Active

Project #: E-20-W80   Cost share #: E-20-389   Rev #: 2
Center # : 10/24-6-R8634-0A0   Center shr #: 10/22-1-F8634-0A0   OCA file #:
                                                                Work type : RES
Contract#: 032856   Mod #: 2   Document : SUBCONT
Prime   #: R819605   Contract entity: GTRC

Subprojects ? : N   CFDA: NA
Main project #:   PE #: NA

Project unit: CIVIL ENGR   Unit code: 02.010.116
Project director(s):
   PENNELL K D   CIVIL ENGR   (404)894-9365

                                                                             |

Sponsor/division names: UNIV OF MICHIGAN   /
Sponsor/division codes: 400   / 058

Award period: 950715   to   970517 (performance)   970517 (reports)

Sponsor amount   New this change   Total to date
     Contract value   35,000.00   70,000.00
     Funded   35,000.00   70,000.00
Cost sharing amount   23,750.00

Does subcontracting plan apply ?: N

Title: ORGANIC VAPOR SORPTION & DESORPTION IN UNSATURATED ZONE: RATES & EQUILIBRIA

PROJECT ADMINISTRATION DATA

OCA contact: Ina R. Lashley   894-4820

 Sponsor technical contact   Sponsor issuing office

 DR. WALTER J. WEBER, JR   RAY HUNTER
 (313)763-1464   (000)000-0000

 THE UNIVERSITY OF MICHIGAN   THE UNIVERSITY OF MICHIGAN
 GREAT LAKES MID-ATLANTIC CENTER FOR 181 EWRE BUILDING
 HAZARDOUS SUBSTANCE RESEARCH   1351 BEAL AVENUE
 181 EWRE BUILDING, 1351 BEAL AVENUE ANN ARBOR, MI 48109-2125
 ANN ARBOR, MI 48109-2125

 Security class (U,C,S,TS) : U   ONR resident rep. is ACO (Y/N): N
 Defense priority rating   : NA   NA supplemental sheet
 Equipment title vests with: Sponsor   GIT X
   PER AGREEMENT, ARTICLE V, P.2
 Administrative comments -
   AMENDMENT 2 ADDS NEW FUNDS OF $35,000 PLUS ADDITIONAL COST-SHARE OF $8,750.
   NO OTHER CHANGES.

CA8120   Georgia Institute of Technology   Page: 1
Office of Contract Administration   18-FEB-1998 08:54
PROJECT CLOSEOUT - NOTICE

4
7

Closeout Notice Date   18-FEB-1998

Project Number E-20-W80   Doch Id   40211

Center Number 10/24-6-R8634-0A0

Project Director PENNELL, KURT

Project Unit   CIVIL ENGR

Sponsor   UNIV OF MICHIGAN/

Division Id   5823

Contract Number 032856   Contract Entity GTRC

Prime Contract Number R819605

Title   ORGANIC VAPOR SORPTION & DESORPTION IN UNSATURATED ZONE: RATES &
      EQUILIBRI

Effective Completion Date   17-MAY-1997 (Performance) 17-MAY-1997 (Reports)

Closeout Action:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	22-JUL-1997
Final Report of Inventions and/or Subcontracts	N	
Government Property Inventory and Related Certificate	N	
Classified Material Certificate	N	
Release and Assignment	Y	30-JUL-1997
Other	N	

Comments

Distribution Required:

Project Director/Principal Investigator	Y
Research Administrative Network	Y
Accounting	Y
Research Security Department	N
Reports Coordinator	Y
Research Property Team	Y
Supply Services Department/Procurement	Y
Georgia Tech Research Corporation	Y
Project File	Y

The Great Lakes Mid-Atlantic Hazardous Substance Research Center

Thrust Area I

Organic Vapor Sorption and Desorption in the Unsaturated Zone:

Rates and Equilibria

1st Quarterly Report

for the period

July 15, 1995 to October 15, 1994

Submitted November 14, 1995

Principal Investigator:

Kurt D. Pennell, Assistant Professor
School of Civil and Environmental Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0512
tel: 404-894-9365
fax: 404-853-3177
e-mail:kurt.pennell@ce.gatech.edu

Project Introduction and Objectives:

Vapor-phase sorption is one of the most important processes influencing the mobility and distribution of volatile organic chemicals (VOCs) in the unsaturated zone. Previous studies have demonstrated that oven-dry soils and clay minerals have a sizable capacity to sorb organic vapors, which is strongly correlated with the specific surface area of the solid phase (Chiou and Shoup, 1985; Rhue et al., 1988). Under natural conditions, however, the sorption of organic vapors usually occurs in the presence of water. As the soil moisture content or relative humidity increases, VOCs are displaced from adsorbent surfaces resulting in the suppression of organic vapor sorption (Chiou and Shoup, 1985; Pennell et al, 1992). This behavior is generally attributed to the ability of water molecules to effectively compete with nonpolar organic vapors for adsorption sites, such as exchangeable metal cations

Although the competitive effects of water on the magnitude of organic vapor sorption by soils are well established, the specific mechanisms responsible for the VOC sorption of organic vapors on hydrated or moist soils remains in debate. Chiou and Shoup (1985) postulated that hydrated soils behave as dual adsorbents, in which soil organic matter functions as a partition medium while mineral surfaces behave as a conventional solid adsorbent. These authors concluded that partitioning into soil organic matter was the dominant mechanisms governing vapor-phase sorption by soils. In contrast, Pennell et al. (1992) reported that sorption isotherms for p-xylene vapors at 90% relative humidity were consistently nonlinear and sorptive capacities were several times greater than could be attributed to partitioning into soil organic matter. In this work, Pennell et al. (1992) demonstrated that adsorption at the gas-liquid interface could account for up to 50% of p-xylene sorption on Webster soil at 90% relative humidity.

Although it is now acknowledged that several mechanisms may contribute to the overall sorption of organic vapors in the unsaturated zone, the effects of these processes contaminant fate and transport have not been considered in detail. Therefore, this research project is designed to quantify the rates, equilibria and energetics of organic vapor sorption in the unsaturated zone. To date, there exists limited information on rates and energetics of vapor-phase sorption, particularly in the presence of water. Such data is critical to the elucidation of mechanisms governing the bioavailability of VOCs in unsaturated soils. In addition, virtually no data exists on the competitive sorption of organic vapors in the presence of water. To address these specific issues the project has been divided into three subtasks listed below.

Task IIIA-Sorption Rates and Equilibria: Quantify the effects of moisture content and organic carbon content and type on the rates and equilibria of organic vapor sorption.

Task IIIB-Sorption of Binary Organic Vapors: Assess the influence of moisture content organic carbon content on the competitive sorption of binary organic vapor mixtures.

Task IIIC-Energetics of Vapor-Phase Sorption: Determine organic vapor heats of adsorption based on sorption isotherms measured at 20, 30 and 40°C.

Progress This Period:

During first three months of the project a significant effort was directed toward integrating our research activities with those of other Thrust Area I scientists. In addition, substantial progress was made with regard to the experimental aspects of the project. An on-line flow through apparatus was constructed to conduct single and binary vapor sorption experiments over a range of moisture contents (relative humidities). Preliminary surface area measurements were performed on Webster soil, and the sorption of toluene vapors by Webster soil was estimated using the multi-component sorption model of Pennell et al. (1992). These research activities are described in the remainder of the progress report.

1. Integration with Thrust Area I Research Groups:

The investigation of VOC sorption in the unsaturated zone has been coordinated with the research to be conducted in Tasks I (Adriaens) and IV (Weber) of Thrust Area I. Collaboration is planned with Dr. Peter Adriaens' research group in order to quantify the factors influencing rates of toluene degradation in moist soils. Measurements of equilibrium toluene sorption isotherms, rates of toluene sorption and desorption, and sorption energetics on moist soils will be utilized by Dr. Adriaens to interpret biodegradation data. Moisture release curves measured as part of Task III will also be used to select appropriate and consistent soil water contents for detailed study. Collaboration is also planned with Dr. Walter Weber (Tasks IV and VI), who is investigating contaminant sorption/desorption in water-saturated systems and the measurement of binding energies by supercritical fluid extraction (SFE). Measurements of VOC sorption rates and equilibria under saturated conditions will be used to evaluate the magnitude of solid-liquid sorption processes in unsaturated soils. In addition, competitive water and organic vapor sorption data obtained in Task III will be compared to SFE results. This information will be used to interpret the effects of polar solvents on SFE extraction efficiencies. Potential for collaboration also exists with Task V (Voice) and II (Fogler) unsaturated transport experiments are performed. In dynamic systems, the gas-liquid interface can play an important role in cell attachment and bioavailability.

Volatile organic chemicals selected for study are shown in Table 1. These compounds were chosen after consensus was reached with all Thrust Area I researchers. Particular emphasis is placed on toluene to provide for direct interaction with the biodegradation studies to be conducted as part of Task I (Adriaens). Sorbents used in the vapor-phase sorption studies were also selected after discussion with Thrust Area I researchers. Special effort was made to select sorbents that provided a range of organic carbon content and type. The matrix of sorbate-sorbent experiments to be conducted over a two-year funding period is shown in Table 2.

3

Table 1. Relevant properties of volatile organic compounds selected for use in Task III..

Chemical	MW (g/mole)	Density (g/cm³)	Solubility (mg/L)	Vapor Pressure (mm Hg)
Toluene	100.2	0.94	500	22
1,2-Dichlorobenzene	147.0	1.31	100	1
Trichloroethylene	131.4	1.46	1,100	58
Tetrachloroethylene	165.8	1.63	200	14

Table 2. Matrix of vapor-phase sorption experiments to be conducted as part of Task III.

Sorbent	Toluene	1,2-DCB	TCE	PCE
Wurtsmith soil	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Webster soil	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Ohio Shale	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Poly(butyl methacrylate)	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM

D=oven-dry organic equilibrium sorption isotherm (Task IIIA)
M=moist organic equilibrium sorption isotherm (Task IIIA)
MR=moist sorption/desorption rates (Task IIIA)
C=competitive equilibrium sorption oven-dry (Task IIIB)
CM= competitive equilibria sorption moist soil (Task IIIB)
E=sorption energetics (Task IIIC)

2. Experimental Methods and Apparatus

During the first few months of the project a flow-through apparatus was constructed as shown in Figure 1. The system is designed for batch sorption measurements and can be modified to accommodate dynamic measurements of organic vapor adsorption and desorption in soil columns. The effluent vapor stream is directly connected to an HP 6000 GC equipped with an internal six-port valve. This allows for accurate and rapid measurements of organic vapor concentrations in the gas stream. The valve system is air-pressure actuated and can be remotely controlled through the computer. As shown in Figure 2, adjustment of nitrogen flow through the needle valves shown on the left-hand side of the diagram permits both the relative humidity and

relative vapor pressure of the organic vapor to be varied over a wide range of values. The concentration of water and organic vapor in the flow stream is determined by direct injection via an internal sample loop. Sorbed (solid-phase) quantities of water and organic vapor will be determined by methanol extraction, using Karl Fisher titration for water and either HPLC or GC analysis of the organic. Additional single component experiments will be conducted using a Micromeritics ASAP 2010 surface area analyzer in collaboration with Dr. Weber's research group..

3. Surface Area Measurements

The primary objective of this work was to obtain specific surface area measurements for the sorbents used in the vapor-phase sorption experiments. These data will also be provided to the other Thrust Area I researchers. In addition to simply measuring baseline sorbent properties, this portion of the project was designed to assess the role of soil organic matter in vapor-phase sorption at 0% RH (oven-dry), and to correlate nitrogen/BET surface area measurements with the adsorption of organic vapors under similar experimental conditions. Initial experiments conducted during the past three months focused on surface area measurements for Webster soil. To investigate the influence the organic carbon content on nitrogen adsorption, a sample of the Webster soil was treated with a buffered solution containing hydrogen peroxide. This treatment resulted in a reduction of organic carbon content from 3.32% to 0.55%. The intent of this procedure was not to oxidize all of the soil organic matter, but rather to determine the effect of removing a significant fraction of the organic carbon. Nitrogen adsorption and desorption experiments were then conducted on the treated and untreated Webster soil using an Autosorb 1 Sorption Analyzer (Quantachrome). Representative adsorption and desorption isotherms for the Webster soils at 77°K are shown in Figure 2.

The Brunauer-Emmett-Teller (BET) equation was fit to the adsorption data over the relative vapor pressure range of 0.05 to 0.35 using a nonlinear least-squares procedure (SYSTAT ver. 5.0). When the number of adsorbed layers (n) is assumed to be infinite, which is valid over the range of relative vapor pressures considered, the BET equation can be written as:

$$\frac{S}{S_m} = \frac{C(P/P_0)}{(1-P/P_0)\left[1 - P/P_0 + C(P/P_0)\right]}$$

where S is the amount sorbed (mg/g), S_m is the monolayer adsorption capacity (mg/g), and P/P_0 is the relative vapor pressure. The dimensionless parameter C is related to the heat of adsorption on the bare surface (Q_a) and the heat of condensation of the liquid adsorbate (Q_{aa}) by the equation:

$$C \approx e^{(Q_a - Q_{aa})/RT}$$

where R is the gas constant and T is the absolute temp (°K). The values of C derived from the BET equation do not provide quantitative measures of heats of adsorption, but rather indicate the relative magnitude of adsorbate-adsorbent interactions. Specific surface areas of the adsorbents were then calculated using a cross-sectional area for N_2 of 0.162 nm^2/molec. Results of the BET analysis are shown in Table 3.

Table 3. BET parameters and specific surface area of treated and untreated Webster soil.

Soil	S_m (mg/g)	C	r^2	Surface Area (m^2/g)
Webster Soil	2.35	190	0.9997	8.2
Webster Soil HP	7.83	304	0.9998	27.3

Note that both the adsorption of nitrogen and the calculated surface areas were greater for the hydrogen peroxide treated Webster soil than the untreated Webster soil. These data demonstrate that removal of organic carbon from the sorbent actually resulted in enhanced nitrogen adsorption. This behavior can be attributed to the removal of organic coatings from mineral surfaces and the division of soil particles held together by soil organic matter. Similar studies will be conducted for the other sorbents listed in Table 2.

4. Predictions of Multi component Sorption of Toluene by Webster Soil

The sorption of organic vapors by hydrated (moist) soils can be described using a multi-mechanistic model which incorporates (a) dissolution into adsorbed water films, (b) adsorption on mineral surfaces, (c) sorption by soil organic matter, and (d) adsorption at the gas-liquid interface (Pennell et al., 1992). As an initial step toward evaluating this conceptual approach, the multi-component sorption of toluene vapors on Webster soil was estimated using specific surface area and organic carbon content measurements given in the previous section, and toluene sorption parameters obtained from the literature. Based on the proposed mechanistic model, organic vapor sorption is considered to be composed of the following components:

$$S_T = S_w + S_s + S_i$$

where S_T is the total sorption (mg/g), S_w is the amount dissolved in the adsorbed water film (mg/g), S_s is the amount sorbed by the solid phase (mg/g), and S_i is the amount adsorbed at the

6

gas-liquid interface (mg/g). Dissolution of the organic vapor into adsorbed water films can be described by the following equation assuming that Henry's Law is valid and that the adsorbed water film behaves as bulk water:

$$S_w = \frac{P\,MW\,w}{K_H}$$

where P is the pressure of the organic vapor (atm), MW is the molecular weight (g/mole), w is the gravimetric water content of the soil (g/g), and K_H is the Henry's Law constant (L atm/mole). Sorption by the solid phase can be described using a water-saturated distribution coefficient based on a linear model (K_d) or nonlinear model, such as the Freundlich equation (K_F). In this case we will assume that the sorption can be described using a linear distribution coefficient:

$$S_s = K_d\,C_{aq}$$

where C_{aq} is the aqueous or dissolved phase concentration of the organic species. For estimation purposes, the value of K_d was obtained from the measured organic carbon content of the soil and the Log K_{oc}-K_{ow} correlation of Karickhoff et al. (1979).

$$Log\,K_{oc} = 1.00\,Log\,K_{ow} - 0.21 \qquad K_d = K_{oc}\,f_{oc}$$

where K_{oc} is the organic carbon partition coefficient (L/kg), K_{ow} is the octanol-water partition coefficient and f_{oc} is fraction of organic carbon in the soil (g/kg). Adsorption at the gas-liquid interface can be described by the following equation:

$$S_i = \Gamma\,MW\,SA$$

where Γ is the surface excess (mol/cm^2), and SA is the surface area (m^2/g). For estimation purposes, the oven-dry surface area was utilized, assuming that the water content was relatively small and thus, the gas-liquid interfacial area could be approximated by the solid phase surface area. The surface excess can be obtained from the Gibbs adsorption equation:

$$\Gamma = -\frac{d\gamma}{d\mu}$$

7

where γ is the surface tension (dyne/cm) and μ is the chemical potential. If the organic vapor obeys the ideal gas law the above equation can be rewritten as:

$$\Gamma = -\frac{P}{RT}\frac{d\gamma}{dP}$$

Using surface tension data reported by Cutting and Jones (1955), the relationship between surface excess and toluene vapor pressure was calculated, as shown in Figure 3. These data were then utilized to obtain the composite isotherm shown in Figure 4. The composite isotherm (solid line) conforms to a Type III isotherm which is typical for the sorption of organic vapors on moist soils (Pennell et al. 1992). It should also be noted that solid-phase sorption and adsorption at the gas-liquid interface were the primary mechanisms contributed to the estimated toluene vapor sorption. For aquifer materials, which typically have low organic carbon contents, adsorption at the gas-liquid interface is likely to be a dominate process. It should be recognized, however, that as the water content of the soil increases, the importance of the gas-liquid interface will diminish due to the reduction in gas-liquid interfacial area. In future experiments we will measure the sorption of toluene vapors on moist Webster soil and compare these experimental results to the theoretical model described above.

