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Influence of Vapor-Phase Sorption and Diffusion on the Fate of Trichloroethylene in an Unsaturated Aquifer System

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■ This research evaluates the influence of vapor-phase sorption and diffusion on the fate and transport of a common volatile pollutant, trichloroethylene (TCE). Vapor-phase sorption of TCE by a porous aluminum oxide surface coated with humic acids (to simulate an aquifer material) was observed to be highly dependent on moisture content. Linear partition coefficients for binding of TCE vapor under a range of unsaturated conditions were 1–4 orders of magnitude greater than the value measured for the saturated sorbent. In addition, laboratory measurement of the TCE diffusion coefficient through the simulated aquifer material indicated that an existing empirical formula used to estimate this parameter can be in error by as much as 400%. The significance of differences in sorptive partition coefficients and diffusion coefficients was examined with an existing one-dimensional vertical transport model for the unsaturated zone. Model calculations indicate that the common practice of assuming saturated partition coefficients apply to unsaturated conditions should be avoided to obtain accurate predictions of volatile contaminant transport.

Introduction

Most studies dealing with the transport and sorption of groundwater contaminants have focused on chemical, biological, and physical activity in the saturated zone. However, a major category of groundwater pollutants are volatile organic compounds that can readily move between the aqueous phase and vapor phase in aquifers that have saturated and unsaturated zones. An understanding of the extent and significance of vapor-phase transport and reaction may be important for accurately forecasting the movement of volatile contaminants and in evaluating the usefulness of alternative remedial methods for removing pollutants.

Compared to our understanding of pollutant behavior in saturated systems, our present knowledge of vapor-phase reactions in soils is relatively deficient. For example, the aqueous-phase sorptive partitioning coefficient of a wide array of nonionic organic compounds may generally be estimated (within a factor of 3–10) from a knowledge of two parameters: (1) a measure of the pollutant hydrophobicity such as the octanol–water partitioning coefficient or aqueous solubility and (2) a measure of soil hydrophobicity such as the weight fraction of organic carbon (*1*, *2*). By comparison, our understanding of organic vapor adsorption allows no such empirical prediction. Vapor-phase sorption reactions are anticipated to depend on specific soil properties that may not play a significant role in control of sorption in saturated systems. For example, the results of Chiou and Shoup (*3*) suggest that competition between organic vapors and water vapor for adsorption sites on soil minerals may be extremely important.

Transport processes for organic solutes in saturated systems include advection, dispersion, and diffusion. In the absence of vapor pressure gradients, gaseous diffusion is expected to be the major mechanism for vapor transport. Since vapor-phase diffusion coefficients greatly exceed those in the aqueous phase, movement of organic vapors in the gaseous headspace of unsaturated aquifers may be a significant aspect of volatile pollutant transport.

It is the purpose of this paper to report the results of a sequence of laboratory experiments and model simulations performed to determine the potential impact of vapor-phase adsorption and gaseous diffusion on the movement of trichloroethylene (TCE) in unsaturated aquifer systems. Linear sorptive partitioning coefficients for TCE were measured both from aqueous solution and from the vapor phase onto a synthetic soil. Vapor-phase sorption was evaluated for several moisture contents. The gaseous diffusion coefficient for TCE in the synthetic soil was also measured. This information was incorporated into an existing one-dimensional behavior assessment model for volatile organic materials to illustrate the impact of vapor-phase sorption and diffusion on the fate of TCE.

TCE was selected as the subject for the study because it is one of the most common groundwater pollutants in the nation. In 1980, 18 states surveyed reported a total of 2894 wells containing volatile organics, of which TCE was the most often detected compound (*4*).

Determination of Partition Coefficients. Methods used to determine sorptive partition coefficients include bottle-point equilibrium and/or soil column retardation studies. We have employed a recently developed headspace technique (*5*) to measure the aqueous partition coefficient for TCE. The procedure was also modified to obtain TCE vapor-phase partition coefficients.

In analysis of solute sorption in aqueous systems, difficulties can arise if results are based on direct sampling of the aqueous phase, particularly if the compound of interest is bound to colloidal solids or dissolved macromolecules that are not removed in separation processes such as filtration or centrifugation. Experimental artifacts of this nature are one of the explanations offered to describe the "solids effect", in which linear sorptive partition coefficients are observed to decrease with increasing solids concentration (*6–8*). Since headspace analysis obviates the need for separation of solids from the aqueous phase, solids effects that result from incomplete separation should be avoided. In the results described below, we have compared the TCE sorptive partitioning coefficient obtained with the headspace batch equilibration procedure (over a range of solids concentrations) with the results of a soil column study.

Headspace Theory: Aqueous-Phase Partition Coefficient. The headspace procedure makes use of Henry's law, which interrelates the concentration of a compound in aqueous and gaseous phases at equilibrium:

$$\gamma C_L = C_G/K_H \qquad (1)$$

where C_L is the liquid concentration, C_G is the gaseous concentration, K_H is Henry's constant (dimensionless), and γ is the aqueous activity coefficient correcting for nonideal behavior. To evaluate the sorption process, a system with known liquid volume, gas volume, and mass of sorbent is compared to a control, which contains no sorbent. If the

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total mass of the volatile compound in each system is the same, then the mass balance equations for each system may be equated. If, in addition, a linear adsorption isotherm is used to describe the relationship between the sorbed and liquid concentrations, then

$$C_s = X/M = K_d C_L \tag{2}$$

where C_s = sorbed concentration (mass sorbed/mass solid), X = mass sorbed, M = mass of solid sorbent, and K_d = the solid–liquid partition coefficient (cm^3/gm). Following the procedure of Garbarini and Lion (*5*), a combination of the mass balance equations for the control and the system containing sorbent, and substitution of eq 1 and 2 gives

$$(C_{G_1}/C_{G_2})\frac{V_{G_1}K_H\gamma + V_{L_1}}{V_{G_2}K_H\gamma + V_{L_2}} = K_d[M/(V_{L_2} + K_H\gamma V_{G_2})] + 1 \tag{3}$$

with V_{L_1} and V_{G_1} being the volume of liquid and gas in a standard control bottle without sorbent (mL), V_{L_2} and V_{G_2} being the liquid and gas volumes in bottles containing sorbent, C_{G_1} being the headspace vapor concentration in the control, and C_{G_2} being the vapor concentration in the bottle with sorbent.

