Application of Modelling Techniques to Test Hypotheses Concerning the Migration of Aviation Gasoline from A Surface Spill

by

Theresa Hutchings
B.A. in Engineering, Cambridge University, 1992

Submitted to the Department of Civil and Environmental Engineering
in partial fulfillment of the requirements for the degree of

Master of Science in Civil and Environmental Engineering

at the

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Abstract

Models are widely accepted as useful tools in the understanding of the groundwater environment. This study uses a physically based computer model to investigate various hypotheses concerning the migration of aviation gasoline from a surface spill. The site considered is the FS-1 site at the Massachusetts Military Reservation, Cape Cod, Massachusetts. Between 1955 and 1970, aircraft maintainance at the FS-1 site caused between 400,000 and 1 million gallons of aviation gasoline to be released into the soil. Field investigation has detected a relatively small area that has been impacted by this source. Uncertainty exists over many of the factors which would govern the fate and transport of contaminant from such a spill. These were investigated using the model developed for the site. Biodegradation was found to be the predominant factor in influencing the extent of contamination emanating from this source area. It was concluded that the development of a model for this site was useful in two ways: it enabled examination of various assumptions, and the model predictions can be used to help direct future field investigations.

Thesis Supervisor: David Marks
Title: Professor, Department of Civil and Environmental Engineering

Acknowledgments

As I finish up this thesis my mind drifts through the crowd of people I'd like to thank for their help in making it possible. This includes not only people who have been directly involved, but all of those who have helped me on my path towards MIT: teachers at school who had enough foresight to see that women could be engineers too, and all those who taught and encouraged me at Cambridge. Particular thanks are due to the British Kennedy Memorial Trust. The generous scholarship awarded to me not only enabled me to undertake this master's program at MIT, but has also given me the opportunity of exploring America.

Studying at MIT can be a tough experience, and it can be difficult to find a niche that suits you. I'd like to thank my advisor, Professor David Marks, for giving me the freedom to explore a project and find what was right for me. My first exposure to groundwater modelling came from Dr. Fernando Miralles-Wilhelm - his lectures were a real inspiration to me. I have also greatly appreciated all the help he has provided over the last year in the use of the DYN system. I would also like to thank Shawn Morrissey for his help and guidance in this project, and for his never ending enthusiasm. This thesis would not have been possible without the involvement of the IRP staff at the Massachusetts Military Reservation. Their continual willingness to help and provide information was greatly appreciated, and the opportunity to become involved in an on-going investigation was invaluable. I hope the MIT-MMR links continue to be productive.

My thanks go to all the people who have helped me cope with the stress of having a thesis deadline fast approaching - in particular I'd like to thank Rachel for sharing that wonderful late night Athena experience, Heidi for being on the other end of the phone at 4am, Rob for letting me take out my anguish on his hair, Ida for being the perfect deskmate (now I've gone you can get some work done!), and Cris for, well, just being there. Last, but definitely not least, I think of my parents. Without their love and support I wouldn't have even been at MIT to write this thesis. I thank them for always encouraging me in everything I have wanted to do, no matter how insane it seemed at the time.

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Chapter 1

Introduction

Over recent years mathematical models, implemented in computer code, have emerged as a useful tool to help us understand and predict the processes occurring in the subsurface environment. The most widely accepted have been physically based models which combine conservation principles with constitutive relationships such as Darcy's and Fick's laws[17]. This type of model has been used extensively in a wide variety of applications from water management studies to groundwater contaminant assessment.

The complex nature of the subsurface environment presents the greatest challenge in the development of successful groundwater models. Although the classical groundwater flow and solute transport equations are reasonably accurate representations of the actual processes, problems are encountered when trying to apply them to real-world situations. Uncertainties arise due to the inaccessibility of this environment and the ensuing scarcity of data, heterogeneity over scales smaller than those considered in a typical groundwater model, physical and chemical interactions among the various phases present, the long time scales involved, and the difficulty of extending laboratory results to the field. However McLaughlin et al.[17] conclude that, although models may not be able to give us completely accurate predictions, they can give us a qualitative insight into a particular situation. This in turn can better our understanding of the processes occurring.

One particular application of models has been in the area of groundwater contamination. Models have been used to assess the migration of contaminants from a source, both to test hypotheses about the processes occurring and to predict future plume migration. This study uses modelling techniques to investigate a case study of this type. The problem addressed is one where there is comprehensive data on groundwater flow, but very little about the actual extent of contamination and factors affecting the fate of pollutants in the groundwater. Various hypotheses concerning these factors are considered, and a numerical model is used to test their respective outcomes. Consideration of this case study will enable us to comment on the widely accepted view that a modelling approach can be useful in such a situation.

The site to be considered is one of the many sites of potential environmental concern at the Massachusetts Military Reservation (MMR) on Cape Cod. This site, referred to as the FS-1 Study Area, has been identified as potential source of environmental impact due to the aircraft maintenance activities which were performed at the site between 1955 and 1967. These activities resulted in the release of aviation gasoline(AVGAS) into the soil, which is thought to have migrated down to the water table and contaminated the groundwater. This study uses the DYN modelling packages developed by Camp Dresser and McKee[3][4] to gain an insight into the fate of the AVGAS released at this site.

1.1 Site Background

MMR occupies approximately 22,000 acres on western Cape Cod (see Figure 1-1). Military activity at MMR dates back to 1911, with the heaviest use being since 1935. Operations have been of two general types: (1) mechanized army training and maneuvers; and (2) military aircraft operations, maintenance, and support. An Installation Restoration Program has been instigated at MMR as part of the U.S. Department of Defense program to investigate and remediate potential problems related to suspected past releases of toxic and hazardous materials at its facilities.This program has iden-

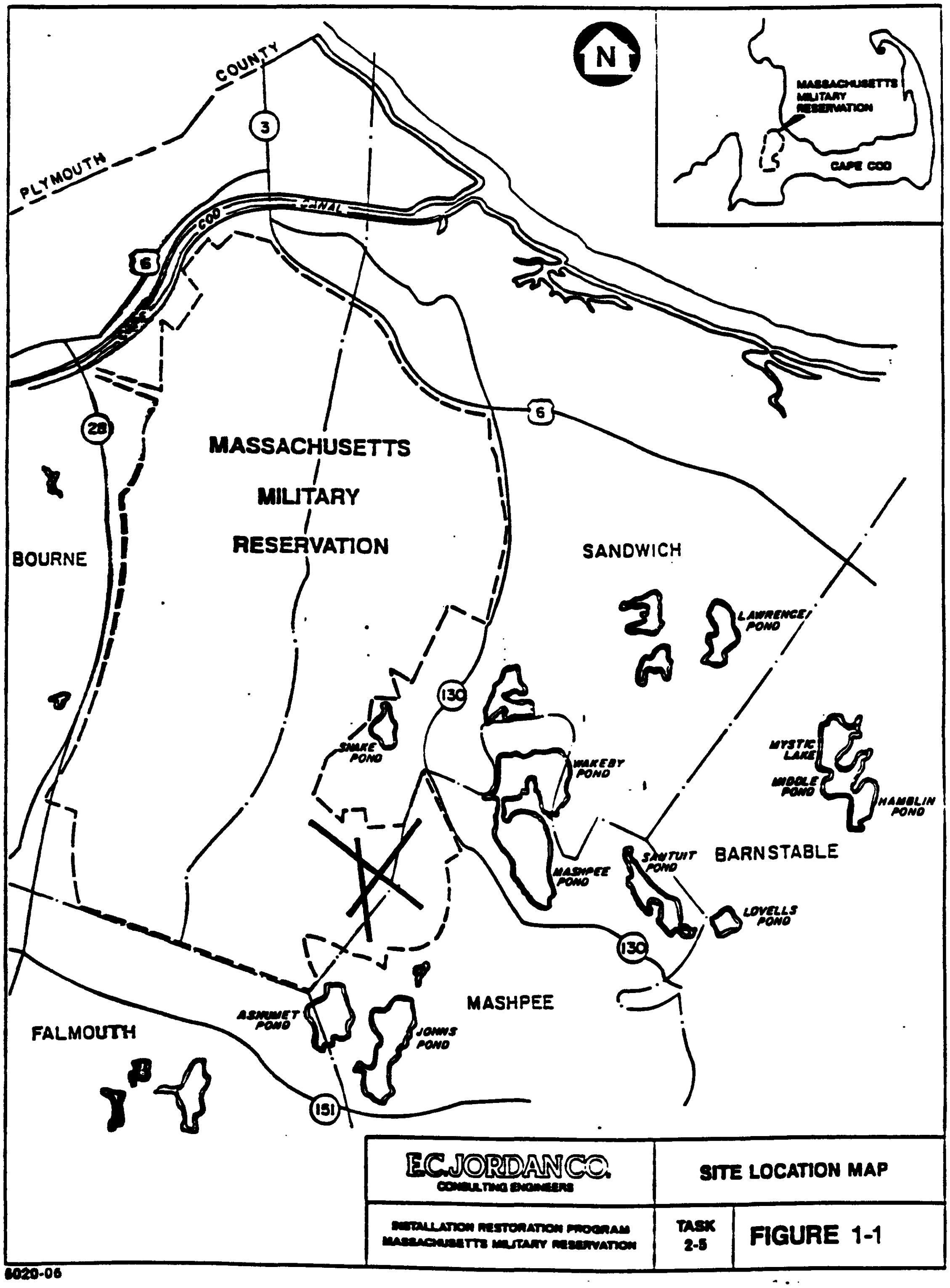


Figure 1-1: Location of Massachusetts Military Reservation

tified a total of 77 sites at MMR as possible sources of environmental contamination. The sites that have been identified are typical of military bases, including fire training areas, landfills, chemical spills, and fuel spills. The FS-1 Study Area is one such site.

1.2 FS-1 Study Area

1.2.1 Location and History

The FS-1 Study Area is located along the southeastern boundary of the base, east of the main aircraft runways (see Figure 1-2). The study area consists of two concrete paved aircraft turnarounds branching one to the east, and one to the west of Taxiway E. From 1955 to 1967, the 551st Airborne Early Warning and Control Wing (AEW&C) assigned to MMR was responsible for maintaining EC-121 Constellation Aircraft in the air at all times. Maintainance activities included testing aircraft fuel dump valves at this site. During the test, the aircraft's four dump valves were opened, which resulted in the dumping of an estimated 100 to 250 gallons of AVGAS per episode. Firefighting crews who witnessed the tests washed the dumped AVGAS into the soils around the pavement so that fuel vapours would not be present when the tow vehicle returned to remove the aircraft. As the aircraft aged, the frequency of the testing was increased. Later, in an effort to limit the quantity of wasted fuel, barrels were used to collect the dumped fuel. Records of AEW&C fuel management practices have since been lost; therefore, a complete inventory of the amount of AVGAS discharged is unknown. It was estimated that fuel dump valve testing released a maximum of 400,000 to 1 million gallons of AVGAS at the FS-1 Study Area.

1.2.2 Previous Investigations

Following the identification of FS-1 as a site of potential environmental concern through a record search by Metcalf and Eddy (1983), the site has been explored by test pitting and borings performed by R.F. Weston (1985) and by Jordan (1989 and 1990). These investigations confirmed the presence of groundwater contamination

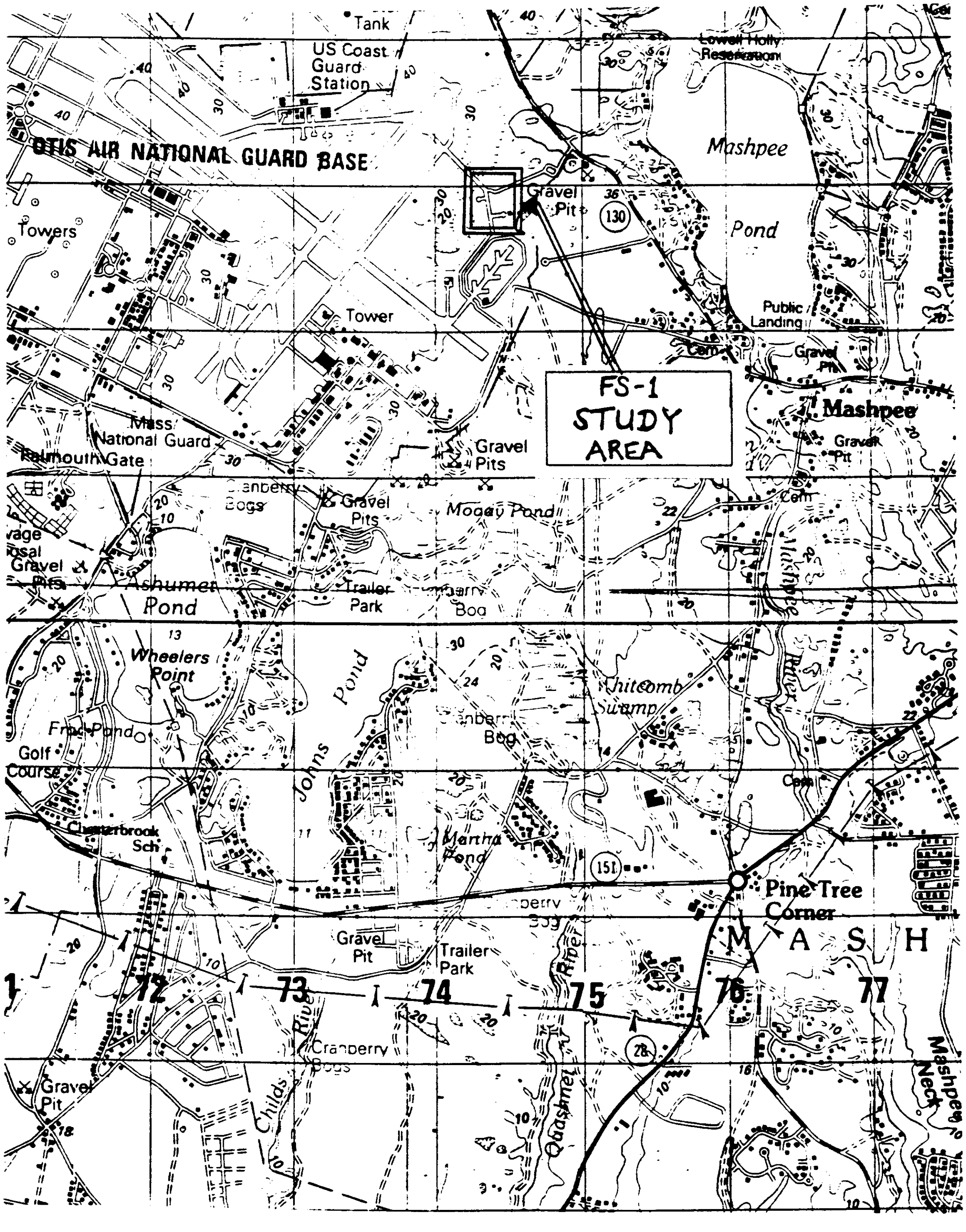


Figure 1-2: Location of FS-1 Study Area

extending from the study area, with benzene, toluene, xylene and lead being detected. The Remedial Investigation conducted by E.C. Jordan Co.[7] further characterized the groundwater contamination. Impact to downgradient groundwater quality was evident at least up to a distance of 1,800ft from the Western Aircraft Turnaround, although the maximum downgradient extent of the regulated fuel volatile organic compounds (i.e., BTEX) was only approximately 500ft downgradient. Beyond this other chemical indicators of AVGAS impact were detected, including the presence of lead, tentatively identified fuel-related compounds, and reduced dissolved oxygen levels.

The Remedial Investigation raised various questions about the fate of the AVGAS released at the FS-1 Study Area. The extent of contamination detected was small compared to the amount of AVGAS thought to have been released into the soil. It has been suggested that a significant amount of biodegradation has been occurring, as indicated by the low dissolved oxygen concentrations detected at the study area, and that this is limiting the extent of the plume. However, there is also the possibility that under anoxic conditions, biodegradation may slow, and "slugs" of degradable chemicals may be transported by advection within the aquifer. A particle tracking model for a conservative contaminant was developed to determine the direction a detached slug may be transported. The result is shown in Figure 1-3. Further studies were suggested into the biodegradation of fuel-related compounds at FS-1. At present an extensive groundwater sampling program using the Geoprobe^{TM} is being implemented. The objectives of this study are to confirm the vertical and horizontal extent of groundwater contamination and low DO concentrations known to exist near the FS-1 source area, and to determine the presence or absence and extent of low DO concentration downgradient of FS-1 and evaluate low DO zones for BTEX and total petroleum hydrocarbons.

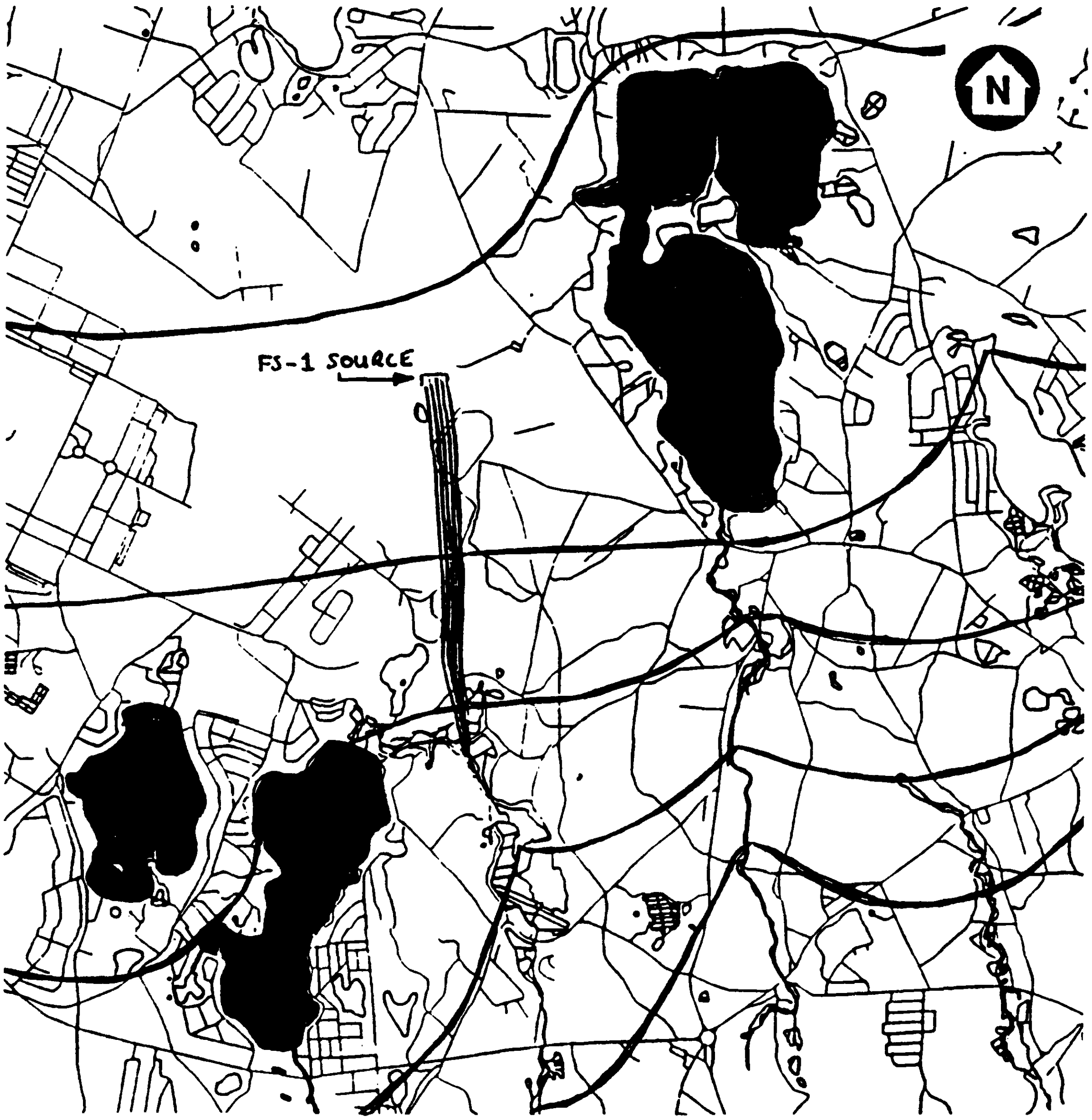


Figure 1-3: Results from the Particle Tracking Model

1.3 Purpose and Scope

This project attempts to model the transport of AVGAS from the FS-1 source area using the DYN modelling packages developed by Camp Dresser and McKee Inc. Various hypotheses concerning the uncertain factors affecting this migration are considered. It is hoped that this analysis will help us determine the relative importance of these factors, and that the conclusions reached will help guide future field investigations.

In preparation for attempting to model this site, a study area characterization (Chapter 2), and assessment of the chemicals of concern (Chapter 3) are carried out. Chapter 4 discusses the processes which determine the fate and transport of the AVGAS, and attempts to determine the dominant migration pathways. The numerical model used in the study is introduced in Chapter 6, and Chapter 7 outlines the development of the model for this site. Finally the results are assessed, and various conclusions made.

Chapter 2

Study Area Characterization

2.1 Climate

Cape Cod has a temperate climate with precipitation distributed year round. The average annual precipitation is about 48 inches, and annual groundwater recharge is reported as being in the range of 17 to 23 inches/year[2]. The one year 24-hour rainfall event is about 2.7 inches. These figures indicate a high potential for runoff and erosion, however this is minimized due to the highly permeable surface soils and low topographic gradient. Hence the contamination migration from the site is primarily via groundwater pathways.

2.2 Geology

The surficial geology of Western Cape Cod is dominated by depositional processes associated with glacial activity during the Wisconsin period (7,000 to 85,000 years ago). A series of glacial advances and retreats resulted in the deposition of the Buzzards Bay Moraine and the Sandwich Moraine along the western and northern edges of this area. Between the two moraines lies a broad outwash plain. It is on this plain that the FS-1 Study Area is located. Sediments which form this outwash plain were carried by rivers flowing off the ice sheet, and hence tend to have a uniform grain-size. Thus the area is characterized by highly permeable soils. Fine-grained, glaciolacustrine sediments and basal till are present below the outwash plain at the base of the unconsolidated sediments. Figures 2-1 through 2-3 show the horizontal and vertical distribution of glacial sediments.

2.3 Regional Hydrogeology

MMR is located over a U.S. Environmental Protection Agency-designated sole source aquifer. The aquifer is unconfined, and is recharged by infiltration from precipitation. The top of the groundwater mound within the western Cape Cod groundwater system is located beneath the northern portion of MMR. Groundwater flow is generally radial from this mound. The lateral boundary of the aquifer is formed by the ocean on three sides, with groundwater discharging into Nantucket Sound on the south, Buzzards Bay on the west, and Cape Cod Bay on the north. The eastern boundary is formed by the Bass River which is at some distance from the areas of interest. The interpretive map of groundwater surface produced from water level data gathered in March 1988 is shown in Figure 2-4.

