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Modeling natural attenuation of benzene with analytical and numerical models[‡]

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Abstract

Natural attenuation of benzene is a much-accepted technology for remediating low risk sites. To date, numerous protocols have been developed for assessing natural attenuation and measuring indicator parameters. Many models have additionally been developed to describe the advection, dispersion, sorption and biodegradation processes involved. It is evident that while there is extensive guidance in natural attenuation protocols for field sampling methodologies, less emphasis is placed on analyzing natural attenuation data for supporting appropriate model development. This paper presents methodologies for data analysis and interpretation that may be undertaken to achieve data reduction for modeling purposes. A case study is presented to illustrate the use of an analytical and a numerical natural attenuation model at the same site for predicting the time required to achieve the remedial goal at the site.

Introduction

During the 1990s, the concept of natural attenuation emerged, and its application as a remedial strategy, especially at sites contaminated with benzene, toluene, ethylbenzene and xylenes (BTEX) where the risk of exposure is within acceptable levels, gained acceptance. Initially, the majority of natural attenuation related research was focused on developing field protocols for demonstrating the occurrence of natural attenuation. The Air Force Center for Environmental Excellence (AFCEE), for example, funded the development of two protocols for fuel hydrocarbons and for chlorinated solvents (Wiedemeier et al. 1995, 1996). Numerous state and federal agencies and industrial and private sector organizations followed suit and developed their own methodologies and procedures for assessing natural attenuation at the field scale (see for example ASTM 1998; Wiedemeier & Chapelle 1998; Yang et al. 1995). Common to all the developed protocols is collecting vast amounts of data to document concentration declines, the presence of electron acceptors and the production of biodegradation by-products.

More recently, researchers and practitioners have recognized the need for quantitatively assessing natural attenuation and its impacts on future site conditions and on plume status. This necessitated the development of natural attenuation models that can be used to simulate advection, dispersion, sorption, and biodegradation. Both analytical and numerical models have been developed. Some examples of analytical models include BIOSCREEN (Newell et al. 1996) and BIOCHLOR (Aziz et al. 1999). Numerical natural attenuation models include two- and three-dimensional tools such as BIOPLUME III (Rifai et al. 1997) and RT3D (Clement 1998), among others. Natural attenuation models are typically applied for three different purposes:

(1) Determine if a plume is going to get longer;
(2) Determine how long will a plume be there; and
(3) Develop a better understanding of the important natural attenuation processes at a given site.

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A key element in applying these models to sites is to be able to integrate the natural attenuation site data into the model development such that an applicable site model may be calibrated and validated prior to being used for predictive simulations. Natural attenuation modeling differs only slightly from a typical fate and transport model application. The main difference arises from simulating the biodegradation processes affecting contaminant concentrations. While many models simulate rather complex kinetics and multi-component interactions, it is evident that many of the requisite kinetic parameters for these models cannot be measured or estimated using the current natural attenuation protocols. Thus the utility of these models is limited to research and to improving our understanding of natural attenuation processes and biologically mediated reactions. Simpler approaches are needed for predicting plume behavior using site data that are currently being collected in natural attenuation studies. Additionally, guidance is needed on how to analyze and interpret natural attenuation data to develop applicable site models that support natural attenuation decision-making.

This paper presents several methodologies and approaches for natural attenuation data analysis and parameter estimation. Furthermore, the paper illustrates the application of an analytical and a numerical natural attenuation model to the same gasoline spill site. Emphasis is placed on conceptual model development for model set-up and on natural attenuation data analysis and interpretation for parameter estimation. The model calibration and validation process using field data is illustrated, as is the reasoning behind selecting an analytical or a numerical model. This paper is intended to provide guidance to model developers and users in terms of the challenges involved in applying models to sites (especially sites with limited data), and to illustrate the difficulties involved in parameter estimation for natural attenuation models.

Natural attenuation data analysis and interpretation for model development

Whether data have been obtained through field work conducted as a natural attenuation investigation or gathered through an analysis of records after the investigation, they must be analyzed so that an appropriate natural attenuation model can be developed. The goals of the modeling should also guide the analysis of the data and its interpretation.

Presumably, monitoring well data will constitute the largest set of data for a site. Potentiometric (or water table) surface maps will show the direction of groundwater flow, and provide the data required for the calculation of the hydraulic gradient. If potentiometric surface maps do not already exist, they should be drawn for multiple sampling dates to observe seasonal and yearly changes in groundwater flow direction and gradient. Other bodies of water that affect flow may be observed on the potentiometric surface map if its scale permits; otherwise, they can be seen on topographic maps of the area. Ideally, hydraulic conductivity should have been determined in the field; if it was not, literature values for different soil types will have to be used as an estimate.

Oftentimes there will be quarterly or annual sampling of the monitoring wells for constituents of concern. Faced with these multiple data sets, how are they to be used to develop a site conceptual model? First, visualizing the data often helps one's understanding of a site. The data should be plotted for each well and contaminant as concentration *versus* time plots to see if any patterns emerge, such as a decrease in concentration at certain wells or an increase in the concentration of metabolic intermediates. Isocontour maps of the contaminant data at several sampling dates should be plotted to see if the plume is stable or decreasing, or even increasing. Examination of concentration data in wells in the source zone may show whether source concentrations are decreasing; comparison with water elevation data will indicate the effect of water level on concentration. If any remediation has been conducted at the site, the behavior of the contaminant plumes before and after the remediation can be investigated.

The monitoring well data should be examined for indicators of biodegradation. If electron acceptor data exist, they should be contoured also, and estimates of electron acceptor capacity should be developed. In the absence of electron acceptor data, a first-order biodegradation rate can be determined using the concentration *versus* distance data or using microcosm studies. The field concentration *versus* time data will give a rate of

attenuation rather than a rate of biodegradation. The field attenuation rate could be reduced to the biodegradation rate if there is a recalcitrant, non-biodegradable compound moving with the contaminant plume. Also, if the plume is at steady state, the method of Buscheck and Alcantar (1995) can be used to obtain a first-order biodegradation rate using concentration *versus* distance data. The biodegradation rate will invariably be altered during model development to fit the model to the data.

