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GROUNDWATER POLLUTION: TECHNOLOGY, ECONOMICS AND MANAGEMENT

Edited by
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and
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Ralph M. Parsons Laboratory
for
Water Resources and Hydrodynamics
Department of Civil Engineering
Massachusetts Institute of Technology

Report No. TR 208

Prepared with the support of the United Nations Food and Agricultural Organization (acting as executing agency for the United Nations Development Program).

January 1976

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ABSTRACT

A review of the technical, economic and management aspects of groundwater pollution is presented. The groundwater pollution problem is described and several of its important characteristics are pointed out.

A description of the physical, chemical and biological aspects of groundwater pollution is given. The technology of groundwater pollution detection and observation is reviewed, including elements in the design and operation of a groundwater quality monitoring system.

The concept of pollution is related to the economic concept of externalities, and the interrelationships of technology, institutions and economics in groundwater pollution management are presented. Technical, institutional, legal and economic measures to induce pollution control in groundwater systems are reviewed. The financial aspects, and the costs and benefits of groundwater pollution control are discussed.

The causes, types and extent of groundwater pollution are described. These include agricultural, industrial, domestic and urban, radiological, and natural or induced sources of pollution. Methods of control for each are given.

Methods of analysis as applied to groundwater pollution management are described within the context of total resource management and long-range planning. Criteria for choosing among alternative plans, systems analysis, and optimization and simulation techniques are discussed.

A case study of integrated groundwater-surface water management with specific groundwater quality considerations is described and discussed.

PREFACE

This work is part of a one-year project entitled, "Training of Engineers in the Field of Groundwater Pollution" which was supported financially by the United Nations Development Program/Food and Agriculture Organization, and the Spanish Government. Administrative support has been provided by the M.I.T. Office of Sponsored Research.

The writing of this report was supervised and edited by Drs. Roberto Lenton and John L. Wilson, Assistant Professors of Civil Engineering. Dr. Jorge Porras and Messrs. Javier Calvin, Pedro Nieto, Luis de Oteyza and Enrique Reyes, Visiting Research Engineers; and Ms. Patricia Deese and Mr. Peter Kitanidis, Research Assistants, collaborated both in researching the material and in preparing the final text.

Different project members participated in preparing different parts of the report. Chapter 1 was written by Professor J. Wilson. Chapter 2 was developed and written principally by Professor J. Wilson and Dr. Jorge Porras, and was supervised and edited by Professor J. Wilson; additionally, Messrs. J. Calvin and P. Nieto collaborated in providing some of the basic material for the chapter. Chapter 3 was developed and written by Mr. Luis de Oteyza and edited by Professors R. Lenton and J. Wilson; additionally, Section 3.2 was developed and written by Ms. P. Deese. Chapter 4 was developed and written principally by Professor J. Wilson, Dr. Jorge Porras, Ms. P. Deese, Mr. J. Calvin, Mr. P. Kitanidis, and Mr. E. Reyes, and was supervised and edited by Professor J. Wilson; additionally, Mr. P. Nieto collaborated in researching material for the chapter. Chapter 5 was developed and written by Dr. Jorge Porras, Ms. P. Deese, and Messrs. Luis de Oteyza and Peter Kitanidis, and was supervised and edited by

Professor R. Lenton. The Case Study, which is presented in Chapter 6, was developed and written by Dr. Jorge Porras and Messrs. J. Calvin, P. Nieto, L. de Oteyza and E. Reyes; the discussion of the Case Study in Section 6.2 was written by Professor R. Lenton. Finally, the conclusions in Chapter 7 were written by Professor J. Wilson.

The authors would like to acknowledge the many valuable comments on the first draft of this report made by the members of the Project Advisory Panel, Messrs. Robert Chun of the California Department of Water Resources, Kenneth Edworthy of the Water Research Centre, United Kingdom, and R. G. Thomas of the Food and Agricultural Organization, Rome, Italy; and Dr. P.F. Teniere-Buchot of the Agence Financiere de bassin Seine-Normandie, Paris, France; furthermore, their friendly cooperation and advice throughout the entire duration of the project is very much appreciated.

The authors would also like to thank Mr. Nguyen Quang Trac of the Food and Agricultural Organization, UNDP, Madrid, Spain. Mr. Trac suggested the training program and through his leadership as project manager has coordinated the several simultaneous activities of the Spanish Government and MIT which resulted in the case study presented in Chapter 6.

The Southern Division of the California Department of Water Resources hosted a month-long visit by project members to facilities and agencies in their area which concerned groundwater quality. The authors wish to thank Mr. Jack J. Coe, District Engineer, Dr. Ahmad Hassan and Messrs. Kiyoshi Mido, Jimmy Koyasako, and Dennis Underwood for thier hospitality during that trip and for their advice and consultation during the preparation of the Case Study.

A special note of thanks is due to Ms. Carole J. Solomon for her assistance in the many different aspects of the project and for her patience and skill in typing the drafts and final version of this report.

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CHAPTER 1

Introduction

1.1 General Purpose

Spain is currently going through a process of very rapid industrial, urban and agricultural development. In response, the Spanish Government has become concerned with the potential for environmental pollution that is associated with the rapid development of a society. In particular, Spain is heavily dependent on groundwater resources and will be even more so in the future due to expected increases in water demands. Groundwater supplies about 23 percent of the present total water supply in Spain, and this ratio is projected to increase to 40 percent of the total by the end of the century. However, very little is known about the pollution, or potential pollution, of groundwater resources in the country. The potential pollution problems, as discussed in Section 2.1 and Chapter 4, are such that the government needs to act rather than wait for the signs of pollution to become acute, possibly including severe damage to public health. This report, which is addressed to the more general aspects of the technology, economics and management of groundwater pollution, is part of the initial program of the Spanish Government to take appropriate action. It constitutes the culmination of one phase of a nine-month training program for four Spanish technicians and an economist at MIT.

1.2 Objectives

The overall approach to handling the effect of development on water resources is through long term water resource planning, stressing in particular groundwater pollution management, at least within the context presented here. And groundwater pollution management has several levels: from the control or evaluation of an individual local pollution problem, to basin wide groundwater quality management. The need to address this wide range of situations requires a broad background in the technological, economic and managerial aspects of groundwater pollution. In light of this, the objectives of this report are:

a. To develop background information of the basic aspects of physics, chemistry and biology as applied to groundwater pollution problems.
b. To analyze and catalog systems and techniques for monitoring groundwater quality.
c. To review and/or develop technological, economic and institutional methods for the control of groundwater pollution.
d. To access particular types of pollution, their causes, extent and control.
e. To review methods of analysis applicable to groundwater pollution management and resource planning; including optimization, simulation, and input-output models.
f. To apply all of these, especially the methods of analysis, to a case study.

1.3 Scope

This report is one part of a two-year integrated program which is being conducted by the Spanish Government, with support from the United Nations Food and Agricultural Organization and the United Nations Development Program. In the first year of this program, which is now complete, four Spanish technicians and an economist received training in the field of groundwater pollution at MIT, with a field trip to California and additional study in Spain, France and England. MIT received a contract from UNDP/FAO to provide training to the Spanish team through formal subjects, visiting lecturers, field trips, a case study, and review of the state of the art. This report constitutes the result of the review process and also presents a summary of the case study.

The results of the first year's effort will be used in the second year's program. The general objective will be to prepare national and regional systems for groundwater management and protection. The specific objectives of the second year will be to analyze specific methods of groundwater pollution control in Spain, and to analyze regional groundwater quality management systems in at least two areas of Spain.

In this report, groundwater, including its pollution aspects, is considered in the context of the total environmental system: hydrologic system, ecological system, economic system, social system, etc. The management of groundwater quality cannot, in general, be separated from the management of groundwater quantity and surface water quality and quantity.

Also, the terms groundwater pollution, groundwater contamination, and groundwater quality degradation are assumed synonymous in this report. Their definition is "the presence of any substance (organic, inorganic, biological, thermal, or radiological) in water at intensity levels which tend to impair, degrade, or adversely affect its quality or usefulness for a specific purpose."

CHAPTER 2

Some Basic Aspects of Groundwater Pollution

The purpose of this chapter is to lay the foundation of the remainder of the report. To this end the chapter is divided into three parts. The first part presents a brief background identification of the types and kinds of groundwater pollution, their transportation and transformation in the subsurface environment, and their effects on man and the environment. A number of general characteristics of groundwater pollution problems are revealed by this review. The second section of the chapter discusses the various physical, chemical and biological processes which influence the movement, distribution and decay of pollutants. Finally, the last section reviews the technology of groundwater quality monitoring. Observation network design and the use of observation wells for sampling are among the topics discussed.

2.1 Identifying the Problem

Groundwater quality changes are brought about through man's introduction of foreign chemical and biological material into the subsurface environment, through quantitative interference with natural flow patterns, by a completely natural process, or through various combinations of these. Sanitary landfills, beefcattle feedlots and leaking petrochemical storage tanks are illustrative sources of materials for the first category. Water supply wells are prime examples of quantitative interference, the second category, which may redistribute man-made or natural chemicals in a manner not otherwise possible. The third category, natural processes, includes mineralization of groundwaters and the process of natural salt-water intrusion.

A number of recent studies, reviews and symposia proceedings have been published discussing the types and sources of groundwater pollution (e.g., Stanley and Eliassen, 1960; U.S. Public Health Service, 1961; Fuhriman et al., 1971; National Water Well Assoc., 1971; Ballentine et al., 1972; Cate, 1972; Amer. Assoc. Petro. Geol. et al., 1973; Calif Dept. of Water Resources and U. of Calif., 1973; Meyer, 1973; Scalf et al., 1973; E.P.A., 1973; Cole, 1974; Karubian, 1974; Miller et al., 1974 and Todd, 1974). Several bibliographies have also been published (e.g., E.P.A., 1972; Bader et al., 1973; Cole, 1974; Summers and Spiegal, 1974; Todd and McNulty, 1974). These publications provide the means for one to obtain either a broad background in this field, or the direction that leads to a detailed analysis of one particular aspect of a groundwater quality problem. A similar presentation is made in Chapter 4, with information organized along the disciplinary lines associated with each kind of problem, from agriculturally related pollution to radioactive waste disposal. To fit this detailed description of each specific problem area, as well as the more general aspects of materials transportation and transformation (Section 2.2), groundwater quality monitoring (Section 2.3), and groundwater quality control (Chapter 3), into an organized package a background description of the problem is required. The following paragraphs are devoted to a brief examination of the various types of human activities that can alter groundwater quality, the ways in which nature responds to these activities, and their effect on man and the environment.

Most ground and surface waters contain some natural dissolved salts. These salts most often originate from contact of the liquid water moving in the hydrologic cycle with various rock and soil minerals. Similarly, water can pick up natural organic matter from leaves, grass and other vegetation in various stages of biodegradation, as well as dissolved gasses native to the atmosphere. The result of these contacts is that water accumulates various amounts of natural impurities due to solution or chemical reaction followed by solution (Hem, 1961). These natural mineralization processes are most important in arid lands, but the resulting quality is a function of nature, not of man and is generally referred to as a background level of quality.

There are other natural sources of lower quality water. Along the seacoast there exists a natural meeting place of fresh groundwater moving toward the ocean, and saline groundwater. As it approaches the ocean the freshwater slowly rises above and mixes with the denser seawater until it discharges to the ocean (see Section 4.5). Over longer periods of time this "interface" between fresh and saltwater may move toward the land or back toward the sea in response to natural changes in the hydrology and climate of the area.

Saline water is underneath us as well. Buried in ancient sedimentary deposits are connate brines; brines that were trapped in the sediments as they were being deposited or as the sea retreated. These brines are often associated with major gas or oil deposits, but occur separately as well. These brine deposits constitute a potentially valuable source of certain minerals if the concentrations are high enough, and in many locations are a potential source of agricultural, industrial or domestic water supply if desalinized.

It is not unusual for these shallow brine deposits to underlie and be hydraulically connected to a major freshwater aquifer. Thus in these aquifers, as well as along the seacoast, man's groundwater extraction activities may serve to redistribute natural waters of low quality. The result may be the eventual abandonment of pumping wells due to the intrusion of salt water. These problems are discussed in Section 4.5.

There are wide numbers of activities that are associated with man's introduction of foreign chemical and biological material in the subsurface environment. The first of these is agriculture, which is responsible for five major sources of materials. In the long run the most hazardous of these may be the use of chemical pesticides. But it is possible that the tremendous use of chemical fertilizers as plant nutrients may be a more significant problem, causing an increasing buildup of nutrients in our surface water and groundwater. Not to be overlooked is the most pressing groundwater quality problem of the current decade in the arid and semi-arid portions of the world: the increasing mineralization of groundwater due to natural leaching processes and irrigation practices. For the most part these pollution sources are incidental to certain of the agricultural activities of man. It is certainly not the intent of the farmer that these materials reach ground or surface waters. These sources, for the most part, can be characterized as distributed, regional or non-point sources.

In contrast to these are other agricultural sources which are associated with agricultural waste disposal activities. First among these are animal wastes, about half of which are produced by animals in concentrated production systems (LeGrand, 1970). Crop wastes, along with pesticide and fertilizer storage facilities, pose other sources of material. It appears that these sources are often point or local sources of material generating local pollution problems. For a further discussion of agricultural pollution, see Section 4.2.

Industry serves as another originator of chemicals for groundwater pollution. Most of these sources are localized or point sources. Some wastes are intentionally disposed to groundwater system via injection wells, and seepage, recharge or infiltration pits. More often, pollution occurs due to leaks from evaporation ponds, holding or oxidation ponds, buried wastes, landfills, or deep well waste disposal activities. From time to time, salts may enter groundwater due to the land spreading of industrial wastes. Seepage from underground mines and leacheate from mine tailings pose other threats. Finally accidental spills and leaks associated with production, storage and transportation facilities sometimes lead to groundwater quality degradation.

There are many thousands of chemicals that may enter the subsurface environment due to these activities. A partial list would include waste oil, petro-chemicals, oil field brines, industrial sludges, inorganic salts and various exotic materials including a vast array of organics. Section 4.1 contains a thorough examination of the industrial pollution problem.

Waste generated domestically, in rural or urban landscapes, find their way to the groundwater system. More and more, the land is being used to treat municipal wastewaters by spray irrigation or some other application technique. Sludges produced in primary and secondary sewage treatment plants have been applied to the land for many years. Household disposal systems form the backbone of rural wastewater treatment and in other cases provide the only treatment system in many towns and villages around the world. All of these systems are sources of nitrate nitrogen which is easily leached to the groundwater. Where the land disposal system is extensive, or when the population of household disposal systems (e.g., septic tank systems) is high, they constitute a distributed or non-point source of nitrate. Some of these systems may also be local sources of biological pollution.

Solid wastes are also generated domestically and leachates from dumps and landfills are classic sources of local pollution of groundwater. There are other miscellaneous domestic pollution sources ranging from highway de-icing salts to lawn fertilizers. The various aspects of domestic pollution are discussed further in Section 4.3.

Radiological contamination from accidents or leaks during the production, storage, transportation, use or disposal of radiological materials is an important threat to the integrity of groundwater supplies. Some of these materials are extremely toxic and would pose a severe limitation on the use of contaminated groundwater supplies. Section 4.4 discusses this topic in detail.

Agricultural, industrial, domestic activities and radiological materials all constitute major sources of chemical or biological material which threaten to degrade the underground water supply. There are other threats which have yet to create severe problems, except in a few restricted locations. Among these are polluted surface water which, like natural salt brines, can be induced by man's groundwater extraction activities to pollute groundwater supplies; artificial recharge with a low quality water will lead to some degree of quality degradation; and air pollution can lead to a change in the amount of dissolved gas in water, or to the introduction of soluble solids which can be transported in the groundwater system. A number of these problems are also described in Section 4.5.

Once foreign chemical or biological material has been introduced in the environment it becomes a possible groundwater pollutant. Materials introduced near ground level (e.g., septic tank leachates, pesticides, fertilizers, toxic wastes from disposal pits) are subject to a sequence of events including leaching, percolation through the zone of aeration and introduction into the groundwater. Some materials may enter the groundwater directly, as in the case of the deep well disposal of sewage to a fresh water aquifer. Once the material has entered the groundwater system (or in the case of natural quality problems it is already there) it is subject to movement following the local flow pattern and, in many cases, to some degree of attenuation. The flow pattern will be influenced by regional and local hydrogeological characteristics, and will often be altered by man's activities (e.g., pumping or recharge wells, abandoned wells or boreholes, and mining activities). The degree of attenuation will depend on the type of contaminant, the type of aquifer porous or fractured media, and the flow itself. A series of effects, including the physical (convection, diffusion, mechanical dispersion, filtration, radioactive decay) chemical (precipitation-solution, oxidation-reduction, ion-exchange, adsorption) and biological (degradation, oxidation-reduction and other transformation influences),may act to 'trap' the pollution on the porous media and to dilute it, or to decay it. Many of these processes are discussed in depth in Section 2.2.

This has been a brief description of the sources of groundwater contaminants, and of their transportation and transformation in the subsurface environment. The final phase of this explanation is to describe the effects of the contamination on man and on the environment. Since the definition of a water pollutant must be tied to the use of the water, it is necessary to describe effects in terms of use and the associated contaminants.

There is little doubt that one important effect is on public health, for groundwater is a major source of drinking water supply. Biological contamination from domestic sources has historically constituted the most important source of poor health associated with water. Now the threat appears to lie with other contaminants as well. Nitrate nitrogen is mobile (moves freely with flowing groundwater) and in high concentrations ($>$ 45 mg/L as NO_3^- or 10 mg/L as NO_3^--N) is a cause of methemoglobinemia in infants. Methemoglobinemia is a condition wherein some of the body's hemoglobin is converted to a form (methemoglobin) which does not allow efficient oxygen transport in the blood. It may cause a bluish color in the skin, if it is not too far advanced, or in the acute stage, it may lead to brain damage and ultimately to death. It is also possible that in high concentrations it can be metabolized to a nitrosamine, a potential carcenogen (cancer causing material). Because of its wide introduction via domestic and agricultural practices it constitutes one of the prime health risks to groundwater supplies.

Inorganic and organic chemicals from agriculture (e.g., pesticides) or industry constitute additional health hazards. Some, like chlorides, are primarily important because of their influence on taste. Others, like many of the pesticides, have proven toxicological effects, sometimes causing death. Radiological contaminants, as discussed in Section 4.4, are not only radiation sources, but may be extremely toxic as well.

Perhaps the second most important effect is on agriculture. The use of groundwater for irrigation is widespread and it is well known that as the amount of dissolved solids increase above a certain level in irrigation water, the crop yield decreases. Crops, like animals, also require trace amounts of inorganics and if these are over supplied or withheld the crop yield decreases. Thus it is not unusual to see a citrus crop yield decrease if water with too much boron is applied. In addition to irrigation, groundwater is used to supply water to farm and range animals. Thus the whole range of health issues described for humans is relevant to this case as well.

Finally, groundwater is a source of water for industry. Certain chemicals contained in the groundwater may lead to corrosion and other difficulties affecting industrial equipment. More often this is due to the natural mineralization of groundwater rather than to the introduction of chemicals by man to the groundwater system.

Further references on the effects of impaired groundwater quality on humans, animals, vegetation and industrial processes can be found in U.S. Public Health Service (1962), McKee and Wolf (1963), F.W.P.C.A. (1968), W.H.O. (1972), Kovda et al. (1973), Meyer (1973), Karubian (1974), and Chapters 3 and 4 of this report.

Several characteristics have been revealed by this brief overview of the problem. First, there are a wide variety of sources and potential pollutants. Second, the sources are widely distributed. Third, for the most part, the source and type of pollutant is associated with land use. Fourth, groundwater quality problems can be characterized as local or regional (point or non-point) in nature. Fifth, as quality impairing material is transported through the subsurface environment it is subject to a range of factors which tend to attenuate it. Sixth, although not previously emphasized, groundwater is a slow motion, slow response resource. This will influence one's attempts to prevent, monitor, or to clean up pollution. Seventh, the primary effect of impaired quality seems to be health related, although effects on agriculture and industry may be economically most significant.

2.2 Physical, Chemical and Biological Aspects of Groundwater Contamination

Most potential groundwater contaminants are released at or slightly beneath the land's surface. Here the wastes are subject to the processes of leaching and percolation which may lead to their introduction into the groundwater. As they move through the unsaturated zone above the groundwater table it is the tendency of contaminants to attenuate; a process which sometimes eliminates potential contamination sources as serious problems, because the contamination simply does not reach the groundwater in sufficient strength (LeGrand, 1965). This sub-section describes the physical, chemical and biological processes that influence the movement of contaminants through the soil of the unsaturated zone and in groundwater aquifers.

2.2.1 Physical Aspects

Contaminants which are introduced into the environment as waste solutions are already mobile, but dry solid materials must be leached; that is, they must be dissolved before they can move. The solution of various contaminants is basically a chemical phenomenon and is discussed later. Once available in mobile form the solute (hydrocarbons and other nonsolubles are not discussed here) is subject to an array of physical properties and characteristics which influence its movement and distribution.

Zone of Aeration

Consider first the movement of a solute through unsaturated zone, or zone of aeration, to the water table. The movement through this zone is primarily vertically downward from the surface, and the solute is suspended to undergo only a mild degree of horizontal displacement. Since the solute movement depends to a great extent on the movement of water, it must also depend on the same physical factors. In unsaturated systems it is known that the following six hydraulic and mass transport properties or characteristics influence the degree of pollutant movement (Biggar and Nielsen, 1967; Thomas, 1970; Bresler, 1973; Wilson and Gelhar, 1974):

a. The hydraulic conductivity (in Darcy's Law) of the soil and its dependence on the soil moisture (water) content. The hydraulic conductivity together with the hydraulic gradient determine the rate of movement of water due to boundary influences (boundary conditions) at the surface and/or water table. If the hydraulic conductivity of the soil is high enough, then the upward movement of salts due to evaporation at the surface is likely to be high and salts may accumulate at the surface. If the solute is available along with a moisture source, like rain, it is likely to penetrate the unsaturated zone deeply, depending on moisture content.

b. The moisture (water) content of a soil represents the relative volume of the soil occupied by water. When the soil is saturated, all of the soil voids are filled with water and the moisture content equals the porosity. The downward movement of solutes is especially influenced by the moisture content. Generally lower moisture contents, as in sandy soils, result in a greater degree of downward movement of the solute.

c. The amount of active pore space vs. the amount of inactive, or 'dead-end' space also influences the relative degree of movement. This is particularly a problem in unsaturated or aggregated soils having large pores which readily transmit water, and much smaller or isolated pores which admit solute primarily via molecular diffusion. As a result the solute moves through the soil more quickly due to the decreased active moisture content; yet, at the same time, some of the solute lags behind as it gets trapped in the inactive pores.

d. The degree of heterogeneity of the soil has two influences. If this refers to the pore size distribution it results in the 'dead-end' pore effect. If it is due to soil sediment stratification it results in spatially varying moisture profile and hydraulic conductivity, which in turn influences the rate of solute movement.

e. The boundary conditions to the unsaturated zone influence the amount of moisture available for percolation and/or evapotranspiration. Consequently it is the boundary conditions which determine whether a given soil will be experiencing upward or downward movement of water and solute at a given time. In humid areas, after the first few centimeters of soil depth, the primary direction of flow is downward. In arid regions it will be upward during periods of high evapotranspiration, and downward during periods when water is available (as during irrigation).

f. As it moves through the unsaturated zone the solute will spread out. In part this may be due to the 'dead-end' effect. But it is also due to dispersion, a process described below for saturated flow. In unsaturated soils, dispersion is often more important than in saturated flow, although it is generally secondary to the process of convection; that is, mixing due to dispersion is often secondary to the average movement of the solute with the percolating water.

The climate of a region also influences these physical properties and characteristics (Thomas, 1970; Parizek, 1973). The distance that solutes move downward depends on the amount of water entering the soil. The more rainfall that occurs the deeper a solute can be expected to penetrate a given soil. If it is in the upper 30 cm of soil, a solute may travel back toward the surface due to evaporation. If enough rain falls to remove the solute from this zone it will probably enter the groundwater. Therefore, in arid regions or during the summer, when evaporation is important, the total rainfall of each storm is just as important as the total precipitation. But when evaporation is negligible, low intensity rainfall is more efficient in moving contaminants since there will be less runoff.

Transpiration becomes important as plants grow larger during the growing season. This, along with evaporation, may serve as an hydraulic trap holding salts and nutrients in the root zone of the plants.

The climate also influences the hydraulic properties of the soil water, viscosity and surface tension, since they depend on temperature. Consequently soils drain slowly during cold weather and not at all when frozen. As the solution freezes salts are concentrated in the non-frozen liquid. It is not unusual to find brines in partially frozen soils resulting from this concentration process; brines that become selectively mobile because of their hydraulic properties.

It may take years for a solute to percolate through the zone of aeration, even in the absence of chemical effects, due to the slow rate of movement of percolating water. On the other hand, it may take a pulse of water only a few weeks or months to move the same distance. The pulse of 'water' is like a flood wave in a river, representing not the actual movement of water particles, but only the movement of a pressure ridge. Even so, under favorable circumstances the solute may reach the water table in a matter of hours, although days or weeks is a more realistic time span. Once the pollution reaches this saturated zone it usually spreads out laterally and moves in the general direction of groundwater flow.

The Groundwater System

Located along the top of the aquifer at the water table the contaminants must either penetrate into the aquifer or float on top. The latter occurs when the contaminated water is buoyant, say due to a high temperature for a miscible pollutant; or more likely in groundwater systems, this is due to an immiscible fluid of low density as in the case of hydrocarbons like fuel oil or gasoline. After entering the groundwater system the pollutant is convected toward the natural discharge area of the aquifer, which may be a stream, river, lake, spring or wetlands; or toward groundwater extraction activities in the vicinity.

The convective movement of the polluted water is subject to a number of physical factors identical or similar to those listed for the zone of aeration. That is, the convective motion of the pollution depends on the groundwater flow field, which in turn depends on the peizometric head (ϕ) distribution (called the water table configuration in an unconfined aquifer), the distribution of hydraulic conductivity, and the sources and sinks of water influencing the aquifer (the boundary conditions). In confined aquifers the flow is primarily horizontal due to the presence of the confining layers, unless there is a significant dip of the formation. In unconfined aquifers the flow is still primarily horizontal, although density effects, additional recharge at the surface and dispersion lead to limited vertical movement.

When dealing with a quantitative analysis of aquifers we often average its properties and characteristics over the vertical (Walton, 1970; Bear, 1972). Thus, for example, the hydraulic conductivity (K) is replaced by a factor called the transmissivity ($T=Kh$, where h is the aquifer height and K is an averaged conductivity). A flow field evaluated on this basis assumes horizontal flow, and since this is often the case in practice, it is usually an adequate representation of reality (see Section 5.5.1). But the rate of movement of the pollutant depends on the effective porosity (n_e), as well as the flow field; and it, too, is often averaged over the vertical. The resulting velocity or rate of movement V is given by

$V_i = (K/n_e)\ \partial\phi/\partial x_i$ where x_i is the direction of flow. In a porous media field observations indicate that the natural rate of movement of pollutants varies from 5 ft/year to 5 ft/day; in fractured or fissued media, because of the low porosity, the rate may approach 1000 ft/day (Todd, 1973a). Naturally the direction of pollution movement is aligned with the flow field. The geohydrologic aspects of groundwater pollution are presented in Brown (1961), Parizek (1973), Todd (1973a) and Blair (1974).

As the pollution moves through the aquifer it mixes due to density effects, if any, and due to a phenomenon described by the term "dispersion". The term really represents a hierarchy of effects, each on a different scale. At the smallest scale there is molecular diffusion, due to the Brownian motion of individual molecules, which results in the mixing of two adjacent miscible liquids even if there is no flow. This phenomenon is generally of no importance in groundwater situations, but it may be very important in the unsaturated system (see, e.g., Wilson and Gelhar, 1974).

On a slightly higher scale there is mechanical dispersion. This is mixing due to the local velocity field in the porous media. Because the media is tortuous and because there is a velocity profile across each individual saturated pore, the local velocity varies from point to point. Consequently, two water particles which are initially adjacent, will experience different velocity histories in strength and direction as they move through the porous media; and at some time later they will arrive at different locations. Their general movement will have been in the direction of flow as shown by the average of many particles initially in the same general location; but their final location will differ from the average with respect to longitudinal (in the direction of flow) and lateral or transverse (in the orthogonal direction)displacements.

Molecular diffusion leads to isotropic mixing with respect to the flow. Mechanical dispersion, which depends on the flow velocity (V_i), causes a greater degree of mixing in the direction of flow, the longitudinal direction, than in the lateral direction. It can be shown that these dispersive phenomena are represented by a Fickian law, in terms of a concentration gradient and a dispersion coefficient (Bear, 1972). For molecular diffusion this coefficient (D_d^*) is the diffusion coefficient (D_d) for the given solute in bulk water at a given temperature and concentration, adjusted for the presence of the porous media ($D_d^* \cong 2/3\ D_d$ for saturated flow). For mechanical dispersion the coefficient is often simplified to linear relationships $D_L = \alpha_L V_i$ for longitudinal dispersion and $D_T = \alpha_T V_i$ for laterial dispersion, where α_L and α_T are "dispersivities" representing the effect of the pore structure on the dispersion (Bear, 1972). Typical laboratory tests indicate α_L is the range of 0.1mm to 10cm, and that it is roughly correlated to the grain size of the porous media. In unsaturated flow the relationship is more complicated (Wilson and Gelhar, 1974), and α depends on the moisture content.

The two effects as characterized by their coefficients can be added to yield a "hydrodynamic" dispersion coefficient (e.g., $D_L' = D_L + D_d^*$), and it is this coefficient which is used in most modelling (see Section 5.5.1). If the flow velocity is high enough, then $D_L' \cong D_L$ and molecular diffusion is neglected. These processes of hydrodynamic dispersion are discussed in Bear et al.(1969), Fried and Combarnous (1971) and Bear (1972).

There is another higher level of dispersive mixing. Natural aquifer materials are made of stratified layers, or fractures and **fissures with** a geometrically consistant pattern. Considering only the case of stratified materials, each layer of the material has its own characteristic hydraulic conductivity. Consequently, the rate of flow and pollutant movement through the different layers varies; for example, the more permeable layer is characterized by a high velocity. At the same time many of models (see Section 5.5.1), mathematical analyses (see Walton, 1970 or Bear 1972) and field data (see Section 2.3) average properties over the vertical to an extent. In the case of field data this is due to the finite vertical length of perforated well casing. Consequently we deal not with the average velocity in each layer and the mixing about it, but with an average velocity in the aquifer and the mixing about this new average. The degree of mixing at this scale will be characterized by the geometry and conductivity variation of the aquifer materials. Mercado (1967) and Marle and Simondoux (1966, as presented in Fried and Combarnous, 1971) have shown that the gross mixing in heterogeneous deposits like these can still be assumed to behave as the mixing due to hydrodynamic dispersion. In this case, however, the dispersivities are much larger reflecting the field conditions. For example, Pinder (1973) found values of α_L = 70 ft. and α_T = 14 ft. for a glacial aquifer on Long Island, New York, which was approximately 110 feet thick.

Combining convection with the average velocity as determined by the flow field and dispersion, we can describe the movement of a conservative, non-interacting pollutant in the aquifer. For example LeGrand (1965, also in Todd, 1973a) has catalogued a range of contamination patterns or plumes which extend downstream of various point pollution sources. He notes that there are two opposing tendencies with respect to groundwater contamination problems. First, there is the tendency of contaminants to be entrained in groundwater flow. Second, there is the tendency for contaminants to be attenuated to varying degrees by dilution with water, decay with time, and sorption on the aquifer materials (see Section 2.2.2). The first tendency and to some extent the second, can be attributed to the dispersive phenomenon. This explains why plumes typically have much larger longitudinal than transverse extents, since $\alpha_L >> \alpha_T$. The attenuation due to dilution can occur by dilution with natural or artificial recharge water as well as by dispersion.

The mechanism of pollution introduction also influences the behavior of the plume. So far, this section has emphasized pollution due to the leaching of soluble materials, percolation through the zone of aeration and introduction to the water table. Pollution can also come from a hydraulic connection with contaminated surface water, direct injection, short-circuiting from one aquifer to another through abandoned well-casings and the like, through leakage via a semi-permeable confining bed, or from salt water intrusion. Each of these either influences the flow field and/or determines the type of contaminant boundary condition on the flow field.

Once introduced into the system the plume is further influenced by local pumping and recharge patterns, so that the flow pattern and the movement of a plume depends on man as well as on nature (Brown, 1961; Deutsch, 1961, 1963; Geraghty and Miller, Inc., 1972; Meyer, 1973; and Todd, 1973a, all provide examples of the effects that these factors and the mechanism of introduction have on the distribution of pollution.)

When the source of pollution is widespread, such as non-point agriculture pollution, plumes do not exist or are unimportant on a regional scale. Instead there is a gradual decline in the quality of water as it moves through the aquifer. Users in the up-gradient portions of the aquifer have relatively high quality water. Users at the downstream end of the aquifer receive all of the non-degradable pollution inputs to the aquifer and have a much lower quality of water. For example, Orange County at the downstream end of the Santa Ana Watershed in Southern California is experiencing total dissolved solids (TDS) concentrations over 600 mg/L. Just over 40 miles up-gradient, near San Bernardino, the same aquifer has TDS values are less than 250 mg/L. Between these points are various urban and, more importantly, agricultural facilities which reuse the water several times.

Even when the regional aquifer system is made up of many small aquifers, such as in the glacial geology of the New England region of the United States, well distributed pollution sources can still be characterized on a regional basis. For example, in Massachusetts the concentration of chloride gradually decreases in local aquifers as one moves inland from the city of Boston, and the sea coast (Gelhar and Wilson, 1974). The source in this case is the use of sodium chloride for highway deicing, a technique which is more common in the densely settled region near the ocast. Naturally the salt concentration in any one particular location can contrast significantly with this regional trend depending on local effects.

2.2.2 Chemical Aspects

As water moves through the soil in the zone of aeration, or through rock or porous material in a groundwater aquifer, its composition changes. The water is in contact with various soil and rock minerals, with the organic and inorganic constituents of soils, and with gases in the atmosphere or produced by biological or other processes. The result of these contacts is solution, or chemical reaction followed by solution, and the water accumulates numerous dissolved impurities (Hem, 1961). This, however, is only the most basic reaction or chemical characteristic that must be considered in an analysis of groundwater pollution. It is this natural leaching process which leads to the background concentration levels of organics, salts, metals, etc. in our groundwater (e.g., see Walton, 1970).

This section is a review of the basic chemical phenomena that are important in many groundwater pollution problems. In a short list these are: volatility, acids and bases, solubility and precipitation-solution, oxidation-reduction (redox), surface phenomenon including ion-exchange and adsorption, and the particular aspects of organics and heavy metals, including hydrolysis. Biochemical phenomenon and nutrient cycling are discussed in the next section.

Volatility

The volatility of a chemical when it has been deposited on the soil surface, or as it moves through the zone of aeration, is an important mechanism for removing that chemical as a possible groundwater pollutant. The loss of a chemical through volatilization is a function of its vapor (partial) pressure and water solubility in the soil in question. For example, volatility is decreased in soils which strongly adsorb the chemical and is also dependent on moisture content. Most of the pollutants typically observed in groundwater systems are not volatile, or they would never have passed through the zone of aeration. But some materials, notably synthetic organics like certain insecticides, are volatile and significant amounts are lost to the atmosphere each year.

Volatility is also important with respect to dissolved gases in water. The amount of dissolved carbon dioxide and oxygen are very important parameters in terms of precipitation-solution and redox reactions. If a sample of groundwater is exposed to the air some CO_2 and O_2 will dissolve in the sample. The result is that the sample may change in several of its chemical characteristics including, as examples, pH, redox potential, and carbonate solutility.

Acids and Bases

The hydrogen-ion (H^+) concentration is expressed as the pH, which is the reciprocal of the logarithm to the base 10 of the hydrogen-ion concentration in moles per liter (M/L). A neutral water has a pH=7.0, indicating equal amounts of H^+ and OH^- ions. Most groundwater has a pH in the range 6-8 (Walton, 1970).

The composition of groundwater is influenced by the reactions of acids and bases. Acids, which have their source from the atmosphere or human activities, are, in a sense titrated in the groundwater system with the bases that have been set free by weathering processes (Stumm and Morgan, 1970). The hydrogen-ion concentration plays an important role in preiciptation-solution and redox reactions, surface phenomenon, and biological processes. It, in turn, is influenced by biological activities and physical phenomena which determine the amount of dissolved carbon dioxide, since $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$. Its been observed that the pH generally decreases during oxidation, and that it increases during processes like sulfate reduction and denitrification (see Section 2.3.3 and Stumm and Morgan, 1970).

The most common bases are bicarbonate (HCO_3^-) and carbonate ($CO_3^=$) because of the widespread distribution of carbonate minerals like calcite. Less important bases are borate, phosphate, arsenate, ammonia and silicate; and they may be available due to natural weathering and solution, or due to human activities. For example ammonia and phosphate are agricultural fertilizers. Acidity may be found due to industrial waste disposal activities, to the hydrolysis of metal ions or due to boric acid, silicic acid, ammonium ions and the like. The most important acid is H_2CO_3 which is formed by the solution of CO_2 in water. The basic aspects of acid-base reactions in aquatic systems are reviewed by Stumm and Morgan (1920); and additional information can be found in Hem (1961, 1972).

Precipitation- Solution

The amounts and kinds of dissolved material in groundwater reflect its history of contact with minerals, organics, inorganic salts and gases. In an aquifer, because the movement of water is very slow, the solution of chemicals is subject to a relatively stable set of conditions. With this slow movement and large surface area for the liquid to interface with the solid matrix, there is a long contact period which is often characterized by the establishment of chemical equilibria between the liquid (solute) and solid phases (Hem, 1961). This equilibrium condition, however, does not hold as well for the zone of aeration, near sources of organic or industrial wastes or near areas that are undergoing large pressure or temperature changes due to pumping or injection.

The major, secondary, minor and trace constituents dissolved in natural groundwaters and information describing the range of background concentrations are given in Table 2.1.

The total dissolved solids (TDS) of a sample of water includes all the solid material in solution. It is often used to characterize the degree of solution and concentration which has occurred, such as due to water re-use. It does not include colloids, dissolved gases or suspended matter. It can be measured chemically or by measuring the electrical conductivity (EC) of a sample. The EC depends not only on the TDS, but on proportion of the various ionic species in solution. In most natural groundwaters EC ranges from 100 to 5000 micromhos /cm at 25°C, where 1 ppm $\cong$ 1.56 (EC) x 10^{6}, depending on the sample (Walton, 1970).

The solubility of a given compound in water is controlled by variations in temperature, pressure, hydrogen-ion concentration (pH), redox potential (Eh), the presence of organic matter, the type of mineral, and the relative concentrations of other substances in solution. Using well established chemical equilibria principles the theoretical amount of dissolved substance can be determined. For example if solid compound

TABLE 2.1

Dissolved Constituents in Groundwater

(After Davis and DeWiest, 1966)

Major constituents (range of concentration 1.0 to 1,000 ppm)

- Sodium
- Calcium
- Magnesium
- Bicarbonate
- Sulfate
- Chloride
- Silica

Secondary constitutents (range of concentration 0.01 to 10.0 ppm)

- Iron
- Strontium
- Potassium
- Carbonate
- Nitrate
- Fluoride
- Boron

Minor constituents (range of concentration 0.00001 to 0.1 ppm)

- Antimony
- Aluminum
- Arsenic
- Barium
- Bromide
- Cadmium
- Chromium
- Cobalt
- Copper
- Germanium
- Iodide
- Lead
- Lithium
- Manganese
- Molybdenum
- Nickel
- Phosphate
- Rubidium
- Selenium
- Titanium
- Uranium
- Vanadium
- Zinc

Trace constituents (range of concentration generally less than 0.001 ppm)

- Beryllium
- Bismuth
- Cerium
- Cesium
- Gallium
- Gold
- Indium
- Lanthanum
- Niobium
- Platinum
- Radium
- Ruthenium
- Scandium
- Silver
- Thallium
- Thorium
- Tin
- Tungsten
- Ytterbium
- Yttrium
- Zirconium

AB is assumed to have a constant surface area, the solubility product K_{eq} is

$$K_{eq} = [A]\ [B]$$

in which [A] and [B] are concentrations in M/L of ions A and B. Observing the slightly more complicated carbonate equilibria, $CaCO_3$ (solid) + $H^+ \rightleftarrows HCO_3^- + Ca^{+2}$ this becomes (Hem, 1961)

$$K_{eq} = \frac{[C_a^{+2}]\ [HCO_3^-]}{[H^+]}$$

or

$$pH(eq) = -\log\ (\frac{[C_a^{+2}]\ [HCO_3^-]}{K_{eq}}$$

This illustrates the dependence of carbonate equilibria on pH, and thus on the amount of dissolved CO_2. Walton (1970) for example, reports on the case of a regional groundwater flow system in which the carbonate hardness of groundwater increases in the direction of flow, until the CO_2 concentration is exhausted. After that the hardness of the groundwater remained constant.

The solubility for other compounds can vary from the simple to the complex. For example, in concentrations and amounts expected in groundwater systems, even polluted ones, NaCl is completely soluble. On the other hand, the solubility of metals and the synthetic organics is influenced by the range of factors mentioned earlier. As an example consider iron. Hem (1961) describes the stability fields of iron in water which has 100 ppm HCO_3^- and 10 ppm SO_4^{-2}, in the range of pH and Eh normally found in groundwater. This system is more precariously balanced than the calcite-carbonate system (Hem, 1961). For example, if the redox potential is raised by adding air, metal Fe(OH$_3$) may precipitate. This can also be brought about by raising the pH. Polluted water can also contain materials that will decrease the redox potential or pH, possibly dissolving previously precipitated metals into solution. Also, note that the stability fields will shift if the amount of HCO_3^- or SO_4^{-2} changes.

Many toxic compounds have extremely low solubilities in soil-water or groundwater systems. But unless this soluble component is removed via surface phenomena like adsorption, it will remain mobile. The difficulty is that even at this low concentration the compound may remain extremely toxic in acute or, more likely, chronic doses. Low solubility cannot be considered a guarantee that a compound is not a groundwater pollution threat.

More information on solubility can be found in Hem (1961), Davis and DeWeist (1966), Stumm and Morgan (1970), Walton (1970), Hem (1972) and Hall (1974).

Oxidation-Reduction

A full description of the chemistry of underground water must include a description of the influence of electrons on reactions. The redox potential of a solution, Eh, is a measure of the relative intensity of oxidizing or reducing conditions in a system. Oxidation refers to a chemical change in which there is an increase in oxidation number and reduction is a decrease in oxidation number; they always occur together and just compensate each other by a shift of electrons.

For example at a lower Eh than typical in groundwater and pH $\cong$ 9 the following precipitation-solution reaction takes placein an iron carbonate system: $FeCO_3$ (solid) + $H^+ \rightleftarrows Fe^{+2} + HCO_3^-$. But for the range shown in groundwater the reaction is a redox equilibria: $Fe(OH)_3$(solid) + $3H^+ + e \rightleftarrows Fe^{+2} + 3H_2O$. The term "e" represents a free electron with a negative charge.

Many of the waste products disposed of, or placed in the soil or groundwater systems are oxidizable materials. Included among these are many of the metals, organics and some of the inorganics. For example fertilizer ammonia is oxidized to nitrite, and this in turn in oxidized to nitrate (see Section 2.2.3) in soil systems. But the approach to equilibrium in reactions like these is very slow in purely chemical systems and, instead, nature depends on the biota to speed up this approach. By the application of highly efficient enzyme catalysts, soil and aquifer micro-organisms use non-equilibrium redox systems for respiration and consequently accomplish the additional job of helping the system approach equilibrium.

The biochemical aspects of redox reactions are discussed in Section 2.2.3. More information on the chemical aspects can be found in Hem (1971), Stumm and Morgan (1970), Hem (1972), and Hall (1974).

Surface Phenomena

The physico-chemical properties of soils and aquifer materials are due principally to the properties of colloidal material: Inorganic clays and organic materials like humus. Non-colloidal material, like sand and silt, have similar properties, but to a lesser extent. In essence these properties depend on the surface properties of the material: adsorption and electrokinetic behavior (Bailey, 1968). Adsorption has two forms: ion exchange and molecular adsorption, like the adsorption of water, waste waters, or polar organic molecules by clay.

Ion exchange is probably the most important property of the colloidal system because it affects all the other properties of the system (Bailey, 1968). Since soils contain significant amounts of colloidal material, as well as organics, this is certainly the case for them.

Cation exchange (cation adsorption) in colloids can be primarily attributed to isomorphic substitution. That is, the exchange of a cation in solution for one of the cations (usually of higher valence) in a layer of the colloid. This accounts for about 80% of the cation exchange capacity of the clay minerals montmorillonite and vermiculite. Exchange capacity, incidentally, is measured in terms of milliequivalents of ions per 100 g of solid. Montmorillonite, for example, has an exchange capacity of 80-150 Meq/100 g. Isomorphic substitution is rate limiting because the exchange sites are not always easily accessible.

In aquifer materials, and in colloids as well, broken bonds along the edges of minerals also provide cation exchange sites. The strength of these bonds is also generally greater for the smaller multivalent ions. However, this kind of bond is more ion specific and is often not reversible in terms of substitution of other ions. Consequently it is sometimes classed as adsorption, but not ion exchange (Ellis, 1973). Hem (1972) suggests that the exchange capacity of aquifer materials is in the order of 10 Meq/100 g. Because the exchange sites in this case are on the edges of the minerals this kind of reaction is much faster than is isomorphic substitution.

We've seen that since both colloids and other minerals (due to a crystal surface dominated by O_2 ions) have edge sites with a net surplus negative charge they tend to adsorb cations, and H_2O molecules as well. Since protons are also attracted to this surface, adsorption is a function of pH. Also we've seen that for both edge sites and isomorphic replacement, the smaller multivalent ions are preferred. Thus the relative ease of exchangeability is given by the series $Li^+ > Na^+ > K^+ > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$ (Davis and DeWeist, 1966). Lithium is held with the least force and barium the most.

The actual rate of exchange varies with the mineral type, the concentration of cations, the concentration of anions, and pH. For example as the surface area and percentage of colloids increases, so does the exchange capacity. Thus the exchange capacity of soils is given by the series (Bailey, 1968):

$$\text{gravels} < \text{sands} < \text{loams} < \text{clay loams}$$

The most studied exchange reaction has been that of sodium for calcium. This is an important reaction in irrigation practice. An unfavorable soil structure develops if the cation exchange complex is sufficiently saturated with Na, so that the soil deflocculates, tending to form impermeable crusts. In order to study this situation, and to provide a criteria for evaluating irrigation waters and soils, the sodium adsorption ratio (SAR) is used.

$$SAR = \frac{Na^+}{\sqrt{(Ca^{++} + Mg^{++})/2}}$$

A soil containing undesirable amounts of sodium can be leached with water containing Ca and Mg to remove some of the sodium.

Anion exchange also occurs, although it usually is not important. The only widely studied anion is phosphate which is easily adsorbed through a number of mechanisms, which are not well understood (see Section 4.2). Most other anions (e.g., Cl^- or NO_3^-) are not adsorbed by most soils.

From this discussion it is apparent that ion-exchange and adsorption are terms that are often used interchangeably. But there are some adsorption mechanisms which cannot be classified in any sense of the word as ion-exchange. These mechanisms fall under the earlier classification, molecular adsorption, which includes physical and chemical adsorption. Physical adsorption is due to van der Waals' attractive forces while chemical adsorption is due to coulombic forces (Bailey and White, 1964). This kind of molecular adsorption is probably the most important process by which chemicals are removed from pollution sources by soil or aquifer material. For example, the anion-exhcange capacity of soils and precipitation cannot account for the capacity of soils to retain phosphates. Instead phosphate interacts with iron and aluminum silicates present at the surface of layered silicates, and with iron and aluminum hydroxides in soil. Initially, this phosphate is relatively free to exchange with other similar anions, like arsenic $H_2AsO_4^{-2}$, but it is eventually so difficult to remove that it may have been incorporated in the soil solid phase as an impurity (Murrmann and Koutz, 1972).

