
Jiang Wu
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Jiang Wu
Organic contaminant transport processes in subsurface systems have been paid increasing attention recently. Sorption of organic compounds on the aquifer solid matrix (retardation) is one of the most important processes influencing contaminant transport. The extent of sorption has been estimated by determination of organic carbon in aquifer materials and assumptions concerning sorption constants.

This paper focuses upon the sensitivity of organic contaminant transport to the total organic carbon (TOC) content in a natural aquifer. This study was composed of two phases. The first phase was methodology development and laboratory analysis of organic carbon contents in soil samples. Acidification and furnace combustion methods were used to determine carbon contents. Profiles of the TOC distribution in natural soil were also determined.

Based on the laboratory TOC data, a three-dimensional ground water flow/solute transport computer model was constructed to evaluate the sensitivity of organic contaminant transport to varying TOC distributions. MODFLOW, MODPATH, and MT3D codes were used to perform the modeling simulations. A very sensitive and semi-logarithmic relation between organic transport and TOC level was observed from evaluation of the modeling results.
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CHAPTER I

INTRODUCTION

Statement of the Problem

Pollution of ground water by organic contaminants has been recognized as a matter of concern in the United States (USEPA, 1980). In recent years, increasing attention and concern have been given to the problems associated with contaminant transport to ground water systems (D. Wildenschild et al., 1994).

Organic contaminants have entered soil and ground water from various waste disposal activities, including industrial impoundments, landfills, septic tanks and cesspools, municipal waste water discharges, spreading of wastes on land, and deep well disposal. Ground water contamination also occurred as a result of other activities, such as accidental spills, irrigation practices, and applications of fertilizer and pesticides.

The basic principles of contaminant transport in the subsurface environment are understood in many aspects. Advection, dispersion, sorption, and degradation are four major processes which may strongly influence organic solute transport in saturated ground water environments.

Sorption is the most important process needed to describe the retention of organic solutes by interactions of ground water and porous media. Recent research indicates that the movement of organic contaminants in the subsurface has been influenced by sorption processes involving the total organic carbon (TOC) content in aquifer solids, at least for TOC levels greater than 0.1% (Powell et al., 1989). This
makes the TOC distribution and concentration levels considered more important in prediction of organic contaminant transport in subsurface environments.

Purpose and Scope of the Study

The purpose of the first phase of the study was to verify the performance of an acidification/combustion based method for organic carbon determination in aquifer materials. The method was then used to determine actual TOC levels and vertical concentration distributions at field sites.

In the second phase of the project, the sensitivity of transport prediction to a range of TOC levels was estimated. To enable better understanding and predictions of organic contaminant transport influenced by sorption onto the solid phase, a series of sensitivity analyses of the organic contaminant transport versus varying TOC levels in a typical sand and gravel aquifer was conducted.

The study including field sampling, laboratory analysis, and numerical modeling was completed with sponsorship by the Institute for Water Sciences, WMU, and Department of Geology, WMU. Profile sampling of aquifer solids and ground water table elevation measurements were conducted at Asylum Lake site (WMU's property) between 1991 and 1992. Laboratory analyses (TOC level) were conducted in Water Quality Lab, WMU, in 1991 and 1992. Field and lab data processing and numerical model simulations were performed in 1993 and 1994.
CHAPTER II

OVERVIEW OF ORGANIC SOLUTE TRANSPORT
IN SUBSURFACE SYSTEMS

Processes Influencing Organic Contaminant Transport

Subsurface Physical Processes

The transport and fate of contaminants in the terrestrial subsurface environment are effected by many processes. Physical processes are the most important factors controlling chemical transport in the subsurface. These physical processes can be simply described by advection-dispersion theory for saturated, porous media. An example, provided below, illustrates the effects of advection and dispersion on chemical transport.

If the concentration of a contaminant is measured at successive time intervals in a monitoring well located between a contaminant source and a receptor such as a water supply well (Figure 1), a concentration breakthrough curve can be obtained (Figure 2). In Figure 2, the concentrations do not immediately increase in a step function but, instead, increase more gently in an S-shaped curve. In an one-dimensional, homogeneous system, the arrival of the center of mass is the result of advection while the spread of the breakthrough curve is the result of dispersion.

Advection is the major transport mechanism for a non-reactive, conservative chemical constituent traveling at an average ground water bulk velocity. The average linear velocity, $v$, at which ground water flows through a porous aquifer is:
Figure 1. Site Containing a Monitoring Well, Contaminant Source, and Receptor. (EPA Seminar Publication 1989)

Figure 2. Concentration of a Contaminant in a Monitoring Well.
Where, \( K \) is the hydraulic conductivity of the formation in the direction of ground water flow. 
\( \theta_i \) is the porosity of the formation. 
\( dh/dx \) is the hydraulic gradient in the direction of ground water flow. 

(Freeze and Cherry, 1979).

Dispersion is also very important since it controls the shape of the breakthrough curve and explains mixing effects. The classical mathematical approach for combined solute transport in porous media is the advection-dispersion equation. The one-dimensional equation form is:

\[
\frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}
\]

Where, \( D \) is the dispersion coefficient. 
\( v \) is the ground water velocity. 
\( C \) is the concentration of the solute . 
\( x \) is the spatial coordinate. 
\( t \) is the time.

This equation is an expression of the mass balance of a contaminant within the aquifer as a result of dispersion (the first term), advection (the second term), and change in storage (the third term). The linear dispersion coefficient \( (D) \) can be written as the sum of two terms: an effective molecular diffusion coefficient, \( D_d \), and mechanical dispersion coefficient, \( D_m \).

\[
D = D_d + D_m
\]
\[ D_m = \alpha v \]
\[ D_d = \tau D_0 \]

Where, \( \alpha \) is the constant of proportionality and is known as the dispersivity parameter.

\( D_0 \) is the free solution diffusion coefficient.

\( \tau \) is the tortuosity of the medium. Tortuosity is a factor that accounts for the increased distance a diffusing ion must travel to get around the aquifer solids.

(Gillham and Cherry, 1982)

The advection-dispersion equation can be solved with appropriate boundary and initial conditions to yield the concentration breakthrough curves or concentration distribution curves. For a one-dimensional system with a constant concentration of solute at the boundary, the concentration at a given distance from the source results in an S-shaped curve (Figure 3).

**Subsurface Chemical Processes**

In the case of a non-conservative or reactive solute, the advection-dispersion equation may be modified with the addition of chemical reaction terms (\( RXN \)) to the basic equation:

\[ D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \pm RXN \]

There are many complex chemical processes in subsurface water systems, such as organic reactions, sorption, complexation reactions, hydrolysis, redox, and ion-exchange reaction. Of all these chemical processes, sorption is probably the most
important and that most studied. In ground water applications, sorption of non-polar organics often has most been treated as an equilibrium-partitioning process between the aqueous phase and the porous medium (Chiou et al., 1979). When solute concentrations are low (e.g., either less than $10^{-5}$ Molar, or less than half the solubility, whichever is lower), partitioning has been described using a linear Freundlich isotherm (Karickhoff et al., 1979, and Karickhoff, 1984):

$$S = K_p C$$

Where, $S$ is the sorbed concentration (mg/g).

