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Partitioning Equilibria of Volatile Pollutants in Three-Phase Systems

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DECEMBER 1983

FINAL REPORT
JUNE 1983 — AUGUST 1983

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PREFACE

This report was prepared by the Southeastern Center for Electrical Engineering Education under Contract F-49620-82-C-0035 for the Air Force Engineering and Services Center, Air Force Engineering and Services Laboratory (AFESC/RD), Tyndall AFB, Florida. This research was sponsored by the Air Force Office of Scientific Research under the Summer Faculty Research Program.

Research documented within this report was performed between June and August 1983, by Dr. Leonard W. Lion and Doug Gabarini of the Department of Electrical Engineering, Cornell University. AFESC/RDVW project officer was Mr. Thomas B. Stauffer.

The authors thank the Air Force Systems Command, the Air Force Office of Scientific Research, and the Southeastern Center for Electrical Engineering Education for providing both the opportunity and financial support for our research on a challenging environmental problem. In particular, we would like to thank Mr. Thomas Stauffer of the Environics Laboratory at Tyndall Air Force Base for his valuable assistance and technical expertise in the separation and analysis of the compounds concerned. We also thank Don Wickman and Sergeants Stacey Brown, Chuck Manikas, Bill Nemeier, Dan Stork, and the rest of the personnel at the Environics Laboratory who assisted us in this research effort.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

The fate of various pollutant organic compounds introduced into groundwater systems is a pressing and ubiquitous environmental problem in many areas of the United States. This problem is of concern to the U.S. Air Force since groundwater contamination has been detected on or near several Air Force Bases.

The U.S. Air Force is currently conducting an active research program designed to both investigate feasible treatment strategies for groundwater cleanup and to study the reactions of groundwater pollutants which may control their transport. Two classes of non-ionic organic pollutants are currently among those of concern to the Air Force: (1) those typically found in cleaning solvents and degreasers such as trichloroethylene (TCE) and (2) those found in jet fuels, such as toluene and naphthalene. These materials may be introduced into soils and, ultimately, into groundwater aquifers in a number of different ways, including spills and rupture or leaking of underground storage containers.

In unsaturated aquifer systems, contaminant compounds may be removed from solution by several mechanisms, including volatilization, sorption and biodegradation. The first two of these processes were examined in the research which was conducted. The reactions are illustrated in schematic fashion in Figure 1 and are briefly discussed below.

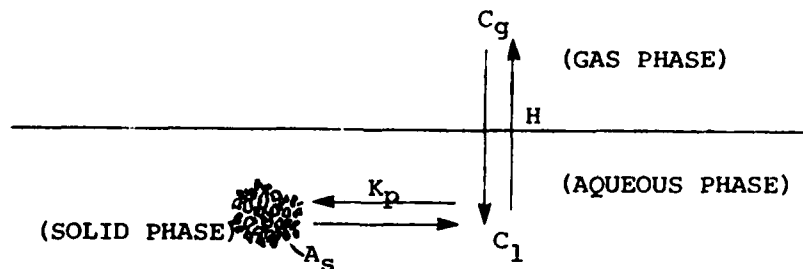


Figure 1. Potential Reactions for a Non-Ionic Organic Pollutant Compound in a Three-Phase Abiotic System

A. VOLATILIZATION

Gas exchange equilibria for compounds are governed by Henry's Law:

$$H = C_g/A_1 \quad (1)$$

where H is the Henry's Law constant
C_g is gas concentration
and A₁ is the activity of the compound in solution.

Compound activity and concentration in solution are interrelated through the activity coefficient:

$$A_1 = \gamma C_1 \quad (2)$$

where γ is the activity coefficient
and C₁ is the aqueous solution concentration.

Activity coefficients for neutral molecules, such as those considered in this study, are commonly related to solution ionic strength by the empirical equation:

$$\log \gamma = kI \quad (3)$$

where k is referred to as the salting coefficient
and I is the ionic strength of solution (Reference 1).

To the author's knowledge, activity coefficients and salting coefficients for many of the constituents of Air Force jet fuels and degreasing compounds have not been determined, however it is clear that these values may need to be known in order to precisely describe both gas exchange and sorption equilibria.

Henry's Law Constants for compounds are often reported as either dimensionless numbers (this convention has been adopted in this report) or with units of atm-l/mole; the two values being interrelated by the universal gas constant and temperature (°K) as follows:

$$H \text{ (dimensionless)} = H \text{ (atm-l/mole)}/RT \quad (4)$$

Henry's Law Constants are sometimes estimated from reported values for compound solubility in water and vapor pressure.

$$H \text{ (dimensionless)} = 16.04 PM / S T \quad (5)$$

where P = vapor pressure in mm Hg
M = molecular weight (grams)
S = solubility (mg/l)
T = absolute temperature (°K)

Unfortunately, reported values for solubility of many organic compounds can often vary over an order of magnitude with a concomitant uncertainty in the calculated value of H. Accurate values for Henry's Law Constants are essential to the description of the fate of volatile compounds in unsaturated groundwater aquifers.

B. SORPTION

Available data for the sorption of non-ionic organic compounds typically reveal linear sorption isotherms (References 2,3,4) and, therefore, the equilibrium between solution and the adsorbing solid may be described by a simple partitioning coefficient:

$$K_p = \Gamma / A_1 \quad (6)$$

where K_p is the partitioning coefficient and Γ is adsorption density (mg adsorbed/g adsorbent).

It is noteworthy that such a linear relationship results from the Langmuir adsorption isotherm:

$$\Gamma = \frac{\Gamma_{\max} A_1}{K + A_1} \quad (7)$$

at low-solution concentrations (i.e., when $A_1 \ll K$). A linear relationship also results from the Freundlich adsorption isotherm:

$$\Gamma = K A_1^n \quad (8)$$

when $n = 1$.

At soil organic carbon concentrations > 1 percent organic solute equilibria appear to be controlled by the organic content of the adsorbent (Reference 5) and, therefore, the observed partitioning coefficient may be normalized to the weight fraction of organic carbon as:

$$K_{oc} = K_p / f \quad (9)$$

where f is the weight fraction of organic carbon on the soil and K_{oc} is the normalized partitioning coefficient.

Although investigators agree on the importance of soil organic matter, the mechanism of the binding reaction between the organic solutes and the solid phase is uncertain. Both the terms "sorption," which is frequently used to refer to a surface reaction, and "partitioning," which refers to an extraction

phenomena, have been employed to describe the binding process (References 2,3,4,6,7).