References

Chiou, C.T. and T.D. Shoup. 1985. Soil sorption of organic vapors and the effects of humidity on sorptive mechanism and capacity. Environ. Sci. Technol. 19:1196-1200.

Cutting, C.L. and D.C. Jones. 1955. Adsorption of insoluble vapors on water surfaces. J.Chem. Soc. 4067-4075.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13:241-248.

Pennell, K.D., R.D. Rhue, P.S.C. Rao, and C.T. Johnston. 1992. Vapor-phase sorption of p-xylene and water on soils and clay minerals. Environ. Sci. Technol. 26:756-763.

Rhue, R.D., K.D. Pennell, P.S.C. Rao, and W.H. Reve. 1989. Competitive adsorption of alkylbenzene and water vapors on predominantly mineral surfaces. Chemosphere 18:1971-1986.

Organic Vapor Sorption/Desorption Experiments
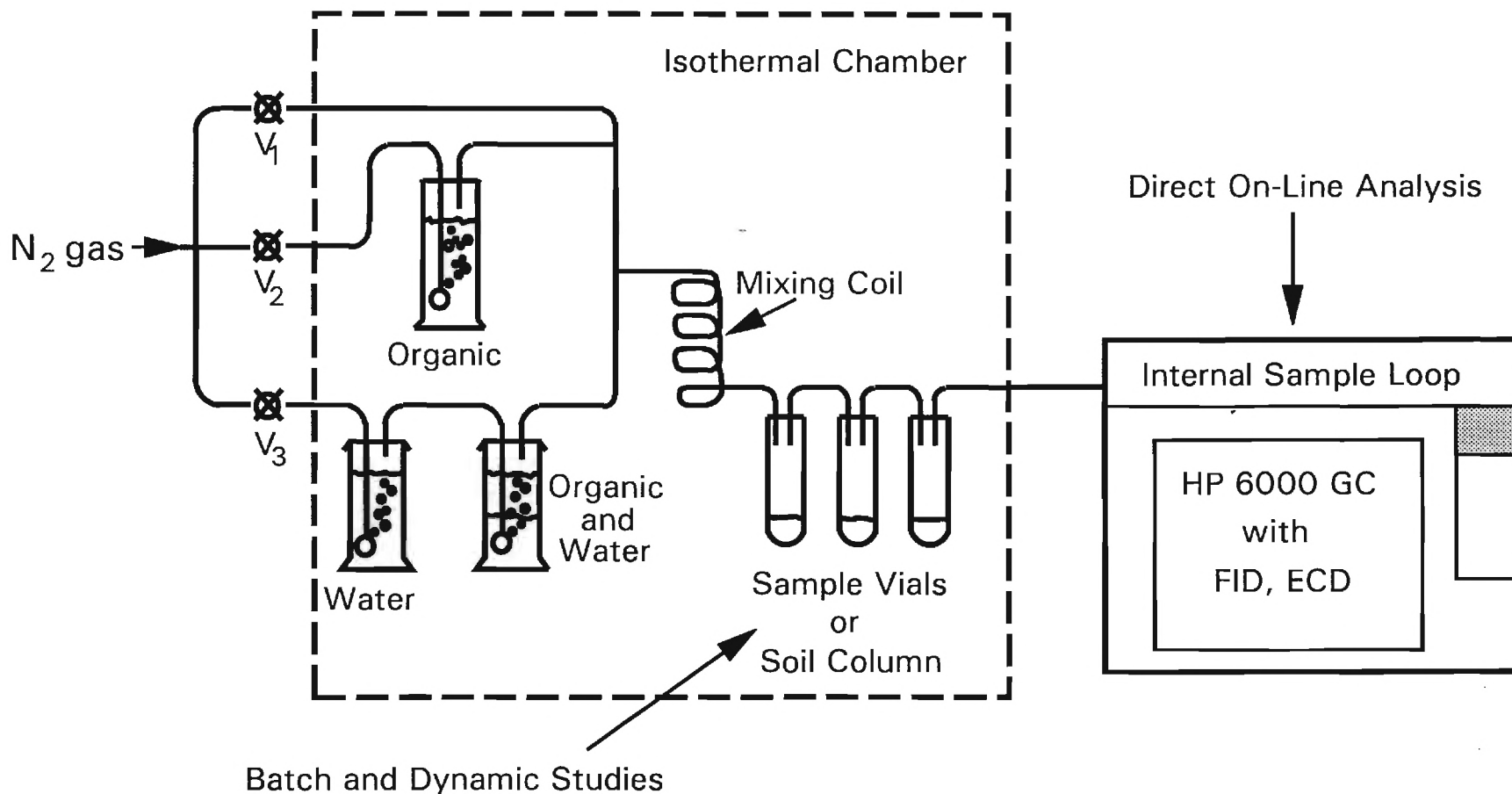
Experimental Apparatus

Figure 1.

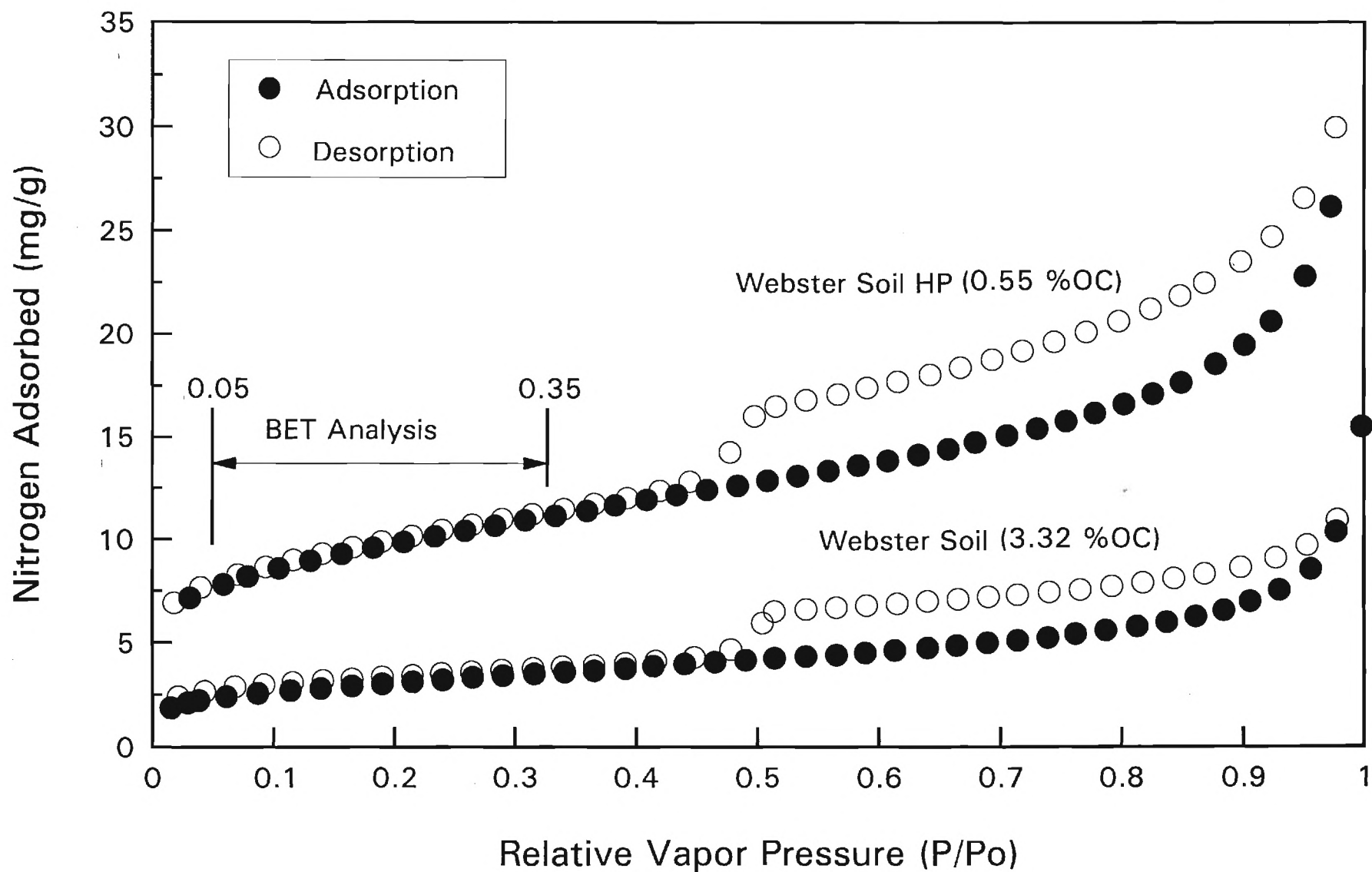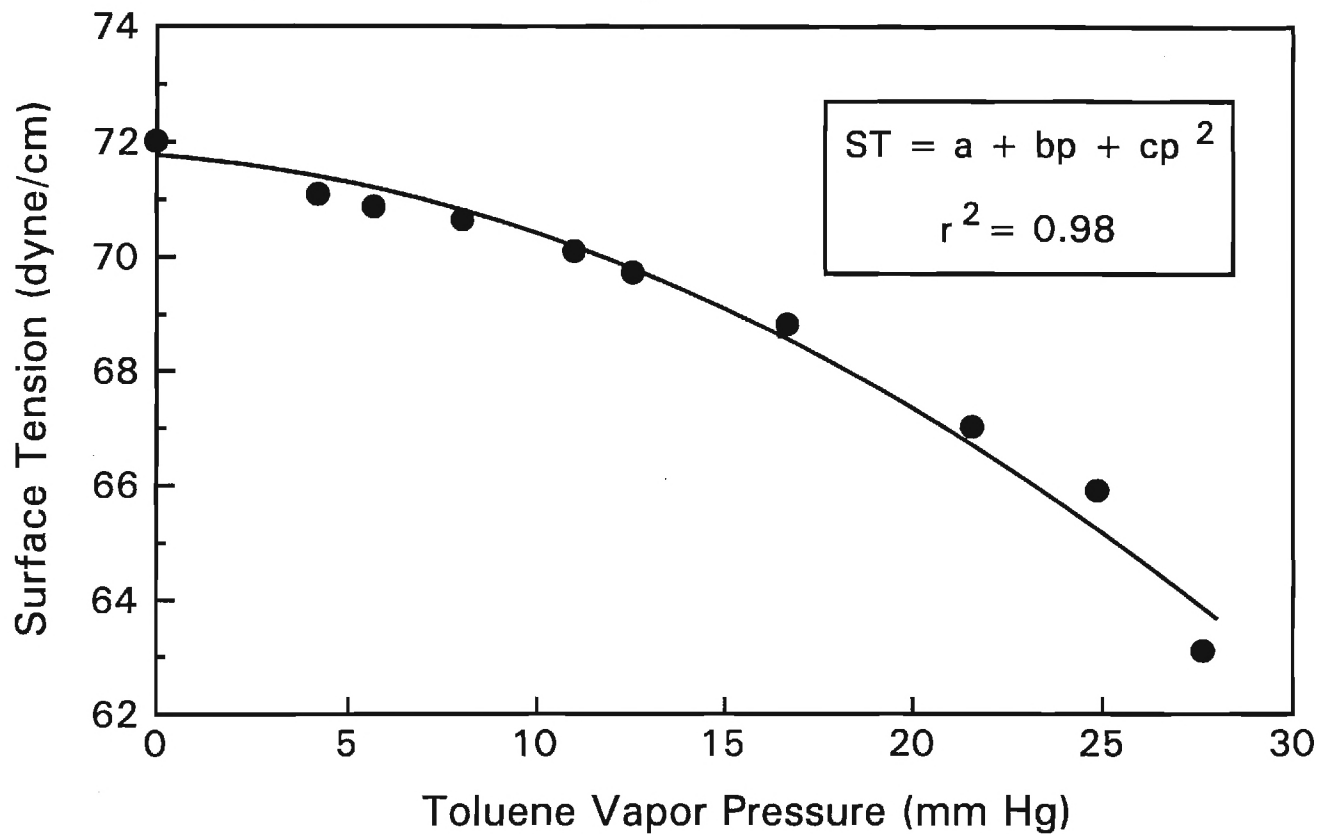*Effect of Organic Carbon Removal on Nitrogen Adsorption*

Figure 2.

Surface Tension

$$ST = a + bp + cp^2$$

$$r^2 = 0.98$$

Surface Excess

$$SE = -\frac{P}{RT}\frac{d\,ST}{d\,P}$$
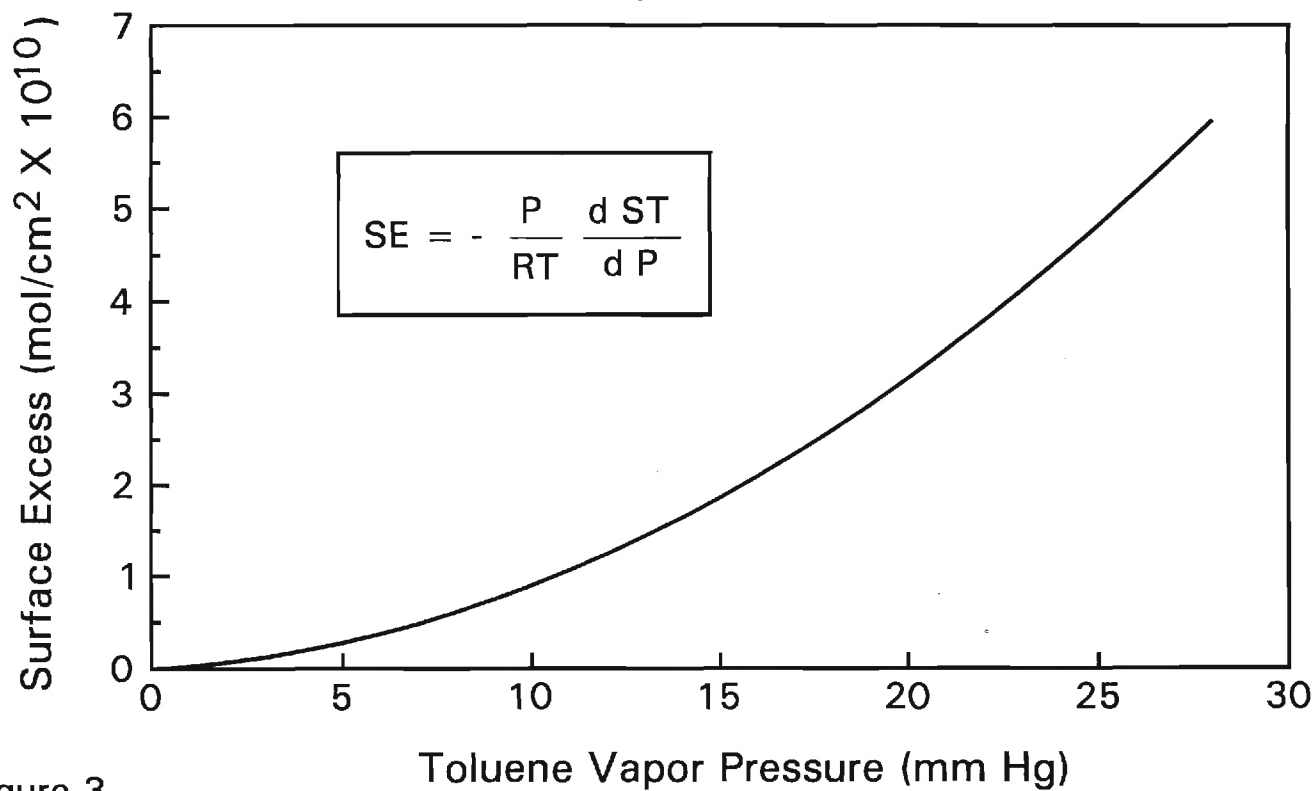
Figure 3.

