UNCLASS

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

①

AD-A158 096

## REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
AFIT/CI/NR 85-99T

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Sorption and Desorption of Volatile Chlorinated Aliphatic Compounds by Soils and Soil Components

5. TYPE OF REPORT & PERIOD COVERED
THESIS/~~DISSERTATION~~

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
Robert G. La Poe

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
AFIT STUDENT AT: Cornell University

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
AFIT/NR
WPAFB OH 45433 - 6583

12. REPORT DATE
June 1985

13. NUMBER OF PAGES
306

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)
UNCLASS

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

DTIC
ELECTE
AUG 1 9 1985
S D
B

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES
APPROVED FOR PUBLIC RELEASE: IAW AFR 190-1

Lynn Wolaver
LYNN E. WOLAVER
Dean for Research and
Professional Development
AFIT, Wright-Patterson AFB OH

5 Aug 1985

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
ATTACHED

DTIC FILE COPY

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASS

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

85 8 13 094

85-99

# AFIT RESEARCH ASSESSMENT

The purpose of this questionnaire is to ascertain the value and/or contribution of research accomplished by students or faculty of the Air Force Institute of Technology (AU). It would be greatly appreciated if you would complete the following questionnaire and return it to:

AFIT/NR
Wright-Patterson AFB OH 45433

RESEARCH TITLE: Scorption and Desorption of Volatile Chlorinated Aliphatic Compounds by Soils and Soil Components

AUTHOR: Robert G. La Poe

RESEARCH ASSESSMENT QUESTIONS:

1. Did this research contribute to a current Air Force project?

( ) a. YES ( ) b. NO

2. Do you believe this research topic is significant enough that it would have been researched (or contracted) by your organization or another agency if AFIT had not?

( ) a. YES ( ) b. NO

3. The benefits of AFIT research can often be expressed by the equivalent value that your agency achieved/received by virtue of AFIT performing the research. Can you estimate what this research would have cost if it had been accomplished under contract or if it had been done in-house in terms of manpower and/or dollars?

( ) a. MAN-YEARS ________ ( ) b. $________

4. Often it is not possible to attach equivalent dollar values to research, although the results of the research may, in fact, be important. Whether or not you were able to establish an equivalent value for this research (3. above), what is your estimate of its significance?

( ) a. HIGHLY SIGNIFICANT ( ) b. SIGNIFICANT ( ) c. SLIGHTLY SIGNIFICANT ( ) d. OF NO SIGNIFICANCE

5. AFIT welcomes any further comments you may have on the above questions, or any additional details concerning the current application, future potential, or other value of this research. Please use the bottom part of this questionnaire for your statement(s).

| | | |
|---|---|---|
| NAME | GRADE | POSITION |
| ORGANIZATION | LOCATION | |

STATEMENT(s):

FOLD DOWN ON OUTSIDE - SEAL WITH TAPE

AFIT/NR
WRIGHT-PATTERSON AFB OH 45433

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE. $300

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY MAIL
FIRST CLASS PERMIT NO. 73236 WASHINGTON D.C.

POSTAGE WILL BE PAID BY ADDRESSEE

AFIT/ DAA
Wright-Patterson AFB OH 45433

FOLD IN

# SORPTION AND DESORPTION OF VOLATILE CHLORINATED ALIPHATIC COMPOUNDS BY SOILS AND SOIL COMPONENTS

A Thesis
Presented to the Faculty of the Graduate School
of Cornell University
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

by
Robert G. La Poe
June 1985

# BIOGRAPHICAL SKETCH

The author, Robert G. Blum, is currently in the process of legally changing his name to Robert G. La Poe. He received his Bachelor of Science Degree (with honors) in Engineering Science and Mechanics from the University of Florida in 1972. Upon graduation he entered the United States Air Force as a Second Lieutenant. Robert was a distinguished graduate from the USAF Navigator Training School, and subsequently served as a C-141 global airlift navigator. In 1976, he entered the master's program in Water Resources Engineering at the University of North Carolina at Chapel Hill, and, in 1977, received the Master of Science degree in Environmental Engineering. Afterwards, he worked with two environmental consulting engineering firms, and, in 1979, Robert returned to the Air Force as a bioenvironmental engineer. He was the distinguished graduate from the Air Force Bioenvironmental Engineering School. Prior to starting the Ph.D. program at Cornell University, Captain La Poe (Blum) was a Research Environmental Engineer at the AF Engineering and Services Center, Tyndall AFB, Florida. Upon graduation from Cornell, Captain La Poe (Blum) will be assigned to the Environmental Health Laboratory in Wiesbaden, Germany, where he will be the Chief of Environmental Engineering for the air bases in Europe.

"Scientific research consists in seeing what everyone else has seen, but thinking what no one else has thought."

Albert Szent-Györgyi
(1893-    )

# ACKNOWLEDGEMENTS

I would like to praise and thank my committee chairman, Professor James M. Gossett, for his keen insight into research problems (and their solutions), unparalleled scientific mind, and uncanny savvy for the intricate workings of laboratory equipment. Furthermore, I appreciate his suggestion many, many months ago, that I "look into the adsorption of these compounds onto soils" as a possible research topic.

I would also like to express my gratitude to my other committee members: Professors L. W. Lion and M. B. McBride, for their input, discussions, suggestions and assistance during this research effort.

I am indeed grateful to the U.S. Air Force (HQ AFESC/RDV) for providing the funds necessary to conduct this research. In addition, a "thank you" is in order to the Air Force Institute of Technology (AFIT) for their assistance during my "tour" at Cornell.

I am indebted to my girl friend, Sarolta (Scarlett), who helped me remain "human" throughout this struggle, and who tried to show me that there is another world which lies beyond scientific explanation.

Lastly, I would like to acknowledge the contributions of the following people: Carol Cook, my very meticulous typist; Paul Jones, who constructed the two tumblers and the centrifuge adaptors; Spyros Pavlostathis, who explained the 'GRAF' computer program to me; and my son Joel, who assisted me in an experiment by carefully placing the septa in the caps with their "shiny sides up".

# SORPTION AND DESORPTION OF VOLATILE CHLORINATED ALIPHATIC COMPOUNDS BY SOILS AND SOIL COMPONENTS

Robert G. La Poe, Ph.D.
Cornell University, 1985

Many groundwater supplies in the industrialized nations of the world are contaminated with low concentrations of certain volatile, chlorinated, aliphatic compounds, such as trichloroethylene ($C_2HCl_3$), tetrachloroethylene ($C_2Cl_4$), carbon tetrachloride ($CCl_4$), and chloroform ($CHCl_3$). One aspect of this problem, about which very little is known, is that of the (potential) sorption of these chemicals (in dilute aqueous systems) by the soils comprising the groundwater aquifers, and by soils and soil components in general. This research was performed to expand our very limited knowledge in this area, and utilized $^{14}C$-labeled sorbates in conjunction with liquid scintillation counting.

This investigation has shown that the above compounds are negligibly adsorbed by the inorganic solids (clays and minerals) which would typically comprise subsurface soils, with some evidence suggesting that they are slightly <u>negatively</u> adsorbed by these solids.

Sorption (and some desorption) isotherms were determined for each sorbate with each of the following sorbents: a mineral soil, a peat soil, a muck soil, activated carbon, graphite, humic acid, and lignin. (K subscript d) The sorption equilibrium distribution coefficients ($K_d$) in the linear, low-concentration regions of these isotherms were determined for each

Cont'd

sorbent-sorbate system. These $K_d$ values were regressed with various properties of the sorbates, which included molecular weight, dipole moment, polarizability, molar volume, parachor, aqueous solubility, and octanol-water partition coefficients. The results of these correlation studies showed that polarizability and aqueous solubility are the best predictors of $K_d$ values investigated in this research.

The sorption free energy ($\Delta G^o$), enthalpy ($\Delta H^o$), and entropy ($\Delta S^o$) were measured by conducting isotherms at three temperatures. The mean $\Delta H^o$ values were approximately -1 to -2 kcal/mol, and the $\Delta G^o$ values ranged from about -1 to -4 kcal/mol. These relatively low values, together with the results of the correlation studies, implicated the London (dispersion) forces and the ion-induced dipole interaction as the most plausible mechanisms to account for the sorption of these compounds by soils.

B

# TABLE OF CONTENTS

# LIST OF TABLES

Table Page

# LIST OF FIGURES

Figure Page

# I. INTRODUCTION

The contamination of groundwater supplies by volatile, chlorinated, hydrocarbon compounds has become a very serious environmental problem for industrialized countries of the world. Chemicals such as trichloroethylene, tetrachloroethylene, carbon tetrachloride, chloroform, methylene chloride, trichloroethanes, vinyl chloride, dichloroethanes, and dichloroethylenes have been found in numerous groundwater aquifers worldwide. (They are also present in some surface waters, but usually at a much lower concentration because of their high volatility.) The above compounds are presently undergoing review for possible inclusion in the National Revised Primary Drinking Water Regulations (Federal Register, 1982) (except for chloroform which is already regulated by the existing National Primary Drinking Water Regulations).

The synthetic chlorinated hydrocarbons named above are principally used as solvents in industrial or domestic applications. For example, trichloroethylene (TCE) has been used for or in: metal degreasing, solvent dyeing, dry cleaning, refrigerants, fumigants, cleaning and drying electronic parts, diluent in paints and adhesives, textile processing, anesthetics, spot removers, rug cleaners, and even air fresheners (Hawley, 1981; Love and Eilers, 1982). Table 1.1 shows the world production capacities for some of these chlorinated hydrocarbons (from McConnell et al., 1975). The largest users of these solvents are industries (e.g., chemical

TABLE 1.1 Estimated World Production Capacities (1973) for Various Chlorinated Hydrocarbons, in Tons per Year (From McConnell *et al*.)

| | |
|---|---|
| Trichloroethylene | 1,010,000 |
| Tetrachloroethylene | 1,050,000 |
| 1,1,1-Trichloroethane | 480,000 |
| Methylene Chloride | 400,000 |
| Vinyl Chloride | 10,500,000 |
| 1,2-Dichloroethane | 19,500,000 |
| Carbon Tetrachloride | 1,000,000 |
| Chloroform | 245,000 |

manufacturing, metal finishing, electronic, and airlines) and maintenance facilities at military bases.

As a result of improper disposal practices, accidental spills, or leaking storage tanks, many groundwater supplies have become contaminated with one or more of these compounds. (Other minor sources of these solvents in groundwater include septic tank degreasers and similar products from households, sewer leaks, water from cleaning and rinsing of storage tanks and machinery, and treated wastewaters used for groundwater recharge [Love, *et al*., 1983]). It is likely that more of these polluted aquifers will be discovered in the future as water sampling programs become more extensive.

The reason for the concern over the trace-level presence of these compounds in drinking water is that most of them are suspected human carcinogens (vinyl chloride is the only one of those listed above which is a "confirmed" human carcinogen) (Council on Environmental Quality, 1981). At high concentrations and doses (acute exposures), these compounds generally cause nausea, dizziness, tremors, blindness, or other health problems. At lower concentrations, skin eruptions can develop, or the central nervous system may be impaired. At still lower concentrations (i.e., those typical of contaminated groundwaters), over a period of many months or years (chronic exposure), some of the health problems are tolerable and some are fatal (Council on Environmental Quality, 1981). There is often a long latency period between the time of exposure, and manifestation of the disease induced by animal or human carcinogens. It should be noted that there is no direct evidence which implicates trace levels of these compounds in drinking water with adverse human health effects. Rather, the adverse health effects are extrapolated from evidence based on occupational exposures, epidemiological studies of populations drinking chlorinated water, and laboratory studies of chemical carcinogen effects on animals.

Nevertheless, it is no doubt prudent policy to prevent contamination of groundwater aquifers by these chemicals, and, if the aquifer is already contaminated, to spare no effort in "cleaning it up". Indeed, the politics of the situation will generally demand that the polluter take measures to reduce the contaminant concentration to a specified level. Fortunately, water treatment technologies are available for the removal of these volatile organics. The most promising techniques presently available are air-stripping and adsorption onto activated carbon. Numerous studies have been performed on these (and other) water treatment technologies.

However, one aspect of this type of groundwater contamination problem which has received very little attention is the sorption of these compounds with soils and soil components. If certain soils or soil fractions sorb these compounds to any extent, then the total amount (mass) of contaminant in the aquifer could be surprisingly more than that estimated by multiplying the aquifer water volume by an average contaminant concentration. In other words, sorption by the soil provides additional "storage capacity" for the contaminant in the aquifer. Therefore, the sorption and desorption characteristics of these compounds with soils could have an impact on the length of time that a treatment system must operate to ensure that a particular groundwater aquifer is "cleaned up". Furthermore, sorption parameters are needed in the transport equations for modeling the movement of groundwater contaminants; and lastly, sorption may affect the kinetics of the compounds' biodegradation, volatilization, or other mechanisms which may bring about their transformation. Therefore, an understanding of the sorption characteristics of these types of compounds with soils is clearly essential.

This study is undertaken with the overall goal of measuring, describing, explaining, modeling, and correlating the equilibrium sorption (and desorption) characteristics of chloroform, carbon tetrachloride, trichloroethylene, and tetrachloroethylene with soils and soil components. Primary emphasis is given to the relationship between sorption and certain fundamental molecular properties. Also, an attempt is made to implicate the predominant sorption mechanism(s) involved, based on the results of the isotherm correlation studies, and estimation of the free energies, enthalpies, and entropies of sorption.

# II. BACKGROUND

## A. Adsorption Versus Absorption

Adsorption is generally defined as the accumulation or concentration of a substance at an interface between two phases. Absorption refers to the penetration or transfer of a substance from one phase into another. The term sorption is used when it is not desired (or is experimentally impossible) to distinguish between adsorption and absorption phenomena. (The term sorption is often used in this thesis since it has not yet been conclusively demonstrated which concept applies to the uptake of neutral [nonionic] organic compounds by certain soils or soil components. However, the term adsorption is used in those cases where it is known to occur, such as in the accumulation of substances at the surfaces of activated carbon, graphite, clays, and minerals.)

For a sorption system consisting of an aqueous soil suspension to which a neutral organic solute is introduced, the two opposing (but not necessarily mutually exclusive) explanations for what occurs are:

1) The solute molecules are adsorbing onto the surfaces of the soil solids.
2) The solute molecules are absorbing into the solid (or semisolid) phase of soil organic matter.

Since virtually all the organic matter in soils is associated with (i.e., coated onto) the clay/mineral fraction (Greenland, 1965; Schnitzer and Kodama, 1977), the two processes are similar in that they involve the distribution of a solute between an aqueous phase and a solid (or semisolid) phase. The mechanisms at work which govern this distribution are theoretically the same, whether the phenomenon is one of adsorption or absorption, since the same intermolecular forces are at work in each case. Nevertheless, the theory and fundamentals of the adsorption and absorption (liquid-liquid extraction) processes are discussed separately below (in Sections B and C, respectively), since the two phenomena are also quite different in many respects. Because adsorption and liquid-liquid extraction are both vast subject areas, discussion is limited to those aspects relevant to sorption in aqueous soil systems containing dilute concentrations of organic solutes.

## B. Adsorption Theory and Fundamentals Relevant to This Research

Adsorption from solution is an extremely complicated phenomenon, and no single theory has yet been developed which adequately explains the process from a molecular standpoint. The main reasons for its complexity are:

1) It not only involves the interaction of the adsorbent with the adsorbate, but also interactions between a solvent (water) with the adsorbate, and with the adsorbent.
2) Molecular interactions in condensed systems differ from those occurring in the gaseous phase because distances between the interacting molecules are much smaller.
3) A rigorous theory for the structure of liquid water is far from being developed (Eisenberg and Kauzmann, 1969). In addition, various thermal anomalies have been reported in the properties of water and aqueous solutions (Drost-Hansen, 1967). That is, it appears that many properties of water (including surface and

interfacial phenomena) exhibit relatively abrupt transitions at certain distinct temperatures (Drost-Hansen, 1967).

### 1. Adsorption Isotherms and Models

Perhaps the most useful way to present equilibrium adsorption data is via an adsorption isotherm. The isotherm is a plot of the mass of solute adsorbed per unit mass (or surface area) of solid (i.e., adsorption density) versus the equilibrium solute concentration* (at constant temperature). According to Giles (1970), equilibrium adsorption data plotted as isotherms can potentially yield a surprising amount of information including: the nature of the adsorption reaction; the heat, free energy, and entropy of the reaction; the specific surface of the solid, its degree of porosity, and the size and shape of its pores; and the size of the adsorbate molecule, its orientation at the surface, and its degree of self association.

By the early part of this century, a great deal of isotherm data (especially on gas-solid adsorption systems) had been generated, and interests were mounting to develop an adsorption theory/model to explain and "fit" these data. Several theories/models have been derived or proposed since that time, but none were specifically applicable to liquid-solid adsorption systems. Each theory/model has its utility, and each has its shortcomings.

---

*To be thermodynamically rigorous, the isotherm should actually plot the activity of the adsorbed solute molecules versus their activity in solution at equilibrium. However, since the activity of an adsorbed species cannot be defined in terms of the usual activity coefficients and standard states, isotherm plots based on the activity of the adsorbed solute are not meaningful. Isotherms may, however, be plotted as sorption density versus the equilibrium solute activity, although this is seldom done.

The major theories and models for adsorption from solution have been "borrowed" from those which were originally derived for adsorption of gases onto solids. Many of the assumptions made in these theoretical derivations are not applicable to the case of adsorption from solution (especially when soil is the adsorbent). For example, the Langmuir (1918) adsorption model was derived for the adsorption of gases onto nonporous solids (such as glass, platinum, and mica), and makes the following assumptions:

1) The energy of adsorption is the same at each site and is independent of surface coverage (i.e., the surface is energetically homogeneous).
2) There are no interactions between adsorbed molecules, and they cannot migrate over the surface.
3) A molecule can only be adsorbed by a vacant site. (In other words, a monomolecular layer represents the maximum amount that can be adsorbed on the solid.)

It is very likely that none of these assumptions are true for the adsorption of solutes by soils. Nevertheless, the Langmuir adsorption isotherm is sometimes used to describe the experimental data for liquid-solid adsorption. (However, a successful fit of experimental data to the Langmuir equation does not imply that its underlying assumptions are valid.)

The Langmuir equation is:

$$C_s = \frac{KC_s^{max}C_\ell}{1 + KC_\ell} \qquad (2\text{-}1)$$

where $C_s$ is the surface concentration of the adsorbate; $C_s^{max}$ is the maximum adsorption possible (complete monolayer coverage); $C_\ell$ is the equilibrium solution concentration of the adsorbate; and K is an equilibrium constant.

Another equation that is much more widely used to describe liquid-solid adsorption data is the Freundlich or exponential, empirical equation which is

$$C_s = KC_\ell^{1/n} \tag{2-2}$$

where $C_s$, $C_\ell$, and K are as previously defined; and 1/n is an exponent which is usually less than or about equal to one (Hamaker and Thompson, 1972). The use of 1/n is an archaic remnant of an attempt to give the Freundlich isotherm physical meaning, and is retained only because its use has become embedded in the literature (Hamaker and Thompson, 1972). Although the Freundlich equation has no established theoretical basis, it is interesting to note that it can be derived through statistical thermodynamics , if one starts with the Langmuir equation, but assumes that the adsorption energy per site decreases exponentially with increasing surface coverage (Adamson, 1982). The major drawbacks of the Freundlich equation are:

1) It does not reduce a "Henry's law" relationship (see next paragraph for explanation) as the system approaches infinite dilution, except for the rare case where n exactly equals one.

2) It predicts that adsorption increases indefinitely with solute concentration, and therefore, could never be applicable to the case of monolayer adsorption (since there are only a finite

number of adsorption sites, which would eventually become saturated).

Therefore, use of the Freundlich equation should be restricted to the region of the isotherm between "Henry's law" regime and the start of site saturation (for the case of monolayer coverage). This restriction very often limits the Freundlich model to representing only a narrow range of the isotherm curve. According to Belfort (1980), many investigators have incorrectly extended this empirical model beyond its valid experimental range.

The simplest possible isotherm equation is the one in which the adsorption density is directly proportional to the equilibrium solution concentration:

$$C_s = KC_\ell \tag{2-3}$$

(where the variables are as previously defined). Equation (2-3) is frequently referred to as Henry's law (for adsorption), since it is analogous to Henry's law in gas-liquid equilibria (i.e., the solubility of a gas in a liquid is directly proportional to its vapor pressure). All adsorption equations (or models) must reduce to this linear (Henry's law) isotherm as infinite dilution is approached, in order to be valid from a theoretical standpoint. (Note that the Langmuir equation obeys this boundary condition, but the Freundlich one does not, except for the trivial case in which the exponent equals one.) The linear isotherm has been used extensively to model the sorption of nonionic, organic compounds by soils.

Although other isotherm models exist, those described above are the ones principally used in the soil sorption literature. Therefore, the discussion herein has been limited to these models.

### 2. Adsorption Forces and Mechanisms

A variety of mechanisms have been proposed in an attempt to explain adsorption phenomena at the molecular level. The principal ones are:

- van der Waals-London Forces
- Ion-Dipole (Direct and Induced) Interactions
- Hydrophobic Interaction
- Charge Transfer
- Hydrogen Bonding
- Ion Exchange
- Ligand Exchange
- Chemisorption
- Magnetic Bonding

Ion exchange can clearly be ruled out as a possible mechanism for the sorption of the compounds under consideration in this research. Also, magnetic bonding would probably not be applicable since it is only significant in large organic molecules with conjugated double bonds (Hirschfelder, 1965). These two mechanisms, therefore, shall not be discussed below.

#### a. van der Waals-London Forces

The van der Waals-London interaction is actually comprised of three distinct interactions*:

---

*Some texts refer only to interaction (3) as being van der Waals-London. However, this thesis will follow the same categorization as Adamson (1982), and group these interaction potentials together since they all vary inversely with the sixth power of intermolecular distance.

(1) Dipole-Dipole

(2) Dipole-Induced Dipole

(3) Induced Dipole-Induced Dipole

The last interaction is better known as the London or "dispersion"* force, and turns out to be the most significant of the three in condensed systems. It will, therefore, be discussed first.

The London interaction is present between all atoms and molecules in close proximity. The force originates from the oscillating motion of electrons in their orbitals around atoms/molecules, which results in an instantaneous dipole. The instantaneous dipole of one molecule/atom will induce a synchronous dipole in a nearby molecule/atom, and an attractive energy will result. This energy, E(r), between two different atoms is given by the following expression:

$$E(r) = -\frac{3}{2}\frac{\alpha_1\alpha_2}{r^6[(1/h\nu_1) + (1/h\nu_2)]} \qquad (2\text{-}4)$$

where

$\alpha_1, \alpha_2$ = polarizability** of atoms 1 and 2, respectively;

$r$ = distance between the two atoms;

$\nu_1, \nu_2$ = oscillating frequency of the electron-nucleus system for atoms 1 and 2, respectively;

$h$ = Planck's constant.

---

*This term originated from the fact that the quantum-mechanical mechanism which causes the London force, also causes the refraction (or dispersion) of light passing through gas molecules (Maitland, et al., 1981).

**An atom's polarizability is a measure of how "loosely" the nucleus controls its electron distribution under the influence of an applied electric field. Quantitatively, it is the proportionality coefficient, $\alpha$, in the following equation: $\mu_{ind} = \alpha\mathbf{E}$, where $\mu_{ind}$ is the dipole induced by the applied electric field, $\mathbf{E}$.

(The quantities $h\nu_1$ and $h\nu_2$ are approximately equal to the ionization potentials of the respective atoms, and it is these values that are normally used in the above equation.)

The dispersion force usually accounts for the majority of the interaction energy between two neutral molecules (see Table 2.1 below). Two important characteristics of the dispersion interaction are that it is independent of molecular orientation; and it is approximately additive for the case of a collection of molecules. This additivity property results in an interaction potential (energy) which is inversely proportional to the cube of the distance ($E(r) \propto 1/r^3$) between an atom (or molecule) and a particle (e.g., colloid); and inversely proportional to the square of the distance ($E(r) \propto 1/r^2$) between two particles. Therefore, the London force generally predominates over the other van der Waals forces in colloidal systems (For example, the London interaction is the principal attractive force in the aggregation [or coagulation] of colloids in suspension, according to some models.) Another prime example of attractive interaction consisting almost exclusively of dispersion forces is the adsorption of nonpolar molecules by covalent solids (e.g., graphite) (Clark, 1970).

The dipole-dipole attractive interaction results when two polar molecules approach each other. It would seem that the random thermal molecular motions in the gas and liquid phases would yield no net attractive force, since on the average, the two molecules' dipole moments would be non-aligned just as often as they would be aligned (i.e., repulsive forces would cancel out attractive ones). However, because of the tendency of one dipole to align the other into a favorable arrangement, the attractive orientations slightly outweigh the repulsive ones. The average dipole-dipole attractive interaction energy between two molecules is given by the following equation:

$$E(r) = -\frac{\mu_1^2\mu_2^2}{24\pi^2\varepsilon_0^2\varepsilon^2 k_B T r^6} \tag{2-5}$$

where

$\mu_1$, $\mu_2$ = dipole moment of molecules 1 and 2, respectively;

$\varepsilon_0$ = permittivity in a vacuum;

$\varepsilon$ = permittivity of the medium;

$k_B$ = Boltzmann constant;

$T$ = temperature;

$r$ = distance between the two molecules.

Note that this interaction energy is inversely proportional to the sixth power of the separation distance, and inversely proportional to temperature. (This latter dependence reflects the fact that the favorable attractive orientations between two dipoles are disrupted by increased thermal agitation.)

The dipole-induced dipole interaction results when a molecule with a permanent dipole moment is in the vicinity of another molecule (which may itself be polar or nonpolar). The first molecule will induce a dipole in the second, and an attractive force will result, whose average interaction energy is:

$$E(r) = -\frac{2\mu_1^2\alpha_2}{16\pi^2\varepsilon_0\varepsilon r^6} \tag{2-6}$$

where the symbols have the same meaning as given previously.

In order to put the three van der Waals-London interactions in perspective, the following table is presented (from Laidler and Meiser, 1982, p. 756). Note that the dipole-induced dipole energy is generally quite small relative to the total interaction potential; and that the dispersion energy is generally the most significant except for those molecules with unusually high dipole moments (such as ammonia and water molecules). It is also important to realize that the total net van der Waals-London interaction energy would be the sum of the three separate attractive interactions (e.g., -479 J/mol for HCl), plus the repulsive interaction potential,

TABLE 2.1 Attractive Energy Contributions Between Neutral Molecules (After Laidler and Meiser, 1982, p. 756)

| Molecule | Dipole Moment, $\mu$ ($10^{-30}$ C-m) | Polarizability,* $\alpha$ ($10^{-30}$ $m^3$) | E(r) (J/mol) due to the separate interaction potentials:** $\mu$-$\mu$ | $\mu$-$\alpha$ | $\alpha$-$\alpha$ |
|---|---|---|---|---|---|
| He | 0 | 2.5 | 0 | 0 | -4.6 |
| Xe | 0 | 50.3 | 0 | 0 | -850.0 |
| CO | 0.40 | 25.0 | -0.012 | -0.22 | -260.0 |
| HCl | 3.43 | 33.0 | -72.0 | -2.0 | -405.0 |
| $NH_3$ | 5.01 | 27.8 | -324.0 | -39.0 | -360.0 |
| $H_2O$ | 6.14 | 18.6 | -732.0 | -39.0 | -180.0 |

*The polarizability values actually given by Laidler and Meiser are a factor of $(1/4\pi)$ lower than those given here, since these authors used "rationalized" units for electromagnetism. To conform with the literature on dielectrics, "unrationalized" units are used in this thesis (see Hill, et al., 1969, p. 7).

**Calculated at an intermolecular separation, r, of 500 pm (= 5 Å)

generally considered to be inversely proportional to the twelfth power of separating distance. That is, the net interaction energy between two molecules is

$$E(r)_{net} = -\frac{A}{r^6} + \frac{B}{r^{12}} \qquad (2\text{-}7)$$

where A and B are constants. (Note that the repulsion term is negligible except at very small values of r.)

Based on the foregoing, it is expected that the dispersion force will be the predominant van der Waals-London mechanism operating in the sorption of those molecules under consideration in this research. The differential heats of adsorption for the van der Waals-London interactions are generally on the order of 1 to 2 kcal/mol for atoms and small molecules (Hamaker and Thompson, 1972). However, values of 5 to 15 kcal/mol (depending on the polarizability of the adsorbate) were calculated by Kiselev (1969 and 1970) for (gas-phase) adsorption (attributable to dispersion forces) of alcohols, ketones, hydrocarbons, and $CO_2$, onto graphitized carbon black.

### b. Ion-Dipole and Ion-Induced Dipole Forces

The electric field surrounding an ion will cause an attractive force toward a polar molecule with an interaction potential given by:

$$E(r) = -\frac{ze\mu \cos \theta}{4\pi\varepsilon_o \varepsilon r^2} \qquad (2\text{-}8)$$

where

z = ion valence;

e = electron charge;

θ = angle between the dipole moment and an imaginary line connecting the ion with the polar molecule.

(The remaining terms have previously been defined.)

An ion can also induce a dipole moment in a molecule which has no permanent dipole. The energy of this interaction is:

$$E(r) = -\frac{\alpha (ze)^2}{8\pi\varepsilon_0 \varepsilon r^4} \qquad (2\text{-}9)$$

where all the symbols are as previously defined.

Ion-dipole forces probably play an important role in the complexation of neutral, polar, ligand molecules with metal cations associated with the solid surface. It is therefore important in the coordination reactions of water molecules with metal cations. However, it is surmised that the solute molecules under consideration in this research will simply not be able to compete with the highly polar water (solvent) molecules in the ion-dipole interaction. In fact, it seems likely that this force could result in exclusion (or negative adsorption) of the solute, since the solute molecules may be excluded from the "enriched water atmosphere" surrounding an ionic solid or clay-type adsorbent. Nevertheless, this mechanism shall not be ruled out unless further evidence warrants it.

The ion-induced dipole interaction energy is a function of the adsorbate molecule's polarizability, $\alpha$. Since all the compounds selected in this research have polarizabilities higher than that of $H_2O$, their induced attractive force to an ion would be stronger than that for $H_2O$. The question is whether or not this induced ion-dipole force between the ion and the organic compound is stronger than the direct ion-dipole force between $H_2O$ and the ion. The answer is that it depends on the distances between the ion and each of the two species. If one equates Equations (2-8) and

(2-9) above (assuming that $\cos \theta \approx 1$, the ion-induced dipole energy for $H_2O$ is negligible, and that $z = +2$) and solves for r, the solution is $r = (\alpha e/\mu)^{\frac{1}{2}}$. Then, substituting in the appropriate values of $\alpha$ for tetrachloroethylene ($151 \times 10^{-30}$ $m^3$ -- the highest polarizability of any compound used in this research), $\mu$ for $H_2O$ ($6.17 \times 10^{-30}$ C-m), and e ($1.602 \times 10^{-19}$ C), the corresponding value of r is calculated to be $1.98 \times 10^{-9}$ m (or 19.8 Å). That is, at separation distances greater than this value, $H_2O$ is more strongly attracted than tetrachloroethylene ($C_2Cl_4$) to the ion, whereas for distances below this value, $C_2Cl_4$ is more strongly attracted. Therefore, the ion-induced dipole interaction must be considered a possible sorption mechanism in this research, unless it is ruled out from experimental evidence.

### c. Hydrophobic Interaction

As previously mentioned in this chapter, the structure of liquid water is not completely understood, and several theories and models have been proposed over the past 60 years. Excellent reviews of these theories and models of liquid water structure have been presented by Eisenberg and Kauzmann (1969), Gurikov (1969), Martin (1970), and Horne (1969). One of the popular theories is the two-state mixture model, which postulates that liquid water is an equilibrium mixture of two different species: (1) bulky and (2) dense. The bulky species is considered to be an open, "ice-like" cluster of $H_2O$ molecules linked by extensive hydrogen bonds; and the dense species is assumed to be amorphous with very little or no hydrogen bonding.

According to many researchers (Frank and Evans, 1945; Kauzmann, 1959; Birshtein, 1969; Sidorova et al., 1971; Zhukovskii and Sidorova, 1971), the dissolution of a nonpolar molecule in water causes a shift in the structural equilibrium, favoring the formation of the open, "ice-like" arrangement. One explanation for this occurrence is that water molecules cannot form hydrogen bonds with these hydrophobic, low-solubility molecules, but instead, form "clathrate cages" (Frank and Quist, 1961) around them to minimize their interaction with other $H_2O$ molecules. This has the effect of making the water much more highly structured, and hence, the entropy of the solution is reduced. In an effort to regain its lost entropy (and thus, lower its free energy) the water molecules attempt to "squeeze" these hydrophobic molecules out of solution, if the opportunity is available. In qualitative terms, this is the basis of the hydrophobic interaction. The thermodynamic favorability for the adsorption of nonpolar solutes onto certain surfaces can, therefore, be dramatically amplified because of the hydrophobic interaction.

It should be emphasized that the hydrophobic interaction (HI) actually does result in an additional attractive force between two hydrophobic species, over and above the presence of other forces (e.g., van der Waals-London). The free energy of the HI for adsorption in solution has been interpreted by Melander and Horvath (1980) as the free energy above and beyond that which would be measured if the adsorption were occurring in the gas phase alone. That is,

$$\Delta G^o_\ell = \Delta G^o_g + \Delta G^o_{HI} \tag{2-10}$$

where

$\Delta G^o_\ell$ = free energy for adsorption from solution;

$\Delta G^o_g$ = free energy for adsorption from the gas phase;

$\Delta G^o_{HI}$= free energy of the hydrophobic interaction.

However, this interpretation is probably not valid since it does not take into account the free energy associated with the displacement (i.e., desorption) of $H_2O$ molecules from the surface, upon adsorption of the solute.

Several investigators (Nemethy and Scheraga, 1962; Birshtein, 1969; Ben-Naim, 1980) have observed that the strength of the HI increases with increasing temperature, and have attempted to relate this phenomenon to changes in water structure with temperature. For the case of a nonpolar solute whose partitioning between aqueous and organic solvent phases is controlled primarily by the HI, this means that the equilibrium partition (or distribution) coefficient increases with increasing temperature, and furthermore, that the standard enthalpy and entropy for this partitioning process are each positive values. In other words, for those cases where the HI predominates (over other mechanisms), the partitioning of a solute between water and an organic solvent is an endothermic process in which the system entropy increases. This is why the HI is sometimes said to be "driven by entropy".

The HI is expected to play a role in the sorption of (at least) the nonpolar molecules studied in this research.

### d. Charge Transfer

This adsorption mechanism involves the partial exchange of electron density between adsorbate and adsorbent molecules, and the partial overlap of their respective molecular orbitals. (Charge transfer is also sometimes referred to as an electron donor-acceptor complex formation.) According to Hamaker and Thompson (1972), the formation of a charge-transfer complex involves the creation of resonance structures between ionic forms of the donor and acceptor molecules. These authors also state that such complexes may be formed between structures containing $\pi$-bonds or lone pair electrons, and cite the alkenes (in addition to many other classes of organic compounds) as possible electron donors because of their electron-rich $\pi$-cloud.

Since two of the adsorbate compounds investigated in this research (trichloroethylene and tetrachloroethylene) are chlorine-substituted alkenes, this adsorption mechanism would appear to be possible. However, the neutral, chlorinated hydrocarbon compounds investigated herein are relatively non-reactive, and have no tendencies (known to this author) to form ionic structures in aqueous solution. Furthermore, in adsorption onto soils, it is generally the electron-rich aromatic structures of soil humic substances which serve as the electron donor, and not the adsorbate molecules. Indeed, the soil adsorption studies which have postulated the charge-transfer mechanism (see Khan, 1978, p. 143) have all been performed using cationic adsorbate molecules, which would behave as electron acceptors. Therefore, the alkenes (as adsorbates) would not be likely candidates for the charge-transfer complex formation with soils, and this particular mechanism is considered highly unlikely in regards to this research.

### e. Hydrogen Bonding

Hydrogen bonding is actually a very strong dipole-dipole interaction, but because of its special importance and uniqueness, it is considered separately. A hydrogen bond is formed when the hydrogen atom serves as a bridge between two electronegative atoms, one being held by covalent bond and the other by electrostatic forces. Because of hydrogen's extremely small size, the resulting attraction between the species is much greater than for other dipoles.

It probably could be argued that hydrogen bonding might be possible between the C-H or C-Cl bonds of the adsorbate molecules of this research, and the amino or oxygen-containing functional groups in soil organic matter. However, according to Berlow et al. (1982), carbon is not sufficiently electronegative to induce a strong enough partial positive charge on the H atom of a C-H bond for this group to engage in hydrogen bonding. Thus, the only other possibility left for the formation of a hydrogen bond (for the compounds used in this research) is if the Cl atom in the C-Cl bond is sufficiently electronegative to acquire a strong partial negative charge; but it appears that it is not. Numerous chemistry texts (Patterson et al., Berlow et al., Masterson and Slowinski, Sisler et al., Meislich et al., Jones et al., Holum) all indicate that virtually the only atoms which participate (with hydrogen) in hydrogen bonding are the small, electronegative ones: oxygen, nitrogen, and fluorine. Although the chlorine atom is fairly electronegative, it is apparently too large to have a high enough "density" of partial negative charge. Even the HCl molecule (which constitutes a much stronger dipole than the C-Cl bond) is not known to form hydrogen bonds.

Reasoning of a different nature also leads to the same conclusion (that hydrogen bonding would not occur for chlorinated hydrocarbons): If hydrogen bonding is possible for these molecules then this implies that they should easily engage in such bonding with $H_2O$ molecules. However, if this occurred, their aqueous solubilities would be very high, which they are not.

For the above reasons, it is concluded that hydrogen bonding would probably not play a role in the adsorption of the solutes examined in this research.

### f. Ligand Exchange

Ligand exchange would occur in adsorption if the adsorbate molecules were stronger ligands (or chelating agents) than those existing on the adsorbent. For example, it is postulated that S-triazines replace the $H_2O$ ligands bound to transition metals in humic acids, and thereby become adsorbed by the soil (Hamaker and Thompson, 1972).

The adsorbate molecules considered in this research are not known (by this author) to have any ligand or chelating agent characteristics. In any event, it is unlikely that they would be able to compete with the ubiquitous solvent ($H_2O$) molecules as a ligand for metal cations associated with the adsorbent. Therefore, the ligand exchange mechanism is probably not applicable in this research.

### g. Chemisorption

The paramount feature which distinguishes chemisorption from the other adsorption mechanisms is that the adsorbent and adsorbate establish a chemical (usually covalent) bond (Atkins, 1978). It is, therefore, an exothermic process which is normally accompanied by a large heat of adsorption, typically in the range of 30 to 50 kcal/mol, and occasionally much higher (see Adamson, 1982, p. 621). A molecule being chemisorbed may actually undergo chemical reaction because of the high adsorption energies involved, and thereby lose its identity (Atkins, 1978).

Two distinguishing characteristics of chemisorption reported by Hamaker and Thompson (1972) are:

(1) It can take place at extremely low adsorbate concentrations and still produce adsorbent site saturation; and

(2) It can occur at elevated temperatures.

Both are consequences of the high enthalpy of adsorption. The former characteristic gives rise to an isotherm which appears to start at a finite value on the adsorption density axis (the ordinate) rather than passing through the origin. This gives the appearance of significant adsorption near zero adsorbate concentration, with almost an immediate flattening of the isotherm (signifying attainment of Langmuir monolayer coverage) at relatively low adsorbate concentrations.

Chemisorption of the compounds in this study is probably unlikely because of their low reactivity, however, it shall not be ruled out. Evidence in the form of adsorption and desorption isotherm characteristics, and energies and enthalpies of adsorption, should indicate whether or not chemisorption is occurring.

### 3. Thermodynamics of Adsorption from Solution

Adsorption, like all other natural phenomena, is a thermodynamic process which occurs because the system (comprised of water, soil, and an organic solute in this case) is attempting to achieve its lowest possible free energy state, which it attains at equilibrium. Theoretically, adsorption equilibrium is a function only of the temperature, pressure, adsorbent surface area, and the total amounts of the chemical species present in the system. An adsorption isotherm experiment is usually performed by holding all these variables constant except for the mass of adsorbate added to the system. An alternative method is to hold all these variables constant except for the adsorbent surface area (i.e., the amount of adsorbent added), and (sometimes) the mass of adsorbate added.*

The adsorption of a hydrophobic, organic solute from aqueous solution (at infinite dilution) can probably best be represented by the following equilibrium expression**:

$$X + S_V + H_2O = SX + H_2O \tag{2-11}$$

where X is the adsorbate molecule, $S_V$ represents a vacant adsorption site, and SX is the adsorbent-adsorbate complex. The equilibrium constant, K, for reaction (2-11) is given by

$$K = \frac{a_{SX}}{(a_X)(a_{S_V})} \tag{2-12}$$

where the $a_i$'s represent the activities of the subscripted species. A key assumption must be made at this point: At infinite dilution, the activity

---

*It would seem that this alternative method should yield an isotherm identical to the one obtained using the first method; however, O'Connor and Connolly (1980), as well as other investigators, have reported that this may not be the case. They cite evidence which indicates that the concentration of solids used in isotherm experiments affects the resulting partition coefficient (see Section D.3 of this chapter).

**Note that water molecules appear in the reaction, but do not participate in it (i.e., they can be cancelled out). I chose to represent the reaction this way because these organic sorbate molecules (in this research) do not solvate with water (in the usual sense). Furthermore, it is highly unlikely that they would replace water at an adsorption site (see "Adsorption Forces and Mechanisms" Section). Water was entered in this equation simply to show that adsorption is taking place in aqueous solution. (It turns out that the results of the derivation which follows are the same even if one assumes displacement of $H_2O$ during adsorption.)

of the "vacant sites" is analogous to the activity of a pure solid phase, and is, therefore, defined as equal to one.* This results in the following expression for K:

$$K = \frac{\gamma_{sx} C_{sx}}{\gamma_x C_x} \qquad (2\text{-}13)$$

where activity coefficients ($\gamma_i$) and concentrations** ($C_i$) have been introduced. At this point, a second problem is encountered: What is the activity coefficient for adsorbed species? The answer to this question has not been completely reconciled in the literature, and usually further assumptions or definitions are introduced at this point to circumvent this complication. Not to go against this trend, one further assumption shall be made: The activity coefficient for the adsorbent-adsorbate complex is considered constant for all cases of adsorption from dilute solution in this research. Therefore, $\gamma_{sx}$ can simply be incorporated into the value of K, and thus be removed from the expression. Thus, we are left with

$$K_d = \frac{C_{sx}}{C_x} \qquad (2\text{-}14)$$

where $\gamma_x$ has also been removed since it would be $\approx 1$ in dilute solution; and the subscript "d" indicates a distribution coefficient† (which

---

*Although this assumption is only valid at infinite dilution, it is still a good approximation as long as the number of occupied sites is negligible relative to the total number of sites.

**The "concentration" of the adsorbate on the surface, $C_{sx}$, is actually the adsorption density (e.g., μg adsorbate/g adsorbent).

† The sorption equilibrium constant is also sometimes called a partition coefficient, but the word "partition" in this thesis shall be used only in conjunction with ab̲sorption phenomena.

distinguishes it from the previously used K; i.e., $K_d = \gamma_x K/\gamma_{sx}$). Thus, the equilibrium adsorption (or distribution) coefficient, which is a measure of the strength adsorption, is simply the slope of the isotherm at infinite dilution (i.e., in the Henry's law region).

Burchill et al. (1981) relate this distribution coefficient to the standard differential Gibbs energy of adsorption ($\Delta G^o_{ads}$) by

$$\Delta G^o_{ads} = -R_g T \ln K_d \qquad (2\text{-}15)$$

where $R_g$ is the universal gas constant, and T is the temperature. They also point out that the infinite dilution criterion does not have to apply in the case of a linear isotherm.

The standard differential enthalpy of adsorption (also called the isosteric heat of adsorption) can be determined from the van't Hoff expression which relates the differential change in an equilibrium constant with respect to a differential change in temperature:

$$\frac{d \ln K_d}{dT} = \frac{\Delta H^o_{ads}}{R_g T^2} \qquad (2\text{-}16)$$

where $\Delta H^o_{ads}$ is the differential heat of adsorption. If Equation (2-16) is integrated, assuming $\Delta H^o_{ads}$ to be independent of temperature,* then one obtains:

$$\ln \frac{K_{d_2}}{K_{d_1}} = \frac{\Delta H^o_{ads}}{R_g} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (2\text{-}17)$$

---

*This is probably a safe assumption over the small temperature ranges reported in the literature and used in this research.

where $\Delta H^o_{ads}$ can be calculated by determining the distribution coefficients for two isotherms, one at temperature $T_1$, the other at $T_2$. An alternative form of the integrated van't Hoff expression is:

$$\ln K_d = -\frac{\Delta H^o_{ads}}{R_g T} + \text{constant}. \qquad (2\text{-}18)$$

In this form, it is apparent that a plot of $\ln K_d$ versus $1/T$ should yield a straight line whose slope is $-\Delta H^o_{ads}/R_g$. Equation (2-18) would be the preferred equation for solving for $\Delta H^o_{ads}$ if more than two isotherm distribution coefficients are measured. Again, both Equations (2-17) and (2-18) assume that $\Delta H^o_{ads}$ is independent of T, and the only thermodynamic variable that changes (among isotherms) is T.

Once $\Delta G^o_{ads}$ and $\Delta H^o_{ads}$ have been determined, it is a simple matter of using the relation:

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \qquad (2\text{-}19)$$

to find the differential entropy of adsorption, $\Delta S^o_{ads}$. A knowledge of the free energies, enthalpies, and entropies of adsorption can provide clues to the type(s) of adsorption mechanism(s) and force(s) involved.

## C. Absorption (Liquid-Liquid Extraction) Theory and Fundamentals Relevant to This Research

Some investigators in this field have postulated that the sorption of nonionic organic compounds by soils can best be explained and modeled as a solvent (i.e., liquid-liquid) extraction process (see Chiou et al., 1979, 1983, and 1984), wherein the organic solute partitions itself between the "liquid" or polymeric soil organic matter phase, and the aqueous phase. Since this hypothesis has neither been adequately proven nor disproven at this point, it was deemed necessary to include a brief discussion of the fundamentals of solvent extraction chemistry, emphasizing those aspects which might be relevant to sorption by soils.

The adsorption forces and mechanisms discussed in Section B.2. of this chapter are also applicable to extraction (absorption).* The primary difference is that in liquid-liquid extraction, intermolecular forces are exerted among the solute and the two bulk solvent phases (e.g., aqueous and organic), whereas in liquid-solid adsorption the forces are among the solute (adsorbate) molecules, the liquid (aqueous) phase, and a solid surface.

The distribution of a species between two solvents (one aqueous and one organic) is generally expressed as a distribution (or partition) coefficient, $K_p$, given by

$$K_p = \frac{a_{org}}{a_{aq}} \tag{2-20}$$

or, in sufficiently dilute solution where the activity coefficients (for the solute in <u>each</u> phase) are unity, then

$$K_p = \frac{C_{org}}{C_{aq}} \tag{2-21}$$

where the subscripts "org" and "aq" denote the organic and aqueous phase

---

*The terms "absorption", "extraction", and "partitioning" are used interchangeably in this thesis.

respectively; and "a" and "C" are the activities and concentrations, respectively, for the solute in each phase.

This partition coefficient is obviously related to the solute's mutual solubility in each of these solvents. In fact, if the mutual solubility of the two solvents is negligible (i.e., the solvents are completely immiscible), and the solute solubilities in each of the organic and aqueous phases are low enough such that activity corrections are negligible over the range from infinite dilution to saturation, then the partition coefficient, $K_p$, is theoretically equal to the ratio of these solute solubilities. Therefore, because of the close connection between solute partitioning and the concept of solubility, the theoretical attempts to explain solvent extraction behavior have generally been based on solubility theory.

The most successful of these solubility theories is the "Regular Solution Theory", which attempts to explain/predict the solubility of substances from the fundamental viewpoint of molecular forces. Although the application of regular solution theory to solvent extraction is somewhat limited, it has been applied to various solution systems with moderate success (Sekine and Hasegawa, 1977). In "regular" solutions, certain intermolecular forces such as chemical interaction, association, and strong dipole-dipole interactions are considered negligible. Because of this assumption, the regular solution theory is not suitable to aqueous solutions due to the highly polar water molecule (Sekine and Hasegawa, 1977). Indeed, Horvath (1982) pointed out that the theory does not give a satisfactory treatment for the solubility of halogenated hydrocarbons in water (and it therefore would not be useful in connection with this research). Nevertheless, certain equations based on regular solution theory have been proposed for aqueous systems. An example of such an equation is (Sekine and Hasegawa, 1977):

$$\log K_p = \frac{\overline{V}_x}{2.3\ RT}\left[(\delta_{aq} + \delta_{org} - 2\delta_x)(\delta_{aq} - \delta_{org}) + RT\left(\frac{1}{\overline{V}_{org}} - \frac{1}{\overline{V}_{aq}}\right)\right] \qquad (2\text{-}22)$$

where the "x" subscript denotes the solute; $\overline{V}_\ell$ is the molar volume ($cm^3$/mol) of species *i* at the system conditions, and $\delta_i$ is the solubility parameter ($[cal/cm^3]^{\frac{1}{2}}$) for species *i* given by:

$$\delta_i = \left(\frac{\Delta\overline{E}_{vap}}{\overline{V}_i}\right)^{\frac{1}{2}} \qquad (2\text{-}23)$$

where $\Delta\overline{E}_{vap}$ is the molar heat of vaporization. It is not known whether Equation (2-22) has been successful in predicting $K_p$ values in aqueous-organic solvent extraction systems; but nonetheless, it would be difficult to apply to aqueous soil systems since the values for $\delta_{org}$ and $\overline{V}_{org}$ would not be known for the soil organic matter phase.

The equilibrium reaction for the partitioning of a solute, X, between two phases can be represented as:

$$X_{aq} \rightleftharpoons X_{org} \qquad (2\text{-}24)$$

At equilibrium, the chemical potentials* of the solute in both phases are equal:

---

*The symbol $\overline{G}$ (partial molar free energy) is used to denote chemical potential since the symbol "$\mu$" in this thesis is used for dipole moment.

$$\overline{G}_{aq} = \overline{G}_{org}$$

then

$$\overline{G}^{o}_{aq} + RT \ln a_{aq} = \overline{G}^{o}_{org} + RT \ln a_{org}$$

or

$$RT \ln C_{org} + RT \ln \gamma_{org} - RT \ln C_{aq} - RT \ln \gamma_{aq} = \overline{G}^{o}_{aq} - \overline{G}^{o}_{org} \quad .$$

Solving for $C_{org}/C_{aq}$ which is equal to the partition coefficient, $K_p$, the result is:

$$K_p = \frac{C_{org}}{C_{aq}} = \frac{\gamma_{aq}}{\gamma_{org}} \exp[(\overline{G}^{o}_{aq} - \overline{G}^{o}_{org})/RT] \quad . \tag{2-25}$$

Since the exponential term in Equation (2-25) is constant at a given temperature, the distribution coefficient, $K_p$, is simply a function of the ratio of solute activity coefficients in each phase, $\gamma_{aq}/\gamma_{org}$. Thus, if $\gamma_{aq}/\gamma_{org}$ is relatively constant (i.e., independent of solute concentrations) then the partition coefficient will also be relatively constant. The constancy of $K_p$ values over a wide range of solute concentrations (in either phase) is, in fact, frequently observed (McCabe and Smith, 1976; Sekine and Hasegawa, 1977), which indicates that the ratio of activity coefficients does indeed remain relatively constant.

For solute partitioning in octanol-water systems, Chiou and Schmedding (1982) derived the following expression:

$$K_{ow} = \frac{1}{S\ \overline{V}^{*}_{o}\gamma^{*}_{o}} \ \frac{\gamma^{*}_{w}}{\gamma_{w}} \tag{2-26}$$

or

$$\log K_{ow} = -\log S - \log \overline{V}^*_o - \log \gamma^*_o + \log(\gamma^*_w/\gamma_w) \qquad (2\text{-}27)$$

where

$K_{ow}$ = octanol-water partition coefficient

$S$ = molar solubility of solute in water (mol/l)

$\overline{V}^*_o$ = molar volume of the organic (octanol)-rich phase (i.e., corrected for the octanol-water mutual saturation) at the system conditions (l/mol)

$\gamma^*_o$ and $\gamma^*_w$ = solute activity coefficients in the water-saturated octanol phase, and octanol-saturated water phase, respectively.

$\gamma_w$ = solute activity coefficient in pure water.

Chiou et al. (1983) then used the "Flory-Huggins theory" (Flory and Huggins have each authored numerous references on polymer chemistry) to define the activity of a solute in a polymer:

$$\ln a_x = \ln \phi + \phi_p \left(1 - \frac{\overline{V}_x}{\overline{V}_p}\right) + \chi \phi_p^2 \qquad (2\text{-}28)$$

where $a_x$ is the solute activity in the polymer, $\phi$ is the volume fraction of solute, $\phi_p$ is the volume fraction of polymer, $\overline{V}_x$ is the solute molar volume, $\overline{V}_p$ is the average molar volume of polymeric substances, and $\chi$ is the Flory-Huggins interaction parameter.* Chiou et al. asserted that

---

*Chiou et al. (1983) did not explain this "Flory-Huggins interaction parameter" in their paper. Flory (1953) described it as a dimensionless quantity which characterizes the interaction energy per solute molecule. The quantity $k_B T \chi$ represents the difference in energy of a solute molecule immersed in the pure polymer, compared with one surrounded by molecules of its own kind (i.e., in the pure solute).

the properties of $a_x$, $\phi$, $\phi_p$, $\overline{V}_p$, and $\chi$, are those corrected for the effect of sorbed water. (For example, $\phi_p$ is the volume fraction of soil organic matter [SOM] and sorbed water, and $\overline{V}_p$ is the average molar volume of water-saturated SOM.) The authors then make the following assumptions: the solute concentration is dilute in each of the solvent phases; $\overline{V}_p$ corresponds to $\overline{V}_o^*$ of Equation (2-27); $\phi_p \approx 1$; $\gamma_w^*/\gamma_w \approx 1$; and $\overline{V}_x/\overline{V}_p << 1$. Upon making the appropriate substitutions into Equation (2-27), the following final result was obtained by the authors:

$$\log K_{om} = -\log S\overline{V}_x - \log \rho - (1 + \chi)/2.303 \qquad (2\text{-}29)$$

where $K_{om}$ is the solute partition coefficient between the SOM and aqueous phases, and $\rho$ is the SOM density. Thus a plot of log $K_{om}$ versus log $S\overline{V}_x$ should be linear for a given soil (i.e., $\rho$ is constant), assuming that $\chi$ remains constant. (The authors also stated that since the variability of $\overline{V}_x$ is small compared to that of S, plots of log $K_{om}$ versus log S should also be linear.)*

The thermodynamic properties of solvent extraction ($\Delta G^o_{ex}$, $\Delta H^o_{ex}$, and $\Delta S^o_{ex}$) are defined analogously to those for adsorption. That is,

$$\Delta G^o_{ex} = -R_g T \ln K_p \quad ,$$

---

*The authors used their experimental findings that log $K_{om}$ versus log S (or log $S\overline{V}_x$) yielded a highly linear relationship as direct support for a partitioning phenomenon. However, the same type of relationship has also been observed in cases where adsorption is known to be occurring.

$$\frac{\partial \ln K_p}{\partial T} = \frac{\Delta H^o_{ex}}{RT^2} \quad , \qquad \text{and}$$

$$\Delta S^o_{ex} = \frac{\Delta H^o_{ex} - \Delta G^o_{ex}}{T} \quad ,$$

where the equilibrium partitioning coefficient, $K_p$, is defined the same way as $K_d$ for a soil-water-solute system. Since the thermodynamic variables are determined identically for both adsorption and extraction phenomena (for the system of interest), the "ads" and "ex" subscripts are henceforth dropped, and it shall be understood that $\Delta G^o$, $\Delta H^o$, and $\Delta S^o$ refer to the free energy, enthalpy, and entropy of sorption, respectively. However, the subscript "d" in $K_d$ shall be retained as a sorption distribution coefficient, which can be applied to both adsorption and extraction phenomena.

## D. Factors Influencing the Sorption of Nonionic, Organic Solutes in Soil Solution

From the previous discussion of thermodynamics, it is clear that the solute concentration, temperature, adsorbent surface area (or sorbent mass), and pressure can all affect the quantity of solute sorbed. (The effect of pressure variations at the earth's surface on sorption from solution is considered negligible, and this parameter is always assumed to be constant at $\approx$ 1 atmosphere in such experiments. Therefore, the influence of pressure shall not be discussed below.) However, in addition to these variables, there are other characteristics and/or properties of the sorbent, sorbate, and solution which can influence (or have been significantly correlated with) the strength of sorption. All of these variables, characteristics, and properties are discussed below. Also, a discussion of reversibility and desorption is presented in Section 4 (below) since this is deemed pertinent to this research.

### 1. Sorbent (Soil) Characteristics

The soil components which account for virtually all sorption phenomena in soils are the clays, hydrous metal oxides, and organic matter. The most important of these components in "controlling" the sorption of nonionic, organic compounds is the soil organic matter (Bailey and White, 1964; Lambert, 1967; Osgerby, 1970; Pierce *et al.*, 1974; Karickhoff *et al.*, 1979; Chiou *et al.*, 1979; Peck *et al.*, 1980; Sharom *et al.*, 1980; Means *et al.*, 1980; Brown and Flagg, 1981; Schwarzenbach and Westall, 1981; Chou *et al.*, 1981; Stevenson, 1982; Means and Wijayaratne, 1982; Weber *et al.*, 1983). In fact, many studies have found that the soil organic matter content is essentially the *only* soil property which affects the sorption of these types of compounds. That is, other soil characteristics such as clay type and content,* surface area, and the cation exchange capacity (CEC) are generally considered to have negligible influence on sorption.** (However, two papers pertaining to the sorption of PCB's by various sorbents [Hiraizumi *et al.*, 1979; Horzempa and Di Toro, 1983] reported strong correlation between sorption and surface area, as well as to organic carbon contents.)

---

*It should be noted that these soil characteristics would certainly influence the sorption of *ionic* solutes.

**Since many soil properties are correlated to each other (e.g., soils high in organic matter content are typically high in CEC) a high correlation between sorption and a particular property may be obtained. However, this does not always mean that this property is influencing sorption.

So many studies have established strong correlation between sorption and soil organic matter content, that the sorption distribution coefficient reported in the literature is usually normalized to the fraction of organic carbon ($f_{oc}$) present in the soil, as indicated in the following equation:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad (2\text{-}30)$$

where $K_{oc}$ is the normalized distribution coefficient. An excellent summary of $K_{oc}$ values reported for numerous pesticides in soils is presented by Hamaker and Thompson (1972, see pp 68-90). Examination of their table reveals that $K_{oc}$ values for any particular chemical are generally not precise constants. (For example, three values of $K_{oc}$ reported for the sorption of silvex by three different soils are: 440, 2786, and 4682.) One possible reason for this variability in $K_{oc}$ values (for a particular chemical) is the variation in organic matter composition among soils. That is, two soils with identical percentages of organic carbon, may have drastically different percentages of humic substances, polysaccharides, proteins, and lipids. If these separate fractions of soil organic matter sorb with different intensities, then this could be a plausible explanation for the high variability of $K_{oc}$ values. Another possible explanation (which would be likely for adsorption phenomena) is the variability of specific surface area among soils.

### 2. Sorbate Properties

The two most popular sorbate properties used in sorption correlation studies have been aqueous solubilities and octanol-water partition coefficients. The general rule for the inverse correlation between sorption and a compound's solubility was first expounded in 1920 by Lundelius. The rule serves as a useful guide, but numerous exceptions have been reported. For example, Harris and Warren (1964) concluded that no general relationship exists between sorption and solubility for the widely differing herbicides which they examined; Weber (1966 and 1970) found that the solubility differences of S-triazines were not reflected in their sorption differences; and Hance (1965 and 1967) found no relationship between the sorption of substituted ureas and their solubilities. The use of a compound's octanol-water partition coefficient ($K_{ow}$) as a correlating parameter probably originated with the works of Lambert (1967) and Hance (1967). These investigators suggested that the sorption of a neutral organic compound to soil was analogous to the liquid-liquid partitioning of a solute between water and an immiscible organic solvent. The use of $K_{ow}$ as a predictor of the $K_{oc}$ value for a given compound has since become widespread, and numerous investigators have reported regression equations relating these two variables (Briggs, 1973; Karickhoff <u>et al</u>., 1979; Means <u>et al</u>., 1980 and 1982; Brown and Flagg, 1981; Schwarzenbach and Westall, 1981).

Other correlating parameters which are used less often are the sorbate's bioconcentration factor and parachor. A compound's parachor, P, is a function of molecular structure and, for liquids, is defined as

$$P = \frac{M\sigma^{\frac{1}{4}}}{\rho_{\ell} - \rho_{v}}$$

where M is the molecular weight, $\sigma$ is the surface tension, $\rho_{\ell}$ the liquid density, and $\rho_{v}$ the vapor density. Since $\rho_{\ell} >> \rho_{v}$, the equation reduces to

$$P = \frac{M\sigma^{\frac{1}{2}}}{\rho_{\ell}} = \overline{V}\sigma^{\frac{1}{4}}$$

where $\overline{V}$ is the molar volume.

Regression equations developed between sorption and the above sorbate properties normally take the form

$$\log K_{oc} = A \log Y + B$$

where A and B are regression coefficients, and Y is the particular sorbate property (i.e., solubility, $K_{ow}$, or bioconcentration factor). (The exception is parachor which is regressed directly with log $K_{oc}$.) It is interesting to note that values of $K_{oc}$ estimated from these regression equations can vary by as much as two orders of magnitude (i.e., 100-fold) for any particular sorbate chemical.

It should be emphasized that these correlations were developed primarily for pesticides (insecticides, herbicides, and fungicides) and, to a lesser extent, aromatic and polynuclear aromatic hydrocarbons. Many of these compounds have high molecular weights, extensive molecular branching, and the presence of a variety of functional groups. Therefore, their sorption characteristics may be quite different from the compounds chosen for study in this research. Furthermore, it appears that virtually no research studies attempt to correlate sorption to more fundamental sorbate properties such as polarizability, dipole moment, and molecular weight and size. (Credit should be given to the fundamental nature of parachor, however, since it is related to molecular volume and surface tension.)

### 3. Solution Properties

Properties of the solution which may affect the sorption of compounds (ionic and nonionic) in soils are: temperature, pH, ionic strength (or salt concentration), sorbate concentration, solids concentration (water content), and the presence of other sorbates. These are each discussed below.

Most references state that since adsorption is an exothermic reaction, it should decrease with increasing temperature. However, only adsorption from the gas phase is strictly exothermic according to the following logic (McBride, 1982): Since adsorption from the gas phase always results in a reduction in entropy for the system, $\Delta S_{ads}$ is always negative. But the Gibb's free energy of adsorption, $\Delta G_{ads}$ (given by $\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$), must also be negative in order for the reaction to occur spontaneously. Therefore, the adsorption enthalpy, $\Delta H_{ads}$, must be negative, and also $|\Delta H_{ads}| > |T\ \Delta S|$ in order to make $\Delta G_{ads} < 0$. (Hence, the reaction is exothermic since $\Delta H_{ads} < 0$; i.e., heat is given off when gas molecules are adsorbed at an interface.) However, sorption from solution is a different matter, since the presence of a third component -- the solvent, must be reckoned with. As mentioned previously in the section on the hydrophobic interaction, the sorption of certain compounds may, in fact, be enhanced by an <u>increase</u> in system entropy during the sorption process. Therefore, the sorption enthalpies in these cases may be either negative or positive. That is, in sorption from solution, the reaction may be endothermic and still occur spontaneously. Nevertheless, the majority of studies on the sorption of organic compounds in soil solution do indicate that sorption decreases with increasing temperature. Some of the exceptions to this trend are: (1) Yaron and Saltzman (1972) found that the equilibrium sorption of parathion in soil solution was not appreciably influenced by temperature; (2) Francis (1972) found that increasing temperatures resulted in increased sorption equilibrium of polyvinylpyrrolidone by several clays; (3) Pierce et al. (1974) reported an endothermic reaction for the sorption of DDT by humic acid in sea water*; and (4) Horzempa and Di Toro (1983) also obtained an endothermic enthalpy of sorption for hexachlorobiphenyl (a PCB) by sediment (i.e., sorption of the PCB increased with increasing temperature). Therefore, the effect of temperature on sorption is not always predictable, and should be verified experimentally.

The pH of the soil solution has a strong influence on sorption for ionizing sorbate species, especially weak acids and weak bases which can undergo ionization in the mid-pH ranges characteristic of soil environments. Therefore, depending upon the pH (and the compound's $pK_a$ or $pK_b$ value) these sorbates (weak acids and weak bases) may exist as an ion or a neutral molecule which would markedly affect their sorption. However, in the case of nonionic sorbate molecules, the literature indicates that pH has virtually no effect unless some pertinent soil change is produced thereby (Hamaker and Thompson, 1972; Lyman, 1982). Since all the sorbate compounds investigated in this research are neutral, no significant pH effects are expected. However, since pH would affect the properties of

---

*Pierce et al. did not use the normal sign convention for $\Delta H$ values (i.e., negative $\Delta H$ denoting an exothermic reaction) and the signs on the $\Delta H$ values reported in Table 4, p. 1068 of this reference should all be reversed.

certain soil organic matter components (e.g., humic polymers), the effect of pH on sorption shall be experimentally assessed.

The solution ionic strength can affect sorption via three possible mechanisms:

(1) Sorbed organic ions can be displaced by the inorganic (salt) ions in an ion exchange reaction.

(2) The activity of the sorbate in solution is altered.

(3) Sorbent structure/characteristics are altered.

Mechanism (1) above would mainly affect the sorption cationic sorbates, since virtually all sorbent soil particles are negatively charged in solution. Mechanism (2) would result in reduced sorption of ions, but enhanced sorption of neutral molecules, with increasing ionic strength. (This is because the activity of ions decreases, but the activity of neutral molecules increases, with ionic strength.) Nevertheless, the sorbate activity effect on the sorption of neutral, organic molecules should be minor since their activity is not significantly altered within the range of ionic strengths (<0.1 M) typically encountered in soil solutions*. Mechanism (3) may or may not affect the sorption of these types of molecules by soils.

Sorbate concentration always influences the amount sorbed (otherwise isotherms would merely be horizontal lines). As the sorbate concentration increases, of course, the amount sorbed increases (but there is not necessarily a linear correspondence), until the sorbent becomes "saturated" with the sorbate. Beyond this point, increasing sorbate concentration will

---

*For example, Gossett and Lincoff (1981) determined an activity coefficient equal to about 1.05 for trichloroethylene in a 0.1 M aqueous KCl solution.

not further increase the quantity sorbed, and the isotherm should become flat. However, it appears that this saturation point is rarely attained in the sorption of neutral, organic molecules by soils. Two possible explanations for this lack of sorbent saturation are: (1) the sorption phenomenon is one of solute partitioning between water and the organic matter "solvent" in the soil, wherein the solute is completely miscible with the soil organic matter "solvent"; or (2) the aqueous solubilities of these types of compounds are too low to approach site saturation on the sorbent (for the case of adsorption).

As the solids concentration or water content of a soil suspension is altered, the amount of solute sorbed and its equilibrium solution concentration will, in general, change. However, the distribution coefficient, $K_d$, should theoretically remain the same. The literature on this topic offers conflicting results, with the bulk of the data indicating that $K_d$ increases as the solids concentration decreases (Grover and Hance, 1970; Cox, 1970; O'Connor and Connolly, 1980 - [this reference contains an excellent review of the phenomenon and cites several other references as well]; Voice et al., 1983; Di Toro et al., 1984; Gschwend and Wu, 1984). On the other hand, Nearpass (1967), Green and Obien (1969), and Garbarini and Lion*(1984) obtained no significant differences in $K_d$ values as a function of solids concentration. O'Connor and Connolly were unable to explain why increasing solids concentration yielded lower $K_d$ values, but Grover and Hance suggested that the degree of soil colloid dispersion is greater in the more dilute suspensions, and hence, more surface area is

---

*Garbarini and Lion measured equilibrium solute concentration via the compound's gas-phase concentration, employing Henry's law. Therefore, the method may have "avoided the cause" of the frequently-observed "solids effect" on $K_d$.

available for sorption. An alternative explanation (Gossett, 1984) is that sorption equilibrium is approached faster in the dilute system than in the concentrated system, resulting in a higher "apparent" $K_d$ value (i.e., the samples containing the higher solids concentration are farther from equilibrium at the time all samples are analyzed, and thus yield a lower measured $K_d$ value). Voice et al. (1983) and Gschwend and Wu (1984) concluded that the "solids effect" (on the partition coefficient) results from the presence of sorbent "microparticles" and/or "macromolecules" which are not removed from the suspension during separation procedures. Since the supernatant of the reaction vessel containing the higher solids concentration would contain a higher concentration of these sorbent microparticles and macromolecules, the experimenter would measure a higher "apparent" solute concentration for this reaction vessel; and since the amount sorbed is calculated by difference in solute concentration, the net effect would be to measure a lower "apparent" $K_d$ value for the reaction vessel containing the higher solids concentration. On the other hand, Di Toro et al. (1984) performed several experiments which seem to refute the above conclusion of Voice et al. Di Toro et al. proposed a "particle interaction induced desorption" model to account for the "solids effect". This model assumes that a binary interaction between particles causes desorption to occur, but the authors are unable to fully explain the mechanism for this proposed reaction. Therefore, assuming that there is a solids concentration effect on $K_d$, there is much controversy in the literature on the specific cause of this effect.

The presence of a mixture of solutes in a sorption system may mutually enhance sorption, may act independently, or may compete with one another for sorption (Weber, 1972). However, this aspect of sorption will not be investigated in this research, and is therefore not further discussed.

### 4. Desorption and Reversibility

Very few desorption studies have been performed, but those that have generally indicate that the desorption process is slower to reach equilibrium than sorption (Hance, 1967; Williams, 1968). Also, it is frequently observed that a portion of the sorbed compound is very difficult to remove (Talbert and Fletchall, 1965; Yaron et al., 1967; Williams, 1968; Peck et al., 1980; Rogers et al., 1980; Horzempa and Di Toro, 1983). Other investigators have found that if sorption equilibration times are relatively short, and are immediately followed by the desorption experiment, that the process is essentially reversible (i.e., sorption and desorption isotherms are coincident) (McGlamery and Slife, 1966; Graham-Bryce, 1967); but that if the soil is dried and rewet after the sorption phase, or if sorption equilibration times are long, then the two isotherms are nonsingular, and the sorbed chemical much more difficult to extract (Hilton and Yuen, 1963; Hamaker et al., 1966; Graham-Bryce, 1967; Saha et al., 1969). Based on the above results, it appears that the sorption of some compounds in soils may be partially irreversible, resulting in hysteresis for the two isotherms (sorption and desorption). Rao and Davidson (1980) have critically reviewed the findings on reversibility and desorption, and have concluded that, while hysteresis in sorption isotherms is often an artifact of the experimental methods used, it can be real and significant for some compounds.

## E. Previous Research on the Sorption of Volatile Chlorinated Hydrocarbons (One and Two-Carbon Chlorinated Aliphatics) by Soils

Our present knowledge of the sorption interactions of these types of compounds with soils or soil components is indeed limited. An extensive, computer-assisted literature search turned up only six papers dealing with this topic. The relevant aspects of these studies are discussed below (in chronological order of publication date).

1) Chiou et al. (1979) found linear sorption isotherms for 1,2-dichloroethane; 1,1,1-trichloroethane, and tetrachloroethylene (and four other halogenated hydrocarbons) in water with a Willamette silt loam. They hypothesized that the uptake of neutral organic chemicals by soil organic matter is essentially a process of solute partitioning rather than physical adsorption. This hypothesis was based on their findings that:

(a) The isotherms for the seven organic compounds tested showed no indication of curvature even at concentrations approaching (aqueous) saturation, and

(b) The extensive data from the literature (and their own work) indicated that sorption distribution coefficients (normalized to fraction organic matter in soil) were highly correlated (inversely) with solubilities and (directly) with octanol-water partition coefficients.

The main criticisms of Chiou's work are:

(a) they did not demonstrate that their isotherms extended into the high surface coverage regime (if one assumes the adsorption concept applies). In fact, a rough calculation (see Appendix A) indicates that fractional surface coverage was less than five percent in all cases. At low surface coverages such as this, adsorption equilibria obey Henry's law, and linear isotherms should always be obtained.

(b) A strong inverse correlation between sorption distribution coefficients and compound solubility does not constitute evidence in favor of a partitioning or absorption phenomenon. In fact, this very same correlation between a_d_sorption and solubility was first expounded by Lundelius in 1920.

(c) The article contains no explanations of materials and methods used to measure the sorption isotherms.

Based on criticisms (a) and (b) above, the partitioning (a_b_sorption) hypothesis proposed by Chiou _et al_. does not seem to be justified.*

2) Rogers and McFarlane (1981) investigated the sorption of carbon tetrachloride (CT) and trichloroethylene (TCE) (and ethylene dibromide) with soil and clay. They found no apparent sorption of either TCE or CT onto a $Ca^{+2}$-saturated montmorillonite, but reported surprisingly high sorption of TCE onto an $Al^{+3}$-saturated montmorillonite (17% of the available TCE sorbed). Sorption of these compounds by all soils and clays tested was

---

*In all fairness, however, it should be pointed out that Chiou _et al_. have published other works (two of these are discussed in Section II. C.) which argue for the partitioning phenomenon. (The reader is also referred to MacIntyre and Smith versus Chiou _et al_. [1984] for an excellent "debate" of the adsorption-absorption issue.) The best support for the a_b_sorption side is probably the recent paper (in press at this time) by Chiou _et al_. (1984), in which they showed that the sorption of parathion and lindane in aqueous soil suspensions is noncompetitive and yields highly linear isotherms (characteristic of a_b_sorption phenomena); whereas the sorption of these compounds with dehydrated and partially dehydrated soils in _nonaqueous_ suspensions is competitive and results in highly curved, "Langmuir-type" isotherms (characteristic of a_d_sorption phenomena).

six percent or less, except for the case of TCE onto $Al^{+3}$-saturated montmorillonite. The authors were unable to explain this anomaly. Another anomalous finding reported by Rogers and McFarlane was that the normalized sorption constant ($K_{oc}$) for CT obtained experimentally was quite different from the values obtained using several predictive relationships which correlate $K_{oc}$ with the compound's aqueous solubility (S) or octanol-water partition coefficient ($K_{ow}$). It therefore appears that it is more than just the S or $K_{ow}$ for these compounds that controls their sorption behavior.

