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Bootstrap estimation of the mass transfer coefficient of a dissolving nonaqueous phase liquid pool in porous media

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[1] A new method for confidence interval estimation of mass transfer coefficients suitable for dissolving dense nonaqueous phase liquid pools in homogeneous, water-saturated porous media is developed. The method is based on the bootstrap resampling technique in conjunction with a least squares regression procedure. The method is successfully applied to experimental data collected from bench scale trichloroethylene pool dissolution experiments. *INDEX TERMS:* 1829 Hydrology: Groundwater hydrology; 1831 Hydrology: Groundwater quality; 1832 Hydrology: Groundwater transport; *KEYWORDS:* NAPL pool dissolution, mass transfer coefficient, bootstrap, estimation, contaminant transport

1. Introduction

[2] Contamination of subsurface formations by nonaqueous phase liquids (NAPLs) originating from industrial and commercial activities is currently recognized as an important worldwide problem. There is a relatively large body of available literature on the migration of NAPLs and dissolution of residual blobs [*Keller et al.*, 1997; *Jia et al.*, 1999; *Brusseau et al.*, 2000; *Nambi and Powers*, 2000; *Saba and Illangasekare*, 2000; *Zhou et al.*, 2000; *Zhu and Sykes*, 2000], as well as dissolution of NAPL pools [*Anderson et al.*, 1992; *Chrysikopoulos et al.*, 1994; *Lee and Chrysikopoulos*, 1995, 1998; *Mason and Kueper*, 1996; *Seagren et al.*, 1999; *Leij and van Genuchten*, 2000; *Tatalovich et al.*, 2000]. Numerous theoretically and experimentally derived mass transfer relationships, expressed in terms of nondimensional parameters, for the dissolution of residual NAPL blobs with simple geometries are also presented in the literature [e.g., *Imhoff et al.*, 1994; *Khachikian and Harmon*, 2000]. Further more, several theoretical as well as experimental mass transfer correlations applicable to NAPL pool dissolution in water-saturated porous media have been developed recently [*Kim and Chrysikopoulos*, 1999; *Chrysikopoulos and Kim*, 2000; *Lee*, 1999].

[3] The dissolution of NAPL pools in porous media is fundamentally different from that of residual blobs. Mass transfer coefficients for NAPL pools are not easily determined with precision because they may vary with location at the NAPL-water interface. For unsteady flow conditions, mass transfer coefficients exhibit temporal dependence due to changes of the contaminated aqueous phase plume thickness above the NAPL pool [*Chrysikopoulos and Lee*, 1998], rendering local mass transfer coefficients to be case specific. Furthermore, in heterogeneous formations the average mass transfer coefficient increases with increasing variability in the hydraulic conductivity, leading to enhanced NAPL pool dissolution [*Vogler and Chrysikopoulos*, 2001]. For simplicity, mathematical models for contaminant transport originating from NAPL pool dissolution often employ average and time invariant mass transfer coefficients which are representative of the entire pool [*Holman and Javandel*, 1996].

[4] In this work, experimental data from a unique set of trichloroethylene (TCE) pool dissolution experiments conducted by *Chrysikopoulos et al.* [2000] and *Lee* [1999] are employed for the development of a reliable methodology for confidence interval estimation of mass transfer coefficients. The estimation methodology involves a statistical tool known as "bootstrap" that involves resampling of the experimental data with replacement and a least squares optimization method.

2. NAPL Pool Dissolution and Contaminant Transport

[5] The mass flux from a NAPL-water interface into the aqueous interstitial fluid within a three-dimensional, saturated porous formation is described by the following relationship [*Chrysikopoulos*, 1995]:

$$-\mathcal{D}_e \frac{\partial C(t,x,y,z)}{\partial z}\bigg|_{z\to 0} = k(t,x,y)[C_s - C(t,x,y,\infty)], \qquad (1)$$

where $C(t, x, y, z)$ is the aqueous phase solute concentration [M/L^3]; x, y, and z are the spatial coordinates in the longitudinal, transverse, and vertical (perpendicular to the NAPL-water interface) directions, respectively [L]; t is time [t]; $\mathcal{D}_e = \mathcal{D}/\tau^*$ is the effective molecular diffusion coefficient [L^2/t] (where $\mathcal{D}$ is the molecular diffusion coefficient [L^2/t] and $\tau^* \geq 1$ is the tortuosity coefficient [-]); $k(t, x, y)$ is the local mass transfer coefficient dependent on time and location at the NAPL-water interface [L/t]; and C_s is the aqueous saturation (solubility) concentration of the NAPL at the interface [M/L^3]. Conventionally, any location above the concentration boundary layer is considered as $z \to \infty$. For the case where the background concentration is constant with respect to time and space, for notational convenience, $C(t, x, y, \infty)$ is replaced by C_b, the constant background aqueous phase concentration. It should be noted that in this study the free stream concentration is assumed to be zero ($C_b = 0$). The left-hand term in (1) represents a diffusive flux given by Fick's law, whereas the right-hand side represents a convective mass transfer flux. The mass transfer