Headspace Theory: Vapor-Phase Partition Coefficient. The linear partition coefficient K_d' (where $C_s = K_d'C_G$) for the vapor–solid adsorption isotherm may also be obtained by mass balance principles. A system with known gas volume and mass of sorbent may again be compared to a control, which contains no sorbent. If the same mass of contaminant vapor is introduced into each system, the mass balance equations must be equal:

$$C_{G_1}V_{G_1} = C_{G_2}V_{G_2} + X \tag{4}$$

where X is the mass of vapor that is adsorbed (g). The quantity X may be determined if the vapor adsorption isotherm is known. The adsorption model of Brunauer et al. (*9*) is commonly used to characterize the adsorption of gases by solids. At low vapor pressures of the adsorbate gas, the Brunauer–Emmett–Teller (BET) model equation reduces to a linear isotherm:

$$X/M = K_d'C_{G_2} \tag{5}$$

where K_d' is the soil–vapor partition coefficient (cm^3/g). Combining eq 4 and 5 results in

$$(C_{G_1}/C_{G_2})(V_{G_1}/V_{G_2}) = K_d'(M/V_{G_2}) + 1 \tag{6}$$

The parameters K_d and K_d' may be determined by calculating the slope of a plot of the left-hand side of eq 3 and 6 vs $M/(V_{L_2} + K_H\gamma V_{G_2})$ or M/V_{G_2}, respectively.

Experimental Methods and Materials

A simulated soil was used in all experiments to ensure the uniformity of sorbent properties and the ability to reproduce samples. Alumina oxide (Fisher Scientific adsorption alumina, 80–200 mesh) was coated with humic acid (Aldrich Chemical Co.) to provide a surface to serve as a sorbent for TCE. The coating procedure described by Garbarini and Lion (*5*) was followed.

The organic carbon content of the coated material was measured as 0.48% by the Walkley–Black method for soil analysis (*10*). This value is characteristic of the low carbon content of aquifer materials, whereas surface soils often have a higher carbon fraction. A specific gravity of 3.04 in the simulated soil was measured by using the method of Lambe (*11*). The BET surface area of the coated particles was determined to be 206 m^2/g by N_2 adsorption with a Quantachrome Quantasorb surface area analyzer.

Measurement of Soil–Liquid Partition Coefficient. Adsorption experiments were carried out in 50-mL glass hypovials of known volume containing various masses of coated alumina. To determine the aqueous-phase partition coefficient, 20 mL of 0.1 M NaCl was added to each bottle. This electrolyte was found to adequately swamp out any ionic influences attributed to the sorbent (*5*). In addition, Garbarini and Lion (*5*) have shown that the sorptive partition coefficient of TCE is unaffected by the presence of the 0.1 M NaCl electrolyte relative to that obtained in distilled water. TCE-saturated water (100 μL) was added, and the bottles were immediately sealed with Teflon-lined rubber septa and an aluminum crimp cap (Supelco, Inc.). Four to six replicates were prepared for each mass of sorbent evaluated. The bottles were then rotated for 6 h in a chamber maintained at 25 °C (±0.1 °C) by a circulating water bath. A 1-mL sample of the gaseous headspace was analyzed with a Varian 1440 gas chromatograph with a column of 20% SP 2100 and 0.1% Carbowax on 100/120 Supelcoport (Supelco, Inc.) operated isothermally at 135 °C.

The measurements of Henry's Law constant for TCE and the activity coefficient for 0.1 M NaCl were not repeated for this study. The values obtained by Garbarini and Lion (*5*), $K_H = 0.397$ and $\gamma = 1.055$, were used and are consistent with other reported values (*12–14*).

Measurement of Soil–Vapor Partition Coefficients. The above experimental procedure required slight modifications to adapt it for vapor sorption analysis. Bottles contained oven-dry or moist (see below) adsorbent in the absence of an aqueous phase. a 1.0-mL sample of TCE vapor taken from the headspace over pure liquid TCE at 25 °C was delivered to each sample bottle with a gas-tight syringe. The adsorbent and vapor were equilibrated for 12 h.

Two different moisture content values were obtained by exposing the synthetic soil sample to water vapor. The soil was placed in a chamber with water maintained at a constant temperature and allowed to equilibrate over a 3-day period. A moisture content of 8.2% (grams of H_2O/g dry weight) was obtained at 15 °C, and at 40 °C the water content achieved was 11.6%. The moist soil was weighed into desiccated 50-mL sample bottles, injected with 1 mL of TCE vapor, and immediately sealed with Teflon/rubber septa and an aluminum crimp cap. The headspace analysis procedure followed was then the same as that described above.

Validation of Headspace Technique with Soil Column Measurements. The validity of the headspace result for the soil–liquid partitioning was confirmed by performing a column study using the simulated soil. The experimental procedure developed by Zhong et al. (*15*) was employed for the column experiments. A Sage Model 220 syringe pump operated two Hamilton 1-mL gas-tight syringes for a continuous, pulse-free delivery. A 60-cm borosilicate glass column (Spectrum) with a 2.5-cm diameter was encased in a water jacket for precise temperature control at 25 °C. The porosity of the packed column was calculated gravimetrically to be 0.56 cm^3/cm^3. A steady-state flow of 0.1 M NaCl at a rate of 6.27 ± 0.02 (±0.4%) mL/h was established, resulting in an estimated pore-water velocity of 2.3 cm/h.

