

WATER-TO-AIR MASS TRANSFER OF VOCs: LABORATORY-SCALE AIR SPARGING SYSTEM

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ABSTRACT: Nonequilibrium air-water mass transfer experiments for six volatile organic compounds (VOCs) were conducted using a bench-scale air sparging system. VOCs used were carbon tetrachloride, trichloroethylene, tetrachloroethylene, chloroform, dichloromethane, and toluene. The average particle size of the porous media used ranged from 0.278 to 1.71 mm. The air-water mass transfer coefficients were estimated by fitting the experimental data to a lumped parameter model. The model assumed that the saturated porous media under air sparging conditions consisted of two zones. In the "mass transfer" zone, VOCs were directly impacted by the flow of air in the air channels, while in the "bulk water" zone, VOCs were not directly affected by the air flow in the air channels. The estimated air-water mass transfer coefficients ($K_G a$) were found to increase for higher injected air flow rates and for larger mean particle sizes of porous media but were inversely proportional to the Henry's law constant of the VOCs. An empirical correlation was developed by correlating the Sherwood number with the Péclet number, the Henry's law constant, and the mean particle size of porous media. The estimated fraction (F) of the total volume of the porous media directly affected by air channels was between 5 and 20% for fine sand, indicating that a small fraction of the porous media was affected by the advecting air stream.

INTRODUCTION

Most hazardous-waste sites, including those on the National Priority List (NPL), are contaminated with volatile organic compounds (VOCs). An emerging technology that has been shown to be effective and economical in the remediation of unconfined VOC-contaminated aquifers is the in-situ air sparging technology (Marley et al. 1992; Johnson et al. 1993). In this technology, contaminant-free air is injected into the contaminated aquifer to volatilize the VOCs. The VOC-contaminated air is then removed by a soil vapor extraction system in the unsaturated zone.

The injected air in the contaminated aquifer has been shown to move in continuous air channels in the saturated porous media (Ji et al. 1993; Johnson et al. 1993) with VOCs volatilizing across the air-water interface of the air channels into the air phase. Several researchers have assumed that local equilibrium conditions may be applicable in the modeling of the VOC transfer across the air-water interface (Rathfelder et al. 1991; Imhoff and Jaffe 1994). On the other hand, several researchers have found that the assumption of local equilibrium may not be applicable under certain conditions (Cho and Jaffe 1990; Armstrong et al. 1994). In addition, several researchers have speculated that the limiting VOC mass transfer mechanism during air sparging may not be the mass transfer at the air-water interface but rather the diffusion of VOCs from the bulk water to the air-water interface (Johnson et al. 1993; Ahlfeld et al. 1994; Hein et al. 1994).

Nonequilibrium mass transfer between air and water phases may be modeled using a first-order kinetic process:

$$J_{aw} = K_G a (H C_w - C_a) \quad (1)$$

where J_{aw} = rate of mass transferred (M/L^3T); K_G = gas-phase mass transfer coefficient (L/T); a = air-water interfacial surface area per unit volume of the saturated porous media ($1/L$); H = Henry's law constant (dimensionless, concentration/concentration); and C_a and C_w = average VOC concentrations in the air and water phases (M/L^3), respectively.

Generally, the interfacial surface area cannot be determined. Therefore, it is common to lump K_G and a together as the overall mass transfer coefficient. In the absence of fundamental theoretical models to predict the mass transfer coefficients, empirical correlations of dimensionless parameters using experimental data are often used to quantify the interphase mass transfer data (Wilkins et al. 1995; Szatkowski et al. 1995). Most of the work done to date on mass transfer coefficients for air sparging or soil venting systems is limited to one or two VOCs and for one type of porous media. In order to successfully model air sparging, there is a need to develop a more general correlation that is applicable for a wide range of porous media and for different types of VOCs.

In this study, air sparging experiments using a bench-scale soil column were conducted with six commonly found VOCs at contaminated sites and for four types of porous media. From the experimental data, the air-water mass transfer coefficients were estimated using a lumped parameter or input-output model. An empirical correlation that reasonably predicted the mass transfer coefficients was developed using several dimensionless numbers.

MATERIALS AND METHODS

Bench-Scale Air Sparging Apparatus

Air sparging experiments were conducted in a Plexiglas column with an inner diameter of 9.5 cm (3.75 in.) and a depth of 40.6 cm (16 in.). The soil depth in the column was 30.5 cm (12 in.), giving a soil volume of approximately 2.17 L (0.035 cu ft). A water level of about 1.27 cm (0.5 in.) was maintained above the soil to simulate a typical unconfined aquifer without an unsaturated zone. Air was injected into the saturated soil through a plate diffuser attached to the bottom of the column. The diffuser used was a porous stone plate (ELE International Inc., Lake Bluff, Ill.), which was made of corundum grain with an average particle size of 120 μ m. The plate diffuser was placed approximately 5 cm above the bottom of the column. A fine paste of concrete was used to seal the space between the porous stone and the wall of the column to minimize preferential air flow along the wall of the sparging column. All experimental runs were carefully conducted to ensure that there was no short-circuiting of air flow along the side of the column.