Often, several years of quarterly sampling data exist. In this case, it might be more suitable to average the four quarters of data over a year to manage the data and incorporate seasonal changes in water levels. If there are several complete data sets, one must be chosen for calibration, and another for verification. Typically, the earliest, most complete data set is chosen for calibration, and a later one is used for verification of the model's predictive abilities. As long as the data exist, running the model over as long a time period as possible with existing data will give some confidence as to the model's predictions. The monitoring well data are the standard against which the model's simulation of site conditions is measured.

The soil data can be used to describe the geological environment and provide some of the transport parameters (e.g., retardation), and information about the source zone. From the boring logs obtained during drilling, cross sections can be prepared, preferably, one in the direction of groundwater flow and one perpendicular to groundwater. The cross sections will enable one to determine the stratigraphic zone of interest. From the soil samples, total organic carbon can be determined, as well as the porosity.

Soil samples collected in the source zone can be used to help determine the mass of contaminants in the source and thus, estimate the lifetime of the source. These data can also be used to estimate the areal extent and depth of residual source zones at a site; information that is critical to modeling current and future plume conditions. The mass in the source area can be estimated in several ways. First, using soil data, the mass of contaminant in the soil (and smear zone) can be determined roughly as the concentration multiplied by the volume and by the soil bulk density (see Wiedemeier et al. 1999). Other methods include partitioning interwell tracer tests and inverse modeling. If there are no soil data, then the monitoring well data can be used to estimate the source mass. By plotting the concentration *versus* time data for wells in the source area, a source half-life can be obtained.

Site description

The study site is a petroleum product storage facility located in central Texas. Petroleum hydrocarbon contamination was first discovered in 1991 during the decommissioning of three tanks (two 4000-gal steel gasoline and diesel tanks, and one 550-gal waste oil tank). The excavated leaking gasoline tank was installed in1973 while the diesel tank was installed in 1977. Field observations at the time of tank removal and subsequent soil sampling investigations indicated the presence of hydrocarbons in the tank backfill material and in the native soil surrounding the tank basin (see Figure 1 for contaminated soil zone). A total of 11 monitoring wells (MW-1 through MW-11) were installed between 1991 and 1992 (Figure 1). The site is underlain by quaternary-age fluvial deposits of upper and lower silty sand units interbedded with silty and sandy clays. Laboratory analysis of soil samples yielded an organic carbon fraction of 0.002 within the silty sand unit.

Generally, groundwater is present at approximately 18 ft below ground surface (bgs) and the ground water flow direction is to the north. Groundwater levels fluctuate between 3 and 5 ft over the course of a year. The average hydraulic conductivity is 0.1473 ft/min (7.52×10^{-2} cm/s) based on pump tests in well MW-4. Two monitoring wells, (MW-1 and MW-2), located near the former tank basin and within the source area, intermittently contained measurable accumulations of phase-separated hydrocarbons between 1991 and 1998. Accumulations ranged from trace amounts to the maximum measured accumulations of 0.45 and 1.63 ft, respectively.

Groundwater sampling data for BTEX, shown as annual averages in Table 1, indicate that a dissolved hydrocarbon plume originated in the former tank basin area and has migrated offsite toward the north. Overall, a steadily decreasing dissolved concentration trend is evident from the concentration histories for the monitoring wells. Increases were observed at MW-1 and MW-2 during 1999, possibly as a result of precipitation and a fluctuating groundwater water table.