The aquifer is characterized by highly permeable, stratified glacial deposits. There is a gradual transition from coarse- to fine-grained sediments with depth. In the southern part of MMR, the highly permeable sediments extend to about 200ft below ground surface (BGS), below which significantly finer-grained sediments which may be of the lacustrine origin are present to a depth of approximately 350 ft BGS. Although the Groundwater Remediation Strategy Report[2] suggests that this finer material may be considered the bottom of the aquifer, this study will include all material down to the bedrock in the aquifer. In the southern portion of MMR hydraulic conductivities in the coarser-grained sediments vary between 160 to 380ft/day[2]. The hydraulic conductivity of the lacustrine sediments is 10 to 50 times lower then the outwash[2]. Due to the stratification of the sediments horizontal hydraulic conductivity is likely to be greater than the vertical hydraulic conductivity. However, the degree of anisotropy is typically influenced by the presence of fine-grained sediments

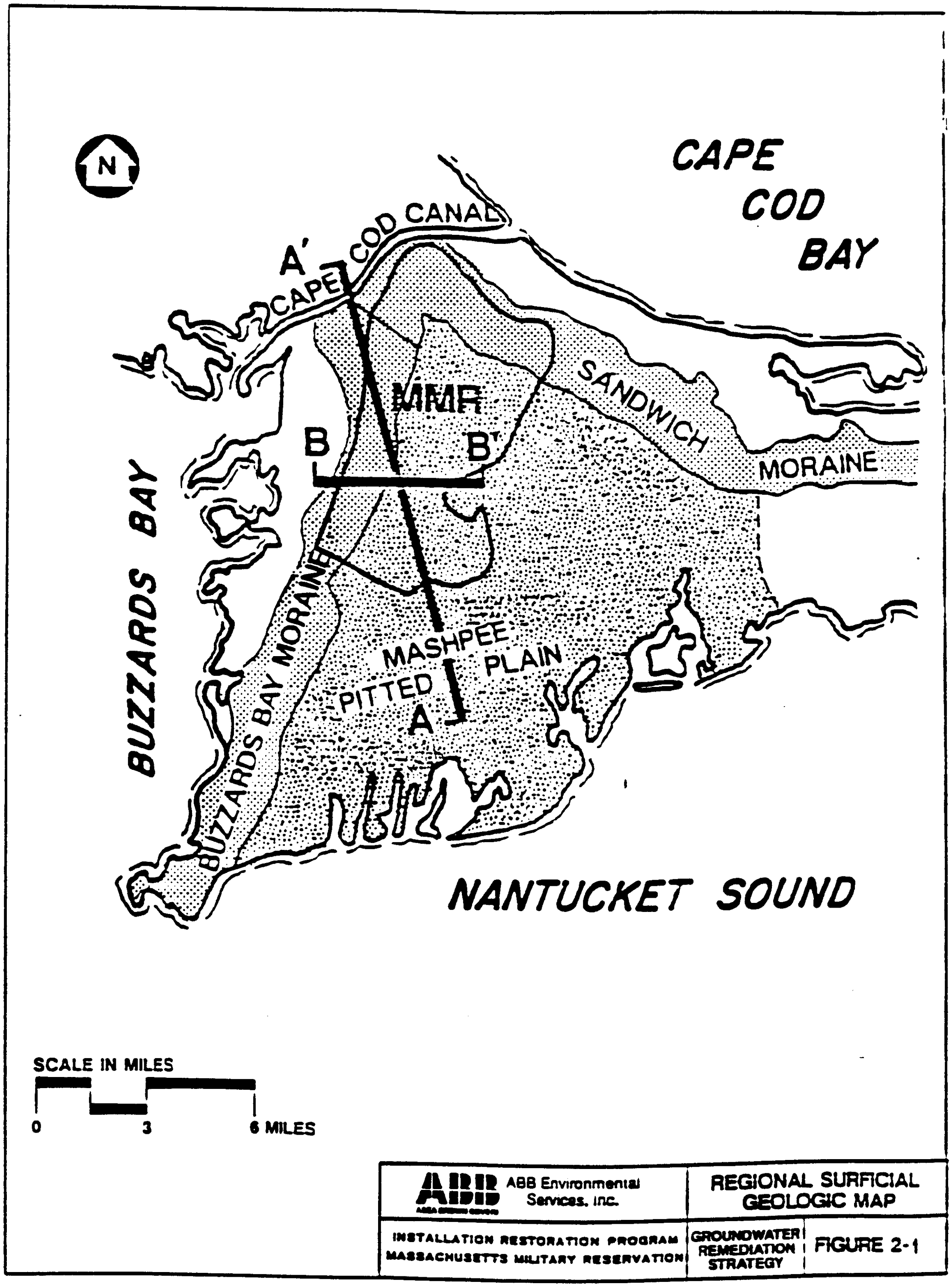


Figure 2-1: Regional Surficial Geologic Map

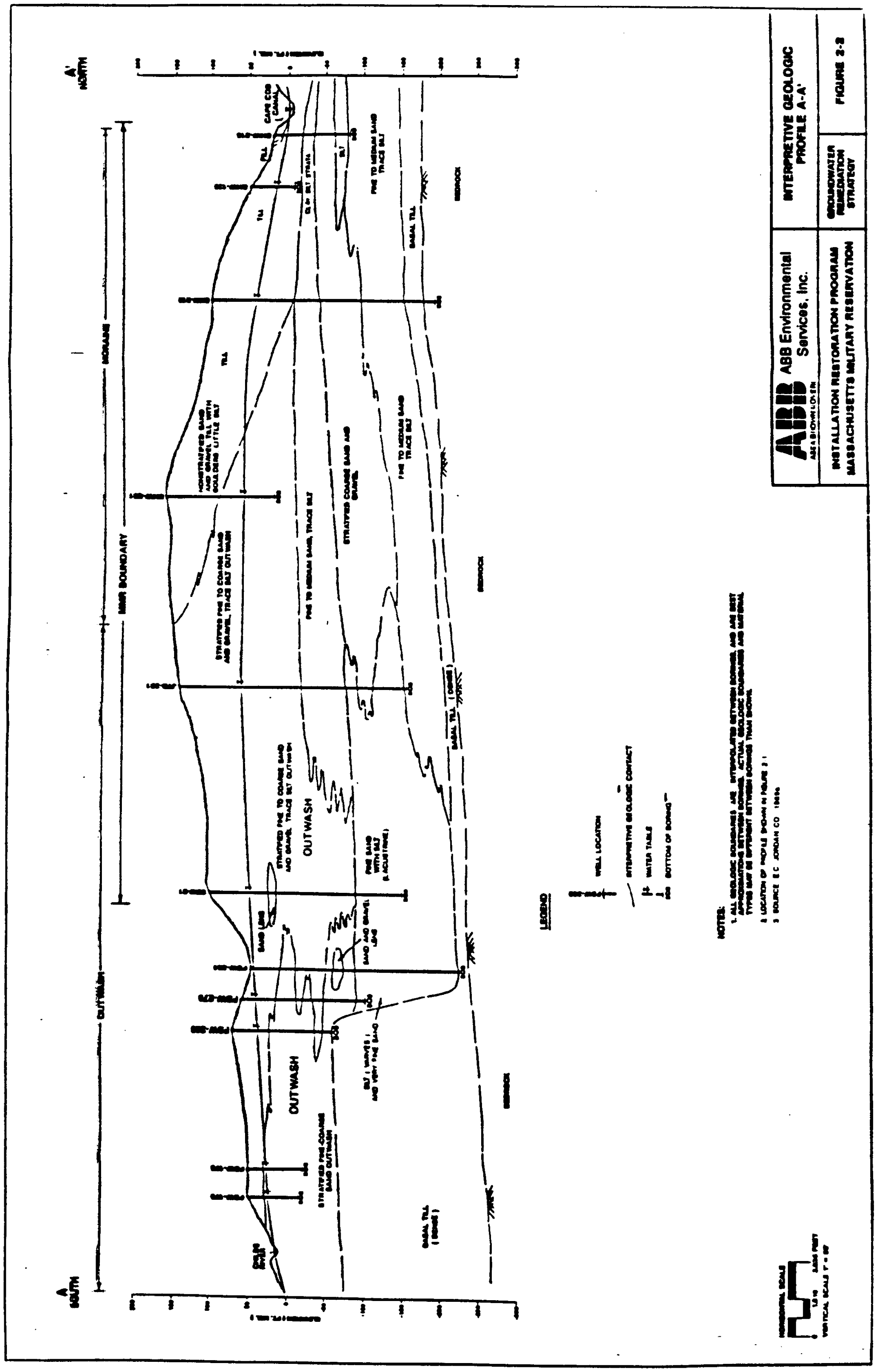
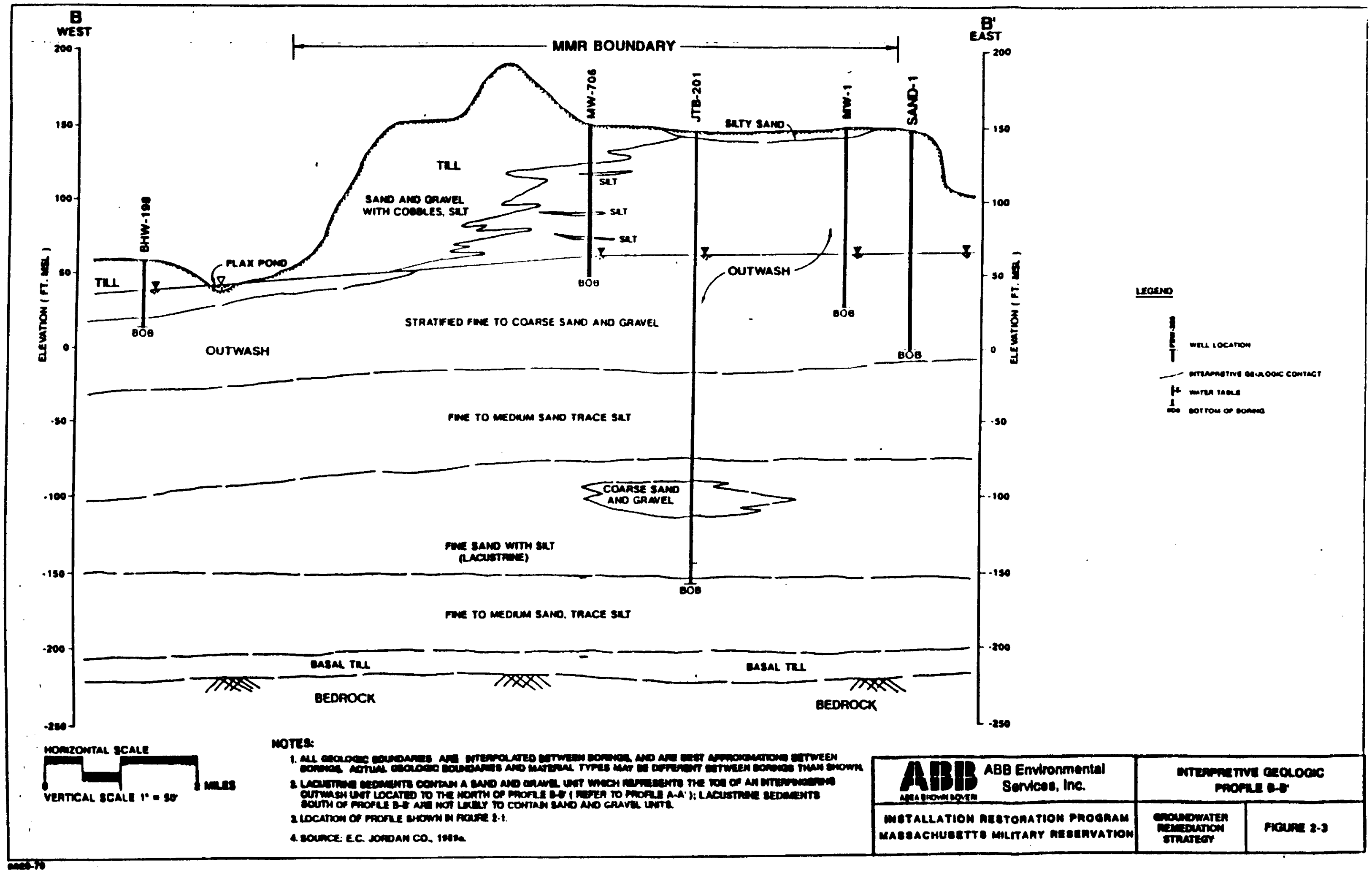


Figure 2-2: Interpretive Geologic Profile A-A'



NOTES:

1. ALL GEOLOGIC BOUNDARIES ARE INTERPOLATED BETWEEN BORINGS, AND ARE BEST APPROXIMATIONS BETWEEN BORINGS. ACTUAL GEOLOGIC BOUNDARIES AND MATERIAL TYPES MAY BE DIFFERENT BETWEEN BORINGS THAN SHOWN.
2. LACUSTRINE SEDIMENTS CONTAIN A SAND AND GRAVEL UNIT WHICH REPRESENTS THE TOE OF AN INTERFINGERING OUTWASH UNIT LOCATED TO THE NORTH OF PROFILE B-B' (REFER TO PROFILE A-A'); LACUSTRINE SEDIMENTS SOUTH OF PROFILE B-B' ARE NOT LIKELY TO CONTAIN SAND AND GRAVEL UNITS.
3. LOCATION OF PROFILE SHOWN IN FIGURE 2-1.
4. SOURCE: E.C. JORDAN CO., 1989a.

Figure 2-3: Interpretive Geologic Profile B-B'

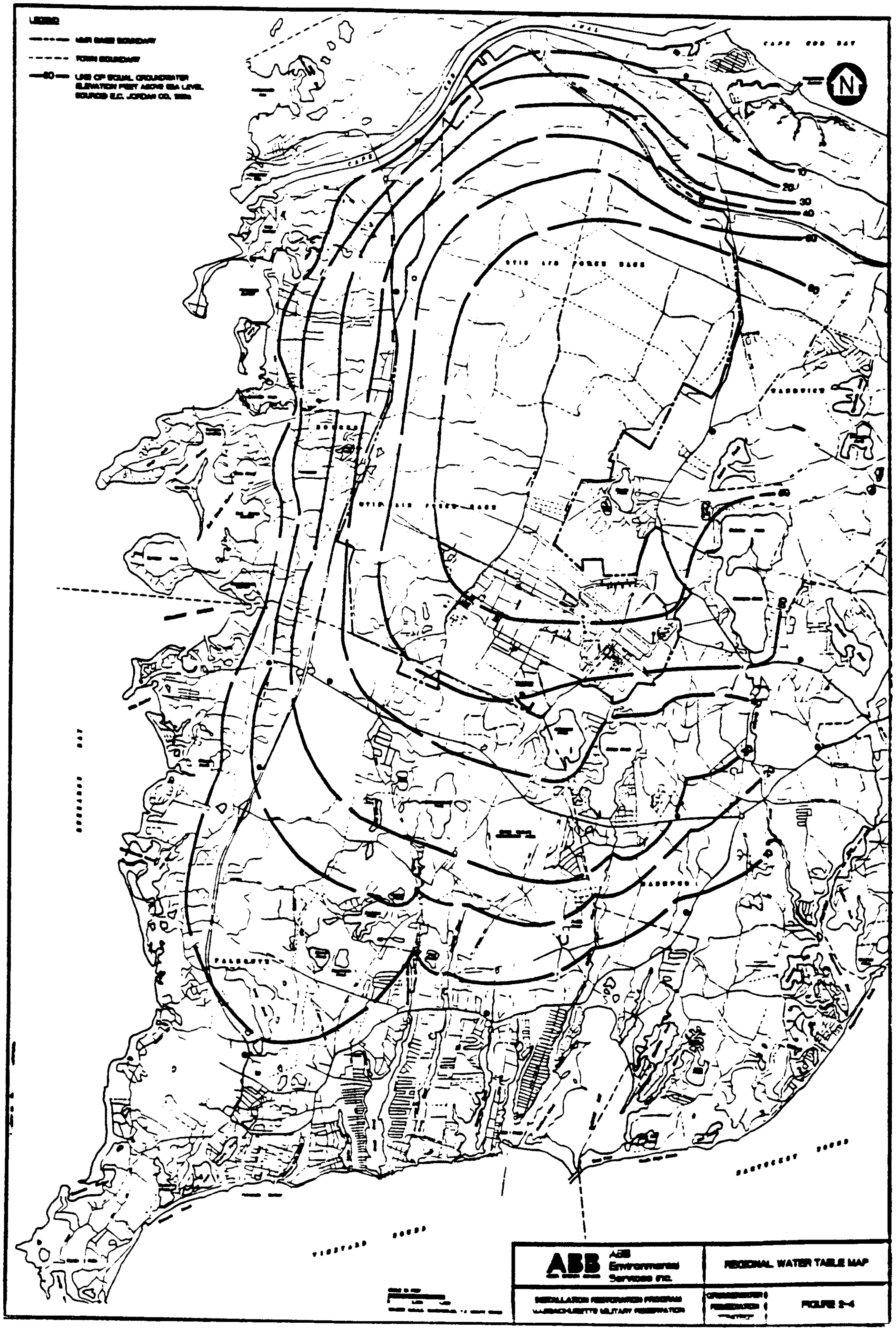


Figure 2-4: Regional Water Table Map

within the strata. Because of the paucity of silt in the outwash sediments, anisotropy may not be as high as would be expected from the observed stratification.

Kettle hole ponds, depressions of the land surface below the groundwater table, are common on the outwash plain. These ponds influence the direction of the groundwater flow in a manner similar to large-scale aquifer heterogeneities. This is evident in the strong changes in the slope and direction of the regional water table in the vicinity of such ponds.

Field studies have shown that piezometric head varies little with depth, apart from in the vicinity of a kettle hole pond. Here the vertical hydraulic gradients are of a similar or greater magnitude than the horizontal hydraulic gradient in the aquifer. These vertical gradients are sufficient to cause groundwater flowing at depth below the water table to discharge to the pond.

Rainfall recharge is observed to cause groundwater flow to have a slight downward component, although the flow is predominantly horizontal.

2.4 Local Geology and Hydrogeology

The local groundwater flow direction at the FS-1 study area is predominantly from north to south. However Johns pond, Ashumet pond, and the Quashnet River all significantly affect the general flow regime. The effect of the Quashnet River and the neighbouring cranberry bogs is of particular interest since the upper reaches of the river lie directly downgradient from the FS-1 source area. Its effect on the groundwater flow regime is considered in the Southeast Region Groundwater Operable Unit Remedial Investigation Report[1]. The river drains water from Johns Pond, however this outlet is controlled by a man-made structure, and is commonly blocked for months when water is not needed for cranberry bog operations. The river is thus primarily groundwater fed along nearly its entire length. The river induces upward vertical head gradients in the groundwater, which produces a flux into the stream. This flux is approximately 0.2 ft^2/s in the upper reaches (first 0.7 miles) of the river.

2.5 Aquifer Characteristics

Hydraulic Conductivity To assess hydraulic conductivity at the FS-1 source area, rising-head tests were performed at seven monitoring wells by Jordan (1989)[7]. Hydraulic conductivities were calculated using the Horslev method, and ranged between 136 and 240ft/day. Well screens were located between 60 and 80ft BGS, hence these conductivities are applicable to the coarse-grained sediments at shallow depths. No tests were made at greater depths. In-situ tests for hydraulic conductivity were also performed at several monitoring wells further downgradient near the Quashnet River[1]. These tests characterized the hydraulic conductivity throughout a significant portion of the aquifer. Hydraulic Conductivity was found to vary between 18 and 123ft/day, with a noticeable decrease of conductivity with depth. The ratio of horizontal to vertical hydraulic conductivities has been found to be between 2:1 and 5:1[14].

Porosity The effective porosity of the outwash material is estimated to be between 0.35[1] and 0.39[14] which is typical of sandy, stratified glacial deposits.

Dispersivity The large-scale natural gradient tracer tests performed in this aquifer by Le Blanc et al.[14][8] yielded field-scale values of dispersivity for a non-reactive contaminant. The movement of the tracer was monitored using a three-dimensional sampling network for about 280m of travel distance. Spatial moments were used to calculate the mass, mean position, and variance for 16 views of the spatial distribution of the non-reactive tracer (bromide). Although there appeared to be a developing dispersion process in the first 26m of distance traveled, the longitudinal dispersivity then remained constant at a limiting value of 0.96m. The calculated transverse horizontal dispersivity was 1.8cm, and transverse vertical dispersivity was 0.15cm.

Chapter 3

Contaminant Assessment

3.1 Contaminants of interest

Aviation gasoline, the contaminant released at the FS-1 Study Area, is made by blending various proportions of distillate stocks such as naphtha, gasoline and kerosene. It is very similar in composition to the later JP-4 Jet Fuel. The individual major components representing at least 0.1% by weight in one JP-4 sample are given in Table 3.1. The predominant organic chemical structures present include aromatic hydrocarbons, straight-chained alkanes, and cyclic hydrocarbons. The gasoline may also contain traces of species containing nitrogen, oxygen or sulphur, and also some trace inorganic elements. Additives may also be added to the fuel as anti-oxidants, metal deactivators, corrosion or icing inhibitors, or electrical conductivity agents. AVGAS differs from JP-4 in that tetraethlyl lead is often added to increase the octane number of AVGAS. Due to the lack of available data for AVGAS, this study shall assume the composition of AVGAS is approximately as given in Table 3.1, with the inclusion of tetraethyl lead.

The factors affecting the fate of contamination, that is solubility, volatility, sorption, and degradation, will vary between constituents, and hence the relative concentrations of the constituents will vary with time and distance from the source. In general, the aromatic compounds tend to preferentially partition into a liquid phase, while more