Some of the problems with the Rogers and McFarlane study are:

(a) An equilibration period ($t_{eq}$) of only 16 hours was selected, even though additional sorption was still occurring beyond this time. (The authors stated that the values of the Freundlich equilibrium coefficients at $t_{eq}$ = 144 h were always within two-times their values at $t_{eq}$ = 16 h, and therefore, 16 hours was chosen for convenience as the equilibrium time period.) Thus, the Freundlich constants reported in the paper cannot be regarded as true equilibrium values. Furthermore, since many of the Freundlich constants determined are within a factor of two-times of each other, it is not clear whether valid comparisons of sorption characteristics can be made. (Perhaps the increased sorption was always by the same fractional amount in all cases, in which case the comparisons would be valid. However, the authors did not state that this was the case.)

(b) The experiments were conducted at a temperature of 25°C, but centrifugation of the reaction vials was done at 5°C. It is not clear why this was done, especially since the settling velocity of suspended particles decreases with decreasing temperature. It is possible that this refrigerated centrifugation affected the accuracy of the resulting isotherms which are supposed to be for T = 25°C.

3) Wilson _et al_. (1981) measured retardation factors* for chloroform, 1,2-dichloroethane, tetrachloroethylene, 1,1,2-trichloroethane, and trichloroethylene (as well as several other halogenated hydrocarbons) in a sandy soil (0.087% organic carbon). For all the compounds named above, they found retardation factors <1.5, except for TCE and tetrachloroethylene whose R.F. values were 1.6 and 2.5, respectively. They concluded that most of the compounds examined in their study would be readily transported through soil (because of their very low retardation factors), and hence, wind up in the groundwater.

The major deficiency in the work of Wilson _et al_. is that they limited their transport/sorption study to a single sorbent: a sandy soil with a very low organic carbon content. Since most of the literature on the sorption of nonionic compounds by soils indicates that it is primarily the organic matter fraction which is responsible for sorption, it is not surprising that the retardation factors (and hence, the sorption coefficients)

---

*The retardation factor of a solute with respect to water is:

$$R.F. = 1 + (\rho_B/\theta_w)K = \upsilon_w/\upsilon_s$$

where:

R.F. = retardation factor
$\rho_B$ = bulk density of soil (g/cm$^3$)
$\theta_w$ = volumetric water content (ml/cm$^3$)
K = sorption equilibrium distribution coefficient (ml/g)
$\upsilon_w$ = interstitial pore water velocity
$\upsilon_s$ = apparent velocity of solute through soil.

determined by these researchers were so low. Furthermore, it is not known whether the sorption which occurred was associated with the sand or the traces of organic matter present.

4) Schwarzenbach and Westall (1981) determined sorption partition coefficients for tetrachloroethylene (and 12 other nonpolar organic chemicals) with a variety of sorbents. They found that:

(a) The sorption isotherms for these nonpolar compounds were linear and reversible at low concentrations ("typically encountered in natural waters").

(b) The sorption partition coefficients were highly correlated with the organic carbon (O.C.) contents of the sorbents (for those sorbents with O.C. content exceeding 0.1%).

(c) Sorbents with very low organic matter contents had small partition coefficients even though their specific surface areas were high.

(d) The logarithms of the partition coefficients of the different compounds and the logarithms of the corresponding octanol/water partition coefficients ($K_{ow}$) had a highly significant linear correlation (for all nonporous sorbents).

(e) For sorbents with O.C. contents greater than 0.1% the partition coefficients can be estimated for many nonpolar organic compounds from their $K_{ow}$'s and the O.C. content of the sorbent. (Predictions within a factor of 2 were possible.)

The main criticisms of this work are:

(a) No sorption isotherms were depicted in the publication.

(b) Isotherm linearity was only substantial at very low solute concentrations (i.e., Henry's law region) using sand as the sorbent.

(c) Their conclusion regarding isotherm reversibility is questionable, and it is not clear from their paper how they came to this conclusion. The authors' only comment about reversibility/desorption was: ". . . the column experiments did indicate that sorption-desorption hysteresis is not too significant for the solutes and sorbents investigated." However, the only sorbent used in the column experiments was sand. Since previous studies on isotherm hysteresis in soil solution implicate the soil organic matter (as the cause of isotherm hysteresis), the authors' selection of sand for these experiments would appear to be inappropriate.

(d) Equilibration time for batch sorption experiments was only about 18 hours, even though no kinetics experiment revealed that equilibrium was achieved by this time.

(e) Sorbent solids in the test tubes were gravity-settled (instead of centrifuged). Thus, it is not clear how the fine fractions of each sorbent were removed from the aqueous phase prior to removing a supernatant sample for analysis.

(f) The coefficients of variation for the measured partition coefficients were relatively high ($\sim$30%) for many of the reported data.

5) Richter (1981) determined sorption isotherms for TCE with various inorganic soil components, organic peat, and a natural soil. He showed that the sorption capacity decreased in the following order: organic peat > montmorillonite > manganese oxide > kaolinite > iron oxide. However, Richter's work suffered from the following problems/inadequacies:

(a) TCE volatilization losses were likely during the experiments, but were neither determined nor accounted for.

(b) Sorbents were dried at 100°C for 1 hour which may have altered their surface properties.

(c) The temperature at which the isotherms were conducted was not reported.

(d) The isotherms were presented as Freundlich log-log plots which tend to "smooth out" the irregularities and imprecision of the data.

It should also be noted that the above work revealed nonlinear isotherms for all sorbents (except possibly the manganese oxide), even though the solute concentration range was relatively low. This anomalous result was neither mentioned nor discussed by Richter in his report.

6) Lion and Garbarini (1983) examined the sorption of TCE (as well as toluene and naphthalene) using several synthetic and natural soils. (The synthetic soils consisted of humic acids, and hydrous aluminum oxide which had been coated with humic acid.) The following observations/findings were made by Lion and Garbarini:

(a) Toluene was "excluded from solution" by $Al_2O_3$ over a wide range of sorbent concentrations. This unusual result could not be explained by the salting-out effect at the low ionic strength (calculated via the measured specific conductance) of the solution. (The authors speculated that the charged $Al_2O_3$ colloids may be affecting the toluene activity.)

(b) TCE and toluene were sorbed by both humic acid (HA) and HA-coated $Al_2O_3$. However, the percentage solute sorbed was consistently higher (for both compounds) with the humic acid alone than with the HA-coated hydrous aluminum oxide (for equal amounts of HA).

Based on this, the authors concluded that the presence of the $Al_2O_3$ suppressed the sorption of these compounds.

(c) The sorption densities of TCE and toluene on HA were independent of their equilibrium solution concentrations, indicating complete coverage of the HA sorbent. (The authors later concluded in a follow-up paper [Garbarini and Lion, 1984] that these sorption isotherms were, in fact, linear with non-zero slopes.)

(d) The sorption of naphthalene by a variety of soils (with O.C. contents ranging from 0.11 to 0.54%) was not controlled by the mass of O.C. present.

My major criticisms of this research are:

(a) The investigators did not distinguish between <u>sorption</u> and <u>binding</u> phenomena in their experiments. That is, the solutes were considered to be "sorbed" by both the particulate <u>and</u> soluble forms of humic acid. Although the distinction between colloidal and dissolved species is somewhat arbitrary, it is useful in connection with groundwater contamination studies, since soluble species are assumed to be transported by dispersion/advection, whereas particulate species are assumed to remain relatively fixed. Thus, a solute that is <u>sorbed</u> is generally considered to be removed from the liquid phase (whether by accumulation at an interface between two phases, or by interpenetrating another phase). Therefore, the sorption concept should perhaps not be applied to the case of compounds binding to soluble HA molecules.

(b) All reaction vessels contained a swamping NaCl electrolyte (0.1 M) in order to minimize any possible effect of the colloidal sorbent on compound activity. Such a high ionic strength is rarely found in natural soils, and may in itself be influencing sorption by increasing the surface tension of water or by altering the structure of the HA polymer.* (However, as pointed out by Lion [1984] in a personal communication, certain comparisons between sorption characteristics made in their paper may still be valid.)

---

*Garbarini and Lion (1984) later demonstrated that these ionic strength effects were negligible.

# III. OBJECTIVES AND PROGRAM OF STUDY

The literature review given in the previous chapter clearly demonstrates how scanty our knowledge is regarding the sorption behavior and characteristics of volatile, chlorinated, aliphatic hydrocarbons (at least relative to our knowledge of pesticide sorption). The following deficiencies, shortcomings, and ambiguities in the literature are evident:

(1) No correlation attempts have been made between sorption and fundamental molecular properties.

(2) The specific sorption mechanism(s) is(are) not clear.*

(3) The constituent of the soil organic matter which is causing sorption of these compounds has not been identified.

(4) Some studies show measurable adsorption of these compounds onto mineral (inorganic) soil components, some show negligible adsorption, and some indicate negative adsorption.

(5) No studies have examined the desorption and reversibility characteristics of these compounds with soils.

(6) There is no convincing experimental evidence to indicate whether it's an a<u>d</u>sorption or a<u>b</u>sorption phenomenon.

(7) Virtually no studies have investigated the influence of various factors such as temperature, pH, ionic strength,

---

*For example, no one has attempted to determine values for the free energy, enthalpy, and entropy of sorption for these compounds by soil, or soil components. A knowledge of these thermodynamic variables should provide clues to the sorption mechanism(s)/force(s) involved.

solids concentration (water content), and sorbent specific surface area, upon sorption of chlorinated aliphatics by soils.

## A. Objectives

In light of the above shortcomings in the scientific literature, the following research objectives have been formulated for this study:

### 1. Primary

(a) Measure, describe, explain, and model/correlate the equilibrium sorption (and desorption) characteristics of the selected compounds with soils or soil components, with primary emphasis given to the relationship between sorption and fundamental molecular properties (such as polarizability, dipole moment, molecular weight, molar volume, and parachor). In addition, attempt to correlate the normalized sorption distribution coefficient ($K_{oc}$) to compound solubility and octanol-water partition coefficient, as is commonly done in the literature.

(b) Attempt to implicate the predominant sorption mechanism(s)/force(s) involved, based on the results from (a) above, and by determining three fundamental thermodynamic properties of the sorption process (free energy, enthalpy, and entropy).

### 2. Secondary

(a) Determine the adsorption/desorption (if any) of the selected compounds onto a variety of common mineral components likely to be present in subsurface soils (i.e., groundwater aquifers).

(b) Attempt to identify the specific constituent(s) of the soil organic matter which is (are) primarily responsible for the sorption of these compounds.

(c) Attempt to determine whether the phenomenon is one of adsorption or absorption.

(d) Determine the influence (if any) of the following factors upon sorption: temperature, pH, ionic strength, solids concentration (water content), and the specific surface area and organic carbon content of the sorbent.

## B. Program of Study

This research was divided into six phases of study discussed below, each corresponding to one of the above objectives (although the chronology was different from that implied above).

### 1. Phase I: Accomplishment of Secondary Objective (a)

A logical beginning for this research was considered to be an investigation of whether or not adsorption of the selected compounds occurs onto inorganic soil components. Since the bulk of soil organic matter occurs within the top few meters of the surface, the mineral components would probably best represent the soil composition of a groundwater aquifer. However, some subsoils are known to contain organic matter (Foster, 1975), and it is not known what effect the coating of mineral soils by trace levels of organic matter might have upon the sorption of these compounds. Nevertheless, there is a need to know the adsorption characteristics of the selected compounds onto "pure" mineral components. The plan was this: if adsorption was observed for certain (or all) mineral components used, then these would also be used as adsorbents in other phases of the study; if no (or negligible) adsorption occurred using these mineral components, then soils (or soil components) containing organic matter would be used in accomplishing the remaining objectives. To this end, the following clays and minerals, commonly found in soils (Bear, 1964; Dixon and Weed, 1977), were examined for their adsorption of the selected compounds:

(1) Montmorillonite

(2) Kaolinite

(3) $SiO_2$ (Silica)

(4) $Al(OH)_3$ (Gibbsite)

(5) $Fe_2O_3$ (Hematite)

(6) $CaCO_3$ (Calcite)

(7) $MnO_2$ (Pyrolusite)

### 2. Phase II: Accomplishment of Primary Objective (a)

Sorption (and some desorption) isotherms were determined for the selected compounds, using the following sorbents:

(1) three "real" surface soils, each with different composition/characteristics;

(2) activated carbon; and

(3) three organic matter components (from Phase III) which yielded significant sorption.

For each sorbent, an attempt was made to correlate the strength of sorption (as measured by the sorption distribution coefficient, $K_d$, determined from the linear Henry's law region of the isotherm) to the compound properties mentioned in Primary Objective (a). (Unfortunately, many of these sorbate properties were mutually correlated with each other.) Also, the organic carbon content of each sorbent was determined in order to calculate the normalized sorption distribution coefficient, $K_{oc}$. These $K_{oc}$ values were then correlated to the compound's solubility, octanol-water partition coefficient, and polarizability.

### 3. Phase III: Accomplishment of Secondary Objective (b)

In this phase, an attempt was made to identify the components of the soil organic matter which are primarily responsible for the sorption of these compounds. According to the literature, the most frequently used method in this regard is to sequentially extract or destroy various organic components from a soil, using a variety of chemical or physical treatments (e.g., 1N NaOH, $H_2O_2$, ignition, benzene-methanol mixtures, etc.). However, the use of these methods has been criticized by Burchill et al. (1981) because they inevitably alter the surfaces of the inorganic components. Furthermore, these methods are not truly selective for the organic components they intend to remove or destroy; and lastly, any chemical used (e.g., as an extractant) may itself sorb with the test soil. Therefore, it may not be valid to interpret the differences in sorption as being caused by the components removed during the treatment.

Therefore, a different technique was employed in this research: a variety of "pure" organic chemicals, which have been identified in soil organic matter, were examined for their sorption characteristics. Three of these organic components yielded significant sorption, and were also used in other phases of this research.

### 4. Phase IV: Accomplishment of Primary Objective (b)

An attempt was made to determine the thermodynamic properties of free energy, enthalpy, and entropy of sorption by performing isotherms for each compound with several sorbents, at three different temperatures. By using the van't Hoff expression, it is theoretically possible to calculate values for the differential (or isosteric) heat of sorption, $\Delta H^o$. Also, the sorption free energy ($\Delta G^o$) is related to the isotherm distribution coefficient, $K_d$, via $\Delta G^o = -RT \ln K_d$. Thus, the only remaining unknown is the sorption entropy, which can be calculated from the relation: $\Delta G^o = \Delta H^o - T\Delta S^o$.

However, as will be evident later, these attempts met with only limited success. Many of the $K_d$ values did not exhibit a trend (with respect to temperature) in accordance with the van't Hoff relation. These unexpected results were attributed to a combination of very low $\Delta H^o$ values, and relatively poor data precision for some of the $K_d$ values. Nevertheless, I was able to establish confidence limits for these thermodynamic properties, and certain conclusions regarding sorption mechanisms and forces were drawn therefrom.

### 5. Phase V: Accomplishment of Secondary Objective (c)

Two methods were used in this research for distinguishing between adsorption and absorption phenomena. The first was to examine isotherm characteristics over a broad range of solute concentrations (and hence, sorption densities). If the phenomenon is one of adsorption, then the isotherms should exhibit significant curvature (either downward due to adsorption site saturation, or upward due to multilayer adsorption); but if it is one of absorption then the characteristic feature should be (virtually) linear isotherms since the partitioning of a solute between two phases is relatively independent of its concentration. For example, octanol-water partition coefficients are fairly constant except at solute concentrations >> 0.01 mole/l (Lyman et al., 1982). In addition, isotherm characteristics and sorption thermodynamic properties for the soils and soil components were compared to those for sorbents (e.g., graphite and activated carbon) for which the phenomenon is known to be one of adsorption.

The second method was to evaluate sorption strength (capacity) as a function of sorbent surface area. If the phenomenon is one of adsorption, then the distribution coefficient ($K_d$) should vary with sorbent surface area; on the other hand, if the phenomenon is one of absorption, then $K_d$ should be (theoretically) independent of sorbent surface area. Therefore, a suitable sorbent was fractionated into two classes of particle size, which also represented two different specific surface areas. (Surface areas were quantitatively verified.) Sorption experiments were then conducted using equal sorbent masses from each of the particle size classes.

### 6. Phase VI: Accomplishment of Secondary Objective (d)

The effects of temperature, pH, ionic strength, solids concentration, and sorbent surface area and organic carbon content, on sorption of one or more of the selected compounds, were determined, by altering each variable in turn, while holding all other variables constant. An attempt was made to explain, from a theoretical standpoint, the observed influence of each factor upon sorption.

# IV. EXPERIMENTAL PROCEDURES AND MATERIALS

This chapter contains only those experimental procedures and materials which are common to all phases of study performed in this research. The remaining experimental procedures and materials (which are phase-specific in nature) are described in the appropriate sections of Chapter V, "Results and Discussion".

## A. Analysis of Sorbate Concentrations and Preparation of Stock Solutions

It was initially intended to use the gas chromatographic headspace technique (see Dietz and Singley, 1979; Richter, 1981; Lincoff and Gossett, 1983; Lion and Garbarini, 1983) as the analytical method for determining sorption data. However, early experiments using this technique yielded unusual results in some cases (some of this early work is discussed in Appendix B). Therefore, other methods for quantitative analysis of these highly volatile organic solutes were investigated. Direct injection of an aqueous phase sample into the gas chromatograph (GC) was considered, but rejected, because of the large volume of water which would have to be injected along with the organic solute (this water would have deleterious effects on the GC column). (Pfaender et al. [1978] described modifications to the GC to enable it to accept direct injections of aqueous samples. However, since our laboratory GC was committed to other researchers injecting only gas-phase samples, this modification idea was rejected.) Another alternative was the liquid-liquid extraction (LLE) procedure, in which the solute is extracted from the aqueous phase by equilibrating it with an organic solvent such as pentane or hexane. A small volume sample of the organic solvent (containing the solute) is then injected into the GC for analysis. However, this method typically yields erratic or low extraction efficiencies for volatile compounds (Bellar and Lichtenberg, 1974; Rhodes and Nulton, 1981; Glaze et al., 1981; Junk et al., 1981), and in some cases, poor analytical precision (Munz and Roberts, 1982). Another procedure used for quantifying volatile solutes is the "purge-and-trap" method, described by Bellar and Lichtenberg (1974). However, this technique requires several pieces of commercial equipment, which then must be modified to meet the needs of the method.

Because of the foregoing problems associated with GC analyses of the sorbate compounds (and since our laboratory had recently acquired a liquid scintillation counter), it was decided to use radiolabeled isotopes in conducting the sorption experiments. Attempts were made to obtain all the chlorinated aliphatics listed previously in Table 1.1 (and several others as well) in radiolabeled form, from several commercial sources. However, the only ones available were:

(1) $^{14}$C-Chloroform
(2) $^{14}$C-Carbon Tetrachloride
(3) $^{14}$C-Trichloroethylene
(4) $^{14}$C-Tetrachloroethylene

Although this represents a limited sample of compounds from which to draw comparisons and correlations in sorption behavior, it is fortuitous that they are quite different in regard to the following properties: (a) polarity (two are polar, and two are nonpolar); (b) aqueous solubility; and (c) octanol-water partitioning. Furthermore, these compounds constitute a "miniature series" of chlorinated alkanes and alkenes. (For a complete discussion of the properties of these compounds, refer to Chapter V.)

All the above compounds were obtained from New England Nuclear, Inc., with a purity of >99%. Table 4.1 lists the pertinent data for these compounds as reported by New England Nuclear.

TABLE 4.1 Compound Data as Reported by New England Nuclear, Inc.

| Compound | Total Activity (mCi)* | Specific Activity (mCi/mmol) | Mass (mg) |
|---|---|---|---|
| Chloroform | 0.1 | 4.6 | 2.6 |
| Carbon Tetrachloride | 0.25 | 2.8 | 13.7 |
| Trichloroethylene | 0.25 | 4.5 | 7.3 |
| Tetrachloroethylene | 0.25 | 15.6 | 2.7 |

---

*A curie (Ci) is equal to 2.2 x $10^{12}$ disintegrations per minute (DPM).

All compounds were shipped in break-seal tubes, in the "neat" form. That is, they were not dissolved in any type of solvent, as many organic radioisotopes are. Also, most of the air in the tubes was evacuated during preparation, so that the isotopes were essentially sealed in a vacuum.

Sorbate stock solutions were prepared as follows: Distilled water was bubbled with high-purity nitrogen gas through a diffuser stone for approximately 1 hour in order to remove dissolved oxygen (since Dilling _et al_. [1975] reported that the presence of oxygen accelerated the decomposition rates for some chlorinated aliphatics). This oxygen-purged water was then quickly transferred into preweighed, 250-ml, amber bottles, and sealed with preweighed Mininert$^{TM}$ valves (Supelco, Inc.) (to be described later). (Amber bottles were selected to contain the stock solutions since a few studies showed that sunlight can also hasten the degradation of these sorbate compounds [McConnell _et al_., 1975; Dilling _et al_., 1975]). Prior to the transfer* of the radiolabeled compounds to the stock solution bottles, the break-seal tubes and stock bottles were immersed in ice-water for several hours. This served to minimize volatilization losses during transfer, and also to "condense out" the radiolabeled compound on the walls of the break-seal tube. The top, open portion of the break-seal tube (which is separated from the closed portion by a glass membrane) was filled with the oxygen-purged, distilled water at 0°C. The seal was then broken with a glass rod and the cold water rushed into the evacuated chamber containing the radioactive compound. Shortly afterwards, a very tiny ball (a few millimeters in diameter) was observed at the bottom of the water column in the break-seal tube (these compounds are all denser than water). The liquid was then immediately poured into a stock bottle, and the break-seal tube was rinsed several times with the $O_2$-purged distilled water and poured into the stock bottle in order to salvage residual traces of the radioisotope. The stock bottles were sealed with the Mininert$^{TM}$ valve, and placed in a dark, locked cabinet** for a minimum of 5 days, to allow the organic solute to completely dissolve. The

---

*It should be emphasized that all procedures involving the transfer of these volatile, radioactive chemicals were performed under a fume hood. Calculations showed that Federal and New York State air quality standards for radioactive emissions would not be exceeded, even in the worst-case event of all the radiolabeled compounds volatilizing up the hood duct simultaneously.

**This locking cabinet had been pre-constructed inside a fume hood for secure storage of all the radiolabeled stock solutions, when not in use. Its secondary purpose was to contain the Beta emissions from the $^{14}C$ nuclei.

filled bottles (with caps) were then reweighed,* and a small sample removed for analysis on the liquid scintillation counter (LSC) (sampling and LSC procedures are described later). Based on the resulting counts per minute (CPM) in each of the above "high-level" stock solutions, corresponding "low-level" stock solutions were prepared by calculating the volume of "high-level" stock solution to add to a known volume of oxygen-purged, distilled water, in order to yield a "low-level" stock solution containing an activity concentration of about 60,000 CPM/ml. (This value was chosen since it yields a target activity concentration of 10,000 CPM/ml, when 1 ml of the stock solution is combined with 5 ml of liquid in the actual reaction vial.) The preparation of these "low-level" stock solutions normally required the transfer of several milliliters (the exact volume was always calculated) from the "high-level" stock solutions to a known volume (usually ~230 ml) of the $O_2$-purged distilled water, contained in the same type bottle and cap. Again, the transfer was made at 0°C, as quickly as possible, in order to minimize volatilization losses. Later, a 1-ml sample of this "low-level" stock solution was analyzed on the LSC in order to verify its activity concentration.

All stock solution bottles were sealed with screw-cap Mininert$^{TM}$ valves which provided a dual-sealing system. The outer seal was a rubber septum, and the inner seal a solid teflon valve. When removing a sample from a stock solution bottle, the bottle was partially

---

*The empty and filled bottles were weighed to calculate the mass of liquid within each bottle, which in turn, was used to determine the total activity of each compound actually received. That is, it was merely done to verify the total activity of the shipment reported by N.E.N., Inc., and was of no experimental relevance.

inverted*, the teflon valve was opened, and a syringe needle inserted through the septa into the solution. After the needle was withdrawn, the teflon valve was closed.

It should be noted that both the "high-" and "low-level" stock solutions for each of the four compounds contained only the radiolabeled compound (i.e., they were not spiked with stable compound). However, for the case of trichloroethylene (TCE), three additional stock solution bottles were prepared with varying amounts of stable TCE (Fisher Scientific Co.) added. These were to be used as "very high-level" stock solutions for examining isotherm characteristics in the high concentration region. The main drawback to spiking a radiolabeled stock solution with stable compound is that the accuracy of the mass of these volatile compounds added to each bottle is extremely difficult to ascertain. Thus, the specific activities for spiked stock solutions are not only likely to be inaccurate, but they are also different because of the different levels of spiking. By contrast, although the specific activity reported by N.E.N., Inc., for a particular radiolabeled compound may not be accurate, it will at least be constant for all unspiked stock solutions of that compound. For example, the low- and high-level stock solutions for chloroform each have the same specific activity, which is reported to be 4.6 mCi/mmol. The specific activity is important because it is one of the factors used in converting the DPM (or CPM) output of the LSC into units of compound mass. However (as will be demonstrated in Section

---

*An apparatus was constructed with rods and clamps to hold the stock bottles at a slight downward angle for withdrawal of samples.

C of this chapter), the sorption equilibrium distribution coefficient, $K_d$, is independent of the accuracy of the specific activity (S.A.). That is, any value can be assumed for the compound's S.A., and it simply cancels out in the calculation of isotherm slope, or $K_d$.

## B. Procedures for Sampling from Sorbent Stock Suspensions

Samples from all suspensions were withdrawn using either a volumetric pipet or an Oxford Precision Macro-Set Pipettor (Fisher Scientific Co.). The clay and mineral suspensions were uniformly mixed by vigorous shaking of the stock bottles. Complete mixing of all other suspensions was accomplished via rapid magnetic stirring for a minimum of 1 minute before the sample was withdrawn. (The suspension was also being stirred during sample removal, to ensure a uniform suspension throughout the bottle.)

## C. Procedures Used in the Determination of Sorption (and Desorption) Isotherms Using Liquid Scintillation Counting Techniques

### 1. Materials and Methods

All sorption (and desorption) equilibrations were performed in 5.0-ml "Micro Reaction Vessels" (Supelco, Inc.), supplied with hole caps (screw-type) and teflon-faced rubber septa. (Care had to be taken to ensure that the "shiny" side of the septa was inserted such that it always faced the vial contents when the cap was screwed on, since this was the teflon-lined face.) These vials were made of borosilicate glass with heavy walls, and could be autoclaved or centrifuged. In setting up a sorption experiment, a series* of these reaction vials (R.V.'s) were usually filled with 5.0 ml** of the desired sorbent suspension, and an equal number of R.V.'s filled with 5.0 ml of distilled water to serve as controls.

Each isotherm data point could be determined from a single sorbent R.V. and a single control R.V., but there would be no way to assess the precision of such an isotherm. Therefore, usually two (but sometimes three or more) replicates were run for each data point, requiring a total of four R.V.'s: two sorbent and two control. (Thus, an isotherm containing six data points would usually require 24 R.V.'s.) Once the R.V.'s were filled with the appropriate liquids, they were transferred to a fume hood where they would each receive a measured volume of a particular radiolabeled stock solution. These volumes were dispensed using three different-sized syringes: 0.1, 0.5, and 1.0 ml. A typical experiment set-up for a six-point isotherm is shown in Table 4.2 below. In addition, a sorbent and control R.V. each containing no radiolabeled compound, were run as indicators of background radiation. (These background counts were subtracted from all results provided by the liquid scintillation counter prior to calculations.)

After each R.V. was injected with its appropriate dose of labeled solution, it was quickly capped and sealed. When this step was completed,

---

*The exact number was determined by the number of isotherm data points desired, and the number of replicates used.

**Some experiments used suspension/distilled water volumes different than 5.0 ml, for reasons explained in the appropriate sections of this thesis.

TABLE 4.2 A Typical Experiment Setup for a Six-Point Isotherm

| Isotherm Data Point No. | Reaction Vial No. and Type | Receives this Volume (ml) | From this Radiolabeled Stock Solution* |
|---|---|---|---|
| 1 | 1,2 Control<br>3,4 Sorbent | 0.1 | LL |
| 2 | 5,6 Control<br>7,8 Sorbent | 0.5 | LL |
| 3 | 9,10 Control<br>11,12 Sorbent | 1.0 | LL |
| 4 | 13,14 Control<br>15,16 Sorbent | 0.1 | HL |
| 5 | 17,18 Control<br>19,20 Sorbent | 0.5 | HL |
| 6 | 21,22 Control<br>23,24 Sorbent | 1.0 | HL |

---

*LL ≡ Low Level
HL ≡ High Level

R.V.'s were transferred to a rotating tumbler* and equilibrated for four days** at constant temperature[†]. At the conclusion of the equilibration period, the R.V.'s were removed from the tumbler, inserted into specially-constructed centrifuge adaptors, and centrifuged (Beckman Model J2-21 Centrifuge) at ∿3000 G for 30 minutes, at the equilibrated temperature.[††] (A preliminary experiment demonstrated that losses of these volatile compounds from the sealed vials occurred when centrifuged with the vacuum system engaged. Therefore, the R.V.'s were always centrifuged with the vacuum system disconnected.) The R.V.'s were then carefully removed from the centrifuge (and their adaptors) so that the settled solids would not be disturbed, and transferred to a vial holder in the fume hood. Using a

---

*Actually, two tumblers were constructed for this research. One was built inside an insulated ice chest where it was positioned just above a thermal reservoir of water contained in the bottom of the chest and connected to a constant temperature circulator (Neslab Instruments, Inc.) thus serving as a miniature constant temperature chamber. The other tumbler was not contained, and was placed in a 20°C room. Both tumblers rotated at ∿7 rpm.

**Some sorbents were equilibrated for 2 days.

[†] The early experiments in this research were subject to poorer precision of temperature control than the remaining experiments. This was because the tumbler used rotated in the vapor phase (above the constant-temperature reservoir) within the insulated ice chest, and the temperature of this vapor phase varied slightly with room temperature. When this discrepancy was first noted, a thermometer was placed in the vapor phase compartment and its temperature was frequently checked at various room temperature and water bath temperature conditions. The temperature range of the vapor phase was generally ±2°C of its mean value, depending on the extremes in room temperature. This problem was corrected by raising the water reservoir level within the ice-chest so that the R.V.'s would be submerged during tumbling. Under these conditions, the control of temperature precision improved to about ±0.1°C. For those experiments performed in the constant-temperature room, the temperature range was also monitored and found to be 20°C ± 0.5°C. (The only experiments in which R.V.'s were tumbled in the vapor phase were those involving TCE with the clays/minerals, and the mineral soil.)

[††] During the early experiments, the control R.V.'s were centrifuged along with the sorbent R.V.'s. Later experiments demonstrated that centrifugation had no effect on solute concentrations in the control R.V.'s, and they were therefore not centrifuged afterward (except when needed to balance the centrifuge).

1.0-ml syringe, 2.0 ml of supernatant liquid were removed from each R.V. (by piercing the syringe needle through the septum seal): the first milliliter was discarded (for the purpose of removing volume for the desorption phase of the experiment; and secondarily, to "clean out" the syringe from the previous sample); the second milliliter was injected into 10 ml of liquid scintillation cocktail (Beckman Ready-Solv$^{TM}$ MP), which had previously been added to an 18-ml scintillation vial (Beckman Poly-Q$^{TM}$). The scintillation vial (S.V.) was then quickly capped, thoroughly shaken, and later placed in a liquid scintillation counter (Beckman Model LS-9800) for analysis.

The desorption phase of the experiment could be started at this point. After the second milliliter of supernatant had been removed from the R.V. and transferred to a S.V., the R.V. was quickly uncapped, the septum removed, 2.0 ml of distilled water added (using an Oxford automatic pipettor), and then recapped and resealed (with a different cap containing a new septum). After all R.V.'s had been processed in this manner, they were again returned to the tumbler for a desorption equilibration period (which was arbitrarily set equal to the adsorption equilibration period). At the end of this tumbling period, the R.V.'s were removed and processed as above, and the LSC data from this phase of the experiment were used to construct a desorption isotherm.

Each scintillation vial (S.V.) was counted for 10 minutes, which resulted in a (theoretical) machine counting error (i.e., coefficient of variation) always <1.5%, and usually <0.5%).[†] Furthermore, each sample (S.V.) count was duplicated (i.e., the entire sample train was processed through a second counting cycle), primarily to detect

---

[†] Consult Wyld (1970) for a good discussion of liquid scintillation counting errors and statistical confidence.

chemiluminescence* (which occurred very rarely). The counts per minute (CPM) determined by the LSC were all converted to disintegrations per minute (DPM) by using a quench** curve developed from a set of Carbon-14 quenched standards (Beckman Instruments, Inc.). Using this method, therefore, it was not necessary to ensure identical quench levels for all samples, but only that the quench level did not exceed the range of the quench curve.

### 2. Calculation of Isotherm Data

In order to construct an isotherm, two pieces of information are needed for each data point - the equilibrium concentration of the compound in the aqueous (liquid) phase ($C_\ell$, μg/l), and the sorption density of the compound in the solid phase ($C_s$, μg/g). The solute equilibrium concentration, $C_\ell$, is measured "directly" by converting the LS-9800 DPM output (resulting from a 1-ml supernatant sample for the sorbent vial) into units of μg/l. The sorption density, $C_s$, is calculated by the difference in solute concentrations between the control and sorbent R.V.'s. Although the headspace present in the reaction

---

*Chemiluminescence is caused by various chemical reactions which generate light within the sample scintillation cocktail, and are not the result of the radioactivity in the sample. Therefore, chemiluminescence results in a higher CPM (or DPM) output by the LSC than is actually present in the sample. However, chemiluminescence typically decays away fairly rapidly, and after ~1 hour is virtually gone.

**The quench level of a sample is a measure of the extent to which various substances present in the sample (e.g., particles, color, water, cocktail, etc.) act to interfere with the counting ability of the machine. The higher the quench level, the lower the machine counting efficiency. The LS-9800 measures quench level using an external standard, which is reported as the sample "H#". Thus, by determining the H#'s for a set of quenched standards (of known DPM), a quench curve of counting efficiency (i.e., CPM/DPM) versus quench level (H#) was generated, and used to assess the DPM for other samples.

vials was minimal, compound partitioning into the gas phase was accounted for in the calculations of sorption density. A small headspace was intentionally retained in the R.V.'s for the following reasons: (a) it promoted more thorough mixing of the vial contents during equilibration (tumbling) (i.e., it probably increased sorption kinetics); and (b) filling the R.V.'s exactly "to the rim" prior to sealing would have been very difficult, and may have resulted in loss of liquid during capping/sealing.

To simplify the explanation for the derivation of the isotherm (sorption and desorption) equations, consider the three-phase sorbent R.V., two-phase control R.V., and their accompanying symbols, shown in Figure 4.1. The solute equilibrium concentration, $C_\ell$, is obtained from $X_\ell$ by the use of a conversion factor (C.F.) which simply converts DPM to units of mass. The C.F. for a particular radiolabeled compound is a function only of its molecular weight and specific activity. For example, the C.F. for TCE is:

$$\frac{131.4\ \text{mg/mmole}}{4.5\ \text{mCi/mmol}} \times 10^{-3}\ \frac{\text{mCi}}{\mu\text{Ci}} \times \frac{1\ \mu\text{Ci}}{2.22 \times 10^{6}\ \text{DPM}} \times 10^{3}\ \frac{\mu\text{g}}{\text{mg}} = 1.32 \times 10^{-5}\ \frac{\mu\text{g}}{\text{DPM}}$$

The conversion factors for the remaining compounds are:

| Compound | Conversion Factor (μg/DPM) |
|---|---|
| $CHCl_3$ (Chloroform) | $1.17 \times 10^{-5}$ |
| $CCl_4$ (Carbon Tetrachloride) | $2.47 \times 10^{-5}$ |
| $C_2Cl_4$ (Tetrachloroethylene) | $4.79 \times 10^{-6}$ |

vials was minimal, compound partitioning into the gas phase was accounted for in the calculations of sorption density. A small headspace was intentionally retained in the R.V.'s for the following reasons: (a) it promoted more thorough mixing of the vial contents during equilibration (tumbling) (i.e., it probably increased sorption kinetics); and (b) filling the R.V.'s exactly "to the rim" prior to sealing would have been very difficult, and may have resulted in loss of liquid during capping/sealing.

To simplify the explanation for the derivation of the isotherm (sorption and desorption) equations, consider the three-phase sorbent R.V., two-phase control R.V., and their accompanying symbols, shown in Figure 4.1. The solute equilibrium concentration, $C_\ell$, is obtained from $X_\ell$ by the use of a conversion factor (C.F.) which simply converts DPM to units of mass. The C.F. for a particular radiolabeled compound is a function only of its molecular weight and specific activity. For example, the C.F. for TCE is:

$$\frac{131.4 \text{ mg/mmole}}{4.5 \text{ mCi/mmol}} \times 10^{-3} \frac{\text{mCi}}{\mu\text{Ci}} \times \frac{1 \ \mu\text{Ci}}{2.22 \times 10^{6} \text{ DPM}} \times 10^{3} \frac{\mu\text{g}}{\text{mg}} = 1.32 \times 10^{-5} \frac{\mu\text{g}}{\text{DPM}}$$

The conversion factors for the remaining compounds are:

| Compound | Conversion Factor (μg/DPM) |
|---|---|
| $CHCl_3$ (Chloroform) | $1.17 \times 10^{-5}$ |
| $CCl_4$ (Carbon Tetrachloride) | $2.47 \times 10^{-5}$ |
| $C_2Cl_4$ (Tetrachloroethylene) | $4.79 \times 10^{-6}$ |

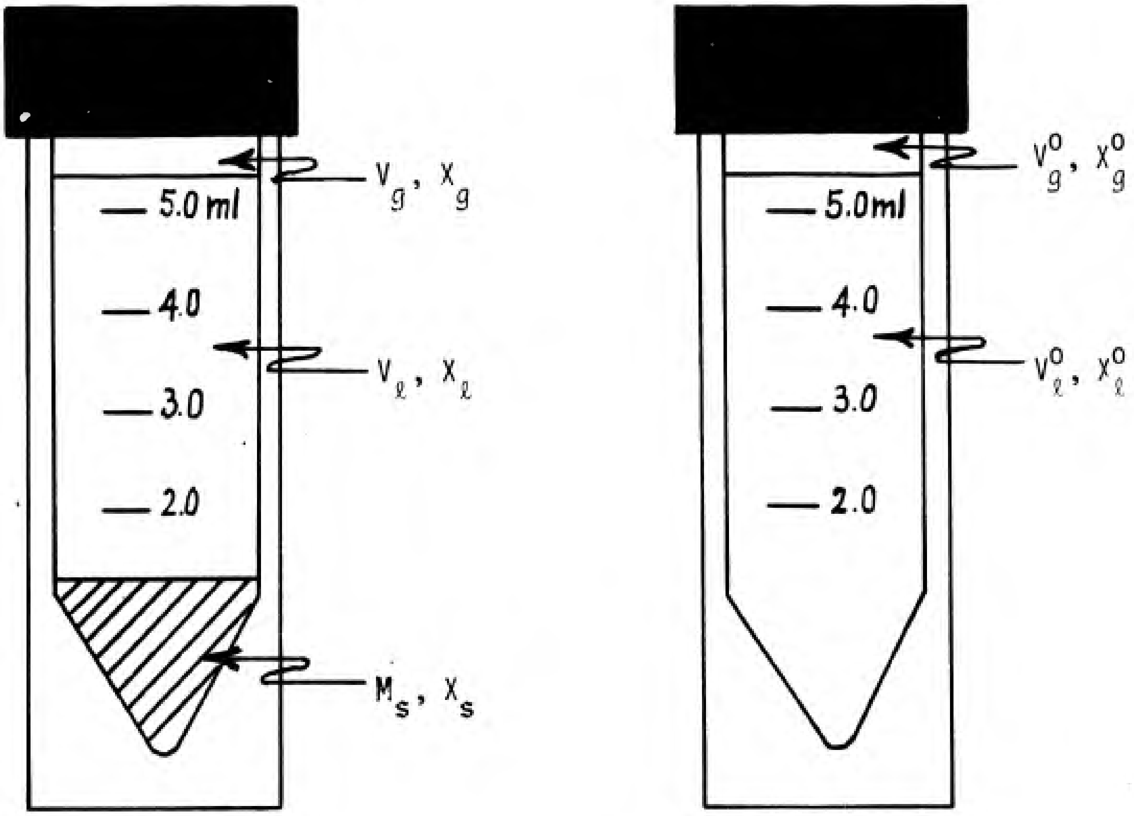

FIGURE 4.1 Three-Phase Sorbent Reaction Vial and Two-Phase Control Reaction Vial Systems, and Their Accompanying Symbols

Definition of Symbols:

(The "o" superscript denotes variables associated with the control R.V.)

$X_\ell$, $X_\ell^o$ ≡ "radioactivity" concentration in the liquid phase (DPM/ml)

$X_s$ ≡ "radioactivity" density on the solid (DPM/g)

$X_g$, $X_g^o$ ≡ "radioactivity" concentration in the gas phase (DPM/ml)

$M_s$ ≡ mass of solid (g)

$V_\ell$, $V_\ell^o$ ≡ liquid volume (ml)

$V_g$, $V_g^o$ ≡ gas (headspace) volume (ml)

As an example of this conversion, suppose the LS-9800 determined an $X_\ell$ value for $CCl_4$ of 7673 DPM/ml; the corresponding $C_\ell$ value would be:

$$\left(2.47 \times 10^{-5}\ \frac{\mu g}{DPM}\right) \left(7673\ \frac{DPM}{ml}\right) \left(1000\ \frac{ml}{l}\right) = 190\ \frac{\mu g}{l} \quad .$$

Thus, the general equation for $C_\ell$ (in units of μg/l) is:

$$C_\ell = (1000)(C.F.)(X_\ell) \quad . \qquad (4\text{-}1)$$

The derivation of the sorption density, $C_s$, is a bit more complicated. Referring back to Figure 4.1, in any sorption experiment, the liquid volumes present in the sorbent and control R.V.'s are the same. Thus, $V_\ell = V_\ell^o$; and $V_g = V_g^o$ (since the total volume of each R.V. is approximately the same). Now, consider a mass balance on the radioactivity <u>initially</u> <u>added</u> to each vial.* For the sorbent R.V., the total added

---

*This mass balance assumes that the volume occupied by the sorbent is negligible compared to $V_\ell$, which is the case for all work reported in this thesis.

quantity of radioactivity, $R_T$ (DPM)* is:

$$R_T = M_s X_s + V_\ell X_\ell + V_g X_g + R_L \tag{4-2}$$

and for the control vial:

$$R_T^o = V_\ell X_\ell^o + V_g X_g^o + R_L^o \tag{4-3}$$

where $R_L$ and $R_L^o$ represent any possible losses of compound mass (in DPM) (e.g., due to leakage, sorption onto glass walls of R.V., or sorption onto septa)* during the equilibration period, from the sorbent and control R.V.'s, respectively. (It is assumed that losses occurring during the delivery of an isotope to both the sorbent and control R.V.'s are identical [and probably also negligible]. Also, loss of compound during sampling is negligible since the samples are withdrawn by piercing the rubber septa with a syringe [i.e., the seal remains intact during sampling].) For any set of R.V.'s used to determine a single isotherm data point, the amount of radiolabeled compound delivered to each R.V. is identical. Therefore, $R_T = R_T^o$. Also, since the volume of each vial is 6.4 ml, $V_g = 6.4 - V_\ell$. Lastly, Henry's law can be used to express the gas-phase concentrations in terms of liquid phase concentrations:

---

*Various experiments which have been performed implicate compound sorption on the teflon lining of the rubber septa as the principal (and perhaps, only) source of these losses. These experiments are detailed in Appendix D, along with a discussion of losses.

$$X_g = \gamma_x H_c X_\ell \tag{4-4}$$

$$X_g^o = \gamma_x H_c X_\ell^o \tag{4-5}$$

where $H_c$ is the compound's "dimensionless" Henry's constant. (The values for Henry's constants used in this research are given in Appendix C, as well as a method for measuring $H_c$ using LSC techniques.) Making these substitutions (assuming that $\gamma_x = 1$, since solution is dilute), and equating the expressions for $R_T$ and $R_T^o$ yields:

$$M_s X_s + V_\ell X_\ell + (6.4 - V_\ell) H_c X_\ell + R_L = V_\ell X_\ell^o + (6.4 - V_\ell) H_c X_\ell^o + R_L^o \tag{4-6}$$

Solving for $X_s$ and collecting terms, we obtain:

$$X_s = \frac{(X_\ell^o - X_\ell)[V_\ell + H_c(6.4 - V_\ell)] + R_L^o - R_L}{M_s} \quad . \tag{4-7}$$

If mass losses from each R.V. (sorbent and control) are identical, then the last two terms in the numerator of Equation (4-7) cancel each other. However, experiments have shown that these mass losses* are approximately proportional to the solute equilibrium concentration in the reaction vial. This indicates that the reaction causing these losses (probably sorption of compound by the septum's teflon lining*) follows simple first-

---

*Compound mass losses are addressed in Appendix D, along with evidence of probable cause. As a matter of interest at this point in the thesis, the following losses were observed for each compound during a 4-day equilibration experiment at 20°C: $CHCl_3 \sim 0$; $CCl_4 \sim 1.3\%$; $C_2HCl_3 \sim 4.4\%$; and $C_2Cl_4 \sim 8.2\%$. These losses were strongly dependent on temperature, with higher temperatures resulting in higher percentage losses. See Appendix D for more detail.

order kinetics. Mass losses occurring from the control R.V. ($R_L^o$) can be determined by the use of another control vial which is analyzed at the beginning of the experiment. This "initial" control vial was prepared identical to the "reaction" control vial, but was only given several minutes of equilibration time (at the same temperature as the sorption experiment). In addition, this "initial" control vial was vigorously hand-shaken for 1 minute in order to establish gas-phase partitioning equilibrium*. If we designate the aqueous concentration of radioactivity in this initial control vial as $X_\ell^i$, then mass loss from the reaction control vial is given by:

$$R_L^o = [V_\ell X_\ell^i + (6.4 - V_\ell)H_c X_\ell^i] - [V_\ell X_\ell^o + (6.4 - V_\ell)H_c X_\ell^o] \tag{4-8}$$

where the terms in each bracket represent the total quantity of radioactivity present in the initial and reaction control vials, respectively; and thus, the difference represents the loss of radioactivity from the reaction control vial during equilibration. Equation (4-8) can be simplified to:

$$R_L^o = (X_\ell^i - X_\ell^o)[V_\ell + H_c(6.4 - V_\ell)] \quad . \tag{4-9}$$

If we assume that the rate of mass loss is proportional to instantaneous solute concentration, and that sorption is rapid, then $R_L^o \propto X_\ell^o$, and

---

*Dietz and Singley (1979) demonstrated that 1 minute of vigorous hand-shaking was sufficient to establish partitioning equilibria for each of the solute compounds used in this research, in serum vials containing dilute aqueous solutions of each compound.

$R_L \propto X_\ell$; or $R_L^o = kX_\ell^o$, and $R_L = kX_\ell$, where k is a proportionality constant which is different for each compound. Instead of assessing this k-value for each compound, we may simply eliminate it via the following ratio:

$$\frac{R_L}{R_L^o} = \frac{\cancel{k}X_\ell}{\cancel{k}X_\ell^o} \quad \text{or} \quad R_L = \left(\frac{X_\ell}{X_\ell^o}\right) R_L^o \quad . \tag{4-10}$$

Substituting the above expressions for $R_L^o$ and $R_L$ (i.e., Equations [4-9] and [4-10]) into Equation (4-7), and letting $V^* = [V_\ell + (6.4 - V_\ell)H_c]$, we obtain:

$$X_s = \frac{(X_\ell^o - X_\ell)V^* + (X_\ell^i - X_\ell^o)V^* - (X_\ell/X_\ell^o)(X_\ell^i - X_\ell^o)V^*}{M_s} \quad . \tag{4-11}$$

Upon simplification, Equation (4-11) reduces to:

$$X_s = \left(\frac{X_\ell^i}{X_\ell^o}\right) (X_\ell^o - X_\ell)V^*/M_s \tag{4-12}$$

and noting that sorption density, $C_s$ (μg/g), is simply equal to the appropriate conversion factor (C.F.) times $X_s$, yields:

$$C_s = (\text{C.F.})\left(\frac{X_\ell^i}{X_\ell^o}\right) (X_\ell^o - X_\ell)V^*/M_s \quad . \tag{4-13}$$

This interesting result shows that, if compound mass losses are proportional to solute concentration, sorption is relatively rapid, and activity corrections are negligible, the correct sorption density, $C_s$, is simply equal to the sorption density that would be calculated if there was no mass losses (or if losses from each vial were equal), times the "correction factor", $(X_\ell^i/X_\ell^o)$. Equation (4-13) is the one used to calculate the sorption density values for all sorption isotherm data in this research.

The derivation of the desorption equation (for the mass of solute sorbed on the solid) is more involved, but leads to the following surprisingly-simple result:

$$C_s' = \frac{(C.F.)[X_\ell^i - X_\ell' + (X_\ell/X_\ell^o)(X_\ell^{o\prime} - X_\ell^i)V^*]}{M_s} \qquad (4\text{-}14)$$

where the "primed" values represent those measured at the end of the desorption experiment. The actual derivation of Equation (4-14) is presented in Appendix E; and this equation was used to calculate all desorption isotherm data used in this research. The equation for the solute equilibrium concentration (at the end of the desorption cycle) remains the same. That is,

$$C_\ell' = 1000(C.F.)(X_\ell') \quad . \qquad (4\text{-}15)$$

Note that the slopes of the linear portions (e.g., the Henry's law region) of the sorption and desorption isotherms (obtained by plotting a series of $C_s$ vs. $C_\ell$, and $C_s'$ vs. $C_\ell'$ data points, respectively) are simply equal to $\Delta C_s/\Delta C_\ell$, or $C_s/C_\ell$ with respect to the origin. Therefore, these slope values are clearly independent of the conversion factor, C.F., since it cancels out in the ratio, $C_s/C_\ell$. The compounds' specific activities provided by New England Nuclear, Inc., being the only questionable "constants" which comprise these conversion factors, are thus shown to have no effect upon the determination of isotherm slopes, and hence, $K_d$ values.*

---

*$K_d$ values reported in this research are actually equal to 1000 ppb/ppm times these isotherm slope values, in order to make them quasi-dimensionless constants. That is, the units of $C_s$(μg/g or ppm) ÷ $C_\ell$(μg/l or ppb) yield slope units of ppm/ppb, which is multiplied by 1000 ppb/ppm in order to make $K_d$ "dimensionless".

# V. RESULTS AND DISCUSSION

## A. Adsorption of the Selected Compounds onto Clays and Minerals

The experimental procedures and materials applicable to this section are detailed first, with the results/discussion given afterwards.

### 1. Preparation of $Na^+$-, $Ca^{+2}$-, and $Al^{+3}$-Saturated Montmorillonite Suspensions

In order to examine the effects of various cations (occupying the exchange sites of the clay) upon adsorption, three montmorillonite suspensions were prepared with three different saturating cations: $Na^+$, $Ca^{+2}$, and $Al^{+3}$. These cations were selected because they are commonly found (especially $Ca^{+2}$ and $Al^{+3}$) as exchange cations in mineral soils (Dixon and Weed, 1977; Brady, 1974).

Distilled water was added to 15 grams of montmorillonite (#25 API standard; Upton, Wyoming; obtained from Professor Murray McBride [Agronomy Department, Cornell University] who, in turn, obtained it from Ward's Natural Science Establishment, Inc., Rochester, NY) and a large excess of the appropriate salt to make a 1-liter suspension. The salts used were reagent grade NaCl, $CaCl_2 \cdot 2H_2O$, and $AlCl_3 \cdot 6H_2O$ (Mallinckrodt Chemical Works). The mass of salt added corresponded to that required to yield a 1 N solution of the particular cation*. These suspensions were occasionally, vigorously stirred and shaken over a period of two days, but it was

---

*Since the montmorillonite has a CEC of approximately 100 meq/100 g, the 15 g of clay in suspension would have a CEC of ∿15 meq (0.015 eq). Therefore, a 1 N (= 1 eq/l) solution of the cation would contain about 67-times as many cations as available exchange sites, and should thus serve to saturate the sites with the desired cation.

observed that several extremely hard clumps of clay resisted dispersion. I decided to place the bottles containing the suspensions in an ultrasonic bath (Branson Cleaning Equipment Company) while stirring frequently with a glass rod. The montmorillonite clumps gradually dispersed (i.e., they were observed to become smaller) and virtually uniform suspensions were obtained after about 30 minutes of this treatment*. The suspensions were removed from the bath and set aside (with occasional shaking) for a period of one day. (This was to ensure that the clay became saturated with the desired cation.) The suspensions were then transferred into dialysis tubes (Carolina Biological Supply Co.) and placed in separate baths containing distilled water. (This allowed the excess salt ions to be removed from the suspensions, while maintaining the montmorillonite in a virtually saturated condition.) The distilled water in the baths was tested daily for chloride ions (note that chloride was the common anion for all the salts used) by removing a sample of bath water and adding to it several drops of a concentrated $AgNO_3$ solution. (AgCl is very insoluble and forms a white precipitate in solution.) If chloride was detected, the bath water was changed and the process repeated each day. Typically, after 5 to 7 days of this procedure, no further chloride was detected in the bath water; and the suspensions were poured into their final 2-liter stock bottles, and sealed with ground-glass stoppers. In order to verify that the excess dissolved salts had been removed from these suspensions,

---

*Other researchers (Rogers et al., 1980) have also used ultrasonics in dispersing their montmorillonite clay suspensions.

their conductivities* were measured and found to be 50, 30, and 60 μmho/cm for the $Na^+$-, $Ca^{+2}$-, and $Al^{+3}$-saturated montmorillonite suspensions, respectively; thus, confirming the salt removal. The pH values† for these suspensions were also determined and found to be 5.6, 5.3, and 4.3, respectively.

### 2. Preparation of Kaolinite, Silica, Gibbsite, Hematite, Calcite, and Pyrolusite Suspensions

The following materials were used to represent these sorbents:

(a) Kaolinite: A water-processed (to reduce soluble salt content) kaolinite clay, obtained from Georgia Kaolin Co. The particular manufacturer's grade was "Hydrite Flat D" with a reported median particle size of 5.0 μm, and BET surface area of 7 $m^2/g$.

(b) Silica: "Min-U-Sil 30" obtained from Pennsylvania Glass Sand Corp., and reported to be 99.7% silicon dioxide ($SiO_2$). Surface area was reported to be 0.54 $m^2/g$ and average particle size 8.8 μm.

(c) Gibbsite: Aluminum Hydroxide [$Al(OH)_3$] (Reagent Grade, Fisher Scientific Co.) and $\gamma$-$Al_2O_3 \cdot 3H_2O$ (Sigma Chemical Co.).

(d) Hematite: Ferric Oxide ($Fe_2O_3$) (Reagent Grade, Allied Chemical Co.)

(e) Calcite: Calcium Carbonate ($CaCO_3$) (Fisher Scientific Co.).

---

*All conductivities reported in this research were determined using a Chemtrix Type 70 Conductivity Meter (Chemtrix, Inc.)

†All pH values reported in this research were determined using a Fisher Accument pH Meter, Model 610A (Fisher Scientific Co.)

(f) Pyrolusite: Manganese Dioxide ($MnO_2$) (K & K Laboratories, Inc.) Distilled water was added to 15 grams* of each of the above sorbents to make 1-liter suspensions. These suspensions were stored in reagent bottles with ground-glass stoppers.

In order to ascertain that ionic strengths for these suspensions would not produce significant effects upon solute activities, the conductivities of each suspension were measured and are listed below. In addition, the pH values of these suspensions were determined and are also given below.

| Sorbent Suspension | Conductivity (μmho/cm) | pH |
|---|---|---|
| Kaolinite | 20 | 5.0 |
| $SiO_2$ | 12 | 5.5 |
| $\gamma\text{-}Al_2O_3 \cdot 3H_2O$ | 23 | 8.4 |
| $Al(OH)_3$ | 25 | 8.3 |
| $Fe_2O_3$ | 23 | 6.0 |
| $CaCO_3$ | 105 | 8.2 |
| $MnO_2$ | 160 | 7.5 |

Using a correlation derived by Russell (1976) (as reported by Snoeyink and Jenkins [1980]) in which

$$I = 1.6 \times 10^{-5} \times \text{Conductivity } (\mu\text{mho/cm})$$

---

*The selection of 15 g/l as the solids concentration for the clay/mineral sorbents was based on striking a balance between having enough sorbent mass present to detect slight amounts of sorption, and at the same time, keeping the sorbent mass low enough so that the error associated with corrections for the volume occupied by the solids would be minimal. Most soil sorption work has been done at solids concentrations much lower than 15 g/l (see Hamaker and Thompson, 1972), but the solutes are generally pesticides which have relatively high sorption intensities.

(where $I$ is ionic strength in moles/l), the estimated ionic strengths of these suspensions ranged from $1.9 \times 10^{-4}$ M to $2.6 \times 10^{-3}$ M. The activity coefficients ($\gamma$) for uncharged species have been approximated by the following equation (Butler, 1964; Drever, 1982): $\gamma = 10^{0.1\,I}$. Using this expression with the above range in $I$ values, the corresponding range in $\gamma$ for these suspensions is calculated to be 1.00004 to 1.0006. Thus, for all practical purposes, the solute activities in all these suspensions are equal to their corresponding solute concentrations. (That is, any differences in ionic strengths among these suspensions would have negligible effect upon sorption equilibria.)

### 3. Brief Summary of Procedures Used in These Experiments

Each sorbent reaction vial (R.V.) contained 5.0 ml (unless otherwise noted) of the appropriate sorbent suspension (at a solids concentration of 15 g/l), and each control R.V. contained 5.0 ml of distilled water. Each R.V. was then spiked with 0.5 ml from a low-level radiolabeled stock solution, and quickly capped/sealed. After all R.V.'s were processed in this manner, they were placed on a rotating tumbler for a minimum of two days. All the adsorption tests with clays and minerals were conducted at a temperature (T) of 20°C ± 2°C for TCE, and T = 20°C ± 0.1°C for the remaining compounds. (See Section IV.C.1. for a discussion of temperature precision, and an explanation of this discrepancy.) At the end of the equilibration period, the R.V.'s were centrifuged, and 1-ml supernatant samples were withdrawn for analysis.

### 4. Results and Discussion

In Table 5.1 below, TCE adsorption onto a particular clay or mineral sorbent can be assessed by comparing the mean "radioactivity" concentration in the control R.V. ($\overline{X}_\ell^o$), to that present in the supernatant of the sorbent R.V. ($\overline{X}_\ell$). Note, however, that in all cases except one ($Na^+$-montmorillonite), the values of $\overline{X}_\ell$ exceed the corresponding value for $\overline{X}_\ell^o$. In order to determine if any of the $\overline{X}_\ell$ values differ significantly from their corresponding $\overline{X}_\ell^o$ value, a two-tailed t-test was performed on each pair of means (sorbent versus control), within each experiment. The t-test revealed that at the 95% confidence level, none of the $\overline{X}_\ell$ values differ significantly from their corresponding $\overline{X}_\ell^o$ value. Also, a one-tailed t-test (to test the hypothesis that $\overline{\mu}_\ell > \overline{\mu}_\ell^o$, where $\overline{\mu}_\ell$ and $\overline{\mu}_\ell^o$ are the <u>population</u> means corresponding to the <u>sample</u> means, $\overline{X}_\ell$ and $\overline{X}_\ell^o$) at the 95% confidence level revealed that none of the $\overline{X}_\ell$ values are significantly greater than their corresponding $\overline{X}_\ell^o$ values. Nevertheless, the interesting fact remains that in eight of the nine pairs of means, $\overline{X}_\ell$ was greater than $\overline{X}_\ell^o$. If neither negative nor positive adsorption of TCE is occurring, and the errors associated with the measurements of the $\overline{X}_\ell^o$ and $\overline{X}_\ell$ variables are strictly random, then the probability of observing eight out of nine values in which $\overline{X}_\ell > \overline{X}_\ell^o$ is 0.0176*. Therefore, the anomalous data given in Table 5.1 are probably not the result of random error.

One possible explanation for these unexpected results is: due to the volume occupied by the solids in the suspensions, the sorbent R.V.'s

---

*Obtained from the binomial distribution under the assumption that the probability of an $\overline{X}_\ell$ value exceeding its corresponding $\overline{X}_\ell^o$ value is 0.5; and the probability that any $\overline{X}_\ell$ value is less than its corresponding $\overline{X}_\ell^o$ value is also 0.5.

TABLE 5.1 Tests for Adsorption of TCE onto Clays and Minerals

| Experiment | Type Solid (for Sorbent R.V.'s) | $\overline{X}_\ell^o$ or $\overline{X}_\ell$ * (CPM/ml) | S.D.** (CPM/ml) | C.V.*** |
|---|---|---|---|---|
| A | Control[†] | 7005 | ± 107 | ± 1.5% |
| | $Ca^{+2}$-montmorillonite[†] | 7055 | ± 61 | ± 0.87% |
| B | Control | 6413 | ± 125 | ± 1.9% |
| | $Na^{+}$-montmorillonite | 6344 | ± 58 | ± 0.91% |
| | $Al^{+3}$-montmorillonite | 6424 | ± 35 | ± 0.54% |
| | Kaolinite | 6519 | ± 95 | ± 1.5% |
| | Silica | 6526 | ± 77 | ± 1.2% |
| C | Control | 6607 | ± 11 | ± 0.17% |
| | $\gamma$-$Al_2O_3 \cdot 3H_2O$ | 6610 | ± 83 | ± 1.3% |
| D | Control | 6402 | ± 141 | ± 2.2% |
| | $CaCO_3$ | 6574 | ± 53 | ± 0.80% |
| | $MnO_2$ | 6578 | ± 27 | ± 0.41% |
| | $Fe_2O_3$ | 6438 | ± 89 | ± 1.4% |

*Mean value of three replicates.

**S.D. ≡ sample standard deviation = $[\sum_{i=1}^{3}(x_i - \overline{x})^2/(n-1)]^{\frac{1}{2}}$.

***C.V. ≡ coefficient of variation = $(S.D./\overline{x})(100\%)$.

[†] These R.V.'s contained 4.5 ml of liquid, to which 0.5 ml of the TCE stock solution was added, yielding a total liquid volume of 5.0 ml.

contained a slightly lower volume of water than the control R.V.'s, which would result in $\overline{X}_\ell$ being greater than $\overline{X}^o_\ell$. In order to determine if this could account for the observed differences between $\overline{X}_\ell$ and $\overline{X}^o_\ell$, the values for $\overline{X}_\ell$ were corrected (adjusted) to what they would be if they had the same water volume as the control R.V. This correction causes the liquid (or suspension) and total volumes in each "adjusted" sorbent R.V. to be slightly greater (by an amount equal to the volume occupied by the solids) than that in the control R.V. A mass balance on the radioactivity delivered to the actual and adjusted R.V.'s leads to the following expression*:

$$X^{\#}_\ell = \frac{V_\omega + H_c(6.4 - V_\ell)}{V^{\#}_\omega + H_c(6.4 - V_\ell)} \overline{X}_\ell \qquad (5\text{-}1)$$

where $V_\omega$ and $V^{\#}_\omega$ are the water volumes contained in the actual and adjusted sorbent R.V.'s, respectively; $H_c$ is the dimensionless Henry's constant; 6.4 ml is the total volume of each R.V.; and $V_\ell$ is the (actual) liquid volume in each R.V. (= 5.5 ml for all experiments in this section, unless otherwise noted). Note that $V^{\#}_\omega = V_\ell$; and that $V_\omega = V_\ell - V_s$, where $V_s$ is the volume occupied by the solids. The key unknown variable in Equation (5-1) is $V_\omega$, which turns out to be strictly a function of the mass of solids ($M_s$) in the sorbent R.V.'s (0.075 g for each of the clay and mineral R.V.'s when 5.0 ml of suspension are used), and the density

---

*The derivation of Equation (5-1) assumes losses are negligible. The inclusion of losses (proportional to solute concentration) simply adds a constant, k (loss proportionality constant), to both the numerator and denominator of the right-hand-side of Equation (5-1). This has the effect of slightly increasing the value of $X^{\#}_\ell$ but this effect is negligible for all practical purposes.

of the solids, $\rho_s$. The volume occupied by the solids is given by:

$$V_s = \frac{M_s}{\rho_s} \qquad . \tag{5-2}$$

Therefore, the water volume in the sorbent R.V.'s is:

$$V_\omega = V_\ell - \frac{M_s}{\rho_s} \qquad . \tag{5-3}$$

Table 5.2 gives the solid densities, $\rho_s$ (Weast and Selby, 1967); the volumes occupied by the solids, $V_s$, calculated from Equation (5-2); the values for $V_\omega$ calculated from Equation (5-3); the values for $X_\ell^\#$ calculated from Equation (5-1); and the experimentally-determined values of $\overline{X}_\ell^o$ (previously given in Table 5.1 -- shown here for comparison purposes). Table 5.2 shows that if the volume occupied by the solids is taken into account, six of the nine sorbent R.V.'s would still have higher solute concentrations than their corresponding control R.V.'s. Although this can perhaps be attributable to random error, it is interesting to note that there doesn't appear to be any correlation between the volume occupied by the solids, and the extent of the "volume exclusion effect" on solute concentration. For example, the $MnO_2$ solids occupy a relatively small volume of the suspension (because of their high density), and yet this sorbent gave the largest fractional difference between $X_\ell^\#$ and $\overline{X}_\ell^o$. Also, the $\gamma$-$Al_2O_3 \cdot 3H_2O$ solids displace the largest volume of water, and yet, resulted in no apparent volume exclusion effect (i.e., $X_\ell^\#$ was less than $\overline{X}_\ell^o$). Therefore, the "solids volume

TABLE 5.2 Solid Densities ($\rho_s$), Solids and Water Volumes in the Sorbent Reaction Vials ($V_s$ and $V_\omega$), Corrected Solute Concentrations in the Sorbent Reaction Vials ($X_\ell^\#$), and (Actual) Mean Solute Concentrations in the Control Reaction Vials ($\overline{X}_\ell^o$)

| Solid | | $\rho_s$ (g/cm$^3$)$^a$ | $V_s$ (cm$^3$ or ml)$^b$ | $V_\omega$ $^c$ | $X_\ell^\#$ $^d$ | $\overline{X}_\ell^o$ $^e$ |
|---|---|---|---|---|---|---|
| Montmorillonite* | $Ca^{+2}$ | ∿2.5 | 0.027 | 4.973 | 7020 | 7005 |
| | $Na^+$ | ∿2.5 | 0.030 | 5.470 | 6311 | 6413 |
| | $Al^{+3}$ | ∿2.5 | 0.030 | 5.470 | 6391 | 6413 |
| Kaolinite | | 2.65 | 0.028 | 5.472 | 6487 | 6413 |
| Silica ($SiO_2$) | | 2.65 | 0.028 | 5.472 | 6494 | 6413 |
| Gibbsite [$Al(OH)_3$ or $\gamma$-$Al_2O_3 \cdot 3H_2O$] | | 2.4 | 0.031 | 5.469 | 6575 | 6607 |
| Calcite ($CaCO_3$) | | 2.8 | 0.027 | 5.473 | 6543 | 6402 |
| Pyrolusite ($MnO_2$) | | 5.06 | 0.015 | 5.485 | 6561 | 6402 |
| Hematite ($Fe_2O_3$) | | 5.26 | 0.014 | 5.486 | 6422 | 6402 |

[a] From Weast and Selby (1967)

[b] Calculated from Equation (5-2)

[c] Calculated from Equation (5-3)

[d] Calculated from Equation (5-1)

[e] Obtained from the experimentally-determined values reported in Table 5.1.

*The R.V.'s used in the $Ca^{+2}$-montmorillonite experiment contained liquid volumes of 5.0 ml instead of 5.5 ml.

exclusion" hypothesis may not completely account for some of the anomalous data (e.g., the cases of $MnO_2$ and $CaCO_3$, in which $X_\ell^\# >> \overline{X}_\ell^o$ [relative to the other data]). However, the differences between the paired values of $X_\ell^\#$ and $\overline{X}_\ell^o$ in Table 5.2 are still not significant at the 95% confidence level, and therefore, definite conclusions cannot be drawn at this point.

Other experiments were performed with TCE and these inorganic components, in order to elucidate the effects of equilibration time and solute concentration. The results are shown in Tables 5.3 and 5.4. Note that in all cases the adjusted sorbent R.V. solute concentrations are higher than their corresponding controls. These two tables demonstrate that the lack of positive adsorption (and the possibility of slight negative adsorption) of TCE with these solids is clearly not an artifact of equilibration time or solute concentration.

An issue that perhaps should be addressed at this point concerns the following question: If negative or positive adsorption is occurring with these inorganic solids, what is the minimum detectable level that is statistically significant (e.g., at the 95% confidence level), given the variances of the pertinent variables? An analysis of error propogation* for the functions defining the dependent variables $C_s$ (given by Equation [4-13]) and $K_d$ (= 1000 $C_s/C_\ell$, where $C_\ell$ is given by Equation [4-1]) revealed that the variances (observed or estimated) for $X_{\underset{\sim}{\ell}}^i$, $V_\ell$, $H_c$, $M_s$, and 6.4 ml, are each negligible relative to the variances for $X_\ell$ and $X_\ell^o$, for the case of the clays and minerals.

---

*See Appendix F for the error propogation analysis for $K_d$.

TABLE 5.3 Effect of Equilibration Time on the Interaction Between TCE and $Ca^{+2}$-Saturated Montmorillonite Clay

| Equilibration Time (days) | $\overline{X}_\ell$ (CPM/ml)* | $X_\ell^{\#}$ (CPM/ml) | $\overline{X}_\ell^{o}$ (CPM/ml)* |
|---|---|---|---|
| 3 | 1068 (± 1.0%) | 1062 | 1024 (± 4.0%) |
| 11 | 835 (± 2.6%) | 831 | 818 (± 3.1%) |

*Mean values based on three replicate R.V.'s; coefficients of variation are given as the ± values in parentheses. (The differences between the 3-day and 11-day values represent TCE losses.)

TABLE 5.4 Effect of TCE Solute Concentration on the Interaction Between TCE and $Ca^{+2}$-Saturated Montmorillonite Clay[†]

| $\overline{X}_\ell$ (CPM/ml)* | $X_\ell^{\#}$ (CPM/ml) | $\overline{X}_\ell^{o}$ (CPM/ml)* |
|---|---|---|
| 1477 (± 2.5%) | 1470 | 1428 (± 2.1%) |
| 7055 (± 0.87%) | 7020 | 7005 (± 1.5%) |
| 14950 (± 1.2%) | 14876 | 14574 (± 3.4%) |

[†] Equilibration Time = 2 days; the R.V.'s used in this experiment contained total liquid volumes of 5.0 ml.

*Mean values based on three replicate R.V.'s; coefficients of variation are given as the ± values in parentheses.

Since $C_s \propto (X_\ell^o - X_\ell)$, or more specifically, for the case of the clay/mineral solids, $C_s \propto |\overline{X}_\ell^o - X_\ell^\#|$, the variance of $X_\ell^\#$ must be estimated before proceeding. An error propogation analysis on the expression for $X_\ell^\#$ (given by Equation [5-1]) revealed that the variances of all terms (independent variables and constants) in Equation (5-1) are negligible compared to the variance of $\overline{X}_\ell$. Therefore, it is assumed that the variance of $X_\ell^\#$ is essentially identical to that for $\overline{X}_\ell$. Therefore, the question of significant positive or negative adsorption really becomes a question of whether the difference between the means $\overline{X}_\ell^o$ and $X_\ell^\#$ is significant at the 95% confidence level. In order to carry out the analysis which answers this question, the following values were considered to represent approximate "averages" for the applicable variables from the previous experiments in this section with TCE:

$$\overline{X}_\ell^o = 6500 \text{ CPM/ml} \qquad \text{C.V.} = \pm 1\% \qquad \therefore \text{S.D.} = \pm 65$$

It was assumed that $\overline{X}_\ell$ (and hence, $X_\ell^\#$) had the same C.V. (and hence, S.D.) as $\overline{X}_\ell^o$, for the sake of simplicity. The key was to solve for that value of $X_\ell^\#$ which yields significant difference between the means ($\overline{X}_\ell^o$ and $X_\ell^\#$) at the 95% confidence level (C.L.). Since three replicate samples were used for control R.V.'s, and three for the sorbent R.V.'s, the student's t-distribution is applicable with $n_1 + n_2 - 2$ $(= 3 + 3 - 2 = 4)$ degrees of freedom. A two-tailed t-test (since we are interested in the minimum detectable [significant] positive or negative adsorption) was employed. The results showed that $|6500 \text{ CPM/ml} - X_\ell^\#| > 170$, or that $X_\ell^\# > 6670$ or $< 6330$ CPM/ml, in order for the difference between the means to be significant at the 95% C.L. or greater. Substituting these values (along with the appropriate values for the other terms) back into the adsorption equation, yields a $C_s$ value of ± 0.17 μg/g. In other words, until the $|C_s|$ value rises to about 0.17 μg/g, we cannot be certain (with 95% confidence) that any adsorption or negative adsorption is, in fact, occurring. Hence, $C_s = \pm 0.17$ μg/g represents the approximate minimum detectable (statistically significant) sorption density, based on the approximate, experimentally-obtained means and variances used in the above analysis. This results in a minimum detectable $K_d$ value (at the 95% C.L.) of about ± 2.0. Therefore, in those cases where the difference between $\overline{X}_\ell^o$ and $X_\ell^\#$ is not statistically significant at the 95% C.L. (which is the case for almost all the results in this section), we can only claim that $|C_s|$ and $|K_d|$ are less than certain values, which for TCE were derived above.

