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# ADSORPTION AND DESORPTION OF HEXACHLOROBIPHENYL

A. Experimental Results and Discussions
B. Analysis of Exchangeable and Nonexchangeable Components

by

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16. ABSTRACT


The purpose of this report is to present the experimental and theoretical results that lead to the development model for the analysis of adsorption and desorption of hexachlorobiphenyl from suspended and sedimented particles.

The reversibility of the adsorption reaction between dissolved organic chemicals and naturally occurring soils, sediments, and suspended particles is of fundamental importance in the understanding of the fate of these chemicals in the environment. The issue of reversibility becomes critical if the adsorption-desorption behavior of a chemical is to be expressed quantitatively within the framework of mass balance equations. In the formulations used to date, with a notable exception to be discussed below, the formulations used to express the adsorption and desorption reactions assume reversible behavior, that is, at equilibrium, the same isotherm applies for adsorption and desorption.

The difficulty with this assumption is that for many organic chemicals and many naturally occurring adsorbents, laboratory adsoption and subsequent desorption experiments demonstrate only partially reversible behavior.

In the experiment described in Part A, Section VIII, this nonsingular behavior was confirmed and, using various experimental procedures, it was found to persist. This suggests that it is necessary to account for this behavior in a quantitative and consistent way.

It is the purpose of Part B of this report to present a framework within which this nonsingular behavior can be analyzed in a manner that can be easily incorporated into mass balance calculations.


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TABLE OF CONTENTS

Part A


| Section | Title | Page |
|---|---|---|
| I | Summary and Recommendations | 1 |
| II | Introduction and Previous Work | 13 |
| III | Experimental Methodology and Initial Experimental Results | 16 |
| IV | Kinetics | 34 |
| V | Effect of Solution Composition | 51 |
| VI | Sediment Composition Effects | 66 |
| VII | Sediment Concentration Effects | 86 |
| VIII | Reversibility of Adsorption and Desorption | 107 |


Part B


| | | |
|---|---|---|
| I | Exchangeable and Nonexchangeable Components Model of Adsorption and Desorption | 139 |
| II | Effect of Sediment Concentration and Composition | 169 |
| III | Resuspension and Dilution: Implications for Fate of PCB | 193 |

FIGURES - Part A

Fig. #


I-1. Exchangeable-Nonexchangeable Component Model of Desorption . . . . . 4

I-2. HCB Isotherm Analysis. Saginaw Bay Station #50 . . . . . 6

I-3. Partition Coefficient vs. Adsorbent Concentration . . . . . 7

I-4. HCB Partition Coefficient versus Adsorbent Concentration. Saginaw Bay Station #50, Distilled Water. . . . . 8

I-5. Particulate fraction versus adsorbent mass for reversible desorption, eq. (15); and exchangeable-nonexchangeable desorption, eq. (17). $\pi_o = 10^4$ ℓ/kg, $\nu_x = 0.5$ . . . . . 11

III-1. Flow Chart of Experimental Procedure . . . . . 17

III-2. Adsorption-Desorption Experimental Procedure . . . . . 19

III-3. Histogram of Mass Balance Error, $e_1$(%). . . . . 23

III-4. Adsorption of HCB to Vessel Walls . . . . . 24

III-5. Adsorption of HCB to Metal Coated Vessels . . . . . 25

III-6. Glass Adsorption Isotherm: Volumetric Concentration of HCB Adsorbed to the Wall versus Aqueous Concentration. Distilled Water . . . . . 27

III-7. Adsorbed HCB Concentration at Adsorption Equilibrium, $mr_a$, versus Total HCB Concentration at Desorption Equilibrium,

$c_{Td}$, for Type 3 Experiments. Histograms of % Error = 100% $(mra - c_{Td})/c_{Td}$. . . . . 29

III-8. Comparison of Glass Adsorption Isotherm (from Fig. III-6) to Glass Adsorbed HCB after Desorption Equilibrium . . . . . 30

IV-1. Effect of Adsorption time, $t_a$, on aqueous concentration, $c_a$, sediment adsorbed HCB, $r_a$, and partition coefficient, $\pi_a$. m = 200 mg/ℓ Montmorillonite, Aqueous phase is supernatant. . . . . 35

IV-2. Effect of Adsorption Time, $t_a$, on aqueous concentration, $c_a$, sediment adsorbed HCB, $r_a$, and partition coefficient, $\pi_a$. m = 200 mg/ℓ Saginaw Bay #50, Aqueous phase = supernatant . . . . . 37

IV-3. HCB Adsorption Isotherms at various Adsorption Times. Saginaw Bay #50, m = 1000 mg/ℓ, Distilled Water . . . . . 38

IV-4. HCB Adsorption Isotherms. Comparison. Saginaw Bay #50 m = 1000-1100 mg/ℓ. Distilled Water . . . . . 41

IV-5. HCB Adsorption Isotherms. Saginaw Bay #50, m = 55 mg/ℓ, Distilled Water . . . . . 42

IV-6. Effect of Desorption Time, $t_d$, on Desorption Aqueous Concentration, $c_d$, Sediment Bound HCB, $r_d$, and Desorption Partition Coefficient $\pi_d$. m = 200 mg/ℓ, montmorillonite supernatant. $t_a$ = 2 hr. . . . . 43

IV-7. Effect of Desorption Time, $t_d$, on desorption aqueous concentration, $c_d$, sediment bound HCB, $r_d$, and desorption partition coefficient, $\pi_d$. m = 200 mg/ℓ Saginaw Bay #50,

Supernatant, $t_a$ = 2 hr. . . . . 44

IV-8. Long Term Desorption. Sediment Bound HCB, $r_d$ and desorption partition coefficient, $\pi_d$(ℓ/g) (x 10 for convenience in plotting) versus desorption time. . . . . 45

IV-9. Adsorption ($r_a$ vs. $c_a$) and Desorption ($r_d$ vs. $c_d$) Isotherms: $t_a$ = 3 hr., $t_d$ = 3 hr. m = 1100 mg/ℓ Saginaw Bay #50. Distilled Water . . . . . 48

IV-10. Adsorption ($r_a$ vs. $c_a$) and Desorption ($r_d$ vs. $c_d$). Isotherms for increasing desorption times: $t_d$ = 72 and 144 hr. m = 1100 mg/ℓ Saginaw Bay #50, Distilled Water. . . . . 49

IV-11. Effect of Increasing Desorption Time. Saginaw Bay #50. . . . . 50

V-1. Effect of Temperature on HCB Adsorption. $t_a$ = 3 hr., m = 1100 mg/ℓ Saginaw Bay #50 . . . . . 52

V-2. Effect of pH on HCB Partitioning to Montmorillonite . . . . . 56

V-3. Effect of Increasing Ionic Strength using NaCl and $CaCl_2$ on HCB Adsorption Partition Coefficient for Montmorillonite. m = 200 mg/ℓ. $t_a$ = 4 hr. . . . . 57

V-4. Adsorption Isotherm for Distilled Water and 0.01M $CaCl_2$ m = 220 mg/ℓ Montmorillonite . . . . . 60

V-5. Adsorption Isotherm for Distilled Water and 0.01M $CaCl_2$. m = 220 mg/ℓ Saginaw Bay #50 . . . . . 61

V-6. Effect of pH on Vessel Adsorption of HCB . . . . . 62

V-7. Effect of Solution Composition on Vessel (Glass) Adsorption of HCB . . . . . 64

VI-1. Location Map for Sediment Samples . . . . . 67

VI-2. HCB Adsorption and Desorption Isotherms for Saginaw Bay sediment samples. m = 1100 mg/ℓ . . . . . 74

VI-3. HCB Adsorption and Desorption Isotherms for Station #69 . . . . . 75

VI-4. HCB Adsorption & Desorption Isotherms for Station #31 on Total and Suspended Solids Samples . . . . . 77

VI-5. Adsorption and Desorption Partition Coefficients versus Specific Surface area and % Volatile Solids . . . . . 82

VI-6. Comparison of Estimated Partition Coefficient using Regression Equation to Observed Values. . . . . 83

VII-1. Adsorption Partition Coefficient vs. Adsorbent Concentration. . . 88

VII-2. Adsorption Isotherms for m = 55, 220, and 1100 mg/ℓ Saginaw Bay #50 . . . . . 89

VII-3. Adsorption Isotherms for m = 50, 200, 1000 mg/ℓ Montmorillonite . . . . . 91

VII-4. Adsorption Isotherms for m = 55 and 1100 mg/ℓ Montmorillonite Aqueous phase = 2 mM $NaHCO_3$ . . . . . 92

VII-5. Variation in Adsorption partition coefficient, $\pi_a$, and Sediment Bound HCB, $r_a$, versus adsorbent concentration, m, at constant equilibrium aqueous concentration, $c_a$. . . . . 94

VII-6. Variation in Adsorption partition coefficient, $\pi_a$, and Sediment Bound HCB, $r_a$, versus adsorbent concentration, m, at constant equilibrium aqueous concentration, $c_a$. . . . . 95

VII-7. Variation in Adsorption partition coefficient, $\pi_a$, and

Sediment Bound HCB, $r_a$ versus adsorbent concentration, m, at constant equilibrium aqueous concentration, $c_a$. . . . . 96

VII-8. Variation in Adsorption partition coefficient, $\pi_a$, and Sediment Bound HCB, $r_a$ versus adsorbent concentration, m, at constant equilibrium aqueous concentration, $c_a$. . . . . 98

VII-9. Variation in Adsorption partition coefficient, $\pi_a$, and sediment bound HCB, $r_a$, versus adsorbent concentration, m, at constant equilibrium aqueous concentration, $c_a$. Effect of increased adsorption time, $t_a$ = 24 hr. versus $t_a$ = 3 hr. (dashed line from fig. VII-6) . . . . . 99

VII-10. Log-log analysis of $\pi_a$ versus m. Straight line slopes & intercepts are given in Table VII-1. . . . . 101

VII-11. Comparison of particulate fraction computed using constant $\pi_a$ to observed data . . . . . 105

VIII-1. Adsorption and Desorption Isotherms - Montmorillonite Distilled Water. Lines have unity slope . . . . . 110

VIII-2. Adsorption and Desorption Isotherms - Montmorillonite, Aqueous phase = 2mM $NaHCO_3$ and Kaolinite, Distilled Water. Lines have unity slope . . . . . 111

VIII-3. Adsorption and Desorption Isotherms - Saginaw Bay #50 Distilled Water. Lines have unity slope . . . . . 112

VIII-4. Effect of Adsorbent Concentration on Degree of Reversibility Adsorption, $\pi_a$, and Desorption, $\pi_d$, Partition Coefficients and their ratio . . . . . 115

VIII-5. Effect of Adsorbent Concentration on Degree of Reversibility Adsorption, $\pi_a$, and Desorption, $\pi_d$, Partition Coefficients and their ratio . . . . . 116

VIII-6. Effect of Dilution on HCB Desorption . . . . . 118

VIII-7. Effect of Adsorption Time on Reversibility m = 55 mg/ℓ Saginaw Bay #50 . . . . . 121

VIII-8. Effect of Adsorption on Reversibility Adsorption $\pi_a$, and Desorption, $\pi_d$, Partition Coefficients versus Adsorbent mass. $t_a$ = 24 hr. Montmorillonite. Supernatant. . . . . 122

VIII-9. Consecutive Desorption Isotherms - Saginaw Bay and Montmorillonite . . . . . 124

VIII-10. Consecutive Desorption Isotherms - Saginaw Bay and Montmorillonite . . . . . 125

VIII-11. Consecutive Desorption. Saginaw Bay #50. m = 1100 mg/ℓ, Distilled Water (a) Sediment Bound HCB, r, and (b) aqueous concentration, c versus desorption cycle. (c) Isotherm. . . . . 127

VIII-12. Consecutive Desorption. Saginaw Bay #50 and Montmorillonite. m = 200 mg/ℓ. Distilled Water (a) Sediment Bound HCB, r, and (b) aqueous concentration, c, versus desorption cycle. (c) Isotherm . . . . . 131

TABLES - Part A


| Table | | Page |
|---|---|---|
| III-1. | Nomenclature and Computational Equations | 20-21 |
| III-2. | Glass Desorption Data | 26 |
| III-3. | Speciation Experiment - Montmorillonite | 32 |
| III-4. | Speciation Experiment - Saginaw Bay #50 | 33 |
| IV-1. | Saginaw Bay Adsorption Isotherms | 39 |
| IV-2. | Long Term Desorption Study | 47 |
| V-1. | Effects of Temperature on Adsorption | 53 |
| V-2. | Adsorption vs. Chemical Composition | 59 |
| VI-1. | Sampling Locations for Saginaw Bay | 68 |
| VI-2. | Sediment Size Distribution for Saginaw Bay | 69 |
| VI-3. | Chemical Characteristics of Saginaw Bay Sediments | 71 |
| VI-4. | Chemical Characteristics of Saginaw Bay Sediments Seived Subsamples | 72 |
| VI-5. | Sediment Partition Coefficients and Freundlich Isotherm Parameters | 73 |
| VI-6. | HCB Partitioning to Saginaw Bay Suspended Matter | 78 |
| VI-7. | Representative PCB Concentrations for Saginaw Bay Suspended Solids* | 80 |
| VI-8. | Multiple Linear Regression Results | 84 |
| VII-1. | Partitioning Coefficient - Adsorbent Mass Regression | 102 |
| VIII-1. | Isotherm Parameters - Saginaw Bay Sediments | 109 |
| VIII-2. | Isotherm Parameters - Effect of Sediment Concentration | 113 |
| VIII-3. | Isotherm Parameters - Effect of Adsorption Time | 120 |
| VIII-4. | Consecutive Desorption Data | 126 |
| VIII-5. | Consecutive Desorption | 128 |
| VIII-6. | Consecutive Desorption | 133 |

# Adsorption and Desorption of

# Hexachlorobiphenyl

## Part A

## Experimental Results and Discussions

## SECTION I

## SUMMARY AND RECOMMENDATIONS

### A. Introduction

The purpose of this report is to present the experimental and theoretical results that lead to the development model for the analysis of adsorption and desorption of hexachlorobiphenyl from suspended and sedimented particles. In contrast to the desorption reaction, a large body of information already exists for the adsorption reaction. Relationships have been developed that relate the extent of adsorption of organic chemicals to their characteristics such as aqueous solubility (Chiou et al., 1979) and adsorbent properties such as specific surface area (Hiraizumi et al., 1979) and organic carbon content (Karickhoff et al., 1979).

This is not the case, however, for the desorption reaction. The available information, to be discussed in more detail subsequently, indicates that for a great many organic adsorbent systems the desorption reaction is not completely or even moderately reversible. As a consequence the assumption of reversible behavior is neither justified nor realistic, and it is not possible to directly apply the large body of adsorption theory and data to describe desorption since, for nonreversible systems, it is not the same reaction.

This is unfortunate since it is not clear how to incorporate nonreversible behavior into modeling frameworks that have been, and are being, developed by EPA and other groups for the computation of the fate of toxic chemicals in natural waters (Baughman and Lassiter, 1978; Thomann and Di Toro, 1979, O'Connor and Schnoor, 1979). If the adsorption were either completely reversible, or completely irreversible so that no desorption occurred, then it would be straightforward to include such behavior in a fate model. What has been found experimentally, however, is that some desorption takes place. The amount is variable and depends on the details of the situation such as the mass of adsorbent and the adsorbate-adsorbent pair involved.

The use of a desorption "partition coefficient" in a way that is analogous to the use of the adsorption partition coefficient in fate computations, is not a solution to the problem since the actual quantity of chemical desorbed when exposed to lower aqueous concentration is not directly related to only the desorption partition coefficient but also to the quantity of chemical previously adsorbed. As it happens, for the desorption model described below, the desorption partition coefficient does have a specific meaning, which the model

clarifies, but it cannot be used directly in fate computations. Without a specific model for nonreversible desorption, it is not surprising that this mechanism has not been explicitly included in fate computations.

The nonreversible behavior of adsorption and desorption can have important consequences for the fate of chemicals in natural waters. As inputs of toxic chemicals are reduced, the desorption of already existing toxic chemical from suspended solids and sediments will constitute the major inputs of dissolved toxicants into the water column. The magnitude and extent of this reaction can control the environmental distribution and the exposure level for the biota. If the quantity of chemical desorbed is much less than the quantity initially adsorbed then assuming completely reversible behavior can significantly overestimate the dissolved chemical in the water column. This overestimate may translate into an underestimation of the impact of remedial measures such as discharge reductions via treatment of effluents. Hence, a quantitative understanding of the factors that influence the behavior of the desorption reaction is an essential component for understanding the fate of toxic chemicals in natural waters and the consequences of remedial actions.

Summary

As part of the effort at Manhattan College to formulate and test mathematical models of the fate of PCB's in the Great Lakes (Thomann, 1977) a series of experiments have been conducted using tritiated hexachlorobiphenyl (abbreviated as HCB) as the adsorbate and natural sediments and inorganic clays as the adsorbents. The experiments concentrated on the desorption behavior as well as conventional adsorption tests. Nonreversible desorption occurred and an effort was made to formulate a model which explained the data.

It was assumed that the adsorbed HCB was made up of two components: an exchangeable component which readily and reversibly desorbes and readsorbes depending upon aqueous phase concentration, and a second component, which was termed nonexchangeable, which resisted desorption until very low (or possibly zero) aqueous concentrations. This idea is often used to explain nonreversible behavior in qualitative terms, e.g. physical versus chemical adsorption. Methods were developed for calculating the quantity of the exchangeable and nonexchangeable components from the experimental adsorption and desorption data. This is the unique feature of the model since it gives quantitative estimates of the magnitudes of these components. An analysis of the individual behavior suggested that each was describable in terms of (distinct) linear isotherms. This regular behavior, for both natural sediments

and inorganic clays, represents a significant simplification and codification of a large quantity of adsorption and desorption data in terms of distinct partition coefficients for the exchangeable and nonexchangeable components. Subsequent consecutive adsorption experiments confirmed the distinct behavior of the two components and supported the validity of the model.

The basic idea is illustrated in fig. 1. A conventional adsorption-desorption data set (assuming three adsorption points and three desorption points for clarity) is shown in fig. 1a. The fact that two distinct isotherms are found for the adsorption and desorption data indicates that the desorption is not completely reversible. Consider a single pair of points corresponding to a single adsorption-desorption experiment, fig. 1b. If it is assumed that continued desorption cycles follow a straight line, then the intersection of this line and the ordinate defines the particulate concentration which is nonexchangeable (since it remains on the particles even at zero aqueous concentration). This concentration, $r_o$, is illustrated in fig. 1b. Once the nonexchangeable component concentration, $r_o$, has been found, the differences between this concentration and that found at adsorption and desorption equilibria must be the exchangeable component since two components are assumed to be present. The fact that it responded to the decrease in aqueous concentration that occurred from adsorption to desorption equilibrium supports its exchangeability. Note that two exchangeable component data points result: at adsorption equilibrium, $r_{xa}$, and at desorption equilibrium, $r_{xd}$. These correspond to the two aqueous concentrations $c_a$ and $c_d$, respectively. If this analysis is repeated for the remaining two adsorption-desorption data pairs in the illustration, the result is six pairs of exchangeable component-aqueous concentration data.

The validity of this analysis depends upon the observation that all the exchangeable component data conform to a single isotherm, fig. 1c. The same isotherm applies to all exchangeable component data, regardless of whether they correspond to the quantity of exchangeable component that is present at adsorption, $r_{xa}$, in equilibrium with aqueous concentration, $c_a$, or at desorption, $r_{xd}$, in equilibrium with aqueous concentration, $c_d$. That is, the exchangeable component is behaving in accordance with classical reversible adsorption-desorption theory.

The three nonexchangeable component concentrations calculated from the data analysis have also been found to follow one isotherm, illustrated in fig. 1d. They are a linear function of the adsorption aqueous concentration as illustrated.

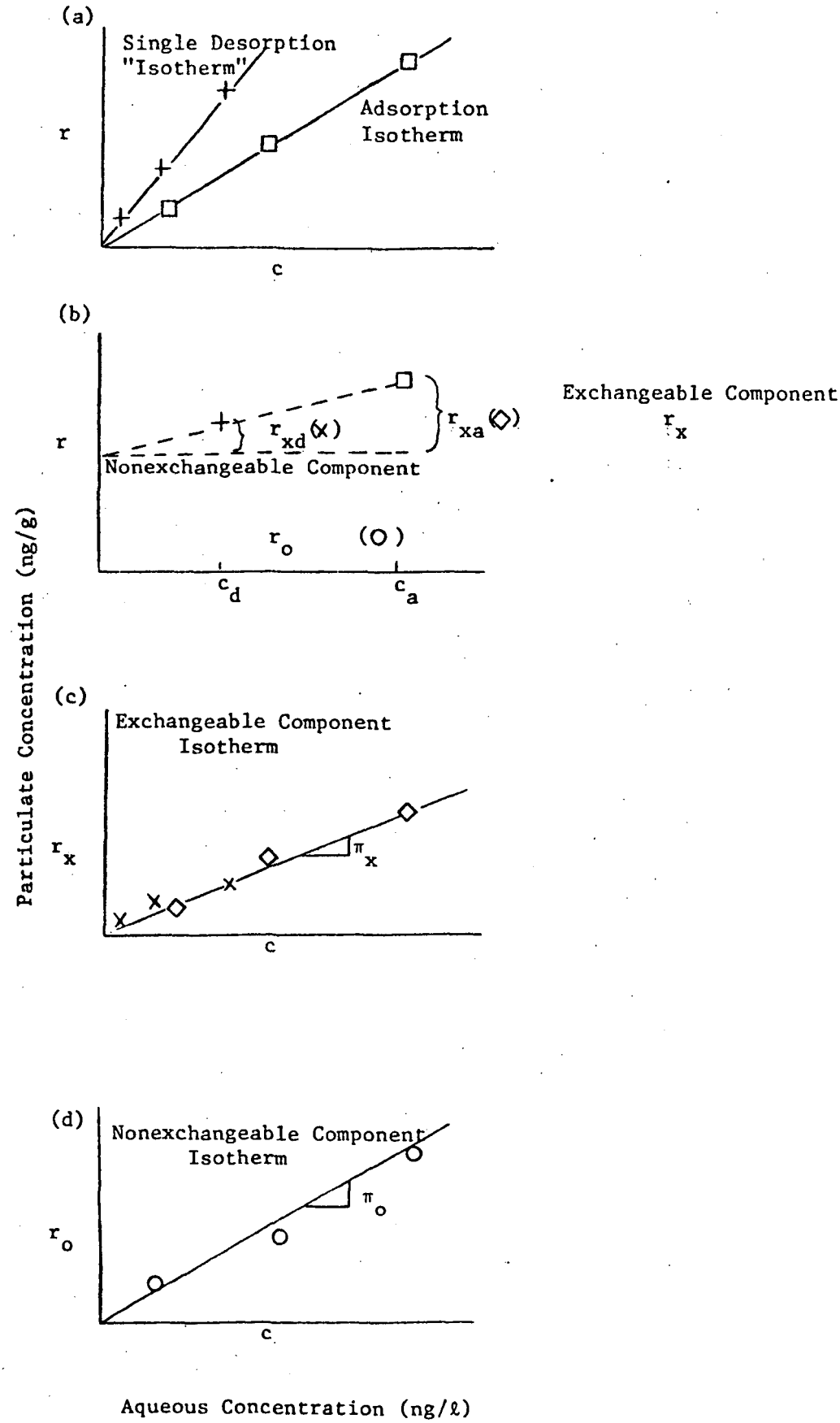



Fig. 1-1. Exchangeable-Nonexchangeable Component Model of Desorption

The actual data set for an HCB adsorption-desorption isotherm experiment, corresponding to the illustrations in fig. 1. are shown in fig. 2. Part B of this report contains additional results of the isotherm analysis for HCB and a full discussion of the development of the proposed adsorption-desorption model. Part A of this report presents further data and the results of experimental modifications designed to eliminate experimental artifacts as the cause of the nonreversible behavior.

A second focus of the experiments conducted with HCB was the effect of the mass of adsorbent on the partition coefficients. It had been observed from an analysis of published data (O'Connor and Connolly, 1980) that adsorption partition coefficients decrease as adsorbent mass increases. ~~Fig. 3~~, reproduced from O'Connor and Connolly, 1980, illustrates the effect. This phenomena was investigated for HCB adsorption and also for desorption. It was found to occur for both reactions. If the data is interpreted in terms of exchangeable and nonexchangeable components, it was found that the nonexchangeable partition coefficient is essentially independent of adsorbent mass whereas the exchangeable partition coefficient is inversely proportional to adsorbent mass. An example is presented in fig. 4. The adsorption and desorption partition coefficients are seen to decrease as adsorbent mass, m, increases (fig. 4a). Note that the extent of irreversibility increases as mass increases. That is, the desorption partition coefficient becomes increasingly larger than the adsorption partition coefficient as adsorbent mass increases. The exchangeable partition coefficient is seen to be inversely proportional to mass (fig. 4b) whereas the nonexchangeable partition coefficient is independent of mass (fig. 4c). This suggests a definition of an exchangeable distribution coefficient: $\nu_x = \pi_x m$ which is also mass independent. The solid lines in fig. 4a are the variations of adsorption and desorption partition coefficients predicted by the exchangeable-nonexchangeable desorption model (See Part B for details).

The variation of these mass-independent parameters as functions of sediment properties has been examined. The details, together with additional data and a more complete description of the adsorbent mass effects are given subsequently in Parts A and B.

The result of this combined experimental and modeling program is a quantitative framework within which it is possible to predict the adsorption, and more significantly, the desorption behavior of hexachlorobiphenyl as a function of adsorbent mass and its characteristics.

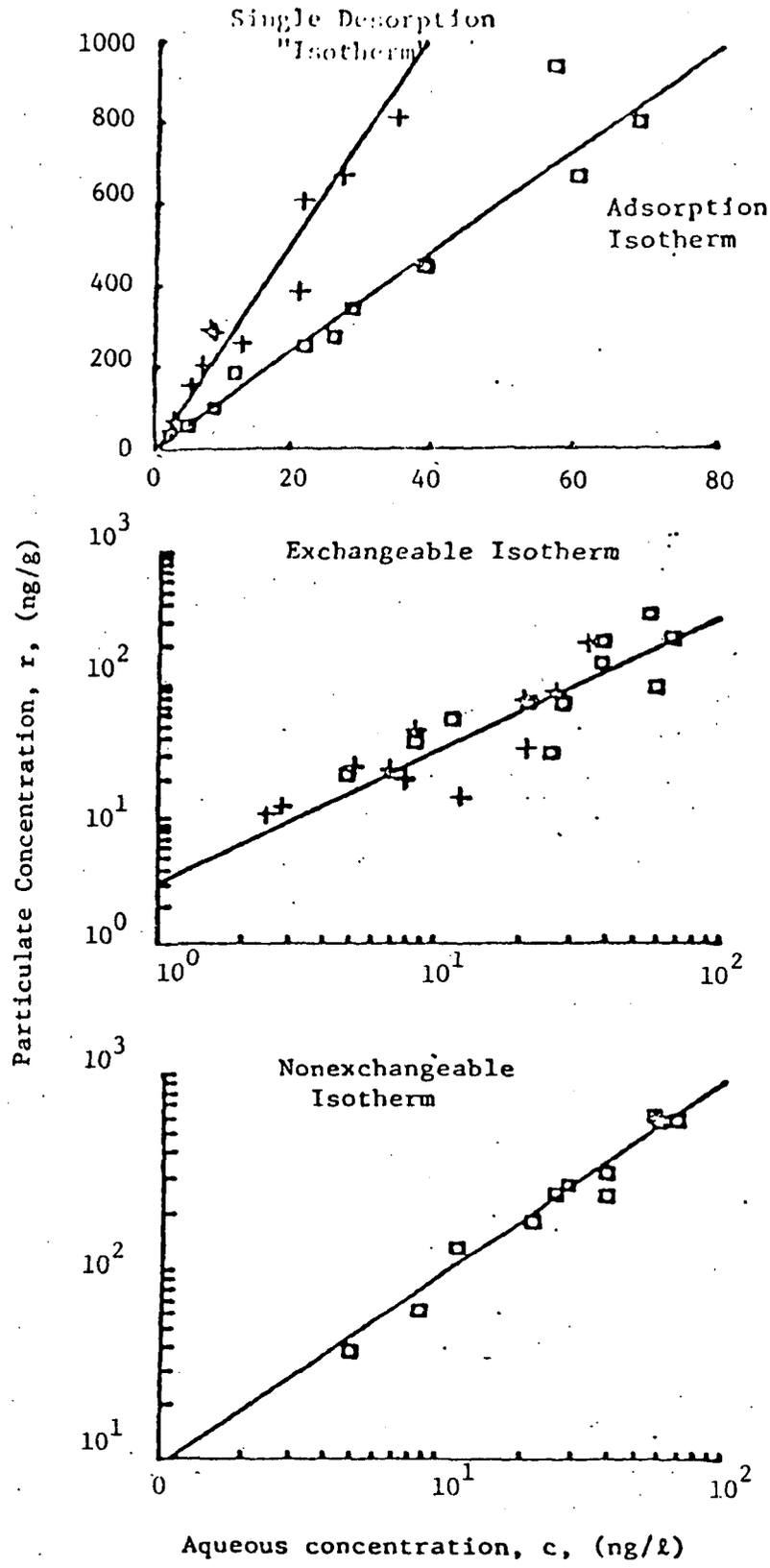



Fig. I-2. HCB Isotherm Analysis. Saginaw Bay Station #50

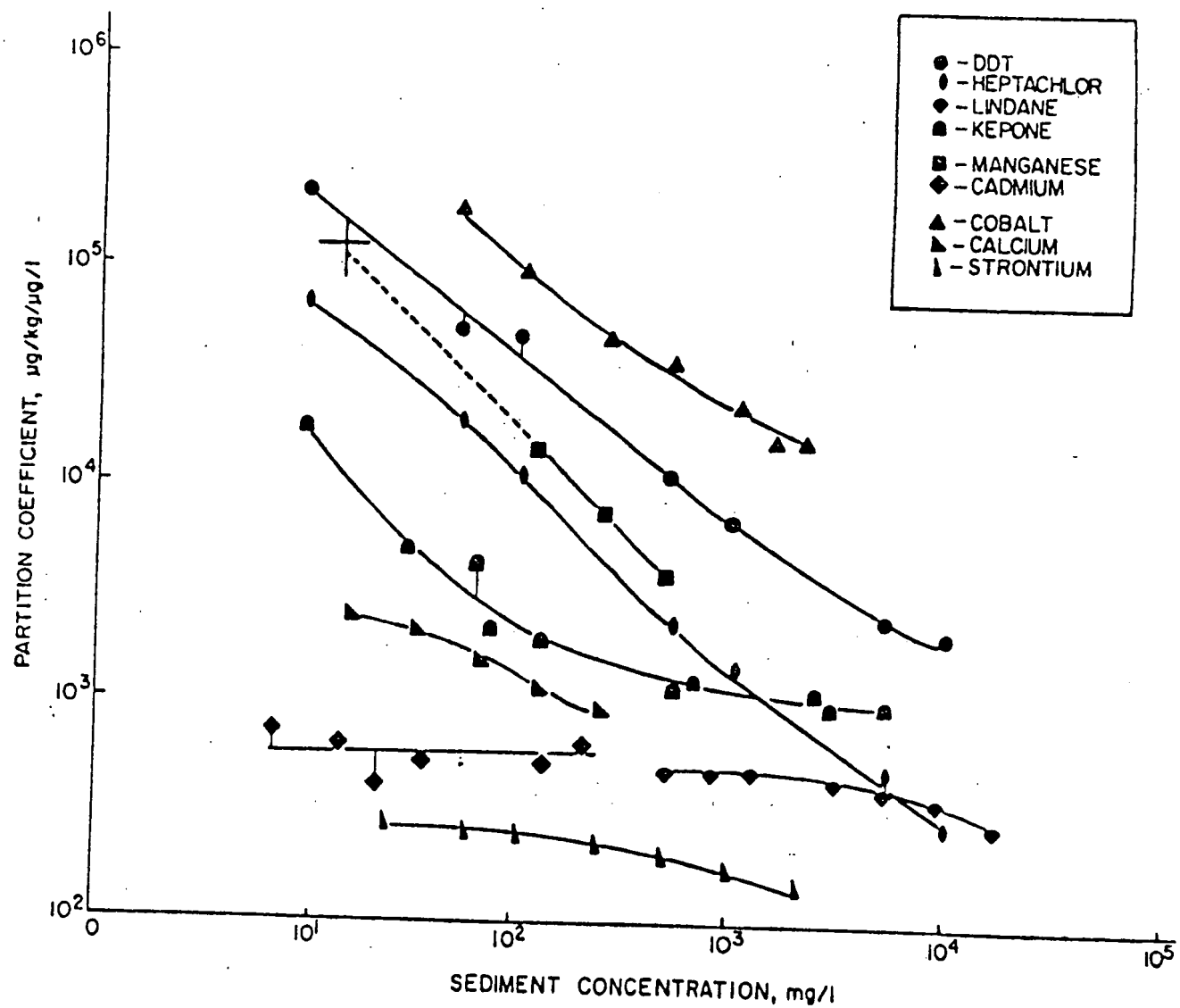



Fig. I-3. Partition Coefficient vs. Adsorbent Concentration
(O'Connor & Connolly, 1980)

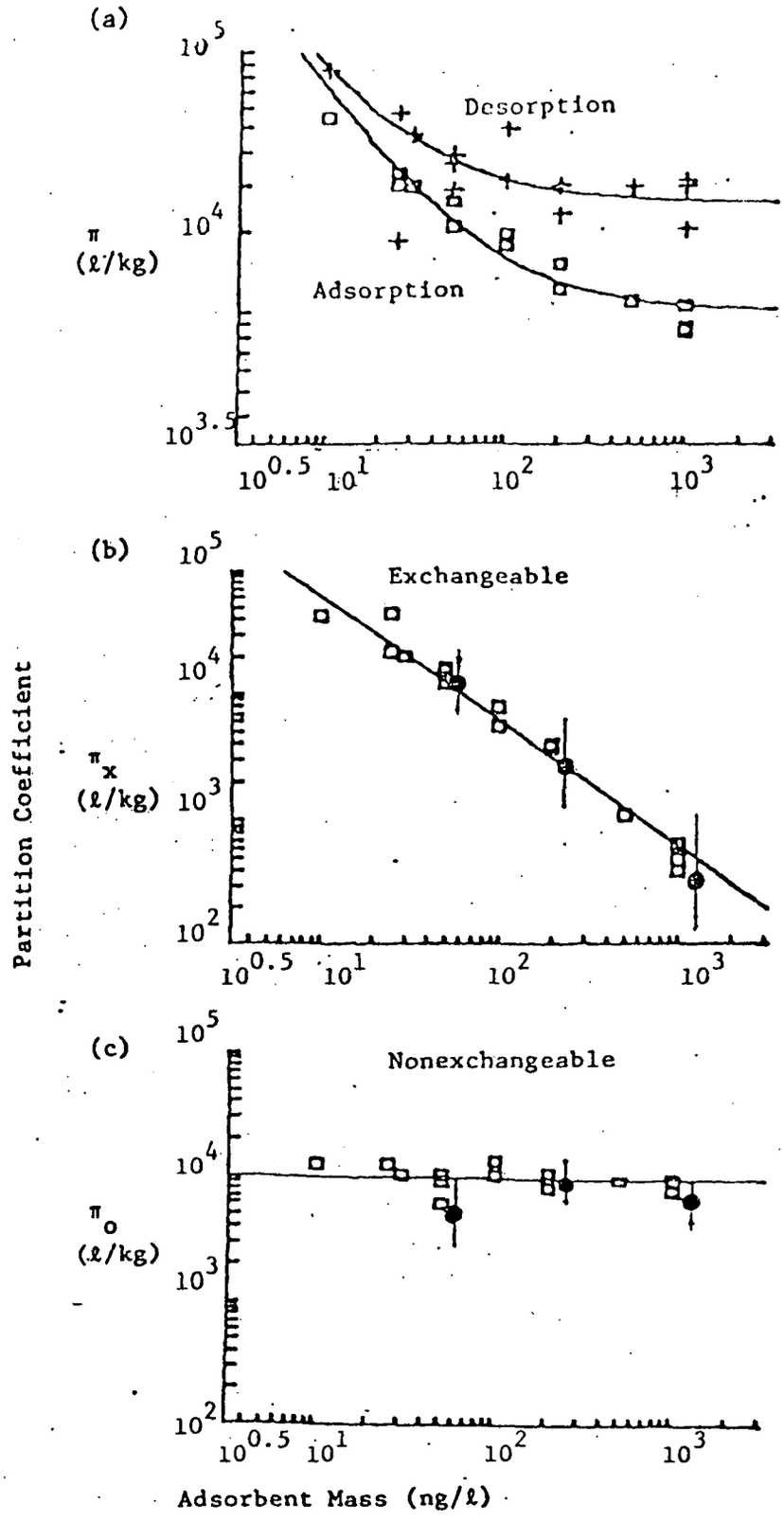



Fig. I-4. HCB Partition Coefficient versus Adsorbent Concentration. Saginaw Bay Station #50, Distilled Water.

The importance of the interaction between modeling analysis and experimental design in such an investigation cannot be overemphasized. The exchangeable-non-exchangeable model was formulated as a consequence of the need to organize, synthesize, and understand the experimental data. Once the hypothesis was formulated in quantitative terms, it was possible to design experiments to test the model predictions and illucidate the relevant features. The dual capability to do the experiments and formulate the models within a cooperating group is essential if progress is to be made in formulating and testing rational, quantitative descriptions of complex phenomena such as the desorption reaction.

C. Implications for Receiving Water Fate Models

The use of models for the computation of toxic chemicals exposure levels in natural waters is currently an important component of rational toxic chemical regulation and control. The development of EXAMS by EPA (Baughman and Lassiter, 1978), models for PCB, radionuclides and toxic heavy metals in the Great Lakes by our group at Manhattan College, and other investigations, are currently in progress. These models have a common approach in dealing with the adsorption-desorption reaction.

The mass balance equations are written in terms of total chemical, $c_T$, with the transport and kinetic terms suitably modified with the fraction of chemical in the dissolved, $f_d$, or particulate, $f_p$, form depending on whether the terms in the equation apply to particulate or dissolved phases. As an example, consider a two layer segmentation representing the water column of depth $H_1$, and an active sediment layer of depth $H_2$. These interact via vertical mixing of the aqueous phases, with mass transfer coefficient $K_L$; and settling and resuspension of the particulate phases, with velocities $w_a$ and $w_{rs}$ respectively. The governing mass balance equations are:

$$H_1 \frac{dc_{T1}}{dt} = K_L(f_{d2}c_{T2} - f_{d1}c_{T1}) - w_a f_{p1} c_{T1} + w_{rs} f_{p2} c_{T2} + W \qquad (1)$$

$$H_2 \frac{dc_{T2}}{dt} = K_L(f_{d1}c_{T1} - f_{d2}c_{T2}) + w_a f_{p1} c_{T1} - w_{rs} f_{p2} c_{T2} \qquad (2)$$

where $c_{T1}$ and $c_{T2}$ are the total chemical concentrations in the water column and sediment layers respectively, and W is the input mass loading rate ($M/L^2/T$).

Note the central role of the dissolved ($f_{d1}$ and $f_{d2}$) and particulate ($f_{p1}$ and $f_{p2}$) fractions, in the water column and sediment segments respectively. They directly affect the magnitudes of the mass transfer coefficients and therefore the fate of the chemical. A more complex fate computation would include terms for outflow, the various appropriate decay mechanisms, and sedimentation losses. However, the principle is still the same. Once the total concentration is computed, the dissolved water column concentration is given by: $c_{d1} = f_{d1}c_{T1}$, with analagous expressions for the particulate concentration. Again the particulate and dissolved fractions play a central role, and these fractions are a direct result of the adsorption-desorption model employed.

For completely reversible adsorption-desorption and a linear isotherm, the dissolved and particulate fractions are given by:

$$f_d = \frac{1}{1 + m\pi} \tag{3}$$

$$f_p = \frac{m\pi}{1 + m\pi} \tag{4}$$

where $\pi$ is the reversible partition coefficient and m is the adsorbent concentrations. The subscripts 1 and 2 in equations (1) and (2) refer to evaluating these fractions using the appropriate adsorbent concentration in segments 1 and 2.

For the HCB exchangeable-nonexchangeable component model of adsorption-desorption, these fractions depend upon the model parameters: $\pi_o$, the partition coefficient for the nonexchangeable component; and $\nu_x$, the distribution coefficient for the exchangeable component; and the maximum dissolved aqueous concentration to which the particle has been exposed: $c_{md}$. This latter concentration sets the magnitude of the nonexchangeable component. It can be shown (Part B) that the dissolved and particulate fractions are given by the expressions:

$$f_d = \frac{1}{1 + \nu_x + m\pi_o(c_{md}/c_d)} \tag{5}$$

$$f_p = \frac{\nu_x + m\pi_o(c_{md}/c_d)}{1 + \nu_x + m\pi_o(c_{md}/c_d)} \tag{6}$$

where $c_d$ is the current dissolved aqueous phase concentration. The particulate fraction as a function of adsorbent solids concentration, m, is shown in fig. 5.

The Effect of Nonreversible Desorption

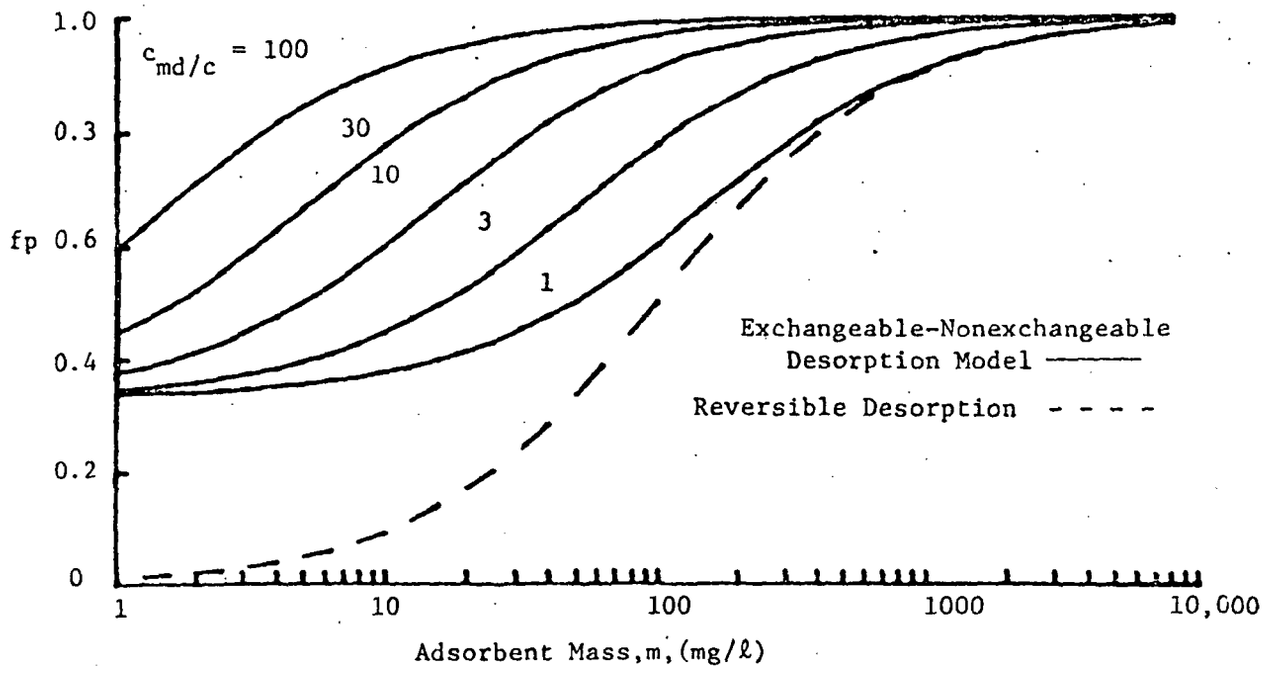



Fig. I-5. Particulate fraction versus adsorbent mass for reversible desorption, eq. (15); and exchangeable-nonexchangeable desorption, eq. (17). $\pi_o = 10^4$ ℓ/kg, $\nu_x = 0.5$

The conventional expression, assuming reversible behavior is also shown. There is a significant difference between the conventional reversible formulation and the exchangeable-nonexchangeable model. The particulate fraction is always a substantial portion of the total chemical concentration, even at low suspended solids concentrations that are characteristic of most receiving waters (10-100 mg/ℓ). This suggests that fate computations using the exchangeable-nonexchangeable model will give quite different results which emphasize the importance of particle transport.

## SECTION II

## INTRODUCTION AND PREVIOUS WORK

### A. Introduction

The construction of accurate computer models designed to predict the behavior of polychlorinated biphenyl compounds (PCB's) in natural waters such as the Great Lakes requires a quantitative knowledge of PCB sediment-water interactions. Current knowledge of PCB behavior in natural waters is based in part on studies pertaining to the general behavior of organics in natural waters (Lambert, 1967; Briggs, 1973; Chiou, 1977; Karickhoff et al., 1979, etc.). There exists a wide body of information on pesticides including reviews by Bailey and White (1970), and Dinauer (1974).

Studies specifically addressing PCB behavior have included many field observations of PCB levels in natural waters such as the Great Lakes (Glooshenko et al., 1976; Haile, 1977; Veith et al., 1977, etc.). Fewer studies have been devoted to analysis of the mechanisms of PCB sediment-water interactions. Studies on sediment-water interactions have included soil (Haque et al., 1974, 1976) fresh water (Steen et al., 1978) and marine (Hiraizumi, 1979) systems. While factors of importance to PCB partitioning to solid phases have been characterized, the available literature includes wide variations in reported equilibrium constant values for PCB adsorption to sediments. These variations suggest that current knowledge of PCB behavior is insufficient to permit direct quantitative prediction of PCB partitioning in specific systems such as the Saginaw Bay region of Lake Huron.

The apparent variability of partitioning data may reflect diversity in the physiochemical properties of the sediments under investigation. Alternately, it is quite possible that results reflect variations in experimental techniques and reaction conditions. There currently exist several factors of particular concern in terms of the potential applicability of experimental data to computer models. The first concerns the need for experimental partitioning data run under conditions reflecting observed natural water PCB concentrations particularly in the Great Lakes. The extrapolation of isotherm data run at high aqueous PCB concentrations to more realistic natural water levels suffers from a number of objections including solubility constraints. The more highly chlorinated PCB isomers (Cl $\geq$ 6) exhibit extremely low water solubility (< 10

μg/ℓ) (Dexter and Pavlov, 1978). Data obtained at aqueous concentrations in excess of solubility levels may not represent true partitioning between adsorbed and dissolved phases. Recent decreases in PCB pollution inputs should result in reductions in the current part per trillion natural water levels. Also of critical importance from the modeling standpoint is the need for quantitative data on PCB desorption from sediments. With reductions in PCB inputs, future aqueous phase concentrations may well be controlled by the extent of PCB movement into the water column from underlying sediments.

The purpose of this study has been to evaluate the problem of PCB sediment-water interactions both in general terms and more specifically in terms of determining the magnitude of such interactions in the Saginaw Bay region of Lake Huron. Studies have been designed to specifically address the need for obtaining data at low aqueous concentrations as well as that of obtaining information on the magnitude of the desorption process. In addition, experiments have been conducted to assess the potential importance of possible physiochemical variations in natural waters to the PCB partitioning process.

## B. Theory

Sediment-water HCB partitioning has been evaluated by determining HCB concentrations in both aqueous, $c_a$(ng HCB/ℓ), and solid phases, $r_a$(ng HCB/kg adsorbent). The mass balance equation relating these quantities is:

$$c_{Ta} = c_a + mr_a \qquad \text{(II-1)}$$

where $c_{Ta}$ is the initial total HCB concentration, and m is the adsorbent concentration (kg/ℓ) . The partition coefficient $\pi_a$ may be defined as:

$$\pi_a = \frac{r_a}{c_a} \quad \frac{(ng/kg)}{(ng/\ell)} \qquad \text{(II-2)}$$

The subscript "a" is used to denote the quantities that apply to adsorption.

In the present study, experimental data has been evaluated both in terms of partition coefficient $\pi_a$ and in terms of the parameters of the Freundlich expression:

$$r_a = Kc_a^{1/n} \qquad \text{(II-3)}$$

where K and 1/n represent constants. This empirical expression has proved useful in describing the behavior of a variety of trace organics and pesticides on soil and sediment systems. Converted to logarithmic form, the Freundlich expression yields:

$$\log x/m = \log K + \frac{1}{n} \log c_a \qquad \text{(II-4)}$$

The intercept, log K, of a Freundlich plot of the log of the solid phase HCB concentration vs. the log of the equilibrium concentration is an indirect measure of relative free energy changes. As such, it provides some measure of the relative strength of attachment of the HCB molecule to the solid phase.

In a review of a large body of adsorption data Hamaker and Thompson (1972) concluded that the routine approximation of $1/n \approx 1$ was probably not justified and could lead to large errors in attempting to extrapolate adsorption data. For this reason it is important that HCB laboratory experiments represent as closely as possible actual aqueous PCB concentrations found in the field.

For this reason radiochemical techniques were employed so the reliable measurements at low aqueous (1-100 ng/ℓ) and sediment (10-1000 ng/g) concentrations could be made, even at low suspended solids levels (10-1000 mg/ℓ). The methodology is discussed in the next section.

## SECTION III

## EXPERIMENTAL METHODOLOGY AND INITIAL EXPERIMENTAL RESULTS

### A. Experimental Methodology

PCB partitioning studies have been conducted using tritiated 2,4,5,2',4',5' hexachlorobiphenyl (HCB). A single isomer was chosen so that experimental results are more directly interpretable. Radiochemical studies were found to combine the advantages of low level HCB detection with ease of sample handling. Tritiated HCB (38.2 Ci/mmole) was obtained from New England Nuclear Corp. Aqueous HCB stock solutions were prepared by addition of hexane-tritiated HCB solutions to a volumetric flask, followed by hexane evaporation. The HCB was subsequently washed in 2 ml of acetone (Burdick & Jackson, non-spectro grade) and the solution re-evaporated. The HCB was then taken up in distilled water. Solutions were refrigerated to minimize HCB evaporation losses. Aqueous HCB concentrations were confirmed by capillary column gas chromatographic analysis (EPA, Grosse Ile, Michigan).

A flowchart of the experimental procedure for adsorption is indicated in Fig. III-1. Partitioning experiments were conducted in 25 ml (Corex-Corning) centrifuge tubes. (These tubes were selected on the basis of extensive experimentation, discussed subsequently.) Samples were equilibrated for specified time periods using a Burell Wrist Action Shaker. With the exception of kinetic studies, adsorption experiments were usually equilibrated for 3 hours and desorption experiments for 2 hours, preceded by an initial adsorption step. Following equilibration, both total HCB (sediment + water) and aqueous HCB samples were taken. Solid and liquid phases were separated by centrifugation (7000 RPM for 15 minutes). Both total and aqueous HCB samples were analyzed for tritium using a Beckman LS-150 liquid scintillation counter. Experimentatio indicated that HCB was efficiently extracted from the sediment particles directly into the scintillation fluid (Aquasol-2, New England Nuclear).

Sorption studies were conducted by equilibrating aqueous HCB stock solutions with a series of natural lake sediment (Saginaw Bay, Lake Huron, Michigan) and montmorillonite (Wards Natural Science Co.). Montmorillonite samples were used as received without cation saturation treatment. Sediment suspensions (<200 mesh solids) were equilibrated at 24 ± 2°C in the 25 ml Corex brand (Corning Glass Co.) centrifuge tubes.

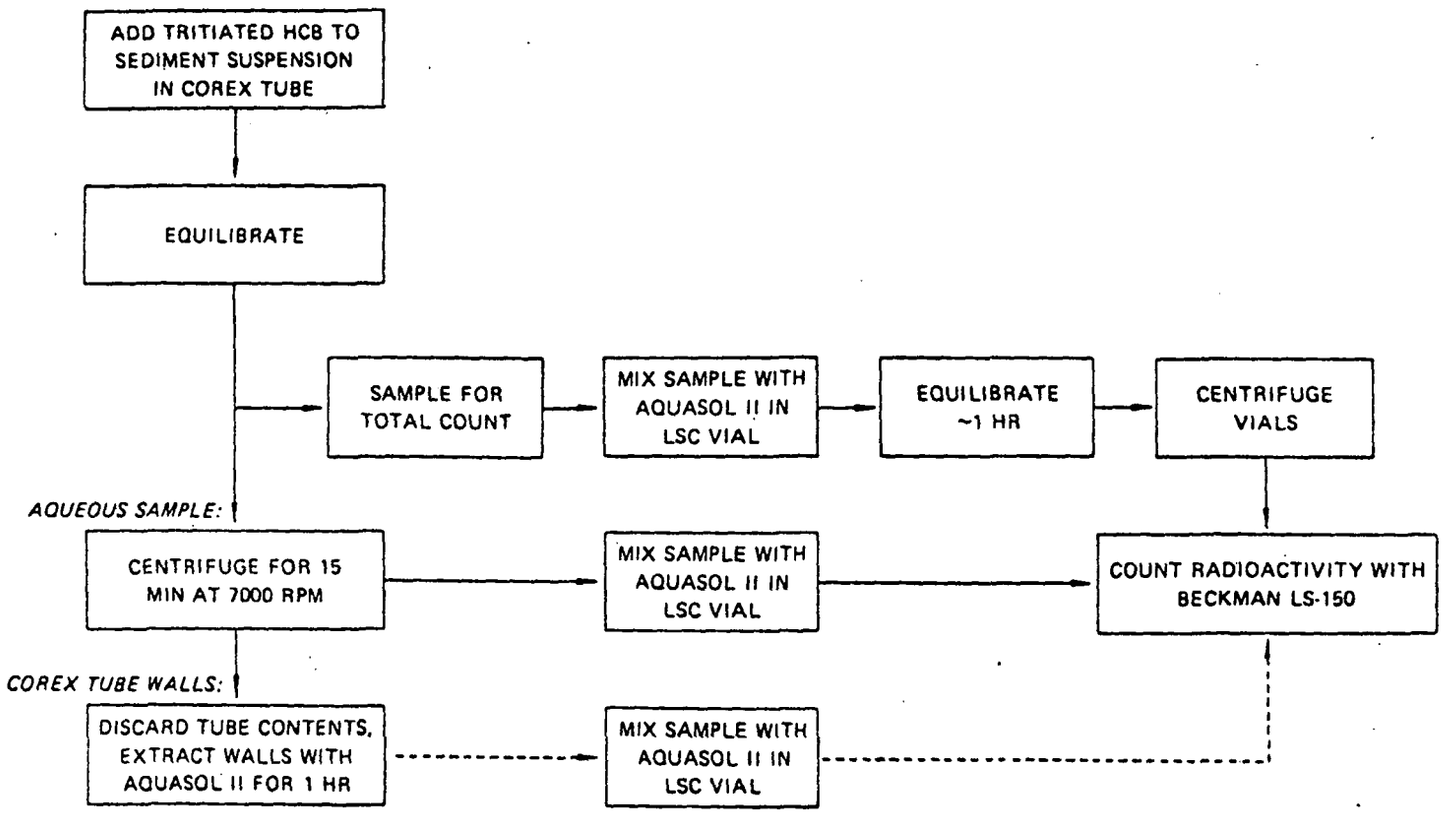



Fig. III-1. Flow Chart of Experimental Procedure

The experimental and measurement procedures for the basic adsorption-desorption measurements are illustrated in fig. (III-2). The aqueous phase, sediment, and HCB stock solutions are combined to achieve the desired concentrations in 15 mℓ of solution in the centrifuge tube. The tube is caped and agitated until adsorption equilibria is achieved. A sample of the sediment-aqueous phase mixture is removed and analyzed for HCB concentration, $c_{Ta}$. After centrifuging, a sample of aqueous phase is removed and analyzed yielding the dissolved concentration at adsorption equilibrium, $c_a$. The particulate concentration at adsorption equilibrium is calculated by difference: $r_a = (c_{Ta}-c_a)/m$, where m is the adsorbent concentration. This completes the adsorption step.

For the desorption step, the contaminated aqueous phase is carefully removed leaving the sedimented solids in the tube, and uncontaminated aqueous phase is added (to achieve a total volume that produces the same adsorbent concentration as initially present at adsorption). The caped tube is agitated until desorption equilibrium is achieved. A sample of sediment-aqueous phase mixture is removed and analyzed yielding $c_{Td}$. After centrifuging an aqueous phase sample is removed and analyzed for $c_d$. The particulate concentration is obtained by difference. $r_d = (c_{Td}-c_d)/m$. The remaining sediment and aqueous phase is either discarded or saved for further analysis. The centrifuge tube is extracted, and the HCB adsorbed to the tube is analyzed. A mass balance calculation is made to insure the integrity of the experiment.

Multiple adsorption and desorption experiments are modifications of these procedures. The data analysis equations for the calculation of the adsorption and desorption concentrations are given in Table III-1. Each experimental point is triplicated in order to reduce the magnitude of the experimental variability.

For the most part three types of experiments were performed:

Type 1: an adsorption cycle only
Type 2: an adsorption followed by a desorption with no $c_{Td}$ measurement
Type 3: an adsorption followed by a desorption with $c_{Td}$ measured.

The only difference between the Type 2 and 3 results is the presence of a $c_{Td}$ measurement. As pointed out subsequently the Type 3 experimental data indicate that no significant glass desorption occurs so that $c_{Td}$ can be calculated from mass balance: $c_{Td} = m_d r_a$.

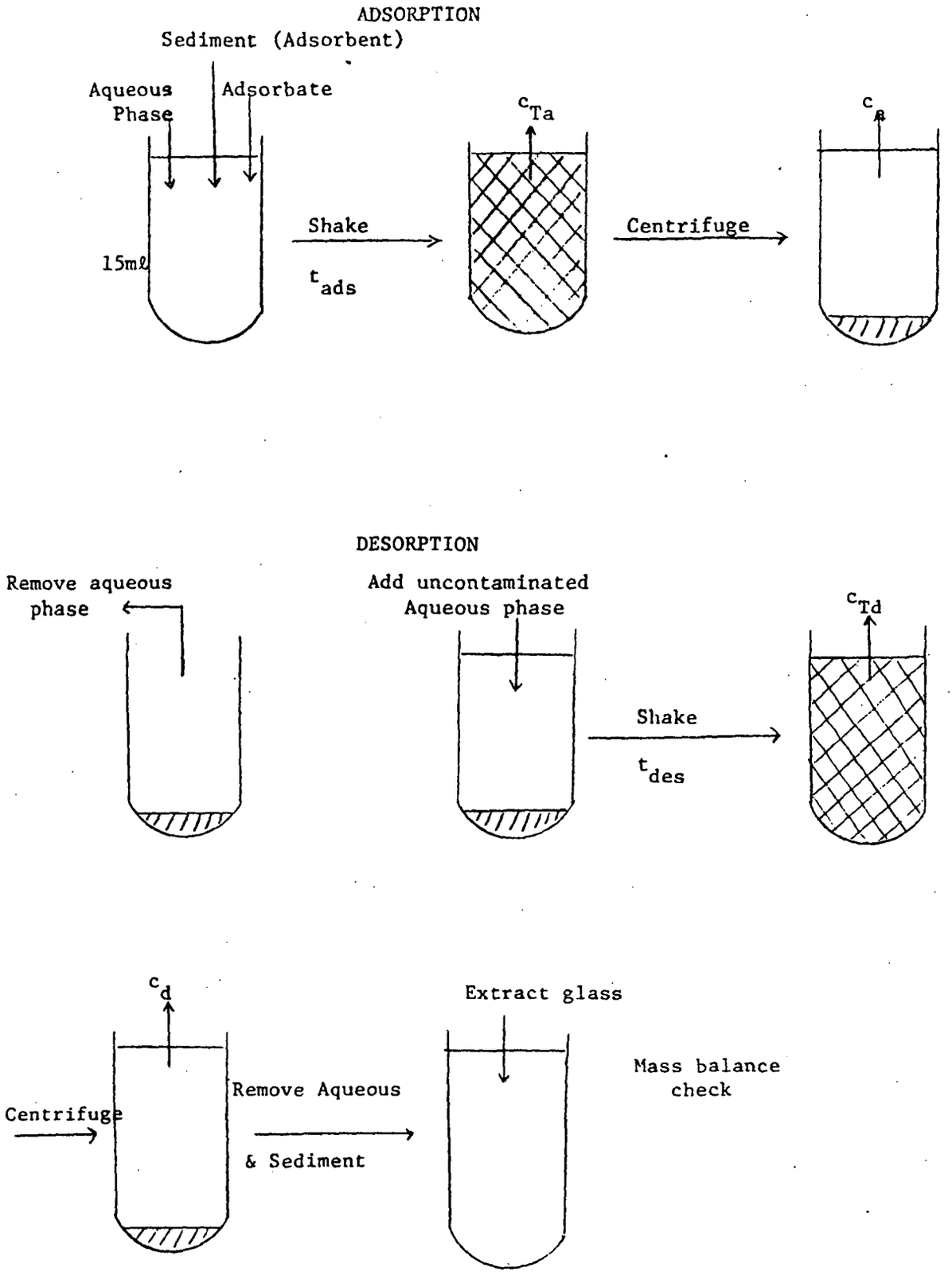



Fig. III-2. Adsorption-Desorption Experimental Procedure

Table III-1

Nomenclature and Computational Equations

Initial Conditions

| | |
|---|---|
| Total Volume (mℓ) | $V_i$ |
| Stock Volume Added (mℓ) | $V_{sk}$ |
| Stock Count (1 mℓ sample) (cpm) | $N_{sk}$ |
| Sediment Concentration (mg/ℓ) | $m_a$ |

Adsorption

| | |
|---|---|
| Total Sample Volume Removed (mℓ) | $V_{Ta}$ |
| Total Count (cpm) | $N_{Ta}$ |
| Aqueous Sample Volume Removed (mℓ) | $V_{aa}$ |
| Aqueous Count (cpm) | $N_{aa}$ |

Desorption

| | |
|---|---|
| Aqueous Phase Volume (mℓ) | $V_d$ |
| Total Sample Volume Removed (mℓ) | $V_{Td}$ |
| Total Count (cpm) | $N_{Td}$ |
| Aqueous Sample Volume Removed (mℓ) | $V_{ad}$ |
| Aqueous Count (cpm) | $N_{ad}$ |

Glass

| | |
|---|---|
| Total Glass Count (cpm) | $N_g$ |

Volumes for all experiments

$V_i$ = 10-15 mℓ

$V_{Ta} = V_{Td}$ = 1 mℓ

$V_{aa} = V_{ad}$ = 1 mℓ

Final Concentrations

Conversion factor

$$f_o = (940 \text{ ng}/\ell)/(515000 \text{ cpm}/m\ell)$$

Initial Concentration

$$c_i = f_o N_{sk} V_{sk}/V_i \qquad (\text{ng}/\ell)$$

Initial HCB Mass

$$h_i = f_o N_{sk} V_{sk} \qquad (\text{pg})$$

Table III-1 (cont'd)

Adsorption

Total Concentration

$c_{Ta} = f_o N_{Ta}/V_{Ta}$ (ng/ℓ)

Aqueous Concentration

$c_a = f_o N_a/V_{aa}$ (ng/ℓ)

Particulate Concentration

$r_a = (c_{Ta} - c_a)/(m_a \cdot 10^{-3}\ g/mg)$ (ng/g)

Desorption (Experiment Type 2 and 3)

Sediment Concentration

$m_d = m_a (V_i - V_{Ta})/V_d$ (mg/ℓ)

Total Concentration

(Expt. Type 3) $c_{Td} = f_o N_{Td}/V_{Td}$ (ng/ℓ)

(Expt. Type 2) $c_{Td} = m_d r_a$ (ng/ℓ)

Aqueous Concentration

$c_d = f_o N_{ad}/V_{ad}$ (ng/ℓ)

Particulate Concentration

$r_d = (c_{Td} - c_d)/(m_d \cdot 10^{-3}\ g/mg)$ (ng/g)

Mass Balance

Final Mass Adsorbed to Glass

$g_2 = f_o N_g$ (pg)

Apparent Initial Glass Adsorption

$g_o = (c_i - c_{Ta})V_i$ (pg)

Apparent Glass Adsorption (+) or Desorption (-) during Desorption

$g_1 = (c_{Td} - r_a m_a \cdot 10^{-3})V_d$ (pg)

Mass Balance Error

Experiment Type 1 and 2

$e_1 = 100\% (g_2 - g_o)/h_i$ (%)

Experiment Type 3

$e_1 = 100\% (g_2 - g_o - g_1)/h_i$ (%)

The data generated during the course of these experiments is presented in tabular form in the Appendix of this report if it is not included in the body of the report.

## B. Mass Balance of HCB

In order to check that the experiments were properly executed, HCB mass conservation was checked. The initial mass of HCB added, $h_i$ must be accounted for at the end of the experiment. The most direct check is to compute the initial HCB mass adsorbed to the vessel:

$$g_o = (c_i - c_{Ta})V_i \qquad \text{(III-1)}$$

where $c_i$ is the initial concentration from the diluted stock solution, $c_{Ta}$ is the total HCB concentration at adsorption equilibrium, and $V_i$ is the volume of solution. This is compared to the computed change in mass adsorbed to the glass after desorption equilibrium (for Type 3 experiments):

$$g_1 = (c_{Td} - r_a m_a)V_d \qquad \text{(III-2)}$$

and the observed glass concentration, $g_2$ at the end of the experiment. The mass balance error is this difference normalized by the total initial HCB mass added to the vessel, $h_i$. Thus the mass balance error in percent is

$$e_1 = 100\% \ (g_2 - g_o - g_1)/h_i \qquad \text{(III-3)}$$

A histogram of this error is shown in figure III-3. Typically the error is ∿10% which indicates that the recovery of HCB mass is on the order of 90%.

## C. Vessel Adsorption of HCB

Preliminary experiments indicated that HCB adsorption to vessel walls is a significant problem. Studies on a variety of potential vessel materials (Figure III-4) indicated potentially serious HCB losses could occur from dilute solutions (<1 μg/ℓ) even during relatively short reaction periods (hours). Aqueous solutions were observed to lose more than 80% of the initial HCB concentration (40 ng/ℓ) to organic reaction vessel surface (polyethylene, polycarbonate, teflon) in less than 2 hours. The results suggested that Corex (Corning Glass Co.) adsorbed slightly less HCB than did Pyrex (Corning Glass Co.). Experiments conducted on metal surfaces (Figure III-5) showed uniformly rapid uptake. Under quiescent conditions chrome, gold, copper and nickel coated surfaces all displayed HCB losses from solutions of > 80% in a matter of hours. Experiments on stainless

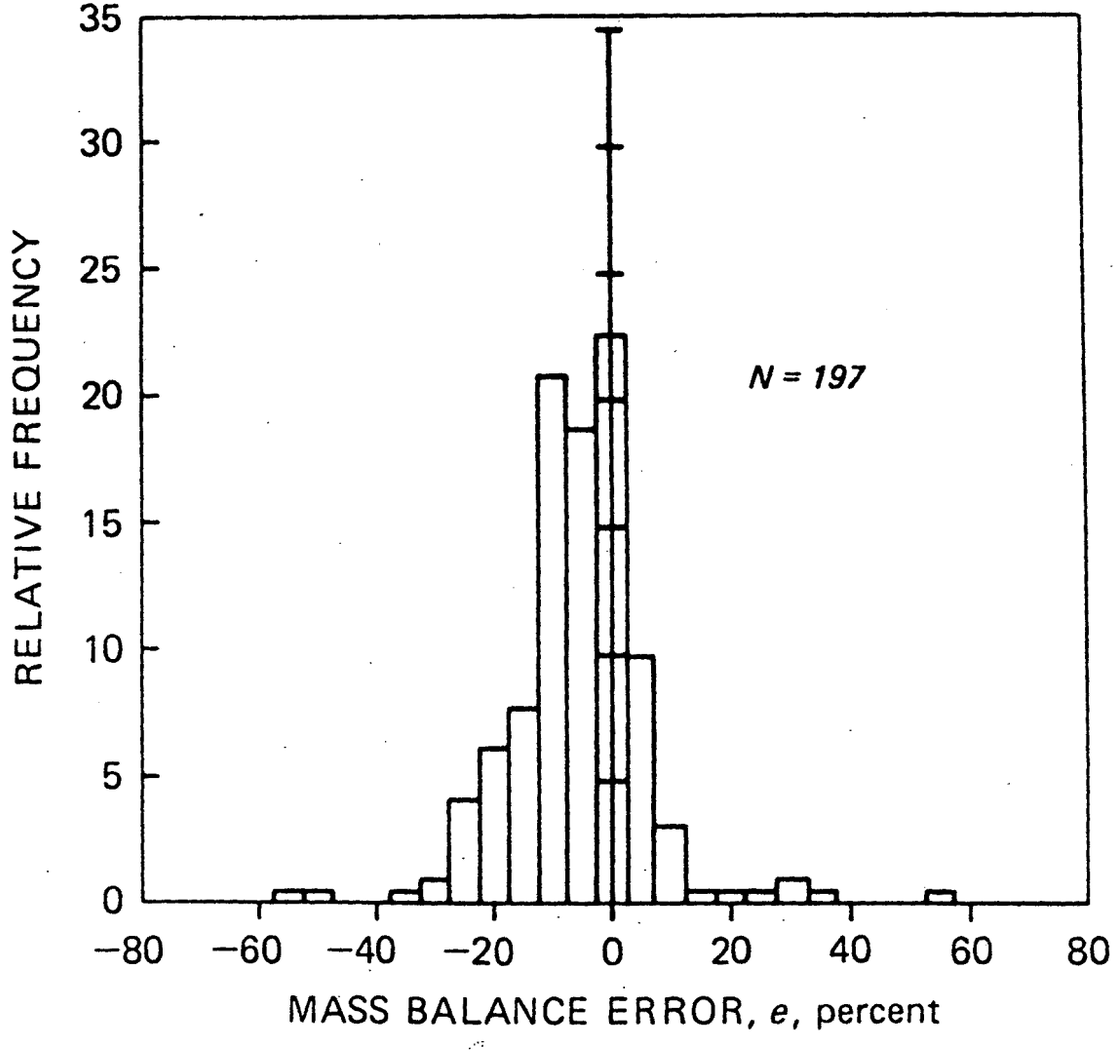



Fig. III-3. Histogram of Mass Balance Error, $e_1$(%)

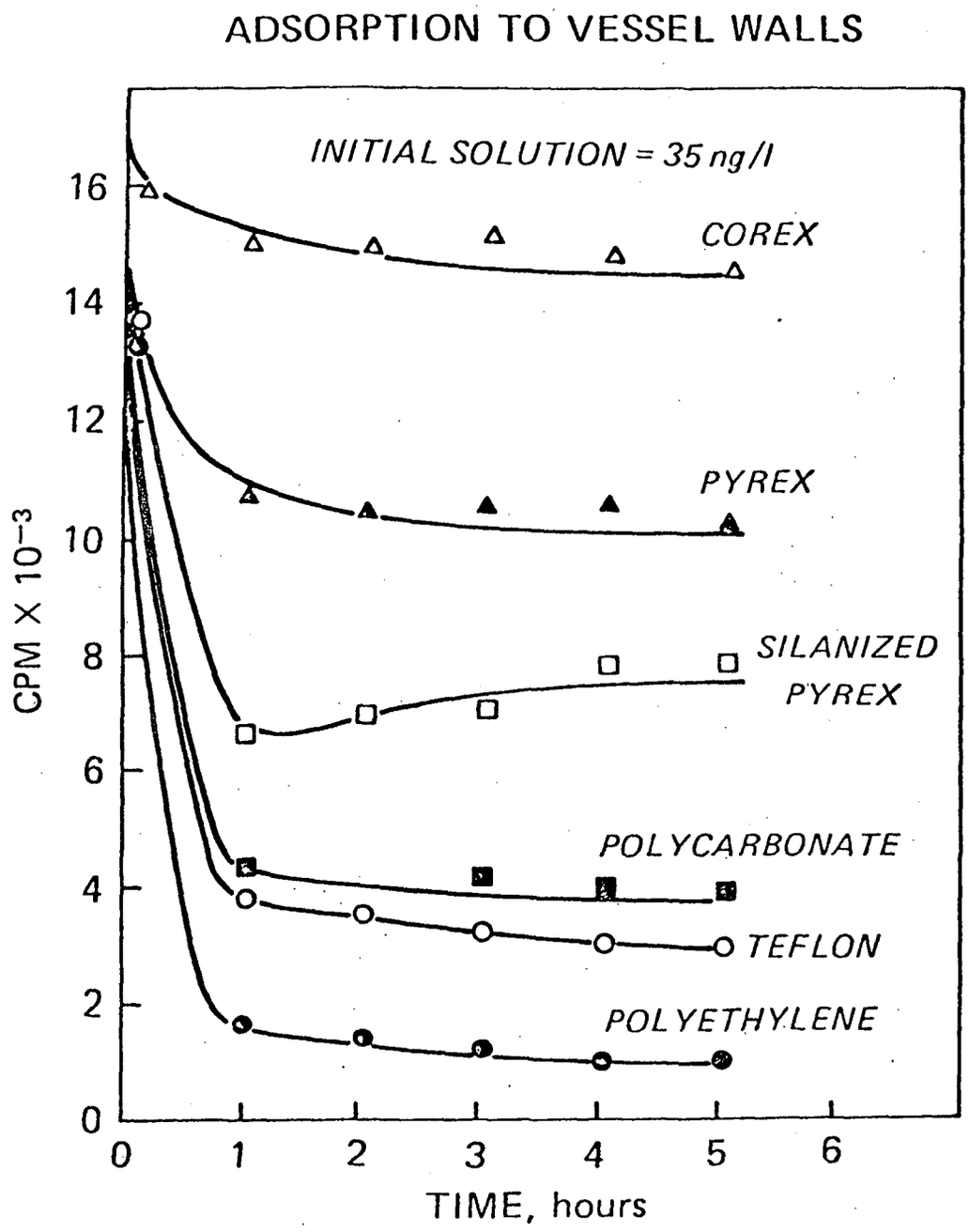



Fig. III-4. Adsorption of HCB to Vessel Walls

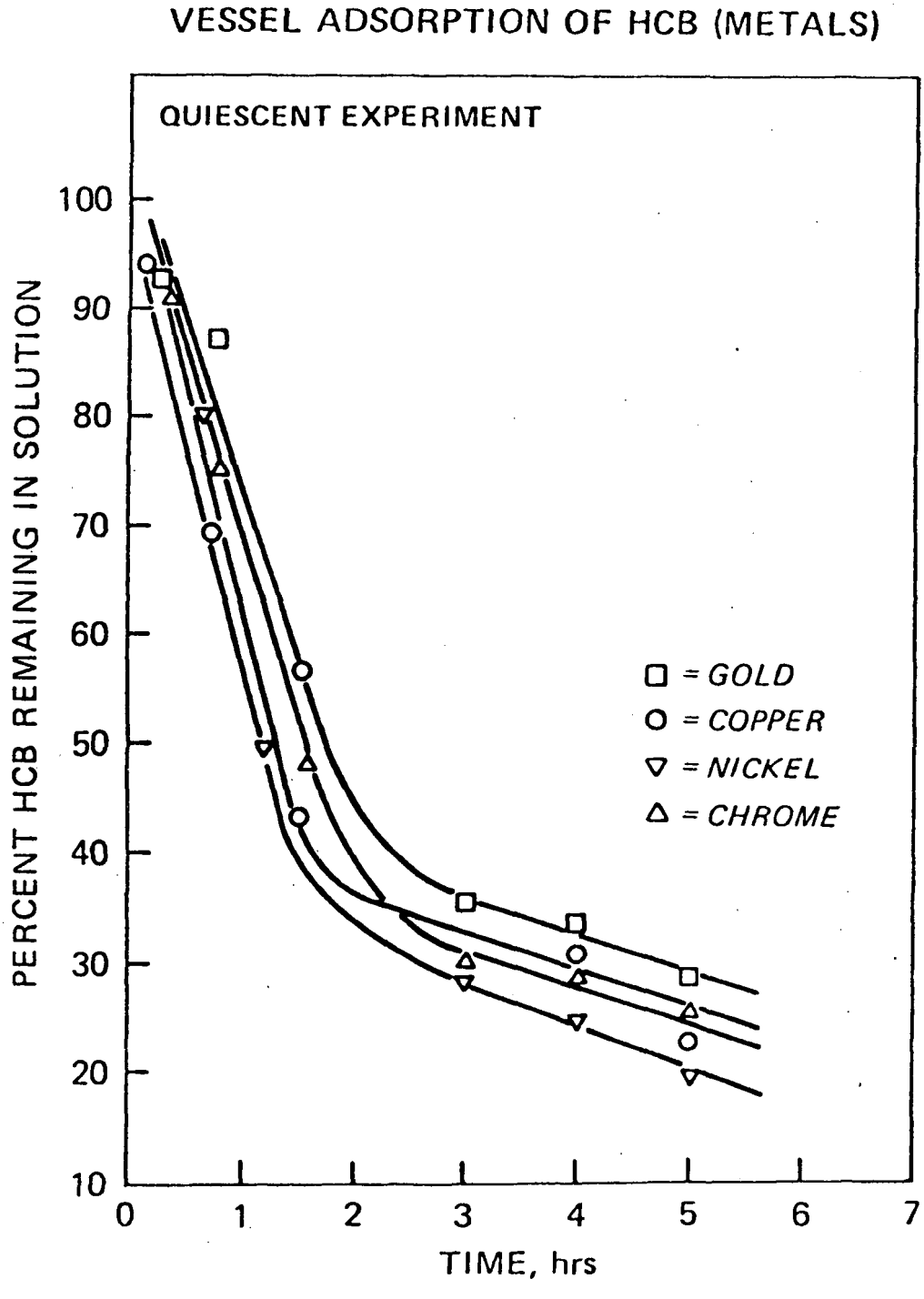



Fig. III-5. Adsorption of HCB to Metal Coated Vessels

steel, lead and aluminum also resulted in similar rapid HCB removal from solution.

Additional studies on Corex glass (Section V) revealed that although solution composition affected the extent of glass adsorption it still did not exceed ∿ 10% of the initial HCB mass. Since these vessels (25 mℓ Corex centrifuge tubes) appeared to be the least adsorptive they were chosen for these experiments. An adsorption isotherm constructed from adsorption experiments (type 1) in distilled water, shown in fig. III-6, confirms that ∿ 10% of equilibrium aqueous concentration, $c_a$, had been adsorbed to the glass wall. Both adsorption and desorption cycles used the same tube in order that HCB adsorption to fresh vessel surfaces was reduced. This is especially important for the desorption phase of the experiment since transfer of solids to a second vessel would cause additional vessel adsorption.

## D. Glass Desorption

A number of experiments were conducted to evaluate the sorption effects of the Corex glass tubes on the desorption process. The purpose of this study was to determine the magnitude of the effect of the glass surfaces on the aqueous HCB concentration, $c_d$, during the desorption process. In these reference studies HCB stock solutions were added to Corex tubes and allowed to equilibrate for time periods equivalent to those used in the sediment studies. After equilibration, aqueous HCB levels, $c_a$, were determined and the stock solutions replaced with distilled water. These solutions were allowed to equilibrate with the vessel walls after which the aqueous concentration, $c_d$, levels were again measured.

Data typical of the results obtained in these experiments are tabulated below.

TABLE III-2

GLASS DESORPTION DATA

Corex Tubes (Contact Surface Area = 38 $cm^2$)

| ADSORPTION | DESORPTION | | |
|---|---|---|---|
| $c_a$ (ng/ℓ) | $c_d$ (ng/ℓ) | $r_{gd}$ ($ng/cm^2$) | HCB Adsorbed (ng) |
| 18.6 | 2.8 | .001 | .037 |
| 41.6 | 4.0 | .005 | .185 |
| 81.8 | 8.5 | .011 | .418 |
| 163.6 | 15 | .018 | .684 |

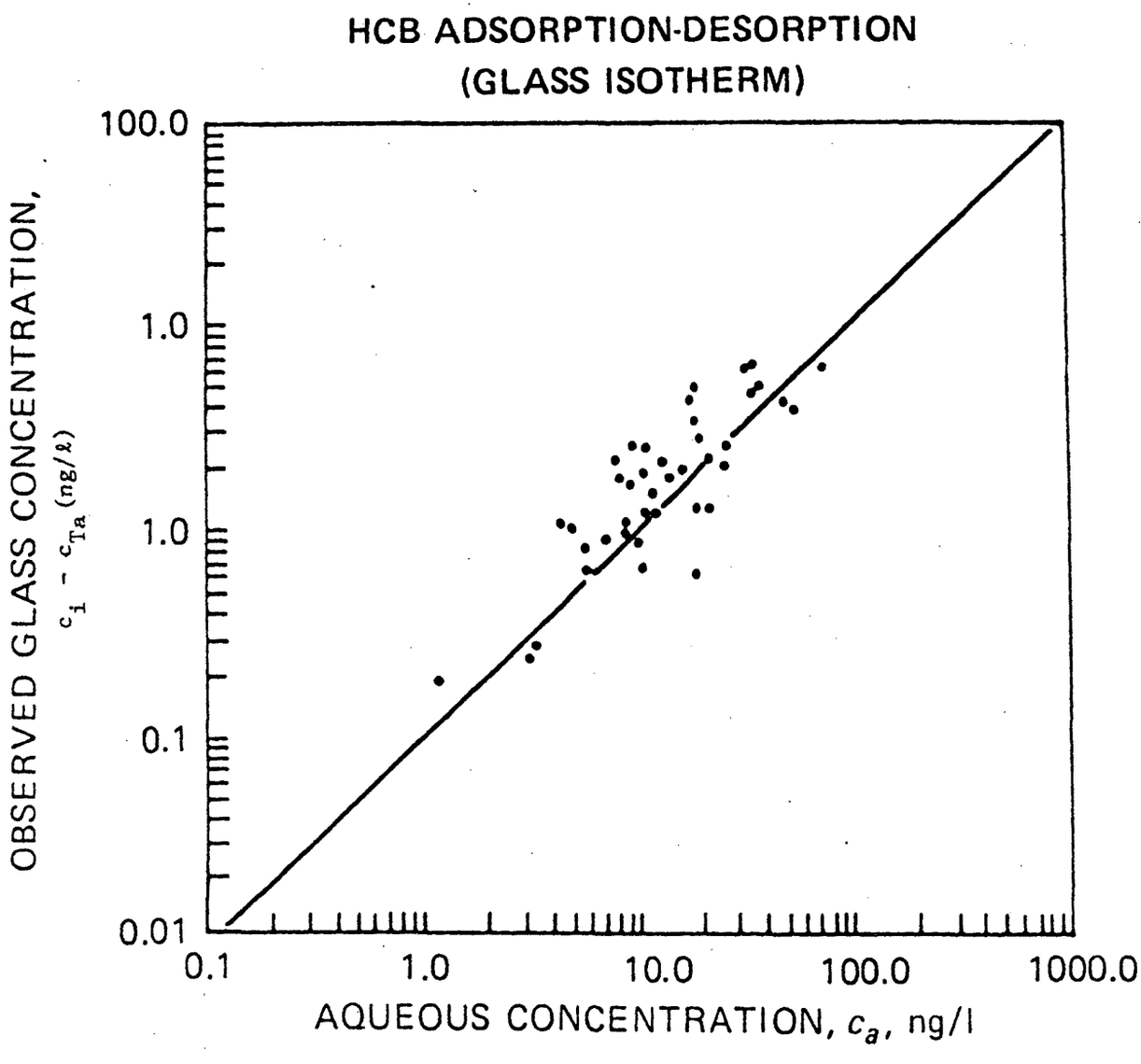



Fig. III-6. Glass Adsorption Isotherm: Volumetric Concentration of HCB Adsorbed to the Wall versus Aqueous Concentration, Distilled Water.

These results suggest an approximate linear relationship between the equilibrium HCB concentration for adsorption, $c_a$, and the equilibrium HCB concentration observed during desorption, $c_d$. Desorption concentrations appear to constitute $\sim$ 10% of the equilibrium adsorption concentrations. It is, therefore, possible that of the total equilibrium HCB concentrations observed during sediment desorption, a fraction (up to 10% of the equilibrium aqueous HCB concentration) may result from desorption from the walls. This would suggest that partitioning studies may overestimate the extent of HCB desorption from sediments and underestimate the magnitude of the desorption partition coefficient. However, since the absolute quantity of HCB adsorbed to the glass walls is small relative to the quantity adsorbed to the sediment, even at low sediment concentrations, the glass desorption contribution is also small. This can be seen in fig. III-7 which compares, on a concentration basis, the mass of HCB on the sediment after adsorption equilibrium, $mr_a$, to the total HCB measured at desorption equilibrium, $c_{Td}$. These observations are from all the experiments in which both quantities were measured (Type 3 experiments). The histogram of percent error: $100\% \ (mr_a - c_{Td})/c_{Td}$ is within ±2.5% for 48% of the observations and within ±7.5% for 72% of the observations. The observed equality indicates that glass desorption is an insignificant contribution.

This fact is also apparent from fig. III-8 which compares the observed glass concentration for type 2 experiments, $g_2$, on a volumetric basis, after the desorption cycle versus the aqueous adsorption concentration, $c_a$. The isotherm is that found from the type 1 adsorption experiments (fig. III-6). Although the glass concentrations are slightly lower indicating some glass desorption has occurred, it is an insignificant quantity compared to the total HCB at desorption equilibrium, $c_{Td}$. (See fig. III-7).

E. HCB Speciation

It is possible that partitioning data may be affected by changes in HCB speciation in aqueous solution. It has been suggested that at aqueous HCB levels in excess of the aqueous solubility, molecules may bind together as aggregates, forming a micro-emulsion rather than a true solution. Such aggregates may display partitioning behavior quite different from that of only dissolved species. Although HCB concentrations in the present studies are well below the solubility limits of 8 μg/ℓ (Dexter and Pavlou, 1977), experiments were conducted to evaluate the possibility of solution speciation.