Molecular adsorption is an important removal mechanism for synthetic organics, heavy metals, anions like orthophosphate, and, to a lesser degree, by some monovalent cations like ammonium or potassium. Soils with higher colloidal and organic content, and with iron and aluminum hydroxides, are usually more active molecular adsorption media. The strength of adsorption depends on the type of soil mineral, the insoluble organic content, the soil moisture, the pH, the chemicals in solution, and the nature of the chemical being adsorbed. Orthophosphate and arsenate are examples of competing species.

These ion-exchange and adsorption phenomena are discussed further in Chapter 4 and in Bailey and White (1964), Davis and DeWeist (1966), Bailey (1968), Society of Chemical Industry (1970), Stumm and Morgan (1970), Hem (1972), Murrmann and Koutz (1972), and Ellis (1973).

The combination of relatively irreversible ion-exchange, molecular adsorption and precipitation of a substance, which removes it from the soluble phase, is called fixation. Chemicals which have been fixed in the soil or in aquifer material cannot by definition be considered short-term pollution threats if the amount of chemical fixed is significant. However, fixation may be partially reversible in the long term leading to the release of chemicals into solution which were once immobile.

Heavy Metals and Organics

The presence or addition of metals to the soil or in an aquifer sometimes results in an interaction between the metal and the water which result in a slightly basic or acidic solution. These interactions are called hydrolysis. For example if solid NaCl is added to water there is no hydrolysis. The Na^+ and Cl^- ions do not appreciably affect the water equilibrium. On the other hand ferric iron would form a slightly acid solution: $Fe^{+3} + H_2O \rightleftarrows FeOH^{+2} + H^+$, a hydrolysis reaction. Certain metals, especially those associated with industrial pollution have to undergo hydrolysis before they can be leached to the groundwater system. Stumm and Morgan (1970) describe the importance of hydrolysis reactions in aquatic systems.

Organics are subject to biochemical oxidation and adsorption in soil systems. Coupled with their generally low solubility this usually means that organics must be transformed (oxidized) to be more mobile compound before they can cause serious problems. However, caution and experience dictates that this is not the case for a variety of circumstances (e.g., some organic herbicides and phenols).

Organic matter is removed from water by a number of processes. First, there is the physical filtration of insoluble matter. This is an important component of septic tank leaching fields and the disposal of waste waters on land. Additional information can be found in McGauhey and Krone (1967), McGauhey (1968), Thomas (1973) and Hall (1974).

The next process is the consumption of organic substance for respiration by soil or aquifer micro-organisms and for cell synthesis. The resulting products are usually more water soluble. There is also the precipitation of humus by microbial fermentation in anaerobic systems. This usually leads to a reduction in water solubility. We primarily deal with oxidation of organic matter because this may lead to increased groundwater pollution. But the last process adds to the adsorptive capacity of the soil, and reduces the threat of pollution from the surface.

Many organic compounds are easily adsorbed onto soil. In part this is due to their large molecular size, and in part to their structure. Organic exchange sites develop from the dissociation of acidic function groups, of which carboxyl is quantitatively the most important; as well as on colloidal or other mineral particles (Ellis, 1973). Consequently, the soluble organic exchange capacity of a soil is proportional to the amount of soil organic or humus. Naturally, aquifer materials have a much lower capacity to hold organics than soils.

Ion-exchange and adsorption of heavy metals by organic matter will limit the mobility of the metals. But there are also soluble organic substances which have similar chemical properties. These form metal/organic complexes, or chelates, with the metals in the soil solution. Chelates are important because in the formation of a new chemical species, metal ions have been made more soluble and less susceptable to adsorption. Because of this, the combination of organic and metal wastes may significantly enhance the mobility of the metals in the zone of aeration and in the groundwater zone.

Organics and their reactions in soils are described in Society of Chemical Industry (1970),Murrimann and Koutz (1972), Adams (1973), Ellis (1973) and Hall (1974).

A description of the various chemical processes is summarized in Table 2.2 and Figure 2.1, both taken from Murrimann and Koutz (1972). The table is organized into classes of elements and substances on the basis of their similar chemical behavior. Groups 1, 2, 5, 6 and 7 are of special note in groundwater pollution problems. The remaining groups are composed of immobile or innocuous species. The first group is composed of species which are common cations in groundwater systems, and are primarily subject to ion exchange, although some of the higher valence ions may form insoluble precipitates (e.g., Na^{++}). Group two includes species which are common anions, and are moderately to highly soluble and relatively mobile (e.g., NO_3^-). Group five is a set of soluble metal species which, to one degree or another, are commonly found in groundwater supplies (e.g., Fe^{++}). Group six forms a set of not so common trace metals, which usually are of low solubility, although they can form soluble organic complexes (e.g., Cu^{++}). Finally, group seven is a rough classification of the various organic compounds.

2.3.2 Biological Aspects

Biological activities have several mechanisms by which they influence groundwater quality. First there is the threat of transmission of pathogenic organisms from organic wastes to the soil, the groundwater, and

TABLE 2.2: Chemical Compounds in Relation to Soil Chemical Processes (Reproduced from Murrimann and Koutz, 1972.)

Elemental name	*Chemical notation*	*Species in solution*	*Soil chemical process*						
			Ion exchange		*Oxidation/Reduction*		*Common insoluble precipitates*	*Specific adsorption*	*Soluble organic complexes*
			Cationic	*Anionic*	*Ox-species*	*Red-species*			
Group One									
Lithium	Li	Li^+	I,O				None	No	No
Sodium	Na	Na^+	I,O				None	No	No
Nitrogen	N	NH_4^+	I,O		NO_3^-, NO_2^-	N_2O, N_2	None	M, I, V (m)	No
Potassium	K	K^+	I,O				None	M, I, V (m)	No
Rubidium	Rb	Rb^+	I,O				None	M, I, V (m)	No
Cesium	Cs	Cs^+	I,O				None	M, I, V (m)	No
Magnesium	Mg	Mg^{+2}	I,O				P, C, Sf	No	w
Calcium	Ca	Ca^{+2}	I,O				P, C, Sf	No	w
Strontium	Sr	Sr^{+2}	I,O				P, C, Sf	No	w
Barium	Ba	Ba^{+2}	I,O				P, C, Sf	No	w
Group Two									
Chlorine	Cl	Cl^-		I, O				No	No
Nitrogen	N	CN^-		I, O			None	No	No
Nitrogen	N	NO_3^-		I, O		NO_2^-, NH_4^+, N_2O, N_2	None	No	No
Sulfur	S	SO_4^{-2}		I, O		SO_2^{-2}, S^{-2}, S	Divalent cations	IH (w)	No
Selenium	Se	SeO_3^{-2}		I, O	SeO_4^{-2}	Se	Divalent cations, Fe^{3+}	IH (w)	No
Group Three									
Fluorine	F	F^-		I, O			CaF_2	IH, AH (s)	No
Phosphorus	P	$H_2PO_4^-$, HPO_4^{-2}		I, O			(Fe, Al, Ca) P	CM, IH, AH (s)	No
Phosphorus	P	Poly-P, Meta-P		I, O				CM, IH, AH (m)	No
Arsenic	As	$H_2AsO_4^{-2}$		I, O			Co-ppt with (Fe, Al, Ca) P	CM, IH, AH (s)	No
Silicon	Si	$Si(OH)_4$		I, O			Fe, Al, SiO_2		No
Molybdenum	Mo	MoO_4^{-2}		I, O			Co-ppt with (Fe, Al, Ca) P	CM, IH, AH (s)	No
Boron	B	$B(OH)_3$						IH, AH (w)	No
		HCO_3^-					$CaCO_3$, $MgCO_3$		No
Group Four									
Aluminum	Al	Al^{3+}, $Al(OH)^{+2}$	I,O				H, P		m
Beryllium	Be	$Be(OH)^+$	I,O				H		
Vanadium	V	VO_2	I,O				H		
Group Five									
Iron	Fe	Fe^{+3}	I,O			Fe^{+2}	H, P, C, Sf, Sd	CM, O (s)	s
Manganese	Mn	Mn^{4+}	I,O			Mn^{+2}	H, Sd	CM, O (m)	m

TABLE 2.2: (continued) (Reproduced from Murrimann and Koutz, 1972.)

			Soil chemical process						
Elemental name	*Chemical notation*	*Species in solution*	*Ion exchange*		*Oxidation/Reduction*		*Common insoluble precipitates*	*Specific adsorption*	*Soluble organic complexes*
			Cationic	*Anionic*	*Ox-species*	*Red-species*			
Group Six									
Silver	Ag	Ag^{+}	I,O				AgCl, Sd	I, O (s)	s
Lead	Pb	Pb^{+2}	I,O				H, Sf, C, Sd	I, O (s)	s
Mercury	Hg	Hg^{+2}	I,O				HgO, Sd	I, O (s)	s
Cadmium	Cd	Cd^{+2}	I,O				Co-ppt (Fe, Al), H	I, O (s)	s
Zinc	Zn	Zn^{+2}	I,O				Co-ppt (Fe, Al), H	I, O (s)	s
Copper	Cu	Cu^{+2}	I,O				Co-ppt (Fe, Al), H	I, O (s)	s
Nickel	Ni	Ni^{+2}	I,O				Co-ppt (Fe, Al), H	I, O (s)	s
Cobalt	Co	Co^{+2}	I,O				Co-ppt (Fe, Al), H	I, O (s)	s
Chromium	Cr	Cu^{+3}	I,O				Co-ppt (Fe, Al), H	I, O (s)	s
Group Seven									
	Organic	Undecomposed			Yes				
	Organic	Macromolecules			Yes			I, (s)	
	Organic	Non-polar			Yes				
	Organic	Polar			Yes			I, (w)	
	Organic	Cationic	I,O		Yes			I, (s)	
	Organic	Anionic		I, O	Yes			I, O	
	Organic	Metal chelates			Yes				

Footnotes:

I = soil inorganic components
O = soil organic components

P = phosphate
C = carbonate
Sf = sulfate
Sd = sulfide
H = hydroxide

M = mica
I = illite
V = vermiculite
Mt = montmorillonite
CM = clay minerals

IH = iron hydroxide
AH = aluminum hydroxide

w = weak interaction
m = moderate interaction
s = strong interaction

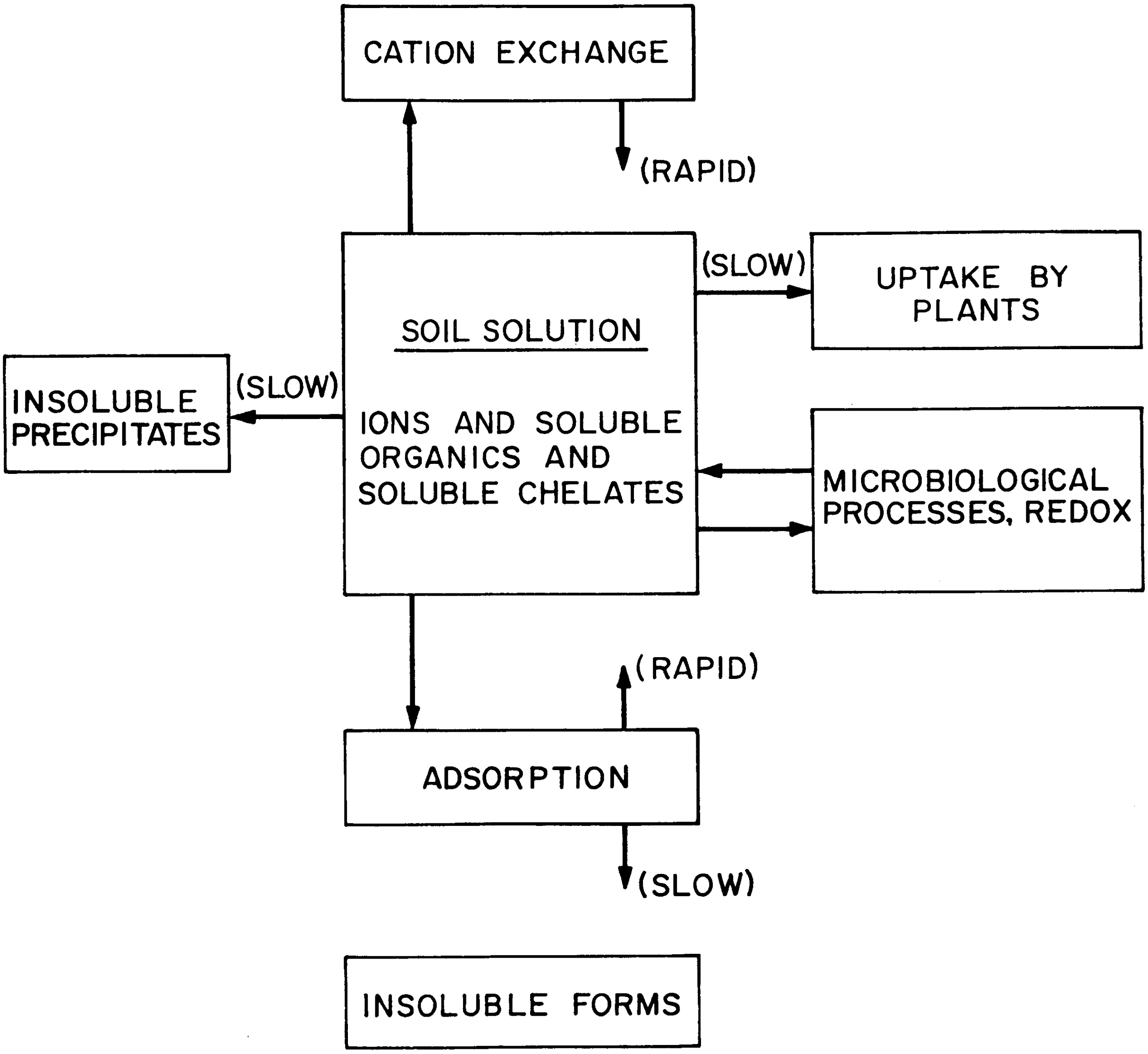

Figure 2.1: Active Chemical-Processes Leading to Pollution Attenuation. (After Murrman and Koutz, 1972.)

eventually to humans. Second, there is the threat of an increase in concentration of organic material which originates as wastes. These two mechanisms are associated with each other. Third there is the presence of micro-organisms which add in oxidation-reduction reactions of organics and inorganics in the subsurface environment. In terms of global nutrient cycling, and the threat of increased inorganic contamination of groundwaters, this may be the most important. We will examine this first.

Biological Actions Within the Soil

The ability of organisms in the soil to oxidize organic and inorganic compounds and to reduce inorganic compounds has long been known. The common use of septic systems and landfills show an understanding that the soil provides some protection to the ground water. Biologically, this protection is provided by all the organisms living in and on the soil complex including bacteria, algae, soil animals, actinomycetes, fungi, protozoa and higher plants. Each of these different groups contributes to the reduction of organic contamination reaching the groundwater. However, for this "Biological Filter" (Miller, 1973) to function properly it must have adequate oxygen, sunlight, and space. Thus the ability of the organisms to function is limited, as most systems are.

"In both agricultural and forest soils the microbial population is concentrated primarily in the surface 15 cm organic matter rich region of the soil and numbers decrease rapidly with depth." (Miller, 1973) Thus, another important limitation on the soil microbial system is the location of the organic or inorganic source relative to the top of the soil. For example, if the drainage field for a septic tank is too deep and the water table too high, there is less chance that the organics contained in the effluent will receive sufficient treatment by soil organisms. Another important limitation in waste treatment is on the amount of organic matter which can be applied. Excessive accumulations of organics can reduce soil aeration and cause the system to go anaerobic. Anaerobic decomposition is much slower, and can result in serious odor problems and reduce the rate of growth of larger plants in agricultural areas.

Perhaps the most serious threat to the "biological filter" is the application of environmental toxins such as phenolic compounds, pesticides, heavy metals, etc. If toxin application rates are not too high, and if the physical and physico-chemical adsorption properties of soil provide sufficient retention time ,the microbial populations are frequently able to eliminate environmental toxins.

Biological action is particularly important in the mobility and plant availability of ions in the soil. It influences biochemical reactions such as mineralization, immobilization, oxidation, reduction, chelation, volitization, precipitation and solution.

One way to study biological action is to examine the cycles of various materials in the soil and groundwater:

a. Nitrogen: The primary biological reactions relating to the nitrogen cycle within the soil are nitrification, denitrification, and mineralization. Nitrogen often reaches the soil in the form of organic nitrogen compounds which break down to ammonia. Frequently, the ammonia is adsorbed (see Section 4.2) onto soil particles until nitrifying bacteria (Nitrosomonas and Nitrobacter) oxidize it to nitrite and finally to nitrate. Once formed, nitrate is very mobile and leaches readily. It is also available to plants. Thus, it is advantageous to have the nitrogen applied to the top of the soil where the largest microbial population exists and where nitrate, once formed, will be within the root zone of higher plants. However, it is important to note that nitrifying bacteria are influenced by soil conditions (pH, ammonium concentration, etc.) and climate.

Denitrification is another important biological reaction within the soil complex. In this process facultative anaerobic, heterotrophic bacteria convert NO_3^- to N_2 and N_2O which are released to the atmosphere thus reducing the threat to ground water quality. The requirements for denitrification include availability of nitrate-nitrogen, nutrients for bacterial metabolism, neutral pH, anaerobic conditions, and sufficient substrates. This condition does not frequently exist in the lower unsaturated zone. It occurs in areas where the saturated zone is very shallow or soil is saturated.

Nitrogen fixing organisms are able to take N_2 from the atmosphere and use it directly in the building of cell materials. Once released to the soil these organic materials will decompose into ammonia and eventually contribute to the nitrogen in the soil complex, thorugh the process of ammonification or mineralization. This process represents an enzymatic reaction which converts organic nitrogen to ammonium.

The various aspects of the nitrogen cycle have been studied extensively in recent years. This is due to the potential health hazard posed by the presence of nitrate in the groundwater (see Section 2.1).

Most of these reactions have been studied extensively under controlled and specified laboratory conditions. But the organisms that promote these biochemical reactions are sensitive to environmental changes, and it is difficult to model and successfully quantify the entire nitrogen cycle.

b. Phosphorus: Although the quantity of phosphorus reaching the soil is usually very much smaller than that of nitrogen, it may not pose a serious threat to groundwater quality since there are mechanisms for its removal. The two means of removing phosphorus are fixation (adsorption) by Fe, Al, Ca, and clay minerals in the soil (see Section 4.2) and utilization by plants.

c. Sulfur: Sulfur does not present the environmental concerns associated with nitrogen. However, the reactions of microbial populations involving sulfur compounds can be quite important. Under aerobic conditions biological reactions can result in the mineralization of organic sulfates and the oxidation of metal sulfides and H_2S to $SO_4^=$ ($SO_4^=$ can be utilized by plants). However, under anaerobic conditions insoluble sulfides can be formed which can cause serious soil clogging.

d. Inorganic Ions: Other inorganic ions pose a serious threat to water quality if they leach to the groundwater. The soil microbial population also provides mechanisms for reducing this threat. These mechanisms influence the mobility of the ions and make them available to plants (Miller, 1973).

Additional information on the influence of the soil and aquifer microbial population and its influence on biochemistry can be found in McGauhey and Krone (1967), Bailey (1968), Pound and Crites (1973) and Hall (1974).

Pathogens

The threat to public health due to the transmission of pathogenic organisms is as real in groundwater as it is in surface water. Although it is generally agreed that the soil complex provides some protection against this threat, it by no means eliminates it. Pathogenic organisms which may reach the soil and eventually the groundwater include bacteria, viruses, protozoa, worms, etc.

Although some diseases caused by protozoa, worms and fungi can be water borne, bacterial water borne infections such as dysentery, cholera, and typhoid fever and viral water borne infections such as infectious hepatitis are the most important. Therefore, for purposes of this report the aspects of bacterial and viral contamination of groundwater will be discussed.

a. <u>Bacterial Contamination</u>: Sewage is the primary source of pathogenic bacterial contamination of water. The traditional methodology for monitoring both surface and groundwater for the presence of pathogenic bacteria has been to test for an indicator organism. Coliform bacteria, the most common indicator used, is a class of harmless organisms found in the intestines of many warm blooded animals including man and it is always present in human feces. However, because coliform can propagate outside of the host and there are other hosts besides man, its presence does not necessarily prove that there is contamination with sewage. Nevertheless the coliform test has been institutionalized into standard public health practice.

Several authors have suggested that specific tests should be made for the various pathogenic bacteria. However, due to the complexities of such tests, the costs and time involved, little has been done to change the standards. In addition, public health officials feel that the coliform test provides a factor of safety. They assume that a source would be closed, based on the coliform test, long before there would be a probable presence of pathogenic bacteria in sufficient numbers to cause illness or be sampled accurately.

When considering the bacterial contamination of groundwater, two factors are important; the ability of the organisms to survive in the soil zone and in the groundwater, and the ability of the organisms to travel through the soil matrix. When sewage or treated effluent reaches the soil complex, physical entrapment and physio-chemical adsorption by the soil slow the movement of pathogenic bacteria.

> "Fortunately most studies indicate a rather rapid die back of coliforms and bacterial pathogens reaching the soil so that the long term hazard to groundwater or surface waters is considered minimal under normal condtions." (Miller, 1973)

However, long survival rates, up to a year or more, have been reported under some unique conditions (Miller, 1973). Factors which effect the survival rate of pathogenic bacteria include physical conditions such as pH, moisture content, oxygen content, temperature, and soil structure as well as biological constraints. The mechanisms by which the soil microorganisms tend to eliminate foreign organisms is subject to some question. Some mechanisms that have been suggested include: "production of microbial toxins; enzymatic lysis; predatory protozoa; parasitic bacteria, fungi, phase; and the inability of aliens to compete effectively with the indigenous community for nutrients." (Miller, 1973).

Studies show that when sewage effluent is recharged directly into the groundwater that bacteria normally travel about 100 feet in the direction of normal groundwater movement and about 60 feet in other directions

(Stanley and Eliassen, 1960). Thus the threat to groundwater quality seems to be controllable. The primary limit to mobility appears to be physical filtering (McGauhey and Krone, 1968).

b. Viruses: The primary source of viral contamination of water is sewage, just as with bacterial contamination. There is no traditional method for testing for viral contamination and public health standards in general, do not contain any criteria on viral contamination (since viruses live longer than bacteria the coliform test cannot be considered applicable) despite several confirmed experiences with infectious hepatitis in water supplies. However, this lack of standards is in part due to the relatively recent understanding of viruses and viral diseases.

In general, very little is known about the survival of viruses in the soil or groundwater, or on the ability of viruses to travel through these media. Most laboratory experiments tend to indicate that viruses are removed from groundwater by entrapment and adsorption after travelling a short distance. The bound viruses are suspected to then be broken down by soil micro-organisms and environmental conditions (Akin et al., 1971). There are several possible explanations for the discrepancy between field, which indicates some viral mobility, and laboratory data, which does not. The possible existance of channels or fractures in the field could allow direct flow of contaminated water without percolation. In addition, lab tests have been carried out with different viral strains, not necessarily those found in the field.

When sewage effluents are applied to the ground surface there are climatic conditions which also may reduce the survival rate. These include desication, ultraviolet radiation, etc. However, at this point there is very little scientific information available to draw any conclusions on the survival rate of viruses within either groundwater or the soil.

More information on viruses can be obtained from the University of Illinois (1971).

2.2.4 Synthesis

The physical, chemical and biological mechanisms influencing the movement and distribution of groundwater pollution can be synthesized and represented conceptually. A mass balance in volume Ꝟ of a certain chemical species "A" requires

$$\underset{(1)}{\begin{bmatrix}\text{Rate of Accumulation}\\ \text{of mass of A in the}\\ \text{volume Ꝟ}\end{bmatrix}} = \underset{(2)}{\begin{bmatrix}\text{Net mass flux of}\\ \text{"A" into Ꝟ due}\\ \text{to convection}\end{bmatrix}} + \underset{(3)}{\begin{bmatrix}\text{Net mass flux of}\\ \text{"A" into Ꝟ due}\\ \text{to dispersion}\end{bmatrix}} + \underset{(4)}{\begin{bmatrix}\text{Source or}\\ \text{sink}\\ \text{of A}\end{bmatrix}}$$

The term flux refers to the rate at which a mass of A is transported through the boundary of Ꝟ. This is a rather simplistic model which lumps all the chemistry and biology into the source or sink term. For example, consider a situation in which adsorption becomes important: term (4) would be negative for adsorption (loss of "A" from liquid) and positive for desorption (gain of "A" to liquid).

Usually this model is presented in mathematical form as a mass transport differential equation. Bear (1972) and Fried and Combarnous (1971) provide descriptions of the resulting equation, with emphasis on the physical aspects. Boast (1973) and Kurtz and Melsted (1973) provide descriptions with more emphasis on the chemistry. Section 5.5.1 reviews numerical simulations which are based on this model.

The source or sink term takes on different forms depending on the chemical and/or biological processes in effect for a certain situation. They can also be used to account for the "dead-end pore effect" (Section 2.2.1) and for the introduction of pollution by man. Examples of chemical-biological sources are solution, desorption, ion-exchange, and the oxidation of species "B" to "A" (including the biodegradation of "B" to "A", e.g., NH_4^+ to NO_2^-). Sinks included are chemical precipitation, adsorption, ion-exchange, the oxidation of "A" to "C" (e.g., NO_2^- to NO_3^-), and the conversion of "A" to a gas (e.g., NO_3^- to $N_2\uparrow$).

A process dmoinated by geochemical processes would necessarily include terms (2) and (4), but not necessarily term (1) and seldom (3).

For example, the solution of carbonates in a limestone aquifer varies with space (hence term (2)), but is relatively steady state (hence term (1) is neglected). An example is given in Walton (1970). A process dominated by strong adsorption of "A" would necessarily include terms (2) and (4), possibly (1) and seldom (3). As the sorptive capacity of soil decreases (1) becomes more important and (3) needs to be considered. For a process involving the movement of a conservative species from a point source (1), (2) and (3) are important, but (4) may be neglected. As we can see from these examples this simple model represents all of the various components of the physical-chemical-biological system which influence groundwater pollution.

2.3 The Technology of Groundwater Pollution Detection and Observation

Action undertaken to manage water quality or, in other terms, to deter water degradation, requires an assessment of water quality status. This is generally based on the periodic observation of a set of parameters relating to water quality and the causes that modify it. A surveillance of these parameters is necessary in order to know whether the objectives of the control measure are attained. This process of observation and surveillance concerning water quality is known as water quality monitoring. The detection of pollution, in this case groundwater pollution, is based on an appropriate monitoring network and/or program.

2.3.1 Definition and Purpose of Groundwater Quality Monitoring

A specific definition of water quality monitoring (a concept not easily expressed with only one word in languages other than English) is given by the U.S. Environmental Protection Agency (Meyer, 1974) in these terms:

> "Monitoring of water quality might be defined as a scientifically designed program of continuing surveillance, including direct sampling and remote quality measurements, inventory of existing and potential causes of change, and analysis of the cause of past quality changes and prediction of the nature of future quality changes.
>
> Unfortunately, monitoring of groundwater is often thought of only in the context of sampling of wells and springs. Such sampling is a dominant or sole practice in most surveillance programs; however, sampling can be minimized and perhaps even eliminated in some cases by thorough inventory of possible causes and prediction of anticipated quality changes.
>
> For example, a situation in which direct sampling could be eliminated would be one where a planned activity is analyzed, major groundwater pollution predicted, and the planned activity is cancelled because of the unacceptable level of predicted pollution. An alternative outcome if the planned activity were implemented after analysis of the anticipated effects would be

> that the location and number of sampling points and the quality parameters analyzed would be minimized by anticipating the location of the source(s) and nature of pollution and by making predictions of rates and direction of pollution travel. The entire process described is thus considered to be monitoring".

Following this definition, the main purpose in monitoring groundwater quality can be stated as, "To obtain the type of information from which control decisions can be made." In terms of pollution this can be further described as, "To obtain an early warning of groundwater pollution" and/or "To determine the progress of pollution or changes in its composition."

Besides these aspects, surveillance of water quality in wells can fulfill other objectives more or less related to the prevention, elimination or research of groundwater pollution. For example, it can be used to determine suitability of water for an intended use, or to determine the treatment requirements for this use and the optimal treatment procedures. Another common use is to develop information on the natural movement of groundwater in an aquifer, or on the geological or natural chemical characteristics of the aquifer.

All these aspects can be expressed in a different way if a monitoring program is included in the water quality planning of a certain area (see Chapter 3). For example in California, or in the case study region of Chapter 6, a monitoring program could be described as having six purposes. First among these the program would measure the achievement of the water quality objectives sought after in the water plan. Second, it would measure the specific effects of water quality changes on the established beneficial uses in the plan. Third, it would measure the background condition of water quality and the long term trends. Fourth, the program would be designed to locate and identify sources of water pollution that can pose an acute or chronic threat to the environment. Fifth and sixth, it would aim at providing data for determining waste discharge compliance with permit conditions and the documentation to support the enforcement of permit conditions required for waste discharges. Finally the program should provide data to carry on the continuing planning process.

As used in this report four types of monitoring may be defined (Todd, 1973):

a. Ambient trend monitoring: Measurement of conditions and trends of groundwater quality in relation to standards and guidelines. These measurements should be representative of the total spatial situation (such as a groundwater basin) as well as local quality modifying influences.

b. Source monitoring: Measurements of effluents entering the groundwater that can affect groundwater quality.

c. Case preparation monitoring: Gathering of evidence for control of local existing or anticipated groundwater pollution situations.

d. Research monitoring: Measurements specifically related to research investigations.

At this point it is interesting to indicate that groundwater quality monitoring has been traditionally considered as the sole process of taking samples of water from wells or springs for chemical analysis. This aspect of monitoring is, of course, an important one; but in fact, it is only an indirect method of assessment of pollution problems, due to one of the following reasons (Karubian, 1974; items a-c):

a. Groundwater movement is very slow. The pollutants travelling with groundwater may reach the sampling well months or years after they have reached the aquifer.
b. As is explained later in the chapter, a sample of water taken in a well represents, in the best of cases, the quality of groundwater in a restricted area around the well. Pollutants move producing a plume which extends in the direction of flow and move very slowly (see Section 2.2), and it is necessary to measure at a great number of points to adequately represent the quality of the aquifer, increasing the costs of monitoring.
c. An attempt to follow the track of a pollutant from the detection point (well or spring) up to the source, without previous knowledge of the location of this source, is very difficult, if not impossible in actual practice; and the establishment of responsibility is risky.
d. The potential changes in well-groundwater quality, where high nutrient concentrations exist, must be taken into account and if possible avoided. Pumping is fine, but it still leaves you with an "average" sample.

Analyses of the pollution potential of a planned activity, and the monitoring of such an activity when already in operation, are more direct methods than the analysis of water in the wells.

In the present section, special attention is given to some practical aspects of monitoring, such as the kinds of parameters to observe in the sampling programs, the methods of sampling groundwater, and the design of an observation network of sampling points (wells, springs, etc.). Some suggestions are made about procedures for source monitoring. In Chapter 4 (as well as E.P.A., 1973; Meyer, 1973; Karubian, 1974) some of the specific aspects of monitoring the different activities are described, leaving to the present part of the report the more general concepts. Additional references may be found in Fuhriman and Barton (1971), Scalf et al. (1973), Todd (1973), Cole (1974) and Miller et al. (1974).

2.3.2 Elements in the Design of a Groundwater Quality Monitoring System

A properly designed monitoring system must take into account, as stated previously, the necessity to monitor not only the composition of water in wells, springs and streams, but some parameters related to the potential sources of pollution. In the establishment of a network of sampling points (wells, etc.) the decisive elements are the kind of parameters to observe, the sampling procedures, the areal distribution of wells in the system and the frequency of sampling. In any case, the purpose of monitoring in the specific area (ambient trend, local problems, etc.) has the greatest influence in the design. Five main elements in the design of a network of wells can be considered:

a. Specific purpose or purposes of monitoring in the area.

b. The geologic and hydrologic characteristics of the aquifer system.

c. Distribution of existing or future activities likely to pollute groundwater or surface waters; that is, classification of point or non-point sources.

d. Types of pollutants involved in those activities.

e. Location of existing or projected groundwater development areas.

f. Actual existing or future value of the groundwater resource.

These factors have a decisive influence in the design variables, and a previous evaluation of them is necessary to develop a successful monitoring system. As stated before, the monitoring system can be developed over the whole aquifer system, around a potential source area, around a zone where many extraction wells exist, etc.

In general, it is expensive to determine the areal distribution of groundwater quality over time. The number of sampling wells must be minimized in order to achieve the objectives at minimum cost. This can be done by analyzing the hydrogeological framework (water table, transmissivities, boundary conditions, recharge and discharge areas), coupled with the characteristics of the pollutants, and the potential pollution sites to determine the expected extent and movement of the pollution. Essentially, the desirable goal for an observation network is to know the degree of pollution at several points around the source of pollution, especially in the direction of groundwater extraction sites. To reduce the number of wells LeGrand (1968) proposes the establishment of four zones around a pollution site, whose previous knowledge based on the above-mentioned elements, can save money and effort; these areas are:

a. Zone of high concentration of pollutants.

b. Zone of moderate pollution in which the water is objectionable for use (later precursor zone).

c. Zone of detectable pollution in which the water quality is not seriously objectionable for use (early precursor zone).

d. Uncontaminated zone.

An early objective of the observation network could be to determine zones b and c and the general trend of movement, so that decisions can be made. An important consideration could be the definition of zone c, in which water is not seriously polluted; small quantities of pollutants or trace elements can provide an early warning of more serious problems. Following this approach, and in view of the high cost, the number of wells must be reduced to a minimum. Any mathematical model or analytical tool able to predetermine (see Chapter 5), even in rough approximation, the four zones mentioned, must be used to minimize the cost of observation. If a mathematical quality model is going to be developed, the observation points may have a direct relationship with the nodes of the model. Deininger (1974) discusses the design of environmental monitoring systems.

2.3.3 Observation Wells and Sampling

The composition of aquifer water is determined through the chemical (and physical) analysis of a sample of groundwater. The way this sample is obtained is of outmost importance in the further interpretation of the results; a properly designed monitoring system must take into account this fact. Erroneous interpretations can be made if the sampling method used is not thoroughly understood. For the purpose of description of the characteristics, limitations and significance of the various possible sampling procedures, a subdivision has been made between sampling a single aquifer (no other aquifers above or below) or multi-layered aquifers.

The most common and accepted method of sampling groundwaters in a single aquifer is to take a sample of water from a pumping well after some time since the start of pumping. In practice, the well is pumped until electric conductivity of water stabilizes. Usually 10 to 30 minutes of pumping is enough. At that time a sample is taken for analysis. The analysis of this sample represents the average quality of water in a zone of the aquifer which areally surrounds the well and that in depth depends upon the length and situation of the well screen.

As a first approximation, if quality variations in a vertical direction are considered negligible, if the bottom of the well reaches the impervious bottom of the aquifer, and if the well screen covers completely the saturated thickness, the sample represents the quality of groundwater around the well in an areal sense. Careful attention must be paid, thus, to depth of the well and the location of the well screen in relationship to the depth to the aquifer bottom and the saturated thickness; to the expected vertical variation in groundwater composition; and to the time since the start of pumping and stabilization of electrical conductivity.

Another method used in many cases is to take the water sample from a well not being pumped. Depending on the characteristic of the well and aquifer, the time since the end of pumping in the well, depth at which the sample is taken, etc., the analysis of a sample obtained in this way can show considerable variations, and is not recommended. If vertical water quality variations are expected in a single layered aquifer (as can be the case in a thick unconfined aquifer under lands used for intensive agricultural practices), some sampling methods can be applied.

a. The simplest one is to send into the well an electric conductivity probe and prepare a well log. The absolute values of E.C. are less important than the trend in variation of such parameters. In fact these variations are the only ones to be considered. This method is of limited value.

b. A special sampling device consisting of a receptacle which can be opened and closed from the surface, the thief sample, can be lowered into the well to different depths and samples taken. If the well has not been pumped for a long time, this method can give erroneous results.

c. Another method to sample at different depths in a single layered, water table aquifer, is to use a small pump. Locating it at different depths, the pump is used at very low rates (5 gallons per minute or so) for periods of(10-30 minutes and samples are taken at the end of these periods.

d. A variation of this method is the multipacker pumping method, mainly used in confined, multi-layered aquifers; above and below the pump, surface controllable packers are installed, giving assurance that water is withdrawn from a particular depth interval. This method, however, requires expensive equipment.

e. A variation of methods e and d employs the ejection of samples with an inert gas. This method is relatively simple and inexpensive and avoids contact of the groundwater with the atmosphere.

To perform water quality surveillance in multi-layered aquifers, some sampling methods have been devised.

a. If periodic surveillance of water quality in different superimposed aquifers has to be performed wells can be drilled to and perforated at different corresponding depths. Each well then is used to pump water from the corresponding aquifer, being sealed from the rest by impermeable layers and seals. This method is expensive, but water levels can also be monitored. It is the most common method used in multilayered aquifers.

b. If only one well, with screens in every permeable interval, is available, the multipacker method previously described can be applied, but in the long term this method can be more expensive than having several wells at different depths.

c. The method of using a telescope arrangement of casings in a single well, each casing corresponding to an aquifer has been utilized mainly to observe water levels, but can be applied for taking samples. The water can be withdrawn from the annular spaces by means of air under pressure. It appears that this arrangement for sampling has not been used in practice.

d. The method listed in paragraph e of the previous page is equally well suited to multi-layered aquifers.

Care must be taken in multi-layered aquifers that the observation method does not accidentally lead to the short circuiting of water from one aquifer to another.

The measurement of some parameters must be done in the field immediately after the sample has been taken. Concentrations of HCO_3^-, alkalinity and pH among others, can vary significantly from field conditions if the analysis is delayed. In the case of some parameters like concentrations of Fe^{++} and Mn^{++} it is necessary to add immediately a fixer to the water sample, since both cations have a great affinity for oxygen. Among the parameters whose measurement is recommended in the field are: temperature, pH, color, odor, electrical conductivity, dissolved oxygen, alkalinity, carbonate, bicarbonate, and dissolved CO_2.

Samples of groundwater can be analyzed for physical, chemical, biological and radiological constituents. Although the number of analyses to which a water sample can be subjected is very large, the number of parameters to observe at a given location is often quite small. Table 2.3 (Todd, 1973) gives the possible components of an exhaustive, pollution-oriented water analysis. Associated water quality standards are given in U.S. Public Health Service (1962), McKee and Wolf (1963), F.W.P.C.A. (1968) and W.H.O.(1972).

Some of the parameters listed in the table are anions, cations or other characteristics, which are normally found in easily measurable amounts in groundwaters (Davis and DeWeist, 1966). Their observation gives an idea of the overall "quality" of water for some common use, in the absence of other nondesirable components. Among these parameters can be included Na^+, K^+, Ca^{++}, Mg^{++}, Cl^-, $SO_4^=$, $CO_3^=$, HCO_3^-, NO_3^-, total dissolved solids, hardness, etc. Because these elements are found in relatively higher concentration in natural groundwaters than other more exotic components, they are easier to quantify, and hence, they are basic components of a standard water analysis.

Table 2.3

Components of a Complete Water Analysis (after Todd, 1973)

Field Data

Date of collection	Modify for reporting ground-water data
Time of collection	
Gage height	
Water discharge (cfs)	
Water temperature (°F)	
Other climatological data	

Silica (SiO_2)

Cations-Heavy metal ions

- Aluminum (Al)
- Iron (Fe), ferrous
- Iron (Fe), ferric
- Iron (Fe), total dissolved
- Iron (Fe), (without qualifying statement, refers to iron in solution when sample collected)
- Iron (Fe), in solution at time of analysis
- Iron (Fe), total (all forms of soluble iron plus iron extracted from suspended materials (turbid samples) with acid)
- Manganese (Mn), (without qualifying statement, refers to Mn in solution when sample collected)
- Manganese (Mn), in solution when analyzed
- Manganese (Mn), total (see total iron)
- Titanium (Ti)
- Chromium (Cr), trivalent
- Chromium (Cr), hexavalent
- Chromium (Cr),(total dissolved)
- Nickel (Ni)
- Copper (Cu)
- Tin (Sn)
- Lead (Pb)
- Zinc (Zn)
- Cobalt (Co)
- Arsenic (As)
- Selenium (Se)
- Cadmium (Cd)
- Antimony (Sb)

Cations-Alkali earths and metals

Calcium (Ca)	Earths
Manganese (Mg)	
Strontium (Sr)	
Barium (Ba)	
Beryllium (Be)	
Sodium (Na)	Metals
Potassium (K)	
Lithium (Li)	
Ammonia nitrogen as NH_4^+	

Free acidity (H^+) (calculated to pH 4.5)

Table 2.3 (continued)

Anions

- Bicarbonate (HCO_3)
- Carbonate (CO_3)
- Hydroxide (OH)
- Sulfite (SO_3)
- Sulfate (SO_4)
- Chloride (Cl)
- Fluoride (F)
- Bromide (Br)
- Iodide (I)
- Nitrite (NO_2)
- Nitrate (NO_3)
- Nitrogen (N), total dissolved
- Orthophosphate (PO_4)
- Phosphorus as PO_4
- Cyanides as (CN)
- Boron (B)

Organic, nonionic, and calculated values

- Phenolic material as C_6H_5OH
- Oils and waxes
- Organic matter (for example: humates, nitrobodies, detergents, weed sprays and insecticides)
- Total solids (dissolved and suspended)
- Loss on ignition
- Dissovled solids
  - Calculated
    - ppm
    - Tons per acre foot
    - Tons per day
  - Residue on evaporation at 180°C
    - ppm
    - Tons per acre foot
    - Tons per day
- Suspended solids at 110°C
- Hardness as $Ca\ CO_3$
- Noncarbonate hardness as $CaCO_3$
- Alkalinity as $CaCO_3$
- Saturation index (Langelier)
- Immediate acidity (H^-) pH 7.0
- Potential free acidity (H^+) pH 7.0
- Total acidity (H^+) pH 7.0
- Percent sodium
- Sodium adsorption ratio

Other data

- Specific conductance (micrombos at 25°C)
- pH
- Color
- Turbidity
- Density at 20°C
- Viscosity (centipoises at 20°C)

Table 2.3 (continued)

Biochemical, dissolved gases, and related measurements

- Odor
- Biochemical oxygen demand (and bacteria and viruses)
- Dissolved oxygen
  - Percent saturation
- Oxygen consumed
- Free carbon dioxide (CO_2)
- Sulfides as H_2S
- Chlorine (Cl_2)

Radioactivity

- Total alpha activity, micromicrocuries per liter
- Total beta + gamma activity, micromicrocuries per liter
- Radium (Ra), micromicrocuries per leter
- Uranium (U), micrograms per liter
- Radioisotopes (radioactive Sr, I, Co, etc.) micromicrocuries per liter

(This table was originally presented in The Water Encyclopedia, D. K. Todd, (Ed.), Water Information Center, Port Washington, N.Y., 1970.)

In an oriented monitoring system not all of these components will be quantified in the analysis. In some cases only one parameter is analyzed; such as, for example, electrical conductivity, which is approximately proportional to the concentration of total dissolved solids (TDS).

The selection of parameters to observe in each well is an important issue, because it affects the effectiveness of the monitoring process directly. The main factor to determine the type and number of parameters to observe is the kind of contamination expected. A previous knowledge of potential pollution sources and the nature and behavior of possible pollutants in the aquifer system is thus desirable.

No systematization in the kind of parameters to observe in each type of expected pollution seems to exist (although Meyer, 1973, and Karubian, 1974, summarize some of this information). For example, in the case of aquifers under areas of irrigated agriculture, the more important element to monitor may be the concentration of nitrates in pumped wastes, especially if they are going to be used for domestic purposes. On the other hand, if the groundwater is pumped for irrigation TDS may be most important (see Section 4.2 for a discussion of agricultural pollution). Some trace elements are often included in the regular analysis; especially when research monitoring is being conducted, or when monitoring the composition of groundwater around municipal supply wells. In any case the determination of observable parameters must take into account the fact that groundwaters dissolve and transport elements taken from the geological formations encountered in their path, whether or not man's activities affect this phenomenon. Biological analysis (coliform bacteria count) is especially recommended in cases where pumped groundwater is used for domestic supply.

In areas where the water management program includes recharge facilities problems with salt buildup can arise. In this case a general parameter such as total dissolved solids (TDS) concentration or electrical conductivity can be enough for the purposes of salts content control.

When organics are expected an organic compound analysis is performed. In general some of the organic compounds found in polluted groundwaters are stable, and their analysis is expensive. Evaluation of the total organic carbon (TOC) may be a comprehensive indicator of organic pollution load. To determine TOC carbonaceous compounds are converted into carbon dioxide, which is measured.

Heavy metals (trace elements) are analyzed in areas where industrial development can lead to higher than tolerable concentrations of these elements. The most typical are Al, As, Cr, Cu, Fe, Mn, Pb and Li.

Further references on methods of water quality analysis can be found in American Public Health Assoc., Inc. (1965), Fisherman et al. (1967), F.W.P.C.A. (1969), the A.S.T.M. Standards, Part 23, Water.

2.3.4 Operations in the Development of an Observation Network

The operations performed in practice to develop an efficient observation network over an aquifer system can be arranged as follows:

a. Evaluation of the design elements of Section 2.3.2.

b. Evaluation of present sampling programs. Historical quality data available in the system, if any, is not only important as a basis for comparison in the future, but it also provides a powerful tool in the assessment of rates of change and the response of the aquifer to changes in quality.

c. Selection of sampling points, including sampling methods and parameters to observe. It is always advisable to use already existing (if any) sampling points.

Usually wells are considered, but quality observation in springs and surface waters is often necessary or convenient due to the hydraulic connection between rivers and the aquifer. In addition electrical resistivity surveys (Davis and DeWeist, 1960; Todd, 1973) may be used to reveal the areal distribution of salinity.

As stated elsewhere in this chapter, samples can be taken at different depths covering different aquifers. In most cases only areal distribution of wells is considered, but the possibility of sampling different aquifers in the same well must be considered. Supply wells are considered as the first choice as sampling points. The distance between wells and the exact location of each well can only be determined in the light of the factors previously stated.

The frequency of sampling is determined taking into account that quality of groundwater in natural conditions varies little with time, and that, as Todd (1973) states, the influence of man's activities tend to cause an increase in the amplitude of annual changes, often due to the intensification of agricultural activity and a progressive deterioration over a period of many years, related to increased pumpage and/or increased production of wastes. The frequency of sampling depends upon the sensitivity of groundwater to changes in quality. Some suggested intervals include (Todd, 1973) daily or weekly sampling for rapid changes (such as effluent wastes directly injected into the ground); or bimonthly or quarterly sampling for annual changes; or annual sampling for background. Todd (1973) further suggests semimonthly, monthly or bimonthly sampling near pollution sources and semiannually sampling near or from pumped wells.

In practice,and if no significant monitoring operations have been developed in an area, its advisable to foresee during the first year a higher number of monitoring wells, sampled more frequently; in successive periods, the network and frequency are modified according to the particular characteristics of the area.