$C$ is the aqueous concentration (mg/mL).

$K_p$ is the partition or distribution coefficient describing the relative concentration of sorbed versus soluble constituent under equilibrium conditions.
conditions.

Under conditions of linear equilibrium partitioning, the sorption process has most often been represented in advection-dispersion formulations as a retardation factor, R:

\[ D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = R \frac{\partial C}{\partial t} \]

Where,

\[ R = 1 + \frac{\rho_b K_p}{\theta_i} \]

\( \rho_b \) is soil bulk density (g/cm\(^3\)).

\( \theta_i \) is porosity of soil.

The dominant influence on sorption of organics is the partitioning of the organic compound between the solution and the natural organic matter associated with aquifer solids (Karickhoff, 1984, Tanford, 1973, and Mackay et al., 1987). The extent of sorption for non-polar organic solutes on natural soils or sediments has been estimated based on the organic carbon content of the sediment (Karickhoff, 1984) using the expression:

\[ K_p = K_{oc} f_{oc} \]

Where, \( f_{oc} \) is the fraction organic carbon content (by weight) of the soil.

\( K_{oc} \) is a proportionality constant characteristic of the specific chemical.

This approach works reasonably well for a wide range of soils, providing the soil organic content is sufficiently high (\( f_{oc} > 0.001 \)). For lower carbon-content soils, sorption of the organic compounds onto the mineral phase may cause significant
errors in the estimate of $K_p$ (Chiou et al., 1985). Nonetheless, use of the $K_{oc}$ relationship allows the estimation of sorption-based retardation developed from actually measured $f_{oc}$ values, rather than more complicated and expensive batch equilibrium sorption experiments.

$K_{oc}$ has also been estimated by empirical regression equations for $K_{oc}$ versus solubility ($S$ in mg/L), octanol/water partition coefficient ($K_{ow}$), and bioconcentration factor (BCF) (see Table 1).

Table 1

Regression Equations

\[
\begin{align*}
K_{oc} &= -0.55 \log S + 3.64 \\
K_{oc} &= 0.544 \log K_{ow} + 1.377 \\
K_{oc} &= 0.681 \log BCF + 1.963
\end{align*}
\]


Biotransformation and other processes, such as volatilization and non-aqueous phase dissolution and transport may also be very important in some subsurface situations. These processes are beyond the scope of this study, however.

The Use of TOC Data in Prediction of Contaminant Transport

From the preceding discussion, it should be evident that the retardation factor (R) may be a critical parameter in estimating the rate of migration of organic contaminants. These estimates are useful in the design of monitoring networks and remediation schemes for contaminated aquifers. Consequently, determination of
physical transport characteristics of the flow field, notably advection and dispersion, may not be sufficient for predicting the migration of contaminant zones or for performing pathway analysis at existing or proposed waste-management site. We have to consider the effects of geochemical processes to ensure the reliability of our transport prediction.

TOC analytical results are commonly used as input data for contaminant transport models. The partition coefficient $K_p$, generated from weight fraction of TOC and $K_{oc}$, can be used in the above partitioning models to predict contaminant retardation and travel time to downgradient points where ground water protection is essential, for example, the entry into a public water supply well (Powell et al., 1989).

TOC data also can be used to make profiles of TOC versus depth (Figure 4). These profiles can provide clues as to where additional samples should be taken for more thorough and expensive analysis, such as GC-MS, that precisely identify and quantify contaminant species (Powell et al., 1990). These profiles may provide the basis for the use of appropriate $K_p$ estimates for estimating relative retardation in specific layers or pathways of transport.

Review of Related Literature

TOC Related Literature

The total organic carbon (TOC) content of aquifer material has been found to have significant effects on the movement of contaminants in the subsurface environment (Roberts et al., 1989). The movement of hydrophobic contaminants, such as neutral pesticides, through natural sediments is dependent on sorption by the organic carbon content of the sediment. Low TOC content (<0.1%) can cause gross errors in estimations of the partition coefficient $K_p$. 
Traditionally, the fraction of organic carbon ($f_{oc}$) used for a model input parameter has been the TOC of the "pristine" or uncontaminated sediment. Some researchers, however, found that when heavy, oily-phase contaminants sorb to aquifer materials they make a significant contribution to the retardation of co-dispersed or subsequently encountered contaminants. So the use of the "pristine" TOC value becomes increasingly questionable. (Scharp et al., 1989)

Recent work by Mravik and Enfield (1990) indicates that the situation may be even more complex, with lighter compounds, possibly even the volatile components, contributing to contaminant partitioning on the solid aquifer materials.
Accurate analytical determinations become increasingly difficult as the total carbon (TC) and TOC ratio increases, due to the mineral carbonate components of TC and the difficulty of removing them without affecting the TOC. Interlaboratory data show variations of ±39% between laboratories analyzing the same sample, even with appropriate pre-treatment (Powell et al., 1989). Volatile organic carbon is not determined by most analytical methods and therefore may contribute to negative bias in analytical results. In most cases, it would be lost during acidification and release of carbonate carbon or CO₂.

Carbonate carbon or total inorganic carbon (TIC) is frequently present at levels 10 to 100 times that of organic carbon. TIC must be completely removed prior to analysis of TOC or it will be driven off as CO₂ during sample combustion. This represents a potential source of positive bias in TOC measurements. Various instruments and detection systems are in use for TOC. The combustion based methods have been found to be quite reliable though TIC removed by acidification remaining a major concern.

In this study, the method of Caughey and Barcelona (1994) was used which relies on sulfurous acid (H₂SO₃) acidification prior to combustion.

