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**COMPETITIVE ADSORPTION OF VOLATILE ORGANIC COMPOUNDS ONTO
NATURAL AND SYNTHETIC ADSORBENTS**

The University of Arizona

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COMPETITIVE ADSORPTION OF VOLATILE ORGANIC COMPOUNDS
ONTO NATURAL AND SYNTHETIC ADSORBENTS

by

Wilbert Irwin Odem, Jr.

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In the Graduate College
THE UNIVERSITY OF ARIZONA

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TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS.....	vi
LIST OF TABLES.....	xi
ABSTRACT.....	xii
INTRODUCTION.....	1
LITERATURE REVIEW.....	6
Adsorption Principles.....	6
Adsorption of Organics onto Soils.....	12
Nonpolar Organic Compound Adsorption onto Soils.....	13
Review of Soil Adsorption Studies.....	15
Other Adsorbents.....	25
Clays.....	25
Activated Carbon.....	26
Synthetic Macroreticular Polymeric Resins..	27
Activated Alumina.....	31
Competitive Adsorption Predictive Models.....	32
EXPERIMENTAL PROCEDURES.....	39
Batch Test Procedure.....	39
Preparation of VOC Stock Solutions.....	43
Sorbates.....	44
Adsorbents.....	48
Adsorbent Preparation.....	52
Activated Carbon.....	52
Macroreticular Resins: Amberlite XAD-8 and Ambersorb XE-340.....	53
Activated Alumina.....	55
Aluminum Montmorillonite.....	56
Humic Acid.....	57
Peat.....	57
Natural Soil.....	58

TABLE OF CONTENTS--Continued

	Page
RESULTS AND DISCUSSION.....	61
Natural Adsorbents.....	61
Al-montmorillonite.....	61
Humic Acid.....	63
Soil.....	64
Peat.....	64
Synthetic Adsorbents.....	84
Activated Carbon.....	84
Amberlite XAD-8.....	98
Ambersorb XE-340.....	105
CONCLUSIONS.....	120
Natural Adsorbents.....	120
Synthetic Adsorbents.....	121
Predictive Models.....	122
RECOMMENDATIONS FOR FURTHER RESEARCH.....	124
APPENDIX: TABLES OF BATCH TEST ADSORPTION DATA.....	130
REFERENCES.....	152

LIST OF ILLUSTRATIONS

Figure	Page
1. Chemical structures of the VOC's of interest...	49
2. Freundlich isotherm for PCE adsorption onto soil; initial PCE concentration = 0.979 mg/l...	65
3. Freundlich isotherm for DCB adsorption onto soil; initial DCB concentration = 1.078 mg/l...	66
4. Freundlich isotherm for PCE adsorption onto peat; initial PCE concentration = 1.055 mg/l...	67
5. Freundlich isotherm for DCB adsorption onto peat; initial DCB concentration = 1.078 mg/l...	68
6. Freundlich isotherm for PCE adsorption onto peat in the presence of TCE; initial PCE concentration = 1.253 mg/l; initial TCE concentration = 1.535 mg/l.....	70
7. Experimental and predicted isotherms for PCE in the presence of TCE on peat; initial PCE concentration = 1.253 mg/l, initial TCE concentration = 1.535 mg/l.....	71
8. Freundlich isotherm for PCE adsorption onto peat in the presence of CT; initial PCE concentration = 0.958 mg/l; initial CT concentration = 0.587 mg/l.....	73
9. Experimental and predicted isotherms for PCE in the presence of CT on peat; initial PCE concentration = 0.958 mg/l; initial CT concentration = 0.587 mg/l.....	74
10. Freundlich isotherms for PCE and DCB adsorption onto peat in the presence of each other; initial PCE concentration = 1.022 mg/l; initial DCB concentration = 0.980 mg/l.....	75

LIST OF ILLUSTRATIONS--Continued

Figure	Page
11. Freundlich isotherm for DCB adsorption onto peat in the presence of TCE; initial DCB concentration = 0.980 mg/l; initial TCE concentration = 1.228 mg/l.....	77
12. Freundlich isotherm for DCB adsorption onto peat in the presence of CT; initial DCB concentration = 0.900 mg/l; initial CT concentration = 0.527 mg/l.....	78
13. Experimental and predicted isotherms for DCB in the presence of TCE on peat; initial DCB concentration = 0.980 mg/l; initial TCE concentration = 1.228 mg/l.....	79
14. Experimental and predicted isotherms for DCB in the presence of CT on peat; initial DCB concentration = 0.900 mg/l; initial CT concentration = 0.527 mg/l.....	80
15. Experimental and predicted isotherms for DCB in the presence of PCE on peat; initial DCB concentration = 0.980 mg/l; initial CT concentration = 1.002 mg/l.....	81
16. Freundlich isotherm for PCE adsorption onto activated carbon; initial PCE concentration = 0.993 mg/l.....	85
17. Freundlich isotherm for DCB adsorption onto activated carbon; initial DCB concentration = 1.078 mg/l.....	86
18. Freundlich isotherm for PCE adsorption onto activated carbon in the presence of TCE; initial PCE concentration = 1.139 mg/l; initial TCE concentration = 1.130 mg/l.....	88
19. Freundlich isotherm for DCB adsorption onto activated carbon in the presence of TCE; initial DCB concentration = 0.900 mg/l; initial TCE concentration = 0.896 mg/l.....	90

LIST OF ILLUSTRATIONS--Continued

Figure	Page
20. Freundlich isotherms for PCE and DCB adsorption onto activated carbon in the presence of each other; initial PCE concentration = 0.993 mg/l; initial DCB concentration = 1.078 mg/l.....	91
21. Experimental and predicted isotherms for PCE in the presence of TCE on activated carbon; initial PCE concentration = 1.139 mg/l; initial TCE concentration = 1.130 mg/l...	93
22. Experimental and predicted isotherms for PCE in the presence of DCB on activated carbon; initial PCE concentration = 0.993 mg/l; initial DCB concentration = 1.078 mg/l...	94
23. Experimental and predicted isotherms for DCB in the presence of TCE on activated carbon; initial DCB concentration = 0.900 mg/l; initial TCE concentration = 0.896 mg/l...	96
24. Experimental and predicted isotherms for DCB in the presence of PCE on activated carbon; initial DCB concentration = 1.078 mg/l; initial PCE concentration = 0.993 mg/l...	97
25. Freundlich isotherm for PCE adsorption onto XAD-8; initial PCE concentration = 0.993 mg/l..	99
26. Freundlich isotherm for DCB adsorption onto XAD-8; initial DCB concentration = 1.078 mg/l..	100
27. Freundlich isotherm for PCE adsorption onto XAD-8 in the presence of TCE; initial PCE concentration = 1.253 mg/l; initial TCE concentration = 1.535 mg/l.....	102
28. Experimental and predicted isotherms for PCE in the presence of TCE on XAD-8; initial PCE concentration = 1.253 mg/l; initial TCE concentration = 1.535 mg/l.....	103

LIST OF ILLUSTRATIONS--Continued

Figure	Page
29. Experimental and predicted isotherms for DCB in the presence of TCE on XAD-8; initial DCB concentration = 0.900 mg/l; initial TCE concentration = 0.896 mg/l.....	104
30. Freundlich isotherm for PCE adsorption onto XE-340; initial PCE concentration = 1.058 mg/l.	106
31. Freundlich isotherm for DCB adsorption onto XE-340; initial DCB concentration = 1.005 mg/l..	107
32. Freundlich isotherm for PCE adsorption onto XE-340 in the presence of TCE; initial PCE concentration = 0.861 mg/l; initial TCE concentration = 0.858 mg/l.....	108
33. Freundlich isotherm for DCB adsorption onto XE-340 in the presence of TCE; initial DCB concentration = 1.010 mg/l; initial TCE concentration = 0.712 mg/l.....	110
34. Freundlich isotherms for PCE and DCB adsorption onto XE-340 in the presence of each other; initial PCE concentration = 0.837 mg/l; initial DCB concentration = 0.979 mg/l...	111
35. Experimental and predicted isotherms for PCE in the presence of TCE on XE-340; initial PCE concentration = 0.861 mg/l initial TCE concentration = 0.858 mg/l.....	113
36. Experimental and predicted isotherms for DCB in the presence of TCE on XE-340; initial DCB concentration = 1.010 mg/l; initial TCE concentration = 0.712 mg/l.....	114
37. Experimental and predicted isotherms for PCE in the presence of DCB on XE-340; initial PCE concentration = 0.837 mg/l; initial DCB concentration = 0.979 mg/l.....	116

LIST OF ILLUSTRATIONS--Continued

Figure		Page
38.	Experimental and predicted isotherms for DCB in the presence of PCE on XE-340; initial DCB concentration = 0.979 mg/l; initial PCE concentration = 0.837 mg/l.....	117
39.	Freundlich single solute isotherms for PCE and DCB adsorption onto soil, peat, activated carbon, XAD-8, and XE-340.....	118
40.	Arithmetic single solute isotherm for PCE and DCB adsorption onto peat, activated carbon, XAD-8, and XE-340.....	119

LIST OF TABLES

Table		Page
1.	Commonly occurring volatile organic compounds..	3
2.	Volatilization losses due to experimental procedure.....	42
3.	Adsorption of methanol onto activated carbon...	45
4.	Comparative adsorbate data.....	47
5.	Moisture content and organic matter content of peat and soil.....	59
6.	Kansas topsoil characterization.....	60

ABSTRACT

This research addresses the phenomenon of competitive adsorption of volatile organics onto natural and synthetic adsorbents. The primary focus of this report is on tetrachloroethylene and 1,4-dichlorobenzene, but also includes information on the competitive interactions of trichloroethylene and carbon tetrachloride. Single-solute and bisolute batch isotherm tests were conducted, and the results were plotted on arithmetic and logarithmic graphs. Several models which predict competitive adsorption were tested using data obtained from the single-solute tests. The predictions were analyzed vs. the bisolute test results. Analysis of the model results is presented, along with an analysis of the viability of each of the models for predicting competitive adsorption. Implications of this research include prediction of subsurface migration of organic compounds for remedial purposes, and treatment of VOC-contaminated water.

INTRODUCTION

In recent years a number of federal and state surveys have documented the occurrence of synthetic organic chemicals in drinking water systems throughout the United States [1]. Systems that utilize groundwater as a source have been particularly plagued by the presence of potentially harmful organic compounds. When one considers that 80% of all public water suppliers in the U.S. rely on groundwater as a raw source [1], the need for control of these compounds becomes apparent.

The major sources of organic contamination of groundwater include municipal landfills, industrial waste impoundments and discharges, leaking underground storage tanks, and outmoded or closed treatment, storage and/or disposal facilities. To date, a relatively small percentage of water source aquifers have been determined to be adversely affected by organic contaminants [2]. However, due to the nature of groundwater hydraulics, which is often characterized by time lags measured in decades, and due to the rapid expansion in the manufacture and use of synthetic organic chemicals since the 1940s, groundwater contamination problems may very likely continue to surface at an

increasing rate for years to come. The scope of the potential problem was estimated in the U.S. government's "Interim Report on Groundwater Contamination" [3]. This report stated that approximately 170,000 waste impoundments exist in the U.S. Of these, 26,000 are industrial sites, 18,000 of which are unlined. About 8,000 of these unlined sites overlay aquifers, 2,600 of which are within a mile of water supply wells.

The compounds that most frequently occur in groundwater supplies are volatile organic compounds (VOC's), especially several chlorinated hydrocarbon solvents [1]. Due to their volatile nature, VOC's are not typically found in surface water--VOC contamination is almost exclusively a groundwater problem. Trichloroethylene (TCE) and tetrachloroethylene (PCE) are the compounds most frequently detected in groundwater [2]. Other commonly found VOC's include carbon tetrachloride (CT), 1,2-dichloroethane, 1,1,1-trichloroethane, vinyl chloride, and 1,4-dichlorobenzene (DCB). A more complete list of commonly occurring VOC's is found in Table 1 [4].

The present study focuses on four of these VOC's: tetrachloroethylene, 1,4-dichlorobenzene, trichloroethylene, and carbon tetrachloride. This report documents experimentally determined properties of PCE and DCB. A related master's thesis by Kalimtgis [5] "Adsorption of

Table 1. Commonly occurring volatile organic compounds.

Vinyl chloride	Bromobenzene
1,1-Dichloroethylene	m-Xylene
1,1-Dichloroethane	o+p-Xylene
1,2-Dichloroethylene	p-Dichlorobenzene
1,2-Dichloroethane	1,1,2-Trichloroethane
1,1,1-Trichloroethane	1,1,1,2-Tetrachloroethane
Carbon tetrachloride	1,1,2,3-Tetrachloroethane
1,2-Dichloropropane	Chlorobenzene
Trichloroethylene	1,2-Dibromo-3-chloropropane
Tetrachloroethylene	n-Propylbenzene
Benzene	o-Chlorotoluene
Toluene	m-Dichlorobenzene
Ethylbenzene	l-Dichlorobenzene

Source: Westrick et al., 1984

Trichloroethylene and Carbon Tetrachloride on Synthetic and Natural Adsorbents," documents the results of the tests concerning TCE and CT. All four of these compounds are considered toxic or potentially carcinogenic [6, 7, 8]. They are also widely used industrial solvents, and thus their potential for entry into water supplies is high.

More specifically, this study addresses the adsorption behavior of these VOC's, both in single component and two component solutions. Adsorption plays a critical role in two relevant areas of concern regarding organic compounds: subsurface contaminant migration, and treatment of contaminated water.

The purpose of this investigation was to examine the competitive and noncompetitive adsorption of these VOC's onto various natural and synthetic adsorbents. The method employed was the batch isotherm technique. The adsorption of each compound from a single component solution onto a number of adsorbents was determined, and the isotherms were graphed. The adsorption of the compound from a bisolute solution with each of the other compounds onto the same adsorbents was then determined. After the experimental data were obtained, a number of models predicting competitive adsorption were tested. The model predictions were compared

to the experimental results and evaluated according to the accuracy of the predictions.

LITERATURE REVIEW

Adsorption Principles

Adsorption at a surface or interface is largely the result of binding forces between individual atoms, ions, or molecules and the adsorbent surface [9]. There are four principal types of adsorption: exchange, physical, chemical, and specific. Exchange refers to ion exchange. Physical adsorption results from Van der Waal's forces. Chemical adsorption, or chemisorption, involves a reaction between the adsorbate and the adsorbent, resulting in a change in the form of the adsorbate. This binding is stronger than that of physical adsorption. Specific adsorption implies a reaction between the adsorbate and a functional group on the adsorbent. The adsorbate is not transformed [9].

Fox makes the point that adsorption onto activated carbon is a combination of physical and chemical adsorption [10]. Weber explains this by describing the activated carbon surfaces. Most of the carbon surface is the basal plane area, composed of polynuclear hydrocarbons, where physical adsorption and solvophobic uptake occurs [9, 11]. The much smaller heterogeneous edges of the carbon plane are

comprised of carbon-oxygen functional groups [9, 11]. These functional groups enable the activated carbon to undergo processes such as oxidation, hydrogenation, or halogenation. They also allow for a variety of chemisorption, hydrogen bonding, and functional group adsorption processes [9].

Fox also states that the adsorption onto synthetic polymeric adsorbents is a physical adsorption. Other interactions such as hydrogen bonding and dipole-dipole interaction may be important, depending on the resin and the adsorbate [10]. Nonionic compound adsorption onto resins has been shown to be a physical adsorption by thermodynamic measurements, especially heat of adsorption and enthalpy. The heat of adsorption for chemisorption is an order of magnitude greater [10].

A number of system characteristics are important in determining adsorption behavior and capacity. Bernardin divides these into adsorbate properties, adsorbent properties, and solution properties [12]. Since this is a convenient way to enumerate important characteristics, it will be followed in this report.

Important adsorbate characteristics include molecular size and molecular form. Molecular size influences the degree of solubility within a homologous series [12]. As size increases, solubility generally decreases, and therefore adsorption out of the solvent increases [12].

This is known as Traube's rule. Weber states that adsorption from solution increases as a homologous series is ascended because expulsion of increasingly larger molecules allows a greater number of water-water bonds to form [9]. Molecular size may also affect the ease of diffusion through the micropores of the adsorbent.

Molecular form is also important. This encompasses the charge of the molecule and the structure of the molecule, i.e., branch, straight chain, ring structure, etc.

The important adsorbent characteristics include the degree of ionization of the surface, types of functional groups present, the physical form of the adsorbent (i.e., granular, bead, powder, etc.), surface area, and pore size and distribution [12]. Weber states that the surface chemistry of activated carbon is important in determining the activity or capacity for specific organic compounds. The surface chemistry is a function of the raw material used, the activation process, and the activation conditions [9].

The important solution characteristics are pH, which affects both the adsorbate and adsorbent; temperature, which affects kinetics and the degree of solubility; and the presence of competing adsorbates [12]. The degree of solubility of the compound in the solvent is also quite important.

Kipling discusses important factors that affect competitive adsorption [11], including the interaction of each of the components with the adsorbent, the porosity of the solid, and the heterogeneity of the solid. The existence of competition between components of a solution depends most frequently on differences in the strength of interactions between the adsorbates and the adsorbent. Quite small differences in these strengths may be responsible for preferential adsorption of one of the compounds. This can be understood qualitatively in terms of the varying degrees of polarity exhibited by the surface and the adsorbates [11].

The heterogeneity of the adsorbent surface can also be important, especially in soils. The existence of functional groups with variable affinities for the solutes results in preferential adsorption [11]. For example, a high-energy functional group may adsorb one solute more than another. When these sites are filled, only lower-energy sites are left, which may not adsorb as effectively.

A thermodynamic approach can be used to describe and, sometimes, predict adsorption. With this approach, adsorption must be viewed as a phase equilibrium mechanism. The adsorbed layer can be treated as a distinguishable phase, though the precise location of the phase boundary may be uncertain [13]. According to Ruthven, two perspectives

are available with this distinct phase approach: (1) the adsorbate and the adsorbent are considered as a single phase having the properties of a solution; (2) the adsorbent is thermodynamically inert and the adsorbed molecules are a distinct phase [13].

The first perspective calls for consideration of the surface tension term, π , which is defined as the difference in surface tension between a clean surface and a surface covered with adsorbate [13]. This term is often considered the intensive variable in surface adsorption. Weber says that the extent of adsorption relates to certain properties of the adsorbate relative to the solution phase, especially surface tension and solubility [9]. Many organic compounds can decrease the surface tension of water, and thus the energy balance of such aqueous systems favors partitioning to a solid/water interface. This process is also influenced by the solvophobicity of the compound; i.e., the greater the solvophobicity, the greater the tendency to move to another phase.

Kipling expresses Traube's rule relative to surface tension. The surface activity, or tension, increases as a homologous series is ascended, and therefore so does adsorption [11].

The second perspective expressed by Ruthven, i.e., viewing the adsorbent as inert and the distinct phase com-

prised solely of adsorbates, involves the concept of surface excess. Kipling defines this as the measure of the extent to which the bulk liquid is impoverished with respect to one component because the surface layer is correspondingly enriched [11]. Sircar and Myers view this particular interface model as being comprised of two homogeneous phases, the bulk liquid and the adsorbed layer, which both extend up to a surface of division [14]. The properties of the homogeneous adsorbed phase are a function of the location of the dividing surface. They develop a characteristic extensive parameter of the liquid-solid interface called the excess property. Chatteraj and Birdi, in Adsorption and the Gibbs Surface Excess, give an extensive, detailed treatment of this approach to adsorption phenomena [15].

A number of different algebraic expressions has been developed to approximate adsorption onto surfaces [16]. Most of these have resulted from attempts to describe experimental data by means of ideal equations derived on the supposition of substrate uniformity. The most common of these are the Freundlich and Langmuir expressions.

The Freundlich model, or description, if you will, was developed on the basis that at sufficiently low surface concentrations, all adsorption isotherm equations reduce to the form of a line through the origin, or Henry's law:

$$p = K\theta \quad (16)$$

The Freundlich equation, $q_c = KC^{1/n}$, reduces to the form of the Henry equation when $1/n = 1$. The Freundlich model is used primarily to describe adsorption data with the parameters K and $1/n$, which can be valuable descriptors but have a tenuous physical significance.

The Langmuir expression was originally developed to represent chemisorption on a set of distinct localized sites [13]. It has been widely applied to adsorption from solution, but it must be regarded as an empirical equation with no thermodynamic validity [17]. The Langmuir constants do not have any physical significance in the case of adsorption from solution [17]. The Langmuir model will be discussed more later.

Adsorption of Organics onto Soils

The adsorption of toxic organic compounds onto soil is of relevance to this study because volatile organic compound contamination of groundwater occurs mainly via leaching through overlying soil regimes. Once they have been introduced into the groundwater, the VOC's must migrate through the saturated soil matrix of the aquifer to pose any threat to water supplies or to sensitive biosystems. A knowledge of potential soil/contaminant interactions can allow accurate prediction of contaminant migration and thus expedite remedial efforts. When siting toxic waste disposal facilities or land-based treatment operations, pertinent

testing of the appropriate soil profiles can provide valuable data for designing for an in situ barrier to off-site migration of wastes. In this section, a simplified explanation of soils uptake of nonionic organic compounds will be presented, followed by a brief review of published studies dealing with adsorption onto soils.

Nonpolar Organic Compound Adsorption onto Soils

Burchill et al., in their chapter "Adsorption of Organic Molecules," in The Chemistry of Soil Processes [18], make the observation that, in general, the higher the solubility of a neutral compound in a solvent medium, the lower the adsorption of the compound from that solvent. The surface tension of the solvent also plays a part. The higher the surface tension of the solvent, the lower its affinity for the adsorbent surface and the more readily will an adsorbate of low surface tension be adsorbed from it. Burchill points out, however, that many of the systems studied involve sparingly soluble species, and the very small differences in solubility may not be able to explain significant differences in adsorption behavior. He cites research where observed thermodynamic parameters of adsorption were corrected for solubility effects to obtain parameters more closely related to adsorbate/adsorbent surface interactions [18].

Concerning the mechanisms of nonpolar organic compound adsorption onto soil, Graham-Bryce states that information can be obtained by investigating the relationship between the extent of adsorption and individual soil properties, e.g., clay and organic matter content, pH, cation exchange capacity (CEC), etc. [19]. Caution must be exercised, though, because these soil properties are often correlated among themselves, e.g., high clay content often goes with high organic matter content. However, one of the strongest correlations that has been found is that between adsorption and organic matter content. Graham-Bryce's description of the process, though simplistic, imparts a general understanding of a widely accepted mechanism. One must consider the strengths of attraction of the components--water, organic matter, sorbate--for themselves and for each other. The adsorbate is nonpolar and has little affinity for the polar solvent, water. It will, therefore, tend to accumulate at a hydrophobic interface, such as that afforded by the soil organic matter [19]. This is similar to the process of accumulation of surfactants at an air/water interface. Viewed in this perspective, we actually have adsorption out of water as opposed to onto a surface, i.e., a partitioning process. Minglegrin and Gerstl [20] discuss partitioning vs. adsorption as

mechanisms for uptake of nonpolar compounds onto soil. Their views will be discussed later.

Burchill et al. agree that the organic matter content is largely responsible for soils uptake of nonpolar organics. They go beyond Graham-Bryce's development and cite evidence that long chain aliphatic acids, probably released from lipid-like structures, and long chain hydrocarbons formed from humic substance degradation reactions may act as hydrophobic anchoring sites for the nonpolar (i.e., hydrophobic) adsorbates [19]. Burchill suggests that the forces of attraction are Van der Waal's forces; the process is therefore a physical adsorption. Burchill terms the process hydrophobic bonding [18]. Both Graham-Bryce and Burchill note that other adsorption mechanisms may be involved due to the great heterogeneity of the soil surfaces. These mechanisms include hydrogen bonding, ligand exchange, chemisorption and others. The contributions of these mechanisms to the overall absorption, though, is probably quite small [18, 19].

Review of Soil Adsorption Studies

The chemistry of soils and soil processes is very complex indeed. Soil particles have a wide range of sizes and generally have quite heterogeneous surfaces. These surfaces can support a wide variety of functional groups and

ionic species, which can often impart a reactive or charged nature to the particles.

The current problem of contaminant leaching into groundwater supplies has focused much attention on the physical and chemical properties of soils. An understanding of the mechanisms involved in transport through soil regimes, including physical, chemical, and biological processes, is critical for protection and remediation of groundwater supplies.

Fortunately, much work has been done prior to this time dealing with the interactions of pesticides with soils [18, 19]. This previous work encompasses investigations on both charged and uncharged organic compounds. Therefore, the theoretical and empirical groundwork has been laid for the present problems of organic contaminant migration in porous media.

Goring [21], in 1962, observed a significant positive correlation between the organic matter content of a soil and the adsorption of neutral organic pesticides. Lambert suggested that only the organic fraction of the soil was adsorbing these neutral compounds, and not the whole soil [22]. He derived a partition coefficient, K_{oc} , determined from experimental data and normalized to the organic carbon content of the soil. This was determined by

$$K_{oc} = \frac{K_d}{O.C.\%} \times 100$$

where K_d is an experimentally determined distribution coefficient

mass of solute adsorbed per unit mass of adsorbent
equilibrium concentration in solution

and O.C.% is the percentage of the total soil comprised of organic carbon. Lambert compared the partitioning between the organic carbon fraction and the water to the partitioning when a low solubility compound is placed in a water/nonpolar solvent mixture [22]. This led to the idea that a possible relationship existed between solvent/water partition coefficients and the organic carbon-based distribution coefficient.

Karickhoff et al., based on Lambert's findings, attempted to derive an empirical equation based on the soil organic carbon fraction and the partition between water and octanol, a nonpolar solvent [23]. They worked with low-concentration solutions of sparingly soluble organic compounds and determined K_{oc} 's for a number of soils which varied in organic carbon content. They plotted $\log K_{oc}$ vs. the log of the octanol/water partition coefficient, $\log K_{ow}$, and determined the following relationship:

$$\log K_{oc} = 1.00 \log K_{ow} - .21 \quad (r^2 = 1.00)$$

Because the octanol/water partition coefficient is basically a function of the compound's solubility, an expression was derived in a similar manner to predict K_{oc} from solubility data:

$$\log K_{oc} = -.54 \log S + .44 \quad (r^2 = .94)$$

Karickhoff et al. found a stronger correlation between K_{oc} and K_{ow} than between K_{oc} and S [23]. The postulated reason for this is that the partition between water and octanol is simply a monomer distribution between two phases. However, saturated aqueous solutions involve equilibrium between dissolved monomers with the crystalline phase, i.e., undissolved monomers. Therefore, crystal energy contributions enter into water solubilities, while they do not affect the monomer-associated properties of K_{ow} and K_{oc} . Karickhoff found that reasonable estimates (within a factor of 2) of adsorption behavior of hydrophobic compounds can be made from knowledge of the organic carbon content of the soil and the K_{ow} of the compound [23].

In later work Karickhoff conducted a review of published sorption data and derived K_{oc} 's for a number of soils and compounds, including some chlorinated hydrocarbons. He also predicted values of K_{oc} using a combination of thermodynamic theory and empirical correlation. He based

his estimates on individual compound K_{ow} 's and aqueous solubilities, some of which were corrected for crystal energy [24].

Twenty-two various hydrocarbon and chlorinated hydrocarbon adsorption studies were reviewed. Three equations were used for K_{oc} estimates and compared to experimental data. The K_{ow} -based relationship was

$$K_{oc} = .411 K_{ow}$$

Log K_{oc} estimates derived from this relation deviated from measured values by an average of .20 log units (absolute value deviation). The following relationship was employed using solubility data corrected for crystal energy:

$$\log K_{oc} = -.921 \log X_{sol} - .00953 (mp - 25) - 1.405$$

where X_{sol} is the compound aqueous solubility and .00953 (mp - 25) is the crystal energy correction term. Estimates of log K_{oc} deviated from measured values by .27 log units. The relationship

$$\log K_{oc} = -.544 \log X_{sol} - .197$$

was used to estimate K_{oc} based on the uncorrected solubility term. The average deviation from measured values was .30 log units.

Karickhoff concluded that all three estimation techniques predicted values within the range of typical measurement variation, which may be caused by measurement error or just reasonable differences in soils adsorption [24].

In a recent paper [25], Karickhoff gives a descriptive explanation of his understanding of the mechanism of uncharged organics adsorption onto soils. He posits that the binding is dominated by hydrophobic interactions. The key thermodynamic property discriminating the adsorption of different chemicals is the aqueous phase coefficient, i.e., the chemical's affinity for water. Therefore, hydrophobic-related adsorption can be estimated by any pollutant property directly related to the aqueous phase activity coefficients, e.g., K_{ow} , solubility, etc. The organic fraction of the soil, due to a hydrophobic nature, dominates the uptake of uncharged compounds [25]. Karickhoff also notes that pollutant sorption to soils may involve kinetic rates in the range of weeks to months. The kinetics depend on the compound's molecular size, the sorbent cohesive properties, and solids concentration [25].

Many researchers proceeded in the same direction as Karickhoff, some using his empirical derivations, while others developed their own, depending on the nature of the compounds studied. Briggs also found K_{ow} to be a better

predictor than solubility for soils/pesticides adsorption coefficients [26].

