A Hydro-GeoChemical Assessment of Groundwater Flow and Arsenic Contamination in the Aberjona River Sub-Basin

by

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Abstract

Because of the increased dependency of groundwater supplies for domestic, agriculture, and industrial purposes, it is necessary to be knowledgeable of the contamination issues that affect groundwater quality. The first step in this process involves understanding the mechanics of groundwater flow, the structure of and effects due to the geologic environment, and the biological and chemical influences on flow and transport. Within the Aberjona River watershed and more specifically, the Aberjona River Sub-Basin, the hydro-geochemistry is dynamic and complex.

The effects of the stream-aquifer interaction are key, with the Aberjona River being hydrologically dominant. The buried valley containing mostly glacial outwash is a defining feature of the sub-basin geology. Additionally, bedrock outcrops and bedrock ridges complicate modeling efforts and may be more important than originally thought in controlling the flow regime. In the vicinity of the hide piles, geochemical conditions affect the speciation and subsequent transportability of arsenic throughout the aquifer.

Using a three-dimensional finite element model, the sub-basin is discretized with specific attention to the areas near the Industriplex and Well G & H Superfund sites, and along the Aberjona River and tributaries. The modeling results confirm much of the information gained by studying the hydro-geochemical behavior of the sub-basin. Additionally, the results of modeling will be beneficial in establishing boundary conditions for more detailed models of both the Industriplex and the Well G & H areas for both flow and transport analysis.

Thesis Supervisor: Dennis McLaughlin
Title: Associate Professor

Dedication

To all those who are the heart and soul of the greatest educational conglomerate the world has ever known...

Historically **B**lack **C**olleges and **U**niversities

...and Southern and Xavier, thanks for Dad, Mom, and Sis!

Acknowledgments

> *And God said, Let the waters under the heaven be gathered together unto one place, and let the dry land appear: and it was so. And God called the dry land Earth; and the gathering together of the waters called he Seas: and God saw that it was good.*
>
> Genesis 1:9,10

Thanks to all who helped, inspired, and prayed...
I will be forever grateful to my advisor, Dennis McLaughlin, for the patience, persistence and brilliance. Dennis, what a special way of providing the balance. Can you imagine if we had both seen that glass as *half-empty* on any given day? Kay Thompson and Lynn Reid, thanks for all the support, encouragement, and direction. MIT was more beautiful and positive because of you, and I have been blessed by your friendship, in as much as I have benefited from your wealth of knowledge and experiences. See you at that conference, real soon, *love* Josh! John Durant, Helena Solo, and Peter Zeeb, your wisdom and information were so timely and essential; thank you. Margaret Talbott and Freddie-Jo Eisenberg thanks for all the help. Stephen Lancaster, words can't even begin to tell (at least, not written here), but I know you know it already. Thanks and continue the fight! Professor Eagleson, you were a big part of my coming to MIT, thanks for the constant encouragement that lifted my spirits on numerous occasions. And Pat Dixon... I can't imagine MIT or the Parsons Lab without your presence and spirit. Thanks for getting me here, I have gained so much! And to all in the Parsons Lab family, good wishes and continued success...

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Chapter 1

Introduction

1.1 Formulation of the Problem

Water is essential to life, and as a fragile resource, must be managed effectively. All environmental concerns are in some way pertinent to some aspect of water resources. Only six percent (6%) of the earth's water lies outside of the saline oceans and seas. Of this percentage of freshwater, groundwater—*the subsurface water that occurs beneath the water table in soils and geologic formations that are fully saturated*—constitutes approximately two-thirds of the world's resources, and 95% of fresh water resources if glaciers and icecaps are excluded (Freeze & Cherry, 1979).

The United States increased its use of freshwater, from 1955 to 1980, by 175 percent. It is possible that a fourfold increase may be felt by the year, 2000 (Viessman & Welty, 1985). Water pollution, broadly categorized as contamination by biological agents, dissolved chemicals, nondissolved chemicals and sediment, and heat (Kupchella & Hyland, 1989) has also increased. Consequently, in many places, water quality, and not quantity is the most critical factor of concern (Viessman et al., 1989). Heath (1989) links the importance of fresh water quantity and quality by stating:

> Subsurface openings large enough to yield water in a usable quantity to wells and springs underlie nearly every place on the land surface and thus make ground water one of the most widely available natural resources.

> When this fact and the fact that ground water also represents the largest reservoir of freshwater readily available to man are considered together, it is obvious that the value of ground water, in terms of both economics and human welfare, is incalculable.

To fully understand the issues related to the management and protection of groundwaters, it is important that one be aware of the geologic environment through which these waters are stored, transmitted, and filtered (Parker, Sr., 1976; Kazmann, 1988). Consequently, future methods of waste disposal—*sometimes hazardous*—will need to properly address the failures that plague today's water quality. Yong et al. (1992) state:

> Regardless of how the waste material is generated (produced), and regardless of the steps taken to reduce, recycle, or treat the waste material, in the final analysis, the ultimate resting place for the industrial or consumer waste that cannot be recycled (or has been recycled) is in the ground.

Because most waste is eventually buried in the sub-surface, the study of hydrogeochemical phenomena below ground is essential.

Subsurface water quality issues have been fueled by the increased dependency on groundwater for domestic, agricultural, and industrial purposes. Additionally, between 1950 and 1980, the ratio of the increase in total water withdrawals to the increase in population for the United States was approximately five to three. Kupchella and Hyland (1989) estimate that each American utilizes four times the amount of water utilized by an American living at the turn of the century.

The Council on Environmental Quality lists groundwater contamination by toxic chemicals as one of the three most important environmental problems for the decade of the eighties. Kupchella and Hyland (1989) cite the following statistics relevant to groundwater and its contamination:

- Ninety-five percent of rural households and one third of the nation's 100 largest cities use groundwater as their main source of drinking water and irrigation

(Sun, 1986).

- In the late 1980's the United States used 100 billion gallons of groundwater per day.
- Groundwater is the source of fully half the irrigation water used in the American West.
- Groundwater is the next largest reservoir of water on earth after the oceans.
- Thirty percent of the stream flow in the United States starts as groundwater (springs, etc.).
- Once contaminated, groundwater may remain contaminated for hundreds of years or more.

As the emphasis shifts from groundwater accessibility to groundwater quality, it is imperative that research initiatives shift to ensure that the needs of the population will be addressed. Groundwater contamination issues are complicated by a complex and heterogeneous geologic matrix. Additionally, with travel times in the subsurface significantly slower than surface water pathways, a contaminant may not be identified until it has reached a pumping or extraction well, at which point the hazards are irreversible and potentially deadly.

The research in this thesis is concerned with industrial pollution and the potential for the resulting contaminants to migrate through the sub-surface via groundwater. The area of concern is the Aberjona River Sub-Basin, located approximately ten (10) miles north of Boston, Massachusetts. This watershed, represented by Figure 1.1, includes the towns of Woburn, Reading, Wilmington, Burlington, Lexington, Winchester, and Stoneham. The research in this area is part of a broad-based interdisciplinary initiative at the Massachusetts Institute of Technology.

Durant et al. (1990) report on the influence of the leather industry on the waste contamination problem of the Aberjona watershed, while Aurilio (1992) looks specifically at the historical and industrial practices that contributed to the arsenic contamination within the watershed. Arsenic was used from approximately 1888 to 1929

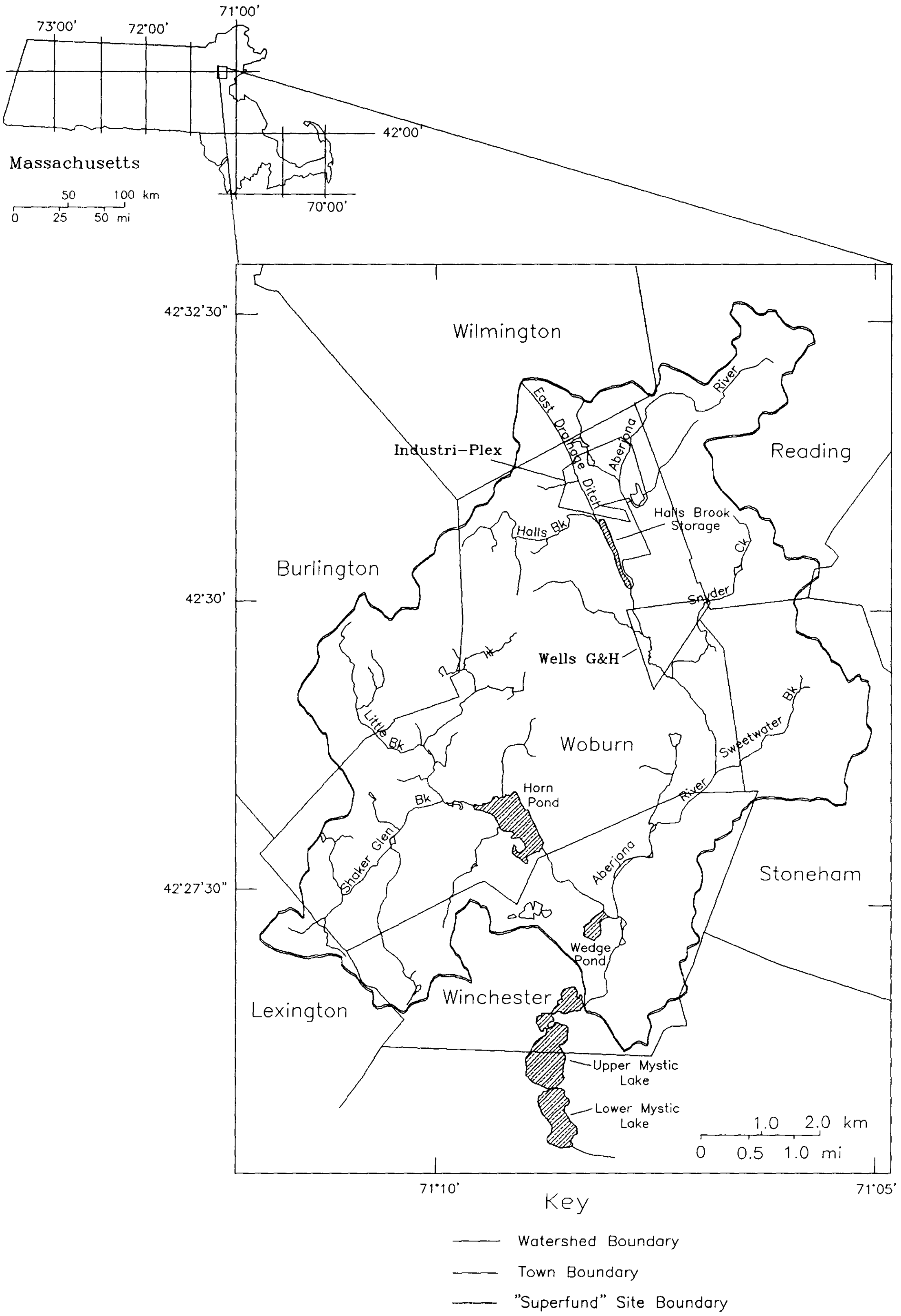

Figure 1-1: Site Map

as a raw material in the manufacturing of chemicals (Haynes, 1939; Aurilio, 1992). Concentrations of arsenic in soils and riverine and lacustrine sediments are a predominant result of this activity. However, consideration of other anthropogenic uses and activity such as, "arsenical pesticides for agriculture and arsenical depilatories (i.e., hair-removing agents) in tanning operations and activities," and earth movement for land development, respectively, further explain arsenic distribution in the watershed (Aurilio, 1992). Aurilio (1992) conservatively estimates that 170 tons of arsenic were released on the watershed from sulfuric acid production, using arsenic-rich pyrites; and that 35 metric tons of wastes from arsenical pesticides, such as lead arsenate, were also released.

This 65 square kilometers ($24.3mi^2$) area—divided into the 26.5 sq. kilometer Horn Pond ($9.9mi^2$) and 38.5 sq. kilometer Aberjona River ($4.4mi^2$) Subbasins (Figure 1.2)—is home to two Environmental Protection Agency (EPA) Superfund sites (under CERCLA, the Comprehensive, Environmental Response, Compensation and Liability Act): Industriplex and Wells G&H. From the onset of the industrial rise in this area in 1837, through the diversification of the industrial base in 1940, to the present situation with approximately 135 manufacturing firms in 1989, waste generation and disposal practices can be linked to the current dangers within the watershed.

Adverse health effects are possible and potentially threatening because of the use of wells *G* and *H* as important sources of domestic drinking water (Lagakos et al., 1984; Brown, 1987). The possible connection between contamination and a childhood leukemia cluster in Woburn was investigated in a study by the Harvard School of Public Health/For A Cleaner Environment Study. This study included data from 20 cases of leukemia in children 19 and under, diagnosed between 1964 and 1983, the regional and temporal distribution of water from wells G and H provided by the state Department of Environmental Quality Engineering, and the health survey. Quoting from Brown (1987):

> On 8 February 1984, the Harvard SPH data were made public. Childhood leukemia was found to be significantly associated with exposure to water from wells G and H, both on a cumulative basis and on a none-

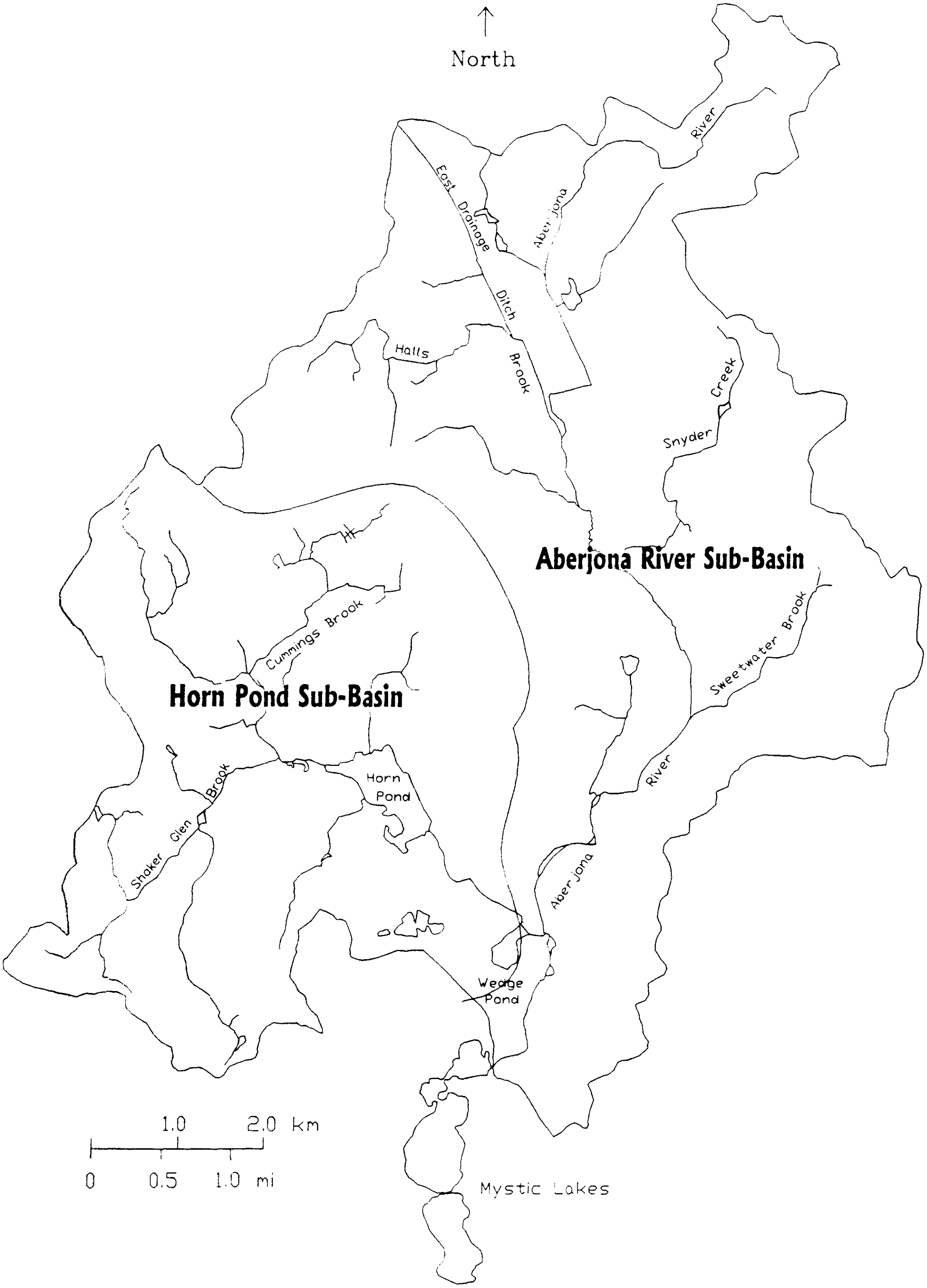

Figure 1-2: Aberjona River Basin with Sub-Basins

> versus-some exposure basis. Children with leukemia received an average of 21.2% of their yearly water supply from the wells, compared to 9.5% for children without leukemia....
>
> Water exposure was associated with perinatal deaths since 1970, eye/ear anomalies, and CNS/chromosomal/oral cleft anomalies. With regard to childhood disorders, water exposure was associated with... kidney/urinary tract and lung/respiratory disease.

Aurilio (1992) provides extensive data on arsenic within the Aberjona watershed. Arsenic is twentieth among elemental abundance in the earth's crust. Natural soil concentrations average 1.5–2 mg/kg. The National Research Council (1977) report arsenic concentrations in soils ranging from 0.1–40 mg/kg and averaging 5–6 mg/kg; however, within the Aberjona watershed there have been arsenic levels reported up to 30,800 mg/kg. The majority of arsenic contamination is near the Industriplex site. Because of high arsenic levels in the sediments of the Aberjona River and the Mystic Lakes (Knox, 1991; Spliethoff & Hemond, 1992) (as shown in Figures 1.3) the river may be a major conduit for transporting arsenic to areas below Industriplex. Therefore, it is imperative that the flow and transport mechanisms near the Industriplex site and within the Aberjona River Sub-basin be critically investigated.

1.2 Scope and Objectives

Broadly, the goals of this research are to (1) gain a better understanding of the flow regime in the Aberjona River Sub-basin, including the three-dimensional impact of vertical gradients and stream-aquifer interaction and behavior; (2) determine the impact of sub-surface geochemical conditions (i.e. stratigraphic layering, hide piles) on flow and arsenic transport; (3) assess the fate of arsenic in the watershed, with an emphasis on the dynamics, equilibria, and kinetics near Industriplex; and (4) model groundwater flow in the sub-basin with appropriate hydraulic parameters.

To gain a better understanding of the groundwater flow regime, the interaction between the groundwater and surface water, and possible contaminant pathways,

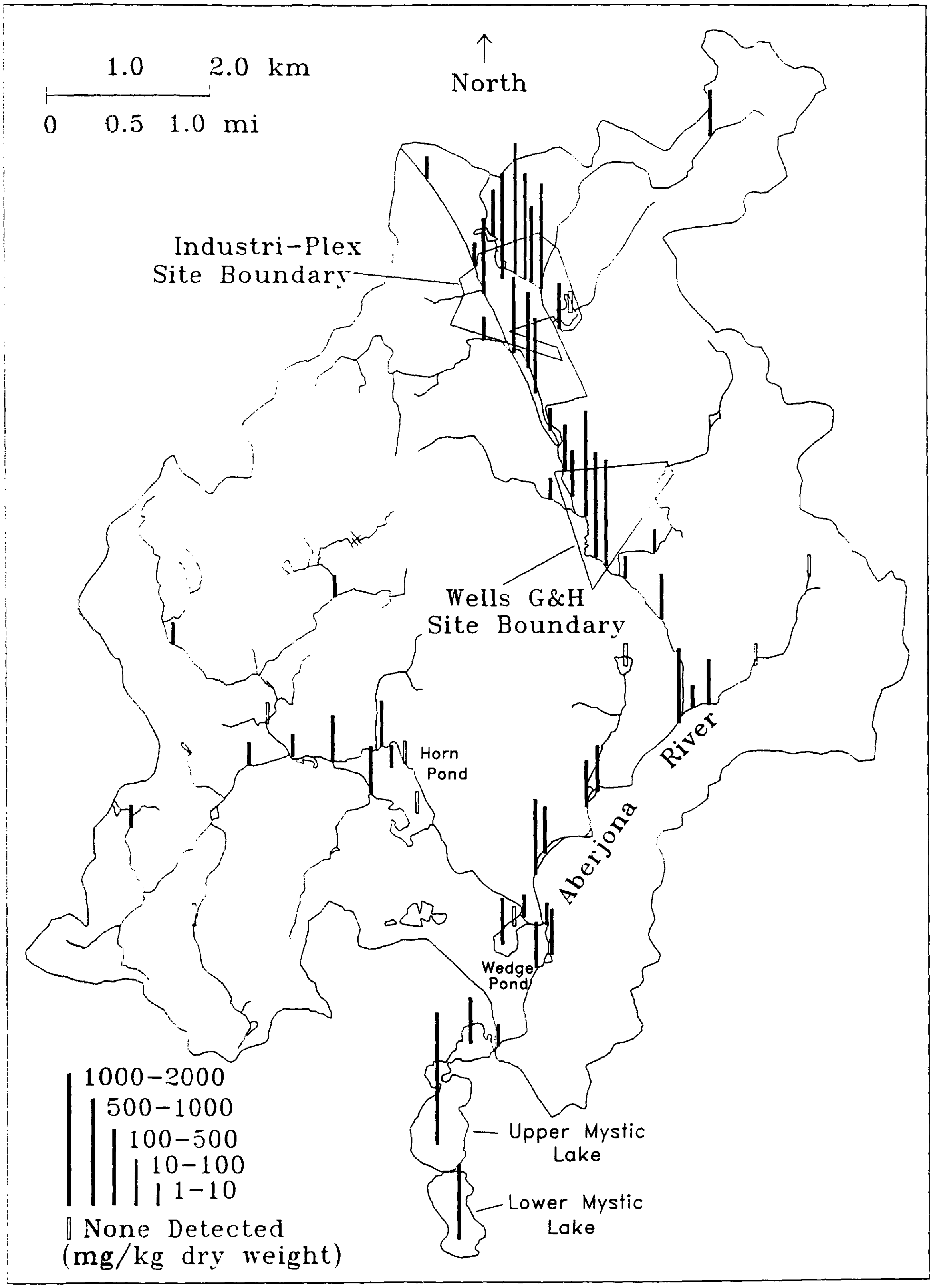

Figure 1-3: Distribution of Arsenic in Surface Sediments of the Aberjona Watershed
Source: Aurilio, 1992

a numerical flow model is used. The flow modeling builds upon the work begun by Brainard (1990) and continued by Reynolds (1993). Brainard modeled two-dimensional flow in the Aberjona River Sub-basin and also examined vertical flow and the effect on transport pathways, analytically. Reynolds' analysis of only a portion of the watershed is based on a three-dimensional model, using vertically uniform stratigraphy, in which she attempts to evaluate the influence of vertical flow and transient behavior. By building on the results of Brainard and Reynolds, this thesis attempts to accurately represent the three-dimensionality of the aquifer, especially along the river where recharge or discharge locations may be governed by local topographic features.

One of the problems in accurately representing sub-surface conditions is the difficulty in properly characterizing the heterogeneity of the geologic medium (Gelhar, 1993). To provide the best description possible of the geology would require extensive and expensive geotechnical procedures that may not reduce the uncertainty of the *true* geology, significantly. In fact it is suggested by McLaughlin et al. (1993) that

> the hydraulic and chemical properties which control subsurface flow and transport are frequently only weakly correlated with readily measured geological properties such as soil texture. As a result hydraulic and chemical heterogeneity are even less well understood than geological heterogeneity.

This research attempts to utilize the available information on the geology of the subsurface, effectively identify stratigraphic layers, and model appropriately. By kriging topographic data and borehole log data that differentiate layers of varying properties and conductivities, the attempt is made to provide a more accurate picture of the subsurface. In contrast to the previous modeling exercises by Brainard and Reynolds, the objective is to access the importance of horizontal layering on the flow regime and to evaluate the ability to quantify anisotropic differences in a geologic unit whereby vertical hydraulic conductivities may be orders of magnitude less than conductivities in the horizontal. The *DYNFLOW* model of Camp Dresser & McKee, Inc. (CDM) is used to model the flow in the watershed.

1.3 Organization of Thesis

This thesis is organized into two major sections. The first includes Chapters 1–4 and establishes the background and theoretical directions. Chapter 1 defines the motivation for this research, states the problem of investigation and establishes the depth to which the problem will be studied. Chapter 2 gives the depositional history of the watershed and discusses the geologic influence on hydrologic parameters. Chapter 3 presents a discussion of the conceptual flow model, based on data from previous studies within the watershed, while Chapter 4 is a chemical characterization of the watershed with particular emphasis on arsenic equilibrium, speciation, and mobility.

In part two, Chapters 5 and 6, results of the flow model are presented. Chapter 5 describes the modeling process using *DYNFLOW*, a three-dimensional finite element flow model. Chapter 6 ties all sections together, linking the hydrology, geology, and chemistry to the results of the flow model and presents recommendations and directions for future research as an outgrowth of this thesis.

Chapter 2

Geological Characterization of the Aberjona Watershed

2.1 Depositional History

The Aberjona watershed overlies the Fresh Pond buried valley which is located between Wilmington and the Charles River, and includes the Aberjona River and the Mystic Lakes (Figure 1.1). The thick glacial ice that formed the buried valley over a duration of hundreds of thousands of years is a result of the last glaciation in the region, more than a million years ago. Climatic fluctuations caused ice sheets up to thousands of feet in thickness to be compacted by the overburden pressure of the weight of this ice-mass and to flow and spread throughout the region. The glacial deposits that are exposed at the surface, developed by hundreds of millions of years of compression, cementation, and solidification into rock are deposits of the last ice sheet that is known to have covered the New England area. (Kaye, 1976; Leet et al., 1978). It is also possible that older ice sheets may have deposited sediments, especially in the buried valley (Chute, 1959).

