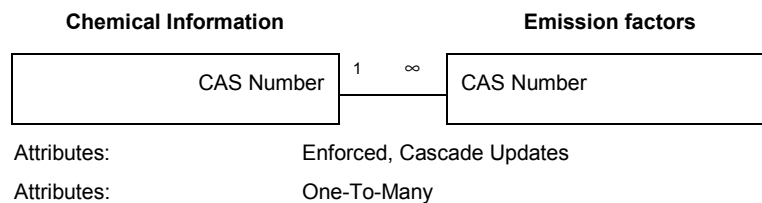
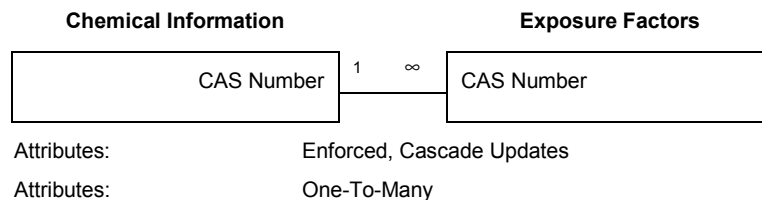
Relationships**Chemical Information - Characterization Factors****Chemical Information - Chemical Names****Chemical Information - Emission factors****Chemical Information - Exposure Factors**

Table Indexes

<u>Name</u>	<u>Number of Fields</u>
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Fields:	Chemical Name, Ascending
PrimaryKey	1
Fields:	CAS Number, Ascending

Table: Chemical Names

Properties

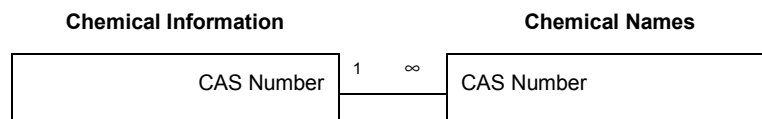
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Columns

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Chemical Name	Text	255
CAS Number	Text	255

Relationships

Chemical Information - Chemical Names



Attributes: Enforced, Cascade Updates
 Attributes: One-To-Many

Table Indexes

Name	Number of Fields
PrimaryKey	1
Fields:	Chemical Name, Ascending

Table: Distributions

Properties

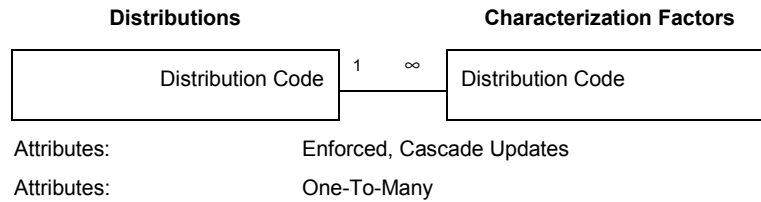
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Columns

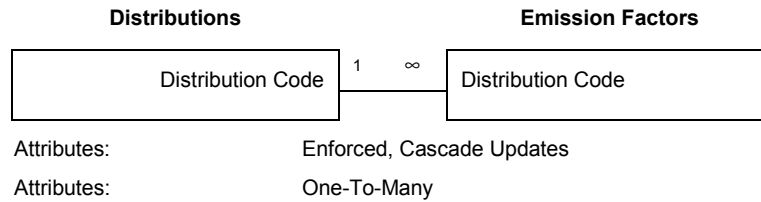
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Parameter 1 definition	Text	255
Parameter 2 definition	Text	255
@Risk Expression	Text	100

Relationships

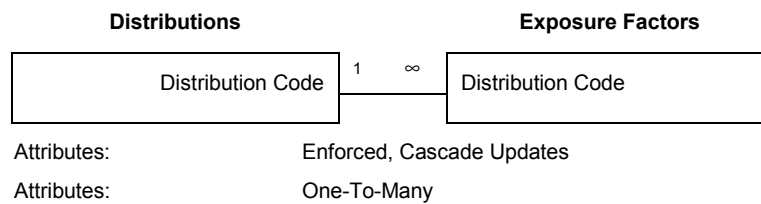
Distributions - Characterization Factors



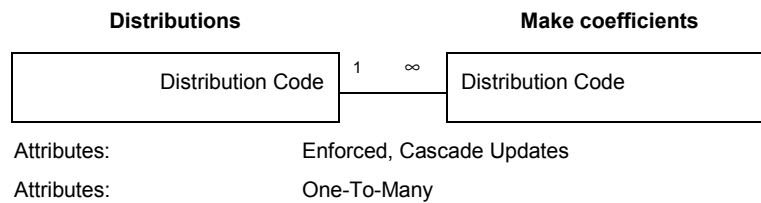
Distributions - Emission factors



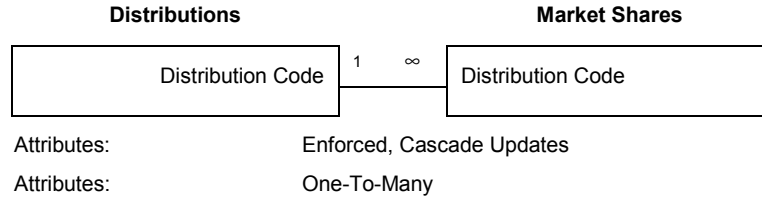
Distributions - Exposure Factors



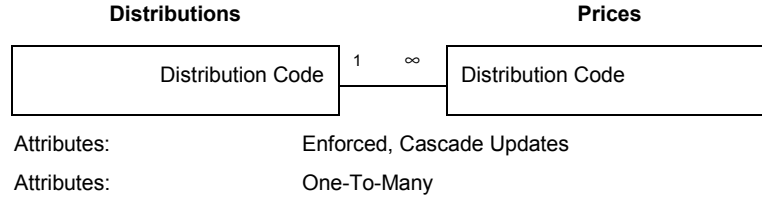
Distributions - Make coefficients



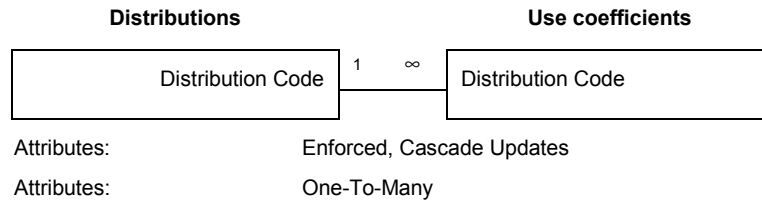
Distributions - Market Shares



Distributions - Prices



Distributions - Use coefficients



Distributions - Valuation Factors

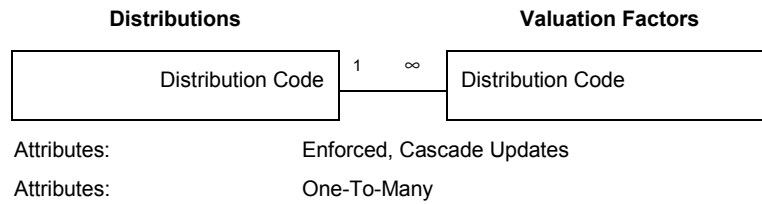


Table Indexes

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Fields:	Distribution Code, Ascending

Table: Emission factors

Properties

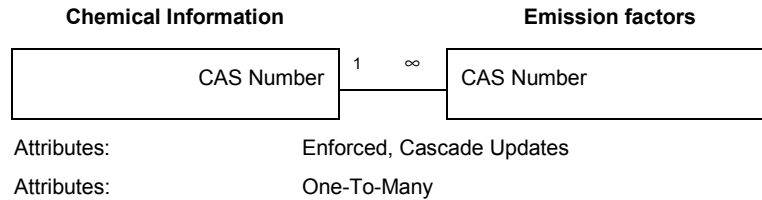
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Columns

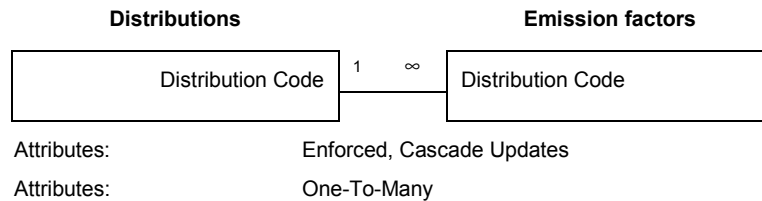
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Source code	Text	50
CAS Number	Text	255
Release Medium	Text	255
Nominal Value	Number (Double)	8
Units	Text	50
Distribution Code	Text	255
Parameter 1	Number (Double)	8
Parameter 2	Number (Double)	8
Date Incorporated	Date/Time	8

Relationships

Chemical Information - Emission factors



Distributions - Emission factors



Sources of Emission Factors - Emission factors

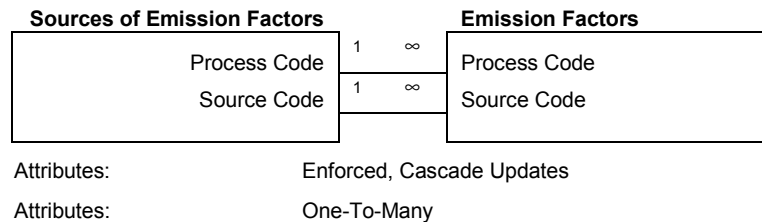


Table Indexes

<u>Name</u>	<u>Number of Fields</u>
PrimaryKey	1
Fields:	Factor_number, Ascending
Sources of Emission Factors	2
Fields:	Process code, Ascending
	Source code, Ascending
Unique	3
Fields:	Process Code, Ascending
	Source Code, Ascending
	CAS Number, Ascending

Table: Exposure Factor Descriptions

Properties

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Columns

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Exposure Factor Name	Text	255
Units	Text	255

Relationships

Exposure Factor Descriptions - Sources of Exposure Factors

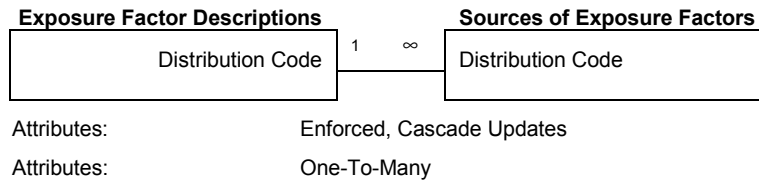


Table Indexes

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PrimaryKey	1
Fields:	Exposure Factor Code, Ascending

Table: Exposure Factors

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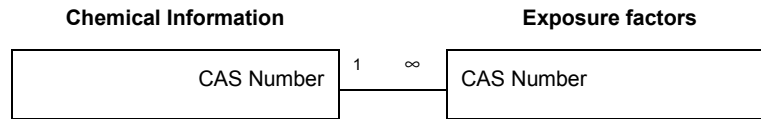
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RecordCount:	36976		

Columns

Name	Type	Size
Factor_number	Number (Long)	4
CAS Number	Text	255
Exposure Factor Code	Text	255
Source Code	Text	255
Nominal Value	Number (Double)	8
Distribution Code	Text	255
Parameter 1	Number (Double)	8
Parameter 2	Number (Double)	8
Date Incorporated	Date/Time	8

Relationships

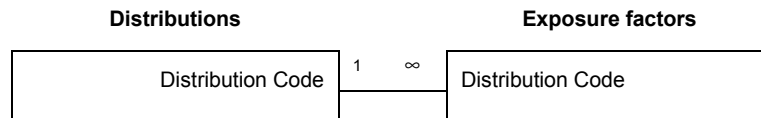
Chemical Information - Exposure Factors



Attributes: Enforced, Cascade Updates

Attributes: One-To-Many

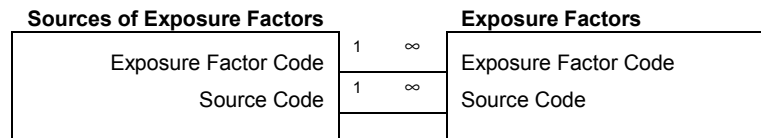
Distributions - Exposure Factors



Attributes: Enforced, Cascade Updates

Attributes: One-To-Many

Sources of Exposure Factors - Exposure Factors



Attributes: Enforced, Cascade Updates

Attributes: One-To-Many

Table Indexes

<u>Name</u>	<u>Number of Fields</u>
PrimaryKey	1
Fields:	Factor_number, Ascending
Sources of Exposure Factors	2
Fields:	Exposure Factor Code, Ascending
	Source Code, Ascending
Unique	3
Fields:	Exposure Factor Code, Ascending
	Source Code, Ascending
	CAS Number, Ascending

Table: Impact Categories

Properties

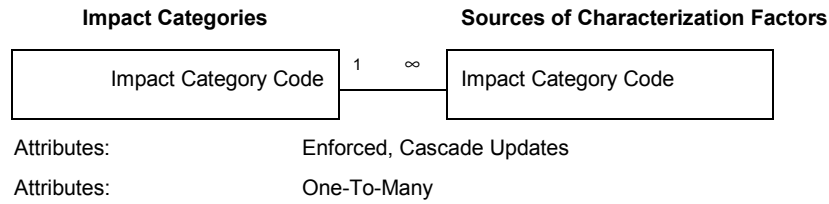
Date Created:	5/21/99 2:32:30 PM	Def. Updatable:	True
Last Updated:	5/29/00 8:04:36 PM	OrderBy:	[Impact Categories].[Impact Category Code]
OrderByOn:	True	RecordCount:	52

Columns

Name	Type	Size
Impact Category Code	Text	255
Impact Category Name	Text	255
Units	Text	255
Broad category	Text	50
Environmental Medium	Text	50
Notes	Text	50
Relevant indicator	Text	50

Relationships

Impact Categories - Sources of Characterization Factors



Impact Categories - Valuation Factors

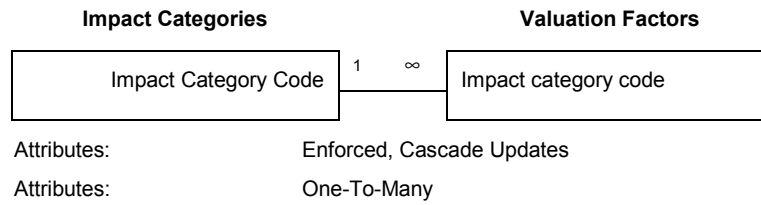


Table Indexes

Name	Number of Fields
PrimaryKey	1
Fields:	Impact Category Code, Ascending

Table: Make coefficients

Properties

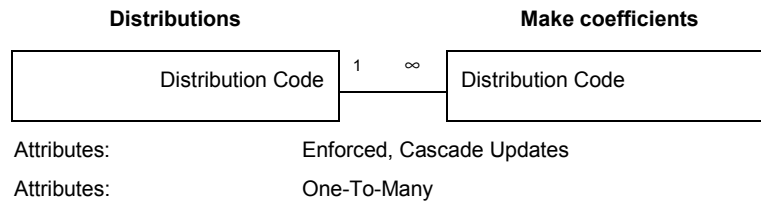
Date Created:	5/22/00 12:10:43 PM	Def. Updatable:	True
Last Updated:	5/22/00 9:33:02 PM	OrderByOn:	False
RecordCount:	42		

Columns

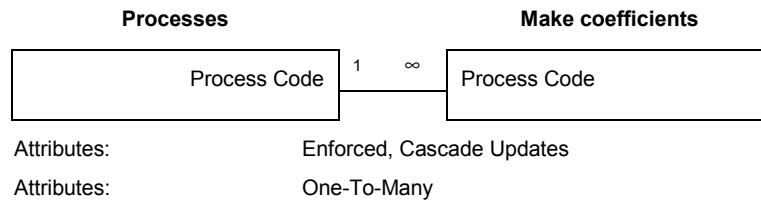
Name	Type	Size
Process Code	Text	50
Product Code	Text	50
Source Code	Text	50
Nominal Value	Number (Double)	8
Distribution Code	Text	50
Parameter 1	Number (Double)	8
Parameter 2	Number (Double)	8
Date Incorporated	Date/Time	8

Relationships

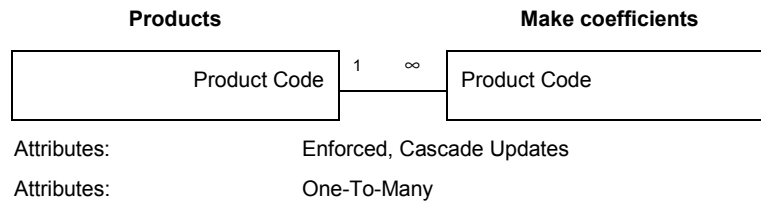
Distributions - Make coefficients



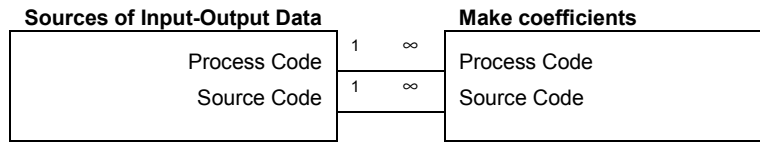
Processes - Make coefficients



Products - Make coefficients



Sources of Input-Output Data - Make coefficients



Attributes: Enforced, Cascade Updates

Attributes: One-To-Many

Table Indexes

Name	Number of Fields
Primary Key	2
Fields:	Process Code, Ascending Product Code, Ascending
Input-Output Data Source	2
Fields:	Process Code, Ascending Source Code, Ascending

Table: Market Shares

Properties

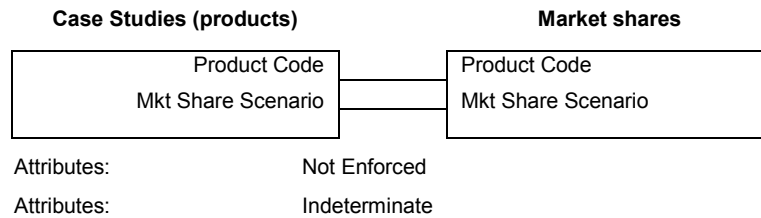
Date Created: 5/29/00 2:08:38 PM Def. Updatable: True
 Last Updated: 6/21/00 11:23:00 AM OrderByOn: False
 RecordCount: 26

Columns

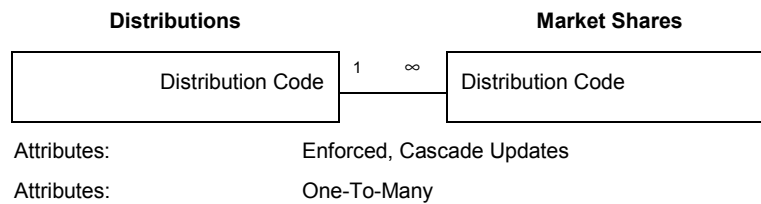
Name	Type	Size
Product Code	Text	50
Mkt Share Scenario	Text	50
Process Code	Text	50
Nominal Value	Number (Double)	8
Distribution Code	Text	50
Parameter 1	Number (Double)	8
Parameter 2	Number (Double)	8
Date Incorporated	Date/Time	8

Relationships

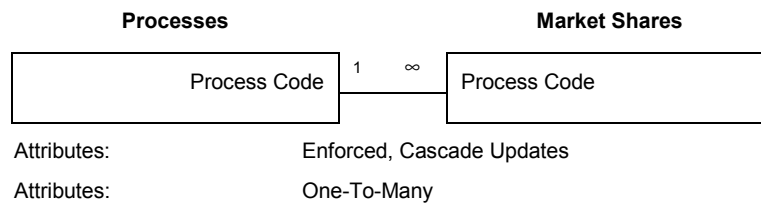
Case Studies (products) - Market Shares



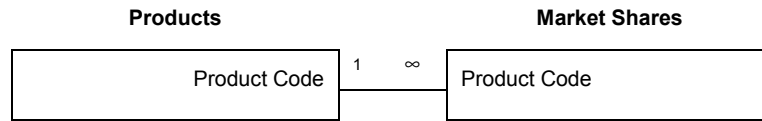
Distributions - Market Shares



Processes - Market Shares



Products - Market Shares



Attributes: Enforced, Cascade Updates

Attributes: One-To-Many

Table Indexes

Name	Number of Fields
PrimaryKey	3
Fields:	Product Code, Ascending Mkt Share Scenario, Ascending Process Code, Descending
Product and Mkt Scenario	2
Fields:	Product Code, Ascending Mkt Share Scenario, Ascending

Table: Prices

Properties

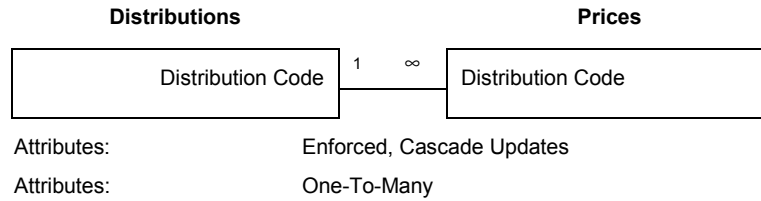
Date Created:	5/29/00 2:06:27 PM	Def. Updatable:	True
Last Updated:	6/21/00 11:30:35 AM	OrderByOn:	False
RecordCount:	5		

Columns

Name	Type	Size
Price Entry Number	Number (Long)	4
Product Code	Text	50
Year	Text	50
Currency	Text	10
Nominal Value	Number (Double)	8
Distribution Code	Text	50
Parameter 1	Number (Double)	8
Parameter 2	Number (Double)	8
Date Incorporated	Date/Time	8

Relationships

Distributions - Prices



Products - Prices

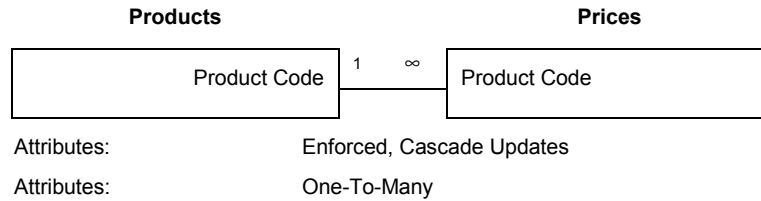


Table Indexes

Name	Number of Fields
PrimaryKey	1
Fields:	Price Entry Number, Ascending

Table: Processes

Properties

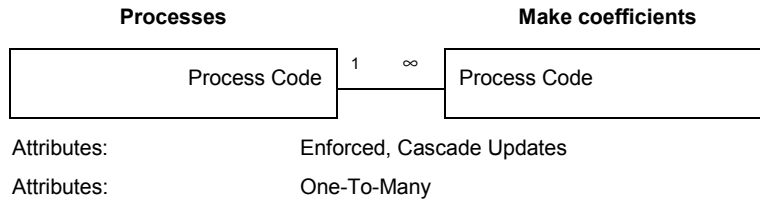
Date Created:	9/8/99 11:20:03 AM	Def. Updatable:	True
Last Updated:	6/21/00 10:36:29 AM	OrderByOn:	False
RecordCount:	46		

Columns

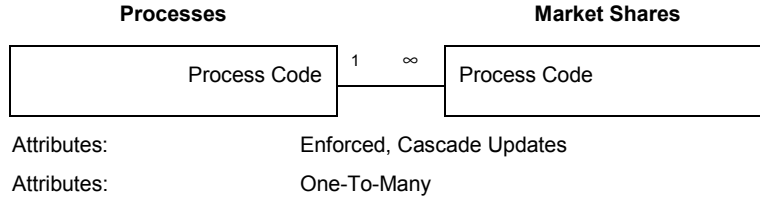
Name	Type	Size
Process Code	Text	50
Throughput basis	Text	100
Emission factor units	Text	50
Comments	Text	200

Relationships

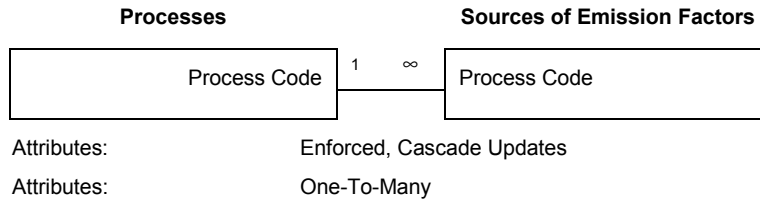
Processes - Make coefficients



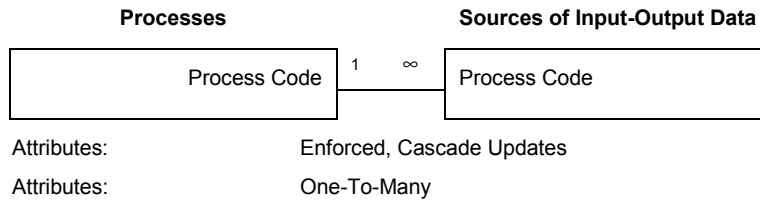
Processes - Market Shares



Processes - Sources of Emission Factors



Processes - Sources of Input-Output Data



Processes - Use coefficients

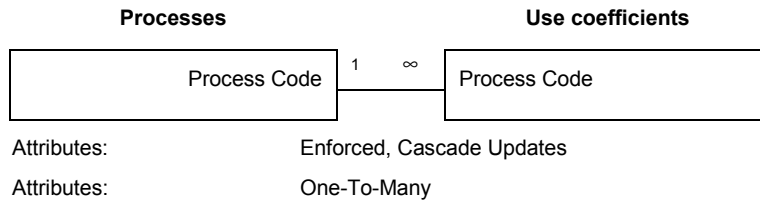


Table Indexes

Name	Number of Fields
PrimaryKey	1
Fields:	Process Code, Ascending

Table: Products

Properties

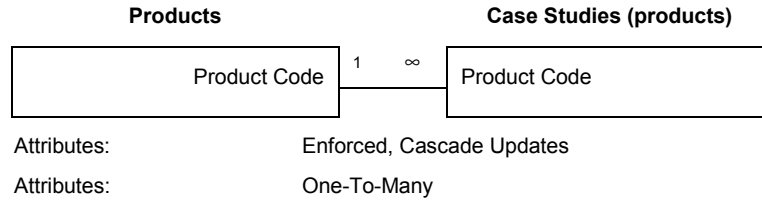
Date Created:	9/8/99 1:30:14 PM	Def. Updatable:	True
Last Updated:	6/21/00 11:18:10 AM	OrderByOn:	False
RecordCount:	30		

Columns

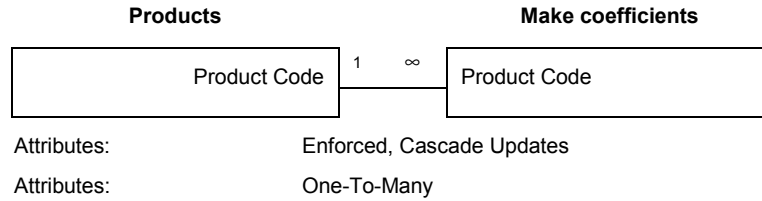
Name	Type	Size
Product code	Text	50
Unit of measurement	Text	100
Comments	Text	200