Hassett et al. studied the uptake of dibenzothiophene by soils and sediments and the effects of various soil properties on this uptake [27]. They found significant correlation between sorption and organic matter content, while other factors tested, clay, clay mineralogy, CEC, and surface area, showed insignificant correlation. The experimental results yielded a distribution coefficient of 11,320. Hassett et al. used Karickhoff's derivation [23]:

$$\log K_{oc} = 1.00 K_{ow} - .21$$

to predict a K_{oc} of 14,798, well within the agreement Karickhoff found of a factor of 2.

Hassett et al. state that the adsorption of dibenzothiophene appears to be an example of hydrophobic adsorption; i.e., it is not due to a strong sorbate/sorbent attraction but to weak solute/solvent interaction [27].

Means et al. also found a high positive correlation between adsorption of polynuclear aromatic hydrocarbons (PAH's) and the organic content of a soil [28]. They also found that organic carbon normalized distribution coefficients were predictive of the compound K_{ow} 's, which were determined experimentally. The researchers also found a highly negative correlation between compound solubility

and K_{oc} . The equations used for predictions are presented below:

$$\log K_{oc} = \log K_{ow} - .317 \quad (r^2 = .98)$$

and

$$\log K_{oc} = -.686 \log S + 4.273 \quad (r^2 = .933)$$

In another investigation of PAH adsorption, Means et al. found predicted K_{oc} values to be within a factor of 2-3 of experimental findings using the same two equations [30]. In these studies, solubility was a better predictor than K_{ow} .

Schwarzenbach and Westall also found a high correlation between the soil organic fraction and nonpolar organic uptake for the compounds and soils studied [31]. There was also a high correlation between experimental K_{oc} 's and estimated K_{oc} 's, determined by

$$\log K_{oc} = .72 \log K_{ow} + .49$$

Schwarzenbach and Westall note that this relationship is valid in principle only for the solutes and sorbents used in this study [28]. Different types of sorbates and sorbents will produce different relationships between K_{ow} and K_{oc} . One needs to determine how unique one's correlation is and how to interpret it.

Wilson et al., using solubility data and the soil organic fraction, predicted retardation of pollutants within a factor of three in soil column experiments [29]. The compounds included TCE, PCE, DCB and other halogenated VOC's. These researchers used Chiou's relationship,

$$\log K_{oc} = 4.04 - .557 S$$

because Chiou looked at many of the same compounds.

Chiou et al. tested soil uptake of twelve aromatic compounds, including the dichlorobenzenes [32]. They observed a significant correlation between organic matter content and adsorption. These researchers claim that their data support the hypothesis of hydrophobic partitioning to the soil organic phase as the primary mechanism of uptake, as opposed to adsorption onto specific sites. Chiou et al. also make an interesting point concerning absolute adsorption data. They state that observed competition would indicate adsorption; no competition indicates a partition process (competition implies a shortage of sites; hydrophobic partitioning does not occur on specific sites) [32].

Kyle challenges Chiou's contention that solubility (or the lack of it) is the primary mechanism or force behind nonionic compound distribution behavior between soil and water [33]. He claims that some true adsorption mechanisms may play a significant role. However, Kyle cites a study

supporting his views which was conducted with hexane as the solvent [33]. Adsorption of nonpolar compounds out of a nonpolar solvent, hexane, onto soils was observed. The mechanism involved here was obviously not due to weak solvent/solute interaction. Though this system is distinctly different from the soil-water-solute matrix, it does indicate that some other adsorption mechanisms may be at work.

Minglegrin and Gerstl also take exception with the idea that nonionic compound adsorption can be explained largely by the hydrophobic partitioning mechanism [20]. They note systems in which a distinct hydrophobic phase at the solvent surface does not exist, but which often exhibit uptake behavior presumed to characterize partitioning. Minglegrin and Gerstl posit that surface uptake cannot be defined simply as "partitioning" or "adsorption," but rather there is a continuum of possible interactions ranging from fixed-site adsorption to true partitioning between the three phases [20].

Minglegrin and Gerstl also criticize the estimation techniques used, claiming that they are overextended without regard to limitations such as compound type [20]. The great heterogeneities of soil surfaces do not allow predictions based on these correlations to apply to all members of the very diverse group of nonionic organic compounds. Nevertheless, the authors concede, these correlations may be

useful and acceptable as long as their limitations are considered.

Other Adsorbents

Clays

Various clays were chosen for adsorption testing in this study, including kaolinite, Na-montmorillonite, and Al-montmorillonite. Only Al-montmorillonite was used in this phase of the experiment, and only for uptake of DCB.

Results reported by Kalimtgis [5] indicated that none of the three clays showed any uptake of trichloroethylene or carbon tetrachloride. The nonpolar nature of these volatile halocarbons was expected to preclude any significant adsorption onto the charged surface of the clays, which are important in the adsorption of ionized species [19].

A number of researchers, however, have observed adsorption of some of these halocarbons onto clays in experiments involving kaolinite and Na- and Al-montmorillonite. Hutzler et al. observed carbon tetrachloride and 1,4-dichlorobenzene adsorption onto Na-montmorillonite, but none on kaolinite [34]. Rogers et al. showed that Ca- and Al-saturated montmorillonite adsorbed less than 5% of available benzene from a dilute aqueous solution [35].

In another study Rogers and McFarlane looked at CT and TCE adsorption onto soils and Al- and Ca-montmoril-

lonite. Insignificant adsorption was measured for all combinations except for a 17% uptake of TCE on Al-montmorillonite [36].

These previously published results warranted at least a cursory investigation into clay adsorption of these VOC's.

Activated Carbon

Granular activated carbon (GAC) columns and beds are commonly used in water and wastewater treatment operations. Powdered activated carbon (PAC) is used to a lesser extent, but its use is not uncommon, e.g., as a control for humic substances in potable water treatment.

Activated carbons have been shown by a number of researchers to adsorb significant amounts of volatile halogenated organics [37, 38, 39], but its greatest promise in treating VOC-contaminated waters appears to be in conjunction with air stripping [39, 40, 41]. Granular activated carbon columns would best be used as an end of pipe polishing step and/or to remove compounds less amenable to air stripping.

The water treatment literature abounds with studies and assessments of AC for removal of organic compounds. Giusti et al. [42] have compiled an extensive list of petrochemicals amenable to carbon adsorption in their review of AC applications. Rizzo and Shepherd [43] give a good

discussion on equipment and economics of AC systems used in industrial wastewater treatment operations. Activated carbon surface chemistry and principles of adsorption onto AC are dealt with in a text by Mattson and Mark [44]. The August 1981 issue of the Journal of the American Water Works Association was devoted entirely to the use of activated carbon for water treatment problems. The EPA has published results of carbon adsorption tests for 143 toxic organics in tabular and graphical form [45]. Suffet and McGuire have edited a very informative 2-volume compilation dealing with the adsorption of organics onto activated carbon [46].

The above-mentioned works should give the reader an overview of the experience and potential of activated carbon for removal of organics from water and wastewater. A thorough review of AC uses, chemistry, and studies in this paper would be redundant and serve no purpose. In the present study, adsorption onto AC was investigated largely to give a baseline to compare the capacities of the synthetic resins and natural sorbents.

Synthetic Macroreticular Polymeric Resins

Several synthetic polymeric resins have been developed in recent years to remove potentially toxic organic compounds from water. Activated carbon is much more commonly used, and, accordingly, has been studied to a much greater extent. Several studies have been conducted,

though, which assess the adsorption properties and capacities of some common synthetic resins [5, 47, 48,49, 50]. Some resins, in fact, are currently in use in industrial wastewater treatment operations which have a well-characterized influent. For instance, macroreticular polymeric resins are being used to remove phenols from process wastewaters [51]. Regeneration of resins involves steam cleaning and sometimes solvent washing.

The two synthetic resins used in this research, Rohm and Haas's Amberlite XAD-8 and Ambersorb XE-340, were designed to remove low molecular weight halogenated organics and pesticides from water [51]. Controlled manufacturing conditions allow the fixing of pore size distributions, uniform surface conditions, and substituent groups. By careful choice of the fixed-based materials used in the polymerization reaction, the manufacturer can control the degree of cross-linking and thus the porous structure and surface characteristics. Typical matrix materials are styrene divinyl benzene and polyacrylic esters [49]. The XAD-8 and XE-340 differ in that the XE-340 is a carbonaceous polymeric resin, which will be discussed later. XAD-8 is available commercially, while the XE-340 is still undergoing lab and pilot scale evaluations.

Amberlite XAD-8 is made from a matrix of polymethacrylic ester. It has a surface area of $140 \text{ m}^2/\text{g}$, a

particle density of $.445 \text{ g/cm}^3$, and an average pore diameter of 410 Å [49]. The XAD-8 resin appears as small white spherical beads.

Generally, XAD-8 has shown little promise in water or wastewater treatment applications. Boening et al. compared activated carbon to a number of synthetic resins for adsorbing humic substances [48]. Isotherms developed on XAD-8 showed unfavorable adsorption. Boening concluded that the humic acid adsorption capacity of XAD-8 was unacceptably low. Kalimgtis, in a study of VOC adsorption onto a variety of adsorbents, showed that XAD-8 had unfavorable adsorption of TCE and CT [5]. Weber and van Vliet looked at the adsorption of phenol, chlorophenol, carbon tetrachloride, toluene sulfonate, and dodecylbenzene sulfonate onto carbons and resins [49]. A statistical analysis of their experimental results [52] concluded that polymeric adsorbents did not compare favorably to the activated carbons tested and do not show promise for water treatment applications. However, Weber and van Vliet note that polymeric adsorbents have performed successfully in analytical situations where it was desired to concentrate and recover organic compounds from water [49]. Activated carbon has a lower ultimate adsorbate yield in these uses because the degree of reversibility of the adsorption reaction on the AC is much lower than that of adsorption onto the resin [49].

Ambersorb XE-340 is a polymeric carbonaceous resin designed for adsorption of low molecular weight organics from water. It is produced by the partial pyrolysis of beads of macroreticular polymer. The polymer chars during pyrolysis but retains its macroreticular structure [53]. Thereby, the great capacity of carbonized organic matter is obtained with the tight structural controls of the engineered synthetic adsorbents. This resin has a surface area of $400 \text{ m}^2/\text{g}$, a particle density of $.995 \text{ g/cm}^3$, and an average pore diameter of 30.1 \AA .

The XE-340 resin has been shown to have a favorable adsorptive capacity relative to activated carbon for a specific, narrow range of compounds [47, 49, 50, 53]. Chudyk et al. found that a carbonaceous polymeric adsorbent had an "excellent capacity for chloroform" [47]. However, 2-methylisoborneol, a taste- and odor-causing organic, adsorbed less favorably and was difficult to remove using standard regenerative techniques. Humic substances were not adsorbed at all onto this resin. Boening et al. also found that XE-340 had a low capacity for humic substances [48]. Wood and DeMarco concluded that XE-340 had approximately three times the capacity of AC for halogenated organics. Weber and van Vliet found that the carbonaceous resins often approached the capacities of the activated carbons studied [49]. Neely observed an "unusually large capacity of XE-340

for chloroform" [53]. Mr. Neely, of the Rohm and Haas Company, attributed this capacity to the resin's macropore and micropore sizes, its chemical composition, and its chemical structure [53].

There is general agreement in the literature that XE-340 and other carbonaceous polymeric resins have application potentials for removing specific, narrow ranges of compounds, e.g., low molecular weight halogenated organics, such as the compounds being investigated in this study. Moreover, no published research to date has focused exclusively on volatile halocarbon adsorption onto polymeric resins, carbonaceous or otherwise. In addition, very little has been reported on competitive adsorption of organic compounds onto synthetic resins. Current concerns regarding volatile organics in drinking water sources renders such treatment studies quite timely.

Activated Alumina

Activated alumina was used in this study to complete the experimental matrix of synthetic adsorbents. Alumina is used in water treatment to remove ionic species, primarily fluorides, from water. It has also been shown to be effective in adsorbing arsenic and selenium [54].

No published work was located that investigated adsorption of organics onto activated alumina. Due to the

nonionic nature of the VOC's, no significant uptake was anticipated.

Competitive Adsorption Predictive Models

Three models were tested to determine their viability in predicting competitive adsorption of VOC's onto a variety of adsorbents. These models are the competitive Langmuir, the Jain-Snoeyink model, and the simplified Ideal Adsorbed Solution Model as presented by Digiano et al. [55]. All three models base their predictions on previously obtained single solute adsorption isotherm data. A brief description of each of these models, along with their basic assumptions, will be presented. Freundlich parameters were also determined for the single and bisolute data for the purpose of characterizing the isotherms.

The Langmuir model is based on three assumptions: (1) maximum adsorption is a saturated monolayer on the adsorbent surface; (2) the energy of adsorption is constant; and (3) there is no transmigration of the adsorbate on the adsorbent surface. The Langmuir model for single-solute adsorption is

$$q_e = \frac{Q_{bc}}{1 + bc}$$

where

q_e = amount of solute adsorbed per unit weight of
adsorbent

Q = maximum capacity of the adsorbent for the
adsorbate

b = constant related to the energy of adsorption

c = equilibrium solution concentration

C and q_e are determined experimentally; Q and b are determined by graphical methods. The competitive Langmuir model as presented by Weber [41] is

$$q_i = \frac{Q_i b_i c_i}{1 + \sum_{j=1}^n b_j c_j}$$

where

n = number of solutes in the solution

Q_i, b_i = single solute parameters

C_i = equilibrium concentration in the mixture

Analysis of the assumptions of the Langmuir model leads to the observation that the adsorbent must have a uniform surface, and that only one adsorption mechanism is operating. However, uniform surfaces are the exception for adsorbents, especially in the case of soils. Both Burchill et al. and Graham-Bryce noted poor fits for the Langmuir model for pesticide adsorption onto soils [18, 19]. The very heterogeneous nature of soil surfaces indicates that the Langmuir model would not be applicable.

Jain and Snoeyink proposed an approach that is an extension of the competitive Langmuir [56]. They point out that the Langmuir model will predict the extent of adsorption only if $X_1 = X_2$, where X_1 is the amount of solute adsorbed, or if there is competition between 1 and 2 for all sites. However, if adsorption of one of the solutes occurs on sites that are not amenable to the other solute, the Langmuir model will not apply. For example, a difference in molecular size could exclude the larger solute from entering pores wide enough for the other solute. Another difference could be caused by affinity for different functional groups [56].

Jain and Snoeyink expanded the competitive Langmuir to account for adsorption onto sites for which there is no competition. Their model is presented below.

$$X_1 = \frac{(x_1 - x_2)b_1c_1}{1 + b_1c_1} + \frac{x_2b_1c_1}{1 + b_1c_1 + b_2c_2}$$

The first term on the right side is a Langmuir expression for the amount of solute 1 that adsorbs without competition. It is assumed that the number of noncompetitive sites equals $X_1 - X_2$ and that $X_1 > X_2$. The second term is simply the expression of the competitive Langmuir for two species [56]. This model uses the Langmuir parameters.

Jain and Snoeyink tested the model on adsorption of bromophenol and benzenesulfonate on carbon, which show different capacities in single-solute systems. They found that their model predicted the results quite well [56].

The simplified Ideal Adsorbed Solution (IAS) model, as presented by Digiano et al. [55], is a modification of the IAS model of Radke and Prausnitz [57]. The fundamentals of the IAS model will be presented, followed by Digiano's modifications.

Radke and Prausnitz made the assumption that the adsorbed phase forms an ideal solution [57]. The concentration of a solute in a mixture is related to the concentration in a single-solute system by

$$C_i(\pi, T, z_i) = Z_i C_i(\pi, T),$$

where

C_i = concentration in mixture

C_i = concentration in single system

π = spreading pressure on the surface, which is a function of surface tension

z_i = mole fraction of surface coverage

T = absolute temperature

This equation holds only when π and T are the same in the mixture and the single-solute system [57].

The spreading pressure is determined by

$$\pi_i = \frac{RT}{A} \int_0^{c_i^0} q_i^0 \frac{dc_i^0}{c_i}$$

where

R = universal gas constant

A = surface area per unit weight of adsorbent

q = solid phase loading

The IAS theory is combined with the Gibbs equation for isothermal adsorption to yield

$$\frac{1}{q_T(\pi, T)} = \sum_j \frac{z_j}{q_j^0(\pi, T)}$$

These three equations allow prediction of adsorption behavior of solutes in a mixture. This procedure requires adsorption data for the entire concentration range of the solutes. Adsorption data in the very low concentration range, however, is often difficult to obtain. In addition, the IAS model becomes increasingly more difficult to use as the number of solutes increases, especially in determining the spreading pressure term, π .

Digiano et al. show that when competing solutes have identical isotherms, the total loading in the mixture is the same as in each single-solute system [55]. The single-solute concentrations are equal to the total concentration of the mixture. There is also an identical relationship between π and C_i for the two solutes.

Digiano proposes an averaging of the Freundlich constants for each single-solute system [55]. Applying these average parameters along with the considerations mentioned above to the IAS development yields the following expression to predict adsorption of competing solutes:

$$q_i = K' [n' - 1/n'] [K_i C_i]^{1/n'} \left[\sum_{N} \left[\frac{K_i}{K'} C_i^n \right]^{1/n'} \right]^{n'-1}$$

where

q_i = amount of solute i adsorbed

K' = adjusted Freundlich K

n' = adjusted Freundlich n

C_i = equilibrium concentration

N = number of solutes in mixture

The Digiano simplification duplicates the IAS model in two situations: (1) when the Freundlich K 's and n 's are in fact equal; and (2) when the K 's are different but the n 's are equal. The closer the n 's are to each other, the better Digiano's model approximates the IAS model [55].

Digiano et al. applied their model to adsorption studies involving nitrophenol, chlorophenol, benzoic acid, and phenol. Their results showed that the simplified model made good approximations of adsorption behavior [55]. One must recognize, though, that the Digiano approach is a curve fitting technique. Single-solute adsorption data must be

analyzed closely to determine if the Digiano model is applicable.

EXPERIMENTAL PROCEDURES

Batch Test Procedure

The adsorption data utilized in this investigation were generated using a bottle point batch isotherm technique. Variable amounts of an adsorbent were introduced into 150 ml serum bottles. The bottles were then filled with distilled water produced in the laboratory. The pH of the distilled water ranged from 5.5-5.7. A constant amount of the volatile organic of concern was introduced into each of the batch bottles using a 50 μ l Hamilton syringe. The VOC was taken from a concentrated stock standard solution composed of the VOC dissolved in methanol. The batch bottle was immediately covered with a 20 mm teflon-faced septum and crimped with a 20 mm aluminum seal. Headspace-free conditions were maintained to prevent volatilization of the VOC and its subsequent loss to the atmosphere. Two additional batch bottles were filled only with distilled water and the VOC, and contained no adsorbent. These two bottles were used as controls and as validation of the introduced VOC concentration.

The batch bottles were then placed on a gyratory shaker and mixed for 24-36 hours. After mixing, the bottles

were centrifuged at 4500 rpm for 10-15 minutes. The centrifuging was performed in order to separate any suspended sorbent material so that it would not interfere with the subsequent water analysis.

The VOC-laced water was analyzed by means of gas chromatography (GC). To prepare samples for the gas chromatographic analysis, 60 ml of the batch bottle contents were poured into a 120 ml serum bottle which already contained 60 ml of distilled water, thus giving a 1:1 ratio of distilled to sample water. The reasons for this procedure were to decrease the potential volatilization losses and to keep the total VOC concentration of the analyzed sample within its linear range of the EC detector for the particular gas chromatograph configuration employed. It was necessary to transfer the sample to another serum bottle because the procedure used for GC analysis, a liquid-liquid extraction technique using pesticide grade pentane extracts the VOC from the water, and would have adsorbed some of the VOC off of the sorbent, thereby invalidating the results. The major problem associated with this sample transfer procedure is the potential loss of the VOC through volatilization, which could be induced by the pouring step. Therefore, control experiments conducted to quantify potential losses due to volatilization during the water transfer. These tests were conducted using carbon

tetrachloride and trichloroethylene, which are the most volatile of the four VOC's studied. This ensured a maximum error estimate due to the water transfer step. The results of these tests are presented in Table 2. The percent errors from each run were calculated and then averaged. The average loss by volatilization during this step was 5.9%. This step, therefore, was the largest contributor to the overall experimental error. However, the amount of adsorption was significantly greater than volatilization losses, except when the clays, soil and humic acid were used. These losses did not adversely affect the experimental results.

After the water was transferred to the adsorbent-free serum bottles and sealed with the teflon septum and aluminum crimp, it was ready for preparation for GC analysis. This preparation involved a liquid-liquid extraction technique using pentane. Five ml of pesticide grade n-Pentane were injected into the sealed serum bottle, with an exhaust needle provided for displacement of 5 ml of the sample. The serum bottle was vigorously shaken for 2.5 minutes to ensure complete contact of pentane with the VOC. The VOC preferentially dissolved into the pentane layer over the water. A 3 μ l aliquot was extracted from the VOC/pentane solution layer using a 10 μ l Hamilton syringe, and injected into the gas chromatograph, a Hewlett Packard

Table 2. Volatilization losses due to experimental procedure.

Sample	Volume (ml)	Initial Concen. ($\mu\text{g/l}$)	Volume Reduction (from/to)	Measured Concen. ($\mu\text{g/l}$)	% Loss
A ₁ (TCE)	150	146.3	150/120	108	6.9
A ₂ (TCE)	150	145.2	150/120	109	6.1
B ₁ (CT)	150	232.1	150/120	165.5	10.5
B ₂ (CT)	150	193.8	150/120	151.3	2.4
C ₁ (TCE)	150	170.0	150/60	80.3	4.4
C ₂ (TCE)	150	168.0	150/60	77.1	8.2
				77.9	7.2
				82.8	1.5
				79.0	6.0
Average % Loss = 5.9					

5794A series Gas Chromatograph equipped with an electron capture detector and linked with a Hewlett Packard 3390 A Integrator. The column consisted of 10% squalane of Chromosorb WAW (80/100) mesh, which afforded excellent separation capabilities for this particular VOC work. The operating conditions of the gas chromatograph were as follows: isothermal oven temperature, 67°C (84°C for DCB); injection temperature, 90°C; detector temperature, 275°C. The readings given by the integrator were doubled to account for the 50% dilution.

Preparation of VOC Stock Solutions

Stock standard solutions of the four VOC's were prepared from which aliquots were drawn to introduce into the batch bottles. These standards were methanol-based solutions. They were prepared in methanol because the VOC's are only slightly soluble in water. However, they are very soluble in methanol, which, in turn, is soluble in water. The VOC standard solutions were prepared according to the procedure recommended by the USEPA (Federal Register, 1979).

There was some concern by the researchers that the methanol itself may have some affinity for the various sorbents, thereby competing with the VOC's for adsorption sites. Research by Manes [58] suggested that methanol adsorption onto carbon was negligible and therefore would not interfere with the VOC adsorption. Tests were

conducted, however, to confirm the findings of Manes. The tests were run using two different methanol concentrations. The test solutions were made at approximately 6.5 mg/l and 340 mg/l total organic carbon. These solutions were put into 120 ml serum bottles and dosed with varying amounts of activated carbon. The bottles were then shaken and the water analyzed to determine if any changes in TOC concentration occurred. The analyses were performed with a Dohrmann DC-80 Total Organic Carbon Analyzer system. The results of these tests are presented in Table 3. These observations indicate that little or no methanol adsorption occurred, and hence would not compete for adsorption sites.

Sorbates

The compounds studied in this research--PCE, DCB, TCE, and CT--are among a group of volatile organic compounds being considered by the EPA for inclusion in the group of chemicals regulated by maximum contaminant level (MCL) standards. Reports published by the EPA indicate that all four of these are toxic and possibly carcinogenic.

These compounds were chosen on the basis of their frequency of occurrence and their chemical and physical properties. TCE and PCE are the most commonly found VOC's in contaminated groundwater [2]. DCB and CT also occur quite frequently. The investigators also wanted to look at compounds from the same homologous grouping (PCE and TCE),

Table 3. Adsorption of methanol onto activated carbon.

Sample	Activated Carbon Dosage (mg/l)	Reading (mg/l TOC)
Control A1	0	341.2
Control A2	0	346.4
Test bottle A1	1000	338.3
Test bottle A2	1200	334.5
Test bottle A3	1500	339.4
Control B1	0	6.59
Test bottle B1	167	6.53
Test bottle B2	333	6.72

compounds from different homologous classes but similar solubilities and octanol water partition coefficients (PCE and TCE vs. CT), and compounds with different structures and different properties (PCE, TCE, and CT vs. DCB). Physical and chemical properties of the four compounds are given in Table 4 [59]. All of these compounds are nonpolar and therefore hydrophobic.

Tetrachloroethylene, C_2Cl_4 , is also known as perchloroethylene, 1,1,2,2-tetrachloroethylene, ethylene tetrachloride, and by a number of trade names [39]. It is a colorless, nonflammable liquid which is produced commercially by chlorinating acetylene or ethylene dichloride. It is widely used as an industrial solvent, in dry cleaning, textile dyeing, metal degreasing, and in the synthesis of fluorocarbons.

Para-dichlorobenzene, $C_6H_4Cl_2$, or 1,4-dichlorobenzene, occurs as colorless or white crystals under normal conditions. It is used as an insecticide, a preservative for furs, wool and rugs, a deoderant, a solvent, and as an intermediate in the manufacture of some resins.

Dichlorobenzene is regulated by the Safe Drinking Water Act, the Food, Drug, and Cosmetic Act, and the Pesticide Control Act. It is soluble in water at concentrations that are toxic to fish. Prolonged exposure to its vapors can cause headaches, nausea, and vomiting in humans [8].

Table 4. Comparative adsorbate data.

Parameter	PCE	DCB	TCE	CT
Molecular weight	165.8	147.0	131.5	153.8
Density	1.62	1.46	1.46	1.59
Boiling point	121	173	87	77
Solubility (mg/l)*	150	49	1100	1160
Vapor pressure (mm Hg)	19	-	74	91
Henry's constant*	1.10	0.1	0.49	1.20
Log K_{ow}	2.60	3.39	2.29	2.72

* At 20°C.

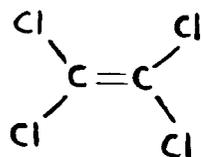
Trichloroethylene, C_2HCl_3 , is a heavy, clear, colorless liquid used principally as a powerful degreasing solvent. It is produced by chlorinating ethylene or acetylene. U.S. production of TCE was 234,000 tons in 1980. However, stringent regulations and controls have led to a decrease in its use. TCE is considered a carcinogen, and its EPA recommended level is zero [5].

Carbon tetrachloride, CCl_4 , is an aliphatic hydrocarbon used mainly in the production of fluorocarbons and as an industrial solvent. U.S. production of CT was 429,000 tons per year prior to 1970. In 1970, carbon tetrachloride was banned from all consumer products in the United States. In 1978 its use as an aerosol propellant was prohibited. See Table 4 for comparative absorbate data. Figure 1 presents the chemical structure of the four compounds.

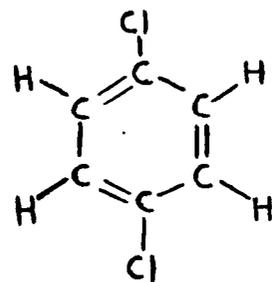
Adsorbents

The adsorbents used in this study were chosen with a focus on two areas of concern involving adsorption phenomena: (1) the movement of non-polar organic compounds through natural adsorbents associated with soils and groundwater regimes; and (2) the treatment of VOC-contaminated water using engineered synthetic adsorbents. The natural adsorbents chosen were aluminum (Al) montmorillonite, a soil-derived humic acid, a peat soil, and a topsoil from Kansas.

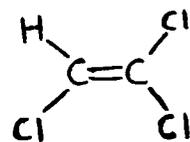
Tetrachloroethylene



1,4-Dichlorobenzene



Trichloroethylene



Carbon Tetrachloride

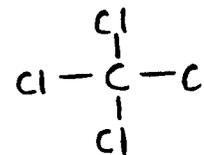


Figure 1. Chemical structures of the VOC's of interest.

The clay, humic acid, and peat were chosen to represent specific soil components which could potentially be involved in the adsorption process. Clays quite often represent a significant fraction of many soils. They are actively involved in ionic exchange mechanisms which can occur in soils. Typically exchanged species include Al^{+3} , Fe^{+3} , Mg^{+2} , and other cations. Reviews of other reported research indicate that the clay would probably not account for a significant amount of adsorption of non-polar volatile organics [29, 34]. However, Rogers et al. have shown that Al-montmorillonite is a more highly adsorbing clay than other clays, e.g., kaolinite or Na-montmorillonite [36]. Therefore, this high adsorption potential clay was chosen to give a maximum estimate of sorption onto clays.

The humic acids represent degradation products of organic material. Highly organic soils are known to be effective in retarding synthetic organic compound migration [22, 23]. It was thought that the humic acids may have shown high adsorption capabilities. Though little research, if any, has been conducted on adsorption by humic materials, these typically large molecules could possibly support a number of substituent groups, some of which may be effective in sorbing the chlorinated hydrocarbons being studied.

The peat soil was chosen to represent the organic component of soils. The organic fraction of soils is

generally accepted to be the predominant adsorbing component for nonionic compounds. The organic fraction, or percentage, is often used with the log of the octanol water partition coefficient of the compound (K_{ow}) to predict the partition coefficient, and thus the retardation factor associated with a particular soil for a particular compound. The peat soil used was determined to have an organic matter content of 80-85%.