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relationship (1) implies that the dissolution at the NAPL-water interface is fast. Therefore the aqueous phase solute concentration is limited only by mass transfer. The concentration along the interface is assumed constant and equal to the saturation concentration, $C(t, x, y, 0) = C_s$.

[6] In view of (1), the time- and space-dependent local mass transfer coefficient is given by

$$k(t,x,y) = \frac{-\mathcal{D}_e}{C_s} \frac{\partial C(t,x,y,z)}{\partial z}\bigg|_{z\to 0}. \tag{2}$$

Furthermore, the average mass transfer coefficient, applicable to the entire pool, can be expressed as [*Incropera and DeWitt*, 1996, p. 285]

$$\bar{k}(t) = \frac{1}{A}\int\limits_A k(t,x,y)\mathrm{d}^2\mathrm{A}, \tag{3}$$

where A is the surface area of the NAPL pool [L^2] and $\mathrm{d}^2\mathbf{A}$ is a differential surface area. At steady state physicochemical and hydrodynamic conditions, the local mass transfer coefficient is independent of time. In this work, it is assumed that at steady state conditions the average mass transfer coefficient is equal to the corresponding time invariant, average mass transfer coefficient

$$k^* = \bar{k}(t). \tag{4}$$

[7] The transient contaminant transport from a dissolving DNAPL circular pool in a water-saturated, three-dimensional, homogeneous porous medium under steady state uniform flow, assuming that the dissolved organic sorption is linear and instantaneous, is governed by

$$\begin{aligned} R\frac{\partial C(t,x,y,z)}{\partial t} &= D_x\frac{\partial^2 C(t,x,y,z)}{\partial x^2} + D_y\frac{\partial^2 C(t,x,y,z)}{\partial y^2} \\ &\quad + D_z\frac{\partial^2 C(t,x,y,z)}{\partial z^2} - U_x\frac{\partial C(t,x,y,z)}{\partial x} \\ &\quad - \lambda RC(t,x,y,z), \end{aligned} \tag{5}$$

where R is the retardation factor [-] and λ is a first-order decay constant [1/t]. Assuming that NAPL pool dissolution is described by (1), the appropriate initial and boundary conditions for this system are

$$C(0,x,y,z) = 0, \tag{6}$$

$$C(t,\pm\infty,y,z) = 0, \tag{7}$$

$$C(t,x,\pm\infty,z) = 0, \tag{8}$$

$$\mathcal{D}_e\frac{\partial C(t,x,y,0)}{\partial z} = \begin{cases} -k(t,x,y)C_s & (x-\ell_{x_o})^2 + (y-\ell_{x_o})^2 \le r^2, \\ 0 & \text{otherwise}, \end{cases} \tag{9}$$

$$C(t,x,y,\infty) = 0, \tag{10}$$

where ℓ_{x_o} and ℓ_{y_o} indicate the x and y Cartesian coordinates of the pool origin, respectively [L]; and r is the pool radius [L]. It should be noted that the decay term λRC in the governing equation (5) indicates that the total concentration (aqueous plus sorbed solute mass) disappears due to possible decay or biological/chemical degradation.

[8] The analytical solution to the governing partial differential equation (5) subject to conditions (6)–(10) has been derived by *Chrysikopoulos* [1995] as follows:

$$\begin{aligned} C(t,x,y,z) = \frac{C_s k^*}{2\pi\mathcal{D}_e}\int\limits_0^t\int\limits_{\mu_1}^{\mu_2}\left(\frac{D_z}{R\tau}\right)^{1/2}\exp\left[-\lambda\tau - \frac{Rz^2}{4D_z\tau}\right] \\ \times\exp\left[-\mu^2\right]\left(\mathrm{erf}[n_2] - \mathrm{erf}[n_1]\right)d\mu\,d\tau, \end{aligned} \tag{11}$$

where

$$\mu_1 = \left(y - \ell_{y_o} + r\right)\left(\frac{R}{4D_y\tau}\right)^{1/2}, \tag{12}$$

