

Assessing uncertainty in remediation by natural attenuation of a petroleum hydrocarbon contaminated site

MONICA P. SUAREZ & HANADI S. RIFAI

University of Houston, 4800 Calhoun Road, Bldg D, Room N107, Houston, Texas 77204-4791, USA

e-mail: rifai@uh.edu

Abstract Over the past decade, natural attenuation has been accepted as a feasible remediation alternative for sites contaminated with petroleum hydrocarbons. Remediation by natural attenuation relies on the physical, chemical and biological processes that contribute to decrease both contaminant concentration and plume size. Extensive analysis of these intrinsically occurring processes is required to assess the time required for cleanup and the extent of future migration of the contaminant plume. A number of protocols, guidance documents and models have been developed for assessing the viability of the technology on a site-specific basis. These tools, have not however, fully addressed the uncertainty associated with field characterization of these processes and mechanisms. In this paper, we determine the potential impacts of uncertainties associated with hydrogeological and geochemical characterizations of the groundwater system and the uncertainties associated with the source term. The implications for remediation by natural attenuation are determined through analytical modelling using different values for key model parameters. The uncertainty modelling is used to demonstrate the feasibility of using natural attenuation at a coastal site contaminated by refined and crude BTX (benzene, toluene and xylene).

INTRODUCTION

The site under investigation is located in a coastal area and immediately west of the mouth of a river. Manufacturing operations at the facility were suspended in 1985 and its eleven operational units have been decommissioned and dismantled. The site exhibits contamination by petroleum hydrocarbons over approximately 24 ha (60 acres) in the northeastern part of the main plant. Several on-site and off-site sources have contributed to BTX (benzene, toluene and xylene) contamination of the underlying soil and groundwater. A number of site assessment and characterization studies have been completed that allowed mapping of the BTX plumes.

Groundwater samples collected in 1979, 1982, 1996, and 1998 indicate that benzene and xylene concentrations in the site monitoring wells are decreasing with time. Furthermore, concentrations in the leading edge wells have remained constant over time and the BTX plumes seem to have reached quasi-steady state even though residual contaminant sources are still present in the aquifer.

A number of on-site and off-site sources of contamination have been reported since 1967. In 1977, an underground pipeline that transported refined BTX from the site to a neighbouring facility ruptured causing the release of 1130 m³ (300 000 gallons)

of BTX (approximately 60% benzene). Pumping operations resulted in the recovery of 1020 m³ (270 000 gallons) of the released BTX. Several oil spills into a drainage ditch that runs along the east boundary of the site have been also reported between 1965 and 1975, and between 1989 and 1995. In addition, the presence of NAPL has been detected in several wells within the facility and in the north-neighbouring site. The on-site NAPLs were found floating above the piezometric surface through a clayey sand layer with thickness varying from 2.5–69.0 cm (1–27 inches). Off-site NAPLs cover about 60 ha (150 acres) with an average thickness of 122 cm (4 ft) adjacent to the north boundary of the site. The delineated NAPLs continue to contribute to hydrocarbon contamination in the groundwater.

GROUNDWATER FATE AND TRANSPORT MODELLING

The analytical model BIOSCREEN (Newell *et al.*, 1996) was used for modelling the observed BTX data at the site. BIOSCREEN is an analytical model for natural attenuation that is based on the Domenico (1987) solution of the advection–dispersion equation. The Domenico (1987) solution was modified to include biodegradation, using first-order and instantaneous reaction kinetics. The model also assumes a fully penetrating vertical plane source perpendicular to groundwater flow to simulate the release of organics to the groundwater.

The site BIOSCREEN model used 1979 as the base year and was calibrated by matching the 1996 monitoring wells along a flow line within the benzene plume. The calibration was carried out using field-measured parameters for hydraulic conductivity, gradient, aquifer thickness, and geochemical data. Typical values from the general literature were used for porosity, dispersivity, and the benzene biodegradation rate. The calibration parameters are listed in Table 1.

It is important to point out that since dissolved phase biodegradation was not sufficient to explain the concentration reduction in the source area between 1979 (1700 mg l⁻¹) and 1996 (580 mg l⁻¹), a decaying source was assumed. The source concentration was determined using the plume in 1979 and the soluble mass was calculated assuming the 1977 spill as the main source of benzene contamination. The predicted benzene concentrations using the calibrated model matched the measured concentrations reasonably well as can be seen in Fig. 1.

Table 1 Input data for calibrated BIOSCREEN site model.

