Uncertainty in Estimated Natural Attenuation Rate due to Uncertainty in Pressure Head Measurement

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Site-specific natural attenuation capacity of contaminated aquifers has a great importance in management of contaminated sites associated with upstream oil and gas industry. The biodegradation rate constant of organic contaminants is particularly important for decision making purposes. 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 source geometry. This study attempts to quantify the resulting uncertainty in the rate constants. First, a synthetic aquifer with known hydrogeological and transport properties is created and transport of dissolved contaminant (BTEX) is simulated across the site. The first-order biodegradation rate constant is then estimated using the method of Buscheck and Alcantar and compared to the known value used in the transport simulation to evaluate the effect of heterogeneity of aquifer on estimation of the rate constant. Next, uncertainty in head measurement and its effect on the estimation is investigated. For this purpose, multiple realizations of transmissivity field are generated conditioned to a number of hydraulic conductivity measurements and hydraulic head observations. These realizations are then combined with realizations of source geometry obtained by a boundary modeling approach to create multiple joint realizations of transmissivity and source geometry. In a Monte Carlo simulation framework, the transport of dissolved contaminant for all joint realizations is simulated and the first-order biodegradation rate is estimated by the method of Buscheck and Alcantar. The results 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 is the other important factor. In the latter case, the applied field approach may overestimate the first order rate by more than one order of magnitude, depending on the level of uncertainty in pressure measurements.

Introduction

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.

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 multi-component interactions (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,

Figure-1: Conceptual illustration of important natural attenuation processes that affect the fate of petroleum hydrocarbons in aquifers

which can be determined using the 'concentration versus distance' techniques (Wiedemeier 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
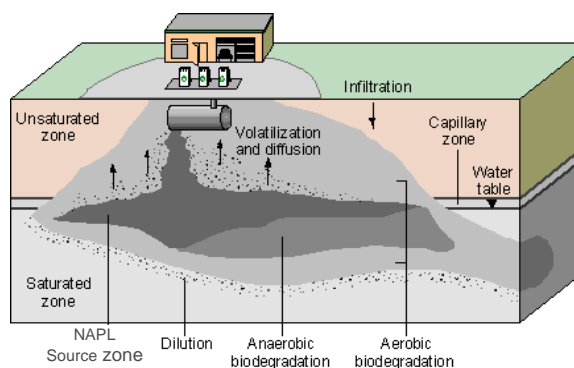
then calculated by matching the first-order curve to the observed concentrations. The method of Buscheck and Alcantar (1995) is a concentration – distance approach commonly used in practice. It is based on the steady-state solution for a 1D transport equation, incorporating advection, longitudinal dispersion 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.

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).

To evaluate the performance of the method of Buscheck and Alcantar (1995) in heterogeneous aquifers, a synthetic aquifer 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 real-world 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.

Modeling domain and input 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 log-normally distributed random variable with a mean of 1.48×10^{-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 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
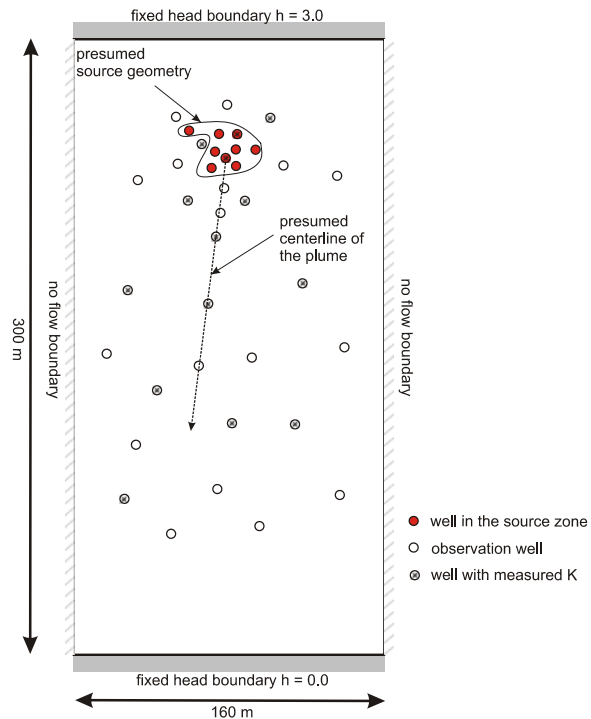

Figure-2: Well configuration and modeling domain associated with the synthetic aquifer

aquifer 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.

