

Degradation of organic vapors in unsaturated soils*

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Abstract

To predict the fate of volatile organic compounds (VOCs) in unsaturated soil, it is necessary to understand the physical and chemical processes that occur in the soil system. Two important removal mechanisms of organic vapors in soil are sorption and biodegradation. Modeling efforts to describe the removal of organic vapors in soil require constitutive relationships that are developed from laboratory data. This paper reports measurements of removal coefficients for three VOCs in a fine sandy loam soil. Sorption coefficients and degradation removal rates were determined from batch reactors for three compounds: benzene, trichloroethylene (TCE) and *o*-xylene. Results indicate organic vapors are sorbed and then removed by biodegradation in the unsaturated soil system. This information has potential for use in the bioremediation of soils contaminated with VOCs and for impacting decisions on air emissions, regulatory limits and on-site controls.

Introduction

The need to provide treatment for soils contaminated with hazardous materials from accidental spills and land based handling operations has become increasingly apparent. Many of these hazardous materials contain VOCs that volatilize and pass through the soil as a vapor. To develop adequate treatment and control for volatile air emissions and to predict the fate of chemical constituents in soil, it is necessary to understand the fundamental processes and interactive mechanisms that occur in the unsaturated soil. Such knowledge can be utilized both to provide criteria for designing soil decontamination processes and to evaluate the feasibility of soil biofilters as an alternative bioremediation technology at hazardous waste sites and for industrial vapors and exhaust gases.

The properties of natural soils have been increasingly utilized for removal of VOCs emitted from waste disposal facilities, from waste air streams, and from soil remediation systems [1-4]. The removal of organic vapors in soil is

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dependent on continuous interaction between the volatilized compounds and the soil properties. While all soil properties have not been evaluated, those showing increasing importance in vapor sorption are surface area (texture), organic/mineral content and moisture content. For degradation, temperature, soil moisture content, VOC concentration and acclimation of the soil microbial population are important.

A major concern with the presence of hazardous compounds in soils is the movement of contaminants into groundwater. Recently, this has been expanded to include air emissions. As a result, numerous contaminant transport models include volatilization and the subsequent movement of vapor through the unsaturated zone as model parameters [5–9]. These models account for the partitioning of the VOCs between air, soil water and soil when the compound is initially in the liquid phase. Recent models of the vadose zone include terms for sorption equilibrium and oxygen utilization or chemical half life in the removal of organic vapors [10,11]. At the present time, limited experimental data of vapor/soil interactions exist to test these models. The identification of important removal mechanisms for volatilized VOCs, the determination of sorption and degradation coefficients, and the evaluation of the significance of these mechanisms in the removal of VOCs was the focus of this research.

This paper presents research that evaluates vapor removal of three VOCs in unsaturated soils. Sorption coefficients for the three VOCs were empirically determined using the Freundlich and BET models. Degradation coefficients were obtained using zero and first order reaction models. These results are part of a larger study directed toward developing protocols for vapor studies, evaluating various removal mechanisms, and determining the role of these mechanisms in vapor removal.

Materials and methods

The compounds used in this study were chosen based on their prevalence in the environment; chemical characteristics (vapor pressure, solubility, partition coefficient, degradation constant); chemical structure and analytical compatibility. The three compounds selected were benzene, TCE and *o*-xylene. The soil used in the study was a fine sandy loam with an organic content of 3.25%. It was slightly alkaline, with a pH of 7.8, and a cation exchange capacity (CEC) of 10.8 meq/100 g. The soil was obtained from an agricultural area not known to have been exposed to these chemicals previously.

The soil was placed in sealed 40 ml VOA vials with PTFE-lined mininert valves. A screening test was conducted with each compound to evaluate leakage from and sorption onto the vials, to determine the equilibration time for the sorption tests, and to estimate removal times for the degradation studies.

The samples were prepared by adding water to a known mass of soil in the vials in order to reach the desired soil water content. A moisture content of

16% (g/g), or about 80% field capacity (determined from Soil Conservation Survey), was chosen as the standard condition based on previous studies for optimizing removal of organic compounds in unsaturated soil. The vials were then placed overnight at 20°C before adding the compound of interest. The pure compound was added to a small glass tube inside the vial where it volatilized before contacting the soil.

For the moisture study, the mass of water added to the soil was adjusted to achieve 1,2,8 and 16% moisture by weight in the vials. To evaluate the effect of organic content on the sorption, the soil was placed in a 550°C muffle furnace to remove the organic content in the soil. After removing the soil from the furnace, it was rehydrated and placed in a 105°C oven overnight.

