To the Graduate Council:

I am submitting herewith a thesis written by William P. Hamilton entitled "Effect of pH, iodide, and organic matter on the mobility of mercury(II) in soils." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

Mriganka M. Ghosh, Major Professor

We have read this thesis
and recommend its acceptance:

Chris D. Cox

Ralph R. Turner

Accepted for the Council:

Associate Vice Chancellor
and Dean of the Graduate School

Effect of pH, Iodide, and Organic Matter on the Mobility of Mercury(II) in Soils

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

William P. Hamilton

May, 1995

DEDICATION

For my wife, Kathy

ACKNOWLEDGMENTS

I would like to thank my major professor, Dr. Mriganka M. Ghosh, for giving me the opportunity of the past two years, and for all the assistance he has given me. I would also like to thank Dr. Ralph R. Turner for his guidance, patience, and friendship. He has taught me a lot about environmental chemistry. I would also like to thank Dr. Chris D. Cox for his comments and suggestions.

On a personal note, I would like to thank my wife, Kathy, for her patience, support, understanding, and love. I would like to thank my parents, Bill and Judy Hamilton, for all that they have done for me before, during and after my graduate school experience. They impressed upon me the importance of an education, and that impression was never lost (even if it appeared clouded at times). Thanks to Mark Barnett for all of the help, advice, and for functioning as a sounding board. Finally, I would like to thank all of the people in Knoxville that have been so good to me for the last 2 years: Chris, Stoli, Jennifer, Stacey, Mike and Julie. Thanks for keeping me sane!

ABSTRACT

This research attempted to determine the effect of pH, iodide concentration, and organic matter on the mobility of mercury in soils. Initial investigations assessed the impact of the above parameters for three initial mercury concentrations (40, 100, and 200 μg/L) in suspensions of the clay mineral, illite, a major component of the inorganic fraction of Eastern Tennessee soils. Subsequent experiments assessed the capability of large concentrations of iodide (> 1 mM) to extract mercury from contaminated floodplain soils.

Results indicate that iodide affects mercury adsorption in a manner similar to that of chloride, but at much lower concentrations. Iodide is very effective in preventing mercury adsorption by illite. Adsorption is particularly inhibited at low pH values. Organic matter acts to increase mercury adsorption. However, in contaminated soils, iodide was less effective in extracting mercury. Even with high iodide concentrations and extended exposure times, little mercury was extracted from contaminated soils, likely due to the chemical form of mercury in the soil.

TABLE OF CONTENTS

1.0 INTRODUCTION 1

1.1 Objectives 2

2.0 LITERATURE REVIEW 5

2.1 Background 5

2.2 Thermodynamics 5

2.2.1 OXIDATION-REDUCTION 5

2.2.2 MERCURY COMPLEXATION 10

2.3 Adsorption 17

2.3.1 THEORY 17

2.3.2 MODELS 21

2.3.2.1 *Non-electrostatic models* 21

2.3.2.2 *Electrostatic models* 25

2.3.3 SPECIATION 26

2.3.4 SOIL CONSTITUENTS 36

3.0 METHODS 39

3.1 Geochemical Modeling 39

3.2 Mercury(II) Adsorption by Illite 40

3.2.1 ILLITE PREPARATION 40

3.2.2 SUSPENSION PREPARATION 40

3.2.3 SPIKING AND SEPARATION 41

3.3 Mercury(II) Adsorption by a Mixed Illite/Organic Matrix 44

3.3.1 MIXED ILLITE-ORGANIC MATRIX PREPARATION 44

3.3.2 SUSPENSION PREPARATION 45

3.3.3 SPIKING AND SEPARATION 46

3.4 Leachability of Mercury from Contaminated Soils 46

3.4.1 SOIL EXTRACTION WITH VARIOUS HALIDES 46

3.4.2 SOIL EXTRACTION WITH IODIDE 47

3.4.3 SOIL WASHING TO REMOVE MERCURY 47

3.4.4 LEACHING WITH RESIDUAL IODIDE 48

3.5 Determination of Natural Organic Matter 49

4.0 RESULTS AND DISCUSSION 50

4.1 Geochemical Modeling 50

4.2 Mercury Adsorption Studies 55

4.2.1 MERCURY ADSORPTION BY ILLITE 55

4.2.1.1 *Mass Balance* 55

4.2.1.2 *Effect of pH and Iodide Concentration* 60

4.2.1.3 *Effect of Mercury Concentration* 68

4.2.2 MERCURY ADSORPTION BY ILLITE IN THE PRESENCE OF NOM 76

4.2.2.1 *Mass Balance* 76

4.2.2.2 *Effect of pH and Iodide Concentration* 79

4.2.2.3 *Effect of Mercury Concentration* 84

4.3 Mercury Desorption from Contaminated Soils 88

4.3.1 MERCURY EXTRACTION WITH IODIDE AND OTHER HALIDES 88

4.3.2 MERCURY EXTRACTION WITH IODIDE LEACHATE 93

4.4 Conclusions 104

BIBLIOGRAPHY 106

APPENDICES 117

APPENDIX A: SUPPLEMENTAL LITERATURE REVIEW 118

APPENDIX B: CALCULATIONS 160

APPENDIX C: INFORMATION ON CONSTRUCTION OF E_H-pH DIAGRAM 162

APPENDIX D: EXPERIMENTAL DATA 166

VITA 173

LIST OF TABLES

Table 2.1: Thermodynamic Data for Mercury-Halide and Other Environmentally-Significant Mercury Species. 6

Table 2.2: Complex Equilibria with Hg(II) in Aqueous Systems. 14

Table 2.3: Formation Constants for Mercury-Halide Complexes at 298 K. . . . 16

Table 2.4: Reported K_D Values for Mercury. 23

Table 4.1: Mercury Losses to Polycarbonate Filters. 61

Table 4.2: Efficiency of Different Halide Solutions at Extracting Mercury from Contaminated Soils. 92

Table 4.3: Mercury Extracted from Mississippi Soils Using 0.001 M KI. 94

Table 4.4: Characteristics of Leachate 1 Generated Using Foust Protocol. . . . 97

Table 4.5: Mercury Extracted Using Dilutions of Soil Washing Leachates. . . . 98

Table 4.6: Percent of Total Mercury Extracted from EFPC Floodplain Soils Using Dilute Acids or Iodide. 101

Table A.1: U.S. Industrial Consumption of Refined Mercury Metal, By Use . . 119

Table A.2: Concentration of Mercury in Select Rocks. 126

Table A.3: Concentration of Mercury in Select Soils. 128

Table A.4: Mercury in Air and Volcanic Emanations. 129

Table A.5: Concentration of Mercury in Natural Waters. 131

Table A.6: Concentration of Mercury in Sediments. 132

Table A.7: Average Residence Times for Mercury in Different

Compartments. 134

Table A.8: Iodine Concentration in Parent Material (ppm). 135

Table A.9: Iodine in Soils. 137

Table A.10: Iodine in the Atmosphere. 140

Table A.11: Iodine in Waters of the Pacific Ocean. 141

Table A.12: Iodine in Natural Waters. 143

Table A.13: Physical Properties of Mercury. 145

Table A.14: Physical Properties of Select Mercury Compounds. 146

Table A.15: Solubility of Mercury and Some Mercury Compounds. 149

Table A.16: Physical and Chemical Properties of Iodine. 151

Table A.17: Composition of Average Igneous Rocks and of Three Surface Soils of Increasing Maturity (%). 154

LIST OF FIGURES

Figure 2.1: E_H-pH Diagram for Hg-H_2O System at 25°C. 8

Figure 2.2: E_H-pH Diagram for I-H_2O System at 25°C. 9

Figure 2.3: E_H-pH Diagram for Hg-I-H_2O System at 25°C. 11

Figure 2.4: E_H-pH Diagram for Hg-I-Cl-S-H_2O System at 25°C. 12

Figure 2.5: Diffuse Double Layer. 19

Figure 2.6: Speciation of Mercury in Water. 28

Figure 2.7: Adsorption as a Function of First Hydrolysis Constant. 29

Figure 2.8: Effect of Cl^- Concentration of Mercury(II) Adsorption. 33

Figure 2.9: Speciation of Mercury(II) in the Presence of Cl^-. 35

Figure 3.1: Titration Curve for Illite. 42

Figure 3.2: Adsorption of Mercury as a Function of Time. 43

Figure 4.1: Speciation of Mercury. 51

Figure 4.2: Effect of Iodide:Chloride Ratio on Mercury Speciation. 54

Figure 4.3: Median Mass Balance During 18-hour Equilibration for Mercury-Illite Suspensions (MB1). 56

Figure 4.4: Median Mass Balance During Filtration for Mercury-Illite Suspensions (MB2). 59

Figure 4.5: Effect of pH and Iodide on Mercury Adsorption by Illite (1 g/L). . 62

Figure 4.6: Median Distribution Coefficients (K_D) for Mercury-Illite Suspensions. 67

Figure 4.7: Adsorption Isotherms for Mercury Adsorption by Illite, pH = 6. . 69

Figure 4.8: Adsorption Isotherms for Mercury Adsorption by Illite, pH = 8.5. 73

Figure 4.9: Median Mass Balance During 18-hour Equilibration for Mercury-Illite-NOM Suspensions (MB1). 77

Figure 4.10: Median Mass Balance During Filtration for Mercury-Illite-NOM Suspensions (MB2). 78

Figure 4.11: Effect of pH and Iodide on the Adsorption of Mercury by Illite-NOM (1 g/L). 80

Figure 4.12: Median Distribution Coefficients (K_D) for Mercury-Illite-NOM Suspensions. 83

Figure 4.13: Adsorption Isotherms for Mercury Adsorption by Illite-NOM, pH = 6. 85

Figure 4.14: Adsorption Isotherms for Mercury Adsorption by Illite-NOM, pH = 8.5. 89

Figure 4.15: Process Diagram for the Generation of Sample Leachates. 95

Figure 4.16: Effect of Iodide Concentration on Mercury Mobility. 103

Figure A.1 Mercury Cycle in the Biosphere. 123

Figure A.2: Iodine Cycle in the Biosphere. 124

Figure A.3: Adsorption of Organics Affecting Particle Charge. 157

Figure A.4: Inner- and Outer-Sphere Surface Complexes. 158

Figure A.5: Possible Surface Complexation Reactions. 159

1.0 INTRODUCTION

Recently, chemical extraction techniques have been proposed as a means of decontaminating mercury-contaminated soils and sediments. Both an ex situ soil washing process and an in situ electrokinetic process are being investigated. Both processes employ an extractant developed by General Electric composed of elemental iodine (I_2) and potassium iodide (I^- as KI). Iodine is able to oxidize both elemental mercury as well as the sulfide of mercuric sulfide (a very common mercuric complex), enabling much more of the mercury in a contaminated matrix to be readily complexed and removed by the iodide.

While both processes have exhibited varying degrees of success, the possible increase in the mobility of residual mercury due to residual iodide remaining in soils after treatment needs to be addressed. Because recoveries are never 100% efficient, some amount of extractant and mercury will remain; these residuals may combine, or the extractant may scavenge native mercury adjacent to the treated site, resulting in an increased mobility and therefore a more threatening contamination problem than may have existed prior to treatment.

It is therefore necessary to investigate the effect of residual mercury and iodide on the overall mobility of mercury in a soil/water system. Because many factors (mercury concentration, iodide concentration, pH, E_H, organic matter concentration, solids concentration, and ionic strength) can affect mercury mobility, those variables thought to control speciation and sorption will be altered independently to assess that

variable's contribution to mobility.

1.1 Objectives

In order to fully assess the effects of iodide on mercury mobility in soils, the following objectives were defined:

1. *The geochemical model MINTEQA2 will be used to predict the speciation of mercury in solutions of different mercury and iodide concentrations.* Qualitative predictions about the adsorption of a given compound can be made based on chemical speciation. When the formation of a electronegative complex is favored, adsorption is assumed to decrease because of electrostatic repulsion between the negatively-charged clay surface and the complex. Additionally, adsorption is likely minimal when an electrostatically-neutral complex is formed, because the influence of charge on attraction will be minimized. However, specific reactions with certain complexes may not conform to strict electrostatic models. By determining the likely speciation of mercury, qualitative predictions about the potential for adsorption can be made.

2. *An investigation of the effect of pH and iodide concentration on the degree of mercury adsorption to the clay mineral, illite, will be made.* Since pH and

ligand concentration often dictate speciation, trials over an environmentally-significant pH range will be conducted using different concentrations of mercury and iodide. The results will show: (1) the effect of pH on the adsorption of given mercury-iodide complexes, and the effect of (2) different mercury concentrations, and (3) iodide concentrations on the adsorption of mercury to illite. Illite will be used due to the prevalence of this mineral in Eastern Tennessee soils.

3. *The effect of organic matter on mercury adsorption will be determined by introducing natural organic matter (NOM) to illite suspensions over the same pH range.* NOM can control the mobility of mercury in soil systems, even at relatively low concentrations. In addition, NOM has been shown to impede the mobility of iodide in the environment. The overall effect of NOM can be determined by introducing NOM to the systems analyzed in step 2. NOM will be added in a concentration that is representative of local soils. Comparisons between the systems with NOM and those systems without can be made to determine the effect of NOM on mercury mobility in the presence of iodide.

4. *Batch studies to determine the ability of iodide to desorb mercury from contaminated soils will be conducted.* Since one of the potential problems with introducing iodide into a mercury-contaminated system is that the iodide may desorb the mercury and make it more mobile, studies will be performed to

determine the capacity of different concentrations of iodide to desorb mercury from mercury-contaminated soils. Soils will be suspended in sub-molar solutions of iodide and in solutions containing dilutions of a leachate from the G.E. soil washing process. After a given contact time, the suspensions will be filtered and analyzed to determine the ability of different concentrations and compositions of iodide to remove mercury from contaminated soils.

2.0 LITERATURE REVIEW

2.1 Background

A detailed discussion of typical environmental concentrations and the physical/chemical properties of mercury and iodide, as well as the fundamentals of soil chemistry is presented in the Appendix.

2.2 Thermodynamics

2.2.1 Oxidation-Reduction

Hepler and Olofsson (1975) have critically reviewed the thermodynamic literature for mercury, and data for some of the more significant mercury species are listed in Table 2.1.

Since both mercury and iodine can exist in several oxidation states, the oxidation-reduction potential of a system is important in determining the dominant form of mercury and iodine present. This characteristic can best be described in terms of a E_H-pH diagram, which relates the oxidation-reduction potential (E_H) to the hydrogen ion concentration (pH) at equilibrium. Although oxygen is not required for chemical oxidation, it is the most common environmental oxidant and systems in contact with air or oxygenated water tend to be fairly oxidized; anaerobic systems such as sediments and subsurface soils tend to be void of air and are usually fairly

Table 2.1: Thermodynamic Data for Mercury-Halide and Other Environmentally-Significant Mercury Species. (Hepler and Olofsson, 1975)

Compound	ΔG_f° (kcal/mol)	ΔH_f° (kcal/mol)	ΔS° (cal/mol • K)
Hg° (aq)	8.9	3.33	-0.5
Hg° (g)	7.613	14.655	41.79
Hg° (l)	0	0	18.17
Hg^{2+}	39.365	40.67	-8.6
Hg_2^{2+}	36.713	39.87	15.7
$HgOH^+$	-12.4	-20.2	16.5
$Hg(OH)_2^\circ$	-65.6	-86.0	30.2
$Hg(OH)_3^-$	-102.1	--	--
$HgCl^+$	-1.2	-4.7	17
$HgCl_2^\circ$	-41.3	-51.9	36
$HgCl_3^-$	-73.8	-93.1	49
$HgCl_4^{2-}$	-106.7	-132.6	69
$HgBr^+$	2.2	1.3	18
$HgBr_2^\circ$	-34.1	-40.8	40
$HgBr_3^-$	-61.9	-38.6	61
$HgBr_4^{2-}$	-88.6	-70.3	73
HgI^+	9.6	10.1	18
HgI_2°	-17.9	-19.2	41
HgI_3^-	-35.4	-36.7	71
HgI_4^{2-}	-50.5	-56.4	85
HgS (s) red	-11.1	-12.9	19.7
HgS (s) black	-10.6	-12.0	21.2
$Hg(CH_3)_2$ (g)	34.9	22.56	73

reductive (Hem, 1970). E_H-pH diagrams have been constructed for mercury (Pourbaix, 1966), iodine (Whitehead, 1984; Pourbaix, 1966), and mercury in natural systems (Hem, 1970). These diagrams can also be constructed using software such as Outakumpu Research's HSC (Roine, 1994); however, the quality of the output is dependant on the quality of the thermodynamic database which the software employs and the understanding of the computer operator; a thorough crosscheck of the database with the published literature and an understanding of the software is required prior to the utilization of these software packages. The area of each stability zone is dependant on the pressure, temperature, available ligands, and ligand concentration, so interpretation of these diagrams should be made with attention to the factors considered in the construction of the diagram.

E_H-pH diagrams for mercury and iodine are illustrated in Figures 2.1 and 2.2. The dashed box indicates the limits of pH and E_H in soils (Bass Becking, 1960). As Figure 2.1 illustrates, only Hg°, Hg_2^{2+}, and mercuric hydroxide ($Hg(OH)_2^\circ$) are thermodynamically stable for the conditions listed; and given the fact that Hg_2^{2+} is unstable in the environment, one only expects to find Hg° and $Hg(OH)_2^\circ$ in aqueous natural systems with no other ligands present. Figure 2.2 reveals that iodide ion (I^-) is the dominant iodine species, except under fairly oxidized conditions, where the tri-iodide (I_3^-) and iodate (IO_3^-) species dominate. These species, while possible, rarely exist in soils; they are prevalent in waters with higher total iodine concentrations and in environments where microorganisms can assist in the oxidation process, such as oceans.

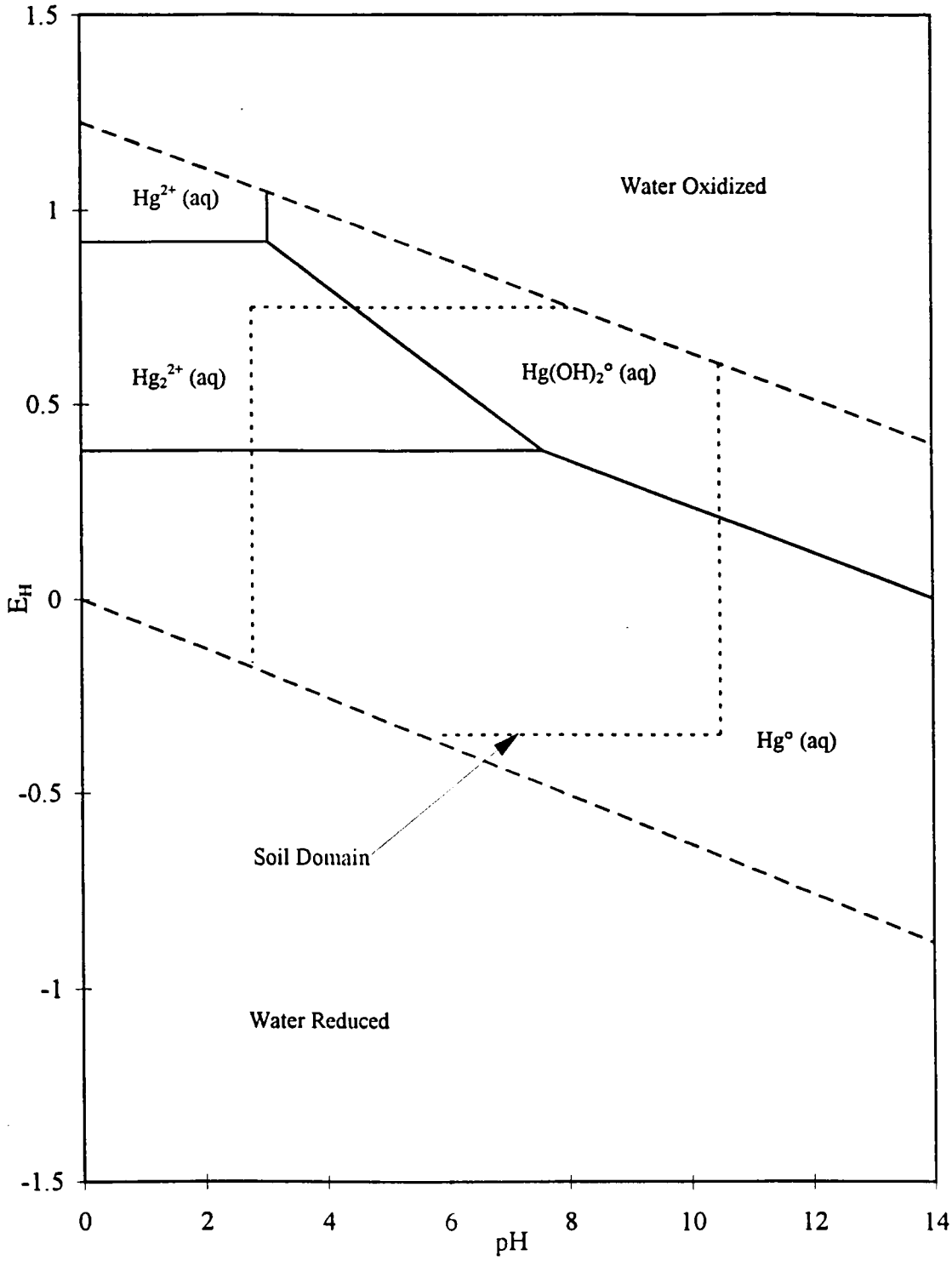


Figure 2.1: E_H-pH Diagram for Hg-H_20 System at 25°C.
Hg_T = 1 mol/L.

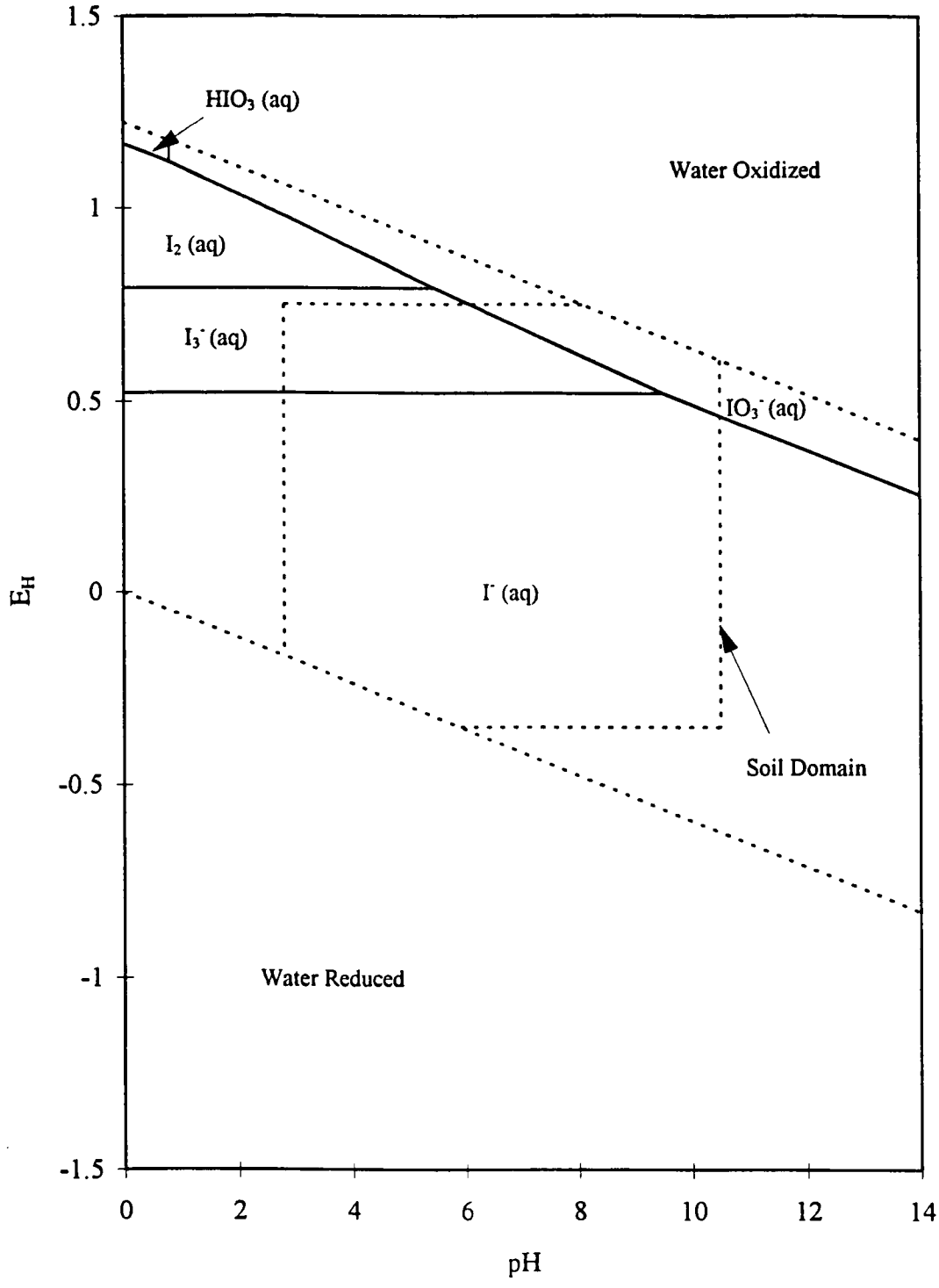


Figure 2.2: E_H-pH Diagram for I-H_2O System at 25°C.
I_T = 1 mol/L

An E_H-pH diagram for the Hg-I system is shown in Figure 2.3. For oxidized conditions, mercury-iodide complexes are thermodynamically stable, except at high pH, where $Hg(OH)_2^*$ will form. It is interesting that nowhere is the free ion, Hg^{2+}, the dominant thermodynamically stable mercury species in soils. This illustrates the importance of speciation in determining adsorption characteristics.

Hem (1970) constructed a E_H-pH diagram for mercury in natural waters by including sulfur and chlorine as potential ligands. A similar diagram which includes iodine in addition to the aforementioned ligands has been constructed (Figure 2.4). Once again, the importance of mercury-iodine complexes is seen. Sulfur complexes (as the reduced sulfur species, sulfide, S^{2-}) become prevalent under reduced conditions, a characteristic that will affect mercury solubility.

2.2.2 Mercury Complexation

According to the HSAB (Hard Soft Acid Base) principle (Stumm and Morgan, 1981), ionic species of relatively small ionic size, high oxidation states, high electronegativity, and low polarizability are classified as hard acids, while large ions with low oxidation state, low electronegativity and high polarizability are considered soft acids. Mercury is considered a soft acid, and therefore favors ligands that are easy to oxidize and are highly polarizable, called soft bases (Stumm and Morgan, 1981). One of the many preference chains for soft acid-base complexation is:

most preferred $\quad S > I > Br > Cl = N > O > F \quad$ least preferred

Unlike hard-hard complexes, which are typically joined by an ionic bond, soft-

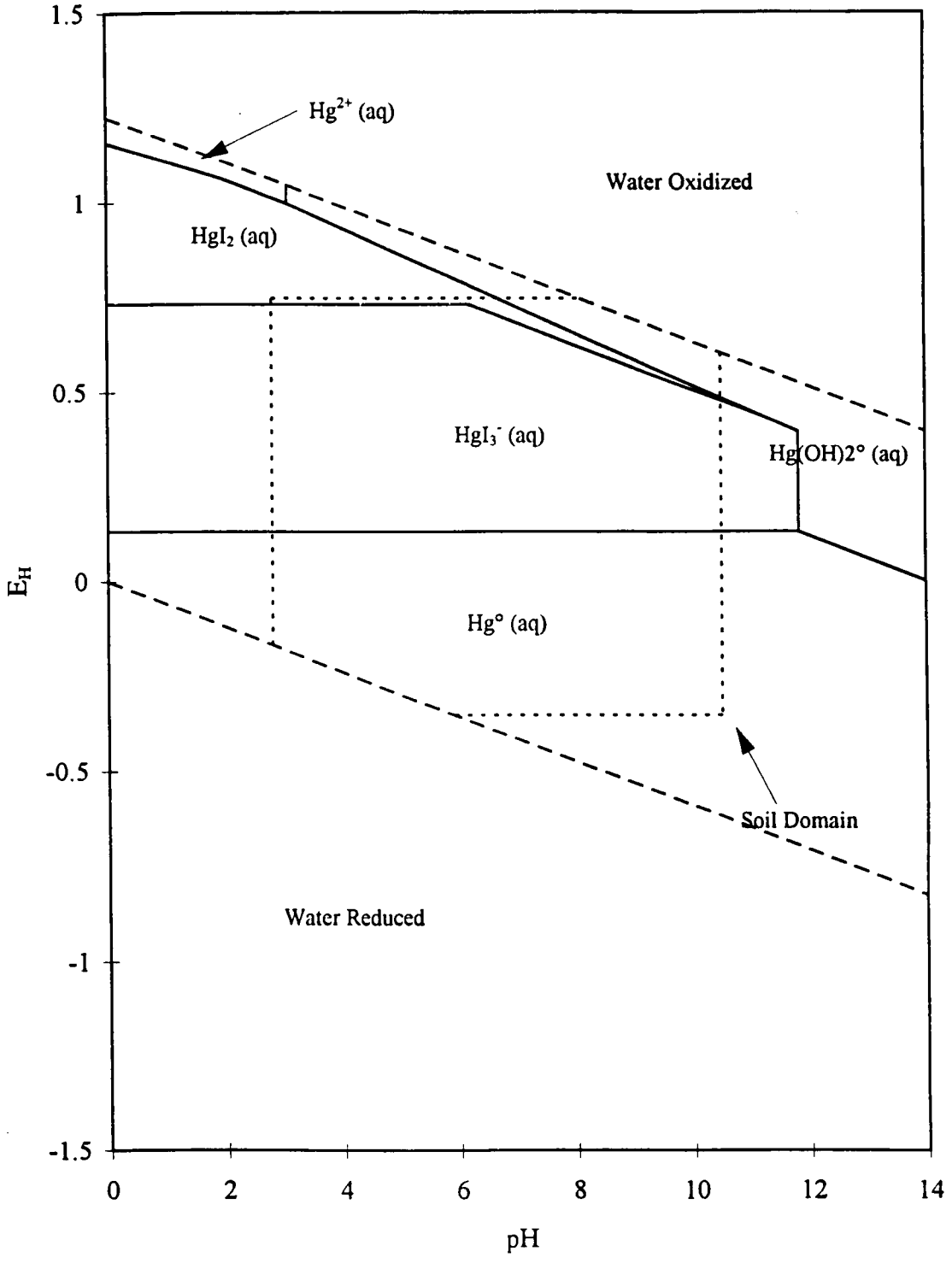


Figure 2.3: E_H-pH Diagram for Hg-I-H_2O System at 25°C.
Hg_T = 100 μg/L; I_T = 50 mg/L

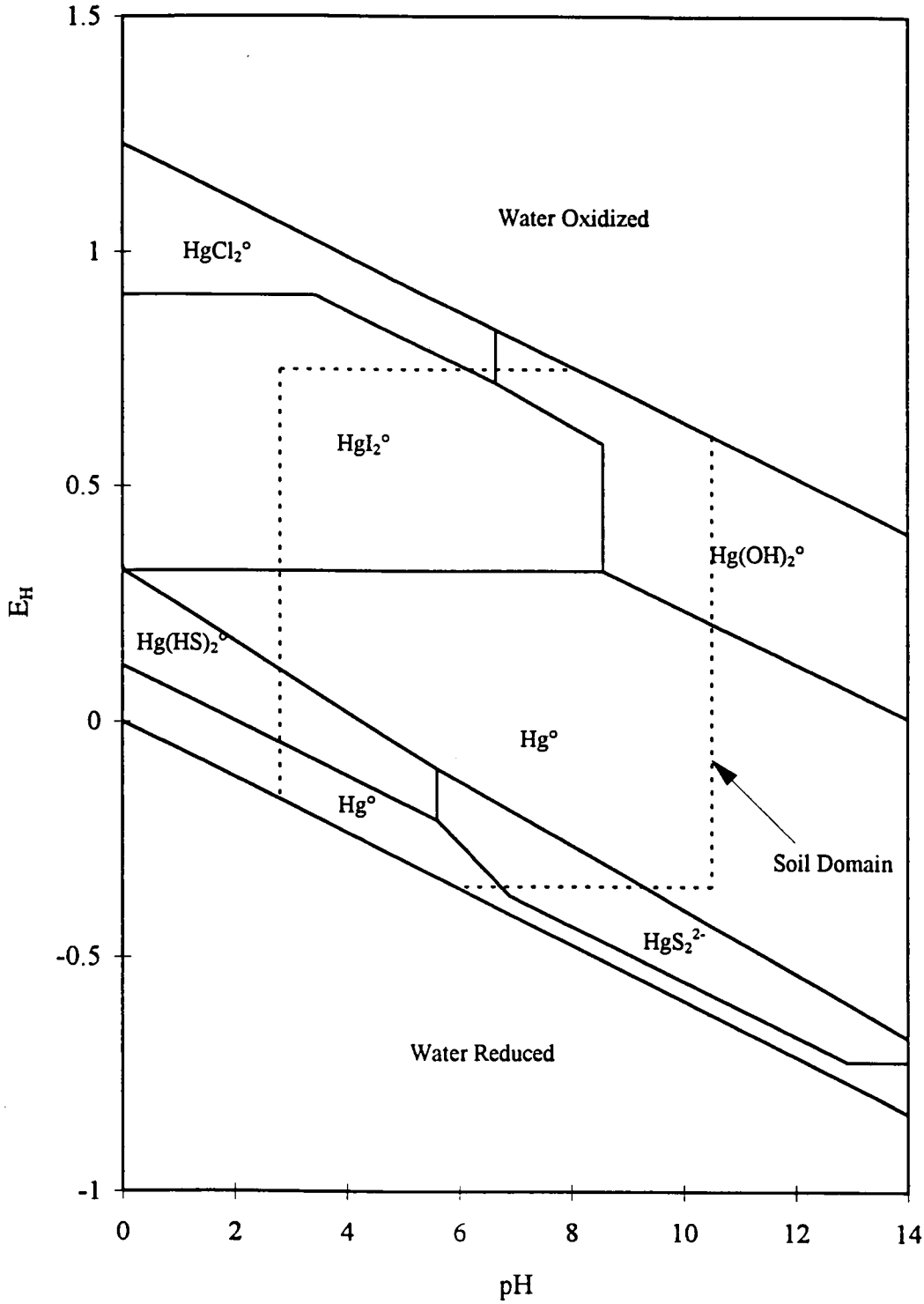


Figure 2.4: E_H-pH Diagram for Hg-I-Cl-S-H_2O System at 25°C.
Hg_T = 100 µg/L; I_T = 50 µg/L; Cl_T = 35 mg/L; S_T = 96 mg/L

soft complexes are typically covalent in nature.