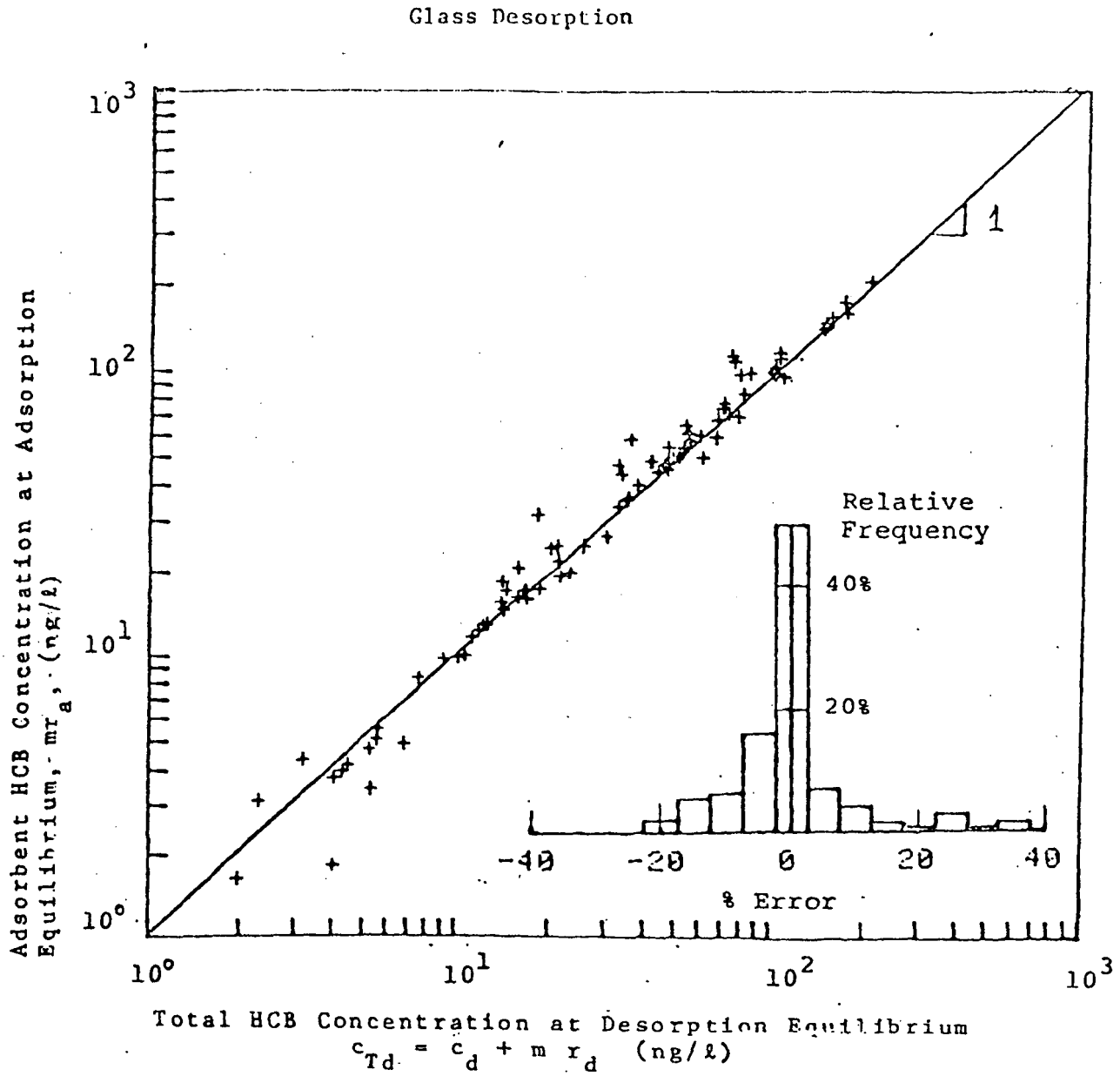



Fig. III-7. Adsorbed HCB Concentration at Adsorption Equilibrium, $mr_a$, versus Total HCB Concentration at Desorption Equilibrium, $c_{Td}$, for Type 3 Experiments. Histograms of % Error = 100% $(mr_a - c_{Td})/c_{Td}$.

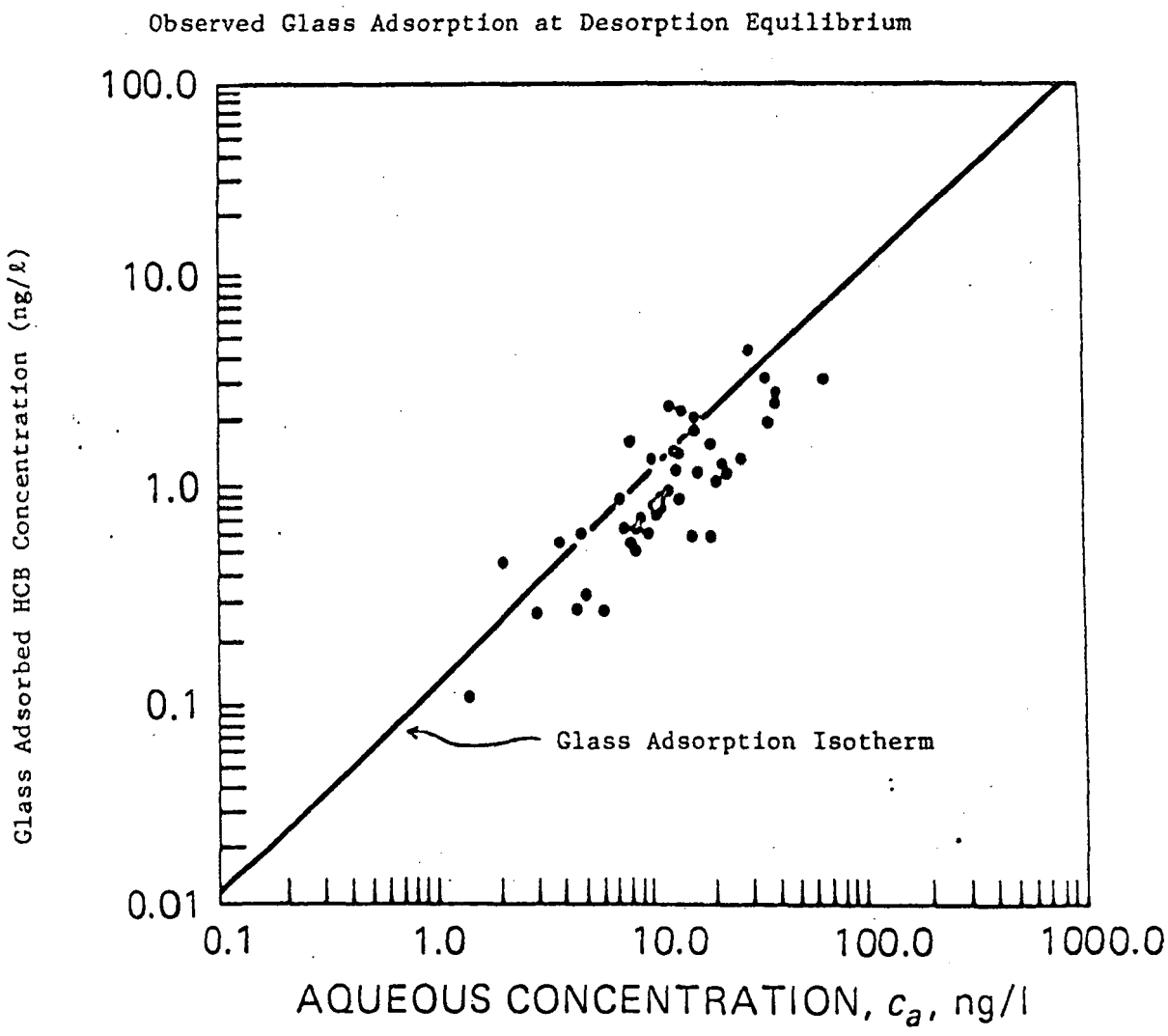



Fig. III-8. Comparison of Glass Adsorption Isotherm (from Fig. III-6) to Glass Adsorbed HCB after Desorption Equilibrium

In these experiments stock HCB solutions were initially equilibrated with 100 mg/ℓ sediment suspensions (montmorillonite clay and Saginaw Bay # 50). After equilibration (3 hr.), the samples were centrifuged, the solid phase discarded and the aqueous phase equilibrated (3 hr.) with additional clean sediment. Sediment concentrations were kept constant during both equilibration cycles. Partitioning data for the individual cycles were compared. If aqueous stock solutions contained more than one HCB species whose partition coefficient values differed, then the consecutive adsorption process would be expected to selectively separate such species. Table III-3 and III-4 contains the data in the replicated experiment using montmorillonite and Saginaw Bay sediments. Although there is a slight tendency for the second adsorption cycle partition coefficient to be less than the first adsorption cycle, especially for the Saginaw Bay sediment, the differences are statistically insignificant as indicated from the Analysis of Variance results. The significance levels of the F test are much larger than the usual critical significance level of 0.05 (95% significance) which indicates no statistical difference between the partition coefficients found in cycle 1 and cycle 2. This suggests that the stock solutions used in the present study did in fact contain dissolved HCB species with no preferential adsorptive properties.

The effect of adsorption and desorption equilibration times are discussed in the next section.

Table III-3

Speciation Experiment - Montmorillonite

Data

| Adsorption Cycle 1 | | | Adsorption Cycle 2 | | |
|---|---|---|---|---|---|
| $c_a$ (ng/ℓ) | $r_a$ (ng/g) | $\pi_a$ (ℓ/kg) | $c_a$ (ng/ℓ) | $r_a$ (ng/g) | $\pi_a$ (ℓ/kg) |
| 23.97 | 125.1 | 5218 | 11.64 | 33.6 | 2886 |
| 23.25 | 127.3 | 5478 | 9.18 | 44.4 | 4832 |
| 25.84 | 117.9 | 4562 | 10.13 | 58.7 | 5799 |
| 26.58 | 115.3 | 4338 | 12.12 | 45.4 | 3746 |

Statistics

Overall Mean $\pi_a$ = 4607 (ℓ/kg)

Number of Observations = 8

$\pi_a$ (ℓ/kg)

| Cycle | N | Mean | Standard Error | 95% Confidence Interval Lower Limit | Upper Limit |
|---|---|---|---|---|---|
| 1 | 4 | 4899 | 487 | 3704 | 6093 |
| 2 | 4 | 4315 | 487 | 3121 | 5509 |

Analysis of Variance

| Source | DF | SS | MS | F-Test | Significance Level |
|---|---|---|---|---|---|
| Total | 7 | 6380997 | | | |
| a | 1 | 680361 | 680361 | 0.716 | 0.429 |
| Error | 6 | 5700636 | 950106 | | |

Table III-4

Speciation Experiment - Saginaw Bay #50

Data

| Adsorption Cycle 1 | | | Adsorption Cycle 2 | | |
|---|---|---|---|---|---|
| $c_a$ (ng/ℓ) | $r_a$ (ng/g) | $\pi_a$ (ℓ/kg) | $c_a$ (ng/ℓ) | $r_a$ (ng/g) | $\pi_a$ (ℓ/kg) |
| 22.12 | 118.0 | 4696 | 10.75 | 53.5 | 4974 |
| 25.98 | 98.1 | 3775 | 12.05 | 52.0 | 4311 |
| 30.53 | 204.3 | 6692 | 14.38 | 51.7 | 3594 |

Statistics

Overall Mean $\pi_a$ = 4673 (ℓ/kg)

Number of Observations = 6

$\pi_a$ (ℓ/kg)

| Cycle | N | Mean | Standard Error | 95% Confidence Interval Lower Limit | Upper Limit |
|---|---|---|---|---|---|
| 1 | 3 | 5054 | 670 | 3176 | 6931 |
| 2 | 3 | 4293 | 670 | 2415 | 6170 |

Analysis of Variance

| Source | DF | SS | MS | F-Test | Significance Level |
|---|---|---|---|---|---|
| Total | 5 | 6269177 | | | |
| a | 1 | 869442 | 869442 | 0.644 | 0.467 |
| Error | 4 | 5399734 | 1349933 | | |

## SECTION IV

## KINETICS

### A. Introduction

An assessment of HCB sediment-water interactions in naural systems requires an evaluation of the rate at which the partitioning process occurs. Specifically, it is necessary to determine how rapidly aqueous suspensions approach equilibrium with respect to adsorbed and dissolved HCB. Previous work on a variety of organic compounds (Wahid and Sethunathan, 1978, Paris, 1978) has suggested that the partitioning process for physical adsorption to sediments occurs quite rapidly (hours). The goals of the present study were to determine time periods required for the hexachlorobiphenyl isomer to approach equilibrium during both adsorption and desorption processes. Experimental studies have been of both short ($\leq$ 24 hours) and longer term (1-10 days) duration.

### B. Effect of Adsorption Time on Adsorption Partition Coefficient

Initial experiments were conducted on both Saginaw Bay and montmorillonite samples for time intervals ranging up to 24 hours. It has been suggested that partitioning of dissolved pesticide molecules to montmorillonite occurs somewhat more slowly than for other clay minerals such as illite and kaolinite (Huang, 1970). In the present study, data for the partitioning of HCB to 200 mg/ℓ montmorillonite suspensions is shown in Figure IV-1. The aqueous phase employed was the supernatant from a previously equilibrated HCB-free 200 mg/ℓ montmorillonite suspension. This procedure was adopted in order that the aqueous phase was in equilibrium with montmorillonite and no further dissolution of montmorillonite (if indeed any occurred) would take place during the kinetic experiments. HCB aqueous and sediment concentration values have been plotted, together with the adsorption partition coefficient. It can be seen that the partitioning process appears to occur quite rapidly. A slight change is observed from $t_a$ = 15 min. to $t_a$ = 2 hours suggesting that the adsorption process is essentially complete in a matter of minutes.

It has been suggested (Huang and Liao, 1970) that bonding of organic molecules to montmorillonite may involve a two stage process. The first state being a rapid adsorption to external particle surfaces occurring in

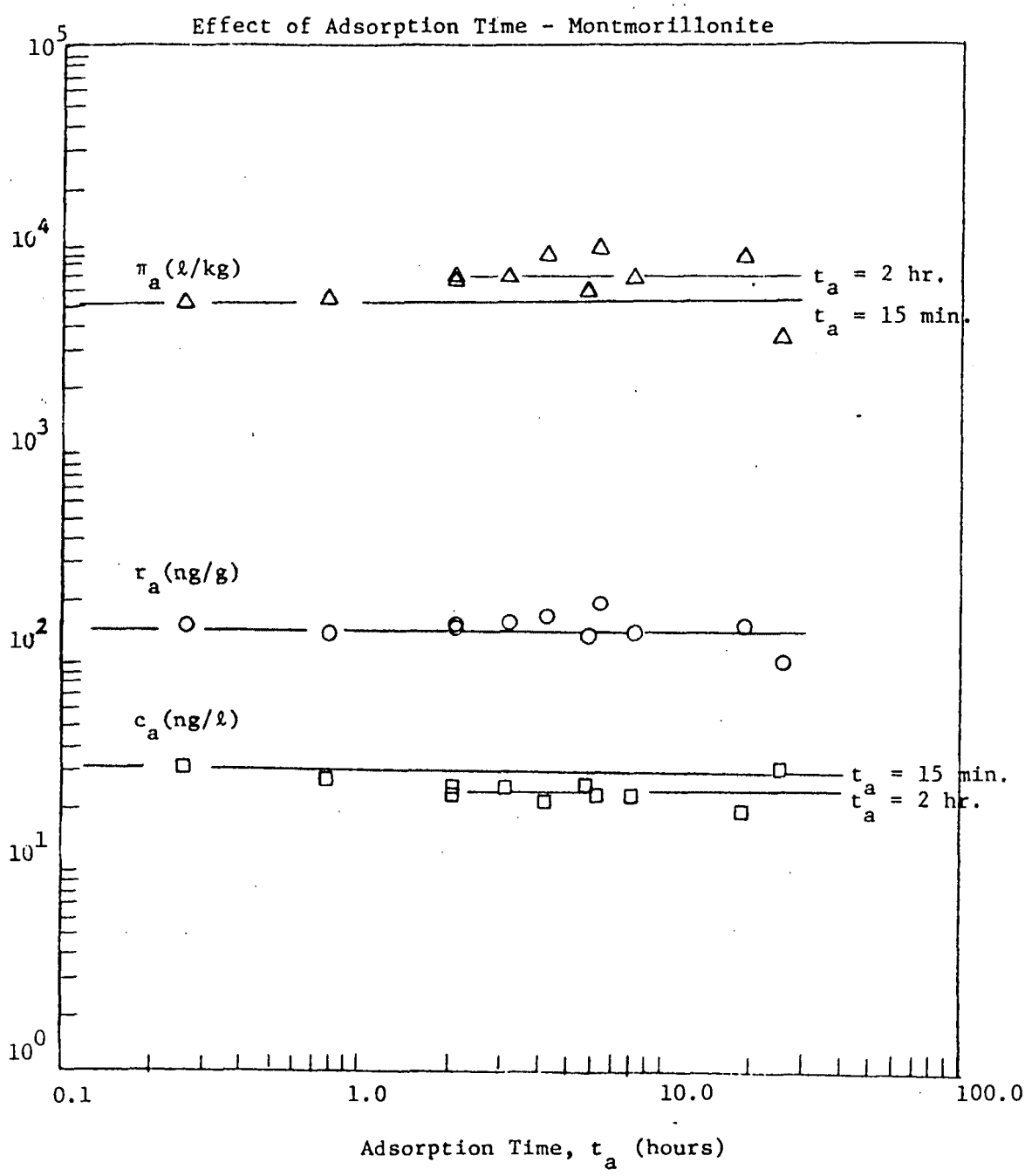



Fig. IV-1. Effect of Adsorption time, $t_a$, on aqueous concentration, $c_a$, sediment adsorbed HCB, $r_a$, and partition coefficient, $\pi_a$. m = 200 mg/ℓ Montmorillonite, Aqueous phase is supernatant.

a matter of minutes or less and the second stage being a slower migration of organic molecules into interlayer spaces. The extent of migration to internal sites appears to be dependent upon the size, conformation, and polarity of the organic molecule. The present results do suggest a small decrease in aqueous HCB concentrations during the first couple of hours. This may be related to additional migration into the solid phase. However, the magnitude of this effect appears to be quite small. Initial studies on 200 mg/ℓ Saginaw Bay sediment #50 suspensions using previously equilibrated supernatant show rapid partitioning behavior similar to that observed for montmorillonite (Figure IV-2). The adsorption appears to be essentially complete within the first 2 hours. The scatter observed in the data precludes a more careful analysis of this type of experiment.

The results of the present experiments are supported by a number of other studies on organic partitioning between sediment and water phases. Sorption studies on parathion (Wahid and Sethurathan, 1978), paraquat (Juo and Ogiani, 1978) and Arachlor mixtures (Steen et al., 1978) all suggest the partitioning process to be complete in less than one hour.

Kinetically rapid partitioning processes such as those observed in the present study appear to result from weak physical adsorption of organic molecules at sediment particle surfaces (Goring and Hamaker, 1972). Conversely, it has been observed that for some porous substrates such as activated charcoal (Crittenden and Weber, 1978) reaction kinetics appear to be controlled by the rate of diffusion or organic molecules into particle interiors. Diffusion processes have also been suggested to be of importance in the uptake of pesticides by clay flocculates (Haque et al., 1968).

To further evaluate this effect a number of experiments were conducted to assess the potential importance of kinetically slow processes on HCB adsorption from Saginaw Bay sediment. In these experiments adsorption isotherms were constructed for experimental shaking times ranging up to one week. The results of long term adsorption studies conducted on 1000 mg/ℓ Saginaw Bay sediment samples are indicated in Figure IV-3. The results suggest that small increases in adsorption may occur during the first 24 hours. However, these results may be due to losses of HCB from the aqueous phase. An examination of the data shows no observable increase in HCB sediment concentrations with time (see Table IV-1).

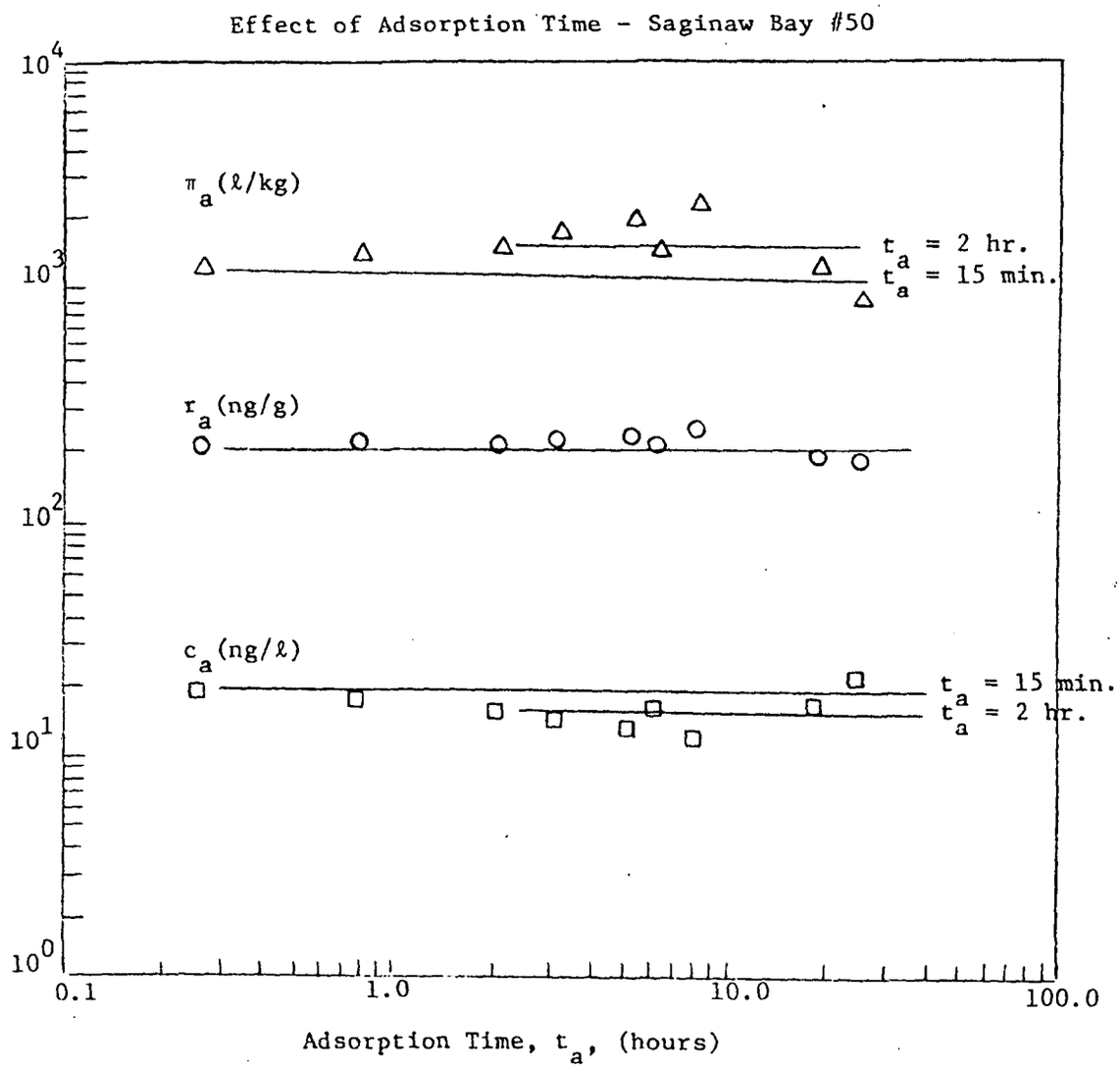



Fig. IV-2. Effect of Adsorption Time, $t_a$, on aqueous concentration, $c_a$, sediment adsorbed HCB, $r_a$, and partition coefficient, $\pi_a$. m = 200 mg/ℓ Saginaw Bay #50, Aqueous phase = supernatant.

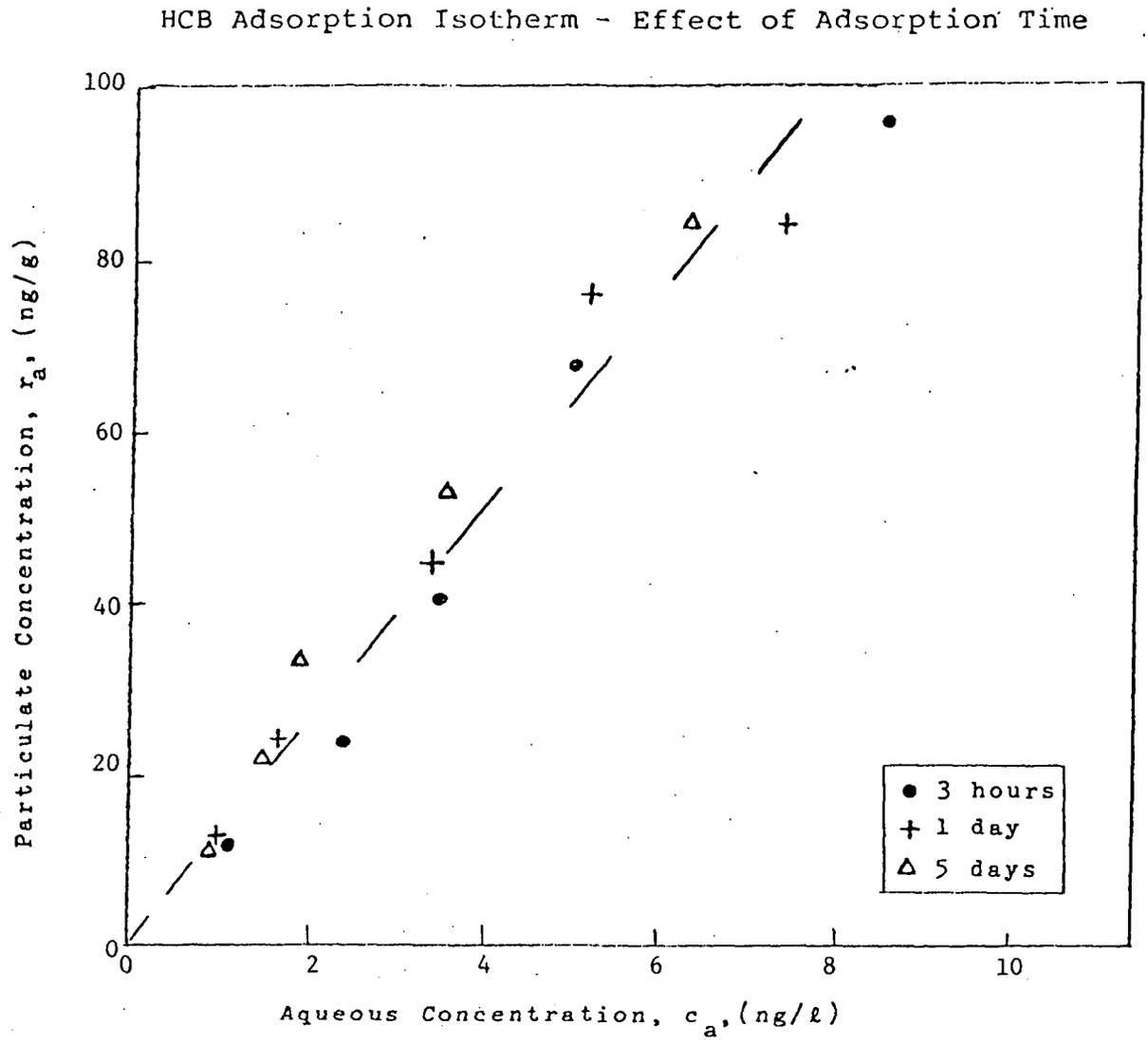



Fig. IV-3. HCB Adsorption Isotherms at various Adsorption Times. Saginaw Bay #50, m = 1000 mg/ℓ, Distilled Water.

TABLE IV-1

SAGINAW BAY ADSORPTION ISOTHERMS

SAGINAW BAY #50, 1000 mg/ℓ

$t_a$ = 3 hr.

| $c_i$ (ng/ℓ) | $c_a$ (ng/ℓ) | $r_a$ (ng/gm) | $\pi_a$ (ℓ/kg) | Freundlich Parameters |
|---|---|---|---|---|
| 16.2 | 1.11 | 12 | 10900 | 1/n = 1.06 |
| 30.1 | 2.50 | 24 | 9600 | K =10.4 |
| 53.8 | 3.46 | 41 | 11700 | |
| 86.2 | 4.92 | 68 | 13600 | |
| - | 8.6 | 96 | 11100 | |

$t_a$ = 24 hr.

| | | | | |
|---|---|---|---|---|
| 15.2 | 1.0 | 12 | 12500 | 1/n = 0.97 |
| 30.4 | 1.7 | 24 | 14200 | K =13.6 |
| 60.8 | 3.4 | 46 | 13600 | |
| 91.3 | 5.2 | 76 | 14500 | |
| 121.7 | 7.4 | 82 | 11000 | |

$t_a$ = 5 day

| | | | | |
|---|---|---|---|---|
| 15.2 | 0.9 | 11 | 12400 | |
| 30.4 | 1.5 | 22 | 15200 | 1/n = 1.02 |
| 45.5 | 1.9 | 34 | 17900 | K =13.9 |
| 75.1 | 3.6 | 53 | 14800 | |
| 121.6 | 6.3 | 84 | 13200 | |

A comparison of all the adsorption data (Saginaw Bay #50, m = 1000 - 1100 mg/ℓ) with adsorption times of 1 to 5 hours generated for other purposes to the longer adsorption time data is shown in figure IV-4. Although the longer adsorption times appear to increase the partitions coefficient somewhat, the effect is not dramatic. A similar plot for isotherms conducted for the same sediment at m = 55 mg/ℓ, figure IV-5, show less increases for $t_a$ = 48 hour when compared to $t_a$ = 2 hour.

It is concluded that although there appears to be slight effect of $t_a$ on adsorption partition coefficient, $\pi_a$, the effect is not large and a two hour absorption time appears to be sufficient.

C. Effect of Desorption Time on the Desorption Partition Coefficient

A major focus of this research is the desorption reaction for HCB since very little information was available. Initial kinetic experiments were conducted to examine the effect of desorption time, $t_d$, on the aqueous and sediment concentrations and the desorption partition coefficient. Vessels were equilibrated for $t_a$ = 2 hour followed by the desorption step. Vessels were analyzed for desorption times of 15 minutes to 24 hours. The results are shown in figures IV-6 and IV-7 for montmorillonite and Saginaw Bay #50 at m = 200 mg/ℓ. Pre-equilibrated supernatants were again employed. Unlike the adsorption experiments the time of desorption experiments displayed no consistent change in sediment or aqueous concentrations as a function of desorption time.

Because of the importance of this observation to the interpretation of the extent of reversibility of HCB adsorption, longer periods of desorption were employed. The difficulty with the kinetic experiment design is that sampling fluctuations obscure the effects if only discrete points are generated at each desorption time even if they are replicated. As shown in figure IV-8, and Table IV-2, the sediment concentration shows a slight initial trend but the partition coefficient varies in apparently random fashion.

A more convincing experiment is to generate full isotherms at fixed adsorption time and at various desorption times. The reference isotherms and data (Saginaw Bay #50, m = 1100 mg/ℓ), for $t_a$ = 3 hr and $t_d$ = 2 hr, are shown in fig. IV-9.

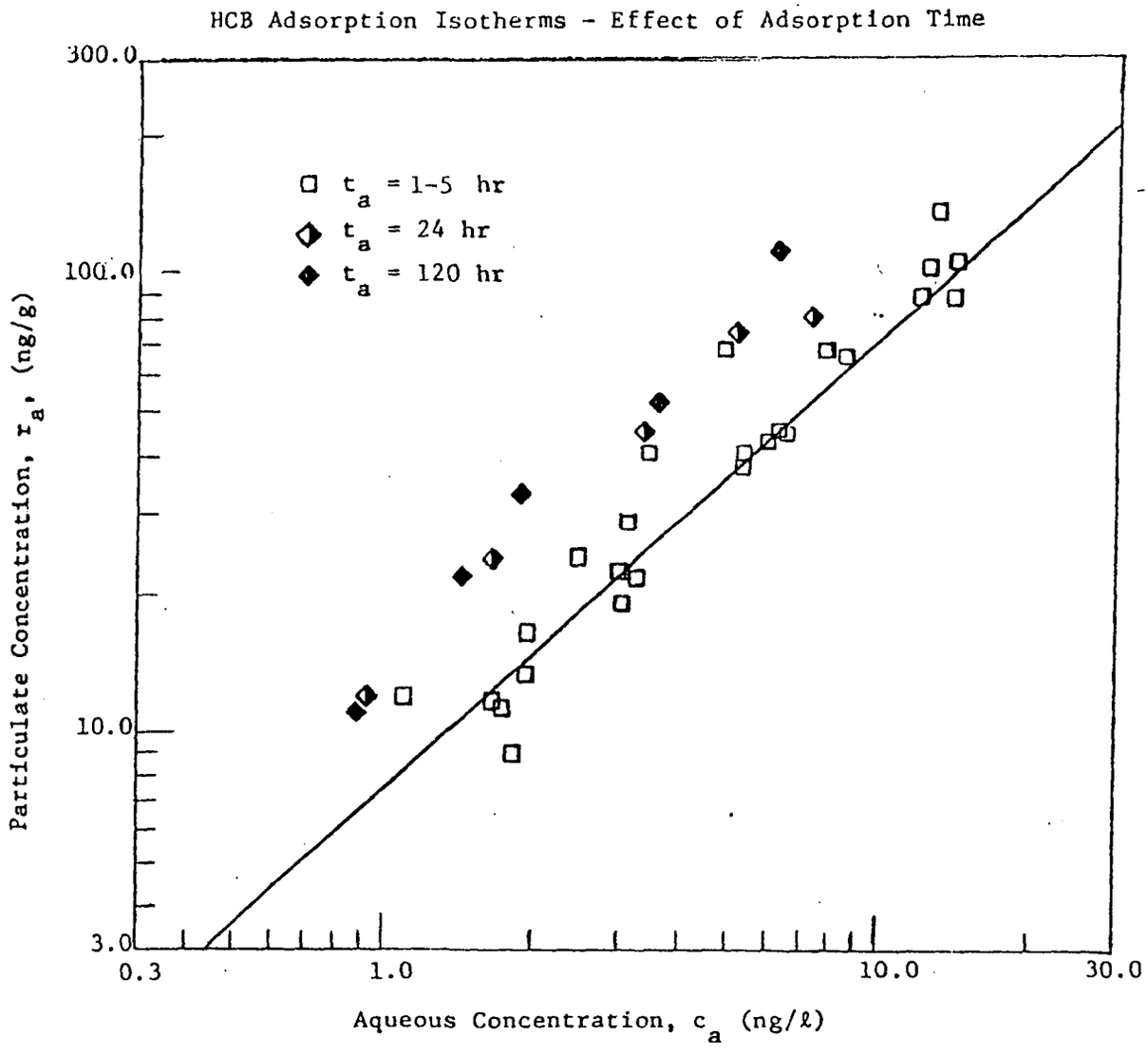



Fig. IV-4. HCB Adsorption Isotherms. Comparison. Saginaw Bay #50
m = 1000-1100 mg/ℓ. Distilled Water

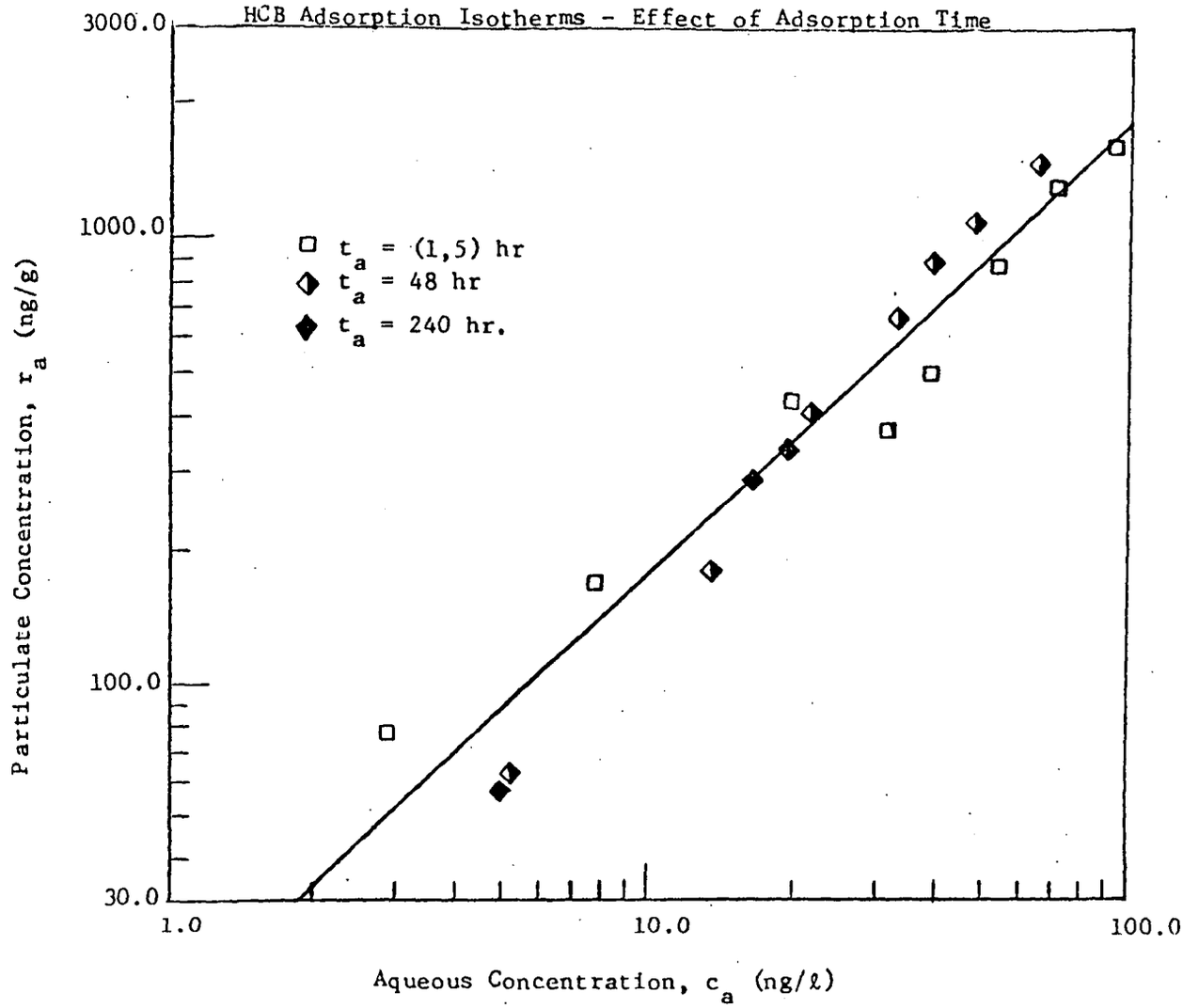



Fig. IV-5. HCB Adsorption Isotherms. Saginaw Bay #50, m = 55 mg/ℓ, Distilled Water

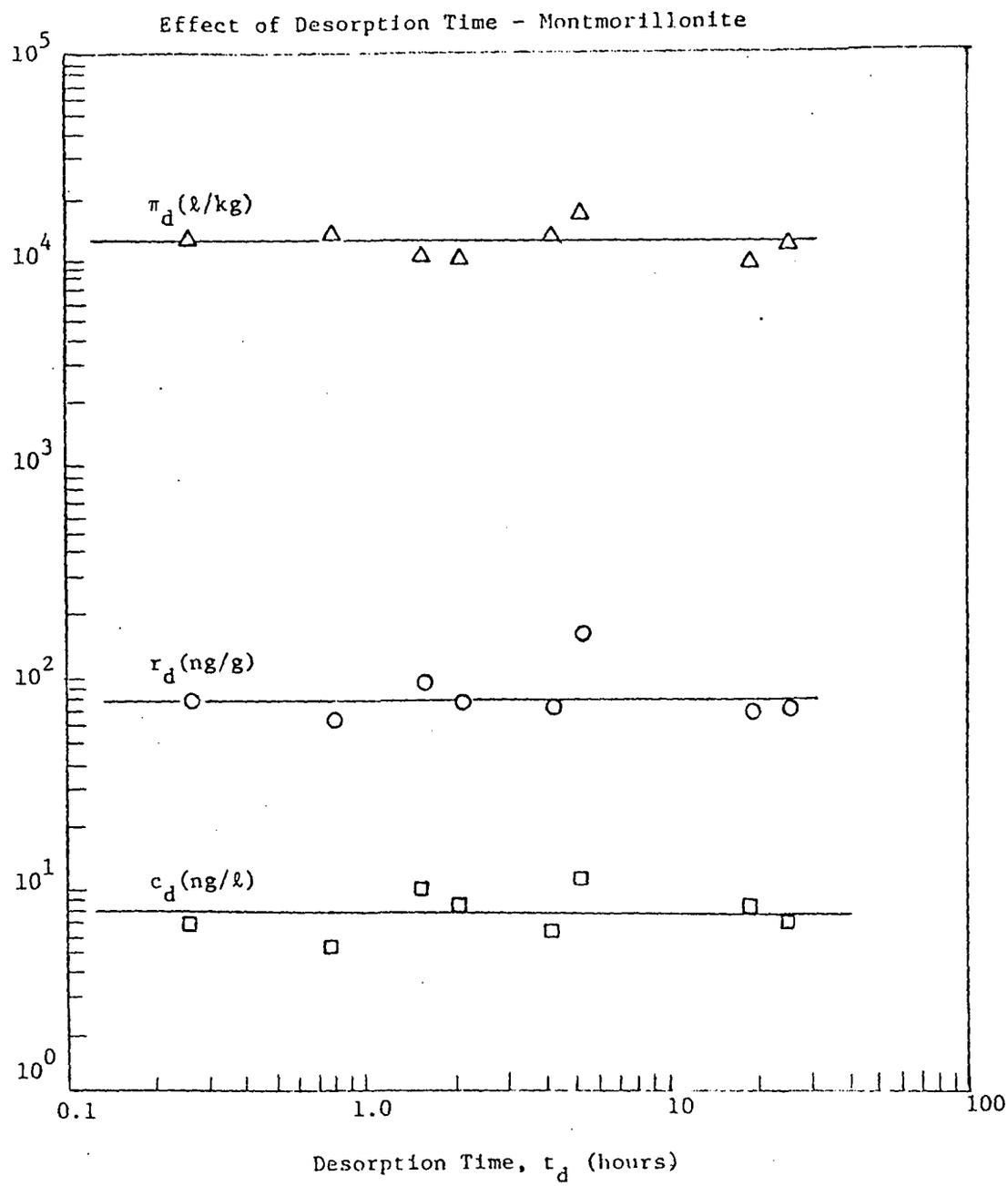



Fig. IV-6. Effect of Desorption Time, $t_d$, on Desorption Aqueous Concentration $c_d$, Sediment Bound HCB, $r_d$, and Desorption Partition Coefficient $\pi_d$. m = 200 mg/ℓ, montmorillonite, supernatant. $t_a$ = 2 hr.

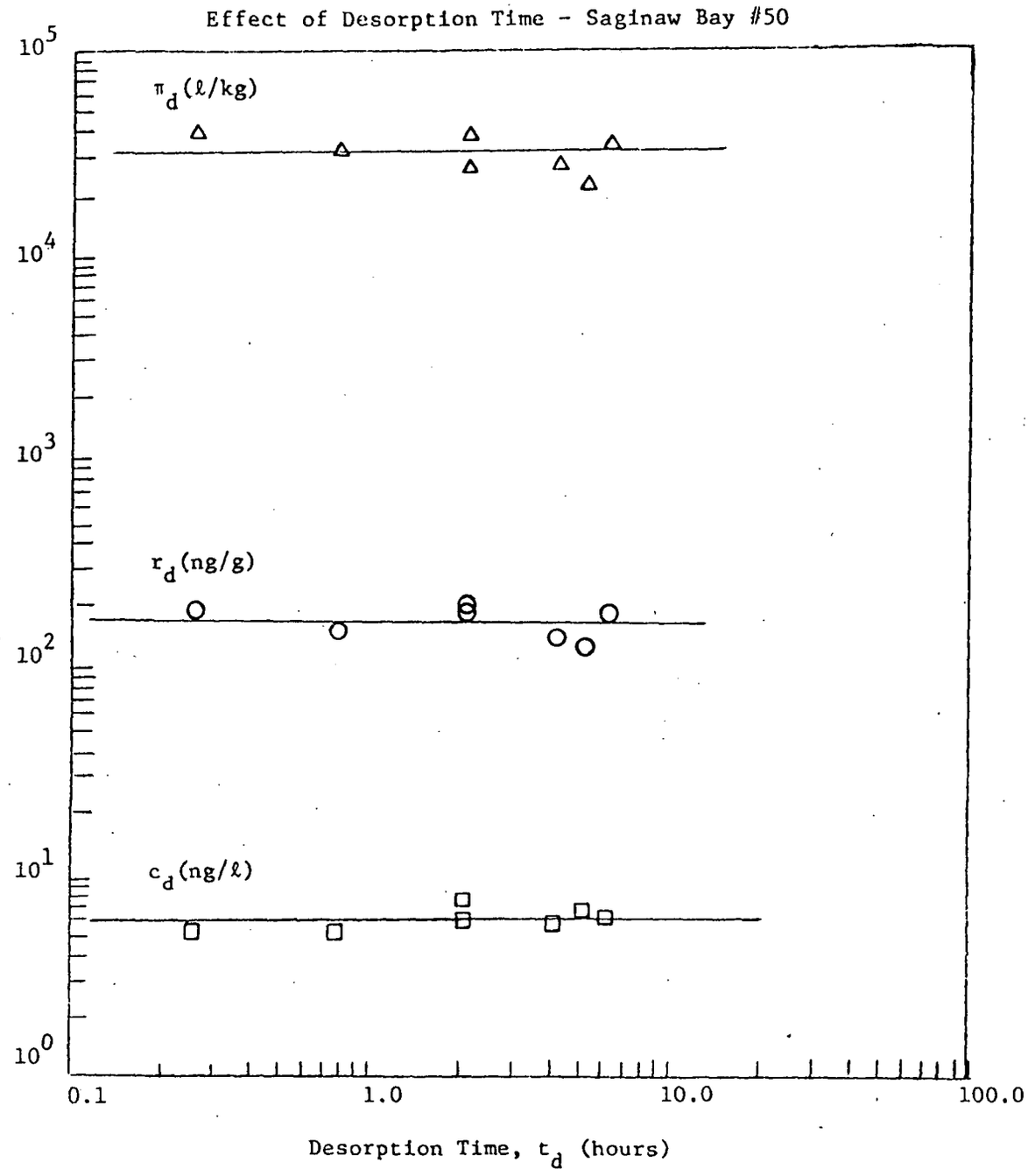



Fig. IV-7. Effect of Desorption Time, $t_d$, on desorption aqueous concentration, $c_d$, sediment bound HCB, $r_d$, and desorption partition coefficient, $\pi_d$. m = 200 mg/ℓ Saginaw Bay #50, Supernatant, $t_a$ = 2 hr.

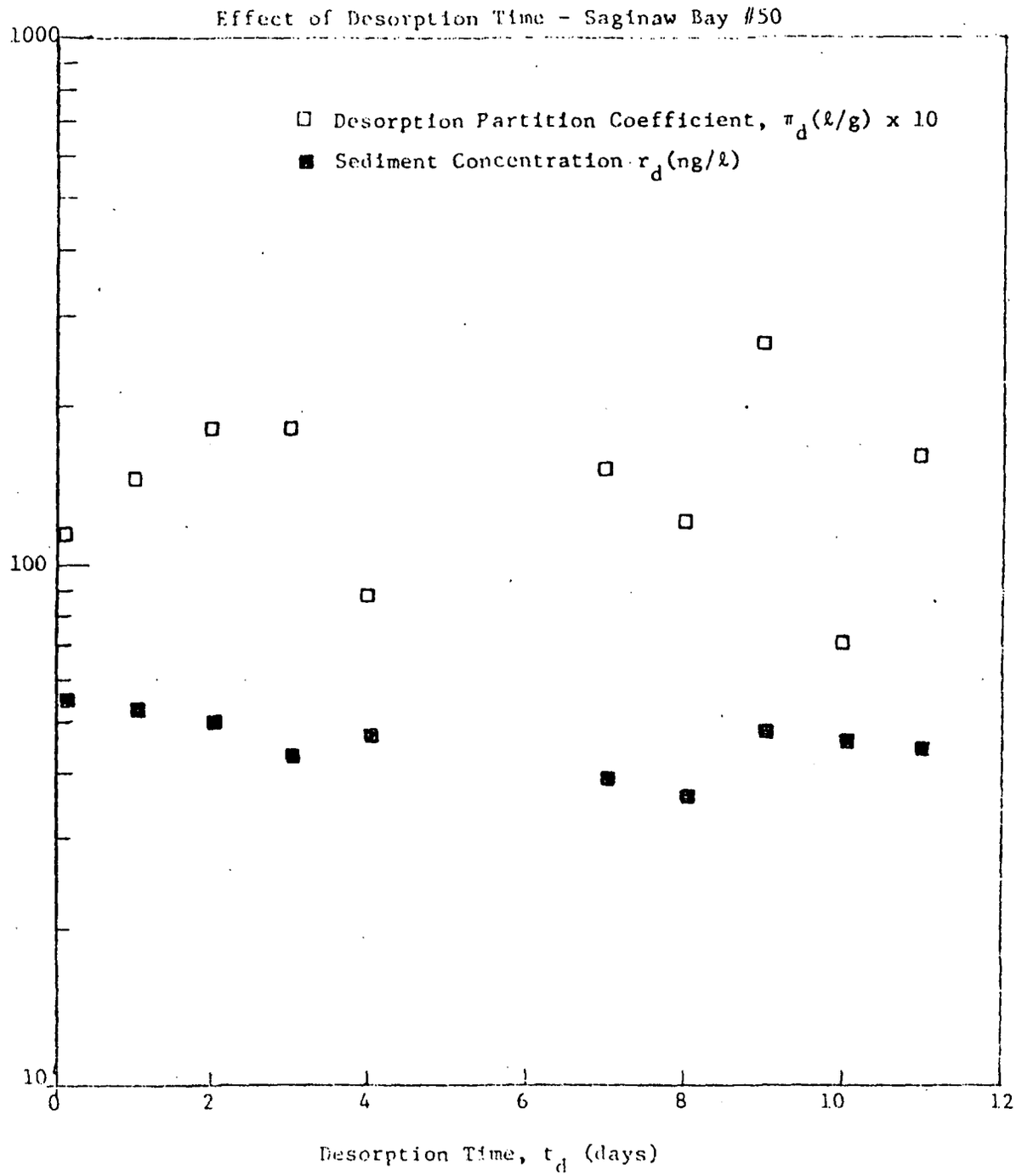



Fig. IV-8. Long Term Desorption. Sediment Bound HCB, $r_d$ and desorption partition coefficient, $\pi_d$(ℓ/g) (x 10 for convenience in plotting) versus desorption time.

These isotherms are compared to the adsorption and desorption data for $t_a$ = 3 hr and $t_d$ = 72 and 144 hrs. in fig. IV-10. A composite plot of all data is shown in fig. IV-11. The results indicate no significant difference for the desorption isotherm employing $t_d$ = 3 hour, 3 days and 6 days.

The conclusion is that the desorption reaction is essentially complete after 1-2 hour and much longer desorption times have no appreciable effect on the desorption partition coefficient obtained.

The apparent lack of full reversibility of the adsorption reaction plays an important role in the experimental investigations that follow and the theoretical treatment of the phenomena developed in Part B of this report. Subsequent chapters of Part A discuss other factors that influence partitioning with a view toward elucidating the possible mechanisms that may cause this behavior.

TABLE IV-2

LONG TERM DESORPTION STUDY

SAGINAW BAY # 50

| Time (Days) | $c_d$ (ng/ℓ) | $r_d$ (ng/gm) | $\pi_d$ (ℓ/kg) |
|---|---|---|---|
| 15 (min) | 4.7 | 55 | 11600 |
| 1 | 3.6 | 53 | 14600 |
| 2 | 2.8 | 50 | 18200 |
| 3 | 2.4 | 43 | 18100 |
| 4 | 5.4 | 47 | 8600 |
| 7 | 2.6 | 39 | 15000 |
| 8 | 3.0 | 36 | 12100 |
| 9 | 2.0 | 48 | 26500 |
| 10 | 6.0 | 42 | 7000 |
| 11 | 2.8 | 45 | 15800 |

$c_i$ = 70.1 ng/ℓ
pH = 7.1 ± 0.1

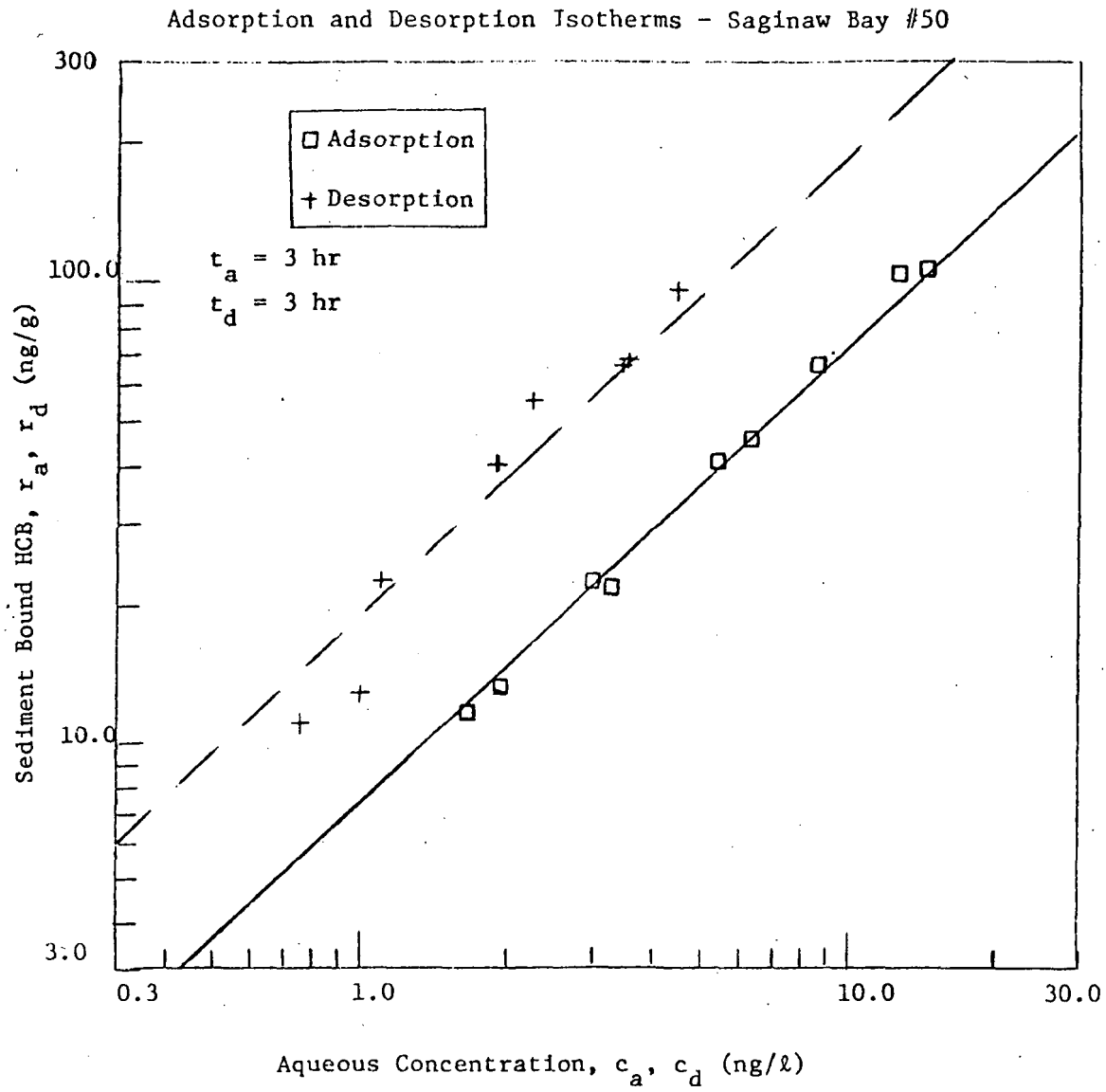



*Fig. IV-9. Adsorption ($r_a$ vs. $c_a$) and Desorption ($r_d$ vs. $c_d$)* Isotherms: $t_a$ = 3 hr., $t_d$ = 3 hr. m = 1100 mg/ℓ Saginaw Bay #50. Distilled Water

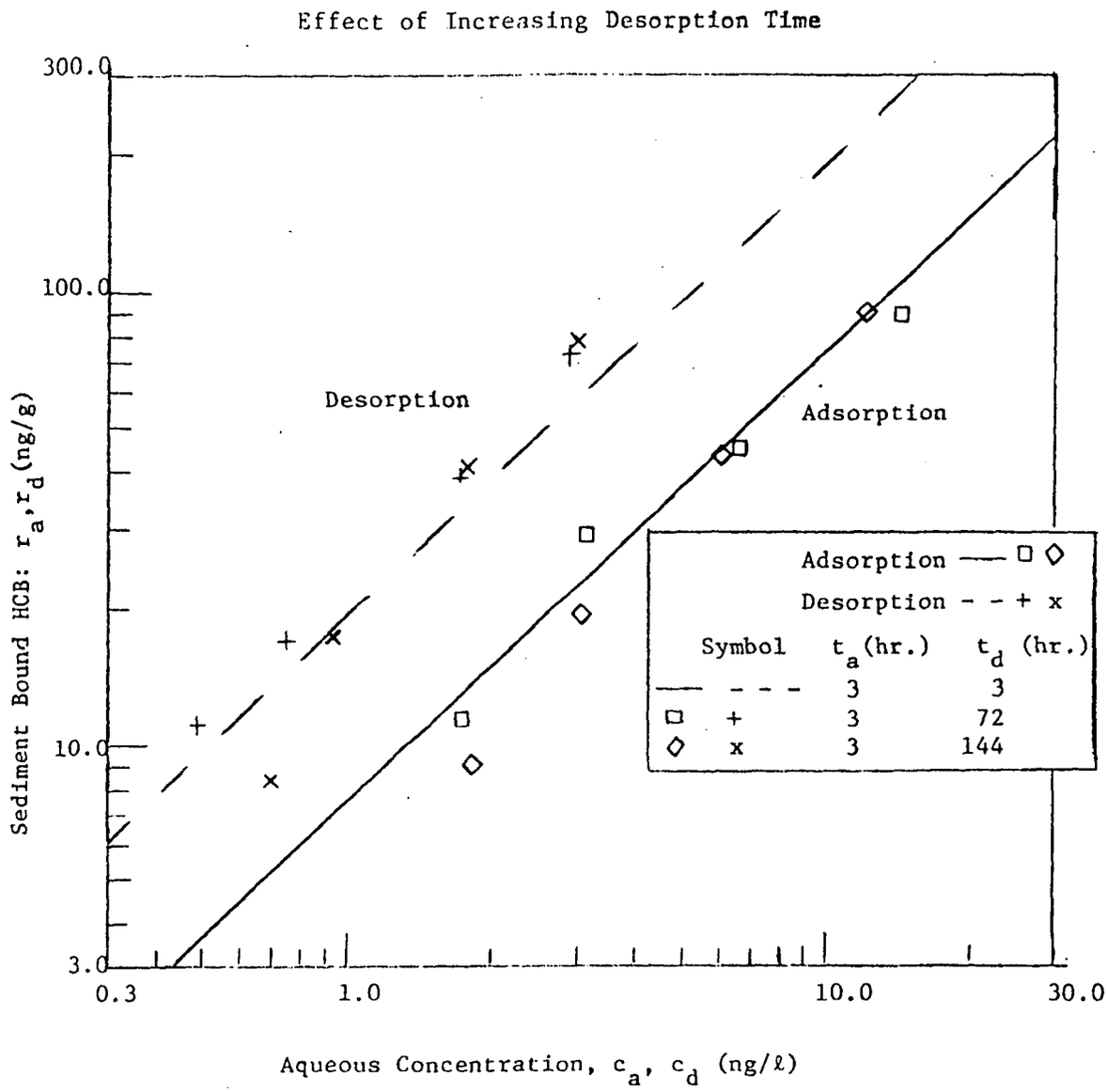



Fig. IV-10. Adsorption ($r_a$ vs. $c_a$) and Desorption ($r_d$ vs. $c_d$). Isotherms for increasing desorption times: $t_d$ = 72 and 144 hr. m = 1100 mg/ℓ Saginaw Bay #50, Distilled Water.

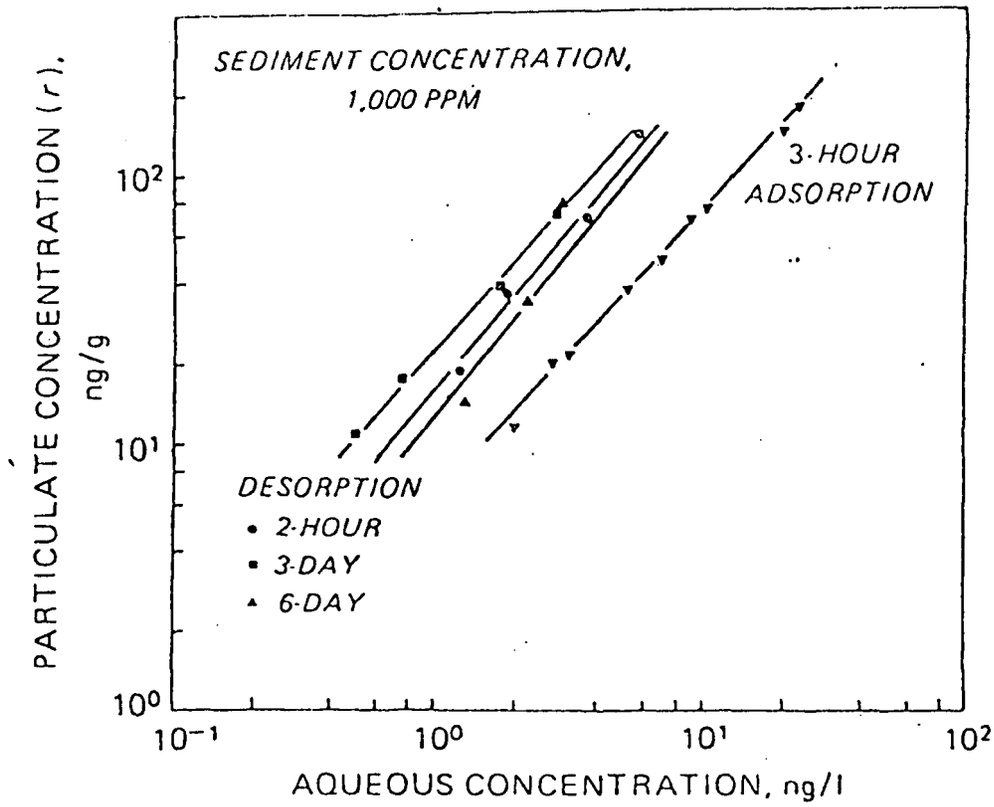



Fig. IV-11. Effect of Increasing Desorption Time. Saginaw Bay #50

## SECTION V

## EFFECT OF SOLUTION COMPOSITION

### A. Introduction

The adsorption of organic chemicals can be affected by the state of the aqueous phase. This is especially true of chemicals which have ionizable groups as part of their structure. The purpose of this section is to present the results of these experiments. Initially temperature variations are considered, followed by pH and ionic strength influences. The unexpected influence of $CaC\ell_2$ is discussed.

### B. Temperature

Similar to many temperate zone water bodies, Great Lakes water column temperatures vary slightly with seasonal changes. In Saginaw Bay, water column temperatures typically range from 0°C - 30°C during a yearly cycle (Smith et al., 1977). Experiments were conducted to determine whether temperature changes of this magnitude would significantly affect HCB partitioning. Using Saginaw Bay sediment (#50), adsorption isotherms were constructed at 1 ± 1°C and at 40 ± 1°C. Equilibration procedures were identical to those used for ambient temperature studies.

Experimental results are indicated in Figure V-1 and Table V-1. Somewhat surprisingly, 1°C data indicates a lower adsorption partition coefficient ($\pi_a$ = 6680 ℓ/kg) than does the 40°C data ($\pi_a$ = 14780 ℓ/kg). Overall, these equilibrium constant values bracket the previously reported value ($\pi_a$ = 7240 ℓ/kg) for ambient temperature and m = 1100 mg/ℓ.

The relatively non-reversible HCB bonding implied by the partitioning studies to be discussed subsequently appears to conflict somewhat with calculations of the enthalpy of adsorption (ΔH) based on variations in adsorption with temperature. A value of ΔH for Saginaw Bay sediment has been estimated from the expression,

$$\ell n \frac{K_2}{K_1} = \frac{\Delta H(T_2 - T_1)}{RT_1T_2} \qquad \text{(V-1)}$$

HCB Adsorption Isotherms - Effect of Temperature

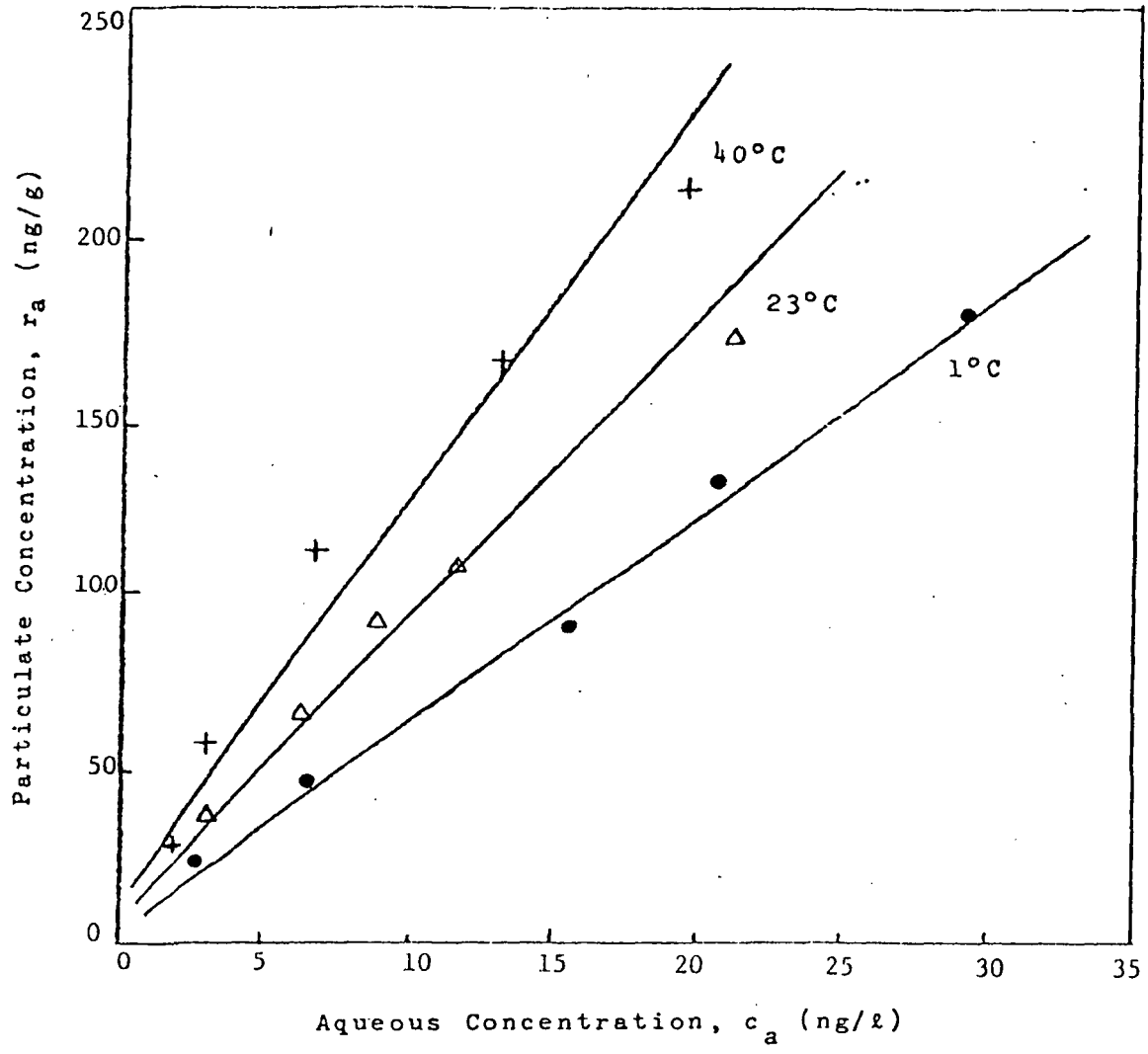



Fig. V. Effect of Temperature on HCB Adsorption. $t_a$ = 3 hr., m = 1100 mg/ℓ Saginaw Bay #50

TABLE V-1

EFFECTS OF TEMPERATURE ON ADSORPTION

Saginaw Bay: #50

$t_a$ = 3 hr.
m = 1100 mg/ℓ

Temperature
1°C ± 1°C

| $c_i$ (ng/ℓ) | $c_a$ (ng/ℓ) | $r_a$ (ng/gm) | $\pi_a$ (ℓ/kg) | Freundlich Constants |
|---|---|---|---|---|
| 29.2 | 2.7 | 24 | 8700 | 1/n = .86 |
| 58.4 | 6.9 | 46 | 6600 | |
| 116.8 | 15.7 | 88 | 5600 | K = 9.3 |
| 175.2 | 20.6 | 132 | 6400 | Corr. = .99 |
| 233.6 | 29.4 | 180 | 6100 | |

Average $\pi_a$ 6680 ± 1190 ℓ/kg

Temperature
40°C ± 1°C

| $c_i$ (ng/ℓ) | $c_a$ (ng/ℓ) | $r_a$ (ng/gm) | $\pi_a$ (ℓ/kg) | |
|---|---|---|---|---|
| 29.2 | 1.8 | 28 | 15300 | 1/n = .87 |
| 58.4 | 3.3 | 55 | 16500 | K = 17.8 |
| 116.8 | 6.9 | 111 | 16000 | Corr. = .99 |
| 175.2 | 13.1 | 164 | 12500 | |
| 233.6 | 19.3 | 214 | 11100 | |

Average $\pi_a$ = 14280 ± 2356 ℓ/kg

where $K_2$ and $K_1$ represent the equilibrium constant values for adsorption ($\pi_a$) at temperatures $T_2$(40°C) and $T_1$(1°C). The resulting positive value of $\Delta H$ ($\sim$ 3.3 kcal/mole) is not what would be predicted for an exothermic adsorption process. The small absolute value of $\Delta H$ is, however, similar in magnitude to values commonly observed for weak physical adsorption to sediment (Hamaker and Thompson, 1972). In contrast, this value is much smaller than values associated with chemisorption processes (> 10 kcal/mole) such as might be implied by the non-singular isotherms for adsorption and desorption discussed previously in Section IV. In addition, it should be noted that the direction of the temperature effect is not unique to HCB and has been observed in soil-pesticide studies (Spencer and Cliath, 1970; Haque and Coshow, 1971).

The observations of the present study may result from a number of factors. First, it is possible that reaction rates for the adsorption process may increase with increasing temperature. Alternately, variations in temperature could affect the aggregation state of the sediment, with increased temperatures resulting in greater dispersion.

In summary, it would appear that water temperature changes within Saginaw Bay will have a relatively small effect on PCB partitioning processes. From an experimental point of view, however, the temperature variation is small enough so that changes in ambient temperature should not cause large changes in partitioning.

C. Aqueous Phase Composition

The chemical composition of natural waters such as Saginaw Bay and its tributaries may differ considerably from the solution conditions of the present study. Interstitial waters, for instance, typically possess higher ionic strength levels than are observed in the overlying water column. Several experiments were conducted to evaluate the effects of changes in solution composition on HCB partitioning.

Initial experiments were conducted on montmorillonite clay samples. The chemical structure of montmorillonite is considerably simpler than that of natural sediments and evaluation of solution composition effects is, therefore, somewhat easier. In addition, a one component adsorbent was used in

order to attempt to characterize some aspects of the nature of HCB bonding to solid surfaces.

Figure V-2 depicts the results of experiments conducted to assess the effect of pH on HCB partitioning to 200 mg/ℓ montmorillonite suspensions. In these experiments, solution pH levels were adjusted by incremental additions of $10^{-3}$M HCl or NaOH and the suspensions allowed to equilibrate for several hours prior to HCB addition. This was done to minimize the occurrence of pH shifts during the course of the experiment. In all reaction solutions the total $Na^+$ and $Cl^-$ concentrations were maintained below $5.10^{-4}$M. The results indicate a significant reduction in HCB adsorption by the clay as pH levels were increased over a range from pH = 4 to pH = 10. The data suggests a rather abrupt decrease in $\pi_a$ as solution pH levels are increased from pH = 6 to pH = 8. Values of $\pi_a$ for acidic solutions (pH<6) are approximately 2-3 times greater ($\pi_a$ ∿12,000 ℓ/kg vs. $\pi_a$ ∿4000 ℓ/kg) than those observed under more basic conditions (pH>7).

The overall variation in $\pi_a$ may reflect changes in montmorillonite particle surface charge characteristics resulting from pH changes. It is known that while montmorillonite particle surfaces are negatively charged above pH ∿ 4, the charge on particle edges is pH dependent (van Olphen, 1963). Under acidic conditions (pH<5) particle edges are positively charged. However, as pH levels are increased from pH = 6 to pH = 8 edges undergo a neutralization reaction which, with continued pH increases, may result in the development of negative charge sites. This would suggest that the abrupt decreases in $\pi_a$ as solution pH levels increase above pH = 6 may be related to changes in the charge characteristics of particle edges.

The potential importance of solid phase charge characteristics to HCB adsorption is also suggested in comparisons of variations in $\pi_a$ with changes in solution composition. In experiments designed to evaluate the effect of solution ionic strength on HCB adsorption, the NaCl concentrations of 200 mg/ℓ montmorillonite suspensions were systematically varied. As indicated by figure V-3, the value of $\pi_a$ was relatively little affected by increasing NaCl concentrations from $10^{-4}$M to $10^{-2}$M. Partition coefficient values fluctuated

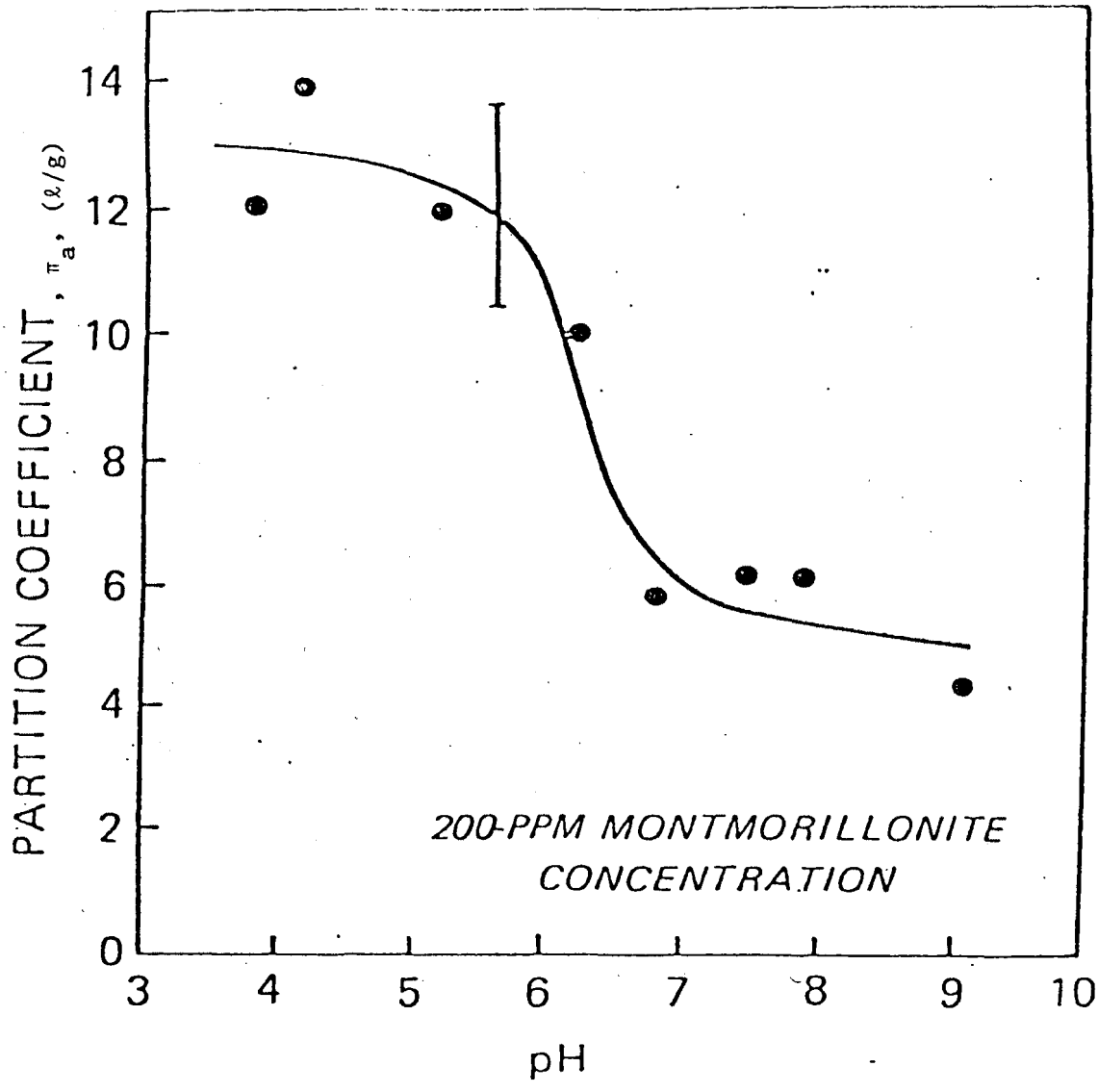



Fig. V-2. Effect of pH on HCB Partitioning to Montmorillonite

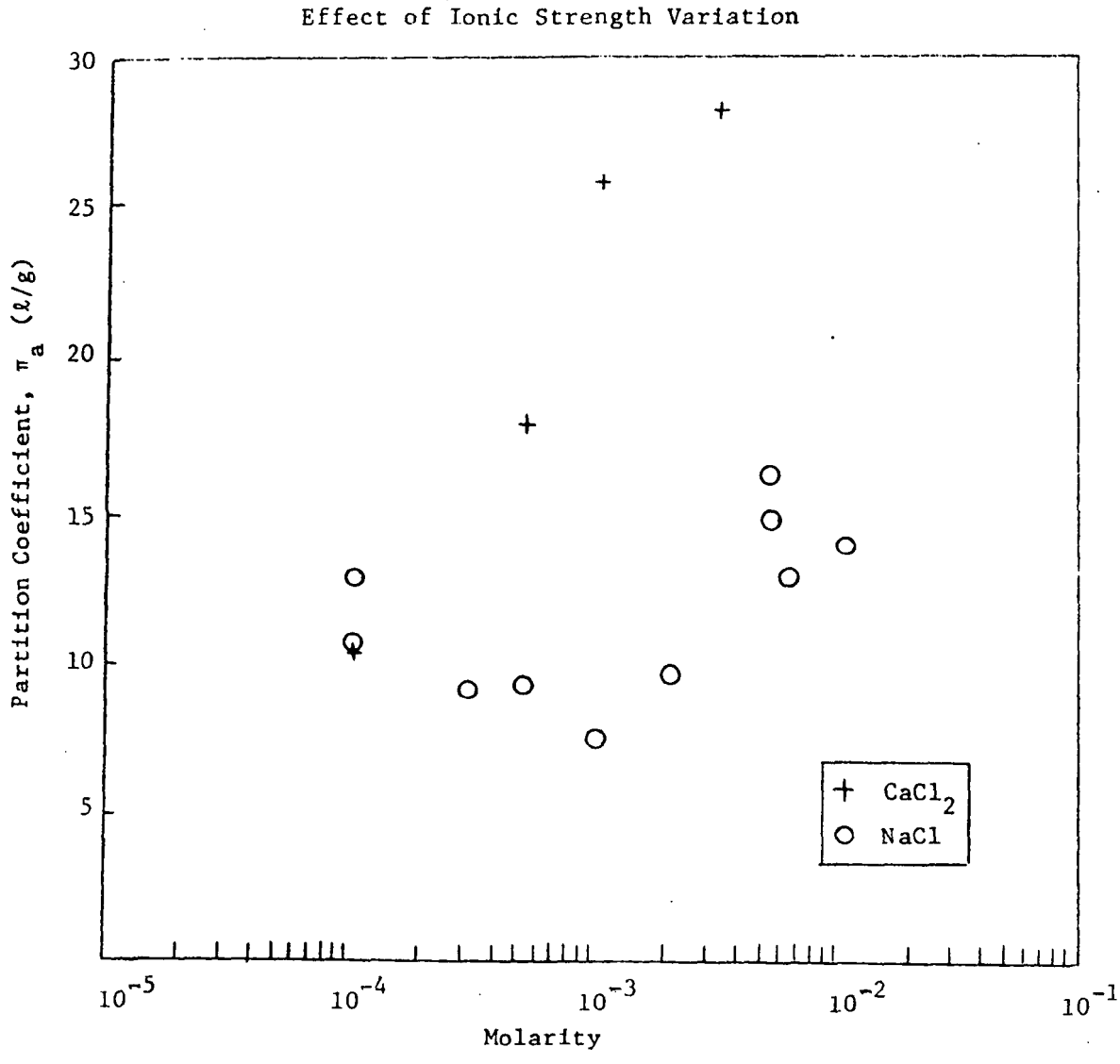



Fig. V-3. Effect of Increasing Ionic Strength using NaCl and $CaCl_2$ on HCB Adsorption Partition Coefficient for Montmorillonite. m = 200 mg/ℓ. $t_a$ = 4 hr.

between 10000 ℓ/kg and 14000 ℓ/kg with some evidence for a gradual increase in $\pi_a$ with increasing NaCl concentration. However, in similar experiments in which $CaCl_2$ concentrations were systematically varied, $\pi_a$ increased from ∿11000 ℓ/kg to >25000 ℓ/kg over a $10^{-4}$M to $10^{-2}$M concentration range. It is unlikely that this effect is the result of changes in HCB solubility since aqueous HCB concentrations were over an order of magnitude below reported HCB solubility limits (Dexter and Pavlov, 1978).

Dilute artificial seawater solutions appear to yield partition coefficient values intermediate between NaCl and $CaCl_2$ solutions (Table V-2). Interestingly, the presence of dissolved humic acid (Aldrich Chemical Co.) at concentrations achievable in natural waters did not appear to significantly alter the observed partition coefficient values. Increases in hunic acid concentrations from 5-50 ppm did not significantly affect partition (Table V-2). Thus it appears that HCB is not being strongly complexed by the organic phase. Nor does the humic acid appear to be competing with HCB adsorption sites on the clay particles.

The effect of $CaCl_2$ on HCB partitioning was confirmed in isotherm studies conducted on both montmorillonite and Saginaw Bay sediment samples. As demonstrated in figure V-4, for HCB adsorption onto 220 mg/ℓ montmorillonite suspensions, $\pi_a$ increased from ∿6000 ℓ/kg in distilled water to ∿35000 in .01M $CaCl_2$. For 220 mg/ℓ Saginaw Bay sediment suspensions (figure V-5), somewhat smaller increases in $\pi_a$ (12,000 to 25,000 ℓ/kg) were observed. For both solid phases the results suggest that isotherms in .01M $CaCl_2$ maintain the linear behavior observed for the distilled water and supernatant systems.

It is interesting to note that in preliminary experiments on vessel absorption it was also observed that the presence of .01M $CaCl_2$ increased the adsorption of HCB by glass surfaces and a pH effect was found. The adsorption process was found to be pH dependent with more extensive adsorption occurring at pH = 3 than at pH = 11 (Figure V-6). By contrast, the solution pH appeared to have little effect on the adsorption of HCB by polyethylene. Under basic conditions the glass surfaces may be expected to display more negatively charged surfaces possibly impeding adsorption of HCB. In this regard it is of interest to observe the effects of electrolyte composition on HCB partitioning to the vessel.