The Kansas topsoil represents a true soil, i.e., a composite of all the various components of a soil. It is relatively high in organic matter (about 5%) and was expected to be a highly adsorbing soil. The soil was donated by Woodward Clyde Inc., who also provided a complete physical characterization of the soil.

The synthetic adsorbents represent the types of materials produced and used as adsorption media in the purification of water. Activated carbon is the most widely used material in water purification processes that utilize adsorption. It has been used in industrial, municipal, and domestic applications. This study also looks at two macroreticular resins designed and produced by the Rohm and Haas Corp. These resins are known by their trade names, XAD-8 and XE-340. These resins can be engineered with certain substituent groups which provide active adsorption sites for the adsorbates. The resins can be designed to

adsorb specific molecules, compounds, and classes of compounds. Adsorption by activated alumina was also investigated. It is most often used to remove fluoride and other ions from water. Activated alumina was not expected to adsorb significant amounts of VOC's, but was chosen to complete the experimental matrix. Descriptions of the preparation of each of the adsorbents investigated are presented in the following section.

Adsorbent Preparation

Activated Carbon

Only one activated carbon, Calgon Corporation's Filtrasorb 400, was used in this study. It has a documented ability to remove chlorinated organics from water [60]. A pulverized form (passing a standard 325 mesh sieve) was used so that the kinetics for the batch adsorption tests would be favorable. Filtrasorb 400 is a bituminous coal based carbon. Its surface area is $1100 \text{ m}^2/\text{g}$, as determined by the Brunnauer-Emmett-Turner (BET) nitrogen coverage test. It has a pore volume of $.757 \text{ cm}^3/\text{g}$ and a density of $.811 \text{ g}/\text{cm}^3$.

The carbon was manipulated by means of a slurry prepared in accordance with procedures outlined in the EPA document "Carbon Adsorption Isotherms for Toxic Organics" [45]. The carbon itself was purified and cleaned of fines prior to the slurry preparation. A quantity of the pulverized activated carbon was placed in a beaker with

distilled water and boiled for 20 minutes. The carbon was allowed to settle, and the supernatant was poured off. The wet carbon was then dried in an oven at 103°C for 24 hours and then cooled in a dessicator. Fifty grams of this purified activated carbon was weighed out on a Mettler Analytical Balance and placed in a 1000 ml volumetric flask. The flask was filled to one liter with distilled water, giving a stock slurry with a 50 mg/l concentration. Lower-concentration slurries were prepared by diluting aliquots of the initial stock. Carbon dosages could then be easily metered out by thoroughly mixing the appropriate slurry and pipetting a given amount into the batch bottles. Care must be taken to maintain the slurries in air-tight bottles so that evaporation of water does not increase the slurry concentrations.

Macroreticular Resins: Amberlite
XAD-8 and Ambersorb XE-340

These resins are manufactured by the Rohm and Haas Company. XAD-8 is commercially available, whereas XE-340 is available only for experimental purposes and is not currently available for commercial purposes. A sample of XE-340 was provided by Rohm and Haas for this investigation. Both of these resins were specifically designed for removal of low-molecular-weight organic compounds.

XAD-8 is a nonionic polymeric macroreticular resin with an acrylic matrix. Macroreticular resins have a highly ordered, netlike internal structure. The matrix structure is controlled by the manufacturing process. It has a BET-N₂ surface area of 200 m²/g, a pore volume of 1.43 cm³/g, and a particle density of .445 g/cm³ [48]. The resin used in these studies came from batch 2-4786.

The XE-340 resin is a carbonaceous resin formed by the partial pyrolysis of macroporous polymer beads. It has a BET-N₂ surface area of 400 m²/g, a pore volume of 1.32 cm³/g, and a particle density of .451 g/cm³ [48]. Robeck has claimed that carbonaceous resins are superior to granular activated carbon for removal of volatile halogenated organics such as PCE, TCE, and 1,1-dichloroethane. Uses are limited to narrower ranges of compounds than activated carbon, but better performance may be obtained for these compound types. The resin used was from lot #JJM3597B.

Rohm and Haas state in their product information brochures that these "polymeric adsorbents are industrial grade products and are not intended for use in analytical applications without extensive purification" [61]. Therefore, a purification step was performed on both resins in order to render them suitable for analytical work. The resins were allowed to soak in methanol for one hour while being slowly agitated by a magnetic stirrer. After

settling, the supernatant was decanted. Distilled water was added to wash off the residual methanol. The resin and water was mixed, allowed to settle, and decanted. This was repeated fifteen times to ensure complete cleaning. Afterward, the resin was dried in a 103°C oven for two hours and then cooled in a dessicator.

The resins were manipulated for the batch tests by weighing out variable amounts on the analytical balance and were added to the serum bottles.

Activated Alumina

Alcoa Corporation provided a sample of its F-1 activated alumina for use in these batch tests. This activated alumina is composed of 92% Al_2O_3 and has a pH_{zpc} of 7.9.

The activated alumina was finely ground to render its adsorption kinetics more favorable. It was passed through a 325 mesh sieve to ensure a uniform particle distribution. The alumina powder was then washed with a .01 N NaOH solution and rinsed with distilled water. It was dried for 24 hours at 103°C and cooled in a dessicator. The alumina was introduced by two means: (1) weighing out portions on the analytical balance, and (2) preparing a slurry and pipetting into the batch bottles.

Aluminum Montmorillonite

Based on work reported by Kalimtgis, only one clay type was investigated. Kalimtgis performed VOC adsorption batch tests using kaolinite, Na-montmorillonite, and Al-montmorillonite. He found that these clays showed very little or no adsorption of TCE or CT. Based on these results, only Al-montmorillonite was studied, as it has been shown by Rogers et al. to have a higher sorption capacity than kaolinite or Na-montmorillonite [36].

Al-montmorillonite is not available commercially, as are Na-montmorillonite and kaolinite. Therefore, using procedures outlined by Rogers et al. [36], Al-montmorillonite was manufactured in the lab. Fifty grams of Na-montmorillonite were slowly added to a large beaker containing 500 mg of 1 M $\text{Al}_2(\text{SO}_4)_3$. (It is necessary to mix the clay in slowly, as it is very expansive when hydrated and will clump if not done slowly.) The mixture was then vigorously mixed for five hours. The Al^{3+} ions will readily replace the Na^+ ions due to their stronger attraction for negatively charged sites. After mixing, the clay was allowed to settle and the supernatant was decanted. Distilled water was added, mixed, and decanted to remove residual Na^+ , Al^{3+} , and SO_4^{2-} ions. The Al-montmorillonite sludge was used to develop a slurry whose concentration was determined by gravimetric methods. The batch tests were

conducted by introducing variable amounts of slurry via pipettes into the serum bottles.

Humic Acid

The humic acid used in these experiments is sold by the Aldrich Chemical Company, lot #121137. The humic material was purportedly mined in West Germany. No molecular weight analysis was performed.

The humic acid was also prepared in a slurry form. The slurry was made by vigorously mixing 25 g of humic acid with 500 ml of distilled water for 3 hours. The humic acid was initially difficult to maintain in suspension due to clumping of the fine particles. However, the prolonged vigorous mixing broke the clumps apart and produced an easily handled slurry amenable to pipetting.

Peat

The peat used in these tests was a bacterially activated peat mined in Michigan by the Michigan Peat Company. Because the peat was used to represent the organic fraction of soils, it was necessary to determine its organic content.

Five weighing pans were preweighed, filled with peat, and weighed again. The pans were allowed to sit in a 180°C oven to drive off water and were then weighed again to determine the total moisture content. The pans were then

placed in a 550°C oven for one hour. At this temperature all the organic material was combusted. The pans were weighed again, and the organic content was determined by the difference from the previous weighings. The results of these determinations are shown in Table 5. The average peat content was 85.2%, and the average water content was 13.2%. The peat was employed in the batch mode experiments by weighing out variable amounts of dried peat.

Natural Soil

Woodward Clyde Consultants provided this study with a sample of topsoil from the state of Kansas. The soil characterization is provided in Table 7. The organic matter content is approximately 5%, which is relatively high for natural soils. The moisture content was determined in the laboratory to be 16.0%.

Two approaches were used in the soil batch tests. The first, following procedures detailed by Fuller [62], involved drying and grinding the soil to obtain particle sizes passing a 2 mm sieve. The second approach entailed using the soil as is, without drying and grinding. This latter approach was used to more closely simulate natural soil conditions. No significant differences in adsorption behavior were observed between the two approaches.

Table 5. Moisture content and organic matter content of peat and soil.

Sample	% Moisture	% Organic Matter
Peat 1	13.2	83.4
Peat 2	12.5	86.0
Peat 3	13.4	86.3
Peat 4	13.3	86.1
Peat 5	13.4	84.4
Average:	13.2%	85.2%
Soil 1	13.7	Determined by previous lab analysis. See Table 6.
Soil 2	16.4	
Soil 3	15.3	
Soil 4	18.4	
Soil 5	16.1	
Average:	16.0%	5.3%

Table 6. Kansas topsoil characterization.

Sample*	Organic Content (%)	Gradation Analysis (% Passing)				
		Sieve Size:	4	10	40	80
1	5.0	97.6	97.2	95.8	94.7	93.3
2	5.5	100	99.7	97.7	95.7	94.4

* The soil tested in this adsorption study was a composite of these two samples.

RESULTS AND DISCUSSION

Batch isotherm tests were conducted to determine adsorption of tetrachloroethylene (PCE) and 1,4-dichlorobenzene (DCB) onto a natural composite soil and onto separate soil components, clay, humic acid, and peat. The soil components were selected to determine the most active soil phase in the adsorption of neutral organics.

Based on the analytical approach employed, no adsorption was observed on the clay or on the humic acid. The soil showed a small amount of adsorption of these two compounds, while the peat displayed an appreciable amount of adsorption. These results are in agreement with some studies previously published, but they do conflict with the findings of some other researchers.

Natural Adsorbents

Al-montmorillonite

Only one batch test was run with Al-montmorillonite, that using DCB as the potential adsorbate since its lower solubility indicated the greatest potential for adsorption. The initial DCB concentration was 1.07 mg/l. The clay loadings were 3.85 g/l, 6.17 g/l, and 15.03 g/l. Gas chromatograph analyses showed that no measurable DCB was

The experimental conditions of this study varied from those of the other researchers. Hutzler et al. used clay loadings ranging from 6 to 125 g/l and solute loadings of .15 to 75 mg/l [34]. Both of these loading ranges were quite different from those employed in this research. Rogers et al. used contact times of up to 136 hours to develop their isotherms, as compared to the 24-36 hour contact times employed here [35].

Other researchers have used sophisticated isotopic analyses to achieve mass balance controls. Means et al. labeled their compounds with C^{14} and H^3 tracers to keep experimental errors low. Not only were techniques such as these unavailable, they were not desirable, as the intent was to obtain relevant data via readily accessible methods.

Humic Acid

The humic acid results showed no measurable adsorption of either PCE or DCB. These results are in agreement with those reported by Kalimgtis for TCE and CT [5]. No other studies were found dealing with humic acid adsorption of neutral organics. Humic acids are generally large, charged, amorphous molecules which support a variety of functional groups. The main adsorption mechanism, therefore, would likely be some type of chemical adsorption, i.e., based on a functional group interaction. Though this

may have occurred to some extent, it was not significant enough to measure.

Soil

The Kansas topsoil showed some adsorption of PCE and DCB, as indicated in Figures 2 and 3. About 19% of the available PCE and 6% of the DCB was adsorbed onto the soil. Hutzler et al. also observed uptake of DCB onto a soil with similar organic matter content, about 5% [34]. No competitive tests were conducted on the soil, as the low uptake would have precluded observing competitive effects.

Peat

Peat was used as an adsorbent so as to typify the organic matter of a soil, i.e., that component acknowledged to be responsible for neutral organics adsorption onto soils. This peat contained about 85% organic matter and therefore was an adequate representation of that soil fraction.

The peat adsorbed significant amounts of both PCE and DCB. About 90% of available PCE was adsorbed onto 13.3 mg/l peat. Eighty-two percent (82%) of the DCB was adsorbed by 6.7 mg/l peat. Figures 4 and 5 give the Freundlich isotherms for PCE and DCB, respectively. Note that while the peat may ultimately have a greater capacity for DCB, the adsorption of PCE is slightly more favorably, as indicated

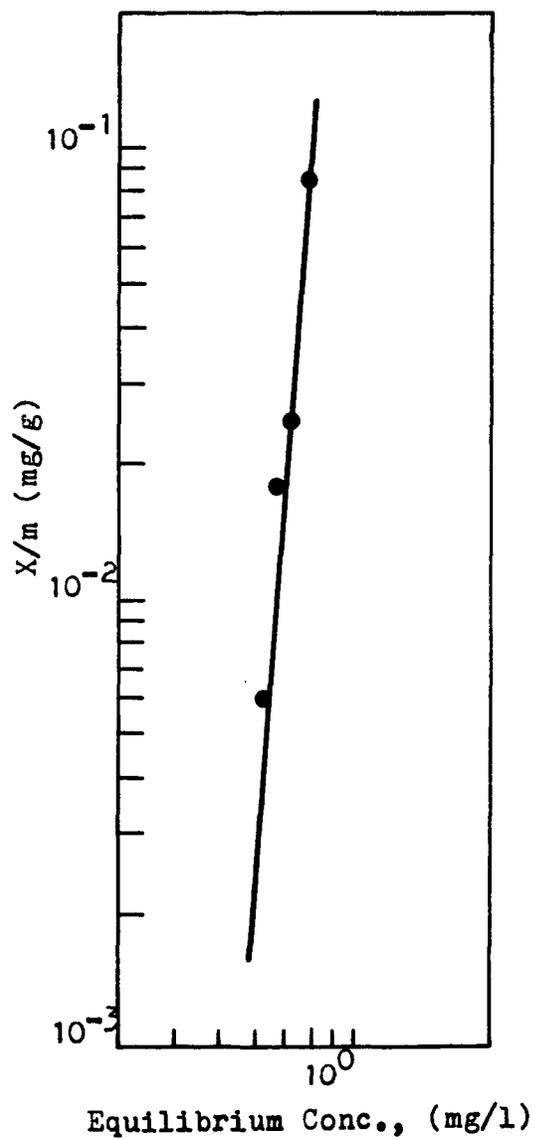


Figure 2. Freundlich isotherm for PCE adsorption onto soil; initial PCE concentration = 0.979 mg/l.

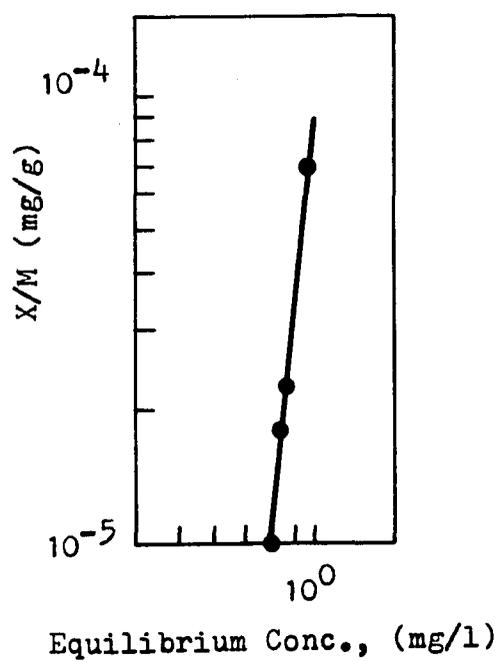


Figure 3. Freundlich isotherm for DCB adsorption onto soil; initial DCB concentration = 1.078 mg/l.

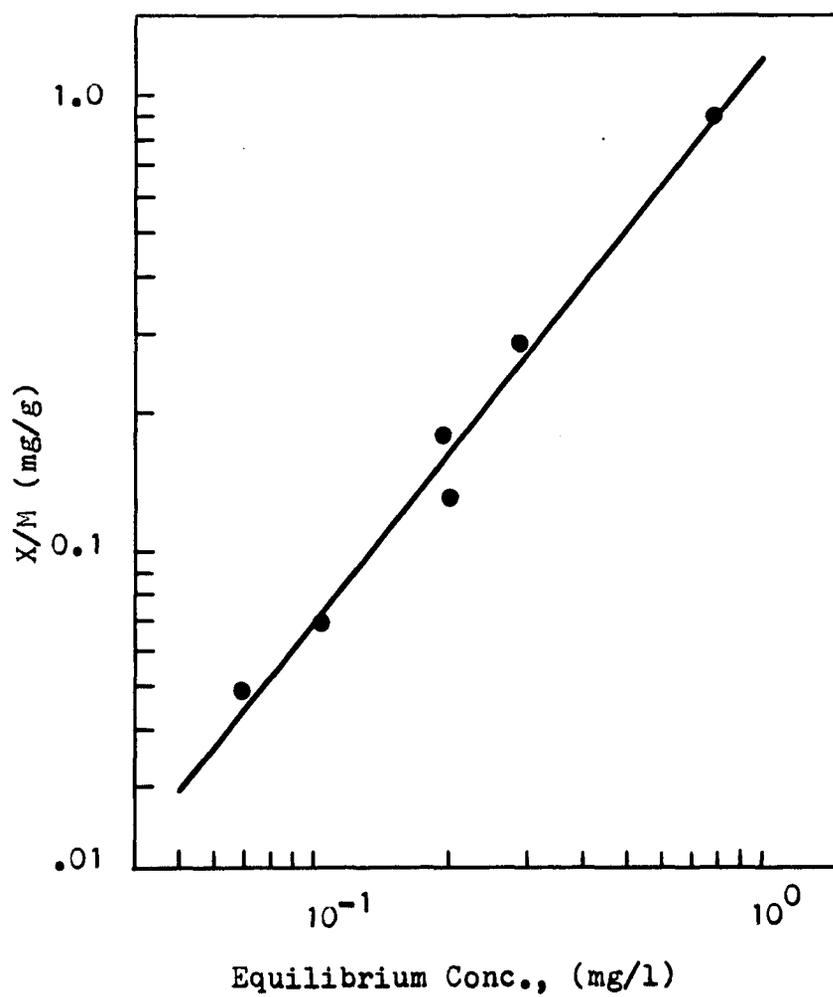


Figure 4. Freundlich isotherm for PCE adsorption onto peat; initial PCE concentration = 1.055 mg/l.

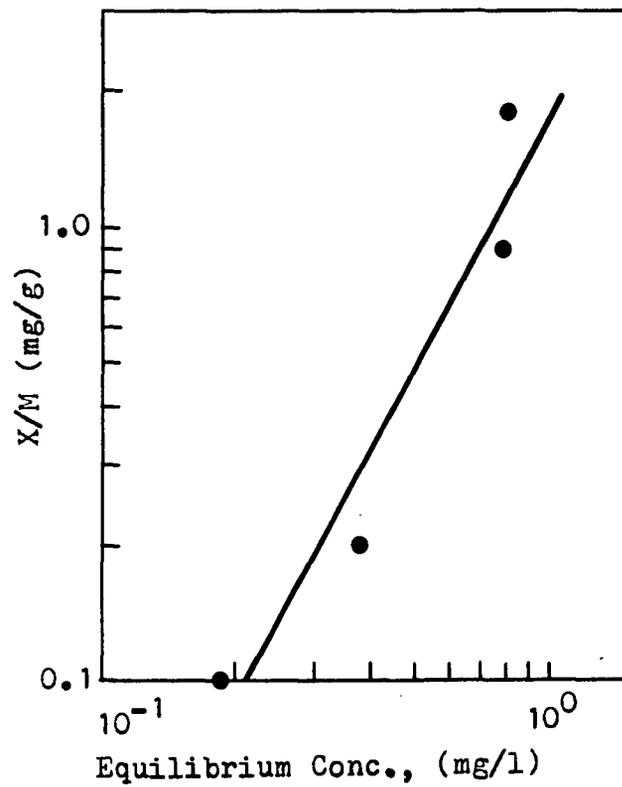


Figure 5. Freundlich isotherm for DCB adsorption onto peat; initial DCB concentration = 1.078 mg/l.

by the smaller slope, the Freundlich $1/n$ value. In other words, the peat absorbs more DCB at higher concentrations, but over the range of concentrations, PCE adsorption is more favorable.

Competitive adsorption tests using peat were performed for PCE and DCB in the presence of each other and in the presence of TCE and CT. The results of each of these tests will be presented, along with an evaluation of the viability of the three predictive models, the Langmuir, Jain-Snoeyink, and simplified IAS, for estimating adsorption competition between VOC's.

Figure 6 shows the Freundlich isotherms for PCE in a single-solute system and PCE in the presence of TCE, a bisolute system. The bisolute system shows a marked decrease in adsorption capacity and favorability compared to the single isotherm. The PCE does adsorb more favorably than TCE, however. The presence of TCE decreased the adsorption of PCE from 90% to 55% on 13.3 mg/l of peat.

Figure 7 gives an arithmetic plot of the single-isotherm and the bisolute and predicted isotherm for PCE in the presence of TCE. The concave upward shape of the isotherms indicates unfavorable adsorption. Only the IAS (Digiano) model was tested, as the data were not amenable to use of the Langmuir and Snoeyink models. Again, it is seen that the effect of the presence of TCE on PCE adsorption in

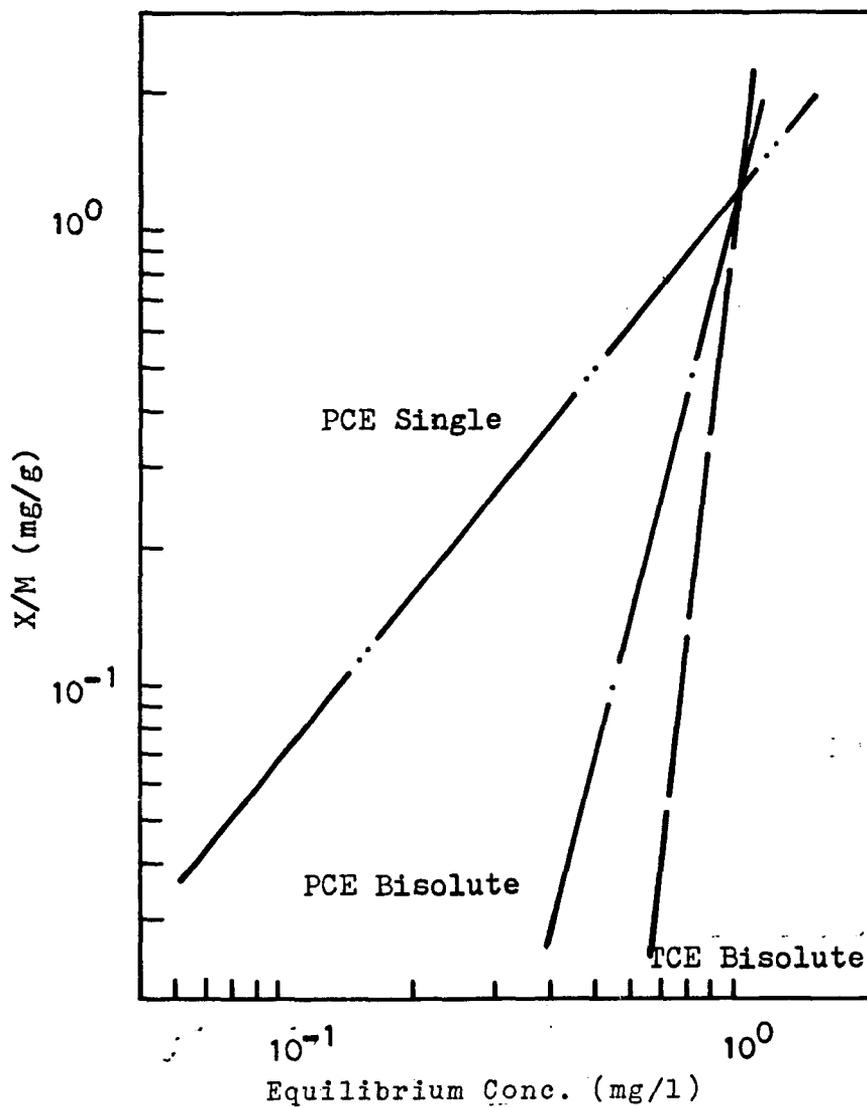


Figure 6. Freundlich isotherm for PCE adsorption onto peat in the presence of TCE; initial PCE concentration = 1.253 mg/l; initial TCE concentration = 1.535 mg/l.

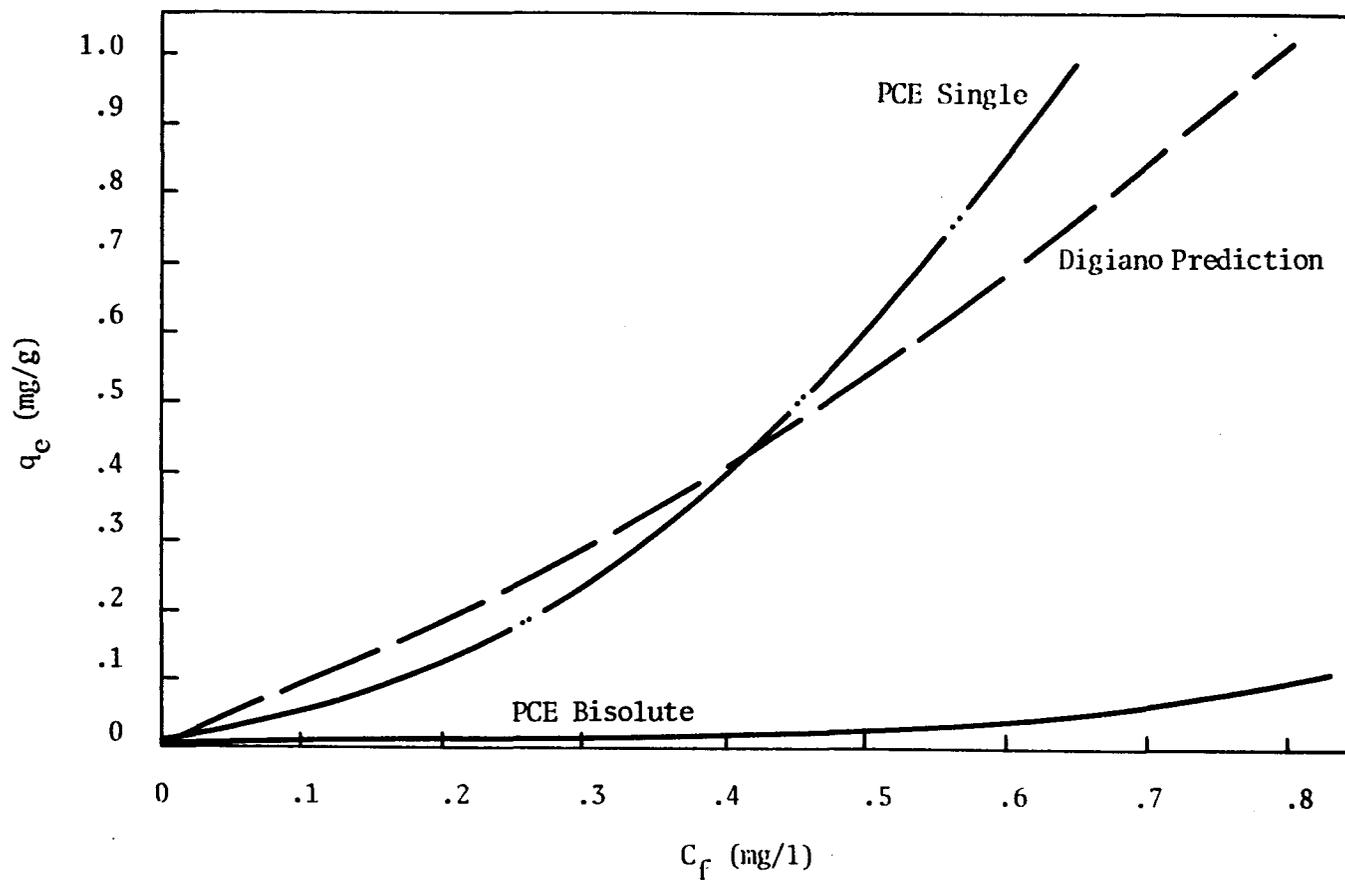


Figure 7. Experimental and predicted isotherms for PCE in the presence of TCE on peat; initial PCE concentration = 1.253 mg/l; initial TCE concentration = 1.535 mg/l.

the significant change of the observed isotherm. The Digiano model poorly represents the experimental data. The model was not able to predict the effect of TCE competition in the system.

Figure 8 shows the adsorption behavior of PCE in the presence of CT on peat. The PCE bisolute isotherm shows much less favorable adsorption than the PCE single-solute isotherm. The steepness of the bisolute slope shows that increase in the sorbent (peat) loading had little effect on decrease in the PCE concentration in the water. The PCE adsorption decreased from 90% to 78% in the presence of CT. Obviously CT was less competitive than TCE.

Figure 9 shows the arithmetic plots for the observed PCE/CT/peat isotherms and the Digiano prediction. Again, the prediction was poor, except at low concentrations.