Fig. 1 shows the schematic flow diagram of the experi-

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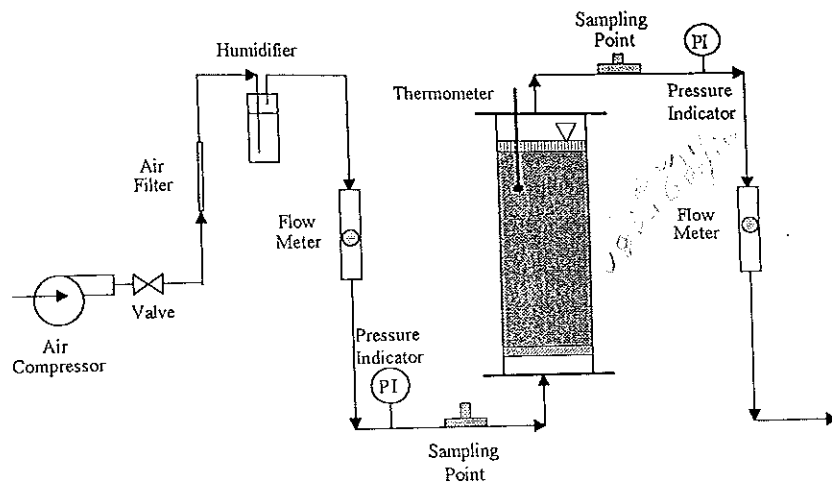


FIG. 1. Sketch of Bench-Scale Air Sparging System

TABLE 1. Physical and Chemical Properties of VOCs

Compound (1)	Abbreviation (2)	Formula (3)	Solubility ^a (mg/L) (4)	H ^b (5)	K _{oc} ^c (mL/g) (6)	D _L ^d (10 ⁻⁶ cm ² /s) (7)	D _a ^e (cm ² /s) (8)
Dichloromethane (ACS grade, EM Science)	DCM	CH ₂ Cl ₂	20,000	0.085	8.8	1.31	0.101
Chloroform (HPLC grade, Fluka)	CLF	CHCl ₃	8,000	0.147	31	1.12	0.089
Toluene (ACS grade, Fisher)	TLN	C ₆ H ₅ CH ₃	515	0.273	300	0.91	0.083
Trichloroethylene (GC grade, Fluka)	TCE	C ₂ HCl ₃	1,100	0.397	126	1.03	0.082
Carbon tetrachloride (ACS grade, Aldrich)	CT	CCl ₄	800	1.241	110	0.99	0.080
Tetrachloroethylene (ACS grade, Fluka)	PCE	C ₂ Cl ₄	140	0.667	364	0.93	0.082

Note: Data are for 25°C.

^aSolubility at 20°C.

^bHenry's law constant (dimensionless).

^cOrganic carbon partition coefficient.

^dDiffusion coefficient in water estimated using Wilke-Chang method (Welty et al. 1976).

^eDiffusion coefficient in gas estimated using Hirschfelder, Bird, and Spotz equation (Welty et al. 1976).

mental apparatus. Two sampling points on the influent and effluent air flow lines were used to collect air samples for analysis. Air for sparging purposes was supplied by an oil-free air compressor (DeVilbiss Air Power Co., Jackson, Tenn.). A 0.1- μ m compressed air filter (Cole Parmer, Vernon Hills, Ill.) was used to remove any oil, water, and solid particles in the injected air flow. To avoid evaporation of water in the soil column, air was saturated with water by passing through a humidifier prior to entering the sparging column. All equipment except the soil column was made of stainless steel, glass, or Teflon, and all parts were connected with the Teflon tubing.