The TCE concentration of the column effluent was monitored with the use of a radiolabeled ^{14}C tracer. A 3-mL pulse input of water containing ^{14}C-labeled TCE was injected into the column with a gas-tight syringe. The

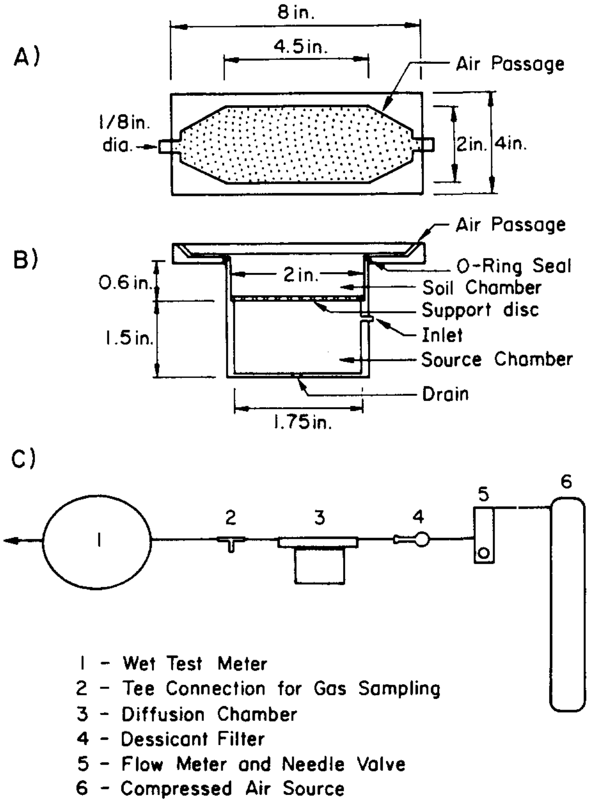

Figure 1. Diffusion test cell [(after Farmer et al. (*16*)]: (A) top view, (B) side view, and (C) schematic of test assembly.

column effluent was collected in scintillation cocktail (Fisher Scinti-Verse E) and analyzed on a Tracor analytic scintillation counter, Model 6882. A mass balance calculation indicated that 79% of the TCE applied was accounted for in the column effluent. The volatile nature of TCE is likely to be the major factor responsible for any loss.

Diffusion of Pollutant Vapors. In an unsaturated system, the steady-state diffusive flux is determined by the diffusion coefficient characteristic of the compound in transport, D_G, and the concentration gradient across the soil layer. This relationship is expressed by Fick's first law:

$$J = -D_G(C_m - C_{vp})/L \qquad (7)$$

with J being the vapor flux through the soil (g/cm^2 day), C_{vp} being the concentration of the volatilizing material at one face of a soil layer, C_m being the measured concentration at the other face (g/mL), and L being the depth of the soil layer (cm).

A diffusion cell was constructed on the basis of the design of Farmer et al. (*16*) to measure diffusion of gaseous TCE through the simulated soil and is shown in Figure 1. An airstream was passed across the synthetic soil and carried TCE vapor out of the cell. The airflow rate through the cell was measured with a wet-test meter. Diffusion experiments were carried out in a constant-temperature room at 21.5 °C. A 1-mL sample of the flowing gas stream was periodically withdrawn by a gas-tight precision sampling syringe and analyzed on a Hewlett-Packard 5890A gas chromatograph with an HP3392A integrator; a standard methanol solution of known TCE concentration was used for calibration.

At a constant temperature, the TCE vapor concentration in the sample chamber below the soil can be calculated from TCE vapor pressure with the ideal gas law. The vapor pressure P of liquid TCE is a temperature-dependent relationship expressed by (*17*)

$$\log P(t) = A - B/(t + C) \qquad (8)$$

where $A = 6.5183$, $B = 1018.6$, $C = 192.7$, t = temperature, and P is in millimeters of Hg (*17*). At the experimental temperature of 21.5 °C, P is 57.9 mmHg, or 0.076 atm.

The vapor flux J through the apparatus at a gasflow rate Q (cm^3/day) and soil-surface area A (cm^2) may be determined from the concentration of diffused pollutant C_m:

$$J = QC_m/A \qquad (9)$$

Combining eq 7 and 9 gives the following equation for the diffusion coefficient:

$$D_G = QC_mL/(C_{vp} - C_m)A \qquad (10)$$

Experimental Results and Discussion

Soil–Liquid Partition Coefficient. The results of the saturated sorption experiments fit to eq 3 are shown in Figure 2A. The mass of sorbent in the saturated system ranged from 0 to 20.000 g (giving a maximum of a 1:1 ratio of grams of sorbent mass to milliliter of solution). The solid–liquid partition coefficient of TCE onto humic-coated alumina adsorption was found to be 0.29 mL/g (or cm^3/g) by calculating the slope of the line ($r^2 = 0.94$). Normalizing this value for organic carbon content yields a K_{oc} of 61.1 cm^3/g ($K_{oc} = K_d$/fraction organic content).

Since the headspace procedure does not require a physical separation of solids, the solids effect that results from such separations should be avoided. As a check of this hypothesis, a TCE column experiment was performed to validate the partition coefficient obtained with the bottle equilibration procedure.

In saturated column experiments, the velocity of a sorbed contaminant (which obeys a linear sorption isotherm) may be related to that of an inert tracer through the retardation factor R where

$$R = 1 + (\rho_b/\phi)K_d \qquad (11)$$

with ρ_b = bulk density of soil (g/cm^3) and ϕ = porosity.

The nonlinear least-squares inversion method of Parker and van Genuchten (*18*) was used to determine the soil retardation factor for TCE from the column breakthrough curve. The model was run for a deterministic linear equilibrium adsorption isotherm and an input of a pulse of known concentration. The degradation rate for TCE was assumed to be negligible. The resulting retardation factor (R) was calculated as 1.79 with an r^2 of 0.83. With a bulk density of 1.17 g/cm^3, the resulting partition coefficient is 0.38 cm^3/g. Given the experimental difficulties inherent in measuring small partition coefficients, this value agrees reasonably well with the value of 0.29 measured with the headspace technique. Since solids effects should result in a lower value of K_d for the column experiment (in which sorbent concentration is highest), differences in the two values may not be attributed to this phenomenon.

