

Expediting Site Closure with the Fate and Transport Models BioTrans and SpillCAD

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Abstract

Closure of gasoline spill sites is often complicated by a persistent low level dissolved phase sourcing from a residual liquid phase. Partitioning from the residual phase to the dissolved phase becomes the rate limiting step toward site closure. For this case study site remediation efforts began in 1986 and consisted of the removal of liquid, dissolved and vapor phase hydrocarbons from the saturated and unsaturated zones. The most successful phase was the recovery of non-aqueous phase liquid (NAPL) hydrocarbons at the onset of remediation. Dissolved phase hydrocarbon recovery was hampered from the start by the relatively low permeability of the aquifer and no convenient means of disposing of treated water other than reinjection. This compromised the effectiveness of the removal of adequate pore volumes of water and especially their recharge to the aquifer. Air sparging was implemented but discontinued after dissolved phase hydrocarbons were detected in a private supply well, possibly as the result of displacement by the sparge system. The regulatory agency that funded the remediation asked its contractor to assess potential impact on down gradient receptors, private supply wells, once remediation efforts ceased. Groundwater transport modeling programs SpillCAD and BioTrans (ES&T, Blacksburg, VA.) were chosen to evaluate the site. These programs were used to estimate the volume of the residual phase and the fate of the dissolved plumes.

Introduction

The site is one of two retail gasoline stations located on Shelter Island, NY. Remediation efforts began in 1986 and have consisted of the removal of liquid, dissolved and vapor phase hydrocarbons from the saturated and unsaturated zones (See **Figure 1. Site Plan** on the following Page).

Geology & Topography

The topography averages 50 feet above sea level in the central portions, and descends toward the shoreline as a rolling plain, pitted with small ponds and dry and marshy depressions (kettles). The topography near the site ranges from about 20-30 ft. above sea level.

The island is underlain by Upper Pleistocene deposits of stratified glacial drift underlain by two Pleistocene clay units, an upper marine and lower non-marine unit. Beneath the clay is the Upper Cretaceous undifferentiated Magothy Formation (Magothy Aquifer). Below the Magothy is the Lloyd Clay and Sand Member (Lloyd Aquifer) of the Raritan Formation underlain by crystalline bedrock. The stratified glacial drift on the island is the groundwater table aquifer that has been impacted by the release of gasoline. These deposits are mostly stratified, poorly sorted, with particle sizes ranging from clay to boulders. The drift contains a high degree of clay and silt along the northwestern coastline from the Jennings Point area to Hay Beach Point where it forms cliffs. It is coarser southeast of the cliffs.