Sorption study

For the sorption study, five mass loadings were used to construct each isotherm, i.e. for benzene: 0.35, 0.70, 0.88, 1.23 and 1.58 mg. The mass added was based on the results of the screening tests, the vapor pressure of the compound, and sampling considerations. Triplicate vials with soil and duplicate controls without soil were used for each input volume. A total of 25 vials were set up for each sorption study. The compound added to the vials was allowed to equilibrate with the soil for 24 to 48 hours depending on the results from the screening test for each compound. Screening tests using abiotic vials fumigated with methyl bromide showed no difference in compound loss between fumigated and nonfumigated vials during the equilibration period. Therefore, abiotic vials were not utilized during the sorption study.

At the end of the equilibration period, the headspace of each vial was sampled with a gas tight syringe and injected directly into a Tracor 540 gas chromatograph (GC). The difference between the mass in the headspace of the control and the mass in the headspace of the sample containing the soil was calculated to be the amount removed on the soil.

The coefficients describing the sorption phenomena were determined using the Freundlich and BET models for analysis. Freundlich coefficients for benzene, TCE and *o*-xylene were obtained at 16% moisture (g/g). The effect of moisture content on vapor sorption was evaluated with benzene at five soil water contents (0-oven dried, 1, 2, 8 and 16%). The appropriate coefficients were obtained for each condition using the two models.

Degradation study

The procedure for the degradation study was similar to that of the sorption study. A single mass loading was used in this study. Therefore, one set of vials consisting of 3 samples and 2 controls (no soil) was required for each sample point. When the mass in the headspace decreased to approximately 0.1 mg, subsequent loadings were added to the remaining vials to evaluate the effect of continual loading and acclimation on removal rates. An example of mass load-

TABLE 1

Typical mass loadings at 16% (g/g) soil moisture

Compound	Volume (μ l)	Input (mg)	Loading (mg VOC/kg soil)
<i>Sorption study</i>			
Benzene	0.4 -1.8	0.35-1.58	35-158
<i>o</i> -Xylene	0.4 -1.5	0.35-1.32	35-132
TCE	0.34-1.6	0.59-2.34	59-234
<i>Degradation study</i>			
Benzene	1.5	1.32	132
<i>o</i> -Xylene	1.0, 1.4	0.88, 1.23	88, 123
TCE	1.0	1.46	146

ings to the soil is given in Table 1 for the three compounds for both the sorption and degradation studies.

At the appropriate time, the headspace of each vial in the sample set was analyzed as described above. In addition, the headspace was sampled for oxygen and carbon dioxide on a gas partitioner to ensure the soil samples maintained aerobic conditions and to obtain oxygen utilization rates. After sampling the headspace, a methanol extraction was used to measure the total mass remaining in the vial. Methanol (10 ml) was added to each vial with a syringe by injection through the mininert valve. After two hours, the valves were removed and an additional 20 ml of methanol was added to each vial. The vials were then capped, inverted and allowed to stand for 20-24 hours. At the end of the extraction period, the vials were centrifuged and the supernatant poured into 8 ml vials which were stored at -15°C until analysis. This method was adapted from Sawhney et al. [12].

The removal rates were determined using data obtained from the methanol extractions. With the extraction data from the sample vials (mass remaining) and control vials (total mass), a percentage mass remaining was calculated. This procedure accounted for loss onto the mininert valves and for daily variations in the analytical equipment. The percentage remaining was multiplied by the initial input mass and the result was used to determine removal rates with zero order reaction kinetics, the most appropriate kinetics for the available data.

Results and discussion

Sorption study

Results from the screening test indicated that an equilibration time of 24 to 48 hours was required for the three compounds; approximately 24 hours for benzene and TCE and 48 hours for *o*-xylene. Benzene vapor has been reported

to equilibrate in shorter periods of time than determined in this study, 30 minutes [13] and in less than 4 hours [14]. The equilibration time for TCE vapor used by Peterson et al. [15] in studies with synthetic soil was 24 hours. Rao et al. [16] established an equilibrium time of less than 24 hours for *o*-xylene vapor in soil.