Soil–Vapor Partition Coefficients. The solid–vapor partition coefficient K_d' for TCE onto the oven-dried (105 °C) simulated soil (calculated from the slope of the adsorption isotherm plotted in Figure 2B) is 11 870 cm^3/g, which is over 10^5 times greater than the aqueous-phase linear partition coefficient. Hence, the percentage of material that would be expected to be sorbed onto the dry soil in much greater than would have been predicted by the partition coefficient measured under saturated conditions (as is often the practice). As the sorptive capacity of the dry soil was much higher than a soil that is saturated, less sorbent was needed in the experiments to yield

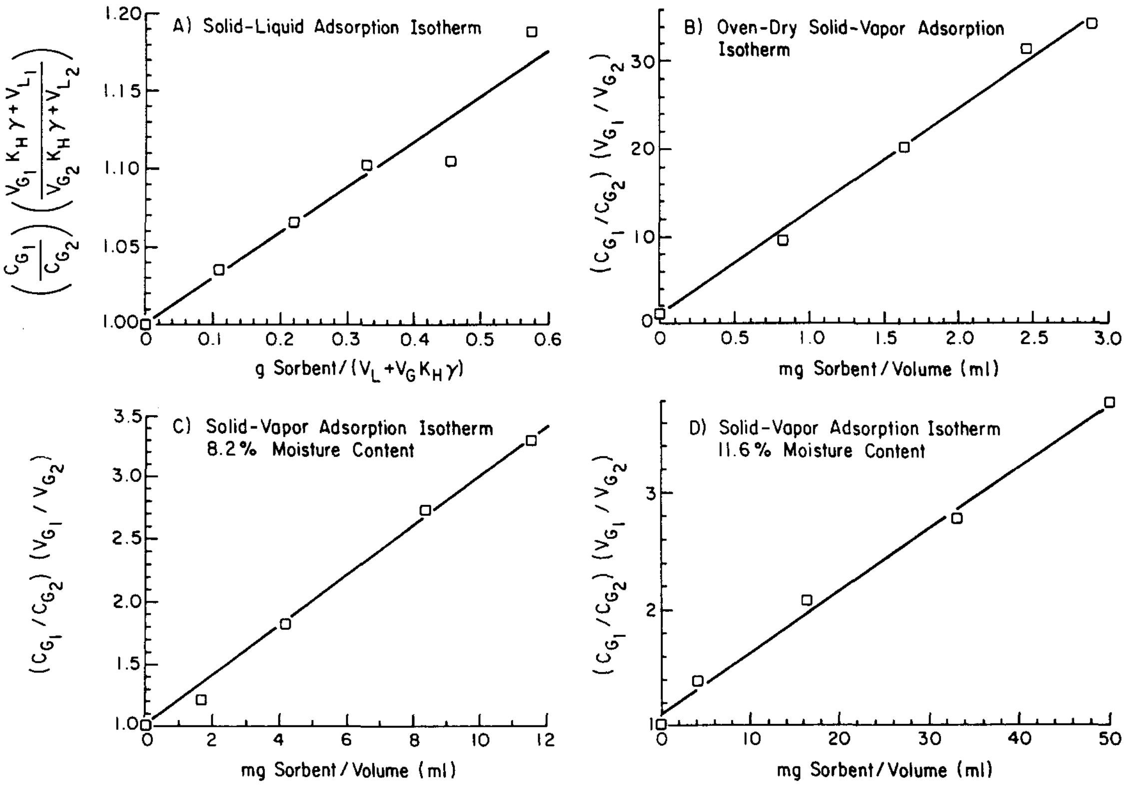

Figure 2. Reaction of TCE with humic-coated alumina: (A) sorption of dissolved TCE (saturated solid), (B) sorption of TCE vapor by oven-dry solid, and (C and D) sorption of TCE vapor by moist solid.

measurable changes in gas concentrations. The mass of sorbent used for sorption of TCE vapor ranged from 0.0500 to 0.1750 g.

Vapor sorption partition coefficients were not normalized with respect to soil organic content. Chiou and Shoup (*3*) have experimentally demonstrated that at subsaturation soil minerals may control organic vapor partitioning. However, in saturated aqueous systems, water displaces nonionic organic sorbates from hydrophilic soil mineral surfaces, and soil organic matter is most likely to account for binding of hydrophobic pollutants.

The soil region overlying the water table could conceivably contain moisture contents ranging from a few percent to near saturation. A typical field moisture content for the intermediate zone of a partially saturated soil layer is approximately 10%. The adsorption isotherms for the synthetic soil with moisture contents of 8.2% and 11.6% are presented in Figure 2, parts C and D. The TCE partition coefficient at 8.2% water content was 207 cm^3/g, and at 11.6% the value decreased to 53.9 cm^3/g. Both of these values are still 2 or more orders of magnitude greater than that determined for the saturated synthetic soil (K_d = 0.29). Therefore, in spite of the fact that hydrophilic mineral surfaces strongly bind water vapor, it may be very important to consider organic vapor-phase partitioning equilibria in unsaturated aquifer systems.

The experimental results given here are specific to the synthetic aquifer material (i.e., humic acid coated alumina) that was employed in this study. This surface's principle characteristics are a high specific area and low carbon content. It can be anticipated that the magnitude of TCE vapor partition coefficients and their dependence on moisture content will be different on different sorbents. The physical–chemical nature of soils can, of course, vary widely. Aquifer sands, for example, have much lower specific surface areas than the synthetic soil and would therefore be expected to have lower vapor partition coefficients. The choice of a commercial humic acid as the experimental organic coating also will influence the results. Malcom and MacCarthy (*19*) have reported pronounced differences between ^{13}C NMR spectra of commercial humic acids and natural organic materials. It is also clear that natural organic materials can vary widely in their pollutant-binding properties depending upon their hydrophobicity (*20*) and degree of aromaticity (*21*).