Materials

VOCs used for the experimental runs were dichloromethane, chloroform, toluene, trichloroethylene, carbon tetrachloride, and tetrachloroethylene. Table 1 gives the physical-chemical properties of the six chlorinated solvents. Three different sizes of sand obtained from Sid's Corp., Brooklyn, N.Y., and one type of glass beads from Fine Industrial Supply Co., Long Island, N.Y., were used for the air sparging experiments. Table 2 summarizes the physical-chemical properties of porous media. The porous media used were coarse sand, medium sand, fine sand, and glass beads with an average particle size (d_{50}) of 1.709, 0.398, 0.278, and 0.788 mm, respectively. The hydraulic conductivities for packed columns of the porous media were estimated using a constant head method with a permeameter (ELE International, Inc., Lake Bluff, Ill.). Total carbon content and organic carbon content of the soils were determined using the wet combustion method (Allison 1960). The organic carbon fractions for all three porous media were approximately the same. Therefore, the effects of sorption may

be assumed to be similar for all three porous media although the extent of sorption for each VOC on a given porous medium would be different.

Experimental Procedures

All porous media were washed thoroughly and dried in an oven at 105°C for at least 48 h. The clean porous media were added to VOC-contaminated water in a closed glass container and mixed thoroughly. VOC-contaminated water was prepared by dissolving neat VOCs in deionized water. The packing was performed carefully by transferring the slurry layer by layer to minimize trapped air bubbles in the saturated porous media. Packing of the column was usually completed within 10 min and efforts were taken to minimize volatilization of VOCs during the packing as much as possible. The column was immediately sealed by closing tightly the influent and effluent air lines. The soil column was then allowed to equilibrate for at least 24 h before air was injected into the column.

Air flow rates used for the experiments varied from 1.5 L/min to 5 L/min. At the start of the experiment, air samples in the headspace of the soil column were analyzed to determine the initial VOC concentrations. During the sparging experiments, air samples were taken from the effluent sampling port every 5 to 15 min and analyzed by direct injection into a gas chromatograph (Shimadzu Model GC-14A, Columbia, Md.) equipped with a flame ionization detector (FID). Throughout the experiments, the temperature of the air sparging system was maintained at $22 \pm 3^\circ\text{C}$. The influent air was also analyzed to ensure that the injected air was contaminant-free. The gas chromatograph column used was a fused-silica phenyl/methylpolysiloxane phase capillary column, and the tempera-

TABLE 2. Physical and Chemical Properties of Porous Media

Soil type (1)	Coarse sand (2)	Medium sand (3)	Fine sand (4)	Glass bead (5)
Grain size (mm)	0.42~2.48	0.106~1.0	0.074~0.5	0.59~0.84
Effective grain size, d_{10} (mm)	1.126	0.187	0.155	0.613
Average grain size, d_{50} (mm)	1.709	0.398	0.278	0.788
Uniformity coefficient, d_{60}/d_{10}	1.6	2.2	2.0	1.36
Porosity	0.410	0.388	0.476	0.397
Hydraulic conductivity, K (cm/s)	0.0549	0.0273	0.0057	0.0506
Specific density, S_w (g/cm ³)	2.891	2.606	2.908	2.629
Bulk density (g/cm ³)	1.561	1.590	1.525	1.586
Total carbon content (%)	0.38	0.44	0.34	0
Organic carbon content, f_{oc} (%)	0.30	0.39	0.31	0

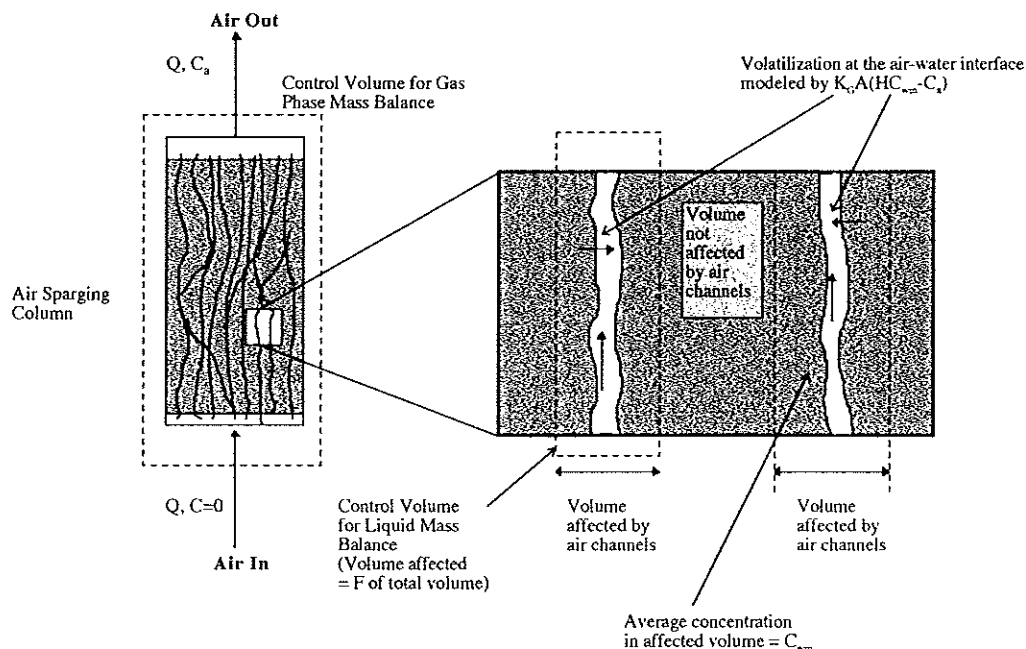


FIG. 2. Sketch Illustrating Two-Zone Concept and Mass Balances Taken

tures of the injection port and detector were maintained at 220°C and 250°C, respectively.