TABLE V-2

Adsorption vs. Chemical Composition

Montmorillonite, m = 200 mg/ℓ

| Composition | pH | $c_a$ (ng/ℓ) | $r_a$ (ng/gm) | $\pi_a$ (ℓ/kg) |
|---|---|---|---|---|
| Distilled $H_2O$ | 6.9 | 15.0 | 79 | 6000 |
| 0.001M $NaKH_2PO_4$* | 7.2 | 12.2 | 98 | 8000 |
| 0.002M NaCl | 6.9 | 10.7 | 96 | 9200 |
| 0.01M NaCl | 6.9 | 9.3 | 126 | 13,500 |
| 0.01M $CaCl_2$ | 6.9 | 4.6 | 130 | 28,000 |
| Artificial Seawater | | | | |
| 1.8 gm/kg | - | 6.3 | 94 | 15,000 |
| 3.8 gm/kg | - | 5.1 | 75 | 14,600 |
| Humic Acid (Dissolved) | | | | |
| 5 mg/ℓ | 6.7 | 14.6 | 76 | 5000 |
| 10 mg/ℓ | 6.7 | 22.8 | 104 | 5000 |
| 50 mg/ℓ | 7.1 | 12.5 | 70 | 5500 |

*Composition: $H_2PO_4$ = 0.001M $K^+$ = 0.001M $Na^+$ = 0.0008M

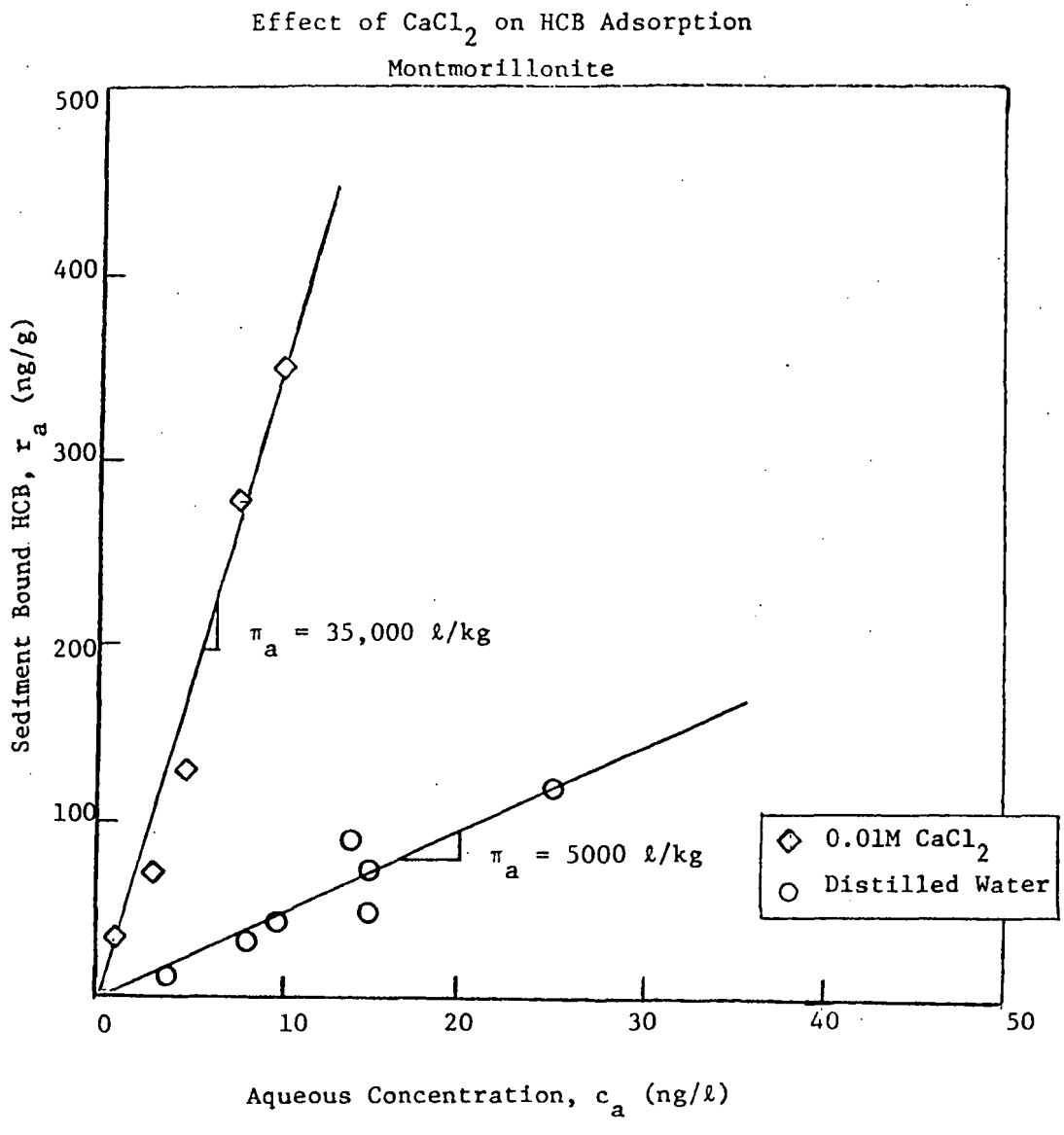



Fig. V-4. Adsorption Isotherm for Distilled Water and 0.01M $CaCl_2$
m = 220 mg/ℓ Montmorillonite

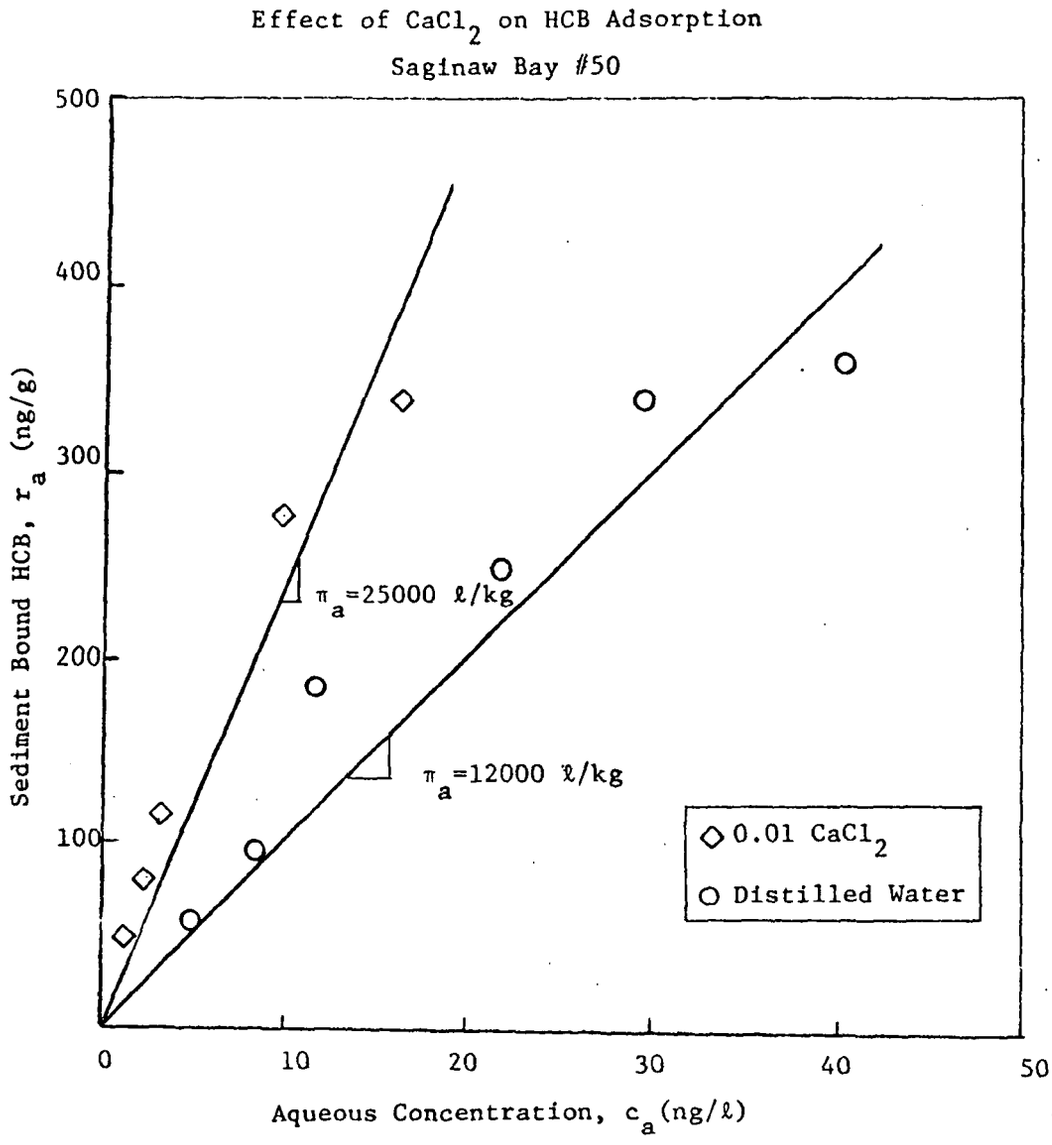



Fig. V-5. Adsorption Isotherm for Distilled Water and 0.01M $CaCl_2$. m = 220 mg/ℓ Saginaw Bay #50

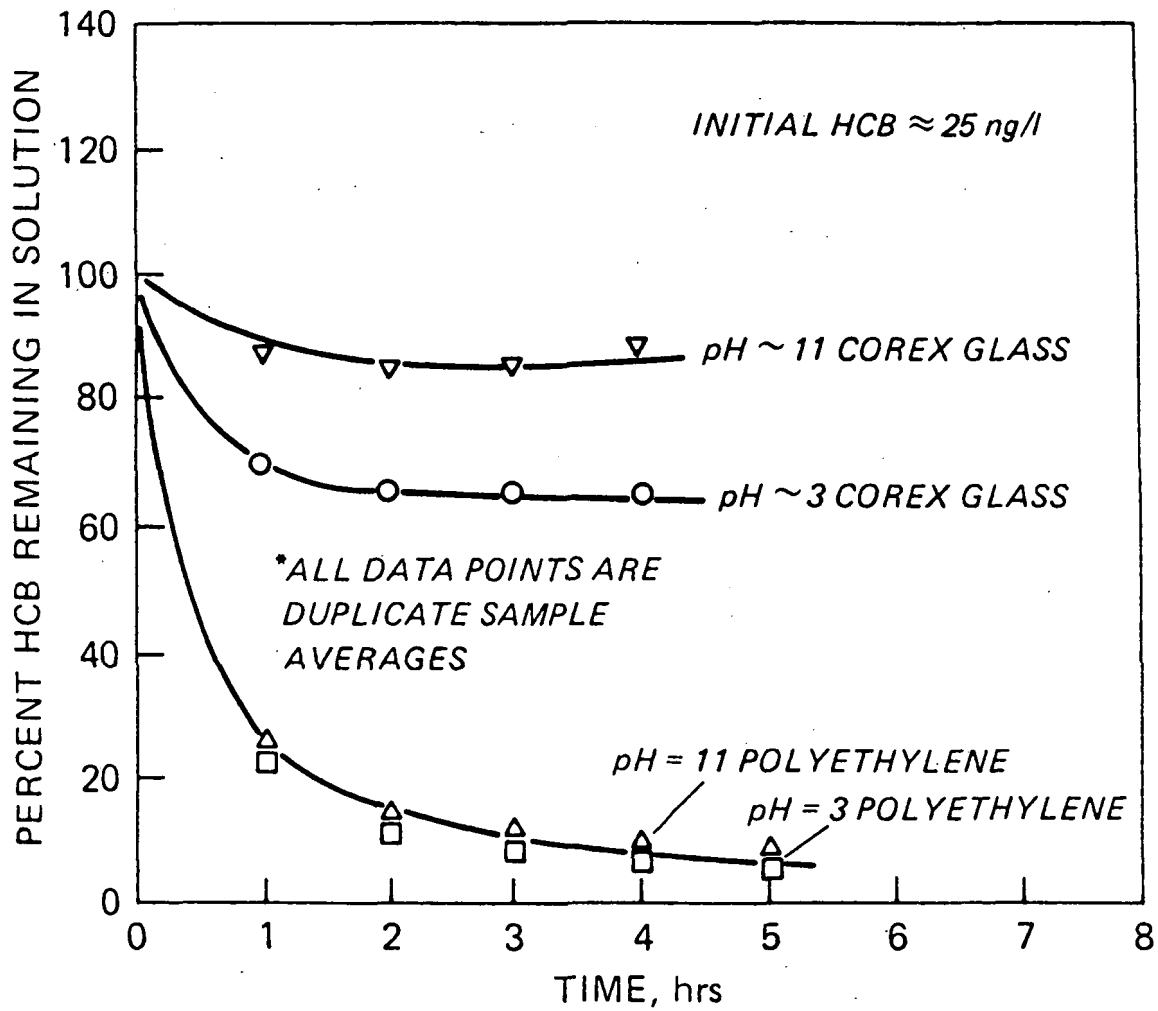



Fig. V-6. Effect of pH on Vessel Adsorption of HCB

Experiments indicated that significantly more HCB adsorption to Corex occurred from 0.1M $CaCl_2$ solutions than from 0.1M NaCl solutions (figure V-7). More than 50% of the initial 40 ng/ℓ HCB concentration was adsorbed onto vessel walls from a 0.1M $CaCl_2$ solution. Once again, solution composition (0.1M NaCl) appeared to have no observable effect on HCB adsorption to polyethylene.

It has been reported that natural sediments as well as clay minerals possess negatively charged surfaces (Neihof and Loeb, 1972). In addition, it is well known that $Ca^{++}$ is more effectively adsorbed at particle surfaces than is $Na^{+}$ (van Olpen, 1963). Thus it would appear that increased sediment adsorption of HCB in the presence of $CaCl_2$ may be the result of neutralization of surface charge. This interpretation of the $CaCl_2$ data would appear to be consistent with the pH results. In these experiments HCB adsorption was significantly reduced under pH conditions (pH>7) which should have favored maximization of negative surface charge. It is interesting that adsorption of the neutral HCB moleclue should be as significantly affected by surface charge as it appears to be.

$CaCl_2$ may also affect sediment aggregation and particle size. It is possible that $CaCl_2$ may increase partitioning by flocculating extremely small sediment particles (<0.1μ) which might otherwise remain suspended in distilled water even after centrifugation. HCB adsorbed on such particles would appear to be dissolved rather than adsorbed. The effect would be to reduce the calculated equilibrium constant value. Experimentation conducted to test this hypothesis proved inconclusive. In one experiment, sediment solutions were added to reaction vessels and subsequently centrifuged. The supernatant solutions were then discarded and replaced with distilled water after which tritiated HCB was added. The results did not show any significant increase in partitioning when compared to samples treated in the standard manner. However, it has been reported (Karickhoff and Brown, 1978) that shaking natural sediment materials may result in redispersion of the sediments into finer and finer particles. This may occur in the present experiments.

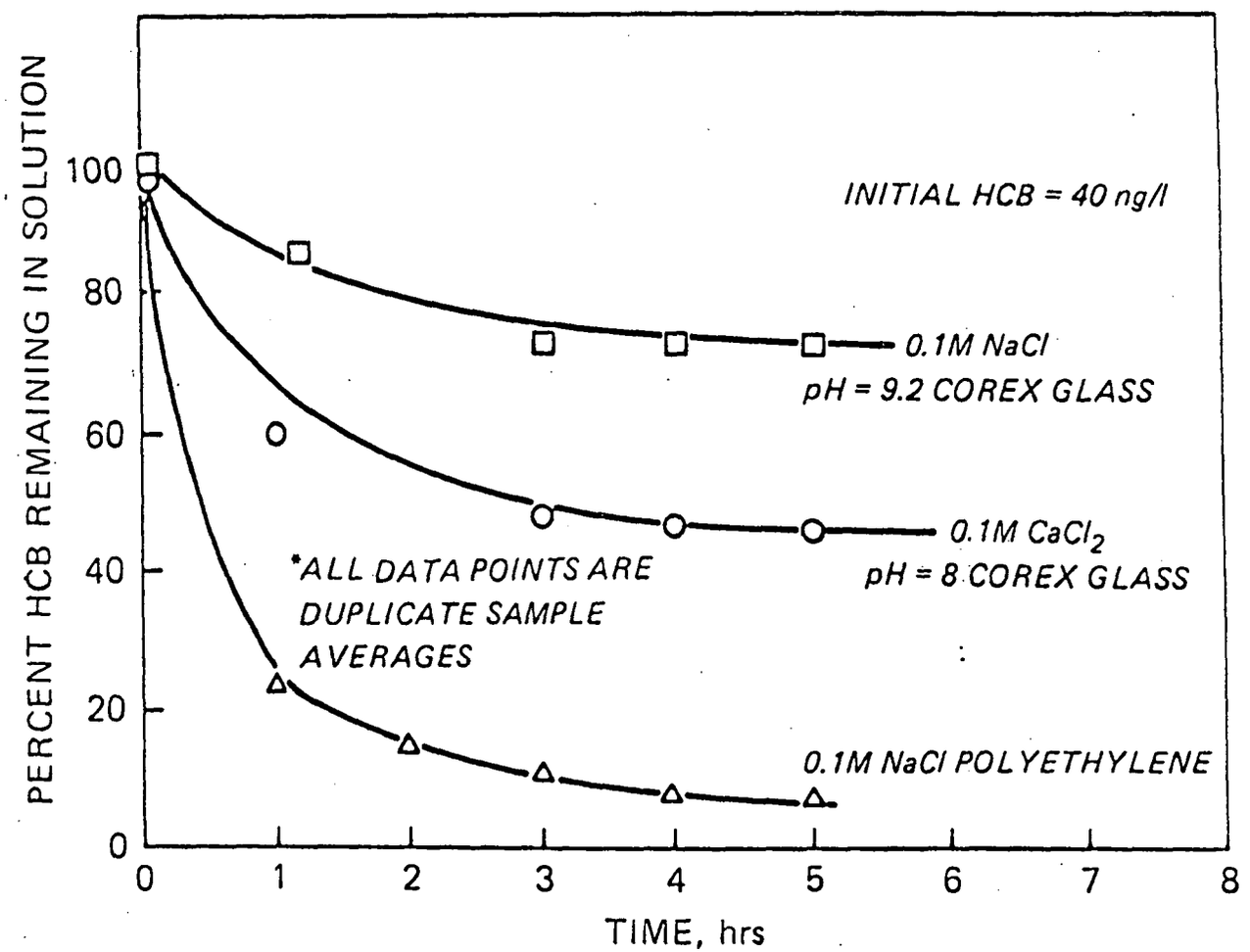



Fig. V-7. Effect of Solution Composition on Vessel (Glass) Adsorption of HCB

In summary, it has been shown that although pH effects are observed in the range pH = 5 to pH = 7, the effects of higher pH values, more common in surface and interstitial waters, is small. Ionic strength effects are slight if $NaC\ell$ is used. However, the effect of $CaC\ell_2$ is marked. This surprising result may be due to neutralization of surface charge changes resulting from $Ca^{++}$ adsorption.

## SECTION VI

## SEDIMENT COMPOSITION EFFECTS

### A. Introduction

The composition of the adsorbent is known to strongly affect the degree of adsorption of organic chemicals. For PCB's a number of investigators have proposed that various sediment properties can be used to correlate to adsorption partition coefficient. This is discussed in more detail below.

From the point of view of an analysis of PCB distributions in Saginaw Bay, it was apparent that PCB adsorption partition coefficients were not well enough known for Saginaw Bay sediment to be used in the fate computations that were planned and are currently underway. Thus Saginaw Bay samples from various locations were analyzed to establish the relevant relationships.

### B. Saginaw Bay Field Samples

Saginaw Bay is a relatively large arm of Lake Huron. The inner half of the Bay is quite shallow (mean depth = 5m) with bottom sediments ranging in composition from sand to clay. The large area and varied bottom composition suggest that HCB partitioning to sediments may vary significantly depending on location. For this reason, HCB partitioning studies were conducted on a series of field samples collected from different inner Bay locations.

Grab samples of the top 6" of the bottom sediments were taken from a number of locations throughout the inner Bay area (Figure VI-1). Locations, given in Table VI-1, were selected in an attempt to gather samples reflecting varying sediment composition. After collection (September 21-22, 1979) samples were refrigerated (5°C) but not frozen. (Station #50 was collected in August, 1978).

Sediment size fractions were characterized in a series of hydrometer studies (Table VI-2). The sediments vary in texture from predominantly sand (#19, #53, #69) to predominantly silt (#31, #43, #50). In general, samples from the middle Bay area contain much higher percentages of fine materials

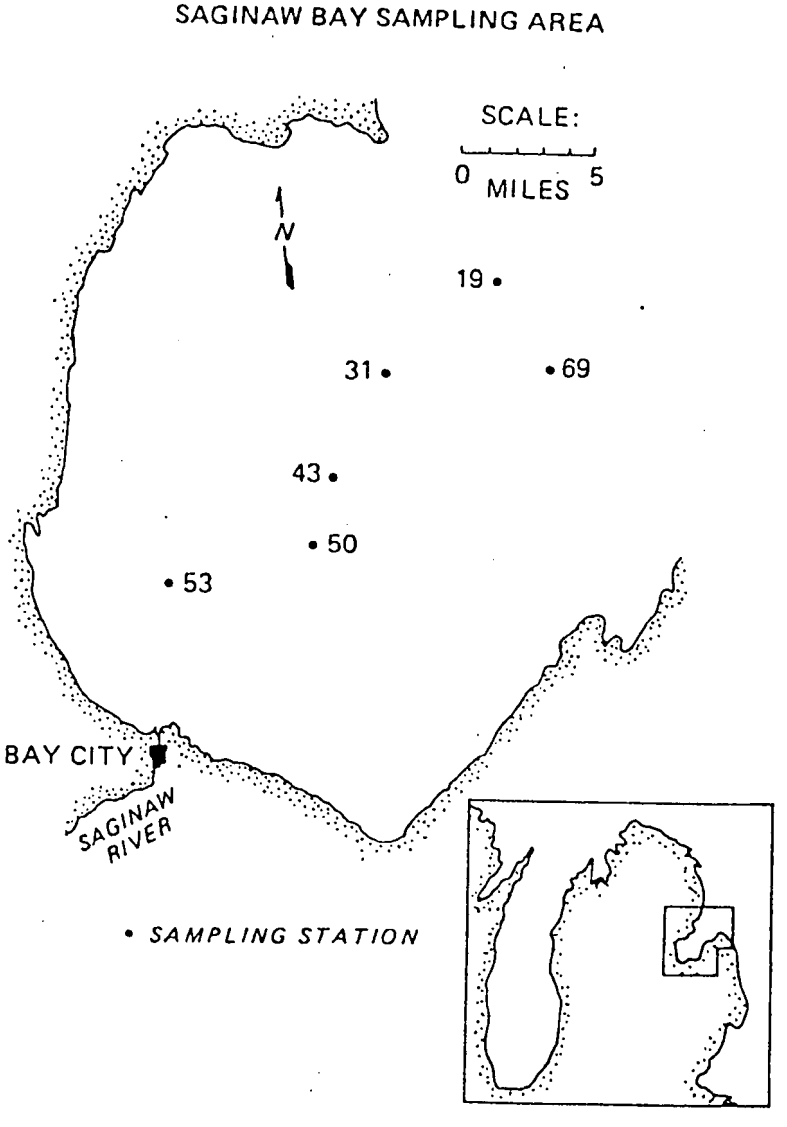



Fig. VI-1. Location Map for Sediment Samples

TABLE VI-1. Sampling Locations for Saginaw Bay

| Station # | Location | | ∿ Water Depth (ft) | Sediment Characteristics |
|---|---|---|---|---|
| 19 | 43°54.2'N | 83°35.7'W | 25 | Muddy Sand |
| 31 | 43°50.8' | 83°40.5' | 26 | Silty Mud |
| 43 | 43°47.3' | 83°42.9' | 24 | Silty Mud |
| 50 | 43°45.5' | 83°42.9' | 25 | Mud |
| 53 | 43°43.8' | 83°50.4' | 15 | Muddy Sand |
| 69 | ∿43°51.5' | 83°33.5' | 12 | Sand |
| Saginaw R. | ∿43°37.5' | 83°51.8' | 15 | Mud |

TABLE VI-2. Sediment Size Distribution For Saginaw Bay

| Station | % Sand | % Silt | % Clay |
|---|---|---|---|
| #19 | 91 | 8 | <1 |
| #31 | 7 | 90 | 4 |
| #43 | 9 | 89 | 2 |
| #50 | 15 | 82 | 3 |
| #53 | 85 | 14 | <1 |
| #69 | 95 | 5 | 0 |
| Saginaw River | 18 | 79 | 3 |

Sand >62μ
Silt 1-62μ
Clay <1μ

Breakdown Of High Silt Fraction

| | Microns(μ) | Weight (% Total) | | |
|---|---|---|---|---|
| Station | | 30-10 | 10-2 | 2-1 |
| #31 | | 30 | 30 | 15 |
| #43 | | 27 | 34 | 10 |
| #50 | | 20 | 15 | 4 |
| Saginaw River | | 25 | 9 | 1 |

than do sites located closer to the shore areas. Fine clay fractions (<1μ) range from ∿ 0.1% for Station #69 in the peripheral sand zone up to ∿ 4% (#31) in the middle Bay.

General chemical characteristics of the sediments are tabulated in Table VI-3. Sediment organic contents were determined by wet digestion using the Wakley-Black method. Surface area values were determined by single point BET nitrogen analysis. Volatile solids were calculated from gravimetric changes resulting from heating to 500°C after initial drying at 100°C. Organic matter varies from 0.1% (Station #69) to 5.4% (Station #31). The organic content appears to be inversely related to general particle size suggesting that most of the organic matter is present in the fine fractions. Organic concentrations in the sandy stations (#19, #69) are <1%. Similar correlations appear to exist between particle size in the major cations and phosphorus. The reason for the high Ca and Mg levels in the Saginaw River sample may reflect high levels of human activity in the immediate area.

HCB adsorption and desorption isotherms were constructed for each sample. Samples were wet seived and the <75μ fraction used in these studies. Station #69 which consisted largely of sand was wet seived and only the >75μ fraction used in the analysis. The characteristics of these seived subsamples are listed in Table VI-4. Adsorption studies were conducted using 1100 mg/ℓ (except #69 for which $m_a$ = 20,000 mg/ℓ) sediment concentrations and 3 hr equilibration times. Following the adsorption phase, 2 hour desorption studies were performed at sediment concentrations of 990 mg/ℓ (except #69 for which $m_d$ = 18,000 mg/ℓ). For each sediment sample, isotherms were constructed on the basis of 5 points, each being the average value of 3 replicates as usual.

The results are presented in Figure VI-2. Tabulated data is included in the Appendix. Freundlich isotherm parameters and partition coefficient values have been summarized in Table VI-5. With the exception of Station #69 the samples appear to display relatively uniform adsorption behavior. $K_a$ values range from 9-16 and $\pi_a$ values from 9500-15000 ℓ/kg. Slope values ($1/n_a$) for the Freundlich plots range from 0.93-1.15 suggesting relatively linear behavior. The desorption data exhibits considerably greater variability with $1/n_d$ values ranging from .94 to 1.47 and $K_d$ ranging from 13.6 to 35.2. Desorption partition coeffi-

TABLE VI-3. Chemical Characteristics of Saginaw Bay Sediments

| | | | Total Sample (mg/ℓ) | | | | |
|---|---|---|---|---|---|---|---|
| Sample # | pH | % Org. Matter | P | K | Mg | Ca | C.E.C. milliequivalents/ 100 gms |
| 19 | 7.8 | 0.4 | 3 | 10 | 30 | 160 | 3.7 |
| 31 | 7.4 | 5.4 | 4 | 95 | 600 | 3600 | 21.4 |
| 43 | 7.4 | 4.9 | 5 | 80 | 450 | 6800 | 24.3 |
| 50 | 7.4 | 4.6 | 8 | 80 | 550 | 2700 | 16.2 |
| 53 | 7.8 | 1.2 | 4 | 20 | 85 | 3900 | 4.6 |
| 69 | 8.1 | 0.1 | 2 | 5 | 12 | 100 | 2.9 |
| Saginaw R. | 7.6 | 4.9 | 37 | 73 | 525 | 22000 | 31.6 |

C.E.C. = cation exchange capacity

TABLE VI-4. Chemical Characteristics of Saginaw Bay Sediments Seived Subsamples

| Saginaw Bay Station # | * Surface area $\sigma(m^2/g)$ | % Volatile Solids |
|---|---|---|
| 19 | 17.0 | 15.0 |
| 31 | 17.8 | 9.9 |
| 43 | 15.9 | 9.3 |
| 50 | 12.8 | 7.6 |
| 53 | 7.0 | 8.7 |
| 69** | 0.2 | 0.3 |
| Saginaw River | 8.4 | 9.6 |
| Montmorillonite | 12.6 | 0.0 |

* Single Point BET Nitrogen Determinations

** For the > 75μ Fraction

TABLE VI-5. Sediment Partition Coefficients and Freundlich Isotherm Parameters

| Saginaw Bay Station # | Adsorption $m_a$ = 1100 mg/ℓ $\pi_a$ (ℓ/g) | $1/n_a$ | $K_a$ | Desorption 990 mg/ℓ $\pi_d$ (ℓ/g) | $1/n_d$ | $K_d$ |
|---|---|---|---|---|---|---|
| 19 | 14.83 | 0.97 | 15.7 | 30.13 | 1.17 | 26.0 |
| 31 | 12.27 | 0.93 | 14.1 | 30.85 | 0.94 | 35.2 |
| 43 | 10.67 | 1.14 | 9.3 | 26.09 | 1.50 | 22.6 |
| 50 | 7.01 | 0.91 | 11.3 | 20.22 | 1.10 | 29.3 |
| 53 | 11.18 | 0.94 | 12.6 | 19.76 | 1.28 | 13.6 |
| 69 | 0.036 | - | - | 0.052 | - | - |
| Saginaw R. | 9.63 | 0.95 | 10.6 | 22.43 | 1.37 | 14.6 |
| Montmorillonite | 2.10 | - | - | 7.23 | - | - |

* 20,000 mg/ℓ sediment concentration for adsorption and 18,000 mg/ℓ for desorption

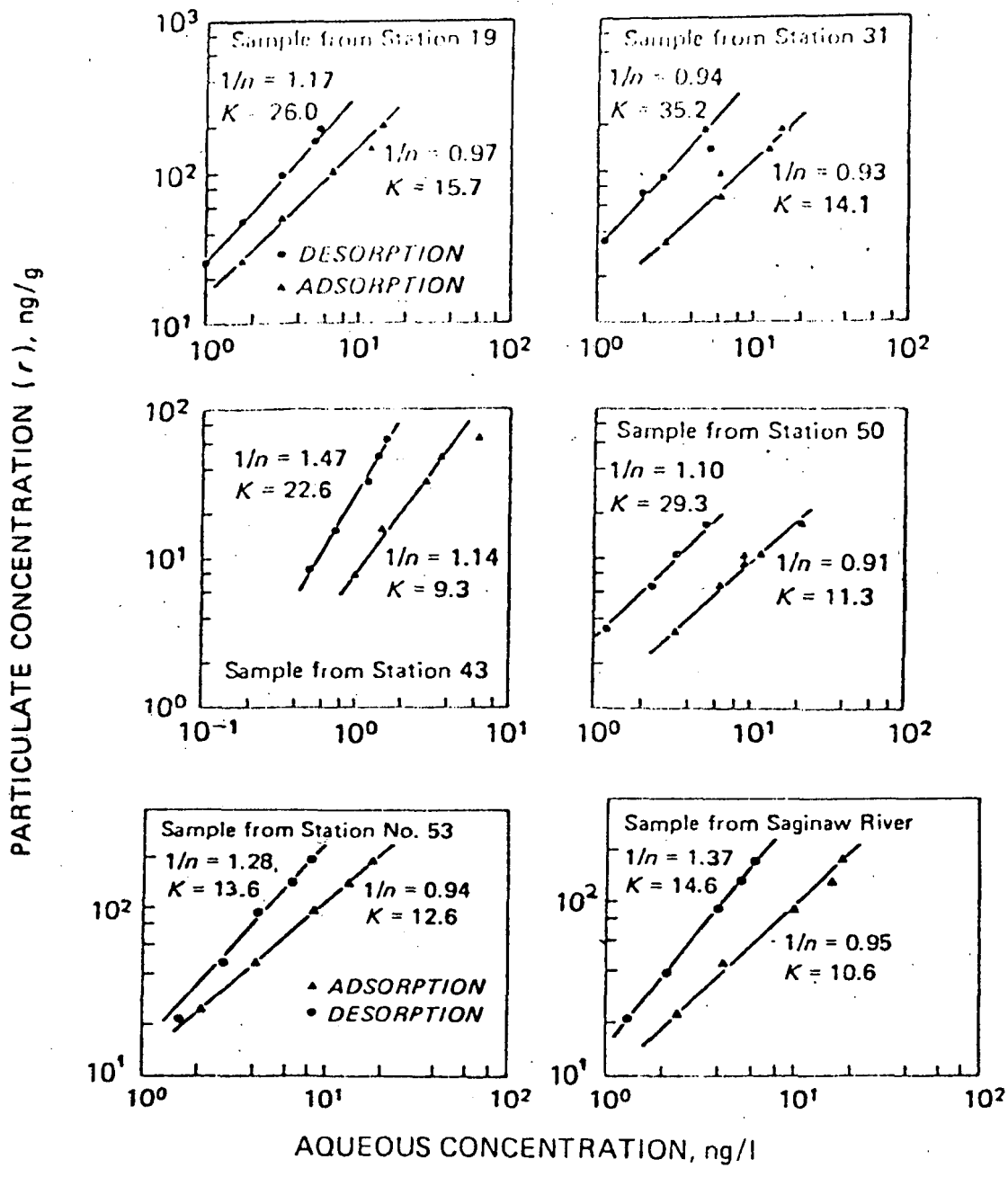



Fig. VI-2. HCB Adsorption and Desorption Isotherms for Saginaw Bay sediment samples m = 1100 mg/ℓ

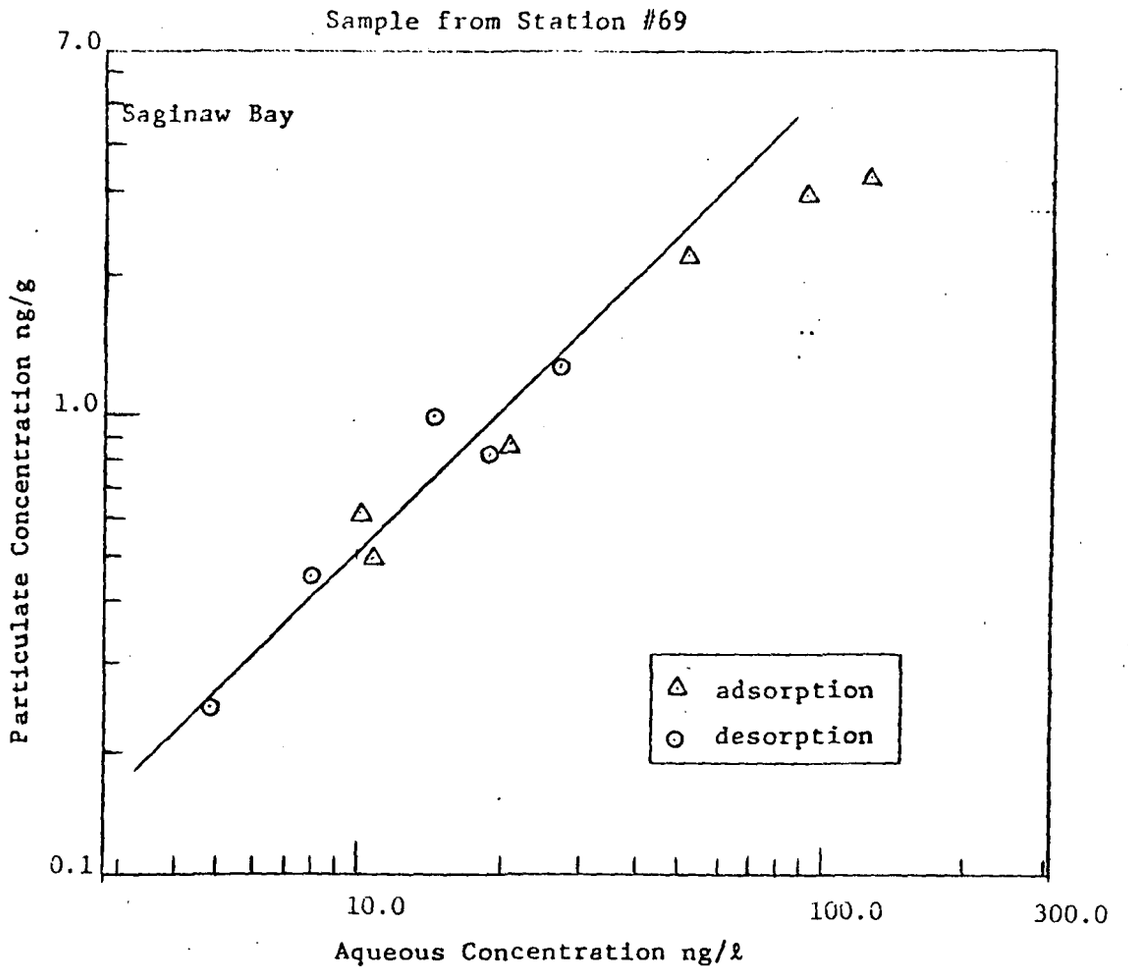



Fig. VI-3. HCB Adsorption and Desorption Isotherms for Station #69

cients, $\pi_d$, ranged from 7000 to 30,000 ℓ/kg. For all of the stations $\pi_a$ and K values were observed to be higher for desorption than for adsorption suggesting that the partitioning process was not completely reversible. Station #69 displayed dramatically reduced partitioning ($\pi_a$ = 36 ℓ/kg) for adsorption and almost reversible behavior, $\pi_d$ = 52 ℓ/kg (see fig. VI-3).

## C. Saginaw Bay Suspended Matter

Samples of suspended matter were collected at Station #31 during a vertical plankton tow (9/30/79). Samples were stored in bay water. A portion of the samples were allowed to settle for 3 days at which time settled and suspended fractions were separated. Subsequent adsorption experiments were conducted on 500 ppm solutions of both total suspended samples and on the fraction remaining in suspension after 3 days. The results of 3 hr adsorption and 2 hr desorption studies are indicated in Figure VI-4 and Table VI-6. Partition coefficient values for adsorption onto total samples were somewhat higher ($\pi_a$ = 6200 ℓ/kg) than values observed for the suspended supernatant ($\pi_a$ = 3400 ℓ/kg). The higher values observed for the mixed samples may reflect higher percentages of organic material. However, no chemical analyses were performed on the sediment material.

Partition coefficient values for the suspended sediment samples appear to be similar to, although somewhat less than, values for Saginaw Bay bottom sediments. In studies on Arochlors 1016 and 1242 Paris et al. (1978) reported partition coefficient values for freshwater pond seston ($\pi_a \sim 1000$ ℓ/kg) to be similar to values observed for bottom sediments but somewhat less than values for suspended bacteria ($\pi_a \sim 6000$ ℓ/kg). Conversely, Hiraizumi et al. (1979) has reported much higher partition coefficients for marine suspended solids compared to bottom sediments suggesting that the former possess higher specific surface areas.

## D. Results and Discussions: Partition Coefficients

The differences in values of $\pi$ for adsorption ($\pi_a \sim 12000$ ℓ/kg) and desorption ($\pi_d \sim 30000$ ℓ/kg) of Saginaw Bay suspended matter appear to indicate

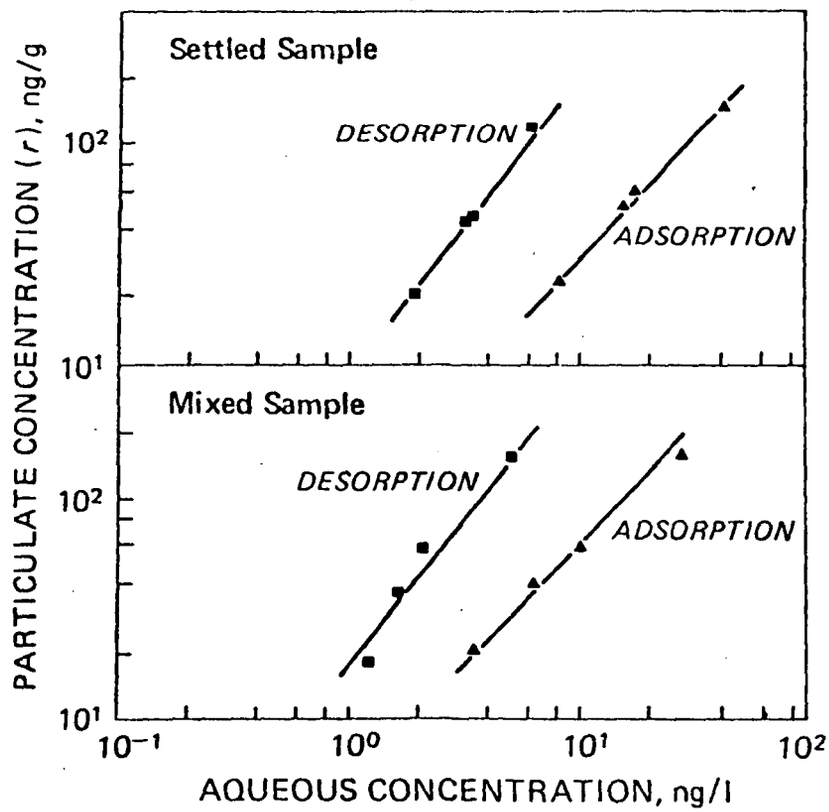



Fig. VI-4 HCB Adsorption and Desorption Isotherms for Station #31 on total and suspended solids samples.

TABLE VI-6. HCB Partitioning to Saginaw Bay Suspended Matter

Adsorption (2 Hr, $m_a$ = 500 mg/ℓ)

| Material | $c_i$ | $c_a$ | $r_a$ | $\pi_a$ |
|---|---|---|---|---|
| Settled | (ng/ℓ) | (ng/ℓ) | (ng/gm) | (ℓ/kg) |
| | 15.3 | 8.3 | 26. | 3100 |
| | 30.6 | 15.5 | 52 | 3500 |
| | 45.9 | 17.1 | 60 | 3400 |
| | 76.5 | 43.9 | 150 | 3400 |
| | | | Average $\pi_a$ | = 3350 ± 160 ℓ/kg |
| Mixed | 15.3 | 3.5 | 22 | 6400 |
| | 30.6 | 6.3 | 42 | 6700 |
| | 45.9 | 10.1 | 62 | 6100 |
| | 76.5 | 28.2 | 164 | 5800 |
| | | | Average $\pi_a$ | = 6230 ± 350 ℓ/kg |

Desorption (2 Hr, $m_d$ = 500 mg/ℓ)

| | | | | |
|---|---|---|---|---|
| Settled | | 1.9 | 20 | 11800 |
| | | 3.2 | 46 | 14400 |
| | | 3.4 | 46 | 15100 |
| | | 6.1 | 118 | 21300 |
| | | | Average $\pi_a$ | = 14400 ± 3660 ℓ/kg |
| Mixed | | 1.4 | 18 | 13100 |
| | | 1.6 | 37 | 23000 |
| | | 2.2 | 60 | 27000 |
| | | 4.9 | 155 | 32000 |
| | | | Average $\pi_a$ | = 23700 ± 8030 ℓ/kg |

that the adsorption process is not readily reversible. Similar results were also obtained for other Saginaw Bay sediments (Table VI-5). Adsorption partition coefficients ($\pi_a \sim$ 9000-14000 ℓ/kg) appeared to be consistently lower than those observed for desorption ($\pi_d \sim$ 20000-33000 ℓ/kg). By comparison, sand from which the fine fractions (< 75μ) had been removed by washing, displayed dramatically reduced HCB adsorption. Partitioning results for 20,000 mg/ℓ sand suspensions (Station #69) showed only small differences between adsorption and desorption isotherms ($\pi_a \sim$ 40 ℓ/kg, $\pi_d \sim$ 60 ℓ/kg) suggesting relatively reversible behavior.

The partition coefficients derived from the isotherm studies have been compared to values of $\pi_a$ calculated from measurements of PCB concentrations in aqueous and suspended sediment samples taken from Saginaw Bay (Richardson, personal cummunication). Mean values of $\pi_a$(ℓ/kg) computed from field data for suspended solids > 0.7μ vary from 13,000-36,000 ℓ/kg closely resembling the range of HCB $\pi_d$ values (Table VI-7). Although possibly fortuitous, this correlation does suggest that Great Lakes PCB concentrations are in fact controlled by sediment-water interactions as has been proposed for estuarine environments (Pavlov and Dexter, 1979). In addition, these results also tend to support the hypothesis that natural water PCB concentrations may be predominantly comprised of the more highly chlorinated PCB compounds.

## E. Effect of Particle Size and Organic Content

In natural waters, such as Saginaw Bay, the physical and chemical variables characterizing the system may undergo significant changes with time. Effective application of laboratory partitioning data to such regimes requires a determination of those factors capable of controlling or altering the magnitude of the partitioning process. The difference in partitioning observed between the sand (Station #69) and the finer sediment fractions suggest that the magnitude of adsorption and possibly the extent of reversibility may be related to the physical and chemical properties of the sediments. Both organic matter (Chiou et al., 1977; Karickhoff et al., 1979) and surface area (Hiraizumi, 1979) have been suggested as controlling the magnitude of partitioning to sediments.

TABLE VI-7. Representative PCB Concentrations For Saginaw Bay Suspended Solids*

| Study Segment** | Suspended Solids (> 0.7μ) mg/ℓ | Dissolved PCB Conc. ng/ℓ | Particulate PCB Conc. ng/g | Partition Coefficient (ℓ/g) |
|---|---|---|---|---|
| | Volume Weighted Averages for Arochlor 1254 | | | |
| 1 | 17.7 | 16.2 | 384 | 23.7 |
| 2 | 12.6 | 13.5 | 482 | 35.7 |
| 3 | 15.5 | 18.0 | 286 | 15.9 |
| 4 | 4.2 | 25.8 | 320 | 25.8 |
| 5 | 13.1 | 41.9 | 548 | 13.1 |

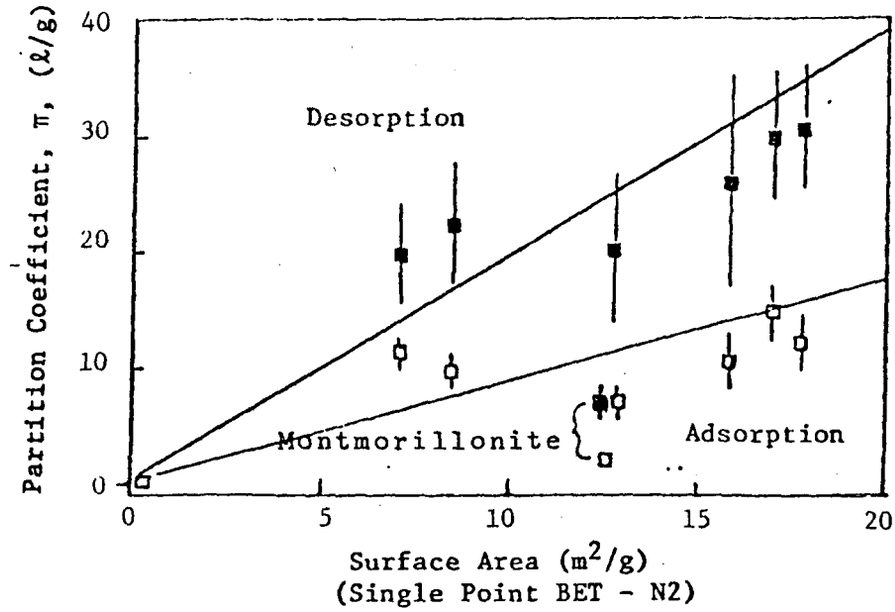
* Data furnished by EPA Large Lakes Research Station, Grosse Ile, Michigan

** Data for each study segment represents mean values for results from 12 cruises

In the present study both effects were investigated for adsorption and desorption partition coefficients. Figure VI-5a presents the relationship between partition coefficients and specific surface area. Although the Saginaw Bay sediments exhibit a reasonable relationship, the montmorillonite results are not in conformity with the trend. Figure VI-5b presents the relationship between partition coefficients and percent volatile solids. Again a trend is evident, however, montmorillonite and the sandy Station #69 sediment are not both in conformity. Although both these samples are low in percent volatile solids montmorillonite has a significantly higher surface area.

In an effort to further clarify the role of the sediment organic matter, samples of Saginaw Bay sediment (#50) were stripped of their organic coatings. In these experiments organic matter was removed by either chemical oxidation ($H_2O_2$) or dry ashing. Partition coefficient values for the remaining inorganic fractions were found to be markedly reduced by both processes ($\pi_a(H_2O_2) \approx 5000$ ℓ/kg, $\pi_a$(ashing) $\sim$ 600 ℓ/kg). These results suggest that loss of the sediment organic fraction reduced HCB partitioning to Saginaw Bay sediments. Results from this type of experiment must, however, be interpreted with caution since the extraction process may significantly alter the chemical characteristics of the inorganic sediment fraction. This suggests that both independent variables (organic matter and surface area) are important and the proper method of analysis is a regression that includes both of these effects.

The results of a multiple linear regression are shown in Figure VI-6 and Table VI-8. The estimated partition coefficients are calculated using the listed equations. The fit is quite good for both equations, as indicated by the magnitude of the variance removed ($R^2$). The small - and for practical purposes negligible - constant terms in the regression correctly reflect the fact that partitioning is small for both small percent volatile solids and specific surface area. Strictly speaking the constant coefficients should be exactly zero. The inset in Figure VI-6 illustrates the cross correlation between surface area and percent volatile solids for the sediments considered. The presence of montmorillonite and the sandy Station #69 sediment prevents a strong cross correlation which would weaken the ability of the analysis to discriminate between these two effects.



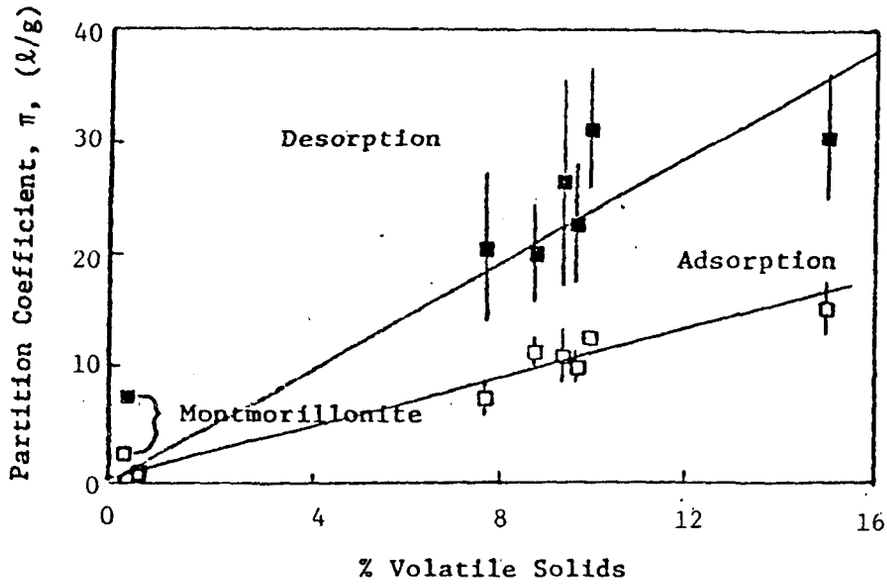




Fig. VI-5. Adsorption and Desorption Partition Coefficients versus Specific Surface area and % Volatile Solids

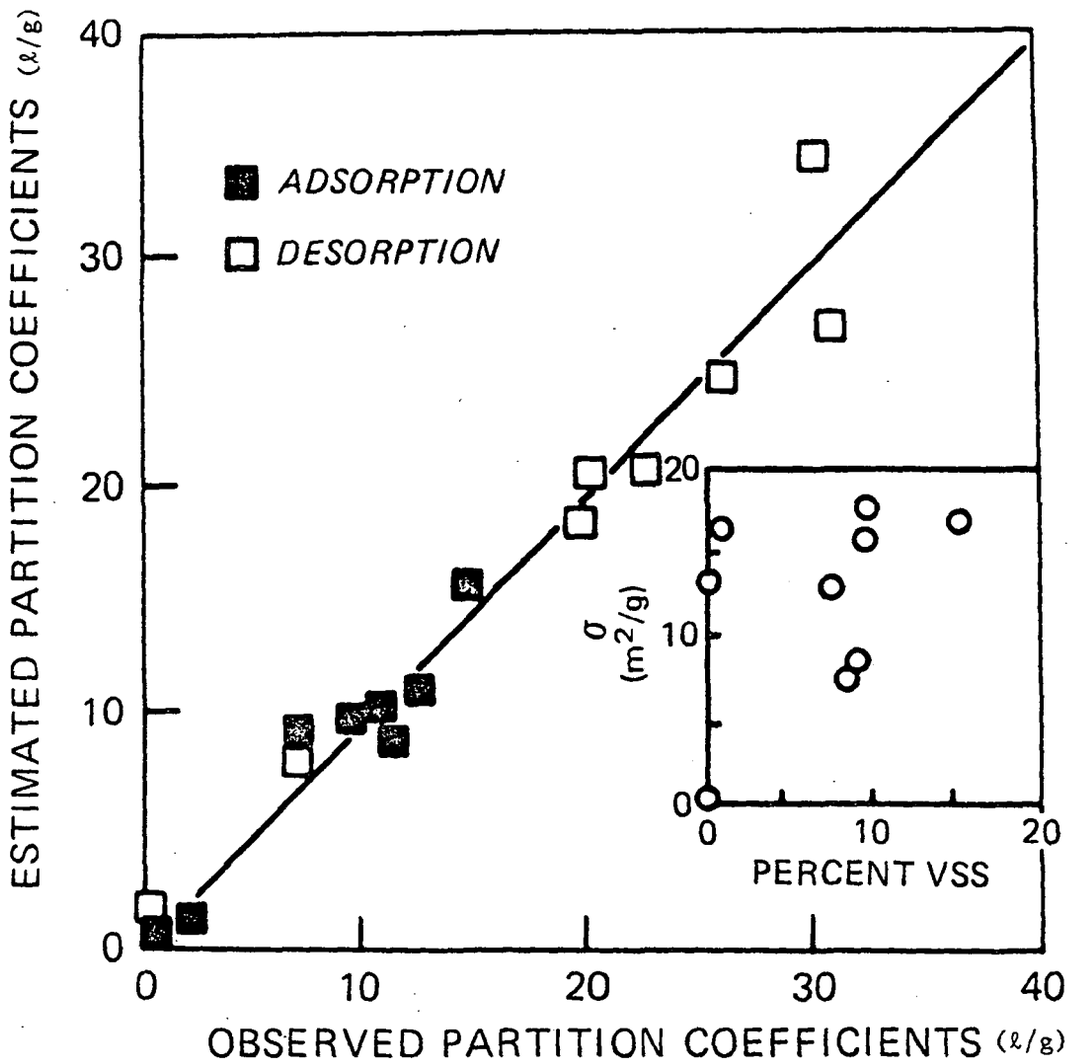



Fig. VI-6. Comparison of Estimated Partition Coefficient using Regression Equation to Observed Values.

TABLE VI-8. Multiple Linear Regression Results

| | Partition Coefficient | |
|---|---|---|
| | Adsorption[1] | Desorption[2] |
| Constant ($\ell/g$) | 0.46 | 0.516 |
| Surface Area Coefficient ($(\ell/g)/(m^2/g)$) | 0.103(0.11)* | 0.652(0.277)* |
| % Volatile Solids ($(\ell/g)/(\%)$) | 0.903(0.13)* | 1.537(0.268)* |
| Multiple Regression $R^2$ | 0.945 | 0.949 |

(1) $\pi_a = 0.46 + 0.103\ \sigma + 0.903\ (\%\ VSS)$

(2) $\pi_d = 0.516 + 0.652\ \sigma + 1.537\ (\%\ VSS)$

* Standard Error of the Coefficient

It does not appear that the observed non-singular HCB isotherms can be readily related to bonding with the organic fraction of the sediments. As shown in Table VI-8, the regression coefficients for both the specific surface area and percent volatile solids increase when desorption is considered relative to adsorption. Further HCB isotherms for montmorillonite and kaolinite clay samples also displayed nonsingular behavior as shown subsequently in Part B of this report. For 1100mg/ℓ clay suspensions, HCB adsorption onto montmorillonite ($\pi_a \approx 2100$ ℓ/kg) was found to be substantially greater than that observed for kaolinite ($\pi_a \approx 1060$ ℓ/kg). Desorption values for both montmorillonite ($\pi_d = 9700$ ℓ/kg) and kaolinite ($\pi_d \sim 3300$ ℓ/kg) were significantly larger than the respective adsorption values. The differences in HCB partitioning between the two clays probably reflects the fact that montmorillonite possesses a substantially greater surface area than does kaolinite.

These results indicate that both organic content and surface area are important determinants of the extent of HCB adsorption. The regression equations can be used to predict the partition coefficient for adsorption and desorption. However it should be pointed out that these partition coefficients apply only to sediment concentration of m = 1100 mg/ℓ. As shown in the next section, the sediment concentration itself exerts a strong influence on the measured adsorption partition coefficient.

## SECTION VII

## SEDIMENT CONCENTRATION EFFECTS

### A. Introduction

The application of the results of laboratory trace organic partitioning studies to natural waters often involves extrapolating experimental data to systems possessing markedly different physical and chemical characteristics. This problem is well recognized with respect to the potential effects on partitioning of variations in the chemical composition of natural waters. Less consideration, however, has been devoted to the possible influence of the large variations in sediment concentrations which can occur in natural systems. Sediment concentrations typically occurring in lake surface waters may differ by many orders of magnitude over those found in bottom sediments or in adjacent drainage basin soils. Suspended solids concentrations in the Saginaw Bay water column typically range from 10 - 500 mg/ℓ (Smith, et. al. 1977). Bottom waters may reach 1000 mg/ℓ while underlying sediments may approach 500,000 mg/ℓ. During sediment erosion within the drainage basin, PCB compounds may be subjected to this entire range of solid phase concentrations.

In the development of models for the fate of chemicals in the environment the experimental results of partitioning studies conducted at one suspended solids level may be extrapolated to systems of very different sediment concentrations. Such extrapolations may be inappropriate if partition coefficient values are affected by sediment concentration variations. Any systematic variations in the HCB partitioning with sediment concentration could have a significant impact on the overall cycling of PCB in the Saginaw Bay water column and the underlying sediments.

An attempt was made to evaluate the possible influence of sediment concentration on HCB partitioning. While there have been a number of studies on PCB binding to soils and sediments (Haque and Schmedding, 1976; Dexter, 1976; Steen et al. 1978; Hiraizumi et al. 1979; Lee et al., 1979; Farquhar et al., 1979) there appears to be relatively little available information on the possible influence of sediment concentration. As previously indicated such information is of potential importance in attempting to accurately predict the chemical cycling of organics compounds such as PCB's.

A review of the literature on organic adsorption to soils and sediments reveals no consistent trend in the reported magnitude of the influence of sediment concentration changes on partitioning. Studies on DDT, heptachlor and dieldrin adsorption to natural clays (Huang and Liao, 1970) suggested that partitioning of these compounds may vary as a function of sediment concentration. Similar effects have been observed in investigations on the adsorption of lindane to lake sediments (Lotse et al., 1968) and kepone to estuarine sediments (Connolly, 1980). Conversely, Karickhoff (1979) did not find evidence that sediment concentration changes significantly affected pyrene and methoxychlor partitioning. Observations of the possible influence of sediment concentration on partitioning do not appear to be limited to organics and have also been reported for trace metals and radionuclides (see the review by O'Connor and Connolly, 1980, and the references contained therein). Figure VII-1 from their report illustrates the effect. It is the purpose of this section to report the results of studies conducted to determine the extent of the effects of sediment concentration variations on HCB partitioning.

B. Isotherms

In initial experiments designed to characterize HCB partitioning, isotherms were constructed for a series of differing sediment concentrations. These studies were conducted on both Saginaw Bay sediment and montmorillonite clay samples. As indicated by figure VII-2, adsorption isotherms constructed at m = 1100, 220 and 55 mg/ℓ concentrations of Saginaw Bay #50 sediment suggest that HCB adsorption increases with decreasing sediment concentration. Partition coefficient values, in order of decreasing sediment concentration, were $\pi_a$ = 9900, 12,300 and 17,100 ℓ/kg respectively. The data suggest that all of the isotherms are essentially linear over aqueous HCB concentration ranges investigated.

The results of similar isotherm studies conducted on montmorillonite clay are depicted in figure VII-3. Again it can be seen that decreasing sediment concentrations resulted in increased HCB partitioning to the solid phase. For m = 1000, 200 and 50 mg/ℓ sediment concentrations, partition coefficient values were found to be $\pi_a$ = 2900, 6690, and 10,600 ℓ/kg, respectively. The isotherms

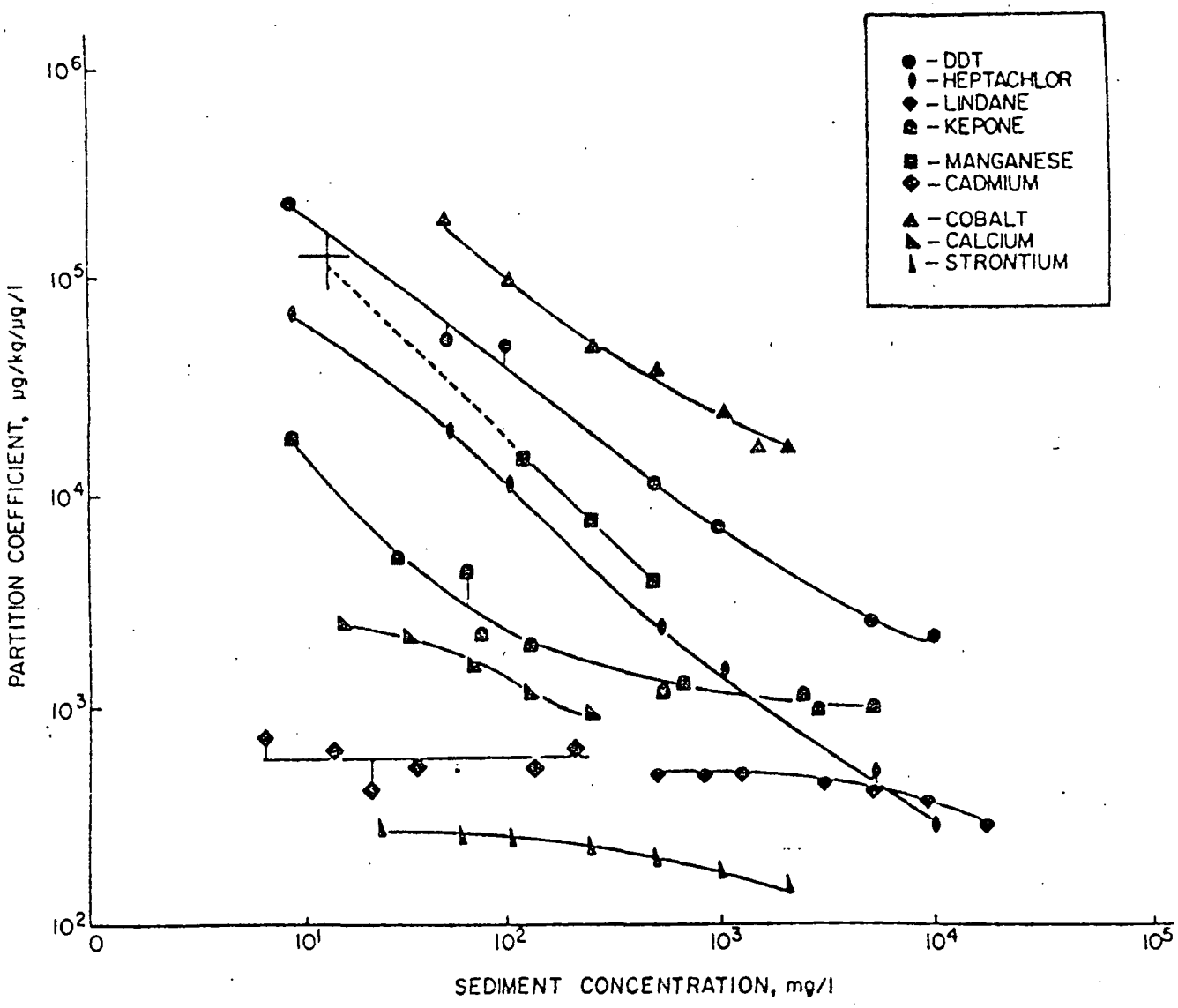



Fig. VII-1. Adsorption Partition Coefficient vs. Adsorbent Concentration (O'Connor & Connolly, 1980)

Effect of Adsorbent Concentration - Saginaw Bay

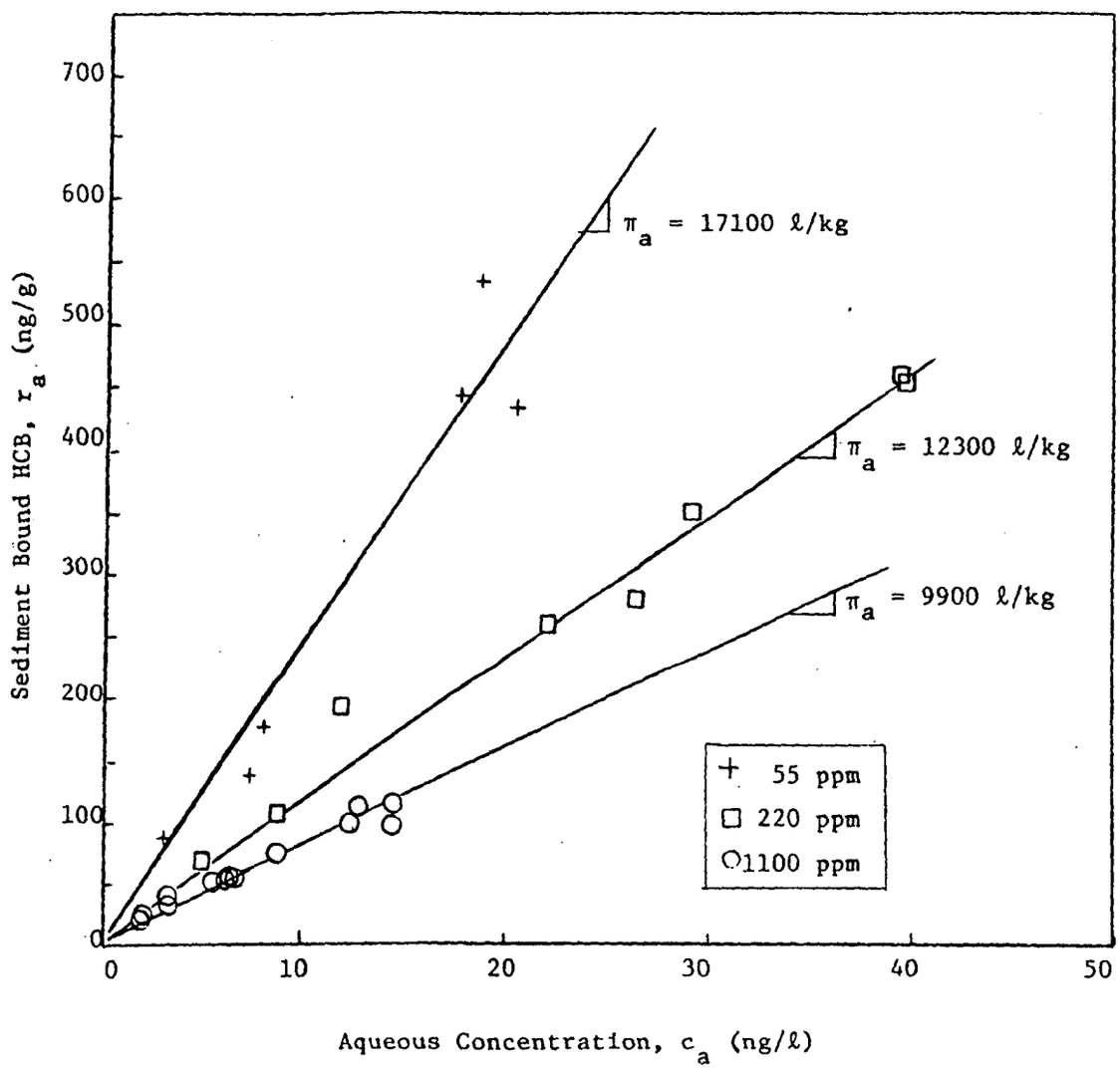



Fig. VII-2. Adsorption Isotherms for m = 55, 220, and 1100 mg/ℓ
Saginaw Bay #50

appear to be essentially linear, although the m = 50 mg/ℓ data does display some scatter. A comparison of these data suggests that montmorillonite displays a more marked variation in HCB partitioning with sediment concentration than does the Saginaw Bay sediment.

There exist a variety of factors which could conceivably be responsible for the apparent affect of sediment concentration on partitioning. Among those of possible importance are isotherm linearity, reaction kinetics, solution composition, and the uniformity of solid phase binding site energies. Investigations were conducted to ascertain the influence of each of these processes on the relationship between sediment concentration and partitioning.

Non-linear adsorption isotherms represent one possible explanation for the apparent sediment concentration effect. However, the available experimental evidence does not appear to support this hypothesis. As already indicated, the isotherms for both the Saginaw Bay sediment and montmorillonite displayed a linear character over the entire aqueous HCB concentration range investigated. In addition, the adsorption isotherms constructed for 1100 mg/ℓ suspensions from a variety of different Saginaw Bay sediment samples (Section VI) also demonstrated a linear relationship between $r_a$ and $c_a$ over a range of 1 ng/ℓ - 100 ng/ℓ in aqueous HCB concentration. Similarly other studies (Lee et al., 1979; Wildish et al., 1980) on PCB adsorption to a variety of sediments over a wide range of aqueous PCB concentrations suggest linear isotherm behavior.

It is possible that the observed effects may be the result of variations in solution chemical composition. Changes in suspended solids concentrations may influence factors such as solution pH and ionic strength. However, as shown in Section IV ionic strength effects are small and pH has an effect only in the range, pH = 5 to 7.

In order to completely eliminate the effect of pH variations, isotherms where constructed using a 2mM $NaHCO_3$ aqueous phase for montmorillonite concentrations of m = 55 and 1100 ppm. The large difference in partition coefficient, as seen in fig. VII-4, cannot be attributed to pH variations since it remained relatively constant (pH = 8.0 - 8.4) and above the inflection point found for montmorillonite (fig. V-2).

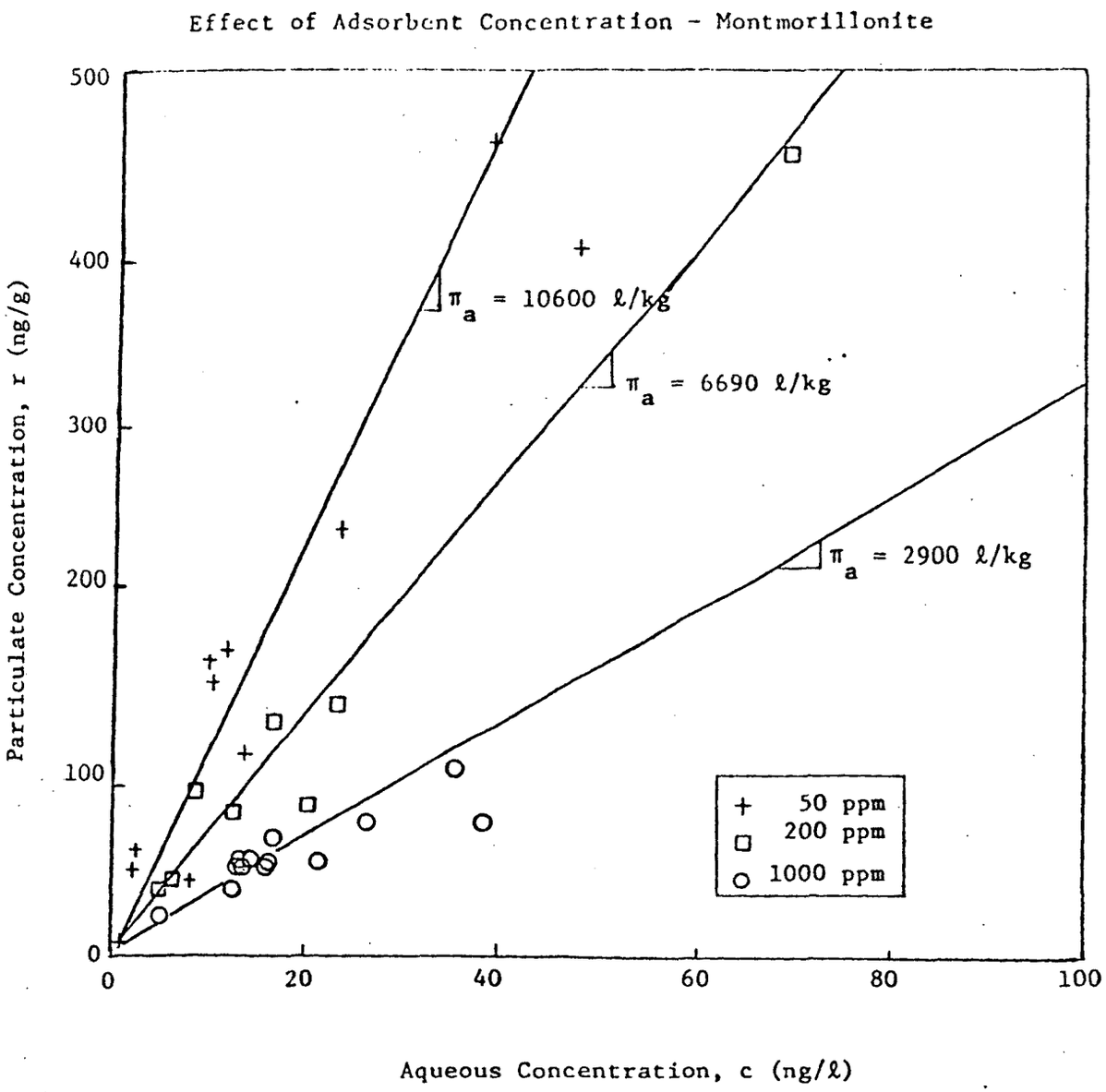



Fig. VII-3. Adsorption Isotherms for m = 50, 200, 1000 mg/ℓ Montmorillonite

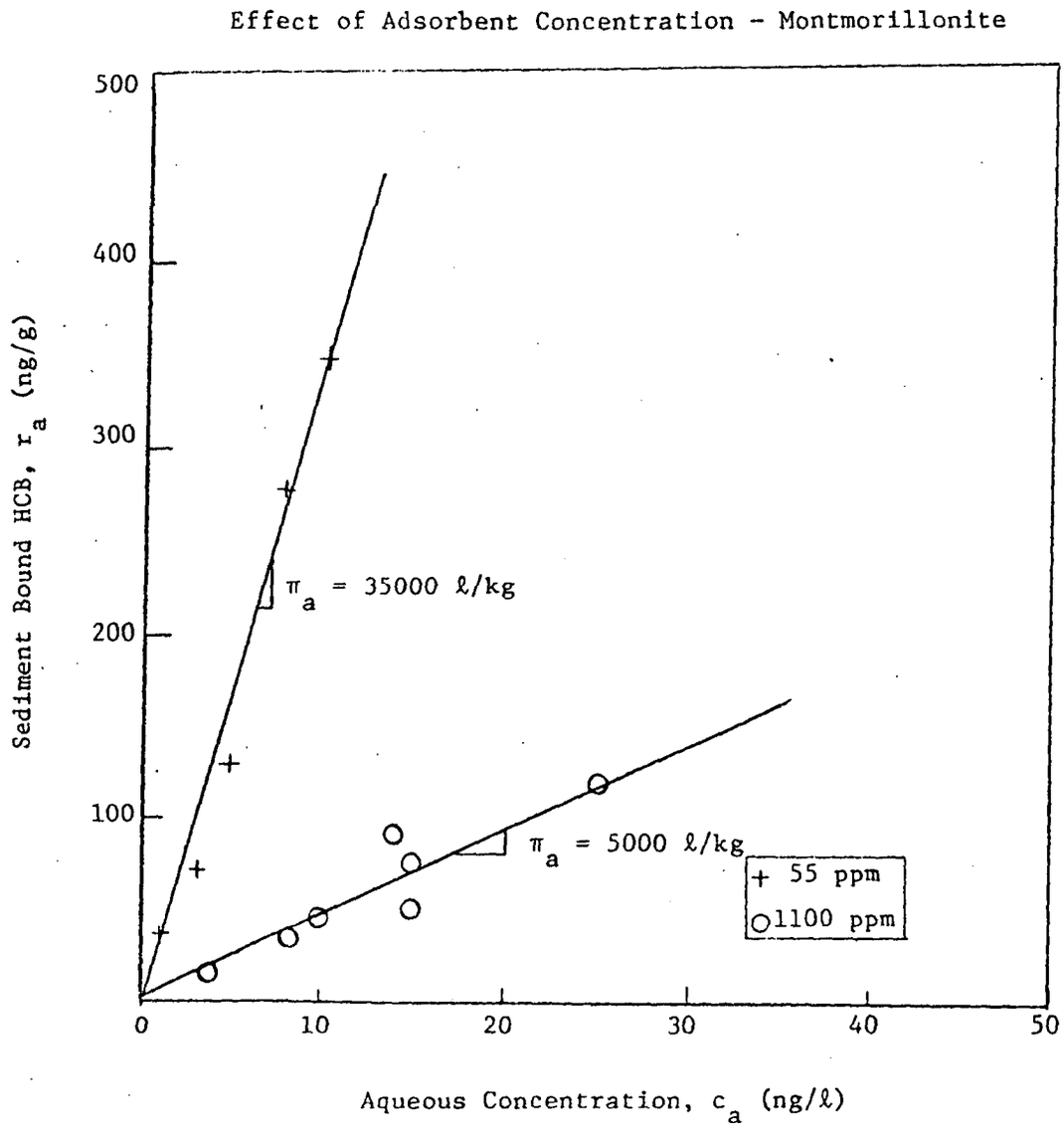



Fig. VII-4. Adsorption Isotherms for m = 55 and 1100 mg/ℓ Montmorillonite
Aqueous phase = 2mM $NaHCO_3$

## C. Variation in Binding Energy of Adsorption Sites

One difficulty in evaluating sediment concentration behavior, results from the manner in which experimental sorption data are gathered. Studies are typically carried out, either by varying the aqueous organic chemical concentrations at constant sediment mass or by varying sediment mass at constant total initial chemical concentration. It is probable that organic molecules are capable of adsorbing onto solid phase sites of varying energy. Under these conditions, variations in adsorption may simply reflect changes in the type of solid phase sites occupied by the organic molecules rather than effects due solely to the sediment concentration. It has been proposed by a number of workers (see review by Hamaker and Thompson (1972) and the references contained therein) that sediment surfaces may present a variety of adsorption sites of differing binding energies to dissolved organic molecules. Previous experimentation suggests that HCB moleclues may also demontrate similar behavior. The nature and fraction of such solid phase binding sites occupied by a dissolved organic molecule such as HCB may depend on the compounds' equilibrium aqueous concentration ($c_a$). However, at a constant initial aqueous concentration ($c_i$), $c_a$ may vary with sediment concentration, as binding sites of differing energy are occupied. Hence, the apparent sediment concentration effect observed for HCB could result from variations in binding site occupation.

A series of studies were conducted in an effort to evaluate this possibility. In these experiments sediment concentrations were varied while maintaining approximately constant equilibrium aqueous HCB concentrations, $c_a$. Under these conditions all HCB adsorption should have been to surface sites of equivalent energy. The results of experiments conducted on the Saginaw Bay sediment are presented in figure VII-5. Under approximately constant equilibrium HCB aqueous concentrations, ($c_a \sim$ constant) values of $r_a$ for adsorbed HCB decreased by approximately a factor of four as sediment concentrations were increased from 10 - 1000 mg/ℓ. The resulting variation in partition coefficient is also shown.

In contrast to the Saginaw Bay data, the results of similar experiments utilizing montmorillonite (figure VII-6) indicated more marked changes in r as sediment concentrations were varied. In adsorption studies conducted

Effect of Adsorbent Concentration on Adsorption -
Saginaw Bay #50, Distilled Water

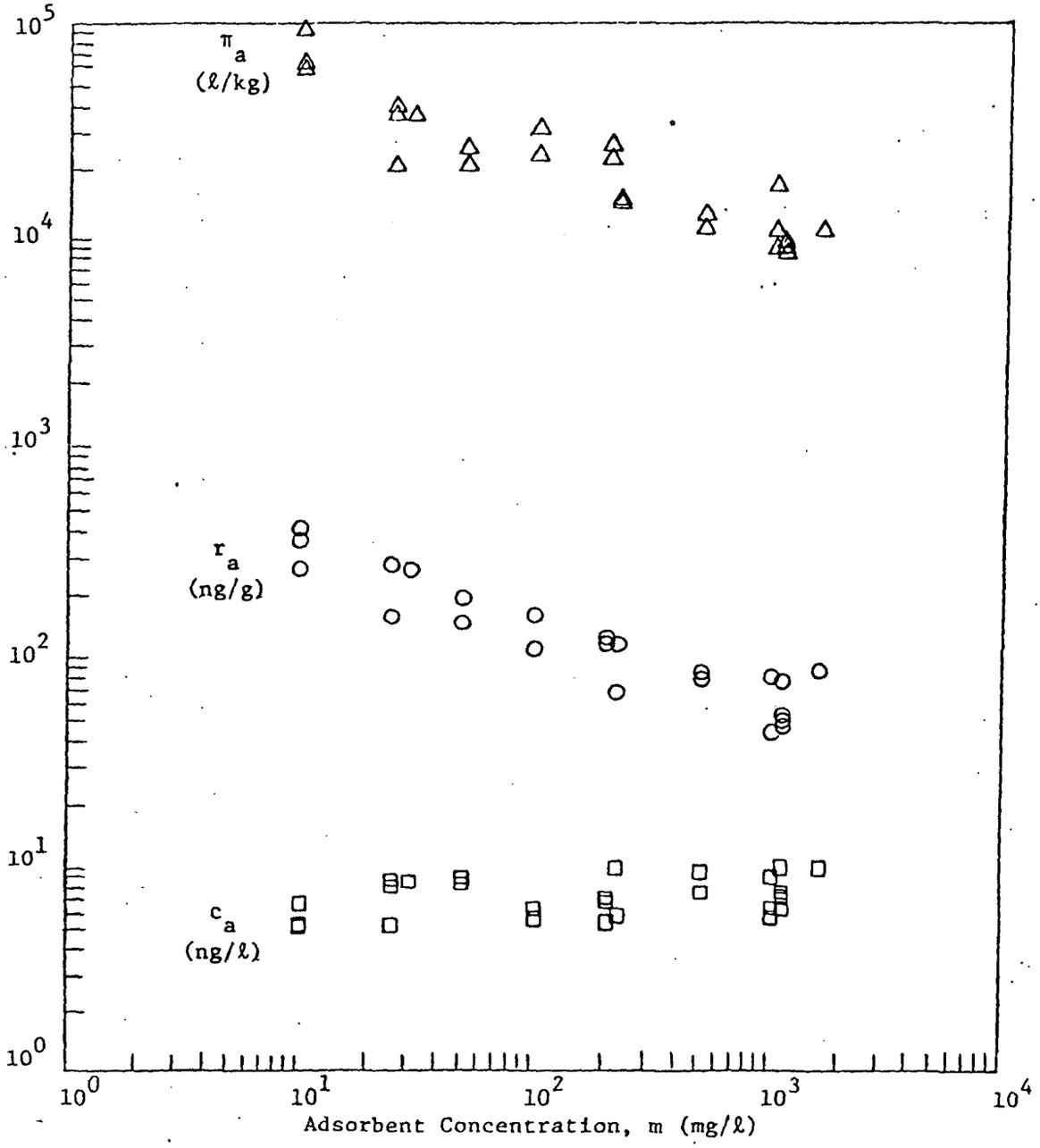



Fig. VII-5. Variation in Adsorption partition coefficient, $\pi_a$, and Sediment Bound HCB, $r_a$, versus adsorbent concentration, m, at constant equilibrium aqueous concentration, $c_a$.

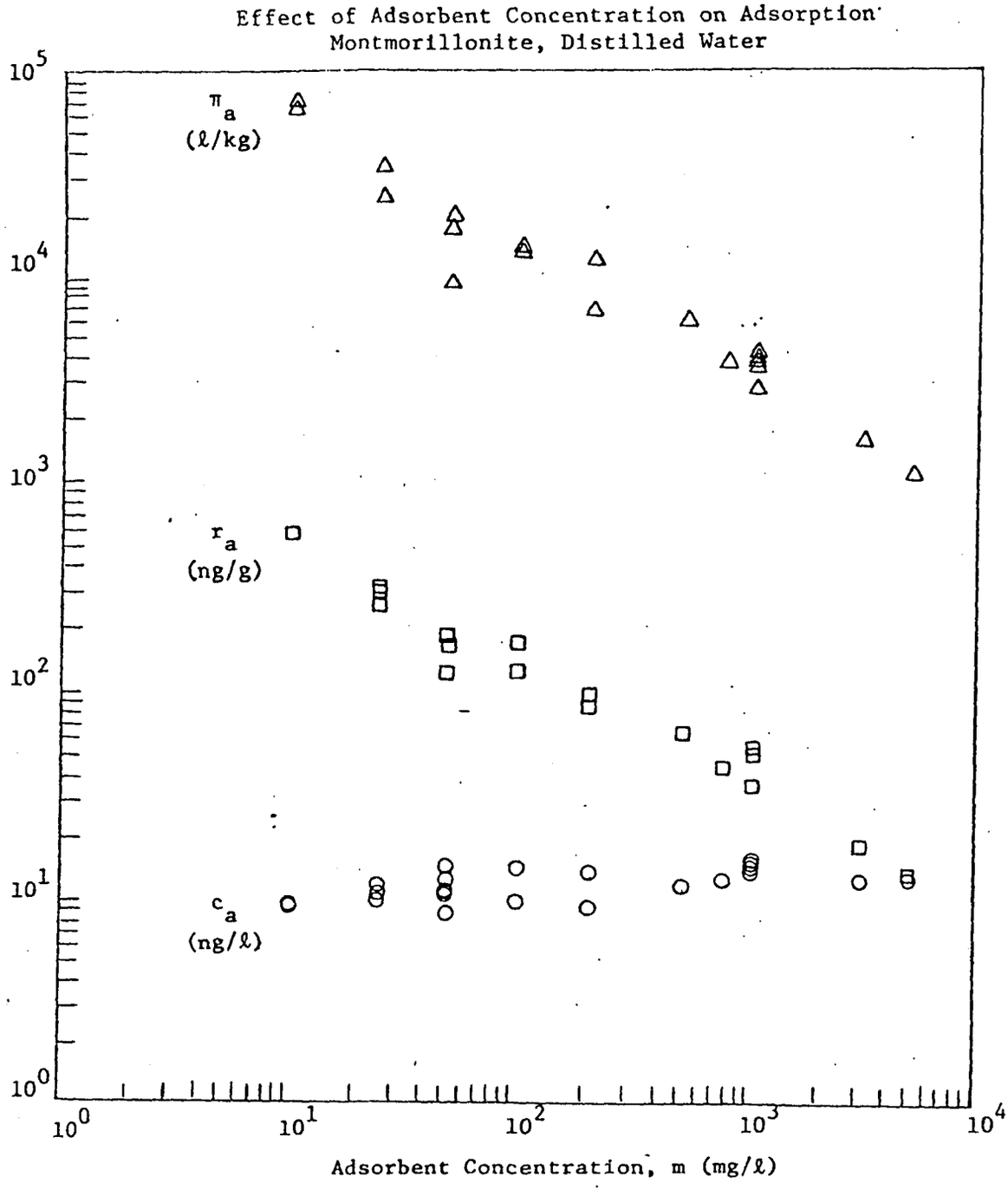



Fig. VII-6. Variation in Adsorption partition coefficient, $\pi_a$, and Sediment Bound HCB, $r_a$, versus adsorbent concentration, m, at constant equilibrium aqueous concentration, $c_a$.

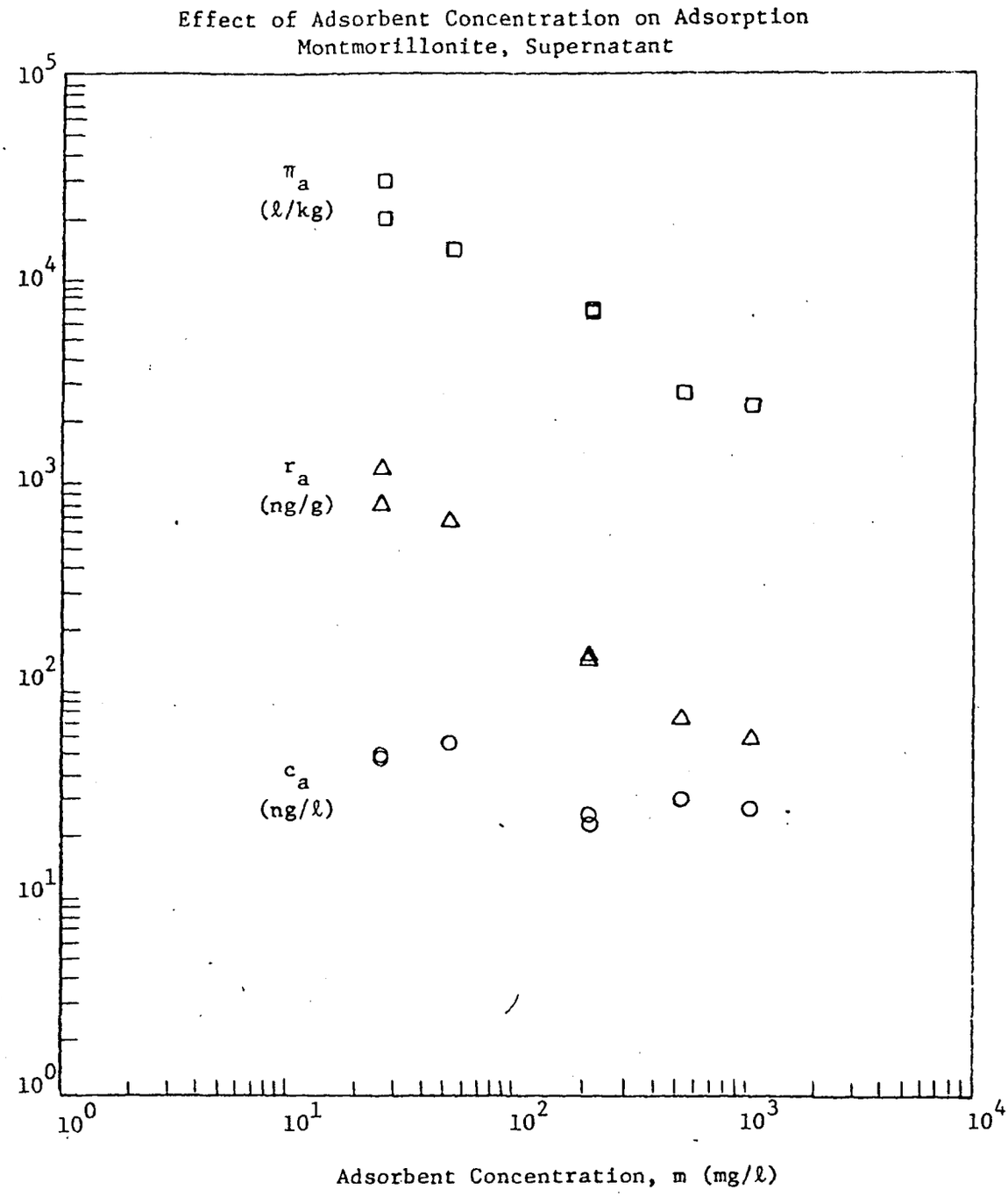



Fig. VII-7. Variation in Adsorption partition coefficient, $\pi_a$, and Sediment Bound HCB, $r_a$ versus adsorbent concentration, m, at constant equilibrium aqueous concentration, $c_a$.

while maintaining essentially constant equilibrium aqueous HCB levels ($c_a \sim$ constant), $r_a$ decreased from ∿500 ng/g at a 10 mg/ℓ montmorillonite concentration to ∿14 ng/g at 5000 mg/ℓ. These data indicate that a two order of magnitude increase in sediment concentration resulted in over an order of magnitude decrease in the partition coefficient as shown.