The experimental procedures used in the test for adsorption of tetrachloroethylene (PCE*) onto the inorganic soil components were identical to those used for TCE, except as follows:

(a) All the solids were tested in a single experiment using a single set of controls (consisting of four replicates).

(b) Two replicates were used for each sorbent R.V.

Figure 5.1 depicts a bar graph of the results. Precision of the data was excellent (as before), and ranged from 0.035% to 2.3% (expressed as the coefficient of variation). Notice again that the $\overline{X}_\ell$ values are each higher than the $\overline{X}_\ell^o$ value.

---

*The symbol "PCE" is sometimes used in this thesis to designate tetrachloroethylene since this chemical is commonly called perchloroethylene.

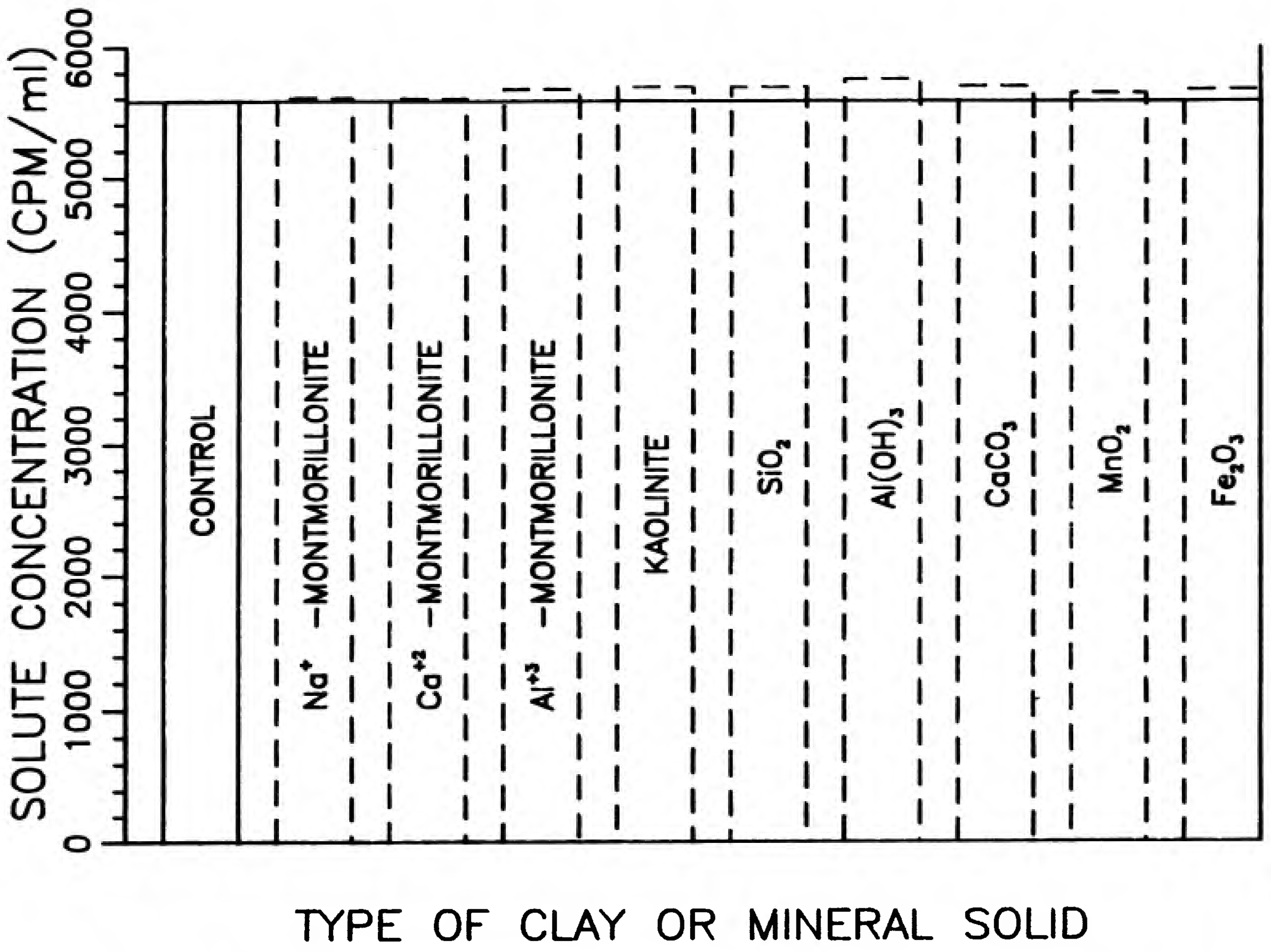

FIGURE 5.1 Test for Adsorption of Tetrachloroethylene ($C_2Cl_4$) onto Clays and Minerals

Figure 5.2 depicts the PCE adsorption test using the corrected (adjusted) values for the sorbent R.V.'s. As in the case of TCE, accounting for the solids volume does not seem to completely explain the general trend of higher solute concentrations in the sorbent versus control R.V.'s.

Figures 5.3 and 5.4 show the results for the adsorption experiments with $CHCl_3$ and $CCl_4$, respectively, in which the sorbent data values have been corrected using Equation (5-1), as in the case of PCE. Figure 5.3 shows that even after correcting for the effect of the solids volume, each of the sorbent R.V.'s still contain higher solute concentrations than the control. The probability of this occurring simply due to random errors in the $\overline{X}^o_\ell$ and $X^\#_\ell$ variables is 0.00195 (i.e., less than two chances in a thousand). Therefore, the cause for these results must either be a systematic error, or the presence of slight negative adsorption of $CHCl_3$ by these solids.

If negative adsorption is occurring then this would mean that the clay and mineral colloids are surrounded by an atmosphere of water molecules which excludes the presence of the $CHCl_3$ molecules. Furthermore, this "water-enriched atmosphere" surrounding the colloids would have to remain intact upon centrifugation. It is not known why these colloids might "repel" $CHCl_3$ molecules. A consideration of molecular properties would lead one to surmise that $CHCl_3$ would be the least likely candidate (of the four compounds in this research) to be negatively adsorbed by these colloids: Since $CHCl_3$ has the greatest dipole moment, it could potentially interact with the colloid-associated ions and their surrounding $H_2O$ molecules via ion-dipole and dipole-dipole interactions. However, this apparently does not occur.

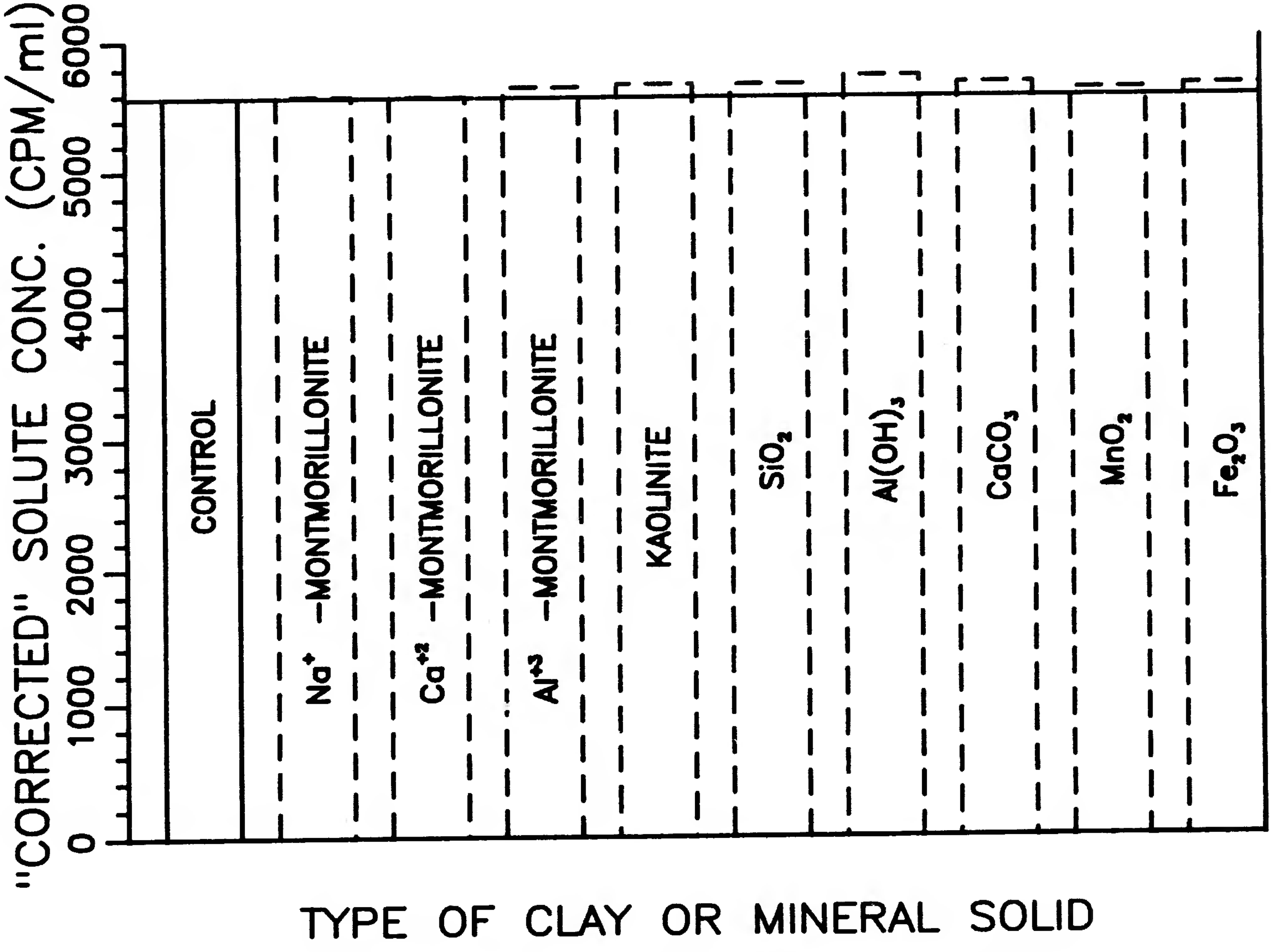

FIGURE 5.2 Test for Adsorption of Tetrachloroethylene ($C_2Cl_4$) onto Clays and Minerals (Using Solute Concentration Corrected for Volume Occupied by the Solids)

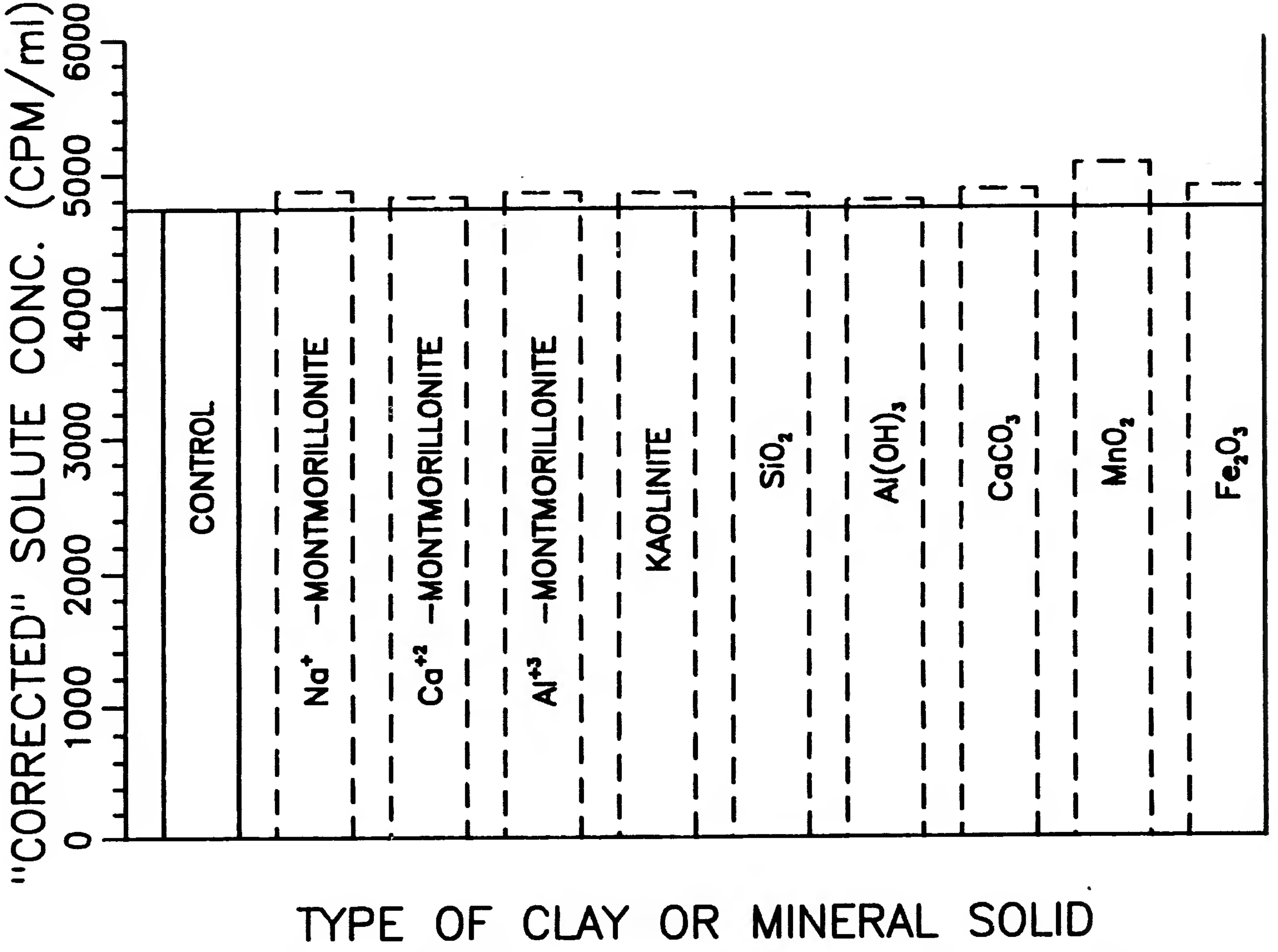

FIGURE 5.3 Test for Adsorption of Chloroform ($CHCl_3$) onto Clays and Minerals (Using Solute Concentration Corrected for Volume Occupied by the Solids)

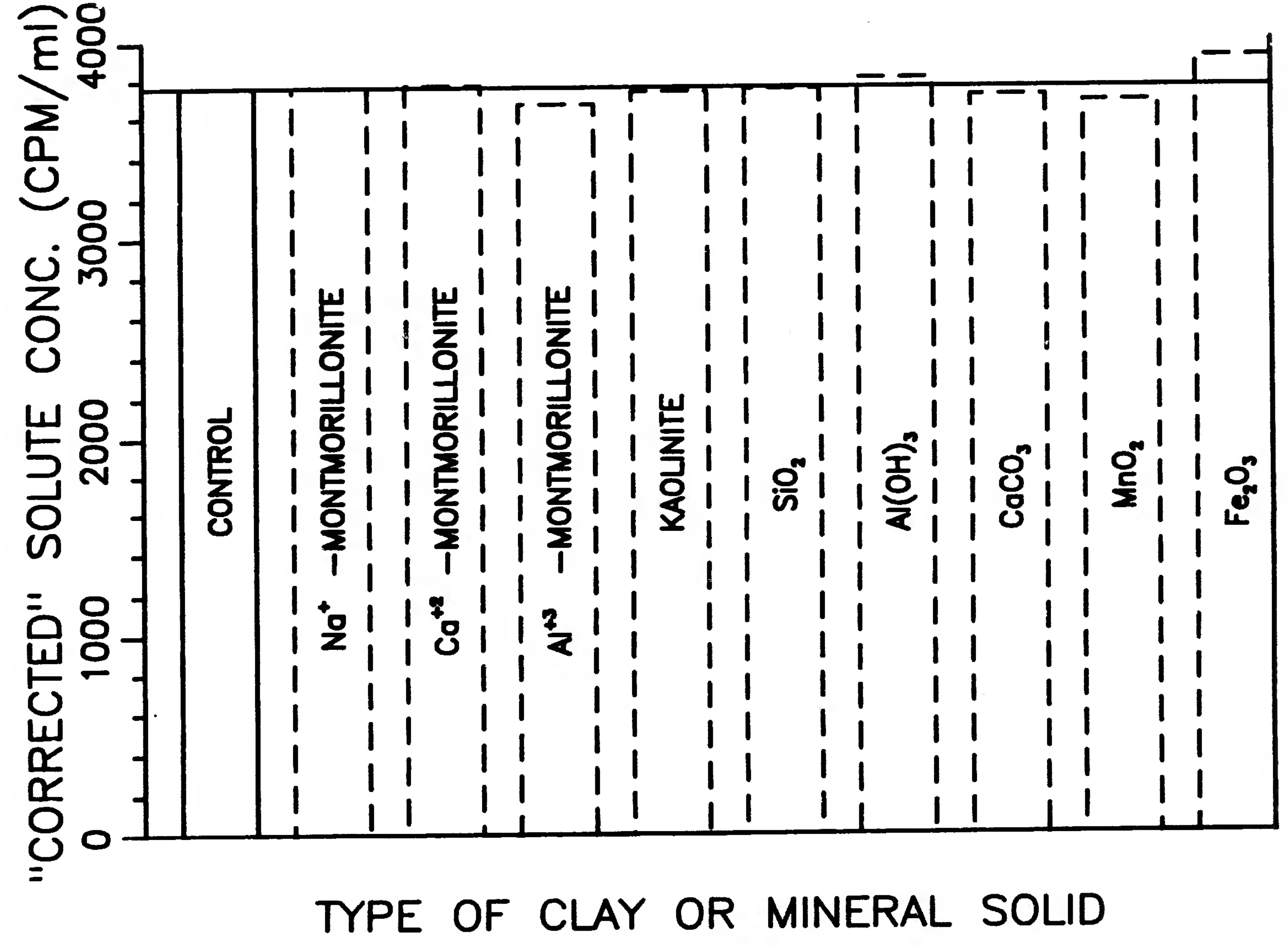

FIGURE 5.4 Test for Adsorption of Carbon Tetrachloride ($CCl_4$) onto Clays and Minerals (Using Solute Concentration Corrected for Volume Occupied by the Solids)

Systematic errors due to experimental procedures (e.g., pipeting) have been considered, but were rejected as a possible cause of these results. An example of one of the hypothesized systematic errors considered was that the presence of the solids somehow reduced the compound loss rate from the sorbent R.V., which, of course, would have resulted in a higher solute concentration for this R.V. However, since losses of $CHCl_3$ (from control R.V.'s) at 20°C over a two-day period are not detectable, this source of error was ruled out. Also, the non-inclusion of losses in Equation (5-1) for determining the value of $X_\ell^\#$ cannot account for the apparent negative adsorption since inclusion of losses in this equation results in a slight increase in apparent negative adsorption. (This is because the inclusion of losses in Equation (5-1) causes a slightly higher value of $X_\ell^\#$.)

Figure 5.4 presents the adsorption test results for $CCl_4$, which seem to contradict the general trend displayed by the other three compounds. That is, only three of the nine sorbents yield higher solute concentrations than the control. However, as in the previous results, the values of $X_\ell^\#$ are too close to the value of $\overline{X}_\ell^0$ to draw any statistically valid conclusions.

Some of the early work in this research (using the gas chromatographic headspace technique with stable compounds) indicated that the headspace concentrations (and, therefore, presumably the solution activities) for methylene chloride and 1,1,1-trichloroethane were significantly increased in the presence of a $Ca^{+2}$-saturated montmorillonite*. Lion and Garbarini (1983) reported similar results

---

*Experimental details are provided in Appendix B.

with toluene in an aqueous suspension of $Al_2O_3$. Such observations could have been due to a real increase in solution concentration caused by exclusion from water associated with the solids (i.e., a true negative adsorption). Alternatively, a high ionic strength induced by the charged colloids could have resulted in an increased activity coefficient for the uncharged solutes (i.e., a "salting out" effect), causing an increased headspace concentration via an increased effective Henry's constant.*

The "salting-out" effect would seem to be ruled out as a plausible explanation because: (a) increased headspace concentrations were not seen in identical experiments performed with TCE and PCE as solutes**, and (b) the later, radio-tracer studies reported in this chapter seem to indicate a real--although often insignificant--increase in solution concentration of the solutes in the presence of solid sorbents. If "salting out" were appreciable, one would, in fact, expect observed <u>decreases</u> in solution concentrations by virtue of greater transfer to the headspaces of samples with sorbents present. However, either or both of the following arguments could be made in regard to the absence of salting out in my experiments:

(a) There was insufficient headspace volume in the R.V.'s for salting out to be detectable.

(b) The sorbent R.V.'s were centrifuged, which thus eliminated the suspected cause of the salting-out effect (i.e., the suspended, charged colloids).

---

*Since the salting out phenomenon is believed to be caused by the same mechanism as negative adsorption (i.e., the ions in solution are surrounded by layers of structured [coordinated] water molecules which exclude the neutral solute molecules), the distinction between the two concepts is somewhat contrived. However, with respect to the experiments performed in this section, an important distinction is that the solids (causing negative adsorption) can be centrifuged from solution, whereas ions (causing salting out) cannot.

**Experimental details are provided in Appendix B.

In order to determine if these arguments had any merit, two additional experiments were performed. In each of these experiments the total liquid volume ($V_\ell$) was fixed at 3.5 ml, which allowed a headspace volume of 2.9 ml; and solute concentrations were sampled from both centrifuged and non-centrifuged, completely-mixed, sorbent R.V.'s. The presence of the solids in the scintillation cocktail (for the completely-mixed samples) had no apparent effect on the LS-9800 counting efficiency of the $^{14}C$ beta emissions. The corrected values (i.e., $X_\ell^{\#}$ and $X_\ell^{cm\#}$)* were calculated by entering the appropriate data into Equations (5-1), (5-2), and (5-3). (For example, the values for $V_\ell$ and $M_s$ in these experiments are 3.5 ml and 0.045 g, respectively.) The first experiment tested the effect at $Al(OH)_3$ on $C_2Cl_4$ solute activity, and the second tested the effect of $Al^{+3}$-montmorillonite on $CHCl_3$ solute activity. Table 5.5 summarizes the results of these experiments.

These data clearly demonstrate that salting out (i.e., increased solution activity) does not occur--even under conditions of increased headspace volume, and complete mixing of the sorbent R.V.'s. Neither one-tailed nor two-tailed t-tests at the 95% confidence level show significant differences between any of the mean values for the $CHCl_3/Al^{+3}$-montmorillonite experiment (but note that $X_\ell^{\#}$ is again slightly higher than $\overline{X}_\ell^{o}$). For the $C_2Cl_4/Al(OH)_3$ data, neither one-tailed nor two-tailed t-tests at the 95% confidence level yield significant differences between the $X_\ell^{cm\#}$ and $\overline{X}_\ell^{o}$ values (which is what would be expected if there were no effects of the solid on the activity coefficient). However, a one-tailed t-test shows that $X_\ell^{\#} > \overline{X}_\ell^{o}$, even at the 99% confidence level. (This provides additional evidence to support the negative adsorption hypothesis proposed earlier.)

---

*$X_\ell^{cm\#}$ ≡ the corrected solute concentration in the completely-mixed, non-centrifuged, sorbent R.V. (DPM/ml).

TABLE 5.5 Effect of Colloidal Solids on the Solution Activities of $C_2Cl_4$ and $CHCl_3$*

| Experiment no. and Solute/Solid | $\overline{X}_\ell$ (centrifuged) | $\overline{X}_\ell^{cm}$ (completely mixed) | $X_\ell^{\#}$ (centrifuged) | $X_\ell^{cm\#}$ (completely mixed) | $\overline{X}_\ell^{o}$ (control) |
|---|---|---|---|---|---|
| 1<br>$C_2Cl_4/Al(OH)_3$ | 7374 (± 110) | 7078 (± 205) | 7347 | 7052 | 6870 (± 70) |
| 2<br>$CHCl_3/Al^{+3}$-mont. | 6377 (± 36) | 6356 (± 10) | 6348 | 6327 | 6340 (± 28) |

*Notes: Data represent mean concentration values from three replicates, with standard deviations given in parentheses; units are DPM/ml; superscripts cm ≡ completely mixed, and # refers to the corresponding value corrected for solids volume [by using the appropriate values in Equation (5-1)].

It is not known why certain solutes exhibit this negative adsorption behavior in the presence of clay or mineral colloids. It was initially thought that perhaps the phenomenon is related to the compound's molecular polarity, since methylene chloride and 1,1,1-trichloroethane have substantially higher dipole moments than the compounds in this research. However, the more recent work of Lion and Garbarini (1983) with toluene caused rejection of this proposed relationship since the dipole moment of toluene is relatively low (even compared to $CHCl_3$ and $C_2HCl_3$).

An interesting question which arises in connection with the findings of this section is: What is the volume of bound (exclusion) water surrounding the colloids which could account for the observed negative adsorption? A balance on the total compound mass in the sorbent and control R.V.'s leads to the following equation for the volume of exclusion water, $V_{ex}$:

$$V_{ex} = \frac{[V_\ell + (6.4 - V_\ell)H_c](X_\ell^\# - X_\ell^o)}{X_\ell^\#} \quad . \qquad (5\text{-}4)$$

[Note that since Equation (5-4) incorporates the variable $X_\ell^\#$, the volume occupied by the <u>solids</u> is already accounted for, and does not need to be included in this expression.] If we consider the case of the $SiO_2$-TCE system, wherein $X_\ell^\# = 6494$ CPM/ml, and $X_\ell^o = 6413$ CPM/ml, the resulting value for $V_{ex}$ is 0.07217 ml (or $cm^3$). Since the specific surface area of the $SiO_2$ is known to be 0.54 $m^2/g$ (Pennsylvania Glass Sand Corp.), the approximate thickness of the exclusion water surrounding each $SiO_2$ colloid would have to be ∿1.78 μm or 17,800 Å. Assuming a water molecule "diameter" of 2.4 Å (McBride, 1982), this would amount to ∼ 7400 monolayers of $H_2O$ molecules surrounding each colloid. Although this seems to be a relatively large amount of bound water, it does not necessarily weaken the negative adsorption hypothesis. For example, the electric (diffuse) double layer "thickness" in aqueous solution at low ionic strength is on the order of 500 to 1000 Å (van Olphen, 1977, p. 35). It could be that the atmosphere of counterions (and their waters of hydration) surrounding each colloid is much thicker than this at the very low ionic strengths characteristic of the experiments herein. However, it is not known if such a large diffuse double layer would lie within the particle's plane of shear (slipping plane), in order to be considered bound (to the particle). Nevertheless, moderately long-range effects of charged surfaces on certain properties of the water phase (e.g., density) are reported to exist (van Olphen, 1977, p. 53), which appear to contradict certain aspects of colloid stability theory. Therefore, negative adsorption still appears to be the best explanation for the anomalous experimental results of this section.

In summary, the results of this section provide some evidence to suggest that the compounds examined (except possibly $CCl_4$) are slightly negatively adsorbed (i.e., excluded) by the clays and minerals investigated herein. Even accounting for the relatively small volume occupied by the solids in suspension could not explain this anomaly. Also, the compounds (based on the results for TCE) appear to be negatively adsorbed regardless of equilibration time or solute concentration. Lastly, the solution activity coefficients of these compounds appear to be unaffected by the presence of clays/minerals in suspension.

## B. Sorption and Desorption of the Selected Compounds with the Mineral Soil, Peat, Muck, and Activated Carbon in the Low Concentration Region

### 1. Collection of "Real" Soil Samples, and Preparation of Their Suspensions

Over 20 different types of soil samples were collected as potential sorbents in this research, with many showing insignificant sorption of the radiolabeled compounds. (It should be pointed out that only the mineral soils* with very low organic matter contents yielded negligible sorption.) All the soils collected fell into one of three categories: (1) mineral soil, (2) peat, and (3) muck (the latter two being considered organic soils). I decided to select a representative soil from each of these categories for examining sorption characteristics in greater detail. Therefore, only three aqueous suspensions of these "real" soils were made.

The mineral soil chosen for study (because of its high sorption capacity for the compounds used in this research) was collected on the bank of the Cascadilla Gorge near Hollister Hall, Cornell University, NY. An undisturbed site was selected, the surface litter (i.e., dead leaves, twigs, etc.) removed, and soil (to a depth of ∿20 cm) was placed in plastic sample bags and sealed. Professor Ray Bryant (Agronomy Department, Cornell University) classified this soil as a *Udifluvents*

---

*A mineral soil is defined as one consisting predominantly of, and having its properties determined predominantly by, mineral matter; and usually contains <20% organic matter (Brady, 1974; Foth, 1978; Hausenbuiller, 1978).

Entisol. A particle size analysis of this soil (see Table 5.6 below) revealed that its textural classification was loam. (This soil shall henceforth be referred to as the "mineral soil" in this research.)

The organic soils (peats and mucks) were collected on separate field trips (led by Professor John Duxbury of the Agronomy Department, Cornell University) as part of his "Organic Soils" course. The particular peat sample chosen to undergo extensive sorption study (a Limnic Sphagnofibrist Histosol) was obtained from a sphagnum moss-covered peat bog near Dryden, NY. The sample was taken from a depth of about 25 cm, and Duxbury (1983) stated that it was "virtually 100% organic matter". The muck soil was obtained from an "Edwards" muck (a Typic Medisaprist Histosol) near Savannah, NY, and was also taken from a depth of ~25 cm. The Fibrist suborder (under which the selected peat is classified) includes organic soils in which the undecomposed, fibrous, organic materials are easily identified. On the other hand, the Saprist suborder (under which the selected muck is classified) represents those Histosols containing highly decomposed organic materials. The selected peat and muck thus represent opposite ends of the suborder classification spectrum, and may shed light on the role of the stage of organic matter decomposition on sorption phenomena.

Table 5.6 below lists some of the characteristics of these soils which are pertinent to this research. These characteristics pertain to the soils, as dried from their respective suspensions, and are therefore representative of the fine particle-size fractions of each respective "whole" soil. The peat and muck soils obey the general rule that

TABLE 5.6 Pertinent Characteristics of "Real Soils"--Mineral Soil, Peat, and Muck (Obtained by Drying Liquid Samples of Their Prepared Suspensions)

| Soil | Fraction Organic Carbon[a] | Fraction Organic Matter[b] | Fraction Humic + Fulvic Acids[c] | Specific Surface Area[d] ($m^2/g$) |
|---|---|---|---|---|
| Mineral Soil[e] | 0.181 | 0.160 ± 0.004 | 0.0436 ± 0.0019 | 6.32 ± 0.08 |
| Peat | 0.410 | 0.903 ± 0.038 | 0.412 ± 0.004 | 0.339 ± 0.006 |
| Muck | 0.296 | 0.573 ± 0.017 | 0.228 ± 0.008 | 2.81 ± 0.02 |

[a] Determined by the "Wet Combustion" procedures described in Sections 29-2.3 and 29-3.3.2 of Methods of Soil Analysis, Part 2, 2nd Edition, Editors: Page, A. L., *et al.*, published by ASA-SSSA, Madison, WI, U.S.A. (1982). Samples were oven-dried at 50°C for 4 days prior to the test.

[b] Determined as the loss on ignition resulting from heating the sample for 24 hours at 430°C. (These values were selected since Davies [1974] showed that a 24-hour heating at 430°C did not destroy $CaCO_3$. Also, other researchers [Mitchell, 1932; Ball, 1964] have found that ignition of samples at 350° to 440°C destroys organic matter without removing the structural water associated with inorganic soil components.) The suspension samples received no prior chemical treatments, but were oven-dried (103°C for 2 days) to drive off non-structural water. That is, the fractions of organic matter reported are based on the oven-dry weights of the samples, and represent the means and standard deviations of three replicates.

[c] Procedure used was as follows: Three replicates of each soil suspension were centrifuged (3000 G for 30 min), the supernatants carefully discarded, then oven-dried for 4 days at 50°C. The R.V.'s + soils were then weighed, 5 ml of 0.1 N NaOH added, and placed on a tumbler (20°C) for 4 days to extract the humic and fulvic acids. Samples were then centrifuged (3000 G for 30 min), and the supernatants carefully discarded. The settled solids were dried for 4 days at 50°C, then reweighed. The resulting mass loss was attributed to the extraction of the HA and FA by the 0.1 N NaOH solution.

Table 5.6 continued

[d] Measured with a Quantasorb™ instrument (Quantachrome Corp.) using single-point B.E.T. isotherms with $N_2$ gas as the adsorbate. All samples were outgassed for a minimum of 1 hour at 90°C with dry $N_2$ gas. Values given represent the mean and standard deviation based on three runs (replicates) per sample. In an attempt to assess the accuracy of the Quantasorb™, the specific surface area of a "known" sample was determined. The solid was $\gamma$-$Al_2O_3$ (Alfa Products), and Professor Leonard Lion (Department of Civil and Environmental Engineering, Cornell University) had previously measured its specific surface area to be 95.8 $m^2/g$. Three runs with this solid on the Quantasorb™ yielded a specific surface area of 89.2 ± 0.8 $m^2/g$. Professor Lion pointed out that this somewhat low value was probably attributable to the accumulation of moisture by the $\gamma$-$Al_2O_3$, which was not removed by 1 hour of outgassing at 90°C. (This would have resulted in a higher apparent mass of solids being measured, and hence, an underestimated surface area per unit mass [i.e., specific surface area]).

[e] A particle size analysis was performed on the mineral soil (as collected--i.e., the whole soil), with the following results:

| Sand | Silt | Clay |
|---|---|---|
| 45.7% | 42.9% | 11.4% |

Therefore, the textural classification of the mineral soil is "loam". The particle size analysis was conducted using the "Pipette Method" described in Section 43-4.1 of *Methods of Soil Analysis, Part I*, Edited by Black, C. A., *et al*., Am. Soc. of Agron., Madison, WI (1965).

$f^*_{om} \approx 2f_{oc}$, but the mineral soil does not. (No explanation can be offered for this apparent discrepancy.) These data also show [by dividing column (c) by column (b)] that the organic matter contents of the mineral soil, peat, and muck are comprised of approximately 27%, 46%, and 39%, respectively, humic acid + fulvic acid (HA + FA). Lastly, the specific surface areas were measured using single-point B.E.T. isotherms with $N_2$ gas as the adsorbate.** By necessity, the sorbents must be completely dry prior to their surface area measurements. Therefore, the specific surface areas given in Table 5.6 are probably not at all representative of what they would be in aqueous suspension. This is especially true of the organic soil sorbents, which would be expected to have specific surface areas much higher (than those given in this table) when immersed in water. Obviously, the dehydration of these sorbents drastically alters their structures. Furthermore, since nitrogen is a relatively weak sorbate, it is probably unable to penetrate any internal structure present in the organic matter, just as it is unable to penetrate the internal surfaces of montmorillonite. Therefore, it is not known if the specific surface areas listed in Table 5.6 are relevant to this research; nevertheless, B.E.T. surface areas for soils are frequently reported in the literature pertaining to sorption by soils.

---

*$f_{om} \equiv$ fraction organic matter.

**A multi-point isotherm, using a sample of the muck soil, demonstrated that a B.E.T. plot of the data was relatively linear. (These data were obtained with the assistance of Professor Murray McBride [Agronomy Department, Cornell University], using the multi-point Quantasorb™ apparatus in the Agronomy Department.) Based on these data it was decided that use of single-point B.E.T. isotherms would be adequate for these sorbents.

The stock suspensions for these three "real" soils were prepared similarly. A large excess of each soil (∿100 g) was vigorously stirred with ∿2 l of distilled water in glass beakers for several minutes. The mixtures were then wet-sieved through a #20 U.S. standard mesh in order to remove twigs, gravel, roots, clumps, etc. The filtrates were then wet-sieved several times through a #70 U.S. standard mesh (which removed soil particles >210 μm size). (This was done to ensure that when the soil suspensions were mixed prior to and during the withdrawal of a sample, that there would be no large particles tending to settle out, creating a nonuniform suspension.) The final filtrates were then transferred to 1-liter, amber bottles, and capped. For the case of peat, the presence of soluble humic substances (as evidenced by the brown color of the supernatant liquid after several days of quiescent settling and 30 minutes of centrifugation at ∿3000 G*) necessitated the removal or reduction of this component.** Therefore, the peat suspension was transferred to several Nalgene™ bottles and centrifuged at ∿3000 G for 30 minutes. The brown supernatant was carefully discarded, replaced with distilled water, and the process repeated twice again. At the end of the third centrifugation, the supernatant was again replaced with distilled water, and the suspension transferred back to the stock bottle.

In order to ensure that pH and ionic strength differences were not factors affecting the relative sorption behaviors of these three

---

*Acceleration due to gravity is represented by the symbol "G" where $G = 9.8$ m/sec$^2$.

**Removal or reduction of the soluble humic material was desired primarily because of the dramatic effect of color on the sample quenching during LSC analyses.

sorbents, they were all adjusted to a common value. Their original pH values and conductivities were measured to be:

| Sorbent | pH | Conductivity (μmho/cm) |
|---|---|---|
| Mineral Soil | 7.7 | 225 |
| Peat (after washing) | 4.5 | 150 |
| Muck | 7.6 | 210 |

The common values selected were pH = 7.7 and conductivity = 225 μmho/cm (i.e., those values corresponding to the mineral soil). Therefore, the pH and conductivity of the peat and muck were raised to these values by adding the necessary amounts of NaOH and NaCl, respectively.

Note that because of the procedure used to prepare these "real" soil suspensions, the sorbent solids concentrations were unknown. The solids concentrations for these suspensions had to be estimated by measuring (in triplicate) the Total Residue (also called Total Solids or TS)* content of three, 10-ml samples withdrawn from each completely-mixed suspension. The mean values of these TS measurements were taken as the approximate solids concentrations for the suspensions and are shown below. (The total dissolved solids were negligible by comparison.)

| Sorbent | Total Solids (g/l) | Coefficient of Variation |
|---|---|---|
| Mineral Soil | 9.6 | 0.5% |
| Peat | 3.8 | 5.4% |
| Muck | 10.1 | 1.5% |

---

*Procedure used was in accordance with Standard Methods for the Examination of Water and Wastewater, 15th Edition, published jointly by APHA, AWWA, and WPCF, Part 209A, page 92 (1981).

### 2. Preparation of Powdered Activated Carbon (PAC) Suspension

The EPA (1983) reported that the organic compounds used in this study all have adsorption densities on the order of 10 mg/g (at a solute concentration ∿0.1 mg/l) on several different activated carbons. Calculations revealed that this corresponds to a PAC solids concentration of about 0.01 g/l (based on ∿50% adsorption of the compound from solution). Indeed, initial experiments within $^{14}$C-trichloroethylene showed that this PAC concentration resulted in ∿½ of the trichloroethylene being adsorbed from solution. Therefore, the PAC suspension was prepared by adding distilled water to 10 mg PAC (No. C-5260, Untreated powder, 250-350 mesh, Sigma Chemical Co.) to make a 1-liter suspension. The pH and conductivity of this suspension were 8.0 and 77 μmho/cm, respectively.

### 3. Results and Discussion

The isotherm calculative procedures for this section (as well as the remainder of this chapter) are described in Chapter IV and Appendix E, unless otherwise noted. All experiments in this section were conducted at T = 20°C ± 0.1°C (except for TCE with the mineral soil, which was 20°C ± 2°C). The pH and approximate ionic strength ($I$)* for the "real" soil suspensions were each 7.7 and ∿0.0036 M, respectively. The pH and $I$ for the PAC suspension were 8.0 and ∿0.0012 M, respectively.

Figure 5.5 presents the sorption kinetics data for $C_2Cl_4$ and $CHCl_3$ with the mineral soil. Note that the bulk of the sorption occurs

---

*Calculated from the previously-given correlation by Snoeyink and Jenkins (1980): $I = 1.6 \times 10^{-5} \times$ conductivity (μmho/cm). (All "$I$" values calculated in this chapter are based on this formula.)

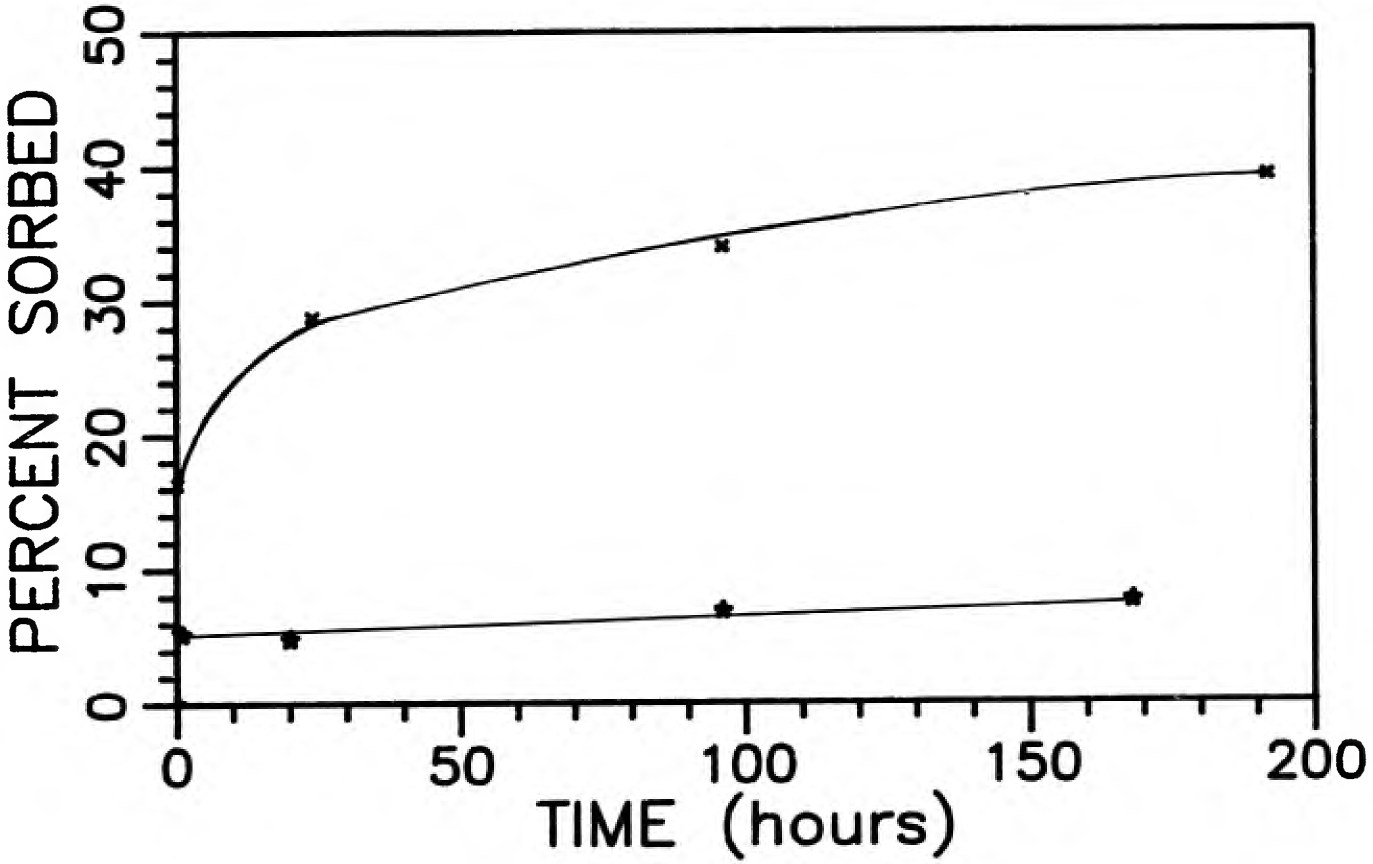

FIGURE 5.5 Sorption Kinetics for $C_2Cl_4$ (x) and $CHCl_3$ (★) with the Mineral Soil

(relatively) rapidly, with (what appears to be) almost complete sorption of $CHCl_3$ occurring within the first hour of the experiment. The rate of sorption for $C_2Cl_4$ is somewhat slower, which is what one would expect if sorption kinetics are diffusion-limited (since diffusivities in liquids generally vary inversely with the solute's molecular weight or volume). Based on these data, I decided to use an equilibration time of 4 days (i.e., 96 hours) for all isotherm experiments with the mineral soil*. (That is, the sorption and desorption cycles were each 4 days long)

Figures 5.6 through 5.9 present the sorption and desorption isotherms for $C_2HCl_3$, $C_2Cl_4$, $CHCl_3$, and $CCl_4$, respectively, with the mineral soil as the sorbent in all cases. These isotherms represent the "low concentration range" which is arbitrarily defined as $C_\ell <$ 200 μg/l, so that at least three data points would be included in

---

*Although some additional sorption of both $CHCl_3$ and $C_2Cl_4$ appears to be occurring beyond 4 days, at the time these data were gathered, this slight increase was believed to be relatively minor. Furthermore, the vast majority of soil sorption isotherms reported in the literature are based on equilibration times of one day or less (with many of these ranging merely from 0.25 to 4 hours). More importantly, with respect to my sorption kinetics data, it was computed that the fractional increment of sorption (by the mineral soil) beyond 4 days was approximately the same for $CHCl_3$ and $C_2Cl_4$. Assuming that this would also hold true for $CCl_4$ and $C_2HCl_3$, the lack of attainment of "true" equilibrium would not affect correlations of $K_d$ to sorbate properties (since the "nonequilibrium" $K_d$ values would have the same relative values as the "true" equilibrium $K_d$ values). However, it would (or might) affect correlations of $K_d$ to sorbent properties. One of the final experiments of this research revealed that some additional sorption by the mineral soil occurs, even up to 22 days (and possibly beyond) (see Section J of this chapter). This appears to be the only sorbent studied which displays this curious behavior, which may, in fact, explain some of the anomalous data obtained for the mineral soil. These issues are discussed in Section J.2. of this chapter.

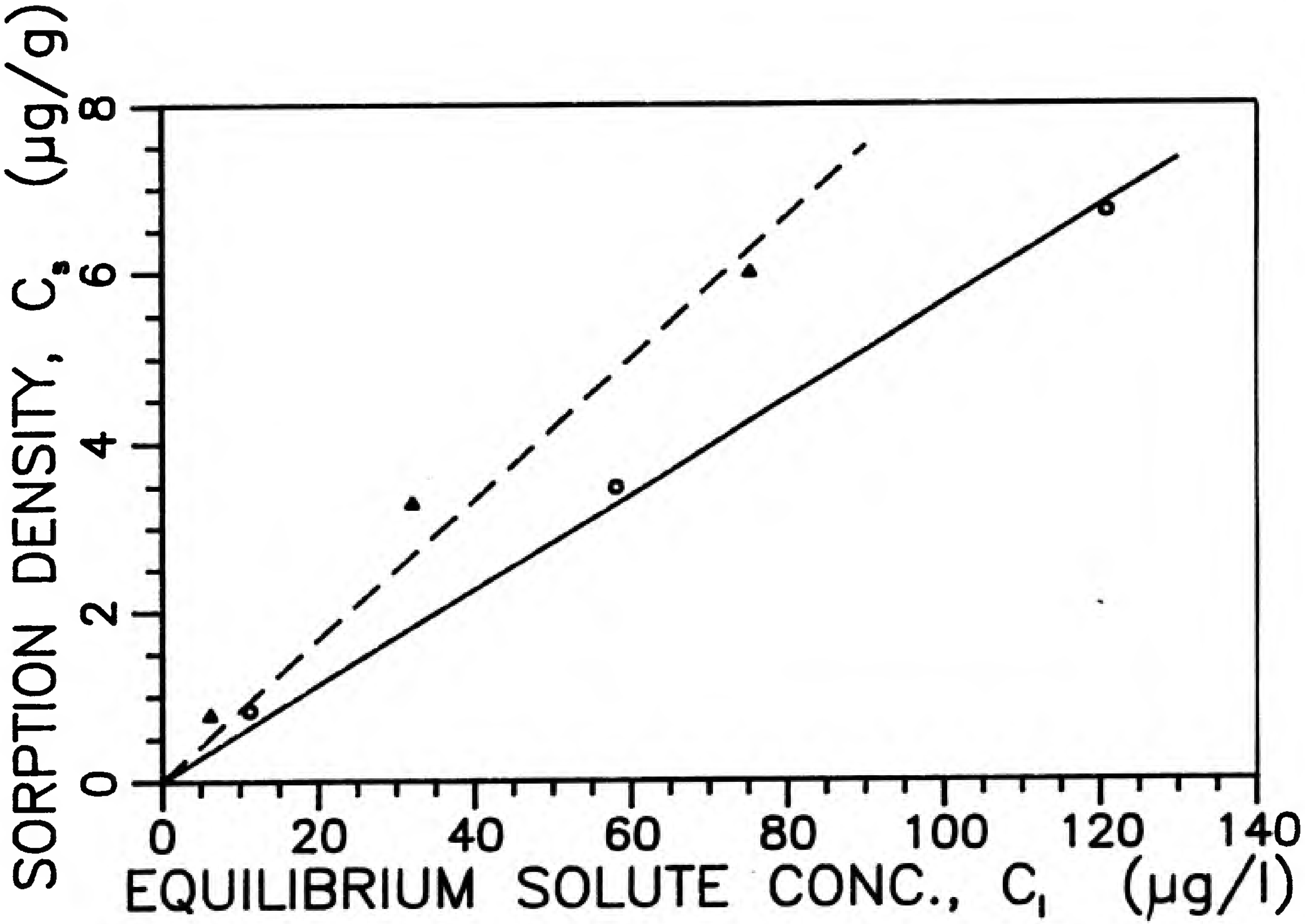

FIGURE 5.6 Sorption (○) and Desorption (Δ) Isotherms for $C_2HCl_3$ with the Mineral Soil

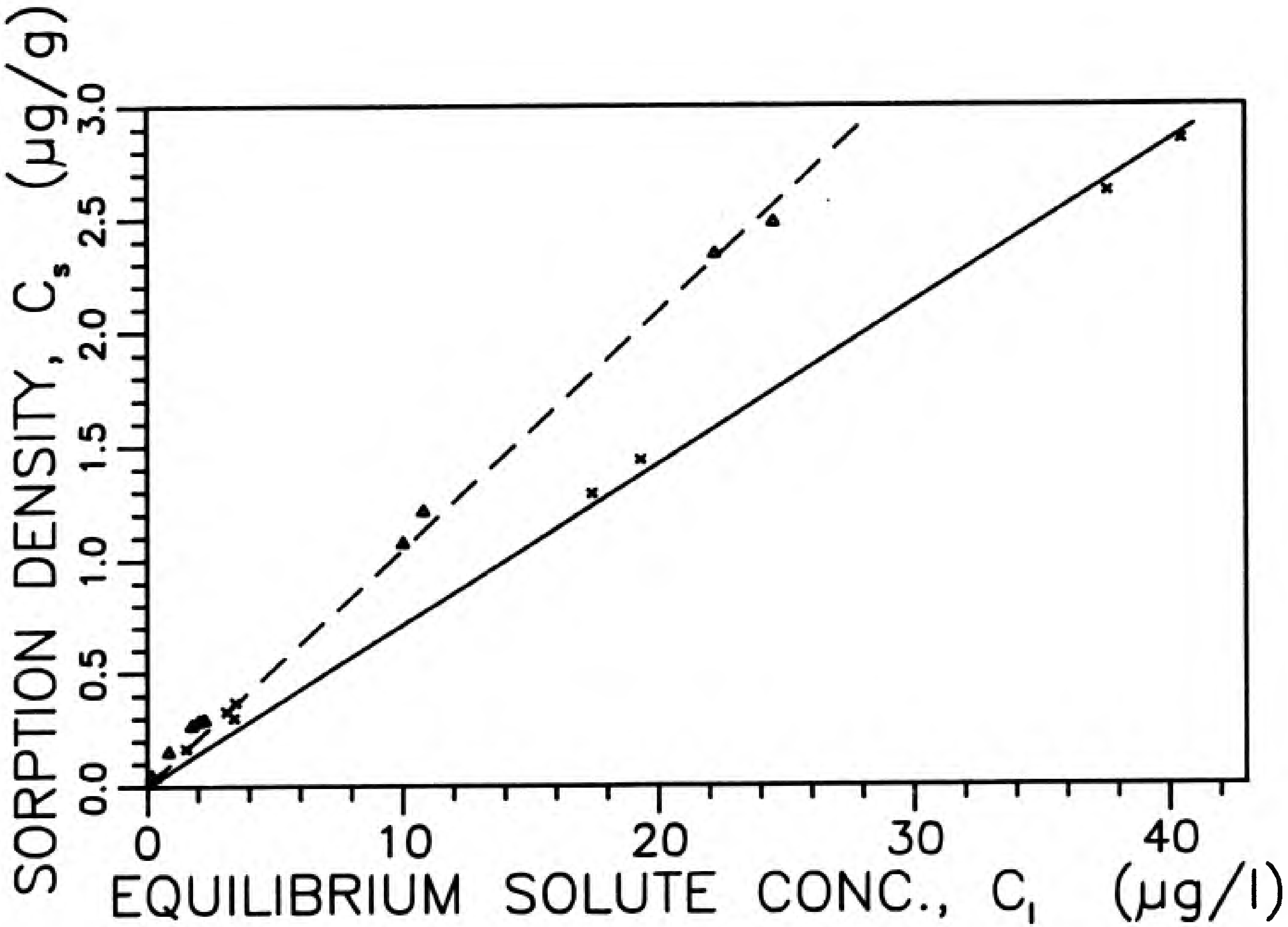

FIGURE 5.7 Sorption (x) and Desorption (Δ) Isotherms for $C_2Cl_4$ with the Mineral Soil

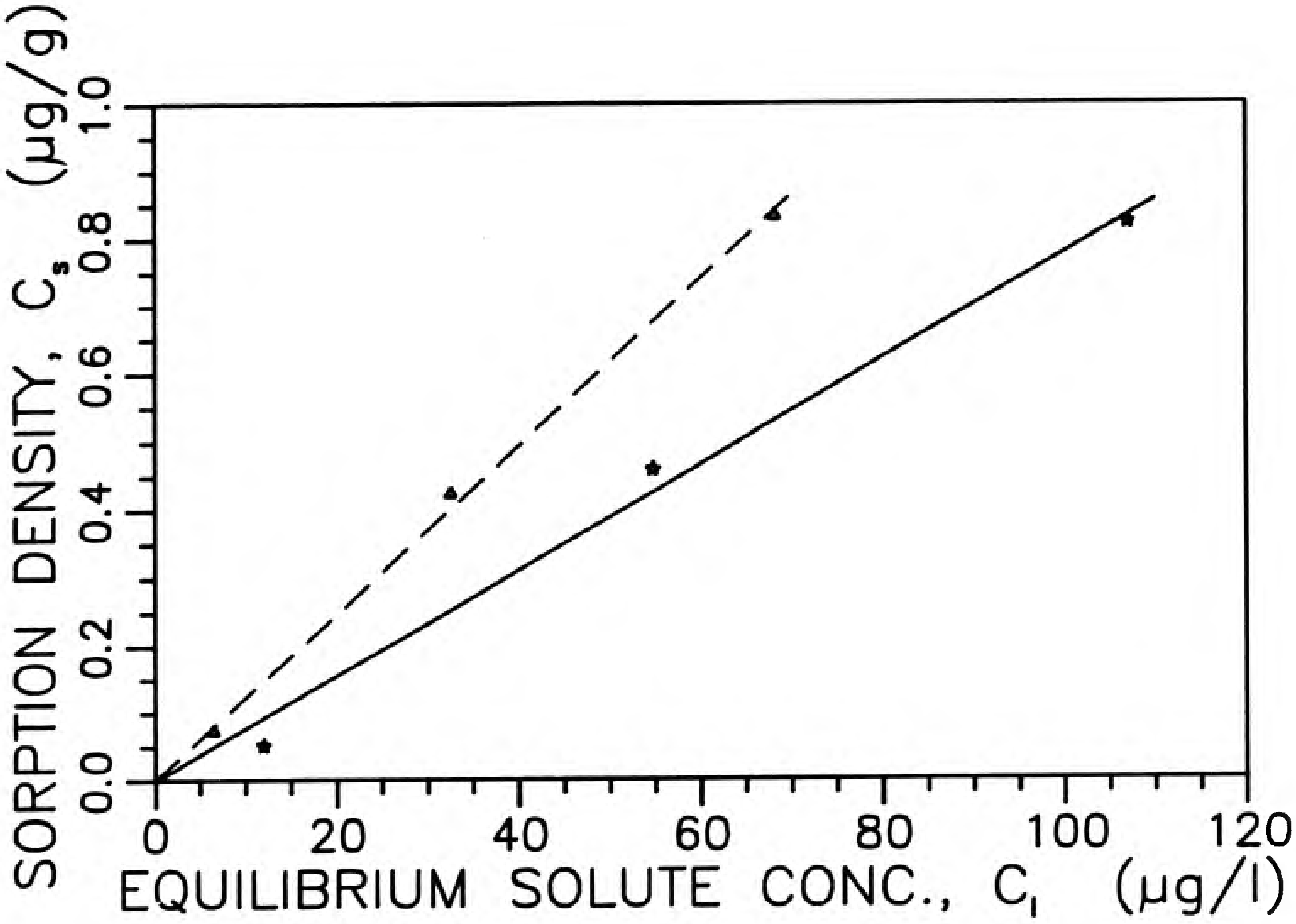

FIGURE 5.8 Sorption (★) and Desorption (△) Isotherms for $CHCl_3$ with the Mineral Soil

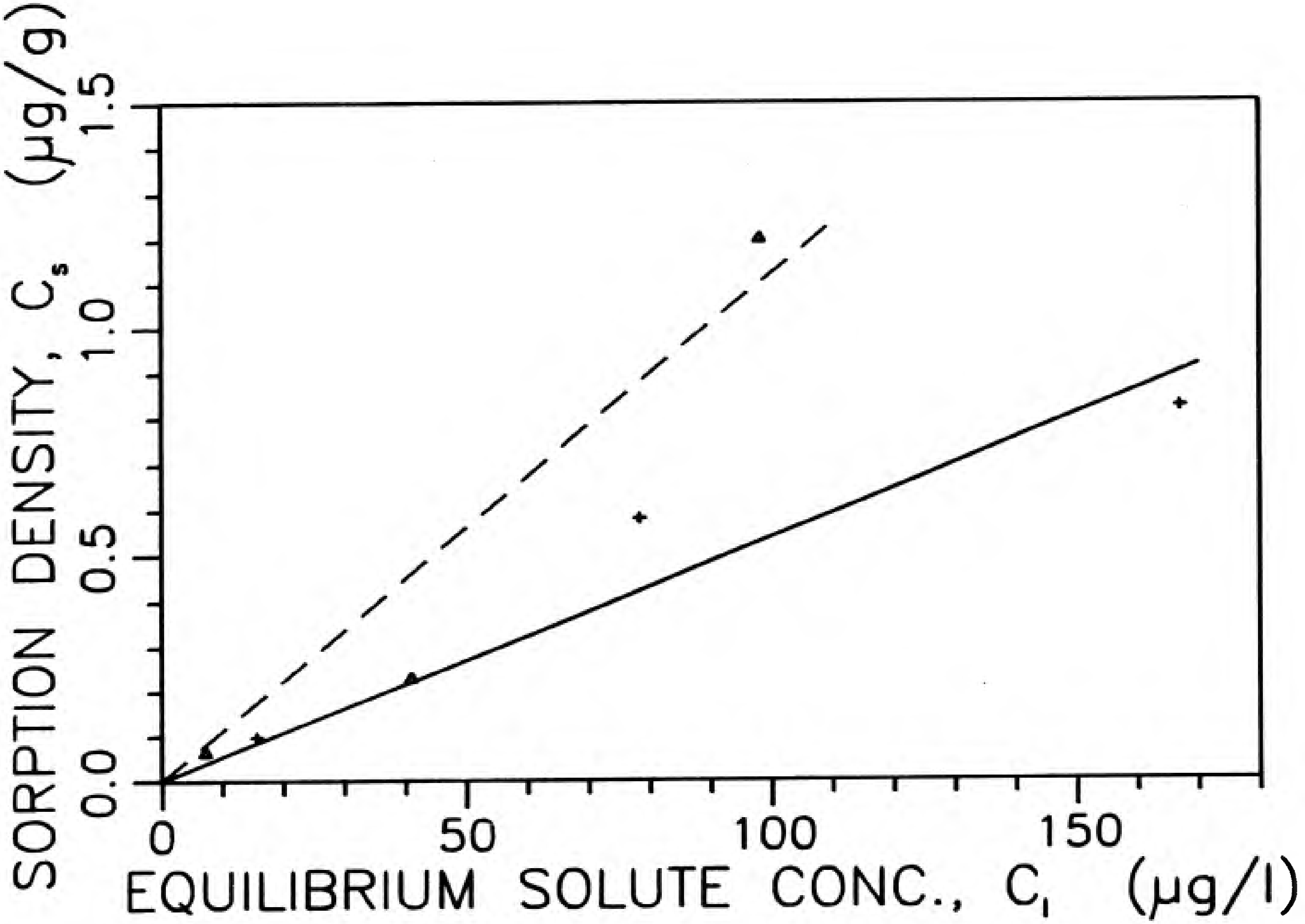

FIGURE 5.9 Sorption (+) and Desorption (Δ) Isotherms for $CCl_4$ with the Mineral Soil

this region. (Extended isotherms, which cover a higher solute concentration range, are presented and discussed in Section H.) Also, the lines depicted in these figures represent least-squares regressions, which have been "forced" through the origin. That is, the origin data point (0, 0) was given "infinite" weighting since all isotherms (whether they describe *ad*sorption or *ab*sorption) must pass through the origin. Note that in most cases the data appear to be fairly linear, which is consistent with the majority of the research findings for sorption of nonionic compounds with soils. However, there is one glaring anomaly in Figures 5.6 through 5.9: The desorption isotherms each lie above their respective sorption isotherms, giving the appearance that sorption of these compounds with the mineral soil is not thermodynamically reversible. Two additional experiments were performed in the final phase of this research in an attempt to determine the cause for this peculiar behavior. The results and discussion of these experiments are presented in the final section of this chapter, "Desorption and Reversibility". However, to satisfy the reader's (likely) curiosity at this point, it was discovered in these later experiments that these "nonsingular" sorption and desorption isotherms for the mineral soil are apparently due to the lack of attainment of *sorption* equilibrium.

Figure 5.10 summarizes the *sorption* isotherms for the four compounds with the mineral soil. (In this thesis, it is assumed that the sorption isotherm [as opposed to the desorption isotherm] more accurately represents the equilibrium relationship between water, sorbent, and solute, due to the possible uncertainties in quantifying mass losses which occur during the desorption experiment. Therefore, only *sorption*

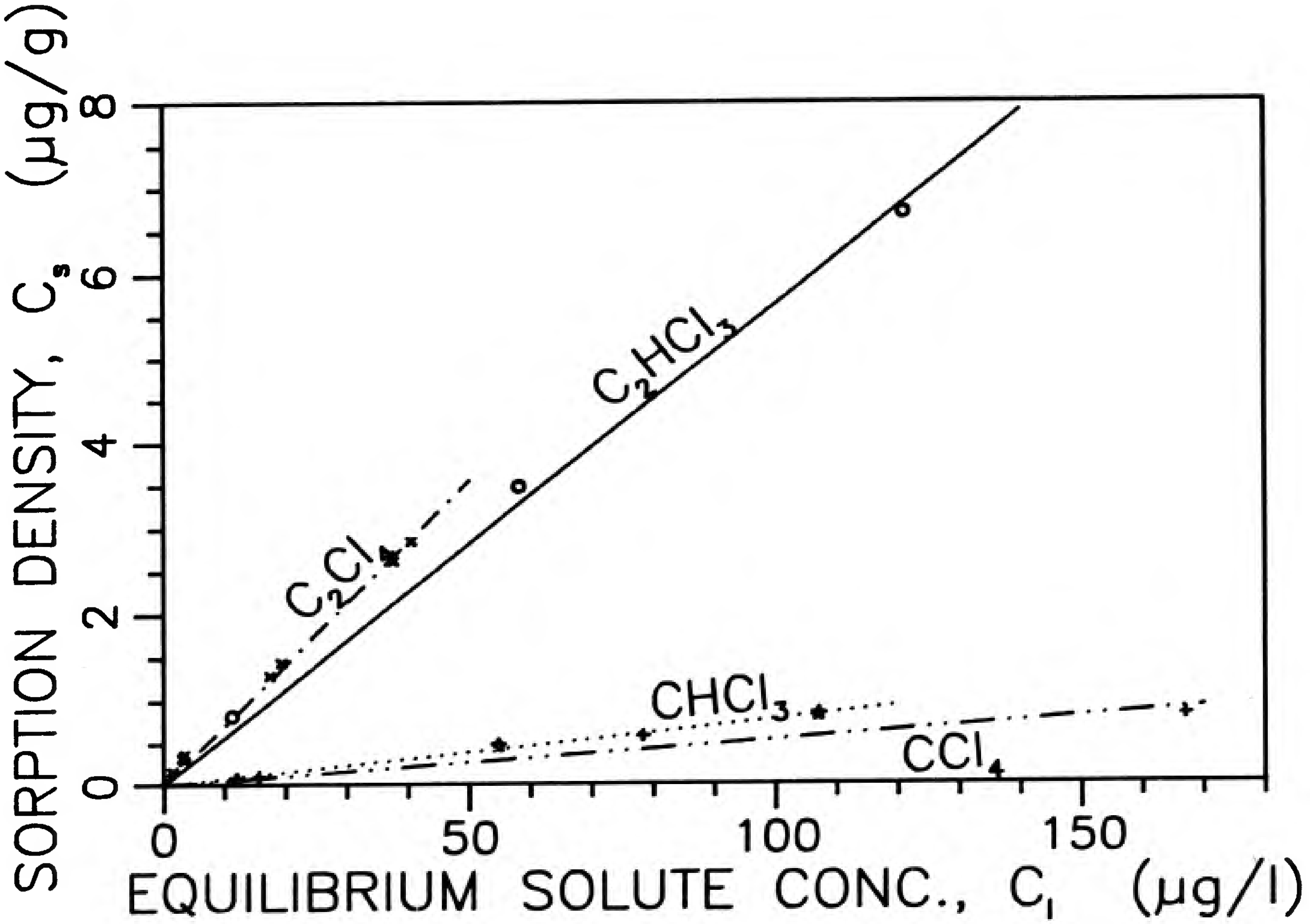

FIGURE 5.10 Sorption Isotherms for All Compounds with the Mineral Soil

isotherms and their distribution coefficients are used in exploring possible interrelationships and correlations reported in this research.) Note that the order of sorptive strength is: $C_2Cl_4 > C_2HCl_3 >> CHCl_3 > CCl_4$.

Figure 5.11 depicts the adsorption kinetics for $C_2HCl_3$ (TCE) onto the powdered activated carbon (PAC). Based on these data, an equilibration time of 48 hours (for each of the adsorption and desorption cycles) was selected for all PAC experiments.

Figures 5.12 through 5.15 show the adsorption and desorption isotherms (low concentration region) for each of the compounds onto PAC. Note that all isotherms appear to be reasonably linear over this solute concentration range, and that there seems to be no consistency in the location of the desorption isotherm (with respect to the adsorption isotherm). That is, the desorption isotherm is slightly higher than the adsorption isotherm for the cases of $C_2HCl_3$ (Figure 5.12) and $CHCl_3$ (Figure 5.14); significantly lower for the case of $C_2Cl_4$ (Figure 5.13); and virtually identical for the case of $CCl_4$ (Figure 5.15). No explanation is offered for this variability in the location of the desorption isotherm (with respect to the adsorption isotherm) except experimental error--most likely in the desorption isotherm determination.

Figure 5.16 summarizes the adsorption isotherms for the four compounds onto PAC. The order of adsorption strength is: $C_2Cl_4 >> C_2HCl_3 >> CCl_4 > CHCl_3$.