In Figure 10 are the Freundlich isotherms for PCE and DCB in a bisolute system on peat. The PCE adsorption decreased from 90% to 62%. Note that PCE and DCB had comparable adsorption in single systems and that both decreased almost identically in the presence of each other. Chiou et al. [32] stated that if competition is observed, the actual mechanism of uptake is a site-specific adsorption, as opposed to hydrophobic partitioning. If this hypothesis is appropriate, then there appears to be adsorption occurring and not just partitioning. Also, notice that

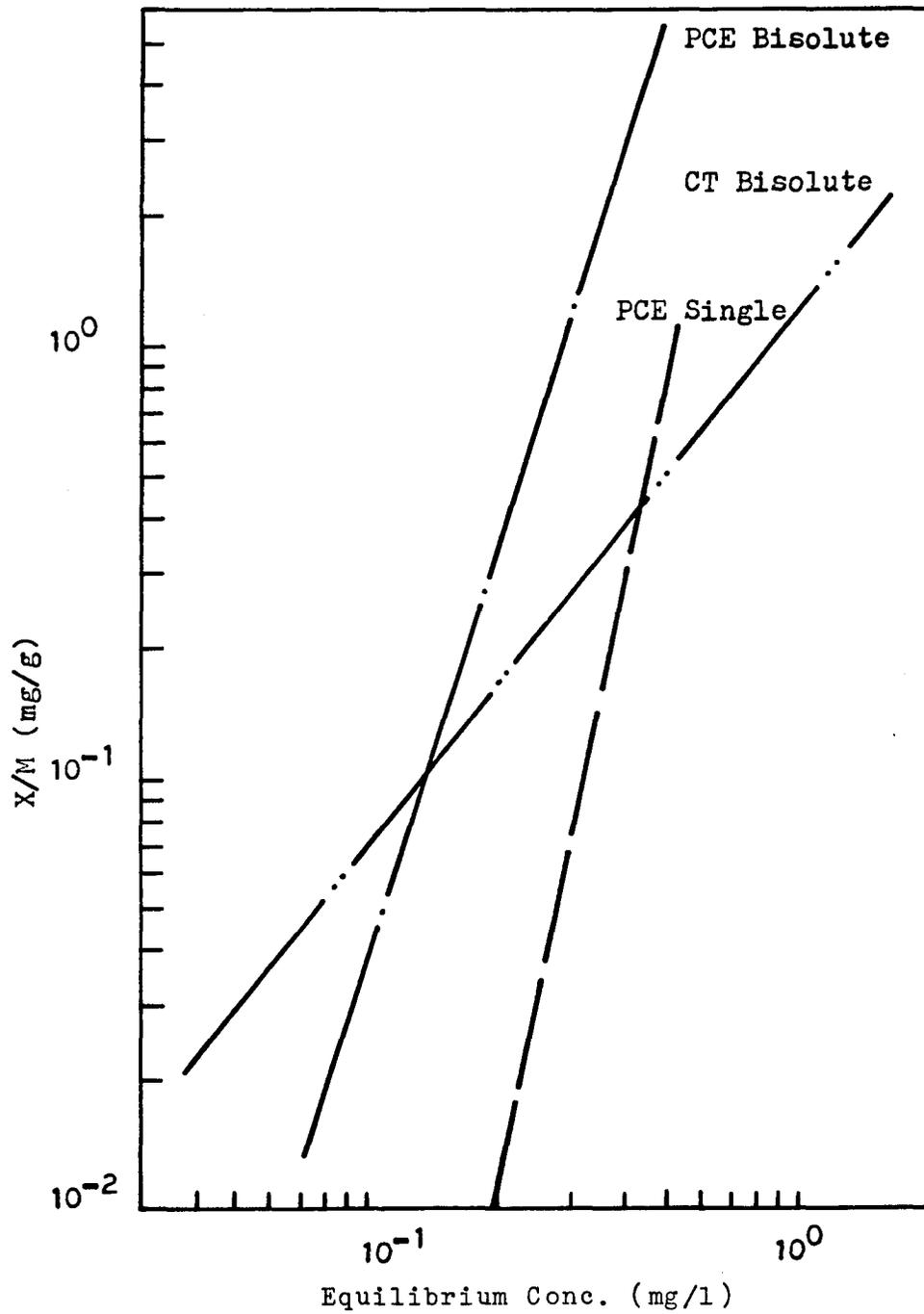


Figure 8. Freundlich isotherm for PCE adsorption onto peat in the presence of CT; initial PCE concentration = 0.958 mg/l; initial CT concentration = 0.587 mg/l.

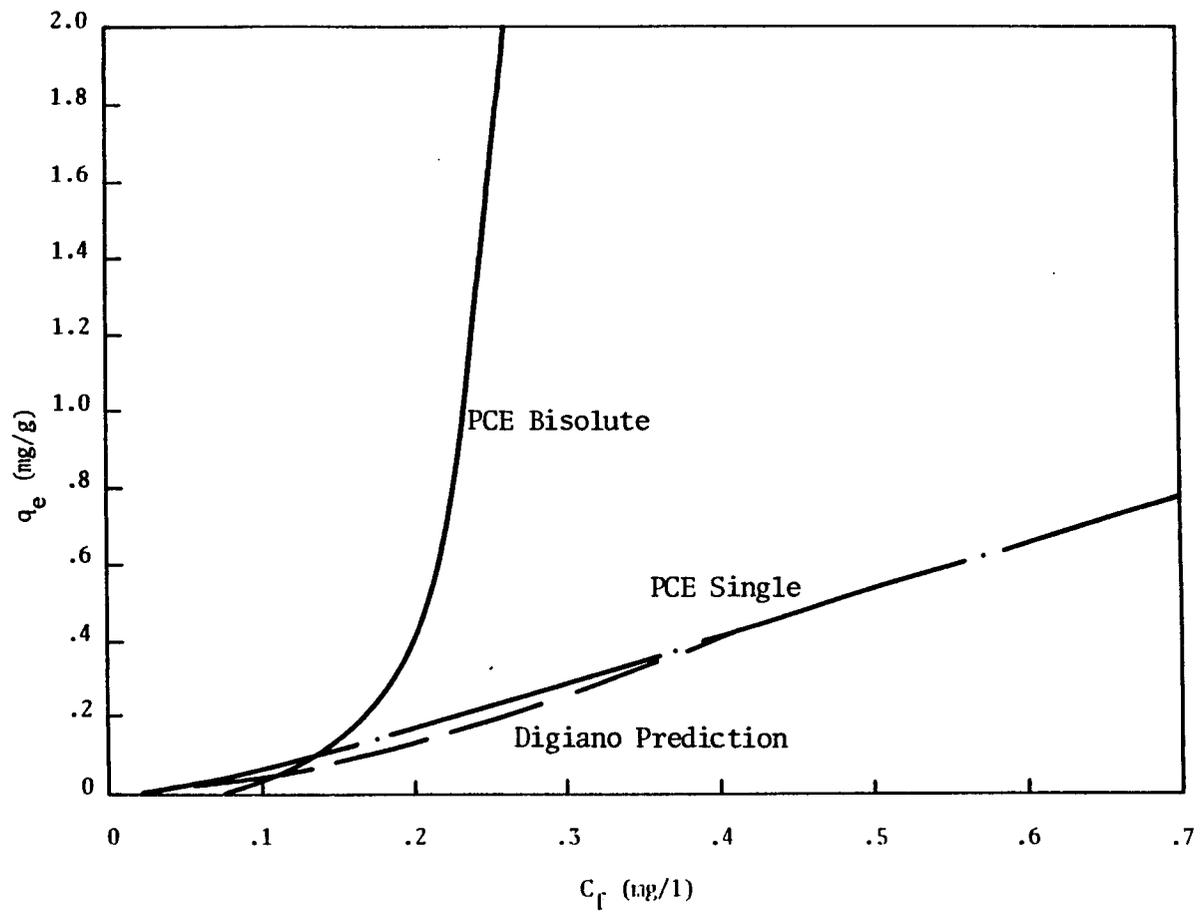


Figure 9. Experimental and predicted isotherms for PCE in the presence of CT on peat; initial PCE concentration = 0.958 mg/l; initial CT concentration = 0.587 mg/l.

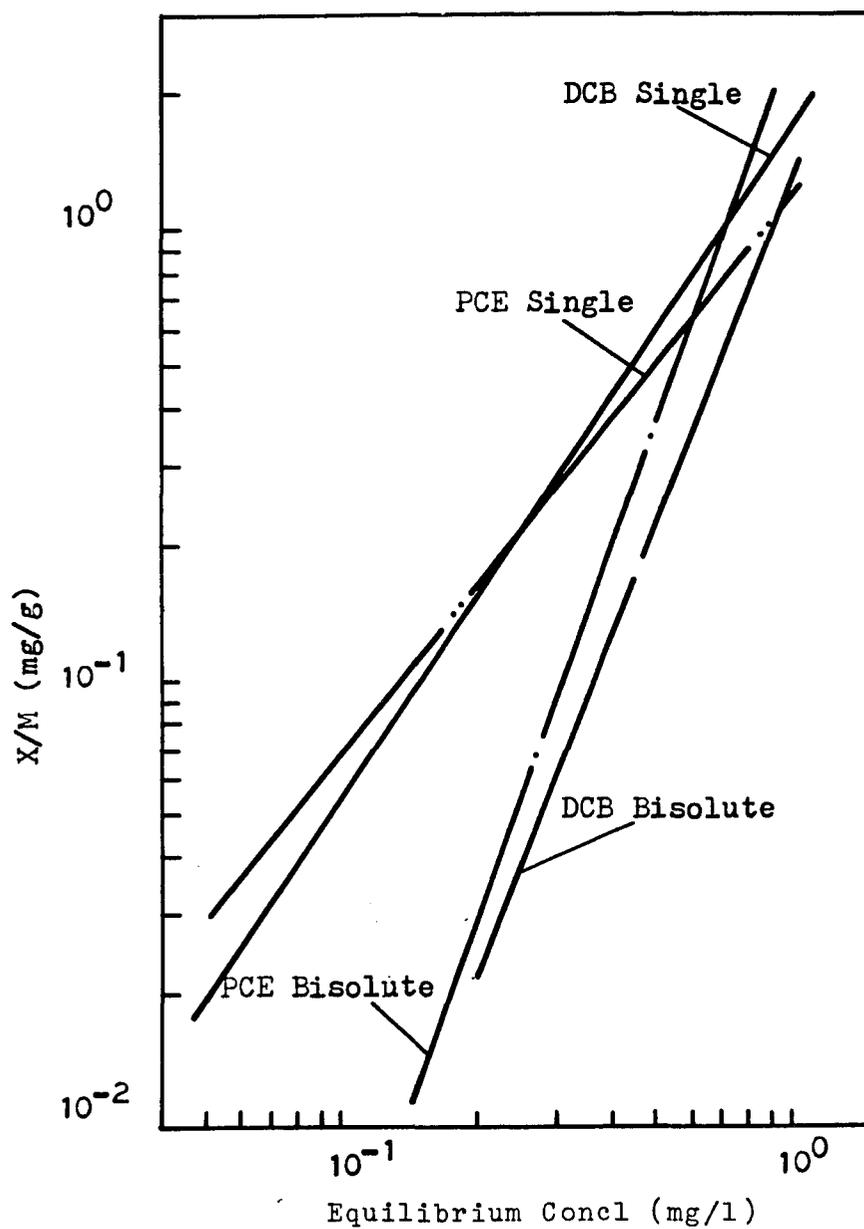


Figure 10. Freundlich isotherms for PCE and DCB adsorption onto peat in the presence of each other; initial PCE concentration = 1.022 mg/l; initial DCB concentration = 0.980 mg/l.

TCE had more effect on PCE adsorption than DCB. TCE and PCE, being structurally very similar, perhaps compete for the same sites, whereas PCE and DCB, though sharing an affinity for some sites, do not compete for others.

The Freundlich isotherms for DCB in the presence of TCE and CT are shown in Figures 11 and 12, respectively. Neither TCE nor CT affect the adsorption of DCB. This trend is indicated by the very steep slopes of the TCE and CT slopes and the similar positions of the DCB single and bisolute isotherms.

The next three figures display the arithmetic plots of DCB in the presence of TCE, CT, and PCE. Figure 13 shows that DCB in a bisolute system with TCE is little affected in adsorption behavior compared with its single isotherm. The Digiano model estimates, although slightly low, predict the actual behavior quite well. The Jain-Snoeyink model predicts the competitive adsorption fairly well, but shows a slightly favorable isotherm, while the actual isotherm is unfavorable.

Figure 14 indicates that the Digiano model again closely approximated DCB uptake, especially in the lower concentration ranges. Figure 15 also shows the Digiano model predicting DCB adsorption fairly well in the presence of PCE. The model tends to dampen any extreme isotherm shapes, but predicts trends quite well. The Digiano model appears

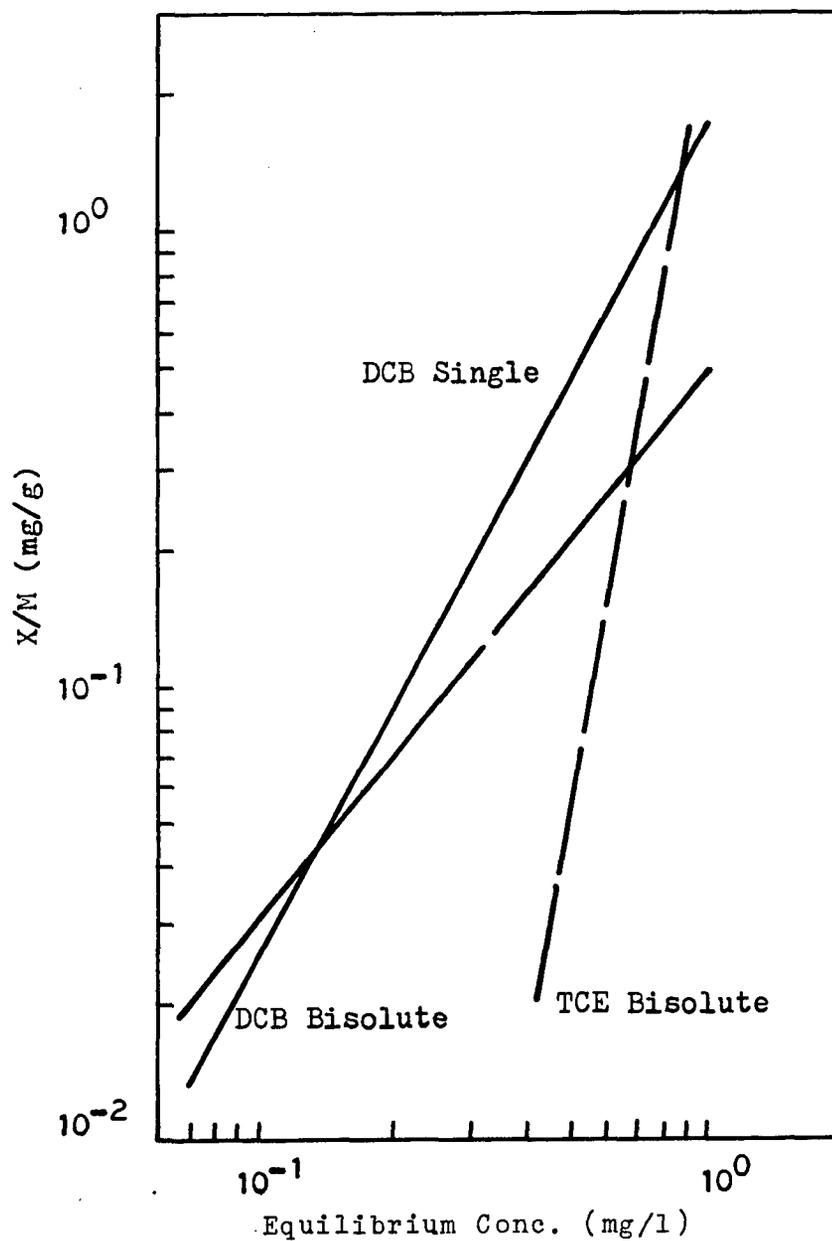


Figure 11. Freundlich isotherm for DCB adsorption onto peat in the presence of TCE; initial DCB concentration = 0.980 mg/l; initial TCE concentration = 1.228 mg/l.

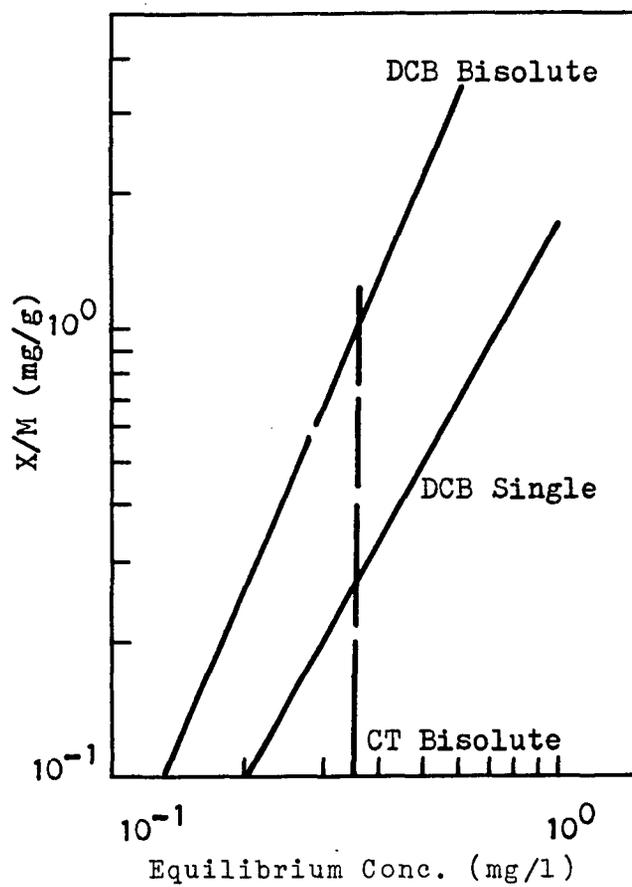


Figure 12. Freundlich isotherm for DCB adsorption onto peat in the presence of CT; initial DCB concentration = 0.900 mg/l; initial CT concentration = 0.527 mg/l.

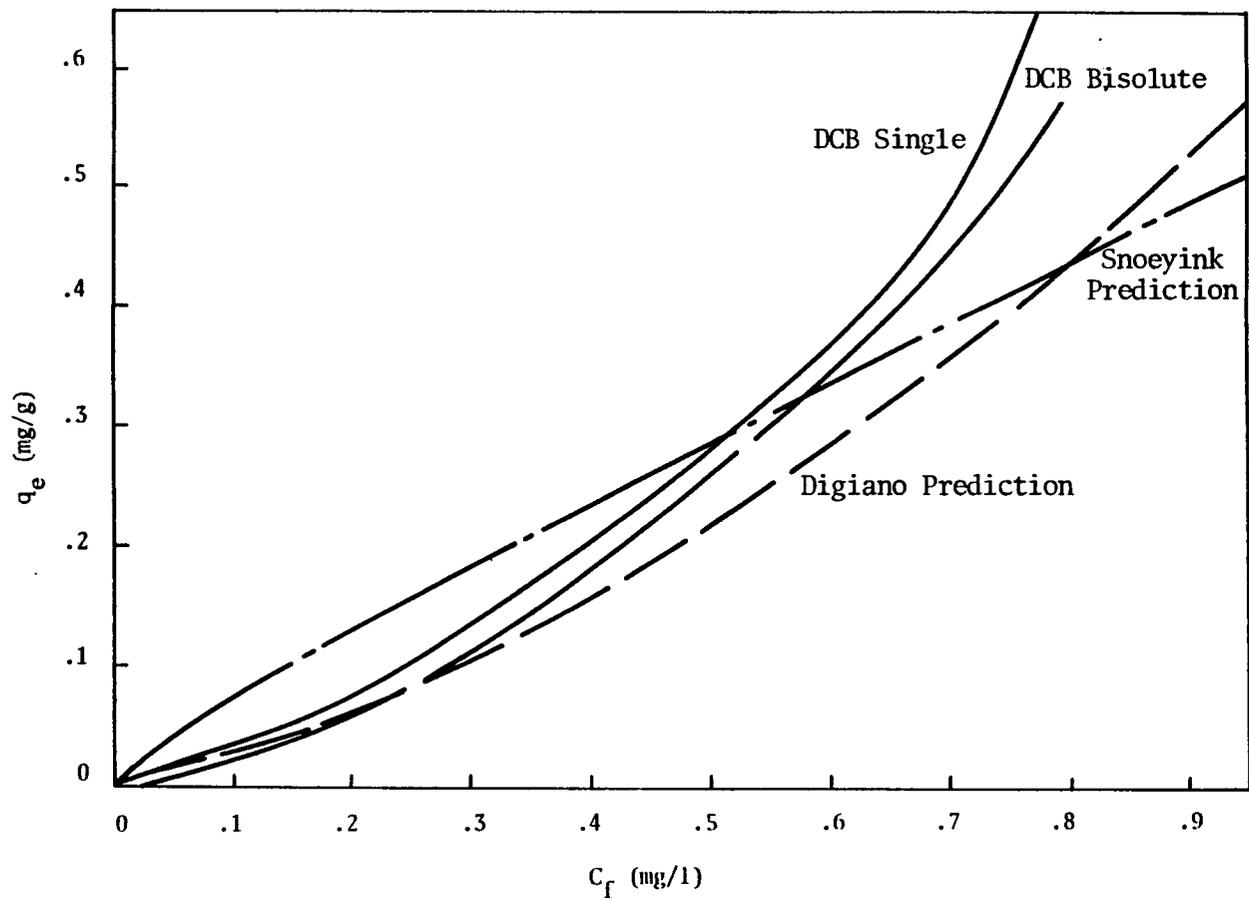


Figure 13. Experimental and predicted isotherms for DCB in the presence of TCE on peat; initial DCB concentration = 0.980 mg/l; initial TCE concentration = 1.228 mg/l.

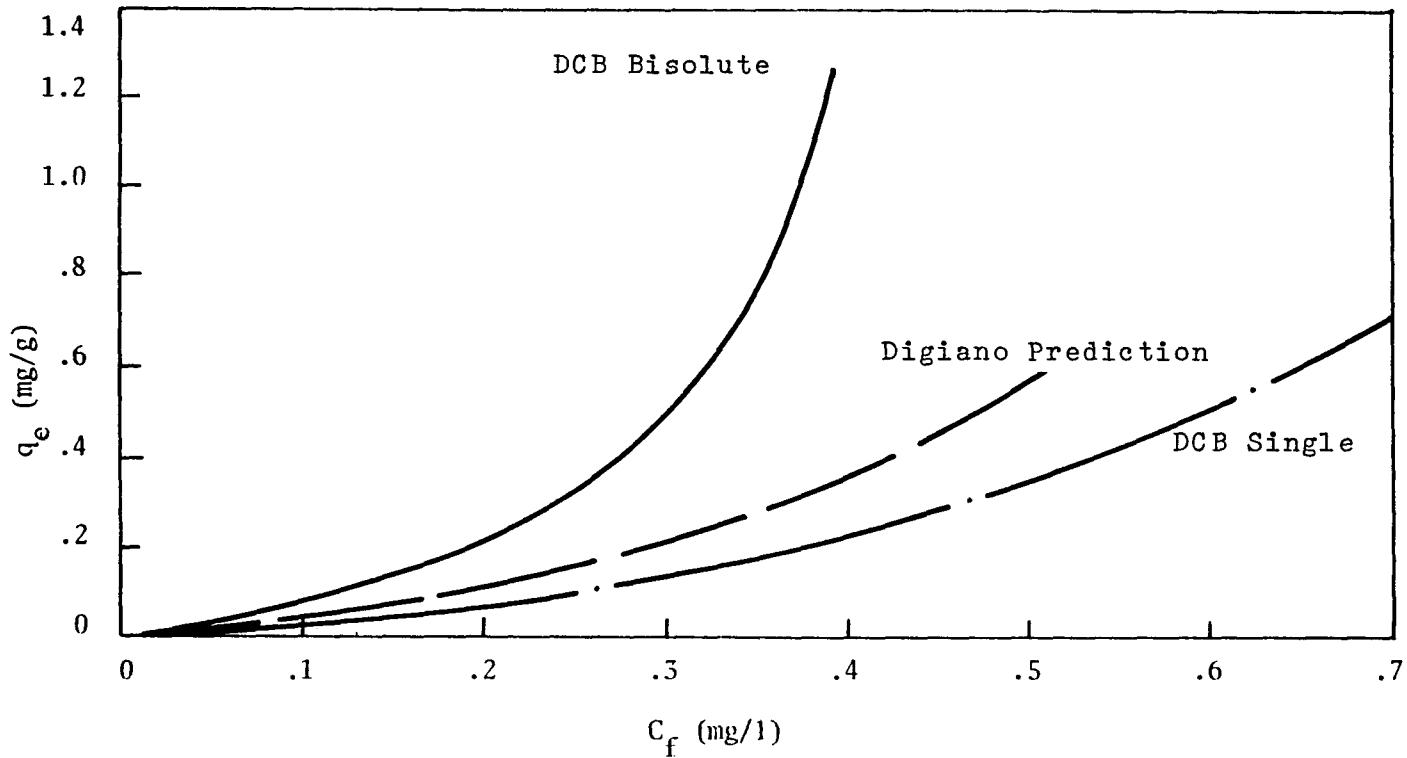


Figure 14. Experimental and predicted isotherms for DCB in the presence of CT on peat; initial DCB concentration = 0.900 mg/l; initial CT concentration = 0.527 mg/l.

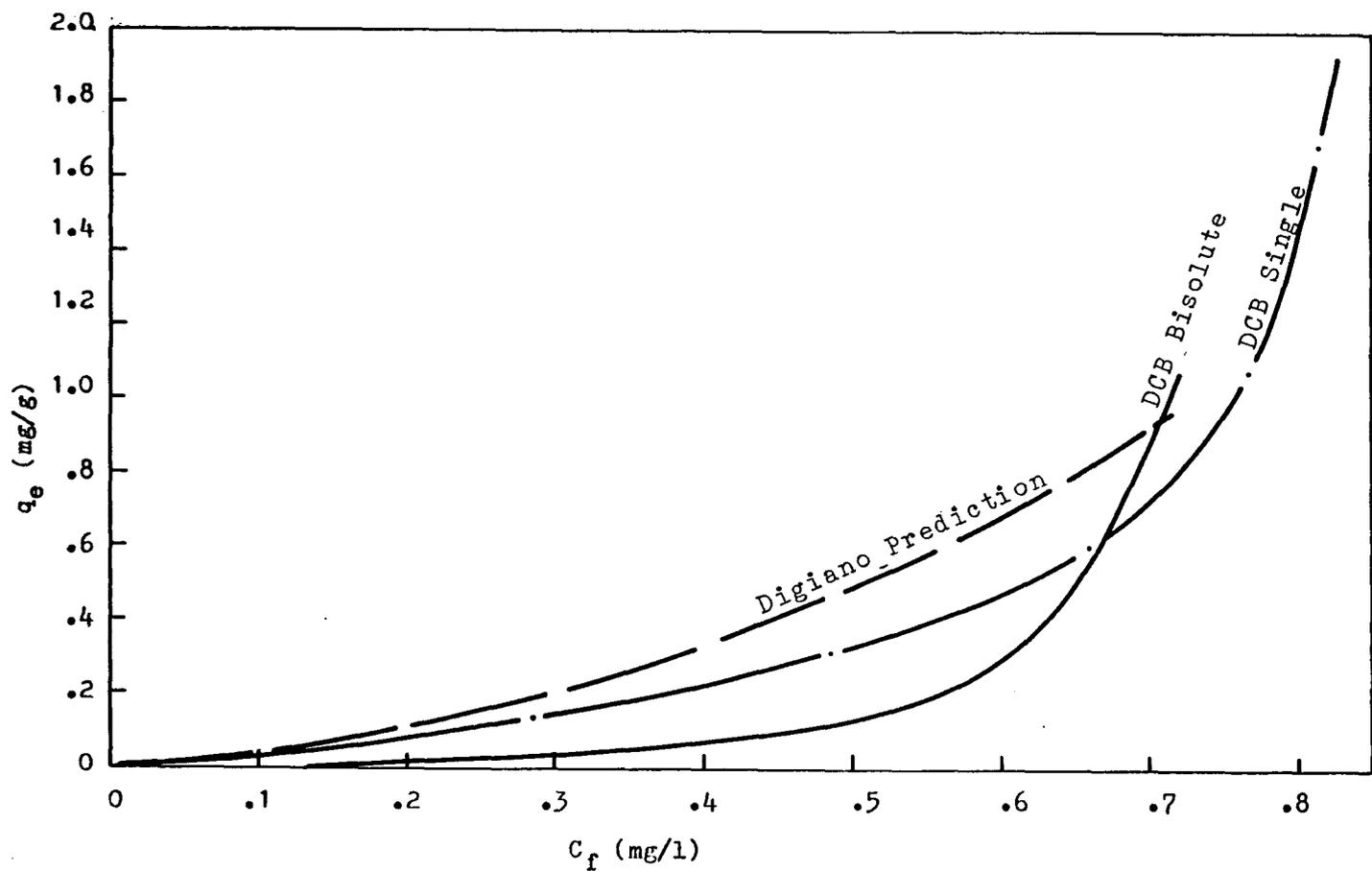


Figure 15. Experimental and predicted isotherms for DCB in the presence of PCE on peat; initial DCB concentration = 0.980 mg/l; initial CT concentration = 1.002 mg/l.

to predict the behavior of more strongly sorbing compounds, such as DCB, quite well. DCB is significantly less soluble than the other compounds and more likely to be adsorbed. Its aromatic structure may also affect its behavior.