Transport Model Related Literature

Many flow and transport models have been developed to simulate the groundwater flow and contaminant transport in the subsurface environment over recent years. Each model has its specific applied conditions and can solve one or more aspects of the subsurface flow and transport system. Generally, these models use finite differences or finite element method to approach the subsurface environments. They are able to simulate steady-state, transient, or both flow status. Transport
models normally require a basis in ground water flow conditions established within a flow model. Contaminant advection, dispersion, sorption/desorption, biodegradation processes generally may be simulated in one to three dimensional scales. Migration of free phase and multi-phase contaminants are also simulated by some transport models based on density, viscosity, and surface tension. Table 2 provides a list of most of the current transport model computer software in ground water systems.
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<td>MOC</td>
<td>solute advection, dispersion, linear/non-linear sorption, and first order decay or chemical reaction in saturated media</td>
<td>2</td>
<td>included</td>
<td>steady-state &amp; transient</td>
<td>finite</td>
<td>numerical</td>
<td>USGS</td>
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<tr>
<td>MT3D</td>
<td>solute advection, dispersion, linear/non-linear sorption, and first order decay or chemical reaction in saturated media</td>
<td>3</td>
<td>MODFLOW</td>
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<td>INTERTRANS</td>
<td>solute advection, dispersion, linear/non-linear sorption, and first order decay or chemical reaction in saturated media</td>
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<td>INTERSAT</td>
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<td>finite</td>
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<td>SUTRA</td>
<td>solute transport in saturated-unsaturated media, fluid density dependent flow</td>
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<tr>
<td>HST3D</td>
<td>heat and solute transport in saturated media with variable density and viscosity</td>
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<td>included</td>
<td>steady-state &amp; transient</td>
<td>finite</td>
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<tr>
<td>BIOPLUME</td>
<td>hydrocarbon transport influenced by oxygen-limited biodegradation</td>
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<td>FEMSEEP</td>
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<td>AQUA</td>
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<tr>
<td>BIO1D</td>
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<td>included</td>
<td>steady-state &amp; transient</td>
<td>finite differences</td>
<td>analytical</td>
<td>EPA</td>
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<tr>
<td>FLOWTRANS</td>
<td>cross-section solute transport based on advection, dispersion, first order decay, and linear adsorption</td>
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<td>FLOWNET</td>
<td>steady-state</td>
<td>finite differences</td>
<td>analytical</td>
<td>Waterloo</td>
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<tr>
<td>ARMOS</td>
<td>areal migration of free phase light hydrocarbon based on density, viscosity, and surface tension</td>
<td>2</td>
<td>included</td>
<td>steady-state &amp; transient</td>
<td>finite differences</td>
<td>numerical</td>
<td>Parker EPA</td>
</tr>
<tr>
<td>MOTRANS</td>
<td>vertical transport of multi-phase (water, dense or light nonaqueous phase liquid, and air)</td>
<td>2</td>
<td>included</td>
<td>transient</td>
<td>finite element</td>
<td>numerical</td>
<td>Parker EPA</td>
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CHAPTER III

THE HYPOTHESIS AND DESIGN OF THE STUDY

This study planned to measure TOC analytical data as inputs to a three-dimensional transport model to explore the sensitivity of the predicted transport to varying $f_{oc}$ levels in subsurface sediments.

A relatively uniform sand and gravel aquifer was selected to conduct the field sampling and numerical modeling. A typical organic contaminant, trichloroethylene (TCE), was selected as the transport solute species for model simulations. These selections represent well understood aquifer and solute characteristics for the study. It should then useful to compare and evaluate the results generated from this study with the literature studies.

The TOC analytical method was originally developed by Dr. Michael Caughey, Illinois State Water Survey (ISWS). A slightly modified procedure was used to get a series of TOC, TC, and TIC data from different depths in the aquifer.

MODFLOW was used to simulate the ground water flow, and MT3D was used in contaminant transport simulation. MODPATH was used to lay out the flowpath and particle travel time. A set of varying $f_{oc}$ levels (due to analytical and natural variability) were input into the transport model to evaluate the quantitative relationship between $f_{oc}$ level and contaminant transport. Two powerful graphical software programs (AUTOCAD and SURFER) were used to portray the simulation results. Figure 5 shows the overall framework of the entire study.
Figure 5. Design of the Study.
CHAPTER IV

HYDROGEOLOGIC CHARACTERISTICS OF THE SELECTED SITE

Site Location

The study site was on Western Michigan University's property in the Asylum Lake area of southwest Kalamazoo. The Asylum Lake site lies north of Parkview Ave. and east of Drake Rd., in Kalamazoo Township. The site location is shown in Figure 6.

Site Geology and Hydrogeology

The sediments of the site and surrounding area are comprised of glacial outwash sand and gravel and postglacial alluvium. These sediments are pale brown to pale reddish brown, fine to coarse sand alternating with layers of small gravel to heavy cobbles. A clay unit at a depth of about 150 feet below land surface was detected by on-site geophysical survey which is believed to be a continuous aquitard of the sand and gravel aquifer. The bedrock top lies at about 220 to 230 feet below land surface is Mississippian Age Coldwater Shale. The topography of the principal area is generally flat, and that of the overall property has a deeper gradient towards Asylum Lake.

The static ground water level is about 50 feet below the grade across the site. The water flow direction is generally from southwest to northeast towards Asylum Lake. A certain base flow is believed to run beneath Asylum Lake and flow towards Kalamazoo River basin. Asylum Lake exhibits relatively stable water levels. Ground
water flows into the lake at the west and central portions of the lake boundary, and flow out of the lake into the aquifer at the east portion of the lake boundary.

This study mainly focuses on the upper unit of the unconfined, sand and gravel aquifer (above the clay layer). An *in-situ* pumping test was conducted by the Geology Department, WMU, in Summer 1991. The measured aquifer transmissivity is 8000 ft$^2$/day.

Figure 7 shows the ground water flow direction and water level elevations measured in Summer, 1992.
Figure 6. Site Location Map.
Figure 7. Site Ground Water Flow Direction and Water Level Elevations.
CHAPTER V

AQUIFER SOLID SAMPLING AND LABORATORY ANALYSIS

Aquifer Solid Sampling

A total of 18 soil samples were collected by split-spoon techniques at 3 locations (AL-1, AL-14, and AL-17) at depths of 3 to 55 feet below land surface in summer, 1991 (see Table 3). The soil samples were put in 500 mL jars, sealed, and delivered directly to the Water Quality Lab, Institute for Water Sciences. A series of unique laboratory identification numbers were assigned to each individual sample (Table 3). The soil samples were stored in a refrigerator at 4°C before analyzing.

Aquifer Solid Analysis

Sample Preparation

Soil samples were prepared in following standard steps (Caughey and Barcelona, 1994):

1. Place each sample in a 40 mL vial and dry in oven at 40°C for 48 hours, then cool down to room temperature.

2. Grind dried samples until more than 90% of total weight can pass #200 sieves.

3. Put ground samples in 40 mL vials without caps in vacuum desiccator until samples reach constant weight.

4. Close vials with caps and store them in refrigerator at 4°C.

The sample grinding procedure was as follows:
Table 3
Aquifer Solid Sample Locations, Depth, and WQL ID Numbers

