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# Field Performance of Air-Sparging System for Removing TCE from Groundwater

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The removal of volatile organic compounds from groundwater by air sparging (AS) is well-established, although reliable methods for predicting the time required to reach site closure have not been established. To develop an improved understanding of mass transfer processes that limit AS performance, two extended controlled shutdowns of an operating AS system were performed. Monitoring of TCE concentrations in source zone groundwater indicated "tailing" and "rebound" behavior similar to that observed for pump-and-treat systems. A simple two-compartment model provided a reasonable description of the 3-year AS history, using parameters calibrated from data collected during the first shutdown period. Comparison of the calibrated rate constants with parameters estimated from laboratory soil columns suggests that, for the study site, aqueous diffusion to discrete air channels has a stronger influence on system performance than rate-limited desorption. Predictions based on the calibrated model indicated that restoration of the source zone to drinking water standards would require approximately 1 decade for the current AS system.

## Introduction

Air sparging (AS) is a popular strategy for removing volatile organic compounds (VOCs) from groundwater (1, 2). The underlying concept behind AS is relatively simple: air is injected into the saturated zone to promote volatilization and/or enhanced biotransformation (Figure 1a). AS systems have been implemented to aggressively remove mass from contaminant source zones and/or to serve as barriers to dissolved plume migration. Reports from case studies have indicated considerable success in reducing groundwater VOC concentrations, although concentration "tailing" and "rebound" have been observed at many sites (3, 4). The focus of this work is on the application of a user-oriented mathematical model to analyze the performance of an AS system designed for source zone remediation at a case study site.

Several simplified reactor models for predicting VOC concentrations in the groundwater influenced by sparge wells have been proposed (5–9). Recently, Rabideau and Blayden (10, hereafter denoted R&B) developed a model capable of describing source zone tailing and rebound behavior with a closed-form solution based on a limited number of site-specific parameters. The region surrounding an individual

sparge well is modeled as a reactor consisting of two completely mixed compartments that exchange mass with each other. Only one of the two compartments exchanges mass with the vapor phase introduced by sparging. Depending on the meaning assigned to the parameters, the governing equations can be interpreted to represent two alternative conceptual models for the rate limitation: (1) nonequilibrium desorption or (2) aqueous diffusion to discrete air channels.

**Nonequilibrium Sorption Model.** Nonaqueous phase contamination was not detected at the study site, and the initial interpretation of the model was considered in terms of an aqueous phase in contact with the vapor phase and a sorbed phase subject to rate-limited desorption (Figure 1b). The resulting model equations are

$$\frac{dC}{dt} = -kC - \frac{\rho_b}{\theta_a} \frac{dX}{dt} \quad (1)$$

$$\frac{dX}{dt} = \alpha(K_d C - X) \quad (2)$$

where  $C$  [ $M L^{-3}$ ] is the contaminant concentration in the aqueous phase,  $X$  is the contaminant mass fraction in the sorbed phase,  $t$  [T] is time,  $\rho_b$  [ $M L^{-3}$ ] is the media bulk density,  $\theta_a$  is the aqueous phase volume fraction,  $\alpha$  [ $T^{-1}$ ] is the sorption rate coefficient,  $K_d$  [ $L^3 M^{-1}$ ] is the sorption distribution coefficient, and  $k$  [ $T^{-1}$ ] is a lumped sparging rate constant that can represent volatilization, biotransformation, and/or advection, as discussed by R&B.

**Air Channel Model.** An alternative model considers aqueous diffusion to discrete air channels as the rate-limiting mechanism. The aqueous phase within the sparge zone is assumed to consist of (1) "clean zones" located in the immediate vicinity of air channels, characterized by accelerated volatilization and/or biotransformation, and (2) adjacent "dirty zones" not in contact with the air channels, in which contaminant is removed only by aqueous diffusion to the adjoining clean zone. In this conceptualization (Figure 1c), field observations of contaminant concentrations are assumed to correspond to the clean zone, advection is neglected, biotransformation is assumed to apply only to the clean zone, and sorption is assumed to be adequately described by the use of a retardation factor. The air channel model is mathematically similar to the popular "mobile-immobile" formulations used to describe solute transport. The corresponding equations are

$$\frac{dC_1}{dt} = -\frac{k}{R_1} C_1 - \frac{\theta_2 R_2}{\theta_1 R_1} \frac{dC_2}{dt} \quad (3)$$

$$\frac{dC_2}{dt} = \alpha'(C_1 - C_2) \quad (4)$$

where the subscripts 1 and 2 refer to the clean and dirty compartments, respectively;  $\theta_i$  is the volume fraction associated with compartment  $i$ ;  $k$  [ $T^{-1}$ ] is the lumped sparging constant;  $\alpha'$  [ $T^{-1}$ ] is the rate constant for mass transfer between the two zones; and the retardation factors are defined as  $R_1 = 1 + f\rho_b K_d/\theta_1$ ,  $R_2 = 1 + (1 - f)\rho_b K_d/\theta_2$ , with  $f$  representing the fraction of the sorption capacity associated with the clean zone.