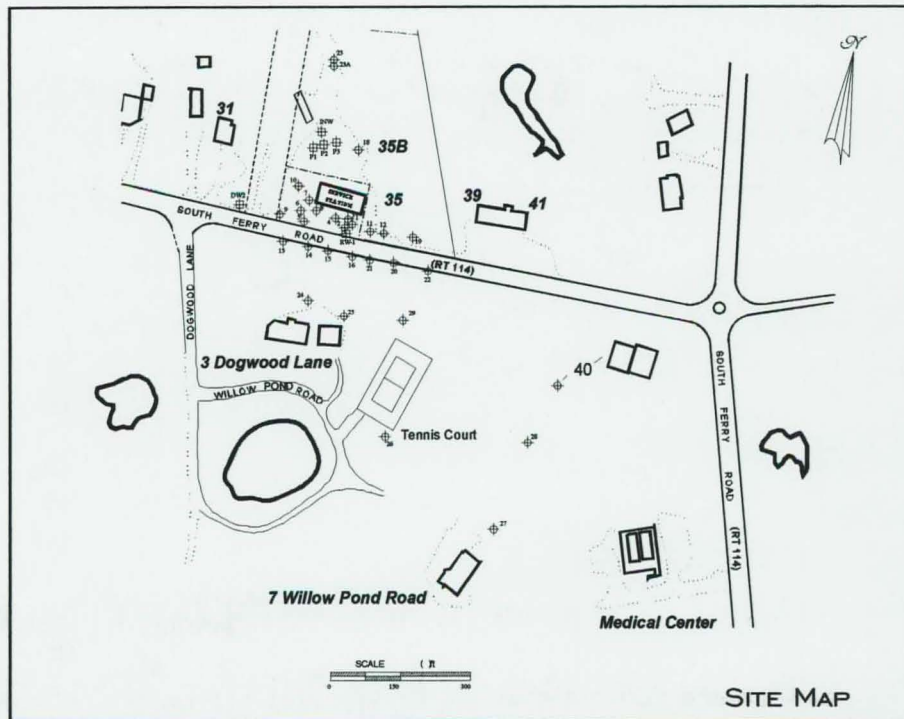


Figure 1

Two east-west trending terminal moraines with extensive outwash cover most of the surface of Long Island. The Ronkonkoma moraine, which passes to the south of Shelter Island, is the older of the two and is at the limit of the Late Wisconsin glaciation. The Harbor Hill moraine passes to the north of Shelter Island, and is the younger of the two major end moraines in the area. The numerous kettles and depressions indicate that the upper Pleistocene drift of Shelter Island is outwash that was deposited during the recessional stage of the younger glacier. A log of an exploratory well advanced near the site is presented below:

Boring Log of Exploratory Well

Description	Thickness (ft)	Depth (ft)	Elevation (ft)
Upper Pleistocene Deposits <i>SAND</i> - Brown very fine to very coarse, mostly coarse with gravel and cobbles up to 5-inch in diameter. Much interstitial silt and clay.	85	0 to 85	+28 to -57
Pleistocene Marine Deposits <i>CLAY</i> - Dark gray/green and dark gray; some laminae and thin beds of sand and granule gravel.	95	85-180	-57 to -152
Upper Pleistocene (?) Deposits <i>SAND</i> - Light gray, very fine to medium with some coarse. Granular to very large pebble gravel up to 2.4 inches in diameter.	67	180-247	-152 to -219

USGS, 1974

* above mean sea level

Hydrogeology

The thin upper glacial water table aquifer is the sole source of freshwater on the island. The freshwater aquifer system is essentially lens shaped, unconfined on top and defined laterally and vertically by increasing concentrations of chloride (Cl⁻). The hydraulic bottom of the aquifer near the site is defined by the Pleistocene marine clay deposits at a depth of approximately 85 feet. The freshwater probably extends to this depth since intrusion from below is likely impeded by the clay unit. The groundwater gradient at the site is relatively flat, approximately 0.0003 ft/ft, and flows to the south east. Hydraulic conductivity at the site has been calculated to 33 ft/day from pump test data.

Contaminant Source

A map of the liquid phase plume from data collected in the fall of 1986, shows the largest recorded extent of the liquid phase plume. This representation is also indicative of the extent of the residual phase which is acting as the continuing source of dissolved phase hydrocarbons (see Figure 2. Below).