Sorption (and desorption) experiments for both the peat and muck samples were run using equilibration periods of 4 days, as with the mineral soil. Desorption experiments for these sorbents were conducted

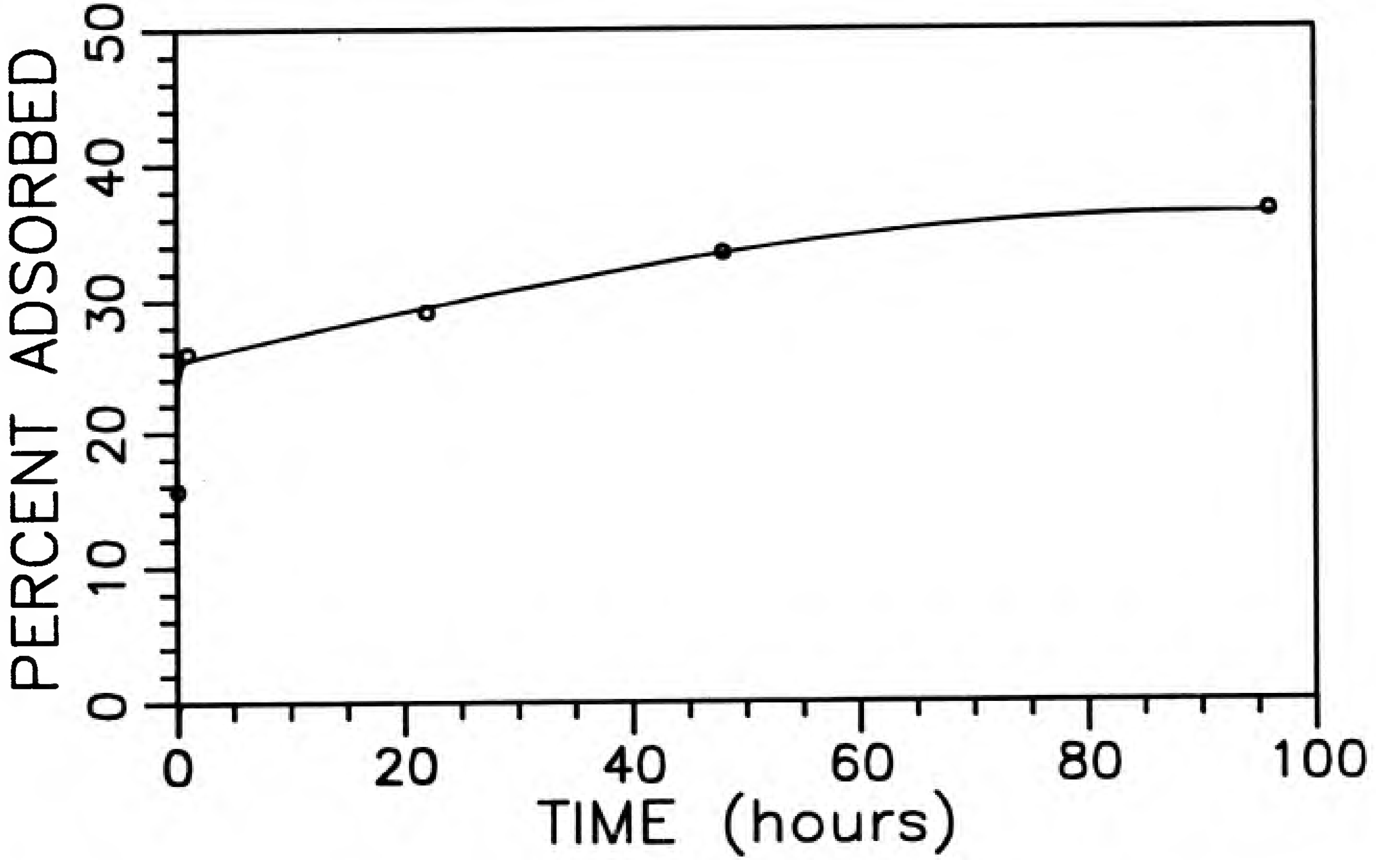

FIGURE 5.11 Adsorption Kinetics for $C_2HCl_3$ with Powdered Activated Carbon (PAC)

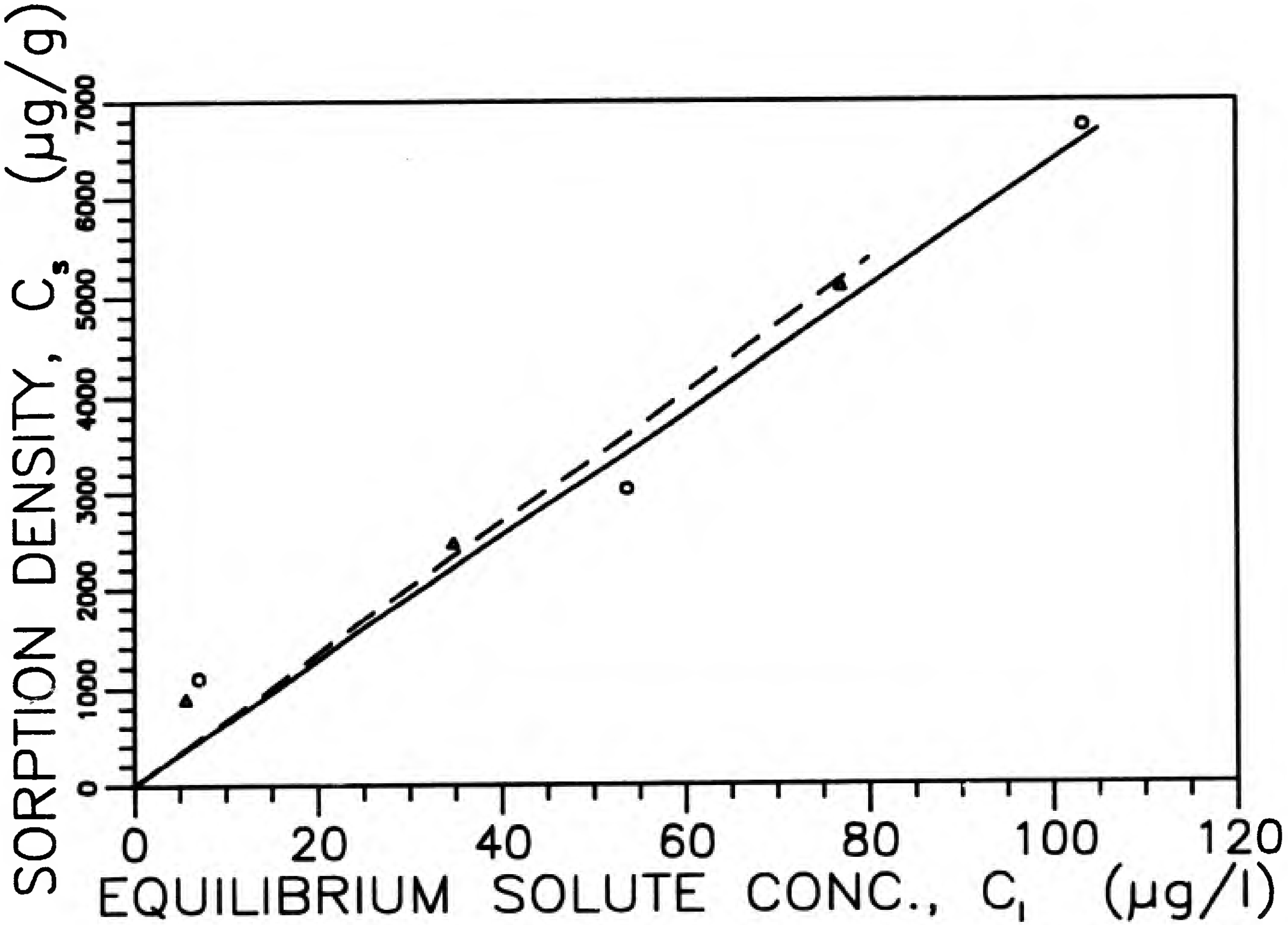

FIGURE 5.12 Adsorption (○) and Desorption (△) Isotherms for $C_2HCl_3$ with Powdered Activated Carbon (PAC)

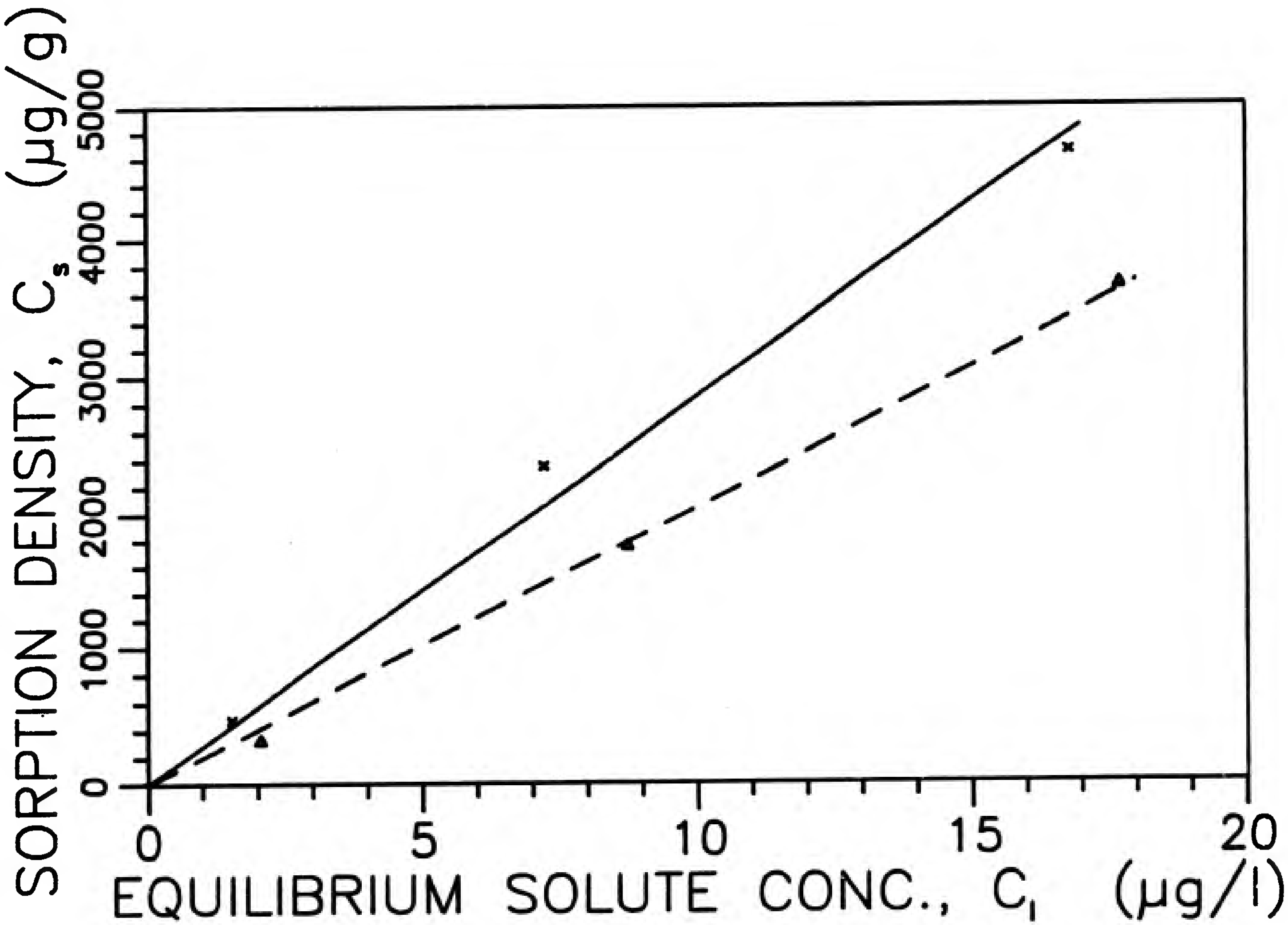

FIGURE 5.13 Adsorption (x) and Desorption (Δ) Isotherms for $C_2Cl_4$ with PAC

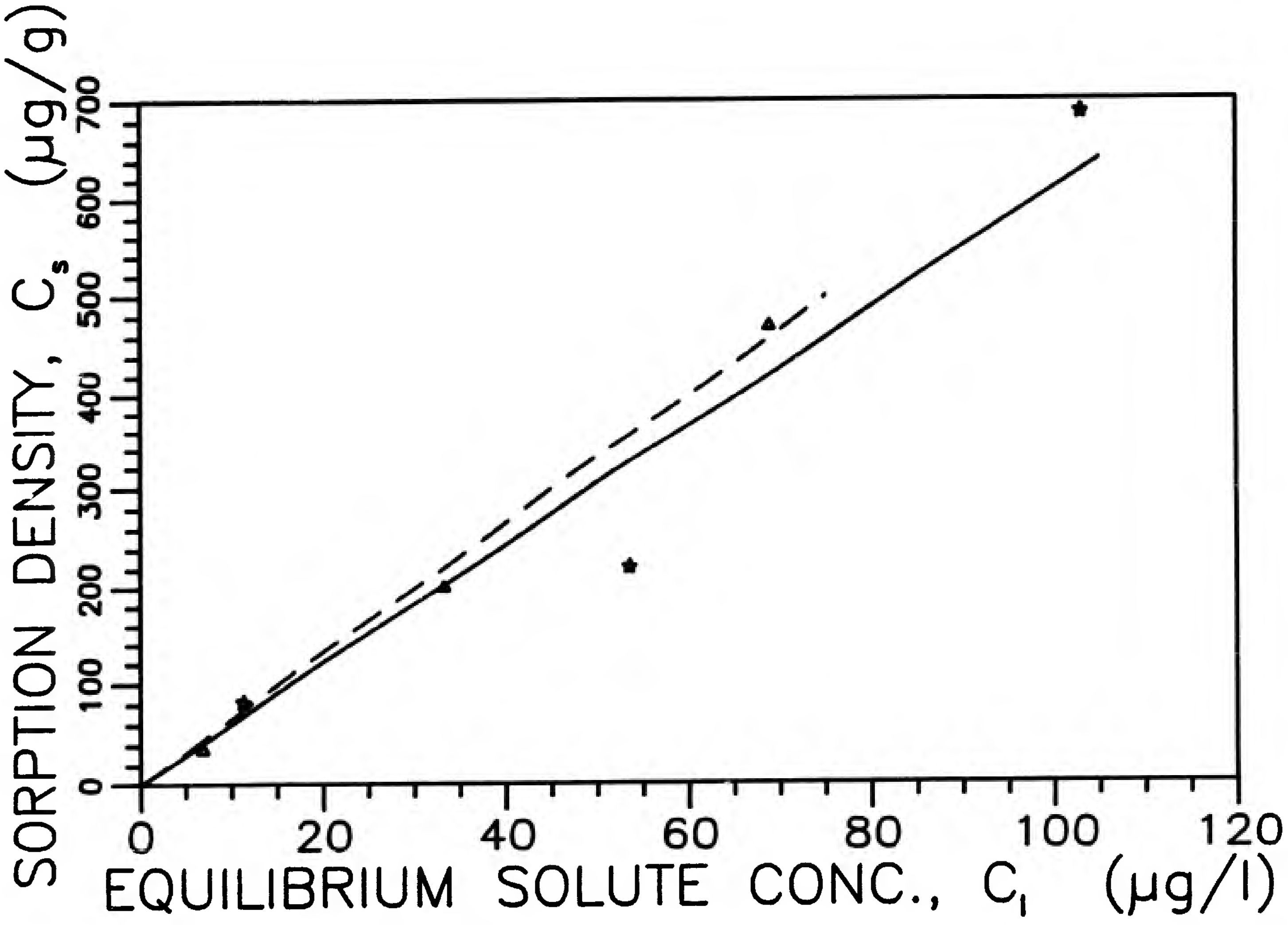

FIGURE 5.14 Adsorption (★) and Desorption (Δ) Isotherms for $CHCl_3$ with PAC

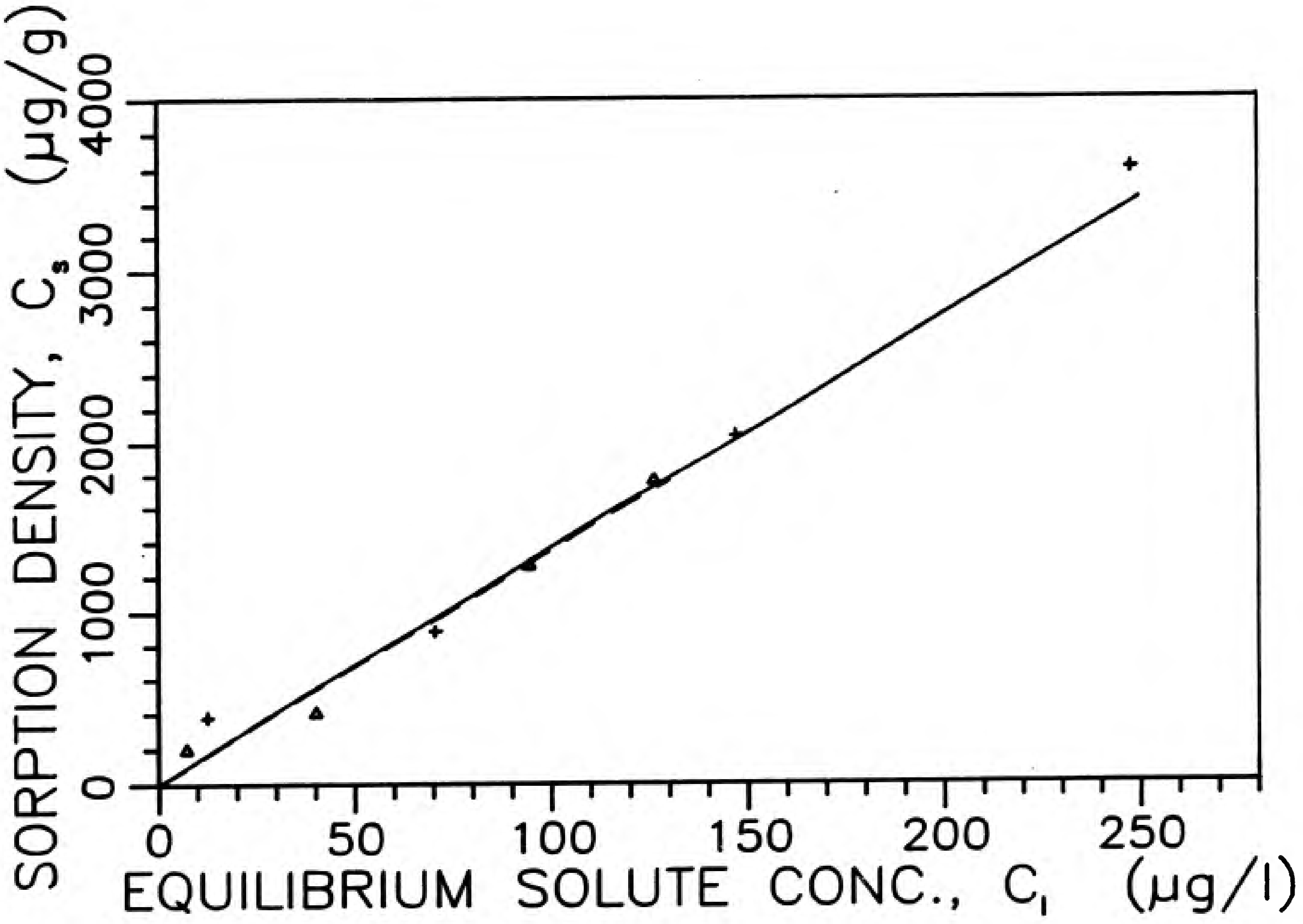

FIGURE 5.15 Adsorption (+) and Desorption (Δ) Isotherms for $CCl_4$ with PAC

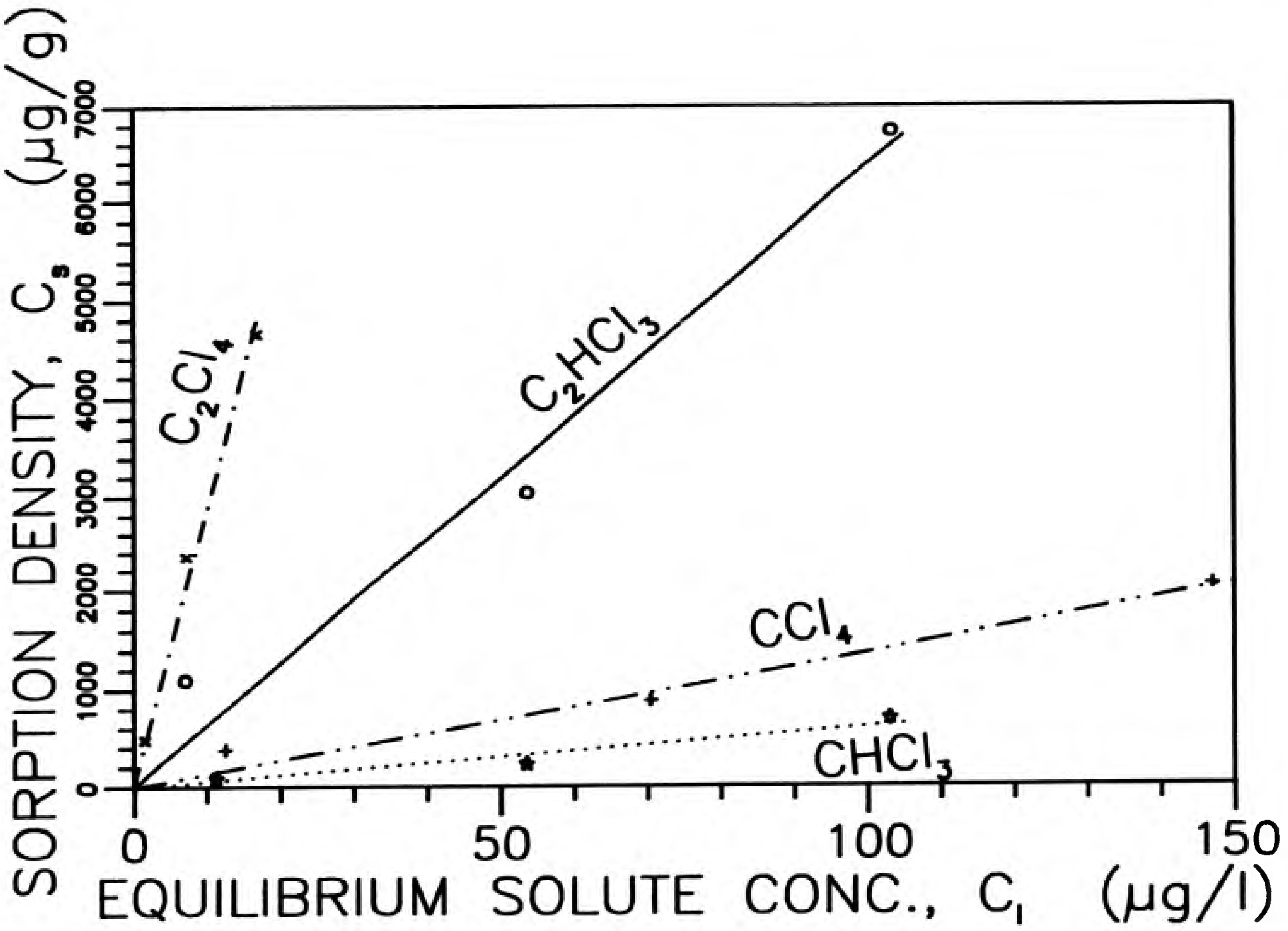

FIGURE 5.16 Adsorption Isotherms for All Compounds with PAC

only for the case of $C_2HCl_3$ (TCE), and the results are shown in Figures 5.17 and 5.19 for peat and muck, respectively. Note that the sorption and desorption isotherms for the peat/$C_2HCl_3$ system are virtually identical, indicating complete thermodynamic reversibility over the 4-day sorption and 4-day desorption cycles. The sorption and desorption isotherms for muck appear to be nonsingular; however, this may be due to experimental error since the extended portion of the muck/$C_2HCl_3$ sorption and desorption isotherms (presented later in this chapter) seems to be singular.

Figures 5.18 and 5.20 summarize the sorption isotherms for all compounds with the peat and muck, respectively. Note that for the case of muck, $CCl_4$ sorbs almost as strongly as $C_2HCl_3$, and for the case of peat, it actually sorbs more strongly.

## C. Sorption of the Selected Compounds with Humic Acid, Lignin, and Graphite in the Low Concentration Region

Sorption experiments using a variety of soil organic matter (SOM) components (discussed in Section F of this chapter) revealed that humic acid, lignin, and graphite* appear to be the principal SOM components responsible for the sorption of the selected compounds.

### 1. Stock Suspension Preparation of Soil Organic Matter Components

The following components of soil organic matter were prepared in suspension form:

(a) Graphite: Graphite powder, Grade #38 (Fisher Scientific Co.)

(b) Humic Acid: Humic Acid, Sodium Salt (Aldrich Chemical Co., Inc.)

---

*Various forms of elemental carbon (such as graphite) are believed to be quite rare in soils (Duxbury, 1983).

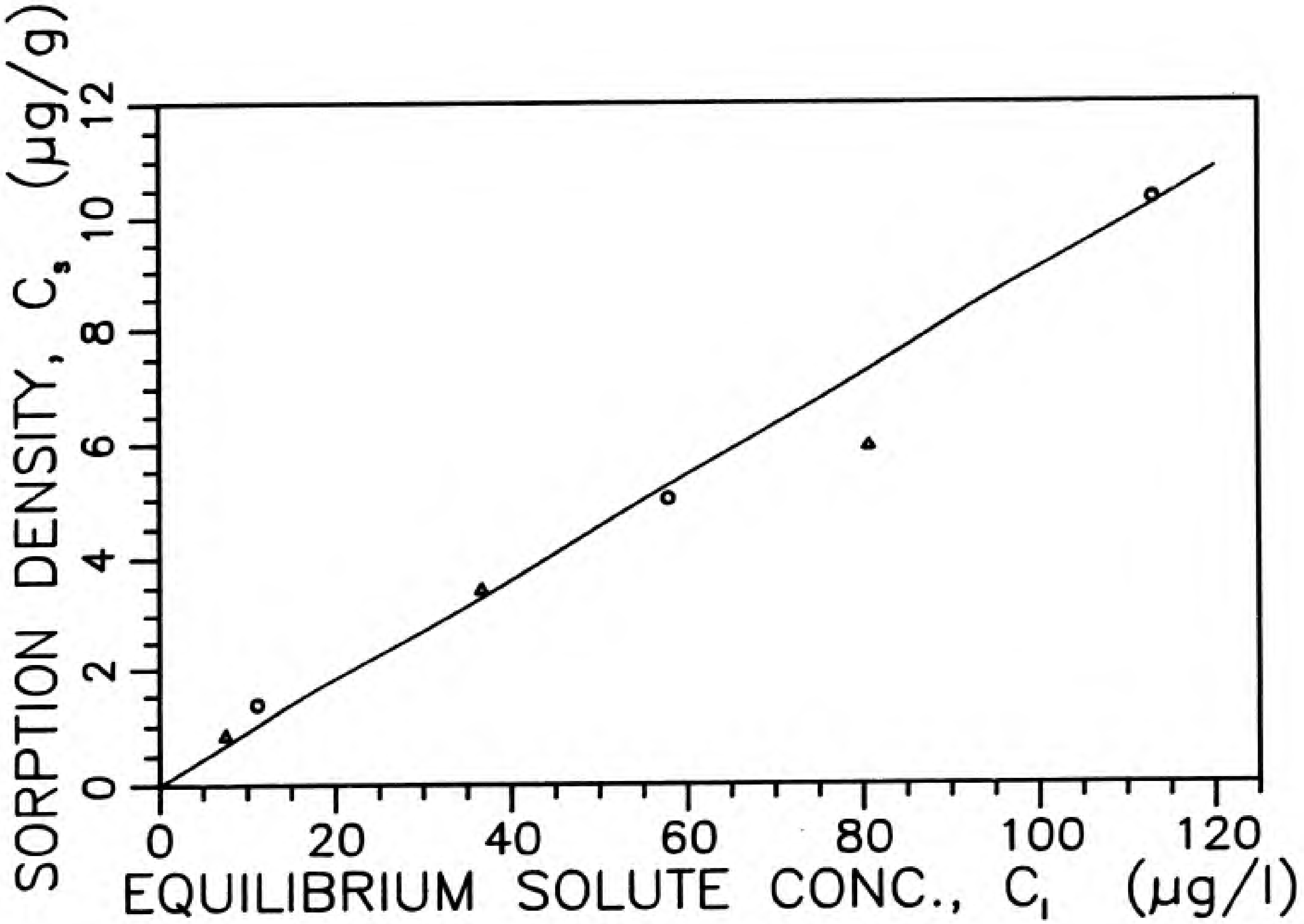

FIGURE 5.17 Sorption (○) and Desorption (△) Isotherms for $C_2HCl_3$ with Peat

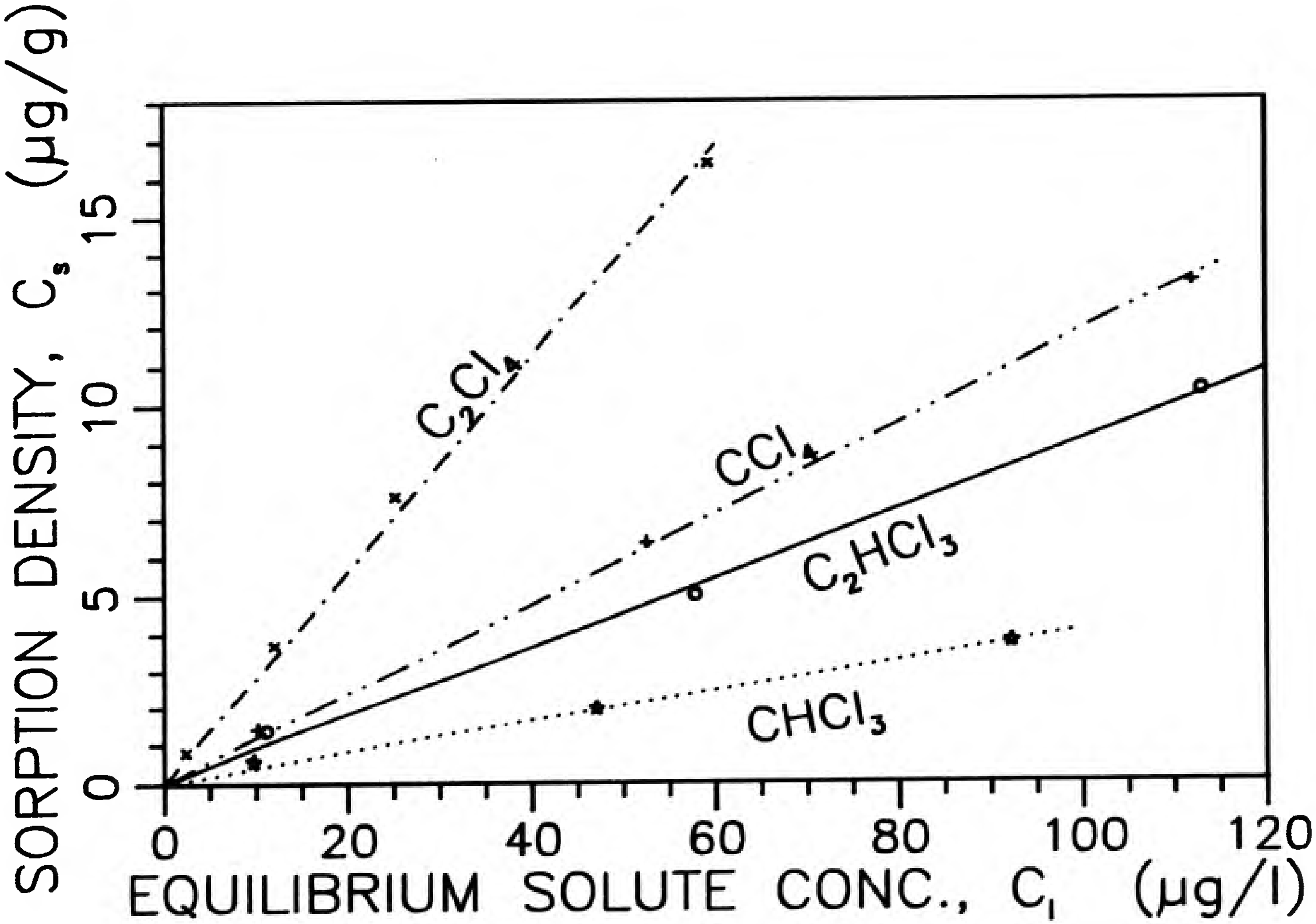

FIGURE 5.18 Sorption Isotherms for All Compounds with Peat

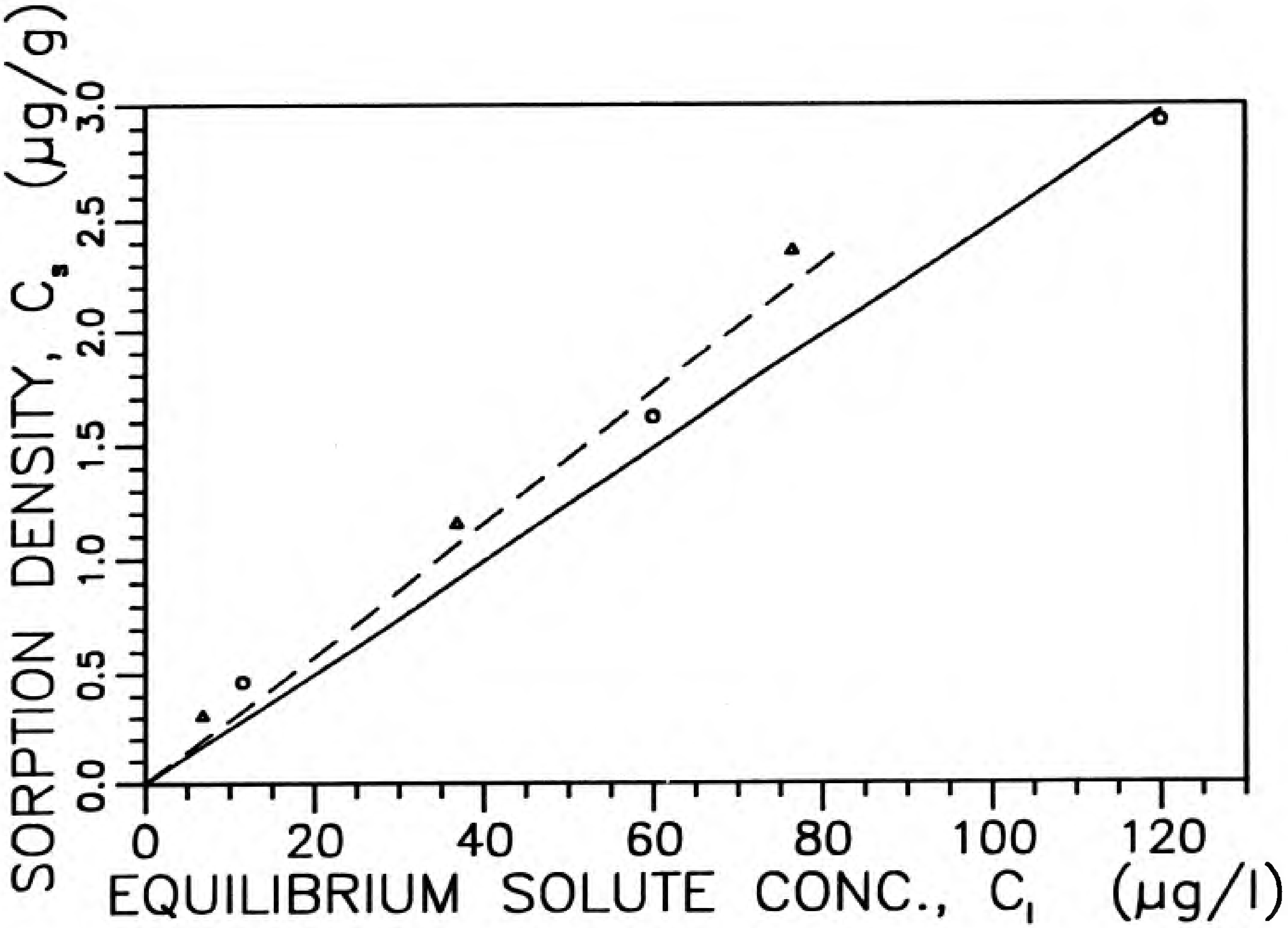

FIGURE 5.19 Sorption (○) and Desorption (△) Isotherms for $C_2HCl_3$ with Muck

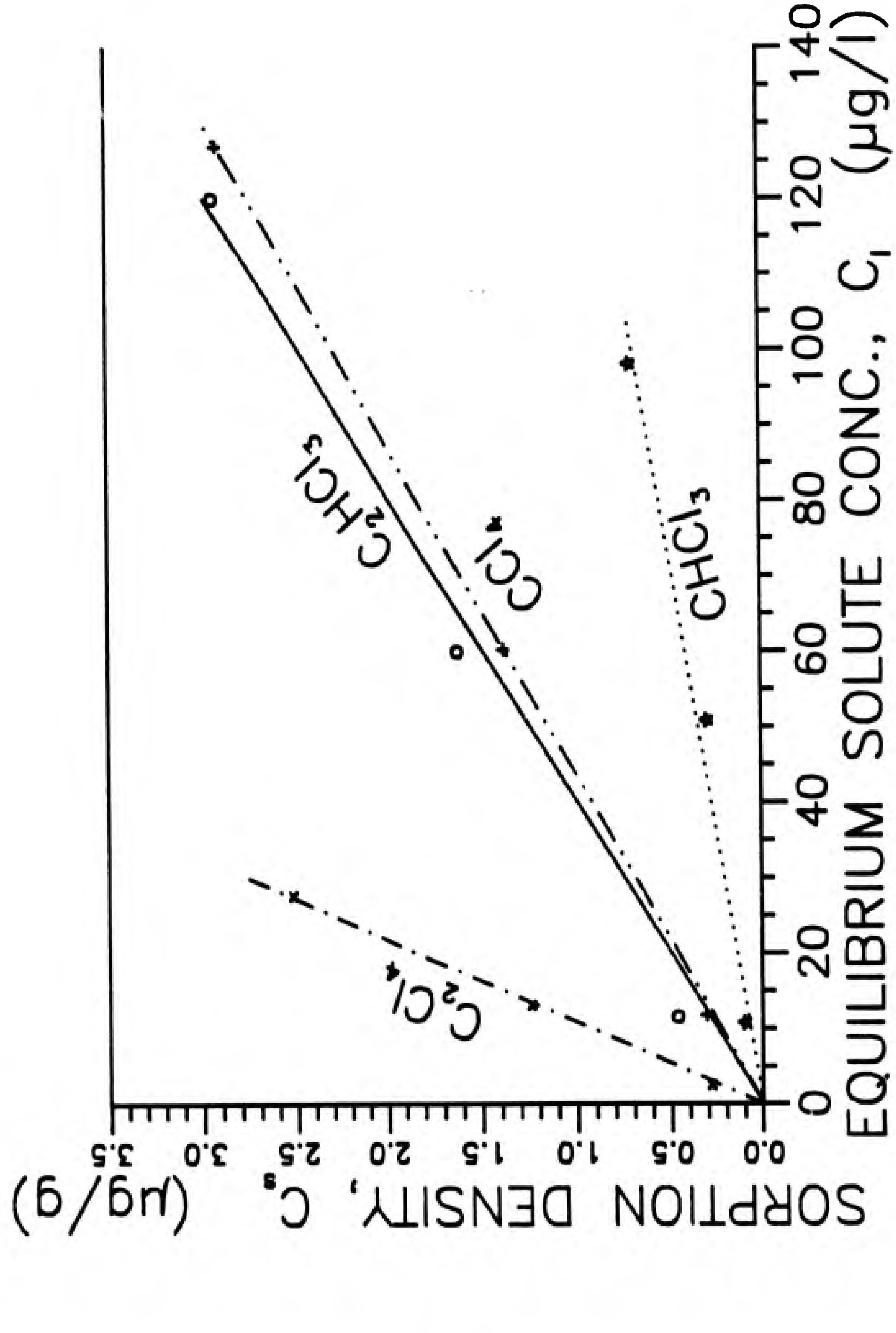

FIGURE 5.20 Sorption Isotherms for All Compounds with Muck

(c) Lignin: Kraft Pine Lignin, "Indulin AT", (Westvaco Chemical Division).

Preliminary tests on the sorption of $^{14}$C-tetrachloroethylene by these materials indicated that the following sorbent concentrations were suitable:

| Sorbent | Solids Concentration (g/l) |
|---|---|
| Graphite | 4 |
| Humic Acid | 2 |
| Lignin | 10 |

Therefore, distilled water was added, in turn, to 2 g of graphite, 1 g of humic acid, and 5 g of lignin, to make 500-ml suspensions of each. In order to keep the humic acid and lignin insoluble, these suspensions were adjusted to pH of 2.0 by the addition of HCl. The pH values, conductivities, and approximate ionic strengths of the three suspensions are given below.

| Suspension | pH | Conductivity (μmho/cm) | Approximate Ionic Strength (M) |
|---|---|---|---|
| Graphite | 6.6 | 25 | 0.00040 |
| Humic Acid | 2.0* | 8400 | 0.13** |
| Lignin | 2.0* | 10500 | 0.17** |

*Adjusted by addition of HCl.
**The potential impact of these non-dilute systems on resulting $K_d$ values is addressed in Section D of this chapter.

The fractions of organic carbon and specific surface areas of these soil organic matter components are listed in Table 5.7. The "pure" material was used for these determinations, and <u>not</u> the dried residue from their liquid suspensions.

TABLE 5.7 Fraction Organic Carbon and Specific Surface Area of Graphite, Humic Acid, and Lignin Sorbents

| Sorbent | Fraction Organic Carbon* | Specific Surface Area† ($m^2/g$) |
|---|---|---|
| Graphite | 0.868 | 8.64 ± 0.38 |
| Humic Acid | 0.355 | 0.336 ± 0.030 |
| Lignin | 0.336 | 2.11 ± 0.02 |

---

*Determined by the "Wet Combustion" method [see Footnote (1) of Table 5.6 for reference citation]. Samples were oven-dried at 50°C for 4 days prior to the test.

†Specific surface areas were measured on a Quantasorb™ (Quantachrome Corp.) by single-point B.E.T. isotherms using $N_2$ as the adsorbate gas. Samples were outgassed with dry nitrogen at 90°C for a minimum of 1 hour. Data represent the mean value ± standard deviation, calculated from three separate desorption signals for the same sample.

### 2. Results and Discussion

The low concentration, "single-point" isotherms for all compounds with the humic acid, lignin, and graphite sorbents are shown in Figures 5.21, 5.22, and 5.23, respectively. (The use of single-point isotherms for these sorbents assumes that these isotherms are linear. Since they were determined in the low concentration region, with a large excess of sorbent mass [or surface area] relative to the sorbate mass [or surface area], there is no reason to expect that these isotherms would not be linear. Furthermore, the extended [very high concentration region] isotherms for these sorbents [with TCE] were virtually linear [see Figure 5.37 in Section H], and therefore, the low concentration region isotherms should be linear, as well.) Equilibration time for these sorbents was 2 days, and two replicates were run for each control and each sorbent R.V.

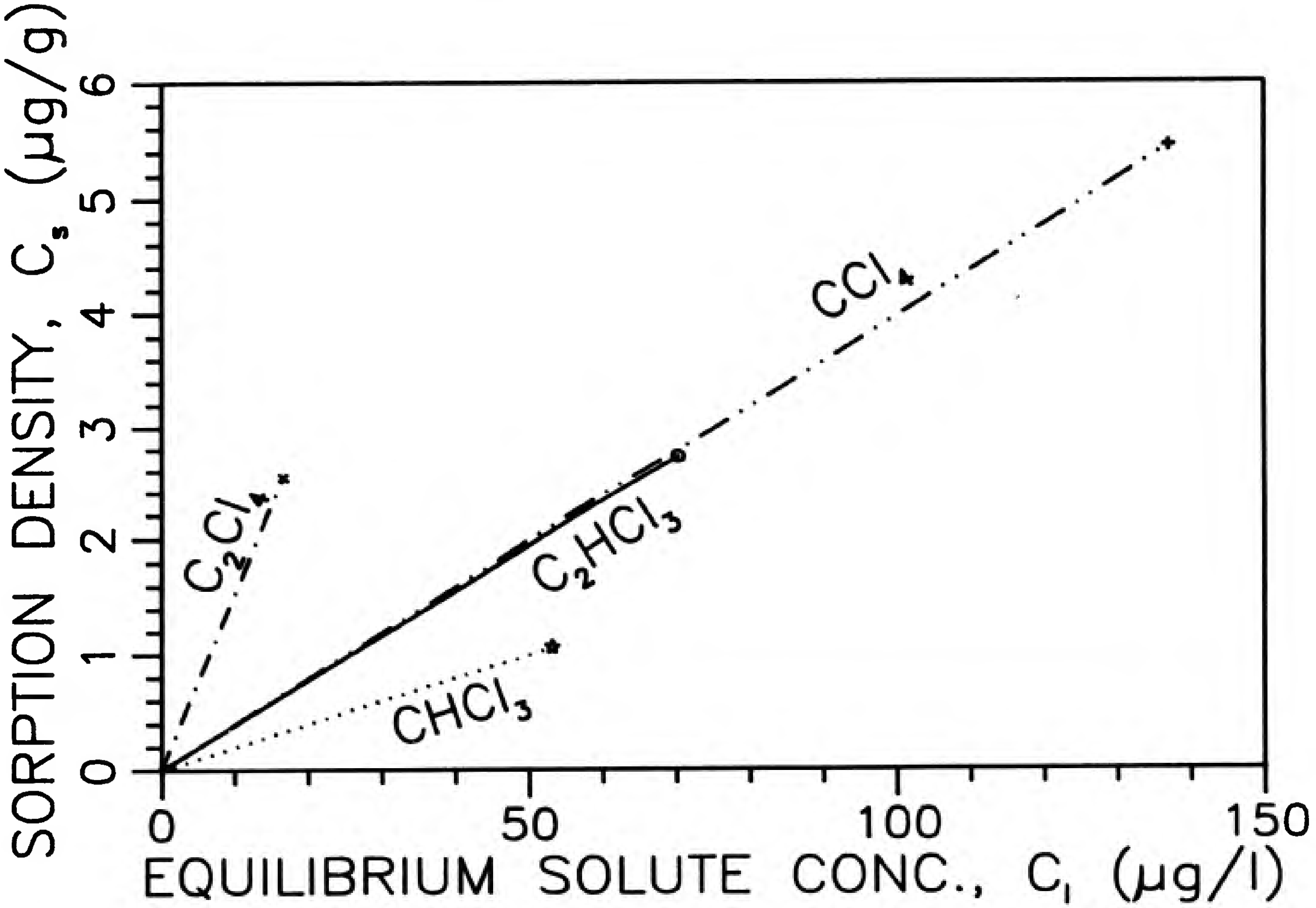

FIGURE 5.21 Sorption Isotherms for All Compounds with Humic Acid

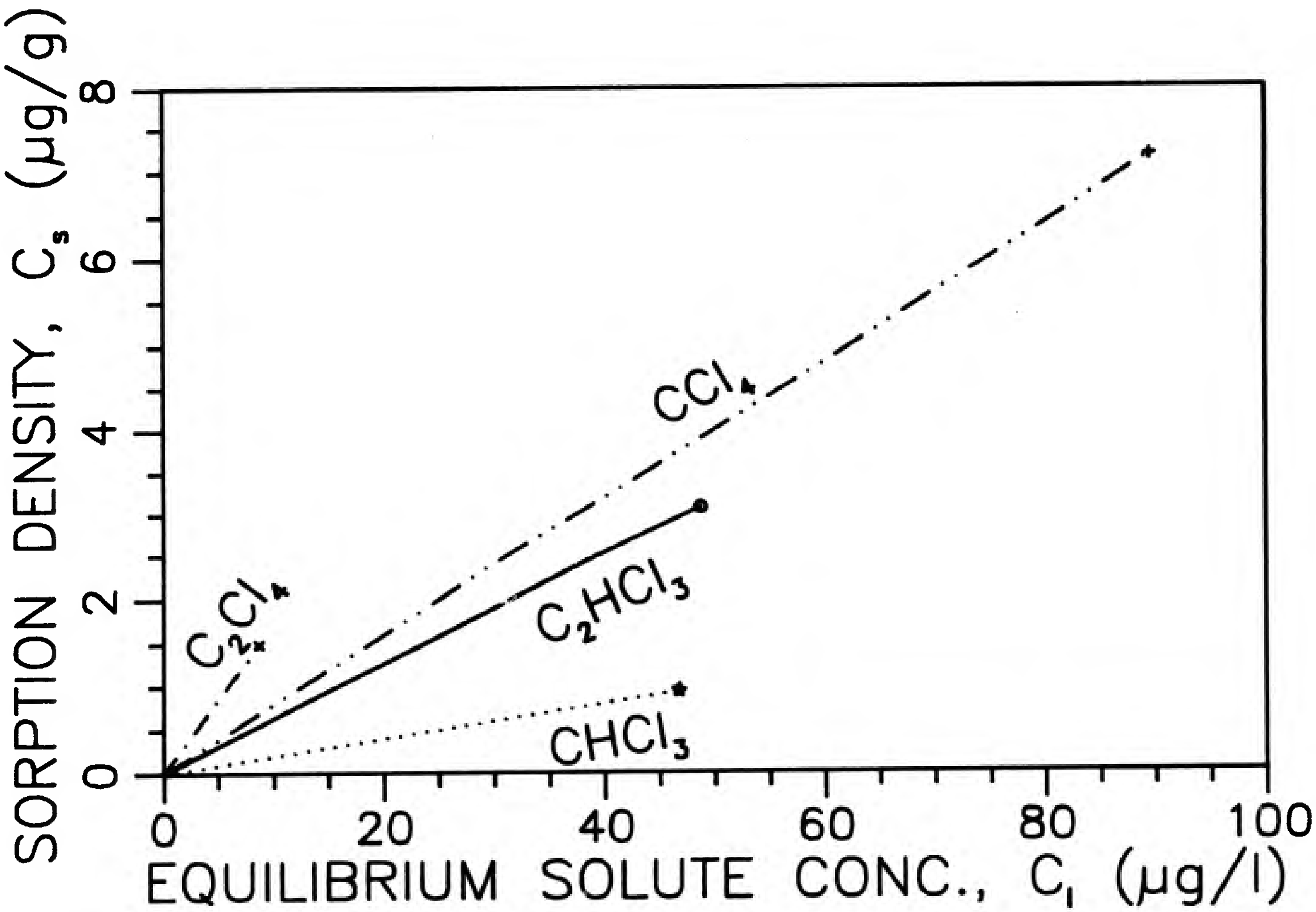

FIGURE 5.22 Sorption Isotherms for All Compounds with Lignin

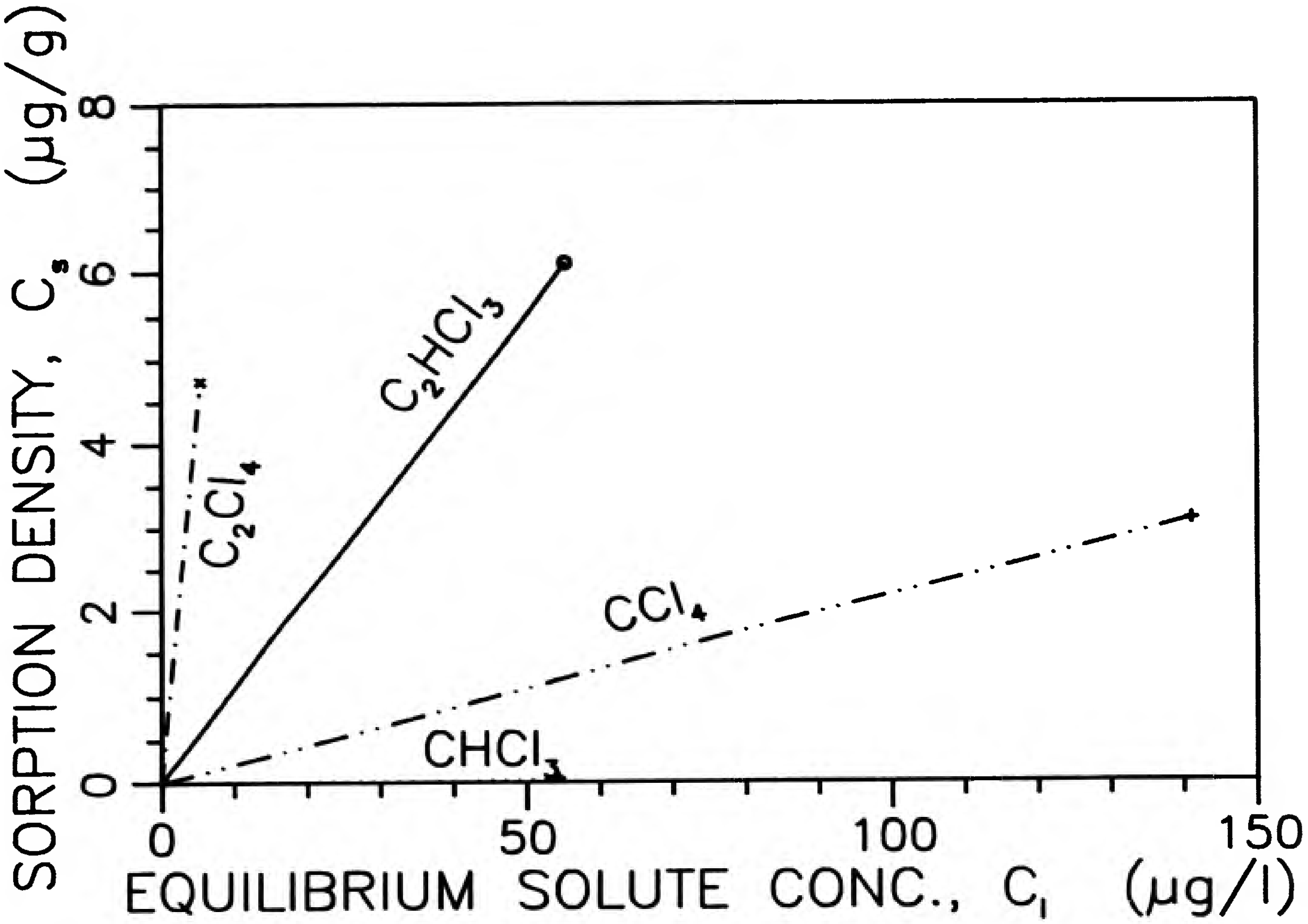

FIGURE 5.23 Sorption Isotherms for All Compounds with Graphite

Note that the interrelationships of sorptive strength among compounds are very similar for humic acid (HA) and lignin, which in turn, are similar to the interrelationships for peat depicted in Figure 5.18 (and, to a lesser extent, for muck shown in Figure 5.20). These observations are not too surprising, since HA and lignin have many structural similarities, and would therefore be expected to sorb in a similar fashion. Also, the extractable humic substance (HA + FA) content for the peat (and muck to a lesser extent) were determined to be relatively high (see Table 5.6). It is also interesting to note that the adsorptive interrelationship among the compounds for graphite (Figure 5.23) closely resemble that of PAC (Figure 5.16). Again, this is to be expected in view of the structural similarities between graphite and activated carbon, the main difference being the vast internal pore structure, and hence, much larger specific surface area for PAC.

## D. Correlation of Sorptive Strength with Various Molecular Properties of the Sorbate

Table 5.8 summarizes the sorption distribution coefficients ($K_d$'s)* and their standard deviations for all sorption isotherms presented in

---

*There is a strong likelihood that the $K_d$ values determined throughout this thesis are "conditional" in that they depend upon the solids concentration employed in the experiment. However, this has no influence on the results and conclusions of this section (i.e., Section V.D.), since the correlations are between the $K_d$ values and compound properties of each sorbate, for a given sorbent. That is, there is no reason to expect that the relative $K_d$ values among the sorbates (for any particular sorbent) would vary with the sorbent concentration, and hence, the correlations should be unaffected. Refer to Section V.I.3. for experimental work pertaining to the "solids effect", and a discussion of how it (potentially) affects the results of other aspects of this research.

TABLE 5.8 Summary of Linear Sorption Distribution Coefficients ($K_d$) and Their Standard Deviations, for Each Compound and Sorbent (T = 20°C)*

| Sorbent | $CHCl_3$ | $CCl_4$ | $C_2HCl_3$ | $C_2Cl_4$ |
|---|---|---|---|---|
| Mineral Soil | 7.80 ± 0.32<br>(0.996) | 5.39 ± 0.68<br>(0.984) | 56.4 ± 1.6<br>(1.000) | 71.1 ± 1.2<br>(0.999) |
| Peat | 40.9 ± 1.0<br>(1.000) | 119 ± 1.5<br>(1.000) | 90.7 ± 2.4<br>(0.998) | 281 ± 5.7<br>(0.999) |
| Muck | 6.89 ± 0.43<br>(0.989) | 22.9 ± 0.2<br>(1.000) | 25.1 ± 1.2<br>(1.000) | 68.6 ± 5.8<br>(0.986) |
| Humic Acid† | 20.0 ± 3.3 | 39.8 ± 19 | 38.9 ± 5.1 | 153 ± 24 |
| Lignin† | 19.9 ± 1.6 | 80.1 ± 7.8 | 63.2 ± 3.0 | 172 ± 11 |
| Graphite | 0.48 ± 3.6 | 21.9 ± 4.8 | 110 ± 8.3 | 878 ± 100 |
| PAC | 6140 ± 735<br>(0.967) | 13700 ± 971<br>(0.990) | 63700 ± 4670<br>(0.987) | 285000± 12700<br>(0.996) |

*Standard deviations are given as the ± values (see Appendix F for the method of their determination). Correlation coefficients (R) are given in parentheses for the multi-point isotherms. NOTE: The $K_d$ values listed above (and others reported throughout this thesis) are probably "conditional" in that they depend upon the solids concentration employed in the experiment. Refer to Section V.I.3. for a discussion of this issue.)

†The $K_d$ values given for HA and lignin may be ∿ 5% higher than their "true" infinite dilution values because of the effect of $I$ upon $K_d$ (see Section V.I.2.). No attempt was made to correct for the influence of $I$ on $K_d$ for these sorbents.

Sections B and C of this chapter. (Consult Appendix F for the procedures used in determining the standard deviations given, and a discussion of error propogation analysis.) The linear correlation coefficients (R) are also given in this table (in parentheses) as a measure of the "linearity" of the data points (for the multi-point isotherms). As stated previously in this thesis, the $K_d$ values are simply equal to the slopes of the linear isotherms (forced through the origin) in the low concentration region, multiplied by a factor of 1000 g/l in order to make them "quasi-dimensionless". The precisions (coefficients of variation) of the $K_d$ values range from ±0.87% (for the $CCl_4$-muck system) to ±750% (for the $CHCl_3$-graphite system). In general, of course, the precision for the multi-point, linear regression $K_d$ values is better than that for the single-point $K_d$ values.

Table 5.9 presents a variety of properties of the sorbate compounds used in this research. The dipole moment and polarizability* are the ones of primary interest (in this research), since they are the only sorbate properties which enter into the equations for intermolecular forces/energies. However, as seen in the Lorentz-Lorenz equation (Footnote [c] of Table 5.9) used to calculate the polarizability, $\alpha$ is directly proportional to M or $M/\rho$--which is the molar volume, $\bar{V}$. Thus, for compounds in general, there is typically a strong correlation between $\alpha$ and $\bar{V}$, and to a lesser extent, between $\alpha$ and M. In addition, the equation defining P also includes $\bar{V}$ (and surface tension [$\sigma$]--which, in turn, is a function of intermolecular

---

*"Polarizability," as used in this thesis, shall always refer to the electronic polarizability, since other types (of polarizability) do exist.

TABLE 5.9 Summary of Compound Properties to be Used in Sorption Correlations

| Property | $CHCl_3$ | $CCl_4$ | $C_2HCl_3$ | $C_2Cl_4$ |
|---|---|---|---|---|
| Molecular Weight[a] (M, g/mol) | 119.38 | 153.82 | 131.39 | 165.83 |
| Dipole Moment[b] ($\mu$, Debye) | 1.01 | 0 | 0.99 | 0 |
| Electronic Polarizability[c] ($\alpha$, $10^{-24}$ $cm^3$) | 106 | 132 | 126 | 151 |
| Molar Volume[d] ($\overline{V}$, $cm^3/mol$) | 80.07 | 96.49 | 89.87 | 102.17 |
| Parachor[e] (P, $cm^3 \cdot dyne^{\frac{1}{4}}/mol \cdot cm^{\frac{1}{4}}$) | 182.8 | 219.8 | 209.4 | 242.5 |
| Aqueous Solubility[f] (S, mmol/l) | 68.8 | 5.23 | 8.24 | 0.899 |
| Octanol-Water Partition[g] Coefficient ($K_{ow}$, dimensionless) | 93 | 437 | 195 | 398 |

[a] From Weast (1967).

[b] From McClellan (1963 and 1974) (Note: 1 Debye = 3.336 x $10^{-30}$ coulomb-meter.)

[c] Values given represent the <u>electronic</u> polarizabilities of the molecules, calculated using the Lorentz-Lorenz equation:

$$\alpha = \frac{3M}{N_o \rho} \frac{(n_D^2 - 1)}{(n_D^2 + 2)}$$

where:
M = the compound's molecular weight (g/mole)
$N_o$ = Avagadro's number (6.023 x $10^{23}$ molecules/mole)
$\rho$ = density of the compound at T = 20°C ($g/cm^3$)
$n_D$ = index of refraction for the compound at T = 20°C, using light of wavelength 589 nm (dimensionless)

Values for $\rho$ and $n_D$ were obtained from either Weast (1967) or Dean (1979). (Note: Some references include a factor of $[1/4\pi]$ on the right-hand-side of the above Lorentz-Lorenz equation.)

Table 5.9 continued

[d] Calculated from $\bar{V} = M/\rho$, where the $\rho$ values are for $T = 20°C$, obtained from Weast (1967).

[e] Calculated from $P = \bar{V}\sigma^{1/4}$, where $\sigma$ = surface tension of the compound at $T = 20°C$ (dyne/cm). Values for $\sigma$ ($T = 20°C$) were obtained from Weast (1967), except for $\sigma_{TCE}$ which was obtained from Dean (1979).

[f] From Horvath (1982) (see pp. 485, 486, 500, and 501).

[g] Values of $K_{ow}$ for $CHCl_3$, $CCl_4$, and $C_2Cl_4$ are from Chiou (1977); and $K_{ow}$ for $C_2HCl_3$ is from Rogers and McFarlane (1981).

forces, and hence, $\alpha$ and $\mu$!). Finally, the extent to which a compound dissolves in water (i.e., its aqueous solubility), or distributes itself between octanol (or any solvent) and water, is partially governed by a competition among intermolecular forces.† Unfortunately, for these types of compounds, these intermolecular forces are principally governed by their polarizabilities. This is because these compounds are either nonpolar or weakly polar, and hence, their intermolecular potentials are primarily controlled by their induced dipole moments, rather than their permanent dipole moments; and these induced dipole moments are directly proportional to the compounds' polarizabilities. Therefore, the unfortunate possibility exists that all these properties (except perhaps dipole moment) are highly inter-correlated.

In order to test for this possible mutual correlation among properties, I decided to (initially) linearly regress each variable (i.e., property) in turn with $\alpha$,* using the regression equation: $Y = A\alpha + B$ where "Y" is the property in question, and "A" and "B" are the regression coefficients. The most important coefficient to be determined in these regressions is the linear correlation coefficient, R, which is a measure of how well the two variables are linearly cor-

---

†Ironically, the other significant property affecting both solubility and partitioning phenomena is the compound's molecular size or volume, since this determines the size of the cavity which must be created in a solvent in order to accomodate the solute molecule. Thus, S and $K_{OW}$ may be strongly correlated to $\overline{V}$ for the solute. But since $\overline{V}$ is, in turn, highly correlated with $\alpha$, S and $K_{OW}$ may also be indirectly (highly) correlated to $\alpha$ via the solvent cavity effect.

*The property, $\alpha$, was selected as the independent variable merely to serve as an example of possible mutual correlations. Obviously, any of the variables listed in Table 5.10 could have been chosen for this purpose.

related. (The value of R ranges from -1 to +1, with values of $R \approx 0$ indicating negligible correlation, and $|R| = 1$ indicating "perfect" linear correlation between the two variables.) Table 5.10 exhibits the results of this regression. As expected, some of the properties ($\overline{V}$, M, and P) do indeed show strong correlation to $\alpha$. Based on this linear regression, neither S nor $K_{ow}$ are (strongly) linearly correlated

TABLE 5.10 Test for Linear Correlation Between Sorbate Properties and Polarizability*

| Property (Y) | Linear Correlation Coefficient (R) |
|---|---|
| M (Molecular Weight) | 0.950 |
| $\mu$ (Dipole Moment) | -0.800 |
| $\overline{V}$ (Molar Volume) | 0.982 |
| P (Parachor) | 0.999 |
| S (Solubility) | -0.868 |
| $K_{ow}$ (Octanol-Water Partition Coefficient) | 0.836 |

*Regression equation is $Y = A\alpha + B$. Each regression is based on four pairs of observations, and the probability that $R \geq 0.950$ if the variables are unrelated is 0.05. Values for "A" and "B" were determined but not given since they are not pertinent to the discussion.

with $\alpha$.[†] In order to test for a nonlinear correlation between these variables, arithmetic plots of S versus $\alpha$, and $K_{ow}$ versus $\alpha$ were made,

---

[†] Since $\mu$ and $\alpha$ are fundamental molecular properties which are independent of each other, there is no reason to expect or attempt any type of correlation between these two variables. The correlation coefficient for $\mu$ versus $\alpha$ was presented in Table 5.10 for the sake of completeness, and also to show that these two variables are indeed not highly correlated (even by chance), (i.e., there is always the possibility that two variables can be highly correlated, even though they have no causal connection to each other.)

and these are displayed in Figures 5.24 and 5.25, respectively. Note that S appears to be an exponential function of $\alpha$, but $K_{ow}$ versus $\alpha$ does not result in a monotonic, nonlinear relationship. In order to test for this suspected exponential relationship between S and $\alpha$, a linear regression was performed between the variables ln S versus $\alpha$. The result was that $R = -0.999$, which verifies that S does in fact have a strong nonlinear correlation with $\alpha$.

Despite the fact that many of the properties exhibit strong intercorrelation, they are by no means "perfectly" correlated with each other. Therefore, it was decided to assess the correlation of sorptive strength to each of these properties, since it is possible that some differences of significance might exist, and conclusions drawn therefrom. Therefore, correlations were attempted between the $K_d$ values for each sorbent (given in Table 5.8), and the molecular properties of the sorbates (given in Table 5.9).

In order to determine which functions of the variables should be regressed, the following reasoning was applied. Since sorption free energy ($\Delta G°$) is proportional to the natural logarithm of the sorption equilibrium distribution coefficient ($K_d$), and intermolecular energies are directly proportional to either $\mu$, $\mu^2$, or $\alpha$, the independent variables in the form of "$\mu$", "$\mu^2$", or "$\alpha$" should be regressed with the dependent variable in the form of "ln $K_d$". The resulting regression equation will then have the form: $\ln K_d = AY + B$ where Y is either $\mu$, $\mu^2$, or $\alpha$.

For the cases of M, $\overline{V}$, and P as the independent variables, I chose to regress them "as is" versus ln $K_d$. (This was mainly because they were shown to be highly [linearly] correlated with $\alpha$.) Also, since ln S

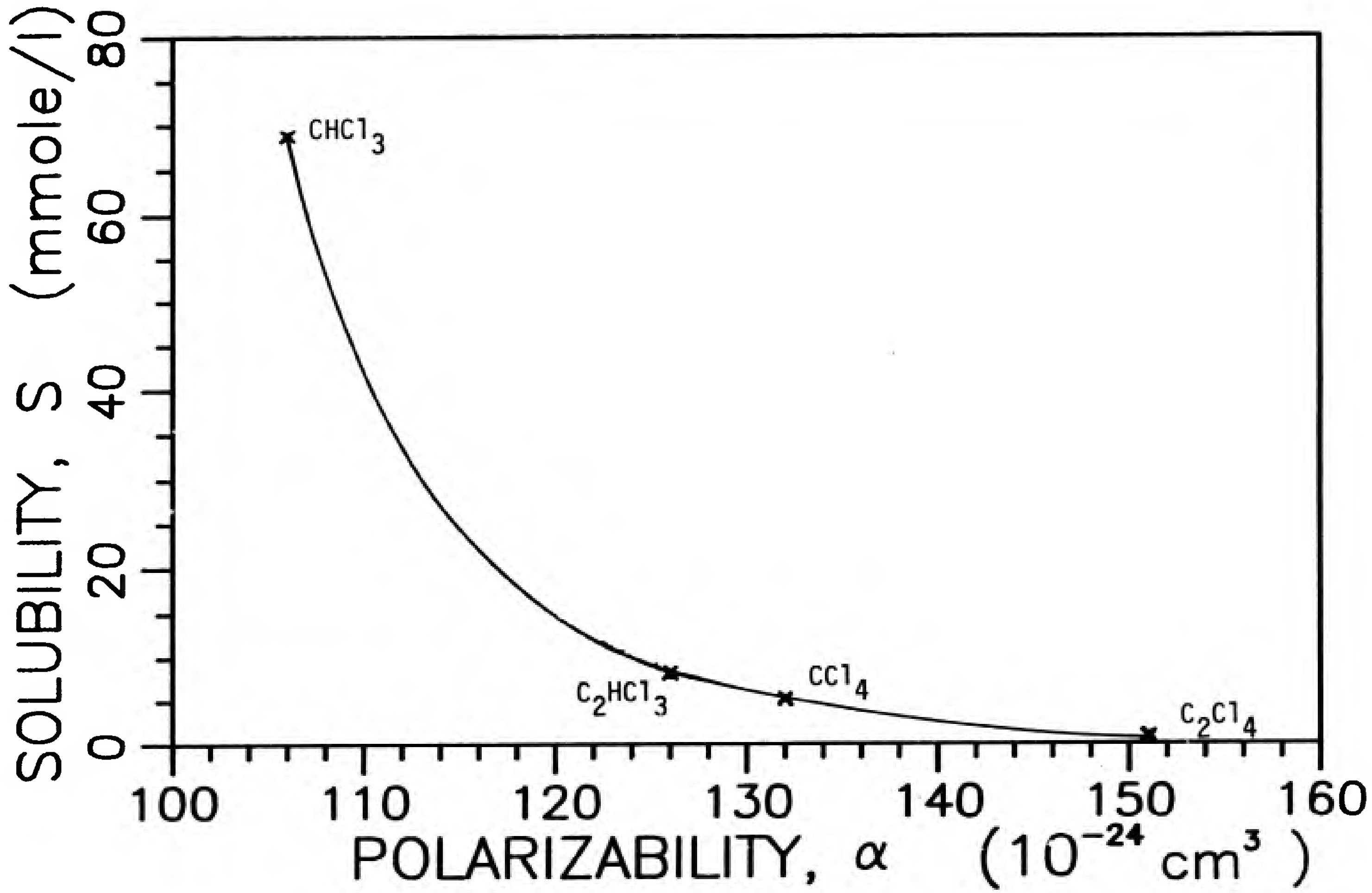

FIGURE 5.24 Plot of Sorbate Aqueous Solubilities Versus Their Polarizabilities

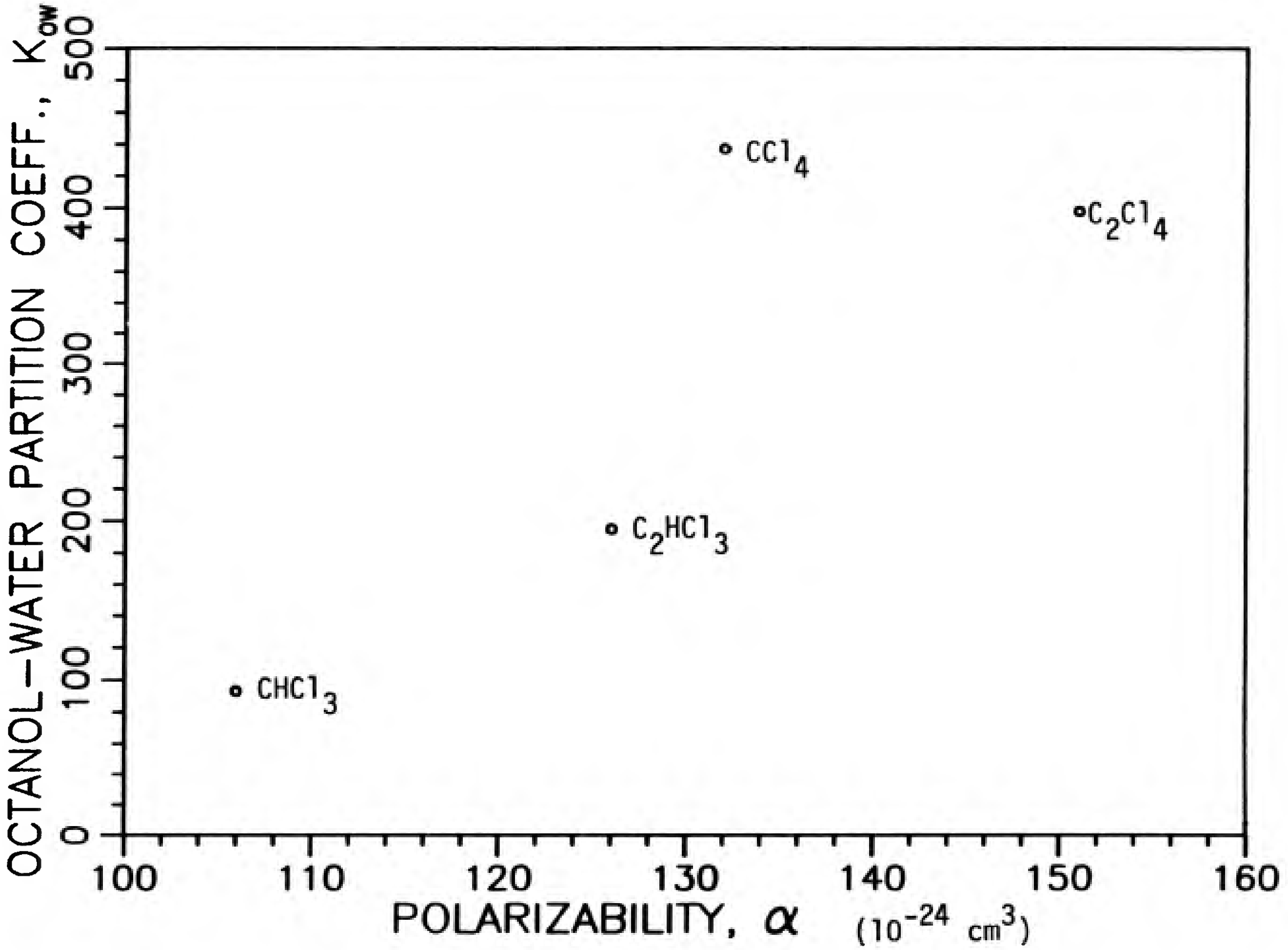

FIGURE 5.25 Plot of Sorbate $K_{ow}$ Values Versus Their Polarizabilities

is highly correlated with $\alpha$, and furthermore, since the free energy of solution ($\Delta G^\circ_{soln}$) for these compounds (with water) is directly proportional to ln S (where S is expressed in moles/l and the activity coefficient is assumed to be unity),* I chose to regress "ln $K_d$" with "ln S". Lastly, since $K_{ow}$ is a partition coefficient, and since $K_d$ would likewise be a partition coefficient if the extraction (i.e., absorption) hypothesis for soil sorption is correct, then perhaps the best way to regress these two variables is simply as $K_d$ versus $K_{ow}$.

Table 5.11 presents the resulting linear correlation coefficients (R) from these regressions. (The regression coefficients "A" and "B" are not given since they are not pertinent to this discussion, and furthermore, are only valid for the particular sorbents used in this research.) The results clearly indicate that the sorption distribution coefficient is strongly correlated (except for the cases of the mineral soil and PAC) to both the polarizability and solubility of the sorbate (and to a lesser extent, parachor and molar volume).

The nature of the statistics applicable to Table 5.11 is somewhat analogous to the situation regarding the (postulated) slight negative adsorption by the clay and mineral solids. In other words, the 95% CI for these correlation coefficients are too wide (in most cases) to

---

*This latter reason (i.e., $\Delta G^\circ_{soln} \propto \ln S$) for choosing this functionality is based on the assumption that the sorption free energy ($\Delta G^\circ$) is much more likely to be directly proportional to the variable "$\Delta G^\circ_{soln}$" than to the variable "S". That is, aqueous solubility, S, simply expresses the number of molecules (or moles) of a substance in a unit volume of solution at saturation. On the other hand, $\Delta G^\circ_{soln}$ expresses the free energy utilized (expended or released) in dissolving a mole of solute (originally part of a pure solute phase) into the aqueous phase (at standard-state conditions). But since $\Delta G^\circ$ expresses the free energy utilized in removing the same mole of solute from the aqueous phase, and placing it in (or on) a sorbent (at standard-state conditions), the two processes are in some respects the reverse of each other.

TABLE 5.11 Correlation Coefficients (R) for Regressions of $\ln K_d$ versus $\mu$, $\mu^2$, $\alpha$, M, $\overline{V}$, P, and ln S; and $K_d$ versus $K_{ow}$[†]

| | $\ln K_d$ versus | | | | | | $K_d$ versus |
|---|---|---|---|---|---|---|---|
| Sorbent | $\mu$ or $\mu^2$ * | $\alpha$ | M | $\overline{V}$ | P | ln S | $K_{ow}$ |
| Mineral Soil | 0.007 | 0.576 | 0.298 | 0.424 | 0.539 | -0.592 | 0.174 |
| Peat | -0.804 | 1.000 | 0.952 | 0.978 | 0.997 | -0.996 | 0.706 |
| Muck | -0.685 | 0.984 | 0.881 | 0.944 | 0.977 | -0.990 | 0.628 |
| Humic Acid | -0.700 | 0.962 | 0.881 | 0.899 | 0.949 | -0.954 | 0.571 |
| Lignin | -0.781 | 0.993 | 0.935 | 0.984 | 0.994 | -0.998 | 0.746 |
| Graphite | -0.546 | 0.932 | 0.779 | 0.878 | 0.921 | -0.946 | 0.469 |
| PAC | -0.399 | 0.863 | 0.670 | 0.756 | 0.839 | -0.870 | 0.449 |

[†] Each regression is based on four pairs of data values, and the probability that $R \geq 0.950$ if the variables are unrelated is 0.05.

*Since $\mu$ values are either zero or $\approx 1.0$, the squaring of $\mu$ has virtually no effect on the outcome of this regression.

draw any statistically significant conclusions between any two R values. Nevertheless, the fact remains that for each sorbent, the variables $\alpha$ or ln S are the best predictors of $\ln K_d$ (and hence, $K_d$).

## E. Determination of the Normalized Sorption Distribution Coefficient ($K_{oc}$) and Its Correlation to the Sorbate's Aqueous Solubility, Octanol-Water Partition Coefficient, and Polarizability

The literature pertaining to the sorption of nonionic, organic compounds with soils usually reports high correlation between sorptive strength and the fraction of organic carbon ($f_{oc}$) in the sorbent; and sometimes reports a correlation between the normalized sorption distribution coefficient, $K_{oc}$*, and the sorbate's solubility (S) and octanol-water partition coefficient ($K_{ow}$). It is therefore of interest to know to what extent these variables are correlated for the data accumulated in this research. Also, it was decided to include the sorbate's polarizability ($\alpha$) in the correlations with $K_{oc}$, since the previous section demonstrated that it was an effective predictor of $K_d$.

From Tables 5.6 and 5.7 the organic carbon contents for the real soils and SOM components are listed again below.**

| Sorbent | Fraction Organic Carbon ($f_{oc}$) |
|---|---|
| Mineral Soil | 0.181 |
| Peat | 0.410 |
| Muck | 0.296 |
| Humic Acid | 0.355 |
| Lignin | 0.336 |
| Graphite | 0.868 |

---

*$K_{oc} = K_d/f_{oc}$.

**Powdered activated carbon (PAC) is intentionally omitted from this section since it is not a (natural) SOM component. Furthermore, PAC is a porous solid, and its high specific surface area clearly makes its adsorption virtually independent of organic carbon content.