**Dimensionless Form.** The two conceptual models for air sparging yield identical dimensionless equations, based

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TABLE 1. Summary of Dimensionless Groupings

grouping	meaning	desorption	air channels
$\bar{C}$	normalized concentration for zone in contact with vapor phase	$C/C_0$	$C_1/C_0$
$\bar{X}$	normalized concentration for zone not in contact with vapor phase	$X/K_d C_0$	$C_2/C_0$
$T$	time normalized to characteristic sparge time	$kt$	$kt/R_1$
$\beta$	solute distribution ratio	$\rho_b K_d/n$	$\theta_2 R_2/\theta_1 R_1$
$\phi$	ratio of mass transfer rate to sparge rate	$\alpha/k$	$\alpha' R_1/k$

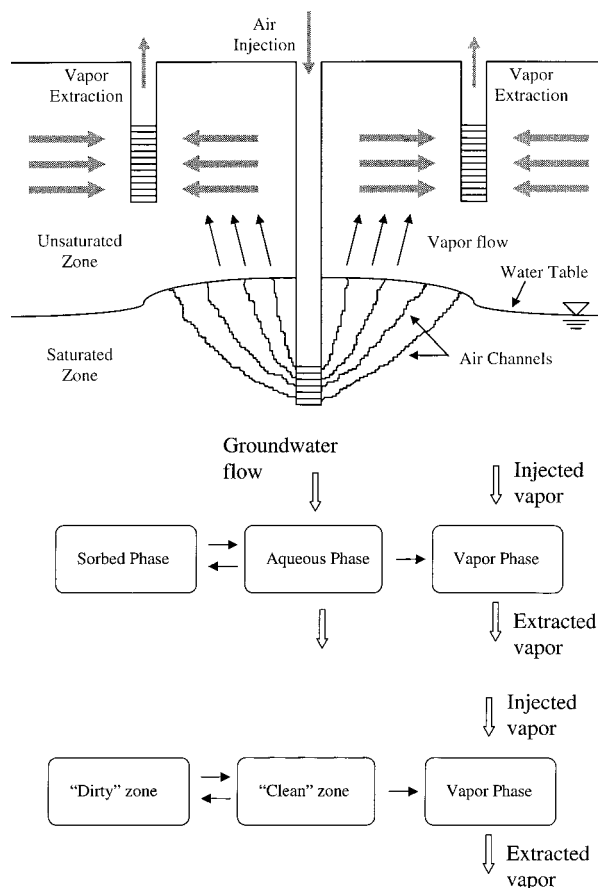


FIGURE 1. (a) Schematic of air-sparging well. (b) Conceptual model for mass transfer limitation: desorption. (c) Conceptual model for mass transfer limitation: diffusion to discrete air channels.

on the groupings defined in Table 1:

$$\frac{d\bar{C}}{dT} = -\bar{C} - \phi\beta(\bar{C} - \bar{X}) \quad (5)$$

$$\frac{d\bar{X}}{dT} = \phi(\bar{C} - \bar{X}) \quad (6)$$

Since most AS systems are operated intermittently, a "resting period" solution can also be considered by eliminating the first term on the right-hand-side of eq 5. Details of the model solutions are provided by R&B.

Application of the model requires estimation of three key parameters: the effective sparge constant ( $k$ ), the solute distribution ratio ( $\beta$ ), and the dimensionless mass transfer coefficient ( $\phi$ ). If the desorption-based interpretation is correct, it may be possible to estimate key components of the sorption parameters ( $K_d$  and  $\alpha$ ) using laboratory columns.

## Research Objectives

The objectives of this study were as follows: (1) to characterize the rebound behavior of the study site by frequently

monitoring the groundwater following periods of controlled AS shutdown, (2) to assess the ability of the R&B model to describe the remediation history of the site using parameters calibrated from the rebound data, and (3) to assess the hypothesis that sorption is the mechanism responsible for tailing/rebound by comparing laboratory measurements of sorption parameters with values calibrated from the field.