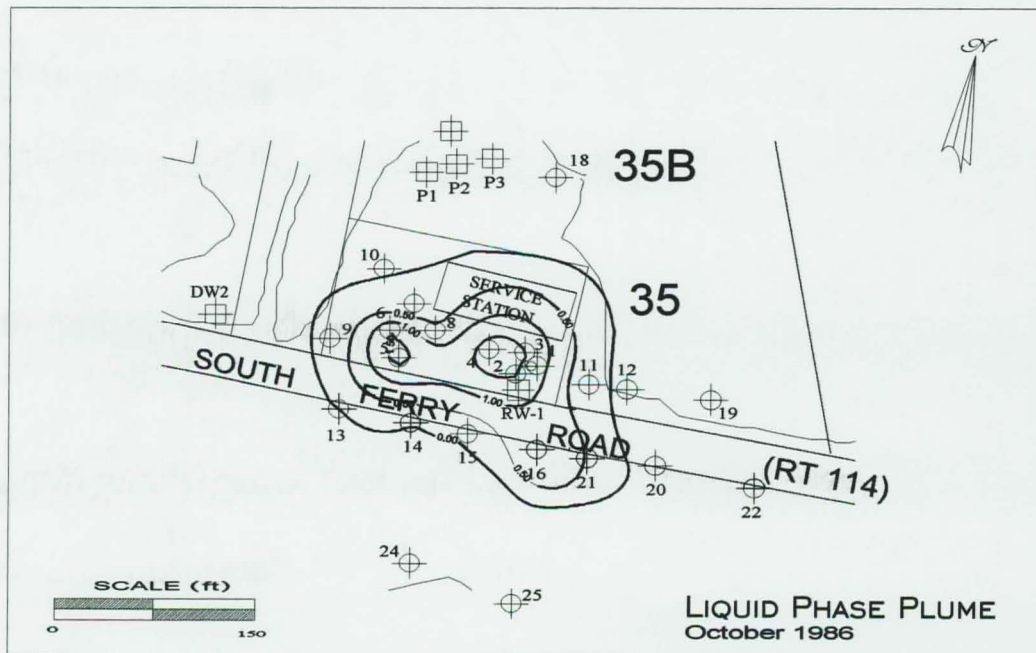


Figure 2.

Contam

inant Characteristics and Chemical Properties

The environmental fate and transport of petroleum hydrocarbons are dependent on the physical and chemical properties of the hydrocarbon, transport mechanisms, environmental transformation processes affecting them, and the media through which they are transported. The principal contaminants of concern on site are benzene, toluene, ethyl benzene, xylene (BTEX), and methyl t-butyl ether (MTBE.)

Physical and Chemical Properties of Modeled Species

Species	Molecular Weight (grams)	Henry's Law Constant (atm*m3/mol)	Vapor Pressure (atm)	Solubility (mg/l)	Type
Benzene	78	5.5 x 10 ⁻³	95	1780	Aromatic
Toluene	92	6.7 x 10 ⁻³	28	515	Aromatic
Ethyl Benzene	106	8.7 x 10 ⁻³	25.9	152	Aromatic
Xylene	106	6.3 x 10 ⁻³	5	200	Aromatic
MTBE	88	5.9 x 10 ⁻⁴	245	48,000	Ether

Migration

Contaminants found in the subsurface environment are subject to a variety of transportation and transformation processes that affect their distribution. These processes include advection, hydrodynamic dispersion, molecular diffusion, adsorption, transformation/degradation (including biological decay), and volatilization.

Transportation of petroleum hydrocarbons in the subsurface occurs within the pore spaces of the soil. Migration of contaminants in the subsurface depends on the chemical and physical properties of the contaminant and the medium through which they travel. The solubility of MTBE is more than an order of magnitude higher than other major gasoline constituents and therefore more mobile in ground water than most hydrocarbons. Relative migration rates follow the pattern: MTBE > Benzene > Toluene > Ethyl benzene/Xylene. Therefore MTBE and Benzene are the first contaminants to migrate off-site and reach sensitive receptors. Ethyl benzene and Xylene have low solubilities and therefore adhere to soil particles which reduce their rate of transport. Additionally, MTBE is relatively resistant to biological decay.

Regulatory Standards

Regulatory standards for site contaminants are based on New York State discharge standards:

Compound	Drinking Water Standards (ppb)
Benzene	0.7
MTBE	50.0
Ethyl benzene	5.0
Toluene	5.0
Xylene	5.0

If hydrocarbon levels on site are less than the generic action levels, apply for closure of the site. If contaminant levels on site are greater than the generic action levels, a corrective action plan should be devised to reduce contaminant levels on site.

Fate and Transport Modeling

The SpillCAD module Soilvol was used to model the distribution of the residual phase from soil analytical data collected in 1996. The SpillCAD module Q-free was used to model the flow net across the site using monitoring data from April of 1996. Both the residual phase distribution and flow net information modeled by SpillCAD are stored in files for use later by BioTrans.