Using the Freundlich model, sorption coefficients greater than zero were obtained for benzene, TCE and *o*-xylene indicating sorption of organic vapor to soil does occur with these three compounds at 16% soil water content. Using the organic soil containing 3.25% organic carbon, *o*-xylene exhibited the greatest capacity for sorption onto the soil of the three compounds tested followed by TCE and benzene (Table 2). The coefficients were obtained using a linear regression of pooled data from four sorption runs at 16% soil water content.

The effect of soil organic content on sorption also is presented in Table 2. Coefficients were determined at 16% soil water for soil treated to remove organic matter. For the three VOCs tested, the sorption coefficient for the non-organic soil was lower than for the soil with organics indicating the soil organic content contributed to the sorption of the organic vapors in unsaturated soils. The role of organic content in sorption of organic liquids in soil has been well documented [17–19].

The effect of moisture content on vapor sorption was evaluated with benzene. Sorption coefficients were determined for moisture in contents of 0% (oven dried), 1%, 2%, 8% and 16%. Results indicated the sorption coefficient, K_f , from the Freundlich analysis was greatest at 0% moisture (oven-dried) and decreased by more than an order of magnitude at 1% moisture, i.e. K_f went from a value of 362 to 11 (Table 3) (mg/g)/(mg/l)^{1/n}. The values continued to

TABLE 2

Freundlich coefficients at 16% (g/g) soil moisture

Compound	Sorption parameters		
	$K_f \times 10^{-3}$ (mg/g)/(mg/l) ^{1/n}	<i>n</i>	<i>r</i> ²
<i>Soil with organics</i>			
Benzene	2.33 ^a	1.08	0.861
TCE	2.83 ^a	1.17	0.868
<i>o</i> -Xylene	6.17 ^a	0.87	0.933
<i>Soil treated for organics removal^b</i>			
Benzene	1.18	1.16	0.616
TCE	0.65	0.99	0.709
<i>o</i> -Xylene	0.36	0.73	0.692

^aLinear regression of pooled data from 4 runs.

^bMuffle furnace at 550°C.

TABLE 3

Sorption coefficients for the moisture content study with benzene

Moisture content (% g/g)	Coefficients					
	Freundlich			BET		
	$K_f \times 10^{-3}$ (mg/g)/(mg/l) ^{1/n}	<i>n</i>	<i>r</i> ²	<i>B</i> ^a	<i>Q</i> ^a	<i>r</i> ²
0	362.2	1.69	0.779	85.0	1.96	0.648
1	11.1	1.35	0.855	18.4	0.19	0.518
2	4.3	1.33	0.874	8.7	0.11	0.357
8	2.0	1.17	0.913	7.6	0.08	0.448
16	2.3	1.08	0.861	3.1	0.22	0.042

^a*B*: related to the heat of adsorption and heat of liquefaction, and *Q*: monolayer adsorption capacity.

decrease more slowly from 1 to 16% moisture and became constant after 2%. The rapid decrease in vapor sorption as water was added to the soil was similar to the results found by Peterson et al. [15], Chiou and Shoup [14] and Rhue et al. [20].

As presented by Valsaraj and Thibodeaux [21], soil water plays a major role in determining the major mechanisms of sorption in unsaturated soils. At less than a monolayer of water around the soil particles, VOC vapors tend to adsorb to the soil surface. After a monolayer of water is present in the soil and the active sorption sites on the soil surface are occupied by water, less vapor is sorbed, the coefficients become constant and the soil organic matter takes on a more important role. This was substantiated by the data from the moisture study. In dry soil, the sorption coefficient was high (362). One monolayer of water was present at approximately 1% moisture based on surface area measurements of the fine sandy loam soil. At greater than 1% soil moisture, sorption coefficients were similar ranging from 4.3 to 2.0.

The Freundlich isotherm modeled the sorption data better than the BET isotherm over all ranges of soil water contents. Even so, the BET model provided information on the thermodynamic term, *B*, and the monolayer capacity value, *Q*, at low moisture content where there is little or no competition for sorption sites with water vapor [14,20,22]. As the soil water increased, the monolayer capacity value, *Q*, was no longer a valid descriptor for the VOC. The soil water was occupying the majority of the active sites on the soil surface.