2.3.5 Pollution Source Monitoring

The periodic observation of some aspects of the potentially polluting activities can be considered as a part of the monitoring system, classically understood as only the network of wells. Among the source monitoring operations can be included (Todd, 1973):

a. Periodic monitoring of quantity and composition of waste fluids or recharge water injected in the ground and the facilities involved (recharge, waste injection in fresh water aquifers, or deep well disposal; see Sections 4.1 and 4.5).

b. Pipeline (oil pipeline, sewage pipes) and storage tank tests.

c. Regular review or inspection of land use, with the purpose of identification of new sources of groundwater pollution, which could then be individually monitored as appropriate (this includes treatment plants operation).

d. Notification and recordation of activities that could affect groundwater quality, such as, for example, volumes of recharged water, kinds and amounts of solid wastes disposed of in landfills, and schedules of truck transport of hazardous wastes.

e. Basin management: Regular surveillance of how a groundwater basin is being managed in terms of quantity will yield advance information on potential pollution. Extrapolation of trends in pumping and water levels could indicate incipient sea water intrusion, upward movement of connate brines and undesirable inter-aquifer or river-aquifer flows. The use of computer models in this regard is desirable (see Chapter 5).

f. Induced recharge of polluted water from rivers must also be regularly observed in those areas in which a hydrodynamic river-aquifer connection exists, as the polluted surface waters can enter the aquifer when the water table is below river level. Computer models can help in the assessment of the possible influent flow from the river due to future trends in pumping.

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CHAPTER 3

Methods and Effects of Controlling Groundwater Pollution

3.1 Introduction

The objective of this chapter is not only to give a list of technical, institutional and economic methods and effects of controlling pollution, but also to show the interrelations among the different methods and how they influence one another in an heuristic way. Control, as used here, means to prevent, if possible, or otherwise, to minimize pollution. Many of the concepts discussed here are treated in a comprehensive way, including not only groundwater but also surface water. The reasons are quite simple and can be explained in two ways. The first is related to the available literature; surface water was examined before groundwater, and a series of methods have been developed to control its pollution problems. Most of the methods for the control of groundwater pollution are simple extrapolations of these. The second reason is that good water resources management within a region or state implies the comprehensive study of surface and groundwater and quantity and quality problems in an integrated fashion.

The chapter starts by reviewing the concept of pollution and its relationship with the concept of externalities. Since pollution and its control involves the interaction between many technical, institutional and economic factors, the interrelationship between these are first discussed in general. The chapter next reviews these different factors in detail: first the technological methods for pollution control, then the different institutional frameworks necessary to achieve the same end, and finally the institutional, legal and economic measures to induce pollution control. In all cases the primary emphasis is on groundwater problems. The chapter ends with a discussion of the economic factors involved in the problem, dealing both with the financial aspects of pollution control and with the estimation of pollution control benefits and costs. A series of appendices which present numerical illustrations and examples of institutional settings in different countries completes the chapter.

3.1.1 The Concept of Pollution and its Relation with the Economic Concept of Externalities

To understand the relationship between pollution and the economic concept of externalities, an examination of a historical institution, the Common Property, is appropriate. The concept of the "commons" is very simple, consisting of a natural resource which cannot be reduced to individual ownership and therefore does not enter into the process of market exchange and the price system. With full ownership, the owner of a natural resource can receive compensation for the use of his property (the examples are so numerous that it is feasible to mention only one, i.e., a coal mine); but if this compensation doesn't exist because there is no owner, the resource is available at zero price, and the common is subject to congestion, overuse and quality degradation. The reason for such a situation is that an additional user will utilize the resource regardless of the costs or disutilities he is causing others, creating what economists call spill-over effects or externalities. A simple, but graphic example of this economic concept is the case of a lake where fish are caught; as soon as the number of fisherman overloads the fishing capacity of the lake, each additional fisherman increases the costs of fishing to the others by an amount (or externality) that he does not consider in his private calculations (Gordon, 1954; Scitovsky, 1954).

If in the economic transactions between a producer and a consumer, third parties are adversely effected, they bear costs that are not included in the private costs calculations of the producer; this causes social costs to be higher than private costs and the result is excessive production. Graphic examples to illustrate these concepts are discussed in detail in Appendix 3.1.

So far, the concept of the commons, the concept of externalities, the failure of the market to attach a price to its services and thence the misallocation of resources have been introduced. But where does the environment enter? The answer lies in the fact that the environment is the modern equivalent of the Common Property, and the pollution problem is a good example of economic externalities. The capacity of the environment to be used as a waste-receptor has historically been provided at a zero price, and the consequence has been the very same overuse, congestion, and quality degradation that plagued the commons years ago.

The ability of the environment to receive, store or assimilate the residuals generated as by-products of economic activity is an important natural resource of increasing value which should not be used at a zero price. How the new tragedy of the commons develops will depend upon the capacity of society to manage the environmental problems that it creates, since leaving it to the private market will necessarily end in complete failure.

3.1.2 Interrelationship Between the Technical, Institutional and Economic Aspects

Although the interrelationship between technical, institutional and economic factors is usually in the mind of all people who deal with pollution problems, in most cases the complexity of each of these factors precludes a more comprehensive and efficient management of the problem. Two kinds of approaches may be useful in understanding these complexities and interactions. The first one is the Materials Balance Approach, which is a positive model which describes the situation as it really is, and which shows the interdependency between the technical and institutional aspects as well as between parts of the economic ones. The second one is a normative model, and it shows how the economic and institutional aspects, as well as the technical ones should relate to each other when trying to establish the optimum level of environmental quality.

The first approach, the materials conservation law, states that nothing is consumed but merely transformed; in other words, the mass of the materials extracted from nature as an input to the economic activity should be equal to the mass of the final goods and residuals. Since final goods follow the same law, the conclusion is that the mass of inputs is equal to the mass of residuals materials (Kneese, Ayres and D'Arge, 1970).

If, with this in mind, one looks at the total weight of input materials, one obtains a good, though exaggerated, idea of what pollution problems can be like. However, it must not be forgotten that a high percentage of the total weight is discharged as hydrogen and carbon dioxide which can be reabsorbed by vegetation and water bodies without manifest harm, that industrial and household accumulation processes exist, and that the increase in the recovery of materials for recycling will ease the total burden.

A graph showing the materials flow is presented in Figure 3.1, in order to provide a better understanding of these concepts. An optimistic person, observing that most of the material ends up in the Residuals Processing Sector, would conclude that since engineers have solved other problems, they will surely find some solution to this one. However, although there is a wide range of treatment methods available for application to residuals, these processes can only change the chemical composition of the residuals or convert them form one form to another, but they can never eliminate the residual. This is because, for a given level of economic activity, a given efficiency of energy conversion, and a given degree of recycling and by-product production, the reduction of one type of residual must come at the expense of creating another type.

As an example, consider only the household sector. If advanced treatment is given to all household sewage, the waste water problem can be solved,but the disposal of the solid or semi-solid sludge will still create problems either to the air, if incineration is chosen, or to the land, if it is disposed of in solid form.

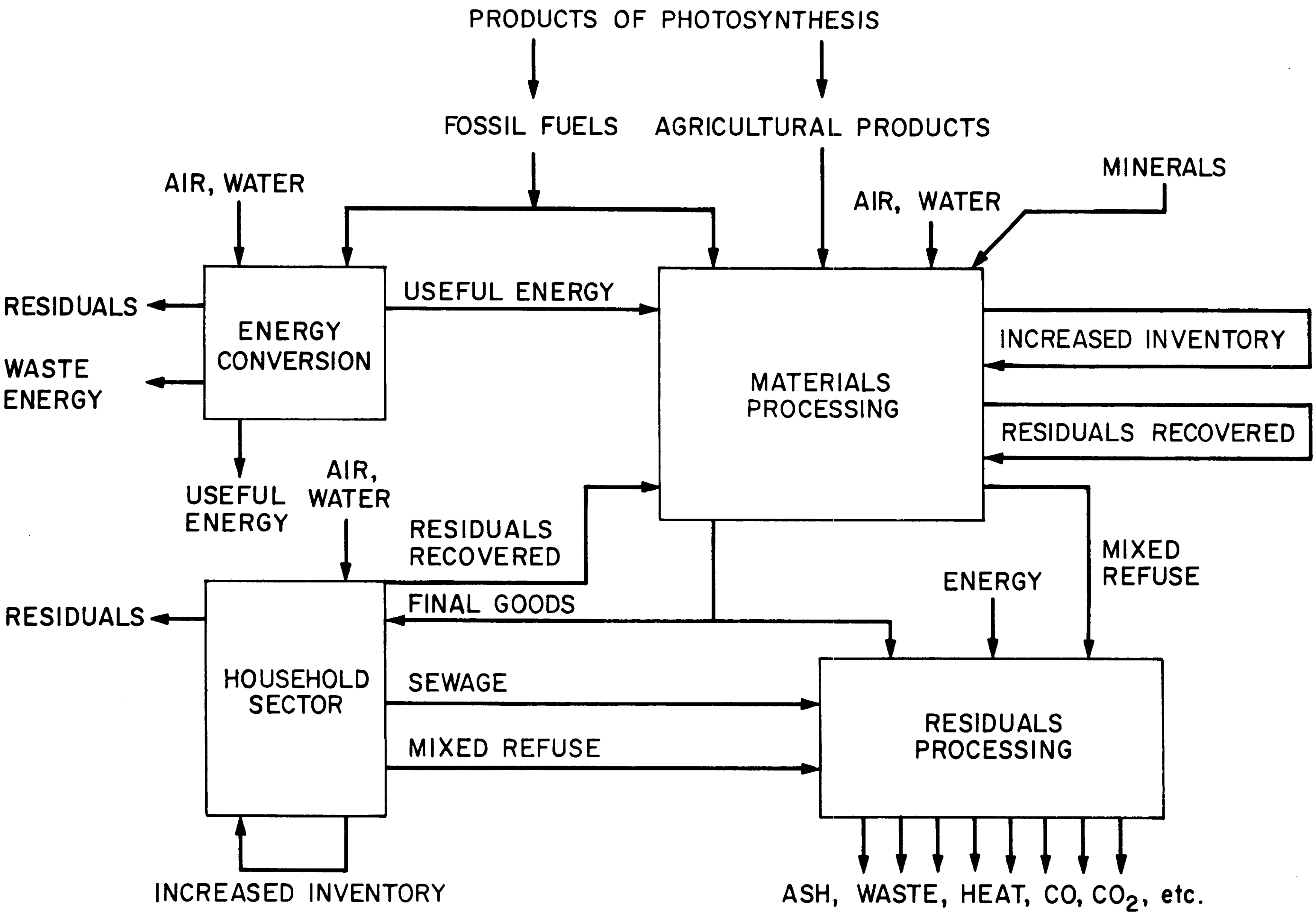

Figure 3.1: Flow of Materials. (From Kneese, Ayres and D'Arge, 1970.)

The challenge therefore is to find an alternative solution to the disposal of residuals, and the best way seems to be the recovery of materials for reincorporation into the productive process. But in this case other problems arise because the cost of recovery is very high relative to the value of the recovered material; these costs may be, and often are, considerably higher than those of obtaining new materials from nature, even when external costs associated with disposal are taken into account (see Kneese, Ayres and D'Arge, 1970; or Kneese and Bower, 1968). Without institutional changes, under the market system the users would still prefer to use the common property (i.e., the environment) at zero price for the disposal of its residuals, than to have to invest in new technology for its recovery and recycling, thus leaving such a technology in a primitive stage relative to the ones available for productive uses.

Consider now the second approach. It is generally agreed that, aside from the difficulties of measurement, pollution causes certain damages in the environment, and that these damages have a cost associated with them. However, it is no less true that the control of pollution has another series of associated costs. The question is therefore how far to go towards improving the environment, or, in other words, how much pollution control should be bought. The solution can be seen as a tradeoff between these two aspects, since if the resources used to control pollution could have produced goods of higher value than the damages or costs avoided by such a control, there would have been too much pollution control. Obviously, this indicates the importance of the value that is assigned to environmental damages, and this will depend upon many different factors, such as the current level of environmental quality or economic development. Because of this, the level of environmental quality desired in a country like India could be quite different from that desired by the U.S. Nevertheless, the normative model which follows could be applied to any of these two countries.

In terms of economic welfare, it can be assumed that costs are minimized and hence economic welfare maximized when the marginal costs of controlling pollution equal the marginal benefits of improving environmental quality; or, in other words, when the costs of controlling the last unit of pollution (i.e., treatment costs in an extensive sense) equal the costs of the last unit of damage.

It can be argued that the inclusion of social objectives instead of, or in addition to economic efficiency will make the optimal solution in terms of economic welfare different from the optimum social level of environmental quality; however, it can also be argued that if social preferences (through public hearings, the Delphi method, or any other method) have been taken into account during the establishment of values to the damages caused by pollution, such a discrepancy between alternative solutions will be minimized.

If it is assumed that environmental quality depends only upon the concentration of a certain index (e.g., B.O.D.), and that this concentration depends only on the rate of discharge of a given residual (e.g., organic wastes), then the optimum level of environmental quality, and consequently the optimum rate of discharge, can conceptually be found through the interaction of the following three factors (Freeman et al.

1973). The first factor is the relationship between residual discharge reduction and treatment costs which, as indicated in Figure 3.2., will produce curve 1. The second factor is the relationship between discharges and environmental quality which will give curve 2 and hence curve 3 in which treatment costs are plotted as a function of environmental quality. The third factor is the relationship between concentrations of residuals and dollar damages due to pollution, which will give curves 4 and 5.

Given this information, the optimum level of environmental quality Q^* and the optimal rate of discharge R^* will be found at the point in which the sum of the treatment and damage costs is minimum. At this point the marginal costs of both functions cross, therefore maximizing economic welfare.

However, in the real world environmental quality will not be a function only of the concentration of some index, nor will this concentration depend only upon the rate of discharge of a certain residual. But even if these two simplifications were to be correct, it would still be difficult to find the treatment cost curve which, of course, is implicitly assumed to be a minimum cost curve (i.e., all the different producers have equalized the marginal costs of the different ways of controlling pollution). And, last but not least, the political and institutional problems of assigning dollar values to find the damage cost curve are not trivial.

Therefore, the relation between institutional decisions, the economics implicit in the treatment costs imposed on the polluter, and

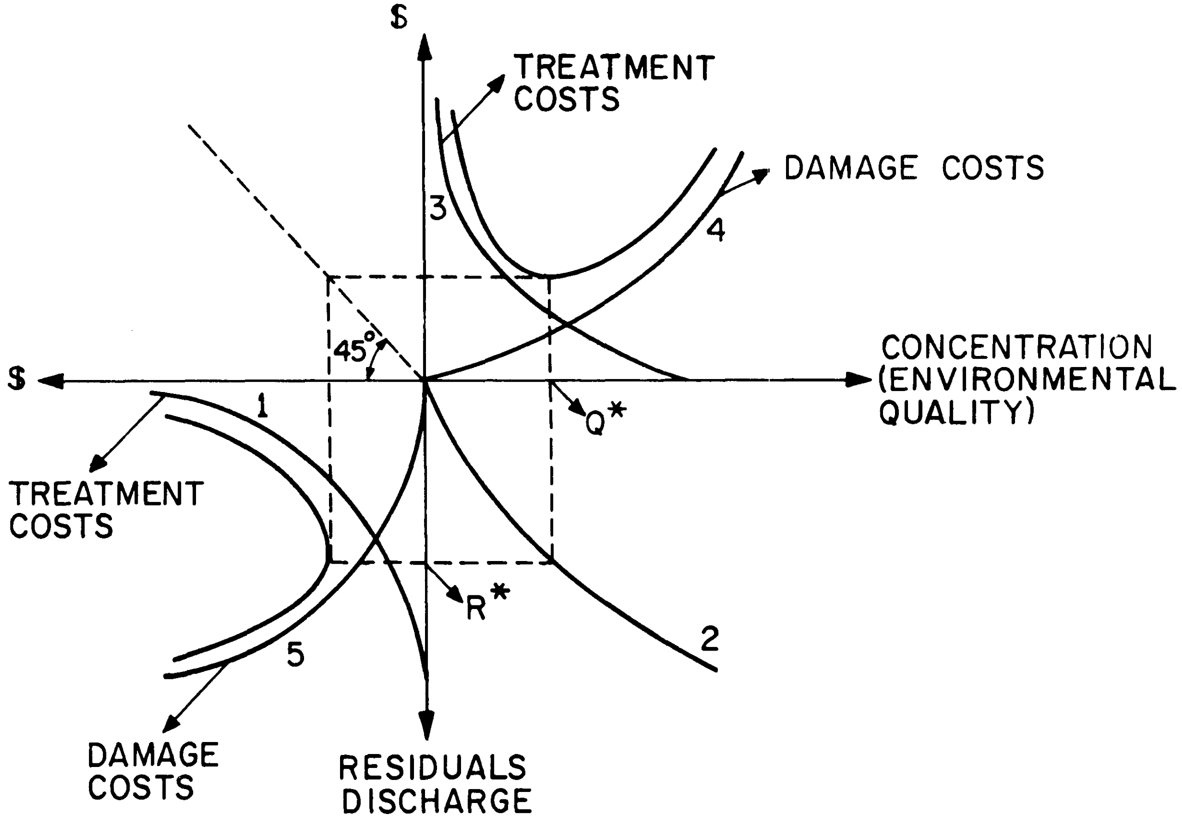

Figure 3.2: Determination of Optimal Level of Environmental Quality and Rate of Discharge.

the benefits derived by the users, is a technological relation, depending mostly on the technology of waste-water treatment and disposal. In the next section, therefore, these technological factors are reviewed.

3.2 Technical Methods of Groundwater Quality Control

In discussing the uses of modern technology in groundwater quality management it is easiest to consider two broad categories. The first is the use of technology to prevent groundwater contamination by controlling the quality of the water which recharges the aquifer. The second involves the use of technology to manipulate the groundwater flows to reduce the spread of contaminated or potentially contaminated groundwater, or to clean it up.

3.2.1 Controlling Sources

Some of the more important sources of groundwater contamination through recharge are wastewater discharges from municipal and industrial plants, drainage from septic tanks, seepage from sewers, percolation from irrigated agriculture, seepage from holding ponds-and leaching of landfills and dumps. These sources of groundwater contamination are all the result of waste disposal activites. It soon becomes obvious that any reduction in the quantity of waste produced will reduce the threat to groundwater quality (Kneese, 1971).

Although it is often difficult, if not impossible, to reduce the quantity of wastes from municipalities, it is often relatively easy to reduce the volume of wastes generated by an industry by the use of a more efficient process. In the case of industrial wastewater, it is sometimes feasible to reduce the total volume of wastewater significantly simply by practicing water conservation and resue within the plant. While conservation will increase the concentration of the wastewater, this usually makes it much easier to treat.

Wastewater treatment processes can be broken down into three categories; physical, chemical, and biological (Kneese, 1971; McGauhey, 1968; Hunter, 1973; Peterson, 1973). The combination of the three most common physical processes, screening, grit removal and sedimentation, is usually referred to as Primary Treatment. This process can remove approximately 33% of the BOD of municipal waste. Another frequently used physical process is flotation and skimming, which removes grease and other light solids. Filtration, a process historically used in water treatment, is now being frequently utilized in waste water treatment to improve the quality of the effluent. Gravity sand and mixed media filters, pressure filters and microscreens are among the filtration processes being used. Perhaps the most sophisticated physical treatment process is adsorption. Activated carbon columns are frequently designed to both filter the waste water and to adsorb dissolved solids. Activated carbon treatment produces a high quality effluent and the method is being used more and more frequently to treat industrial wastes which cannot be readily treated biologically (EPA, 1973).

Chemical treatment includes a variety of processes, including oxidation, correction of pH, disinfection, and chemical coagulation. Chlorine is used almost universally to disinfect municipal effluents before discharge, while chemical coagulants are being used to increase the efficiency of sedimentation and filtration processes. Chemical treatment methods usually involve low initial costs but high operating costs.

Biological treatment of waste water, which is limited to non-toxic, biodegradable wastes, is either aerobic or anaerobic. Municipal facilities generally utilize the aerobic processes which require that sufficient oxygen be supplied to maintain the aerobic organisms. Activated sludge and trickling filters are the two most common aerobic processes used and, either combined with primary treatment or not, are referred to as secondary treatment. The primary use of anaerobic decomposition is in septic tanks and sludge digestion. Other treatment methods include stabilization ponds and spray irrigation (EPA, 1973).

Wastewater treatment is a complex and rapidly changing field. Modern facilities often combine all three methods--physical, chemical and biological--to achieve the treatment desired.

In addition to wastewater production and treatment, steps can be taken to prevent potentially polluted water from entering the groundwater once it has been applied to the land. One method is to install an underdrain system to intercept the water as it percolates. This method has been used in Southern California to reduce contamination from irrigated agriculture and in Michigan to collect effluent after land application of wastewater.

Another method to reduce the contamination of groundwater is to line agricultural and industrial holding ponds to eliminate seepage. In the case agricultural non-point pollution sources the problem is more difficult to solve (see Section 4.2).

Solid waste presents municipalities with an equally important disposal problem. Dumps, incinerators and landfills have been used by municipalities and industries to deal with the solid waste problem. Dumps pose a great threat to groundwater quality (Weddle, 1974). The exposure of the waste to precipitation greatly increases the potential for leachate production. Although incinerators greatly reduce waste volumes, the ash must be disposed of. If this ash is placed in an open dump the leachate produced will be extremely polluted. Any management program should include an effort to eliminate the use of open dumps.

The alternative to open dumps is the use of sanitary landfills. Careful site selection, the covering of the waste each night, and the control of the waste disposed of, characterize the landfill process. The California State Water Resources Control Board's "Waste Discharge Requirements for Waste Disposal to Land" provides a good outline of the landfill process.

3.2.2 Control of Polluted Groundwater

Once a portion of an aquifer has been contaminated, as in the case with salt water intrusion or leachate contamination, groundwater quality management efforts sift from prevention to either removal or isolation. In either case it is important to remember the effect of groundwater pumping on the movement of polluted water within the aquifer. Pumping sets up artificial pressure gradients which can increase (or decrease) the movement of contaminated water through the aquifer.

Some of the techniques used to control the movement of contaminated groundwater are outlined below. For a more detailed outline of the techniques used for control of pollution see Todd (1959) or Todd (1973), who describes the technology as applied to the control of sea water intrusion.

a. Modification of Pumping: Contamination of an aquifer can often be accelerated when it is overdrawn by too much ground water pumping. This is particularly true in the case of salt water intrusion. The only real solution to this problem is the modification of the pumping patterns to eliminate overdraw. In cases of salt water intrusion this can be done by reducing the amount pumped, which requires an alternate water source, or relocation of the pumping sites further away from the coast. In cases of isolated pollution of a small portion of an aquifer, such as leachate contamination, wells are frequently moved with no real effort made to improve the ground water quality. The contamination is simply avoided.

b. Pressure Ridge: A line of pumps recharging an aquifer will produce a pressure ridge, or line of high piezometric head, isolating the source of contamination from the main aquifer. Although theoretically quite simple, this process involves very high capital and operational costs and requires large amounts of water. The California experience with a pressure ridge system to prevent salt water intrusion near Los Angeles is discussed in Todd (1959).

c. Pressure Trough: A pressure through is exactly the reverse of a pressure ridge. A line of pumps withdrawing water is used to produce a pressure trough, or line of low piezometric head, between the source of the contamination and the fresh water aquifer. In this case a mixture of contaminated water and pure water is pumped from the wells and must be disposed of. Although some contaminated water is removed in this method the real barrier to further movement of contaminated water is the low pressure ridge. This method involves the same capital and operational costs as the pressure ridge method, but a source of supplemental water to recharge the aquifer is not needed. However, the storage capacity of the aquifer is reduced significantly, since some good water is removed along with the contaminated water. Additional costs may also be incurred if the contaminated water pumped from these wells must be treated.

d. Interception and Withdrawal: In dealing with small isolated sources of contamination (such as leachate from a dump or landfill) the groundwater quality manager may wish to actually remove the contaminated water from the aquifer. In order to do this the means of intercepting the contaminated water must be selected. A line of wells similar to that used to form a pressure trough may be used. An alternative method of intercepting contaminated groundwater has been used in Southern California at a landfill site used for disposing of liquid wastes. In this case a dry well has been installed over the entire depth of the aquifer to intercept the leachate. The dry well can then be pumped out from time to time.

e. Subsurface Barriers: In some cases physical subsurface barriers can be installed to isolate a fresh water aquifer from a source of contamination. These barriers can be installed by excavation and installation or by pumping material into the aquifer which will form a physical barrier. The high cost of installing an impermeable barrier can often be prohibitive. In addition, the required impermeability is often very difficult to achieve, and may be even more difficult to monitor and maintain.

3.3 Institutions for Groundwater Quality Control

Before dealing with methods of pollution control and institutional approaches, two points--the system of property rights and the capabilities of institutional bodies--should be mentioned, since they can have a major impact on the results of any water management plan.

The influence of property rights can be considered from two different points of view. One of these is the relationship between the owner of a well and the institution in charge of water management; with full ownership of the water under the owner's land, the institution can be precluded from the use of some methods of controlling pollution (as, for example, a charge over the pumping of water). On the other hand, for example, the riparian owner is "held to be entitled to have water flow by him undiminished in either quantity or quality" and therefore in the case of some reduction in either aspects of the water, he can ask for the elimination of such damages. Such a problem has arisen many times with surface waters, where the water laws usually give the upstream users the right to discharge their waste waters, and the downstream users the right to have the water without damages in its quality. In the past, priority was given to the upstream user, since otherwise it would have represented a threat to economic development and growth, but in present times the trend is towards a compromise between both users (Levi and Coyler, 1972). In practice, this compromise takes the form of a mutual agreement between users of the same water body, whenever the external effects can be internalized.

The influence of the institutional bodies will depend upon their different capabilities. A Water Quality Authority should at the very least be able to prescribe levels of effluent treatment for individual waste dischargers, or to set limits on the quantities of pollutants the dischargers may release. However, if the aim is, as it ideally should be, a comprehensive water management plan, another set of capabilities should be authorized:

a. Coordinated management of water quantity and quality. The existence of water quantity and quality relationships should include the consideration of water quality aspects during the planning, design and implementation of water quantity projects.

b. Coordinated management of surface and groundwater resources, both because of their hydrological interaction and because of the fact that the consideration of any one of the two alone will normally result in high discrepancy with the socially optimum.

c. Location patterns may greatly influence the costs associated with waste disposal and therefore with water quality. Institutions for land and water management should therefore be interrelated.

d. A difficult problem for the institutional body is the fact that, quite typically, the advantages of high quality water and the costs of obtaining it ,accrue to distinct groups of epople whose conflicting claims must be weighted. Because of this, the capability to articulate private and government decisions is an important factor (see Kneese and Bower, 1968; and Dorfman et al., 1974).

In Appendix 3.2, a summary of the characteristics of various institutional bodies created in different countries for pollution management is presented. The characteristics of these agencies should be compared with the ideal characteristics outlined above.

3.4 Institutional, Legal and Economic Measures to Induce Pollution Control

This section will examine various water pollution control devices and, whenever necessary, will emphasize the effect of such a device on groundwater pollution control. Although each measure is described individually, this does not mean that they should not be used conjunctively.

3.4.1 Legal Remedies

One of the best ways for a state (including the legislative and executive powers) to handle a problem is to create a law or decree regulating it. Therefore, it is not surprising that the first type of remedies to pollution problems were legal remedies.

However, two different aspects should be considered here. The first is related to the legislative processes which deal with specific pollution problems, such as the creation of stream or aquifer standards. In this case the main problem is the possibility of enforcement, since it is not uncommon to find laws that have never been enforced since their establishment. Another problem, though less significant, is that, even if the law is enforced with any degree of precision, delays in deciding cases might themselves cause substantial inefficiencies.

The second aspect is related to the laws which protect private rights against actions causing nuisances or trespassing damages and which have greater difficulties dealing with pollution problems due to several factors:

1) The wide dispersion of damages often associated with waste discharges into either surface or groundwater makes it hard to bring suit for full damages, and even harder to find the person to be sued.
2) Since waste discharges impose costs in a highly variable fashion over time and space due to both hydrologic events and the time pattern of waste discharges, it would be difficult to frame laws with sufficient flexibility.
3) Damages may be dispersed over a wide area and in aquifers may be longlasting or even permanent.
4) Regardless of the difficulties of the former points, the laws would provide remedies through damages already committed and through the potential to halt such acts in the future,but they do not eliminate pollution, prevent irreversible acts, or provide any sort of general approach to the problem. Therefore, although they can be (and, in fact, are) useful tools, they should still be supplemented with other kinds of measures (Levi and Coyler, 1972; Kneese and Bower, 1968).

3.4.2 Stream or Aquifer Standards

The difficulties mentioned in the introduction regarding the determination of a socially optimum level of environmental quality can, in some way, be overcome through the use of the political process to produce such a value. This is closely related to the concept of stream or aquifer standards, which fix a certain level of quality in the river or aquifer that should not be violated.

However, although the establishment of quality standards is actually an institutional measure to induce pollution control, it should not be considered as an alternative,but rather as a complement to other measures, such as effluent standards or effluent charges; its existence is necessary to establish an effluent standard and very useful to establish an effluent charge.

Such a control method was implemented in Spain, for surface waters, through the Department of Public Works in 1959 (regulated in 1960) and in the United States through the Water Quality Act of 1965, but in neither of these countries is there legislation regarding groundwater. One of the reasons for this, perhaps, is that the characteristics of water flowing through porous media can cause one part of the aquifer to be badly polluted, while a nearby region remains totally unpolluted (Ballantine et al, 1972; Todd, 1959).

3.4.3 Effluent Standards

Once an environmental quality goal has been set*, a useful measure could be the introduction of effluent standards which allow the different polluters to discharge a certain amount of residuals in such a way

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*The problem of determining an environmental quality goal is a very difficult one since the natural selfpurification of the water body, the economic development of the areas, and the social preferences of the inhabitants must be taken into account.

that the sum of all residuals do not exceed a predetermined level of quality. If a polluter discharges more than the assigned level, he is liable to receive an injunction or may be fined.

The virtues of this measure are impaired by the information difficulties that it involves and minimizing the total social costs. As a matter of fact, in determining an effluent standard for each individual polluter, the agency (or institutional body) in charge has two alternatives. The first alternative consists of introducing different standards for different polluters so as to minimize the total social cost of achieving the desired quality level; but this has two major difficulties. The first and most important difficulty is a technical one regarding the estimation of the different marginal cost curves of the polluters. The second difficulty is political and is related to the difficulties of passing a bill which theoretically (though not practically) is discriminatory among the different polluters (Roberts, 1974).

The second and easier alternative for determining the effluent standard is by dividing the maximum amount of residuals to achieve the desired level of quality by the number of polluters. This solution is easier for the agency since it does not require such a large amount of information and is politically feasible because, in theory, it is not discriminatory. However, it does in fact involve a misallocation of resources and differs highly with the least cost solution since it can and probably will imply large differences in the marginal costs of the different polluters, as can be easily seen in Figure 3.3.

Another consideration which diminishes even more the benefits of

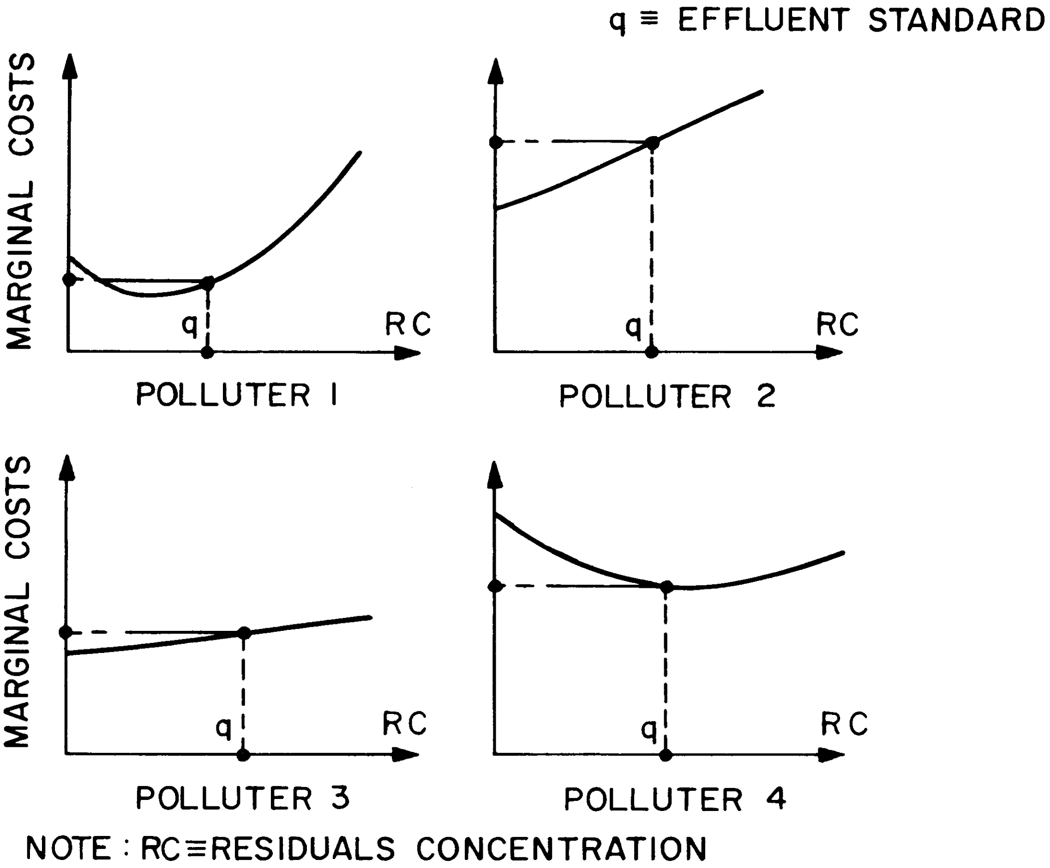

Figure 3.3: Variations in Marginal Costs Among Different Polluters.

the effluent standard is that the polluter does not have an incentive to develop technologies which diminish the amount of pollutants, since he is interested merely in reaching the standard and will not go further in reducing pollution even if he could do so at a low price. There are also other kinds of problems related to effluent standards, such as the possibility of enforcement, and the polluter's incentive to cheat the agency when stating the amount of pollutant he discharges (Roberts, 1974; Dorfman and Dorfman, 1974; Freeman, 1973; Kneese and Bower, 1968).

With respect to groundwater, however, it is possible to argue that such a measure would act quite efficiently to control injection well pollution. In fact, it is known that an injection well should not be considered a pollution point source, in the sense given to surface waters, since the pollutants will not normally go directly to the fresh groundwater which is to be protected, but indirectly (and randomly) through permeable ground between the brine aquifer in which the pollutant is injected and the fresh aquifer to be protected. This characteristic of the pollutant flow precludes the use of the usually more efficient effluent charge and gives priority to the establishment of an effluent standard which determines the maximum amount of pollutant that can be injected.

In addition to the problems of standard determination, there are difficulties involved in the compliance of such standards. Furthermore, social costs have to include compliance costs which are generally high.

3.4.4 Effluent Charges

The philosophy of effluent charges, whereby polluters are charged an amount proportional to their emissions of pollutants, is that equity and efficiency require payments for the use of valuable resources.

Many are the virtues that economists have found in this measure. To begin with, it is assumed that the introduction of such a charge will make the different polluters equate the marginal costs of their respective treatment cost curve (in an extensive sense) to the effluent charge, thereby minimizing the cost of reaching a given stream or aquifer standard.

Other virtues of this measure are that the effluent charge will be reflected in the price of the product, thus causing a shift in the demand to other products with lesser environmental costs. Moreover, because the charge would be proportional to the discharge and not as high as the effluent standard penalty, the polluter will not have such an incentive to cheat the agency in charge. It is also important to note that such a system is easier to enforce, since the cost to the polluter will not usually be large enough to throw him out of the market (which can happen with the effluent standard). Last, but not least, it will yield revenue to the agency which can be used to further increase environmental quality, with the possibility of taking advantage of economies of scale.

However, this method also has some disadvantages that should be taken into account. One of them, common to all measures to induce pollution control, is the determination of a multi-criteria index over which to levy the charge; this will pose many important problems due to the different characteristics of the wastes discharged through different or even the same outlet.

Another problem is to find the correct level of the charge in dollar values. In this case three answers are possible:

a. As indicated in Figure 3.4, if the average marginal treatment cost curve of the different pollutors were known, the intersection with the quality standard will give the correct charge; here the standard acts as if it were a damage function.

b. If the agency does not know the treatment cost curve, but instead knows the damage cost curve, it could establish a charge equal to the marginal damage for each unit of residual. Again, the residual charge would act as an incentive to economize on the use of the environment. Discharges would decrease their residual flow as long as the marginal costs of doing so are less than the charge for discharging. The sum of the treatment costs of all discharges would then be minimized because each discharger would be equating his marginal cost to the common charge. Hence, marginal costs of all options among all dischargers are made equal.

c. If the agency knows neither the damage cost curve nor the marginal treatment cost curve, which is the most likely case, a way of finding the best charge would begin by determining a low level charge which would allow the agency to obtain information, initiating a trial and error process. Further information can be obtained from Roberts (1974), Kneese and Bower (1968), Dorfman and Dorfman (1974), Solow (1971), Lefrou (1972), Delogu (1971) and Teniere-Buchot (1973).

There are some other disadvantages of the effluent charge. So far, it has been seen that the equalization of marginal costs of the different pollution control measures (recycling, increasing technical efficiency, treating residuals) within an outfall will minimize the cost in this part-

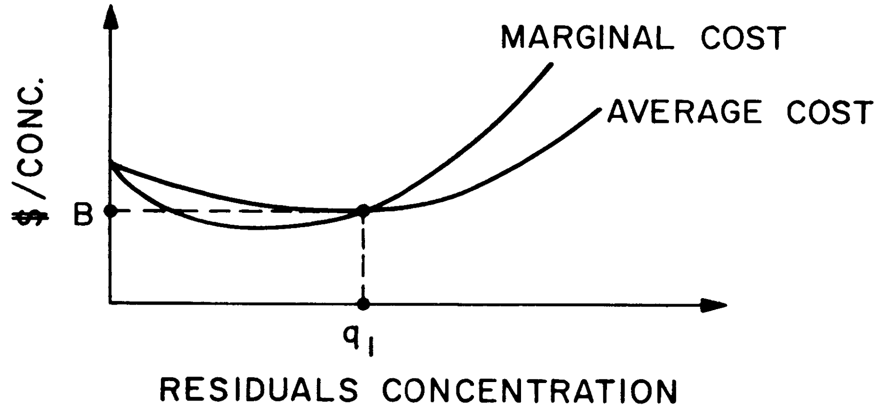

Figure 3.4: Determination of Effluent Charges.

icular outfall; and that the equalization of marginal costs among different outfalls will minimize the total cost. However, this last assumption is not necessarily correct, and an example illustrating this fact is presented in Appendix 3.3.

The last theoretical disadvantage of the effluent charge is that when only a low level of treatment is needed for achieving a given quality standard, no effluent charge will achieve this reduction. As shown in Figure 3.5, if the reduction necessary to achieve the standard were less than q, no charge under B would achieve it, and the charge B would be too high; however, this situation is very unlikely to take place in the real world.

With respect to groundwater it could be argued that this measure would perhaps be very useful to control one of the major sources of groundwater pollution: sea water encroachment. This occurs as a result of changes in the relative hydraulic pressure which are caused, among other reasons, by the pumping of wells; therefore a system of charges, not on the effluent, but on the influent, should be levied upon the pumpers.

Such a system could be established on the basis of the damages caused by pumping. An aquifer quantity model could determine how a certain amount of pumping affects the piezometric surface, this being the main factor in sea water intrusion. Therefore, by finding the amount of freshwater which is going to be lost and assigning a value to it, one could derive the charge to be levied upon the pumper. Alternatively, if the agency in charge of water quality is willing to control saline intrusion through a system of injection and/or extraction wells, the cost of this process can be considered as the charge (or whichever is smaller).

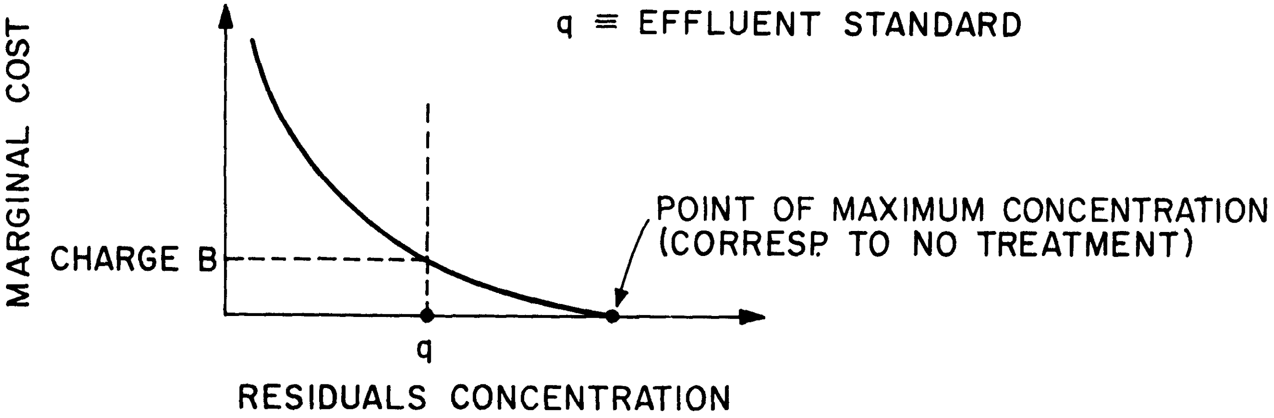

Figure 3.5: Effluent Charges for Low Levels of Waste Treatment.

Another application is in association with the problem of high nitrate concentrations due to the utilization of inorganic fertilizers in agriculture (see Abrams and Barr, 1974), in which a charge is levied on the use of fertilizers.

Some examples of effluent charges in European countries are presented in Appendix 3.4.

3.4.5 Payments

Another measure to induce pollution control is through payments, which is analogous but opposite to the effluent charge. While the charge method requires the polluter to pay for each unit of residual discharged, the payment system gives the polluter an amount of money for each unit of residual reduced. Thus the objective is just the same: to equal the marginal treatment cost of the payment or charge (Roberts, 1974, Kneese and Bower, 1968).

The main differences between payments and charges are the greater amounts of information and administrative requirements that the payment method demands. In practice, while the trial and error method of determining a proper effluent charge allows information to be obtained regarding the different amounts of pollutants discharged, therefore allowing modifications of the charge, the payment method needs accurate information before the distribution of funds.

Furthermore, the payment system is in contradiction with the international principles approved by the O.C.D.E. that establish that polluters are responsible for the pollution they cause. The payment system, on the contrary, is equivalent to a transfer from the non-polluter to the polluter. A final but important difference is that payment, instead of yielding revenue to the agency, will further strain its budget.

However, in the field of groundwater pollution, it could be argued that such a measure would have greater possibilities than others in trying to control agricultural groundwater pollution. If the return flow which percolates from these activities is found to be of such a poor quality that it adversely affects the aquifer, the objective would be to avoid it or reduce its magnitude. With this purpose in mind, two methods might be possible: an increase in irrigation efficiency through the use of a better, though more costly, technology (e.g., drip irrigation) which will produce a return flow of even poorer quality, or, alternatively, to construct a tail drainage system which would similarly be quite costly leading to a lack of the farmers' willingness to do so. However, the establishment of a system of payments over the reduction of return flow to the drainage channel could act as an incentive for its construction. The additional problems of such behavior (i.e., the lower water table, since the return water has been eliminated, or the strain on the agency's budget) could in some way be eliminated through the posterior treatment and sale of this water to supply industrial demands, if these indeed were to exist.

3.4.6 Markets in Transferable Pollution Economic Rights

This measure consists of a series of pollution economic rights which could be sold by an agency in a free market, say in the stock exchange, and which would allow the dumping of as many residuals as the economic rights the polluter had bought; therefore, the quantity of rights to be sold, and hence the ambient quality level, would be controlled by the agency.

To test this new concept, one can compare it to the better known effluent standards or charges. With respect to the first one, transfer-ability lessens the possibility of inefficient allocation of waste control efforts, since voluntary transactions will tend to equate the prices of economic rights to the polluters' marginal treatment costs. Compared with the system of charges, although it will equate marginal costs with the prices of rights, reaching a high degree of efficiency, it lacks the continuous incentive for obtaining a better technology.

The resulting increase in prices for dumping rights would be the outgrowth of impersonal market forces and this would be turn provide increased incentives to all waste sources to limit their discharges. However, in the long run, too high prices could result in paying penalties being less costly than trying to obtain permits, and the selling of more permits to augment the supply and lower prices could result in a lower quality level (Roberts, 1974).

3.4.7 Land Use

Land use controls form another important optional method for the control of groundwater pollution. By controlling regional land use, basin wide groundwater quality is managed. By controlling local zoning, industry and other point sources of pollution, can be confined to areas which are hydrogeologically protected from pollution, or in which there are no economically exploitable groundwater resources for other uses. Land use controls are better suited to widespread non-point sources of contamination, than are many of the previously mentioned economic controls. For example land use controls can be applied to the site selection of sanitary landfills; the density and location of septic tank leaching fields and cesspools; the location of agricultural fields, the types of crops grown and the amount of pesticides and fertilizers used; the site selection for areas for the disposal of animal wastes; site selection for nuclear power plants and radioactive waste disposal operations; and the location and regulation of fuel storage tanks.

In practice the land use plans would not only designate areas for restricted uses, but regulations would lay out requirements for the use of the land as described in the plan. In summary, land use controls are better suited for the regulation of some types of sources, than are many of the other methods of control which require more data, much of which is not obtainable.

A depiction of the interactions between water quality and land use, as well as the main determinants in land use policy is indicated in Figure 3.6.

3.4.8 Summary and Conclusions Regarding Pollution Control Measures

a. Although the above methods have been analyzed separately, this, does not mean that they should be considered as alternatives, but rather, most of them can and should be used conjunctively.

b. Although some measures can be used for controlling both surface and groundwater pollution, there are some differences which should be taken into account: the longer effects of pollutants on groundwaters and the lesser capability of the aquifer to purify itself; the fact that an important amount of pollution reaching surface waters comes from point sources,while in groundwater non-point sources are as important; and the difficulties involved in monitoring groundwater pollution and in being able to correctly consider the monitoring data.

c. It is necessary to recall the main conclusion provided by the material balance approach: if the pollution in a river, lake or aquifer is to be reduced, it should not be (if the costs are higher) at the expense of polluting land or air. This is the main reason for the existence of an agency on a regional basis.