The glacial deposits are linked to the Pleistocene epoch of the Cenozoic era, while the bedrock is Pre-Quaternary (Kaye, 1976). Figure 2.1 shows the surficial geology in the watershed, with the more transmissive glacial outwash lying along the axis of the buried valley and,the glacial till located between the outwash and the boundary

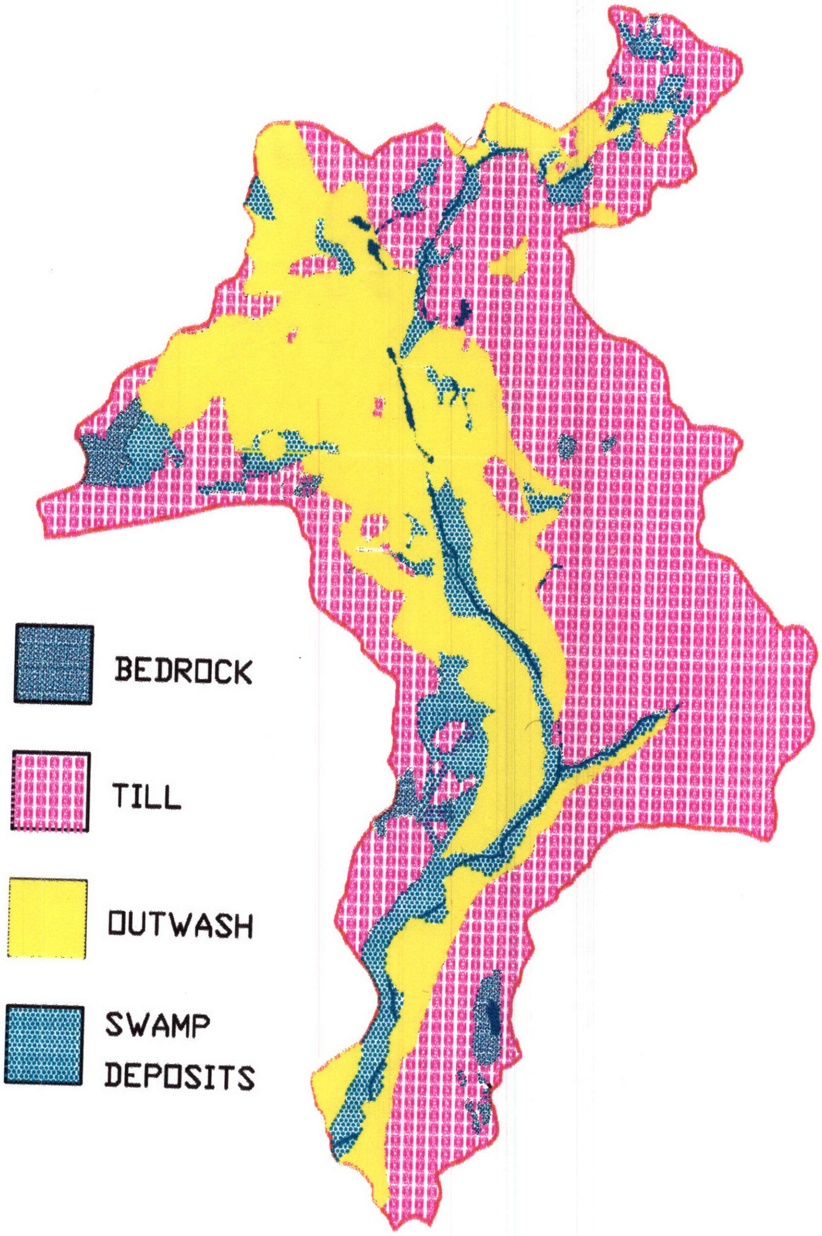

Figure 2-1: Surficial Geology

of the watershed. The lower boundary of the watershed is crystalline bedrock which may be encountered up to approximately $30m$ below the surface (Roux, 1991) and also present as outcrops throughout the watershed (Figure 2.2).

Stratigraphic layering may significantly influence the flow regime and the transport pathways for arsenic. Although the depositional nature of this formation is extremely complex, the major geologic events that create the stratigraphy are itemized below. The major events in the formation of this Aberjona River valley are based on the description by Chute (1959). While it is impossible to accurately date the following events, the chronological history is presumed sufficient to chronicle the development of the important geological features.

- The advance of the ice and deposition of ground moraine produced till deposits that cover the highlands in the buried valley. These deposits also contain gravel, sand, and clay.
- The retreat of the ice front allowed for the deposition of outwash material which varies in composition throughout the area. While the layering represents an ordered bedding pattern inclined southward, the deposits range from boulders to poorly sorted gravel resembling till.
- Deposition of clay occurs in the topographic lows of the sub-basin, deposited as the ice melted away from the Boston lowland. The clay layer contains interbedded sand and gravel deposits.
- The readvancement of the glacial ice was sufficient to disturb and transport previously deposited clay. The clay does not appear stratified; although, within the Aberjona River Sub-basin, there is a variety of material ranging from boulders and pebbles to sand and gravel.
- As the majority of the glacial ice in the Aberjona River valley melted, more outwash material was deposited, with the composition mainly silt, sand, and pebble-sized gravel.

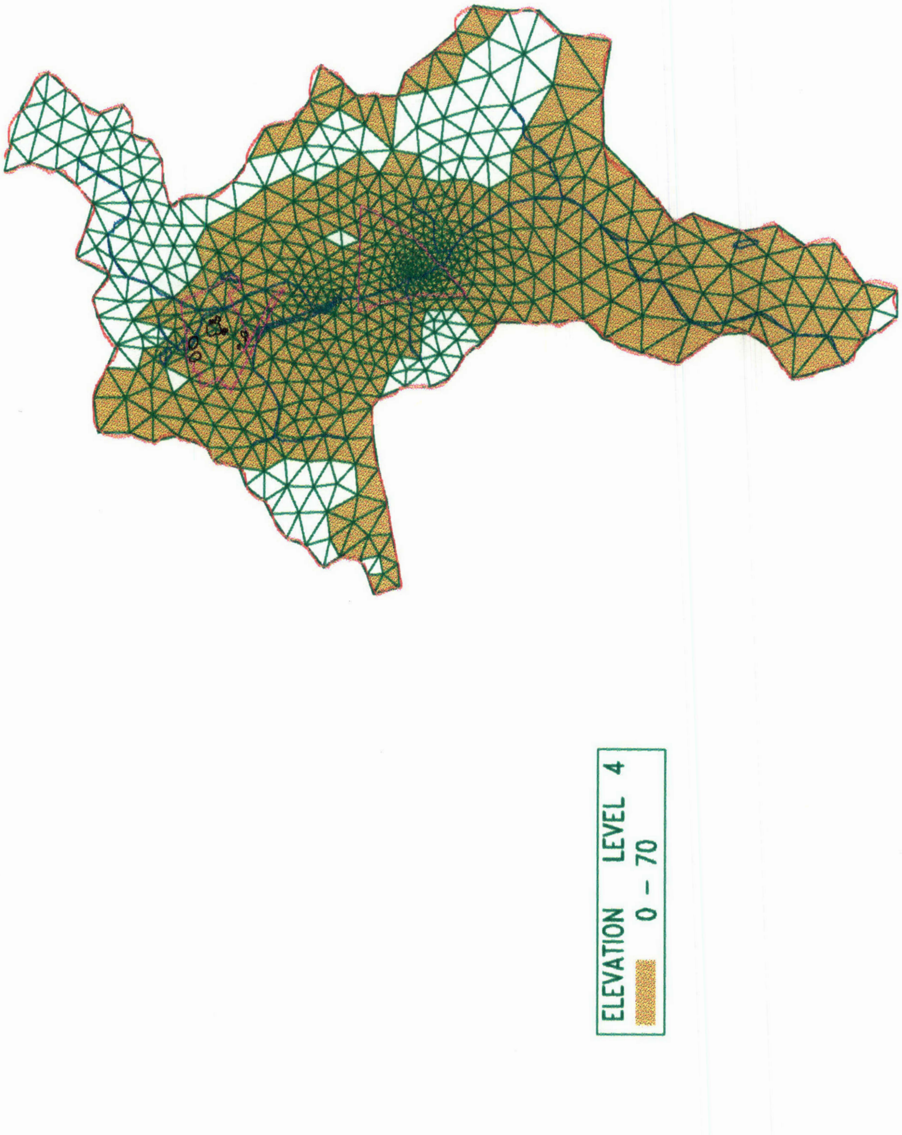

Figure 2-2: Extent of Sand Layer (Shaded) and Bedrock/Till Outcrops (Unshaded)

- Clay deposits, with some interbedded sand and gravel, were deposited concurrent with the glacial ice melt. This deposition occurred primarily in lake or marine environments.

- The deposits of outwash in the northern portion of Aberjona River valley are mostly clay, while in the southern portion of the valley, the outwash is predominantly sand and pebble-sized gravel—in places, the sand and gravel are interbedded. There are significant variations in elevation due to differences in the surface elevation of the underlying clay, influenced by compaction, erosion, and melting ice.

- Eroding valleys of the Aberjona River and Horn Pond Brook may have produced a majority of the aforementioned outwash. It appears the melting of the ice blocks was the controlling process as late glacial streams eroded outwash deposits in the valley, becoming more deeply eroded as the blocks of ice melted.

- The melting of the last remains of glacial ice marked the end of the period of outwash deposition some 12,000 years ago. The melting of the remaining, separated ice blocks formed the current water-filled depressions such as the Mystic Lakes and Wedge Pond.

- There have been clay, silt, sand, gravel, and peat deposits in the streams, ponds, and marshes subsequent to the melting of the last masses of glacial ice. However, most of these deposits are covered by the ponds and marshes.

It is evident through interpretation of the surface geology and observation of borehole logs that this buried valley contains a wide range of glacial material with various mechanical and hydraulic properties, including interbedded till, gravel, sand, silt, clay, and peat (Chute, 1959). Because of the variety of material types and their associated properties, it is critical that the sub-surface conditions modeled reflect the properties provided by borehole logs and other information. Figure 2.3 shows the location of the boreholes used to determine geologic layering for the modeled area.

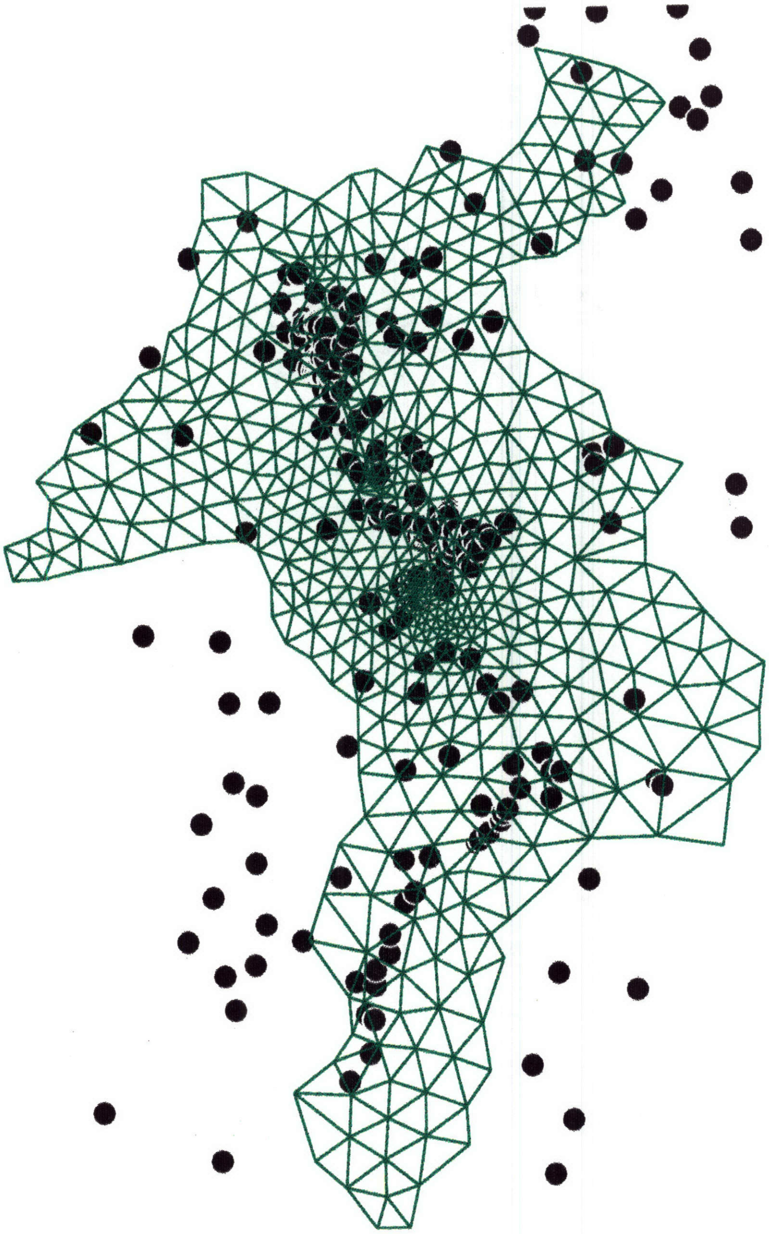

Figure 2-3: Geologic Borehole Locations

Additional points are a reflection of data obtained from topographic and surficial geologic maps from the U.S. Geologic Survey.

2.2 Geologic Data and Hydrologic Influence

2.2.1 North of Highway 128 (*Industriplex*)

Within the Aberjona Sub-basin, there are two (2) Superfund sites—Industriplex, located north of Highway 128 and Wells G&H, south of Highway 128 (Figure 3.1). Significant portions of the data for the area are concentrated within and around the site boundaries as illustrated in the aforementioned figure. Because of the distribution of sampling and the various geologic materials and properties, a more accurate geological characterization is provided by highlighting the major properties of the watershed both north and south of the the highway.

Crystalline Bedrock can be encountered up to $33m$ below the ground surface and exists in other areas as outcrops. Because of the relatively smooth surface topography, the depth to bedrock is primarily dependent on the bedrock topography. The bedrock is fractured within a meter of the surface and becomes more permeable with depth. However, in the northern portion of the Aberjona River sub-basin the fractures are effectively sealed with finer-grained material that reduces the transmissive ability of the bedrock. Thus, the bedrock may serve as a no-flow boundary to the aquifer (Roux, 1991).

Glacial Till—as thick as $10m$—is not generally found along the axis of the buried valley. Up to $9m$ below ground, the till is a combination of unsorted boulders, cobbles, sand and gravel, silt and some clay. This dense poorly sorted material has a lower effective conductivity than the sand and gravel, above (Roux, 1991; Stauffer, 1983).

Sand and Gravel is thickest in the southern portion of the Industriplex area ranging to $35m$ Roux, 1991). From the surface, sand and gravel may be met up to $3m$ below ground. This unconsolidated aquifer unit of glacial outwash consists of fine sand and coarse gravel with silt, silt lenses and some cobbles and is the most permeable of the watershed (Roux, 1991).

Peat and Swamp Deposits are present throughout the watershed, however there is no continuous layer of this material. In places as thick as $4m$, the peat will extend from the ground surface to approximately $5m$ below ground. Containing peat, organic silt, clay, and fine sand, these deposits are not very permeable (Roux, 1991).

Fill is the most varied of the geologically classified units. Fill in some areas are as thick as $3m$, but always extending from the ground surface. Construction debris, fine sands, blasted bedrock fragments, and animal hides may be considered fill. Depending on the ratio of the mixture, the conductivity of a fill deposit may be extremely varied (Roux, 1991).

2.2.2 South of Highway 128 (*Wells G&H*)

The groundwater, in the southern portion of the Aberjona Sub-basin, is primarily found in the bedrock underlying the entire area and the overlying glacial drift. In areas the two geologic layers are separated by a thin and discontinuous sheet of till. Due to weathering and erosion of materials, the till is exposed in several places in the watershed. Figure 2.1 shows the where the till is at the surface. In the wetland areas peat of variable thickness and expanse overlies the glacially stratified drift. The groundwater is both confined and unconfined—confined in the bedrock and unconfined in the drift, except where overlain by peat.

Crystalline Bedrock The majority of the bedrock underlying most of the valley is Salem Gabbro-Diorite—a medium-grained igneous rock of the early Paleozoic age (Myette et al., 1987). On either side of the bedrock valley, there is more weathered and fractured medium-to-fine-grained igneous rock of the Late Proterozoic age—Dedham Granite (Myette et al., 1987; Kaye, 1976). Water within the bedrock is found primarily in fractures and joints. The bedrock can supply significant yields of water where there are many open and connected joints. The depth to bedrock varies. At the surface where bedrock outcrops are present, depth ranges from zero to greater than 40 meters in the center of the valley. Also, bedrock hills and depressions that were influenced by the extreme climatic fluctuations that caused glacial ice to advance and retreat, may significantly affect the local groundwater flow regime. Wells screened in the bedrock east of the Wells G&H produced yields in excess of $500m^3/day$, approximately 1-2 orders of magnitude greater than typical bedrock wells (Delaney and Gay, 1980; Myette et al., 1987).

Glacial Till The glacial till, as in the northern portion of the Aberjona watershed is found generally on the hilltops along the eastern and western boundaries. This till is composed of clay, silt, sand, gravel, and boulders and is of similar composition to the glacial drift (Castle, 1959; Myette et al., 1987). In several areas, the till was observed to be compacted and relatively dense, significantly reducing discharge or flow through this layer of material. Reported yields are on the order of less than $10m^3/day$ (Delaney and Gay, 1980; Myette et al., 1987).

Sand and Gravel The stratified glacial drift is composed primarily of sand and gravel and produces significant quantities of the domestic water supply. As the drift overlies the bedrock, its thickness is zero in the vicinity of bedrock outcrops and may reach in excess of 40 meters in the valley of the watershed. The lithology of the drift varies both horizontally and vertically ranging from a mixture of silt, clay and fine sand to coarser sand and gravel. In some areas the stratified drift may yield up to $3000m^3/day$ with an estimated transmissivity of approximately $400m^2/day$ (Delaney and Gay, 1980; Myette et al., 1987).

Peat and Swamp Deposits The peat is located in wetland area of the Aberjona watershed and is a nearly continuous layer which confines the the groundwater in the aquifer below. The average thickness of the peat deposits ranges from approximately $0.6m$ - $2m$; however, core samples have revealed peat as thick as $8m$ (Myette et al., 1987). The peat may be an important link in the steam-aquifer interaction. Because it is relatively loose and nearly saturated, groundwater is discharged to the river through the peat under normal conditions, while streamwater infiltrates through the peat into the groundwater under pumping conditions (Myette, et al., 1987).

2.3 Summary

To model the transport of arsenic within the Aberjona River sub-basin, it is important that the flow regime be modeled as accurately as possible. The subsurface geology should be represented in sufficient detail to capture the macroscopic properties of the region and, potentially, local effects due to layering or other small scale depositional features. It is nearly impossible to provide detailed information on the structure and permeability of bedrock environments that significantly affect flow and transport; however, in granular environments, more information is usually available, but not exhaustive (Mackay, 1990).

The transport of arsenic dissolved in groundwater will be governed, primarily, by advection—as the particles of arsenic move with the groundwater flow field. By utilizing available geologic information, the potential for the model to reproduce field data is increased. It is expected that arsenic will be more mobile in layers with higher conductivities, conforming to preferential flow paths through the variable soil medium. Information on the differences in horizontal and vertical hydraulic conductivities of layers is essential to modeling the dispersion of arsenic—where more lateral dispersion is expected in layers with extremely small vertical conductivities.

Additionally, geochemical influences may affect arsenic transport; as the organic nature of the peat deposits may cause arsenic to be trapped and removed from solution. In the vicinity of the hide piles, the geochemistry creates an environment favorable for reducing the arsenate species to arsenite which is also more mobile and more toxic. A detailed model of the subsurface geology is, therefore, necessary to depict the hydro-geochemistry within the Aberjona watershed with some degree of confidence.

Chapter 3

Hydrologic Characterization of the Aberjona Watershed

3.1 Introduction

The most dominant of the hydrologic influences on contaminant transport in the Aberjona Watershed is the Aberjona River and its tributaries. The river extends from the northern portion of the Aberjona River Sub-Basin, through the Industriplex and Wells G & H sites, and to the southern sub-basin area, into the Mystic Lakes (Figures 1.2 & 3.1). The river slopes approximately $0.0016 m/m$ while draining the watershed. Three major tributaries of the river include "Halls Brook which drains northwestern of Woburn, Sweetwater Brook which originates in Stoneham, and Horn Pond Brook which drains western Woburn and feeds Horn Pond (Brainard, 1990)." The Halls Brook Storage Area is another important feature of the sub-basin hydrology as it was constructed to reduce flood flow in the Aberjona River (Figure 1.1) (Roux, 1991). The relation between the surface-water bodies and the sub-surface groundwater defines the stream-aquifer interaction, a relationship with important physical effects.

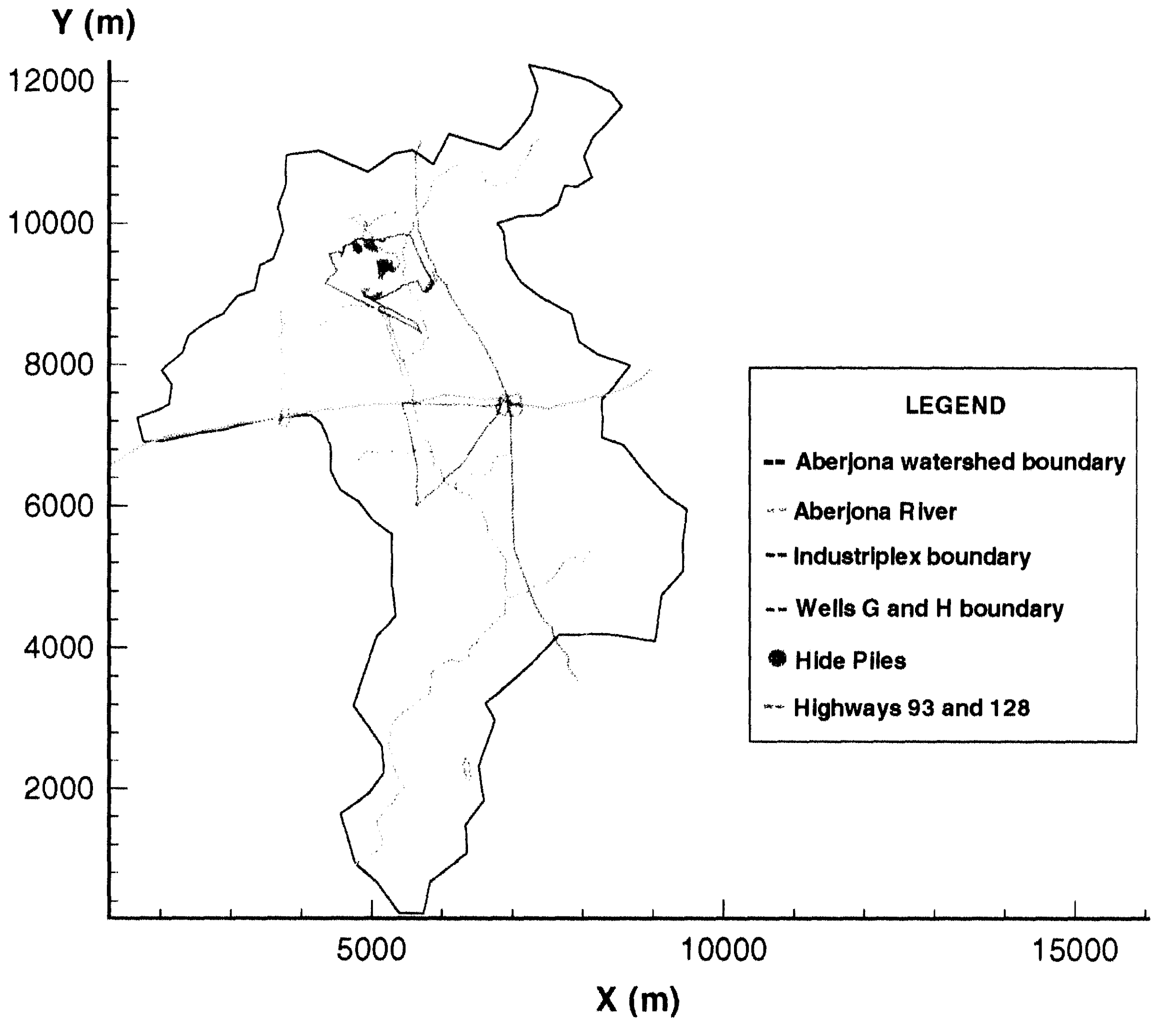

Figure 3-1: Aberjona River Sub-Basin

3.2 Conceptual Flow Model

In the northern portion of the Aberjona River Sub-Basin, the surface-water drainages at the Industriplex site are predominantly gaining streams—characterized by an increase in flow from inflowing groundwater (Roux, 1991; Fetter, Jr., 1980). The more shallow groundwater—*groundwater at approximately the same depth below the water-table surface as the depth of the bottom of the stream*—is influenced by the vertical gradients that forces the flow towards and into the surface-water streams (Roux, 1991). As the lithology within the sub-basin is variable, so is the stream-aquifer interaction that defines whether recharging or discharging conditions exist. Although, the stream is predominantly a gaining stream, there is a reversal in the relationship during periods of intense rainfall and high runoff events when the stream becomes a loosing stream—characteristically replenishes/ recharges the aquifer (Roux, 1991).

Seasonal variations in precipitation do not effect the overall flow patterns and directions; however, the magnitude of the heads do change. Because the direction of groundwater flow is not altered by the transient conditions observed through various seasons, there are implications that contaminants may be advected from the subsurface to the surface waters, where the potential for danger is increased dramatically (Roux, 1991). Although "a recharge boundary to the aquifer, [under pumping conditions, Halls Brook] is not a constant-head boundary because the brook only penetrates [approximately 1 m] into the total saturated thickness of the water-table aquifer [up to 20+ m] (Roux, 1991)."

Field data suggest the potential for vertical movement of groundwater from the unconsolidated outwash material into the bedrock only in the northern portion of the watershed (Roux, 1991). The thinness of the layers, particularly, the thinness of the glacial outwash in the north and near the model boundaries increase the potential for recharge to the unconsolidated and bedrock flow systems (Roux, 1991).