Degradation study

Degradation studies were carried out on benzene and *o*-xylene. Triplicate runs were conducted for benzene and *o*-xylene. Results showed that removal of benzene and *o*-xylene vapor occurred under aerobic conditions. (Typical degradation data are presented in Fig. 1 for one run using benzene.) With

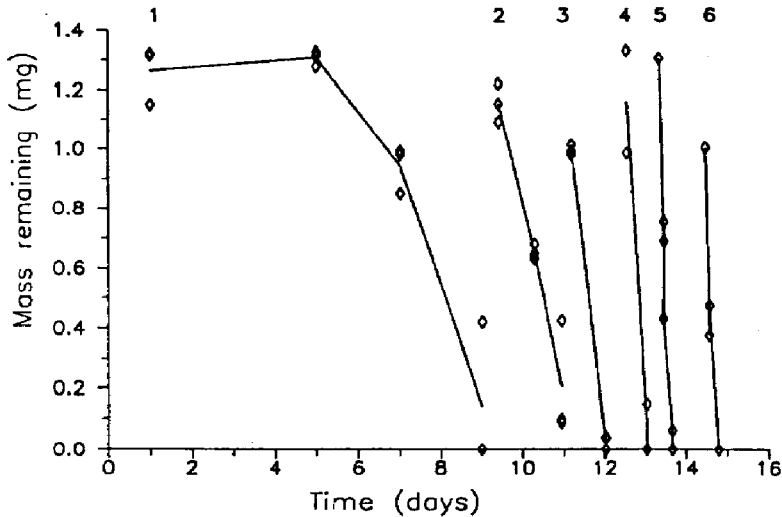


Fig. 1. Benzene removal over time.

TABLE 4

Zero order removal rates for benzene and *o*-xylene from triplicate runs (mg/d)

VOC additions	Benzene	<i>o</i> -Xylene
1	0.292	0.227
2	0.696	0.369
3	1.277	0.668
4	2.264	1.192
5	3.333	1.336
6	3.196	1.464
7	No data	-
8	4.255	-

benzene as the test compound, results from triplicate runs indicated an initial lag period of approximately 5 days before vapor removal was evident. Results from the *o*-xylene studies indicated a lag period of approximately 10 days occurred before removal began. Commonly found in biologically mediated systems, the lag period is the result of a combination of factors including mass transfer rates, microbial acclimation and mass loading. The lag phase for several aromatics has been shown to decrease when acclimated soil from a polluted aquifer is added to contaminated groundwater [23].

Removal rates for benzene and *o*-xylene using the zero order rate model are presented in Table 4. The rates were obtained from pooled data from triplicate runs for benzene and *o*-xylene. The results indicated the removal rates for benzene were faster than the rates for *o*-xylene by as much as a factor of two.

As part of the degradation studies, sequential applications of the compound were added to the vials. For benzene and *o*-xylene, the lag phase disappeared and removal rates increased with repeated additions to the vials. During these studies, steady rates were not achieved; the rates increased over the duration of the study for both benzene and *o*-xylene.

Soil bacteria are known to have the capacity to degrade benzene and *o*-xylene once the compounds are in the aqueous phase [24]. In the degradation studies, the volatile organic compound (VOC) was initially sorbed into the soil water system and then became available to the soil microorganisms. The removal of benzene and *o*-xylene was mainly due to biological degradation as evident by the disappearance of the lag phase and the increased removal rates due to sequential inputs. The role of biodegradation in these studies was verified with ^{14}C benzene studies and with headspace oxygen and CO_2 measurements.

The increase in VOC removal rates can be attributed to either the result of microbial acclimation to the presence of the compound in the soil or to an increase in the number of soil microorganisms due to the available substrate. A study was conducted to measure the increase in biomass over the sequential additions of benzene. The general population of soil microorganisms was counted using standard agar plating techniques. Results showed that the number of microbial colonies increased with each addition of benzene. A linear regression of the increased biomass count (sample soil plate counts minus control soil plate counts) versus benzene removal rates resulted in the following equation:

$$a = 1.28 \times 10^{-15} b^{0.814} \quad r^2 = 0.959 \quad (1)$$

where a is the benzene removal rate (mg/d) and b the increased biomass (expressed as number of colony forming units, CFU).

From the data, the increase in removal rates was paralleled with an increase in the soil microorganisms indicating the importance of high biomass concentration for VOC removal.

Conclusions

In this study, it was determined that VOCs in the vapor phase are removed in the unsaturated zone. The results indicate both that sorption of VOCs can occur in soil and that degradation is rapid in acclimated soils. The results indicate VOCs are retained and subsequently removed by soil in the unsaturated zone. Parameters that need to be evaluated further for organic vapor removal include soil organic content, moisture content/relative humidity, mass loading, acclimation and mass transfer kinetics.

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