<table>
<thead>
<tr>
<th>WQL ID</th>
<th>Sampling Location</th>
<th>Sampling Depth (feet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0020</td>
<td>Well AL-14</td>
<td>3.5 - 5.0</td>
</tr>
<tr>
<td>A0021</td>
<td>Well AL-14</td>
<td>8.0 - 10.0</td>
</tr>
<tr>
<td>A0022</td>
<td>Well AL-14</td>
<td>13.5 - 15.0</td>
</tr>
<tr>
<td>A0023</td>
<td>Well AL-14</td>
<td>18.5 - 20.0</td>
</tr>
<tr>
<td>A0024</td>
<td>Well AL-14</td>
<td>23.5 - 25.0</td>
</tr>
<tr>
<td>A0025</td>
<td>Well AL-14</td>
<td>28.5 - 30.0</td>
</tr>
<tr>
<td>A0026</td>
<td>Well AL-14</td>
<td>33.5 - 35.0</td>
</tr>
<tr>
<td>A0027</td>
<td>Well AL-14</td>
<td>38.5 - 40.0</td>
</tr>
<tr>
<td>A0028</td>
<td>Well AL-17</td>
<td>5.0 - 5.5</td>
</tr>
<tr>
<td>A0029</td>
<td>Well AL-17</td>
<td>7.0 - 7.5</td>
</tr>
<tr>
<td>A0030</td>
<td>Well AL-17</td>
<td>9.0 - 9.5</td>
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<td>A0031</td>
<td>Well AL-17</td>
<td>3.0 - 3.5</td>
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<td>A0103</td>
<td>Well AL-1</td>
<td>33.5 - 35.0</td>
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<td>A0104</td>
<td>Well AL-1</td>
<td>13.5 - 15.0</td>
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<td>Well AL-1</td>
<td>53.5 - 55.0</td>
</tr>
<tr>
<td>A0106</td>
<td>Well AL-1</td>
<td>43.5 - 45.0</td>
</tr>
<tr>
<td>A0107</td>
<td>Well AL-1</td>
<td>23.5 - 25.0</td>
</tr>
<tr>
<td>A0109</td>
<td>Well AL-1</td>
<td>3.5 - 5.0</td>
</tr>
</tbody>
</table>
1. Measure out about 20 g of dried sample.

2. Grind samples by agate mortar/pestle set or mechanical grinder, about 5 g of sample each time.

3. Mix ground sample well.

4. Use about 5 g sample to check percentage passing through #200 sieves.

5. Transfer remaining sample into a labeled 40 mL vial.

6. Clean mortar/pestle or grinder.

**Analytical Methods**

In this study, two methods were used to generate TIC and TOC data. The first method was to use a weak acid (H$_2$SO$_3$, 6%) to remove inorganic carbon (carbonate and bicarbonate) from the samples at low temperature (40°C) in order to maintain only the organic carbon content of the samples:

$$H_2SO_3 = H^+ + HSO_3^-$$

$$HCO_3^- + H^+ = H_2O + CO_2$$

$$CO_3^{2-} + 2H^+ = H_2O + CO_2$$

After the samples were acidified in ceramic boats, a high-temperature furnace (950°C) with O$_2$ supplied was used to combust the organic carbon (assume all inorganic carbon was removed) into CO$_2$ and H$_2$O. A photometric, automated coulometric titrator was used to determine the CO$_2$ evolved and quantitation was done relative to pure organic standard compounds. In this way, the readings from the titrator represented TOC levels directly.

The second method was to determine total inorganic carbon (TIC) and total
carbon (TC) contents in sample separately. Acidification and coulometric titration of off-gases was used to determine TIC level. Combustion of an unacidified sample was used to determine TC level. The theoretical TOC level was determined by the difference between TC and TIC:

\[ \text{TOC} = \text{TC} - \text{TIC} \]

In this study, the first method was used to analyze TOC content in soil samples, and the second method was used to quality control (QC) the accuracy of the analytical data.

The analytical procedures for the two methods were as follows:

The first method:
1. Ceramic boat cleanup.
2. Weigh samples (leave two boats as blanks) to nearest 0.1 mg.
3. Acidification: add 1-3 mL H$_2$SO$_3$ solution (6%) to each boat and dry them on heater (40°C). For the samples with high inorganic carbon content, this step needs to be repeated a couple more times.
4. Combust each boat (the first and the last one should be blanks) in furnace (950°C) for 9 minutes. Record the TOC readings.

The second method:
1. Vial cleanup.
2. Weigh samples.
3. Acidification: add 2-3 mL HCl (2N) to each vial on heater (≈100°C) for 9 minutes. Record the TIC readings (run two blanks).
4. Clean ceramic boats.
5. Weigh samples (leave two blank boats) to nearest 0.1 mg.
6. Combust each boat (run blanks at first and end) in furnace (950°C) for 9 minutes. Record the TC readings.

7. Subtract TIC value from TC value (unit: µgC/g sample) and get TOC value.

Analytical Results

All raw laboratory data were processed using Lotus 1-2-3 (version 2.3) and Microsoft EXCEL (version 4.0). A summary of the organic, inorganic, and total carbon analytical results is included in Table 4. The entries in Table 6 show that the analyzed organic carbon content in the aquifer solid samples was between 0.099 and 3.627 µgC/g sample.

The data in Table 4 indicate that the TOC generated from the first method matches well with those from the second method (-14.318% to 13.447% residuals). It is within acceptable analytical procedures. A visual relationship of TOC levels between the first method and the second method is illustrated in Figure 8.

Figure 9 illustrates the distribution of TOC (mg/g) in natural unsaturated and saturated soil with depth at the Asylum Lake site. The figure shows that a higher TOC levels are likely to appear at shallow zones (in the top soil at the ground surface or just above the water table), and that TOC level generally decrease with the increasing depth. These results agree qualitatively with those of Powell et al. (1989) shown in Figure 4.
Table 4

Summary of Carbon Analytical Results for Aquifer Solids
(The Asylum Lake Site)

<table>
<thead>
<tr>
<th>WQL ID</th>
<th>TC</th>
<th>TOC</th>
<th>TIC</th>
<th>(TOC+TIC-TC)/TC</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0020</td>
<td>5.142</td>
<td>3.627</td>
<td>2.208</td>
<td>13.477</td>
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<td>A0021</td>
<td>13.655</td>
<td>0.099</td>
<td>12.142</td>
<td>-10.355</td>
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<tr>
<td>A0022</td>
<td>10.808</td>
<td>0.131</td>
<td>10.142</td>
<td>-4.950</td>
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<td>A0023</td>
<td>9.796</td>
<td>0.030</td>
<td>9.937</td>
<td>-4.950</td>
</tr>
<tr>
<td>A0024</td>
<td>15.615</td>
<td>0.068</td>
<td>13.395</td>
<td>-13.782</td>
</tr>
<tr>
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<td>19.277</td>
<td>0.177</td>
<td>17.350</td>
<td>-9.078</td>
</tr>
<tr>
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<td>16.535</td>
<td>0.213</td>
<td>15.251</td>
<td>-1.787</td>
</tr>
<tr>
<td>A0027</td>
<td>11.604</td>
<td>0.242</td>
<td>11.029</td>
<td>-5.378</td>
</tr>
<tr>
<td>A0028</td>
<td>20.548</td>
<td>0.951</td>
<td>18.418</td>
<td>-5.738</td>
</tr>
<tr>
<td>A0029</td>
<td>3.097</td>
<td>0.570</td>
<td>2.844</td>
<td>10.236</td>
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<td>17.821</td>
<td>0.602</td>
<td>16.613</td>
<td>3.800</td>
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<td>1.899</td>
<td>0.004</td>
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<td>0.806</td>
<td>11.126</td>
<td>6.314</td>
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<td>25.279</td>
<td>0.615</td>
<td>25.092</td>
<td>1.693</td>
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<td>A0105</td>
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<td>10.199</td>
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<td>A0107</td>
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<td>0.317</td>
<td>10.994</td>
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<td>A0109</td>
<td>1.422</td>
<td>1.223</td>
<td>0.066</td>
<td>-9.353</td>
</tr>
</tbody>
</table>