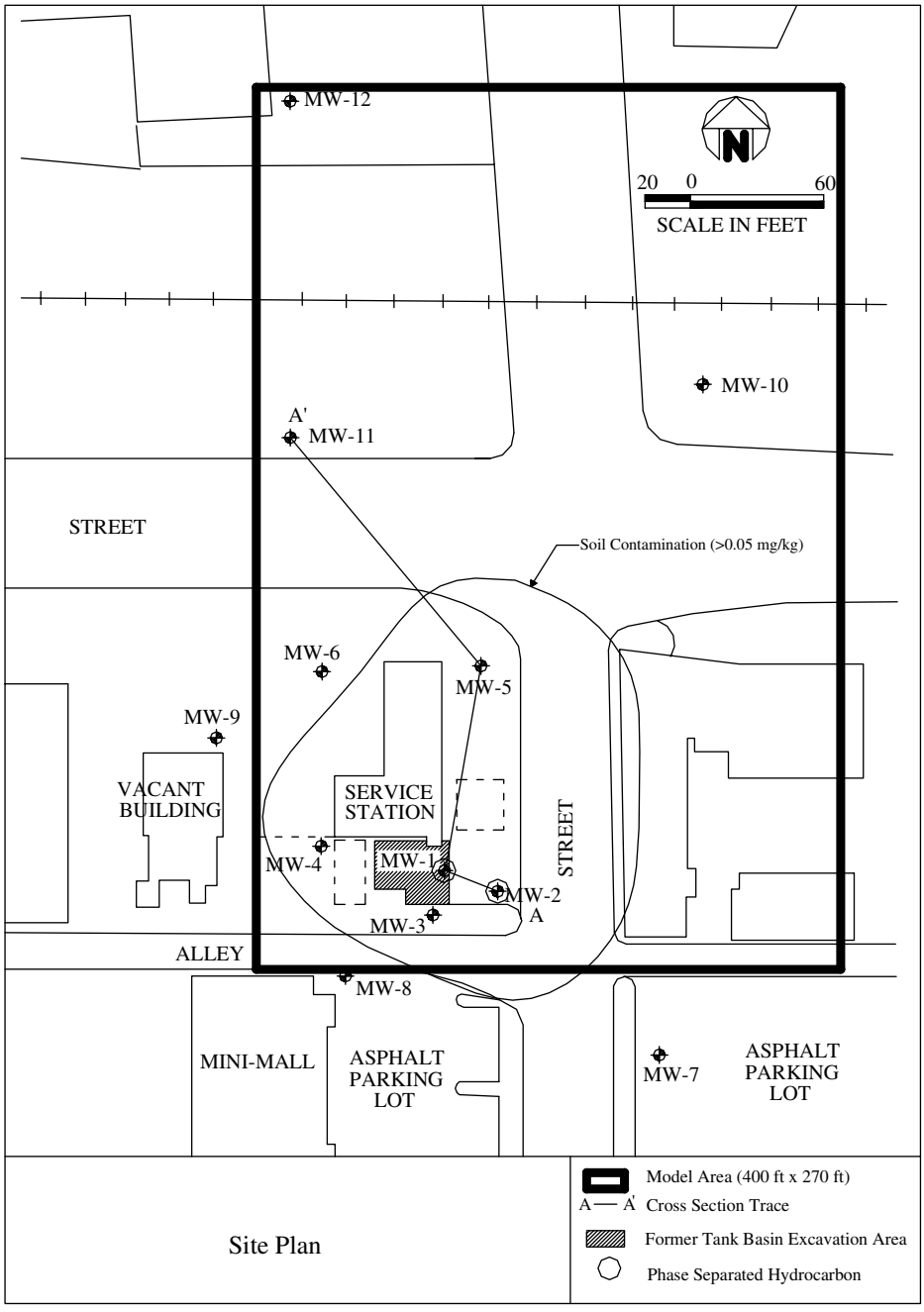

Figure 1. Site plan.

Remediation activities at the site have been limited to excavating approximately 450 cubic yards of backfill and native material during tank removal. Product accumulations in wells MW-1 and MW-2 were bailed between 1992 and 1999. A remedial goal of 0.47 mg/l for benzene concentrations at the site was established via a risk analysis.

Table 1. Average annual benzene concentrations (μg/l)

Monitor well	1991	1992	1994	1995	1996	1997	1998	1999
MW-1	20,138	–	–	–	–	7810	8930	18,0000
MW-2	18,635	–	–	–	–	7990	8995	14,0000
MW-3	13,837	9828	2710	3195	4025	3135	2200	910
MW-4	1,405	1,012	3.8	9.5	13.6	0.5	2	8
MW-5	16,926	14,599	13,400	11,400	8505	8500	6900	8200
MW-6	1311	1502	788	330	316.5	474	833	620
MW-7	1.3	1.0	0.5	0.5	0.5	0.5	–	0.5
MW-8	1,026	174	0.5	0.5	0.5	0.5	–	0.5
MW-9	0.5	625	0.5	0.5	0.5	0.5	–	0.5
MW-10	–	0.5	0.5	0.5	0.5	0.5	–	0.5
MW-11	–	1538	156	106.5	119.1	58.9	169	26
MW-12	–	–	–	–	–	950	283.3	200

Notes: No benzene data available for 1993. –No sampling conducted.

BIOSCREEN modeling

The BIOSCREEN model (Newell et al. 1996) is a screening tool for simulating the natural attenuation of petroleum hydrocarbons in groundwater. The model, which uses an Excel spreadsheet interface, is based on the Domenico (1987) analytical solution that includes first-order decay of the solute. The Domenico solution simulates groundwater flow using a fully penetrating vertical plane perpendicular to groundwater flow, a linear isotherm sorption, and three-dimensional dispersion. Newell et al. (1996) modified the Domenico solution to include a decaying source and an electron acceptor limited instantaneous reaction for biodegradation.

The BIOSCREEN model requires a limited number of input variables that include the seepage velocity, the dispersivity (longitudinal, transverse and vertical), the retardation coefficient, biodegradation parameters and source variables. Biodegradation variables include estimating the biodegradation rate when using a first-order process or providing the electron acceptor capacities when using the instantaneous reaction assumption (see Wiedemeier et al. (1999) for a detailed description of these kinetic expressions). Source definition can be accomplished using an infinite source or a decaying source. A source half-life or source mass is required for a finite source. The BIOSCREEN model conceptualizes the geometry of the source in the ground water as a plane with a given depth and width perpendicular to the direction of ground water flow (Figure 2). The source concentration can vary across the defined source width. While the model is relatively simple in of itself, there are some complexities associated with estimating the biodegradation and source parameters using site data as will be seen in the next section.

BIOSCREEN conceptual model

The goal of the modeling is to determine how long it will take for benzene concentrations to attenuate to the risk-based target of 0.47 mg/l in the groundwater, given the observed historical attenuation patterns. Therefore, it is important to calibrate the model to current site conditions and use the calibrated model to predict the site concentrations in the future. Figure 3 illustrates the sequence of events at the site beginning with tank installation and ending in 1999 when the last data set was collected. Assuming that leakage occurred 7 yr after tank installation (previous studies have shown that to be a typical timeframe for tank failure) leaves 11 yr of attenuation prior to excavating the tanks in 1991. It seems reasonable to select 1991 as a calibration date and to select 1998 as a validation or verification data set (recall that concentrations at MW-1 and MW-2 experienced concentration increases due to water table fluctuations in 1999). Finally, and in order to complete model set-up, it is important to identify the centerline of the plume and its associated concentrations in 1991 and 1998 so that the model

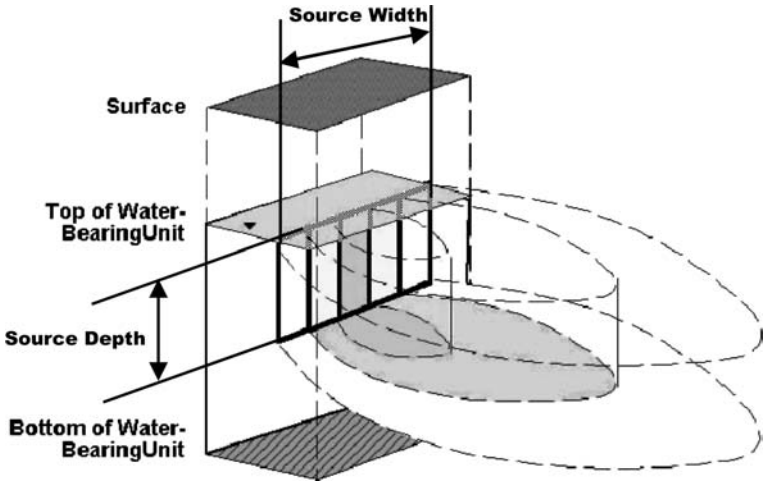

Figure 2. Source geometry in BIOSCREEN.