## Methods

**Field Study.** The study site is a 16-ha plot that includes an active gravel pit operated by the town of Machias, NY; an inactive gravel pit that is the subject of ongoing remediation; and two small streams that run along the northern and eastern property lines. Unconsolidated fluvio-glacial deposits overlie the shale bedrock, which has been estimated to be approximately 27 m below ground surface (BGS). The soil consists mainly of sands and gravels with intermittent deposits of silty sand. Groundwater at the site is under unconfined conditions and varies in depth from approximately 1.5 to 18 m.

In 1986, waste drums were removed from the inactive gravel pit (henceforth designated as the source zone), and subsequent site investigations revealed the presence of a dissolved plume containing trichloroethylene (TCE) (11). A combined soil vapor extraction/air-sparging system was installed to remove contaminant mass from the source zone, with continuous operation beginning in January 1994 and continuing until the summer of 1996, when the periods of intermittent operation associated with the current study began. A preliminary review of the system performance resulted in the hypothesis of mass transfer limitations that led to the research described in this paper (12).

The AS system is operated by cycling two groups of sparge wells (36 total) located within the 2500 m<sup>2</sup> source zone and a third "defensive" grouping of five AS wells located approximately 60 m downgradient. Periodic compliance monitoring of the site groundwater has continued since the initial startup of the AS system. In conjunction with this study, portions of the system were shut down beginning June 24, 1996. During the subsequent period, groundwater samples were collected from selected monitoring wells at intervals of 1–3 weeks and analyzed for TCE. The entire system was restarted on October 22, 1996. Monitoring during a second shutdown period was performed from April 2 to October 26, 1997, and the system was subsequently returned to continuous operation.

**Laboratory Studies.** In conjunction with the field monitoring, three soil borings were installed at the site using conventional hollow stem auger techniques. Soil samples from two of the borings (located outside the contaminated areas) were used for batch isotherm tests and physical characterization, which indicated a median grain size of 2.2 mm, a total porosity of 0.28, a bulk density of 1.91 g/cm<sup>3</sup>, and an organic fraction of 0.013 ± 0.002 (ASTM 2374-87).

Soil used for a 10-day adsorption isotherm experiment was allowed to air-dry for 24 h and passed through a 1.70-mm sieve. The sieved material was mixed until the sample was homogeneous and allowed to dry for another 24 h. For each of the six TCE concentration levels, approximately 4 g

TABLE 2. Summary of Column Parameters

parameter	column 1	column 2	comment
cross-sectional area [cm <sup>2</sup> ]	11.4	11.4	
length [cm]	20.56	20.56	
flow rate (tracer) [cm <sup>3</sup> /min]	0.65	0.59	measured
tracer pulse length [pore volumes]	1.52	1.38	measured
effective porosity ( $\theta_e$ )	0.24	0.22	fitted from tracer data
dispersivity ( $\alpha_L$ ) [cm]	2.4	3.0	fitted from tracer data
flow rate (flushing) [cm <sup>3</sup> /min]	0.073	0.076	measured
sorption coefficient ( $K_d$ ) [cm <sup>3</sup> /g]	0.28	0.36	fitted from flushing data
initial aqueous TCE concn [ $\mu$ g/L]	809	626	fitted from flushing data
sorption rate ( $\alpha$ ) [day <sup>-1</sup> ]	0.23	0.32	fitted from flushing data
initial total TCE concn [ $\mu$ g/kg]	365	332	calculated

of the sieved soil was added to five 12-mL amber Borosilicate glass sample vials, which were then filled with Nanopure water. Three blanks containing only Nanopure water were also prepared for each concentration level. Small amounts of a TCE stock solution were injected into the vials prior to sealing with Teflon-lined screw caps. The samples were tumbled at 30 rpm for 10 days, followed by gravity separation and analysis for aqueous TCE as described below. The total TCE mass in each vial was estimated from the blanks, and the sorbed fraction was computed by subtracting the mass associated with the measured aqueous concentrations.

**Column Flushing Experiments.** One soil sample was collected from the saturated interval in an area of elevated TCE concentrations, using a three-section stainless steel split-spoon liner. One of the three subsamples was used to measure the total TCE concentration, as described below, while the remaining two cores were used for column flushing experiments designed to estimate the sorption parameters. A schematic of the column apparatus is shown in the supplemental Figure 1s (see Supporting Information). The adaptation of field sampling tubes to serve as laboratory columns followed the general strategy developed by Mackay et al. (13).