The peat adsorption data give insight regarding adsorption onto soils. Neither the humic acid nor the clay displayed any measurable uptake. The natural soil adsorption was low and therefore difficult to run tests on. The peat data, though, displayed some interesting relationships and interactions. First and most obvious is the effect of solubility. PCE and DCB, with solubilities of 150 and 49 mg/l, respectively, were adsorbed to a greater extent than either CT or TCE, which have solubilities of 1160 and 1100 mg/l. This order of magnitude difference in solubilities between the two pairs satisfactorily explains the difference in adsorption. However, solubility does not adequately explain the adsorption differences between PCE and DCB. In fact, in the single-solute systems, PCE adsorbs more favorably than DCB, though its solubility is greater by a factor of 3. In the high concentration range they adsorb almost equally. However, in the lower concentration ranges, PCE exhibits greater uptake by the peat. It appears that solubility is not so important in this lower range; instead, other adsorption mechanisms may be more predominant.

Soil surfaces are quite heterogeneous. They can support a wide variety of functional groups, the nature of which depends on the local geological, biological, and environmental conditions. The functional groups on this particular peat appear to have a greater affinity for PCE than DCB, enough to override the effects of solubility in lower concentration ranges. One simplistic explanation may be that the difference in the molecular structure, i.e., the straight carbon chain of PCE vs. the aromatic ring structure of DCB, renders the PCE more amenable to interaction with the available functional groups.

Note in Figures 6 and 10 the effect of TCE and DCB on PCE adsorption onto peat. The presence of TCE causes a noticeably greater decrease in PCE adsorption than does the presence of DCB. The data of Kalimtgis [5] show that the presence of PCE causes a greater decrease in TCE adsorption than does the presence of DCB also. The point here is that PCE and TCE, which have very similar structures, offer each other more competition than does DCB, despite the fact that DCB is much less soluble. PCE and TCE are competing for the same sites, or functional groups, whereas DCB has little or no affinity for these sites. Therefore, in the higher concentration ranges, solubility (actually solvophobicity) appears to be the main mechanism of uptake. As the concentration decreases, though, the effect of functional

group adsorption (or possibly chemisorption) becomes more and more important.

Synthetic Adsorbents

Batch isotherm tests were also conducted using four different synthetic, or engineered, adsorbents. These sorbents include Calgon Corporation's Filtrasorb 400, a granular activated carbon, Rohm and Haas's Amberlite XAD-8 and Ambersorb XE-340, two macroreticular resins, and Alcoa Corporation's activated alumina. The activated alumina was tested for adsorption of PCE at two different concentrations and showed no uptake propensity for either. Designed for removal of ionic species in water, especially fluoride, the activated alumina was not expected to exhibit significant adsorption. The other three adsorbents, though, all showed appreciable adsorption of PCE and DCB in both single-solute and bisolute systems. A full suite of batch tests was run with these adsorbents to compare their relative abilities in removing these low molecular weight halogenated organics from water.

Activated Carbon

The single-solute Freundlich isotherms for PCE and DCB are presented in Figures 16 and 17, respectively. The Freundlich K value for PCE is 24.9, while that for DCB is 193; they have similar slopes, or $1/n$ values, indicating,

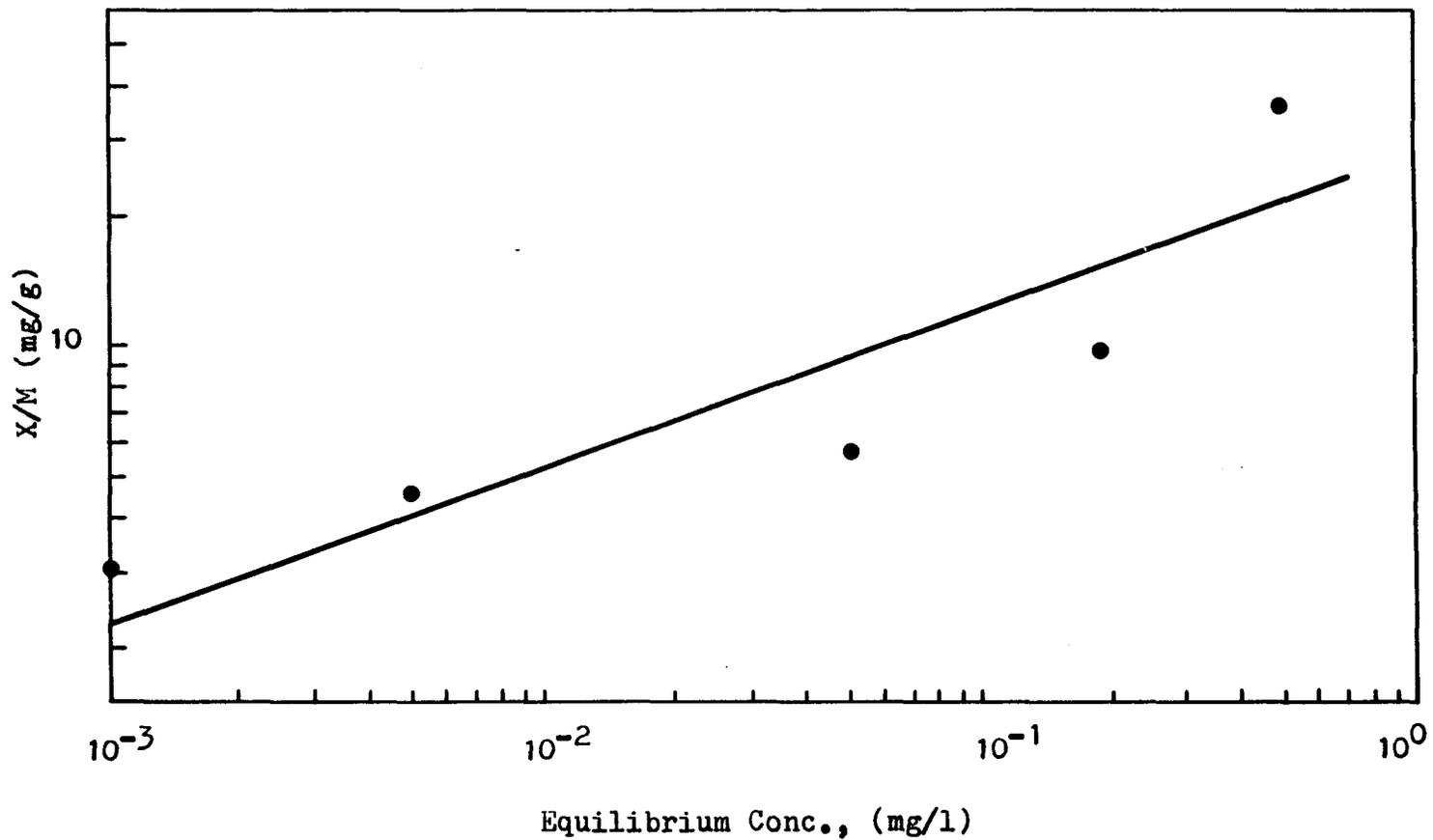


Figure 16. Freundlich isotherm for PCE adsorption onto activated carbon; initial PCE concentration = 0.993 mg/l.

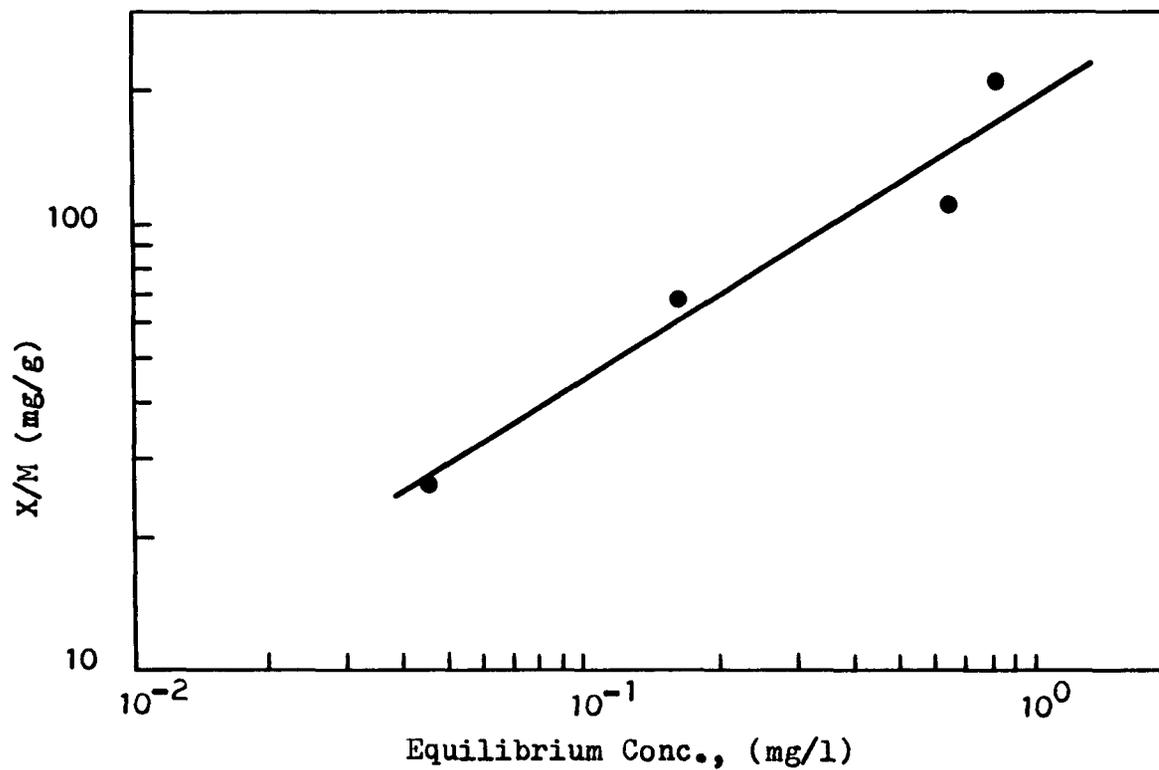


Figure 17. Freundlich isotherm for DCB adsorption onto activated carbon; initial DCB concentration = 1.078 mg/l.

therefore, that the capacity of the carbon for DCB is significantly higher than that for PCE. The reason for this difference is DCB's greater hydrophobicity; in other words, DCB has less tendency to remain in association with the liquid phase than PCE. This hydrophobic partitioning appears to be the primary mechanism of uptake in the batch tests using activated carbon.

The predominance of partitioning as the mechanism of uptake is supported by the findings from the competitive tests. Recall Chiou's observation that a lack of competition indicates partitioning, i.e., there are no individual sites where adsorption occurs, just an extensive nonpolar surface to which the nonpolar compounds will migrate to, resulting in an equilibrium type partitioning between the water and the nonpolar solid [58]. Figure 18 depicts the results of PCE adsorption onto activated carbon in the presence of TCE. The bisolute isotherm, though slightly less favorable in the mid and low concentration, is actually somewhat higher in the higher ranges. This apparent greater capacity may be the result of experimental inconsistencies, but the interpretation remains that very little competition was observed in the presence of the structurally similar TCE. Recall the marked effect that TCE had on PCE uptake onto peat. Also note that PCE adsorbs to

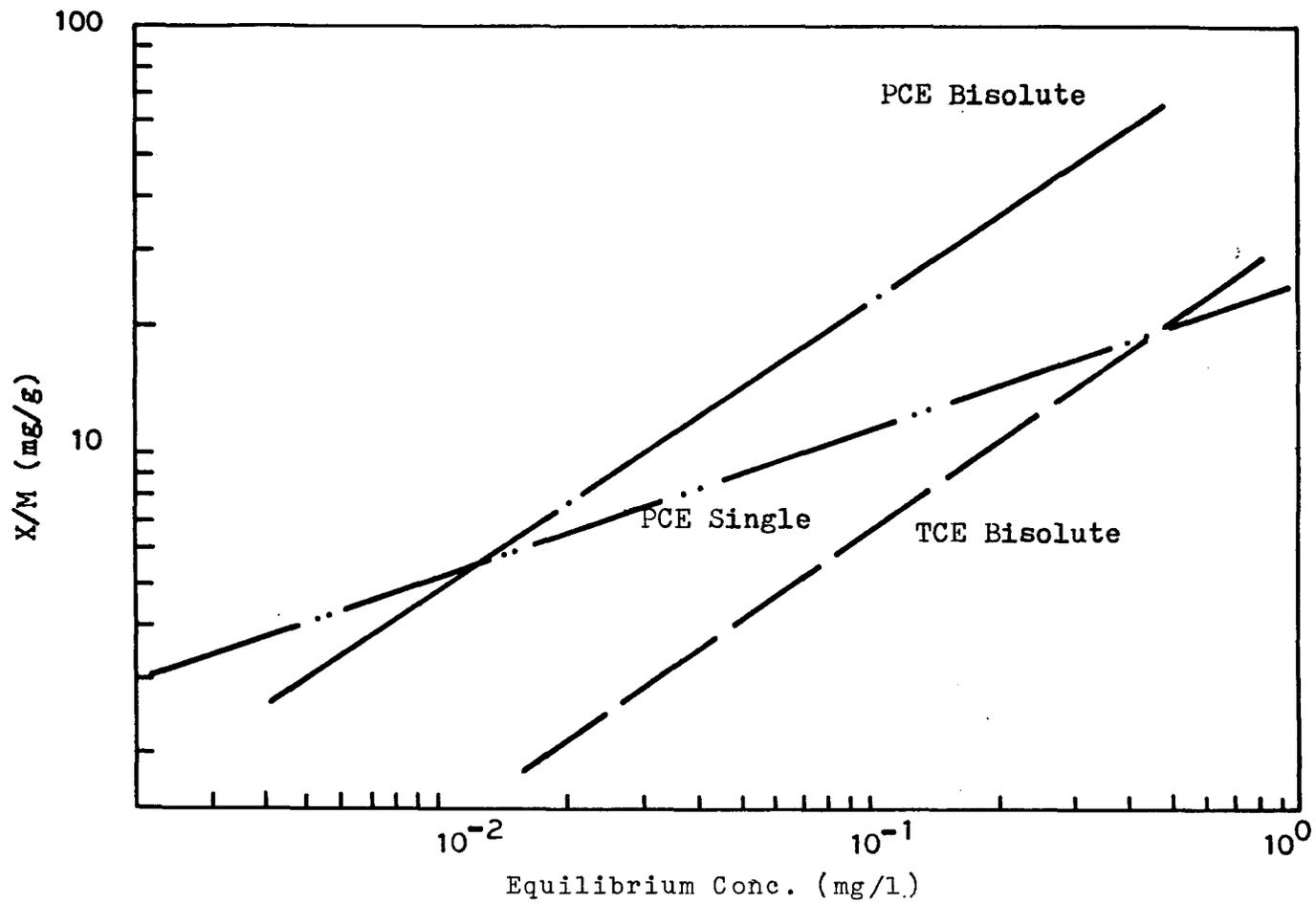


Figure 18. Freundlich isotherm for PCE adsorption onto activated carbon in the presence of TCE; initial PCE concentration = 1.139 mg/l; initial TCE concentration = 1.130 mg/l.

a greater extent than TCE, a behavior anticipated due to its lower solubility.

Figure 19 illustrates this point even more graphically. There is no significant difference between the DCB single-solute and bisolute isotherms. Again, compare the effect that TCE presence had on DCB adsorption onto peat. There appears to be no site competition exerted by TCE; the differential adsorption of the two compounds in the mixture is reflected by the large difference respective solubilities.

Figure 20 presents the single and bisolute isotherms for PCE and DCB in the presence of each other. Again, very little difference is observed between the respective single and bisolute isotherms.

To conclude that hydrophobic bonding, or partitioning, is the only mechanism of uptake occurring in these tests on activated carbon would be inaccurate. Both Kipling and Weber made note of the carbon-oxygen complexes that exist on the edges of the activated carbon surfaces which are potential functional group adsorption sites [9, 11]. However, if these groups are interactive with these VOC's of concern, and if there is competition for these sites, their contribution to the overall adsorption is quite small.

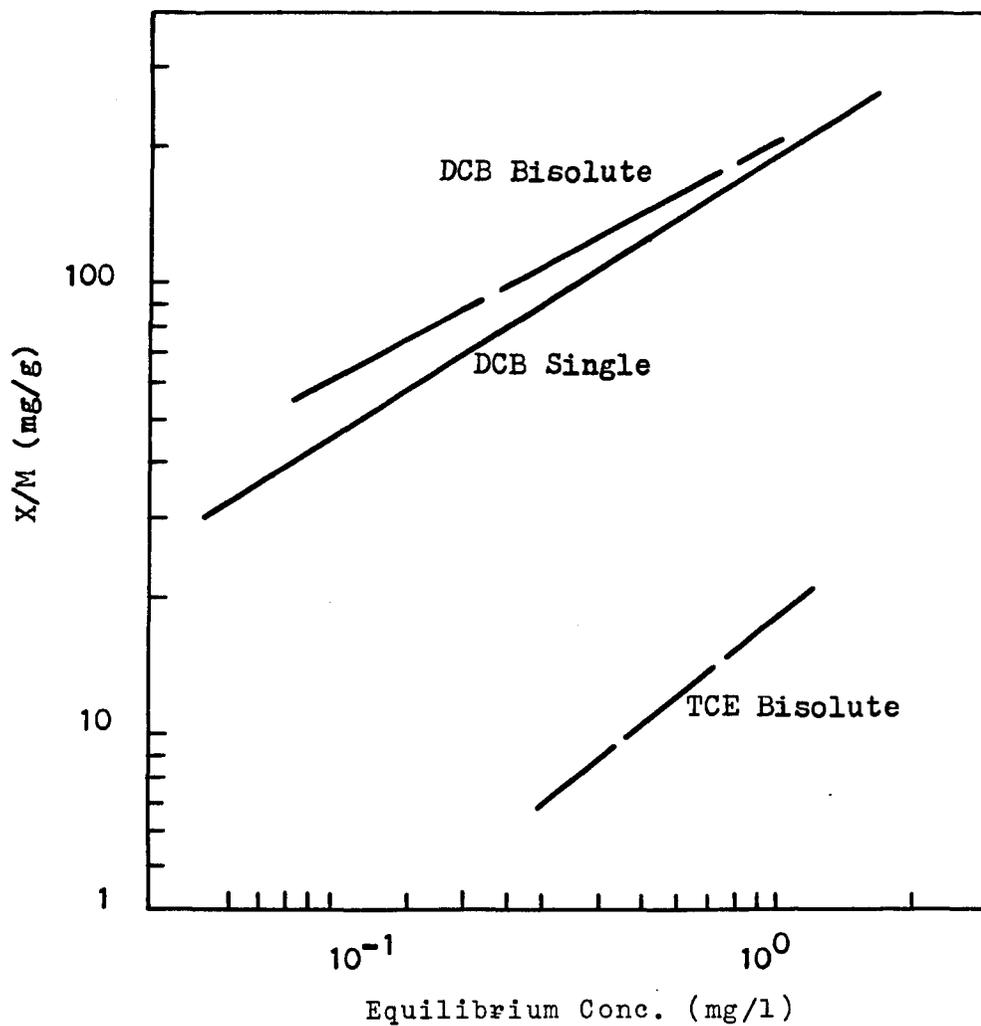


Figure 19. Freundlich isotherm for DCB adsorption onto activated carbon in the presence of TCE; initial DCB concentration = 0.900 mg/l; initial TCE concentration = 0.896 mg/l.

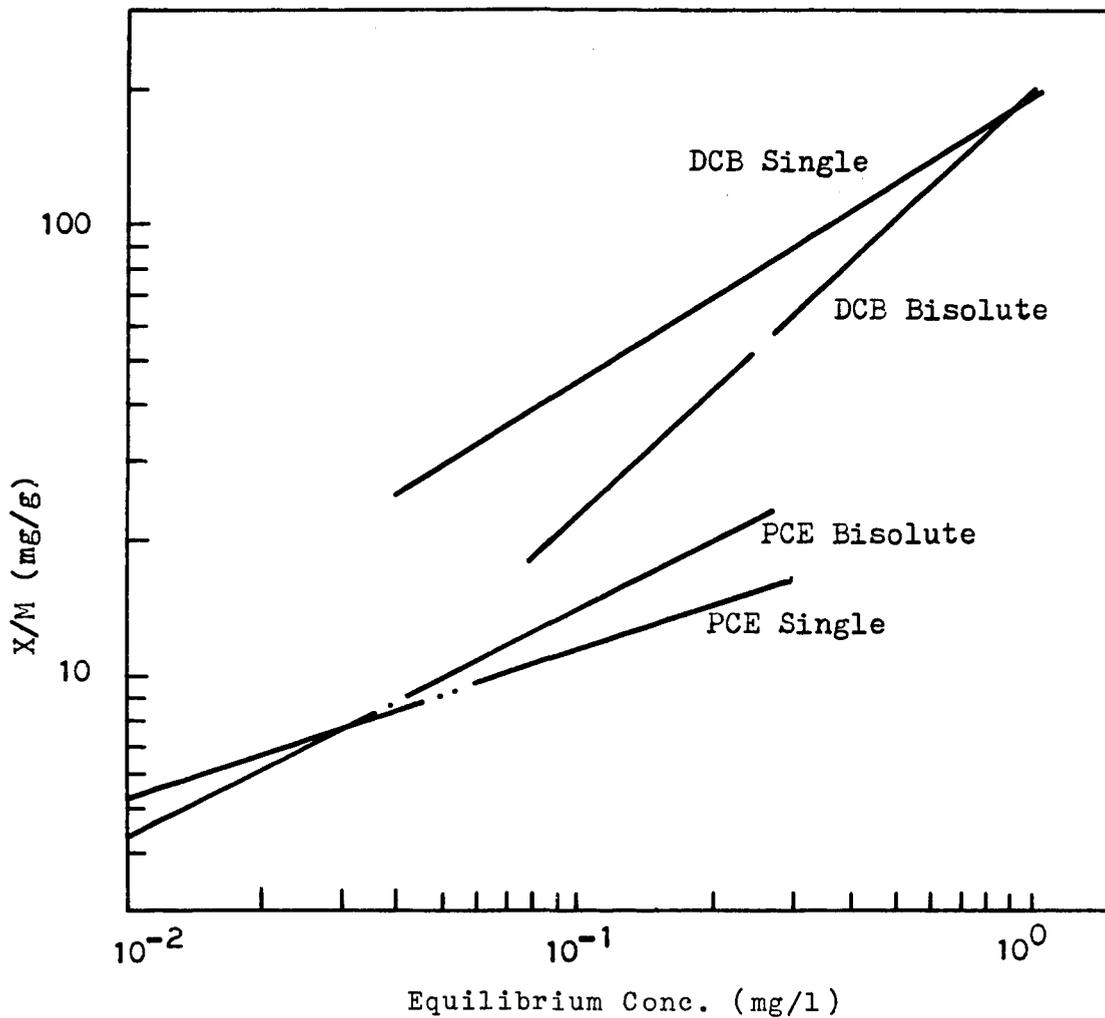


Figure 20. Freundlich isotherms for PCE and DCB adsorption onto activated carbon in the presence of each other; initial PCE concentration = 0.993 mg/l; initial DCB concentration = 1.078 mg/l.

Figures 21 and 22 present the experimental and predicted isotherms for PCE in the presence of TCE and DCB, respectively. In Figure 21, for PCE in the presence of TCE, the Digiano simplified IAS and the Jain-Snoeyink models provide accurate predictions for the lower part of the isotherms. They diverge from the experimental data in the upper range, but in general give good approximations of the adsorption behavior. The competitive Langmuir model, however, gives a very poor prediction. The model's assumptions, i.e., a monolayer of specific adsorption sites and equal energies of adsorption, are much too conservative, and hence, grossly underestimate the observed results.

For PCE in the presence of DCB, as reflected by Figure 22, the Digiano and Snoeyink models do not perform as well. The Snoeyink model is significantly lower in its prediction. The Digiano model simulates the data better, predicting accurately in the lower concentration and loading range, but its predictions level off too early, underestimating the ultimate capacity. Both models do, however, correctly show favorable adsorption, as indicated by the concave downward shape of the curves. The Langmuir model not only predicted very low values; it also indicated unfavorable adsorption, as shown by the concave upward curve.

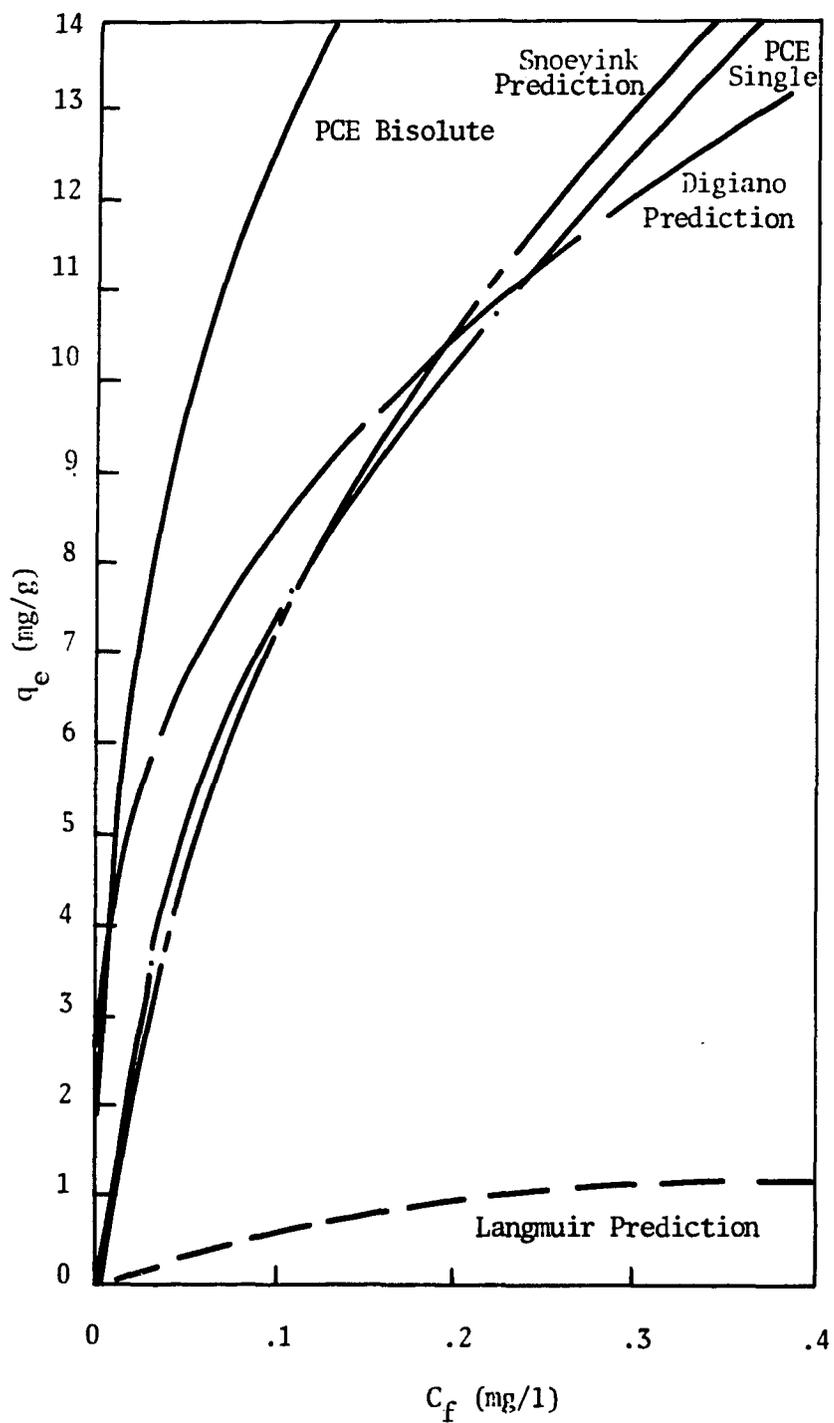


Figure 21. Experimental and predicted isotherms for PCE in the presence of TCE on activated carbon; initial PCE concentration = 1.139 mg/l; initial TCE concentration = 1.130 mg/l.