The volume of the air channels, V_{ac} , during air sparging was estimated by measuring the rise in the water level in the soil column. V_{ac} was found to vary between 0.015 L for fine sand at an air flow rate of 1.5 L/min and 0.089 L for coarse sand at an air flow rate of 5.0 L/min. At the end of the experimental run, soil and water samples were collected from the column and analyzed for residual VOCs. VOC concentrations in the dewatered soil samples were determined using a methanol extraction procedure (Pavlostathis and Mathavan 1992).

Lumped Parameter Model

Air channels were assumed to be formed and were evenly distributed throughout the saturated porous media during air sparging of the column. Furthermore, it was assumed that there were no air holdups and that the air velocities in the air channels were the same. As VOCs volatilized from the air-water interface of the air channels, an aqueous concentration gradient zone around the air channels will develop whereby VOCs present in the bulk water away from the air channels will have to diffuse through this zone to the air-water interface. Therefore, under air sparged conditions, the saturated porous media may be assumed to consist of a zone that was directly impacted by the air channels and a zone that was not directly affected by the air channels (see Fig. 2). The two zones may be designated as the "mass transfer" zone and the "bulk media" zone, respectively. Due to the slow diffusion of VOCs in

the aqueous phase to the air-water interface as compared to the rapid volatilization of VOCs at the air-water interface, the mass of VOCs present in the "bulk media" zone may be assumed to remain constant during air sparging.

For modeling purposes, the volume fraction of the porous media directly affected by the air channels may be defined as F , which is the volume of the "mass transfer" zone divided by the total volume of the saturated porous media ("mass transfer" zone and "bulk media" zone). The fraction F is dependent on the size and number of the air channels formed, the distance between two air channels, the aqueous-phase diffusivity of the VOC, and the physical-chemical properties of the porous media. The larger the distance between two air channels, the smaller will be the F value and, therefore, less volume of the porous media will be impacted by the air channels.

Under constant air flow conditions, the governing equations may be derived by taking mass balances for the air phase and the "mass transfer" zone only (see Fig. 2). Since the air channels did not impact the "bulk media" zone, a mass balance for the "bulk media" was not needed. The effects of air compressibility were assumed to be negligible, while the porous media were assumed to be homogeneous within the sparging column. In addition, the aqueous concentrations of the VOCs throughout the soil column were assumed to be uniform prior to the initialization of the air sparging experiments. The VOC concentration of the influent air was assumed to be zero. The mass balance equation for the air phase of the sparging column is given by

TABLE 3. Experimental Conditions for Air Sparging Column

Soil type (1)	Coarse sand (2)	Medium sand (3)	Fine sand (4)	Glass bead (5)
Total headspace volume of air, V_a (L)	0.271	0.271	0.271	0.271
Total volume of water, V_w (L)	0.98	0.93	1.12	0.95
Total mass of porous media, M_s (kg)	3.70	3.46	3.31	3.44
Air flow rate, Q (L/min)	1.5~5	1.5~4.5	1.5~3	1.5~4.5

$$V_a \frac{dC_a}{dt} = K_G A (HC_{wm} - C_a) - Q C_a \quad (2)$$

where A = air-water interfacial area of the air channels (L^2); Q = air flow rate (L^3/T); V_a = total volume of the air channels within the sparging column (L^3); C_a = average VOC concentration in the air phase (M/L^3); and C_{wm} = average VOC water concentration of the "mass transfer" zone (M/L^3).

For the "mass transfer" zone in the aqueous phase, the change in mass per unit time in the "mass transfer" zone is equal to the mass volatilized per unit time, i.e.,

$$\frac{d[F(M_s K_p + V_w)C_{wm}]}{dt} = -K_G A (HC_{wm} - C_a) \quad (3)$$

where F = volume fraction as defined earlier (dimensionless); M_s and V_w = total mass of porous media (M) and the total volume of water within the saturated porous media (L^3), respectively; and K_p = soil-water partition coefficient (L^3/M). Since F , M_s , V_w , and K_p were assumed to be constants, the foregoing equation may be written as

$$F(M_s K_p + V_w) \frac{dC_{wm}}{dt} = -K_G A (HC_{wm} - C_a) \quad (4)$$

For porous media with high organic carbon content greater than 0.1%, the soil-water partition coefficient may be estimated from the empirical equation $K_p = f_{oc} K_{oc}$, where K_{oc} is the organic carbon partitioning coefficient (L^3/M) (Karickhoff 1984).

