Uncertainty in measured biodegradation rate constant for heterogeneous aquifers



Amir H Hosseini, Clayton V Deutsch Department of Civil and Environmental Engineering, University of Alberta, Edmonton, AB, Canada Carl A Mendoza Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB, Canada Kevin W Biggar BGC Engineering, Edmonton, AB, Canada

ABSTRACT

The biodegradation rate constant of organic contaminants are particularly important for decision making and management of contaminated sites. A number of field approaches that estimate the rate constants by using concentration - distance relations along the plume centerline are commonly used. However, the estimated rate constants will be affected by heterogeneity in transmissivity, uncertainty in hydraulic head measurements and uncertainty in source geometry. This study attempts to quantify the resulting uncertainty in the rate constants. First, a synthetic aguifer with known hydrogeological and transport properties is created and transport of dissolved BTEX is simulated across the site. The first-order biodegradation rate constant is then estimated using the method of Buscheck and Alcantar (1995) and compared to the known value used in the transport simulations. Next, uncertainty in head measurements and its effect on the estimated first-order rate constant is investigated. For this purpose, multiple realizations of the transmissivity field are generated conditioned to a number of hydraulic conductivity measurements (static data) and hydraulic head observations (dynamic data). These realizations are then combined with the realizations of source geometry obtained by a distance-function approach to create multiple joint realizations of transmissivity and source geometry. In a Monte Carlo Simulation framework, transport of dissolved BTEX is simulated for all joint realizations and the first-order biodegradation rate constant is estimated by the method of Buscheck and Alcantar. The results of the simulations show that the first-order biodegradation rate constant can be easily overestimated due to missing the centerline of the plume in heterogeneous aquifers. Uncertainty in head measurements also affects the estimated first-order rate. In this case the method of Buscheck and Alcantar may overestimate the first-order rate constant by more than one order of magnitude.

RÉSUMÉ

La constante de vitesse de biodégradation des contaminants organiques sont particulièrement importantes pour la prise de décision et la gestion des sites contaminés. Un certain nombre d'approches domaine estimer que le taux constantes en utilisant la concentration - les relations à distance le long de l'axe du panache sont couramment utilisés. Toutefois, le taux estimé constantes seront touchés par l'hétérogénéité dans transmissivité, l'incertitude dans les mesures hydraulique et de l'incertitude dans la source la géométrie. Cette étude tente de quantifier l'incertitude qui en résulte pour le taux des constantes. Tout d'abord, un aquifère de synthèse dont on connaît hydrogéologiques et propriétés de transport est créé et le transport des BTEX dissous est simulé à travers le site. Le premier ordre de biodégradation constante de vitesse est alors estimée en utilisant la méthode de Buscheck et Alcantar (1995) et par rapport à la valeur connue utilisée pour le transport des simulations. Ensuite, l'incertitude des mesures dans la tête et son effet sur l'estimation du premier ordre est constante de vitesse d'une enquête. À cet effet, de multiples réalisations de la transmissivité domaine sont générés conditionné à un certain nombre de mesures de la conductivité hydraulique (données statiques) et hydraulique observations (données dynamiques). Ces réalisations sont ensuite combinés avec les réalisations de la source géométrie obtenu par une distance fonction de créer plusieurs réalisations conjointes de transmissivité et la source la géométrie. Dans une simulation Monte Carlo cadre, le transport des BTEX dissous est simulée pour toutes les commissions paritaires et les réalisations de premier ordre biodégradation constante de vitesse est estimé par une concentration communément utilisés distance technique. Les résultats des simulations montrent que le premier ordre de biodégradation constante de vitesse peut être facilement sous-estimée en raison de l'absence de l'axe du panache dans les aquifères hétérogènes. Incertitude sur la tête mesures influe également sur l'estime de premier ordre. Dans ce cas, la méthode de Buscheck et Alcantar mai surestimer le premier ordre constante de vitesse de plus de un ordre de grandeur.

1 INTRODUCTION

Active clean up of upstream oil and gas contaminated sites has both practical and financial limitations, which has led to extensive interest in remediation techniques that utilize the natural attenuation (NA) capacity of the subsurface. Reduction in concentrations of organic contaminants in the subsurface is due to combination of physical, geochemical and biochemical processes (Figure 1). Among these, aerobic and anaerobic biodegradation are the main processes for the destructive removal of organic contaminants (Chiang et al. 1989).