Observed Koc values have been related to compound solubilities in water and to compound octanol-water partitioning coefficients (Kow) (References 2,4,6). An implication of these results is that sorption of non-ionic organic pollutants on a given aquifer material may be predicted solely on the basis of the sorbent's organic content. In addition, these results suggest that the specific nature and form of the soil organic material may not be relevant to sorption equilibria. These implications have not been rigorously tested.

SECTION II

OBJECTIVES OF RESEARCH EFFORT

Major research objectives were as follows:

1. To evaluate the applicability of an equilibrium head space technique to the determination of Henry's Law Constants for individual compounds typical of JP-4 fuels. Initial method verification was performed using TC, a compound for which the experimental procedure had previously been successfully employed. TCE was also included as a compound of interest in subsequent experiments in which compound activity coefficients and sorption equilibria were evaluated.

2. To determine the effect of solution composition on compound activity in solution. Variables examined included the effect of compound concentration, the effect of the presence of additional compounds in solution - both polar and nonpolar, the effect of ionic strength, and the effect of electrolyte composition.

3. To examine the applicability of a modification of the equilibrium head space technique to the measurement of compound sorption from solution and to study the influence of organic carbon on compound sorption behavior. Variables considered included the effect of the presence of an organic (e.g. humic acid) coating on compound sorption by a hydrous oxide (Al_2O_3), the effect of the form of the organic material (e.g. humic acids coated on Al_2O_3 vs. humic acids in the absence of Al_2O_3) and the effect of the nature of the organic material (varied by carrying out sorption experiments on both synthetic and naturally occurring soils).

SECTION III

GAS EXCHANGE EQUILIBRIA AND MEASUREMENT OF ACTIVITY COEFFICIENTS

A. INTRODUCTION

Recently equilibrium partitioning in closed systems (EPICS) has been shown by Lincoff and Gossett (Reference 8) to be a reliable procedure for the determination of Henry's Law Constants for compounds with dimensionless Henry's constants < 3 . For two identical bottles (1 and 2) containing the same compound mass but with different liquid and gas volumes, Lincoff and Gossett (Reference 8) show that:

$$H = \frac{(C_{g1}/C_{g2})V_{l1}-V_{l2}}{V_{g2}-(C_{g1}/C_{g2})V_{g1}} \quad (10)$$

where C_{g1} and C_{g2} are compound concentrations in the bottle head spaces. V_{l1} , and V_{l2} are the liquid volumes in the bottles. and V_{g1} and V_{g2} are the gas volumes in each bottle.

Thus, Henry's Law Constant may be determined by G.C. head space analysis of gas concentration, and is independent of the compound mass employed in the experiment.

For compounds of low volatility or high molecular weight, G.C. head space analysis may not be feasible. However, liquid phase analysis may also be employed since for the same two identical bottles, it may be shown that:

$$H = \frac{(C_{l1}/C_{l2})V_{l1}-V_{l2}}{V_{g2}-(C_{l1}/C_{l2})V_{g1}} \quad (11)$$

Equations (10) and (11) are written assuming the aqueous phase behaves as an ideal solution and therefore $\gamma = 1$. However, the EPICS technique may also be employed to evaluate compound activity coefficients.

For two identical bottles containing the same compound mass and the same liquid and gas volume, but in only one of which (Bottle 1) the compound behaves ideally, the following relationship applies:

$$M_T = C_{g1}V_{g1} + C_{l1}V_{l1} = C_{g1} + \frac{C_{g1}}{H} V_{l1} \quad (12)$$

and

$$M_T = C_{g2}V_{g2} + C_{l2}V_{l2} = C_{g2} + \frac{C_{g2}}{\gamma H} V_{l2} \quad (13)$$

Combining Equations (12) and (13) and solving for γ gives:

$$\gamma = (V_1/H) \{ (C_{g_1}/C_{g_2}) (V_g + V_1/H) \}^{-1} \quad (14)$$

Therefore γ may be determined using the ratio of gas concentrations determined in the two bottles.

B. MATERIALS AND METHODS

The chemical constituents of JP-4 jet fuels have been analyzed and reported by Smith et al. (Reference 9). Seventy-seven major components were identified. A subset of 15 components of JP-4 was utilized by MacIntyre et al. (Reference 10) for investigation of sorption equilibria on soils listed in Table 1. Compounds from this list, available at the USAF Environics Laboratory at Tyndall AFB, were used in this study.

TABLE 1. REPRESENTATIVE COMPONENTS OF JP-4 FUELS


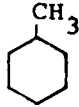
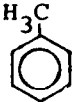
Compound	Structure	Molecular Weight (gm)	Vapor Pressure* (mm Hg)	Solubility (mg/l)	H** (dimensionless)
n-hexane	$\begin{array}{ccccccc} & H & H & H & H & H & H \\ & & & & & & \\ H & -C & -C & -C & -C & -C & -C-H \\ & & & & & & \\ & H & H & H & H & H & H \end{array}$	86.17	107 ¹¹ 120 ¹²	13 ¹²	41.2
cyclohexane		84.16	66.5 ¹¹ 77 ¹²	55 ¹²	6.0
n-heptane	$\begin{array}{ccccccc} & H & H & H & H & H & H \\ & & & & & & \\ H & -C & -C & -C & -C & -C & -C-H \\ & & & & & & \\ & H & H & H & H & H & H \end{array}$	100.20	32.8 ¹¹ 35 ¹²	2.4 ¹²	77. ⁵
methylcyclohexane		98.19	34.25 ¹¹	14 ¹³	13.2
toluene		92.13	20.9 ¹¹ 22. ¹¹	515 ¹²	0.27 ¹³ (25°C)

TABLE 1. REPRESENTATIVE COMPONENTS OF JP-4 FUELS (CONCLUDED)

Compound	Structure	Molecular Weight (gm)	Vapor Pressure* (mm Hg)	Solubility (mg/l)	H** (dimensionless)
n-octane		114.22	10.411 1112	0.66 ¹²	101.5
ethylcyclohexane		112.2	9.411		
p-xylene		106.2	6.5 ¹²	198 ¹²	0.19
isopropyl- benzene		120.2	3.411 3.2 ¹²	50 ¹²	.42
1,3,5 trimethyl- benzene		120.2	2.1 ¹¹	97.7 ¹⁴	.14
indan		118.17			
naphthalene		128.16	.053 ¹¹	31.7 ²	.020 ¹³ (25°C)
2-methylnaphthalene		142.2		25.4 ²	
n-tetradecane	C ₁₄ H ₂₀	198.4	.024 ¹¹ .0022 ¹²		
2,3 dimethyl- naphthalene		156.2			

* vapor pressures reported at 20°C

** H calculated from average reported vapor pressure and solubility unless otherwise noted.

Henry's Law Constants were measured using glass hypo vials sealed with Teflon® rubber laminated discs (Pierce Chemical Co.). Discs and bottles were precleaned by washing with distilled water and heating overnight at 105°C.