$$\mu_2 = \left(y - \ell_{y_o} - r\right)\left(\frac{R}{4D_y\tau}\right)^{1/2}, \tag{13}$$

$$n_1 = \left\{x - \frac{U_x\tau}{R} - \ell_{x_o} + \left[r^2 - \left(v - \ell_{y_o}\right)^2\right]^{1/2}\right\}\left(\frac{R}{4D_x\tau}\right)^{1/2}, \tag{14}$$

$$n_2 = \left\{x - \frac{U_x\tau}{R} - \ell_{x_o} - \left[r^2 - \left(v - \ell_{y_o}\right)^2\right]^{1/2}\right\}\left(\frac{R}{4D_x\tau}\right)^{1/2}, \tag{15}$$

$$v = y - \mu\left(\frac{4D_y\tau}{R}\right)^{1/2}, \tag{16}$$

where μ and τ are dummy integration variables. Note that in view of (1) it is evident that the analytical solution (11) can also be employed for cases of finite but constant free stream concentration ($C_b = \text{const} \neq 0$) by replacing C_s by $C_s - C_b$.

3. Resampling and Parameter Estimation

[9] The basic idea of interval estimation is intuitively simple, but its application can lead to considerable difficulties. For models that are linear with respect to the parameters, there are several methods available for exact confidence interval estimation, that is, intervals which maintain nominal coverage probability. However, for nonlinear models the most widely used techniques for interval estimation are linearization methods. Such methods assume that the nonlinear model may be approximated by a linear function throughout the section covered by the confidence interval. Consequently, linearization methods provide only approximate confidence intervals which quite frequently are very poor; that is, they underestimate nominal coverage probability [*Donaldson and Schnabel*, 1987]. On the other hand, nonlinear intervals constructed by resampling methods are also approximate but have proven to be accurate [*Duncan*, 1978].

[10] There are several resampling techniques available for dependable construction of confidence intervals. The jackknife, cross-validation, balanced repeated-replication, and bootstrap are conceptually similar and computationally intensive statistical methods that require very little modelling effort [*Diaconis and Efron*, 1983]. Each of these methods generates numerous artificial data sets from the original experimental data and evaluates of a statistical property of interest from its observed

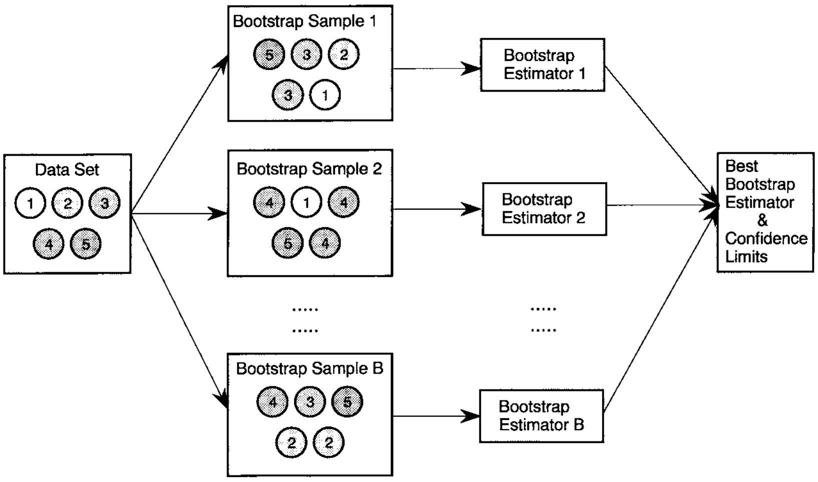

Figure 1. Illustrative example of the bootstrap method for a set of five data points and *B* bootstrap replications.

variability over all of the generated artificial data sets. A major advantage of a resampling technique is that the error in the experimental data does not necessarily have to be homoscedastic or normally distributed. Among the available resampling techniques available, bootstrap is considered more efficient for confidence interval estimation [*Efron and Tibshirani*, 1993]. Consequently, in this work only the bootstrap resampling technique is employed.