Estimating the amount of time required for NA processes to lower contaminant levels to given regulatory goals is required when assessing 'monitored natural attenuation' (MNA) as a remedial alternative. The need for quantitative assessment of this 'time of remediation' problem has resulted in the development of numerical models that simulate complex kinetics and multicomponent interactions (Zheng 1990, Rifai et al. 1997 and Chapelle et al. 2003). Unfortunately, many of the kinetic parameters and electron acceptor data required by these models are either quite uncertain or very difficult to determine using the current natural attenuation guidelines and protocols (Rifai and Rittaler 2005). When electron acceptor data are uncertain or do not exist, one approach is to use a first-order biodegradation rate, which can be determined using the 'concentration versus distance' techniques or microcosm studies (Chapelle et al. 1996, Widemeier et al. 1999). In a concentration versus distance approach, contaminant concentrations are plotted along the centerline of the plume, which is assumed to be in the direction of groundwater flow. The biodegradation rate constants are then calculated by matching the first-order curve to the observed concentrations. The method of Buscheck and Alcantar (1995) is a concentration – distance approach commonly used in practice. It is based on the steady-state solution for a 1D transport equation, incorporating advection, longitudinal dispersion and first-order biodegradation. An estimate of longitudinal dispersivity is required for this approach, which may introduce additional uncertainty in estimation of biodegradation rate constant.



Figure 1. Conceptual illustration of important natural attenuation processes that affect the fate of petroleum hydrocarbons in aquifers (Bekins et al. 2001)

The concentration – distance techniques are affected by the level of heterogeneity of aquifer material. In fact, the centerline of a plume can easily be missed by monitoring wells installed based on assumed (but incorrect) groundwater flow directions (Wilson et al. 2004). The uncertainty inherent in source zone geometry may also contribute to uncertainty in the estimated biodegradation rate constant. It has been also observed that, in the method of Buscheck and Alcantar (1995), estimation of dispersivities by common approaches may also introduce large uncertainties in the biodegradation rate estimates (Bauer et al. 2006).

The work of Bauer et al. (2006) is a similar work which investigates the uncertainty in the measured

biodegradation rate constant as a direct result of uncertainty in a heterogeneous transmissivity field. Similar to the study of Bauer et al. (2006), in this work we investigate the uncertainty in measured biodegradation rate constant in a Monte Carlo Simulation framework. However, there are two improvements to the work of Bauer et al. (2006): (1) in this work transmissivity realizations are conditioned to head observations (dynamic data) as well as direct transmissivity measurements (static data), and (2) the effect of uncertainty in source geometry is also investigated. The first improvement ensures that we can study the effect of uncertain hydraulic head measurements on the estimated first-order rates. The second improvement is useful to investigate the effect of uncertainty in source geometry on the results. The proposed improvements render the simulations more realistic.

To evaluate the performance of the method of Buscheck and Alcantar (1995) in heterogeneous aquifers, a synthetic aguifer with a known transmissivity field is considered and steady-state pressure (head) response is simulated. For a given monitoring well configuration, a few transmissivity measurements and head observations are then recorded from the synthetic aquifer. In a realworld application, these transmissivity measurements and head observations are usually the only site-specific data available about the hydrogeologic regime of the site. So, in this work we only use these data to model the uncertainty in transmissivity field. In the next step, a distance function based approach is used to model the uncertainty in source geometry; and multiple combined source-transmissivity realizations are created. Fate and transport of dissolved BTEX is then simulated for all combined realizations with pre-specified values of biodegradation rate constant and dispersivity. The method of Buscheck and Alcantar (1995) is then applied to estimate the biodegradation rate constant for all simulated plumes. To investigate the effects of uncertain source geometry alone, the simulations are repeated for a fully characterized source zone geometry with uncertain transmissivity field, and the variability in the rate constants are compared for the two sets of simulations.

2 SYNTHETIC AQUIFER

2.1 Modeling domain and parameters

The synthetic aquifer developed for this work is a fairly heterogeneous two-dimensional aquifer with 300m length and 160m width. The well configuration and modeling domain associated with the synthetic aquifer is shown in figure 2. The heterogeneous transmissivity field (Figure 3) is created by a single unconditional realization simulated by sequential Gaussian simulation (Deutsch and Journel 1997). Thus, transmissivity is considered as a lognormally distributed random variable with a mean of 1.48 $\times 10^{-5}$ m/s and a standard deviation of 2.1 (in natural logarithmic units). The correlation structure of the heterogeneous field follows a spherical variogram model with a range of 25m and with 5% nugget effect. The statistical properties of the synthetic aquifer are similar to

that of Columbus Air Force Base site (Rehfeldt et. al. 1992) with slight modifications.