Fuel Component	Molecular Formula	Percent by Weight	Molecular Weight (g/mol)	T melt °C	T boil °C	Vapour Pressure at 25°C (atm) $-\log p^{o}$	Aqeous Solubility at 25°C (mol /L) $-\log C_{w}^{sat}$	Henry's Law Constant at 25°C (Latm/mol) $\log K_H$	Octanol-Water Partition Coefficient at 25°C [(mol/L octanol)/(mol/L water)] logKow	NOTES
n-Butane	C4H10	0.12	58.10	-138.40	-0.50	-0.39	2.59	2.98	2.89	
Isobutane	(CH3)2CHCH2	0.66	58.12	-159.40	-11.70	-0.47	3.07	*3.54*	1.95	soly meas & v.p. estimated at 20C
n-Pentane	C5H12	1.06	72.20	-129.70	36.10	0.16	3.25	3.09	3.62	
2,2-Dimethylbutane	CH3CH2C(CH3)3	0.10	86.18	-99.90	49.70	0.39	4.79	4.40	3.68	
2-Methylpentane	C3H7CH(CH3)2	1.28	86.18	-153.70	60.30	0.56	4.95	4.39	3.81	
3-Methylpentane	(C2H5)2CHCH3	0.89	86.18		63.30	0.61	4.95	4.34	3.81	
n-Hexane	C6H14	2.21	86.20	-95.00	69.00	0.69	3.83	3.14	4.11	
Methylcyclopentane	CH3C5H9	1.16	84.16	-142.40	71.80	0.76	4.53	3.77	3.47	
2,2-Dimethylpentane	C3H7C(CH3)3	0.25	100.20	-123.80	79.20	0.88	5.46	4.57	4.22	
Benzene	C6H6	0.50	78.10	5.50	80.10	0.90	1.64	0.74	2.13	
Cyclohexane	C6H12	1.24	84.20	6.60	80.70	0.90	3.15	2.25	3.44	
2-Methylhexane	C4H9CH(CH3)2	2.35	100.20	-118.30	90.00	1.07	5.62	4.55	4.35	
3-Methylhexane	(CH3)C2H5	1.97	100.20	-114.00	92.00	1.11	5.62	4.51	4.35	
trans-2,3-Dimethylcyclopentane	2,3-(CH3)2C5H8	0.36	98.19	-120.00	91.80	1.10	5.19	4.08	4.00	
cis-1,3-Dimethylcyclopentane	1,3-(CH3)2C5H8	0.34	98.19				5.19		4.00	
cis-1,2-Dimethylcyclopentane	1,2-(CH3)2C5H8	0.54	98.19	-62.00	99.25	1.24	5.19	3.95	4.00	
n-Heptane	C7H16	3.67	100.20	-90.60	98.40	1.21	4.51	3.30	4.66	
Methylcyclohexane	CH3C6H11	2.27	98.19	-126.60	100.90	0.72	3.85	3.12	4.04	v.p. & soly measured at 20C
2,2,3,3-Tetramethylbutane	CH3C(CH3)2C(CH3)2CH3	0.24	114.23	100.70	106.50	1.37	5.51	4.14	4.26	
Ethylcyclopentane	C2H5C5H9	0.26	98.19	-138.40	103.50	1.31	5.20	3.89	4.01	
2,5-Dimethylhexane	(CH3)2CHCH2CH2CH(CH3)2	0.37	114.23	-91.20	109.00	1.41	6.12	4.71	4.76	
2,4-Dimethylhexane	C2H5CH(CH3)CH2CH(CH3)2	0.58	114.23		111.00	1.45	6.12	4.68	4.76	
1,2,4-Trimethylcyclopentane	1,2,4-(CH3)3C5H7	0.25	112.22				5.84		4.53	
3,3-Dimethylhexane	C3H7C(CH3)2C2H5	0.26	114.23	-126.10	112.00	1.46	6.12		4.76	
1,2,3-Trimethylcyclopentane	1,2,3-(CH3)3C5H7	0.25	112.22				5.84		4.53	
Toluene	C7H8	1.33	92.10	-95.00	110.60	1.42	2.25	0.83	2.69	
2,2-Dimethylhexane	(CH3)2CHCH2CH2CH(CH3)2	0.71	114.23	-121.00	106.80	1.37	6.12	4.75	4.76	
2-Methylheptane	C4H9C(CH3)3	2.70	114.23	-109.00	117.60	1.57	6.28	4.72	4.89	
4-Methylheptane	(C3H7)2CHCH3	0.92	114.23	-121.00	117.70	1.57	6.28	4.72	4.89	
cis-1,3-Dimethylcyclohexane	1,3-(CH3)2C6H10	0.42	112.22	-75.60	120.10	1.61	5.80	4.19	4.50	
3-Methylheptane	C4H9CH(CH3)C2H5	3.04	114.23	-120.50	119.00	1.59	6.28	4.69	4.89	
1-Methyl-3-ethylcyclohexane	3-C2H5(C6H10)CH3	0.17	126.24				6.47		5.04	
1-Methyl-2-ethylcyclohexane	2-C2H5(C6H10)CH3	0.39	126.24				6.47		5.04	
Dimethycyclohexane	1,1-(CH3)2C6H10	0.43	112.22	-33.50	119.50	1.60	5.80	4.20	4.50	
n-Octane	C8H18	3.80	114.20	-56.80	125.70	1.73	5.20	3.47	5.18	
1,3,5-Trimethylcyclohexane	1,3,5-(CH3)3C6H9	0.99	126.24	-49.70	138.50	1.95	5.64	3.69	4.37	
1,1,3-Trimethylcyclohexane	1,1,3-(CH3)3C6H9	0.48	126.24				5.64		4.37	
2,5-Dimethylheptane	C2H5CH(CH3)(CH2)2CH(CH3)2	0.52	128.26		136.00	1.91	6.94	5.03	5.42	
Ethylbenzene	C8H10	0.37	106.20	-95.00	136.20	1.90	2.80	0.90	3.15	
m-Xylene	1,3-(CH3)2C6H4	0.96	106.20	-48.05	139.10	1.95	3.82	1.87	3.20	v.p. calc. by interpolating bet. 20C and 30C
p--Xylene	1,4-(CH3)2C6H4	0.35	106.20	13.05	138.30	1.91	2.69	0.78	3.18	v.p. calc. by interpolating bet. 20C and 30C
3,4-Dimethylheptane	CH3CH2CH(CH3)CH(CH3)C3H7	0.43	128.26		140.10	1.98	6.94	4.96	5.42	
4-Ethylheptane	(C3H7)2CHC2H5	0.18	128.26		141.20	2.00	6.95	4.95	5.43	
4-Methyloctane	C4H9CH(CH3)C3H7	0.86	128.26	-113.20	142.40	2.03	6.95	4.92	5.43	
2-Methyloctane	C6H13CH(CH3)2	0.88	128.26	-80.10	142.80	2.03	6.95	4.92	5.43	
3-Methyloctane	C5H11CH(CH3)C2H5	0.79	128.26	-107.60	143.00	2.04	6.95	4.91	5.43	
o-Xylene	1,2-(CH3)2C6H4	1.01	106.20	-25.35	144.40	2.03	2.68	0.65	3.13	v.p. calc. by interpolating bet. 20C and 30C
1-Methyl-4-ethycyclohexane	4-C2H5(C6H10)CH3	0.48	126.24		150.00	2.17	6.47	4.30	5.04	
n-Nonane	C9H20	2.25	128.30	-51.00	150.80	2.24	5.94	3.70	5.56	
Isopropylbenzene	(CH3)2CHC6H5	0.30	120.20	-96.60	154.20	2.37	3.38	1.01	3.74	v.p. & soly measured at 20C
n-Propylbenzene	C9H12	0.71	120.20	-101.60	159.20	2.35	3.34	0.99	3.63	
1-Methyl-3-ethylbenzene	3-C2H5C6H4CH3	0.49	120.19	-95.50	161.30	2.39	3.77	1.38	3.99	
1-Methyl-4-ethylbenzene	4-C2H5C6H4CH3	0.43	120.19	-62.30	162.00	2.40	3.77	1.37	3.99	
1,3,5-Trimethylbenzene	C9H12	0.42	120.20	-44.70	164.70	2.48	3.40	0.92	3.42	
1-Methyl-2-ethylbenzene	2-C2H5C6H4CH3	0.23	120.20	-80.95	165.20	2.46	3.21	0.75	3.53	
1,2,4-Trimethybenzene	C9H12	1.01	120.20	-43.80	169.40	2.57	3.33	0.76	3.65	
n-Decane	C10H22	2.16	142.30	-29.70	174.10	2.76	6.57	3.81	6.10	

Table 3.1: Major Components of one JP-4 Sample - Chemical Properties

Fuel Component	Molecular Formula	Percent by Weight	Molecular Weight (g/mol)	T melt °C	T boil °C	Vapour Pressure at 25°C (atm) $-\log p^{L}$	Aqeous Solubility at 25°C (mol /L) $-\log C_{W}^{sat,L}$	Henry's Law Constant at 25°C (Latm/mol) $\log K_{H}$	Octanol-Water Partition Coefficient at 25°C [(mol/L octanol)/(mol/L water)] logKow	NOTES
n-Butylcyclohexane	C4H9C6H11	0.70	140.27	-74.70	181.00	2.77	7.15	4.38	5.59	
1,3-Diethylbenzene	1,3-(C2H5)2C6H4	0.46	134.22	-83.90	181.00	2.77	4.40	1.63	4.53	
1-Methyl-4-propylbenzene	4-C3H7C6H4CH3	0.40	134.24				4.40		4.53	
1,3-Dimethyl-5-ethylbenzene	1,3-(CH3)2-5-C2H5C6H3	0.61	134.24				4.53		4.65	
1-Methyl-2-isopropylbenzene	2-i-C3H7C6H4CH3	0.29	134.24	-71.50	178.10	2.71	4.24	1.53	4.40	
1,4-Dimethyl-2-ethylbenzene	1,4-(CH3)2-2-C2H5C6H3	0.70	134.24				4.53		4.65	
1,2-Dimethyl-4-ethylbenzene	1,2-(CH3)2-4-C2H5C6H3	0.77	134.24				4.53		4.65	
n-Undecane	C11H24	2.32	156.24	-25.60	196.00	3.06	8.44	5.38	6.64	
1,2,3,4-Tetramethylbenzene	1,2,3,4-(CH3)4C6H2	0.75	134.22	-6.20	205.00	3.24	4.67	1.43	4.77	
Napthalene	C10H8	0.50	128.20	80.60	217.90	3.43	3.06	-0.37	3.36	
2-Methylundecane	C9H19CH(CH3)2	0.64	170.38				8.95		7.05	
n_Dodecane	C12H26	2.00	170.30	-9.60	216.30	3.80	7.52	3.72	*7.18*	
2,6-Dimethylundecane	C5H11CH(CH3)C3H6CH(CH3)2	0.71	184.41				9.46		7.46	
2-Methylnaphthalene	2-CH3C10H7	0.56	142.20	34.45	241.00	3.97	3.74	3.86	4.02	
1-Methylnaphthalene	1-CH3C10H7	0.78	142.20	-22.15	244.60	4.04	3.70	3.87	4.02	
n-Tridecane	C13H28	1.52	184.30	-5.50	235.40	3.86	9.78	5.92	7.72	
2,6-Dimethylnaphthalene	2,6-(CH3)2C10H6	0.25	156.20	107.85			4.89		4.31	
n-Tetradecane	C14H30	0.73	198.30	5.90	253.70	4.23	7.95	3.72	8.38	

Explanatory Notes:

1. Experimental data used where available. Sources:[19][20][21]
2. Underlined figures are estimated values. Estimation methods are detailed in Appendix B.

Table 3.1: Major Components of one JP-4 Sample - Chemical Properties

volatile constituents favour a vapour phase. Compounds which will dissolve easily in water will tend to migrate faster from the source area, and hence the compounds which present the most likely hazard to downgradient water supply wells are the aromatics, in this case benzene, toluene, ethylbenzene and xylene (BTEX).

Table 3.1 gives estimated values for the chemical properties of each of the major constituents. From this we can see that the least retarded constituents (lowest octanol-water partition coefficients) while be Isobutane and then Benzene. Isobutane is a gas at ambient temperature, and so we can assume that any present will vaporize as soon as the AVGAS is released. Hence it is benzene which will migrate furthest from the source, due to it's relatively high solubility in water. Other relatively mobile constituents are toluene (K_{ow}=2.69), ethylbenzene (K_{ow}=3.15) and the xylenes(K_{ow}=3.13 to 3.20).

Any tetraethyl lead present in the AVGAS will be highly immobile since it sorps strongly to soil. Any lead that has been solubilized is expected to be predominantly in the lead (II) species.

The degradation rates will also vary between the constituents of AVGAS, depending on their chemical structure. For hydrocarbons in groundwater, the primary mechanism of degradation will be by microorganisms. Estimates of degradation rates are not available for all the constituents of AVGAS. However, Table 3.2 gives a range of estimates for several of the constituents. It can be seen that the aromatics exhibit a wide range of biodegradation rates, with benzene tending to be the least rapidly degraded. Tetraethyl lead is rapidly degraded. Information on the growth rate of bacterial species can lead us to a qualitative understanding of the biodegradation rates of other constituents. The shorter-chained alkanes (up to C_8) are utilized by relatively few bacterial species and so will tend not to be biodegraded. Conversely, utilization of long-chained alkanes is widespread among microorganisms, and n-alkanes with 10-18 carbons are utilized with the greatest frequency and rapidity. Hence biodegradation rates of these compounds will tend to be high[9]. The cyclic alkanes are also subject

Compound	*Estimated Half Life[12]* $t_{\frac{1}{2}}$ *(days)*		*Biodegradation Rate* k *(day^{-1})*	
	Low	*High*	*Fast*	*Slow*
Benzene	10	730	0.070	0.001
Toluene	7	28	0.099	0.025
Ethylbenzene	6	228	0.116	0.003
Xylenes	14	365	0.050	0.002
Tetraethyl lead	14	56	0.050	0.012
Cyclohexane	56	365	0.012	0.002

Table 3.2: Estimated Degradation Rates of Selected AVGAS Constituents

to biodegradation. The most persistent compounds will be those that are least susceptible to biodegradation. This assessment of the relative biodegradability of the constituents of AVGAS leads to the conclusion that the most persistent compounds will be benzene, and the short-chained alkanes. The short-chained alkanes, however, are not considered as great a threat to downgradient water supplies since they are much less soluble, and hence less mobile.

Hence we can conclude that the constituent of AVGAS that is of most concern will be benzene, due to its high solubility and relatively low susceptibility to biodegradation.

3.2 Observed distributions

The most extensive field investigation of FS-1 was undertaken during the Remedial Investigation[7]. Both the residual contamination in the soil near the source, and the groundwater contamination at the source and downgradient were investigated. Summaries of the results, along with an interpretive groundwater contamination profile from the Groundwater Remediation Strategy Report[2], are included in Appendix A.

The results indicate that there is residual fuel-related contamination of the soil at both turnarounds, although a different set of compounds was found at each source area. The soils beneath the Western Aircraft Turnaround exhibit greater residual contamination with lead, tetraethyl lead, and total petroleum hydrocarbons being detected in deep soils just above the water table. At the Eastern Aircraft Turnaround several tentatively identified (that is, non-regulated and therefore not specifically tested for) alkane isomers commonly related with fuel products were detected in the soil just below the water table. The compounds detected included methylated isomers of octane, hexane, cyclohexane, and pentane, and heptane. Except in these deep soils, there was no evidence of residual contamination due to AVGAS in the unsaturated sands.

Fuel-related compounds were detected in groundwater samples from both source areas, though to a much lesser extent at the Eastern Aircraft Turnaround. Toluene and xylene were detected up to 200ft downgradient of the Western Aircraft Turnaround, and benzene was detected in one monitoring well, 500ft downgradient. The detection of lead, fuel-related tentatively identified compounds (including methylated isomers of butane, pentane, hexane, heptane, octane, cyclohexane, and cyclopentane), and low dissolved oxygen levels indicating biodegradation has taken place, suggest a zone extending up to 1,800ft downgradient that has been impacted.

The Remedial Investigation concludes that the Western Aircraft Turnaround is the major source area, with significant amounts of fuel-related constituents still persisting in the capillary zone and high levels of regulated fuel-related compounds being detected in the groundwater.

Chapter 4

Migration of AVGAS from FS-1

This chapter will consider the processes which determine the fate and transport of the AVGAS released at the FS-1 Study Area. The migration of AVGAS away from the source area can be described by considering the processes occuring at three distinct stages. These are:

- contaminant present on the surface
- transport through the unsaturated zone
- transport in the saturated zone

The fate of each constituent of AVGAS in each of these stages will vary depending on the physical and chemical properties of the compound, and the characteristics of the environment it is in. The model developed by this study will quantatively assess the migration of AVGAS within the groundwater. However we must also assess the behaviour of the AVGAS prior to reaching the water table in order to predict the rate in which contaminant arrives at the water table to determine the input into this model. This assessment will also help us determine the likely composition of the contaminant which reaches the groundwater.

4.1 Source Assessment

AVGAS was released at the FS-1 Study Area as a result of testing the fuel dump valves of the aircraft being maintained at the site. During this test the valves were opened for a short time, and fuel was dumped directly onto the ground below. In assessing the probable extent of contamination from the source area it is necessary to ascertain how much fuel was dumped in this procedure, and how often aircraft were tested at this site. As previously mentioned, records of this procedure have been lost, and so we must infer this information from the interviews with personnel involved in the testing, and from known specifications of the aircraft. Each aircraft is known to have had 3 dump valves per wing, the flow rate through which was 37.5 gpm. From the interviews it was judged that approximately one aircraft was tested per day during the period testing took place at this site (1955 to 1967). Using this information, and the assumption that the valves were left open for 30 seconds (consistent with the description of the vavles being left open for a minimum amount of time), the volume of AVGAS dumped per episode is estimated as 112.5 gallons. Hence over the 12 years of testing a total of about 500,000 gallons of AVGAS was released at FS-1. This is judged to be the most logical case scenario. Other more conservative calculations yield an estimate of the total amount of AVGAS released to be up to about 1 million gallons.

4.2 Migration from the Source

Once the AVGAS has been released into the environment there are several potential migration routes the constituents may follow. Figure 4-1 summarizes these routes. It is not necessarily true that all the contaminant will follow one particular route, in fact it is likely that there will be some partitioning between the different routes. To fully quantify the exact partitioning between these routes would require a detailed model of each stage of migration. This is beyond the scope of this study. However we can qualitatively determine the likely partitioning by considering the physical properties

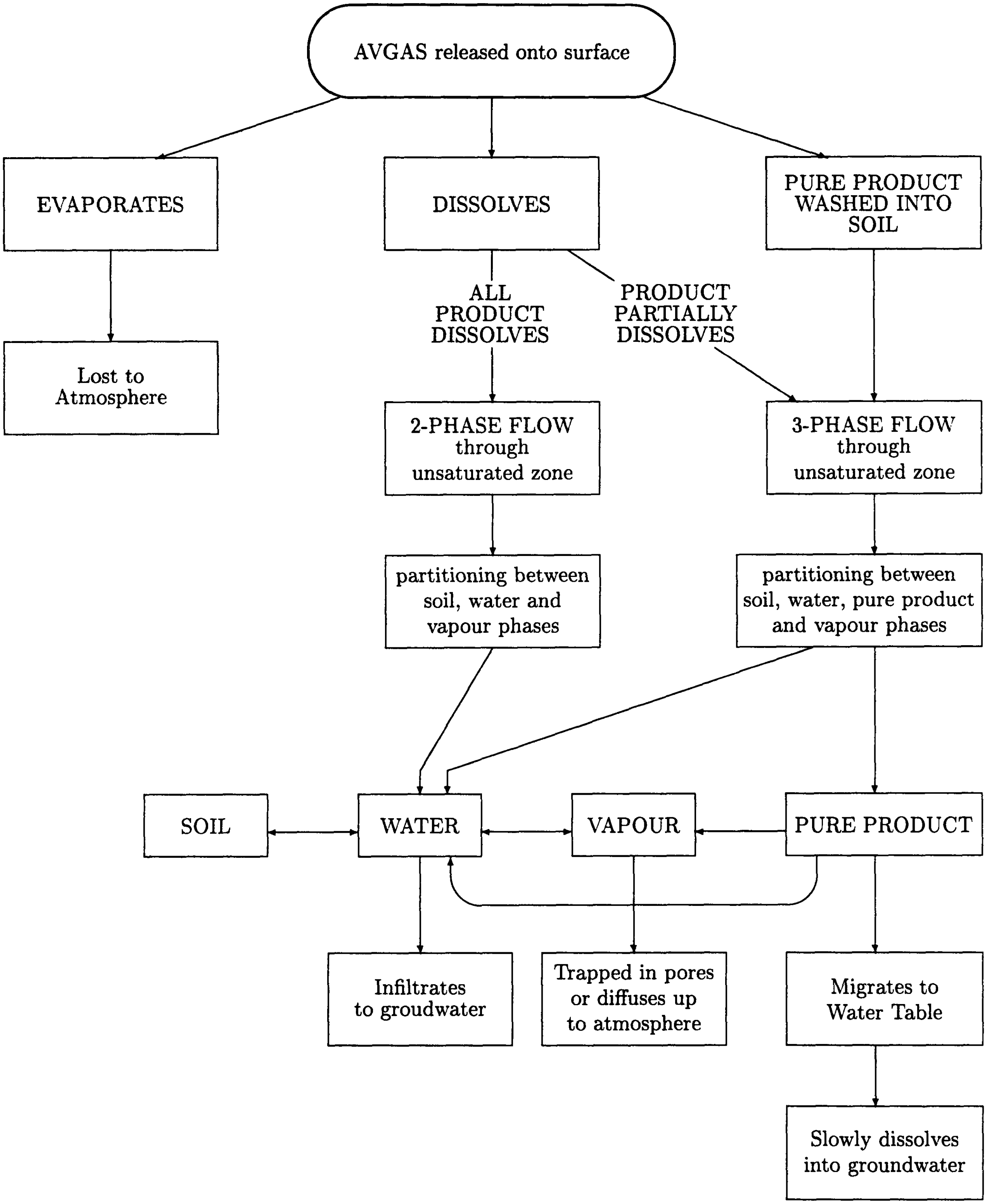


Figure 4-1: **Potential Routes of Migration of the Contaminant**
On release into the environment there are several potential routes the constituents of AVGAS may follow. Partitioning between these routes will depend on the chemical properties of the constituents.

of the various constituents.

4.2.1 Contaminant Present on the Surface

AVGAS released during the testing would probably have landed on the asphalt of the aircraft turnarounds. This is a reasonable assumption given the size of the turnarounds, and also the presence of the firefighters, whose task was to prevent the fuel evaporating by washing it away from the testing area. If the AVGAS had fallen onto the dirt surrounding the turnarounds this task would have been unnecessary since infiltration into the soil would prevent significant evaporation. If the AVGAS did fall onto asphalt, there would have been no immediate infiltration, and hence the potential for rapid evaporation is high. In fact if the released AVGAS had been left undisturbed on the asphalt, it would only take in the order of an hour for the entire slick to evaporate (see calculation in Appendix C). This was not the case, however, since firefighters were on hand specifically to prevent this occuring.

Water added by the firefighters would have had the dual effect of dissolving a portion of the AVGAS , whilst washing the remaining pure product towards the soil. The process is also likely to induce some increased evaporation since it will increase the surface area of the contaminant (both dissolved and pure product) and the relative wind speed to this surface. Hence there will be an initial partitioning between contaminant which evaporates, and thus escapes to the atmosphere, contaminant which is dissolved, and pure product which is washed into the soil along with the water. This partitioning will depend on the physical properties of the constituents, given in Table 3.1. The highly volatile constituents, such as butane and isobutane which are gases at atmospheric temperatures, are likely to evaporate more rapidly than they would dissolve, and hence will not migrate to the groundwater. The detection of dimethylbutane (one of the more volatile constituents) in the groundwater suggests that the application of water was successful in it's attempt to limit the occurrence of evaporation, and in fact most of the constituents will have been washed into the soils before significant evaporation could take place. Thus we conclude that the loss of contaminant due to evaporation from the surface is a relatively small effect.

The partitioning between contaminant that dissolves and that which remains as pure product will depend on the solubilities of each of the constituents. The more soluble constituents, such as the aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylene), will tend to dissolve readily, whereas the less soluble constituents, such as the longer chained alkanes (octane, nonane etc.) may remain as pure product. The fraction of AVGAS which dissolves will depend on the quantity of water added by the firefighters. Unfortunately the exact procedure followed by the firefighters during the testing is not known. A possible scenario is that four hoses were used to wash down the area for a period of 10 minutes during and after the time when the dump valves were open. This would result in a total of 10,000 gallons being added to the area (see calculation in Appendix C). This would dissolve approximately 3.6% of the spilt AVGAS. The more soluble constituents would be preferentially dissolved.

Contaminant entering the unsaturated zone is thus likely to be both pure product and in an aqueous solution. The majority of the contaminant will exist as pure product, consisting of the less soluble constituents such as the longer-chained alkanes and cyclic alkanes. The dissolved fraction of the contaminant will primarily consist of the aromatic hydrocarbons and the short-chained alkanes.

4.2.2 Migration through the Unsaturated Zone

As the contaminant migrates through the unsaturated zone there is a continuous exchange of contaminant between the different possible phases as shown in Figure 4-1. Pure product may dissolve or evaporate. Dissolved contaminant may evaporate or undergo adsorption. Contaminant that has evaporated and is thus existing in a vapour phase may redissolve, and finally contaminant that has become sorped to the soil particles may desorp as water continues to flush past. The movement of the contaminant through this zone is thus a three-phase problem, with pure product, and contaminated water and air all free to migrate. To quantify this process a model would not only have to consider the relative motions of each of these three phases, but also the partitioning kinetics. A frequent assumption is that an equilibrium partitioning between each of these phases is reached within a much shorter timescale than the migration process. Hence the fraction of the contaminant present in each phase would remain relatively constant.

The presence of pure product will have the effect of increasing the time it takes for contaminant, both in aqueous and non-aqueous phases, to reach the water table. In this three-phase flow, water is the wetting fluid, AVGAS is the non-wetting fluid with respect to water, but the wetting fluid with respect to air, and air is the non-wetting fluid. As they move the three phases will interfere with one another thus inhibiting flow to a certain degree. The relative permeability of the soil matrix, and hence the velocity of flow, will depend on the relative saturations of each phase. Flow of aqueous or non-aqueous phase liquid will only occur once the residual saturation has been exceeded.

As the contaminant travels downwards through the unsaturated zone, sorption to the soil particles will occur. This partitioning will depend on the properties of the constituent considered. Constituents with a high octanol-water partitioning coefficient (K_{ow}) will tend to sorp more readily onto the soil particles. Table 3.1 gives values of K_{ow} for each of the constituents. This sorption has the effect of retarding the rate of transport of contaminant down to the water table. This process will also reduce the rate at which contaminant is added to the groundwater, since the sorption reduces the concentration in the infiltrating water. Sorption is noncompetitive[6], with many nonpolar chemicals able to partition between water and the available volume of natural organic matter at the same time without interfering with each other. However, the soil underlying the FS-1 source area has been found to have a very low organic carbon content ($f_{oc} = 0.0001$), and hence it is likely that there is a limit to the amount of contaminant that can sorp onto this soil. The source at FS-1 is continuous over a long period of time, and hence a state may be reached where no further sorption is possible. In this case, the dissolved contaminant will migrate through the unsaturated zone unretarded. After testing has ceased contaminant will undergo desorption from the soil as uncontaminated rainwater seeps through this zone. Also, the recharge due to precipitation will mobilize the residual pure product present in the soil pores. This is consistent with the lack of detection of hydrocarbons in the soils of much of the unsaturated zone, which indicates that there is no longer any AVGAS sorped onto these soil particles. These two processes will have caused a continuing source after the testing ceased.