The results of field data is shown in the contour plots of Figure 3.2. The results are based on measurements taken at the locations displayed in Figure 3.3. The reader, however, is cautioned that the data points are extremely dense in the area

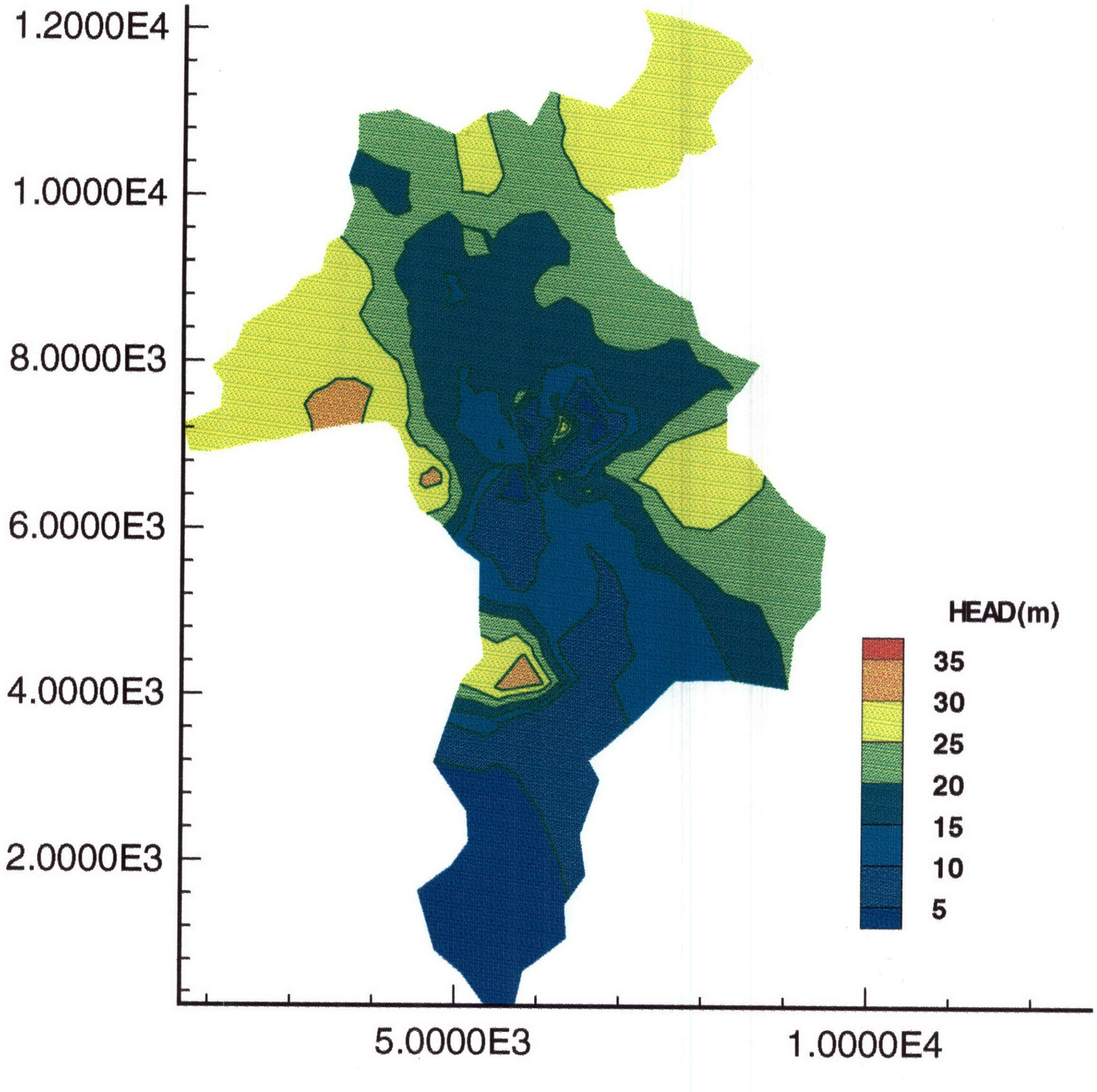

Figure 3-2: Field Head Data Interpolated to Model Grid

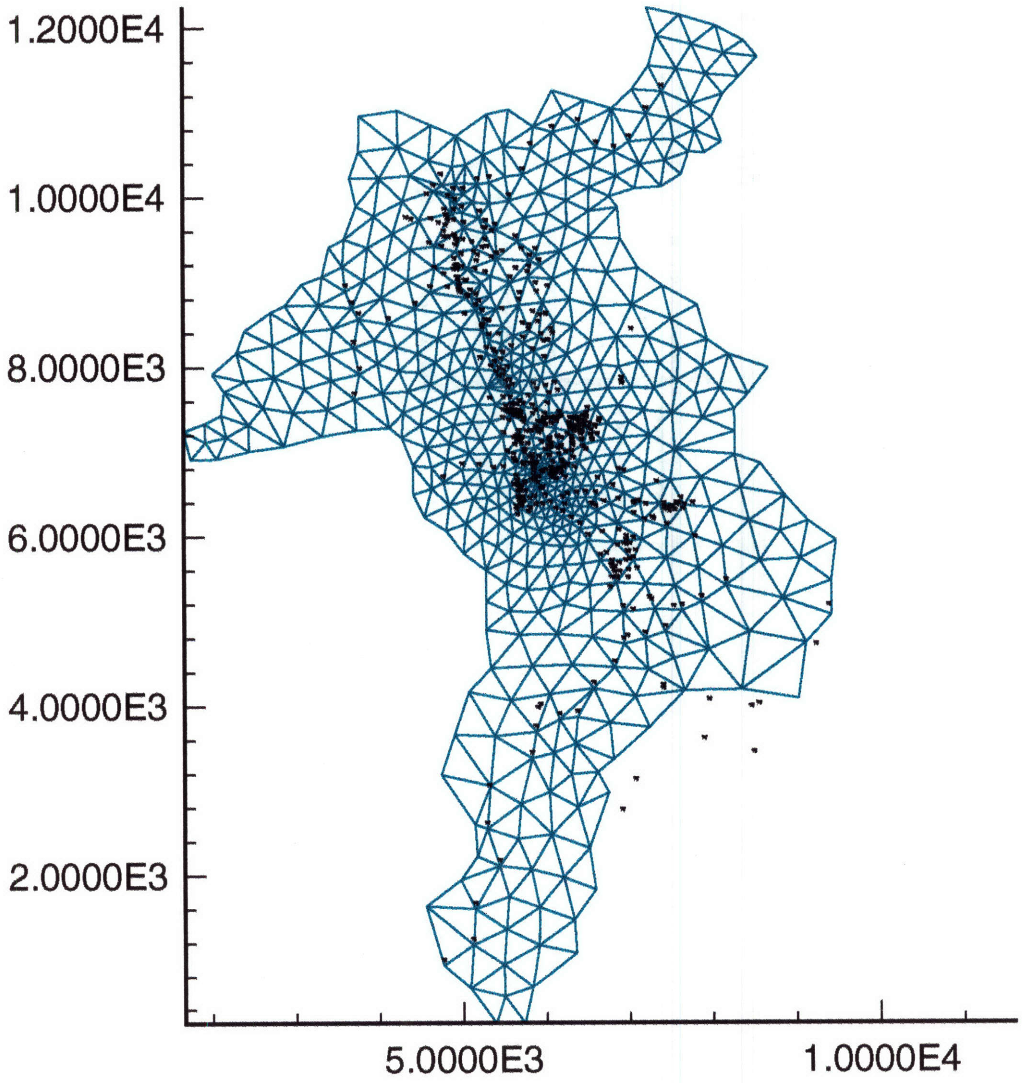

Figure 3-3: Location of Hydrologic Field Data Points

near Wells G & H and Industriplex and sparsely scattered in the remainder of the Aberjona River Sub-basin. Thus, Figure 3.2 represents a qualitative description of the head variation within the sub-basin. The higher portions of the Aberjona River Sub-basin are recharge zones where groundwater flow begins and moves toward the Aberjona River and Hall's Brook. The shallow groundwater flow patterns are driven primarily by the relationship between the stream and the aquifer, while the deeper groundwater flow is heavily influenced by the aquifer geometry. Also, there is the potential for the reversal of flow fr om the surface to groundwaters during periods of intense surface-water flow (Roux, 1991; Reynolds, 1993).

3.3 Horizontal and Vertical Gradients

Additionally, upward vertical gradients that allow for the upward flow of groundwater from the bedrock into the glacial till and outwash layers are possible. The potential for "leakage from the till and crystalline bedrock into the overlying unconsolidated deposits may occur as indicated by vertical and horizontal gradients near the [outwash]/till-bedrock boundaries within the area south of the Industriplex site (Roux, 1991; Myette, et al., 1987)." Note however, that the exception is north of the Industriplex site where recharge may be occurring, and thus the flow reversed (Roux, 1991).

"The principal direction of [groundwater] flow on the western side of the Aberjona River valley is southeast on an average horizontal gradient of $0.005 m/m$. Vertical hydraulic-head gradients in the [glacial outwash] range from $0.002 m/m$ [downward] to $0.0006 m/m$ [upward] (Myette, et al., 1987)." In the outwash—stratified drift—east of the Aberjona River, the groundwater flow moves "toward the southwest with an average horizontal gradient of $0.02 m/m$ (Myette, et al., 1987)." The vertical head gradients east of the river are usually of greater magnitude than the gradients to the west. In the east, the vertical gradients are downward of magnitude ranging from $0.008 m/m$ to $0.01 m/m$ (Myette, et al., 1987). Roux (1991) concludes that "the upward or downward gradients [measured in the Industriplex area] do not reflect the potential for significant upward or downward vertical flow in the unconsolidated aquifer."

In the center of the Aberjona River Sub-Basin, the horizontal gradient is approximately $0.001 m/m$ and the flow is southward and parallel to the axis of the buried valley. The corresponding vertical head gradients are "upward toward the streambed of the Aberjona River (Myette, et al., 1987)."

3.4 Summary

The hydrology within the Aberjona River Sub-Basin is dominated by the Aberjona River. Detailed hydrologic information is critical to modeling the groundwater flow regime and accounting for vertical gradients within the aquifer, the relationship between the groundwater and surface waters, and potential contaminant pathways. Because the river is a predominantly gaining stream in the northern portion of the sub-basin, there is an increased potential for dissolved contaminants to be transported to a larger area in a shorter time span when contaminated groundwater recharges surface waters. Also, because of the horizontal gradients, the groundwater tends to flow to the center of the sub-basin—toward the river—and then, to the southern portion of the basin. The direction of groundwater flow is toward the Wells G & H site, providing a potential link to contaminant migration and human exposure with the natural flow regime. With a greater understanding of the hydrologic conditions, it is possible to more acc urately simulate field conditions during modeling, which is discussed in the following chapter.

Chapter 4

Arsenic Chemistry in the Aberjona Watershed

4.1 Occurrence of Arsenic

At the Industriplex Site concentrations of arsenic have been reported in the soil up to and exceeding 100 μg/kg. Also, groundwater data indicate that dissolved arsenic concentrations in wells near the largest of the hide piles—East Central Hide Pile—range above 28,000 μg/L. The 1976 drinking water standards for arsenic set the upper concentration limit at 50 μg/L. Because of the toxicity of arsenic, there is concern about its distribution within the watershed and possible effects through human consumption or exposure. Figures 4.1 and 4.2 show contours of arsenic concentrations in the groundwater and soil, respectively. The occurrence of arsenic in the Aberjona Watershed is linked to the industrial practices in the area during the late nineteenth and early to mid-twentieth century (Durant et al., 1990).

Several factors have influenced the movement and distribution of arsenic at the Industriplex site. Arsenical pesticides were manufactured at the site beginning in the late 1800's, possibly including lead m-arsenate, monolead o-arsenate, trilead arsenate and calcium arsenate compounds (Thompson, 1973). In the early 1900's magnesium and zinc arsenates were produced in substitution for lead arsenate (Roux, 1991). The use of herbicides within the area seems to have introduced several methylated arsenic

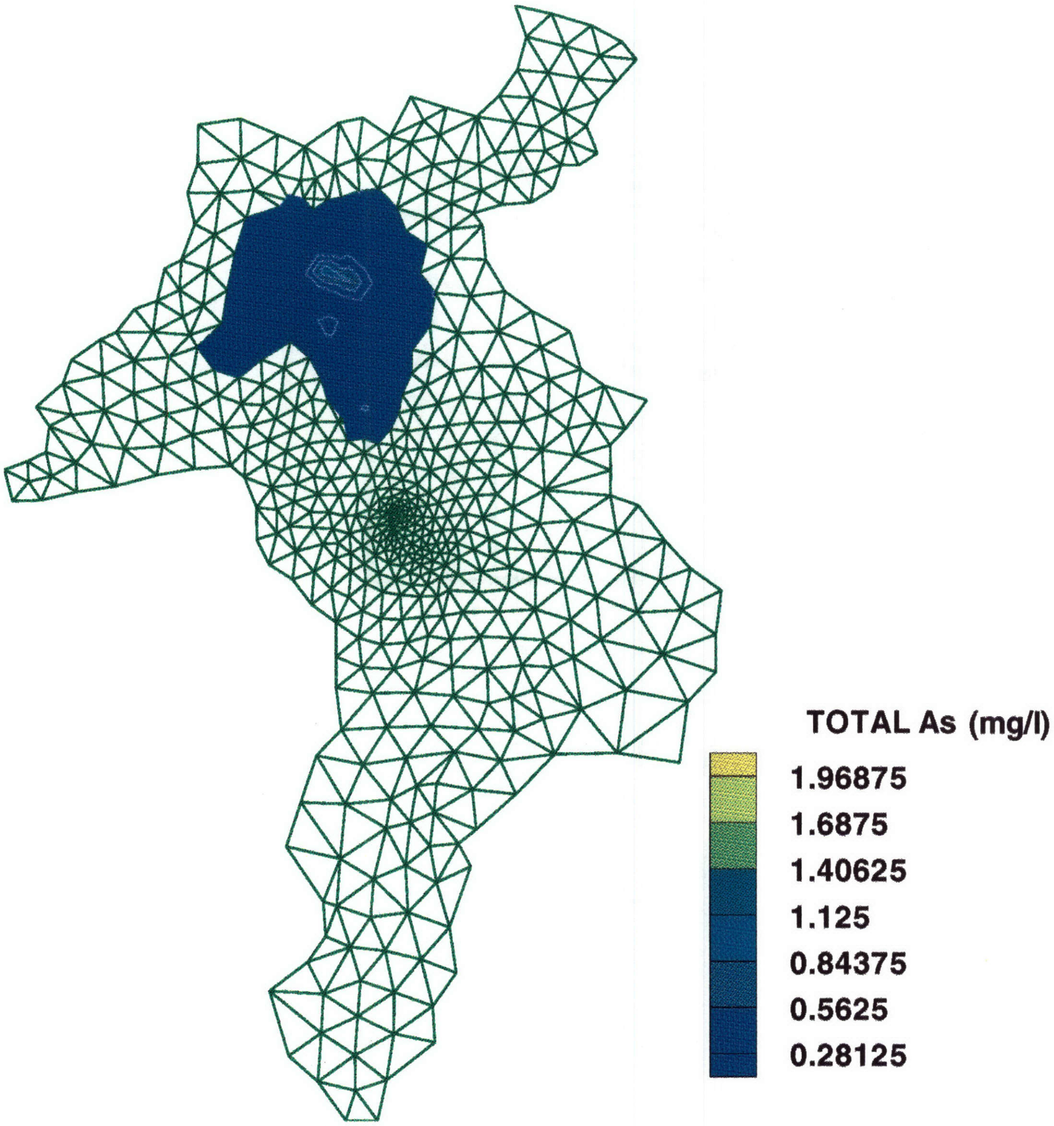

Figure 4-1: Arsenic in Groundwater at the Industriplex Site

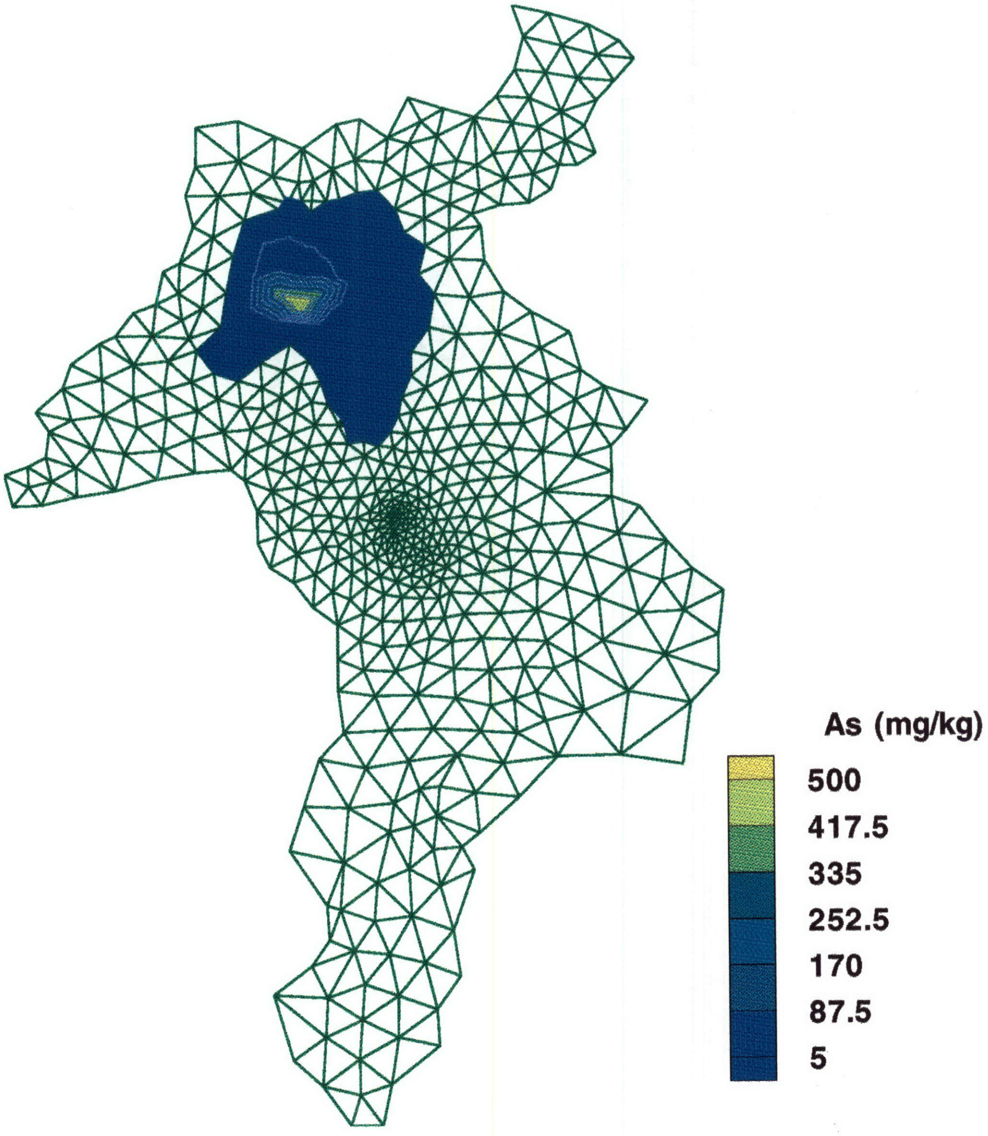

Figure 4-2: Arsenic in Soil at the Industriplex Site

Table 4.1: Arsenic Species Present in Aquatic Environments

Species	Formula	Oxidation Number
Arsenic	As	0
Arsenate	As^{5+}	+5
Inorganic Monovalent	$H_2AsO_4^-$	+5
Inorganic Divalent	$HAsO_4^{2-}$	+5
Arsenite	As^{3+}	+3
Inorganic	H_3AsO_3	+3
Uncharged	$HAsO_2(aq)$	+3
Arsine	AsH_3	-3
Monomethylarsonate	$CH_3AsO(OH)_2$	+5
Dimethylarsenate	$(CH_3)_2AsOOH$	+5

compounds to the site, as well. Additionally, arsenic may have been a minor impurity in pyrite, used at the site in the production of sulfuric acid (H_2SO_4) (Barnes, 1979). Further detail of these processes (Aurilio, 1993) present evidence that several hundred metric tons now present can be attributed to the production of sulphuric acid from arsenic-rich pyrites (approximately 170 tons of released As) and arsenical pesticides in the form of lead arsenate (approximately 35 metric tons)(Hemond, 1994).

4.2 Equilibrium Chemistry of Arsenic

Dissolved in water, arsenic is stable as arsenate (V) or arsenite (III) oxyanions (Table 4.1). Hem (1977) shows the importance of pH-Eh to conditions that dictate the field distribution of aqueous arsenates. Results of measurements in monitoring wells at Industriplex (Roux, 1991) show the dominance of the monovalent arsenate anion ($H_2AsO_4^-$) within a pH range of 3-7 and the divalent species ($HAsO_4^{2-}$) within the 7-11 range. In mildly reducing conditions, the arsenite uncharged ion $HAsO_2(aq)$ is dominant (Figure 4.3)(Roux, 1991; Hem, 1985; Aurilio, 1992).

Within natural environments, other factors that may reduce the concentration of aqueous arsenic are adsorption by hydrous iron oxide (Pierce and Moore, 1980) co-precipitation (as particles precipitate out of solution, the attached arsenic is removed,

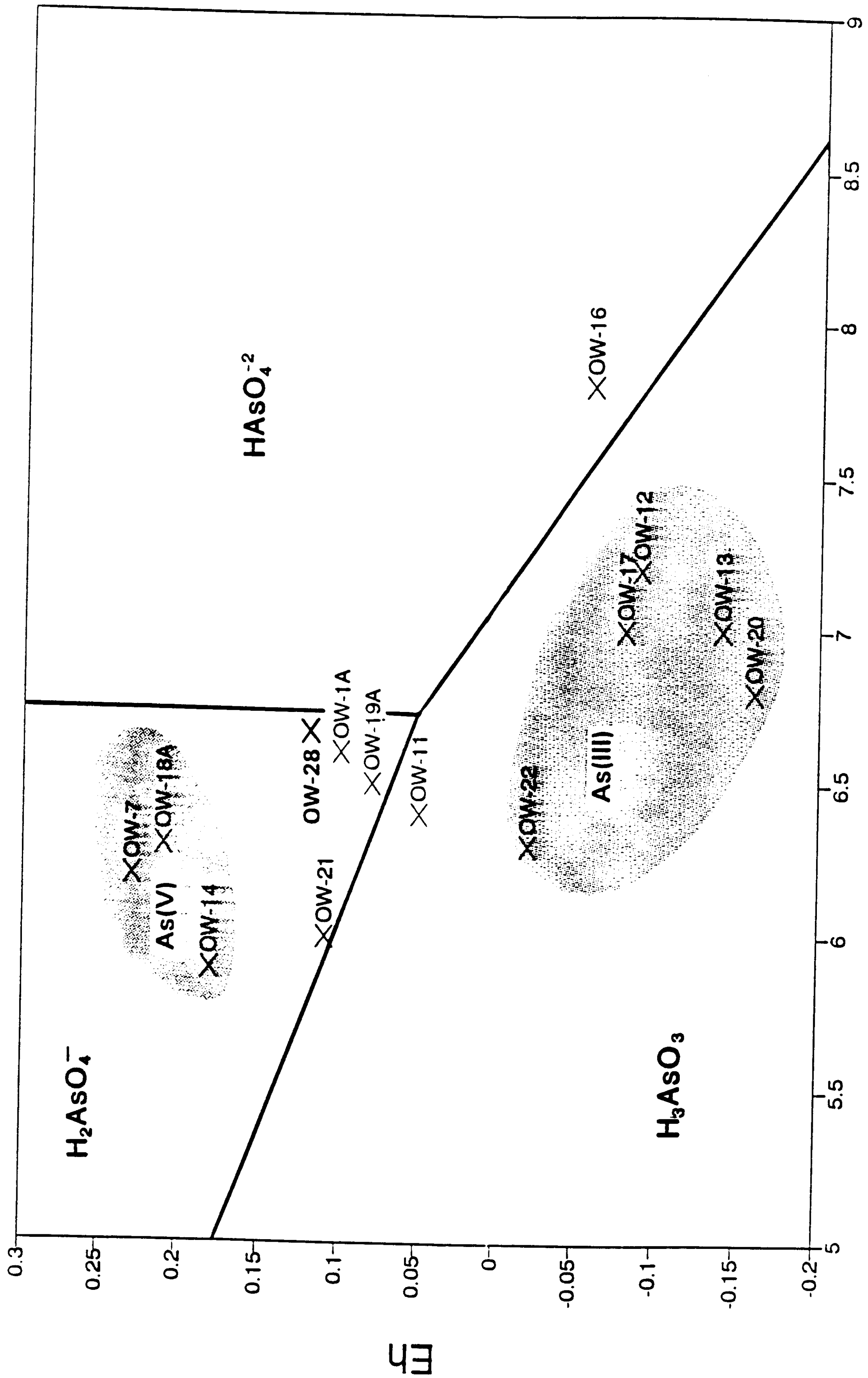

Figure 4-3: Theoretical Arsenic Speciation Based on pH and Eh
Source: Roux, 1991

also), or combination with sulfide in reduced bottom sediment (Kobayashi and Lee, 1978). Arsenic is an important element in biochemical processes. The synthesis of dimethyl arsenic ($(CH_3)_2AsOOH$) and methyl arsonic acids ($CH_3AsO(OH)_2$) is a result of biologically mediated methylation (Hem, 1985). Because of the difficulty of oxidizing dimethyl arsenic acid, it may remain a major constituent of total dissolved arsenic in surface water (Braman and Foreback, 1973).