In a related experiment designed to minimize the potential effects of solution composition on partitioning, the supernatant solution resulting from the centrifugation of a 1000 mg/ℓ montmorillonite suspension was used in place of distilled water. Use of this solution should have minimized solution composition changes as well as any solid surface area alterations resulting from clay solubilization at low sediment concentrations. This supernatant stabilized suspension pH levels within a relatively narrow range (pH = 6.7±0.3). However, as indicated in figure VII-7, the use of this supernatant did not appear to significantly reduce the magnitude of the effect of sediment concentration on partitioning. Adsorption results indicated an order of magnitude decrease in $\pi_a$ over a 10 - 1000 mg/ℓ sediment concentration range. A similar experiment using potassium phosphate buffer ($2 \cdot 10^{-4}$ M, pH = 7.25) gave similar results as shown in fig. VII-8.

In order to consider the possible effects of kinetic factors on adsorption, an evaluation was made of the influence of equilibration time on the relationship between sediment concentration and partitioning. If sediment concentrations affected the rate of adsorption, then increasing the equilibration time to longer time periods should have resulted in significant increases in HCB adsorption. Preliminary kinetic experiments indicated possible small increases in HCB adsorption during time increases of up to 24 hours and no significant changes for longer time periods (Section IV). However, as indicated in figure VII-9, increasing the equilibration time to 24 hours appeared to have little effect on the variation in $\pi_a$ with sediment concentration. For montmorillonite concentrations ranging from 20 mg/ℓ to 1000 mg/ℓ values of $\pi_a$ decreased from ∿30,000 ℓ/kg to <2000 ℓ/kg. The magnitude and direction of this change was quite similar to that observed for a 3 hour equilibration period as shown. While these results do not entirely rule out kinetic effects, it does not appear that such factors are responsible for the observed sediment concentration behavior.

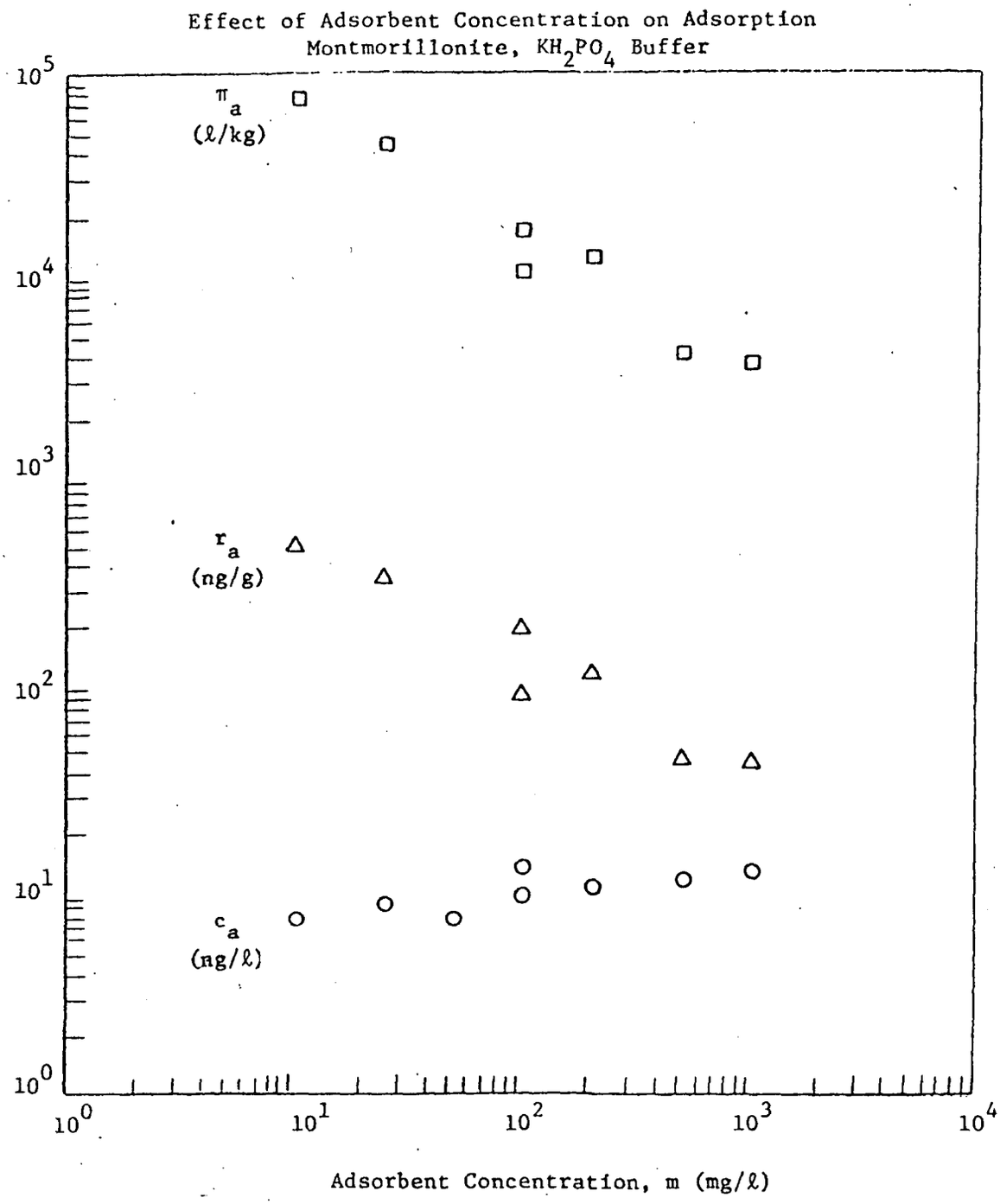



Fig. VII-8. Variation in Adsorption partition coefficient, $\pi_a$, and Sediment Bound HCB, $r_a$ versus adsorbent concentration, m, at constant equilibrium aqueous concentration, $c_a$.

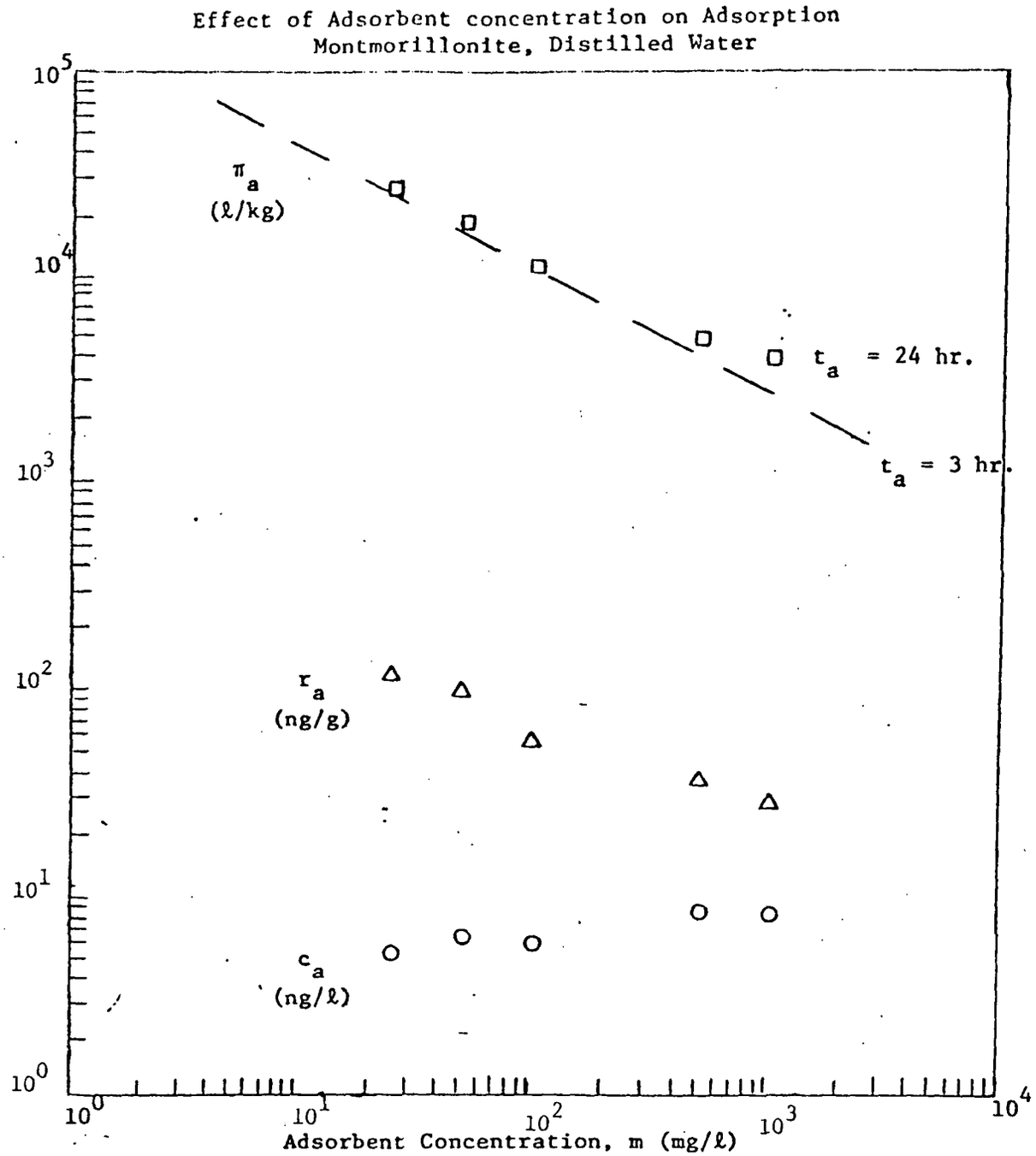



Fig. VII-9. Variation in Adsorption partition coefficient $\pi_a$, and sediment bound HCB, $r_a$, versus adsorbent concentration, m, at constant equilibrium aqueous concentration, $c_a$. Effect of increased adsorption time, $t_a$ = 24 hr. versus $t_a$ = 3 hr. (dashed line from fig. VII-6).

The preceding experimental results appear to suggest that the effect of sediment concentration on HCB is not readily explained by kinetic factors, solution ionic strength or variations in the binding sites utilized during adsorption. While it appears that solution composition changes can affect partioning, the evidence does not seem to indicate that those changes which were investigated (pH, ionic strength, etc.) can account for the magnitude of the observed sediment concentration effect.

It has been suggested (O'Connor and Connolly, 1980) that an empirical relationship exists between partition coefficient and sediment concentration of the form.

$$\pi_a = am^b \qquad \text{(VII-1)}$$

Figure VII-10 presents the HCB data analyzed in this way. Table VII-1 gives the regression coefficients and their standard errors. The exponent for Saginaw Bay sediment is $\sim$ - 0.36 to -0.40 whereas montmorillonite has an exponent of -0.52 to -0.67 indicating the stronger sediment mass dependency. The partition coefficients at m = 1 mg/ℓ. ($\pi_a$ = a) range from a = 90 - 100 ℓ/g for Saginaw Bay and 110-290 ℓ/g for montmorillonite. Thus at low concentrations of sediment, the extrapolated partition coefficients are quite large. It is interesting to note that the available data consistently indicates that the sediment concentration effect is larger for montmorillonite than for the Saginaw Bay sediment. The results also indicate that at the higher sediment concentrations ($\geq$ 1000 ppm) the lake sediment was significantly more effective in adsorbing HCB than montmorillonite.

## D. Discussion

A variety of studies (including Haque and Schmedding, 1976; Steen et al., 1978; Karickhoff et al., 1979) have suggested that the magnitude of the partitioning of organic molecules to natural sediments is related to the sediment organic content. In studies on PCB distributions in sediments (Hiraizumi, 1978) it has also been suggested that sediment surface areas may play a significant role in partitioning. The results of the experimental data and analysis presented in Section VI, on a series of Saginaw Bay sediments and montmorillonite clay, indicated that both factors were highly correlated with HCB partition coefficient values and appear to be important to the HCB adsorption process. This would imply that any variables which affect either of these

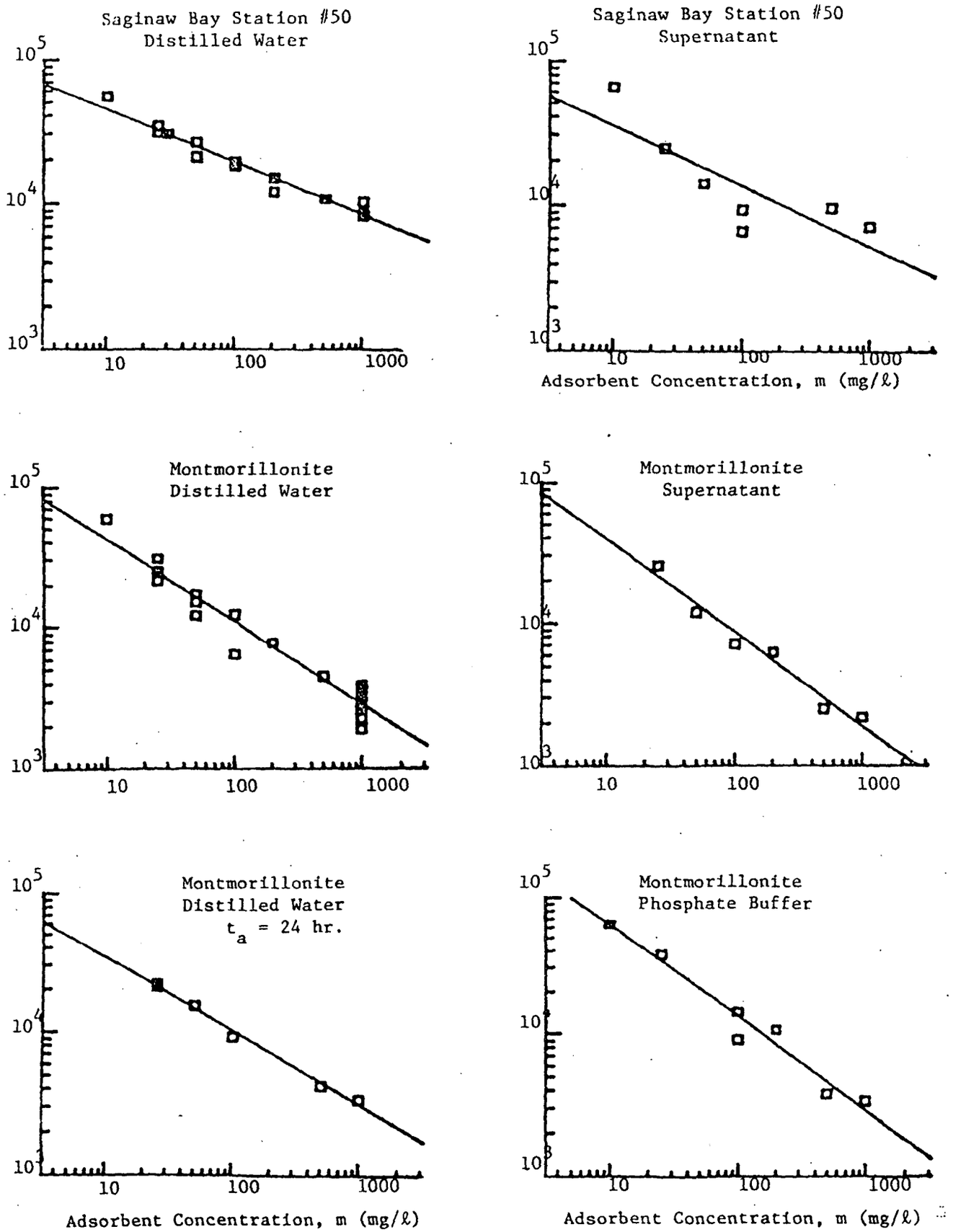



Fig. VII-10 Log-log analysis of $\pi_a$ versus m. Straight line slopes and intercepts are given in Table VII-1.

TABLE VII-1. Partitioning Coefficient - Adsorbent Mass Regression[§]

| Adsorbent | Aqueous Phase | Adsorption time (hr) | a $(\ell/g)(mg/\ell)^{-b}$ | b |
|---|---|---|---|---|
| Saginaw Bay #50 | Distilled Water | 2.0 | 101 (90.6, 113)* | -0.358 (-0.336, -0.381)* |
| " | Supernatant | 2.0 | 89.5 (48.6, 165) | -0.408 (-0.28, -0.536) |
| Montmorillonite | Distilled Water | 2.0 | 162 (136, 192) | -0.585 (-0.555, -0.615) |
| " | " | 24.0 | 113 (101, 126) | -0.518 (-0.494, -0.541) |
| " | Supernatant | 2.0 | 182 (131, 251) | -0.662 (-0.599, -0.784) |
| " | $2 \times 10^{-4}$ M $KH_2PO_4$ pH = 7.25 | 2.0 | 293 (217, 394) | -0.668 (-0.608, -0.728) |

§ Regression Equation $\pi_a = am^b$

* Mean ± Standard Error

factors might significantly affect partitioning.

The lack of organic matter in the montmorillonite clay suspensions would rule out changes in this fraction as the cause of the observed sediment mass-partition coefficient variations. It does, however, appear possible that unanticipated changes in surface area might occur within the sediment suspensions. Specifically, it is suggested that linear increases in sediment concentration (mass/unit volume) may not necessarily result in analogous linear increases in surface area. Conceivably, the area of a sediment surface available for adsorption could be influenced by interactions occurring between suspended sediment particles. For instance, electrostatic interactions arising from surface sites of differing charge might result in a certain amount of interparticle association. Interactions of this nature could result in a reduction in the number of solid phase binding sites accessible for adsorption of a molecule such as HCB. In the case of montmorillonite suspensions, interparticle associations have, in fact, been reported (Laffer et al., 1969; Schweitzer and Jennings, 1971; Gilbert and Laudelout, 1971).

Controversy appears to exist over the precise geometrical arrangement of such associations with a variety of structures having been proposed. Nor does detailed information appear to be available on the influence of sediment concentration or chemical composition on such interactions. Ascribing the HCB partitioning results of the present study to such interactions requires that increasing montmorillonite and, to less an extent, Saginaw Bay sediment concentrations result in a decrease in the number of available binding sites on a per unit mass basis. The relationship between HCB partitioning and solid phase surface area would, however, depend upon the location of principal binding sites. If HCB molecules preferable bond at clay particle edges then available clay edge surface area and not total surface area would be of importance to partitioning.

Under this interpretation, at high sediment concentrations (> 1000 mg/ℓ) the Saginaw Bay sediment is a much more effective HCB adsorber probably as a result of the dominance of interactions involving the sediment organic phase. However, as sediment concentrations are decreased, $\pi_a$ increases more rapidly for montmorillonite than for the Saginaw Bay sediment. This increase is presumably due to a significant increase in the total or edge surface area to mass

ratio for the clay. The Saginaw Bay sediment would not be expected to possess the same surface charge characteristics as montmorillonite and hence particle interactions are unlikely to be of the same magnitude. A more detailed analysis of the relationship between the nature of the solid phase binding sites and the effects of sediment concentration is presented in Part B of this report.

E. Implications

The potential implications of the relationship between partitioning and sediment concentration to natural water PCB distributions may be illustrated by a consideration of HCB adsorption ratios. The fraction of a given total HCB concentration, $c_{Ta}$, which is adsorbed on suspended particles, $mr_a$, may be calculated from the relationship:

$$f_p = \frac{m\pi_a}{1 + m\pi_a} \qquad \text{(VII-2)}$$

Values for $f_p$ have been determined from previously discussed Saginaw Bay and montmorillonite data (figures VII-5 and VII-6) and the results plotted against sediment concentration (figure VII-11). For comparison, curves representing the partitioning behavior expected from measurements made at high sediment concentrations (1000 mg/ℓ and 10000 mg/ℓ) in the absence of any concentration effect ($\pi_a$ assumed constant and equal to 2000 ℓ/kg for montmorillonite and 10,000 ℓ/kg for Saginaw Bay sediment) have also been plotted. The results demonstrate the relatively large differences in the predicted fraction of HCB adsorbed onto dilute montmorillonite suspensions (<10 mg/ℓ) in the absence of a sediment concentration effect ($f_p \sim 0.02$) and the values calculated on the basis of the observed experimental data ($f_p \sim 0.35$). It would appear that at suspended solids concentrations typical of many quiescent fresh water bodies (1-50 mg/ℓ), inorganic clay materials may be capable of carrying a significant fraction of the overall total aqueous PCB loading, possibly initially outcompeting more organic rich sediment fractions. However, since HCB is more readily desorbed from montmorillonite than from organic containing lake sediment, as shown in the next section it is uncertain that clay particles would act as a significant PCB sink.

It is somewhat more difficult to evaluate the overall implications of the partitioning results for PCB cycling through sediment transport. Processes such as the shoreline erosion of red clays into Lake Superior (Bahnick et al., 1979) may involve, first, sequential reductions in suspended clay concentrations

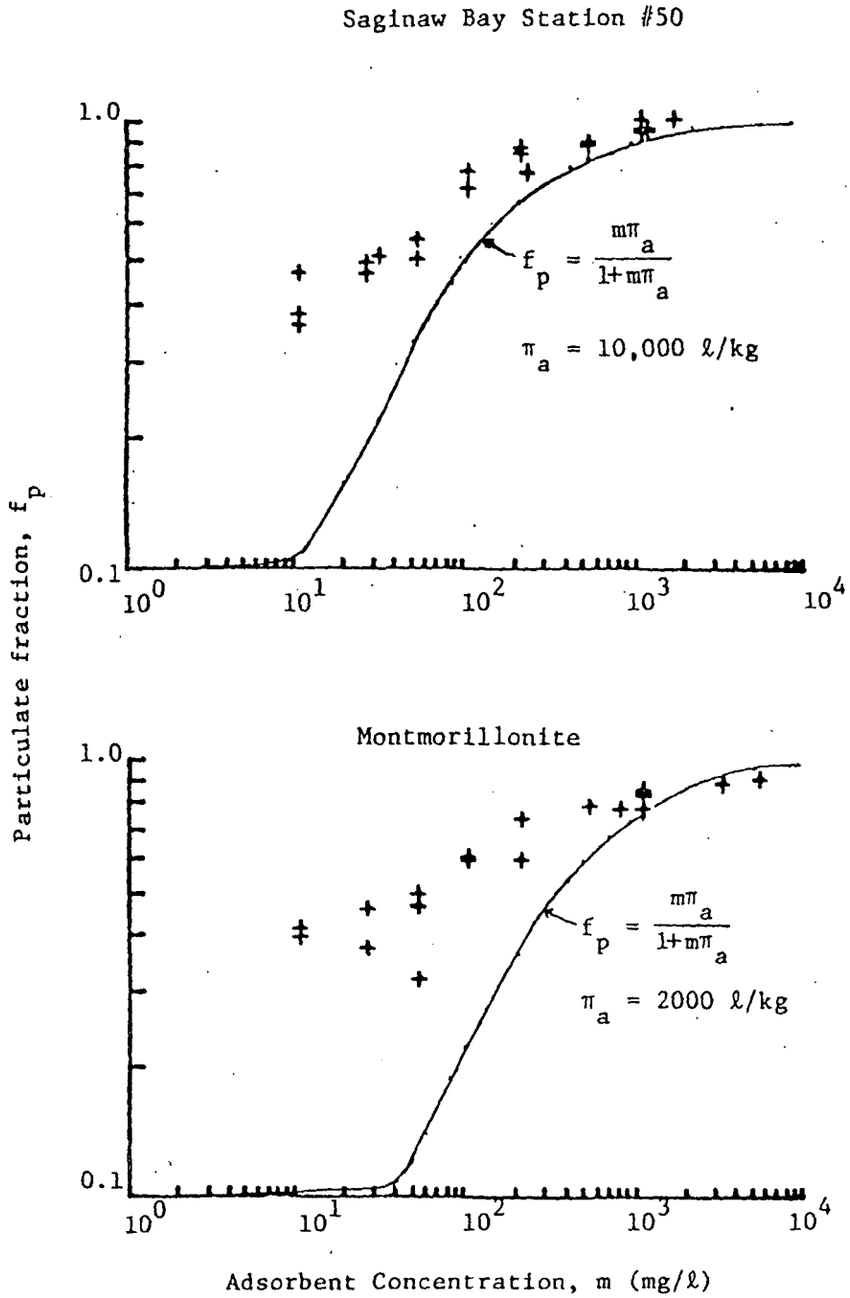



Fig. VII-11. Comparison of particulate fraction computed using constant $\pi_a$ to observed data

through dilution and subsequent increases in solid phase concentrations as material settles into lake bottom sediments. The preceding results suggest that conceivably during such a cycle aqueous dissolved PCB molecules might first be adsorbed from solution only to be later partially desorbed in response to increases in sediment concentration. Clearly, interactions between sediment concentration and partitioning may suggest a rather more dynamic cycling of PCB's between aqueous and solid phases than is generally accepted.

In summary, the results of these studies suggest that the partitioning of HCB to both Saginaw Bay sediment and montmorillonite clay is affected by the sediment concentration. Decreasing the sediment concentration from 1000 mg/ℓ to 10 mg/ℓ resulted in a considerably larger increase in $\pi_a$ for montmorillonite than for the Saginaw Bay sediment. Experiments failed to demonstrate that this effect was the result of non-linear isotherms, kinetics or changes in solution chemistry. It is tentatively suggested that this effect may be the result of direct interactions between solid phase particles which result in changes in the amount of sediment surface area, available for HCB adsorption. The occurrence of such effects in natural systems could result in significant variations in HCB sorption as sediment concentrations change during erosional and depositional processes.

## SECTION VIII

## REVERSIBILITY OF ADSORPTION AND DESORPTION

### A. Introduction

A principle focus of this experimental investigation is the issue of reversibility. Although some information from previous studies was available for the PCB adsorption reaction on sediments, less information is available on the magnitude of PCB desorption from sediments. As PCB usage declines, it is likely that the extent of desorption may determine future changes in natural water concentrations. PCB desorption studies include measurements of Arochlor 1254 release from contaminated soils (Farquhar et al., 1979) and sediments (Halter and Johnson, 1977). In addition, Freundlich isotherm parameters have been determined for Arochlor 1254 partitioning to sand and silt (Wildish et al., 1980). There appears to be relatively little information on the desorption of individual highly chlorinated (Cl $\geq$ 6) PCB isomers from natural sediments. Studies (Furukawa, 1978) have suggested that it is the more highly chlorinated PCB compounds which are likely to be the most environmentally persistent. Thus it is these species which may exert the greatest long term influence on natural water PCB levels.

In addition, there is a need for information on the extent of PCB desorption at the << 1 ppb aqueous concentrations typically reported for natural waters (Pavlov and Dexter, 1979). As pointed out by Hamaker and Thompson (1970), such information is important to avoid the possibility of erroneous estimates of the magnitude of partitioning resulting from the extrapolation of high concentration data to more dilute solutions.

It is the purpose of this section to evaluate the extent of reversibility of HCB sorption to natural sediment materials. As in the experiments discussed in previous sections, studies have been conducted with a single hexachlorobiphenyl isomer at aqueous concentrations similar to PCB levels which have been reported in natural waters.

## B. Isotherm Results

The partition coefficients for the fine fraction of the Saginaw Bay sediment samples discussed in Section VI all exhibited significant non-reversibility: Adsorption partition coefficients were consistently lower ($\pi_a \sim 12{,}000$ ℓ/kg) than the desorption partition coefficients ($\pi_d \sim 25{,}000$ ℓ/kg). The coarse fraction of Station #69 also exhibited nonreversible behavior although the magnitude of both coefficients was much lower ($\pi_a = 0.036$ ℓ/kg, $\pi_d = 0.052$ ℓ/kg).

A useful index of reversibility is the ratio of desorption to adsorption partition coefficient: $\pi_d/\pi_a$, which approaches unity for complete reversibility and increases as nonreversibility increases. Table VIII-1 lists the isotherm parameters, their coefficients of variation, and the reversibility index which ranges from $\pi_d/\pi_a = 1.44$ to 3.44. Since they are all statistically greater than unity (except Station #53) the evidence is that significant nonreversibility exists for the Saginaw Bay sediment samples.

In addition to these sediment samples, inorganic clays were used as adsorbents for isotherm at various clay concentrations with various aqueous phases. These isotherms are shown in figure VIII-1, for montmorillonite at adsorbent concentrations of m = 50, 200, and 1000 mg/ℓ with distilled water as the aqueous phase; in figure VIII-2 for montmorillonite (m = 55 and 1100 mg/ℓ) and a 2mM $NaHCO_3$ buffer as the aqueous phase, which corresponds to the alkalinity of Saginaw Bay water, and kaolinite (m = 1000 mg/ℓ in distilled water); and in figure VIII-3 for Saginaw Bay Station #50 at sediment concentrations of m = 50, 220, and 1100 mg/ℓ.

It is apparent that both the inorganic clays and the Saginaw Bay sediment exhibit significant nonreversibility. The reversibility ratio ranges from $\pi_d/\pi_a \sim 2$ for the lower sediment concentration ($m \sim 50$ mg/ℓ) and $\pi_d/\pi_a \sim 3$ for the higher sediment concentration ($m \sim 1000$ mg/ℓ). Table VIII-3 presents the partition coefficients and the reversibility factor for these isotherms.

The experimental design used to investigate the effect of sediment concentration on adsorption partition coefficient (Section VII) can also be used to investigate reversibility since a desorption followed the adsorption step. The adsorption and desorption partition coefficients and the reversibility index versus sediment concentration is shown in fig. VIII-4 for Saginaw Bay

TABLE VIII-1

Isotherm Parameters[§] - Saginaw Bay Sediments

| Station # | Partition Coefficients | | Reversibility Ratio |
|---|---|---|---|
| | Adsorption $\pi_a$ (ℓ/g) | Desorption $\pi_d$ (ℓ/g) | $\pi_d/\pi_a$ |
| 19 | 14.8 (0.10) | 30.1 (0.17) | 2.03 (0.20) |
| 31 | 12.3 (0.17) | 30.9 (0.14) | 2.51 (0.22) |
| 43 | 10.7 (0.21) | 26.1 (0.40) | 2.45 (0.45) |
| 50 | 7.01 (0.13) | 20.2 (0.27) | 2.88 (0.30) |
| 53 | 11.2 (0.04) | 19.8 (0.21) | 1.44 (0.21) |
| 69* | 0.036 (0.26) | 0.052 (0.15) | 2.33 (0.30) |
| Saginaw R. | 9.63 (0.08) | 22.4 (0.23) | 3.44 (0.24) |

*Sediment concentration = 20,000 mg/ℓ

[§]Numbers in parentheses are coefficients of variation

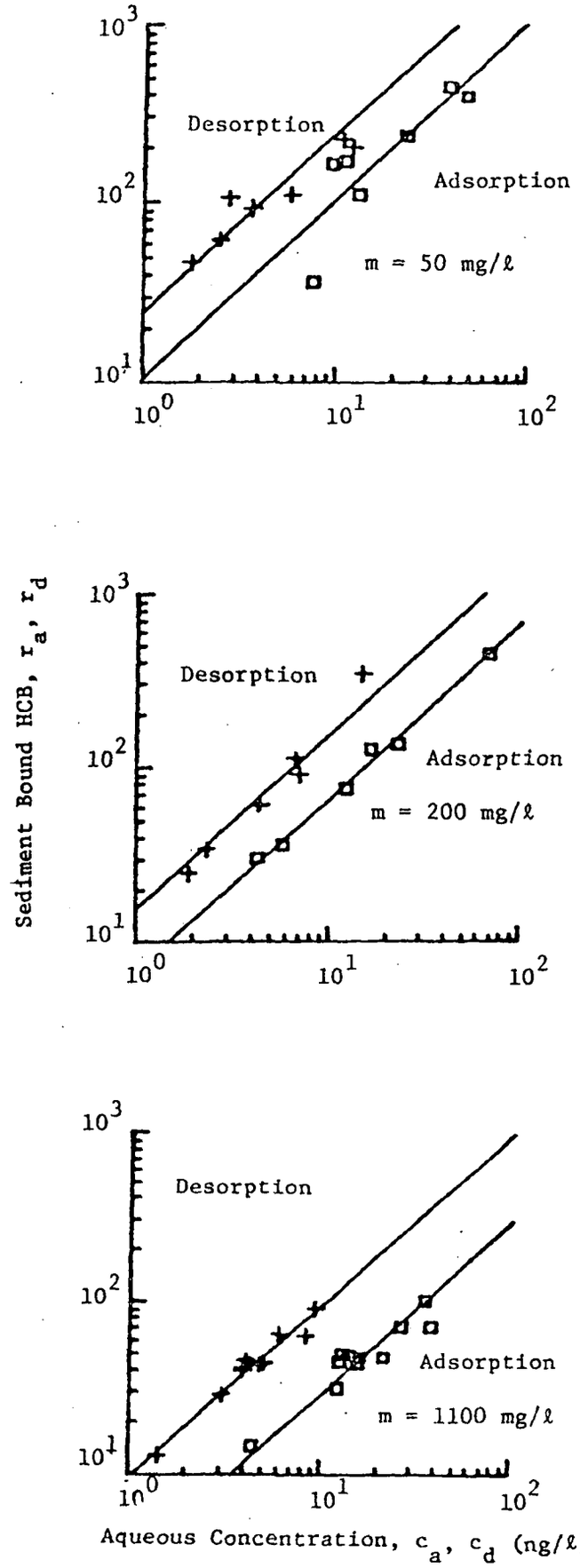



Fig. VIII-1. Adsorption and Desorption Isotherms - Montmorillonite Distilled Water. Lines have unity slope

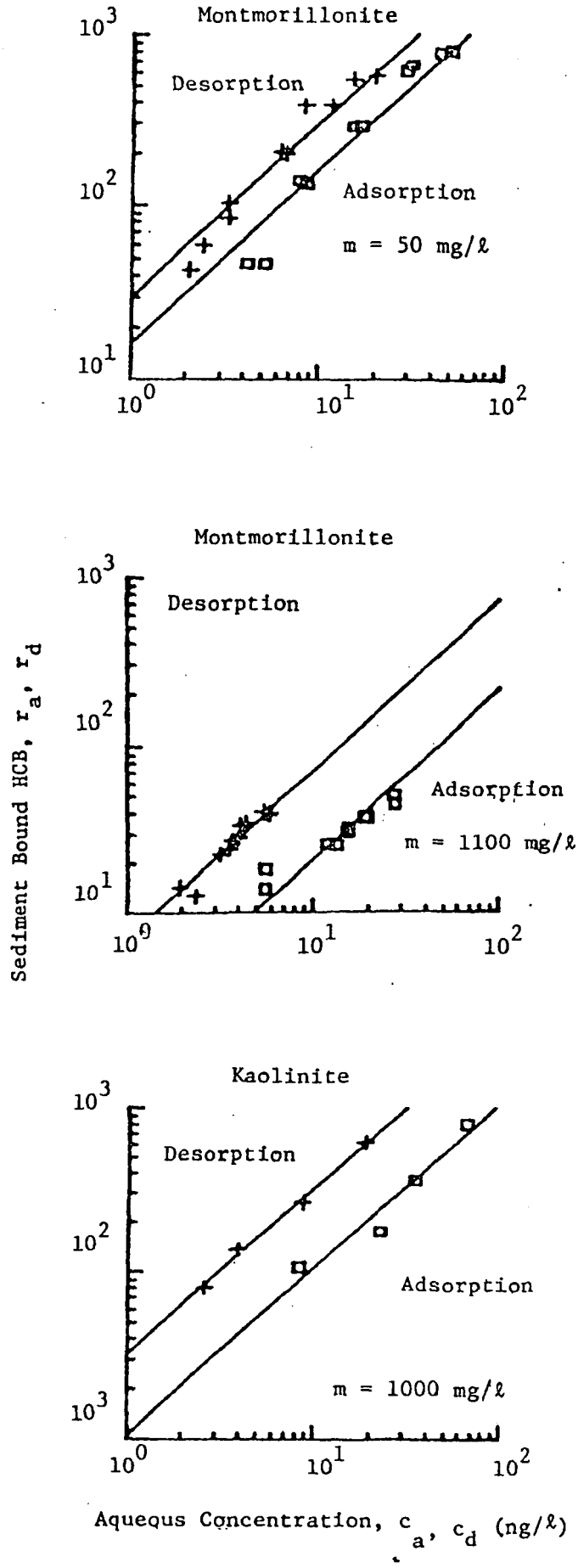



Fig. VIII-2. Adsorption and Desorption Isotherms - Montmorillonite, Aqueous phase = 2mM $NaHCO_3$ and Kaolinite, Distilled Water. Lines have unity slope.

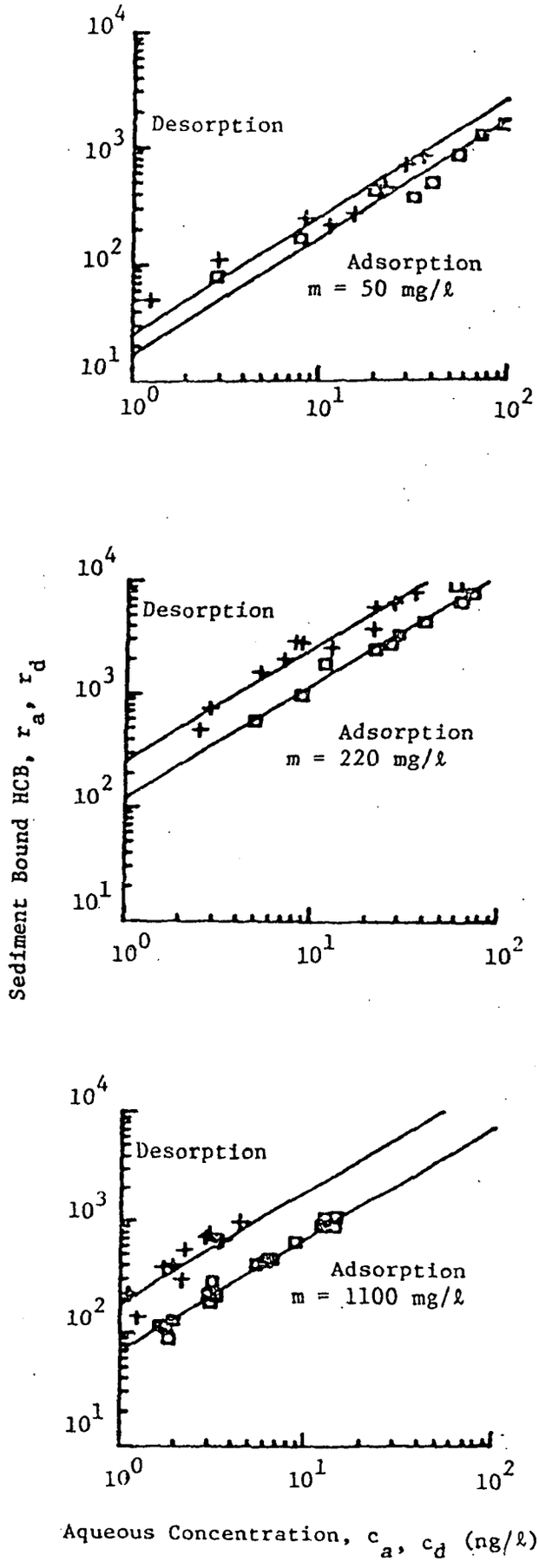



Fig. VIII-3. Adsorption and Desorption Isotherms - Saginaw Bay #50 Distilled Water. Lines have unity slope

TABLE VIII-2

Isotherm Parameters[§] - Effect of Sediment Concentration

| Sediment* | Aqueous Phase | Sediment Concentration m (mg/ℓ) | Partition Coefficients Adsorption $\pi_a$ (ℓ/g) | Partition Coefficients Desorption $\pi_d$ (ℓ/g) | Reversibility Ratio $\pi_d/\pi_a$ |
|---|---|---|---|---|---|
| Montmorillonite | $H_2O$ | 50 | 10.6 (0.40) | 24.9 (0.26) | 2.35 (0.48) |
| Montmorillonite | $H_2O$ | 200 | 6.69 (0.09) | 15.7 (0.21) | 2.35 (0.23) |
| Montmorillonite | $H_2O$ | 1000 | 2.90 (0.20) | 9.65 (0.10) | 3.33 (0.22) |
| Montmorillonite | Buffer+ | 55 | 16.2 (0.26) | 30.4 (0.21) | 1.88 (0.33) |
| Montmorillonite | Buffer+ | 1100 | 2.10 (0.19) | 7.15 (0.11) | 3.40 (0.22) |
| Kaolinite | $H_2O$ | 1000 | 1.08 (0.20) | 3.26 (0.05) | 3.02 (0.21) |
| Saginaw Bay #50 | $H_2O$ | 50 | 17.1 (0.27) | 25.2 (0.29) | 1.47 (0.40) |
| Saginaw Bay #50 | $H_2O$ | 220 | 12.3 (0.14) | 25.9 (0.21) | 2.11 (0.25) |
| Saginaw Bay #50 | $H_2O$ | 1100 | 7.05 (0.13) | 18.9 (0.27) | 2.68 (0.30) |

*Adsorption time = 2 hours

§Numbers in parentheses are coefficients of variation

+Buffer is 2mM $NaHCO_3$

and fig. VIII-5 for montmorillonite. The two cases are for aqueous phases consisting of distilled water and supernatant, as described in Section VII. The gradual increase in separation between $\pi_d$ and $\pi_a$, and the increase in $\pi_d/\pi_a$ as mass increases indicates that the extent of nonreversibility is increasing as sediment concentration increases. The exception is montmorillonite in supernatant. An interpretation of these results in terms of exchangeable and nonexchangeable components is presented in Part B of this report. However, it is also possible that the nonreversibility is the result of an experimental artifact. Experiments designed to address this issue are described below.

## C. Irreversibility

A review of the literature on soil-organic interactions reveals that nonsingular isotherm behavior is not unique to hexachlorobiphenyl. Studies on picloram (Farmer and Aochi, 1974), 2,4,5,-T (van Genuchten et al., 1977), Diuron (Peck et al., 1980) and DDT (Pierce et al., 1974) among others, all suggest distinct differences between adsorption and desorption isotherms. A variety of factors have been postulated to account for this behavior. Rao and Davidson (1980) in a review of literature on the subject indicate that nonsingularity may result from lack of attainment of equilibrium during desorption, chemical or microbial transformations, or experimental artifact. Experiments were conducted to test the potential effects of these factors on the HCB isotherms of the present studies.

Evidence suggests that microbial transformations are not responsible for causing non-singular HCB isotherms. In experiments conducted using activated sludge cultures, no evidence of HCB degradation (as measured by $^{14}C\text{-}CO_2$ evolution) was obtained during a two month test period. Since it is likely that such cultures contain far greater densities of microbial organisms than would be expected in either the natural sediment or montmorillonite suspensions, they probably represent optimal degradation conditions. Other studies (Tucker et al., 1975; Furukawa et al., 1978) have confirmed these findings and indicate that the rate of microbial degradation decreases as the degree of PCB chlorination increases. Thus if microbial degradation of HCB occurs at all, it requires time periods much longer than the reaction times of the present study.

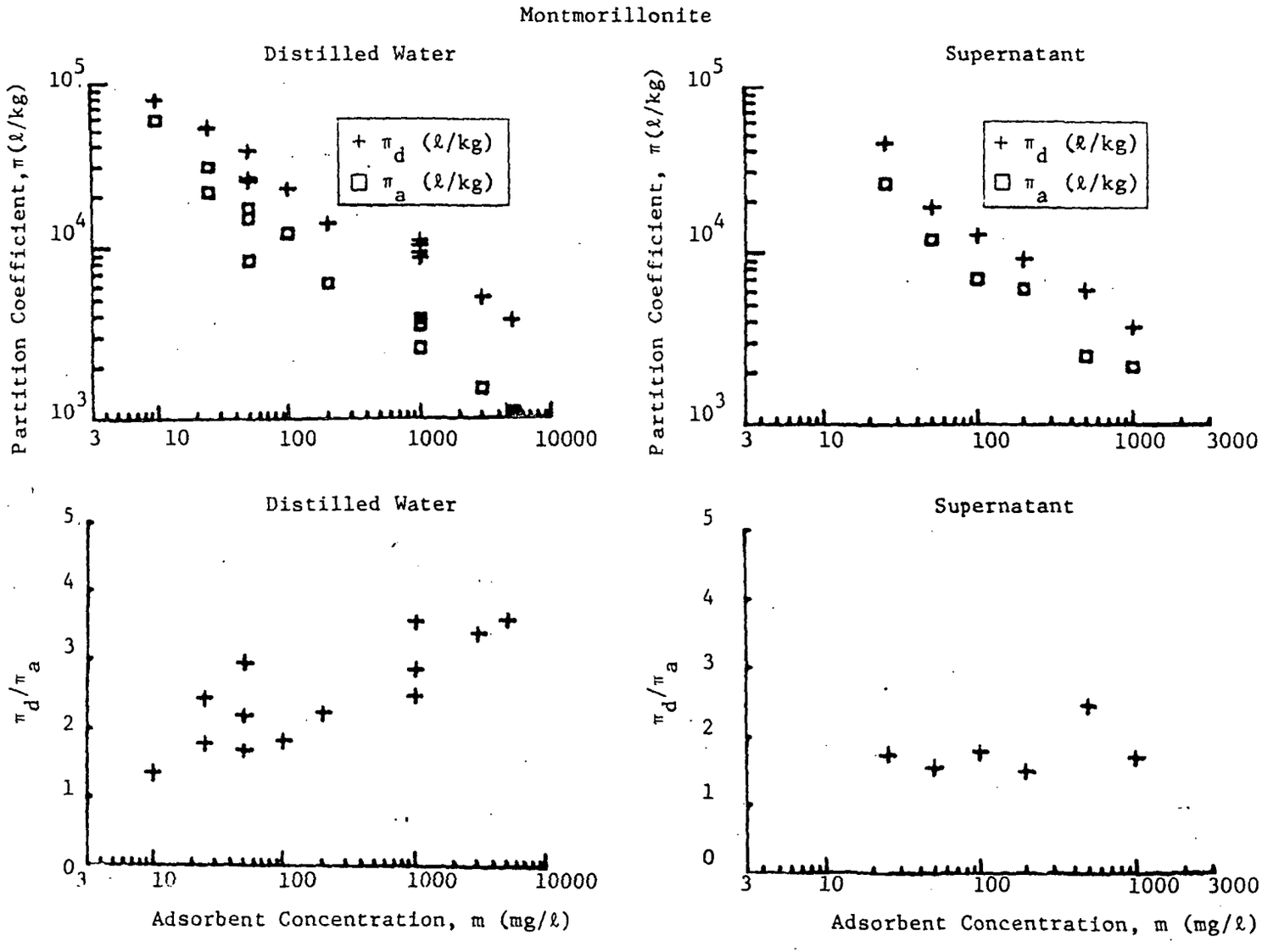



Fig. VIII-4. Effect of Adsorbent Concentration on Degree of Reversibility Adsorption, $\pi_a$, and Desorption, $\pi_d$, Partition Coefficients and their ratio

Saginaw Bay #50

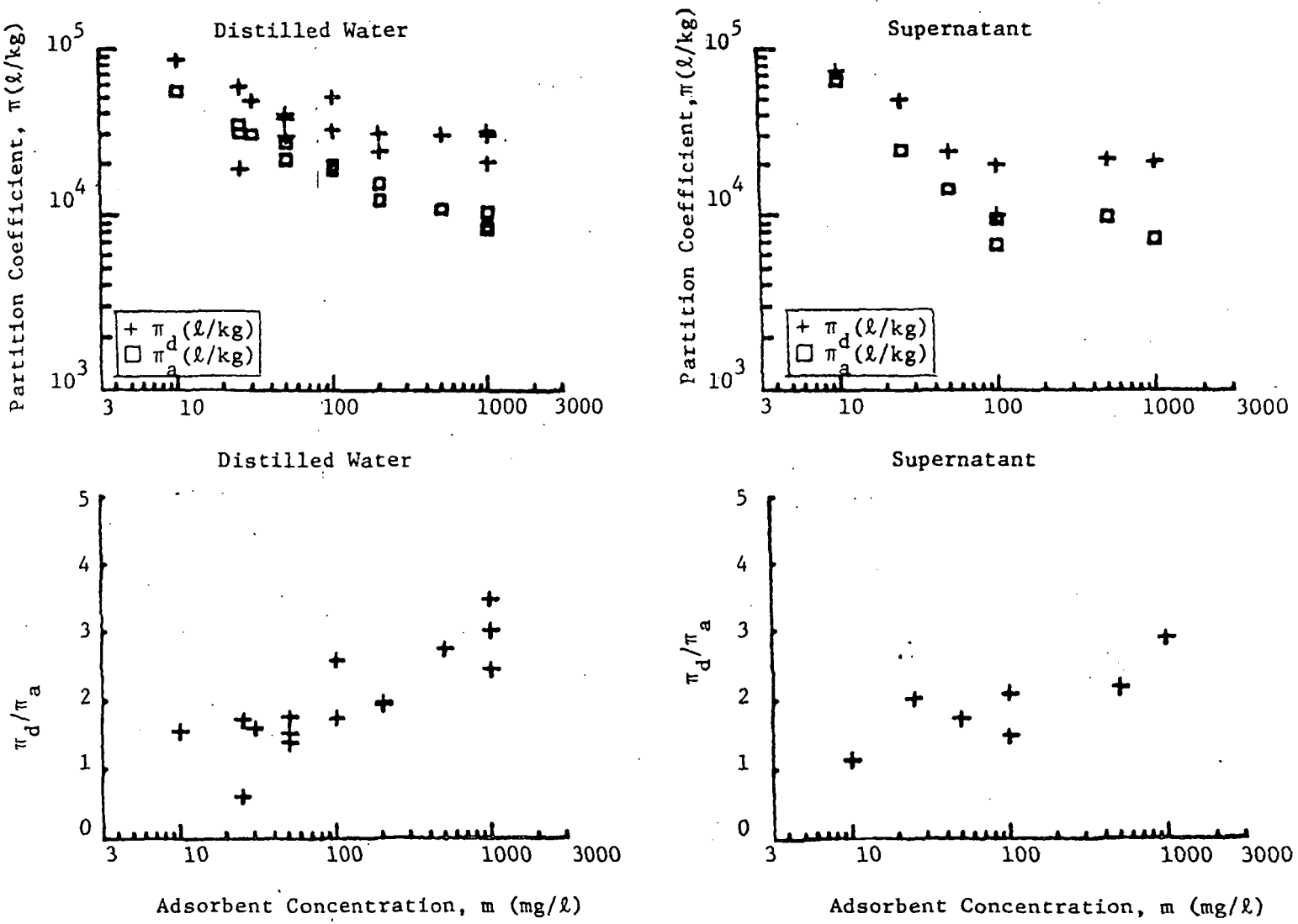



Fig. VIII-5. Effect of Adsorbent Concentration on Degree of Reversibility Adsorption, $\pi_a$, and Desorption, $\pi_d$, Partition Coefficients and their ratio

## D. Dilution Experiment

It has been suggested (Rao and Davidson, 1980) that for some soil-pesticide systems, non-singular isotherms may be an experimental artifact caused by centrifugation. The possibility exists that centrifuging may alter the manner in which an organic molecule is bonded to the solid phase resulting in a displacement of the desorption isotherm. To test this hypothesis, desorption isotherms were constructed by varying the sediment and aqueous concentrations through dilution. Following HCB equilibrium adsorption to 1100 mg/ℓ sediment suspensions, solid and liquid phase concentrations were diluted by replacing varying volumes of the suspension with equal volumes of distilled water. Samples were then re-equilibrated, subsequently centrifuged to determine the amount of HCB desorbed from the solid phase, and the results used to construct desorption isotherm.

Desorption isotherms based on this dilution technique (Figure VIII-6) indicate that HCB adsorption to Saginaw Bay #50 and montmorillonite is not readily reversible. For both sediments the results suggest that decreases in aqueous concentration, c, do not result in significant reductions in adsorbed particulate concentration, r, which is not what would be expected if the adsorption process was readily reversible. The horizontal isotherms obtained imply even less reversibility than is indicated from isotherms constructed in the usual manner. Hence it does not appear that centrifugation is responsible for the observed non-singular isotherms. This conclusion is supported by observations (Rao et al., 1978) suggesting that centrifugation effects appear to be more pronounced for ionic water soluble molecules than for neutral non-ionic species.

The interpretation of the dilution experiment ignores the effect of varying sediment concentration on desorption. This is inherent in the dilution method which relies on removing a portion of the total suspension and replacing it with particle free aqueous phase. In fact, the analysis of dilution experiments is fairly complicated. In Part B, the dilution experiments are analyzed in terms of the exchangeable and nonexchangeable model of adsorption and desorption. This clarifies the mechanism which produces the almost horizontal dilution isotherms.

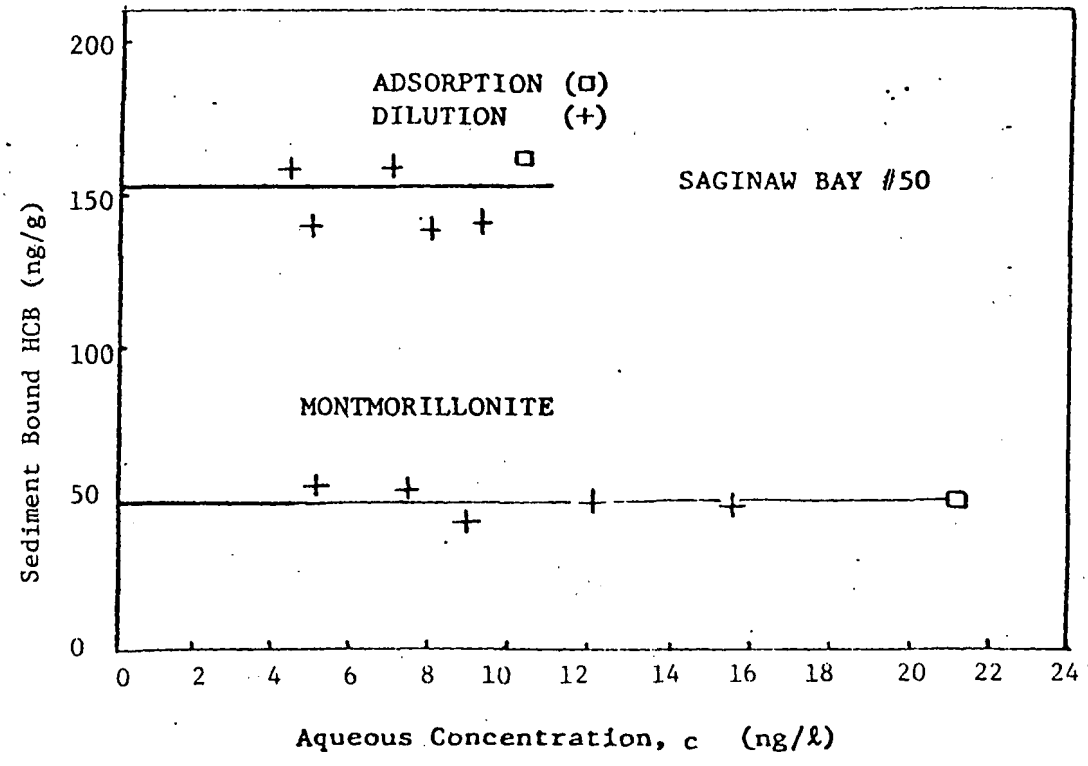



Fig. VIII-6 Effect of Dilution on HCB Desorption

## E. Kinetic Effects

Previous studies (Steen et al., 1978) have suggested that PCB adsorption to sediments is a rapid process reaching equilibrium in a matter of minutes. In the present study, experiments suggest that while adsorption time exerts an influence on reversibility, it does not appear to account for the non-singular isotherm behavior. As discussed in Section IV (Kinetics), a series of isotherms were constructed for HCB adsorption to 1100 ppm Saginaw Bay sediment (#50) suspensions for time periods of 3 hrs, 1 day and 5 days. The results suggested that small increases in adsorption may occur during the first 24 hours with little evidence for significant changes at longer equilibration periods.

The effect of desorption time on reversibility was also tested experimentally. For a fixed adsorption time (3 hr) a series of desorption isotherms for varying desorption times (2 hr, 3 day, 6 day) are shown in fig. IV-11 of Section IV. Although some differences occurred the trend is not consistent: the 2 hr desorption isotherm is bracketed by the 3 day and 6 day isotherms. Further, the differences between the three desorption isotherms are much less than the difference between the adsorption isotherm and any of the desorption isotherms. Hence although there appears to be some effect of time of desorption it is not sufficient to eliminate non-reversible behavior. Overall, it appears that small increases in HCB adsorption may occur between 3 and 24 hours while no consistent evidence of changes in desorption with time were observed.

What was not discussed in Section IV is the effect of adsorption time on the desorption partition coefficient. As shown in fig. VIII-7, for adsorption times of $t_a$ = 2, 48 and 240 hrs, the adsorption partition coefficient increased slightly ($\pi_a$ = 17000 to 18000 ℓ/kg) but the desorption coefficient increased markedly ($\pi_d$ = 25200 to 61000 ℓ/kg) after 48 hrs of adsorption and little thereafter. The reversibility ratio increased from $\pi_d/\pi_a$ = 1.5 to 3.4 (Table VIII-3). This result suggests that whatever the binding reaction is that increases irreversibility, for this sediment concentration at least, it requires ∿ 2 days for it to reach equilibrium.

This result is contradicted by the results of a sediment concentration experiment for montmorillonite for which the adsorption time is $t_a$ = 24 hr (fig. VIII-8). The results are not substantially different from the equivalent shorter term adsorption time experiment (fig. VIII-4). The aqueous

TABLE VIII-3

Isotherm Parameters[§] - Effect of Adsorption Time

| Sediment* | Adsorption Time | Partition Coefficients Adsorption | | Partition Coefficients Desorption | | Reversibility Ratio | |
|---|---|---|---|---|---|---|---|
| Saginaw Bay | $t_a$ (hr) | $\pi_a$ (ℓ/g) | | $\pi_d$ (ℓ/g) | | $\pi_d/\pi_a$ | |
| Station #50 | 2.0 | 17.1 | (0.27) | 25.2 | (0.29) | 1.47 | (0.40) |
| Station #50 | 48.0 | 18.2 | (0.24) | 61.3 | (0.25) | 3.37 | (0.35) |
| Station #50 | 240.0 | 16.3 | (0.27) | 54.0 | (0.42) | 3.31 | (0.50) |

*Sediment concentration = 55 mg/ℓ; Aqueous phase is $H_2O$

[§]Numbers in parentheses are coefficients of variation

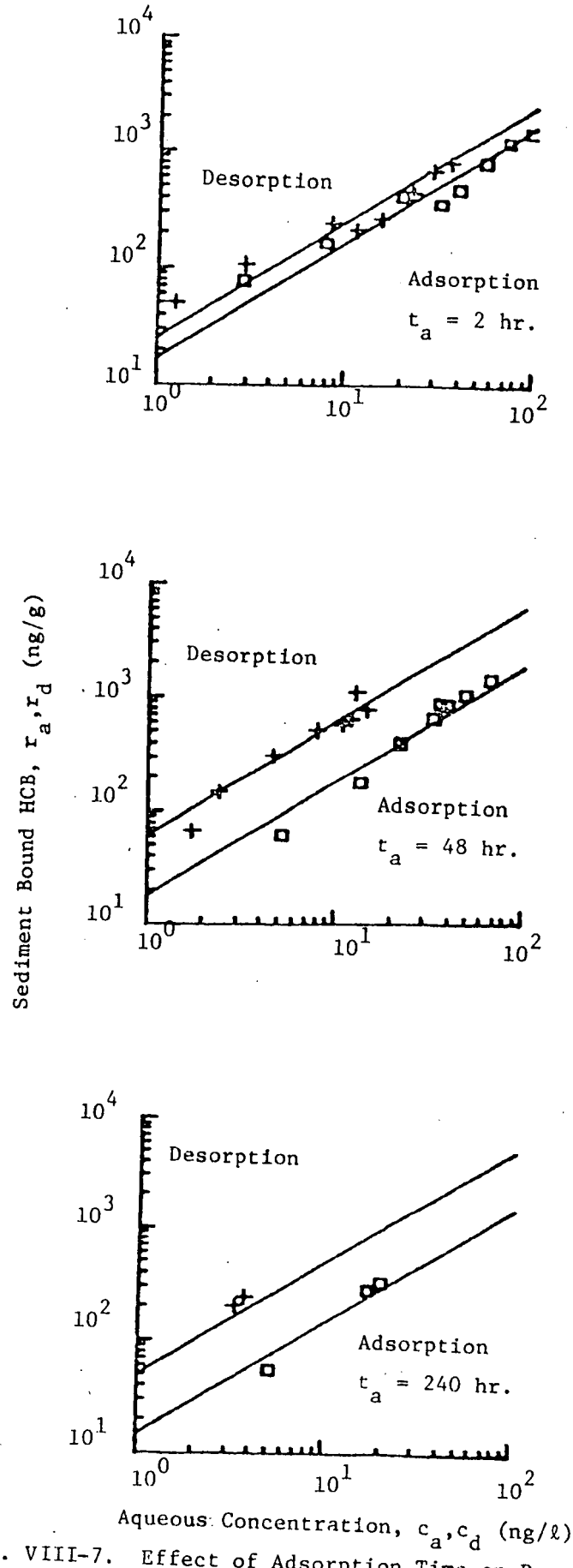
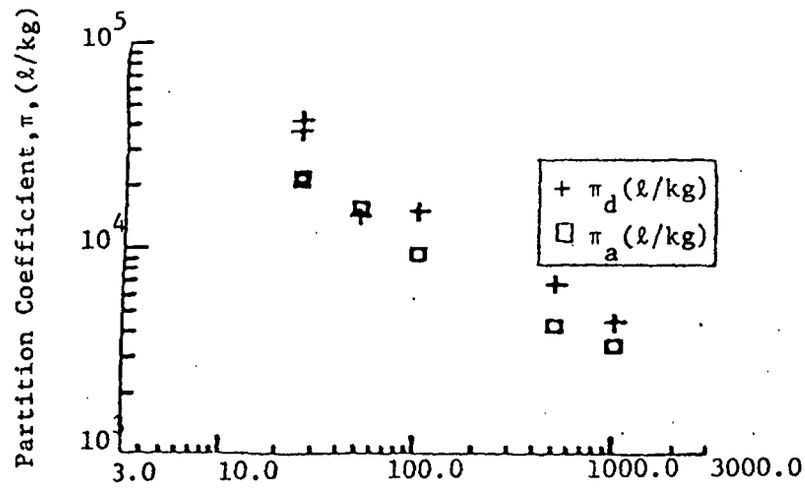



Fig. VIII-7. Effect of Adsorption Time on Reversibility
m = 55 mg/ℓ Saginaw Bay #50



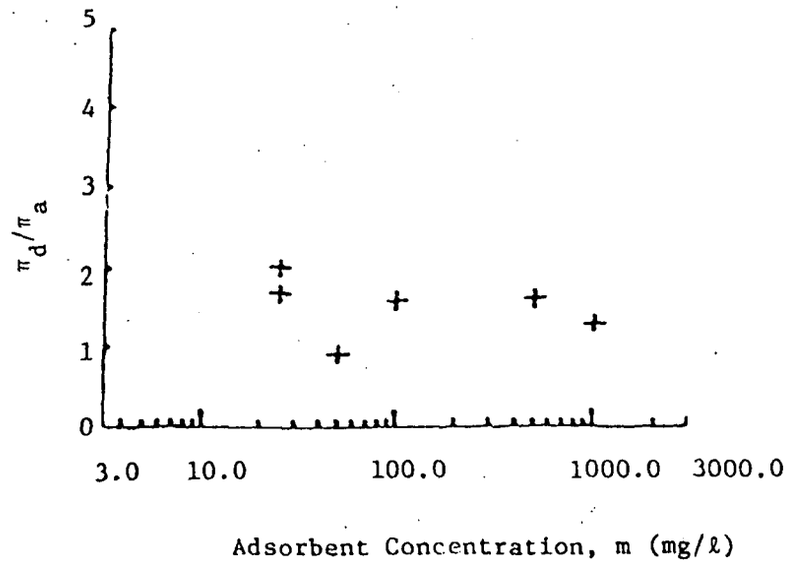




Fig. VIII-8. Effect of Adsorption on Reversibility Adsorption $\pi_a$, and Desorption, $\pi_d$, Partition Coefficients versus Adsorbent mass. $t_a$ = 24 hr. Montmorillonite, Supernatant

phase is supernatant for both experiments.

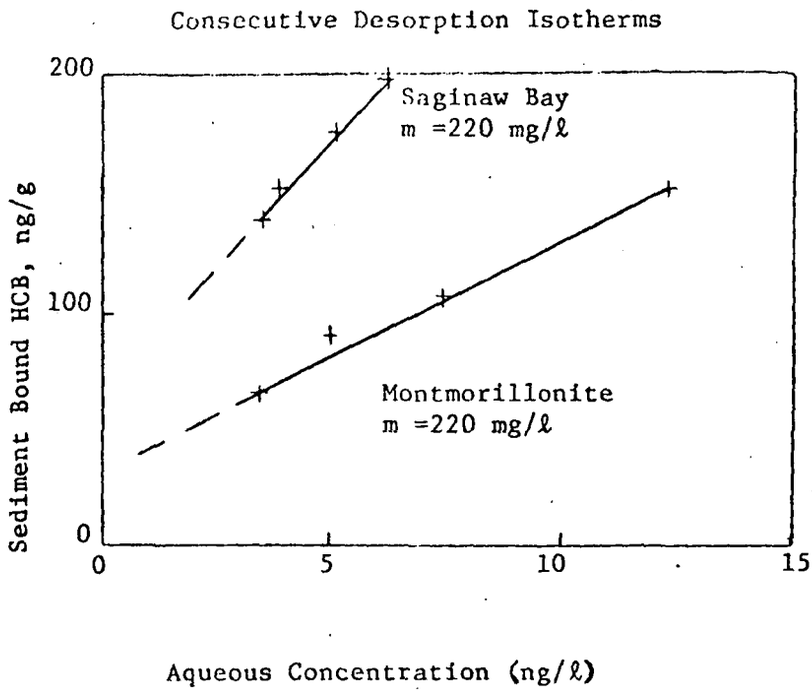
These conflicting results indicate that further experimental investigations are required to elucidate the details of the mechanism by which the irreversibility occurs and its relationship to kinetic effects.

## F. Consecutive Desorption

In an attempt to more clearly define the extent of reversibility of HCB adsorption, a series of consecutive desorption studies were performed. In these experiments, HCB was initially adsorbed onto sediment samples (Saginaw Bay #50 and montmorillonite) and subsequently subjected to a series of consecutive desorption cycles. After 1 hour equilibration periods, the samples were centrifuged and the aqueous phase replaced with distilled water. Samples were analyzed for aqueous and sediment HCB concentrations. Figure VIII-9 displays the results of initial experiments for sediment concentrations of m = 80 mg/ℓ and 220 mg/ℓ. The consecutive desorption isotherms are essentially linear with the exception of the 80 mg/ℓ montmorillonite isotherm.

In order to evaluate the effect of longer desorption times, a second experiment was performed with adsorption and desorption times of 24 hrs. The data (fig. VIII-10a), although more scattered, indicates a linear isotherm although it is difficult to judge the shape of the isotherm at low aqueous concentrations. The effect of changing the aqueous phase (2mM $NaHCO_3$) for montmorillonite is shown in fig. VIII-10b. As with the Saginaw Bay sediment at m = 1100 mg/ℓ the small aqueous concentrations that result at each desorption makes it difficult to judge the exact shape of the consecutive desorption isotherm. Table VIII-4 presents the data for these experiments.

In order to further define the consecutive desorption isotherm, the number of desorption cycles was increased to ten. Figures VIII-11a and 11b present the variation in sediment bound HCB and aqueous phase HCB concentrations with desorption cycle, for 15 mℓ, 1100 ppm Saginaw Bay #50 suspensions. To maintain a constant sediment concentration, solution volumes were appropriately adjusted (0.5 mℓ per cycle) following the removal of each total suspension sample to determine $c_T$. At both initial HCB concentrations, the results suggest a sharp initial decrease in aqueous HCB levels (desorption cycles 1 and 2) followed by almost constant levels (2.8 ng/ℓ and 5.5 ng/ℓ) during the remaining cycles (fig.



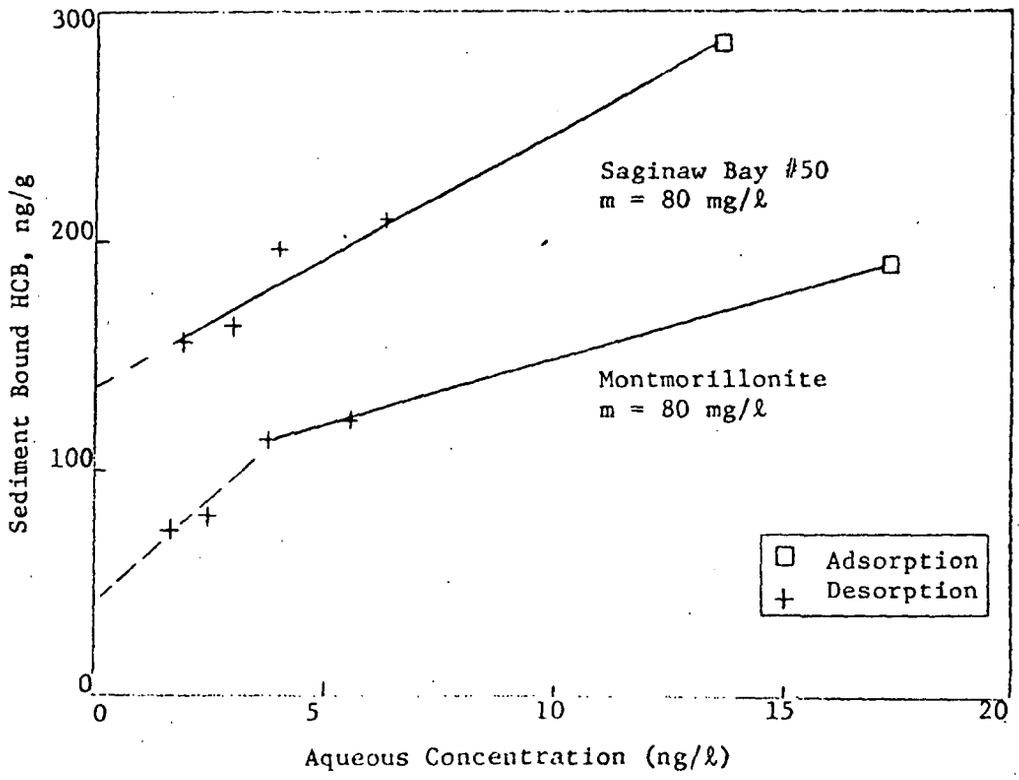
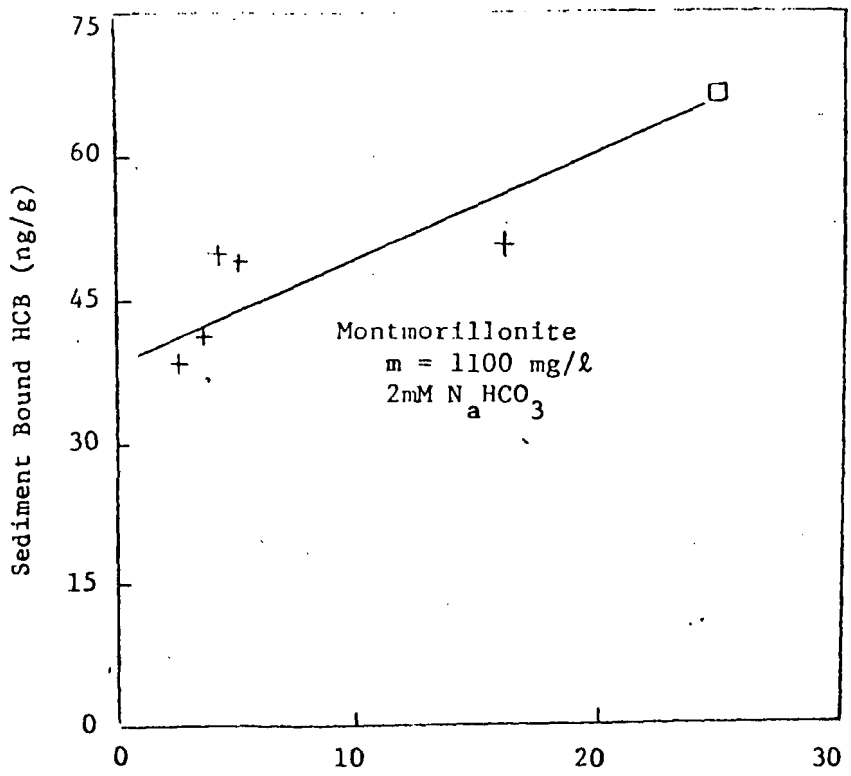




Fig. VIII-9. Consecutive Desorption Isotherms Saginaw Bay and Montmorillonite

Consecutive Desorption Isotherms



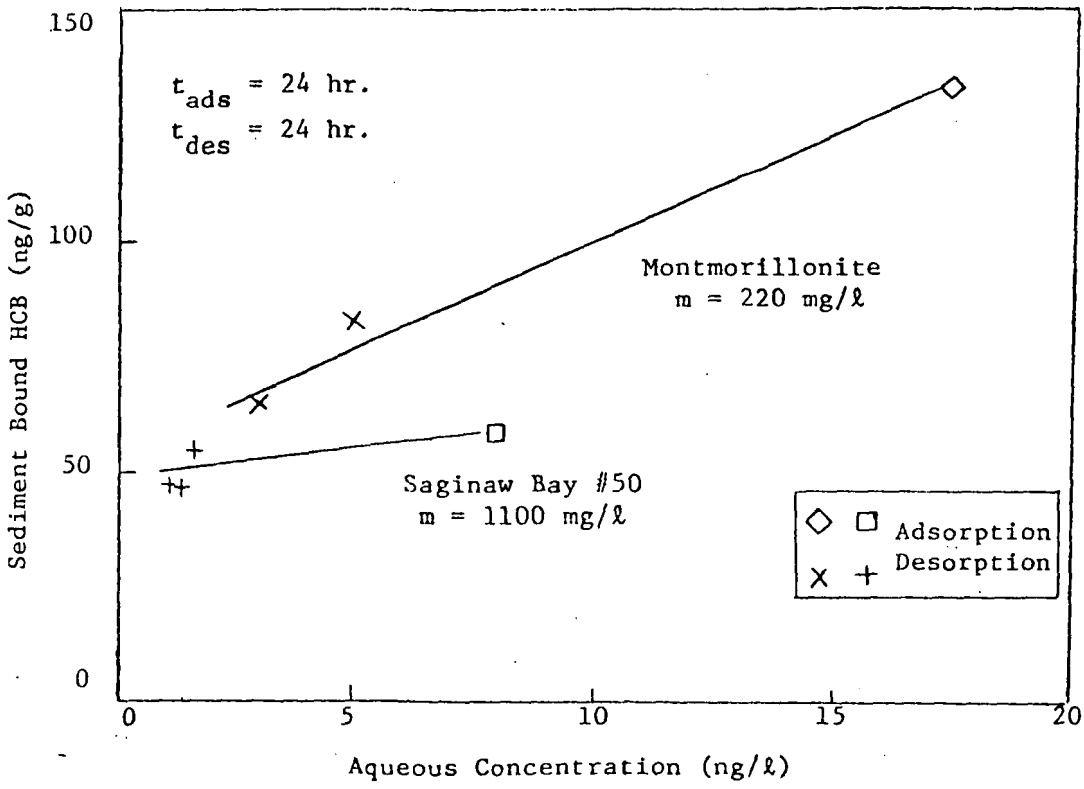




Fig. VIII-10. Consecutive Desorption Isotherms - Saginaw Bay and Montmorillonite

TABLE VIII-4

Consecutive Desorption Data

| Cycle | Sediment Conc. m (mg/ℓ) | Montmorillonite Aqueous Conc. c (ng/ℓ) | Montmorillonite Particulate Conc. r (ng/g) | Saginaw Bay #50 Aqueous Conc. c (ng/ℓ) | Saginaw Bay #50 Particulate Conc. r (ng/g) |
|---|---|---|---|---|---|
| 0 | 80 | 17.3 | 191 | 13.6 | 287 |
| 1 | 76 | 5.5 | 122 | 6.3 | 209 |
| 2 | 72 | 3.8 | 113 | 3.9 | 195 |
| 3 | 68 | 2.4 | 89.4 | 2.9 | 162 |
| 4 | 64 | 1.6 | 77.1 | 1.9 | 157 |
| 1 | 220 | 12.3 | 153 | 6.2 | 207 |
| 2 | 209 | 7.4 | 106 | 5.1 | 177 |
| 3 | 199 | 5.0 | 90 | 3.9 | 154 |
| 4 | 189 | 3.4 | 66 | 3.5 | 140 |
| $t_a = t_d = 24$ hr. | | | | | |
| 0 | 220 | 17.5 | 134 | 14.4 | 178 |
| 1 | 209 | 5.0 | 84 | 5.4 | 141 |
| 2 | 199 | 2.5 | 65 | 5.9 | 114 |
| 3 | 189 | 6.4 | 53 | 6.2 | 86 |
| 4 | 179 | 3.3 | 50 | 4.3 | 58 |
| $t_a = t_d = 24$ hr. | | | | | |
| 0 | 1100 | - | - | 7.6 | 59 |
| 1 | 1045 | - | - | 1.65 | 55 |
| 2 | 993 | - | - | 1.4 | 48 |
| 3 | 943 | - | - | 1.3 | 47.6 |
| 4 | 896 | - | - | 1.1 | 48 |
| Aqueous Phase = 2mM $NaHCO_3$ | | | | | |
| 0 | 1100 | 26 | 66 | - | - |
| 1 | 1063 | 13 | 51 | - | - |
| 2 | 1028 | 5.3 | 55 | - | - |
| 3 | 994 | 4.4 | 50 | - | - |
| 4 | 961 | 3.9 | 40 | - | - |
| 5 | 928 | 2.8 | 39 | - | - |

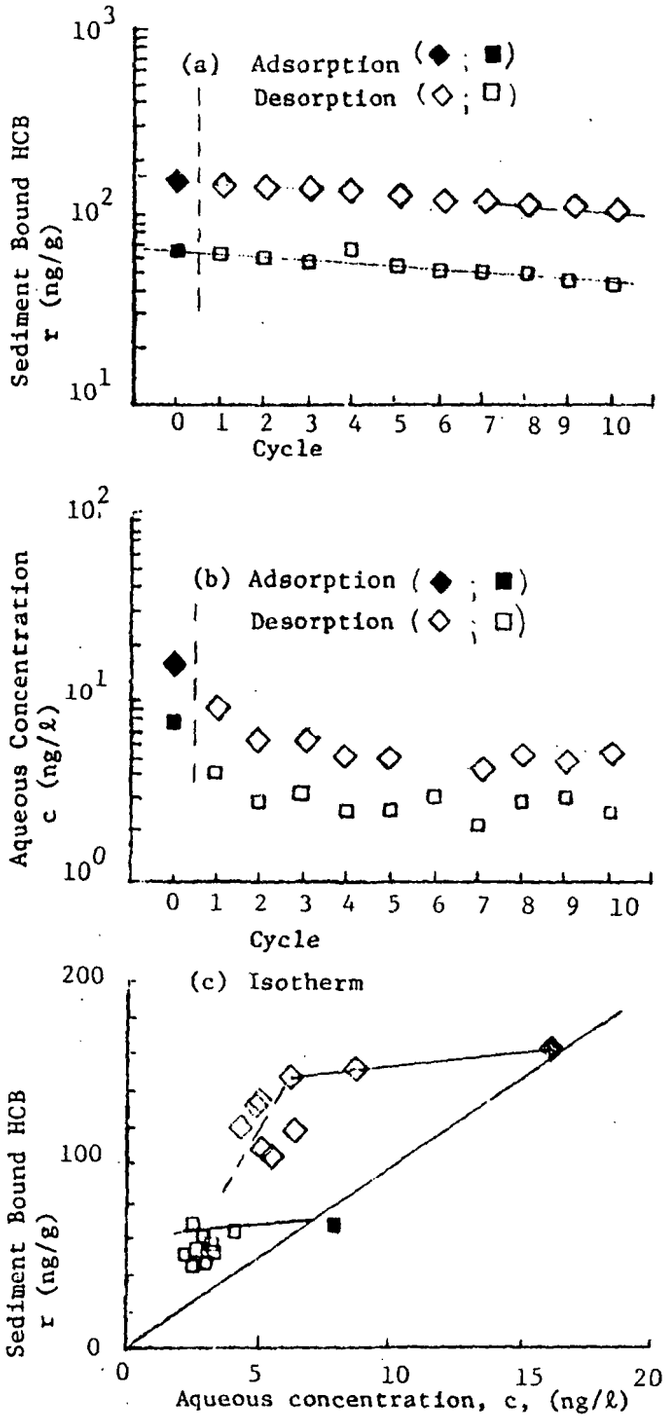



Fig. VIII-11. Consecutive Desorption, Saginaw Bay #50 m = 1100 mg/ℓ, Distilled Water (a) Sediment Bound HCB, r, and (b) aqueous concentration, c versus desorption cycle. (c) Isotherm

TABLE VIII-5

Consecutive Desorption

Saginaw Bay #50 m = 1100 mg/ℓ

| Cycle | $c_T$ (ng/ℓ) | c (ng/ℓ) | r (ng/g) | $c_T$ (ng/ℓ) | c (ng/ℓ) | r (ng/g) |
|---|---|---|---|---|---|---|
| 0 | 81.00 | 7.96 | 66.40 | 190.25 | 16.15 | 158.22 |
| 1 | 74.28 | 4.15 | 63.73 | 174.37 | 8.85 | 150.41 |
| 2 | 70.36 | 2.87 | 61.34 | 164.92 | 6.20 | 144.29 |
| 3 | 66.66 | 3.22 | 57.60 | 167.68 | 6.32 | 146.69 |
| 4 | 77.52 | 2.56 | 68.02 | 153.08 | 5.10 | 134.50 |
| 5 | 62.88 | 2.58 | 54.81 | 149.43 | 5.01 | 131.29 |
| 6 | 61.55 | 3.07 | 53.17 | 128.12 | 7.65 | 109.08 |
| 7 | 58.80 | 2.13 | 51.51 | 139.32 | 4.54 | 122.50 |
| 8 | 59.15 | 2.90 | 51.09 | 134.29 | 6.21 | 116.32 |
| 9 | 54.63 | 3.10 | 46.82 | 121.60 | 4.89 | 106.06 |
| 10 | 51.20 | 2.50 | 44.27 | 119.27 | 5.37 | 103.90 |

VIII-11b). Table VIII-5 presents the data. By comparison, values of sediment bound HCB concentrations appear to decrease exponentially as the number of desorption cycles increases (figure VIII-11a). An extrapolation of the sediment concentration results appears to suggest that s sufficiently large number of washing cycles may result in desorption of all of the adsorbed HCB. However, the curvilenear variation in aqueous HCB concentration is not what would be expected if a single reversible isotherm described HCB sorption behavior.

A single reversible isotherm would result in parallel curves for the particulate and aqueous data on a logarithmic scale, as implied by the linear partition equation $r = \pi c$. Figure VIII-11c presents the isotherm for these data. The first two desorption cycles produce essentially linear and distinct consecutive desorption isotherms. The remaining data is quite scattered due to the experimental variability of the low aqueous concentrations.

Conceivably, the variations in sediment bound HCB concentration, r, with desorption cycle, could be an experimental artifact caused by reductions in sediment particle sizes resulting from abrasion during shaking. The formation of extremely fine particles which resist contrifuging has been previously observed for other natural sediments (Karickhoff and Brown, 1979). The creation of such particles during the desorption cycle could result in losses of sediment and could account for the observed reductions in r. However, it seems unlikely that shaking should consistently lead to the formation of equivalent amounts of fine particles as would be required to produce the observed data.

In a further effort to determine whether all of the HCB may be eventually desorbed, studies were conducted on 220 ppm sediment suspensions. It can be shown that the ratio of the dissolved phase HCB concentration, $c_a$, to the total HCB concentration in suspension, $c_{Ta}$, may be expressed as:

$$c_a/c_{Ta} = \frac{1}{1 + \pi_a m} \qquad \text{(VIII-1)}$$

where m is the solid phase concentration. Therefore, decreasing the experimental value of m from 1100 ppm to 220 ppm should result in a significantly greater fraction of the total HCB concentration being removed during each desorption cycle.

The results of these 220 ppm experiments appear to confirm the decreases in sediment HCB concentration observed for the 1100 ppm suspensions. In these 220 ppm experiments, solution volumes were kept constant and as a result sample analysis resulted in small changes in the suspension sediment concentrations. The results are shown in fig. VIII-12 for montmorillonite and Saginaw Bay sediment (#50). The data are presented in Table VIII-6. A more rapid decrease in particulate HCB concentration during each desorption cycle is apparent, in agreement with eq. (VIII-1) which predicts a larger HCB fraction associated with the dissolved phase at m = 220 ppm. However the particulate and aqueous phase concentrations are again not parallel: whereas the particulate concentrations decrease exponentially the aqueous concentrations decrease rapidly at first and then more slowly. The isotherm plot (fig. VIII-12c) suggests a two phase process: an initial linear consecutive isotherm, followed by a second linear isotherm which appears to intersect the origin, implying that eventually it is possible to eventually desorb all the HCB.

A detailed quantitative evaluation of the adsorption and initial consecutive desorption isotherms in terms of two adsorbed components: an exchangeable and initially non-exchangeable component is presented in Part B of this report. The data presented in figs. VIII-11 and 12 suggest that low aqueous concentrations must be reached in order that the "non-exchangeable" component eventually desorbs. It is also apparent that the mass of solids, m, influences the aqueous concentration at which this desorption commences.