3.1. The Bootstrap

[11] Since the bootstrap estimator was introduced by *Efron* [1979], the literature on the bootstrap method has grown rapidly [e.g., *Efron and Tibshirani*, 1993; *Chernick*, 1999; *Politis et al.*, 1999]. The concept of the bootstrap is conceptually simple, and its theoretical foundations are described elsewhere [*Efron*, 1982]. The method is outlined in just a few steps. Consider a data set composed of m observations. Select a random sample with replacement of size m from the original data set. This random resample or bootstrap sample may contain a certain observation more than once. Using the random resample, obtain a bootstarp vector of estimated model parameters $\hat{\mathbf{b}}$, by some parametric or nonparametric procedure. Repeat the resampling process a large number of times B and keep a record of the bootstrap parameter estimates $\hat{\mathbf{b}}_i$, where subscript i denotes bootstrap iteration ($1 \leq i \leq B$). The mean of multiple bootstrap estimated model parameters is the "best" bootstrap vector of parameter estimates [*Efron*, 1982]

$$\hat{\mathbf{b}}_\beta = \sum_{i=1}^{B} \frac{\hat{\mathbf{b}}_i}{B}, \tag{17}$$

and the standard error is the square root of the sample variance of bootstrapped parameter values

$$\hat{\sigma}_\beta = \left[\sum_{i=1}^{B} \frac{\left(\hat{\mathbf{b}}_i - \hat{\mathbf{b}}_\beta\right)^T \left(\hat{\mathbf{b}}_i - \hat{\mathbf{b}}_\beta\right)}{B-1} \right]^{1/2}. \tag{18}$$

Efron [1982] has shown via Monte Carlo experiments that the bootstrap standard error is slightly downward biased; thus it is not conservative. For an illustration of the bootstrap procedure see Figure 1.

3.2. Confidence Intervals by Bootstrap Percentiles

[12] Although several bootstrap methods for obtaining confidence intervals are available [*Efron and Tibshirani*, 1993], in this study the percentile method which makes use of the bootstrap distribution is employed. That is, the estimation of a confidence interval

$$\left[\hat{\mathbf{b}}_\ell(\alpha), \hat{\mathbf{b}}_u(\alpha)\right], \tag{19}$$

where subscripts ℓ and u denote the lower and upper limits, respectively, of the vector of true model parameters $\mathbf{b}$, is approximated by the α central confidence interval. The probability α ($0 < \alpha < 1$) indicates a 100α% confidence that $\mathbf{b} \in [\hat{\mathbf{b}}_\ell, \hat{\mathbf{b}}_u]$ or a 100($1-\alpha$)% confidence that $\mathbf{b} \notin [\hat{\mathbf{b}}_\ell, \hat{\mathbf{b}}_u]$. The larger the α, the greater the chance that the unknown parameter is included in the confidence interval. For example, the 95% confidence limits for $\mathbf{b}$ based on 2000 bootstrap replications are given by $\hat{\mathbf{b}}_\ell$ = 50th and $\hat{\mathbf{b}}_u$ = 1950th largest estimates of $\mathbf{b}$. Obviously, each element of the vector of model parameters is treated individually. For simple parameter estimation, approximately 100 bootstrap replications are sufficient. However, for confidence interval estimation the number of bootstrap iterations should be of the order of 1000 [*Efron and Tibshirani*, 1993].

4. Estimation of Mass Transfer Coefficients

[13] The experimental data used in this work were obtained from the three-dimensional experiment of a TCE pool dissolution in a water-saturated bench-scale aquifer described by *Chrysikopoulos et al.* [2000]. The experimental aquifer is constructed of glass sides with a specially designed aluminum bottom plate. The unique aspect of the 150 × 21.6 × 40 cm model aquifer design is the formation of a well-defined, circular TCE pool with 7.6 cm diameter at the bottom of the model aquifer. The aquifer material is kiln-dried Monterey sand (RMC Lonestar, Monterey, California). The fundamental parameters characterizing the experimental conditions are solubility of TCE in the aqueous phase, C_s^{TCE} = 1100 mg/L (at 20°C); molecular diffusion coefficient of the dissolved TCE in the aqueous-phase, $\mathcal{D}^{\mathrm{TCE}}$ = 0.0303 cm^2/h (at 20°C); pool radius r = 3.8 cm; retardation factor for the dissolved TCE in the aqueous-

Table 1. Experimental Mean Aqueous Phase TCE Concentrations and Bootstrap Estimates of k^*

U_x, cm/h	Time,[a] h	C^{TCE} (mg/L) at Sampling Node[b]					$\hat{k}^*_\beta$, cm/h	Confidence Limits	
		4	34	63	95	144		Lower	Upper
0.25	804	628.1±1.1	204.3±1.9	151.7±3.2	141.3±0.2	71.1±0.8	0.02591	0.02571	0.02619
0.51	360	541.2±133.9	145.4±9.3	114.1±0.7	97.4±0.9	56.7±0.2	0.03373	0.03371	0.03376
0.75	250.5	403.8±13.8	104.5±13.2	80.5±1.8	144.7±1.2	43.6±0.6	0.03850	0.03849	0.03851
1.21	180	382.4±3.9	135.6±1.1	94.9±2.5	108.4±2.5	24.3±0.2	0.04482	0.04472	0.04488
1.50	131.5	365.5±2.6	114.4±7.5	62.6±2.9	101.6±2.5	37.7±0.2	0.04734	0.04731	0.04737
1.96	132	237.0±3.6	82.1±4.7	54.7±0.2	51.3±0.1	17.7±0.3	0.04759	0.04275	0.05103
3.35	66	209.0±4.4	70.4±1.4	44.6±2.2	40.1±5.9	4.8±0.3	0.05563	0.05558	0.05566