One of the characteristics of group IIB metals is their ability to form a multitude of complexes with soluble ligands (Petrucci, 1985). Complex strength can be assessed by examining the magnitude of the complex's equilibrium constant. For a metal in solution with a ligand, the following reaction may occur:

$$Me^{m+} + L^{l-} \rightleftharpoons Me_lL_m \qquad (2.1)$$

where Me^{m+} = metal
L^{l-} = ligand
Me_lL_m = aqueous complex

The ratio of the activities of each component at equilibrium is the equilibrium constant, which is calculated as follows:

$$K = \frac{\{Me_lL_m\}}{\{Me^{m+}\}\{L^{l-}\}} = \frac{\gamma_{MeL}[Me_lL_m]}{\gamma_{Me}[Me^{m+}]\gamma_L[L^{l-}]} \qquad (2.2)$$

where γ = activity coefficient
$\{\}$ = activity
$[]$ = concentration

In the dilute solutions commonly found in the environment, activity coefficients are typically 1, so that the equilibrium constant is simply a ratio of concentrations of products to reactants (see Equation 2.2). Therefore, a reaction with a large equilibrium constant indicates the formation of a strong complex, while relatively smaller equilibrium constants reflect the formation of weaker, ion pairs.

Gilmour (1971) composed a list of common mercury(II) compounds (Table 2.2) and assessed their importance in the natural environment. He noted, based on equilibrium constants, that OH^-, Cl^-, NH_3, CN^-, F^-, SO_4^{2-}, NO_3^-, S^{2-}, and SCN^- were

Table 2.2: Complex Equilibria with Hg(II) in Aqueous Systems. (Gilmour, 1971)

Equilibrium	$\log K_{eq}$
$Hg^{2+} + Cl^- \rightleftharpoons HgCl^+$	7.33, 7.36
$Hg^{2+} + 2\ Cl^- \rightleftharpoons HgCl_2^\circ$	14.15, 14.16
$Hg^{2+} + 3\ Cl^- \rightleftharpoons HgCl_3^-$	15.15, 15.01
$Hg^{2+} + 4\ Cl^- \rightleftharpoons HgCl_4^{2-}$	15.81, 15.72
$Hg^{2+} + Cl^- + OH^- \rightleftharpoons HgClOH^\circ$	18.87, 18.25, 18.28
$Hg^{2+} + OH^- \rightleftharpoons HgOH^+$	10.53, 10.92
$Hg^{2+} + 2\ OH^- \rightleftharpoons Hg(OH)_2^\circ$	21.89, 22.64
$Hg^{2+} F^- \rightleftharpoons HgF^+$	1.56
$Hg^{2+} + NH_3 \rightleftharpoons HgNH_3^{2+}$	8.80
$Hg^{2+} + 2\ NH_3 \rightleftharpoons Hg(NH_3)_2^{2+}$	17.50
$Hg^{2+} + 3\ NH_3 \rightleftharpoons Hg(NH_3)_3^{2+}$	18.50
$Hg^{2+} + 4\ NH_3 \rightleftharpoons Hg(NH_3)_4^{2+}$	19.28
$Hg^{2+} + CN^- \rightleftharpoons HgCN^+$	18.44
$Hg^{2+} + 2\ CN^- \rightleftharpoons Hg(CN)_2^\circ$	34.5, 35.36
$Hg^{2+} + 3\ CN^- \rightleftharpoons Hg(CN)_3^-$	38.7, 39.19
$Hg^{2+} + 4\ CN^- \rightleftharpoons Hg(CN)_4^{2-}$	41.0, 41.95
$Hg^{2+} + CN^- + OH^- \rightleftharpoons HgCNOH^\circ$	29.43
$Hg^{2+} + 2\ SCN^- \rightleftharpoons Hg(SCN)_2^\circ$	17.26, 18.37
$Hg^{2+} + 3\ SCN^- \rightleftharpoons Hg(SCN)_3^-$	19.97
$Hg^{2+} + 4\ SCN^- \rightleftharpoons Hg(SCN)_4^{2-}$	21.69
$Hg^{2+} + SO_4^{2-} \rightleftharpoons HgSO_4^\circ$	2.60
$Hg^{2+} + NO_3^- \rightleftharpoons HgNO_3^+$	0.16
$HgS\ (s) + S^{2-} \rightleftharpoons HgS^{2-}$	0.48
$HgS\ (s) + 2\ HS^- \rightleftharpoons HgS(HS)_2^\circ$	-3.60
$HgS\ (s) + 2\ H_2S \rightleftharpoons Hg(H_2S)_2^\circ$	-4.31
$HgS\ (s) + HS^- + 2\ H_2S \rightleftharpoons Hg(HS)_3^-$	-3.59

the most significant ligands to be considered in mercury complexation in natural waters; of these, he excluded from consideration NH_3, CN^-, F^-, SO_4^{2-}, NO_3^-, and SCN^-, because of inadequate natural concentrations, and S^{2-} because of the insolubility of HgS. He therefore concluded that mercury complexes with Cl^- and OH^- dominate in natural waters.

Among the strongest complexes formed with mercury are the mercury-halide complexes. Table 2.3 (Hepler and Olofsson, 1975) gives an indication of the magnitude of the formation constants of different mercury-halide complexes. As the table indicates, the strength of the complexes increase as the atomic number of the halide increases. Therefore, mercury and iodide form the strongest complex, while mercury-fluoride complexes are the weakest.

Many investigations of the Hg-Cl system have been conducted due to the abundance of Cl^- in both fresh and sea waters. Hahne and Kroontje (1973a) performed theoretical calculations for a suite of heavy metals to determine the effect of pH (i.e. OH^- concentration) and Cl^- concentration on the distribution of metal complexes. They noted that for pH values above 3.8, the solubility of mercury is determined by the solubility of $Hg(OH)_2$ (about 53 mg/L) in systems without appreciable amounts of Cl^-. However, the presence of complexing ligands, specifically Cl^-, will act to significantly increase the solubility of mercury. They note that a concentration of 3.5 ppm Cl^- will increase the solubility of $Hg(OH)_2$ and HgS by a factor of 55 and 408, respectively. The effect of Cl^- and pH on mercury mobility was considered further by Hahne and Kroontje (1973b). They determined

Table 2.3: Formation Constants for Mercury-Halide Complexes at 298 K. (Hepler and Olofsson, 1975)

Reaction		F	Cl	Br	I
$Hg^{2+} + X^- \rightleftharpoons HgX^+$	K_1	38	5.8×10^6	1.1×10^9	6.4×10^{12}
$HgX^+ + X^- \rightleftharpoons HgX_2^{\bullet}$	K_2	--	2.5×10^6	2.5×10^8	1.3×10^{11}
$HgX_2^{\bullet} + X^- \rightleftharpoons HgX_3^-$	K_3	--	6.7	1.5×10^2	6.2×10^3
$HgX_3^- + X^- \rightleftharpoons HgX_4^{2-}$	K_4	--	13	23	1.1×10^2
$Hg^{2+} + 4\ X^- \rightleftharpoons HgX_4^{2-}$	β_4	--	1.3×10^{15}	9.2×10^{20}	5.6×10^{29}

(by calculation) that at pH 5, Cl^- concentrations of as little as 14 ppm were adequate to mobilize all mercury as $HgCl_2^\circ$ for a given mercury concentration, a fact that was shown experimentally in a leaching study. At higher pH values, complete mobilization of mercury was possible, but it required greater Cl^- concentrations. Feick, Horne and Yeaple (1972) noted that increased concentrations of Cl^- in soils, sediments, and streams due to the abundant use of de-icing salt could increase the mercury concentration by two to five orders of magnitude, leading to widespread environmental contamination.

Very little research has been conducted on the effect of other halides on mercury mobility, presumably because of the low abundance of these other halogens in most circumstances. The role of bromide in the extraction of mercury from cinnabar mines was investigated (Ballester et al., 1988). Iodine has also been investigated as a potential mercury extractant in cinnabar mines (Nuñez and Espiell, 1983; Nuñez and Espiell, 1984). No references to the environmental significance of Hg-F interactions were found.

2.3 Adsorption

2.3.1 THEORY

Net particle charge, σ_P, is due to the contribution of several charges:

σ_O	Charge due to isomorphic substitution, i.e. permanent charge
σ_H	Charge due to bound protons or hydroxides, i.e. net proton charge
σ_{IS}	Charge due to inner-sphere surface complexes
σ_{OS}	Charge due to outer-sphere surface complexes

The charge on the particle must be neutralized by counterions in suspension because suspensions have no net electrical charge. Particles in suspension may therefore be viewed in terms of an electrical double layer (Figure 2.5) (Stumm, 1992). The first layer is composed of the surface and solutes that make up the net particle charge. This layer is surrounded by a cloud of oppositely charged ions (called the diffuse layer) that act to neutralize the particle charge with a counter charge (σ_D).

Because of the primary charge of the particle, an electrostatic potential exists between the particle and the bulk solution. This potential is important because it represent the work required to move ions through the double layer (Stumm, 1992). This potential (ψ) is defined as (Stumm, 1992):

$$\psi = \frac{\Delta G^{\circ}_{COUL}}{\Delta Z\ F} \qquad (2.3)$$

where ΔG°_{COUL} = coulombic free energy which varies with distance from the surface
ΔZ = change in the charge of the surface species for a given reaction
F = Faraday's constant = 9.6485×10^4 C/mol

Much like aqueous complexation, reactions at a surface can be viewed as complex or ion pair formation between solutes and an individual chemical member of a surface. Surface complexes can be described by a surface equilibrium constant which has a form similar to the aqueous equilibrium constant. For a surface with no charge, the surface equilibrium constant (termed the intrinsic surface equilibrium constant, $K^s(int)$) is the same as any other chemical equilibrium constant:

$$K^s(int) = \exp\left(\frac{\Delta G^{\circ}_{CHEM}}{RT}\right) \qquad (2.4)$$

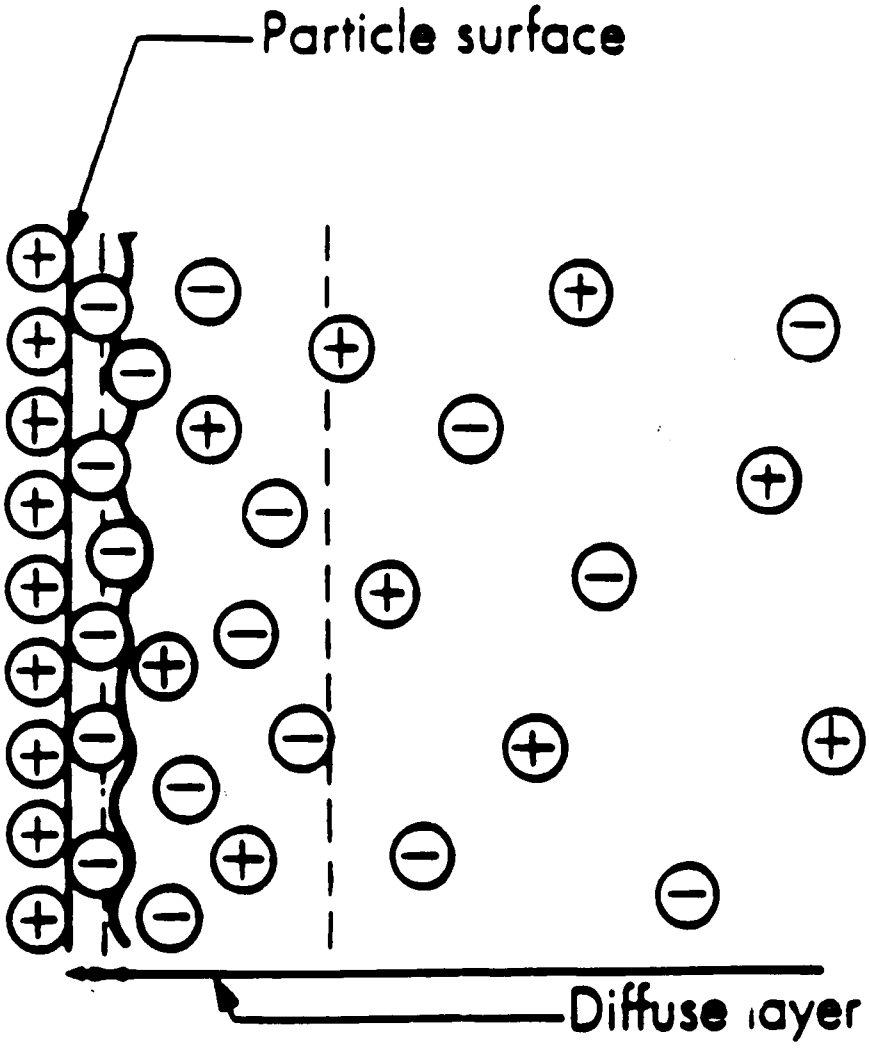


Figure 2.5: Diffuse Double Layer.
(Stumm, 1992)

For charged surfaces, the total free energy for the reaction is the sum of the chemical free energy and the electrical free energy, so that

$$\Delta G = \Delta G^{\circ}_{CHEM} + \Delta G^{\circ}_{COUL} \tag{2.5}$$

and (from Equation 2.4) the overall surface equilibrium constant $K^s(app)$ (taking into account the effect of the charged surface) is

$$-RTlnK^s(app) = -RTlnK^s(int) + \Delta ZF\psi; \therefore K^s(app) = K^s(int)\exp(-\frac{F\psi}{RT}) \tag{2.6}$$

Therefore, for the reaction of mercury with a solid phase, the concentration of mercury must be corrected by the exponential term (called the boltzman factor) so that the effect of electrostatics is considered. For the reaction

$$=SOH^o + Hg_s^{2+} \rightleftharpoons =SOHg^+ + H_s^+; \; K^s(app) = K^s(int)\exp(-\frac{\psi F}{RT}) \tag{2.7}$$

where the subscript "s" denotes an ion near the surface, the activity of a solute near the surface is a function of the surface potential of the solid.

$$\{Hg_s^{2+}\} = \{Hg^{2+}\}e^{(-\frac{\psi F}{RT})} \tag{2.8}$$

2.3.2 MODELS

2.3.2.1 *Non-electrostatic models*

Non-electrostatic models are those relationships used to describe adsorption that do not include a factor to account for the electrostatic interaction between the dissolved ionic species and the charged surface. As such, these models are empirical, and their application is limited to the system in question. A discussion of the three most common non-electrostatic models follows.

Distribution Coefficient (K_D) model: The Distribution Coefficient model assumes that there are an unlimited number of surface sites available for adsorption, and that the concentration of species adsorbed at equilibrium is directly proportional to the concentration of aqueous species at equilibrium. Therefore, if the reaction of a solute with a surface is described as follows:

$$\equiv SOH + Me \rightleftharpoons \equiv SOH \cdot Me; \qquad K = \frac{[\equiv SOH \cdot Me]}{[\equiv SOH][Me]} \tag{2.9}$$

then the distribution coefficient, K_D, is simply the ratio of concentrations of total adsorbed species [$\equiv$SOH$\cdot$Me] to total dissolved species [Me] at equilibrium, or

$$K_D = \frac{[\equiv SOH \cdot Me]}{[Me]} \tag{2.10}$$

Data collected at constant pH and temperature conforms to a distribution model if a

graph of adsorbed concentration versus total dissolved concentration at equilibrium yields a straight line whose slope is the distribution coefficient.

Many describe the partitioning of mercury in terms of the K_D, and the published values range over 4 orders of magnitude (Table 2.4).

Langmuir model: The Langmuir model is identical to the Distribution Coefficient model except it assumes a limited number of available surface sites, so:

$$[\equiv SOH_T] = [\equiv SOH] + [SOH \cdot Me] \qquad (2.11)$$

The Langmuir isotherm is derived by combining substituting the new value of $[\equiv SOH]$ ($[\equiv SOH] = [\equiv SOH_T] - [\equiv SOH \cdot Me]$) into the equilibrium expression in Equation 2.9:

$$[\equiv SOH \cdot Me] = \frac{K_L\ [SOH_T]\ [Me]}{1 + K_L\ [Me]} \qquad (2.12)$$

The constants K_L (a constant related to bonding energy) and $[\equiv SOH_T]$ (adsorption capacity) can be obtained by plotting the linear form of the Langmuir isotherm.

$$\frac{[Me]}{[\equiv SOH \cdot Me]} = \frac{1}{K_L\ [SOH_T]} + \frac{[Me]}{[SOH_T]} \qquad (2.13)$$

The slope of this line will be equal to $1/(K_L[\equiv SOH_T])$ and the y-intercept will be

Table 2.4: Reported K_D Values for Mercury.

Source	K_D (L/kg)	Reference
various soil/water systems	10.2 - 115.3	Butcher et al., 1989
various soil/water systems	0.41 - 408	Rai and Zachara, 1984
Hg in suspended solids of natural water	134 - 188	Moore and Ramamoorthy, 1984
Hg in suspended solids and solution	118	Glass et al., 1990
Dissolved Hg and particulate-associated Hg in six streams in North Carolina (Polluted)	86.8	Robinson and Shuman, 1989
Dissolved Hg and particulate-associated Hg in six streams in North Carolina (Background)	113	Robinson and Shuman, 1989
Hg-bentonite suspensions (2 g/L)	119 - 408	Newton et al., 1976
Hg-bentonite suspensions (2 g/L) in 0.01 M $CaCl_2$	29 - 224	Newton et al., 1976
^{203}Hg added to lake enclosures (suspended particles)	360	Diamond et al., 1990
Savannah River soils	26.6 - 23,600	Bibler and Marson, 1992
Savannah River soils (1 M Ca^{2+})	3.08 - 13,900	Bibler and Marson, 1992
Savannah River soils (2 M Ca^{2+})	6.37 - 15,100	Bibler and Marson, 1992
^{203}Hg added to lake enclosures (sediment trap)	160	Diamond et al., 1990
1 mg/L suspended solids	3000	Mills et al., 1985
10 mg/L suspended solids	200	Mills et al., 1985

equal to [Me]/[$\equiv SOH_T$].

Hogg et al. (1978) used the Langmuir model to describe the adsorption of several different chemical forms of mercury to two soils of different organic matter content. They determined values of SOH_T in each soil for $HgCl_2$ (2,475 and 323 μg/g), phenylmercuric acetate (719 and 309 μg/g), and methylmercuric chloride (606 and 20 μg/g). The largest values corresponded to soils of high organic matter content which were doped with $HgCl_2$.

Freundlich model: The Freundlich model was originally an empirically-derived model. If Equation 2.11 is rewritten

$$\equiv SOH + \frac{1}{n} \cdot Me \rightleftharpoons \equiv SOH \cdot Me; \qquad K = \frac{[\equiv SOH \cdot Me]}{[\equiv SOH][Me]^{1/n}} \tag{2.14}$$

and if the number of available surface sites is assumed constant ($\equiv$SOH = constant), an expression for the Freundlich isotherm can be written:

$$[\equiv SOH \cdot Me] = K_F[Me]^{1/n} \tag{2.15}$$

By plotting the linear form of Equation 17, the constants K_F and n can be determined:

$$\log(\equiv SOH \cdot Me) = \log(K_F) + 1/n \log(Me) \tag{2.16}$$

The slope of this plot is 1/n and the y-intercept is $\log(K_F)$.

Lockwood and Chen (1974) modeled the adsorption of mercury by iron oxide. they found the data fit the Freundlich model well when n = 1.316 and K_F = 2.467. Barrow and Cox (1992a) used the Freundlich isotherm to describe the relationship between mercury adsorption and the equilibrium mercury concentration at constant pH in a suspension of goethite, and determined a value of log(K_F) of 0.743. This value was independent of pH. They later (1992b) used a modified version of the Freundlich isotherm to relate mercury adsorption to $HgOH^+$ concentration at pH 5.8. In their equation, 1/n is not a constant, but a function of $HgOH^+$ concentration:

$$[\equiv SOH{\cdot}Me] = K_F[Me]^{1/N} \qquad (2.17)$$

where $1/N = b[Me]^c$.

They determined values of K_F, b, and c of 2.01×10^5, 0.087, and -0.0496, respectively.

2.3.2.2 *Electrostatic models*

Recently, the use of surface complexation models (SCM) has become a popular method of defining adsorption. Unlike the empirical approaches, SCMs strive to be comprehensive (i.e. applicable to a wide range of conditions), realistic, and predictive (Goldberg, 1991). Instead of relying on empirical constants, the SCM's use thermodynamic data, experimentally-derived surface equilibrium constants, and physical/electrical characteristics of the adsorbing media to predict adsorption. A model's ability to predict speciation varies according to the quality of its thermodynamic database, its flexibility (handling multiple chemical reactions and

phases), and the various complexes considered (Goldberg, 1991).

One example of a SCM is the geochemical model MINTEQA2/PRODEFA2, which is a hybrid of several classic geochemical models. The original MINTEQ was developed using the mathematical structure of MINEQL (Westall and Hohl, 1980) with the thermodynamic database of WATEQ3 (Allison et al., 1991). Later releases of MINTEQ have improved upon the original version by offering more options, altering the method of calculation, and improving its thermodynamic database (Allison et al., 1991).

2.3.3 SPECIATION

An important factor when considering adsorption is the speciation of the compound of interest. Mercury can exist in a variety of forms in the environment, and each form will have a different affinity for a surface. Most metals do not exist at significant activities in nature as the "free metal," i.e. Hg^{2+}; instead, depending on pH, one or more waters from the solvation sheath will deprotonate to yield a hydrated complex. The hydrolysis constant, K, is a specific example of the equilibrium constant for complexes (Equation 2.2), and relates hydrolyzed products to reactants. The mercuric ion undergoes the following reaction

$$Hg^{2+} + H_2O \rightharpoonup Hg(OH)^{+} + H^{+}, \text{ or } Hg(H_2O)_6^{2+} \rightharpoonup Hg(H_2O)_5(OH)^{+} + H^{+} \quad (2.18)$$

For mercury, the first hydrolysis product, K_1, can be written

$$K_1 = \frac{\{H^+\}\{Hg(OH)^+\}}{\{Hg^{2+}\}} \qquad (2.19)$$

Therefore, when pK_1 = pH, the concentrations of each metal species is equal. Figure 2.6 shows the speciation of mercury. The pK_1 is found at the pH where the line representing Hg^{2+} crosses the line representing $Hg(OH)^+$.

Elliott and Huang (1979) illustrated a common trend among hydrolyzable metals (Figure 2.7). At low pH, little adsorption was noticed. However, adsorption abruptly increased in a narrow pH range, and this range corresponded to the pK_1 of the metal. Therefore, it was proposed that hydroxo complexes increased adsorption of metal cations.