Two bottle sizes were employed. Bottle volumes were determined by weighing when full of water and averaged 156.10 ± 0.24 ml ($n=9$) and 120.98 ± 0.78 ml ($n=12$). Liquid volumes normally employed in the 156.1 ml bottle size were 10 and 125 ml. Typically, five or more replicate bottles of each liquid volume were equilibrated over at least a 24-hour period in a circulating water bath at 25°C. Other experimental procedures were comparable to those described by Lincoff and Gossett (Reference 8). Henry's Law Constants and activity coefficients for TCE and toluene were determined by removing 1 ml of bottle head space with a gastight syringe and analysis with a Perkin Elmer model 900 gas chromatograph. Concentrations were measured isothermally at temperatures of approximately 135°C for TCE and 175°C for toluene using a Carbopack[®] (60/80) with 1 percent SP-1000 column (Supelco, Inc). Compound concentration was measured as peak area determined by interface of the GC signal with a Hewlett-Packard model 3388A Integrator. A linear relationship between gas concentration and GC peak area was established by analysis over a range of gas concentrations. A typical calibration curve is shown in Figure 2.

Henry's Law Constants for naphthalene, indan, 2-3 dimethylnaphthalene, and 1,2,3 trimethylbenzene were measured by UV analysis of the aqueous solution, using a Cary 219 spectrophotometer. Analytical wavelengths were 219.2 nm for naphthalene, 247 nm for indan, 201.5 nm for 2,3 dimethylnaphthalene, and 196 nm for 1,2,3 trimethylbenzene. With the exception of 1,2,3 trimethylbenzene, wavelengths employed correspond to those at which maximum absorbance was determined to occur by scan of the UV region. UV absorbance for naphthalene and indan was determined to be directly proportional to solution concentration by analysis of standard decane solutions; an example calibration is shown in Figure 3.

After equilibration, samples for aqueous phase analysis were uncapped, and an aliquot was rapidly transferred to a stoppered quartz cuvette for measurement of UV absorbance. The compounds handled in this manner all had dimensionless H values $\leq .04$ and, therefore, aqueous concentration changes caused by volatilization are likely to have been minimal.

C. RESULTS AND DISCUSSION

The Henry's Law Constants determined in this study are given in Table 2.