(1) Water Quality Lab sample identification number.
(2) Total Carbon content in soil sample (unit in mg C/g sample).
(3) Total Organic Carbon content in soil sample (unit in mg C/g sample).
(4) Total Inorganic Carbon content in soil sample (unit in mg C/g sample).
Figure 8. Comparison of TOC Analytical Results Between Method 1 and Method 2.
Figure 9. TOC Profile Distribution in Natural Soil (Asylum Lake Site).
CHAPTER VI

COMPUTER MODEL SIMULATIONS

Introduction of the Software

A ground water flow and contaminant transport model was developed for the Asylum Lake study site to evaluate the ground water flow pattern and selected contaminant transport characteristics.

The model software used to simulate ground water flow system was developed by M.G. McDonald and A.W. Harbaugh (1988) of the U.S. Geological Survey and is entitled "A Modular Three-Dimensional Finite-Difference Ground Water Flow Model (MODFLOW)". The modular design of MODFLOW allows the assignment of specific modules of computer code to simulate different aspects of the hydrogeologic system. MODFLOW is capable of simulations of three-dimensional ground water flow in either confined, unconfined, or a combination of confined and unconfined conditions. Flow associated with external stresses, such as wells, areal recharge, evapotranspiration, river, drain, and general head boundary, can also be simulated. This program was written in FORTRAN 77 and will run without modification on most computers that have a FORTRAN 77 compiler.

A model software named "MODPATH" was developed by David W. Pollock (1989) of USGS to compute and display pathlines using output from steady-state simulations obtained with MODFLOW. This software was used in this study to describe the conservative (non-reactive, no retardation) particle tracking under the existing or predicting flow conditions. MODPATH can display flow pathlines in areal or 3D view, and the program will post travel time periods on each pathline.
This program is written in FORTRAN 77.

MT3D was selected to simulate contaminant transport in this study. MT3D was developed by C. Zheng of S.S. Papadopulos & Associates, Inc. and is entitled "A Modular Three-Dimensional Transport Model for Simulation of Advection, Dispersion, and Chemical Reaction of Contaminants in Ground Water Systems" (1992). The model program uses a modular structure similar to that implemented in MODFLOW, and MODFLOW may be used in conjunction with MT3D to provide ground water flow information. MT3D can simulate advection, dispersion, sink/source mixing, and chemical reactions. The chemical reactions included in the model are equilibrium-controlled linear or non-linear sorption and first-order irreversible decay or biodegradation. This program was written in FORTRAN 77 and uses the same computer hardware used for MODFLOW.

AUTOCAD (release 12) developed by Autodesk, Inc. was used to finalize and output all modeled figures and other charts in this study. SURFER (version 4.1) developed by Golden Software, Inc. was used to transfer modeled data matrix into contour maps. A preprocessor, MODELCAD\textsuperscript{386} (version 2.0) developed by Geraghty & Miller, Inc., was used to setup the input data files of MODFLOW and MT3D. EXCEL (version 4.0), Lotus 1-2-3 (version 2.3), and Microsoft Word (version 2.2) were used to process, transfer, and format data during the model simulations.

A GATEWAY 2000 33MHz 486DX (IBM/PC compatible) was used to perform the simulations. It was equipped with: (a) Intel 80486 processor, (b) 64K cache RAM, (c) 8 MB RAM, (d) 1.2MB 5.25" drive, (e) 1.44MB 3.5" drive, (f) 200MB 15ms IDE drive with 64K multi-segmented cache, (g) ATI graphics ultra video, (h) 14" crystal scan 1024NI color VGA monitor, (i) 1 parallel/2 serial ports, (j) 124-key AnyKey keyboard, (k) Microsoft mouse, (l) MS DOS 5.0, and (m) MS
Modeling of the Ground Water Flow System

Conceptual Model

A conceptual model of hydrogeologic system at the Asylum Lake site was developed prior to construction of the ground water flow model. Chapter IV contains a detailed description of the site geology and hydrology. The sediments consist of fine to coarse grained sand with occasional layers of gravel which overlie the clay unit at the base of the water table aquifer. The aquifer thickness is about 100 feet.

The regional ground water flow direction is generally from southwest to northeast towards Asylum Lake and the ponds in the vicinity. The average measured hydraulic gradient was approximately 0.0025.

The hydrostratigraphy was viewed as a three-layer system to simulate vertical distribution of TOC and solute transport. The grid boundaries were set a sufficient distance away from the area of investigation to eliminate model boundary effects and diminish the need to measure precise boundary values.

Model Setup

In MODFLOW, computer code sets (packages) were used to simulate the different aspects of the hydrogeologic system. Within these packages, the Basic, Block Centered Flow, Recharge, and Well packages were used in this study to evaluate the existing site ground water flow patterns and to predict the potential contaminant transport. The strongly implicit procedure solver was selected to permit convergance of the model with successive iterations.
Basic Package Input

A 3,800-foot by 3,400-foot grid of three layers was constructed using a uniform node of 50-foot spacing (68 rows by 76 columns). Figure 10 shows the model grid setup. The model grid was oriented to correspond to the regional groundwater flow direction. Figure 11 illustrates the model grid locations. The northeast boundary of the model grid was set to the edge of Asylum Lake and the nearby ponds as the major discharge boundary. The southwest boundary was set at a highland upgradient as the major recharge boundary. The northwest and southeast boundaries are generally perpendicular to the flow direction, and were set as no-flow boundaries. Figure 12 illustrates the boundary setup of the model. A downward vertical gradient (0.005 to 0.01) was set at the southwest boundary between layers to simulate the vertical flow caused by recharge. An upward vertical gradient (0.005 to 0.01) was set to the northeast boundary between layers to reflect discharge to the lake.

Block Centered Flow Package

An aquifer pumping test was conducted on the site in Summer 1991, and the calculated hydraulic transmissivity was 8,000 ft²/day. Based on the pumping test and grain size analysis results, the horizontal hydraulic conductivity was in the range of 100 to 200 feet/day. Vertical conductivity used in specific layers or between layers was set as one tenth of the horizontal conductivity to simulate the leakage between layers. Flat bottoms were set for all three layers. The bottom elevation of the lowest layer was set on top of the clay unit. The bottom elevation of the middle layer was set 30 ft above the clay, and the bottom of the top layer was set 60 feet above the clay. An average porosity for sand and gravel sediments of 0.25 was set in the model.
MODEL GRID AREA
(3800 ft x 3400 ft – 68 rows x 76 columns)

76 COLUMNS

Model Grid Spacing is 50 ft.