As shown in Figure 2, there are a total of 38 monitoring wells at which steady-state hydraulic heads are to be recorded. The configuration of wells is chosen similar to a natural attenuation study site in west-central Alberta with some modification. Transmissivity values are recorded at 14 wells marked in Figure 2. Also shown in Figure 2 is the location of wells deemed inside the source zone. Boundary conditions of the synthetic aguifer include constant head boundary conditions on the north and south boundaries and no-flow boundary conditions on the east and west boundaries. A hydraulic gradient equal to 1% has been imposed to the synthetic aquifer through the constant head boundary conditions on the north and south boundaries. For all simulations, biodegradation rate constant, and longitudinal and transverse dispersivities are set at 0.0031 day⁻¹, 1.0 m and 0.2 m, respectively.



Figure 2. Well configuration and modeling domain associated with the synthetic aquifer

In practical applications, appropriate detection of the centerline of the plume is important when the intention is to use any one of the concentration-versus-distance techniques. In our synthetic contaminated aquifer, we assume that the centerline of the plume starts somewhere in the middle of the source zone with observed non-aqueous-phase-liquid (NAPL) in the observation wells (solid circles in Figure 2). The direction of the centerline of the plume is the same as the direction of groundwater flow in the vicinity of the source zone which is usually detected using a 'hydrogeologic triangle', early in life of a remediation project. Following the same procedure, the presumed centerline of the plume can be

plotted as shown in Figure 2. In practical applications, a number of wells are often installed along the presumed centerline of the plume to record the concentrations for subsequent concentration-versus-distance calculations. There are a total of 6 wells along the centerline of the plume that are used in the calculation of first-order biodegradation rate constant.

In remediation projects associated with petroleum hydrocarbons, distribution of mobile LNAPL (light-nonaqueous-phase-liquid) sitting on top of groundwater table is often delineated by observation wells. A few source removal techniques are available to subsequently reduce the volume of mobile LNAPL in a practical way. After removal of much of mobile LNAPL still there may be a large plume of residual LNAPL in soil in the source zone area. The focus of this work is on contamination of groundwater exposed to residual LNAPL. In this work, we assume that the residual LNAPL concentration in soil is equal to 1127 mg/kg and it is uniformly distributed within the source geometry shown in Figure 2. Due to limited number of sampling points, there is always uncertainty in the source zone geometry. This uncertainty will be addressed in subsequent sections of this work through a distance-function algorithm.

The other important source zone property is NAPL dissolution rate. In general, the dissolution rate of NAPL into groundwater depends on interfacial area between the NAPL and water (Imhoff 1993), aquifer heterogeneity (Mayer and Miller 1996), the size and shape of the NAPL blobs (Powers et al. 1994) and groundwater velocity (Pfannkuch 1984). Thus, if transport processes occur at a high rate relative to the NAPL dissolution rate, aqueous concentration (C_s) may remain lower than NAPL-water

equilibrium concentration ($C_s^{\rm eq}$). This effect can be described mathematically (Parker et al. 1991, Imhoff et al. 1993) by a mass transfer rate coefficient ($k^{\rm NAPL}$), such that the NAPL dissolution into groundwater can be explained by:

$$R^{\text{NAPL}} = \max[0, k^{\text{NAPL}} (C_s^{\text{eq}} - C_s)]$$
^[1]

According to Raoult's law, C_s^{eq} can be calculated as:

$$C_s^{eq} = f_s C_s^{sol}$$
 [2]

where, $\rm f_s$ is the mole fraction of the substrate (e.g. BTEX) in NAPL and $\rm C_s^{sol}$ is solubility of the pure substrate in water. Average BTEX solubility in water and its mole fraction in NAPL are set to 1500 mg/L and 0.26, respectively. The mass transfer rate coefficient ($\rm k^{NAPL}$) has been set to 0.035 day⁻¹ for all simulations (Waddill and Widdowson 1998). The concentration of residual NAPL in soil is also dependent on rate of mass transfer between the soil and groundwater. This rate of change in concentration of residual NAPL in soil may be expressed by:

$$\frac{\mathrm{d}C_{\mathrm{s}}^{\mathrm{NAPL}}}{\mathrm{d}t} = -\frac{\theta_{\mathrm{T}}}{\rho_{\mathrm{b}}} R^{\mathrm{NAPL}}$$
[3]

in which, $C_s^{\rm NAPL}$ is the NAPL mass of substrate per unit mass of dry soil, θ_T is total porosity and ρ_b is the bulk density of porous medium. θ_T and ρ_b are set to 0.35 and 1600 kg/m³, respectively.