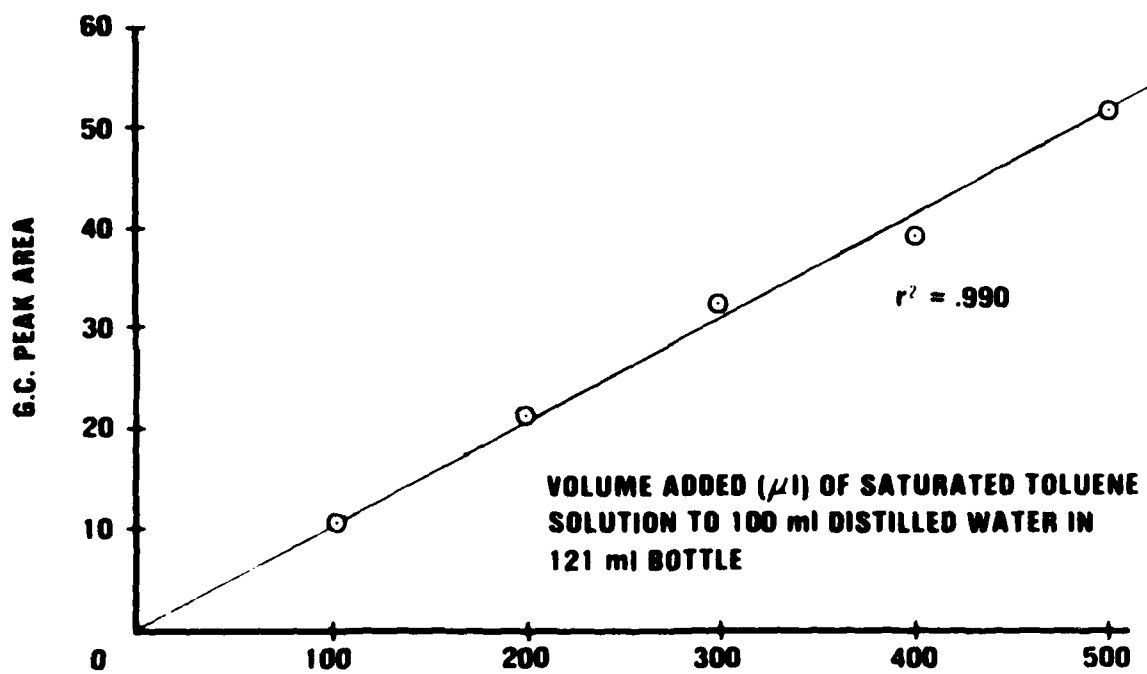


Figure 2. G.C. Calibration Curve For Toluene Head Space Analysis

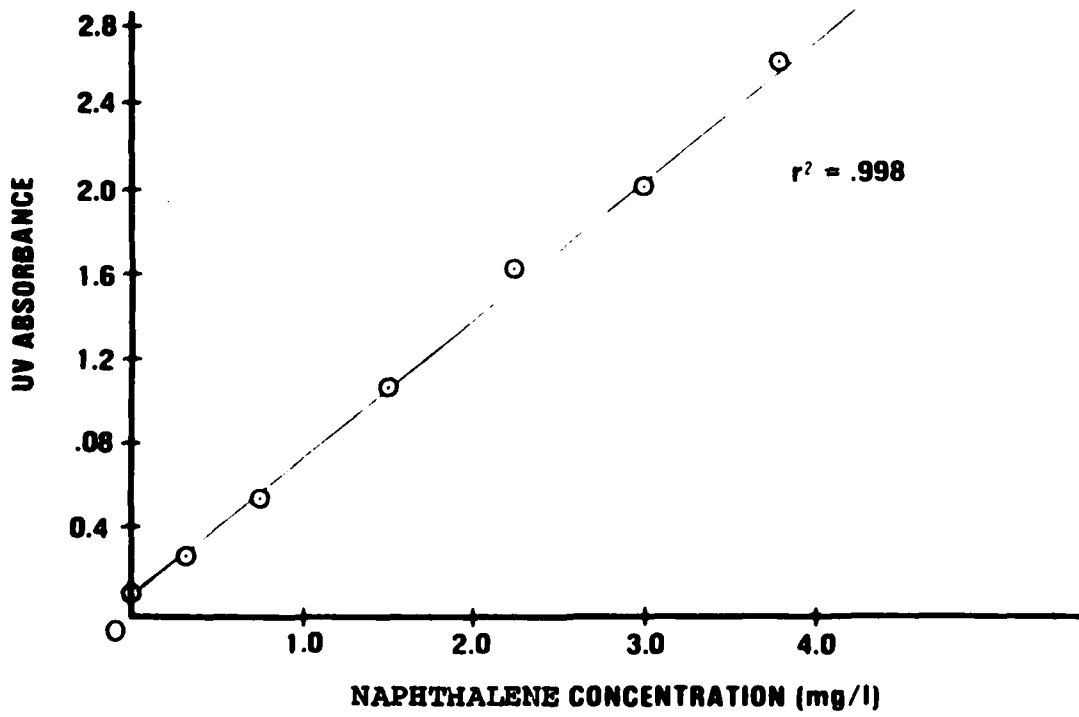


Figure 3. UV Calibration Curve for Naphthalene Analysis

TABLE 2. HENRY'S LAW CONSTANTS FOR TCE AND JP-4 FUEL COMPONENTS

<u>Compound</u>	<u>Measured Value @ 25°C</u>	<u>Literature Value</u>	<u>Reference</u>	<u>Remarks</u>
TCE	.397	.411	8	reference value calculated for T=25°C from regression equation for H vs. temperature
toluene	.261	.270	13	
naphthalene	.0209	.0196	13	
2,3, dimethyl-naphthalene	.0376			
indan	.0082			
1,2,3 trimethylbenzene*	.086	.141		reference value calculated from reported values for vapor pressure (11) and solubility (14) of 1,3,5 trimethylbenzene

* the experimental compound used was technical grade (90 percent purity) and, therefore, the measured value for H is suspect.

The measured H value for TCE is in good agreement with the value previously determined, using the EPICS technique. H values measured for toluene and naphthalene also agree closely with reported literature values. Neither water solubility and vapor pressure data from which H could be calculated nor measured H values for 2,3 dimethylnaphthalene; indan; or 1,2,3 trimethylbenzene could be located by the authors for comparison with the measured values.

A Henry's Law constant was also measured for methylcyclohexane. The measured value ($H = 9.81$) was beyond the range in which the EPICS technique is sensitive (ie $H < 3$) and therefore is not considered to be reliable. Henry's Law constants calculated from reported values for vapor pressure and solubility for hexane, cyclohexane, heptane and octane are all greater than 6.0 (see Table 1). It is therefore likely that Henry's Law Constants for these components of JP-4 Fuels cannot be accurately determined with the EPICS procedure.

Activity coefficients obtained for TCE and toluene at four ionic strengths are given in Table 3.

TABLE 3 - ACTIVITY COEFFICIENTS FOR TCE AND TOLUENE*

compound	γ			
	$I = .1$	$I = .3$	$I = .6$	$I = 1.0$
TCE	1.055	1.16	1.32	1.58
toluene	1.054	1.14	1.31	1.62

* values obtained in NaCl electrolyte at 25°C

Based on these data, the calculated salting coefficients (k) for TCE and toluene are .197 and .207, respectively. Considering the precision of replicate GC analyses ($\pm 2\%$) the difference in these values is not considered to be statistically significant. Gossett (Reference 15) has previously reported a salting coefficient of .207 for TCE from KCl electrolyte, which agrees closely with the measured value.

The activity of toluene in solution was measured over a threefold range in solution concentration and was unaffected over the toluene concentration range of 0.5 to 1.5 mg/l.

The activity of toluene in solution was also measured in the presence of other nonpolar (cyclohexane) and polar (acetone) solutes and was unaffected by the presence of these compounds.

Finally, the influence of electrolyte composition on toluene activity was evaluated by measuring activity coefficients in CaCl_2 and AlCl_3 electrolytes with ionic strengths of 0.10 and 0.30; results are shown in Table 4.

TABLE 4. EFFECT OF ELECTROLYTE COMPOSITION ON TOLUENE ACTIVITY

Ionic Strength	Toluene Activity Coefficient		
	NaCl	CaCl_2	AlCl_3
0.10	1.054	1.022	1.043
0.30	1.136	1.077	1.057

Activity coefficients for toluene in both AlCl_3 and CaCl_2 were significantly lower than that determined for toluene in NaCl at $I = 0.30$. These data are consistent with reported values for other non-ionic compounds which also vary with electrolyte composition (Reference 1).

D. SUMMARY

The EPICS technique has been demonstrated to be a reliable method for measurement of Henry's Law Constants and activity coefficients for many constituents of JP-4 Fuels. The procedure loses sensitivity for compounds with dimensionless H values ≥ 3 and is therefore not applicable to compounds such as hexanes, heptanes and octanes. For unsaturated compounds of low volatility UV analysis of the equilibrated aqueous solution is seen to be a viable analytical procedure. Gas exchange equilibria of volatile compounds is a function of their activity in the aqueous phase (see Equation (1)) and solution activity has been shown to be influenced by both electrolyte composition and concentration. Activity coefficients determined for TCE and toluene suggest that corrections for nonideality are likely to be negligible in most freshwater aquifers.

SECTION IV

SORPTION EQUILIBRIA

A. INTRODUCTION

At equilibrium, the gas concentration of a volatile compound in a closed bottle serves as a direct measure of the aqueous solution concentration providing the compound's Henry's Law Constant and activity coefficient are known (see Equations (1) and (2)). It is therefore reasonable to extend the EPICS technique to the study of sorption equilibria of volatile compounds such as toluene and TCE. A major advantage of this procedure is that separation of the solid from solution is no longer required in order to measure the equilibrium concentration in solution.

For compounds of low volatility, such as naphthalene, direct analysis of the solution is required, necessitating separation of solid from the aqueous phase.

B. MATERIALS AND METHODS

Sorption equilibria for toluene, naphthalene and TCE were determined on an artificial soil created by coating humic acids onto a hydrous aluminum oxide (Al_2O_3). Sorption equilibria were also measured for these compounds onto humic acids in the absence of Al_2O_3 . Finally, naphthalene and TCE sorption equilibria were evaluated, using naturally occurring Air Force base soils.