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-non-aqueous-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, aquifer heterogeneity, the size and shape of the NAPL blobs and groundwater velocity. Thus, if transport processes occur at a high rate relative to the NAPL dissolution rate, aqueous concentration may remain lower than NAPL-water equilibrium concentration. This effect can be described mathematically (Imhoff et al. 1993) by a mass transfer rate coefficient (k^{NAPL}), such that the NAPL dissolution into groundwater can be explained by:

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

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

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

where, f_s is the mole fraction of the substrate (e.g. BTEX) in NAPL and 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 (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:

$$\frac{dC_s^{NAPL}}{dt} = -\frac{\theta_T}{\rho_b} R^{NAPL} \qquad [3]$$

in which, C_s^{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.

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):

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(\theta v_i C) + \theta R^{NAPL} + R_n \qquad [4]$$

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}.
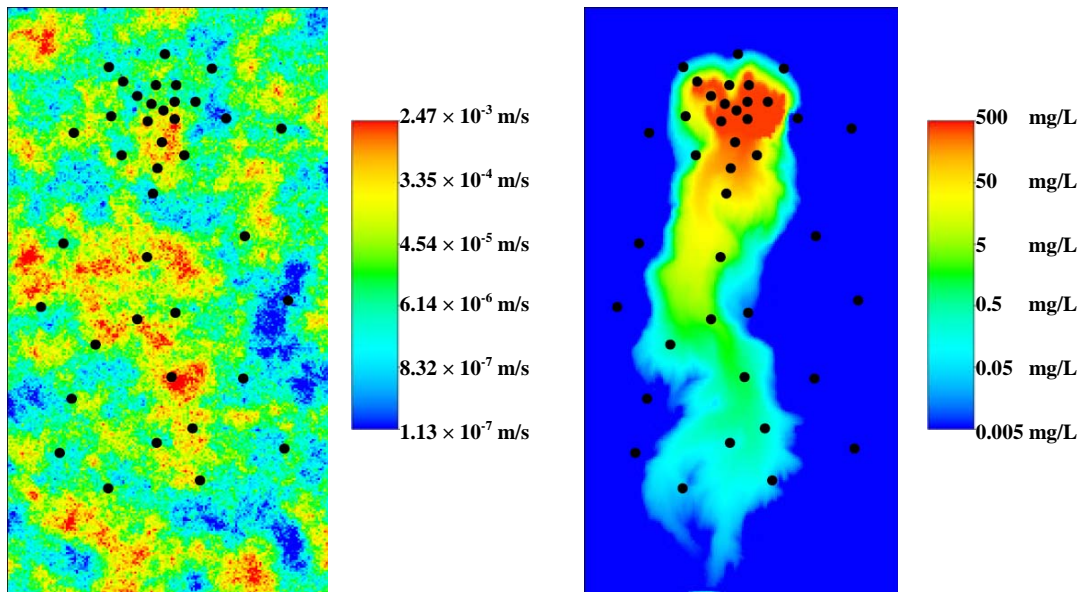

Figure-3: Synthetic transmissivity field (left); the dissolved BTEX plume in steady-state condition (right).

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) and a GSLIB-like program snasim was prepared and tested for this purpose (Appendix A). 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 × 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 Buscheck and Alcantar (1995) is based on the solution to one-dimensional 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.

Estimation of biodegradation rate constant

There are several methods to determine the site specific biodegradation rate coefficients. 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:

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

where, $C(x)$ is concentration at a distance x downstream of the source, C_0 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:

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

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:

$$\lambda = \left(\frac{v_c}{4\alpha_L}\right) \left\{ \left[1 + 2\alpha_L \left(\frac{k}{v}\right) \right]^2 - 1 \right\} \quad [7]$$

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).
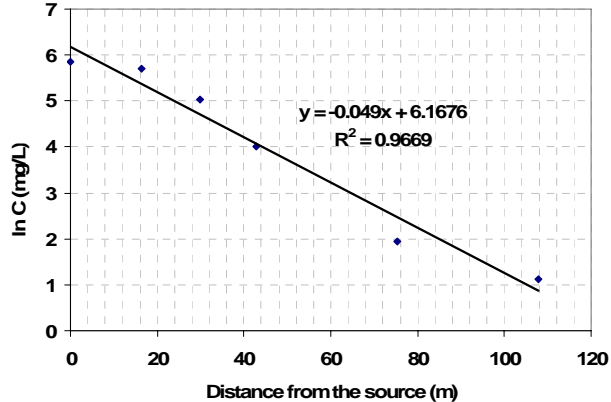

Figure-4: Determination of k / v by linear regression, to be used in the method of Buscheck and Alcantar

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. Longitudinal dispersivity is often estimated as 0.1 of the maximum observed plume length. The maximum observed plume length is 235 m, giving 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. 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, pressure head measurement and source geometry.