calibration and verification can be completed. The average concentrations shown in Table 1 are used to generate plume contours for 1991 and 1998 (Figures 4 and 5). The resulting plumes are then used to estimate the concentration profiles shown below:

1991 centerline calibration concentrations					
Distance from the source (ft)	0	48	98	188	248
Concentration (mg/l)	20	18	16.9	6	2
1998 centerline verification concentrations					
Distance from the source (ft)	0	57	120	165	229
Concentration (mg/l)	8.9	8	6	4	2

Velocity, dispersivity and sorption

Based on the horizontal groundwater gradients observed at the site, the average horizontal hydraulic gradient across the aquifer was calculated to be 0.001 ft/ft. Using a horizontal hydraulic conductivity of 7.52×10^{-2} cm/s, and an estimated effective porosity of 0.32, the seepage velocity was calculated to be 243.1 ft/yr. Utilizing the Xu and Eckstein equation (1995), the longitudinal dispersivity was calculated to be 11.9 ft and the transverse dispersivity was estimated to be 1.2 ft based on the assumption that the transverse dispersivity is 10% of the longitudinal value. The vertical dispersivity was neglected. Using an organic carbon partition coefficient of 38 l/kg (ASTM, 1995), an organic carbon content of 0.002 and a bulk density of 1.72 kg/l, the retardation coefficient was estimated to be 1.4.

Biodegradation

The geochemistry of the site had not been sufficiently characterized to allow estimating the electron acceptor capacity, therefore the first-order decay approximation in BIOSCREEN is used for biodegradation. In a review by Suarez and Rifai (1999), the estimated range of biodegradation rates for benzene was between 0 and 0.087 day^{-1} with a median rate of 1.283 yr^{-1}. In the absence of site-specific biodegradation data, the first-order biodegradation rate is used as a calibration parameter and is estimated using a trial-and-error method. It is noted that this approach assumes benzene decay is independent of the benzene concentration since a constant decay rate is used. It is also noted that this approach does not account for limitations imposed by electron acceptor availability. Finally, the first-order reaction assumption is only reasonable if the concentration of benzene is low. However, and since electron acceptor data were not collected and because the modeling is addressing one component only (benzene), the first-order decay approach is used. The data range reported in Suarez and Rifai provided a useful starting point as did their estimated median rate.

Source definition

As mentioned previously, BIOSCREEN requires source width and depth and benzene concentration

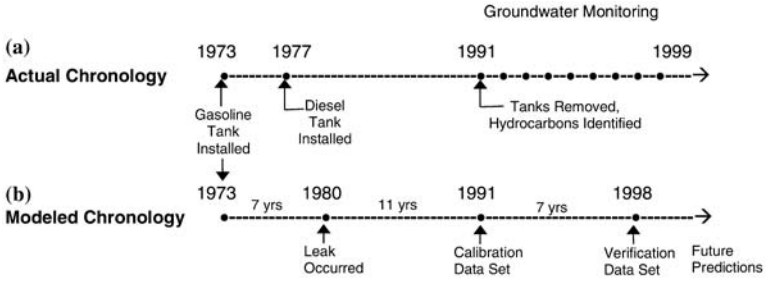

Figure 3. Site timeline.

in the source area as input. These variables are not directly measured in the field and have to be estimated from the soil and ground water data collected at the site. Source depth can be assumed to equal the thickness of the smear zone defined by the maximum fluctuation in water levels (5 ft in this case). Source width can be estimated from the 1991 plume data by drawing a transect across the highest benzene concentration contour within the plume and perpendicular to the defined plume centerline (see Figure 4). Benzene concentrations along this transect can then be estimated:

BIOSCREEN also requires the residual mass in the source area or the source half-life to be entered as input. In the case of an infinite source, the source half-life can be set to a relatively large number, e.g., 100 yr to simulate an excess of benzene in the source area. However, in the case of a finite release (as in this case), it is necessary to estimate the source half-life between 1980 and 1991. This is not possible using the existing natural attenuation data since the volume of the original spill is unknown. Also, no soil data were collected prior to tank excavation so the mass could not be determined from residual soil data before the tank was removed. Once the tank is removed, the source half-life is expected to shorten since no more product will be released into the ground water. The source half-life after the tank was removed can be approximated by analyzing the decline in concentrations in wells located in the source area. Such an analysis yields half-lives in the range of 2.7–9 yr for the period between 1991 and 1998. It is reasonable then to assume that the half-life for the period 1980–1991 would be <100 and >9 years. In this case, the source half-life (or source mass) is used as a calibration variable and estimated through trial and error.

BIOSCREEN calibration

In developing the conceptual model for BIOSCREEN modeling, it was clear that two parameters would have to be estimated through trial and error: the biodegradation rate and the source half-life. The calibration process was started by predicting the ground water concentrations assuming an infinite source and no biodegradation and comparing the modeled concentrations to the measured values (Figure 6). The results of this comparison illustrated that while the maximum concentrations near the source area matched the measured ones relatively well, the in-plume concentrations were overestimated. The next step was to incorporate biodegradation into the model. The median rate of 1.28 yr^{-1} reported in Suarez and Rifai (1999) was used as a first-guess. The results shown in Figure 6 indicate that this rate is not high enough to provide a reasonable match with the measured data. Using trial and error, the closest match was obtained using a rate of 1.53 yr^{-1} as shown in Figure 6.