Legend
- Model Grid lines
- Observation Wells
- Lakes
- Ground Water
- Flow Direction

Figure 10. Ground Water Model Grid Setup.
Figure 11. Ground Water Model Grid Location Map.
Boundary Conditions: (Layer 1 though Layer 3)

- Constant Head Boundary
- No-Flow Boundary
- Inactive Cells

LEGEND

- Model Grid Lines
- Observation Wells
- Lakes
- Ground Water
- Flow Direction
- Wetland

Figure 12. Model Boundary Condition Setup.
to be used later in particle tracking and contaminant transport simulations.

Well Package

To eliminate the effects on transport simulation from the complex lake boundary, a proposed purge well was set between source area and the lake boundary. The purge well was assumed to fully penetrate all layers. The purge rate in each layer was set at 50 gpm (i.e., the total purge rate from the purge well was 150 gpm).

Recharge Package

The recharge package was used to simulate the infiltration of precipitation across the site. Based on available climatic data, an average annual precipitation of 32 inches was received by the region. Annual infiltration or recharge to the aquifer was represented as one-third of the precipitation (10 inches per year) during the model calibration and simulation scenarios.

Strongly Implicit Procedure Package

The strongly implicit procedure (SIP) package was used to solve the ground water flow equations resulting from the model input by iteration. All flow model runs were converged by using the SIP solver in this study.

Model Calibration

Upon completion of the model setup, the ground water flow model was calibrated to the Summer 1992 ground water elevation data. The model was calibrated by adjusting the hydraulic conductivity, vertical leakance, and hydraulic boundary heads until an acceptable match to the target data was obtained. The
calibrated ground water flow contours in each layer are included in the modeling result section.

Upon the calibration, the proposed purge well was emplaced, and the model was used to assess the sensitivity of the contaminant transport to TOC levels.

Ground Water Flow Pathline and Travel Time

MODPATH was applied to evaluate travel times for a group of conservative particles (non-reactive, no retardation) which started from the upgradient area (source area) and were allowed to flow through the majority of the model. The particle pathlines were simulated in each layer, and travel times were posted on each of the pathlines. These travel times theoretically represent ground water flow pathways and velocities.

Modeling of Contaminant Transport

Model Setup

The input structure for MT3D was similar to the ground water flow model (MODFLOW). The input data were formatted into packages which contained input parameters needed to simulate the different aspects of contaminant transport. Of the available packages the Basic Transport, Advection, Dispersion, Chemical Reaction, and Source/Sink Mixing packages were used to simulate the contaminant migration. The application of each of these packages is described below.

Basic Transport Package

Due to the similarity of the input formats between MODFLOW and MT3D,
most of the information for definition of the modal domain was obtained directly from the existing MODFLOW Basic and Block Center Flow input files.

In this model, trichloroethylene (TCE) was selected as the source transport solute. The initial concentration of 1000 µg/L was input in four cells (100-foot by 100-foot) and in all three layers as constant concentration source to simulate continuous TCE entered into the aquifer. A typical porosity value of 0.25 for sand and gravel aquifer was used in all transport simulations.

**Advection Package**

The advection package simulated the change in chemical concentration due to advection. MT3D provides three types of Eulerian-Lagrangian algorithms to solve the advection portion of contaminant transport. The Method of Characteristics (MOC) was used in this model. It uses a conventional particle tracking technique to solve the advection term. One important feature of the MOC technique is that it is virtually free of numerical dispersion, which creates serious difficulty in many standard numerical solution schemes.

**Dispersion Packages**

The dispersion package simulated the change in contaminant concentrations due to hydrodynamic dispersion. Hydrodynamic dispersion occurs due to mechanical mixing during advection through porous medium and because of molecular diffusion due to the thermal-kinetic energy of the contaminant particles.

The dispersion term was broken down into three orthogonal components of spreading: (1) longitudinal dispersivity ($\alpha_L$) which accounts for spreading in the direction of ground water flow, (2) horizontal transverse dispersivity ($\alpha_{TH}$), and (3)
vertical transverse dispersivity ($\alpha_{tv}$).

In this model, the values of longitudinal, horizontal, and vertical dispersivity were set as 10 feet, 2 feet, and 2 feet, respectively. These values were considered appropriate considering the homogeneous nature of the aquifer. Spreading due to molecular diffusion was not considered during the transport simulations because the average linear ground water flow velocities at the site fell within an advection dominated flow regime (i.e., diffusion was negligible for the simulations).

**Source/Sink Mixing Package**

The source/sink mixing package simulated dissolved contaminants entering the simulated domain through sources (i.e., recharge), or leaving the simulated domain through sinks (i.e., wells or drains). In this model, this package was used to simulate the TCE input as a constant concentration source, and the removal of TCE due to pumping at the proposed purge well (PW-1). The location of the point source was set upgradient of the model. The location and flow rate of the point sink (PW-1) were obtained directly from the output of the ground water flow model.

**Chemical Reaction Package**

The chemical reaction package was used to simulate the retardation of contaminant migration due to sorption and desorption of the contaminants with the aquifer matrix. A linear isotherm was selected to simulate the adsorption and desorption process. A soil bulk density of 120.6 lb/ft$^3$ and $K_{oc}$ of 1.26X10$^2$ were input into the model. A range of varying $f_{oc}$ values from 0.0001 to 0.01 were input to conduct the sensitivity analysis.
Model Scenarios

Three transient transport simulations were conducted based on the calibrated ground water flow characteristics. A stress period of 25 years was used and the TCE concentration distribution was output at a 5-year intervals. Scenario 1 was designed to simulate the transport characteristics of TCE in the sand and gravel aquifer with a \( f_{oe} \) level of 0.001 which is the most realistic case based on the laboratory analytical results and the literature references. Scenarios 2 and 3 were designed to simulate the TCE transport in the aquifer with \( f_{oe} \) levels of 0.01 and 0.0001 which were one order magnitude larger and smaller than the value for realistic case. The retardation factor (R) was calculated by the model as 1.10, 1.97, and 10.73, corresponding to the \( f_{oe} \) input values of 0.0001, 0.001, and 0.01. In these three scenarios, all flow and transport parameters were kept constant except for \( f_{oe} \) values. This helped to acquire the sensitivity of the relation between net contaminant transport and \( f_{oe} \) level.

Modeling Results

The ground water flow model (MODFLOW) was calibrated to within 0.38 foot of the observed water levels (Summer, 1992) for the entire modeled area. The majority of water levels were calibrated to less than 0.23 foot. Table 5 presents the model calibration statistical results with the target head, modeled head, and residuals for the corresponding monitoring wells at the site. The residual standard deviation over the head range for all layers was 6.5%. Figure 13 shows the graphical view of modeled ground water contours in each layer. The head residuals are also posted.