After the columns reached room temperature, they were flushed with Nanopure water containing 1.5 mM sodium azide (added to inhibit microbial activity) from an influent reservoir fitted with a floating cover. To reduce the potential for volatilization losses during sample collection, the effluent from each column was collected in 25 × 200 mm culture tubes sealed with Teflon-lined septa and screw caps. Deflected point, noncoring septum penetration needles (30 cm, 18 gauge) were connected to the effluent tubing with the ends submerged in 3–5 mL of hexane placed in the culture tubes. The needles and tubes were replaced every 12 h, and the effluent was analyzed for TCE as described below. For each column, 25 effluent samples representing aqueous sample volumes of 31–66 mL were collected, corresponding to a total of approximately 16 pore volumes. Following the flushing experiments, a tracer study was performed by introducing a pulse containing 1000 mg/L sodium bromide. Upon completion of the tracer study, the soil was removed from the two columns. Visual inspection did not indicate any observable large void areas; the columns appeared to be completely packed. However, the grain size distributions were quite heterogeneous, including a large pebble in one of the columns.

**Analytical Methods.** Groundwater samples collected during the rebound study were analyzed for TCE at the SUNY Buffalo Environmental Engineering Laboratory. The samples were subjected to liquid/liquid extraction using hexane, followed by GC analysis for TCE using a Hewlett-Packard (HP) 5890 gas chromatograph equipped with an HP 6890 automatic sampler and an electron capture detector. Measurement of the total TCE concentration in the soil core was

performed using a hot methanol extraction procedure similar to that described by Ball et al. (14). Aqueous samples from the column tracer tests were analyzed for bromide using a Shimadzu LC10AS ion chromatograph with an anion column (Shimadzu IC-A1) and a conductivity detector operating at 40 °C.

## Results

**Isotherm.** The batch sorption data (Sorting Information Figure 2s) were fit with several isotherm models by nonlinear regression assuming constant relative error. Although the nonlinear models provided somewhat better fits, the linear isotherm was adopted for consistency with the analytical AS model. The estimated  $K_d$  ( $0.42 \pm 0.02$  cm<sup>3</sup>/g) was lower than predictions based on various literature correlations (15) using the measured organic content of 1.3% ( $0.5$ – $1.0$  cm<sup>3</sup>/g). One possible explanation for this difference is that sorption equilibrium was not achieved during the 10-day test period.

**Column Flushing.** The conditions and results from the column tests are summarized in Table 2. The bromide breakthrough curves for the two soil columns (Sorting Information Figures 3s and 4s) were reasonably symmetrical, suggesting that physical nonequilibrium was not a significant factor. Both the tracer tests and the column flushing experiments were analyzed by fitting the appropriate form of the advective–dispersive–reactive equation (ADRE) to the data by nonlinear regression. For the flushing experiments, the cumulative mass removed, rather than effluent concentration, was considered as the dependent variable (16). A numerical solution to the ADRE incorporating the kinetic sorption model of eq 2 was developed using the split-operator finite element method (17) with the output expressed both in terms of concentration and cumulative mass.

The effective porosity and dispersivity were calibrated from the bromide tracer test effluent assuming negligible sorption, a third-type Danckwerts influent boundary condition, and a zero-gradient effluent condition. The average calibrated effective porosity (0.23) was approximately 8% less than the independently measured total porosity (0.28). For the column flushing simulations, the effective porosity and dispersivity were fixed at the values calibrated from the tracer study, and the boundary conditions were set as zero-concentration entrance and zero-gradient exit. Unknowns included the sorption distribution coefficient ( $K_d$ ), the sorption rate constant ( $\alpha$ ), and the initial aqueous TCE concentration  $C_0$ , which was assumed to be uniform throughout the column. Initial equilibrium was assumed between the aqueous and sorbed phases.