Contaminant will also be removed from the infiltrating water and pure product via the process of evaporation. Contaminant existing in the vapour phase may get trapped between the soil particles, however, it's eventual fate will be to escape upwards to the atmosphere. Following the same reasoning described in the consideration of evaporation from the surface, we can conclude that the amount of contaminant lost by this process is likely to be relatively small.

On reaching the water table, contaminant that is in the aqueous phase will enter the groundwater directly, whereas the pure product will form a layer of floating non-aqueous phase liquid in the capillary fringe. This floating product may then be dissolved into the groundwater beneath it, acting as a secondary source of contamination. It will result in a slower addition of contaminant to the groundwater than if the contaminant were already in the aqueous phase when it reached the water table. As previously discussed the fraction of contaminant arriving at the water table in the aqueous phase is likely to consist of the most soluble constituents of AVGAS such as the aromatics, whereas the pure product will consist of the less soluble constituents. Hence the more soluble constituents will contaminate the groundwater immediately, whilst there is a delay before the groundwater becomes contaminated by the less soluble constituents.

Hence the dominant migration pathway of the constituents of AVGAS from FS-1 is as a non-aqueous phase liquid seeping downwards through the unsaturated zone, forming layer of floating product in the capillary fringe, and subsequently dissolving into the groundwater. Of more concern, however, is the fraction of contaminant that was dissolved on the surface and hence reached the water table as an aqueous solution. This fraction will contaminate the groundwater directly and so will have had longer to migrate from the source area. After testing ceased, contaminant that had sorped onto the soil particles of this zone will desorp as clean rainwater infiltrates, and provide a continuing source. The continuing source will also be contributed to by residual contamination being flushed out of the pores by recharge.

4.2.3 Migration in the Saturated Zone

Once the contaminant is dissolved within the groundwater it will migrate as dictated by the flow field at the point of injection. At the FS-1 Study Area the direction of groundwater flow is from north to south, and so contaminant will migrate in a southerly direction. Recharge due to precipitation will induce a slight downwards drift of the contaminant plume with distance from the source. As in the unsaturated zone, there will be some partitioning of contaminant between the groundwater and the soil particles. Again, this sorption will cause the migration of AVGAS to be retarded, and so reduce the current extent of contamination.

Biodegradation of the contaminant may occur at any of the stages of migration of AVGAS after its release into the atmosphere. The rate of biodegradation will vary for each constituent, and will depend on that constituent's chemical structure. It will also depend on the amount of oxygen available to support the process. This can often be a limiting factor of biodegradation within groundwater. For example, Chiang et al.[5] found that if the dissolved oxygen level drops below about 2 mg, aerobic biodegradation of BTEX will cease. Field results show, however, that in this aquifer the average dissolved oxygen level is well above this limiting value. Oxygen deficiency will only become a limiting factor in areas where significant biodegradation has occurred, consuming the dissolved oxygen, as was found at the FS-1 source area. Biodegradation will have the effect of reducing the total volume of contaminant present in the aquifer at the current time.

The dissolved oxygen level is also a good indicator of whether biodegradation has occurred in particular part of the aquifer. The process of biodegradation consumes oxygen, and hence if the DO level is found to be below the average level detected in the aquifer, it can be inferred that biodegradation has occurred there. Chiang et al.[5] found there to be an inverse correlation between contaminant concentration and biodegradation. A similar inverse correlation was found within the plume emanating from FS-1. Hence we can infer that biodegradation has been occuring to some extent.

4.3 Summary

The above discussion qualitatively describes the likely migration routes of AVGAS after release at the FS-1 Study Area. It is thought that loss of contaminant by evaporation both from the surface and whilst migrating through the unsaturated zone will be a relatively small effect. Contaminant is likely to enter the unsaturated zone both as pure product and as an aqueous solution, with both migrating downwards to the water table. Sorption will act to retard the migration through the unsaturated zone. Pure product reaching the water table will form a floating layer and will subsequently be either biodegraded by microorganisms or slowly dissolved by the moving groundwater. Contaminant that has migrated down through the unsaturated zone in the aqueous phase will enter the groundwater directly, and will hence have longer to migrate downgradient and so is of more concern when considering the safety of the downgradient monitoring wells. After testing has ceased, desorption from the soil particles in the unsaturated zone and mobilization of residual contamination will act as a continuing source. Migration away from the source area will follow the groundwater flow field, with the contaminant undergoing sorption and biodegradation.

Figure 4-2 shows the dominant migration pathways from the initial release of AVGAS onto the surface. The initial partitioning of AVGAS is between dissolved and pure product, both of which enter the soil. This partitioning will depend on the amount of water added by the firefighters. The flow through the unsaturated zone is then a three-phase flow with continuous exchange of contaminant between soil, water, pure product and vapour. Contaminant will reach the water table in two ways: either as an aqueous solution, which enters the groundwater directly, or as pure product which slowly dissolves into the groundwater.

The greatest hazard to downgradient water supplies is presented by the constituents which migrate through the unsaturated zone in an aqueous solution,and therefore enter the groundwater directly. These will be the more soluble constituents. As we saw in Chapter 3, the most soluble constituent that is not a gas at atmospheric temperature (and therefore is not lost by evaporation) is benzene. Consideration of the extent of the benzene plume will thus reveal the furthest extent of contaminant from the source area. The most likely migration pathway of benzene is shown by the bold lines on Figure 4-2. It is thought that all the benzene in the AVGAS is completely dissolved at the surface due to its high solubility. Thus it enters the soil as an aqueous solution. Uncertainties arise at every stage of its migration. However, the uncertainty in its migration once it reaches the groundwater can be reduced to three factors: the strength and duration of the source of benzene at the water table, which will be determined by its migration through the unsaturated zone; the rate at which biodegradation occurs; and the amount by which it undergoes sorption out of the groundwater. These three factors will determine the extent of the benzene plume.

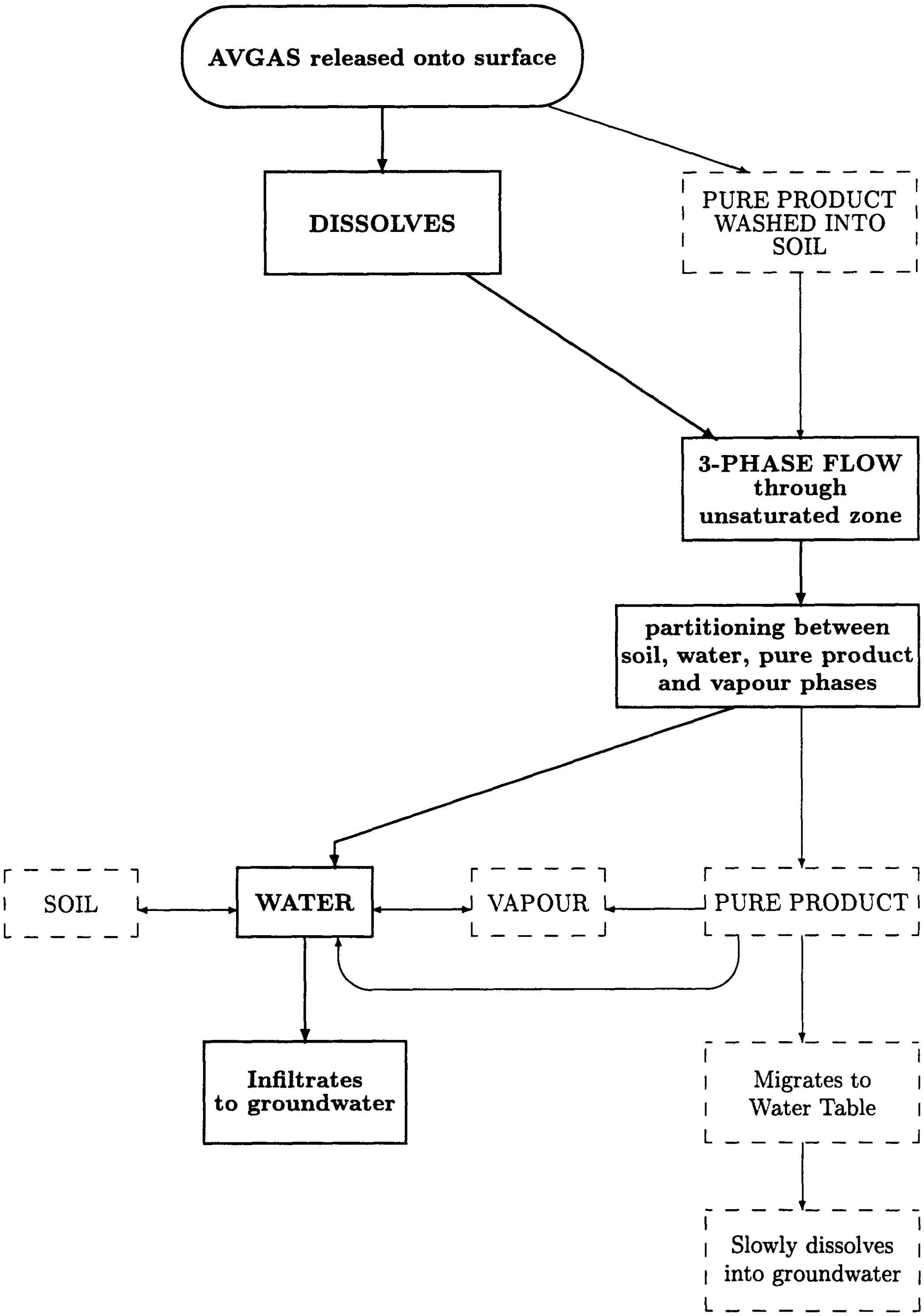


Figure 4-2: **Dominant migration pathways of AVGAS from FS-1**
Consideration of the testing procedures, chemical properties of AVGAS constituents, and processes occurring at each stage on migration lead to the conclusion that some migration pathways are more important than others. Likely migration pathway for benzene is shown in bold face.

Chapter 5

Numerical Models

The governing equations of groundwater flow, and of contaminant transport are formulated by considering the conservation of mass, along with constitutive relationships such a Darcy's and Fick's laws. The classical groundwater flow equation may be written as

$$S_s \frac{\partial h}{\partial t} = \frac{\partial}{\partial X_i}\left[K_{ij}\frac{\partial h}{\partial X_j}\right] + f(X_i, t) \tag{5.1}$$

where the piezometric head, h, is the dependent variable, and the specific storage S and hydraulic conductivity tensor K are coefficients which describe the aquifer's capacity to store and conduct water. The function $f(X_i, t)$ accounts for point singularities, such as pumping from a well.

Contaminant transport can be described by the Advection-Dispersion-Reaction (ADR) Equation, which can be written as

$$\frac{\partial C}{\partial t} + v_i \frac{\partial C}{\partial X_i} = \frac{\partial}{\partial X_i}\left[\alpha_{ij} v \frac{\partial C}{\partial X_j}\right] + r \tag{5.2}$$

where r is taken symbolically as the mass produced (or consumed) per unit volume of water per unit time, C is the solute concentration, α is the dispersivity coefficient, and v is the local flow velocity. If the only processes contributing to the production term, r, are sorption and biodegradation, and if we model biodegradation by a first-order model, this equation becomes

$$\frac{\partial C}{\partial t} + \frac{v_i}{R}\frac{\partial C}{\partial X_i} = \frac{\partial}{\partial X_i}\left[\alpha_{ij}\frac{v}{R}\frac{\partial C}{\partial X_j}\right] - \frac{kC}{R} \tag{5.3}$$

where R is the retardation factor due to sorption, and k is the first-order decay coefficient.

For some simple scenarios these equations can be solved analytically, however most situations are too complex to take this approach, and we must look to a numerical solution. The general motivation behind a model is to approximated the continuous solution of a given differential equation by solving algebraic equations for a finite number of discrete values of the solution. The basic idea underlying most groundwater models is to split the region under consideration into a finite number of discrete sub-regions (elements) and write local equations for flux in terms of the dependent variable (head for groundwater flow, and conconcentration for contaminant transport) at selected points (nodes) on the boundary of the element by making some assumptions about the variation of the variable across the element. One of two methods can be used to formulate these local equations, either a Finite Difference method, or a Finite Element method. These local equations can then be solve simultaneously to yield values of the dependent variable at each node. This process can be repeated for each timestep in a transient problem. The inputs to this type of model will be the boundary conditions, the parameters of the governing equations and some "initial guess" of the distribution of the dependent variable.

5.1 Dynflow, Dyntrack and Dynplot

This study uses the DYN modelling system to develop a model of the contaminant transport from the FS-1 source area. This system consists of three components, Dynflow, Dyntrack and Dynplot. Dynflow is a three-dimensional flow code based on the governing equations of flow in a porous media, Dyntrack provides a simulation of three-dimensional contaminant transport driven by the flow field generated by

Dynflow, and Dynplot is an interactive visualization tool used in both model creation and to view the results generated by Dynflow and Dynplot.

Dynflow uses the finite element method to solve the groundwater flow equations. This method is seen to be preferable to the finite difference method since the element geometry is more flexible and hence it enables us to cope with irregular boundary geometries. However, this method can prove to be more complicated to apply, and requires more sophisticated grid generation capacity.

Dyntrack does not solve the governing equations of contaminant transport directly, but rather utilizes the "Random Walk" method, which follows discrete amounts of contaminant mass as they move through the aquifer. This Lagrangian method considers a statistically significant number of particles injected into the groundwater, each with an associated weight, decay rate, and retardation rate. At each timestep the translation of a particle has two components. The first component is deterministic, and simulates the advection of the particle as driven by the groundwater flow field. If the particle is retarded, this factor is included into the deterministic translation. The second component is probabilistic, and simulates the dispersion of the particles. The weight of the particle is also decreased over the timestep if biodegradation is occurring. The weight of the particle at the end of the timestep is given by

$$W_{(t+\delta t)} = W_t exp(-k\delta t) \tag{5.4}$$

where δt is the length of the timestep. The probability density function for the location of a particle yields the concentration distribution. At any time, the concentration in a given element can be calculated by summing the mass of all the particles in that element and dividing by the volume of the element.

The advantages of using this particle tracking method over the more traditional Eulerian methods are that the solution is stable, there is no numerical dispersion, and no "overshoot" (negative concentrations) can occur. Above all it is often a much quicker method since there is no large system of equations to solve, and coarser discretization in space is allowed. It does, however, have two disadvantages in that it does not solve for concentrations directly, and that there are no "hard" criteria to select the number of particles used to model a particular plume. The number of particles must be selected by a trial and error method and relies upon the experience of the modeller.

5.2 Model Parameters

The success of a model depends largely on the selection of suitable values for the parameters introduced in the governing equations. These parameters vary over scales smaller than those considered in a typical groundwater flow problem. It is, however, impossible to fully characterize this small-scale variability of the parameters and hence we use regionalised effective parameters[17]. This method accounts for large-scale spatial variations by separating the region under consideration into smaller regions of constant effective parameters which average out the effects of local variability.

Chapter 6

Model of FS-1

6.1 Conceptual Model

Prior to developing the numerical model of transport of AVGAS within the saturated zone, it is helpful to consider a conceptual model of the processes that are occuring. This section outlines the conceptual model of both the flow field and the contaminant migration, developed from the discussion of aquifer characteristics, chemicals of concern, history of the spill, and migration of the contaminant from the surface discussed in Chapters 2 through 4. In particular, it is necessary to determine the migration pathway of the constituents to be modelled, in order to quantify the source strength of these constituents at the water table.

6.1.1 Flow Field

Extensive field investigation of the western part of Cape Cod led to the interpretive water table profile presented in Figure 2-4. This study will refer to this map, rather than the original field data, in its assessment of the flow field. This is judged to be more accurate than using a small subset of the data that this map was created from. Consideration of the full data set is beyond the scope of this study.

From Figure 2-4 we see flow is predominantly north to south in the area of FS-1. The average head gradient for the region of interest is approximately 0.0025. Most contaminant transport will take pace in the layer of stratified fine to coarse sand and gravel which extends to 120ft below the ground surface. Taking the representative hydraulic conductivity for this material to be 200ft/day, and an effective porosity of 0.35, the pore velocity would be 1.43ft/day.

Flow within the aquifer is predominantly horizontal, apart from in the vicinity of surface water bodies. The surface water of interest in this particular case is the Quashnet River. This stream is primarily groundwater fed and so we would expect upward head gradients in the aquifer near the stream, producing a discharge of groundwater into the stream. Since the stream is fairly shallow, it is expected that discharge will only occur from the upper part of the aquifer, whilst the deeper groundwater underflows the stream and continues downgradient. The magnitude of the discharge from the aquifer along the length of the stream can be inferred from the plot of streamflow at various points along the stream (Figure 6-1[1]). The total discharge from the aquifer into the stream is between 11.3cfs and 15.8cfs.

6.1.2 Contaminant Migration

The fate and transport of AVGAS away from the FS-1 source area was discussed in Chapter 4. We saw that there are several potential migration pathways, and the partitioning between these is complex. It was concluded that the greatest threat to the downgradient water supplies came from the more soluble constituents of AVGAS. These will have either been dissolved on the surface by the water added by the firefighters, or will be quickly dissolved at the groundwater interface. This study will thus consider the migration of the most soluble constituent (after those which are gases at atmospheric temperature) of AVGAS, that is, benzene. Various hypotheses concerning the uncertain properties which determine the migration of the benzene, as outlined in Section 4.3, are considered. Toluene is also modelled, since several detections of toluene were made at FS-1 allowing us to fully characterize the extent of the toluene plume. This will enable us to verify the model.

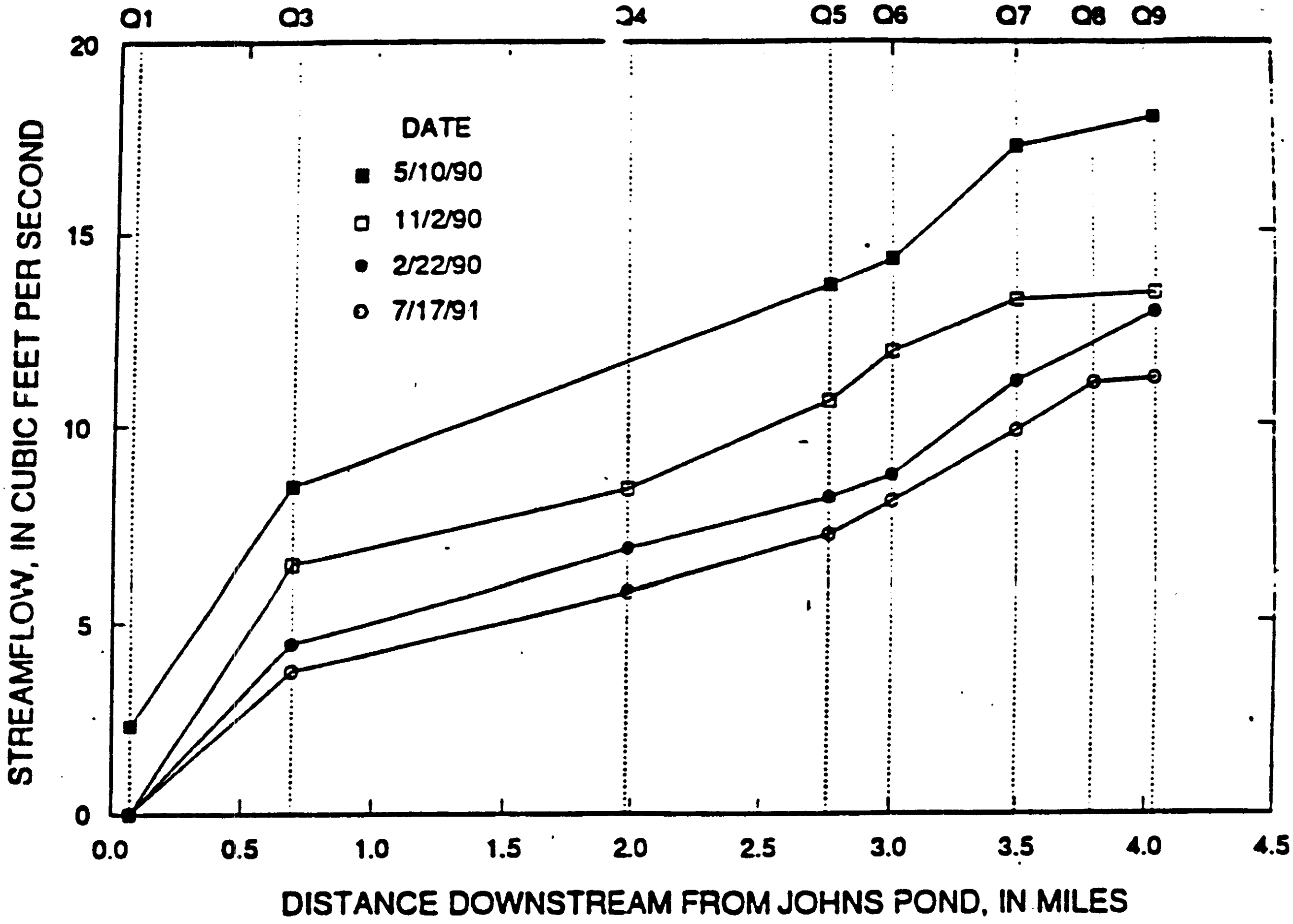


Figure 6-1: Streamflow measured at selected sites along the Quashnet River, 1990-91

The primary source area was determined in Section 3.2 to be the Western Aircraft Turnaround. The most logical case scenario for the testing procedure, described in Section 4.1, estimated that approximately 112.5 gallons were spilled at this site each day for the period between 1955 and 1957. Benzene constitutes on average 0.5% by weight of this amount, hence the mass of benzene released is 1.6kg/day. The dumped AVGAS was promptly washed off the asphalt by attendant firefighters.

As discussed in Chapter 4, contaminant will enter the unsaturated zone in both the aqueous and non-aqueous phases. It is possible that benzene will occur in both these phases. However, due to its relatively high solubility, for the purposes of this study it is assumed that the benzene is completely dissolved at the surface. The benzene will thus migrate downwards at the velocity of the infiltrating water. Since this is a three-phase flow situation, the rate of infiltration will depend on the relative saturation of each of the three phases: water, pure product, and air. Transport downwards is driven by gravity and the vertical gradient of tension head, for each phase. However, since the testing occurred continuously over a long period of time, we can conclude that these relative saturations will reach a steady state where they are constant throughout the unsaturated zone beneath the area of impact. In this case the infiltration is driven purely by gravity. Hence, vertical flux of water, q_{water} is given by

$$q_{water} = K(s_{water}) \tag{6.1}$$

The recharge rate, q, is taken as constant and is determined by the amount of water the firefighting crews used to wash the AVGAS off the turnaround. This was estimated in Section 4.2.1 to be in the region of 10,000 gallons/day. Hence the recharge rate, q, is approximately 0.059ft/day, which yields the value of $K(s_{water})$ to be 0.059ft/day also. In order to estimate the infiltration velocity of the water, we need to determine the relative saturation of water, s_{water}. One possibility is to use our calculated value for the conductivity, K, which is dependent on s_{water}, along with known relationships of conductivity versus saturation for three-phase problems. However, in this case, we know that the relative saturation of pure product to water is likely to be small, due to the respective volumes of each of these released at the surface (the volume of water entering soil is 10,000 gallons/day, whereas pure product entering the soil would be less than 112.5 gal/day). Thus as a first approximation we ignore the presence of the pure product, and consider only a two-phase situation (see Appendix C). This would imply that the relative saturation of water is 20%. Hence the infiltration velocity of the water ($q/\eta_e s$) is 0.84ft/day.

As the benzene travels through the unsaturated zone it may undergo sorption to the organic carbon in the soil particles. This would act to retard the migration of the benzene, with the apparent velocity being given by velocity/retardation factor. As discussed in Section 4.2.2, a state will be reached where no further sorption is possible. When this case has been reached, benzene will migrate at the velocity of the infiltrating water, that is, 0.84ft/day. Hence the benzene will take 60 days to reach the water table. This delay time for transport through the unsaturated zone is small compared to the total time period being considered (1955 to present day) and so can be neglected.