The initial vapor phase concentration, C_a^0 , was obtained experimentally while the initial aqueous phase concentration, C_{wm}^0 , was estimated from the following expression:

$$C_{wm}^0 (M_s K_p + V_w) = M^0 - V_a C_a^0 \quad (5)$$

where M^0 = initial mass of VOC in the sparging column; and V_a = volume of headspace above the sparging column. Since the total air-water interfacial area of the air channels cannot be determined, K_G and A were lumped together as an overall air-water mass transfer coefficient, $K_G A$ (L^3/T). Eqs. (2) and (4) have four unknowns. By selecting various values of $K_G A$ and F and using the initial aqueous phase concentration, C_{wm}^0 , and the air phase concentration, C_a^0 , the air phase concentration at time t was estimated by solving numerically (2) and (4). The predicted air phase concentrations were compared with the experimentally determined air phase concentrations, and the $K_G A$ and F values were adjusted to minimize the sum of squares of deviations. The best combination of $K_G A$ and F that gave the minimum sum of squares of deviations was selected. Table 3 presents the experimental conditions used for the numerical calculations of the model.

RESULTS AND DISCUSSION

The average experimental mass balances of VOCs before and after air sparging were found to be approximately 90%. This indicated that sorption of VOCs to the Plexiglas column and losses during the experiment were minimized. The differences in the masses before and after the experiment were prob-

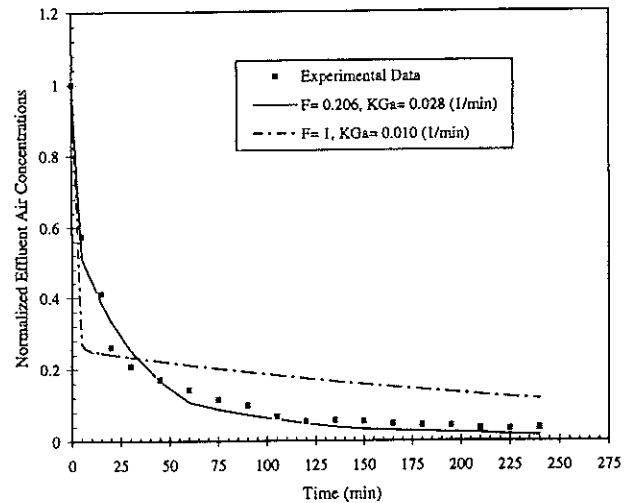


FIG. 3. Curve Fitting of Experimental Data with Two-Zone Model for TCE in Medium Sand at Air Flow Rate of 1.5 L/min

ably due to losses during the packing of the column and analytical errors. Fig. 3 shows the change in trichloroethylene effluent air concentrations over time for a typical air sparging experiment, as well as the modeling results for $F = 0.206$. Also plotted in Fig. 3 is the model prediction for $F = 1$. By assuming the whole media volume was affected by the air flow ($F = 1$), the model did not fit the experimental data well. However, if only a fraction of the media volume was affected by the air channels, a better-fit curve was obtained. It is obvious that the fraction of the media volume that was affected by air flow cannot be predicted a priori. However, the curve fitting approach adopted here may provide a rough estimate of the fraction of the porous media that was affected by the air channels.

Air-Water Mass Transfer Coefficients

Table 4 summarizes the estimated mass transfer coefficients, $K_G a$, for five VOCs and eight air flow rates in three different sands. The $K_G a$ values were computed using $K_G A/V$, where V is the total volume of saturated porous media. As observed in Table 4, the smaller the particle size of the soil, the smaller were the $K_G a$ values. In addition, the $K_G a$ values were proportional to the air flow rate for the coarse and medium sand but somewhat erratic for fine sand. With regard to the Henry's law constant of the VOCs, a weak inversely proportional trend was observed with the $K_G a$ values. The overall gas phase mass transfer coefficient, $K_G a$, is related to overall liquid phase mass transfer coefficient, $K_L a$, by the relationship $K_L a/H$ (Mackay et al. 1979), thus making the overall liquid phase mass transfer coefficient directly proportional to the Henry's law constant. Ji et al. (1993) showed in a two-dimensional laboratory-scale experiment that the size and number of air channels increased for an increase in the air flow rate. Since the total air-water interfacial surface area is proportional to the number and size of the air channels, an increase in an air flow rate will result in an increase in the $K_G a$ values.