The purpose of this research was to illustrate the possible importance of vapor-phase sorption reactions. The experimental results for humic-coated alumina indicate that the assumption that vapor sorption partition coefficients may be equated with saturated partition coefficients can lead to large errors unless experimental data are available demonstrating that this assumption is reasonable for the soil of interest. The functional dependencies of specific soil characteristics on vapor-phase sorptive partitioning will be the subject of later research.

Estimation of the Wet versus Dry Sorption-Site Distribution in an Unsaturated Soil. As a first approximation, the sorptive partitioning coefficients for the oven-dried and water-saturated synthetic soil may be considered as end members of a continuum of possible sorption partition coefficients that will be observed at intermediate moisture contents. By using this approach it is possible to estimate the fraction of dry surface sites that would be needed to account for the measured partition coefficients of the partially wet synthetic soil. If the sorbent mass M is considered to be composed of some fraction F_w of water-saturated sites of mass M_{ws} and a fraction F_d of dry sites of mass M_{ds}, then $F_w + F_d = 1.0$ and

$$F_w = M_{ws}/M \tag{12}$$

$$F_d = M_{ds}/M \tag{13}$$

If each site type is also assumed to obey a linear isotherm, then

$$M_{sl} = C_L K_d M_{ws} \tag{14}$$

$$M_{\mathrm{sg}} = C_{\mathrm{G}} K_{\mathrm{d}}{}'_{\mathrm{dry}} M_{\mathrm{ds}} \qquad (15)$$

where M_{sl} and M_{sg} are contaminant masses sorbed onto the wet and dry sites, respectively, and $K_{\mathrm{d}}{}'_{\mathrm{dry}}$ is the vapor partition coefficient for the dry surface. The mass sorbed onto the partially wet solid X is considered to be the sum of the contribution of each site type. Therefore, from eq 5

$$X = M_{\mathrm{sl}} + M_{\mathrm{sg}} = K_{\mathrm{d}}{}'_{\mathrm{obsd}} C_{\mathrm{G}} M \qquad (16)$$

where $K_{\mathrm{d}}{}'_{\mathrm{obsd}}$ is the vapor partition coefficient at an intermediate moisture content.

Combination of eq 12–16 and Henry's law ($C_{\mathrm{G}} = K_{\mathrm{H}} C_{\mathrm{L}}$) gives

$$K_{\mathrm{d}}{}'_{\mathrm{obsd}} = F_{\mathrm{w}} K_{\mathrm{H}} K_{\mathrm{d}} + F_{\mathrm{d}} K_{\mathrm{d}}{}'_{\mathrm{dry}} \qquad (17)$$

Given the values of $K_{\mathrm{d}}{}'_{\mathrm{obsd}}$ in Figure 2 and given $K_{\mathrm{d}} = 0.29$ cm^3/g (our measured value for the saturated synthetic soil) as well as $K_{\mathrm{d}}{}'_{\mathrm{dry}} = 11\,870$ cm^3/g (the value for the oven-dry soil), the values of F_{w} calculated from eq 17 are 0, 0.983, and 0.995 at 0, 8.2, and 11.6% moisture contents, respectively. Hence, F_{w} is a highly nonlinear function of the moisture content. Apparently only a very small fraction of dry sites would be required to mathematically account for the higher partitioning coefficient of the moist, unsaturated solid relative to saturated conditions.

An alternative explanation for the magnitude of K_{d}' vs K_{d} is that totally dry sites do not exist on the unsaturated moist solid but that (for reasons which are not known) the moist surface has a sorptive binding strength that is greater than that of the saturated sorbent. In this regard it is noteworthy that taking the surface area occupied by a water molecule as 11.4 Å^2 (*22*) and the measured BET surface area of 206 m^2/g gives an average coverage of 1.6 and 2.4 monolayers of water on the Al_2O_3 surface at the moisture contents of 8.2 and 11.6%. Multiple layers of water were therefore likely to have been present. Regardless of the interpretation of the results, the relationship between soil moisture and linear TCE sorption coefficients is highly nonlinear. Identifying the specific sorption mechanisms responsible for this relationship will require further study.

Gaseous Diffusion Coefficient. The TCE vapor diffusion coefficient of a soil system was monitored over a 6-day period. The carrier (air) flow rate was 1.70 ± 0.21 ft^3/h. The system stabilized (i.e., reached steady state) after 69 h, and the average diffusion coefficient (D_{G} computed from eq 10) after this point in time was 1195 ± 108 (±9.0%) cm^2/day at a soil porosity of 0.722.

It is instructive to compare the measured value of D_{G} to the value that would be predicted by empirical formulas such as the model proposed by Millington and Quirk (*23*), which is often used to estimate the vapor-phse diffusion coefficient for a soil system. This formula predicts the soil–vapor diffusion coefficient D_{G} (cm^2/day) on the basis of the known diffusion coefficient of the compound in air $D_{\mathrm{G_{air}}}$. The specific geometric effects of the soil are accounted for by applying a retardation factor based on the soil's volumetric air content a and porosity ϕ:

$$D_{\mathrm{G}} = a^{10/3}/\phi^2 D_{\mathrm{G_{air}}} \qquad (18)$$

A $D_{\mathrm{G_{air}}}$ value of 6875 cm^2/day at 21.5 °C was estimated for TCE with the Hirschfelder correlation (*24*). Given this value, the value of D_{G} predicted by eq 18 was 4450 cm^2/day, 3.7 times greater than the experimentally measured coefficient. The experiment was repeated for a second porosity of 0.56, and again the predicted and measured values differed significantly. The measured diffusion coefficient was 700 cm^2/day (±5.1), and the predicted value was 3160 cm^2/day, which is over 4 times greater than the measured value.