The presence of arsenic at Industriplex is complicated by the speciation of arsenic in naturally occurring environments. Under oxidizing conditions, As(V) is predominant as is As(III) under reducing conditions (Roux, 1990)

$$H_3As(V)O_4 + 2H^+ + 2e^- \Longleftrightarrow H_3As(III)O_3 + H_2O \tag{4.1}$$

Conditions in the vicinity of the hide piles (Figure 4.4) are favorable to reduction because of the low values of dissolved oxygen (DO). Additionally, reduced arsenic has the potential to form organic complexes. There is a strong correlation between arsenic and iron (Fe) and manganese (Mn). Arsenate sorptivity is controlled by Fe and Mn oxides and hydroxides. Arsenite dominates in the reducing environment of the hide piles. The bio-geochemical conditions may be significant in influencing the further speciation of arsenic, as methane is formed by the bacterial decomposition of organic matter under water (Gillespie et al., 1986; Bloomfield, 1980; Roux, 1990) represented as

$$CH_2O + 2H^+ + 2e^- \Longleftrightarrow CH_3OH \tag{4.2}$$

Due to the biological and chemical processes that influence methylation, monomethylarsonic acid (MMAA) or dimethylarsinic acid (DMAA) are produced. After the formation of methanol in the vicinity of the hide piles, the methanol is then free to combine with arsenite to produce monomethylarsonic acid through bacterially mediated respiration (Roux, 1990)

$$CH_3OH + H_3AsO_3 \Longleftrightarrow CH_3AsO(OH)_2 + H_2O \tag{4.3}$$

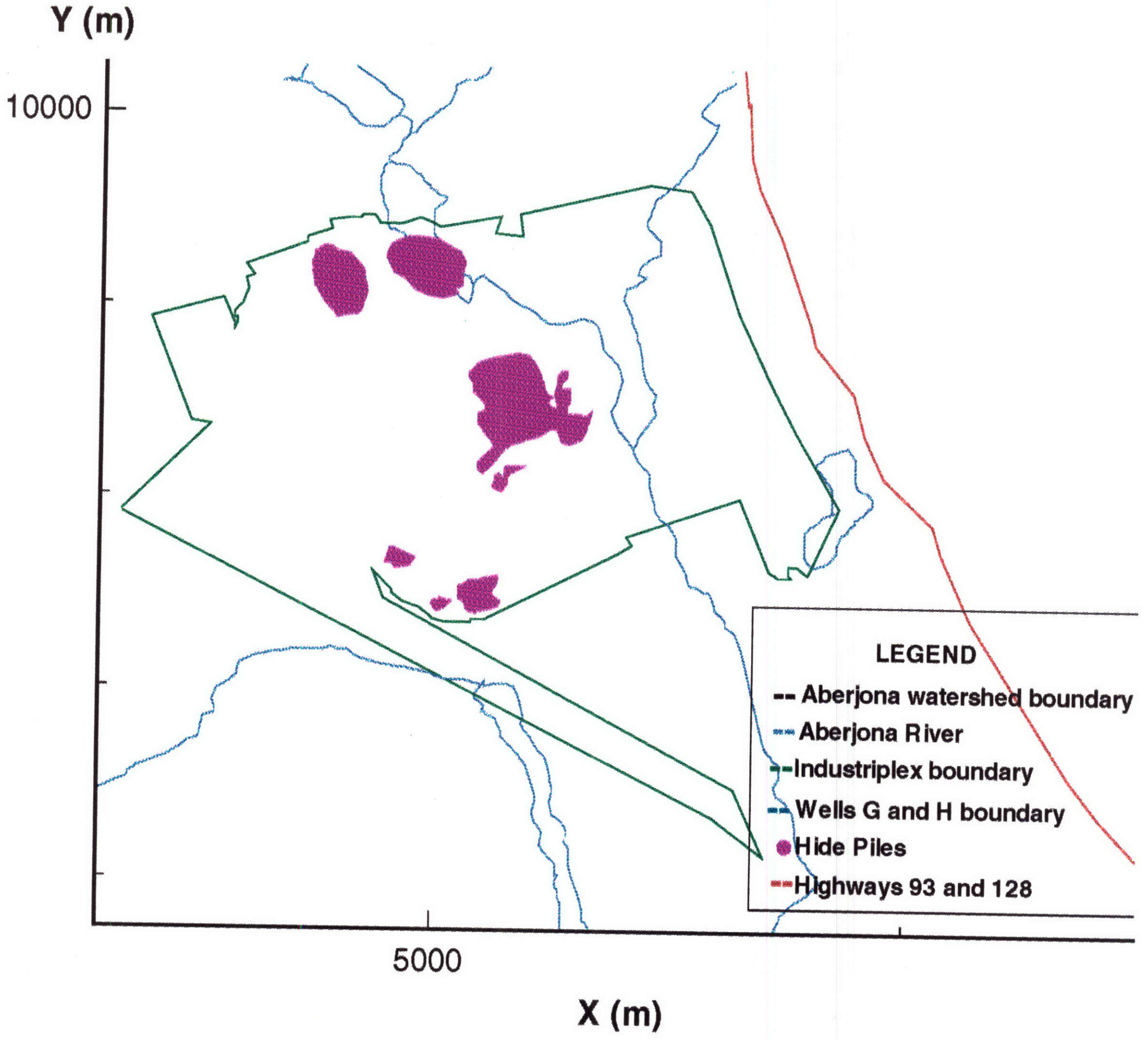

Figure 4-4: Hide Piles at the Industriplex Site

As the bacterially mediated respiration (Bloomfield, 1980) proceeds, the reaction produces dimethylarsinic acid. The following equation describes a potential step in the reaction pathway for arsenic reduction that produces dimethylarsenate (Roux, 1990)

$$CH_3AsO(OH)_2 + CH_3OH + 2H^+ + 2e^- \Longleftrightarrow (CH_3)_2AsO(OH) + 2H_2O \qquad (4.4)$$

Evidence suggests that organoarsenical complexes are less sorptive (Wauchope, 1975; 1983) while Mohan et al. (1982) and Holm et al. (1980) show that in aerobic and anaerobic environments, respectively, the order of affinity for arsenic speciation within sediments is arsenate > arsenite > MMAA > DMAA (Roux, 1991).

In summary, the arsenite species and the methylated species of arsenic are likely to migrate farther from the source than the arsenate species. Because arsenite is more toxic than arsenate, it is important to account for the full range of bio-geochemical processes and reactions that might impact this transport phenomenon. Accurate parameterization near the hide piles is critical to understanding the interactions between the hydrology, geology, and chemistry.

4.3 Effects of Organics from Hide Piles

The hide piles—a large source of organics—create an environment that is favorable for arsenic transport.

> Under reducing conditions, infiltration of precipitation through the soils containing metals at a hide pile leaches metals, the mobility of which is influenced through complexing with organic conjugate bases released from the hide piles (Roux, 1991).

Hence, the transport of arsenic is not only influenced by the hydraulic and geological conditions, but by the geochemical and biochemical processes that drive arsenic speciation and influence the sorption chemistry of arsenic, especially in the vicinity of the waste hide piles.

The hide piles were placed on top of the existing grade during the middle 1900's after the metal-containing soils were placed on the pre-1931 grade (Roux, 1991). The volume of buried hide material at the site is estimated at 260,546 m^3, including the East (95508 m^3), West (38203 m^3), East-Central (80991 m^3), and South-Central Hide Piles (45844 m^3) (Roux, 1984).

The hide piles are important because data suggests that "arsenic mobility is *only* facilitated downgradient from the hide piles." In the vicinity of the hide piles, particularly below the East, West, and East-Central Hide Piles, the environment is strongly reducing characterized by Eh < 0 mV and DO < 1 mg/L. Throughout the remainder of the Industriplex site conditions are favorable for oxidation with Eh potentials > 0 mV, DO > 1 mg/L, and the chemical oxygen demand (COD) < 25 mg/L (Roux, 1991).

High alkalinity values measured in the groundwater that intersects the East-Central Hide Pile indicate the presence of organic acids at the Industriplex site. These organic acids are generated from the breakdown of the hides and form strong aqueous complexes with metal cations, increasing the solubility and mobility of arsenic. Dissolved organic carbon can be a nutrition source for bacteria in the sub-surface which influences the bacterially-mediated methylation of arsenic (Roux, 1991; Rai, et al., 1984).

4.4 Conceptual Transport Model

4.4.1 Mobility and Speciation of Arsenic

The ability to trace Arsenic in the vicinity of the hide piles is extremely important. As precipitation infiltrates the ground near the hide piles, arsenate and arsenite salts are dissolved into the groundwater and transported to the water table. Here, any arsenate is reduced to arsenite because of the reducing environment and methyl groups from hide breakdown (Roux, 1991). Subsequent methylation allows for the forma-

Table 4.2: Pearson Correlation Matrix of Arsenic for Transformed, Standardized Groundwater Data

Parameter	Correlation Coef.	Parameter	Correlation Coef.
Fe	0.618	Mg	0.530
Ni	0.640	K	0.615
V	0.767	Alk	0.718
Eh	-0.518	pH	0.614
PO_4	0.624	COD	0.758

tion of MMAA and DMAA. Figures 4.5 & 4.6—contours of arsenate and arsenite, respectively—show that concentrations are highest in the vicinity of the hide piles along the upper reach of the Aberjona River.

At the Hall's Brook Holding Area (HBHA), the surface waters are recharged by the groundwaters and arsenic is removed from solution by sorption, indicated by contaminant analysis of sediment. This infiltration creates a reduction in surface water concentrations. Also, the biological activity in HBHA results in the sorbing of neutral organic complexes, such as DMAA, to the large amounts of organic carbon. The reducing environment near HBHA is capable of removing metals from solution (Roux, 1991)

4.4.2 Effects of Influencing Parameters

The speciation and mobility of arsenic is influenced by the concentrations and levels of other chemicals, as well as parameters that govern the geochemistry at the Industriplex site. Table 4-2 lists correlations in the groundwater data collected at the site and Figures 4.7–4.11 illustrate the contours of iron, DO, COD, Eh, and pH data, respectively.

The data indicates a strong correlation between arsenic and iron (Fe). The Fe(II):Fe(III) ratio may be used to assess the redox potential of the ground water (Figure 4.7). The distribution of iron, especially in the vicinity of the hide piles, is consistent with the occurrence of corresponding species of arsenic.