The observed consecutive desorption data might be explained if HCB molecules were capable of forming bonds of differing strength with sediment surfaces. The consecutive desorption data for Saginaw Bay sediment (#50) indicates that a majority of the adsorbed HCB is more strongly bound than would be predicted by a reversible adsorption isotherm. A smaller amount of HCB appears to be relatively exchangeable. This behavior could result from HCB adsorption to both inorganic and organic components of the natural sediment. Under this hypothesis, the desorption behavior displayed by montmorillonite could imply adsorption to differing inorganic sites on the clay particles, possibly particle edges versus particle faces. Alternately, it is possible that HCB molecules may adsorb in geometrically different arrangements to relatively uniform

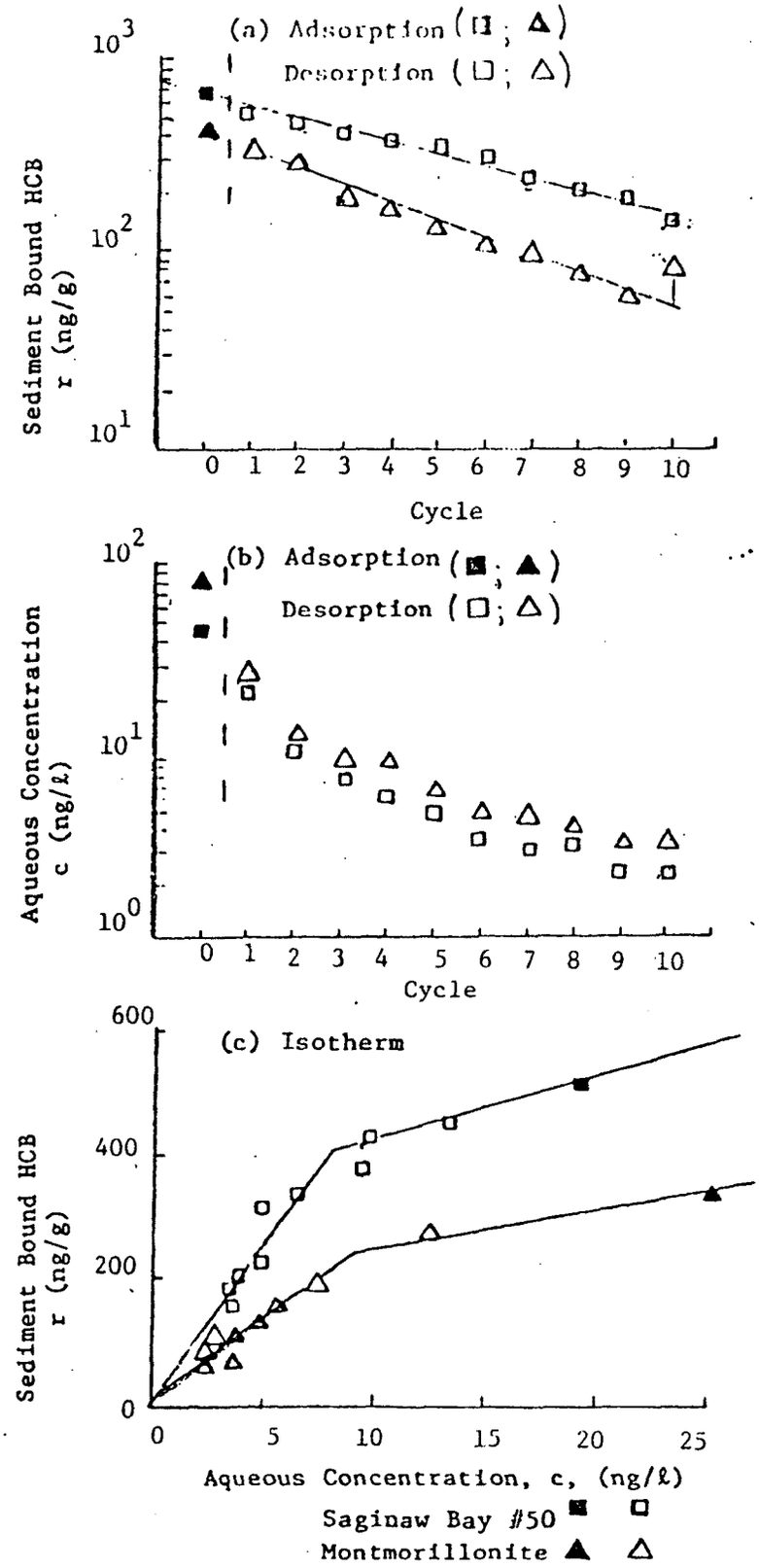



Fig. VIII-12. Consecutive Desorption. Saginaw Bay #50 and Montmorillonite. m = 200 mg/ℓ. Distilled Water (a) Sediment Bound HCB, r, and (b) aqueous concentration, c, versus desorption cycle. (c) Isotherm

surfaces. The formation of face to face versus edge to face bonds could result in differing degrees of desorption. Such behavior has been suggested to account for the adsorption of certain pesticides to sediments (Huang, 1970).

## G. Conclusion

It appears that while HCB adsorption to sediments may be ultimately reversible, the process does not appear to be defined by a single reversible isotherm. Partition coefficient values for desorption isotherms are substantially greater than those obtained for adsorption. Consecutive desorption data suggests the possibility of the formation of HCB-sediment bonds of differing strengths. Overall, the results indicate that the use of adsorption isotherms alone, will result in overestimates of the amount of HCB released from sediments to natural waters.

TABLE VIII-6

Consecutive Desorption

m = 220 mg/ℓ

| Cycle | Montmorillonite | | | Saginaw Bay #50 | | |
|---|---|---|---|---|---|---|
| | $c_T$ (ng/ℓ) | c (ng/ℓ) | r (ng/g) | $c_T$ (ng/ℓ) | c (ng/ℓ) | r (ng/g) |
| 0 | 176.36 | 81.04 | 433.10 | 195.03 | 47.25 | 671.01 |
| 1 | 95.72 | 25.20 | 335.28 | 126.67 | 19.15 | 514.43 |
| 2 | 66.83* | 12.44 | 272.62 | 102.33* | 13.34 | 448.04 |
| 3 | 45.36 | 7.47 | 190.24 | 94.02 | 9.71 | 424.61 |
| 4 | 35.96* | 5.67 | 159.06 | 80.19* | 9.48 | 374.46 |
| 5 | 30.06* | 4.82 | 131.99 | 70.73* | 6.64 | 339.48 |
| 6 | 24.95* | 3.66 | 111.90 | 64.11* | 4.97 | 313.48 |
| 7 | 21.52 | 2.71 | 99.21 | 46.62 | 4.81 | 221.13 |
| 8 | 17.81* | 3.66 | 73.75 | 39.67* | 3.98 | 198.43 |
| 9 | 13.27* | 2.31 | 59.32 | 35.60* | 3.43 | 179.22 |
| 10 | 17.48 | 2.23 | 82.08 | 28.32 | 3.54 | 137.97 |

*These values are not measurements but are calculated by mass balance

## REFERENCES


Bailley, G.W., and J.L. White. Factors Influencing the Adsorption, Desorption and Movement of Pesticides in Soil. Residue Rev., 32. pp. 29-92, 1970.

Baughman, G.L., Lassiter, R.R. "Prediction of Environmental Pollutant Concentration" in Estimating the Hazard of Chemical Substances to Aquatic Life eds. J. Cairns, K.L. Dickson, K.L. Maki. ASTM STP 657, p. 35. 1978.

Briggs, G.G. A Simple Relationship between Soil Adsorption of Organic Chemicals and their Octanol/Water Partition Coefficients. Proc. 7th British Insecticide and Fungicide Conf. p. 475-478. 1973.

Chiou, C.T., V.H. Freed, D.W. Schmedding, R.L. Kohnert. Partition Coefficient and Bioaccumulation of Selected Organic Chemicals, Environmental Science and Technology, Vol. 11, #5, pp. 475-478.

Connolly, J. The Effect of Sediment Suspension on Adsorption and Fate of Kepone. Ph.D. Thesis, University of Texas, Austin, Texas. 208 pages. 1980.

Crittenden, J.C. and W.J. Weber. Model for Design of Multicomponent Adsorption Systems, J. Environ. Engr. Div. ASCE, p. 1175. 1978.

Dexter, R.N. An Application of Equilibrium Adsorption Theory to the Chemical Dynamics of Organic Compounds in Marine Ecosystems. Ph.D. Dissertation, University of Washington, 1976.

Dexter, R.N. and S.P. Pavlov. Mass Solubility and Aqueous Activity Coefficients of Stable Organic Chemicals in the Marine Environment: Polychlorinated Biphenyls. Marine Chemistry, Vol. 6, pp. 41-53.

Dinauer, R.C., ed. Pesticides in Soil and Water. Soil Science Society of Am. Inc. Madison Wis. 1974.

Farquhar, G.J., T.W. Constable, A. Van Norman and H. Mooij. PCB Interactions with Soil, J. Environ. Sci. Health. A 14(7), pp. 547-557. 1979.

Furukawa, K., K. Tonomuru, and A. Kamibayashi. Effect of Chlorine Substitution on the Biodegradability of Polychlorinated Biphenyls, Applied and Environmental Microbiology, Vol. 34, #2, pp. 223-227. 1978.

Gilbert, M. and H. Laudelout. Tactoids in Hydrogen Montmorillonite Suspensions. J. Colloid Interface Science, Vol. 36, pp. 486-489. 1971.

Glooschenko, W.A., W.M.J. Strachan, R.C. Sampson. Distribution of Pesticides and PCBs in Water, Sediments, and Seston of the Upper Great Lakes. Pestic. Monit. J. Vol. 10, p. 61-67, 1976.

Haile, C.L., G. Veith, G.F. Lee, W.C. Boyle. Chlorinated Hydrocarbons in the Lake Ontario Ecosystem (IFYGL) EPA-660/3-75-002. NERC, EPA, Corvallis, Or. 1975.

Halter, M.T. and H.E. Johnson. A Model System to Study the Desorption and Biological Availability of PCB in Hydrosoils, in Aquatic Toxicology and Hazard Evaluation, A.S.T.M. STP 634, F.L. Mayer and J.L. Hamelink, eds., American Society for Testing and Materials, pp. 178-195. 1977.

Hamaker, J.W. and J.M. Thompson. "Adsorption", in Organic Chemicals in the Soil Environment, edited by C.A. Goring and J.W. Hamaker, Marcel Dekker, Inc., New York. 1972.

Haque, R., F.T. Lindstrom, V.H. Freed, R. Sexton. Kinetic Study of the Sorption of 2,4-D on Some Clays. Envir. Sci. Tech. 2(3). p. 207, 1968.

Haque, R., and W.R. Coshow. Adsorption of Isocil and Bromocil from Aqueous Solution onto Some Mineral Surfaces. Environ. Sci. Technol. Vol. 5, pp. 139-141, 1971.

Haque, R., D.W. Schmedding and V. Freed. Aqueous Solubility Adsorption and Vapor Behavior of Polychlorinated Biphenyl Arochlor 1254, Environmental Science and Technology, Vol. 8, #2, pp. 139-142. 1974.

Haque, R. and D. Schmedding. Studies on the Adsorption of Selected Polychlorinated Biphenyl Isomers on Several Surfaces, J. Environ. Sci. Health, B 11(2), pp. 129-137. 1976.

Hiraizumi, Y., M. Takahashi and H. Nishimura. Adsorption of Polychlorinated Biphenyl onto Sea Bed Sediment Marine Plankton and Other Adsorbing Agents, Environ. Sci. Technology, Vol. 13, #5, pp. 580-584. 1979.

Huang, Ju-C, Liao, C. Adsorption of Pesticides by Clay Minerals. J. Sanit. Engr. Div., ASCE, Vol. 96, SA5, pp. 1057-1078. 1970.

Huang, J.C. Effect of Selected Factors on Pesticide Sorption and Desorption in the Aquatic System, J. of Water Pollution Control Federation, pp. 1739-1748. 1971.

Karickhoff, S.W., D.S. Brown and T.A. Scott. Sorption of Hydrophobic Pollutants on Natural Sediments, Water Research, Vol. 13, pp. 241-248. 1979.

Laffer, B.G., A.M. Posner, and J.P. Quirk. Optical Density of Montmorillonite Suspensions During Sodium-Calcium Exchange, J. Colloid Interface Sci., 20/30 #3. pp. 355-358. 1969.

Lambert, S.M. Functional Relationship between Sorption in Soil and Chemical Structure. J. Agric. Food Chem. Vol. 15, pp. 572-576, 1967.

Lee, M.C., R.A. Griffin, M.L. Miller, and E.S.K. Ghian. Adsorption of Water Soluble Polychlorinated Biphenyl Arochlor 1242 and Used Capacitor Fluid by Soil Materials and Coal Char, J. Environ. Sci. Health, A 14(5), pp. 415-442. 1979.

Lotse, E.G., D.A. Graetz, G. Chesters, G.B. Lee, and L.W. Newland. Lindane Adsorption by Lake Sediments, Environ. Sci. Technol., Vol. 2 #5, pp. 353-357. 1968.

Neihof, R. and G. Loeb. Dissolved Organic Matter in Seawater and the Electric Charge of Immersed Surfaces. J. Mar. Res. 32, pp. 5-12. 1974.

O'Connor, D.J., Connolly, J.P. The Effect of Concentration of Adsorbing Solids on the Partition Coefficient". Water Research, 14, p. 1517. 1980.

O'Connor, D.J. Schnoor, J.L. Distribution of Organic Chemicals and Heavy Metals in Lakes and Reservoirs, Manhattan College Technical Report. 1980.

Paris, D.F., W.C. Steen, G.L. Baughman. Role of Physico-Chemical Properties of Aroclors 1016 and 1242 in Determining their Fate and Transport in Aquatic Environments. Chemosphere, 4 pp. 319-325. 1978.

Pavlov, S.P. and R.N. Dexter. Distribution of Polychlorinated Biphenyls (PCB) in Estuarine Ecosystems. Testing the Concept of Equilibrium Partitioning in the Marine Environment, Environ. Sci. Technology, Vol. 13, #1, pp. 65-70. 1979.

Peck, D.E., D.L. Corwin and W.J. Farmer. Adsorption-Desorption of Diuron by Freshwater Sediments, J. Environ. Quality, Vol. 9, #1, pp. 101-106. 1980.

Pierce, R.H., Jr., Olney, C.E., Felbeck, G.T., Jr. pp'-DDT Adsorption to Suspended Particulate Matter in Sea Water. Geochim. Cosmochim. Acta, Vol. 38, pp. 1061-1073. 1974.

Rao, P.S.C., J.M. Davidson, D.P. Kilcrease. Examination of Desorption Isotherms for Soil Pesticide Systems. Agronomy Abstracts, 34. 1978.

Rao, P.S.C. and J.M. Davidson. Estimation of Pesticide Retention and Transformation Parameters Required in Nonpoint Source Pollutant Models, in Environmental Impact of Nonpoint Source Pollution, edited by M.R. Overcash and J.M. Davidson, Ann Arbor Science Publishers, Inc., pp. 23-67. 1980.

Smith, V.E., K.W. Lee, J.C. Filkins, K.W. Hartwell, K.R. Rygwelski, J.M. Townsend. Survey of Chemical Factors in Saginaw Bay (Lake Huron) Ecol. Res. Series. USEPA, Duluth, MN. No. EPA-600/3-77-125. 1977.

Steen, W.C., D.F. Paris and G.L. Baughman. Partitioning of Selected Polychlorinated Biphenyls to Natural Sediments, Water Research, Vol. 12, pp. 655-657. 1978.

Sweitzer, J. and B.R. Jennings. The Association of Montmorillonite by Light Scattering in Electric Fields. J. Colloid Interface Sci., Vol. 37 #2, pp. 443-457. 1971.

REFERENCES (cont'd)

Thomann, R.V., Di Toro, D.M. Preliminary Model of Recovery of the Great Lakes following Toxic Substance Pollution Abatement. Workshop on Scientific Basis for Dealing with Toxic Chemical Substances in the Great Lakes. Great Lakes Basin Commission, Ann Arbor, Mich. Submitted to J. Great Lakes Res.

Tucker, E.S., V.W. Saeger, O. Hicks. Activated Sludge Primary Biodegradation of Polychlorinated Biphenyls, Bulletin of Environmental Contamination and Toxicology, 14; 705-713. 1975.

van Genuchten, M.Th., Wierenga, P.J., O'Connor, G.A. Mass Transfer Studies in Sorbing Porous Media: III. Experimental Evaluation with 2,4,5-T. Soil Sci. Soc. Am. J., Vol. 41, pp. 278-285. 1977.

van Olphen, H. An Introduction to Clay Colloid Chemistry. Wiley Interscience, New York. 1963.

Veith, G.D., D.W. Kuehl, F.A. Puglisi, G.E. Glass, and J.G. Easton. Residues of PCB's and DDT in the Western Lake Superior Ecosystem. Firch Environ. Contam. Toxicol., 5, pp. 487-499. 1977.

Wahid, P.A. and N. Sethunathan. Sorption-Desorption of Parathion in Soils. J. Agric. Food Chem. Vol. 26, p. 101-105. 1978.

Weber, Jr., W.J., Sherrill, J.D., Pirbazari, M., Uchrin, C.G., Lo, T.Y., Transport and Differential Accumulation of Toxic Substances in River-Harbor-Lake Systems, in Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. ed. R. Haque. Ann Arbor Science Pub., Inc., Ann Arbor, Mich., pp 191-213. 1980.

Wildish, D.J., Metcalfe, C.D., Akagi, H.M., McLeese, D.W. Flux of Aroclor 1254 Between Estuarine Sediments and Water. Bull. Environ. Contam. Toxicol., Vol. 24, pp 20-26. 1980.

# Adsorption and Desorption of

# Hexachlorobiphenyl

## Part B

## Exchangeable and Nonexchangeable Components

FIGURES - Part B

FIG. #


I-1. Hexachlorobiphenyl Adsorption-Desorption Isotherms Saginaw Bay Sediment, Station #50. (a) Adsorption and Single Desorption data, m = 220 mg/ℓ (b) Adsorption and Consecutive Desorption data, m = 1100 mg/ℓ. Data on averages of three replicates . . . . . 141

I-2. Schematic illustration of the definitions of nonexchangeable, $r_o$, and the exchangeable components at adsorption, $r_{xa}$, and desorption, $r_{dx}$, assuming a linear consecutive desorption isotherm . . . . . 144

I-3. Exchangeable-Nonexchangeable Component Model of Desorption: Illustration of Data Analysis . . . . . 146

I-4. Hexachlorobiphenyl Adsorption-Desorption Isotherms, Saginaw Bay Sediment, Station #50, m = 220 mg/ℓ. (a) Adsorption and Single Desorption data and Linear Isotherms. (b) Nonexchangeable component estimates from eq. (I-3) and linear isotherm. (c) Exchangeable linear isotherm: adsorption (eq. I-1) and desorption (eq. I-2). estimates of the exchangeable component . . . . . 147

I-5. Hexachlorobiphenyl Adsorption-Desorption Isotherms - Montmorillonite m = 220 mg/ℓ, Kaolinite, m = 1000 mg/ℓ. (a) Adsorption and Single Desorption data and linear isotherms. (b) Nonexchangeable component estimate (eq. I-3) and linear isotherm. (c) Exchangeable linear isotherm, adsorption (eq. I-1) and desorption (eq. I-2) estimates of the exchangeable component . . . . . 151

I-6. Hexachlorobiphenyl Adsorption-Desorption and Consecutive Adsorption, Saginaw Bay Sediment, Station #50 (m = 1100 ppm) and Montmorillonite (m = 1100 ppm and 2 meq/ℓ $NaHCO_3$ buffer) . . . . . 158

| FIG # | | Page |
|---|---|---|
| I - 7. | Hexachlorobiphenyl Adsorption-Desorption Isotherms Saginaw Bay Sediment, Station #50 m = 55 mg/ℓ, effect of adsorption time. See fig. 3 caption. Dotted isotherms are the two hour results replotted for visual reference . . . . . | 159 |
| II- 1. | Adsorption and Desorption Partition Coefficient variation with Adsorbent concentration. Saginaw Bay Station #50 and Montmorillonite. Distilled water and supernatant aqueous phases . . . . . | 172 |
| II- 2. | Nonexchangeable and Exchangeable Partition Coefficient variation with adsorbent concentration Saginaw Bay Station #50. Distilled water and supernatant as aqueous phase . . . . . | 174 |
| II-3. | Nonexchangeable and Exchangeable Partition Coefficient variation with adsorbent concentration, Montmorillonite. Distilled water and supernatant as aqueous phase. . . . . | 175 |
| II-4. | Adsorption and Desorption Isotherms for Saginaw Bay Stations and Montmorillonite. Aqueous phase is Distilled Water except for Montmorillonite (2mM $NaCHO_3$) m = 1100 mg/ℓ except for Station #69 (m = 20,000 mg/ℓ) . . . . . | 179 |
| II-5. | Variation of Nonexchangeable Partition Coefficient and exchangeable distribution coefficient with respect to percent volatile solids and specific surface area . . . . | 182 |
| II-6. | Comparison of Calculated (using the regression equations) and observed coefficients . . . . . | 184 |
| II-7. | Ratio of Particulate to Dissolved fraction of HCB versus adsorbent concentration . . . . . | 187 |

| FIG. # | | Page |
|---|---|---|
| II- 8 | Ratio of Particulate to Dissolved fraction of PCB versus suspended solids concentration for Saginaw Bay. All cruises. Line if regression equation: $\log_{10} f_p/f_d = a + bm$; $a = -0.532$; $b = 0.0343$ . . . . . | 188 |
| II- 9. | Particulate Fraction versus adsorbent concentration with and without adsorbent dependent partitioning . . . . . | 190 |
| III-1. | Resuspension Experimental Procedure . . . . . | 194 |
| III-2. | Resuspension Experiment - Model Predictions and Observations | 200 |
| III-3. | Exchangeable and Nonexchangeable Component Behavior at Adsorption and Resuspension Equilibria . . . . . | 201 |
| III-4. | Experimental Procedure for Dilution Experiment . . . . . | 203 |
| III-5. | Comparison of Observed Particulate to Dissolved Fraction Ratio-Adsorbent Mass Relation Without Correction due to the Dilution Equilibration . . . . . | 206 |
| III-6. | Comparison of Observed Particulate to Dissolved Fraction Ratio to Adsorbent Mass, modified by $c_a/c_{d\ell}$ as predicted from the Exchangeable-Nonexchangeable Model . . . . . | 208 |
| III-8. | Exchangeable Partition Coefficient at Adsorption and Dilution Equilibrium Estimated from the Subsequent Desorption, versus Adsorbent Concentration, $m_a$ and $m_{d\ell}$ respectively . | 211 |
| III-9. | Particulate fraction versus adsorbent mass for reversible desorption, eq. (III-28); and exchangeable-nonexchangeable desorption, eq. (III-30). $\pi_o = 10^4 \ell/kg$, $\nu_x = 0.5$ . . . | 215 |

TABLES - Part B


| TABLE | | Page |
|---|---|---|
| I-1. | Isotherm Parameters for HCB Adsorption-Desorption | 149 |
| I-2. | Adsorption and Consecutive Desorption Isotherm Parameters | 153 |
| II-1. | Regression Analyses[§] of Adsorbent Concentration Effect | 176 |
| II-2. | Experimental Data for Partition Coefficients | 180 |
| II-3. | Multiple Linear Regression Analysis* | 183 |
| III-1. | Resuspension Experiment - Saginaw Bay #50 | 196 |

## SECTION I

## EXCHANGEABLE AND NONEXCHANGEABLE COMPONENTS MODEL OF ADSORPTION AND DESORPTION

### A. Introduction

The reversibility of the adsorption reaction between dissolved organic chemicals and naturally occurring soils, sediments, and suspended particles is of fundamental importance in the understanding of the fate of these chemicals in the environment. The strong particle binding tendency of persistent organic chemicals such as DDT and PCB is well known and its importance has been stressed many times (1,2,3). The issue of reversibility becomes critical if the adsorption-desorption behavior of a chemical is to be expressed quantitatively within the framework of mass balance equations. These are used in mathematical models of the transport of chemicals in soil column leaching laboratory and field experiments (4) and in models of the fate of chemicals in natural water systems (5,6,7) In the formulations used to date, with a notable exception to be discussed below, the formulations used to express the adsorption and desorption reactions assume reversible behavior, that is, at equilibrium, the same isotherm applies for adsorption and desorption.

The difficulty with this assumption is that for many organic chemicals and many naturally occurring adsorbents, laboratory adsorption and subsequent desorption experiments demonstrate only partially reversible behavior. That is, the measured desorption does not conform to the adsorption isotherm. This troublesome behavior has been ascribed to a number of possible experimental artifacts but the weight of the evidence so far suggests that indeed the effect is real (8). It is described as a nonsingular or hysteretic isotherm.

In the experiments described in Part A, Section VIII, this nonsingular behavior was confirmed and, using various experimental procedures, it was found to persist. This suggests that it is necessary to account for this behavior in a quantitative and consistent way.

It is the purpose of Part B of this report to present a framework within which this nonsingular behavior can be analyzed in a manner that can be easily incorporated into mass balance calculations. The presentation is

restricted to linear isotherms since these have been found to be applicable to HCB adsorption-desorption, at least until small aqueous concentrations are achieved. However, the basic framework is not restricted to only this class of isotherms.

## B. Previous Methods of Analysis

A typical desorption experiment follows an adsorption experiment in which, at equilibrium, the sediment bound chemical concentration $r_a = q/m$, (the mass of adsorbate/mass of adsorbent), and the dissolved aqueous concentration, $c_a$, are measured. The solids are separated, the supernatant is discarded and replaced by adsorbate-free aqueous phase. At desorption equilibrium the particulate, $r_d$, and aqueous, $c_d$, concentrations are measured. If this procedure is repeated at constant temperature for different initial adsorbate concentrations, an isotherm results. The adsorption isotherm relates $r_a$ to $c_a$ and for the linear case a partition coefficient for adsorption, $\pi_a$, can be defined as the slope of the isotherm: $r_a = \pi_a c_a$. Similarly, if the desorption points fall on a straight line, a desorption "isotherm" can be defined, $r_d = \pi_d c_d$, with "partition coefficient", $\pi_d$. The result is illustrated in fig. I-1a for HCB adsorption-desorption with Saginaw Bay sediment.

Strictly speaking, it is incorrect to use the term isotherm for the desorption curve since in the presence of nonreversibility the desorption points obtained depend on the previous adsorption and the details of the desorption step rather than being strictly governed by the causal relationship $r_d = \pi_d c_d$. However, with this restriction kept in mind, the procedure is well defined and, for the sake of a simple nomenclature, this curve is called a single desorption isotherm. Many examples of these isotherm pairs exist in the literature: for various adsorbate-absorbent systems: Dieldrin - Montmorillonite (10); pp'-DDT - Humic Acid (11); Aldicarb, Terbufos - Soil (12); and PCB (Aroclor 1254) - Estuarine Sediment (13). The nonsingular nature of the isotherms is consequence of the desorption partition coefficient, $\pi_d$, being greater than the adsorption partition coefficient, $\pi_a$.

A more refined and time-consuming experimental procedure is, after adsorption, to extend each initial desorption step by performing subsequent multiple

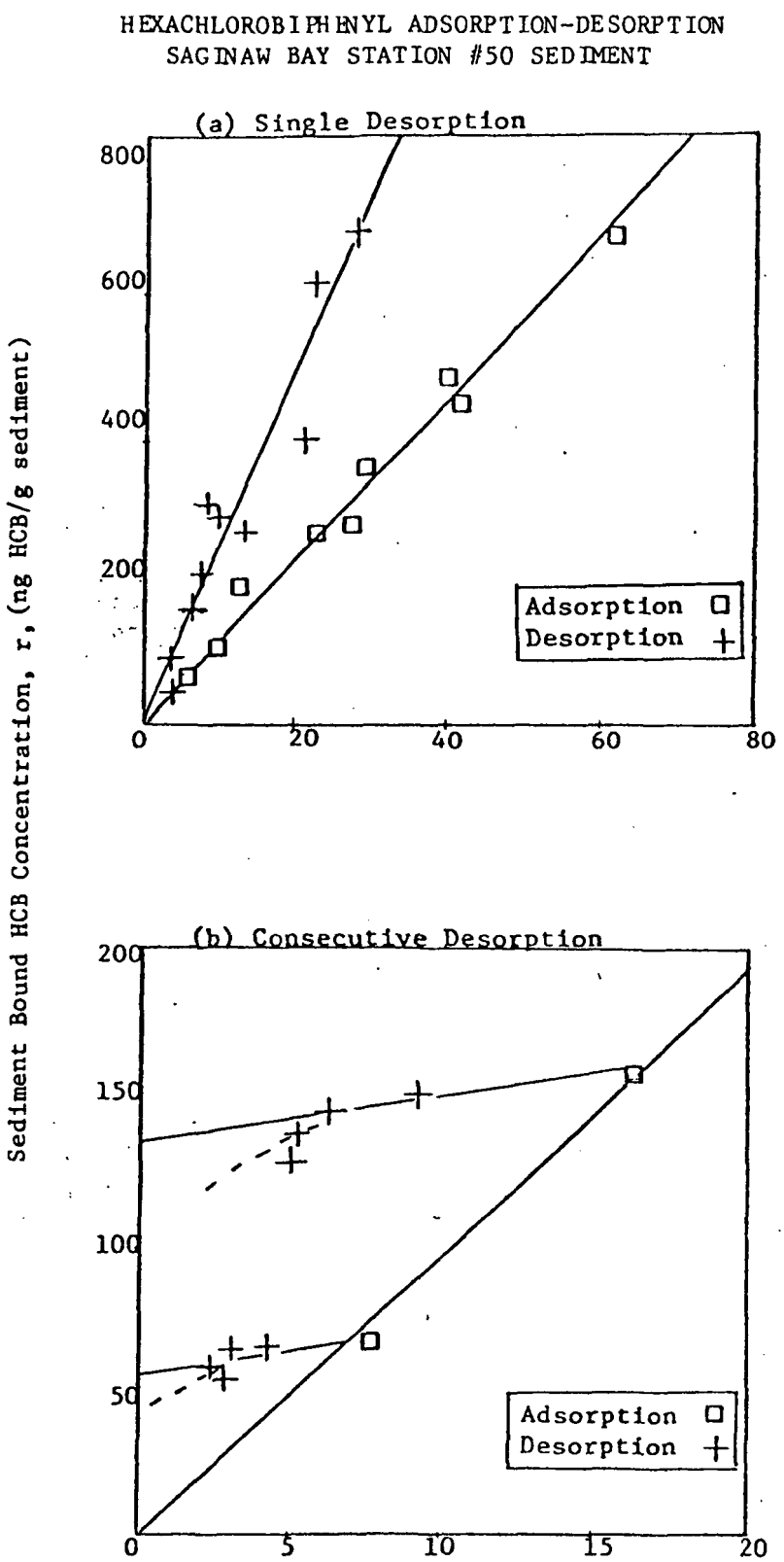



Fig. I-1. Hexachlorobiphenyl Adsorption-Desorption Isotherms Saginaw Bay Sediment, Station #50. (a) Adsorption and Single Desorption data, m = 220 mg/ℓ (b) Adsorption and Consecutive Desorption data, m = 1100 mg/ℓ. Data on averages of three replicates.

desorptions. The points generated in this fashion can also be described by an isotherm, which may be termed the consecutive desorption isotherm as shown in fig. I-1b and discussed in Part A, Section VIII. Examples of these consecutive desorption isotherms with significant nonreversibility have also been reported for various adsorbate-adsorbent systems: Atrazine - Soil (14,15); Picloram - loam (4) Fluometuron - fine sandy loam (16); 2,4,5-T - clay (17) and loam (18) Parathion - Soil (19), Montmorillonite (20), and sandy loam (21); and Diuron - Soil (15), and lake sediment (22). It was first shown for Atrazine (14) that each consecutive desorption isotherm, corresponding to each adsorption point, can be represented as a Freundlich isotherm. However the isotherm parameters were found to depend upon the individual adsorption concentrations. Thus although the description of the desorption data is adequate, it is not concise.

This framework has been successfully applied to a mass balance analysis of Picloram - soil column leaching experiments (4). At the start of the experiment the initial adsorption at each computational node within the column follows the adsorption isotherm as concentrations increase. Then the influent concentration is decreased and as the concentrations within the column which are computed to begin decreasing, the isotherm branches off along the appropriate desorption isotherm with the appropriate interpolated parameters. An interesting question arises if the influent concentration to the column were again to increase. What is the proper isotherm relationship in this case. Such questions, and the desire for a more concise description of the adsorption-desorption data leads to the model described below.

The results of experimental consecutive desorption studies indicate that there exists a significant component of the adsorbed HCB which is extremely difficult to desorb. The problems involved in experimentally achieving zero aqueous concentration make it uncertain as to whether or not all of this fraction is ultimately desorbable under the varying physical chemical conditions of natural waters. However, it is clear that for HCB, see fig. I-1b, and the other data in Part A and for other adsorbates - adsorbent systems cited previously, that the particulate HCB concentrations for the initial few desorptions are significantly above the adsorption isotherm. That is, a portion of the adsorbate does not significantly desorb even at low aqueous concentrations.

To idealize the situation, consider fig. I-2. The adsorption isotherm is assumed to be linear as is the initial stages of the consecutive desorption isotherm which is presumed to describe the behavior of the readily reversible fraction. This idealization is important since it limits the applicability of the analysis to those aqueous concentrations for which the consecutive desorption data conform to the linear assumption. Define the nonexchangeable component concentration, $r_o$, as the extrapolated intersection of the consecutive desorption isotherm and the ordinate. Define the exchangeable components at adsorption, $r_{xa}$, and at the first desorption, $r_{xd}$, as the difference between the observed adsorption and desorption particulate concentration and the extrapolated nonexchangeable concentration:

$$r_{xa} = r_a - r_o \tag{I-1}$$

$$r_{xd} = r_d - r_o \tag{I-2}$$

This component is exchangeable since it responds to the change in aqueous concentration from $c_a$ at adsorption equilibrium to $c_d$ at desorption equilibrium.

From the geometry of the linear isotherms, or from an algebraic derivation given in Appendix I of this section, the exchangeable and nonexchangeable components can be computed from each pair of adsorption ($r_a$, $c_a$) and single desorption ($r_d$, $c_d$) values. The equation for the nonexchangeable component is:

$$r_o = \frac{r_d - \beta\, r_a}{1 - \beta} \tag{I-3}$$

where $\beta = c_d/c_a$. The exchangeable components follow by difference, eqs. (I-1) and (I-2). The analysis of a hypothetical set of data is illustrated in fig. I-3. A conventional adsorption-desorption data set (assuming three adsorption points and three desorption points for clarity) is shown in fig. I-3a. The two distinct isotherms are shown. Each single pair of points, corresponding to a single adsorption-desorption experiment, are linearly extrapolated and the intersection of this line and the ordinate defines the particulate concentration, $r_o$, which is nonexchangeable (since it remains on the particles even at zero aqueous concentration). Once the nonexchangeable component concentration, $r_o$, has been found, the differences between this concentration

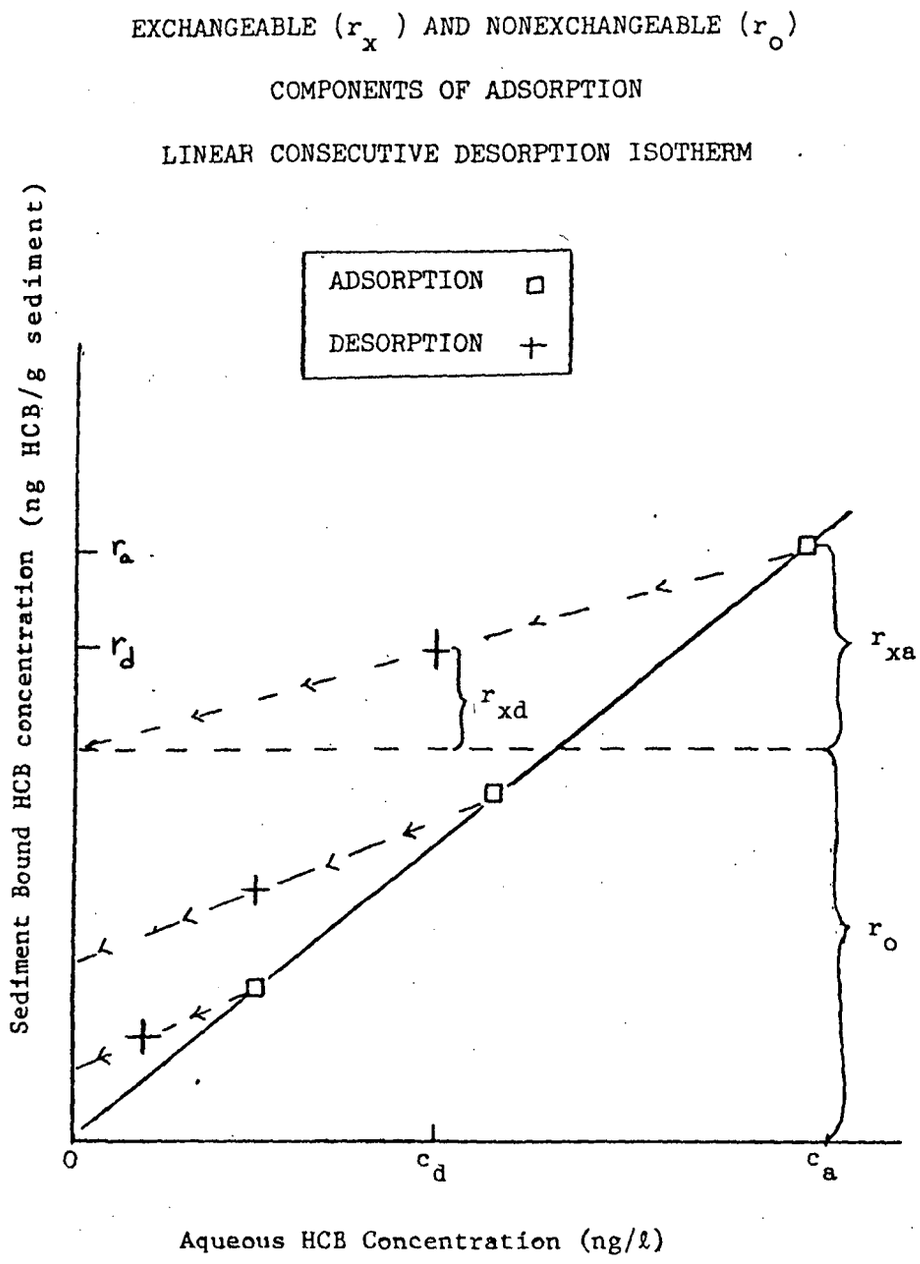



Fig. I-2. Schematic illustration of the definitions of nonexchangeable, $r_o$, and the exchangeable components at adsorption, $r_{xa}$, and desorption, $r_{dx}$, assuming a linear consecutive desorption isotherm.

and that found at adsorption and desorption equilibria must be the exchangeable component since two components are assumed to be present. The fact that it responded to the decrease in aqueous concentration that occurred from adsorption to desorption equilibrium supports its exchangeability. Note that two exchangeable component data points result: at adsorption equilibrium, $r_{xa}$, and at desorption equilibrium, $r_{xd}$. These correspond to the two aqueous concentrations $c_a$ and $c_d$, respectively. If this analysis is repeated for the remaining two adsorption-desorption data pairs in the illustration, the result is six pairs of exchangeable component-aqueous concentration data.

The validity of this analysis depends upon the observation that all the exchangeable component data conform to a single isotherm, fig. I-3c. The same isotherm applies to all exchangeable component data, regardless of whether they correspond to the quantity of exchangeable component that is present at adsorption, $r_{xa}$, in equilibrium with aqueous concentration, $c_a$, or at desorption, $r_{xd}$, in equilibrium with aqueous concentration, $c_d$. That is, the exchangeable component is behaving in accordance with classical reversible adsorption-desorption theory.

The three nonexchangeable component concentrations calculated from the data analysis have also been found to follow one isotherm, illustrated in fig. I-3d. They are a linear function of the adsorption aqueous concentration as illustrated.

Figure I-4, which are the experimental data in fig. I-1a analyzed using eqs. (I-1,2,3), shows that indeed all the exchangeable adsorption and desorption points are described by a single, in this case linear, exchangeable isotherm:

$$r_x = \pi_x c \qquad \text{(I-4)}$$

independent of which adsorption experiment is considered, and whether $r_x = r_{xa}$ or $r_{xd}$ and $c = c_a$ or $c_d$ respectively (Figure I-4c).

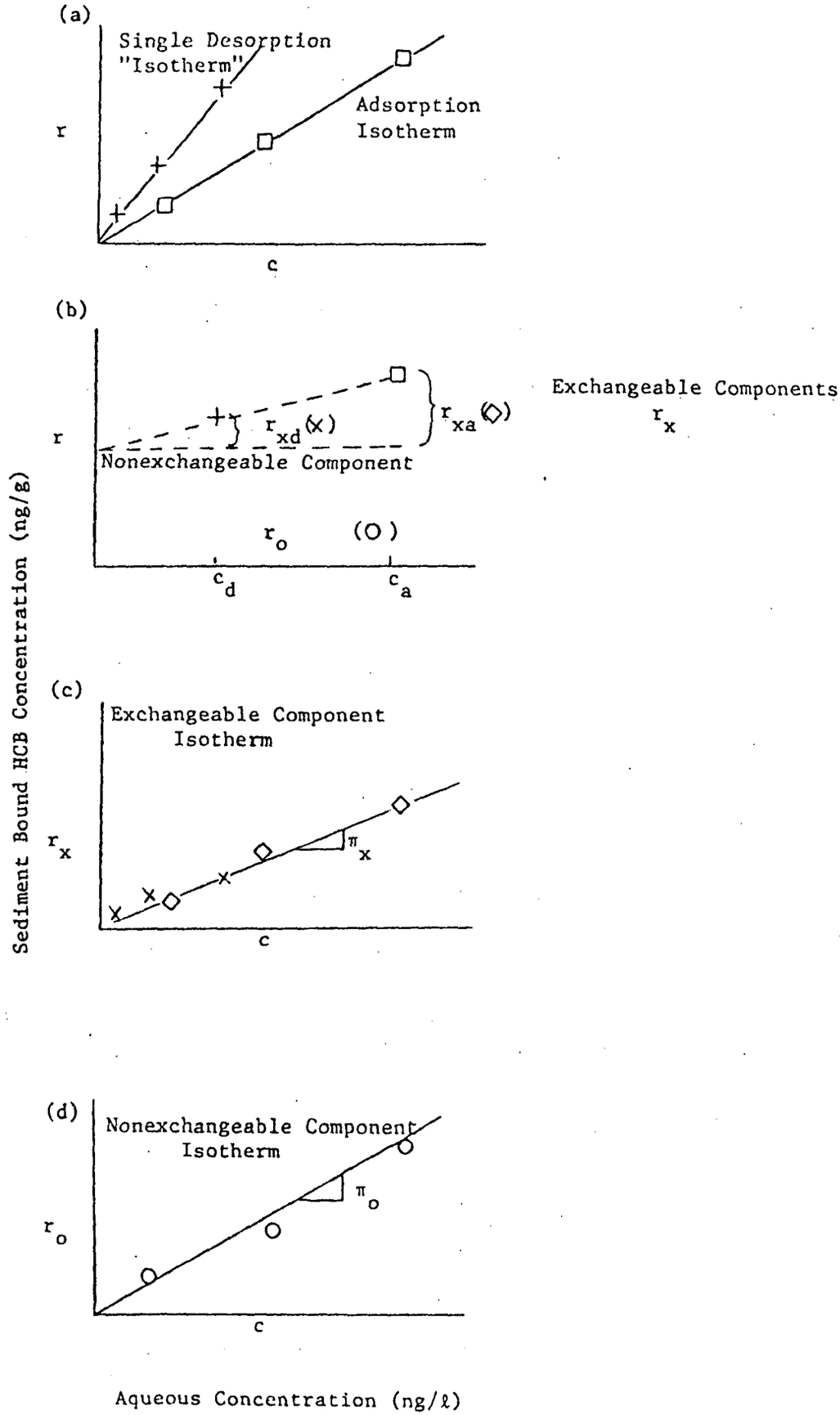
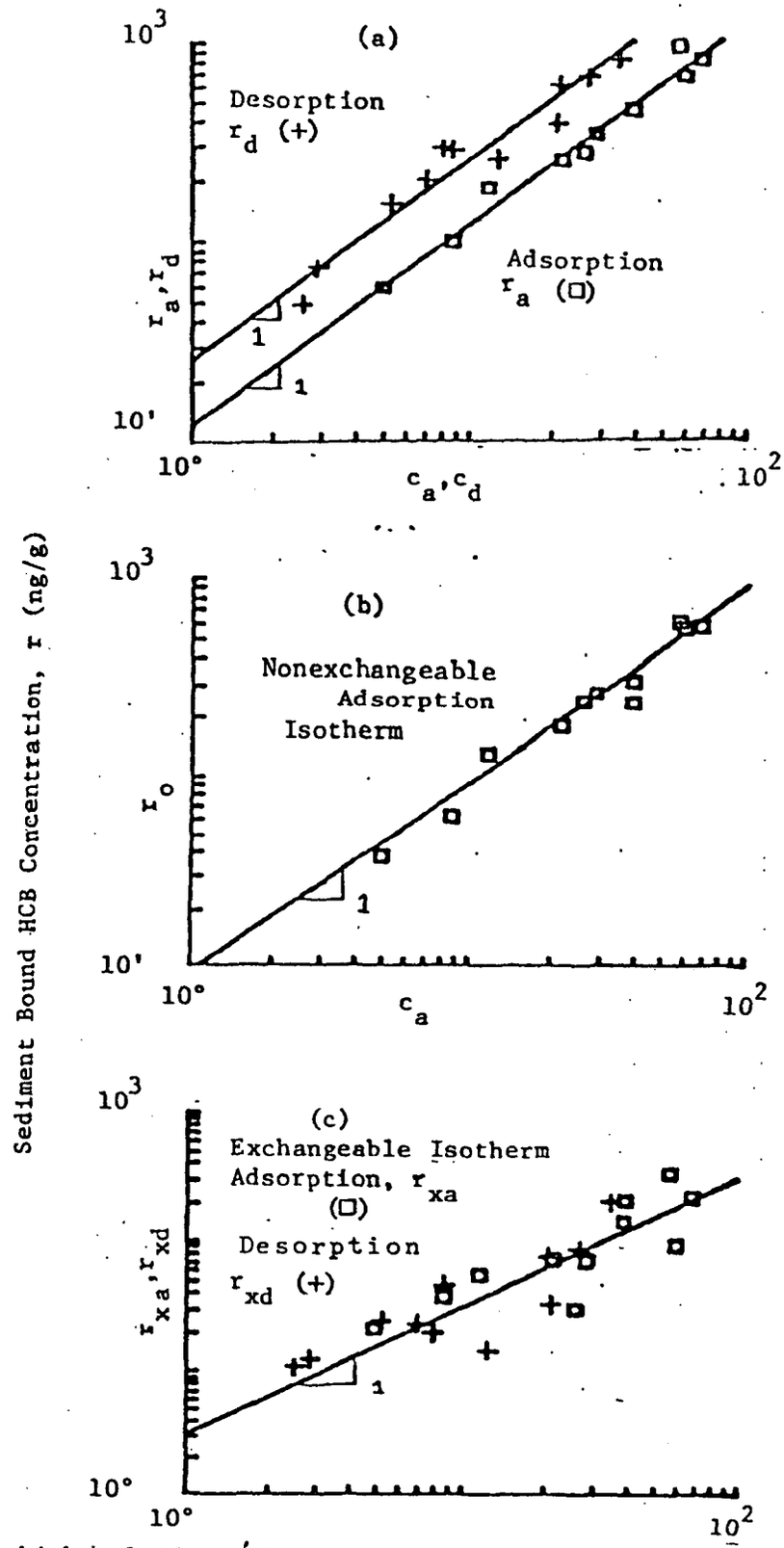



Fig. I-3. Exchangeable-Nonexchangeable Component Model of Desorption: Illustration of Data Analysis

HEXACHLOROBIPHENYL ADSORPTION-DESORPTION
SAGINAW BAY STATION #50 SEDIMENT




I-4. Hexachlorobiphenyl Adsorption-Desorption Isotherms, Saginaw Bay Sediment, Station #50, m = 220 mg/ℓ. (a) Adsorption and Single Desorption data and Linear Isotherms. (b) Nonexchangeable component estimates from eq. (I-3) and linear isotherm. (c) Exchangeable linear isotherm: adsorption (eq. I-1) and desorption (eq. I-2). estimates of the exchangeable component.

Figure I-4b illustrates that for these isotherm pairs the nonexchangeable component is a linear function of the equilibrium adsorption aqueous concentration, $c_a$, leading to a nonexchangeable isotherm:

$$r_o = \pi_o c_a \tag{I-5}$$

Since the adsorption isotherm is linear, the nonexchangeable component can also be expressed in terms of the particulate adsorption concentration: $r_o = \pi_o r_a/\pi_a$. Which is the more useful characterization is discussed subsequently. The experimental conditions and isotherm parameters are listed in Table I-1.

## D. Relationship to Single Desorption Isotherm

The formulation presented above is based upon the consecutive desorption isotherm (fig. I-1b). It is of interest to inquire what is the relationship of this analysis to the single desorption isotherm (fig. I-1a). It can be shown (Appendix II of this section) that, if the single desorption and adsorption isotherms are linear, and essentially all the adsorbate mass is associated with the particles at the start of the desorption, that is, that the glass desorption is small and $mr_a = c_{Td}$ as is the case for these experiments (Section II of Part A), then the exchangeable and nonexchangeable components also follow linear isotherms, eq. (I-4) and (I-5) with partition coefficients:

$$\pi_x = \frac{\pi_a}{1 + m(\pi_d - \pi_a)} \tag{I-6}$$

$$\pi_o = \frac{m\pi_a(\pi_d - \pi_a)}{1 + m(\pi_d - \pi_a)} \tag{I-7}$$

These relationships provide the connection between the conventional adsorption, $\pi_a$, and single desorption $\pi_d$, partition coefficients and the partition coefficients of the exchangeable, $\pi_x$, and nonexchangeable, $\pi_o$ components. In addition, they establish the fact that linear adsorption and single desorption isotherms imply linear exchangeable and nonexchangeable isotherms.

TABLE I-1

Isotherm Parameters for HCB Adsorption-Desorption

| Adsorbent* | Adsorbent Concentration m (mg/ℓ) | Adsorption Time (hr) | Desorption Time (hr) | Partition Coefficients (ℓ/kg) $\pi_a$ | $\pi_d$ | $\pi_o$ | $\pi_x$ | fig. |
|---|---|---|---|---|---|---|---|---|
| Saginaw Bay #50 | 55 | 2 | 3 | 17000 | 25100 | 5270 | 11700 | (I-6) |
| " | 55 | 48 | 48 | 18100 | 60900 | 12700 | 5400 | (I-6) |
| " | 220 | 3 | 3 | 12200 | 25800 | 9170 | 3070 | (I-3) |
| Montmorillonite | 220 | 3 | 3 | 6600 | 15600 | 4250 | 2350 | (I-4) |
| Kaolinite | 1000 | 3 | 3 | 1060 | 3290 | 730 | 327 | (I-5) |

* Aqueous Phase is Distilled Water for all experiments, Temperature = 23°C

Since the exchangeable isotherm applies at both the adsorption and single desorption aqueous concentration, and $r_o$ is constant for an adsorption-desorption experiment, each consecutive desorption isotherm can be expressed as:

$$r = r_o + \pi_x c \tag{I-8}$$

which is linear. Thus these results lead to the conclusion that an analysis using linear adsorption and consecutive desorption isotherms (fig. I-2) is consistent with linear adsorption and single desorption isotherms (fig. I-1a), and both types of isotherms are reasonable representations of linear desorption data.

The exchangeable and nonexchangeable partition coefficients can be obtained either from an analysis of the individual data, eqs. (I-1,2,3), or from the partition coefficients, $\pi_a$, $\pi_d$, and eqs. (I-6,7). This symmetry is especially useful in analyzing previously published adsorption-desorption data for which only the adsorption and single desorption isotherms are presented.

A comparison of both these methods is presented in fig. (I-5): HCB adsorption and single desorption data for montmorillonite and kaolinite respectively. The nonexchangeable (fig. I-5b) and exchangeable component estimates (fig. I-5c) are computed using eqs. (I-1,2,3). The linear isotherms are eqs. (I-4,5) using average $\pi_a$ and $\pi_d$ computed from a fit of the adsorption and single desorption data, fig. (I-5a), and eqs. (I-6) and (I-7) for the partition coefficients. Table I-1 lists the isotherm parameters. The agreement is basically due to the observed linearity of the adsorption and single desorption isotherms.

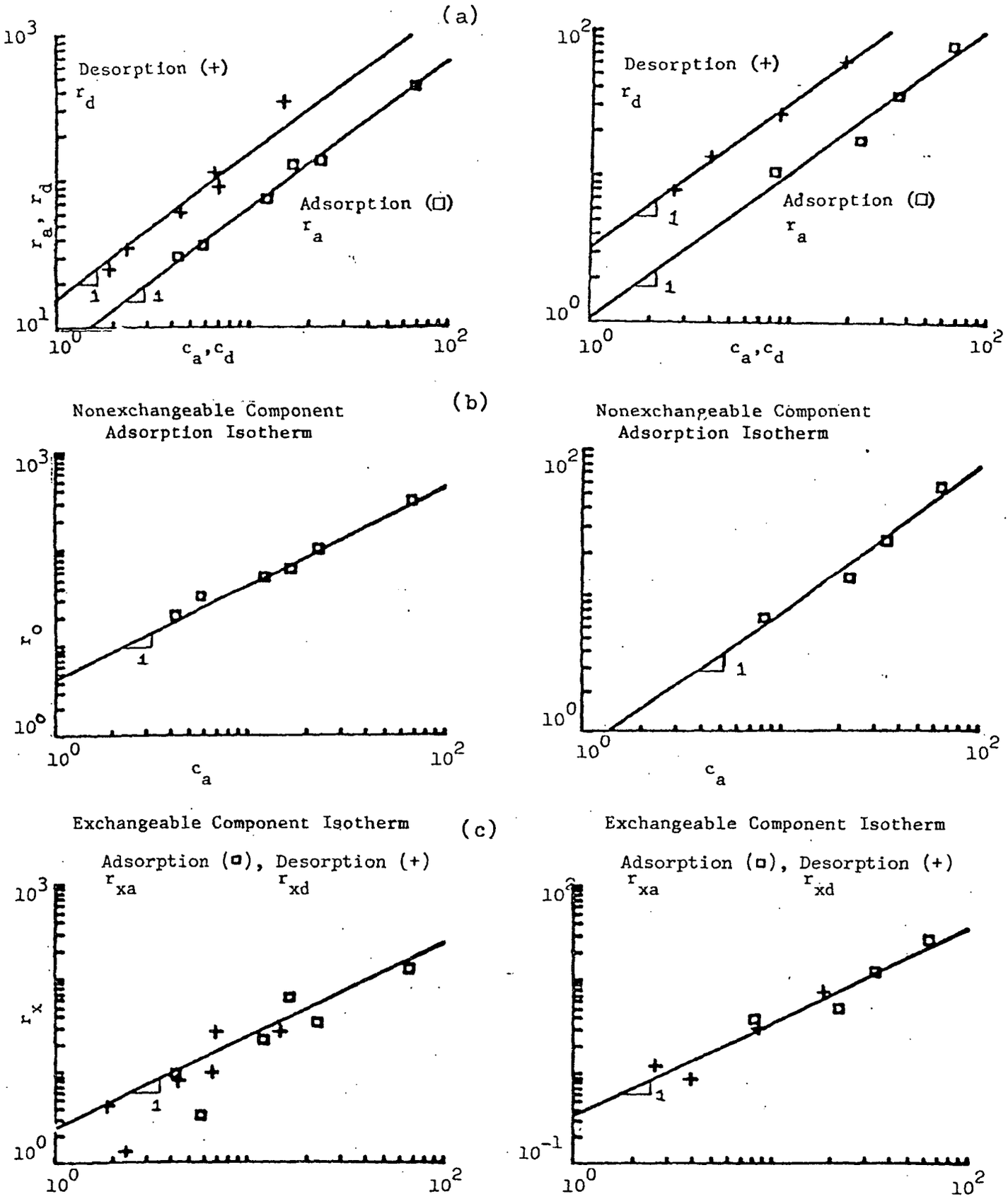
## E. Relationship to Freundlich Consecutive Desorption Isotherms

Consecutive desorption isotherms have been analyzed within the framework of Freundlich isotherms (4, 14, 17). The adsorption isotherm is represented by:

$$r_a = K_a c_a^{N_a} \tag{I-9}$$

HEXACHLOROBIPHENYL ADSORPTION-DESORPTION

MONTMORILLONITE KAOLINITE




I-5. Hexachlorobiphenyl Adsorption-Desorption Isotherms - Montmorillonite, m = 220 mg/ℓ Kaolinite, m = 1000 mg/ℓ. (a) Adsorption and Single Desorption data and linear isotherms. (b) Nonexchangeable component estimate (eq. I-3) and linear isotherm. (c) Exchangeable linear isotherm, adsorption (eq. I-1) and desorption (eq. I-2) estimates of exchangeable component.

and each consecutive desorption isotherm is represented by:

$$r_d = K_d c_d^{N_d} \tag{I-10}$$

Since the consecutive desorption isotherm intersects the adsorption isotherm at the adsorption concentration, $r_d = r_a$ at $c_d = c_a$, so that:

$$K_d = K_a c_a^{N_a - N_d} \tag{I-11}$$

which indicates that the consecutive desorption Freundlich parameter, $K_d$, is a nonlinear function of the initial adsorption concentration, $c_a$.

However a peculiar result has been noted: the ratio $N_a/N_d$ is approximately constant, $N_a/N_d \approx 2.3$. Table I-2 presents some examples. It is of interest to investigate the implication of this result with respect to an analysis based upon exchangeable and nonexchangeable components.

As shown in Table I-2, the adsorption isotherms are almost linear, $N_a \approx 1$, and the partition coefficient is the slope of the isotherm:

$$\pi_a = \frac{dr_a}{dc_a} = K_a N_a c_a^{N_a - 1} \tag{I-12}$$

The consecutive desorption isotherm, when approximated as a straight line with a non-zero intercept, eq. (I-8), has a slope $\pi_x$. If this slope is equated to the slope of the Freundlich consecutive desorption isotherm at the point of intersection of the adsorption isotherm, then:

$$\pi_x = \left.\frac{dr_d}{dc_d}\right|_{c_d = c_a} = K_d N_d c_a^{N_d - 1} \tag{I-13}$$

and using the equality of the isotherms at the intersection, eq. (I-11), yields:

$$\pi_x = K_a N_d c_a^{N_a - 1} \tag{I-14}$$

and using eq. (I-12) for $K_a$ yields:

TABLE I-2

Adsorption and Consecutive Desorption Isotherm Parameters

| Adsorbate | Adsorbent | $K_a$ $(ng/kg)/(ng/\ell)^{N_a}$ | $N_a$ | $N_a/N_d$ | $\pi_o$ (1) $(\ell/kg)$ | $\pi_x$ (1) $(\ell/kg)$ | Ref |
|---|---|---|---|---|---|---|---|
| Atrazine | Mohave Soil | 0.21 | 1.0 | 2.3 | 0.12 | 0.091 | (14) |
| Atrazine | Walla Walla Soil | 2.61 | 0.85 | 2.3 | 0.87-1.08 | 0.77-0.96 | (14) |
| Picloram | Norge Loam | 0.18 | 0.94 | 2.22-2.98 | 0.095-0.125 | 0.060-0.073 | (14) |
| 2,4,5-T | Glendale Clay Loam | 0.616 | 0.792 | 2.30 | 0.20 -0.24 | 0.12 -0.15 | (17) |

(1) $\pi_o$ and $\pi_x$ calculated using eq. (I-17) and eq. (I-13) and the experimental range in $c_a$.

$$\pi_x = \frac{N_d}{N_a} \pi_a \tag{I-15}$$

Since $N_d/N_a$ is approximately constant and $\pi_a$ is constant for linear adsorption isotherms, and almost constant for $N_a \sim 1$, the exchangeable partition coefficient is the same for each consecutive desorption isotherm. Hence to the extent that a linear approximation of the consecutive desorption isotherm is a reasonable representation, the fact that $N_d/N_a$ is the same for each consecutive desorption isotherm is a reflection of the fact that <u>all</u> the consecutive desorption isotherms can be represented by a single exchangeable component with partition coefficient, $\pi_x$.

The fact that the desorption Freundlich constant, $K_d$, is a function of the adsorption concentration, $c_a$, eq. (I-11), is reflected in the fact that the nonexchangeable component given by eq. (I-8),

$$r_o = r_a - \pi_x c_a \tag{I-16}$$

can be expressed in terms of the Freundlich parameters, eq. (I-9) and (I-15), yielding:

$$r_o = (1 - \frac{N_d}{N_a}) K_a c_a^{N_a} \tag{I-17}$$

Since $N_d/N_a$ is constant for every consecutive desorption isotherm, $r_o$ is a function only of the adsorption concentration, $c_a$. For a linear adsorption isotherm, $N_a = 1$, and the nonexchangeable partition coefficient is:

$$\pi_o = (1 - \frac{N_d}{N_a}) K_a \tag{I-18}$$

which is, again, the same for <u>each</u> consecutive desorption isotherm. Hence, eqs. (I-15) and (I-18) represent all the consecutive desorption isotherms consistently in terms of two parameters: $\pi_o$ and $\pi_x$, as compared to the individual Freundlich isotherms for each consecutive desorption isotherm. The observational fact that $N_d/N_a$ is constant for each isotherm is the key to this simplification.

The nonexchangeable and exchangeable partition coefficients corresponding to the Freundlich parameters are listed in Table I-2. The indicated ranges are the effect of the slight nonlinear adsorption isotherm. The linear approximation of the adsorption isotherm results in only slight changes in $\pi_o$ and $\pi_x$. The critical approximation is that the consecutive desorption isotherm is linear. This is reasonable until fairly low aqueous concentration achieved after multiple desorptions, as discussed previously.

## F. Discussion

The proposed linear approximation describing the binding of organics to sediments is clearly an oversimplification of the actual process. In the case of HCB, experimental evidence suggests that under certain chemical conditions the binding to sediments during consecutive desorption may be described by a curvilinear isotherm which may or may not ultimately demonstrate complete desorbability. It is also quite possible that the actual adsorption process may involve binding to sites of a gradation of energies rather than the two arbitrarily defined fractions (exchangeable and nonexchangeable). Nevertheless, there exist distinct advantages for data analysis which result from treating HCB and other organic adsorption study results in terms of this approximation.

For a sediment adsorbed organic molecule such as HCB, it may not be experimentally feasible to generate consecutive desorption isotherms under all of the chemical conditions of concern from an environmental modeling standpoint.

For instance, it will be shown that the magnitude of the adsorbed and readily desorbed HCB sediment fractions is a function of a variety of parameters including aqueous composition and sediment concentration. This suggests that a large number of consecutive desorption isotherms would be required to adequately define the environmental behavior of HCB. However, for certain chemcial conditions (such as high (> 1000 mg/ℓ) sediment concentrations) it is extremely difficult to obtain consecutive desorption isotherms at the aqueous HCB concentrations of concern in natural water systems. The extremely small aqueous HCB concentrations which result from sediment HCB release during successive desorption cycles possess large experimental uncertainties, require a prohibitive number of experimental data points, and lead to ill defined isotherms.

From the standpoint of environmental modeling the linear approximation offers a means of refining currently used assumptions such as complete reversibility for organic adsorption to sediments. From the environmental chemical perspective the approximation can be utilized to separate reaction variables and provide an aid in interpreting organic binding mechanisms. These applications may be demonstrated by examining derivation results for both experimental binding mechanism and multiple cycle adsorption-desorption studies.

G. Consecutive Adsorption

In order to incorporate environmental cycling within mass balance calculations there exists a need to provide a method of analyzing the behavior of adsorption and desorption under changing aqueous PCB concentrations. (An example would be sediments initially exposed to high PCB concentrations subsequently migrating into environments characterized by lower but varying aqueous PCB levels.) The isotherm treatment of the present study has been utilized to predict how such changes would affect the sediment adsorbed PCB fractions. Model predictions have been compared with the results of laboratory experiments designed to simulate the cycling process described above. As discussed in detail in the methods section these experiments involved an adsorption step followed by a single desorption (the standard isotherm experiment) and following this a series of consecutive adsorptions. For small incremental increases in the aqueous concentration during the adsorption steps, small such that they do not exceed the initial adsorption concentration, $c_a$, the nonexchangeable component should be constant and only the exchangeable component should vary. That is, this portion of the data should follow the consecutive desorption isotherm:

$$r = r_o + \pi_x c \qquad c_d < c < c_a \qquad \text{(I-19)}$$

where $r_o = \pi_o c_a$. When the aqueous concentration exceeds $c_a$, more nonexchangeable sites should be available and the data should follow the adsorption isotherm:

$$r = (\pi_o + \pi_x)c \qquad c > c_a \qquad \text{(I-20)}$$

Figure I-6 presents the results for HCB binding to Saginaw Bay sediment and montmorillonite. The initial adsorption, single desorption, and the subsequent consecutive adsorption data are differentiated in the legend. The range of the quadruplicated data are as indicated. For Saginaw Bay sediment, the theoretical prediction is followed almost exactly. The agreement for montmorillonite is less satisfactory although it also clearly shows a change in behavior as the aqueous concentration exceeds $c_a$. These results provide at least a preliminary answer to the question posed at the outset: namely, how are these isotherms to be interpreted if the aqueous concentration, c(t), is changing in time during a mass balance calculation. Assuming local equilibria the nonexchangeable component reacts in response to the maximum aqueous concentration achieved up to that time:

$$r_o = \pi_o \, c_{ma}(t), \tag{I-21}$$

$$c_{ma}(t) = \max_t c(t) \tag{I-22}$$

whereas the exchangeable component follows the linear reversible isotherm:

$$r_x = \pi_x c(t) \tag{I-23}$$

in all circumstances. Since this interpretation is based upon rather limited experimental data it should be regarded with caution. However it does suggest the advantages of applying the proposed model to scenarios of this type as opposed to assuming a completely reversible formulation for HCB adsorption-desorption.

## H. Kinetic Effects

The assignment of exchangeable and nonexchangeable sediment HCB components in accordance with the method described above also offers potential advantages in the utilization of kinetic data to evaluate binding mechanisms. Of particular interest is the effect of time on the relationship between the exchangeable and nonexchangeable HCB components. The results of experiments designed to assess these effects can be seen from the comparison (presented in figure I-7) of the adsorption, single desorption, exchangeable and nonexchangeable iso-

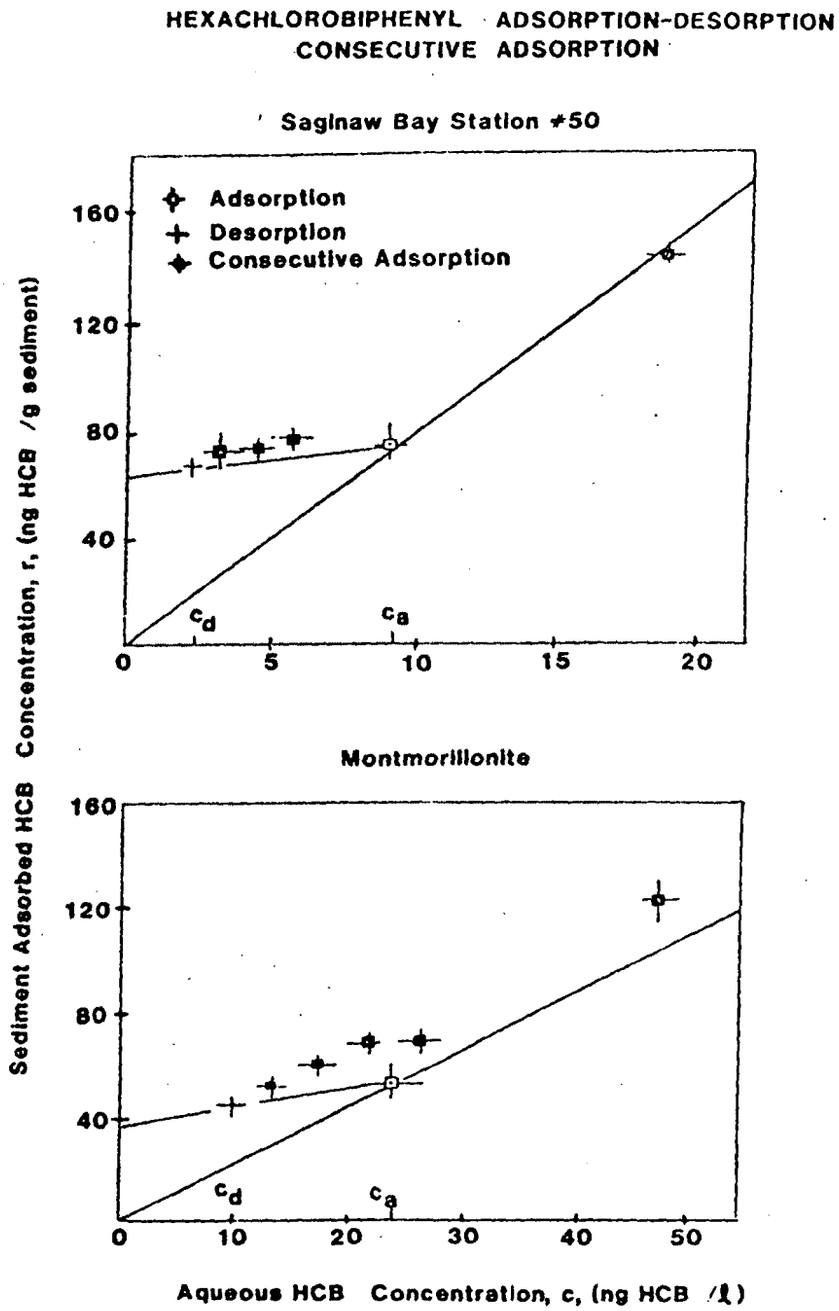



Fig. I-6. Hexachlorobiphenyl Adsorption-Desorption and Consecutive Adsorption, Saginaw Bay Sediment, Station #50 (m = 1100 ppm) and Montmorillonite (m = 1100 ppm and 2 meq/ℓ $NaHCO_3$ buffer)

Saginaw Bay Station #50

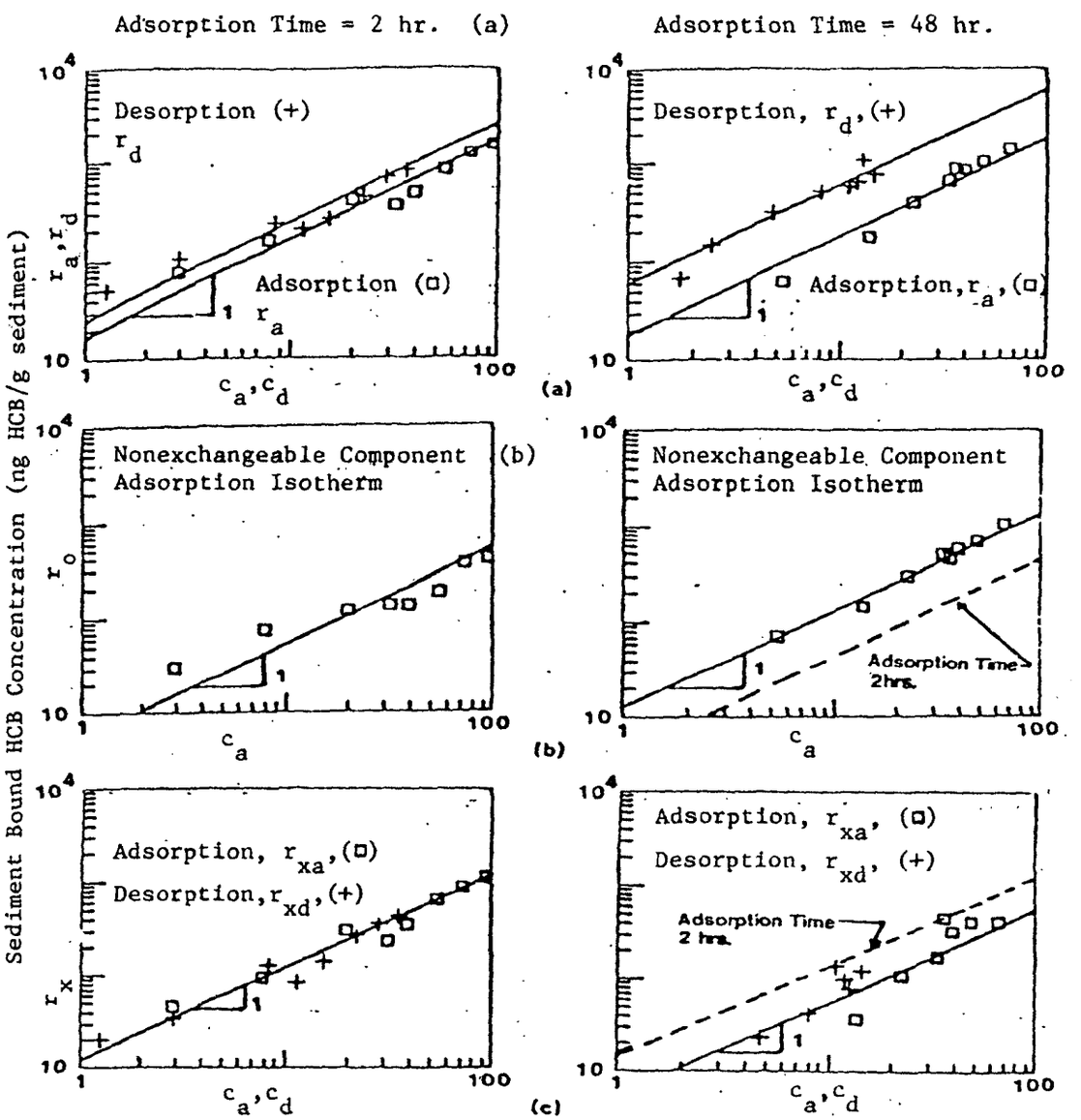



Fig. I-7. Hexachlorobiphenyl Adsorption-Desorption Isotherms, Saginaw Bay Sediment, Station #50 m = mg/ℓ, effect of adsorption time. See fig. 3 caption. Dotted isotherms are the two hour results replotted for visual reference.

therms found for 2 hour and 48 hour adsorption times. (It has been found that increasing the desorption time has no effect on the desorption isotherms.) The adsorption partition coefficient is slightly increased ($\pi_a$ = 1700 → 1800 ℓ/kg) but the desorption partition coefficient is markedly increased ($\pi_d$ = 25000 → 61000 ℓ/kg). As result the nonexchangeable component partition coefficient increases by approximately a factor of two ($\pi_o$ = 5100 → 12800 ℓ/kg) and the exchangeable component partition coefficient decreases ($\pi_x$ = 11800 → 5400 ℓ/kg) by approximately the same factor.

Since the partition coefficient can be thought of as the product of a binding strength constant and a capacity factor, the question arises as to which factor is responsible for the increase in $\pi_o$ with time. That is, are HCB molecules being bound more strongly at a fixed number of sites or is the number of strongly bound sites increasing with time. Although the exchangeable component data are quite scattered there is some suggestion that the increase in the nonexchangeable fraction is accompanied by an equal and opposite decrease in the magnitude of the exchangeably bound fraction. This would seem to imply that a change in the capacity factor of the nonexchangeable component is occurring rather than a change in the binding strength. Such an effect could conceivably result from a transformation of reversible binding sites to strong binding sites (metastable complex → stable configuration). If the magnitude of the exchangeable partition coefficient had remained constant during the experiment it would have implied that separate sites are responsible for reversible and resistant binding of HCB. Clearly, more experimental data is warranted before a choice of change in capacity factor versus binding strength constant can be made with certainty. However, the results again illustrate the utility of considering the data in terms of reversible and resistant components.

## I. Summary

It is useful to summarize the experimental basis for the component hypothesis. The definition of the nonexchangeable or perhaps better termed the resistant component follows from two observations: (1) that the single desorption isotherm is not coincident with the adsorption isotherm, that is that this pair of isotherms display hystersis; and (2) that the consecutive desorption isotherm can be approximated by a straight line, at least for the first few consecutive

desorptions. These are distinct observations and each can be examined in the light of experimental evidence.

The presence of hystersis in the adsorption and single desorption isotherms can be ascribed to a number of phenomena and possible experimental artifacts. A recent review (8) concluded that hystersis persists in most cases in spite of experimental modifications designed to eliminate the phenomena. Our experimental investigations for HCB have evaluated the influence of increasing the desorption times (no reduction in hystersis was observed) and the influence of using the dilution method to produce the desorption isotherm (hystersis was still present). Thus HCB hystersis is not being caused by insufficient desorption time or by the centrifugation used to separate the solids prior to the desorption experiment.

The second observation, that the consecutive desorption isotherm is linear is experimentally observed for the first few consecutive desorptions. After that the data are inconclusive in one case (fig. I-1B) and, at a lower sediment concentration, they suggest that in fact the consecutive desorption isotherm decreases toward the origin (fig. VIII-12 of Part A). It is for this reason that the "nonexchangeable" component responsible for this behavior is more appropriately termed resistant. That is the resistant component does not desorb at all for the first few consecutive desorption (i.e. nonexchangeable), and may or may not subsequently desorb. Its existence accounts for the observed hystersis in the single desorption experiments, and it has been argued above that experimental artifacts are not the cause for hystersis.

The question of the linearity of the consecutive desorption isotherm can be interpreted in terms of the resistant component consecutive desorption isotherm: is it a horizontal straight line indefinitely (as shown in fig. I-2) or is it initially a horizontal straight line which eventually curves to the origin as aqueous concentrations approach zero. In either case it is clear that the resistant component consecutive desorption isotherm is a straight line initially and that it is linear for the consecutive adsorption data presented in fig. I-6. These observations justify the assumption employed in this analysis. Further detailed experimental investigations are required to establish the shape of the resistant component consecutive desorption isotherm.

The issue is significant since it relates to the ultimate desorbability of PCB from previously contaminated sediments. But this issue should not be confused with the existence of hysteretic isotherms. The hypothesis employed in this analysis sharpens the question of ultimate desorbability since it is clear that the issue is the behavior of the resistant component at aqueous concentrations approaching zero rather than the overall utility of separating the data into the two components using the method proposed above.

## J. Conclusions

From an empirical point of view, the analysis of HCB isotherm data in terms of exchangeable and resistant components is quite successful in providing a concise and unified description. The full adsorption and desorption isotherm data set is represented by two partition coefficients, $\pi_o$ and $\pi_x$. The relationship between consecutive desorption isotherms and a single desorption isotherm has been clarified for the linear isotherm case at least, and they have been shown to be equivalent in the sense that either can be used to obtain the relevant partition coefficients for the components. The consecutive adsorption experiments provide preliminary confirmation that the exchangeable and resistant components behave in accordance with their expected properties. The exchangeable component exhibits no hystersis in response to changes in aqueous concentrations, and the resistant component reacts only to increases in aqueous concentrations that exceed the initial adsorption concentration. The use of the method described above to estimate the exchangeable and resistant components of adsorption-desorption provides additional insight into the influence of kinetics, sediment type, aqueous phase modifications (e.g. altering the pH) since it is possible to observe the effects on each of the components individually. Perhaps such investigations will help to clarify the mechanisms responsible for hysteretic isotherms and clairfy the issue of ultimate desorbability.

## Notation

$c_a$ = dissolved aqueous concentration of HCBP at adsorption equilibria (ng/ℓ)

$c_d$ = dissolved aqueous concentration of HCBP at desorption equilibria (ng/ℓ)

$K_a$ = Freundlich adsorption parameter $(ng/kg)/(ng/\ell)^{N_a}$

$K_d$ = Freundlich consecutive desorption parameter $(ng/kg)/(ng/\ell)^{N_d}$

$m$ = adsorbent concentration (kg/ℓ)

$N_a$ = Freundlich adsorption exponent

$N_d$ = Freundlich consecutive desorption exponent

$r_a$ = sediment bound concentration of HCBP at adsorption equilibria (ng/g)

$r_d$ = particulate concentration of HCBP at desorption equilibria (ng/g)

$r_o$ = resistant component of adsorbed HCBP (ng/g)

$r_{xa}$ = reversible component of adsorbed HCBP at adsorption equilibria (ng/g)

$r_{xd}$ = reversible component of adsorbed HCBP at desorption equilibria (ng/g)

$\pi_a$ = partition coefficient for adsorption (ℓ/kg)

$\pi_d$ = partition coefficient for single desorption (ℓ/kg)

$\pi_o$ = partition coefficient for the resistant component (ℓ/kg)

$\pi_x$ = partition coefficient for the reversible component (ℓ/kg)

## Appendix I

Derivation of Exchangeable and Nonexchangeable Components.

The equilibrium particulate concentrations that result from an adsorption experiment, $r_a$ at aqueous concentration $c_a$, and a subsequent desorption, $r_d$ at aqueous concentration $c_d$, are assumed to be the sum of a nonexchangeable component, $r_o$, and the exchangeable components, $r_{xa}$ and $r_{xd}$, that is:

$$r_a = r_o + r_{xa} \tag{A1}$$

$$r_d = r_o + r_{xd} \tag{A2}$$

The nonexchangeable component is the same for both adsorption and desorption since it is assumed to be nonexchangeable and therefore not affected by the desorption step, whereas the exchangeable component reacts to the lower aqueous concentration at desorption and decreases from $r_{xa}$ to $r_{xd}$ at equilibrium.

It is further assumed for this derivation that the exchangeable component follows a linear isotherm with partition coefficient, $\pi_x$, so that the exchangeable components are related to the aqueous concentration by the equations:

$$r_{xa} = \pi_x c_a \tag{A3}$$

$$r_{xd} = \pi_x c_d \tag{A4}$$

Using eq. (A2) to solve for $r_o$ and substituting eq. (A4) for $r_{xd}$ yields:

$$r_o = r_d - \pi_x c_d \tag{A5}$$

Substituting eq. (A3) for $\pi_x$ and using eq. (A1) for $r_{xa}$ yields:

$$r_o = r_d - \frac{c_d}{c_a}(r_a - r_o) \tag{A6}$$

The final result for the nonexchangeable component is:

$$r_o = \frac{r_d - \beta r_a}{1 - \beta} \tag{A7}$$

where $\beta = c_d/c_a$. The exchangeable components are obtained by subtraction using the defining eqs. (A1,A2):

$$r_{xa} = r_a - r_o \tag{A8}$$

$$r_{xd} = r_d - r_o \tag{A9}$$

The assumption of a linear exchangeable isotherm is checked by examining a composite plot of $r_{xa}$ versus $c_a$ and $r_{xd}$ versus $c_d$ for linearity.

It is significant to note that the derivation does not involve a mass balance argument so that the equations are applicable even if the experimental vessel is acting as a third phase with adsorption and desorption characteristics of its own. Also it is not necessary that the desorption be carried out by removing all the supernatant after centrifugation or that a correction be made for any residual aqueous phase. In fact the equations apply to whatever method is used to accomplish the desorption; for example by using an immiscible organic solvent as a third phase to accomplish the desorption (15). It is only necessary that the linearity assumption for the exchangeable component is satisfied and that its partition coefficient is unaffected by the desorption method employed.

If the linearity assumption is found to be inappropriate, it is still possible to separate the components. The derivation using nonlinear exchangeable isotherms (e.g. a Langmuir or Freundlich equation) is similar with the exception that an unknown parameter (the Langmuir binding constant and the Freundlich exponent respectively) remain in the equations for $r_o$ and $r_x$. Thus an iterative fitting procedure is required to make the estimates.

## Appendix II

Relationship between Linear Adsorption, Single Desorption, Nonexchangeable, and Consecutive Desorption Isotherms.

It is the purpose of this derivation to show that if the adsorption and single desorption isotherm are linear, then the nonexchangeable and the consecutive desorption isotherm are also linear. The linearity assumptions for adsorption and desorption are expressed by the equations:

$$r_a = \pi_a c_a \tag{A10}$$

$$r_d = \pi_d c_d \tag{A11}$$

The nonexchangeable component concentration is given by (eq. A7):

$$r_o = \frac{r_d - \beta\, r_a}{1 - \beta} \tag{A12}$$

which can be expressed in terms of aqueous concentrations only using eqs. (A10, A11):

$$r_o = \frac{c_d\,(\pi_d - \pi_a)}{1 - c_d/c_a} \tag{A13}$$

A relationship is available between $c_d$ and $c_a$ if the desorption is carried out by removing essentially all the supernatant and replacing it with adsorbate-free solvent (or equivalently that the mass of adsorbate associated with the residual supernatant is negligible) and that the vessel desorption is negligible. Then the mass of adsorbate prior to solvent addition, $m\, r_a$, is equal to the total mass of adsorbate in the dissolved and particulate phases:

$$m\, r_a = c_d + m\, r_d \tag{A14}$$

where m is the mass of adsorbent present. Substituting eqs. (A10, A11) yields the desired relationship:

$$c_d = \frac{m\, \pi_a c_a}{1 + m\, \pi_d} \tag{A15}$$

This relationship in eq. (A13) yields:

$$r_o = \frac{m\, \pi_a\, (\pi_d - \pi_a)}{1 + m(\pi_d - \pi_a)}\, c_a \tag{A16}$$

so that $r_o$ is linearly related to $c_a$ and by the definition of $\pi_o$, eq. (4):

$$\pi_o = \frac{m\,\pi_a(\pi_d - \pi_a)}{1 + m(\pi_d - \pi_a)} \tag{A-17}$$

Hence, if the linearity and mass balance equations are applicable, the resistant component partition coefficient can be computed from the adsorption and single desorption partition coefficients.

Similarly the consecutive desorption isotherm can also be shown to be linear. This is equaivalent to showing that the slope of the consecutive desorption isotherm, which is the partition coefficient of the reversible component, is the same at the adsorption and desorption aqueous concentrations. The reversible component concentration at adsorption equilibrium is given by eq. (A8):

$$r_{xa} = r_a - r_o \tag{A18}$$

or, using eqs. (A10) and (A16):

$$r_{xa} = \pi_a c_a = \frac{m\,\pi_a(\pi_d - \pi_a)}{1 + m(\pi_d - \pi_a)}\, c_a \tag{A19}$$

which simplifies to:

$$r_{xa} = \frac{\pi_a}{1 + m(\pi_d - \pi_a)}\, c_a \tag{A20}$$

Similarly the reversible component concentration at desorption equilibrium is given by eq. (A9):

$$r_{xd} = r_d - r_o \tag{A21}$$

$$= \pi_d c_d - \frac{m\,\pi_a(\pi_d - \pi_a)}{1 + m(\pi_d - \pi_a)} \frac{1 + m\,\pi_d}{m\,\pi_a}\, c_d \tag{A22}$$

where eq. (A11) and eq. (A16) have been used for $r_d$ and $r_o$ and eq. (A15) for $c_a$. Combining terms and simplifying yields:

$$r_{xd} = \frac{\pi_a}{1 + m(\pi_d - \pi_a)}\, c_d \tag{A23}$$

Hence the reversible component isotherm has the same slope at $c_a$, eq. (A20), and $c_d$, eq. (A23) so that the consecutive isotherm is linear and further the reversible component partition coefficient is given by:

$$\pi_x = \frac{\pi_a}{1 + m(\pi_d - \pi_a)} \tag{A24}$$

It should be noted that these relationships can be easily corrected for the mass associated with the residual supernatant if its volume is known by simply adding that mass to the left hand side of eq. (A14).

## SECTION II

## EFFECT OF SEDIMENT CONCENTRATION AND COMPOSITION

### A. Introduction

The effect of sediment concentration on the extent of partitioning of HCB has been investigated in Part A, Section VIII, of this report. It is related to the well-known phenomena that the fraction of adsorbate in the particulate phase increases as the mass of adsorbent increases. What is surprising is that in the case of HCB, the extent to which the particulate fraction increases is inconsistent with the conventional assumption that the isotherm parameters are independent of the sediment concentration.

The experiments which reproduce this effect for HCB adsorption have been discussed in Part A of this report. Possible experimental artifacts which may explain the effect have also been investigated. It has been found that the effect is not caused by nonlinear isotherms improperly characterized by a single partition coefficient, or by aqueous or particulate phase changes that result as a consequence of adsorbent concentration increases. The conclusion from these experiments is that the phenomena is real and must be considered systematically in the description of HCB adsorption and desorption.

The second focus of the experiments described in this report is the extent of reversibility of the adsorption reaction. Since both adsorption and desorption are occurring in natural systems, the experiments were designed to address both processes. It was consistently found that the adsorption reaction was not completely reversible, and, depending upon the details of the experiment, a substantial quantity of adsorbed HCB remained in the particulate phase after desorption, in excess of that which would be predicted by the adsorption isotherm.

This disturbing result implies that the conventional reversible description of adsorption-desorption is inadequate and that a refined quantitative desorption is required. It has been shown in Section I that the process can be consistently described if the adsorbed HCB is assumed to be composed of two components: an exchangeable component which readily adsorbs and desorbs reversibly; and a nonexchangeable, or resistant, component which resists desorption during

the single desorption phase of the experiment, and may or may not ultimately desorb during consecutive desorptions. The irreversibility has been found to persist under a variety of experimental modifications: it is not affected by either the time of desorption or the manner of phase separation, and it occurs for clay adsorbents as well as Saginaw Bay sediments.

The dual focus of these experiments makes it possible to investigate the effect of sediment concentration on both the exchangeable and nonexchangeable components of HCB adsorption. It is shown below that the observed systematic variation of adsorption and single desorption partition coefficient as a function of sediment concentration can be explained in terms of the behavior of the exchangeable and nonexchangeable partition coefficients. The latter has been found to be approximately constant with respect to adsorbent concentration variations, as would be expected from conventional adsorption theory; whereas the exchangeable partition coefficient has been found to be inversely proportional to adsorbent concentration. The interplay of these two components determine the variation of the adsorption and single desorption partition coefficients as a function of sediment concentration. It is the purpose of this section to present the analysis of these experimental data and to relate these findings to the conventional descriptions of adsorption-desorption as applied to the computation of the fate of PCB in natural water systems.