Relationships

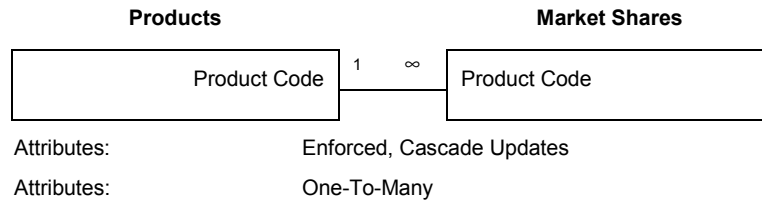
Products - Case Studies



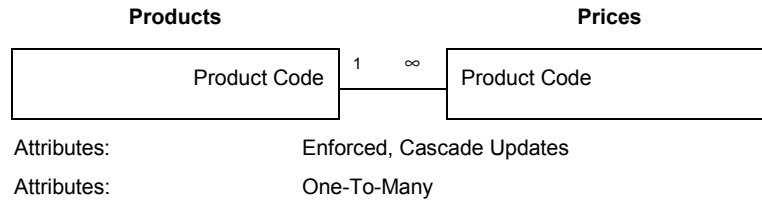
Products - Make coefficients



Products - Market Shares



Products - Prices



Products - Use coefficients

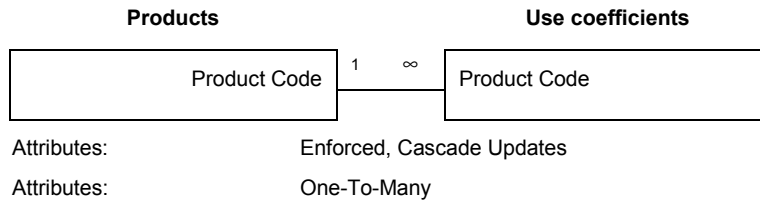


Table Indexes

Name	Number of Fields
PrimaryKey	1
Fields:	Product code, Ascending

Table: References

Properties

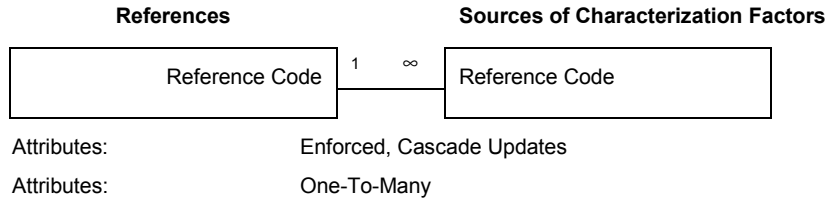
Date Created: 5/27/99 11:16:37 AM Def. Updatable: True
 Last Updated: 6/21/00 11:42:23 AM OrderByOn: True
 RecordCount: 65

Columns

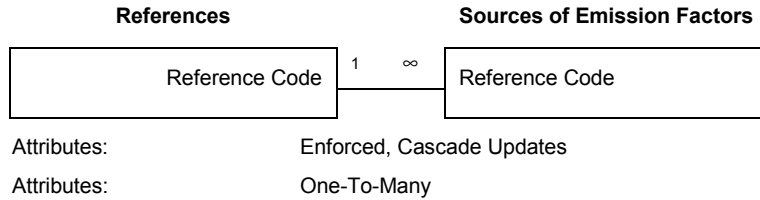
Name	Type	Size
Reference Code	Text	50
Reference	Text	255
Date Published	Date/Time	8
Date Downloaded	Date/Time	8
EndNote Code	Text	50

Relationships

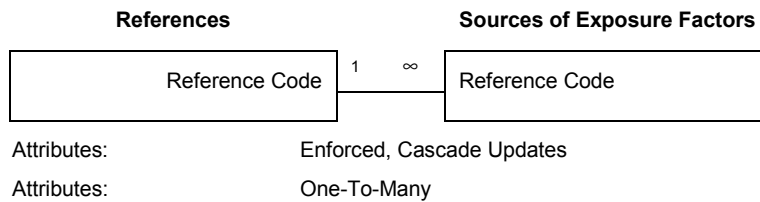
References - Sources of Characterization Factors



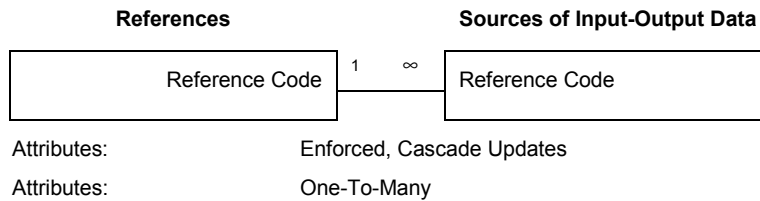
References - Sources of Emission Factors



References - Sources of Exposure Factors



References - Sources of Input-Output Data



References - Valuation Methods

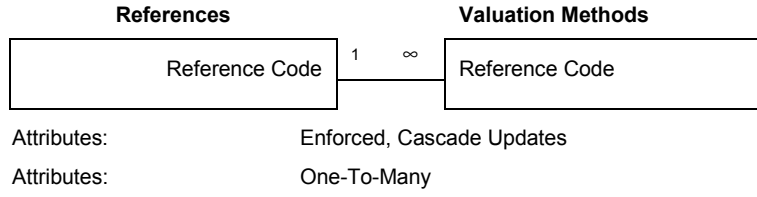


Table Indexes

Name	Number of Fields
PrimaryKey	1
Fields:	Reference Code, Ascending

Table: Sources of Characterization Factors

Properties

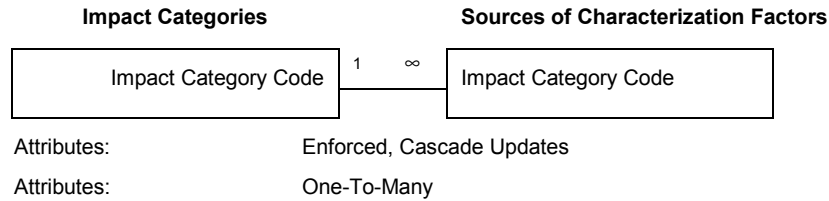
Date Created: 5/27/99 2:28:45 PM Def. Updatable: True
 Last Updated: 6/21/00 12:32:35 PM
 OrderBy: [Sources of Characterization Factors].[Impact Category Code] OrderByOn: False
 RecordCount: 220

Columns

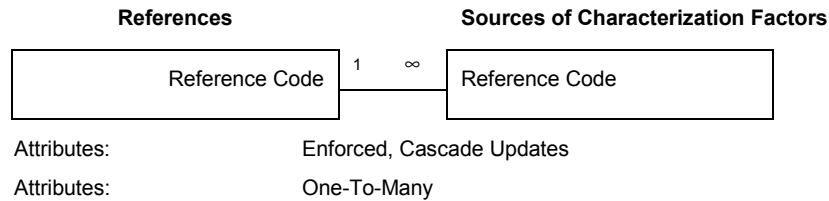
Name	Type	Size
Impact Category Code	Text	255
Source Code	Text	255
Priority	Number (Long)	4
Source of Data	Text	255
Reference Code	Text	50
Default Distribution Code	Text	50
Default Parameter 1	Text	50
Default Parameter 2	Text	50
Comments	Text	255

Relationships

Impact Categories - Sources of Characterization Factors



References - Sources of Characterization Factors



Sources of Characterization Factors - Characterization Factors

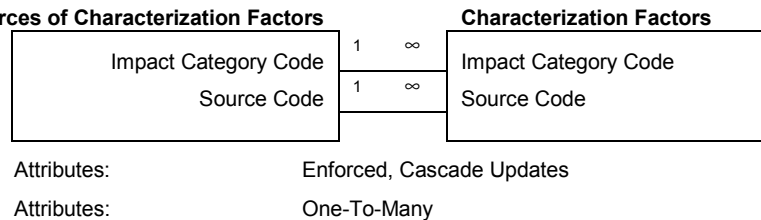


Table Indexes

<u>Name</u>	<u>Number of Fields</u>
Category+Priority	2
Fields:	Impact Category Code, Ascending Priority, Ascending
PrimaryKey	2
Fields:	Impact Category Code, Ascending Source Code, Ascending

Table: Sources of Emission Factors

Properties

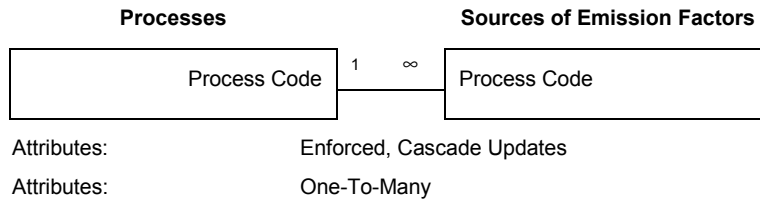
Date Created: 9/21/99 2:28:45 PM Def. Updatable: True
 Last Updated: 3/26/00 11:01:40 PM OrderByOn: False
 RecordCount: 55

Columns

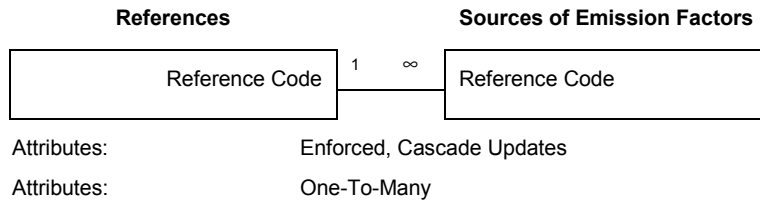
Name	Type	Size
Process Code	Text	255
Source Code	Text	255
Priority	Text	255
Source of Data	Text	255
Reference Code	Text	50
Comments	Text	255

Relationships

Processes - Sources of Emission Factors



References - Sources of Emission Factors



Sources of Emission Factors - Emission factors

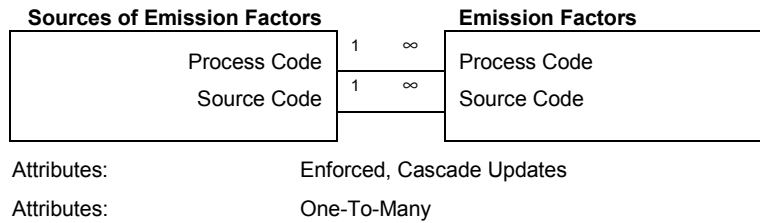


Table Indexes

Name	Number of Fields
PrimaryKey	2
Fields:	Process Code, Ascending Source Code, Ascending

Table: Sources of Exposure Factors

Properties

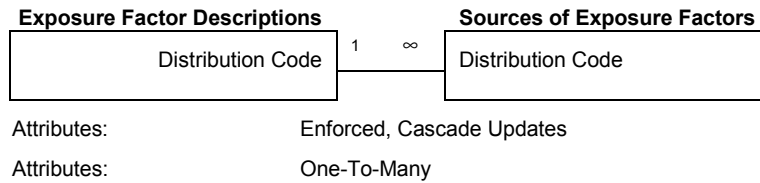
Date Created: 5/27/99 2:31:39 PM Def. Updatable: True
 Last Updated: 6/21/00 12:32:57 PM
 OrderBy: [Sources of Exposure Factors].Priority OrderByOn: False
 RecordCount: 113

Columns

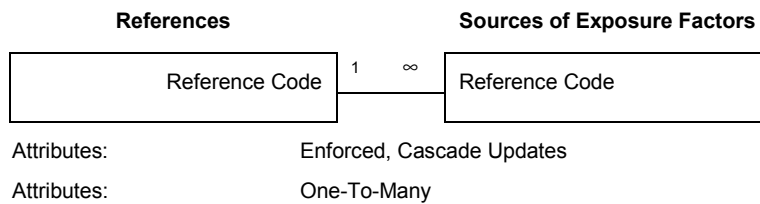
Name	Type	Size
Exposure Factor Code	Text	255
Source Code	Text	255
Priority	Number (Long)	4
Source of Data	Text	255
Reference Code	Text	50
Comments	Text	255

Relationships

Exposure Factor Descriptions - Sources of Exposure Factors



References - Sources of Exposure Factors



Sources of Exposure Factors - Exposure Factors

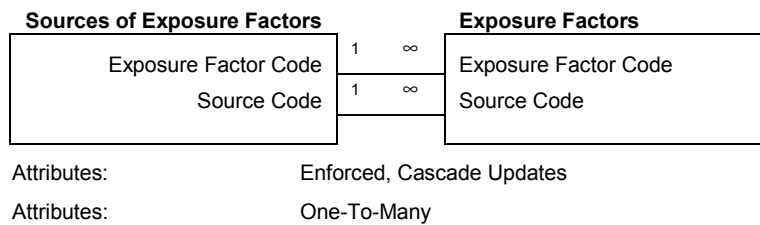


Table Indexes

<u>Name</u>	<u>Number of Fields</u>
PrimaryKey	2
Fields:	Exposure Factor Code, Ascending Source Code, Ascending

Table: Sources of Input-Output Data

Properties

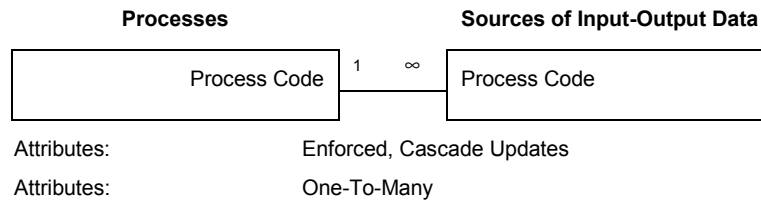
Date Created:	5/22/00 2:59:39 PM	Def. Updatable:	True
Last Updated:	5/22/00 10:11:46 PM	OrderBy:	[Sources of Input-Output Data].[Process Code]
OrderByOn:	True	RecordCount:	81

Columns

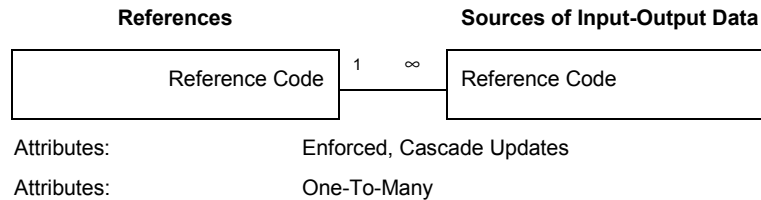
Name	Type	Size
Process Code	Text	255
Source Code	Text	255
Priority	Text	255
Source of Data	Text	255
Reference Code	Text	50
Comments	Text	255

Relationships

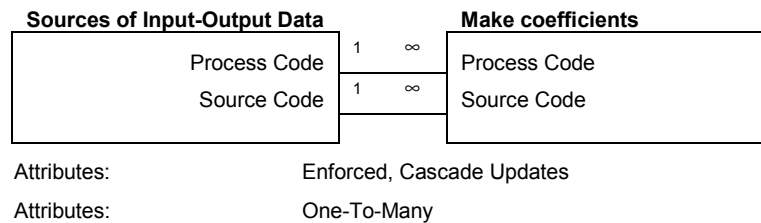
Processes - Sources of Input-Output Data



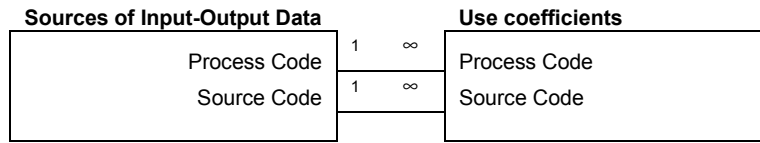
References - Sources of Input-Output Data



Sources of Input-Output Data - Make coefficients



Sources of Input-Output Data - Use coefficients



Attributes: Enforced, Cascade Updates

Attributes: One-To-Many

Table Indexes

Name	Number of Fields
PrimaryKey	2
Fields:	Process Code, Ascending Source Code, Ascending

Table: Use coefficients

Properties

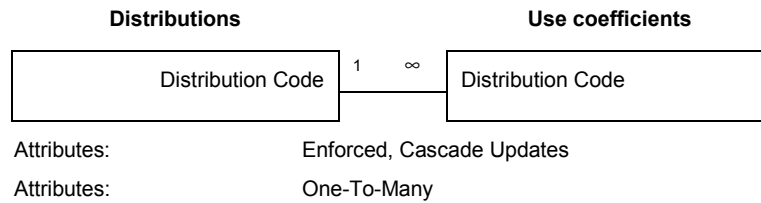
Date Created:	5/22/00 12:10:58 PM	Def. Updatable:	True
Last Updated:	6/19/00 2:51:21 PM	OrderBy:	[Use coefficients].[Product
OrderByOn:	True	RecordCount:	65

Columns

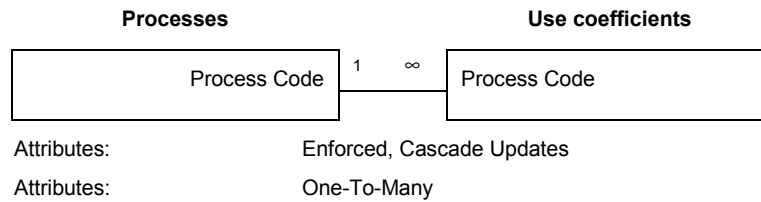
Name	Type	Size
Process Code	Text	50
Product Code	Text	50
Source Code	Text	50
Nominal Value	Number (Double)	8
Distribution Code	Text	50
Parameter 1	Number (Double)	8
Parameter 2	Number (Double)	8
Date Incorporated	Date/Time	8

Relationships

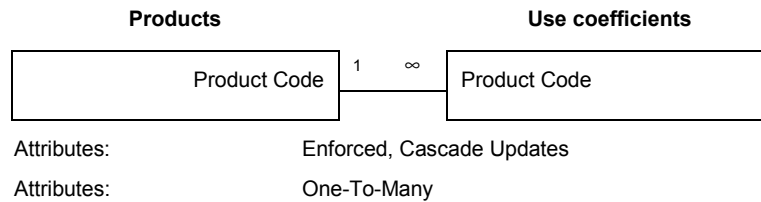
Distributions - Use coefficients



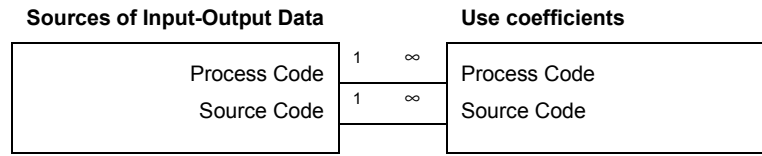
Processes - Use coefficients



Products - Use coefficients



Sources of Input-Output Data - Use coefficients



Attributes: Enforced, Cascade Updates

Attributes: One-To-Many

Table Indexes

Name	Number of Fields
Primary Key	2
Fields:	Process Code, Ascending Product Code, Ascending

Table: Valuation Factors

Properties

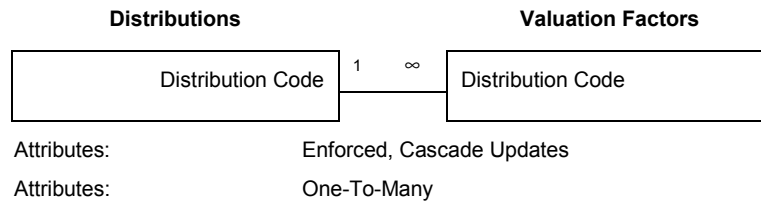
Date Created:	6/1/99 9:48:14 AM	Def. Updatable:	True
Last Updated:	6/21/00 10:51:28 AM	OrderBy:	[Valuation Factors].[Method]
OrderByOn:	True	RecordCount:	62

Columns

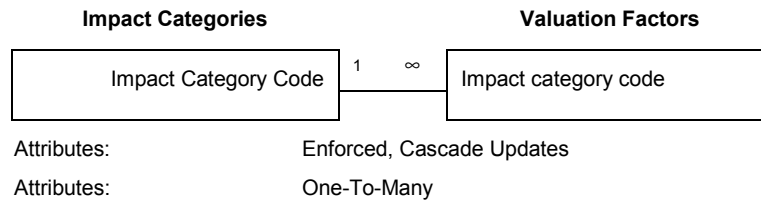
Name	Type	Size
Factor_number	Number (Long)	4
Method code	Text	50
Impact category code	Text	50
Nominal Value	Number (Double)	8
Distribution Code	Text	50
Parameter 1	Number (Double)	8
Parameter 2	Number (Double)	8
Date Incorporated	Date/Time	8

Relationships

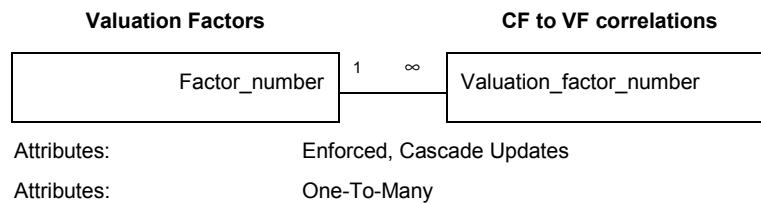
Distributions - Valuation Factors



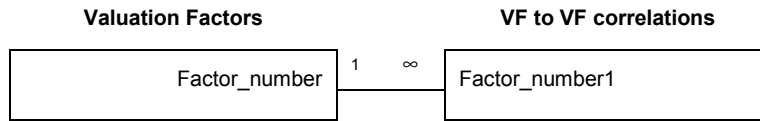
Impact Categories - Valuation Factors



Valuation Factors - CF to VF correlations



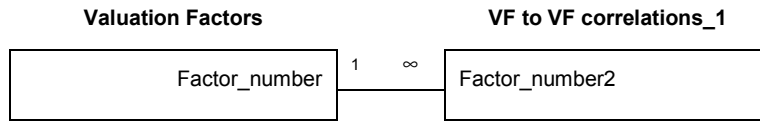
Valuation Factors - VF to VF correlations



Attributes: Enforced, Cascade Updates

Attributes: One-To-Many

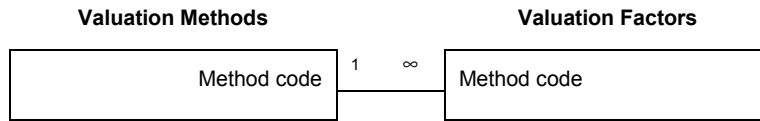
Valuation Factors - VF to VF correlations_1



Attributes: Enforced, Cascade Updates

Attributes: One-To-Many

Valuation Methods - Valuation Factors



Attributes: Enforced, Cascade Updates

Attributes: One-To-Many

Table Indexes

Name	Number of Fields
PrimaryKey	1
Fields:	Factor_number, Ascending

Table: Valuation Methods

Properties

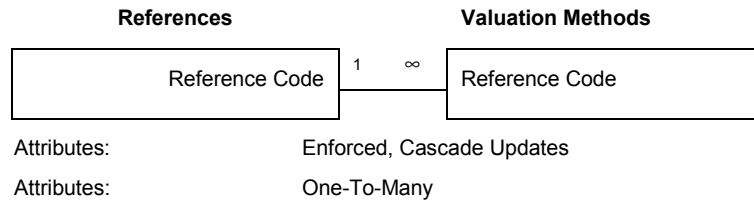
Date Created:	6/21/00 10:40:02 AM	Def. Updatable:	True
Last Updated:	6/21/00 11:20:15 AM	OrderByOn:	False
RecordCount:	4		

Columns

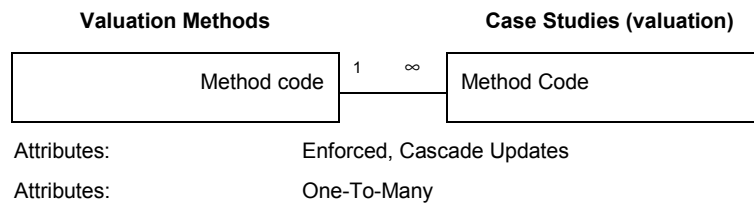
Name	Type	Size
Method code	Text	50
Method name	Text	50
Reference Code	Text	50

Relationships

References - Valuation Methods



Valuation Methods - Case Studies (valuation)



Valuation Methods - Valuation Factors

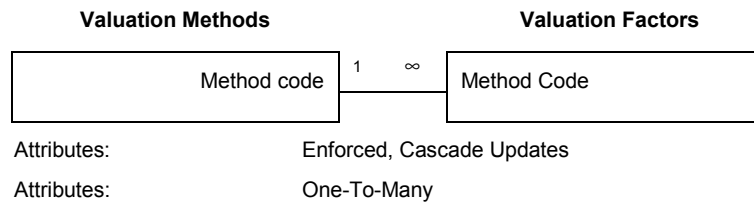


Table Indexes

Name	Number of Fields
Method code	1
Fields:	Method code, Ascending
PrimaryKey	1
Fields:	Method code, Ascending
ReferencesValuation Methods	1
Fields:	Reference Code, Ascending

Table: VF to VF correlations

Properties

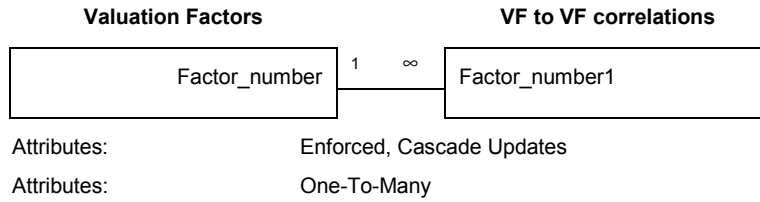
Date Created: 9/16/99 11:18:09 PM Def. Updatable: True
 Last Updated: 5/26/00 7:36:32 PM OrderByOn: False
 RecordCount: 227

Columns

Name	Type	Size
ID	Number (Long)	4
Factor_number1	Number (Long)	4
Factor_number2	Number (Long)	4
Correlation_coefficient	Number (Double)	8

Relationships

Valuation Factors - VF to VF correlations



Valuation Factors - VF to VF correlations_1

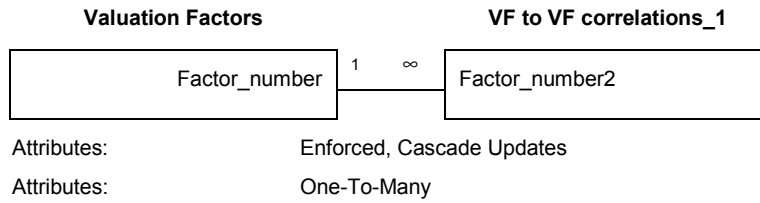


Table Indexes

Name	Number of Fields
Factor_numbers	2
Fields:	Factor_number1, Ascending Factor_number2, Ascending
PrimaryKey	1
Fields:	ID, Ascending

B.2 Queries and Visual Basic code used to export data to the human exposure model

B.2.1 Overview

This section presents the code used to export data from the EnvEvalTool Access database to the spreadsheet-based fate, transport, and exposure model used to generate probability distributions for human exposure factors and human toxicity potentials (cancer and non-cancer).

SOFTWARE REQUIRED

The EnvEvalTool database used in this project implemented in Microsoft Access version 97 SR-1. The fate, transport and exposure model was implemented in version 97 SR-1 of Microsoft Excel. Monte Carlo simulations are carried out in Excel using the @Risk Add-on (Palisade Corporation). Version 3.5 of @Risk was used in this work.

EXECUTION SEQUENCE

The user first needs to define the list of chemicals to be included in the fate, transport, and exposure model. This is done within the EnvEvalTool database through the use of the auxiliary table **Chemical List**. This table has a single column for CAS numbers. For chemicals for which a CAS number does not exist, the internal chemical code used as primary key in the **Chemical Information** table should be used instead of the CAS number.