Another indicator in the ground water is the dissolved oxygen (DO) which can

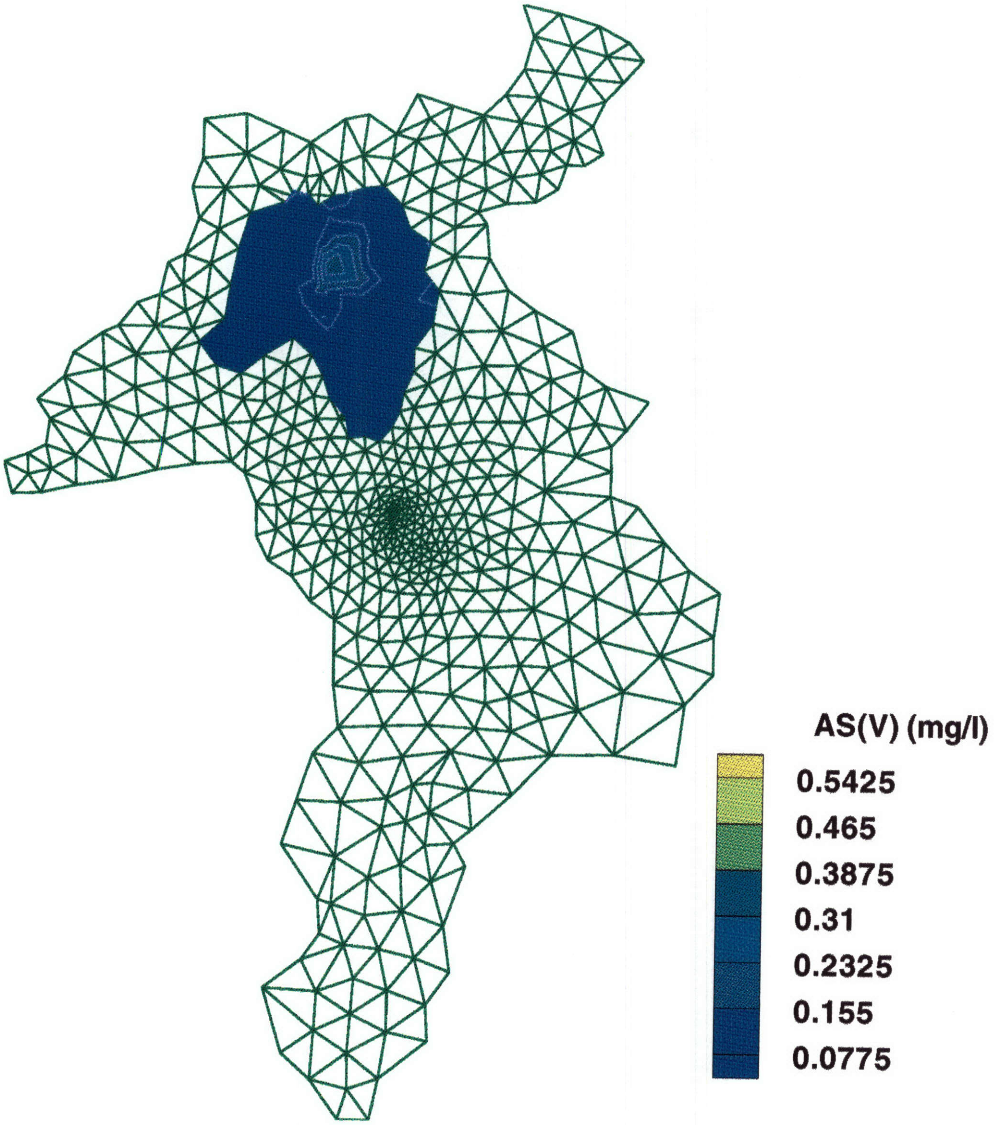

Figure 4-5: Arsenate Concentrations in Groundwater at the Industriplex Site

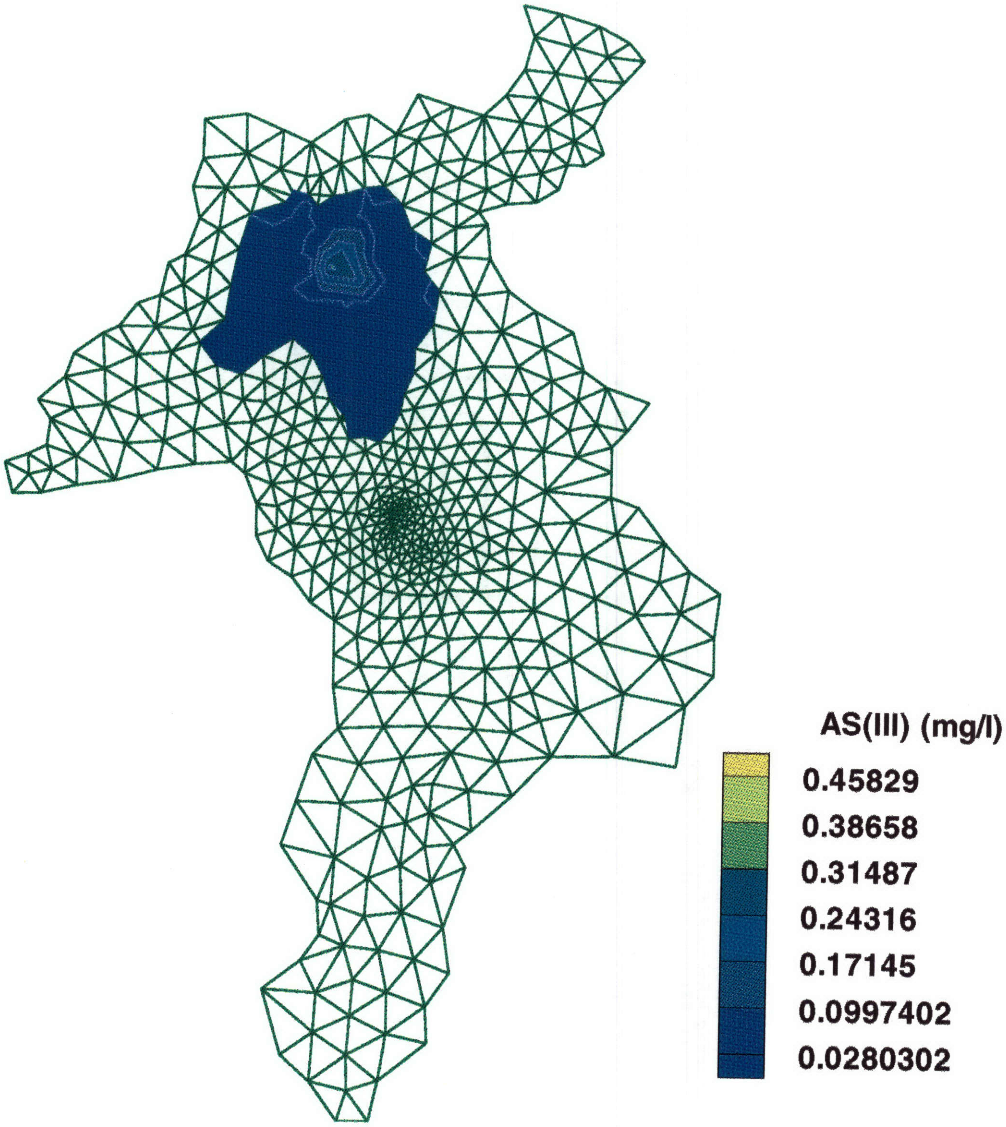

Figure 4-6: Arsenite Concentrations in Groundwater at the Industriplex Site

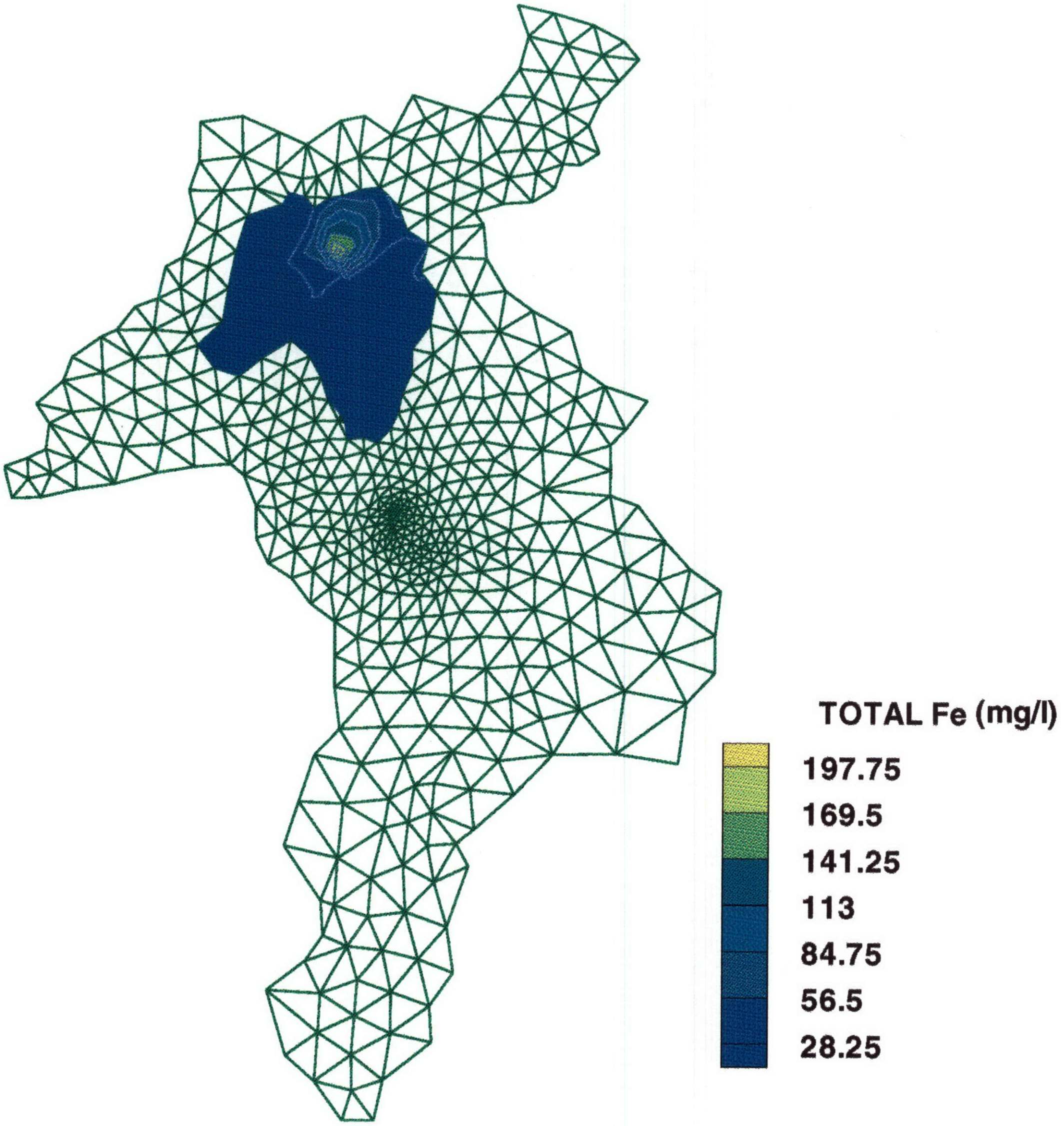

Figure 4-7: Iron in Groundwater at the Industriplex Site

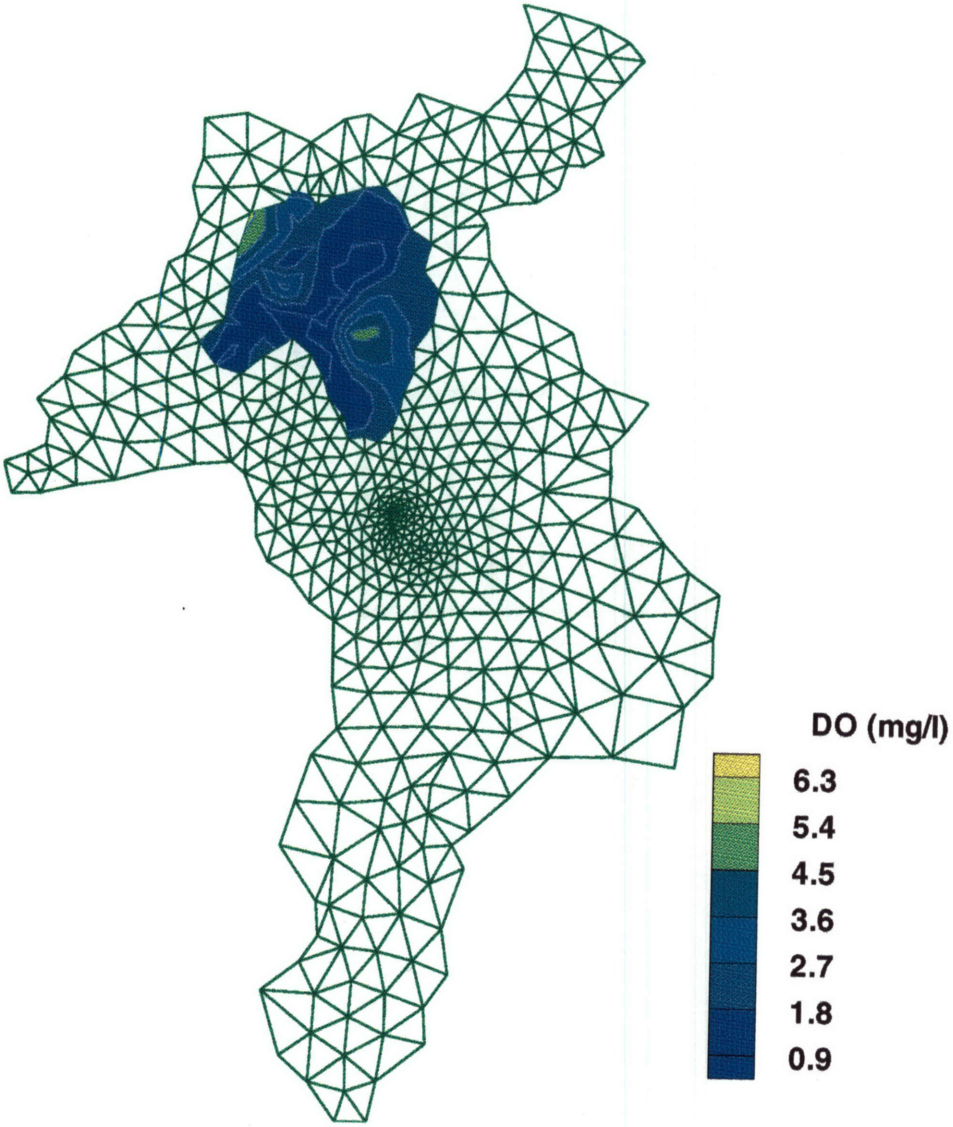

Figure 4-8: Dissolved Oxygen in Groundwater at Industriplex Site

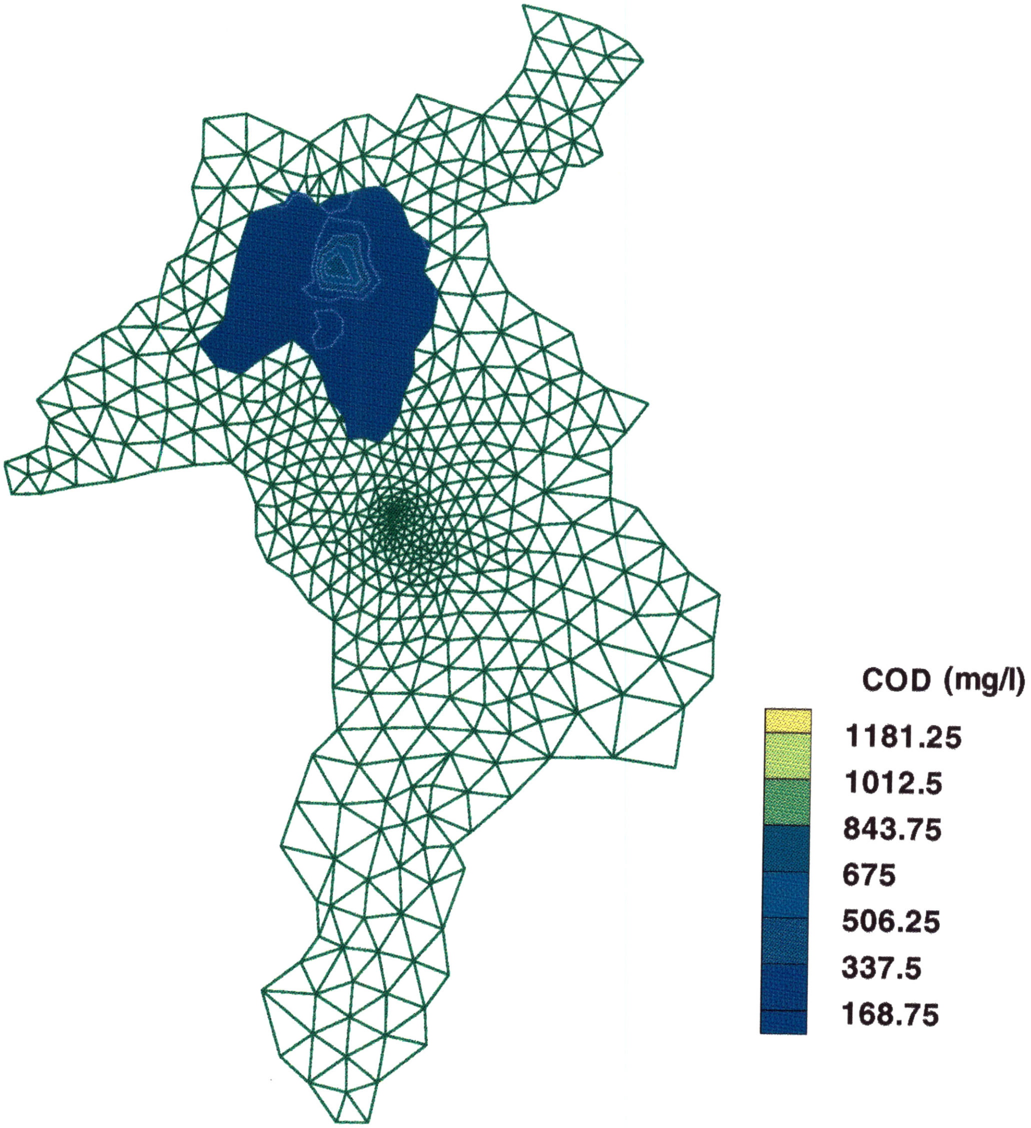

Figure 4-9: Chemical Oxygen Demand in Groundwater at the Industriplex Site

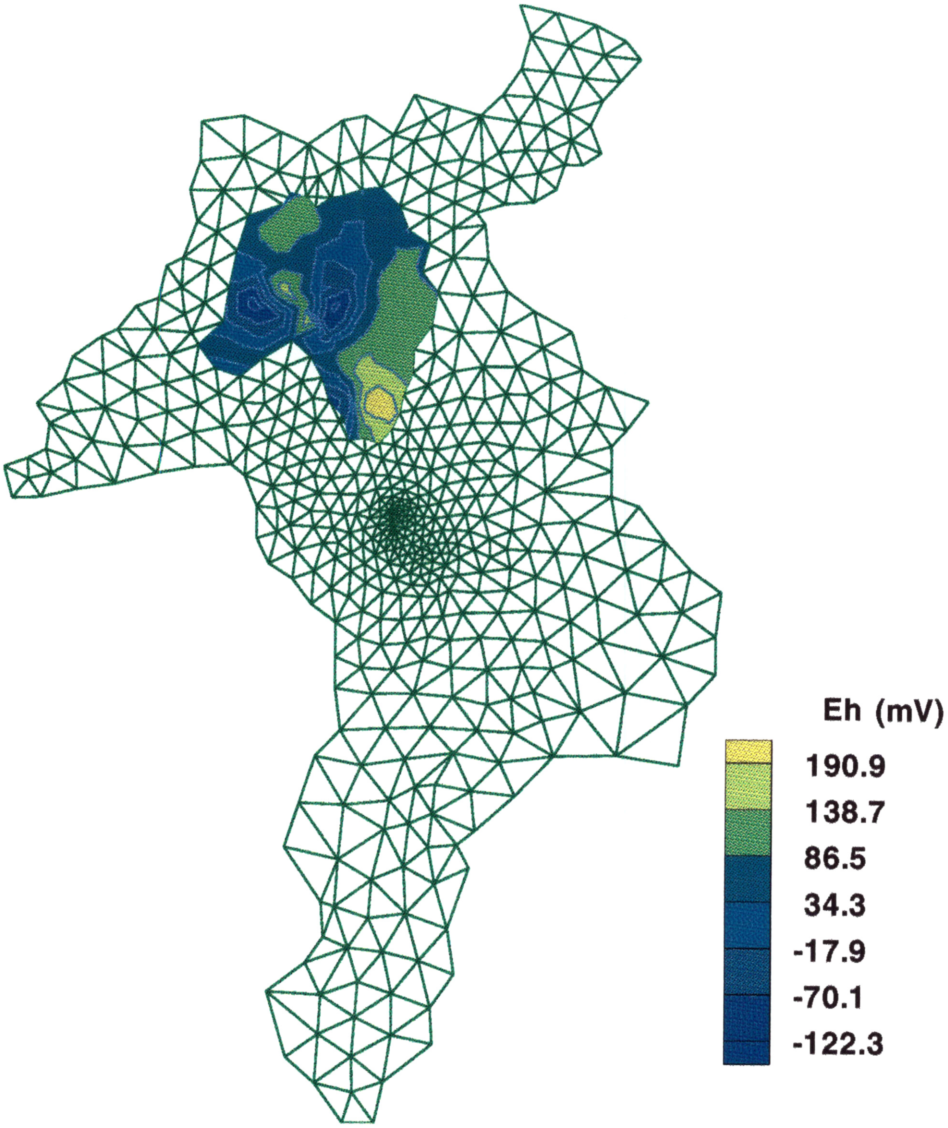

Figure 4-10: Redox Potential in Groundwater at the Industriplex Site

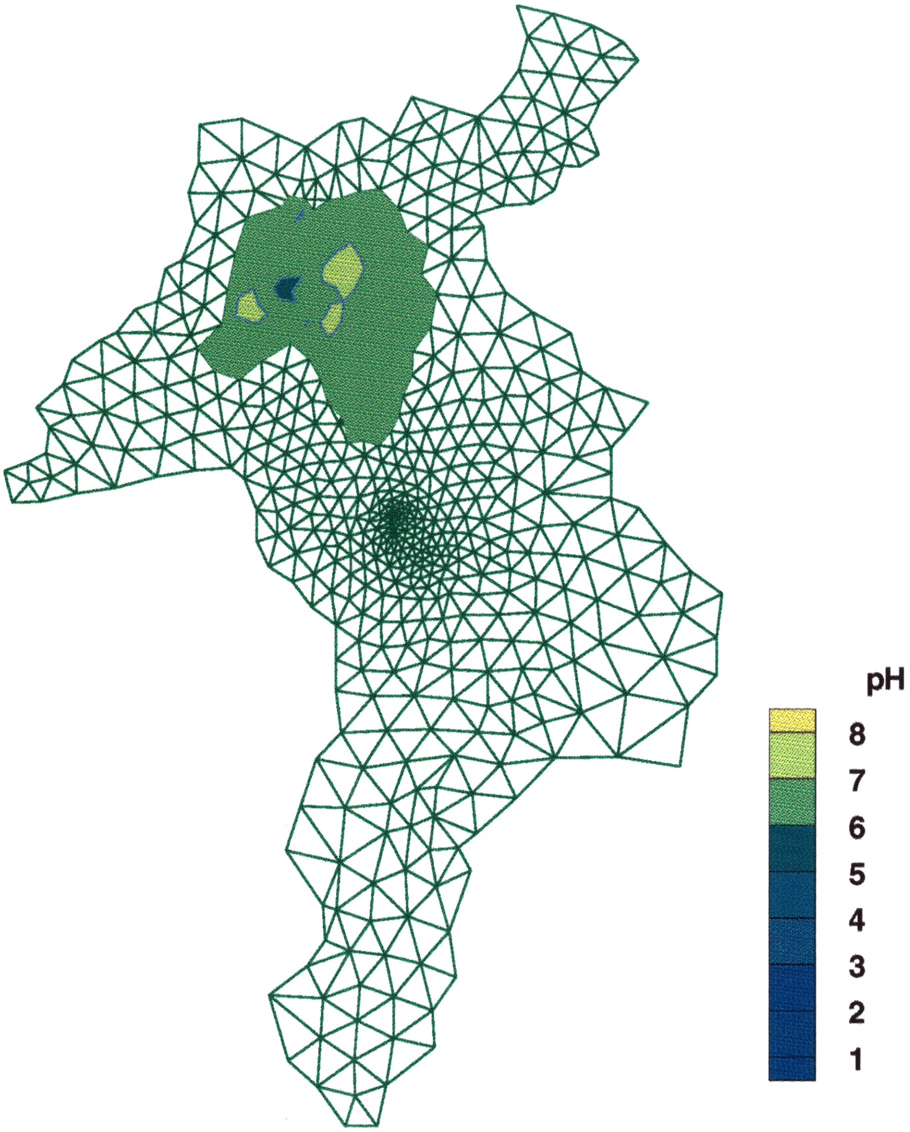

Figure 4-11: pH at the Industriplex Site

provide information about oxidation-reduction (redox) potentials (Eh). The DO is negatively correlated to COD. Therefore, in a strongly reducing environment in which DO is low and COD is high, higher values of arsenite are expected. Eh and pH are critical parameters for effective representation of geochemistry in aqueous environments as low Eh values (< 0 mV) indicate reducing conditions coupled with high electron availability and while low pH represents the high availability of protons for reaction (Roux, 1992).

The organic matter, in the vicinity of the hide piles, mediates the reduction of sulfate to aqueous sulfide forms. Volatile hydrogen sulfide gas is produced, as concentrations of aqueous sulfide increase (Roux, 1992). The field data collected at the Industriplex site (Roux, 1992), suggest an important relationship between sulfide and methylated arsenic aqueous species. Because MMAA is more mobile than arsenate and arsenite and more toxic, there are concerns that arise surrounding the transport potential within the area. However, once MMAA migrates out of the sulfidic ground waters, it is demethylated. Consequently, in the ground water zone where sulfide < 1 mg/l, DMAA—the most mobile of arsenic species—is less than measurable and MMAA is unstable.

Downgradient of the East-Central Hide Pile, phosphorous (P) is present. Phosphate (PO_4)is a limiting nutrient which controls microbial growth rates. PO_4 may influence arsenic mobility because it may appear chemically, similar to arsenate (AsO_4) (Roux, 1991). Arsenic mobility may be increased as PO_4 attempts to compete with AsO_4 for the same adsorption sites (Goldberg, 1986).

4.5 Summary

Through analyses conducted by various agencies and groups associated with the Industriplex site assessment and remediation, results indicate the present of arsenic plumes downgradient of the West and East-Central Hide Piles and arsenic, also downgradient of the South Hide Pile. Further, it is observed that the arsenic has migrated significantly, near the West and East-Central Hide Piles. The presence of these discrete dissolved inorganic plumes near the hide piles is influenced by the geochemical factors in the hide piles and metal adsorption properties (Roux, 1991).

Arsenic (as arsenate) in the groundwaters in the northern portion of the Aberjona River Sub-Basin is reduced to arsenite and is transported through the groundwater, eventually recharging into the surface water. At this point, arsenite may be re-oxidized and return to the arsenate form. Arsenate is the predominant species that is transported by the river (Hemond, 1994). The Halls Brook Storage Area is, also, important in the geochemical balance within the sub-basin. The Storage Area acts as a contaminant trap by filtering metals, arsenic included, from the groundwater and reducing concentrations in surface waters (Roux, 1991).

The most effective model for simulating conditions within the Aberjona Rivers Sub-Basin would provide an effective mechanism to accurately measure the geochemical behavior of the aquifer, including the ability to model chemical equilibrium, speciation, and mobility.

Chapter 5

Flow Modeling

5.1 Flow Model Description

The goals of modeling the groundwater flow through the Aberjona River Sub-Basin are to provide a simplified, yet informative, hydrologic representation of the flow regime in this complex and heterodynamic river valley aquifer system; observe the interdependency of hydrogeologic influences on stream-aquifer interactions; and to assist in the prediction of contaminant migratory pathways. This general and large scale simulation is performed to assess the holistic and macro-scale effects characteristic of the Aberjona River Sub-Basin and to form the basis for more local models, specifically focusing on the areas near the *Industriplex* and *Wells G&H* sites. Local models are needed to capture smaller-scale effects and provide greater resolution for estimating mass balances and concentrations that could have harmful toxicological influences on the biota, especially humans.

The model used is **DYNFLOW:** *A 3-Dimensional Finite Element Groundwater Flow Model* (CDM, 1984) developed by Camp Dresser & McKee Inc. Coded in FORTRAN, this code uses the Galerkin finite element formulation. *DYNFLOW* uses the basic equations of groundwater flow. Darcy's law, which states that the flow rate $[length(L)^3/time(T)]$ is proportional to the *hydraulic gradient* (L/L) and the *hydraulic conductivity* (L/T) (Freeze and Cherry, 1979), is mathematically represented in one dimension as

$$Q = -K\frac{dh}{dl}A \tag{5.1}$$

where:

Q = flow rate
K = hydraulic conductivity
h = hydraulic head
l = length
A = area (L^2).

For transient flow in a saturated porous medium, Darcy's law is combined with the continuity equation:

$$-\frac{\partial(\rho v_x)}{\partial x} - \frac{\partial(\rho v_y)}{\partial y} - \frac{\partial(\rho v_z)}{\partial z} = \frac{\partial(\rho n)}{\partial t} \tag{5.2}$$

requiring that (Freeze and Cherry, 1979):

> the *net* rate of fluid mass flow into any elemental control volume be equal to the time rate of change of fluid mass storage within the element

where:

v = specific discharge (Q/A) (L/T)in each of three (3) coordinate directions (x, y, z)
ρ = density ($mass/volume$) (M/L^3)
t = time (T).

The result is

$$S_s\frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\left(K_x\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y\frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z\frac{\partial h}{\partial z}\right) + q \tag{5.3}$$

where (Freeze and Cherry, 1979):

$S_s = S_s$(x,y,t) = specific storage (L^{-1})
h = h(x,y,z,t) = hydraulic head
$K_x = K_x$(x,y,z) = hydraulic conductivity in the x direction
$K_y = K_y$(x,y,z) = hydraulic conductivity in the y direction
$K_z = K_z$(x,y,z) = hydraulic conductivity in the z direction
q = q(x,y,z,t) = source or sink (i.e. recharge) [$volume/area/time(L/T)$].

The finite element method used to solve for *h(x,y,z,t)* assumes a linear variation of hydraulic potential within each element. Gauss Elimination is used to solve the discretized flow equations at every node in the model. The solution is simultaneous if the flow equations remain linear. In an unconfined aquifer system, the flow equations are non-linear and the solution proceeds through successive iterations until converging.

5.1.1 Assumptions

Because of the inherent difficulties associated with producing a regional model of watershed behavior, several assumptions are necessary to more effectively simulate flow behavior. The modeling assumptions are listed below.

1. The aquifer is a three-dimensional, shallow, unconfined aquifer with a free surface.
2. The unsaturated zone above the water table is not modeled.
3. The top of the model is free surface. The head at the surface is set to the elevation of the node if head exceeds elevation. Otherwise, the surface flux is set equal to recharge.
4. The head is restricted from falling below the elevation of the bottom of the model.

5. The sides of the model are represented as *no-flow* boundaries to the North, East, and West. At the southern edge of the model, head is specified, allowing flow out to the South.

6. Geological layers are based on boring logs and cross-sections from studies conducted near the Industriplex and Well G&H sites, where the the bottom of the bedrock layer is modeled as horizontal and the till a continuous layer of 4 m, except where bedrock outcrops.

7. Properties are uniform and unvarying in the horizontal.

8. A transient simulation will approach steady state at a large enough simulation time.

9. Initial heads are set at the bottom of the outwash layer.

While these assumptions may not hold for extremely localized areas of the model, they are appropriate for a regional scale model that simulates basin-wide conditions. The three-dimensional modeling of the aquifer is necessary to capture the effects of vertical gradients that influence and are influenced by the stream-aquifer interaction. Because of the shallowness of this unconfined aquifer, the unsaturated zone does not contribute significantly to the sub-basin hydraulics and is assumed to only provide recharge to the underlying aquifer. The above assumptions are consistent with establishing this modeling analysis as a well-posed calibration problem which is able to converge to a solution.

5.1.2 Network and Boundary Conditions

The finite element grid representing the Aberjona sub-basin consists of 1063 elements connected by 584 nodes in four levels. The terms *level* and *layer* are used to define the vertical discretization of the model. *Level* defines the upper and lower boundary of the model and also separates layers within the model. A *layer* is a geologically defined unit, where the number of layers is equal to $n - 1$, n being the number of levels in the vertical. Constructed with DYNPLOT8—developed by Camp Dresser & McKee, the grid is finely discretized along the Aberjona River and connected tributaries, including the Halls Brook Storage Area. Also, the grid has greater resolution near the Industriplex and Wells G&H sites—where the bulk of the data are located and head gradients are steep when the wells are pumped. The finite element network is coarsest around the outer edge of the basin near the flow divide, where the data are sparse. Figures 5.1 and 5.2 illustrate the model network with elemental and nodal numbering schemes, respectively.

The finite element boundary was chosen to reflect the fact that the edges of the model coincide with a *no-flow* boundary along the flow divide to the North, East, and West. To the South, flow is allowed out of the model, which corresponds to the mouth of the Aberjona River—draining the sub-basin into the Upper and Lower Mystic Lakes. The western boundary separates the Horn Pond and Aberjona River sub-basins. Here we consider only the Aberjona river sub-basin, which contains the *Industriplex* and *Wells G&H* Superfund sites.

The upper boundary of the flow model is set at the elevation of the ground surface. All nodes in the uppermost level—LEVEL 4—are specified as *Rising Water Nodes.* This condition imposes an upper limit on the head in the top level; once the head at a node reaches the elevation of the ground surface at that node it is fixed for that iteration at the surface. The nodes in the bottom level of the aquifer—LEVEL 1—are assigned an implied *DRY* condition that prevents the head from dropping below the elevation of LEVEL 1.

5.1.3 Choice of Nominal Model Parameters

The model property set consists of values of hydraulic conductivities in the x, y, and z directions; specific storage, specific yield and recharge for each layer represented. The initial parameters were selected based on information from field data (Roux, 1991; Reynolds, 1993; Brainard, 1990; Myette et al., 1987) and information about average parameters for groundwater study (Freeze and Cheery, 1979). The initial pre-calibration values are presented in Table 5.1.

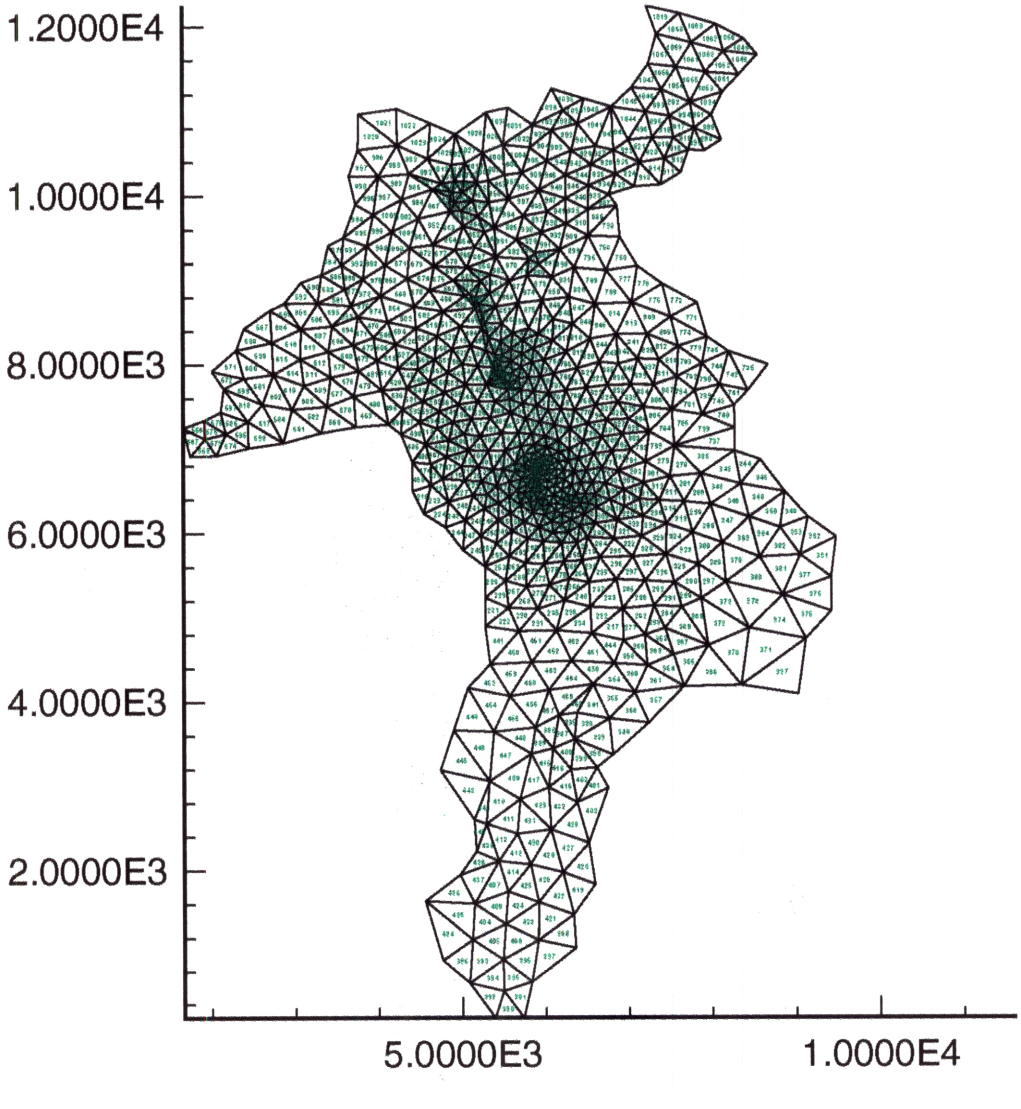

Figure 5-1: Elements of the Aberjona Model Grid

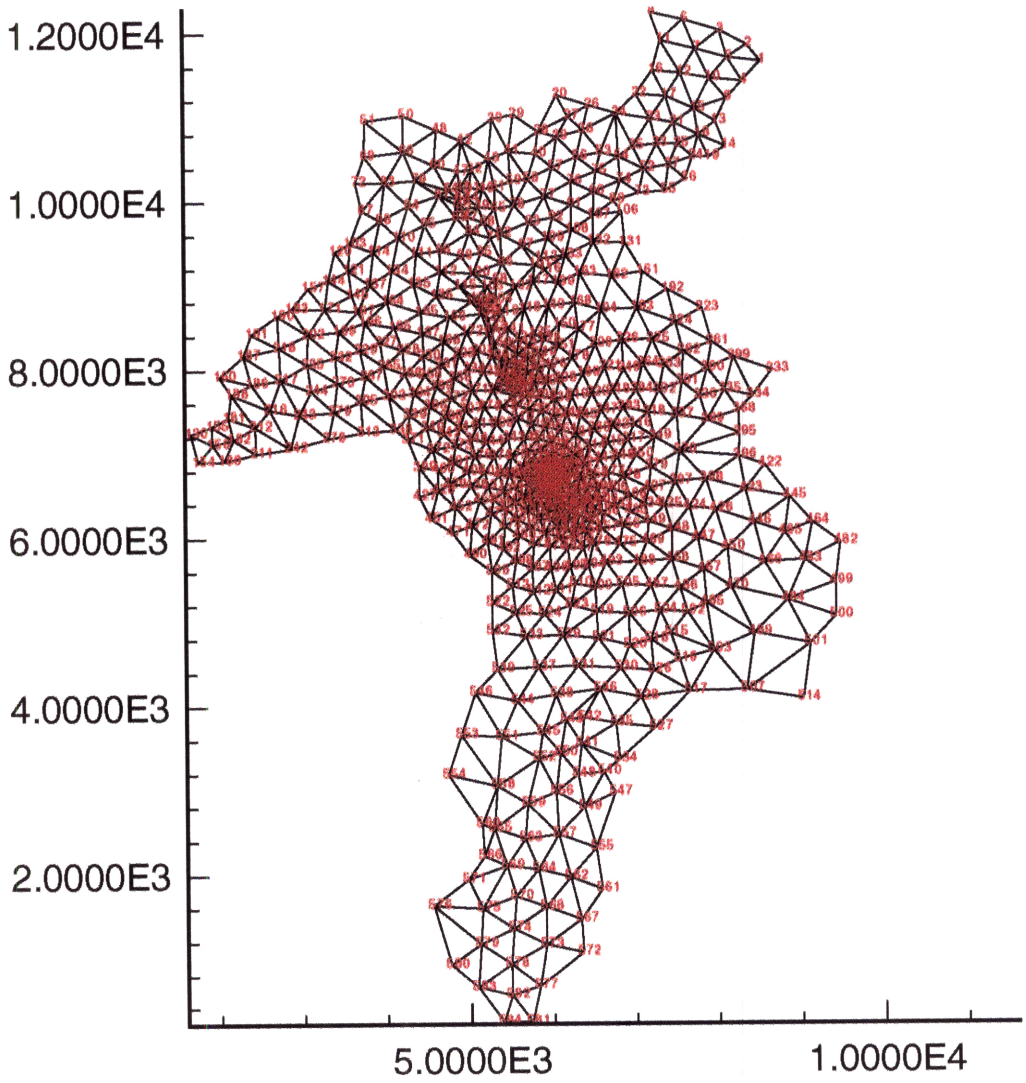

Figure 5-2: Nodes of the Aberjona Model Grid

Table 5.1: Pre-Calibration Model Parameters

Geologic Layer	Parameter	Estimated Value
Outwash	K_x	10.0
	K_y	10.0
	K_z	10.0
Till	K_x	10.0
	K_y	10.0
	K_z	10.0
Bedrock	K_x	10.0
	K_y	10.0
	K_z	10.0

5.2 Model Calibration Process

To achieve a representative steady-state flow regime, a transient simulation was run, starting with a plausible initial condition, in order to allow the heads to gradually converge to steady-state values. The transient simulation was carried out to 125 days, the approximate time at which the aquifer reached steady-state. The pumping wells at *G* and *H* were not turned on during the calibration because the field data used to calibrate the model were collected after these wells were shut off.

After the initial model run, the heads calculated for each node in each layer were used as initial head conditions for all subsequent runs. To achieve the best fit against field data the hydraulic conductivities and recharge were adjusted until the fit was considered acceptable. Only the hydraulic conductivity values for layers were adjusted, but were assumed horizontally uniform. It is important to note that the model does not capture the small-scale effects that are common in an aquifer as large and complex as the Aberjona River Sub-Basin. However, the goal is to produce a model which captures the regional effects and uses the results as the basis of one or more local models.

Once calibrated, the pumping wells are turned on at the wells *G* and *H*. The purpose of pumping at the wells is to determine the deviation from steady-state that reflect historical conditions during the time the wells were pumping. The further

Table 5.2: Post-Calibration Model Parameters

Geologic Layer	Parameter	Estimated Value	Parameter	Estimated Value
Outwash	K_x	30.0	S_s	0.001
	K_y	30.0	S	0.1
	K_z	6.0	Q_r	0.0006756
Till	K_x	3.0	S_s	0.001
	K_y	3.0	S	0.1
	K_z	0.6	Q_r	0.0000563
Bedrock	K_x	0.001	S_s	0.001
	K_y	0.001	S	0.1
	K_z	0.001	Q_r	0.0

implication is that the resultant drawdown may be used to define a smaller hydrologically efficient unit for future analysis that may link the Aberjona River and the aquifer to human exposure pathways created by the pumping of the wells for public drinking water.

The parameters that result from model calibration are summarized in Table 5.2. The data suggest that the most influential effects on flow may be due to the extreme heterogeneities in the geology. The parameters shown above represent a large-scale characterization of the Aberjona River Sub-Basin. By varying the hydraulic conductivities, anisotropy ratios, and recharge values, it is observed in Table 5.3 that the average differences between flow results and model results are within the same order of magnitude. The histogram in Figure 5.3 indicates that the majority of the differences fall between 0 and $-10m$. It is also observed that the areas with the larger absolute differences are either in areas where data are scarce—close to the model boundaries—or in the area near Wells G&H, where the data are dense and highly variable. Both areas are characterized by steep gradients that prevent the model from more accurately representing micro-scale features. The statistics of the calibrated model for differences at 755 field data points are shown below.