It is apparent that the uncertainty associated with empirical relationships can, in some cases, be high. As two empirical formulas (Millington–Quirk and Hirschfelder) must be applied to estimate the soil gaseous diffusion coefficient for TCE, the uncertainty associated with the predicted coefficient D_{G} is the result of the combination of errors for the two equations. Reid and Sherwood (*24*) evaluated several methods of estimating diffusion coefficients and reported an average error of 6% in the Hirschfelder correlation. However, deviations as high as 39% were observed. Millington and Quirk (*23*) compared, predicted, and measured soil diffusion coefficients using the data of several researchers and found an average deviation of approximately 15%, with variations of 100% resulting in some cases. The results of Farmer et al. (*16*) show a closer agreement between the measured and predicted values for the diffusivity of hexachlorobenzene (approximate error of 15%).

Impact of Vapor-Phase Sorption on Contaminant Transport: Model Analysis

The significance of the uncertainty in vapor diffusivity on volatile pollutant behavior as well as the importance of considering the soil–vapor partitioning equilibria may be evaluated through the use of models. To illustrate effects, the model developed by Jury et al. (*25–28*) for contaminant transport in the unsaturated zone was employed. This model incorporates the effects of volatilization, leaching, and degradation to describe the major loss pathways of soil-applied organic chemicals as a function of specific environmental variables and soil conditions.

The model is an analytical solution to the one-dimensional advection–diffusion equation describing the vertical transport and volatilization loss of soil-applied compounds. Model equations are summarized in the Appendix. A homogeneous porous medium, a linear equilibrium adsorption isotherm, and a linear equilibrium liquid–vapor partitioning are assumed. Initial conditions include a uniform concentration of a compound incorporated to a specified depth L (cm). Volatilization at the soil surface is assumed to be controlled by gaseous diffusion through a stagnant air boundary layer of thickness d (cm). The model is intended for use as a screening tool to assess behavior under prototype conditions rather than to make precise predictions under specific circumstances.

As is the common practice for models of contaminant transport in the unsaturated zone, Jury et al. (*25*) assume that sorption is described by the partitioning coefficient determined by experiments on the basis of saturated conditions. However, as the preceding results indicate, the sorption partitioning coefficient can vary considerably with the phase in which the reaction occurs.

Figure 3 indicates the impact of changes in the value of the partition coefficient on model predictions of the transport of TCE through the unsaturated zone. Each line on the graph represents the results of the Jury et al. (*25*) model for a different value of the partition coefficient. For the "saturated" case, a K_{d} of 0.76 cm^3/g was used on the basis of our measured $K_{\mathrm{oc}} = 61.1$ and a model soil with weight-fraction organic content $f_{\mathrm{oc}} = 1.25\%$. The vapor partition coefficients at 11.6% moisture, 8.2% moisture, and 0.0% moisture were $K_{\mathrm{d}}' = 53.9$, 207, and 11 870, respectively, and are based on our measured values for the vapor-phase partitioning coefficient. These were converted to an aqueous-phase basis [by noting $K_{\mathrm{d}} = C_{\mathrm{s}}/C_{\mathrm{L}} = C_{\mathrm{s}}/(C_{\mathrm{G}}/K_{\mathrm{H}}\gamma) = K_{\mathrm{d}}' K_{\mathrm{H}}\gamma$] prior to use in the model. Other

Table I. Model Input Parameters

symbol	term	units	value	source
$D_{G_{air}}$	TCE air diffusion coefficient	cm^2/day	7030	Hirschfelder formula at 25 °C, Reid and Sherwood (*24*)
$D_{L_{water}}$	TCE water diffusion coefficient	cm^2/day	0.8304	Wilke and Chang (*29*) at 25 °C
ϕ	porosity	cm^3/cm^3	0.5	
ρ_b	bulk density	g/cm^3	1.35	
f_{oc}	fraction organic content	%	1.25	
θ	water content		0.25	
a	air content		0.25	
L	incorporation depth	cm	10	
d	boundary layer thickness	cm	0.475	
K_H	Henry's Law constant		0.397	Garbarini and Lion (*5*)
C_0	uniform initial concentration	$\mu g/(cm^3 \cdot ppm)$	100	
T	elapsed time	days	10	
J_w	groundwater velocity	cm/day	1	
μ	degradation rate	day^{-1}	0	

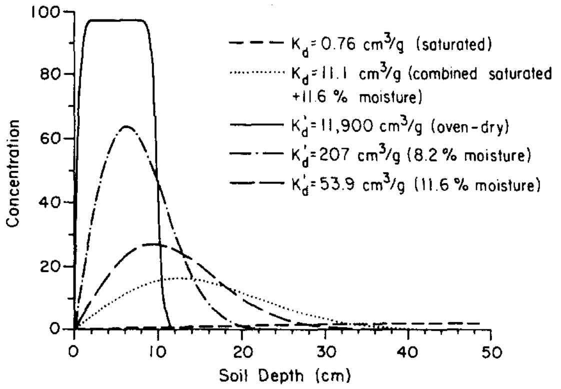

Figure 3. Calculated TCE concentration profiles assuming uniform sorption of TCE equivalent to that observed in saturated systems and unsaturated systems of varying moisture content.

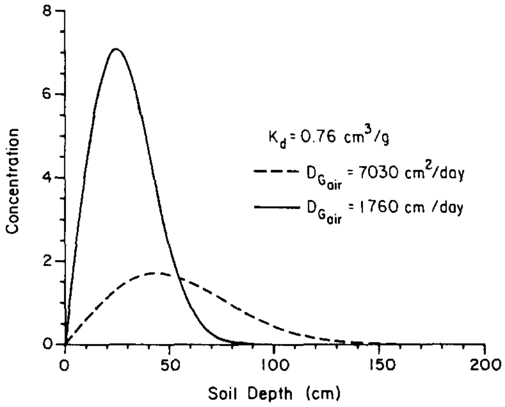

Figure 4. Calculated TCE concentration profiles with differing soil diffusion coefficients.

model input parameters are summarized in Table I.