After populating the **Chemical List** table, the user should execute the macro **Export FTT data** from within the EnvEvalTool database. This will generate three temporary Excel files.

After executing the macro, the user should open the spreadsheet containing the fate and transport model. Clicking on the **BuildTable** button executes the Visual Basic code that loads the data, including @Risk probability distribution functions and comments on each cell citing the data source used. Data are loaded for exposure factors whose internal exposure factor code coincides with the appropriate column heading in the fate and transport model spreadsheet (see Figure B-3).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	Metal													
1	INPUTS			MW	Metal Classification	Tm	Solub	Pvap	K Henry	Log Kow	BCF	logKds	logKDsed	logKDss
2		BuildTable		Molecular mass (g/mol)		Melting Point (K)	Water solubility (g/m3)	Vapor pressure (Pa)	K Henry (atm-m3/mol)	Log Kow	Bioconcentration factor	logKd3 = soil-water partition coefficient	logKd4 = sediment-water partition coefficient	logKd5= suspended solids-water partition coefficient
3	Air	7440-50-8	Copper	63.546	M	1356.15	897				14000	2.99		
4														
5														

	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG
1	t_air	t_aerobic	t_hydrolysis	t_water	t_soil	t_sed	Cancer CSF oral	Cancer UR inh	Cancer CSF	NonCancer invRfD oral	NonCancer invRfC inh	NonCancer invRfD	WWTP_ to_air	WWTP_ to_water	WWTP_ to_sludge	Emission Scenario		
2	Air half life (hr)	Aerobic degradation half life (hr)	Hydrolysis half life (hr)	Surface Water half life (hr)	Soil Half life (hr)	Sediment half life (hr)	Oral cancer slope factor [1/(mg/kg/d)]	Inhalation Unit Risk [1/(ug/m3)]	Cancer slope factor [1/(mg/kg/d)]	NonCancer inverse oral reference dose [1/(mg/kg/d)]	NonCancer inverse inhalation reference conc. [1/(mg/m3)]	NonCancer inverse reference dose [1/(mg/kg/d)]				Emission to Air (kg/h)	Emission to Water (kg/h)	Emission to ground soil (kg/h)
3									27.027027	50000	51	0	0.2753	0.7247	1000	0	0	
4																		
5																		

Figure B-1: Layout of the chemical properties data entry of the fate, transport and exposure spreadsheet model

B.2.2 Visual Basic code implemented within the Access database

Macro: Export FTT data

Properties

Date Created: 6/21/00 4:42:18 PM Last Updated: 6/21/00 4:42:42 PM
 Owner: admin

Actions

Name	Condition	Action	Argument	Value
		RunCode	Function Name:	Export_FTT_data ()
<i>Used to access the function Export_FTT_data()</i>				

Module: Export data for fate transport exposure model

Properties

Date Created: 6/21/00 4:38:08 PM Last Updated: 6/21/00 4:42:02 PM

Code

```

1 Attribute VB_Name = "Export data for fate transport exposure model"
2 Option Compare Database
3 Option Explicit
4
5 '-----
6 ' Export_FTT_data()
7 '
8 '-----
9 Function Export_FTT_data()
10 On Error GoTo Export_FTT_Err
11 Dim PathName As String
12 PathName = "F:\Work in Progress\Environmental Evaluation Tool\Temp\"
13 SetOption "Confirm Action Queries", False
14 Export_query "QFT Chemical Information for spreadsheet", PathName
15 Export_query "QFT Exposure factors for spreadsheet", PathName
16 Export_query "QTI Toxicity Indices for FT spreadsheet", PathName
17 SetOption "Confirm Action Queries", True
18
19 Export_FTT_Exit:
20 Exit Function
21
22 Export_FTT_Err:
23 MsgBox Error$
24 Resume Export_FTT_Exit
25
26 End Function
27
28 Sub Export_query(QueryName As String, PathName As String)
29 DoCmd.OpenQuery QueryName, acNormal, acReadOnly
30 DoCmd.TransferSpreadsheet acExport, 8, QueryName, PathName + QueryName, True
31 DoCmd.Close
32 End Sub

```

Module: Uncertainty description functions

Properties

Date Created: 5/24/99 3:24:23 PM Last Updated: 3/28/00 7:54:53 PM

Code

```

1 Attribute VB_Name = "Uncertainty description functions"
2 Option Compare Database
3 Option Explicit
4
5 Function MakeRiskExpression(Mask, NomVal, Param1, Param2)
6 ' This function generates @Risk Expressions for uncertainty
7 ' distributions based on the templates stored in the
8 ' "Distributions" table
9 Dim position, MaskLength, BracketedLength, j As Integer
10
11 ' Substitute "[Nominal Value]" occurrences
12 position = InStr(1, Mask, "[Nominal Value]", vbTextCompare)
13 MaskLength = Len(Mask)
14 BracketedLength = Len("[Nominal Value]")
15 If position > 0 Then
16 Mask = Left(Mask, position - 1) & Format(NomVal, "0.00E+00")
17 & Right(Mask, MaskLength - BracketedLength - (position - 1))
18 End If
19
20 ' Substitute "[Parameter 1]" occurrences
21 For j = 1 To 2
22 position = InStr(1, Mask, "[Parameter 1]", vbTextCompare)
23 MaskLength = Len(Mask)
24 BracketedLength = Len("[Parameter 1]")
25 If position > 0 Then
26 Mask = Left(Mask, position - 1) & Format(Param1, "0.00E+00")
27 & Right(Mask, MaskLength - BracketedLength - (position - 1))
28 End If
29 Next j
30
31 ' Substitute "[Parameter 2]" occurrences
32 position = InStr(1, Mask, "[Parameter 2]", vbTextCompare)
33 MaskLength = Len(Mask)
34 BracketedLength = Len("[Parameter 2]")
35 If position > 0 Then
36 Mask = Left(Mask, position - 1) & Format(Param2, "0.00E+00")
37 & Right(Mask, MaskLength - BracketedLength - (position - 1))
38 End If
39
40 ' Return generated expression
41 MakeRiskExpression = Mask
42
43 End Function

```

B.2.3 Queries and auxiliary tables

Table: Chemical List

Properties

Date Created: 5/24/00 12:09:43 AM Def. Updatable: True
Last Updated: 5/24/00 12:09:43 AM RecordCount: 14

Columns

<u>Name</u>	<u>Type</u>	<u>Size</u>
CAS Number	Text	255

Query: QFT Chemical Information for spreadsheet

Properties

Date Created: 10/7/99 11:04:19 AM Def. Updatable: True
Last Updated: 3/4/00 11:01:27 PM MaxRecords: 0
ODBCTimeout: 60 OrderByOn: True
Record Locks: No Locks Records Affected: 0
RecordsetType: All Records ReturnsRecords: True
Type: Select

SQL

```
SELECT DISTINCT [Chemical Information].[CAS Number],  
                [Chemical Information].[Chemical Name],  
                [Chemical Information].[Molecular Weight],  
                [Chemical Information].[Metal Classification]  
FROM ( [Chemical List]  
      INNER JOIN [Chemical Information]  
              ON [Chemical List].[CAS Number] = [Chemical Information].[CAS Number] )  
INNER JOIN [Chemical Names] ON [Chemical Information].[CAS Number] = [Chemical Names].[CAS Number]  
ORDER BY      [Chemical Information].[Molecular Weight] DESC ,  
              [Chemical Information].[Metal Classification];
```

Columns

<u>Name</u>	<u>Type</u>	<u>Size</u>
CAS Number	Text	255
Chemical Name	Text	255
Molecular Weight	Number (Double)	8
Metal Classification	Text	3

Query: QFT Exposure factors for spreadsheet

Properties

Date Created:	6/6/99 5:42:16 PM	Def. Updatable:	True
Last Updated:	4/17/00 1:24:50 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```

SELECT DISTINCTROW [Exposure Factors].[Exposure Factor Code],
[Chemical Information].[CAS Number],
[Chemical Information].[Chemical Name],
[Sources of Exposure Factors].Priority,
[Exposure Factors].[Nominal Value],
MakeRiskExpression([Distributions].[@Risk Expression],
[Exposure Factors].[Nominal Value],
[Exposure Factors].[Parameter 1],
[Exposure Factors].[Parameter 2]) AS Expr1,
[Exposure Factor Descriptions].Units,
[Sources of Exposure Factors].[Source Code],
References.[Reference Code]
FROM ([References]
INNER JOIN ([Exposure Factor Descriptions]
INNER JOIN [Sources of Exposure Factors]
ON [Exposure Factor Descriptions].[Exposure Factor Code] =
[Sources of Exposure Factors].[Exposure Factor Code])
ON References.[Reference Code] = [Sources of Exposure Factors].[Reference Code])
INNER JOIN ([Distributions]
INNER JOIN ([Chemical List]
INNER JOIN [Chemical Information]
ON [Chemical List].[CAS Number] = [Chemical Information].[CAS Number])
INNER JOIN [Chemical Names]
ON [Chemical Information].[CAS Number] = [Chemical Names].[CAS Number])
INNER JOIN [Exposure Factors]
ON [Chemical Information].[CAS Number] = [Exposure Factors].[CAS Number])
ON Distributions.[Distribution Code] = [Exposure Factors].[Distribution Code])
ON ([Sources of Exposure Factors].[Source Code] = [Exposure Factors].[Source Code])
AND ([Sources of Exposure Factors].[Exposure Factor Code] = [Exposure Factors].[Exposure Factor Code])
ORDER BY [Exposure Factors].[Exposure Factor Code],
[Chemical Information].[CAS Number],
[Sources of Exposure Factors].Priority;
    
```

Columns

Name	Type	Size
Exposure Factor Code	Text	255
CAS Number	Text	255
Chemical Name	Text	255
Priority	Number (Long)	4
Nominal Value	Number (Double)	8
Expr1	Text	0
Units	Text	255
Source Code	Text	255
Reference Code	Text	50

Query: QTI Toxicity Indices for FT spreadsheet

Properties

Date Created:	3/10/00 3:07:48 PM	Def. Updatable:	True
Last Updated:	3/28/00 8:05:20 PM	MaxRecords:	0
ODBCTimeout:	60	OrderBy:	[QTI Toxicity Indices for FT spreadsheet].Expr1
OrderByOn:	True	Record Locks:	No Locks
Records Affected:	0	RecordsetType:	All Records
ReturnsRecords:	True	Type:	Select

SQL

```

SELECT DISTINCTROW [Characterization Factors].[Impact Category Code],
[Chemical Information].[CAS Number],
[Chemical Information].[Chemical Name],
[Sources of Characterization Factors].Priority,
[Characterization Factors].[Nominal Value],
MakeRiskExpression([Distributions]![@Risk Expression],
[Characterization Factors]![Nominal Value],
[Characterization Factors]![Parameter 1],
[Characterization Factors]![Parameter 2]) AS Expr1,
[Impact Categories].Units,
[Sources of Characterization Factors].[Source Code],
References.[Reference Code]
FROM [References]
INNER JOIN (([Distributions]
INNER JOIN ((([Chemical List]
INNER JOIN [Chemical Information]
ON [Chemical List].[CAS Number] = [Chemical Information].[CAS Number])
INNER JOIN [Characterization Factors]
INNER JOIN [Impact Categories]
ON [Characterization Factors].[Impact Category Code] = [Impact Categories].[Impact Category Code])
ON [Chemical Information].[CAS Number] = [Characterization Factors].[CAS Number])
INNER JOIN [Chemical Names]
ON [Chemical Information].[CAS Number] = [Chemical Names].[CAS Number])
ON Distributions.[Distribution Code] = [Characterization Factors].[Distribution Code])
INNER JOIN [Sources of Characterization Factors]
ON ([Sources of Characterization Factors].[Source Code] = [Characterization Factors].[Source Code])
AND ([Sources of Characterization Factors].[Impact Category Code]
= [Characterization Factors].[Impact Category Code])
AND ([Impact Categories].[Impact Category Code]
= [Sources of Characterization Factors].[Impact Category Code]))
ON References.[Reference Code] = [Sources of Characterization Factors].[Reference Code]
WHERE ((([Characterization Factors].[Impact Category Code]) Like "Cancer UR*"
Or ([Characterization Factors].[Impact Category Code]) Like "Cancer CSF*"
Or ([Characterization Factors].[Impact Category Code]) Like "NonCancer inv*")
ORDER BY [Characterization Factors].[Impact Category Code],
[Chemical Information].[CAS Number],
[Sources of Characterization Factors].Priority;

```

Columns

Name	Type	Size
Impact Category Code	Text	255
CAS Number	Text	255
Chemical Name	Text	255
Priority	Number (Long)	4
Nominal Value	Number (Double)	8
Expr1	Text	0
Units	Text	255
Source Code	Text	255
Reference Code	Text	50

B.2.4 Visual Basic code implemented within the Excel workbook

```
' This code is attached to the button in the top-left corner of the model spreadsheet

Private Sub CommandButton1_Click()
    BuildTable
End Sub
```

```
' The following subroutines and functions are implemented within a VisualBasic Module

Public Sub BuildTable()

    ' Declare variables
    Dim rowLabel As String
    Dim columnLabel As String
    Dim chemName As String, CASNumber As String
    Dim CurrentWorkbook As String
    Dim fileName1 As String
    Dim fileName2 As String
    Dim fileName3 As String

    CurrentWorkbook = Application.ActiveWorkbook.Name

    ' Open files with output from Access database
    PathName = "F:\Work in Progress\Environmental Evaluation Tool\Temp\"
    fileName2 = "QFT Chemical Information for spreadsheet.xls"
    fileName1 = "QFT Exposure factors for spreadsheet.xls"
    fileName3 = "QTI Toxicity Indices for FT spreadsheet.xls"
    Workbooks.Open (PathName + fileName2)
    Workbooks.Open (PathName + fileName1)
    Workbooks.Open (PathName + fileName3)

    Windows(CurrentWorkbook).Activate

    ' Assemble table
    RowNumber = 2
    Do While Workbooks(fileName2).Sheets(1).Cells(RowNumber, 1).Value <> ""
        ' Get chemical information
        CASNumber = Workbooks(fileName2).Sheets(1).Cells(RowNumber, 1).Value
        chemName = Workbooks(fileName2).Sheets(1).Cells(RowNumber, 2).Value
        molWt = Workbooks(fileName2).Sheets(1).Cells(RowNumber, 3).Value
        metalClass = Workbooks(fileName2).Sheets(1).Cells(RowNumber, 4).Value
        ' Check whether the chemical is already in the table
        thisRowNumber = getRowNumber(CurrentWorkbook, CASNumber, chemName, CASNumber)
        ' Add name, molecular weight and metal classification information
        Workbooks(CurrentWorkbook).Sheets(2).Cells(thisRowNumber, 3).Value = chemName
        Workbooks(CurrentWorkbook).Sheets(2).Cells(thisRowNumber, 4).Value = molWt
        Workbooks(CurrentWorkbook).Sheets(2).Cells(thisRowNumber, 5).Value = metalClass
        RowNumber = RowNumber + 1
    Loop
    Workbooks(fileName2).Close

    GetInfo fileName1, CurrentWorkbook
    GetInfo fileName3, CurrentWorkbook

End Sub
```

```
Sub GetInfo(fileName As String, CurrentWorkbook As String)

    Dim rowLabel As String
    Dim columnLabel As String
    Dim chemName As String, CASNumber As String

    RowNumber = 2
    Do While Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value <> ""

        ' Get chemical name and check whether it exists in the table
        CASNumber = Workbooks(fileName).Sheets(1).Cells(RowNumber, 2).Value
        chemName = Workbooks(fileName).Sheets(1).Cells(RowNumber, 3).Value
        thisRowNumber = getRowNumber(CurrentWorkbook, CASNumber, chemName, CASNumber)

        ' Get Exposure factor code and check whether it exists in the table
        columnLabel = Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value
```

```

ColNumber = getColumnNumber(CurrentWorkbook, columnLabel)

' If a higher priority value has not been entered into the table, enter the factor
' (Table created by Access is sorted by
' Impact Category, Chemical Name, and Priority Level)
If IsEmpty(Workbooks(CurrentWorkbook).Sheets(2).Cells(thisRowNumber, ColNumber)) Then
    Workbooks(CurrentWorkbook).Sheets(2).Cells(thisRowNumber, ColNumber).Formula = "=" & Workbooks(fileName).Sheets(1).Cells(RowNumber, 5).Value
    Workbooks(CurrentWorkbook).Sheets(2).Cells(thisRowNumber, ColNumber).AddComment "Source: " & Workbooks(fileName).Sheets(1).Cells(RowNumber, 8).Value

    ' Check whether a distribution exists
    Distribution = Workbooks(fileName).Sheets(1).Cells(RowNumber, 6).Value
    If Not IsEmpty(Distribution) Then
        Workbooks(CurrentWorkbook).Sheets(2).Cells(thisRowNumber, ColNumber).Formula = "=" & Workbooks(CurrentWorkbook).Sheets(2).Cells(thisRowNumber, ColNumber).Value & "*" & Distribution
    End If

End If
RowNumber = RowNumber + 1
Loop
Workbooks(fileName).Close

End Sub

```

```

Function getColumnNumber(CurrentWorkbook As String, columnLabel As String) As Integer
    topRow = Workbooks(CurrentWorkbook).Sheets(2).Range("c1:AD1")
    On Error Resume Next
    getColumnNumber = Application.WorksheetFunction.Match(columnLabel, topRow, 0) + 2
    If Err.Number > 0 Then 'display error message
        MsgBox "Can't find the column heading " & columnLabel, vbOKOnly, "ERROR!"
        getColumnNumber = -1
    End If
    On Error GoTo 0
End Function

```

```

Function getRowNumber(CurrentWorkbook As String, rowLabel As String, _
    chemName As String, CASNumber As String) As Integer
    labelColumn = Workbooks(CurrentWorkbook).Sheets(2).Range("B" & FirstAvailRow & ":B" & MaxRows)
    numRows = Application.WorksheetFunction.CountA(labelColumn)

    On Error Resume Next
    getRowNumber = Application.WorksheetFunction.Match(rowLabel, labelColumn, 0) _
        + FirstAvailRow - 1
    If Err.Number > 0 Then 'new row is needed
        Workbooks(CurrentWorkbook).Sheets(2).Cells(numRows + FirstAvailRow, 3).Value = chemName
        Workbooks(CurrentWorkbook).Sheets(2).Cells(numRows + FirstAvailRow, 2).Formula = "=" & CASNumber
    End If
    getRowNumber = numRows + FirstAvailRow
End If
On Error GoTo 0

End Function

```

B.3 Queries and Visual Basic code used to export data to the PIO-LCA model

B.3.1 Overview

This section presents the code used to export data from the EnvEvalTool Access database to the spreadsheet-based PIO-LCA model. The actual building of the output vectors and matrices in the PIO-LCA method is done by the code presented in Appendix C.

SOFTWARE REQUIRED

The EnvEvalTool database used in this project implemented in Microsoft Access version 97 SR-1. The PIO-LCA model was implemented in version 97 SR-1 of Microsoft Excel. Monte Carlo simulations are carried out in Excel using the @Risk Add-on (Palisade Corporation). Version 3.5 of @Risk was used in this work.

EXECUTION SEQUENCE

A case study is defined by entering its name in the **Case Studies** table, specifying the products of interest and market share scenarios in the **Case Studies (products)** table, and selecting a valuation method, by entering the name of the case study and valuation method in the **Case Studies (Valuation)** table¹⁰³.

After defining the case study, the user should execute the macro **Export to spreadsheet** from within the EnvEvalTool database. This will generate a set of 11 temporary Excel files.

After executing the macro, the user should open the PIO-LCA excel workbook. Clicking on the **Load Table** button on Sheet1 of the workbook executes the Visual Basic code that loads the data and arranges them into the appropriate input matrices and vectors of the PIO-LCA method. The code also incorporates @Risk probability distribution functions and places comments on each cell citing the data source used.

¹⁰³ See section B.1 for information regarding the structure of these tables.

B.3.2 Visual Basic code implemented within the Access database

Macro: Export to spreadsheet

Properties

Date Created: 11/23/99 5:40:59 PM Last Updated: 11/23/99 5:40:59 PM
 Owner: admin

Actions

Name	Condition	Action	Argument	Value
		RunCode	Function Name:	Export_to_spreadsheet ()
<i>Used to access the function Export_to_spreadsheet()</i>				

Module: Converted Macro- Export to spreadsheet

Properties

Date Created: 9/9/99 10:54:53 AM Last Updated: 5/29/00 3:32:06 PM
 Owner: admin

Code

```

1 Attribute VB_Name = "Converted Macro- Export to spreadsheet"
2 Option Compare Database
3 Option Explicit
4
5 '-----
6 ' Export_to_spreadsheet
7 '
8 '-----
9 Function Export_to_spreadsheet()
10 On Error GoTo Export_to_spreadsheet_Err
11 Dim PathName As String
12 PathName = "F:\Work in Progress\Environmental Evaluation Tool\Temp\"
13 SetOption "Confirm Action Queries", False
14 DoCmd.OpenQuery "QIO Select Case Study", acNormal, acReadOnly
15 Generate_List_of_Products
16 Export_query "QIO Products Made", PathName
17 Export_query "QIO Processes", PathName
18 Export_query "QIO Exchanges", PathName
19 Export_query "QIO Prices", PathName
20 Export_query "QIO Market shares", PathName
21 Export_query "Make table factors for spreadsheet", PathName
22 Export_query "Use table factors for spreadsheet", PathName
23 Export_query "Emission factors for spreadsheet", PathName
24 Export_query "Characterization factors for spreadsheet", PathName
25 Export_query "Valuation factors for spreadsheet", PathName
26 SetOption "Confirm Action Queries", False
27 DoCmd.OpenQuery "CF with distributions for spreadsheet", acNormal, acReadOnly
28 DoCmd.OpenQuery "VF with distributions for spreadsheet", acNormal, acReadOnly
29 SetOption "Confirm Action Queries", True
30 Export_query "Correlation coefficients for spreadsheet", PathName
31 DoCmd.DeleteObject acTable, "Temporary CF"
32 DoCmd.DeleteObject acTable, "Temporary VF"
33 DoCmd.DeleteObject acTable, "TEMP Case Study"
34
35
36 Export_to_spreadsheet_Exit:
37 Exit Function
38
39 Export_to_spreadsheet_Err:
40 MsgBox Error$
41 Resume Export_to_spreadsheet_Exit
42
43 End Function

```

```

44
45 Sub Export_query(QueryName As String, PathName As String)
46     DoCmd.OpenQuery QueryName, acNormal, acReadOnly
47     DoCmd.TransferSpreadsheet acExport, 8, QueryName, PathName + QueryName, True
48     DoCmd.Close
49 End Sub

```

Module: Converted Macro- Generate List of Products

Properties

Date Created: 5/22/00 7:50:47 PM Last Updated: 5/22/00 9:14:13 PM
Owner: admin

Code

```

1 Attribute VB_Name = "Converted Macro- Generate List of Products"
2 Option Compare Database
3 Option Explicit
4
5 '-----
6 ' IO_Macro
7 '
8 '-----
9 Function Generate_List_of_Products()
10 On Error GoTo IO_Macro_Err
11
12     Dim NumOfProducts, NumOfProductsNew As Integer
13
14     SetOption "Confirm Action Queries", False
15     ' QIO Generate Temporary List of Products
16     DoCmd.DeleteObject acTable, "Temporary List of Products"
17     DoCmd.OpenQuery "QIO Generate Temporary List of Products", acNormal, acEdit
18     ' Get the Number of Records
19     DoCmd.OpenForm "FIO CountOfProducts", acNormal, acEdit
20     NumOfProducts = Forms![FIO CountOfProducts]!NumOfProducts.Value
21     DoCmd.Close acForm, "FIO CountOfProducts"
22     Do While True
23         ' QIO Copy NLOfProd into TLOfProd2
24         DoCmd.OpenQuery "QIO Copy NLOfProd into TLOfProd2", acNormal, acEdit
25         DoCmd.DeleteObject acTable, "Temporary List of Products"
26         DoCmd.Rename "Temporary List of Products", acTable, _
27             "Temporary List of Products New"
27         ' Check whether the new list has more records than the old list
28         ' Get the Number of Records
29         DoCmd.OpenForm "FIO CountOfProducts", acNormal, acEdit
30         NumOfProductsNew = Forms![FIO CountOfProducts]!NumOfProducts.Value
31         DoCmd.Close acForm, "FIO CountOfProducts"
32         If NumOfProductsNew > NumOfProducts Then
33             NumOfProducts = NumOfProductsNew
34         Else
35             Exit Do
36         End If
37     Loop
38
39     SetOption "Confirm Action Queries", True
40
41 IO_Macro_Exit:
42     Exit Function
43
44 IO_Macro_Err:
45     MsgBox Error$
46     Resume IO_Macro_Exit
47
48 End Function
49
50

```

Module: Uncertainty description functions

Properties

Date Created: 5/24/99 3:24:23 PM Last Updated: 3/28/00 7:54:53 PM
Owner: admin

Code

```
1 Attribute VB_Name = "Uncertainty description functions"
2 Option Compare Database
3 Option Explicit
4
5 Function MakeRiskExpression(Mask, NomVal, Param1, Param2)
6 ' This function generates @Risk Expressions for uncertainty
7 ' distributions based on the templates stored in the
8 ' "Distributions" table
9 Dim position, MaskLength, BracketedLength, j As Integer
10
11 ' Substitute "[Nominal Value]" occurrences
12 position = InStr(1, Mask, "[Nominal Value]", vbTextCompare)
13 MaskLength = Len(Mask)
14 BracketedLength = Len("[Nominal Value]")
15 If position > 0 Then
16 Mask = Left(Mask, position - 1) & Format(NomVal, "0.00E+00")
17 & Right(Mask, MaskLength - BracketedLength - (position - 1))
18 End If
19
20 ' Substitute "[Parameter 1]" occurrences
21 For j = 1 To 2
22 position = InStr(1, Mask, "[Parameter 1]", vbTextCompare)
23 MaskLength = Len(Mask)
24 BracketedLength = Len("[Parameter 1]")
25 If position > 0 Then
26 Mask = Left(Mask, position - 1) & Format(Param1, "0.00E+00")
27 & Right(Mask, MaskLength - BracketedLength - (position - 1))
28 End If
29 Next j
30
31 ' Substitute "[Parameter 2]" occurrences
32 position = InStr(1, Mask, "[Parameter 2]", vbTextCompare)
33 MaskLength = Len(Mask)
34 BracketedLength = Len("[Parameter 2]")
35 If position > 0 Then
36 Mask = Left(Mask, position - 1) & Format(Param2, "0.00E+00")
37 & Right(Mask, MaskLength - BracketedLength - (position - 1))
38 End If
39
40 ' Return generated expression
41 MakeRiskExpression = Mask
42
43 End Function
```


B.3.3 Queries, forms, and auxiliary tables

The following list gives the page numbers in which details are given on the different queries, forms, and auxiliary tables used by the Visual Basic code in section B.3.2.

Form: FIO CountOfProducts, 562
Query: CF with distributions for spreadsheet, 546
Query: Correlation Coefficients for spreadsheet, 549
Query: Emission factors for spreadsheet, 550
Query: Make table factors for spreadsheet, 551
Query: QIO Copy NlofProd INTO TlofProd2, 552
Query: QIO Count Products, 552
Query: QIO Direct Processes, 553
Query: QIO Exchanges, 553
Query: QIO First List of Used Products, 554
Query: QIO Generate Temporary List of Products, 554
Query: QIO Market Shares, 555
Query: QIO New List of Products, 556
Query: QIO Prices, 556
Query: QIO Processes, 557
Query: QIO Products made, 557
Query: QIO Products Used but not Made, 558
Query: QIO Products used by direct processes, 558
Query: QIO Select Case Study, 559
Query: Use table factors for spreadsheet, 560
Query: Valuation factors for spreadsheet, 561
Query: VF with distributions for spreadsheet, 562
Table: TEMP Case Study, 559
Table: Temporary CF, 546
Table: Temporary List of Products, 554
Table: Temporary List of Products New, 552
Table: Temporary VF, 562

Query: CF with distributions for spreadsheet (creates Table: Temporary CF)

Properties

Date Created:	9/17/99 1:05:32 AM	Def. Updatable:	True
Last Updated:	5/29/00 4:33:39 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	Edited Record	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Make-table	UseTransaction:	False

SQL