The output from MODPATH indicated that modeled ground water flow velocity in majority grid area was 319.2 ft/year or 0.87 ft/day with the proposed purge well PW-1 (see Figure 14).
Table 5
Model Calibration Results

Calibration Statistics

<table>
<thead>
<tr>
<th>MODFLOW BCF File Name</th>
<th>MODFLOW BAS File Name</th>
<th>Target Information in</th>
<th>Model-Computed Heads in</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Well Name</th>
<th>Target Head</th>
<th>Model Head</th>
<th>Residual</th>
</tr>
</thead>
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<tr>
<td>AL-11</td>
<td>873.50</td>
<td>873.35</td>
<td>0.15</td>
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<td>AL-17</td>
<td>870.60</td>
<td>870.72</td>
<td>-0.12</td>
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<tr>
<td>AL-15</td>
<td>871.00</td>
<td>870.96</td>
<td>0.04</td>
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<tr>
<td>AL-4</td>
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<td>-0.33</td>
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<td>AL-2</td>
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<td>LB-2</td>
<td>873.00</td>
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<td>-0.38</td>
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</table>

---- Summary Statistics For Entire Model -----
Residual Mean = -0.083899
Residual Standard Dev. = 0.230884
Residual Sum of Squares = 0.422424
Absolute Residual Mean = 0.000000
Minimum Residual = -0.377319
Maximum Residual = 0.286133
Observed Range in Head = 3.550476
Res. Std. Dev./Range = 0.065029

----------Statistics for Layer 1----------
Number of Targets = 7
Residual Mean = -0.083899
Residual Standard Dev. = 0.230884
Residual Sum of Squares = 0.422424
Absolute Residual Mean = 0.000000
Minimum Residual = -0.377319
Maximum Residual = 0.286133
Observed Range in Head = 3.550476
Res. Std. Dev./Range = 0.065029
Layer 1:

Layer 2:

Layer 3:

LEGEND

-0.33 Head Residual (ft)
-872.0 Modeled Ground Water
Contour Lines

Ground Water Flow Direction

Figure 13. Ground Water Flow Calibration.
Modeled Ground Water Flow Characteristics:

Layer 1:  
Layer 2:  
Layer 3:  

Notes:
(1) Proposed purge well (full penetrating): Purge rate = 150 gpm (50 gpm in each layer)
(2) Conservative particle (non-reactive) travel time interval: 1 year between dots
(3) Modeled ground water flow velocity in majority grid area: \( V = 319.2 \text{ ft/year} \) (0.87 ft/day)

LEGEND
- Travel Time Interval Mark
- Proposed Purge Well
- Modeled Ground Water Flow Contour Lines
- Ground Water Flow Path line

Figure 14. Modeled Flow Pathlines and Particle Travel Times.
The results of Scenario 1 are presented in Figures 15 and 16. Figure 15 illustrates the horizontal and vertical transport of TCE under a uniform $f_{oc}$ distribution in each layer (at transport time $t = 5$ years). The results indicate that net TCE transport in each layer was quite similar. The results also imply that groundwater flow paths were primarily horizontal rather than vertical, negligible vertical flow occurred between layers. Figure 16 illustrates the TCE transport in Layer 1 at transport periods of 5, 10, 15, 20, and 25 years. The results indicate that under a uniform $f_{oc}$ level of 0.001, the TCE plume front would be expected to move about 1150 feet in 5 years, towards well PW-1 (2250 feet from the source area) in 10 years. The TCE concentration distribution achieved equilibrium at about 20 years.

Scenario 2 evaluated TCE transport at a uniform $f_{oc}$ level of 0.01. Figure 17 illustrates the TCE transport characteristics in Layer 1 at 5, 10, 15, 20, and 25 years. The results show that the plume front would be expected to move approximately 350 feet in 5 years and 1100 feet in 25 years. Obviously, the TCE plume migrated much slower in a high $f_{oc}$ level aquifer.

Scenario 3 evaluated TCE transport characteristics under a uniform $f_{oc}$ level of 0.0001. Figure 18 illustrates the TCE transport in Layer 1 at 5, 10, 15, 20, and 25 years. It shows that the TCE plume front would be expected to move about 1950 feet in 5 years, and achieve the equilibrium at 10 years. These results indicate that the TCE plume would migrate much faster in a low $f_{oc}$ level aquifer.

A summary of migration distance in each time period from Scenario 1 through Scenario 3 is presented in Table 6.
Layer 1:  
Layer 2:  
Layer 3:  

Cross Section A-A':

**LEGEND**

- TCE: $K_{oc} = 1.26 \times 10^2$  
- $R = 1.97$  
- $f_{oc} = 0.001$  
- $n = 0.25$

**Figure 15.** Modeled Contaminant (TCE) Transport in a Three-Dimensional Aquifer System ($t = 5$ years).
Figure 16. Modeled Contaminant (TCE) Transport in Layer 1 Under a Medium TOC Level. 

TCE:

\[ K_{oc} = 1.26 \times 10^4 \text{ ml/g} \]
\[ f_{oc} = 0.001 \]
\[ K_d = 0.126 \text{ ml/g} \]
\[ R = 1.97 \]
\[ n = 0.25 \]
Figure 17. Modeled Contaminant (TCE) Transport in Layer 1 Under a High TOC Level.
Figure 18. Modeled Contaminant (TCE) Transport in Layer 1 Under a Low TOC Level.
Table 6

Modeled Contaminant (TCE) Plume Front Migration Under Varying foc Levels

<table>
<thead>
<tr>
<th>foc Level (ug/L)</th>
<th>TCE Transport Distance from Source (feet)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 years</td>
</tr>
<tr>
<td>0.01 1</td>
<td>42.29</td>
</tr>
<tr>
<td>0.01 10</td>
<td>35.59</td>
</tr>
<tr>
<td>0.01 100</td>
<td>30.43</td>
</tr>
<tr>
<td>0.01 500</td>
<td>17.02</td>
</tr>
<tr>
<td>0.001 1</td>
<td>97.76</td>
</tr>
<tr>
<td>0.001 10</td>
<td>81.93</td>
</tr>
<tr>
<td>0.001 100</td>
<td>70.81</td>
</tr>
<tr>
<td>0.001 500</td>
<td>16.90</td>
</tr>
<tr>
<td>0.0001 1</td>
<td>153.93</td>
</tr>
<tr>
<td>0.0001 10</td>
<td>128.54</td>
</tr>
<tr>
<td>0.0001 100</td>
<td>110.34</td>
</tr>
<tr>
<td>0.0001 500</td>
<td>17.08</td>
</tr>
</tbody>
</table>
An additional evaluation of TCE transport in an aquifer with a vertical $f_{oc}$ gradient was conducted based on above model simulations. The results are presented in Figure 19. The $f_{oc}$ level was set 0.01 in Layer 1, 0.001 in Layer 2, and 0.0001 in Layer 3. The profile of TCE migration in Figure 19 shows the quantitative transport vs. $f_{oc}$ relationship. The vertical gradient of $f_{oc}$ used in this evaluation represents one of the typical natural distributions of $f_{oc}$ in the sand and gravel aquifer at the study site. Therefore, the TCE transport characteristics shown in Figure 19 basically represent the expected solute transport in this sand and gravel aquifer.