Characterizing the Uncertainty in transmissivity field

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), pressure 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 as well as measurement errors.

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 are always prone to variability due to seasonal groundwater fluctuations. Uncertainty in head measurements coupled with the non-uniqueness problem that arises from sparse hydraulic conductivity 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 pressure heads and is given by:

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

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. An inefficient way of performing this is by an acceptance/rejection algorithm for a large number of SGS realizations. About 4000 realizations would be needed to be flow simulated and accepted or rejected based on their fit to the observation data. The most efficient way to accomplish this is to condition the generated SGS transmissivity fields to uncertain head data using an inverse modeling approach such as Sequential Self-Calibrated (SSC) approach (Gomez-Hernandez et l. 1997, Wen et al. 1999). The uncertainty in head data is accounted for by setting the weights in the objective function equal to inverse of standard deviation of error, which has been set to 10 cm for all observation wells. In this way, 100 realizations with RMS < 0.1 m can be obtained that honor both static data (point transmissivity measurements) and dynamic data (pressure head observations with their uncertainty).

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. 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:

$$Z_{ID}^*(u_0) = \sum_{i=1}^{N} \alpha^{\frac{Z(u_i)}{|Z(u_i)|}} \cdot \lambda_{ID}(u_i) \cdot \left[Z(u_i) + \beta \cdot \frac{Z(u_i)}{|Z(u_i)|} \right] \qquad [9]$$

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 $\lambda_{ID}(u_i)$ is the weight calculated by:

$$\lambda_{ID}(u_i) = \frac{\dfrac{1}{(d(u_i))^\omega + c}}{\displaystyle\sum_{j=1}^{N} \dfrac{1}{(d(u_j))^\omega + c}} \qquad [10]$$

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:

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

where, P_j represents the true probabilities corresponding to quantiles $q_1, ..., q_M$ used in optimization. The calculated probabilities $P_j^*(\alpha, \beta, R)$ 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.
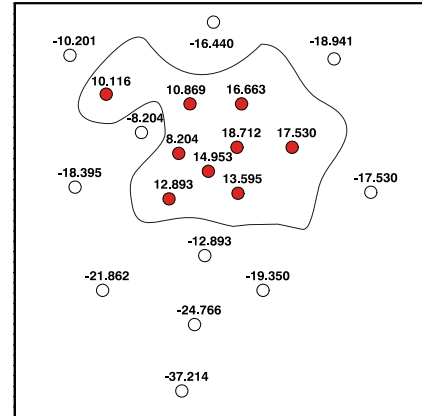

Figure-5: Coding the well locations and calculating DF values

Uncertainty in estimated first-order rate constant

Uncertainty in the transmissivity field and pressure head measurement of the heterogeneous aquifer, as well as uncertainty in the source zone geometry results translate into 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 source-transmissivity 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 (corresponding to a presumed measurement error in the observed pressure heads) 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 first-order 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 pre-specified value is 0.0031 day^{-1}. This overestimation is largely due to missing the centerline of the plume by the observation wells.

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.

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 over-estimated 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
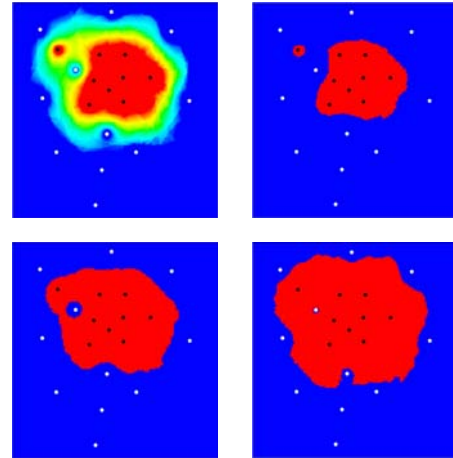