```
SELECT DISTINCTROW [Characterization factors for spreadsheet].Factor_number,
[Characterization factors for spreadsheet].[Impact Category Code] AS ColumnLabel,
[Characterization factors for spreadsheet].RowLabel,
[Characterization factors for spreadsheet].[Environmental Medium] AS firstRowLabel,
[Characterization factors for spreadsheet].[Chemical Name] AS secondRowLabel,
[Characterization factors for spreadsheet].Priority,
[Characterization factors for spreadsheet].[Source Code],
[Characterization factors for spreadsheet].[Nominal Value],
[Characterization factors for spreadsheet].[@Risk expression]
INTO [Temporary CF]
FROM [Characterization factors for spreadsheet]
INNER JOIN [Select CF distributions for spreadsheet]
ON ([Characterization factors for spreadsheet].Priority =
[Select CF distributions for spreadsheet].MinOfPriority)
AND ([Characterization factors for spreadsheet].[Chemical Name] =
[Select CF distributions for spreadsheet].[Chemical Name])
AND ([Characterization factors for spreadsheet].[Impact Category Code] =
[Select CF distributions for spreadsheet].[Impact Category Code]);
```

Query: Characterization factors for spreadsheet

Properties

Date Created:	9/8/99 12:11:48 PM	Def. Updatable:	True
Last Updated:	5/29/00 3:19:15 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```

SELECT DISTINCTROW [Impact Categories].[Environmental Medium],
[Characterization Factors].[ImpactCategory Code],
[QIO Exchanges].[Chemical Name],
[Sources of Characterization Factors].Priority,
[Characterization Factors].[Nominal Value],
MakeRiskExpression([Distributions].[@Risk Expression],
[Characterization Factors].[Nominal Value],
[Characterization Factors].[Parameter 1],
[Characterization Factors].[Parameter 2]) AS [@Risk expression],
[Impact Categories].Units,
[Characterization Factors].[Source Code],
References.[Reference Code],
[Characterization Factors].Factor_number,
[Chemical Names].[Chemical Name]+ " to "+[Environmental Medium] AS RowLabel,
[Characterization Factors].[Impact Category Code]
+ " ("+[Impact Categories].[Units]+)" AS ColumnLabel

FROM [TEMP Case Study]
INNER JOIN ([References]
INNER JOIN (([Distributions]
INNER JOIN ((([Characterization Factors]
INNER JOIN [Chemical Names]
ON [Characterization Factors].[CAS Number] = [Chemical Names].[CAS Number])
INNER JOIN [QIO Exchanges]
ON [Chemical Names].[Chemical Name] = [QIO Exchanges].[Chemical Name])
INNER JOIN [Impact Categories]
ON [QIO Exchanges].[Release Medium] = [Impact Categories].[Environmental Medium])
ON Distributions.[Distribution Code] = [Characterization Factors].[Distribution Code])
INNER JOIN [Sources of Characterization Factors]
ON ([Sources of Characterization Factors].[Source Code] = [Characterization Factors].[Source Code])
AND ([Sources of Characterization Factors].[Impact Category Code]
= [Characterization Factors].[Impact Category Code])
AND ([Impact Categories].[Impact Category Code]
= [Sources of Characterization Factors].[Impact Category Code]))
INNER JOIN ([Case Studies (valuation)]
INNER JOIN [Valuation Factors]
ON [Case Studies (valuation)].[Method Code] = [Valuation Factors].[Method code])
ON [Impact Categories].[Impact Category Code] = [Valuation Factors].[Impact category code])
ON References.[Reference Code] = [Sources of Characterization Factors].[Reference Code])
ON [TEMP Case Study].[Case Study] = [Case Studies (valuation)].[Case Study])
ORDER BY [Impact Categories].[Environmental Medium],
[Characterization Factors].[Impact Category Code],
[QIO Exchanges].[Chemical Name],
[Sources of Characterization Factors].Priority;
    
```

Columns

<u>Name</u>	<u>Type</u>	<u>Size</u>
Environmental Medium	Text	50
Impact Category Code	Text	255
Chemical Name	Text	255
Priority	Number (Long)	4
Nominal Value	Number (Double)	8
@Risk expression	Text	0
Units	Text	255
Source Code	Text	255
Reference Code	Text	50
Factor_number	Number (Long)	4
RowLabel	Text	0
ColumnLabel	Text	0

Query: Correlation Coefficients for spreadsheet

Properties

Date Created:	9/20/99 1:11:23 PM	Def. Updatable:	True
Last Updated:	5/29/00 4:43:02 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Union		

SQL

```

SELECT [CF_1].FirstRowLabel AS FirstRowLabel1,
       [CF_1].SecondRowLabel AS SecondRowLabel1,
       [CF_1].ColumnLabel AS ColLabel1,
       [CF_2].FirstRowLabel AS FirstRowLabel2,
       [CF_2].SecondRowLabel AS SecondRowLabel2,
       [CF_2].ColumnLabel AS ColLabel2,
       [CF to CF correlations].Correlation_coefficient AS CorrCoeff
FROM [Temporary CF] AS [CF_2]
INNER JOIN ([Temporary CF] AS [CF_1]
INNER JOIN [CF to CF correlations]
         ON [CF_1].Factor_number = [CF to CF correlations].Factor_number1)
         ON [CF_2].Factor_number = [CF to CF correlations].Factor_number2

UNION

SELECT [CF_1].FirstRowLabel AS FirstRowLabel1,
       [CF_1].SecondRowLabel AS SecondRowLabel1 ,
       [CF_1].ColumnLabel as ColLabel1 ,
       null as firstRowLabel2,
       [VF_1].RowLabel as secondRowLabel2 ,
       [VF_1].ColumnLabel ,
       [CF to VF correlations].Correlation_coefficient
FROM [Temporary VF] AS [VF_1]
INNER JOIN ([Temporary CF] AS [CF_1]
INNER JOIN [CF to VF correlations]
         ON [CF_1].Factor_number = [CF to VF correlations].Charact_factor_number)
         ON [VF_1].Factor_number = [CF to VF correlations].Valuation_factor_number

UNION

SELECT null As FirstRowLabel1,
       [VF_1].RowLabel As SecondRowLabel ,
       [VF_1].ColumnLabel ,
       null as FirstRowLabel2,
       [VF_2].RowLabel ,
       [VF_2].ColumnLabel ,
       [VF to VF correlations].Correlation_coefficient
FROM [Temporary VF] AS [VF_2]
INNER JOIN ([Temporary VF] AS [VF_1]
INNER JOIN [VF to VF correlations]
         ON [VF_1].Factor_number = [VF to VF correlations].Factor_number1)
         ON [VF_2].Factor_number = [VF to VF correlations].Factor_number2;

```

Columns

Name	Type	Size
FirstRowLabel1	Text	0
SecondRowLabel1	Text	0
ColLabel1	Text	0
SecondRowLabel2	Text	0
ColLabel2	Text	0
CorrCoeff	Number (Double)	8

Query: Emission factors for spreadsheet

Properties

Date Created:	9/8/99 11:59:06 AM	Def. Updatable:	True
Last Updated:	5/22/00 10:15:13 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```

SELECT Processes.[Process Code],
       [Emission factors].[Release Medium],
       [Chemical Information].[Chemical Name],
       [Sources of Emission Factors].Priority,
       [Emission factors].[Nominal Value],
       MakeRiskExpression([Distributions]![@Risk Expression],
                          [Emission Factors]![@Nominal Value],
                          [Emission Factors]![@Parameter 1],
                          [Emission Factors]![@Parameter 2]) AS Expr1,
       [Emission factors].Units,
       References.[Reference Code],
       [Chemical Name]+ " to "+[Release Medium] AS RowLabel,
       [Emission Factors].[Process Code]+ " ("+[Units]+)" AS ColumnLabel,
       [Emission factors].Factor_number
FROM (([References]
INNER JOIN ([Processes]
INNER JOIN ([Sources of Emission Factors]
ON Processes.[Process Code] = [Sources of Emission Factors].[Process Code])
ON References.[Reference Code] = [Sources of Emission Factors].[Reference Code])
INNER JOIN ([Distributions]
INNER JOIN ([Chemical Information]
INNER JOIN ([Emission factors]
ON [Chemical Information].[CAS Number] = [Emission factors].[CAS Number])
ON Distributions.[Distribution Code] = [Emission factors].[Distribution Code])
ON ([Sources of Emission Factors].[Source Code] = [Emission factors].[Source code])
AND ([Sources of Emission Factors].[Process Code] = [Emission factors].[Process code]))
INNER JOIN ([QIO Processes]
ON Processes.[Process Code] = [QIO Processes].[Process Code])
ORDER BY Processes.[Process Code],
         [Emission factors].[Release Medium],
         [Chemical Information].[Chemical Name],
         [Sources of Emission Factors].Priority;

```

Columns

Name	Type	Size
Process Code	Text	50
Release Medium	Text	255
Chemical Name	Text	255
Priority	Text	255
Nominal Value	Number (Double)	8
Expr1	Text	0
Units	Text	50
Reference Code	Text	50
RowLabel	Text	0
ColumnLabel	Text	0
Factor_number	Number (Long)	4

Query: Make table factors for spreadsheet

Properties

Date Created:	5/22/00 9:17:21 PM	Def. Updatable:	True
Last Updated:	5/23/00 5:10:28 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```

SELECT Processes.[Process Code],
       [QIO Products made].[Product Code],
       [Make coefficients].[Source Code],
       [Sources of Input-Output Data].Priority,
       [Make coefficients].[Nominal Value],
       MakeRiskExpression([Distributions]![@Risk Expression],
                          [Make Coefficients]![Nominal Value],
                          [Make Coefficients]![Parameter 1],
                          [Make Coefficients]![Parameter 2]) AS Expr1
FROM ([QIO Products made]
INNER JOIN Products
      ON [QIO Products made].[Product Code] = Products.[Product code])
INNER JOIN ((Processes
INNER JOIN [QIO Processes]
          ON Processes.[Process Code] = [QIO Processes].[Process Code])
INNER JOIN (Distributions
INNER JOIN [Make coefficients]
          ON (Distributions.[Distribution Code] = [Make coefficients].[Distribution Code])
          AND (Distributions.[Distribution Code] = [Make coefficients].[Distribution Code]))
          ON Processes.[Process Code] = [Make coefficients].[Process Code])
INNER JOIN [Sources of Input-Output Data]
          ON ([Sources of Input-Output Data].[Source Code] = [Make coefficients].[Source Code])
          AND ([Sources of Input-Output Data].[Process Code] = [Make coefficients].[Process Code])
          AND (Processes.[Process Code] = [Sources of Input-Output Data].[Process Code]))
          ON Products.[Product code] = [Make coefficients].[Product Code]
ORDER BY Processes.[Process Code],
         [QIO Products made].[Product Code],
         [Sources of Input-Output Data].Priority;
    
```

Columns

Name	Type	Size
Process Code	Text	50
Product Code	Text	50
Source Code	Text	50
Priority	Text	255
Nominal Value	Number (Double)	8
Expr1	Text	0

Query: QIO Copy NlofProd INTO TLoProd2

(creates Table: Temporary List of Products New)

Properties

Date Created:	5/22/00 7:42:29 PM	Def. Updatable:	True
Last Updated:	5/22/00 7:43:45 PM	MaxRecords:	0
ODBCTimeout:	60	Record Locks:	Edited Record
Records Affected:	0	ReturnsRecords:	True
Type:	Make-table	UseTransaction:	True

SQL

```
SELECT [QIO New List of Products].[Product Code]
INTO [Temporary List of Products New]
FROM [QIO New List of Products];
```

Query: QIO Count Products

Properties

Date Created:	5/22/00 8:01:49 PM	Def. Updatable:	True
Last Updated:	5/22/00 8:01:49 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```
SELECT Count([Temporary List of Products].[Product Code]) AS [CountOfProduct Code]
FROM [Temporary List of Products];
```

Columns

<u>Name</u>	<u>Type</u>	<u>Size</u>
CountOfProduct Code	Number (Long)	4

Query: QIO Direct Processes

Properties

Date Created:	5/22/00 7:16:34 PM	Def. Updatable:	True
Last Updated:	5/29/00 3:21:42 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```
SELECT [Make coefficients].[Process Code]
FROM [TEMP Case Study]
INNER JOIN ([Make coefficients]
INNER JOIN [Case Studies (products)]
ON [Make coefficients].[Product Code] = [Case Studies (products)].[Product Code])
ON [TEMP Case Study].[Case Study] = [Case Studies (products)].[Case Study];
```

Columns

Name	Type	Size
Process Code	Text	50

Query: QIO Exchanges

Properties

Date Created:	5/23/00 1:44:14 PM	Def. Updatable:	True
Last Updated:	5/23/00 1:50:03 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```
SELECT DISTINCT [Emission factors].[Release Medium],
                [Chemical Information].[Chemical Name],
                [Emission factors].Units
FROM [Chemical Information]
INNER JOIN ([QIO Processes]
INNER JOIN [Emission factors]
ON [QIO Processes].[Process Code] = [Emission factors].[Process code])
ON ([Chemical Information].[CAS Number] = [Emission factors].[CAS Number])
AND ([Chemical Information].[CAS Number] = [Emission factors].[CAS Number]);
```

Columns

Name	Type	Size
Release Medium	Text	255
Chemical Name	Text	255
Units	Text	50

Query: QIO First List of Used Products

Properties

Date Created:	5/22/00 7:22:30 PM	Def. Updatable:	True
Last Updated:	5/29/00 7:42:30 PM	MaxRecords:	0
ODBCTimeout:	60	Record Locks:	No Locks
Records Affected:	0	ReturnsRecords:	True
Type:	Union		

SQL

```
SELECT [Case Studies (products)].[Product Code]
FROM [TEMP Case Study]
INNER JOIN [Case Studies (products)]
    ON [TEMP Case Study].[Case Study]= [Case Studies (products)].[Case Study]
```

UNION

```
SELECT [QIO Products used by direct processes].[Product Code]
FROM [QIO Products used by direct processes];
```

Columns

Name	Type	Size
Product Code	Text	50

Query: QIO Generate Temporary List of Products

(creates Table: Temporary List of Products)

Properties

Date Created:	5/22/00 7:28:18 PM	Def. Updatable:	True
Last Updated:	5/22/00 7:34:12 PM	MaxRecords:	0
ODBCTimeout:	60	Record Locks:	Edited Record
Records Affected:	0	ReturnsRecords:	True
Type:	Make-table	UseTransaction:	True

SQL

```
SELECT [QIO First List of Used Products].[Product Code]
INTO [Temporary List of Products]
FROM [QIO First List of Used Products];
```

Query: QIO Market Shares

Properties

Date Created:	5/29/00 3:15:06 PM	Def. Updatable:	True
Last Updated:	5/29/00 3:21:20 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```

SELECT DISTINCT [QIO Products made].[Product Code],
                [QIO Processes].[Process Code],
                [Case Studies (products)].[Mkt Share Scenario],
                [Market Shares].[Nominal Value],
                MakeRiskExpression([Distributions].[@Risk Expression],
                                [Market Shares].[Nominal Value],
                                [Market Shares].[Parameter 1],
                                [Market Shares].[Parameter 2]) AS Expr1

FROM [TEMP Case Study]
INNER JOIN (Distributions
INNER JOIN (([QIO Products made]
INNER JOIN ([QIO Processes]
INNER JOIN [Market Shares]
            ON [QIO Processes].[Process Code] = [Market Shares].[Process Code])
            ON [QIO Products made].[Product Code] = [Market Shares].[Product Code])
INNER JOIN [Case Studies (products)]
            ON ([Market Shares].[Product Code] = [Case Studies (products)].[Product Code])
            AND ([Market Shares].[Mkt Share Scenario] = [Case Studies (products)].[Mkt Share Scenario]))
            ON Distributions.[Distribution Code] = [Market Shares].[Distribution Code])
            ON [TEMP Case Study].[Case Study] = [Case Studies (products)].[Case Study]
ORDER BY      [QIO Products made].[Product Code],
                [Market Shares].[Nominal Value] DESC;
    
```

Columns

Name	Type	Size
Product Code	Text	50
Process Code	Text	50
Mkt Share Scenario	Text	50
Nominal Value	Number (Double)	8
Expr1	Text	0

Query: QIO New List of Products

Properties

Date Created:	5/22/00 7:31:55 PM	Def. Updatable:	True
Last Updated:	5/22/00 7:37:40 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Union		

SQL

```

SELECT [Use coefficients].[Product Code]
FROM [QIO Processes]
INNER JOIN [Use coefficients]
    ON [QIO Processes].[Process Code] = [Use coefficients].[Process Code]

UNION

SELECT [Temporary List of Products].[Product Code] FROM [Temporary List of Products];

```

Columns

Name	Type	Size
Product Code	Text	50

Query: QIO Prices

Properties

Date Created:	5/29/00 3:06:54 PM	Def. Updatable:	True
Last Updated:	5/29/00 3:34:40 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```

SELECT [QIO Products made].[Product Code],
    Prices.[Nominal Value],
    MakeRiskExpression([Distributions]![@Risk Expression],
        [Prices]![Nominal Value],
        [Prices]![Parameter 1],
        [Prices]![Parameter 2]) AS Expr1,
    Prices.Currency,
    [QIO Products made].[Unit of measurement],
    Prices.Year
FROM (Distributions
INNER JOIN Prices
    ON Distributions.[Distribution Code] = Prices.[Distribution Code])
INNER JOIN [QIO Products made]
    ON Prices.[Product Code] = [QIO Products made].[Product Code]

```

Columns

Name	Type	Size
Product Code	Text	50
Nominal Value	Number (Double)	8
Expr1	Text	0
Currency	Text	10
Unit of measurement	Text	100
Year	Text	50

Query: QIO Processes

Properties

Date Created:	5/22/00 7:24:18 PM	Def. Updatable:	True
Last Updated:	5/22/00 7:33:16 PM	MaxRecords:	0
ODBCTimeout:	60	Record Locks:	No Locks
Records Affected:	0	ReturnsRecords:	True
Type:	Select		

SQL

```
SELECT DISTINCT [Make coefficients].[Process Code]
FROM [Temporary List of Products]
INNER JOIN [Make coefficients]
ON [Temporary List of Products].[Product Code] = [Make coefficients].[Product Code];
```

Columns

<u>Name</u>	<u>Type</u>	<u>Size</u>
Process Code	Text	50

Query: QIO Products made

Properties

Date Created:	5/22/00 8:58:37 PM	Def. Updatable:	True
Last Updated:	5/23/00 3:46:03 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```
SELECT DISTINCT [Make coefficients].[Product Code],
Products.[Unit of measurement]
FROM Products
INNER JOIN ([QIO Processes]
INNER JOIN [Make coefficients]
ON [QIO Processes].[Process Code] = [Make coefficients].[Process Code])
ON Products.[Product code] = [Make coefficients].[Product Code];
```

Columns

<u>Name</u>	<u>Type</u>	<u>Size</u>
Product Code	Text	50
Unit of measurement	Text	100

Query: QIO Products Used but not Made

Properties

Date Created:	5/22/00 9:07:20 PM	Def. Updatable:	True
Last Updated:	5/22/00 9:07:20 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```
SELECT [Temporary List of Products].[Product Code]
FROM [Temporary List of Products]
LEFT JOIN [QIO Products made]
    ON [Temporary List of Products].[Product Code] = [QIO Products made].[Product Code]
WHERE ((([QIO Products made].[Product Code]) Is Null));
```

Columns

Name	Type	Size
Product Code	Text	255

Query: QIO Products used by direct processes

Properties

Date Created:	5/22/00 7:18:13 PM	Def. Updatable:	True
Last Updated:	5/22/00 7:18:13 PM	MaxRecords:	0
ODBCTimeout:	60	Record Locks:	No Locks
Records Affected:	0	ReturnsRecords:	True
Type:	Select		

SQL

```
SELECT DISTINCT [Use coefficients].[Product Code]
FROM [QIO Direct Processes]
INNER JOIN [Use coefficients]
    ON [QIO Direct Processes].[Process Code] = [Use coefficients].[Process Code];
```

Columns

Name	Type	Size
Product Code	Text	50

Query: QIO Select Case Study (Creates Table: TEMP Case Study)

Properties

Date Created:	5/29/00 3:18:05 PM	Def. Updatable:	True
Last Updated:	5/29/00 3:18:43 PM	MaxRecords:	0
ODBCTimeout:	60	Record Locks:	Edited Record
Records Affected:	0	ReturnsRecords:	True
Type:	Make-table	UseTransaction:	True

SQL

```
SELECT DISTINCT [Case Studies (products)].[Case Study]
INTO [TEMP Case Study]
FROM [Case Studies (products)]
WHERE ((([Case Studies (products)].[Case Study])=[Enter Case Study Name:]));
```

Query Parameters

Name	Type
[Enter Case Study Name:]	Text

Query: Use table factors for spreadsheet

Properties

Date Created:	5/22/00 10:09:41 PM	Def. Updatable:	True
Last Updated:	5/23/00 5:10:15 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```

SELECT Processes.[Process Code],
       [QIO Products made].[Product Code],
       [Sources of Input-Output Data].[Source Code],
       [Sources of Input-Output Data].Priority,
       [Use coefficients].[Nominal Value],
       MakeRiskExpression([Distributions].[@Risk Expression],
                          [Use Coefficients].[Nominal Value],
                          [Use Coefficients].[Parameter 1],
                          [Use Coefficients].[Parameter 2]) AS Expr1
FROM (Distributions
INNER JOIN (([QIO Products made]
INNER JOIN Products
         ON [QIO Products made].[Product Code] = Products.[Product code])
INNER JOIN ([Processes]
INNER JOIN [QIO Processes]
         ON Processes.[Process Code] = [QIO Processes].[Process Code])
INNER JOIN [Use coefficients]
         ON (Processes.[Process Code] = [Use coefficients].[Process Code])
         AND (Processes.[Process Code] = [Use coefficients].[Process Code])
         ON (Products.[Product code] = [Use coefficients].[Product Code])
         AND (Products.[Product code] = [Use coefficients].[Product Code]))
         ON (Distributions.[Distribution Code] = [Use coefficients].[Distribution Code])
         AND (Distributions.[Distribution Code] = [Use coefficients].[Distribution Code]))
INNER JOIN [Sources of Input-Output Data]
         ON ([Sources of Input-Output Data].[Source Code] = [Use coefficients].[Source Code])
         AND ([Sources of Input-Output Data].[Process Code] = [Use coefficients].[Process Code])
         AND (Processes.[Process Code] = [Sources of Input-Output Data].[Process Code])
ORDER BY Processes.[Process Code],
         [QIO Products made].[Product Code],
         [Sources of Input-Output Data].Priority;

```

Columns

Name	Type	Size
Process Code	Text	50
Product Code	Text	50
Source Code	Text	255
Priority	Text	255
Nominal Value	Number (Double)	8
Expr1	Text	0

Query: Valuation factors for spreadsheet

Properties

Date Created:	5/22/00 10:22:14 PM	Def. Updatable:	True
Last Updated:	5/29/00 3:28:52 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	No Locks	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Select		

SQL

```

SELECT DISTINCT [Valuation Factors].Factor_number,
                [Valuation Factors].[Method code],
                [Valuation Factors].[Impact category code],
                [Valuation Factors].[Nominal Value],
                MakeRiskExpression([Distributions].[@Risk Expression],
                [Valuation Factors].[Nominal Value],
                [Valuation Factors].[Parameter 1],
                [Valuation Factors].[Parameter 2]) AS Expr1,
                "Valuation factor" AS RowLabel,
                [Impact Categories].[Impact Category Code]+" ("+[Impact Categories].[Units]+")" AS ColumnLabel,
                [Impact Categories].Units
FROM [QIO Exchanges]
INNER JOIN ([Impact Categories]
INNER JOIN ([Distributions]
INNER JOIN ([TEMP Case Study]
INNER JOIN ([Valuation Factors]
INNER JOIN [Case Studies (valuation)]
                ON [Valuation Factors].[Method code] = [Case Studies (valuation)].[Method Code])
                ON [TEMP Case Study].[Case Study] = [Case Studies (valuation)].[Case Study])
                ON [Distributions].[Distribution Code] = [Valuation Factors].[Distribution Code])
                ON [Impact Categories].[Impact Category Code] = [Valuation Factors].[Impact category code])
                ON [QIO Exchanges].[Release Medium] = [Impact Categories].[Environmental Medium]
ORDER BY [Valuation Factors].[Method code],
        [Valuation Factors].[Impact category code];
    
```

Columns

Name	Type	Size
Factor_number	Number (Long)	4
Method code	Text	50
Impact category code	Text	50
Nominal Value	Number (Double)	8
Expr1	Text	0
RowLabel	Text	0
ColumnLabel	Text	0
Units	Text	255

Query: VF with distributions for spreadsheet (Creates Table: Temporary VF)

Properties

Date Created:	9/17/99 1:42:48 AM	Def. Updatable:	True
Last Updated:	5/29/00 4:34:11 PM	MaxRecords:	0
ODBCTimeout:	60	OrderByOn:	False
Record Locks:	Edited Record	Records Affected:	0
RecordsetType:	All Records	ReturnsRecords:	True
Type:	Make-table	UseTransaction:	False

SQL

```
SELECT [Valuation factors for spreadsheet].Factor_number,  
       [Valuation factors for spreadsheet].[Method code],  
       [Valuation factors for spreadsheet].RowLabel, "" AS firstRowLabel,  
       [Valuation factors for spreadsheet].RowLabel AS secondRowLabel,  
       [Valuation factors for spreadsheet].[Impact category code] AS ColumnLabel,  
       [Valuation factors for spreadsheet].[Nominal Value],  
       [Valuation factors for spreadsheet].Expr1  
INTO [Temporary VF]  
FROM [Valuation factors for spreadsheet]  
WHERE ((([Valuation factors for spreadsheet].Expr1) Is Not Null));
```

Form: FIO CountOfProducts

Properties

Date Created:	5/22/00 8:07:59 PM
Last Updated:	5/22/00 8:10:51 PM
Record Source:	QIO Count Products

Objects**Text Box: NumOfProducts**

Control Source:	CountOfProduct Code
Name:	NumOfProducts

B.3.4 Visual Basic code implemented within the Excel workbook

The following list gives the page numbers in which the various subroutines and functions used within the Excel workbook to import the data generated by the macro in the Access database. The code is launched by clicking on the “Load Data” button on Sheet1 of the PIO-LCA workbook.