The factor F represents the fraction of the saturated porous media that was affected by the air channels during air sparging. As presented in Table 5, the values of F were larger for coarse sand as compared to fine sand. This was as expected since the air would probably flow more easily through coarse sand than fine sand. Depending on the VOC sparged, the estimated fraction of the total volume affected by air sparging varied from 5 to 20% for fine sand but may be as high as 50% for coarse sand. These differences were attributed to the properties of the porous media, where more channels were expected to form for coarser materials than fine materials. This would mean that the

TABLE 4. Air-Water Mass Transfer Rate Coefficients for Air Sparging Experiments

Air flow rate (L/min) (1)	Air-Water Mass Transfer Coefficient, $K_G a$ (1/min)				
	Dichloromethane (2)	Chloroform (3)	Toluene (4)	Trichloroethylene (5)	Carbon tetrachloride (6)
(a) Coarse sand ($d_{50} = 1.709$ mm)					
1.5	0.083	0.056	0.082	0.033	0.011
2.0	0.129	0.077	0.121	0.049	0.021
2.5	0.130	0.086	0.090	0.042	0.019
3.0	0.186	0.104	0.156	0.053	0.024
3.5	0.157	0.120	0.184	0.066	0.028
4.0	0.129	0.108	0.149	0.049	0.022
4.5	0.288	0.213	0.299	0.096	0.056
5.0	0.228	0.176	0.327	0.109	0.052
(b) Medium sand ($d_{50} = 0.398$ mm)					
1.5	0.054	0.040	0.061	0.028	0.013
2.0	0.074	0.050	0.073	0.034	0.015
2.5	0.122	0.067	0.136	0.043	0.022
3.0	0.127	0.081	0.147	0.052	0.025
3.5	0.139	0.083	0.151	0.053	0.024
4.0	0.091	0.060	0.100	0.045	0.019
4.5	0.137	0.106	0.160	0.050	0.035
(c) Fine sand ($d_{50} = 0.278$ mm)					
1.5	0.042	0.030	0.033	0.013	0.009
2.0	0.035	0.025	0.043	0.018	0.009
2.5	0.047	0.038	0.059	0.025	0.012
3.0	0.038	0.030	0.047	0.019	0.010
3.5	0.054	0.042	0.062	0.025	0.014

TABLE 5. Values of F for Air Sparging Experiments

Air flow rate (L/min) (1)	F (Dimensionless)				
	Dichloromethane (2)	Chloroform (3)	Toluene (4)	Trichloroethylene (5)	Carbon tetrachloride (6)
(a) Coarse sand ($d_{50} = 1.709$ mm)					
1.5	0.221	0.218	0.202	0.216	0.233
2.0	0.239	0.221	0.251	0.224	0.289
2.5	0.270	0.290	0.291	0.283	0.331
3.0	0.308	0.302	0.306	0.308	0.369
3.5	0.327	0.365	0.349	0.359	0.423
4.0	0.371	0.428	0.411	0.456	0.512
4.5	0.356	0.413	0.400	0.437	0.558
5.0	0.301	0.335	0.359	0.398	0.515
(b) Medium sand ($d_{50} = 0.398$ mm)					
1.5	0.151	0.165	0.198	0.206	0.243
2.0	0.175	0.174	0.197	0.203	0.238
2.5	0.191	0.194	0.199	0.220	0.252
3.0	0.227	0.255	0.228	0.278	0.367
3.5	0.222	0.250	0.239	0.258	0.326
4.0	0.214	0.253	0.255	0.283	0.351
4.5	0.198	0.231	0.217	0.229	0.387
(c) Fine sand ($d_{50} = 0.278$ mm)					
1.5	0.059	0.068	0.068	0.072	0.102
2.0	0.076	0.090	0.090	0.101	0.143
2.5	0.094	0.116	0.133	0.131	0.206
3.0	0.092	0.120	0.134	0.134	0.193
3.5	0.086	0.097	0.095	0.097	0.146

distance between the air channels would be closer for coarse materials, resulting in a larger volume of the porous media that would be affected by the air channels. Similarly, the aqueous effective diffusion of VOCs would be faster in coarser materials than in fine materials. Because of the difference in the properties of VOCs such as the aqueous diffusivity and in the properties

of the porous media, the fraction of the porous media affected by air sparging was also different for different VOCs.