Estimated Toluene Vapor Sorption on Webster Soil

Surface Area = 8.2 m^2/g
Kd = 12.38 ml/g
Organic Carbon = 3.3 %
Water Content = 0.07 g/g
Surface Tension Data
Cutting and Jones, 1955

Multicomponent Sorption
Solid Phase
G-L Interface
Adsorbed Water
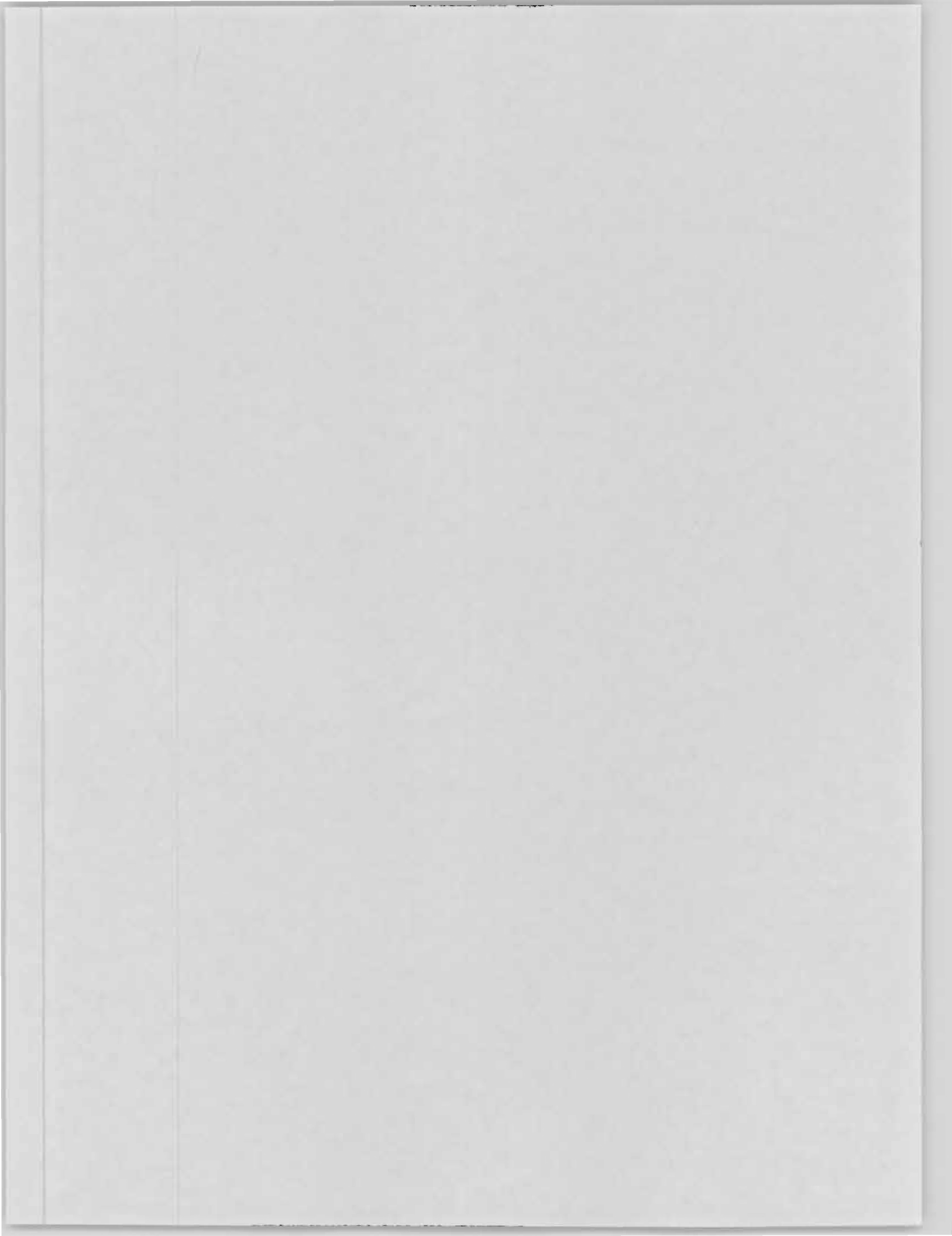
Toluene Sorbed (mg/g)

Relative Vapor Pressure (P/Po)

Figure 4.

The Great Lakes Mid-Atlantic Hazardous Substance Research Center

Thrust Area I

Organic Vapor Sorption and Desorption in the Unsaturated Zone:

Rates and Equilibria

2nd Quarterly Report

for the period

October 16, 1995 to January 15, 1996

Submitted February 14, 1996

Principal Investigator:

Kurt D. Pennell, Assistant Professor
School of Civil and Environmental Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0512
tel: 404-894-9365
fax: 404-853-3177
e-mail:kurt.pennell@ce.gatech.edu

Project Introduction and Objectives:

Vapor-phase sorption is one of the most important processes influencing the mobility and distribution of volatile organic chemicals (VOCs) in the unsaturated zone. Previous studies have demonstrated that oven-dry soils and clay minerals have a sizable capacity to sorb organic vapors, which is strongly correlated with the specific surface area of the solid phase (Chiou and Shoup, 1985; Rhue et al., 1988). Under natural conditions, however, the sorption of organic vapors usually occurs in the presence of water. As the soil moisture content or relative humidity increases, VOCs are displaced from adsorbent surfaces resulting in the suppression of organic vapor sorption (Chiou and Shoup, 1985; Pennell et al, 1992). This behavior is generally attributed to the ability of water molecules to effectively compete with nonpolar organic vapors for adsorption sites, such as exchangeable metal cations

Although the competitive effects of water on the magnitude of organic vapor sorption by soils are well established, the specific mechanisms responsible for the VOC sorption of organic vapors on hydrated or moist soils remains in debate. Chiou and Shoup (1985) postulated that hydrated soils behave as dual adsorbents, in which soil organic matter functions as a partition medium while mineral surfaces behave as a conventional solid adsorbent. These authors concluded that partitioning into soil organic matter was the dominant mechanisms governing vapor-phase sorption by soils. In contrast, Pennell et al. (1992) reported that sorption isotherms for p-xylene vapors at 90% relative humidity were consistently nonlinear and sorptive capacities were several times greater than could be attributed to partitioning into soil organic matter. In this work, Pennell et al. (1992) demonstrated that adsorption at the gas-liquid interface could account for up to 50% of p-xylene sorption on Webster soil at 90% relative humidity.

Although it is now acknowledged that several mechanisms may contribute to the overall sorption of organic vapors in the unsaturated zone, the effects of these processes contaminant fate and transport have not been considered in detail. Therefore, this research project is designed to quantify the rates, equilibria and energetics of organic vapor sorption in the unsaturated zone. To date, there exists limited information on rates and energetics of vapor-phase sorption, particularly in the presence of water. Such data is critical to the elucidation of mechanisms governing the bioavailability of VOCs in unsaturated soils. In addition, virtually no data exists on the competitive sorption of organic vapors in the presence of water. To address these specific issues the project has been divided into three subtasks listed below.

Task IIIA-Sorption Rates and Equilibria: Quantify the effects of moisture content and organic carbon content and type on the rates and equilibria of organic vapor sorption.

Task IIIB-Sorption of Binary Organic Vapors: Assess the influence of moisture content organic carbon content on the competitive sorption of binary organic vapor mixtures.

Task IIIC-Energetics of Vapor-Phase Sorption: Determine organic vapor heats of adsorption based on sorption isotherms measured at 20, 30 and 40°C.

Progress This Period:

During 2nd quarter of the project (16 October 1995 to 15 January 1996) our research efforts were directed toward completing the construction of the organic vapor flow apparatus and conducting initial measurements of toluene vapor sorption on oven-dried Webster soil. These research activities are described in the following sections of the progress report.

1. Experimental Methods and Apparatus

Over the last three months, construction of the organic vapor flow apparatus was completed (Figure 1). The system is designed for batch sorption measurements, but can be modified to accommodate dynamic measurements of organic vapor adsorption and desorption in soil columns. The effluent vapor stream is directly connected to an HP 6000 GC equipped with an internal six-port valve. This allows for accurate and rapid measurements of organic vapor concentrations in the gas stream. The valve system is air-pressure actuated and can be remotely controlled through the computer. As shown in Figure 1, adjustment of nitrogen flow through the needle valves shown on the left-hand side of the diagram permits both the relative humidity and relative vapor pressure of the organic vapor to be varied over a wide range of values. The concentration of water and organic vapor in the flow stream is determined by direct injection via an internal sample loop. Sorbed (solid-phase) quantities of water and organic vapor will be determined by methanol extraction, using Karl Fisher titration for water and either HPLC or GC analysis of the organic. Volatile organic chemicals selected for study are shown in Table 1. These compounds were chosen after consensus was reached with all Thrust Area I researchers. Particular emphasis is placed on toluene to provide for direct interaction with the biodegradation studies to be conducted as part of Task I (Adriaens). Sorbents used in the vapor-phase sorption studies were also selected after discussion with Thrust Area I researchers. Special effort was made to select sorbents that provided a range of organic carbon content and type. The matrix of sorbate-sorbent experiments to be conducted over a two-year funding period is shown in Table 2.

2. Toluene Vapor Sorption Measurements

A representative isotherm for the equilibrium sorption of toluene vapors on webster soil is shown in Figure 2. The isotherm is expressed as the amount of organic vapor sorbed (mg/g) versus the relative vapor pressure of toluene (P/Po), where the saturated vapor pressure (Po) is equal to 22 mm Hg. The toluene sorption data conform to a Type-II Brunauer-Emmett-Teller (BET) isotherm, which is characteristic of organic vapor sorption on oven-dried (0% relative humidity) soils and clay minerals (e.g., see Pennell et al., 1992). Assuming that the number of adsorbed layers is infinite, the BET equation may be written as:

$$\frac{S}{S_m} = \frac{C(P/P_0)}{(1-P/P_0)\left[1-P/P_0+C(P/P_0)\right]} \tag{1}$$

3

where S is the amount sorbed (mg/g), S_m is the monolayer adsorption capacity (mg/g), and P/P_0 is the relative vapor pressure. The dimensionless parameter C is related to the heat of adsorption on the bare surface (Q_a) and the heat of condensation of the liquid adsorbate (Q_{aa}) by the equation:

$$C \approx e^{(Q_a - Q_{aa})/RT} \tag{2}$$

where R is the gas constant and T is the absolute temp (°K). The values of C derived from the BET equation do not provide quantitative measures of heats of adsorption, but rather indicate the relative magnitude of adsorbate-adsorbent interactions. The sorption data shown in Figure 2 were fit to the BET equation over the relative vapor pressure range of 0.05 to 0.35 using a nonlinear least-squares procedure (SYSTAT, ver. 5.0). The resulting values of S_m and C are shown in Table 3, along with values obtained from the N_2 adsorption measurements presented in our first quarterly report.

The surface area available for the adsorption of an organic vapor can be estimated from the value of S_m and the area occupied by each adsorbed molecule. The cross-sectional area (a_m) of toluene was calculated to be 0.343 nm^2/molecule, using the following equation:

$$a_m = 1.09(MW/\tau A)^{2/3} \tag{3}$$

where MW is the molecular weight, τ is the liquid density, and A is Avogadro's number. This equation assumes that the adsorbed molecules are oriented in a hexagonal close packing at a density similar to the bulk liquid. The BET surface area calculated in this manner is shown in Table 3. Notice that this value is similar to the surface area previously obtained from N_2 adsorption data. It is widely recognized that N_2 adsorption provides a measure of the external surface area of soils and clay minerals. The similarity in surface area values determined by N2 and toluene sorption suggests that (a) nonpolar organic vapors are adsorbed on the external surfaces of oven-dried soil materials and (b) N_2 surface area measurements provide a useful tool for predicting the magnitude of organic vapor sorption under anhydrous conditions.

Future Plans: Over the next three months, toluene vapor sorption iostherms will be measured for the remainder of sorbents in the experimental matrix (Wurtsmith soil, Ohio shale, and Poly(butyl methacrytale). In addition, we have recently submitted a request for the purchase of a Micromeretics Surface Area Analyzer (Model ASAP 2100) which will be used to conduct additional nitrogen and organic vapor sorption measurement, as well as characterization of sorbent microporosity.

Table 1. Relevant properties of volatile organic compounds selected for use in Task III..

Chemical	MW (g/mole)	Density (g/cm³)	Solubility (mg/L)	Vapor Pressure (mm Hg)
Toluene	100.2	0.94	500	22
1,2-Dichlorobenzene	147.0	1.31	100	1
Trichloroethylene	131.4	1.46	1,100	58
Tetrachloroethylene	165.8	1.63	200	14

Table 2. Matrix of vapor-phase sorption experiments to be conducted as part of Task III.

Sorbent	Toluene	1,2-DCB	TCE	PCE
Wurtsmith soil	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Webster soil	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Ohio Shale	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Poly(butyl methacrylate)	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM

D=oven-dry organic equilibrium sorption isotherm (Task IIIA)
M=moist organic equilibrium sorption isotherm (Task IIIA)
MR=moist sorption/desorption rates (Task IIIA)
C=competitive equilibrium sorption oven-dry (Task IIIB)
CM= competitive equilibria sorption moist soil (Task IIIB)
E=sorption energetics (Task IIIC)

Table 3. BET parameters and specific surface area of webster soil based on N_2 and toluene sorption isotherms.