Adjustments to either or both local hydraulic conductivities and recharge may provide a better representation of the micro effects within the aquifer. However, the purpose is to estimate parameters for a watershed-scale model and define appropriate

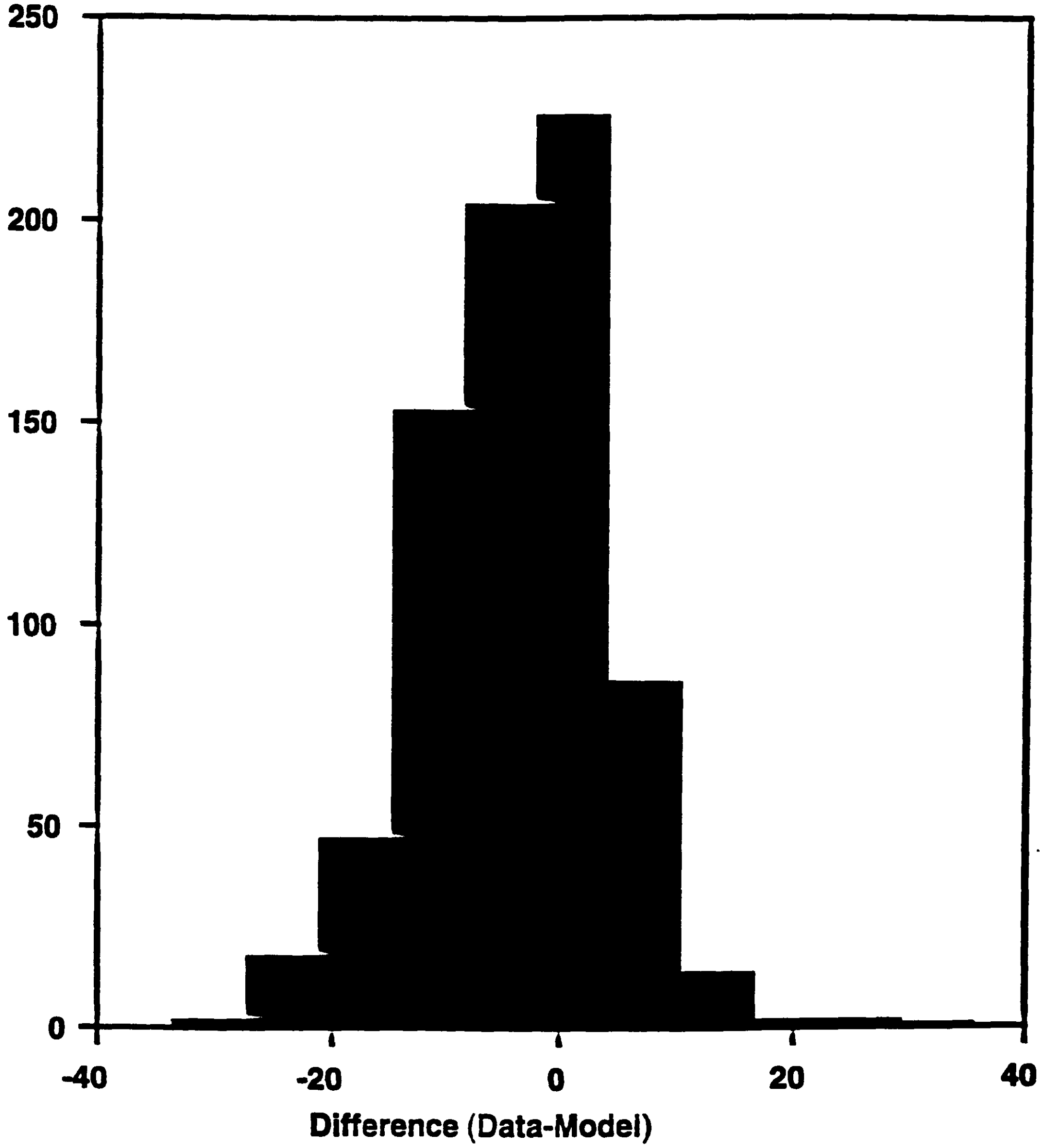

Figure 5-3: Histogram of Differences Between Field and Model Heads

Table 5.3: Statistics of Post-Calibration Differences (Data - Model)

Measure	Value	Measure	Value
Mean	-3.40	Variance	63.50
Median	-3.00	Minimum	-32.10
Std. Dev.	8.00	Maximum	37.60

boundary conditions for more detailed and discretized models within the sub-basin, specifically at the Industriplex and Wells G&H sites. In the following sections, unless otherwise stated, references to average and either minimum or maximum values will refer to the differences between the field data and model results.

5.3 Simulation Results without Pumping

5.3.1 Effects Due to Changes in Hydraulic Conductivity

The results indicate that the model consistently overpredicted the heads within the sub-basin. Therefore, the model results with closest agreement to the field results were obtained using values of hydraulic conductivity in excess of $100m/day$ for both the outwash and till layer. The averages were within an absolute difference of $2m$ and a minimum value of $-28.60m$. The differences within this data set are influenced by the anisotropy ratio and recharge estimates. The difficulty in using such a high estimate for hydraulic conductivity for a regional macro-scale model is that $100m/day$ is at the maximum of the range of field estimates of hydraulic conductivity indicated in reports by Roux (1991) and Myette et al. (1987) for the most transmissive of geological layers. A true regional model could not be represented appropriately using such high estimates.

Also, the relatively continuous and thin till layer was tested (Roux, 1991) to be of a lower conductivity than the outwash, although composed of similar materials of different size and sorting (Myette et al., 1987). The bedrock layer was represented as a limited—practically *no flow*—flow geologic zone. Estimates of conductivity in excess of $0.001 m/day$ did not effect the results. This was compared to results from simulations using hydraulic conductivity values of $0.0001 m/day$. A bedrock hydraulic conductivity estimate of $0 m/day$ produced solution convergence difficulties and therefore, could not be used.

5.3.2 Effects Due to Changes in the Anisotropy Ratio

Changes in the anisotropy ratio were not very significant. The ratios were evaluated at 1:1, 2:1, 5:1, and 10:1. While the results with a 10:1 ratio produced lower averages and a reduced range of values, there was no field data to support a ratio in excess of 5:1 was physically representative of macro properties. Reynolds (1993) did use an outwash ratio of 20:1, however, those results are on a smaller scale with increased layering in the vertical, and may not be representative of macro properties within the sub-basin. At the values of hydraulic conductivity selected, outwash, $30 m/day$ and till, $3 m/day$, the differences due to an increased anisotropy ratio were minimal; therefore, a value of 5 was preferred to 2 because of the close association with field data (Roux, 1991; Myette et al., 1987). Also, the larger anisotropy ratio creates vertical stress and produces more significant vertical flow effects, especially while wells G and H are pumping.

5.3.3 Effects Due to Changes in Recharge

The final parameter that could be varied was the recharge. The original recharge of $0.001126 m/day$ was based upon an average precipitation rate of approximately $1.2 m/yr$ and a negative 30% evaporative flow rate—approximately $0.35 m/yr$ (Brainard, 1990) and a river discharge of approximately $0.41 m/yr$ (Solo, 1994). Initially, the recharge was applied equally to all elements within the modeled sub-basin. Because of the overestimation of head values, the recharge was decreased both for the sub-basin and within the geologic properties of the sub-basin. Further reduction in the recharge could have reduced the averages more, but would not have been consistent with field data from the watershed (Roux, 1991; Myette et al., 1987; and Solo, 1994).

5.3.4 Plots of Unpumped Conditions

The modeled flow results are shown in plan view for each of the levels modeled—Levels 1-4, with Level 4 representing the surface and Level 1 the bottom of the bedrock—in Figures 5.4-5.7.

By analyzing cross-sections throughout the sub-basin, it is possible to gain a better understanding of the significance of both the lateral flow pattern towards the Aberjona River and also of the longitudinal flow pattern along the river. At steady-state, the geological influence and flow patterns are illustrated in Figures 5.8-5.10 as cross-sections showing the variability of geological elevations, the bedrock valley, and the steady-state head contours. Figure 5.8 represents the two flow patterns, visible in the northern portion of the sub-basin. The flow cells before the 1000 m point indicated lateral flow toward the center of the sub-basin, while the flow cells after the 1000 m point show flow directly toward one of the Aberjona River tributaries. Figure 5.9, taken across the center of the sub-basin intersecting the Wells G & H site, represents a predominantly lateral flow pattern, with groundwater flow converging toward the Aberjona River from both west and east of the river valley. Directly below the river, the closed contours represent a longitudinal movement of groundwater down the axis of the valley, following the reach of the Aberjona River. Figure 5.10 is taken across the Industriplex site. This cross-section captures both flow patterns in two different regions. In the northwestern portion of the watershed flow is both toward the center of the valley and toward one of the river tributaries. In the north-central region, flow is again toward the center of the valley, which is at a much lower elevation, and down the river toward the southern portion of the sub-basin.

The cross-sections shown in Figures 5.11 and 5.12 are taken across the Wells G & H site. These cross-sections without pumping (Figures 5.11 & 5.12) illustrate both the lateral and longitudinal flow patterns toward the Aberjona River and along the river, as well. These figures will be used for comparison with the results due to pumping in the next section.