As expected, the model predictions of transport down through the unsaturated zone vary markedly with the values used for the partition coefficient. Using the saturated partition coefficient to describe sorption in the unsaturated zone results in model predictions of much faster transport than is predicted when any of the unsaturated partition coefficients are used.

The results in Figure 3 illustrate only the impact of changing sorptive characteristics of the soil; they do not incorporate the impact of changes in vertical velocity associated with changes in soil moisture. Soil moisture and vertical velocity are positively correlated. Clearly decreases in vertical velocity will retard the downward transport of a contaminant. The results of Figure 3 illustrate that the decreases in soil moisture and associated increases in sorption will also retard the downward transport. The combined effect of reduction in soil moisture and in vertical transport is expected to be greater than either process acting by itself.

In saturated soils, it is reasonable to assume that portions of the solid phase behave as though they are surrounded by liquid water, and therefore their reactions with a nonionic organic pollutant may be described by a saturated sorptive partition coefficient. Other portions of the soil may behave as though they are in contact with both water and organic vapors, and a vapor-phase partition coefficient for the moist (but unsaturated) sorbent would be appropriate. Therefore, if a single partition coefficient for an organic pollutant is to be used in a model, a value that is intermediate between the saturated and moist–unsaturated partition coefficients may be a reasonable choice. As a first approximation for the selection of a value for a single partition coefficient in a soil with heterogeneous moisture conditions, we may wish to weigh the saturated and moist but unsaturated partition coefficients by the volumetric moisture content of the soil θ giving

$$K_{d\,\text{combined}} = (\theta/\phi)K_d + (a/\phi)K_d'K_H\gamma \qquad (19)$$

where a and ϕ are as previously defined (see eq 18).

Figure 3 also shows the results of a simulation trial using a partition coefficient K_d of 11.1 cm^3/g, which results from $\theta = 0.25$, $a = 0.25$, and $\phi = 0.5$, a saturated $K_d = 0.76$ cm^3/g (based on our $K_{oc} = 61.1$ and $f_{oc} = 0.0125$), and our unsaturated (11.6% moisture) $K_d' = 53.9$ cm^3/g values. It may be seen that the calculated profile for this case still lies nearer to the results for the case based on the K_d' for 11.6% moisture.

A more appropriate procedure for handling the unsaturated case where both gas- and liquid-phase partitioning occur would be to compartmentalize the unsaturated soil phase into portions that behave as though they are saturated (from the perspective of sorption reactions) and portions in which vapor-phase partitioning occur. The modified model could then employ both a soil–liquid and soil–vapor partition coefficient. Such a model has been developed (*30*) and will be the subject of a subsequent paper.

Sensitivity of Results to Gaseous Diffusion Rates. The model of Jury et al. (*25*) was also used to evaluate the significance of gaseous diffusion in determining the concentration profile. The results obtained for a case in which the gaseous diffusion coefficient was predicted with empirical models is compared to a trial in which this value was reduced by a factor of 4. This was roughly the magnitude of difference between the measured value for TCE in this study and the predicted diffusion coefficient estimated from empirical relationships. Figure 4 illustrates the expected slower net transport of TCE when the diffusion coefficient is reduced.

Conclusions

This study demonstrates that an experimental headspace procedure can be used to measure linear solid–vapor partition coefficients. A significant range of values for the vapor sorptive partition coefficient for TCE was observed depending upon the moisture content of the sorbent.

Vapor-phase partition coefficients for a simulated soil were substantially greater than the saturated aqueous partition coefficient. The results of our study indicate that the current practice of using saturated partition coefficients in models of the unsaturated zone may underestimate the amount of sorption and hence overestimate the amount and rate of material moving into the groundwater. We note that the curves obtained are model dependent and that calculations performed with a different model may result in smaller or larger differences between predictions based on saturated vs unsaturated partition coefficients. The magnitude of differences in partition coefficients will also depend on the physical–chemical characteristics of the sorbent. However, if the saturated and unsaturated partition coefficients vary by several orders of magnitude (as they do for the synthetic sorbent employed in this research), the differences in predictions are expected to be similar to those described here.

The vapor-phase diffusion coefficient measured for TCE did not agree with the value predicted empirically. The model results indicate that the differences in calculation using measured vs empirically estimated values are significant. These results are important since field measurements of vapor diffusion coefficients are experimentally difficult and field conditions are likely to be heterogeneous. The model results indicate that any pollutant transport analysis based on empirically estimated values of the gaseous diffusion coefficient should be subjected to extensive sensitivity analysis to examine how the results of the analysis would change over a range of values.

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Appendix

The one-dimensional equations governing mass flux of solute and solute mass balance are respectively

$$J_s = -D_E \frac{dC_T}{dZ} + V_E C_T \qquad (A1)$$

$$\frac{dC_T}{dt} = D_E \frac{d^2C_T}{dZ^2} - V_E \frac{dC_T}{dZ} - \mu C_T \qquad (A2)$$

where J_s = solute mass flux in the soil (g/cm^2 day), C_T = total mass of solute per soil volume (g/cm^3), i.e., $C_T = C_L \theta + C_G a + C_s \rho_b$, Z = distance from surface (cm), t = time (day), μ = net degradation rate (day^{-1}), D_E = effective diffusion coefficient (cm^2/day), V_E = effective velocity (cm/day), and θ = volumetric water content ($\theta + a = \phi$).

The effective diffusivity D_E and velocity V_E take into account the retardation of transport due to sorption and volatilization and are functions of K_d, D_G, and K_H as derived by Jury et al. (*23*):

$$D_E = (K_H D_G + D_L)/(\rho_b K_d + \theta + a K_H)$$

and

$$V_E = J_w/(\rho_b K_d + \theta + a K_H)$$

where D_L is the aqueous diffusion coefficient of the solute in soil and J_w is the groundwater advective velocity.