BioTrans was used to spatially and temporally model the distribution and natural attenuation of dissolved species that partition from the residual phase. The model calculates concentrations of each species at each node of a specified grid at specified time steps. BioTrans can model the fate of four different species and dissolved oxygen. The characteristics of each species being modeled are input into BioTrans. The following hydrocarbon species were modeled for this site:

BENZENE, **MTBE**, **TEX** (a pseudo species consisting of the average characteristics of toluene, ethyl benzene and xylene), and **OTHERS** (a pseudo species which combines the remaining mass fraction of gasoline). **OTHERS** was modeled because their assimilation by microorganisms accounts for a percentage of dissolved oxygen consumption.

SpillCAD Data Requirements

SpillCAD was used to model the petroleum product distribution in the residual phase from data obtained from split spoon sampling performed in April 1996. For SpillCAD to model the amount and distribution of the residual phase specific information about the aquifer and contaminant must be input. SpillCAD provides estimators for various soil types and petroleum products. Sieve analyses performed on the samples show that the saturated aquifer near the water table is a medium fine to fine sand with practically no fines (silt or clay) or gravel, therefore, the Soil Properties Estimator for Sand was used:

SpillCAD Soil Properties Estimator

Parameter	Range of Possible Values	Estimator Values
K_{sw}	10^{-4} to 10^{+4} ft/day	*23.3 ft/day
ϕ	0.1 - 0.7	0.43
S_m	0.05 - 0.95	0.13
α	0.01 - 100 ft.	4.5
n	1.1 - 10.0	2.7
S_{or}	0 - 0.5	0.261
S_{og}	0 - 0.4	0.0339

* A K_{sw} of 33 ft/day was used which was calculated from pump test data collected during the pump and treat design phase and corresponds well with the estimator value.

SpillCAD Fluid Estimator for Gasoline

Parameter	Estimator Values
ρ_{ro}	0.73
η_{ro}	0.62
β_{ao}	3.3
β_{aw}	1.4

Calculating the Source Term

The SoilVol Module in SpillCAD was used to model the volume of residual soil contamination acting as the ongoing source of dissolved phase contamination from the soil samples collected from the site in April of 1996. The samples were analyzed for petroleum hydrocarbons using EPA method 418.1 and for volatiles using EPA method 8020 + MTBE. Analytical data was collectively input into the SpillCAD Database as TPH with the associated coordinate positions and depths for each sample.

The Hydrocarbon Volume Module of SoilVol scans the database for TPH data and vertically integrates concentrations using linear interpolation between sample depths and areal interpolation using a two-dimensional kriging algorithm. The file that SpillCAD creates for showing residual hydrocarbon volume from soil concentration data is intended for viewing within SpillCAD and not as an output file for use by BioTrans or other ES&T programs. The file was modified using an ASCII editor to insert a header with the proper grid and node information and saving it with the prescribed name format (vo*.sem - the same file format that represents a liquid phase).

SpillCAD was also used to generate the groundwater gradient file for use by BioTrans (ve*.sem). The VE file was generated using actual field data and did not require any modification.

Modeling the Fate of Dissolved Species with BioTrans

The following data for BioTrans model input were used:

Time Step Control Menu

- *Starting Time* - The beginning of the simulation is based on the soil samples, monitoring and dissolved data collected in April of 1996.
- *Ending Time* - The simulation was run long enough for a conservative species (such as MTBE) to migrate from the source area to the furthest down gradient receptor, the Medical Center Well. Based on the expression for Darcian Velocity:

$$v = ki/n$$

Where:

$$k = \text{hydraulic conductivity} = 33 \text{ ft/day}$$

$$I = \text{gradient} = 0.0003 \text{ ft/ft}$$

$$n = 0.43 \text{ (porosity)}$$

$$v = (33 \text{ ft/day})(0.001 \text{ ft/ft})/(0.40) \\ = 0.083 \text{ ft/day (or 30 feet/year)}$$

It is approximately 750 feet from the source area to the Medical Center well. It would require roughly 910 days, or 25 years, for MTBE to migrate the entire distance. It should be noted that the accuracy of any model decreases with time. For this reason the run time of the model was limited to 10 years.