[a] Time since the initiation of each individual experiment (sample collection time).
[b] Adopted from *Lee* [1999].

phase R = 1.31; longitudinal aquifer dispersivity α_L = 0.259 cm; transverse aquifer dispersivity α_T = 0.019 cm; bulk density of sand ρ = 1.61 kg/L; aquifer porosity, θ = 0.415; and aquifer tortuosity τ^* = 1.43.

[14] The experimental aqueous phase TCE concentrations at specific locations within the aquifer downstream from the TCE pool for seven different interstitial fluid velocities (0.25, 0.51, 0.75, 1.21, 1.50, 1.96, and 3.35 cm/h) and steady state conditions were collected by *Chrysikopoulos et al.* [2000] and *Lee* [1999]. For each TCE dissolution experiment, samples were simultaneously collected from sampling ports 4 (located at x = 0.0, y = 0.0, z = 0.8 cm), 34 (15.0, 0.0, 1.8), 63 (30.0, 2.5, 1.8), 95 (45.0, −2.5, 1.8), and 144 (70.0, 0.0, 3.8). It should be noted that the origin of the Cartesian coordinate (0, 0, 0) is directly below port 4, and the center of the circular TCE pool is located at (−3.8, 0, 0). The duplicate aqueous phase TCE concentration experimental data are averaged and presented in Table 1 together with the corresponding standard deviations.

[15] The bootstrap resampling technique in conjunction with a regression procedure based on the Levenberg-Marquardt method are employed in this work for parameter estimation and confidence interval determination of k^*. Each of the seven sets of experimental aqueous phase TCE concentrations corresponding to a different interstitial velocity is treated separately. A FORTAN program was

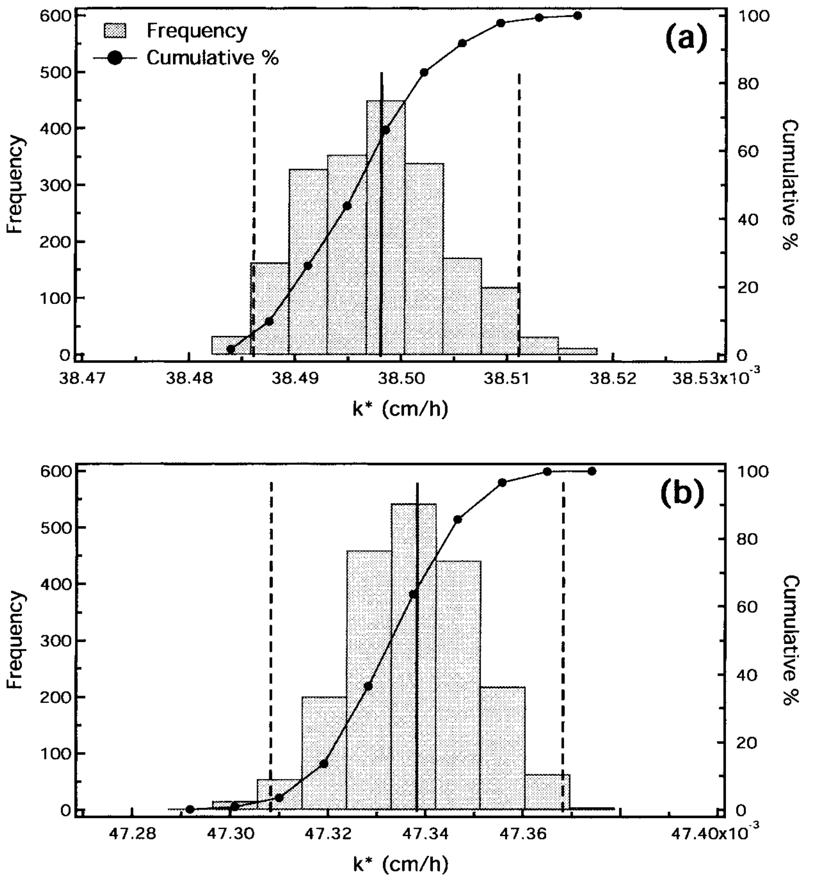

Figure 2. Histograms of 2000 bootstrap estimates of the time invariant average mass transfer coefficient $\hat{k}^*$, evaluated from the aqueous phase trichloroethylene concentrations collected for interstitial velocity of (a) 0.75 cm/h and (b) 1.50 cm/h. The bars represent frequency, and the curves with solid circles represent cumulative percentage. The best bootstrap estimator value $\hat{k}^*_\beta$ is indicated by a solid line, and its lower and upper confidence limits $\hat{k}^*_\ell$ and $\hat{k}^*_u$, respectively, are represented by dashed lines.