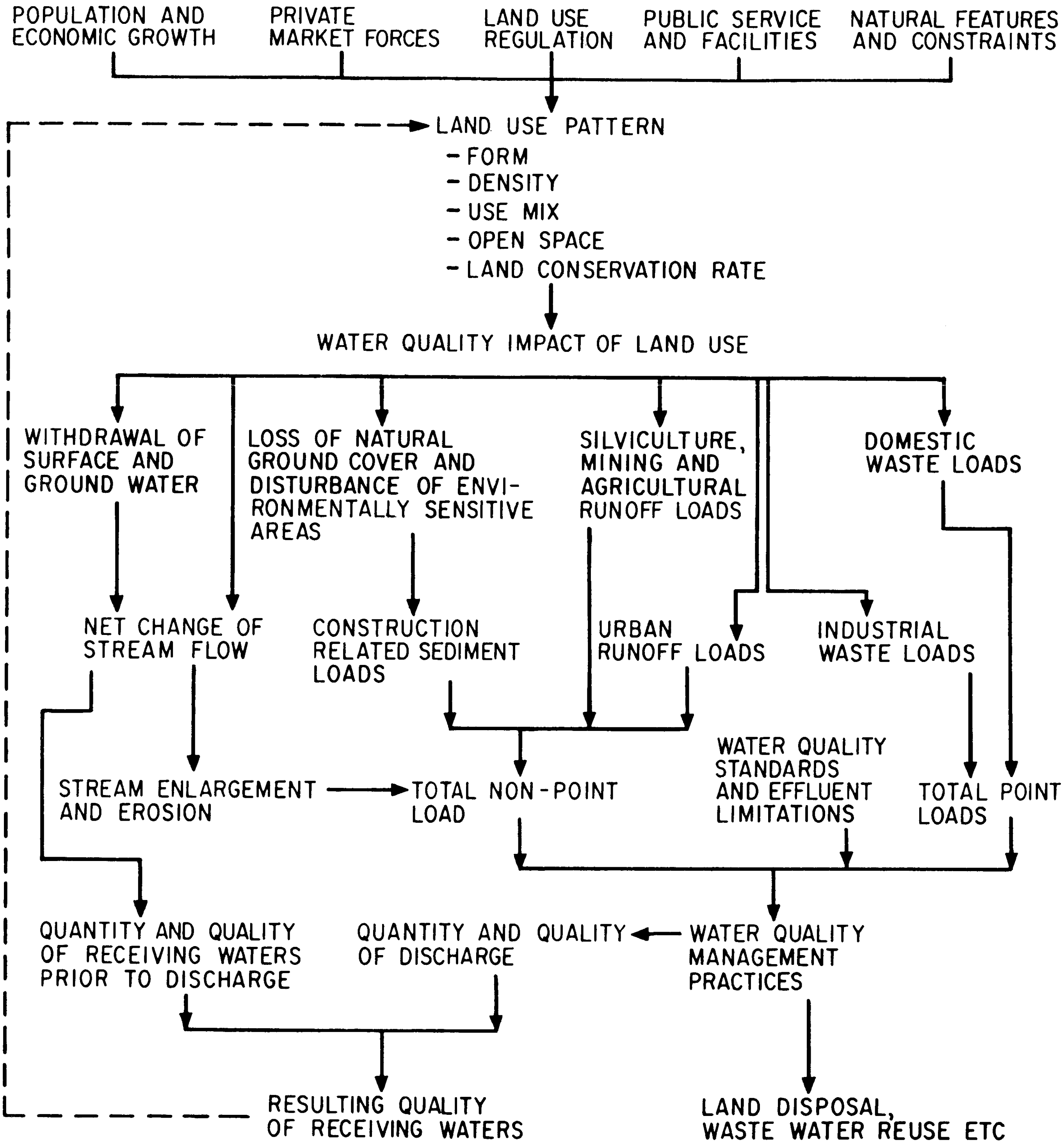

Figure 3.6: Interactions Between Water Quality and Land Use.

d. As mentioned previously, Appendix 3.2 presents a summary of various institutional bodies created in different countires for pollution control, considering the practical implementation of the institutional, legal and economic measures which have been described in this section.

3.5 Economics

This section deals primarily with the financial aspects of pollution control and with the estimation of benefits and costs of pollution control. However, it should be mentioned that up to recent times, economists have been primarily concerned with the development of the control measures which were studied in Section 3.4, rather than with the financial aspects to be discussed here.

3.5.1 Financial Aspects

The first point that should be mentioned is the groundwater budget. The management of groundwater resources in a comprehensive way to include both water quantity and quality, needs an important amount of money which must be matched by a correspondingly important budget. The relatively new techniques of Planning Programming Budgeting System (P.P.B.S.) help to identify these needs and to relate them to the relative benefits to be derived by the actions involved in planned management. In this context, the budget for pollution control techniques should be considered part of the whole groundwater management budget, its relative significance being determined by sound P.P.B.S. techniques.

The generation of a groundwater budget can take different forms which can be grouped according to whether they affect the general, state, local, or private budget. In Spain, because of the small significance of the local corporation budgets, and the infeasibility of private budgets unless a regional institutional body as defined in the preceding section exists, the only possibility for generating a groundwater budget is by setting aside a part of the general state budget,which on the other hand seems to be correct, given that 23% of the Spanish water demand is supplied by groundwaters.

Under these circumstances, however, some comments should be made. First of all, the problem of generating the budget becomes a political decision for which P.P.B.S. techniques are more needed than in the two other cases mentioned. P.P.B.S. processes, however, require good information circulation and transfer under a fair and commonly accepted "play". On the other hand, the generation of the budget in this way permits a comparison with the parts of the general state budget set aside for surface water, agriculture, the state budget itself and other major sources related to groundwater.

However, an additional problem is that groundwater management in general and pollution control regulations in particular are directly related to the financial possibilities. Because of the limitations of the state budget, some additional system of charging, either in the form of new taxes, increases in existing taxes, specific charges over water pumping, or any other way of increasing state budget possibilities will very likely be needed.

A second point that should be mentioned is the system of aids. The argument that pollution occurs as a result of externalities arising from production and consumption activities, and that therefore what is required is a method of introducing the costs associated with these externalities into the user's private calculations is definitely a sound one, lying at the root of many of the measures of inducing pollution control described in previous sections. Nevertheless, the levels of activity involved in pollution control will very often involve substantial costs which may not be successful unless some system of aids is developed.

In this respect, it is important to ask who should give these aids (a question that is directly related with the generation of the groundwater budget and therefore does not need additional comments) and who should benefit from them. In the latter case the main differences concern whether any polluter should have the right to use the aids or whether they should be limited to municipalities, individuals or juristic persons. The institutional approaches presented in Appendix 3.2 differ in this respect; while in the case of Germany and France all polluters can benefit from these aids, in the California approach the emphasis is given to municipalities. These differences are, on the other hand, related to the way in which the budgets are generated; in the first two approaches the private (or the institutional body) generation is relevant, while in the third case the most important part of the budget is the money obtained from the state treasury.

With respect to the kind of aids required, some careful thought is needed, since to establish one or another kind will have very different effects. A quick examination will show that subsidies can be effective for all kinds of polluters whenever the remaining part of the operations needed are not so large that the polluters cannot afford, say, to install a treatment plant that they may be obliged to build; this will create different problems. In the case of a marginal industry obliged to build a a treatment plant, strict enforcement will oblige the industry to go out of the market. The economic system will not suffer an impact due to the marginal situation of the industry, but for the municipality some alternative would have to be found.

The establishment of loans, either substituting or complementing the subsidy will also be effective for all polluters and will not constrain the budget as much as the subsidies; however, a kind of subsidy can be hidden in a long repayment loan and low interest rate. The other two (more common) kinds of aids are reductions in taxes or allowances of quick depreciation; in practice these will be effective only for industries, and within them, only for the competitive ones which paradoxically, are the ones that need less help.

Finally it should be mentioned that any program developed to aid in the implementation of a water quality management plan must carefully measure the advantages and disadvantages of the reasons for determining the payers (who should give the aids), the receivers (who should benefit from them), and the kinds of aids (loans, tax reductions, quick depreciation, subsidies, etc.) and whether these aids should focus on capital costs, on operations and maintenance costs or on both.

3.5.2 Estimation of Groundwater Pollution Control Costs and Benefits

Water pollution control benefits encompass all water uses, both direct and indirect, that result in the satisfaction of improvement of social welfare. However, cleaner water will not yield benefits unless the water is used (or at least desired) for potential use and enjoyment; i.e., the important issues are the human and ecological responses to cleaner water.

Unfortunately there are no direct measures of welfare, and since the objective of water quality management is to maximize net benefits*, economists have been motivated to discover criteria that could serve as conceptually and operationally meaningful proxies for the measurement of welfare.

Conceptually speaking, benefits derived from water-quality management and control can be classified into three broad categories.

The first one is what can be called "Preservation of the Natural State" and had given the name of "preservationists" or "conservationists" to the people who claim these benefits. They state that decisions should not be made on the basis of probabilities or on the availability of alternative decisions; for them the protection of the natural state is an end in itself. These benefits arise from the fact that many people derive comfort and satisfaction simply from the knowledge that the ecosystem is being preserved or restored, even if they do not benefit in other ways. Quantification of such benefits is very hard, although the willingness to pay and the Delphi methods, which will be explained later on, or any method implying public participation, can be a great advantage.

The second category can be grouped under the heading of "Risk Aversion or Minimization" and its main reasoning is that if the level of pollution is reduced, the probability of straining the assimilative capacity of water bodies until a major ecological system collapses with possibly catastrophic results, is reduced. These benefits seem to be the underlying ones involved in controlling marine pollution, and here the point of

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*Note that multi-objective analysis focusses on maximization of net benefits through a series of objectives instead of the maximization of net benefits as defined solely by national income.

collapse would be the interruption of the food chain. Probably, the best method for estimating these benefits is the dose response relationship which has great difficulties involved in modelling effects.

Finally, the third category can be considered the reduction in damages to health, production and consumption activities, caused by poor water quality.

There are many different methods of benefit estimation. Some of the most important are the following:

a. Associated Costs of Control - Although subject to many criticisms, since there is often no a priori reason to believe that benefits equal or exceed costs, this method has long been applied, and it will still be used in the future. The idea is that the cost of the project is assumed to represent the lower boundary of economic benefits, and the rationale involved is that a project is funded if it is worth at least what it costs. It could be said that such an idea is behind the U.S. 1972 Ammendments, since the goal established there says that by 1985 there cannot be any discharge of pollutants to the navigable waters of the U.S.

The social benefits of such a measure (which will involve benefits from the three categories mentioned previously) will be at least as great as the costs needed to attain this goal. However, it should be noted that these benefits are not quantifiable.

b. Dose-Response Relationships - This method, perhaps the most used in the U.S., consists of two phases of analysis. The first phase is the derivation of a model relating total damages, of whatever kind (physical, biological, or chemical), to water quality. The second phase then translates these damages into an economic equivalent.

This has been the approach taken by a number of economists in trying to derive what have been called the "Quality Related Consumer Costs". These are derived from models which relate damages to household, industrial and agricultural users to water quality. However, such a model is still in evolution and involves quite a number of simplifications; water quality is usually assumed to be just the mineral content of water expressed as TDS in mg/L., and damages to the three beneficial uses mentioned above are derived on the basis of mineral content and hardness.

On the other hand, the translation of these damages into an economic equivalent is still quite misleading; such items as the increased use of soap, the scaling of pipes, and the rapid deterioration of plumbing fixtures and water-using appliances are common examples of damages which the household user will suffer. But when it comes to giving a certain value to these factors, many different studies give very different results. As an example, the increase in soap cleaning costs due to an increase in 100 ppm hardness varies from $1.55 in an Illinois study to $8.21 in a California survey. An example of the application of this technique can be found in Porras (1975).

c) Delphi Technique - The procedure involved in this method of estimating benefits is explained in greater detail in Chapter 5. It consists of gathering various individuals with different fields of expertise, who are asked to estimate benefits derived from a water quality program. After a series of meetings the estimates are refined, resulting in a narrow range of values considered as the benefits of the project.

d) Willingness to Pay Surveys - A recent method of estimating water quality control benefits which is primarily used for estimating recreational benefits, can best be explained through the use of a simple example, which is presented in Appendix 3.5. The major difficulty involved in such a method is the derivation of the proper demand curve and thus the use of a survey as a way of discovering the attitudes of the people.

So far, different kinds of benefits have been introduced and some of the methods used for their estimation have been shown; however, any economic analysis of a pollution control program still needs additional information on water quality control costs.

Two different approaches, with varying difficulties involved, can be taken. The first and simpler one, consists of a water management program, which focusses not on the quality of the water resource, but on the quality of the water supply. In this case, the problem reduces to the estimation of cost functions for water treatment, both conventional (coagulation, sedimentation, filtration and disinfection) and more advanced (softening, demineralization). This would be quite simple if there is enough data, since these cost functions will not be hard to estimate.

However, if the water management program focusses on the elimination of pollutants before they reach the water resource, the problem is far more complicated. Nevertheless, two kinds of approaches can be taken; the first one is the use of the accounts of firms with pollution control expenses to determine capital and operation and maintenance costs. This approach has some difficulties involved, since companies often do not record expenditures in sufficient detail to permit cost determination, and even if they do keep records, they may not be willing to publicize them. Moreover, the approach does not permit the consideration of costs of new technology and systems not yet in operation.

The second approach which can overcome these difficulties is through detailed engineering and design specifications of individual treatment processes which can be used to extrapolate plant costs. However, this approach suffers from the problem of accuracy.

The development of these kinds of cost functions received federal support in the mid-sixties, and there are now, in the U.S., several good estimates of them.

Additional problems also arise when trying to determine pollution abatement costs of a process change which results in abatement and increased productivity, as will normally be the case after the introduction of some incentive (e.g., effluent charges). For example, in the northwest part of the Netherlands, to the north of Amsterdam, five years after the introduction of an effluent charge, industrial discharges were reduced to 30% of the original figure.

But perhaps, the worst problems of cost estimation appear when one changes from point source estimations to non-point or regional sources. Here the economist will find it extremely difficult to estimate costs due to the implementation of a well construction and destruction standards program, or direct and indirect costs related to a sanitary landfill policy, or costs related to sounder agricultural procedures.

Finally, it is important to note that when benefits are compared with costs, the economist will find that cost curves are derived on the basis of source control whereas benefits are a function of ambient quality. What is needed, then, is a reliable quality model to relate changes in emissions to variations of ambient quality, of the type developed in Section 3.1.

Further references on this topic include Abel and Tihansky (1971), Moore et al. (1974), Tihansky (1974a), Tihanksy (1974b), Nedeness (1972), Tihanksy (1973), Tihanksy (1974c), Akiyama (1974), Hassan (1969), Tihanksy (1974d), Smith et al. (1974), Fisher (1975), Shah and Raid (1970) and Smith (1967).

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APPENDIX 3.1

Social and Private Costs

As mentioned in Section 3.1, if third parties are already affected in the economic transactions between a producer and a consumer, they bear costs that are not included in the private cost calculations of the producer. These cause social costs that are higher than private costs, resulting in excessive production.

This effect can be illustrated by means of the following example. It is known that the supply curve is related to the marginal costs; if in Figure 3.7 the market is represented by a demand schedule D-D and the supply schedule (private marginal costs) is S, then the equilibrium output will be Q_1 at a price P_1. But if the social costs had been taken into account, their being equal to the private costs plus the externalities, the supply curve would have been S' and the point of equilibrium would have been one with a lower output Q_2 and a higher price P_2.

Another way of considering this problem is from the consumer's point of view. Assume that the index utility function of a consumer is

$$i = f(x, \ldots x_n, y_1)$$

This means that the consumer's utility (i.e., the satisfaction that he gets) is a function of the n activities $(x_1, \ldots, x_n)$ over which it is possible to assume that he has control, as well as a function of y_1 over which it is possible to assume he has no control. As an example, y_1 could be the quality of the water supply.

Neglecting budgetary constraints, the consumer will maximize his utility be setting the partial derivatives of i with respect to the x's

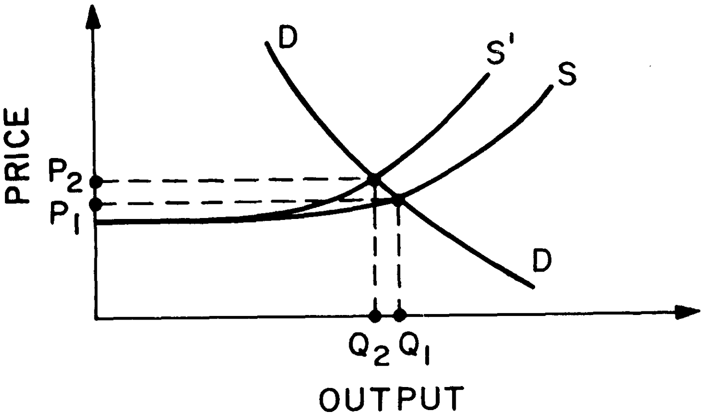

Figure 3.7: Social and Private Costs.

to zero, but he will not be able to do this in regard to y_1, which he cannot control. Thus, a marginal externality exists when $\frac{\partial i}{\partial y} \neq 0$, and a marginal external diseconomy exists when $\frac{\partial i}{\partial y_1} < 0$. Further details can be obtained from Ayres and Kneese (1969) or Kneese (1971).

APPENDIX 3.2

Examples of Pollution Management Agencies

This appendix presents a summary of the characteristics of various institutional bodies created in different countries for pollution control. These characteristics should be compared with those of an ideal agency as outlined in Section 3.3. It is felt that these agencies could serve as examples of what could be done in Spain in this respect.

The Genossenschaften (Germany)

This rather complicated word is the plural of Genossenschaft (or river basin association), six of which deal with the problems of water quantity and quality in the Ruhr District in Germany. Given the similarity among the six of them with respect to both their institutional organization and operation, only the Emscher genossenschaft, which is the oldest one (created in 1904), will be summarized.

The legal structure of the Association was designed to permit it to investigate, plan, design, construct, operate, maintain and replace all necessary installations or engineering works for the abatement of pollution in a given river basin, and for the general management of its waters. The association was to accomplish its task in cooperation and codetermination with all public and private corporations or persons that were themselves polluters or drew benefits from proposed investments.

The administrative organs of the Association or Genossenschaft are:

a. The Assembly: This is the governing organ in all the Associations. The memberships are divided in two categories: The first is composed of Associates, which include municipalities or rural administrative districts that discharge all or part of their waste water in the Emscher or its tributaries; the second is composed of Participants which include mines, industries and public administrative bodies (not municipalities or rural districts) within the basin. However, some of the other associations have only one category of membership. Representation in the Assembly is in proportion to annual contributions: one delegate for each 5% of the annual budget, but not fewer than one. On the other hand, people related to agriculture are given a voice in the assembly to further protect the interests of agriculture. The Assembly elects the members of the Board of Appeals that are not appointed by the supervisory public authority. Meetings of the Assembly are normally biennial.

b. The Board of Directors: This is the lawful representative of the Association, and conducts all the business not specifically reserved for the Assembly. As mentioned above, its members are elected by the Assembly and its president becomes the chairman of the Board.

c. The Board of Appeals: As its name indicates, it decides any appeal made against any action or omission of the association. As mentioned above, some of the members are elected by the Assembly (six) and some by the public authorities (three); furthermore, the supervisory public authority is in charge of naming the public official who chairs the hearings of the Board.

d. The District President: Public supervision of the Association is exercised in the person of the District President (similar to the charge of Governor in the Spanish Administrative Body), who is designated by the administratively competent Ministry.

With respect to the financial approach, the financing aspects were to take the form of public loans for capital improvements and internal allocation of running expenses, in proportion to the distribution of benefits from investments and costs of preventing or rectifying damage to the members of the Association insofar as expenses were not covered by income.

On the other hand, allocation assessments in the form of effluent charges, which are discussed in Section 3.4.4, have the same legal status as tax liabilities; accordingly they can be collected by force, although this is rarely necessary due to the well-mounted institutional body. Any member feeling aggrieved by his assessment can ask to be heard by the Board of Directors in the first instance and by the Board of Appeals in the second instance; furthermore, recourse to court against the decision of the Board of Appeals is possible.

As can be seen, this institutional body has all the conditions which were described in Section 3.3, and which are necessary for optimal management--i.e., the coordination of water quality and quantity, surface and groundwater, and water and land use; and the capability to articulate private and governmental decisions. More information can be obtained from Gordon (1961), Kneese and Bower (1968).

The River Authorities (England and Wales)

The Water Resources Act of 1963 introduced some water management changes in Great Britain which can be summarized as follows. At the national level, it complemented the concern for water of the Housing and Agriculture Ministries, with that of the Ministry of Land and Natural Resources and the Water Resources Board which, under the Ministry of Land and Water Resources, had specific approval and directive authority over the river authorities in performing their functions.

With respect to the basin level, the 29 River Authorities took the role of the former River Boards, but broadening their functions to deal with the whole field of "clean" water management in a comprehensive manner. With such a goal, the Act gave them authority to operate a comprehensive system of licensing water withdrawals from surface and groundwater; to introduce charging schemes over water withdrawers; to license all discharges of wastewater to underground strata as well as to streams; and to construct, operate and finance multipurpose facilities. Regarding financial aspects, the River Authorities operate through grants and loans from the central government, by effecting a part of their local budget through licenses, fees, and through charging schemes over water withdrawers. Finally, the composition of the River Authorities was made up of representatives of the central and local governments, in such a proportion as to always assure local governments a bare majority.

The way in which this institutional body fits into the ideal one described in Section 3.3 should be viewed step by step. With respect to the coordination of water quantity and quality management, the River Authorities had no authority to implement a water quality management plan as such, although they could construct reservoirs and operate them for streamflow regulation. On the other hand, the practice of placing almost complete reliance on treatment at individual points (direct control), and the little use of charges, should be counted as a deficiency. The coordination of surface and groundwater, however, was well attained. With respect to water and land planning, the system, although not ideal, had arrangements with local planning agencies to receive reviews and advice from the River Authorities. Finally, the capability to articulate private and government decisions was challenged by the lack of private representatives in the institutional body. Further information can be obtained from Kneese and Bower (1968).

The system as described above was modified by the 1973 Act which instituted Regional Water Authorities. The whole of England and Wales is covered by ten of these Authorities, which now have a multifunctional activity and are financed through a system of charges for water withdrawal and waste discharges.

The Agences du Bassin (France)

As the result of the work carried out by the Commission on Water created in 1959, in December 1964 the Parliament passed a comprehensive water law whose principal characteristics are:

a. It establishes agencies in each of the six river basins of France to serve as regional branches of the national government.

b. It gives powers to these agencies to implement regional programs of water quality management.

c. It places primary emphasis on charges, particularly effluent charges, to finance the program and to coordinate private and local government waste discharge decisions with the objectives of the regional agency.

However, although water quality problems are given great emphasis and broad scope covering "any occurrence liable to cause or increase the pollution of water by altering the physical, chemical, biological and bacteriological problems of surface water, groundwater or seawater within territorial limits", the law considers overall water resources problems and gives the agencies general water management powers.

The administrative organization of the agencies is a Basin Committee which sets up the main lines of action of the agency regarding desirability of programs and financial possibilities; these Committees are composed of representatives of national, state, community and direct users in equal number. The executive is the Board of Commissioners of the Basin Agency, composed of national, state and direct users on a half and half basis. Its role is the development of programs under the advice of the Basin Committee. Furthermore, there exists an Interdepartmental Mission (or Mission Deleguee), composed of representatives of the Ministries of Agriculture, Equipment and Housing, Industry, Quality of Life, Health and Welfare, Interior and Finance which supervises, co-ordinates, and approves the water management programs.

Regarding the financial aspects, the agencies received as a source of income the charges over the users. These charges are classified in two categories: over withdrawal of water, and over pollution loads intended to internalize the costs of pollution. The purpose of such income is to develop quantity and quality water management in the form of subsidies, loans and diverse aids for regional facilities in the general interest. The beneficiaries are industries and municipalities which formerly paid the charges. Municipalities can also receive grants directly from the government.

A comparison with the "ideal" institutional body, as defined in Section 3.3, indicates good coordination of quantity and quality water management. The only exception is the need for a new law authorizing the construction and operation of collective facilities, since the law of 1964 establishes the primary action of agencies through grants, loans and contracts with private and public bodies, but not directly. The coordination of water and land use policies seems to be obtained at a level less than the "ideal", through the setting up of protective zones, and zoning, around sources of water supply. On the other hand, surface and groundwater have coordinated management, and the organizational arrangement offers the capability to articulate private and government decisions. More details can be obtain from Levy-Lambert (1967) and Teniere Buchot (1975).

The Delaware River Basin Commission (D.R.B.C.)

The D.R.B.C. was established by a federal-interstate compact approved by the U.S. Congress in 1961. The central objective was to create a river basin commission that would devise and administer a comprehensive multi-purpose water resources plan which would "bring the greatest benefits and produce the most efficient services in the public welfare".

The D.R.B.C. has five members--the Governors of the four member States, and the Secretary of the Interior representing the President. It has power over the control and development of water supply, water quality control, flood protection, management of watersheds, the promotion of recreational uses, and hydroelectric power. It also has powers to establish cost sharing standards and formulas to allocate costs among the different signatory parties of multipurpose programs, public bodies, groups and private enterprise. The D.R.B.C. is the only interstate-federal compact agency in the U.S. and the only regional agency to be given such comprehensive powers. With respect to the financial aspects, the compact authorizes broad borrowing powers and the power to issue bonds. On the other hand, the parties agree to provide capital funds for the projects of the Commission in accordance with the cost-sharing provisions established by it.

Following the usual process of comparison, the D.R.B.C. shows that, although the act gives recognition to interdependencies between water quantity and quality, it is somewhat doubtful whether an optimal account of all interrelations will actually be accomplished. On the other hand, the Commission has authority to construct, operate and finance any measure for water management only if it can do so more efficiently than other agencies.

Surface and groundwater resources seem to be well coordinated; however, although there are some relationships with land-use policies through the stream classification and watershed practices, these do not seem to go too far. Finally, the articulation of private and government decisions would have to take place through public hearings. Additional information can be obtained from Kneese (1968) and Howe (1974).

The California Approach

The information presented here is a summary of the booklet published in July 1974 for the California State Water Resources Control Board, containing the Porter-Cologne Water Quality Control Act and related code sections.

The State Water Resources Control Board was established by the 1967 legislature and is included in the Resources Agency of the State of California. It is composed of five members designated by the Governor, who also designates the Chairman of the Board. It has, by law, two divisions, one of Water Quality and the other of Water Rights; furthermore, it has established by itself some additional divisions--a Legal Division, Divisions of Planning and Research, and a Division of Administrative Services. The Board may also represent state or local agencies in any matters involving the Federal Government which are within the scope of its powers and duties.

With respect to decision arrangements, the law established that although any member of the Board may, with prior authorization, conduct any hearing or investigation, all final actions of the Board should be taken by a majority of all the members at a formal meeting.

The Board prepared a report which was sent to the legislature in 1969 and passed as the Porter-Cologne Act, which established that the health, safety and welfare of the people requires a state-wide program which should be administered regionally, for the control of the quality of all the waters of the state. As a result, the Board has to formulate and adopt state policy for water quality control consisting of:

a. Water quality principles and guidelines for long-range resource planning, including groundwater and surface water management programs and control and use of reclaimed water.

b. Water quality objectives at key locations for planning and operation of water resources development projects and for water quality control activities.

c. Other principles and guidelines deemed essential by the state board for water quality control.

The regional administration of the state-wide program is implemented by the Regional Water Quality Control Boards. For this purpose, the State of California is divided into nine regions.

Each Regional Board consists of nine members appointed by the Governor for a term of four years, who represent and act on behalf of all the people of the region. The Chairman of the Regional Board is elected by the members, and there are at least six yearly regular meetings, plus additional meetings or hearings if called by the Chairman or any two members. Each region obtains coordinated action, within the region, for water quality control, including the prevention and abatement of water pollution and nuisances; in order to accomplish this they have powers to adopt water quality control plans, prescribe waste discharge requirements and perform other functions concerning water quality control which are deemed essential. Statewide corrdination is reached through the review and/or approval by the State Board of the actions of the Regional Boards, and by the creation of a Water Quality Coordination Committee, consisting of at least one member of each of the nine Regional Boards, to assist the State Board in carrying out its responsibilities in water quality control.

Regarding financial aspects, the sources of income consist of the State Treasury, which is authorized to sell bounds through the Clean Water Bond Laws of 1970 and 1974; money contributed by any person and accepted by the Board; money collected through waste discharge permits; and penalties for any violation of provisions, or by way of criminal penalties. This income is utilized primarily for loans and subsidies for construction, studies and investigations related with water quality.

Regarding the coordinated management of water quality and quantity, it must be stated that there are aspects such as construction and operation of facilities which are out of their context. However, these institutional bodies may approve appropriation by storage of water to be released for the purpose of protecting or enhancing quality; moreover, there is some coordination with the Department of Water Resources in the sense that the Department plans for water projects should include plans and recommendations for protection of water quality which have to be transmitted to the State and Regional Boards. Additionally, the coordination of surface and groundwaters is well established, as it should be in a state so dependent on its groundwater. It should be pointed out that Water Quality Control Plans prepared by the SWRCB and accepted by the State Legislature became part of the California Water Plan.

Regarding water and land-use management, there is some coordination which can be observed through their water quality control plans; however, the role of the Boards in this respect is based on recommendations rather than on implementations. Regarding the capability to articulate private and government decisions, these take place only by public hearings which must be held before any action is approved.

Further information can be obtained from California State Water Resources Control Board (1974).

APPENDIX 3.3

Necessary Conditions for Waste Discharge Cost Minimization

In Section 3.4.4, it was stated that the assumption that the equalization of marginal costs among different waste discharge outfalls will minimize the total cost was not necessarily correct. The falseness of this assumption can be illustrated by the following example. Let:

$c_1 = f(x_1)$

$c_2 = f(x_2)$

where

x_1 = waste discharge from plant 1

x_2 = waste discharge from plant 2

and

c_1, c_2 = costs of reducing waste discharge

Both plants discharge the residuals into a lake. Let us assume that the standard in the lake is to get a dissolved oxygen (D.O.) level of at least 5 mg/L, and that a_1, a_2 are the coefficients which relate the units of discharge x_1 and x_2 with the D.O. in the lake.

The problem then will be

$\text{Min } (c_1 + c_2)$

$\text{s.t. } 5 = a_1x_1 + a_2x_2$

The above can be solved through the use of Lagrange multipliers, and the Lagrangean function can be written:

$$L = c_1 + c_2 + \lambda\ (5 - a_1x_1 - a_2x_2)$$

The necessary conditions for cost minimization are thus

$$\frac{\partial L}{\partial x_1} = \frac{\partial c_1}{\partial x_1} - a_1\lambda = 0$$

$$\frac{\partial L}{\partial x_2} = \frac{\partial c_2}{\partial x_2} - a_2\lambda = 0$$

$$\frac{\partial L}{\partial \lambda} = 5 - a_1x_1 - a_2x_2 = 0$$

From the first two equations, it is seen that a necessary condition is also

$$\frac{\partial c_1}{\partial x_1} = \frac{\partial c_2}{\partial x_2} + \lambda\,(a_1 - a_2)$$

Unless $a_1 = a_2$, it is easily seen that the condition $\frac{\partial c_1}{\partial x_1} = \frac{\partial c_2}{\partial x_2}$ does not satisfy the above necessary condition which signifies that the equalization of marginal costs at different outfalls is not a necessary condition for cost minimization unless all the coefficients in the transfer matrix (a_i) are equal. When they are not, cost minimization requires that prices be tailored to each outfall. Further information can be obtained from Ayres and Kneese (1969).

APPENDIX 3.4

Some Examples of Effluent Charges

Given the growing acceptance of effluent charges as the best available system to deal with pollution control problems, this appendix shows how three European countries--Germany, France and Netherlands--have dealt with the problems of levying charges from the discharges of wastes into SURFACE WATERS of sewage treatment plants, in proportion to the quantity and concentration of the wastes discharged.

Germany

As is evident, one of the main difficulties in establishing an effluent charge is the determination of an index with the ability to integrate the different compositions of the different wastes discharged. The two approaches shown here belong to two of the Genossenschaften described in Appendix 3.2.

a. Die Emschergenossenschaften-Lippeverband system: This system achieves commensureability between various effluents by determining their propensity to kill a given type of fish. Indeed, the formula indicates the amount of clean water required to dilute the effluent in order to avoid harm to fish which is called the dilution factor. The choice of the objective of maintaining fish life does not necessarily mean the absence of other objectives; it is simply considered a useful summary surrogate for a wide range of values. The dilution factor is calculated by the following equation:

$$D = -1 + \frac{S}{S_p} + \frac{1}{2}\frac{B}{B_p} + \frac{1}{2}\frac{P-30}{P_p} + F$$

where D = dilution factor

S = materials subject to sedimentation in cm^3/L

S_p = permitted S in cm^3/L

B = BOD_5 (5 -day Biochemical Oxygen Demand) in mg/L after sedimentation

B_p = permitted BOD_5 in mg/L

P = potassium permanganate oxygen used in mg/L after sedimentation (stands for chemical oxidation)

P_p = permitted potassium permanganate in mg/L

F = necessary dilution for toxic materials, its value is derived directly from a fish toxicity test

-1 = compensates for the volume of dilution water included in the waste discharge.

The actual permitted values used in the equation are as follows:

$$D = -1 + \frac{S}{0.4} + \frac{1}{2}\frac{B}{40} + \frac{1}{2}\frac{P-30}{42} + F$$

b. <u>Die Ruhrverband system</u>: This system is a special form of the population equivalent BOD which aims to include both oxygen-demanding and toxic wastes. The rationale is that the self-purification of a stream is similarly affected by both types of wastes; in the first case, this is due to additional pollution, and in the second case, this is due to the inhibition of the self-purification process. The idea is to assign a population equivalent of, say, 3 to the quantity of industrial effluent that has the same inhibiting effect or self-purification as a household effluent of 162 grams BOD (54 grams BOD = 1 population equivalent).

The procedure followed is to simultaneously test the potassium permanganate (which stands for chemical oxidation of materials and is not influenced by the presence of toxic materials) used by a household effluent of known BOD, and the industrial waste. The result is expressed in a chart. For the above example, the points for 54, 108 and 162 BOD (1, 2, 3 population equivalents) are found in the curve of household effluent, translated to the curve of the indsutrial effluent, and read on the abcissa. The new points are 18.34 and 42 mg/L. Accordingly, $\frac{18+34+42}{1+2+3} = \frac{94}{6}$ = 15.7 liters of the effluent being tested are to be valued at one population equivalent. More information can be obtained from Kneese (1966) and Kneese and Bower (1968).

France

The basis of the effluent charge of the River Basin Agencies is the average pollution load discharged in a day during the month in which this pollution is maximal in the year. This pollution load consists of the load of suspended solids, the load of oxidizable material (given by $\frac{2BOD + COD}{3}$), and the level of salinity estimated by electrical conductivity.

Each user's effluent charges are estimated by a contract estimate (what they call estimation forfiture). The charge for communities is based on the number of permanent inhabitants and summer visitors; for industries the basis is the industrial activities (products, raw materials, number of workers, etc.). A table is available for each industrial branch, and the pollution load for characteristic operations. Alternatively, the daily pollution load may be individually measured.

To illustrate the procedure, some of the industries with their specific pollution coefficients and the units to which these coefficients are referred (the total pollution will be the product of the coefficient by the number of units the industry being tested has) are shown in the following table:

Table 3.1

Industrial Pollution Coefficients

Industry	Unit Referred	Pollution Coefficients (grams/day)			
		Susp. Solids	Oxid. Met.	Dis. Solid	Toxic Met.
Iron Extraction	Person employed	100	50	-	-
Soap Manufacture	kg. soap produced	18	52	-	-
Hotels	Room	180	114	-	-

In 1974, the amount of the charge to be levied upon was:

Oxidizable Material (kg per day) ... 30 F/year

Suspended Solids (kg per day) ...... 30 "

For each inhabitant................. 4.41 "

Toxic Material (kg per day)........ 800 "

It should be mentioned that the French river basin agencies take into account the effects of a treatment plant over the effluents and give the users a bonus according to the characteristic of the plant and its efficiency. Further information can be obtained from Lefrou (1972) and Redevances Pour Deterioration de la Qualite de l'eau (1974).

Netherlands

The way in which the charge is levied over the effluent in the Netherlands is very similar to that of France, although with some differences. Perhaps one of the most important differences is the fact that the pollutancy of a waste effluent is determined in such a way that the same amount is paid per inhabitant per year and per corresponding industrial unit.

As in France, however, the agencies have developed a system by which the pollutancy caused by several branches of industry is related to units of production, raw materials used, or number of persons employed. This relationship is expressed as a waste-water coefficient, and the multiplication of the above unit for a particular year with the waste water coefficient gives the pollution caused by that particular industry.

As an illustration, Table 3 gives the waste water coefficients for some industries:

Table 3.2

Waste Water Coefficients

Industry	Unit Referred	Waste-Water Coefficient
Vegetable washing	1000 kg. carrots	0.09
Glue factories	1000 kg. bone glue	3.30
Dry cleaning	Person employed	0.50

Nevertheless, at the request of an industry, the pollutancy of its waste water can be determined by measurement.

The amount of the charge was 2.50 Fl in 1966. The charge, however, rose to 7 Fl per population equivalent per year in 1972, to 8 Fl in 1973, and is expected to raise up to 20 Fl by 1985. Further information can be obtained from Koot et al. (1972).

APPENDIX 3.5

Willingness to Pay Surveys

This appendix presents a numerical example of a willingness to pay survey. Assume a village with an underlying aquifer used for water supply, whose water quality is 1.700 ppm of TDS and further assume that a survey has shown that the village would be willing to pay $10,000 for the reduction of the first 100 ppm TDS (i.e., a change in water quality from 1.700 ppm to 1.600 ppm), and $0 for the reduction of the last 10 ppm. This means the village would not be willing to pay any money for water quality improvement once the water quality reaches 10 ppm TDS. Further assume that the demand curve is linear.

If there exists a project which would change the water quality to 700 ppm TDS (either through artificial recharge of the aquifer with water of better quality or by the construction of a demineralization plant) the benefits of the project should be considered as the area under the demand curve ABCO, indicated in Figure 3.8.

A major weakness of this approach is that the survey can lead to misleading results, since if the individual is sure he would not have to pay, he is likely to say that his willingness to pay is higher than what he would actually pay.

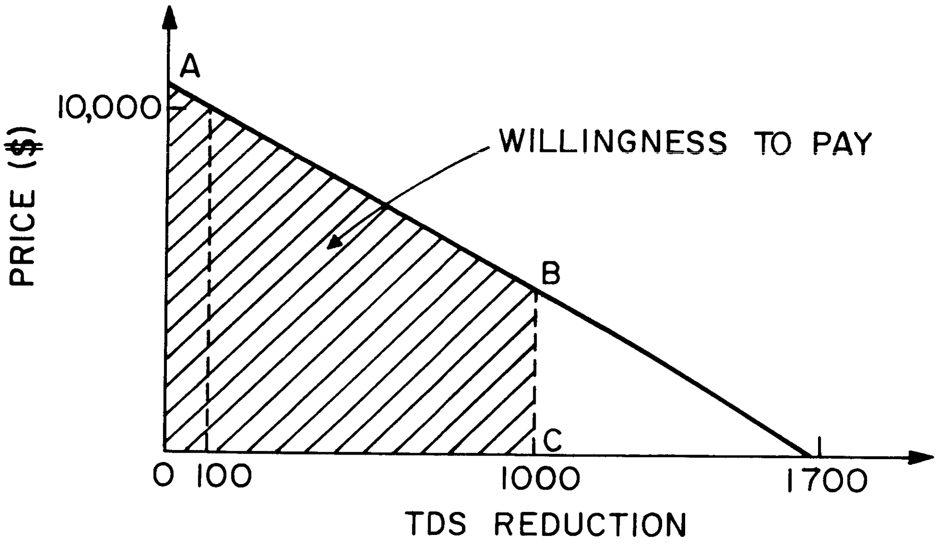

Figure 3.8: Demand Curve for TDS Reduction-Willingness to Pay.

CHAPTER 4

Causes, Types and Extent of Groundwater Pollution and its Control

Groundwater pollution is characterized by many different types and sources (causes) of pollution (Section 2.1). These are distributed over the landscape from sources at the surface to those in buried sediments. Many of these are associated with particular land uses, and can be characterized by the areal extent of the resulting pollution as local or regional (basin-wide) problems. This chapter reviews the important pollution sources, and the type and extent of pollution associated with each. The extent of pollution is only briefly discussed because the particulars depend on the part of the world or nation that is under consideration. Specific methods of control for each pollution source are given, or references to source material is cited. Industrial, agricultural, domestic and urban and radiological pollution sources are discussed. So too is the man-induced pollution associated with salt water intrusion, the induced recharge of polluted surface waters, air pollution, thermal pollution and artificial recharge.

A number of other reviews have been published in the last few years that are similar to this chapter, but which present more detail. Some of these are cited in Section 2.1, but Meyer (1973) deserves special attention because it catalogues control methodologies along with the sources and types of pollution.

All of the fields discussed in the section are the subject of continued theoretical, laboratory and field investigation. Our understanding of, and ability ot describe each problem or situation, and to recommend control technology is rapidly changing. The references quoted here are only representative, and for a more detailed picture of a particular situation the latest literature should be consulted.

4.1 Industrial Pollution of Groundwater

The pollution of groundwater by industry is characterized by the tremendous variety of organic and inorganic chemicals which are potential pollutants, and the degree to which the sources of pollution can be regarded as local, or point sources. In this section we analyze the sources of pollution, the characteristics of industrial pollutants, and the control of the pollution sources. Special sections are devoted to the deep well disposal of industrial wastes and to pollution by mining activities.

4.1.1 Sources of Industrial Pollution

There are three primary sources of the industrial pollution of groundwater. In terms of quantity the most important source is the waste generated by industry, which is discharged to the air, land, or surface water or groundwater. Leaks, which are often undetected and so untreated, are important because of their continuity and insidious nature. Finally, there are the unforeseen acts represented by accidents.

Wastes

In its effort to produce products, industry is also faced with the production of residuals, or wastes. These are materials for which there is seemingly no use and which must be disposed of. However, the definition of what is a waste fluctuates with the economic market and regulatory decisions and guidelines (see Section 4.1.3 and Chapter 3). Industrial wastes are released to the air and surface water, sources which are treated in terms of their groundwater pollution potential in Section 4.5, and to the land and groundwater, sources treated here.

Liquid wastes, which may be extremely dangerous acids or organic complexes, more often consist only of high concentrations of various salts. In some cases these are injected through wells into the saline groundwater zones or dry strata, for storage or disposal. The primary threat to groundwater in this case is an accident at the well, or leakage from the injection horizon through the well hole or intermediate strata, to a useful freshwater aquifer. These elements are treated in Section 4.1.4. Liquid wastes are also commonly discharged into surface reservoirs, pits, lagoons, basins, etc. The purpose for this may be the further treatment of an already treated waste, evaporation and concentration, infiltration or storage (Meyer, 1973). Those basins intended to be watertight are now usually lined with a relatively impermeable material like clay, asphalt or plastic and sited in areas of low permeability. In times past, however, many reservoirs were constructed without consideration of the possible infiltration to, and contamination of, shallow aquifers. When not discharged to wells or reservoirs, or to surface water, liquid wastes may be spread or sprayed on the ground. This is most common with the organic wastes of the food processing industry. This process is similar to the increasingly popular municipal land waste disposal concept, and many of the same principles and concepts apply (see Section 4.3). The process depends on the zone of aeration and its ability to bio-chemically degrade organic matter and to physically and chemically remove wastewater constituents (Section 2.2). The ability of this kind of operation to function properly depends on the physical-chemical characteristics of the soil and waste water, as well as on secondary factors such as the crop, the method of application, and the climate (Hassan, 1974).

Solid wastes form another component of the industrial waste disposal problem. These have been disposed of to open dumps in the past, but are now most often taken to landfills (see Section 4.3). The landfills are then subject to leaching from infiltrating rainwater, or liquid wastes injected into the landfill. A survey by the Manufacturing Chemists Association (1967) of the solid waste disposal of chemical process wastes indicates that 71% of the waste was disposed of by landfill on company property. The leaching of landfills and the subsequent introduction of pollution to the groundwater depends on a source of water (Zanoni, 1971). Some landfills must depend on natural precipitation, surface water infiltration, percolation from surrounding high ground, or the direct contact with groundwater. But industrial landfills may also receive liquid wastes directly. Landfills are discussed further in Zanoni (1971), Meyer (1973) and Section 4.3.

Leaks and the Leaching of Stored Materials

Leaks are a particular problem because they may go undetected for long periods of time, and there is increasing evidence that leaking pipelines and storage tanks are more common than is generally realized (Meyer, 1973).

Tanks and pipelines have been used for many years for the storage and transmission, respectively, of liquids. The predominant use of storage tanks in home or industry is for the storage of fuels. Industry also stores chemicals in tanks. The installation and maintenance of small tanks, especially is homes, is not well regulated and there are numerous instances of these leaking. Larger tanks are usually designed and sited to minimize the potential threat of leakage. The most numerous underground storage tanks are at gasoline stations, which Matis (1971) has shown to be significant sources of pollution in Maryland due to leaks.

Pipelines for the collection, distribution or transportation of liquids are another source of pollution (Meyer, 1973). Collection lines and distribution lines in industrial plants or oil fields are not regulated and may be one of the sources of contaminated water in industrial areas. Transportation pipelines, on the other hand, are usually regulated. Their heaviest use is for petroleum products, with natural gas and water second and third on the list (Meyer, 1973). Leaks from pipelines can be classified as accidental spills if the duration of the leak is short enough. Meyer (1973) has summaried data for 1971 taken from the Office of Pipeline Safety (1972), U.S. Department of Transportation, which is shown in Table 4.1. This table represents only accidents and leaks associated with interstate carriers. The table demonstrates that petroleum products constitute the major source of potential pollution. The Office of Pipeline Safety (1972, see Table 3.3 in Meyer, 1973) found that in 1971 the major cause of leakage was external corrosion. The second most important causal factor was the rupture of a pipeline by earth moving equipment, leading to a more acute spill type of situation. The former is more difficult to detect and may lead to a greater groundwater pollution hazard. The second is detected immediately but significant amounts of liquid can be lost before the line is shut off.

Since most of the liquids associated with tank and piepline leakage are petroleum products their particular behavior in the ground should be reviewed. Most petroleum products are lighter than water, and all are characterized by different surface tension characteristics. Consequently these products and water are immiscible and the comments in Section 2.2.1 on movement are not altogether appropriate. Meyer (1973) and the Committee on Environmental Affairs review the physics of petrochemical movement in soils and groundwater.

TABLE 4.1

Summary of Interstate Liquid Pipeline Accidents for 1971

(From Meyer, 1973; and Office of Pipeline Safety, 1972)

Commodity	No. of Accidents	% of Total	Loss (Barrels)	% of Total
Crude Oil	172	55.9	115,760	47.2
Gasoline	51	16.6	42,001	17.1
L. P. G.	39	12.7	39,887	16.3
Fuel Oil	21	6.8	13,724	5.6
Diesel Fuel	5	1.6	6,953	2.8
Condensate	5	1.6	3,658	1.5
Jet Fuel	4	1.3	2,236	.9
Natural Gasoline	4	1.3	8,743	3.6
Anhydrous Ammonia	3	1.0	9,810	4.0
Kerosene	2	.6	700	.3
Alkylate	2	.6	1,585	.7
Total	308	100.0	245,057	100.0

Outside storage areas for salts and other solid chemicals, if exposed to water sources, can be leached into the soil and eventually introduced into the groundwater. If they are placed on an impermeable surface, but left uncovered, the resulting runoff contains dissolved material which may enter the soil at some point downstream. If the storage area is covered by a roof or sheet of plastic, etc., the potential for leaching and runoff is greatly reduced.

Accidents

Accidental spills associated with pipelines has been discussed, but there are other accidents associated with transportation that may lead to pollution. Chemicals spilled in highway truck accidents or railway derailments are usually treated for their fire and/or explosion hazard first. This often involves washing the area with water which moves the chemicals into roadside ditches and surface drainage. This provides an excellent opportunity for infiltration into the soil. Spills over fractured bedrock are most critical because there is little opportunity for the chemicals to attenuate in strength. Meyer (1973) cites examples of spills which have caused groundwater pollution and summarizes the special characteristics of the movement of a spilled chemical in groundwater.

4.1.2 Characteristics of Industrial Pollution

Inorganics

Inorganics from industrial sources can be broadly divided into metals, salts and acids and bases, The metals (see Table 2.1) are usually found in low concentrations near localized sources of pollution, but this is balanced by their high human toxicity. Because they are adsorbed (Section 2.2.2) onto minerals their mobility is restricted. Nevertheless, chromium and cadmium wastes from electroplating plants have been observed to move considerable distances in sand and gravel water table aquifers (Deutsch, 1963; Perlmutter and Lieber, 1970).

Salts are derived from a variety of sources, many of which are associated with agriculture or local governments (Sections 4.2 and 4.3). Many anions from salts are very mobile and move with the groundwater. Most cations are less mobile and undergo ion-exchange or adsorption. The salts of group 1 (Table 2.1) contribute to pollution primarily by their high concentration levels. Other salts, like arsenic or cyanide, contribute to pollution because of the extreme toxicity, even though they are not found in large concentrations. Salts from oil field brines are historically common pollutants (Krieger, 1961; Deutsch, 1963; Pettyjohn, 1973). Arsenic (Koppe and Gieber, 1965) and cyanides (Csanady, 1968) from waste disposal operations have also been found in groundwater supplies.