The boundary conditions employed for solution were as follows: $C(Z,O) = C_o$ if $O < Z < L$, $C(Z,O) = O$ if $Z > L$, $C(\infty,t) = O$, and $J_s(O,t) = -hC_G(O,t)$. Here h is a transport coefficient across the boundary layer of thickness d (cm) and $C_G(O,t)$ is the gaseous concentration at the soil surface below the boundary layer. Equations A1 and A2 were solved for the above boundary and initial conditions (*23*); other input parameters used in the calculations performed here were based on the soil properties assumed in the original calculations of Jury et al. (*23*) and are summarized in Table I.

The analytic solution is as follows [note that the original paper by Jury et al. (*23*) contained a typographical error in this equation]:

$$\begin{aligned} C_T(Z,t) = {} & (1/2)C_o \times \\ & \exp(-\mu t)\left\{\left[\operatorname{erfc}\frac{Z - L - V_E t}{\sqrt{4D_E t}} - \operatorname{erfc}\frac{Z - V_E t}{\sqrt{4D_E t}}\right] + \right. \\ & [(1 + V_E/H)\exp(V_E Z/D_E)] \times \\ & \left(\operatorname{erfc}\frac{Z + L + V_E t}{\sqrt{4D_E t}} - \operatorname{erfc}\frac{Z + V_E t}{\sqrt{4D_E t}}\right) + \\ & [(2 + V_E/H)\exp\{[H(H + V_E)t + (H + V_E)Z]/D_E\}] \times \\ & \left(\operatorname{erfc}\frac{Z + [(2H + V_E)t]}{\sqrt{4D_E t}} - [\exp(HL/D_E)] \times \right. \\ & \left.\left.\operatorname{erfc}\frac{Z + L + (2H + V_E)t}{\sqrt{4D_E t}}\right)\right\} \qquad (A3) \end{aligned}$$

where $H = D_{G_{air}}(\rho_b C_s/C_G + \theta C_L/C_G + a)^{-1}/d$.

Registry No. $Cl_2C{=}CHCl$, 79-01-6; Al_2O_3, 1344-28-1.

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Atmospheric Reactions of a Series of Dimethyl Phosphoroamidates and Dimethyl Phosphorothioamidates

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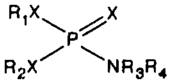
■ The kinetics of the atmospherically important gas-phase reactions of a series of dimethyl phosphoroamidates and dimethyl phosphorothioamidates with OH and NO_3 radicals and O_3 were investigated at 296 ± 2 K and ~740 Torr total pressure of air. The rate constants obtained for the OH radical, NO_3 radical, and O_3 reactions (in units of cm^3 $molecule^{-1}$ s^{-1}) were respectively as follows: $(CH_3O)_2P(O)N(CH_3)_2$, $(3.19 \pm 0.24) \times 10^{-11}$, $<3.9 \times 10^{-14}$, and $<2 \times 10^{-19}$; $(CH_3O)_2P(S)N(CH_3)_2$, $(4.68 \pm 0.14) \times 10^{-11}$, $(3.1 \pm 1.0) \times 10^{-14}$, and $<2 \times 10^{-19}$; $(CH_3O)_2P(S)NHCH_3$, $(2.32 \pm 0.13) \times 10^{-10}$, $(3.0 \pm 0.4) \times 10^{-13}$, and $<2 \times 10^{-19}$; $(CH_3O)_2P(S)NH_2$, $(2.44 \pm 0.09) \times 10^{-10}$, $(3.9 \pm 0.8) \times 10^{-13}$, and $<4 \times 10^{-19}$. These data show that for the dimethyl phosphorothioamidates both the OH and NO_3 radical reactions are important atmospheric loss processes, with calculated lifetimes ranging from ~1 h to ~1 day. The mechanistic implications of these data are discussed.

Introduction

It is now known that chemicals emitted into the troposphere, including volatilization from soil and aqueous systems (*1*), are removed from the troposphere by photolysis, by chemical reaction (mainly with OH and NO_3 radicals and O_3), and by wet and dry depositions (*2, 3*). In order to assess the atmospheric lifetimes and dominant loss process(es) for organic chemicals emitted into the troposphere, and hence human exposures to such compounds and their atmospheric reaction products, it is necessary to know, or to reliably predict, the reaction rates for the potentially important atmospheric processes.

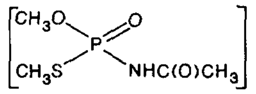
While a large data base is now available for the kinetics and mechanisms of the gas-phase reactions of organic compounds with OH radicals (*4*), O_3 (*5*), and NO_3 radicals (*2*), the only organophosphorous compounds for which data exist are trimethyl phosphate (*6*) and a series of trimethyl phosphorothioates (*7*), despite the fact that organophosphorous compounds are widely used in agricultural operations as insecticides and herbicides (*8*).

A class of organophosphorous compounds related to the phosphorothioates are the phosphoroamidates and the phosphorothioamidates:

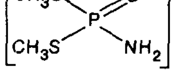


where X = O or S, respectively, R_1 and R_2 are alkyl groups, and R_3 and R_4 are H or alkyl. The insecticidal properties of many of these compounds have been investigated (*9, 10*).

Acephate



and methamidophos



are two examples of this class of organophosphorous compounds presently used as insecticides (*8*), with several more having been in use previously (*8*).

In order to investigate the atmospherically important reaction pathways of this class of structurally interesting chemicals, and to further extend structure–reactivity relationships (*4, 7, 11*) to these compounds, we have investigated the gas-phase atmospheric chemistry of the dimethyl phosphoroamidates and dimethyl phosphorothioamidates (DMPs) $(CH_3O)_2P(O)N(CH_3)_2$, $(CH_3O)_2P(S)N(CH_3)_2$, $(CH_3O)_2P(S)NHCH_3$, and $(CH_3O)_2P(S)NH_2$. The DMP $(CH_3O)_2P(O)NHCH_3$ could not be studied, presumably due to its low volatility and/or to adsorption onto the reaction chamber walls, and hence we did not attempt to

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