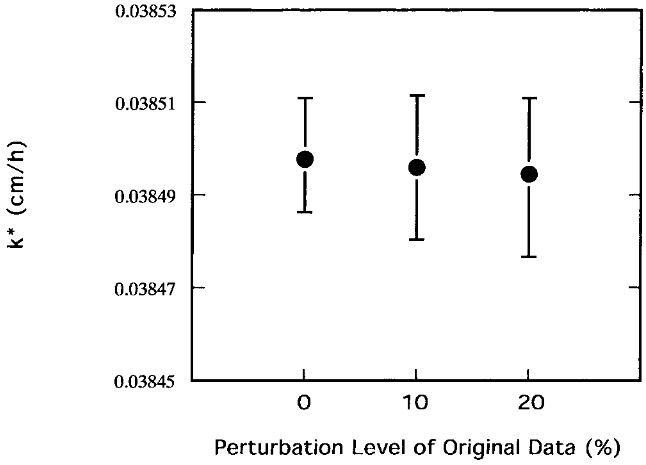

Figure 3. Bootstrap estimated average mass transfer coefficients and confidence intervals for various levels of random perturbation of the original experimental data set for U_x = 0.75 cm/h.

developed in order to select a random sample (bootstrap sample) from an aqueous phase TCE concentration data set, to fit the bootstrap sample with the analytical solution (11), and to estimate the corresponding value of k^*. The bootstrap sample of size 5 is randomly selected with replacement from the original experimental data set that contains five aqueous phase TCE concentrations (one for each of the five sampling ports). Consequently, multiple repetitions of the same aqueous phase TCE concentration may occur in a bootstrap sample. The subroutine *ran2* [*Press et al.*, 1992] is used to generate five random integers between 1 and 5. For each random number the corresponding aqueous phase TCE concentration and its standard deviation (required by the fitting routine) as well as the sampling location (x, y, and z coordinates) are selected from the original data set and stored. The subroutine mrqmin [*Press et al.*, 1992] is used to obtain the desired bootstrap parameter estimate $\hat{k}^*$ by fitting the analytical solution (11) to the five aqueous phase TCE concentrations of the bootstrap sample together with an additional datum representing the TCE saturation at the pool-water interface. It should be noted that k^* is the only unknown parameter in the transport model employed here; all other model parameters were evaluated independently.

[16] The complete resampling procedure is repeated 2000 times for each set of the original experimental data. Consequently, a bootstrap vector of 2000 estimated model parameters $\hat{\mathbf{b}} = (\hat{k}^*_1, \hat{k}^*_2, \ldots, \hat{k}^*_{2000})^{\mathrm{T}}$ is created for each of the seven experimental data sets. In view of (17), averaging the bootstrapped parameter values yields the "best" bootstrap estimate $\hat{k}^*_\beta$. In this work, determination of confidence limits is based on bootstrap percentiles. The 95% confidence limits of $\hat{k}^*_\beta$ (95% confidence that $\hat{k}^*_\beta \notin [\hat{k}^*_\ell, \hat{k}^*_u]$) are given by $\hat{k}^*_\ell$ = 50th and $\hat{k}^*_u$ = 1950th largest bootstarp estimates of k^*, respectively.

[17] For each of the seven TCE pool dissolution experimental data sets available, a $\hat{k}^*_\beta$ and its cofidence limits are determined and listed in Table 1. A histogram and cumulative percentage of 2000 bootstrap replications of k^* for the experimental data collected under interstitial velocities of 0.75 and 1.50 cm/h are presented in Figure 2. The histogram for the dissolution experiment with interstitial velocity of 0.75 cm/h indicates that the mean or best bootstrap estimator is $\hat{k}^*_\beta$ = 0.038498 cm/h with a 95% confidence interval ranging between $\hat{k}^*_\ell$ = 0.038486 cm/h and $\hat{k}^*_u$ = 0.038511 cm/h (Figure 2a). For the dissolution experiment with interstitial velocity of 1.50 cm/h, $\hat{k}^*_\beta$ = 0.047338 cm/h, and its 95% confidence interval ranges between $\hat{k}^*_\ell$ = 0.047308 cm/h and $\hat{k}^*_u$ = 0.047368 cm/h (Figure 2b). A dotted line drawn at the parameter estimate and dashed lines drawn at the two confidence limits are included with each histogram of Figure 2. Both histograms are roughly Gaussian in shape, suggesting that confidence interval evaluation based on bootstrap percentiles is a reasonable approach.