Two calibrations were performed: (1)  $K_d$  fixed at the batch isotherm value with  $\alpha$  and  $C_0$  calibrated, and (2) all three parameters calibrated (Figure 2). A significantly better fit was obtained when  $K_d$  was calibrated from the column data, and the average calibrated value ( $0.32$  cm<sup>3</sup>/g) was 25% lower



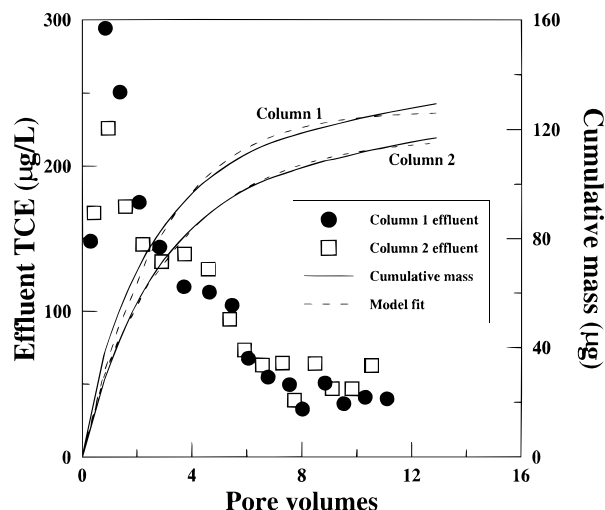


FIGURE 2. Results from column flushing experiments.

than the batch isotherm value. This difference could be attributable to the reduced contact with soil organic matter in the columns (18), the removal by sieving of the larger particles (mostly gravel) from the media used for the batch experiments, or heterogeneity effects. Regardless of the reason for the difference, the column value was considered more representative of field conditions and adopted for subsequent use. The calibrated sorption rates were similar for both approaches, and the values obtained from the three-parameter calibration were adopted ( $\alpha = 0.27 \text{ day}^{-1}$ ). The total column TCE mass corresponding to the calibrated initial aqueous concentrations and sorption distribution coefficients was similar for the two columns (365 and  $332 \mu\text{g/kg}$ ) and fell within 3–12% of the mass measured from the total extraction of the third core ( $376 \mu\text{g/kg}$ ).

**Field Rebound Behavior.** During the initial period of the first AS shutdown over summer 1996, five monitoring wells were sampled regularly and analyzed for TCE. Of these wells, only one source zone well (GW5) was located in an area where the AS system operation schedule could be reliably inferred. During both shutdown periods, the TCE concentration in GW5 increased from approximately 150 to  $400 \mu\text{g/L}$  over a 3–5-month period and began stabilizing near the higher value. When the system was restarted after the first shutdown, the concentration decreased rapidly, although the time to return to pre-shutdown conditions could not be determined due to uncontrolled intermittent operation caused by mechanical problems. The extended tailing and significant rebound observed for this source zone well suggest that a point of diminishing return has been reached in the operation of the current AS system.

**Sparging Model Calibrations.** A primary objective of this study was to evaluate the ability of the R&B model to simulate the observed field performance. Because the AS system records were considered most reliable during the periods of controlled shutdown, the following calibration strategy was adopted:

(a) The initial concentrations were established based on the measured aqueous concentration immediately prior to the AS startup (January 13, 1994), and initial equilibrium was assumed between the compartments.

(b) An approximate history of the AS operation was constructed by identifying on/off cycles from the available maintenance records.

(c) The AS model was calibrated by nonlinear regression using only aqueous concentration data from the first controlled shutdown period (June–October 1996).

Three sets of model calibrations were performed, based on the desorption interpretation (eqs 1–2): (1)  $K_d$  and  $\alpha$

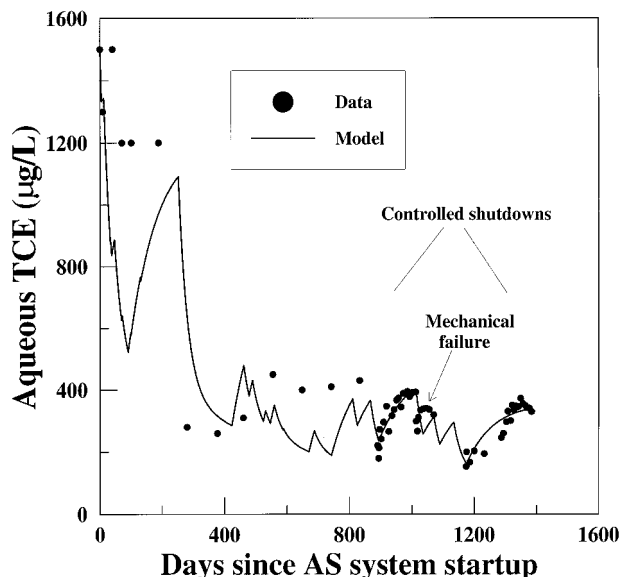


FIGURE 3. Measured TCE concentrations in source zone groundwater and model predictions based on parameters calibrated using data from first controlled shutdown.

fixed at the laboratory values, with  $k$  calibrated; (2)  $K_d$  fixed at the laboratory value, with  $\alpha$  and  $k$  calibrated; and (3) all three parameters calibrated.