Al_2O_3 organic coatings were created by dissolving 9 grams of humic acid (Aldrich Chemical Co. or ICN Pharmaceuticals Inc.) in 1 liter of water at pH 10. Al_2O_3 was added (approximately 450 grams) and the pH lowered to approximately 4. After equilibration, excess humic acids and water were decanted. Solids were rinsed once with 1 liter of distilled water acidified to pH = 4 and dried overnight at 105°C.

Soil samples from Air Force bases were obtained from cores, and shipped to the Environics Laboratory at Tyndall AFB, wrapped in foil sealed in paraffin. Moisture contents for the soils were measured by weight loss after drying for 108 hours at 105°C. The dried soils were ground and material passing through an 850 μ sieve was used in the sorption experiments.

The organic content of all adsorbents was characterized by dichromate oxidation using the Walkley-Black method for analysis of soil organic carbon (Reference 16). Samples were analyzed in triplicate and the mean result is shown in Table 5.

Since sorption equilibria were conducted in sealed bottles with a gas headspace (see discussion below) knowledge of adsorbent densities was required to determine the volume displaced by the solid. Solid densities were determined by measuring the water volume displaced by a weighed amount of soil in a 10 ml graduated cylinder and are summarized in Table 5.

The protocol used for sorption experiments was as follows:

1. The calculation of compound mass remaining at equilibrium necessitated precise knowledge of the headspace in each bottle. The individual bottle volumes were determined by weighing when full with water. Results for the gas and/or liquid concentrations in individual bottle were normalized to a uniform standard bottle size, using the following relationships:

$$C_g(\text{normalized}) = C_g(\text{observed}) \frac{(V_1 + \gamma HV_g)_{\text{actual}}}{(V_1 + \gamma HV_g)_{\text{std.}}} \quad (15)$$

$$C_l(\text{normalized}) = C_l(\text{observed}) \frac{(V_1 + \gamma HV_g)_{\text{actual}}}{(V_1 + \gamma HV_g)_{\text{std.}}} \quad (16)$$

2. A stock solution of the compound of interest was prepared. For toluene this was accomplished by delivering 500 ml of toluene with an Eppendorf pipette to a 2-liter volume of water. The mass delivered was determined by weight to be $.422 \pm .001$ grams ($n = 4$) giving a stock solution concentration of 211 mg/l. The toluene concentration in the stock solution was verified by microextraction as follows:

- a. 1 ml methylene chloride (MeCl) and 8.5 ml distilled water were delivered to a 10 ml glass bottle and sealed with a Teflon[®] disc.
- b. 250 μ l of the toluene stock solution was delivered through the disk, using a syringe while venting the bottle head space gas through a second syringe needle.
- c. The remaining bottle head space was displaced by injecting distilled water into the bottle and venting the head space gas as in (b).
- d. bottle contents were shaken to extract toluene into MeCl and the MeCl phase analyzed for toluene by gas chromatography.

TABLE 5. ADSORBENT CHARACTERISTICS

<u>Solid Phase</u>	<u>% organic carbon</u>	<u>density (g/cm³)</u>	<u>moisture content</u>	<u>depth of core</u>
Al ₂ O ₃ (Fisher Scientific Co. adsorption alumina; 80-200 mesh)	varied from 0 to 0.54%	2.49 ± .055 (n = 5)		
Whiteman AFB soil Knobnoster, MO	0.40%	2.27 ± 0.148 (n = 6)	21.4%	3'-4.7'
Lowry AFB soil Denver, CO	0.11%	2.28 ± .049 (n = 3)	15.3%	5.3'-6.9'
Offutt AFB soil Omaha, NB	0.23%	2.50 ± .041 (n = 3)	22.2%	11'-13'
Minot AFB soil Minot, ND	0.12%	2.36 ± .078 (n = 3)	14.5%	10'-12'
Humic Acid, ICN Pharmaceuticals Inc.	33.46%			
Humic Acid, Aldrich Chemical Co.	32.05%			

- e. G.C. peak areas were calibrated against standard toluene solutions in MeCl prepared by delivering a weighed amount of toluene into MeCl and serial dilution.

The toluene concentration in the stock solution determined by microextraction was $214.1 \text{ mg/l} \pm 12.4 \text{ mg/l}$ ($n = 4$). Based on these data it was assumed that toluene loss in preparation of the stock solution was negligible and a stock concentration of 211 mg/l was assumed. Aliquots of the stock solution were added to bottles containing solids for sorption experiments.

For naphthalene, a saturated aqueous stock solution was prepared by equilibrating an excess of naphthalene with water. Prior to each experiment, an aliquot of stock solution was filtered through Number 5 Whatman filter paper and additions were made to experimental bottles containing solids. Identical additions were made to bottles without solids and used to establish the stock solution concentration. This aqueous solution was analyzed for naphthalene concentration by UV at $\lambda = 219.2 \text{ nm}$. UV absorbance was calibrated against decane solutions of known naphthalene concentration made by dilution of a stock solution consisting of a weighed amount of naphthalene in decane.

For TCE, aliquots of a saturated aqueous stock solution were delivered to experimental bottles containing solids for equilibration. Aliquots delivered to bottles without solids were used to determine TCE concentration. Solution concentration was measured by rapidly transferring a portion of the aqueous phase to a stoppered cuvette and measuring its UV absorbance at 198 nm . UV absorbance was calibrated against decane solutions of known TCE concentration made by dilution of a stock solution prepared by adding $500 \text{ } \mu\text{l}$ of TCE ($.693 \pm .013 \text{ grams}$ ($n = 10$)) to 250 ml decane.

3. Sorption equilibria were measured by adding aliquots of toluene, naphthalene or TCE stock solutions to glass bottles containing variable amounts of adsorbent and distilled water or 0.1 m NaCl electrolyte. Bottles were rapidly capped with Teflon[®] laminated discs and continuously rotated at room temperature for at least 12 hours. The bottles were then placed in a 25°C water bath overnight prior to analysis of the liquid or gas phases.

4. After equilibration vapor phase concentrations of TCE and toluene were determined by gas chromatography using the methods described in Section IIIB.

The liquid phase from bottles containing naphthalene was analyzed by high-performance liquid chromatography (HPLC). Sample volumes of $25 \text{ } \mu\text{l}$ were removed through the bottle disc by syringe and injected into a Waters liquid

chromatograph fitted with a Bondpack C-18 column (Waters, Inc.). An in-line prefilter was used to remove any colloidal solids sampled by the syringe. A mobile phase of 75/25 acetonitrile - H₂O was employed at a flow rate of 2.0 ml/min. Peak detection was by UV at $\lambda = 254$ nm. Concentrations were quantified by comparison of sample peak heights to those of naphthalene standards in decane.