The notion that the formation of complexes of reduced charge would increase adsorption is counter-intuitive, since one would expect, based on electrostatics, that adsorption of a metal cation to a negatively-charged surface would decrease as the ionic charge of the species decreases (see Equation 2.3). Stumm and O'Melia (1968; summarized in Elliott and Huang, 1979) offered several possible explanations for why this is not so:

1. A specific interaction with the surface that is independent of charge is invoked with the addition of a hydroxy ligand. These proposed interactions include hydrogen bonding with the surface oxygen atoms, or the replacement of a water of hydration on the surface with a hydroxy ligand of the cation.
2. The hydroxy complex may be more hydrophobic than the "free metal" ion.
3. The presence of one hydroxy ligand may facilitate the adsorption of a

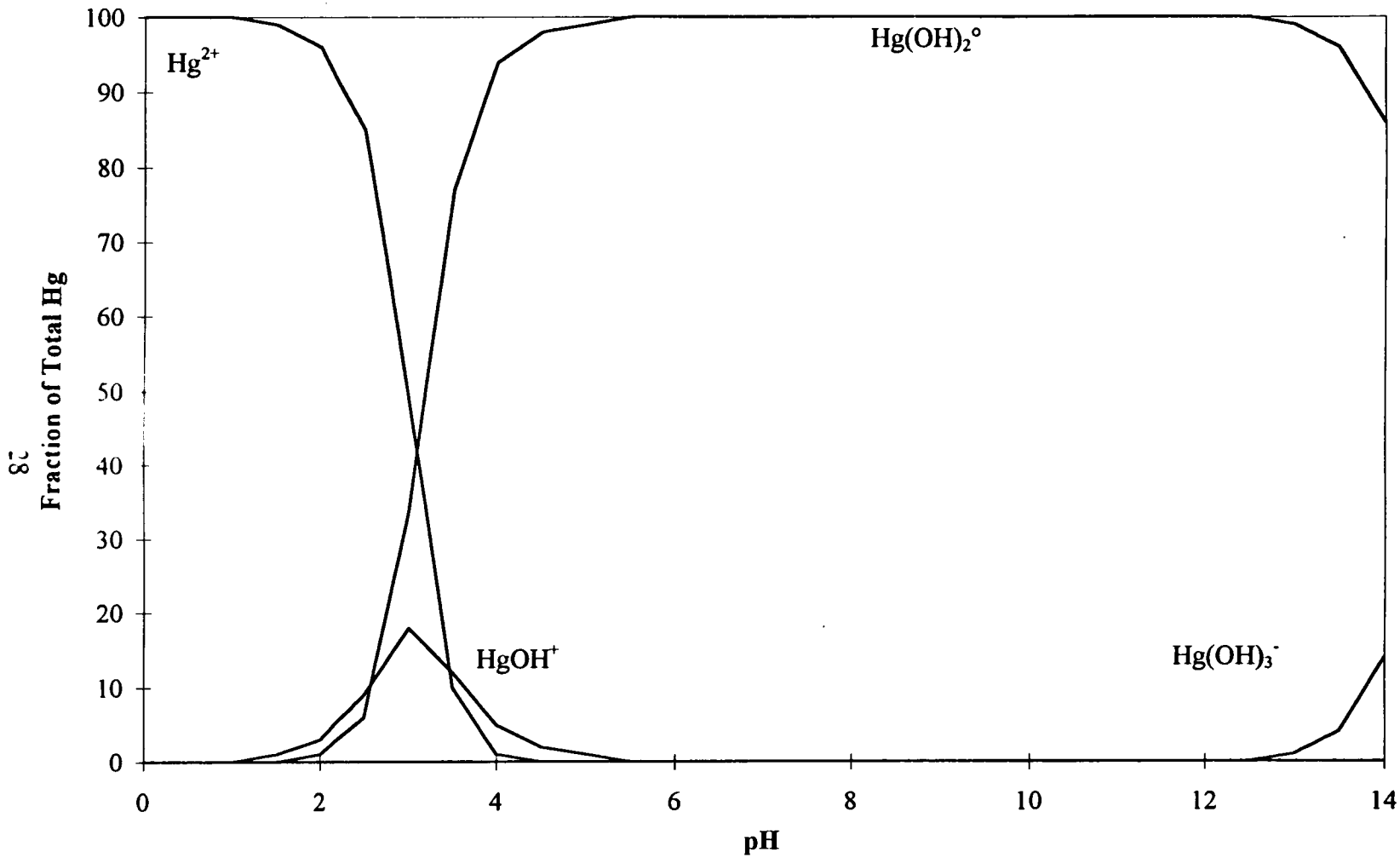


Figure 2.6: Speciation of Mercury in Water. $Hg_T = 5x10^{-7}$ M

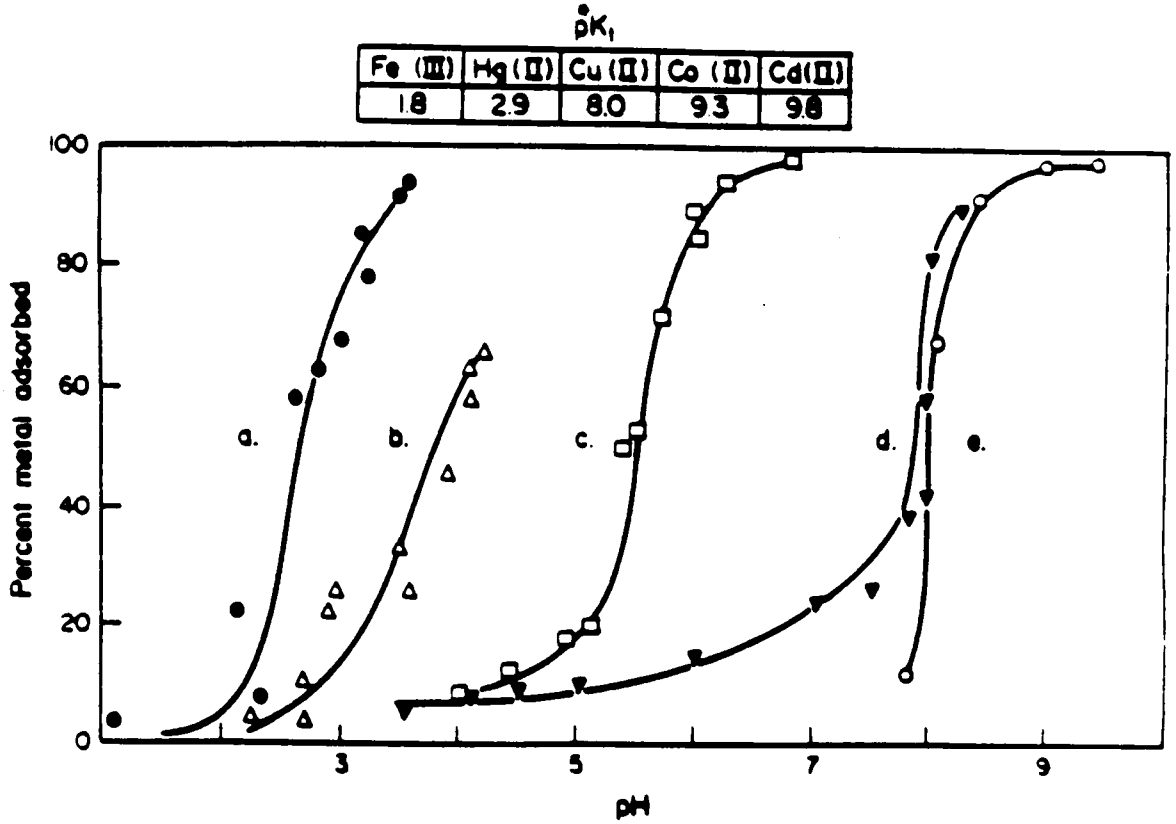


Figure 2.7: Adsorption as a Function of First Hydrolysis Constant.
(a) Fe(III); (b) Hg(II); (c) Cu(II); (d) Co(II); (e) Cd(II)
(Elliott and Huang, 1979)

cation into the surface lattice of a particular mineral.

Many researchers have studied the effects of hydroxide ligands on mercury adsorption. Forbes et al. (1974) studied the adsorption of mercury to goethite (α-FeOOH) and observed a correlation between the formation of mercury-hydroxide complexes and adsorption. A maximum in adsorption occurred at pH = 4.13, and speciation calculations predict that at this pH, all mercury is present as $Hg(OH)_2^\circ$. They concluded that the hydroxo ligands of $Hg(OH)_2^\circ$ act as bridging ligands between the oxide surface and the metal cation. Similar patterns in mercury adsorption (i.e. apparent dependance on hydroxo species) were noted for bentonite (Newton et al., 1976), iron hydrous oxide gel (Kinniburgh and Jackson, 1978) and kaolin and illite (Farrah and Pickering, 1978). Barrow and Cox modeled the adsorption of mercury to goethite (1992a) and a sandy-loamy soil (1992b). Their adsorption maxima was located just below pH 4 in a goethite system without competitive ligands. They concluded that the $HgOH^+$ species described adsorption, since the adsorption maxima occurred at the pH of maximum $HgOH^+$ concentration. In their studies of mercury adsorption to soil (1992b), they once again used a model to describe mercury adsorption based on changes in $HgOH^+$ concentration over a narrow pH range ($4 < pH < 5.8$). However, their model did not perform consistently. MacNaughton and James (1974) studied mercury adsorption to quartz (SiO_2). They also noted an abrupt increase in adsorption to a maximum at a pH of 2 - 3, and noted the correlation in adsorption with the formation of $Hg(OH)_2^\circ$. Lockwood and Chen (1974) compared the adsorption behavior of mercury on ferric hydroxide ($Fe(OH)_3$) and manganese

dioxide (MnO_2). They found that $Hg(OH)_2^\circ$ was the most likely species responsible for adsorption of mercury, and that at low mercury concentrations, the difference between the effectiveness of the two substrates was small. However, at higher concentrations of mercury, MnO_2 had a higher capacity than $Fe(OH)_3$. Thanabalasingam and Pickering (1985) studied mercury adsorption to γ-MnO_2. They proposed that adsorption was due to the migration of mercury species into the internal structure of the MnO_2, where the mercury ligands either undergo ligand exchange with the surface hydroxyl groups, or are transformed into the solid hydroxy phase.

According to Stumm (1992), hydrolyzable metals adsorb as the free metal, not as the hydrolyzed complex. The correlation between the formation of hydrolyzed products and adsorption is due not to the adsorption of the hydroxo complex, but to the likelihood of the cation to interact with either the oxygen donor groups of surface silonol/aluminol groups or free OH^-.

Farrah and Pickering (1978) observed a *decrease* in the adsorption of mercury to montmorillonite (bentonite) with increasing pH. The authors attribute this decrease to the decrease in concentration of Hg^{2+} and $Hg(OH)^+$; however, the authors assume that adsorption is based solely on electrostatics (i.e., they assume that adsorption will be a minimum when $Hg(OH)_2^\circ$ is dominant), so the quality of their interpretation must be questioned.

The effect of other inorganic ligands on mercury adsorption has also been studied. Although they failed to consider the adsorbing substrate in their calculations of mercury mobility, Hahne and Kroontje (1973b) used aqueous speciation to argue a

decrease in mercury mobility with increasing chloride concentration. They found that total chloride concentrations were as important a parameter as pH in determining solubility and mobility of mercury. Leckie and James (1974) studied the effect of chloride on mercury adsorption (Figure 2.8). They noted that the adsorption edge for mercury on SiO_2 shifted to increasingly higher pH with the addition of increasingly higher concentrations of chloride. The onset of the adsorption edge occurred in the pH range where mercury-hydroxo species began to dominate all mercury-chloro and mixed mercury-chloro-hydroxo species. Thanabalasingam and Pickering (1985) found that sulfate was more effective at mobilizing mercury than an equivalent concentration of chloride, and that, in a sulfate system, an increase in pH decreased the amount of mercury adsorbed. They speculated that this was due to the formation of HSO_4^- or the protonation of the MnO_2 surface. Newton et al. (1976), while noting that chloride prevents mercury adsorption, also noticed a maxima in mercury adsorption when the mixed hydroxy-chloro species, $HgClOH^\circ$, was dominant. They concluded that this species was the most strongly adsorbed mercury species. This is in contrast to the more generally held notion that adsorption increases when the formation of $Hg(OH)_2^\circ$ is favored (Stumm, 1992; Thanabalasingam and Pickering, 1985; Lockwood and Chen, 1974; Kinniburgh and Jackson, 1978; MacNaughton and James 1974). The authors also noted that a further decrease in adsorption could result when significant chloride concentrations were achieved through the formation of negatively-charged mercury-chloro complexes (see Table 2.3). Forbes et al., (1974) believed that the reduction in mercury adsorption in the presence of chloride was due to the strength of

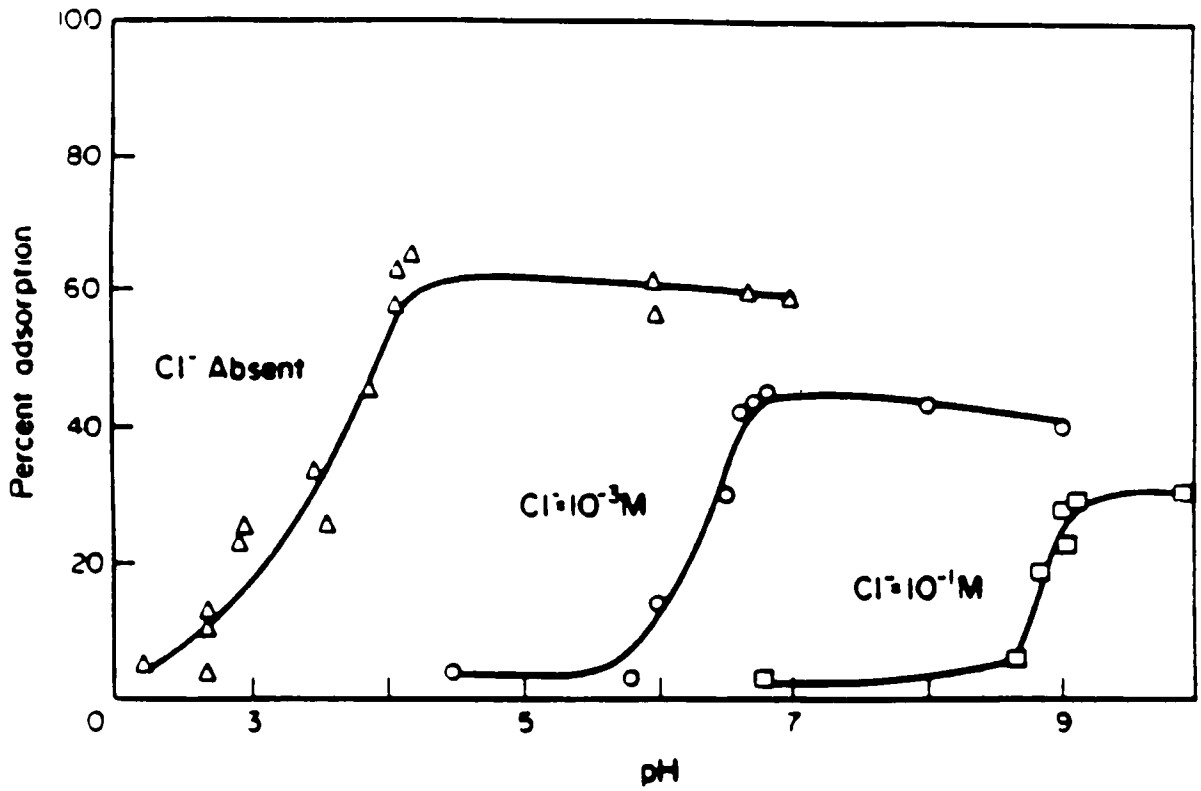
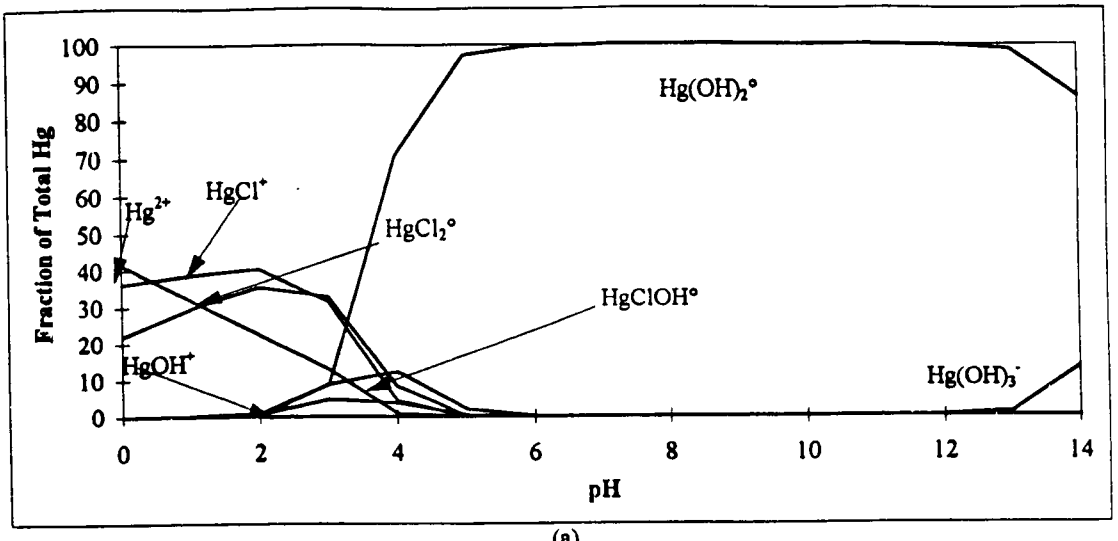


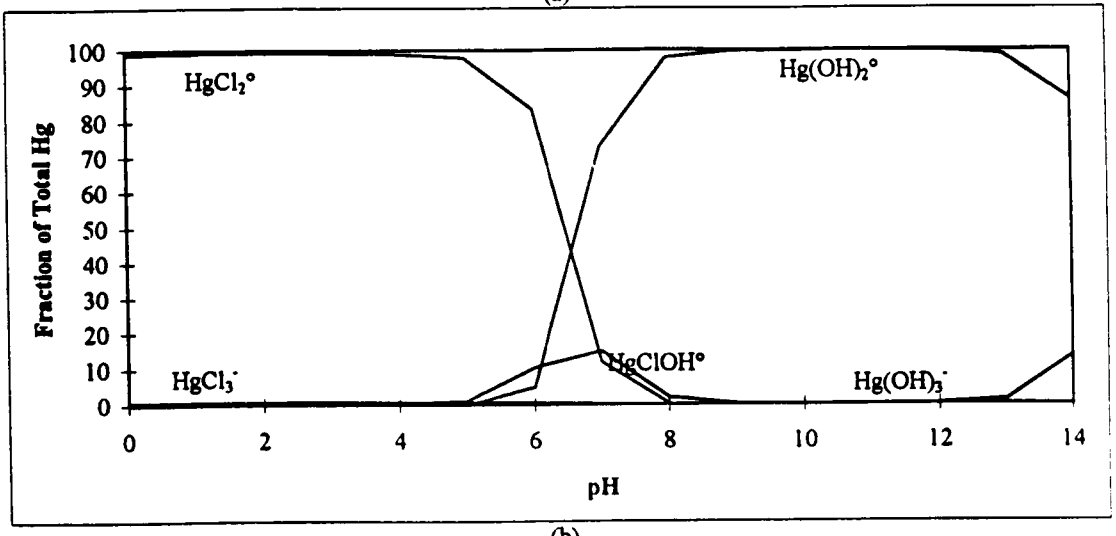
Figure 2.8: Effect of Cl^- Concentration of Mercury(II) Adsorption.
$Hg_T = 10^{-6}$ M.
(Leckie and James, 1974)

the Hg-Cl bond, which prevents the formation of a bridging ligand between the complex and the surface. MacNaughton and James (1974) also observed a decrease in mercury in the presence of chloride, and attempted to model their results. Their model performed well, but it failed to account for a decrease in adsorption after the maximum. They postulated this decrease was due to (i) a decrease in the number of adsorption sites as pH increases, (ii) a decrease in free energy with increasing pH, or (iii) other species not included in their analysis that adsorb less strongly than $Hg(OH)_2^\circ$.

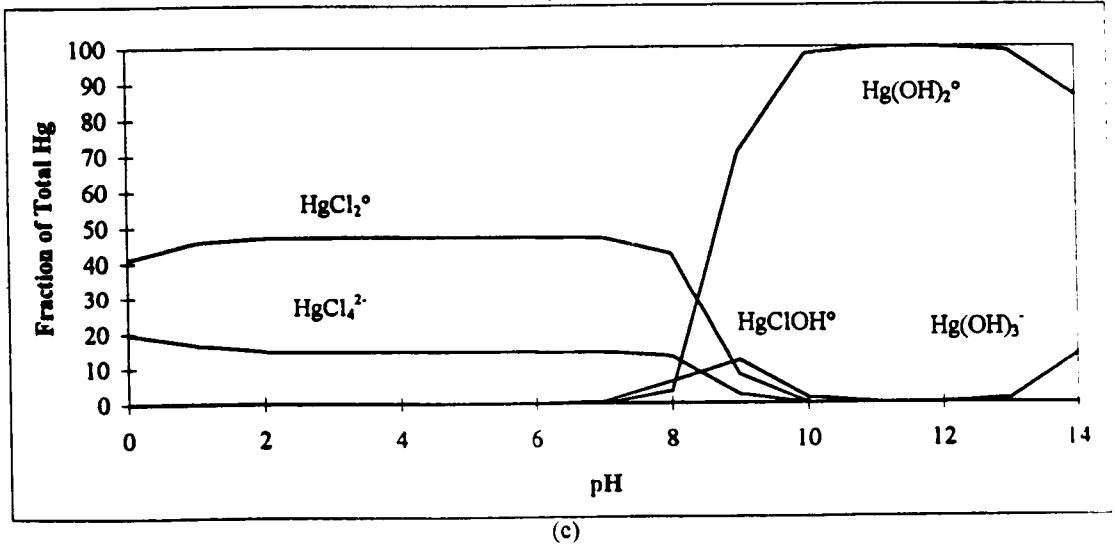
Some have seen an increase in mercury adsorption with the addition of chloride. Lockwood and Chen (1974) observed an increase in mercury adsorption in the presence of chloride, and mistakenly concluded that $HgCl_2^\circ$ may also adsorb. For the mercury and chloride concentrations that they considered, the formation of $Hg(OH)_2^\circ$ is possible within this range, and is the likely adsorbate (Figure 2.9). Barrow and Cox (1992a) noticed an offset in the adsorption edge and the pH of maximum adsorption with increasing chloride concentration, the same pattern observed by Leckie and James (1974) and Newton et al. (1976). They found that they could model the adsorptive behavior with an adaptation of their model ZNCL2.BAS, a type of Triple Layer Model, based on the adsorption of $HgOH^+$ and $HgCl^+$ ions. Although their modeling results agreed well with their experimental findings, the significance in their model of $HgCl^+$ as an adsorbed species is questionable, not only because others have argued that chloro complexes reduce mercury adsorption (Forbes et al., 1974; MacNaughton and James, 1974; Thanabalasingam and Pickering, 1985;



(a)



(b)



(c)

Figure 2.9: Speciation of Mercury(II) in the Presence of Cl^-.
$Hg_T = 5x10^{-7}$ M; Cl^- = (a) $1x10^{-6}$ M; (b) $1x10^{-3}$ M; (c) $1x10^{-1}$ M.

Kinniburgh and Jackson, 1978; Newton et al., 1976; Leckie and James, 1974; and others), but also because the contribution of both the $HgOH^+$ and $HgCl^+$ complexes to the total fraction of mercury species in solution is quite small, particularly at high pH (Figures 2.6 and 2.9). Farrah and Pickering (1978) noticed an increase in mercury adsorption to illite and kaolin with the addition of chloride, but these results are suspect.

The adsorption of organic mercury compounds (methyl mercuric chloride (MMC) and phenyl mercuric acetate (PMA)) and mercuric chloride to two soil columns was studied by Hogg et al. (1978). They found that soils with higher organic and clay content retained more mercury overall, and that adsorption maxima (as determined by Langmuir isotherms) decreased in the order: $HgCl_2$ > PMA > MMC. They also found that, in spite of the mercury complex present (organic vs. inorganic) and the application of organic (EDTA, NH_2OAc, DTPA) or inorganic ($CaCl_2$) extractants, little mercury leached below 20 cm. They speculated that this was due to strong binding between mercury and the soil. Farrah and Pickering (1978) found that mercury complexes with nitrilo triacetate (NTA), cyanide (CN^-), and acetate (Ac) decreased mercury adsorption to kaolin and illite; thiocyanate (SCN^-) decreased mercury adsorption to kaolin and illite, but increased adsorption to montmorillonite at high (> 7) pH.

2.3.4 Soil Constituents

Soil physical and chemical properties have also been correlated to metal mobility.

Korte et al. (1976) investigated the effect of different soil properties on the mobility of eleven trace elements. They found that the most important property for predicting metal mobility in soils was the soil texture. Soils with a high clay content typically retained metals, while sandy soils showed little capability of retaining metals. Soils with a large surface area showed a greater capability to retain metals than soils of lower surface area, presumably due to the availability of more surface sites. Lime content was also shown to reduce the mobility of metals in soils, due to an increase in pH that results in a metal species favorable for adsorption. The electrical conductivity of the leachate was found to be unrelated to metal mobility.

Soil organic matter has also been shown to be a major factor in a soil's ability to retain mercury. Xu and Allard (1991) studied the effect of fulvic acids (FA) on the adsorption of mercury to aluminum oxide. Using formation constants for FA's reported by others, they predicted that in the presence of as little as 1 mg/L FA, virtually all mercury in their system was complexed as Hg-FA. Although they expected the FA's to enhance the mobility of mercury above the zero point of charge (pH_{zpc}) because of electrostatics, they found that the FA's reduced mercury mobility over the entire pH range studied ($2.5 < pH < 9.5$). Mantoura et al. (1978) determined the formation constants for several metal-humic complexes, and found that the magnitude of the formation complex increased according to the Irving-Williams order of stabilities of chelates formed by metal ions with ligands:

$$Mg < Ca < Cd \approx Mn < Co < Zn \approx Ni < Cu < Hg$$

In their investigation, the found that humic compounds were of major importance for

mercury in freshwaters (100% of mercury was complexed with humic compounds), but the significance of humics in seawater decreased due to the abundance of halide ligands. Randle and Hartman (1987) also noted the competition between chloride and humic compounds for mercury. Their results indicate that mercury adsorption to humic compounds can be described by the Langmuir model. Mierle and Ingram (1991) correlated the amount of mercury transported to reservoirs with color (a measure of the humic content of water), underscoring the strong adsorption of mercury to these insoluble organics.

3.0 METHODS

3.1 Geochemical Modeling

The geochemical model MINTEQA2 (version 3.10, USEPA, Athens, GA) was used. The model's thermodynamic database especially that for mercury was compared with data from other sources (Hepler and Oloffson, 1975; Lange's Handbook of Chemistry, 1973; CRC Handbook of Chemistry and Physics, 1992), and was found to be consistent. Input variables consisted of only the solutes to be used in later studies, namely mercury (as $Hg(OH)_2$) and iodide (as NaI) as reactants, potassium and nitrate (as KNO_3) to control ionic strength effects, and hydrogen ion (H^+) to alter pH. No attempt was made to simulate natural waters.

Although MINTEQA2 has the capacity to model adsorption as surface complexation, no attempt was made to model adsorption in this study because of a lack of required data. In addition, no redox couples were specified in the model for iodide or mercury; the different oxidation states could not be considered. The sweep function in MINTEQA2 was utilized to generate speciation data at a series of pH values. Equilibrium speciation data for individual species (as molar concentration) were added to data files. The mole fraction of each species represented was calculated as follows:

$$fraction\ (\%) = \frac{aqueous\ species\ concentration\ (M)}{total\ mercury\ concentration\ (M)} \times 100 \qquad (3.1)$$

3.2 Mercury(II) Adsorption by Illite

3.2.1 Illite Preparation

Fithian illite [$(Al_{1.22}Fe^{(III)}_{0.45}Fe^{(II)}_{0.22}Mg_{0.15}Ti_{0.04})(Si_{3.33}Al_{10.67})O_{10}(OH)_2(K_{0.57}Na_{0.05}Ca_{0.07})$] was chosen as a substrate for these studies because of its abundance in the soils of Eastern Tennessee (Toran and Saunders, 1992). The illite (obtained from Wards Natural Science Establishment) was ground in a mortar and pestle and passed through a series of stainless steel sieves. The less than 32 μm fraction was suspended in 0.1 N KNO_3 and agitated on a horizontal shaker table for 2 hours. The suspension was then centrifuged for 15 minutes at 2000 rpm and the supernatant was discarded. The solids were resuspended in 0.1 N KNO_3 and centrifuged three additional times to convert illite to its potassium form. The suspension was next continually resuspended in DI water and centrifuged until the suspension would not settle upon repeated centrifugation (the suspension was stable), and then air-dried in a fume hood.

3.2.2 Suspension Preparation

Illite suspensions (1g/L) were prepared by combining 1 g of the K^+-saturated illite with 10 mL of 1 N KNO_3 (to control ionic strength effects) and adequate DI water to achieve a volume of 1 L. The suspension was agitated on a horizontal shaker for several hours.

Several suspensions with pH values in the range of 4 to 11 were prepared. Various volumes of 0.01 N HNO_3 or 0.01 N NaOH were added to 100-mL samples

of suspension. After a three-day equilibration period, pH values for each suspension were measured. A titration curve was plotted (Figure 3.1), and from this graph, the specific volume of acid or base required to achieve a target pH could be determined.

One hundred milliliters of the test suspension was placed in 125-mL polyethylene (PE) bottles to which an appropriate volume of 0.01 N HNO_3 or 0.01 N NaOH was added to achieve a desired pH in the range of 4 to 11. Samples were equilibrated for at least 3 days to obtain a stable pH values.

3.2.3 Spiking and Separation

Aliquots (10 mL) from each bottle were transferred into 14-mL PE culture vials. Suspensions were spiked with iodide (as NaI) to achieve a final solution concentration between 0 and 50 mg/L, and with mercury to achieve final solution concentrations between 0 and 200 μg/L (as $^{203}Hg(NO_3)_2$). Immediately after spiking, 1 mL aliquots from each suspension were transferred into 7-mL PE scintillation vials and preserved in 1 mL of 4 N HNO_3. Culture vials were mixed on a horizontal shaker for at least 18 hours, determined to be the time needed to attain mercury adsorption equilibrium (Figure 3.2).

The suspensions were removed from the shaker and 1 mL aliquots of each sample were transferred into 7-mL PE scintillation vials and preserved in 1 mL of 4

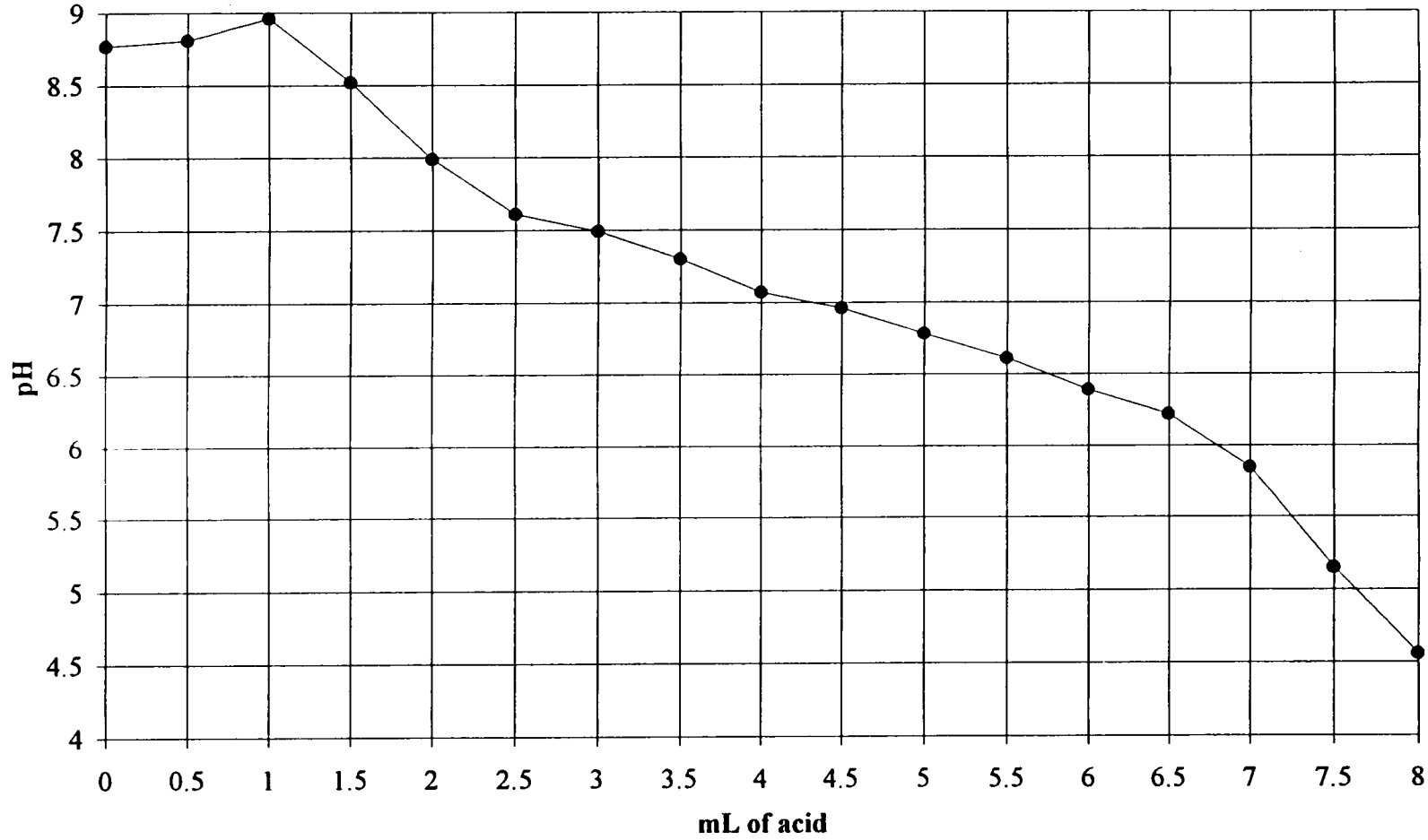


Figure 3.1: Titration Curve for Illite. Suspension Concentration = 1 g/L; Acid = 0.01 N HNO_3.