Acids and bases, that is, extreme pH values, have been introduced into groundwater systems. In the most optimistic cases, these liquids are neutralized by aquifer rocks resulting in a salinity increase.

Organics

Synthetic organics include a list of thousands of chemicals. Each chemical behaves differently in the soil and/or aquifer and has different toxicological properties. Several generalizations about their characteristics in soils were presented in Table 2.1. In addition some organics have the property of physically coating soil particles. This coating process essentially removes part of the organic from active transport, but it also coats adsorption sites and greatly reduces the capacity of a soil to attenuate pollution by ion-exchange or adsorption. Viscous immiscible hydrocarbons are important examples of this kind of organic material. Other organic materials, surfactants, influence the surface tension properties of soil and this can lead to an alteration of its hydraulic response to waste and water inputs.

The most serious synthetic organic threat may be from pesticides and their application in agricultural fields (Section 4.2.2) or the waste disposal from pesticide manufacturing. For example, 2,4 D (2,4 dichlorophenoxyacetic acid), an organochlorine herbicide could have formed in situ in the waste disposal pits of a pesticide manufacturing operation in Colorado. The groundwater pollution resulting from the percolation of the waste water may have contaminated over fifty wells in the vicinity with 2,4 D (Bonde and Krone, 1962).

Hydrocarbons have been described as important pollution sources with respect to leaks and spills. They are characterized by their immiscible behavior in groundwater (see Dracos, 1974) and are common pollutants.

Organics from the food processing, paper and similar industries provide the most significant amounts of these materials, although they are secondary organic sources compared to agriculture and domestic activities (Sections 4.2 and 4.3). When applied to land these wastes are degraded in the soil, and the primary effect is an increase in the inorganic load to the aquifer. They are usually not mobile until oxidized. James M. Montgomery (1974) reports the result of the application of citrus processing wastes to a field in California.

4.1.3 Control of Industrial Pollution

Wastes

A key element in the control of waste from industrial facilities is waste and water management. Through improved practices the volume and/or concentration of waste water can be reduced. A reduction in volume is often associated with an increase in concentration. One way by which either or both of these ends can be achieved is through a change in industrial processes resulting in greater efficiency. This option is one of the elements of the effluent charge control schemes described in Chapter 3. Closely associated is the option of finding a useful application for one or more of the waste products. Water reuse after treatment decreases the volume of water used, and although the effluent concentration may be higher, the total amount of waste is lower. Finally, there is wastewater treatment technology, which is used to reduce the concentration of liquid or air waste streams, but which often results in greater amounts of solid waste to dispose of, or small amounts of extremely concentrated liquid wastes.

Surface reservoirs, pits, lagoons, basins, etc., can be controlled by a number of measures taken to reduce pollutant strength, prevent leakage, or to confine the pollution. Meyer (1973) described the following methods for the E.P.A.:

a. "Require pretreatment of wastes for removal of at least the toxic chemicals

b. "Require lining with impervious barriers of all lagoons, basins and pits that contain noxious fluids...

c. "Use barrier wells, pumped to intercept plumes of contaminated groundwater from existing industrial basins where leakage has occurred... The water removed must be treated before redisposal

d. "Ban the use of pits...

e. "Locate and identify unauthorized pits on industrial sites on a case-by-case basis and apply appropriate regulatory action.

To these one should add a monitoring program to insure that the method of technical control is functioning properly (Section 2.3).

Land disposal operations are controlled through the correct location and design of the facility (see Section 4.3.1). Pretreatment will often be required to remove toxic material, like the heavy metals, or to reduce solids content. A monitoring system to insure proper operation is a must, and a collection system to be used in the case of system failure may be incorporated.

Solid wastes, as a groundwater pollution source, are controlled by limiting the amount of water available for leaching. In arid climates this is done through the control of waste types permitted in a landfill. In humid climates there is little control over water availability. The landfill site should be properly located and designed and if a leachate problem is expected linings and collection systems may be required. Zanoni (1971) and Meyer (1973) provide more detail.

Leaks and Accidents

Leaks are prevented through the proper design and maintenance of facilities, incorporating, for example, corrosion prevention. Storage tank leaks can be contained on site by surrounding the tanks with a lined excavation. Pipeline leaks can be minimized similarly by installing automatic shut-off valves which will limit the amount of liquid spilled in an accident. There is no containment option for slow, undetected pipeline leaks.

Once the material has entered the soil, it can be removed along with soil and treated. This option is used most often to clean up hydrocarbon spills or leaks and is limited to action soon after the leak or spill occurrs. If the liquid pollutant has reached the water table it can be removed by pumping a well as described in Chapter 3, or by excavating a ditch to intercept the pollution and act as a sump. For some pollutants chemical or biological agents can be added that will speed biodegradation, or cause chemical precipitation or chemical reactions that can immobilize the pollution. The Committee on Environmental Affairs (1972) and Meyer (1973) present different options for controlling leaks and spills.

4.1.4 Deep Well Waste Disposal

For the purposes of the present report, deep well disposal is defined as the injection of liquid wastes (industrial wastes, brines, etc.) into permeable subterranean geologic strata, usually of large volume, containing non-commercial native waters (saline waters). The purpose of the operation is to eliminate the waste from the surface, storing it permanently and with no harmful effect on the environment.

Increasing emphasis on surface water quality control, connected with apparently lower costs (in comparison with waste treatment) in operation, has made the alternative of deep well disposal increasingly popular. Due to the nature of the wastes involved (some of them highly toxic or undesirable), and because of the methods and techniques of injection, serious damage to the quality of fresh groundwaters can take place if the necessary precautions and controls are not properly developed. There is extensive information available on methods, controls, monitoring, economic and legal issues, and case histories relating to deep well disposal. Only a brief description of the problems connected with fresh groundwater pollution shall be presented here. The main characteristics of the potential pollution of groundwaters by deep well disposal are (Meyer, 1973):

a. Some of the wastes are very dangerous and/or stable, or very concentrated.

b. The monitoring of operations is difficult and costly, due to the depths of injection, usually from 300 to 3,000 m.

c. As a result of the nature of wastes and the polluted medium, decontamination is very difficult.

Possible Mechanisms of Pollution

The usual practice is to inject the waste through a tube from the surface to the bottom of the disposal well. This tube may or may not be sealed against the well casing, but the annulus is always filled with fresh water or a light oil. Wastes are injected at rates lower than 25 liters per second (400 g.p.m.) in 95% of the examples, known in the United States, with well-head pressures of less than 1500 p.s.i. (90 kg/cm^2) in 99% of the cases (Warner, 1972).

The chances of groundwater pollution from this practice can be summarized as follows (Meyer, 1973):

a. Escape of waste through the well bore into a freshwater aquifer due to insufficient casing by corrosion or other casing failures.

b. Vertical escape outside of the well casing from the injection zone into a fresh water aquifer.

c. Vertical escape of waste through confining beds not completely impervious.

d. Vertical escape through other deep wells improperly plugged or with corroded casing.

e. Direct contamination due to lateral travel of polluted water or displacement of native saline water due to injection.

Types of Wastes Injected

There are three main types of wastes that, in current practice, are injected by deep wells (for more complete detailed information see Donaldson, 1972). Oil field brines, with concentrations from less than 100 ppm TDS to more than 10,000 ppm are injected in thousands of wells in the United States for the displacement of crude oil or for disposal purposes. Inorganic industrial wastes, in an enormous range of compositions, which vary in pH, and organic industrial wastes, such as aldehydes, phenols, alcohols, glycols, organic acids, nitrites, etc., are injected. More than 50% of existing wells in United States have been constructed by chemical, petrochemical or pharmaceutical companies, 22% by refineries and natural gas plants, and 7% by metal product companies (Warner, 1972).

Methods of Control

Meyer (1973) describes several control methods based on proper siting, design, construction, operation, abandonment, and monitoring. First there should be an evaluation of hydrogeologic framework and restriction on unsuitable locations and aquifers for waste water injection. A successful operation depends on four primary requirements: permeable reservoir rock of adequate capacity, with recognizable and finite vertical dimensions; infinite or well-known lateral dimensions; impermeable seals above and below, to prevent migration of fluids; adequate data on hydrogeologic parameters; and compatibility between waste fluids and native fluids. It is always risky to choose the injection site in an area where many holes have been previously drilled and abandoned.

Second there should be an evaluation of injection fluids. This includes an estimation of the nature and extent of chemical reactions between injected fluids and receiving formation fluids and minerals. Third the injection wells must be properly designed and constructed. Fourth, a complete hydrogeologic evaluation is required during the construction and testing of wells. Fifth, the aquifer response to injection is determined. Sixth, restrictions on the operating programs for injection wells are specified. Seventh, surface equipment and programs for emergency procedures in the event of malfunction are required. Eighth, abandonment procedures for all wells are required. Ninth, a monitoring system is required, including: the well; monitoring of injection and annulus pressure; the surface equipment; and the subsurface, to establish that the waste is going into and staying where intended. This can be accomplished using the injection well itself, using a shallow well located in the fresh water aquifer likely to be polluted, or using a deep well, especially when the thickness of confining strata is small.

4.1.5 Mining Activities

The activities relating to the extraction and preparation of minerals create, like other types of industries, environmental impacts, of which one may be the pollution of groundwaters.

Mechanisms of Pollution

Mine dewatering by pumping of groundwater can affect the quality of water withdrawn from wells in the surrounding area. For example, saline or poor quality water may appear in supply wells as a result of the modification of the ambient groundwater flow pattern by the pumping activity in the mine (induced pollution, see Section 4.5.1).

Acid mine water is produced in many cases when certain minerals (e.g., FeS_2, pyrite) are exposed to the atmosphere, and as a result, are oxidized. In the case of pyrite, sulfuric acid is released. Secondary reactions produce concentrations of Al, Mn, Ca and Na in coal mining areas; in metal mining areas, Cu, Pb, Zn, Ni, Ag, F, U, Sb, Hg, Cr, Se, Cd and As have been found in mine waters in excessive concentrations (Warner, 1974). All of these elements can pollute the aquifer by the infiltration of polluted waters through mine excavations. Or, groundwater pollution may occur from the infiltration of pumped water as long as the mine is being operated and the water discharged into the surface without the proper precautions.

Although not due directly to the mining activity itself, the disposal of wastes into abandoned quarries, gravel pits and strip mines can cause groundwater pollution from leachates. Solution mining practices, as applied to strata containing water soluble salts, can cause groundwater pollution due to interaquifer flow of the saline water. Pollution mechanisms are similar to those described in the chapter on deep well waste disposal.
In the process of recovery of metals from metallic ores, groundwater pollution can occur as a result of loss of the leaching agent into the groundwater system.

Sites for the disposal of solid and liquid wastes from mining and mineral processing are potential groundwater pollution sources, due to the composition of leachates. In these cases, the mechanism of pollution is like that associated with sanitary landfills and lagoons for other liquid wastes.

Methods to Avoid or Reduce Pollution

Different methods for avoiding or reducing water pollution, and groundwater pollution in particular, from mining activities can be considered (Warner, 1974). In underground mines, where dewatering can cause depletion of nearby aquifers and subsequent groundwater pollution, the amount of infiltrating water can be diminished by roof fracture control, increasing surface runoff by the elimination of depressions and grading of the surface, and sealing boreholes and fracture zones. In the case of surface activities, pollution of groundwaters can occur by leaching of pollutants from the spoiled material and waste heaps and can be avoided by placing impervious barriers (clay, concrete, plastic, etc.) on or around the waste material, establishing vegetation cover or constructing underdrains.

Additional information on mining activities and pollution control can be found in E.P.A. (1973b) and Warner (1974).

4.2 Agricultural Pollution of Groundwater

A primary characteristic of most agriculturally related groundwater pollution is that it is often well distributed(non-point source). From these sources come animal wastes, irrigation salts and the various chemiclas applied to fields. In this later category are pesticides, and the organic and inorganic compounds of nitrogen, phosphorus and potassium that originate in commercial fertilizers. Localized animal, agrichemical or crop waste disposal or storage activities may lead to point pollution sources.

4.2.1 Plant Nutrients as Water Pollutants

The rapid increase in fertilizer usage has been due largely to low fertilizer costs and the necessity for higher economic yields. This increase of use has raised many questions concerning nutrient pollution of the surface and groundwaters. Since population is rapidly increasing, it probably will be essential that the land produce food at capacity levels in the future. This will necessitate the continued rise of high rates of fertilizer use. The three main nutrients applied to crops are nitrogen, phosphorus and potassium fertilizers, which are added to supplement nutrients already in the top soil.

Types of Compounds

Nitrogen compounds are the most important nutrients from the point of view of groundwater pollution due to the mobility of nitrate nitrogen. A significant percentage of nitrogen (N) applied to soil is in organic form like manure or urea $(NH_2)_2CO$. The remainder is in inorganic form like anhydrous ammonia NH_3, ammonium sulfate $(NH_4)_2SO_4$, ammonium nitrate NH_4NO_3, ammonium carbonate $(NH_4)_2CO_3$ or calcium nitrate $(NO_3)_2Ca$. The rate of application of these fertilizers is based on the total quantity of nitrogen needed per unit area of a given crop.

Since plants can only use nitrogen in the nitrate form, the type of fertilizer chosen determines the rate at which nitrogen is available to plants. As we shall see it also determines the degree to which the nitrogen is subject to leaching in the mobile nitrate form (see Section 2.2). Thus the organic nitrogen compounds are very slow acting, as the nitrogen must first be ammonified and then nitrified (Section 2.2.3). The stabilized inorganics like ammonium sulfate release their nitrogen slowly because it must be nitrified. Finally the quick-acting nitrate compounds are both readily available to plants and to leaching to the groundwater.

As expected,field and laboratory experiments have demonstrated that the organic nitrogen compounds are not very mobile in soils (Bailey, 1968); consequently it is only their degraded products that may lead to pollution problems. The two primary mechanisms leading to this lack of mobility are (1) the limited solubility of the organic compounds and (2) the ease of adsorption and resistance to desorption of the organics in the soil.

Most research dealing with the leaching of inorganic nitrogen compounds has focussed on nitrate-nitrogen (NO_3^--N), ammonium-nitrogen (NH_4^+-N) and nitrite-nitrogen (NO_2^--N). These studies indicate that ammonium and nitrite represent only insignificant portions of the total nitrogen leached to groundwater, often less than one percent. The low nitrite level can be attributed to rapid oxidation to nitrate and low concentration in the soil, while the low ammonium level is attributed to its fixation by the soil exchange complex or oxidation to nitrates. The fixed ammonium NH_4^+ (or ammonia NH_3 as well) has been chemically adsorbed by soil particles and various kinds of organic matter and is in a non-exchangeable form. Ammonium (or ammonia) is also easily physically adsorbed on soil particles like clay minerals and is available in a readily exchangeable form. Ammonium favors this last adsorption reaction, while ammonia favors fixation. Note that the fixation of ammonium greatly reduces nitrification and thus limits the availability of its degradation product, nitrate, for leaching. This generally involves only a small amount of the total nitrogen. For a further discussion of these reactions see Bailey (1968).

Nitrate (NO_3^-), which results from the degradation process and constitutes almost all the nitrogen in leaching waters, has the general reputation of being quite mobile in soils and groundwater (Bailey, 1968). The usual description is that the nitrate behaves as if it were a tracer. Generally this is true, but under some conditions the nitrate may be adsorbed. For example, if there are appreciable concentrations of the oxides of iron and aluminum, a pH value of 6 or below, and particularly in unsaturated soils, it may be weakly adsorbed, in a fashion similar to chloride (Thomas, 1970). Neglecting this as an unusual process the movement of nitrate from the plant root zone to and through the groundwater system can be described as in Section 2.2.1. That is, the movement of nitrate is primarily influenced by the movement of water and so depends on the same factors. Ayers and Branson describe some elements of nitrate percolation through the zone of aeration and groundwater (Ayers and Branson,1973).

Nitrate nitrogen concentrations in water percolating to the groundwater are dependent on the rate of application and the type of fertilizer, the amount of fertilizer applied, and the amount of organic and inorganic nitrogen already in the soil; as well as the physical factors mentioned in Section 2.2 like soil permeability, soil moisture, the amount of water applied as irrigation water or from natural causes, and soil stratification. Concentrations of total nitrogen in the drainage systems of the San Joaquin Valley of California have ranged from 0.4 to 103.4 mg/L with an average of 21 mg/L about 95% of which was nitrate nitrogen (Hassan, 1974). Data from the upper Santa Ana Basin of Southern California indicates, as expected, that once nitrate enters the groundwater system it moves very slowly. Observed rates of movement in this valley range from 0.003 to 0.1 mile per year; so that a specific particle of water needs as much as 300 years to as little as 10 years to travel 1 mile in the basin (Ayers and Branson, 1973).

The water pumped from wells perforated at different depths within the zone of saturation of basins like these indicate that higher nitrate concentrations occur in wells perforated near the top of the saturated zone, and the lower concentrations occur in wells perforated near the bottom of the zone of saturation. This may be explained by the fact that vertical velocities are slight, so that vertical mixing of nitrate water resulting from accumulation of percolating nitrated waters in the upper saturated zone is slow. Where the zone of saturation is relatively thin, mixing takes place more completely and nitrates appear to be more uniformly mixed with depth. Some vertical mixing of nitrates takes place locally in the zone of saturation as a result of fluctuations of water tables produced by the pumping of individual wells. It is probable, however, that these effects are secondary to regional fluctuations in the water table.

Phosphorus compounds occur in organic and inorganic forms and most of these become fixed in the soil. Although usually applied as P_2O_5 the inorganic forms of phosphorus found in soils are mainly iron and aluminum phosphates in acids soils and calcium phosphates in alkaline soils; these are all salts of orthophosphoric acid. These inorganics are fixed in a process in which readily soluble compounds are changed into these less soluble forms by reaction with inorganic or organic components of the soil.

The result is that these compounds have severely limited mobility. The fixation is usually attributed to (1) physical adsorption, (2) anion exchange (isomorphic replacement) and (3) a double decomposition reaction involving solubility-product relationships (Bailey, 1968). The latter is especially important in aluminum systems.

Organic phosphorus consists primarily of inositol phosphates with secondary amounts as nucleic acids and phospholipids. These compounds are adsorbed or fixed in the soil such that their mobility is as restricted as the inorganic phosphorus compounds. The nature of the reactions for organic and inorganic compounds is discussed in Bailey (1968).

Any phosphorous added as fertilizer or released by the decomposition of organic matter is quickly converted to an insoluble form and fixed in the soil. It is for this reason that most water quality problems involving phosphorous occur in surface waters and are due to the erosion of soil carrying phosphorous compounds. The movement of these compounds to groundwater is greatly restricted, but it may occur in cases in which the soil column has been overloaded, and all the fixation sites have been utilized.

Phosphorous concentrations have been observed in tile drain waters of the San Joaquin Valley ranging from 0.06 to 0.39 mg/L, with an average

of 0.11 mg/L (Hassan, 1974). Because of the low solubility of phosphorus compounds and their affinity for the soil these concentrations are probably not directly related to fertilizer application.

Potassium is usually applied to the soil as potash K_2CO_3. It does not generally lead to groundwater pollution because of its susceptibility to adsorption/ion-exchange on the soil (see Section 2.2.2).

Factors Affecting Fertilizer Movement to Surface and Groundwaters

As seen here and in Chapter 2 there are several factors which stand out as affecting the loss of plant nutrients to the groundwater or to surface water (E.P.A., 1973a).

a. Precipitation and Irrigation: Nitrogen in the water percolating below the root zone may contribute to the nitrogen concentration in aquifers, whether the water is from rainfall or irrigation. The nutrient content of rainfall and irrigation water varies with local atmospheric conditions and the source of water. Irrigation can be controlled to reduce the leaching of nutrients.

b. Type of crop: The type of crop affects nutrient losses to surface water or groundwater through erosion and leaching, respectively. Erosion of soil and loss of phosphorus and organic nitrogen associated with sediment are much lower for sod crops (pasture and grasses) than, for example, corn and soybeans. When more water enters the soil than is lost by evapotranspiration of the crop, the excess water can leach nitrate.

c. Temperature: This factor affects the mineralization (ammonification) of nitrogen. During cold periods, plant activity is retarded, reducing the rate of nutrient utilization and water consumption. Surface runoff by rainfall occurs when a frozen sublayer exists. During spring nutrients are leached.

d. Ammonification and Nitrification of Nitrogen.

e. Denitrification (see Section 2.2.3): This is usually not an important factor. It may lead to the removal of nitrate from the root zone of crops such as rice, that are submerged in water for a long enough time to go anaerobic.

Methods of Control

The control of phosphate pollution depends largely on control of soil erosion. Control of nitrate movement to surface water or to aquifer depends on the control of runoff and leaching.

To reduce the percolation of fertilizers which may contribute to groundwater pollution, from agricultural nonpoint sources, several methods have been developed. These methods include determining and applying the necessary quantity at the proper time and place; improving practices such as conservation tillage and crop rotation; and contouring and terracing to control soil and water losses (E.P.A., 1973a;Ayers and Branson, 1973).

a. Timing and placement: The timing is very important for nitrogen fertilizers because they are leached much easier than, for example, the phosphorus. The best time is determined by considering the soil, climatic conditions and the kind of crop. Nitrogen fertilizer should never be broadcast on frozen land. The placement of fertilizers include: broadcasting, plowing before planting, and top dressing after the crop has been established.

b. Slow-released fertilizers: Chemical inhibitors that can be incorporated with nitrogen fertilizer have been developed to retard nitrification. Presently, the general use of these inhibitors in agriculture is restricted by the high cost. These materials are most effective on pastures or with plants having a long growing season.

4.2.2 Pesticides

The word pesticide is a general term that covers fungicides, herbicides, insecticides, fumigants and rotenticides. A classification table for pesticides is given in Appendix 4.1. The synthetic organic chemicals are the most important compounds because of their toxicity and popularity in use; and these are the compounds which are emphasized here. The three main insecticides of importance in relation to groundwater pollution are the organochlorines because of their persistence in the environment, the organophosphorous because of their relative mobility, and the carbonates because they are relatively new and little is known about their behavior in the ground. These insecticides are toxic to humans and animals. Most herbicides are important from a groundwater pollution point-of-view because they are very mobile and toxic to plants (phytotoxic) in low to moderate concentrates and to humans and animals in high concentrations. Pesticide dusts, sprays and granules are applied by aircraft and ground equipment to fields, and in some cases are worked into the soil. From here they may be leached into the groundwater system.

Types of Compounds

The synthetic organochlorine pesticides have been widely used since 1945. They are characterized by a long-term residual effect (persistence), by a low solubility, and by a relatively specific effect upon target organisms. Over the years, however, the various target insects have developed resistant strains which has limited their usefulness. This, coupled with their persistence and toxicity has lead to recent bans on the best known of the organochlorine compounds, DDT. Despite their low solubility they are extremely toxic, and groundwater containing parts per billion of these compounds may be unsafe for drinking purposes. Most organochlorine insecticides are strongly adsorbed on soils (Adams, 1973) and, because of this the threat to groundwater quality is limited (Eye, 1968). However, Swoboda et al. (1971) and Johnson et al. (1967) have demonstrated the organochlorines can move via leaching. What's more, they can also move with soil particles onto which they are adsorbed, as these particles move through cracks in the soil, or in a well gravel pack.

The organophosphorus and carbamate compounds degrade relatively quickly and have only limited residual action against pests. Their solubility is also limited, but it is much greater than that of the organochlorines. Because of this greater solubility, the organophosphorous compounds may move great distances underground, although there is data indicating that they are adsorbed moderately to strongly (Swoboda and Thomas, 1968). The degree of movement depends on the particular pesticide and soil.

Most herbicides are relatively soluble and mobile. Dregne et al. (1969) found that 2,4D was only slightly adsorbed in laboratory columns. Schneider et al. (1970) performed an aquifer field test which confirmed that some heribicdes essentially move with the water. There are some less mobile herbicides for which Adams (1973) has summarized the adsorption properties.

A further description of pesticides and their behavior in soil can be found in Bailey and White (1964), International Symposium on Pesticides in the Soil (1970), Society of Chemical Indsutry (1970), and Adams (1973). The Department of Health,Education and Welfare (1969) or McKee and Wolf (1963) provide other, more general, information.

Factor Affecting Pollution by Pesticides

Some of the most important factors affecting pollution of groundwater by pesticides, besides those associated with the adsorption of pesticides on the soil itself, are (E.P.A., 1973a).

a. Methods of Application: Pesticides escape during the application, and also by their solubility and volatility. Pesticides are applied in liquid form into the soil or as a spray, or in solid form as a dust or granule. These are imperfect methods of application because some of the pesticide reaches nontarget areas. Various emulsifiers and oils can be added to the spray to increase droplet size and thereby to reduce drift. Improved application of dusts may be possible with electrostatic equipment which produces charged particles.

b. Container Disposal: Pesticides can enter the environment through careless or improper disposal of containers and unused materials. If they are deposited or buried in permeable materials, the groundwater can be polluted. Section 19 of the Federal Insecticide, Fungicide and Rodenticide Act as amended in 1972 (Public Law 92-516) directs the administrator of EPA to issue procedures and regulations governing the disposal of pesticide containers.

Methods of Control of Pollution by Pesticides

There are two catagories into which the control of pesticide use can be classified. In the first of these a substitute for chemical pesticides is used (E.P.A., 1973a). In the second case chemical pesticides are used, but with greater efficiency (E.P.A., 1973a).

Among the non-chemical pest control methods cultural practices rank high. These practices include changes in the methods of cultivating and harvesting crops that make the environment less hospitable to pests. So, for example, tobacco stalks remaining after harvest support large numbers of tobacco worms and diseases. Destruction or removal of the stalks immediately after harvest aids in controlling these pests. Crop rotation is one of the most ancient methods for pest control.

Through biological control, a pest's natural enemies can be a major factor in its control. The introduction of predators or pathogens to fight a specific pest has been used for a long time, but at the present time biological methods of controlling disease, pests, etc. do not appear reliable. For example, the Helliothis virus was recently registered for control of bollworms on cotton, but the virus is not yet sufficiently persistent (E.P.A., 1973a).

Insect sterilization is another method, one of the most selective, for suppressing insect populations. An example is the protection of 364, 372 hectares of cotton in the San Joaquin Valley of California from incipient populations of the pink bollworm (E.P.A., 1973a).

The use of resistant crop varieties, plant varieties that are resistant to diseases, insects, and nematodes, is one means of solving pest provlems in an economical and relatively desirable manner. Although, absolute resistance to pests is rare, even a modest resistance can greatly reduce the need for pesticides.

Among the methods increasing efficiency is the use of a minimum amount of pesticide. In current practice, more pesticides are used than is necessary for proper pest control. Continuous careful monitoring should make it possible to reduce the number of scheduled treatments. Unnecessary applications can also be reduced by determining the critical period for treatment. Also we can control by treating only those areas that are heavily infested by the pest (E.P.A., 1973a).

A second efficiency technique is to use more effective pesticides. Only compounds that degrade rapidly in the environment should be used, but that is extremely difficult. There are some instances like Mirex (a chlorinated hydrocarbon) that has not caused a residue problem or harm to wildlife or the aquatic environment. The biological efficacy of pesticides might also be increased by synergists. Certain synergists have increased the insecticidal action of organophosphorus applied to boll weevils. Many studies of synergism have been made to solve problems caused by insects that have become resistant to pesticides, but the same principle could be applied to increase the efficacy of the materials before their use is developed extensively (American Chemical Society, 1969; E.P.A., 1973 a).

There is more information on pesticides and their control in American Chemical Society (1969) and E.P.A. (1973 a).

4.2.3 Animal Wastes

Animal wastes have received considerable attention in recent years because of the major trend toward large confined livestock and poultry operations. The runoff and solid organic matter from these operations is a source of nitrogen and phosphorus, which can pollute surface water and/or groundwater.

In the past feedlots and other confined animal facilities have been located and designed without regard to soil, topographic or hygeologic conditions. As a result the organic matter from these facilities directly entered surface water, and nitrates from the decomposing waste leached into groundwater systems (Resnik and Rademacher, 1970). In most current operations the runoff is now collected and either treated, or applied to the land. The solid wastes, too, are removed and they are often spread on the ground (E.P.A., 1973a). Both of these operations lead to an increasing nitrate load to the groundwater; and if the animals are ingesting inorganic feed additives like sodium chloride, this combined with the NO_3^- leads to an increase in TDS (Adriano et al., 1971). These same problems can arise, although to a much lesser degree, where animals graze.

When the wastes are applied to land, the rate of application should be based on the range of physical chemical and climatic factors which influence its decomposition and movement (Section 2.2). If proper guidelines are followed the soil-plant system will not be overloaded and the soil as a treatment system should function efficiently (E.P.A., 1973a).

Besides the application of wastes to the land (which is also the lowest cost method), there are other methods for the biological treatment of animal wastes. Among these are anaerobic degradation in lagoons which has received the most attention from livestock producers. Evaporation ponds have been used in arid or semi-arid areas for disposing of surface runoff.

Appendix 4.2 presents guidelines given by the California State Water Resources Control Board for the protection of surface water and groundwater from animal wastes from confined facilities. In addition further information on animal wastes and groundwater can be found in Resnik and Rademacher (1970) and E.P.A. (1973a).

4.2.4 Irrigation

The pollution of groundwater by salts introduced due to agricultural practices is most common in areas experiencing extensive irrigation. Irrigation return flow, or water which is diverted for irrigation purposes and eventually returns to a surface water or groundwater supply, is the irrigation water not consumed by evapotranspiration. Because the amount of water decreases during this process, but the dissolved salts in the irrigation water do not, the salts are concentrated in the return. Additionally, the irrigation water may leach some natural salts and accelerate the leaching of fertilizers and pesticides (Sections 4.2.1 and 4.2.2). The concentrated salts in the return flow, usually represented in terms of TDS or electrical conductivity (EC), are a source of low quality water for both surface water and groundwater (Peterson et al., 1970).

Irrigation efficiency is the ratio of the amount of consumptive use or evapotranspiration, to the amount of applied irrigation water. By definition low irrigation efficiencies lead to large amounts of return water, which are only moderately degraded in quality. High efficiency leads to low amounts of return water, but with a very concentrated salt solution. The total amount of salt returned to groundwater, however, is often lower in the high efficiency case (Hassan, 1974).

The amount of salt returned to the groundwater depends on the irrigation efficiency, the type of soil, the amount and distribution of rainfall, and the salt content of the soil and irrigation water (Kovda et al., 1973). Since the salts are ions, the ion exchange complex of the soil is important. Usually, the return flow indicates the appropriate total dissolved solids content as calculated by a mass (salt) balance. But the distribution of types of ions depends on the type of ions in solution and in the soil. Typically, the return flow chemistry from younger irrigated fields reflect the chemistry of the natural soil, while older fields reflect more the type of irrigation water applied historically (Kovda et al., 1973).

The salt balance (Kovda et al., 1973) is often used as a technique for determining the salinization threat to a soil, and/or groundwater reservoir. The main concern in agricultural practice is to maintain a low enough salt content in the root zone to provide for high crop yields. This often involves the leaching of salts to the groundwater where they mix with the ambient system and are eventually reapplied in irrigation water. The degraded groundwater is not pumped in every case, but it is the source of base flow to streams which is used for irrigation water downstream.

When there is an excess of sodium in the soil, the soil colloidal fraction floculates (see Section 2.2.2) and clogs the soil pores. This prevents drainage and makes it difficult to irrigate. The sodium can be removed by adding a soil conditioner, like gypsum ($CaSO_4$ $2H_2O$) to displace the sodium. That is the gypsum exchanges with the sodium which is leached downward, and the soil defloculates restoring its permeability.

Groundwater quality degradation from irrigation return flows can be controlled in a number of relatively indirect ways (Law, 1971). These include, for general management, improvements in the water delivery system and on-the-farm water management. Or more directly, a drainage water removal system can be installed which prevents the recharge of degraded water and provides for its treatment or disposal to the ocean or a drain line. Drainfields are usually installed for other primary purposes, however, including waterlogging and soil salinization prevention (Kovda et al., 1973).

Kovda et al (1973) provides excellent further reading on the subject of irrigation. In addition there are references by Law (1970, 1971).

4.3 Urban and Domestic Pollution

Two major forms of domestic wastes generated by modern society threaten groundwater quality: solid waste and municipal waste water (sewage). These wastes, or their residues from the treatment of the wastes, must be disposed of in some way. If the wastes are ultimately disposed of to the land or in subsurface excavations, groundwater contamination can result. The effect of the disposal of these wastes into surface waters, which may indirectly affect the groundwater quality, is discussed in Section 4.5.

4.3.1 Municipal Waste Water Disposal

The extent to which the direct discharge of municipal waste water on land will affect groundwater quality depends on the amount of the discharge, the degree of treatment, the local hydrologic and geologic conditions, and the method of application (Collins, 1973).

In addition to the direct application of waste water to the land, sludge, the solids residue produced during conventional primary and secondary waste water treatment, is frequently applied to the land. Although it is primarily considered a means of disposal, land application of sludge is often also thought of as a beneficial means of soil conditioning. The potential threat of groundwater quality posed by the application of waste water or sludge to the land is focussed on its biological and chemical effects, and these are generally related to public health.

The threat to public health resulting from the transfer of pathogenic organisms from sewage to sources of drinking water has long been known. This threat is as real in the case of groundwater as in that of surface water. However, the ability of the soil to provide some protection (Section 2.2.3) has been studied a great deal in the past few years due to the great interest in land treatment methods (Boyd, 1969; Morrill, 1973). Miller has concluded that:

> "...it seems likely that the soil filter will effectively eliminate the pathogenic bacteria and protozoa reaching the soil from applications of secondary effluent or sewage sludge. Survival of viruses is still an open question because of the paucity of information on this topic. The limiting factor in the elimination of all pathogens may be the effectiveness of the physical and chemical processes of the soil filter in retaining the pathogens long enough for their elimination by the soil microbial population." (Miller, 1973)

This aspect of the elimination of pathogens is discussed in Section 2.2.3.

To prevent the possible contamination of groundwater by pathogenic organisms as a result of land application most large municipal facilities chlorinate the effluents before they are discharged. In the case of individual septic systems and sludge digestion long contact times with anaerobic populations are used to reduce the possibility of pathogenic survival.

Another form of pollution is the result of organic matter in the sewage, characterized by a biochemical oxygen demand or BOD. Organic pollution is common when disposal is to surface water. It is much less common with groundwater because of the soil treatment factor. Organic material in waste water is decomposed by bacteriological enzymatic reactions (Section 2.2.3, Sabey, 1973). If sufficient oxygen is available, the process is aerobic. However, if insufficient oxygen is available, which is usually the case in groundwater systems, the process will be anaerobic. Anaerobic decomposition can cause serious odor and color problems in the groundwater. This leads to the necessity of a relatively large distance through the zone of aeration from the surface or point of application of sewage to the groundwater table.

Chemical components of waste water and sludge, which threaten groundwater quality, include the residuals of biodegradation and organic and inorganic substances which are considered potential environmental toxins. These components are usually not removed by the standard treatment processes. Many chemical reactions alter the character of waste water or leachate as they pass through the soil (Sections 2.2.2 and 2.2.3). These alterations may lessen the environmental impact (for example, through the adsorption of organics on the soil), or may increase the environmental hazard (for example, through the conversion of organic nitrogen to nitrate, a much more mobile and therefore, hazardous material). The most important chemical reactions which occur in the soil in these cases are ion exchange, adsorption, precipitation, and biochemical alteration. The influence of these soil characteristics, as well as the climate and hydrolgeology, is usually studied as part of the site selection procedure. Parizek discusses the importance of site selection for large municipal land disposal operations (Parizek, 1973; Evans, 1973) and some requirements for site selection for individual septic tank systems are discussed by Bernhart (1973), Morrill (1973) and Miller (1972). Various methods of treatment of waste water prior to discharge are discussed in Chapter 3, but the different methods of application are discussed in this section.

The effect of domestic waste water disposal on nitrate concentration in groundwater has been studied in some detail. Miller (1972) discusses the relationship between the water table depth and the concentration of nitrates verses organic nitrogen in the groundwater in areas where septic tanks are used to treat domestic waste. Morrill (1973) has attempted to establish a relationship between nitrates concentration and dwelling unit densities.

Several branches of the U.S. Government have funded extensive studies on the effect of septic tank on groundwater quality (FWQA, 1969).

In order to deal with the potential effect of land application of domestic wastes on nitrate concentrations in the groundwater, most state regulatory agencies have established standardized field tests and minimum requirements for the location and design of septic tanks (e.g., California Regional Water Quality Control Board - Guide Lines for Waste Disposal from Land Developments). However, most present standards are based on intuition and experience and not on scientific experimentation. Some of the standards are being challenged as more becomes known about the nature of the processes involved (Miller, 1972; Bernhart, 1973).

The problems created by the introduction of environmental toxins from waste water is not clearly understood. Municipal waste effluents and sewage sludges contain a number of organic and inorganic substances which are considered potential environmental toxins. A list of these materials would include phenolic compounds, the chlorinated hydrocarbon pesticides, and chlorinated biphenyls, detergent residues like ABS and NTA, petroleum products and heavy metals (Miller, 1973). Although the soil profile shows a considerable ability to remove or detoxify these compounds, the effect on groundwater is not clearly understood at this time (Miller, 1973; Ellis, 1973).

Municipal waste water which is not discharged into surface water bodies can be applied to the land in several ways. Individual homes frequently employ septic tanks or cesspools as a means of treatment, with the effluent being applied to the land either through leaching fields or pits. This is a very common means of domestic waste treatment in suburgan and rural areas. The use of septic systems seems quite adequate providing the density of the units is maintained at a sufficiently low level to insure that the soil system will be able to treat the waste load. Many studies on the spacing and operation of septic tank systems have been made and standard regulations exist in most areas controlling the use of these systems (Meyer, 1973; Miller et al., 1974).

Large municipal waste disposal systems may include infiltration basins, irrigation, or ponding as means of land application. These are forms of artificial recharge (Section 4.5). The Environmental Protection Agency has sponsored a detailed study of land application in the United States which includes an analysis of the effectiveness of the various methods in reducing the threat to groundwater quality (E.P.A., 1973c;other studies include Godfrey, 1973; Sopper and Kardos, 1973; Collins, 1973; Kerfoot, 1974).

The land application of sludge has been practiced for many years. The effects of sludge application on groundwater quality are of interest due to the increase in the use of sludge as a soil conditioner. The increasingly difficult task of sludge disposal is making the ultimate use of land disposal more attractive. In particular the use of sludge to recondition acid soil (from strip mining areas) is being suggested. In general the effects of sludge disposal on groundwater quality are the same as those of waste water disposal, although varying in degree (Peterson, 1973; Lejcher, 1973; Kudrha, 1973; Pratt, 1973).

4.3.2 Solid Waste Disposal

Large scale solid waste disposal facilities include dumps, incinerators and land-fills. Ultimately most solid waste is disposed of on land either in the original form or as incinerator ash (Burch, 1973).

Open dumps have proven to be disasterous to groundwater quality. In dumps the wastes are exposed to precipitation which greatly increases the amount of leachate produced. Due to the high concentrations of pollutants in the leachates from dumps the soil profile is frequently unable to provide sufficient treatment and the groundwater is often seriously polluted (Cummins, 1968; Weddle and Garland, 1974).

The procedures which are used in a sanitary landfill operation were developed partly as a result of experience with pollution caused by open dumps. These procedures include the spreading of the waste in layers and covering of each layer with a layer of soil. Compaction is used to reduce to volume and to reduce the rate of decomposition. These general procedures reduce the public health hazard resulting from exposed wastes (flies, rats, etc.) and reduce the potential or groundwater contamination by reducing the amount and rate of leachate production.

Several studies have been done on the production of leachate in landfills. Numerous studies have demonstrated that the concentrations of pollutants in the leachate produced by an experimental landfill were very high. Qasim (1970) studied the production of leachate in landfills of different depths and concluded that deep landfills pose less threat to the groundwater because the leachate is produced at a slower rate (for a longer time) and that the soil is better able to adsorb the pollution. Zanoni (1971) has reviewed the literature with respect to these attenuation processes.

As in the case of municipal sewage disposal, site selection is an important component in the control of groundwater pollution by landfills. Cartwright and Sherman (1969), Farvolden and Hughes (1969) and Zanoni (1971) describe landfill site selection criteria for humid areas. The landfill design also influences the eventual degree of leachate production. Salvato et al. (1971) and Zanoni (1971) describe the various alternatives: impermeable barriers, surface and subsurface drains, sumps which are pumped out periodically, and monitoring wells.

In their booklet "Waste Discharge Requirements for Waste Disposal to Land," the California State Water Resources Board describes California's landfill system. Four categories of landfills are described based on site characteristics, waste characteristics, and operating procedures. The booklet describes the standards and restrictions for each category of landfill.

4.3.3 Highway De-icing Salts and Other Sources

Urban areas concentrate people, and domestic, commercial and industrial activities that lead to groundwater pollution. For example, urban groundwater is subject to recharge of water which is contaminated by polluted air and atmospheric precipitation, or has leached various street chemicals through porous asphalt pavements; not to mention possible septic tank or landfill pollution. One of the most publicized sources of contamination is highway de-icing salts. Salts, primarily sodium chloride, are applied to northern streets during the winter to cut and melt know and ice. Part of this runs off in surface streams, but the remaining part can percolate into the soil and eventually reach the groundwater. This is a serious source of water pollution in the Northeastern United States (Miller et al., 1974). Another common source of urban pollution is leaking sewer lines, which leads to organic, bacterial and nitrate groundwater contamination. A description of these and other secondary domestic pollution sources is given in Meyer (1973) and Miller et al. (1974) along with suggested control and monitoring measures.

4.4 Radiological Pollution of Groundwater

The International Atomic Energy Agency predicts, in its publication "Nuclear Power and Environment", that nuclear plant orders will account for half the capacity of all orders for electric power generation in some industrialized countries within the next decade. That total installed electric power generating capacity, worldwide, will be 50% nuclear by the year 2000; and by that year nuclear power will account for as much as 90% of new plant orders. Based on this assumption, by the year 2000 the accumulative stored activity of nuclear waste worldwide, would be 700,000 megacuries of fission products and it seems logical to consider those radioactive wastes as potential groundwater pollutants depending on the method of storage.

In Spain there are already several nuclear power plants completed or under construction; and with the anticipated shift to this source of power in the future the potential contamination of groundwater by radiological materials must be seriously considered. Therefore, the main intention of this section is to emphasize the examination of potential risks from the atomic energy industry.

4.4.1 Definition of Radiological Pollution

Radiological pollution is the man-made or man-induced alteration of the radiological integrity of groundwater. All radioactive materials are agents of the pollution. Radioactive materials consist of unstable atoms, and radiation is a process which accompanies the transformation of unstable atoms to states of complete or greater stability. Unstable atoms can become stable through the emission of either alpha or beta particles and both of them may or may not be accompanied by gamma radiation. Whereas alpha or beta radiation brings about a change in the size of the nucleus or in the number of a particular type of particles therein, the emission of gamma radiation represents only a release of energy. Radionuclides lose their radioactivity through physical decay, which unit of measurement is the physical half-life: the period of time characteristic of each radionuclide in which one-half of the initial radioactivity is lost through decay. The frequency or rate of decay is generally expressed in curies (c), microcuries ($\mu c = 10^{-6}$) and picocuries ($pc = 10^{-12}$). A curie is defined as 3.7×10^{10} disintegrations per second, the approximate specific activity of one gram of radium in equilibrium with its disintegration products.

4.4.2 Sources of Radiological Pollution

Radiological pollution may originate from radiation of natural origin, weapons testing fallout or the peaceful uses of atomic energy. The nature of these sources and their influence on groundwater quality is reviewed in Appendix 4.3. Radiation of natural origin and tritium from weapons testing fallout are probably not important sources of groundwater contamination except in a few isolated cases. Although, the tritium ion is used as a tracer for determining rates of groundwater flow, the primary radiological threat to groundwater comes from nuclear power plants and associated industries. Table 4.2 shows radionuclides of interest in groundwater aquifers.

The sources of groundwater contamination from the nuclear power industry may be categorized as follows: mining and milling of uranium ores, nuclear power plants,chemical reprocessing plants, radioactive waste disposal, and the transportation of nuclear fuel and radioactive waste

Table 4.2

Radionuclides of Interest in Hydrogeology (Federal Register, November 17, 1960)

Element	Mass Number of Radioisotope	Half-Life years, y; days, d; hours, h	Radiation	MPC above Natural Background μc/ml in Solution in Water
Barium	131	13 d	γ	2×10^{-4}
	140	12.8 d	β^-,γ	3×10^{-5}
Bromine	82	36 h	β^-,γ	3×10^{-4}
Calcium	45	153 d	β^-	9×10^{-6}
Carbon	14	5600 y	β^-	8×10^{-4}
Cerium	144	290 d	β^-,γ	1×10^{-5}
Cesium	135	2.9×10^{6} y	β^-	1×10^{-4}
	137	33 y	β^-,γ	2×10^{-5}
Chlorine	36	4×10^{5} y	β^-	8×10^{-5}
Chromium	51	27.8 d	γ	2×10^{-3}
Cobalt	57	270 d	β^+,γ	5×10^{-4}
	60	5.3 y	β^-,γ	5×10^{-5}
Hydrogen	3	12.4 y	β^-	3×10^{-3}
Iodine	129	1.72×10^{7} y	β^-,γ	4×10^{-7}
	131	8.04 d	β^-,γ	2×10^{-6}
Phosphorus	32	14.3 d	β^-	2×10^{-5}
Plutonium	238	92 y	α,γ	5×10^{-6}
	239	2.4×10^{4} y	α,γ	5×10^{-6}
	240	6580 y	α	5×10^{-6}
	242	5×10^{5} y	α	5×10^{-6}

Table 4.2 (continued)

Element	Mass Number of Radioisotope	Half-Life years, y; days, d; hours, h	Radiation	MPC above Natural Background μ c/ml in Solution in Water
Radium	226[a]	1620 y	α, γ	1×10^{-8}
	228	6.7 y	β^-	3×10^{-8}
Radon	222	3.83 d	α	A gas
Rubidium	86	18.7 d	β^-, γ	7×10^{-5}
	87	6×10^{10} y	β^-	1×10^{-4}
Ruthenium	103	40 d	β^-, γ	8×10^{-5}
	106	1 y	β^-	1×10^{-5}
Sodium	22	2.6 y	β^+, γ	4×10^{-5}
Strontium	89	51 d	β^-	1×10^{-5}
	90[a]	29 y	β^-	1×10^{-7}
Sulfur	35	88 d	β^-	6×10^{-5}
Uranium	235	7.1×10^{8} y	α	3×10^{-5}
	238	4.5×10^{9} y	α, γ	4×10^{-5}
Zinc	65	245 d	β^+, γ	1×10^{-4}

MPC = Maximum permissible concentration

(Appendix 4.3). Mining and milling of uranium ores results primarily in pollution from mine tailings (see Section 4.1). Nuclear power plants may be the source of leaks or other accidental releases, from storage tanks or pipes. Chemical reprocessing plants may also be sources of accidental releases from storage facilities.

The primary threat to the groundwater comes, however, from the disposal of radioactive wastes, which must be carefully managed to ensure that development of nuclear energy will not impose future limitations on human activities.