5. The sorption of solute in each experiment was calculated as follows:
 - a. Measured bottle concentrations were normalized to those in a standard bottle of uniform size using Equation (15) or (16) and replicate sample results were averaged. In bottles containing solids, gas volumes were corrected for the volume displaced by the adsorbent.
 - b. The fraction of solute remaining (f) was calculated as the ratio of normalized concentration in bottles with adsorbent to those in bottles containing the same addition of solute but with no solid. the percent solute sorbed is therefore:

$$\% \text{ Sorbed} = (1-f)100 \quad (17)$$

It should be noted that the percent solute sorbed (a ratio) may be accurately determined without knowing the precise mass of solute added in the experiment.

- c. The mass sorbed was calculated as the product of the total mass added to the experimental bottles and the calculated percent sorbed (see (b) above). Total solute mass added was computed from the product of the solute stock solution concentration (measured as described in (2) above) and the volume of stock solution added to the experimental bottles.

C. RESULTS AND DISCUSSION

Several experiments were performed to evaluate toluene sorption by Al₂O₃. In the absence of humic acid coatings, toluene concentration in the bottle head space indicated that it was consistently excluded from solution by the oxide adsorbent. Exclusion was observed at adsorbent additions ranging from 5 to 60 gm to a 50 ml volume of distilled water. The specific conductance of the equilibrated solution was measured and results are shown in Figure 4. The conductance in the equilibrated solution containing humic-coated Al₂O₃ was substantially lower than that in solution equilibrated with the pure oxide.

Approximate ionic strengths may be computed from specific conductance using the relationship developed by Langlier (Reference 17):

$$I = 1.6 \times 10^{-5} \times \text{specific conductance } (\mu\text{mho/cm}) \quad (18)$$

Calculated ionic strengths and corresponding toluene activity coefficients are shown in Figure 4. The calculated values are insufficient to explain the observed toluene exclusion from solution. As an example, the 15-gram addition of Al_2O_3 produced a head space concentration of toluene which would require a toluene activity coefficient in solution of 1.05 (conservatively estimated, assuming no toluene was sorbed) while the calculated toluene activity coefficient based on measured specific conductivity was 1.006. Although no explanation for these results has been established, we speculate that colloidal Al_2O_3 carrying a surface charge may be affecting toluene activity. Such charged colloids are unlikely to be sufficiently mobile to influence the measured solution conductance which would explain the disparity between the calculated toluene activity coefficients and those which were observed.

Toluene was found to be consistently sorbed from aqueous solution by Al_2O_3 coated with humic acids. The control of sorption by humic acids was tested by performing parallel experiments in which one set of bottles contained variable amounts of Al_2O_3 coated with humic acids and a second set contained the same mass of humic acids without Al_2O_3 . A swamping NaCl electrolyte (0.1M) was used in all bottles to prevent toluene activity changes from influencing the results. Four or more replicate bottles of each solid addition were analyzed; mean results are shown in Figure 5.

Sorption of toluene was observed to be greater by humic acids in the absence of Al_2O_3 . This difference suggests that the form of the humic acid in solution (e.g., as a coating material vs. free humic acid), influences its sorptive properties.

It is noteworthy that the toluene sorption isotherm on humic acids without Al_2O_3 is a plateau (i.e., mg of toluene sorbed/g humic acid is independent of the equilibrium toluene concentration). This suggests that toluene sorption on the humics obeys a Langmuir isotherm and that full-sorption site occupancy has occurred.

Sorption kinetics for naphthalene on humic-coated Al_2O_3 were studied over a 72-hour time period. Results show that equilibrium conditions were obtained within the 18 minutes which elapsed prior to analysis of the first sample.