Given the uncertainty associated with parameter estimates, it is necessary to evaluate the sensitivity of the calibrated model to changes in the parameter values. Both plume length and maximum plume concentration were used as model outcomes for comparison to the calibrated base case. As would be expected for an analytical model, the seepage velocity (including the retardation coefficient) and the biodegradation first-order rate parameter had a significant impact on

Source zone benzene concentrations – 1991			
Width (ft)	26	11.25	15
Concentration (mg/l)	20	16	10

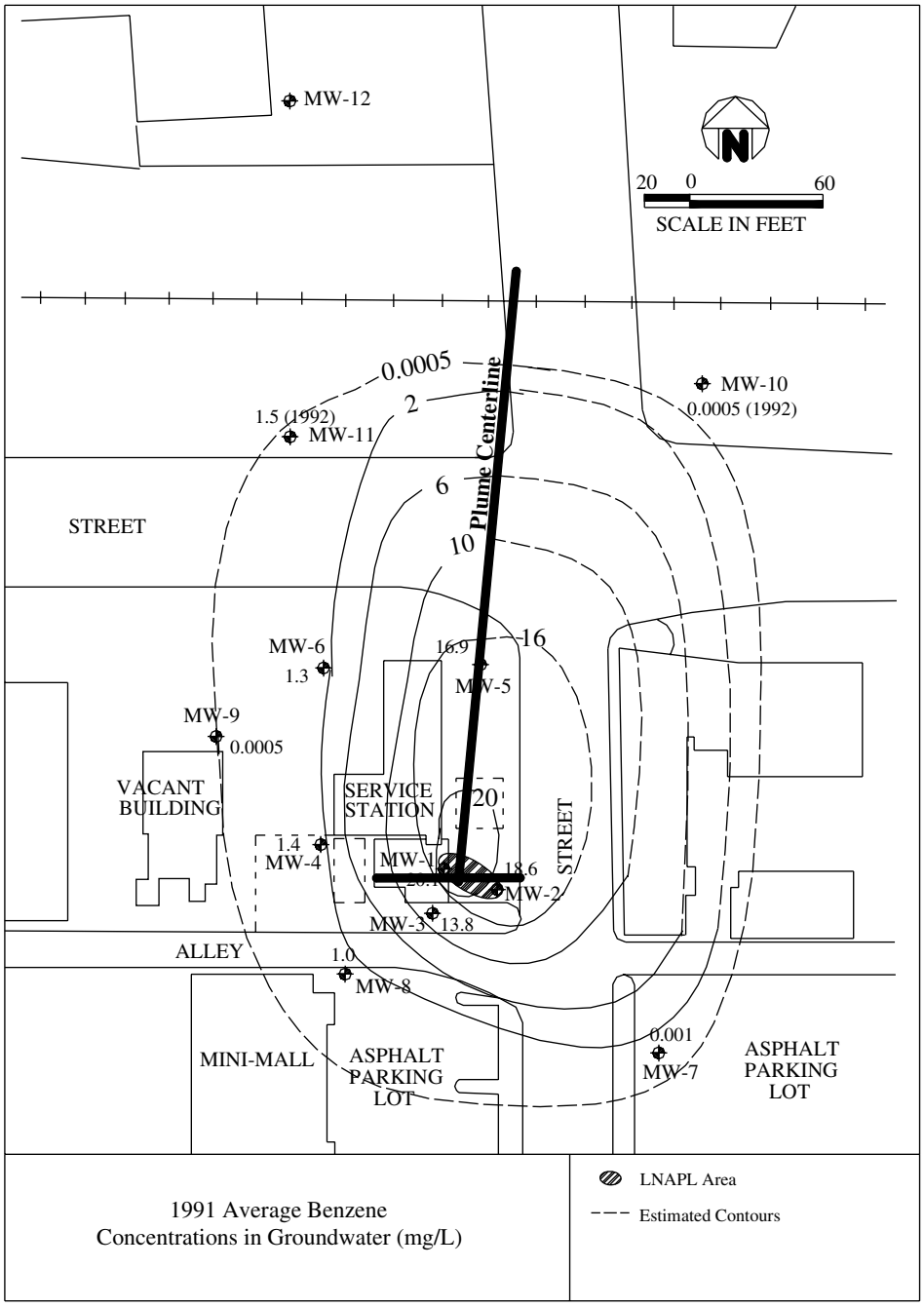

Figure 4. 1991 average benzene concentrations in groundwater (mg/l).

the predicted plume length and maximum concentration. Increases in velocity and decreases in the rate coefficient resulted in an equivalent relative increase in plume length.

BIOSCREEN verification

The calibrated model was used to predict the concentrations at the site for the year 1998 in an effort to validate that the model adequately represents