Very poor results were obtained when the desorption rate ( $\alpha$ ) was fixed at the laboratory value. When  $\alpha$  was treated as a calibration parameter, reasonable agreement with the field data was noted regardless of whether  $K_d$  was fixed at the column value or calibrated. Using the parameters obtained from the three-parameter calibration ( $k = 0.034 \text{ day}^{-1}$ ,  $\beta = 4.43$ ,  $\phi = 0.10$ ), the entire history of GW5 was simulated (Figure 3). While significant differences between measurements and predictions were apparent for several sampling points, reasonable agreement was noted for the overall trends, including the second rebound study period. The location of several large TCE peaks during periods of AS system operation highlights the approximate nature of the operating schedule reconstructed from the site maintenance records. For example, uncontrolled mechanical failures were believed to be responsible for the TCE concentration fluctuations immediately following the first rebound study, as noted in Figure 3.

## Discussion

Given the many uncertainties associated with the field data, the description of the sparging history provided by the R&B model was considered reasonable for the Machias site, which suggests that the model could be used to predict performance for a proposed design if appropriate procedures could be developed to estimate the model parameters. The calibrated mass transfer coefficient under the desorption interpretation ( $\alpha = 0.0034 \text{ day}^{-1}$ ) was approximately 2 orders of magnitude lower than the desorption rate inferred from the laboratory columns ( $0.27 \text{ day}^{-1}$ ). On this basis, it was concluded that the air channel model (eqs 3–4) was more appropriate for the site, and the parameters were re-interpreted using the dimensionless groupings of Table 1. Although the development of a mechanistic understanding of the complex processes involved in air sparging is in the early stages, it is useful to consider a "reality check" of the model calibrations against current conceptual models.

**Interpretation of Solute Distribution Ratio.** Under the air channel interpretation, it is reasonable to assign equivalent sorption capacities to the two zones, which implies that  $\beta$  represents the ratio of the respective volume fractions. For

the measured media porosity of 0.28, the computed volume fractions associated with the clean zone ( $\theta_1$ ) and dirty zone ( $\theta_2$ ) are 0.05 and 0.23, respectively. A rough check on the reasonableness of this interpretation is provided by considering the air-sparging conceptual model proposed by P. Johnson (19). In this approach, the region surrounding an air channel is divided into three concentric cylinders: (1) an air channel of radius  $R_c$ , (2) a clean zone of outer radius  $\delta$ , and (3) a dirty zone of outer radius  $\xi$ , which may also be interpreted as the radius of influence of an individual air channel. In terms of the Johnson model, the distribution ratio  $\beta$  can thus be understood as

$$\beta \approx \frac{\xi^2 - \delta^2}{\delta^2 - R_c^2} \quad (7)$$

Johnson suggested an approximate dimension for the air channel radius ( $R_c$ ) of 0.01 m and performed sensitivity analyses to calculate a range for  $\delta$  of approximately 0.02–0.1 m. For the calibrated  $\beta = 4.43$ , the calculated values of  $\xi$  range from approximately 0.04 to 0.23 m, which implies a separation distance of 0.08–0.46 m between air channels, a value consistent with the suggestion of ~0.20 m previously advanced by R. Johnson (20).

**Interpretation of the Sparge Constant.** The calibrated sparge constant ( $k = 0.034 \text{ day}^{-1}$ ) was consistent with the previous estimate obtained from early-time groundwater data (12). Since biotransformation was not believed to occur at the study site and advection is neglected in the air channel model,  $k$  is believed to primarily represent volatilization. Gvirtzman and Gorelick (21) proposed a simple volatilization model for in-well air stripping, which is adapted here for the case of vapor transfer to air channels:

$$k = \frac{Q_v H}{\theta_1 R_1 V} \left[ 1 - \exp\left(\frac{-K_L a h}{H U_a}\right) \right] \quad (8)$$

where  $V [\text{L}^3]$  is the volume of porous media influenced by the AS system,  $Q_v [\text{L}^3 \text{ T}^{-1}]$  is the vapor flow rate for the sparge system,  $H$  is the contaminant dimensionless Henry's constant,  $K_L a [\text{T}^{-1}]$  is a lumped rate constant for contaminant mass transfer between the aqueous and vapor phases,  $h [\text{L}]$  is the vertical height of the sparge zone, and  $U_a [\text{L T}^{-1}]$  is the air velocity.