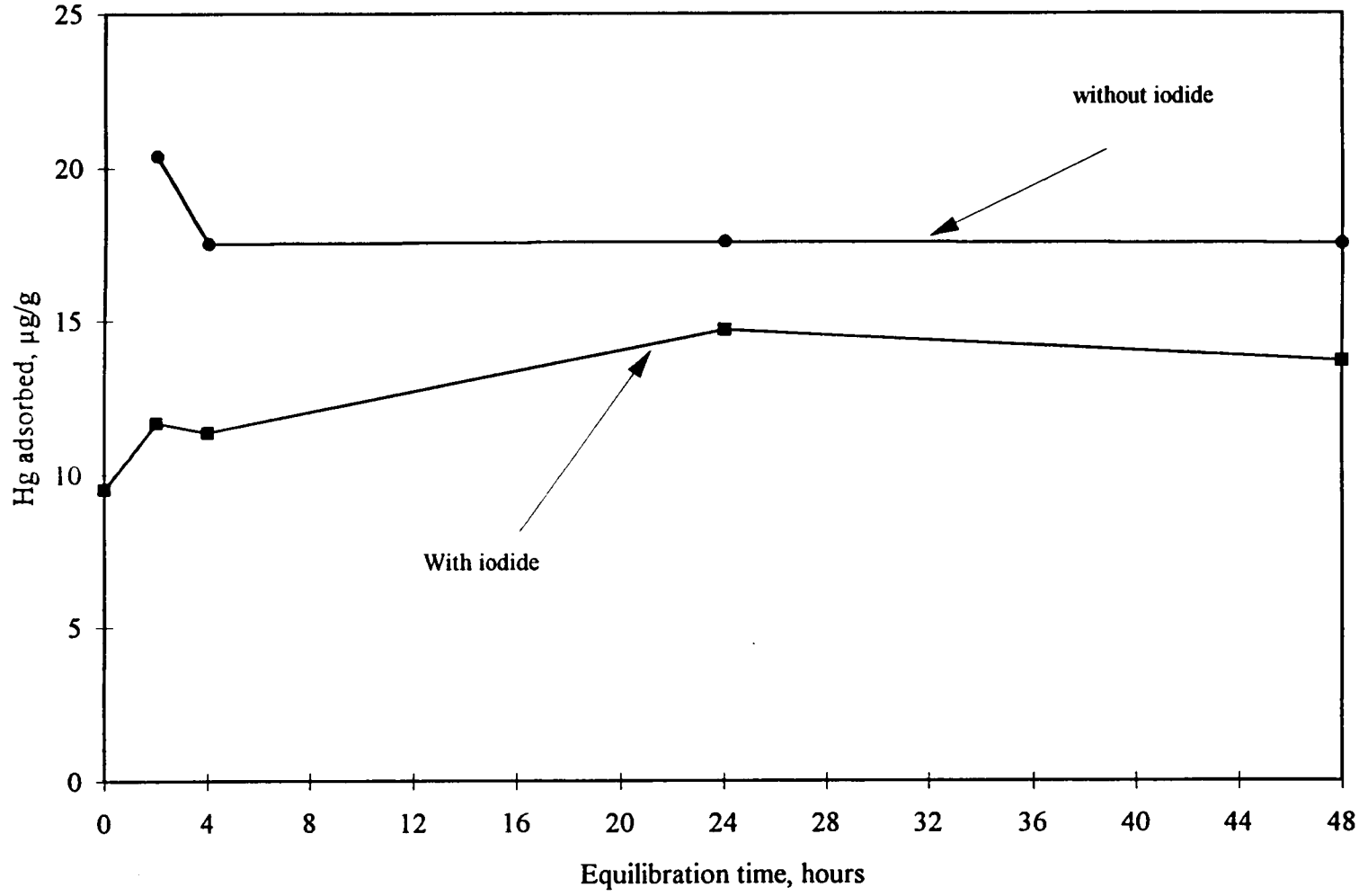


Figure 3.2: Adsorption of Mercury as a Function of Time. Hg_T = 20 µg/L.

N HNO_3. Aliquots (3 mL) of each suspension were filtered through 0.2 μm Nucleopore filter membranes. The filtrate was collected in 14-mL PE culture vials containing 1 mL of 4 N HNO_3. Filtration was followed by two successive 1-mL washes with DI water to collect any aqueous sample entrained in the filter membrane or filter apparatus. Aliquots (1 mL) of each of the diluted filtrates were transferred to 7-mL PE scintillation vials and preserved in 1 mL of 4 N HNO_3. Filters were transferred into 7-mL PE scintillation vials. The pH of each of the remaining suspensions was recorded.

All 7-mL vials were capped and placed inside 30-mL PE scintillation vials for analysis. Samples were accounted for a period of 5 to 15 minutes using a 3" x 3" Bicron NaI deep-well crystal and a Nuclear Data Accuspec gamma spectrometer.

3.3 Mercury(II) Adsorption by a Mixed Illite/Organic Matrix

3.3.1 Mixed Illite-Organic Matrix Preparation

Soils from an old-growth forest in N.W. North Carolina (Joyce Kilmer-Slickrock Wilderness Area of the Nantahala National Forest) were collected. The forest is primarily deciduous; tree species include yellow poplar, hemlock, sycamore, basswood, dogwood, beech, and several species of oak. In addition, there are a variety of shrubs, vines, ferns, and mosses (U.S. Department of Agriculture, 1994). All of these species contribute to the Natural Organic Matter (NOM) of the soil. Soils from this area (JK soil) were selected because they are relatively undisturbed

and contain a relatively high concentration of NOM. NOM was determined by loss on ignition (LOI) analysis (see Section 3.6).

3.3.2 Suspension Preparation

The mass of JK soil (M_{soil}) required to prepare a 1 g/L mixed soil suspension with a organic matter content of 4% was calculated as follows:

$$M_{soil} = \frac{M_{organic}}{NOM} \times 100 \qquad (3.2)$$

where M_{soil} = mass of JK soil required (g)
$M_{organic}$ = mass of organic matter required (g)

The mass of illite per liter of mixed suspension was

$$M_{illite} = 1 - M_{soil} \qquad (3.3)$$

where M_{illite} = mass of illite required (g)

Suspensions were prepared in the same manner as those described in Section 3.2.2 with the following exceptions/alterations:

- pH-adjusted suspensions were prepared in 125-mL brown glass bottles instead of 125-mL PE bottles, and stored in a refrigerator to inhibit microbial growth or activity.
- Soils were not saturated with potassium because of the possibility of losing organic acids in the process.
- A new titration curve was not produced since most of the substrate was illite.
- The soil added to the suspension had a larger particle size (between 250 and 125 μm) than that of illite (<32 μm). It was hoped that this would reduce the effect of other clay minerals that may be introduced into the suspension, since larger particles would have a smaller specific surface area.

3.3.3 Spiking and Separation

Mixed clay-organic suspensions were subjected to the same protocol used to determine the effect of pH and iodide on mercury adsorption to illite (Section 3.2.3).

3.4 Leachability of Mercury from Contaminated Soils

Three studies were conducted to determine the ability of iodide to extract mercury. The first two examined the potential of various concentrations of iodide and other halides to extract mercury from contaminated soil, and the second examined the ability of the leachate from soil washing to extract mercury from contaminated soils.

3.4.1 Soil Extraction with Various Halides

A highly-contaminated soil (2700 μg/g) from the East Fork Poplar Creek (EFPC) floodplain was extracted with various halide solutions. Solutions of each halide (F^-, Cl^-, Br^-, and I^-) were prepared at several concentrations (0.1, 0.01, 0.001 M). Twenty milliliters of each solution were combined with 1 g of soil in a 50 mL PE centrifuge tube. Samples were prepared in triplicate, and process blanks were also prepared using the solution of the middle concentration (0.01 M) to determine mercury contribution from sources other than the soil. Soils were extracted for 48 hours on a horizontal shaker table. Suspensions were filtered through 0.2 μm polycarbonate membranes. The filtrate was preserved in 2 N HNO_3, and analyzed using cold vapor atomic adsorption spectrometry (CVAA).

3.4.2 Soil Extraction with Iodide

Two mildly contaminated soils (< 100 μg/g) from a site in Mississippi were extracted with 0.001 M KI. Twenty milliliters of each solution were combined with 1 g of soil in a 50 mL PE centrifuge tube. One sample was prepared in duplicate. Soils were extracted for 48 hours on a horizontal shaker table. Suspensions were filtered through 0.2 μm polycarbonate membranes. The filtrate was preserved in 2 N HNO_3, and analyzed using cold vapor atomic adsorption spectrometry (CVAA).

3.4.3 Soil Washing to Remove Mercury

A well-characterized soil from the EFPC floodplain was selected to undergo chemical extraction using the method of Foust (1993). This soil has been characterized by others (IT Corporation, 1994) for mercury and other contaminants; it had an average mercury concentration of 258 μg/g.

A soil extraction was conducted to generate a leachate that may be typical of post-treatment soils. Four suspensions were prepared by mixing 115 g of EFPC soil (soil 1) with 500 mL of lixiviant (I^- = 0.4 M; I_2 = 0.2 M) in 1-L PE bottles. The suspensions were shaken for 2.5 hours at 350 rpm at 52°C. They were then centrifuged at 2000 rpm for 15 minutes on an IEC CRU-5000 centrifuge. The supernatant was decanted and replaced with 500 mL of distilled water. The solids were resuspended and centrifuged for 15 minutes to wash out excess lixiviant; the supernatant was decanted.

An additional extraction was performed to remove excess iodide from soils

that had been extracted with I^-/I_2. Five hundred milliliters of distilled water was added and the solids were resuspended. The pH of the solution was adjusted to 10 to 11 using lime (CaO). The suspensions were then returned to the orbital shaker and agitated for 2 hours at 60°C and 350 rpm. After mixing, the samples were centrifuged again for 15 minutes at 2000 rpm. The supernatant was decanted, and the solids were washed in 500 mL of distilled water and centrifuged. These solids are considered treated solids.

In order to generate a leachate from these treated solids, the soil was suspended a final time in DI water, agitated on a horizontal shaker overnight, and then centrifuged. The supernatant from this wash was filtered and reserved as leachate. The leachate was analyzed for pH, total Hg (using cold vapor atomic adsorption spectrometry (CVAA)) and total I^- (using an iodide-specific electrode).

3.4.4 Leaching with Residual Iodide

Leachate 1 was applied to a second soil from the EFPC floodplain (soil 2) with a mercury concentration of 28 μg/g (Barnett and Turner, 1994). Two, 20 g/L suspensions were prepared using undiluted the leachate and a solution of diluted (100:1) leachate.

One hundred milliliter samples were prepared from each suspension and mixed on the shaker table. Three samples of each dilution were removed at 4 and 24 hours. Samples were centrifuged, and the supernatant was analyzed for total mercury using CVAA.

3.5 Determination of Natural Organic Matter

Loss on ignition (LOI) analysis was performed on the three soils and the illite clay standard to estimate the natural organic matter (NOM) content of each. Soils were sieved to remove bulk aggregates and large organic particles such as sticks and roots. Sieved soils were then air-dried for 24 hours in a fume hood and then softly ground in a mortar and pestle. Ground soils and a sample of prepared illite (Section 3.2.1) were dried further in a drying oven to remove excess water, cooled in a desiccator and weighed on an analytical balance to determine dry weight (M_{total}). Samples were baked in a furnace at 500°C overnight to fully oxidize any organic matter, cooled in a desiccator, and weighed to determine the mass of the inorganic fraction ($M_{inorganic}$). Organic matter content (NOM) was determined as follows:

$$NOM = \frac{M_{total} - M_{inorganic}}{M_{total}} \times 100 \qquad (3.4)$$

4.0 RESULTS AND DISCUSSION

4.1 Geochemical Modeling

The geochemical model MINTEQA2 (Allison et al., 1991) was employed to predict the effect of iodide and pH on mercury speciation. Based on the published literature describing the aqueous chemistry of mercury and chloride (Newton and Ellis, 1976), as well as the reported equilibrium constants for mercury-halide complexes (Hepler and Oloffson, 1975), it was expected that neutrally- and negatively-charged mercury-iodide complexes (HgI_2°, HgI_3^- and HgI_4^{2-}) would readily form in solutions of relatively low iodide concentration. In addition it was hypothesized that these complexes would show little affinity for solid surfaces, and, in the case of the negatively-charged complexes, would exhibit electrostatic repulsion.

Several combinations of mercury (0, 2.0×10^{-7}, 5.0×10^{-7}, and 1.0×10^{-6} M) and iodide (3.9×10^{-7}, 3.9×10^{-6}, 1.2×10^{-5}, and 3.9×10^{-4} M) were investigated at constant ionic strength (I = 0.1) over an environmentally-significant pH range ($3.5 < pH < 11$), and a representative plot of the resulting speciation of aqueous mercury ($Hg_T = 5 \times 10^{-7}$ M) is depicted in Figure 4.1. Figure 4.1a shows the species distribution of aqueous mercury over a pH range of 3.5 to 11 with no iodide present. The dominance of the hydolyzed species ($Hg(OH)_2^\circ$) suggests that a large fraction of the mercury in this system should be adsorbed. Figures 4.1b to 4.1d show the distribution of mercury-iodide species for four initial iodide concentrations. Figure

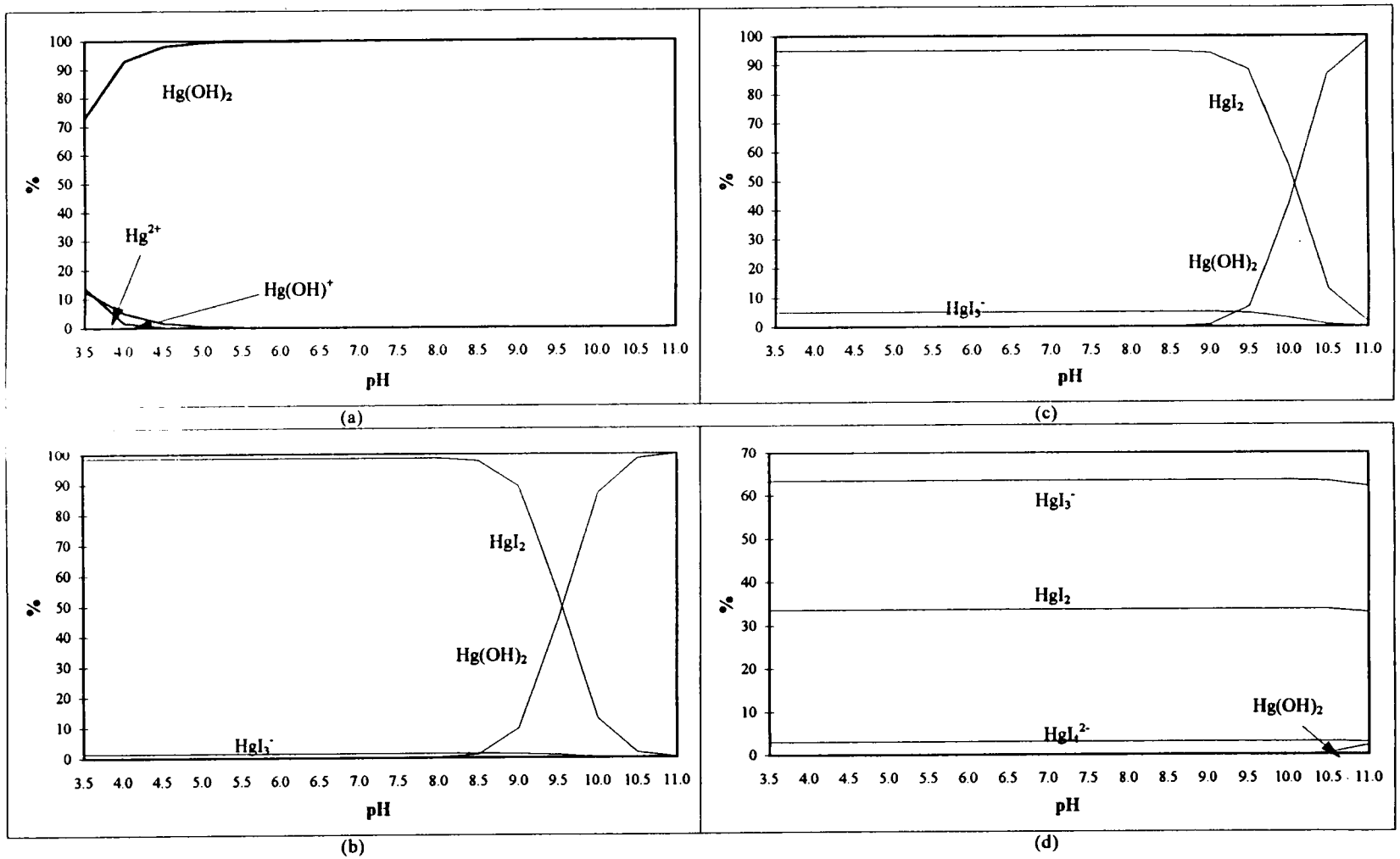


Figure 4.1: Speciation of Mercury. Hg = 100 µg/L.
I = (a) 0 µg/L; (b) 500 µg/L; (c) 1.5 mg/L; (d) 50 mg/L.

4.1b shows that as little as 500 μg/L of iodide may significantly increase mercury mobility due to the formation of HgI_2°. Further increases in iodide concentration (Figures 4.1c and 4.1d) result in an increase in the proportion of HgI_2°, HgI_3^-, and HgI_4^{2-}, and therefore should further increase the mobility and bioavailability of mercury.

Because of large equilibrium constants, seemingly small concentrations of iodide can complex essentially all available mercury in an aqueous system. The total concentration of mercury in an aqueous system ($C_{T,Hg}$) is:

$$C_{T,Hg} = Hg^{2+} + \{Hg\ complexes\} \tag{4.1}$$

where each mercury complex can be written in the form of Equation 2.3. Therefore, in an aqueous solution of mercury and iodide:

$$\begin{aligned} C_{T,Hg} = {} & Hg^{2+} + K_1(Hg^{2+})(I^-) + \beta_2(Hg^{2+})(I^-)^2 + \beta_3(Hg^{2+})(I^-)^3 \\ & + \beta_4(Hg^{2+})(I^-)^4 + K'_1(Hg^{2+})(OH^-) + \beta'_2(Hg^{2+})(OH^-)^2 \end{aligned} \tag{4.2}$$

where K_1 = first equilibrium constant for Hg-I complex (Equation 2.19)
$\beta_2, \beta_3, \beta_4$ = overall equilibrium constant for each successive mercury-iodide reaction (i.e. $\beta_n = (HgI_n^{2-n})/[(Hg)(I^-)^n]$).
K'_1, β'_2 = first and overall mercury hydrolysis constant.

The fraction, f, of a particular species (HgL_n^{2-n}; L = I^- or OH^-, n = stoichiometric coefficient) at equilibrium can be calculated in terms of the reactants and the total mercury concentration:

$$f_{HgL_n^{2-n}} = \frac{(HgL_n^{2-n})}{C_{T,Hg}} = \frac{\beta_n(Hg^{2+})(L^-)^n}{C_{T,Hg}} \qquad (4.3)$$

An examination of Equation 4.3 illustrates why low concentrations of iodide can affect mercury speciation. Since mercury hydrolysis constants are less than mercury-iodide equilibrium constants (Tables 2.3 and 2.4), hydrolyzed mercury products will only become significant when the concentration of iodide is small and hydroxide is in excess (i.e., at high pH). However, above a certain iodide concentration, hydroxide complexes constitute only a minor fraction of the total aqueous mercury.

Increasing the concentration of soluble mercury over the narrow concentration range studied will have little effect on speciation; Equation 4.3 indicates that for iodide concentrations above 500 μg/L, the product $\beta_n(L^-)^n$ masks the effect of slight changes in the concentration of mercury.

Modeling also revealed that only a small amount of iodide is required to complex mercury, even in the presence of chloride. Figure 4.2 shows the effect of increasing I^-:Cl^- ratios on mercury speciation. The figure relates the fraction of species concentration as a function of p(I:Cl) ($Hg_T = 1x10^{-6}$ M). Assuming an aqueous chloride concentration of 35 mg/L (Hem, 1970), a p(I/Cl) of 2.8 or less will result in the formation of an appreciable amount of Hg-I complexes. In fact, essentially all mercury will be in the iodide form given a p(I/Cl) of 2 or less.

Fuge (1972) reports the p(I/Cl) for rainwater to be approximately 2.78. Others (Chilean Iodide Educational Bureau, 1951) have reported average chloride concentrations in rainwater to be about 1 to 15 mg/L. Therefore, the iodide in

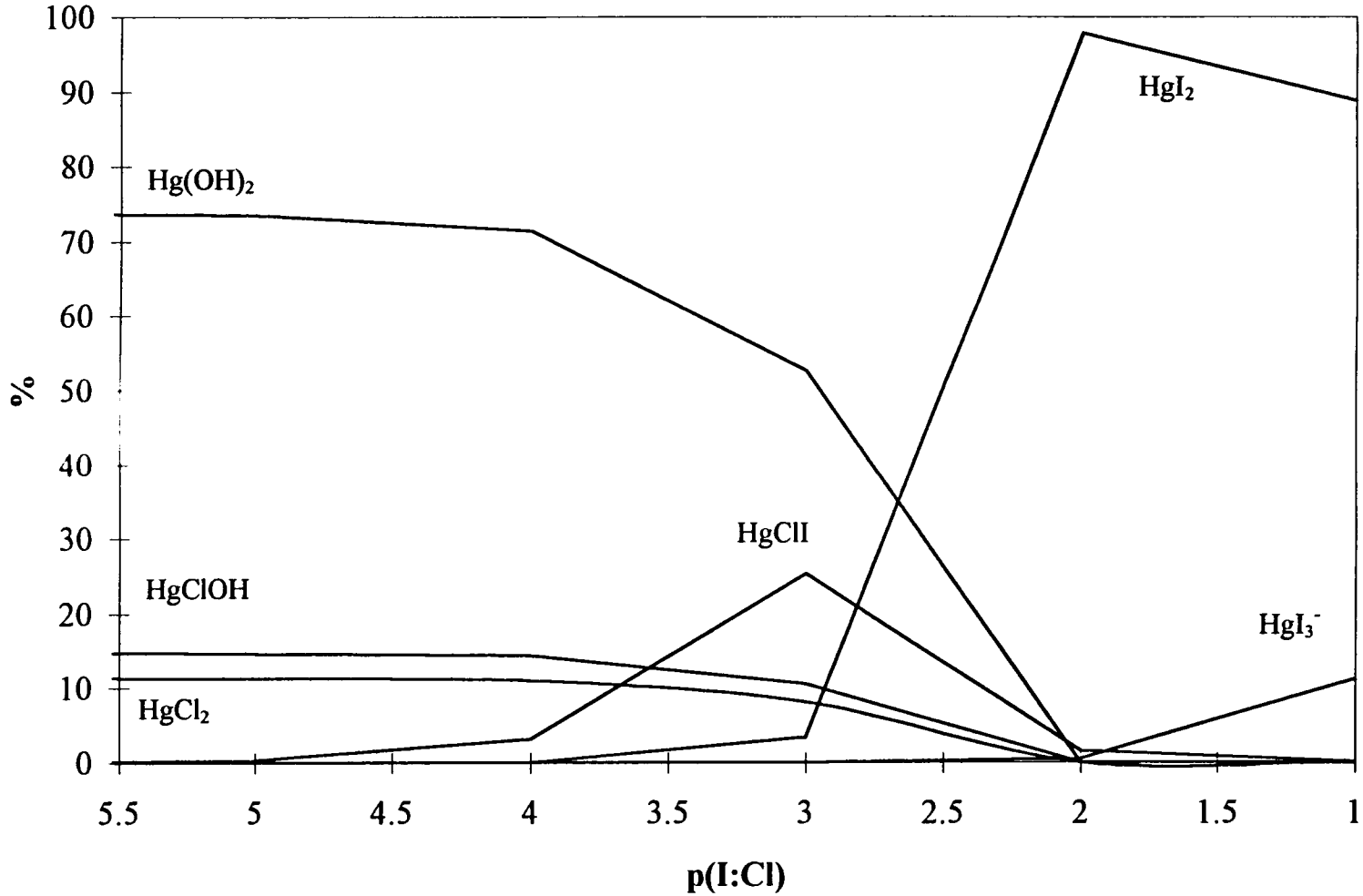


Figure 4.2: Effect of Iodide:Chloride Ratio on Mercury Speciation.
$Hg_T = 1x10^{-6}$ M; $Cl^- = 1x10^{-3}$ M.

rainwater may affect the speciation and mobility of mercury in soils immediately after a rain storm. Fuge also reported typical p(I/Cl) values for soils (1 - 1.4) and sedimentary rocks (1 - 3), and commented that the p(I/Cl) of subsurface brines is typically low. Depending on weathering conditions, the concentration of iodide in these environments may also act to increase mercury mobility. Using the chloride concentration of 35 mg/L for natural waters (Hem, 1970), and a riverwater iodide concentration of 2.2 μg/L (Fuge, 1972), the p(I/Cl) is calculated to be 4.77, which is clearly too large for iodide to affect mercury speciation. However, chloride concentrations in the range of 10^{-2} to 10^{-5} M have been reported by Gilmour (1971), and Fuge reports iodide concentrations ranging from $3x10^{-7}$ to 10^{-8} M, so it is possible for iodide to affect mercury speciation in natural waters, although it appears that under typical conditions, the effects of iodide will be suppressed by chloride concentration.

4.2 Mercury Adsorption Studies

4.2.1 Mercury Adsorption by Illite

4.2.1.1 *Mass Balance*

Using the procedure outlined in section 3.0, two different mass balances were performed on each sample. The first (MB1) was measured during the 18 hour equilibration period, and median values for this mass balance are illustrated in Figure 4.3. MB1 values represent the percent of total mercury that could be accounted for.

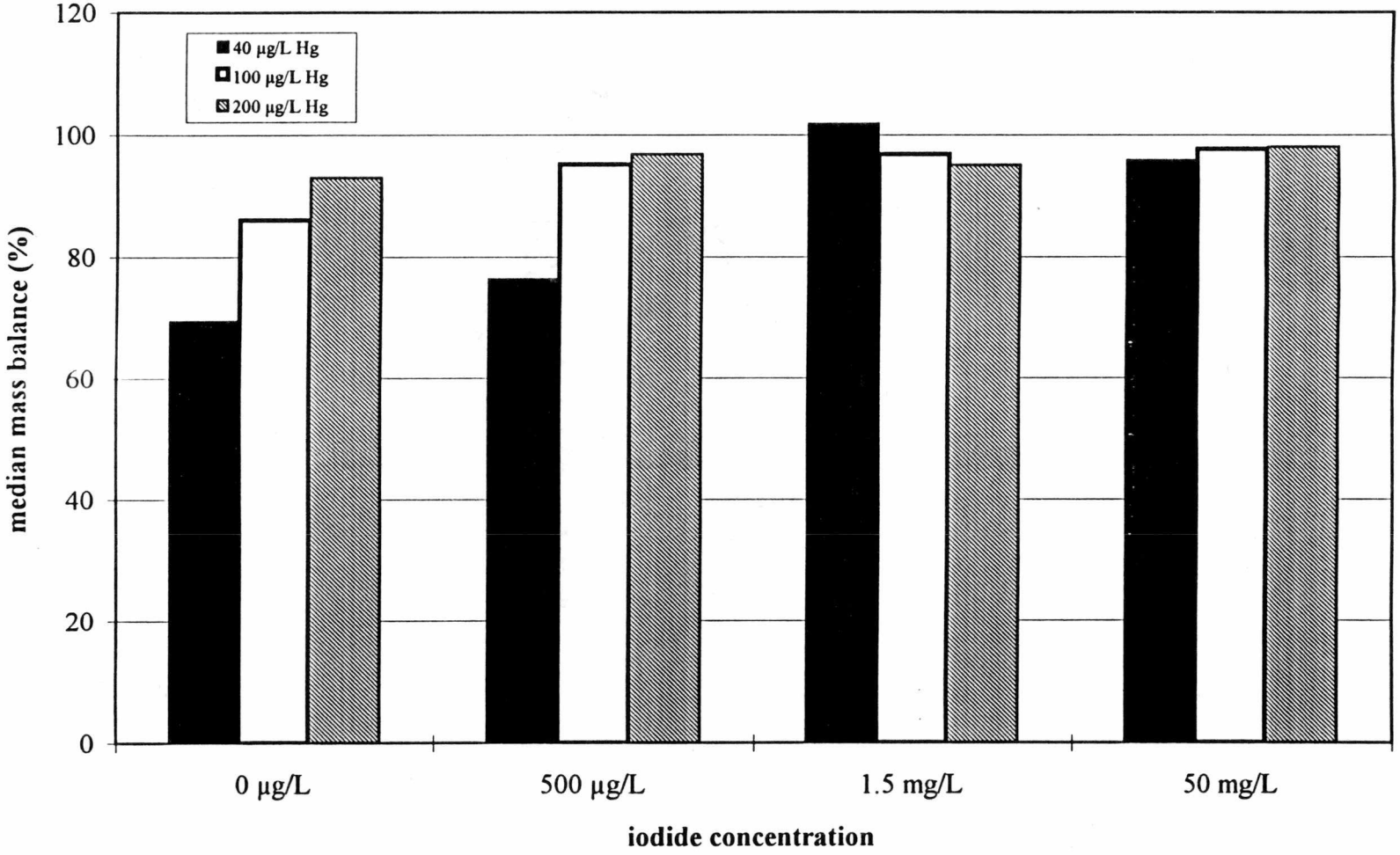


Figure 4.3: Median Mass Balance During 18-hour Equilibration for Mercury-Illite Suspensions (MB1).

Different quantities of mercury were lost from suspension, depending on both the mercury and iodide concentrations. In suspensions with no iodide and low mercury concentrations, losses often exceeded 30%. Losses were high at high pH, up to 60% in some cases, likely due to mercury adsorption by and incorporation in container walls. Similar losses have been documented by others (Feldman, 1974; Newton and Ellis, 1974; Jeanne and Avotins, 1975). It is believed that losses due to volatilization of Hg°, if any, were small since the containers were agitated in the presence of atmospheric oxygen and therefore should have been well oxidized; however, others (Oki and Watanabe, 1971; Shimomura et al., 1969) have postulated that volatilization due to disproportionation could be responsible for mercury losses.