Soil	S_m (mg/g)	C	r^2	Surface Area (m²/g)
Webster Soil/N_2	2.35	190	0.9997	8.2
Webster Soil/Toluene	5.07	18	0.992	10.5

Organic Vapor Sorption/Desorption Experiments
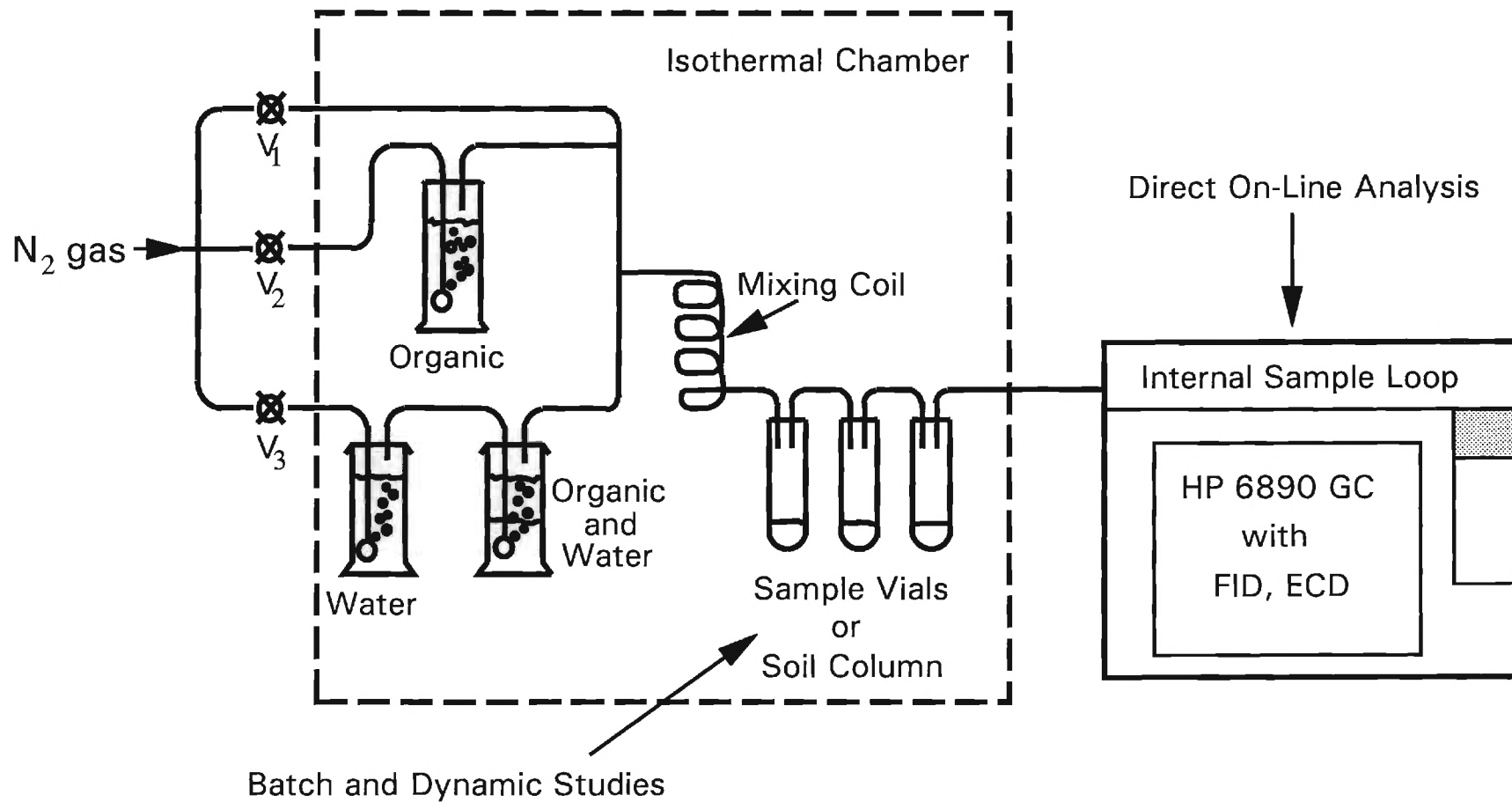
Experimental Apparatus

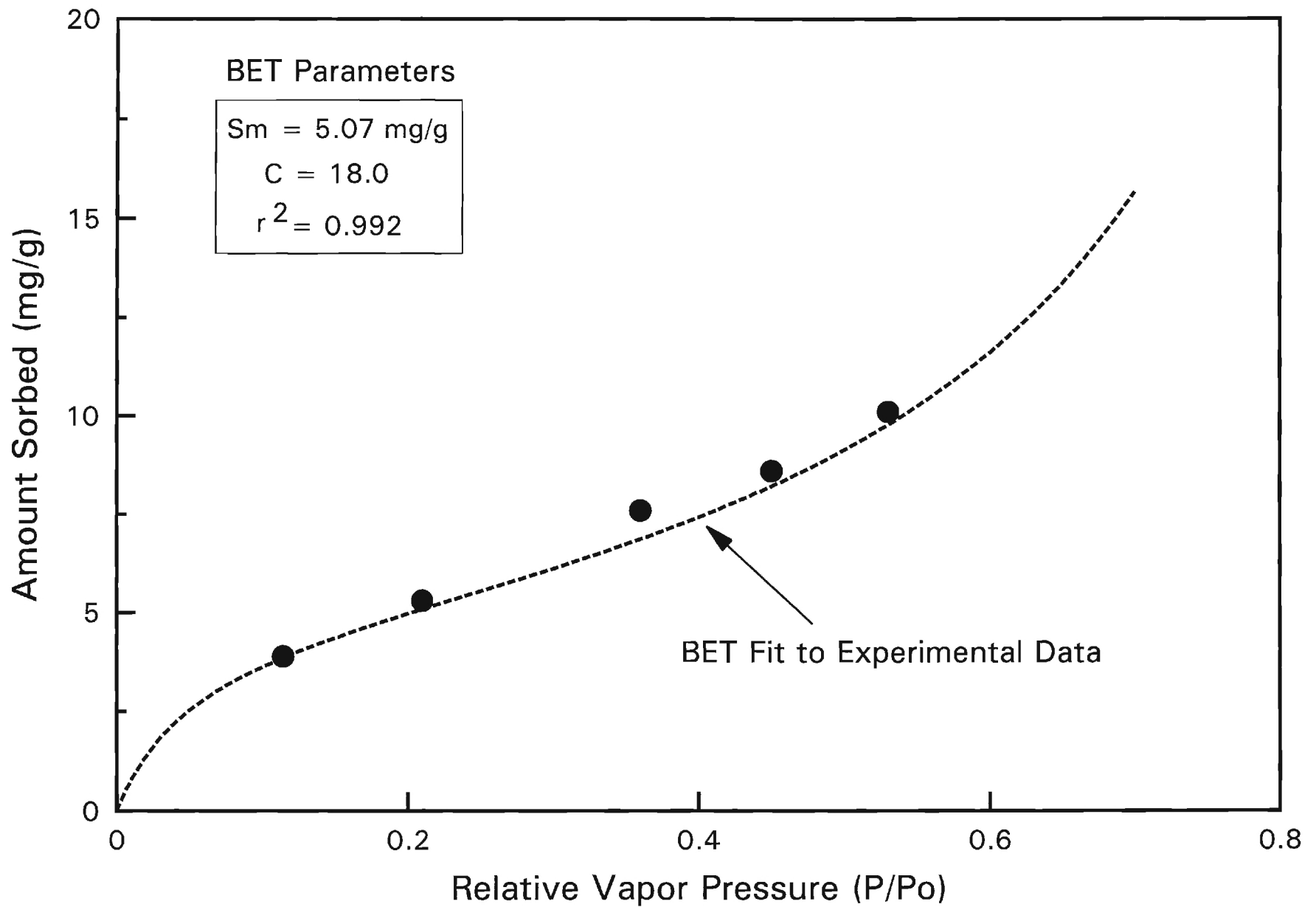Figure 1.

Toluene Sorption by Oven-Dried Webster Soil

BET Parameters

Sm = 5.07 mg/g

C = 18.0

r^2 = 0.992

BET Fit to Experimental Data

Amount Sorbed (mg/g)

Relative Vapor Pressure (P/Po)

Figure 2.

The Great Lakes Mid-Atlantic Hazardous Substance Research Center

Thrust Area I

Organic Vapor Sorption and Desorption in the Unsaturated Zone:

Rates and Equilibria

3rd Quarterly Report

for the period

January 16, 1996 to April 15, 1996

Submitted May 14, 1996

Principal Investigator:

Kurt D. Pennell, Assistant Professor
School of Civil and Environmental Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0512
tel: 404-894-9365
fax: 404-853-3177
e-mail:kurt.pennell@ce.gatech.edu

Project Introduction and Objectives:

Vapor-phase sorption is one of the most important processes influencing the mobility and distribution of volatile organic chemicals (VOCs) in the unsaturated zone. Previous studies have demonstrated that oven-dry soils and clay minerals have a sizable capacity to sorb organic vapors, which is strongly correlated with the specific surface area of the solid phase (Chiou and Shoup, 1985; Rhue et al., 1988). Under natural conditions, however, the sorption of organic vapors usually occurs in the presence of water. As the soil moisture content or relative humidity increases, VOCs are displaced from adsorbent surfaces resulting in the suppression of organic vapor sorption (Chiou and Shoup, 1985; Pennell et al, 1992). This behavior is generally attributed to the ability of water molecules to effectively compete with nonpolar organic vapors for adsorption sites, such as exchangeable metal cations

Although the competitive effects of water on the magnitude of organic vapor sorption by soils are well established, the specific mechanisms responsible for the VOC sorption of organic vapors on hydrated or moist soils remains in debate. Chiou and Shoup (1985) postulated that hydrated soils behave as dual adsorbents, in which soil organic matter functions as a partition medium while mineral surfaces behave as a conventional solid adsorbent. These authors concluded that partitioning into soil organic matter was the dominant mechanisms governing vapor-phase sorption by soils. In contrast, Pennell et al. (1992) reported that sorption isotherms for p-xylene vapors at 90% relative humidity were consistently nonlinear and sorptive capacities were several times greater than could be attributed to partitioning into soil organic matter. In this work, Pennell et al. (1992) demonstrated that adsorption at the gas-liquid interface could account for up to 50% of p-xylene sorption on Webster soil at 90% relative humidity.

Although it is now acknowledged that several mechanisms may contribute to the overall sorption of organic vapors in the unsaturated zone, the effects of these processes contaminant fate and transport have not been considered in detail. Therefore, this research project is designed to quantify the rates, equilibria and energetics of organic vapor sorption in the unsaturated zone. To date, there exists limited information on rates and energetics of vapor-phase sorption, particularly in the presence of water. Such data is critical to the elucidation of mechanisms governing the bioavailability of VOCs in unsaturated soils. In addition, virtually no data exists on the competitive sorption of organic vapors in the presence of water. To address these specific issues the project has been divided into three subtasks listed below.

Task IIIA-Sorption Rates and Equilibria: Quantify the effects of moisture content and organic carbon content and type on the rates and equilibria of organic vapor sorption.

Task IIIB-Sorption of Binary Organic Vapors: Assess the influence of moisture content organic carbon content on the competitive sorption of binary organic vapor mixtures.

Task IIIC-Energetics of Vapor-Phase Sorption: Determine organic vapor heats of adsorption based on sorption isotherms measured at 20, 30 and 40°C.

2

Progress This Period:

During 2nd quarter of the project (16 October 1995 to 15 January 1996) our research efforts were directed toward completing the construction of the organic vapor flow apparatus and conducting initial measurements of toluene vapor sorption on oven-dried Webster soil. These research activities are described in the following sections of the progress report.

1. Experimental Methods and Apparatus

Over the last three months, construction of the organic vapor flow apparatus was completed (Figure 1). The system is designed for batch sorption measurements, but can be modified to accommodate dynamic measurements of organic vapor adsorption and desorption in soil columns. The effluent vapor stream is directly connected to an HP 6000 GC equipped with an internal six-port valve. This allows for accurate and rapid measurements of organic vapor concentrations in the gas stream. The valve system is air-pressure actuated and can be remotely controlled through the computer. As shown in Figure 1, adjustment of nitrogen flow through the needle valves shown on the left-hand side of the diagram permits both the relative humidity and relative vapor pressure of the organic vapor to be varied over a wide range of values. The concentration of water and organic vapor in the flow stream is determined by direct injection via an internal sample loop. Sorbed (solid-phase) quantities of water and organic vapor will be determined by methanol extraction, using Karl Fisher titration for water and either HPLC or GC analysis of the organic. Volatile organic chemicals selected for study are shown in Table 1. These compounds were chosen after consensus was reached with all Thrust Area I researchers. Particular emphasis is placed on toluene to provide for direct interaction with the biodegradation studies to be conducted as part of Task I (Adriaens). Sorbents used in the vapor-phase sorption studies were also selected after discussion with Thrust Area I researchers. Special effort was made to select sorbents that provided a range of organic carbon content and type. The matrix of sorbate-sorbent experiments to be conducted over a two-year funding period is shown in Table 2.

2. Toluene Vapor Sorption Measurements

A representative isotherm for the equilibrium sorption of toluene vapors on webster soil is shown in Figure 2. The isotherm is expressed as the amount of organic vapor sorbed (mg/g) versus the relative vapor pressure of toluene (P/Po), where the saturated vapor pressure (Po) is equal to 22 mm Hg. The toluene sorption data conform to a Type-II Brunauer-Emmett-Teller (BET) isotherm, which is characteristic of organic vapor sorption on oven-dried (0% relative humidity) soils and clay minerals (e.g., see Pennell et al., 1992). Assuming that the number of adsorbed layers is infinite, the BET equation may be written as:

$$\frac{S}{S_m} = \frac{C(P/P_0)}{(1-P/P_0)\left[1 - P/P_0 + C(P/P_0)\right]} \tag{1}$$

where S is the amount sorbed (mg/g), S_m is the monolayer adsorption capacity (mg/g), and P/P_0 is the relative vapor pressure. The dimensionless parameter C is related to the heat of adsorption on the bare surface (Q_a) and the heat of condensation of the liquid adsorbate (Q_{aa}) by the equation:

$$C \approx e^{(Q_a - Q_{aa})/RT} \qquad (2)$$

where R is the gas constant and T is the absolute temp (°K). The values of C derived from the BET equation do not provide quantitative measures of heats of adsorption, but rather indicate the relative magnitude of adsorbate-adsorbent interactions. The sorption data shown in Figure 2 were fit to the BET equation over the relative vapor pressure range of 0.05 to 0.35 using a nonlinear least-squares procedure (SYSTAT, ver. 5.0). The resulting values of S_m and C are shown in Table 3, along with values obtained from the N_2 adsorption measurements presented in our first quarterly report.

The surface area available for the adsorption of an organic vapor can be estimated from the value of S_m and the area occupied by each adsorbed molecule. The cross-sectional area (a_m) of toluene was calculated to be 0.343 nm²/molecule, using the following equation:

$$a_m = 1.09 (MW/\tau A)^{2/3} \qquad (3)$$

where MW is the molecular weight, τ is the liquid density, and A is Avogadro's number. This equation assumes that the adsorbed molecules are oriented in a hexagonal close packing at a density similar to the bulk liquid. The BET surface area calculated in this manner is shown in Table 3. Notice that this value is similar to the surface area previously obtained from N_2 adsorption data. It is widely recognized that N_2 adsorption provides a measure of the external surface area of soils and clay minerals. The similarity in surface area values determined by N2 and toluene sorption suggests that (a) nonpolar organic vapors are adsorbed on the external surfaces of oven-dried soil materials and (b) N_2 surface area measurements provide a useful tool for predicting the magnitude of organic vapor sorption under anhydrous conditions.

Future Plans: Over the next three months, toluene vapor sorption iostherms will be measured for the remainder of sorbents in the experimental matrix (Wurtsmith soil, Ohio shale, and Poly(butyl methacrytale). In addition, we have recently submitted a request for the purchase of a Micromeretics Surface Area Analyzer (Model ASAP 2100) which will be used to conduct additional nitrogen and organic vapor sorption measurement, as well as characterization of sorbent microporosity.

4

Table 1. Relevant properties of volatile organic compounds selected for use in Task III..

Chemical	MW (g/mole)	Density (g/cm^3)	Solubility (mg/L)	Vapor Pressure (mm Hg)
Toluene	100.2	0.94	500	22
1,2-Dichlorobenzene	147.0	1.31	100	1
Trichloroethylene	131.4	1.46	1,100	58
Tetrachloroethylene	165.8	1.63	200	14

Table 2. Matrix of vapor-phase sorption experiments to be conducted as part of Task III.

Sorbent	Toluene	1,2-DCB	TCE	PCE
Wurtsmith soil	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Webster soil	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Ohio Shale	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Poly(butyl methacrylate)	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM

D=oven-dry organic equilibrium sorption isotherm (Task IIIA)
M=moist organic equilibrium sorption isotherm (Task IIIA)
MR=moist sorption/desorption rates (Task IIIA)
C=competitive equilibrium sorption oven-dry (Task IIIB)
CM= competitive equilibria sorption moist soil (Task IIIB)
E=sorption energetics (Task IIIC)

Table 3. BET parameters and specific surface area of webster soil based on N_2 and toluene sorption isotherms.

Soil	S_m (mg/g)	C	r^2	Surface Area (m^2/g)
Webster Soil/N_2	2.35	190	0.9997	8.2
Webster Soil/Toluene	5.07	18	0.992	10.5

The Great Lakes Mid-Atlantic Hazardous Substance Research Center

Thrust Area I

Organic Vapor Sorption and Desorption in the Unsaturated Zone:

Rates and Equilibria

4th Quarterly Report

for the period

April 16, 1996 to July 15, 1996

Submitted August 14, 1996

Principal Investigator:

Kurt D. Pennell, Assistant Professor
School of Civil and Environmental Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0512
tel: 404-894-9365
fax: 404-853-3177
e-mail:kurt.pennell@ce.gatech.edu

Organic Vapor Sorption and Transport in Unsaturated Soils

Kurt D. Pennell[1] and Joshua L. Schlanger[1]

[1]School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332

Vapor-phase sorption is one of the most important processes influencing the mobility and distribution of volatile organic chemicals (VOCs) in the unsaturated zone. Previous studies have demonstrated that oven-dry soils and clay minerals have a sizable capacity to sorb organic vapors (Chiou and Shoup, 1985; Rhue et al., 1988). As the soil moisture content or relative humidity increases, however, VOCs are displaced from adsorbent surfaces resulting in the suppression of organic vapor sorption (Chiou and Shoup, 1985; Pennell et al., 1992). Although the competitive effects of water on the magnitude of organic vapor sorption by soils are well established, the specific mechanisms responsible for the VOC sorption of organic vapors on moist soils remain in debate. In addition, there exists only limited information on the rates and energetics of vapor-phase sorption, particularly in the presence of water.