BuildBCmatrix, 568
BuildEMatrix, 569
BuildHMatrix, 569
BuildMktShrMatrix, 571
Buildpvector, 571
BuildSheet1, 564
BuildSheet2, 566
BuildSheet3, 566
BuildSheet4, 567
BuildSheet5, 567
Buildwvector, 570
CommandButton2_Click(), 564
FormatMatrix, 573
FormatVector, 573
getColumnNumber, 572
Getncat, 574
Getnex, 574
Getnproc, 574
Getnprod, 574
getPosition, 573
getRowNumber, 572
getRowNumber2labels, 572
getRowNumber3labels, 573
Global declarations, 564

```

Private Sub CommandButton2_Click()
    Dim PathName As String
    Dim CurrentWorkbook As String

    PathName = "F:\Work in Progress\Environmental Evaluation Tool\Temp\"
    CurrentWorkbook = Application.ActiveWorkbook.Name

    BuildSheet1 CurrentWorkbook, PathName, _
        "QIO Processes.xls", _
        "QIO Products made.xls", _
        "QIO Exchanges.xls", _
        "Use table factors for spreadsheet.xls", _
        "Make table factors for spreadsheet.xls", _
        "Emission factors for spreadsheet.xls"

    BuildSheet2 CurrentWorkbook, PathName, _
        "QIO Prices.xls"

    BuildSheet3 CurrentWorkbook, PathName, _
        "Valuation factors for spreadsheet.xls", _
        "Characterization factors for spreadsheet.xls"

    BuildSheet4 CurrentWorkbook, PathName, _
        "QIO Market Shares.xls"

    BuildSheet5 CurrentWorkbook, PathName, _
        "Correlation coefficients for spreadsheet"
End Sub

```

```

' Global declarations

Public nproc As Integer ' number of processes
Public nprod As Integer ' number of products
Public nex As Integer ' number of environmental exchanges
Public ncat As Integer ' number of impact categories

```

```

Sub BuildSheet1(CurrentWorkbook As String, PathName As String, _
    fileName1 As String, fileName2 As String, _
    fileName3 As String, fileName4 As String, _
    fileName5 As String, fileName6 As String)

    ' Open files with output from Access database
    Workbooks.Open (PathName + fileName1)
    Workbooks.Open (PathName + fileName2)
    Workbooks.Open (PathName + fileName3)
    Windows(CurrentWorkbook).Activate

    ' Copy names of processes and count them
    nproc = 0
    runOutOfProcesses = False
    Do While Not runOutOfProcesses
        ProcessLabel = Workbooks(fileName1).Sheets(1).Cells(2 + nproc, 1).Value
        If ProcessLabel = "" Then
            runOutOfProcesses = True
        Else
            nproc = nproc + 1
            Workbooks(CurrentWorkbook).Sheets(1).Cells(1, 4 + nproc).Value = _
                ProcessLabel
        End If
    Loop
    ' format process labels
    Range(Cells(1, 5), Cells(1, 5 + nproc - 1)).Select
    With Selection
        .Orientation = 90
        .ColumnWidth = 5
    End With
    ' close file with process labels
    Workbooks(fileName1).Close

    ' Count the number of products
    nprod = 0
    runOutOfProducts = False
    Do While Not runOutOfProducts
        If Workbooks(fileName2).Sheets(1).Cells(2 + nprod, 1).Formula = "" Then
            runOutOfProducts = True
        Else
            nprod = nprod + 1
        End If
    End If

```

```

Loop

' Make space for Use Matrix
Rows("3:" & nprod + 2).Select
Selection.Insert Shift:=xlDown
Selection.Font.Bold = False
' Copy product labels and units
For i = 1 To nprod
    ' Copy label
    Cells(2 + i, 2).Select
    Selection.Value = _
        Workbooks(fileName2).Sheets(1).Cells(1 + i, 1).Value
    ' Copy units
    Cells(2 + i, 3).Select
    Selection.Value = _
        Workbooks(fileName2).Sheets(1).Cells(1 + i, 2).Value
Next i
Workbooks(fileName2).Close
FormatMatrix 3, 5, nprod, nproc

' Make space for Make Matrix
Rows(nprod + 5 & ":" & 2 * nprod + 4).Select
Selection.Insert Shift:=xlDown
Selection.Font.Bold = False
' Insert formulas
Range(Cells(nprod + 5, 2), Cells(2 * nprod + 4, 3)).Select
For i = 1 To nprod
    ' Copy label
    Cells(nprod + 4 + i, 2).Select
    Selection.FormulaR1C1 = "=+R[-" & nprod + 2 & "]"C"
    ' Copy units
    Cells(nprod + 4 + i, 3).Select
    Selection.FormulaR1C1 = "=+R[-" & nprod + 2 & "]"C"
Next i
FormatMatrix nprod + 5, 5, nprod, nproc

' Insert Environmental Exchanges Labels
nex = 0
runOutOfExchanges = False
Do While Not runOutOfExchanges
    ExchangeLabel = Workbooks(fileName3).Sheets(1).Cells(2 + nex, 2).Value
    If ExchangeLabel = "" Then
        runOutOfExchanges = True
    Else
        Cells(2 * nprod + 7 + nex, 2).Value = _
            ExchangeLabel
        Cells(2 * nprod + 7 + nex, 1) = _
            Workbooks(fileName3).Sheets(1).Cells(2 + nex, 1).Value
        Cells(2 * nprod + 7 + nex, 3) = _
            Workbooks(fileName3).Sheets(1).Cells(2 + nex, 3).Value
        nex = nex + 1
    End If
Loop
Workbooks(fileName3).Close
FormatMatrix 2 * nprod + 7, 5, nex, nproc

BuildBCmatrix CurrentWorkbook, PathName, fileName4, 3
BuildBCmatrix CurrentWorkbook, PathName, fileName5, 5 + nprod
BuildEMatrix CurrentWorkbook, PathName, fileName6

' Fill B matrix with zeros
For i = 1 To nprod
    For j = 1 To nproc
        If Cells(2 + i, 4 + j).Value = "" Then Cells(2 + i, 4 + j).Value = 0
    Next j
Next i

' Fill C matrix with zeros
For i = 1 To nprod
    For j = 1 To nproc
        If Cells(4 + nprod + i, 4 + j).Value = "" Then Cells(4 + nprod + i, 4 + j).Value = 0
    Next j
Next i

' Fill E matrix with zeros
For i = 1 To nex
    For j = 1 To nproc
        If Cells(6 + 2 * nprod + i, 4 + j).Value = "" Then _
            Cells(6 + 2 * nprod + i, 4 + j).Value = 0
    Next j
Next i

```

```

Next i
End Sub

```

```

Sub BuildSheet2(CurrentWorkbook As String, PathName As String, _
                fileName As String)
    Dim Units As String

    Getnprod
    Workbooks(CurrentWorkbook).Sheets(2).Activate
    For i = 1 To nprod
        Cells(2 + i, 1).Value = Sheets(1).Cells(2 + i, 2).Value
        ' Enter default price
        Cells(2 + i, 3).Value = 999
        Units = Sheets(1).Cells(2 + i, 3).Value
        Cells(2 + i, 4).Value = "$/" + Units
        Cells(2 + i, 8).Value = 0
        Cells(2 + i, 9).Value = Units
    Next i
    FormatMatrix 3, 3, nprod, 2
    FormatMatrix 3, 8, nprod, 2

    Buildpvector CurrentWorkbook, PathName, fileName
End Sub

```

```

Sub BuildSheet3(CurrentWorkbook As String, PathName As String, _
                fileName1 As String, fileName2 As String)

    ' Open files with output from Access database
    fileName1 = "Valuation factors for spreadsheet"
    Workbooks.Open (PathName + fileName1)
    Windows(CurrentWorkbook).Activate
    Sheets(3).Activate

    ' Copy names of impact categories and count them
    ncat = 0
    runOutOfCategories = False
    Do While Not runOutOfCategories
        CategoryLabel = Workbooks(fileName1).Sheets(1).Cells(2 + ncat, 3).Value
        If CategoryLabel = "" Then
            runOutOfCategories = True
        Else
            Cells(1, 5 + ncat).Value = CategoryLabel
            Cells(2, 5 + ncat).Value = Workbooks(fileName1).Sheets(1).Cells(2 + ncat, 8).Value
            ncat = ncat + 1
        End If
    Loop
    ' format category labels
    Range(Cells(1, 5), Cells(2, 5 + ncat - 1)).Select
    With Selection
        .ColumnWidth = 12
        .WrapText = True
    End With
    ' close file with valuation factor labels
    Workbooks(fileName1).Close

    ' Count the number of products and exchanges
    Getnprod
    Getnex
    Sheets(3).Select

    ' Make space for H Matrix
    Rows("4:" & nex + 3).Select
    Selection.Insert Shift:=xlDown
    Selection.Font.Bold = False
    ' Copy labels for environmental exchanges
    For i = 1 To nex
        Cells(3 + i, 1).Value = Sheets(1).Cells(nprod * 2 + 6 + i, 1).Value
        Cells(3 + i, 2).Value = Sheets(1).Cells(nprod * 2 + 6 + i, 2).Value
        Cells(3 + i, 3).Value = Sheets(1).Cells(nprod * 2 + 6 + i, 3).Value
    Next i
    FormatMatrix 4, 5, nex, ncat
    FormatMatrix nex + 6, 5, 1, ncat

    BuildHMatrix CurrentWorkbook, PathName, fileName2
    Buildwvector CurrentWorkbook, PathName, fileName1

    ' Fill H matrix with zeros
    For i = 1 To nex

```

```

        For j = 1 To ncat
            If Cells(3 + i, 4 + j).Value = "" Then Cells(3 + i, 4 + j).Value = 0
        Next j
    Next i
End Sub

```

```

Sub BuildSheet4(CurrentWorkbook As String, PathName As String, _
    fileName As String)

    ' Get matrix size
    Getnprod
    Getnproc
    Workbooks(CurrentWorkbook).Sheets(4).Activate

    For i = 1 To nproc
        ' Copy process labels
        Cells(2 + i, 1).Value = Sheets(1).Cells(1, 4 + i).Value
        For j = 1 To nprod
            ' Copy product labels
            If i = 1 Then Cells(1, 2 + j).Value = Sheets(1).Cells(2 + j, 2).Value
            ' Enter default market shares
            If Sheets(1).Cells(4 + nprod + j, 4 + i).Value > 0 Then
                Cells(2 + i, 2 + j).Formula = "100%"
            End If
        Next j
    Next i
    Range(Cells(1, 3), Cells(1, 3 + nprod - 1)).Select
    With Selection
        .Orientation = 90
        .ColumnWidth = 5
    End With
    FormatMatrix 3, 3, nproc, nprod

    BuildMktShrMatrix CurrentWorkbook, PathName, fileName
End Sub

```

```

Sub BuildSheet5(CurrentWorkbook As String, PathName As String, _
    fileName As String)

    Dim firstRowLabel As String
    Dim secondRowLabel As String
    Dim colLabel As String
    Dim firstRowLabel1 As String
    Dim secondRowLabel1 As String
    Dim colLabel1 As String
    Dim firstRowLabel2 As String
    Dim secondRowLabel2 As String
    Dim colLabel2 As String
    Dim numEntries As Integer

    ' Add matrix of correlation coefficients
    Workbooks.Open (PathName + fileName)
    Workbooks(CurrentWorkbook).Sheets(5).Activate

    ' Loop through all the records in the correlation coefficients file
    RowNumber = 2
    numEntries = 0
    Do While Workbooks(fileName).Sheets(1).Cells(RowNumber, 2).Value <> ""

        ' Get labels for first factor and check whether entries exist in the table
        firstRowLabel1 = Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value
        secondRowLabel1 = Workbooks(fileName).Sheets(1).Cells(RowNumber, 2).Value
        colLabel1 = Workbooks(fileName).Sheets(1).Cells(RowNumber, 3).Value
        position1 = getPosition(firstRowLabel1, secondRowLabel1, _
            colLabel1, numEntries)
        If position1 > numEntries Then numEntries = position1

        ' Get labels for second factor and check whether entries exist in the table
        firstRowLabel2 = Workbooks(fileName).Sheets(1).Cells(RowNumber, 4).Value
        secondRowLabel2 = Workbooks(fileName).Sheets(1).Cells(RowNumber, 5).Value
        colLabel2 = Workbooks(fileName).Sheets(1).Cells(RowNumber, 6).Value
        position2 = getPosition(firstRowLabel2, secondRowLabel2, _
            colLabel2, numEntries)
        If position2 > numEntries Then numEntries = position2

        ' Get correlation coefficient value and enter it in the matrix
        corrCoeff = Workbooks(fileName).Sheets(1).Cells(RowNumber, 7).Value
    
```

```

Cells(position1 + 3, position2 + 3).Value = corrCoeff
Cells(position2 + 3, position1 + 3).Value = corrCoeff

RowNumber = RowNumber + 1
Loop
Workbooks(fileName).Close
LastCellAddress = Cells(3 + numEntries, 3 + numEntries).Address()
MatrixRangeAddress = "Sheet5!$D$4:" + LastCellAddress

' Insert CorrMat functions
Getnex
Getncat
For i = 1 To numEntries
    firstRowLabel = Sheets(5).Cells(i + 3, 1).Value
    secondRowLabel = Sheets(5).Cells(i + 3, 2).Value
    colLabel = Sheets(5).Cells(i + 3, 3).Value
    Sheets(3).Activate
    rowNum = getRowNumber2labels(firstRowLabel, secondRowLabel, _
        4, nex + 3)
    colNum = getColumnNumber(colLabel, 5, ncat)
    Formula = Cells(rowNum, colNum).Formula
    riskExpLocation = Application.WorksheetFunction.Find("Risk", Formula) - 1
    riskExpLength = Len(Formula)
    newFormula = Left(Formula, riskExpLocation) + "RiskCorrMat(" + _
        MatrixRangeAddress + "," & i & ") + " & _
        + Right(Formula, riskExpLength - riskExpLocation)
    Cells(rowNum, colNum).Formula = newFormula
Next i
End Sub

```

```

Sub BuildBCmatrix(CurrentWorkbook As String, PathName As String, _
    fileName As String, firstRow As Integer)
' This code builds the use matrix (B matrix) or the make matrix (C matrix)

Dim ProductLabel As String
Dim ProcessLabel As String

' Open file with output from Access database
Workbooks.Open(PathName + fileName)
Windows(CurrentWorkbook).Activate

' Assemble table
RowNumber = 2
Do While Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value <> ""
    ' Get product name and check whether it exists in the table
    ProductLabel = Workbooks(fileName).Sheets(1).Cells(RowNumber, 2).Value
    thisRowNumber = getRowNumber(ProductLabel, firstRow, nprod, 2)

    ' Get Process category code and check whether it exists in the table
    ProcessLabel = Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value
    colNumber = getColumnNumber(ProcessLabel, 5, nproc)

    ' If a higher priority value has not been entered into the table, enter the factor
    ' (Table created by Access is sorted by Process, Product, and Priority Level)
    If IsEmpty(Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, colNumber)) Then
        Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, colNumber).Formula = _
            "=" & Workbooks(fileName).Sheets(1).Cells(RowNumber, 5).Value
        Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, colNumber).AddComment _
            "Source: " & Workbooks(fileName).Sheets(1).Cells(RowNumber, 3).Value
    End If

    ' If a higher priority uncertainty distribution has not been entered into the table,
    ' append the distribution to the nominal value
    If InStr(1, Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, _
        colNumber).Formula, "Risk", 1) = 0 Then
        ' Check whether a distribution exists
        Distribution = Workbooks(fileName).Sheets(1).Cells(RowNumber, 6).Value
        If Not IsEmpty(Distribution) Then
            Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, _
                colNumber).Formula = "=" & _
                Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, colNumber).Value & _
                "*" & Distribution
        End If
    End If
    RowNumber = RowNumber + 1
Loop

```



```

Workbooks(fileName).Close
End Sub

```

```

Sub BuildEMatrix(CurrentWorkbook As String, PathName As String, _
                fileName As String)
' This code builds the exchanges matrix (E matrix)

    Dim ProcessLabel As String
    Dim relMedium As String
    Dim chemName As String
    Dim relUnits As String

    ' Open file with output from Access database
    Workbooks.Open (PathName + fileName)
    Windows(CurrentWorkbook).Activate

    ' Assemble table
    RowNumber = 2
    Do While Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value <> ""

        ' Get chemical name and release medium and check whether it exists in the table
        relMedium = Workbooks(fileName).Sheets(1).Cells(RowNumber, 2).Value
        chemName = Workbooks(fileName).Sheets(1).Cells(RowNumber, 3).Value
        relUnits = Workbooks(fileName).Sheets(1).Cells(RowNumber, 7).Value
        thisRowNumber = getRowNumber3labels(relMedium, chemName, relUnits, nprod * 2 + 7, nex)

        ' Get Process category code and check whether it exists in the table
        ProcessLabel = Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value
        colNumber = getColumnNumber(ProcessLabel, 5, nproc)

        ' If a higher priority value has not been entered into the table, enter the factor
        ' (Table created by Access is sorted by Impact Category, Chemical Name,
        ' and Priority Level)
        If IsEmpty(Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, colNumber)) Then
            Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, _
                colNumber).Formula = "=" & _
                Workbooks(fileName).Sheets(1).Cells(RowNumber, 5).Value
            Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, colNumber).AddComment _
                "Source: " & Workbooks(fileName).Sheets(1).Cells(RowNumber, 8).Value
        End If

        ' If a higher priority uncertainty distribution has not been entered into the table,
        ' append the distribution to the nominal value
        If InStr(1, Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, _
            colNumber).Formula, "Risk", 1) = 0 Then

            ' Check whether a distribution exists
            Distribution = Workbooks(fileName).Sheets(1).Cells(RowNumber, 6).Value
            If Not IsEmpty(Distribution) Then
                Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, _
                    colNumber).Formula = "=" & _
                    Workbooks(CurrentWorkbook).Sheets(1).Cells(thisRowNumber, _
                    colNumber).Value & "*" & _
                    Distribution
            End If
        End If

        RowNumber = RowNumber + 1
    Loop

    Workbooks(fileName).Close
End Sub

```

```

Sub BuildHMatrix(CurrentWorkbook As String, PathName As String, _
                fileName As String)
' This code builds the characterization factor matrix (H matrix)

    Dim CategoryLabel As String
    Dim relMedium As String
    Dim chemName As String
    Dim relUnits As String

    ' Open file with output from Access database
    Workbooks.Open (PathName + fileName)
    Windows(CurrentWorkbook).Activate
    Sheets(3).Activate

```

```

' Assemble table
RowNumber = 2
Do While Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value <> ""

' Get chemical name and release medium and check whether it exists in the table
relMedium = Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value
chemName = Workbooks(fileName).Sheets(1).Cells(RowNumber, 3).Value
thisRowNumber = getRowNumber2labels(relMedium, chemName, 4, nex)

' Get Impact category code and check whether it exists in the table
CategoryLabel = Workbooks(fileName).Sheets(1).Cells(RowNumber, 2).Value
colNumber = getColumnNumber(CategoryLabel, 5, ncat)

' If a higher priority value has not been entered into the table, enter the factor
' (Table created by Access is sorted by Impact Category, Chemical Name,
' and Priority Level)
If IsEmpty(Cells(thisRowNumber, colNumber)) Then
    Cells(thisRowNumber, colNumber).Formula = "=" & _
        Workbooks(fileName).Sheets(1).Cells(RowNumber, 5).Value
    Cells(thisRowNumber, colNumber).AddComment
        "Source: " & Workbooks(fileName).Sheets(1).Cells(RowNumber, 8).Value
End If

' If a higher priority uncertainty distribution has not been entered into the table,
' append the distribution to the nominal value
If InStr(1, Cells(thisRowNumber, colNumber).Formula, "Risk", 1) = 0 Then
    ' Check whether a distribution exists
    Distribution = Workbooks(fileName).Sheets(1).Cells(RowNumber, 6).Value
    If Not IsEmpty(Distribution) Then
        Cells(thisRowNumber, colNumber).Formula = "=" & _
            Cells(thisRowNumber, colNumber).Value & "*" & _
            Distribution
    End If
End If

RowNumber = RowNumber + 1
Loop
Workbooks(fileName).Close

End Sub

```

```

Sub Buildwvector(CurrentWorkbook As String, PathName As String, _
    fileName As String)
' This code builds the valuation factor vector (w vector)

Dim CategoryLabel As String

' Open file with output from Access database
Workbooks.Open (PathName + fileName)
Windows(CurrentWorkbook).Activate
Sheets(3).Select

thisRowNumber = nex + 6

' Assemble table
RowNumber = 2
Do While Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value <> ""

' Get Impact category code and check whether it exists in the table
CategoryLabel = Workbooks(fileName).Sheets(1).Cells(RowNumber, 3).Value
colNumber = getColumnNumber(CategoryLabel, 5, ncat)

' If a higher priority value has not been entered into the table, enter the factor
If IsEmpty(Cells(thisRowNumber, colNumber)) Then
    Cells(thisRowNumber, colNumber).Formula = "=" & _
        Workbooks(fileName).Sheets(1).Cells(RowNumber, 4).Value
    Cells(thisRowNumber, colNumber).AddComment
        "Source: " & Workbooks(fileName).Sheets(1).Cells(RowNumber, 8).Value
End If

' If a higher priority uncertainty distribution has not been entered into the table,
' append the distribution to the nominal value
If InStr(1, Cells(thisRowNumber, colNumber).Formula, "Risk", 1) = 0 Then
    ' Check whether a distribution exists
    Distribution = Workbooks(fileName).Sheets(1).Cells(RowNumber, 5).Value
    If Not IsEmpty(Distribution) Then
        Cells(thisRowNumber, colNumber).Formula = "=" & _
            Cells(thisRowNumber, colNumber).Value & "*" & _

```

```

        Distribution
    End If
End If

    RowNumber = RowNumber + 1
Loop
Workbooks(fileName).Close

End Sub

```

```

Sub Buildpvector(CurrentWorkbook As String, PathName As String, _
    fileName As String)
' This code builds the price vector (p vector)

    Dim ProductLabel As String

    ' Open file with output from Access database
    Workbooks.Open (PathName + fileName)
    Windows(CurrentWorkbook).Activate
    Sheets(2).Activate

    colNumber = 3

    ' Assemble table
    RowNumber = 2
    Do While Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value <> ""

        ' Get product code and check whether it exists in the table
        ProductLabel = Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value
        thisRowNumber = getRowNumber(ProductLabel, 3, nprod, 1)

        Cells(thisRowNumber, colNumber).Formula = "=" & _
            Workbooks(fileName).Sheets(1).Cells(RowNumber, 2).Value
        Cells(thisRowNumber, colNumber).AddComment _
            Workbooks(fileName).Sheets(1).Cells(RowNumber, 6).Value _
            & " " & Workbooks(fileName).Sheets(1).Cells(RowNumber, 4)

        ' If a higher priority uncertainty distribution has not been entered into the table,
        ' append the distribution to the nominal value
        If InStr(1, Cells(thisRowNumber, colNumber).Formula, "Risk", 1) = 0 Then
            ' Check whether a distribution exists
            Distribution = Workbooks(fileName).Sheets(1).Cells(RowNumber, 3).Value
            If Not IsEmpty(Distribution) Then
                Cells(thisRowNumber, colNumber).Formula = "=" & _
                    Cells(thisRowNumber, colNumber).Value & "*" & _
                    Distribution
            End If
        End If

        RowNumber = RowNumber + 1
    Loop

    Workbooks(fileName).Close

End Sub

```

```

Sub BuildMktShrMatrix(CurrentWorkbook As String, PathName As String, _
    fileName As String)

    Dim ProductLabel As String
    Dim ProcessLabel As String

    ' Open file with output from Access database
    Workbooks.Open (PathName + fileName)
    Windows(CurrentWorkbook).Activate
    Sheets(4).Activate

    ' Assemble table
    RowNumber = 2
    Do While Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value <> ""
        ' Get process name and check whether it exists in the table
        ProcessLabel = Workbooks(fileName).Sheets(1).Cells(RowNumber, 2).Value
        thisRowNumber = getRowNumber(ProcessLabel, 3, nproc, 1)

        ' Get Product code and check whether it exists in the table
        ProductLabel = Workbooks(fileName).Sheets(1).Cells(RowNumber, 1).Value
    
```

```

colNumber = getColumnNumber(ProductLabel, 3, nprod)

Cells(thisRowNumber, colNumber).Formula = "=" & _
    Workbooks(fileName).Sheets(1).Cells(LineNumber, 4).Value
Cells(thisRowNumber, colNumber).AddComment " " & _
    Workbooks(fileName).Sheets(1).Cells(LineNumber, 3).Value & _
    " market share"

' If a higher priority uncertainty distribution has not been entered into the table,
' append the distribution to the nominal value
If InStr(1, Cells(thisRowNumber, colNumber).Formula, "Risk", 1) = 0 Then
    ' Check whether a distribution exists
    Distribution = Workbooks(fileName).Sheets(1).Cells(LineNumber, 5).Value
    If Not IsEmpty(Distribution) Then
        Cells(thisRowNumber, colNumber).Formula = "=" & _
            Cells(thisRowNumber, colNumber).Value & "*" & _
            Distribution
    End If
End If

LineNumber = LineNumber + 1
Loop

Workbooks(fileName).Close

End Sub

```

```

Function getColumnNumber(columnLabel As String, _
    firstCol As Integer, numCols As Integer) As Integer
    Dim thisLabel As String

    i = 1
    Do While i < numCols + 1
        thisLabel = Cells(1, firstCol + i - 1).Value
        If thisLabel = columnLabel Then
            getColumnNumber = firstCol + i - 1
            i = numCols + 1
        Else
            i = i + 1
        End If
    Loop

End Function

```

```

Function getRowNumber(rowLabel As String, _
    firstRow As Integer, numRows As Integer, _
    labelCol As Integer) As Integer

    i = 1
    Do While i < numRows + 1
        thisLabel = Cells(firstRow + i - 1, labelCol).Value
        If thisLabel = rowLabel Then
            getRowNumber = firstRow + i - 1
            i = numRows + 1
        Else
            i = i + 1
        End If
    Loop

End Function