An interesting point to note is that the values of F reached a maximum value but then decreased for a further increase in air flow rates. The number of air channels may increase with higher air flow rates but beyond a certain air flow rate the air channels may coalesce to form larger air channels (Ji et al. 1993). With fewer but larger air channels instead of a larger number of smaller air channels, the distance between two air channels may increase. This may lead to a corresponding decrease in the fraction of media volume affected by the air channels.

Air-Water Mass Transfer Correlation

The estimated mass transfer coefficients, $K_G a$, for five VOCs (trichloroethylene, dichloromethane, chloroform, toluene, and carbon tetrachloride) in three porous media were correlated with several dimensionless numbers. The results for tetrachloroethylene and the aforementioned five VOCs in glass beads were reserved for the validation of the correlation. The dimensionless numbers used were Sherwood number (Sh), Péclet number (Pe), and several physical-chemical properties of VOCs and porous media. Definition of Sherwood number and Péclet number are as follows:

$$Sh = \frac{K_G a(d_{50})^2}{D_G} \tag{6}$$

$$Pe = \frac{v_G d_{50}}{D_G} \tag{7}$$

where d_{50} = mean particle size of the porous media (L); D_G = molecular diffusion of VOCs in the air (L^2/T); μ_G and ρ_G = dynamic viscosity (M/LT) and density (M/L^3) of air, respectively; and v_G is the average air velocity (L/T). Both the Henry's law constant and the normalized mean particle size were considered for the correlation. The normalized mean particle size was defined as $d_0 = d_{50}/d_m$, where d_m (=0.05 cm) is the mean grain size of medium sand (Wilkins et al. 1995). The empirical dimensionless correlation may be presented as

$$Sh = \beta_0 Pe^{\beta_1} d_0^{\beta_2} H^{\beta_3} \tag{8}$$

where $\beta_0, \beta_1, \beta_2,$ and β_3 = constants. The parameters β_i were estimated by stepwise multiple regression analysis using the statistical software package SPSS to obtain the best fit param-

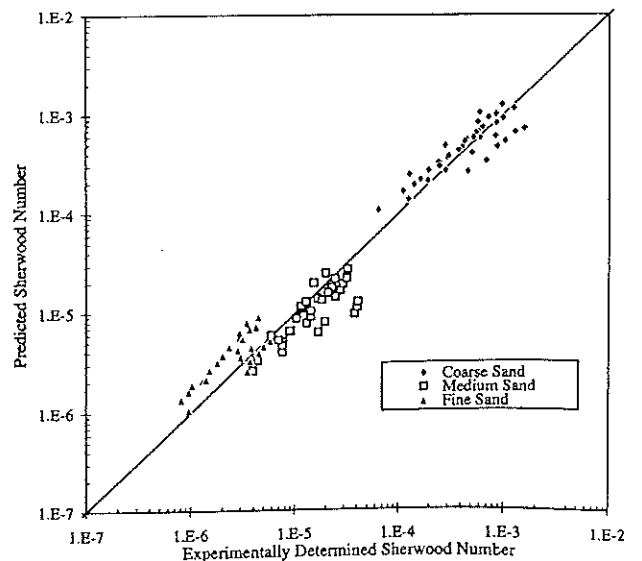


FIG. 4. Comparison of Experimentally Determined Sherwood Numbers with Predicted Sherwood Numbers

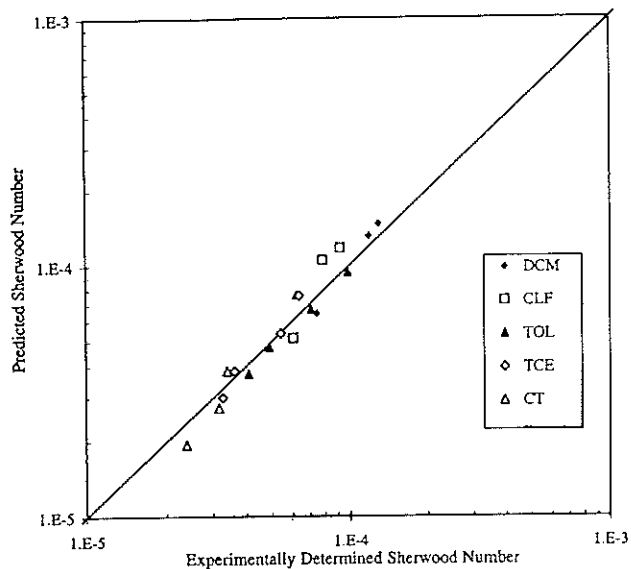


FIG. 5. Comparison of Experimentally Determined Sherwood Numbers for Glass Beads with Predicted Sherwood Numbers (DCM = Dichloromethane; CLF = Chloroform; TOL = Toluene; TCE = Trichloroethylene; CT = Carbon Tetrachloride)