Thus, the overall objective of this project was to quantify the rates, equilibria and energetics of organic vapor sorption in the unsaturated zone. Specifically, this research focuses on the sorption and transport of single and binary mixtures of organic vapors in the presence of water. Results of this work will be directly linked to the biogedradation and aqueous-phase sorption studies currently being conducted by other researchers involved in Thrust Area I (Fundamental Aspects of Bioavailability) of the GLMAC HSRC. It is anticipated that this integrated approach will lead to a more basic understanding of VOC bioavailability in the unsaturated zone. From a practical perspective, such information could be used to improve the design of bioventing systems and modify unsaturated zone conditions to enhance biotransformation rates.

Organic vapor sorption and transport experiments were conducted in a temperature-controlled chamber containing several gas-washing bottles and flow control valves. The system, originally designed for batch sorption measurements, was modified to accommodate dynamic measurements of organic vapor sorption and desorption in soil columns. Adjustment of nitrogen flow through needle valves permitted both the relative humidity and relative vapor pressure of the organic vapor of the influent flow stream to be varied over a wide range of values. The effluent flow stream was directly connected to an Hewlett Packard 6890 GC equipped with an internal six-port valve. The concentration of water and organic vapor in the flow stream was determined by direct injection into the internal sample loop. Sorbed-phase concentrations of water and organic vapor were determined by methanol extraction, using Karl Fisher titration for water and GC analysis for the organic species. Single component vapor sorption experiments and surface area measurements were conducted using a Micromeritics ASAP 2010 surface area analyzer. Properties of the VOCs selected for study are shown in Table 1. Sorbents used in this work included Wurtsmith aquifer material, Ohio shale, Webster soil and a polymer (methyl methacrylate).

Table 1. Relevant properties of volatile organic compounds used in vapor sorption studies.

Chemical	MW (g/mole)	Density (g/cm^3)	Solubility (mg/L)	Vapor Pressure (mm Hg)
Toluene	92.1	0.94	500	27
1,2-Dichlorobenzene	147.0	1.31	100	1
Trichloroethylene	131.4	1.46	1,100	58
Tetrachloroethylene	165.8	1.63	150	14

Sorption isotherms were expressed as the amount of organic vapor sorbed (S, mg/g) versus the relative vapor pressure of toluene (P/Po), where the saturated vapor pressure (Po) is given in

Table 1. Organic vapor sorption on oven-dry (0% RH) sorbents conformed to the Type-II Brunauer-Emmett-Teller (BET) isotherm. Assuming that the number of adsorbed layers is infinite, these data may be described by the BET equation:

$$\frac{S}{S_m} = \frac{C\,(P/P_0)}{(1-P/P_0)\left[1-P/P_0+C\,(P/P_0)\right]}$$

where S is the amount sorbed (mg/g), S_m is the monolayer adsorption capacity (mg/g), and P/P_0 is the relative vapor pressure. The dimensionless parameter C is related to the heat of adsorption on the bare surface (Q_a) and the heat of condensation of the liquid adsorbate (Q_{aa}). The 0% RH sorption data were fit to the BET equation over the relative vapor pressure range of 0.05 to 0.35 using a nonlinear least-squares procedure (SYSTAT). As an example, the values of S_m and C for toluene vapor sorption on dry Webster soil were 5.07 and 18, respectively, with an r^2 value of 0.992. The surface area available for the adsorption of organic vapors can be estimated from the value of S_m and the area occupied by each adsorbed molecule. The cross-sectional area (a_m) of toluene was calculated to be 0.343 nm^2/molecule, using the following equation:

$$a_m = 1.09\,(MW/\tau A)^{2/3}$$

where MW is the molecular weight, τ is the liquid density, and A is Avogadro's number. This equation assumes that the adsorbed molecules are oriented in a hexagonal close packing at a density similar to the bulk liquid. The surface area calculated in this manner was 10.5 m^2/g, which is close to the surface area obtained from N_2 adsorption data (8.2 m^2/g). Similar results were observed for the other sorbate-sorbent systems investigated. The similarity in surface area values determined from N_2 and organic vapor sorption suggests that: (1) nonpolar organic vapors are adsorbed on the external surfaces of dry soil materials and (2) N_2 surface area measurements can be utilized to predict the extent of organic vapor sorption under anhydrous conditions.

As the relative humidity or moisture content was increased, the magnitude of organic vapor sorption decreased and the shape of the sorption isotherm shifted from Type II to Type III. The measured sorption of toluene vapors on moist webster soil was described using a multi-mechanistic approach which incorporates (1) dissolution into adsorbed water films, (2) adsorption on mineral surfaces, (3) absorption (uptake) by the solid phase, and (d) adsorption at the gas-liquid interface (Pennell et al., 1992). Using independently determined values of aqueous solubility, aqueous-phase sorption, and the Gibbs surface excess, a composite isotherm was developed which closely matched the experimental data. For this system, solid-phase sorption and adsorption at the gas-liquid interface were the primary mechanisms contributing to toluene vapor sorption. Results of the toluene vapor column experiments conducted at a P/Po of 0.5 were described using a two-site, linear sorption model, and will be discussed in more detail in the poster presentation.

References
Chiou, C.T. and T.D. Shoup. 1985. Soil sorption of organic vapors and the effects of humidity on sorptive mechanism and capacity. Environ. Sci. Technol. 19:1196-1200.

Pennell, K.D., R.D. Rhue, P.S.C. Rao, and C.T. Johnston. 1992. Vapor-phase sorption of p-xylene and water on soils and clay minerals. Environ. Sci. Technol. 26:756-763.

Rhue, R.D., K.D. Pennell, P.S.C. Rao, and W.H. Reve. 1989. Competitive adsorption of alkylbenzene and water vapors on predominantly mineral surfaces. Chemo. 18:1971-1986.
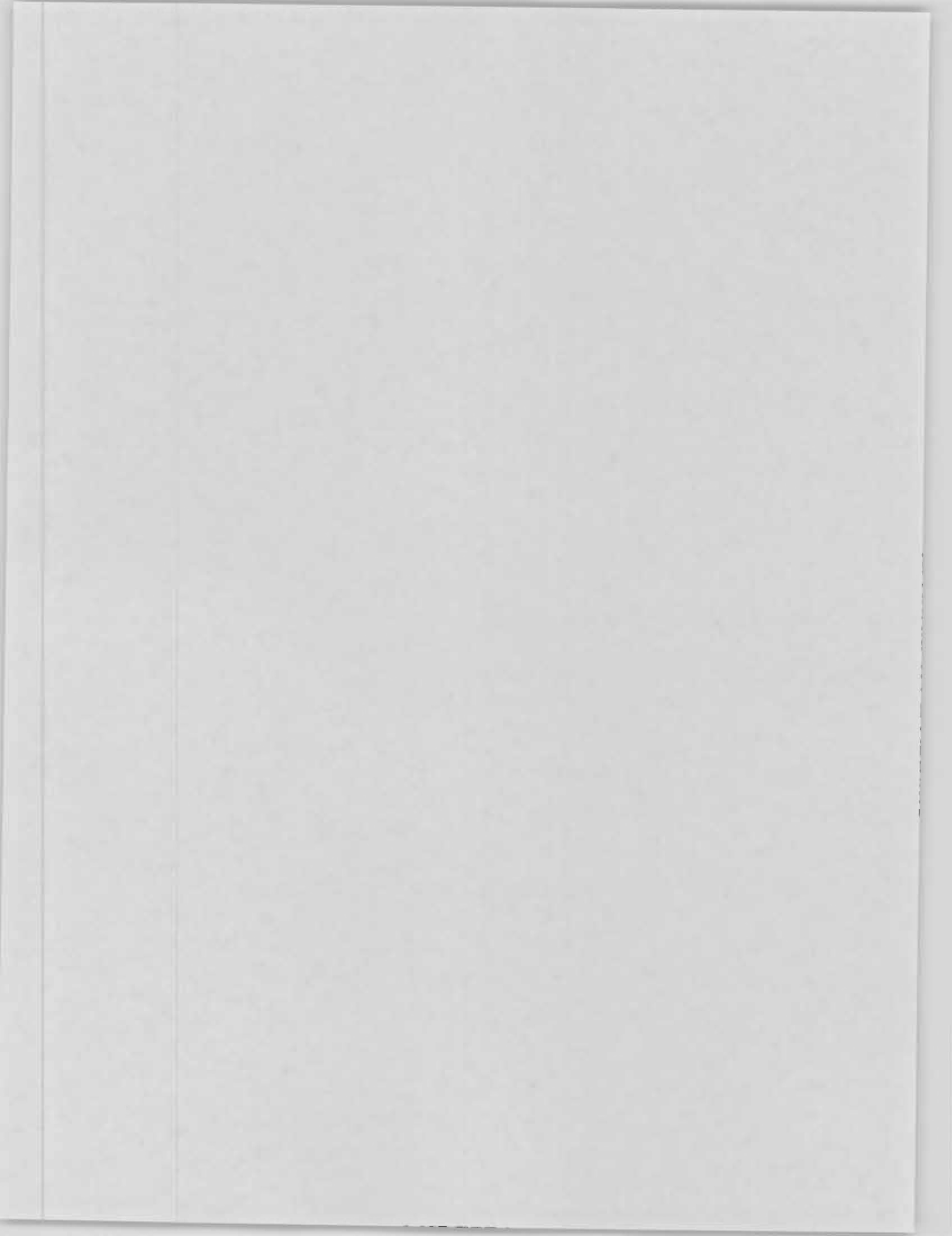
The Great Lakes Mid-Atlantic Hazardous Substance Research Center

Thrust Area I

Organic Vapor Sorption and Desorption in the Unsaturated Zone:

Rates and Equilibria

5th Quarterly Report

for the period

August 1, 1996 to October 31, 1996

Submitted January 13, 1997

Principal Investigator:

Kurt D. Pennell, Assistant Professor
School of Civil and Environmental Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0512
tel: 404-894-9365
fax: 404-853-3177
e-mail:kurt.pennell@ce.gatech.edu

Project Introduction and Objectives:

Vapor-phase sorption is one of the most important processes influencing the mobility and distribution of volatile organic chemicals (VOCs) in the unsaturated zone. Previous studies have demonstrated that oven-dry soils and clay minerals have a sizable capacity to sorb organic vapors, which is strongly correlated with the specific surface area of the solid phase (Chiou and Shoup, 1985; Rhue et al., 1988). Under natural conditions, however, the sorption of organic vapors usually occurs in the presence of water. As the soil moisture content or relative humidity increases, VOCs are displaced from adsorbent surfaces resulting in the suppression of organic vapor sorption (Chiou and Shoup, 1985; Pennell et al, 1992). This behavior is generally attributed to the ability of water molecules to effectively compete with nonpolar organic vapors for adsorption sites, such as exchangeable metal cations

Although the competitive effects of water on the magnitude of organic vapor sorption by soils are well established, the specific mechanisms responsible for the VOC sorption of organic vapors on hydrated or moist soils remains in debate. Chiou and Shoup (1985) postulated that hydrated soils behave as dual adsorbents, in which soil organic matter functions as a partition medium while mineral surfaces behave as a conventional solid adsorbent. These authors concluded that partitioning into soil organic matter was the dominant mechanisms governing vapor-phase sorption by soils. In contrast, Pennell et al. (1992) reported that sorption isotherms for p-xylene vapors at 90% relative humidity were consistently nonlinear and sorptive capacities were several times greater than could be attributed to partitioning into soil organic matter. In this work, Pennell et al. (1992) demonstrated that adsorption at the gas-liquid interface could account for up to 50% of p-xylene sorption on Webster soil at 90% relative humidity.

Although it is now acknowledged that several mechanisms may contribute to the overall sorption of organic vapors in the unsaturated zone, the effects of these processes contaminant fate and transport have not been considered in detail. Therefore, this research project is designed to quantify the rates, equilibria and energetics of organic vapor sorption in the unsaturated zone. To date, there exists limited information on rates and energetics of vapor-phase sorption, particularly in the presence of water. Such data is critical to the elucidation of mechanisms governing the bioavailability of VOCs in unsaturated soils. In addition, virtually no data exists on the competitive sorption of organic vapors in the presence of water. To address these specific issues the project has been divided into three subtasks listed below.

Task IIIA-Sorption Rates and Equilibria: Quantify the effects of moisture content and organic carbon content and type on the rates and equilibria of organic vapor sorption.

Task IIIB-Sorption of Binary Organic Vapors: Assess the influence of moisture content organic carbon content on the competitive sorption of binary organic vapor mixtures.

Task IIIC-Energetics of Vapor-Phase Sorption: Determine organic vapor heats of adsorption based on sorption isotherms measured at 20, 30 and 40°C.

2

Progress This Period:

During 5th quarter of the project (August 1 1996 to October 31 1996) our research efforts focused on the investigation of coupled sorption and transport of organic vapors in soil columns. These research activities are described in the following section of the progress report.

1. Soil Column Experiments

A series of soil column experiments was conducted to investigate the coupled sorption and transport of toluene vapors through Wurtsmith soil. Aluminum columns (5 cm i.d. X 10 cm length) were packed with Wurtsmith soil that had been uniformly wetted with water (6% by wt). The soil columns were then transferred to the temperature-controlled flow equilibration apparatus previously described in our 3rd Quarterly Progress Report. A pulse of toluene vapor was then displaced through the soil column. Effluent concentrations of toluene were measured gas chromatography using a HP 6800 GC equipped with an internal sample loop and flame ionization detector. The flow sequence used in each soil column experiment conformed to the following specifications: moist air (95% RH); toluene vapor (65% P/Po) and moist air (95% RH); moist air (95% RH). The results of a representative soil column experiment are shown in Figure 1. In this column experiment (Figure 1), a pulse (45 pore volumes) of toluene vapor was injected through the soil column, followed by the reintroduction of moist air. The experimental breakthrough curve (BTC) for toluene vapor transport through the Wurtsmith soil was fit to a one-dimensional form of the advective-dispersive reactive (ADR) transport equation which may written as:

$$ns_g \frac{\partial C_g}{\partial t} + \rho_b \frac{\partial S_T}{\partial t} = ns_g D_g \frac{\partial^2 C_g}{\partial x^2} - q_g \frac{\partial C_g}{\partial x}$$

where n is the soil porosity, s_g is the gas-phase saturation, C_g is the concentration in the gas phase, t is time,

The sorption of organic vapors by hydrated (moist) soils was described using a multi-mechanistic model which incorporates (a) dissolution into adsorbed water films, (b) adsorption on mineral surfaces, (c) sorption by soil organic matter, and (d) adsorption at the gas-liquid interface (Pennell et al., 1992). Based on the proposed mechanistic model, organic vapor sorption is considered to be composed of the following components:

$$S_T = S_w + S_s + S_i$$

where S_T is the total sorption (mg/g), S_w is the amount dissolved in the adsorbed water film (mg/g), S_s is the amount sorbed by the solid phase (mg/g), and S_i is the amount adsorbed at the gas-liquid interface (mg/g). Dissolution of the organic vapor into adsorbed water films can be described by the following equation assuming that Henry's Law is valid and that the adsorbed water film behaves as bulk water:

3

$$S_w = \frac{P\,MW\,w}{K_H}$$

where P is the pressure of the organic vapor (atm), MW is the molecular weight (g/mole), w is the gravimetric water content of the soil (g/g), and K_H is the Henry's Law constant (L atm/mole). Sorption by the solid phase can be described using a water-saturated distribution coefficient based on a linear model (K_d) or nonlinear model, such as the Freundlich equation (K_F). In this case we will assume that the sorption can be described using a linear distribution coefficient:

$$S_s = K_d\,C_{aq}$$

where C_{aq} is the aqueous or dissolved phase concentration of the organic species. For estimation purposes, the value of K_d was obtained from the measured organic carbon content of the soil and the Log K_{oc}-K_{ow} correlation of Karickhoff et al. (1979). Adsorption at the gas-liquid interface can be described by the following set of equations:

$$S_i = \Gamma\,MW\,SA; \qquad \Gamma = \frac{d\gamma}{d\mu}; \qquad \Gamma = -\frac{P}{RT}\frac{d\gamma}{dP}$$

where Γ is the surface excess (mol/cm^2), and SA is the surface area (m^2/g). For estimation purposes, the oven-dry surface area was utilized, assuming that the water content was relatively where γ is the surface tension (dyne/cm) and μ is the chemical potential. Using surface tension data reported by Cutting and Jones (1955), the relationship between surface excess and toluene vapor pressure was calculated. These data were then utilized to obtain the composite isotherm shown in Figure 1. A linear estimate of the composite isotherm was then utilized for model simulations of toluene breakthrough as shown in Figure 1 (solid line).