```

```

Function getRowNumber2labels(Label1 As String, _
    Label2 As String, firstRow As Integer, _
    numRows As Integer) As Integer

    i = 1
    Do While i < numRows + 1
        thisLabel1 = Cells(firstRow + i - 1, 1).Value
        thisLabel2 = Cells(firstRow + i - 1, 2).Value
        If thisLabel1 = Label1 And thisLabel2 = Label2 Then
            getRowNumber2labels = firstRow + i - 1
            i = numRows + 1
        Else
            i = i + 1
        End If
    Loop

End Function

```

```

Function getRowNumber3labels(Label1 As String,
    Label2 As String, Label3 As String, firstRow As Integer, _
    numRows As Integer) As Integer
    i = 1
    Do While i < numRows + 1
        thisLabel1 = Cells(firstRow + i - 1, 1).Value
        thisLabel2 = Cells(firstRow + i - 1, 2).Value
        thisLabel3 = Cells(firstRow + i - 1, 3).Value
        If thisLabel1 = Label1 And thisLabel2 = Label2 And thisLabel3 = Label3 Then
            getRowNumber3labels = firstRow + i - 1
            i = numRows + 1
        Else
            i = i + 1
        End If
    Loop
End Function

```

```

Function getPosition(firstRowLabel As String, _
    secondRowLabel As String, colLabel As String, _
    numEntries As Integer) As Integer

    getPosition = 0
    offset = 0

    rowNum = getRowNumber3labels(firstRowLabel, _
        secondRowLabel, colLabel, 4, numEntries)
    If rowNum = 0 Then ' rowlabels were not found
        ' new row and column are needed
        Sheets(5).Cells(1, 3 + numEntries + 1).Value = firstRowLabel
        Sheets(5).Cells(2, 3 + numEntries + 1).Value = secondRowLabel
        Sheets(5).Cells(3, 3 + numEntries + 1).Value = colLabel
        Sheets(5).Cells(3 + numEntries + 1, 1).Value = firstRowLabel
        Sheets(5).Cells(3 + numEntries + 1, 2).Value = secondRowLabel
        Sheets(5).Cells(3 + numEntries + 1, 3).Value = colLabel
        ' Enter diagonal element
        Sheets(5).Cells(3 + numEntries + 1, 3 + numEntries + 1).Value = 1
        getPosition = numEntries + 1
        Exit Function
    Else
        getPosition = rowNum - 3
    End If
End Function

```

```

Sub FormatVector(intStartRow As Integer, intVectorCol As Integer, _
    intVectorLength As Integer, intLabelRow As Integer, _
    sngColWidth As Single)
    Cells(intStartRow, intVectorCol).Select
    Selection.ColumnWidth = sngColWidth
    ' add brackets
    InsertBracket intVectorCol - 1, _
        intStartRow, intStartRow + intVectorLength - 1, "Left"
    InsertBracket intVectorCol + 1, _
        intStartRow, intStartRow + intVectorLength - 1, "Right"
    ' format label area
    Range(Cells(intLabelRow, intVectorCol - 1),
        Cells(intLabelRow, intVectorCol + 1)).Select
    With Selection
        .HorizontalAlignment = xlCenter
        .WrapText = True
        .MergeCells = True
        .Font.Bold = True
    End With
End Sub

```

```

Sub FormatMatrix(intStartRow As Integer, intStartCol As Integer, _
    intNumRows As Integer, intNumCols As Integer)

    ' Format label area
    Range(Cells(intStartRow - 1, intStartCol),
        Cells(intStartRow - 1, intStartCol + intNumCols - 1)).Select
    With Selection
        .WrapText = True
        .MergeCells = True
    End With

```

```
        .Font.Bold = True
    End With

    ' Insert Brackets
    InsertBracket intStartCol - 1, intStartRow, intStartRow + intNumRows - 1, "Left"
    InsertBracket intStartCol + intNumCols, intStartRow, intStartRow + intNumRows - 1, "Right"
End Sub
```

```
Sub Getnproc()
    ' Count the number of processes
    Sheets("Sheet1").Select
    nproc = 0
    runOutOfProcesses = False
    Do While Not runOutOfProcesses
        If Cells(1, 5 + nproc).Formula = "" Then
            runOutOfProcesses = True
        Else
            nproc = nproc + 1
        End If
    Loop
End Sub
```

```
Sub Getnprod()
    ' Count the number of products
    Sheets("Sheet1").Select
    nprod = 0
    runOutOfProducts = False
    Do While Not runOutOfProducts
        If Cells(3 + nprod, 2).Formula = "" Then
            runOutOfProducts = True
        Else
            nprod = nprod + 1
        End If
    Loop
End Sub
```

```
Sub Getnex()
    ' Count the number of environmental exchanges
    Sheets("Sheet1").Select
    nex = 0
    Getnprod
    runOutOfExchanges = False
    Do While Not runOutOfExchanges
        If Cells(2 * nprod + 7 + nex, 2).Formula = "" Then
            runOutOfExchanges = True
        Else
            nex = nex + 1
        End If
    Loop
End Sub
```

```
Sub Getncat()
    ' Count the number of impact categories
    Sheets("Sheet3").Select
    ncat = 0
    runOutOfCategories = False
    Do While Not runOutOfCategories
        If Cells(1, 5 + ncat).Formula = "" Then
            runOutOfCategories = True
        Else
            ncat = ncat + 1
        End If
    Loop
End Sub
```

Appendix C PIO-LCA method spreadsheet implementation

This Appendix contains the Visual Basic code needed to generate all the vectors and matrices in the PIO-LCA method (Chapter 7)¹⁰⁴. The code listed here was written for Microsoft Excel 97. The required inputs are organized into four spreadsheets with the default names “Sheet1”, “Sheet2”, “Sheet3” and “Sheet4”, as shown in the figures in the next few pages.

C.1 Input requirements

Sheet1 contains the button to which the first subroutine listed in this Appendix is linked. It also contains data for the use, make, and environmental exchanges matrices (matrices **B**, **C**, and **E** according to the nomenclature used in Chapter 7). As many rows and columns as needed can be used, subject to the limitation of the number of columns in the version of Excel used. It is very important that the rows of the **C** matrix be entered in the same order as the rows in the **B** matrix. This is the reason why the cells used for the product names and units of the **C** matrix shown in Figure C-1 are not shaded (shading is used to emphasize optional inputs). **It is very important that a value of zero be entered for each matrix or vector element for which no other data are available.** Excel will enter a #VALUE error in cells containing formulas involving matrices with blank elements.

Sheet2 is used to store information on product prices and demands. As explained in Chapter 7, prices are only required for products made in multiproduct processes. For all other products a default value of 999 (or any other nonzero value) may be used. For consistency it is recommended that the product names and units be copied from Sheet1 through the use of Excel formulas.

Characterization and valuation factors for the environmental valuation model are entered in Sheet3. The type, name, and units for the environmental exchanges should be copied via formula from Sheet1.

¹⁰⁴ To obtain a working spreadsheet with the Visual Basic code listed here contact the author at alexcano@alum.mit.edu

Sheet4 is used to store market share information. The product and process names are copied via formula from Sheet1 (the matrix function =TRANPOSE(Range) can be used to facilitate the copying from row labels to column labels and vice versa).

A fifth spreadsheet (“Sheet5”) is left blank. This sheet is used to store rank correlation coefficients when the PIO-LCA is run in stochastic mode using the @Risk add-in. No other spreadsheets should be present in the workbook used to implement this code prior to clicking the “Build PIO-LCA tables” button.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X
	Build PIO-LCA tables																							
1				PROCESS	diphragm chloralkali	membrane chloralkali	mercury chloralkali	Brine pumping	coal production	natural gas production	oil production	diesel production	coal-fired plant	oil-fired plant	gas-fired plant	nuclear plant	hydroelectric plant	diesel engine	methane reforming	Railroad	coal-fired boiler	oil-fired boiler	gas-fired boiler	
2	PRODUCT INPUTS			UNITS	B = [use matrix]																			
3		Salt from brine	kg	1.65	1.65	1.65	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
4		coal	kg	0	0	0	0	0	0	0	0	0	0	0.34	0	0	0	0	0	0	0	34.82	0	
5		oil	kg	0	0	0	0	0	0	0	0	1	0.24	0	0	0	0	0	0	0	0	0	23.24	
6		diesel	kg	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.024	0	0	0	0	0	
7		Natural gas	kg	0	0	0	0	0	0	0	0	0	0	0	0.22	0	0	0	2.25	0	0	0	19.5	
8		electricity	MJ	10.8	11	11.7	0.36	0.052	0.124	0.142	0.144	0	0	0	0	0	0	0	0	0	0	0	0	
9		mechanical energy diesel engines	MJ	0	0	0	0	2.53	0	0	0	0	0	0	0	0	0	0	0	0.269	0	0	0	
10		Chlorine	kg	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
11		NaOH	kg	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
12		H2	kg	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
13		Railroad transport	kg-km	0	0	0	0	0	0	0	0	158.8	0	0	0	0	0	0	0	0	0	0	0	
14		Thermal energy from coal	MJ	0	0	0	0	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
15		Thermal energy from oil	MJ	0	0	0	0	0	0.027	0.064	0.545	0	0	0	0	0	0	0	0	0	0	0	0	
16		Thermal energy from gas	MJ	9	1.35	0	0	0	1.271	0.53	1.839	0	0	0	0	0	0	0	84.97	0	0	0	0	
17																								
18	PRODUCT OUTPUTS			UNITS	C = [make matrix]																			
19		Salt from brine	kg	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
20		coal	kg	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
21		oil	kg	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	
22		diesel	kg	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	
23		Natural gas	kg	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
24		electricity	MJ	0	0	0	0	0	0	0	0	3.6	3.6	3.6	3.6	3.6	0	0	0	0	0	0	0	
25		mechanical energy diesel engines	MJ	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	
26		Chlorine	kg	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
27		NaOH	kg	1.12	1.12	1.12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
28		H2	kg	0.028	0.028	0.028	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	
29		Railroad transport	kg-km	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1000	0	0	0	
30		Thermal energy from coal	MJ	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1055	0	0	
31		Thermal energy from oil	MJ	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1055	0	
32		Thermal energy from gas	MJ	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1055	
33																								
34	EXCHANGE TYPE	ENVIRONMENTAL EXCHANGE	UNITS	E = [Environmental exchanges matrix]																				
35	Emission to air	CFC-21	kg	2E-05	2E-05	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
36	Emission to air	Dichloromethane	kg	0	0	4E-05	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
37	Emission to air	Tetrachloromethane	kg	6E-06	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
38	Emission to air	Chlorine	kg	1E-06	2E-06	3E-05	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
39	Emission to air	Hydrogen	kg	0.001	0.001	1E-04	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
40	Emission to air	Mercury	kg	0	0	3E-06	0	0	0	0	0	0	8E-09	7E-10	2E-12	0	0	0	0	0	0	0	0	
41	Emission to air	Carbon dioxide	kg	0	0	0	0	0	0	0	0	1.071	0.94	0.667	6E-05	0	0.075	5.5	0	103.5	88.08	60.84	0	
42	Emission to air	Sulfur dioxide	kg	0	0	0	0	0	0	0	0	0.01	0.005	5E-04	6E-04	0	5E-05	0	0	1.13	0.158	0.043	0	
43	Emission to air	Nitrogen oxides	kg	0	0	0	0	0	0	0	0	0.005	0.002	0.003	2E-04	0	9E-04	0	0	0.432	0.084	0.077	0	
44	Emission to air	Carbon monoxide	kg	0	0	0	0	0	0	0	0	0.002	3E-04	3E-04	0	0	9E-04	0	0	0.238	0.031	0.028	0	
45	Emission to air	Hydrocarbons	kg	0	0	0	0	0	0.008	0	0	2E-04	0.002	0.007	0	0	6E-04	0.25	0	0.021	0.22	0.631	0	
46	Emission to air	Particulates	kg	0	0	0	0	0	0	0	0	0.002	3E-04	4E-05	2E-04	0	4E-04	0	0	0.221	0.012	0.004	0	
47	Solid waste	Total mass	kg	0	0	0	0	0	0	0	0	0.139	0.003	8E-04	0.028	0	0	0	0	12.85	0.271	0.077	0	
48	Discharge to water	Dissolved solids	kg	0	0	0	0	0	0	0	0	2E-05	0.004	5E-05	0	0	0	0	0	0.002	0.336	0.005	0	
49	Discharge to water	Sulfuric acid	kg	0	0	0	0	0	0	0	0	9E-04	1E-05	5E-06	0	0	0	0	0	0.085	0.001	5E-04	0	
50																								

Figure C-1: Layout of Sheet1 in the PIO-LCA workbook

	A	B	C	D	E	F	G	H	I	J	K
1											
2	PRODUCT										
3	Salt from brine										
4	coal										
5	oil										
6	diesel										
7	Natural gas										
8	electricity										
9	mechanical energy diesel engines										
10	Chlorine										
11	NaOH										
12	H2										
13	Railroad transport										
14	Thermal energy from coal										
15	Thermal energy from oil										
16	Thermal energy from gas										
17											

		p = price vector				d = demand vector			
		\$ 6.7200	/kg			0	kg		
		\$ 0.0300	/kg			0	kg		
		999	/kg			0	kg		
		999	/kg			0	kg		
		999	/kg			0	kg		
		\$ 0.0167	/MJ			0	MJ		
		999	/MJ			0	MJ		
		\$ 0.4000	/kg			1000	kg		
		\$ 0.2000	/kg			0	kg		
		\$ 0.0001	/kg			0	kg		
		999	/kg-km			0	kg-km		
		999	/MJ			0	MJ		
		999	/MJ			0	MJ		
		999	/MJ			0	MJ		

Figure C-2: Layout of Sheet2 in the PIO-LCA workbook

	A	B	C	D	E	F	G	H	I	J
1										
2										
3	EXCHANGE TYPE	ENVIRONMENTAL EXCHANGE								
4	Emission to air	CFC-21	kg							
5	Emission to air	Dichloromethane	kg							
6	Emission to air	Tetrachloromethane	kg							
7	Emission to air	Chlorine	kg							
8	Emission to air	Hydrogen	kg							
9	Emission to air	Mercury	kg							
10	Emission to air	Carbon dioxide	kg							
11	Emission to air	Sulfur dioxide	kg							
12	Emission to air	Nitrogen oxides	kg							
13	Emission to air	Carbon monoxide	kg							
14	Emission to air	Hydrocarbons	kg							
15	Emission to air	Particulates	kg							
16	Solid waste	Total mass	kg							
17	Discharge to water	Dissolved solids	kg							
18	Discharge to water	Sulfuric acid	kg							
19										
20										
21		Valuation factors								
22										
23										
24										

		H = [Characterization factor matrix]			
		0	0.04	0	0
		9	0	11	1.4E-08
		0	1.1	480	0
		0	0	0.02	0
		0	0	0	0
		0	0	29000	0
		1	0	0	0
		0	0	0.16	0.00006
		0	0	0.26	0.000077
		0	0	0.012	0.00000073
		0	0	0	0.0000013
		0	0	0	0.00011
		0	0	0	0
		0	0	0	0

		w' = Transpose of valuation factor vector				
		\$	0.0136	50	3.3	50000

Figure C-3: Layout of Sheet3 in the PIO-LCA workbook

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
1																		
2	PROCESS																	
3	diaphragm chloralkali																	
4	membrane chloralkali																	
5	mercury chloralkali																	
6	Brine pumping																	
7	coal production																	
8	natural gas production																	
9	oil production																	
10	diesel production																	
11	coal-fired plant																	
12	oil-fired plant																	
13	gas-fired plant																	
14	nuclear plant																	
15	hydroelectric plant																	
16	diesel engine																	
17	methane reforming																	
18	Railroad																	
19	coal-fired boiler																	
20	oil-fired boiler																	
21	gas-fired boiler																	
22																		
23																		

PRODUCT	Salt from brine	coal	oil	diesel	Natural gas	electricity	mechanical energy	diesel engines	Chlorine	NaOH	H2	Railroad transport	Thermal energy from coal	Thermal energy from oil	Thermal energy from gas	
F = [market share matrix]																
3	0	0	0	0	0	0	0	0	78%	78%	7.8%	0	0	0	0	
4	0	0	0	0	0	0	0	0	6%	6%	0.6%	0	0	0	0	
5	0	0	0	0	0	0	0	0	16%	16%	1.6%	0	0	0	0	
6	100%	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
7	0	100%	0	0	0	0	0	0	0	0	0	0	0	0	0	
8	0	0	0	0	100%	0	0	0	0	0	0	0	0	0	0	
9	0	0	100%	0	0	0	0	0	0	0	0	0	0	0	0	
10	0	0	0	100%	0	0	0	0	0	0	0	0	0	0	0	
11	0	0	0	0	0	57%	0	0	0	0	0	0	0	0	0	
12	0	0	0	0	0	3%	0	0	0	0	0	0	0	0	0	
13	0	0	0	0	0	9%	0	0	0	0	0	0	0	0	0	
14	0	0	0	0	0	20%	0	0	0	0	0	0	0	0	0	
15	0	0	0	0	0	11%	0	0	0	0	0	0	0	0	0	
16	0	0	0	0	0	0	100%	0	0	0	0	0	0	0	0	
17	0	0	0	0	0	0	0	0	0	90%	0	0	0	0	0	
18	0	0	0	0	0	0	0	0	0	0	100%	0	0	0	0	
19	0	0	0	0	0	0	0	0	0	0	0	100%	0	0	0	
20	0	0	0	0	0	0	0	0	0	0	0	0	100%	0	0	
21	0	0	0	0	0	0	0	0	0	0	0	0	0	100%	0	

Figure C-4: Layout of Sheet4 in the PIO-LCA workbook

C.2 Visual Basic Code

The following list gives the page number in which the different subroutines used by the Build PIO-LCA Tables program are listed:

AddLabels, 594
BuildAproc, 581
BuildAprod, 581
buildD, 581
BuildDiagMatrix, 596
BuildDinvAprod, 582
BuildEDinvAprod, 584
BuildEinvAproc, 584
buildG, 580
BuildI, 582
BuildInvAproc, 582
BuildInvAprod, 582
BuildInventory, 584
BuildInvProcContrib, 585
BuildProcUnitValContrib, 591
BuildProdOutputs, 583
BuildProdUnitValContrib, 593
buildThroughputs, 582
BuildUnitImpacts, 588
BuildValExchContrib, 586
BuildValProcContrib, 587
buildw, 586
CommandButton1 Click(), 580
FormatMatrix, 597
FormatVector, 597
GetMatrixSizes, 598
Getncat, 598
Getnex, 597
Getnproc, 597
Getnprod, 597
Global Declarations, 580
InsertBracket, 594
SelectSheet, 596

```

Private Sub CommandButton1_Click()
    GetMatrixSizes
    buildG
    buildD
    BuildAprod
    BuildAproc
    BuildI
    BuildInvAprod
    BuildInvAproc
    BuildDinvAprod
    buildThroughputs
    BuildProdOutputs
    BuildEDinvAprod
    BuildEinVAproc
    BuildInventory
    BuildInvProcContrib
    buildw
    BuildValExchContrib
    BuildValProcContrib
    BuildUnitImpacts
    BuildProcUnitValContrib
    BuildProdUnitValContrib
End Sub

```

```
' Global Declarations
```

```

Public nproc As Integer ' number of processes
Public nprod As Integer ' number of products
Public nex As Integer ' number of environmental exchanges
Public ncat As Integer ' number of impact categories

```

```

Public coords_ProcProc_matrix As String
Public coords_ProcProd_matrix As String
Public coords_ProcIcat_matrix As String
Public coords_ProdProc_matrix As String
Public coords_ProdProd_matrix As String
Public coords_ProdIcat_matrix As String
Public coords_ExchProc_matrix As String
Public coords_ExchProd_matrix As String
Public coords_ExchIcat_matrix As String

```

```

Public range_B_matrix As String
Public range_C_matrix As String
Public range_E_matrix As String
Public range_d_vector As String
Public range_H_matrix As String
Public range_wtranspose As String
Public range_D_matrix As String
Public range_w_vector As String
Public range_Diag As String
Public range_x_vector As String
Public range_Diagx As String
Public range_e_vector As String
Public range_Diage As String

```

```

Sub buildG()
'
' buildG Macro
' Macro recorded 11/16/99 by Alejandro Cano
' Macro builds the allocation matrix (matrix "G")
'
' first build G transpose matrix
SelectSheet 6, "G transpose", "Transpose of allocation matrix"
AddLabels "Row", "Product", 0, True, "per ", ""
AddLabels "Column", "Process", 0, False, "", ""
' if C(i,j) > 0, G(i,j) = p(i)/C(i',j)*SUM(p(i'))
Cells(3, 3).Select
ActiveCell.FormulaR1C1 = _
    "=IF(Sheet1!R[" & nprod + 2 & "]C[2]>0,Sheet2!RC3" & _
    "/SUMPRODUCT(Sheet1!R" & nprod + 5 & "C[2]:R" & 2 * nprod + 4 & _
    "C[2],Sheet2!R3C3:R" & nprod + 2 & "C3),0)"
Selection.Copy
Range(Cells(3, 3), Cells(nprod + 2, nproc + 2)).Select
ActiveSheet.Paste
FormatMatrix 3, 3, nprod, nproc

```

```

' now build matrix G
SelectSheet 7, "G", "Allocation matrix"
AddLabels "Row", "Process", 0, False, "", ""
AddLabels "Column", "Product", 0, True, "per ", ""
' G = transpose(G transpose)
Range(Cells(3, 3), Cells(2 + nproc, 2 + nprod)).Select
Selection.FormulaArray =
    "=TRANSPOSE('G transpose!' & coords_ProdProc_matrix & )"
FormatMatrix 3, 3, nproc, nprod
End Sub

```

```

Sub buildD()
'
' buildD Macro
' Macro written on 11/16/99 by Alejandro Cano
'
'
    SelectSheet 8, "D",
        "Process by product throughput matrix"

    AddLabels "Row", "Process", 0, False, "", ""
    AddLabels "Column", "Product", 0, True, "per ", ""
    Cells(3, 3).Select
    ' Dij = Fij * Gij
    ActiveCell.FormulaR1C1 = "=Sheet4!RC*G!RC"
    Selection.Copy
    Range(Cells(3, 3), Cells(nproc + 2, nprod + 2)).Select
    ActiveSheet.Paste
    FormatMatrix 3, 3, nproc, nprod
End Sub

```

```

Sub BuildAprod()
'
' BuildAprod Macro
' Macro recorded 11/16/99 by Alejandro Cano
'
'
    SelectSheet 9, "Aprod",
        "Product by product direct requirements matrix"
    AddLabels "Row", "Product", 0, True, "", ""
    AddLabels "Column", "Product", 0, True, "per ", ""
    ' Aprod = BD
    Range(Cells(3, 3), Cells(2 + nprod, 2 + nprod)).Select
    Selection.FormulaArray = "=MMULT(" & range_B_matrix & "," & _
        range_D_matrix & ")"
    FormatMatrix 3, 3, nprod, nprod
End Sub

```

```

Sub BuildAproc()
'
' BuildAproc Macro
' Macro recorded 11/16/99 by Alejandro Cano
'
'
    SelectSheet 10, "Aproc",
        "Process by process direct requirements matrix"
    AddLabels "Row", "Process", 0, False, "", ""
    AddLabels "Column", "Process", 0, False, "", ""
    ' Aproc = DB
    Range(Cells(3, 3), Cells(2 + nproc, 2 + nproc)).Select
    Selection.FormulaArray = "=MMULT(" & range_D_matrix & "," & _
        range_B_matrix & ")"
    FormatMatrix 3, 3, nproc, nproc
End Sub

```

```

Sub BuildI()
'
' BuildI Macro
' Macro recorded 11/16/99 by Alejandro Cano
' Builds identity matrix large enough to use in process or
' product requirement matrix inversions
'
    Dim intSize As Integer

    SelectSheet 11, "I", ""
    intSize = Application.WorksheetFunction.Max(nproc, nprod, nex, ncat)
    Range(Cells(3, 3), Cells(2 + intSize,
        2 + intSize)).Select
    Selection.FormulaR1C1 = "=IF(column(RC)=row(RC),1,0)"
    Selection.ColumnWidth = 1.5
    FormatMatrix 3, 3, intSize, intSize
End Sub

```

```

Sub BuildInvAprod()
'
' BuildInvAprod Macro
' Macro recorded 11/16/99 by Alejandro Cano
'
'
    SelectSheet 12, "Inv(I-Aprod)", _
        "Product by product total requirements matrix"
    AddLabels "Row", "Product", 0, True, "", ""
    AddLabels "Column", "Product", 0, True, "per ", ""
    Range(Cells(3, 3), Cells(2 + nprod, 2 + nprod)).Select
    Selection.FormulaArray = "=MINVERSE(I!" & coords_ProdProd_matrix & _
        "-Aprod!" & coords_ProdProd_matrix & ")""
    FormatMatrix 3, 3, nprod, nprod
End Sub

```

```

Sub BuildInvAproc()
'
' BuildInvAproc Macro
' Macro recorded 11/16/99 by Alejandro Cano
'
'
    SelectSheet 13, "inv(I-Aproc)", _
        "Process by process total requirements matrix"

    AddLabels "Row", "Process", 0, False, "", ""
    AddLabels "Column", "Process", 0, False, "", ""
    Range(Cells(3, 3), Cells(2 + nproc, 2 + nproc)).Select
    Selection.FormulaArray = "=MINVERSE(I!" & coords_ProcProc_matrix & _
        "-Aproc!" & coords_ProcProc_matrix & ")""
    FormatMatrix 3, 3, nproc, nproc
End Sub

```

```

Sub BuildDinvAprod()
'
' BuildDinvAprod Macro
' Macro recorded 11/16/99 by Alejandro Cano
'
'
    SelectSheet 14, "Dinv(I-Aprod)", _
        "Process by product direct requirements matrix"
    AddLabels "Row", "Process", 0, False, "", ""
    AddLabels "Column", "Product", 0, True, "per ", ""
    Range(Cells(3, 3), Cells(2 + nproc, 2 + nprod)).Select
    Selection.FormulaArray = "=MMULT(" & range_D_matrix & _
        ", 'inv(I-Aprod)!' & coords_ProdProd_matrix & ")""
    FormatMatrix 3, 3, nproc, nprod
End Sub

```

```

Sub buildThroughputs()
'
' buildThroughputs Macro
' Macro recorded 11/16/99 by Alejandro Cano
'
'
    SelectSheet 15, "Process throughputs", ""

```

```

' insert process labels
AddLabels "Row", "Process", 0, False, "", ""

' build vector of direct process requirements
Range(Cells(3, 3), Cells(2 + nproc, 3)).Select
' xdirect = Dd
Selection.FormulaArray = "=MMULT(" & range_D_matrix & "," & _
                        range_d_vector & ")"
FormatVector 3, 3, nproc, 1, 12
Range("C1").Select
ActiveCell.FormulaR1C1 = _
    "xdirect = vector of direct process throughput requirements"
ActiveCell.Characters(Start:=2, Length:=6).Font.Subscript = True

' build vector of total process requirements
Range(Cells(3, 7), Cells(2 + nproc, 7)).Select
' x = Dinv(I-Aprod)d
Selection.FormulaArray = "=MMULT('Dinv(I-Aprod)!' & _
                        coords_ProcProd_matrix & _
                        "," & range_d_vector & ")"
FormatVector 3, 7, nproc, 1, 12
Range("G1").Select
ActiveCell.FormulaR1C1 = _
    "x = vector of total process throughput requirements"

' build diag(x) matrix
BuildDiagMatrix 3, 7, nproc, True
Cells(2, 11).Select
ActiveCell.FormulaR1C1 = "Diag(x)"

Rows("1:1").RowHeight = 63.75

End Sub