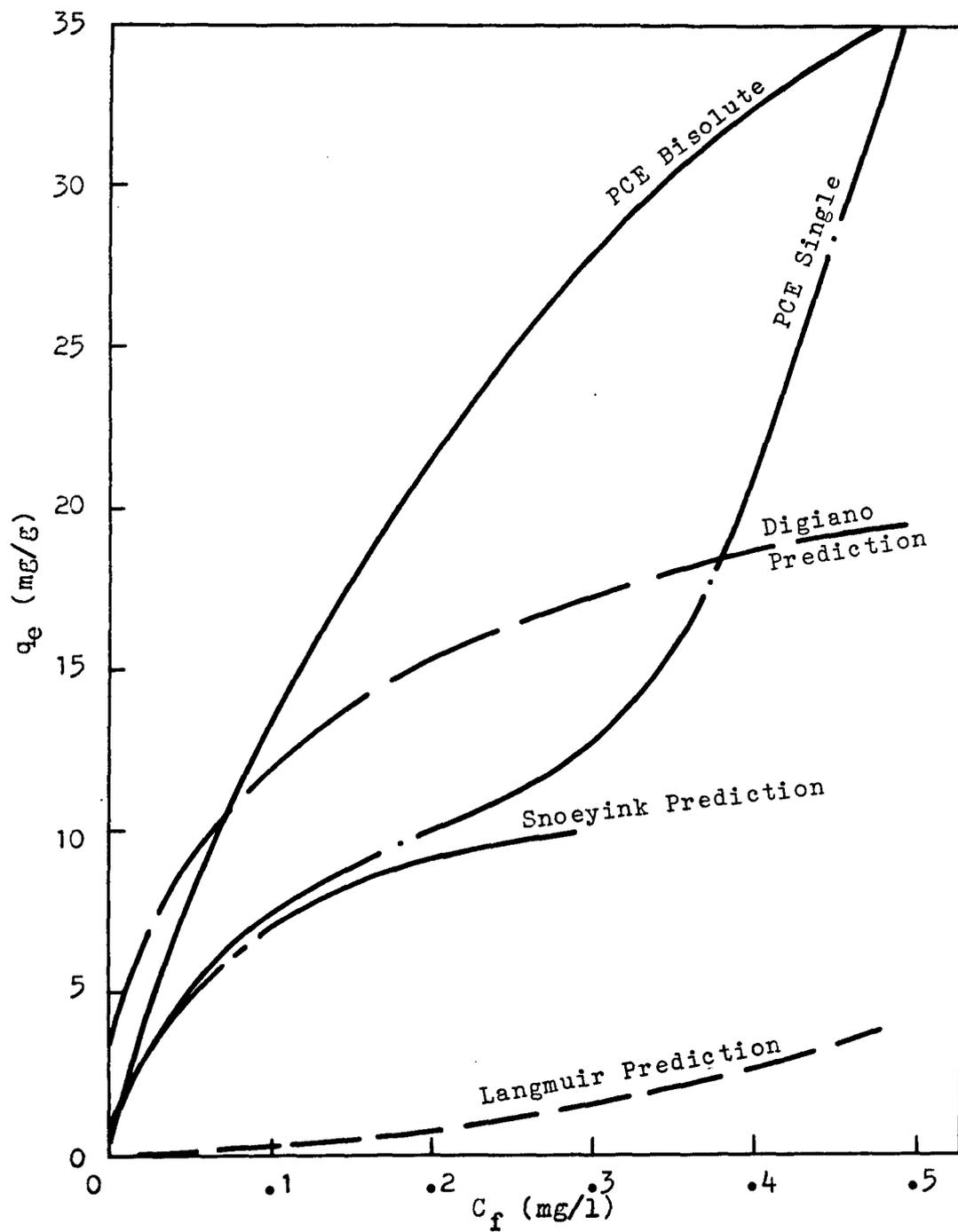


Figure 22. Experimental and predicted isotherms for PCE in the presence of DCB on activated carbon; initial PCE concentration = 0.993 mg/l; initial DCB concentration = 1.078 mg/l.

Figure 23 shows the adsorption of DCB in the presence of TCE. The Digiano and Snoeyink models provide almost identical predictions. Both models accurately predict the trend and shape of the isotherm, but are low in the estimate of ultimate loading. Both predict about 100 mg/g, while the observed data indicate an ultimate capacity of about 275 mg/g. The Langmuir model again was quite inadequate in simulating the data.

Figure 24 gives the isotherm data for DCB in the presence of PCE on activated carbon. Again, the Digiano and Snoeyink models yield similar predictions, this time slightly overestimating the observed results. The model predictions, however, are quite good over the entire range of concentration and loading. Even the Langmuir model predictions are closer to the experimental results. Though its S-shaped curve is not reflected by the data, it does give a good idea of the adsorption trend and capacity.

The candidate activated carbon studied during this research displayed a large capacity for both PCE and DCB, in single-solute as well as bisolute systems. During this research, it was also observed that no significant diminishing of capacity occurred in the presence of other VOC's.

The performance of the predictive models was inconsistent. The Digiano simplified IAS model predicted observed results more accurately and more consistently than

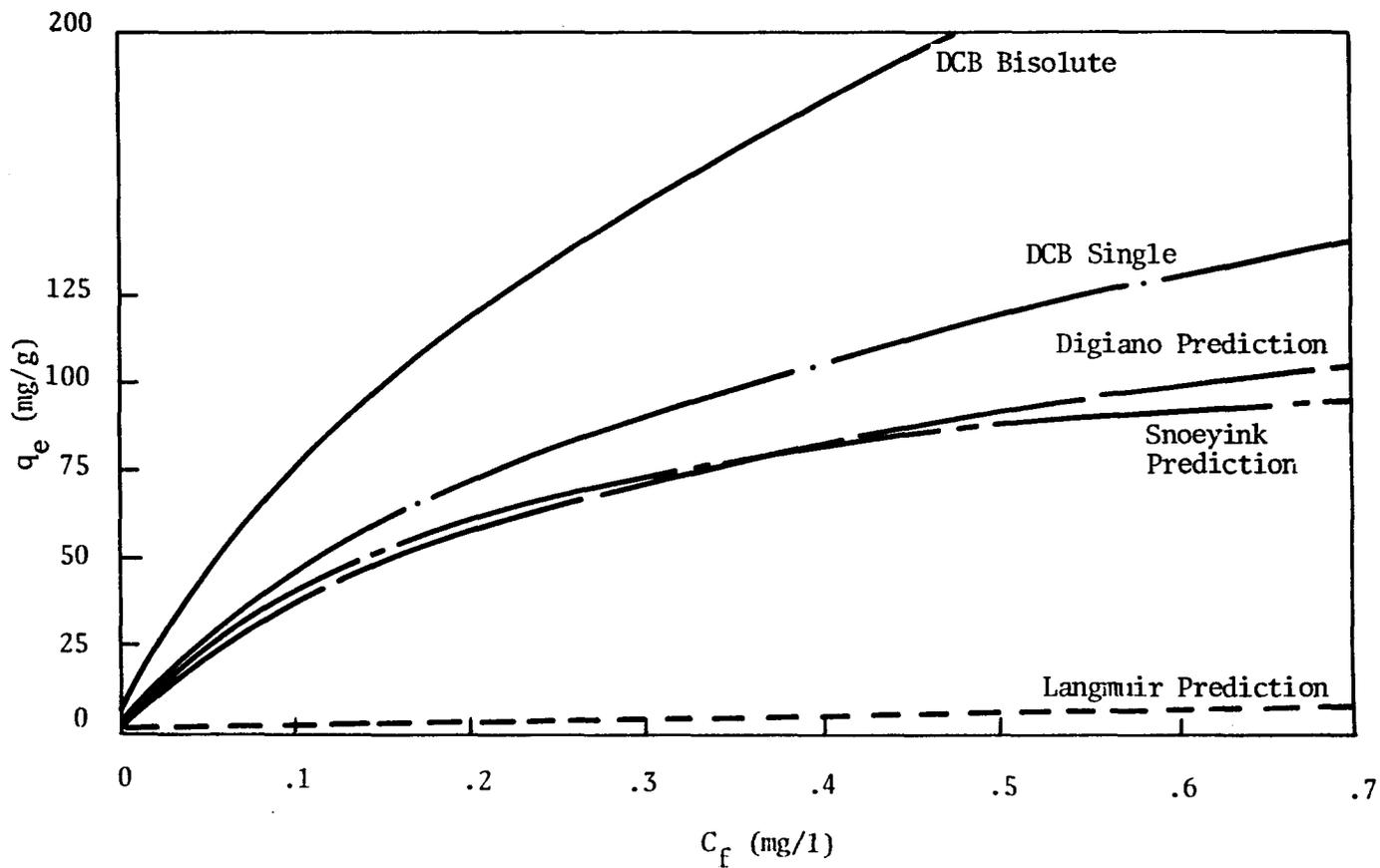


Figure 23. Experimental and predicted isotherms for DCB in the presence of TCE on activated carbon; initial DCB concentration = 0.900 mg/l; initial TCE concentration = 0.896 mg/l.

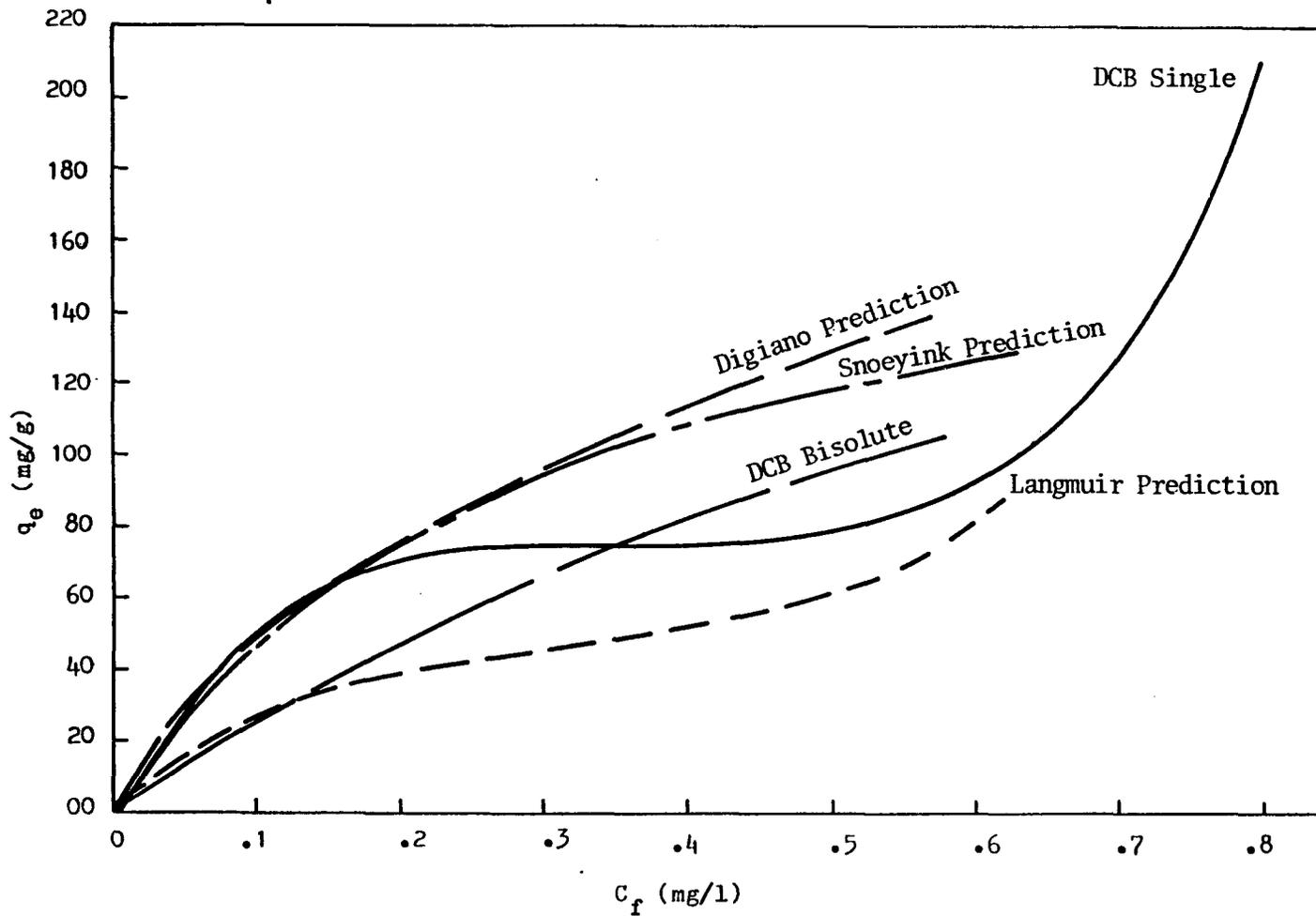


Figure 24. Experimental and predicted isotherms for DCB in the presence of PCE on activated carbon; initial DCB concentration = 1.078 mg/l; initial PCE concentration = 0.993 mg/l.

the Jain-Snoeyink. The Langmuir model was inadequate in all but one test. Generally, the predictions were lower than observed results. Possible reasons for this trend will be discussed later.

Amberlite XAD-8

This macroreticular resin was found by Weber and van Vliet to be useful in laboratory situations where it is desired to concentrate and recover a contaminant from water [49]. However, they note, it has little potential for applications in the water treatment industry. They observed that this resin showed unfavorable adsorption over a range of concentrations and had an unacceptably low capacity.

In the present study similar conclusions were reached. The XAD-8 had a much lower capacity than activated carbon and a noticeably lower capacity than the XE-340 for the VOC's studied. Furthermore, if it was necessary to reduce VOC concentrations to less than 5 $\mu\text{g}/\text{l}$, which is currently the recommended maximum contaminant level for TCE in Arizona, the XAD-8 resin would be incapable of delivering that level of performance.

Figures 25 and 26 show the single-solute Freundlich isotherms for PCE and DCB, respectively, on XAD-8 resin. The capacity for DCB is slightly higher than that for PCE, presumably due to solubility differences. The steep slopes, though, indicate a less than favorable adsorption pattern.

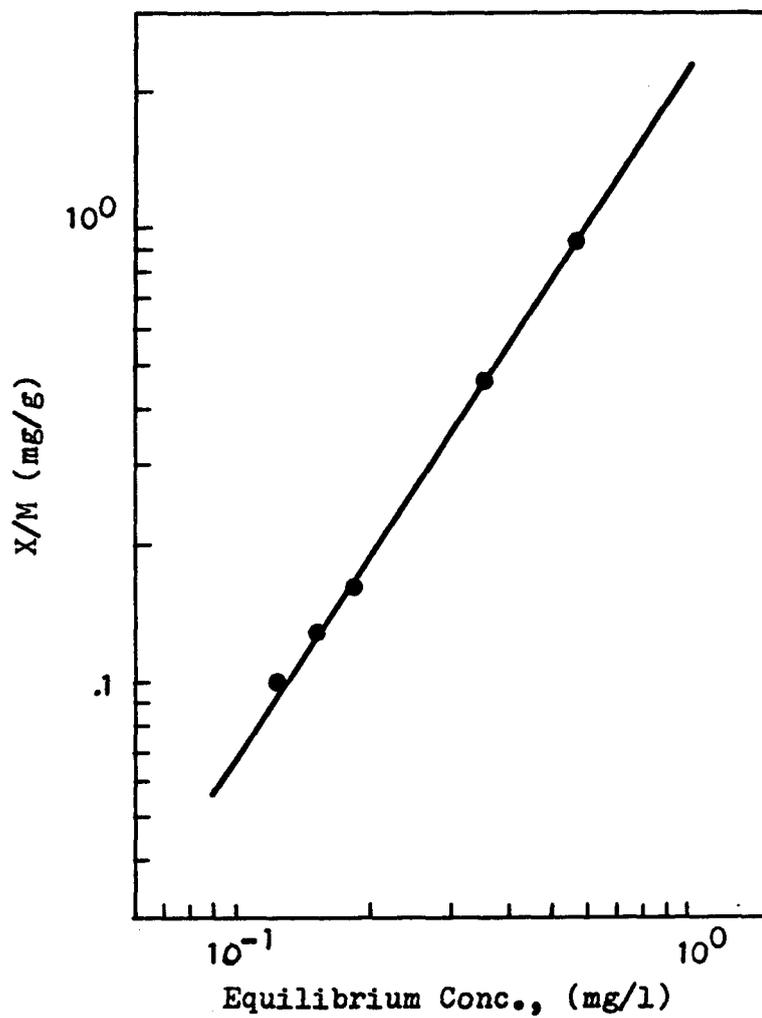


Figure 25. Freundlich isotherm for PCE adsorption onto XAD-8; initial PCE concentration = 0.993 mg/l.

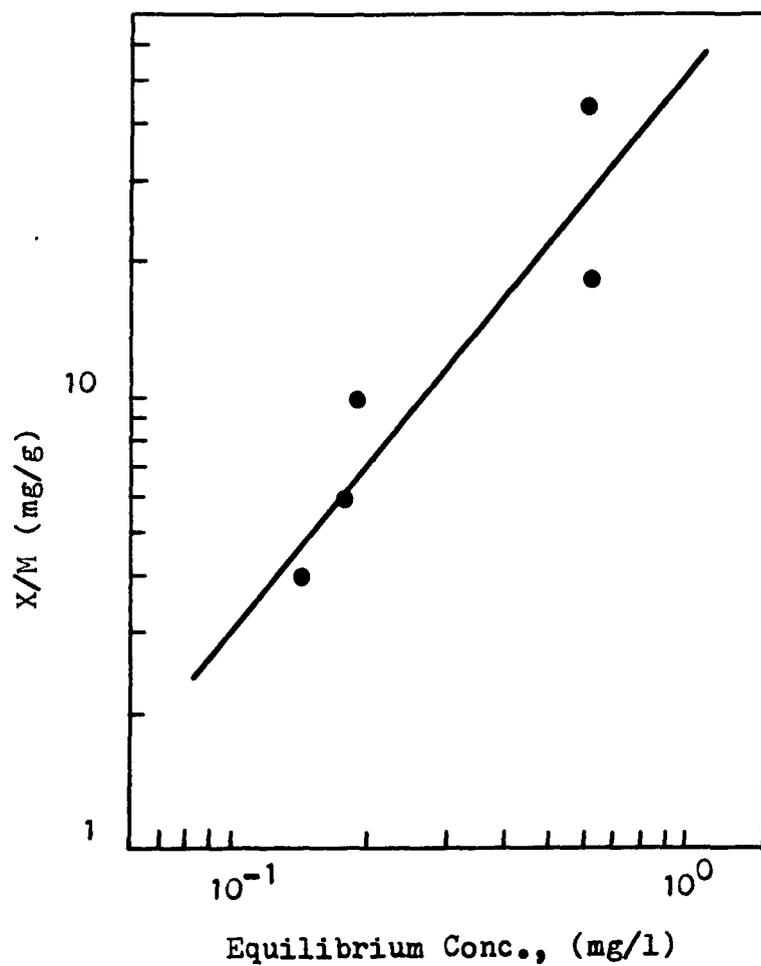


Figure 26. Freundlich isotherm for DCB adsorption onto XAD-8; initial DCB concentration = 1.078 mg/l.

Figure 27 indicates that the presence of TCE had little if any effect on the uptake of PCE. This leads to the conclusion that individual sites are not responsible for the VOC adsorption; rather, it is again a partitioning process being observed. Because both compounds are structurally and chemically similar, the presence of TCE would have a deleterious effect on PCE adsorption if functional group adsorption was a primary mechanism of uptake.

Figure 28 gives the experimental and predicted isotherms for PCE in the presence of TCE on XAD-8. The Digiano model is accurate in the low concentration range, but departs significantly in the higher ranges, tending toward a duplication of the single-solute data. The Snoeyink and Langmuir models were not applied as the Langmuir parameters, which both models depend on, were not obtainable.

Experimental and predicted results for DCB in the presence of TCE are presented in Figure 29. The Digiano model predicts the adsorption behavior quite well, though it is a bit low on the adsorption capacity. The Snoeyink and Langmuir models predict similar behavior, but both are low in the loading estimates and both indicate a favorable adsorption, whereas the experimental data show a slightly unfavorable adsorption.

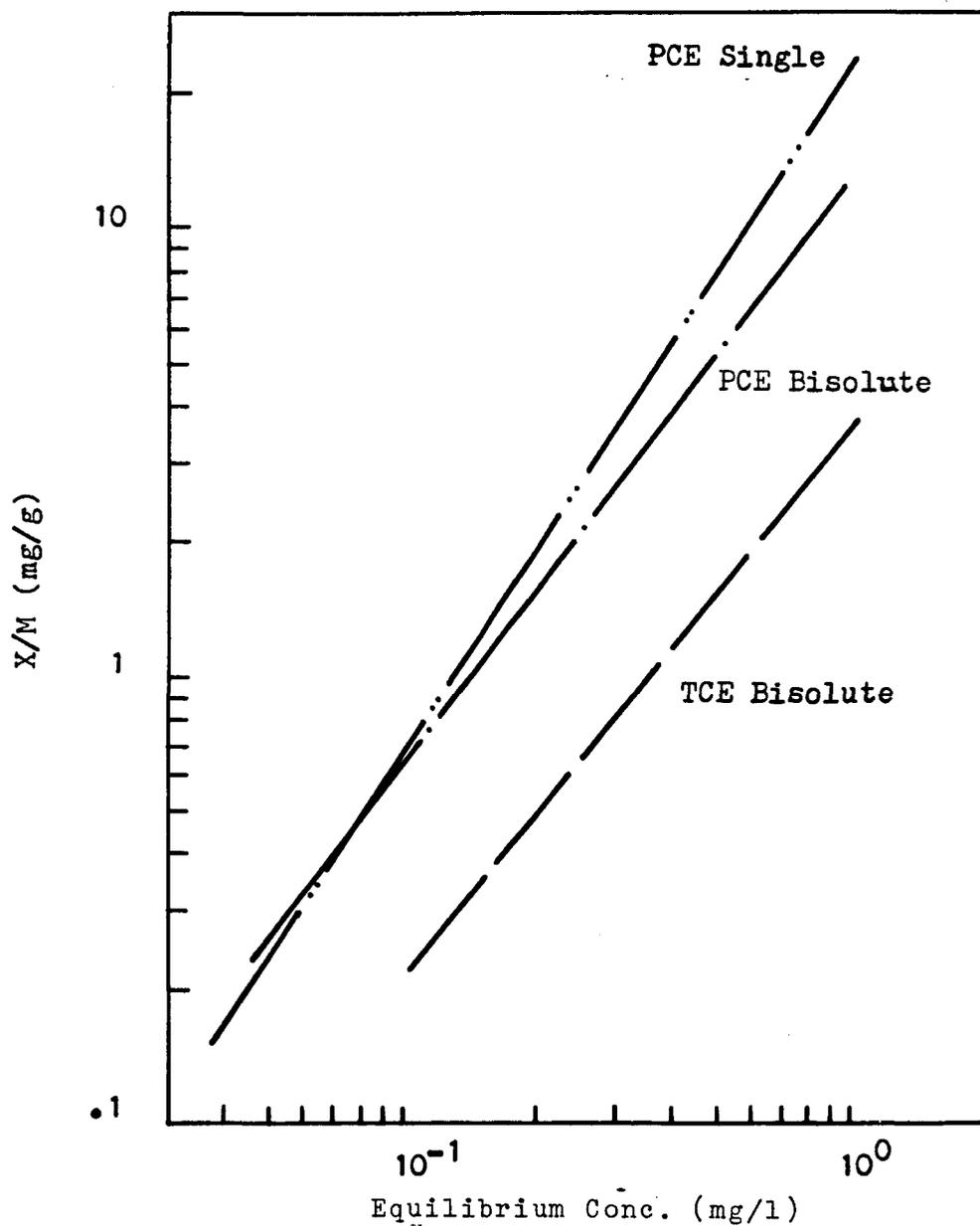


Figure 27. Freundlich isotherm for PCE adsorption onto XAD-8 in the presence of TCE; initial PCE concentration = 1.253 mg/l; initial TCE concentration = 1.535 mg/l.

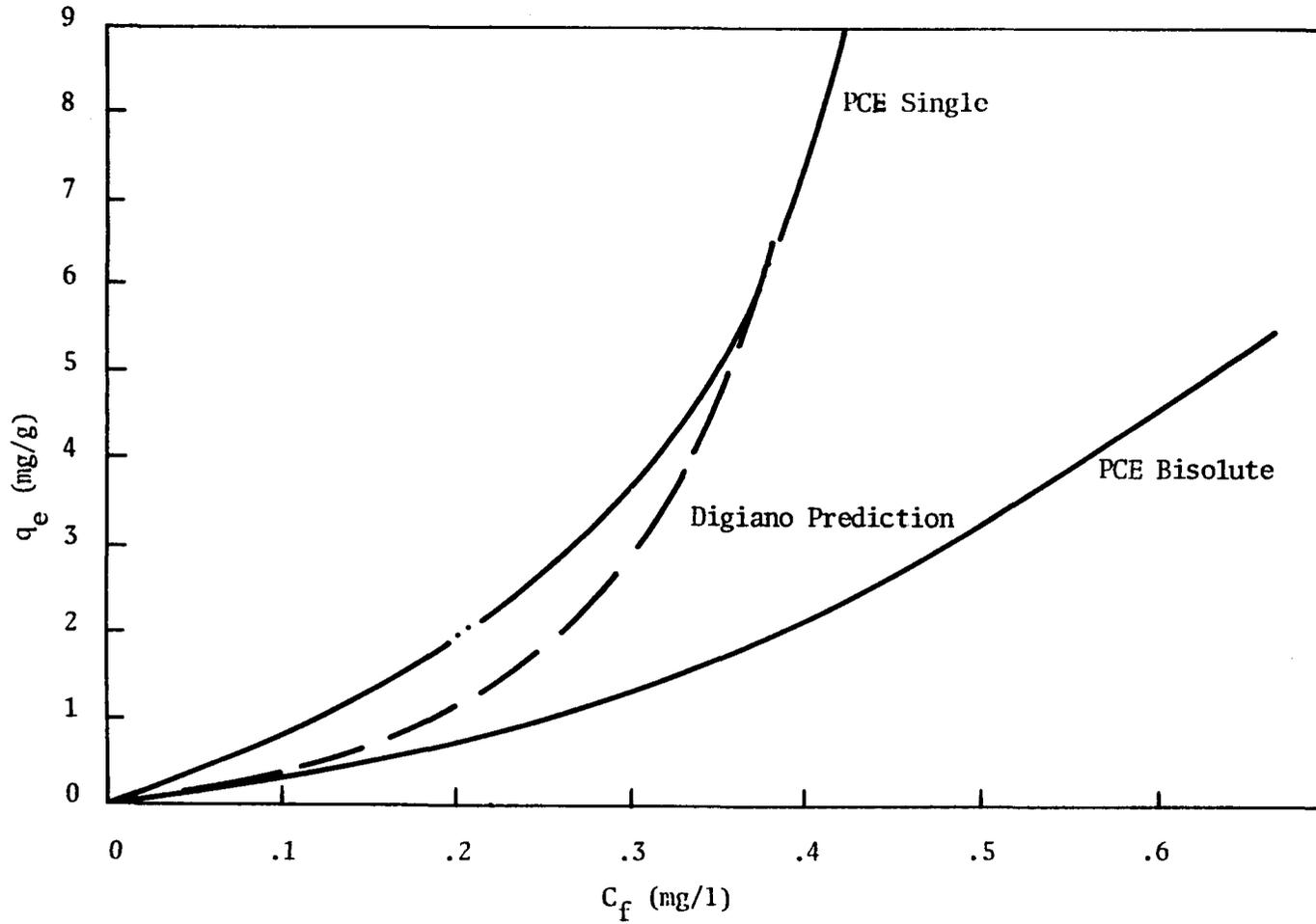


Figure 28. Experimental and predicted isotherms for PCE in the presence of TCE on XAD-8; initial PCE concentration = 1.253 mg/l; initial TCE concentration = 1.535 mg/l.

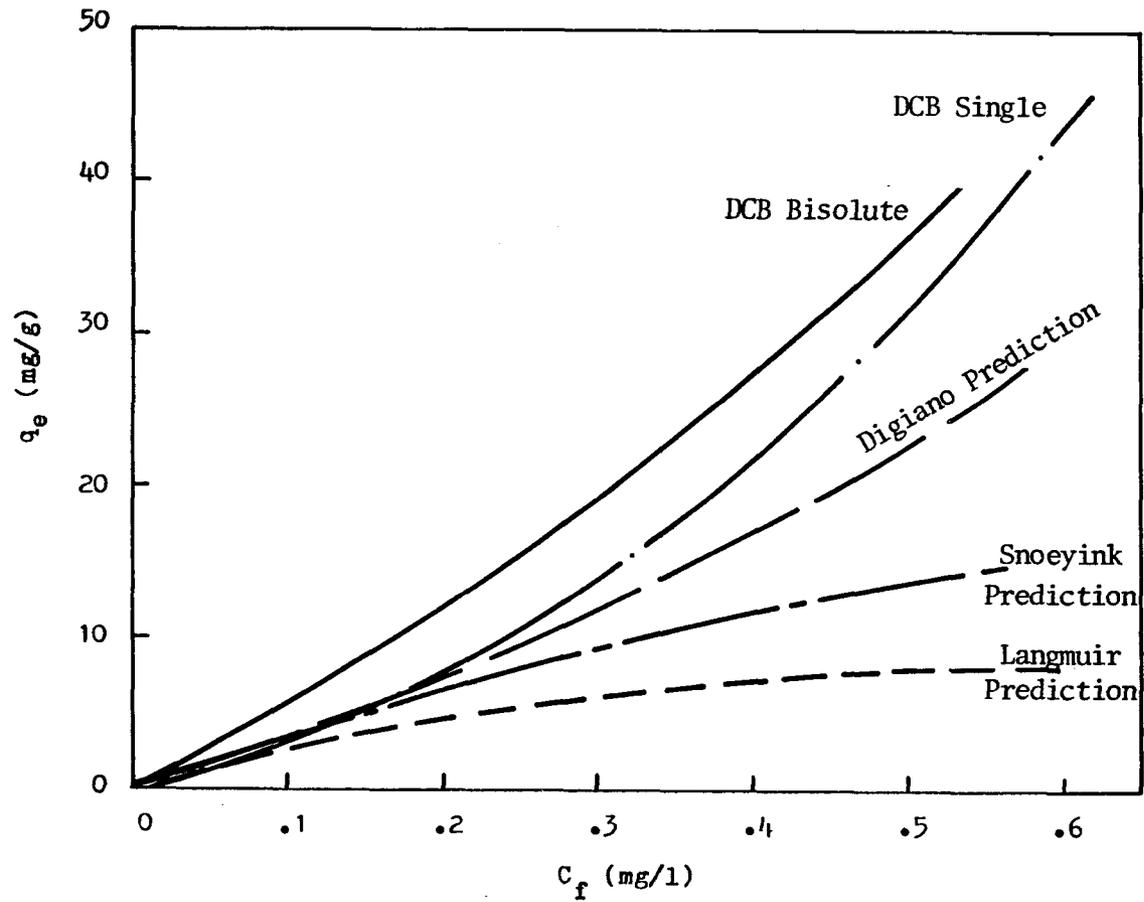


Figure 29. Experimental and predicted isotherms for DCB in the presence of TCE on XAD-8; initial DCB concentration = 0.900 mg/l; initial TCE concentration = 0.896 mg/l.