Future Plans: During the next quarter, we will continue to conduct column experiments to investigate the coupled sorption and transport of organic vapors. In addition, we have received and installed of a Micromeritics Surface Area Analyzer (Model ASAP 2100) which will be used to conduct additional nitrogen and organic vapor sorption measurements. Initial surface area measurements will be made during the next quarter.
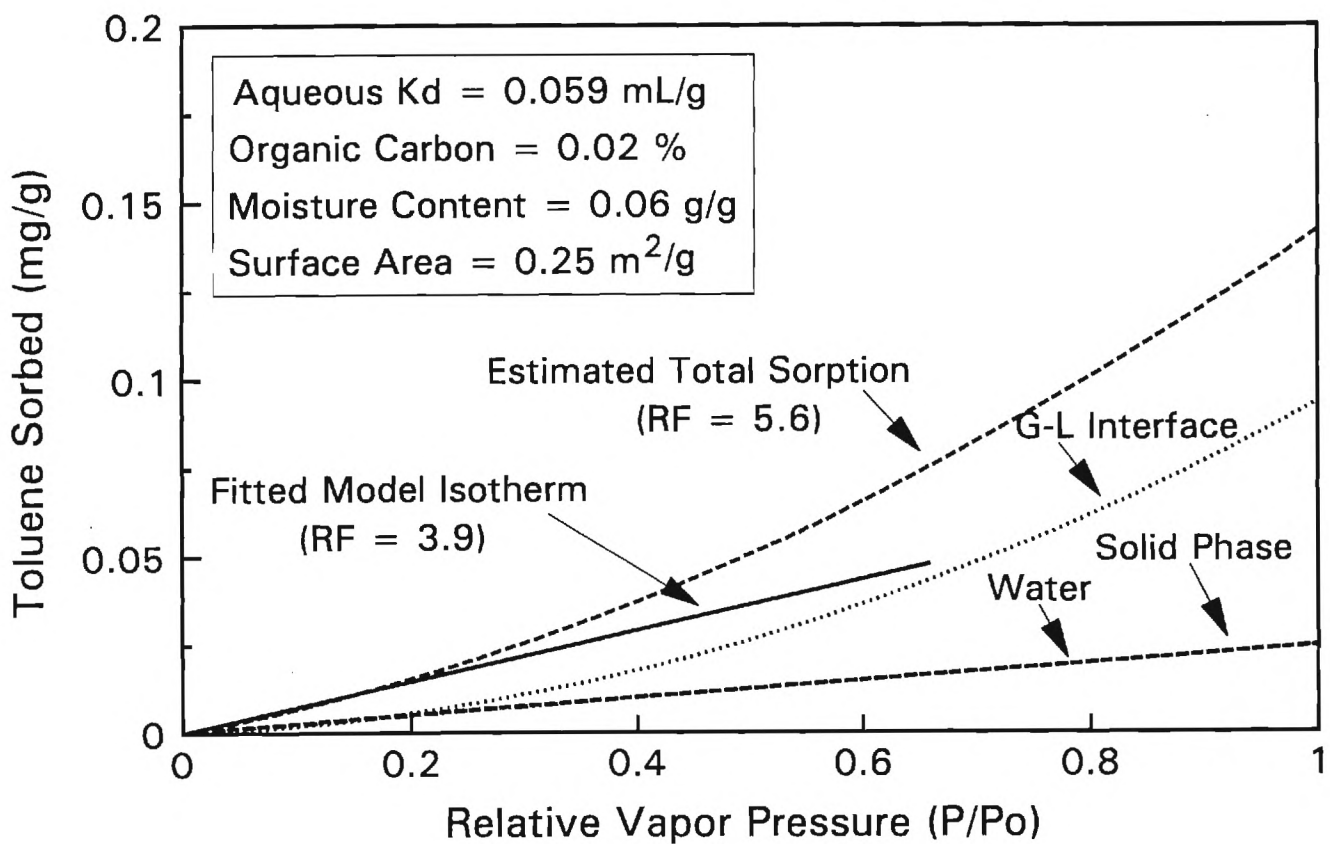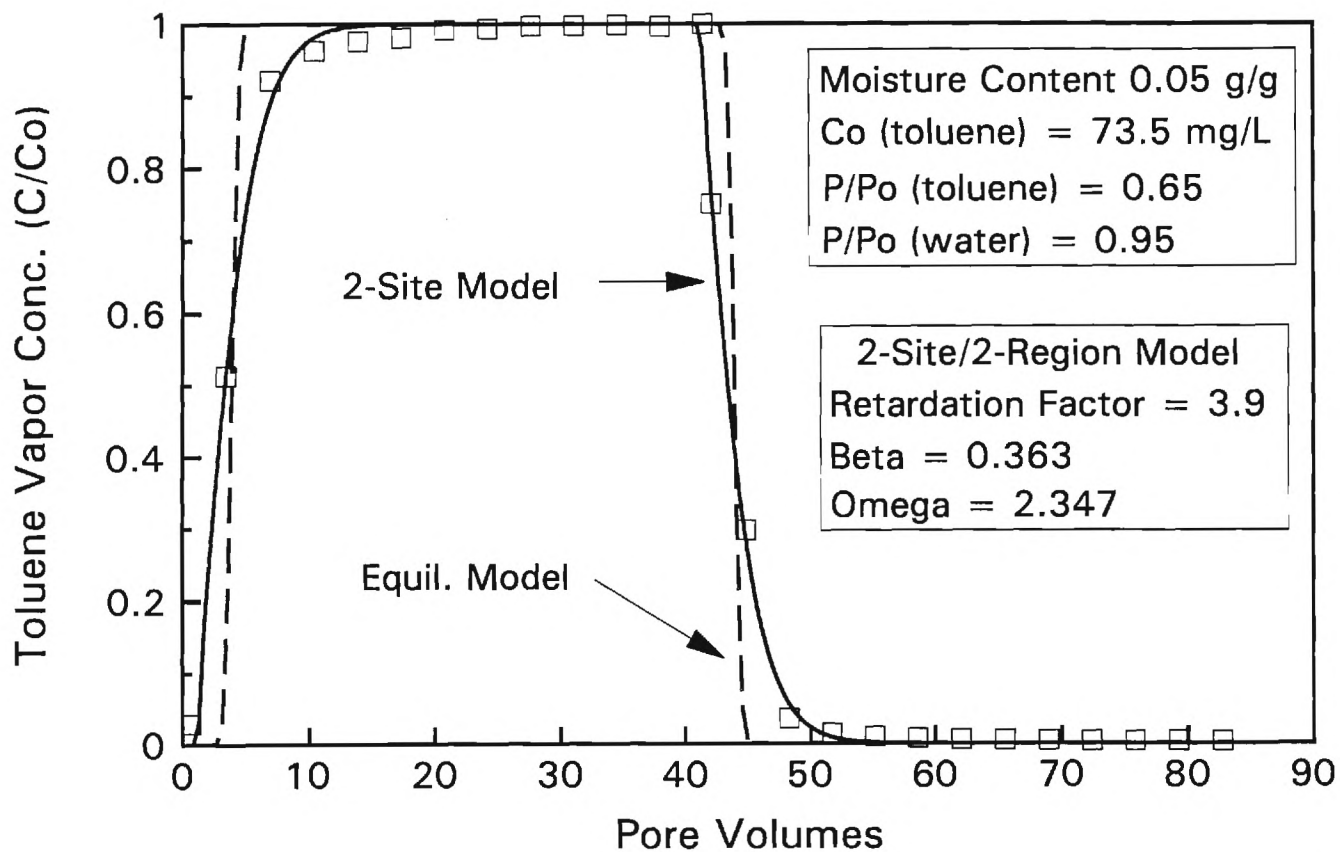
4

Figure 1. Toluene Vapor BTC and Sorption for Wurtsmith Soil

Top panel labels:
- Toluene Vapor Conc. (C/Co)
- Pore Volumes
- 2-Site Model
- Equil. Model
- Moisture Content 0.05 g/g
- Co (toluene) = 73.5 mg/L
- P/Po (toluene) = 0.65
- P/Po (water) = 0.95
- 2-Site/2-Region Model
- Retardation Factor = 3.9
- Beta = 0.363
- Omega = 2.347

Bottom panel labels:
- Toluene Sorbed (mg/g)
- Relative Vapor Pressure (P/Po)
- Aqueous Kd = 0.059 mL/g
- Organic Carbon = 0.02 %
- Moisture Content = 0.06 g/g
- Surface Area = 0.25 m^2/g
- Estimated Total Sorption (RF = 5.6)
- G-L Interface
- Fitted Model Isotherm (RF = 3.9)
- Solid Phase
- Water

The Great Lakes Mid-Atlantic Hazardous Substance Research Center

Thrust Area I

Organic Vapor Sorption and Desorption in the Unsaturated Zone:

Rates and Equilibria

6th Quarterly Report

for the period

November 1, 1996 to January 15, 1997

Submitted March 14, 1997

Principal Investigator:

Kurt D. Pennell, Assistant Professor
School of Civil and Environmental Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0512
tel: 404-894-9365
fax: 404-853-3177
e-mail:kurt.pennell@ce.gatech.edu

Project Introduction and Objectives:

Vapor-phase sorption is one of the most important processes influencing the mobility and distribution of volatile organic chemicals (VOCs) in the unsaturated zone. Previous studies have demonstrated that oven-dry soils and clay minerals have a sizable capacity to sorb organic vapors, which is strongly correlated with the specific surface area of the solid phase (Chiou and Shoup, 1985; Rhue et al., 1988). Under natural conditions, however, the sorption of organic vapors usually occurs in the presence of water. As the soil moisture content or relative humidity increases, VOCs are displaced from adsorbent surfaces resulting in the suppression of organic vapor sorption (Chiou and Shoup, 1985; Pennell et al, 1992). This behavior is generally attributed to the ability of water molecules to effectively compete with nonpolar organic vapors for adsorption sites, such as exchangeable metal cations

Although the competitive effects of water on the magnitude of organic vapor sorption by soils are well established, the specific mechanisms responsible for the VOC sorption of organic vapors on hydrated or moist soils remains in debate. Chiou and Shoup (1985) postulated that hydrated soils behave as dual adsorbents, in which soil organic matter functions as a partition medium while mineral surfaces behave as a conventional solid adsorbent. These authors concluded that partitioning into soil organic matter was the dominant mechanisms governing vapor-phase sorption by soils. In contrast, Pennell et al. (1992) reported that sorption isotherms for p-xylene vapors at 90% relative humidity were consistently nonlinear and sorptive capacities were several times greater than could be attributed to partitioning into soil organic matter. In this work, Pennell et al. (1992) demonstrated that adsorption at the gas-liquid interface could account for up to 50% of p-xylene sorption on Webster soil at 90% relative humidity.

Although it is now acknowledged that several mechanisms may contribute to the overall sorption of organic vapors in the unsaturated zone, the effects of these processes contaminant fate and transport have not been considered in detail. Therefore, this research project is designed to quantify the rates, equilibria and energetics of organic vapor sorption in the unsaturated zone. To date, there exists limited information on rates and energetics of vapor-phase sorption, particularly in the presence of water. Such data is critical to the elucidation of mechanisms governing the bioavailability of VOCs in unsaturated soils. In addition, virtually no data exists on the competitive sorption of organic vapors in the presence of water. To address these specific issues the project has been divided into three subtasks listed below.

Task IIIA-Sorption Rates and Equilibria: Quantify the effects of moisture content and organic carbon content and type on the rates and equilibria of organic vapor sorption.

Task IIIB-Sorption of Binary Organic Vapors: Assess the influence of moisture content organic carbon content on the competitive sorption of binary organic vapor mixtures.

Task IIIC-Energetics of Vapor-Phase Sorption: Determine organic vapor heats of adsorption based on sorption isotherms measured at 20, 30 and 40°C.

2

Progress This Period:

Surface Area Measurements

During the past six months (November 1 1996 to January 15 1997) a significant portion of our research activity has focused on the measurement of the specific surface area of natural soils and reference materials (Subtask IIIA). Initially, nitrogen adsorption and desorption isotherms for three natural sorbents (Wurtsmith soil, Webster soil, and Ohio Shale) were measured using a Micromeretics ASAP 2010 Surface Area Analyzer. In all cases the nitrogen exhibited hysteresis upon desorption, and thus, the isotherm were classified as Type IV. The adsorption leg of the isotherm was utilized to calculate the specific surface area of the solids using the Brenauer, Emmett and Teller (BET) equation. Assuming that the number of adsorbed layers is infinite, the BET equation may be written as:

$$\frac{S}{S_m} = \frac{C(P/P_0)}{(1-P/P_0)\left[1-P/P_0+C(P/P_0)\right]} \tag{1}$$

where S is the amount sorbed (mg/g), S_m is the monolayer adsorption capacity (mg/g), and P/P_0 is the relative vapor pressure. The dimensionless parameter C is related to the heat of adsorption on the bare surface (q_1) and the heat of condensation of the liquid adsorbate (q_L) by the equation:

$$C \approx e^{(q_1-q_L)/RT} \tag{2}$$

where R is the gas constant and T is the absolute temp (°K). The nitrogen adsorption data were fit to the BET equation over the relative vapor pressure range of 0.05 to 0.35 using a nonlinear least-squares procedure (SYSTAT, ver. 5.0). The resulting values of S_m and C are shown in Table 1. The specific surface area of the solid can then be estimated from the value of S_m and the area occupied by each adsorbed molecule. Using the cross-sectional area of nitrogen (16.2 X 10^{-20} m^2/molecule), the surface can be calculated from the value of S_m (Table 1). These values were consistent with previously reported values. The experimental method was also checked using reference standards of kaolinite (KGa-1) and smectite (SAaz-1) obtained from the Clay Minerals Society.

The effect of organic carbon content on measured values of N_2/BET surface area was also investigated. Four soils (Webster, Marlette A, Marlette B, and Houghton) were treated with hydrogen peroxide (HP) to remove organic carbon. In addition, a sample of Oshtemo soil was treated with a cationic surfactant (HDTMA) to increase its organic carbon content. Measured BET parameters and calculated specific surface areas are shown in Table 2 for each sorbent. Following treatment with HP, the measured surface area of each soil increased. In a similar fashion, the addition of organic carbon as HDTMA led to a reduction in the N_2/BET surface area. In our previous report, it was shown that N_2 surface area measurements can be used to estimate the magnitude of organic vapor sorption under anhydrous conditions. Coupled with the data presented herein, this suggests that organic carbon plays a minimal role in organic vapor sorption

3

under anhydrous conditions. This is the exact opposite of what one might expect based on sorption data for water-saturated conditions. To further evaluate this hypothesis, single component organic vapor sorption isotherms will be measured for all of the soils presented in Table 2, and compared to both N_2/BET and CO_2/BET surface area measurements.

Upcoming Presentations:

Schlanger, J.L. and K.D. Pennell. Sorption and transport of organic vapors in unsaturated soils. Proceedings Abstract (EOS), American Geophysical Union Spring Meeting, May 27-30, 1997, Baltimore, MD.

Schlanger, J.L. and K.D. Pennell. Effect of soil organic matter content on vapor-phase heats of adsorption. American Chemical Society Fall Meeting, August, 1997, Las Vegas, NV.

Table 1. BET Analysis of Nitrogen Adsorption/Desorption Isotherms at 77°K.

Soil	Sm (mg/g)	C (dimensionless)	Corr. R^2	Surface Area (m^2/g)
Wurtsmith Soil	0.195	58.63	0.998	0.67
Webster Soil	2.19	170.09	0.991	7.66
Ohio Shale	3.87	142.72	0.999	13.48
Kaolinite (KGa-1)	3.58	174.63	0.999	12.47
Smectite (SAz-1)	22.27	667.81	0.999	77.55

Table 2. Effect of Organic Carbon Removal or Addition on Nitrogen/BET Surface Area.