```

```

Sub BuildProdOutputs()
'
' BuildProdOutputs Macro
' Macro recorded 11/16/99 by Alejandro Cano-Ruiz
'
    SelectSheet 16, "Product Outputs", ""

' insert product labels
AddLabels "Row", "Product", 0, True, "", ""

' copy d vector
Range(Cells(3, 3), Cells(2 + nprod, 3)).Select
Selection.FormulaArray = "=" & range_d_vector
FormatVector 3, 3, nprod, 1, 8.43
Range("C1").Select
ActiveCell.FormulaR1C1 = "d = product demand vector"

' calculate qdirect vector
Range(Cells(3, 7), Cells(2 + nprod, 7)).Select
' qdirect = (I+Aprod)d
Selection.FormulaArray = _
    "=+MMULT(I!" & coords_ProdProd_matrix & _
    "+Aprod!" & coords_ProdProd_matrix & "," & _
    range_d_vector & ")"
FormatVector 3, 7, nprod, 1, 12
Range("G1").Select
ActiveCell.FormulaR1C1 = "qdirect = direct product requirements vector"
ActiveCell.Characters(Start:=2, Length:=6).Font.Subscript = True

' calculate q vector
Range(Cells(3, 11), Cells(2 + nprod, 11)).Select
' q = inv(I+Aprod)d
Selection.FormulaArray = _
    "=+MMULT('inv(I-Aprod)!' & coords_ProdProd_matrix & _
    "," & range_d_vector & ")"
FormatVector 3, 11, nprod, 1, 12
Range("K1").Select
ActiveCell.FormulaR1C1 = "q = total product requirements vector"

' calculate Cxdirect vector
Range(Cells(3, 15), Cells(2 + nprod, 15)).Select
Selection.FormulaArray = _
    "=+MMULT(" & range_C_matrix & "," & _
    "'Process throughputs'!R3C3:R" & nproc + 2 & "C3)"

```

```

FormatVector 3, 15, nprod, 1, 10
Range("O1").Select
ActiveCell.FormulaR1C1 = "Cxdirect = equivalent direct production vector"
ActiveCell.Characters(Start:=3, Length:=6).Font.Subscript = True

' calculate Cx vector
Range(Cells(3, 19), Cells(2 + nprod, 19)).Select
Selection.FormulaArray = _
    "+MMULT(" & range_C_matrix & "," & _
        range_x_vector & ")"
FormatVector 3, 19, nprod, 1, 10
Range("S1").Select
ActiveCell.FormulaR1C1 = "Cx = equivalent total production vector"

Rows("1:1").RowHeight = 63.75
End Sub

```

```

Sub BuildEDinvAprod()
'
' BuildEDinvAprod Macro
' Macro recorded 11/16/99 by Alejandro Cano
'
'
    SelectSheet 17, "EDinv(I-Aprod)", _
        "Life cycle environmental exchanges by product matrix"
    AddLabels "Row", "Exchange", 0, True, "", ""
    AddLabels "Column", "Product", 0, True, "per", ""
    Range(Cells(3, 3), Cells(2 + nex, 2 + nprod)).Select
    Selection.FormulaArray = "=MMULT(" & range_E_matrix & _
        ",'Dinv(I-Aprod)'!" & coords_ProcProd_matrix & ")"
    FormatMatrix 3, 3, nex, nprod
End Sub

```

```

Sub BuildEinvAproc()
'
' BuildEinvAproc Macro
' Macro recorded 11/16/99 by Alejandro Cano
'
'
    SelectSheet 18, "Einv(I-Aproc)", _
        "Life cycle environmental exchanges by process matrix"
    AddLabels "Row", "Exchange", 0, True, "", ""
    AddLabels "Column", "Process", 0, False, "", ""
    Range(Cells(3, 3), Cells(2 + nex, 2 + nproc)).Select
    Selection.FormulaArray = "=MMULT(" & range_E_matrix & _
        ",'inv(I-Aproc)'!" & coords_ProcProc_matrix & ")"
    FormatMatrix 3, 3, nex, nproc
End Sub

```

```

Sub BuildInventory()
'
' BuildInventory Macro
' Macro recorded 11/16/99 by Alejandro Cano-Ruiz
'
'
    SelectSheet 19, "Inventory", ""

' add labels
AddLabels "Row", "Exchange", 0, True, "", ""

' compute e vector
Range(Cells(3, 3), Cells(2 + nex, 3)).Select
' e = EDinv(I-Aprod)d
Selection.FormulaArray = _
    "+MMULT('EDinv(I-Aprod)'!" & coords_ExchProd_matrix & _
        " & range_d_vector & ")"
FormatVector 3, 3, nex, 1, 14
Range("C1").Select
ActiveCell.FormulaR1C1 = _
    "e = life cycle environmental exchanges inventory vector"

' Build Diag(e) matrix
BuildDiagMatrix 3, 3, nex, True
Cells(2, 7).Select
ActiveCell.FormulaR1C1 = "Diag(e)"

```



```

Rows("1:1").RowHeight = 89.25

End Sub

Sub BuildInvProcContrib()
'
' BuildInvProcContrib Macro
' Macro recorded 11/16/99 by Alejandro Cano-Ruiz
' Builds matrices of process contributions to the
' life-cycle environmental exchanges inventory
'
'
SelectSheet 20, "Process contrib to inv", _
    "Process contributions to life-cycle environmental exchanges"

' build matrix of direct process contributions
' add matrix labels
AddLabels "Row", "Exchange", 0, True, "", ""
AddLabels "Column", "Process", 0, False, "", ""
' process contributions = E Diag(x)
Range(Cells(3, 3), Cells(2 + nex, 2 + nproc)).Select
Selection.FormulaArray = _
    "=+MMULT(" & range_E_matrix & ", " & _
        range_Diagx & ")"
FormatMatrix 3, 3, nex, nproc
Cells(2, 3).Select
ActiveCell.FormulaR1C1 = _
    "Direct Process Contributions"

' copy life cycle environmental exchanges vector
Range(Cells(3, nproc + 6), Cells(2 + nex, nproc + 6)).Select
Selection.FormulaArray = "=" & range_e_vector
FormatVector 3, nproc + 6, nex, 1, 14
Cells(1, nproc + 6).Select
ActiveCell.FormulaR1C1 = _
    "e = life cycle environmental exchanges inventory vector"

' build matrix of direct process contributions (in relative terms)
Cells(5 + nex, 3).Select
Selection.FormulaR1C1 = "=R[-" & nex + 2 & "]C/R[-" & nex + 2 & _
    "]"C" & nproc + 6
Selection.NumberFormat = "0%;0%;"
Selection.Copy
Range(Cells(5 + nex, 3), Cells(4 + 2 * nex, 2 + nproc)).Select
ActiveSheet.Paste
FormatMatrix 5 + nex, 3, nex, nproc
AddLabels "Row", "Exchange", nex + 2, True, "", ""
Cells(4 + nex, 3).Select
ActiveCell.FormulaR1C1 = _
    "Direct Process Contributions, relative to total inventory"

' build matrix of total process contributions
' direct + indirect process contributions = Einv(I-Aproc) Diag(x)
Range(Cells(7 + 2 * nex, 3), Cells(6 + 3 * nex, 2 + nproc)).Select
Selection.FormulaArray = _
    "=+MMULT('Einv(I-Aproc)'! " & coords_ExchProc_matrix & _
        ", " & range_Diagx & ")"
FormatMatrix 7 + 2 * nex, 3, nex, nproc
Cells(6 + 2 * nex, 3).Select
ActiveCell.FormulaR1C1 = _
    "Total (direct + indirect) process contributions"

' build matrix of total process contributions (in relative terms)
Cells(3 * nex + 9, 3).Select
Selection.FormulaR1C1 = "=R[-" & nex + 2 & "]C/R[-" & 3 * (nex + 2) & _
    "]"C" & nproc + 6
Selection.NumberFormat = "0%;0%;"
Selection.Copy
Range(Cells(3 * nex + 9, 3), Cells(8 + 4 * nex, 2 + nproc)).Select
ActiveSheet.Paste
FormatMatrix 3 * nex + 9, 3, nex, nproc
AddLabels "Row", "Exchange", 3 * (nex + 2), True, "", ""
Cells(8 + 3 * nex, 3).Select
ActiveCell.FormulaR1C1 = _
    "Total (direct + indirect) process contributions, relative to total inventory"

End Sub

```

```

Sub buildw()
'
' buildw Macro
' Macro recorded 11/17/99 by Alejandro Cano
'
'
'   SelectSheet 21, "w", ""
'
'   insert impact category labels
AddLabels "Row", "Category", 0, True, "", "Both"
'
'   untranspose valuation vector
Range(Cells(3, 3), Cells(2 + ncat, 3)).Select
Selection.FormulaArray = "=TRANSPOSE(" & range_wtranspose & ")"
FormatVector 3, 3, ncat, 1, 8
Range("C1").Select
ActiveCell.FormulaR1C1 = _
    "w = vector of valuation factors"
'
'   Build Diag(w) matrix
BuildDiagMatrix 3, 3, ncat, True
Cells(2, 7).Select
ActiveCell.FormulaR1C1 = "Diag(w)"
'
Rows("1:1").RowHeight = 63.75
End Sub

```

```

Sub BuildValExchContrib()
'
' BuildValExchContrib Macro
' Macro recorded 11/17/99 by Alejandro Cano-Ruiz
' Builds matrices of environmental exchange contributions
' to the environmental impact valuation
'
'   SelectSheet 22, "Valuation by exchange", _
'       "Environmental Impact Valuation " + _
'       "with Environmental Exchange Contributions"
'
'   build matrix of exchange contributions by impact category indicator
'   add matrix labels
AddLabels "Row", "Exchange", 0, False, "", ""
AddLabels "Column", "Category", 0, True, "", "Category"
Range(Cells(3, 3), Cells(2 + nex, 2 + ncat)).Select
'   exchange contributions = Diag(e) H
Selection.FormulaArray = _
    "=+MMULT(" & range_Diag_e & ", " & range_H_matrix & ")"
FormatMatrix 3, 3, nex, ncat
Cells(2, 3).FormulaR1C1 = "Impact Category Indicators"
'
'   build matrix of exchange contributions by impact category valuation
'   add matrix labels
AddLabels "Column", "Category", ncat + 3, True, "", "Valuation"
Range(Cells(3, ncat + 6), Cells(2 + nex, 2 * ncat + 5)).Select
'   exchange contributions to category valuation = Diag(e) H Diag(w)
Selection.FormulaArray = "=+MMULT(" & coords_ExchIcat_matrix & _
    ", " & range_Diagw & ")"
FormatMatrix 3, ncat + 6, nex, ncat
Cells(2, ncat + 6).FormulaR1C1 = "Impact Category Valuations"
'
'   build vector of exchange contributions to overall valuation
Range(Cells(3, 2 * ncat + 9), Cells(2 + nex, 2 * ncat + 9)).Select
'   exchange contributions to category valuation = Diag(e) H w
Selection.FormulaArray = "=+MMULT(" & coords_ExchIcat_matrix & _
    ", " & range_w_vector & ")"
FormatVector 3, 2 * ncat + 9, nex, 1, 14
Cells(1, 2 * ncat + 8).FormulaR1C1 = "=Concatenate(" + Chr(34) + _
    "life-cycle environmental impact valuation (" + Chr(34) + _
    ",Sheet3!R" & nex + 6 & "C3," + Chr(34) + " " + Chr(34) + ")")"
'
'   add row label
Cells(nex + 5, 1).Select
Selection.FormulaR1C1 = "System Total"

```

```

Selection.Font.Bold = True

' add impact category indicator totals
Range(Cells(nex + 5, 3), Cells(nex + 5, ncat + 2)).Select
' indicator totals = e' H
Selection.FormulaArray =
    "=+MMULT(TRANSPOSE(" & range_e_vector & ")," & _
    range_H_matrix & ")"
FormatMatrix nex + 5, 3, 1, ncat
Cells(nex + 4, 3).Select
ActiveCell.FormulaR1C1 =
    "Y = Vector of impact category indicators"
ActiveCell.Characters(Start:=1, Length:=1).Font.Name = "Symbol"

' add impact category valuation totals
Range(Cells(nex + 5, ncat + 6), Cells(nex + 5, 2 * ncat + 5)).Select
' indicator totals = e' H Diag(w)
Selection.FormulaArray = "=+MMULT(RC3:RC" & ncat + 2 & "," & _
    & range_Diagw & ")"
FormatMatrix nex + 5, ncat + 6, 1, ncat

' add overall valuation (scalar)
Cells(nex + 5, 2 * ncat + 9).Select
' overall valuation = e' Hw
Selection.FormulaR1C1 = "=+MMULT(RC3:RC" & ncat + 2 & "," & _
    & range_w_vector & ")"
' Insert label
Cells(nex + 4, 2 * ncat + 9).Select
ActiveCell.FormulaR1C1 = "W"
Selection.Font.Name = "Symbol"
Selection.HorizontalAlignment = xlCenter

' add vector of exchange relative contributions
Range(Cells(3, 2 * ncat + 13), Cells(2 + nex, 2 * ncat + 13)).Select
Selection.FormulaR1C1 = "=+RC[-4]/R" & nex + 5 & "C[-4]"
Selection.NumberFormat = "0%"
FormatVector 3, 2 * ncat + 13, nex, 1, 12
Cells(1, 2 * ncat + 12).FormulaR1C1 = "% contribution"

' add vector of impact category relative contributions
Range(Cells(nex + 7, ncat + 6), Cells(nex + 7, 2 * ncat + 5)).Select
Selection.FormulaR1C1 = "=+R[-2]C/R[-2]C" & 2 * ncat + 9
Selection.NumberFormat = "0%"
FormatMatrix nex + 7, ncat + 6, 1, ncat
Cells(nex + 7, 1).Select
ActiveCell.FormulaR1C1 = "% contribution"
Selection.Font.Bold = True

```

End Sub

```

Sub BuildValProcContrib()
'
' BuildValProcContrib Macro
' Macro recorded 11/17/99 by Alejandro Cano-Ruiz
' Builds matrices of process contributions
' to the environmental impact valuation

SelectSheet 23, "Valuation by process", _
    "Environmental Impact Valuation with Process Contributions"

' build matrix of process contributions by impact category indicator
' add matrix labels
AddLabels "Row", "Process", 0, False, "", ""
AddLabels "Column", "Category", 0, True, "", "Category"
Range(Cells(3, 3), Cells(2 + nproc, 2 + ncat)).Select
' exchange contributions = Diag(x) E' H
Selection.FormulaArray =
    "=+MMULT(" & range_Diagx & _
    ",MMULT(TRANSPOSE(" & range_E_matrix & ")," & _
    range_H_matrix & ")"
FormatMatrix 3, 3, nproc, ncat
Cells(2, 3).FormulaR1C1 = "Impact Category Indicators"

' build matrix of process contributions by impact category valuation
' add matrix labels
AddLabels "Column", "Category", ncat + 3, True, "", "Valuation"
Range(Cells(3, ncat + 6), Cells(2 + nproc, 2 * ncat + 5)).Select
' exchange contributions to category valuation = Diag(x) E' H Diag(w)

```

```

Selection.FormulaArray = "="+MMULT(" & coords_ProcIcat_matrix & _
                                "," & range_Diagw & ")"
FormatMatrix 3, ncat + 6, nproc, ncat
Cells(2, ncat + 6).FormulaR1C1 = "Impact Category Valuations"

' build vector of process contributions to overall valuation
Range(Cells(3, 2 * ncat + 9), Cells(2 + nproc, 2 * ncat + 9)).Select
' exchange contributions to category valuation = Diag(x) E' H w
Selection.FormulaArray = "="+MMULT(" & coords_ProcIcat_matrix & _
                                "," & range_w_vector & ")"
FormatVector 3, 2 * ncat + 9, nproc, 1, 14
Cells(1, 2 * ncat + 8).FormulaR1C1 = "=Concatenate(" + Chr(34) + _
    "life-cycle environmental impact valuation (" + Chr(34) + _
    ",Sheet3!R" & nex + 6 & "C3," + Chr(34) + ")" + Chr(34) + ")"

' add row label
Cells(nproc + 5, 1).Select
Selection.FormulaR1C1 = "System Total"
Selection.Font.Bold = True

' add impact category indicator totals
Range(Cells(nproc + 5, 3), Cells(nproc + 5, ncat + 2)).Select
' indicator totals = x' E' H
Selection.FormulaArray = _
    "="+MMULT(TRANSPOSE(" & range_x_vector & _
                        "),MMULT(TRANSPOSE(" & range_E_matrix & _
                        ")," & range_H_matrix & "))"
FormatMatrix nproc + 5, 3, 1, ncat
Cells(nproc + 4, 3).Select
ActiveCell.FormulaR1C1 = _
    "Y = Vector of impact category indicators"
ActiveCell.Characters(Start:=1, Length:=1).Font.Name = "Symbol"

' add impact category valuation totals
Range(Cells(nproc + 5, ncat + 6), Cells(nproc + 5, 2 * ncat + 5)).Select
' indicator totals = x' E' H Diag(w)
Selection.FormulaArray = "="+MMULT(RC3:RC" & ncat + 2 & "," & _
    range_Diagw & ")"
FormatMatrix nproc + 5, ncat + 6, 1, ncat

' add overall valuation (scalar)
Cells(nproc + 5, 2 * ncat + 9).Select
' overall valuation = x' E' H w
Selection.FormulaArray = "="+MMULT(RC3:RC" & ncat + 2 & "," & _
    range_w_vector & ")"

' Insert label
Cells(nproc + 4, 2 * ncat + 9).Select
ActiveCell.FormulaR1C1 = "W"
Selection.Font.Name = "Symbol"
Selection.HorizontalAlignment = xlCenter

' add vector of process relative contributions
Range(Cells(3, 2 * ncat + 13), Cells(2 + nproc, 2 * ncat + 13)).Select
Selection.FormulaR1C1 = "="+RC[-4]/R" & nproc + 5 & "C[-4]"
Selection.NumberFormat = "0%"
FormatVector 3, 2 * ncat + 13, nproc, 1, 12
Cells(1, 2 * ncat + 12).FormulaR1C1 = "% contribution"

' add vector of impact category relative contributions
Range(Cells(nproc + 7, ncat + 6), Cells(nproc + 7, 2 * ncat + 5)).Select
Selection.FormulaR1C1 = "="+R[-2]C/R[-2]C" & 2 * ncat + 9
Selection.NumberFormat = "0%"
FormatMatrix nproc + 7, ncat + 6, 1, ncat
Cells(nproc + 7, 1).Select
ActiveCell.FormulaR1C1 = "% contribution"
Selection.Font.Bold = True

```

End Sub

```

Sub BuildUnitImpacts()
'
' BuildUnitImpacts Macro
' Macro recorded 11/17/99 by Alejandro Cano-Ruiz
' Builds matrices of process contributions
' to the environmental impact valuation

    SelectSheet 24, "Unit Impacts", _

```

```

"Unit Impact Environmental Impact Indicators and Valuations"

' build matrix of product unit environmental impact indicators
' add matrix labels
AddLabels "Row", "Product", 0, True, "per ", ""
AddLabels "Column", "Category", 0, True, "", "Category"
Range(Cells(3, 3), Cells(2 + nprod, 2 + ncat)).Select
' product unit indicators = (EDinv(I-Aprod))' H
Selection.FormulaArray =
    "=+MMULT(TRANSPOSE('EDinv(I-Aprod)!' & coords_ExchProd_matrix & _
        )," & range_H_matrix & ")" _
FormatMatrix 3, 3, nprod, ncat
Cells(2, 3).Select
With Selection
    .FormulaR1C1 =
        "Yd = Matrix of environmental impact indicators per unit of " _
        + "product demand"
    .Characters(Start:=1, Length:=1).Font.Name = "Symbol"
    .Characters(Start:=2, Length:=1).Font.Subscript = "True"
    .Font.Size = 8
    .Characters(Start:=1, Length:=2).Font.Size = 10
End With

' build matrix of product unit impact category valuation
' add matrix labels
AddLabels "Column", "Category", ncat + 3, True, "", "Valuation"
Range(Cells(3, ncat + 6), Cells(2 + nprod, 2 * ncat + 5)).Select
' product unit impact category valuations = (EDinv(I-Aprod))' H Diag(w)
Selection.FormulaArray = "=+MMULT(" & coords_ProdIcat_matrix & _
    ", " & range_Diagw & ")"
FormatMatrix 3, ncat + 6, nprod, ncat
Cells(2, ncat + 6).Select
Selection.FormulaR1C1 =
    "Matrix of impact Category valuations per unit of product demand"
Selection.Font.Size = 8

' build vector of product unit environmental impact valuations
Range(Cells(3, 2 * ncat + 9), Cells(2 + nprod, 2 * ncat + 9)).Select
' product unit valuations = (EDinv(I-Aprod))' H w
Selection.FormulaArray = "=+MMULT(" & coords_ProdIcat_matrix & _
    ", " & range_w_vector & ")"
FormatVector 3, 2 * ncat + 9, nprod, 2, 14
Cells(2, 2 * ncat + 9).Select
ActiveCell.FormulaR1C1 = "Wd = vector of environmental impact " + _
    "valuations per unit of product demand" _
With ActiveCell
    .Characters(Start:=1, Length:=1).Font.Name = "Symbol"
    .Characters(Start:=2, Length:=1).Font.Subscript = "True"
    .Font.Size = 8
    .Characters(Start:=1, Length:=2).Font.Size = 10
    .RowHeight = 70
End With

Cells(1, 2 * ncat + 9).Select
ActiveCell.FormulaR1C1 = "=Concatenate(" + Chr(34) + _
    "Overall valuation (" + Chr(34) + _
    ",Sheet3!R" & nex + 6 & "C3," + Chr(34) + ") " + Chr(34) + ")"
With Selection
    .HorizontalAlignment = xlGeneral
    .VerticalAlignment = xlBottom
    .WrapText = False
    .Orientation = 90
    .RowHeight = 150
End With

' generate Diag(Omegad) matrix
BuildDiagMatrix 3, 2 * ncat + 9, nprod, False
Cells(2, 2 * ncat + 13).Select
ActiveCell.FormulaR1C1 = "Diag(Wd)"
ActiveCell.Characters(Start:=6, Length:=1).Font.Name = "Symbol"
ActiveCell.Characters(Start:=7, Length:=1).Font.Subscript = "True"

' build matrix of process direct unit environmental impact indicators
' add matrix labels
AddLabels "Row", "Process", nprod + 2, False, "", ""
Range(Cells(nprod + 5, 3), Cells(nprod + nproc + 4, 2 + ncat)).Select
' process direct unit indicators = E'H
Selection.FormulaArray =
    "=+MMULT(TRANSPOSE(" & range_E_matrix & "), " & _

```

```

                                range_H_matrix & ") "
FormatMatrix nprod + 5, 3, nproc, ncat
Cells(nprod + 4, 3).Select
ActiveCell.FormulaR1C1 =
    "Yxdirect = Matrix of direct environmental impact indicators " + _
    "per unit of process throughput"
ActiveCell.Characters(Start:=1, Length:=1).Font.Name = "Symbol"
ActiveCell.Characters(Start:=2, Length:=7).Font.Subscript = "True"
ActiveCell.Font.Size = 8
ActiveCell.Characters(Start:=1, Length:=8).Font.Size = 10

' build matrix of direct process unit impact category valuation
Range(Cells(nprod + 5, ncat + 6), _
    Cells(nprod + nproc + 4, 2 * ncat + 5)).Select
' direct process unit impact category valuations = E' H Diag(w)
Selection.FormulaArray = "=+MMULT(" & coords_ProcIcat_matrix & _
    ", " & range_Diagw & ")"
FormatMatrix nprod + 5, ncat + 6, nproc, ncat
Cells(nprod + 4, ncat + 6).Select
ActiveCell.FormulaR1C1 =
    "Matrix of direct impact category valuations per unit of " + _
    "process throughput"
Selection.Font.Size = 8

' build vector of direct process unit environmental impact valuations
Range(Cells(nprod + 5, 2 * ncat + 9), _
    Cells(nprod + nproc + 4, 2 * ncat + 9)).Select
' direct process unit valuations = E'H w
Selection.FormulaArray = "=+MMULT(" & coords_ProcIcat_matrix & _
    ", " & range_w_vector & ")"
FormatVector nprod + 5, 2 * ncat + 9, nproc, nprod + 4, 12
Cells(nprod + 4, 2 * ncat + 9).Select
ActiveCell.FormulaR1C1 = "Wxdirect = vector of direct " + _
    "environmental impact valuations per unit of process throughput "
With Selection
    .Characters(Start:=1, Length:=1).Font.Name = "Symbol"
    .Characters(Start:=2, Length:=7).Font.Subscript = "True"
    .Font.Size = 8
    .Characters(Start:=1, Length:=8).Font.Size = 10
    .RowHeight = 70
End With

' generate Diag(Omegaxdirect) matrix
BuildDiagMatrix nprod + 5, 2 * ncat + 9, nproc, False
Cells(nprod + 4, 2 * ncat + 13).Select
ActiveCell.FormulaR1C1 = "Diag(Wxdirect)"
ActiveCell.Characters(Start:=6, Length:=1).Font.Name = "Symbol"
ActiveCell.Characters(Start:=7, Length:=7).Font.Subscript = "True"

' build matrix of total process unit environmental impact indicators
' add matrix labels
AddLabels "Row", "Process", nprod + nproc + 4, False, "", ""
Range(Cells(nprod + nproc + 7, 3), _
    Cells(nprod + 2 * nproc + 6, 2 + ncat)).Select
' total process unit indicators = (Einv(I-Aproc))'H
Selection.FormulaArray =
    "=+MMULT(TRANSPOSE('Einv(I-Aproc)') & coords_ExchProc_matrix & _
    ", " & range_H_matrix & ")"
FormatMatrix nprod + nproc + 7, 3, nproc, ncat
Cells(nprod + nproc + 6, 3).Select
ActiveCell.FormulaR1C1 =
    "Yx = Matrix of total (direct + indirect) environmental " + _
    "impact indicators per unit of process throughput"
ActiveCell.Characters(Start:=1, Length:=1).Font.Name = "Symbol"
ActiveCell.Characters(Start:=2, Length:=2).Font.Subscript = "True"
ActiveCell.Font.Size = 8
ActiveCell.Characters(Start:=1, Length:=2).Font.Size = 10

' build matrix of total process unit impact category valuations
Range(Cells(nprod + nproc + 7, ncat + 6), _
    Cells(nprod + 2 * nproc + 6, 2 * ncat + 5)).Select
' total process unit impact category valuations =
' (Einv(I-Aproc))' H Diag(w)
Selection.FormulaArray = "=+MMULT(" & coords_ProcIcat_matrix & _
    ", " & range_Diagw & ")"
FormatMatrix nprod + nproc + 7, ncat + 6, nproc, ncat
Cells(nprod + nproc + 6, ncat + 6).Select
ActiveCell.FormulaR1C1 =
    "Matrix of total (direct + indirect) impact category " + _
    "valuations per unit of process throughput"
Selection.Font.Size = 8