## B. Definitions and Methodology

For isotherm experiments at a fixed sediment concentration with many pairs of adsorption $(r_a, c_a)$ and desorption $(r_d, c_d)$ data, the adsorption, $\pi_a$, and desorption, $\pi_d$, partition coefficients are obtained as the slopes of $r_a$ versus $c_a$ and $r_d$ versus $c_d$ respectively. For experiments that are designed to investigate the effect of sediment concentration variations it is inconvenient to evaluate a complete isotherm at each sediment concentration of interest. Rather the concentration of sediment is varied systematically. In order to reduce the effect of systematically varying aqueous concentrations - for example if a constant initial HCB concentration is used, then the equilibrium dissolved concentration would decrease systematically as adsorbent concentration increases - the initial concentration is varied to produce sim-

ilar equilibrium dissolved concentrations as discussed in Section VIII of Part A. The results of this experimental design are (triply replicated) pairs of adsorption ($c_a$,$r_a$) and desorption ($c_d$,$r_d$) points at varying adsorbent concentrations, m. The partition coefficients are then calculated from the ratio of r and c, i.e., $\pi_a = r_a/c_a$ and $\pi_d = r_d/c_d$.

For some of the initial experiments which were focused on desorption, the total HCB concentration at adsorption equilibria, $c_{Ta}$, was not measured (Type 2 experiment) so that a direct estimate of $r_a$ is not available. If it is assumed that no significant vessel adsorption or desorption occurs during the desorption phase of the experiment then the mass balance relationship: $m\,r_a = c_{Td}$ can be used to estimate $r_a$. Figure III-7 of Part A presents the experimental confirmation of this relationship for those experiments in which both $r_a$ and $c_{Td}$ are available. No significant bias is observed which confirms the assumption that no significant vessel adsorption or desorption occurs during the desorption phase of the experiment.

The variations of the adsorption, $\pi_a$, and desorption, $\pi_d$, partition coefficients as a function of adsorbent concentration are shown in fig. II-1 for Saginaw Bay sediment (Sta. #50) and montmorillonite, and two aqueous phases, distilled water and supernatant - which is distilled water previously equilibrated with uncontaminated adsorbent - are shown. The data points are averages of triplicate replicates as usual, the curves are discussed below. The systematic decrease of both adsorption and single desorption partition coefficients as adsorbent concentration increases is apparent, as is the irreversibility of adsorption-desorption, illustrated by the fact that $\pi_d$ exceeds $\pi_a$. It can be seen that the extent of irreversibility increases as adsorbent concentration increases as pointed out in Part A, Section VIII, which contains a more complete description of these experiments and the experimental modifications employed to insure that the results are not experimental artifacts. The purpose of this section is to analyze these results in terms of exchangeable and nonexchangeable component behavior.

The definitions of the exchangeable and nonexchangeable components are given in Section I. From the geometry of the relationships it is clear that

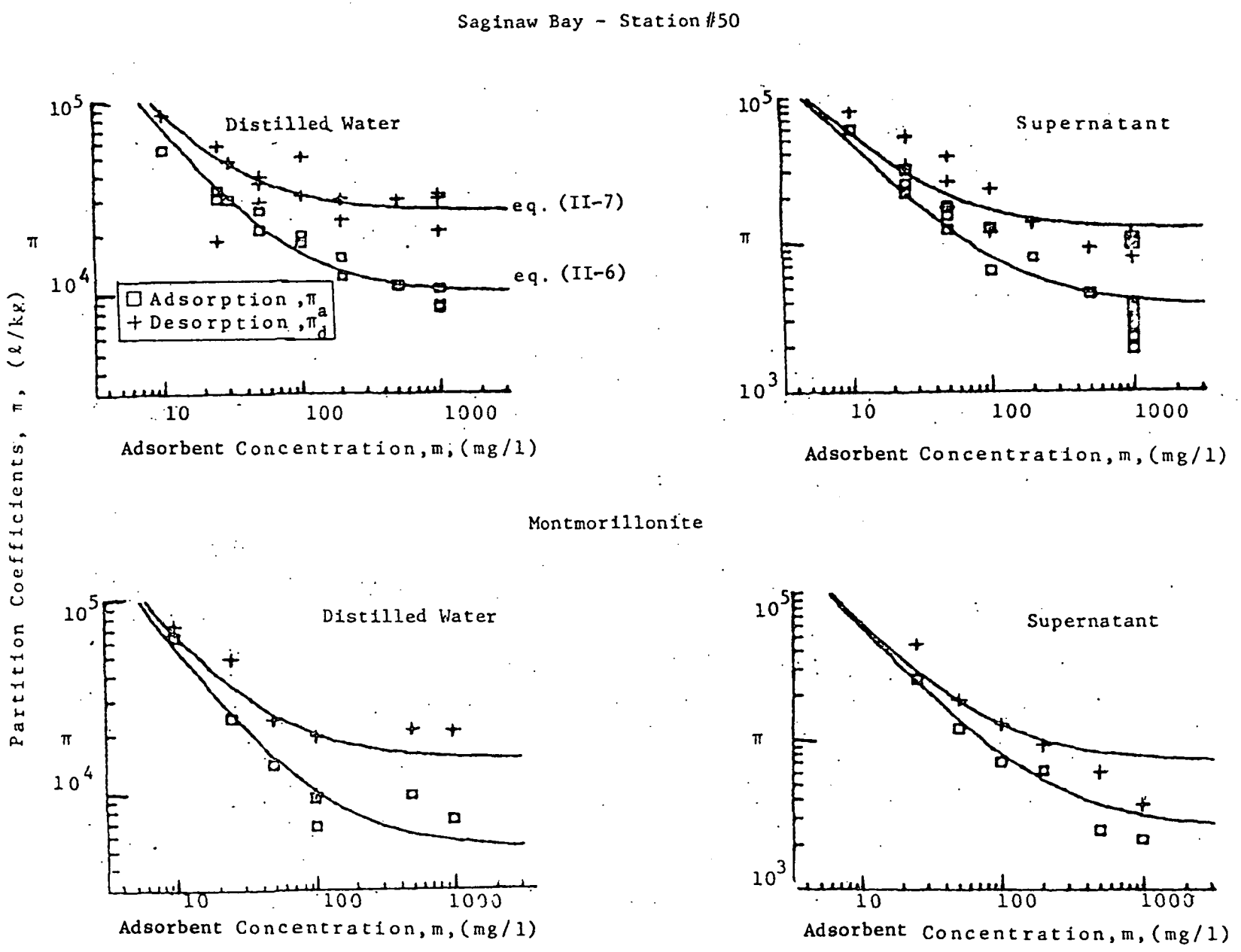



Fig. II-1. Adsorption and Desorption Partition Coefficient variation with Adsorbent concentration. Saginaw Bay Station #50 and Montmorillonite. Distilled water and supernatant aqueous phases.

the partition coefficients for the exchangeable and nonexchangeable components are given by:

$$\pi_x = \frac{r_a - r_d}{c_a - c_d} \qquad \text{(II-1)}$$

and

$$\pi_o = \frac{r_a}{c_a} - \frac{r_a - r_d}{c_a - c_d} \qquad \text{(II-2)}$$

The second equation follows from the fact that $\pi_a = \pi_o + \pi_x$. These equations are re-expressions of eqs. (I-6) and (I-7) of the previous section.

## C. Sediment Mass Effects for Exchangeable and Nonexchangeable Partition Coefficients

The results of these experiments analyzed in terms of exchangeable and nonexchangeable partition coefficients, eq. (II-1) and eq. (II-2), are shown in fig. (II-2) for Saginaw Bay sediment (Sta. #50) and fig. (II-3) for montmorillonite. They correspond to the adsorption-desorption data presented in fig. I-1. The open squares represent triplicate logarithmic averages of the partition coefficients. The filled circles are the logarithmic average ± the standard error of the average from isotherm experiments each of which was conducted at the fixed adsorbent concentrations as indicated in the figure. (These isotherms were only available for distilled water as the aqueous phase.)

For the Saginaw Bay sediment, fig. (II-2), it is found that the nonexchangeable partition coefficient, $\pi_o$, is independent of sediment concentration whereas the exchangeable partition coefficient, $\pi_x$, is inversely proportional to sediment concentration. The lines on the plot have slopes of zero and minus one respectively. For montmorillonite, fig. (II-3), the nonexchangeable partition coefficient appears to decrease slightly for distilled water and more markedly for supernatant as the aqueous phase. However, the exchangeable partition coefficients are both inversely proportional to sediment concentration as was the case for Saginaw Bay sediment.

Regression analyses of these data, using the relationship: $\pi = am^n$ (O'Connor and Connolly, 1980) are given in Table II-1. The slopes, n, for

SAGINAW BAY - STATION #50

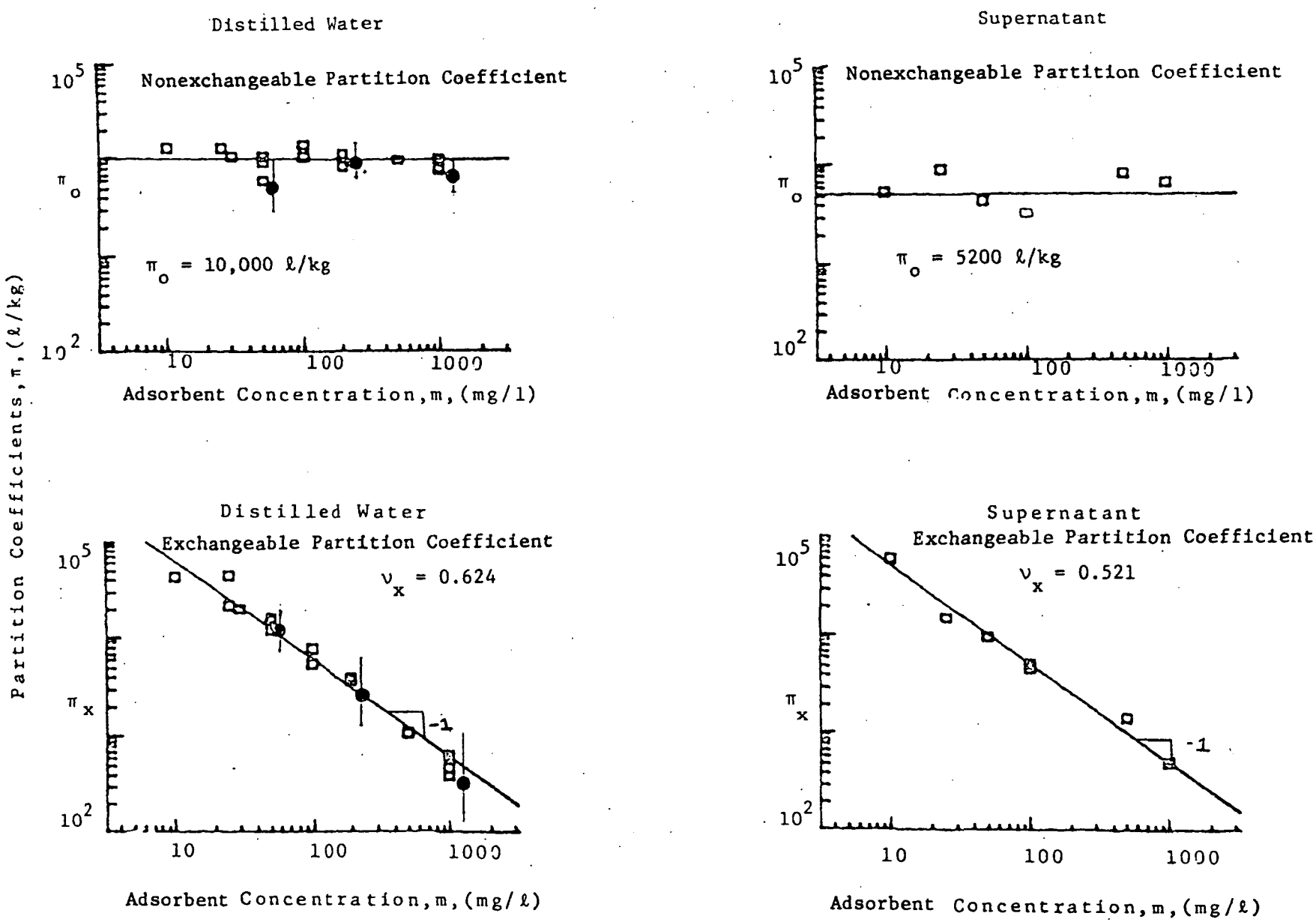



Fig. II-2. Nonexchangeable and Exchangeable Partition Coefficient variation with adsorbent concentration Saginaw Bay Station #50. Distilled water and supernatant as aqueous phase

MONTMORILLONITE

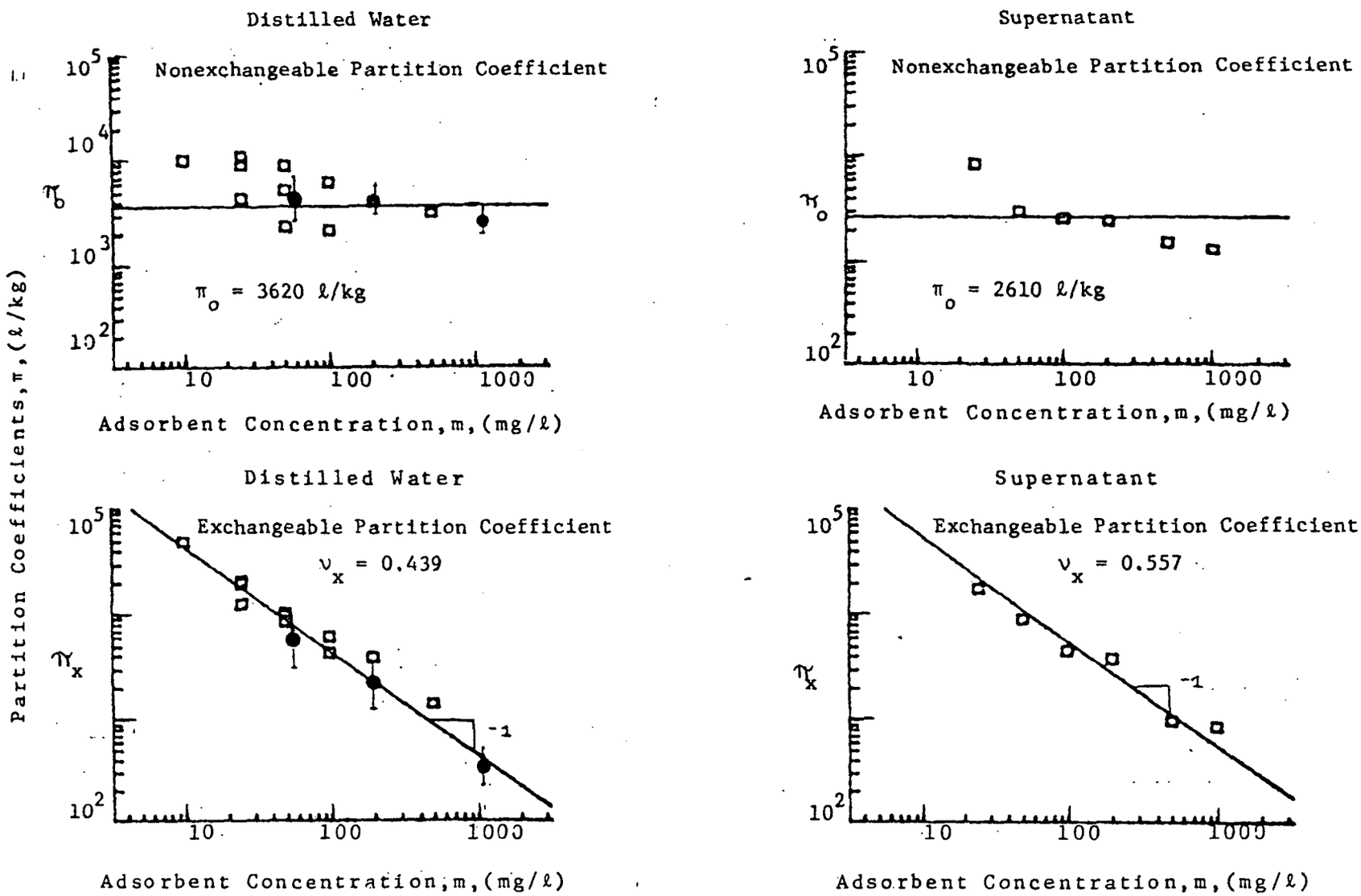



Fig. II-3. Nonexchangeable and Exchangeable Partition Coefficient variation with adsorbent concentration, Montmorillonite. Distilled water and supernatant as aqueous phase.

TABLE II-1

REGRESSION ANALYSES[§] OF ADSORBENT CONCENTRATION EFFECT

| Adsorbent | Aqueous Phase | Nonexchangeable Partition Coefficient* | | | Exchangeable Partition Coefficient* | | |
|---|---|---|---|---|---|---|---|
| | | $\pi_o$ (ℓ/kg) | | | $\pi_x$ (ℓ/kg) | | |
| | | Slope (n) | Intercept (a) ($\times 10^{-3}$) | Average $\pi_o$ (ℓ/g) | Slope (n) | Intercept (a) ($\times 10^{-6}$) | Average $\nu_x$ |
| Saginaw Bay #50 | Distilled Water | -0.015 (0.039, -0.070) | 9.64 (12.6, 7.33) | 10.0 | -1.025 (-0.98, -1.07) | 0.681 (.862, .538) | 0.624 |
| Saginaw Bay #50 | Supernatant | 0.011 (0.093, -0.07) | 5.83 (8.72, 3.90) | 5.29 | -0.952 (-0.90, -1.01) | .410 (.534, .315) | 0.521 |
| Montmorillonite | Distilled Water | -0.247 (-0.21, -0.29) | 13.6 (16.9, 10.9) | 3.62 | -1.04 (-1.01, -1.06) | .541 (.635, .461) | 0.439 |
| Montmorillonite | Supernatant | -0.421 (-0.35, 0.49) | 2.12 (3.09, 1.45) | 2.61 | -0.855 (-0.79, -0.92) | .261 (.367, 1.86) | 0.557 |

[§]Regressions performed on individual data points rather than the triplicate averages.

*Values in parentheses are regression coefficients ± standard errors of the estimates.

the exchangeable partition coefficient relationship are all found to be n = -1 within 95% confidence limits, whereas for the nonexchangeable partition coefficients, only the Saginaw Bay sediment yields n = zero within the confidence limits.

Nevertheless it is a useful approximation to assume that the nonexchangeable partition coefficient, $\pi_o$, is constant with respect to sediment concentration, m. The inverse relationship between $\pi_x$ and m, i.e.:

$$\pi_x = \nu_x m^{-1} \tag{II-3}$$

defines $\nu_x$, a dimensionless distribution coefficient for the exchangeable component. Hence a consistent description of the exchangeable and nonexchangeable partition coefficient - sediment concentration relationships requires two parameters only: a nonexchangeable partition coefficient: $\pi_o$ and an exchangeable distribution coefficient: $\nu_x$.

The utility of this assumption is that it provides a concise description of the behavior of the variation of adsorption, $\pi_a$, and desorption, $\pi_d$, partition coefficients as functions of adsorbent concentration. It has been shown in Section I that there are relationships which express $\pi_o$ and $\pi_x$ in terms of $\pi_a$ and $\pi_d$. These equations can be derived as follows. For $\pi_x$, it follows from eq. (II-1) that:

$$\pi_x = \frac{\pi_a - \pi_d(c_d/c_a)}{1 + (c_d/c_a)} \tag{II-4}$$

The relationship between $c_a$ and $c_d$ follows from the mass balance relationship: $mr_a = c_{Td}$ and the fact that $c_{Td} = c_d + m\, r_d$ so that:

$$\frac{c_d}{c_a} = \frac{m\pi_a}{1 + m\pi_d} \tag{II-5}$$

Using these equations, solving for $\pi_a$ and $\pi_d$ in terms of $\pi_o$ and $\pi_x$, and using eq. (II-3) for $\pi_x$ yields:

$$\pi_a = \pi_o + \frac{\nu_x}{m} \tag{II-6}$$

$$\pi_d = \pi_o(1 + \frac{1}{\nu_x}) + \frac{\nu_x}{m} \qquad \text{(II-7)}$$

The curves in fig. (II-1) for $\pi_a$ and $\pi_d$ versus m are these relationships using constant $\pi_o$ and $\nu_x$ represented by lines in fig. (II-2) and (II-3), and the average values given in Table I-1. The extent of the goodness of fit reflects the assumption of constant $\pi_o$: the fit is better for Saginaw Bay sediment than for montmorillonite, as is expected, since the assumption of constant $\pi_o$ is more appropriate for the former data.

## D. Effect of Sediment Characteristics

It has been proposed in the previous section that the adsorption and desorption behavior of HCB can be described in terms of two parameters, $\pi_o$ and $\nu_x$, which are essentially independent of the sediment concentration. However, they may be functions of the types of sediment used. To investigate these relationships the Saginaw Bay sediment isotherms generated for sediment samples from seven locations can be used (Section VI, Part A).

The results of the adsorption-desorption isotherm experiments are shown in fig. II-4. The straight lines are linear isotherms for the average adsorption and desorption partition coefficients, which are listed in Table II-2. Although there is some tendency for the desorption isotherm to be nonlinear the fits are reasonable representations of the data. Nonreversible behavior is found in all cases but is quite small for Station #69 in contrast to the other stations. Note that the Station #69 particulate concentrations are an order of magnitude smaller and the dissolved concentrations are an order of magnitude larger than the other stations. In addition the adsorbent concentration used is much larger (m = 20,000 mg/ℓ) than for the rest of the adsorbents (m = 1100 mg/ℓ). This was necessary in order that appreciable particulate concentrations resulted for this sediment.

The variation in adsorption partition coefficient has been correlated to organic carbon content of the sediment (Karickhoff et al., 1979) and to the sediment surface area (Hiraizumi et al., 1979). Similar correlation studies have been made for the adsorption and desorption partition coefficients found in the present studies (Section VI).

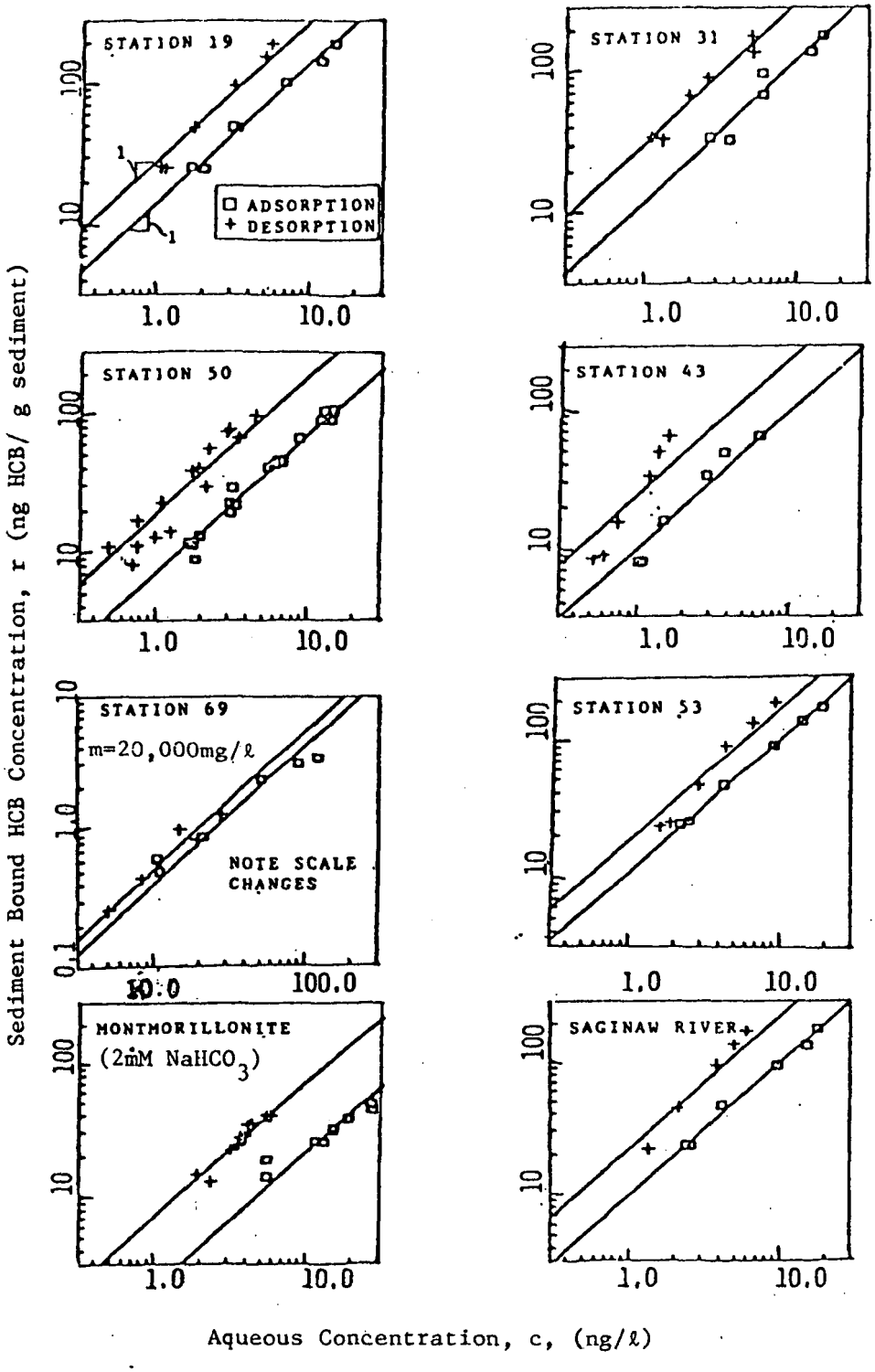



Fig. II-4 Adsorption and Desorption Isotherms for Saginaw Bay Stations and Montmorillonite. Aqueous phase is Distilled Water except for Montmorillonite (2mM $NaHCO_3$) m = 1100 mg/ℓ except for Station #69 (m = 20,000 mg/ℓ)

TABLE II-2

EXPERIMENTAL DATA FOR PARTITION COEFFICIENTS

| Sediment | Volatile Solids (%) | Specific Area ($m^2/g$) | Adsorbent Concentration (mg/ℓ) | $\pi_a$* (ℓ/g) | $\pi_d$* (ℓ/g) | $\pi_o$* (ℓ/g) | $\nu_x$* |
|---|---|---|---|---|---|---|---|
| Saginaw Bay | | | | | | | |
| 19 | 15.0 | 17.0 | 1100 | 14.8 (15) | 30.1 (18) | 14.0 (14) | 0.915 (44) |
| 31 | 9.9 | 17.8 | 1100 | 12.3 (18) | 30.9 (17) | 11.7 (18) | 0.630 (39) |
| 43 | 9.3 | 15.9 | 1100 | 10.7 (21) | 26.1 (35) | 10.1 (21) | 0.653 (66) |
| 50 | 7.6 | 12.8 | 1100 | 7.01(17) | 20.2 (32) | 6.56(17) | 0.496 (52) |
| 53 | 8.7 | 7.0 | 1100 | 11.2 ( 7) | 19.8 (22) | 10.1 ( 8) | 1.18 (48) |
| 69 | 0.3 | 0.2 | 22000 | 0.036(27) | 0.052(25) | 0.0087(64) | 0.545 (46) |
| Saginaw River | 9.6 | 8.4 | 1100 | 9.63(12) | 22.4 (23) | 8.99 (12) | 0.702 (43) |
| Montmorillonite | 0.0 | 12.6 | 1100 | 2.10(17) | 7.23(15) | 1.79 (16) | 0.349 (29) |

*The numbers in parentheses are the standard errors of the experimental data, in percent.

As suggested above, the most concise description of adsorption and desorption is in terms of the nonexchangeable partition coefficient, $\pi_o$, and the exchangeable distribution coefficient, $\nu_x$. The variation of these coefficients (mean ± standard deviation) as functions of percent volatile solids (% VSS) and specific surface area ($\sigma$) as determined by a single point $N_2$-BET isotherm, are shown in fig. II-5. The variation of nonexchangeable partition coefficient, $\pi_o$, with % VSS (fig. II-5a) is fairly regular for the Saginaw Bay stations, but montmorillonite does not conform to the relationship since it has a significant $\pi_o$ and no volatile solids fraction. The surface area correlation (fig. II-5b) is more erratic and again montmorillonite does not conform.

The variation of exchangeable distribution coefficient, $\nu_x$, with volatile solids fraction (fig. II-5c) and surface area (fig. II-5d) is not systematic although there is a slight trend for $\nu_x$ to increase with volatile solids fraction. The surprising result is that to within approximately a factor of three the exchangeable distribution coefficient is nearly constant and independent of sediment properties. The value obtained for the coarse fraction (>75μ) of Station #69 sediment ($\nu_x$ = 0.545) is consistent with the range for the fine fraction (<75μ) of the other Saginaw Bay Stations ($\nu_x$ = 0.496 - 1.18) and for montmorillonite ($\nu_x$ = 0.349). This weak variation of the exchangeable distribution coefficient as a function of sediment properties contrasts sharply with the strong variation of the nonexchangeable partition coefficient: whereas the range of $\nu_x$ is 0.349-1.18, the range of $\pi_o$ is 0.036-14.8 (ℓ/g).

A multiple linear regression analysis of these data, shown in Table II-3, further illustrates this result. Whereas the regression equation for $\pi_o$ has a small constant term relative to the contribution of the volatile solids fraction and surface area, the reverse is true for $\nu_x$. The goodness of fit of the prediction equations are illustrated in fig. II-6. The observed nonexchangeable partition coefficients are well represented by the linear relationship (Table II-3) as indicated by the large fraction of the variance removed by the regression ($R^2$ = 0.953) whereas the exchangeable distribution coefficient is less well represented, although a significant fraction of the variance is removed by the regression ($R^2$ = 0.66).

Both the nonexchangeable and exchangeable coefficients tend to increase

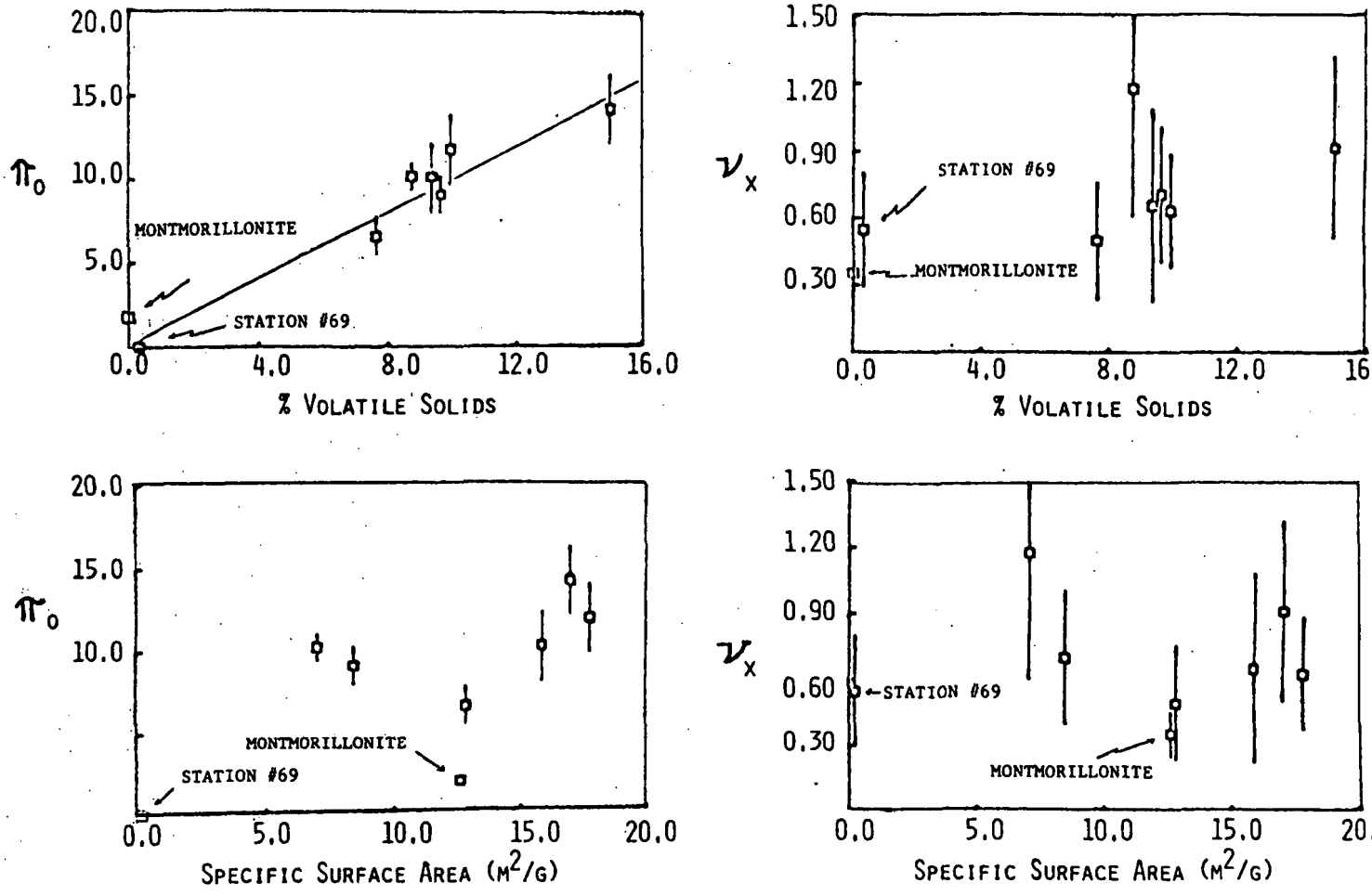



Fig. II-5. Variation of Nonexchangeable Partition Coefficient and exchangeable distribution coefficient with respect to percent volatile solids and specific surface area.

TABLE II-3

MULTIPLE LINEAR REGRESSION ANALYSIS*

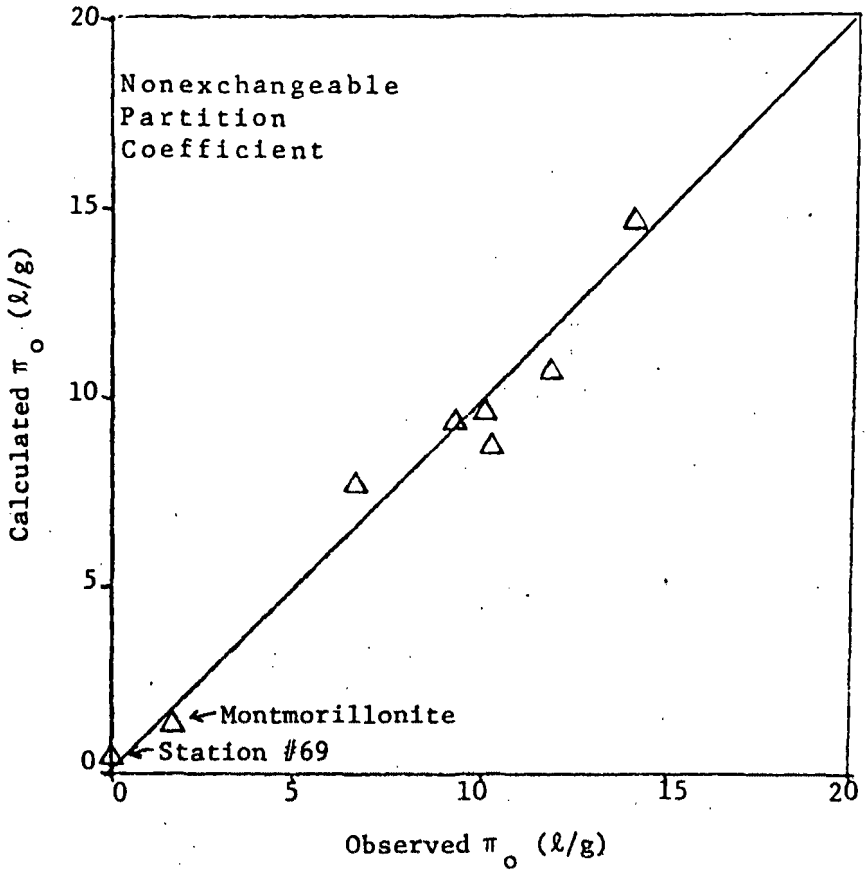
| | Constant | Volatile Solids** VSS(%) | Surface Area** $\sigma(m^2/g)$ | Multiple Regression Coefficient $R^2$ |
|---|---|---|---|---|
| $\pi_o(\ell/g)$ | 0.219 | 0.850(0.115) | 0.110(0.097) | 0.953 |
| $\nu_x$ | 0.625 | 0.0507(0.0163) | -0.028(0.0138) | 0.660 |

*Prediction Equations are:

$$\pi_o = 0.219 + 0.850\ (\%\ VSS) + 0.110\ \sigma$$

$$\nu_x = 0.625 + 0.0507\ (\%\ VSS) - 0.028\ \sigma$$

**The numbers in parentheses are the estimated standard errors of the coefficients.



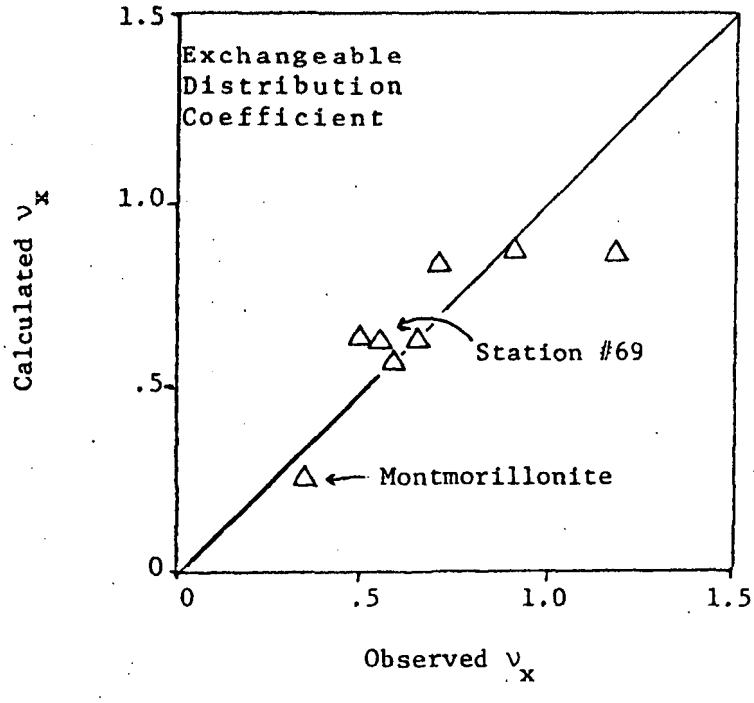




Fig. II-6. Comparison of Calculated (using the regression equations) and observed coefficients.

as volatile solids fraction increases and the standard errors of the regression coefficients are small (14% and 32% respectively). The influence of increasing surface area is to tend to increase $\pi_o$, as a result of montmorillonite which shows a significant nonexchangeable partition coefficient with no fraction volatile solids. However, the standard error of this regression coefficient is large (88%). In contrast the exchangeable distribution coefficient tends to decrease as surface area increases. This puzzling result may be spurious and due to the cross correlation between volatile solids fraction and surface area. In any case the regression equation is not a dramatic improvement over the assumption of a constant $\nu_x$. Further experimental information is required in order to refine the relationship for $\nu_x$, if indeed they exist.

## E. Implications for Modeling PCB Fate in Natural Waters

The results of these experiments and their analysis in terms of a nonexchangeable partition coefficient and an exchangeable distribution coefficient directly impact the formulations used to model the fate of chemicals which adsorb to suspended and sedimented particles. The conventional assumptions are that the adsorption-desorption reaction is reversible and, for a linear isotherm relationship, that the partition coefficients are constant with respect to adsorbent concentration. Both of these assumptions have been shown to be inappropriate approximations of the experimentally observed behavior of HCB.

The issue of the impact of the nonexchangeable component on the eventual fate of HCB is still uncertain since it has been shown that apparently this component does eventually desorb at very low aqueous concentration (Section VIII, Part A). Whether the desorption is complete is uncertain at present.

The sediment concentration effects, however, can have a substantial impact on the computation of the fate of PCB. The transport processes and kinetic reactions are significantly different for adsorbed (= particulate) and dissolved chemical fractions. These are estimated using the relationships for dissolved and particulate fraction :

$$f_d = \frac{1}{1 + m\pi_a} \qquad \text{(II-8)}$$

$$f_p = \frac{m\pi_a}{1 + m\pi_a} \qquad \text{(II-9)}$$

where $f_d = c_a/c_{Ta}$ and $f_p = 1 - f_d$. These equations follow directly from the mass balance equation $c_{Ta} = c_a + mr_a$, and the linear isotherm: $r_a = \pi_a c_a$. A useful quantity is the ratio of particulate to dissolved fraction:

$$\frac{f_p}{f_d} = m\,\pi_a \qquad \text{(II-10)}$$

since if the adsorption partition coefficient is independent of the adsorbent concentration, m, then one would expect that a graph of $f_p/f_d$ versus m would be a straight line.

It has been shown above, however, that $\pi_a$ is indeed a function of m and that eq (II-6) provides an expression of this variation. The result is that the ratio of particulate to dissolved fraction should vary as:

$$\frac{f_p}{f_d} = \nu_x + m\,\pi_o \qquad \text{(II-11)}$$

where $\nu_x$ and $\pi_o$ are constant with respect to m. Thus at low suspended solids concentrations the particulate fraction should approach $\nu_x$ following eq. (II-11) and not zero, as implied by eq. (II-10).

The experimental adsorption data, presented in this way is shown in fig. II-7. The straight line is eq. (II-10) using $\pi_a = \pi_o$, the curved line is eq. (II-12) with $\nu_x = 0.5$ for all cases and $\pi_o$ as indicated. The marked deviation from straight line behavior is a consequence of the sediment concentration dependent adsorption partition coefficient. The data for quartz and kaolinite as adsorbents also appear to conform to this relationship, as shown in fig. II-7.

These data are all laboratory experimental results. The fact that $\nu_x$ is approximately independent of adsorbent properties, however, suggests that field data would also exhibit the same solids dependency if $\pi_o$ is not fluctuating too widely. Fig. II-8 illustrates the relationship for $\log_{10} f_p/f_d$ versus m for Saginaw Bay suspended particulates. The line is a linear re-

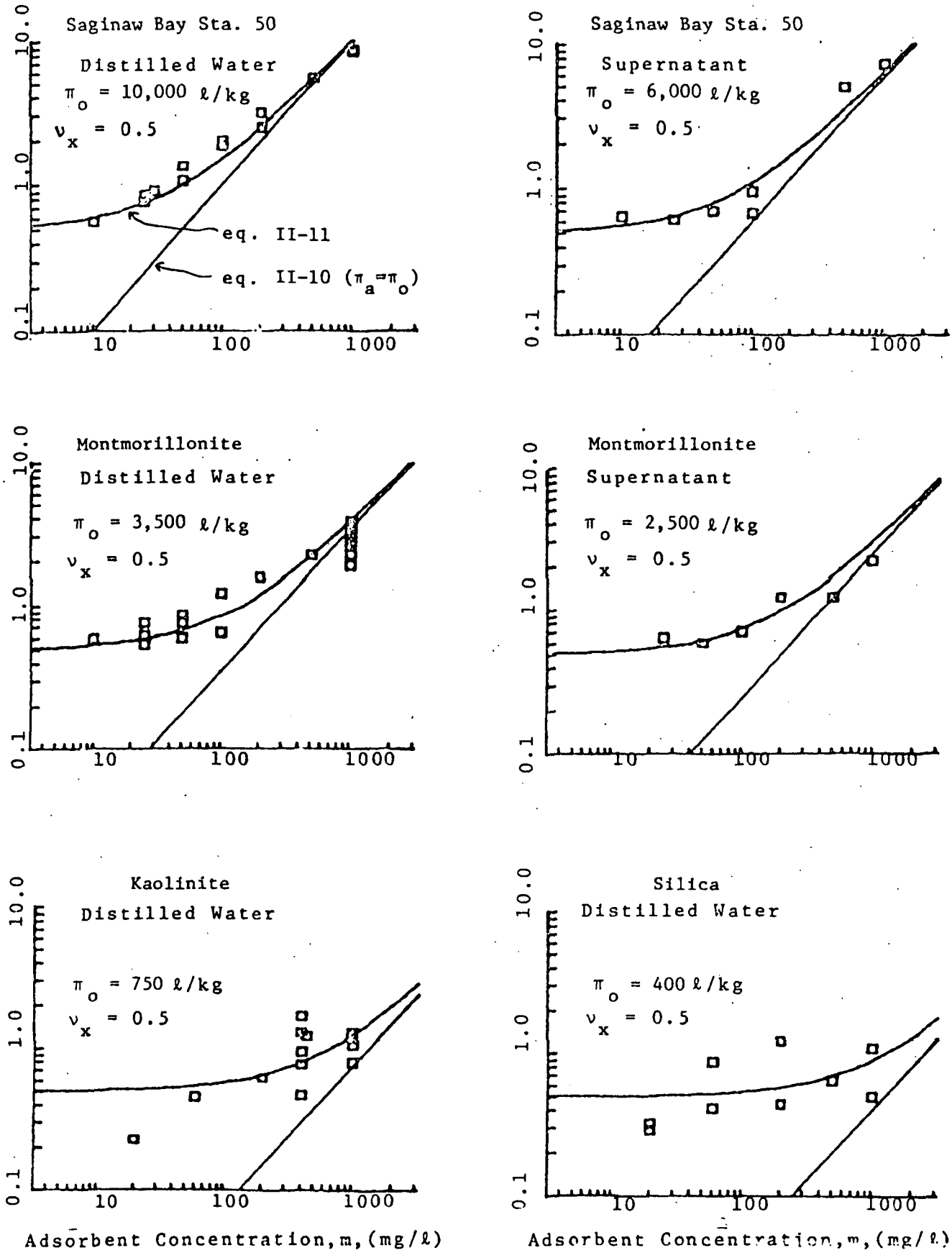



Fig. II-7 Ratio of Particulate to Dissolved fraction of HCB versus adsorbent concentration.

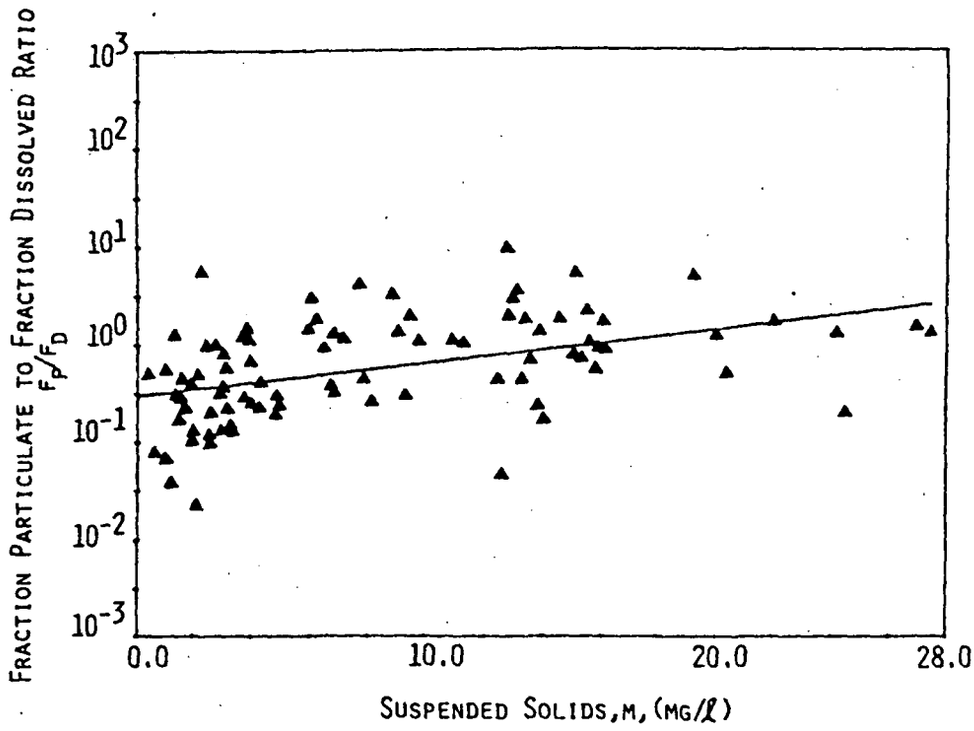



Fig. II-8 Ratio of Particulate to Dissolved fraction of PCB versus suspended solids concentration for Saginaw Bay. All cruises. Line is regression equation: $\log_{10} f_p/f_d = a + bm$; $a = -0.532$; $b = 0.0343$.

gression. Using eq. (II-11) for the particulate to dissolved ratio, and the approximation: $\ell n\ (1 + \varepsilon) \simeq \varepsilon$ for $\varepsilon$ small yields:

$$\log_{10}(\nu_x + m\ \pi_o) \simeq \frac{1}{2.303}\ (\ell n \nu_x + m\ \pi_o/\nu_x) \qquad \text{(II-12)}$$

The regression slope (0.0343 ℓ/mg) and intercept (-0.532) yields $\nu_x$ = 0.294 and $\pi_o$ = 23.2 ℓ/g. The exchangeable distribution coefficient is at the lower range of the experimental values ($\nu_x$ = 0.35 - 1.2) and the nonexchangeable partition coefficient is larger than those observed experimentally ($\pi_o$ = 0.036 - 14.8 ℓ/g). The latter result suggests that the percent volatile solids of the suspended particulates in Saginaw Bay is on the order of 20% (see fig. II-5) which is not unreasonable since a substantial fraction of the suspended particulate fraction is phytoplankton and detrital organic matter. Thus it appears that the Saginaw Bay suspended particulate PCB field data is in reasonable conformity with the experimental results, and, in particular, exhibits the relationship implied by the exchangeable-nonexchangeable model of PCB partitioning.

The implication of these results is that the expressions for dissolved and particulate fractions should be modified. In particular the particulate fraction, eq. (II-9), becomes:

$$f_p = \frac{\nu_x + m\pi_o}{1 + \nu_x + m\pi_o} \qquad \text{(II-13)}$$

A comparison of this equation to the conventional expression (eq. (II-10)) is shown in fig. II-9. Whereas at adsorbent concentrations of less than 10 mg/ℓ the conventional expression predicts no significant particulate fraction in the water column ($f_p$ = 0.09), the revised expression, eq. (II-13) predicts a substantial fraction ($f_p$ = 0.38). Although this may be compensated for by suitably increasing the "apparent" partition coefficient, the shapes of the two curves are quite different. The influence of this modification on detailed PCB fate calculations in Saginaw Bay is currently under way.

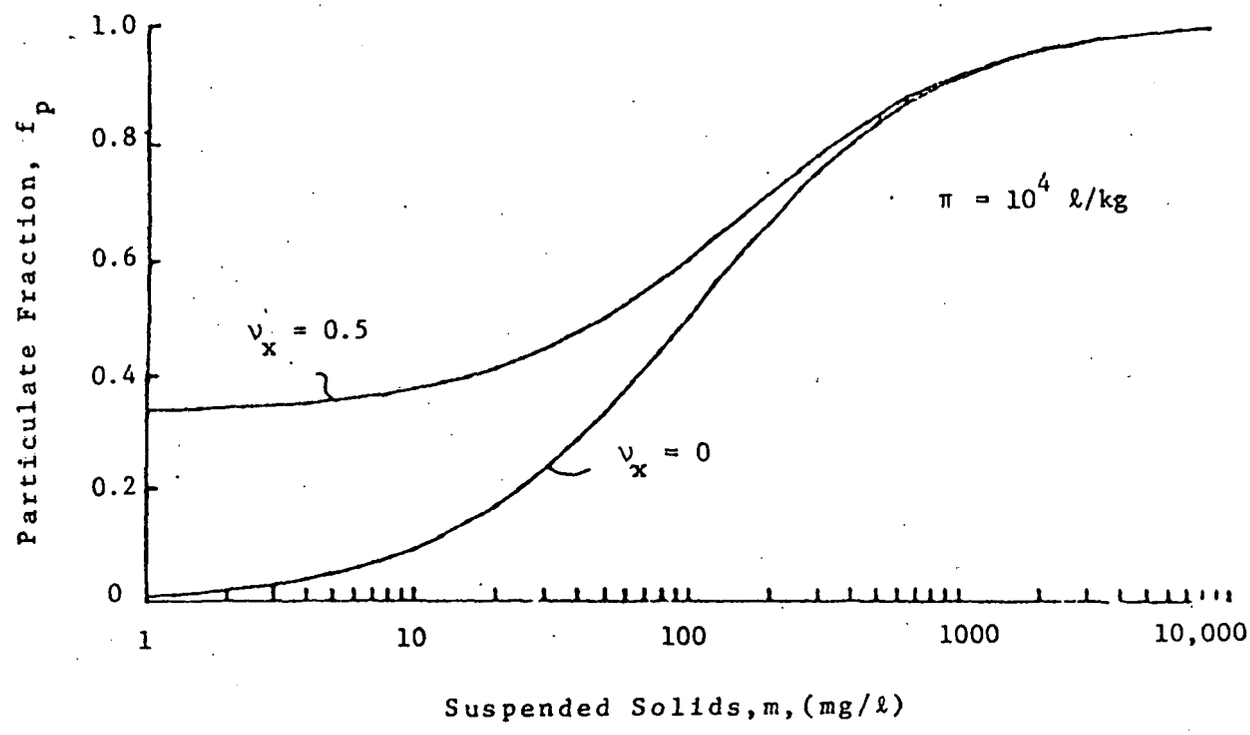



Fig. II-9 Particulate Fraction versus adsorbent concentration with and without adsorbent dependent partitioning.

## F. Discussion and Conclusions

The data presented for HCB adsorption and desorption for various Saginaw Bay sediments and clay adsorbents clearly indicates that sediment concentration has a significant effect on the extent of partitioning. The behavior of the particulate fraction is quite different from that which is expected if $\pi_a$ is constant.

The behavior of both the adsorption, $\pi_a$, and single desorption, $\pi_d$, partition coefficients as a function of sediment concentration is somewhat more complicated. They are nearly equal at low adsorbent concentrations ($m = 10$ mg/ℓ) and both decrease as m increases. They appear to reach asymptotic values in the range of $m = 200 - 1000$ mg/ℓ. However, the desorption partition coefficient varies less markedly than the adsorption partition coefficient (fig. II-1).

In contrast, the behavior of the partition coefficients for the exchangeable and nonexchangeable components is quite regular. The former is inversely proportional to adsorbent concentration and the parameter describing this behavior, $\nu_x$, is found to be nearly a constant regardless of adsorbent type or properties. This is a remarkable result and suggests that some ubiquitous mechanism is the cause for the behavior of the exchangeable component.

In contrast, the nonexchangeable component partition coefficient has been found to be constant with respect to adsorbent concentration but to vary quite markedly with adsorbent type. The interplay of these two parameters determines the extent of the adsorbent concentration effect and the degree of reversibility observed, i.e., the extent to which $\pi_d \simeq \pi_a$. Equations (II-6) and (II-7) specify the relationships. In particular if the ratio of $\pi_d$ to $\pi_a$ is used as the measure of irreversibility as was done in Section VIII of Part A, then they predict that:

$$\frac{\pi_d}{\pi_a} \rightarrow \frac{1 + \nu_x}{\nu_x} \quad \text{as } m \rightarrow \infty \qquad \text{(II-14)}$$

and

$$\frac{\pi_d}{\pi_a} \rightarrow 1 \quad \text{as } m \rightarrow o \qquad \text{(II-15)}$$

Hence PCB adsorption-desorption should appear to be quite reversible at low adsorbent concentrations, $\pi_d/\pi_a \rightarrow 1$, and to exhibit moderately nonreversible characteristics, $\pi_d/\pi_a \rightarrow 3$, at high adsorbent concentrations. Indeed, this is what was observed in Part A, fig. VIII-4 and 5.

However, if the measure of irreversibility is the difference between $\pi_d$ and $\pi_a$, then eqs. (II-6) and (II-7) predict that:

$$\pi_d - \pi_a = \frac{\pi_o}{\nu_x} \qquad \text{(II-16)}$$

which is independent of sediment concentration, and so, also, is the extent of irreversibility. The point is that the more fundamental description of HCB adsorption and desorption and their behavior as a function of sediment concentration is in terms of $\pi_o$ and $\nu_x$ and that $\pi_a$ and $\pi_d$ are simply a result of the behavior of the exchangeable and nonexchangeable components.

The description of HCB adsorbent concentration effects for both adsorption and desorption is certainly parsimonious and empirically quite successful. In addition it describes the behavior of experiments in which both aqueous phase and adsorbent concentrations are varied together as discussed in the next section. The difficulty that remains is to ascribe the results to mechanistic models. Partition coefficients that decrease as sediment concentration increases suggest that particle-particle interactions are responsible. But why should the variation be exactly inverse to mass and for the exchangeable component, why should $\nu_x$ be independent of adsorbent type.

Conversely the nonexchangeable partition coefficient appears to be constant with respect to sediment concentration but a strong function of sediment type. The mechanism that accounts for this behavior is also unknown at present. Thus although the description of adsorbent concentration effects in terms of the exchangeable and nonexchangeable component behavior is successful, it is not yet complete and additional experimental and theoretical investigations are required to determine what mechanisms are responsible for this regular, if puzzling, behavior.

## SECTION III

## RESUSPENSION AND DILUTION: IMPLICATIONS FOR FATE OF PCB

### A. Introduction

The formulation and validation of a desorption model is guided by the use for which this model is being developed: namely as a portion of the computation of toxic chemical fate. An important interaction in such models is the settling and resuspension of the adsorbent particles. Consider the situation in which particles settle into a region near the sediment-water interface. The concentration of adsorbent particles will increase in this region. Since the experimental information indicates that the exchangeable partition coefficient decreases as adsorbent mass increases, it might be expected that some desorption from the particles will take place. This mechanism would liberate PCB's to the dissolved phase and thereby increase the exposure concentration for the biota.

Conversely, decreases in suspended solids concentrations can occur if influents, which carry both PCB's and suspended solids, are dispersed in the receiving water. For example, a tributary with a high concentration of both PCB's and suspended solids enters a deeper, more quiescent, region of a lake. The mass dependent partitioning for the exchangeable components would interact to produce a redistribution of the total quantity of PCB among the adsorbed components and the soluble fraction. Both of these situations are of practical significance and are discussed below.

### B. Resuspension

An experimental design to investigate this mechanism, called a resuspension experiment, is shown in fig. III-1. Following adsorption equilibrium and adsorbent separation, a portion of the contaminated aqueous phase is removed. No new aqueous phase is added. Rather the adsorbent is then resuspended into the previously contaminated aqueous phase and equilibriated. The only change has been to increase the concentration of the adsorbent, since it is now resuspended into only a portion of the aqueous phase volume.

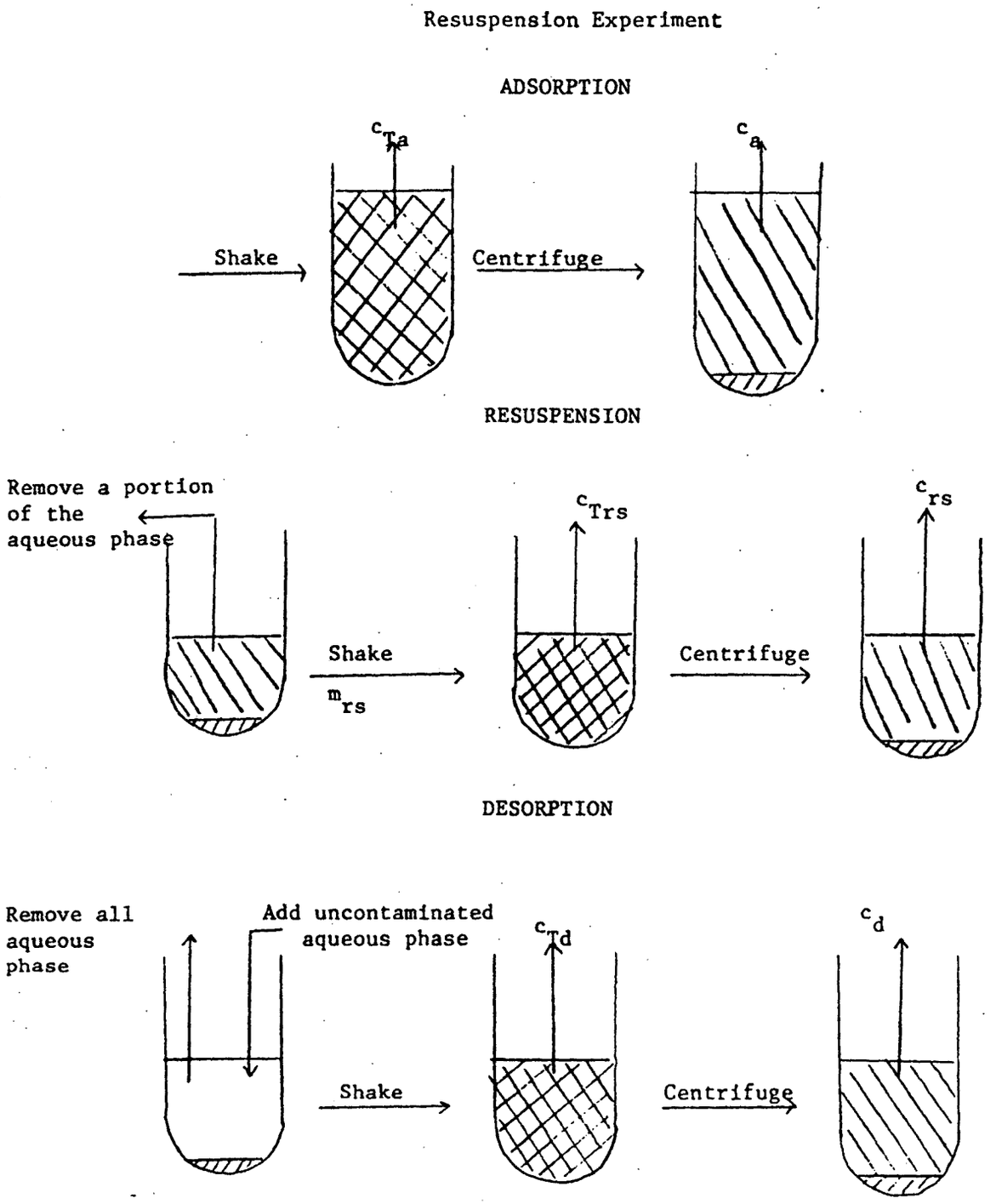



Fig. III-1. Resuspension Experimental Procedure

If the exchangeable-nonexchangeable model of desorption is valid, then it is expected that the exchangeable partition coefficient should decrease since it is inversely proportional to adsorbent mass (refer to fig. II-2). This should cause an increase of dissolved chemical in the aqueous phase. Hence, the first prediction is that the aqueous phase concentration at resuspension equilibrium should increase.

This is a somewhat surprising prediction since during resuspension equilibrium the only change that has occurred is in the number of particles per unit volume. The aqueous phase is the same as that which resulted from adsorption equilibrium. Thus each particle is exposed to the same aqueous phase concentration as it was previously exposed to, and with which it was in equilibrium. The only difference is that the particle-particle interaction is increased: each particle is exposed to more particles than at adsorption equilibria. Accordingly, one would expect no change if the particle concentration has no effect on this desorption.

But the sediment concentration experiments indicate that it does have an effect on the exchangeable component partition coefficient. Hence the resuspension experiment is a direct check on the validity of the sediment concentratopm effects and the formulation of the desorption model.

Three experiments were performed; for the first two experiments, the sediment concentration was increased four-fold from the adsorption sediment concentration of (1) $m_a$ = 55 mg/ℓ to the resuspension sediment concentration of $m_{rs}$ = 220 mg/ℓ; and (2) from $m_a$ = 220 mg/ℓ to $m_{rs}$ = 1100 mg/ℓ. For the third experiment a twenty-fold change was examined: (3) from $m_a$ = 55 mg/ℓ to $m_{rs}$ = 1100 mg/ℓ. Saginaw Bay #50 sediment was employed. The results are shown in Table III-1 where each replicate is listed. In all cases the aqueous concentration at resuspension equilibrium, $c_{rs}$, is larger than at adsorption equilibrium, $c_a$, in conformity with the rather unexpected model prediction.

The experiment is a clear confirmation of the sediment concentration on partitioning that was observed in the conventional adsorption-desorption experiments at different solids concentrations. What is unexpected is that by simply resuspending the solids into a reduced volume of supernatant but with the same HCB concentration as at adsorption equilibrium, causes any

TABLE III-1

Resuspension Experiment - Saginaw Bay #50

| Experiment No. | Adsorption $m_a$ (mg/ℓ) | Adsorption $c_a$ (ng/ℓ) | Adsorption $r_a$ (ng/g) | Resuspension $m_{rs}$ (mg/ℓ) | Resuspension $c_{rs}$ (ng/ℓ) | Resuspension $r_{rs}$ (ng/g) | Dissolved Concentration Ratio $c_{rs}/c_a$ |
|---|---|---|---|---|---|---|---|
| (1) | 55 | 41.8 | 692. | 220 | 104. | 345. | 2.49 |
| | 55 | 37.1 | 647. | 220 | 58.3 | 575. | 1.57 |
| | 55 | 38.1 | 663. | 220 | 70.9 | 443. | 1.86 |
| (2) | 220 | 22.1 | 300. | 880 | 32.2 | 286. | 1.46 |
| | 220 | 23.3 | 269. | 880 | 42.3 | 298. | 1.82 |
| | 220 | 21.5 | 259. | 880 | 27.5 | 301. | 1.28 |
| (3) | 55 | 29.8 | 497. | 1100 | 84.8 | 488. | 2.85 |
| | 55 | 29.3 | 480. | 1100 | 74.4 | 458. | 2.54 |
| | 55 | 27.6 | 511. | 1100 | 63.6 | 487. | 2.30 |

change at all. The only difference is that the solids concentration has increased. What seems to be occurring is that the particle-particle interactions are increased and that either the quantity of available exchangeable sites are decreased, causing desorption, or, more likely, that the binding strength of all the exchangeable sites is decreased by the particle-particle interactions, causing desorption from all exchangeable sites.

Note that the effect is more pronounced for adsorption at (1) $m_a = 55$ mg/ℓ and resuspension at $m_{rs} = 220$ mg/ℓ for which $c_{rs}/c_a \simeq 2.0$ then at (2) $m_a = 220$ mg/ℓ and $m_{rs} = 1100$ mg/ℓ for which $c_{rs}/c_a \simeq 1.5$. This is due to the fact that the quantity of the exchangeable component is larger at the lower sediment concentration $m_a = 55$ mg/ℓ than at $m_a = 220$ mg/ℓ. To see this, consider the fraction of adsorbed HCB that is exchangeable:

$$\frac{r_x}{r_a} = \frac{\pi_x c_a}{\pi_a c_a} = \frac{\nu_x m^{-1}}{\pi_o + \nu_x m^{-1}} = \frac{\nu_x}{\nu_x + m\pi_o} \qquad \text{(III-1)}$$

so that for $\pi_o \simeq 10{,}000$ ℓ/kg and $\nu_x = 0.5$, $r_x/r_a \simeq 0.5$ at $m_a = 55$ mg/ℓ, whereas at $m_a = 220$ mg/ℓ, $r_x/r_a \simeq 0.2$.

The largest change in dissolved HCB occurs for the twenty-fold increase in sediment concentration (3) $m_a = 55$ mg/ℓ and $m_{rs} = 1100$ mg/ℓ for which $c_{rs}/c_a \simeq 2.6$, which is the result of the initially large fraction of exchangeable component present and the large change in sediment concentration.

The quantitative predictions are derived as follows. Consider the ratio of the particulate fraction of total HCB:

$$f_p = mr_a/c_{Ta} \qquad \text{(III-2)}$$

and the dissolved fraction:

$$f_d = c_a/c_T \qquad \text{(III-3)}$$

That is:

$$\frac{f_p}{f_d} = \frac{mr_a}{c_a} = \nu_x + m_a\pi_o \qquad \text{(III-4)}$$

where the second equality is what is predicted from the exchangeable-nonexchangeable model. As shown in section II, fig. II-7 the varying sediment concentration experiments are in agreement with this equation.

Now consider the effect of resuspension. The aqueous concentration at resuspension equilibrium $c_{rs}$, is increased, $c_{rs} > c_a$, due to increased sediment concentration $m_{rs} > m_a$. Hence additional nonexchangeable HCB should adsorb. This was verified by the consecutive adsorption experiment (fig. I-7). Thus the total HCB concentration at resuspension equilibrium, $c_{Trs}$, is given by:

$$c_{Trs} = c_{rs} + m_{rs} r_{rs} \qquad \text{(III-5)}$$

$$= c_{rs} + m_{rs}(r_o + r_x) \qquad \text{(III-6)}$$

since $r_{rs}$ is the sum of the exchangeable and nonexchangeable components. Since the aqueous concentration increased, the nonexchangeable component concentration should be given by the nonexchangeable isotherm: $r_o = \pi_o c_{rs}$. The exchangeable component is always determined by the reversible exchangeable isotherm: $r_x = \pi_x c_{rs}$. Therefore eq. (III-6) becomes:

$$c_{Trs} = c_{rs} + m_{rs}(\pi_o + \pi_x) c_{rs}$$

and since the exchangeable partition coefficient is mass dependent: $\pi_x = m^{-1}\nu_x$, the final formula is:

$$c_{Trs} = c_{rs}(1 + \nu_x + m_{rs}\pi_o) \qquad \text{(III-7)}$$

The dissolved fraction is:

$$f_d = \frac{c_{rs}}{c_{Trs}} = \frac{1}{1 + \nu_x + m_{rs}\pi_o} \qquad \text{(III-8)}$$

the fraction particulate is:

$$f_p = 1 - f_d \qquad \text{(III-9)}$$

and the ratio is:

$$\frac{f_p}{f_d} = \nu_x + m_{rs}\pi_o \qquad \text{(III-10)}$$

which is the same form as the particulate to dissolved ratio at adsorption equilibrium (eq. III-4) except that it is evaluated at the sediment concentration at resuspension, $m_{rs}$. Figure III-2 presents the results for both the adsorption and resuspension ratios, which also contains the desorption model prediction for this experiment. The ratio of the fraction of particulate to dissolved chemical is predicted to increase as sediment mass is increased. As shown the experimental results are in conformity with the quantitative prediction. The data, although somewhat scattered, is consistent with $\nu_x = 0.5$ and $\pi_o = 10{,}000$ ℓ/kg, which are in fairly close agreement to the results of the adsorption-desorption experiments at varying sediment concentrations (fig. II-2, $\pi_o = 10{,}000$ ℓ/kg and $\nu_x = 0.624$).

## C. Component Behavior at Resuspension Equilibrium

Since the desorption model is based upon the distinct behavior of the exchangeable and nonexchangeable components, the experimental design includes a final desorption step (fig. II-1). Its purpose is analogous to the desorption phase of the previous experimental designs: namely to allow the determination of the concentration of exchangeable and nonexchangeable components actually on the particles at resuspension equilibrium. The increased aqueous phase concentration at resuspension equilibrium should interact with the particles. Since the nonexchangeable partition coefficient is constant with respect to sediment concentrations (fig. II-2), this increased aqueous concentration should cause the nonexchangeable component concentration to increase via increased adsorption until it is in equilibrium with the increased aqueous phase. These quantities, expressed as partition coefficients, are compared to the model predictions in fig. III-3. The lines represent the theoretical behavior inferred from the sediment concentration experiments. The results of the desorption following the resuspension experiments are shown as are parallel adsorption-desorption experiments. Although quite scattered, the component behavior is in rough conformity with expectations: the observed exchangeable partition coefficients do decrease, and the observed nonexchangeable partition coefficient are approximately constant. The data are given in the Appendix.

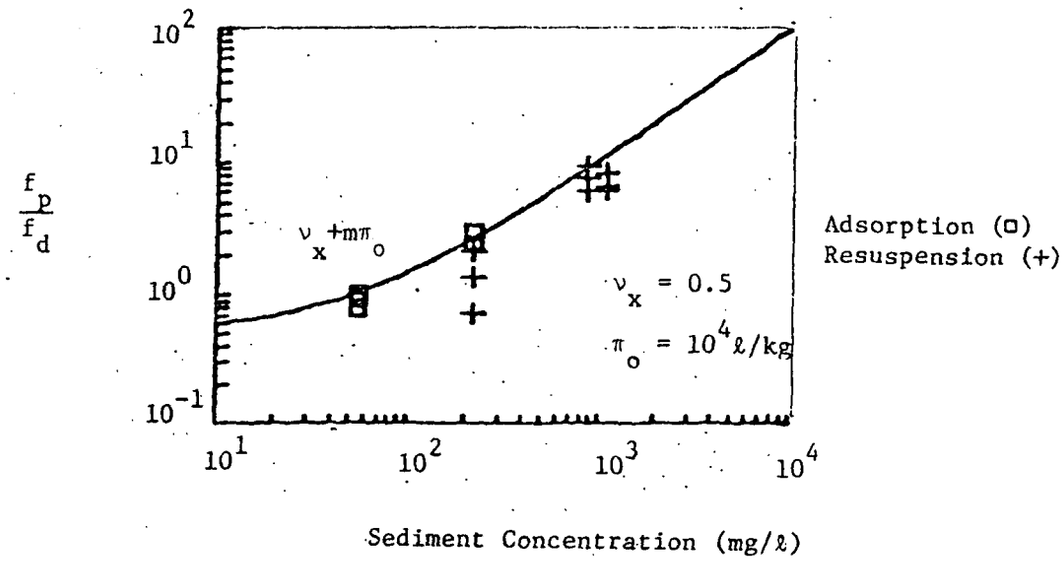



Fig. III-2. Resuspension Experiment - Model Predictions and Observations

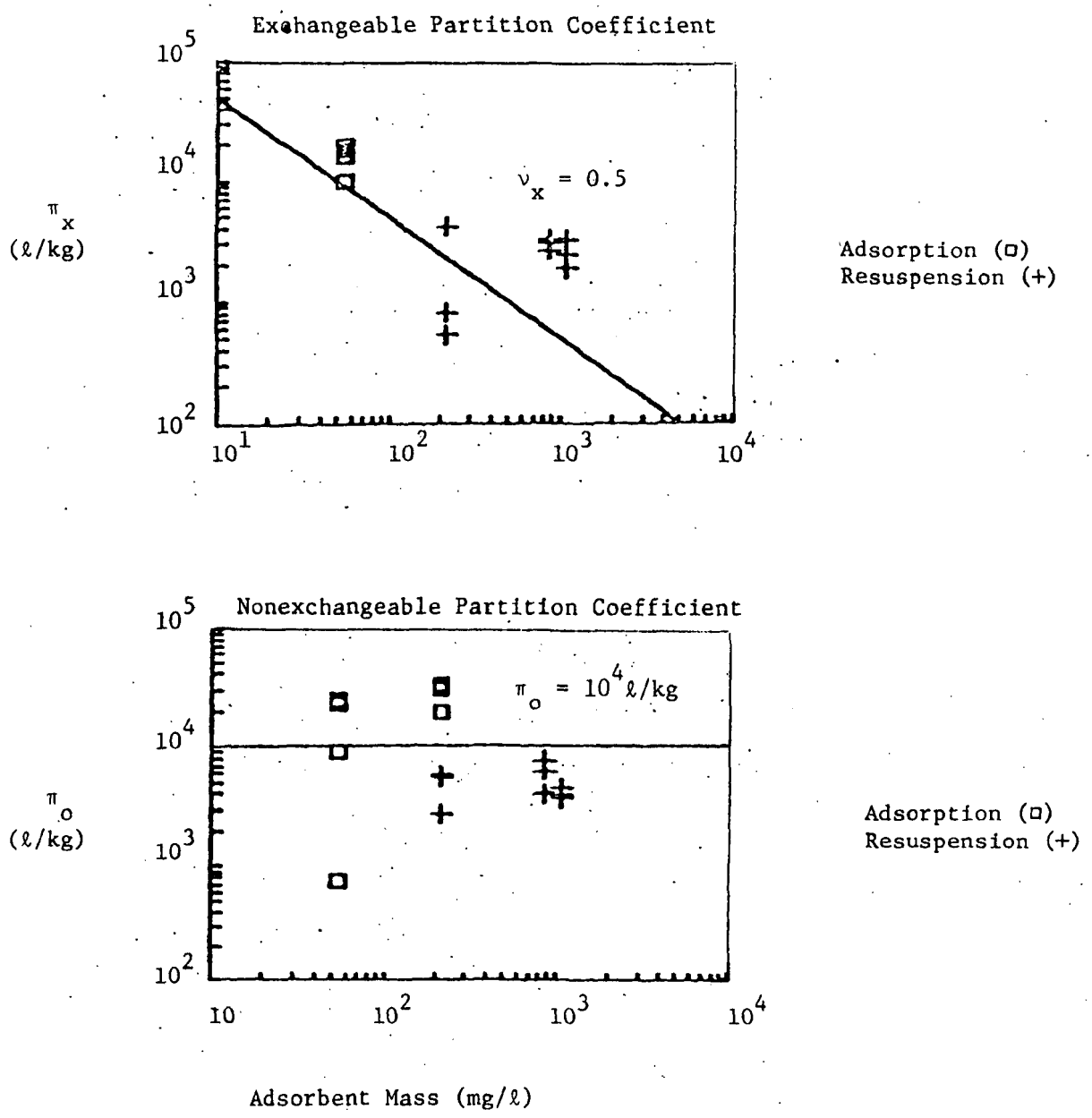



Fig. III-3. Exchangeable and Nonexchangeable Component Behavior at Adsorption and Resuspension Equilibria

However the agreement is not sufficient to firmly establish that component behavior is in absolute accord with model predictions. More experiments of this type would be required to firmly establish the detailed validity of component behavior.

## D. Dilution Experiment

The dilution experiment is, in a sense the reverse of the resuspension experiment, in that the concentration of sediment is reduced by adding uncontaminated aqueous phase to the vessel after adsorption equilibrium is achieved. This procedure is sometimes used to construct adsorption isotherms without an intervening solids separation step. It has been suggested that a possible cause of the nonsingularity of adsorption and desorption isotherm is the solids separation step, which involves centrifuging and subsequent resuspension into adsorbate-free aqueous phase. This mechanical procedure can conceivably alter the particle aggregations so that the available sites and, therefore, the observed desorption partition coefficient increases.

The dilution isotherm avoids the solids separation step. As shown in fig. III-4: following adsorption equilibrium, a fraction of the mixed aqueous-solids phase is removed and replaced by adsorbate-adsorbent-free aqueous phase. This step lowers the aqueous phase adsorbate concentration and causes desorption to occur. Unfortunately the dilution step also lowers the solids concentration so that the analysis of this experiment must account for that effect as well. If sediment concentrations affect the partitioning then the dilution "isotherm" is not a direct experimental determination of the desorption isotherm because of the sediment concentration reduction which occurs at dilution. However if the sediment concentration effect has been quantified, as it has for the model of adsorption and desorption proposed in this report, then it is possible to account for this effect.

An analysis of the dilution experiment can be made using the predicted ratio of particulate to dissolved fractions at adsorption and dilution equilibrium in the same way as the resuspension experiment. At adsorption equilibrium, the ratio of $f_p = 1 - f_d$, to the dissolved fraction: $f_d = c_a/c_{Ta}$ is

Dilution Experiment

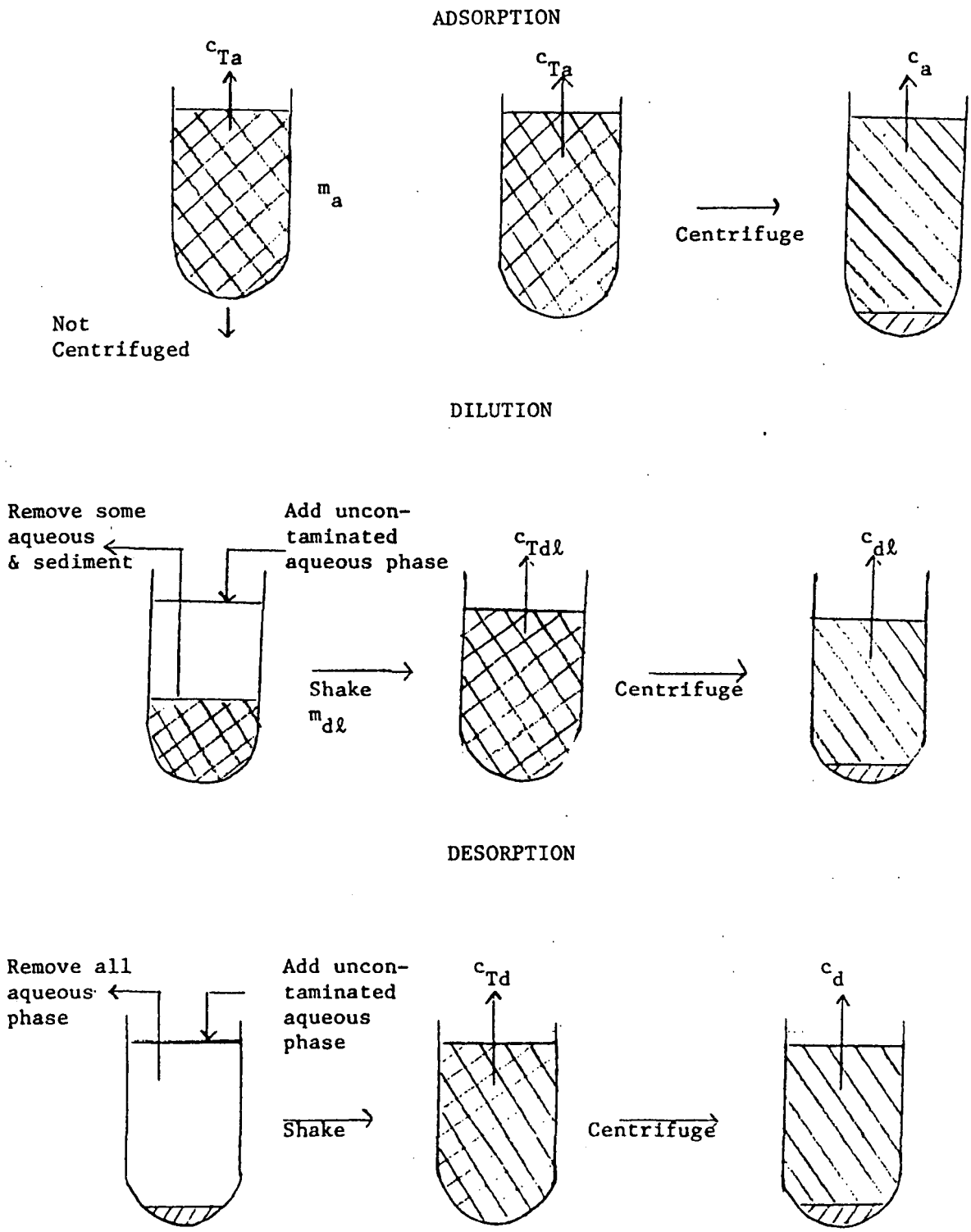



Fig. III-4. Experimental Procedure for Dilution Experiment

given by: (eq. II-1)

$$\frac{f_p}{f_d} = \nu_x + m_a \pi_o \qquad \text{(III-11)}$$

The sediment concentration effect accounts for the difference between this expression and the conventional expression: $f_p/f_d = m_a \pi_a$.

Consider the situation at dilution equilibrium. The total concentration is given by:

$$c_{Td\ell} = c_{d\ell} + m_{d\ell} r_{d\ell} \qquad \text{(III-12)}$$

where $c_{d\ell}$ and $r_{d\ell}$ are the aqueous and particulate concentrations and $m_{d\ell}$ is the sediment concentration at dilution equilibrium. The particulate concentration is made up of the sum of the nonexchangeable, $r_{od\ell}$, and exchangeable, $r_{xd\ell}$, components, that is:

$$r_{d\ell} = r_{od\ell} + r_{xd\ell} \qquad \text{(III-13)}$$

The exchangeable component has reacted to the lowered aqueous concentration caused by the dilution and it is given by the exchangeable isotherm:

$$r_{xd\ell} = \pi_x c_{d\ell} \qquad \text{(III-14)}$$

However, the nonexchangeable component does not react, since it is nonexchangeable. Rather it remains at the concentration that is determined by the nonexchangeable isotherm at adsorption equilibrium:

$$r_{od\ell} = r_o = \pi_o c_a \qquad \text{(III-15)}$$

Hence the particulate concentration at dilution equilibrium is, from eqs. (III-13, 14 and 15):

$$r_{d\ell} = \pi_o c_a + \pi_x c_{d\ell} \qquad \text{(III-16)}$$

Using this expression in eq. (III-12) yields:

$$c_{Td\ell} = c_{d\ell} + m_{d\ell}(\pi_o c_a + \pi_x c_{d\ell}) \qquad \text{(III-17)}$$

and since $m_{d\ell}\pi_x = \nu_x$ from the exchangeable-partition coefficient - sediment concentration relationship, the result is that:

$$c_{Td\ell} = c_{d\ell}(1 + \nu_x + m_{d\ell}\pi_o c_a/c_{d\ell}) \qquad \text{(III-18)}$$

and the dissolved fraction at dilution equilibrium is given by:

$$f_d = \frac{c_{d\ell}}{c_{Td\ell}} = \frac{1}{1 + \nu_x + m_{d\ell}\pi_o(c_a/c_{d\ell})} \qquad \text{(III-19)}$$

and finally, the particulate to dissolved fraction ratio is:

$$\frac{f_p}{f_d} = \nu_x + m_{d\ell}\pi_o\left(\frac{c_a}{c_{d\ell}}\right) \qquad \text{(III-20)}$$

Note the difference between this formula, which applies at dilution equilibrium, and eq. (III-11) which applies at adsorption equilibrium. The ratio is larger for dilution equilibrium due to the presence of the factor: $c_a/c_{d\ell}$, which is due to the assumption that the nonexchangeable component concentration is determined by the aqueous concentration at adsorption equilibrium: $r_o = \pi_o c_a$ and that it remains constant at dilution equilibrium and does not decrease in response to the decreased aqueous concentration that is: $c_{d\ell} < c_a$, whereas: $r_{od\ell} = r_o$ (eq. III-15).

The experimental data is compared to the (incorrect) expression for the particulate to dissolved ratio that applies only at adsorption equilibrium:

$$\frac{f_p}{f_d} = \nu_x + m\pi_o \qquad \text{(Adsorption)} \qquad \text{(III-21)}$$

in fig. III-5. Note that the ratio found for the dilution experiment is significantly larger than that predicted from the adsorption sediment concentration effect alone. This suggests that indeed dilution equilibration is not simply another technique to produce adsorption isotherms even if the sediment concentration effect is taken into account. In fact the nonreversibility persists and the particulate fraction is larger than expected. It is not linearly related to sediment concentration as is predicted by the adsorption equilibrium expression (eq. III-21).