By adding iodide, mercury could be preserved in solution. With 500 μg/L of iodide, losses were less than 10%; increasing iodide concentration decreased mercury losses from less than 5% (I^- = 1.5 mg/L) to less than 3% (I^- = 50 mg/L). Similar observations were made by Shimomura et al. (1969). Newton and Ellis (1974) found that over 50% of mercury in a suspension of bentonite containing 10^{-6} M $CaCl_2$ was lost after 1 day of storage, and only 5% remained after 15 days. By comparison, less than 10% of the mercury in illite suspensions containing similar concentrations of iodide was lost. Therefore, ambient iodide in the environment could conceivably keep mercury mobile as iodo complexes at unacceptably high levels.

It is likely that Hg-I complexes do not strongly adsorb to aquatic surfaces because of the nature of the Hg-I bond. The bond is strongly covalent and prevents

stable bonds from forming between the mineral surface and the mercury cation (Forbes et al., 1974).

An additional mass balance (MB2) was performed to assess the loss of mercury to the filtration unit (filter membrane, filter support and sample receptacle). These losses were expected to be relatively small, since the filtration time was always less than 3 minutes. Figure 4.4 illustrates the effect of increasing iodide concentration on median MB2 values.

In suspensions without iodide, losses were greatest, and the results were variable. On average, MB2 values were greater than 80% for all suspensions without iodide, but several individual values were less than 75%. MB2 values improved with the addition of iodide. Values were always greater than 85%, and generally exceeded 90% for solutions with iodide added. MacNaughton and James (1974) have suggested that losses of mercury to the filter and support could be "relatively high," and Lockwood and Chen (1974) applied a "filter factor" because losses of mercury to the filter in the absence of chloride averaged 20%, and the losses showed considerable variance. The fact that mercury was lost to the filter apparatus (sometimes in large amounts) suggests that the kinetics of mercury adsorption are fast.

A fraction of the mercury loss (MB2) can be attributed to the irregular geometry of the filter during counting. Radiochemical analysis depends on the physical configuration of the sample within the container. Therefore, differences in the orientation of the sample can result in a different number of registered counts. Unlike aqueous suspensions, with a fairly uniform geometry, filter activity could not

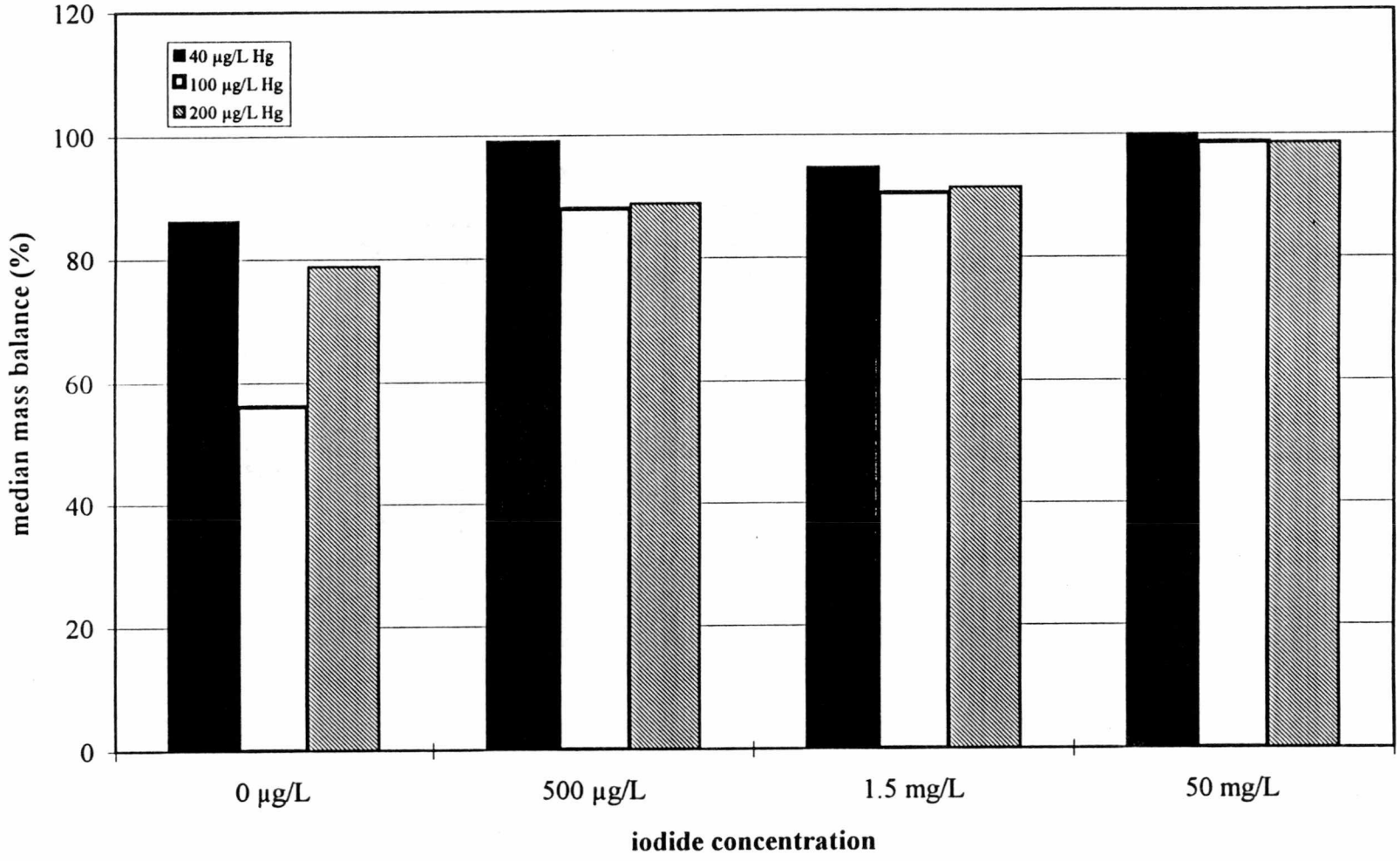


Figure 4 4: Median Mass Balance During Filtration for Mercury-Illite Suspensions (MB2).

be counted with a uniform geometry. Although there was no way to quantitatively determine the effect of the irregular geometry of the filter on the counting efficiency, it is believed that differences of greater than 5% may result from irregular geometries.

Losses to the membrane (i.e., aqueous mercury adsorption by the polycarbonate membrane) must be considered to prevent overestimation of adsorption. To estimate uptake of mercury by the filters, aqueous solutions of mercury at relatively high concentrations ($\sim$ 200 μg/L) and pH (pH > 9.0) were passed through the filter. These parameters were chosen because mercury losses were expected to be greatest under conditions of high pH and mercury concentration. The filtration results in Table 4.1 indicate that mercury uptake by the filters was very small. Even if the adsorptive capacity of the filters is assumed to be independent of the aqueous mercury concentration, less than 10% of the lowest concentration of aqueous mercury (40 μg/L) would be removed by the filter.

4.2.1.2 *Effect of pH and Iodide Concentration*

The effect of pH on mercury adsorption in suspensions with different iodide concentrations is illustrated in Figure 4.5. Because of the poor mass balances in suspensions without iodide, only data with both MB1 and MB2 greater than 70% were considered. In suspensions without iodide, mercury adsorption slightly decreased between pH 4 and pH 7; above pH 7, adsorption dropped precipitously in some suspensions (Figure 4.5a and 4.5b). Barrow and Cox (1992a), who claimed that $HgOH^+$ controls the adsorption of mercury, argued that this decrease is due to

Table 4.1: Mercury Loss to Polycarbonate Filters.

Hg Applied (µg)	pH	I (µg/L)	Filtrate (µg)	Solids (µg)	Loss to Filter (%)
155.7	9.53	0	156.6	3.9	2.5
155.7	9.51	0	149.9	3.0	1.9
155.7	9.58	0	145.7	2.8	1.8
139.4	9.51	500	124.1	1.8	1.3
139.4	9.46	500	137.8	1.6	1.1
139.4	9.39	500	129.3	1.6	1.1

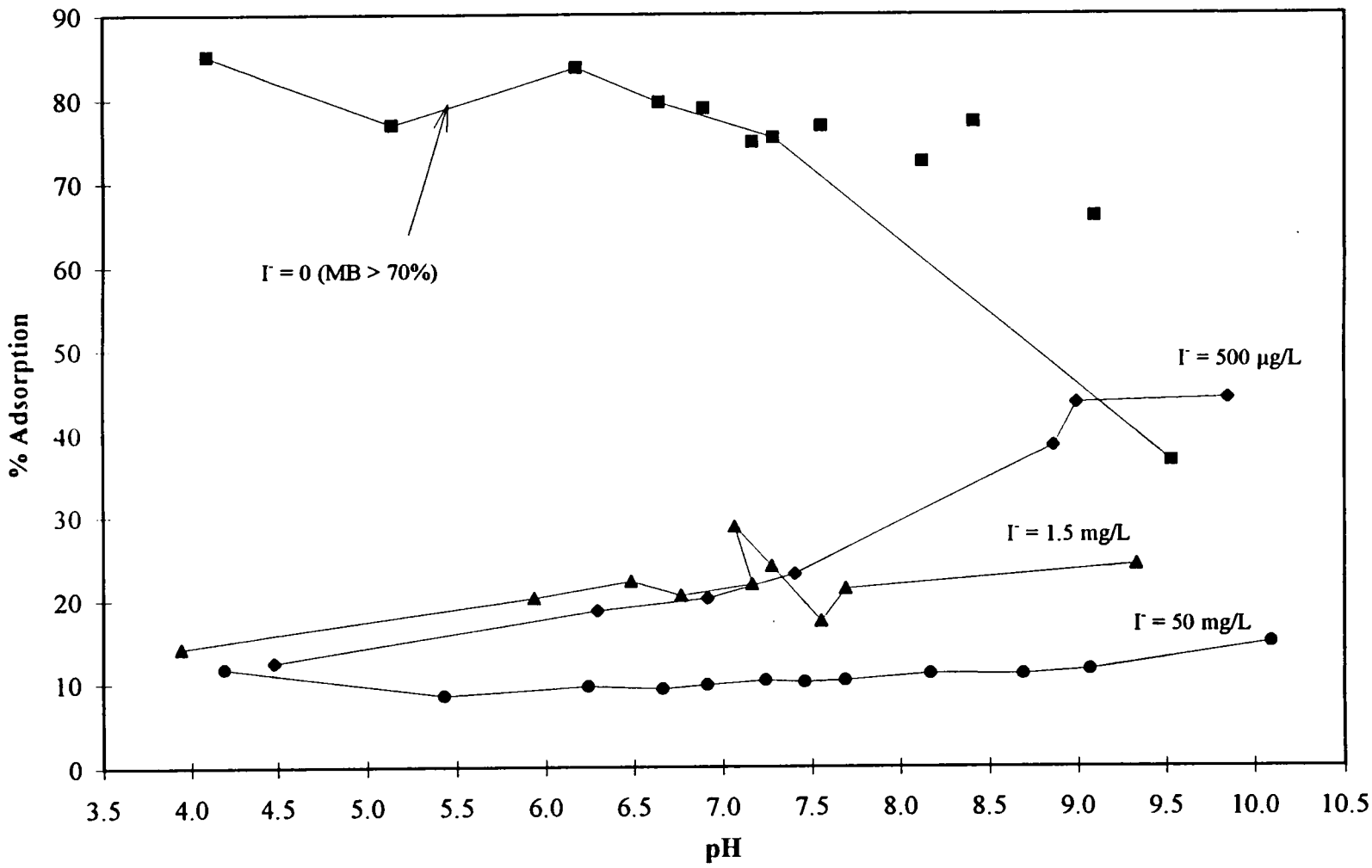


Figure 4.5: Effect of pH and Iodide on Mercury Adsorption by Illite (1 g/L).
(a) Hg_T = 40 µg/L.

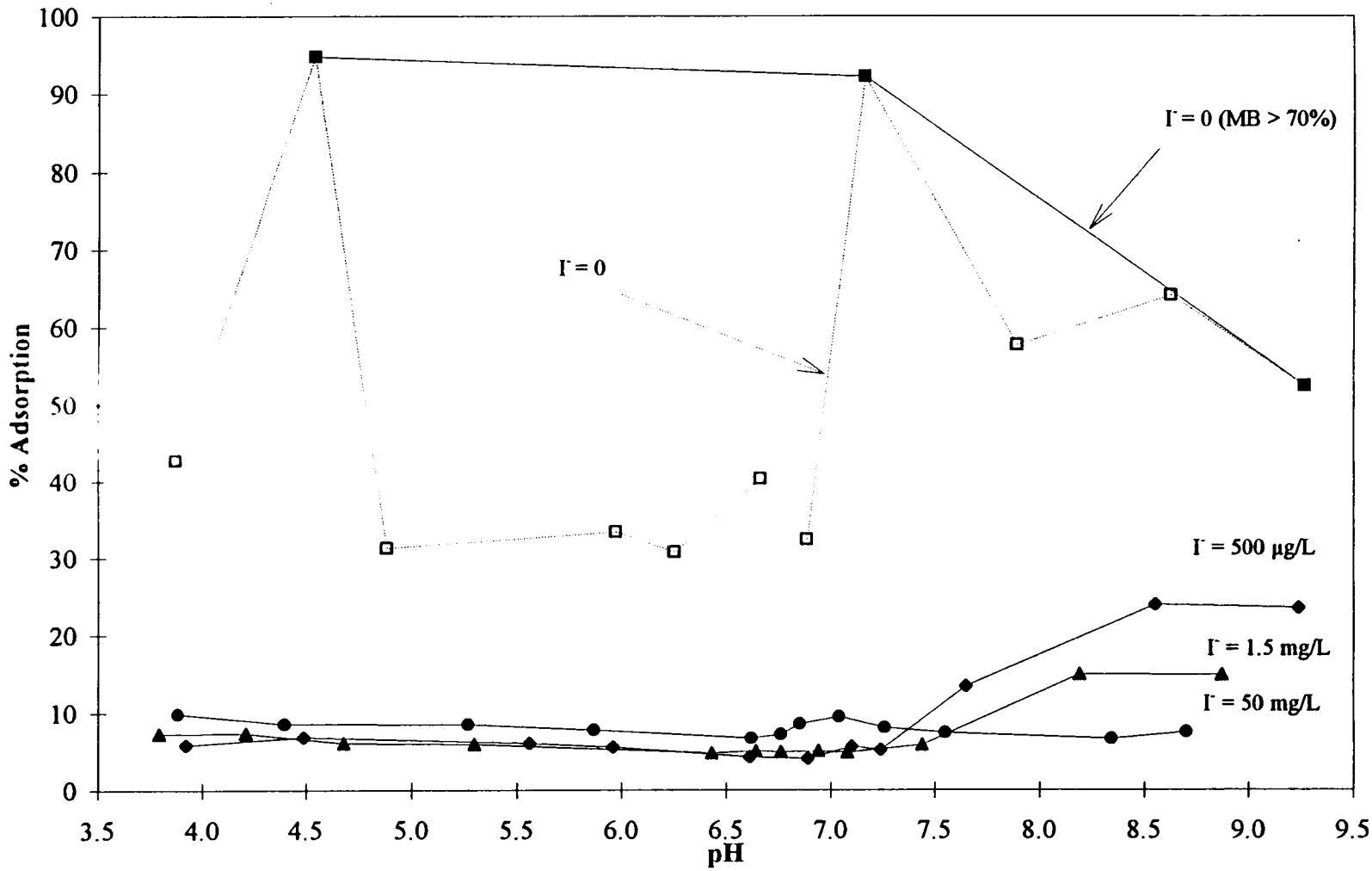


Figure 4.5 continued.
(b) Hg_T = 100 µg/L.

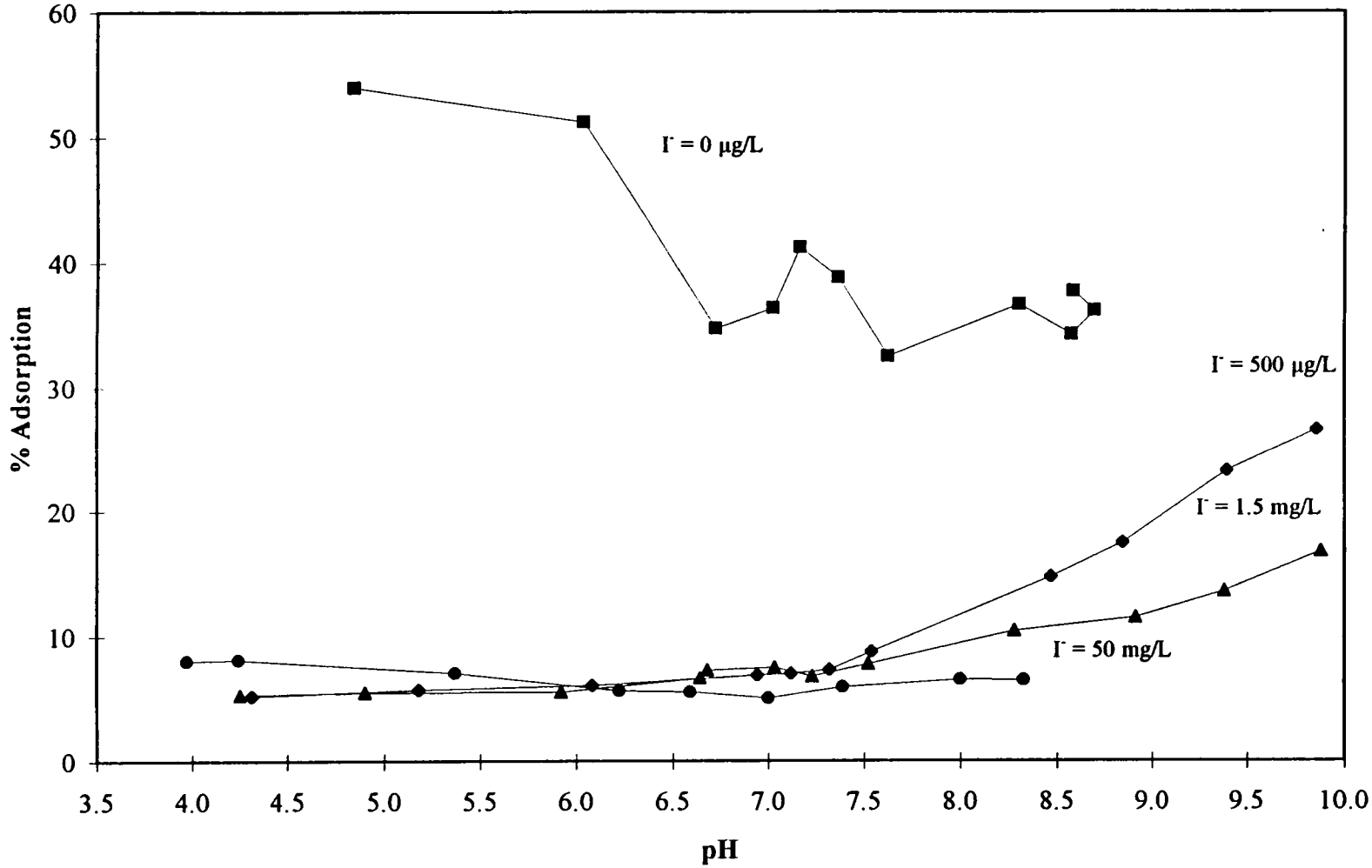


Figure 4.5 continued.
(c) Hg_T = 200 µg/L.

the decrease in the amount of $HgOH^+$ in solution coupled with the increasing negative character of the solid surface. As the pH rises, the concentration of $HgOH^+$ decreases (Figure 4.1a); however, the mineral surface becomes more negative due to deprotonation of surface sites. The result is a slight decrease in adsorption. Kinniburgh and Jackson (1978) argued that the decrease is instead due to the exceptional stability of $Hg(OH)_2^\circ$. This complex competes for a significant fraction of the total mercury in the suspension, and as pH increases, the activity of $Hg(OH)_2^\circ$ "increases proportionately more rapidly than the activity of the Hg(II)-surface complex." Because of the fairly large losses, adsorption may be overestimated or underestimated by up to 30% in suspensions with initial mercury concentrations less than 100 μg/L.

The effect of pH is clear in suspensions with iodide concentrations of 500 μg/L and 1.5 mg/L. At low pH (pH $<$ 7), adsorption remains containing iodide. However, because mass balances improved in all suspensions to which iodide was added, losses will have little effect on the data.

The addition of iodide greatly reduces adsorption, particularly at low pH values. Mercury adsorption decreased to below 20% and was fairly constant (independent of pH) in all suspensions in all suspensions below pH 7. Above a threshold pH, increases in adsorption (termed adsorption edges) are seen over a fairly narrow pH range. A notable exception is seen in suspensions with 1.5 mg/L iodide and 40 μg/L mercury (Figure 4.5a). No adsorption edge is evident since ample iodide is available to suppress mercury adsorption over the entire pH range

considered. Adsorption decreases with the addition of iodide even after the development of the adsorption edge. Adsorption typically rose to about 15% in suspensions with I^- = 1.5 mg/L and to 25% in suspensions with I^- = 500 μg/L (40% for Hg = 40 μg/L). Adsorption values are greater in similar suspensions (constant Hg and pH) without iodide.

The effect of iodide on adsorption is evident in the magnitude of the values of the distribution coefficient, K_D. Figure 4.6 illustrates the effect of iodide on median K_D values for several initial iodide and mercury concentrations. The large values of K_D for suspensions without iodide indicate that mercury prefers the solid phase. An increase in iodide concentration caused a concomitant decrease in the magnitude of K_D, indicating a greater preference of mercury for the aqueous phase.

Adsorption edge development is in part a function of iodide concentration. As iodide concentration increases, adsorption edges shift to higher pH values (Figure 4.5). Similar observations were made by Leckie and James (1974) for mercury adsorption by silica in the presence of chloride (see Figure 2.8). They speculated that the shifts in adsorption edge development to higher pH values were due to an increase in the amount of hydroxide required for the formation of a significant fraction of mercury-hydroxy species in solution.

Adsorption edges are indistinguishable in suspensions with iodide concentrations of 50 mg/L and in one suspension with an iodide concentration of only 1.5 mg/L (Hg = 40 μg/L). Iodide negates the effects of pH on adsorption over the entire pH range studied (the fraction of hydroxo species is always insufficient to

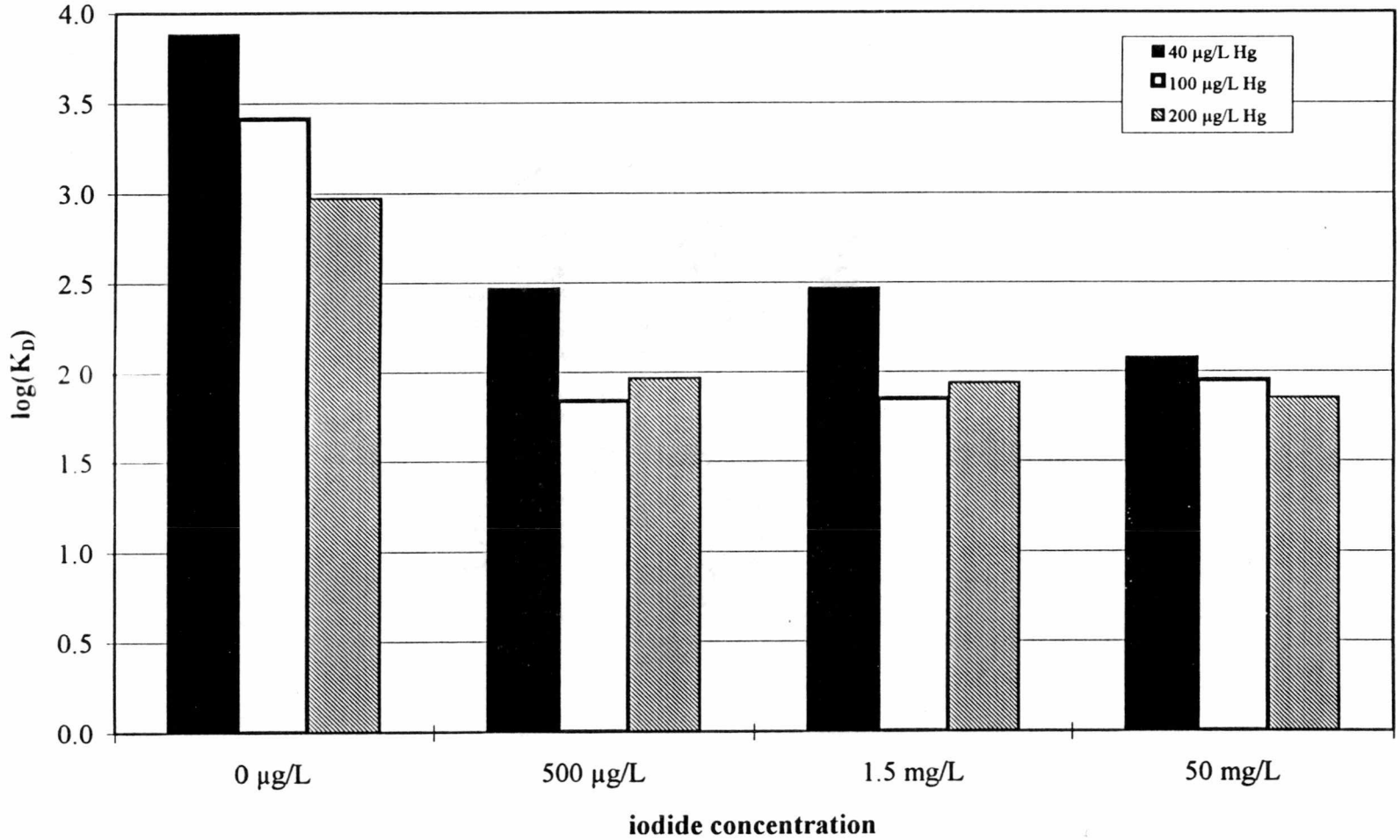


Figure 4.6: Median Distribution Coefficients (K_D) for Mercury-Illite Suspensions.

significantly affect adsorption). Only 50 mg/L of iodide may increase the mobility of mercury over the entire environmentally-significant pH range, and suggests that little iodide is necessary to increase the mobility and bioavailability of mercury in illitic soil environments.

A comparison of the experimental results and MINTEQA2 model predictions indicates that the adsorption edges develop close to the pH at which the formation of the hyroxo species are predicted. Adsorption edges develop around pH 7 when I^- = 500 μg/L and around pH 7.5 when I^- = 1.5 mg/L; MINTEQA2 predicts $Hg(OH)_2^\bullet$ to occur around pH 8 (I^- = 500 μg/L) or pH 8.5 (I^- = 1.5 mg/L). These results indicate that the presence of relatively little $Hg(OH)_2^\bullet$ can be correlated to a significant increase in adsorption (Barrow and Cox, 1992a, b).

4.2.1.3 *Effect of Mercury Concentration*

To determine the effect of mercury concentration on adsorption, adsorption isotherms were constructed for each iodide concentration at two pH values (6 and 8.5). Values for aqueous mercury concentration (C_{eq}) and adsorbed mercury concentration (q) were obtained by interpolation from plots of these values as a function of pH. Data were plotted according to Linear, Langmuir, and Freundlich models. Lines of best fit were constructed and coefficients of regression (R^2) were calculated to determine which model best described the data.

Figure 4.7 shows the correspondence of the data to the different adsorption models at pH 6. Based on the values of R^2 for each of the models, adsorption is best

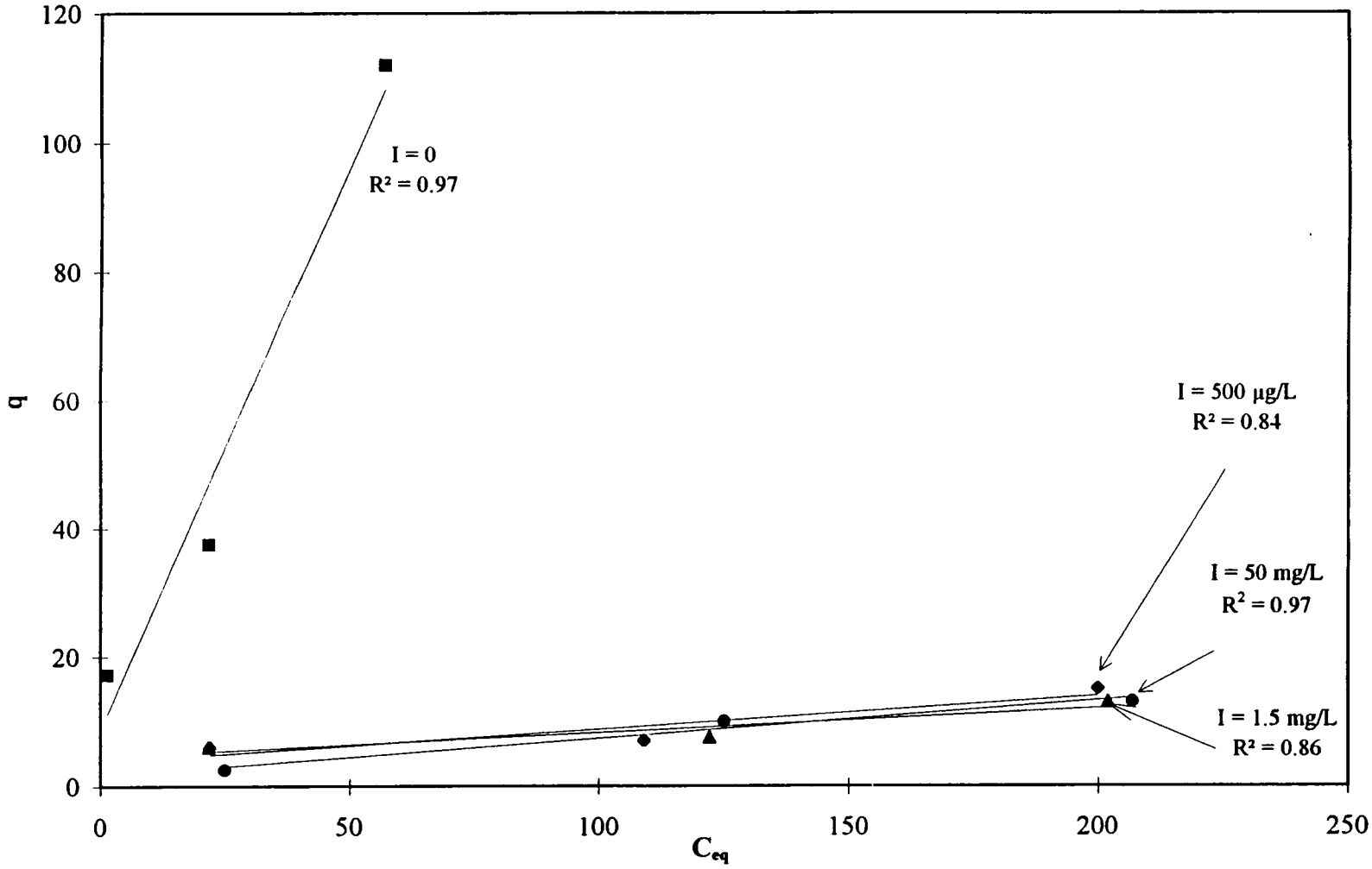


Figure 4.7: Adsorption Isotherms for Mercury Adsorption by Illite. pH = 6.
(a) Linear Isotherm.