2.2 Reactive mass transport simulation

The governing mass-conservation equation for fate and transport of dissolved BTEX in groundwater may be expressed by (Chapelle et al. 2003):

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial x_{i}} \left(\theta D_{ij} \frac{\partial C}{\partial x_{j}} \right) - \frac{\partial}{\partial x_{i}} \left(\theta v_{i} C \right) + \theta R^{\text{NAPL}} + R_{n}$$
 [4]

where, C is dissolved concentration of BTEX, θ is the effective porosity, x_i is the distance along the respective Cartesian coordinate, D_{ij} is the hydrodynamic dispersion coefficient tensor, v_i is pore water velocity, R^{NAPL} is NAPL dissolution term (Equation 1) and R_n is the chemical reaction term. As stated previously, the chemical reaction term is assumed to be a first-order irreversible reaction given by ($-\theta\lambda C$), where λ is the first-order biodegradation rate constant set to 0.0031 day^1.



Figure 3. Synthetic transmissivity field (left) and dissolved BTEX plume in steady – state condition (right)

The partial differential equation describing the reactive transport of dissolved hydrocarbons (Equation 4) is mathematically solved by the method of characteristics (KoniKow and Bredhoef 1978). The method of characteristics (MOC) uses a conventional particle tracking technique for solving the advection term. At the beginning of the simulation, a large number of moving particles are distributed in the flow field with a random or fixed pattern. A concentration and position in the Cartesian coordinate system are associated with each of these particles. Particles are tracked forward through flow field using a small time increment. At the end of each time increment, the average concentration at each cell is evaluated from the concentrations of moving particles which are located within that cell. Changes in cell concentrations due to dispersion, sink/source mixing and

chemical reactions are then simulated by implicit or explicit finite difference method (FDM).

The simulation cells are $1m \times 1m$. This is considerably smaller than the range of spherical variogram (25m) that is used to create the transmissivity field and justifies the use of small dispersivity values (Fernandez-Garcia and Gomez-Hernandez 2007). The method of Bucheck and Alcantar (1995) is based on the solution to onedimensional steady-state transport equation. To reach to a steady-state condition, all transport simulations are run for 7 years. Figure 3 shows the synthetic heterogeneous transmissivity field and associated steady-state dissolved BTEX plume.

2.3 Estimation of biodegradation rate constant

There are several methods to determine the site specific biodegradation rate coefficients (Alvarez and Illman 2006). These methods include mass balances, the technique of Buscheck and Alcantar (1995), normalization of contaminant concentrations to those of a recalcitrant cocontaminant that was present in the initial release, the use of in situ microcosms and direct push tests. The method of Buscheck and Alcantar is based on an analytical solution to one-dimensional, steady-state contaminant transport that considers advection, longitudinal dispersion, sorption and first-order biodegradation:

$$C(x) = C_0 exp\left\{\left(\frac{x}{2\alpha_L}\right) \left[1 - \left(1 + \frac{4\lambda\lambda_L}{v_c}\right)^{1/2}\right]\right\}$$
[5]

where, C(x) is concentration at a distance x downstream of the source, C₀ is the source concentration, α_L is longitudinal dispersivity, and v_c is the contaminant velocity. Buscheck and Alcantar (1995) recognized that contaminant concentrations usually decrease exponentially along the centerline of the plume as a function of distance from the source:

$$C(x) = C_0 exp\left(\frac{-kx}{v}\right)$$
[6]

where k is the decay coefficient, which incorporates biodegradation, dilution, etc. The variable x in Equation 6 represents the distance from the source, and x / v is the time it takes groundwater to travel a distance x. Buscheck and Alcantar (1995) equated Equations [5] and [6] and solved for λ :

$$\lambda = \left(\frac{v_{c}}{4\alpha_{L}}\right) \left\{ \left[1 + 2\alpha_{L}\left(\frac{k}{v}\right)\right]^{2} - 1 \right\}$$
[7]

in which, k/v is the negative of the slope of a line obtained from a log-linear plot of the (centerline) contaminant concentration versus distance downgradient along the flow path. According to Equation 7, determination of λ using this approach requires knowledge of the longitudinal dispersivity (α_L) and contaminant (retarded) velocity (v_c). As stated previously, sorption is considered to be negligible in this work. Also, a reasonable assumption would be to consider that biodegradation occurs solely in aqueous phase. Thus, v_c can be replaced by groundwater seepage velocity (v_{por}). In a real-world application, seepage velocity can be determined based on Darcy's law and by using the measured hydraulic conductivities, effective porosity and observed hydraulic gradient. In this work, hydraulic conductivities have been measured at 16 wells locations (Figure 2).