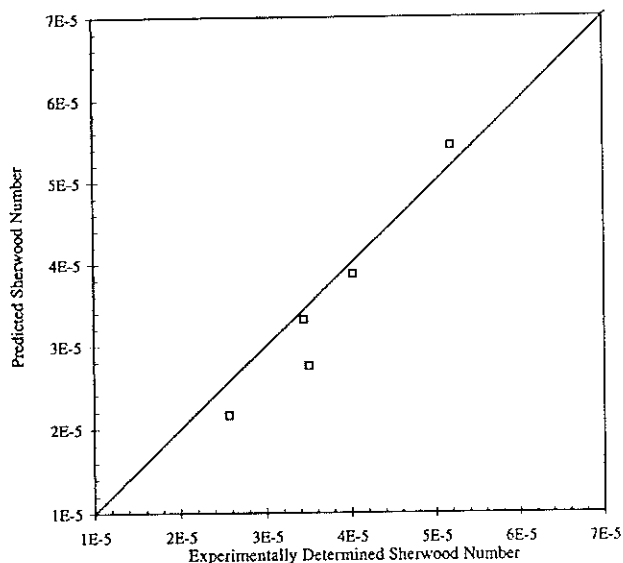


FIG. 6. Comparison of Experimentally Determined Sherwood Numbers for Glass Beads and Tetrachloroethylene (PCE) with Predicted Sherwood Numbers

eters for the log-linearized form of (8). With a significance level $\alpha = 0.05$ (95% confidence limit) and a total of 100 data points, the best fit correlation ($R^2 = 0.96$) was

$$Sh = 10^{-4.71} Pe^{0.84} d_0^{1.71} H^{-0.61} \quad (9)$$

Eq. (9) shows that mass transfer was affected by the physical properties of the porous media such as the particle size, air flow rate, the diffusivity of the VOCs, and the volatility of the VOCs as represented by the Henry's law constant. Fig. 4 presents a comparison of experimentally determined Sherwood numbers with Sherwood numbers predicted by (9). To assess the utility of the foregoing empirical correlation, the correlation was used to predict the mass transfer coefficients for experiments conducted with glass beads as the porous media. Fig. 5 presents the predicted results of the correlation and the experimental results obtained using glass beads. As indicated in Fig. 5, the predictions of the correlation agreed well with the experimental Sherwood numbers for the five different VOCs using glass beads as the porous media. To further assess

the utility of the correlation, a separate experiment was conducted using glass beads as the porous media and tetrachloroethylene (PCE) as the VOC. Fig. 6 shows that the predicted values of (9) agreed well ($R^2 \approx 0.92$) with the experimentally estimated values for PCE and glass beads as the porous media.

CONCLUSIONS

Air sparging column experiments were conducted to investigate the nonequilibrium air-water mass transfer of VOCs in the saturated porous media. The saturated porous media under air sparging conditions may be viewed as consisting of two zones: a "mass transfer" zone, in which VOCs were affected by the flow of air in the air channels resulting in the transfer of VOCs from the aqueous phase to the gas phase, and a "bulk media" zone, in which air channels have low or no direct impact. Air-water mass transfer rate coefficients were found to be higher for higher air flow rates and for larger mean particle size of the porous media. Based on the two-zone concept, the volume fraction F (the volume of the mass transfer zone divided by the total volume of the saturated porous media) affected by the air channels varied from as low as 5 to 20% for fine sand but as high as 50% for coarse sand. The mass transfer coefficients and F -values obtained in this study implied that the volatilization rates for air sparging in the saturated zone may not be as efficient as that for a soil vacuum extraction systems in the unsaturated zone and that only a fraction of the porous media will be affected by the advecting air stream.

An air-water mass transfer correlation was developed using the Sherwood number, the Péclet number, the Henry's law constant, and the mean particle size of porous media. Data from air sparging experiments for five different VOCs and three types of sand (fine, medium, and coarse) were used for the correlation. The correlation was found to predict the experimental air-water mass transfer coefficients for the five VOCs in a different porous media. In addition, the correlation was found to predict the mass transfer coefficients for an additional VOC, tetrachloroethylene, in glass beads. Since the correlation developed may be used to predict the mass transfer coefficients for a variety of VOCs and porous media, the correlation developed in this work is more versatile and applicable than currently available correlations. It must be pointed out that the results obtained in the study are for mass transfer in the immediate vicinity of a sparging well only, and expected behavior in the field of an in-situ air sparging system away from the vicinity of the well may be different.

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