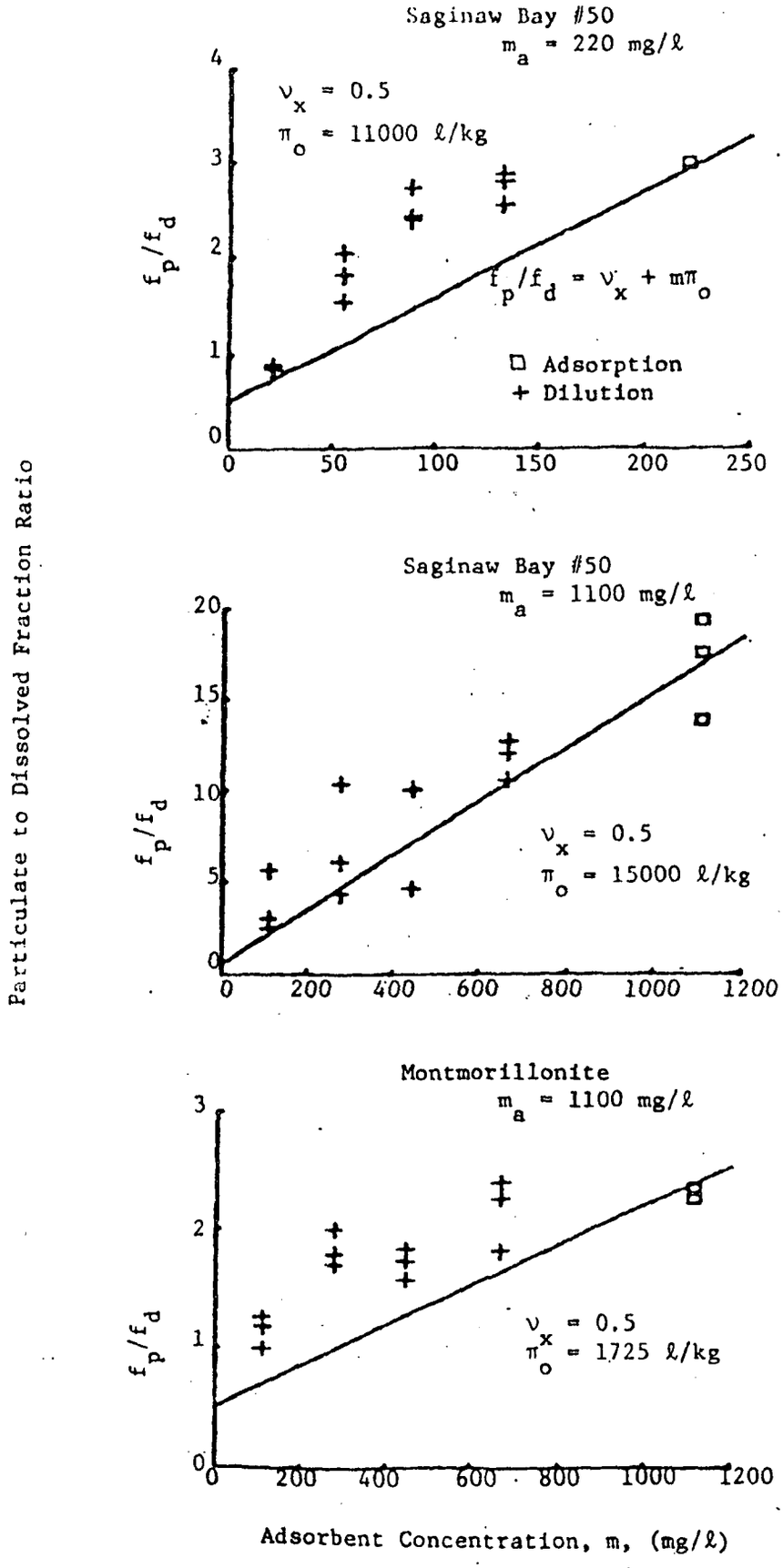



Fig. III-5. Comparison of Observed Particulate to Dissolved Fraction Ratio-Adsorbent Mass Relation Without Correction due to the Dilution Equilibration

By contrast, if the nonreversibility is taken into account, then the particulate-dissolved concentration ratio is given by:

$$\frac{f_p}{f_d} = \nu_x + m\pi_o\left(\frac{c_a}{c_{d\ell}}\right) \qquad \text{(Adsorption and Dilution)} \qquad \text{(III-22)}$$

This expression predicts a straight line if the ratio is plotted against sediment concentration, m, modified by the ratio of aqueous concentration of adsorption equilibrium, $c_a$, to aqueous concentration at dilution equilibrium, $c_{d\ell}$. Since the former concentration is not measured in the dilution experiment, it is estimated from the total concentration at adsorption equilibrium, $c_{Ta}$, which is measured and the adsorption partition coefficient, $\pi_a$, which is available from the parallel adsorption experiment, as described previously. The results are shown in fig. III-6 where $f_p/f_d$ are plotted against $mc_a/c_{d\ell}$. The straight line corresponds to eq. (III-22), the prediction of the exchangeable-nonexchangeable model. The values of $\pi_o$ and $\nu_x$ (from which $\pi_a = \pi_o + \nu_x m_a^{-1}$ is also calculated) are shown in the figure.

The value of the exchangeable distribution coefficient is $\nu_x = 0.5$ in all cases, in conformity with the experiments for which sediment concentration was varied. The nonexchangeable partition coefficient, $\pi_o$, is chosen to conform with the parallel adsorption experiment.

Note that the dilution experimental data are in conformity with the prediction except at the largest dilution, corresponding to the lowest aqueous concentrations. This suggests that, although the exchangeable-nonexchangeable model is certainly more successful than the model which accounts for only the adsorption sediment concentration (compare fig. III-5 to fig. III-6), it is not fully descriptive of the behavior of the experiments at large dilutions. This failure was also noted at low aqueous concentrations in the analysis of consecutive desorption isotherms, where for $m_a = 220$ mg/ℓ, it appeared that eventually it may be possible to desorb the nonexchangeable component (fig. VIII -12 of Part A). This point is discussed below in more detail.

## E. Component Behavior at Dilution Equilibrium

The utility of the division of adsorbed HCB into exchangeable and nonexchangeable components depends upon the applicability of the isotherms

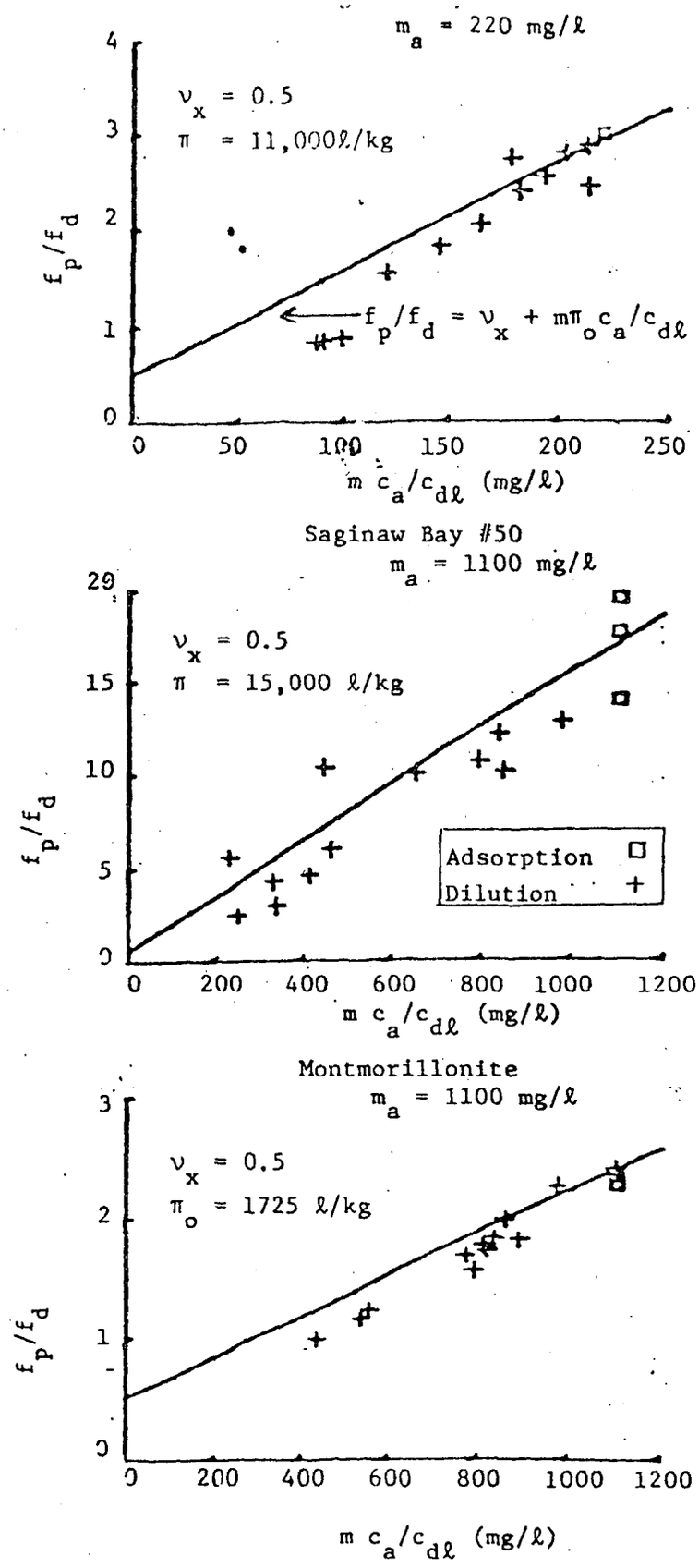



Fig. III-6. Comparison of Observed Particulate to Dissolved Fraction Ratio to Adsorbent Mass, modified by $c_a/c_{d\ell}$ as predicted from the Exchangeable-Nonexchangeable Model

$r_o = \pi_a c_a$ and $mr_x = \nu_x c$ to all situations that may be encountered during simulations of mixing phenomena in natural waters. In particular the dilution experiment can be thought of as the experimental analog of the mixing that would occur if a tributary stream carrying a high HCB and suspended solids concentration enters a relatively uncontaminated, suspended solids free receiving water. The question is: are the isotherms capable of predicting the results. More specifically, is each component behaving as expected. The analysis of the ratio of particulate to dissolved fractions suggest that it is. However a more detailed answer to this question involves a direct measurement of the component concentrations at dilution equilibrium. This can be determined if a desorption step follows dilution step in the experiment. The final desorption step generates the desorption points ($c_d$, $r_d$), which when extrapolated, can be used to calculate the exchangeable and nonexchangeable components at dilution equilibrium in a way that is directly analogous to the method employed in the conventional adsorption-desorption experiment with the exception that the dilution concentrations replace the adsorption concentrations.

That is the nonexchangeable particulate concentration is estimated using:

$$r_{od} = \frac{r_d - \beta_d r_{d\ell}}{1 - \beta_d} \qquad \text{(III-23)}$$

where $\beta_d = c_d/c_{d\ell}$, and the exchangeable partition coefficient, is given by:

$$\pi_{xd} = \frac{r_{od} - r_{d\ell}}{c_{d\ell}} \qquad \text{(III-24)}$$

The model is based upon the hypothesis that the nonexchangeable component concentration achieved at adsorption equilibrium, $r_o$, showed no change during dilution since the aqueous concentration decreases. By performing the subsequent desorption step an estimate, $r_d$, is made of the nonexchangeable component concentration. If it were entirely nonexchangeable it should remain constant, as aqueous concentrations decrease. The experimentally estimated nonexchangeable component concentrations (eq. III-23) are shown in fig. III-7 for the three dilution experiments. The parallel adsorption-desorption experimental estimates are shown as well. They are plotted against $c_a$ and $c_{d\ell}$ respectively. It can be seen that for the lower initial sediment concentration experiment

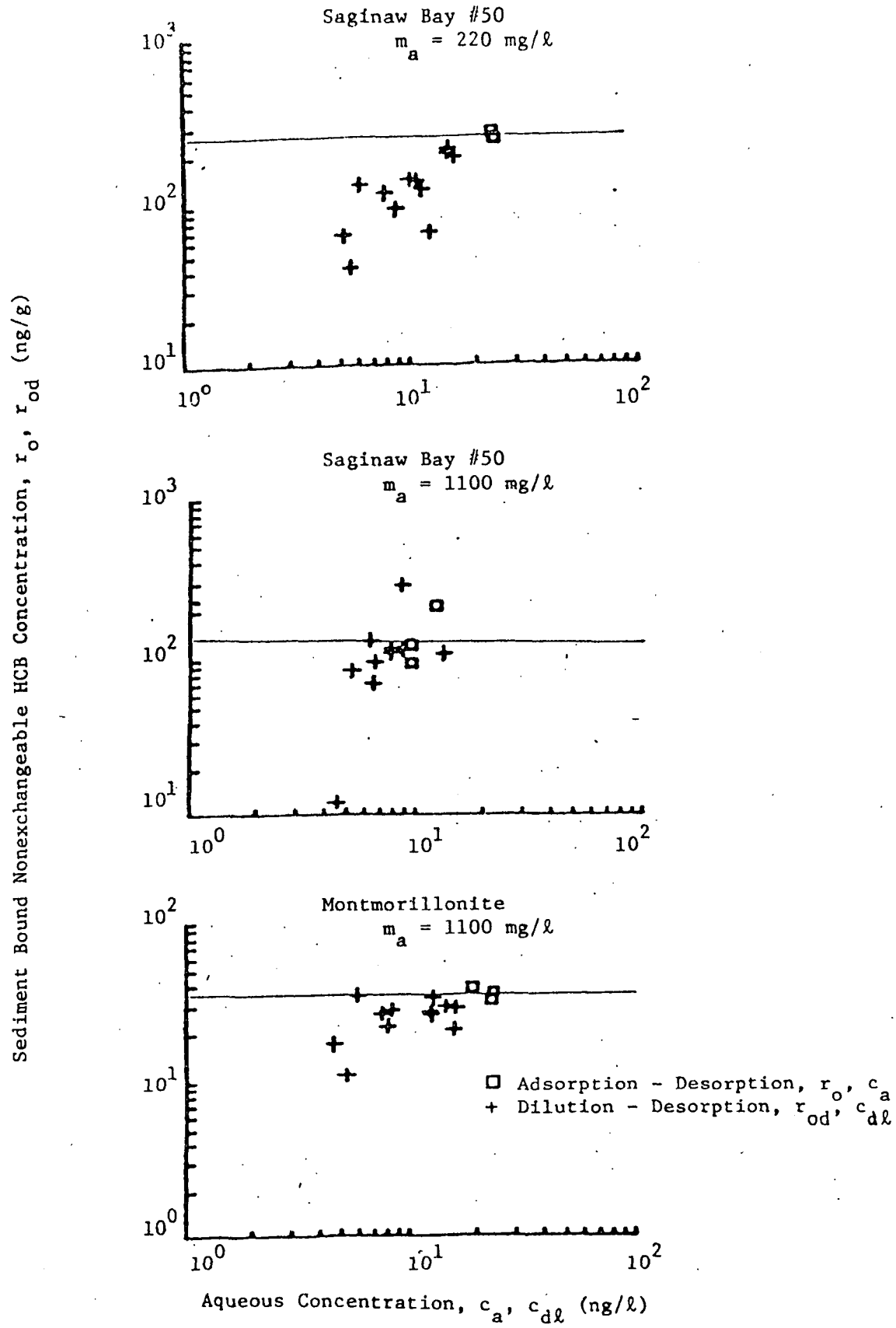



Fig. III-7. Nonexchangeable Component Concentration at Adsorption and Dilution Equilibrium, estimated using a subsequent desorption, versus aqueous HCB concentration at adsorption and dilution equilibrium respectively

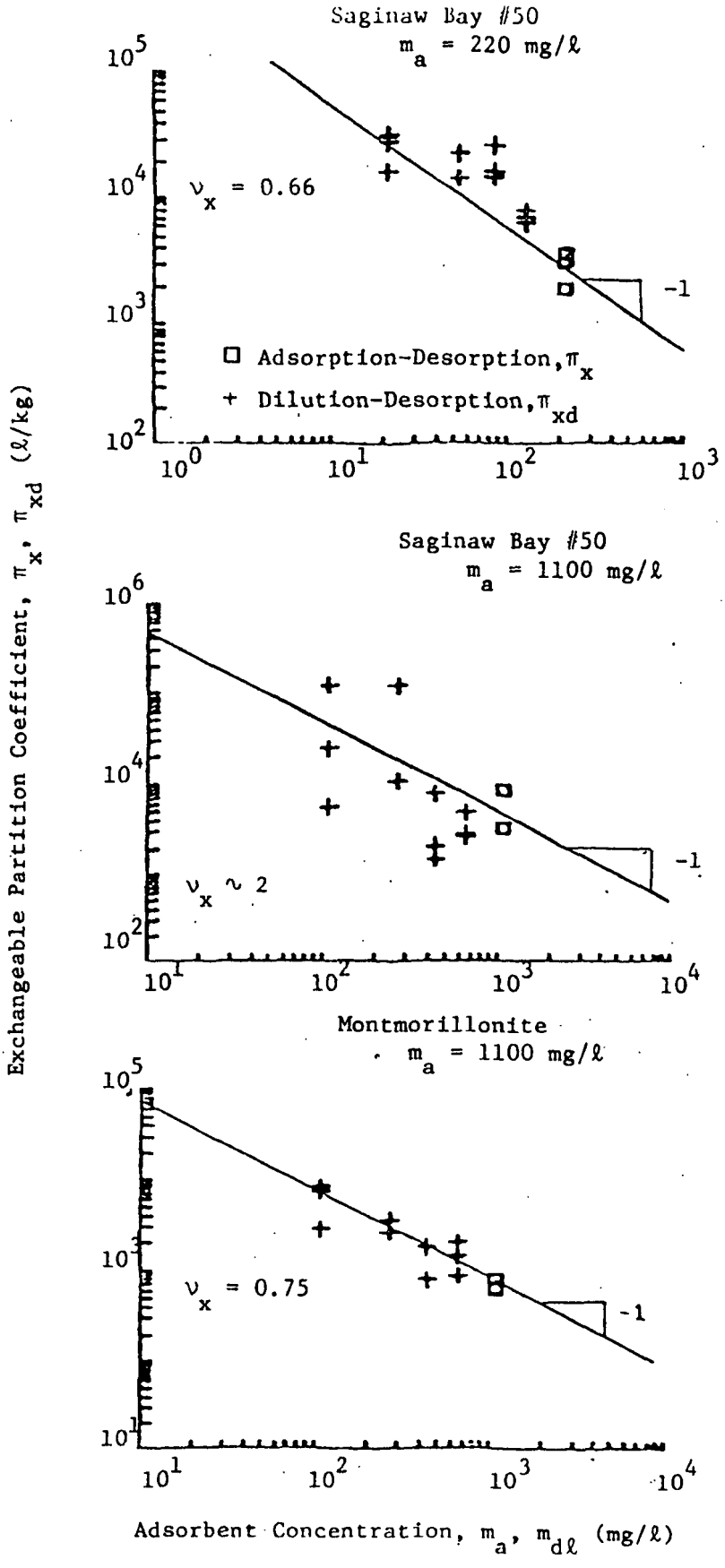



Fig. III-8. Exchangeable Partition Coefficient at Adsorption and Dilution Equilibrium Estimated from the Subsequent Desorption, versus Adsorbent Concentration, $m_a$ and $m_{d\ell}$ respectively

(Saginaw Bay, $m_a$ = 220 mg/ℓ) the nonexchangeable concentration appears to decrease with decreasing aqueous concentrations in violation of the assumption of nonexchangeability whereas for the higher initial sediment concentrations, the nonexchangeable hypothesis is roughly supported.

By contrast, the experimentally estimated exchangeable partition coefficients appear to conform to an inverse relationship to sediment concentration as shown in fig. III-8 although the scatter in the data is substantial. The lines have a slope of minus one in conformity with the relationship: $\pi_x \sim m^{-1}$ and $\nu_x \sim 0.5$ except for the scattered data at $m_a$ = 1100 mg/ℓ for Saginaw Bay.

Hence, while the exchangeable component behavior appears to be in agreement with the model hypothesis, the nonexchangeable component appears to be more exchangeable at lower sediment concentrations than assumed in the model formulation.

## F. Application to Receiving Water Fate Models

The use of models for the computation of toxic chemicals exposure levels in natural waters is currently an important component of rational toxic chemical regulation and control. The development of EXAMS by EPA (Baughman and Lassiter, 1978), models for PCB, radionuclides and toxic heavy metals in the Great Lakes by our group at Manhattan College, and other investigations, are currently in progress. These models have a common approach in dealing with the adsorption-desorption reaction.

The mass balance equations are written in terms of total chemical, $c_T$, with the transport and kinetic terms suitably modified with the fraction of chemical in the dissolved, $f_d$, or particulate, $f_p$, form depending on whether the terms in the equation apply to particulate or dissolved phases. As an example, consider a two layer segmentation representing the water column of depth $H_1$, and an active sediment layer of depth $H_2$. These interact via vertical mixing of the aqueous phases, with mass transfer coefficient $K_L$; and settling and resuspension of the particulate phases, with velocities $w_a$ and $w_{rs}$ respectively. The governing mass balance equations are:

$$H_1 \frac{dc_{T1}}{dt} = K_L(f_{d2}c_{T2} - f_{d1}c_{T1}) - w_a f_{p1} c_{T1} + w_{rs} f_{p2} c_{T2} + W \qquad \text{(III-25)}$$

$$H_2 \frac{dc_{T2}}{dt} = K_L(f_{d1}c_{T1} - f_{d2}c_{T2}) + w_a f_{p1} c_{T1} - w_{rs} f_{p2} c_{T2} \qquad \text{(III-26)}$$

where $c_{T1}$ and $c_{T2}$ are the total chemical concentrations in the water column and sediment layers respectively, and W is the input mass loading rate ($M/L^2/T$). Note the central role of the dissolved ($f_{d1}$ and $f_{d2}$) and particulate ($f_{p1}$ and $f_{p2}$) fractions, in the water column and sediment segments respectively. They directly affect the magnitudes of the mass transfer coefficients and therefore the fate of the chemical. A more complex fate computation would include terms for outflow, the various appropriate decay mechanisms, and sedimentation losses. However, the principle is still the same. Once the total concentration is computed, the dissolved water column concentration is given by: $c_{d1} = f_{d1}c_{T1}$, with analagous expressions for the particulate concentration. Again the particulate and dissolved fractions play a central role, and these fractions are a direct result of the adsorption-desorption model employed.

For completely reversible adsorption-desorption and a linear isotherm, the dissolved and particulate fractions are given by:

$$f_d = \frac{1}{1 + m\pi} \qquad \text{(III-27)}$$

$$f_p = \frac{m\pi}{1 + m\pi} \qquad \text{(III-28)}$$

where $\pi$ is the reversible partition coefficient and m is the adsorbent concentrations. The subscripts 1 and 2 in equations (III-25 and III-26) refer to evaluating these fractions using the appropriate adsorbent concentration in segments 1 and 2.

For the HCB exchangeable-nonexchangeable component model of adsorption-desorption, these fractions depend upon the model parameters: $\pi_o$, the partition coefficient for the nonexchangeable component; and $\nu_x$, the distribution coefficient for the exchangeable component; and the maximum dissolved aqueous concentration to which the particle has been exposed: $c_{md}$. This latter concentration sets the magnitude of the nonexchangeable component. It is shown in the previous section that the dissolved and particulate fractions are given

by the expressions:

$$f_d = \frac{1}{1 + \nu_x + m\pi_o(c_{md}/c_d)} \qquad \text{(III-29)}$$

$$f_p = \frac{\nu_x + m\pi_o(c_{md}/c_d)}{1 + \nu_x + m\pi_o(c_{md}/c_d)} \qquad \text{(III-30)}$$

where $c_d$ is the current dissolved aqueous phase concentration. The particulate fraction as a function of adsorbent solids concentration, m, is shown in fig. III-9. The conventional expression, assuming reversible behavior is also shown. There is a significant difference between the conventional reversible formulation and the exchangeable-nonexchangeable model. The particulate fraction is always a substantial portion of the total chemical concentration, even at low suspended solids concentrations that are characteristic of most receiving waters (10-100 mg/ℓ). This suggests that fate computations using the exchangeable-nonexchangeable model will give quite different results which emphasize the importance of particle transport.

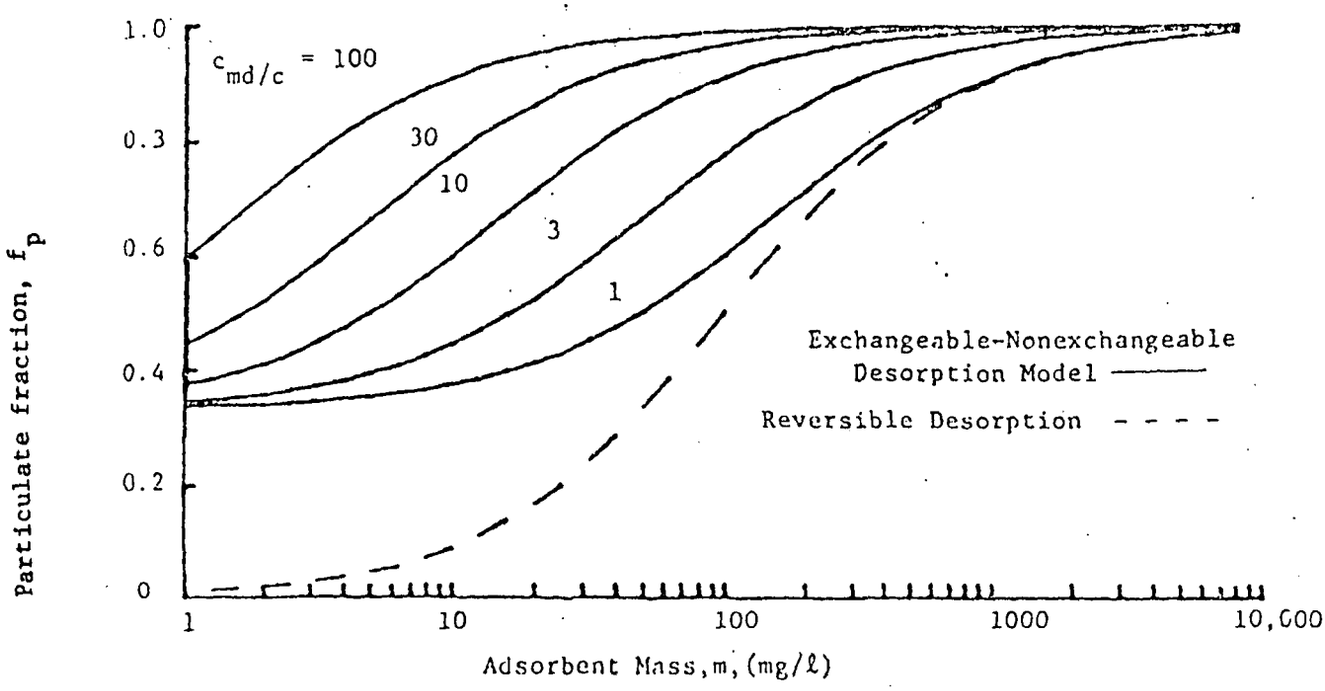



Fig. III-9. Particulate fraction versus adsorbent mass for reversible desorption, eq. (III-28); and exchangeable-nonexchangeable desorption, eq. (III-30). $\pi_o = 10^4$ ℓ/kg, $\nu_x = 0.5$

## REFERENCES


Baughman, G.L., Lassiter, R.R. Prediction of Environmental Pollutant Concentration in Estimating the Hazard of Chemical Substances to Aquatic Life. Cairns, J., Dickson, K.L., Maki, A.W. eds. ASTM STP 657. 1978, pp. 35-70.

Bowman, B.T., Sans, W.W. Adsorption of Parathion, Fenitroghion, Methyl Parathion, Aminoparathion and Paraoxon by Na, Ca, and Fe Montmorillonite Suspension. Soil Soc. Am. J., Vol. 41, pp. 514-519. 1977.

Bowman, B.T. Method of Repeated Additions for Generating Pesticide Adsorption-Desorption Isotherm Data. Can. J. Soil Sci., Vol. 59, pp. 435-437. Nov. 1979.

Connolly, J.P. The Effect of Sediment Suspension on Adsorption and Fate of Kepone. Ph.D. Thesis, University of Texas, Austin, Texas. 208 p. 1980.

Felsot, A., Dahm, P.A. Sorption of Organophosphorus and Carbamate Insecticides by Soil, Agricul. Food Chem., Vol. 27, pp. 557-563. 1979.

Hague, R. ed. Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. Ann Arbor Science Publ. Inc., Ann Arbor, Mich. 48106. 1980.

Hiraizumi, Y.M., Takahashi, M., Nishimura, H. "Adsorption of Polychlorinated Biphenyl onto Sea Bed Sediment, Marine Plankton, and other Adsorbing Agents." Environ. Sci. Tech., Vol. 13(5), p. 580. 1979.

Huang, Ju-C, Liao, C. Adsorption of Pesticides by Clay Minerals. J. Sanit. Engr. Div., ASCE, Vol. 96, SA5, pp. 1057-1078. 1970.

Karickhoff, S.W., Brown, D.S., Scott, T.A. Sorption of Hydrophobic Pollutants on Natural Sediments. Water Research, Vol. 13, p. 241. 1979.

Kishk, F.M., Abu-Sharar, T.M., Bakry, N.M., Abou-Donia, M.B. Sorption-Desorption Characteristics of Methyl Parathion by Clays. Arch. Environ. Contam. Toxicol., Vol. 8, pp. 637-645. 1979.

Koskinen, W.C., O'Connor, G.A., Cheng, H.H. Characterization of Hystersis in the Desorption of 2,4,5-T in Soils. Soil Sci. Soc. Am. J., Vol. 43, pp. 871-874. 1979.

Lotse, E.G., Graetz, D.A., Chesters, G., Lee, G.B., Newland, L.W. Lindane Adsorption by Lake Sediments. Environ. Sci. Technol., Vol. 2, No. 5, p. 353. 1968.

Marking, L.L., Kimberle, R.A., eds. Aquatic Toxicology Proc. Second Annual Symposium on Aquatic Toxicology. ASTM STP 667. 1979.

Mayer, F.L., Hamelink, J.L., eds. Aquatic Toxicology and Hazard Evaluation. Proc. First Annual Symposium on Aquatic Toxicology. ASTM STP 634. 1916 Race St. Phil. Pa. 19103. 1977.

O'Connor, D.J., Connolly, J.P. The Effect of Concentration of Adsorbing Solids on the Partition Coefficient". Water Research, 14, p. 1517. 1980.

O'Connor, D.J., Schnoor, J.L. Distribution of Organic Chemicals and Heavy Metals in Lakes and Reservoirs, in press.

Peck, D.E., Corwin, D.L., Farmer, W.J. Adsorption-Desorption of Diuron by Freshwater Sediments. J. Environ. Qual., Vol. 9, pp. 101-106. 1980.

Pierce, R.H., Jr., Olney, C.E., Felbeck, G.T., Jr. pp'-DDT Adsorption to Suspended Particulate Matter in Sea Water. Geochim. Cosmochim. Acta, Vol. 38, pp. 1061-1073. 1974.

Rao, P.S.C., Davidson, J.M. Estimation of Pesticide Retention and Transformation Parameters Required in Nonpoint Source Pollution Models in Environmental Impact of Nonpoint Source Pollution, ed. M.R. Overcash, J.M. Davidson. Ann Arbor Science Publishers, Inc., pp. 23-67. 1980.

Rao, P.S.C., Davidson, J.M. Nonsingularity of Pesticide Adsorption-Desorption Isotherms: Effect of Experimental Method, submitted to J. Environ. Qual. 1980.

Savage, K.E., Wauchope, R.D. Fluometuron Adsorption-Desorption Equilibria in Soil. Weed Sci., Vol. 22, pp. 106-110. 1974.

Swanson, R.A., Dutt, G.R. Chemical and Physical Processes that Affect Atrazine Distribution in Soil Systems. Soil Sci. Soc. Am. Proc., Vol. 37, pp. 872-876. 1973.

Thomann, R.V., Di Toro, D.M. Preliminary Model of Recovery of the Great Lakes Following Toxic Substances Pollution Abatement. Workshop on Scientific Basis for Dealing with Chemical Toxic Substances in the Great Lakes. Great Lakes Basin Commission, Ann Arbor, Mich. 1979. Submitted, J. Great Lakes Res. 1980.

van Genuchten, M.Th., Davidson, J.M., Wierenga, P.J. An Evaluation of Kinetic and Equilibrium Equations for the Prediction of Pesticide Movement Through Porous Media. Soil Sci. Soc. Amer. Proc., Vol. 38, pp. 29-35. 1974.

van Genuchten, M.Th. Wierenga, P.J., O'Connor, G.A. Mass Transfer Studies in Sorbing Porous Media: III. Experimental Evaluation with 2,4,5-T. Soil Sci. Soc. Am. J., Vol. 41, pp. 278-285. 1977.

Wildish, D.J., Metcalfe, C.D., Akagi, H.M., McLeese, D.W. Flux of Aroclor 1254 Between Estuarine Sediments and Water. Bull. Environ. Contam. Toxicol. Vol. 24, pp. 20-26. 1980.

# APPENDIX

## DATA APPENDIX

| Table No. | Sediment | Aqueous Phase | Sedi. Conc. (mg/ℓ) | Time of Ads. (hours) | Time of Des. (hours) |
|---|---|---|---|---|---|
| KINETIC STUDY | | | | | |
| 1 | Montmorillonite | Supernatant | 200 | 0.75-24 | |
| 2 | Sag Bay Sta.#50 | Supernatant | 200 | 0.25-24 | |
| 3 | Montmorillonite | Supernatant | 200 | 2 | 0.25-24 |
| 4 | Sag Bay Sta.#50 | Supernatant | 200 | 2 | 0.25-6 |
| ISOTHERM | | | | | |
| 5 | Sag Bay Sta.#50 | Dist. Water | 50-55 | 2-3 | 1.5-3 |
| 6 | Sag Bay Sta.#50 | Dist. Water | 55 | 48 | 48 |
| 7 | Sag Bay Sta.#50 | Dist. Water | 55 | 240 | 240 |
| 8 | Sag Bay Sta.#50 | Dist. Water | 200 | 4 | |
| 9 | Sag Bay Sta.#50 | Dist. Water | 220 | 3 | 3 |
| 10 | Sag Bay Sta.#50 | Dist. Water | 1000 | 2-4 | 1.5 |
| 11 | Sag Bay Sta.#50 | Dist. Water | 1100 | 3 | 3 |
| 12 | Sag Bay Sta.#50 | Dist. Water | 1100 | 24 | |
| 13 | Sag Bay Sta.#50 | Supernatant | 1100 | 120 | |
| 14 | Sag Bay Sta.#50 | Dist. Water | 1100 | 3 | 72 |
| 15 | Sag Bay Sta.#50 | Dist. Water | 1100 | 3 | 144 |
| 16 | Montmorillonite | Dist. Water | 50 | 2-3 | 1.5-3 |
| 17 | Montmorillonite | Dist. Water | 200 | 2-3 | 1.5-3 |
| 18 | Montmorillonite | Dist. Water | 1000 | 2 | 1.5-3 |
| 19 | Montmorillonite | $NaHCO_3$ Buffer | 50 | 3 | 3 |
| 20 | Montmorillonite | $NaHCO_3$ Buffer | 1100 | 3 | 3 |
| 21 | Kaolinite | Dist. Water | 1000 | 2.0 | 1.5 |
| SOLUTION COMPOSITION | | | | | |
| 22 | Montmorillonite | NaCl | 200 | 4 | |
| 23 | Montmorillonite | HCl & NaOH | 200 | 4 | |
| 24 | Montmorillonite | $CaCl_2$ | 200 | 4 | |
| ISOTHERM-SEDIMENT COMPOSITION | | | | | |
| 25 | Sag Bay Sta.#43 | Dist. Water | 1100 | 3 | 3 |
| 26 | Sag Bay Sta.#50 | Dist. Water | 1100 | 3 | 3 |
| 27 | Montmorillonite | $NaHCO_3$ Buffer | 1100 | 3 | 3 |
| 28 | Sag Bay Sta.#69 | Dist. Water | 20000 | 3 | 3 |
| 29 | Sag Bay Sta.#19 | Dist. Water | 1100 | 3 | 3 |
| 30 | Saginaw River | Dist. Water | 1100 | 3 | 3 |
| 31 | Sag Bay Sta.#53 | Dist. Water | 1100 | 3 | 3 |
| 32 | Sag Bay Sta.#31 | Dist. Water | 1100 | 3 | 3 |

| Table No. | Sediment | Aqueous Phase | Sedi. Conc. (mg/ℓ) | Time of Ads. (hours) | Time of Des. (hours) |
|---|---|---|---|---|---|
| SEDIMENT CONCENTRATION | | | | | |
| 33 | Montmorillonite | Dist. Water | | 2 | 1-3 |
| 34 | Montmorillonite | Supernatant | | 2 | 1.5-5 |
| 35 | Sag Bay Sta.#50 | Dist. Water | | 2 | 1.5 |
| 36 | Sag Bay Sta.#50 | Supernatant | | 2 | 1.5-5 |
| 37 | Montmorillonite | Dist. Water | | 24 | 24 |
| 38 | Montmorillonite | Phosphate Buffer | | 2-4 | 1.5-4 |
| 39 | Silica | Dist. Water | | 3 | 3 |
| RESUSPENSION EXPERIMENT | | | | | |
| 40 | Sag Bay Sta.#50 | Dist. Water | 55-220 | | |
| 41 | Sag Bay Sta.#50 | Dist. Water | 220-880 | | |
| 42 | Sag Bay Sta.#50 | Dist. Water | 55-1100 | | |
| DILUTION EXPERIMENT | | | | | |
| 43 | Montmorillonite | $NaHCO_3$ Buffer | 1100 | | |
| 44 | Sag Bay Sta.#50 | Dist. Water | 1100 | | |
| 45 | Sag Bay Sta.#50 | Dist. Water | 220 | | |

TABLE 1. KINETIC STUDY

Sediment = Montmorillonite Aqueous Phase = Supernatant

Mass = 200 mg/ℓ Time of Adsorption = 0.75-24 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 6229.00 | 6229.00 | 6229.00 | 6229.00 | 7039.00 | 6229.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Aq. Phase | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| pH | 7.20 | 7.25 | 7.30 | 7.30 | 7.20 | 7.30 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 0.75 | 2.00 | 5.50 | 7.75 | 18.00 | 0.25 |
| Md (mg/l) | -- | -- | -- | -- | -- | -- |
| Td (hr) | -- | -- | -- | -- | -- | -- |
| Ci (mg/l) | 56.40 | 54.76 | 54.76 | 54.76 | 54.76 | 54.76 |
| CTa (mg/l) | 48.17 | 48.74 | 45.99 | 44.62 | 43.27 | 53.70 |
| Ca (mg/l) | 24.26 | 22.04 | 22.38 | 20.05 | 16.93 | 27.57 |
| Ra (mg/g) | 119.56 | 133.51 | 118.06 | 122.84 | 131.69 | 130.65 |
| Rxa (mg/g) | -- | -- | -- | -- | -- | -- |
| CTd (mg/l) | -- | -- | -- | -- | -- | -- |
| Cd (mg/l) | -- | -- | -- | -- | -- | -- |
| Rd (mg/g) | -- | -- | -- | -- | -- | -- |
| Rxd (mg/g) | -- | -- | -- | -- | -- | -- |
| Ro (mg/g) | -- | -- | -- | -- | -- | -- |
| Glass (pg) | 21.54 | 16.18 | -- | 69.89 | 24.53 | 15.55 |
| MB Er. (%) | -10.77 | -8.04 | -- | -5.75 | -16.51 | 0.92 |

TABLE 1. (cont'd) KINETIC STUDY

Sediment = Montmorillonite | Aqueous Phase = Supernatant

Mass = 200 mg/ℓ | Time of Adsorption = 0.75-24 hr.

| | | | | | |
|---|---|---|---|---|---|
| Date | 6229.00 | 6269.00 | 6279.00 | 6119.00 | 6119.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 | 2.00 |
| Aq. Phase | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| pH | 7.25 | 7.20 | 7.35 | 6.70 | 6.60 |
| Ionic | -- | -- | -- | -- | -- |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 3.00 | 6.00 | 24.00 | 4.00 | 2.00 |
| Md (mg/l) | -- | -- | -- | -- | 200.00 |
| Td (hr) | -- | -- | -- | -- | 1.50 |
| Ci (mg/l) | 56.40 | 55.85 | 54.21 | 55.30 | 55.30 |
| CTa (mg/l) | 49.63 | 54.29 | 44.72 | 48.30 | 45.56 |
| Ca (mg/l) | 22.09 | 20.08 | 27.08 | 18.85 | 20.26 |
| Ra (mg/g) | 137.72 | 171.07 | 88.22 | 147.23 | 126.53 |
| Rxa (mg/g) | -- | -- | -- | -- | 77.50 |
| CTd (mg/l) | -- | -- | -- | -- | 25.28 |
| Cd (mg/l) | -- | -- | -- | -- | 8.77 |
| Rd (mg/g) | -- | -- | -- | -- | 82.56 |
| Rxd (mg/g) | -- | -- | -- | -- | 33.54 |
| Ro (mg/g) | -- | -- | -- | -- | 49.02 |
| Glass (pg) | 73.73 | 11.80 | 2.52 | 14.18 | 9.73 |
| MB Er. (%) | 1.07 | -0.68 | -17.04 | -10.11 | -15.85 |

TABLE 2. KINETIC STUDY

Sediment = Saginaw Bay Station #50 Aqueous Phase = Supernatant

Mass = 200 mg/ℓ Time of Adsorption = 0.25-24 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 7039.00 | 6229.00 | 6229.00 | 6229.00 | 6229.00 | 6229.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Aq. Phase | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| pH | 7.05 | 6.75 | 6.75 | 6.75 | 6.75 | 6.75 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 18.00 | 0.25 | 2.00 | 7.75 | 0.75 | 3.00 |
| Md (mg/l) | -- | -- | -- | -- | -- | -- |
| Td (hr) | -- | -- | -- | -- | -- | -- |
| Ci (ng/l) | 54.76 | 54.76 | 54.76 | 54.76 | 56.40 | 56.40 |
| CTa (ng/l) | 49.38 | 53.63 | 51.66 | 56.24 | 54.27 | 52.84 |
| Ca (ng/l) | 14.55 | 16.61 | 13.73 | 10.48 | 15.22 | 12.42 |
| Ra (ng/g) | 174.14 | 185.06 | 189.65 | 228.80 | 195.24 | 202.09 |
| Rxa (ng/g) | -- | -- | -- | -- | -- | -- |
| CTd (ng/l) | -- | -- | -- | -- | -- | -- |
| Cd (ng/l) | -- | -- | -- | -- | -- | -- |
| Rd (ng/g) | -- | -- | -- | -- | -- | -- |
| Rxd (ng/g) | -- | -- | -- | -- | -- | -- |
| Ro (ng/g) | -- | -- | -- | -- | -- | -- |
| Glass (pg) | 13.37 | 12.55 | 13.70 | 33.17 | 17.21 | 11.53 |
| MB Er. (%) | -7.38 | 0.23 | -3.15 | 8.77 | -0.73 | -4.27 |

TABLE 2. (cont'd) KINETIC STUDY

Sediment = Saginaw Bay Station #50 Aqueous Phase = Supernatant

Mass = 200 mg/ℓ Time of Adsorption = 0.25-24 hr.

| | | | |
|---|---|---|---|
| Date | 6279.00 | 6309.00 | 6309.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 |
| Aq. Phase | 2.00 | 2.00 | 2.00 |
| pH | 6.80 | 6.75 | 6.75 |
| Ionic | -- | -- | -- |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 24.00 | 5.00 | 6.00 |
| Md (mg/l) | -- | -- | -- |
| Td (hr) | -- | -- | -- |
| Ci (ng/l) | 54.21 | 58.04 | 58.04 |
| CTa (ng/l) | 52.98 | 54.49 | 52.48 |
| Ca (ng/l) | 19.70 | 11.59 | 14.13 |
| Ra (ng/g) | 166.40 | 214.47 | 191.71 |
| Rxa (ng/g) | -- | -- | -- |
| CTd (ng/l) | -- | -- | -- |
| Cd (ng/l) | -- | -- | -- |
| Rd (ng/g) | -- | -- | -- |
| Rxd (ng/g) | -- | -- | -- |
| Ro (ng/g) | -- | -- | -- |
| Glass (pg) | 10.20 | 25.97 | 12.87 |
| MB Er. (%) | -0.40 | -1.65 | -7.37 |

TABLE 3. KINETIC STUDY

Sediment = Montmorillonite | Aqueous Phase = Supernatant

Mass = 200 mg/ℓ | Time of Adsorption = 2 hr. | Time of Desorption = 0.25-24 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 7039.00 | 7039.00 | 6289.00 | 6269.00 | 6269.00 | 6279.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| pH | 7.40 | 7.40 | 7.85 | 8.50 | 8.50 | 8.50 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Td (hr) | 24.00 | 18.00 | 5.00 | 0.25 | 2.00 | 0.75 |
| Ci (ng/l) | 47.09 | 54.76 | 55.85 | 55.85 | 55.85 | 54.21 |
| CTa (ng/l) | -- | -- | -- | -- | -- | -- |
| Ca (ng/l) | -- | -- | -- | -- | -- | -- |
| Ra (ng/g) | -- | -- | -- | -- | -- | -- |
| Rxa (ng/g) | -- | -- | -- | -- | -- | -- |
| CTd (ng/l) | 18.31 | 19.10 | 38.22 | 19.95 | 20.65 | 15.72 |
| Cd (ng/l) | 5.95 | 7.08 | 9.60 | 6.05 | 7.31 | 4.63 |
| Rd (ng/g) | 61.81 | 60.10 | 143.11 | 69.49 | 66.72 | 55.48 |
| Rxd (ng/g) | -- | -- | -- | -- | -- | -- |
| Ro (ng/g) | -- | -- | -- | -- | -- | -- |
| Glass (pg) | 8.26 | 9.44 | 10.55 | 5.06 | 6.72 | 11.39 |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 3.(cont'd) KINETIC STUDY

Sediment = Montmorillonite | Aqueous Phase = Supernatant

Mass = 200 mg/ℓ | Time of Adsorption = 2 hr. | Time of Desorption = 0.25-24 hr.

| | | |
|---|---|---|
| Date | 6279.00 | 6119.00 |
| Expt. Type | 2.00 | 2.00 |
| Aq. Phase | 2.00 | 2.00 |
| pH | 7.90 | 6.60 |
| Ionic | -- | -- |
| Ma (mg/l) | 200.00 | 200.00 |
| Ta (hr) | 2.00 | 2.00 |
| Md (mg/l) | 200.00 | 200.00 |
| Td (hr) | 4.00 | 1.50 |
| Ci (ng/l) | 54.21 | 55.30 |
| CTa (ng/l) | -- | 45.56 |
| Ca (ng/l) | -- | 20.26 |
| Ra (ng/g) | -- | 126.53 |
| Rxa (ng/g) | -- | 77.50 |
| CTd (ng/l) | 17.92 | 25.28 |
| Cd (ng/l) | 5.39 | 8.77 |
| Rd (ng/g) | 62.68 | 82.56 |
| Rxd (ng/g) | -- | 33.54 |
| Ro (ng/g) | -- | 49.02 |
| Glass (pg) | 9.85 | 9.73 |
| MB Er. (%) | -- | -15.85 |

TABLE 4. KINETIC STUDY

Sediment = Saginaw Bay Station #50 | Aqueous Phase = Supernatant

Mass = 200 mg/ℓ | Time of Adsorption = 2 hr. | Time of Desorption = 0.25-6 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 6289.00 | 6289.00 | 6269.00 | 6269.00 | 6269.00 | 6279.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| pH | 6.80 | 6.75 | 6.75 | 6.80 | 6.75 | 6.75 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Td (hr) | 5.00 | 6.00 | 0.25 | 2.00 | 2.00 | 0.75 |
| Ci (mg/l) | 55.85 | 55.85 | 55.85 | 55.85 | 55.85 | 54.21 |
| CTa (mg/l) | -- | -- | -- | -- | -- | -- |
| Ca (mg/l) | -- | -- | -- | -- | -- | -- |
| Ra (mg/g) | -- | -- | -- | -- | -- | -- |
| Rxa (mg/g) | -- | -- | -- | -- | -- | -- |
| CTd (mg/l) | 28.11 | 38.13 | 38.88 | 39.13 | 40.90 | 31.57 |
| Cd (mg/l) | 5.76 | 5.42 | 4.76 | 6.77 | 5.25 | 4.68 |
| Rd (mg/g) | 111.77 | 163.58 | 170.59 | 161.81 | 178.28 | 134.45 |
| Rxd (mg/g) | -- | -- | -- | -- | -- | -- |
| Ro (mg/g) | -- | -- | -- | -- | -- | -- |
| Glass (pg) | 5.30 | 7.60 | 7.35 | 4.80 | 21.71 | 13.93 |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 4. (cont'd) KINETIC STUDY

Sediment = Saginaw Bay Station #50 Aqueous Phase = Supernatant

Mass = 200 mg/ℓ Time of Adsorption = 2 hr. Time of Desorption = 0.25-6 hr.

| | |
|---|---|
| Date | 6279.00 |
| Expt. Type | 2.00 |
| Aq. Phase | 2.00 |
| pH | 6.75 |
| Ionic | -- |
| Ma (mg/l) | 200.00 |
| Ta (hr) | 2.00 |
| Md (mg/l) | 200.00 |
| Td (hr) | 4.00 |
| Ci (ng/l) | 54.21 |
| CTa (ng/l) | -- |
| Ca (ng/l) | -- |
| Ra (ng/g) | -- |
| Rxa (ng/g) | -- |
| CTd (ng/l) | 30.00 |
| Cd (ng/l) | 5.08 |
| Rd (ng/g) | 124.57 |
| Rxd (ng/g) | -- |
| Ro (ng/g) | -- |
| Glass (pg) | 7.69 |
| MB Er. (%) | -- |

TABLE 5. ISOTHERM

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 50-55 mg/ℓ | Time of Adsorption = 2-3 hr. | Time of Desorption = 1.5-3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 4189.00 | 6079.00 | 5239.00 | 5280.00 | 5280.00 | 5280.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 5.60 | 5.60 | 5.50 | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 50.00 | 50.00 | 50.00 | 55.00 | 55.00 | 55.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 7.37 | -- | 18.07 | 56.40 | 75.20 | 112.80 |
| CTa (ng/l) | 6.72 | 41.22 | 16.24 | 51.95 | 66.15 | 100.42 |
| Ca (ng/l) | 2.89 | 20.00 | 7.89 | 31.86 | 39.35 | 54.49 |
| Ra (ng/g) | 76.69 | 424.36 | 167.17 | 365.27 | 487.16 | 835.13 |
| Rxa (ng/g) | 46.13 | 304.67 | 93.32 | 232.45 | 353.89 | 652.66 |
| CTd (ng/l) | 3.80 | 20.86 | 8.35 | 22.32 | 29.01 | 44.99 |
| Cd (ng/l) | 1.26 | 8.44 | 2.92 | 11.49 | 15.41 | 22.43 |
| Rd (ng/g) | 50.72 | 248.31 | 108.45 | 216.66 | 271.87 | 451.17 |
| Rxd (ng/g) | 20.16 | 128.62 | 34.60 | 83.84 | 138.60 | 268.70 |
| Ro (ng/g) | 30.56 | 119.69 | 73.86 | 132.82 | 133.27 | 182.47 |
| Glass (pg) | 2.40 | 9.51 | 14.38 | 17.69 | 27.88 | 33.60 |
| MB Er. (%) | -5.60 | -- | -2.14 | -11.96 | -14.51 | -10.86 |

TABLE 5. ISOTHERM (cont'd)

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 50-55 mg/ℓ | Time of Adsorption = 2-3 hr. | Time of Desorption = 1.5-3 hr.

| | | |
|---|---|---|
| Date | 5280.00 | 5280.00 |
| Expt. Type | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 |
| pH | -- | -- |
| Ionic | -- | -- |
| Ma (mg/l) | 55.00 | 55.00 |
| Ta (hr) | 3.00 | 3.00 |
| Md (mg/l) | 50.00 | 50.00 |
| Td (hr) | 3.00 | 3.00 |
| Ci (ng/l) | 150.40 | 188.00 |
| CTa (ng/l) | 140.76 | 178.62 |
| Ca (ng/l) | 72.46 | 94.49 |
| Ra (ng/g) | 1241.89 | 1529.75 |
| Rxa (ng/g) | 892.57 | 1138.58 |
| CTd (ng/l) | 64.01 | 76.88 |
| Cd (ng/l) | 28.80 | 35.77 |
| Rd (ng/g) | 704.09 | 822.18 |
| Rxd (ng/g) | 354.77 | 431.01 |
| Ro (ng/g) | 349.32 | 391.17 |
| Glass (pg) | 20.26 | 27.25 |
| MB Er. (%) | -6.33 | -3.75 |

TABLE 6. ISOTHERM

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 55 mg/ℓ | Time of Adsorption = 48 hr. | Time of Desorption = 48 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 3280.00 | 3280.00 | 3280.00 | 3280.00 | 3280.00 | 4280.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 |
| Ta (hr) | 48.00 | 48.00 | 48.00 | 48.00 | 48.00 | 48.00 |
| Md (mg/l) | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 |
| Td (hr) | 48.00 | 48.00 | 48.00 | 48.00 | 48.00 | 48.00 |
| Ci (ng/l) | 9.49 | 28.47 | 47.46 | 75.93 | 207.17 | 93.63 |
| CTa (ng/l) | 8.67 | 23.37 | 44.08 | 68.41 | 209.28 | 84.26 |
| Ca (ng/l) | 5.26 | 13.59 | 22.11 | 32.82 | 111.81 | 35.59 |
| Ra (ng/g) | 61.99 | 177.74 | 399.52 | 647.04 | 1772.22 | 884.80 |
| Rxa (ng/g) | -8.75 | 36.68 | 107.50 | 171.91 | 98.19 | 445.39 |
| CTd (ng/l) | 5.13 | 9.78 | 20.46 | 33.83 | 103.21 | 39.58 |
| Cd (ng/l) | 1.73 | 2.40 | 4.71 | 7.98 | 18.69 | 10.83 |
| Rd (ng/g) | 67.86 | 147.54 | 314.92 | 516.94 | 1690.45 | 574.99 |
| Rxd (ng/g) | -2.88 | 6.48 | 22.90 | 41.81 | 16.42 | 135.58 |
| Ro (ng/g) | 70.74 | 141.06 | 292.02 | 475.13 | 1674.03 | 439.41 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 6. ISOTHERM (cont'd)

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 55 mg/ℓ | Time of Adsorption = 48 hr. | Time of Desorption = 48 hr.

| | | | |
|---|---|---|---|
| Date | 4280.00 | 4280.00 | 4280.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- |
| Ionic | -- | -- | -- |
| Ma (mg/l) | 55.00 | 55.00 | 55.00 |
| Ta (hr) | 48.00 | 48.00 | 48.00 |
| Md (mg/l) | 50.00 | 50.00 | 50.00 |
| Td (hr) | 48.00 | 48.00 | 48.00 |
| Ci (ng/l) | 124.85 | 156.06 | 187.27 |
| CTa (ng/l) | 86.49 | 106.07 | 143.51 |
| Ca (ng/l) | 39.16 | 48.31 | 65.57 |
| Ra (ng/g) | 860.58 | 1050.06 | 1417.16 |
| Rxa (ng/g) | 320.23 | 404.37 | 407.77 |
| CTd (ng/l) | 43.76 | 52.68 | 67.04 |
| Cd (ng/l) | 11.88 | 14.38 | 12.64 |
| Rd (ng/g) | 637.51 | 766.06 | 1087.98 |
| Rxd (ng/g) | 97.16 | 120.36 | 78.59 |
| Ro (ng/g) | 540.36 | 645.69 | 1009.39 |
| Glass (pg) | -- | -- | -- |
| MB Er. (%) | -- | -- | -- |

TABLE 7. ISOTHERM

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 55 mg/ℓ | Time of Adsorption = 240 hr. | Time of Desorption = 240 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 4240.00 | 4240.00 | 4240.00 | 4240.00 | 4240.00 | 4240.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 |
| Ta (hr) | 240.00 | 240.00 | 240.00 | 240.00 | 240.00 | 240.00 |
| Md (mg/l) | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 |
| Td (hr) | 240.00 | 240.00 | 240.00 | 240.00 | 240.00 | 240.00 |
| Ci (ng/l) | 10.04 | 10.04 | 50.19 | 50.19 | 50.19 | 80.31 |
| CTa (ng/l) | 9.25 | 8.62 | 39.97 | 47.82 | 29.02 | 31.85 |
| Ca (ng/l) | 4.69 | 5.26 | 22.18 | 26.92 | 12.59 | 18.71 |
| Ra (ng/g) | 82.97 | 61.06 | 323.57 | 379.98 | 298.68 | 238.94 |
| Rxa (ng/g) | 76.45 | 30.22 | 78.84 | 221.68 | 141.27 | -39.69 |
| CTd (ng/l) | 2.45 | 2.65 | 16.66 | 12.63 | 12.23 | 18.43 |
| Cd (ng/l) | 1.17 | 0.86 | 3.76 | 3.34 | 2.79 | 5.04 |
| Rd (ng/g) | 25.55 | 35.77 | 258.09 | 185.81 | 188.73 | 267.95 |
| Rxd (ng/g) | 19.04 | 4.93 | 13.37 | 27.50 | 31.33 | -10.69 |
| Ro (ng/g) | 6.52 | 30.84 | 244.72 | 158.31 | 157.40 | 278.63 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 7. ISOTHERM (cont'd)

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 55 mg/ℓ | Time of Adsorption = 240 hr. | Time of Desorption = 240 hr.

| | | |
|---|---|---|
| Date | 4240.00 | 4240.00 |
| Expt. Type | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 |
| pH | -- | -- |
| Ionic | -- | -- |
| Ma (mg/l) | 55.00 | 55.00 |
| Ta (hr) | 240.00 | 240.00 |
| Md (mg/l) | 50.00 | 50.00 |
| Td (hr) | 240.00 | 240.00 |
| Ci (ng/l) | 80.31 | 80.31 |
| CTa (ng/l) | 54.76 | 19.80 |
| Ca (ng/l) | 29.93 | 8.29 |
| Ra (ng/g) | 451.33 | 209.41 |
| Rxa (ng/g) | 220.30 | -14.42 |
| CTd (ng/l) | 17.39 | 13.32 |
| Cd (ng/l) | 4.27 | 2.34 |
| Rd (ng/g) | 262.47 | 219.76 |
| Rxd (ng/g) | 31.43 | -4.07 |
| Ro (ng/g) | 231.04 | 223.82 |
| Glass (pg) | -- | -- |
| MB Er. (%) | -- | -- |

TABLE 8. ISOTHERM

Sediment = Saginaw Bay Station 50 Aqueous Phase = Distilled Water

Mass = 200 mg/ℓ Time of Adsorption = 4 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 6079.00 | 2289.00 | 3019.00 | 3029.00 | 3079.00 | 3079.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 6.80 | 6.90 | 6.90 | 6.90 | 6.90 | 6.90 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 |
| Md (mg/l) | -- | -- | -- | -- | -- | -- |
| Td (hr) | -- | -- | -- | -- | -- | -- |
| Ci (ng/l) | -- | 43.81 | 195.30 | 97.65 | 17.70 | 88.52 |
| CTa (ng/l) | 65.92 | 45.17 | 198.81 | 90.75 | 15.61 | 75.81 |
| Ca (ng/l) | 17.38 | 11.42 | 67.14 | 16.98 | 2.95 | 17.77 |
| Ra (ng/g) | 242.71 | 168.73 | 658.35 | 368.87 | 63.29 | 290.23 |
| Rxa (ng/g) | -- | -- | -- | -- | -- | -- |
| CTd (ng/l) | -- | -- | -- | -- | -- | -- |
| Cd (ng/l) | -- | -- | -- | -- | -- | -- |
| Rd (ng/g) | -- | -- | -- | -- | -- | -- |
| Rxd (ng/g) | -- | -- | -- | -- | -- | -- |
| Ro (ng/g) | -- | -- | -- | -- | -- | -- |
| Glass (pg) | 28.60 | 10.34 | 52.39 | 28.43 | 2.14 | 11.28 |
| MB Er. (%) | -- | 5.47 | 4.48 | -4.15 | -10.65 | -13.09 |

TABLE 8. ISOTHERM (cont'd)

Sediment = Saginaw Bay Station 50 Aqueous Phase = Distilled Water

Mass = 200 mg/ℓ Time of Adsorption = 4 hr.

| | | | | | |
|---|---|---|---|---|---|
| Date | 3079.00 | 3089.00 | 3089.00 | 3269.00 | 1040.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 6.90 | 6.90 | 6.90 | -- | -- |
| Ionic | -- | -- | -- | -- | -- |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 4.00 | 4.00 | 4.00 | 4.00 | 3.00 |
| Md (mg/l) | -- | -- | -- | -- | -- |
| Td (hr) | -- | -- | -- | -- | -- |
| Ci (ng/l) | 141.64 | 47.09 | 94.18 | 29.39 | 30.12 |
| CTa (ng/l) | 124.51 | 49.42 | 92.39 | 24.84 | 27.30 |
| Ca (ng/l) | 24.02 | 10.16 | 20.25 | 4.65 | 5.79 |
| Ra (ng/g) | 502.43 | 196.27 | 360.69 | 100.94 | 107.55 |
| Rxa (ng/g) | -- | -- | -- | -- | -- |
| CTd (ng/l) | -- | -- | -- | -- | -- |
| Cd (ng/l) | -- | -- | -- | -- | -- |
| Rd (ng/g) | -- | -- | -- | -- | -- |
| Rxd (ng/g) | -- | -- | -- | -- | -- |
| Ro (ng/g) | -- | -- | -- | -- | -- |
| Glass (pg) | 17.61 | 10.54 | 19.40 | 8.86 | -- |
| MB Er. (%) | -10.85 | 7.18 | 0.16 | -12.46 | -- |

TABLE 9. ISOTHERM

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 220 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 7269.00 | 7269.00 | 7269.00 | 7319.00 | 7319.00 | 7319.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 7.08 | 7.08 | 7.05 | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 220.00 | 220.00 | 220.00 | 220.00 | 220.00 | 220.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 198.00 | 198.00 | 198.00 | 220.00 | 220.00 | 220.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 17.16 | 51.47 | 102.94 | 31.76 | 79.40 | 127.04 |
| CTa (ng/l) | 17.97 | 52.52 | 104.31 | 30.68 | 77.37 | 137.47 |
| Ca (ng/l) | 4.93 | 11.66 | 28.59 | 8.66 | 21.65 | 38.99 |
| Ra (ng/g) | 59.26 | 185.76 | 344.19 | 100.12 | 253.28 | 447.62 |
| Rxa (ng/g) | 21.24 | 54.48 | 71.63 | 37.77 | 72.03 | 206.80 |
| CTd (ng/l) | 12.18 | 36.09 | 65.89 | 19.30 | 52.07 | 71.80 |
| Cd (ng/l) | 2.51 | 5.25 | 7.97 | 2.85 | 7.04 | 8.69 |
| Rd (ng/g) | 48.83 | 155.80 | 292.53 | 74.77 | 204.67 | 286.90 |
| Rxd (ng/g) | 10.81 | 24.52 | 19.97 | 12.42 | 23.43 | 46.07 |
| Ro (ng/g) | 38.02 | 131.28 | 272.56 | 62.34 | 181.25 | 240.82 |
| Glass (pg) | 4.96 | 6.62 | 12.06 | 5.88 | 14.12 | 13.38 |
| MB Er. (%) | 5.05 | 4.66 | 4.69 | 7.06 | 3.83 | 30.26 |

TABLE 9. ISOTHERM (cont'd)

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 220 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 3 hr.

| | | | | | |
|---|---|---|---|---|---|
| Date | 5270.00 | 5270.00 | 5270.00 | 5270.00 | 5270.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- |
| Ma (mg/l) | 220.00 | 220.00 | 220.00 | 220.00 | 220.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 198.00 | 198.00 | 198.00 | 198.00 | 198.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 98.56 | 164.27 | 229.98 | 262.83 | 295.69 |
| CTa (ng/l) | 86.36 | 138.56 | 207.45 | 245.58 | 264.61 |
| Ca (ng/l) | 25.96 | 38.78 | 60.17 | 68.52 | 56.71 |
| Ra (ng/g) | 274.54 | 453.56 | 669.46 | 804.81 | 945.02 |
| Rxa (ng/g) | 30.09 | 141.94 | 93.68 | 218.95 | 333.05 |
| CTd (ng/l) | 63.83 | 97.65 | 141.80 | 160.01 | 196.04 |
| Cd (ng/l) | 12.55 | 20.84 | 21.25 | 26.96 | 34.62 |
| Rd (ng/g) | 258.99 | 387.91 | 608.86 | 672.00 | 815.28 |
| Rxd (ng/g) | 14.55 | 76.29 | 33.08 | 86.14 | 203.31 |
| Ro (ng/g) | 244.45 | 311.62 | 575.78 | 585.86 | 611.97 |
| Glass (pg) | 18.26 | 61.91 | 59.53 | 32.51 | 58.97 |
| MB Er. (%) | -20.14 | -16.66 | -11.23 | -5.58 | -11.54 |

TABLE 10. ISOTHERM

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 1000 mg/ℓ | Time of Adsorption = 2-4 hr. | Time of Desorption = 1.5 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 2289.00 | 1070.00 | 1070.00 | 1070.00 | 1040.00 | 4119.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 7.30 | -- | -- | -- | -- | 6.90 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |
| Ta (hr) | 4.00 | 3.00 | 3.00 | 3.00 | 3.00 | 2.00 |
| Md (mg/l) | -- | -- | -- | -- | -- | 1000.00 |
| Td (hr) | -- | -- | -- | -- | -- | 1.50 |
| Ci (ng/l) | 43.81 | 16.15 | 53.84 | 86.15 | 30.12 | 19.17 |
| CTa (ng/l) | 43.26 | 13.01 | 44.54 | 73.21 | 26.58 | 18.53 |
| Ca (ng/l) | 5.37 | 1.11 | 3.46 | 4.92 | 2.49 | 1.96 |
| Ra (ng/g) | 37.90 | 11.91 | 41.08 | 68.30 | 24.09 | 16.56 |
| Rxa (ng/g) | -- | -- | -- | -- | -- | 1.26 |
| CTd (ng/l) | -- | -- | -- | -- | -- | 16.56 |
| Cd (ng/l) | -- | -- | -- | -- | -- | 0.77 |
| Rd (ng/g) | -- | -- | -- | -- | -- | 15.80 |
| Rxd (ng/g) | -- | -- | -- | -- | -- | 0.49 |
| Ro (ng/g) | -- | -- | -- | -- | -- | 15.31 |
| Glass (pg) | 6.91 | -- | -- | -- | -- | 3.97 |
| MB Er. (%) | 0.34 | -- | -- | -- | -- | -1.25 |

TABLE 10. ISOTHERM (cont'd)

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 1000 mg/ℓ | Time of Adsorption = 2-4 hr. | Time of Desorption = 1.5 hr.

| | | |
|---|---|---|
| Date | 4119.00 | 4119.00 |
| Expt. Type | 2.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 |
| pH | 6.90 | 6.90 |
| Ionic | -- | -- |
| Ma (mg/l) | 1000.00 | 1000.00 |
| Ta (hr) | 2.00 | 2.00 |
| Md (mg/l) | 1000.00 | 1000.00 |
| Td (hr) | 1.50 | 1.50 |
| Ci (ng/l) | 76.66 | 153.32 |
| CTa (ng/l) | 76.26 | 151.45 |
| Ca (ng/l) | 7.89 | 13.13 |
| Ra (ng/g) | 68.37 | 138.32 |
| Rxa (ng/g) | 3.09 | 6.22 |
| CTd (ng/l) | 68.34 | 138.32 |
| Cd (ng/l) | 2.20 | 4.22 |
| Rd (ng/g) | 66.15 | 134.10 |
| Rxd (ng/g) | 0.86 | 2.00 |
| Ro (ng/g) | 65.29 | 132.11 |
| Glass (pg) | 4.88 | 12.85 |
| MB Er. (%) | 0.12 | -0.38 |

TABLE 11. ISOTHERM

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 7189.00 | 7189.00 | 7189.00 | 7189.00 | 10109.00 | 10109.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 16.79 | 50.38 | 83.96 | 134.34 | 15.33 | 30.66 |
| CTa (ng/l) | 16.60 | 50.66 | 81.26 | 132.25 | 14.52 | 27.79 |
| Ca (ng/l) | 1.95 | 5.40 | 8.63 | 14.35 | 1.66 | 3.01 |
| Ra (ng/g) | 13.31 | 41.15 | 66.03 | 107.19 | 11.69 | 22.53 |
| Rxa (ng/g) | 0.90 | 0.97 | -0.34 | 15.44 | 1.08 | -0.12 |
| CTd (ng/l) | 13.73 | 42.00 | 69.00 | 99.92 | 11.74 | 23.48 |
| Cd (ng/l) | 0.99 | 1.89 | 3.43 | 4.40 | 0.75 | 1.10 |
| Rd (ng/g) | 12.87 | 40.51 | 66.23 | 96.48 | 11.10 | 22.61 |
| Rxd (ng/g) | 0.46 | 0.34 | -0.13 | 4.74 | 0.49 | -0.05 |
| Ro (ng/g) | 12.41 | 40.17 | 66.37 | 91.75 | 10.61 | 22.65 |
| Glass (pg) | 2.33 | 3.72 | 8.17 | 7.82 | 1.10 | 1.36 |
| MB Er. (%) | -3.06 | -1.21 | -6.56 | 3.65 | -5.65 | -12.78 |

TABLE 11. ISOTHERM (cont'd)

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 10107.00 | 10109.00 | 10109.00 | 10129.00 | 10129.00 | 10129.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 30.66 | 61.33 | 122.66 | 15.33 | 30.66 | 61.33 |
| CTa (ng/l) | 27.34 | 56.95 | 127.42 | 14.18 | 35.10 | 56.08 |
| Ca (ng/l) | 3.30 | 6.32 | 12.55 | 1.75 | 3.16 | 6.59 |
| Ra (ng/g) | 21.85 | 46.02 | 104.43 | 11.30 | 29.04 | 44.99 |
| Rxa (ng/g) | -1.18 | -15.15 | 50.87 | 0.43 | 15.87 | 8.38 |
| CTd (ng/l) | 23.51 | 57.51 | 70.65 | 11.37 | 17.50 | 40.08 |
| Cd (ng/l) | 1.10 | 2.22 | 3.52 | 0.49 | 0.75 | 1.70 |
| Rd (ng/g) | 22.64 | 55.85 | 67.81 | 10.99 | 16.92 | 38.77 |
| Rxd (ng/g) | -0.39 | -5.33 | 14.25 | 0.12 | 3.76 | 2.17 |
| Ro (ng/g) | 23.03 | 61.18 | 53.56 | 10.88 | 13.16 | 36.61 |
| Glass (pg) | 1.66 | 5.21 | 11.35 | 1.31 | 13.01 | 11.65 |
| MB Er. (%) | -16.40 | -25.78 | 31.50 | -7.84 | 55.39 | 0.61 |

TABLE 11. ISOTHERM (cont'd)

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 3 hr.

| | | | | | |
|---|---|---|---|---|---|
| Date | 10129.00 | 10179.00 | 10179.00 | 10179.00 | 10179.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 122.66 | 16.61 | 33.22 | 66.44 | 132.88 |
| CTa (ng/l) | 112.97 | 11.60 | 24.14 | 53.73 | 111.86 |
| Ca (ng/l) | 14.21 | 1.83 | 3.07 | 6.01 | 12.09 |
| Ra (ng/g) | 89.78 | 8.89 | 19.16 | 43.38 | 90.69 |
| Rxa (ng/g) | 21.10 | 1.18 | 8.55 | 20.86 | 17.04 |
| CTd (ng/l) | 75.10 | 8.78 | 15.18 | 31.80 | 80.13 |
| Cd (ng/l) | 2.88 | 0.70 | 1.25 | 2.14 | 3.01 |
| Rd (ng/g) | 72.95 | 8.16 | 14.08 | 29.96 | 77.89 |
| Rxd (ng/g) | 4.27 | 0.45 | 3.47 | 7.43 | 4.24 |
| Ro (ng/g) | 68.67 | 7.71 | 10.61 | 22.52 | 73.65 |
| Glass (pg) | 19.16 | -- | -- | -- | -- |
| MB Er. (%) | 4.90 | -- | -- | -- | -- |

TABLE 12. ISOTHERM

Sediment = Saginaw Bay Station 50 Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ Time of Adsorption = 24 hr.

| | | | | | |
|---|---|---|---|---|---|
| Date | 11289.00 | 11289.00 | 11289.00 | 11289.00 | 11289.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 24.00 | 24.00 | 24.00 | 24.00 | 24.00 |
| Md (mg/l) | -- | -- | -- | -- | -- |
| Td (hr) | -- | -- | -- | -- | -- |
| Ci (ng/l) | 15.15 | 30.30 | 60.60 | 90.90 | 121.20 |
| CTa (ng/l) | 14.11 | 28.20 | 53.81 | 87.95 | 96.96 |
| Ca (ng/l) | 0.94 | 1.68 | 3.37 | 5.19 | 7.35 |
| Ra (ng/g) | 11.97 | 24.11 | 45.86 | 75.24 | 81.46 |
| Rxa (ng/g) | -- | -- | -- | -- | -- |
| CTd (ng/l) | -- | -- | -- | -- | -- |
| Cd (ng/l) | -- | -- | -- | -- | -- |
| Rd (ng/g) | -- | -- | -- | -- | -- |
| Rxd (ng/g) | -- | -- | -- | -- | -- |
| Ro (ng/g) | -- | -- | -- | -- | -- |
| Glass (pg) | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- |

TABLE 13. ISOTHERM

Sediment = Saginaw Bay Station 50 Aqueous Phase = Supernatant

Mass = 1100 mg/ℓ Time of Adsorption = 120 hr.

| | | | | | |
|---|---|---|---|---|---|
| Date | 12109.00 | 12109.00 | 12109.00 | 12109.00 | 12109.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Aq. Phase | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| pH | 7.35 | 7.45 | 7.45 | 7.40 | 7.35 |
| Ionic | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 120.00 | 120.00 | 120.00 | 120.00 | 120.00 |
| Md (mg/l) | -- | -- | -- | -- | -- |
| Td (hr) | -- | -- | -- | -- | -- |
| Ci (ng/l) | 15.15 | 30.30 | 45.45 | 75.75 | 121.20 |
| CTa (ng/l) | 13.14 | 25.87 | 39.41 | 62.21 | 130.57 |
| Ca (ng/l) | 0.89 | 1.45 | 1.90 | 3.63 | 6.29 |
| Ra (ng/g) | 11.14 | 22.20 | 34.09 | 53.26 | 112.98 |
| Rxa (ng/g) | -- | -- | -- | -- | -- |
| CTd (ng/l) | -- | -- | -- | -- | -- |
| Cd (ng/l) | -- | -- | -- | -- | -- |
| Rd (ng/g) | -- | -- | -- | -- | -- |
| Rxd (ng/g) | -- | -- | -- | -- | -- |
| Ro (ng/g) | -- | -- | -- | -- | -- |
| Glass (pg) | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- |

TABLE 14. ISOTHERM

Sediment = Saginaw Bay Station #50 | Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 72 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 10129.00 | 10129.00 | 10129.00 | 10129.00 | 10129.00 | 10129.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 72.00 | 72.00 | 72.00 | 72.00 | 72.00 | 72.00 |
| Ci (ng/l) | 15.33 | 15.33 | 15.33 | 30.66 | 30.66 | 61.33 |
| CTa (ng/l) | 15.11 | 13.73 | 13.74 | 20.33 | 28.51 | 58.30 |
| Ca (ng/l) | 1.95 | 1.62 | 1.68 | 3.10 | 3.16 | 6.11 |
| Ra (ng/g) | 11.96 | 11.00 | 10.97 | 15.66 | 23.05 | 47.44 |
| Rxa (ng/g) | 0.07 | 1.27 | -0.10 | 5.94 | 3.10 | 4.34 |
| CTd (ng/l) | 12.32 | 10.48 | 11.39 | 11.96 | 21.15 | 45.07 |
| Cd (ng/l) | 0.53 | 0.47 | 0.46 | 0.80 | 0.71 | 1.41 |
| Rd (ng/g) | 11.91 | 10.10 | 11.04 | 11.26 | 20.65 | 44.10 |
| Rxd (ng/g) | 0.02 | 0.37 | -0.03 | 1.54 | 0.70 | 1.00 |
| Ro (ng/g) | 11.89 | 9.73 | 11.07 | 9.73 | 19.95 | 43.10 |
| Glass (pg) | 2.45 | 0.80 | 1.15 | 124.04 | 3.72 | 4.64 |
| MB Er. (%) | -2.94 | -7.25 | -13.07 | 18.35 | -0.39 | -1.09 |

TABLE 14, (cont'd) ISOTHERM

Sediment = Saginaw Bay Station #50 Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ Time of Adsorption = 3 hr. Time of Desorption = 72 hr.

| | | | | | |
|---|---|---|---|---|---|
| Date | 10129.00 | 10129.00 | 10129.00 | 10129.00 | 10129.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 72.00 | 72.00 | 72.00 | 72.00 | 72.00 |
| Ci (ng/l) | 61.33 | 61.33 | 122.66 | 122.66 | 122.66 |
| CTa (ng/l) | 63.96 | 47.31 | 111.14 | 115.72 | 112.11 |
| Ca (ng/l) | 6.41 | 7.32 | 17.83 | 12.41 | 12.98 |
| Ra (ng/g) | 52.32 | 36.36 | 84.82 | 93.92 | 90.12 |
| Rxa (ng/g) | 11.80 | 9.04 | 18.27 | 21.72 | 23.43 |
| CTd (ng/l) | 44.39 | 32.20 | 71.77 | 77.81 | 75.84 |
| Cd (ng/l) | 1.51 | 2.32 | 2.92 | 2.32 | 3.52 |
| Rd (ng/g) | 43.31 | 30.18 | 69.54 | 76.25 | 73.05 |
| Rxd (ng/g) | 2.79 | 2.86 | 2.99 | 4.06 | 6.36 |
| Ro (ng/g) | 40.52 | 27.32 | 66.55 | 72.20 | 66.69 |
| Glass (pg) | 4.69 | 72.72 | 8.54 | 7.06 | 116.51 |
| MB Er. (%) | 17.13 | -4.81 | 1.26 | 7.29 | 11.80 |

TABLE 15. ISOTHERM

Sediment = Saginaw Bay Station #50 | Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 144 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 10179.00 | 10179.00 | 10179.00 | 10179.00 | 10179.00 | 10179.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 144.00 | 144.00 | 144.00 | 144.00 | 144.00 | 144.00 |
| Ci (ng/l) | 16.61 | 16.61 | 16.61 | 33.22 | 33.22 | 66.44 |
| CTa (ng/l) | 10.55 | 11.32 | 13.09 | 24.66 | 25.12 | 52.06 |
| Ca (ng/l) | 1.81 | 2.01 | 1.68 | 3.34 | 2.92 | 6.35 |
| Ra (ng/g) | 7.95 | 8.46 | 10.37 | 19.38 | 20.18 | 41.55 |
| Rxa (ng/g) | 0.82 | 0.58 | 2.26 | 0.78 | 8.68 | 4.09 |
| CTd (ng/l) | 8.09 | 8.74 | 9.56 | 19.40 | 15.84 | 39.95 |
| Cd (ng/l) | 0.71 | 0.73 | 0.66 | 0.80 | 1.13 | 1.75 |
| Rd (ng/g) | 7.45 | 8.09 | 9.00 | 18.79 | 14.86 | 38.59 |
| Rxd (ng/g) | 0.32 | 0.21 | 0.88 | 0.19 | 3.36 | 1.13 |
| Ro (ng/g) | 7.12 | 7.88 | 8.11 | 18.60 | 11.50 | 37.46 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 15 (cont'd) ISOTHERM

Sediment = Saginaw Bay Station #50 | Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 144 hr.

| | | | | |
|---|---|---|---|---|
| Date | 10179.00 | 10179.00 | 10179.00 | 10179.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 144.00 | 144.00 | 144.00 | 144.00 |
| Ci (ng/l) | 66.44 | 132.88 | 132.88 | 132.88 |
| CTa (ng/l) | 60.63 | 114.57 | 114.15 | 107.01 |
| Ca (ng/l) | 6.02 | 12.16 | 12.16 | 11.97 |
| Ra (ng/g) | 49.65 | 93.10 | 92.72 | 86.40 |
| Rxa (ng/g) | 9.85 | 13.04 | 18.04 | 19.58 |
| CTd (ng/l) | 44.13 | 85.59 | 81.55 | 73.70 |
| Cd (ng/l) | 1.81 | 3.07 | 3.08 | 2.88 |
| Rd (ng/g) | 42.75 | 83.35 | 79.26 | 71.53 |
| Rxd (ng/g) | 2.95 | 3.29 | 4.58 | 4.72 |
| Ro (ng/g) | 39.80 | 80.06 | 74.68 | 66.82 |
| Glass (pg) | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- |

TABLE 16. ISOTHERM

Sediment = Montmorillonite

Aqueous Phase = Distilled Water

Mass = 50 mg/ℓ

Time of Adsorption = 2-3 hr.

Time of Desorption = 1.5-3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 6069.00 | 6019.00 | 5309.00 | 4010.00 | 4010.00 | 4010.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 5.70 | 5.70 | 5.70 | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 50.00 | 50.00 | 50.00 | 45.00 | 45.00 | 45.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 77.57 | 22.54 | 22.54 | 10.95 | 21.90 | 43.81 |
| CTa (ng/l) | 60.53 | 19.52 | 17.60 | 9.44 | 18.60 | 34.78 |
| Ca (ng/l) | 37.85 | 11.10 | 9.43 | 7.61 | 13.07 | 22.90 |
| Ra (ng/g) | 453.77 | 168.38 | 163.38 | 36.64 | 110.58 | 237.55 |
| Rxa (ng/g) | 365.64 | 111.22 | 80.28 | -13.01 | 58.84 | 168.82 |
| CTd (ng/l) | 22.24 | 8.40 | 8.16 | 3.88 | 5.37 | 10.86 |
| Cd (ng/l) | 12.03 | 3.69 | 2.81 | 1.78 | 2.53 | 5.83 |
| Rd (ng/g) | 204.33 | 94.15 | 107.03 | 46.61 | 63.14 | 111.74 |
| Rxd (ng/g) | 116.21 | 36.99 | 23.93 | -3.05 | 11.39 | 43.00 |
| Ro (ng/g) | 88.12 | 57.16 | 83.10 | 49.65 | 51.74 | 68.74 |
| Glass (pg) | 24.82 | 7.99 | 5.42 | -- | -- | -- |
| MB Er. (%) | -18.77 | -9.86 | -19.50 | -- | -- | -- |

TABLE 16. ISOTHERM (cont'd)

Sediment = Montmorillonite

Aqueous Phase = Distilled Water

Mass = 50 mg/ℓ

Time of Adsorption = 2-3 hr.

Time of Desorption = 1.5-3 hr.

| | | |
|---|---|---|
| Date | 4010.00 | 4010.00 |
| Expt. Type | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 |
| pH | -- | -- |
| Ionic | -- | -- |
| Ma (mg/l) | 50.00 | 50.00 |
| Ta (hr) | 3.00 | 3.00 |
| Md (mg/l) | 45.00 | 45.00 |
| Td (hr) | 3.00 | 3.00 |
| Ci (ng/l) | 87.61 | 204.43 |
| CTa (ng/l) | 66.27 | 167.88 |
| Ca (ng/l) | 46.52 | 98.35 |
| Ra (ng/g) | 394.92 | 1390.62 |
| Rxa (ng/g) | 222.32 | 707.87 |
| CTd (ng/l) | 20.66 | 64.28 |
| Cd (ng/l) | 10.62 | 25.34 |
| Rd (ng/g) | 223.32 | 865.16 |
| Rxd (ng/g) | 50.73 | 182.41 |
| Ro (ng/g) | 172.60 | 682.75 |
| Glass (pg) | -- | -- |
| MB Er. (%) | -- | -- |

TABLE 17. ISOTHERM

Sediment = Montmorillonite

Aqueous Phase = Distilled Water

Mass = 200 mg/ℓ

Time of Adsorption = 2-3 hr.

Time of Desorption = 1.5-3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 5309.00 | 3215.00 | 3215.10 | 3215.20 | 3215.30 | 3215.40 |
| Expt. Type | 2.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 5.70 | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 2.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 200.00 | 180.00 | 180.00 | 180.00 | 180.00 | 180.00 |
| Td (hr) | 1.50 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 43.35 | -- | -- | -- | -- | -- |
| CTa (ng/l) | 42.03 | 10.38 | 13.09 | 27.33 | 50.45 | 157.22 |
| Ca (ng/l) | 16.32 | 4.28 | 5.77 | 12.15 | 22.76 | 67.76 |
| Ra (ng/g) | 128.59 | 30.48 | 36.61 | 75.93 | 138.41 | 447.31 |
| Rxa (ng/g) | 63.02 | 9.63 | 3.31 | 22.13 | 34.06 | 124.88 |
| CTd (ng/l) | 25.46 | 6.40 | 8.56 | 15.53 | 27.20 | 77.68 |
| Cd (ng/l) | 6.96 | 1.88 | 2.33 | 4.40 | 6.63 | 14.75 |
| Rd (ng/g) | 92.47 | 25.09 | 34.64 | 61.82 | 114.28 | 349.61 |
| Rxd (ng/g) | 26.90 | 4.24 | 1.33 | 8.02 | 9.92 | 27.18 |
| Ro (ng/g) | 65.57 | 20.85 | 33.30 | 53.80 | 104.36 | 322.43 |
| Glass (pg) | 10.50 | -- | -- | -- | -- | -- |
| MB Er. (%) | -0.62 | -- | -- | -- | -- | -- |

TABLE 18. ISOTHERM

Sediment = Montmorillonite

Aqueous Phase = Distilled Water

Mass = 1000 mg/ℓ

Time of Adsorption = 2 hr.

Time of Desorption = 1.5-3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 4059.00 | 4059.00 | 4059.00 | 4029.00 | 4029.00 | 4029.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 6.30 | 6.30 | 6.30 | 6.30 | 6.30 | 6.30 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| Ci (ng/l) | 54.76 | 91.26 | 146.02 | 18.07 | 54.21 | 90.35 |
| CTa (ng/l) | 43.69 | 68.63 | 109.50 | 18.78 | 59.39 | 97.22 |
| Ca (ng/l) | 12.08 | 21.10 | 37.58 | 4.40 | 15.50 | 25.97 |
| Ra (ng/g) | 31.61 | 47.52 | 71.92 | 14.38 | 43.89 | 71.25 |
| Rxa (ng/g) | 4.08 | 6.15 | 10.52 | 2.17 | 5.32 | 8.19 |
| CTd (ng/l) | 31.61 | 47.46 | 71.91 | 14.31 | 43.84 | 71.04 |
| Cd (ng/l) | 3.05 | 4.71 | 8.21 | 1.40 | 3.93 | 6.07 |
| Rd (ng/g) | 28.56 | 42.75 | 63.69 | 12.90 | 39.91 | 64.97 |
| Rxd (ng/g) | 1.03 | 1.37 | 2.30 | 0.69 | 1.35 | 1.91 |
| Ro (ng/g) | 27.53 | 41.37 | 61.40 | 12.21 | 38.56 | 63.06 |
| Glass (pg) | 8.55 | 11.43 | 22.03 | 2.48 | 5.29 | 11.97 |
| MB Er. (%) | -18.65 | -23.55 | -23.50 | 5.33 | 10.53 | 8.93 |

TABLE 18. ISOTHERM (cont'd)

Sediment = Montmorillonite

Aqueous Phase = Distilled Water

Mass = 1000 mg/ℓ

Time of Adsorption = 2 hr.