As previously discussed, this estimate of travel time assumed that the effect of the pure product was negligible. The effect of the pure product would be to increase the travel time. It is likely that, even if this were taken into consideration, the travel time would continue to be small compared to the total time period being considered. Hence it is not necessary to quantify this effect.

As benzene migrates to the water table, it will be biodegraded by any microorganisms present in the water. This will reduce the mass of benzene which arrives at the water table. The range of biodegradation rates of benzene found in literature are given in Chapter 3. Taking a relatively conservative biodegradation rate of $0.001 day^{-1}$, the mass loss in the unsaturated zone would be 100g/day. Hence the magnitude of the benzene source at the water table is 1500g/day.

Once the contaminant has reached the water table it is transported away from the source area by the groundwater flow in the aquifer. It is assumed to be a passive source, that is it does not alter the existing groundwater flow pattern. As it migrates, it will again undergo both sorption and biodegradation. Using the retardation factor for benzene given in Chapter 3, the apparent velocity, and hence the farthest downgradient extent of benzene can be estimated. The pore velocity of the groundwater was found in Section 6.1 to be approximately 1.43ft/day, hence the apparent velocity of the benzene is calculate as 1.35ft/day. Hence the farthest possible downgradient extent of the plume would be around 19,000ft.

6.2 Model Development

6.2.1 Discretization

In order to carry out the Finite Element analysis, we first need to generate a three-dimensional grid to define the nodes to be considered. The horizontal grid used in the numerical simulations is shown in Figure 6-2. The extent of the grid was determined by physical features which provided convenient boundaries. The vertical discretization is determined by the choice of stratigraphy. Due to the absence of any borings deep enough to capture the stratigraphy in the vicinity of FS-1, a uniform stratigraphy was assumed. This is consistent with the cross-sections of the aquifer presented in the Groundwater Remediation Strategy Report[2]. The east end of cross-section BB' (Figure 2-3) was used to determine the elevations of the five layers used. Details of the model stratigraphy can be found in Table 6.1.

6.2.2 Flow Simulation

DYNFLOW was used to simulated the flow field in the area surrounding FS-1. The aim was to reproduce observed heads measured in the aquifer, and particular to reproduce the interpretive water table profile of Figure 2-4. The results were also calibrated to the known discharges into the Quashnet River. Since the flow field

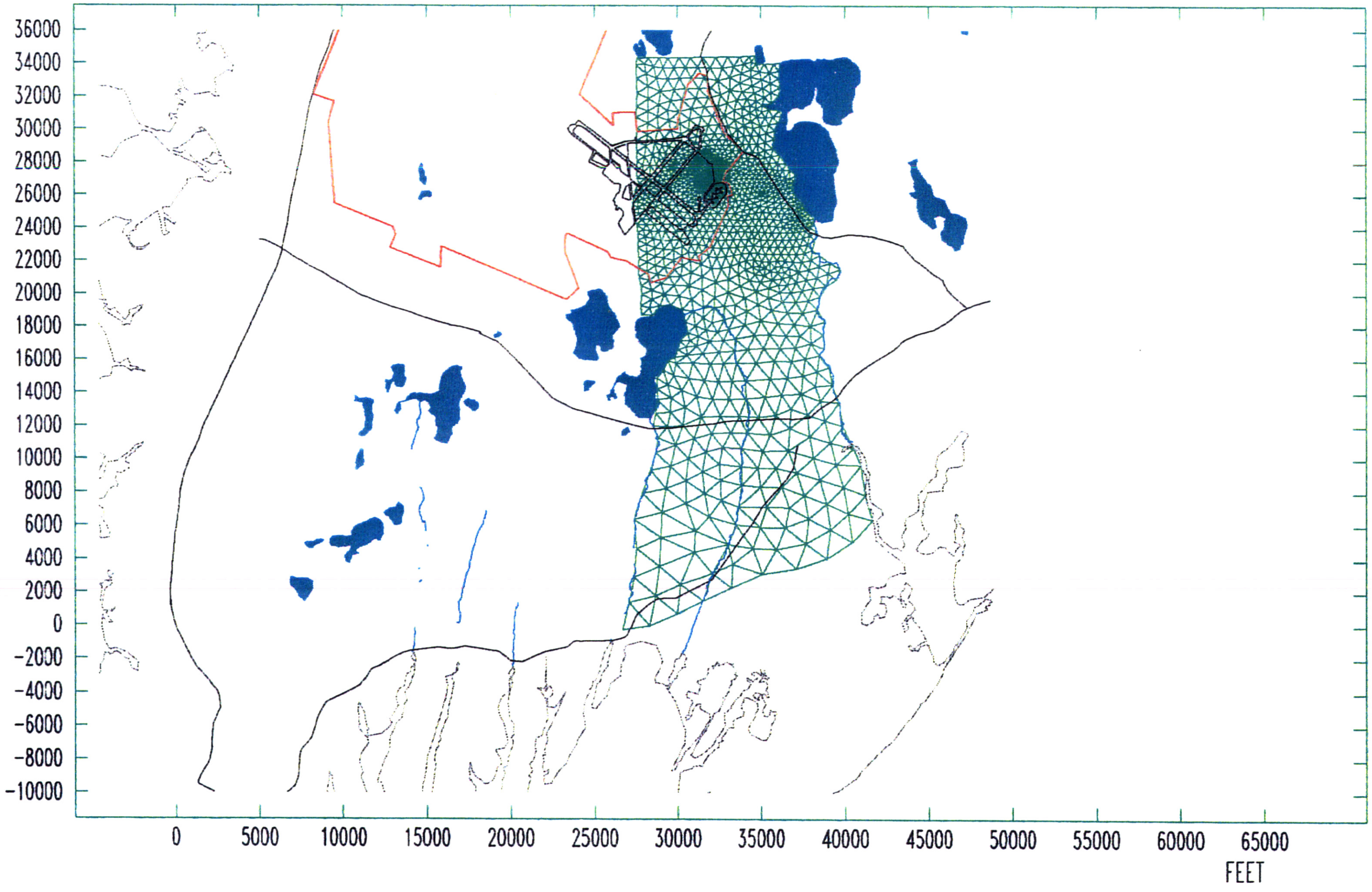


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FIGURE 6-2 : HORIZONTAL GRID USED IN DYNFLOW AND DYNTRACK

FS-1

Layer	*Elevation (ft.MSL)*	*Soil description*
Layer 1	-220 to -200	Basal Till
Layer 2	-200 to -150	Fine to Medium Sand, Trace Silt
Layer 3	-150 to -70	Find Sand with Silt (Lacustrine)
Layer 4	-70 to -10	Fine to Medium Sand, Trace Silt
Layer 5	-10 to 108.3	Stratified Fine to Coarse Sand and Gravel

Table 6.1: Model Stratigraphy

produced will be used in the simulation of contaminant transport over a long period of time, a steady state simulation was performed, that is heads are invariant with time.

Boundary Conditions

The boundary conditions for the flow simulation were fixed such that the pattern of head contours of Figure 2-4 was reproduced. The northern part of the west boundary is a no flow boundary taken perpendicular to the head contours of the interpretive map of the groundwater surface. The southern part of this boundary is taken as a fixed head defined by Johns Pond and the Childs River. The east boundary is taken as a fixed head defined by the Mashpee Pond and River. The south boundary was chosen to coincide with a head contour, and is taken as a fixed head. The nodes on the north boundary are defined as fixed heads to reproduce the pattern of head contours predicted by the Figure 2-4. In reality, neither the north, nor south boundary would truly behave as a fixed head boundary, however they are positioned far enough up and down gradient from the area of interest for this inaccuracy to not be apparent.

The Quashnet River, which flows initially east out of Johns Pond, and then south, also imposes a boundary on the flow field. It is included in the model as a fixed head boundary, with the heads being determined from the USGS topographic map of the area.

Layer	*Groundwater Flow Properties*				*Transport Properties*		
	K_x ft/day	K_y ft/day	K_z ft/day	η_e	α_L ft	α_T ft	a
1	1	1	0.2	0.35	3.15	0.06	0.1
2	150	150	30	0.35	3.15	0.06	0.1
3	3	3	0.6	0.35	3.15	0.06	0.1
4	150	150	30	0.35	3.15	0.06	0.1
5	200	200	40	0.35	3.15	0.06	0.1

Table 6.2: Flow and Transport Properties

Input Parameters

The parameters required by DYNFLOW in the flow simulation are the hydraulic conductivities in each direction for each layer, the effective porosity of the material, and the recharge due to precipitation. The specific storage is not required since we desire a steady state solution. Due to the limited amount of field data, values of hydraulic conductivity typical to the region were used. These values will then be verified in the calibration part of model development. All the layers were assumed to be isotropic in the horizontal direction, and a vertical anisotropy ratio of 1:5 was used.

The parameters used for each layer of the model are detailed in Table 6.2, where K_x, K_y, and K_z, are the hydraulic conductivity in the two horizontal directions and the vertical direction, and η_e is the effective porosity. A constant recharge of 0.0046ft/day was used, consistent with the climate of the region.

Calibration

The flow model was calibrated in two ways. First, boundary conditions were adjusted such that the water table profile of the model coincided with that predicted by the interpretive map. Secondly, the discharge from the aquifer into the Quashnet River was checked against the field data of stream discharge with distance from the streams head at Johns Pond. This second method of calibration will verify both the choice of hydraulic conductivity for the most superficial layer, and also the fixed heads

Distance Downstream From Johns Pond (miles)	*Measured Increase in Discharge (cfs)*				*Model Predicted Increase in Discharge (cfs)*
	5/10/90	11/2/90	2/22/90	7/17/91	
0.1 to 0.7	6.2	6.6	4.3	3.6	4.38
0.7 to 2.8	5.4	4.3	3.8	3.6	6.63
2.8 to 3.0	0.7	1.2	0.7	0.8	1.16
3.0 to 3.5	2.8	1.4	2.4	2.0	0.95

Table 6.3: Measured and Model Predicted Discharge into the Quashnet River with Distance Downstream from Johns Pond

at the river.

Results

The piezometric head contours produced are shown in Figure 6-3. A good match with the interpretive water table contours of Figure 2-4 was obtained. The head distribution produced is uniform with depth of the aquifer, except in the vicinity of the Quashnet River, as seen in Figure 6-4. The total discharge into the Quashnet River predicted by the model is 13.1cfs. This is within the range of that inferred from the field data. The comparison of the discharge into the river predicted by the model to that measured in the four rounds of field investigations is detailed in Table 6.3. Here it becomes apparent that the model does not accurately reproduce the measured discharge into the stream when we consider it section by section. However it should be noted that calculation of the model predicted discharge is highly dependent on the node positions, and so the margin of error in these quantities is considered to be acceptable.

6.2.3 Contaminant Transport Simulation

Model Inputs

As discussed in the conceptual model, the contaminant transport model will initially be run for toluene, adopting a most logical case scenario. The model will then

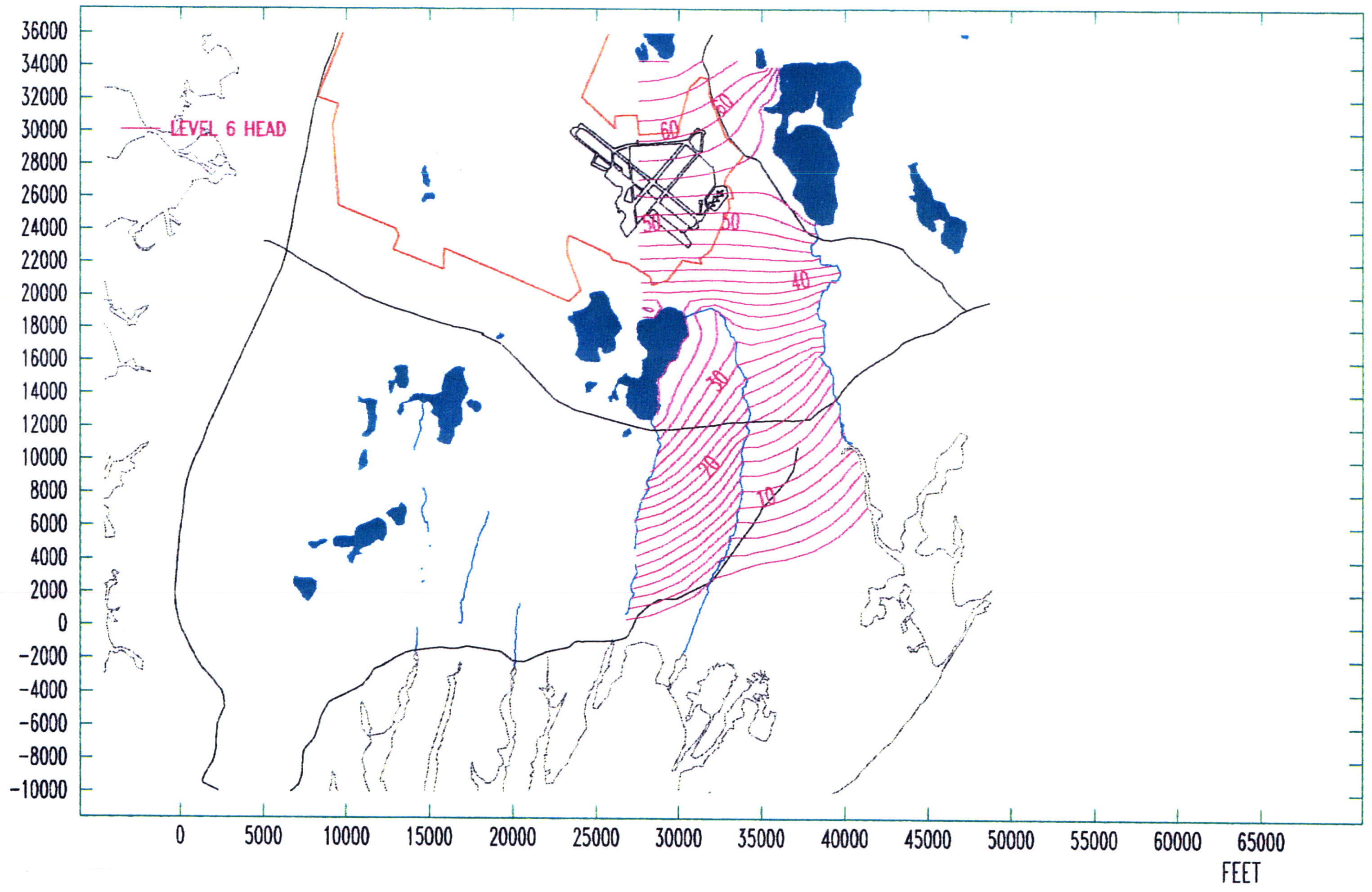

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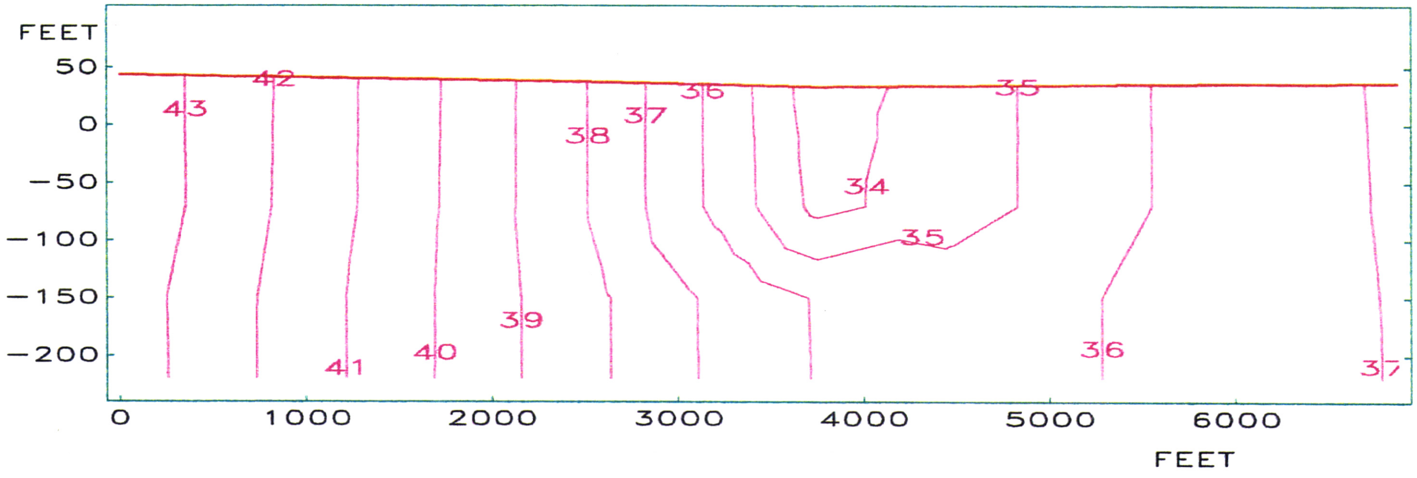
FIGURE 6-3 : PIEZOMETRIC HEAD CONTOURS PRODUCED BY DYNFLOW

FS-1



— HEAD

CROSS SECTION AA

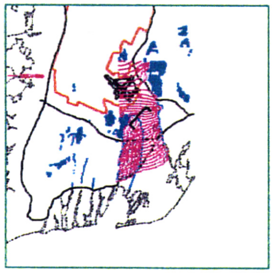


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FIGURE 6−4 : EFFECT OF QUASHNET RIVER ON PIEZOMETRIC HEAD

FS−1

RUN	*Compound*	*Source Strength g/day*	*Continuing Source Decay Rate* day^{-1}	*Retardation Factor*	*Biodegradation Rate* day^{-1}
1	Toluene	973	NONE	1.16	0.025
2	Benzene	1500	NONE	1.06	0.001
3	Benzene	1000	4×10^{-3}	1.06	0.001
4	Benzene	1600	NONE	1.06	0
5	Benzene	1185	NONE	1.06	0.005
6	Benzene	1500	NONE	1	0.001

Table 6.4: Inputs to Contaminant Transport Model

be run for benzene for various scenarios, in order to investigate some of the factors over which there is uncertainty.

The model requires various input parameters, relating to both the transport properties of the aquifer, and of the compound in question. These parameters are: dispersion in the longitudinal and transverse directions (α_L and α_T), and an estimate of the vertical anisotropy ratio (a); source strength; decay rate of any continuing source; biodegradation rate of the compound; and retardation factor for the compound. The parameters relating to the transport properties of the aquifer are given in Table 6.2. These values for dispersivities are those obtained from the large scale field experiment conducted in this aquifer[14], and are so the uncertainty associated with this parameter is low. Table 6.4 details the inputs used for the various runs of the model.

Results

Figure 6-5 shows the model results for toluene. The plume is predicted to extend approximately 300ft downgradient. The results show that the plume is confined near to the source area. This is due to the high degree of sorption and biodegradation that toluene is believed to undergo.

Figures 6-6 through 6-10 show the results for the various scenarios considered for benzene. The results are shown in plan view, with the shaded contours indicating the concentration at the water table, and the open contours indicating the concentrations at level 5 (approximately 70ft below the water table). These results will be discussed in more detail in Chapter 7. Run 2 was considered the most logical case scenario, with retardation of the benzene, moderate biodegradation and no continuing source. The results from run 6, which considered the case of no biodegradation, also indicates the direction any detatched undegraded "slugs" of benzene may have migrated.

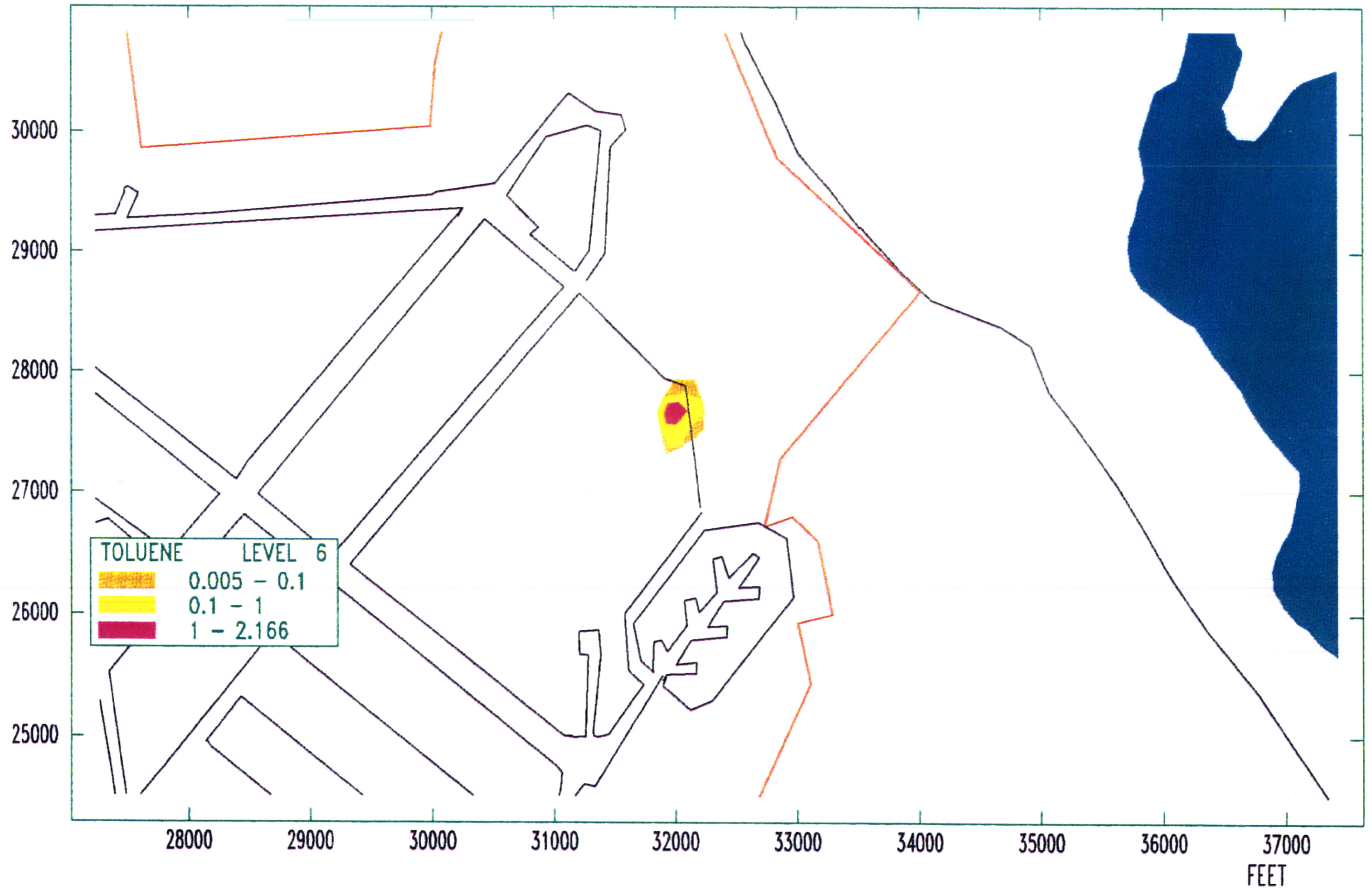

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FIGURE 6–5 : MODEL PREDICTED TOLUENE PLUME IN 1994