Transport Parameters Menu

- *Total Porosity* - 0.43 (SpillCAD Soil Estimator).
- *Bulk Density* - The density of the aquifer material per unit volume is a function of density of the solid material and the porosity (Φ) of the aquifer. The density of the solid matrix is a function of the minerals that are present and their average density (ρ_s). Quartz is the predominant mineral and its density is 2.65g/cm³. The bulk density (ρ_b) is calculated below:

$$\rho_b = \rho_s (1 - \Phi)$$

$$\rho_b = 2.65 \text{ g/cm}^3 (1 - 0.43)$$

$$= 1.59 \text{ g/cm}^3$$
- *Product Specific Gravity* - This value is the specific gravity of gasoline, 0.73
- *Longitudinal Dispersivity* - A typical value for the scale of this model is 1 to 10 feet.
- *Transverse Dispersivity* - Typically a tenth of longitudinal Dispersivity, or .1 to 1 feet.
- *Oil/Water Mass transfer Coefficient* - The possible range of values are 0 to 2 and typically less than 1.
- *Molecular weight of inert NAPL* - The typical value for gasoline is 210 grams/mole.

Chemical Properties Menu

- *Species* - Benzene, MTBE, TEX and Others.
- *Initial Mass Fraction in NAPL* - The Species Mass module in SpillCAD was used to determine the mass of each of the modeled species in the residual hydrocarbon from the soil TPH data and determine their individual mass fractions (see Table Below).
- *Molecular Weight* - Literature
- *Solubility* - Literature
- *Mobile Zone Adsorption Coefficient (k_d)* - SpillCAD manual

Chemical Input Properties

Parameter	Benzene	TEX	Others	MTBE
Initial mass fraction in NAPL	0.42	0.16	0.4	0.02
Molecular weight (g/mole)	78.11	98.15	205.7	88
Solubility (mg/l)	1780	360	3	48,000
Mobile zone adsorption coefficient (cm ³ /g)	0.07	0.32	1375	0

Oxygen transport

BioTrans allows for first order and oxygen limited decay of species. Oxygen limited decay is appropriate when the concentration of substrate is high and one or more nutrients is available at a rate below that which allows for maximum growth of microorganisms. It is appropriate to model the aromatic species this way as their decay competes for the available oxygen. It is not appropriate to model MTBE with a biological decay rate since it is practically unbiodegradable and does not compete for the oxygen.

To realistically model all species the model was run with oxygen limited decay for aromatic species and zero decay for MTBE. The following parameters are applicable for oxygen limited decay:

- *Oxygen Solubility* - This is a function of groundwater temperature.
- *Oxygen Concentration in Recharge* - Assumed to be similar to that measured in groundwater.
- *Background oxygen concentration in groundwater* - This is the dissolved oxygen present from up gradient and was measured in the field.
- *Maximum Total Decay Rate* - A measure of the amount of decay of all hydrocarbon species combined. Typical values are between 1 and 5 mg/l*day.
- *Stoichiometric Coefficient* - A measure of the amount of the mass of oxygen required to degrade a unit mass of all hydrocarbon species. Typical values are between 2.5 and 3.
- *Initial Oxygen Concentration* - For this simulation the same as Background Oxygen Concentration in Groundwater.

Spatial Data

- Contaminant distribution, VO*.SEM file from SpillCAD.
- Groundwater flow field, VE*.SEM file from SpillCAD.
- BioTrans does not allow for the input of an established dissolved phase at the start of a simulation. It does allow for a model run to be stopped and restarted. The file it writes at the end of a model run records the concentration of all contaminant species and dissolved oxygen at every node in the model domain. This file, designated *.txf can be modified in an ASCII editor. To start a simulation with actual dissolved levels of the modeled species and dissolved oxygen, actual field data collected in April of 1996 was used. This was done by contouring the distribution of benzene, TEX, MTBE and dissolved oxygen with Surfer using the same grid and node structure as the BioTrans model and input by hand for each species at each of 400 nodes into the restart file (*.TXF). The model is initially run for one day to generate the TXF file with the correct grid and node structure. The model is then run in the restart mode using the modified TXF file

Model Calibration

Calibration of a model is the process of adjusting input for which data are not available. It was assumed that the dissolved phases of all species would be gradually decreasing asymptotically over time (as is typically observed at this stage of a site remediation as a function of dissolution from an ever decreasing residual phase to the dissolved phase and natural attenuation). To calibrate the model the Mass in Water vs. Time utility in the Post Processor module of BioTrans was used. The mean values of the five estimated parameters were used initially to gauge model response. This produced the dissolved benzene and TEX phases increasing with time.