In the context of groundwater contamination, several factors determine the radiological significance of the different radionuclides existing in radioactive wastes. The half-life is important because the transport processes through the soil are generally slow and because permissible ingestion limits are, approximately, inversely proportional to half-life. Also one must consider the abundance and energy of radionuclides released during decay and the biochemistry of human physiology. Martin and Apsimon (1972; see also Kaufman, 1973) have computed the relative radiological significance of the n^{th} radionuclide at any time by the expression

$$\frac{\frac{A_n}{MPAI_n}}{\sum_o^N \frac{A_n}{MPAI_n}}$$

where A_n is the activity of the n^{th} of N radionuclides and $MPAI_n$ is the maximum permissible annual intake of the n^{th} radionuclide. From the standpoint of abundance, hazard and persistence, Sr^{90} and Cs^{137} are the most significant radionuclides for the first 500 years.

Wastes are disposed by different techniques under different safety conditions depending on their classification (see Appendix 4.3 for an explanation of the classification system and details on disposal techniques). High level wastes must be isolated from the remainder of the environment and are stored in tanks, salt mines or deep caverns. Low to intermediate wastes pose the greater threat to groundwater quality, because the product of their treatment is usually released to the environment. For example, by burial of solid wastes or the infiltration of liquid wastes. Some, however, are relatively isolated via injection wells to deep strata or seams created by hydraulic fracturing.

Transportation accidents is the last category of possible waste entry to the groundwater. Considering the vast increase expected in radioactive materials transfers it looks as if the number of accidents will increase, with an attendant possibility of groundwater pollution.

4.4.3 Introduction and Evolution of Radionuclides within the Aquifer

Radionuclides can enter the aquifer either directly by the introduction of liquid wastes, or indirectly by water infiltrating through the soil and leaching contaminants from the surface of solid waste buried with insufficient protection. The release may not be deliberate but may result, for example, from the accidental rupture of a buried pipe-line causing the escape of a radioactive solution. However the release occurs, the soil and soil water become contaminated, and this leads to the special case of radioactive pollution of groundwater. The pollution may disperse and become diluted or may remain close to the point of introduction, according to the chemical composition of both the soil constituents and the water. The contaminants may retain their toxicity for long periods, depending on their radioactive decay rates; so even though they may stay underground for many years, there remains the possibility that the longer-lived radionuclides will survive in a large enough quantity and more far enough below ground to pollute a potable source of water (IAEA, 1965).

As described in Chapter 2 the soil is a medium in which many pollutants are reduced in potency. Radionuclides, normally, attenuate through adsorption, dispersion, dilution and with the passage of time. Thus the environment has a potential capacity to receive limited quantities of radioactive materials without creating an unacceptable exposure potential. Among the four factors mentioned above two of them have the strongest influence to delay and reduce the amount of a radionuclide arriving at some point of concern: adsorption and radioactive decay.

The adsorption of a radionuclide depends on its chemistry in relation to the mineralogy of the formation. In Chapter 2 the velocity of a sorbed chemical, in this case a radionuclide, into the aquifer can be described by the expression (Kaufman, 1973):

$$V_R = V \frac{1}{1 + k_d \frac{\rho}{n}} = k\ V$$

where V and V_R are the average seepage velocity of the water and the transport velocity of the radionuclide, R, respectively; k_d is the distribution coefficient (adsorbed radionuclide per gram of soil dissolved radionuclide per cm^3 of solution) in the formation media, and ρ/n is the ratio of bulk density of soil to porosity. For example, if H^3, Sr^{90} and Cs^{137} are injected simultaneously, H^3 moves with the water and advances the greatest, Cs^{137} is moderately adsorbed (Table 2.1) and doesn't advance very far, while Sr^{90} is exchanged and is somewhere in between.

The effect of radioactive decay is to reduce the concentration of a radionuclide. The activity of a radionuclide is described by the expression

$$A_t = A_o \ k^{t/T}$$

where t and T are the time and half-life respectively, and k is a constant which depends on the radionuclide. Inoue and Kaufman (1963) demonstrated that with a knowledge of the distribution of residence times of water flow between two points and with reasonable estimates of the distribution coefficient in the porous media, as well as the density and porosity of the media, quite accurate radionuclide arrival patterns can be predicted. More recent developments along these lines are described in Chapter 5 and in Robertson and Barraclough (1973).

4.4.4 Groundwater Protection Criteria

The control of groundwater pollution by radioactive materials must focus on prevention because of the extreme hazard these materials represent. In order to avoid radiological pollution of groundwater several basic principles may be applied: containment of the radioactivity can best be achieved if contact between the radioactive material and percolating groundwater can be prevented; leaching can be prevented if the geological structure is impermeable; however, if leaching should occur, the ion exchange capacity of the geological materials can be expected to restrict the migration of radionuclides through the ground. Therefore, before making a final decision about the most suitable location for any of the facilities belonging to the atomic energy industry, it is necessary to conduct an extensive geological, hydrogeological and geochemical investigation.

Among the sources of groundwater pollution mentioned in this report, radioactive waste disposal, and especially ground burial, appear to be one of the most intimately connected with groundwater. All disposal schemes for radioactive wastes have in common the selection of an environment without circulating groundwater; and in the case of ground burial the basic problem is to avoid contamination of groundwater which could finally lead to an unacceptable contamination of drinking water supplies and food chain products.

Peckham and Belter (1962), Appendix 4.4, considered several factors for the selection of radioactive waste burial sites including meterorology, surface hydrology, groundwater hydrology, geology and the physical-chemical characteristics of earth materials. In 1965 the International Atomic Energy Agency assembled a table to summarize the significant natural phenomena affecting ground disposal (IAEA, 1965). Obviously the factors listed in Table 4.3 must be considered individually since certain combinations of so-called favorable features are inconsistent with naturally occurring situations. They are therefore an indication only of the qualities generally found to be favorable, but many exceptions are possible. LeGrand (1962) provides a third approach for analyzing sites.

If the waste is injected by a deep well into a permeable zone or hydraulically fractured seam, other criteria must be considered. Especially leakage from the disposal zone to a zone of potable water supply must be prohibited. Criteria for this kind of evaluation can be found in Section 4.1 or Belter (1972).

There are several good references on radioactive materials and groundwater pollution: AEC (1962), Davis and DeWeist (1966), OECD-ENEA (1971), and Kaufman (1973).

Table 4.3

Assessment of Ground Disposal Factors

(from IAEA, 1965)

Factors	Favorable Characteristics	Unfavorable Characteristics
Physical state of waste	Solids	Liquids; sludges
Chemical composition of waste	Alkaline; neutral low salt	Acid; high salt
Radiochemical composition of waste	Presence of short-lived nuclides	Presence of (a) long-lived nuclides, (b) anionic species
Geographical situation	Low precipitation; remote from open water sources; remote from population centres	High precipitation; close to rivers, lakes; close to population centres
Geology (geochemistry)	Uniform unconsolidated materials; high sorptive soil; low soluble calcium content	Fissured rocks; inert materials; high content of calcium or other soluble salts
Hydrology	Deep water table; slow-moving ground water; slow ion migration; long path to point of discharge	Shallow water table; fast fround water; fast ion migration; short underground flow path

4.5 Natural and/or Induced Groundwater Pollution

In Sections 2.1 and 2.2.2 the background level of water quality in groundwater aquifers was associated with the natural process of leaching and/or precipitation-solution. Taking this for granted, there are other sources of naturally low quality water: sea water and connate salt water. These waters may be redistributed by pumping or recharge activities, which may lead to pollution and the eventual abandonment of groundwater water supplied. This section also describes the pollution of groundwater due to air pollution, the induced recharge of polluted surface recharge, thermal pollution and artificial recharge.

4.5.1 Salt Water Intrusion

Fresh water in aquifers often comes or can come into contact with saline water. The sources of saline water are classified by the Task Committee on Saltwater Intrusion of the American Society of Civil Engineers (1969) as: encroachment of sea water in coastal aquifers; sea water that entered aquifers during deposition or during a high stand of the sea in past geologic time; salt in salt domes, thin beds, or disseminated in the geologic formations; slightly saline water concentrated by evaporation in tidal lagoons, playas, or other enclosed areas; return flows to streams from irrigated lands (see Section 4.2); and man's own saline wastes (see Section 4.1-4.3). In this section we will examine the first source under the title "Sea Water Intrusion in Coastal Aquifers" and the next three under the title "Saline Water in Inland Aquifers". This category of contamination is often called "contamination from natural sources", although it is an inadvertent effect of some human activities. The last two cases are examined in other sections. Each of these is a source of present or potential contamination of freshwater aquifers.

Sea Water Intrusion in Coastal Aquifers

This section briefly describes the historic development and occurrence of the problem, its physical model, its causes and modes, and the environmental consequences.

The problem of salt water intrusion was first noticed in highly populated coastal areas, where the demand for freshwater was most pressing. For example, Braithwaite described the increasing salinity of waters pumped from wells in London and Liverpool, England, as early as 1855 (Todd, 1959). The first physical interpretation of the problem was given by Ghyben and Herzberg, some 70 years ago. Today the problem of sea water intrusion is encountered as a present or potential threat in most coastal aquifers in Europe, the United States, Japan and other countries. In recent years sophisticated physical interpretation models and methods of analysis have been developed, together with technology for monitoring, controlling, and preventing this kind of problem.

The earliest and simplist historical interpretation of the mechanism of intrusion was the "static equilibrium" concept of Ghyben and Herzberg. They noticed that salt water in coastal aquifers was observed at a depth below sea level equal to about forty times the height of the fresh water above sea level. They attributed this distribution to the hydrostatic equilibrium between two non-mixing fluids of different densities. This model gives a very simple interpretation of the intrusion, but very seldom does it give realistic results. Actually both the basic assumptions (no flow and no mixing) are invalid. The fresh water flows into the sea, moving at very low velocities, and near the shoreline creates a seepage face for outflow. This picture was improved by introducing the Dupuit approximation and finding the shape and characteristics of a stationary interface. A number of studies retained the assumption of immiscibility of fresh and salt water and found approximate analytical (e.g., Bear and Dagan, 1964; Rumer and Harleman, 1963; see summary in Bear, 1972) or numerical solutions (e.g., Shamir and Dagan, 1971).

In reality, however, fresh water and sea water are miscible, and thus a transition zone, rather than an abrupt interface, exists between the two fluids. This transition is mainly caused by dispersion, while molecular diffusion is usually a minor factor. Note that since the dispersion coefficient is a function of the aquifer characteristics and the velocity of flow, it is also a function of the tidal characteristics of the surface water. The transition zone can vary in size from several meters to 300 meters (Tyagi and Todd, 1975). In certain cases therefore, the assumption of the existence of an abrupt interface can lead to serious errors.

The sea water intrusion is almost always the inadvertent effect of man's activities. Increased pumping lowers the water table, or the piezometric surface, to the extent that the fresh water potential becomes less than the potential of adjacent sea water. The result is spreading and movement of the transition zone inland. Another cause is the destruction of natural barriers which have historically prevented sea water intrusion.

The seriousness of the problem varies and depends mainly on the flow conditions. Tyagi and Todd (1975) gave the following classification of interfacial regimes.

a. Recharge flow regime: The fresh water moves in the aquifer towards its outcrop. The interface is usually near-flat and parabolic in shape.

b. Reduced flow regime: Due to overpumping or reduced recharge the fresh water flow is reduced. The seepage face gets smaller while the transition zone moves slowly inland until it reaches a new equilibrium point.

c. No flow regime: The seepage face disappears, while the transition zone moves inland with decreasing velocity.

d. Reversed flow regime: The rate of intrusion of the interface accelerates.

e. Overdraft regime: In this case, due to very severe reversed flow conditions, the interface develops a steep gradient and both fluids,sea and fresh waters, move inland. This may be considered as a displacement phenomenon, with very unstable interface.

The intruding salt water makes large zones of the aquifers unusable for all human needs. Only two percent of sea water in fresh groundwater gives a chloride content higher than that permitted by U.S. Public Health Service standards for drinking water; so that most of the transition zone between fresh and salt water, which is often very long, consists of unusable water, too. Once an aquifer is intruded by sea water, it remains polluted for years, given the slow rates of groundwater flow and the long transition zone left behind by the retreating saltwater.

The degradation of the freshwater is not always restricted to an increase of chlorides (Revell, 1941). Some modifications in the composition of salt water can take place because of ion exchange between salt water and the porous media, or due to sulphate reduction and substitution of carbonates or other weak acid radicals (Todd, 1959). However, the total dissolved solids content is not altered significantly through those modifications, except if they are combined with solution and precipitation of salts. Since chlorides are not significantly influenced by these processes a chloride-bicarbonate ratio is suggested as a criterion for sea water intrusion (Revell, 1941).

The control of sea water intrusion is established through the measures described in Section 3.2.2 (also in Todd, 1959, 1973; and Meyer, 1973).

Saline Water in Inland Aquifers

The Task Committee on Salt Water Intrusion in the United States (1969) reported that problems of saline water intrusion are acute not only in coastal aquifers, but also in many inland areas. Two-thirds of the continental U.S. is underlain in part by saline groundwater. Such problems are also very common in Europe (see Examples in Cole, 1974).

The basic mechanisms causing mixing of saline water with fresh waters in inland aquifers are changes of pressure heads, where the two fluids are hydraulically connected, destruction of natural barriers separating the two fluids (Meyer, 1973). For example, it is common to find an aquifer underlain by saline water and separated from it through a fairly impermeable stratum. Destruction of this barrier (e.g., during the drilling of water or oil wells or by leakage through abandoned wells or bore holes) or the development of steep pressure gradient towards the freshwater (e.g., due to overpumping) can cause the saline water intrusion. Upcoming of salt water toward a pumping well is a fairly common phenomenon and has been studied both analytically and in the field (e.g., Dagan and Bear, 1967, Schmotak and Mercado, 1969). Other examples are associated with changes in recharge conditions, or by increases of pressure head created by a new surface water reservoir forcing saline water to move (Meyer, 1973).

The increase of TDS content in fresh groundwater, caused by its mixing with saline waters, makes the water unusable. Those phenomena are usually of local character but nevertheless cause long-lasting contamination. The method of control is similar to that of sea water intrusion (see Section 3.2.2), but also includes the sealing of abandoned wells and proper well construction to prevent leakage (Meyer, 1973; Todd, 1973).

4.5.2 Induced Recharge of Aquifers by Polluted Surface Water

Polluted water from almost any kind of body of surface water (e.g., rivers, channels, lakes, etc.) can infiltrate and cause pollution of the groundwaters beneath them. In the case of rivers or lakes,polluted water will enter unconfined shallow aquifers in areas where groundwater levels are lower than adjacent surface water levels. Pumping from wells near a polluted stream forms a classical example of this kind of pollution. Many different kinds of pollutants enter aquifers through the mechanism of flow from surface water to groundwater. These include many types of inorganic and organic compounds, as well as bacteria and viruses (Meyer, 1973). This is a common occurrence in heavily industrialized areas (Miller et al., 1974) and arid areas (Fuhriman and Barton, 1971).

The reverse problem, involving the degradation of surface water from polluted groundwater can occur when hydrogeological conditions are reversed. That is to say, it occurs when a contaminated aquifer discharges to an adjacent stream. A large fraction of streamflow is derived from drainage of existing aquifers, thus long term degradation of surface water can be anticipated in areas where groundwater pollution continues to exist.

The classical case here involves the movement of salts from irrigation return flows through an aquifer to surface drainage (Fuhriman and Barton, 1971).

The methods of control of groundwater pollution from surface waters can be arranged in two classes (Meyer, 1973). The first class involves effective programs to improve surface water quality; for example, by the control of waste disposal into streams. The second class involves control of pumping and recharge and the proper siting of wells in accordance with hydrogeological characteristics. This helps to minimize infiltration of polluted surface water into the aquifers.

Meyer (1973) provides a good review of the quality interaction of surface water and groundwater.

4.5.3 Recharge of Water Contaminated by Air Pollution

As described in Sections 2.1 and 2.2.2, raindrops pick up various natural impurities as they fall through the atmosphere and come into contact with atmospheric gases and suspended particles. Salt from sea water constitutes one type of suspended particle. However, much higher concentrations of suspended particles and many more constituents result from man's air polluting activities. These include industrial, automotive and urban sources. Where air pollution exists, raindrops may dissolve enough suspended solids to become a source of groundwater pollution (Meyer, 1973).

In the process of infiltration, pollutants present in rainwater plus those picked up by the water passage through the soil become groundwater pollutants when the water reaches the aquifer. Pollutants in precipitation falling on surface water may later reach the aquifer in points downstream.

In the United States the classical example of this contaminant source is related to groundwater chromium pollution, due to airborne chrome-laden dust carried from the air to the aquifer by rainwaters. In this example an electroplating firm was the source of contamination. The chrome-laden dust was discharged through ventilators on the factory roof, and was picked up by rainwater (Deutsch, 1961).

The obvious and most straight forward approach for the control of this kind of groundwater pollution is the control and improvement of air quality. An alternative method of control via land use planning would locate this kind of source in areas without economically important groundwater resources.

4.5.4 Thermal Pollution of Groundwaters

Thermal pollution (raise in temperature) of surface waters in rivers and estuaries is a well recognized environmental hazard, mainly interfering with aquatic life and ecology. Thermal pollution of groundwaters, though, has never been considered as a major problem. As a recent E.P.A. report states:

> "In the case of cooling water returned to the same aquifer from which it has been pumped, the quality of the water may be unchanged from that of the native water except for an increase in temperature. Increased solubility of aquifer materials due to a rise in temperature is believed to be insignificant, except perhaps in carbonate aquifers." (Meyer, 1973)

On the other hand some groundwaters have natural temperatures higher than surface waters in the same area due to the geothermal gradient, depending on depth from which the groundwater is withdrawn. Hence, temperature is a natural characteristic of groundwater. It appears that there are few cases in which a major use of groundwater was detered by a man-induced change in temperature.

4.5.5 Artificial Recharge of Aquifers

The use of the storage capacity in the unsaturated zone of an aquifer system can be, in some cases, an important element in the management of water resources (Brown and Signor, 1973). The objective of the technique is to store and retrieve water of good quality. This objective is quite different from deep well disposal where the objective is to store permanently water of objectionable quality (see Section 4.1). The most common recharge technique is by surface spreading through basins or by induced recharge from adjacent surface water bodies like streams or lakes (Todd, 1959). Less common is the use of injection wells.

The recharge water is usually good quality water, but in many cases treated sewage effluent is used as input for recharge facilities. This practice, in fact, helps to improve the water quality of the effluent since, in the infiltration process, treated sewage waste improves in quality (see Section 4.3). The major problems are the total dissolved solids present in the treated sewage and the nitrates which eventually enter the aquifer. As Brown and Signor (1973) state, in most areas, the recharge spreading basin is a more economical method of improving the quality of available surface water than any other system now in use. Excellent examples of recharge of treated sewage can be found in some areas of Southern California (see Todd, 1959).

Recharge techniques in the case of wells are very similar to the well disposal of liquid wastes (Section 4.1), except for the depths of injection which are, in general, much shallower for recharge wells. Recharge wells are used in two ways. First, they are used to simply add to the total stored volume of water in an aquifer. As in an aquifer recharged via spreading, the water is withdrawn later at some point downgradient. Second, wells may be used to cyclically recharge and then withdraw water depending on the availability and demand. In either case the aquifer material does not perform as nearly well as the soil zone of aeration (the soil filter) as a treatment system, although it can do an adequate job (Brown and Signor, 1973). The main mechanisms in treating the injected water are adsorption and ion-exchange, precipitation-solution, and biochemical degradation in a biologically active area around the well (Ragone et al., 1973). In any case, when stored water is withdrawn through the injection well it resembles the quality of the injected fluid for several hours or days. Later the quality will tend to improve as water which has received more treatment is withdrawn (Sellinger and Aberbach, 1973).

Besides TDS and nitrates groundwater pollution problems in these practices arise when, for different reasons, the recharge water carries some other undesirable element. For instance, when treated sewage water is used and the sewer systems collect both domestic and industrial waste waters, the treated sewage can carry heavy metals or other components not removed in the secondary treatment (see Section 4.3).

The control of pollution from spreading grounds or induced stream infiltration depends on site selection criteria similar to Table 4.3 and on pre-treatment requirements, if waste water is to be used. Control of the potential pollution from well recharge depends on similar criteria. If the well recharge water is of sufficiently low quality this should be classed as a waste injection which is treated in Section 4.1. Control criteria for artificial recharge as a source of pollution can be found in

Meyer (1973). Other information on artificial recharge is available in Todd (1959), Fuhriman and Barton (1971), Brown and Signor (1973) and Sellinger and Aberbach (1973).

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APPENDIX 4.1

Classification of Pesticides

Chlorinated Hydrocarbon Insecticides

aldrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endoexo-5,8-dimethanonaphthalene
dieldrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene
endrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8a-octahydro-1,4,-endo-endo-5,8-dimethanonaphthalene
heptachlor	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-endomethanoindene
DDT	2,2-bis (p-chlorophenyl)-1,1,1-trichloroethane
DDD, TDE	2,2-bis (p-chlorophenyl)-1,1-dichloroethane
DDE	Dichlorodiphenyl, dichloroethylene
methoxychlor	2,2-bis (p-methoxyphenyl)-1,1,1-trichloroethane
BHC lindane (gamma isomer)	1,2,3,4,5,6-Hexachlorocyclohexane
toxaphene	Synthesized by chlorination of camphene to chlorine content of 67-69%.
mirex	Dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta [cd] pentalene

Organophosphorus Insecticides

diazinon	0-0-Diethyl 0-[2-isopropyl-4-methyl-6pyrimidyl) phosphorothioate
malathion	0-0-dimethyl S-(1,2-dicarbethoxyethyl) phosphorodithioate
parathion	0-0-Diethyl-0-p-nitrophenyl, phosphorothioate

Carbamate Insecticides

carbaryl	N-Methyl-1-naphthyl-carbamate
	4-dimethylamino-3,5-xylyl N-methylcarbamate

Herbicides

2,4-D	2,4-dichlorophenoxyacetic acid
2,4,5-T	2,4,5-trichlorophenoxyacetic acid
fenoprop	2-(2,4,5-Trichlorophenoxy) propionic acid
2,3,6-TBA	2,3,6-trichlorobenzoic acid
fenac	2,3,6-trichlorophenylacetate

APPENDIX 4.2

Guidelines for the Protection of Water Quality from Animal Wastes (from California State Water Resources Control Board)

First of all it is important to give some definitions that normally will appear in the following pages. Animal confinement--cattle, calves, sheep, swine, horses, mules, goats, fowl or other domestic animals--corraled, penned, tethered or otherwise caused to remain in restricted areas where feeding is other than by grazing. Manure storage areas--corrals, feedyards, retention ponds, manure collection area of any kind and areas used for storage, composting and or drying of animal wastes. Ten-year 24-hour storm--A storm of 24-hour duration which yields a total precipitation of a magnitude that has a probability of recurring only once every ten years. Washwater--Water which has been used for washing animals or equipment or for cleaning manure storage areas. Retention pond--Pond used to retain washwater or surface drainage from manure sotrage areas until proper disposal on land or other suitable disposal means can be accomplished. Twenty-year peak stream flow-- Stream flow magnitude that is expected to be equalled or exceeded on the average of once every 20 years. One hundred-year peak stream flow--Stream flow magnitude that is expected to be equalled or exceeded on the average of once every 100 years.

a. <u>Guidelines for protection of surface water</u>

1. Animal confinement facilities plus adjacent crop lands under the control of the operator shall have the capacity to retain surface drainage form manure storage areas plus any washwater during a 10-year 24-hour storm.

2. Surface drainage, including water from roofed areas, shall be prevented from running through manure storage areas.

3. Animal confinement facilities, including retention ponds, shall be protected from overflow from stream channels during 20-year peak stream flows for existing facilities and 100-year peak stream flows for new facilities.

4. Washwater and surface drainage from manure storage areas shall be applied to crop lands, or discharged to treatment systems subject to approval by the appropriate regional water quality control board.

5. Animals in confinement shall be prevented from entering surface waters.

6. Lands that have received animal wastes shall be managed to minimize erosion and runoff. Dry manures applied to cultivated crop lands should be incorporated into the soil soon after application.

7. Animal wastes shall be managed to prevent nuisances in manure storage areas.

b. Guidelines for protection of groundwater

1. Manure storage areas shall be managed to minimize percolation of water into underlying soils.

2. Animal confinement facilities shall have adequate surface drainage to prevent continuous accumulation of surface waters in corrals and feedyards.

3. The use of special sealants for retention ponds is not usually necessary when these ponds are constructed on sandy loams or finer textured soil materials.

4. Application of manures and washwaters to crop lands shall be at rates which are reasonable for the crop, soil, climate, special local situations, management systems and type of manure.

5. The salt in animal rations should be limited to that required to maintain animal health and optimum production.

APPENDIX 4.3

Sources of Radiological Pollution

Three sources of radiological pollution may be considered: radiation of natural origin, weapons testing fallout and peaceful uses of atomic energy.

Radiation of Natural Origin

Man is continuously exposed to ionizing radiation of natural origin. This has three components: cosmic radiation originating in outer space and reaching the earth's surface after reacting with, and being partidally absorbed by, the earth's atmosphere; terrestial radiation coming from natural radionuclides present in the earth's crust; and radiation from natural radionuclides that have been accumulated in the body as a result of the consumption of food and water and the inhalation of air containing such radionuclides.

The most abundant primordial radionuclides are K^{40}, Rb^{87}, Th^{232}, U^{235} and U^{238}. The daughter products Rn^{222} and Ra^{226}, which come from U^{238}, are the most important from the standpoint of groundwater. The common isotope of radium, Ra^{226}, is the principal naturally occurring radionuclide found in groundwater and it is the most toxic among all inorganic materials (Davis and DeWeist, 1966). Table 4.2 shows radionuclides of interest in hydrogeology.

The maximum permissible radiation concentrations values for the general population are set low enough so that biological effects are so slight or infrequent that they are impossible to detect. The 1962 United States Public Health Service Drinking Water Standards are: supplies containing not in excess of 3 and 10 pc/L, respectively for Ra^{226} and Sr^{90} would be acceptable without consideration of other radioactive sources. In the known absence of Sr^{90} and alpha-emitting radionuclides, the water supply is considered acceptable if the gross beta activity does not exceed 1,000 pc/L. Several studies have shown that a natural background level of radioactivity in groundwater at levels appreciably above the standard limit is not uncommon.

Weapons Testing Fallout

The amount of activity contributed from fallout due to weapons testing varies and is dependent upon geographical positions, climatological conditions, and the frequency of weapons tests. Fortunately, the longer lived radioactive materials are subjected to natural purification, and the only extensive contamination of groundwater has been by tritium. This is not considered to be significant from a health standpoint because the resulting increase in whole body dose (compared to permissible limits) has not been appreciable.

Peaceful Uses of Atomic Energy

Radioactive materials are processed or used for peaceful purposes in the application of radioisotopes and radiation sources to medicine, industry, agriculture, research and in the nuclear power industry. Compared with nuclear power indsutry, the other sources are relatively minor potential sources of groundwater pollution and are only likely to cause localized problems where poor handling results in spillage or minor accidental releases. The sources of groundwater contamination from the nuclear power industry may be categorized as follows: mining and milling of uranium ores, nuclear power plants, chemical reprocessing plants, radioactive waste disposal, and the transportation of nuclear fuel and radioactive waste (Rubin, 1972).

a. Mining and Milling of Uranium Ores

The raw material of the nuclear power industry is uranium, an element which in its natural state is about as toxic as most other heavy metals. Its chemical toxicity is, in fact, greater than its radiotoxicity. In its uranium ore it is associated with its radioactive decay products, of which radium deserves special mention as it constitutes an important radioactive hazard. When uranium is extracted from ores, the radium remains as a very insoluble sulphate in the uranium mill tailings (ore residues). The main objective of managing the uranium mill tailings is to minimize the dust nuisance. Hence it is necessary to spray the tailings with water to hold down the dust. Here, some solution of contaminates may result with the attendent possibility of leakage to the ground. For additional information see Rubin (1972).

b. Nuclear Power Plants

In analyzing the potential problems associated with the nuclear power industry it is appropriate to distinguish between accident-induced releases of radioactivity and planned releases. The permissible amounts and concentrations of radioactivity that can be released from a nuclear power plant are very small (maximum 5 mrem/year, see definition of terms); these releases are much more likely to cause air or surface water contamination problems and groundwater may be reasonably expected free of contamination. Storage tanks are used to store the irradiated fuel during the necessary time (weeks or months) it takes to reduce the activity of fission products.

This facilitiates its transport to the chemical reprocessing plant. Accidental releases from these tanks may occur and some pollution may result (IAEA, 1968).

c. Chemical Reprocessing Plants

Irradiated fuel from the nuclear power plant is shipped, intact, in heavily shielded casks, to the chemical reprocessing plant where the unburned fissile and fertile materials generated in the fuel by reactor operations are separated and purified for reuse. The effluents from the chemical reprocessing plant are: plutonium and uranium to recycle; treated effluents to discharge; precipitates, sludges or ion exchange resins containing radioactive materials removed by treatment of liquid effluents; and high-level wastes.

The high-level wastes deserve special mention. The fuel, after chop-leaching, is dissolved in nitric acid; then an organic solvent is used to extract the plutonium and uranium from the acidic solution. The remainder of this acidic solution containing almost all the fission products, is the origin of the high-level liquid wastes. The trend is toward direct conversion of the high-level wastes to cintered solid, thus avoiding the current practice of interim liquid storage. The resulting solid must be cooled to avoid meltdown, and where water is used for cooling purposes some contamination may result with the attendent possibility of leakage to the ground (Rubin, 1972).

d. Radioactive Waste Disposal

The peaceful uses of nuclear energy generate enormous quantities of radioactive wastes (Martin and Apsimon, 1972) which need the adoption of a careful waste management polocy to ensure that development of nuclear energy will not impose future limitations on human activities.

Radioactive wastes may be classified according to different criteria: physical (solid, liquid, gaseous) and chemical (organic or aqueous wastes) properties, type of radiation emitted (alpha, beta, gamma) and the composition and degree of contamination. This following classification criteria is adopted here

LIQUID WASTES	High-level activity (10^4 to 10^6 cm^3)
	Low and intermediate activity (10^{-6} to 1 cm^3)
SOLID WASTES	High-level activity (> 10^3 c/ft^3)
(Morgan et al., 1962)	Low and intermediate activity (< 10^3 c/ft^3)

High-level liquid wastes include fission-products solutions which are concentrated by evaporation techniques and then stored in stainless steel tanks contained in protective concrete shields. This interim method is used to take advantage of radioactive decay for a given period after which it will be possible to solidify the wastes. The potential danger of leaking during extended storage of such residues is eliminated by the final process of solidification.

During the past 20 years the emphasis of ground-disposal research and development programs has been directed toward establishing the suitability of using underground salt formations for the disposal of high-level solidified radioactive wastes (Kühn, 1973; Lomenick and Boch, 1973). Bedded salt formations are conceptually desirable in that they are dry, mainly impervious to water, and not associated with usable sources of groundwater.

Low to intermediate level liquid wastes, except in certain cases where there are favorable conditions for immediate disposal into the environment, must be treated to remove most of the contained radioactivity. The liquid wastes remaining after decontamination treatment can be safely disposed of into the environment. The discharge of liquid wastes on the surface or at shallow depth, through seepage basins, swamps, etc., as applied in the United States and Canada (IAEA, 1965) has not been authorized in Western Europe where the water table in many regions is only 3 to 15 meters below ground levels and groundwater is extensively used as a drinking water supply.

In some cases low and intermediate level liquid wastes may be disposed of at suitable sites by deep well injection or hydraulic fracturing (Ionue and Kaufman, 1962; IAEA, 1965; Belter, 1972; Kondratiev, 1972). Deep well injection appears to be a useful method, especially in the case of tritium because it is unresponsive to separation by conventional procedures; and furthermore, because the possibility exists that process dilution water in the plant will be insufffficient for assuring that these effluents meet radiation-protection standards prior to release to surface water. In some cases the wastes are mixed with a concrete slurry that sets into a solid, thereby preventing the possible migration of radionuclides.

In particular, liquid waste disposal into the ground must be carefully evaluated since it is not possible to retrieve the radioactivity discharge. Factors such as the climate, the type of soil and geological structure, the hydrology, particularly in relation to the direction of groundwater movements, and the proximity to population centers have to be taken into account.

High-level solid wastes arise, most of them, from the solidification of fission products, therefore the methods of disposal described for high-level liquid wastes are, here, equally suitable.

Low-to-intermediate-level solid wastes are handled most economically by burial above or slightly below ground level (Morgan et al., 1962; Peckham and Belter, 1962; IAEA, 1965). Usually, the waste is dumped directly into trenches and then covered with earth. Waste with a somewhat higher radioactivity content is usually dumped in concrete lined trenches and covered with concrete and earth. Storage in the ground should not be used for significant quantities of long-lived radionuclides, such as Sr^{90} or Cs^{137}, unless satisfactory containment can be assured for the period required for decay, and it is unsuitable for transuranium elements (IAEA, 1965).

One special item in connection with land burial concerns the presence of plutonium. Although the migration of plutonium through soil is extremely limited, the long half-life and high specific radiotoxicity of plutonium require very prolonged surveillance of the sites where plutonium-contaminated solids have been buried. Some consideration is being given to the burial of these wastes in deep geologic formations, under conditions of extreme isolation from groundwaters (DECD-NEA, 1972).

Ground burial at or near the surface cannot always be carried out (densely populated countries, unfavorable geology, high water table, etc.). In these cases, other methods have to be found, and the possibilities of using abandoned mines or deep geological formations as possible sites have been the subject of extensive investigations. The result of such investigations indicate that the storage in salt formations is particularly attractive as repositories for solid radioactive wastes of all activity levels (DCED-NEA, 1972).

e. Transportation of Nuclear Fuel and Radioactive Wastes

The movements of "new fuel" to nuclear power plants, irradiated fuel and radioactive wastes from N.P.P. and chemical reprocessing plants, are made according to rules usually covered in the International Atomic Energy Agency "Regulations for the Safe Transport of Radioactive Materials". Compliance with these regulations, which are applicable to all modes of transport, insures that the transport of radioactive materials will not result in unacceptable radiation hazards to man and the environment, both in normal circumstances and in accident situations.

It is possible to say, in general, that the method of transporting any single shipment of radioactive material is determined more by convenience than by economy. Rail routes, in general, are inflexible. Truck routes are chosen for their convenience; it is easier for trucks to avoid heavily populated areas and significant watersheds than for rail shipments.

Depending on their chemical and physical characteristics, the type and intensity of the radiation emitted, the activity concentration, etc., radioactive materials may be simply transported in strong industrial packages, such as conventional oil drums, or in more elaborate containers with shielding and even, in the case of very active materials, cooling equipment. Radiological safety is the overriding requirement; and the protection of the public, transportation workers and the environment is achieved by a combination of standards and requirements applicable to packaging, to limitations on the contents of packages and to radiation levels from packages.

APPENDIX 4.4

Factors for the Selection of Radioactive Burial or Waste Pond Sites

(Peckham and Belter, 1962)

a. Meteorology: Precipitation is an important consideration because it is the source of surface and groundwater potentially capable of transporting activity from a burial ground into the surrounding environment.

b. Surface Hydrology:

i) Density of Surface Streams: With respect to burial ground operations, stream density is important in that it controls the distance that groundwater in the upper zone of active circulation must move from points of recharge between streams to points of discharge along streams.

ii) Flow Characteristics of Receiving Streams: With reference to streams that drain burial ground operations, the concern is with the magnitude of flow, and its variation in time. These factors control the amount of dilution of fission products that might enter the stream.

iii) Chemical and Physical Quality: This information may be an aid in evaluation of possible reactions between the more hazardous nuclides, and mineral and organic materials suspended in the water on the stream bed.

c. Groundwater Hydrology:

i) Depth to water table: The depth to the water table is of major importance in burial ground operations. Circulating groundwater is the only natural vehicle capable of transporting significant quantities of activity from points of burial to points of discharge at the surface.

For this reason the bottoms of the trenches in which radioactive waste is buried should be above the water table.

ii) Direction and Rates of Groundwater Movement: To adequately assess directions and rates of groundwater movement, it is essential to examine the permeability distribution below the burial area and through the area to points of groundwater discharge at the surface.

iii) Chemistry of Groundwater: A knowledge of the chemical characteristics of water and soil in the unsaturated zone above the water table and in the near surface zone of groundwater flow, and their effect on possible reactions between the more critical nuclides and local materials is required.

iv) Groundwater Use Down Gradient from Burial Ground: Assessment of existing and potential groundwater utilization is required to assure that no valuable resources are in jeopardy.

d. Geology: The composition of the overburden should permit easy excavation and the texture should permit the trenches to stand open without support. The overburden should be sufficiently porous and permeable to permit adequate drainage of burial trenches. In a granular material, however, a certain minimum of fine clay material should be present to provide optimum opportunity for sorption. The tendency for water to move readily through fractures in bedrock, and the tendency for bedrock fractures to furnish little opportunity for sorption of radionuclides eliminates most sites from consideration where bedrock would be exposed in trenches.

e. Physical-Chemical Characteristics of Earth Materials: The physical and geochemical information should provide a description of the mineralogy, the grain size distribution; the permeability and porosity distribution below and surrounding the site. Sorptive capacities for the potentially hazardous radionuclides such as Sr^{90}, Cs^{137}, Ce^{60}, Pu, etc., should be determined for the complete range of earth materials occurring at the site. The ability of earth materials to adsorb, or otherwise immobilize or slow down the movement of water-borne fission product activity, is a major reason that in some environments radioactive wastes can be disposed of safely by land burial. For this reason it is essential that the interactions of soil and rock from the site with the more hazardous nuclides should be investigated in considerable detail.

CHAPTER 5

Methods of Analysis

Previous chapters of this report have discussed different methods of achieving, through technological, economic or legal means, various desired goals with respect to both the prevention and the control of groundwater contamination. This chapter deals with the techniques that are available to evaluate these different methods, and to select the method or set of methods that achieves the desired goals in the most appropriate way. To this end, in this chapter we first discuss some general concepts related to groundwater quality management; next we review different possible criteria for choosing among alternatives,and finally we discuss how the techniques of systems analysis, including both optimization and simulation, can be used to aid planners in selecting the "best" alternative for achieving desired goals for groundwater quality in terms of the defined criteria. The chapter ends with a short summary of the different techniques presented, together with appendices presenting simple examples to illustrate the application of systems analysis techniques.

5.1 Groundwater Quality Management

Due to agricultural, urban and industrial development, regional water requirements will grow considerably in the future. At the same time this development may create problems of pollution, both in surface and in groundwater resources. If planning for water resource development isn't established in the region, the water requirements will tend to be met in an uncontrolled and perhaps very costly manner, and the quality of water may degrade. If plans for future water quantity management are undertaken, but changes in quality (and other environmental effects) are not foreseen,the same danger exists. Ideally, plans for regional water development should be formulated in such a way as to fulfill all quantity, quality and environmental objectives.

The planning process, in which systems analysis techniques are useful tools, could be said to be composed of the following steps:

a. Establishment of quantity and quality (or environmental) objectives.

b. Analysis of the quantity and quality factors playing decisive roles in the area.

c. Analysis of the capability of the region to fulfill objectives without any planning action.

d. Formulation of alternative plans or policies to achieve the objectives in a feasible way.

e. Analysis of each alternative plan, together with their impacts and degree of achievement of objectives. The results of this step should be fed back to Step d in order to modify the alternative plans.

f. Selection of the plan that obtains the highest degree of achievement of objectives.

g. Plan implementation.

An alternative plan or policy is a set of controlled actions to be performed following a certain schedule. These actions may need legal, economic or institutional arrangements in order to be developed as originally planned. They can be of a very different nature, and, as explained in detail further on, the variables which measure their quantitative characteristics are denoted decision variables.

Each alternative plan produces a different degree of achievement of the relevant objectives. If a mathematical expression indicating this degree of achievement can be developed, it is called, in systems analysis language, the objective function. An alternative plan or policy is identified, thus, by the values given to its decision variables and to the objective function specified for the planning process.

As has been said, the impact of the plan may not be easily expressed in terms of a single objective function, and other methods of evaluation must be established. For example, a water resources plan in which water quality considerations have been taken into account, can be tested in order to determine its feasibility and adequacy. This test could include an analysis of the plan's acceptability to the public and local government in the region, its effectiveness in meeting relevant objectives, its efficiency in meeting quality objectives at minimum cost, and its completeness in accounting for all investments and required actions.

5.2 Criteria for Choosing Among Alternative Policies

Among the different alternatives available to achieve the proposed objective the decision maker must choose the one that achieves them to the highest degree. Economical, social and environmental considerations are the key elements in the selection of the "best" alternative.

Perhaps the simplest way to formulate the problem is to consider as an objective the present value of net benefits; in this case the "best" alternative is the one which generates the highest net benefits. However, in many cases this alternative may not be the "best" one from an environmental or social point of view, as in the case of a water quantity plan in which quality aspects have been neglected. If net benefits in the economic sense are commeasurable with the benefits produced by water quality improvements, the two objectives could be associated in a single objective function whose maximum would indicate the best alternative. However, if the benefits produced for each one of these partial objectives (economic efficiency, water quality, etc.) are not commeasurable, the "best" alternative cannot be obtained so simply, and multiobjective analysis must be employed. A thorough analysis of this methodology can be found in Major (1975), but, for completeness,the basic concepts are discussed below.

Evidently, if the regional water planning objectives are different in nature, as in the above examples, the selection of the best alternative plan is subject to a tradeoff between the degree of achievement of each plan in fulfilling the different objectives.

In the best of cases, a transformation curve, or upper limit of achievement of feasible plans, can be drawn. All points inside the curve represent the different feasible plans (Fig. 5.1)·Plan B, for example, is the best in terms of net economic benefits, but the worst in terms of environmental quality, while Plan D achieves greater environmental quality but less economic net benefits than Plan D. Evidently the best plan lies on the curve BCED, the points outside being infeasible (due to the characteristics of the system) and the points inside being sub-optimum.

The selection of the best plan lying on the transformation curve must be a compromise between the relative importance given (in the part-

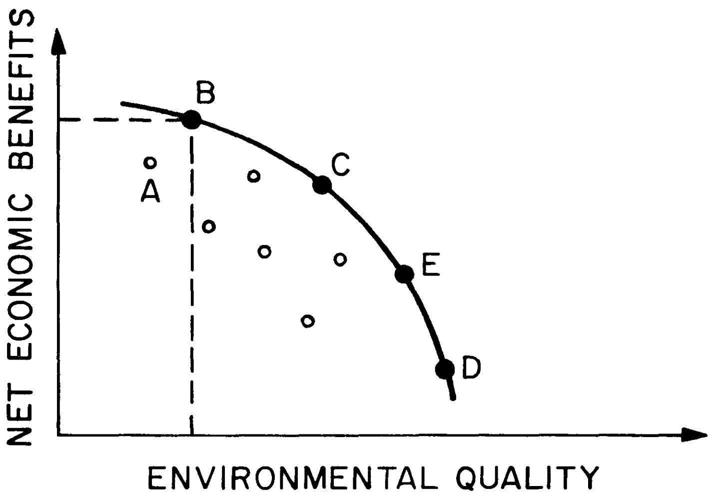

Figure 5.1: The Transformation Curve.

icular region and for the people concerned) to economic development versus environmental quality. As will be seen later on, these two objectives are of central interest in problems of groundwater quality. In other cases the objectives may be national income, regional income, or any other economic, social or environmental measure.

Some more practical methods have also been developed to choose among alternatives with multi-objectives, such as the Delphi method or the Cross-impact method. The Delphi method uses an iterative questionnaire format to obtain different experts' opinions regarding their choice of a "best" alternative under given conditions. The numerically rated answers given by the experts are evaluated statistically to obtain a group median and (in some instances) quartile answers. The median and quartile answers are then given to the participants who are asked to re-evaluate their answers in the light of the group response. When they have done so the answers are again analyzed and new group answers are computed for the second time. The process is usually repeated three times.

In the Cross-impact method, the alternative plans are compared, tabulating the major economic, socioeconomic and environmental impacts of each alternative in a matrix format. In this manner, the major implications of each alternative can be readily evaluated. For each type of impact, major elements of the various alternative plans to be compared are analyzed.

As an example, the plan elements considered for the Santa Clara Basin in California consisted of the water treatment and supply cost, the wastewater facilities cost, the wholesale water costs, and the penalty costs. These items were evaluated in terms of dollars, but in the case of impacts on the physical environment, biological communities, or socioeconomic conditions, only qualitative measures of the impact were given. The final evaluation was performed by giving each aspect a range of values from 1 to 3, in terms of the following:

a. Project performance (water quality enhancement, fulfillment of EPA requirements, and ease of management)
b. Economic evaluation (economic impact and facilities cost-local share)
c. Socioeconomic effects
d. Environmental effects (physical and biological)
e. Plan acceptance (compatible with Federal, state and regional regulations, local institutions, construction requirements)
f. Plan flexibility (accommodate demographic changes, accommodate technological changes, accommodate institutional changes)

As can be seen, great importance was given in this particular case to plan acceptance and flexibility, two evaluation elements which are less evident in a theoretical approach, but which are of great importance if the plan is to be implemented in real life.

5.3 Systems Analysis Techniques

The first sections of this chapter have contained an overall review of the application of planning procedures to water resources systems in which surface and groundwater quality are considered as important elements. The next sections focus on specific systems analysis methods that systematically lead to the determination of the "best" (or optimum) alternative plan.

5.3.1 Important Definitions

To make a clear connection between the general concepts of planning and the equivalent concepts used in systems analysis, some definitions must be stated, although some introductory ideas have been advanced in the first section. Most of the concepts given below are taken directly from Hall and Dracup (1970).

A system may be defined as a set of objects which interact in a regular, interdependent manner. Systems analysis is concerned with making decisions with respect to those aspects of the system which are subject to some degree of control in order to attain certain objectives.

A system can be characterized, as seen in Figure 5.2, by the following:

a. A rule which determines whether any particular object is to be considered a part of the system or of the environment (the system boundary).

b. A statement of the input and output interactions with the environment.

c. A statement of the interrelationships between the elements of the system, the inputs and the outputs, including any external interaction between outputs and inputs.

The controllable and partially controllable inputs are called decision variables. When each decision variable is assigned a particular value, the resulting set of decisions is called a policy or, as in preceeding paragraphs, an alternative plan.

In general, there will be constraints which limit the possible policies. A policy which does not violate any constraints is called a

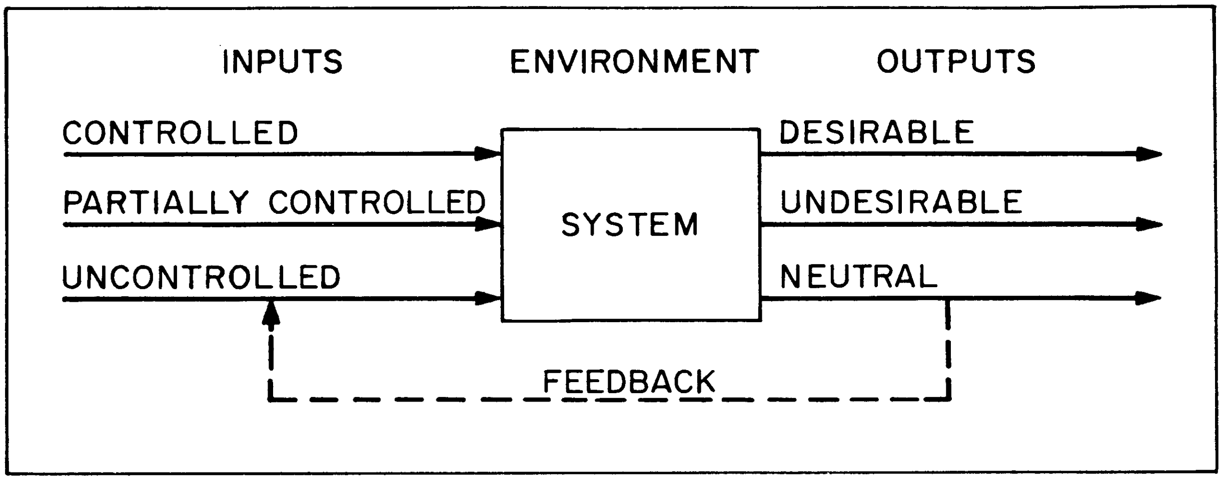

Figure 5.2: Systems Input-Output (After Hall and Dracup, 1970.)

feasible policy. The subset consisting of all possible feasible policies is termed the policy space. This policy space may vary over time and space.