FS–1

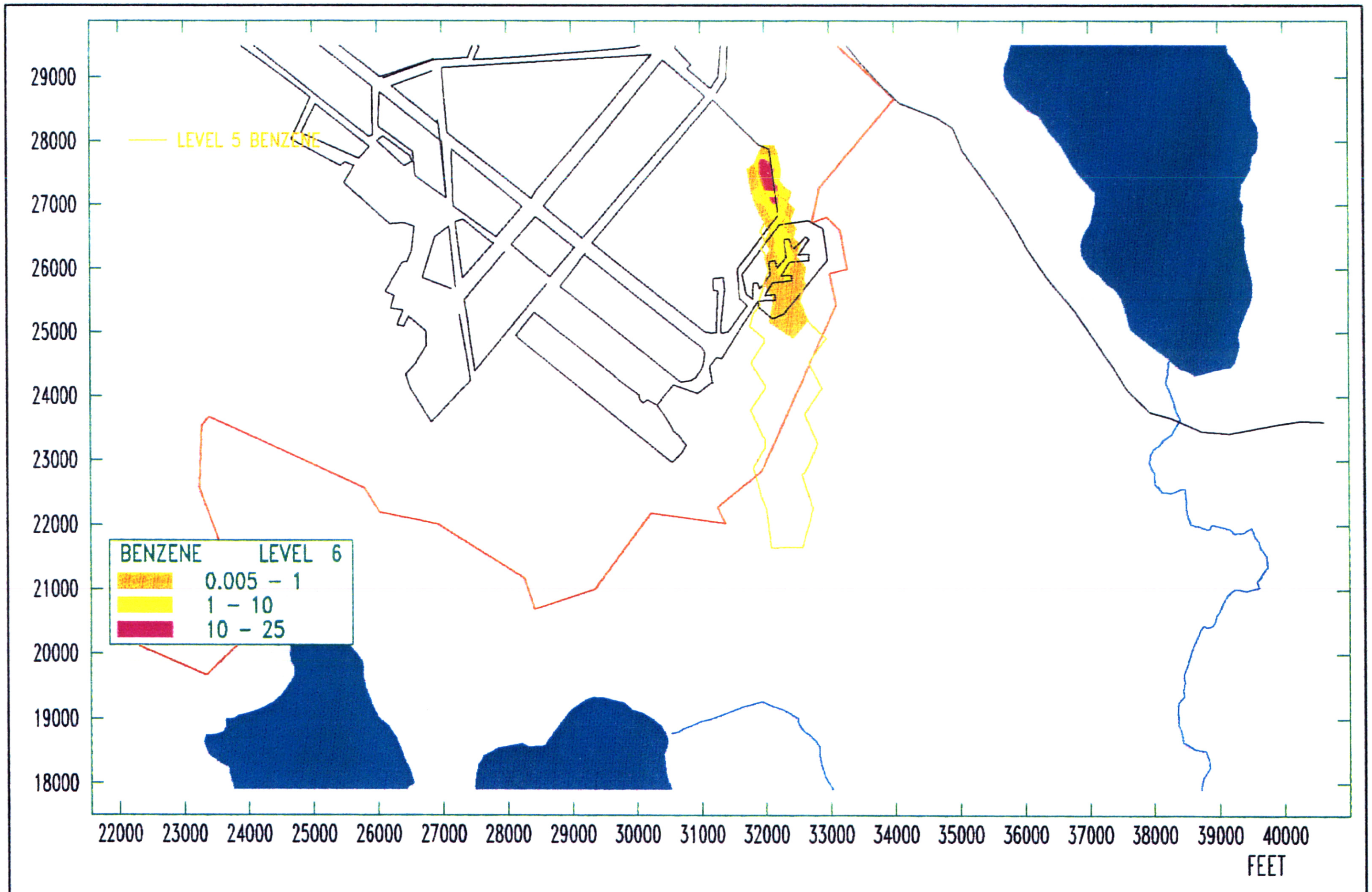

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FIGURE 6–6 : MODEL PREDICTED BENZENE PLUME – RUN 2
Biodegradation Rate = 0.001; Retardation Factor = 1.06; no continuing source

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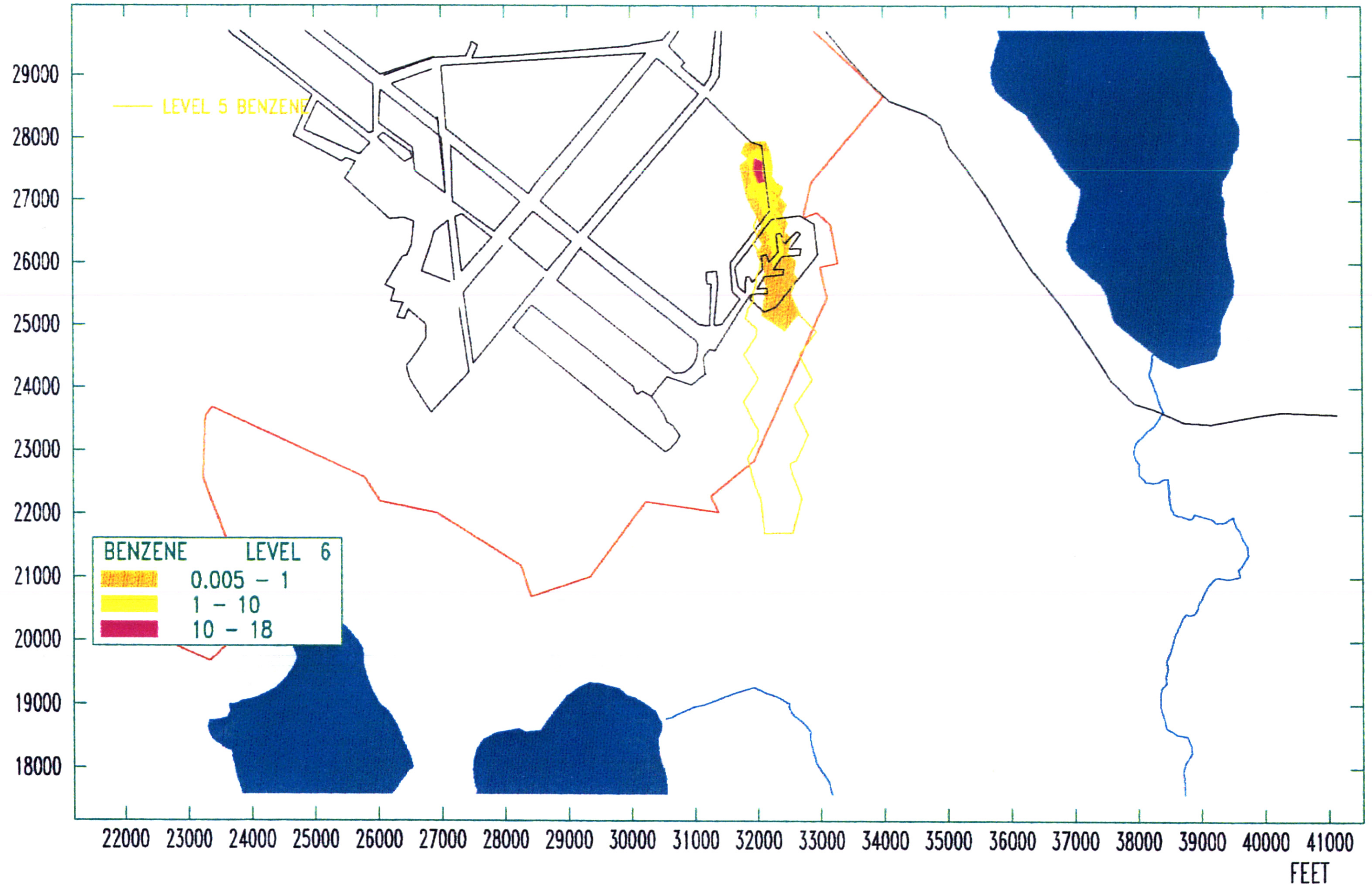

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FIGURE 6-7 : MODEL PREDICTED BENZENE PLUME – RUN 3
Biodegradation Rate = 0.001; Retardation Factor = 1.06; continuing source

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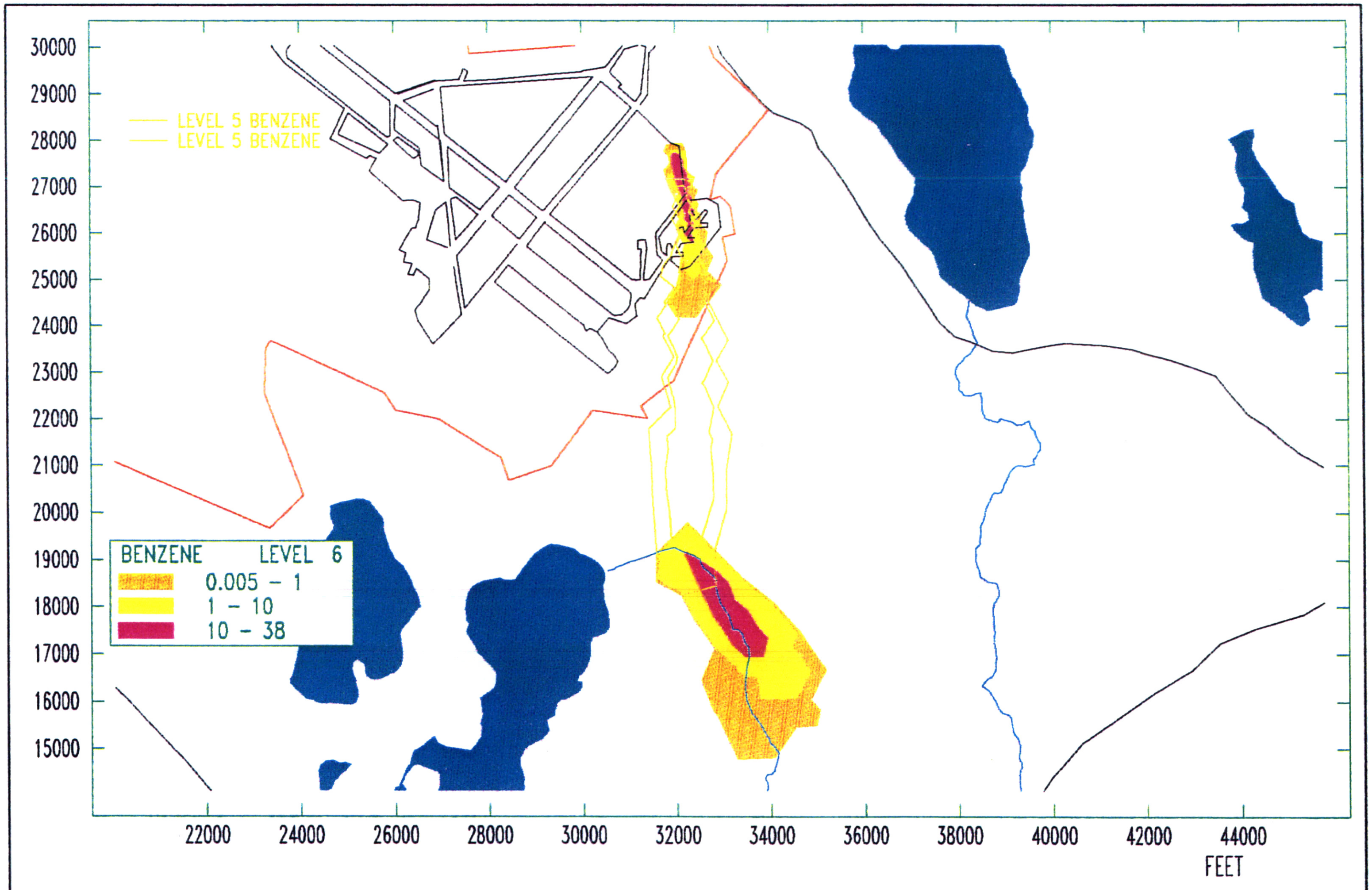

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FIGURE 6–8 : MODEL PREDICTED BENZENE PLUME – RUN 4
Biodegradation Rate = 0; Retardation Factor = 1.06; no continuing source

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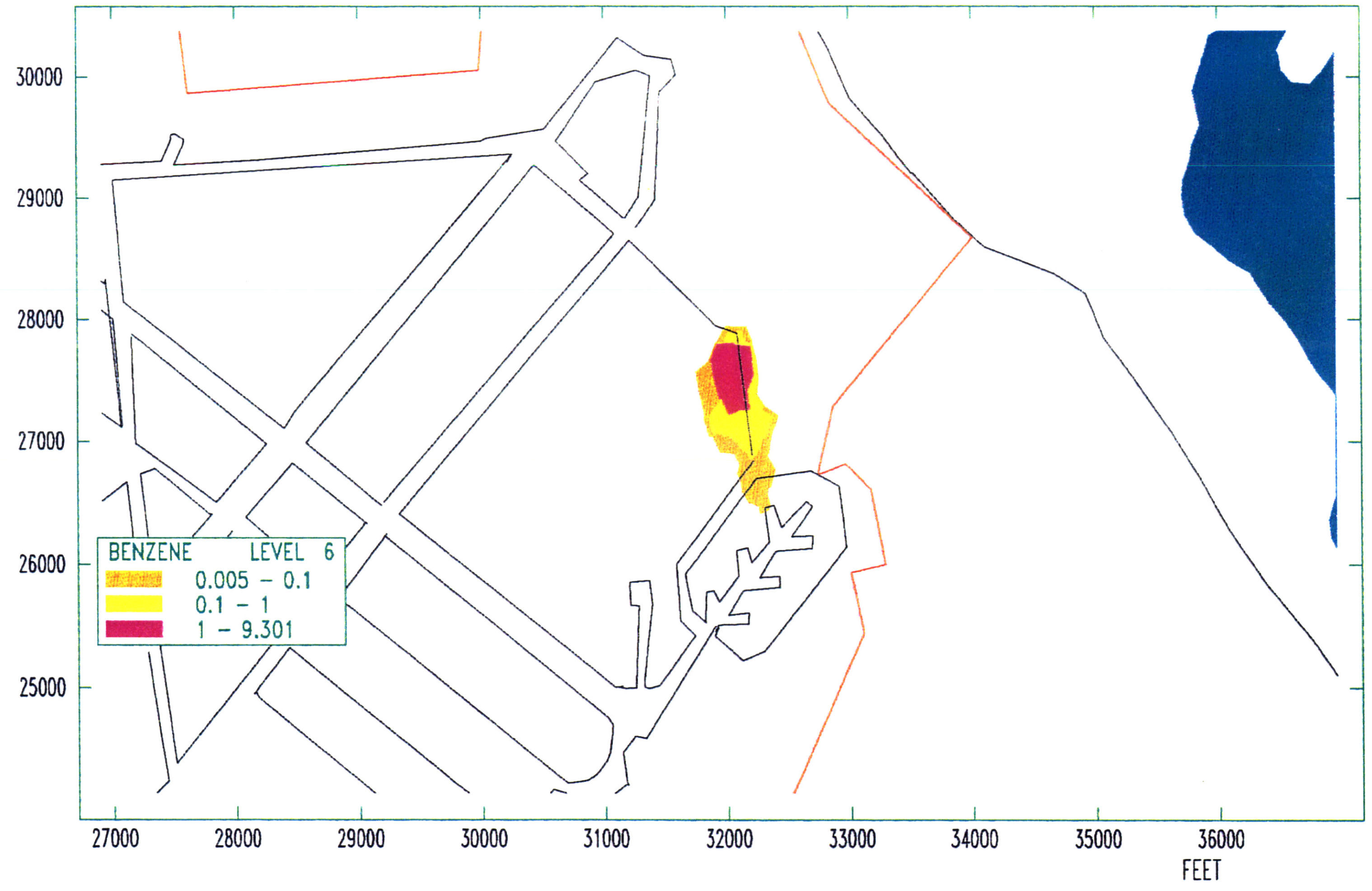

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FIGURE 6–9 : MODEL PREDICTED BENZENE PLUME – RUN 5
Biodegradation Rate = 0.005; Retardation Factor = 1.06; no continuing source

FS–1

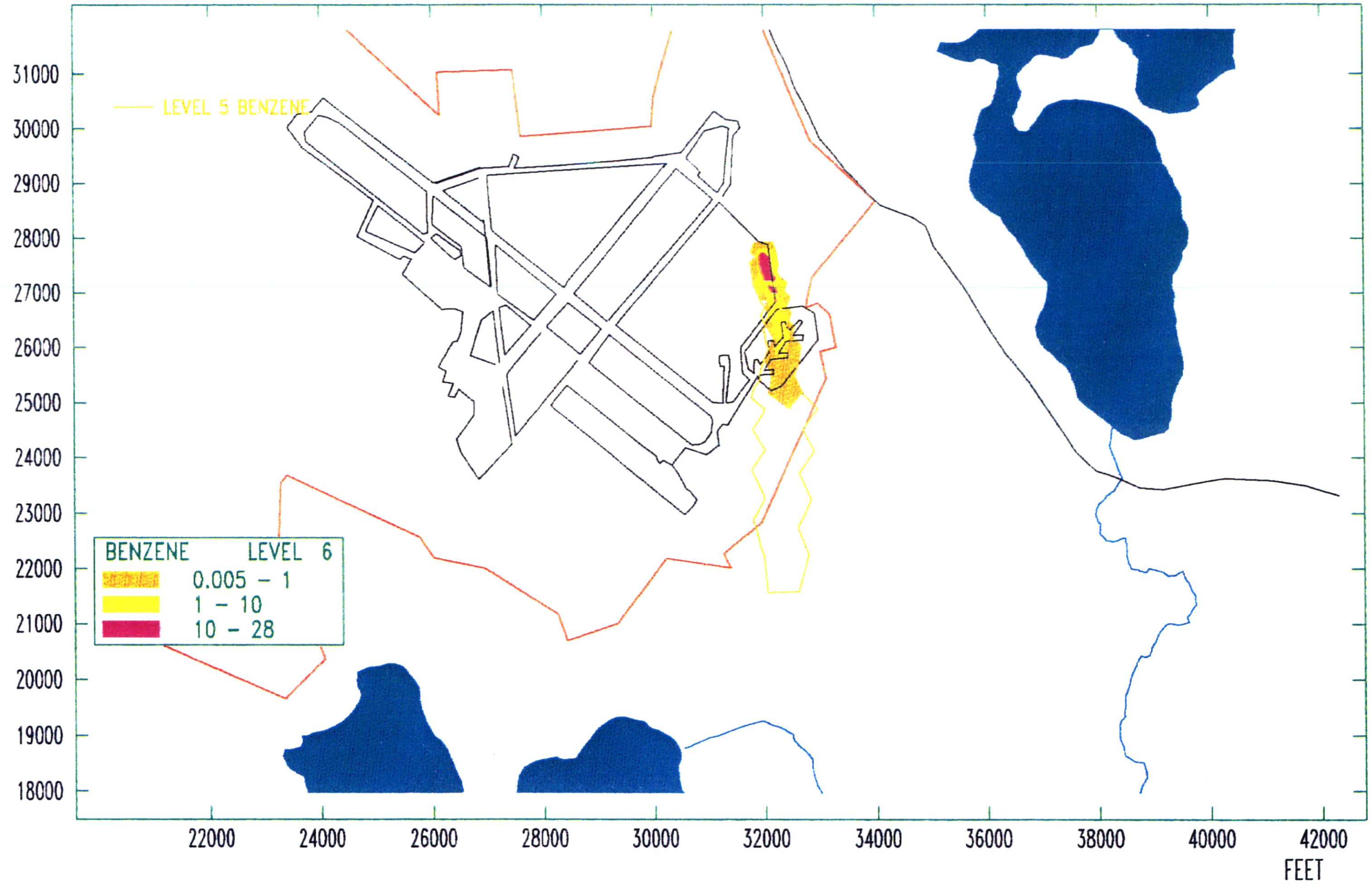

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FIGURE 6–10 : MODEL PREDICTED BENZENE PLUME – RUN 6
Biodegradation Rate = 0.001; Retardation Factor = 1; no continuing source

FS–1

Chapter 7

Assessment of Model Results

7.1 Toluene

The large number of detections of toluene at FS-1 allow us to use this constituent to verify the model. As seen in the presentation of the results (Section 6.2.3) the scenario considered as the most logical case produced a plume of toluene extending 300ft downgradient of the source, and having a peak concentration of $2166\mu g/\ell$. Field investigations found the maximum extent of toluene to be 200ft with the peak concentration detected being $2500\mu g/\ell$. Thus our model shows a great deal of agreement with the observed distributions.

It should be noted that a similar distribution could be obtained with differing estimates of the source strength and biodegradation rate (an increased biodegradation rate would reduce an increased source strength to a similar distribution). The only way to truly verify the relative magnitudes of these two factors would be to monitor the concentrations of toluene over time. Since we can assume that there is no longer any addition of mass to the plume (toluene was not found in the capillary fringe), this would yield a direct estimate of the biodegradation rate.

7.2 Benzene

The results for benzene reveal the relative importance of the factors which determine its migration from the source. The best way to compare the effect of each of these parameters is to view the plume in cross-section. The following discusses each of the uncertainties associated with the migration of benzene in turn.

Continuing Source

One area of uncertainty in determining the extent of benzene from the source area, was the possibility that not all the benzene entered the groundwater during the same period as testing occurred, but that some acted as a continuing source after testing ceased. One mechanism which would cause a continuing source would be the desorption of benzene that had previously been sorped to the soil particles in the unsaturated zone. Alternatively there is the possibility that some benzene reached the water table as pure product, and hence its entry to the groundwater was delayed. This was judged not to be the case in the conceptual model.

Figure 7-1 shows the model predictions of the plume distribution with and without the assumption of a continuing source. The continuing source hypothesis assumed that the entry of approximately one third of the benzene arriving at the groundwater was delayed by the mechanisms described above. This is considered to be an extreme case. The results presented assume a retardation factor of 1.06 and a biodegradation rate of 0.001. The results showed only a small difference between the two scenarios, with the extent of the plume being marginally reduced by the presence of the continuing source. The peak concentration in the plume was also reduced from $25\mu g/\ell$ to $18\mu g/\ell$.

Biodegradation

It is thought that some biodegradation of the plume is occuring. This is indicated by the reduced dissolved oxygen levels along the plumes axis. However, the specific rate of biodegradation of benzene in this aquifer is not known. It is also thought that this rate may not be constant in time and space. Therefore it is important to understand the consequences of various biodegradation rates.

Figure 7-2 shows the extent of the benzene plume assuming various rates of biodegradation. The cases of no biodegradation occuring, and a fast degradation rate of $0.005 day^{-1}$ are compared with a more conservative estimate of $0.001 day^{-1}$. All these cases are for a retardation factor of 1.06 and assume that there is no continuing source. It is clearly shown that process of biodegradation is of considerable importance in determining the extent of the plume. With a fast biodegradation rate the plume would extend only 1500ft downgradient, whereas with a slightly slower rate the plume would extend 6200ft downgradient. The case of no biodegradation is of particular concern, since we see that the plume would migrate 14,200ft downgradient. Furthermore, the Quashnet River has the effect of re-converging this plume, such that an area of high concentrations is created 10,000ft downgradient from the source. Some of the plume will discharge into the Quashnet River, while the rest will be diverted along its direction of flow, but remain in the groundwater. Thus the hazard for downgradient water supplies is high.

Retardation

It is thought that, although the organic carbon content of the soil is low, there will still be some retardation of the benzene plume due to sorption. However, due to the relatively high solubility of benzene this will be a minor factor in determining the extent of the plume. This is shown in Figure 7-3, in which the extent of the plume with and without retardation is compared. Both of these cases assume a biodegradation rate of $0.001 day^{-1}$, and no continuing source. The figure shows that the effect of retardation would be to reduce the current extent of the plume by less than 100ft. This is a relatively small effect, as anticipated.