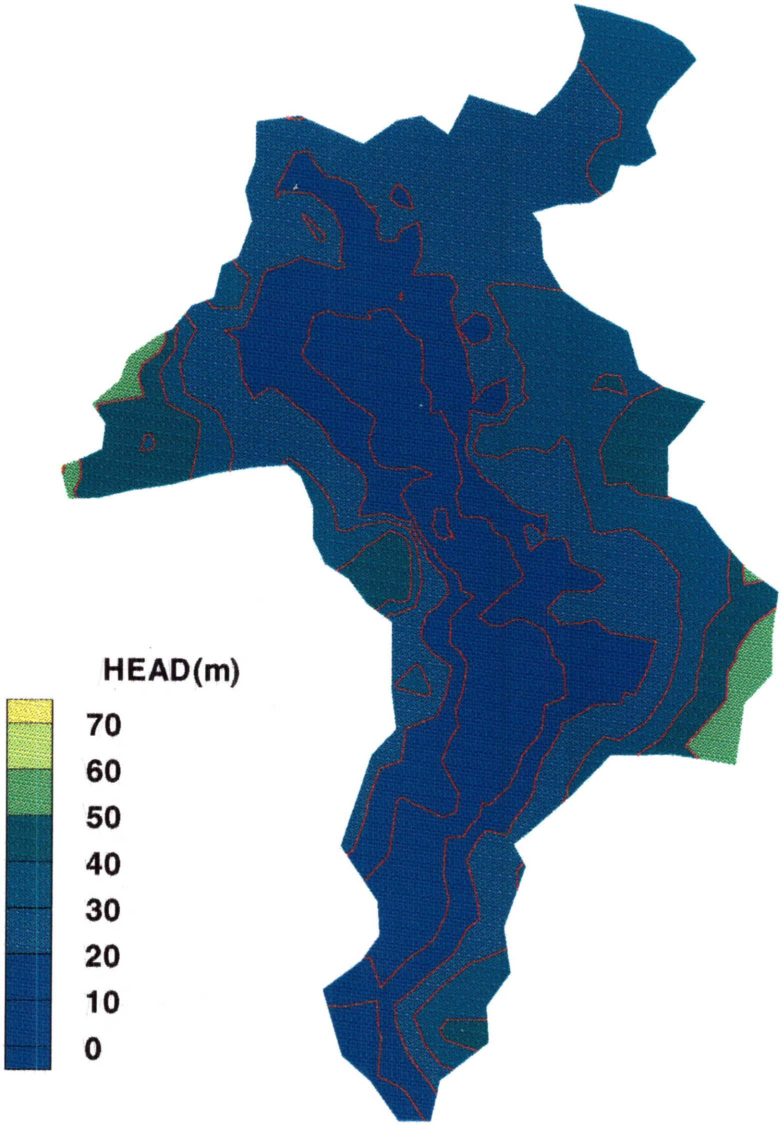

Figure 5-4: Model Results without Pumping—Level 1

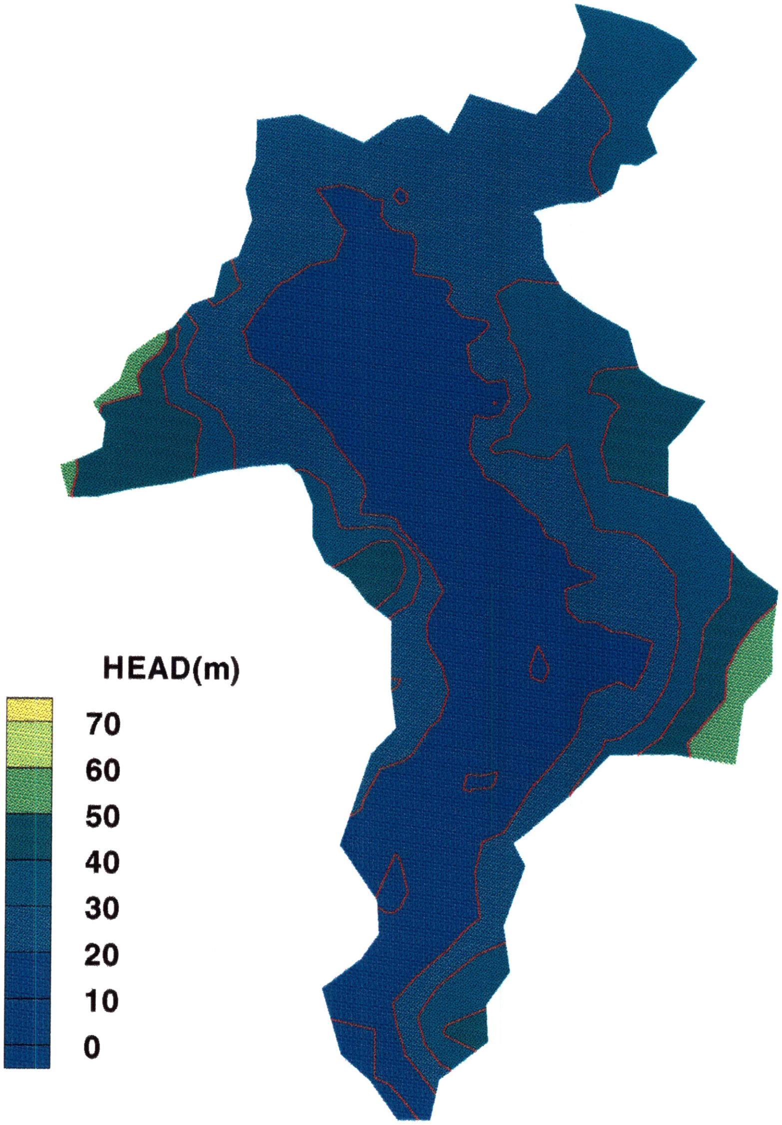

Figure 5-5: Model Results without Pumping—Level 2

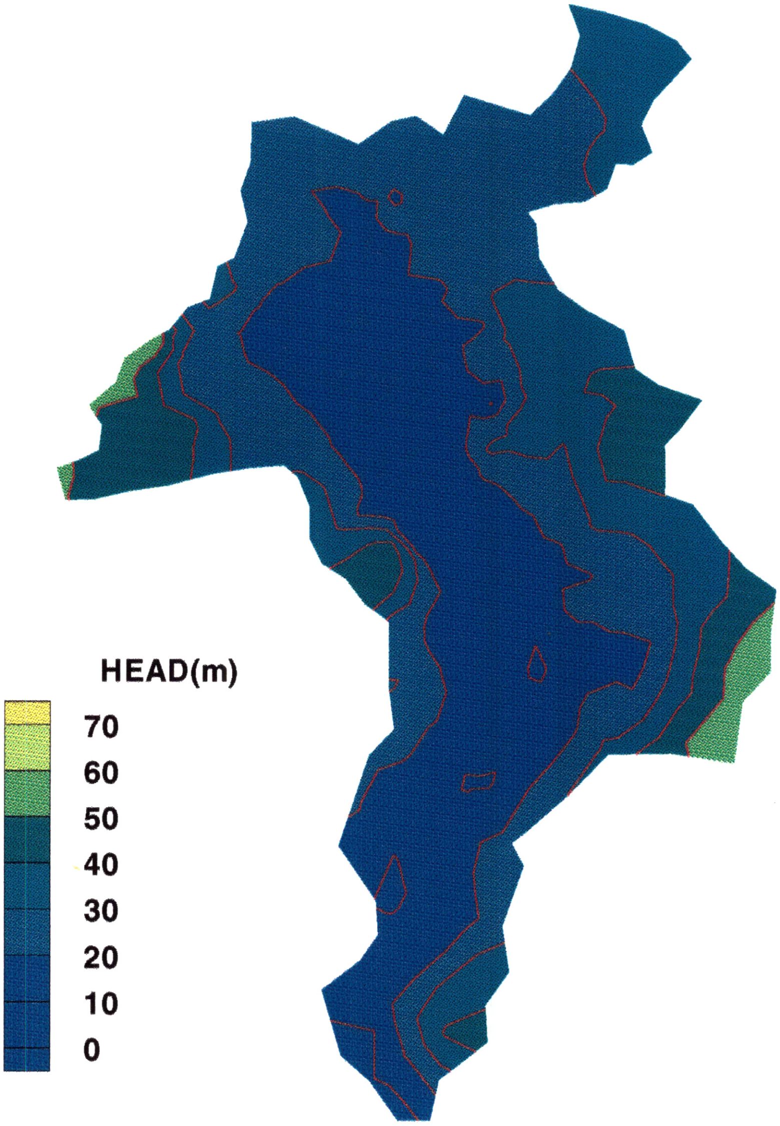

Figure 5-6: Model Results without Pumping—Level 3

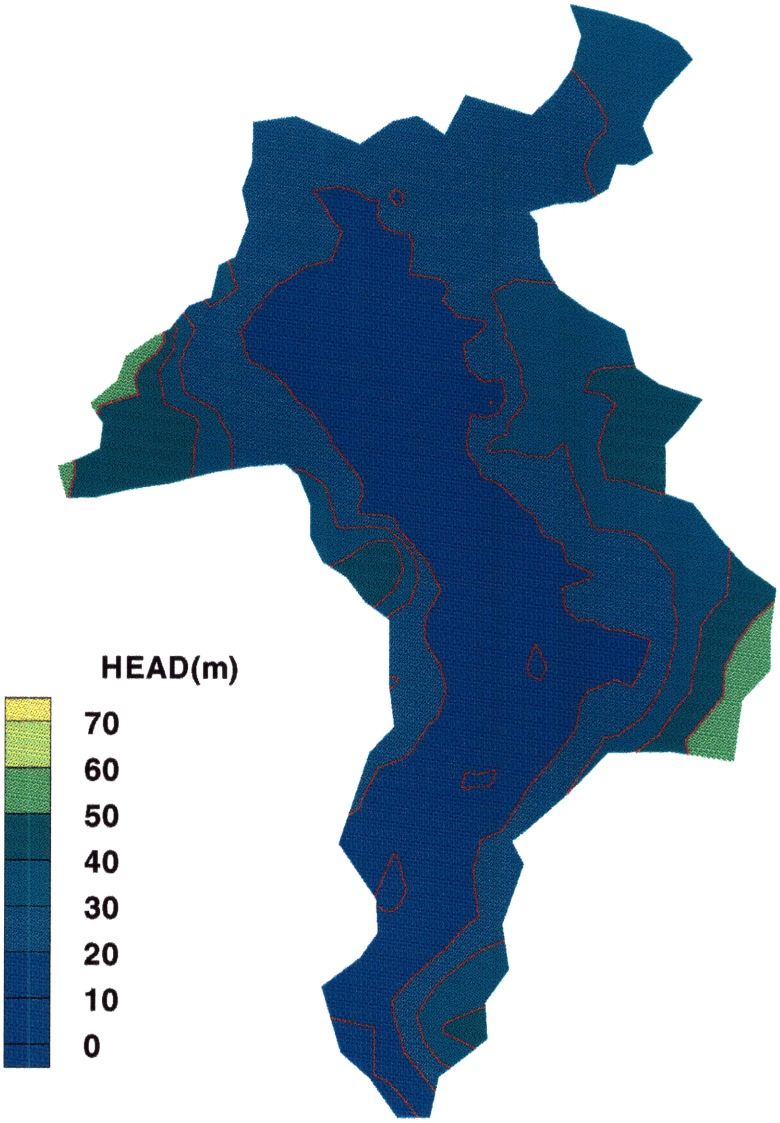

Figure 5-7: Model Results without Pumping—Level 4

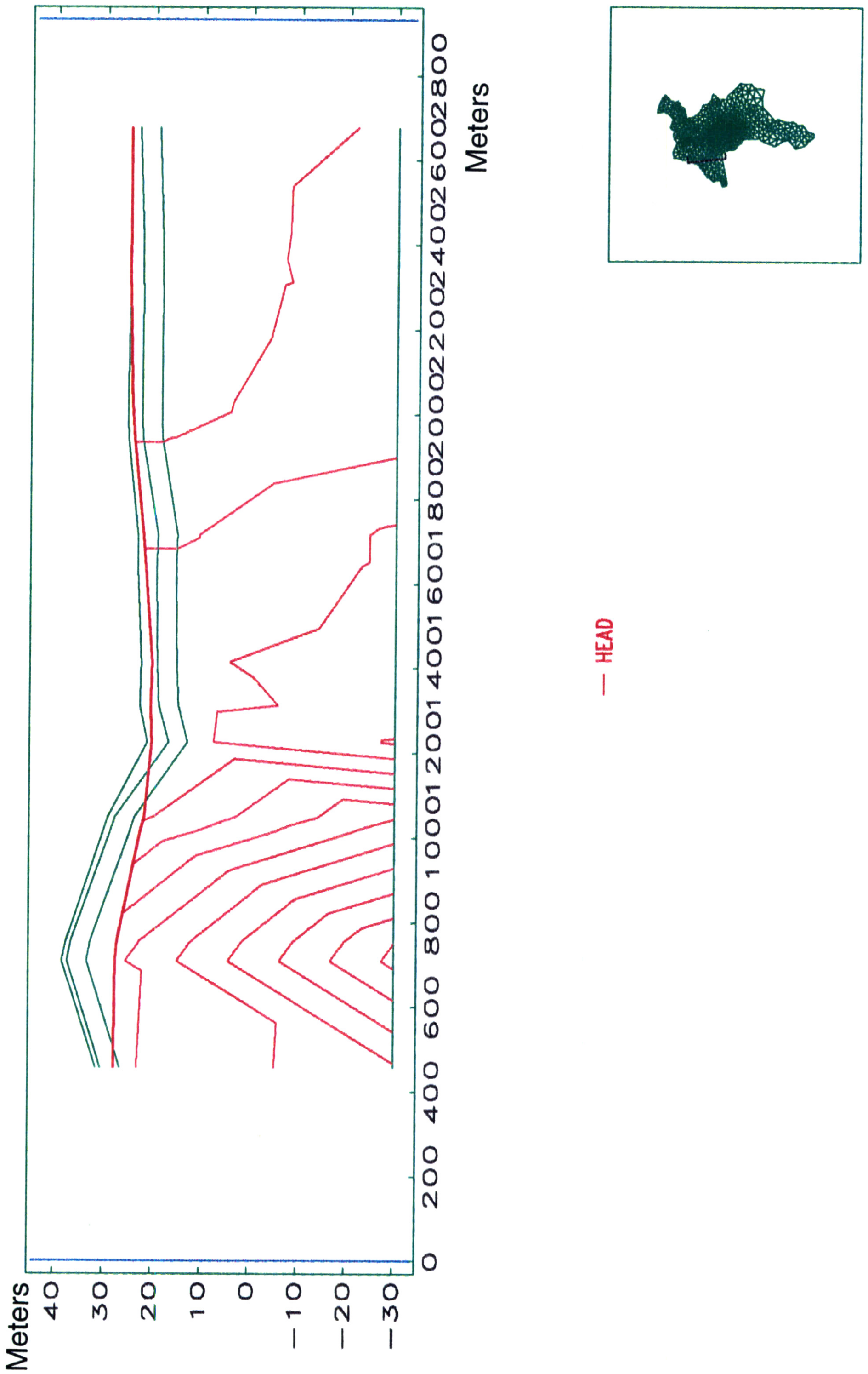

Figure 5-8: Cross-Section Showing Geology and Steady-State Head

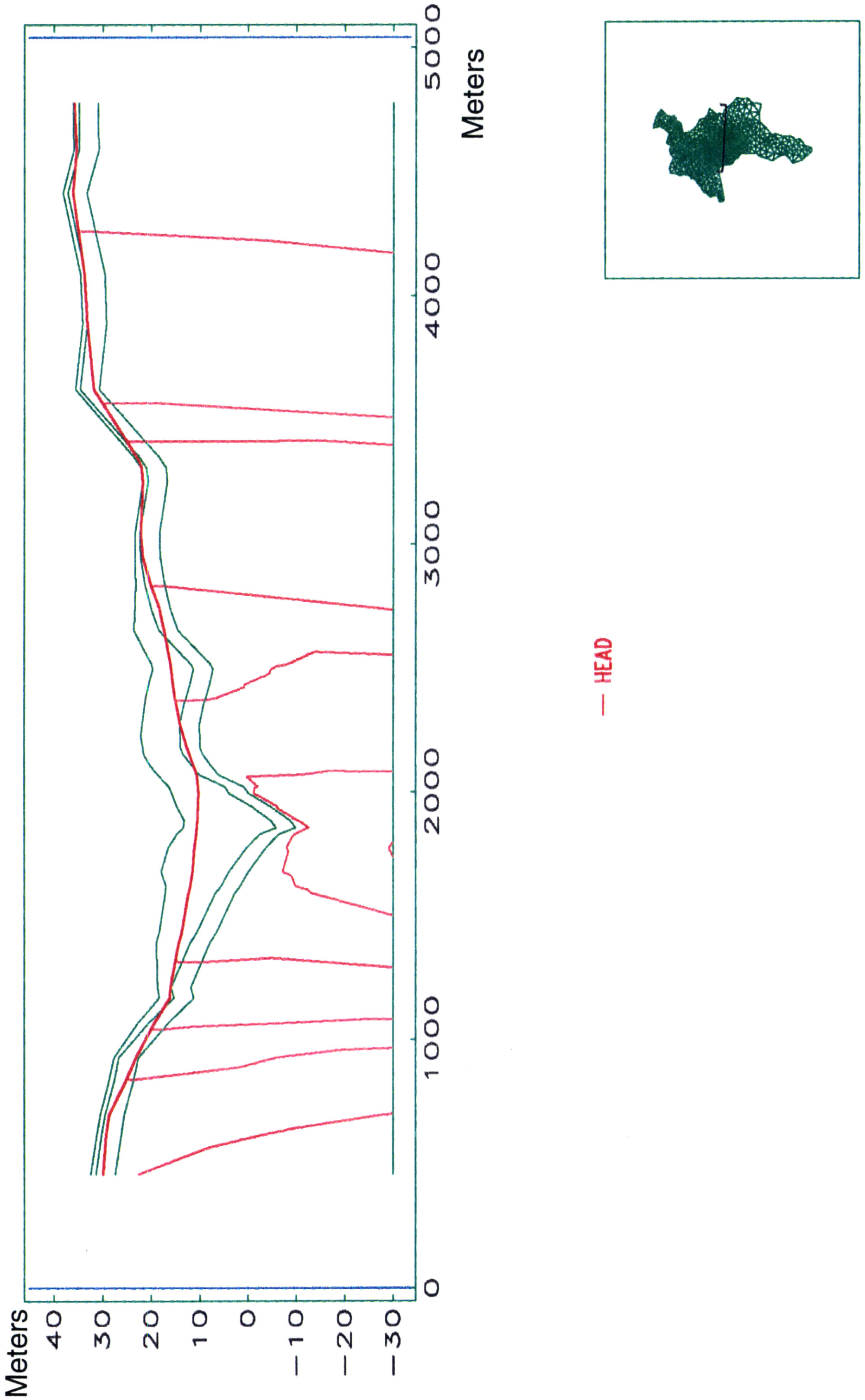

Figure 5-9: Cross-Section Showing Geology and Steady-State Head

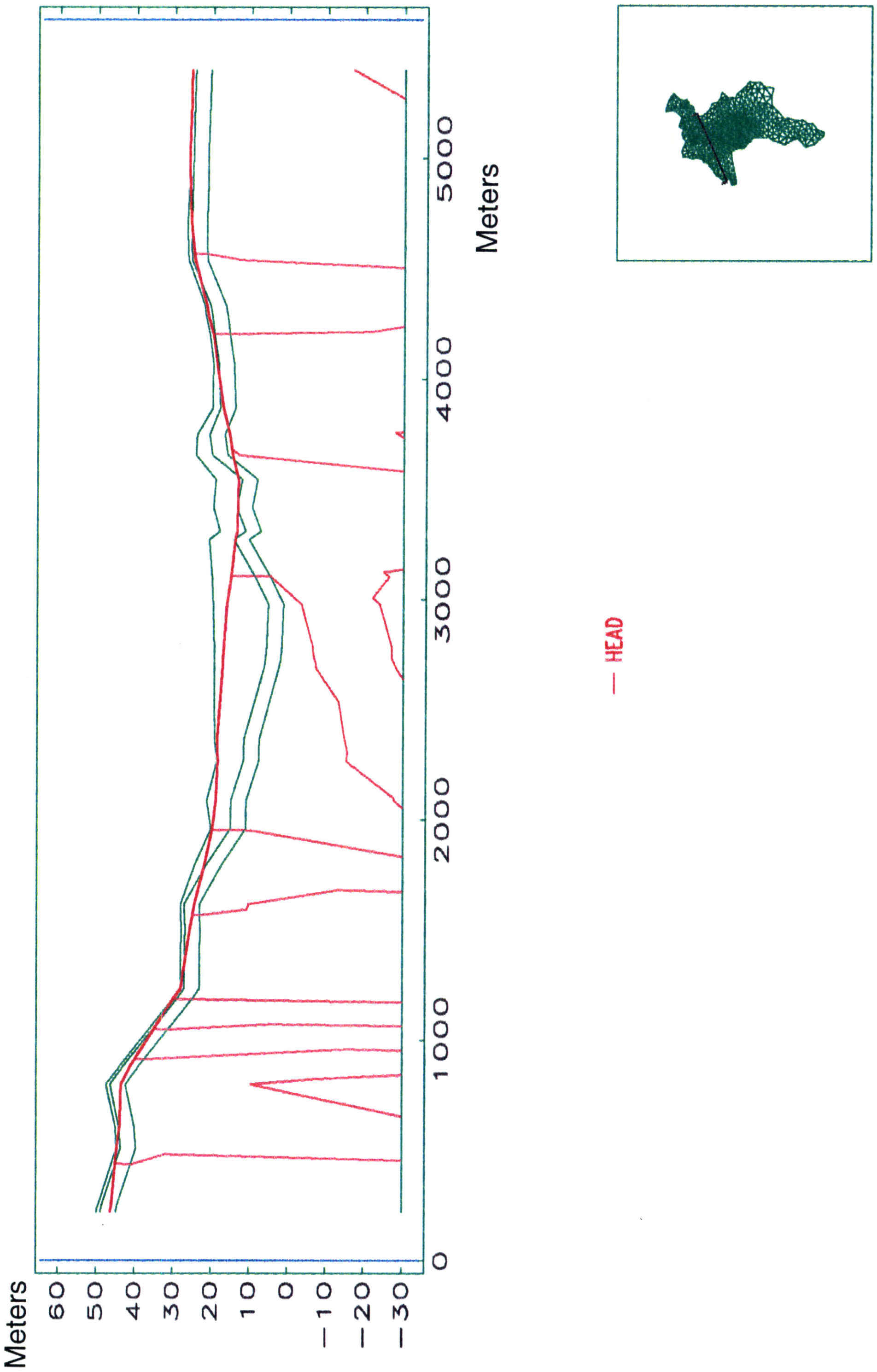

Figure 5-10: Cross-Section Showing Geology and Steady-State Head

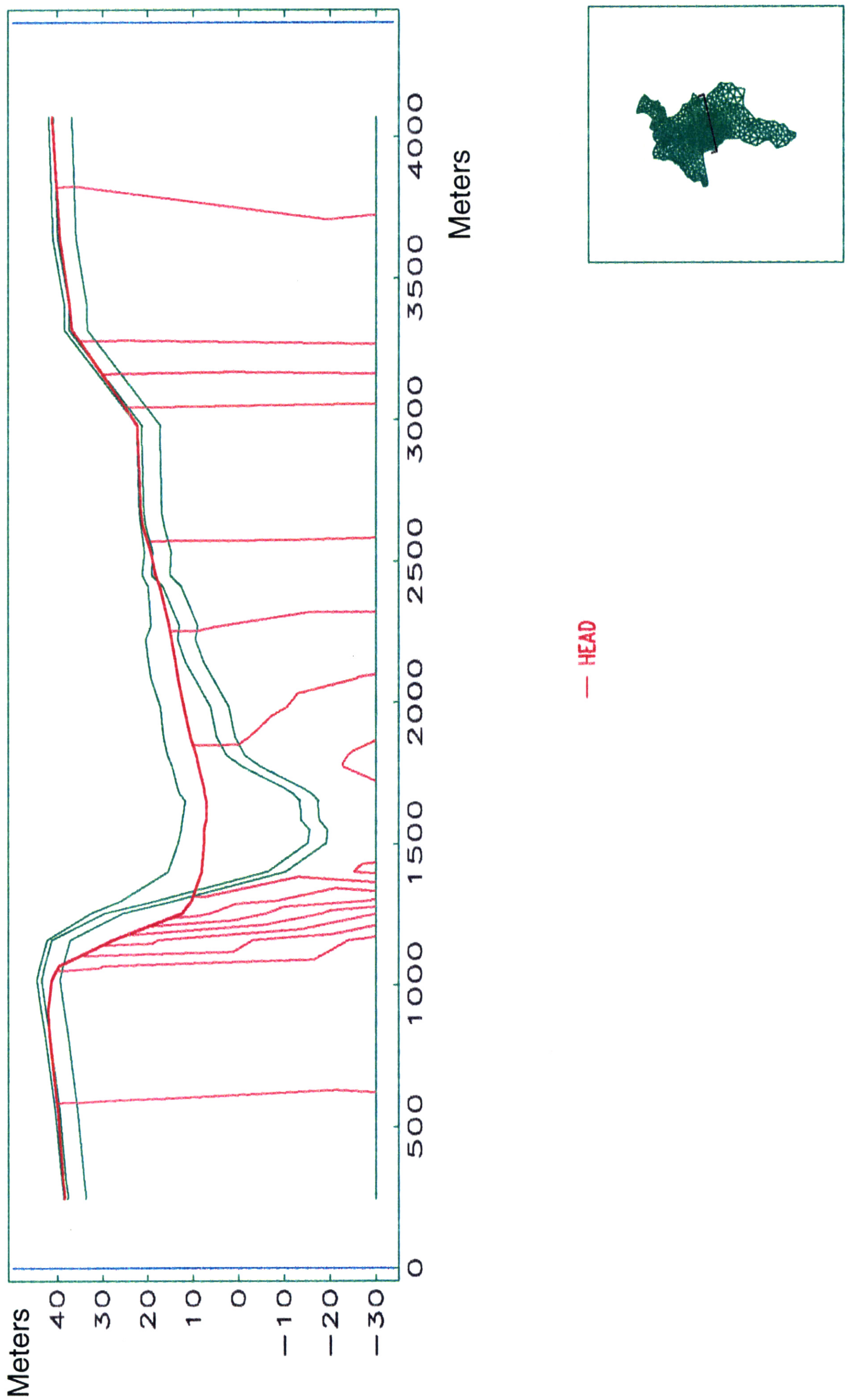

Figure 5-11: Cross-Section Showing Geology and Head without Pumping

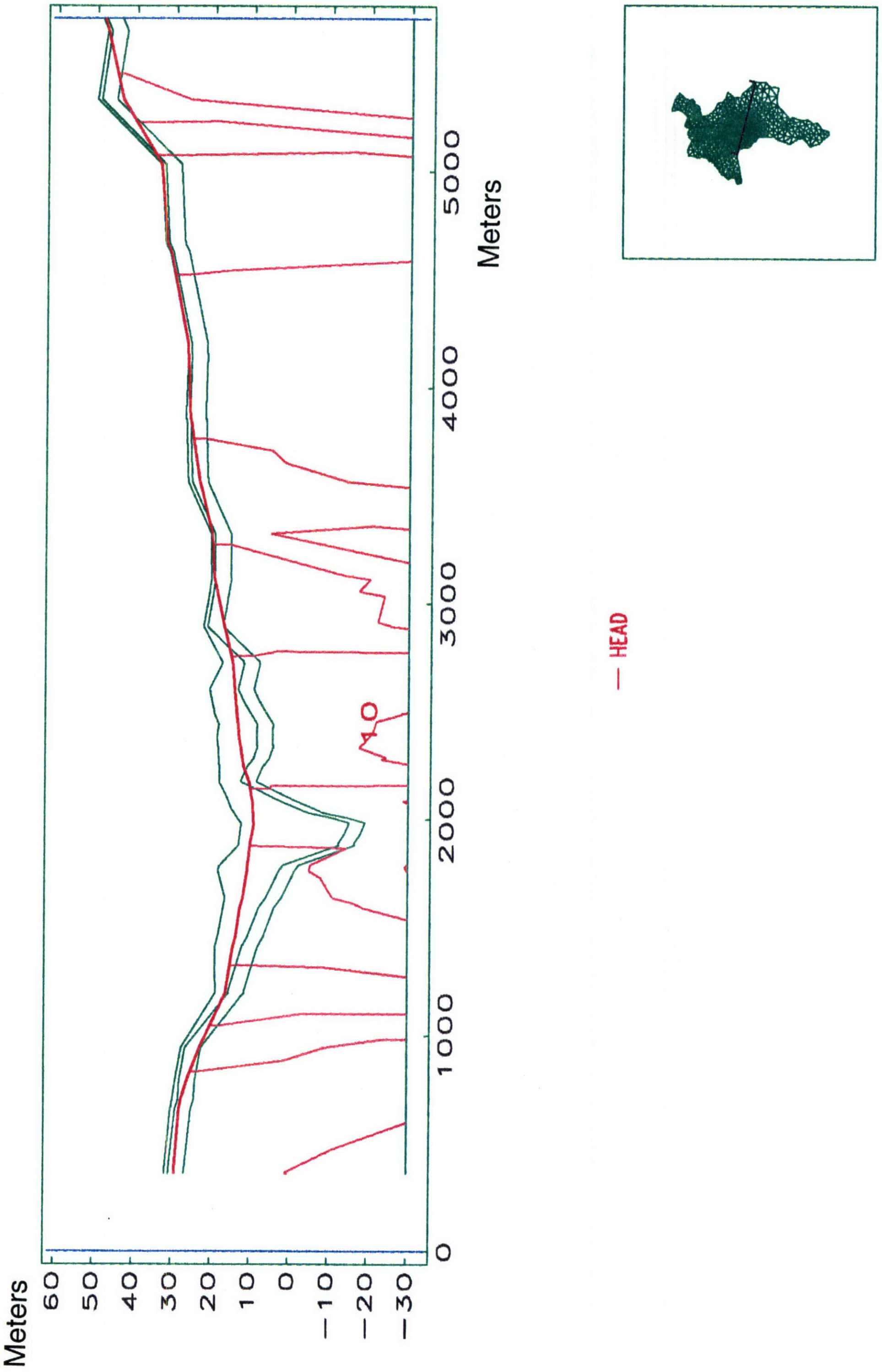

Figure 5-12: Cross-Section Showing Geology and Head without Pumping

Table 5.4: Drawdown Statistics for Pumping at Wells it G and *H*

	Level 1	**Level 2**	**Level 3**	**Level 4**
Measure	*Value*	*Value*	*Value*	*Value*
Mean	-0.075	-0.445	-0.445	-0.445
Median	5E-05	-1.3E-04	-1.15E-04	-9E-05
Std. Dev.	0.635	1.271	1.269	1.240
Variance	0.403	1.616	1.611	1.537
Maximum	-5.501	-7.186	-7.259	-6.129

5.4 Simulation Results with Pumping

By turning on the wells at *G* and at *H*, a pumping zone of influence is created. The following table (Table 5.4) gives the drawdown and summary statistics for each level.

The zone is approximately $1.76km^2$ and is shown in Figure 5.13. As expected, the zone of influence is larger in the more transmissive layer of the aquifer which is shown by the drawdown in Level 4 and smaller in the less transmissive bedrock layer of the aquifer (Figure 5.14) represented by the drawdown in Level 1. The drawdown zone in Levels 2 and 3 (Figures 5.15, 5.16) are intermediate size zones, but with significant drawdown values, greater than the drawdown in Level 1. These intermediate drawdown zones are less than the zone in Level 4 and greater than the zone in Level 1. Drawdown is greatest at the locations of the pumping wells and decreasing with distance away from the pumping locations. Outside of the oblong zone of influence defined along the reach of the Aberjona River in the center of the sub-basin the influence drawdown from pumping is minimal; therefore, the boundary established for a more highly-discretized model of the Wells G & H area, emphasizing the effects of pumping and and local heterogeneities.

5.4.1 Plots of Pumped Conditions

The modeled flow results are also shown for the scenario with pumping the wells *G* and *H* in Figures 5.17-5.20. Results, based upon analysis of Figures 5.4-5.7 & 5.17-5.20 in conjunction with Figures 5.13-5.16, do show a significant zone of influence