Time of Desorption = 1.5-3 hr.

| | | | | | |
|---|---|---|---|---|---|
| Date | 4029.00 | 3299.00 | 3299.00 | 3299.00 | 3299.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 6.30 | 6.30 | 6.30 | 6.30 | 6.30 |
| Ionic | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |
| Td (hr) | 1.50 | 1.00 | 1.50 | 2.00 | 3.00 |
| Ci (ng/l) | 144.56 | 72.83 | 72.83 | 72.83 | 72.83 |
| CTa (ng/l) | 136.80 | 62.91 | 62.37 | 57.07 | 63.14 |
| Ca (ng/l) | 34.93 | 13.88 | 12.80 | 12.37 | 15.80 |
| Ra (ng/g) | 101.86 | 49.02 | 49.57 | 44.70 | 47.34 |
| Rxa (ng/g) | 12.58 | 7.85 | 6.02 | 5.73 | 6.17 |
| CTd (ng/l) | 101.77 | 49.00 | 49.55 | 44.70 | 47.19 |
| Cd (ng/l) | 9.18 | 5.00 | 4.08 | 3.91 | 4.33 |
| Rd (ng/g) | 92.58 | 44.00 | 45.47 | 40.78 | 42.87 |
| Rxd (ng/g) | 3.31 | 2.82 | 1.92 | 1.81 | 1.69 |
| Ro (ng/g) | 89.28 | 41.18 | 43.55 | 38.97 | 41.18 |
| Glass (pg) | 17.84 | 20.23 | 10.77 | 21.11 | 16.14 |
| MB Er. (%) | -4.14 | -10.84 | -12.88 | -18.74 | -11.08 |

TABLE 19. ISOTHERM

Sediment = Montmorillonite

Aqueous Phase = $NaHCO_3$ Buffer

Mass = 50 mg/ℓ

Time of Adsorption = 3 hr.

Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 7010.00 | 7010.00 | 7010.00 | 7010.00 | 7010.00 | 7010.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 11.00 | 11.00 | 11.00 | 11.00 | 11.00 | 11.00 |
| pH | 8.00 | -- | 8.00 | -- | 8.00 | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 45.00 | 45.00 | 45.00 | 45.00 | 45.00 | 45.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (mg/l) | 9.17 | 9.17 | 18.34 | 18.34 | 36.69 | 36.69 |
| CTa (mg/l) | 7.47 | 6.47 | 14.80 | 15.15 | 29.59 | 30.91 |
| Ca (mg/l) | 5.13 | 4.14 | 7.85 | 8.51 | 15.20 | 16.44 |
| Ra (mg/g) | 46.73 | 46.55 | 139.08 | 132.83 | 287.66 | 289.25 |
| Rxa (mg/g) | -23.56 | 7.51 | 93.47 | 46.81 | 155.81 | 137.92 |
| CTd (mg/l) | 5.07 | 3.99 | 7.15 | 7.97 | 15.59 | 15.43 |
| Cd (mg/l) | 2.41 | 2.06 | 3.32 | 3.29 | 6.61 | 6.26 |
| Rd (mg/g) | 59.22 | 42.78 | 85.18 | 104.10 | 199.56 | 203.85 |
| Rxd (mg/g) | -11.07 | 3.74 | 39.56 | 18.09 | 67.71 | 52.51 |
| Ro (mg/g) | 70.29 | 39.04 | 45.62 | 86.01 | 131.85 | 151.34 |
| Glass (pg) | 1.84 | 5.23 | 3.63 | 6.24 | 10.46 | 5.06 |
| MB Er. (%) | -49.00 | -44.40 | -22.21 | -24.87 | -23.71 | -20.97 |

TABLE 19. ISOTHERM (cont'd)

Sediment = Montmorillonite

Aqueous Phase = $NaHCO_3$ Buffer

Mass = 50 mg/ℓ

Time of Adsorption = 3 hr.

Time of Desorption = 3 hr.

| | | | | |
|---|---|---|---|---|
| Date | 7010.00 | 7010.00 | 7010.00 | 7010.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 11.00 | 11.00 | 11.00 | 11.00 |
| pH | 7.95 | -- | 8.00 | -- |
| Ionic | -- | -- | -- | -- |
| Ma (mg/l) | 50.00 | 50.00 | 50.00 | 50.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 45.00 | 45.00 | 45.00 | 45.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 73.37 | 73.37 | 110.06 | 110.06 |
| CTa (ng/l) | 64.34 | 59.69 | 91.23 | 82.90 |
| Ca (ng/l) | 31.03 | 28.79 | 50.41 | 43.48 |
| Ra (ng/g) | 666.21 | 618.04 | 816.25 | 788.50 |
| Rxa (ng/g) | 385.75 | 393.21 | 375.21 | 389.13 |
| CTd (ng/l) | 25.57 | 28.70 | 40.05 | 45.52 |
| Cd (ng/l) | 8.30 | 11.51 | 15.13 | 19.64 |
| Rd (ng/g) | 383.71 | 381.99 | 553.66 | 575.15 |
| Rxd (ng/g) | 103.25 | 157.16 | 112.62 | 175.78 |
| Ro (ng/g) | 280.46 | 224.83 | 441.04 | 399.38 |
| Glass (pg) | 5.69 | 14.34 | 9.49 | 32.64 |
| MB Er. (%) | -5.53 | -17.90 | -19.26 | -30.83 |

TABLE 20. ISOTHERM

Sediment = Montmorillonite | Aqueous Phase = $NaHCO_3$ Buffer

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 6200.00 | 6200.00 | 6200.00 | 6200.00 | 6200.00 | 6200.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 11.00 | 11.00 | 11.00 | 11.00 | 11.00 | 11.00 |
| pH | 8.40 | -- | 8.40 | -- | 8.40 | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 22.27 | 22.27 | 44.54 | 44.54 | 55.67 | 55.67 |
| CTa (ng/l) | 25.88 | 20.81 | 39.94 | 41.01 | 48.88 | 50.69 |
| Ca (ng/l) | 5.55 | 5.48 | 11.79 | 13.24 | 15.20 | 15.38 |
| Ra (ng/g) | 18.48 | 13.93 | 25.59 | 25.25 | 30.61 | 32.10 |
| Rxa (ng/g) | 9.86 | -0.86 | 4.31 | 1.62 | 4.14 | 5.36 |
| CTd (ng/l) | 14.99 | 16.25 | 25.39 | 27.39 | 30.86 | 31.80 |
| Cd (ng/l) | 2.34 | 1.91 | 3.18 | 3.56 | 3.67 | 3.96 |
| Rd (ng/g) | 12.78 | 14.49 | 22.44 | 24.06 | 27.47 | 28.12 |
| Rxd (ng/g) | 4.15 | -0.30 | 1.16 | 0.44 | 1.00 | 1.38 |
| Ro (ng/g) | 8.63 | 14.79 | 21.28 | 23.63 | 26.47 | 26.74 |
| Glass (pg) | 2.23 | 2.67 | 6.37 | 5.16 | 11.44 | 14.80 |
| MB Er. (%) | 32.11 | -16.43 | -9.03 | -12.13 | -11.14 | -6.32 |

TABLE 20. ISOTHERM (cont'd)

Sediment = Montmorillonite

Aqueous Phase = $NaHCO_3$ Buffer

Mass = 1100 mg/ℓ

Time of Adsorption = 3 hr.

Time of Desorption = 3 hr.

| | | | | |
|---|---|---|---|---|
| Date | 6200.00 | 6200.00 | 6200.00 | 6200.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 11.00 | 11.00 | 11.00 | 11.00 |
| pH | 8.40 | -- | 8.50 | -- |
| Ionic | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 66.80 | 66.80 | 87.96 | 87.96 |
| CTa (ng/l) | 60.40 | 59.95 | 80.75 | 75.67 |
| Ca (ng/l) | 19.27 | 18.93 | 26.98 | 27.06 |
| Ra (ng/g) | 37.38 | 37.30 | 48.88 | 44.19 |
| Rxa (ng/g) | 4.54 | 2.96 | 12.06 | 5.01 |
| CTd (ng/l) | 37.58 | 39.03 | 44.83 | 45.21 |
| Cd (ng/l) | 4.11 | 4.36 | 5.80 | 5.42 |
| Rd (ng/g) | 33.81 | 35.02 | 39.42 | 40.19 |
| Rxd (ng/g) | 0.97 | 0.68 | 2.59 | 1.00 |
| Ro (ng/g) | 32.85 | 34.33 | 36.82 | 39.19 |
| Glass (pg) | 8.30 | 10.53 | 22.60 | 29.34 |
| MB Er. (%) | -9.20 | -11.83 | -1.57 | -12.29 |

TABLE 21. ISOTHERM

Sediment = Kaolinite | Aqueous Phase = Distilled Water

Mass = 1000 mg/ℓ | Time of Adsorption = 2.0 hr. | Time of Desorption = 1.5 hr.

| | | | | |
|---|---|---|---|---|
| Date | 4099.00 | 4099.00 | 4099.00 | 4099.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 8.70 | 8.70 | 8.70 | 8.70 |
| Ionic | -- | -- | -- | -- |
| Ma (mg/l) | 1000.00 | 1000.00 | 1000.00 | 1000.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 1000.00 | 1000.00 | 1000.00 | 1000.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 | 1.50 |
| Ci (ng/l) | 18.43 | 36.87 | 73.74 | 147.48 |
| CTa (ng/l) | 18.93 | 39.93 | 69.90 | 145.26 |
| Ca (ng/l) | 8.22 | 22.23 | 34.13 | 64.42 |
| Ra (ng/g) | 10.70 | 17.70 | 35.77 | 80.83 |
| Rxa (ng/g) | 3.84 | 4.95 | 12.11 | 26.11 |
| CTd (ng/l) | 10.68 | 17.54 | 35.35 | 80.66 |
| Cd (ng/l) | 2.60 | 3.92 | 8.62 | 18.46 |
| Rd (ng/g) | 8.08 | 13.62 | 26.73 | 62.20 |
| Rxd (ng/g) | 1.21 | 0.87 | 3.06 | 7.48 |
| Ro (ng/g) | 6.87 | 12.75 | 23.67 | 54.72 |
| Glass (pg) | 4.59 | 10.44 | 28.34 | 28.91 |
| MB Er. (%) | 5.15 | 11.12 | -1.36 | 0.45 |

TABLE 22. SOLUTION COMPOSITION

Sediment = Montmorillonite  Aqueous Phase = NaCl

Mass = 200 mg/ℓ  Time of Adsorption = 4 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 5099.00 | 5099.00 | 5099.00 | 5099.00 | 5179.00 | 5179.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Aq. Phase | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 |
| pH | 6.60 | 6.60 | 6.60 | 6.60 | 6.60 | 6.60 |
| Ionic | 1.00 | 5.00 | 10.00 | 50.00 | 1.00 | 3.00 |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 |
| Md (mg/l) | -- | -- | -- | -- | -- | -- |
| Td (hr) | -- | -- | -- | -- | -- | -- |
| Ci (ng/l) | 31.96 | 31.96 | 31.96 | 31.96 | 30.10 | 30.10 |
| CTa (ng/l) | 41.75 | 27.28 | 28.53 | 27.33 | 24.34 | 24.43 |
| Ca (ng/l) | 12.01 | 9.81 | 11.77 | 6.55 | 7.98 | 8.92 |
| Ra (ng/g) | 148.72 | 87.34 | 83.79 | 103.93 | 81.81 | 77.54 |
| Rxa (ng/g) | -- | -- | -- | -- | -- | -- |
| CTd (ng/l) | -- | -- | -- | -- | -- | -- |
| Cd (ng/l) | -- | -- | -- | -- | -- | -- |
| Rd (ng/g) | -- | -- | -- | -- | -- | -- |
| Rxd (ng/g) | -- | -- | -- | -- | -- | -- |
| Ro (ng/g) | -- | -- | -- | -- | -- | -- |
| Glass (pg) | 9.14 | 13.21 | 10.36 | 21.65 | 30.92 | 22.23 |
| MB Er. (%) | 33.49 | -10.50 | -7.49 | -7.71 | -8.85 | -11.46 |

TABLE 22, (cont'd) SOLUTION COMPOSITION

Sediment = Montmorillonite

Aqueous Phase = NaCl

Mass = 200 mg/ℓ

Time of Adsorption = 4 hr.

| | | | | |
|---|---|---|---|---|
| Date | 5179.00 | 5229.00 | 5229.00 | 5259.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 |
| Aq. Phase | 4.00 | 4.00 | 4.00 | 4.00 |
| pH | 6.60 | 6.60 | 6.60 | 6.60 |
| Ionic | 50.00 | 20.00 | 60.00 | 100.00 |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 4.00 | 4.00 | 4.00 | 4.00 |
| Md (mg/l) | -- | -- | -- | -- |
| Td (hr) | -- | -- | -- | -- |
| Ci (ng/l) | 30.10 | 33.29 | 33.29 | 35.03 |
| CTa (ng/l) | 27.01 | 30.25 | 30.59 | 32.95 |
| Ca (ng/l) | 6.96 | 10.60 | 8.76 | 8.84 |
| Ra (ng/g) | 100.28 | 98.25 | 109.15 | 120.56 |
| Rxa (ng/g) | -- | -- | -- | -- |
| CTd (ng/l) | -- | -- | -- | -- |
| Cd (ng/l) | -- | -- | -- | -- |
| Rd (ng/g) | -- | -- | -- | -- |
| Rxd (ng/g) | -- | -- | -- | -- |
| Ro (ng/g) | -- | -- | -- | -- |
| Glass (pg) | 19.81 | 13.50 | 12.57 | 10.78 |
| MB Er. (%) | -3.67 | -5.09 | -4.35 | -2.84 |

TABLE 23. SOLUTION COMPOSITION

Sediment = Montmorillonite

Mass = 200 mg/ℓ

Aqueous Phase = HCl and NaOH

Time of Adsorption = 4 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 5219.00 | 5219.00 | 5189.00 | 5189.00 | 5229.00 | 5229.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Aq. Phase | 5.00 | 5.00 | 5.00 | 5.00 | 6.00 | 6.00 |
| pH | 6.25 | 6.25 | 4.17 | 3.73 | 6.70 | 6.70 |
| Ionic | 0.10 | 0.30 | 0.60 | 1.20 | 0.20 | 0.50 |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 |
| Md (mg/l) | -- | -- | -- | -- | -- | -- |
| Td (hr) | -- | -- | -- | -- | -- | -- |
| Ci (ng/l) | 33.29 | 33.29 | 33.99 | 33.99 | 33.29 | 33.29 |
| CTa (ng/l) | 28.94 | 28.49 | 29.99 | 32.51 | 35.74 | 31.59 |
| Ca (ng/l) | 9.66 | 8.16 | 7.80 | 9.46 | 16.95 | 14.22 |
| Ra (ng/g) | 95.90 | 101.62 | 110.97 | 115.25 | 93.97 | 86.82 |
| Rxa (ng/g) | -- | -- | -- | -- | -- | -- |
| CTd (ng/l) | -- | -- | -- | -- | -- | -- |
| Cd (ng/l) | -- | -- | -- | -- | -- | -- |
| Rd (ng/g) | -- | -- | -- | -- | -- | -- |
| Rxd (ng/g) | -- | -- | -- | -- | -- | -- |
| Ro (ng/g) | -- | -- | -- | -- | -- | -- |
| Glass (pg) | 10.78 | 12.71 | 14.57 | 11.16 | 10.66 | 10.56 |
| MB Er. (%) | -10.14 | -10.62 | -7.46 | -1.06 | 10.57 | -1.95 |

TABLE 23(cont'd) SOLUTION COMPOSITION

Sediment = Montmorillonite

Mass = 200 mg/ℓ

Aqueous Phase = HCl and NaOH

Time of Adsorption = 4 hr.

| | | |
|---|---|---|
| Date | 5189.00 | 5189.00 |
| Expt. Type | 1.00 | 1.00 |
| Aq. Phase | 6.00 | 6.00 |
| pH | 7.75 | 9.30 |
| Ionic | 1.00 | 2.00 |
| Ma (mg/l) | 200.00 | 200.00 |
| Ta (hr) | 4.00 | 4.00 |
| Md (mg/l) | -- | -- |
| Td (hr) | -- | -- |
| Ci (mg/l) | 33.99 | 33.99 |
| CTa (mg/l) | 31.65 | 33.31 |
| Ca (mg/l) | 14.11 | 16.82 |
| Ra (mg/g) | 87.69 | 82.45 |
| Rxa (mg/g) | -- | -- |
| CTd (mg/l) | -- | -- |
| Cd (mg/l) | -- | -- |
| Rd (mg/g) | -- | -- |
| Rxd (mg/g) | -- | -- |
| Ro (mg/g) | -- | -- |
| Glass (pg) | 10.90 | 10.53 |
| MB Er. (%) | -3.67 | 1.10 |

TABLE 24. SOLUTION COMPOSITION

Sediment = Montmorillonite

Mass = 200 mg/ℓ

Aqueous Phase = $CaCl_2$

Time of Adsorption = 4 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 6149.00 | 6149.00 | 6149.00 | 6199.00 | 6199.00 | 6199.00 |
| Expt. Type | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Aq. Phase | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 |
| pH | 6.50 | 6.50 | 6.60 | 6.60 | 6.50 | 6.60 |
| Ionic | 1.00 | 5.00 | 10.00 | 9.00 | 30.00 | 80.00 |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 |
| Md (mg/l) | -- | -- | -- | -- | -- | -- |
| Td (hr) | -- | -- | -- | -- | -- | -- |
| Ci (ng/l) | 28.44 | 28.44 | 28.44 | 28.44 | 33.29 | 33.29 |
| CTa (ng/l) | 27.14 | 28.00 | 28.67 | 23.93 | 24.08 | 24.60 |
| Ca (ng/l) | 9.09 | 6.21 | 4.73 | 9.51 | 3.67 | 10.32 |
| Ra (ng/g) | 90.24 | 108.91 | 119.72 | 72.09 | 102.06 | 71.36 |
| Rxa (ng/g) | -- | -- | -- | -- | -- | -- |
| CTd (ng/l) | -- | -- | -- | -- | -- | -- |
| Cd (ng/l) | -- | -- | -- | -- | -- | -- |
| Rd (ng/g) | -- | -- | -- | -- | -- | -- |
| Rxd (ng/g) | -- | -- | -- | -- | -- | -- |
| Ro (ng/g) | -- | -- | -- | -- | -- | -- |
| Glass (pg) | 11.02 | 16.81 | 8.16 | 13.93 | 8.88 | 27.15 |
| MB Er. (%) | -0.68 | 4.36 | 3.70 | -10.95 | -25.00 | -17.96 |

TABLE 25. ISOTHERM - SEDIMENT COMPOSITION

Sediment = Saginaw Bay Station 43 Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ Time of Adsorption = 3 hr. Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 1210.00 | 1210.00 | 1210.00 | 1210.00 | 1210.00 | 1210.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | -- | -- | -- | -- | -- | -- |
| CTa (ng/l) | 10.00 | 9.74 | 18.79 | 39.61 | 56.85 | 77.50 |
| Ca (ng/l) | 1.08 | 1.01 | 1.47 | 2.80 | 3.65 | 6.27 |
| Ra (ng/g) | 8.11 | 7.93 | 15.75 | 33.46 | 48.37 | 64.82 |
| Rxa (ng/g) | -1.79 | -1.23 | 0.61 | 0.68 | -1.51 | 0.43 |
| CTd (ng/l) | 9.42 | 8.96 | 16.03 | 33.93 | 50.18 | 65.44 |
| Cd (ng/l) | 0.60 | 0.52 | 0.74 | 1.19 | 1.36 | 1.58 |
| Rd (ng/g) | 8.90 | 8.53 | 15.45 | 33.07 | 49.31 | 64.51 |
| Rxd (ng/g) | -1.00 | -0.63 | 0.31 | 0.29 | -0.56 | 0.11 |
| Ro (ng/g) | 9.91 | 9.16 | 15.14 | 32.78 | 49.88 | 64.40 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 26. ISOTHERM - SEDIMENT COMPOSITION

Sediment = Saginaw Bay Station 50 Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ Time of Adsorption = 3 hr. Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 7189.00 | 7189.00 | 7189.00 | 7189.00 | 10109.00 | 10109.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 16.79 | 50.38 | 83.96 | 134.34 | 15.33 | 30.66 |
| CTa (ng/l) | 16.60 | 50.66 | 81.26 | 132.25 | 14.52 | 27.79 |
| Ca (ng/l) | 1.95 | 5.40 | 8.63 | 14.35 | 1.66 | 3.01 |
| Ra (ng/g) | 13.31 | 41.15 | 66.03 | 107.19 | 11.69 | 22.53 |
| Rxa (ng/g) | 0.90 | 0.97 | -0.34 | 15.44 | 1.08 | -0.12 |
| CTd (ng/l) | 13.73 | 42.00 | 69.00 | 99.92 | 11.74 | 23.48 |
| Cd (ng/l) | 0.99 | 1.89 | 3.43 | 4.40 | 0.75 | 1.10 |
| Rd (ng/g) | 12.87 | 40.51 | 66.23 | 96.48 | 11.10 | 22.61 |
| Rxd (ng/g) | 0.46 | 0.34 | -0.13 | 4.74 | 0.49 | -0.05 |
| Ro (ng/g) | 12.41 | 40.17 | 66.37 | 91.75 | 10.61 | 22.65 |
| Glass (pg) | 2.33 | 3.72 | 8.17 | 7.82 | 1.10 | 1.36 |
| MB Er. (%) | -3.06 | -1.21 | -6.56 | 3.65 | -5.65 | -12.78 |

TABLE 26. (cont'd) ISOTHERM - SEDIMENT COMPOSITION

Sediment = Saginaw Bay Station 50 Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ Time of Adsorption = 3 hr. Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 10107.00 | 10109.00 | 10109.00 | 10129.00 | 10129.00 | 10129.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 30.66 | 61.33 | 122.66 | 15.33 | 30.66 | 61.33 |
| CTa (ng/l) | 27.34 | 56.95 | 127.42 | 14.18 | 35.10 | 56.08 |
| Ca (ng/l) | 3.30 | 6.32 | 12.55 | 1.75 | 3.16 | 6.59 |
| Ra (ng/g) | 21.85 | 46.02 | 104.43 | 11.30 | 29.04 | 44.99 |
| Rxa (ng/g) | -1.18 | -15.15 | 50.87 | 0.43 | 15.87 | 8.38 |
| CTd (ng/l) | 23.51 | 57.51 | 70.65 | 11.37 | 17.50 | 40.08 |
| Cd (ng/l) | 1.10 | 2.22 | 3.52 | 0.49 | 0.75 | 1.70 |
| Rd (ng/g) | 22.64 | 55.85 | 67.81 | 10.99 | 16.92 | 38.77 |
| Rxd (ng/g) | -0.39 | -5.33 | 14.25 | 0.12 | 3.76 | 2.17 |
| Ro (ng/g) | 23.03 | 61.18 | 53.56 | 10.88 | 13.16 | 36.61 |
| Glass (pg) | 1.66 | 5.21 | 11.35 | 1.31 | 13.01 | 11.65 |
| MB Er. (%) | -16.40 | -25.78 | 31.50 | -7.84 | 55.39 | 0.61 |

TABLE 26. (cont'd) ISOTHERM - SEDIMENT COMPOSITION

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 3 hr.

| | | | | | |
|---|---|---|---|---|---|
| Date | 10129.00 | 10179.00 | 10179.00 | 10179.00 | 10179.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 122.66 | 16.61 | 33.22 | 66.44 | 132.88 |
| CTa (ng/l) | 112.97 | 11.60 | 24.14 | 53.73 | 111.86 |
| Ca (ng/l) | 14.21 | 1.83 | 3.07 | 6.01 | 12.09 |
| Ra (ng/g) | 89.78 | 8.89 | 19.16 | 43.38 | 90.69 |
| Rxa (ng/g) | 21.10 | 1.18 | 8.55 | 20.86 | 17.04 |
| CTd (ng/l) | 75.10 | 8.78 | 15.18 | 31.80 | 80.13 |
| Cd (ng/l) | 2.88 | 0.70 | 1.25 | 2.14 | 3.01 |
| Rd (ng/g) | 72.95 | 8.16 | 14.08 | 29.96 | 77.89 |
| Rxd (ng/g) | 4.27 | 0.45 | 3.47 | 7.43 | 4.24 |
| Ro (ng/g) | 68.67 | 7.71 | 10.61 | 22.52 | 73.65 |
| Glass (pg) | 19.16 | -- | -- | -- | -- |
| MB Er. (%) | 4.90 | -- | -- | -- | -- |

TABLE 27. ISOTHERM - SEDIMENT COMPOSITION

Sediment = Montmorillonite

Aqueous Phase = $NaHCO_3$ Buffer

Mass = 1100 mg/ℓ

Time of Adsorption = 3 hr.

Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 6200.00 | 6200.00 | 6200.00 | 6200.00 | 6200.00 | 6200.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 11.00 | 11.00 | 11.00 | 11.00 | 11.00 | 11.00 |
| pH | 8.40 | -- | 8.40 | -- | 8.40 | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 22.27 | 22.27 | 44.54 | 44.54 | 55.67 | 55.67 |
| CTa (ng/l) | 25.88 | 20.81 | 39.94 | 41.01 | 48.88 | 50.69 |
| Ca (ng/l) | 5.55 | 5.48 | 11.79 | 13.24 | 15.20 | 15.38 |
| Ra (ng/g) | 18.48 | 13.93 | 25.59 | 25.25 | 30.61 | 32.10 |
| Rxa (ng/g) | 9.86 | -0.86 | 4.31 | 1.62 | 4.14 | 5.36 |
| CTd (ng/l) | 14.99 | 16.25 | 25.39 | 27.39 | 30.86 | 31.80 |
| Cd (ng/l) | 2.34 | 1.91 | 3.18 | 3.56 | 3.67 | 3.96 |
| Rd (ng/g) | 12.78 | 14.49 | 22.44 | 24.06 | 27.47 | 28.12 |
| Rxd (ng/g) | 4.15 | -0.30 | 1.16 | 0.44 | 1.00 | 1.38 |
| Ro (ng/g) | 8.63 | 14.79 | 21.28 | 23.63 | 26.47 | 26.74 |
| Glass (pg) | 2.23 | 2.67 | 6.37 | 5.16 | 11.44 | 14.80 |
| MB Er. (%) | 32.11 | -16.43 | -9.03 | -12.13 | -11.14 | -6.32 |

TABLE 29. ISOTHERM - SEDIMENT COMPOSITION

Sediment = Saginaw Bay Station 19 | Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 1180.00 | 1180.00 | 1180.00 | 1180.00 | 1180.00 | 1180.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 30.30 | 30.30 | 60.60 | 121.20 | 181.79 | 242.39 |
| CTa (ng/l) | 29.88 | 30.13 | 58.39 | 120.22 | 174.61 | 231.31 |
| Ca (ng/l) | 2.01 | 1.65 | 3.04 | 6.74 | 11.68 | 14.11 |
| Ra (ng/g) | 25.34 | 25.89 | 50.31 | 103.17 | 148.11 | 197.46 |
| Rxa (ng/g) | 0.05 | 0.52 | 1.84 | 9.40 | -20.66 | -2.30 |
| CTd (ng/l) | 26.19 | 26.49 | 50.74 | 100.20 | 163.37 | 202.32 |
| Cd (ng/l) | 1.13 | 1.04 | 1.72 | 3.10 | 4.96 | 5.44 |
| Rd (ng/g) | 25.31 | 25.70 | 49.52 | 98.08 | 160.01 | 198.87 |
| Rxd (ng/g) | 0.03 | 0.33 | 1.04 | 4.32 | -8.77 | -0.89 |
| Ro (ng/g) | 25.28 | 25.38 | 48.48 | 93.77 | 168.78 | 199.76 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 28. ISOTHERM - SEDIMENT COMPOSITION

Sediment = Saginaw Bay Station 69 Aqueous Phase = Distilled Water

Mass = 20,000 mg/ℓ Time of Adsorption = 3 hr. Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 3050.00 | 3050.00 | 3050.00 | 3050.00 | 3050.00 | 3050.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 20000.00 | 20000.00 | 20000.00 | 20000.00 | 20000.00 | 20000.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 18000.00 | 18000.00 | 18000.00 | 18000.00 | 18000.00 | 18000.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 40.70 | 40.70 | 81.41 | 162.81 | 244.22 | 325.62 |
| CTa (ng/l) | 22.83 | 20.90 | 38.52 | 95.71 | 150.22 | 188.57 |
| Ca (ng/l) | 10.55 | 11.02 | 21.10 | 51.08 | 91.30 | 123.62 |
| Ra (ng/g) | 0.61 | 0.49 | 0.87 | 2.23 | 2.95 | 3.25 |
| Rxa (ng/g) | 0.68 | 500.28 | 0.70 | 1.76 | 2.68 | 2.54 |
| CTd (ng/l) | 9.69 | -5020.48 | 16.37 | 32.48 | 34.28 | 50.12 |
| Cd (ng/l) | 5.04 | 4.86 | 8.33 | 14.81 | 19.32 | 27.26 |
| Rd (ng/g) | 0.26 | -279.19 | 0.45 | 0.98 | 0.83 | 1.27 |
| Rxd (ng/g) | 0.33 | 220.60 | 0.28 | 0.51 | 0.57 | 0.56 |
| Ro (ng/g) | -0.07 | -499.79 | 0.17 | 0.47 | 0.26 | 0.71 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 31. ISOTHERM - SEDIMENT COMPOSITION

Sediment = Saginaw Bay Station 53 Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ Time of Adsorption = 3 hr. Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 1170.00 | 1170.00 | 1170.00 | 1170.00 | 1170.00 | 1170.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 30.30 | 30.30 | 60.60 | 121.20 | 181.79 | 242.39 |
| CTa (ng/l) | 31.23 | 29.16 | 55.52 | 113.77 | 171.12 | 222.35 |
| Ca (ng/l) | 2.43 | 2.09 | 4.06 | 8.63 | 13.11 | 17.92 |
| Ra (ng/g) | 26.18 | 24.61 | 46.78 | 95.58 | 143.65 | 185.85 |
| Rxa (ng/g) | 3.48 | 3.01 | 0.26 | 2.73 | 5.50 | -26.85 |
| CTd (ng/l) | 26.85 | 25.12 | 48.96 | 97.36 | 145.45 | 206.39 |
| Cd (ng/l) | 1.81 | 1.54 | 2.73 | 4.14 | 6.14 | 8.65 |
| Rd (ng/g) | 25.30 | 23.82 | 46.69 | 94.16 | 140.72 | 199.74 |
| Rxd (ng/g) | 2.59 | 2.22 | 0.18 | 1.31 | 2.57 | -12.96 |
| Ro (ng/g) | 22.71 | 21.60 | 46.52 | 92.85 | 138.15 | 212.70 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 30. ISOTHERM - SEDIMENT COMPOSITION

Sediment = Saginaw River | Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 1160.00 | 1160.00 | 1160.00 | 1160.00 | 1160.00 | 1160.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | 30.30 | 30.30 | 60.60 | 121.20 | 181.79 | 242.39 |
| CTa (ng/l) | 27.93 | 28.01 | 54.72 | 111.38 | 159.31 | 212.96 |
| Ca (ng/l) | 2.57 | 2.39 | 4.21 | 9.81 | 15.51 | 17.91 |
| Ra (ng/g) | 23.05 | 23.29 | 45.92 | 92.33 | 130.73 | 177.32 |
| Rxa (ng/g) | 3.00 | 3.26 | 2.42 | -1.87 | -5.79 | 7.51 |
| CTd (ng/l) | 22.80 | 23.03 | 46.42 | 96.41 | 138.34 | 176.65 |
| Cd (ng/l) | 1.37 | 1.36 | 2.14 | 3.88 | 5.05 | 6.04 |
| Rd (ng/g) | 21.64 | 21.89 | 44.73 | 93.47 | 134.63 | 172.34 |
| Rxd (ng/g) | 1.59 | 1.86 | 1.23 | -0.74 | -1.88 | 2.53 |
| Ro (ng/g) | 20.05 | 20.03 | 43.50 | 94.21 | 136.52 | 169.81 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 32. (cont'd) ISOTHERM - SEDIMENT COMPOSITION

Sediment = Saginaw Bay Station 31 | Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 3 hr.

| | | |
|---|---|---|
| Date | 1150.00 | 1150.00 |
| Expt. Type | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 |
| pH | -- | -- |
| Ionic | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 |
| Td (hr) | 3.00 | 3.00 |
| Ci (ng/l) | 171.94 | 229.25 |
| CTa (ng/l) | 164.34 | 217.16 |
| Ca (ng/l) | 12.57 | 14.88 |
| Ra (ng/g) | 137.97 | 183.89 |
| Rxa (ng/g) | 2.15 | 5.88 |
| CTd (ng/l) | 140.63 | 183.29 |
| Cd (ng/l) | 5.27 | 5.07 |
| Rd (ng/g) | 136.73 | 180.02 |
| Rxd (ng/g) | 0.90 | 2.01 |
| Ro (ng/g) | 135.83 | 178.02 |
| Glass (pg) | -- | -- |
| MB Er. (%) | -- | -- |

TABLE 32. ISOTHERM - SEDIMENT COMPOSITION

Sediment = Saginaw Bay Station 31 | Aqueous Phase = Distilled Water

Mass = 1100 mg/ℓ | Time of Adsorption = 3 hr. | Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 1150.00 | 1150.00 | 1150.00 | 1150.00 | 1150.00 | 1150.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | -- | -- | 990.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | -- | -- | 3.00 |
| Ci (ng/l) | 42.98 | 42.98 | 85.97 | 85.97 | 114.63 | 114.63 |
| CTa (ng/l) | 39.70 | 40.16 | 80.91 | 82.81 | 111.75 | 111.70 |
| Ca (ng/l) | 3.58 | 2.66 | 5.93 | 6.26 | 6.10 | 5.99 |
| Ra (ng/g) | 32.84 | 34.09 | 68.16 | 69.59 | 96.04 | 96.11 |
| Rxa (ng/g) | -0.41 | -0.84 | 2.40 | -- | -- | 10.98 |
| CTd (ng/l) | 34.08 | 35.34 | 67.84 | -- | -- | 91.57 |
| Cd (ng/l) | 1.31 | 1.11 | 1.95 | -- | -- | 2.59 |
| Rd (ng/g) | 33.09 | 34.58 | 66.56 | -- | -- | 89.88 |
| Rxd (ng/g) | -0.15 | -0.35 | 0.79 | -- | -- | 4.75 |
| Ro (ng/g) | 33.24 | 34.93 | 65.77 | -- | -- | 85.12 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 33. SEDIMENT CONCENTRATION (cont'd)

Sediment = Montmorillonite

Aqueous Phase = Distilled Water

Time of Adsorption = 2 hr.

Time of Desorption = 1-3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 5309.00 | 6019.00 | 5299.00 | 5309.00 | 5299.00 | 4059.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 5.70 | 5.70 | 5.65 | 5.70 | 6.27 | 6.30 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 50.00 | 100.00 | 100.00 | 200.00 | 500.00 | 1000.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 50.00 | 100.00 | 100.00 | 200.00 | 500.00 | 1000.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| Ci (ng/l) | 22.54 | 31.21 | 30.88 | 43.35 | 60.05 | 54.76 |
| CTa (ng/l) | 17.60 | 30.57 | 28.09 | 42.03 | 51.39 | 43.69 |
| Ca (ng/l) | 9.43 | 18.59 | 12.59 | 16.32 | 15.81 | 12.08 |
| Ra (ng/g) | 163.38 | 119.80 | 154.99 | 128.59 | 71.16 | 31.61 |
| Rxa (ng/g) | 80.28 | 79.75 | 76.68 | 63.02 | 21.84 | 4.08 |
| CTd (ng/l) | 8.16 | 11.94 | 15.49 | 25.46 | 35.56 | 31.61 |
| Cd (ng/l) | 2.81 | 5.55 | 4.76 | 6.96 | 6.45 | 3.05 |
| Rd (ng/g) | 107.03 | 63.87 | 107.30 | 92.47 | 58.23 | 28.56 |
| Rxd (ng/g) | 23.93 | 23.82 | 28.99 | 26.90 | 8.91 | 1.03 |
| Ro (ng/g) | 83.10 | 40.05 | 78.31 | 65.57 | 49.32 | 27.53 |
| Glass (pg) | 5.42 | 5.29 | 12.97 | 10.50 | 18.47 | 8.55 |
| MB Er. (%) | -19.50 | -0.36 | -4.83 | -0.62 | -11.34 | -18.65 |

TABLE 33. SEDIMENT CONCENTRATION

Sediment = Montmorillonite

Aqueous Phase = Distilled Water

Time of Adsorption = 2 hr.

Time of Desorption = 1-3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 5309.00 | 6069.00 | 6019.00 | 5309.00 | 6069.00 | 6019.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 5.50 | 5.60 | 5.60 | 5.50 | 5.70 | 5.70 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 10.00 | 25.00 | 25.00 | 25.00 | 50.00 | 50.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 10.00 | 25.00 | 25.00 | 25.00 | 50.00 | 50.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| Ci (ng/l) | 13.87 | 62.06 | 17.34 | 17.34 | 77.57 | 22.54 |
| CTa (ng/l) | 13.42 | 46.58 | 16.35 | 15.41 | 60.53 | 19.52 |
| Ca (ng/l) | 8.46 | 28.81 | 10.63 | 8.77 | 37.85 | 11.10 |
| Ra (ng/g) | 495.83 | 710.69 | 228.87 | 265.39 | 453.77 | 168.38 |
| Rxa (ng/g) | 411.26 | 585.77 | 132.00 | 169.47 | 365.64 | 111.22 |
| CTd (ng/l) | 4.93 | 17.50 | 5.60 | 6.56 | 22.24 | 8.40 |
| Cd (ng/l) | 2.75 | 9.53 | 2.43 | 2.80 | 12.03 | 3.69 |
| Rd (ng/g) | 218.28 | 318.71 | 127.03 | 150.09 | 204.33 | 94.15 |
| Rxd (ng/g) | 133.72 | 193.80 | 30.16 | 54.17 | 116.21 | 36.99 |
| Ro (ng/g) | 84.57 | 124.91 | 96.87 | 95.92 | 88.12 | 57.16 |
| Glass (pg) | 5.72 | 39.46 | 6.68 | 6.38 | 24.82 | 7.99 |
| MB Er. (%) | 0.83 | -18.58 | -1.87 | -7.46 | -18.77 | -9.86 |

TABLE 33. SEDIMENT CONCENTRATION (cont'd)

Sediment = Montmorillonite

Aqueous Phase = Distilled Water

Time of Adsorption = 2 hr.

Time of Desorption = 1-3 hr.

| | | | | |
|---|---|---|---|---|
| Date | 3299.00 | 3299.00 | 3299.00 | 3299.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 6.30 | 6.30 | 6.30 | 6.30 |
| Ionic | -- | -- | -- | -- |
| Ma (mg/l) | 1000.00 | 1000.00 | 1000.00 | 1000.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 1000.00 | 1000.00 | 1000.00 | 1000.00 |
| Td (hr) | 1.00 | 1.50 | 2.00 | 3.00 |
| Ci (ng/l) | 72.83 | 72.83 | 72.83 | 72.83 |
| CTa (ng/l) | 62.91 | 62.37 | 57.07 | 63.14 |
| Ca (ng/l) | 13.88 | 12.80 | 12.37 | 15.80 |
| Ra (ng/g) | 49.02 | 49.57 | 44.70 | 47.34 |
| Rxa (ng/g) | 7.85 | 6.02 | 5.73 | 6.17 |
| CTd (ng/l) | 49.00 | 49.55 | 44.70 | 47.19 |
| Cd (ng/l) | 5.00 | 4.08 | 3.91 | 4.33 |
| Rd (ng/g) | 44.00 | 45.47 | 40.78 | 42.87 |
| Rxd (ng/g) | 2.82 | 1.92 | 1.81 | 1.69 |
| Ro (ng/g) | 41.18 | 43.55 | 38.97 | 41.18 |
| Glass (pg) | 20.23 | 10.77 | 21.11 | 16.14 |
| MB Er. (%) | -10.84 | -12.88 | -18.74 | -11.08 |

TABLE 33. SEDIMENT CONCENTRATION (cont'd)

Sediment = Montmorillonite

Aqueous Phase = Distilled Water

Time of Adsorption = 2 hr.

Time of Desorption = 1-3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 4059.00 | 4059.00 | 4029.00 | 4029.00 | 4029.00 | 4029.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 6.30 | 6.30 | 6.30 | 6.30 | 6.30 | 6.30 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| Ci (ng/l) | 91.26 | 146.02 | 18.07 | 54.21 | 90.35 | 144.56 |
| CTa (ng/l) | 68.63 | 109.50 | 18.78 | 59.39 | 97.22 | 136.80 |
| Ca (ng/l) | 21.10 | 37.58 | 4.40 | 15.50 | 25.97 | 34.93 |
| Ra (ng/g) | 47.52 | 71.92 | 14.38 | 43.89 | 71.25 | 101.86 |
| Rxa (ng/g) | 6.15 | 10.52 | 2.17 | 5.32 | 8.19 | 12.58 |
| CTd (ng/l) | 47.46 | 71.91 | 14.31 | 43.84 | 71.04 | 101.77 |
| Cd (ng/l) | 4.71 | 8.21 | 1.40 | 3.93 | 6.07 | 9.18 |
| Rd (ng/g) | 42.75 | 63.69 | 12.90 | 39.91 | 64.97 | 92.58 |
| Rxd (ng/g) | 1.37 | 2.30 | 0.69 | 1.35 | 1.91 | 3.31 |
| Ro (ng/g) | 41.37 | 61.40 | 12.21 | 38.56 | 63.06 | 89.28 |
| Glass (pg) | 11.43 | 22.03 | 2.48 | 5.29 | 11.97 | 17.84 |
| MB Er. (%) | -23.55 | -23.50 | 5.33 | 10.53 | 8.93 | -4.14 |

TABLE 34. SEDIMENT CONCENTRATION (cont'd)

Sediment = Montmorillonite

Aqueous Phase = Supernatant

Time of Adsorption = 2 hr.

Time of Desorption = 1.5-5 hr.

| | | | |
|---|---|---|---|
| Date | 6119.00 | 6119.00 | 6119.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 2.00 | 2.00 | 2.00 |
| pH | 6.60 | 6.60 | 6.80 |
| Ionic | -- | -- | -- |
| Ma (mg/l) | 200.00 | 500.00 | 1000.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 200.00 | 500.00 | 1000.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 |
| Ci (ng/l) | 55.30 | 73.74 | 92.17 |
| CTa (ng/l) | 45.56 | 58.78 | 75.23 |
| Ca (ng/l) | 20.26 | 26.10 | 23.60 |
| Ra (ng/g) | 126.53 | 65.36 | 51.63 |
| Rxa (ng/g) | 77.50 | 25.64 | 20.39 |
| CTd (ng/l) | 25.28 | 31.29 | 51.57 |
| Cd (ng/l) | 8.77 | 7.66 | 10.90 |
| Rd (ng/g) | 82.56 | 47.25 | 40.66 |
| Rxd (ng/g) | 33.54 | 7.53 | 9.42 |
| Ro (ng/g) | 49.02 | 39.72 | 31.24 |
| Glass (pg) | 9.73 | 16.54 | 13.23 |
| MB Er. (%) | -15.85 | -18.04 | -16.95 |

TABLE 34. SEDIMENT CONCENTRATION

Sediment = Montmorillonite

Aqueous Phase = Supernatant

Time of Adsorption = 2 hr.

Time of Desorption = 1.5-5 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 6139.00 | 6139.00 | 6139.00 | 6289.00 | 6269.00 | 6279.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| pH | 7.00 | 6.50 | 6.60 | 7.85 | 8.50 | 7.90 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 25.00 | 50.00 | 100.00 | 200.00 | 200.00 | 200.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 25.00 | 50.00 | 100.00 | 200.00 | 200.00 | 200.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 | 5.00 | 2.00 | 4.00 |
| Ci (ng/l) | 73.74 | 92.17 | 110.61 | 55.85 | 55.85 | 54.21 |
| CTa (ng/l) | 67.71 | 78.88 | 99.32 | -- | -- | -- |
| Ca (ng/l) | 41.06 | 49.23 | 57.68 | -- | -- | -- |
| Ra (ng/g) | 1065.97 | 593.04 | 416.36 | -- | -- | -- |
| Rxa (ng/g) | 723.81 | 445.71 | 267.10 | -- | -- | -- |
| CTd (ng/l) | 26.41 | 29.29 | 41.36 | 38.22 | 20.65 | 17.92 |
| Cd (ng/l) | 12.40 | 15.09 | 18.07 | 9.60 | 7.31 | 5.39 |
| Rd (ng/g) | 560.67 | 283.99 | 232.93 | 143.11 | 66.72 | 62.68 |
| Rxd (ng/g) | 218.50 | 136.66 | 83.66 | -- | -- | -- |
| Ro (ng/g) | 342.17 | 147.33 | 149.27 | -- | -- | -- |
| Glass (pg) | 27.20 | 22.30 | 18.47 | 10.55 | 6.72 | 9.85 |
| MB Er. (%) | -4.49 | -12.00 | -8.54 | -- | -- | -- |

TABLE 35, SEDIMENT CONCENTRATION (cont'd)

Sediment = Saginaw Bay Station 50

Aqueous Phase = Distilled Water

Time of Adsorption = 2 hr.

Time of Desorption = 1.5 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 5239.00 | 4189.00 | 5249.00 | 6079.00 | 5239.00 | 4189.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 5.50 | 6.00 | 6.00 | 6.25 | 6.30 | 6.50 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 50.00 | 100.00 | 100.00 | 200.00 | 200.00 | 500.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 50.00 | 100.00 | 100.00 | 200.00 | 200.00 | 500.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| Ci (ng/l) | 18.07 | 14.75 | 33.51 | -- | 45.17 | 73.74 |
| CTa (ng/l) | 16.24 | 14.37 | 30.86 | 65.61 | 40.41 | 67.13 |
| Ca (ng/l) | 7.89 | 4.84 | 10.90 | 18.97 | 9.88 | 10.31 |
| Ra (ng/g) | 167.17 | 95.32 | 199.67 | 233.18 | 152.63 | 113.64 |
| Rxa (ng/g) | 93.32 | 26.51 | 84.70 | 71.55 | 39.56 | 11.10 |
| CTd (ng/l) | 8.35 | 9.23 | 19.96 | 46.49 | 30.27 | 56.69 |
| Cd (ng/l) | 2.92 | 1.52 | 4.76 | 8.07 | 4.25 | 3.52 |
| Rd (ng/g) | 108.45 | 77.11 | 151.97 | 192.08 | 130.09 | 106.33 |
| Rxd (ng/g) | 34.60 | 8.30 | 37.01 | 30.45 | 17.02 | 3.79 |
| Ro (ng/g) | 73.86 | 68.81 | 114.96 | 161.63 | 113.07 | 102.54 |
| Glass (pg) | 14.38 | 2.87 | 6.98 | 14.23 | 11.83 | 7.20 |
| MB Er. (%) | -2.14 | -0.60 | -5.81 | -- | -7.93 | -7.98 |

TABLE 35. SEDIMENT CONCENTRATION

Sediment = Saginaw Bay Station 50 | Aqueous Phase = Distilled Water

Time of Adsorption = 2 hr. | Time of Desorption = 1.5 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 5249.00 | 5299.00 | 5239.00 | 5249.00 | 4189.00 | 6079.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | 5.35 | 5.40 | 5.40 | 5.40 | 5.60 | 5.60 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 10.00 | 25.00 | 25.00 | 30.00 | 50.00 | 50.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 10.00 | 25.00 | 25.00 | 30.00 | 50.00 | 50.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| Ci (ng/l) | 9.31 | 13.73 | 9.03 | 14.89 | 7.37 | -- |
| CTa (ng/l) | 9.04 | 13.10 | 8.09 | 14.32 | 6.72 | 41.22 |
| Ca (ng/l) | 5.82 | 7.06 | 4.57 | 7.51 | 2.89 | 20.00 |
| Ra (ng/g) | 322.69 | 241.61 | 140.63 | 227.02 | 76.69 | 424.36 |
| Rxa (ng/g) | 247.30 | 149.97 | 198.59 | 147.52 | 46.13 | 304.67 |
| CTd (ng/l) | 3.21 | 6.04 | 3.47 | 6.81 | 3.80 | 20.86 |
| Cd (ng/l) | 1.72 | 2.45 | 2.36 | 2.78 | 1.26 | 8.44 |
| Rd (ng/g) | 148.72 | 143.62 | 44.51 | 134.16 | 50.72 | 248.31 |
| Rxd (ng/g) | 73.33 | 51.97 | 102.47 | 54.66 | 20.16 | 128.62 |
| Ro (ng/g) | 75.39 | 91.64 | -57.96 | 79.50 | 30.56 | 119.69 |
| Glass (pg) | 2.43 | 7.88 | 5.35 | 5.79 | 2.40 | 9.51 |
| MB Er. (%) | -0.24 | 1.16 | -4.53 | 0.03 | -5.60 | -- |

TABLE 36. SEDIMENT CONCENTRATION

Sediment = Saginaw Bay Station 50

Aqueous Phase = Supernatant

Time of Adsorption = 2 hr.

Time of Desorption = 1.5-5 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 6059.00 | 6059.00 | 6059.00 | 6049.00 | 6049.00 | 6289.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| pH | 6.70 | 6.80 | 7.00 | 6.90 | 6.90 | 6.80 |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 10.00 | 25.00 | 50.00 | 100.00 | 100.00 | 200.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 10.00 | 25.00 | 50.00 | 100.00 | 100.00 | 200.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 5.00 |
| Ci (ng/l) | 14.60 | 14.60 | 18.98 | 31.54 | 29.20 | 55.85 |
| CTa (ng/l) | 13.37 | 17.72 | 22.43 | 30.31 | 29.95 | -- |
| Ca (ng/l) | 8.10 | 10.98 | 13.14 | 15.53 | 17.80 | -- |
| Ra (ng/g) | 526.58 | 269.77 | 185.78 | 147.87 | 121.56 | -- |
| Rxa (ng/g) | 482.61 | 168.05 | 127.40 | 74.01 | 91.89 | -- |
| CTd (ng/l) | 5.14 | 6.68 | 8.91 | 14.60 | 12.16 | 28.11 |
| Cd (ng/l) | 2.95 | 2.99 | 4.04 | 4.88 | 6.06 | 5.76 |
| Rd (ng/g) | 219.60 | 147.52 | 97.53 | 97.13 | 60.96 | 111.77 |
| Rxd (ng/g) | 175.63 | 45.80 | 39.15 | 23.27 | 31.29 | -- |
| Ro (ng/g) | 43.97 | 101.72 | 58.38 | 73.86 | 29.67 | -- |
| Glass (pg) | 5.28 | 2.91 | 4.64 | 6.90 | 13.63 | 5.30 |
| MB Er. (%) | -4.83 | 23.34 | 20.61 | -1.71 | 7.23 | -- |

TABLE 35. SEDIMENT CONCENTRATION (cont'd)

Sediment = Saginaw Bay Station 50

Aqueous Phase = Distilled Water

Time of Adsorption = 2 hr.

Time of Desorption = 1.5 hr.

| | | | |
|---|---|---|---|
| Date | 4119.00 | 4119.00 | 4119.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 |
| pH | 6.90 | 6.90 | 6.90 |
| Ionic | -- | -- | -- |
| Ma (mg/l) | 1000.00 | 1000.00 | 1000.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 1000.00 | 1000.00 | 1000.00 |
| Td (hr) | 1.50 | 1.50 | 1.50 |
| Ci (ng/l) | 19.17 | 76.66 | 153.32 |
| CTa (ng/l) | 18.53 | 76.26 | 151.45 |
| Ca (ng/l) | 1.96 | 7.89 | 13.13 |
| Ra (ng/g) | 16.56 | 68.37 | 138.32 |
| Rxa (ng/g) | 1.26 | 3.09 | 6.22 |
| CTd (ng/l) | 16.56 | 68.34 | 138.32 |
| Cd (ng/l) | 0.77 | 2.20 | 4.22 |
| Rd (ng/g) | 15.80 | 66.15 | 134.10 |
| Rxd (ng/g) | 0.49 | 0.86 | 2.00 |
| Ro (ng/g) | 15.31 | 65.29 | 132.11 |
| Glass (pg) | 3.97 | 4.88 | 12.85 |
| MB Er. (%) | -1.25 | 0.12 | -0.38 |

TABLE 37. SEDIMENT CONCENTRATION

Sediment = Montmorillonite

Aqueous Phase = Distilled Water

Time of Adsorption = 24 hr.

Time of Desorption = 24 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 11069.00 | 11069.00 | 11069.00 | 11069.00 | 11069.00 | 11069.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | -- | -- | -- | -- | -- | -- |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 25.00 | 25.00 | 50.00 | 100.00 | 500.00 | 1000.00 |
| Ta (hr) | 24.00 | 24.00 | 24.00 | 24.00 | 24.00 | 24.00 |
| Md (mg/l) | 23.00 | 23.00 | 45.00 | 90.00 | 450.00 | 900.00 |
| Td (hr) | 24.00 | 24.00 | 24.00 | 24.00 | 24.00 | 24.00 |
| Ci (ng/l) | -- | -- | -- | -- | -- | -- |
| CTa (ng/l) | 7.34 | 7.30 | 9.94 | 10.19 | 23.73 | 32.49 |
| Ca (ng/l) | 4.80 | 4.69 | 5.59 | 5.25 | 7.63 | 7.32 |
| Ra (ng/g) | 101.48 | 104.57 | 87.05 | 49.40 | 32.19 | 25.16 |
| Rxa (ng/g) | 46.51 | 54.93 | 90.56 | 15.67 | 12.75 | 16.12 |
| CTd (ng/l) | 3.34 | 3.61 | 3.06 | 6.61 | 15.33 | 28.25 |
| Cd (ng/l) | 1.70 | 1.94 | 1.86 | 2.82 | 3.76 | 4.06 |
| Rd (ng/g) | 71.42 | 72.39 | 26.60 | 42.14 | 25.72 | 17.98 |
| Rxd (ng/g) | 16.45 | 22.76 | 30.11 | 8.41 | 6.28 | 8.94 |
| Ro (ng/g) | 54.98 | 49.63 | -3.51 | 33.73 | 19.44 | 9.05 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 36. SEDIMENT CONCENTRATION (cont'd)

Sediment = Saginaw Bay Station 50

Aqueous Phase = Supernatant

Time of Adsorption = 2 hr.

Time of Desorption = 1.5-5 hr.

| | | | | | |
|---|---|---|---|---|---|
| Date | 6269.00 | 6269.00 | 6279.00 | 6089.00 | 6089.00 |
| Expt. Type | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Aq. Phase | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| pH | 6.80 | 6.75 | 6.75 | 7.05 | 7.05 |
| Ionic | -- | -- | -- | -- | -- |
| Ma (mg/l) | 200.00 | 200.00 | 200.00 | 500.00 | 1000.00 |
| Ta (hr) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Md (mg/l) | 200.00 | 200.00 | 200.00 | 500.00 | 1000.00 |
| Td (hr) | 2.00 | 2.00 | 4.00 | 1.50 | 1.50 |
| Ci (ng/l) | 55.85 | 55.85 | 54.21 | 96.56 | 193.11 |
| CTa (ng/l) | -- | -- | -- | 96.35 | 190.72 |
| Ca (ng/l) | -- | -- | -- | 16.12 | 22.85 |
| Ra (ng/g) | -- | -- | -- | 160.45 | 167.88 |
| Rxa (ng/g) | -- | -- | -- | 23.88 | 11.78 |
| CTd (ng/l) | 39.13 | 40.90 | 30.00 | 80.08 | 167.54 |
| Cd (ng/l) | 6.77 | 5.25 | 5.08 | 6.77 | 7.55 |
| Rd (ng/g) | 161.81 | 178.28 | 124.57 | 146.61 | 159.99 |
| Rxd (ng/g) | -- | -- | -- | 10.03 | 3.89 |
| Ro (ng/g) | -- | -- | -- | 136.57 | 156.09 |
| Glass (pg) | 4.80 | 21.71 | 7.69 | 10.27 | 17.19 |
| MB Er. (%) | -- | -- | -- | 0.85 | -0.35 |

TABLE 38. SEDIMENT CONCENTRATION (cont'd)

Sediment = Montmorillonite

Aqueous Phase = Phosphate Buffer

Time of Adsorption = 2-4 hr.

Time of Desorption = 1.5-4 hr.

| | |
|---|---|
| Date | 5049.00 |
| Expt. Type | 1.00 |
| Aq. Phase | 8.00 |
| pH | 7.25 |
| Ionic | 5.90 |
| Ma (mg/l) | 1000.00 |
| Ta (hr) | 4.00 |
| Md (mg/l) | -- |
| Td (hr) | -- |
| Ci (ng/l) | 52.38 |
| CTa (ng/l) | 50.26 |
| Ca (ng/l) | 11.55 |
| Ra (ng/g) | 38.71 |
| Rxa (ng/g) | -- |
| CTd (ng/l) | -- |
| Cd (ng/l) | -- |
| Rd (ng/g) | -- |
| Rxd (ng/g) | -- |
| Ro (ng/g) | -- |
| Glass (pg) | 15.49 |
| MB Er. (%) | -1.10 |

TABLE 38. SEDIMENT CONCENTRATION

Sediment = Montmorillonite

Aqueous Phase = Phosphate Buffer

Time of Adsorption = 2-4 hr.

Time of Desorption = 1.5-4 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 5049.00 | 5319.00 | 5049.00 | 5319.00 | 5189.00 | 5049.00 |
| Expt. Type | 1.00 | 2.00 | 1.00 | 2.00 | 1.00 | 1.00 |
| Aq. Phase | 8.00 | 8.00 | 8.00 | 8.00 | 8.00 | 8.00 |
| pH | 7.25 | 7.20 | 7.25 | 7.20 | 7.25 | 7.25 |
| Ionic | 5.90 | 5.90 | 5.90 | 5.90 | 5.90 | 5.90 |
| Ma (mg/l) | 10.00 | 25.00 | 100.00 | 100.00 | 200.00 | 500.00 |
| Ta (hr) | 4.00 | 2.00 | 4.00 | 2.00 | 4.00 | 4.00 |
| Md (mg/l) | -- | 25.00 | -- | 100.00 | -- | -- |
| Td (hr) | -- | 1.50 | -- | 1.50 | -- | -- |
| Ci (ng/l) | -- | 17.16 | 17.96 | 34.31 | 33.99 | 37.42 |
| CTa (ng/l) | 11.25 | 15.90 | 17.28 | 29.70 | 30.78 | 30.78 |
| Ca (ng/l) | 6.87 | 8.16 | 8.96 | 12.15 | 9.71 | 10.68 |
| Ra (ng/g) | 437.66 | 309.62 | 83.17 | 175.54 | 105.31 | 40.20 |
| Rxa (ng/g) | -- | 209.49 | -- | 104.54 | -- | -- |
| CTd (ng/l) | -- | 7.61 | -- | 17.55 | -- | -- |
| Cd (ng/l) | -- | 3.11 | -- | 5.62 | -- | -- |
| Rd (ng/g) | -- | 180.05 | -- | 119.35 | -- | -- |
| Rxd (ng/g) | -- | 79.92 | -- | 48.34 | -- | -- |
| Ro (ng/g) | -- | 100.13 | -- | 71.00 | -- | -- |
| Glass (pg) | 6.90 | 3.68 | 7.57 | 10.18 | 12.57 | 17.37 |
| MB Er. (%) | -- | -5.17 | 0.41 | -10.48 | -5.75 | -13.10 |

TABLE 39. SEDIMENT CONCENTRATION (cont'd)

Sediment = Silica

Aqueous Phase = Distilled Water

Time of Adsorption = 3 hr.

Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 11149.00 | 11149.00 | 11149.00 | 11089.00 | 11149.00 | 11149.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 200.00 | 500.00 | 500.00 | 1000.00 | 1000.00 | 1000.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 180.00 | 450.00 | 450.00 | 900.00 | 900.00 | 900.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | -- | -- | -- | -- | -- | -- |
| CTa (ng/l) | 21.19 | 25.61 | 26.87 | 47.93 | 33.22 | 33.22 |
| Ca (ng/l) | 14.69 | 16.45 | 15.44 | 22.85 | 22.21 | 22.21 |
| Ra (ng/g) | 32.49 | 18.33 | 22.85 | 25.08 | 11.01 | 11.01 |
| Rxa (ng/g) | 26.78 | 9.80 | 18.22 | 17.74 | 5.69 | 5.69 |
| CTd (ng/l) | 7.06 | 9.95 | 9.55 | 19.75 | 10.42 | 10.42 |
| Cd (ng/l) | 4.54 | 4.82 | 4.87 | 7.74 | 4.58 | 4.58 |
| Rd (ng/g) | 13.99 | 11.40 | 10.38 | 13.34 | 6.49 | 6.49 |
| Rxd (ng/g) | 8.28 | 2.87 | 5.75 | 6.01 | 1.17 | 1.17 |
| Ro (ng/g) | 5.71 | 8.53 | 4.63 | 7.34 | 5.32 | 5.32 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 39. SEDIMENT CONCENTRATION

Sediment = Silica

Aqueous Phase = Distilled Water

Time of Adsorption = 3 hr.

Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 11089.00 | 11149.00 | 11149.00 | 11089.00 | 11149.00 | 11089.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 20.00 | 20.00 | 20.00 | 60.00 | 60.00 | 200.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 18.00 | 18.00 | 18.00 | 54.00 | 54.00 | 180.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | -- | -- | -- | -- | -- | -- |
| CTa (ng/l) | 13.18 | 12.38 | 12.28 | 20.39 | 15.00 | 31.14 |
| Ca (ng/l) | 10.22 | 9.49 | 9.20 | 10.81 | 10.64 | 13.98 |
| Ra (ng/g) | 147.84 | 144.19 | 154.23 | 159.71 | 72.71 | 85.79 |
| Rxa (ng/g) | 134.25 | 109.43 | 134.48 | 156.30 | 66.38 | 78.94 |
| CTd (ng/l) | 3.83 | 3.89 | 3.47 | 5.84 | 4.64 | 11.43 |
| Cd (ng/l) | 2.90 | 2.70 | 2.46 | 3.18 | 3.21 | 5.06 |
| Rd (ng/g) | 51.72 | 65.91 | 55.77 | 49.35 | 26.36 | 35.39 |
| Rxd (ng/g) | 38.12 | 31.14 | 36.02 | 45.94 | 20.04 | 28.55 |
| Ro (ng/g) | 13.60 | 34.77 | 19.75 | 3.41 | 6.33 | 6.84 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 39. SEDIMENT CONCENTRATION (cont'd)

Sediment = Silica

Aqueous Phase = Distilled Water

Time of Adsorption = 3 hr.

Time of Desorption = 3 hr.

| | | | | | | |
|---|---|---|---|---|---|---|
| Date | 11149.00 | 11149.00 | 11149.00 | 11089.00 | 11149.00 | 11149.00 |
| Expt. Type | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Aq. Phase | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| pH | -- | -- | -- | -- | -- | -- |
| Ionic | -- | -- | -- | -- | -- | -- |
| Ma (mg/l) | 200.00 | 500.00 | 500.00 | 1000.00 | 1000.00 | 1000.00 |
| Ta (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Md (mg/l) | 180.00 | 450.00 | 450.00 | 900.00 | 900.00 | 900.00 |
| Td (hr) | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Ci (ng/l) | -- | -- | -- | -- | -- | -- |
| CTa (ng/l) | 21.19 | 25.61 | 26.87 | 47.93 | 33.22 | 33.22 |
| Ca (ng/l) | 14.69 | 16.45 | 15.44 | 22.85 | 22.21 | 22.21 |
| Ra (ng/g) | 32.49 | 18.33 | 22.85 | 25.08 | 11.01 | 11.01 |
| Rxa (ng/g) | 26.78 | 9.80 | 18.22 | 17.74 | 5.69 | 5.69 |
| CTd (ng/l) | 7.06 | 9.95 | 9.55 | 19.75 | 10.42 | 10.42 |
| Cd (ng/l) | 4.54 | 4.82 | 4.87 | 7.74 | 4.58 | 4.58 |
| Rd (ng/g) | 13.99 | 11.40 | 10.38 | 13.34 | 6.49 | 6.49 |
| Rxd (ng/g) | 8.28 | 2.87 | 5.75 | 6.01 | 1.17 | 1.17 |
| Ro (ng/g) | 5.71 | 8.53 | 4.63 | 7.34 | 5.32 | 5.32 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB Er. (%) | -- | -- | -- | -- | -- | -- |

TABLE 40. RESUSPENSION EXPERIMENT

Sediment = Saginaw Bay Station #50 Mass = 55-220 mg/ℓ Aqueous Phase = Distilled Water

| | | | | | | |
|---|---|---|---|---|---|---|
| Ma (mg/l) | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 |
| CTa (ng/l) | 80.91 | 73.91 | 76.05 | 79.83 | 72.68 | 74.54 |
| Ca (ng/l) | 41.20 | 41.66 | 37.24 | 41.75 | 37.07 | 38.07 |
| Ra (ng/g) | 722.00 | 586.30 | 705.57 | 692.36 | 647.43 | 663.19 |
| πa (l/kg) | 17523.75 | 14071.85 | 18944.55 | -- | -- | -- |
| M rs (mg/l) | -- | -- | -- | 220.00 | 220.00 | 220.00 |
| CT rs (ng/l) | -- | -- | -- | 180.49 | 184.85 | 168.25 |
| Ca rs (ng/l) | -- | -- | -- | 104.61 | 58.32 | 70.87 |
| Ra rs (ng/g) | -- | -- | -- | 344.92 | 575.17 | 442.65 |
| Ro rs (ng/g) | -- | -- | -- | -- | -- | -- |
| πx rs (l/kg) | -- | -- | -- | -- | -- | -- |
| Md (mg/l) | 18.72 | 19.32 | 19.82 | 220.00 | 220.00 | 220.00 |
| CTd (ng/l) | 888.85 | 790.24 | 534.22 | 81.40 | 106.02 | 102.84 |
| Cd (ng/l) | 1027.83 | 966.61 | 339.34 | 15.80 | 16.93 | 15.25 |
| Rd (ng/g) | -- | -- | 9833.24 | 298.20 | 404.98 | 398.12 |
| Ro d (ng/g) | -- | -- | -- | 289.89 | 335.37 | 385.91 |
| πxd (l/kg) | 35.69 | 33.06 | 25.73 | 526.05 | 4112.06 | 800.76 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB error (%) | -- | -- | -- | -- | -- | -- |

TABLE 41. RESUSPENSION EXPERIMENT

Sediment = Saginaw Bay Station #50 Mass = 220-880 mg/ℓ Aqueous Phase = Distilled Water

| | | | | | | |
|---|---|---|---|---|---|---|
| Ma (mg/l) | 220.00 | 220.00 | 220.00 | 220.00 | 220.00 | 220.00 |
| CTa (ng/l) | 79.90 | 80.19 | 80.02 | 88.05 | 82.53 | 78.46 |
| Ca (ng/l) | 23.03 | 19.92 | 19.51 | 22.08 | 23.25 | 21.52 |
| Ra (ng/g) | 258.46 | 273.99 | 275.01 | 299.86 | 269.47 | 258.82 |
| πa (l/kg) | 11220.65 | 13758.01 | 14093.42 | -- | -- | -- |
| M rs (mg/l) | -- | -- | -- | 880.00 | 880.00 | 880.00 |
| CT rs (ng/l) | -- | -- | -- | 283.91 | 304.34 | 292.39 |
| Ca rs (ng/l) | -- | -- | -- | 32.19 | 42.28 | 27.45 |
| Ra rs (ng/g) | -- | -- | -- | 286.04 | 297.80 | 301.06 |
| Ro rs (ng/g) | -- | -- | -- | -- | -- | -- |
| πx rs (l/kg) | -- | -- | -- | -- | -- | -- |
| Md (mg/l) | 13.05 | 13.31 | 12.81 | 880.00 | 880.00 | 880.00 |
| CTd (ng/l) | 340.99 | 381.95 | 397.45 | 242.76 | 234.60 | 245.38 |
| Cd (ng/l) | 448.94 | 599.64 | 631.38 | 19.80 | 23.33 | 15.28 |
| Rd (ng/g) | -- | -- | -- | 253.36 | 240.08 | 261.48 |
| Ro d (ng/g) | -- | -- | -- | 201.14 | 168.99 | 211.82 |
| πxd (l/kg) | 46.92 | 51.90 | 53.49 | 2637.40 | 3047.02 | 3250.99 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB error (%) | -- | -- | -- | -- | -- | -- |

TABLE 42. RESUSPENSION EXPERIMENT

Sediment = Saginaw Bay Station #50 Mass = 55-1100 mg/ℓ Aqueous Phase = Distilled Water

| | | | | | | |
|---|---|---|---|---|---|---|
| Ma (mg/l) | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 |
| CTa (ng/l) | 58.01 | 58.71 | 59.06 | 57.12 | 55.66 | 55.61 |
| Ca (ng/l) | 28.63 | 30.55 | 30.45 | 29.77 | 29.26 | 27.51 |
| Ra (ng/g) | 534.18 | 512.03 | 520.16 | 497.28 | 480.04 | 510.92 |
| ϖa (l/kg) | 18660.61 | 16758.90 | 17083.19 | -- | -- | -- |
| M rs (mg/l) | -- | -- | -- | 1100.00 | 1100.00 | 1100.00 |
| CT rs (ng/l) | -- | -- | -- | 622.03 | 578.47 | 599.44 |
| Ca rs (ng/l) | -- | -- | -- | 84.80 | 74.41 | 63.56 |
| Ra rs (ng/g) | -- | -- | -- | 488.39 | 458.24 | 487.16 |
| Ro rs (ng/g) | -- | -- | -- | -- | -- | -- |
| ϖx rs (l/kg) | -- | -- | -- | -- | -- | -- |
| Md (mg/l) | 5.22 | 4.21 | 4.23 | 1038.89 | 1038.89 | 1038.89 |
| CTd (ng/l) | 72.57 | 90.20 | 51.19 | 395.04 | 337.43 | 357.70 |
| Cd (ng/l) | -- | 22.77 | -- | 17.41 | 13.54 | 14.61 |
| Rd (ng/g) | 19723.43 | 16013.56 | 17889.87 | 363.49 | 311.77 | 330.25 |
| Ro d (ng/g) | 57.82 | 57.82 | 57.82 | 331.21 | 279.19 | 283.43 |
| ϖxd (l/kg) | 37.72 | 37.72 | 28.81 | 1853.44 | 2406.32 | 3205.37 |
| Glass (pg) | 61.46 | 82.52 | 38.63 | 250.82 | 298.35 | 320.99 |
| MB error (%) | 11.16 | 14.77 | -0.37 | -2.30 | -7.76 | -9.00 |

TABLE 43. DILUTION EXPERIMENT

Sediment = Montmorillonite  Mass = 1100 mg/ℓ  Aqueous Phase = $NaHCO_3$ Buffer

| | | | | | | |
|---|---|---|---|---|---|---|
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| CTa (ng/l) | 74.28 | 77.61 | 78.21 | 80.02 | 72.69 | 77.57 |
| Ca (ng/l) | 22.76 | 18.74 | 23.23 | -- | -- | -- |
| Ra (ng/g) | 46.83 | 53.52 | 49.99 | -- | -- | -- |
| πa (l/kg) | 2057.34 | 2855.56 | 2152.24 | -- | -- | -- |
| M dl (mg/l) | -- | -- | -- | 660.00 | 660.00 | 660.00 |
| CT dl (ng/l) | -- | -- | -- | 48.18 | 44.78 | 50.51 |
| Ca dl (ng/l) | -- | -- | -- | 14.13 | 15.89 | 15.48 |
| Ra dl (ng/g) | -- | -- | -- | 51.59 | 43.79 | 53.07 |
| Ro dl (ng/g) | -- | -- | -- | -- | 58.69 | 24.94 |
| πx dl (l/kg) | -- | -- | -- | 13827.56 | -- | 1816.61 |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 594.00 | 594.00 | 594.00 |
| CTd (ng/l) | 48.96 | 55.41 | 50.13 | 27.46 | 27.10 | 25.83 |
| Cd (ng/l) | 9.74 | 8.94 | 8.45 | 5.02 | 6.25 | 5.92 |
| Rd (ng/g) | 39.61 | 46.95 | 42.10 | 37.78 | 35.10 | 33.52 |
| Ro d (ng/g) | 33.06 | 39.54 | 36.74 | 30.18 | 29.47 | 21.43 |
| πxd (l/kg) | 672.31 | 828.43 | 633.77 | 1515.72 | 901.11 | 2043.52 |
| Glass (pg) | 29.46 | 8.12 | 13.02 | 6.36 | 6.13 | 5.82 |
| MB error (%) | -7.83 | -7.91 | -9.83 | -9.91 | -12.34 | -11.33 |

TABLE 43.(cont'd) DILUTION EXPERIMENT

Sediment = Montmorillonite  Mass = 1100 mg/ℓ  Aqueous Phase = $NaHCO_3$ Buffer

| | | | | | | |
|---|---|---|---|---|---|---|
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| CTa (ng/l) | 77.63 | 78.26 | 75.46 | 78.58 | 78.34 | 78.49 |
| Ca (ng/l) | -- | -- | -- | -- | -- | -- |
| Ra (ng/g) | -- | -- | -- | -- | -- | -- |
| ma (l/kg) | -- | -- | -- | -- | -- | -- |
| M dl (mg/l) | 440.00 | 440.00 | 440.00 | 275.00 | 275.00 | 275.00 |
| CT dl (ng/l) | 33.61 | 34.27 | 31.72 | 21.77 | 22.03 | 22.06 |
| Ca dl (ng/l) | 12.27 | 12.11 | 12.35 | 7.84 | 8.19 | 7.39 |
| Ra dl (ng/g) | 48.52 | 50.36 | 44.02 | 50.66 | 50.34 | 53.36 |
| Ro dl (ng/g) | 53.64 | 49.83 | 59.69 | 49.82 | 50.15 | 39.78 |
| mx dl (l/kg) | -- | 43.73 | -- | 107.09 | 23.14 | 1838.17 |
| Md (mg/l) | 396.00 | 396.00 | 396.00 | 247.50 | 247.50 | 247.50 |
| CTd (ng/l) | 18.11 | 18.74 | 20.09 | 11.56 | 12.88 | 14.61 |
| Cd (ng/l) | 4.50 | 4.44 | 5.00 | 3.17 | 3.51 | 4.20 |
| Rd (ng/g) | 34.36 | 36.09 | 38.11 | 33.89 | 37.83 | 42.07 |
| Ro d (ng/g) | 26.16 | 27.83 | 34.09 | 22.52 | 28.43 | 27.15 |
| mxd (l/kg) | 1822.81 | 1860.08 | 803.99 | 3588.54 | 2676.51 | 3547.22 |
| glass (pg) | 3.16 | 3.91 | 6.84 | 6.19 | 2.03 | 5.07 |
| MB error (%) | -7.83 | -6.65 | -6.75 | -6.68 | -5.45 | -3.77 |

TABLE 43. (cont'd) DILUTION EXPERIMENT

Sediment = Montmorillonite  Mass = 1100 mg/ℓ  Aqueous Phase = $NaHCO_3$ Buffer

| | | | |
|---|---|---|---|
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 |
| CTa (ng/l) | 78.45 | 86.42 | 78.25 |
| Ca (ng/l) | -- | -- | -- |
| Ra (ng/g) | -- | -- | -- |
| πa (l/kg) | -- | -- | -- |
| M dl (mg/l) | 110.00 | 110.00 | 110.00 |
| CT dl (ng/l) | 10.23 | 11.24 | 11.55 |
| Ca dl (ng/l) | 4.55 | 5.17 | 5.80 |
| Ra dl (ng/g) | 51.60 | 55.16 | 52.24 |
| Ro dl (ng/g) | 49.08 | 55.78 | 48.91 |
| πx dl (l/kg) | 555.19 | -- | 573.18 |
| Md (mg/l) | 99.00 | 99.00 | 99.00 |
| CTd (ng/l) | 5.23 | 5.80 | 6.09 |
| Cd (ng/l) | 2.01 | 2.55 | 2.00 |
| Rd (ng/g) | 32.52 | 32.91 | 41.26 |
| Ro d (ng/g) | 17.45 | 11.33 | 35.49 |
| πxd (l/kg) | 7499.67 | 8475.58 | 2886.28 |
| Glass (pg) | 3.29 | 2.92 | 1.98 |
| MB error (%) | -5.55 | 4.17 | -3.47 |

TABLE 44. DILUTION EXPERIMENT

Sediment = Saginaw Bay Station #50 Mass = 1100 mg/ℓ Aqueous Phase = Distilled Water

| | | | | | | |
|---|---|---|---|---|---|---|
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| CTa (ng/l) | 179.57 | 193.32 | 176.23 | 188.42 | 204.60 | 176.20 |
| Ca (ng/l) | 12.06 | 9.46 | 9.48 | -- | -- | -- |
| Ra (ng/g) | 152.28 | 167.14 | 151.60 | -- | -- | -- |
| ϰa (l/kg) | 12623.56 | 17668.08 | 15996.99 | -- | -- | -- |
| M dl (mg/l) | -- | -- | -- | 660.00 | 660.00 | 660.00 |
| CT dl (ng/l) | -- | -- | -- | 101.06 | 105.83 | 101.01 |
| Ca dl (ng/l) | -- | -- | -- | 8.71 | 7.69 | 7.71 |
| Ra dl (ng/g) | -- | -- | -- | 139.93 | 148.70 | 141.36 |
| Ro dl (ng/g) | -- | -- | -- | 218.59 | 389.08 | 183.14 |
| ϰx dl (l/kg) | -- | -- | -- | -- | -- | -- |
| Md (mg/l) | 990.00 | 990.00 | 990.00 | 594.00 | 594.00 | 594.00 |
| CTd (ng/l) | 189.72 | 142.97 | 143.41 | 80.33 | 84.02 | 82.12 |
| Cd (ng/l) | 5.05 | 5.19 | 4.93 | 4.28 | 4.58 | 4.15 |
| Rd (ng/g) | 186.54 | 139.18 | 139.89 | 128.04 | 133.73 | 131.27 |
| Ro d (ng/g) | 216.34 | 95.61 | 123.86 | 116.55 | 111.67 | 119.52 |
| ϰxd (l/kg) | -- | 8401.67 | 3252.72 | 2685.07 | 4812.50 | 2832.63 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB error (%) | -- | -- | -- | -- | -- | -- |

TABLE 44 (cont'd) DILUTION EXPERIMENT

Sediment = Saginaw Bay Station #50 Mass = 1100 mg/ℓ Aqueous Phase = Distilled Water

| | | | | | | |
|---|---|---|---|---|---|---|
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 | 1100.00 |
| CTa (ng/l) | 174.72 | 215.97 | 224.52 | 186.61 | 195.55 | 171.97 |
| Ca (ng/l) | -- | -- | -- | -- | -- | -- |
| Ra (ng/g) | -- | -- | -- | -- | -- | -- |
| ϖa (l/kg) | -- | -- | -- | -- | -- | -- |
| M dl (mg/l) | 440.00 | 440.00 | 440.00 | 275.00 | 275.00 | 275.00 |
| CT dl (ng/l) | 72.27 | 69.15 | 74.15 | 45.42 | 45.40 | 67.11 |
| Ca dl (ng/l) | 6.55 | 6.22 | 13.21 | 8.60 | 6.44 | 5.88 |
| Ra dl (ng/g) | 149.38 | 143.01 | 138.49 | 133.87 | 141.65 | 222.66 |
| Ro dl (ng/g) | 150.91 | 329.26 | 225.74 | 171.59 | 187.04 | 96.14 |
| ϖx dl (l/kg) | -- | -- | -- | -- | -- | 21526.91 |
| Md (mg/l) | 396.00 | 396.00 | 396.00 | 247.50 | 247.50 | 247.50 |
| CTd (ng/l) | 54.53 | 59.68 | 51.48 | 56.28 | 34.84 | 33.11 |
| Cd (ng/l) | 3.82 | 4.24 | 4.20 | 4.53 | 4.62 | 4.96 |
| Rd (ng/g) | 128.06 | 139.98 | 119.37 | 209.09 | 122.09 | 113.73 |
| Ro d (ng/g) | 98.22 | 133.50 | 110.46 | 292.87 | 72.43 | -- |
| ϖxd (l/kg) | 7815.94 | 1528.19 | 2121.43 | -- | 10739.86 | 99999.00 |
| Glass (pg) | -- | -- | -- | -- | -- | -- |
| MB error (%) | -- | -- | -- | -- | -- | -- |

TABLE 44. (cont'd) DILUTION EXPERIMENT

Sediment = Saginaw Bay Station #50 Mass = 1100 mg/ℓ Aqueous Phase = Distilled Water

| | | | |
|---|---|---|---|
| Ma (mg/l) | 1100.00 | 1100.00 | 1100.00 |
| CTa (ng/l) | 179.53 | 249.80 | 209.52 |
| Ca (ng/l) | -- | -- | -- |
| Ra (ng/g) | -- | -- | -- |
| πa (l/kg) | -- | -- | -- |
| M dl (mg/l) | 110.00 | 110.00 | 110.00 |
| CT dl (ng/l) | 31.83 | 18.06 | 18.00 |
| Ca dl (ng/l) | 4.82 | 4.53 | 5.18 |
| Ra dl (ng/g) | 245.53 | 122.99 | 116.55 |
| Ro dl (ng/g) | 130.23 | 254.96 | 198.25 |
| πx dl (l/kg) | 23927.92 | -- | -- |
| Md (mg/l) | 99.00 | 99.00 | 99.00 |
| CTd (ng/l) | 14.19 | 13.69 | 12.89 |
| Cd (ng/l) | 3.68 | 3.65 | 2.73 |
| Rd (ng/g) | 106.21 | 101.42 | 102.62 |
| Ro d (ng/g) | -- | 12.20 | 87.12 |
| πxd (l/kg) | 99999.00 | 24464.10 | 5678.81 |
| Glass (pg) | -- | -- | -- |
| MB error (%) | -- | -- | -- |

TABLE 45 DILUTION EXPERIMENT

Sediment = Saginaw Bay Station #50 Mass = 220 mg/ℓ Aqueous Phase = Distilled Water

| | | | | | | |
|---|---|---|---|---|---|---|
| Ma (mg/l) | 220.00 | 220.00 | 220.00 | 220.00 | 220.00 | 220.00 |
| CTa (ng/l) | 91.89 | 94.66 | 92.91 | 91.38 | 94.75 | 90.15 |
| Ca (ng/l) | 23.03 | 23.78 | 23.33 | -- | -- | -- |
| Ra (ng/g) | 312.98 | 322.20 | 316.29 | -- | -- | -- |
| πa (l/kg) | 13589.53 | 13548.45 | 13557.06 | -- | -- | -- |
| M dl (mg/l) | -- | -- | -- | 132.00 | 132.00 | 132.00 |
| CT dl (ng/l) | -- | -- | -- | 55.71 | 57.09 | 55.99 |
| Ca dl (ng/l) | -- | -- | -- | 15.68 | 14.76 | 14.77 |
| Ra dl (ng/g) | -- | -- | -- | 303.24 | 320.68 | 312.32 |
| Ro dl (ng/g) | -- | -- | -- | 367.56 | 377.73 | 245.15 |
| πx dl (l/kg) | -- | -- | -- | -- | -- | 4549.23 |
| Md (mg/l) | 198.00 | 198.00 | 198.00 | 118.80 | 118.80 | 118.80 |
| CTd (ng/l) | 66.41 | 64.06 | 64.32 | 34.85 | 37.94 | 37.81 |
| Cd (ng/l) | 8.88 | 8.97 | 9.10 | 6.38 | 7.00 | 6.66 |
| Rd (ng/g) | 290.59 | 278.25 | 278.87 | 239.63 | 260.44 | 262.20 |
| Ro d (ng/g) | 273.82 | 246.53 | 250.26 | 196.00 | 206.07 | 220.98 |
| πxd (l/kg) | 1889.00 | 3535.15 | 3144.52 | 6839.74 | 7762.04 | 6186.18 |
| Glass (pg) | 6.77 | 4.17 | 6.03 | 7.35 | 8.18 | 4.23 |
| MB error (%) | -1.51 | 0.32 | -1.74 | -3.30 | 0.76 | -1.85 |

TABLE 45.(cont'd) DILUTION EXPERIMENT

Sediment = Saginaw Bay Station #50 Mass = 220 mg/ℓ Aqueous Phase = Distilled Water

| | | | | | | |
|---|---|---|---|---|---|---|
| Ma (mg/l) | 220.00 | 220.00 | 220.00 | 220.00 | 220.00 | 220.00 |
| CTa (ng/l) | 103.44 | 92.61 | 98.70 | 87.12 | 91.37 | 91.29 |
| Ca (ng/l) | -- | -- | -- | -- | -- | -- |
| Ra (ng/g) | -- | -- | -- | -- | -- | -- |
| πa (l/kg) | -- | -- | -- | -- | -- | -- |
| M dl (mg/l) | 88.00 | 88.00 | 88.00 | 55.00 | 55.00 | 55.00 |
| CT dl (ng/l) | 36.79 | 38.20 | 45.93 | 25.62 | 24.70 | 23.60 |
| Ca dl (ng/l) | 10.71 | 11.24 | 12.27 | 9.97 | 8.70 | 7.70 |
| Ra dl (ng/g) | 296.35 | 306.41 | 382.47 | 284.54 | 291.01 | 289.09 |
| Ro dl (ng/g) | 2142.30 | 358.01 | 141.16 | 311.22 | 349.82 | 373.98 |
| πx dl (l/kg) | -- | -- | 19665.01 | -- | -- | -- |
| Md (mg/l) | 79.20 | 79.20 | 79.20 | 49.50 | 49.50 | 49.50 |
| CTd (ng/l) | 24.12 | 22.81 | 25.45 | 14.42 | 13.48 | 14.37 |
| Cd (ng/l) | 6.03 | 5.65 | 6.60 | 4.30 | 4.14 | 4.04 |
| Rd (ng/g) | 228.48 | 216.68 | 237.95 | 204.35 | 188.68 | 208.70 |
| Ro d (ng/g) | 141.10 | 125.95 | 69.65 | 143.44 | 95.93 | 119.99 |
| πxd (l/kg) | 14497.80 | 16061.05 | 25492.37 | 14153.13 | 22425.05 | 21964.28 |
| Glass (pg) | 12.41 | 4.95 | 3.68 | 16.81 | 3.94 | 2.48 |
| MB error (%) | 6.17 | -2.21 | 6.08 | -2.03 | -2.30 | -2.63 |

TABLE 45.(cont'd) DILUTION EXPERIMENT

Sediment = Saginaw Bay Station #50 Mass = 220 mg/ℓ Aqueous Phase = Distilled Water

| | | | |
|---|---|---|---|
| Ma (mg/l) | 220.00 | 220.00 | 220.00 |
| CTa (ng/l) | 91.55 | 94.77 | 89.79 |
| Ca (ng/l) | -- | -- | -- |
| Ra (ng/g) | -- | -- | -- |
| ϰa (l/kg) | -- | -- | -- |
| M dl (mg/l) | 22.00 | 22.00 | 22.00 |
| CT dl (ng/l) | 9.62 | 11.11 | 10.17 |
| Ca dl (ng/l) | 5.09 | 6.00 | 5.46 |
| Ra dl (ng/g) | 206.17 | 232.05 | 214.13 |
| Ro dl (ng/g) | 398.60 | 382.15 | 370.02 |
| ϰx dl (l/kg) | -- | -- | -- |
| Md (mg/l) | 19.80 | 19.80 | 19.80 |
| CTd (ng/l) | 5.03 | 5.59 | 5.17 |
| Cd (ng/l) | 2.40 | 2.22 | 2.67 |
| Rd (ng/g) | 132.93 | 170.26 | 126.20 |
| Ro d (ng/g) | 67.50 | 133.95 | 42.29 |
| ϰxd (l/kg) | 27259.69 | 16346.47 | 31467.52 |
| Glass (pg) | 1.96 | 4.03 | 3.95 |
| MB error (%) | -1.77 | 3.11 | -2.68 |