Figure-6: Calibrated uncertainty band (top-left) and p$_{90}$, (top-right), p$_{50}$ (bottom-left), and p$_{10}$ (bottom-right) maps.
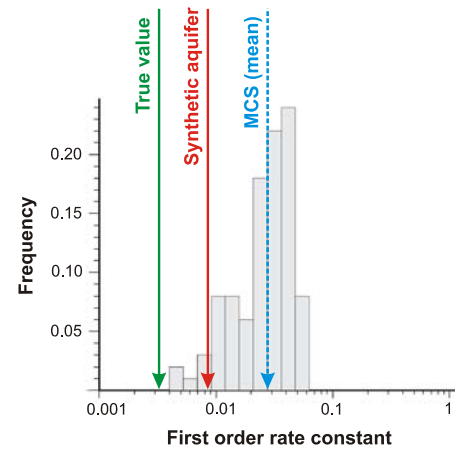

Figure-7: Histogram of estimated rate constants under uncertain transmissivity, pressure head and source zone geometry
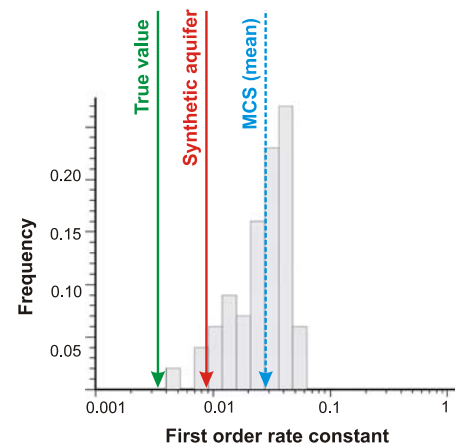

Figure-8: Histogram of estimated rate constants under uncertain transmissivity and pressure head

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.

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Appendix A: Parameter file for snasim

Below is the parameter file for the GSLIB-like program snasim, which can be used to simulate the 2D reactive mass transport (advection, dispersion, reaction) of a dissolved species in both steady-state and transient flow field condition. It accepts uncertain input for source geometry and concentration, and transmissivity field. Both dissolution rate coefficient and biodegradation rate constant can be drawn from uniform or log-normal distributions or be pre-specified.

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                    Parameters for SNASIM
                    *********************

START OF PARAMETERS:
../data/initial.dat              -file with initial condition
3                                -   column for solute conc(gr/cm3)
../data/source.dat               -file with source zone distribution
3                                -   column for NAPL conc(gr/gr)
-1.0e21   1.0e21                 -   trimming limits
1.6       0.35                   -dry soil density(gr/cm3),total porosity
0.00178   0.01                   -substrate solubility(gr/cm3),mass fraction
78.1      101.56                 -substrate,tracer molecular weight(gr/mole)
1                                -dissolution rate (0=specified,1=random)
0                                -   dissolution rate constant(specified)
0                                -   rate distribution (0=uniform,1=Gaussian)
0.01    0.05                     -   min,max (or mean and s.d. for Gaussian)
../data/Kxy.dat                  -file with transmissivity data
3                                -   column for Txy
0.3                              -effective porosity
../data/heads.out                -file with calculated heads
1                                -   column for calculated head
../data/FBC.dat                  -file with flow boundary condition
1   2                            -   columns for ID and head/flux
../data/TBC.dat                  -file with transport boundary condition
1   2                            -   columns for ID and TBC
30      0.5      1.0             -nx,xmn,xsiz
30      0.5      1.0             -ny,ymn,ysiz
2                                -simulation mode
0       12                       -lower and higher no of random cell particles
67097                            -   random number seed
-1.0e5                           -relative cell concentration gradient
4       24                       -minimum and maximum no of particles
1.0                              -grid courant number
3.0     0.6                      -longitudinal and transverse dispersivity(m)
1                                -biodegradation rate (0=specified,1=random)
0.0025                           -   biodegradation rate constant(specified)
0                                -   rate distribution (0=uniform,1=lognormal)
0.001  0.005                     -   min,max (or mean and s.d. for lognormal)
365    3650                      -number of time steps, simulation time(days)
4                                -number of output events
37    73    183    365           -   time steps
snasim.dbg                       -file for debugging output
1                                -   debugging level
snasim.out                       -file for output concentrations
sns-source.out                   -output file for source concentrations


simulation mode:
1 = source dissolution + advection + biodegradation
2 = source dissolution + advection + dispersion + biodegaradtion
3 = source dissolution + advection + dispersion
```