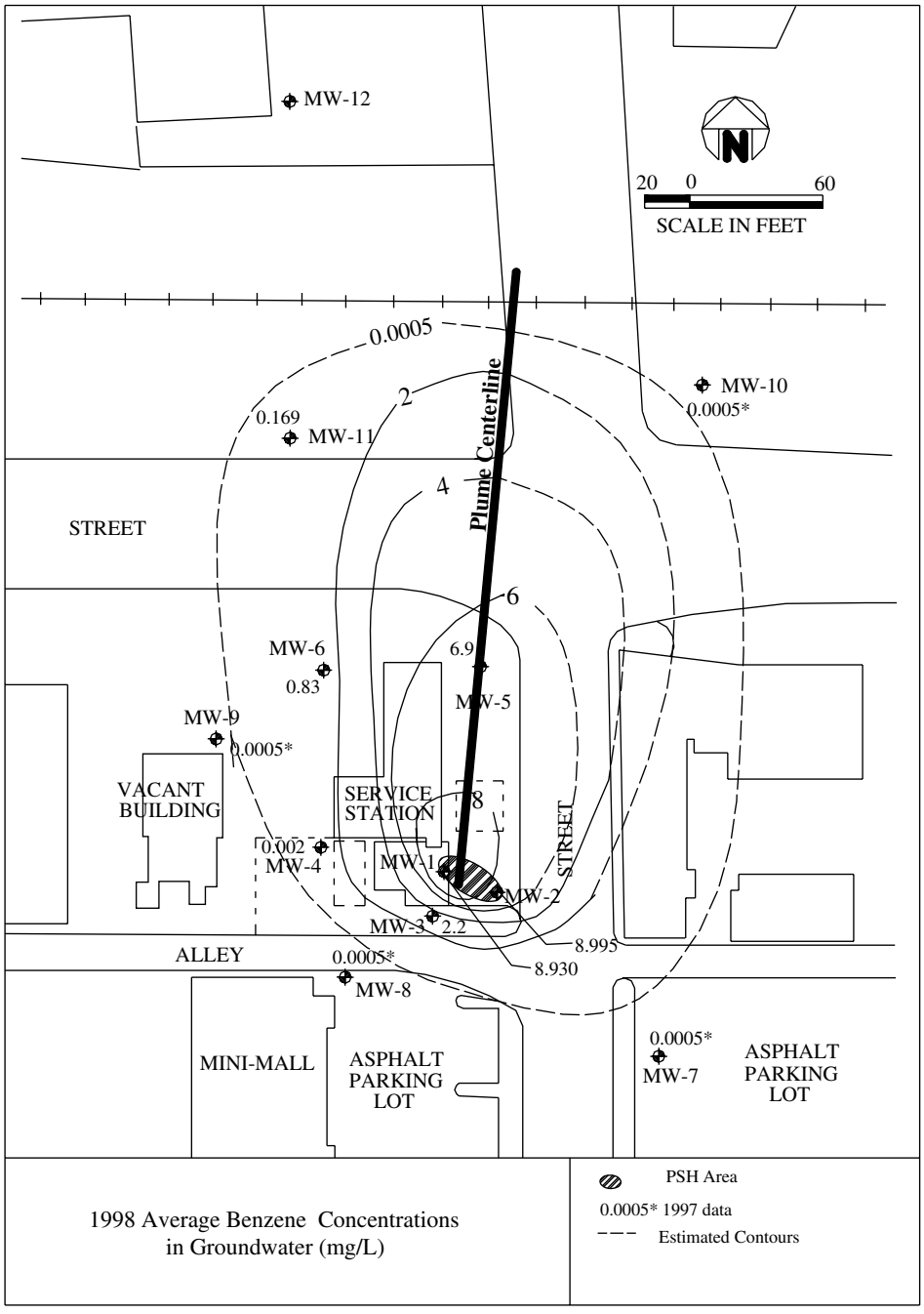

Figure 5. 1998 average benzene concentrations in groundwater (mg/l).

site conditions. This was accomplished by increasing the time variable from 11 to 18 yr. As can be seen in Figure 6, the predicted 1998 benzene concentrations do not match their measured counterparts well. This basically points to the fact that our assumption of an infinite source is not valid and does not incorporate the change in source conditions due to removal of the tank in 1991.

Therefore, the source parameters were changed to reflect a decaying source. The source decay rate

was estimated by trial and error by decreasing the 100 yr half-life until the concentrations in 1998 were matched. A source half-life of 30 yr provided a reasonable match to the 1998 benzene levels (Figure 6). It is noted that this is not a true validation in the sense that the source parameters had to be modified to match the 1998 data. However, this was necessary because of the changes in the source after the tank was removed.

BIOSCREEN predictions

In predicting future site conditions, the validated model results indicate that it would take more than 100 years for benzene concentrations to attenuate to the risk-based cleanup goal of 0.47 mg/l. These results are based on the assumption that the source half-life is around 30 yr and that the biodegradation rate is 1.53 yr^{-1}. The predicted remediation time estimate can be further refined as more field data are gathered.

It is clear from this modeling analysis that there are limitations associated with the use of an analytical model. Analytical models do not have the capabilities to simulate spatial variations in model parameters or to reflect the effects of remediation activities. Numerical models are better suited for handling spatial and temporal changes in flow or contaminant conditions at sites and for modeling remediation. In the next section, the BIOPLUME III model is used to examine the validity of the 100-yr remediation estimate obtained with BIOSCREEN for this site.

BIOPLUME III modeling

BIOPLUME III is a two-dimensional, finite difference model for simulating aerobic and anaerobic biodegradation of hydrocarbons in groundwater in addition to advection, dispersion, sorption and ion exchange. In BIOPLUME III, three different kinetic expressions can be used to simulate biodegradation. These are first-order decay, instantaneous reaction, and Monod kinetics (Rifai et al. 1997). Model parameters closely mimick those for BIOSCREEN with several notable exceptions: BIOPLUME III requires a flow calibration step whereby the observed ground water levels are predicted using the hydraulic conductivity and gradient estimates across the site. Since the model is two-dimensional, most parameters can be spatially variable thus involving more complexity and effort in grid design and parameter estimation. Additionally, the benzene source is represented using injection wells by defining the