Parameter	Units	Value
Hydraulic conductivity	cm s ⁻¹	0.003
Hydraulic gradient	–	0.006
Porosity	–	0.3
Longitudinal dispersivity	m	7.63 (25 ft)
Retardation factor	–	1.2
Biodegradation half-life	year	6
Source thickness	m	0.91 (3 ft)
Source width	m	610 (2000 ft)
Source maximum concentration	mg l ⁻¹	1700
Soluble mass	kg	60 000
Source half-life	year	10

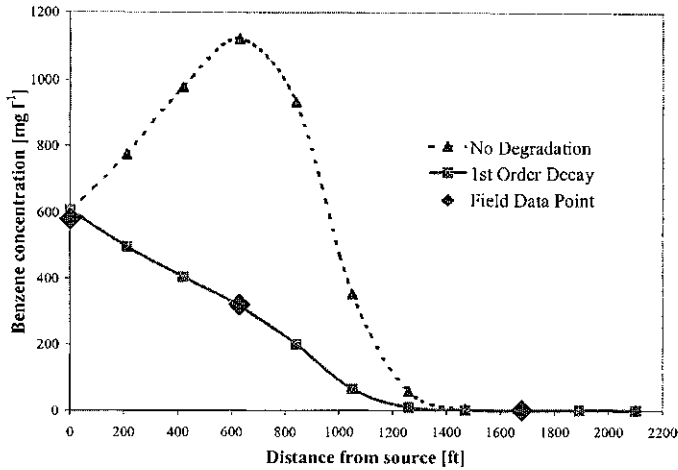


Fig. 1 Predicted concentrations using the BIOSCREEN site model.

SENSITIVITY ANALYSIS

Much uncertainty is associated with groundwater contamination. The majority of aquifer characteristics are spatially variable and contaminant concentrations vary in space and over time. It is very difficult and costly to collect sufficient data to adequately characterize these systems. For the purposes of natural attenuation assessments, it is important to understand the impact of these uncertainties on plume geometry and concentrations particularly with regard to potential risks associated with the contamination. In this paper and due to the limited site database, a sensitivity analysis approach was used to address this issue.

Once the calibrated model for the site was developed, model parameters were varied individually, within the range 10%–2000% of the base case, to evaluate their relative impact on plume geometry. This generic approach was taken in the absence of more specific ranges for site parameters. The variations were quantified using two different criteria: concentrations at the monitoring wells and plume length (using 5 ppb as the minimum concentration). The root mean squared (RMS) error was calculated to express the average difference between simulated and measured concentrations for all model runs in order to compare the relative importance of each of the parameters. For the purposes of this analysis, twenty different simulations were used for each parameter.

Since the BIOSCREEN model is analytical in nature, the source is defined using four parameters: source depth, source width, source concentration and source mass. The model calculates the source decay rate using these data and the flow rate through the source zone. Therefore, changing any of the source parameters or the flow characteristics will result in a change in the source decay rate. For the purposes of this analysis, two sets of model runs were completed. These runs are labelled A and B for ease of identification. The A simulations varied the source mass and held the source decay constant; the B simulations allowed the source decay rate to vary while holding source mass constant. In this manner, a better understanding of source impacts could be developed.