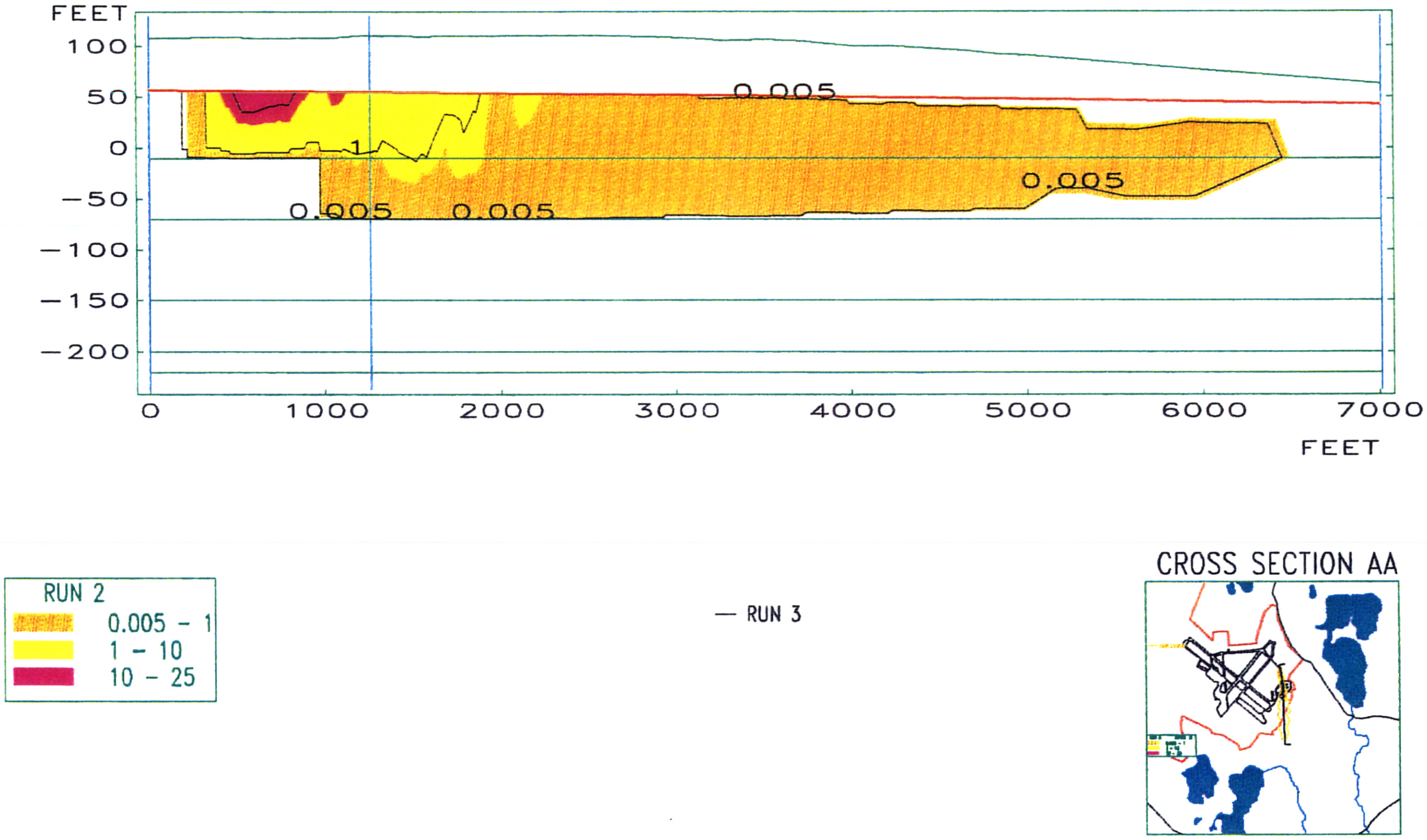

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FIGURE 7-1 : EFFECT OF CONTINUING SOURCE ON BENZENE PLUME

FS-1

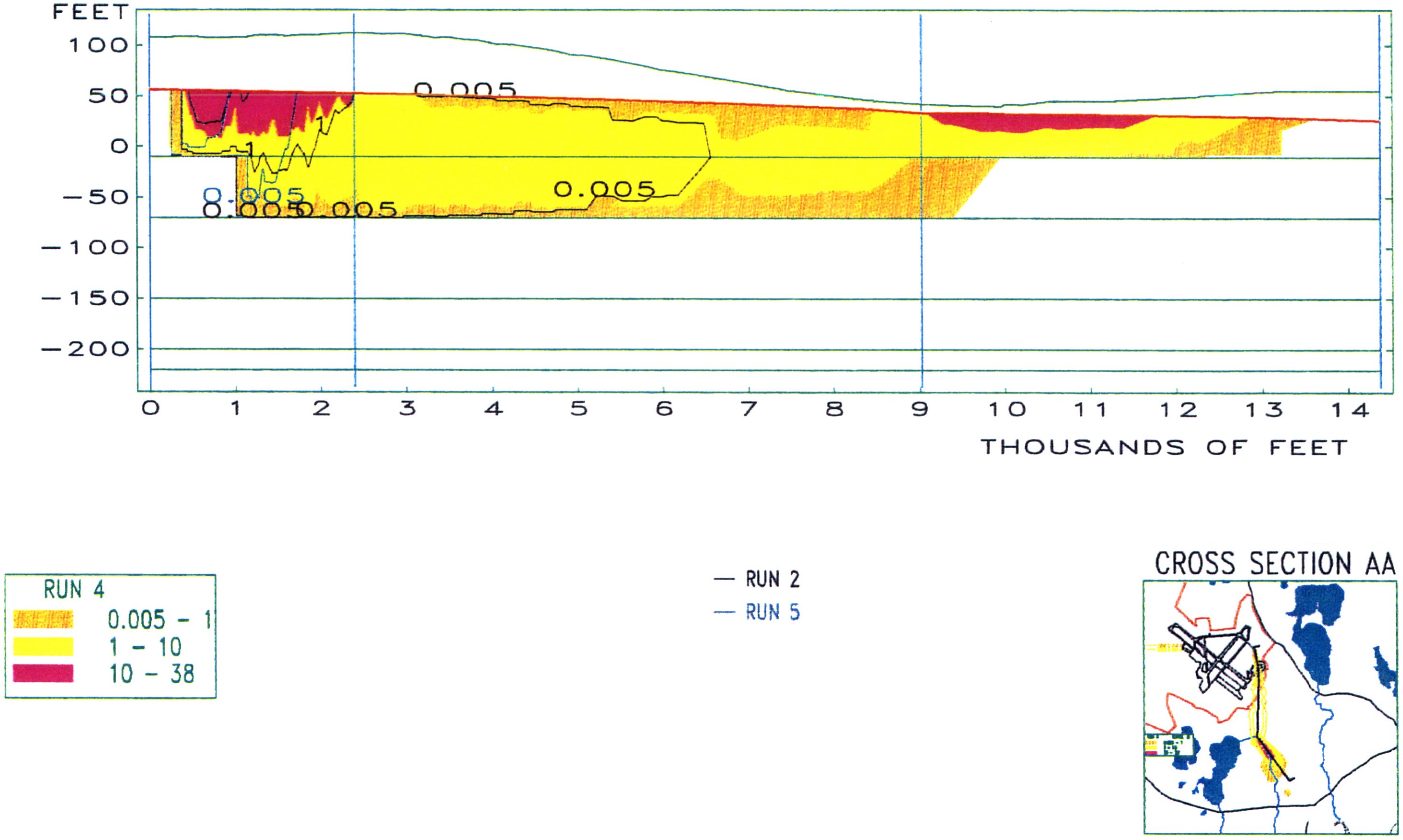

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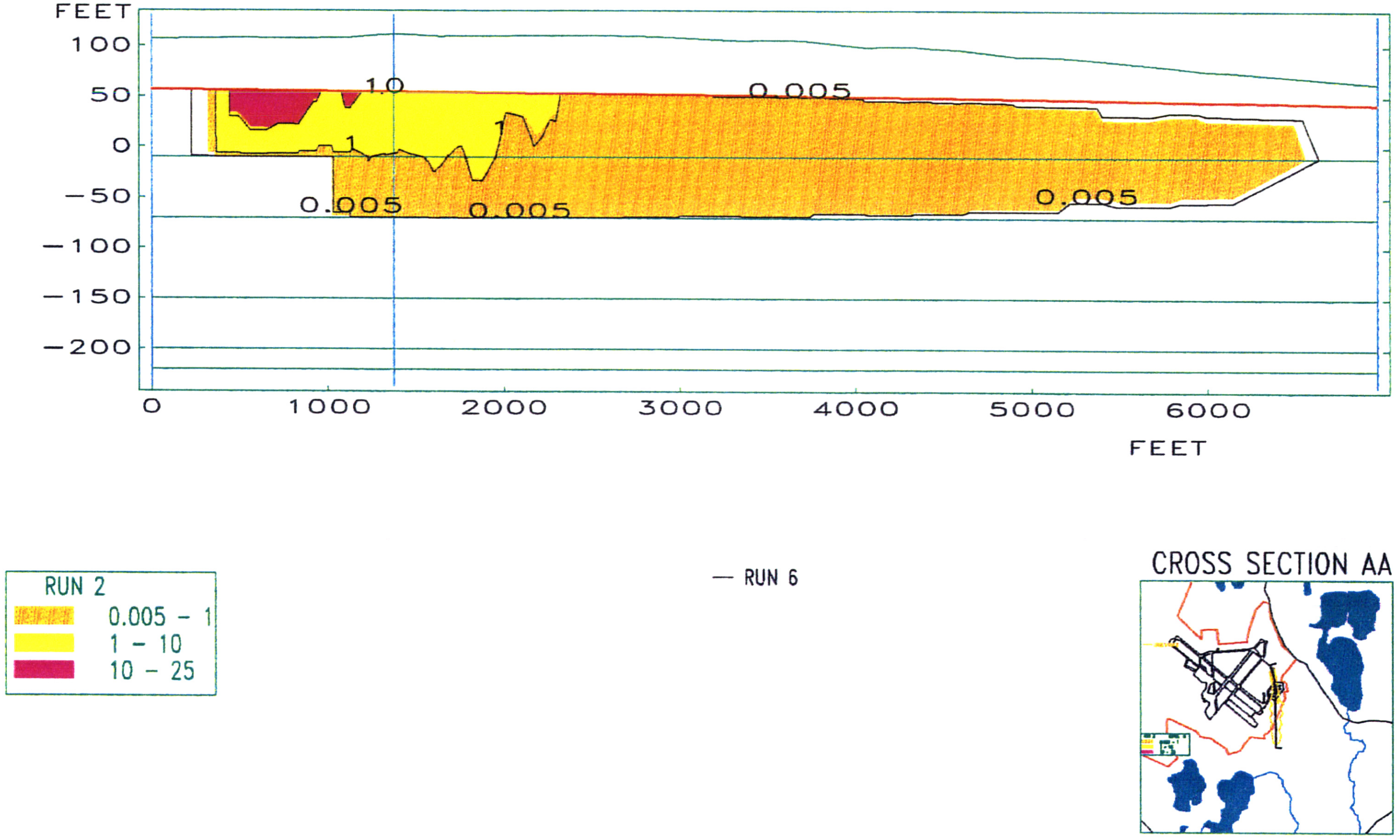
FIGURE 7-2 : EFFECT ON BIODEGRADATION ON BENZENE PLUME

FS-1



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FS-1 STUDY AREA, MASSACHUSETTS MILITARY RESERVATION

FIGURE 7-3 : EFFECT OF SORPTION ON BENZENE PLUME

FS-1

Chapter 8

Conclusions

8.1 Plume Characterization

The fate and transport of aviation gasoline from such a release as occurred at the FS-1 site depends on many factors. Chapter 4 discussed these factors, and qualitatively assessed the dominant routes of migration from this site. This chapter concluded that the initial hazard to downgradient water supplies would come from the more soluble constituents of AVGAS, and in particular, **benzene**. Benzene is thought to be almost entirely dissolved by the water added by the firefighters to prevent evaporation, and thus be transported through the unsaturated zone as an aqueous solution. It will therefore contaminate the groundwater immediately on arrival at the water table. It was suggested that three factors determine the current extent of the benzene plume:

1. The source strength at the water table, and whether a continuing source existed after testing ceased.
2. The rate at which biodegradation has been occuring.
3. The sorption of the contaminant to the soil matrix.

The magnitude of each of these factors is unknown.

The relative importance of each of these factors was assessed using the computer model developed for the site in Chapter 6. The model was used to predict the extent of the plume for various biodegradation rates, with and without sorption, and for two possible source scenarios. The results were then compared in Chapter 7. A continuing source scenario caused the extent of the plume to be marginally reduced, and the peak concentration in the plume to be reduced from $25\mu g/\ell$ to $18\mu g/\ell$. The effect of sorption would be to retard the migration of the contaminant. It was seen that with sorption the extent of the plume was reduced by less than 100ft. The consequences of different assumptions of the rate of biodegradation were much more marked. The model was run for three different assumptions of the biodegradation rate: $k = 0.005$, $k = 0.001$, and no biodegradation ($k = 0$). The extent of the plume from the source area was seen to range from only 1500ft up to 14,200ft downgradient.

Hence, neither the assumptions concerning the source, nor the sorption of benzene, significantly affected the predicted contaminant distribution. Of the three factors considered, **biodegradation** appears to be the dominant factor in controlling the extent of the plume. Variation of the biodegradation rate by relatively small amounts resulted in vastly differing predictions of the current distribution of contaminant. In particular, in the case of no biodegradation occuring we saw that the plume would be converged by the Quashnet River, and some contaminant would discharge into this stream. High concentrations of benzene were predicted in the vicinity of the stream. Thus biodegradation is the process that we need to investigate in order to determine the hazard to downgradient water supplies from benzene.

The rate of biodegradation occuring will be dependent not only on the concentration of the contaminant, but also on the local conditions of the aquifer. It will be dependent on the availability of oxygen, and also on the presence of suitable microorganisms. Thus it is aquifer specific. Hence the most accurate method of determining this rate would be to undertake further field investigations to assess the concentration distribution of benzene, and compare these results to those predicted by the model for various biodegradation rates. This would be possible with further characterization of the plume near the source area. However, the effect of different biodegradation rates is not so pronounced here. A more accurate method would be to determine the maximum extent of the plume. This is seen to be the most obvious feature related to the biodegradation rate.

Hence, we conclude that:

1. The initial hazard to downgradient water supplies comes from the benzene present in the AVGAS.
2. The factor determining the extent of the benzene plume is biodegradation.
3. The rate of biodegradation of benzene is best assessed by determining the extent of the plume by field investigation.

8.2 Usefulness of a Modelling Approach

The previous section has suggested that to determine the extent of the plume we need to quantify the biodegradation occuring, and that the most accurate method to do this is to determine the extent of the plume by field investigation. This would appear to negate the usefulness of developing a model for the site. However, this study has highlighted various benefits of such a model.

1. The computer model enabled us to quantatively examine each of our assumptions concerning the migration of a particular contaminant from the source. This in turn aided us in assessing the relative importance of these assumptions, and help indicate which parameter required further investigation. This would not be possible from a purely intuitive approach.
2. The model also enabled us to predict the distribution of contaminant under each set of assumptions. This will help direct future field investigations. Results from these field investigations can then be fed back into the model to help assess

some of the sources of uncertainty. This will further our understanding of the processes occuring at the specific site, and enable consideration of the potential risk associated with the contamination.

Hence this study has shown us that a computer model, such as the one developed, has limited application unless in is developed in conjunction with field investigation of the site. However, it can be a powerful tool when used concurrently with ongoing field investigations. Each of these two processes can be used to drive the other. In the particular case study considered, the model developed can direct future field investigations, which in turn can be used to calibrate the model and allow us to assess the biodegradation rate. This calibrated model can then be used to predict the future behaviour of the plume, and hence the to determine the potential hazards associated with it. Ongoing monitoring of concentration levels can be used to continuously verify the model.

8.3 Recommendations

The conclusions from this modelling study allow us to make certain tentative recommendations concerning future investigation of this site. It should be recognized that the model does not provide exact predictions of the plume distribution, but rather explores the effect of various scenarios. The results suggest that the distribution of benzene detected in previous site investigations is not fully characteristic of the benzene plume emanating from the FS-1 Study Area. The results imply that further field investigation is necessary to determine the current extent of contamination. The model can potentially be used to help direct these investigations. It appears that the issue of immediate importance is the determination of whether contaminant has been discharging into the Quashnet River. This is predicted by the model in the situation where no biodegradation of the benzene is occurring in the aquifer. In this case, the stream also has the effect of converging the plume such that high concentrations would be present in the groundwater immediately underneath the stream. This would be extremely hazardous to the downgradient water supplies.

If this proves not to be the case, then the results would suggest that investigations should be directed towards assessing the downgradient extent of the plume. Downgradient wells should extend deep enough into the aquifer (at least 100ft below ground surface), since the model results show us that the plume will sink significantly within the aquifer. Once the extent of the plume has been determined, the model could be used to predict the biodegradation rate, and the future hazards associated with the plume.

Appendix A

Observed Distributions

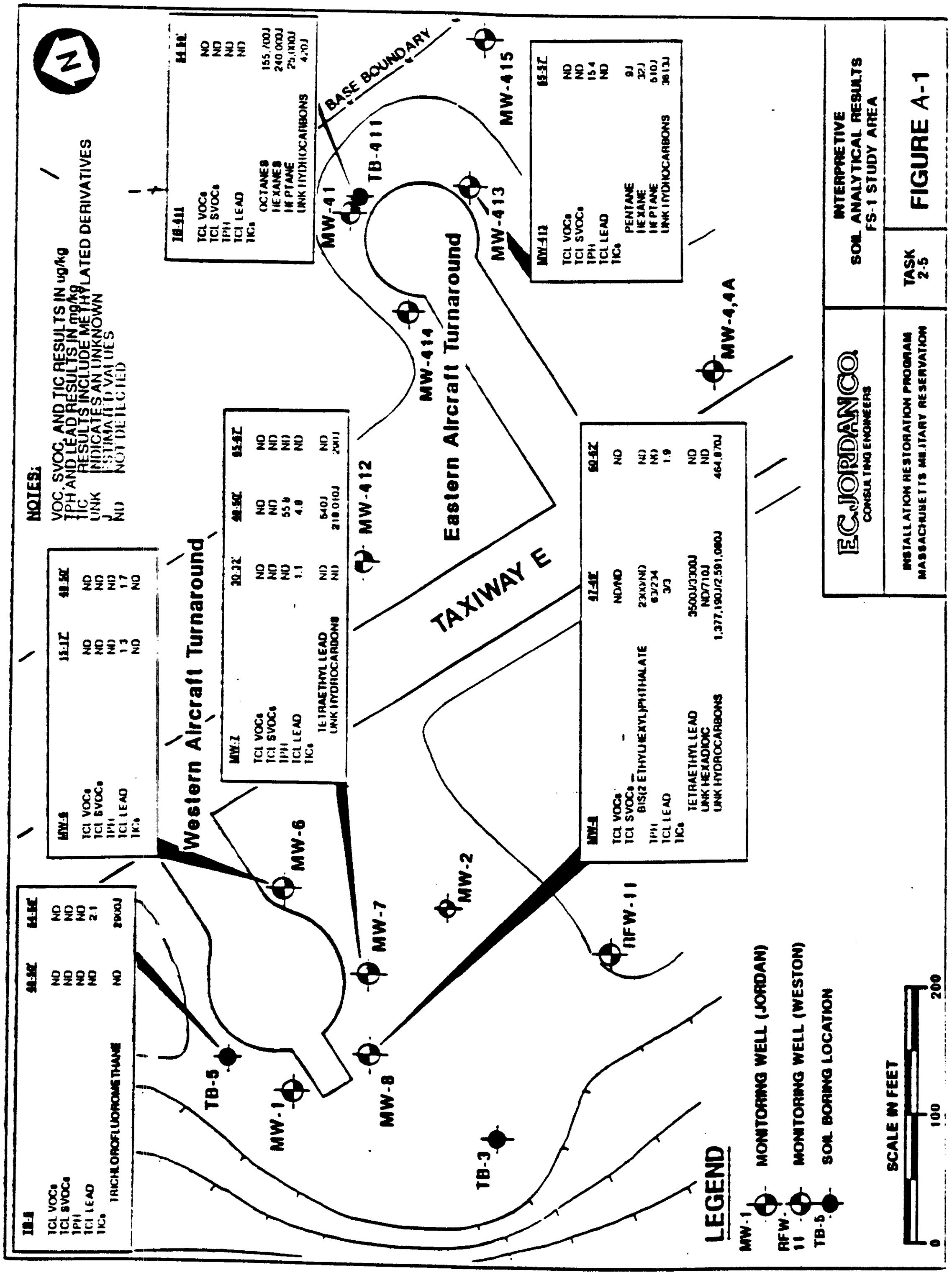

Figure A-1: Interpretive Soil Analytical Results, FS-1 Study Area

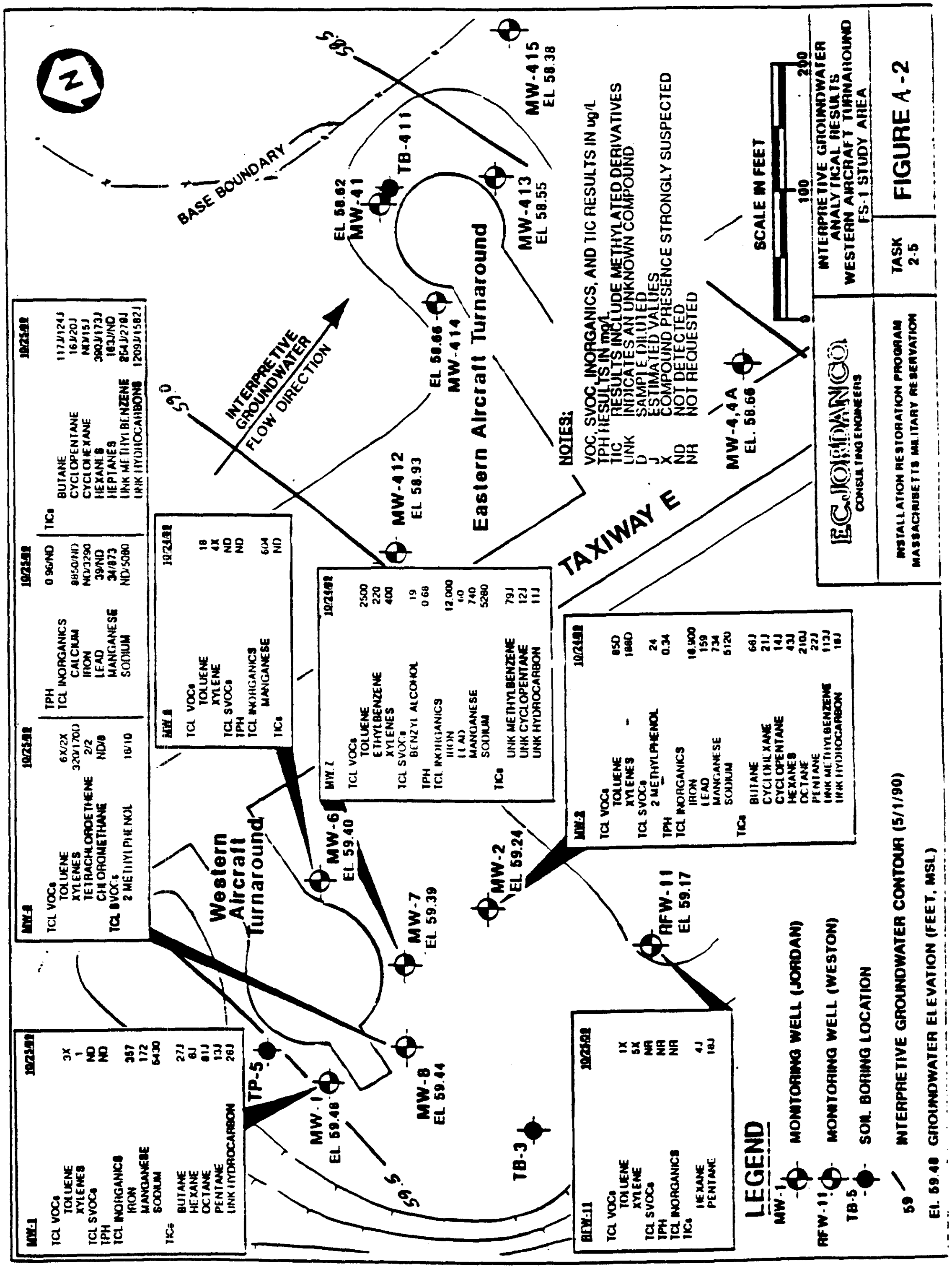

Figure A-2: Interpretive Groundwater Analytical Results, Western Aircraft Turnaround, FS-1 Study Area