Mean Value of Estimated Parameters

Parameter	Mean Values
Oil/Water Mass Transfer Coefficient	0.5
Longitudinal Dispersivity (ft)	5.0
Transverse Dispersivity (ft)	0.5
Maximum Total Decay Rate (mg/l*day)	3
Stoichiometric Coefficient	2.75

By changing a parameter, one at a time, over its range of possible values for each estimated parameter and comparing model output the relative sensitivity of the parameters was established in the following order of decreasing sensitivity:

1. Oil/Water Mass Transfer Coefficient
2. Longitudinal and Transverse Dispersivity
3. Maximum Total Decay Rate
4. Stoichiometric Coefficient

The sensitivity of a model parameter is the degree it effects model output. The oil/water mass transfer coefficient was by far the most sensitive parameter. Significant changes in output were produced with changes in input of as little as five one thousands. Only minor changes were produced with major changes in Longitudinal and Transverse Dispersivity, the Maximum Total Decay Rate and the Stoichiometric Coefficient.

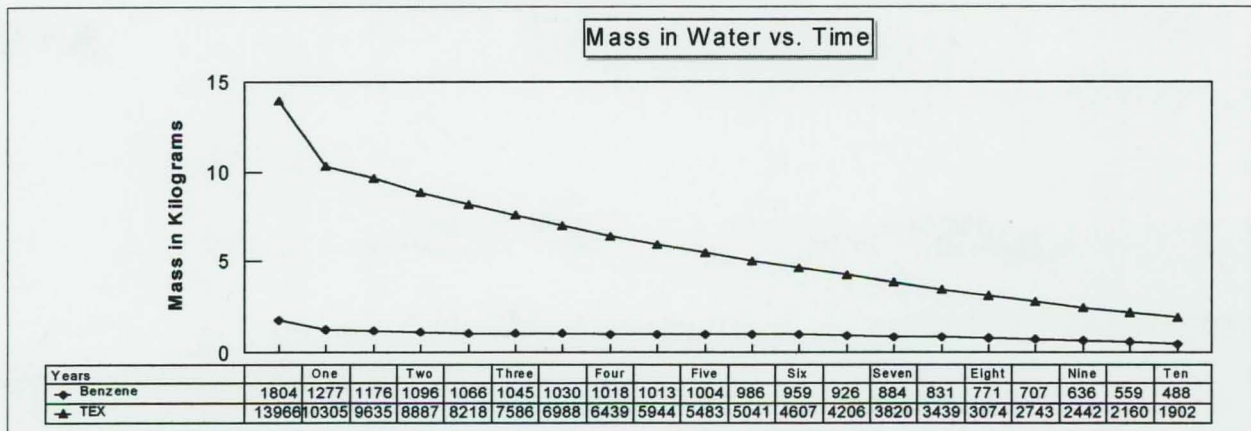
Based on the sensitivity of the estimated parameters the mean values for the relatively insensitive parameters were used. As a conservative measure the highest value for the Oil/Water Mass Transfer Coefficient that would produce a decrease in the concentration of all dissolved species was deemed appropriate.

Value of Estimated Parameters Modeled

Parameter	Value Used
Oil/Water Mass Transfer Coefficient	0.0005
Longitudinal Dispersivity (ft)	5.0
Transverse Dispersivity (ft)	0.5
Maximum Total Decay Rate (mg/l*day)	3.0
Stoichiometric Coefficient	2.75