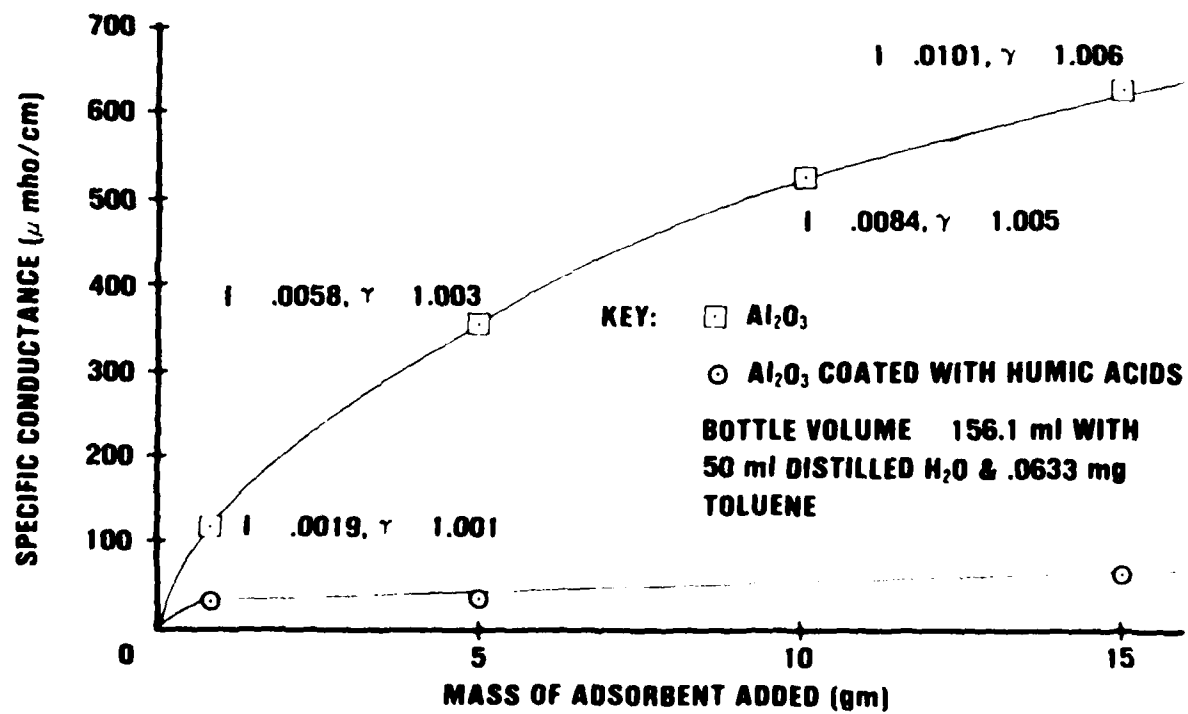


Figure 4. Conductance of Equilibrated Solutions

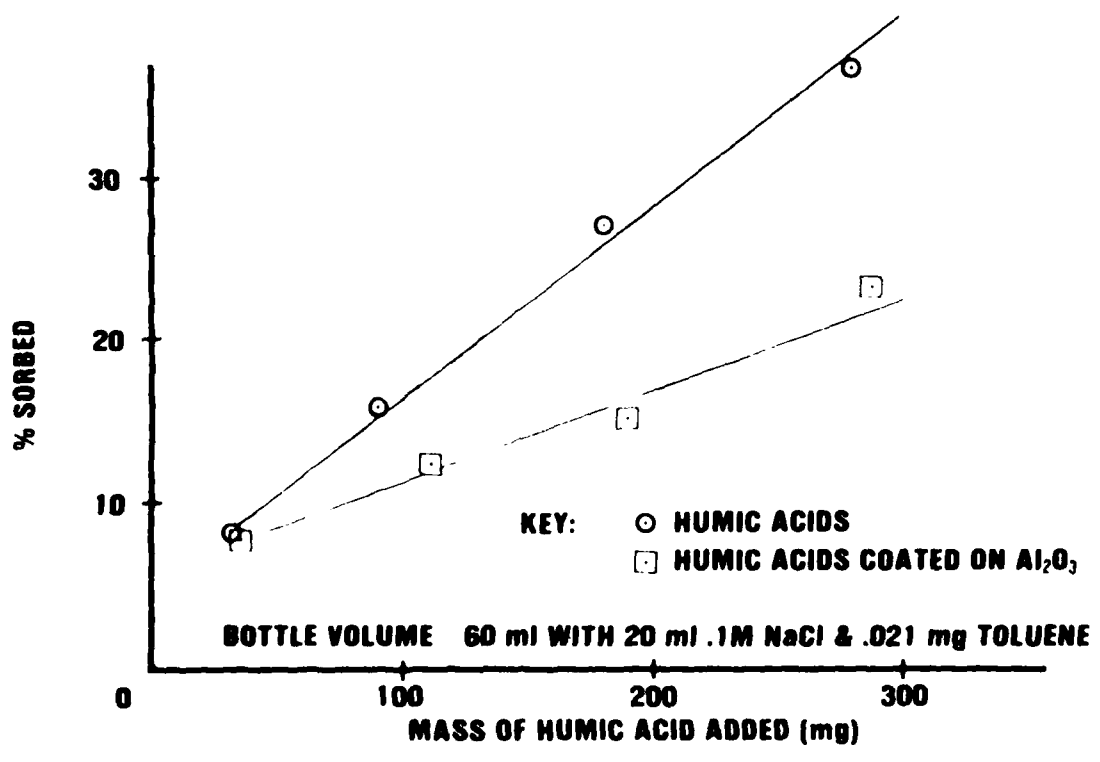


Figure 5. Toluene Head Space Analysis

Naphthalene sorption on humic-coated Al_2O_3 and naturally occurring Air Force Base soils were evaluated under conditions in which each experimental bottle contained the same mass of organic carbon. Triplicate bottles of each solid were analyzed; mean results are shown in Table 6.

TABLE 6. NAPHTHALENE SORPTION NATURAL AND ARTIFICIAL SOILS*

<u>Soil</u>	<u>solid mass(g)</u>	<u>mass of organic carbon (mg)</u>	<u>% naphthalene sorbed</u>
Al_2O_3 with humic acid	13.9	75	48.0%
Offutt AFB soil	32.8	75	100%
Whiteman AFB soil	18.3	75	39.8%
Lowry AFB soil	68.2	75	32.9%
Minot AFB soil	62.0	75	100%

* bottle volumes were 121 ml, containing soil, 50 ml 0.1 m NaCl and 5ml of naphthalene stock solution.

These results clearly show that, at the soil carbon concentrations employed (.11 to .54 percent), soil sorption capacity is not controlled solely by the mass of organic carbon present. In addition, sorption did not co-vary with the total mass of solid added, suggesting that the specific nature of the adsorbent and/or organic matter on the adsorbent must influence sorption equilibria.

The sorption of TCE onto Al_2O_3 coated with humic acids and onto humic acids in the absence of Al_2O_3 was evaluated in an experiment comparable to that previously described for toluene. Results are shown in Figure 6. As was the case with toluene, the sorption of TCE was enhanced in the absence of Al_2O_3 . The observed sorption density of TCE (mg sorbed/g sorbent) onto the humic material was independent of the equilibrium concentration of TCE in solution suggesting that the humic materials have finite binding capacity of approximately 7×10^{-7} moles TCE/gm (vs 3×10^{-7} moles toluene/gm) and that humic binding sites were saturated in the experiment performed.

D. SUMMARY

The head space technique has been demonstrated to be a reliable method for measuring the sorption of volatile components of JP-4 fuels and degreasers.

High-performance liquid chromatography permits separation and analysis of compounds of low volatility which absorb in the UV region.

Sorption of toluene and TCE has been shown to be suppressed by the presence of a hydrous Al_2O_3 oxide. Sorption of these compounds by humic acids was enhanced when this sorbent was not present as a coating material on Al_2O_3 . These data suggest that the physical state of the organic sorbent may influence the binding of non-ionic solutes. The sorption density (mg sorbed/g sorbent) of toluene and TCE on humic acid was observed to be independent of the equilibrium concentration in solution indicating that the humic acid sorbent had a limited number of binding sites and that full-site occupancy was achieved.

Sorption of naphthalene by Al_2O_3 coated with humic acids and naturally occurring Air Force base soils was not controlled solely by the organic content of these sorbents or by the mass of sorbent present. These data establish that the sorption behavior of non-ionic solutions on some naturally occurring aquifer materials is likely to be a complex phenomena in which the nature of both the inorganic soil matrix and the soil organic matter may play a role. Additional research is required to establish the interdependency between sorption of non-ionic solutes and the detailed physical and chemical characteristics of the adsorbent.