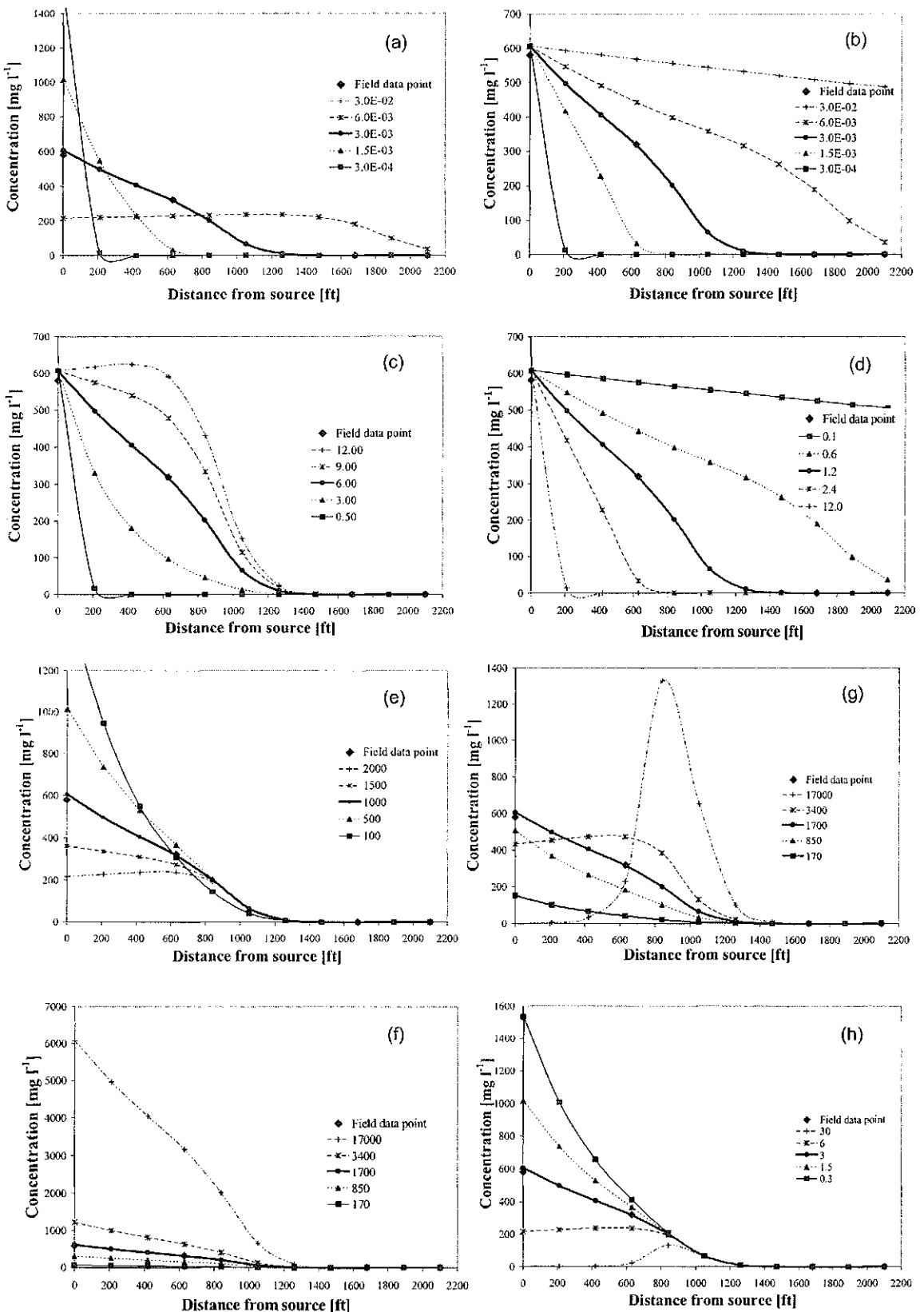


Fig. 2 Relationship between parameters and predicted concentrations (a) hydraulic conductivity A runs, (b) hydraulic conductivity B runs, (c) biodegradation rate, (d) retardation factor, (e) source width A runs, (f) source concentration A runs, (g) source concentration B runs, (h) source thickness. A runs: source half-life 10 years; B runs: source mass constant.

The effect of the different parameters on the predicted concentrations along the centre line of the plume is presented in Fig. 2. Figure 2 does not include variations due to dispersion because the effect of this parameter was very small; when source width was varied as well as the soluble mass of the source (to maintain the source half-life equal to 10 years), concentrations along the plume centre line were almost the same for the different width values, thus this case was not included in Fig. 2 either.

Comparison of the RMS errors in concentrations for the different scenarios is presented in Fig. 3. The bars represent the total error in predicted concentrations with respect to the four field data points for variations of 10% and 2000% of the base case for each parameter. It can be seen in Fig. 3 that the model is most sensitive to source concentration, elapsed time and hydraulic conductivity when predicting concentrations.

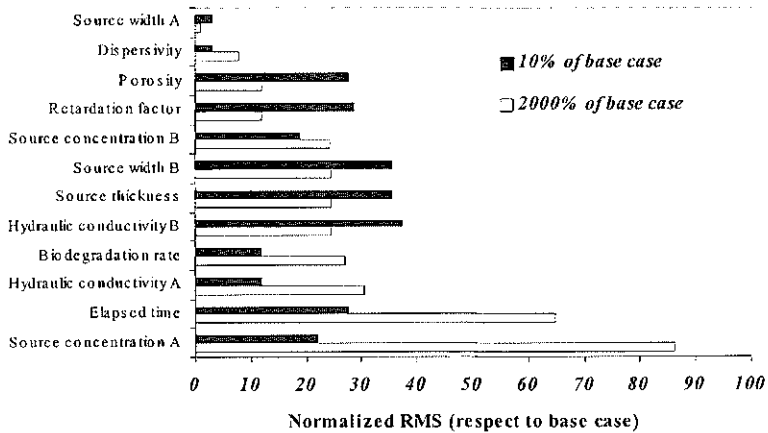


Fig. 3 Concentration RMS errors for different parameters.