Figure 4. Determination of k / v by linear regression, to be used in the method of Buscheck and Alcantar

A representative value for hydraulic conductivity can be obtained as geometric average of all hydraulic conductivity measurements, which is equal to 2.77×10^{-5} m/s in this work. Given that hydraulic gradient is equal to 0.01 and the effective porosity is equal to 0.3, the average seepage velocity will be 9.23×10^{-7} m/s. In practice, longitudinal dispersivity is often estimated as 0.1 times the maximum observed plume length. Considering a BTEX concentration value of 0.005 mg/L as the end of the BTEX plume and based on the well configuration displayed in Figure 2, the maximum observed plume length will be 235 m, which gives an estimated value of 23.5 m for α_L . As shown in figure 3, the BTEX concentrations can be measured at six wells in the simulated steady-state plume along the presumed centerline. Figure 4 shows these concentration measurements plotted against the distance from the source. When applied in the synthetic aquifer, the method of Buscheck and Alcantar (1995) results in a biodegradation rate constant equal to 0.0084 day⁻¹ and overestimates the actual known first-order rate used in transport simulations which is 0.0031 day⁻¹. The higher value of the first-order rate constant by the method of Buscheck and Alcantar is largely due to missing the centerline of the plume as well as oversimplifying assumption of 1D transport. These effects have been explained to some extent by Zhang and Heathcote (2003) and Wilson et al. (2004).

So far, we have estimated the first order biodegradation rate constant for the 2D synthetic aquifer while assuming no uncertainty exists in transmissivity filed, head measurements and areal extent of the residual NAPL zone. In the rest of this work, we investigate the uncertainty in the estimated first-order rates as a result of uncertainty in transmissivity field and source geometry.

3 MONTE CARLO SIMULATIONS

In real-world applications, we have access neither to the exhaustive distribution of transmissivity field nor to the true distribution and geometry of residual NAPL source zone. The only data often available are point measurements of hydraulic conductivity (e.g. by slug tests), hydraulic head observations and sparse soil samples in the source area. According to stochastic hydrogeology principles, the available data cannot uniquely characterize the contaminated aquifer. In other words, there are multiple plausible scenarios that jointly honour all available data. In addition to this, we know that hydraulic head measurements always incorporate some level of uncertainty. This uncertainty usually comes into play mostly due to seasonal groundwater table fluctuations. The uncertainty in hydrogeological and source zone properties translate into uncertainty in estimated first-order biodegradation rate constant.

A large number of joint realizations of sourcezone/transmissivity-field have been built by geostatistical techniques to determine the potential uncertainty in the estimated first order rates. The constructed realizations honour all available data and incorporate uncertainty in hydraulic head measurements. Performing Monte Carlo Simulations, fate and transport of dissolved BTEX is then simulated for every joint realization and concentrations are recorded at the locations of six monitoring wells along the presumed centerline of the contaminant plume (Figure 2). Using the method of Buscheck and Alcantar, first-order biodegradation rate constant is then estimated for all realizations and compared to the original value used in simulations.

3.1 Characterizing uncertainty in the transmissivity field

As shown in Figure 2, hydraulic conductivity is measured at 14 locations across the synthetic aquifer. Hydraulic heads are recorded at all 38 wells installed for site investigation. As stated earlier, head measurements always prone to variability due to seasonal are aroundwater fluctuations. Uncertainty in head measurements coupled with the non-uniqueness problem arises from sparse hydraulic conductivity that measurements motivates us to construct multiple realizations for the transmissivity field.