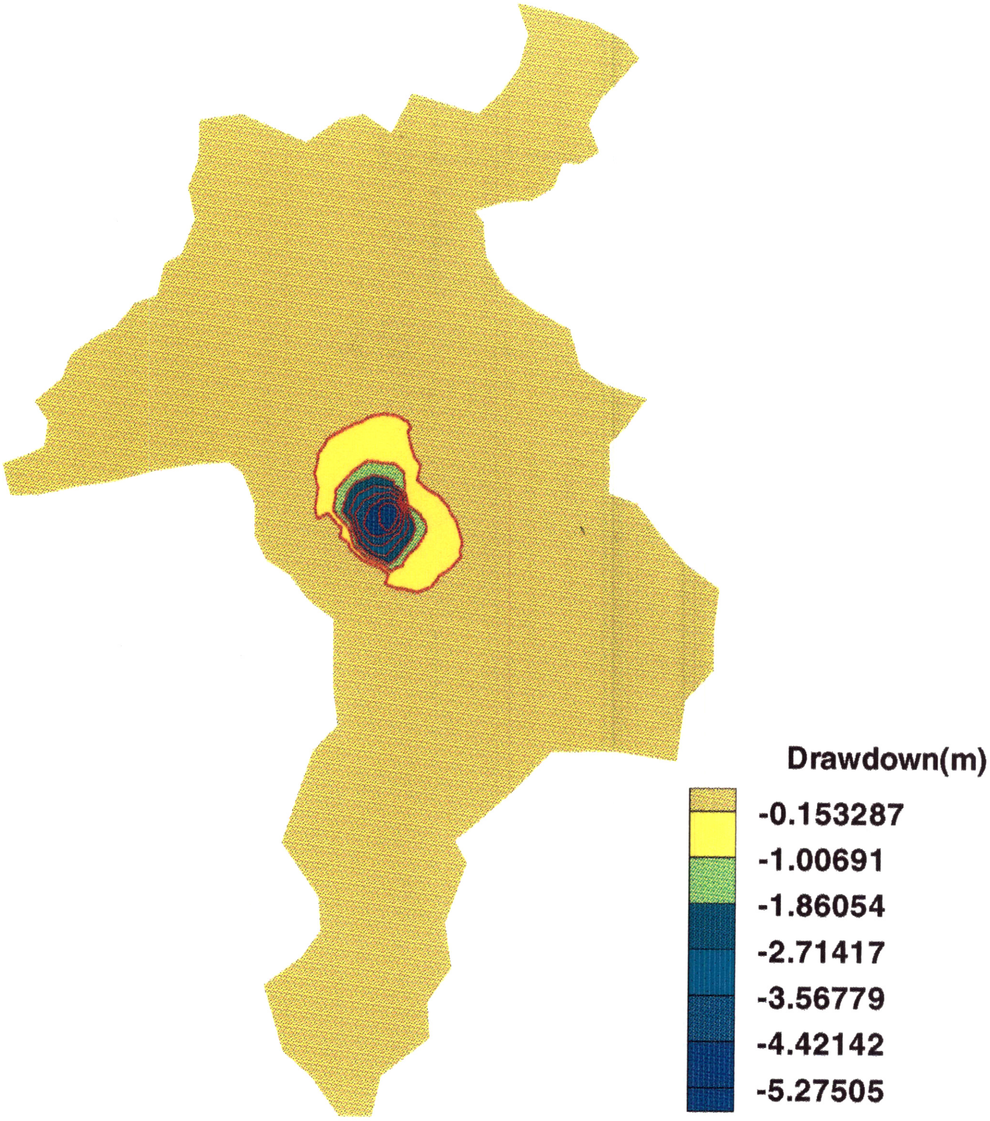

Figure 5-13: Drawdown—Level 4

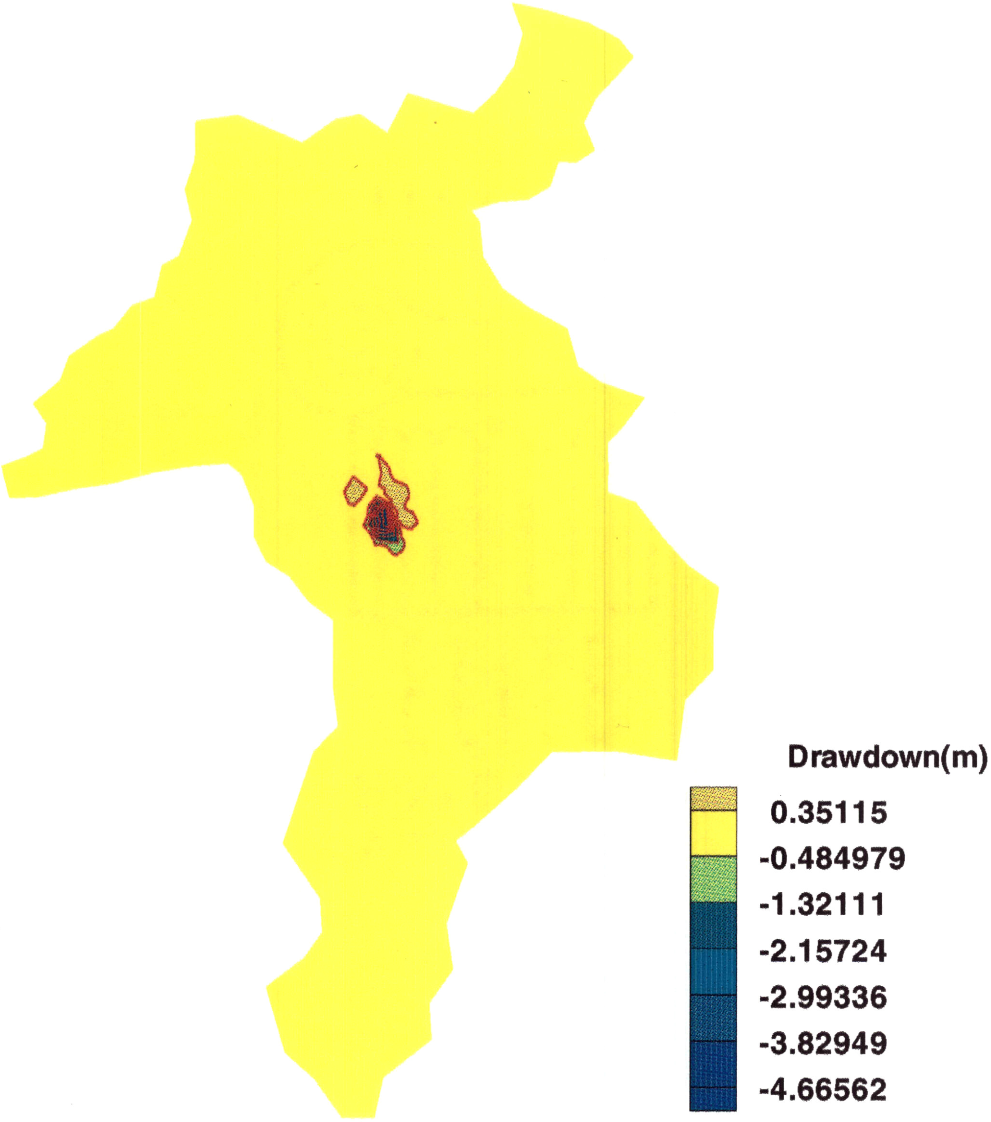

Figure 5-14: Drawdown—Level 1

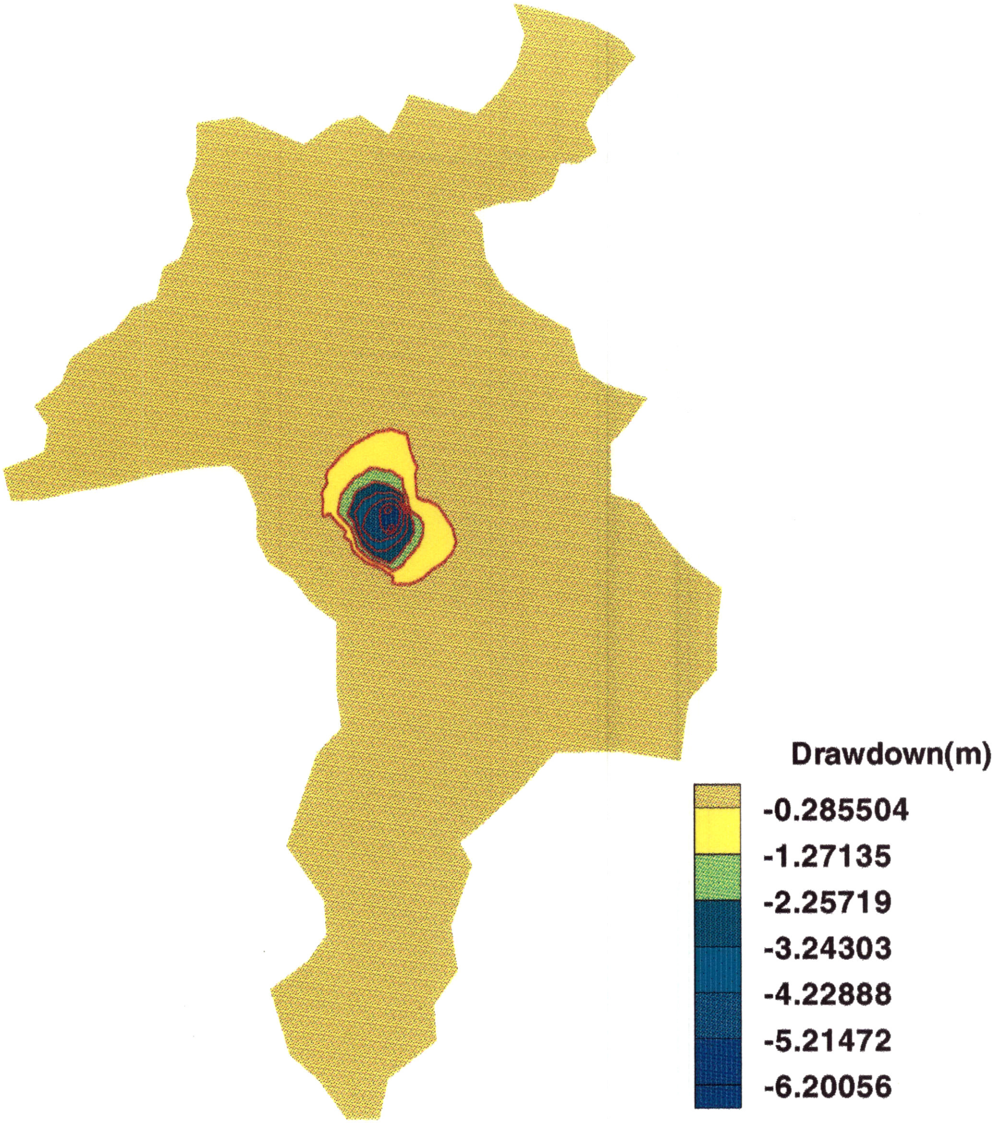

Figure 5-15: Drawdown—Level 2

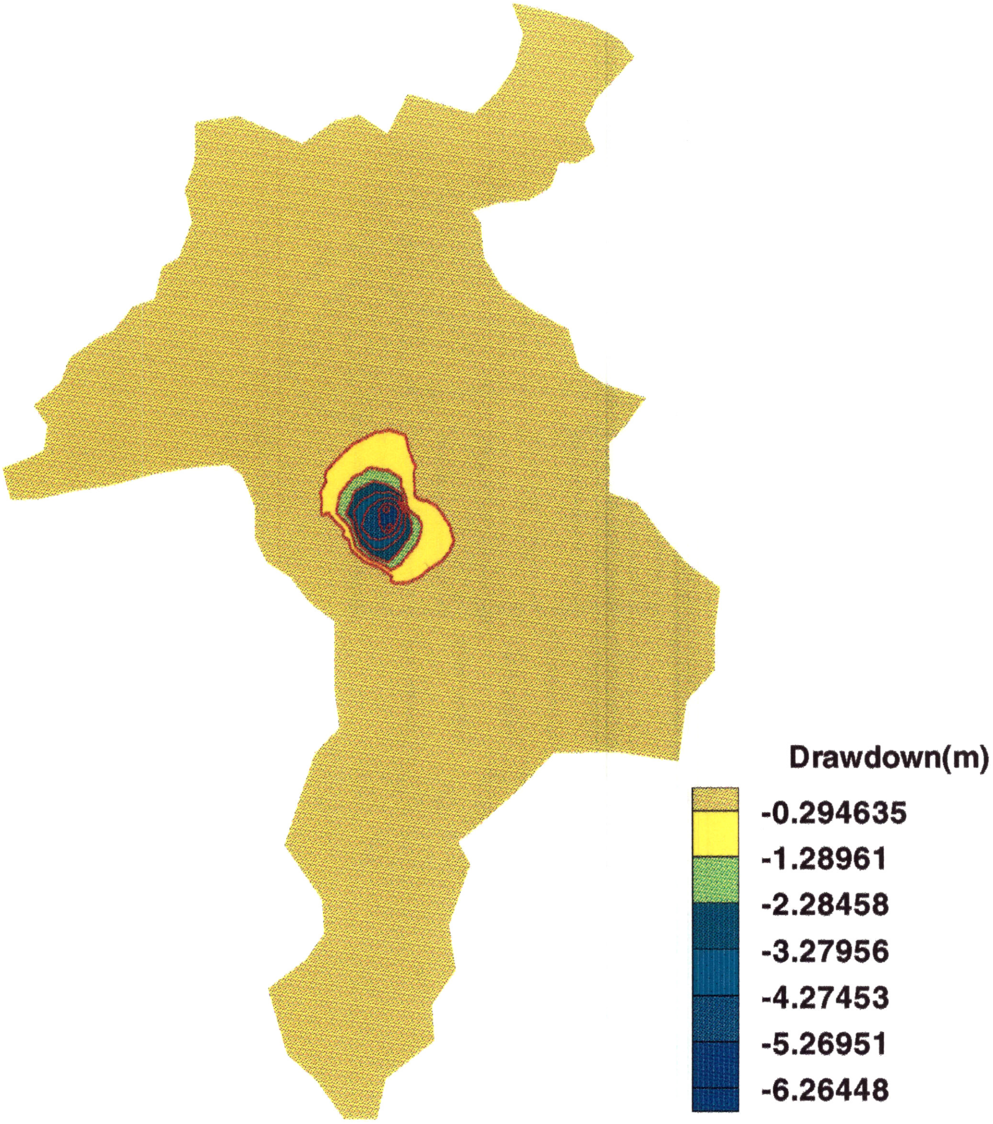

Figure 5-16: Drawdown—Level 3

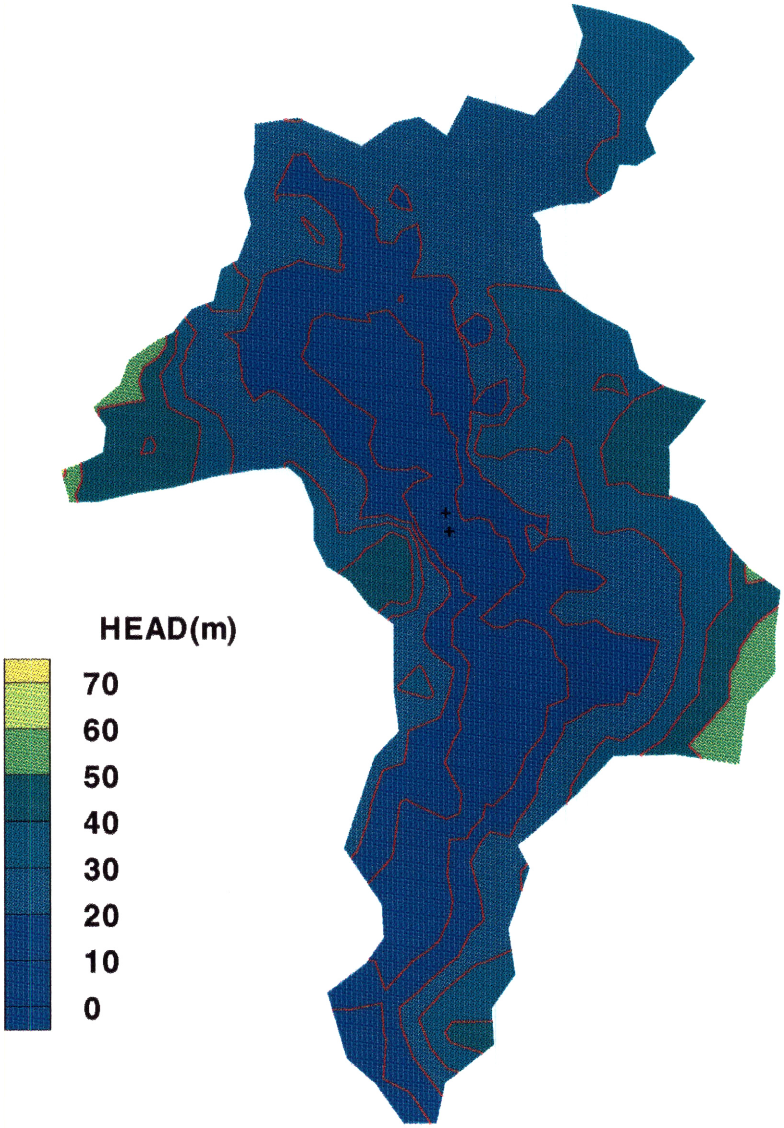

Figure 5-17: Model Results with Wells G and H Pumping—Level 1

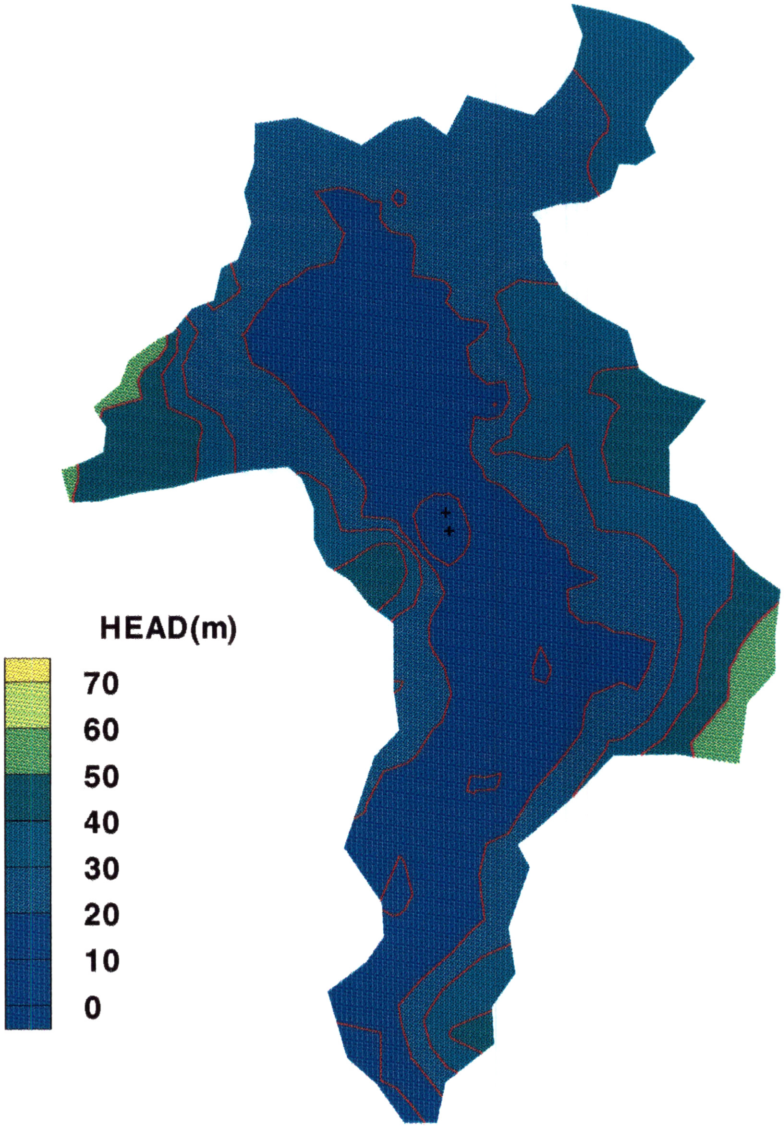

Figure 5-18: Model Results with Wells *G* and *H* Pumping—Level 2

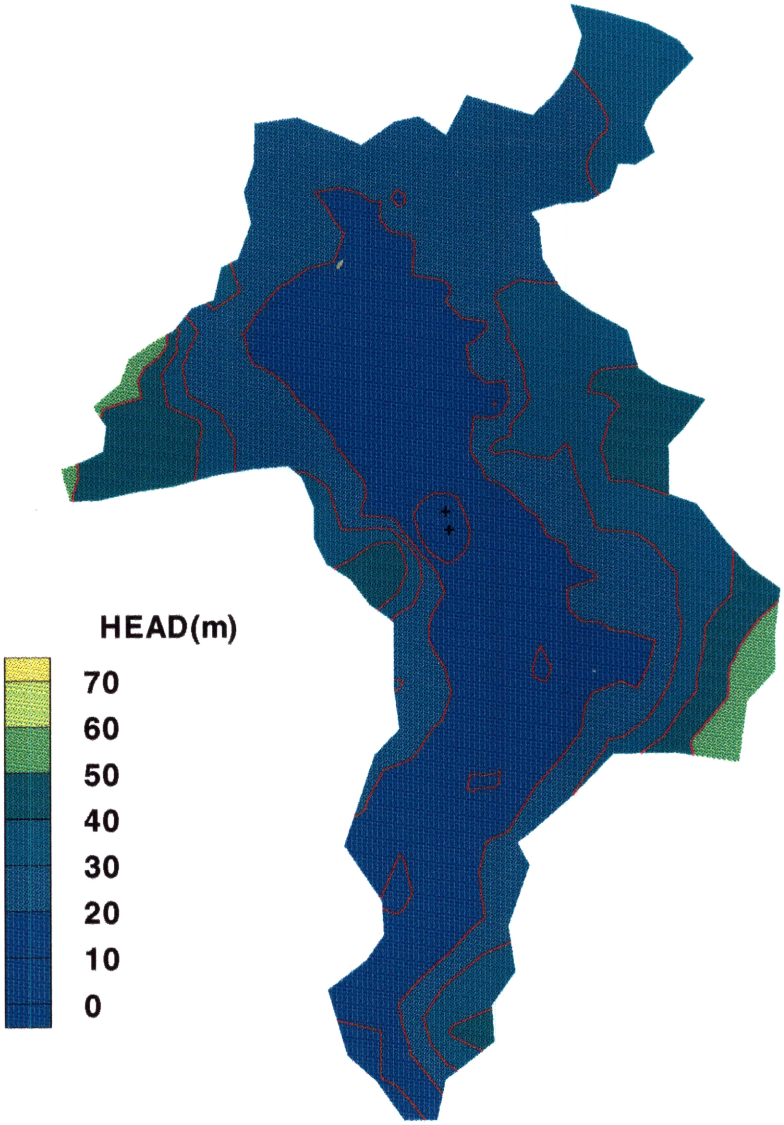

Figure 5-19: Model Results with Wells *G* and *H* Pumping—Level 3

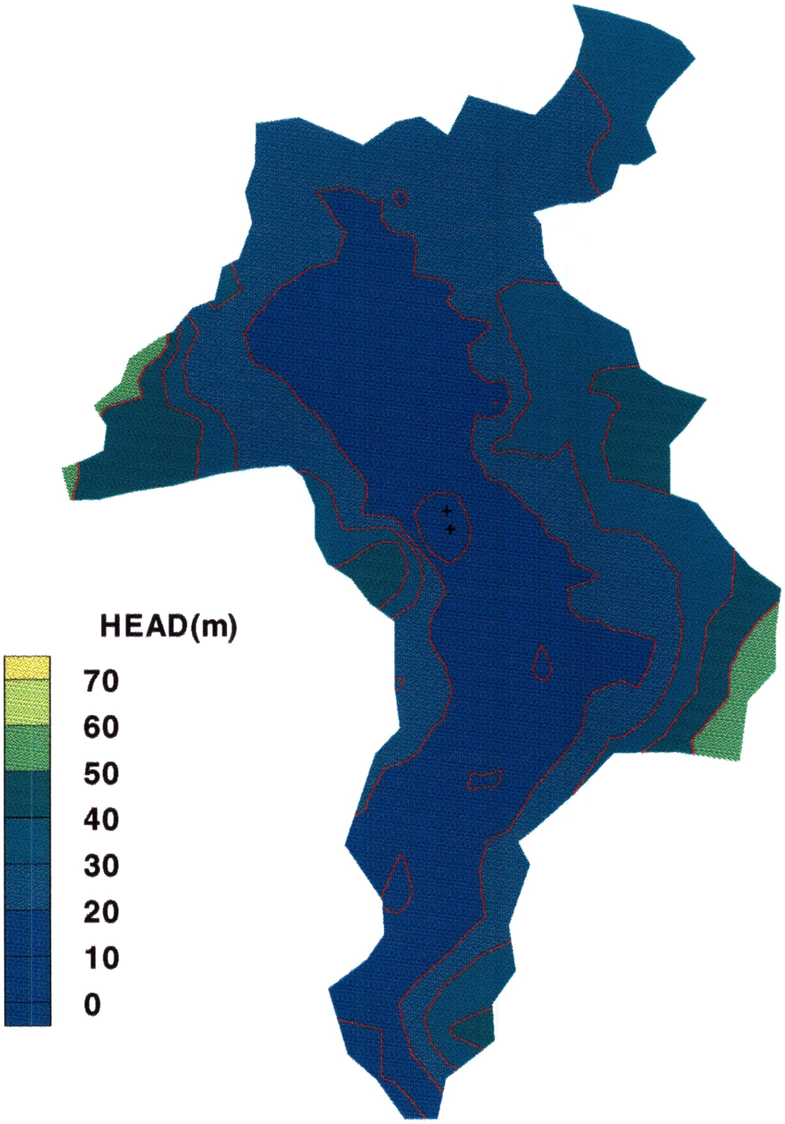

Figure 5-20: Model Results with Wells *G* and *H* Pumping—Level 4

that is identifiable in all four (4) levels of the model. The prominence of the zone of influence—approximately $1.76km^2$—surrounding the Wells G & H site (Figure 5.4) is greatest in the uppermost level of the model and bears important significance for the potential of contaminant transport through the saturated zone of flow.

Cross-sections showing the influence of pumping are shown in Figures 5.21 and 5.22. The cross-sections, taken across the Wells G & H site, show the areas with the most significant effect from drawdown, as the maximum drawdown in each of the four (4) levels exceeds 5.5 m. In Figures 5.21 and 5.22 it is possible to observe the added drawdown effects resulting from the pumping of the wells at G and H that might be compared to the cross-sections in Figures 5.11 and 5.12, without pumping. In Figures 5.21 and 5.22, the heads are lowered and expanded resulting in a prominent vertical drawdown effect. Once the pumping wells are turned on, the heads are lowered, but stably, as controlled by the importance of the river in regulating flow patterns and dynamic changes to those flow patterns.

5.5 Summary of Results

The model results indicate two predominant flow patterns in the Aberjona River Sub-Basin. The first pattern is that flow moves laterally across the basin from areas of higher elevations to areas at lower elevations; and secondly, flow in moving from the northern portion of the sub-basin to the southern portion of the sub-basin. Both of these flow effects are influenced predominantly by the gradients that are very steep along the sub-basin perimetry; however, more gradual along the reach of the Aberjona River.

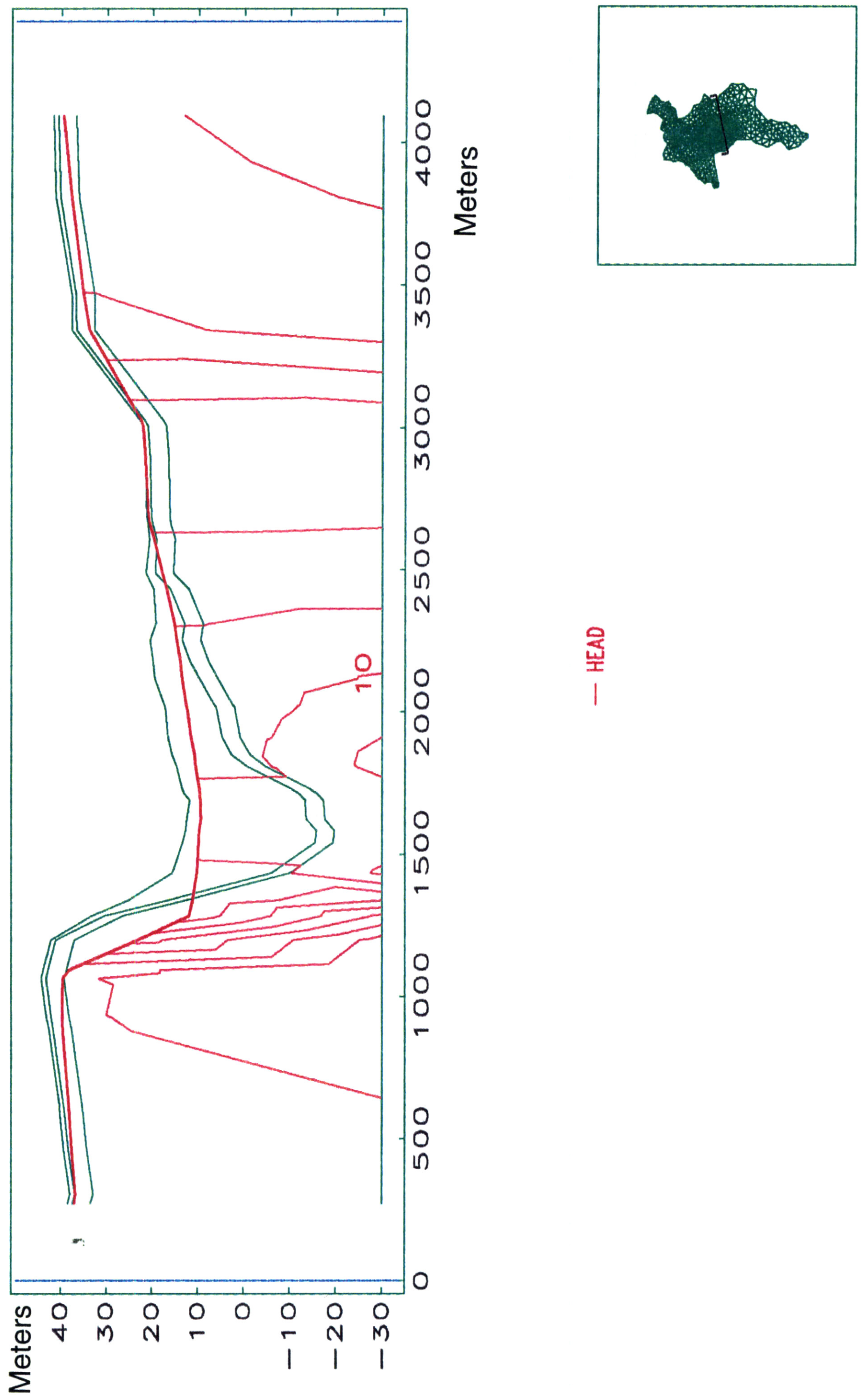

Figure 5-21: Cross-Section Showing Geology and Head with Pumping

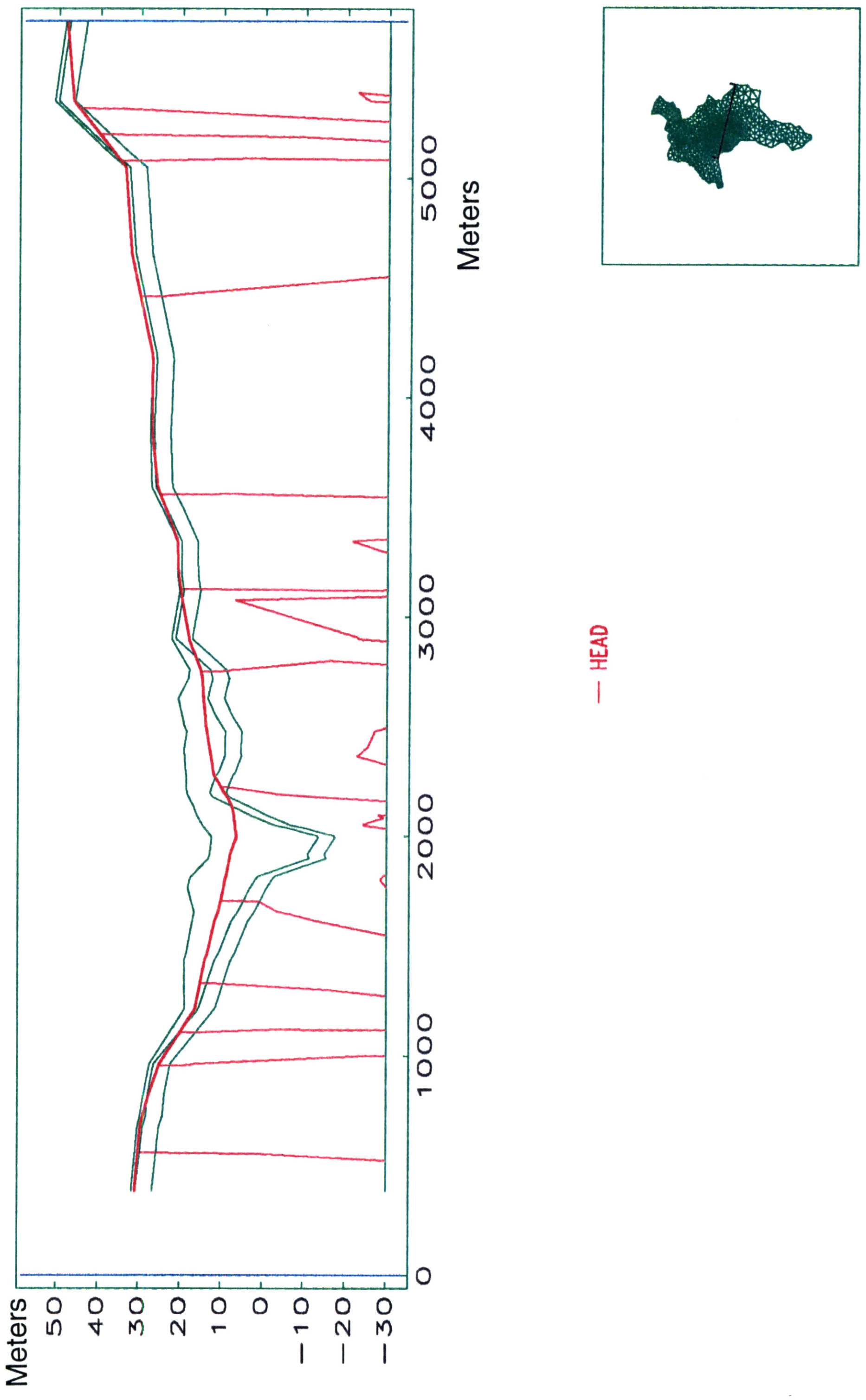

Figure 5-22: Cross-Section Showing Geology and Head with Pumping

Chapter 6

Conclusion and Recommendations

6.1 Conclusion

This thesis consists of two (2) main sections that investigate the mechanics of groundwater flow. This research project, located in the Aberjona River Sub-Basin, approximately 10 miles north of Boston and a part of the Aberjona Watershed, presents an analysis of the hydro-geochemistry of a sub-basin scale aquifer system in an attempt to characterize the large-scale features and influences that affect both flow and transport properties and parameters. The first section presents a description of the hydrology, geology, and chemistry that exists in the sub-basin, and is based primarily on field data and field investigations that have been conducted within the watershed. Section two builds upon this analysis and field data in a modeling exercise that accurately represents the three-dimensionality of the aquifer.

Section one investigates the influence of sub-surface geochemical conditions on flow and arsenic transport. Stratigraphic layers play significant roles in defining the mechanism of flow. While exact information on the structure and permeability of the bedrock environments is not as complete and detailed as with the glacially stratified drift, it can be concluded that preferential flow and transport pathways exist in the upper, unconsolidated layers with higher conductivities. Also, the geochemistry near the hide piles creates an environment favorable for reducing the arsenic species to arsenite—more mobile and more toxic.

Within the same section, discussion continues and provides a better understanding of the flow regime in the Aberjona River Sub-basin, including the three-dimensional impact of vertical gradients and stream-aquifer interaction and behavior. The Aberjona River is the dominant hydrologic influence within the Aberjona Watershed. The stream-aquifer interaction is a phenomena which may vary over the extent of the basin or by transient conditions, seasonally. However, the river is predominantly a gaining stream, characterized by an increased flow of groundwater supply from the aquifer. Recharge zones are located in the upland portions of the sub-basin, along the edges of the sub-basin boundary. The principle directions of flow are toward the center of the sub-basin and the Aberjona River and downgradient from the northern to the southern portion of the sub-basin. The final part of Section 1 assesses the fate of arsenic in the watershed. The occurrence and distribution of arsenic can be linked, directly, to past industrial activity within the watershed. Under oxidizing conditions arsenate (V) is predominant, while arsenite (III) dominates under reducing conditions. Further, in the reduced environment of the hide piles biochemical processes allow the methylation of arsenite to monomethylarsonic acid and dimethylarsinic acid, through bacterially mediated respiration.

The last section presents a synthesis of field results through the numerical model DYNFLOW. This section of the thesis allows for a simple and informative hydrologic representation of the flow regime in the complex and heterodynamic river valley aquifer system; observation of the interdependency of hydrogeologic influences on stream-aquifer interactions, and assistance in the prediction of contaminant migratory pathways. Transient simulations were run to 125 days to approximate steady-state conditions for the aquifer. Hydraulic conductivities and recharge were adjusted for each of the stratigraphic layers which were assumed horizontally uniform. While the model does not capture the small-scale effects, common and varied in large and complex aquifers, it does capture the regional effects that can be used for boundary conditions and input to one or more local and more discretized models. Pumping the wells at *G* and *H* reflect the historical conditions that may have increased the potential for contaminant exposure for residents within the Aberjona watershed, dependent on the supply of groundwater from those two wells for a significant portions of drinking water.

The modeling confirms much of the theoretical analysis presented in Section 1. The modeling results suggest geological heterogeneities may provide the most influence to flow, locally. The Aberjona River has the more significant effect on the behavior of the entire aquifer system. The two predominant patterns of flow within the Aberjona River Sub-basin are lateral movement across the basin from areas of higher elevations to areas of lower elevations, and secondly, flow from the northern portion of the sub-basin to the southern portion of the sub-basin. Because advection is the major factor in contaminant transport, the results of the model indicate migratory pathways extending from the northern portion of the basin—near Industriplex, to the central and southern portion of the sub-basin—near and beyond Wells G & H. Also, contaminant migration is possible from the outer boundaries of the sub-basin, toward the inner portion of the sub-basin—defined by the buried glacial valley—along the Aberjona Ri ver. Once there is interaction with the gaining river, arsenic within the river becomes more mobile and widespread throughout the watershed, and in a shorter amount of time.

6.2 Recommendations

It is highly recommended that work continue to focus on the geological conditions within the watershed and the geochemistry that influences contaminant transport. By utilizing a model that is able to better represent the geological layering—especially, the very thin layers of glacial outwash and till near the model boundaries and the bedrock ridges within the sub-basin interior—one may be able to capture more significant flow effects. Also, by modeling the chemistry—dynamics, equilibria, and kinetics—it will be possible to model the advection and dispersion of contaminant transport, effectively simulating the complex geochemical environments near the hide piles at Industriplex, the Halls Brook Storage Area, and the peat deposits near Wells G & H.

To gain a better understanding of the small-scale aquifer behavior that may have a large bearing on flow mechanisms and transport on a grand scale, the Aberjona River Sub-basin should be further divided into more discretized zones that isolate specific areas of study. One zone of concentration should be the Industriplex area, and another, the Wells G & H area. Using the results presented above allow for a smooth and informative transition to either of these local and highly discretized models.

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