An upper bound on  $k$  can be calculated by assuming equilibrium between the aqueous and vapor phases (equivalent to neglecting the bracketed term in eq 8). The initial AS pilot study (22) yielded estimates of 202  $\text{m}^3/\text{day}$  for the vapor flow rate, 6 m for the average depth of a sparge well below the water table, and 3.8 m for the sparge well radius of influence. Assuming a TCE Henry's constant of 0.26 at groundwater temperature, a volume fraction of  $\theta_1 = 0.05$  (calculated above), and a retardation factor of 3.18 (column measurement), the calculated equilibrium  $k$  is 0.29  $\text{day}^{-1}$ , which is much higher than the value calibrated from the field (0.034  $\text{day}^{-1}$ ), implying that liquid/vapor mass transfer plays a significant role. Further quantification of the volatilization process requires estimating the lumped mass transfer term ( $K_L a/U_a$ ). The values suggested by Gvirtzman and Gorelick for in-well stripping reduce  $k$  by only 20% from the equilibrium value, highlighting the need for improved estimates of vapor/water mass transfer parameters specific to AS systems.

**Interpretation of Mass Transfer Coefficient.** As discussed above, the difference between the column and field mass transfer coefficients suggests that aqueous diffusion to air channels is a more plausible explanation than nonequilibrium desorption for the observed tailing and rebound, although both may contribute. When considered in terms

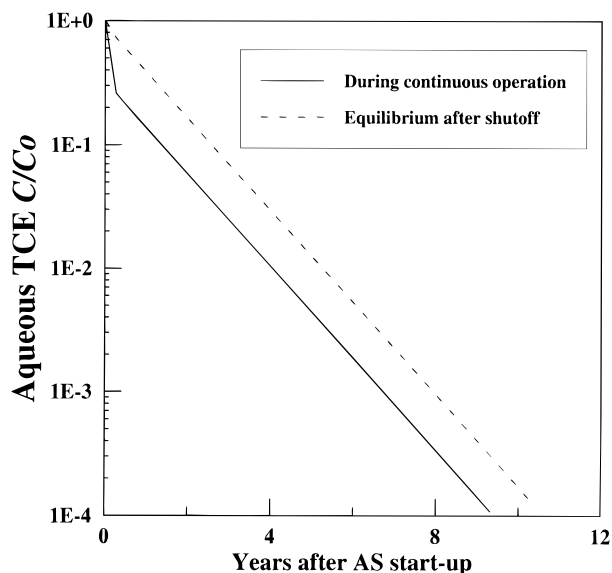


FIGURE 4. Simulation of continuous sparging using calibrated model ( $k = 0.034 \text{ day}^{-1}$ ,  $\beta = 4.43$ ,  $\phi = 0.10$ ).

of the air channel model, the calibrated mass transfer rate corresponds to  $\alpha' = k\phi/R_1 \sim 10^{-3} \text{ day}^{-1}$ . If the cylindrical air channel geometry is adopted,  $\alpha'$  may be estimated using established relationships for approximating diffusion to cylindrical macropores as a first-order process (23):

$$\alpha \approx \frac{1.36\theta_2(D_o)}{r^2(H_p)} \quad (9)$$

where  $D_o$  is the contaminant aqueous diffusion coefficient,  $H_p$  is a porous media hindrance factor, and  $r$  is the diffusion path length.

Assuming a TCE aqueous diffusion coefficient of approximately  $8.64 \times 10^{-5} \text{ m}^2/\text{day}$ , a calculated porous media hindrance factor of 1.5 based on the relationship proposed by Millington (24), and  $\theta_2 = 0.23$  (calculated above), the calculated diffusion path length is approximately 0.13 m, a value again consistent with P. Johnson's concept of diffusion across a clean zone. While the calculations described above involve many approximations, they demonstrate that the calibrations of the simple two-compartment formulation do not contradict current air sparging conceptual models.

**Implications for Remediation.** Using the parameters estimated from the rebound study, an extended model simulation of the source zone aqueous TCE concentration was performed. As shown in Figure 4, the mass transfer limitation is expressed in the two-stage behavior of the observed concentrations during AS operation (solid line), with a rapid concentration reduction during the first months of operation followed by more gradual removal. The dashed line corresponds to the calculated equilibrium aqueous concentration after sparging is discontinued, which is higher due to continued mass transfer from the dirty zone. For a given target concentration, the predicted operation time required to ensure post-rebound compliance is approximately 1 year longer than would be suggested by consideration of the pre-rebound concentrations.