[18] To demonstrate the high-quality performance of the proposed parameter estimation and confidence interval determination methodology, the original experimental data set for the interstitial velocity 0.75 cm/h (listed in Table 1) was perturbed with random noise corresponding to 10 and 20% of the actual concentration values and the bootstrapping procedure was repeated. The determined k^* and confidence limits for the original and the two perturbed data sets are plotted in Figure 3. The results indicate that the proposed methodology is successful in consistent determination of the parameter estimate. Furthermore, the observed confidence interval increase with increasing random noise in the experimental data is relatively small. Therefore the proposed estimation technique is considered to perform effectively under difficult circumstances where the available experimental data may not be error free.

5. Summary

[19] A procedure for the estimation of mass transfer coefficients for dissolving NAPL pools in water-saturated, three-dimensional porous media was proposed. The bootstrap resampling technique was employed to obtain best estimates of mass transfer coefficients and associated confidence limits from available TCE pool dissolution experimental data. Histograms of 2000 bootstrap replications of k^* were shown to be roughly normally distributed, thus verifying that the procedure of confidence interval evaluation based on bootstrap percentiles used in this work is appropriate. Estimates of mass transfer coefficients based on randomly perturbed experimental TCE dissolution data compared well with those obtained with the original TCE dissolution data, demonstrating the high-quality performance of the proposed methodology.

References

Anderson, M. R., R. L. Johnson, and J. F. Pankow, Dissolution of dense chlorinated solvents into groundwater, 3, Modeling contaminant plumes from fingers and pools of solvent, *Environ. Sci. Technol.*, *26*, 901–908, 1992.

Brusseau, M. L., N. T. Nelson, M. Oostrom, Z. Zhang, G. R. Johnson, and T. W. Wietsma, Influence of heterogeneity and sampling method on aqueous concentrations associated with NAPL dissolution, *Environ. Sci. Technol.*, *34*, 3657–3664, 2000.

Chernick, M. R., *Bootstrap Methods: A Practitioner's Guide*, 246 pp., John Wiley, New York, 1999.

Chrysikopoulos, C. V., Three-dimensional analytical models of contaminant transport from nonaqueous phase liquid pool dissolution in saturated subsurface formations, *Water Resour. Res.*, *31*(4), 1137–1145, 1995.

Chrysikopoulos, C. V., and K. Y. Lee, Contaminant transport resulting from multicomponent nonaqueous phase liquid pool dissolution in three-dimensional subsurface formations, *J. Contam. Hydrol.*, *31*, 1–21, 1998.

Chrysikopoulos, C. V., and T.-J. Kim, Local mass transfer correlations for nonaqueous phase liquid pool dissolution in saturated porous media, *Transp. Porous Media*, *38*, 167–187, 2000.

Chrysikopoulos, C. V., K. Y. Lee, and T. C. Harmon, Dissolution of a well-defined trichloroethylene pool in saturated porous media: Experimental design and aquifer characterization, *Water Resour. Res.*, *36*(7), 1687–1696, 2000.

Chrysikopoulos, C. V., E. A. Voudrias, and M. M. Fyrillas, Modeling of contaminant transport resulting from dissolution of nonaqueous phase liquid pools in saturated porous media, *Transp. Porous Media*, *16*, 125–145, 1994.

Diaconis, P., and E. Efron, Computer-intensive methods in statistics, *Sci. Am.*, *248*(5), 116–129, 1983.

Donaldson, J. R., and R. B. Schnabel, Computational experience with confidence regions and confidence intervals for nonlinear least squares, *Technometrics*, *29*(1), 67–93, 1987.

Duncan, G. T., An emperical study of jackknife-constructed confidence regions in nonlinear regression, *Technometrics*, *20*(2), 123–129, 1978.

Efron, B., Bootstrap methods: Another look at the jackknife, *Ann. Sta.*, *7*(1), 1–26, 1979.