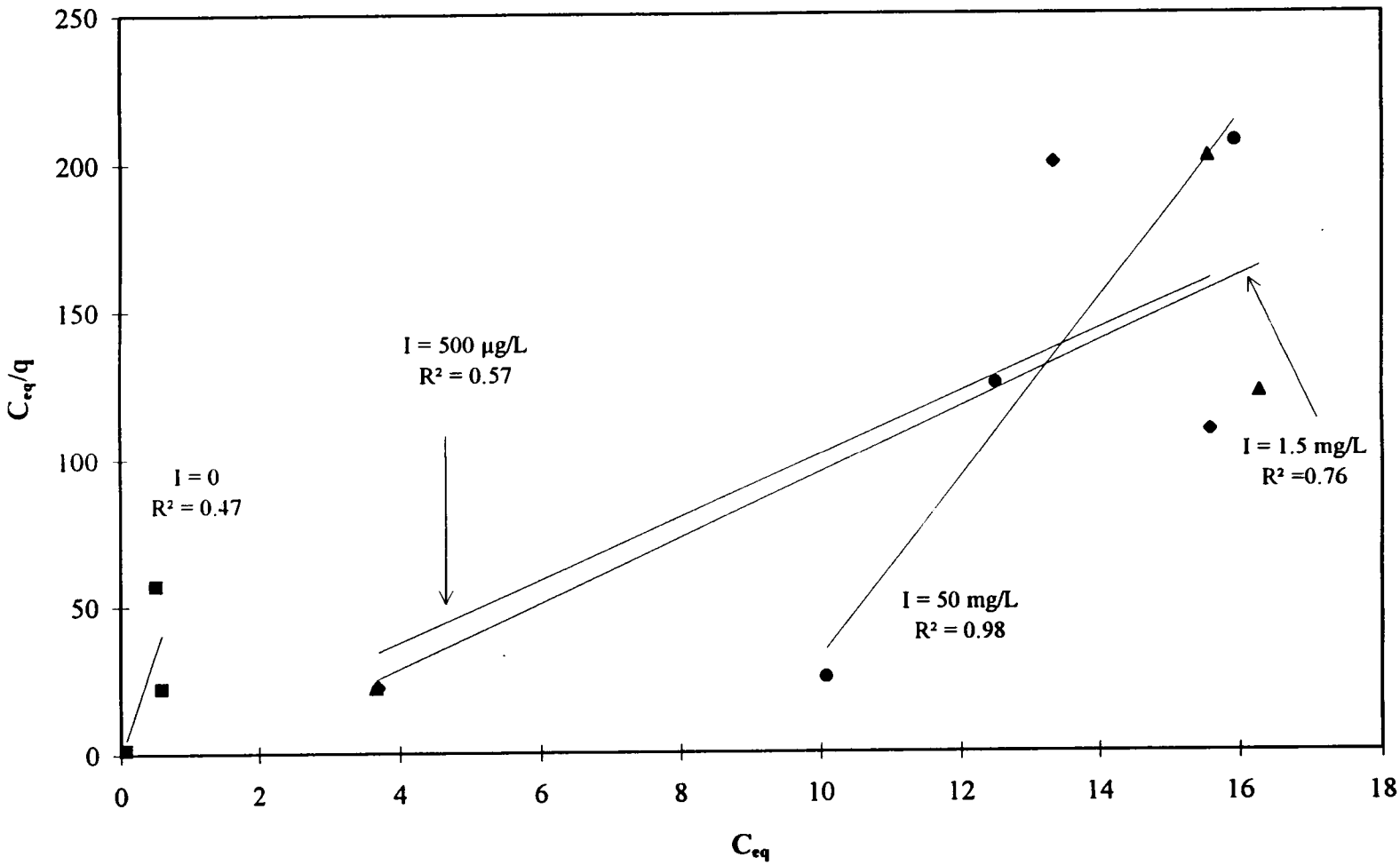


Figure 4.7 continued.
(b) Langmuir Isotherm.

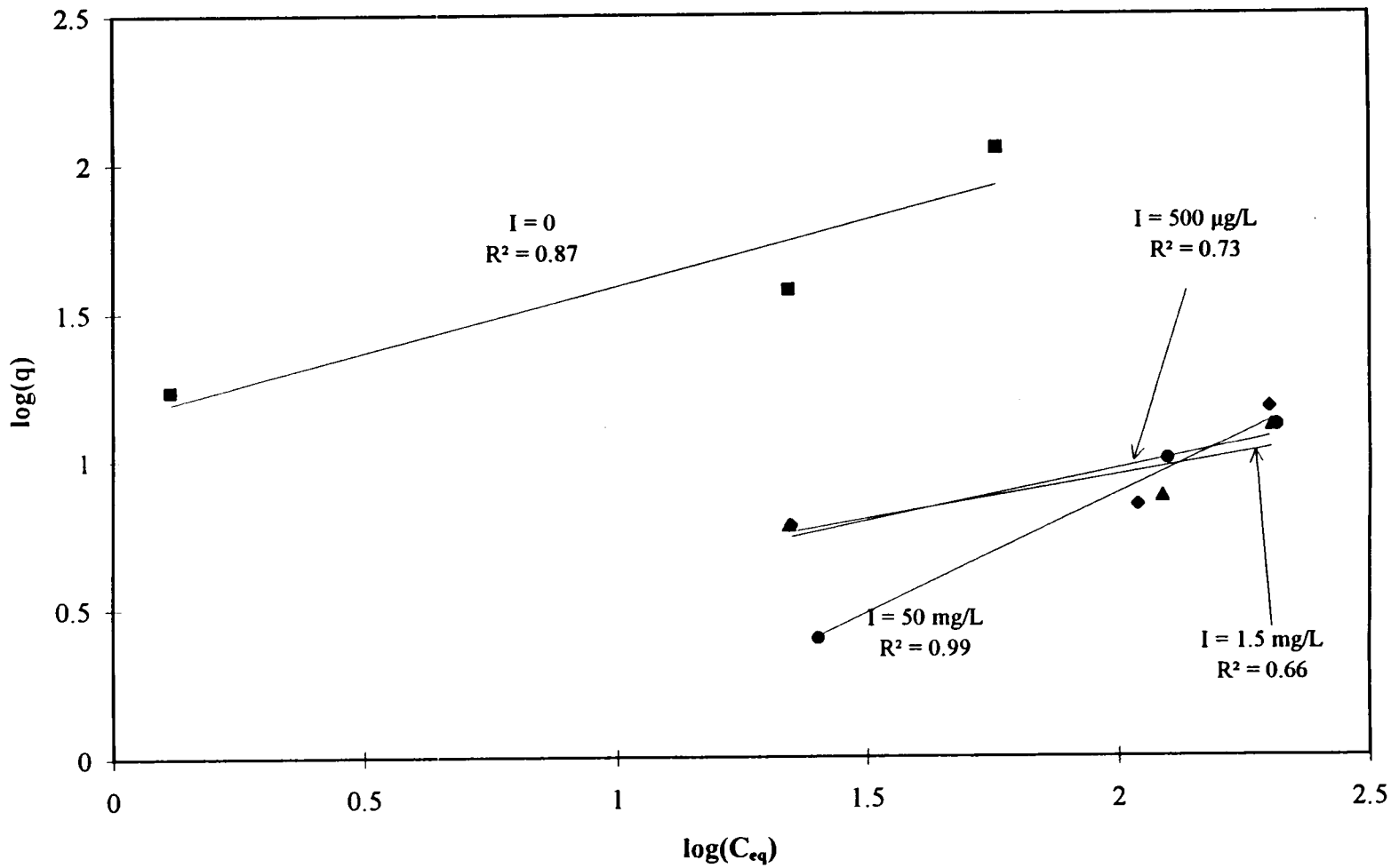


Figure 4.7 continued.
(c) Freundlich Isotherm.

approximated by the linear adsorption model, although none showed particularly good fit at all iodide concentrations. Only suspensions without iodide showed significant increases in adsorption with increasing aqueous mercury concentration. With the addition of iodide, mercury adsorption increased slightly with increasing aqueous mercury concentration.

Figure 4.8 illustrates the adsorption of mercury by illite with increasing concentration of aqueous mercury at pH 8.5. The data follows the Langmuir model of adsorption, indicating a limited number of surface sites and an adsorption maxima for a given iodide concentration. The difference in the adsorption models at high and low pH is likely due to the species of mercury present in solution. At low pH, essentially all mercury in solution is in the iodide form with the exception of the suspensions with no iodide added. Since iodide complexes with essentially all mercury in solution, little mercury is available to adsorb, so the surface sites available for adsorption are not limiting. With the increase in pH, $Hg(OH)_2^\circ$ becomes the dominant species, and is initially (specifically) adsorbed by the surface. As the concentration of mercury increases, surface sites become occupied, and adsorption tapers off. The effect of decreasing adsorption with increasing aqueous mercury concentration is evident in the magnitude of the distribution coefficient (K_D). For a given iodide concentration, K_D values decreased with increasing mercury concentration (Appendix), reflecting the non-linear nature of the increase in mercury adsorption.

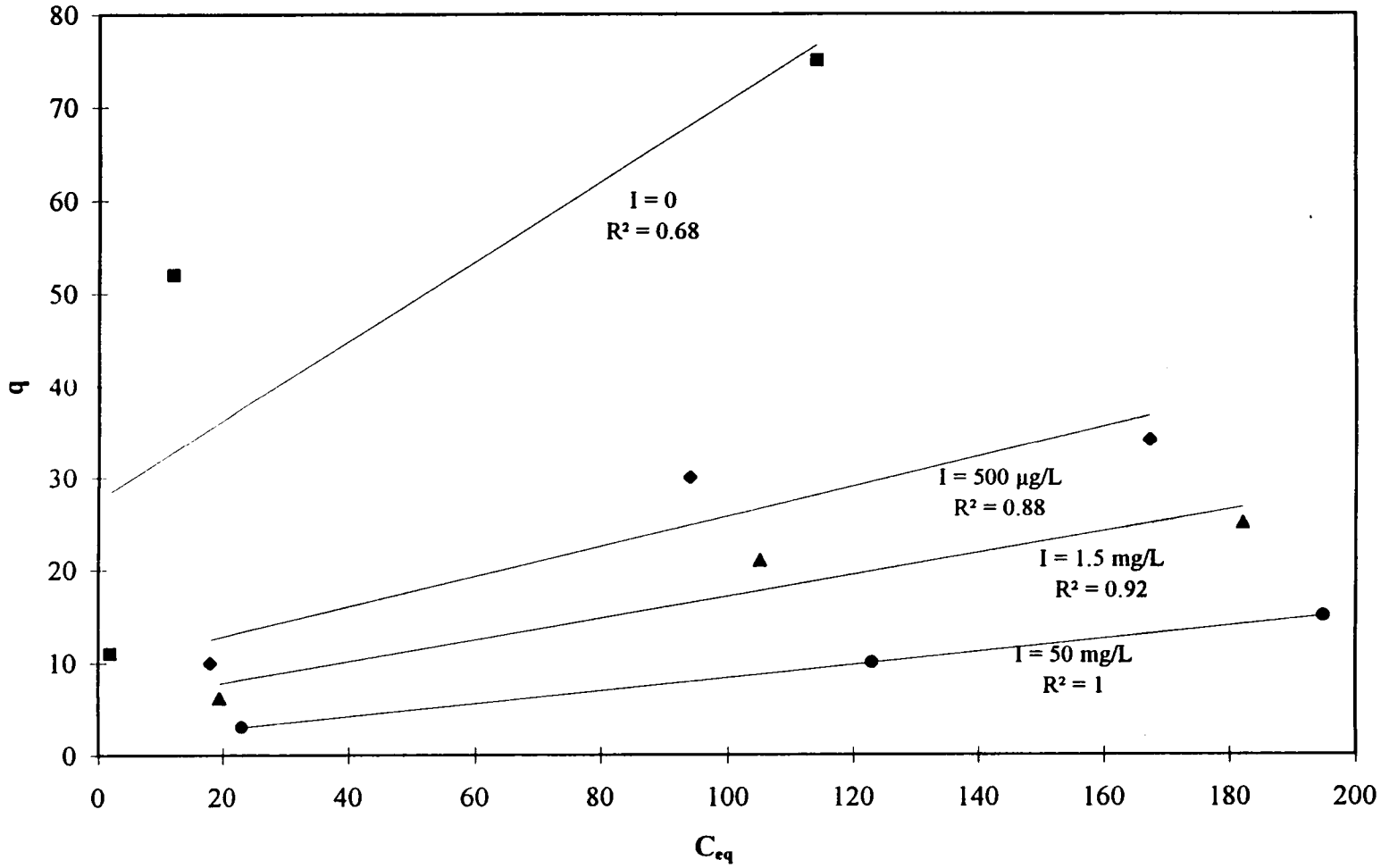


Figure 4.8: Adsorption Isotherms for Mercury Adsorption by Illite, pH = 8.5.
(a) Linear Isotherm.

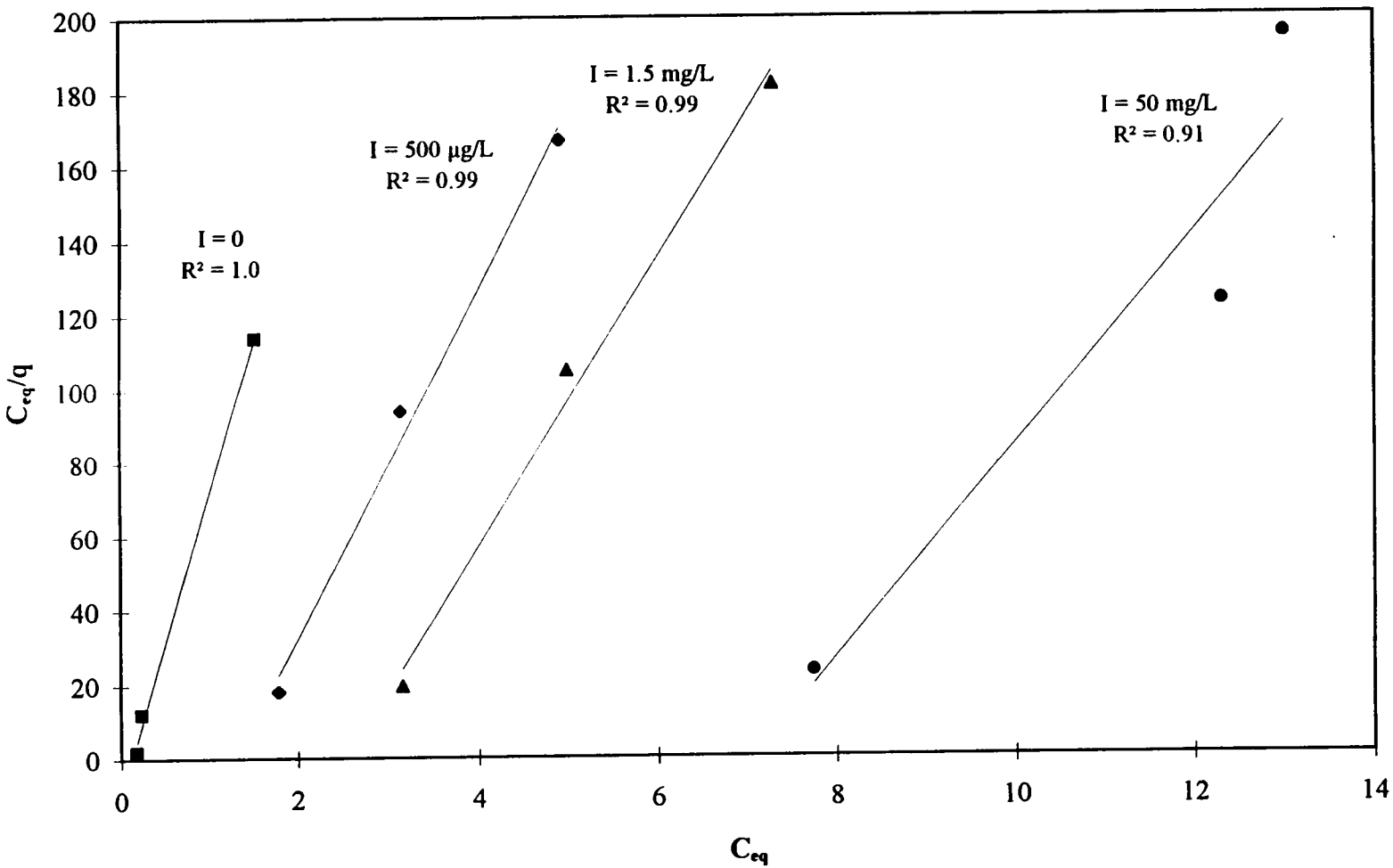


Figure 4.8 continued.
(b) Langmuir Isotherm.

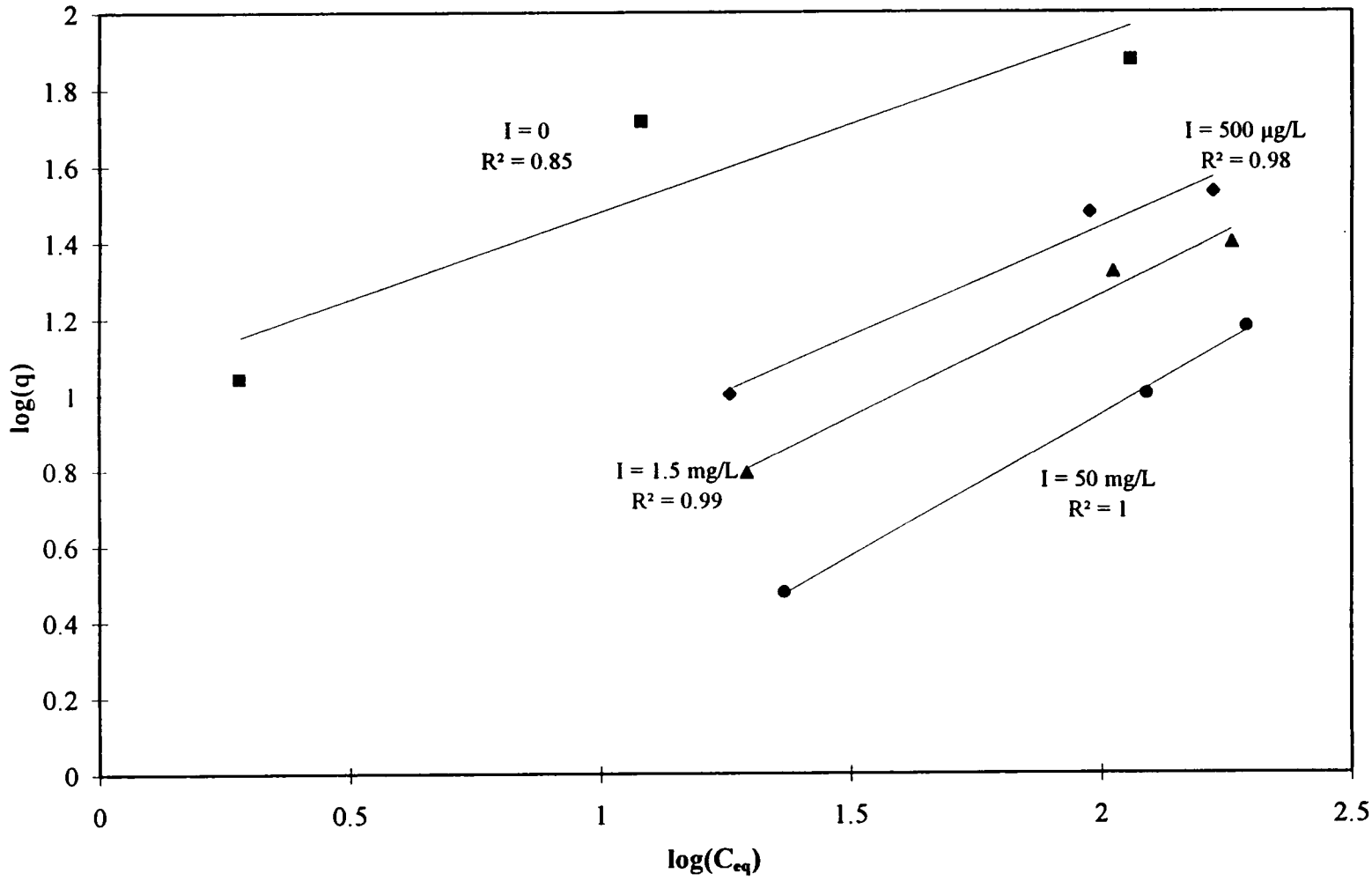


Figure 4.8 continued.
(c) Freundlich Isotherm.

4.2.2 Mercury Adsorption by Illite in the Presence of NOM

4.2.2.1 *Mass Balance*

The addition of organic matter caused an improvement in the overall mass balance during equilibration (MB1). Figure 4.9 illustrates the effect of iodide concentration on median MB1 values in suspension containing the illite-NOM matrix. Minimum MB1 values were typically greater than 70% in all suspensions, even in suspensions with no iodide added. Losses in suspensions with no iodide were typically less than 25%, with a few exceptions when Hg = 100 μg/L, and were close to 10% at low pH. The improved mass balance suggests that organic matter also plays a role in the preservation of mercury. More mercury is adsorbed, preventing less loss from solution; in addition, the mercury that remains in solution is tied up as a soluble organic complex that further prevents losses to the container.

In illite/NOM suspensions with iodide added, MB1 values also improved. Losses ranged from 29% to 0% when I^- = 500 μg/L, from 38% to 0% when I^- = 1.5 mg/L, and from 32% to 0 % when I^- = 50 mg/L. Losses depended on both pH and mercury concentration. At high pH values and lower mercury concentrations the losses were greater. For the range 4.0 < pH < 8.5, MB1 values were greater than 80% for all iodide and mercury concentrations. At pH < 7.0, MB1 values were 87% or higher.

The addition of organic matter improved MB2 values (Figure 4.10). MB2 values were consistently greater than 90%, and only rarely less than 85% in suspensions of high pH and low (< 500 μg/L) iodide concentrations. The improved

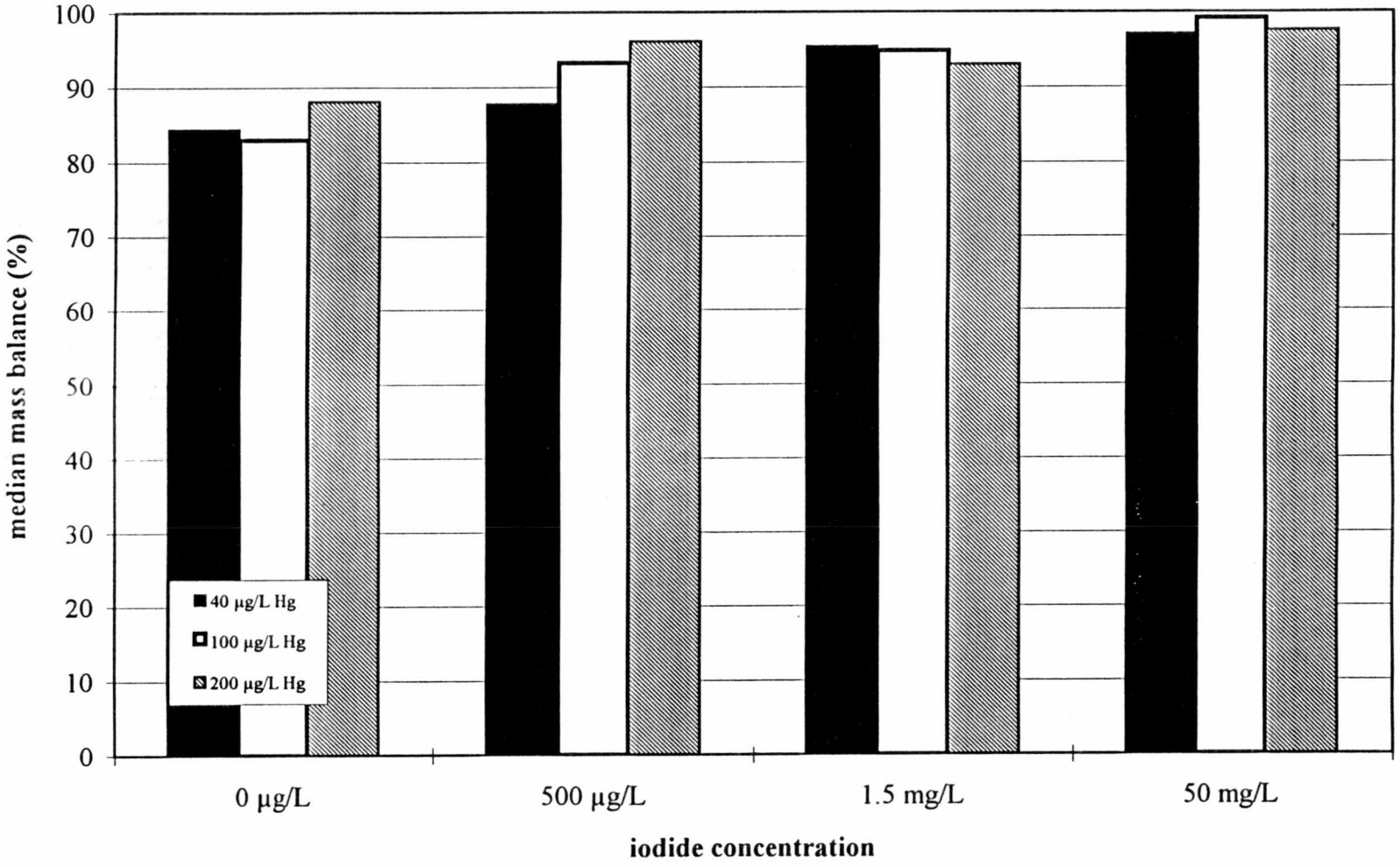


Figure 4.9: Median Mass Balance During 18-hour Equilibration for Mercury-Illite-NOM Suspensions (MB1).

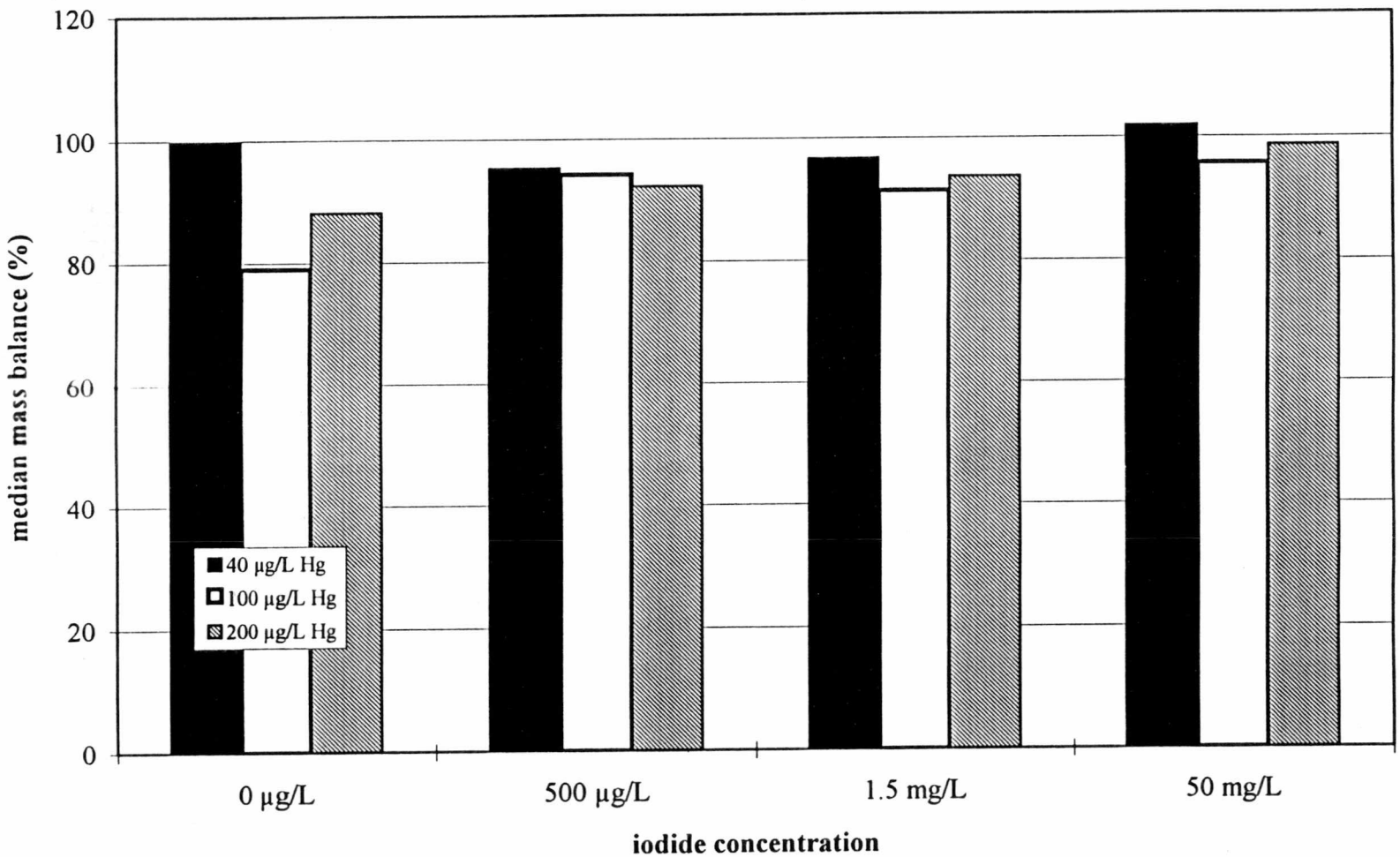


Figure 4.10: Median Mass Balance During Filtration for Mercury-Illite-NOM Suspensions (MB2).

MB2 values suggest that soluble organic acids or other natural ligands form mercury complexes and thereby decrease loss due to sorption to the filter apparatus.