To examine the relationship between sorptive strength and fraction of organic carbon, a least-squares linear regression was performed between the $K_d$ values for each sorbent (within each sorbate category) and their corresponding $f_{oc}$ values. These regressions were of the form $K_d = Af_{oc}$, where "A" is the slope linear regression coefficient. That is, the regression lines were forced through the origin since the "normalization" of $K_d$ with $f_{oc}$ assumes this form of equation. Table 5.12 shows the linear correlation coefficients obtained from these regressions, which indicate that the correlation between $K_d$ and $f_{oc}$ is poor for $CHCl_3$ and $CCl_4$, and fairly high for $C_2HCl_3$ and $C_2Cl_4$.

---

Table 5.12 Linear Correlation Coefficients (R) for the Regression of $K_d$ versus $f_{oc}$*

| $CHCl_3$ | $CCl_4$ | $C_2HCl_3$ | $C_2Cl_4$ |
|---|---|---|---|
| 0.599 | 0.676 | 0.951 | 0.946 |

*R values based on six pairs of data, and the probability that $R \geq 0.881$ if the variables are unrelated is 0.05.

---

Inspection of Table 5.8 reveals that the $K_d$ values for graphite (with $CHCl_3$ and $CCl_4$) are unusually low considering its high $f_{oc}$ value. Indeed, if graphite is excluded from the linear regression for $K_d$ versus $f_{oc}$, the corresponding R values increase significantly for $CHCl_3$ and $CCl_4$; (on the other hand, it slightly decreases the R value for $C_2HCl_3$). The revised linear regression correlation coefficients, resulting from the deletion of graphite from the analysis, are depicted in Table 5.13. Note that now, the correlation of sorptive strength to fraction of organic carbon is moderately high.

Table 5.13 Linear Correlation Coefficients (R) for the Regression of $K_d$ versus $f_{oc}$, Excluding Graphite*

| $CHCl_3$ | $CCl_4$ | $C_2HCl_3$ | $C_2Cl_4$ |
|---|---|---|---|
| 0.922 | 0.892 | 0.934 | 0.953 |

*R values based on five pairs of data, and the probability that $R \geq 0.878$ if the variables are unrelated is 0.05.

Since adsorption by graphite is apparently not controlled by its organic carbon content (as evidenced by the previous correlation analyses for the cases of $CHCl_3$ and $CCl_4$), it was decided to exclude this sorbent from further analyses in this section. As an added justification, the occurrence of graphite (and other forms of elemental carbon) in soils is believed to be quite rare (Duxbury, 1983).

The calculated $K_{oc}$ values are given in Table 5.14. If $K_d$'s are, in fact, "perfectly" (linearly) correlated with $f_{oc}$'s (hypothetically speaking), then the $K_{oc}$ values for a given sorbate would be identical, regardless of the sorbent. Therefore, the wide range in $K_{oc}$ values (for a given sorbate) is simply another way of expressing the observation that, in this research, sorption is not solely a function of the sorbent's organic carbon content.

Table 5.14 Summary of the Normalized Sorption Distribution Coefficients, $K_{oc}$ (and their standard deviations*), for Each Compound and Sorbent (Except PAC and Graphite)

| Sorbent | $CHCl_3$ | $CCl_4$ | $C_2HCl_3$ | $C_2Cl_4$ |
|---|---|---|---|---|
| Mineral Soil | 43.1 (±1.8) | 29.8 (±3.8) | 312 (±8.8) | 393 (±6.6) |
| Peat | 99.8 (±2.4) | 290 (±3.7) | 221 (±5.9) | 685 (±14) |
| Muck | 23.3 (±1.5) | 77.4 (±0.68) | 84.8 (±4.1) | 232 (±20) |
| Humic Acid | 56.3 (±9.3) | 112 (±54) | 110 (±14) | 431 (±68) |
| Lignin | 59.2 (±4.8) | 238 (±23) | 188 (±8.9) | 512 (±33) |

---

*Standard deviations were determined using the general formula for error propogation on the function $K_{oc} = K_d/f_{oc}$. That is, $\sigma_{K_{oc}} = [(\partial K_{oc}/\partial K_d)^2 \sigma_{K_d}^2]^{\frac{1}{2}}$, which yields $\sigma_{K_{oc}} = \sigma_{K_d}/f_{oc}$ as the final result. (This analysis assumes that the error contributed by the $f_{oc}$ values is negligible relative to that for $K_d$.)

Table 5.15 below gives the means and standard deviations for the $K_{oc}$ values listed in Table 5.14.

Table 5.15 Mean ($\overline{K}_{oc}$) and Standard Deviation (S.D.) Values of the Normalized Sorption Distribution Coefficient for Each Sorbate*

| | $CHCl_3$ | $CCl_4$ | $C_2HCl_3$ | $C_2Cl_4$ |
|---|---|---|---|---|
| $\overline{K}_{oc}$ ± S.D.: | 56.3 ± 28 | 149 ± 110 | 183 ± 91 | 451 ± 166 |

*The $K_{oc}$ values for PAC and graphite have been omitted from this analysis.

The coefficients of variation for these data range from 37 to 74 percent, which indicate that $K_{oc}$ values for a given compound are not very precise constants.

These results seem to be somewhat contrary to those generally reported in the literature for the relationship between sorptive strength and fraction of organic carbon. However, it should be pointed out that some workers in this field believe that $K_{oc}$ values within an order of magnitude of each other (for a given sorbate) represent "good" constants. For example, Lyman (1982) stated that numerous studies showed that $K_{oc}$ values for a specific chemical are relatively constant and reasonably independent of the soil or sediment used, even though these same studies yielded $K_{oc}$ values whose coefficients of variation ranged from 10 to 140 percent! Under this criterion, the $\overline{K}_{oc}$ values which I obtained (Table 5.15) would all be considered "relatively constant". (In this sense, my $\overline{K}_{oc}$ values may not be contrary to some of those reported in the literature.)

My results are in accord with those of Lion and Garbarini (1983), who also obtained a range in $K_{oc}$ values for the sorbates (toluene and TCE) which they examined. As these researchers concluded, the sorption of these compounds does not appear to be controlled solely by organic carbon content of the sorbents. It could be that such factors as the composition of the SOM, the specific surface area of the SOM, or the presence of an inorganic fraction, influence sorptive strength.*

Using the $\overline{K}_{oc}$ values in Table 5.15, and the S, $K_{ow}$, and $\alpha$ values from Table 5.9, linear regressions were performed to determine the relationship between log $\overline{K}_{oc}$ and log S, and log $\overline{K}_{oc}$ and log $K_{ow}$ (which represent the regression relationships most commonly reported

---

*It should be pointed out that the "solids effect" may also be partially responsible for the variability in the $K_{oc}$ values. (See Section V.I.3.)

in the literature), and $\log \overline{K}_{oc}$ and $\alpha$. The resulting regression equations are:

$$\log \overline{K}_{oc} = -0.468 \log S + 2.61 \quad (S \text{ in mmol/l}) \quad (R = -0.980) \quad (5\text{-}5)$$

$$\log \overline{K}_{oc} = 0.930 \log K_{ow} + 0.0019 \quad (R = 0.786) \quad (5\text{-}6)$$

$$\log \overline{K}_{oc} = 0.0195\, \alpha - 0.295 \quad (\alpha \text{ in } 10^{-24} \text{ cm}^3) \quad (R = 0.974) \quad (5\text{-}7)$$

According to the correlation coefficients, S and $\alpha$ are better predictors than $K_{ow}$, for $\overline{K}_{oc}$.

Equations (5-5) and (5-6) seem to be in fairly good agreement with some of the regressions reported in the literature for these variables. For example, Lyman (1982) presented the following regression equations which had been determined by various investigators:

$$\log K_{oc} = -0.55 \log S + 3.64 \ (S \text{ in mg/l}) \quad (R = -0.84)$$

$$\log K_{oc} = -0.557 \log S + 4.277 \ (S \text{ in } \mu\text{mol/l}) \quad (R = -0.99)$$

$$\log K_{oc} = 0.544 \log K_{ow} + 1.377 \quad (R = 0.86)$$

$$\log K_{oc} = 0.524 \log K_{ow} + 0.855 \quad (R = 0.92)$$

$$\log K_{oc} = 0.94 \log K_{ow} + 0.02 \quad (R \text{ not available})$$

$$\log K_{oc} = 1.029 \log K_{ow} - 0.81 \quad (R = 0.95) \quad .$$

Also, the following additional equations were reported in various publications by the authors indicated:

| Authors | Equation | |
|---|---|---|
| Karickhoff *et al.* | $\log K_{oc} = -0.54 \log S + 0.44$ (S in mole fraction) | (R = -0.97) |
| Karickhoff *et al.* | $\log K_{oc} = 1.00 \log K_{ow} - 0.21$ | (R = 1.00) |
| Brown and Flagg | $\log K_{oc} = 0.937 \log K_{ow} - 0.006$ | (R = 0.97) |
| Means *et al.* | $\log K_{oc} = -0.686 \log S + 4.273$ (S in mg/l) | (R = -0.97) |
| Means *et al.* | $\log K_{oc} = \log K_{ow} - 0.317$ | (R = 0.99) |
| Schwarzenbach and Westall | $\log K_{oc} = 0.72 \log K_{ow} + 0.49$ | (R = 0.97) |

It is interesting to note that although the correlation coefficients for most of these regressions are quite high, if the regression equations are compared amongst one another, some show significant differences. This observation is illustrated by plotting all the equations given above which relate $K_{oc}$ with $K_{ow}$. (The $K_{oc}$ vs. S equations are not plotted since most of the S variables have different units.) These plots are shown in Figure 5.26. Note that the $\log K_{oc}$ vs. $\log K_{ow}$ regression line obtained from the data in this research [Equation (5-6)] is in good agreement with the majority of those reported in other studies.

## F. Identification of the Principal Soil Organic Matter Components Responsible for the Sorption of the Selected Compounds

### 1. Discussion

Based on the results presented thus far in this chapter (and also on the profuse research findings of others), it is clear that the sorption of the compounds in this research (and of other neutral, organic

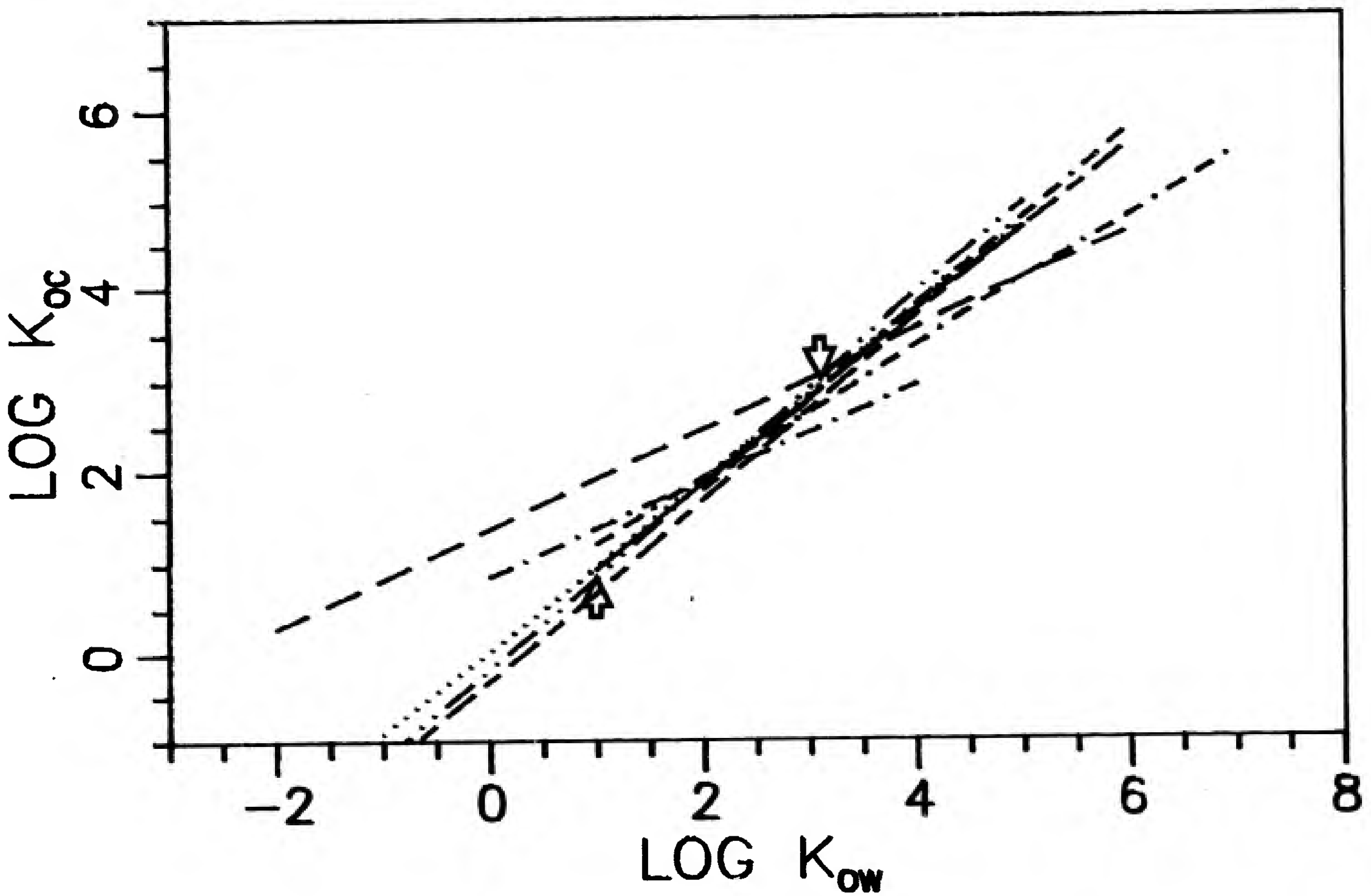

FIGURE 5.26 Plot of Log $K_{oc}$ Versus Log $K_{ow}$ for Various Regression Equations Reported in the Literature and From This Research. (End-points of the regression line determined in this research are indicated by the arrows.)

sorbates as well) with soils is attributable primarily to soil organic matter. The question addressed herein is: Which component(s) of this soil organic matter (SOM) is(are) responsible for this sorption? The answer to this question is important since therein may lie the reason for the high variability of $K_{oc}$ values for the same sorbate among several types of soils. For example, if it is found that the soil lipid fraction is responsible for virtually all the sorption of these types of compounds, then this could explain why two soils with identical organic carbon contents (but different lipid fractions) would sorb the same compound with different intensity.

As previously stated in the "Background" Chapter, the techniques normally employed by investigators attempting to answer the above question, involve the "selective" removal/destruction of certain organic fractions via physical and/or chemical treatments of a soil. However, these techniques suffer from the following potential problems:

(a) The techniques are (generally) not truly selective for the organic component(s) which they intend to remove or destroy. For example, Flagg _et al_. (1975) noted that the usual sodium hydroxide extraction procedure for the separation of humic and fulvic acids, results in the dissolution of various non-humic components such as hemicellulose and lignin; and chemical alteration or condensation reactions which affect the protein and carbohydrate fractions of the soil.

(b) The treatment may modify surface properties (e.g., by altering or removing various surface functional groups).

(c) The chemical used in an extraction procedure may itself sorb with the soil, and thus (potentially) result in different sorption characteristics for the "test" sorbate (which would inadvertently be attributed to the soil component presumably extracted). For example, various organic solvents (such as benzene, ether, ethanol, methanol, or mixtures of these solvents) are typically used to extract the lipid fraction of soil organic matter. However, if these compounds sorb with the soil in the process, then they would likely affect any future sorption by this soil.

In view of the above problems, I decided to use a different method for identifying the organic components responsible for sorption. A variety of "pure" organic materials were selected to represent the various classes of soil organic matter, and used as the sorbents in the sorption tests. The selection of these organic materials is discussed below, preceded by a brief discussion of SOM classification.

Components of soil organic matter are commonly categorized as either humic or non-humic substances. The latter category includes those substances which retain clearly defined physical-chemical properties, such as exact elementary composition, sharp melting point, definite infrared spectrum, and exact refractive index (Schnitzer and Khan, 1978). The non-humic substances therefore include the SOM sub-categories of carbohydrates (polysaccharides), lipids (fats, waxes, and resins), organic nitrogen/phosphorus/sulfur compounds (e.g., proteins, peptides, amino acids, nucleic acids, and phospholipids), and various small organic molecules (which may not fit in any of these sub-categories).

In addition, Allison (1965) included "inert forms of nearly elemental carbon, such as charcoal, coal, or graphite" as a sub-category of SOM. The humic substances, by contrast, do not exhibit specific physical-chemical properties, and are (generally) further classified by the following fractions: (1) humic acid, which is soluble in dilute alkaline solution, but precipitates upon acidification of the alkaline extract; (2) fulvic acid, which remains soluble when the alkaline extract is acidified; and (3) humin, the humic fraction which cannot be extracted from soil by either dilute base or acid. These humic substances are amorphous, three-dimensional polymers (with molecular weights ranging from several hundred to several hundred thousand), and tend to be aromatic structures with acidic functional groups (Ahlrichs, 1972). The humic substances constitute approximately 60 to 70 percent of total soil organic matter (Schnitzer and Khan, 1978); the polysaccharides about 5 to 20 percent (Duxbury, 1983); and the lipids about 1 to 5 percent for mineral soils, and 10 to 20 percent for organic soils (Braids and Miller, 1975).*

Humic acid was selected as the representative component from the class (i.e., sub-category) of humic substances, primarily because it was readily available, and can be maintained in the solid (i.e., insoluble) form during sorption experiments by reducing pH (i.e., the sorption experiments [using the methods in this research] would not be possible with fulvic acid since this component would be soluble). Furthermore, the structure and properties of humin are reported to be

---

*Data on the relative abundance of the other SOM sub-categories were not available.

very similar to that of HA (rather than FA) (Schnitzer and Khan, 1978). Lignin was also selected for study under this class of SOM, even though it is not generally classified as a humic substance. (However, lignin would meet the operational definition of a humic substance, since it would solubilize in dilute alkaline solution.) According to current theory, lignin is one of the "building blocks" of humic substance formation (Stevenson, 1982), and it might be of interest to know how its sorption (if any) compares with that of HA. Furthermore, this constituent was readily available (and remains insoluble at low pH). I therefore decided to test its sorption capability, along with that of HA.

Cellulose was chosen as the representative carbohydrate (polysaccharide) since most of the carbohydrate added to the soil is in the form of cellulose (Greenland and Oades, 1975). Furthermore, it is highly insoluble in water, and was also readily available.

Numerous compounds have been identified in the soil lipid fraction, and many of these were listed by Braids and Miller (1975). The selection of compounds to "represent" the lipid class from this list was done primarily on the basis of availability. That is, many of the compounds listed by Braids and Miller (see pp. 346-355 of this reference) were not available from various suppliers. Also, an attempt was made to obtain a variety of lipid components with respect to their molecular structures and compositions. As a result, the following compounds were obtained for representing the lipid fraction: pyrene, carbazole, lignoceric acid, and L-$\alpha$-phosphatidylcholine.

I decided to select a single amino acid--L-glutamic acid, to represent the organic nitrogen/phosphorus/sulfur class of SOM components. This was done because the nitrogenous organic compounds are the most abundant of the three, and furthermore, glutamic acid is a fairly common amino acid in soils (Parsons and Tinsley, 1975--see Table 4, p. 285).

Lastly, graphite was selected as the representative form of elemental carbon solely on the basis of availability. (Charcoal was available only in the "activated" form.)

It should be emphasized that because of the plethora of organic components in SOM, it would be virtually impossible to conclude that _only_ certain components are responsible for sorption of the compounds in this research. However, it is believed that the components selected for examination serve as worthy representatives of their respective classes; and since these SOM classes (i.e., sub-categories) include the bulk of all soil organic matter, valid conclusions can probably be drawn regarding which of these SOM classes are causing _most_ of the sorption.

### 2. Materials and Methods

The following "pure" organic materials (underlined below) were selected to represent the various classes of soil organic matter in these experiments:

(a) Humic Substances: _Humic Acid_, Sodium Salt (Aldrich Chemical Co., Inc.) and _Lignin_*, Kraft Pine, "Indulin AT", (Westvaco Chemical Division).

---

*Although (technically) lignin is not classified as a humic substance, it is believed to be a precursor, and also would be removed along with the humic and fulvic acids during the extraction procedure. Therefore, for purposes of this research, it is grouped in this category.

(b) Carbohydrates (Polysaccharides): Cellulose, "Sigmacell", Type 20, microcrystalline cellulose, 20 μm average particle size (Sigma Chemical Co.).

(c) Lipids (Fats, Waxes, and Resins):

(1) Pyrene, $C_{16}H_{10}$--a hydrocarbon (Sigma Chemical Co.).

(2) Carbazole, $C_{10}H_9N$--a heterocyclic (Sigma Chemical Co.).

(3) Lignoceric Acid, $CH_3(CH_2)_{22}COOH$--a high molecular weight fatty acid; also called tetracosanoic acid (Sigma Chemical Co.).

(4) L-α-Phosphatidylcholine--a phospholipid; also called L-α-lecithin; obtained from soybean (Sigma Chemical Co.).

(d) Nitrogenous Substances (Proteins): L-glutamic Acid, free acid; crystalline (Sigma Chemical Co.).

(e) Elemental Carbon: Graphite, powder, Grade #38 (Fisher Scientific Co.).

A "target" mass of 0.05 g (or slightly more) of each organic material (except for graphite and HA) was added to a reaction vial.* For the cases of graphite and HA, the masses used were approximately 0.02 and 0.01 g per R.V., respectively.** Also, for the lignin, glutamic acid,

---

*The "exact", final mass delivered to each R.V. was always measured, using a Mettler Instruments Corp. analytical balance.

**The concentration of HA was limited to ∿0.01 g per 5.5 ml of solution in order to remain within the quench curve of the LSC. That is, the soluble HA content at higher concentrations caused the quench level of the scintillation vial sample to exceed the applicable range of the quench curve.

For the case of graphite, it was thought that 0.05 g of this adsorbent might result in excessive adsorption. Therefore, a preliminary ("ballpark") test was run, which showed that 0.02 g graphite per R.V. was a suitable amount to use.

(GA), and HA sorbents, I was interested in assessing the effect on sorption, of the presence of an inorganic solid. For this purpose, an $Al^{+3}$-saturated montmorillonite suspension (with a solids concentration of 15 g/l) was used. Since the adsorption of lignin, GA, and HA to montmorillonite are maximized at low pH, the pH of these suspensions was lowered to 2.0* by the addition of HCl. In addition, sorption by the lignin, GA, and HA were measured at pH = 2.0 in the absence of the clay; and for lignin and GA (at pH of 6.3 and 3.3, respectively, without the clay present (i.e., simply lignin or GA with distilled water). Therefore, depending on its use, each sorbent R.V. received (after the appropriate solids were weighed into them) either: (a) 5.0 ml of distilled water (DW), (b) 5.0 ml of DW adjusted to pH = 2 (by addition of HCl), or (c) 5.0 ml of an $Al^{+3}$-montmorillonite suspension adjusted to pH = 2 (by addition of HCl). The control R.V.'s were also prepared as (a), (b), or (c) above, as necessary (without the organic sorbent, of course). In addition, a control R.V. of $Al^{+3}$-montmorillonite suspension at pH = 4.3 (i.e., non-buffered) was prepared to assess any (possible) effect of pH alone on the adsorption (of the sorbate compound) by the clay. Two replicates were used for each sorbent R.V. and each control R.V. Once prepared, each R.V. was injected with 0.5 ml of the low-level $^{14}C$-$C_2Cl_4$ stock solution. (Tetrachloroethylene was selected

---

*This is well below the isoelectric point of GA, and the $pK_a$'s of the phenolic-OH and carboxylic acid (-COOH) functional groups predominant in HA and lignin. Thus, adsorption of these SOM components to the clay should have occurred. The adsorption of the HA and lignin to the $Al^{+3}$-montmorillonite was in fact confirmed visually. That is, within a matter of minutes of adding the acidified clay suspension to these SOM components (and mixing), the previously white, clay solids were coated brown; and the liquid phases were virtually clear, indicating removal of the soluble HA and lignin components.

as the sorbate in these experiments since it consistently sorbed more strongly than the other compounds for any given sorbent.) The experiments were conducted at T = 20°C and $t_{eq}$ = 2 days. Conductivities of the suspensions used in these experiments were not measured, and thus, ionic strengths are not reported.

### 3. Results

Table 5.16 exhibits the outcome of these experiments. A one-tailed t-test* at the 95 percent C.L. revealed that, of the organic components tested, only lignoceric acid, graphite, lignin, and HA were significant sorbents for PCE. However, the sorptive capacity and $K_d$ value of the lignoceric acid was judged to be negligible (i.e., only 0.161 μg/g and 7.22, respectively) compared with that for the other three, and far too low to account for the sorption observed with the "real" soils.

Therefore, it is postulated that the principal soil organic matter components responsible for the sorption of the compounds studied herein are humic acid, humin, lignin, and forms of elemental carbon (e.g., charcoal and graphite). This postulation assumes that the humin fraction would sorb similar to the HA fraction, since their structures are basically similar;** and likewise regarding various forms of elemental carbon and graphite. Because only a limited number of many possible soil organic components were examined, the possibility that other (less common or abundant) organic matter components could contribute to the sorption of these

---

*The (alternative) hypothesis tested was that $\overline{X}_\ell < \overline{X}_\ell^o$ for each sorbent and its corresponding control.

**The FA fraction is more hydrophillic than the HA and humin fractions since it possesses more oxygen-containing functional groups. Furthermore, Garbarini (1985) found that TCE (and toluene) was much more strongly sorbed by the HA than by the FA fractions extracted from a surface soil.

TABLE 5.16 Test for Sorption of Tetrachloroethylene ($C_2Cl_4$) with Various Soil Organic Matter Components (T = 20°C; $t_{eq}$ = 2d)

-- Experiment A --

| Component | $\overline{X}_\ell^o$ or $\overline{X}_\ell$ (DPM/ml) | $C_\ell$ (μg/l) | $C_s$ (μg/g) | $K_d$ |
|---|---|---|---|---|
| Control (Distilled Water) | 4923 ± 3 | ---- | ---- | ---- |
| Cellulose | 4933 ± 80 | ---- | ---- | ---- |
| Carbazole | 4864 ± 64 | ---- | ---- | ---- |
| Lignoceric Acid | 4648 ± 63 | 22.3 | 0.161 | 7.22 ± 1.75 |
| Pyrene | 4897 ± 40 | ---- | ---- | ---- |
| L-α-phosphatidyl choline* | ---- | ---- | ---- | ---- |

---

*This component formed a colloidal phase which could not be separated via centrifugation.

-- Experiment B --

| | | | | |
|---|---|---|---|---|
| Control (DW) | 4310 ± 25 | ---- | ---- | ---- |
| Graphite | 1130 ± 74 | 5.41 | 4.75 | 878 ± 100 |

TABLE 5.16 (continued)

-- Experiment C --

| System Components | pH | $\bar{X}^o_\ell$ or $\bar{X}_\ell$ (DPM/ml) | $C_\ell$ (μg/l) | $C_s$ (μg/g) | $K_d$ |
|---|---|---|---|---|---|
| Control (DW + HCl) | 2 | 4389 ± 184 | ---- | ---- | ---- |
| Control (DW) | 5.6 | 4398 ± 131 | ---- | ---- | ---- |
| Control ($Al^{+3}$-mont. suspension + HCl) | 2 | 4366 --- | ---- | ---- | ---- |
| Control ($Al^{+3}$-mont. suspension) | 4.3 | 4420 ± 21 | ---- | ---- | ---- |
| Lignin + $Al^{+3}$-mont. + HCl | 2 | 1575 ± 88 | 7.54 | 1.60 | 212 ± 22 |
| GA + $Al^{+3}$-mont. + HCl | 2 | 4391 ± 88 | ---- | ---- | ---- |
| Lignin + HCl + DW | 2 | 1755 ± 62 | 8.41 | 1.51 | 180 ± 15 |
| GA + DW + HCl | 2 | 4391 ± 6 | ---- | ---- | ---- |
| Lignin + DW | 6.3 | 1852 ± 26 | 8.87 | 1.46 | 165 ± 10 |
| GA + DW | 3.3 | 4354 ± 42 | ---- | ---- | ---- |
| -- Experiment D -- | | | | | |
| Control ($Al^{+3}$-mont. + HCl) | 2 | 4688 ± 23 | ---- | ---- | ---- |
| HA + $Al^{+3}$-mont. + HCl | 2 | 4174 ± 2 | 20.0 | 3.07 | 154 ± 8 |
| -- Experiment E -- | | | | | |
| Control (DW + HCl) | 2 | 4310 ± 25 | ---- | ---- | ---- |
| HA + DW + HCl | 2 | 3458 ± 81 | 16.6 | 2.54 | 153 ± 24 |

Abbreviations:
DW ≡ Distilled Water
GA ≡ Glutamic Acid
HA ≡ Humic Acid
Mont. ≡ Montmorillonite

TABLE 5.16 (continued)

Notes:

Standard deviations are given for $\overline{X}_\ell^o$, $\overline{X}_\ell$, and $K_d$, as the ± values. (Consult Appendix F for the error propagation analysis used in determining the standard deviations for the single-point $K_d$'s.) Values for $C_\ell$, $C_s$, and $K_d$ are given only for cases where sorption is significant at the 95-percent confidence level. Each sorbent reaction vial contained a target organic component concentration of ≈ 10 g/l, except for graphite and HA whose concentrations were ≈ 4 g/l and ≈ 2 g/l, respectively. (The "exact" mass added to each vial was always measured.) The $Al^{+3}$-montmorillonite concentration was 15 g/l.

compounds cannot be ruled out.* On the other hand, since 60 to 70 percent of the total soil carbon occurs in humic materials (Schnitzer and Khan, 1978), and the presence of elemental forms of carbon in soils is probably quite rare (Duxbury, 1983), it seems probable that in most cases, humic substances (including lignin, but probably excluding FA) could account for virtually all the sorption of these types of compounds.

Other conclusions can also be drawn from examination of the data in Table 5.16. Experiment "C" shows that for the GA, neither the presence of the clay, nor the pH affected sorption by this component (i.e., GA did not sorb PCE under any conditions). Whereas for lignin, the presence of the clay resulted in the highest sorption, followed by lignin + HCl (pH = 2), and lignin alone (pH = 6.3). This trend is attributed to the decrease in the fraction of lignin associated with the solid phase for the systems: clay > pH = 2 > pH = 6.3. (This trend in the fraction of particulate lignin was verified by the sample H#'s provided by the LSC, which yields an indirect measure of the soluble lignin content.)

Experiments "D" and "E" in Table 5.16 reveal that the presence of the $Al^{+3}$-saturated montmorillonite had no apparent effect on the sorption by HA. This can be readily seen by comparing the "single-point" $K_d$ values (i.e., 1000 $C_s/C_\ell$), computed from each experiment as 154 (± 8) and 153 (± 24), for Experiments "D" and "E", respectively. That is,

---

*For example, Garbarini (1985) found significant sorption of TCE by the lipid fraction extracted from a real soil. On the other hand, he measured a higher $K_{oc}$ value for the lipid-extracted soil than for the whole (untreated) soil. Garbarini stated that an "unmasking" effect (i.e., the lipid fraction has been surmised to mask active sorption sites) may account for his observed results, if it is assumed that all the ethyl ether extractant was removed from the sorbents prior to the actual sorption tests.

the distribution of $C_2Cl_4$ between the HA and aqueous phase seems to be independent of the presence of the clay. (This result is somewhat contrary to that of Lion and Garbarini [1983] who observed that the presence of $Al_2O_3$ inhibited the sorption of toluene by HA.)

## G. Determination of Sorption Thermodynamic Properties (Free Energy, Enthalpy and Entropy) and Discussion of Probable Sorption Mechanisms

### 1. Experimental Procedures

The standard Gibb's free energy ($\Delta G^o$), enthalpy ($\Delta H^o$), and entropy ($\Delta S^o$) of sorption can be determined from isotherm $K_d$ values, and the equations given in Chapter II.* The $\Delta G^o$ value can be calculated from a single (linear) isotherm using the relationship $\Delta G^o = -RT \ln K_d$; however, $\Delta H^o$ (and thus, $\Delta S^o$) requires the determination of $K_d$ values for at least two isotherms, each performed at different temperatures.

Most studies of sorption thermodynamics reported in the literature use only two isotherms for this analysis. In an attempt to improve upon the reliability of the resulting thermodynamic variables ($\Delta H^o$ and $\Delta S^o$), I chose to perform isotherms at three different temperatures for each soil and SOM component (including graphite). (The only exception to this was for the system of TCE with the mineral soil, for which isotherms at five different temperatures were determined, since this was the first system to be analyzed.)

---

*Although the actual values for $\Delta G^o$, $\Delta H^o$, and $\Delta S^o$ determined in this section are not "rigorously" correct because of the problems associated with the activity (or activity coefficient) of a sorbed species, they are nevertheless useful values for comparative purposes. Furthermore, if the assumptions made in Chapter II for the derivation of $K_d$ are valid, then the values for these thermodynamic properties are probably quite reasonable.

A temperature (T) of 20°C was an obvious choice for one of the temperatures, since all the previous isotherms had been determined at this value. For the other two temperatures, I had initially selected 2°C and 50°C, in an attempt to cover a fairly broad range. However, occasional experimental problems were encountered during equilibration at 50°C (i.e., some of the vial caps would loosen, and poor data precision in a few cases suggested that compound leakage from the vials was occurring ). Dropping the temperature to 45°C (and checking cap tightness daily) eliminated this problem, and all the experiments were repeated at this temperature. Therefore, the three isotherm temperatures used in the analyses of thermodynamic properties were 2°, 20°, and 45°C.

The experimental procedures used in the determination of isotherms at the low (2°C) and high (45°C) temperatures were the same as those used for the 20°C isotherm experiments, with the following exceptions: (1) the 2°C and 45°C $K_d$ values were determined from "single-point" isotherms,* whereas the $K_d$ values for the 20°C isotherms (for the real soils) were based on linear regressions from a minimum of three data points; (2) the "single-point" isotherms were determined from three replicate samples for the case of the real soils, and two replicate samples for the case of the SOM components; (3) the R.V.'s (and their liquid contents) for the high temperature experiments were preheated to ~50°C prior to the injection of the radiolabeled compound and vial sealing, so that equilibration at 45°C would not create a positive

---

*The slope of these isotherms was simply the value of $C_s/C_\ell$ for the single data point (i.e., the slope of a line from the origin through the data point).

pressure in the R.V.'s (which would have potentially caused compound leakage from the R.V.'s); (4) centrifugation was performed at the temperature corresponding to that of the isotherm (i.e., not 20°C as in the case of all previous isotherms); and (5) during the (short) period between centrifugation and actual sampling, the R.V.'s were maintained at (approximately) their corresponding isotherm temperature, by immersing them in a water bath (at approximately this temperature).

The pH and approximate ionic strength of each of these sorbent suspensions are summarized in Table 5.17.

TABLE 5.17 pH and Approximate Ionic Strength ($I$) of the Sorbent Suspensions

| Sorbent | pH | $I^*$(M) |
|---|---|---|
| Mineral Soil | 7.7 | 0.0036 |
| Peat† | 7.7 | 0.0036 |
| Muck† | 7.7 | 0.0036 |
| Humic Acid# | 2.0 | 0.13 |
| Lignin# | 2.0 | 0.17 |
| Graphite | 6.6 | 0.0004 |

*Calculated using the correlation of Snoeyink and Jenkins (1980):

$$I = 1.6 \times 10^{-5} \times \text{Conductivity } (\mu\text{mho/cm}).$$

†The pH and $I$ for these sorbents were adjusted (by addition of NaOH and NaCl) to correspond to that for the mineral soil.

#The pH for these sorbents was adjusted to 2.0 (by addition of HCl) to minimize their solubility.

## 2. Results

Table 5.18 presents the matrix of $K_d$ values and their standard deviations* determined for each sorbent-sorbate pair at the three different temperatures. Note that in most cases sorptive strength either decreases with increasing temperature, or shows no apparent trend.

The following additional observations are made with regard to Table 5.18:

(1) Most of those instances where no apparent trend is revealed, the $K_d$ value at 20°C is the lowest of the three. (Note that this observation is always true for the case of peat.)

(2) The only cases where $K_d$ values clearly increase with temperature are for $C_2HCl_3$ and $C_2Cl_4$ with the mineral soil. [The $CCl_4$-G system is not mentioned since $K_d(2°C) \approx K_d(20°C)$.]

(3) The sorption by lignin and HA were roughly comparable ($K_d$ values were within a factor of two for any given sorbate and temperature), reflecting the similar chemical natures of these components.

(4) The ordering of sorptive strength among the compounds (for any given sorbent) was roughly the same for the three different temperatures. For example, the sorptive strength of the compounds for graphite decreased in the order $C_2Cl_4 > C_2HCl_3 > CCl_4 > CHCl_3$ for all temperatures; and the ordering for peat was $C_2Cl_4 > CCl_4 > C_2HCl_3 > CHCl_3$ for all temperatures.

(5) The sorptive strength of peat was greater than any other sorbent (for any given sorbate, at all temperatures) except for the $C_2Cl_4$-G system, and $C_2HCl_3$-G (at 20°C) system.

---

*Refer to Appendix F for the methods used to determine the standard deviations of the $K_d$ values.

TABLE 5.18 Sorption Distribution Coefficients ($K_d$'s) (and Their Standard Deviations) as a Function of Temperature

| Sorbate | Sorbent* | $K_d$ (2°C)** | $K_d$ (20°C)** | $K_d$ (45°C)** | Trend with Respect to Increasing Temperature |
|---|---|---|---|---|---|
| $CHCl_3$ | MS | 9.60 (± 1.1) | 7.80 (± 0.32) | 9.24 (± 1.8) | --- |
| | P | 91.5 (± 10) | 40.9 (± 1.0) | 72.0 (± 8.6) | --- |
| | M | 12.9 (± 0.87) | 6.89 (± 0.43) | 2.28 (0.29) | ↓ |
| | HA | 19.4 (± 7.5) | 20.0 (± 3.3) | 15.3 (± 18) | --- |
| | L | 32.3 (± 2.5) | 19.9 (± 1.6) | 19.1 (± 3.3) | ↓ |
| | G | 5.52 (± 4.5) | 0.48 (± 3.6) | 0.00 (± 7.0) | ↓ |
| $CCl_4$ | MS | 10.1 (± 1.3) | 5.39 (± 0.68) | 5.58 (± 5.5) | --- |
| | P | 197 (± 16) | 119 (± 1.5) | 173 (± 23) | --- |
| | M | 32.0 (± 2.9) | 22.9 (± 0.2) | 19.2 (± 2.5) | ↓ |
| | HA | 49.0 (± 8.1) | 39.8 (± 19) | 84.1 (± 11) | --- |
| | L | 58.2 (± 4.7) | 80.1 (± 7.8) | 73.8 (± 3.6) | --- |
| | G | 20.7 (± 4.6) | 21.9 (± 4.8) | 48.3 (± 44) | ↑ |
| $C_2HCl_3$ | MS† | 39.3 (± 2.1) | 56.4 (± 1.6) | 69.8 (± 11) | ↑ |
| | P | 159 (± 15) | 90.7 (± 2.4) | 154 (± 40) | --- |
| | M | 37.8 (± 2.5) | 25.1 (± 1.2) | 31.1 (± 9.7) | --- |
| | HA | 53.1 (± 5.9) | 38.9 (± 5.1) | 48.2 (± 24) | --- |
| | L | 85.2 (± 3.7) | 63.2 (± 3.0) | 51.8 (± 5.7) | ↓ |
| | G | 129 (± 20) | 110 (± 8.3) | 61.2 (± 38) | ↓ |
| $C_2Cl_4$ | MS | 50.2 (± 1.8) | 71.1 (± 1.2) | 129 (± 37) | ↑ |
| | P | 407 (± 17) | 281 (± 5.7) | 312 (± 53) | --- |
| | M | 97.9 (± 2.4) | 68.6 (± 5.8) | 52.5 (± 25) | ↓ |
| | HA | 194 (± 20) | 153 (± 24) | 144 (± 64) | ↓ |
| | L | 191 (± 10) | 172 (± 11) | 141 (± 11) | ↓ |
| | G | 979 (± 69) | 878 (± 100) | 359 (± 67) | ↓ |

Footnotes to Table 5.18

*MS ≡ Mineral Soil; P ≡ Peat; M ≡ Muck; HA ≡ Humic Acid; L ≡ Lignin; G ≡ Graphite.

**$K_d$ values determined from single-point isotherms, except for the real soils (with all sorbates) at T = 20°C, which were determined from multipoint isotherms. Refer to Appendix F for the determination of the standard deviations (given in parentheses).

† Multipoint isotherms for the $C_2HCl_3$-MS system were also determined at T = 7°C and T = 50°C, with $K_d$ values of 48 and 75, respectively. (Note that these values are also in accord with indicated trend.)

The lack of trend in $K_d$ versus temperature (in accordance with the van't Hoff expression [refer to Equations (2-16)-(2-18)]) for certain sorbent-sorbate pairs can probably best be explained by a combination of unexpectedly high uncertainties in some of the $K_d$ values--coupled with, what appears to be (in many cases), a very small enthalpy of sorption.* Nevertheless, the following (less probable) explanations are offered, since they cannot entirely be ruled out:

(a) The enthalpy of sorption ($\Delta H^o$), which is assumed to be relatively independent of temperature over the 2 to 45°C range in this study, may, in fact, be significantly dependend on temperature. (For example, if the $\Delta H^o$ value for a particular sorbent-sorbate pair is near zero [i.e., very low], but is slightly negative in the low temperature range, and becomes slightly positive in the high temperature range, then this could explain those cases wherein the $K_d$ value at 20°C is the lowest of the three.

---

*That is, the variation of $K_d$ with respect to temperature was relatively small.

(b) The structural properties and characteristics of the sorbents may be affected by temperature, which may, in turn, affect their sorption characteristics.

(c) As previously mentioned in Chapter II, various thermal anomalies ("kinks") in the properties of water and aqueous solutions have been reported (Drost-Hansen, 1967). These "kinks" have been observed for equilibrium and transport properties related to interfacial phenomena, and there is good evidence for these thermal anomalies in the properties at water-solid, water-air, or other water-interface surfaces (Martin, 1970). These thermal anomalies are most frequently observed at transition temperatures of 15°, 30°, 45°, and 60°C, and thus, could account for some of the "anomalous" variations in $K_d$ (as a function of temperature) determine in this research.

The assumption is made that the general lack of (expected) trend in $K_d$ with respect to temperature was principally due to experimental error (and that the "true" $K_d$ values would, in fact, have followed a van't Hoff-type of trend). In addition, I assume that the sorption enthalpy ($\Delta H^o$) is relatively constant over the 2° to 45°C temperature range, and thus, the following integrated form of the basic van't Hoff expression* could be used:

$$\ln K_d = \frac{\Delta H^o}{R_g T} + \text{constant} \quad . \tag{2-18}$$

---

*That is, $(\partial \ln K/\partial T) = (\Delta H^o/R_g T^2)$, which defines the change in an equilibrium constant, K, with respect to temperature.

A plot of $\ln K_d$ versus $1/T$ should therefore result in a straight line whose slope is equal to $-\Delta H^o/R_g$. Since the variances in the $K_d$ measurements were known (i.e., calculated), I chose to use a weighted, least-squares, linear regression of $\ln K_d$ versus $1/T$ in determining this slope (and hence, $\Delta H^o$). In other words, the regressions were performed by weighting each of the data points by a factor equal to the reciprocal of the variance of the corresponding $K_d$ for that data point. That is, $W_i = 1/\sigma^2_{K_{d_i}}$, where $\sigma^2_{K_{d_i}}$ is the variance*, and $W_i$ is the weighting factor, of the $i$th $K_d$ value. It is assumed that errors in the measurement of T (and hence, $1/T$) were negligible compared with that for $K_d$.

The $\Delta H^o$ values (and their corresponding standard deviations) which result from the weighted, least-squares regressions are depicted in Table 5.19. Note that in some cases the magnitude of the standard deviation is larger than its corresponding $\Delta H^o$ value, indicating the high degree of uncertainty in these data. Also, since each regression line is determined from three data points, the possibility exists that the (apparent) high precision (i.e., low S.D.) in some of the $\Delta H^o$ values is strictly due to chance. Table 5.19 also shows that 17 of the 23 $\Delta H^o$ values were negative quantities. The null hypothesis that $\Delta H^o = 0$ (and that the fluctuations of the $\Delta H^o$ values [about zero] in Table 5.19 are strictly due to the random error), can be rejected at the 95 percent confidence level (CL), but not at the 99 percent CL. Therefore, the predominantly negative $\Delta H^o$ values are <u>probably</u> significant, and not attributable to random error.

---

* It is assumed that the best estimate of this population variance is provided by the sample variance (i.e., the sample standard deviations [given in Table 5.18] squared).

TABLE 5.19 Sorption Enthalpies ($\Delta H^o$) and Their Standard Deviations Calculated Using Weighted, Least-Squares Regressions* on Plots of ln $K_d$ versus 1/T

| Sorbate | Sorbent** | $\Delta H^o$ (kcal/mol)† | S.D. (kcal/mol)†† |
|---|---|---|---|
| $CHCl_3$ | MS | -0.71 | ± 1.4 |
| | P | +0.31 | ± 5.3 |
| | M | -7.6 | ± 0.71 |
| | HA | -0.27 | ± 0.88 |
| | L | -2.4 | ± 1.6 |
| | G# | ---- | ---- |
| $CCl_4$ | MS | -5.0 | ± 1.6 |
| | P | -1.5 | ± 3.5 |
| | M | -1.9 | ± 0.79 |
| | HA | +2.1 | ± 1.3 |
| | L | +0.88 | ± 0.60 |
| | G | +0.74 | ± 0.91 |
| $C_2HCl_3$ | MS | +3.1 | ± 0.41 |
| | P | -3.4 | ± 3.3 |
| | M | -3.0 | ± 1.5 |
| | HA | -2.1 | ± 1.3 |
| | L | -2.1 | ± 0.44 |
| | G | -2.4 | ± 1.3 |
| $C_2Cl_4$ | MS | +3.1 | ± 0.09 |
| | P | -2.7 | ± 1.4 |
| | M | -3.0 | ± 0.28 |
| | HA | -1.6 | ± 0.55 |
| | L | -1.2 | ± 0.15 |
| | G | -4.1 | ± 1.2 |

*The weighting factors were equal to the reciprocal of the variances of the $K_d$ values. Errors in the measurement of T (and hence 1/T) were assumed to be negligible relative to that for $K_d$.

**MS ≡ Mineral Soil; P ≡ Peat; M ≡ Muck; HA ≡ Humic Acid; L ≡ Lignin; G ≡ Graphite.

† Calculated as $-R_g$ (= $1.987 \times 10^{-3}$ kcal/mol °K) times the slope of the weighted, least-squares regression line for the plot of ln $K_d$ versus 1/T.

††Calculated as the standard deviation of the slope coefficient multiplied by $R_g$.

# The $\Delta H^o$ value for this case was undefined since two of its $K_d$ values were about equal to zero.

In an attempt to determine the 95 percent confidence limits on the $\Delta H^o$ values, I assumed that the "true" sorption enthalpies for each sorbent-sorbate pair within each sorbate group would be approximately equal. (The implicit assumption here is that heats of sorption are predominantly controlled by properties of the sorbate, rather than the sorbent.) Furthermore, I chose to use a "normal" mean for the $\Delta H^o$ data, rather than a weighted mean, since I did not want to assign (possibly) "undeserved" weighting to the $\Delta H^o$ values which "appeared" to have greater precision.* The resulting mean $\Delta H^o$ values (designated by $\Delta \overline{H}^o$) and their 95 percent confidence intervals (CI) are:

| Sorbate | $\Delta \overline{H}^o$ ± 95% CI (kcal/mol) |
|---|---|
| $CHCl_3$ | -2.1 ± 4.0 |
| $CCl_4$ | -0.78 ± 2.7 |
| $C_2HCl_3$ | -1.7 ± 2.5 |
| $C_2Cl_4$ | -1.6 ± 2.6 |

The sorption free energies and entropies (and their corresponding errors) were also calculated (for T = 20°C), and are presented in Table 5.20. The standard deviations given in this table were calculated by error propagation analyses through the corresponding equations defining $\Delta G^o$ and $\Delta S^o$ (refer to Table 5.20 footnotes). The free energies of sorption (at T = 20°C) for these compounds by the various sorbents examined, range from -0.98 to -3.9 kcal/mol, with $\Delta G^o$ values within each

---

*In other words, the variances of the $\Delta H^o$ values were assumed to be statistically the same. This assumption is supported by an F-test at the 95 percent CL, which showed that the majority of these variances are not statistically different.

TABLE 5.20 Sorption Free Energies ($\Delta G^o$) and Entropies ($\Delta S^o$) (and Their Standard Deviations) Determined at T = 20°C

| Sorbate | Sorbent* | $\Delta G^o$ (kcal/mol)† | $\Delta S^o$ ($10^{-3}$ kcal/mol °K)†† |
|---|---|---|---|
| $CHCl_3$ | MS | -1.2 (± 0.02) | +1.7 (± 4.8) |
| | P | -2.2 (± 0.01) | +8.6 (± 18) |
| | M | -1.1 (± 0.03) | -22. (± 2.4) |
| | HA | -1.7 (± 0.10) | +1.4 (± 3.0) |
| | L | -1.7 (± 0.05) | -0.07(± 5.5) |
| | G# | ---- | ---- |
| $CCl_4$ | MS | -0.98(± 0.08) | -14. (± 5.5) |
| | P | -2.8 (± 0.01) | +4.4 (± 12.) |
| | M | -1.8 (± 0.01) | -0.34(± 2.7) |
| | HA | -2.1 (± 0.28) | +14. (± 4.7) |
| | L | -2.6 (± 0.06) | +12. (± 2.1) |
| | G | -1.8 (± 0.13) | + 8.7 (± 3.1) |
| $C_2HCl_3$ | MS | -2.3 (± 0.02) | +18 (± 1.4) |
| | P | -2.6 (± 0.02) | -2.7 (± 11) |
| | M | -1.9 (± 0.03) | -3.8 (± 5.1) |
| | HA | -2.1 (± 0.08) | 0.0 (± 4.5) |
| | L | -2.4 (± 0.03) | +1.0 (± 1.5) |
| | G | -1.7 (± 0.05) | +1.0 (± 4.4) |
| $C_2Cl_4$ | MS | -2.5 (± 0.01) | +19 (± 0.31) |
| | P | -3.3 (± 0.01) | +0.6 (± 4.8) |
| | M | -2.5 (± 0.05) | -1.7 (± 0.99) |
| | HA | -2.9 (± 0.09) | +4.4 (± 2.0) |
| | L | -3.0 (± 0.03) | +1.8 (± 0.52) |
| | G | -3.9 (± 0.06) | -0.68(± 4.1) |

*MS ≡ Mineral Soil; P ≡ Peat; M ≡ Muck; HA ≡ Humic Acid; L ≡ Lignin; G ≡ Graphite.

† Calculated from the formula $\Delta G^o = -RT \ln K_d$ where the $K_d$ value used is that for T = 20°C. The standard deviations (given as the ± values in parentheses) are calculated using the general error propagation equation:

$$\sigma_{\Delta G^o} = [(\partial\Delta G^o/\partial K_d)^2 \sigma^2_{K_d}]^{\frac{1}{2}}$$

or

$$\sigma_{\Delta G^o} = \frac{RT}{K_d} \sigma_{K_d}$$

where it is assumed that $K_d$ makes the only significant contribution to error.

†† Calculated from the formula $\Delta S^o = (\Delta H^o - \Delta G^o)/T$ where a temperature of 293°K (20°C) was used. The standard deviations (given as the ± values

TABLE 5.20 (continued)

in parentheses) were determined using the general error propagation formula:

$$\sigma_{\Delta S^o} = \left[\left(\frac{\partial \Delta S^o}{\partial \Delta H^o}\right)^2 \sigma^2_{\Delta H^o} + \left(\frac{\partial \Delta S^o}{\partial \Delta G^o}\right)^2 \sigma^2_{\Delta G^o}\right]^{\frac{1}{2}}$$

or

$$\sigma_{\Delta S^o} = \frac{1}{T}\left(\sigma^2_{\Delta H^o} + \sigma^2_{\Delta G^o}\right)^{\frac{1}{2}}$$

where it is assumed that the error contributed by T is negligible.

[#] The $\Delta G^o$ and $\Delta S^o$ values for this case were undefined since $K_d(20°C) \approx 0$, and also $\Delta H^o$ was undefined.

---

sorbate group generally decreasing in the order $C_2Cl_4 > C_2HCl_3 \approx CCl_4 > CHCl_3$.

The establishment of 95 percent confidence limits were also desired for the $\Delta S^o$ variable. Since most of the errors associated with the $\Delta S^o$ values were contributed by their corresponding $\Delta H^o$ values, the same approach (as that used for the $\Delta \overline{H}^o$ values) was used in establishing their 95 percent CI's. That is, it was assumed that the "true" sorption entropies for each sorbent-sorbate pair within each sorbate group would be about the same; and that each of the measured $\Delta S^o$ values in Table 5.20 have statistically comparable variances*. Therefore, a

---

*An F-test for the difference between variances at the 95% CL supports this assumption, by showing that most of these variances are not statistically different.

simple "normal" mean of the sample $\Delta S^o$ values would constitute the best estimate for the population $\Delta S^o$ values. The mean $\Delta S^o$ values ($\Delta\overline{S}^o$) and their 95 percent CI which result are:

| Sorbate | $\Delta\overline{S}^o$ ± 95% CI ($10^{-3}$ kcal/mol°K) |
|---|---|
| $CHCl_3$ | -2.2 ± 15. |
| $CCl_4$ | +4.1 ± 10. |
| $C_2HCl_3$ | +2.3 ± 8.0 |
| $C_2Cl_4$ | +3.9 ± 7.7 |

### 3. Discussion of Probable Sorption Mechanisms

The relatively low values for the sorption free energies and enthalpies determined in this research are characteristic of the weaker physical sorption forces (e.g., van der Waals-London, ion-dipole, ion-induced dipole, and HI), and therefore, chemisorption of these compounds with soils and soil components can now be ruled out. It is interesting to note that the experimentally-determined heats of sorption ($\Delta H^o$) (even considering their wide CI's) are generally less than the compounds' aqueous heats of solution ($\Delta H^o_{soln}$). For example, Horvath (1982) reported a $\Delta H^o_{soln}$ value for $CHCl_3$ of -9.8 kcal/mol at 25°C; and a $\Delta H^o_{soln}$ for $CCl_4$ of -6.0 kcal/mol at 15°C. This is analogous to the physical adsorption energies in gas-phase systems being similar to the heats of condensation of the adsorbate gases, and is thus further evidence to support the rejection of chemisorption.

The remaining sorption mechanisms discussed in Chapter II, which were not _entirely_ ruled out _a priori_, are*:

---

*The only mechanisms which were _definitely_ ruled out in Chapter II were ion exchange and magnetic bonding.

(a) van der Waals-London forces
    (1) dipole-dipole
    (2) dipole-induced dipole
    (3) induced dipole-induced dipole (London or dispersion force)
(b) ion-dipole and ion-induced dipole
(c) hydrophobic interaction (HI)
(d) charge transfer
(e) hydrogen bonding
(f) ligand exchange.

As demonstrated in Section D of this chapter, the sorptive strengths of these compounds with most of the sorbents are very well correlated with the compounds' polarizabilities, but very poorly correlated with their dipole moments. Since $\alpha$ and $\mu$ are the only sorbate properties which enter into the fundamental equations of intermolecular forces, this finding tends to implicate the following "induction" forces as the ones responsible for the sorption observed in this research:

(1) London (dispersion)
(2) ion-induced dipole
(3) dipole-induced dipole (the case in which the sorbate's dipole is the one being induced).

Since these three forces are all directly proportional to the sorbate's polarizability, they cannot be distinguished from one another based on methods used in this research. However, since the London and ion-induced dipole interactions are typically much stronger than the dipole-induced dipole interaction, it is surmised that these two mechanisms are the ones primarily involved in the sorption observed in this research.

Unfortunately, it is not clear from the experimental data gathered whether or not the HI played a role in the sorption under investigation in this research. Since sorptive strength was also shown to be highly correlated (inversely) with aqueous solubility (see Section V.D.), one might be tempted to suggest that this constitutes evidence for the HI. However, the literature pertaining to HI theory does not link this phenomenon with aqueous solubility. In my search and review of the HI literature, I attempted to find some type of property which might be exclusively characteristic of the HI. My efforts met with some success while reading the book Hydrophobic Interactions by Ben-Naim (1980). This author reported that large positive values of $\Delta H^o$ (for the distribution of a nonpolar solute between water and a variety of organic solvents) may be the result of structural changes induced in the water due to the HI. Therefore, I had originally intended on using this criterion to implicate the HI. (For example, if $\Delta H^o > 0$ for $CCl_4$ and $C_2Cl_4$ [the nonpolar solutes], but $\Delta H^o < 0$ for $CHCl_3$ and $C_2HCl_3$ [the polar solutes], then this could have suggested the presence of HI.) However, the mean sorption enthalpies ($\Delta \overline{H}^o$) determined herein were relatively small negative values for each of the sorbates. Even considering their relatively wide CI's, none of the 95 percent confidence limits (on $\Delta \overline{H}^o$) for any sorbate exceeded a value of +2.0 kcal/mol. A re-examination of Table 5.19 shows that the sorption of $C_2HCl_3$ and $C_2Cl_4$ by the mineral soil resulted in the highest observed (positive) enthalpies (+3.1 kcal/mol in each case) in this research. However, the implication of HI in these two cases is not logically sound, since if HI were present, one would expect that sorption of the nonpolar $CCl_4$ and $C_2Cl_4$ species would be enhanced with respect to sorption of the polar $CHCl_3$ and $C_2HCl_3$ species. But for sorption by the mineral soil, the exact opposite occurred: This sorbent either inhibited sorption of the nonpolar species, or enhanced sorption of the polar species (or maybe both). Therefore, no definite conclusions can be drawn from the experimental data regarding the presence of the HI mechanism in the sorption systems investigated herein.

The charge transfer, hydrogen bonding, and ligand exchange mechanisms were each considered highly unlikely to occur (for the sorption systems used in this research) for the reasons given in Chapter II. The possibility of these mechanisms is further discussed below, in light of the experimental results.

If charge transfer is the predominant sorption mechanism then it must involve ionic forms of the sorbate molecule. Although these aliphatic, chlorinated alkanes and alkenes are not known to undergo ionization in aqueous solution, the (remote) possibility exists that a sorbent may serve, for example, as a catalyst which would promote such a transformation. However, if such a reaction occurred, then (by definition) the process would be one of chemisorption. But since the sorption $\Delta G^o$ and $\Delta H^o$ values determined are far too low to involve chemisorption, the charge transfer mechanism is rejected. Furthermore, even if one disregards the above chemisorption argument against this mechanism, if charge transfer is occurring, it would most likely involve ionic forms of $CHCl_3$ and $C_2HCl_3$, since these molecules already possess a partial charge differential (i.e., they are polar). Therefore, if charge transfer were the primary mechanism, one would expect the sorption of $CHCl_3$ and $C_2HCl_3$ to be consistently stronger than for $CCl_4$ and $C_2Cl_4$. But this was not observed to occur, and thus, this second argument also supports the contention that the charge transfer mechanism is not relevant to this research.

Hydrogen bonding is not believed to occur for the chlorinated compounds used in this research (Horvath, 1982). Nevertheless, if it was the principal sorption mechanism, then once again it would be expected that $CHCl_3$ and $C_2HCl_3$ would be much more strongly sorbed than either $CCl_4$ or $C_2Cl_4$. Since this was not observed to occur, hydrogen bonding is ruled out as a predominant mechanism.

Lastly, the same argument can be used to reject ligand exchange as a significant mechanism, since the ligand-exchanging strength of the sorbate would be related to its polarity. Furthermore, if ligand exchange for these compounds was a significant sorption mechanism, then they should have been able to replace $H_2O$ molecules serving as ligands to the ions associated with the clay and mineral surfaces. But no sorption of these molecules to the clays and minerals was observed, which is further evidence to reject ligand exchange in this research.

In conclusion, the sorption of $CHCl_3$, $CCl_4$, $C_2HCl_3$, and $C_2Cl_4$ with soils and soil components is believed to occur principally via the weak induction forces of London (dispersion) and/or ion-induced dipole,* with possible contributions from the HI neither being ruled out nor demonstrated.

---

*These two forces cannot be distinguished by the methods used in this research.

An interesting theoretical question relevant to sorption mechanisms in this research is: Why did adsorption of these compounds not occur with the clay and mineral sorbents, and furthermore, why was exclusion (negative adsorption) possibly occurring? The explanation is as follows. Since these clays and minerals are all ionic solids and/or possess a surface charge due to isomorphous substitution (e.g., montmorillonite), they are very hydrophilic due to the strong ion-dipole interactions between the ions (associated with the solid surface) and the highly polar water molecules. Therefore, in order for these hydrophobic, organic molecules to be adsorbed to the clays or minerals, the cumulative adsorption forces operating between the solid and a sorbate molecule must exceed the cumulative adsorption forces operating between the same solid and a water molecule. Otherwise, the adsorption of $H_2O$ molecules to the solid surface will predominate. One way of expressing the energy of interaction between ions and $H_2O$ molecules is simply via the hydration energy. For example, the hydration free energies for $Na^+$, $Ca^{+2}$, and $Al^{+3}$ (i.e., the cations used to saturate the montmorillonite clay) are -97, -378, and $\sim$ -1100 kcal/mol, respectively; and for $OH^-$ (a common mineral surface functional group) is -110 kcal/mol (McBride, 1982). Since the free energies of sorption (for the other soils and soil components) were determined to range from about -1 to -4 kcal/mol, it is hardly surprising that no adsorption to the clays and minerals was observed. That is, the free energies of hydration for most ions are typically about two orders of magnitude higher than the sorption free energies for the compounds investigated. Furthermore, the ion-dipole interaction would appear to be the predominant force involved in the hydration of ions, and since this interaction energy is proportional to $1/r^2$, it would be considered a "long range" force. Thus, the interaction potential between an ion and $H_2O$ molecule is not only very strong (relatively speaking), but is also exerted over large distances (at the molecular level). Thus, each clay/mineral colloid is probably surrounded by an "atmosphere" enriched in water which excludes the presence of the adsorbate molecules.

## H. Experimental Attempts to Distinguish Between Adsorption and Absorption Phenomena

Examination of Tables 5.19 and 5.20 reveals that the sorption thermodynamic variables for graphite (for which the phenomenon is known to be one of adsorption) are roughly comparable with those for the soils and soil components. Although it is tempting to assert that this provides some evidence in favor of the adsorption phenomenon, it could simply be an outcome of the likelihood that similar sorption forces and mechanisms are at work in each case. That is, whether the phenomenon is one of adsorption or absorption, it is highly likely that the same (weak) intermolecular forces (postulated in the previous section) are working. Therefore, no convincing conclusions can be drawn from the thermodynamic data, with respect to this issue.

Extended sorption isotherms were determined (for many sorbent-sorbate pairs) for the purpose of examining isotherm characteristics in the regions of higher solute concentration (and hence, higher sorption density). The experimental procedures used in determining these isotherms were identical with those employed in Sections B or C of this chapter (depending on the sorbent). All isotherms were performed at

T = 20°C unless otherwise noted, and the pH and ionic strength of all suspensions were previously given in Table 5.17.

These extended isotherms are shown in Figures 5.27 through 5.37.* (For the sake of clarity, the "curves of best fit" were drawn only with respect to the sorption data points.) Note that Figures 5.27 and 5.37 actually cover the "very high concentration" region (relatively speaking) as a result of using the "very high-level"** TCE stock solutions in these experiments. Although this results in attaining a TCE solute concentration of ∿ 80 mg/l, it is still far from aqueous saturation since the solubility of TCE is ∿ 1100 mg/l (Horvath, 1982).

Most of the isotherms exhibit some degree of curvature toward the $C_\ell$-axis, while a few systems ($CCl_4$-mineral soil, $C_2HCl_3$-peat, $CHCl_3$-peat, and $C_2HCl_3$ with graphite, HA, and lignin) display virtually linear isotherms over the entire solute concentration range. It is very difficult (if not impossible) to draw any conclusions with respect to the adsorption-absorption issue from these isotherm characteristics, since the same degree of curvature might also be observed for the solvent extraction "isotherms" of these compounds. However, if Lyman's (1982) criterion of virtually linear octanol-water partitioning isotherms occurring over solute concentrations up to (at least 0.01 M, also applies to (an assumed) SOM-water partitioning process,† then perhaps the downward isotherm curvatures in most of the above figures lend

---

*The reader should note that the curves in Figures 5.27 through 5.37 have been drawn to illustrate possible curvature in the data. Since the curves were not mathematically fit to the data their position is admittedly arbitrary.

**Refer to Section IV.A for the procedures used in preparing the various "levels" of solute concentrations in the stock solutions.

† The aqueous solute concentrations for the isotherms in this section are well below 0.01 M for any of the compounds. The solute concentrations in the SOM phase are estimated by assuming an SOM (particle) density of 1.35 g/cm$^3$ (Brady, 1974, p. 50), and using the organic matter contents ($\approx 2 \times f_{oc}$) of the respective sorbents. These calculations show that the solute concentrations in the SOM phase are < 0.01 M in all cases except $C_2HCl_3$ with HA and lignin (Figure 5.37), for which it is on the order of 1.0 M.