Soil	OC (%C)	Sm (mg/g)	C (dimensionless)	Corr. R^2	Surface Area (m^2/g)
Webster Soil	3.32	2.19	170.09	0.991	7.66
HP-Webster Soil	0.55	8.26	134.55	0.999	28.76
Marlette A	2.14	1.38	85.43	0.997	4.79
HP-Marlette A	0.89	2.53	87.91	0.999	8.81
Marlette B	0.79	3.02	141.19	0.998	10.52
HP-Marlette B	0.29	3.48	160.85	0.996	12.13
Houghton Muck	44.57	0.35	28.91	0.992	1.24
HP-Houghton Muck	18.20	2.62	32.92	0.998	9.12
Oshtemo	0.06	2.70	320.93	0.986	9.41
HDTMA-Oshtemo	0.40	1.33	63.52	0.999	4.63
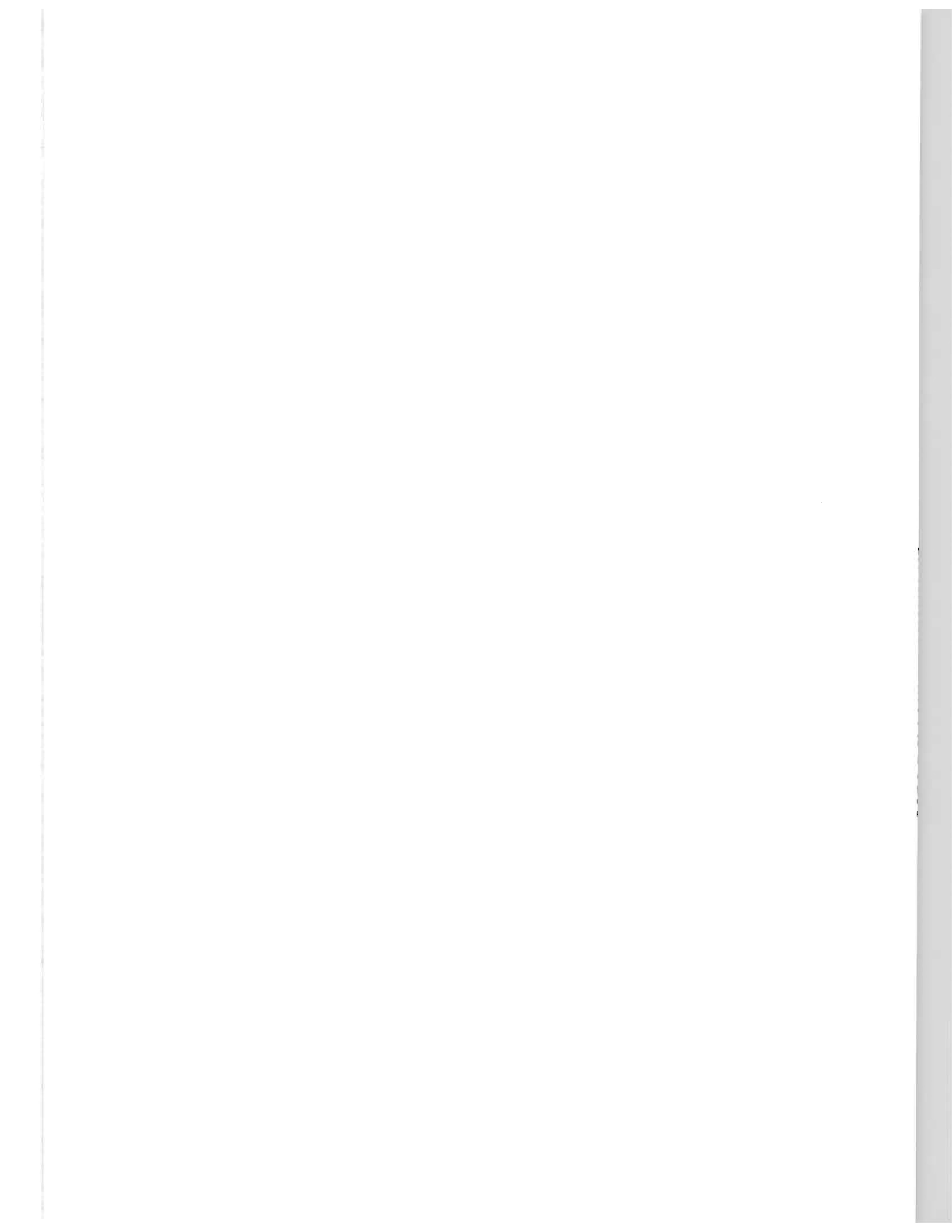
THRUST AREA I

FUNDAMENTAL ASPECTS OF BIOAVAILABILITY

TASK III

ORGANIC VAPOR SORPTION AND DESORPTION IN THE UNSATURATED ZONE: RATES AND EQUILIBRIA

Kurt D. Pennell
Georgia Institute of Technology
School of Civil & Environmental Engineering

June 28, 1995

Submitted to the Great Lakes/Mid-Atlantic Hazardous Substance Research Center

Address: Dr. Kurt D. Pennell
            School of Civil & Environmental Engineering
            200 Bobby Dodd Way
            Georgia Institute of Technology
            Atlanta, GA 30332-0512
            tel: 404-894-9365
            fax: 404-853-3177
            e-mail: kurt.pennell@ce.gatech.edu

1. Introduction and Background

Vapor-phase sorption is one of the most important processes influencing the mobility and distribution of volatile organic chemicals (VOCs) in the unsaturated zone. Previous studies have demonstrated that oven-dry soils and clay minerals have a sizable capacity to sorb organic vapors, which is strongly correlated with the specific surface area of the solid phase (Call, 1957; Chiou et al., 1985; Rhue et al., 1988). Under natural conditions, however, the sorption of organic vapors usually occurs in the presence of water. As the soil moisture content or relative humidity increases, VOCs are displaced from adsorbent surfaces resulting in the suppression of organic vapor sorption (Chiou and Shoup, 1985; Pennell et al, 1992a). This behavior is generally attributed to the ability of water molecules to effectively compete with nonpolar organic vapors for adsorption sites, such as exchangeable metal cations (Rhue et al., 1989; Pennell et al., 1992b).

Although the competitive effects of water on the magnitude of organic vapor sorption by soils is well established, the specific mechanisms responsible for the VOC sorption of organic vapors on hydrated or moist soils remains in debate. Chiou and Shoup (1985) postulated that hydrated soils behave as dual adsorbents, in which soil organic matter functions as a partition medium while mineral surfaces behave as a conventional solid adsorbent. These authors concluded that partitioning into soil organic matter was the dominant mechanisms governing vapor-phase sorption by moist soils. However, Pennell et al. (1992a) reported that sorption iostherms for p-xylene vapors at 90% relative humidity were consistently nonlinear and sorptive capacities were several times greater than could be attributed to partitioning into soil organic matter. These results were described by a mechanistic model which incorporates (a) adsorption

2

on mineral surfaces, (b) sorption by soil organic matter, (c) dissolution into adsorbed water films, and (d) adsorption at the gas-liquid interface (Figure 1). In this work, Pennell et al. (1992a) demonstrated that adsorption at the gas-liquid interface could account for up to 50% of p-xylene sorption on Webster soil at 90% relative humidity. These data were later confirmed by Hoff et al. (1993), who reported that the gas-liquid interface was responsible for approximately half of the observed alkane sorption in unsaturated aquifer materials.

Although it is now widely acknowledged that several mechanisms may contribute to the overall sorption of organic vapors in the unsaturated zone, the effects of this behavior on the bioavailability of VOCs has not been considered. Specifically, the proposed research is designed to elucidate the rates, energetics and relative contribution of each mechanism governing the sorption of single and binary mixtures of organic vapors by natural soils and a representative polymer. The effects of organic carbon type and content, and moisture content on these processes will be studied in detail. A detailed description of the experimental approach and methodology is provided in Section 2 of the proposal.

1.1 Relevance to NCIBRD Mission

The overall objective of the proposed research, to investigate the sorption of organic vapors in the unsaturated zone, is consistent with NCIBRD's mission of establishing a national field center for the assessment of natural and active in-situ bioremediation. The project is designed to provide fundamental information on the sorption and bioavailability of volatile organic chemicals in the unsaturated zone. Such data is essential for the accurate identification and assessment of mechanisms governing contaminant bioavailability in moist soils. This

information could then be used in the interpretation of field trials conducted to assess the effectiveness of bioventing and air-sparging. In addition, the fundamental studies described herein could be used in the development of numerical simulators designed to predict the natural attenuation of VOCs in the unsaturated zone.

1.2 Interaction with Thrust Area I Research Groups

The investigation of VOC sorption in the unsaturated zone is closely integrated with research proposed in Tasks I (Adriaens) and IV (Weber) of Thrust Area I. Collaboration is planned with Dr. Peter Adriaens' research group to assist in the quantification of factors influencing rates of toluene degradation in moist soils. Measurements of equilibrium toluene sorption isotherms, rates of toluene sorption and desorption, and sorption energetics on moist soils will be utilized by Dr. Adriaens to interpret their experimental data. Moisture release curves measured as part of Task III will be used to select appropriate and consistent soil water contents for detailed study. Collaboration is also planned with Dr. Walter Weber (Tasks IV and VI), who is investigating contaminant sorption/desorption in water-saturated systems and the measurement of binding energies by supercritical fluid extraction (SFE). Measurements of VOC sorption rates and equilibria will be utilized in Task III to evaluate the magnitude of solid-liquid sorption processes in unsaturated soils. In addition, competitive water and organic vapor sorption data obtained in Task III will be compared to SFE results to investigate the effect of polar solvents on SFE extraction efficiencies. Potential for collaboration also exists with Task V (Voice) and II (Fogler) if unsaturated transport experiments are performed. In these systems the gas-liquid interface may play an important role in cell attachment and bioavailability in

4

dynamic systems.

2. Research Scope

The research proposed herein is designed to quantify the rates, equilibria and energetics of organic vapor sorption in the unsaturated zone. To date, there exists limited information on rates and energetics of vapor-phase sorption, particularly in the presence of water. Such data is critical to the elucidation of mechanisms governing the bioavailability of VOCs in unsaturated soils. In addition, virtually no data exists on the competitive sorption of organic vapors in the presence of water. To address these issues the project has been divided into three subtasks: Task IIIA-Sorption Rates and Equilibria; Task IIIB-Sorption of Binary Organic Vapors; and Task IIIC-Energetics of Vapor-Phase Sorption.

Single and binary vapor sorption experiments will be conducted using the flow-equilibration apparatus shown in Figure 2. By adjusting the flow of nitrogen through the needle valves shown on the left-hand side of the diagram both the relative humidity and relative vapor pressure of the organic vapor can be varied over a wide range of values. The concentration of water and organic vapor in the flow stream will be determined by direct connection of the line to a GC sample loop. Sorbed amounts of water and organic vapor will be determined by methanol extraction, followed by Karl Fisher titration for water and either HPLC or GC analysis of the organic. Additional single component experiments will be conducted using a Micromeritics ASAP 2010 surface area analyzer.

Properties of the volatile organic chemicals selected for study are shown in Table 1. These compounds were chosen after consensus was reached with all Thrust Area I researchers.

5

Particular emphasis will be placed on toluene to provide for direct interaction with the biodegradation studies to be conducted as part of Task I (Adriaens). Sorbents to be used in the vapor-phase sorption studies were also selected after discussion with Thrust Area I researchers. Special effort was made to select sorbents that provided a range of organic carbon content and type. The matrix of experiments to be performed over the two-year funding period of this project is shown in Table 2.

Table 1. Selected chemical and physical properties of organic compounds proposed for vapor-phase sorption experiments.

Chemical	MW (g/mole)	Density (g/cm³)	Solubility (mg/L)	Vapor Pressure (mm Hg)
Toluene	100.2	0.94	500	22
1,2-Dichlorobenzene	147.0	1.31	100	1
Trichloroethylene	131.4	1.46	1,100	58
Tetrachloroethylene	165.8	1.63	200	14

Table 2. Proposed organic-sorbent experimental matrix for vapor-phase sorption studies.

Sorbent	Toluene	1,2-DCB	TCE	PCE
Wurtsmith soil	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Webster soil	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Ohio Shale	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM
Poly(butyl methacrylate)	D, M, MR, E	D, M, MR	D, M, MR, C	D, M, C, CM

D=oven-dry organic equilibrium sorption isotherm (Task IIIA)
M=moist organic equilibrium sorption isotherm (Task IIIA)
MR=moist sorption/desorption rates (Task IIIA)
C=competitive equilibrium sorption oven-dry (Task IIIB)
CM= competitive equilibria sorption moist soil (Task IIIB)
E=sorption energetics (Task IIIC)

6

2.1 Task IIIA-Sorption Rates and Equilibria

The objective of Task IIIA is to quantify the effects of (a) moisture content and (b) organic carbon content and type on organic vapor sorption rates and equilibria. Initial experiments will focus on equilibrium isotherms for the sorption of toluene, DCB, TCE, and PCE vapors on oven-dry and moist soils (4% wt.). The second phase of experimentation will address rates of organic vapor sorption and desorption. For these experiments the sorbents will be exposed to organic vapors at different relative vapor pressures and destructively sampled over time. The results of these experiments will be used to assess the effects of organic vapor properties, soil organic carbon content, and organic carbon type on sorption rates and equilibria. Toluene sorption data obtained from Task IIIA will be provided to Dr. Adriaens' research group to aid in the interpretation of their degradation studies. Sorption rates and capacities will also be compared to aqueous-phase sorption measurements conducted by Dr. Weber's research group.

2.2 Task IIIB-Sorption of Binary Organic Vapor Mixtures

The objective of Task IIIB is to quantify the competitive sorption of binary organic vapor mixtures on oven-dry and moist (4% wt.) soils. This work will focus on the sorption of PCE and TCE over a range of relative vapor pressures. Results of equilibrium sorption isotherm experiments will be used to evaluate the multi-component sorption models of Gu and Hill (see Pennell et al., 1992b for description). In effect, these models extend the BET equation to account for competitive sorption based on single component sorption data. If these models are found to provide reasonable estimates of competitive sorption, they may prove useful in modeling organic vapor sorption at field sites, which are often contaminated with a mixture of

VOCs. The second phase of experimentation will address rates competitive TCE/PCE sorption and desorption in the presence and absence of water.

2.3 Task IIIC-Energetics of Vapor-Phase Sorption

The objective of Task IIIC is to determine the energetics of vapor-phase sorption. Heats of adsorption will be obtained from sorption isotherms measured at three temperatures (20, 30, 40 C). The derivation of heats of adsorption is based on the Classius-Clayperon equation and is analogous to the derivation of the heat of vaporization from the temperature dependence of the saturated vapor pressure. Sorption experiments will be conducted using oven-dry and moist (4% wt) soils to determine the effect of moisture content on sorption energetics. Data from these studies will be compared to aqueous-phase sorption energetics measured in Task IV (Weber). It is anticipated that the results of these studies will provide valuable information for assessing the bioavailability of sorbed contaminants in the unsaturated zone.

3. Project Schedule

Task	7/95-12/95	1/96-6/96	7/96-12/96	1/97-6/97
Task IIIA-Sorption Rates and Equilibria	equ. sorption on oven-dry and moist soils	rates of sorption and desorption	equ. and rates of sorption by polymers	
Task IIIB-Sorption of Binary Mixtures		equ. sorption of TCE/PCE on dry soils	equ. sorption of TCE/PCE on moist soils	rates of competitive sorption
Task IIIC-Sorption Energetics			tol. sorption at 20, 30, 40 C on dry soils	tol. sorption at 20, 30, 40 C on moist soils

4. References

Hoff, J.T., R. Gillham, D. Mackay, and W.Y. Shiu. 1993. Sorption or organic vapors at the air-water interface in a sandy aquifer material. Environ. Sci. Technol. 27:2789-2794.

Pennell, K.D., R.D. Rhue, P.S.C. Rao, and C.T. Johnston. 1992a. Vapor-phase sorption of p-xylene and water on soils and clay minerals. Environ. Sci. Technol. 26:756-763.

Pennell, K.D, R.D. Rhue, and A.G. Hornsby. 1992b. Competitive adsorption of para-xylene and water vapors on calcium, sodium, and lithium saturated kaolinite. J. Environ. Qual. 21:419-426.

Rao, P.S.C., R.A. Ogwada, and R.D. Rhue 1989. Adsorption of volatile organic compounds on anhydrous and hydrated sorbents: Equilibrium adsorption and energetics. Chemosphere 18:2177-2191.