Ambersorb XE-340

Rohm and Haas's Ambersorb XE-340 is a carbonaceous-type polymeric macroreticular resin designed to adsorb low molecular weight halogenated organics. A number of researchers have reported that XE-340 has a higher capacity for chloroform than activated carbon [___]. No previously published work has dealt with single-solute and/or competitive adsorption of VOC's onto XE-340. As this resin has been shown to be effective in removing other halocarbons, it was desired to determine its capacity for the VOC's in this study.

The Freundlich single-solute isotherms for PCE and DCB are shown in Figures 30 and 31, respectively. The XE-340 displays a similar capacity for both compounds. The low $1/n$ values indicate that it adsorbs favorably throughout the concentration range of interest. However, reference to Figures 16 and 17 show that activated carbon has a higher capacity for both compounds and also adsorbs favorably in a similar concentration range.

Figure 32 shows the Freundlich isotherm for PCE in the presence of TCE on XE-340. There is a distinct lowering of PCE uptake, though the isotherm does not change slope, indicating, therefore, a decrease in overall capacity but still favorable adsorption behavior.

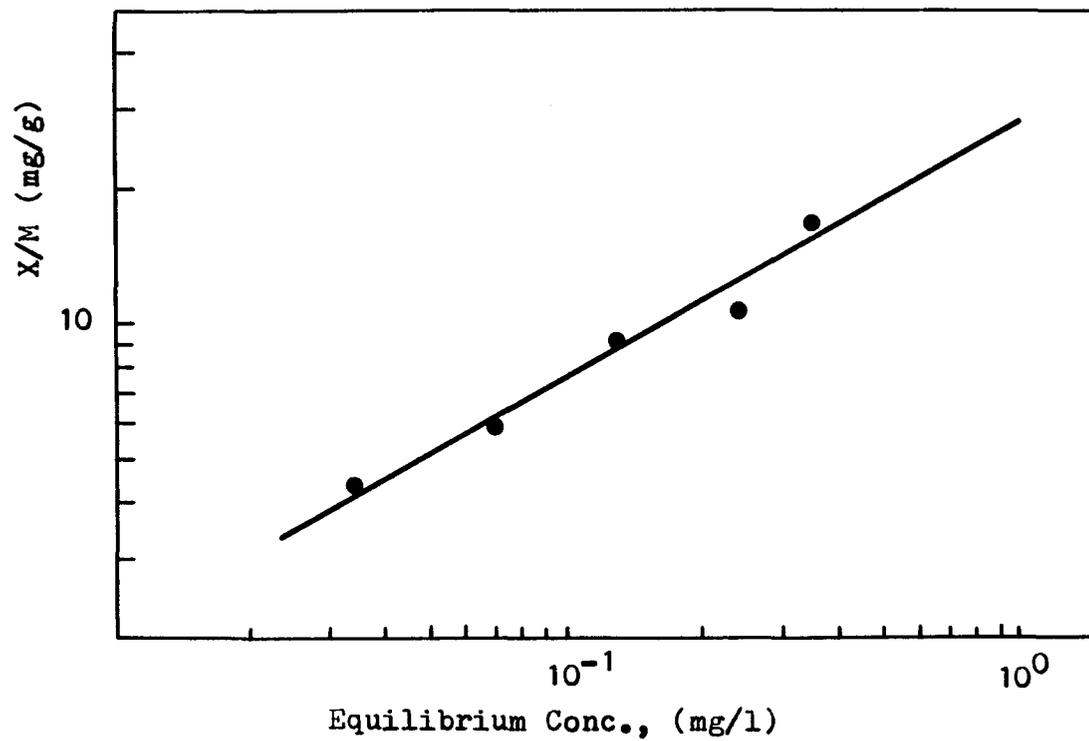


Figure 30. Freundlich isotherm for PCE adsorption onto XE-340; initial PCE concentration = 1.058 mg/l.

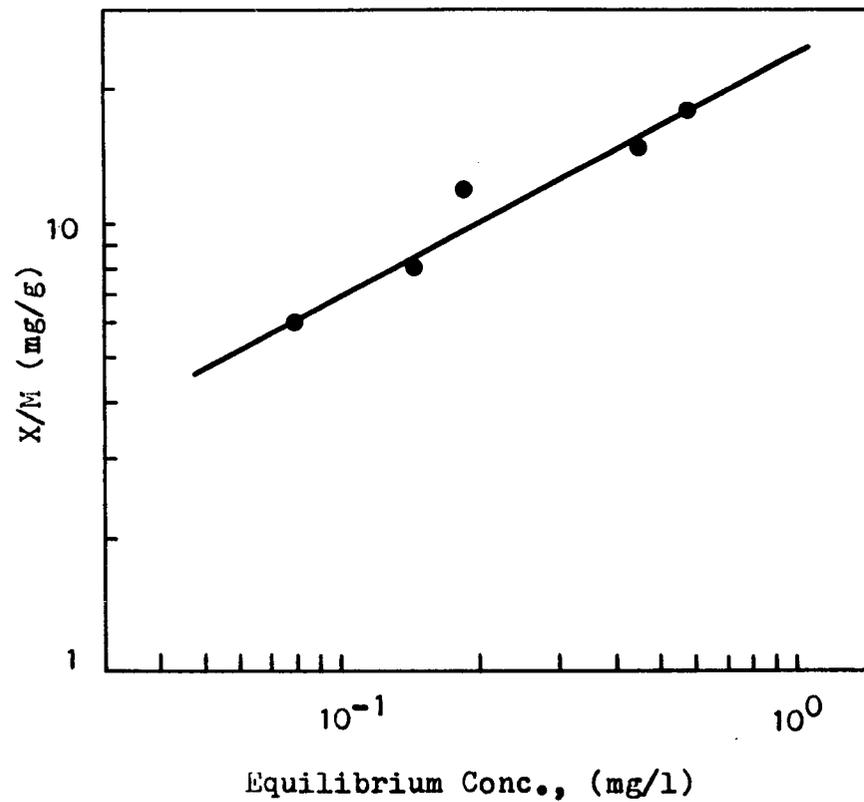


Figure 31. Freundlich isotherm for DCB adsorption onto XE-340; initial DCB concentration = 1.005 mg/l.

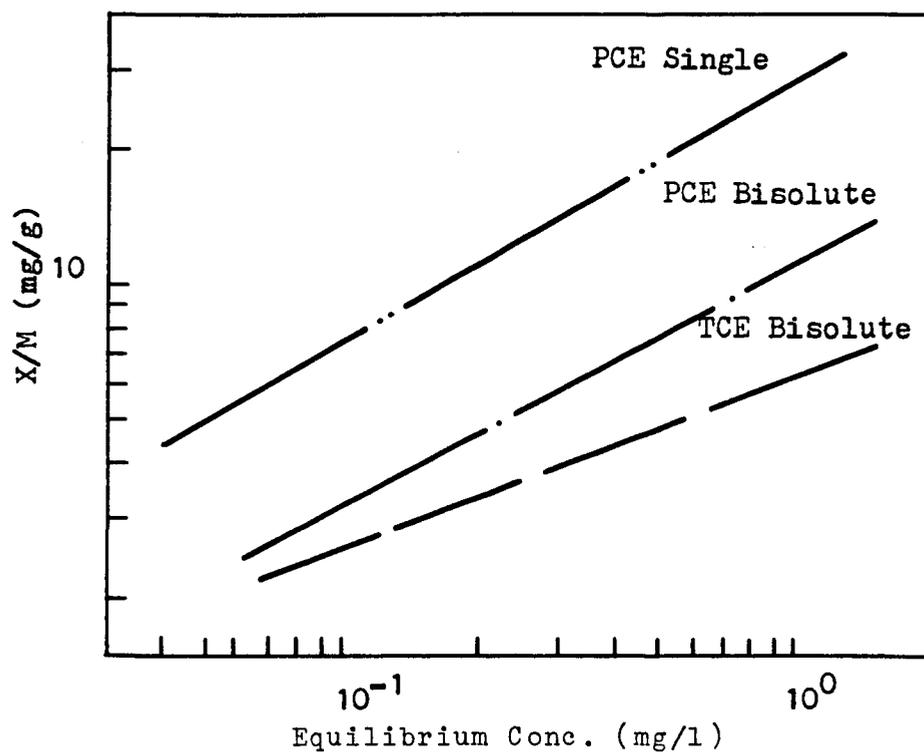


Figure 32. Freundlich isotherm for PCE adsorption onto XE-340 in the presence of TCE; initial PCE concentration = 0.861 mg/l; initial TCE concentration = 0.858 mg/l.

The lowering of the adsorptive capacity for PCE indicates that TCE is providing competition for specific sites. Therefore, the XE-340 must be employing functional group adsorption along with the hydrophobic partitioning mechanism. In fact, the similar capacity exhibited by PCE and DCB in Figures 30 and 31 reveal the same thing. If partitioning, which is a function of solubility, were the primary mechanism of uptake, a larger capacity for DCB would have been observed. The XE-340 apparently has sites that have a greater affinity for PCE than for DCB.

Figure 33 shows the Freundlich isotherm for DCB in the presence of TCE on XE-340. A significant decline in capacity for DCB is observed. TCE probably has a similar affinity as PCE for the same sites for which DCB is less attracted. In a single solute system, DCB could adsorb onto these sites. But in the presence of a compound which has a higher energy of adsorption for those sites, DCB uptake is diminished. DCB experiences an overall adsorption slightly greater than that of TCE, but this is due to its much lower solubility, which implies a different adsorption mechanism.

The Freundlich isotherms for PCE and DCB in the presence of each other are shown in Figure 34. The uptake of both compounds is diminished. DCB does obviously compete effectively for some of the sites. However, PCE is adsorbed

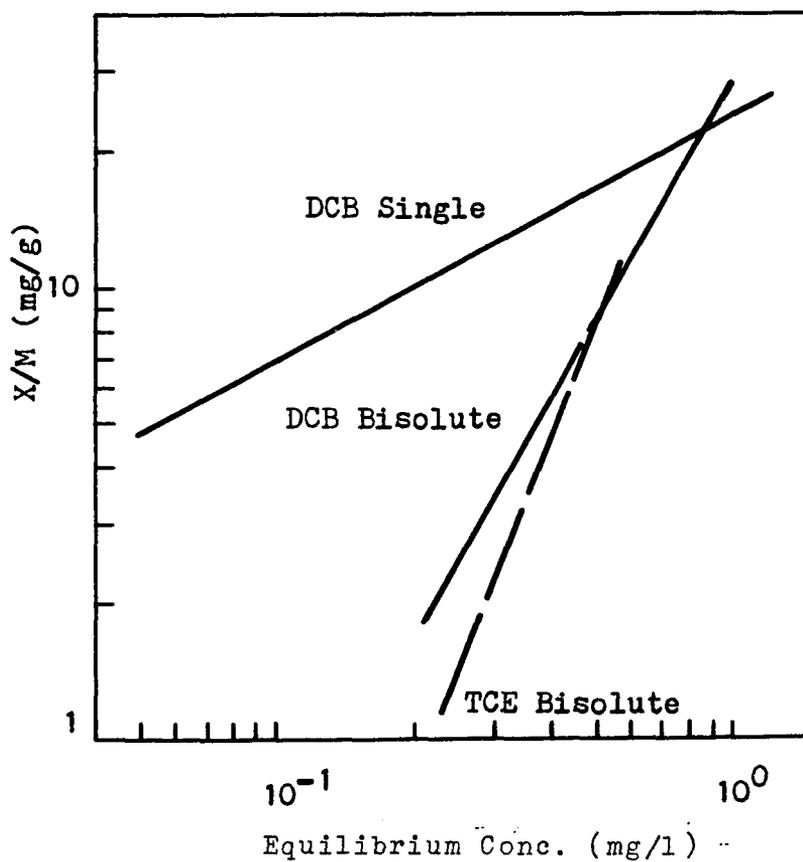


Figure 33. Freundlich isotherm for DCB adsorption onto XE-340 in the presence of TCE; initial DCB concentration = 1.010 mg/l; initial TCE concentration = 0.712 mg/l.

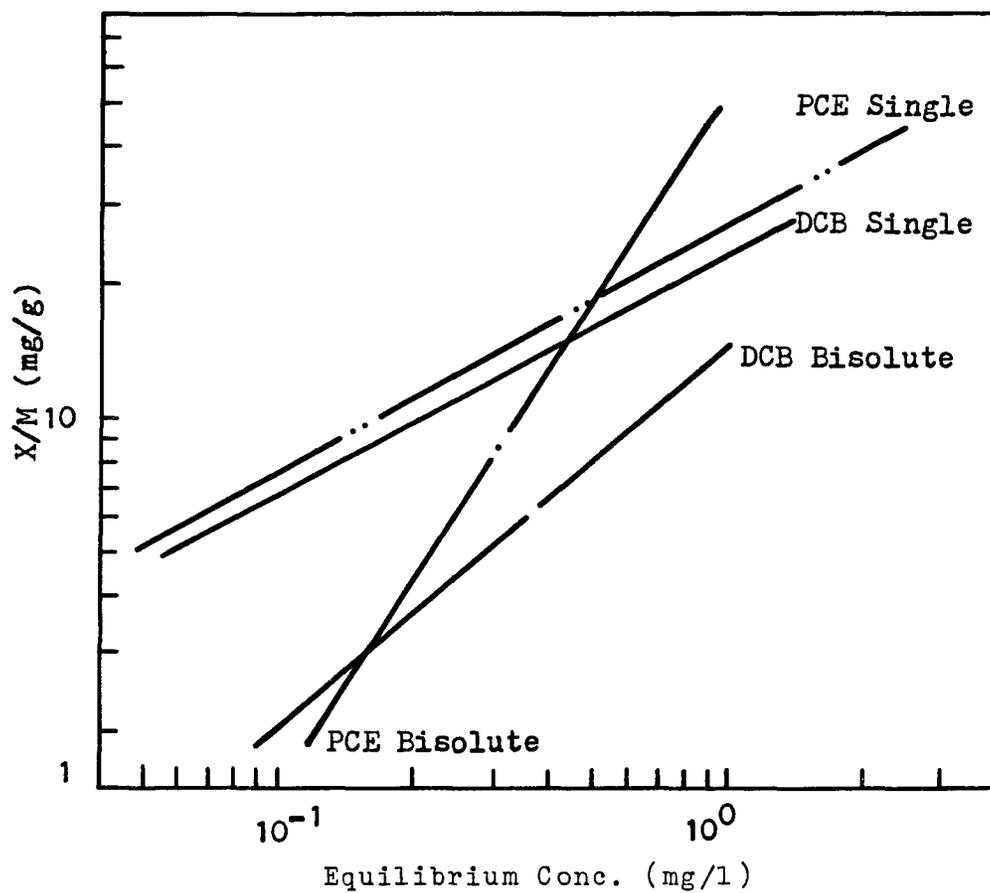


Figure 34. Freundlich isotherms for PCE and DCB adsorption onto XE-340 in the presence of each other; initial PCE concentration = 0.837 mg/l; initial DCB concentration = 0.979 mg/l.

to a significantly greater degree than DCB in the bisolute mixture.

Figure 35 displays the experimental and predicted isotherms for PCE in the presence of TCE. The Digiano model accurately depicts a favorable isotherm, but it well overestimates the actual results. It basically duplicates the single solute isotherm. One problem with the Digiano model is that it relies on Freundlich parameters to make its estimates. The Freundlich K values for PCE and TCE are 28 and 11, respectively. Because the PCE value is a good deal larger than the TCE value, the competitive effects of TCE be masked and underestimated. Also, two adsorption mechanisms are predominant here--specific adsorption and hydrophobic partitioning--and the model cannot distinguish between the two, one of which displays competition while the other does not. At its best, therefore, the simplified IAS model can only grossly predict trends. It does not verify or imply any mechanistic explanations.

Figure 36 shows experimental and predictive isotherms for DCB in the presence of TCE on XE-340. The same interpretation of Figure 35 holds for this analysis. The Digiano model, simply because it is in essence a curve fitting device, cannot adequately predict competitive data when more than one adsorption mechanism is involved. The system is mechanistically more complicated and does not lend

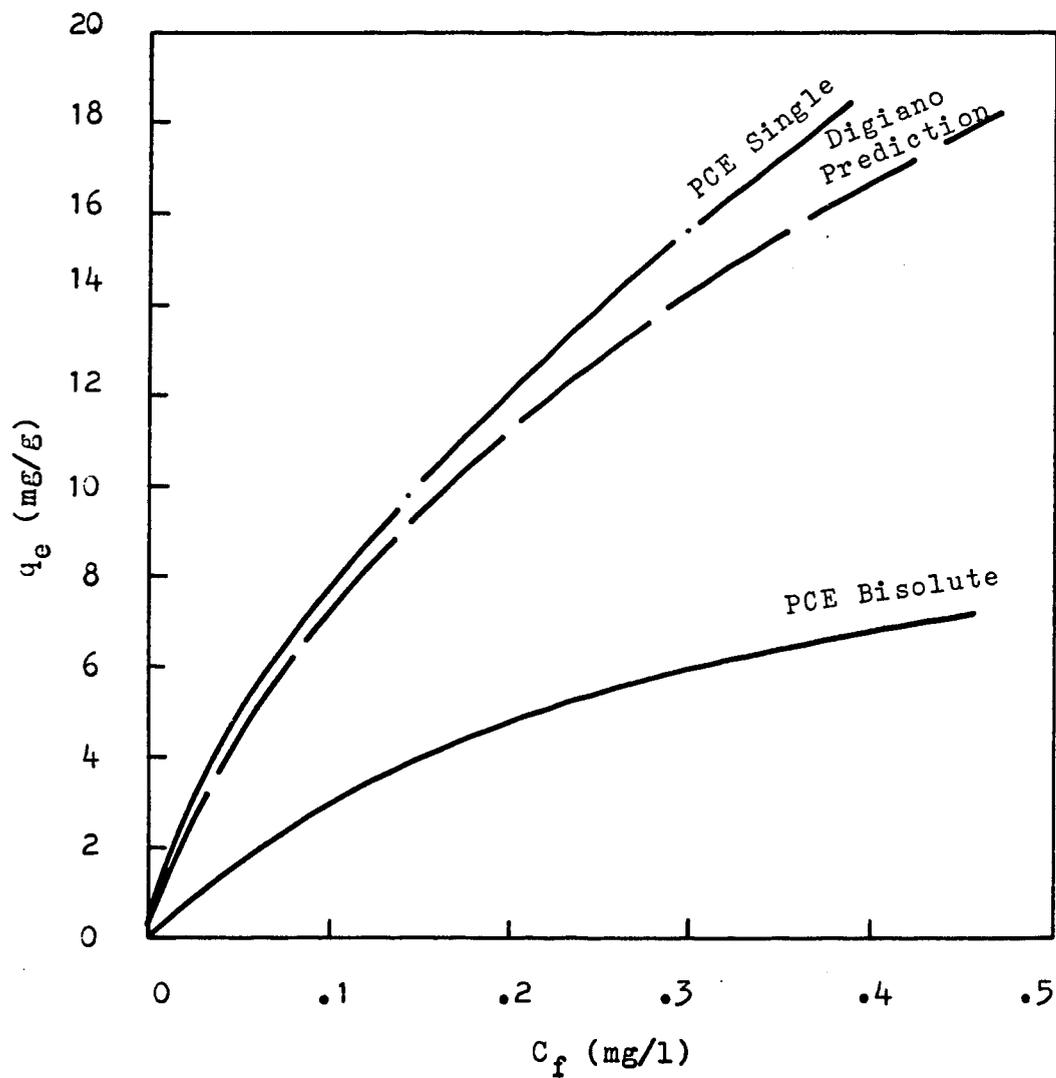


Figure 35. Experimental and predicted isotherms for PCE in the presence of TCE on XE-340; initial PCE concentration = 0.861 mg/l; initial TCE concentration = 0.858 mg/l.

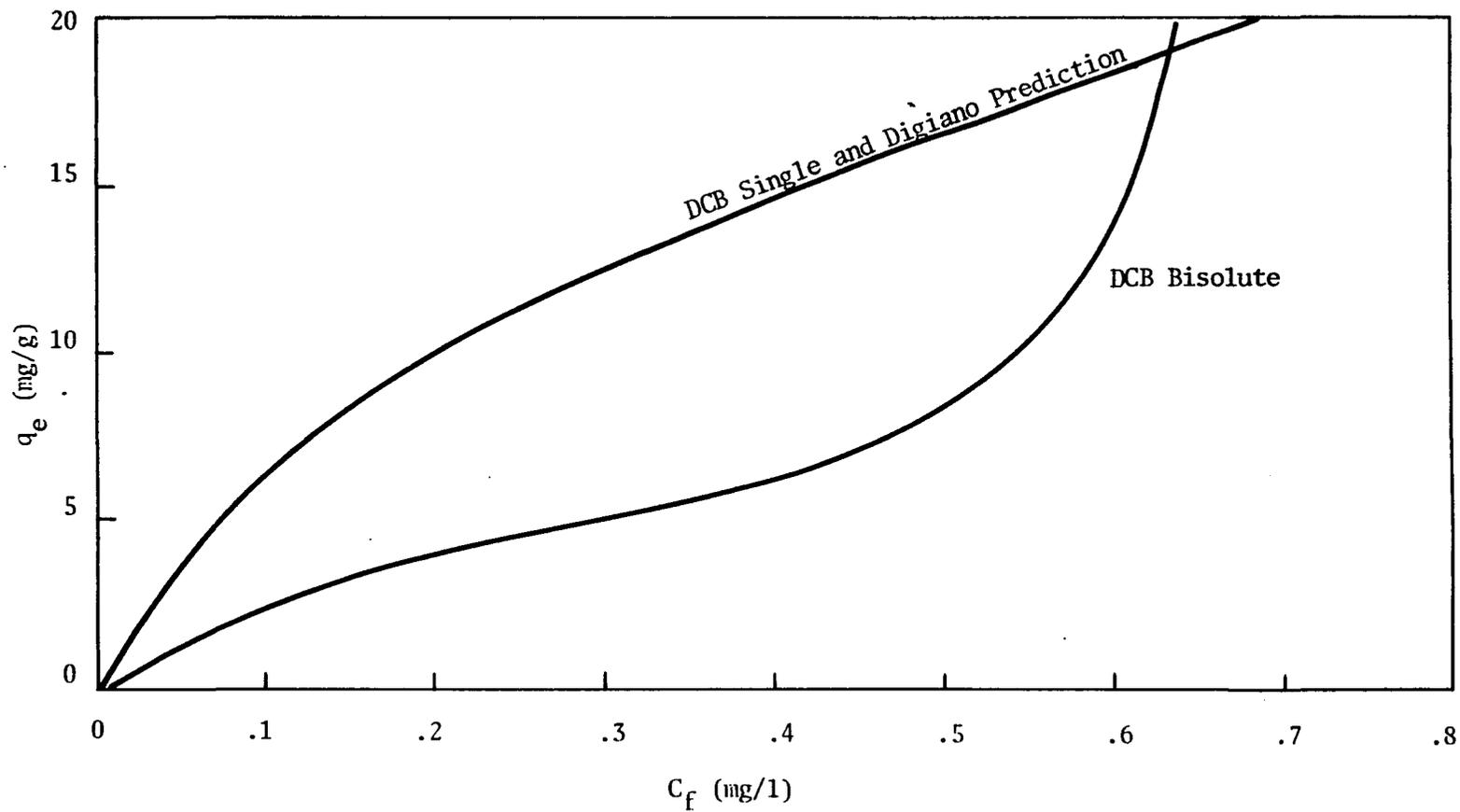


Figure 36. Experimental and predicted isotherms for DCB in the presence of TCE on XE-340; initial DCB concentration = 1.010 mg/l; initial TCE concentration = 0.712 mg/l.

itself to simplistic interpretations. The Snoeyink and Langmuir models were not able to be applied to these data.

Figures 37 and 38 depict the experimental and predicted isotherms for PCE and DCB in the presence of each other, respectively. In Figure 37 the Digiano model inaccurately estimates the isotherm shape and the capacity over the range of concentrations. In Figure 38 the Digiano model correctly predicts the isotherm shape but is somewhat high on the loading estimates. The Langmuir and Snoeyink models were able to be applied to both of these last two batch tests, but their predictions deviated so significantly from the observed results that their isotherms were not plotted.

Figures 39 and 40 present the Freundlich and arithmetic isotherms, respectively, of the compounds and most of the adsorbents studied. Figure 39 gives a good idea of the orders of magnitude differences that exist from one adsorbent to the other. Figure 40 shows whether or not the adsorption of a particular compound onto a particular adsorbent is favorable. Note that only the activated carbon and XE-340 display favorably isotherms. Also note that the XAD-8, though its capacity is not much less than that of the XE-340, has a distinctly unfavorably isotherm.

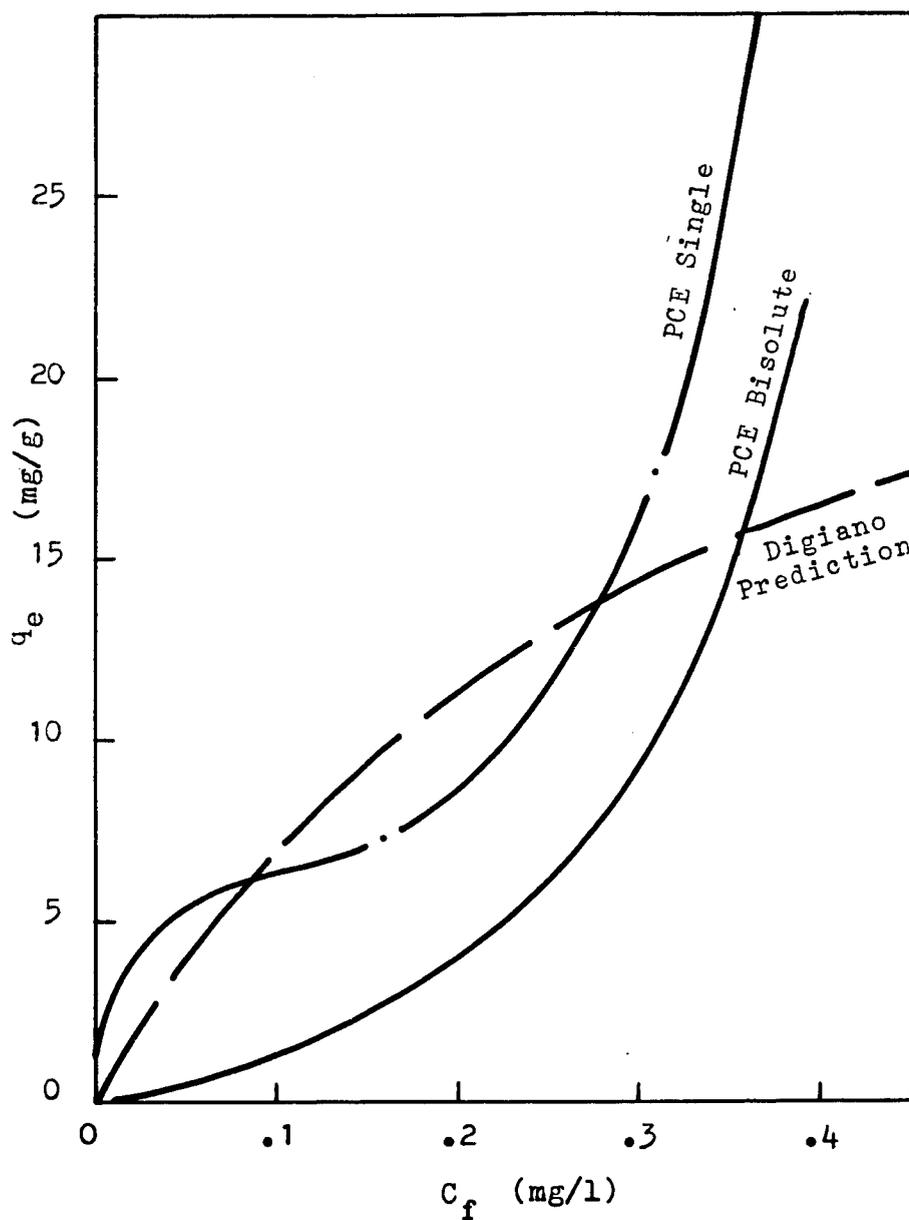


Figure 37. Experimental and predicted isotherms for PCE in the presence of DCB on XE-340; initial PCE concentration = 0.837 mg/l; initial DCB concentration = 0.979 mg/l.