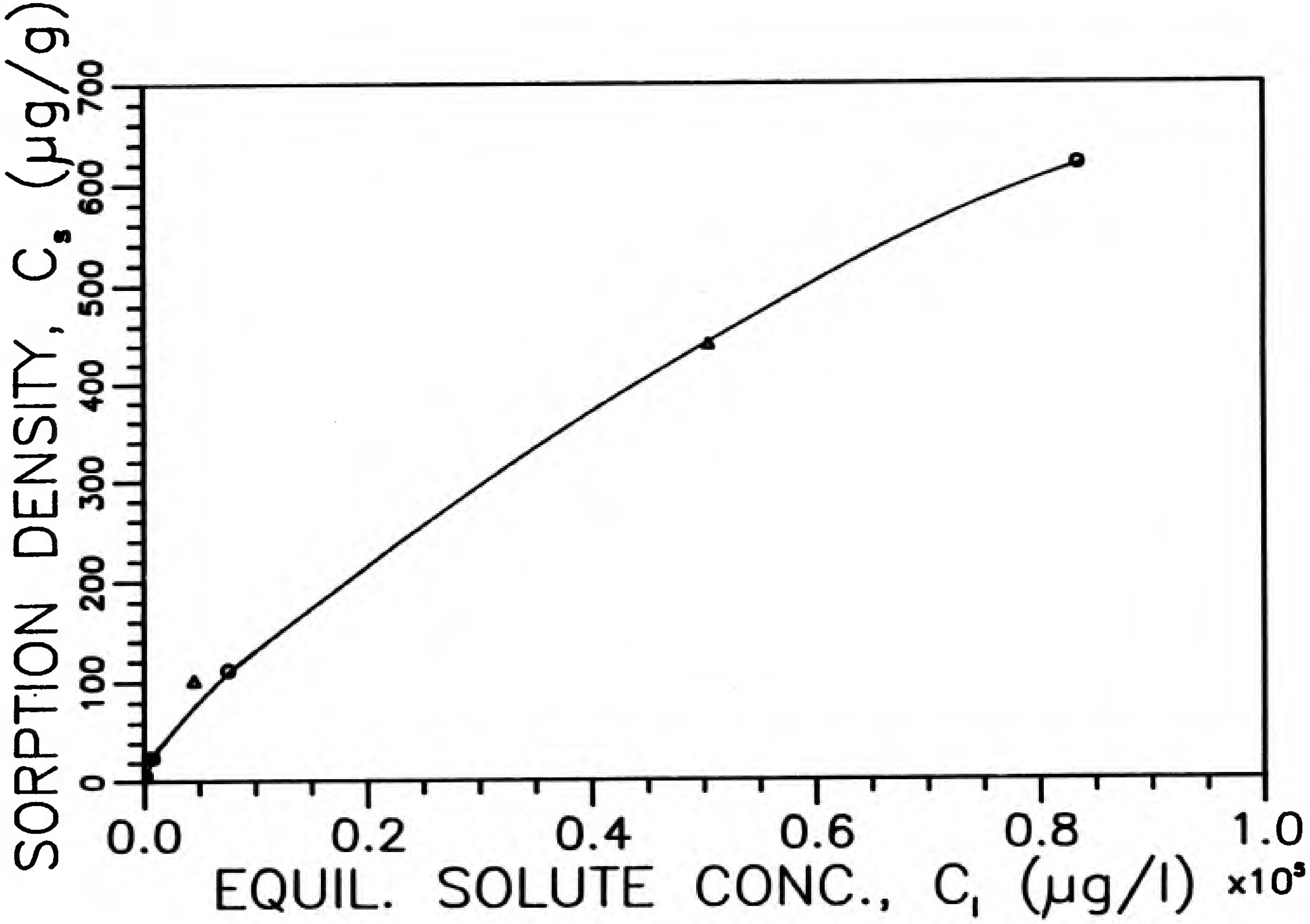

FIGURE 5.27 Extended Sorption (O) and Desorption (Δ) Isotherms for $C_2HCl_3$ with Mineral Soil (Very High Concentration Region)

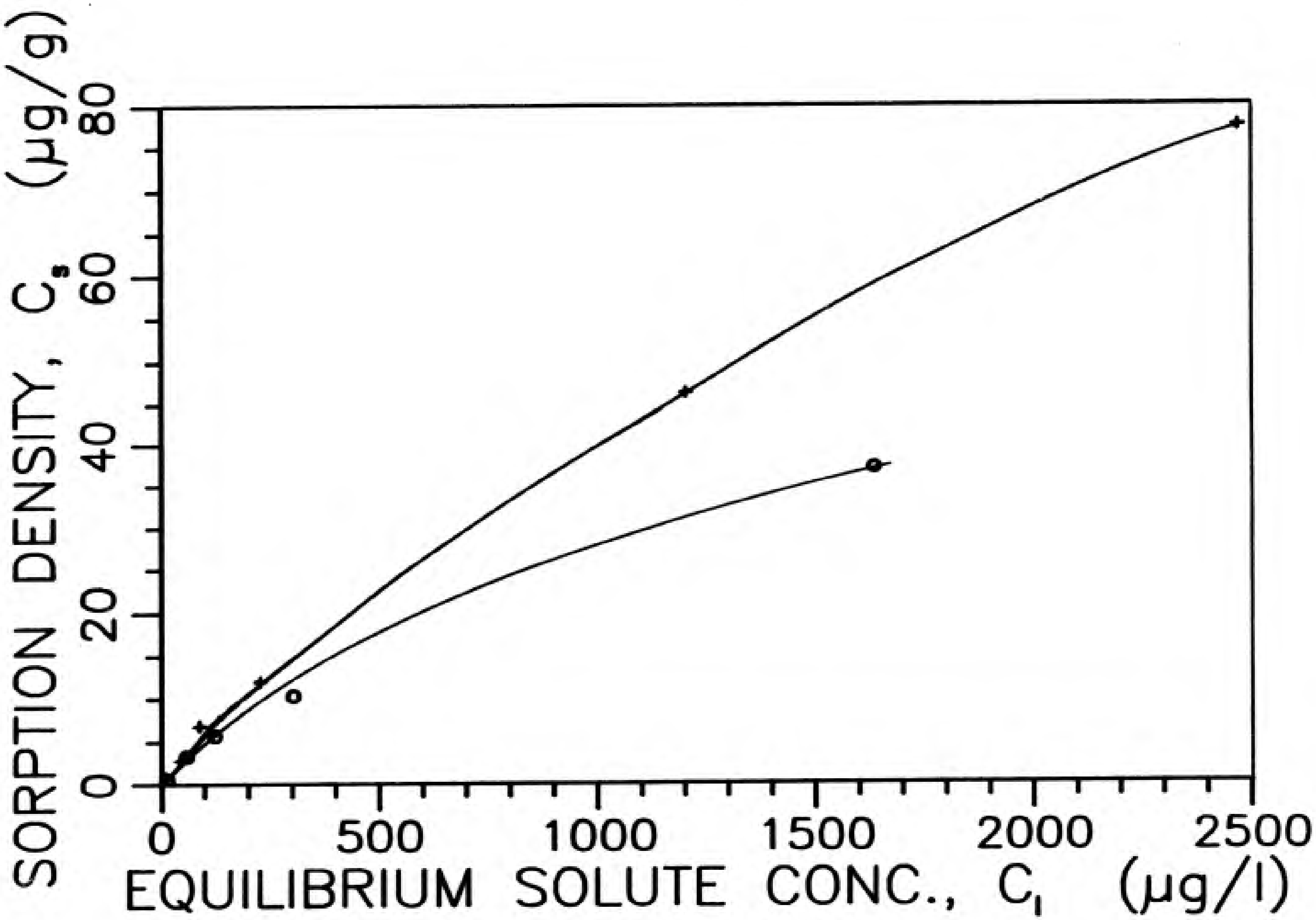

FIGURE 5.28 Extended Sorption Isotherms for $C_2HCl_3$ (TCE) with the Mineral Soil at T = 7°C (o) and T = 50°C (+)

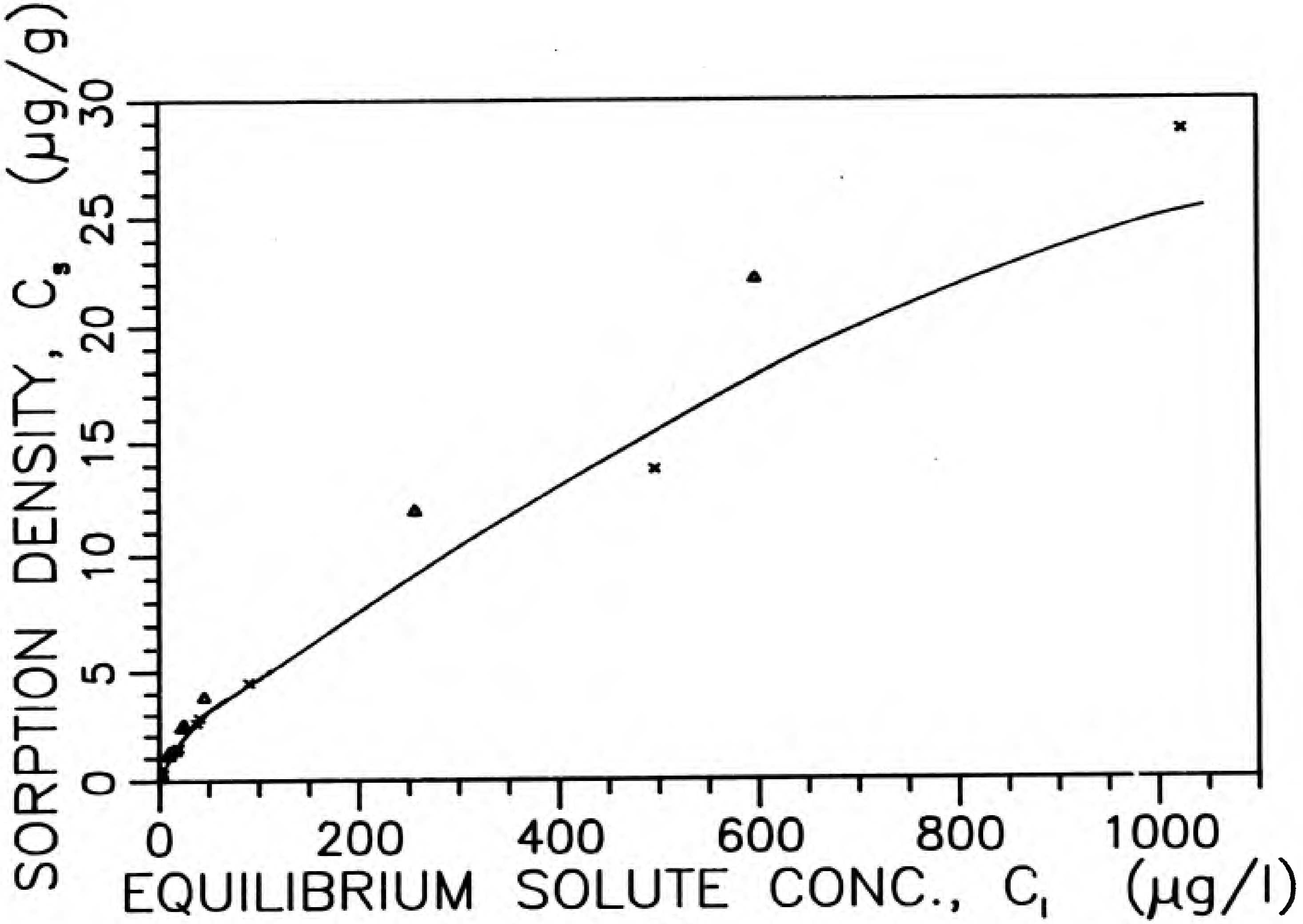

FIGURE 5.29 Extended Sorption (x) and Desorption (Δ) Isotherms for $C_2Cl_4$ with the Mineral Soil

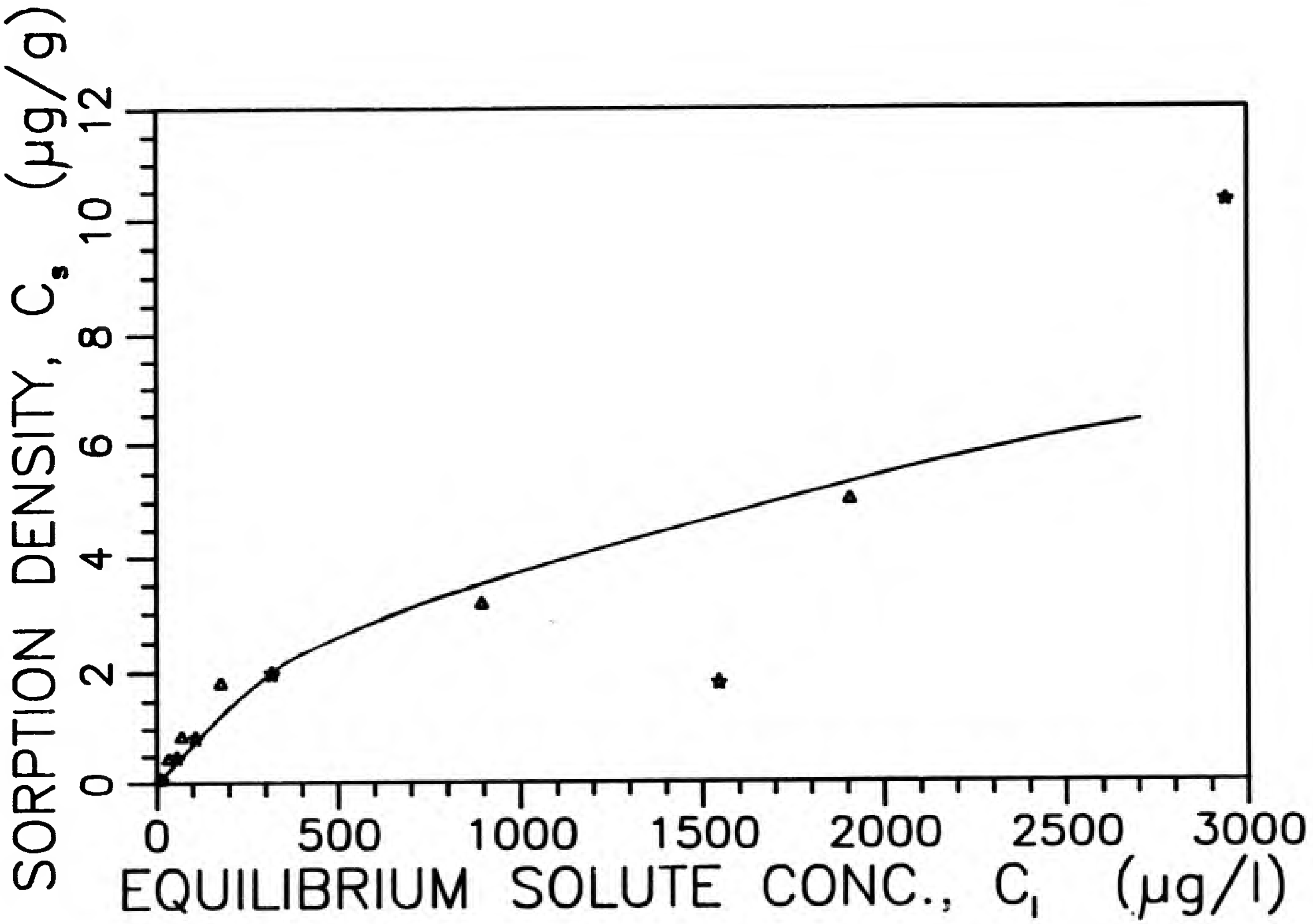

FIGURE 5.30 Extended Sorption (★) and Desorption (△) Isotherms for $CHCl_3$ with the Mineral Soil

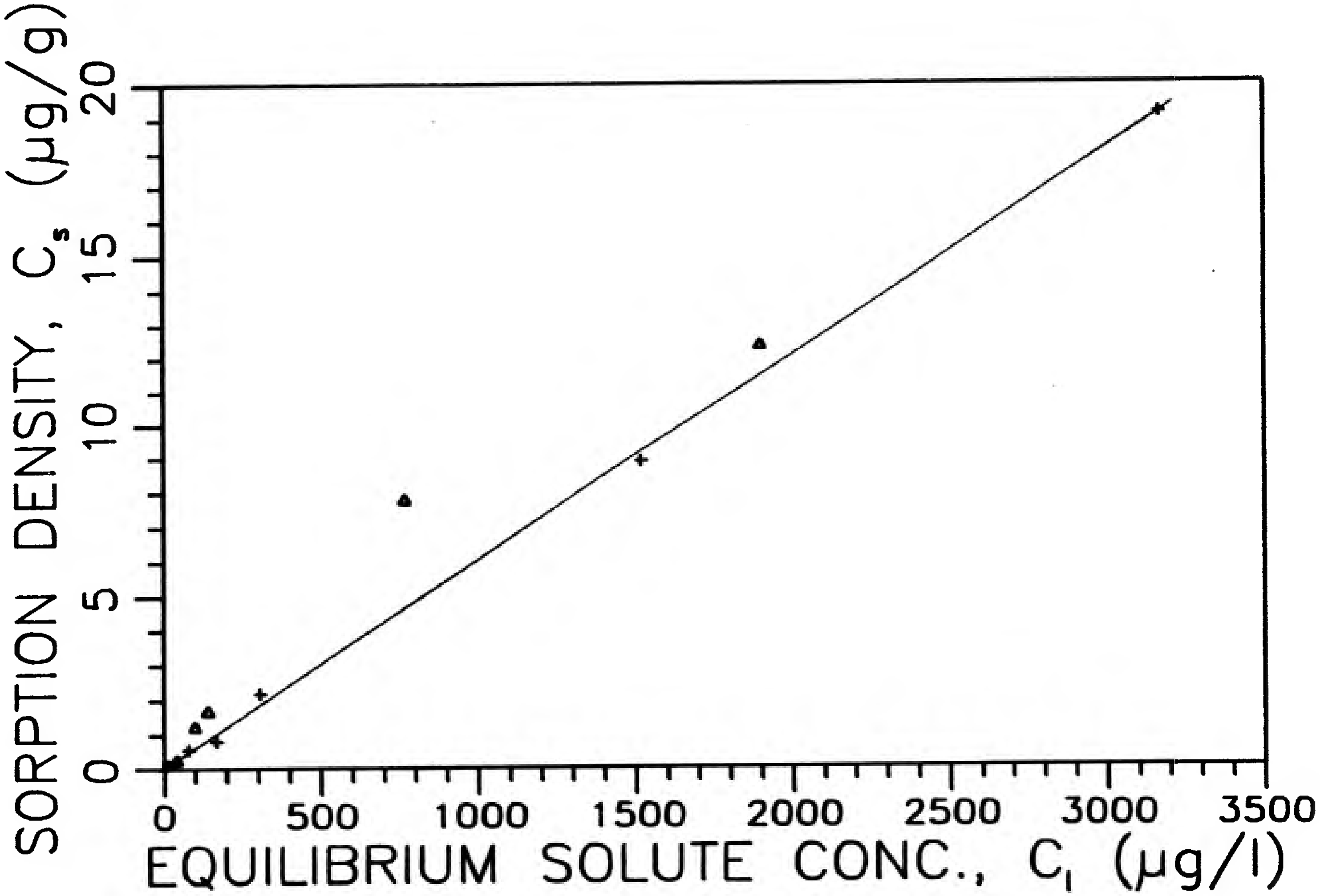

FIGURE 5.31 Extended Sorption (+) and Desorption (Δ) Isotherms for $CCl_4$ with the Mineral Soil

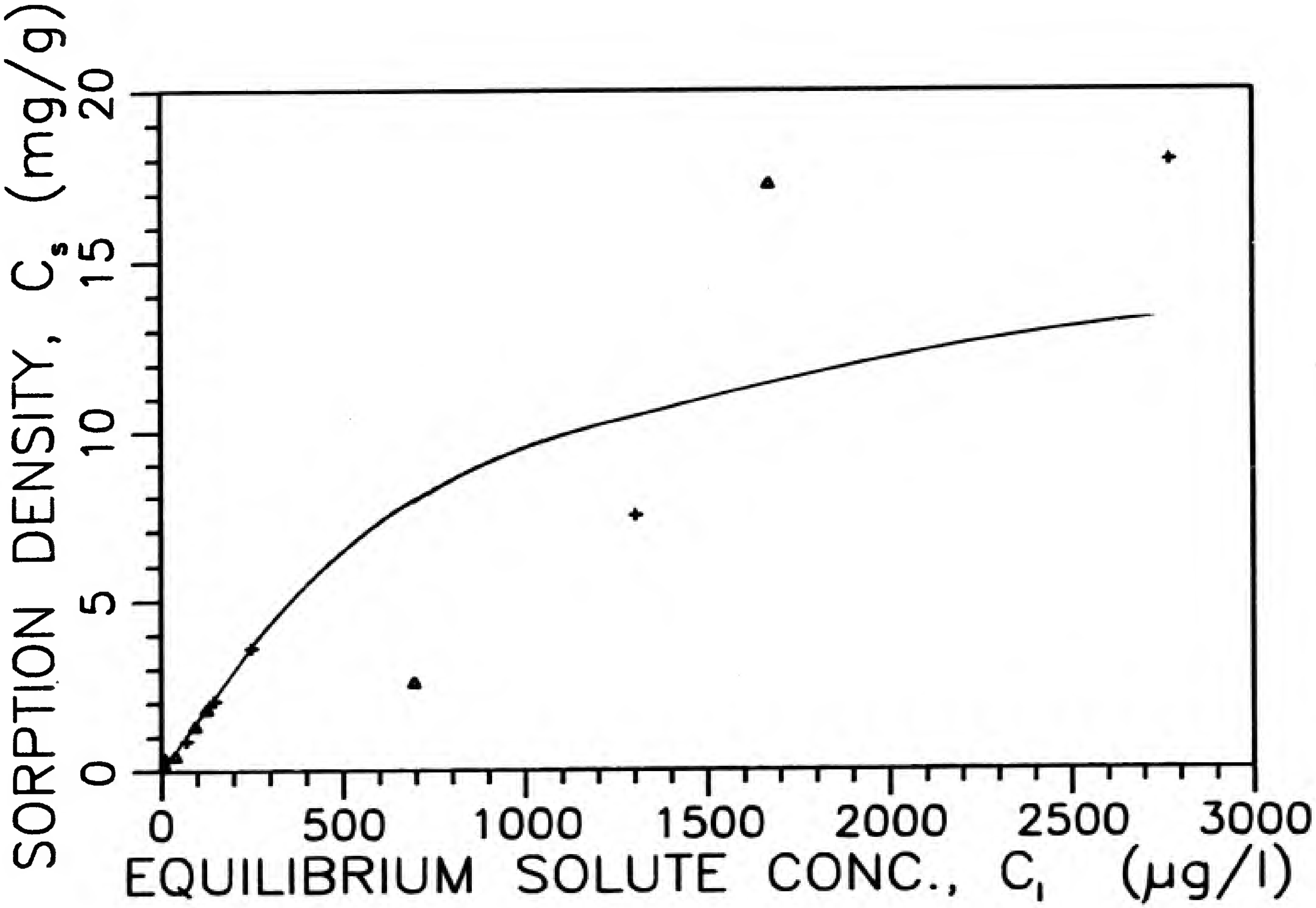

FIGURE 5.32 Extended Adsorption (+) and Desorption (Δ) Isotherms for $CCl_4$ with Powdered Activated Carbon (PAC)

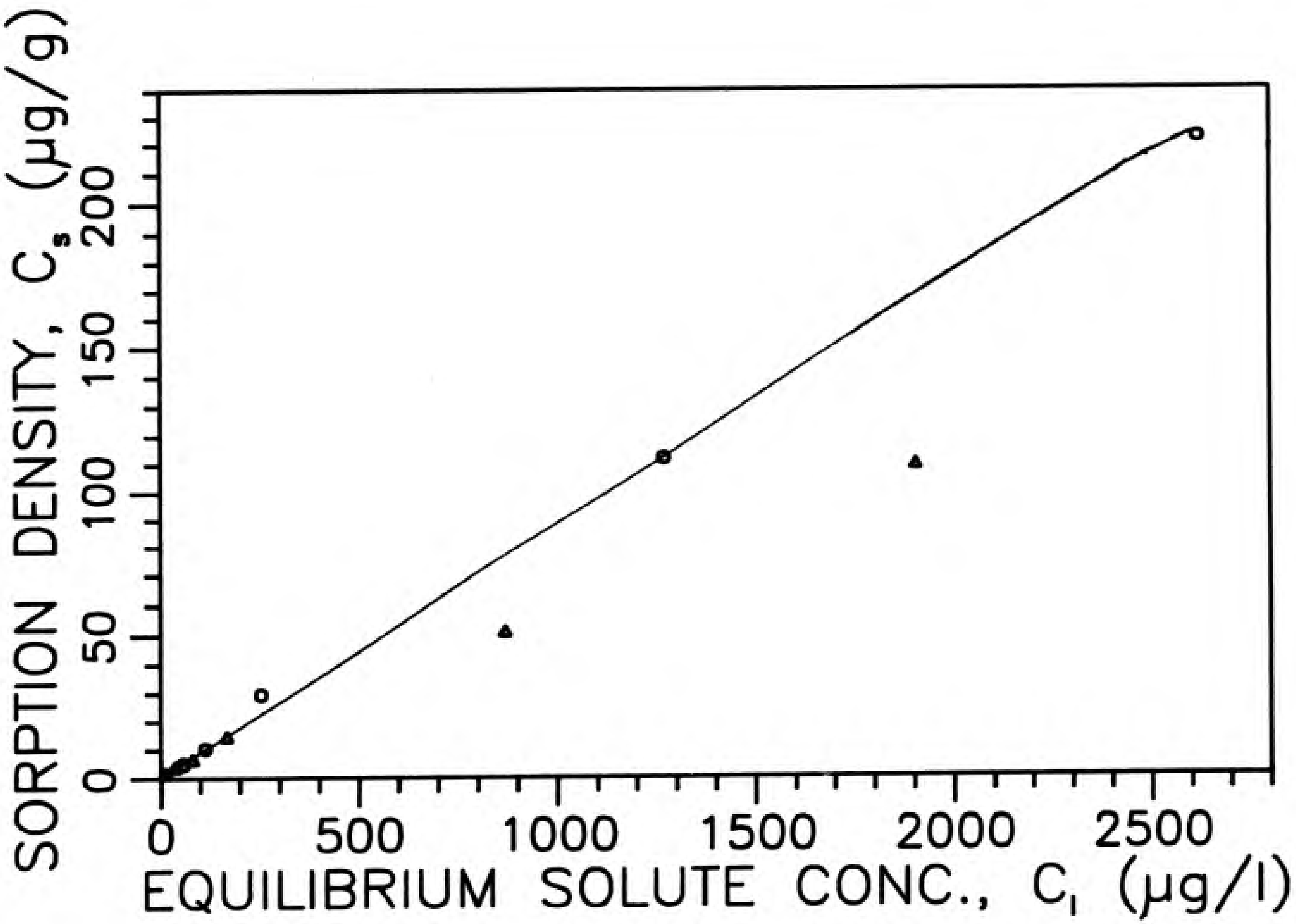

FIGURE 5.33 Extended Sorption (O) and Desorption (Δ) Isotherms for $C_2HCl_3$ with Peat

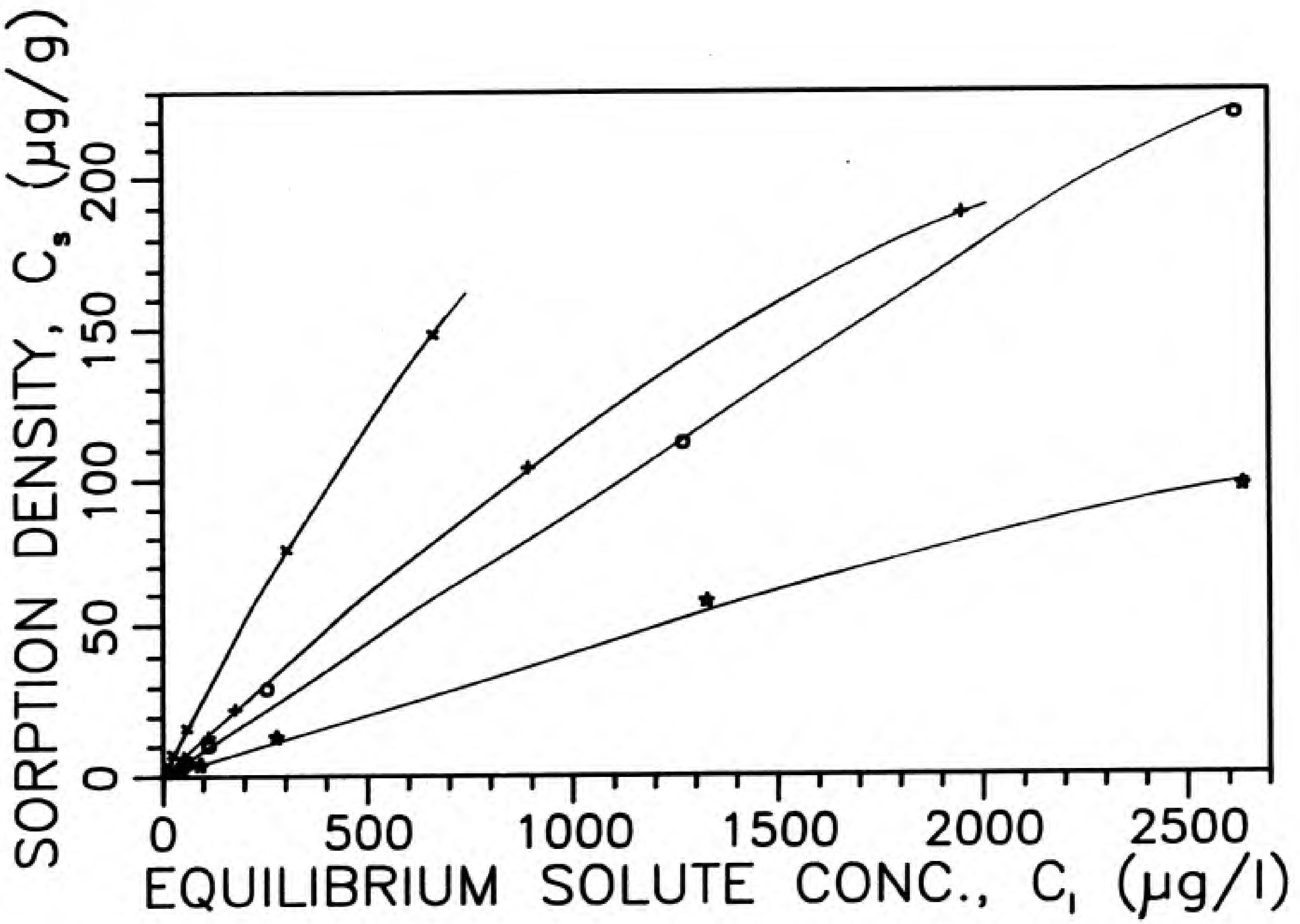

FIGURE 5.34 Extended Sorption Isotherms for $CHCl_3$ (★), $CCl_4$ (+), $C_2HCl_3$ (o), and $C_2Cl_4$ (x) with Peat

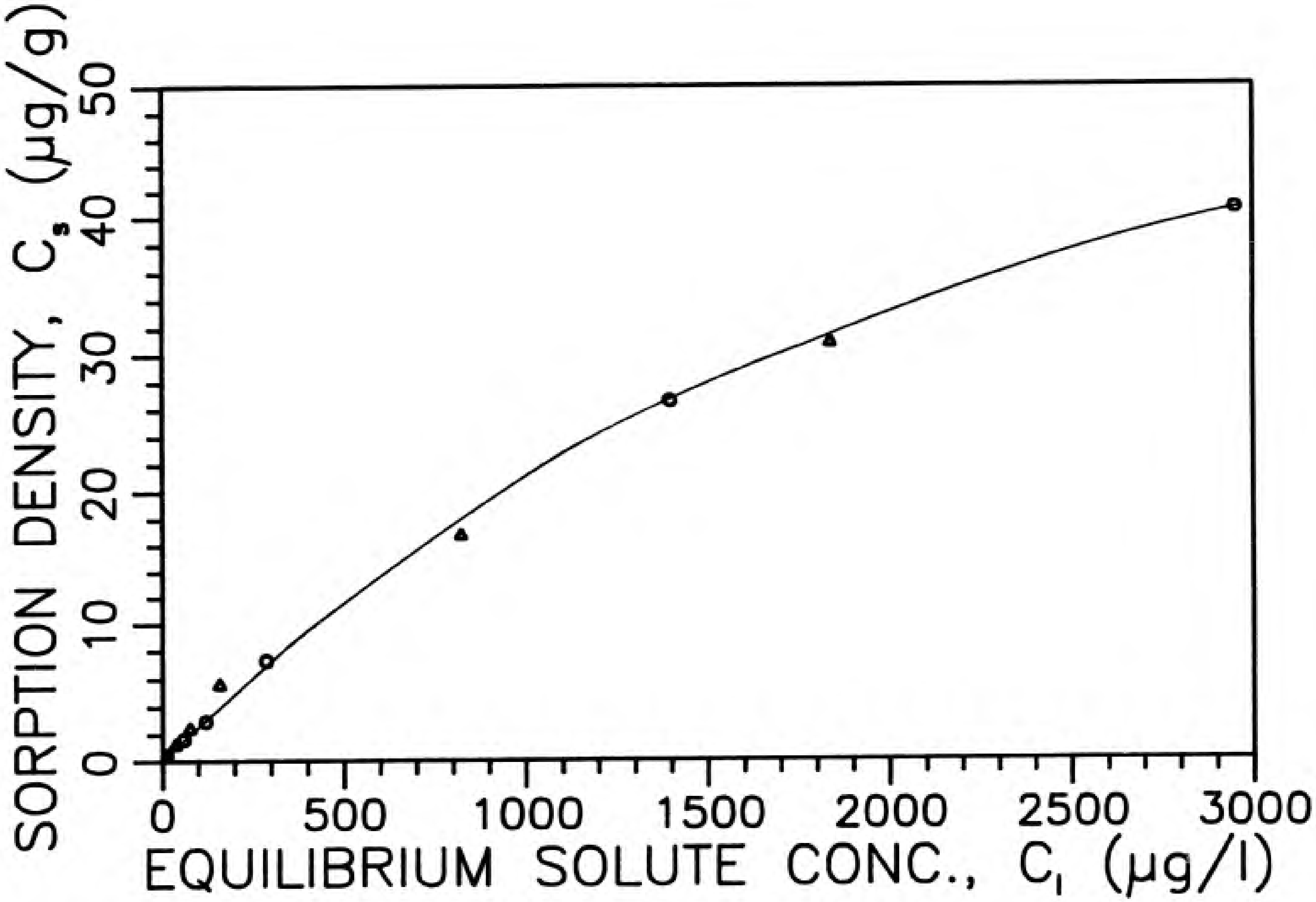

FIGURE 5.35 Extended Sorption (○) and Desorption (△) Isotherms for $C_2HCl_3$ with Muck

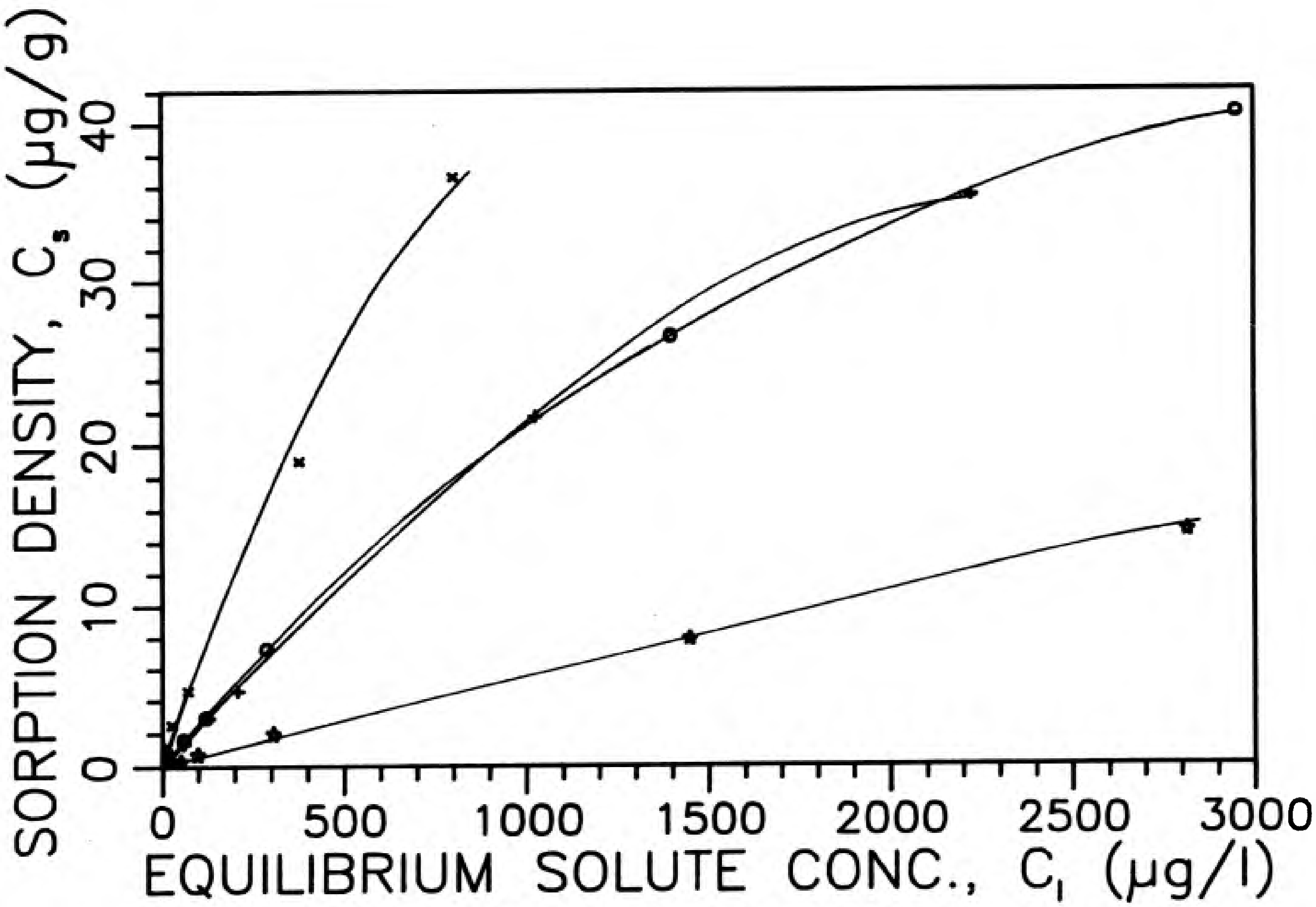

FIGURE 5.36 Extended Sorption Isotherms for $CHCl_3$ (★), $CCl_4$ (+), $C_2HCl_3$ (○), and $C_2Cl_4$ (x) with Muck

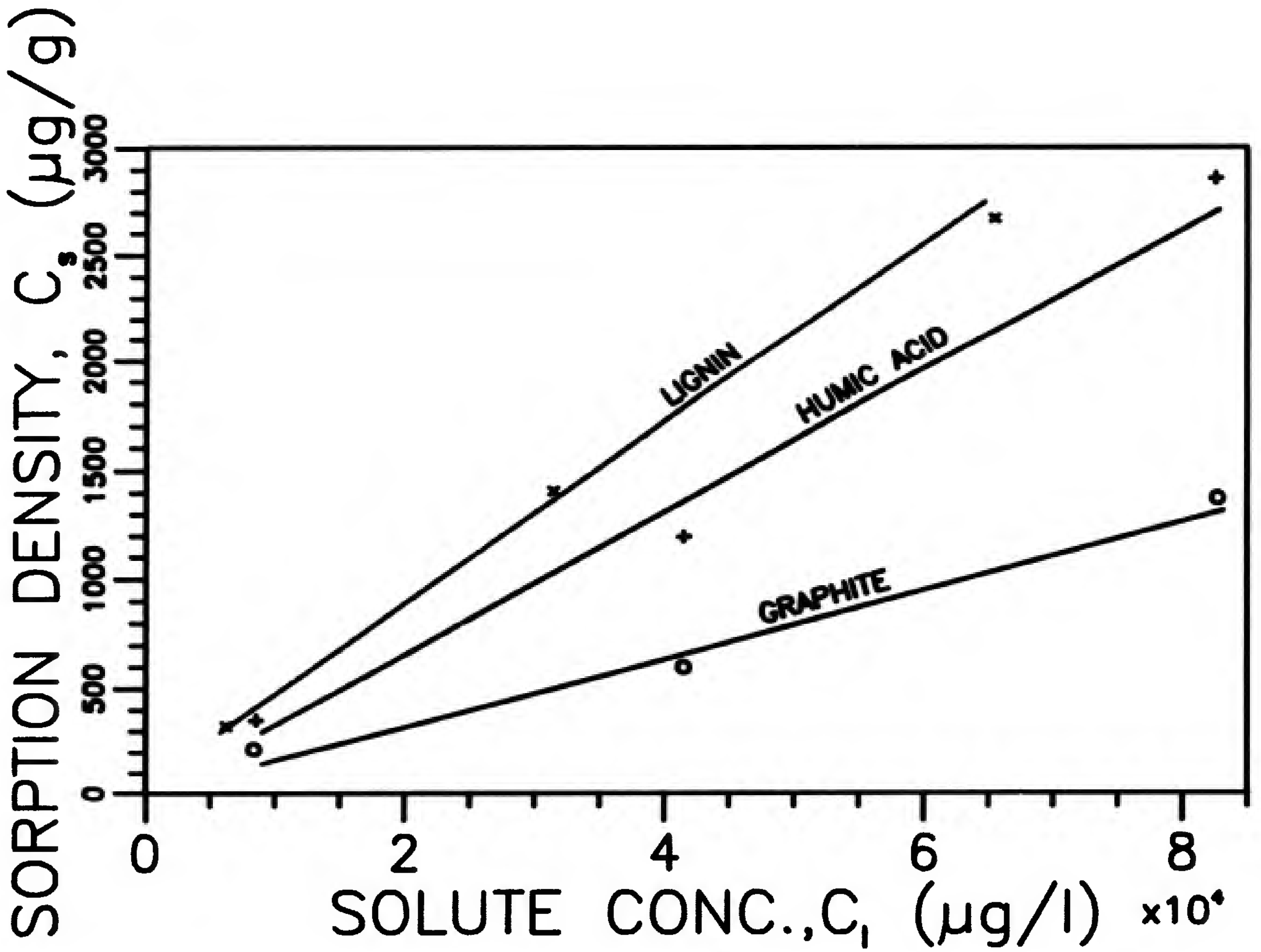

FIGURE 5.37 Extended Sorption Isotherms for $C_2HCl_3$ with Graphite (O), Humic Acid (+), and Lignin (x) (Very High Concentration Region)

some support to the adsorption phenomenon. But it is not known whether the solute behavior in SOM is similar to that in octanol, and therefore, the application of the above criterion is questionable.

Figure 5.37 is rather interesting since it depicts virtually linear isotherms for $C_2HCl_3$ with HA and lignin, even though the estimated solute concentration in the SOM phase is >> 0.01 M. A comparison of this figure with the isotherms for the same systems in the low concentration region, shown in Figure 5.38, reveals a striking difference: The sorption intensity of the graphite is decreased dramatically with respect to HA and lignin. Table 5.21 exhibits the $K_d$ values for these systems over the two solute concentration regimes. These data yield

Table 5.21 Comparison of the Sorption Distribution Coefficients ($K_d$'s) for $C_2HCl_3$ with Graphite, Humic Acid, and Lignin over the "Low" and "Very High" Solute Concentration Regimes*

| | $C_2HCl_3$ Concentration Regimes | |
|---|---|---|
| Sorbent | Low$^{\dagger}$ (0 to ∿70 μg/l) | Very High$^{\dagger\dagger}$ (∿6000 to ∿80000 μg/l) |
| Graphite | 110 (± 8.3) | 15.7 ± 2.0 |
| Humic Acid | 38.9 (± 5.1) | 34.2 ± 4.3 |
| Lignin | 63.2 (± 3.0) | 39.5 ± 1.6 |

*Standard deviations are given in parentheses--consult Appendix F for the method of their determination.

$^{\dagger}K_d$ values based on slopes of single-point isotherms.

$^{\dagger\dagger}K_d$ values based on slopes of least-squares regression lines through each set of three data points, not forced through the origin (since these are high concentration region isotherms).

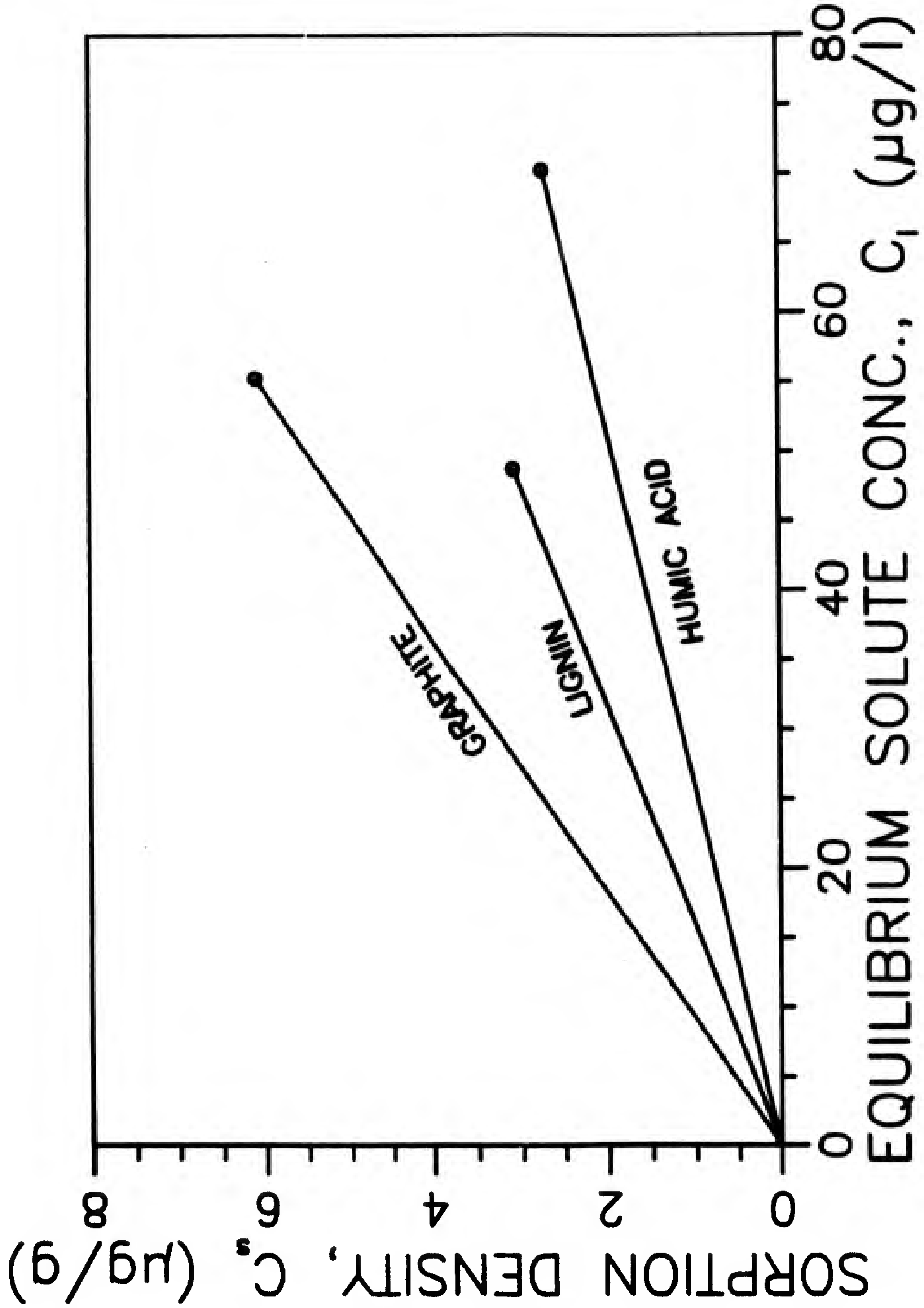

FIGURE 5.38 Sorption Isotherms (in the Low Concentration Region) for $C_2HCl_3$ with Humic Acid, Lignin, and Graphite

reductions in the $K_d$ values (from the low to very high concentration regimes) of 85.7%, 12.1%, and 37.5%, respectively, for the graphite, HA, and lignin sorbents. However, even these data don't really prove anything--since it could be argued that the specific surface areas for the lignin and HA in solution far exceed that of graphite. (For example, the SSA for graphite in solution is probably not too different from that measured in the dry form [$\sim$ 9 $m^2/g$], whereas the SSA for humic materials ranges from 500 to 800 $m^2/g$ [Ahlrichs, 1972]). Thus, the data in Table 5.21 could be explained by either the adsorption or absorption concepts.

A final experiment was performed in an attempt to unravel the adsorption-absorption enigma. The objective of this experiment was to determine if sorptive strength (as measured by $K_d$) varied with the specific surface area of a "suitable" sorbent. The sorbent chosen was lignin since this could be considered a "pure" organic material; and more importantly, its organic composition would remain uniform regardless of particle size. Furthermore, lignin was shown (Section V.F.) to sorb the solute compounds with (relatively) high intensity, and is similar in many respects to the humic substances which predominate soil organic matter.* Tetrachloroethylene ($C_2Cl_4$) was selected as the sorbate.

---

*The reader might be wondering why humic acid (HA) was not selected as the sorbent in this experiment. The reason is that a much higher mass of lignin (than HA) could be sustained in the sorbent R.V. without significantly affecting the quench level of the scintillation sample. That is, even low HA solids concentrations resulted in sorbent R.V. supernatants (following centrifugation) with a brown tint, which had a dramatic effect on scintillation sample quench level. Although the sample DPM/ml was always corrected for quench level, this could only be done if the quench level was within the limits of the established

The experimental procedures were as follows. Distilled water (DW) was added to 10 g of lignin to make a 500-ml suspension. This suspension was placed in an ultrasonic bath for 10 minutes (and frequently stirred) to completely disperse the lignin particles. (The purpose of this step was to disperse the lignin prior to the 4-day tumbling step [i.e., the equilibration period], so that [hopefully], no further dispersion of the lignin would occur during the tumbling process.) The suspension was then thoroughly mixed and quickly poured into two, 250-ml Nalgene$^{TM}$ bottles and capped. The two bottles (and their suspensions) were then centrifuged at 4000 rpm (∿ 1500 G) for 15 minutes, and the supernatants (containing the unsettled colloidal fraction) were discarded and replaced with DW. This step was repeated until the supernatants were virtually clear, requiring four repetitions. (The purpose of this step was to eliminate the non-settling, colloidal lignin fraction, so that this component would not be an influential factor in this experiment.) After the fourth centrifugation, the supernatants were replaced with DW which had been adjusted to pH = 2.0 (by addition of HCl), in order to keep the (remaining) lignin virtually insoluble. The two Nalgene$^{TM}$ bottles were then thoroughly shaken (to resuspend the previously-settled lignin), and their contents transferred to a 500-ml graduated cylinder and allowed to gravity-settle. After several minutes of quiescent settling, 5-ml aliquots of the supernatant were periodically removed with a pipet and transferred to a 250-ml (amber) glass bottle.

---

quench curve. An HA solids concentration >∿ 1.0 g/l resulted in a quench level exceeding the upper limit of the quench curve; whereas a lignin solids concentration many times this (e.g., even ∿ 25 g/l) did not result in exceeding the upper limit of the quench curve.

A large sorbent mass was desirable since it reduced the uncertainty in the $K_d$ value. That is, the error propagation analyses (reported in Appendix F) revealed that the variance of $K_d$ is (approximately) inversely proportional to the square of solids mass (i.e. $\sigma^2_{K_d} \propto 1/M_s^2$).

(This was to eventually become the "fine lignin fraction" [FLF]). After removing and transferring ∿ 200 ml of the supernatant, I noticed that the remaining suspension constituted a region of zone settling, and no further aliquots were withdrawn. This zone-settling suspension was thoroughly mixed, and re-transferred back to a Nalgene$^{TM}$ bottle, and centrifuged for 10 seconds at ∿ 10 G. Most of the supernatant from this bottle was then added to the FLF suspension, again using a 5-ml pipet. The DW (buffered at pH = 2.0) was then added to the lignin suspension remaining in the (centrifuged) Nalgene$^{TM}$ bottle, vigorously shaken (to resuspend the settled lignin), and decanted into a second 250-ml (amber) glass bottle. (This suspension contained the "coarse lignin fraction" [CLF].) The pH of each suspension was measured and found to be 2.3. Therefore, several drops of concentrated HCl were added to each suspension (while mixing) until a pH of 2.0 was attained. Three replicate, 10-ml aliquots of each uniformly-mixed suspension were withdrawn for determination of total solids* concentration. The results showed that the lignin concentration in the fine fraction was 3.5 g/l (± 0.066 g/l), and that in the coarse fraction was 12.7 g/l (± 0.14 g/l). A target lignin concentration of ≈ 10 g/l was selected, which required that the FLF suspension be concentrated, and the CLF suspension be diluted. Therefore, the FLF suspension was centrifuged (3000 G for 30 minutes), and a pre-computed volume of supernatant withdrawn to yield the target lignin concentration. For the CLF suspension, a pre-computed

---

*Procedure used was in accordance with Standard Methods, 15th Edition, published jointly by APHA, AWWA, and WPCF, Part 209A, page 92 (1981).

volume of DW (buffered at pH = 2.0 with HCl) was added, to attain the target concentration. After these adjustments were made, the total solids (TS) of each suspension were again measured (using procedures identical to those used before).* The results (which were obtained after the actual experiment had begun) revealed that the solids concentration of the adjusted FLF suspension was 8.96 g/l (± 0.02 g/l), and that of the adjusted CLF suspension was 9.72 g/l (± 0.052 g/l). This small difference between the lignin concentrations of the two suspensions would result in a negligible "solids concentration effect" on the $K_d$ values determined for the two suspensions. (This can be verified by referring to Figure 5.41 of Section V.I.3.b.). The conductivity for the CLF and FLF suspensions were measured to be about 10,000 μmho/cm for each suspension which corresponds to an $I$ of ∿ 0.16 M.

The experiment was set up in the usual manner except that four replicate R.V.'s were used for each of the suspensions, and four R.V.'s for the controls. Each sorbent R.V. contained 5.0 ml from its corresponding suspension, and each control R.V. contained 5.0 ml of DW (adjusted to pH = 2.0 with HCl). Each R.V. was then injected with 0.5 ml from the low-level, $^{14}C\text{-}C_2Cl_4$ stock solution. (Other procedures are as described in Chapter IV.) The R.V.'s were tumbled for 4 days at T = 20°C.

---

*It should be mentioned that visual verification of a difference in particle size between the two suspensions was possible during these TS tests. When the suspension volumes were transferred into the evaporating dishes, the particles were easily visible against the white background of the dish. The lignin particles comprising the CLF were observed to settle rapidly to the bottom of the evaporating dishes, whereas the FLF particles were not observed to settle out.

Table 5.22 exhibits the resulting $K_d$ values and their standard deviations. The specific surface areas (SSA's) of each lignin fraction were measured using B.E.T. isotherms (with $N_2$ gas as the adsorbate), and these values are also given in this table. The S.V. samples from the CLF and FLF sorbent R.V.'s had mean $H^{\#}$'s (97 and 96, respectively) almost as low as that for the control R.V.'s (92), indicating that the washing procedure was indeed effective, and that the soluble lignin component removed, did not reform during the 4-day tumbling period.

Table 5.22 Sorption Distribution Coefficients (and Specific Surface Areas) for Two Particle-Size Fractions of Lignin Used in a Sorption Experiment with $C_2Cl_4$

| Lignin Fraction | Specific Surface Area* ($m^2/g$) | $K_d^{\dagger}$ |
|---|---|---|
| Coarse | 5.39 (± 0.023) | 239 (± 14) |
| Fine | 7.04 (± 0.095) | 228 (± 16) |

*Specific surface areas were measured on a Quantasorb$^{TM}$ (Quantachrome Corp.) by single-point B.E.T. isotherms using $N_2$ as the adsorbate gas. Samples were outgassed at 90°C for a minimum of 1 hour. Data represent the mean value (± standard deviation), calculated from three separate desorption signals for the same sample. Samples were obtained from the residue remaining after drying liquid samples of each (uniformly-mixed) suspension for 2 days at 103°C.

†Values represent the means (± standard deviations) based on four replicate sorbent R.V.'s for each lignin fraction, and four replicate R.V.'s for the controls. Standard deviations were determined via error propagation methods, detailed in Appendix F.

A two-tailed t-test at the 95-percent CL showed that there is no statistically significant difference between the two mean $K_d$ values given in Table 5.22. A one-tailed t-test also at the 95-percent CL, revealed that the SSA for the fine lignin fraction is significantly greater (statistically, that is) than that for the coarse lignin fraction. These data show that the $K_d$ value for the sorption of PCE (and presumably other nonionic, organic compounds as well) by lignin is not a function of surface area, and thus provide strong evidence to support the absorption concept. Furthermore, assuming that the humic substances (which, in addition to lignin, were shown in Section V.F. to be primarily responsible for the sorption of these types of compounds) would sorb similarly to lignin; and assuming that this sorption behavior would remain the same when these SOM components are bound with (or in the presence of) the soil mineral fraction,* it can be concluded that sorption of these compounds by soils in general is probably one of absorption, rather than adsorption.

Although the B.E.T. surface areas determined for the two lignin fractions were significantly different statistically, their magnitudes were relatively close (i.e., the SSA for the FLF was only 31 percent higher than that for the CLF). Furthermore, it could perhaps be argued that these SSA's bear no relationship to what they would be in solution.

Therefore, it was decided to quantitatively verify that these two lignin fractions indeed represented two different classes of particle

---

*Several "incidental" pieces of data gathered in this research (see Section V.F.) suggest that this assumption is correct.

size. Samples from each suspension were examined using a HIAC$^{TM}$ Particle Size Analyzer (Model PC-320) with a sensor range of 5 to 300 μm. According to Garbarini (1984), a lignin concentration of ∿ 2 mg/l resulted in a satisfactory counting level. Thus, each suspension was diluted to this level by adding 0.1 ml of each completely-mixed suspension to 500 ml of DW buffered at pH = 2.0 with HCl.* The background "particle" counts of the diluent were also determined for each particle size interval, and subtracted from the corresponding particle counts for the suspensions. Three replicates were run for each of the suspensions, and also for the background counts.

Table 5.23 depicts the results, which show that (of particles > 5.0 μm) the FLF has a greater proportion of its particles in the smallest particle size interval (i.e., 5 to 10 μm), and the CLF has a greater proportion of its particles in the larger particle size intervals (i.e., > 15 μm). It is clear from Table 5.23 that many (if not most) of the particles in each of these lignin fractions are less than 5 μm in size. Since a good portion of the actual particle size distribution (for each lignin fraction) is not represented, any determination of mean particle diameters would not be representative of the respective distributions.

However, a rough idea of the <u>relative</u> particle sizes for each fraction was obtained as follows. Note that the <u>total</u> number of counted particles per milliter in the FLF is about four-times that in the CLF. Since

---

*This was done to avoid possible pH effects on particle size, since the previous experiment had been performed at a pH of 2.0.

TABLE 5.23 Particle Size Analysis of the Coarse and Fine Lignin Fractions as Determined by the HIAC$^{TM}$ Particle Size Analyzer*

| Channel | Size Interval (μm) | $\bar{N}_i^{CLF}$ | Percent of Total | $\bar{N}_i^{FLF}$ | Percent of Total |
|---|---|---|---|---|---|
| 1 | 5 - 10 | 268 (± 1.1) | 48.8 | 1243 (± 15) | 61.8 |
| 2 | 10 - 15 | 108 (± 6.1) | 19.7 | 404 (± 5.8) | 20.1 |
| 3 | 15 - 25 | 94.6(± 2.7) | 17.2 | 266 (± 4.3) | 13.2 |
| 4 | 25 - 40 | 49.8(± 0.20) | 9.1 | 83.2(± 1.6) | 4.1 |
| 5 | 40 - 55 | 18.4(± 0.50) | 3.3 | 12.5(± 0.75) | 0.62 |
| 6 | 55 - 75 | 7.35(± 0.35) | 1.3 | 1.7(± 0.25) | 0.08 |
| 7 | 75 - 100 | 2.50(± 0.50) | 0.45 | 0.19(± 0.12) | $\sim$0 |
| 8 | 100 - 150 | 0.55(± 0.10) | 0.10 | 0.065(± 0.029) | $\sim$0 |
| 9 | 150 - 200 | 0.0165(±0.030) | $\sim$0 | 0 | 0 |
| 10 | 200 - 250 | 0 | 0 | 0 | 0 |
| 11 | 250 - 300 | 0 | 0 | 0 | 0 |
| | | $\bar{N}_T^{CLF}$ = 549.2 | | $\bar{N}_T^{FLF}$ = 2011 | |

*Notation:

$\bar{N}_i^{CLF}$, $\bar{N}_i^{FLF}$ ≡ mean number of particles per milliliter in the ith channel (corrected for corresponding background count of diluent) for the coarse and fine lignin fractions, respectively.

$\bar{N}_T^{CLF}$, $\bar{N}_T^{FLF}$ ≡ total (mean) number of particles per milliliter in all channels (corrected for background count) for the coarse and fine lignin fractions, respectively.

Notes:

Values for $\bar{N}_i^{CLF}$ and $\bar{N}_i^{FLF}$ represent the mean (and standard deviation) for three replicates. Percent of total = $\bar{N}_i^j/\bar{N}_T^j$ x 100% (where $j$ = CLF or FLF).

the suspension samples analyzed by the HIAC$^{TM}$ contained approximately the same concentration (i.e., ∿ 2 mg/l)*, this means that the FLF must consist of smaller particles. (An alternative explanation is that the CLF particles are denser, but this seems highly unlikely since the lignin particles would be expected to have reasonably uniform composition.) Furthermore, if it is assumed that the particles > 5 μm constitute most of the mass for each suspension, and that these masses are approximately equal for each lignin fraction, then the average particle volume (since volume is proportional to mass) for the CLF must be about four-times larger than that for the FLF; and since diameter is proportional to the cube-root of volume (assuming approximately spherical particles), the CLF must be about 1.6-times larger in diameter (on average). However, it is surmised that the ratio of FLF to CLF particles in the undetected range of < 5 μm is much greater than four**, and therefore the above factor of 1.6 probably represents a minimum value. (In other words, if the entire particle size distribution of each fraction could be determined, it is speculated that the ratio of total particles counted for the FLF to CLF would be greater than four.) Thus the two lignin fractions do indeed contain different particle size classes.

If the CLF particles have nominal diameter > 1.6 times that of the FLF particles, then one would expect the specific surface area ($m^2/g$)

---

*To be exact, the concentrations of the FLF and CLF were 1.79 and 1.94 mg/l, respectively, based on their original suspension concentrations and the dilution factor.

**This conjecture is supported by the trend in the FLF to CLF particle ratios, which can be obtained from the data of Table 5.23.

of the FLF to be > 1.6 times that of the CLF, in the extreme where only the particles' external, superficial areas are considered. On the other hand, since lignin is an amorphous, polymeric substance whose structure may be quite open with respect to its sorption of small, neutral, organic molecules, then lignin particles may possess considerable, available internal surface area for adsorption. In the extreme case where the entire polymeric internal structure is sufficiently open so as to "receive" potential sorbates, then the specific surface area would be constant, independent of particle size.

At this extreme, distinction between a<u>b</u>sorption and a<u>d</u>sorption becomes irrelevant; for what is absorption other than the complete interpenetration of a sorbent? The BET data of Table 5.22 suggest that the situation with lignin--and perhaps, by extension, with "real" SOM--is somewhere between these two extremes. (That is, the specific surface area ratio between FLF and CLF samples was only 1.3--greater than 1.0, but less than 1.6.)

In summary, one has to conclude that these results support the a<u>b</u>sorption theory more so than the a<u>d</u>sorption theory, since significantly-different specific surface areas were generated and found to result in insignificant differences in $K_d$. However, the less-than-dramatic difference in specific surface area between the two fractions, coupled with the usual concerns with relevance of BET data (and the obvious concerns with the relevance of experiments with lignin as a representation of SOM), prompt this support to be regarded as tenuous.

## I. Influence of Various Factors on Sorption

The effects of temperature and organic carbon content ($f_{oc}$) on sorption have been addressed in other sections of this chapter. Therefore, the discussions below are limited to the influence of pH, ionic strength ($I$), solids (particle) concentration, and specific surface area.

### 1. pH

#### a. Experimental Procedures

The mineral soil (MS) and TCE were selected as the sorbent and sorbate, respectively. Each sorbent R.V. was filled with 5.0 ml of one of three MS suspensions, whose pH values had been pre-adjusted to 4.0, 6.5, and 9.0, by addition of small amounts of concentrated HCl or NaOH, as appropriate. (The original [unadjusted] pH of the MS suspension was 7.7.) The control R.V.'s each received 5.0 ml of distilled water (DW) from one of three solutions which had been pre-buffered to a pH of 4.0, 6.5, or 9.0, by addition of HCl or NaOH, as appropriate. Two sorbent, and two control replicates were run for each pH level. Each R.V. was injected with 0.5 ml from the low-level $^{14}$C-TCE stock solution, capped and sealed, then tumbled for four days at T = 20°C. (Remaining procedures were identical with those described in Chapter IV.) The conductivities of the pH-adjusted suspensions were 240, 230, and 225 μmho/cm, for the suspensions at pH of 4.0, 6.5, and 9.0, respectively. These conductivities correspond to an ionic strength of approximately 0.004 M.

### b. Results and Discussion

The $K_d$ values and their corresponding uncertainties (i.e., standard deviations) determined via error propagation analyses (described in Appendix F) are presented in Table 5.24. The previously-determined $K_d$ value from the TCE-MS sorption experiment at pH = 7.7 (i.e., non-adjusted), and T = 20°C, is also incorporated into the results of this experiment. (The $K_d$ value resulting from the set of R.V.'s corresponding to the 0.5-ml injection by the low-level, $^{14}C-C_2HCl_3$ stock solution was used.) Obviously, a two-tailed t-test at the 95 percent CL does not yield any differences among these $K_d$ values. The effect of pH on sorption for this experiment is also illustrated in Figure 5.39, wherein the percent of TCE sorbed is plotted against pH. Clearly, pH has negligible influence on TCE sorption by the mineral soil over the pH ranges normally encountered in soil solution. (It is assumed that this also holds true for the other compounds, and the other soils and soil

Table 5.24 Equilibrium Sorption Distribution Coefficients ($K_d$) as a Function of pH, for the Mineral Soil-$C_2HCl_3$ (TCE) System

| pH | $K_d$ | Standard Deviation of $K_d$* |
|---|---|---|
| 4.0 | 62.4 | ± 4.2 |
| 6.5 | 59.2 | ± 4.9 |
| 7.7 | 59.9 | ± 3.6 |
| 9.0 | 59.0 | ± 3.6 |

*Calculated from error propagation analyses on the function defining $K_d$, as described in Appendix F.

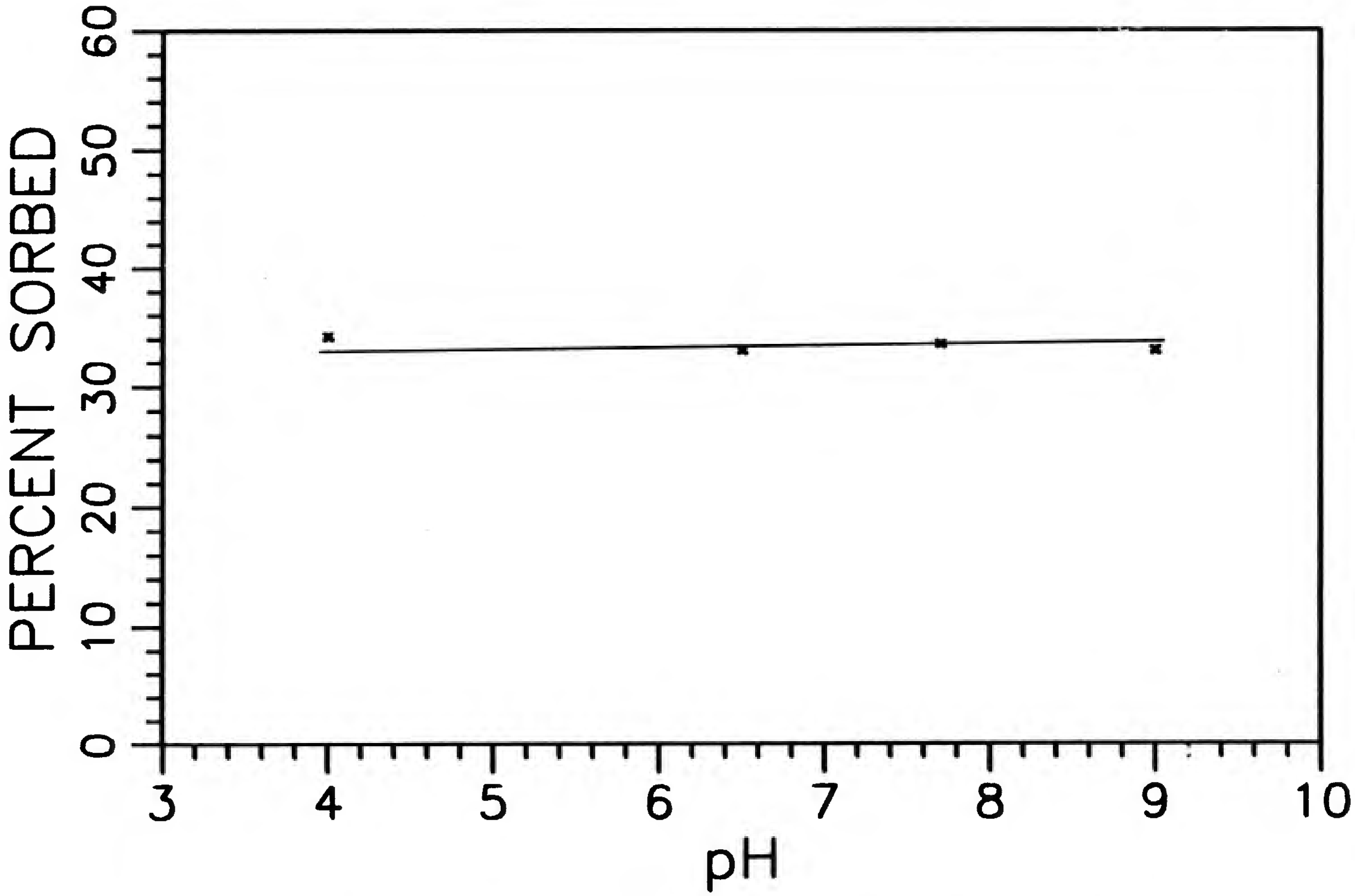

FIGURE 5.39 Percent $C_2HCl_3$ Sorbed by the Mineral Soil as a Function of pH

components. Recall the previous experiments in Section V.F., wherein the sorption of $C_2Cl_4$ by lignin increased slightly with decreasing pH. However, this was attributed to the effect of pH on lignin solubility, and not on the sorption process per se.) The experimental results depicted in Table 5.24 and Figure 5.39 are in accord with the majority of the literature, which reports negligible effects of pH on the sorption of nonionic compounds by soils.

Since pH would have negligible effect upon the sorbates' molecular properties, the real question being addressed by the experiment herein was: Would the effect of pH upon SOM properties have a measurable impact on sorption characteristics? Schnitzer and Kodama (1975) and Chen and Schnitzer (1976) (using an electron microscope and scanning electron microscope, respectively) observed that the shape, size, and degree of aggregation of humic and fulvic acid particles varied with pH, over a range of 2 to 10. Apparently, sorption of these compounds by soils is not significantly affected by these pH-effects on their humic components. But as stated previously, pH may indirectly influence sorption by controlling the solubility of certain SOM constituents, such as HA and lignin.

### 2. Ionic Strength

#### a. Experimental Procedures

The experimental procedures used were identical to those used in the previous pH experiment, except that the R.V.'s received the appropriate mass of KCl (instead of HCl or NaOH) to yield suspension (or solution) ionic strengths ($I$) of either $\sim$ 0.0, 0.1 or 1.0 M. Also, the $K_d$ values determined from the experimental data (and reported below), take into account the increased partitioning of TCE into the headspace of the R.V.'s by using the appropriate values for (effective) Henry's constant as a function of $I$, as determined by Gossett and Lincoff (1981). (The values for Henry's constants used in all experimental work of this research are given in Appendix C.)

### b. Results and Discussion

The influence of $I$ on the sorption of TCE by the mineral soil is depicted in Table 5.25. Also, Figure 5.40 illustrates the percent TCE sorbed as a function of $I$ (based on the same raw data from this experiment). The increases in sorption with increasing ionic strength are probably attributable to increases in TCE solution activity with increasing $I$. For example, the activity coefficient for TCE in aqueous solution at an ionic strength of 1.0 M was estimated (from liquid-vapor equilibrium

TABLE 5.25 "Effective" Equilibrium Sorption Distribution Coefficients ($\gamma_{TCE}K_d$) as a Function of Ionic Strength ($I$), for the Mineral Soil-$C_2HCl_3$ (TCE) System

| $I$ (M) | $\gamma_{TCE}K_d$* | Standard Deviation |
|---|---|---|
| 0.0 | 54.8 | ± 5.0 |
| 0.1 | 64.3 | ± 5.2 |
| 1.0 | 81.8 | ± 4.5 |

*$\gamma_{TCE}$ is the solute (TCE) activity coefficient in the aqueous phase.

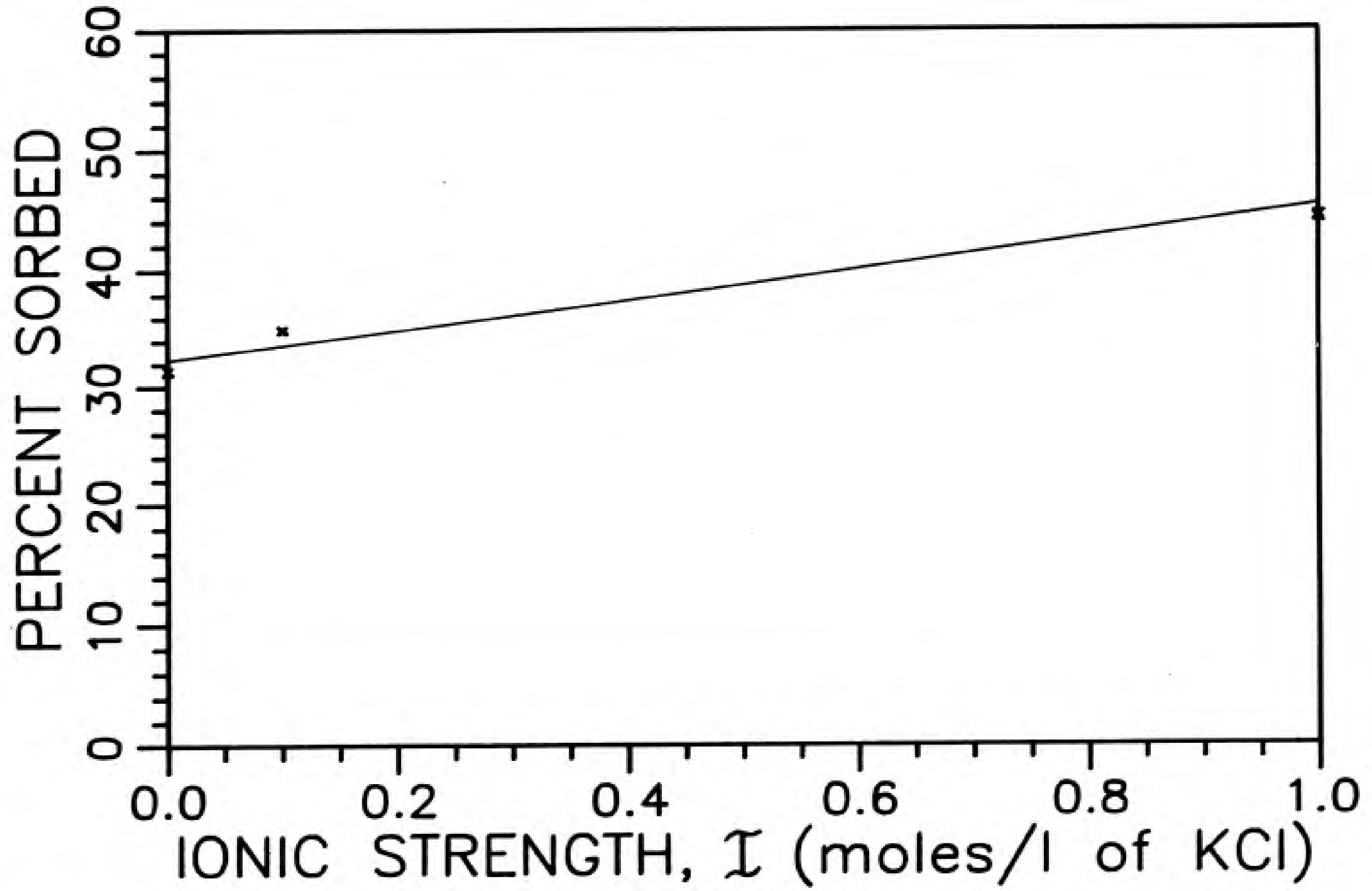

FIGURE 5.40 Percent $C_2HCl_3$ Sorbed by the Mineral Soil as a Function of Ionic Strength

experiments) by Gossett and Lincoff (1981) to be $\approx$ 1.6. The aqueous-phase TCE activity coefficient (at $I$ = 1.0 M) based on the sorption experiment is calculated to be $\approx$ 1.5.* This compares favorably with the previous value, and suggests that the effect of $I$ on sorption of TCE is simply caused by its effect on the aqueous-phase activity coefficient of TCE.

### 3. Solids Concentration

#### a. Preliminary Discussion

As mentioned in Section II.D.3., the bulk of the experimental evidence from the literature indicates that $K_d$ increases as solids concentration decreases, for any given sorbent-sorbate pair. There are presently several theories which attempt to explain this unusual and unexpected (from a thermodynamic viewpoint) result, two of which are discussed below.

One of the theories, proposed by Voice et al. (1983), and later corroborated by Gschwend and Wu (1984), states that the "solids concentration effect" (i.e., the observation that $K_d$ increases as solids concentration decreases, or vice versa) is due to the presence of sorbent microparticles or macromolecules which are not removed from the

---

*This value was calculated from the ratio of the effective sorption distribution coefficients at $I$ = 1.0 M to that for $I$ = 0.0 M. Since $\gamma_{TCE}$ $\approx$ 1 when $I$ = 0.0 M, then

$$\gamma_{TCE}(@\ I = 1.0\ M) = \frac{\gamma_{TCE}\ K_d(@\ I = 1.0\ M)}{(1)\ K_d(@\ I = 0.0\ M)} = \frac{81.8}{54.8} \approx 1.5$$

This method for determining $\gamma$ assumes that changes in TCE solution activity are solely responsible for changes in sorption; and that the presence of the salt does not significantly affect the activity of the sorbed species.

supernatant during the solid-liquid phase separation process (e.g., centrifugation).* Since the reaction vessels (samples) containing the higher concentration of solids will also contain the higher concentration of these microparticles and macromolecules in their supernatants, the result is that the experimenter (unknowingly) determines a lower "apparent" $K_d$ value for these samples. In other words, the sorbent microparticles and macromolecules bind with the sorbate molecules, but remain in the supernatant phase which is sampled and analyzed for determining the equilibrium solute concentration (i.e., $C_\ell$). Thus, the samples containing a higher sorbent solids concentration not only yield a higher apparent "dissolved" sorbate concentration, but also a lower apparent sorption density, $C_s$.** The net result is, therefore, a lower (apparent) $K_d$ value.

The other theory, propounded by Di Toro et al. (1984) explains the solids concentration effect by invoking a mechanism referred to as "particle interaction induced desorption". The hypothesized mechanism assumes that a binary interaction between particles causes desorption to occur, but the authors are uncertain about the further details of this mechanism. The kinetic equations which include the "particle interaction induced desorption" step, lead to a sorption equilibrium

---

*Additional (indirect) support for this theory comes from the works of Lion and Garbarini (1983) and Garbarini and Lion (1984). These investigators found $K_d$ to be independent of solids concentration using the gas-chromatographic headspace technique to determine solute concentration (and hence, $C_s$ and $K_d$). Since this technique employs sampling and analysis of the gas phase, no liquid phase separation process is necessary, and the presence of microparticles and macromolecules does not "interfere" with the measurement of the dissolved sorbate concentration.

**This occurs because sorption density, $C_s$, is typically determined by the difference in solute concentrations between sorbent and control reaction vessels.

expression which seems to account for the observed solids concentration effect. (However, this does not substantiate their proposed mechanism.) Various experiments performed by Di Toro et al. seem to refute the first theory discussed above.

### b. Experimental Procedures

To determine if the solids concentration effect occurs for the sorbents and sorbates of this research, an experiment was undertaken to measure $K_d$ as a function of solids concentration. Lignin and $C_2Cl_4$ were selected as the sorbent and sorbate, respectively. Various masses of lignin were weighed into 13 different sorbent R.V.'s and afterwards, 5.0 ml DW was added to each of these R.V.'s. Three replicate controls were prepared by adding 5.0 ml DW to each control R.V. Each R.V. was then injected with 0.5 ml from the low-level $^{14}C$-$C_2Cl_4$ stock solution. (Remaining procedures were as described in Chapter IV.) The lignin concentrations which resulted, spanned a range of 0.44 to 24.7 g/l (a 56-fold range). Equilibration temperature and time were 20°C and 2 d, respectively. The pH and ionic strength of the resulting suspensions in each sorbent R.V. were not determined. However, based on another experiment with lignin (in which these values were measured), the pH and $I$ are estimated to range from 6.0 to 7.0, and 0.002 to 0.04 mol/l, respectively (wherein pH decreases, and $I$ increases, with increasing lignin concentration).

### c. Results and Discussion

Figure 5.41 displays a plot of $K_d$ versus lignin solids concentration (S.C.), which clearly demonstrates the presence of the solids concentration effect.