Sequential Gaussian simulation (Deutsch and Journel 1997) is performed using 14 hydraulic conductivity measurements as conditioning data. The correlation structure is defined by a spherical variogram with the range of 25m and with 5% nugget effect. This is the same as the variogram used to construct the synthetic aquifer. The root mean of squared residual errors (RMS) criterion is used to evaluate the goodness of fit to observed hydraulic heads and is given by (Zheng and Bennet 2002):

$$RMS = \left[\frac{1}{N}\sum_{i=1}^{N} (h_i^{cal} - h_i^{obs})^2\right]^{1/2}$$
[8]

where, h_i^{cal} and h_i^{obs} are calculated and observed hydraulic heads, and N is the number of head observations. It is assumed that all 38 head observations are uncertain and the distribution of errors is normal with a mean of zero and a standard deviation of 0.1 m. Thus, the calculated RMS should be less than 0.1 m for every geostatistical realization to be accepted and used in subsequent simulations. To accomplish this, 4000 realizations of transmissivity field were generated and flow simulated; and ultimately 100 realizations with RMS < 0.1 m were selected for subsequent MCS.

3.2 Characterizing the uncertainty in source geometry

The model of uncertainty for the geometry of the residual NAPL source is constructed by the distance function (DF) approach. Details of the DF approach and its application in modeling the distribution of residual NAPL is discussed in Hosseini et al. (2008). In this work, we only apply the methodology to model the uncertainty in areal limits of the source zone.

First, initial coding of the available sample data in terms of being 'inside' or 'outside' the source zone is implemented and DF values are calculated (Figure 5). It should be noted that the area shown in Figure 5 is the suspected source zone area in the synthetic aquifer shown in Figure 2.



Figure 5. Coding the well locations and calculating DF values for wells inside and outside of the source zone

An interpolation technique is employed to define the boundary interface in the presence of sparse sample data. As discussed in Hosseini et al. (2008), a data value dependent inverse distance approach is used for this purpose:

$$Z_{\text{ID}}^{*}(\boldsymbol{u}_{0}) = \sum_{i=1}^{N} \alpha^{\frac{Z(\boldsymbol{u}_{i})}{|Z(\boldsymbol{u}_{i})|}} \cdot \lambda_{\text{ID}}(\boldsymbol{u}_{i}) \cdot \left[Z(\boldsymbol{u}_{i}) + \beta \cdot \frac{Z(\boldsymbol{u}_{i})}{|Z(\boldsymbol{u}_{i})|} \right]$$
[9]

where, α and β are scaling and separation factors, respectively. $Z(u_i)$ represents the DF value at sampling location u_i , N is the number of data points used in interpolation, and $\lambda_{\rm ID}(u_i)$ is inverse distance weight calculated by:

$$\lambda_{\rm ID}(u_{\rm i}) = \frac{\frac{1}{(d(u_{\rm i}))^{\circ} + c}}{\sum_{j=1}^{N} \frac{1}{(d(u_{\rm j}))^{\circ} + c}}$$
[10]

where, $d(u_i)$ is the Euclidian distance between the estimation location u_0 and $Z(u_i)$ sample data, ω is distance exponent (set to 1.5) and c is a small constant.

The scaling and separation factors α and β control the centerline and width of an 'uncertainty band' conditioned to the calculated set of DF values. For a given well arrangement, an 'uncertainty band' is defined as a probabilistic areal interval that includes the actual boundary which is unknown. The α and β values are calibrated against a large number of synthetic plumes using the following objective function:

$$S(\alpha,\beta,R) = \sum_{j=q_1}^{q_M} \left[P_j - P_j^*(\alpha,\beta,R) \right]^2$$
[11]

where, P, represents the true probabilities corresponding to quantiles q_1, \dots, q_M used in optimization. The calculated probabilities $P_i^*(\alpha,\beta,R)$ are defined as the proportion of synthetic plumes (R) whose areas completely fall inside the $q_1,...,q_M$ quantile maps. These quantile maps are derived from the conditional cumulative distribution function (CCDF) of an uncertainty band calculated for some α and β values. A downhill simplex optimization algorithm is then adapted to minimize the objective function given in [11] and to calibrate the values of α and β . As a result, in this study, the calibrated values of α and β are determined to be 1.441 and 21.1, respectively. Figure 6 shows the calibrated uncertainty band and corresponding p10, p50 and p90 maps. A total of 100 equi-probabale realizations of source geometry are drawn from the uncertainty band shown in Figure 6 to be used in subsequent MCS.