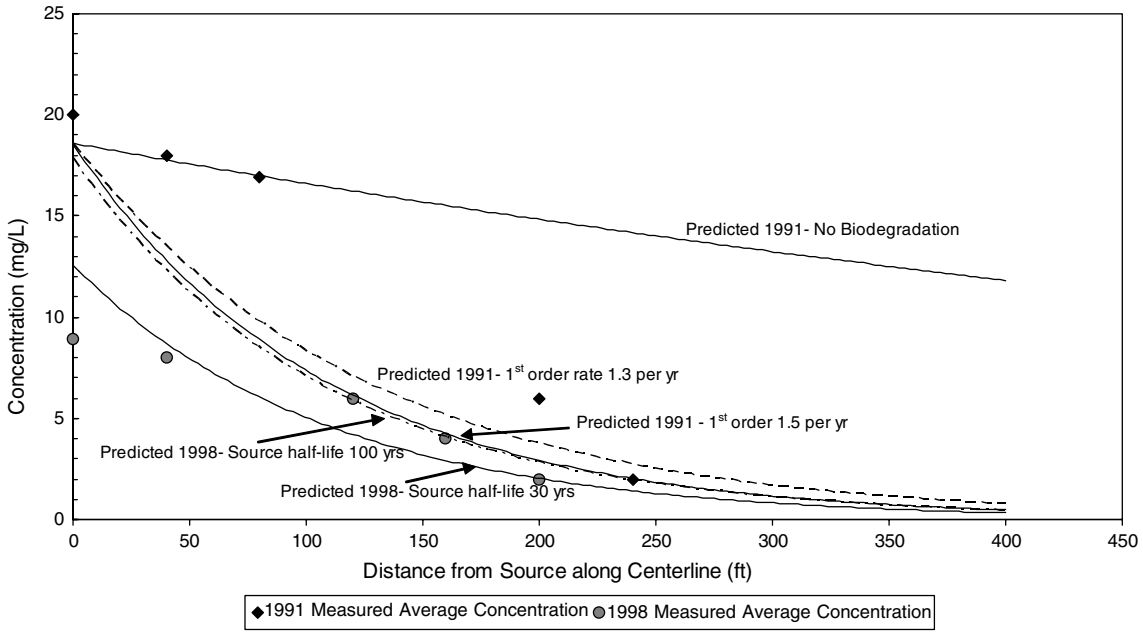

Figure 6. BIOSCREEN run results.

rate of benzene injection and the concentration of benzene in the injected water. Finally, model output is also spatially variable across the model grid which means that more effort is involved in comparing modeled heads concentrations to the measured ones.

The BIOSCREEN modeling presented in the previous section was limited because the model was not designed to simulate excavation and its impacts on the groundwater plume. The BIOPLUME III model allows the use of multiple pumping periods with a changing source definition from period to period thus enabling users to simulate excavation and other remedial activities. The goal for utilizing the two-dimensional BIOPLUME III model, therefore, is the same as that for BIOSCREEN: to predict the distribution and concentration of the dissolved benzene concentrations in 1991 and 1998 at the site and the time at which the concentrations will attenuate to below 0.47 mg/l. The main difference between BIOSCREEN and BIOPLUME III in this case is that the BIOPLUME III model set-up will involve the use of more than one time period to better represent the chronology of events at the site.

BIOPLUME III conceptual model

Based on the estimated maximum dissolved benzene plume length, the BIOPLUME III grid size was designed to be 920 ft long and 500 ft wide. The grid dimensions were defined such that all regions with dissolved benzene concentrations greater than 0.47 mg/l were included in the model. A total of 20 columns and 23 rows were overlain on the base image of the site and used in the modeling. The dimensions of each cell are 25×40 feet (Figure 7).

Flow system

In contrast with BIOSCREEN, the BIOPLUME III model calculates two-dimensional groundwater velocities based on the water table conditions at the site. In order to adequately estimate velocities, it is important to calibrate the flow conditions using the model such that predicted heads match their measured counterparts. Since the designed model grid extends beyond the plume boundary, measured water table contours in 1992 were used to develop the boundary conditions for the model domain. Conceptually, the flow delineation and gradient within the model grid are controlled by defining 'constant head' boundaries at the upgradient and downgradient edges of the plume. In a sense, this represents a modeling mechanism for forcing groundwater to flow from high to low levels within the model grid. The 'water level' is effectively held constant at the upgradient and downgradient boundaries throughout the simulation. Water levels within the grid are, however, allowed to change in response to localized sources and sinks.

Biodegradation

As in BIOSCREEN, biodegradation was modeled as a first-order decay process. A biodegradation rate of 1.52 yr^{-1} (same as calibrated value for BIOSCREEN) was used.

Source definition

As mentioned previously, BIOPLUME III represents benzene leakage into groundwater using injection wells. An injection rate (or source leakage rate) and a source concentration are required input for the model. Both of these variables are considered calibration parameters since their values are unknown. The source injection rate is usually determined to be the smallest flow rate that would not cause mounding or changes in the ground water flow contours within the model grid. Source concentrations are varied until observed concentrations in the source area are matched. Unlike BIOSCREEN, the BIOPLUME III model simulates 'dilution' within the mixing zone in source areas. The source injected mass (flow $\times$ concentration) is diluted by the volume of groundwater already present in the injection cell. Thus, the resulting groundwater concentrations leaving the injection cell are generally lower than the injected concentration.

For this site model a total of two injection wells (one near MW-1 and MW-2 and one near MW-5) were used to represent the tank leakage. Injection rates and injected concentrations used were 0.002 cfs, and 40 mg/l, respectively.

BIOPLUME III calibration

As discussed in the BIOSCREEN model application, initial leakage from the tank was assumed to have started in 1980 and the hydrocarbon source is

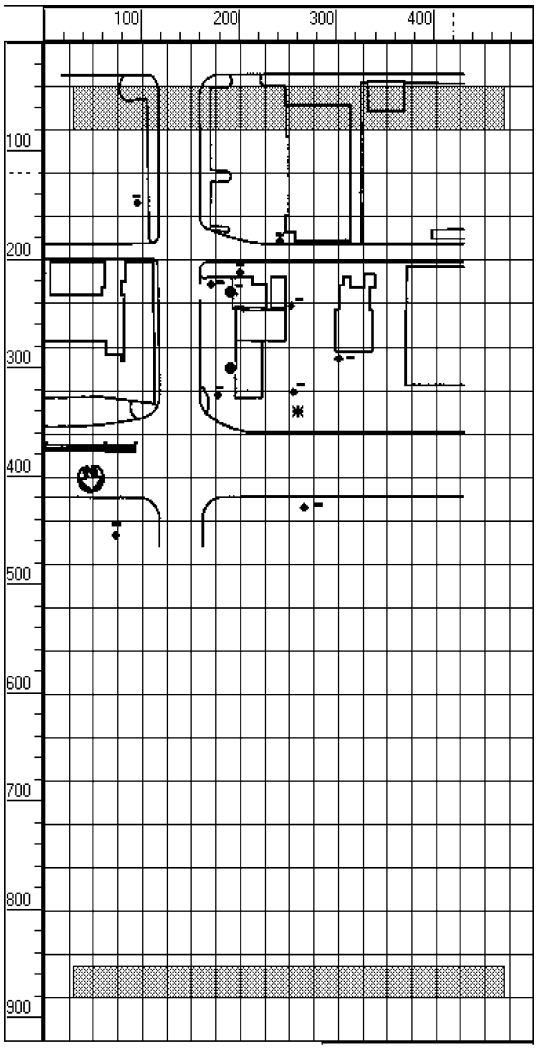

Figure 7. BIOPLUME III model grid.

assumed to be constant between 1980 and 1991. After the majority of the source was excavated in 1991, both the rate of source loading (i.e., injection rate and injected concentration) and the degradation rate are expected to have changed. Therefore, two time steps were incorporated into the BIOPLUME III model to model the pre-excavation and post-excavation time periods.