```

```

' build vector of total process unit environmental impact valuations
Range(Cells(nprod + nproc + 7, 2 * ncat + 9),
      Cells(nprod + 2 * nproc + 6, 2 * ncat + 9)).Select
' total process unit valuations = (Einv(I-Aproc))' H w
Selection.FormulaArray = "=MMULT(" & coords_ProcIcat_matrix & _
                        "," & range_w_vector & ")"
FormatVector nprod + nproc + 7, 2 * ncat + 9, _
             nproc, nprod + nproc + 6, 12
Cells(nprod + nproc + 6, 2 * ncat + 9).Select
ActiveCell.FormulaR1C1 = "Wx = vector of total (direct + indirect) " + _
                        "environmental impact valuations per unit of process throughput"
With Selection
    .Characters(Start:=1, Length:=1).Font.Name = "Symbol"
    .Characters(Start:=2, Length:=1).Font.Subscript = "True"
    .Font.Size = 8
    .Characters(Start:=1, Length:=2).Font.Size = 10
    .RowHeight = 70
End With

' build matrix of environmental exchange impact category valuations
' add matrix labels
AddLabels "Row", "Exchange", nprod + 2 * nproc + 6, True, "per ", ""
Range(Cells(nprod + 2 * nproc + 9, ncat + 6),
      Cells(nprod + 2 * nproc + nex + 8, 2 * ncat + 5)).Select
' exchange impact category valuations = H Diag(w)
Selection.FormulaArray =
    "=MMULT(" & range_H_matrix & "," & range_Diagw & ")"
FormatMatrix nprod + 2 * nproc + 9, ncat + 6, nex, ncat
Cells(nprod + 2 * nproc + 8, ncat + 6).Select
ActiveCell.FormulaR1C1 =
    "Matrix of impact category " + _
    "valuations per unit of environmental exchange"
Selection.Font.Size = 8

' build vector of env exchange unit environmental impact valuations
Range(Cells(nprod + 2 * nproc + 9, 2 * ncat + 9),
      Cells(nprod + 2 * nproc + nex + 8, 2 * ncat + 9)).Select
' env exchange unit valuations = Hw
Selection.FormulaArray =
    "=MMULT(" & range_H_matrix & "," & range_w_vector & ")"
FormatVector nprod + 2 * nproc + 9, 2 * ncat + 9, _
             nex, nprod + 2 * nproc + 8, 12
Cells(nprod + 2 * nproc + 8, 2 * ncat + 9).Select
ActiveCell.FormulaR1C1 = "We = vector of " + _
                        "environmental impact valuations per unit of environmental exchange"
With Selection
    .Characters(Start:=1, Length:=1).Font.Name = "Symbol"
    .Characters(Start:=2, Length:=1).Font.Subscript = "True"
    .Font.Size = 8
    .Characters(Start:=1, Length:=2).Font.Size = 10
    .RowHeight = 70
End With

' generate Diag(Omegae) matrix
BuildDiagMatrix nprod + 2 * nproc + 9, 2 * ncat + 9, nex, False
Cells(nprod + 2 * nproc + 8, 2 * ncat + 13).Select
ActiveCell.FormulaR1C1 = "Diag(We)"
ActiveCell.Characters(Start:=6, Length:=1).Font.Name = "Symbol"
ActiveCell.Characters(Start:=7, Length:=1).Font.Subscript = "True"

End Sub

```

```

Sub BuildProcUnitValContrib()
'
' BuildProcUnitValContrib Macro
' Macro recorded 11/17/99 by Alejandro Cano-Ruiz
' Builds matrices of contributions
' to the process unit environmental impact valuation

SelectSheet 25, "Proc unit valuation contrib", _
    "Contributions to environmental " + _
    "impact valuations per unit of process throughput"

' add matrix labels
AddLabels "Column", "Process", 0, False, "", ""
AddLabels "Column", "Process", nproc + 3, False, "", ""

```

```

AddLabels "Row", "Exchange", 0, False, "", ""
Cells(nex + 3, 1).FormulaR1C1 = "Direct environmental exchanges"
AddLabels "Row", "Product", nex + 1, False, "", ""
Cells(nex + nprod + 4, 1).FormulaR1C1 =
    "Total valuation, including indirect exchanges"

' fill contributions from direct exchanges
Range(Cells(3, 3), Cells(2 + nex, 2 + nproc)).Select
' contributions = Diag(Omegae)E
Selection.FormulaArray =
    "=+MMULT('Unit Impacts'!R" & nprod + 2 * nproc + 9 & _
    "C" & 2 * ncat + 13 & ":R" & nprod + 2 * nproc + nex + 8 _
    & "C" & 2 * ncat + nex + 12 & ", " & range_E_matrix & ")" _
' copy direct unit process valuations (transpose(Omegaxdirect))
Range(Cells(nex + 3, 3), Cells(nex + 3, 2 + nproc)).Select
Selection.FormulaArray =
    "=TRANSPOSE('Unit Impacts'!R" & nprod + 5 & _
    "C" & 2 * ncat + 9 & ":R" & nprod + nproc + 4 & _
    "C" & 2 * ncat + 9 & ")"
' fill contributions from product inputs to processes
Range(Cells(nex + 4, 3), Cells(nex + nprod + 3, 2 + nproc)).Select
' contributions = Diag(Omegad)B
Selection.FormulaArray =
    "=+MMULT('Unit Impacts'!R" & 3 & _
    "C" & 2 * ncat + 13 & ":R" & nprod + 2 & _
    "C" & 2 * ncat + nprod + 12 & ", " & range_B_matrix & ")"
' copy total unit process valuations (transpose(Omegax))
Range(Cells(nex + nprod + 4, 3),
    Cells(nex + nprod + 4, 2 + nproc)).Select
Selection.FormulaArray =
    "=TRANSPOSE('Unit Impacts'!R" & nprod + nproc + 7 & _
    "C" & 2 * ncat + 9 & ":R" & nprod + 2 * nproc + 6 & _
    "C" & 2 * ncat + 9 & ")"

' compute relative contributions
Range(Cells(3, nproc + 6),
    Cells(nex + nprod + 4, 2 * nproc + 5)).Select
Selection.FormulaR1C1 = "=if(R" & nex + nprod + 4 _
    & "C[-" & nproc + 3 & "]">0,RC[-" & nproc + 3 & "]"/R" & _
    nex + nprod + 4 & "C[-" & nproc + 3 & "],0)"
Selection.NumberFormat = "0%;0%;"

' Insert brackets and formatting
InsertBracket 2, 3, nprod + nex + 4, "Left"
InsertBracket nproc + 3, 3, nprod + nex + 4, "Right"
InsertBracket nproc + 5, 3, nprod + nex + 4, "Left"
InsertBracket 2 * nproc + 6, 3, nprod + nex + 4, "Right"
Columns("A:A").EntireColumn.AutoFit
Range(Cells(nex + 2, 3), Cells(nex + 2, nproc + 2)).Select
With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlContinuous
    .Weight = xlThin
    .ColorIndex = xlAutomatic
End With
Range(Cells(nex + 2, nproc + 6),
    Cells(nex + 2, 2 * nproc + 5)).Select
With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlContinuous
    .Weight = xlThin
    .ColorIndex = xlAutomatic
End With
Range(Cells(nex + nprod + 3, 3),
    Cells(nex + nprod + 3, nproc + 2)).Select
With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlDouble
    .Weight = xlThick
    .ColorIndex = xlAutomatic
End With
Range(Cells(nex + nprod + 3, nproc + 6),
    Cells(nex + nprod + 3, 2 * nproc + 5)).Select
With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlDouble
    .Weight = xlThick
    .ColorIndex = xlAutomatic
End With

```

End Sub


```

Sub BuildProdUnitValContrib()
'
' BuildProdUnitValContrib Macro
' Macro recorded 11/17/99 by Alejandro Cano-Ruiz
' Builds matrices of contributions
' to the product unit environmental impact valuation

    SelectSheet 26, "Prod unit valuation contrib", _
        "Contributions to environmental " + _
        "impact valuations per unit of product demand"

    ' add matrix labels
    AddLabels "Column", "Product", 0, True, "per ", ""
    AddLabels "Column", "Product", nprod + 3, True, "per ", ""
    AddLabels "Row", "Process", 0, False, "", ""
    Cells(nproc + 3, 1).FormulaR1C1 = "Total valuation"
    AddLabels "Row", "Exchange", nproc + 2, False, "", ""
    Cells(nex + nproc + 5, 1).FormulaR1C1 = "Total valuation"

    ' fill contributions from processes
    Range(Cells(3, 3), Cells(2 + nproc, 2 + nprod)).Select
    ' contributions = Diag(Omegaxdirect)Dinv(I-Aprod)
    Selection.FormulaArray = _
        "=MMULT('Unit Impacts'!R" & nprod + 5 & _
        "C" & 2 * ncat + 13 & ":R" & nprod + nproc + 4 _
        & "C" & 2 * ncat + nproc + 12 & _
        ", 'Dinv(I-Aprod)'!" & coords_ProcProd matrix & ")"
    ' copy unit product valuations (Transpose(Omegad))
    Range(Cells(nproc + 3, 3), Cells(nproc + 3, 2 + nprod)).Select
    Selection.FormulaArray = "=TRANSPOSE('Unit Impacts'!R3C" & _
        2 * ncat + 9 & ":R" & nprod + 2 & _
        "C" & 2 * ncat + 9 & ")"
    ' fill contributions from env exchanges to products
    Range(Cells(nproc + 5, 3), Cells(nex + nproc + 4, 2 + nprod)).Select
    ' contributions = Diag(Omegae)EDinv(I-Aprod)
    Selection.FormulaArray = _
        "=MMULT('Unit Impacts'!R" & nprod + 2 * nproc + 9 & _
        "C" & 2 * ncat + 13 & ":R" & nprod + 2 * nproc + nex + 8 & _
        "C" & 2 * ncat + nex + 12 & _
        ", 'EDinv(I-Aprod)'!" & coords_ExchProd matrix & ")"
    ' copy unit product valuations (Transpose(Omegad))
    Range(Cells(nex + nproc + 5, 3), _
        Cells(nex + nproc + 5, 2 + nprod)).Select
    Selection.FormulaArray = "=TRANSPOSE('Unit Impacts'!R3C" & _
        2 * ncat + 9 & ":R" & nprod + 2 & _
        "C" & 2 * ncat + 9 & ")"

    ' compute relative contributions
    Range(Cells(3, nprod + 6), _
        Cells(nex + nproc + 5, 2 * nprod + 5)).Select
    Selection.FormulaR1C1 = "=if(R" & nex + nproc + 5 _
        & "C[-" & nprod + 3 & "]>0,RC[-" & nprod + 3 & _
        "]/R" & _
        nex + nproc + 5 & "C[-" & nprod + 3 & "],0)"
    Selection.NumberFormat = "0%;0%";
    Range(Cells(nproc + 4, nprod + 6), _
        Cells(nproc + 4, 2 * nprod + 5)).Clear

    ' Insert brackets and formatting
    InsertBracket 2, 3, nproc + 3, "Left"
    InsertBracket nprod + 3, 3, nproc + 3, "Right"
    InsertBracket 2, nproc + 5, nproc + nex + 5, "Left"
    InsertBracket nprod + 3, nproc + 5, nproc + nex + 5, "Right"
    InsertBracket nprod + 5, 3, nproc + 3, "Left"
    InsertBracket 2 * nprod + 6, 3, nproc + 3, "Right"
    InsertBracket nprod + 5, nproc + 5, nproc + nex + 5, "Left"
    InsertBracket 2 * nprod + 6, nproc + 5, nproc + nex + 5, "Right"
    Columns("A:A").EntireColumn.AutoFit

    ' Insert separation lines
    Range(Cells(nproc + 2, 3), Cells(nproc + 2, nprod + 2)).Select
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlDouble
        .Weight = xlThick
        .ColorIndex = xlAutomatic
    End With
    Range(Cells(nex + nproc + 4, 3), Cells(nex + nproc + 4, nprod + 2)).Select
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlDouble
        .Weight = xlThick
        .ColorIndex = xlAutomatic
    End With

```

```

End With
Range(Cells(nproc + 2, nprod + 6),
      Cells(nproc + 2, 2 * nprod + 5)).Select
With Selection.Borders(xlEdgeBottom)
.LineStyle = xlDouble
.Weight = xlThick
.ColorIndex = xlAutomatic
End With
Range(Cells(nex + nproc + 4, nprod + 6),
      Cells(nex + nproc + 4, 2 * nprod + 5)).Select
With Selection.Borders(xlEdgeBottom)
.LineStyle = xlDouble
.Weight = xlThick
.ColorIndex = xlAutomatic
End With

End Sub

Sub InsertBracket(colNumber, topRowNumber, bottomRowNumber, bracketType)
Range(Cells(topRowNumber, colNumber),
      Cells(bottomRowNumber, colNumber)).Select
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
With Selection.Borders(xlEdgeTop)
.LineStyle = xlContinuous
.Weight = xlThick
.ColorIndex = xlAutomatic
End With
With Selection.Borders(xlEdgeBottom)
.LineStyle = xlContinuous
.Weight = xlThick
.ColorIndex = xlAutomatic
End With
If bracketType = "Left" Then
Selection.Borders(xlEdgeRight).LineStyle = xlNone
With Selection.Borders(xlEdgeLeft)
.LineStyle = xlContinuous
.Weight = xlThick
.ColorIndex = xlAutomatic
End With
ElseIf bracketType = "Right" Then
Selection.Borders(xlEdgeLeft).LineStyle = xlNone
With Selection.Borders(xlEdgeRight)
.LineStyle = xlContinuous
.Weight = xlThick
.ColorIndex = xlAutomatic
End With
End If
Cells(topRowNumber, colNumber).ColumnWidth = 0.67
End Sub

Sub AddLabels(LabelType As String, DataType As String, _
             offset As Integer, _
             IncludeUnits As Boolean, UnitsPrefix As String, _
             UnitType As String)

' Procedure created on 11/17/99 by Alejandro Cano
' Parameters:
' LabelType:      "Row" or "Column"
' DataType:      "Process", "Product", "Exchange", or "Category"
' Offset:        Number of cells by which first label is offset from
'               the standard R3 or C3 position
' IncludeUnits:  True or False. If True text processing is used
'               to add units to the label
' UnitsPrefix:   Text to be added before the units
'               (e.g. "per " as used in column product labels
' UnitType:      "Category", "Valuation", or "Both". This is only
'               used for the "Category" data type. If UnitType =
'               "Category", the units for the impact category are used;
'               If UnitType = "Valuation", the valuation units are used;
'               If UnitType = "Both", the units are valuation units/
'               impact category unit

If LabelType = "Row" Then
If DataType = "Process" Then

```

```

Range(Cells(3 + offset, 1),
      Cells(2 + nproc + offset, 1)).Select
Selection.FormulaArray =
  "=TRANSPOSE(Sheet1!R1C5:R1C[" & nproc + 4 & "])"
ElseIf DataType = "Product" Then
  For i = 1 To nprod
    Cells(2 + i + offset, 1).Select
    If IncludeUnits Then
      Selection.FormulaR1C1 = "=Concatenate(Sheet1!R" & _
        2 + i & "C2," & Chr(34) & " (" & _
        UnitsPrefix & Chr(34) & ",Sheet1!R" & _
        2 + i & "C3," & Chr(34) & ")" & _
        Chr(34) & ")"
    Else
      Selection.FormulaR1C1 = "=Sheet1!R" & 2 + i & "C2"
    End If
  Next i
ElseIf DataType = "Exchange" Then
  For i = 1 To nex
    Cells(2 + i + offset, 1).Select
    If IncludeUnits Then
      Selection.FormulaR1C1 = "=Concatenate(Sheet3!R" & _
        3 + i & "C1," & Chr(34) & ":" & Chr(34) & _
        ",Sheet3!R" & _
        3 + i & "C2," & Chr(34) & " (" & UnitsPrefix _
        & Chr(34) & ",Sheet3!R" & 3 + i & "C3," & _
        Chr(34) & ")" & Chr(34) & ")"
    Else
      Selection.FormulaR1C1 = "=Concatenate(Sheet3!R" & _
        3 + i & "C1," & Chr(34) & ":" & Chr(34) & _
        ",Sheet3!R" & 3 + i & "C2)"
    End If
  Next i
ElseIf DataType = "Category" Then
  For i = 1 To ncat
    Cells(2 + i + offset, 1).Select
    If IncludeUnits Then
      If UnitType = "Both" Then
        Selection.FormulaR1C1 = "=Concatenate(Sheet3!R1C" & _
          & 4 + i & "," & Chr(34) & " (" & Chr(34) & _
          ",Sheet3!R" & nex + 6 & "C3," & Chr(34) & "7" & _
          & Chr(34) & ",Sheet3!R2C" & 4 + i & "," & _
          Chr(34) & ")" & Chr(34) & ")"
      End If
    Else
      Selection.FormulaR1C1 = "=Sheet3!R1C" & 4 + i
    End If
  Next i
End If
Cells(1, 1).EntireColumn.AutoFit

ElseIf LabelType = "Column" Then
  If DataType = "Process" Then
    Range(Cells(1, 3 + offset),
          Cells(1, 2 + nproc + offset)).Select
    Selection.FormulaArray = "=Sheet1!R1C5:R1C" & nproc + 4
  ElseIf DataType = "Product" Then
    If IncludeUnits Then
      For i = 1 To nprod
        Cells(1, 2 + i + offset).Select
        Selection.FormulaR1C1 = "=Concatenate(Sheet1!R" & _
          2 + i & "C2," & Chr(34) & " (" & UnitsPrefix & _
          Chr(34) & ",Sheet1!R" & 2 + i & "C3," & Chr(34) & _
          ")" & Chr(34) & ")"
      Next i
      Range(Cells(1, 3 + offset),
            Cells(1, 2 + nprod + offset)).Select
    Else
      Range(Cells(1, 3 + offset),
            Cells(1, 2 + nprod + offset)).Select
      Selection.FormulaArray =
        "=TRANSPOSE(Sheet1!R3C2:R[" & nprod + 2 & " ]C2)"
    End If
  ElseIf DataType = "Category" Then
    If IncludeUnits Then
      For i = 1 To ncat
        Cells(1, 2 + i + offset).Select
        If UnitType = "Category" Then
          Selection.FormulaR1C1 = "=Concatenate(Sheet3!R1C" & _
            & 4 + i & "," & Chr(34) & " (" & Chr(34) & _
            ",Sheet3!R2C" & 4 + i & "," & Chr(34) & _

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```

        )" & Chr(34) & ")"
    ElseIf UnitType = "Valuation" Then
        Selection.FormulaR1C1 = "=Concatenate(Sheet3!R1C" & _
            & 4 + i & ", " & Chr(34) & " (" & Chr(34) & _
            ",Sheet3!R" & nex + 6 & "C3" & ", " & _
            & Chr(34) & ")" & Chr(34) & ")"
    End If
    Next i
    Range(Cells(1, 3 + offset),
        Cells(1, 2 + ncat + offset)).Select
Else
    Range(Cells(1, 3 + offset),
        Cells(1, 2 + ncat + offset)).Select
    Selection.FormulaArray = "=Sheet3!R1C4:R1C" & ncat + 3
End If
End If
With Selection
    .HorizontalAlignment = xlGeneral
    .VerticalAlignment = xlBottom
    .WrapText = True
    .Orientation = 90
    .ColumnWidth = 5.2
    .RowHeight = 150
End With
End If
End Sub

```

```

Sub BuildDiagMatrix(intStartRow, intVectorCol, intVectorLength, _
    blnFullRightBracket As Boolean)

    Cells(intStartRow, intVectorCol + 4).Select
    ActiveCell.FormulaR1C1 = "=IF(ROW(RC)=COLUMN(RC)+(" & _
        intStartRow - (intVectorCol + 4) & "),RC" & intVectorCol & ",0)"
    Selection.Copy
    Range(Cells(intStartRow, intVectorCol + 4),
        Cells(intStartRow + intVectorLength - 1,
            intVectorCol + intVectorLength + 3)).Select
    ActiveSheet.Paste
    Selection.ColumnWidth = 5.2

    ' add brackets
    InsertBracket intVectorCol + 3, _
        intStartRow, intStartRow + intVectorLength - 1, "Left"

    If blnFullRightBracket Then
        InsertBracket intVectorCol + intVectorLength + 4, _
            intStartRow, intStartRow + intVectorLength - 1, "Right"
    End If
    ' formal label area
    Range(Cells(intStartRow - 1, intVectorCol + 4), _
        Cells(intStartRow - 1,
            intVectorCol + intVectorLength + 3)).Select
    With Selection
        .MergeCells = True
        .Font.Bold = True
    End With
End Sub

```

```

Sub SelectSheet(SheetNumber, SheetName, SheetTitle)
    numberOfSheets = Sheets.Count
    If numberOfSheets < SheetNumber Then
        Sheets.Add
        Application.ActiveSheet.Move After:=Sheets(SheetNumber)
    End If
    Sheets(SheetNumber).Select
    Application.ActiveSheet.Name = SheetName
    Cells.Select
    Selection.Delete Shift:=xlUp
    Range("A1").Select
    ActiveCell.FormulaR1C1 = SheetTitle
    Selection.Font.Bold = True
    Selection.WrapText = True
    Range("B2").Select
    ActiveWindow.FreezePanes = True
End Sub

```

```

Sub FormatVector(intStartRow As Integer, intVectorCol As Integer, _
                intVectorLength As Integer, intLabelRow As Integer, _
                sngColWidth As Single)
Cells(intStartRow, intVectorCol).Select
Selection.ColumnWidth = sngColWidth
' add brackets
InsertBracket intVectorCol - 1, _
              intStartRow, intStartRow + intVectorLength - 1, "Left"
InsertBracket intVectorCol + 1, _
              intStartRow, intStartRow + intVectorLength - 1, "Right"
' format label area
Range(Cells(intLabelRow, intVectorCol - 1), _
      Cells(intLabelRow, intVectorCol + 1)).Select
With Selection
    .HorizontalAlignment = xlCenter
    .WrapText = True
    .MergeCells = True
    .Font.Bold = True
End With
End Sub

```

```

Sub FormatMatrix(intStartRow As Integer, intStartCol As Integer, _
                intNumRows As Integer, intNumCols As Integer)

' Format label area
Range(Cells(intStartRow - 1, intStartCol), _
      Cells(intStartRow - 1, intStartCol + intNumCols - 1)).Select
With Selection
    .WrapText = True
    .MergeCells = True
    .Font.Bold = True
End With

' Insert Brackets
InsertBracket intStartCol - 1, intStartRow, intStartRow + intNumRows - 1, "Left"
InsertBracket intStartCol + intNumCols, intStartRow, intStartRow + intNumRows - 1, "Right"

End Sub

```

```

Sub Getnproc()
' Count the number of processes
Sheets("Sheet1").Select
nproc = 0
runOutOfProcesses = False
Do While Not runOutOfProcesses
    If Cells(1, 5 + nproc).Formula = "" Then
        runOutOfProcesses = True
    Else
        nproc = nproc + 1
    End If
Loop
End Sub

```

```

Sub Getnprod()
' Count the number of products
Sheets("Sheet1").Select
nprod = 0
runOutOfProducts = False
Do While Not runOutOfProducts
    If Cells(3 + nprod, 2).Formula = "" Then
        runOutOfProducts = True
    Else
        nprod = nprod + 1
    End If
Loop
End Sub

```

```

Sub Getnex()

```

```

' Count the number of environmental exchanges
Sheets("Sheet1").Select
nex = 0
Getnprod
runOutOfExchanges = False
Do While Not runOutOfExchanges
  If Cells(2 * nprod + 7 + nex, 2).Formula = "" Then
    runOutOfExchanges = True
  Else
    nex = nex + 1
  End If
Loop
End Sub

```

```

Sub Getncat()
' Count the number of impact categories
Sheets("Sheet3").Select
ncat = 0
runOutOfCategories = False
Do While Not runOutOfCategories
  If Cells(1, 5 + ncat).Formula = "" Then
    runOutOfCategories = True
  Else
    ncat = ncat + 1
  End If
Loop
End Sub

```

```

Sub GetMatrixSizes()

Getnproc
Getnprod
Getnex
Getncat

' generate strings with matrix and vector locations

coords_ProcProc_matrix = "R3C3:R" & 2 + nproc & "C" & 2 + nproc
coords_ProcProd_matrix = "R3C3:R" & 2 + nproc & "C" & 2 + nprod
coords_ProcIcat_matrix = "RC3:R[" & nproc - 1 & "]C" & 2 + ncat
coords_ProdProc_matrix = "R3C3:R" & 2 + nprod & "C" & 2 + nproc
coords_ProdProd_matrix = "R3C3:R" & 2 + nprod & "C" & 2 + nprod
coords_ProdIcat_matrix = "RC3:R[" & nprod - 1 & "]C" & 2 + ncat
coords_ExchProc_matrix = "R3C3:R" & 2 + nex & "C" & 2 + nproc
coords_ExchProd_matrix = "R3C3:R" & 2 + nex & "C" & 2 + nprod
coords_ExchIcat_matrix = "RC3:R[" & nex - 1 & "]C" & 2 + ncat

range_B_matrix = "Sheet1!R3C5:R" & nprod + 2 & "C" & nproc + 4
range_C_matrix = "Sheet1!R" & nprod + 5 & "C5:R" & nproc + 4
& (2 * nprod) + 4 & "C" & nproc + 4
range_E_matrix = "Sheet1!R" & 2 * nprod + 7 & "C5:R" & nproc + 4
& 2 * nprod + nex + 6 & "C" & nproc + 4
range_d_vector = "Sheet2!RC8:R" & nprod + 2 & "C8"
range_H_matrix = "Sheet3!R4C5:R" & nex + 3 & "C" & ncat + 4
range_wtranspose = "Sheet3!R" & nex + 6 & "C5:R" & nex + 6 & "C" & ncat + 4

range_D_matrix = "D!" & coords_ProcProd_matrix

range_w_vector = "w!R3C3:R" & ncat + 2 & "C3"
range_Diagw = "w!R3C7:R" & ncat + 2 & "C" & ncat + 6

range_x_vector = "'Process throughputs!R3C7:R" & nproc + 2 & "C7"
range_Diagx = "'Process throughputs!R3C11:R" & nproc + 2 & "C" & nproc + 10

range_e_vector = "Inventory!R3C3:R" & nex + 2 & "C3"
range_Diage = "Inventory!R3C7:R" & nex + 2 & "C" & nex + 6

End Sub

```