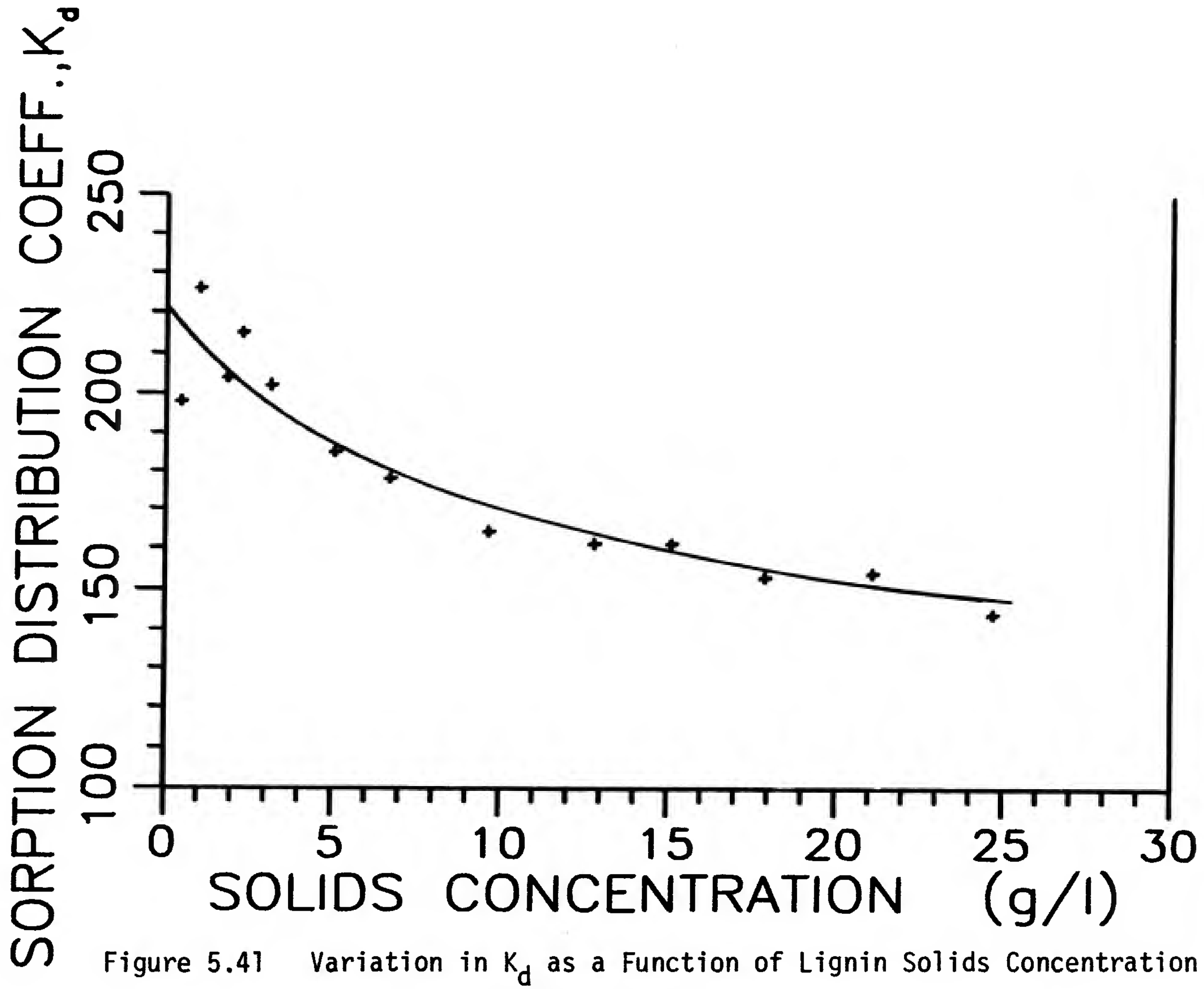

Figure 5.41 Variation in $K_d$ as a Function of Lignin Solids Concentration, Using $C_2Cl_4$ as the Sorbate

In order to assess the possibility that the "effect" was due to differences in sorption rates among the R.V.'s (i.e., that sorption kinetics increases as S.C. decreases), another experiment was conducted, this time using lignin and $C_2HCl_3$.* In this experiment, the variation in $K_d$ as a function of time was determined at two levels of lignin concentration, 2.0 and 20.0 g/l. These suspensions were prepared by combining the appropriate amounts of lignin and DW. The pH and (approximate) I for the 2.0 g/l suspension were 6.5 and 0.004 mol/l, respectively; and for the 20.0 g/l were 6.2 and 0.03 mol/l, respectively. The pH and I for the 2.0 g/l suspension were adjusted (by addition of HCl and NaCl) to the corresponding values of the 20.0 g/l suspension, to eliminate any possible influences of pH and I on sorption. The sorbent R.V.'s each received 5.0 ml from their respective suspensions, and each control R.V. received 5.0 ml DW.

The results of this experiment are shown in Figure 5.42, which clearly demonstrate that the S.C. effect is not due to kinetic considerations. That is, the $K_d$ values corresponding to the two different lignin concentration levels, show no sign of converging even after almost nine days of equilibration.

In both of the above experiments, the "dissolved" lignin fraction (defined as that which remained in the supernatant following centrifugation) increased with increasing lignin (solids) concentration, as evi-

---

*A different sorbate was selected since the S.C. effect could then be confirmed (or denied) for a different sorbate while simultaneously investigating the role (if any) of kinetics. The implicit assumption is, of course, that if kinetics is shown to be responsible for the S.C. effect in the lignin-$C_2HCl_3$ system, it is also responsible for the S.C. effect in the lignin-$C_2Cl_4$ system.

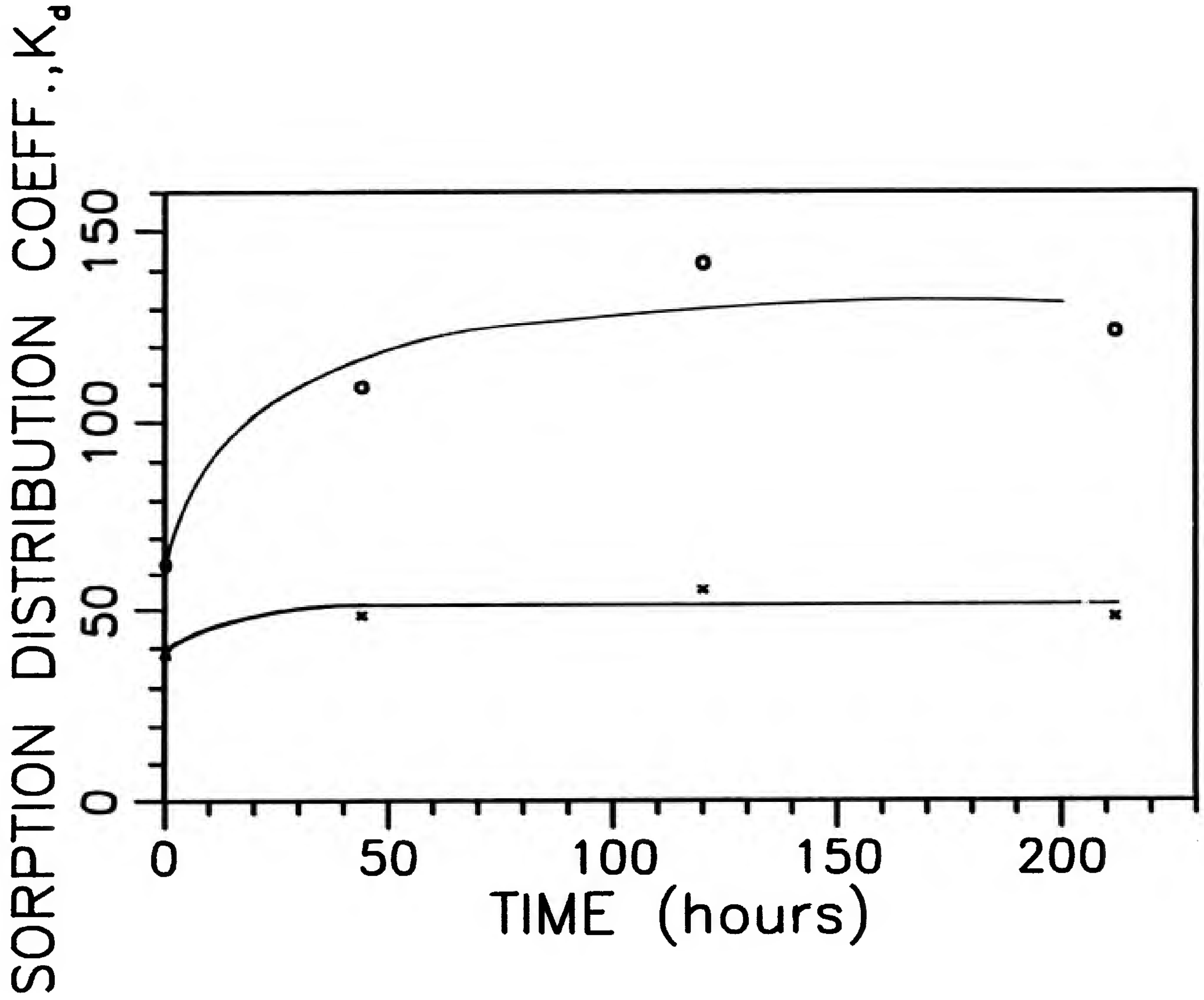

FIGURE 5.42 Variation in $K_d$ as a Function of Time at Lignin Solids Concentrations of 2 g/l (○) and 20 g/l (x), Using $C_2HCl_3$ as the Sorbate

denced by the $H^{\#}$ reported by the LS-9800* (and also by visual inspection of the supernatants). Figure 5.43 gives the sample $H^{\#}$ as a function of lignin solids concentration added to the reaction vials. This figure shows that the level of lignin microparticles and macromolecules indeed increases as S.C. increases, which could account for the observed discrepancies in "apparent" $K_d$ values. Therefore, these two experiments seem to support the microparticle-macromolecule explanation of the solids concentration effect.

A final experiment was performed regarding the S.C. effect, in which an attempt was made to remove the microparticles and macromolecules from the system prior to equilibration. For this experiment, graphite was used as the sorbent since it should have minimal "solubility" in the aqueous phase (i.e., the presence of graphite "macromolecules" in solution can probably be ruled out). The graphite was thoroughly mixed with distilled water, then centrifuged at ∿ 1000 G for 30 minutes. The supernatant was discarded and replaced with distilled water, the suspension thoroughly shaken, and again centrifuged at ∿ 1000 G for 30 minutes. The supernatant was again discarded, and the settled graphite was oven-dried (103°C) for two days to remove the remaining water. The treated, dried graphite was then used to prepare two stock suspensions having graphite concentrations of 2.0 and 20.0 g/l, respectively. Three replicate samples were run for each graphite concentration (as well as three replicates for the control samples), and all samples were equilibrated for two days at 20°C. The graphite R.V.'s were then centrifuged at

---

*As the reader will recall, the $H^{\#}$ is the (external standard) value provided by the LSC as a measure of sample quench level. In this instance, it can be interpreted as an indirect measure of the color (and hence, dissolved lignin) present in the sample.

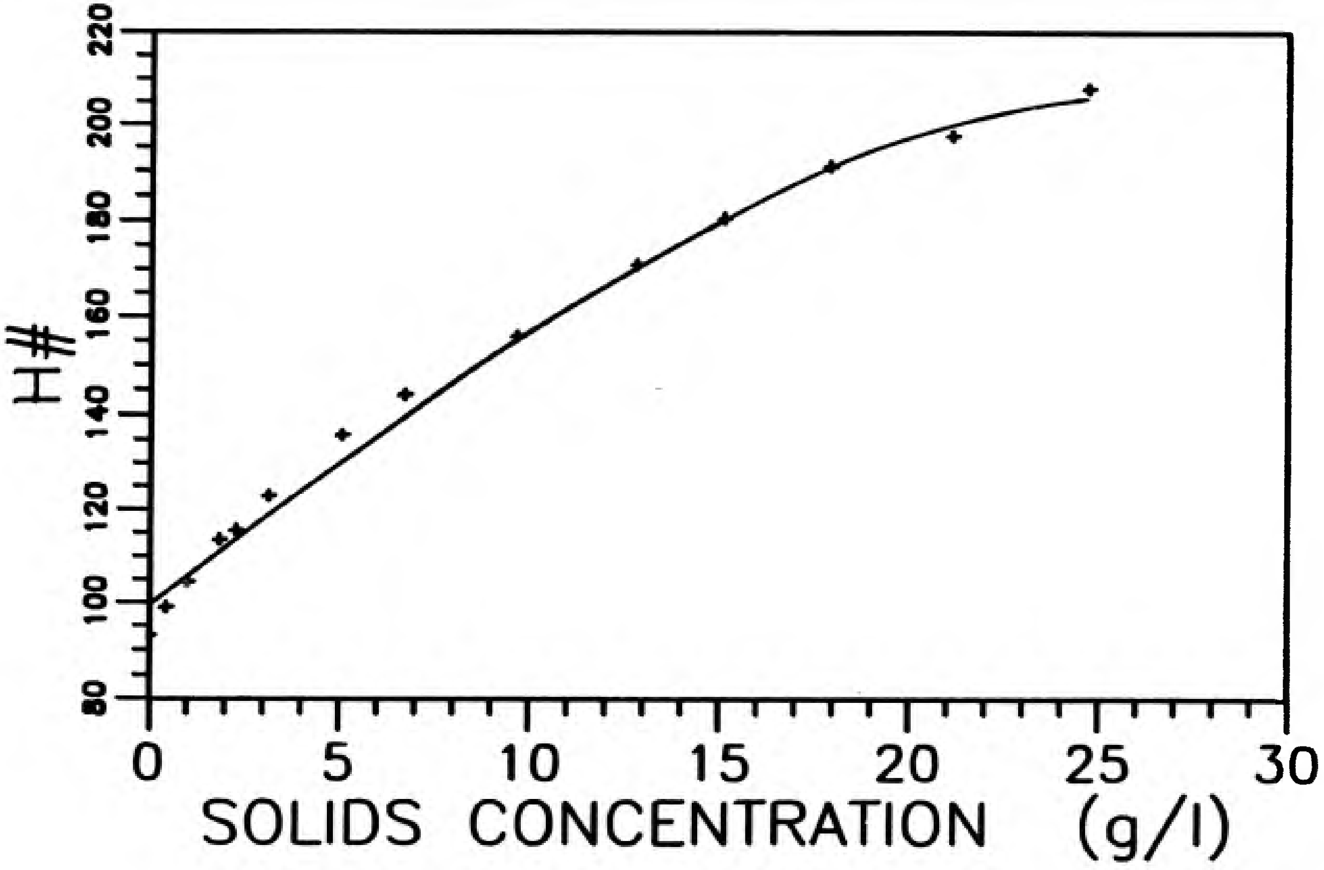

FIGURE 5.43 Sample $H^{\#}$ (Which is Proportional to Soluble Lignin Concentration) as a Function of Lignin Solids Concentration

∿ 3000 G for 30 minutes to achieve phase separation. (Note that this final centrifugation force was three-times stronger than the centrifugation force used during the removal of the graphite colloids. This was done intentionally so that more of the graphite fines would be discarded in the supernatant, or if still remaining, would be centrifuged out in the final step.)

Table 5.26 shows the $K_d$ values determined for each of the graphite concentration levels. As with lignin, a solids concentration effect is evident, even though an attempt was made to remove any graphite microparticles.

TABLE 5.26 Adsorption Distribution Coefficient ($K_d$) for $C_2HCl_3$ and Graphite at Two Different Solids Concentrations

| Solids (Graphite Concentration) (g/l) | $K_d$ | Uncertainty Due to Error Propagation |
|---|---|---|
| 2.0 | 153.3 | ± 3.4 |
| 20.0 | 91.5 | ± 7.3 |

To determine whether or not the two graphite suspensions had different levels of graphitic colloids (i.e., microparticles), a large-volume sample (∿ 200 ml) of each completely-mixed suspension was withdrawn, placed in 250-ml Nalgene$^{TM}$ bottles, and centrifuged at ∿ 3000 G for 30 minutes. Several aliquots of supernatant from each of the two bottles were analyzed for turbidity level using a HACH Model 2100 Turbidimeter. The supernatant samples for the 2.0 g/l and 20.0 g/l graphite suspensions were found to have a turbidity of 0.17 ± 0.035 NTU and 0.16 ± 0.017 NTU, respectively. In other words, based on turbidity measurements, the supernatants for each of the suspensions had virtually identical colloidal particle contents. However, it should be pointed out that the suspensions used in the turbidity measurements had not undergone a two-day tumbling process prior to analysis. The possibility that graphite microparticles were formed during this tumbling process (i.e., the equilibration period) cannot be ruled out. (However, based on a previous experiment using washed lignin, the "soluble" lignin fraction did not reform during a four-day tumbling period.) It could also be possible that the turbidimeter is simply not sensitive to the levels of graphite microparticles present in the two suspensions. Therefore, although the above experimental results with graphite cast some uncertainty upon the microparticle-macromolecule theory of the solids concentration effect, it by no means disproves it.

In summary, it appears that in many instances the S.C. effect can be attributed to the non-separation of colloidal particles during the experiment; but in other cases (in particular, the various experiments conducted by Di Toro et al., and the experiment with graphite performed herein) the experimental procedures and results seem to rule it out as a possible cause. Thus, the solids concentration enigma remains unsolved.

### d. Impact of the "Solids Effect" on Other Facets of this Research

Assuming that the other sorbents used in this research exhibit a similar type of solids concentration effect upon $K_d$ (as discovered above for the cases of lignin and graphite), then the $K_d$ values reported in this thesis would all be conditional ones. That is, they would be valid only for the particular particle concentration employed in the experiment. The impact of using these (assumed) conditional $K_d$ values on the other facets of this research would be as follows.

For Section V.D., in which $K_d$ values were correlated with compound properties, the use of conditional $K_d$ values should have had no effect on the resulting correlations (and conclusions). This is because the same sorbent suspension (and hence, particle concentration) was used for each sorbate, for each correlation.

In the determination of $K_{oc}$ values and their correlation to several sorbate properties (Section V.E.), use of conditional $K_d$ values probably resulted in under-estimating the "true" $K_{oc}$ and $\overline{K}_{oc}$ values* for each sorbate. The extent of this under-estimation is most likely a function of the sorbent, and the solids concentration employed. For example, the $K_d$ values for the lignin-$C_2HCl_3$ system decreased from about 130 to 50 (a reduction of 62%), and those for the graphite-$C_2HCl_3$ system decreased from 153.3 to 91.5 (a 40% reduction), in going from a solids concentration of 2 to 20 g/l (in both cases). Therefore, the "solids effect" may very well be (at least partially) responsible for the high variability in the $K_{oc}$ values obtained in this research, and elsewhere in the literature. However, the use of conditional $K_d$ values is surmised to have had little effect on the R values which resulted from the correlation of $\overline{K}_{oc}$ with the sorbate properties S, $K_{ow}$, and $\alpha$.

---

*The term "true", as used here, refers to the values which would have been obtained at infinitely dilute solids concentration.

This is because the individual sorbate $K_{oc}$ values for a *particular* sorbent were determined at identical particle concentrations. Therefore, the *relationship* of these $K_{oc}$ values (for any given sorbent) to the sorbate properties should be virtually independent of S.C. However, the $\overline{K}_{oc}$ values predicted by these regression equations [(Equations (5-5), (5-6), and (5-7)] would probably under-estimate the "true" value of $\overline{K}_{oc}$.

In Section V.G., where the $\Delta G^o$, $\Delta H^o$, and $\Delta S^o$ values were determined, the use of conditional $K_d$ values probably resulted in under-estimating the "true" (absolute) values of $\Delta G^o$ and $\Delta S^o$. That is, the "true" $\Delta G^o$ values would probably be slightly more negative, but the "true" $\Delta S^o$ values slightly more positive, than those reported in Section V.G. On the contrary, the $H^o$ values are probably not affected by S.C. since they were calculated from the *variation* in $K_d$ with respect to temperature, and not the actual (i.e., conditional) $K_d$ values themselves. However, the "solids effect" itself could be a function of temperature, in which case the $\Delta H^o$ values would, of course, have been affected; but it is surmised that such a relationship (between solids effect and temperature) is unlikely, and probably negligible (if it does exist).

The "solids effect" should not have influenced isotherm linearity (or nonlinearity) used in Section V.H. in attempting to distinguish between *ad*sorption and *ab*sorption. This is because each isotherm (for a given sorbent) was determined at a constant sorbent concentration. Also, the use of conditional $K_d$ values in the lignin particle size fractionation experiment (probably) had no bearing on the results, since roughly the same S.C. was used for each lignin fraction.

### 4. Specific Surface Area

It was hoped that the specific surface areas (SSA's) of the various sorbents used in this research, as measured by their B.E.T. isotherms, would be more representative of what they were in aqueous suspension. But as shown in Tables 5.6 and 5.7, the only sorbents whose SSA's might correspond to that which exist in suspension are perhaps the mineral soil (SSA = 6.32 $m^2/g$) and graphite (SSA = 8.64 $m^2/g$). The peat, muck, humic acid, and lignin, would definitely have SSA's significantly higher in aqueous suspension that those determined by their B.E.T. isotherms.

Nevertheless, a few conclusions can be drawn regarding the role of sorbent surface area in the sorption of the compounds studied. To begin with, sorbent SSA is clearly not the sole determinant for the sorption of these compounds. The negligible sorption of these compounds by the soil minerals and clays, some of which have extremely high SSA's (e.g., montmorillonite SSA $\approx$ 800 $m^2/g$), is perhaps the best corroboration for this conclusion. On the contrary, for those solids which do absorb these compounds, SSA can dramatically influence sorptive strength. This is exemplified by comparing the adsorption of these compounds by graphite and powdered activated carbon (PAC). The structures of these two sorbents are quite similar except for the vast network of internal pores which characterize the activated carbon, and provide it with an enormous SSA (on the order of 1000 $m^2/g$). The $K_d$ values for the PAC are noted to range from two to three orders of magnitude higher than those for graphite (see Table 5.8) reflecting the large difference in SSA's between these sorbents. For the case of polymeric humic substances (including lignin), the role of SSA is a bit more elusive, and depends on how "surface area" is defined. Refer to the latter part of Section V.H. for a discussion of this issue.

## J. Desorption and Reversibility

### 1. Procedures, Results and Discussion

In Section B of this chapter it was shown that the desorption isotherms for each of the compounds with the mineral soil lay above their respective sorption isotherms. Two additional experiments were performed in an attempt to determine the cause for this anomaly, and these experiments and results are discussed below.

The procedures used in this Section were as described in Chapter IV and Section B of this chapter, unless otherwise noted. The pH and $I$ of the mineral soil suspension were 7.7 and ∿ 0.0036 M, respectively.

The first experiment explored the possibility that slow desorption kinetics (relative to sorption kinetics) caused the nonsingular isotherms observed in Figures 5.6 through 5.9. That is, if the desorption cycle was longer, the desorption isotherm data points would ultimately "migrate" toward the sorption isotherm and yield a singular, reversible isotherm.

To test this hypothesis, a single-point sorption isotherm was determined for the mineral soil with $CHCl_3$,* using 12 sorbent R.V. replicates, and 12 control R.V. replicates, equilibrated over the usual four-day sorption cycle. The mean sorption $K_d$ value and its 95 percent

---

*$CHCl_3$ was selected as the sorbate so that compound mass losses would be minimal during the experiments (since long-term equilibration periods were involved). (Compound mass losses are discussed in Appendix D.)

CI for these 12 replicate samples was 8.75 ± 1.17. Following the sorption cycle, the desorption cycle was set up in the usual manner (described in Section IV.C.1.) except that samples were analyzed at various desorption equilibration times. A total of five, single-point, desorption isotherm data points were determined (corresponding to various desorption equilibration times), with two replicates used for each of the first four data points, and four replicates used in the final data point.

The results of these experiments are shown in Figures 5.44 and 5.45. Figure 5.44 illustrates the desorption isotherms (determined at the indicated desorption equilibration times) relative to the sorption isotherm. Figure 5.45 depicts the same data but presented in different format, which better illustrates the variation in $K_d'$ (the desorption distribution coefficient) with respect to time. These two figures plainly demonstrate that slow desorption kinetics has nothing to do with the observed discrepancy between sorption and desorption isotherms. In fact, instead of the desorption isotherms (or $K_d'$ values) converging to the sorption isotherm (or $K_d$ value) with respect to increasing desorption equilibration time, they appear to be diverging!

Having eliminated slow desorption rates as a possible explanation, an alternative hypothesis (which could also account for the results obtained in the previous experiment) is that the sorption data do not reflect equilibrium conditions (i.e., 4 days was insufficient time to attain sorption equilibrium). To test this hypothesis, a long-term sorption experiment was set up, again using the mineral soil-$CHCl_3$ system. Each single-point, sorption isotherm data point was determined from three replicate samples (three sorbent and three control R.V.'s), which

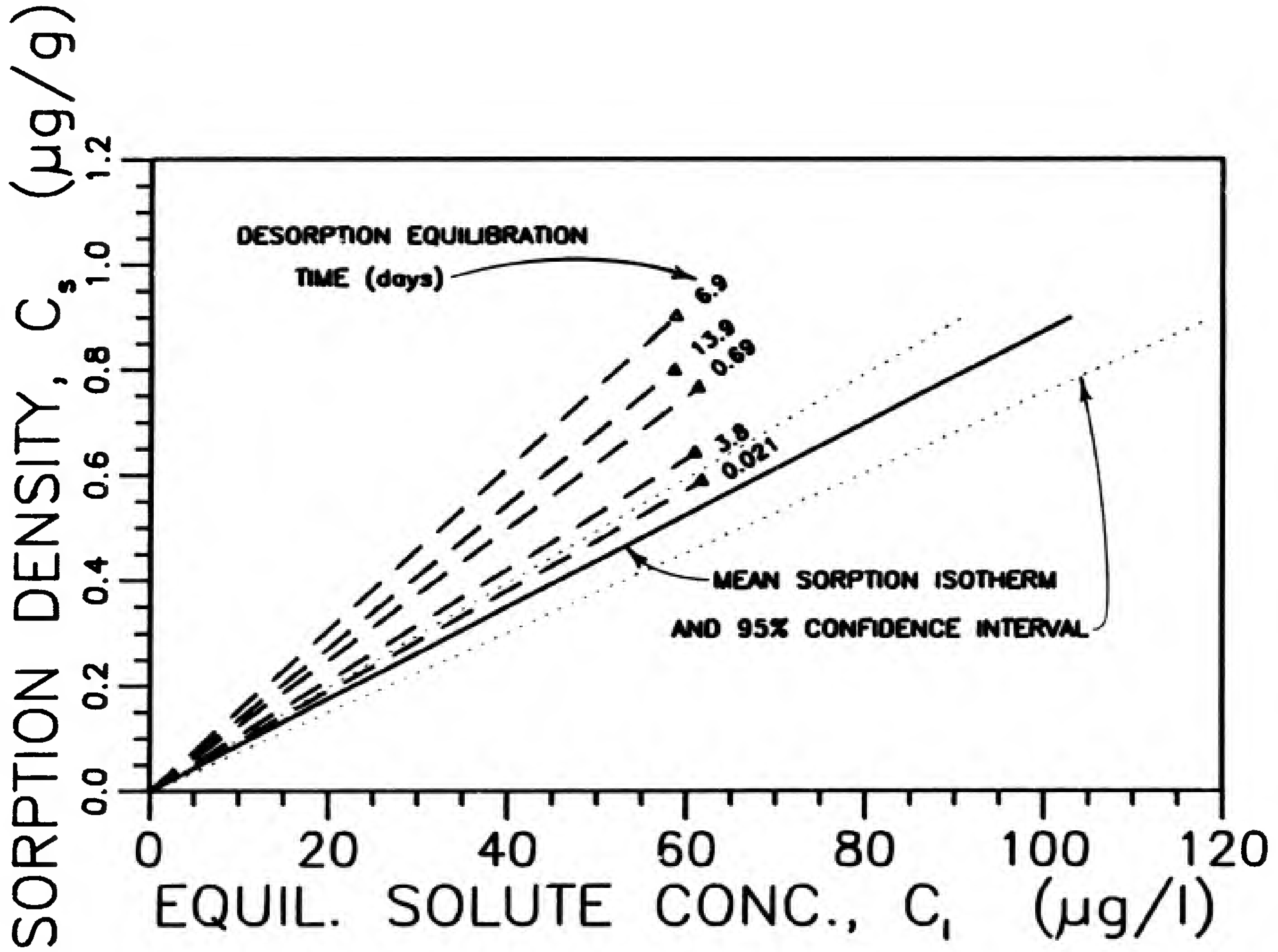

FIGURE 5.44 Location of Desorption Isotherms (Determined at Various Equilibration Times) with Respect to the Mean Four-day Sorption Isotherm for the Mineral Soil-$CHCl_3$ System

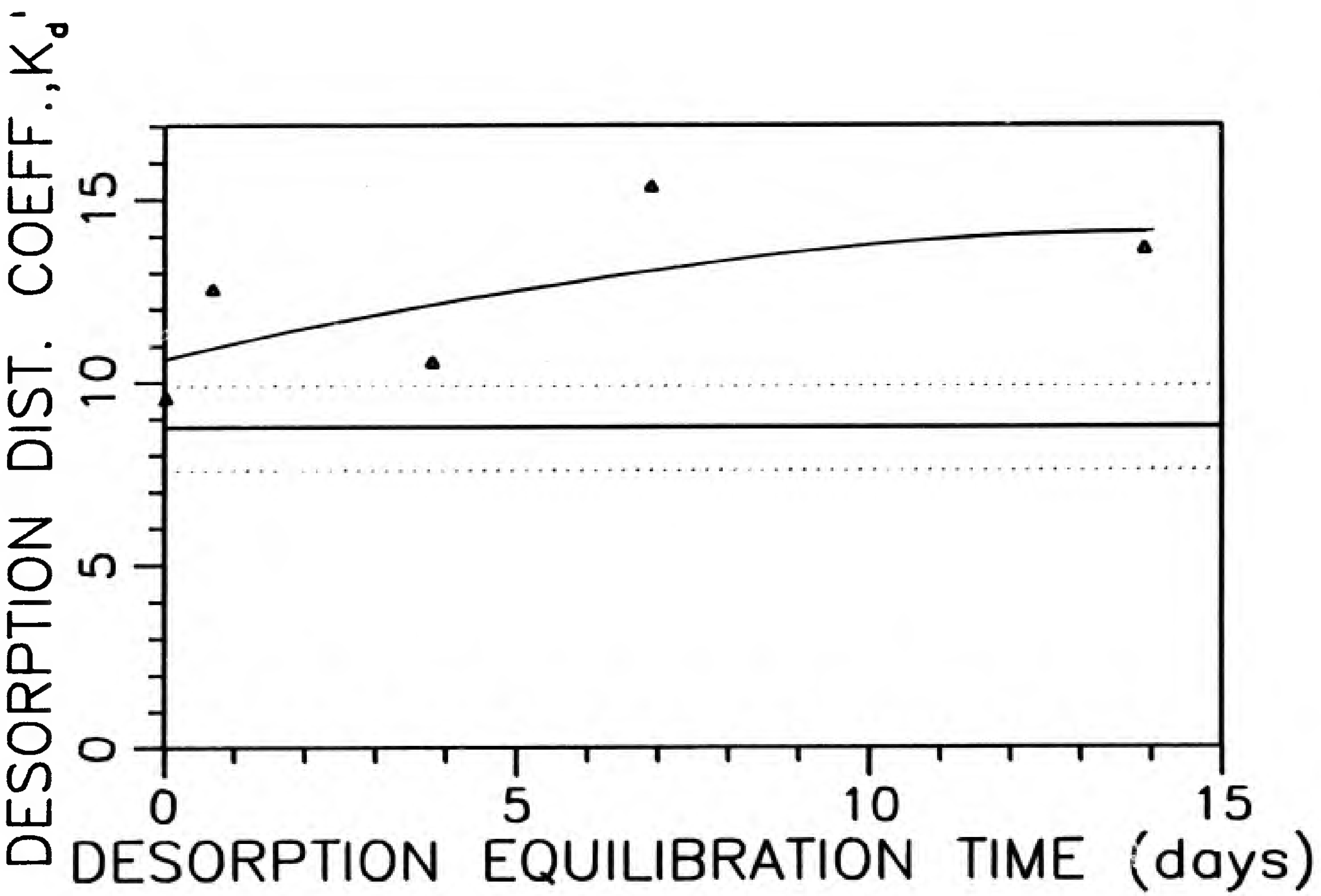

FIGURE 5.45 Variation of $K_d'$ Values (Δ) as a Function of Desorption Equilibration Time for the Mineral Soil-$CHCl_3$ System. (The mean 4-d sorption $K_d$ value is indicated by the solid horizontal line, with the dotted lines representing its 95% confidence limits.)

were analyzed as a function of sorption equilibration time. (All other procedures were as previously described in Chapter IV and Section V.B.)

The results of this experiment are depicted in Figure 5.46, which shows that sorption by the mineral soil appears to continue indefinitely (although at a very slow rate). Therefore, it is apparently slow sorption kinetics which accounts for the anomalous, non-singular isotherms for this soil with each of the sorbates.

### 2. Discussion of Possible Cause of Slow Sorption Kinetics for the Mineral Soil and Impact of Using (Apparent) Non-equilibrium $K_d$ Values for the Mineral Soil on Other Facets of This Research

Unfortunately, the lack of attainment of true sorption equilibrium for the mineral soil was not known until the final phase of this research. (In fact, it would not have been discovered if not for the investigation of the anomalous, non-singular isotherms for this sorbent.)

It is not known for certain why this sorbent behaves in this manner, but a possible explanation (in light of other findings in this research) is: Perhaps the humic materials (presumably causing the sorption of these compounds) in this sorbent are very tightly bound to the mineral fraction*, and therefore, do not exhibit their typical, open structure that they would in the "pure" form. If this is true, then the sorbate molecules might have greater difficulty sorbing into the tightly-bound, polymeric humic materials (which coat the inorganic surfaces of this sorbent), and therefore require more time to completely

---

*This supposition is supported by the fact that only a small portion of the organic carbon fraction of the mineral soil was extractable with 0.1 N NaOH, relative to the other soils.

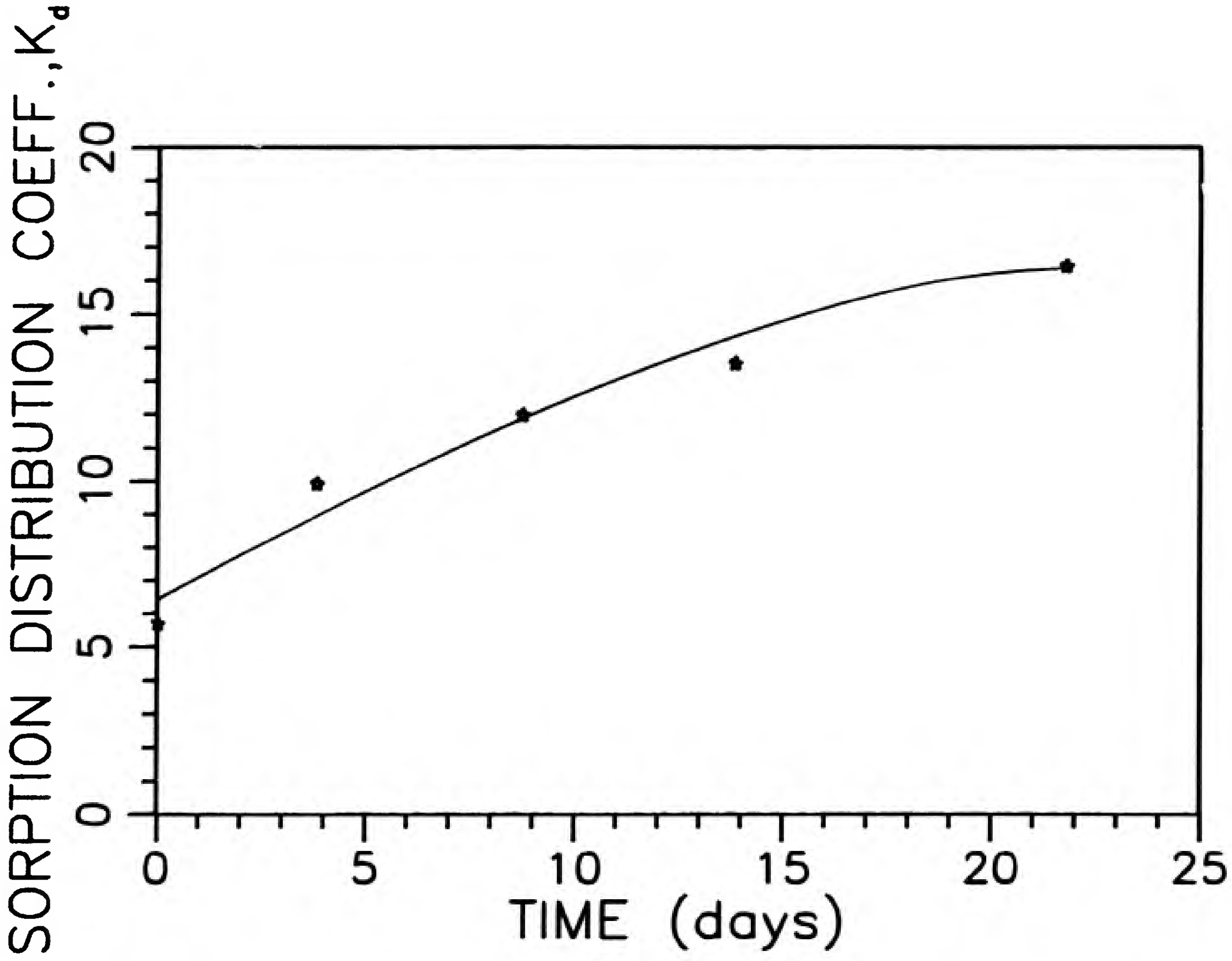

FIGURE 5.46 Variation of $K_d$ Values as a Function of Time for the Mineral Soil-$CHCl_3$ System

diffuse into its structure in attempting to achieve equilibrium. Furthermore, the implication is that other mineral soils may behave in this fashion, and the above explanation could therefore apply to many of the other findings in the (soil sorption) literature, of non-singular sorption and desorption isotherms.

The impact of using the (apparent) non-equilibrium $K_d$ values for the mineral soil upon the other facets of this research may or may not be significant. The only aspects which it might affect are discussed below.

For Section V.D., in which $K_d$ values were correlated with sorbate properties, recall that the mineral soil (MS) was poorly correlated to all sorbate properties. If one assumes that the non-equilibrium $K_d$ values (for the mineral soil) used in these correlations have the same relative values, then the results of Section V.D. would not be affected. But if the "true" equilibrium $K_d$ values do not have the same relative values (as those shown in Table 5.8 for the mineral soil), then obviously, this would affect the correlations (for the mineral soil only), and might explain the poor correlations for this sorbent.

For Section V.E., where the $K_{oc}$ values were determined and correlated to several sorbate properties (S, $K_{ow}$, and $\alpha$), the use of non-equilibrium $K_d$ values for the MS would have the effect of making the resulting $K_{oc}$ values lower than what they should be. However, inspection of Table 5.14 shows that the $K_{oc}$ values for the MS seem to be "in line" with the $K_{oc}$ values for the other sorbents for $CHCl_3$ and $C_2Cl_4$; whereas the $K_{oc}$ value for $CCl_4$ is significantly lower, and that for $C_2HCl_3$ is significantly higher, than their corresponding $K_{oc}$ values for the other sorbents. Nevertheless, the use of higher "true" $K_d$ values for the MS would result in slightly higher $\overline{K}_{oc}$ values in Table 5.15 for each sorbate. But if the fractional change in these $\overline{K}_{oc}$ values is assumed to be approximately the same for each sorbate, then the outcome of this change on the resulting correlations with S, $K_{ow}$, and $\alpha$ would be negligible.

In Section V.G., where it was attempted to measure various thermodynamic sorption properties, $K_d$ values were determined at three different temperatures. If the 20°C $K_d$ values for the MS do not represent equilibrium, then one would expect the 2°C $K_d$ value to be even further from equilibrium, and the 45°C value to be closer to equilibrium, since sorption kinetics increases with increasing temperature. Examination of Table 5.18 shows that this does not hold true for $CHCl_3$ and $CCl_4$; but does for $C_2HCl_3$ and $C_2Cl_4$. (In fact, the $K_d$ values for $C_2HCl_3$ were also determined for 7°C and 50°C, which also fit the trend.) Therefore, lack of attainment of true equilibrium for the MS <u>may</u> have resulted in this observed $K_d$ trend for $C_2HCl_3$ and $C_2Cl_4$. (These two cases were, in fact, the only ones where $K_d$ clearly increased with temperature.) On the other hand, it is not known why this trend was not observed for $CHCl_3$ and $CCl_4$. Nevertheless, if the anomalous trend in $K_d$ with temperature for the MS-$C_2HCl_3$ and MS-$C_2Cl_4$ systems is attributed to sorption kinetics, then it would result in measuring a higher (more positive) than actual $\Delta H^o$ (and $\Delta S^o$) value for this sorbent. This, of course, would also have the effect of computing a slightly higher than actual $\Delta\overline{H}^o$ (and $\Delta\overline{S}^o$) values for these sorbates.

The mineral soil was also used in Section V.I. to test the effects of pH and I on sorption. However, the variation of pH and I in these experiments should have had negligible influence on sorption rate.

Also, the results of these tests were not dependent on achieving equilibrium. That is, the effect of pH and $I$ would be detectable without achieving complete equilibrium. Therefore, the impact of non-equilibrium for the mineral soil in these experiments is judged to be inconsequential.

# VI. FINDINGS AND CONCLUSIONS

The principal findings and conclusions of this research are:

1. The free energies and enthalpies of sorption for $CHCl_3$, $CCl_4$, $C_2HCl_3$, and $C_2Cl_4$, in dilute aqueous systems with soils or soil organic matter (SOM) components, were relatively low, and characteristic of weak physical sorption forces. The sorption free energies determined ranged from about -1 to -4 kcal/mol; the mean sorption enthalpies ranged from -1 to -2 kcal/mol; and the 95 percent confidence limits determined for the sorption enthalpies (for all compounds) were about -6 to +2 kcal/mol. Based on these results, sorption of these compounds via the chemisorption mechanism was ruled out.

2. Strong correlations were found between sorption distribution coefficients, $K_d$, and the fundamental molecular property of electronic polarizability, $\alpha$; but very poor correlations were found between the $K_d$ values and the compounds' dipole moments, $\mu$. This suggests that the following induction-type of intermolecular forces might be primarily responsible for the sorption of these compounds by soils and SOM components:

   a. London (dispersion) forces
   b. ion-induced dipole
   c. dipole-induced dipole*.

---

*The case in which the sorbate's dipole moment is the one being induced.

Although there was no experimental evidence to suggest the presence of the hydrophobic interaction, it could not be rejected on the basis of deductive reasoning, and therefore, should be considered a possible contributing mechanism.

3. The natural logarithm of the compounds' aqueous solubilities (S) was also found to be highly correlated with sorption strength ($K_d$), but the octanol-water partition coefficients ($K_{ow}$) were poorly correlated to $K_d$. However, there is no fundamental consequence of the high correlation between $K_d$ and S; whereas $\alpha$ appears in most of the fundamental equations defining intermolecular forces/energies, upon which all sorption phenomena depend. Furthermore, the solubilities for nonpolar or weakly polar solutes are in most cases controlled by their polarizabilities. (Indeed, $\alpha$ and S were shown to be significantly mutually correlated in this research.) Nevertheless, S would probably be the more useful compound property for prediction or estimation of sorptive strength (especially from an engineering standpoint) since these values are (generally) readily available. On the other hand, $\alpha$ values are not well publicized, and usually must be calculated.

4. The correlation of $K_d$ to fraction of organic carbon (in the sorbent) was only moderately high (R values ranged from 0.892 to 0.953). Also, the mean $K_{oc}$ values ($\overline{K}_{oc}$) determined for each sorbate were not very precise constants, suggesting that sorption of these compounds by soils and SOM components is not controlled solely by the sorbent organic carbon content. The $\overline{K}_{oc}$ values and their standard deviations were:

| $CHCl_3$ | $CCl_4$ | $C_2HCl_3$ | $C_2Cl_4$ |
|---|---|---|---|
| 56.3 ± 28 | 149 ± 110 | 183 ± 91 | 451 ± 166 |

5. The following regression equations were determined between the normalized sorption distribution coefficient, $K_{oc}$, and:

   a. the compound's octanol-water partition coefficient, $K_{ow}$

   $$\log K_{oc} = 0.930\ K_{ow} + 0.0019 \qquad (R = 0.786)$$

   b. the compound's aqueous solubility, S (mmol/l)

   $$\log K_{oc} = -0.468 \log S + 2.61 \qquad (R = -0.980)$$

   c. the compound's polarizability, $\alpha$ ($10^{-24}$ $cm^3$)

   $$\log K_{oc} = 0.0195\ \alpha - 0.295 \qquad (R = 0.974) \quad .$$

Although the correlation between $K_{oc}$ and $K_{ow}$ is rather poor, the regression equation itself agrees quite well with others reported in the literature.

6. These compounds appeared to have very little affinity for some of the common inorganic constituents of soils, yielding negligible adsorption ($|K_d| < 2$) onto the following clays and minerals:

   a. $Na^+$-montmorillonite
   b. $Ca^{+2}$-montmorillonite
   c. $Al^{+3}$-montmorillonite
   d. kaolinite
   e. $SiO_2$ (silica)

f. $Al(OH)_3$ or $\gamma$-$Al_2O_3 \cdot 3H_2O$ (gibbsite)
g. $Fe_2O_3$ (hematite)
h. $CaCO_3$ (calcite)
i. $MnO_2$ (pyrolusite)

In fact, there was some evidence to suggest that negative adsorption of these compounds was occurring with these solids. This possible negative adsorption was attributed to the very hydrophilic nature of these clay and mineral colloids in aqueous suspension. It was postulated that water molecules are so strongly attracted to their surfaces that a significant region (volume) surrounding each colloid is composed of virtually solute-free water (i.e., the solute is excluded from this region).

7. Experiments demonstrated that this negative adsorption (in 6. above) is apparently the cause of increased (equilibrium) gas-phase concentrations (characteristic of certain other organic compounds) in closed systems containing suspensions of various clays or minerals. The effect was originally believed to be caused by the influence of the clay or mineral colloids on the solute's activity coefficient (i.e., salting out); but the experiments performed herein seemed to reject this hypothesis.

8. Sorption experiments using a variety of "pure" organic chemicals to represent the different classes of soil organic matter showed that only humic acid, lignin, and graphite sorbed the chlorinated aliphatics with sufficient intensity to account for their sorption in real soils.

Therefore, it was postulated that the humic substances (with the possible exception of fulvic acid) and lignin are principally responsible for the sorption of these compounds by soils, since the occurrence of graphite (and other forms of elemental carbon) in soils is quite rare.

9. The sorption isotherms for these compounds were reasonably linear in the low concentration regime (i.e., an equilibrium solute concentration range from 0 to ∿ 200 μg/l), and was therefore modeled by the equation:

$$C_s = \frac{K_d C_\ell}{1000}$$

where $C_s$ is the sorption density (μg/g); $C_\ell$ is the equilibrium solute concentration (μg/l); $K_d$ is the sorption equilibrium distribution coefficient (quasi-dimensionless); and 1000 (g/l) is a factor inserted to make $K_d$ quasi-dimensionless (which is commonly done in the literature). The portions of the isotherms representing the high concentration regimes (i.e., equilibrium solute concentrations greater than 200 μg/l, and ranging up to as high as ∿ 80,000 μg/l in some cases) were generally curved slightly downward (i.e., toward the $C_\ell$-axis), but a few were virtually linear over the complete range.

10. The general order of affinity of the sorbates for the sorbents tested in this research was: $C_2Cl_4 > C_2HCl_3 \approx CCl_4 > CHCl_3$.

11. Sorption $K_d$ values for the lignin-$C_2Cl_4$ system were independent of lignin particle size and measured B.E.T. surface area. If sorption by lignin and the humic substances in "real" soils is similar (in

this respect) to their sorption in the pure form, then this provides evidence in support of the absorption (rather than adsorption) concept as the appropriate model for soil sorption of nonionic, organic compounds. However, for sorbates capable of free penetration of three-dimensional, polymeric organic sorbent structures, nearly the entire sorbent macromolecular structure would be accessible, making distinctions between ad- and absorption both impossible and--thankfully--irrelevant.

12. Variations in pH over the range normally encountered in soil solution (4 to 9) were found to have negligible effect upon the sorption of $C_2HCl_3$ by the mineral soil. However, for highly organic soils, pH may have the effect of reducing the solubility of certain organic matter components (such as humic acid and lignin), resulting in a higher apparent $K_d$ value.

13. Sorption of $C_2HCl_3$ by the mineral soil increased with increasing ionic strength. The $K_d$ values measured at 0.0, 0.1, and 1.0 mol/l (as KCl) ionic strength were 54.8, 64.3, and 81.8. The effect of $I$ on sorption was attributed to its influence on the solute activity coefficient.

14. The "solids concentration effect" (i.e., measuring higher $K_d$ values at lower sorbent concentrations, and vice versa) was observed for both the lignin and graphite sorbents (which were the only sorbents tested for this effect). For the case of lignin the effect appeared to be due--at least in part--to an increased amount of lignin in the supernatants of the reaction vials (following centrifugation) as the

lignin particle concentration increased. However, for the case of graphite, wherein the non-settling fraction of this sorbent was presumably removed, the effect was still evident. Therefore, no definite conclusions can be drawn regarding the cause of the solids concentration effect. Because of this effect, the $K_d$ values determined in this research are probably conditional, in that they depend on the concentration of solids employed in the experiment.

15. The nonsingular sorption and desorption isotherms, determined using the mineral soil for all sorbates, were shown to be caused by a very slow, but continuous sorption by this soil, beyond the four-day equilibration period employed. Such behavior could be characteristic of other mineral soils as well, and may explain the frequently-observed nonsingularity (hysteresis) for sorption and desorption isotherms reported in the literature.

# APPENDIX A

## ESTIMATE OF FRACTIONAL SURFACE COVERAGE FOR THE ISOTHERMS OF CHIOU _et_ _al_. (1979)

Chiou _et_ _al_. used a ("Willamette") silt loam in their sorption experiments. Although these authors did not report a specific surface area for this soil, Ahlrichs (1972) gave a range of 50 to 150 $m^2/g$ for silt loams. Therefore, 100 $m^2/g$ shall be assumed for the silt loam used by Chiou _et_ _al_. for purposes of these calculations. The sorbates used by Chiou _et_ _al_. are low molecular weight, halogenated, aliphatic compounds (except for one chlorinated aromatic). The sorbate used for purposes of this computation is 1,1,1-trichloroethane ($H_3C$-$CCl_3$), which Horvath (1982) reported as having a _total_ molecular surface area of 264 $Å^2$. It is assumed that the actual area which each $CH_3CCl_3$ molecule occupies on the surface of the solid is somewhat less than this, and 100 $Å^2$ is chosen as a "ballpark" figure. The mass of soil used in the reaction vessels was 5 g.* Lastly, the maximum sorption density represented by the $CH_3CCl_3$ isotherm was ∿900 μg/g. Using the above assumed, estimated, or known values, the fraction surface coverage (which I shall symbolize as $\theta_s$) can be calculated.

First, the total surface area available ($A_s$) on the 5 g of soil is:

---

*This figure, as well as the experimental procedures in general, were not reported in the article by Chiou _et_ _al_. Therefore, I mailed a request for these procedures to the authors, which they graciously sent to me. (The mass of sorbent used [5 g] was in this separate summary of the experimental procedures which I received.)

$$A_s = (5\text{ g})(100\text{ m}^2/\text{g}) = 500\text{ m}^2 \quad .$$

Second, the number of $CH_3CCl_3$ molecules required for complete monolayer coverage (i.e., $\theta_s = 1$) of this soil is:

$$\frac{(500\text{ m}^2)(10^{20}\text{ Å}^2/\text{m}^2)}{100\text{ Å}^2/\text{molecule}} = 5 \times 10^{20}\text{ molecules}$$

which corresponds to $8.3 \times 10^{-4}$ mole (= 830 μmol) of $CH_3CCl_3$. Now, the <u>actual</u> number of moles of the sorbate on the soil surface (at a sorption density of 900 μg/g) is:

$$\frac{(900\text{ μg/g})(5\text{ g})}{133.4\text{ μg/μmol}} = 33.7\text{ μmol}$$

where 133.4 μg/μmol is the molecular weight of $CH_3CCl_3$.

$$\therefore \quad \theta_s = \frac{33.7\text{ μmol}}{830\text{ μmol}} = 0.04\text{ or }4\% \quad .$$

Since ∿900 μg/g represents the maximum sorption density for all the isotherms reported by Chiou *et al*., and since the molecular surface areas and weights for all the sorbates used are *roughly* the same as for $CH_3CCl_3$, it is concluded that $\theta_s$ would be less than 5 percent for *all* the isotherms reported in their paper.

# APPENDIX B

# EARLY EXPERIMENTS USING THE GAS CHROMATOGRAPHIC HEADSPACE TECHNIQUE WITH STABLE COMPOUNDS

## Experimental Procedures

Several experiments were performed to test the adsorption of various (stable) chlorinated, aliphatic compounds onto montmorillonite clay (in the early stages of this research). The adsorbates examined were: $C_2HCl_3$ (TCE), $C_2Cl_4$ (PCE), $CH_2Cl_2$ (methylene chloride), and $C_2H_3Cl_3$ (1,1,1-trichloroethane). The montmorillonite clay was saturated with $Ca^{+2}$ ions (according to the procedures described in V.A.1. of this thesis) prior to the experiments. (The solids concentration, pH, and ionic strength of this particular batch of $Ca^{+2}$-montmorillonite were 13.4 g/l, 5.5, and $\sim 8.8 \times 10^{-4}$ M, respectively.)

Saturated stock solutions of each solute (i.e., adsorbate) were prepared by adding an excess amount of the pure compound to distilled water. These saturated stock solutions were contained in 120-ml serum vials, sealed with teflon-faced rubber septa and aluminum crimp-caps. Aqueous solute samples were removed by piercing the septa with a syringe needle, and withdrawing the desired volume of solution from the aqueous phase. These saturated stock solutions were maintained in a 20°C water bath to maintain a constant aqueous solubility for each solution. The aqueous solubilities for each of these compounds at 20°C (according to Horvath [1982]) are:

| Adsorbate | Solubility (mg/l) |
|---|---|
| $C_2HCl_3$ | 1100 |
| $C_2Cl_4$ | 150 |
| $CH_2Cl_2$ | 14000 |
| $C_2H_3Cl_3$* | 1550 |

These aqueous solubilities were used to determine the mass of solute withdrawn from a particular stock solution.

The reaction vessels used in these experiments consisted of 120-ml serum vials. The sorbent vials were filled with a certain volume of suspension (usually 50 ml), and the control vials received the same volume of distilled water. Each vial was then injected with either 10, 100, or 1000 μl from the aqueous phase of the appropriate saturated stock solution, then quickly capped and sealed (using teflon-faced rubber septa with aluminum crimp-caps). The vials were then mounted on a wrist-action shaker and equilibrated for a minimum of one day at room temperature (which varied from 20° to 24°C for the experiments reported herein). After equilibration, a 0.5 ml gas-phase sample was withdrawn using a 0.5 ml gas-tight syringe (Precision Sampling Corp.), and injected into a gas chromatograph (GC). The GC was a Varian Aerograph, Model 1440, with a flame ionization detector. The chromatographic column was stainless steel, 3 M by 0.32 cm, packed with 20% SP-2100/0.1% Carbowax 1500 on 100/120 Supelcoport (Supelco, Inc.). The column temperature was 100°C, and gas flow rates were as follows:

---

*Solubility is for the 1,1,1-isomer (i.e., $H_3C\text{-}CCl_3$).

| Gas | Flow Rate (ml/min) |
|---|---|
| $N_2$ (carrier gas) | 30 |
| $H_2$ | 30 |
| Air | 300 |

## Results

In the following table, the mean peak height responses ($\bar{\mathfrak{P}}$) for the replicate vials are given where applicable. (In addition, the value of the peak height ($\mathfrak{P}$) for *each* vial is actually the average from two injections into the GC.) Previous work by Lincoff (1983) showed that solute concentration ($C_\ell$) was directly proportional to $\mathfrak{P}$ for the concentration ranges used herein. The data of Table B.1 reveal negligible adsorption of $C_2HCl_3$ and $C_2Cl_4$ by the clay (which was later substantiated by the work with these compounds in radio-labeled form), and quite significant *negative* adsorption of $CH_3CCl_3$ and $CH_2Cl_2$.

An experiment was also performed using stable TCE, to test the effect of the clay suspension on the solute activity coefficient. That is, an alternative explanation for the greater peak height from the sorbent vial than the control vial is that perhaps the clay colloids in suspension are increasing the solute activity coefficient (also referred to as "salting out"). If this were the case, then spinning down the solids in the sorbent vials should eliminate (or at least significantly reduce) this (postulated) effect. Therefore, a set of four serum vials were each filled with 50 ml of the $Ca^{+2}$-montmorillonite suspension, then injected with 50 μl from the TCE-

TABLE B.1 Comparison of Gas Chromatographic Peak Heights ($\bar{P}$) Between Sorbent ($Ca^{+2}$-Montmorillonite) and Control Serum Vials, Using Various Adsorbates

| Adsorbate | Approximate Solute Concentration in the Control Vial[1] (mg/l) | Values of $\bar{P}$ (± S.D.) Sorbent | Control |
|---|---|---|---|
| | -- Experiment A[2] | | |
| $C_2HCl_3$ | 0.1 | 40 | 37 |
| | 10 | 64 | 65 |
| | -- Experiment B[2] -- | | |
| $CH_2Cl_2$ | 0.2 | 85.7 | 78.8 |
| | 2 | 97.7 | 90.9 |
| | 20 | 102.0 | 97.0 |
| | -- Experiment C[3] -- | | |
| $CH_3CCl_3$ | 2 | 65.2 (±0.85) | 51.5 (±5.5) |
| $C_2Cl_4$ | 0.2 | 80.8 (±2.9) | 82.3 (±4.7) |
| | -- Experiment D[4] -- | | |
| $CH_2Cl_2$ | 2 | 69.1 (±2.9) | 59.9 (±1.4) |

---

[1] Estimated from the volume of stock solution delivered to the vial, adsorbate aqueous solubility, and compound (i.e., adsorbate) partitioning into the serum vial headspace. (Henry's constants determined by Lincoff [1983] were used.)

[2] Values of $\bar{P}$ in these experiments are based on a single sorbent and single control vial for each concentration level.

[3] The $CH_3CCl_3$ $\bar{P}$ value is based on two replicate samples; and the $C_2Cl_4$ $\bar{P}$ value is based on three replicate samples; (for each of the sorbent and control vials).

[4] Value of $\bar{P}$ is based on six replicate samples for the sorbent vial and three replicate samples for the control vial.

saturated stock solution. (This resulted in an approximate TCE solute concentration [assuming negligible adsorption] of 0.7 mg/l.) After capping and sealing, the vials were then placed on a wrist-action shaker for 2 days. The serum vials were then placed in a 20°C water bath for 2 hours, centrifuged at ∿800 G* for 45 minutes, then returned to the 20°C water bath for 1 hour. The headspace samples of these centrifuged vials were then injected into the GC. The vials were then vigorously shaken to resuspend the settled clay, and returned to the 20°C water bath for 1 hour. (Vials were maintained at constant temperature during and between headspace samplings, in order to eliminate the effects of changing temperature upon the compound's gas-phase concentration. [That is, Henry's constant is very sensitive to changes in temperature.]) The vials were removed from the water bath, thoroughly shaken again, and samples of their headspace re-injected into the GC.

The resulting mean peak heights were 47.5 (± 1.54) for the centrifuged vials, and 48.2 (± 1.90) for the completely mixed vials (subsequent to centrifugation). Obviously, the null hypothesis that there is no difference between these means, cannot be rejected at the 95 percent confidence level. Therefore, this experiment (as well as a later experiment using $^{14}C\text{-}C_2HCl_3$) disproves the salting out hypothesis, leaving negative adsorption as the only viable explanation for some of the data in Table B.1.

---

*These serum vials were not centrifugable, and spinning them at higher G-forces frequently resulted in breakage.

# APPENDIX C

## HENRY'S CONSTANTS USED IN THIS RESEARCH AND A METHOD FOR DETERMINING THESE CONSTANTS WHEN USING RADIOLABELED COMPOUNDS

The dimensionless Henry's constants ($H_c$) for all compounds used in this research except $CCl_4$, are from the work of Lincoff and Gossett (1983). These researchers reported the following values of Henry's constants at 20°C, along with regression equations which define the temperature dependence of these constants:

| Compound | Henry's Constant at 20°C ($m^3$-atm/mol) | Temperature Dependence Regression Equation |
|---|---|---|
| $CHCl_3$ | 0.0033 | H = exp(8.553 - 4180/T) |
| $C_2HCl_3$ | 0.00764 | H = exp(11.94 - 4929/T) |
| $C_2Cl_4$ | 0.0130 | H = exp(13.12 - 5119/T) |
| $CH_2Cl_2$† | 0.00215 | H = exp(8.200 - 4191/T) |
| $CH_3CCl_3$† | 0.0132 | H = exp(10.21 - 4262/T) |

The dimensionless* Henry's constants ($H_c$) are obtained by dividing the above values by the quantity '$R_gT$', where $R_g$ is $82.05 \times 10^{-6}$ atm $m^3$/mol $^oK$. This operation results in the following $H_c$ values at 20°C:

---

† The experiments using these compounds (in my research) are reported only in Appendix B.

*The dimensionless Henry's constant is the more useful form in connection with this research, since it represents the ratio of gas-phase concentration to liquid-phase concentration for the compound (i.e., $H_c = C_g/C_\ell$).

| Compound | $H_c$ (20°C) |
|---|---|
| $CHCl_3$ | 0.139 |
| $C_2HCl_3$ | 0.318 |
| $C_2Cl_4$ | 0.541 |
| $CH_2Cl_2$ | 0.0936 |
| $CH_3CCl_3$ | 0.549 |

Also, for $CHCl_3$, $C_2HCl_3$, and $C_2Cl_4$, the $H_c$ values at 2° and 45°C were needed, since isotherms were also conducted at these temperatures. The regression equations given above were used to estimate these values, which are as follows:

| Compound | $H_c$ (2°C) | $H_c$ (45°C) |
|---|---|---|
| $CHCl_3$ | 0.0575 | 0.388 |
| $C_2HCl_3$ | 0.112 | 1.09 |
| $C_2Cl_4$ | 0.182 | 1.95 |

For the case of $CCl_4$, $H_c$ values at 2°, 20°, and 45°C were determined by experiment using labeled $CCl_4$. If two R.V.'s are filled with different amounts of distilled water, but injected with identical masses of $CCl_4$, then a mass balance on the two systems (equated through the equal compound mass term) ultimately yields the following equation, using the nomenclature of this research (refer to "List of Symbols" in Appendix G, if necessary).

$$H_c = \frac{\left[(X^o_{\ell,b}/X^o_{\ell,a})V_{\ell,b} - V_{\ell,a}\right]}{\left[V_{g,a} - (X^o_{\ell,b}/X^o_{\ell,a})V_{g,b}\right]} \tag{C-1}$$

where the "a" and "b" subscripts denote the values associated with vial "a" and vial "b", each containing a different volume of solution. Volumes of 2.5 and 4.5 were selected, and two replicates were run for each volume. Each R.V. received either 2.0 or 4.0 ml of DW, and was then injected with 0.5 ml from the low-level $^{14}C$-$CCl_4$ stock solution. The R.V.'s were then tumbled for a minimum of one day (Lincoff and Gossett [1983] demonstrated that this was sufficient time to achieve gas-liquid equilibrium for these types of compounds). The values applicable to Equation (C-1) which were obtained in this experimental determination of $H_c$ for $CCl_4$ at 20°C, are summarized below:

$X^o_{\ell,a}$ = 3198 (± 8) DPM/ml ; $V_{\ell,a}$ = 2.5 ml ; $V_{g,a}$ = 3.9 ml

$X^o_{\ell,b}$ = 3249 (±29) DPM/ml ; $V_{\ell,b}$ = 4.5 ml ; $V_{g,b}$ = 1.9 ml .

Substitution of these values into Equation (C-1) results in $H_c(20°C) = 1.05$. Identical experiments performed at 2° and 45°C yielded the $H_c$ values for $CCl_4$ of 0.368 and 1.78, respectively.

Using the above technique, values of $H_c$ at 20°C for $CHCl_3$, $C_2HCl_3$, and $C_2Cl_4$ were also determined, and found to be 0.180, 0.277, and 0.478. These values compare reasonably well with the corresponding $H_c$ values from Lincoff and Gossett (1983), given previously.

In the experiment of Section V.I.2. of this thesis, there was a need to know the value of the "effective" Henry's constant at various ionic strengths ($I$). The effective Henry's constant is simply $\gamma_X H_c$, where $\gamma_X$ is the activity coefficient of the solute, X. The values for

$\gamma_{TCE}$ as a function $I$ (as moles/l KCl) were determined by Gossett and Lincoff (1981), who found that the following equation satisfactorily modeled this function:

$$\log_{10} \gamma_{TCE} \approx 0.21 \, I \tag{C-2}$$

where 0.21 is referred to as the salting-out coefficient (which is a function of the type of salt used). Using Equation (C-2), the values of $\gamma_{TCE}$ corresponding to $I$ values of 0.1 and 1.0 M, are 1.05 and 1.62, respectively. Therefore, the effective $H_c$ values for TCE at 20°C, corresponding to $I$ values of 0.1 and 1.0 M, are 0.334 and 0.516, respectively.

# APPENDIX D

## SORBATE LOSSES FROM THE REACTION VIALS AND DETERMINATION OF PROBABLE CAUSE

The sorption kinetics experiments performed in this research revealed that the sorbate "activity" (i.e., DPM/ml) in the control reaction vials (R.V.'s) (and presumably, the sorbent R.V's*) would decrease slightly with time. The quantity (mass) lost seemed to be proportional to solute concentration, and was also characteristic of the sorbate. The loss-rate for each sorbate decreased in the following order: $C_2Cl_4 > C_2HCl_3 > CCl_4 > CHCl_3$. (It is interesting to note that this was also the general order of decreasing sorptive strength for many of the sorbents examined in this research.)

Figures D.1 through D.3 illustrate arithmetic plots of control R.V. solute activity (DPM/ml) versus time for all of the kinetic-type experiments (T = 20°C) conducted in this research. If loss rate, defined as $dX_\ell^o/dt$ (i.e., the instantaneous slopes of the curves in these figures), is proportional to instantaneous solute concentration, then:

$$\frac{dX_\ell^o}{dt} \propto X_\ell^o \qquad \text{or}$$

$$\frac{dX_\ell^o}{dt} = -kX_\ell^o \tag{D-1}$$

---

*Obviously, losses from the sorbent R.V.'s could not be measured since they cannot be distinguished from sorbate removal by sorption.

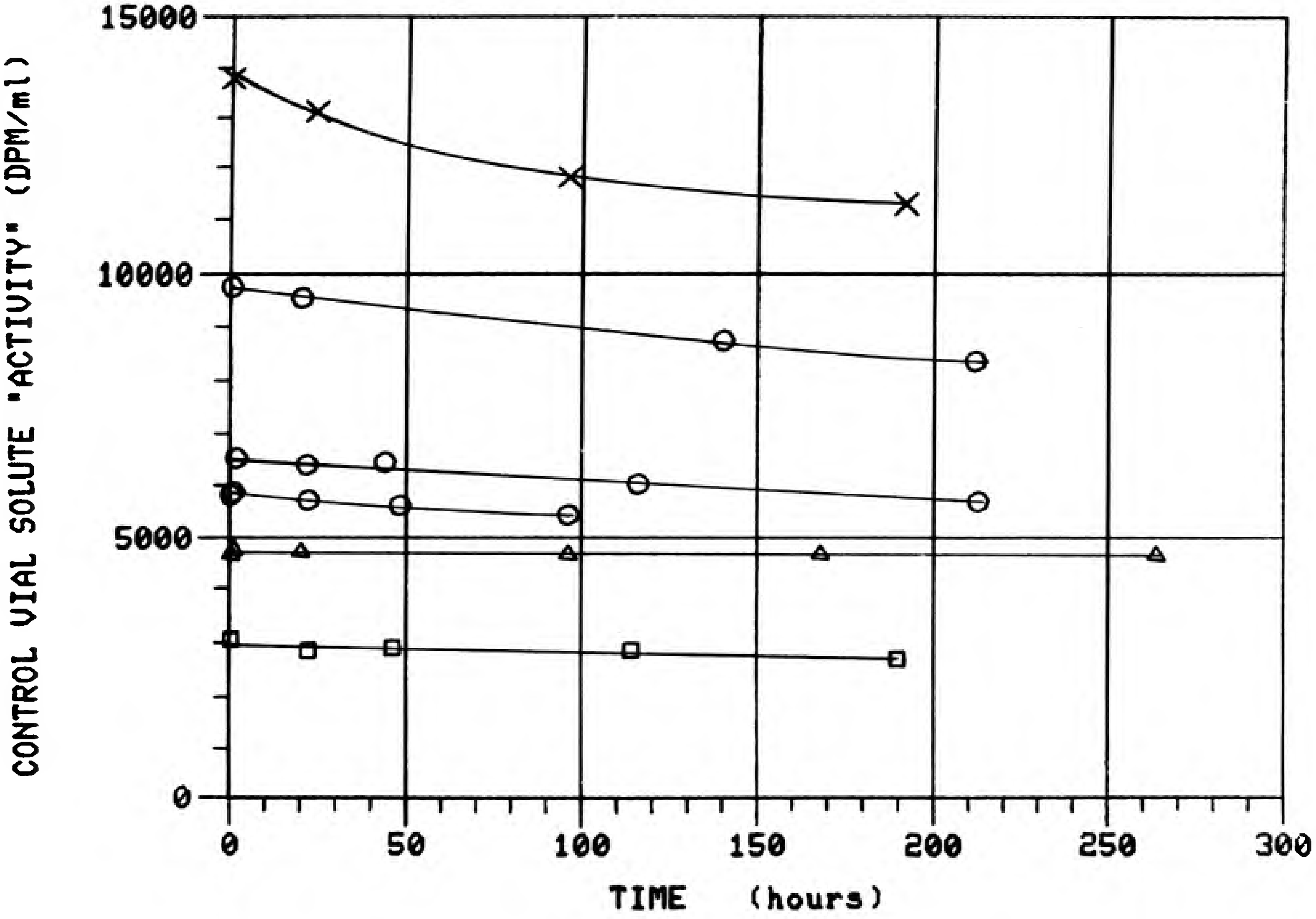

FIGURE D.1 Arithmetic Plots of Control Vial Solute "Activity" (i.e., Radioactivity Concentration, DPM/ml) Versus Time for $CHCl_3$ (△), $CCl_4$ (□), $C_2HCl_3$ (○), and $C_2Cl_4$ (x)

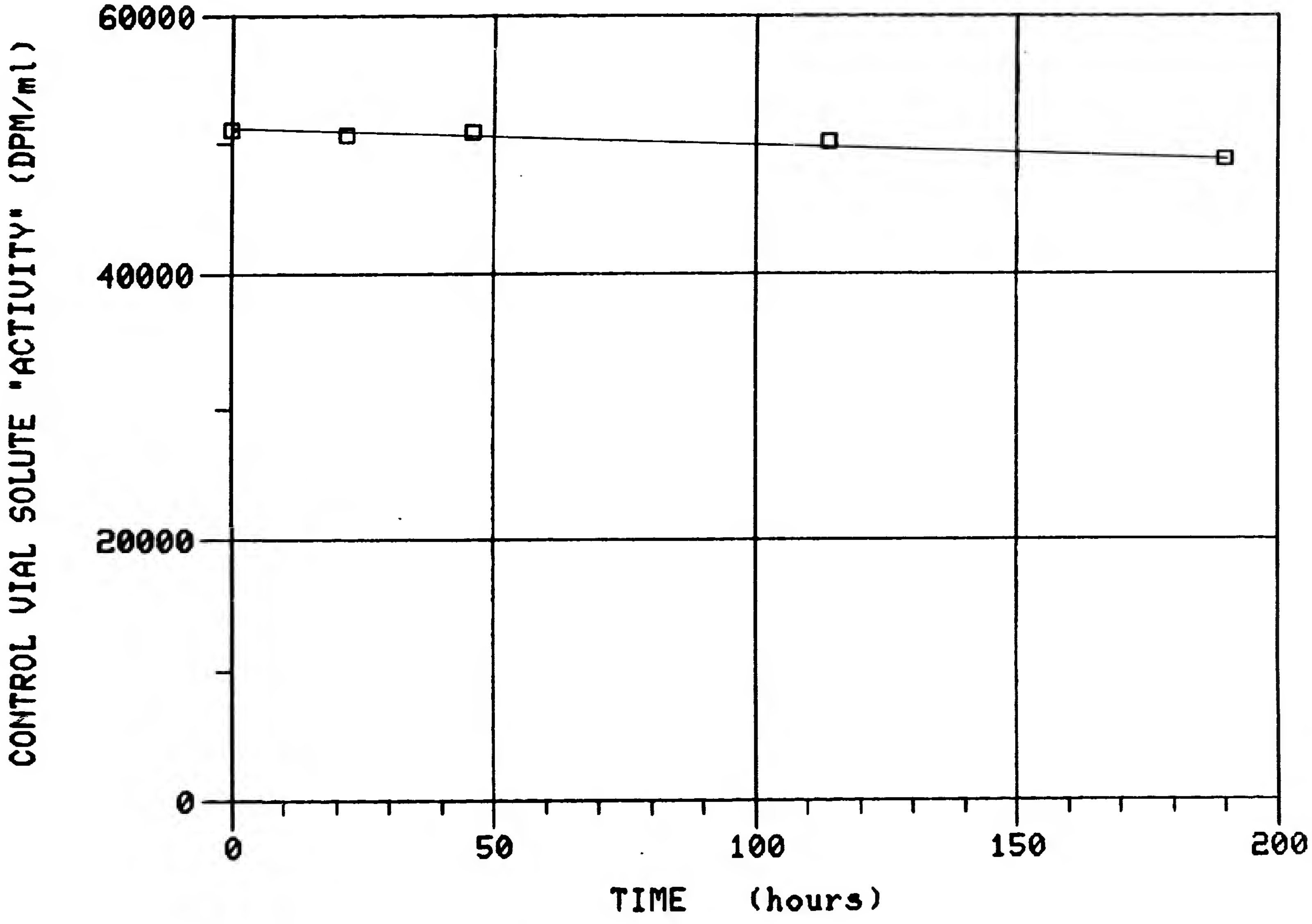

FIGURE D.2 Arithmetic Plot of $CCl_4$ Control Vial Solute "Activity" (DPM/ml) Versus Time

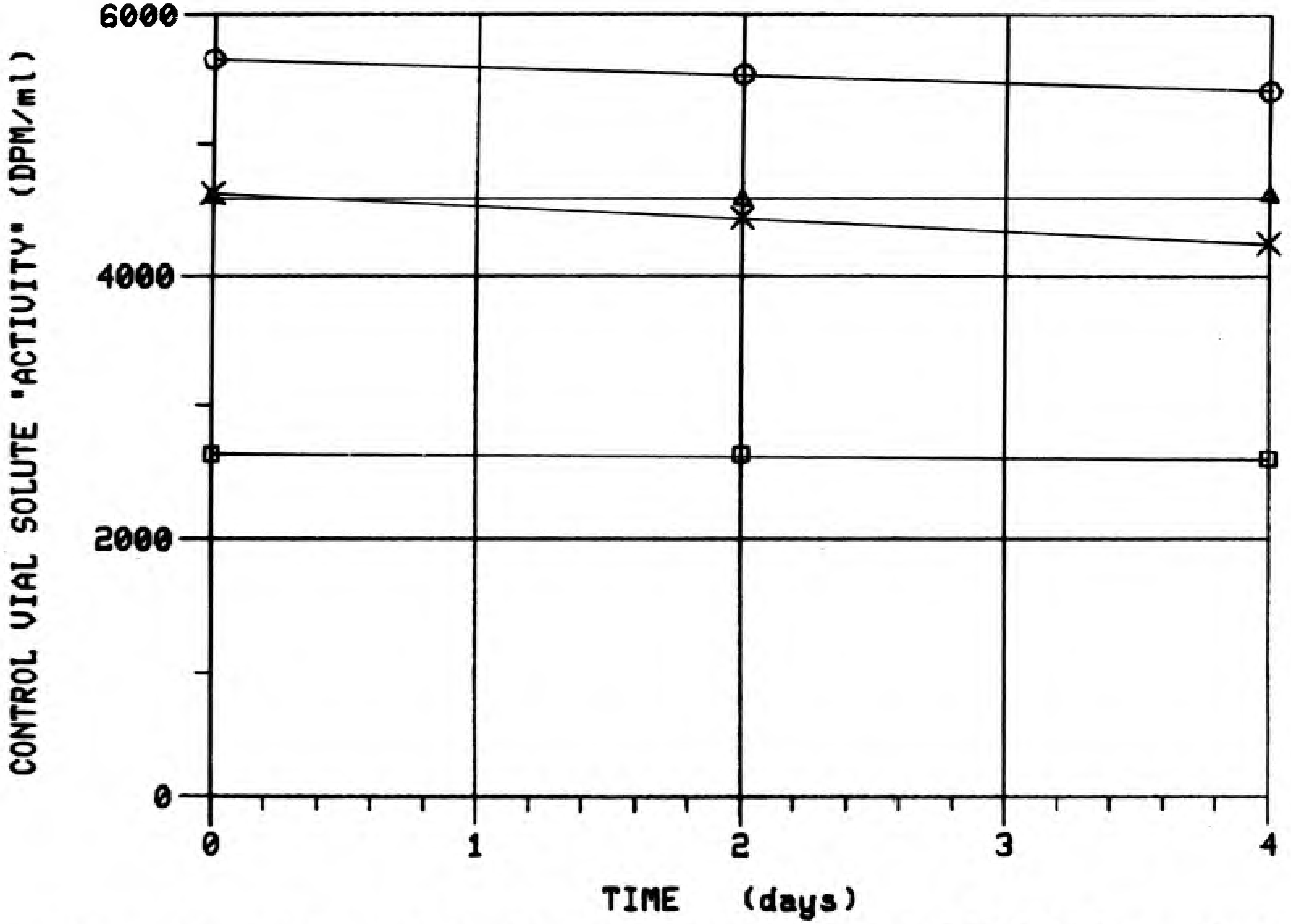

FIGURE D.3 Arithmetic Plots of Control Vial Solute "Activity" (DPM/ml) Versus Time for $CHCl_3$ (△), $CCl_4$ (□), $C_2HCl_3$ (○), and $C_2Cl_4$ (x) where k is a proportionality constant. Integration of Equation (D-1) yields:

$$\ln X_\ell^o + B = -kt \tag{D-2}$$

where B is the integration constant. Therefore, the plots of $\ln X_\ell^o$ versus t should be linear if loss rate is proportional to instantaneous solute concentration.