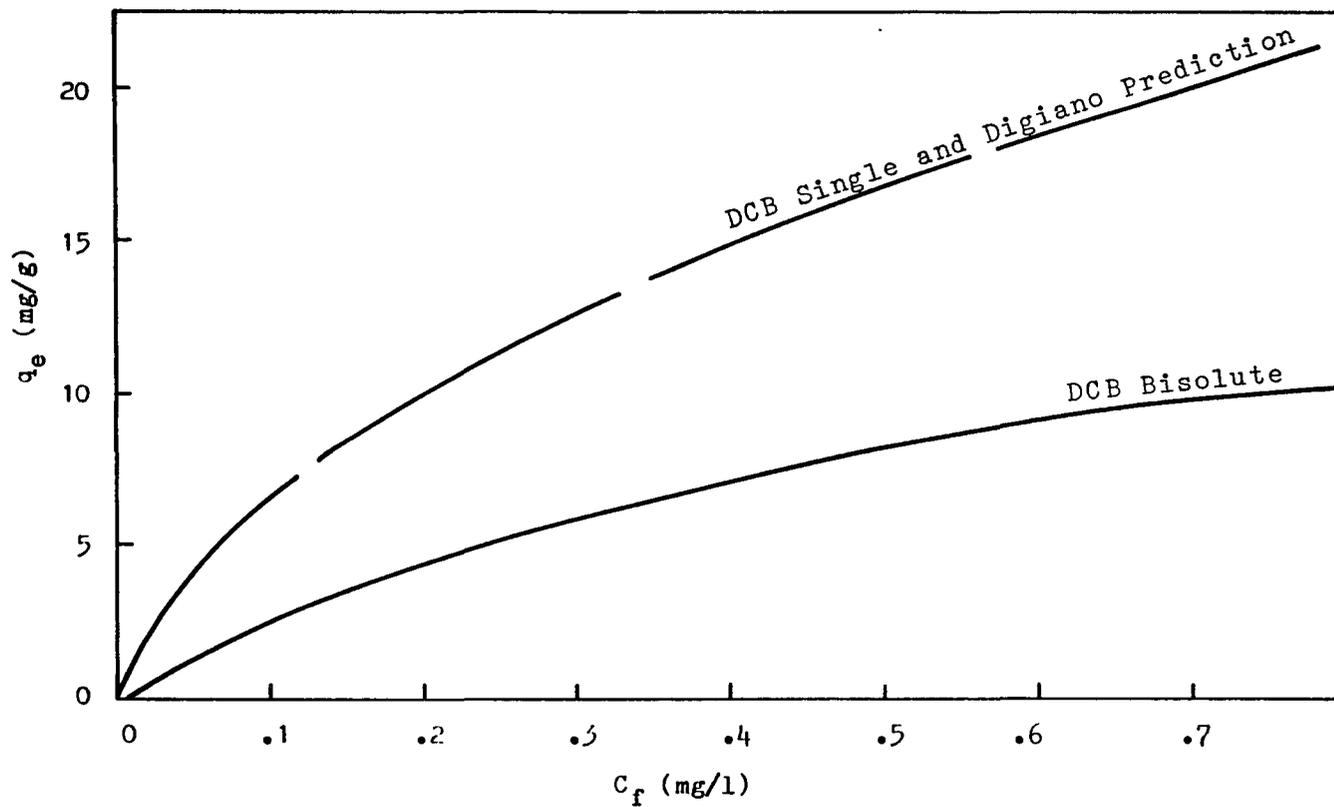


Figure 38. Experimental and predicted isotherms for DCB in the presence of PCE on XE-340; initial DCB concentration = 0.979 mg/l; initial PCE concentration = 0.837 mg/l.

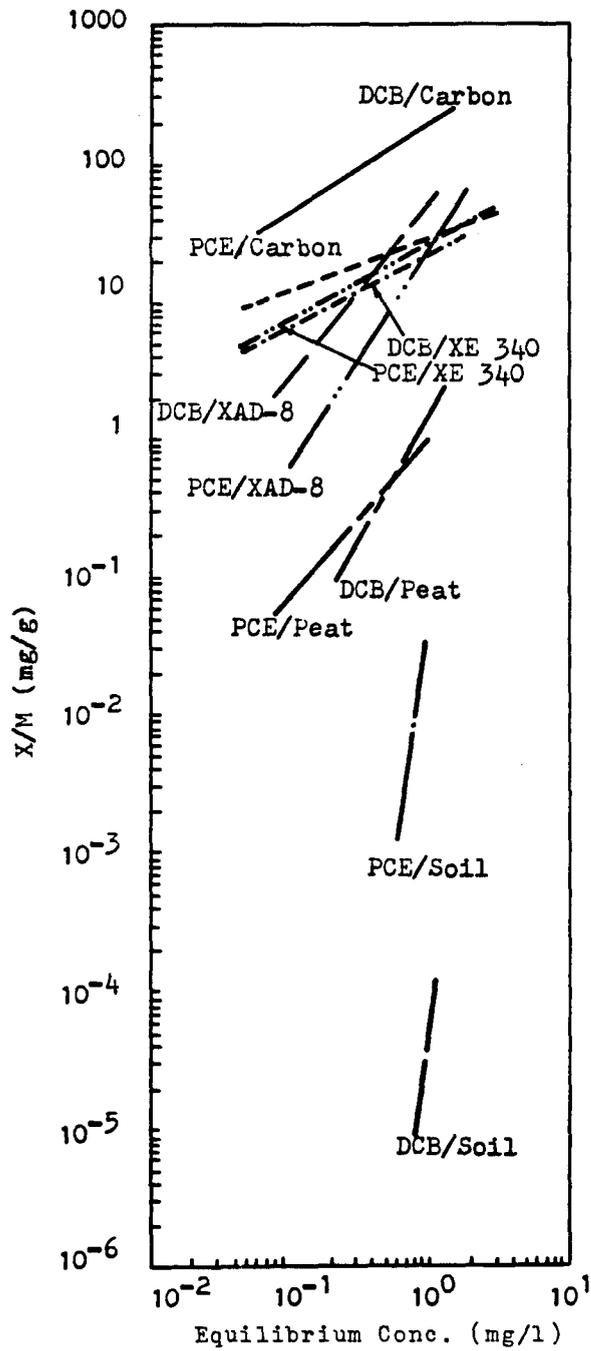


Figure 39. Freundlich single solute isotherms for PCE and DCB adsorption onto soil, peat, activated carbon, XAD-8, and XE-340.

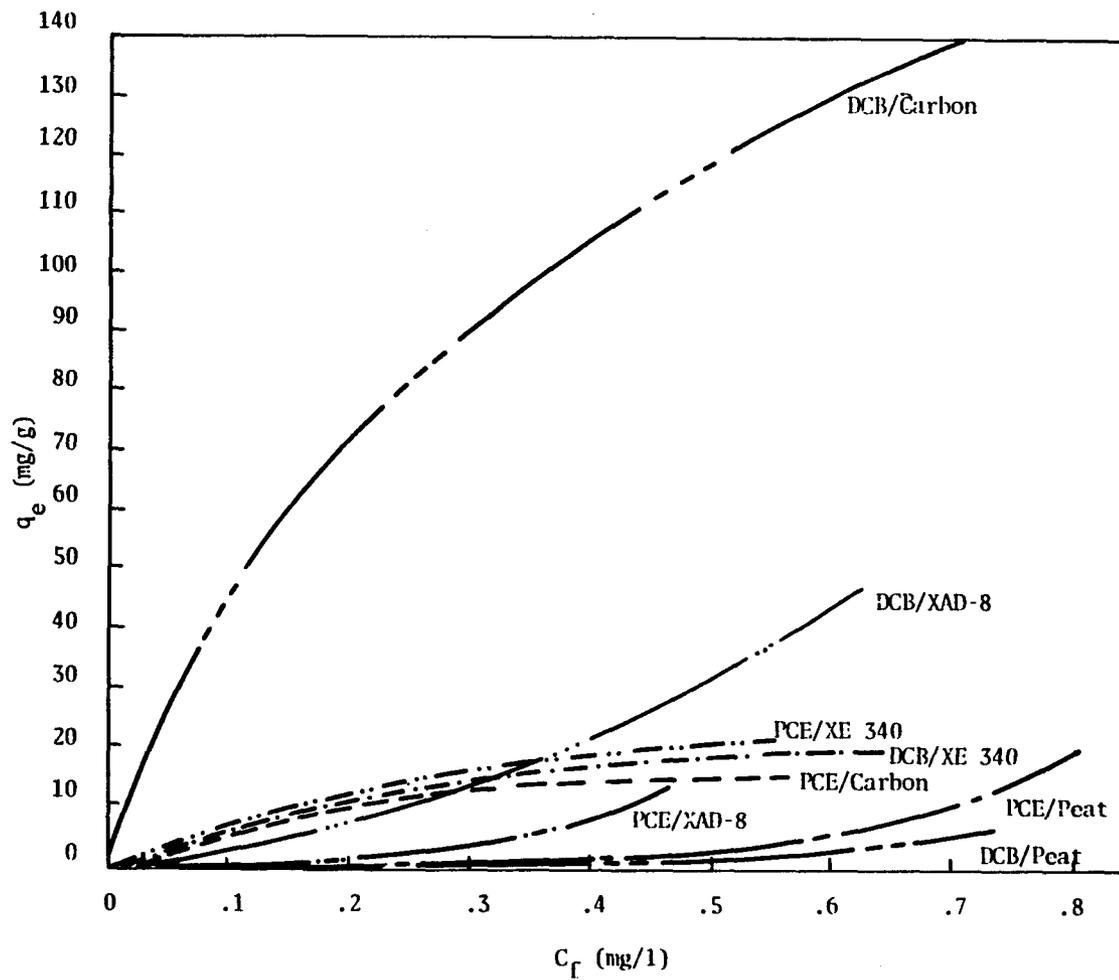


Figure 40. Arithmetic single solute isotherm for PCE and DCB adsorption onto peat, activated carbon, XAD-8, and XE-340.

CONCLUSIONS

This study focused on the adsorption of PCE and DCB onto various natural and synthetic adsorbents. The tests were conducted using single solute and bisolute systems of these compounds and also TCE and CT.

Natural Adsorbents

The adsorbents employed include a natural soil, clays, humic acid, and organic matter (as peat).

1. The clays exhibited insignificant adsorption of the VOC's. This soil component would offer little adsorptive retardation of these compounds.
2. The humic acid was also determined to be unimportant in assessing the movement of these VOC's through a soil.
3. Peat was observed to adsorb significant amounts of both PCE and DCB. The organic matter fraction, about 85%, was responsible for this uptake.
4. This peat supported functional groups which have a stronger affinity for PCE and DCB. The single solute tests show slightly greater uptake of PCE onto peat, despite PCE's greater solubility. The bisolute tests exhibit greater competition with PCE

from chemically similar TCE than from DCB. If the prevalent adsorption mechanism was a function of solubility, TCE would have little effect on either PCE or DCB adsorption.

There has been no attempt to identify the functional groups on the peat that absorb these compounds. More sophisticated analytical techniques would be necessary to make such a determination.

Synthetic Adsorbents

Batch tests were conducted on four engineered materials to determine their adsorption capacity and applicability for removing PCE and DCB in single solute and bisolute systems.

1. The activated carbon, a pulverized form of Calgon Corp.'s Filtrasorb 400, showed the largest capacity for PCE and DCB. The primary adsorption mechanism is hydrophobic partitioning.
2. The Amberlite XAD-8 resin exhibited unfavorable adsorption and is not a practical adsorbent for water treatment applications. Again, the adsorption process is dominated by partitioning.
3. The Amberlite XE-340 resin exhibited favorable adsorption of both PCE and DCB. Its capacity was greater than that of XAD-8, but slightly less than

that of the activated carbon. Consideration must be given to the fact that the kinetics for the activated carbon tests was more favorable than those for the XE-340 due to the much smaller grain size of the carbon. Determination of adsorption kinetics for the XE-340 would be desirable.

4. The competitive adsorption tests indicate that site-specific adsorption is important in uptake of these VOC's by XE-340. TCE competed more strongly with PCE than did DCB. TCE also significantly decreased DCB adsorption. Adsorption sites exist that "prefer" TCE and PCE over DCB.

Predictive Models

Three models were tested to determine their accuracy in predicting the observed competitive test results.

1. The Langmuir competitive model is ineffective in predicting adsorption of VOC's out of multisolute systems. The model assumptions are overly conservative, causing a consistent underestimation of adsorption capacities.
2. The Jain-Snoeyink model is generally not effective in predicting competitive VOC adsorption. This model includes the Langmuir assumptions, but makes allowances for noncompetitive adsorption reactions.

The model predicts adsorption trends well, but also underestimates the capacity.

3. The simplified IAS model, as presented by Digiano et al., was the most accurate in predicting adsorption behavior. This model predicted the adsorption trends well and was accurate in the estimation of capacity for most of the bisolute tests. This model can predict general patterns and trends, and is therefore useful as a first approximation tool when bisolute or multisolute systems are involved.

All three of these models are essentially curve-fitting techniques and employ simplifying assumptions. In many situations, however, adsorption is a complex process which does not lend itself to simplistic descriptions. The mechanisms involved are rarely simply hydrophobic partitioning or site-specific adsorption, but more commonly something on the continuum that exists between these two extremes. To accurately predict and describe the processes involved would require careful determination of complex thermodynamic parameters. The results of such efforts, though, may not justify the expenditure of the time and money that would be required for such determinations.

RECOMMENDATIONS FOR FURTHER WORK

This investigation has revealed some general and some specific adsorption characteristics of volatile halogenated organic compounds on natural and synthetic adsorbents. These results are useful in and of themselves, but also lend themselves to further study in the areas of water treatment, organic compound adsorption in soils, and pollutant migration.

Volatile compounds, by definition, are amenable to removal from water by aeration. Packed column and other aeration methods could be studied to determine optimum conditions (water and gas flow, packing depth, etc.) for removal of these VOC's from water. Armed with these results, those from this study and the study by Kalimtgis [5], an optimization scheme could be developed to achieve the most effective and cost effective linkage of the aeration and adsorption processes. Some contaminants are more susceptible to treatment by adsorption and some to treatment by aeration. How would one best combine these removal mechanisms to treat a polluted water, especially a water with different classes of contaminant compounds?

Many researchers, for example Karichoff and Lambert, have reported that the organic fraction of soils accounts for the adsorption of nonionic organic compounds [16, 17]. The present study supports these results. But which component of the organic material actually adsorbs the compound? Is it the lipid, protein, or perhaps the carbohydrate fraction? Mengelgrin and Gerstl have suggested that the lipid fraction is responsible [25]. Batch tests could be conducted using peat as a stock from which each of the organic components have in turn been removed. This type of work may help explain why soils with similar organic content have different adsorption capacities. Different organic matter source material may contain different lipid, protein, and carbohydrate fractions. This information would allow greater depth in the evaluation of soil properties as related to contaminant migration or containment strategies.

A direct spinoff of these batch tests would be adsorption studies utilizing lab or pilot scale columns filled with soil, carbon, resins, or peat. The results obtained in the batch tests could be used to predict retardation, migration, and breakthrough of the VOC's. Again, various predictive models could be tested against experimental results.

Another direct followup to this study would be an investigation of the desorption characteristics of VOC's off

of soils and peat. Many remediation schemes for contaminated aquifers involve pumping and treatment, followed by direct use or reinjection. Contaminated soils would need flushing to rid them of the harmful adsorbates. What are the kinetics involved and how much flushing would be required? Very little has been published regarding desorption phenomena and kinetics.

APPENDIX

TABLES OF BATCH TEST ADSORPTION DATA

Table A.1. Batch test data for PCE adsorption onto activated carbon.

Adsorbent Dose = M (mg/l)	C_f (mg/l)	$X = C_o - C_f$	X/M (mg/g)
0	0.993	0	0
14	0.488	0.505	36.1
83	0.187	0.806	9.7
166	0.051	0.942	5.7
222	0.005	0.988	4.5
333	0.001	0.992	3.0

Freundlich Parameters:

$$K = 24.9$$

$$1/n = .33$$

$$\text{Corr. Coeff.} = .89$$

Table A.2. Batch test data for PCE adsorption onto XAD-8.

Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
0	0.993	0	0
46.7	0.556	0.437	9.4
140	0.350	0.643	4.6
507	0.184	0.809	1.6
667	0.154	0.839	1.3
873	0.124	0.869	1.0

Freundlich Parameters

K = 22.6

1/n = 1.52

Corr. Coeff. = .99

Table A.3. Batch test data for PCE adsorption onto peat.

Adsorbent Dose = M (mg/l)	C_f (mg/l)	$X = C_o - C_f$	X/M (mg/g)
0	1.055	0	0
293	0.792	0.263	0.90
2667	0.292	0.763	0.29
4667	0.196	0.859	0.18
6667	0.203	0.852	0.13
13,333	0.105	0.950	0.071
20,000	0.069	0.986	0.049

Freundlich Parameters

$$K = 1.2$$

$$1/n = 1.22$$

$$\text{Corr. Coeff.} = .99$$

Table A.4. Replication data for PCE adsorption onto XE-340.

Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
Run #1			
0	1.058	0	0
20.7	0.461	0.597	28.8
42.0	0.348	0.710	16.9
76.7	0.238	0.820	10.7
99.3	0.129	0.929	9.4
166.7	0.070	0.988	5.9
233.0	0.038	1.020	4.4
Run #2			
20	0.367	0.691	34.6
42.7	0.320	0.738	17.3
69.3	0.334	0.724	10.4
100.0	0.197	0.861	8.6
167.3	0.066	0.992	5.9
234.7	0.024	1.034	4.4
Run #3			
19.3	0.416	0.642	33.3
45.3	0.329	0.729	16.1
65.3	0.365	0.693	10.6
104.0	0.182	0.876	8.4
170.0	0.062	0.996	5.9
234.7	0.017	1.041	4.4
<u>Freundlich Parameters</u>			
	Run #1	Run #2	Run #3
K	28.3	23.7	20.4
1/n	0.58	0.47	0.40
Corr. Coeff.	.98	.94	.94

Table A.5. Batch test data for PCE adsorption onto soil.

Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
0	1.055	0	0
3333	0.775	0.280	0.084
13,333	0.725	0.330	0.025
20,000	0.690	0.365	0.018
66,667	0.648	0.407	0.006

Freundlich Parameters

K = 2.92

1/n = 14.2

Corr. Coeff. = .99

Table A.6. Batch test data for PCE adsorption onto activated carbon in the presence of TCE.

Solute	Adsorbent Dose = M (mg/l)	C_f (mg/l)	$X = C_o - C_f$	X/M (mg/g)
PCE	0	1.139	0	0
	14	0.320	0.819	58.5
	83	0.062	1.077	13.0
	167	0.015	1.124	6.7
	222	0.007	1.132	5.1
	333	0.009	1.130	3.4
TCE	0	1.130	0	0
	14	0.752	0.378	27.0
	83	0.410	0.720	8.7
	167	0.101	1.029	6.2
	222	0.057	1.073	4.8
	333	0.034	1.096	3.3

Table A.7. Batch test data for PCE adsorption onto XAD-8 in the presence of TCE.

Solute	Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
PCE	0	1.253	0	0
	367	0.370	0.883	2.4
	667	0.215	1.038	1.6
	987	0.126	1.127	1.1
	1380	0.185	1.068	0.8
	2007	0.088	1.165	0.6
	2673	0.063	1.190	0.5
TCE	0	1.535	0	0
	367	0.692	0.843	2.3
	667	0.503	1.032	1.5
	987	0.370	1.165	1.2
	1380	0.385	1.150	0.8
	2007	0.210	1.275	0.6
	2673	0.198	1.337	0.5

Table A.8. Batch test data for PCE adsorption onto XE-340 in the presence of TCE.

Solute	Adsorbent Dose = M (mg/l)	C_f (mg/l)	$X = C_o - C_f$	X/M (mg/g)
PCE	0	0.861	0	0
	21	0.439	0.422	19.8
	68	0.400	0.461	6.8
	103	0.297	0.564	5.5
	171	0.151	0.710	4.2
	233	0.108	0.753	3.2
TCE	0	0.858	0	0
	21	0.637	0.221	10.5
	68	0.560	0.298	4.4
	103	0.434	0.424	4.1
	171	0.213	0.645	3.8
	233	0.154	0.704	3.0

Table A.9. Batch test data for PCE adsorption onto peat in the presence of TCE.

Solute	Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
PCE	0	1.253	0	0
	187	0.996	0.257	1.40
	760	0.833	0.420	0.55
	2133	0.660	0.593	0.28
	4800	0.603	0.650	0.14
	13,333	0.566	0.687	0.05
	20,000	0.425	0.828	0.04
	26,667	0.368	0.885	0.03
TCE	0	1.535	0	0
	187	1.121	0.414	2.20
	760	1.005	0.530	0.70
	2133	0.869	0.667	0.31
	4800	0.850	0.685	0.14
	13,333	0.729	0.806	0.06
	20,000	0.736	0.799	0.04
	26,667	0.682	0.853	0.03

Table A.10. Batch test data for PCE adsorption onto peat in the presence of CCl_4 .

Solute	Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
PE	0	0.958	0	0
	207	0.399	0.559	2.70
	793	0.229	0.729	0.92
	2153	0.194	0.764	0.35
	13,467	0.148	0.810	0.06
	26,667	0.085	0.873	0.03
CCl_4	0	0.587	0	0
	207	0.462	0.125	0.60
	793	0.339	0.248	0.31
	2153	0.320	0.267	0.12
	13,467	0.308	0.279	0.02
	26,667	0.201	0.386	0.01

Table A.11. Batch test data for DCB adsorption onto activated carbon.

Adsorbent Dose = M (mg/l)	C_f (mg/l)	$X = C_o - C_f$	X/M (mg/g)
0	1.078	0	0
1.26	0.813	0.265	210
3.80	0.657	0.421	111
13.3	0.163	0.915	69
40.0	0.045	1.033	26

Freundlich Parameters

$K = 193$

$1/n = 0.63$

Corr. Coeff. = .97

Table A.12. Batch test data for DCB adsorption onto XAD-8.

Adsorbent Dose = M (mg/l)	C_f (mg/l)	$X = C_o - C_f$	X/M (mg/g)
0	1.078	0	0
10.7	0.609	0.469	44
24.7	0.622	0.456	18
93.3	0.190	0.888	10
149.3	0.183	0.895	6
236.7	0.147	0.931	4

Freundlich Parameters

$$K = 52$$

$$1/n = 1.22$$

$$\text{Corr. Coeff.} = .91$$

Table A.13. Batch test data for DCB adsorption onto XE-340.

Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
0	1.005	0	0
23	0.593	0.412	18
36	0.452	0.553	15
69	0.187	0.818	12
105	0.149	0.856	8
167	0.079	0.926	6

Freundlich Parameters

K = 24

1/n = .53

Corr. Coeff = .97

Table A.14. Batch test data for DCB adsorption onto peat.

Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
0	1.078	0	0
140	0.822	0.256	1.8
340	0.780	0.298	0.9
2733	0.385	0.693	0.2
6733	0.190	0.888	0.1
14,000	-	-	-

Freundlich Parameters

$$K = 1.75$$

$$1/n = 1.85$$

$$\text{Corr. Coeff} = .96$$

Table A.15. Batch test data for DCB adsorption onto soil.

Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
0	1.078	0	0
913	1.014	0.064	0.070
6667	0.931	0.147	0.022
13,333	0.838	0.240	0.018
26,667	0.886	0.192	0.006

Freundlich Parameters

$$K = 0.09$$

$$1/n = 9.7$$

$$\text{Corr. Coeff.} = .97$$

Table A.16. Batch test data for DCB adsorption onto activated carbon in the presence of TCE.

Solute	Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
CDB	0	0.900	0	0
	1.3	0.682	0.218	172
	3.8	0.412	0.488	128
	13.3	0.098	0.802	60
	40.0	-	-	-
	53.3	0.033	0.867	16
TCE	0	0.896	0	0
	1.3	0.818	0.078	60
	3.8	0.834	0.062	16
	13.3	0.744	0.152	11
	40.0	0.482	0.414	10
	53.3	0.432	0.464	9

Table A.17. Batch test data for DCB adsorption onto XE-340 in the presence of TCE.

Solute	Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
DCB	0	1.010	0	0
	20.7	0.635	0.375	18.0
	38.7	0.584	0.426	11.0
	74.7	0.541	0.469	6.3
	105.3	0.383	0.627	5.9
	135.3	0.337	0.673	4.9
	174.7	0.334	0.676	3.9
TCE	0	0.712	0	0
	20.7	0.509	0.203	9.8
	38.7	0.494	0.218	5.6
	74.7	0.471	0.241	3.2
	105.3	0.349	0.363	3.4
	135.3	0.310	0.402	3.0
	174.7	0.308	0.404	2.3

Table A.18. Batch test data for DCB adsorption onto peat in the presence of TCE.

Solute	Adsorbent Dose = M (mg/l)	C_f (mg/l)	$X = C_o - C_f$	X/M (mg/g)
DCB	0	0.980	0	0
	187	0.908	0.072	0.40
	860	0.647	0.333	0.40
	2133	0.474	0.506	0.20
	4807	0.344	0.636	0.10
	13,333	0.135	0.845	0.06
	20,133	0.163	0.817	0.04
TCE	0	1.228	0	0
	187	0.904	0.324	1.70
	860	0.717	0.511	0.60
	2133	0.612	0.616	0.28
	4807	0.566	0.662	0.14
	13,333	0.541	0.687	0.05
	20,133	0.487	0.741	0.04

Table A.19. Batch test data for DCB adsorption onto peat in the presence of CCl_4 .

Solute	Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
DCB	0	0.900	0	0
	153	0.390	0.510	3.0
	360	0.384	0.516	1.0
	807	0.340	0.560	0.7
	2787	0.246	0.654	0.2
	6667	0.123	0.777	0.1
CCl_4	0	0.527	0	0
	153	0.359	0.168	1.10
	360	0.368	0.159	0.40
	807	0.359	0.168	0.20
	2787	0.368	0.159	0.06
	6667	0.231	0.296	0.04

Table A.20. Batch test data for DCB adsorption onto activated carbon in the presence of PCE.

Solute	Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
DCB	0	1.078	0	0
	3.8	0.547	0.531	140
	5.1	0.559	0.519	102
	14.0	0.276	0.802	57
	41.3	0.103	0.975	24
	113.3	-	-	-
	220.0	-	-	-
PCE	0	0.993	0	0
	3.0	0.458	0.535	141
	5.1	0.494	0.499	98
	14.0	0.493	0.500	36
	41.3	0.205	0.788	19
	113.3	0.052	0.941	8
	220.0	0.008	0.985	5

Table A.21. Batch test data for DCB adsorption onto XAD-8 in the presence of PCE.

Solute	Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
DCB	0	0.980	0	0
	7.1	0.757	0.223	31
	21.0	0.308	0.672	32
	43.0	-	-	-
	75.0	-	-	-
	101.5	-	-	-
	130.0	-	-	-
PCE	0	1.002	0	0
	7.1	0.596	0.406	57
	21.0	0.388	0.614	29
	43.0	0.277	0.725	17
	75.0	0.233	0.769	10
	101.5	0.167	0.835	8
	130.0	0.148	0.854	7

Table A.22. Batch test data for DCB adsorption onto XE-340 in the presence of PCE.

Solute	Adsorbent Dose = M (mg/l)	C_F (mg/l)	$X = C_o - C_f$	X/M (mg/g)
DCB	0	0.979	0	0
	21	0.780	0.200	10
	34	0.588	0.392	12
	74	0.473	0.507	7
	141	0.274	0.706	5
	169	0.240	0.740	4
PCE	0	0.837	0	0
	21	0.383	0.454	22
	34	0.360	0.477	14
	74	0.220	0.617	8
	141	0.206	0.631	5
	169	0.202	0.635	4

Table A.23. Batch test data for DCB adsorption onto peat in the presence of PCE.

Solute	Adsorbent Dose = M (mg/l)	C_f (mg/l)	$X = C_o - C_f$	X/M (mg/g)
DCB	0	0.980	0	0
	340	0.689	0.291	0.86
	847	0.642	0.338	0.40
	2067	0.601	0.379	0.18
	4873	0.358	0.622	0.13
	20,000	-	-	-
	26,667	0.260	0.954	0.04
PCE	0	1.002	0	0
	340	0.590	0.412	1.20
	847	0.556	0.446	0.53
	2067	-	-	-
	4873	0.423	0.579	0.12
	20,000	0.186	0.816	0.04
	26,667	0.212	0.790	0.03

Table A.24. Batch test data for TCE adsorption onto XE-340.

Adsorbent Dose = M (mg/l)	C_f (mg/l)	$X = C_o - C_f$	X/M (mg/g)
0	1.000	0	0
22	0.786	0.241	9.7
101	0.426	0.574	5.7
171	0.310	0.690	4.0
237	0.210	0.790	3.3
339	0.142	0.858	2.5

Freundlich Parameters

$$K = 11.2$$

$$1/n = .79$$

$$\text{Corr. Coeff.} = .99$$

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