A mathematical regression procedure was applied to define more quantitatively the relation between the TCE transport and $f_{oc}$ level. Tables 7 through 10 include the linear regression efforts which show an extremely high correlation between simulated TCE migration and $f_{oc}$ level. Figure 20 illustrates these relations in a semilogarithm chart. All data used in mathematics regressions in this study were from the transport model output results simulated at 5 years.
Cross Section A-A':

- Constant Conc. \( (C_o = 1000 \, \text{ug/L TCE}) \)
- Modeled top of Layer 1
- Layer 1
- Layer 2
- Modeled Bottom of the Aquifer

LEGEND
- TCE Concentration (500 - 1000 \, \text{ug/L})
- TCE Concentration (100 - 500 \, \text{ug/L})
- TCE Concentration (10 - 100 \, \text{ug/L})
- TCE Concentration (1 - 10 \, \text{ug/L})
- Ground Water Flow Direction

NOTES:
- Layer 1: \( f_{oe} = 0.01, \, R = 10.73 \)
- Layer 2: \( f_{oe} = 0.001, \, R = 1.97 \)
- Layer 3: \( f_{oe} = 0.0001, \, R = 1.10 \)

Figure 19. Modeled Contaminant (TCE) Transport in a Varying \( f_{oc} \) Level Aquifer System.
### Table 7

Regression Statistics Results - TCE Conc. = 1.0 ug/L

<table>
<thead>
<tr>
<th>Regression Statistics</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiple R</td>
<td>0.999993</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R Square</td>
<td>0.999987</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adjusted R Squared</td>
<td>0.999974</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard Error</td>
<td>0.285774</td>
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<td>Observations</td>
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</tbody>
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<tr>
<th>Analysis of Variance</th>
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<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F</th>
<th>Significance F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
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<td>6231.7448</td>
<td>6231.7448</td>
<td>76307.0792</td>
<td>0.0023</td>
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<tr>
<td>Residual</td>
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<td>0.0817</td>
<td>0.0817</td>
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</tr>
<tr>
<td>Total</td>
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<td>6231.8265</td>
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<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Standard Error</th>
<th>t Statistic</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>x1</td>
<td>-55.8200</td>
<td>-276.2374</td>
<td>0.0000</td>
<td>-58.3876</td>
<td>-53.2524</td>
</tr>
</tbody>
</table>
Table 8
Regression Statistics Results - TCE Conc. = 10.0 ug/L

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<thead>
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<th>Regression Statistics</th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiple R</td>
<td>0.9999999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R Square</td>
<td>0.999997</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adjusted R Squa</td>
<td>0.999994</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard Error</td>
<td>0.110227</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Observations</td>
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<td></td>
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</table>

<table>
<thead>
<tr>
<th>Analysis of Variance</th>
<th>df</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F</th>
<th>Significance F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>1</td>
<td>4319.8513</td>
<td>4319.8513</td>
<td>355543.3128</td>
<td>0.0011</td>
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<tr>
<td>Residual</td>
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<td>0.0121</td>
<td>0.0121</td>
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<td>Total</td>
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<td>4319.8634</td>
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<table>
<thead>
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<th>Standard Error</th>
<th>t Statistic</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-10.9300</td>
<td>-64.9148</td>
<td>0.0002</td>
<td>-13.0694</td>
<td>-8.7906</td>
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<tr>
<td>x1</td>
<td>-46.4750</td>
<td>-596.2745</td>
<td>0.0000</td>
<td>-47.4653</td>
<td>-45.4847</td>
</tr>
</tbody>
</table>
Table 9

Regression Statistics Results - TCE Conc. = 100.0 ug/L

<table>
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<tbody>
<tr>
<td>Multiple R</td>
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<tr>
<td>R Square</td>
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<tr>
<td>Adjusted R Squa</td>
<td>0.999925</td>
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<tr>
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<td>0.347011</td>
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<td>Observations</td>
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<table>
<thead>
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<td></td>
<td>df</td>
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<tr>
<td>Regression</td>
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</tr>
<tr>
<td>Residual</td>
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<tr>
<td>Total</td>
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<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Standard Error</th>
<th>t Statistic</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-9.3833</td>
<td>-17.7021</td>
<td>0.0032</td>
<td>-16.1185</td>
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<td>xl</td>
<td>-39.9550</td>
<td>-162.8332</td>
<td>0.0000</td>
<td>-43.0728</td>
<td>-36.8372</td>
</tr>
</tbody>
</table>
### Table 10

Regression Statistics Results - TCE Conc. = 500.0 ug/L

<table>
<thead>
<tr>
<th>Regression Statistics</th>
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</thead>
<tbody>
<tr>
<td>Multiple R</td>
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<tr>
<td>R Square</td>
</tr>
<tr>
<td>Adjusted R Square</td>
</tr>
<tr>
<td>Standard Error</td>
</tr>
<tr>
<td>Observations</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Analysis of Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>df</td>
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<tr>
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<tr>
<td>Regression</td>
</tr>
<tr>
<td>Residual</td>
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<tr>
<td>Total</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Standard Error</th>
<th>t Statistic</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>27.4200</td>
<td>5.0887</td>
<td>5.3885</td>
<td>-37.2372</td>
<td>92.0772</td>
</tr>
<tr>
<td>x1</td>
<td>3.9000</td>
<td>2.3556</td>
<td>1.6556</td>
<td>-26.0305</td>
<td>33.8305</td>
</tr>
</tbody>
</table>
Figure 20. Sensitivity Analysis Regression Results: $D_x$ vs. $f_{oc}$.

TCE:

$t = 5$ years

LEGEND

- $C = 1$ ug/L
- $C = 10$ ug/L
- $C = 100$ ug/L
- $C = 500$ ug/L
CHAPTER VII

CONCLUSIONS

Based on the laboratory analysis of organic carbon in actual samples, the following conclusions may be drawn:

1. Laboratory TOC analytical data indicate that a high TOC zone normally appeared near water table, and decreased with increasing depth.

2. A generally acceptable match of TOC analytical results can be obtained from the two analytical methods although direct TOC determination is preferable to the difference between TC and TIC.

Based on the flow and transport modeling evaluations, the following conclusions may be drawn:

1. Contaminant transport of TCE is very sensitive to the TOC ($f_{oc}$) content in a natural sand and gravel aquifer.

2. A negative semilog regression correlation exists between TCE transport distance and $f_{oc}$ level: TCE transport distance ($D_x$) increases linearly as $f_{oc}$ decreases logarithmically.

Overall, the variability of TOC contents with depth and the sensitivity of net chemical transport to $f_{oc}$ levels in a typical glacial aquifer setting strongly suggest that: (a) aquifer solid sampling must be performed through a vertical section of an aquifer to properly characterize the TOC levels within the aquifer, (b) actual measurements of TOC levels are necessary in prospective model settings to achieve realistic transport predictions.