The model was run for the initial time period of 11 yrs and the resulting groundwater elevations were compared to the measured values as shown in Table 2 (note that the 1992 groundwater data were used since 1991 data were incomplete). Steady-state conditions were assumed for the flow component of the model. This is a reasonable assumption since the model covers an extensive time frame and model results are unlikely to be sensitive to the relatively small seasonal variation in groundwater levels. Overall, the modeled direction of flow and gradients compared well to the contoured groundwater levels from measured data. The modeled concentrations for the various wells also compare reasonably well to the measured benzene values in 1991 as shown in Table 2.

BIOPLUME III validation

The calibrated model was used to predict the observed concentrations in 1998 as a model validation/verification step. It is be noted, however, that this evaluation required one change in model input and that is a change in model parameters for source definition. This was necessary because of the excavation that occurred in 1991. Concentrations were assigned to the two injection wells based on the measured values obtained during site monitoring: 21 mg/l at the injection well close to MW-1, and 22.5 mg/l at the second injection well near MW-5. Injection rates of 0.0015 and 0.0009 cfs were assigned to the wells, respectively. These rates were estimated using trial and error to obtain the best fit for the 1998 concentration data. The resulting concentration data, shown in Table 3, were generally consistent with the measured values.

As with BIOSCREEN and in an effort to understand the effect of the various parameters on model results, a sensitivity analysis was undertaken. The same parameters that had been analyzed in the BIOSCREEN sensitivity analysis were examined as well as other ones that are specific to the BIOPLUME III model (e.g., ratio transverse/longitudinal dispersivity, source injection rate, and source concentration). The results from the sensitivity model runs were compared to the calibrated model predictions at two points: the maximum concentration observed in the source area (MW-1) and at the property boundary, approximately 120 ft downgradient of the source. Variations in the maximum plume length were also assessed, based on a hydrocarbon (benzene) concentration of 0.47 mg/l. It is noted that the calibrated modeled concentration at the property boundary was 5.9 mg/l in 1998 and the total plume length, based on a concentration of 0.47 mg/l, was 420 ft from the source. The largest concentration variations

were observed in the source area if the injection rates and/or concentrations were either increased or decreased. A decrease in the biodegradation rate also resulted in a large concentration variation, mostly observed at the edge of the plume or the further downgradient from the source. Porosity and hydraulic conductivity had minimal to no effect on the model concentration output. The largest plume length variation was observed when the biodegradation rate was either increased or decreased, with lengths increasing to greater than 600 ft or decreasing to 140 ft.

Table 2. BIOPLUME calibration data 1991–1992

Monitoring well	1992 measured elevations (ft)	Model output elevations (ft)	Difference (ft)
1	81.42	81.536	0.01346
2	81.36	81.531	0.02924
3	81.43	81.530	0.01000
4	81.53	81.498	0.00102
5	81.52	81.410	0.01210
6	81.48	81.403	0.00601
7	81.49	81.590	0.01000
8	81.53	81.563	0.00109
9	81.54	81.424	0.01346
10	81.30	81.227	0.00533
11	81.29	81.278	0.00014
		Root mean square error	0.09622
	Measured concentrations (mg/l)	Model output concentrations (mg/l)	Difference (mg/l)
1	20.1	20.118	0.00032
2	18.6	13.425	26.7806
3	13.8	13.899	0.00980
4	1.4	1.260	0.01974
5	16.9	16.801	0.00980
6	1.3	2.880	2.49640
7	0.0013	0.015	0.00019
8	1.03	0.443	0.34457
9	0.0005	0.772	0.59521
10	0.0005	1.080	1.16532
11	1.5386	2.805	1.60377
		Root mean square error	1.73273

Model predictions

The calibrated and validated model was used to predict how long it would take for site concentrations to attenuate to below 0.47 mg/l. Model results indicated that 99 yr of attenuation are required to reach this goal. These results are very similar to those predicted with BIOSCREEN confirming the screening assessment completed with the analytical model. The benefit from using BIOPLUME III is that various remediation scenarios can be now explored using the calibrated model (e.g., source reduction).

Summary

Natural attenuation models are often used to esimate the length of time required to achieve a remediation goal and to determine if a plume is going to get longer. While many natural attenuation models have been developed for this purpose, very little guidance exists on how to analyze and condense field data collected in support of natural attenuation to develop models that appropriately represent site conditions. This paper demonstrates data analysis and data reduction strategies for natural attenuation modeling. An analytical and a numerical model are applied to a BTEX plume. Calibrated and verified site models are used to

Table 3. BIOPLUME verification data for 1998 (t = 18 years)

Monitoring well	Measured concentrations (mg/l)	Model output concentrations (mg/l)	Difference (mg/l)
1	8.93	8.967	0.00137
2	8.995	6.522	6.11820
3	2.2	6.002	14.45520
4	0.002	0.512	0.26010
5	6.9	6.899	0
6	0.833	1.115	0.07952
7	**0.0005**	0.003	0.00001
8	**0.0005**	0.151	0.02265
9	**0.0005**	0.271	0.07290
10	**0.0005**	0.375	0.14025
11	0.169	1.026	0.73445
		Root mean square error	1.41

Bold – 1999 data.

predict the required cleanup time using natural attenuation. It is clear from the case study that difficulties are still encountered in estimating field based biodegradation rates and developing estimates for source parameters required by natural attenuation models.

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