The condition of the system proper at any time and place is represented by variables known as state variables. Supplementing the state variables are the system parameters which essentially can be considered as constraints for the purposes of the study.

The concept of a "best" decision set or policy implies criteria whereby the effect of any feasible policy on the desirable and undesirable outputs can be gauged. These criteria are called objectives. The overall objectives in most instances consist of many component objectives, some of which are quantitative objectives, measurable with some degree of numerical accuracy, while others are non-quantitative objectives, measurable at most in an ordinal or qualitative sense. As explained in the previous section, if two objectives can be measured or described in the same units or terms with the same general degree of accuracy, they are termed commensurate objectives. Non-commensurate objectives either cannot be expressed in common units, or the order of magnitude of errors inherent in the evaluation of one masks the significance of the magnitude of the other.

The objective function is any statement by which the consequences or output of the system can be determined, given the policy, the initial values of the state variables and the system parameters. However, usage has generally limited the term to the determination of those quantitative objectives which are fully commensurate. As was mentioned in the previous section, when a system can only be evaluated in terms of non-commensurate objectives, the "best" policy can, in theory, only be selected through the use of multi-objective analysis.

In practice, systems analysis techniques have never been applied comprehensively to groundwater quality problems. Rather, most studies have relied on a straightforward selection process between a discrete number of alternative plans in terms of easily quantifiable objectives (see, for example, California State Water Resources Control Board, 1974). Nevertheless the possibility of establishing the use of systems analysis in groundwater quality problems has great potential; with this in mind, some examples of possible objective functions, decision variables and system constraints are given below.

5.3.2 Possible Objective Functions for Groundwater Quality

In a broad sense, objective functions can be considered as being either economical or physical.

Formulated from an economical point of view, an objective function in groundwater quality could perhaps be defined in terms of maximizing the net benefits derived from pollution control, minimizing or eliminating groundwater pollution, or minimizing the costs plus expected value of possible damages produced by pollution. It is evident that in all cases serious problems arise in the economic evaluation of the benefits and costs involved in groundwater pollution.

From other more general viewpoints, if groundwater quality management is integrated in the general management of water resources, the objective function could perhaps be to maximize net benefits produced by water supply availability, defined in terms of both quantity and quality.

In some cases, quality may be directly related to quantity; in others, quality enters the system as a constraint; and in others, it could be represented by a set of development alternatives.

Objective functions of the physical type include, for example, the maximization of the quantity of waste to be disposed of by underground injection, subject to water quality standards at some other points in the aquifer. In very industrialized and contaminated areas, the objective function could perhaps be to optimize water quality in given points of the aquifer, while maintaining the development of the area. In all cases, it is of special importance to give the time factor its correct weight.

The choice between one or another type of objective function can bring about a large amount of discussion. It seems safe to say that an objective function expressed in terms of net benefits (even if the relationship between the alternatives and the costs and benefits involved is difficult to estimate) can more adequately express the broad objectives of any ambitious project. However, because of the difficulties indicated above, most water quality studies have approached the problem through the establishment of water quality standards (see, for example, Kneese and Bower, 1968). These standards usually select some measurable property of quality which is related to the actual objective in such a way that the specification of a maximum or minimum value of that property will accomplish the objective in a qualitative sense. This applies both to surface and groundwater, and, for example, total dissolved solids (TDS in mg/ℓ) is used as one of the several indices required to measure the quality factors which are deleterious to agricultural production.

Under this approach, the systems analysis problem becomes one of determining the least cost method of meeting a given set of standards. In the process, the standard can be varied in order to determine the optimal cost as a function of the level at which the standard is set. With this information the socio-political processes can take over and the level of quality that is worth the cost could be determined.

This approach, which has been applied to surface waters (river standards), is, at present, the most representative of the application of systems analysis to the problems of water pollution. As can be seen, under this approach water quality is not viewed as an objective in itself, but rather as a constraint on the system, while the objective function is stated as the cost necessary to attain or to meet these quality standards. This same approach could be applied to groundwater, establishing "aquifer standards" which should be met at least cost.

This approach has been used, although in a simple fashion, in the Water Quality Control Plan of the State of California, which integrates both surface and groundwater quality in a complex system. However, the systems approach to groundwater quality management tends to be more complex than that of surface waters, mainly due to the fact that the response of the aquifer to quality related inputs is slow, areally distributed, and usually very difficult to predict. Control actions taken to maintain aquifer standards may only be noticed a long time after their application, and they affect only a small portion of the aquifer body. Furthermore, the legal and institutional measures necessary to implement the cost-bearing operations could be very complex, especially when groundwater is privately owned.

5.3.3 Decision Variables

Some examples of the types of decision variables that could be considered in a systems approach to groundwater pollution include those related to regulatory programs for domestic and industrial waste water disposal, and for solid waste disposal; procedures for accidental spills of pollutants; regulatory programs for artificial recharge of aquifers with fresh or treated waste water; injection and/or pumping programs for sea or saline water intrusion control; water well standards; monitoring and surveillance systems; systems of treatment plants for water supply; regulatory programs for pesticides; and regulatory programs for irrigation practices.

In general, decision variables could be classified into the following types:

a. Geographical: e.g., location of pumping and/or injection wells, or location (given the choice) of sources of contaminants, development and irrigation areas, etc. These usually appear as sets of alternatives, rather than in continuous form.

b. Those relating to any quantitative aspect of waste produced: Industrial or agricultural production or the amount of waste generated by any kind of activity, accident, etc. Examples include the amount of waste injected in the ground for disposal purposes, or the amount of fertilizer used in agriculture.

c. Operating policies. For example, time rates of withdrawal from an aquifer.

d. Those relating to engineering alternatives: for example, the design of treatment plants (size, type of treatment) or the modification of production processes (reuse of waste water, flow rate for recycling, etc.).

e. Those of a quantitative character usually considered in general water resources management, such as the physical dimensions of structures or targets for development.

In all cases groundwater quality has to be related to quantity factors. In sea water intrusion, for instance, the quality of water pumped from a coastal aquifer depends upon the quantity withdrawn.

5.3.4 Constraints

The first type of constraint on the values of the decision variables that must be considered is that given by the nature of the physical system itself. Constraints of this type can range from the simple application of the continuity equations or mass balance equations, to more complex relationships that can only be determined through the solution of the differential equations which govern the behavior of the groundwater system.

A second type of constraint is that established by the planner or by the nature of the technological and administrative system. Perhaps the most direct example is that produced by the water quality standard (current or desired) established in the area for the different water uses (recall that we can also consider the water quality standards as decision variables, in the cases in which the possibility of modifying these standards exists). These constraints are likely to be present in the form of limitations on the quantity of non-desirable elements in the water, or perhaps, in special cases, in terms of water temperature.

Among other kinds of constraints, we can consider the technological or administrative limitations in the design of structural or non-structural alternatives for groundwater pollution control.

5.3.5 Statement of Mathematical Programming Problem

In the previous sections we have presented a discussion of the types of objective functions, decision variables and constraints that are most relevant to problems in groundwater quality management. If we denote:

$\underline{x} = (x_1, x_2, \ldots x_n)^T$ = Vector of decision variables

$f(\underline{x})$ = Objective function (scalar)

$g_i(\underline{x}) \geq b_i$ = i^{th} constraint function, $i = 1, 2, \ldots, m$

then we can often state a problem in groundwater quality management as a <u>mathematical programming</u> problem of the type

Max or Min $f(\underline{x})$

subject to $g_i(\underline{x}) \geq b_i$, $i = 1, 2, \ldots, m$

<u>Mathematical optimization techniques</u> (or optimization models) are used to solve the above type of problems, that is to say, to obtain the "optimum" values $x_1^*, \ldots, x_n^*$ such that $f(\underline{x})$ is maximized or minimized and the constraints are met.

In most cases water resource systems are so complex that the best alternative cannot be obtained directly through the use of mathematical programming techniques. In these cases simulation (or descriptive) methods are often employed to test and suggest improvements to the alternatives obtained through the use of mathematical programming. Descriptive or simulation models attempt to evaluate the effect, both physical and otherwise, of a particular policy or control scheme on the environment; whereas "prescriptive" or optimization models are concerned with determining the "best" policy or control scheme in terms of its effects with respect to specific criteria.

In the next sections we review both these techniques and present some examples of their application to groundwater quality problems. However, it should be pointed out that in actual practice, because of the complexity of aquifer systems, only simulation has been applied to the analysis of groundwater quality problems, although some simple optimization techniques have been applied to groundwater quantity problems.

5.4 Optimization Techniques

There are many different types of mathematical optimization techniques, such as linear programming, dynamic programming, or calculus. Each technique has different characteristics which make it particularly applicable to different types of problems. A general review of these techniques can be found in de Neufville and Stafford (1969) or Wagner (1969).

Prior to the development of computers and mathematical programming, the methods of calculus provided the only means of mathematical optimization. However, since the use of calculus requires that the problem be expressed through continuous functions which have continuous first derivatives, they are generally not suited to the solution of problems in water resources, especially in groundwater quality. Even if a problem can be expressed in this manner, the differential equations may be impossible to solve.

Linear programming, on the other hand, is a powerful procedure which can be used in many instances. A more detailed discussion of linear programming techniques and their use can be found in many texts, as for example, Dantzig (1963), Hadley (1962), or Simmons (1972).

The basic form of the linear programming problem is as follows:

$$\text{Max (or Min) } z = c_1x_1 + c_2x_2 + \ldots c_nx_n$$

subject to the constraints

$$a_{i1}x_1 + a_{i2}x_2 + \ldots a_{in}x_n \geq b_i, \quad i = 1, \ldots, m$$

and to the non-negativity restrictions

$$x_j \leq 0 \quad j = 1, \ldots, n$$

Powerful computerized tools based on what is known as the "simplex method" can be used to solve problems of the above type, containing very many constraints and decision variables.

In general, linear programming (L.P.) is very useful in the solution of problems which involve many variables. Although it is possible to include some elements of stochasticity, L.P. is primarily used in deterministic contexts, considering, for example, a typical year which may, however, be divided into seasons which repeat themselves each year. The use of deterministic L.P. allows the planner to take full advantage of this relatively simple and inexpensive optimization tool. L.P. is often used to screen out the least productive alternatives, giving a preliminary solution which can then be improved with the use of more detailed simulation models.

Although at first one may think that more complex versions of L.P. that include uncertainty, such as linear programming under uncertainty or chance constraint programming (de Neuville and Stafford, 1969), may provide a more accurate first approximation to the optimum solution than a deterministic L.P., this is not necessarily so. Often the additional data required for the more complex models cannot be accurately determined. In addition, the exponential increase in the cost of running the model may greatly reduce the number of runs which the planner can make. In many cases, additional runs made with a deterministic model will provide good sensitivity analyses, and the end result may be as accurate at much less cost.

An enumeration technique, which is a systematic search through all possible combinations of decision variables, will, by definition, define the optimal solution. However, it will take an incredible amount of time. Because of this, methods have been developed which permit the identification of the optimum solution through the examination of a limited range of the possible combinations. Dynamic programming is one of the mathematical programming methods which utilizes this limited search technique.

Dynamic programming techniques can be used in many situations when L.P. cannot. Specifically, non-linear, discrete, and non-convex functions can be handled by this method. However, dynamic programming is restricted by the fact that all the decision variables must be separable in the objective function. Although dynamic programming does not necessarily require the consideration of time as a parameter, it can be particularly useful in determining the optimal allocation of a limited resource (in our case groundwater) over a period of time. The optimum is determined through an iterative process of finding the optimum for each step and combining these optima with those of the previous steps.

While dynamic programming enables the analyst to solve non-linear, non-convex problems, it is restricted to problems in which the number of interactive constraints is very small. A thorough discussion of dynamic programming may be found in Bellman (1957)or Wagner (1969). Many applications of dynamic programming and linear programming to water resources problems may be found in Buras (1972) and Hall and Dracup (1970).

In order to better explain the use of optimization models as an aid to the analysis of groundwater quality problems, an example involving linear programming is presented in Appendix 5.1.

5.5 Simulation Techniques

5.5.1 Numerical Models of Groundwater Quality

Simulation consists essentially of synthesizing a real or abstract system. The outputs of this system are supposed to approximate the outputs of the protctype within a given degree of accuracy. Through the simulation model we try to reproduce some of the characteristics of the prototype, leading to the evaluation of alternatives or policies in terms of a given objective function, as discussed in Section 5.3.5. That is why they are sometimes called "performance-prediction models" (Remson, et al., 1971).

According to Dooge (1973), "...the various types of simulation (also called models) could be grouped under the headings of regression models, analog simulation, digital simulation and physical models". All of them are of interest in groundwater hydrology (see Bear, 1972 ;or Todd, 1959). However, the recent development of high speed digital computers provides us with the possibility of developing numerical models which reproduce our complex prototype systems with increasing accuracy. Since almost all the developed groundwater quality models are numerical, the emphasis in this report will be on them.

A numerical model can be defined as a set of mathematical expressions that is solved numerically and which is supposed to describe the various relations within the system. It can be in the form of differential equations with their auxiliary conditions or of semi-empirical relations,or a combination of both. According to Remson, et al. (1971) two types of information must be available in preparing a numerical model:

a. laws or relations governing the phenomenon

b. auxiliary conditions such as geometry, hydraulic or chemical characteristics,and initial and boundary conditions.

The numerical model, as any other type of simulation, reproduces some but not all the characteristics of the prototype. Of course, it is quite legitimate to try to simplify the model by eliminating all characteristics which are unimportant for the purposes of the study. We may fix the required accuracy and drop out all characteristics which have a negligible contribution to the features we try to reproduce. So there should be a tradeoff between sophisticated but costly models and simple but inexpensive ones. However, as usually happens in groundwater quality models, we may have to neglect important features or we may have to simplify our model considerably because of: lack of physical knowledge, very complex quantitative relations bewteen our parameters, lack of a proper numerical schematic, very high computer costs or limited capacity of available computers, or limited data (perhaps the most important factor).

It is because of these restrictions that it is important to know what a groundwater quality numerical model can and cannot do. A thorough understanding of the potential of groundwater quality models is necessary for the organization of data collection and management, for obtaining available help to the planning and management process, and for directions for future research.

From the modeler's point of view (Freeze, 1972), pollutants move in groundwater by a complex interaction of four processes which are discussed in Section 2.2:

a. Convection is the transfer of pollutants by the moving water with the same velocity and direction. Freeze (1972) suggests that this is the primary mechanism, so that in cases in which the other processes can be ignored, any groundwater flow model can be used for groundwater quality modeling.

b. Mechanical dispersion is the spreading phenomenon caused by velocity variations. This must be included in the model whenever there are strong concentration gradients that may influence the distribution of pollutants as would be observed by a pumping or observation well or other observation technique.

c. Molecular diffusion is usually unimportant compared to dispersion, except if the flow is very slow (e.g., in the unsaturated zone). The molecular diffusion coefficient is often lumped together with the mechanical dispersion coefficient into what is known as the "hydrodynamic dispersion coefficient."

d. Hydrochemical interaction between fluid and soil is sometimes an important process that can change the quality of the groundwater.

Basically soil scientists and agricultural engineers have studied some of the complex interactions between dissolved chemical constituents and the soil (see Section 2.2.2). Unfortunately, we are only at the beginning of incorporating this body of knowledge into our models (Evenson et al., 1973).

Most of the work done in groundwater quality modeling is centered on large scale groundwater basins facing salinity problems, or on coastal aquifers with saltwater intrusion. These studies model only conservative pollutants and, although concerned with a very special kind of pollution, are of great practical importance. They are by far the most developed and we will mainly refer to them in the next paragraphs.

By assuming that the quality constituents have conservative properties, we can describe the mass transport phenomenon by a set of equations which can be called (Fried, 1971) the dispersion scheme (see also Chapter 2). This scheme can be applied to describe miscible kinds of pollution or immiscible ones, provided that the pollutant behaves like a tracer. It consists of the dispersion equation, the continuity equation, Darcy's law and the state equations of the mixture. A major simplification, which is always included, is to assume that the density and viscosity of the mixture are constant. This implies that the quality constituent behaves like a tracer.

To solve the dispersion scheme, both analytical and numerical methods can be applied (Remson et al., 1971). However, the analytical solutions are only found for very simple cases or for research purposes (Remson et al., 1971, Bear, 1972). The numerical solutions, which take full advantage of the digital computer's capacity, are of more practical interest to regional groundwater modeling.

It is interesting to note that the groundwater quality models were developed as extensions of groundwater flow models, and along the same three lines:

a. Finite differences. This was the first to be used, on the basis of the experience gained from groundwater quantity problems (e.g., the Boussinesq equation as solved by Pinder and Bredehoeft, 1968). The finite difference scheme is derived by replacing the differential equation by finite difference approximations. A rectangular mesh is superimposed on the region and the system of difference equations is solved at every node. At each step we first solve for the heads and then for the concentrations. The methods of solution can be classified into explicit and implicit methods. The explicit methods are conceptually and operationally simple to apply, but require a very small time-step in order to converge; the implicit methods require the simultaneous solution of large systems of differential equations, but are more economical to run on a computer, because of the longer time steps. Usually the alternating direction procedure is used to solve the flow equation and the method of characteristics is used to solve the dispersion equation (Pinder and Cooper, 1970, or Reddell and Sunada, 1970); further information can be obtained from standard textbooks on finite difference methods for the solution of differential equations. The finite difference solution was the first to be applied on the basis of experience gained in groundwater flow modeling. However, it was very soon realized that the method of characteristics "... is tedious to program for the computer and is not suitable for several situations commonly encountered in the field" (Pinder, 1973).

b. To avoid the drawbacks of the finite difference method, Price et al., (1968) developed a numerical approach based on a Galerkin approximation of the partial differential equation in conjunction with the finite element method. The Galerkin method is a technique of high accuracy and versatility (Rubin and James, 1973; Pinder, 1973; Lee and Chen, 1974; Pinder and Frind, 1972). The main drawback of this method is the effort needed at the stage of formulating the problem mathematically and programming it (Rubin and James, 1973). But it permits better representation of the boundaries, higher accuracy, more flexibility and it is usually more economical.

c. The third kind of numerical models could be described as 'mixing-cells models' (Water Resources Engineers, 1969; Weber and Hassan, 1972; California State Department of Water Resource, Southern District, 1974). The region is divided into polygons on the horizontal plane and into layers in the vertical direction. For the flow problem, the continuity equation is used, combined with a specific equation based on Darcy's law. The quality part of the model estimates the concentration of TDS or any other conservative constituent by simply "...accounting for the movement of salt in each flow" (California State Department of Water Resources, Southern District, 1974). The model program is structured to calculate the average TDS concentration of extracted groundwater from the zone penetrated by wells. The dispersion phenomenon is not accounted for directly in this model. Several assumptions have to be made in order to cope with many problems arising in the formulation and application of the model. The calibration of the model from the historical data is rather laborious, requiring many runs.

The 'mixing-cells model' although lacking in rigor and direct representation of the various phenomena, is less demanding in data than the first two model types. The semi-empirical character of this model requires more user insight in the specific situation which is being modelled, and in the model itself than is usual for the other models.

As mentioned above, convection and dispersion are not the only mechanisms that govern the spreading of a pollutant. A recent step in modelling more quality parameters than those in the dispersion scheme, was taken by Thomas, et al. (1972). They developed a simple model that predicts the concentrations of six different cations as they percolate through a soil profile. Willis and Dracup (1973), in their "optimization" model,take into account dispersion and adsorption (in both the saturated and unsaturated zone). Rubin and James (1973) account for dispersion and ion exchange of one-dimensional transport of solutes in saturated porous media. They utilize the high-accuracy Galerkin procedure described in previous paragraphs.

Most of the literature has focused on the saturated zone. However, the unsaturated zone can be of equal interest since in this zone water is stored while moving upward or downward, the slow motion of water permits diffusion phenomena to become significant, and important biochemical reactions as well as aeration take place.

Freeze (1972) simulated the convective process in both the saturated and unsaturated zone, neglecting dispersion and chemical reactions. The models of Water Resource Eng., Inc. (1969), and Perez et al. (1972) include the unsaturated phase, but only as far as transient effects and storage are concerned. Much more developed is the model by Bresler (1973) that takes into account diffusion and dispersion in both phases. Data for proper modelling of the unsaturated zone are usually lacking, which reduces the usefulness of the modelling effort.

Most groundwater quality models are two-dimensional: in plane for basin models and in profile for seawater encroachment. This is attributed to the very high computer costs for a three-dimensional model, and/or the poor data that are usually available, which is not sufficient for a three-dimensional model. On the other hand, when the neglect of the third dimension is thought to lead to major errors, quasi-three-dimensional models (e.g., the heuristic method of Bredehoeft and Pinder, 1970) can be used. These are usually based on very crude assumptions, which still can be useful.

In the opposite direction, simple lumped parameter models have been developed (e.g., Gelhar and Wilson, 1974). They usually consist of one or more mixing cells in a simple combination. They could be especially useful in optimization studies.

The modeling and data collection activities are based on the premise that an increased understanding of the physical system will improve the manager's decision capabilities (Maddock, 1973).

A certain amount of care should be taken, however, to insure that the model is not used to simulate a specific strategy, which a given agency might wish to promote, but instead is used to simulate a variety of different strategies to achieve given objectives. In order to accomplish this most effectively, a systematic search technique would be very useful; however, as yet these have only been developed in very few cases, and this fact certainly weakens the importance of the simulation model as a tool in the decision making procedure.

The development (or even acquisition) and running of a groundwater quality model is a difficult and expensive task. On the other hand, the data are usually so poor and the cost of obtaining additional data are usually so high, that the modeler must ask himself:

a. What kind of a model (if any) should he use?
b. Should he look for additional data?

It is impossible, however,to answer the above questions in a systematic way before the following points are cleared:

a. What are, explicitly, the evaluation criteria?
b. What is the cost and accuracy of each model? How does the accuracy of the model affect the decision (Maddock, 1973)?
c. What is the sensitivity to the given data (Gillham and Farvolden, 1974)? How does it affect the decision (Gates and Kisiel, 1974)?
d. What is the cost of additional data?

Unfortunately very little has been done in this direction. Nevertheless this aspect of the problem is as important as the development of more sophisticated models.

5.5.2 Input-Output Analysis

In the last section we focused primarily on models that can be used to determine the physical response of the aquifer system. However, in most groundwater quality management problems we are not only interested in the physical response of the system, but in the economic response as well. By this we mean the impact of, for example, different levels of water quality in the aquifer (produced by different management alternatives) on the economy of the region. In this section we present a review of input-output methods which can be used for estimating the economic impact described above. This analysis deals not only with groundwater pollution, but rather it also helps the decision maker to prepare integrated water pollution control plans in which solid land use policies play a major part.

Although many authors have discussed the conflict between environmental quality and economic growth, very little thorough investigation has been done so far to determine the actual impact on the environment of a certain rate of economic growth. Any discussion of economic growth and the environment can, however, greatly benefit from a systematic and dissaggregated model of a particular economy, and the materials link between the economy and the environment which supports it.

In doing so, great advantage can be derived from the use of input-output models. These are the only economic models that, available in most developed countries, explicitly recognize the many industrial sectors forming the economic system; they attempt to explain the spatial distribution of output and consumption of goods and services, and their growth or decline. A detailed explanation of these models may be found in Leontieff (1970) and Victor (1975).

Two different problems can be dealt with through the use of input-output models. The first one is the evaluation of the requirements for water and raw materials, and the waste discharge associated with increases in the forecasted final demands. This approach is relatively simple, and the main problems arise in estimating the waste load coefficients, and the utilized water and raw materials in terms of gallons or tons per dollar of output, corresponding to the different industrial sectors. Given these estimates, the input-output model can be used to estimate the level of output needed in each industry to meet both the final demand as well as the intermediate demand (or input to other industries), the waste loads, and the amount of water and raw materials used, all associated with the forecasted level of final demand.

Table 5.1 presents an outline for an economic and environmental model for planning and forecasting. The input-output models of the national economy determine the industry outputs in dollars; applying location coefficients to it, regional input-output models can be built giving as a result the industry outputs in dollars/region. In these cases the application of the waste-load, water use and raw materials coefficients will give as a final result the total regional waste loads in tons/region and the total regional water and raw materials requirements. These will aid in the analysis of whether the current pattern of economic development is feasible given the desired level of environmental quality; which are the factors that can influence the actual results of the model; and which governmental policy should be undertaken.

For example, if the forecasted growth in demand is considered necessary or beneficial for social welfare, but such a demand pattern would cause waste loadings that could overwhelm the waste assimilation capacities of some regions while in other regions this capacity would remain under-used, a new regional development incentive and/or a new land use policy undertaken by the government could produce changes in location of industries, and therefore changes in the regional waste loadings.

Table 5.1

Outline for an Economic and Environmental Model for Planning and Forecasting

Government Policy Instruments	Factors Influencing Model Components	Framework of the Model	
	Growth in demand	Forecasted Final Demands $	
		Consum. Govern. Capital Exp. Trade	
Financial Assistant to Industry	Changes in Produce. Methods and Pollution Control	Input-Output Coefficients $/$	
		Industry Outputs $	
Land-Use Planning of Neg. Development Incentives	Changes in Location of Industry	Location Coefficients %	
		Industry Output by Region $/region	
Regulations and Financial Assistance and Incentives to Industry	Changes in Pollution Control and Production Methods	Regional Waste Load Coefficients Tons/$/region	Regional Water and Raw Mat. Coefficients Tons/$/region
		Regional Waste Loading Tons/Region	Regional Water and Raw Mat. Requirements Tons/Region

The second problem which can be solved through the use of input-output economic models is not only the estimation of the above factors, but furthermore, the evaluation of the economic impact that the introduction of pollution control measures would create. The control concept is that the technical interdependence between the levels of desirable and undesirable outputs (i.e., the waste loads coefficients per output of a certain industry) can be described and analyzed as an integral part of the system. However, problems of costing and pricing will arise as soon as the analysis moves from explaining and measuring pollution (as was done in the first approach), towards doing something about it. A numerical example explaining the use of input-output models in this context is presented in Appendix 5.2.

5.5.3 Joint Use of Optimization and Simulation Techniques

From the discussion above it is clear that optimization and simulation techniques each have definite advantages and limitations. In general optimization techniques, by nature of the algorithmic procedures for their solution, must treat the problem on a much simpler level. However, a simulation model can only give the value of the objective function for a given alternative or policy, while the optimization model can select the best alternative among a given set of feasible solutions.

A possible approach, which was first proposed by the Harvard Water Program in 1960 (Maass, et al., 1960) and which has been utilized in many case studies since then (e.g., Argentina Project, 1972), is to use both optimization and simulation models in a complementary fashion. In this approach the analyst uses an optimization technique to locate a good feasible alternative (or preliminary optimal solution). Then, using this alternative as a starting point, the analyst examines this solution and similar solutions more carefully using simulation techniques. For example, a deterministic linear programming model can be used to select a good feasible alternative for the allocation of groundwater based on average hydrological conditions. This configuration can then be subjected to examination with the use of a simulation model which can take into account the true non-linear and stochastic nature of the water system.

When these additional considerations are included, the value of the objective function will change. The analyst may wish to proceed with a hand crafted optimization by slightly changing the proposed solution and seeing if the objective function of the simulation model increases or decreases. The logic behind this approach is that without the use of the L.P. model to give a starting point, the use of the simulation model in the search for an optimum would be too time consuming.

In addition, simulation models are frequently used to provide information on the various functions and parameters used in the L.P. models (for example, the mass balance of salts in the aquifer).

5.6 Summary and Conclusions

In this chapter we have reviewed the different techniques that are available to aid in the evaluation and selection of alternative plans to achieve given groundwater quality management goals in the most effective way. Among the techniques of analysis that have been reviewed are those of optimization and simulation. Although it is noted that, at the present time, very little work has been done in the use of these techniques to systematically solve the different problems that arise in groundwater quality management, it is felt that a thorough discussion of the power and limitations of these different techniques will enable them to be used more effectively in the future, both in Spain and in other areas of the world.

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APPENDIX 5.1

An Application of Linear Programming: The "Optimum" Level of Allowed Groundwater Contamination

The example considered in this section is an attempt to examine groundwater quality management as part of a resource management problem, the resource in this case being groundwater and surface water. The many types of development of the resource can be divided into four broad categories: domestic, commercial, industrial, and agricultural. Each of these primary uses requires water of specific quality and results in the secondary use of the water resource as a medium for the disposal of wastes.

The objective of this study is to determine the optimal level of water development in a region (based on Maximum Net Benefits), when the effects of that development on the groundwater quality are taken into account. The objective is not to maintain the groundwater quality at or below a given level, but rather to determine, in a systematic way, what level of groundwater pollution can be allowed before the increased cost (including the public health risk) reduces the net benefits of the system.

The hypothetical region studied in this case has two components of water development: municipal and agricultural. Groundwater and surface water provide alternative sources of supply. The quality of the water (both surface water and groundwater) is characterized by the concentration of the pollutant. For simplicity, in this discussion water quality will be measured using only one characteristic (NO_3^-, BOD, TDS, etc.).

For actual application, the model could be made more realistic by modifying it to include several compounds.

Each of the water projects needed to fulfill the municipal and agricultural requirements of this region have an associated cost (capital investiment, treatment, pumpage, transportation, etc.). For our simple model, benefits will be derived only from the sale of crops.

The effect of the water development projects on the groundwater quality will be the result of (1) infiltration of irrigation water into the groundwater (2) percolation from septic tanks (3) pumpage and (4) natural recharge. The model assumes a steady state condition. Therefore, there is no time element and the model cannot capture the storage characteristics of the system.

In order to operate the model the user must assume a final concentration of the pollutant in the groundwater (C_F). The model will then calculate the optimal scale of development which will result in the given C_F after a given time period. The maximum net benefits that can be realized from the system for this optimum level of development will also be given. A series of runs with different values of C_F will result in different scales of development, with different net benefits. Through an iterative process, the optimal scale of development with the corresponding value of C_F could then be determined from a plot of net benefits versus C_F.

Figure 5.3 shows the region with the interactions of the various components. Tables 5.2 and 5.3 define the decision variables and parameters of the system. The decision variables describe various compon-

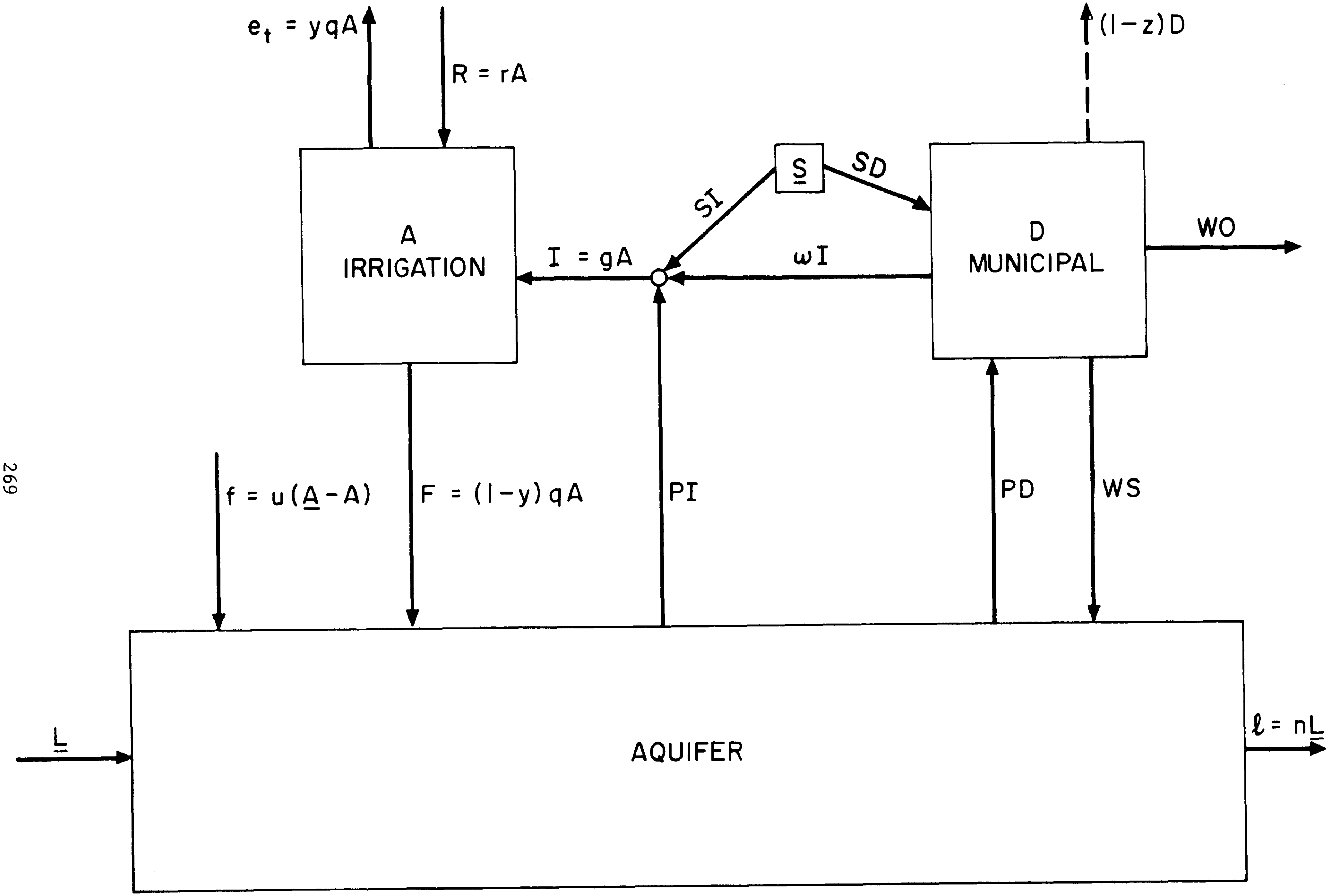


Figure 5.3: Interactions of the System.

Table 5.2

System Decision Variables

Decision Variable		Definition
Direct Decision Variables	PD	Pumpage for municipal water supply
	SD	Surface water for municipal water supply
	WO	Waste water which is discharged outside of the system
	WI	Waste water which is used in irrigation
	WS	Waste water which is treated by means of septic tanks
	SI	Surface water for irrigation
	PI	Groundwater pumped for irrigation
	A	Area irrigated
Indirect Decision Variables	e_t	Evapotransporation (consumptive use)
	F	Infiltration from irrigation areas
	f	Infiltration from non-irrigated areas
	g	Quantity of irrigation water required (quantity/acre/year)
	q	Quantity of applied water required (quantity/acre/year)
	ℓ	Lateral outflow
	R	Total precipitation on irrigated land
	I	Total quantity of irrigation water

Table 5.3

System Parameters

Parameter	Definition
$\underline{A}$	Total area of the region
$\underline{D}$	Total demand for municipal water
$\underline{S}$	Total surface water resources available
r	Average precipitation (quantity/year)
$\underline{L}$	Lateral inflow into the aquifer
n	Factor describing the ratio of lateral outflow to lateral inflow. [Note: through this variable many natural phenomena can be taken into account. The operator may wish to decrease the lateral outflow to allow consumption of the groundwater as part of the development.]
u	Average infiltration for non-irrigated fields (quantity/acre/year)
x	Total amount of water required for the specific crop per acre per year. For more detail the region could be subdivided into sub-regions, each with a different x.
y	Irrigation efficiency
z	Ratio between the amount of waste water and the municipal demand (an expression of consumptive use of municipal water). Since $z = (WO+WS+WI)/D$, we can write $WO+zD-(WS+WI)$
C_F	Final concentration of the pollutant in the aquifer
C_I	Concentration of the pollutant in the irrigation water
C_S	Concentration of the pollutant in the surface water
C_W	Concentration of the pollutant in the waste water
C_R	Concentration of the pollutant in precipitation
C_U	Concentration of the pollutant in natural recharge

ents of potential water development and are expressed in terms of quantity (m^3 or acre-ft) of water per year. Each decision variable can have a lower and upper bound supplied by the user. The parameters are known values input to the model. Table 5.4 defines the benefit and cost coefficients of the system.

Given the above definitions, the model can be formulated in terms of the following linear objective function and constraints.

Objective Function

The objective of this model is to maximize net benefits (Z) given a final concentration of pollutant in the aquifer (C_F). This can be written

$$\text{Max } Z = b\,A - [c_1 PD + c_2 SD + c_3 WO + c_4 WI + c_5 WS + c_6 SI + c_7 PI + c_8 I + c_9 A]$$

System Constraints

The first type of constraints give the relationship between the direct and indirect decision variables, which are a result of their definition. These can be written

$$e_t = y\,q\,A \qquad (1)$$

$$F = (1-y)\,q\,A \qquad (2)$$

$$f = u(\underline{A}-A) \qquad (3)$$

$$g = q-r \qquad (4)$$

$$q = x/y \qquad (5)$$

$$\ell = n\underline{L} \qquad (6)$$

$$R = rA \qquad (7)$$

$$I = g\,A \qquad (8)$$

Table 5.4

System Benefit and Cost Coefficients

Coefficient	Definition
b	Benefits derived from the sale of crops per acre (all annaul costs discounted to present value)
c_1	Cost of pumping groundwater for domestic use. It includes capital cost of pumps and treatment facilities (if required by C_F), annual pumping costs and annual cost of treatment. It is clear that c_1 will be a function of C_F
c_2	Cost of using surface water for domestic water supply. Includes annual treatment costs, capital and annual cost of diverting the surface water plus any annual cost to purchase the water, and will be a function of C_F
c_3	Capital and operation and maintenance (O&M) cost of any additional facilities required to treat or discharge waste water outside the system
c_4	Capital and O&M costs of any additional facilities required to treat or transport waste water for irrigation and annual operational costs
c_5	Capital and O&M costs of any additional septic tanks required
c_6	Capital and O&M costs of diversion for the surface supply of irrigation water
c_7	Capital and O&M costs of pumping groundwater for use in irrigation
c_8	Capital and O&M costs of delivering irrigation water to the fields
c_9	Farming costs, including capital investment to put acreage into agricultural use and annual operational costs

The second type of constraint that must be considered is the continuity constraint that ensure a mass balance in the system. Since the system is considered to be at steady state, it is analyzed during one time period only; no changes in storage take place during the given time period. These constraints can be written:

$$(1-n)\underline{L} + u\underline{A} = PI + PD + ((y-1)q + u)\ A - WS \qquad \text{(Aquifer)} \tag{9}$$

$$(1-z)D = PD + SD - WO - WS - WI \qquad \text{(Municipal supply)} \tag{10}$$

$$SI + WI + PI = I = gA \qquad \text{(Irrigation supply)} \tag{11}$$

$$y(qA) + (1-y)\ (qA) = gA + rA \qquad \text{(Irrigation area)} \tag{12}$$

$$SD + SI = \underline{S} \qquad \text{(Surface supply)} \tag{13}$$

A third and important class of constraints are the quality constraints. There are two types of quality constraints: those that are simple proportionalities and those that are related to the overall effect of development on groundwater. The first can be written

$$C_I\ I = WS\ C_W + SI\ C_S + PD\ C_F \tag{14}$$

The second one involves the quality of the aquifer C_F, which is not only a function of most of the model decision variables, but also of the climatic conditions, geology, hydrology, soil conditions, etc. In this case groundwater quality can be considered to be affected by three main areas of development: pumpage (PI + PD), waste disposal by septic tanks (WS), and irrigated agriculture (A). Under the extremely simplifying assumptions of additivity and linearity, we could write

$$a_0\ C_F(PI + PD) = a_1 + a_2\ A + a_3\ WS \tag{15}$$

Note that this relationship could be interpreted as a mass balance relationship, and is linear, since C_F is constant for each run. The coefficients a_0 through a_3 would have to be determined by simulation models of the area for a given design period. This could be done by running the simulation model for different values of A, WS, PI and PD, and obtaining the coefficient a_0, a_1, a_2 and a_3 through regression. In order to avoid non-linearity C_I is selected by the operator for each run, hence resulting in different coefficients for different values of C_I.

The objective function and constraints (1) to (15) define the model. As written above, the model would apply to the development of a new area where annual costs and capital costs would be based on the same quantities. If an existing area were to be studied the costs would have to be broken down. For example, assume the model recommends the discharge of WO^* from the system, and that an existing treatment plant can handle nWO^*. Then capital cost would be calculated on the value $(1-n)\ WO^*$, while annual operation and maintainance cost would be based on WO^*. However, this would greatly increase the complexity of the model.

To use this groundwater quality model the operator must first assign values to all the parameters ($\underline{A}, \underline{D}, \underline{S}, r, \underline{L}, n, u, x, z, C_S, C_W, C_R, C_U$ and all upper and lower bounds). Then using simulation techniques and a fixed value of C_I the operator must determine the coefficients a_0, a_1, a_2 and a_3, which might be different for the different values of C_F. The operator then tuns the LP model several times for different values of C_F. A plot of Net Benefits versus C_F will give the optimal value of $C_F = C_F^*$ for the value of C_I used as shown in Figure 5.4. It is hoped that by using this iterative technique the linear programming method can be used on this extremely non-linear problem.

It is relatively easy to formulate, as above, a systematic approach to the solution of groundwater problems. However, the problems of data collection could be enormous. The evaluation of all the cost coefficients and quantity relationships is difficult, though not impossible. For any real application, data collection will be both expensive and time consuming. The additional need for quality data and the development of quality coefficients (a_i) through simulation make the data collection problems for this type of model even greater.

This lump parameter approach could be expanded to include other sources of groundwater pollution if we can assume that the effects of each source of pollution are additive and we are able to determine the coefficients (a_i) for each source. However, in this approach we can only consider the aquifer as a whole and assume complete mixing which makes dealing with point sources very difficult.

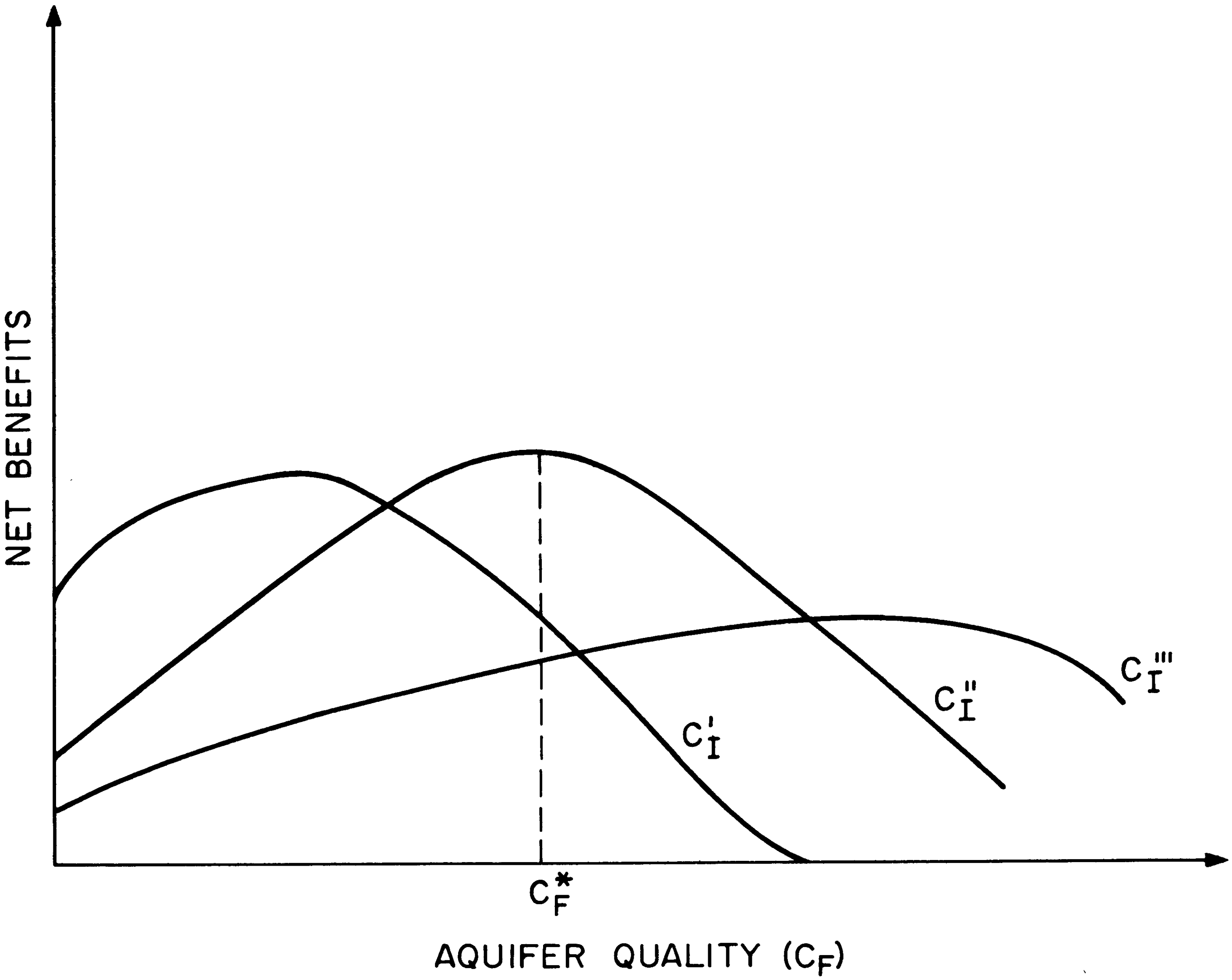


Figure 5.4: Determination of Optimum Aquifer Quality Level.

APPENDIX 5.2

The Use of Input Output Models to Evaluate the Economic Impact of Pollution Control Measures

As explained in Section 5.5.2, input-output models can be used to evaluate the economic impact of the introduction of pollution control measures. This appendix contains a numerical example taken from Leontieff (1970) that illustrates the use of input-output models in this context. More information can be obtained from Leontieff, (1970) and Victor (1975).

Assume a simplified economy represented by the input-output coefficients outlined in Table 5.5. These coefficients represent the amount of input of one sector required to produce one unit of the same or another sector.

Table 5.5

Assumed Input-Output Coefficients

from \ into	Agriculture	Manufacturing
Agriculture	0.25	0.40
Manufacture	0.14	0.12
Labor man-hour (at $1 per hour)	0.80 ($0.80)	3.60 ($3.60)

If the final (external) demands were, say, 55 bushels of wheat and 30 units of manufactured product, and there were no labor employed by the "final demand" sectors, the solution of the equations of the input-output model would give as a result the values indicated in Table 5.6.

Table 5.6

Resultant Input-Output Values

from \ into	Agriculture	Manufacturing	Final Demand	Total Output
Agriculture	25	20	55	100
Manufacture	14	6	30	50
Labor man-hour (Value added)	80 (\$80)	180 (\$180)	--	260

Considering now the prices, P, at which they have to be sold and assuming for simplicity that labor wages constitute the value added V, we obtain:

$$P_1 - 0.25 P_1 - 0.14 P_2 = V_1$$

$$P_2 - 0.40 P_1 - 0.12 P_2 = V_2$$

where the subscripts 1 and 2 refer to agriculture and manufactured products respectively. Assuming the values of $V_1 = 0.8$ and $V_2 = 3.6$ the solution of the above system of equations shows that the price of wheat would have to be \$2 per bushel and that of manufactured products (P_2), \$5 per unit.

To introduce the pollution aspects, assume that agricultural activities produce 0.50 grams of a certain pollutant per bushel of wheat, and that the manufacturing sector produces 0.20 grams per unit of product; further assume, that you can eliminate one gram of pollutant S by using 2 man-hours of input requirements and 0.20 units of manufactured product. Then, the very much simplified economy could be represented by the input-output coefficients indicated in Table 5.7.