Efron, B., (Ed.), *The Jackknife, the Bootstrap, and Other Sampling Methods*, *CBMS-NSF Reg. Conf. Ser. Appl. Math.*, vol. 38, 92 pp., Soc. for Indust. and Appl. Math., Philadelphia, Pa., 1982.

Efron, B., and R. Tibshirani,. *An Introduction to the Bootstrap*, 436 pp., Chapman and Hall, New York, 1993.

Holman, H.-Y. N., and I. Javandel, Evaluation of transient dissolution of slightly water-soluble compounds from a light nonaqueous phase liquid pool, *Water Resour. Res.*, *32*(4), 915–923, 1996.

Imhoff, P. T., P. R. Jaffé, and G. F. Pinder, An experimental study of complete dissolution of a nonaqueous phase liquid in saturated porous media, *Water Resour. Res.*, *30*(2), 307–320, 1994.

Incropera, F. P., and D. P. DeWitt, *Fundamentals of Heat and Mass Transfer*, 4th ed., John Wiley, New York, 1996.

Jia, C., K. Shing, and Y. C. Yortsos, Advective mass transfer from stationary sources in porous media, *Water Resour., Res.*, *35*(11), 3239–3251, 1999.

Keller, A. A., M. J. Blunt, and P. V. Roberts, Micromodel observation of the role of oil layers in three-phase flow, *Transp. Porous Media*, *26*, 277–297, 1997.

Khachikian, C., and T. C. Harmon, Nonaqueous phase liquid dissolution in porous media: Current state of knowledge and research needs, *Transp. Porous Media*, *38*, 3–28, 2000.

Kim, T.-J., and C. V. Chrysikopoulos, Mass transfer correlations for nonaqueous phase liquid pool dissolution in saturated porous media, *Water Resour. Res.*, *35*(2), 449–459, 1999.

Lee, K. Y., Dissolution of nonaqueous phase liquid pools in saturated media, Ph. D. dissertation, Dep. of Civ. and Environ. Eng. Univ. of Calif., Irvine, Irvine, Calif., 1999.

Lee, K. Y., and C. V. Chrysikopoulos, Numerical modeling of three-dimensional contaminant migration from dissolution of multicomponent NAPL pools in saturated porous media, *Environ. Geol.*, *26*, 157–165, 1995.

Lee, K. Y., and C. V. Chrysikopoulos, NAPL pool dissolution in stratified and anisotropic porous formations, *J. Environ. Eng.*, *124*(9), 851–862, 1998.

Leij, F. J., and M. T. van Genuchten, Analytical modeling of nonaqueous phase liquid dissolution with Green's functions, *Transp. Porous Media*, *38*, 141–166, 2000.

Mason, A. R., and B. H. Kueper, Numerical simulation of surfactant-enhanced solubilization of pooled DNAPL, *Environ. Sci. Technol.*, *30*, 3205–3215, 1996.

Nambi, I. M., and S. E. Powers, NAPL dissolution in heterogeneous systems: An experimental investigation in a simple heterogeneous system, *J. Contam. Hydrol.*, *44*, 161–184, 2000.

Politis, D. N., J. P. Romano, and M. Wolf, *Subsampling*, 365 pp., Springer-Verlag, New York, 1999.

Press, W. H., S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran: The Art of Scientific Computing*, 963 pp., Cambridge Univ. Press, New York, 1992.

Saba, T., and T. H. Illangasekare, Effect of groundwater flow dimensionality on mass transfer from entrapped nonaqueous phase liquid contaminants, *Water Resour. Res.*, *36*(4), 971–979, 2000.

Seagren, E. A., B. E. Rittman, and A. J. Valocchi, An experimental investigation of NAPL-pool dissolution enhancement by flushing, *J. Contam. Hydrol.*, *37*, 111–137, 1999.

Tatalovich, M. E., K. Y. Lee, and C. V. Chrysikopoulos, Modeling the transport of contaminants originating from the dissolution of DNAPL pools in aquifers in the presence of dissolved humic substances, *Transp. Porous Media*, *38*, 93–115, 2000.

Vogler, E. T., and C. V. Chrysikopoulos, Dissolution of nonaqueous phase liquid pools in anisotropic aquifers, *Stochastic Environ. Res. Risk Assess.*, *15*, 33–46, 2001.

Zhou, D., L. A. Dillard, and M. J. Blunt, A physically based model of dissolution of nonaqueous phase liquids in the saturated zone, *Transp. Porous Media*, *39*, 227–255, 2000.

Zhu, J., and J. F. Sykes, Stochastic simulations of NAPL mass transport in variably saturated heterogeneous porous media, *Transp. Porous Media*, *39*, 289–314, 2000.

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