3.3 Uncertainty in estimated first-order rate constant

As explained earlier, uncertainty in the transmissivity field of the heterogeneous aquifer and the source zone geometry results in uncertainty in the estimated first-order biodegradation rate constant. To investigate this uncertainty, we generated 100 realizations of the hydraulic conductivity field and 100 realizations of the source zone geometry. These realizations are then randomly combined to create 100 joint sourcetransmissivity realizations. Then, in a Monte Carlo Simulation framework, contaminant transport simulations are implemented for the realizations and the first-order biodegradation rate constant is estimated by the method of Buscheck and Alcantar (1995). Except for the transmissivity distribution and source geometry, all other parameters remain the same as the parameters used for the synthetic aquifer.

Figure 7 shows the histogram of the estimated firstorder biodegradation rate constants, where the transmissivity field, hydraulic head observations and source zone geometry are uncertain. It can be observed that for heterogeneous aquifers, even when there is no uncertainty in head observations (Figure 7 – synthetic aquifer), the method of Buscheck and Alcantar considerably overestimates the true biodegradation rate constant, in this instance by 171%. According to Figure 7, the estimated first-order biodegradation rate constant for the synthetic aquifer is 0.0084 day⁻¹, while the prespecified value is 0.0031 day⁻¹. This overestimation is largely due to missing the centerline of the plume by the observation wells.



Figure 6. Calibrated uncertainty band (top-left) and p90 (top-right), p50 (bottom-left), and p10 (bottom-right) maps.

The situation becomes even worse when there is uncertainty in head observations (Figure 7 – MCS). In this case the first-order biodegradation rate constant can easily be over-estimated by one order of magnitude or more. In this case the mean estimated first-order rate will be 0.0289 day⁻¹ which is one order of magnitude higher than the pre-specified value being 0.0031 day⁻¹ that was used in the simulations.

The histogram of the estimated first-order rate under uncertain transmissivity field and head observation is shown in Figure 8. Comparing Figures 7 and 8, we observe that uncertainty in geometry of the source zone appears to have a minor impact on the distribution of estimated first-order rate. In this case, the mean estimated first-order rate constant is 0.0288 day⁻¹. The variability in this case is slightly lower as it could be expected. The coefficient of variation for the case 2 (no uncertainty in source geometry) is 0.4303 whereas that for case 1 is 0.4433.



Figure 7. Histogram of estimated biodegradation rate constants under uncertain transmissivity distribution, hydraulic head observations and source zone geometry



Figure 8. Histogram of estimated biodegradation rate constant under uncertain transmissivity field and hydraulic head observations

4 CONCLUSIONS

The method of Buscheck and Alcantar (1995) is a widely used field technique for estimation of first-order biodegradation rate constant based on the measured field data. Uncertainty in the first-order constant estimated by the method of Buscheck and Alcantar was investigated using a synthetic heterogeneous aquifer with known properties. It was initially assumed that there is no uncertainty in the head observations and source geometry. Under this condition, the method of Buscheck and Alcantar was used to estimate the first-order rate

constant. The estimated value considerably overestimated the true value by 171%.

To investigate the performance of the Buscheck and Alcantar methodology under uncertain head observations, it was assumed that head observations are uncertain and the unknown errors are normally distributed with a mean of zero and standard deviation of 10 cm. One hundred realizations of the transmissivity field were then generated conditioned to a number of transmissivity measurements. For all realizations the root mean squared error was smaller than the standard deviation of observation errors. The realizations of the transmissivity field were then combined with the realizations of source geometry to create 100 joint transmissivity-source geometry realizations. Then, the transport of dissolved BTEX was simulated for all joint realizations in a Monte Carlo Simulation framework, and first-order rate constant was estimated using the Buscheck and Alcantar approach. The results show that uncertainty in head observations can result in overestimation of the first-order rate by more than one order of magnitude. The results also show that, for the given hydrogeological setting, uncertainty in the geometry of the source zone does not play an important role in propagation of uncertainty in the estimated first-order rate. However, this may not be the more general case. Further investigation should be carried out to study the effect of uncertain source geometry on the first order rate in more stagnant aquifers.

AKNOWLEDGEMENT

The first author would like to acknowledge the Alberta Ingenuity Fund for providing support for this research.