4.2.2.2 *Effect of pH and Iodide Concentration*

The effect of pH on adsorption was more pronounced in the presence of NOM (Figure 4.11). When no iodide was added, increasing pH above the pH of the adsorption maxima caused a decrease in mercury adsorbed. Maximum adsorption (~90%) was achieved around pH 4.5, regardless of initial mercury concentration. Newton et al. (1976) reported a similar maxima at about pH 4.5 for mercury adsorption by bentonite in the absence of chloride.

The presence of iodide in suspensions of illite and NOM caused a decrease in mercury adsorption from approximately 90% ($I^- = 0$) to less than 20% (500 μg/L $\leq$ I $\leq$ 50 mg/L) at pH < 5.5. At higher pH values, adsorption increased regardless of iodide concentration. Iodide concentrations of 500 μg/L or less had no effect on adsorption at high pH values (pH > 9.5). In suspensions without NOM, no adsorption occurred at iodide concentrations over 50 mg/L regardless of the pH. With the addition of organic matter, adsorption of mercury occurred in all suspensions, particularly at high pH. The fact that overall adsorption percentages were greater in suspensions with NOM than in the suspensions with illite above, and that pH effects were noticed at lower pH values in suspensions with organic matter, suggests that NOM may be as strong a ligand of mercury as iodide.

K_D values increased dramatically in suspensions with organic matter, reflecting the preference of mercury for the organic phase. Table 4.12 shows the values of K_D

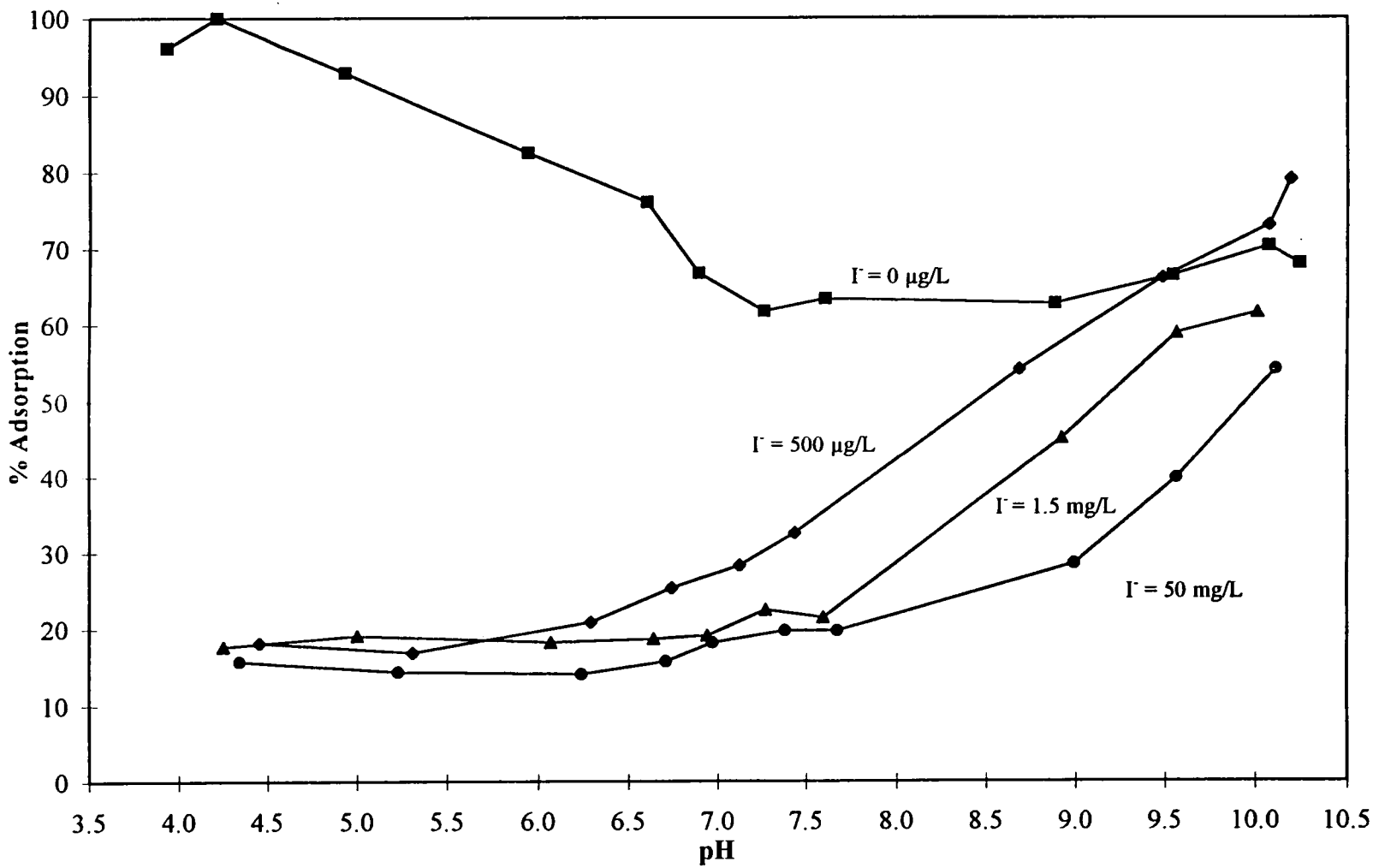


Figure 4.11: Effect of pH and Iodide on the Adsorption of Mercury by Illite-NOM (1 g/L).
(a) Hg_T = 40 µg/L.

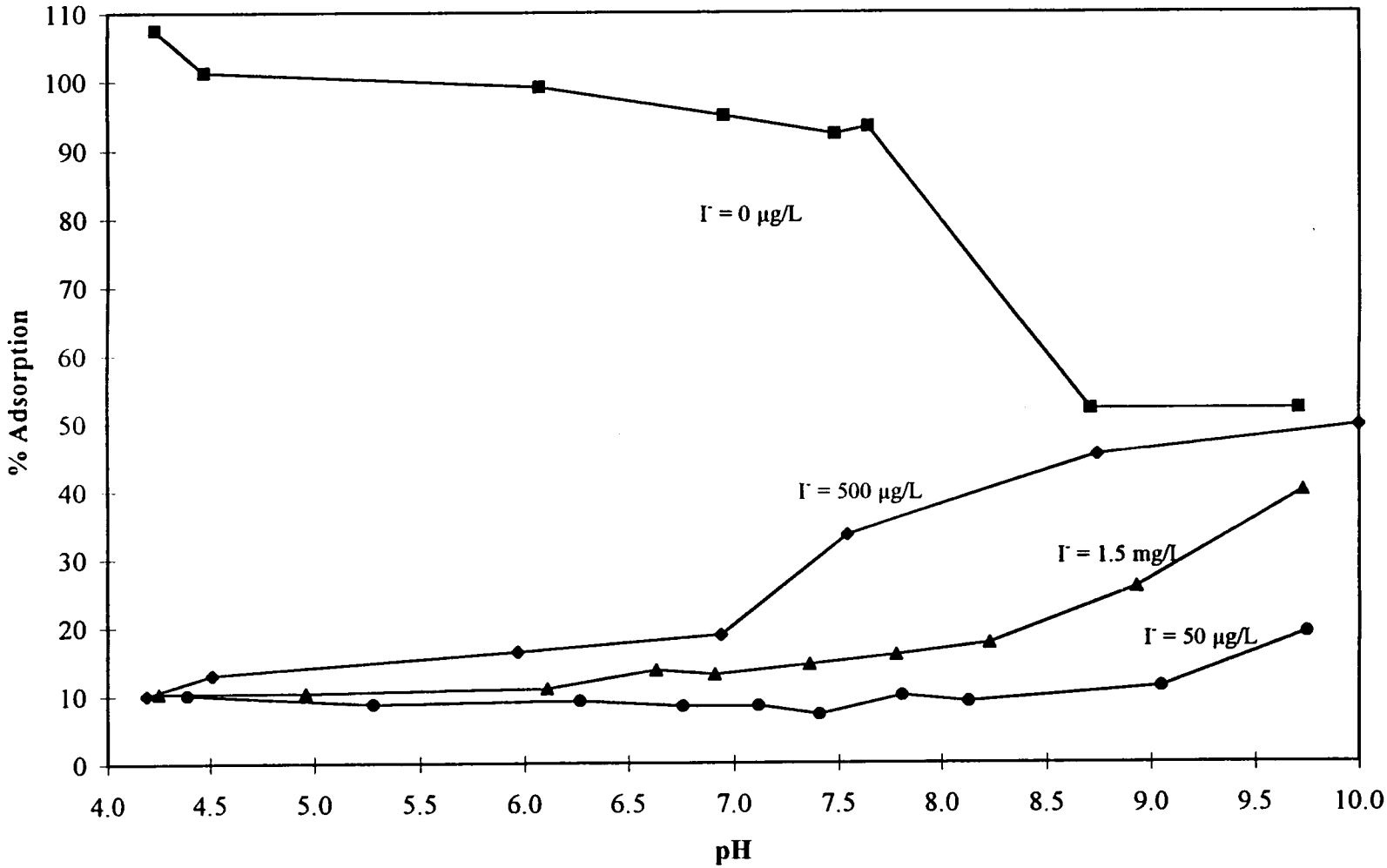


Figure 4.11 continued.
(b) Hg_T = 100 µg/L.

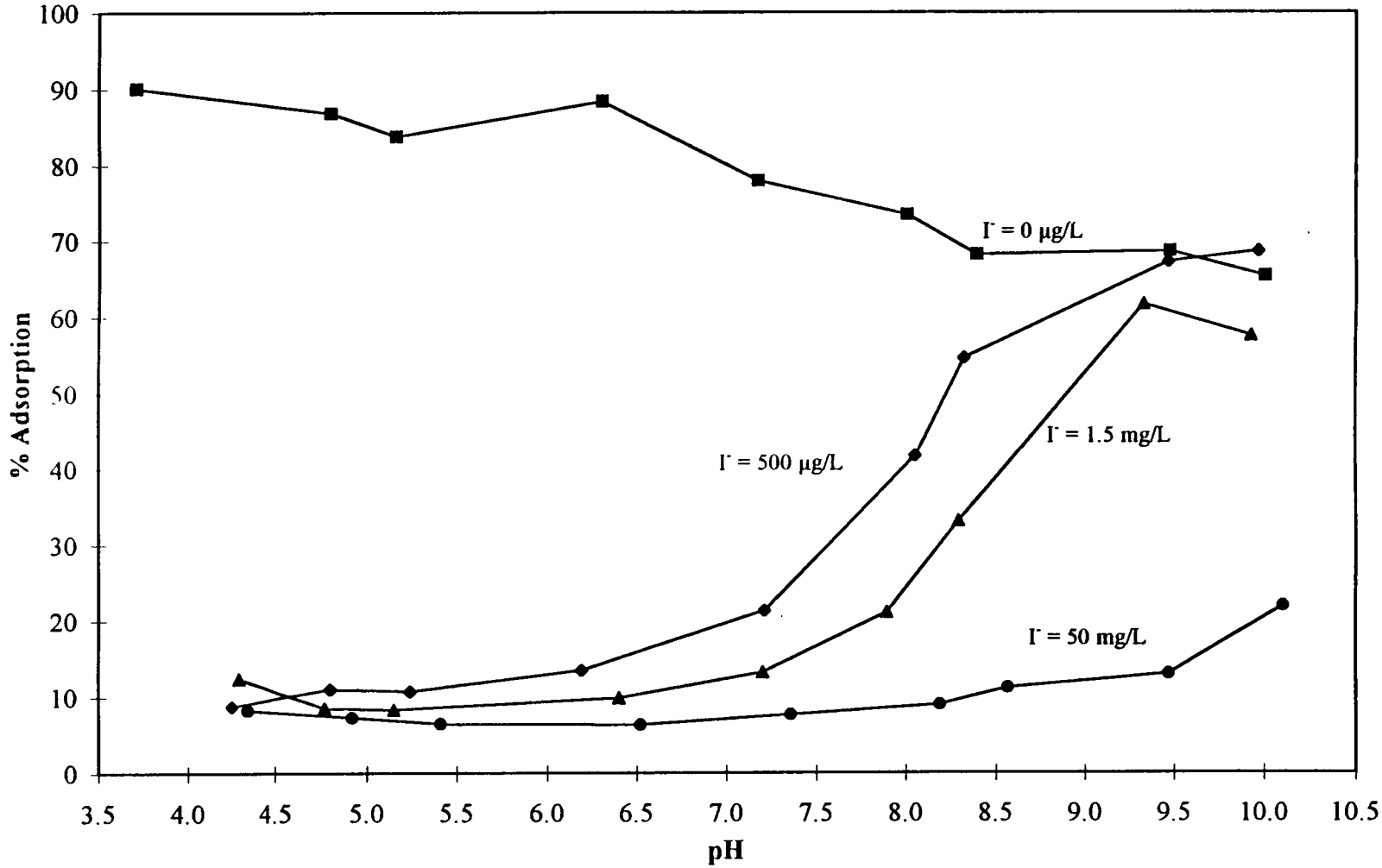


Figure 4.11 continued.
(c) Hg_T = 200 µg/L.

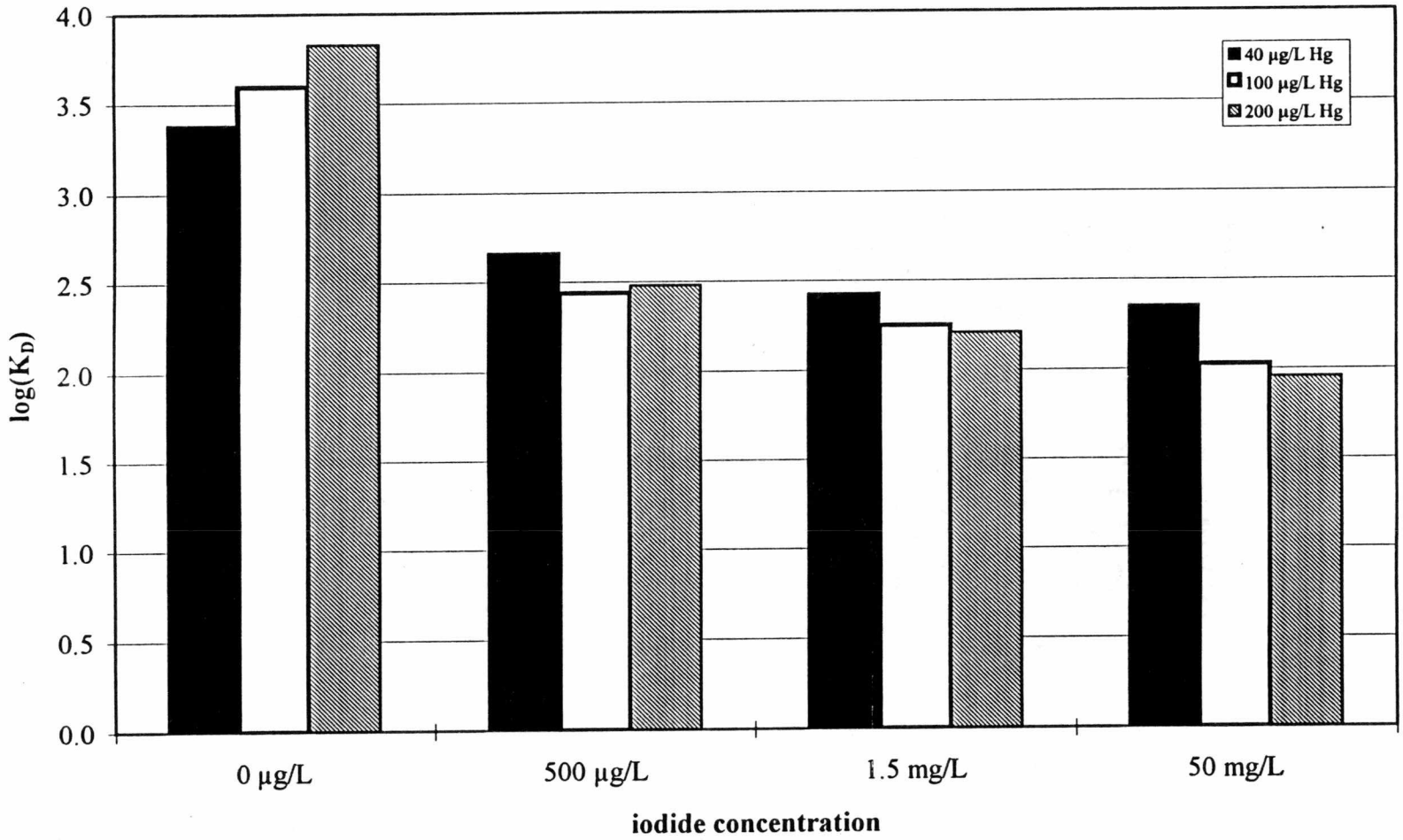


Figure 4.12: Median Distribution Coefficients (K_D) for Mercury-Illite-NOM Suspensions.

for several pH values and initial mercury and iodide concentrations. Comparing with Figure 4.6, the effect of NOM on K_D becomes clear; K_D's increased, sometimes by close to an order of magnitude when organic matter was added.

In the absence of iodide, the addition of NOM resulted in a decrease in K_D values at high pH, yet mercury uptake was not greater in suspensions without NOM. Instead, the concentration of aqueous mercury in suspensions without NOM is affected by significant losses to the container (MB1) and the filtration unit (MB2). In suspensions with NOM, the concentration of adsorbed mercury increases due to the more favorable organic surface; likewise, the concentration of aqueous mercury also increases due to improved preservation from organic acids. The result is an increase in the aqueous mercury concentration in suspensions with NOM causing a misleading decrease in the magnitude of K_D.

Adsorption edges develop at lower pH in suspensions with iodide and NOM. In addition, adsorption edges were more gradual in suspensions with NOM than in suspensions without NOM. While the exact reason for this is unknown, it is possible that soluble organics compete with soil particles for aqueous mercury and that changes in pH cause a gradual improvement in the potential for mercury adsorption, either by weakening the soluble Hg-NOM complex or improving the insoluble surface.

4.2.2.3 *Effect of Mercury Concentration*

Adsorption isotherms were constructed for suspensions of illite-NOM, interpolating data when necessary (Section 4.2.1.3). Figure 4.13 shows the fit of the data to the

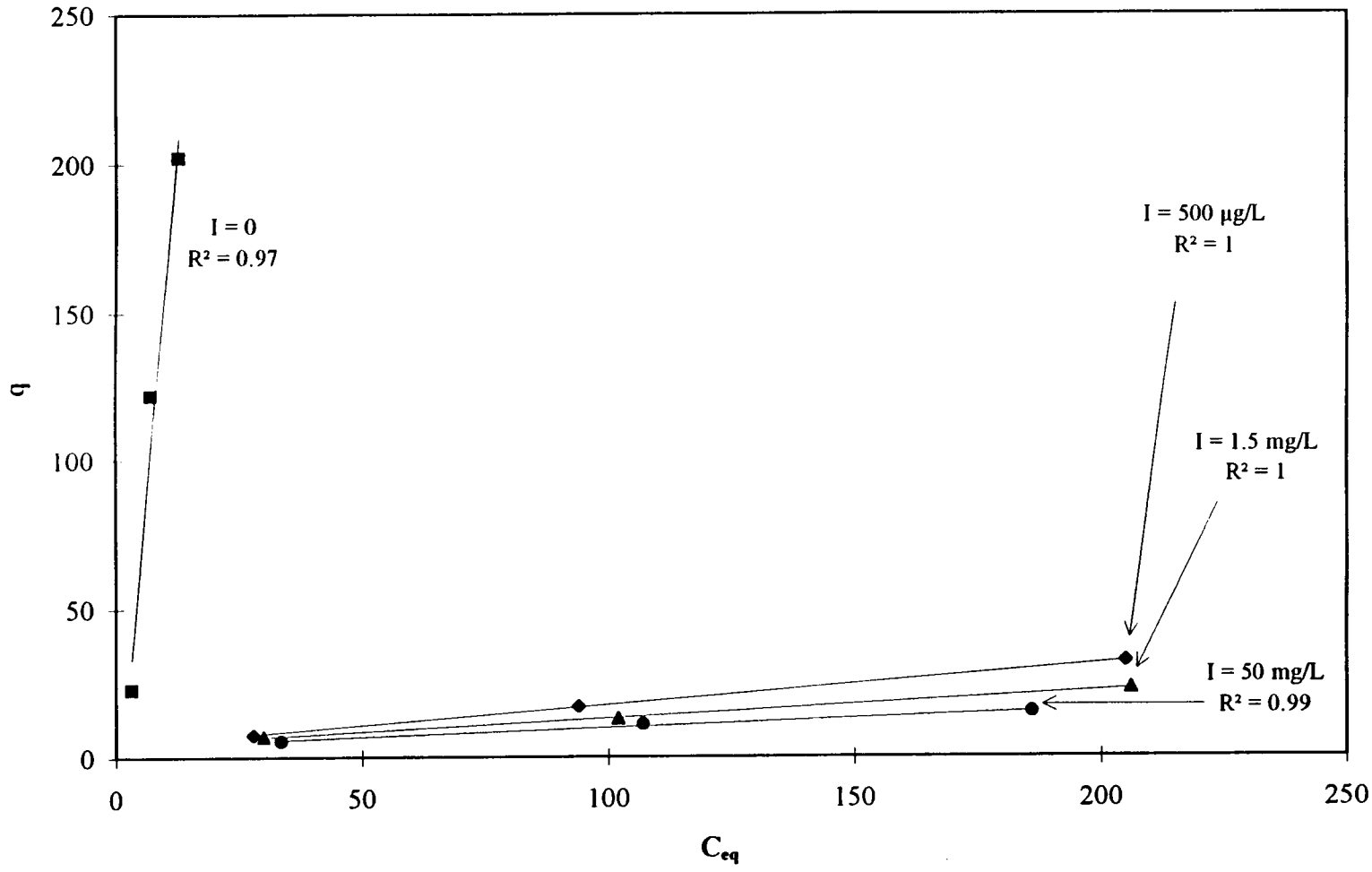


Figure 4.13: Adsorption Isotherms for Mercury Adsorption by Illite-NOM, pH = 6.
(a) Linear Isotherm.

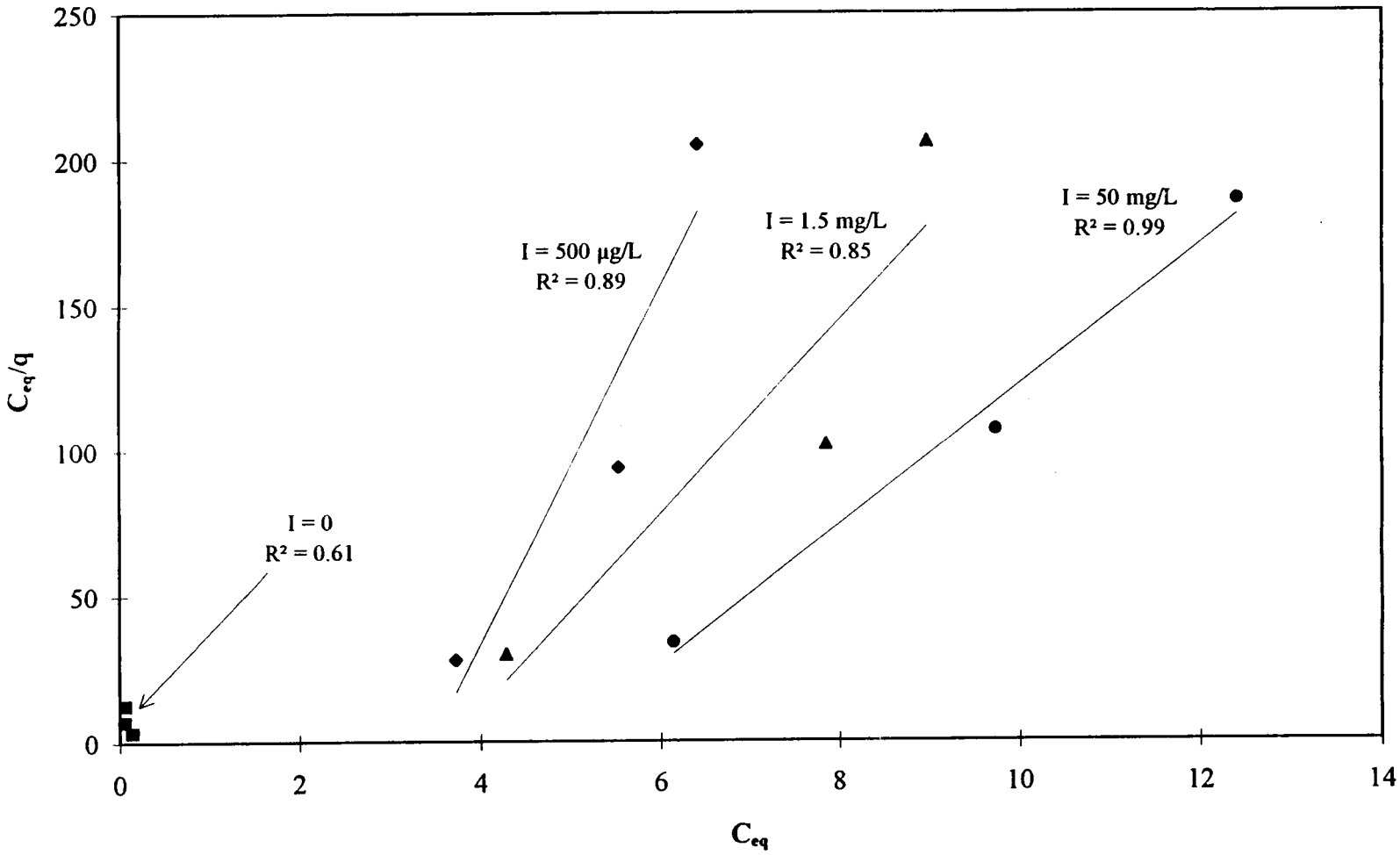


Figure 4.13 continued.
(b) Langmuir Isotherm.

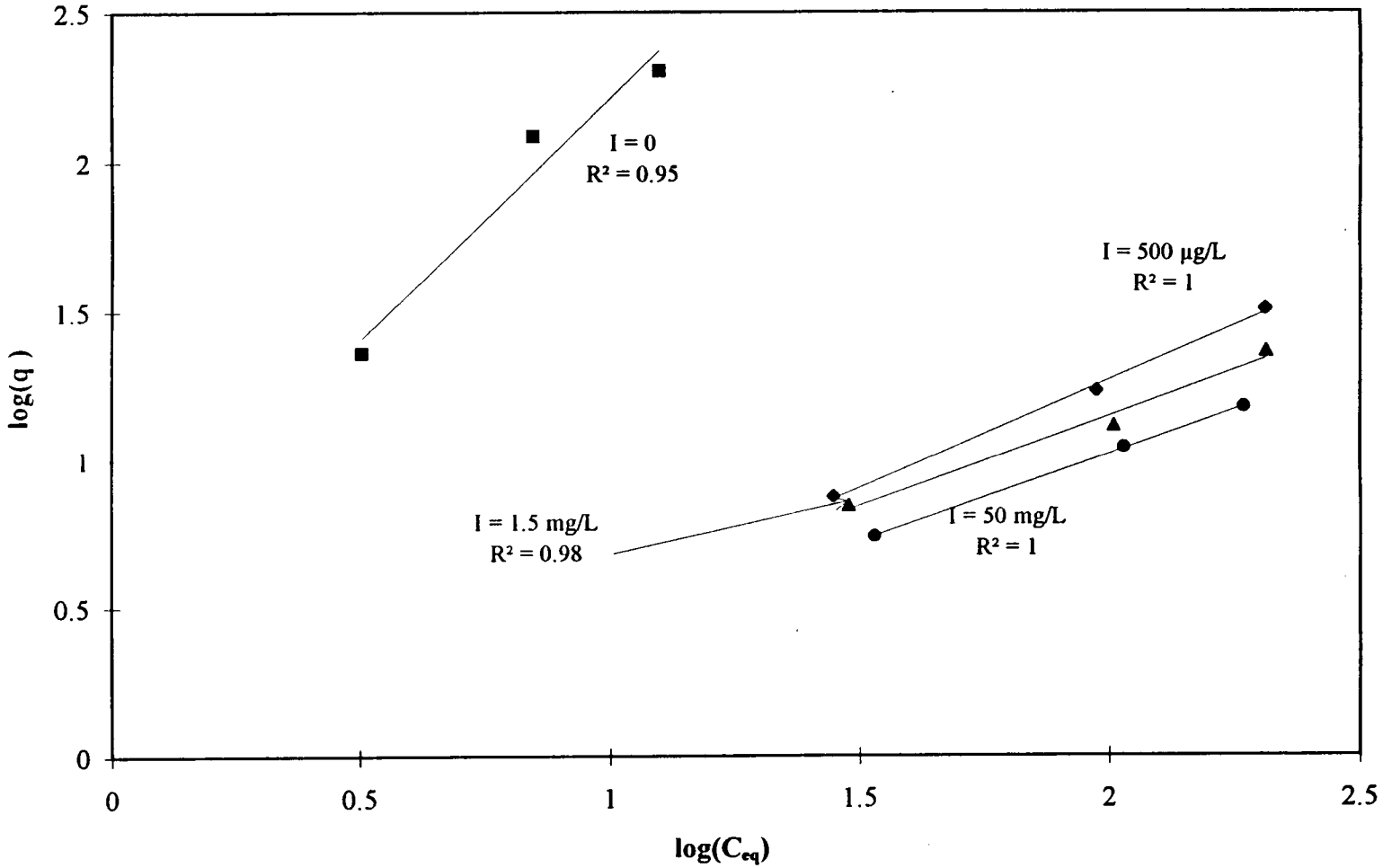


Figure 4.13 continued.
(c) Freundlich Isotherm.

three models at pH 6. Once again, the linear adsorption model exhibited the best fit of the experimental data at pH 6. As the pH was increased to 8.5 (Figure 4.14) in suspensions with NOM, adsorption remains fairly linear. The surface sites are not limiting when NOM was added; therefore adsorption increases linearly with increased aqueous mercury concentrations.

4.3 Mercury Desorption from Contaminated Soils

Ideally, desorption of mercury from soils should retrace the adsorption pattern observed in artificially-contaminated soils. However, the natural soil environment can differ greatly from the artificially-contaminated samples in the laboratory. Temperature, complexing ligands, solution to solid ratio, pH, and E_H vary, and kinetic limitations affect the natural environment so that equilibrium is rarely attained. Therefore, the ability of iodide to desorb mercury from a contaminated natural soil was investigated.