The case study site represented a fairly simple scenario because NAPL was not present and TCE was not expected to undergo biotransformation. For other sites, it may be appropriate to extend the AS model by adding more compartments (e.g., address NAPL dissolution, kinetic desorption, and diffusion to air channels). Similar to the sparge term, first-order decay could be used to represent advection and/or biotransformation in the dirty zone. The use of a

numerical solution technique would also allow consideration of isotherm nonlinearity. Given the need for additional model fitting parameters and the relative success of the current approach, extension of the model in this fashion was not pursued at this time. Future work will attempt to establish the applicability of the two-compartment framework to other site and contaminant conditions.

### Acknowledgments

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### Supporting Information Available

Four figures showing the column flushing apparatus, TCE sorption data and best-fit isotherms, and tracer test results. Ordering information is given on any current masthead page.

### Literature Cited

- (1) Johnson, R. L.; Johnson, P. C.; McWhorter, D. B.; Hinchee, R. E.; Goodman, I. *Ground Water Monit. Rem.* **1993**, *13* (4), 127–135.
- (2) Hinchee, R. E. In *Air Sparging for Site Remediation*; Hinchee, R. E., Ed.; Lewis Publishers: Boca Raton, 1994; pp 1–13.
- (3) Marley, M. C.; Bruell, C. J. *API Publication No. 4609*; API: Washington, DC, 1995.
- (4) Bass, D. H.; Brown, R. A. *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration Conference*, Houston, 1995.
- (5) Pankow, J. F.; Johnson, R. L.; Cherry, J. A. *Ground Water* **1993**, *31* (4), 654–663.
- (6) Sellers, K. L.; Schreiber, R. P. *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration Conference*, Houston, 1992.
- (7) Elder, C. R.; Thorstad, P.; Eykholt, G. R.; Benson, C. H. In *In situ Remediation of the Geoenvironment*; Evans, J. C., Ed.; ASCE Geotechnical Special Publication 71; American Society of Civil Engineers: Reston, VA, 1998; pp 83–97.
- (8) Wilson, D. J.; Kayano, S.; Mutch, R. D.; Clark, A. N. *Sep. Sci. Technol.* **1992**, *27*, 1023–1041.
- (9) Wilson, D. J. *Sep. Sci. Technol.* **1992**, *27*, 1675–1690.
- (10) Rabideau, A. J.; Blayden, J. M. *Ground Water Monit. Rem.* **1998**, *18* (4), 120–130.
- (11) Hydro-Search, Inc. *Machias Gravel Pit Feasibility Study*; Golden, CO, 1991.
- (12) Russell, K.; Rabideau, A. J. *Proceedings of WEFTEC '96, Annual Water Environment Federation Conference*, Dallas, 1996.
- (13) Mackay, A. A.; Chin, Y. P.; MacFarlane, J. K.; Gschwend, P. M. *Environ. Sci. Technol.* **1996**, *30*, 3223–3231.
- (14) Ball, W. P.; Xia, G.; Durfee, D. P.; Wilson, R. D.; Brown, M. J.; Mackay, D. M. *Ground Water Monit. Rem.* **1997**, *17* (1), 104–121.
- (15) Fetter, C. W. *Contaminant Hydrogeology*; Macmillan: New York, 1993.
- (16) Shackelford, C. D. *ASCE J. Geotech. Eng.* **1995**, *121*, 355–372.
- (17) Rabideau, A. J.; Khandelwal, A. *ASCE J. Environ. Eng.* **1998**, *124*, 329–335.
- (18) Holmen, B. A.; Gschwend, P. M. *Environ. Sci. Technol.* **1997**, *31*, 105–113.
- (19) Johnson, P. C. *Environ. Sci. Technol.* **1996**, *32*, 14–22.
- (20) Johnson, R. L. In *Air Sparging for Site Remediation*; Hinchee, R. E., Ed.; Lewis Publishers: Boca Raton, 1994; pp 1–13.
- (21) Gvirtzman, H.; Gorelick, S. M. *Transp. Porous Media* **1992**, *8*, 71–92.
- (22) Vapex Environmental Technologies, Inc. *Air sparging pilot study summary and design report for the Machias Gravel Pit Site*, Machias, NY; Canton, MA, 1993.
- (23) Young, D. F.; Ball, W. P. *Water Resour. Res.* **1995**, *31*, 2181–2192.
- (24) Millington, R. J. *Science* **1959**, *130*, 100–102.

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