REFERENCES

- Alvarez, P. J. J., and Illman, W.A. 2006: *Bioremediation* and Natural Attenuation: Process Fundamentals and Mathematical Models. John Wiley & Sons, 609 pp.
- Bauer, S., Beyer, C. and Kolditz, O. 2006: Assessing measurement uncertainty of first order degradation rates in heterogeneous aquifers. *Water Resources. Research*, 42(1): W01420.
- Bekins, B., Rittmenn, B.E. and MacDonald, J.A. 2001. Natural Attenuation: a groundwater remediation strategy based on demonstrating cause and effect. *EOS, Transactions, AGU* 82, 53-58.
- Buscheck, T.E. and Alcantar, C.M. 1995. Regression techniques and analytical solutions to demonstrate intrinsic bioremediation. *Proc. of 1995 Battelle Int. Conference on In Situ and On Site Bioreclamation*, San Diego, CA. Battelle Press, Columbus, OH.
- Chapelle, F.H., Bradley, P., Lovely, D.R. and Vroblesky, D.A. 1996: Measuring rates of biodegradation in a contaminated aquifer using field and laboratory methods. *Ground Water* 34, 691-698.
- Chapelle, F.H., Widdowson, M.A., Brauner, J.S., Mendez, E. and Casey, C.C. 2003. Methodology for estimating Times of Remediation Associated with Monitored Natural Attenuation. *Water-Resources Investigations Report 034057*, US Geological Survey, Columbia, SC.

- Chiang, C.Y., Salanitro, J.P., Chai, E.Y., Colthart, J.D. and Klein, C.L. 1989. Aerobic biodegradation of benzene, toluene, and xylene in a sandy aquifer: data anal. and comp. modeling. *Groundwater*. 27, 823-834.
- Deutsch, C.V. and Journel, A.G. 1997. *GSLIB: Geostatistical Software Library and User's Guide*, Oxford University Press, New York, NY, 396 pp.
- Hosseini, A.H., Deutsch, C.V. Biggar, K.W. and Mendoza, C.A. 2008. Uncertainty in spatial distribution of residual NAPL and its downstream impacts. 61th Annual Canadian Geotechnical Conf. and 9th Joint CGS/IAH-CNC Conference, September 21 - 24, Edmonton, AB, Canada.
- Imhoff, P.T., Jaffe, P.R. and Pinder, G.F. 1993. An experimental study of complete dissolution of a nonaqueous phase liquid in saturated porous media. *Water Resources Research*, 30(2): 307 - 320.
- Mayer, A.S. and Miller, C.T. 1996. The influence of mass transfer characteristics and porous media heterogeneity on nonaqueous phase dissolution. *Water Resources Research*, 32(6): 1551 1567.
- Pfannkuch, H.O. 1984. Determination of contaminant source strength from mass exchange processes at the petroleum-ground-water interface in shallow aquifer systems. *Proc. NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Groundwater*, NWWA, 5-7 Nov, Worthington, Ohio.
- Powers, S.E. Abriola, L.M. and Weber, W.J. 1994. An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: Transient mass transfer rates. *Water Res. Res.*, 30(2), 321-332.
- Rehfeldt, K.R., Boggs, J.M. and Gelhar, L.W. 1992. Field study of dispersion in a heterogeneous aquifer: 3. Geostatistical analysis of hydraulic conductivity, *Water Resources Research*, 28(12): 3309 - 3324.
- Rifai, H. S., Newell, C.J. Gonzales, J.R. Dendrou, S. Kennedy, L. and Wilson, J.T. 1997. Bioplume III Natural Attenuation Decision Support System, version 1.0, *user's manual*. EPA/600/R-98/010.
- Rifai, H.S., and Rittaler, T. 2005. Modeling natural attenuation of benzene with analytical and numerical models. *Biodegradation*, 16, 291-304.
- Wiedemeier, T. H., Rifai, H.S., Newell, C.J. and Wilson, J.T. 1999. *Natural Attenuation of Fuel Hydrocarbons and Chlorinated Solvents in the Subsurface*. John Wiley & Sons, Hoboken, N.J.
- Wilson, R.D., Thornton, S.F. and Mackay, D.M. 2004. Challenges in monitoring the natural attenuation of spatially variable plumes. *Biodegradation*, 15: 359-369.
- Zhang, Y.K., and Heathcote, R.C. 2003. An improved method for estimation of biodegradation rate with field data. *Groundwater Mon. & Remed*, 23, 112-116.
- Zheng, C. 1990. *MT3D: A Modular, 3D Transport Model* for Simulation of Advection, Dispersion and Chemical Reactions of Contaminants in Groundwater Systems. Report to the U.S. EPA, Ada, OK, 170 pp.
- Zheng, C., Bennett, G.D. 1995. *Applied Contaminant Transport Modeling: Theory and Practice.* Van Nostrand Reinhold Pub., New York, 440 pp.