Table 5.7

Input-Output Coefficients Including Pollution

Pollutant's Output / Input	Agriculture	Manufacturing	Elimination of Pollutant
Agriculture	0.25	0.40	0
Manufacture	0.14	0.12	0.20
Pollutant	0.50	0.20	--
Labor (Value added)	0.80 ($0.80)	3.60 ($3.60)	2.00 (2.00)

Now, given the same final demand for the outputs of the agricultural and manufacturing sectors as before, and assuming that the final demand for pollutant (which in this case is not desired but rather tolerated) is 30 grams, the solution of the equations of the input-output model would give as a result the values indicated in Table 5.8.

Table 5.8

Resultant Input-Output Values Including Pollution Control

Output Sectors / Input and Poll. Output	Agriculture	Manufacturing	Pollution Control	Final Demands	Totals
Agriculture	26.12	23.37	0	55	104.50
Manufacture	14.63	7.01	6.79	30	58.43
Pollutant	52.25	11.68	-33.93	30	--
Labor	83.60	210.34	67.86	0	361.80

Note that the output of the Pollution Control Sector is the elimination of 33.93 grams of pollutant, which enter negatively in the table to obtain the 30 grams of the final "tolerated" demand ($101.80 paid for elimination of the 33.93 grams of pollutant).

To obtain now the price that society has had to pay for the 30 grams of its final pollution demand (i.e., for the elimination of 33.93 grams of pollutant), the process is the same as before; i.e., the following system of linear equations must be written:

$$P_1 - 0.25P_1 - 0.14P_2 = V_1$$

$$P_2 - 0.40P_1 - 0.12P_2 = V_2$$

$$P_3 \qquad - 0.20P_2 = V_3$$

where the subscripts 1, 2 and 3 refer to agriculture, manufactured products and pollution control respectively.

Given Value Added values of $V_1 = \$0.80$, $V_2 = \$3.60$, $V_3 = \$2.00$, the solution of the system of linear equations gives as a result

$$P_1 = \$2.00$$

$$P_2 = \$5.00$$

$$P_3 = \$3.00$$

Note that the prices of wheat and manufactured products remain constant, but there is a price of \$3.00 per gram of eliminated pollutant. The Input-Output table of the National Economy can then be expressed in dollar values as in Table 5.9.

The results of Table 5.9 indicate that the final demand sectors will receive a total of \$361.80, which they will use in the amount of \$260.00 for wheat and manufactured products, having to pay \$101.80 for the elimination of the 33.93 grams of pollutants.

Comparing this situation with the former one, one realizes that now the final demand sectors can buy the same amount of goods as before

Table 5.9

Input-Output Table of National Economy in Dollar Values

Output Sectors / Input and Poll. Output	Agriculture	Manufacturing	Pollution Control	Final Demands	Totals
Agriculture	\$ 52.24	\$ 46.74	0	\$110.00	\$208.99
Manufacture	\$ 73.15	\$ 35.04	\$ 33.94	\$150.00	\$292.13
Pollution	--	--	--	\$101.80	\$101.80
Labor	\$ 83.60	\$210.34	\$ 67.86	0	\$361.80
Total	\$208.99	\$292.13	\$101.80	\$361.80	

at the same price, but instead of having over 60 grams of pollutants they have only 30. Since the second situation is definitely the better one, why is there any controversy? The answer lies in the fact that if society (or the economic system), instead of having used the \$101.80 in "buying" a pollutant reduction of 33.93 grams had used them in the other two sectors, they would have produced greater "tangible" outputs.

It should be mentioned that if instead of an independent pollution control sector, there had been controls to make both the agricultural and manufactured products sectors reduce their own pollution, the result would have been similar; however, society, instead of having to pay equal prices per bushel of wheat and unit product and a separate amount to the antipollution sector, would have had to pay nothing to the latter sector but larger prices per output of the agricultural and manufacturing sectors.

CHAPTER 6

Groundwater Management - A Case Study

Parallel to the writing of this report, a case study was undertaken in order to apply the techniques discussed in previous chapters to a real world context. This chapter will present the basic formulation and results of the case study, together with a discussion of its interrelationship with the theoretical methods of analysis of groundwater problems which were discussed in Chapter 5.

It should be pointed out that, although the context of the case study is real, many simplifications were made and much of the data utilized was generated in order to permit the development of the study. Therefore the case study should be viewed as an illustration of the application of planning techniques rather than as a real planning study whose end result is the recommendation of a given plan for implementation.

6.1 Brief Description of the Case Study

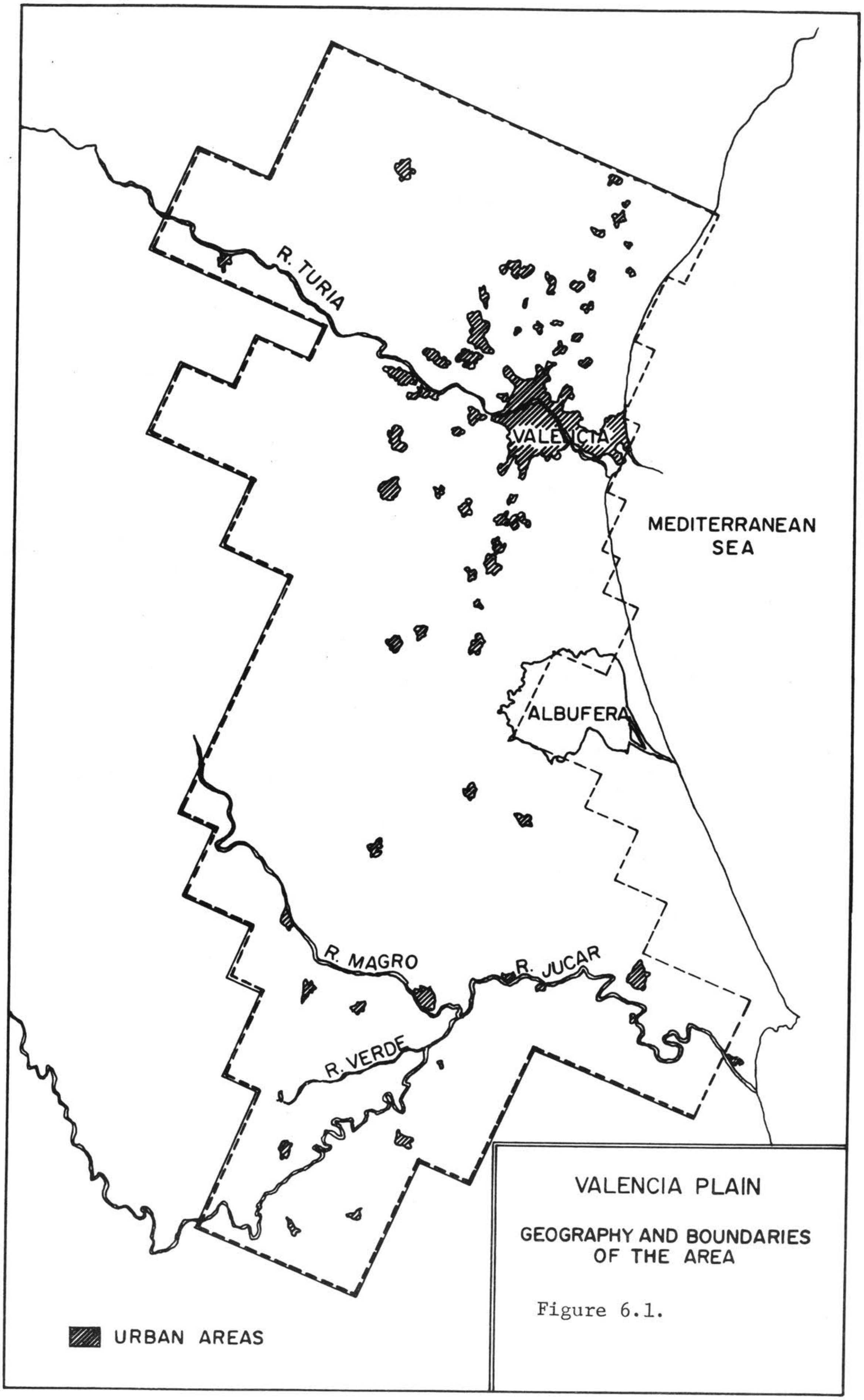
The case study was concerned with the management of water resources in the Valencia Plain area in Eastern Spain. The general objective of the case study was the evaluation of two different plans for supplying water to the Valencia Plain area; these plans involved a description of the pertinent structural designs, together with their corresponding schemes for water quality control and schedules of implementation. The plans were evaluated in terms of National Income and Quality Related Consumer Costs; additionally, their effect on the environment was taken into account. On the basis of these factors, a plan that called for the integrated use of groundwater as well as surface water was recommended as the better plan.

In the following sections, a very brief description of the case study is presented. First, the region itself is described; second, the alternative water resource plans are discussed, and finally, the methodology for choosing the best plan is presented. Further details can be obtained from Porras (1975).

6.1.1 Description of Case Study Area

The case study area is known in Spanish as the "Plana de Valencia", or Valencia Plain; this area is indicated in Figure 6.1. From the viewpoint of agricultural production, as well as that of industry, the zone is among the most important in Spain, and the fruits and citrus from it are exported in great quantities to many other countries. However, due to the fact that most of the land is already being used for agriculture, the development of new agricultural areas in the future will be very small. Since a large amount of industrial development is foreseen, some areas will be lost for agricultural practices and transformed into urban and industrial areas.

The Plain has a length of 31 miles (50 km) along the coast, and the average distance between the coastline and the hills and low mountains that limit the zone toward the west is about 13 miles (21 km.) It has an extension of approximately 344,000 acres. As indicated in Figure 6.1, two main rivers cross the plain before discharging into the sea—the Turia River in the North and the Júcar River in the South. The Magro River, a tributary to the Júcar, rises outside the area, as do



VALENCIA PLAIN

GEOGRAPHY AND BOUNDARIES OF THE AREA

Figure 6.1.

the Túria and Júcar Rivers. The Albufera is a fresh water pond where part of the surface runoff of the plain discharges; in turn, it discharges to the sea through two canals.

A coastal aquifer underlies the totality of the plain. The inputs to the aquifer are the lateral inflow from adjacent aquifers in the western boundaries, rainfall percolation, and percolation of irrigation return flow. The outputs are pumpage from wells, outflowing springs, flow to streambeds, and subsurface flow directly to the sea. No overdraft of groundwater from wells is currently taking place; on the contrary, the aquifer is underdeveloped. Groundwater quality in the aquifer is apparently poor; from the available chemical analysis, TDS ranges between 600 to more than 1500 mg/L, and nitrates vary from 30 to more than 150 mg/L. However, the water samples analyzed have usually been taken from shallow, non-operating wells, and hence these data must be carefully examined.

In the case study, only three beneficial uses, water supply for agriculture, domestic and industrial purposes have been considered. In terms of groundwater quality, irrigation water will not have serious problems in the future, unless industries indiscriminately dump their wastes without treatment in irrigation canals. However, the main concern is related to the quality of groundwater for domestic supply. First of all, the quality of groundwater in the upper part of the saturated thickness is relatively poor, due to the high TDS in some areas, and NO_3^- concentrations. This quality, given the intense agricultural practices, will degrade very slowly but constantly and in a widespread form. Furthermore, if strong waste water effluent standards for surface waters are set, industries will dispose of polluting wastes by means of infiltration into the aquifer, and point source problems could appear in the future.

6.1.2 Alternative Plans

Two alternative plans for water quality and quantity management to be implemented during the period 1975-1985 were developed. The general objective of the alternative plans was to meet the water demands of the area, with special attention to water quality for domestic, industrial and agricultural supply and to try to meet the external demands of neighboring areas, all at least cost and with the least environmental impact.

The two alternative plans selected had a very different nature. Plan 1 relies almost entirely on surface water. Plan 2 is a modification of Plan 1, and uses groundwater resources to a greater extent,thus eliminating the need to import water from another basin.

In Plan 1, since little use is made of groundwater, 511 Hm^3/year have to be imported in order to be able to meet external demands of neighboring areas. In this plan, the Valencia Plain area contributes less than 50% to meeting the total demand. Groundwater is not used to supply municipalities included in the neighborhood de Valencia; surface water from the Júcar River is used instead. Valencia is supplied from the same source. Figure 6.2 shows the volumes of surface and groundwater used in this plan.

From the point of view of water quality management, an important

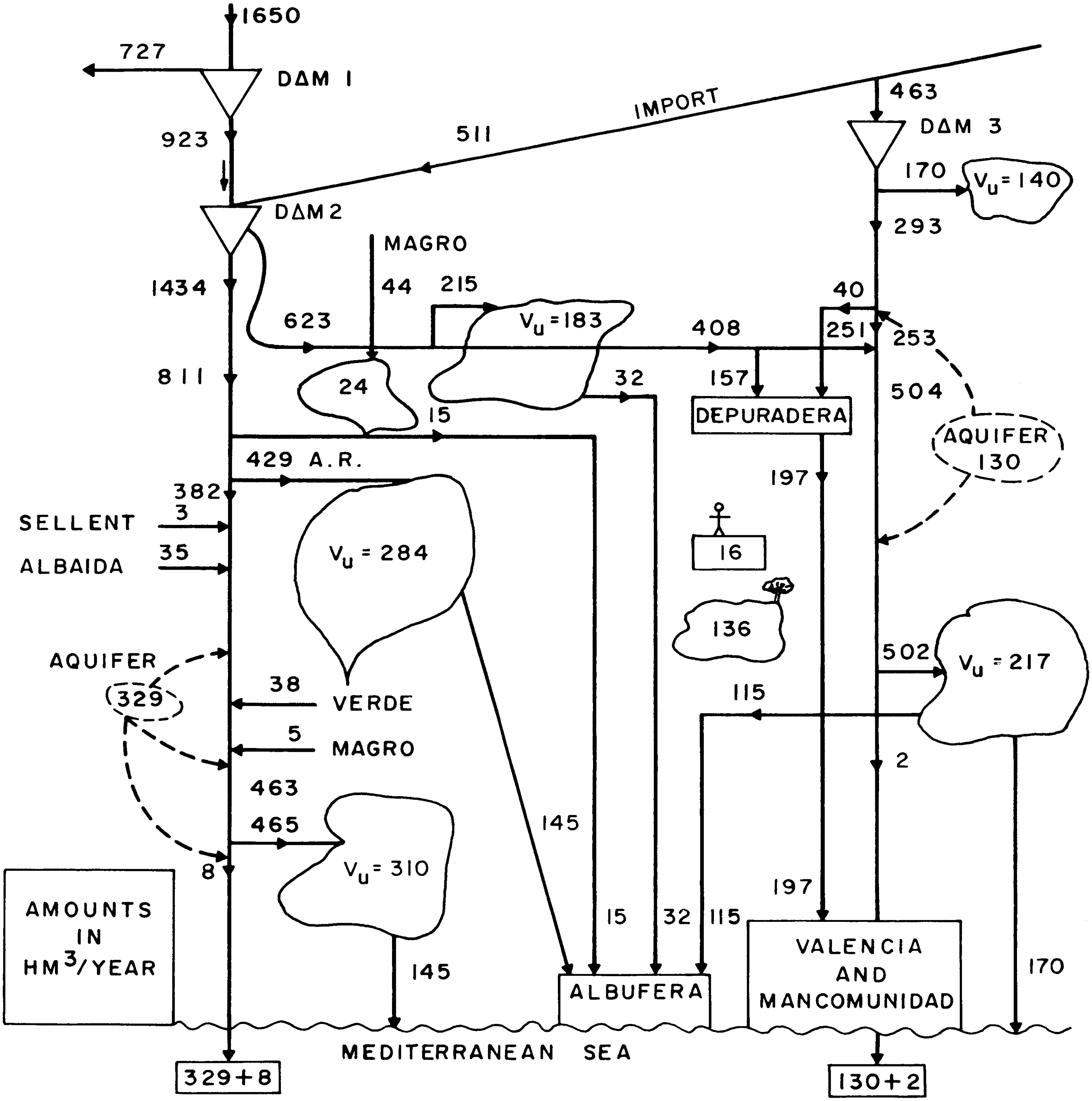


Figure 6.2: Annual Surface and Groundwater Use - Plan 1.

characteristic of this plan is that only a small part of the water demands for domestic and industrial supply are met by groundwater, and these occur in villages which are generally in the western part of the region, where lateral subflow from adjacent limestone aquifers is of good quality. Nevertheless, as in these areas irrigation with groundwater takes place, salt buildup continues to be a problem for the upper part of the aquifer. The groundwater quality management elements which are necessary in this plan, are well standards, solid waste and underground waste disposal regulatory programs, and programs for pesticide control.

In Plan 2, groundwater resources are used to meet part of the internal demands so that external demands can be met by available surface resources, thereby eliminating the need to import water. Groundwater is used to meet a greater part of the total demand for domestic supply. Valencia City and two towns are supplied mainly by surface water. Figure 6.3 indicates volumes of annual water use under this plan.

Special attention must be paid in this plan to the groundwater quality management elements and the monitoring system, due to the fact that domestic supply requires the highest degree of quality. The research program will, in this case, concentrate more on groundwater pollution problems.

The schemes devised for the control of groundwater quality include those devised for Plan 1, but modified in order to account for the greater quality problems foreseen under this plan.

In both plans, various assumptions were made regarding the schedule of implementation in order to properly account for the present value

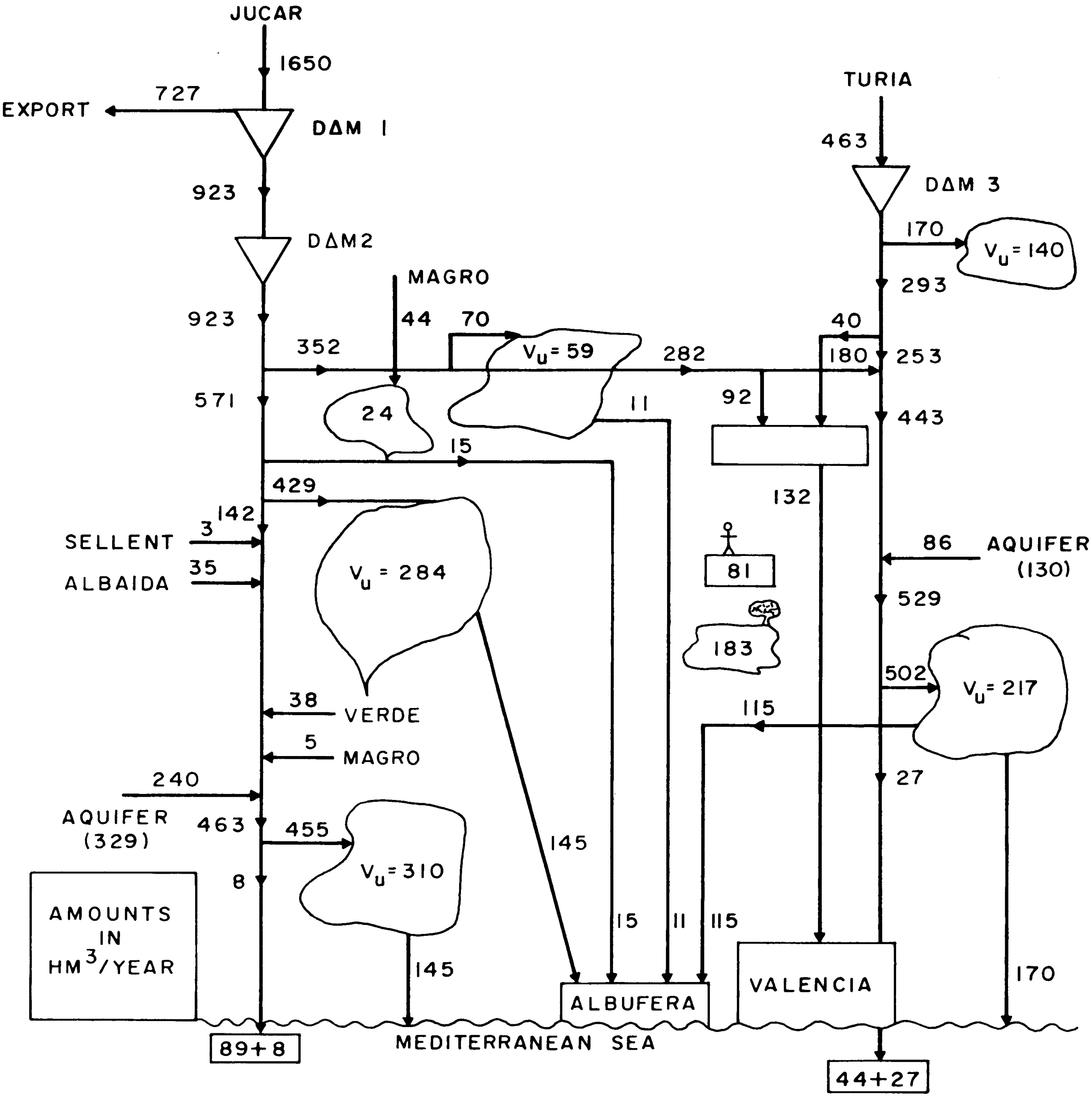


Figure 6.3: Annual Surface and Groundwater Use - Plan 2.

of the different costs.

6.1.3 Selection of Best Alternative

The two alternatives were compared in terms of their environmental and economic impact. In terms of the former, no great difference was found between them; hence the economic assessment of the plans determined the choice.

The economic evaluation focussed only on the costs of each plan, and not on their benefits. The reason for this was that, since both alternatives satisfy the same requirements, i.e., irrigate the same amount of hectares and supply the same amount of water to the municipalities in the area, the benefits which were to be obtained would be the same in both alternatives. Although not absolutely true, this assumption was sufficient for the purpose of the case study.

A second important simplifaction was that the only costs taken into account were the costs which are differential to both alternatives. Furthermore, no distribution costs or associated costs were considered.

Two types of differential costs were estimated. On the one hand were the National Income Costs, or costs which would have to be paid by the corresponding municipality, agency or individual for the physical construction of part or parts of the project; and on the other were the Quality Related Consumer Costs (QRCC), or costs that the individual users must suffer (though paying only indirectly).

Figure 6. 4 indicates the present value of both the National Income Costs and the Quality Related Consumer Costs corresponding to both plans, in which the import costs of Plan 1 are not included. The

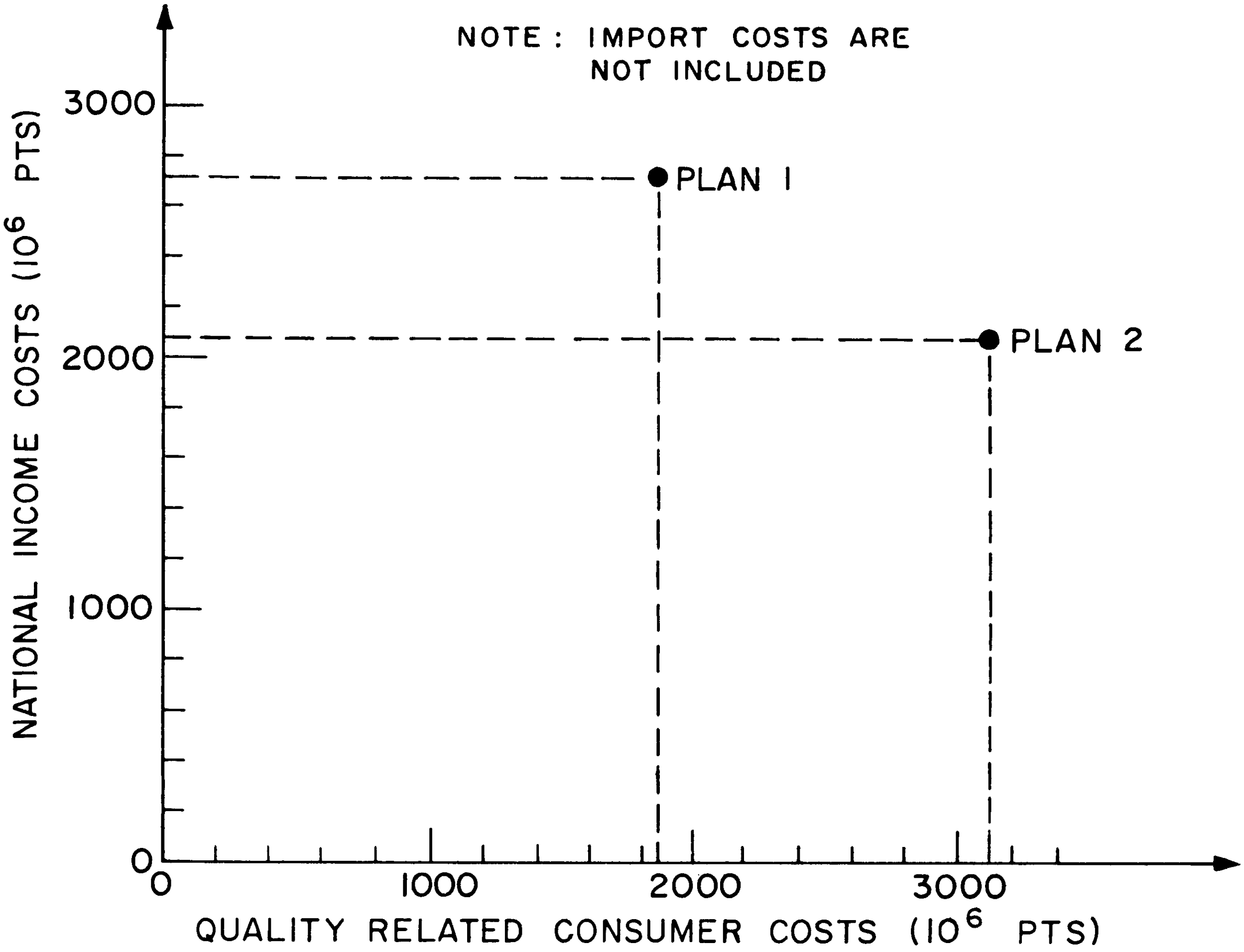


Figure 6.4: Present Value of National Income and Quality Related Consumer Costs for Plans 1 and 2.

Quality Related Consumer Costs are higher for Plan 2, since this plan relies to a greater extent on groundwater, whose salinity level is higher than that of the available surface water. On the other hand, the National Income Costs are higher for Plan 1, due primarily to the additional structures needed in this plan for surface water diversion.

Although a comparison between the two plans in terms of both the National Income and the Quality Related Consumer Costs, as shown by Figure 6.4, does not clearly indicate which is the better plan, it must be remembered that these values do not include the import costs. If the corresponding costs (estimated at 17,000 million pts) are added to Plan 1, it is evident that Plan 2 will be the preferred alternative, regardless of the weight that is attached to the Quality Related Consumer Costs. For this reason, Plan 2 was recommended as the best alternative, meeting water demands both in quantity and quality at the least total cost. It should be recalled that the environmental effects of both plans are very similar. Moreover, Plan 2 is more flexible in meeting the demands and thus would result in higher gross benefits.

6.2 Discussion

The objective of this section is to discuss the case study in the light of the theoretical methods of analysis of groundwater problems which were presented in Chapter 5. The main objective of the case study was its use as an illustration of the application of techniques described in previous chapters, and hence, as mentioned in the introduction, it was necessary to make a series of simplifications both to the data and to the methodology in order to be able to accomplish this objective. In order to make the case study more complete, this section will attempt to show the way in which the formulation of the case study fits into the theoretically correct procedures for systems design, and will discuss the additional factors which should be considered in a "real" planning study when the simplifications included in this case study would not be necessary.

As was mentioned in Chapter 5, the Harvard Water Program (Maass et al, 1962) first proposed the complementary use of different mathematical models for the design of Water Resource Systems. This proposal was part of an overall methodology for system design, which involved four related steps: identifying the objectives of design; translating these objectives into design criteria; using the criteria to devise plans for the development of specific water-resource systems that fulfill the criteria in the highest degree; and evaluating the consequences of the plans that have been developed.

The four basic steps outlined above have formed the basis for most of the work undertaken in Water Resources planning in the last 15 years. Because of this, they will be used as a basis for discussing the case study; in this manner, the way in which the case study undertook each step, together with the additional factors that should be considered in future "real" planning studies, will be discussed.

6.2.1 Identification of the Objectives of Design

The case study dealt with the problem of supplying water for municipal, agricultural and industrial purposes; thus it involved the design of many different structural alternatives, together with their corresponding schemes for water quality control, and their schedule of construction. Although the direct objective of this design was to supply water to the Valencia region, and to preserve its quality, the overall objective behind the design was one of economic efficiency (as later reflected by the National Income Costs minimization), and environmental quality (as witnessed by the Quality Related Consumer Costs and the environmental impact assessment). In analyzing the case study, it is important to point out the fundamental role that the proper choice of objectives plays in water resource planning. Major (1975) suggests as a useful criterion for the selection of objectives, that only those objectives which are important to decision makers and which are likely to be significantly affected by the range of measures under consideration should be included in the analysis.

Upon applying the above criterion to the Valencia plain, it is clear that objectives other than economic efficiency and environmental quality should perhaps also be considered. Possible candidates include increasing regional income, (i.e., the objective of increasing real income flows to the Valencia area) or increasing other regional objectives such as regional employment or the growth of tourism in the area. Evidently, in a real life case study it would be very desirable to have close interaction between analysts and government representatives on this issue.

6.2.2 Translating Objectives into Design Criteria

The second step in the design methodology, that of translating broad objectives into design criteria, essentially involves greater precision in the statement of the objectives and the design constraints.

This means that such matters as the value of the discount rate, and the existence or not of budget constraints should be clearly defined; furthermore, in many cases surrogate measures for such objectives as environmental quality must be established and quantified.

In terms of the case study, many aspects regarding the translation of the objectives of economic efficiency and environmental quality into design criteria may be discussed. In the first place, it was mentioned in Section 6.1.3, that water supply costs were taken as a surrogate measure of National Income Net Benefits, since it was assumed that gross benefits derived from water use would be constant regardless of the method of supply. Although for practical purposes this assumption is a good one, the use of cost minimization rather than benefit maximization as a design criterion in water supply problems leaves unanswered the question of which is the optimum level of water supply. In the case study, this question was avoided by assuming a given water demand level which corresponded to a fixed development plan (determined prior to the water supply study), and assuming that supply must equal or exceed the demand.

The objective of maximizing Environmental Quality was taken into account both qualitatively and quantitatively. The first involved an assessment of the environmental impact of the plans, and lead to the conclusion that both plans are about equal in this respect. The second involved the use of the quality related consumer costs as a surrogate measure of Environmental Quality Benefits, the advantages and disadvantages of which were discussed in Chapter 3.

A second factor that must be discussed is the presence of budget or institutional constraints within the design criteria. As was mentioned, Plan 2 was recommended solely on the basis of lower costs; no constraints entered into the selection process. Evidently, the existence of budgetary, institutional or other constraints might have modified the choice, due to the varying characteristics of the alternative plans when analyzed from this point of view.

A third factor which must be introduced explicitly in the design criteria is the choice of the discount rate, which accounts for the relative values placed on benefits and costs in the present and in the future. In the case study, a single value of 8% was chosen; however, in "real-world" planning studies it is very important that a thorough analysis of the choice of discount rate be undertaken, since there are so many different criteria for choice. A very useful approach is to design projects with several sets of discount rates, so that the sensitivity of the design to the choice of discount rate may be ascertained.

6.2.3 From Design Criteria to System Design

The third step in the proposed methodology for the design of water resources systems involves using the design criteria discussed in the last section to devise development alternatives that fulfill the criteria to the highest degree. It is in this step that the case study has employed the greatest simplification: in the process of selecting the plan that best fulfilled the design criteria, only two alternative plans were considered, whereas in reality the "best" plan should be chosen from among an infinity of contending plans.

As was discussed in Chapter 5, given a set of design objectives and a set of constraints upon the system, it is possible to use powerful mathematical techniques, such as linear programming, to identify optimum solutions to many water resource problems. In the case of the Valencia Plain Case Study, the system is so complex that the best alternative could not be obtained solely through the use of mathematical programming techniques, and hence it would be necessary to use the optimization models in conjunction with simulation models, as was explained in Section 5.5.3. The optimization model would identify an "optimal" solution under simplified conditions, and, using this solution as a starting point, the simulation model would evaluate a number of modified solutions in order to choose the one that best fulfilled the design criteria.

6.2.4 Evaluation of the Consequences of the Plan

In the third step, the plan that best fulfilled the design criteria was identified; in this step, the overall consequences of the plan are determined to see if the choice of plan was a correct one. Part of this step is, of course, accomplished in the previous one; however, because of the simplifications of the analysis, in some cases not all the effects of the chosen development alternative can be properly considered.

In the case study, this step was partially accomplished through the environmental impact assessment, and of course, through the cost analysis. However, many simplifications were made in the analysis, such as the use of a yearly time period, (which ignores the possible effects of within-year water supply shortages), the assumption of a deterministic system (which ignores possible problems of inter-year variabilities and storage requirements), or the drawdown of the aquifer due to the increased use of groundwater resources (with its consequences in terms of groundwater quality). The evaluation of the chosen plan in terms of the above factors could best be accomplished through the use of a stream-aquifer simulation model of the region that can calculate, amongst other things, the water supply shortages due to variability in the streamflow, or the changes in groundwater quality due to the increased use of groundwater.

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CHAPTER 7

Summary and Conclusion

7.1 Summary

An investigation of the technical, economic and institutional aspects of groundwater pollution is presented. Groundwater pollution is shown to be characterized by a wide variety of sources and types of potential pollutants. The pollution sources are widely scattered with effects ranging from the actue and local, to the chronic and regional. The source and type of pollution is often associated with land use.

Groundwater moves slowly and responds slowly to quality changes, influencing efforts to predict, monitor and control groundwater pollution. The movement of pollution is determined, for the most part, by the movement of water and therefore depends on the same physical factors. Pollution tends to attenuate as it moves through soil and groundwater systems, due to physical dilution and dispersion, and a combination of chemical and biochemical actions. Of these precipitation-solution, ion-exchange and adsorption, and biochemical degradation (oxidation-reduction) are most significant to groundwater quality. The importance of the various physical, chemical or biological processes depends on the type and source of pollution, the nature of the soil and/or aquifer material, the geohydrology, and the flow field.

Groundwater pollution detection and observation is based on an appropriate monitoring network and/or program. Most systems are designed to sample existing wells, but a well-designed monitoring system goes beyond this to consider pollution sources now and in the future, as well as the development of groundwater extraction activities. Groundwater quality samples should be analyzed carefully, and the technique of sample extraction and observation well design should be compatible with the objectives of the observation program. Source monitoring is an important component of such a program.

Groundwater pollution is but one part of the complex interactive system describing water quality and quantity and the growth and development of communities. Within this context the economic concept of externalities and the interaction between technical, institutional and economic factors are discussed.

The technical factors for carrying out institutional or economic policies are described in terms of source control, such as waste water treatment, or aquifer rehabilitation and/or control through, for example, the withdrawal of polluted water. A series of institutional, legal and economic measures to induce pollution control are examined including stream or aquifer standards, effluent standards and effluent charges. The nature of the groundwater resource, as a slow motion, slow response medium, plays a role in determining the efficacy of these measures. The various aspects of financing a groundwater pollution control program and methods for determining the costs and benefits of pollution control are presented.

The causes, types and extent of groundwater pollution range from the widespread agricultural use of nitrogen fertilizers to a single incident of an industrial chemical spill. Industrial sources of contamination are classed as waste disposal activities, leaks and/or leaching from industrial facilities and accidental releases. They are usually local in nature and characterized by a wide variety of pollutant types, although the density of industrial activities in cities insures the widespread contamination of their surface aquifers. Agricultural pollution sources include fertilizer and pesticide use and irrigation return flows as non-point sources. Animal wastes from confined animal habitats constitute a local contamination threat. Nitrate nitrogen is the primary pollutant of agricultural activities, but the total dissolved solids is important for water to be used for irrigation. The primary domestic pollution sources are solid and liquid waste disposal. Individual septic tanks cause local contamination problems if malfunctioning, to regional problems of nitrate buildup if their density is high. The land disposal of municipal sewage is a potential nitrate source, and landfills are sources of metals and variety of organic and inorganic compounds. These are primarily local contamination sources. Radiological pollution is a future threat of the development of nuclear power. Ore mining and processing, transportation,power plant and reprocessing plant leaks, and accidents threaten acute local pollution, which is probably less significant to groundwater than to other portions of the environment. Fuel and waste storage, however, constitute severe long-term threats to groundwater quality. Man can also induce low quality water to redistribute leading to the pollution of wells. Along the sea coast and wherever connate brines contact fresh water aquifers, the potential for quality degradation by salt water intrusion increases with the amount of groundwater extraction. So too, does the recharge of polluted surface water to an adjacent, hydraulically connected aquifer. The artificial recharge of aquifers leads to the introduction of dissolved constituents into the aquifer, which can is many cases, degrade water quality.

There are a number of methods of analysis for evaluating these pollution sources and the technology and economics of their control. The analysis should be done in the context of integrated long-term water resources planning. Criteria are described for choosing among alternative policies and systems analysis techniques for carrying out the analysis are reviewed. The use of optimization models in the analysis of groundwater quality for determining the best alternative is reviewed, along with the state of the art of simulation models. Simulation models have achieved a relatively large degree of acceptance and their use in assessing existing pollution or predicting future trends is becoming standard. The economic input-analysis technique is evaluated for its possible use in analyzing groundwater pollution control alternatives.

A Case Study is described which was used to illustrate the application of planning techniques to real world problems. The study involved evaluating alternative water supply plans for the Valencia Plain Area of Spain, taking into account water quality impacts. This description is followed by a discussion of the methodology used in the Case Study in light of the systems analysis techniques described earlier.

7.2 Conclusions and Recommendations

The following conclusions may be drawn from this report.

a. Groundwater system characteristics such as the slow movement of water and pollution, and the slow response to change, must be taken into account in the design and operation of monitoring systems, and in the selection of control and management measures.

b. Most groundwater pollution sources are associated with a particular land use.

c. The principal influence on the potential distribution of a pollutant is the flow field associated with the movement of water. Pollution, however, seldom achieves this potential due to dilution, dispersion, and attenuation by biological and chemical influences.

d. There are a variety of economic, institutional and legal means for the control of groundwater pollution. They vary in their effectiveness with the type of pollution situation. Effluent standards are most appropriate for deep well waste disposal. Withdrawal charges are appropriate for salt water intrusion control. Payments are an attractive means of controlling agricultural pollution. But the principal control may be associated with land use management.

e. If pollution in one portion of the air and water environment is to be reduced, it should not be at the expense of polluting another portion of the environment. Consequently, air pollution control should not come at the expense of aquifer pollution and vice versa.

f. A systems analysis approach in terms of long range water resource planning is the appropriate framework for the control of groundwater pollution.

These conclusions and the material covered in the report indicate several areas for which recommendations are important. Inevitably, as it should, future research will be directed to all of the areas addressed in this report, but several deserve special recommendations.

a. The chemistry associated with the movement of pollutants through aquifer material is currently an extraction of our knowledge of soils. Specific analyses of aquifer materials for pollution attenuation must be emphasized.

b. Our knowledge of the dispersion mechanism is based primarily on laboratory column experiments of hydrodynamic dispersion. Dispersion due to the stratified layers of aquifer material is the primary mixing mechanism in aquifers and it requires further research in the field and laboratory.

c. More emphasis should be placed on analyzing the various institutional, economic and legal control measures for groundwater pollution control.

d. An effort should be made to gather more data on the costs and benefits associated with groundwater pollution control.

e. The systematic methods of analysis must be incorporated into the planning and control process. The available simulation techniques should be used to assist decision makers. The optimization techniques should be improved in conjunction with their use for management.

APPENDIX A

Glossary of Terms

Adsorption--The physico-chemical attraction of a chemical to a soil particle or soil organic matter.

Advanced Waste Treatment--Additional treatment designed to reduce concentrations of selected constituents present in wastewater after secondary treatment.

Alternative Plan, Plan, or Policy--A set of controlled actions to be performed following a certain schedule.

Ammonification--The biochemical process whereby ammoniacal nitrogen is released from nitrogen-containing organic compounds.

Aquifer--A geologic formation or strata that contains water and transmits it from one point to another in quantities sufficient to permit economic development.

Artificial Recharge--The addition of water to the groundwater reservoir by activities of man, such as irrigation or induced infiltration from streams, wells, or spreading basins.

Beneficial Use of Water--The use of water for any purpose from which benefits are derived, such as domestic, irrigation, or industrial supply.

Biochemical Oxygen Demand (BOD)--The quantity of oxygen utilized primarily in the biochemical oxidation of organic matter in a specified time and at a specified temperature. The time and temperature are usually five days and 20^{o}C.

Concentration--The weight of solute dissolved in a unit volume of solution.

Connate Water--Sea water held in the interstices of sedimentary deposits and sealed in by the deposition of overlying beds.

Contamination--See Pollution

Control--The prevention if possible, or otherwise the minimization of pollution (in the sense of pollution control only).

Curie (ci)--The physical unit of radioactivity, as distinct from a measure of its biological significance. It is equal to 37,000 million disintegrations per second.

Daughter Decay Products--Nuclides formed by the radioactive decay of other nuclides, which may be called "parents".

Deep Well Disposal--The disposal of waste materials by injection into a subsurface formation, usually at much greater depth than known freshwater aquifers.

Decision Variables--The variables which measure quantitative characteristics of policies or plans.

Degradation of Water Quality--See Pollution.

Denitrification--The biochemical reduction of nitrate or nitrite to gaseous nitrogen, either as molecular nitrogen or as an oxide of nitrogen.

Dispersion--The mixing induced by molecular diffusion, the structure of a porous medium, or the stratigraphy of an aquifer,caused by Brownian motion on the lowest scale, and velocity variations for the larger scales.

Externality--A term used to describe other positive or negative effects which occur, but which are not accounted for in the private calculation of the results of a certain activity.

Feasible Policy--A policy which does not violate any constraints.

Fertilizer--Any organic or inorganic material of natural or synthetic origin that is added to a soil to supply elements essential to plant growth.

Fixation--A combination of physical and chemical mechanisms in the soil that act to retain wastewater constituents within the soil, including adsorption, chemical precipitation, and ion exchange.

Groundwater--The underground body of water that is the saturated zone, which tends to move by hydraulic gradient to lower levels.

Groundwater Basin--A groundwater reservoir together with all the overlying land surface and the underlying aquifers that contribute water to the reservoir. In some cases, the boundaries of successively deeper aquifers may differ in a way that creates difficulty in defining the limits of the basin.

Groundwater Recharge--Inflow to a groundwater reservoir.

Groundwater Reservoir--An aquifer or aquifer system in which groundwater is stored. The water may be placed in the aquifer by artificial or natural means.

Herbicide--A chemical substance used for killing plants, especially weeds.

Infiltration--The flow of a liquid into a substance through pores or other openings, connoting flow into a soil in contradistinction to the word percolation which connotes flow through a porous substance.

Ion-exchange--The process by which easily exchangeable ions are held by mineral surfaces and/or colloids.

Irrigation--Application of water to the land to meet the growth needs of plants.

Land-Use--The type of use to which land is put. General classifications are undeveloped agricultural, industrial, commercial, housing, and institutional.

Leaching--The removal of materials in solution from the soil.

Manure--The excreta of animals, with or without the admixture of bedding or litter, in varying stages of decomposition.

Marginal--This is a term related with the concept of derivatives; marginal cost is the derivative of the cost function with respect to the independent variable or more graphically, the cost of producing the last unit of product; in the same way, marginal utility will be the utility derived through the use or consumption of the last unit of a certain good.

Mineralization--The conversion of an element from an organic form to an inorganic form as a result of microbial decomposition (and/or)

Mineralization--The process of accumulation of mineral elements and/or compounds in soil or water.

Mobility--The ability of a dissolved or undissolved species to migrate in the soil or groundwater. The most mobile chemical is one that moves with the water.

Nitrification--The biological oxidation of ammonium salts to nitrites and the further oxidation of nitrites to nitrates.

Normative Model--A model which describes situations as they ought to be.

Objective Function--A statement by which the consequences of a policy can be determined.

Oxidation-Reduction Potential--Denotes the potential required to transfer electrons from the oxidized form to the reduced form.

Pathogenic Organisms--Microorganisms that can transmit diseases.

Percolation--The movement of water within a porous medium such as soil.

Permeability--The property of a material which permits appreciable movement of water through it when actuated by hydrostatic pressure of the magnitude normally encountered in natural subsurface water.

Pesticides--Chemical compounds used for the control of undesirable plants, animals, or insects. The term includes insecticides, weed killers, rodent poisons, nematode poisons, fungicides, and growth regulators.

Plan--See Alternative Plan.

Plant Nutrients--The elements or groups of elements taken in by a plant which are essential to its growth and used in elaboration of its food and tissues. Includes nutrients obtained from fertilizer ingredients.

Policy--See Alternative Plan.

Pollution--The presence of any substance (organic, inorganic, biological, thermal, or radiological) in water at intensity levels which tend to impair, degrade, or adversely affect its quality or usefulness for a specific purpose. In this report it is synonymous with "contamination" and "the degradation of water quality".

Porosity--The relative volume of the pore spaces between mineral grains in a rock or soil as compared to the total rock or soil volume.

Positive Model--A model which describes a situation as it actually is.

Primary Treatment (Sewage)--The removal of larger solids by screening, and of more finely divided solids by sedimentation.

Radioactivity--The property possessed by some atoms of disintegrating or decaying spontaneously with the emission of ionizing radiation.

Radionuclide--Any radioactive species of atom that exists for a measurable length of time. Individual radionuclides are distinguished by their atomic weight and atomic number.

Recharge--See Groundwater Recharge.

Recharge Basin--A basin designed for the purpose of adding water to the groundwater reservoir.

Rem--The radioactive dose which is biologically equivalent to one roentgen of gamma or x-radiation.

Return Flow--That part of a diverted flow which is not consumptively used and which returns to a source of supply (surface or underground).

Salt Balance--A condition in which specific or total dissolved solids removed from a specified field, stratigraphic zone, political area, or drainage basin equals the comparable dissolved solids added to that location from all outside sources during a specified period of time.

Salinity--Salt content concentration of dissolved mineral salts in water or soil.

Salt Water--Water containing dissolved salts.

Salt Water Barrier--A physical facility or method of operation designed to prevent the intrusion of salt water into a body of fresh water. In underground water management, a barrier may be created by injection of relatively fresh water to create a hydraulic barrier against salt water intrusion.

Salt Water Intrusion--The invasion of a body of fresh water by salt water. It can occur either in surface or ground water bodies.

Saturation, Zone of--The zone in which interconnected interstices are saturated with water under pressure equal to or greater than atmosphere.

Secondary Treatment--The oxidation of organic matter in sewage through bacterial action.

Soil Water or Soil Moisture--That water present in the soil pores in an unsaturated zone above the groundwater table.

Surface Water--That portion of water that appears on the land surface.

System--A set of objects which interact in a regular, interdependent manner.

Tertiary Treatment--Advanced waste treatment which removes additional impurities which remain in the effluent after secondary treatment.

Total Dissolved Solids (TDS)--The total dissolved solids in water, usually expressed in milligrams per liter (mg/L).

Transmissivity--The rate at which water is transmitted through a unit width of the aquifer under a unit hydraulic gradient.

Transpiration--The net quantity of water absorbed through plant roots and transpired, plus that used directly in building plant tissue.

Utility--Satisfaction that an individual receives through the use or consumption of certain goods.

Viruses--Submicroscopic biological structures containing all the information necessary for their own reproduction.

Water Quality--Pertaining to the chemical, physical and biological constituents found in water and its suitability for a particular purpose.

Water Table--That surface in an unconfined water body at which the pressure is atmospheric. It is defined by the levels at which water stands in wells that penetrate the water body just far enough to hold standing water.

Water-Table Aquifer--An aquifer containing water under water-table conditions.