Figures D.4 and D.5 show the same data as in the previous graphs, except plotted as $\log X_\ell^o$ versus t.* The plots appear to be reasonably linear, which justifies the original assumption that loss rate is proportional to instantaneous solute concentration. This implies that the mechanism(s) causing sorbate mass loss is(are) probably a first-order reaction, which is not too surprising since the two mechanisms that could be causing sorbate losses--volatilization and/or sorption (by the vial itself) are frequently found to be first-order with respect to solute concentration.

Since the sorbate loss rate is approximately proportional to solute concentration, and the bulk of the sorption (by the sorbents used in this research) occurs relatively rapidly, the mass losses occurring from the sorbent R.V.'s are approximately proportional to their final solute concentrations. In the derivation of the sorption density ($C_s$) equation (Section IV.C.2.), it was shown that the correction factor, $X_\ell^i/X_\ell^o$,

---

*Since $\ln X_\ell^o = 2.303 \log X_\ell^o$, Equation (D-2) can also be expressed as:

$$\log X_\ell^o + B/2.303 = -(k/2.303)t \quad .$$

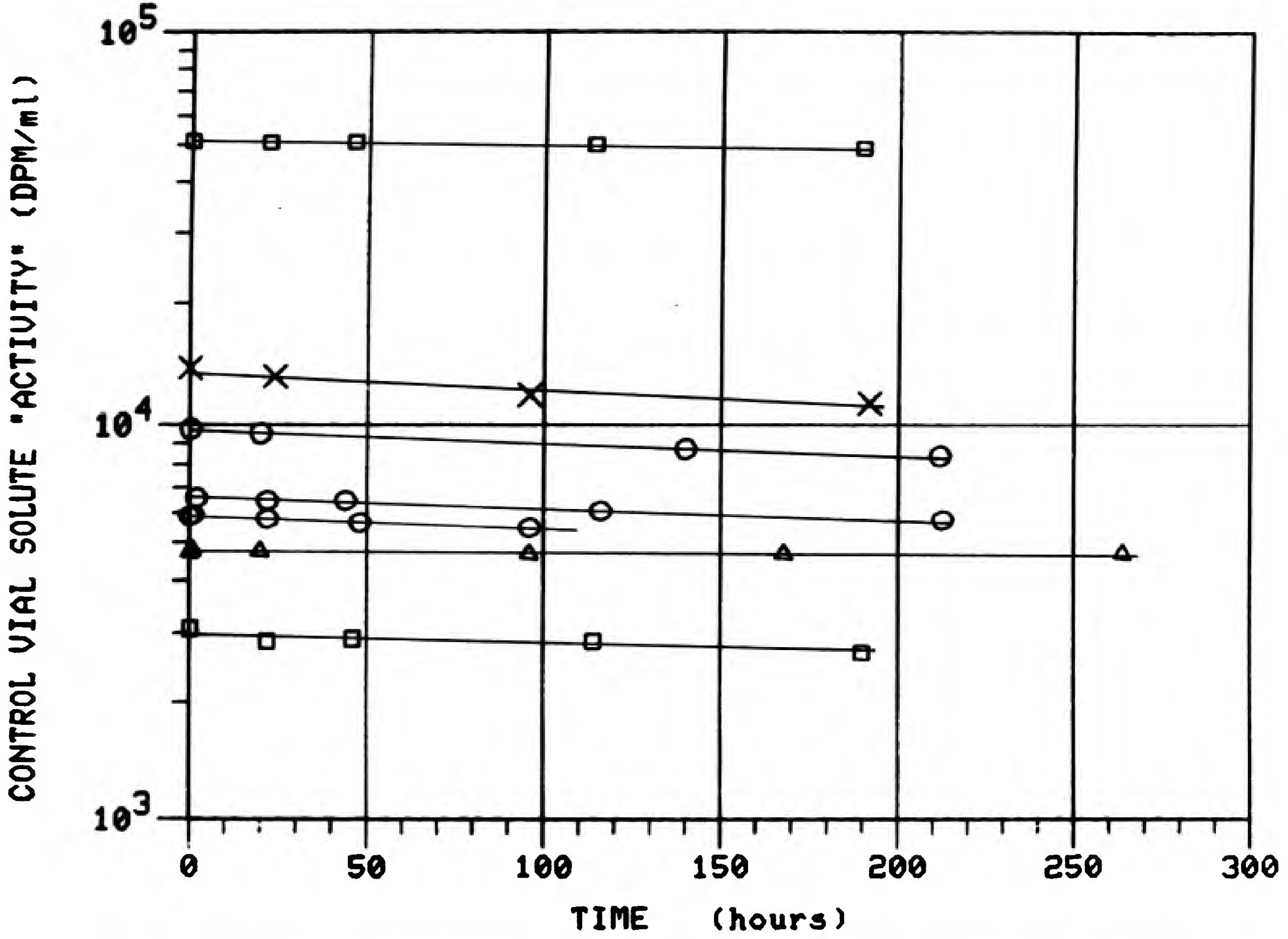

FIGURE D.4 Logarithmic Plots of Control Vial Solute "Activity" (DPM/ml) Versus Time for $CHCl_3$ (△), $CCl_4$ (□), $C_2HCl_3$ (○), and $C_2Cl_4$ (x)

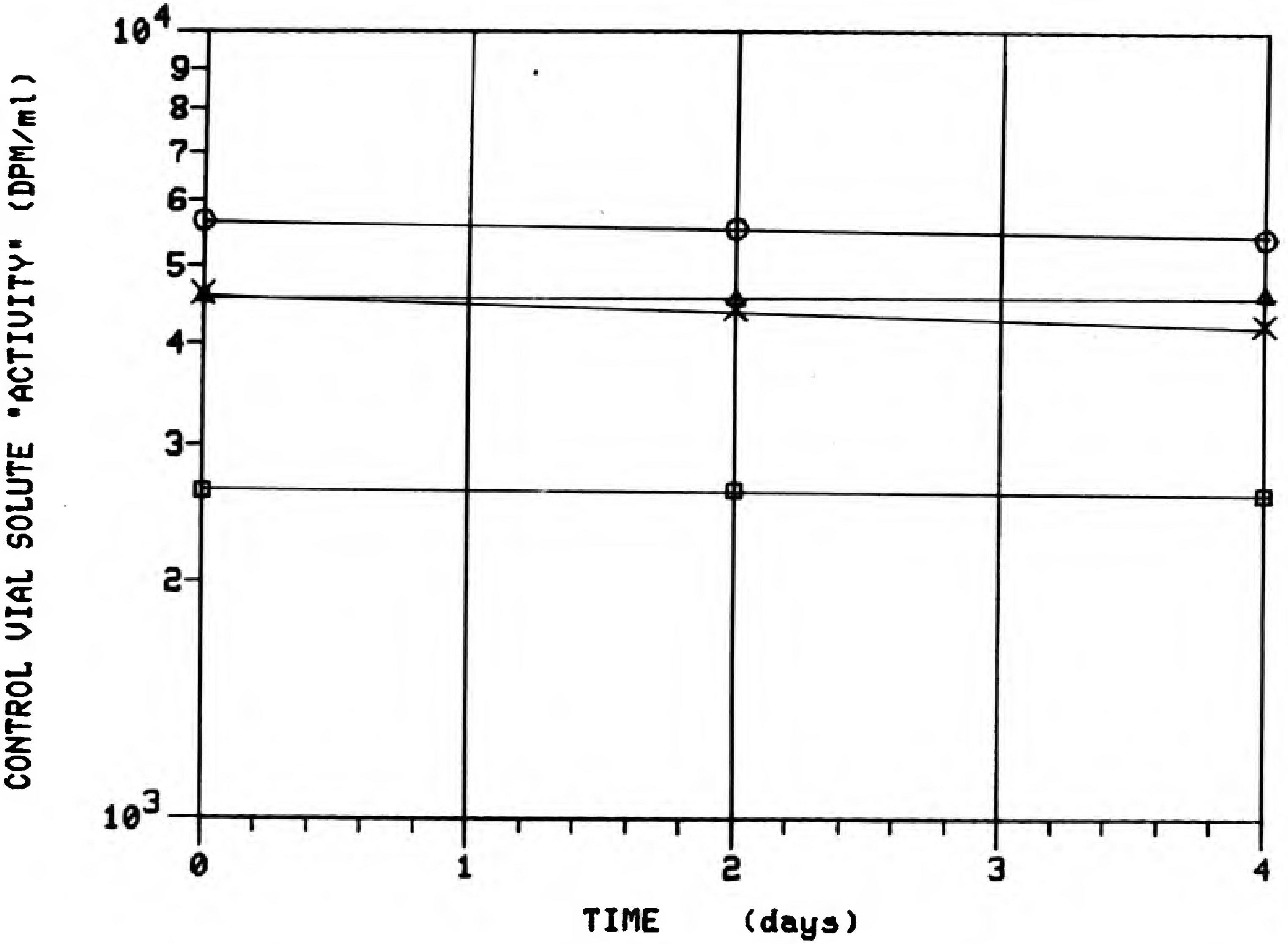

FIGURE D.5 Logarithmic Plots of Control Vial Solute "Activity" (DPM/ml) Versus Time for $CHCl_3$ (△), $CCl_4$ (□), $C_2HCl_3$ (○), and $C_2Cl_4$ (x) completely accounted for these losses, based on the above assumptions. The values for these loss correction factors for two- and four-day sorption experiments are given in Table D.1 (based on the data presented in Figure D.3).

TABLE D.1 Loss Correction Factors ($X_\ell^i/X_\ell^o$) for Each Sorbate for Two- and Four-day Sorption Experiments (T = 20°C)

| Sorbate | $(X_\ell^i/X_\ell^o)_{t_{eq}} = 2d$ | $(X_\ell^i/X_\ell^o)_{t_{eq}} = 4d$ |
|---|---|---|
| $CHCl_3$ | 1.000 | 1.000 |
| $CCl_4$ | 1.000 | 1.013 |
| $C_2HCl_3$ | 1.022 | 1.046 |
| $C_2Cl_4$ | 1.042 | 1.089 |

The loss correction factors were also required for the experiments performed at 2° and 45°C. These factors were determined to range from approximately unity for all sorbates at 2°C, to 2.125 for $C_2Cl_4$ at 45°C (in the 4-d experiment). Thus, the loss rates were strongly temperature-dependent.

I was also interested in finding the cause of these sorbate mass losses. Two mechanisms were postulated:

(1) compound volatilization from the R.V.; and

(2) compound sorption by the R.V. itself.

It would be very difficult to "prove" mechanism (1) experimentally, whereas mechanism (2) could be tested fairly easily. I decided that if mechanism (2) was ruled out as the cause of these losses, then mechanism (1) must be responsible by implication.

Therefore, an experiment was set up, first to determine whether sorption of these compounds occurred onto the glass walls of the R.V.'s. For this test, a previously-broken R.V. was thoroughly washed with distilled water, then ground into "sand-sized" particles using a mortar and pestle. These grindings were then thoroughly washed with distilled water (DW), then oven-dried (103°C for 60 minutes). Two sorbent R.V.'s were created, one containing 0.175 g of the ground glass, the other containing 0.350 g. To ensure that this glass had no residual background count (from its prior usage in experiments), two background control R.V.'s were also employed, one containing 0.178 g, and the other 0.353 g of the ground glass. Also, two regular control R.V.'s were utilized. Each R.V. received 5.0 ml of DW and 0.5 ml from the low-level $^{14}C$-$C_2Cl_4$ stock solution (except for the background controls which <u>only</u> received DW). (Tetrachloroethylene was selected as the sorbate since its loss rate was consistently higher than that of the other compounds.) All R.V.'s were tumbled for 4d at 20°C. Other procedures are as described in Chapter IV.

The results of this experiment are shown below, from which it can be concluded that sorption of these compounds by the glass walls of the R.V.'s is negligible.

The next step was to test for sorption of these compounds by the teflon$^{TM}$ lining of the rubber septa (since this is the only other

| R.V. Type | Mass of Ground Glass (g) | $X_\ell^o$ or $X_\ell$ (DPM/ml) |
|---|---|---|
| Control | 0 | 4458 (± 2) |
| Sorbent<br>(ground glass) | 0.175<br>0.350 | 4356<br>4349 |
| Background<br>Control | 0.178<br>0.353 | $\sim$ 0<br>$\sim$ 0 |

material which comes into contact with the solution). It was initially desired to peel off this teflon$^{TM}$ lining from several septa, and use it directly as the sorbent. However, I was concerned that if any sorption was observed, it could be attributed to the glue or tiny fragments of rubber adhering to this lining. Therefore, I decided to use "pure" teflon$^{TM}$ as the sorbent in these experiments. There are several types of teflon$^{TM}$, and the one used as the lining for the rubber septa (used throughout this research) is type "PTFE" (which stands for polytetrafluoroethylene, $[C_2F_4]_n$). Two sources of PTFE were used in these experiments: One consisted of the shavings (i.e., very small slivers) from a (new) teflon$^{TM}$-coated, magnetic stirring bar; the other was teflon$^{TM}$ tape, which was cut-up into many small pieces. Various amounts (masses) of each of these teflon$^{TM}$ sorbents were added to the sorbent R.V.'s, and three replicate control R.V.'s were run. Each R.V. received 5.0 ml DW and 0.5 ml from the LL $^{14}C$-$C_2Cl_4$ stock solution. All R.V.'s were tumbled for 4d at 20°C. (Other procedures used are described in Chapter IV.)

The results of the teflon$^{TM}$ sorption experiment are given below. These data demonstrate that PTFE-type teflon$^{TM}$ does indeed sorb significant amounts of $C_2Cl_4$. Therefore, although loss due to volatilization

| R.V. Type | Teflon$^{TM}$ Source* | Teflon$^{TM}$ Mass (g) | $X_\ell^o$ or $X_\ell$ (DPM/ml) | Percent Sorbed |
|---|---|---|---|---|
| Control | ---- | 0 | 4648 (± 8) | ---- |
| Sorbent | MSBS | 0.114 | 2052 | 57.9 |
| | MSBS | 0.116 | 1962 | 59.8 |
| | MSBS | 0.419 | 982 | 80.3 |
| | TT | 0.114 | 3937 | 16.4 |
| | TT | 0.114 | 3868 | 18.0 |
| | TT | 0.306 | 3176 | 33.5 |

*MSBS ≡ magnetic stirring bar shavings
TT ≡ teflon$^{TM}$ tape.

cannot be ruled out, it appears that the losses of these compounds incurred in this research can be attributed primarily to sorption by this teflon$^{TM}$ lining.*

---

*One possible mechanism of this sorption is that the sorbate molecules become incorporated into the PTFE structure, or substitute themselves for TFE molecules. This would not be too surprising since the structure of tetrafluoroethylene is very similar to that of tetrachloroethylene and trichloroethylene (to a lesser extent), and could explain why these two sorbates typically exhibited the highest loss rates.

# APPENDIX E

## DERIVATION OF DESORPTION EQUATION USED TO CALCULATE THE SOLUTE'S SORPTION DENSITY (AT THE CONCLUSION OF THE DESORPTION EXPERIMENT)

Symbols used in this derivation are defined as follows:

$R_T$, $R_T^o$ ≡ radioactivity initially delivered to sorbent and control reaction vials, respectively, at the beginning of the <u>sorption</u> experiment (DPM);

$V_\ell$ ≡ liquid volume in each vial (ml);

$H_c$ ≡ dimensionless Henry's constant;

$M_s$ ≡ mass of solid (sorbent) (g);

6.4 ≡ total volume of each vial (ml);

$X_\ell$, $X_\ell^o$ ≡ radioactivity concentration in the liquid phases of the sorbent and control reaction vial (R.V.'s), respectively (DPM/ml);

$X_\ell^i$ ≡ radioactivity concentration in the liquid phase of the "initial" control vial, measured at the beginning of the sorption experiment (DPM/ml);

$X_s$ ≡ radioactivity density on the solid (sorbent) (DPM/g);

$R_L$, $R_L^o$ ≡ radioactivity ($\propto$ mass) losses from the sorbent and control R.V.'s, respectively (DPM).

All "primed" variables represent those measured at the end of the desorption experiment; or, in the case of losses, those occurring <u>during</u> the desorption experiment (which includeslosses incurred upon opening and refilling the vial). The "non-primed" variables pertain to the previous sorption experiment.

A mass balance on the total radioactivity initially delivered to the sorbent and control R.V.'s (at the start of the sorption experiment), but applicable to the desorption experiment, is given below. Note that the 2 ml of supernatant removed from each R.V. at the end of the sorption experiment is accounted for by the terms $2X_\ell$ and $2X_\ell^o$:

$$R_T = M_s X_s' + V_\ell X_\ell' + (6.4-V_\ell)H_c X_\ell' + 2X_\ell + R_L + R_L'$$

$$R_T^o = V_\ell X_\ell^{o'} + (6.4-V_\ell)H_c X_\ell^{o'} + 2X_\ell^o + R_L^o + R_L^{o'} \quad .$$

Again, equating $R_T$ and $R_T^o$ (since the quantity of radioactivity delivered to each R.V. in the set defining a given isotherm data point is the same), yields:

$$M_s X_s' + V^* X_\ell' + 2X_\ell + R_L + R_L' = V^* X_\ell^{o'} + 2X_\ell^o + R_L^o + R_L^{o'}$$

where $V^* = [V_\ell + (6.4-V_\ell)H_c]$. Solving for $X_s'$ yields:

$$X_s' = \frac{(X_\ell^{o'} - X_\ell')V^* + 2(X_\ell^o - X_\ell) + (R_L^o - R_L) + (R_L^{o'} - R_L')}{M_s} \quad .$$

The expressions for $R_L$ and $R_L^o$ were derived previously for the sorption equation, and the quantity $R_L^o - R_L$ is thus given by:

$$R_L^o - R_L = (X_\ell^i - X_\ell^o)V^* - \frac{X_\ell}{X_\ell^o}(X_\ell^i - X_\ell^o)V^*$$

$$= \left\{X_\ell^i - X_\ell^o - \frac{X_\ell X_\ell^i}{X_\ell^o} + X_\ell\right\}V^* \quad .$$

Now, the radioactivity lost from the control R.V. during the desorption experiment (not including the 2 ml intentionally removed at the end of the sorption experiment) is given by:

$$R_L^{o\prime} = (X_\ell^o V^* - 2X_\ell^o) - X_\ell^{o\prime} V^* \quad .$$

Again, assuming losses proportional to solute concentration, losses from the sorbent R.V. may be expressed as:

$$R_L^{\prime} = \frac{X_\ell}{X_\ell^o} R_L^{o\prime} = X_\ell(V^* - 2) - \frac{X_\ell X_\ell^{o\prime}}{X_\ell^o} V^* \quad .$$

(An implicit assumption in this expression for $R_L^{\prime}$ is that the majority of mass loss occurs during opening of each vial, and the addition of 2 ml distilled water, prior to resealing. The experimental data generally support this assumption.) Substitution of these equations for $R_L^{\prime}$ and $R_L^{o\prime}$ into the above equation for $X_s^{\prime}$ yields:

$$X_s^{\prime} = \Bigg\{(X_\ell^{o\prime} - X_\ell^{\prime})V^* + 2(X_\ell^o - X_\ell) + \left(X_\ell^i - X_\ell^o - \frac{X_\ell X_\ell^i}{X_\ell^o} + X_\ell\right) V^* +$$

$$(X_\ell^o V^* - 2X_\ell^o - X_\ell^{o\prime} V^*) - \left[X_\ell(V^*-2) - \frac{X_\ell X_\ell^{o\prime}}{X_\ell^o} V^*\right]\Bigg\} \div M_s \quad .$$

This expression can be expanded, and many terms thus cancel out:

$$X'_s = \left( X^{o\prime}_\ell V^* - X'_\ell V^* + 2X^o_\ell - 2X_\ell + X^i_\ell V^* - X^o_\ell V^* - \frac{X_\ell X^i_\ell}{X^o_\ell} V^* + \right.$$

$$\left. X_\ell V^* + X^o_\ell V^* - 2X^o_\ell - X^{o\prime}_\ell V^* - X_\ell V^* + 2X_\ell + \frac{X_\ell X^{o\prime}_\ell}{X^o_\ell} \right) V^* \div M_s .$$

We are left with the following expression for [illegible]

$$X'_s = \frac{[X^i_\ell - X'_\ell + (X_\ell/X^o_\ell)(X^{o\prime}_\ell - X^i_\ell)]V^*}{M_s}$$

and

$$C'_s = \frac{(\mathrm{C.F.})[X^i_\ell - X'_\ell + (X_\ell/X^o_\ell)(X^{o\prime}_\ell - X^i_\ell)]V^*}{M_s}$$

where C.F. is the appropriate conversion factor (unique and constant for each radiolabeled compound) to convert units of DPM into units of mass.

# APPENDIX F

## ERROR PROPAGATION ANALYSIS OF THE SORPTION DISTRIBUTION COEFFICIENT, $K_d$

The values for $K_d$ were determined by two methods in this research: (1) For the case of a multi-point (Henry's law) isotherm, the $K_d$ value was equal to 1000-times* the slope of the least-squares regression line, forced through the origin; and (2) for the case of a single-point (Henry's law) isotherm, the value of $K_d$ was simply 1000-times the slope of the line from the origin to the data point (i.e., 1000 $C_s/C_\ell$). The uncertainty of $K_d$ associated with the former method (i.e., the multi-point isotherm) is simply (1000-times) the standard deviation of the slope regression coefficient.** However, the error in $K_d$ associated with the latter method must be calculated using error propagation analysis on the equation defining $K_d$. This analysis is presented below.

The equation defining $K_d$ for a single-point isotherm is given by 1000 $C_s/C_\ell$, or 1000-times Equation (4-13) divided by Equation (4-1), the result of which is given by Equation (F-1) below.

$$K_d = \frac{1000\ C_s}{C_\ell} = \frac{1000(\text{C.F.})(X_\ell^i/X_\ell^o)(X_\ell^o - X_\ell)[V_\ell + H_c(6.4 - V_\ell)]/M_s}{1000(\text{C.F.})\ X_\ell} \quad . \qquad \text{(F-1)}$$

---

*As stated previously in this thesis, the factor of 1000 (ppb/ppm) was employed so that $K_d$ would be a "quasi-dimensionless" number.

**These $K_d$ values and their standard deviations were obtained using the "MINITAB" statistical computer program. The command 'NOCONSTANT' forced the least-squares, linear regression through the origin, thus eliminating the intercept coefficient.

Equation (F-1) simplifies to:

$$K_d = \frac{X_\ell^i(X_\ell^o - X_\ell)[V_\ell + H_c(6.4 - V_\ell)]}{X_\ell^o \, X_\ell \, M_s} \qquad \text{(F-2)}$$

or

$$K_d = \frac{X_\ell^i[V_\ell + H_c(6.4 - V_\ell)]}{X_\ell M_s} - \frac{X_\ell^i[V_\ell + H_c(6.4 - V_\ell)]}{X_\ell^o M_s} \quad . \qquad \text{(F-3)}$$

(Equation [F-3] is given since some of the partial derivatives which follow are simplified by using it.)

The general equation used to determine the propagation of errors in a function, Q, of several variables, x, y, z, ... [i.e., Q = f(x, y, z, ...)] is given by

$$\sigma_Q \cong \left[\left(\frac{\partial Q}{\partial x}\right)^2 \sigma_x^2 + \left(\frac{\partial Q}{\partial y}\right)^2 \sigma_y^2 + \left(\frac{\partial Q}{\partial z}\right)^2 \sigma_z^2 + \ldots\right]^{\frac{1}{2}} \qquad \text{(F-4)}$$

where the $\sigma_i^2$ represent the variances of the $i$th variable, and $\sigma_Q$ is the standard deviation of the dependent variable, Q. However, Equation (F-4) is only exact if the errors associated with the independent variables (x, y, z, ...) are <u>independent</u> and <u>random</u>. Unfortunately, the errors associated with the "independent variables" ($X_\ell^i$, $X_\ell^o$, $X_\ell$, $V_\ell$, $H_c$, 6.4, and $M_s$) in the $K_d$ expression are <u>not</u> independent. For example, errors in the values of $V_\ell$, $H_c$, 6.4, or $M_s$, can affect the errors in the values of $X_\ell^i$, $X_\ell^o$, or $X_\ell$. Therefore, an appropriate error propagation expression to use is (Taylor, 1982):

$$\sigma_Q \leq \left|\frac{\partial Q}{\partial x}\right|\sigma_x + \left|\frac{\partial Q}{\partial y}\right|\sigma_y + \left|\frac{\partial Q}{\partial z}\right|\sigma_z + \ldots \qquad \text{(F-5)}$$

where the $\sigma_i$ are the standard deviations of the $i$th variable. The value of $\sigma_Q$ given by Equation (F-5) represents the upper limit on the uncertainty (standard deviation) of Q, regardless of whether or not the errors in x, y, and z are independent (and whether or not they are normally distributed).

Equation (F-5), applied to the function for $K_d$, yields:

$$\sigma_{K_d} \leq \left|\frac{\partial K_d}{\partial X_\ell^i}\right| \sigma_{X_\ell^i} + \left|\frac{\partial K_d}{\partial X_\ell^o}\right| \sigma_{X_\ell^o} + \left|\frac{\partial K_d}{\partial X_\ell}\right| \sigma_{X_\ell} + \left|\frac{\partial K_d}{\partial V_\ell}\right| \sigma_{V_\ell} +$$

$$+ \left|\frac{\partial K_d}{\partial H_c}\right| \sigma_{H_c} + \left|\frac{\partial K_d}{\partial (6.4)}\right| \sigma_{(6.4)} + \left|\frac{\partial K_d}{\partial M_s}\right| \sigma_{M_s} \quad . \qquad \text{(F-6)}$$

A few subtleties regarding Equation (F-6) are noted. First, the value for $V_\ell$ is actually comprised of two separate measurements: the suspension volume (which shall be symbolized as $V_{susp}$), and the radiolabeled stock solution volume (which shall be symbolized as $V_x$). That is, $V_\ell = V_{susp} + V_x$. The application of Equation (F-4) to determine the error (variance) in $V_\ell$ yields $\sigma^2_{V_\ell} = \sigma^2_{V_{susp}} + \sigma^2_{V_x}$.* Second, the value for $M_s$ (solids mass) is actually the product of solids concentration (S.C.) and suspension volume $V_{susp}$. That is, $M_s = (S.C.)(V_{susp})$, and therefore,

$$\sigma^2_{M_s} = \left(\frac{\partial M_s}{\partial (S.C.)}\right)^2 \sigma^2_{S.C.} + \left(\frac{\partial M_s}{\partial V_{susp}}\right)^2 \sigma^2_{V_{susp}} \quad .^*$$

---

*Equation (F-4) can be utilized in these instances since errors in the independent variables are independent of each other.

Taking these partial derivatives yields: $\sigma^2_{M_s} = V^2_{susp}\sigma^2_{S.C.} + (S.C.)^2\sigma^2_{V_{susp}}$. Thus, the uncertainties in the measurements of $V_\ell$ and $M_s$ are each dependent on two other variables.

The seven partial derivatives of $K_d$ in Equation (F-6) were determined from Equations (F-2) or (F-3), and are given below:

$$\frac{\partial K_d}{\partial X^i_\ell} = \frac{(X^o_\ell - X_\ell)V^*}{X^o_\ell X_\ell M_s} \tag{F-7}$$

$$\frac{\partial K_d}{\partial X^o_\ell} = \frac{X^i_\ell V^*}{X^{o2}_\ell M_s} \tag{F-8}$$

$$\frac{\partial K_d}{\partial X_\ell} = -\frac{X^i_\ell V^*}{X^2_\ell M_s} \tag{F-9}$$

$$\frac{\partial K_d}{\partial V_\ell} = \frac{X^i_\ell(X^o_\ell - X_\ell)(1 - H_c)}{X^o_\ell X_\ell M_s} \tag{F-10}$$

$$\frac{\partial K_d}{\partial H_c} = \frac{X^i_\ell(X^o_\ell - X_\ell)(6.4 - V_\ell)}{X^o_\ell X_\ell M_s} \tag{F-11}$$

$$\frac{\partial K_d}{\partial (6.4)} = \frac{X^i_\ell(X^o_\ell - X_\ell)H_c}{X^o_\ell X_\ell M_s} \tag{F-12}$$

$$\frac{\partial K_d}{\partial M_s} = -\frac{X^i_\ell(X^o_\ell - X_\ell)V^*}{X^o_\ell X_\ell M^2_s} \tag{F-13}$$

where V* represents the term $[V_\ell + H_c(6.4 - V_\ell)]$.

In order to assess which terms in Equation (F-6) might be significant, and which might be negligible, the following "average" values for the variables were assumed, and their corresponding standard deviations (errors) were either measured, provided by the manufacturer (e.g., for the syringes and pipets), or estimated:

$X_\ell^i = 5500 \pm 110$ DPM/ml$^{(1)}$
$X_\ell^o = 5400 \pm 108$ DPM/ml$^{(1)}$
$X_\ell = 4000 \pm 80$ DPM/ml$^{(1)}$
$V_\ell = 5.5 \pm 0.0275$ ml$^{(2)}$
$H_c = 0.5 \pm 0.015^{(3)}$
$6.4 = 6.40 \pm 0.02$ ml$^{(4)}$
$M_s = 0.03 \pm 0.0003$ g$^{(5)}$

(NOTE: Please refer to next page for footnotes.)

The contribution of each source of error can now be estimated by substituting the above values into Equations (F-6) through (F-13). The following results are obtained:

| Error Term | | Error Value | Percent of Total Error |
|---|---|---|---|
| $\left\lvert\frac{\partial K_d}{\partial X_\ell^i}\right\rvert \sigma_{X_\ell^i}$ | = | 1.41 | 11.7% |
| $\left\lvert\frac{\partial K_d}{\partial X_\ell^o}\right\rvert \sigma_{X_\ell^o}$ | = | 4.04 | 33.5% |
| $\left\lvert\frac{\partial K_d}{\partial X_\ell}\right\rvert \sigma_{X_\ell}$ | = | 5.46 | 45.3% |
| $\left\lvert\frac{\partial K_d}{\partial V_\ell}\right\rvert \sigma_{V_\ell}$ | = | 0.163 | 1.35% |

---

(1) Based on a "typical" precision (i.e. coefficient of variation) of ±2.0%.

(2) Based on the manufacturer's reported precision for the pipet and syringes of ±0.5%.

(3) Based on an "average" precision value for measured Henry's constants of ±3%, reported by Lincoff (1983, refer to p. 93).

(4) Measured from a random sample of 10 R.V.'s.

(5) Estimated using the previously-derived expression: $\sigma_{M_s} = [V^2_{susp}\sigma^2_{S.C.} + (S.C.)^2\,\sigma^2_{V_{susp}}]^{\frac{1}{2}}$, where $V_{susp}$ = 5.0 ml, $\sigma_{V_{susp}}$ = 0.025 ml (from pipet precision of ±0.5%), S.C. = 0.03 g/5 ml = 0.006 g/ml, and $\sigma_{S.C.} = 3 \times 10^{-5}$ g/ml. (This is based on an assumed precision of ±0.5% for solids concentration--which is probably much higher than it actually is, since all aliquots were withdrawn from completely-mixed suspensions. That is, the suspensions were [theoretically, at least] isotropic with respect to solids concentration, and the removal of repeated, large-volume samples [i.e., relative to the size of a single sorbent particle--which 5.0 ml certainly is] should [theoretically] contain identical solids concentrations. Nevertheless, I decided to use a precision of ±0.5% for the S.C. variable so that a "worst-case" error would be represented.) Substitution of these values into the expression for $\sigma_{M_s}$ (given in this footnote) yields a value of $2.1 \times 10^{-4}$ g. However, I decided to round this up to $3 \times 10^{-4}$ g (= 0.0003 g), (which represents a precision of ±1% for the $M_s$ variable), to remain on the high side for the estimate of error. The numerous total solids tests performed in this research had coefficients of variation ranging from ±0.05% to 5.4%, with ±1% representing the approximate mode of this distribution. Therefore, the use of $\sigma_{M_s} = 0.01\,M_s$ is herein justified, and shall also be used in the error propagation analysis for the actual data obtained in this research.

| Error Term | | Error Value | Percent of Total Error |
|---|---|---|---|
| $\left\|\frac{\partial K_d}{\partial H_c}\right\| \sigma_{H_c}$ | = | 0.160 | 1.33% |
| $\left\|\frac{\partial K_d}{\partial (6.4)}\right\| \sigma_{6.4}$ | = | 0.119 | 0.987% |
| $\left\|\frac{\partial K_d}{\partial M_s}\right\| \sigma_{M_s}$ | = | 0.707 | 5.86% |
| Total Error | = | 12.06 | 100% |

As a matter of interest, the $K_d$ value which results from the above "average" values for the variables is 70.7, and $\sigma_{K_d} \leq 12.06$ (obtained by summing the above error values).

This analysis shows that (based on the values given above) only three of these variables are significant sources of error: $X_\ell^i$, $X_\ell^o$, and $X_\ell$. However, a sensitivity analysis (employing the full range of the variables encountered in this research), revealed that when the mass of solids gets below $\sim 0.025$ g, or when the precisions for the $X_\ell^i$, $X_\ell^o$, and $X_\ell$ variables are $< \pm 2\%$, this source of error (i.e., $M_s$) starts to become significant. (This is a result of the error term for $M_s$ being inversely proportional to $M_s^2$.) Therefore, the standard deviations of the single-point $K_d$ values include the error contributed by $M_s$ as well as by $X_\ell^i$, $X_\ell^o$, and $X_\ell$.

The issue now addressed is whether to use an expression of the form of Equation (F-4) or Equation (F-5) to assess the uncertainty in $K_d$. Since $\sigma_{X_\ell}$ is (theoretically) dependent on $\sigma_{M_s}$, the use of Equation

(F-4) would be justified only if this dependency is demonstrated to be statistically insignificant. One method of accomplishing this is to statistically compare the variance of a sample of $X_\ell^o$ data with the variance of a sample of $X_\ell$ data. Since $\sigma^2_{X_\ell^o}$ is completely independent of $\sigma^2_{M_s}$, if the variances of $X_\ell$ and $X_\ell^o$ are found to be statistically indistinguishable, then the influence of $\sigma_M$ on $\sigma_{X_\ell}$ must be insignificant. That is, if $\sigma_{X_\ell}$ is significantly dependent on $\sigma_{M_s}$, then this should cause the variance of the $X_\ell$ variable to be (significantly) greater than the $X_\ell^o$ variable.

To accomplish this comparison, a normal sorption experiment ($T = 20°C$; $t_{eq} = 4d$) was performed, except that 12 replicate sorbent, and 12 replicate control R.V.'s were run. (The mineral soil was used as the sorbent, with $CHCl_3$ as the sorbate.) The standard deviations for the 12 control and 12 sorbent R.V.'s were ±58 DPM/ml and ±80 DPM/ml, respectively. The F distribution was used to choose between the null hypothesis, that the population variances of $X_\ell^o$ and $X_\ell$ are the same, or the alternative hypothesis, that the population variance of $X_\ell$ is greater than that of $X_\ell^o$. Therefore, a one-tailed F-test (applicable to the ratio of variances) was used at the 95 percent confidence level, with 11 degrees of freedom in both the numerator and denominator. The result showed that the null hypothesis cannot be rejected. Therefore, it is concluded that errors associated with the $M_s$ variable have an insignificant effect on $X_\ell$. Thus, for all practical purposes, the four error-determining variables ($X_\ell^i$, $X_\ell^o$, $X_\ell$, and $M_s$)can be considered to have independent errors, and an expression of the form of Equation (F-4) can be used. This is quite fortunate since Equation (F-4) yields a definite value for the error in the dependent variable (e.g., $K_d$), whereas Equation (F-5) yields an upper limit to this error.

Equation (F-4) is recast below, using the variables of interest.

$$\sigma_{K_d} = \left[ \left(\frac{\partial K_d}{\partial X_\ell^i}\right)^2 \sigma^2_{X_\ell^i} + \left(\frac{\partial K_d}{\partial X_\ell^o}\right)^2 \sigma^2_{X_\ell^o} + \left(\frac{\partial K_d}{\partial X_\ell}\right)^2 \sigma^2_{X_\ell} + \left(\frac{\partial K_d}{\partial M_s}\right)^2 \sigma^2_{M_s} \right]^{\frac{1}{2}} \qquad \text{(F-14)}$$

Substituting in the appropriate partial derivatives, given by Equations (F-7), (F-8), (F-9), and (F-13), yields:

$$\sigma_{K_d} = \frac{V^*}{M} \left[ \frac{(X_\ell^o - X_\ell)^2}{X_\ell^{o2}\, X_\ell^2} \sigma^2_{X_\ell^i} + \frac{X_\ell^{i2}}{X_\ell^{o4}} \sigma^2_{X_\ell^o} + \frac{X_\ell^{i2}}{X_\ell^4} \sigma^2_{X_\ell} + \frac{X_\ell^{i2}(X_\ell^o - X_\ell)^2}{X_\ell^{o2}\, X_\ell^2\, M_s^3} \sigma^2_{M_s} \right]^{\frac{1}{2}} \qquad \text{(F-15)}$$

Equation (F-15) is used in this thesis to determine the uncertainty (standard deviation) in the single-point $K_d$ values. The application of Equation (F-15) to the "average" values of the variables given previously, results in a $\sigma_{K_d}$ of ±8.05. (Recall that $K_d$ for these "average" values was determined to be 70.7, and $\sigma_{K_d} \leq 12.06$ [based on Equation (F-6)].)

# APPENDIX G

## LIST OF SYMBOLS AND ABBREVIATIONS

### 1. Variables and Constants*

#### a. Roman Symbols

| | |
|---|---|
| $a_i$ | activity of species '$i$', or the activity of a solute in phase '$i$' |
| $C_i$ | concentration of a solute in phase '$i$' |
| $C_\ell$ | equilibrium solute concentration at the end of the sorption experiment |
| $C'_\ell$ | equilibrium solute concentration at the end of the desorption experiment |
| $C_s$ | sorption density at the end of the sorption experiment |
| $C'_s$ | sorption density at the end of the desorption experiment |
| $C_s^{max}$ | maximum possible sorption density for the case of monolayer coverage |
| $e$ | charge of electron (= $1.602 \times 10^{-19}$ C) |
| $\mathcal{E}$ | electric field intensity |
| $E(r)$ | interaction (potential) energy between two species (e.g., atoms, molecules, or particles) separated by distance r. |
| $\Delta\overline{E}_{vap}$ | molar heat of vaporization |

---

*Some of the variables listed here are given in the text with a bar over the top (e.g., $\Delta\overline{H}^o$, $\overline{X}_\ell$, and $\overline{X}_\ell^{CM}$). Unless otherwise noted, the bar designates the mean value for that particular variable.

| | |
|---|---|
| $f_{oc}$ | fraction of organic carbon |
| $f_{om}$ | fraction of organic matter |
| $G$ | acceleration due to gravity (= $9.8\ m/s^2$) |
| $\overline{G}$ | partial molar free energy, or chemical potential |
| $\Delta G^o$ | standard Gibb's free energy of sorption |
| $h$ | Planck's constant (= $6.63 \times 10^{-34}$ Js) |
| $\Delta H^o$ | standard enthalpy of sorption |
| $H_c$ | dimensionless Henry's constant |
| $\Delta H^o_{soln}$ | standard enthalpy of solution |
| $I$ | ionic strength |
| $k$ | used as a general proportionality constant |
| $k_B$ | Boltzmann constant (= $1.38 \times 10^{-23}\ J/^oK$) |
| $K$ | used as a general sorption equilibrium constant |
| $K_d$ | equilibrium sorption distribution coefficient |
| $K_{oc}$ | equilibrium sorption distribution coefficient normalized to fraction of organic carbon (i.e., $K_{oc} = K_d/f_{oc}$) |
| $K_{ow}$ | octanol-water partition coefficient |
| $K_p$ | equilibrium solvent extraction partition coefficient |
| $M$ | molecular weight |
| $M_s$ | mass of solid (sorbent) |
| $n$ | Freundlich exponent |
| $n_D$ | index of refraction |
| $P$ | parachor |
| $r$ | distance between two species (e.g., atoms, molecules, or particles) |
| $R$ | linear correlation coefficient |

| | |
|---|---|
| $R_g$ | universal gas constant (= $1.987 \times 10^{-3}$ kcal/mol $^oK$ or $82.05 \times 10^{-6}$ atm $m^3$/mol $^oK$) |
| $R_T$, $R_T^o$ | quantity of radioactivity delivered to the sorbent and control reaction vials, respectively |
| $R_L$, $R_L^o$ | quantity of radioactivity lost from the sorbent and control reaction vials, respectively, during the sorption experiment |
| $R_L'$, $R_L^{o'}$ | quantity of radioactivity lost from the sorbent and control reaction vials, respectively, during the desorption experiment |
| R.F. | retardation factor |
| S | aqueous solubility |
| $S_v$ | vacant site on the adsorbent |
| SX | sorbent-sorbate complex |
| $\Delta S^o$ | standard entropy of sorption |
| T | temperature |
| $t_{eq}$ | equilibration (i.e., tumbling) time |
| $\nu_w$ | interstitial pore water velocity |
| $\nu_s$ | apparent velocity of solute through soil |
| $V_g$, $V_g^o$ | gas volumes in the sorbent and control reaction vials, respectively |
| $V_\ell$, $V_\ell^o$ | liquid volumes in the sorbent and control reaction vials, respectively |
| $V_s$ | volume occupied by the solids |
| $V_w$ | volume occupied by the water |
| $V_\ell^\#$, $V_w^\#$ | liquid and water volumes, respectively, in the (hypothetical), corrected (for the volume occupied by the solids), sorbent reaction vial |

| | |
|---|---|
| $V^*$ | represents the (repetitive) term--$[V_\ell + (6.4-V_\ell)H_c]$ |
| $\bar{V}$ | molar volume |
| $\bar{V}_i$ | molar volume of species '$i$' |
| $\bar{V}_i^*$ | molar volume of species '$i$', corrected for non-ideal conditions |
| X | general symbol used to represent a solute |
| $X_g$, $X_g^o$ | concentration of radioactivity in the gas phases of the sorbent and control reaction vials, respectively |
| $X_\ell$, $X_\ell^o$ | concentration of radioactivity in the liquid phases of the sorbent and control reaction vials, respectively, at the end of the sorption experiment |
| $X_\ell^i$ | concentration of radioactivity in the liquid phase of the <u>initial</u> control vial |
| $X_s$ | density of radioactivity in (or on) the sorbent, at the end of the sorption experiment |
| $X_\ell'$, $X_\ell^{o'}$ | concentration of radioactivity in the liquid phases of the sorbent and control reaction vials, respectively, at the end of the desorption experiment |
| $X_s'$ | density of radioactivity in (or on) the sorbent at the end of the desorption experiment |
| $X_\ell^{CM}$,$X_\ell^{CM\#}$ | concentration of radioactivity in the completely-mixed, liquid phases of the sorbent, and corrected sorbent, reaction vials, respectively |
| z | ion valence |

### b. Greek Symbols

| | |
|---|---|
| $\alpha$ | electronic polarizability |
| $\gamma_i$ | activity coefficient of species '$i$', or the activity coefficient of a solute in phase '$i$' |
| $\gamma_i^*$ | solute activity coefficient in phase '$i$', corrected for the presence of a third component |
| $\delta$ | solubility parameter |
| $\varepsilon$ | permittivity of the medium |
| $\varepsilon_0$ | permittivity of a vacuum (= 8.854 x $10^{-12}$ $C^2$/ J m) |
| $\theta$ | angle between the dipole moment vector and an imaginary line connecting the two atoms or molecules |
| $\theta_s$ | fractional surface coverage of a sorbent |
| $\theta_w$ | volumetric water content |
| $\mu$ | dipole moment |
| $\mu_{ind}$ | induced dipole moment |
| $\nu_i$ | oscillating frequency of the $i$th electron-nucleus system |
| $\rho$ | density of soil organic matter |
| $\rho_B$ | bulk density of soil |
| $\rho_\ell$ | liquid density |
| $\rho_v$ | vapor density |
| $\sigma$ | surface tension |
| $\sigma_i$ | standard deviation of variable '$i$' |
| $\sigma_i^2$ | variance of variable '$i$' |
| $\phi$ | volume fraction of solute |
| $\phi_p$ | volume fraction of polymer |
| $\chi$ | Flory-Huggins interaction parameter |

## 2. Abbreviations

| | |
|---|---|
| API | American Petroleum Institute |
| B.E.T. | Brunauer, Emmett, Teller (authors who derived the B.E.T. isotherm model) |
| CEC | cation exchange capacity |
| C.F. | conversion factor |
| CI | confidence interval |
| CL | confidence level |
| CLF | coarse lignin fraction |
| CPM | counts per minute |
| CT | carbon tetrachloride |
| C.V. | coefficient of variation |
| DPM | disintegrations per minute |
| DW | distilled water |
| FLF | fine lignin fraction |
| GA | glutamic acid |
| GC | gas chromatograph |
| HA | humic acid |
| HI | hydrophobic interaction |
| HL | high level |
| LL | low level |
| LLE | liquid-liquid extraction |
| LSC | liquid scintillation counter (or counting) |
| MS | mineral soil |
| N.E.N. | New England Nuclear |
| O.C. | organic carbon |

| | |
|---|---|
| PAC | powdered activated carbon |
| PCE | tetrachloroethylene (perchloroethylene) |
| R.F. | retardation factor |
| rpm | revolutions per minute |
| R.V. | reaction vial |
| S.A. | specific activity |
| S.C. | solids concentration |
| S.D. | standard deviation |
| SOM | soil organic matter |
| SSA | specific surface area |
| S.V. | scintillation vial |
| TCE | trichloroethylene |
| TS | total solids |

# LIST OF REFERENCES

Adamson, A. W., Physical Chemistry of Surfaces (Fourth Edition), John Wiley & Sons, New York, 1982.

Ahlrichs, J. L., "The Soil Environment", In: Organic Chemicals in the Soil Environment, Marcel Dekker, Inc., New York, 1972.

Allison, L. E., "Organic Carbon", In Black, C. A. (Editor), Methods of Soil Analysis, Part 2, Amer. Soc. of Agron., Inc., 1965.

Atkins, P. W., Physical Chemistry, Oxford University Press, 1978.

Bailey, G. W. and White, J. L., "Review of Adsorption and Desorption of Organic Pesticides by Soil Colloids, with Implications Concerning Pesticide Bioactivity", J. Agric. Fed. Chem., 12, 324-332, 1964.

Ball, D. F., "Loss-on-Ignition as an Estimate of Organic Matter and Organic Carbon in Noncalcareous Soils", J. Soil Science, 15, 84-92, 1964.

Bear, F. E., Chemistry of the Soil (Second Edition), Reinhold Publishing Corp., New York, 1964.

Belfort, G. S., "Adsorption on Carbon: Theoretical Considerations", Environ. Sci. & Tech., 14, 910-914, 1980.

Bellar, T. A. and Lichtenberg, J. J., "Determining Volatile Organics at Microgram-per-Litre Levels by Gas Chromatography", Journal AWWA, 739-744, December 1974.

Ben Naim, A., Hydrophobic Interactions, Plenum Press, New York, 1980.

Berlow, P. P., Burton, D. J., and Routh, J. I., Introduction to the Chemistry of Life, Saunders College Publishing, 1982.

Birshtein, T. M., "Hydrophobic Interactions of Nonpolar Molecules", In: Water in Biological Systems, Edited by Kayushin, L. P. (Translated from Russian), Consultants Bureau, New York, 9-19, 1969.

Brady, N. C., The Nature and Properties of Soils (Eighth Edition), Macmillan Publishing Co., New York, 1974.

Braids, O. C. and Miller, R. H., "Fats, Waxes, and Resins in Soil", In: Soil Components, Volume 1, Edited by Gieseking, J. E., Springer-Verlag, New York, 1975.

Briggs, G. G., "A Simple Relationship Between Soil Sorption of Organic Chemicals and Their Octanol/Water Partition Coefficients", Proc. 7th Bri. Insecticide Fungicide Conf., 11, 475-478, 1973.

Brown, D. S. and Flagg, E. W., "Empirical Prediction of Organic Pollutant Sorption in Natural Sediments", J. Environ. Qual., 10, 382-386, 1981.

Burchill, S., Hayes, M.H.B. and Greenland, D. J., "Adsorption", In: The Chemistry of Soil Processes (Chapter 6), Edited by Greenland, D. J. and Hayes, M.H.B., John Wiley & Sons, Ltd., 221-401, 1981.

Butler, J. N., Ionic Equilibrium, Addison-Wesley Publishing Co., 1964.

Chen, Y. and Schnitzer, M., "Scanning Electron Microscopy of a Humic Acid and Its Metal and Clay Complexes", Soil Sci. Soc. Amer. J., 40, 682-686, 1976.

Chiou, C. T., Freed, V. H., Schmeddling, D. W., and Kohnert, R. L. "Partition Coefficient and Bioaccumulation of Selected Organic Chemicals", Environ. Sci. & Tech., 11, 475-478, 1977.

Chiou, C. T., Peters, L. J. and Freed, V. H., "A Physical Concept of Soil-Water Equilibria for Nonionic Organic Compounds", Science, 206, 831-832, 1979.

Chiou, C. T. and Schmeddling, D. W., "Partitioning of Organic Compounds in Octanol-Water Systems", Environ. Sci. & Tech., 16, 4-10, 1982.

Chiou, C. T., Porter, P. E., and Schmeddling, D. W. "Partition Equilibrium of Nonionic Organic Compounds Between Soil Organic Matter and Water", Environ. Sci. & Tech., 17, 227-231, 1983.

Chiou, C. T., Shoup, T. D., and Porter, P. E. "Mechanistic Roles of Soil Humus and Minerals in the Sorption of Nonionic Organic Compounds from Aqueous and Organic Solutions", Paper Submitted to Organic Geochemistry, 1984 (in press).

Chou, S. J., Fisher, B. W., and Griffin, R. A. "Aqueous Chemistry and Adsorption of Hexachlorocyclopentadiene by Earth Minerals", In: EPA-600/9-81-002b, 29-43, March, 1981.

Clark, A., The Theory of Adsorption and Catalysis, Academic Press, New York, 1970.

Council on Environmental Quality, Contamination of Ground Water by Toxic Organic Chemicals, CEQ, January, 1981.

Cox, J. L., "DDT Residues in Marine Phytoplankton: Increase from 1955 to 1969", Science, 170, 71-73, 1970.

Davies, B. E., "Loss-on-Ignition as an Estimate of Soil Organic Matter", Soil Sci. Soc. Am. Proc., 38, 150-151, 1974.

Dean, J. A., Editor, Lange's Handbook of Chemistry, 12th Edition, McGraw-Hill Book Co., 1979.

Dietz, E. A. and Singley, K. F., "Determination of Chlorinated Hydrocarbons in Water by Headspace Gas Chromatography", Analytical Chemistry, 51, 1809-1814, 1979.

Dilling, W. L., Tefertiller, N. B., and Kallos, G. J., "Evaporation Rates and Reactivities of Methylene Chloride, Chloroform, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and Other Chlorinated Compounds in Dilute Aqueous Solutions", Environ. Sci. & Tech., 9, 833-837, 1975.

Di Toro, D. M., Mahony, J. D., Kirchgraber, P. R., O'Byrne, A. L., Pasquale, L. R., and Piccirilli, D. C., "The Effects of Nonreversibility, Particle Concentration, and Ionic Strength on Heavy Metal Sorption", Manhattan College, New York, Unpublished Manuscript (as of October 1984) (June 1984).

Dixon, J. B. and Weed, S. B., Editors, Minerals in Soil Environments, Soil Science Society of America, 1977.

Drever, J. I., The Geochemistry of Natural Water, Prentice-Hall, Inc., 1982.

Drost-Hansen, W., Adv. Chem. Ser., 67, 70, 1967.

Duxbury, J. M., Professor, Agronomy Department, Cornell University, Ithaca, New York, personal communication or course notes, 1983.

EPA, "Treatment of Volatile Organic Compounds in Drinking Water", Report No. EPA-600/8-83-019, May 1983.

Eisenberg, D. and Kauzmann, W., The Structure and Properties of Water, Oxford University Press, 1969.

Federal Register, "National Revised Primary Drinking Water Regulations, Volatile Synthetic Organic Chemicals in Drinking Water", Volume 47, No. 43, p. 9350, March 4, 1982.

Flaig, W., Beutelspacher, H., and Rietz, E., "Chemical Composition and Physical Properties of Humic Substances", In: Soil Components, Volume 1, Edited by Gieseking, J. E., Springer-Verlag, New York, 1975.

Flory, P. J., Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.

Foster, R. J., Physical Geology (Second Edition), Merill Publishing Co., 1975.

Foth, H. D., Fundamentals of Soil Science, John Wiley & Sons, Inc., 1978.

Francis, C. W., "Adsorption of Polyvinylpyrrolidone on Reference Clay Minerals", *Soil Sci.*, *115*, 40-54, 1973.

Frank, H. S. and Evans, M. W., *J. Chem. Phys.*, *13*, 507, 1945.

Frank, H. S. and Quist, A. S., *J. Chem. Phys.*, *34*, 604, 1961.

Garbarini, D. R., M.S. Candidate, Cornell University, Ithaca, New York, personal communication, 1984.

Garbarini, D. R., *Sorption of Nonionic Volatile Organic Compounds: Headspace Analysis and Effect of the Nature of the Sorbent*, M.S. Thesis, Cornell University, Ithaca, New York, 1985.

Garbarini, D. R. and Lion, L. W., "Evaluation of Sorptive Partitioning of Nonionic Organic Pollutants in Closed Systems by Headspace Analysis", Submitted as a Note to *Environ. Sci. & Tech.*, 1984.

Giles, C. H., "Interpretation and Use of Sorption Isotherms", In: *Sorption and Transport Processes in Soils*, Society of Chemical Industry, London, 14-32, 1970.

Glaze, W. H., Rawley, R., Barleson, J. L., Mapel, D., and Scott, D. R., "Further Optimization of the Pentane Liquid-Liquid Extraction Method for the Analysis of Trace Organic Compounds in Water", In: *Advances in the Identification & Analysis of Organic Pollutants*, Edited by Keith, L. H., Ann Arbor Science, 1981.

Gossett, J. M. and Lincoff, A. H., "Solute-Gas Equilibria in Multi-Organic Aqueous Systems", Final Report to the Air Force Office of Scientific Research, November 30, 1981.

Gossett, J. M., Professor, Department of Environmental Engineering, Cornell University, Ithaca, New York, personal communication, 1984.

Graham-Bryce, I. J., "Adsorption of Disulfoton by Soil", *J. Sci. Fd. Agric.*, *18*, 72-77, 1967.

Green, R. E. and Obien, S. R., *Weed Sci.*, *17*, 514, 1969.

Greenland, D. J., "Interaction Between Clays and Organic Compounds in Soils. II. Adsorption of Soil Organic Compounds and Its Effects on Soil Properties", *Soils Fert.*, *28*, 521-532, 1965.

Greenland, D. J. and Oades, J. M., "Saccharides", In: *Soil Components*, Volume 1, Edited by Gieseking, J. E., Springer-Verlag, New York, 1975.

Grover, R. and Hance, R. J., *Soil Sci.*, *109*, 136, 1970.

Gschwend, P. M. and Wu, S., "On the Constancy of Sediment-Water Partition Coefficients of Hydrophobic Organic Pollutants", Submitted to Environ. Sci. & Tech., March, 1984.

Gurikov, Y. V., "Current State of the Problem of Water Structure", In: Water in Biological Systems, Edited by Kayushin, L. P. (Translated from Russian), Consultants Bureau, New York, 1-8, 1969.

Hamaker, J. W., Goring, C.A.I., and Youngson, C. R., In: Organic Pesticides in the Environment, Advs. in Chem., No. 60, 23, 1966.

Hamaker, J. W. and Thompson, J. M., "Adsorption", In: Organic Chemicals in the Soil Environment, Marcel Dekker, Inc., New York, 1972.

Hance, R. J., Weed Res., 5, 98-114, 1965.

Hance, R. J., Weed Res., 7, 29-36, 1967.

Harris, C. I. and Warren, G. F., Weeds, 12, 120-126, 1964.

Hausenbuiller, R. L., Soil Science (Second Edition), W. C. Brown Co., Publishers, Dubuque, Iowa, 1978.

Hawley, G. G., The Condensed Chemical Dictionary, 10th Edition, Van Nostrand Reinhold Co., 1981.

Hill, N. E., Vaughan, W. E., Price, A. H. and Davies, M., Dielectric Properties and Molecular Behaviour, Van Nostrand Reinhold Co., London, 1969.

Hilton, H. W. and Yuen, Q. H., "Adsorption of Several Pre-emergence Herbicides by Hawaiian Sugar Cane Soils", J. Agric. Fd. Chem., 11, 230-234, 1963.

Hiraizumi, Y., Takahashi, M., and Nishimura, H., "Adsorption of PCB onto Sea Bed Sediment, Marine Plankton, and Other Adsorbing Agents", Environ. Sci. & Tech., 13, 580-584, 1979.

Hirschfelder, J. O., In: Molecular Biophysics, Edited by Pullman, B. and Weissbluth, M., Academic Press, New York, 325-342, 1965.

Holum, J. R., Elements of General and Biological Chemistry (Second Edition), John Wiley & Sons, Inc., New York, 1968.

Horne, R. A., Marine Chemistry, John Wiley & Sons, Inc., New York, 1969.

Horvath, A. L., Halogenated Hydrocarbons (Solubility-Miscibility with Water), Marcell Dekker, Inc., New York, 1982.

Horzempa, L. M. and Di Toro, D. M., "The Extent of Reversibility of PCB Adsorption", Water Research, 17, 851-859, 1983.

Jones, M. M., Netterville, J. T., Johnston, D. O., and Wood J. L., Chemistry, Man and Society (Second Edition), W. B. Saunders, Co., 1976.

Junk G. A. and Richard J. J., "Anionic and Neutral Organic Components in Water by Anion Exchange", In: Advances in the Ident. & Anal. of Organic Pollutants in Water, Edited by Keith, L. H., Ann Arbor Science, 1981.

Karickhoff, S. W., Brown, D. S., and Scott, T. A., "Sorption of Hydrophobic Pollutants on Natural Sediments", Water Research, 13, 241-248, 1979.

Kauzmann, W., Advances in Protein Chemistry, 14, 1, 1959.

Khan, S. V., "The Interaction of Organic Matter with Pesticides", In: Soil Organic Matter, Edited by Schnitzer, M. and Khan, S. V., Elsevier Scientific Publishing Co., 137-171, 1978.

Kiselev, A. V., "Adsorption Properties of Hydrophobic Surfaces", In: Hydrophobic Surfaces, Edited by Fowkes, F. M., Academic Press, 88-100, 1969.

Kiselev, A. V., "Problems of Molecular Adsorption Chromatography", J. Chromatog., 49, 84-129, 1970.

Laidler, K. J. and Meiser, J. H., Physical Chemistry, Benjamin/Cummings Publishing Co., 1982.

Lambert, S. M., "Functional Relationship Between Sorption in Soil and Chemical Structure", J. Agric. Fd. Chem., 15, 572-576, 1976.

Langmuir, I., "The Adsorption of Gases on Plane Surfaces of Glass, Mica, and Platinum", J. Am. Chem. Soc., 40, 1361-1403, 1918.

Lincoff, A. H. and Gossett, J. M., "The Determination of Henry's Constant for Volatile Organics by Equilibrium Partitioning in Closed Systems", In: Gas Transfer at Water Surfaces, Edited by Brutsaert, W. and Gerhard, J. H., D. Reidel Publishing Co., 17-34, 1984.

Lincoff, A. H., The Determination of Henry's Constant for Volatile Compounds by Equilibrium Partitioning in Closed Systems, M.S. Thesis, Cornell University, Ithaca, New York, 1983.

Lion, L. W. and Garbarini, D., "Partitioning Equilibria of Volatile Pollutants in Three-Phase Systems", Final Report to the U.S. Air Force Engineering and Services Laboratory, Report No. ESL-TR-83-51, December 1983.

Love, O. T., Jr. and Eilers, R. G., "Treatment of Drinking Water Containing Trichloroethylene and Related Industrial Solvents", Journal AWWA, 413-425, August 1982.

Love, O. T., Jr., Miltner, R. J., Eilers, R. G., and Fronk-Leist, C. A., "Treatment of Volatile Organic Compounds in Drinking Water", EPA-600/8-83-019, May 1983.

Lundelius, E. F., "Adsorption and Solubility", Kolloid Z., 26, 145, 1920.

Lyman, W. J., Reehl, W. F., and Rosenblatt, D. H., Handbook of Chemical Property Estimation Methods, McGraw Hill Book Co., 1982.

MacIntyre, W. G. and Smith, C. L. (versus) Chiou, C. T., Porter, P. E., and Shoup, T. D., "Comment on 'Partition Equilibria of Nonionic Organic Compounds Between Soil Organic Matter and Water'", Environ. Sci. & Tech., 18, 295-297, 1984.

Maitland, G. C., Rigby, M., Smith, E. G., and Wakeham, W. A., Intermolecular Forces, Their Origin and Determination, Clarendon Press, Oxford, 1981.

Martin, D. F., Marine Chemistry, Volume 2, Marcel Dekker, Inc., New York, 1970.

Masterson, W. L. and Slowinski, E. J., Chemical Principles, W. B. Saunders Co., 1977.

McBride, M. B., Professor, Agronomy Department, Cornell University, Ithaca, New York, Course Notes, 1982.

McCabe, W. L. and Smith, J. C., Unit Operations of Chemical Engineering (Third Edition), McGraw Hill, Inc., 1976.

McClellan, A. L., Tables of Experimental Dipole Moments, Volume 1, W. H. Freeman, San Francisco, California, 1963.

McClellan, A. L., Tables of Experimental Dipole Moments, Volume 2, Rahara Enterprises, El Cerrito, California, 1974.

McConnell, G., Ferguson, D. M., and Pearson, C. R., "Chlorinated Hydrocarbons and the Environment", Endeavor, 34, 13-18, 1975.

McGlamery, M. D. and Slife, F. W., Weeds, 14, 237, 1966.

Means, J. C., Wood, S. G., Hassett, J. J., and Banwart, W. L., "Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils", Environ. Sci. & Tech., 14, 1524-1528, 1980.

Means, J. C. and Wijayaratne, R., "Role of Natural Colloids in the Transport of Hydrophobic Pollutants", Science, 215, 968-970, 1982.

Meislich, H., Nechamkin, H., and Sharefkin, J., Theory and Problems of Organic Chemistry, McGraw Hill Co., 1977.

Melander, W. and Horvath, C., "Thermodynamics of Hydrophobic Adsorption", In: Activated Carbon Adsorption of Organics from the Aqueous Phase, Volume 1, Edited by Suffet, I. H. and McGuire, M. J., Ann Arbor Science Publishers, 65-89, 1980.

Mitchell, J., "The Origin, Nature, and Importance of Soil Organic Constituents Having Base Exchange Properties", J. Am. Soc. Agron., 24, 256-275, 1932.

Munz, C. and Roberts, P. V., "Transfer of Volatile Organic Contaminants into a Gas Phase During Bubble Aeration", Technical Report No. 262, Department of Civil Engineering, Stanford University, January, 1982.

Nearpass, D. C., Soil Sci., 103, 177, 1967.

Nemethy, G. and Scheraga, H. A., J. Chem. Phys., 36, 3401, 1962.

O'Connor, D. J. and Connolly, J. P., "The Effect of Concentration of Adsorbing Solids on the Partition Coefficient", Water Research, 14, 1517-1523, 1980.

Osgerby, J. M., "Sorption of Un-Ionised Pesticides by Soils", In: Sorption and Transport Processes in Soils, Society of Chemical Industry, London, 63-78, 1970.

Parsons, J. W. and Tinsley, J., "Nitrogenous Substances", In: Soil Components, Volume 1, Edited by Gieseking, J. E., Springer-Verlag, New York, 1975.

Patterson, C. S., Kuper, H. S., and Nanney, T. R., Principles of Chemistry, Appleton Century Crofts, Meredith Publishing Co., 1967.

Peck, D. E., Corwin, D. L., and Farmer, W. J., "Adsorption-Desorption of Diuron by Freshwater Sediments", J. Environ. Qual., 9, 101-106, 1980.

Pfaender, F. K., "Evaluation of Direct Aqueous Injection Method for Analysis of Chloroform in Drinking Water", Environ. Sci. & Tech., 12, 432-441, 1978.

Pierce, R. H., Olney, C. E., and Felbeck, G. T., "pp'-DDT Adsorption to Suspended Particulate Matter in Seawater", Geochimica et Cosmochimica Acta, 38, 1061-1073, 1974.

Rao, P.S.C. and Davidson, J. M., "Estimation of Pesticide Retention and Transformation Parameters Required in Nonpoint Source Pollutant Models", In: Environ. Impact of Nonpoint Source Pollution, Ann Arbor Science, 1980.

Rhodes, J. W. and Nulton, C. P., "Microextraction as an Approach to Analysis for Priority Pollutants in Industrial Wastewater", In: Advances in the Identification and Analysis of Organic Pollutants in Water, Edited by Keith, L. H., Ann Arbor Science, 1981.

Richter, R. O., "Adsorption of Trichloroethylene by Soils from Dilute Aqueous Systems", Final Report to the U.S. Air Force Office of Scientific Research, Contract No. F49620-79-C-0038, August 1981.

Rogers, R. D., McFarlane, J. C., and Cross, A. J., "Adsorption and Desorption of Benzene in Two Soils and Montmorillonite Clay", Environ. Sci. & Tech., 14, 457-460, 1980.

Rogers, R. D. and McFarlane, J. C., "Sorption of Carbon Tetrachloride, Ethylene Dibromide, and Trichloroethylene on Soil and Clay", Environmental Monitoring and Assessment, 1, 155-162, 1981.

Russell, L. L., Chemical Aspects of Groundwater Recharge with Wastewaters, Ph.D. Thesis, University of California, Berkeley, December 1976.

Saha, J. G., Bharati, B., Lee, Y. W., and Randall, R. L., J. Agr. Food Chem., 17, 877, 1969.

Schnitzer, M. and Kodama, H., "Reactions of Minerals with Soil Humic Substances", In: Minerals in Soil Environments, Edited by Dixon, J. B. and Weed, S. B., Soil Science Society of America, 1977.

Schnitzer, M. and Khan, S. U., Soil Organic Matter, Elsevier Scientific Publishing Co., 1978.

Schwarzenbach, R. P. and Westall, J., "Transport of Nonpolar Organic Compounds from Surface Water to Groundwater. Laboratory Sorption Studies", Environ. Sci. & Tech., 15, 1360-1367, 1981.

Sekine, T. and Hasegawa, Y., Solvent Extraction Chemistry, Marcel Dekker Inc., 1977.

Sharom, M. S., Miles, J.R.W., Harris, C. R., and McEwen, F. L., "Behavior of 12 Insecticides in Soil and Aqueous Suspensions of Soil and Sediment", Water Research, 14, 1095-1100, 1980.

Sidorova, A. I., Khaloimov, A. I., and Zhukovskii, A. P., "Hydrophobic Bonding in Dilute Aqueous Nonelectrolyte Solutions", In: Water in Biological Systems (Translated from Russian), Consultants Bureau, New York, 1-4, 1971.

Sisler, H. H., VanderWerf, C. A., and Davidson, A. W., College Chemistry (Third Edition), Macmillan Co., 1967.

Snoeyink, V. L. and Jenkins, D., Water Chemistry, John Wiley & Sons, Inc., New York, 1980.

Stevenson, F. J., Humus Chemistry, John Wiley & Sons, Inc., New York, 1982.

Talbert, R. E. and Fletchall, O. H., Weeds, 13, 46, 1965.

Taylor, J. R., An Introduction to Error Analysis, University Science Books, 1982.

van Olphen, H., An Introduction to Clay Colloid Chemistry, Second Edition, John Wiley & Sons, Inc., New York, 1977.

Voice, T. C., Rice, C. P., and Weber, W. J., "Effect of Solids Concentration on the Sorptive Partitioning of Hydrophobic Pollutants in Aquatic Systems", Environ. Sci. & Tech., 17, 513-518, 1983.

Weast, R. C., Editor, Handbook of Chemistry and Physics, 48th Edition, The Chemical Rubber Co., 1967.

Weber, J. B., Am. Miner., 51, 1657-1661, 1966.

Weber, J. B., "Mechanisms of Adsorption of S-Triazines by Clay Colloids and Factors Affecting Plant Availability", Residue Rev., 32, 93-130, 1970.

Weber, W. J., Physicochemical Processes for Water Quality Control, Wiley-Interscience, 1972.

Weber, W. J., Voice, T. C., Pirbazari, M., Hunt, G. E., and Ulanoff, D. M., "Sorption of Hydrophobic Compounds by Sediments, Soils and Suspended Solids - II Sorbent Evaluation Studies", Water Research, 17, 1443-1452, 1983.

Williams, J.D.H., Weed Res., 8, 327, 1968.

Wilson, J. T., Enfield, C. G., Dunlap, W. J., Cosby, R. L., Foster, D. A., and Baskin, L. B., "Transport and Fate of Selected Organic Pollutants in a Sandy Soil", J. Environ. Qual., 10, 501-506, 1981.

Wyld, G.E.A., "Statistical Confidence in Liquid Scintillation Counting", In: The Current Status of Liquid Scintillation Counting, Bransome, E. D., Jr. (Editor), Grune & Stratton, Inc., 69-75, 1970.

Yaron, B., Swoboda, A. R., and Thomas, G. W., J. Agric. Food Chem., 15, 671, 1967.

Yaron, B. and Saltzman, S., "Influence of Water and Temperature on Adsorption of Parathion by Soils", Soil Sci. Soc. Amer. Proc., 36, 583-586, 1972.

Zhukovskii, A. P. and Sidorova, A. I., "Mechanism of Water-Structure Ordering in Solutions of Nonpolar Molecules", In: Water in Biological Systems (Translated from Russian), Consultants Bureau, New York, 76-79, 1971.