Rhue, R.D., K.D. Pennell, P.S.C. Rao, and W.H. Reve. 1989. Competitive adsorption of alkylbenzene and water vapors on predominantly mineral surfaces. Chemosphere 18:1971-1986.

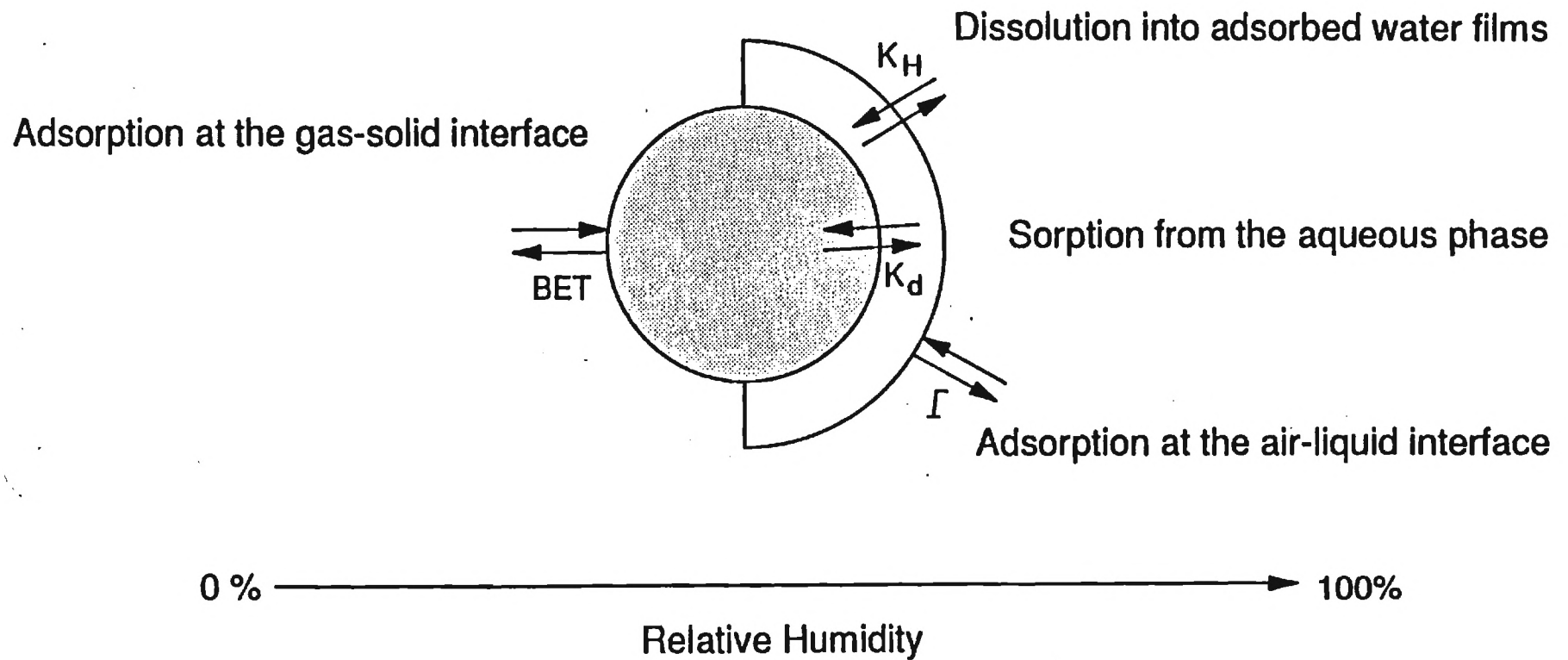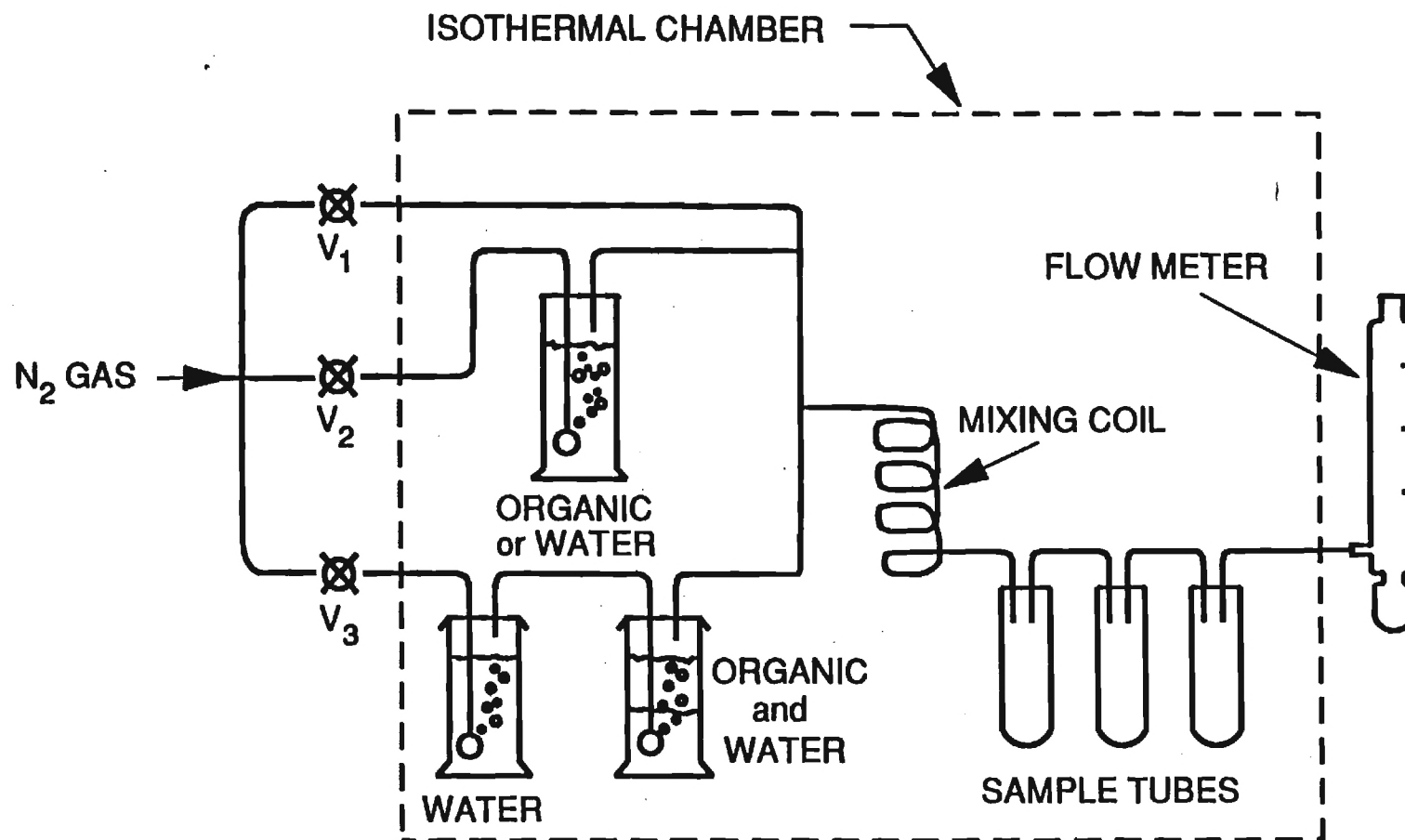# Vapor-Phase Sorption of VOCs

A Mechanistic Approach

Dissolution into adsorbed water films

K_H

Adsorption at the gas-solid interface

Sorption from the aqueous phase

BET

K_d

Γ

Adsorption at the air-liquid interface

0 % ⟶ 100%

Relative Humidity

Figure 1.

Figure 2.

The Great Lakes Mid-Atlantic Hazardous Substance Research Center

TRAC I

Organic Vapor Sorption and Desorption in the Unsaturated Zone: Rates and Equilibria

Summary Progress Report

Submitted April 14, 1997

Principal Investigator:

Kurt D. Pennell, Assistant Professor
School of Civil and Environmental Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0512
tel: 404-894-9365
fax: 404-853-3177
e-mail:kurt.pennell@ce.gatech.edu

Project Introduction and Objectives:

Vapor-phase sorption is one of the most important processes influencing the mobility and distribution of volatile organic chemicals (VOCs) in the unsaturated zone. Previous studies have demonstrated that oven-dry soils and clay minerals have a sizable capacity to sorb organic vapors, which is strongly correlated with the specific surface area of the solid phase (Chiou and Shoup, 1985; Rhue et al., 1988). Under natural conditions, however, the sorption of organic vapors usually occurs in the presence of water. As the soil moisture content or relative humidity increases, VOCs are displaced from adsorbent surfaces resulting in the suppression of organic vapor sorption (Chiou and Shoup, 1985; Pennell et al, 1992). This behavior is generally attributed to the ability of water molecules to effectively compete with nonpolar organic vapors for adsorption sites, such as exchangeable metal cations

Although the competitive effects of water on the magnitude of organic vapor sorption by soils are well established, the specific mechanisms responsible for the VOC sorption of organic vapors on hydrated or moist soils remains in debate. Chiou and Shoup (1985) postulated that hydrated soils behave as dual adsorbents, in which soil organic matter functions as a partition medium while mineral surfaces behave as a conventional solid adsorbent. These authors concluded that partitioning into soil organic matter was the dominant mechanisms governing vapor-phase sorption by soils. In contrast, Pennell et al. (1992) reported that sorption isotherms for p-xylene vapors at 90% relative humidity were consistently nonlinear and sorptive capacities were several times greater than could be attributed to partitioning into soil organic matter. In this work, Pennell et al. (1992) demonstrated that adsorption at the gas-liquid interface could account for up to 50% of p-xylene sorption on Webster soil at 90% relative humidity.

Although it is now acknowledged that several mechanisms may contribute to the overall sorption of organic vapors in the unsaturated zone, the effects of these processes contaminant fate and transport have not been considered in detail. Therefore, this research project is designed to quantify the rates, equilibria and energetics of organic vapor sorption in the unsaturated zone. To date, there exists limited information on rates and energetics of vapor-phase sorption, particularly in the presence of water. Such data is critical to the elucidation of mechanisms governing the bioavailability of VOCs in unsaturated soils. In addition, virtually no data exists on the competitive sorption of organic vapors in the presence of water. To address these specific issues the project has been divided into three subtasks listed below.

Task IIIA-Sorption Rates and Equilibria: Quantify the effects of moisture content and organic carbon content and type on the rates and equilibria of organic vapor sorption.

Task IIIB-Sorption of Binary Organic Vapors: Assess the influence of moisture content organic carbon content on the competitive sorption of binary organic vapor mixtures.

Task IIIC-Energetics of Vapor-Phase Sorption: Determine organic vapor heats of adsorption based on sorption isotherms measured at 20, 30 and 40°C.

the gravimetric water content of the soil (g/g), and K_H is the Henry's Law constant (L atm/mole). Sorption by the solid phase can be described using a water-saturated distribution coefficient based on a linear model (K_d) or nonlinear model, such as the Freundlich equation (K_F). In this case we will assume that the sorption can be described using a linear distribution coefficient:

$$S_s = K_d \, C_{aq} \tag{8}$$

where C_{aq} is the aqueous or dissolved phase concentration of the organic species. For estimation purposes, the value of K_d was obtained from the measured organic carbon content of the soil and the Log K_{oc}-K_{ow} correlation of Karickhoff et al. (1979). Adsorption at the gas-liquid interface can be described by the following set of equations:

$$S_i = \Gamma MWSA; \quad \Gamma = \frac{d\gamma}{d\mu}; \quad \Gamma = -\frac{P}{RT}\frac{d\gamma}{dP} \tag{9}$$

where Γ is the surface excess (mol/cm^2), and SA is the surface area (m^2/g). For estimation purposes, the oven-dry surface area was utilized, assuming that the water content was relatively where γ is the surface tension (dyne/cm) and μ is the chemical potential. Using surface tension data reported by Cutting and Jones (1955), the relationship between surface excess and toluene vapor pressure was calculated. These data were then utilized to obtain a composite isotherm, presented in our previous progress reports. Additional column experiments are now being conducted with Webster soil, which has a much higher organic carbon content than the Wurtsmith aquifer materia.

Presentations:

Schlanger, J.L. and K.D. Pennell. Sorption and transport of organic vapors in unsaturated soils. Proceedings Abstract (EOS), American Geophysical Union Spring Meeting, May 27-30, 1997, Baltimore, MD.

Schlanger, J.L. and K.D. Pennell. Effect of soil organic matter content on vapor-phase heats of adsorption. American Chemical Society Fall Meeting, August, 1997, Las Vegas, NV.
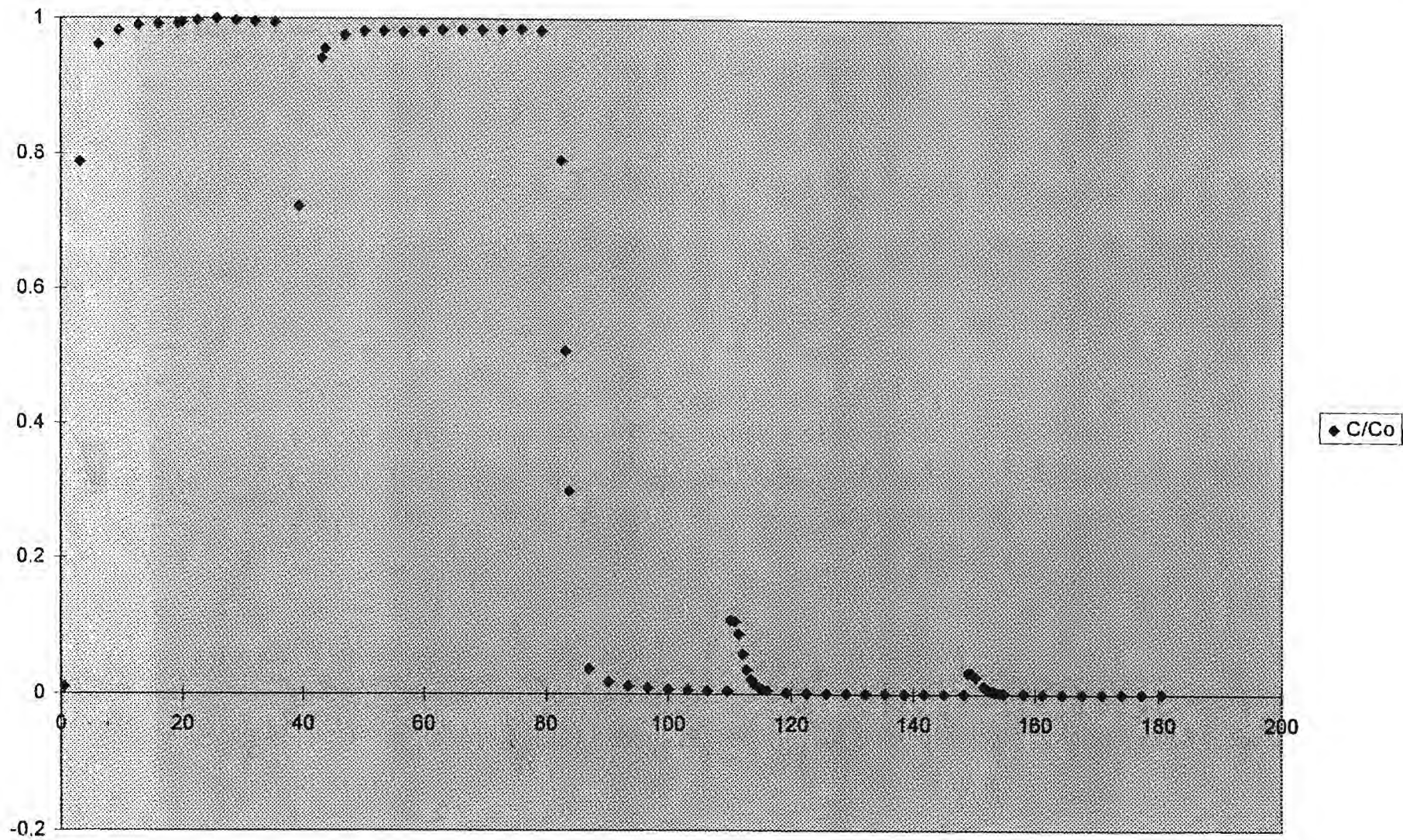
Figure 2. Breakthrough curve for toluene vapor transport through moist Wurtsmith soil.