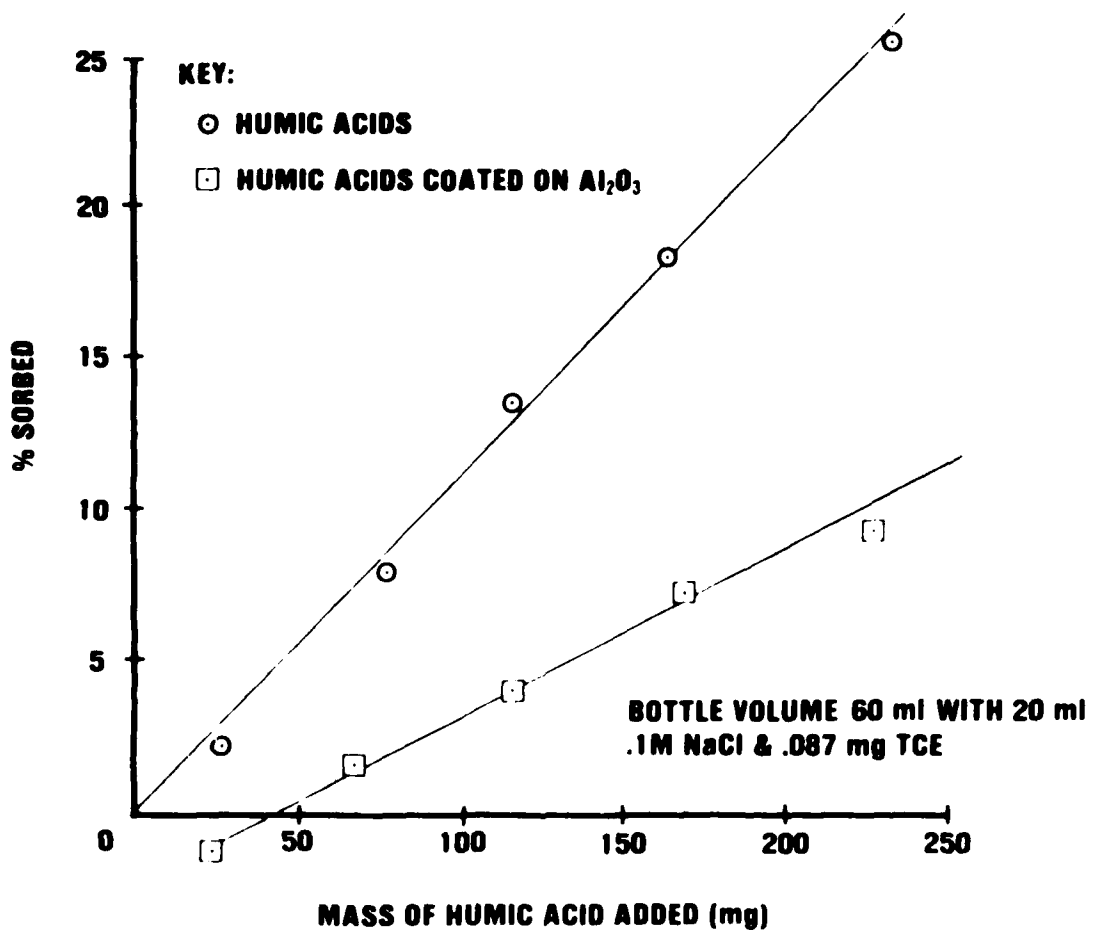


Figure 6. Sorption of TCE by Humic Acid and Humic-Coated Al_2O_3

SECTION V

RECOMMENDATIONS

The research performed was designed to evaluate the equilibria for pertinent reactions of volatile non-ionic organic compounds in unsaturated groundwater systems.

Gas exchange equilibria may be evaluated through knowledge of a compound's Henry's Law constant and its activity coefficient in solution. An equilibrium head space technique has been demonstrated to be applicable to the determination of these parameters for many of the components of distillate fuels and degreasers.

Sorption equilibria may also be evaluated, using head space measurements for volatile compounds for which Henry's Law constants and solution activity coefficients are known. The observed sorption of organic solutes typical of degreasers (TCE) and distillate fuels (toluene and naphthalene) was seen to be a complex phenomena. Although our results confirm the importance of organic materials in the binding of non-ionic solutes, the data indicate that the physical and perhaps chemical nature of the soil organics are likely to influence results. Additional investigation is required to explore these interdependencies.

Specific recommendations for further research are as follows:

1. Experiments should be conducted to determine those characteristics of soil organics which influence their binding with non-ionic organic solutes. Pertinent variables include but are not limited to (a) elemental composition (percent carbon, nitrogen, etc.) (b) molecular size (c) physical state, e.g., particulate vs. dissolved vs. coating materials and (d) exchangeable acidity.

2. Experiments are needed to evaluate the sorption of volatile compounds from the vapor phase onto soils. The importance of soil organic carbon in these sorption reactions requires evaluation.

3. The equilibria of mixed solutes with soil organic materials should be evaluated. Our data suggest humic acids have a finite binding capacity and compound competition for binding sites may therefore occur.

4. Henry's Law constants and activity coefficients for all of the identified components of distillate fuels should be evaluated as a prerequisite for the prediction of their gas exchange and sorption equilibria.

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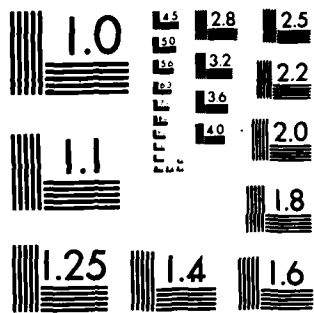
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ERRATA - FEBRUARY 1984

The following corrections are applicable to ESL-TR-83-51, " Partitioning Equilibrium of Volatile Pollutants in Three-Phase Systems," December 1983

Page i: Second paragraph, line 2 - replace "Gabarini" with "Garbarini"
line 3 - replace "Electrical" with "Environmental".

Page 3: Third paragraph, line 1 - insert "," after "percent".

Page 6: Replace Equations (12) and (13) as follows:

$$M_T = C_{g1} V_{g1} + C_{l1} V_{l1} = C_{g1} V_{g1} + \frac{C_{g1} V_{l1}}{H} \quad (12)$$

$$M_T = C_{g2} V_{g2} + C_{l2} V_{l2} = C_{g2} V_{g2} + \frac{C_{g2} V_{l2}}{\gamma H} \quad (13)$$

Page 7: Replace Equation (14) as follows:

$$\gamma = (V_l/H) \{ (C_{g1}/C_{g2}) (V_g + V_l/H) - V_g \}^{-1} \quad (14)$$

Page 9: Third paragraph, line 4 - replace .04 with .09.

Page 16: Third paragraph, line 2 - replace "ml" with "μl"

Page 24: Last paragraph, line 4 - replace "solution" with "solutes".

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