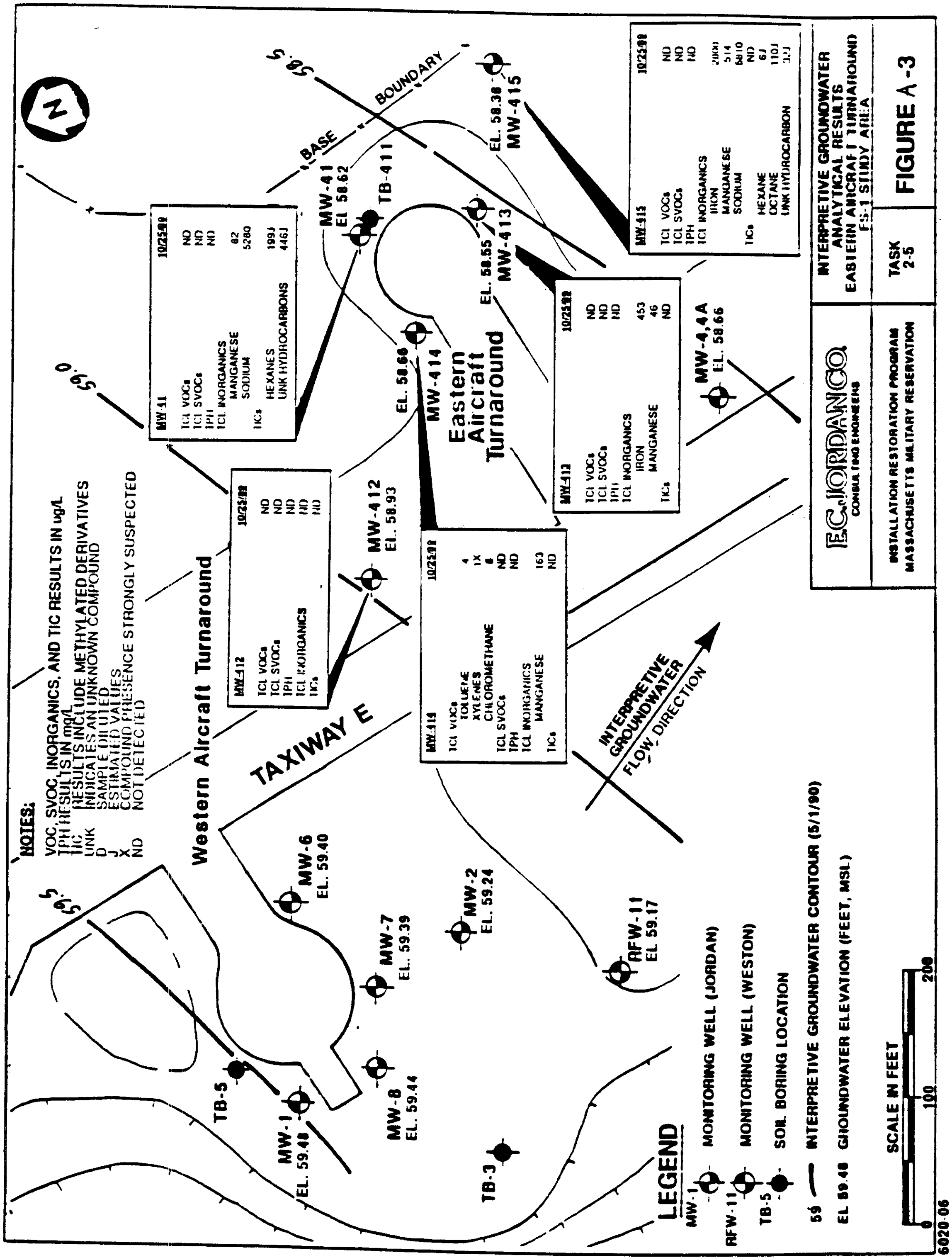

Figure A-3: Interpretive Groundwater Analytical Results, Eastern Aircraft Turnaround, FS-1 Study Area

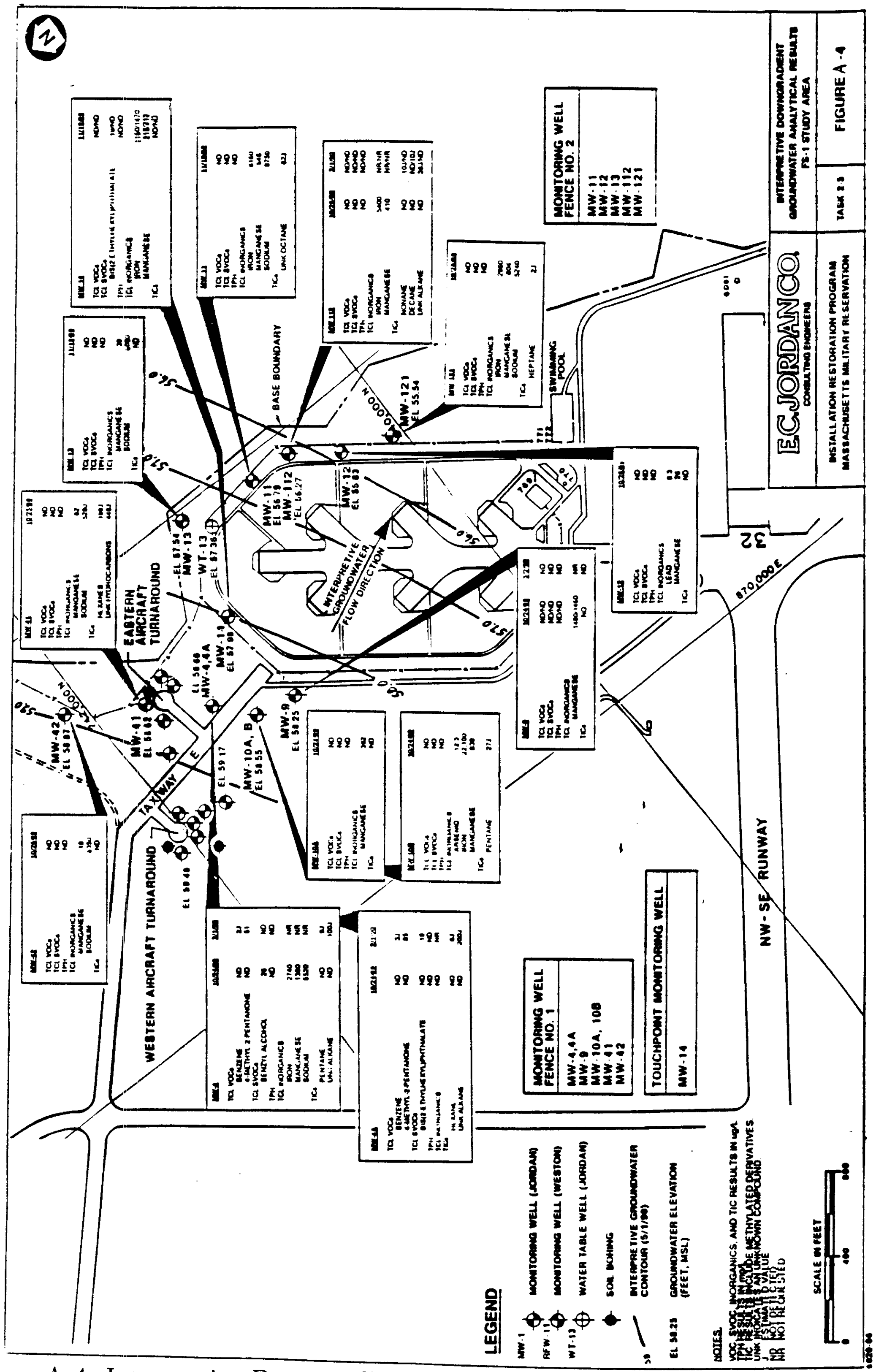

Figure A-4: Interpretive Downgradient Groundwater Analytical Results, FS-1 Study Area

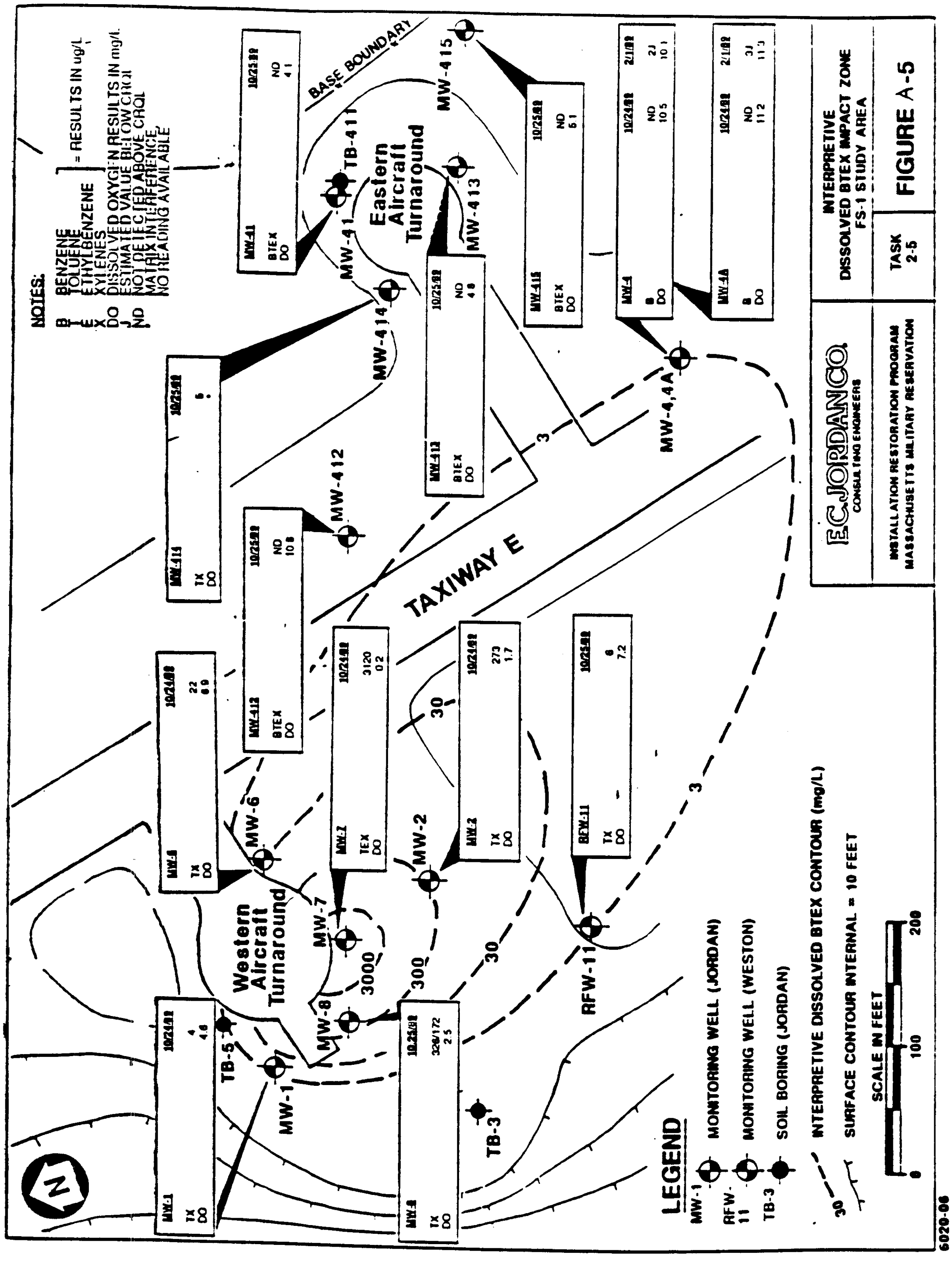

Figure A-5: Interpretive Dissolved BTEX Impact Zone, FS-1 Study Area

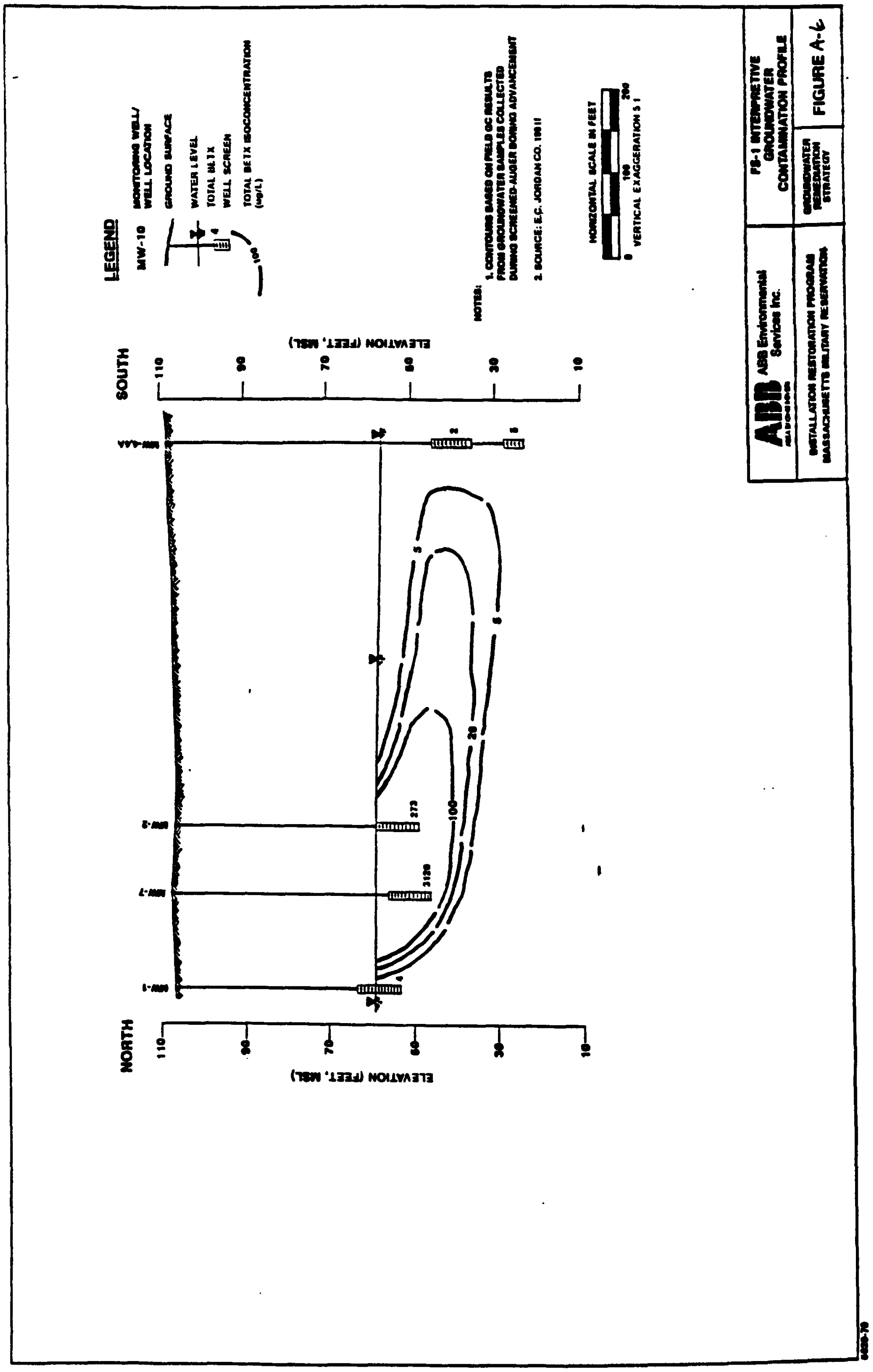

Figure A-6: FS-1 Interpretive Groundwater Contamination Profile

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Appendix B

Estimation Methods

This appendix details the estimation methods used to obtain values of the chemical properties of the constituents of AVGAS listed in Table 3.1 in the cases where experimental data was not available.

B.1 Vapour Pressure

The vapour pressure is defined as the pressure of the vapour of a compound at equilibrium with its pure condensed phase, be it liquid or solid. It can be estimated from the normal boiling point of the compound as outlined by Scharzenbach et al.[19]. For an organic compound the vapour pressure, p^o, at temperature T, is related to its boiling point, T_b, by the following equation.

$$ln P^o \simeq 19\left(1 - \frac{T_b}{T}\right) + 8.5\left(ln\frac{T_b}{T}\right) \tag{B.1}$$

In which p^o is in atmospheres, and both T and T_b are in Kelvin.

B.2 Aqueous Solubility

The aqueous solubility is defined as the abundance of the chemical per unit volume in the aqueous phase when the solution is in equilibrium with the pure compound in its actual aggragation state (gas, liquid, solid) at a specified temperature and pressure.

Since both K_{ow} and solubility depend on the structure of the chemical, it is possible to relate these two properties. Varies empirical relationships have been derived each relating to different groups of organic chemicals. They are all of the form:

$$logK_{ow} = -alogC_w^{sat}(1, L) + b \tag{B.2}$$

The regression constants, a and b, will depend on which particular group this analysis is performed for.

This is commonly used as a method of estimating K_{ow} given experimental data for the solubility. However for many of the constituents of AVGAS experimental data is not available for either. The approach taken in this study was to estimate K_{ow} using method below, and then to use these relationships to determine the solubility. It should be noted that this dependence on estimation methods to determine these quantities will result in the accruing of errors, leading to a fairly inaccurate result. However, this very approximate value will be sufficient to compare the relative behaviour of each of the constituents.

The regression constants for the estimation equation for the groups of compounds found in AVGAS are given in Table B.1.

Set of Compounds	*a*	*b*
Alkanes	0.81	-0.20
Substituted benzenes	0.86	0.75

Table B.1: Regression Constants for Linear Free-Energy Relationships Between Octanol-Water Partition Constants and Aqueous Solubilities for Sets of Compounds Found in AVGAS.

B.3 Henry's Law Constant

The Henry's Law Constant, K_H, can be thought of as the ratio of a compound's abundance in the gas phase to that in the aqueous phase at equilibrium. If the vapour pressure and the solubility of a particular compound are known (or have been estimated), the Henry's Law Constant can be estimated as

$$K_H = \frac{p_i}{C_w} \simeq \frac{p^o}{C_w^{sat}} \tag{B.3}$$

where p_i is the partial pressure of the compound in air which is in equilibrium with an aqueous concentration of the compound, C_w. This method of estimating the Henry's Law Constant assumes that K_H remains relatively constant with concentration.

B.4 Octanol-Water Partition Coefficient

The Octanol-Water Partition Coefficient of a compound can be estimated by considering its chemical structure. This methods attempts to express the free energy of transfer of a compound in the octanol-water system as the sum of free-energy contributions of the different parts of the molecule. Consequently, we have,

$$logK_{ow} = \sum_i f_i + \sum_j F_j \tag{B.4}$$

where f_i values quantify the contributions arising from each building block i in the chemical, and F_j values account for any special *intra*molecular attraction. These intramolecular interactions arise from the particular structure of a given compound, and can be due to a number of factors, both geometric and electronic. Geometric factors include effects caused by the existence of unsaturated bonds, flexing of the molecule and branching. Electronic factors include the effect of polyhalogenation and intramolecular hydrogen bonding.

For more complex chemicals, it is possible to employ known $logK_{ow}$ values for closely related compounds. Thus K_{ow} can be estimated from

$$logK_{ow}(new) = logK_{ow}(old) - \sum_{removed} f + \sum_{added} f - \sum_{removed} F + \sum_{added} F \tag{B.5}$$

Table B.2 gives the fragment constants necessary to estimate $logK_{ow}$, and Table B.3 gives the Intramolecular Interaction Factors.

Fragment	f	f^{ϕ}
$-\overset{\mid}{\underset{\mid}{C}}-$	0.20	0.20
$-H$	0.23	0.23
$-CH_3$	0.89	0.89

Table B.2: Fragment Constants Used in Estimation of $logK_{ow}$. Note : The superscript ϕ indicates constant for substituents bonded to aromatic carbons.

Structural Feature	Symbol	F Value
Skeletal Arrangement		
Long-chain flexing	F_{ch}	(n-1)(-0.12)
Ring flexing	F_r	(n-1)(-0.09)
Nonpolar chain branch	F_{br}	(-0.13)

Table B.3: Intramolecular Interaction Factors Used in Estimation of $logK_{ow}$

Appendix C

Calculations

C.1 AVGAS released during testing

Most Logical Case Scenario Assume valves are left open a full 30 seconds with all fuel being spilled directly on the pavement for one aircraft every day for 12 years.

$13yrs \times 365days = 4,745$

$6valves \times 18.75gal/30sec = 112.5gal$

$4,745 \times 112.5gal = 533,800gallonsspilled$

C.2 Evaporation of Spill

A rough estimation of the time it would take the entire slick to evaporate can be made using a thin film model[11]. Such a model would predict that the evaporative flux, J, is related to the chemical concentration in the air by the equation

$$J = v \cdot C_a \tag{C.1}$$

where v is the piston velocity. The concentration of the chemical in the air can be determine from its vapour pressure:

$$C_a = \frac{p^0}{RT}(MW) \tag{C.2}$$

where p^0 is the vapour pressure of the chemical, R is the universal gas constant, T is absolute temperature, and MW is the molecular weight of the chemical. The piston velocity can be approximated by the following equation

$$v(cm/hr) = 1100 v_w (m/sec) \tag{C.3}$$

where v_w is the wind speed.

So for the case of the aviation gasoline spilled at FS-1:

Vapour pressure of AVGAS, $p^0 = 20 mmHg = 0.0264 atm.$[13]
Average molecular weight $MW = 165.4 g/mol$
Hence, at 20^oC, $J = 0.604 g/cm^2 hr$

Volume of spill $= 112.5 gallons = 15.04 ft^3$
Assuming spill thickness $= 0.25 in$, area of slick $= 722 ft^2$
Rate of mass loss $= 6,754 g/min$

Mass of spill $= 319,397 g$
Time for entire slick to evaporate $= 47.3 minutes$

C.3 Dissolved Fraction of AVGAS

A standard firefighting hose delivers water at the rate of 250 gallons/min (courtesy of the Somerville Fire Department). Assuming four hoses were used for a period of 10 minutes, 10,000 gallons of water would be added to the area.

Solubility of AVGAS $= 300 mg/\ell$[13]
Mass of AVGAS dissolved $= 11,356 g$

C.4 Source Area Recharge Rate

Assume area of impact $= 150^2 ft^2$

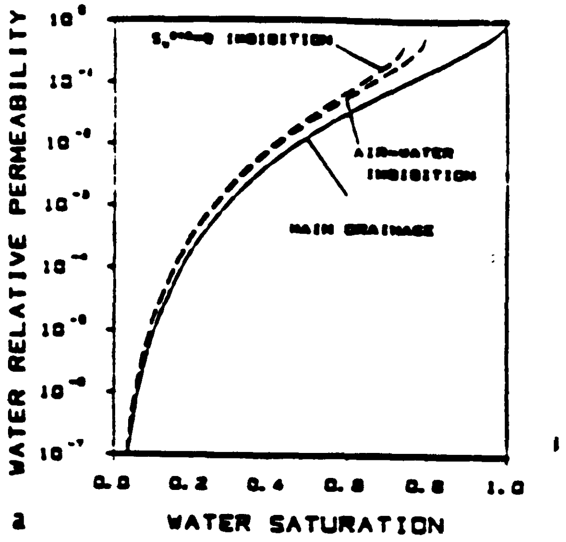

Figure C-1: Water relative permeability vs. Saturation for a Sandy Soil[18]

Recharge Rate, $q = 0.059 ft/day$

Hence relative permeabilty, $k_r = \frac{K(\theta)}{K(1)} = 2.95 \times 10^{-4}$

From Figure C-1, water saturation $s = 20\%$

C.5 Sources at Water Table

Mass of AVGAS released per day $= 319,397g$

Time to reach water table $= 60days$

Toluene

1.33% by weight, mass of toluene released per day $= 4,248g/day$

Assuming biodegradation rate of $0.025day^{-1}$, mass of toluene reaching water table = $948 g/day$

Benzene

0.5% by weight, mass of toluene released per day = $1,597 g/day$

Mass of benzene reaching water table = $1,597 exp(-60k)$

Continuing Source Conservation of mass, and source completion at current time were assumed. In this case,

$$\frac{Q_o}{k'}(1 - e^{-26*360*k'}) + 13 * 360 * Q_o = 13 * 360 * Q \tag{C.4}$$

where Q_o, magnitude of constant source at the water table between 1955 and 1967 is assumed to be 2/3 of Q, mass of compound released on the surface. The magnitude of the decay constant, k' was found to be 4.2×10^{-4}.

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