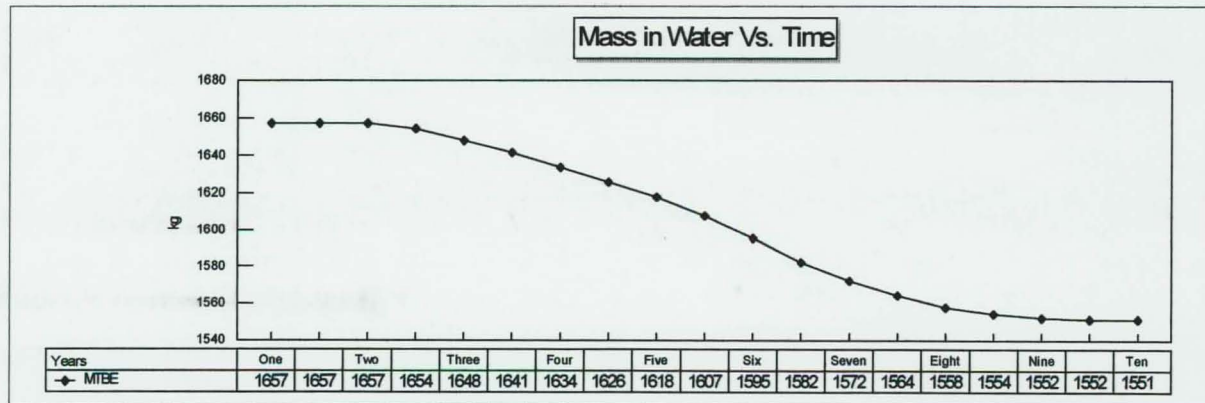
The model output for Mass in Water vs. Time for these values is graphically represented on the following page:

Mass of Benzene and TEX in Water vs. Time



Once the flow parameters that produced an output that realistically attenuated the aromatic species were established, the oxygen limiting decay rate was eliminated for modeling the fate of MTBE. The flow parameters are a function of the aquifer and not the individual species. For the model to be realistic the mass of dissolved MTBE should also gradually attenuate over time with this set of parameters. The model output for Mass in Water vs. Time of MTBE for these values is graphically represented below:

Mass of MTBE in Water vs. Time



Model Results

The output locations of all of the private domestic supply wells in the area were checked for dissolved concentrations of benzene, TEX and MTBE from the start of the simulation (t_0 , March 1996) and run out for 10 years. The following locations were checked: 3, 7, 31, 35, 35b, 40 and The Medical Center (see Figure 1.). All locations were below 10 $\mu\text{g}/\text{l}$ or free of dissolved phase for all species for the 10 year model run time except at 35 South Ferry Road. (This is the source area and simulates conditions at the water table. The service station supply well is screened at some depth below the water table).

Assumptions

It must be stated that all models make several necessary assumptions about the nature of the system that is under study. The following assumptions were made:

- **The aquifer is homogeneous and isotropic.** The major assumption when Darcy's Law is used to describe fluid flow through a porous medium. The study area is a rather complicated geologic Province where glacier ice passed over and retreated. The numerous kettle depressions in the area indicate that multiple depositional regimes occurred over time. The aquifer characteristics modeled for the entire domain are based on conditions near the water table at the source area.
- **The Mass Transfer Coefficient is the maximum rate that will produce attenuation of all species in the dissolved phase.** The Mass Transfer Coefficient could be lower than that modeled. However, the value that was used should produce the highest concentrations in the dissolved phase and have the greatest impact on the private wells.
- **Accuracy of the model decreases with time from the start of the model.** Due to the complexity of the model it was run for a maximum of 10 years.
- **Decay of the aromatic species is oxygen limited.** This seems a realistic assumption since measured dissolved oxygen in the field is greatly depleted where dissolved concentrations of aromatic species are the highest.
- **MTBE does not decay.** This is a generally held assumption based on empirical evidence and studies. If the decay rate is not zero it is realistic enough to model it as such.

Conclusion

Model output indicates that the residual phase contaminants still present are partitioning into the dissolved phase at a rate that allows for natural attenuation to prevent significant impact of down gradient receptors within the next 10 years. However, heterogeneities in the aquifer, and necessary assumptions made to model the site, leave open the possibility that contaminants could impact down gradient receptors at concentrations higher than those predicted by the model.

Acknowledgments

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