Variations in plume length due to the 2000% variation in the parameters were also analysed and compared to the observed plume length of 2097 ft (assuming a 5 ppb limit), Fig. 4. It is most sensitive to the retardation factor and to hydraulic conductivity.

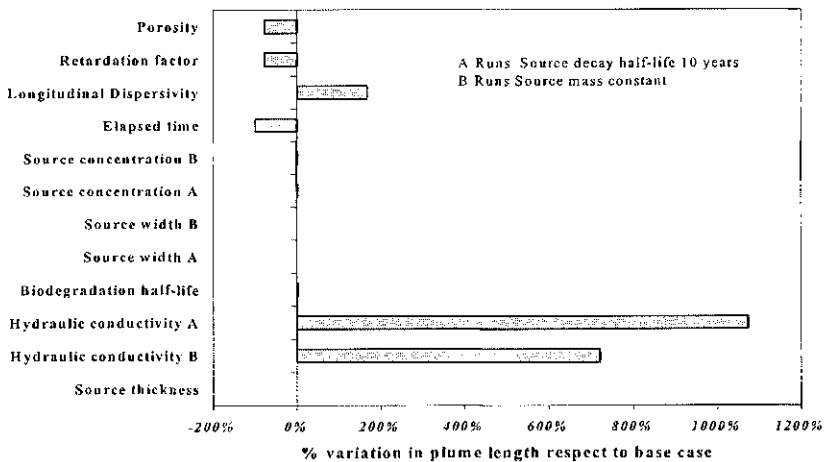


Fig. 4 Plume length variations for different parameters.

Finally, concentrations in a well located in the source area were evaluated for the different scenarios. The percentage of variation in parameter value was plotted against percentage variation in concentration (Fig. 5) in order to determine the curves with the highest slopes, which represent the parameters to which the model is most sensitive. For this criterion, the model was most sensitive to source concentration and biodegradation half-life.

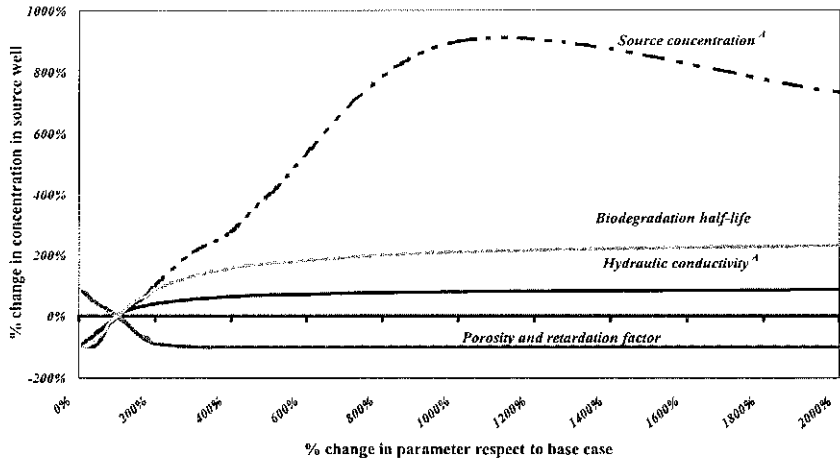


Fig. 5 Relative importance of parameters on concentrations in source well.

CONCLUSIONS

For most cases of groundwater contamination, there is a primary concern with respect to the migration of contaminants to downgradient water supply wells or to points of human exposure. Therefore, in order to determine whether or not natural attenuation is a feasible alternative at a site, it is necessary to demonstrate that there is a high probability that the plume will not reach an exposure point. For this reason, uncertainty analyses should be conducted to evaluate the differences in predicted concentrations and plume lengths at a given site.

The research presented in this paper demonstrated that natural attenuation model predictions using the BIOSCREEN model are most sensitive to hydraulic conductivity and source definition. The results indicate that for sites with an active source area, it may be necessary to obtain an accurate assessment of residual source areas in order to quantify their impacts on plume length and concentrations.

REFERENCES

- Domenico, P. A. (1987) An analytical model for multidimensional transport of a decaying contaminant species. *J. Hydrol.* 91, 49–58.
- Newell, C. J., McLeod, R. K. & Gonzales, J. R. (1996) BIOSCREEN natural attenuation decision support system user's manual, version 1.3. EPA/600/R-96/087, Environmental Protection Agency, USA.