4.3.1 Mercury Extraction with Iodide and Other Halides

A simple experiment was developed to assess the ability of different halide salts to desorb mercury from contaminated soils obtained from the EFPC floodplain. The results are shown in Table 4.2. Suspensions were prepared by adding solutions of

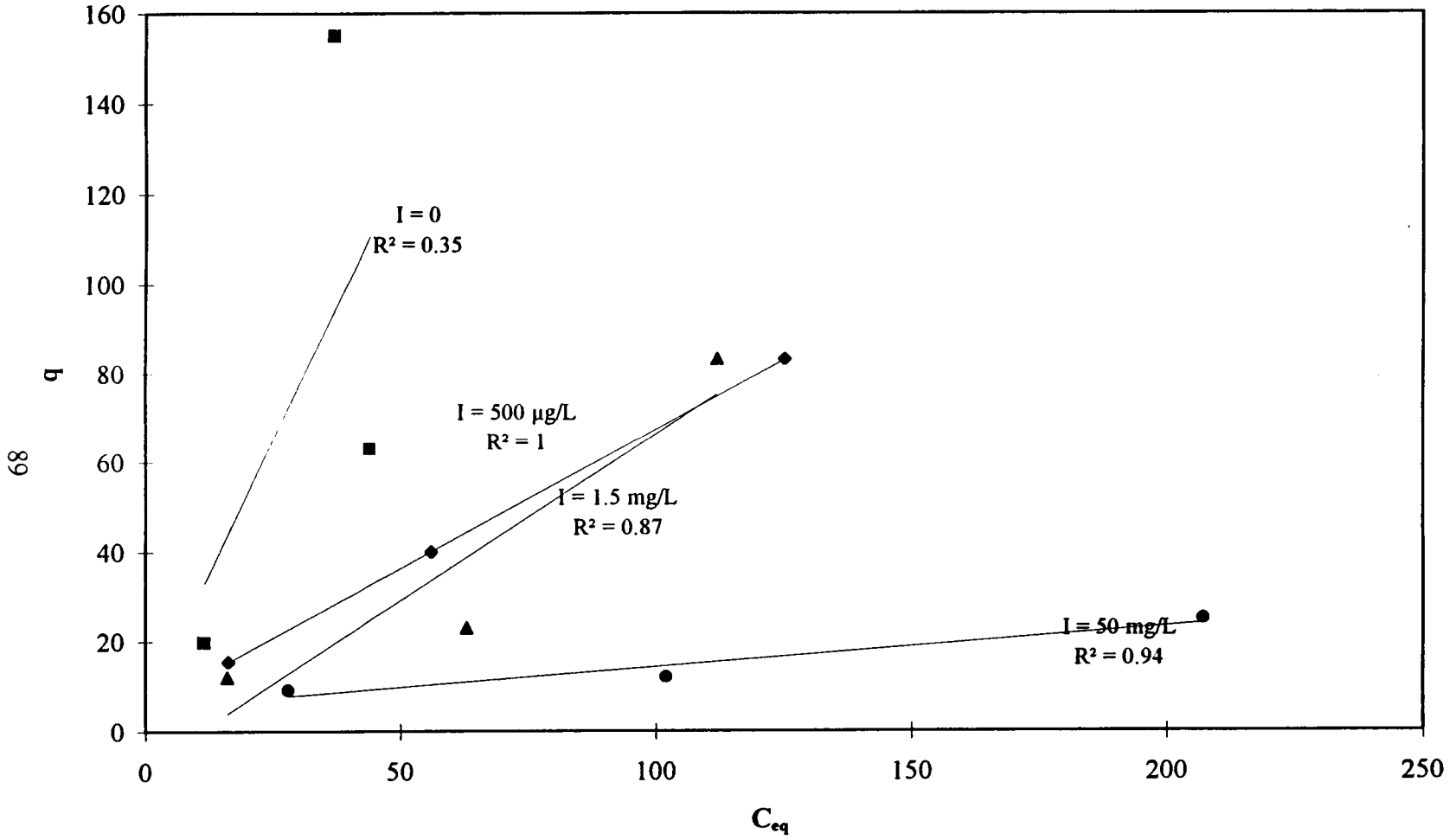


Figure 4.14: Adsorption Isotherms for Mercury Adsorption by Illite-NOM, pH = 8.5.
(a) Linear Isotherm.

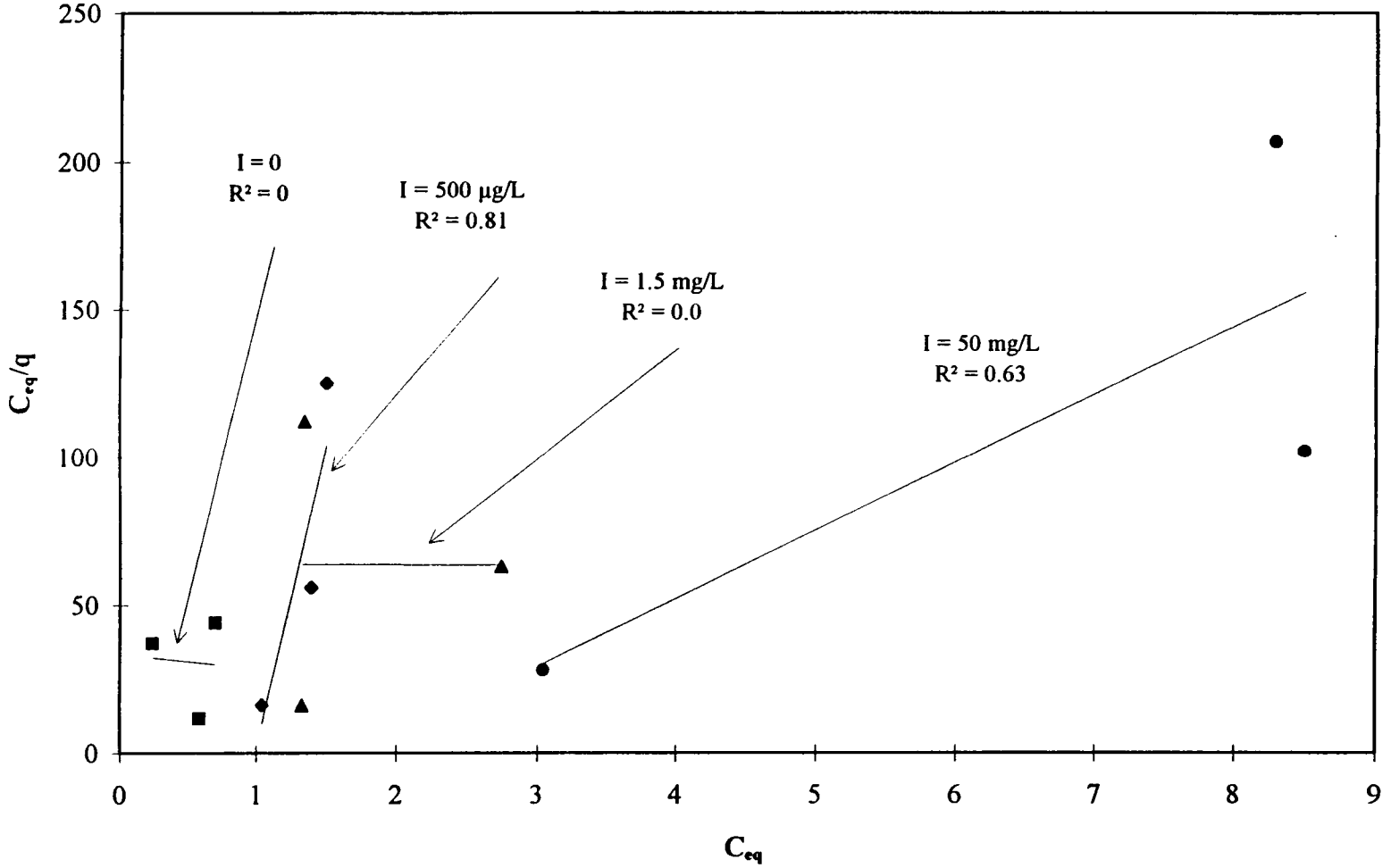


Figure 4.14 continued.
(b) Langmuir Isotherm.

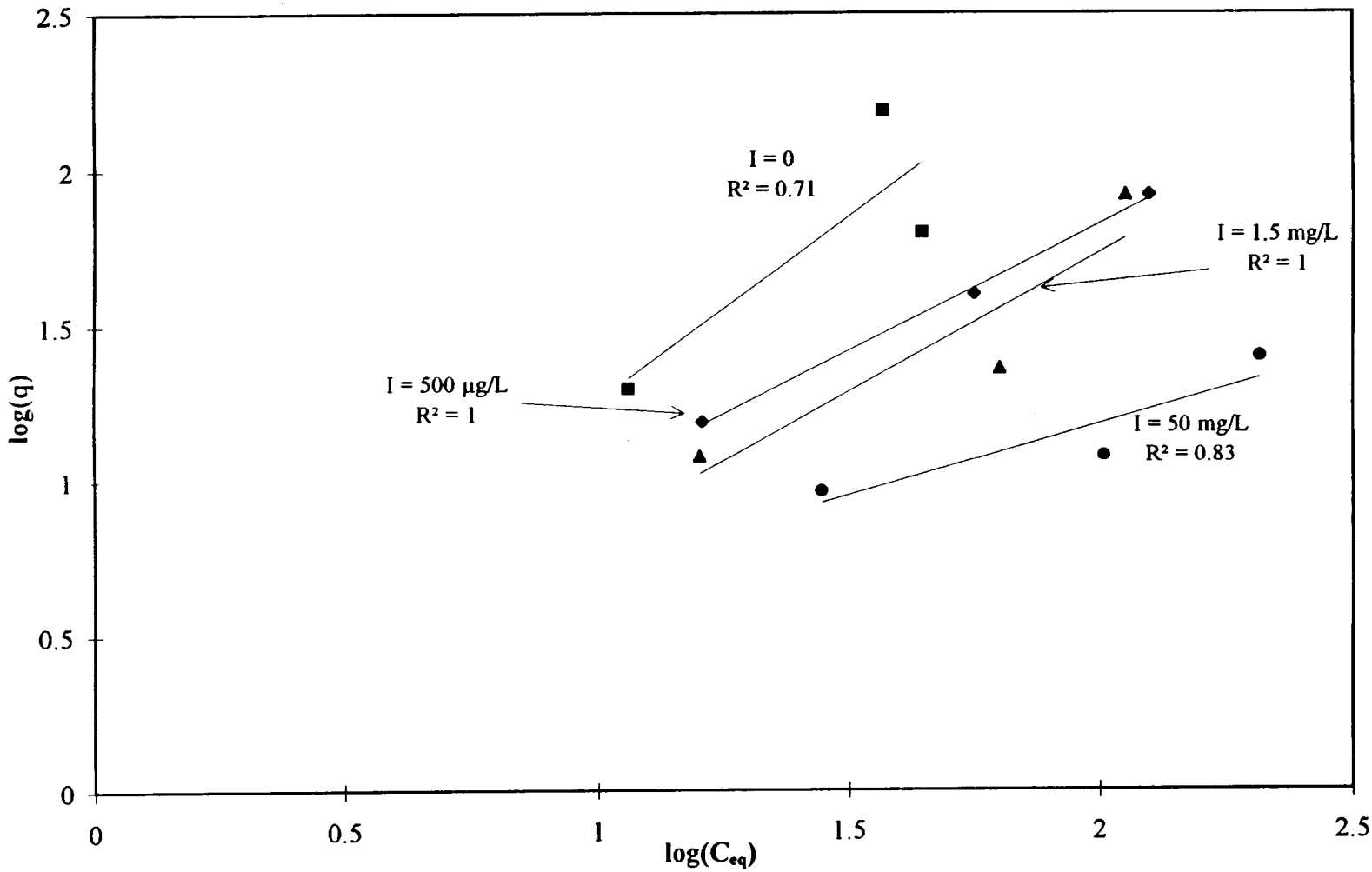


Figure 4.14 continued.
(c) Freundlich Isotherm.

Table 4.2: Effeciency of Different Halide Solutions
at Extracting Mercury from Contaminated Soils.

Concentration	Percent Extracted (%)			
M	F^-	Cl^-	Br^-	I^-
0.001	0.0056	0.0073	0.013	0.041
0.01	0.01	0.012	0.023	1.1
0.1	0.01	0.017	0.04	5.9

each halide salt (0.1 M, 0.01 M, and 0.001 M) to the highly contaminated soil (Hg = 2700 mg/kg) from the EFPC floodplain. Desorption of mercury was measured by CVAA after 48 hours of mixing.

Iodide was the most effective mercury extractant of all halides; more mercury was extracted at the lowest iodide concentration (0.001 M) than at the highest (0.1 M) concentration of any other halide. However, copious quantities of iodide (0.01 M or 1.27 g/L) were required to extract an appreciable amount of mercury. A 0.001 M iodide solution (127 mg/L) was capable of extracting only, on average, 0.041% of the total mercury; desorption increased to 1.1% when I = 0.01 M (1.27 g/L), and 5.9% when I = 0.1 M (12.7 g/L). Such high concentrations of iodide will rarely occur.

A second extraction using 0.001 M iodide was performed on several surface soils from a contaminated site in Mississippi (Table 4.3). Iodide extracted between 25% and 86% of the total mercury in these soils (no mercury was extracted with distilled water).

4.3.2 Mercury Extraction with Iodide Leachate

An actual leachate generated from soils treated with the Foust (1993) protocol was tested for its ability to mobilize soil-bound mercury. The generation of this leachate (Leachate 1) is illustrated in Figure 4.15. Soils extracted with KI/I_2 were resuspended for 24 hours in distilled water and then filtered. This filtrate (considered Leachate 1) contained other mercury-reactive substances, such as residual iodine (I_2), capable of

Table 4.3: Mercury Extracted from Mississippi Soils
Using 0.001 M KI

Sample	Total Hg in Soil	Percent Extracted
	µg/kg	%
Soil 1	69	43
Soil 1 (duplicate)	61	25
Soil 2	13	86

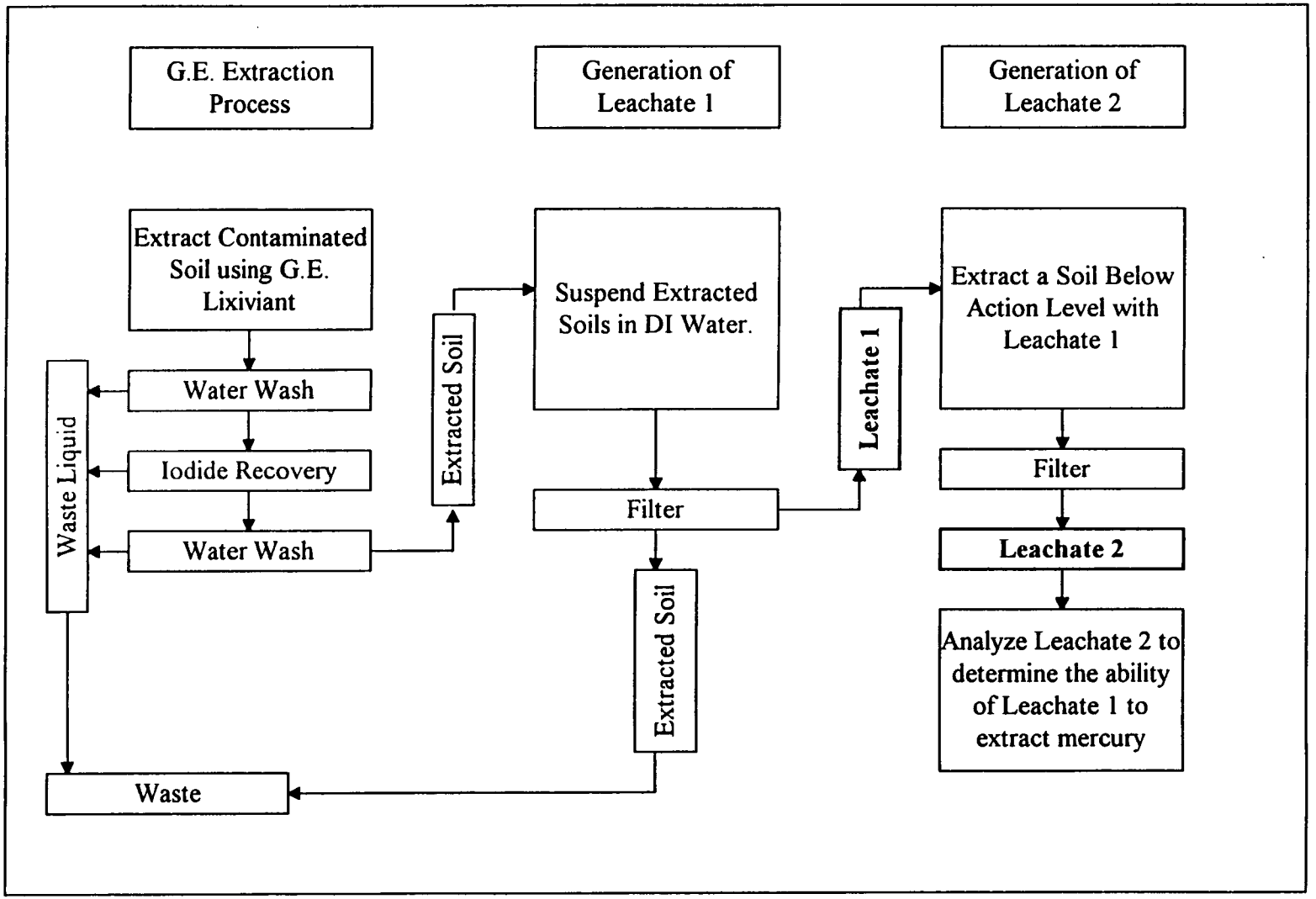


Figure 4.15: Process Diagram for the Generation of Sample Leachates

oxidizing HgS(s) and making available more Hg^{2+} for iodide complexation. Leachate 1 also contained dissolved NOM that could improve the leaching of mercury. Table 4.4 lists some characteristics of Leachate 1.

Leachate 1 was applied to an EFPC soil with a low mercury content (28 mg/kg), well below the most conservative action level (50 mg/kg) suggested (Barnett et al., 1994). Therefore, the soil would not qualify for cleanup; however, it is representative of soil which could experience unintended extraction with iodide. Leachate 1 was applied to this soil in two concentrations: (1) the undiluted form, and (2) a 1:100 dilution typically utilized by the EPA to account for the effects of advection, dispersion, and other dilution factors when determining the hazard potential of a waste as per 40 CFR 261.

A second leachate (Leachate 2) was generated after this extraction and analyzed for total mercury (Figure 4.15). The results of this extraction are shown in Table 4.5, and resemble those for the extraction of a more contaminated floodplain soil. Diluted Leachate 1 (I^- = $1.67x10^{-5}$ M or 2.12 mg/L) was ineffective in extracting mercury. No mercury was detected (detection limit = 0.4 μg/L) in Leachate 2, regardless of the time of contact; less than 0.007% of the mercury was extracted. Undiluted Leachate 1 (I^- = $1.67x10^{-3}$ M or 212 mg/L) showed some capacity to extract mercury over a long time period; while none was detected in Leachate 2 after 4 hours, suspensions agitated over 24 hours extracted, on average, 0.079% of the total mercury in the suspension. This corresponds well to typical

Table 4.4: Characteristics of Leachate
Generated Using Foust (1993) Protocol.

iodide concentration	212 mg/L (1.67×10^{-3} M)
mercury concentration	< 0.4 μg/L (< 2×10^{-9} M)
pH	7.12
suspended solids	0 mg/L
color	yellow, clear
odor	distinct iodine aroma

Table 4.5: Mercury Extracted Using Dilutions of Soil Washing Leachate.

Sample	% extracted (4 hours)	% extracted (24 hours)
1:100 dilution, rep 1	< 0.007	--
1:100 dilution, rep 2	< 0.007	--
1:100 dilution, rep 3	< 0.007	--
no dilution, rep 1	< 0.018	--
no dilution, rep 2	< 0.018	--
no dilution, rep 3	0.079	--
1:100 dilution, rep 1	--	< 0.007
1:100 dilution, rep 2	--	< 0.007
1:100 dilution, rep 3	--	< 0.007
no dilution, rep 1	--	0.079
no dilution, rep 2	--	0.088
no dilution, rep 3	--	0.069

extraction of mercury from highly contaminated soil (2700 μg/g) using 0.001 M iodide.

The inability of either Leachate 1 or iodide to extract mercury from EFPC soils is likely due to the chemical form of the mercury in the soil matrix. Many have attempted to determine the chemical form of mercury in EFPC soils. Revis (1989) used sequential extraction to conclude that most mercury in the EFPC floodplain is mercuric sulfide (HgS(s)). However, Barnett et al. (1994) applied three different sequential extraction protocols (Sakamoto, et al., 1992; Revis, et al., 1989; and Miller, 1994) to several soils from the EFPC floodplain (including the EFPC soil used in Section 4.3.1 and 4.3.2) and found that different protocols yielded different fractions of total mercury as HgS(s). Depending on the extraction procedure, the 2700 μg/g soil contained either 63% (Sakamoto), 59% (Revis), or 41% (Miller) HgS(s), while the 28 μg/g soil contained either 66% (Sakamoto), 33% (Revis), or 6.1% (Miller) HgS(s). Barnett et al. (1994) used hydrometallugic separation methods in conjunction with X-Ray diffraction to positively identify HgS(s) particles in EFPC soils, strengthening the conclusion that mercury in EFPC soils was in part HgS(s). Additional evidence that the dominant form of mercury was HgS(s) was supplied by Barnett and Turner (1994) who noticed a 1:1 relationship between the total mercury and the total sulfur concentration in EFPC soils, possibly indicating that mercury in EFPC soils is bound as HgS(s).

While no speciation information exists for the Mississippi soils, the mercury is believed to be adsorbed divalent mercury rather than crystalline HgS(s), since the

soils are surface soils, and therefore are not subject to seasonal oxic/anoxic conditions typical of EFPC soils. That large percentages of mercury were extracted from these soils indicates that adsorbed mercury may be vulnerable to extraction by concentrations of iodide typical in residual soil washing leachates.

The proportion of adsorbed mercury desorbed from floodplain soils with iodide solution (0.001 M NaI) or undiluted leachate (1.67 mM) can be estimated by comparing these values with the amount of "dilute acid-extractable" mercury observed from two sequential extractions. "Dilute acid-extractions" are intended to remove non water-soluble mercury compounds (including adsorbed mercury) other than $Hg^{\circ}(l)$ and HgS(s). Both the Sakamoto and Miller extractions contain a dilute acid extraction, and the percent of total mercury extracted from the two soils investigated in this work during the dilute acid step are tabulated in Table 4.6. The two acid-extractable percentages give a possible range of the percent of mercury adsorbed in each soil. The similarity of the iodide-extractable and dilute acid-extractable percentages (particularly in reference to the Sakamoto extraction) suggests that much of the adsorbed mercury is extracted from floodplain soils; the mercury remaining is likely HgS(s) and $Hg^{\circ}(l)$.

Low concentrations of iodide alone are unable to extract mercury when it is present as HgS(s) due to thermodynamic limitations. The reaction of aqueous iodide with solid mercuric sulfide (metacinnibar) above pH 7.1 can be represented by:

$$HgS(s) + H^{+} + nI^{-} \rightleftharpoons HgI_n^{2-n} + HS^{-} \qquad (4.4)$$

Table 4.6: Percent of Total Mercury Extracted from EFPC Floodplain Soils Using Dilute Acids or Iodide.

EFPC Floodplain Soil	Percent Total Mercury Extracted (%)		
	Sakamoto*	Miller*	Iodide
(μg/g Hg)	(0.05 M H_2SO_4)	(0.2 M HNO_3)	(0.001 M I^-)
2700	0.0007	22	0.041
28	0.04	0.03	0.079

* from Barnett and Turner, 1994

and below pH = 7.1 by:

$$HgS(s) + 2\ H^+ + nI^- \rightleftharpoons HgI_n^{2-n} + H_2S \qquad (4.5)$$

An equilibrium constant, K, can be calculated from the free energy of the reaction (ΔG°_{rxn}), the temperature (°K), and the gas constant (R):

$$K = e^{-\frac{\Delta G^\circ_{rxn}}{RT}} \qquad (4.6)$$

where $\Delta G^\circ_{rxn} = \Delta G^\circ_{products} - \Delta G^\circ_{reactants}$

Values of K less than 1 indicate a reaction that is not thermodynamically favored. Using the thermodynamic data in Table 2.1 and additional data from Stumm and Morgan (1981), equilibrium constants can be calculated for reactions 4.4 and 4.5. When n = 4 (i.e. HgI_4^{2-}), the equilibrium constants for reactions 4.4 and 4.5 are $10^{-9.14}$ and $10^{-2.11}$ respectively; smaller equilibrium constants are calculated when n = 3 (K = $10^{-11.18}$ and $10^{-4.15}$ respectively) and n = 2 (K = $10^{-14.98}$ and $10^{-7.96}$ respectively).

Figure 4.16 illustrates the effect of pH and several iodide concentrations on the solubility of HgS(s). Clearly, only soils with high iodide concentrations (> 0.1 M or 12.7 g/L) will result in significant (> 1 μg/L or 5×10^{-9} M) mercury extraction. For conditions with lower iodide concentrations ($<3.94\times10^{-4}$ M or 50 mg/L), the pH values required to affect HgS(s) solubility will not be encountered in the environment.

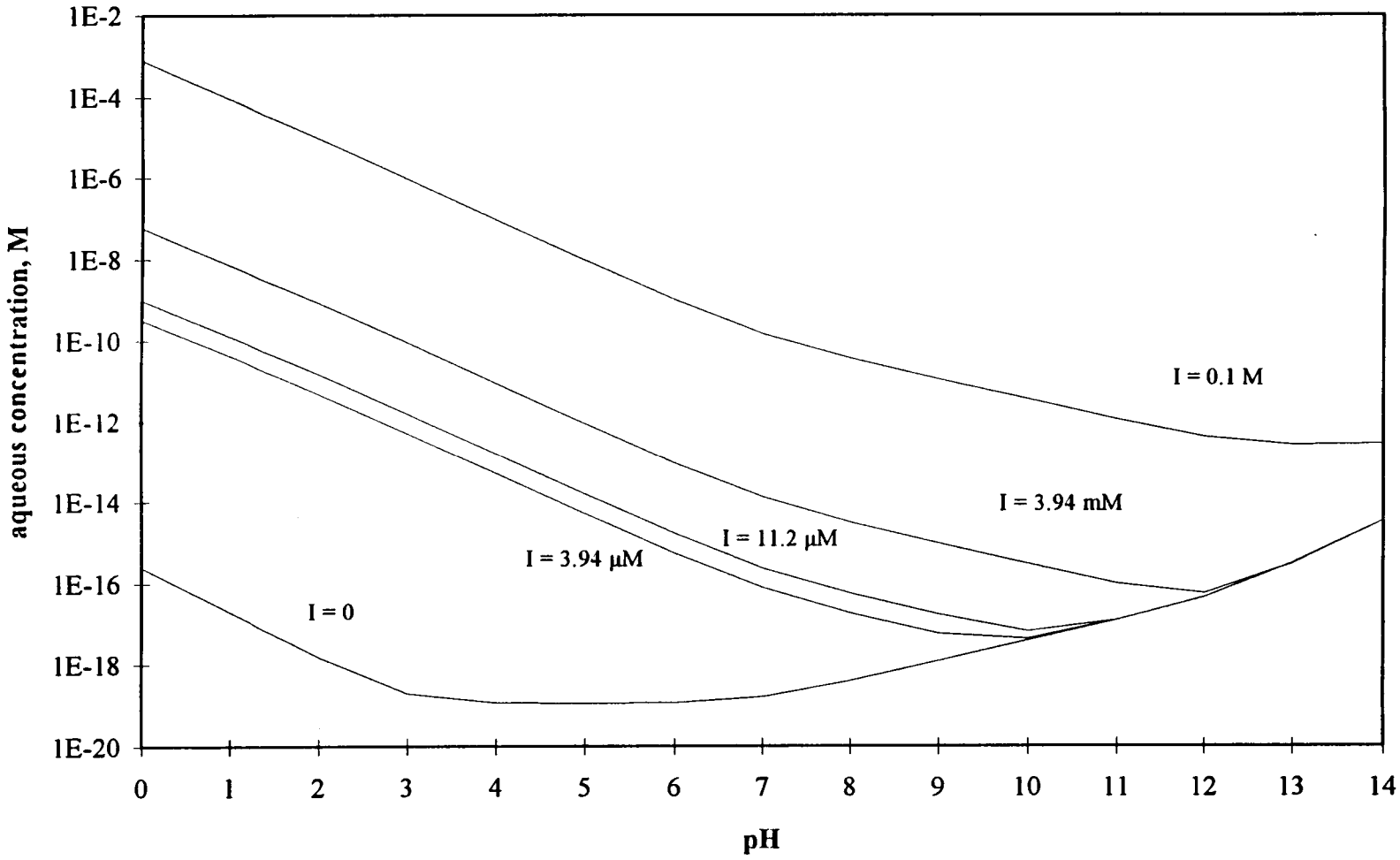


Figure 4.16: Effect of Iodide Concentration on Mercury Mobility.

4.4 Conclusions

Based on the aforementioned discussion, the following conclusions can be made:

- Iodide influences mercury adsorption in a manner similar to chloride.
  - Iodide, even at relatively low concentrations, is very effective at preventing mercury adsorption by illite. Iodide suppresses mercury adsorption at low pH (< 7), shifts the formation of adsorption edges to higher pH values, and reduces overall adsorption after the formation of adsorption edges.
  - Increases in pH may increase mercury adsorption by illite if hydrolyzed mercury complexes can form; however, if iodide concentrations are adequate, adsorption will be independent of pH.
  - Organic matter increases overall mercury adsorption for all iodide concentrations and pH values considered. Greater concentrations of iodide are required to affect a similar reduction in mercury adsorption for a given pH and mercury concentration, due to the increase in the variety of surface adsorption sites introduced to the suspensions with the addition of organic matter, and to the hydrophobic nature of mercury.
- Of all halides, iodide is the most effective mercury extractant; however, large concentrations of iodide are required to extract any appreciable amount (< 1%) of mercury from contaminated floodplain soils.

- Large residual concentrations of iodide from soil decontamination processes are unlikely to affect the mobility of mercury in floodplain soils when the likely chemical form of mercury in the soil is HgS(s); residual iodide is an effective extractant in surface soils (soils not subjected to seasonal oxic/anoxic fluctuations) when the mercury is adsorbed.
- Specific information on the speciation and weathering rates of mercury in a particular soil matrix is required in order to fully assess the impact of iodide on the mobility of mercury within that matrix.

BIBLIOGRAPHY

BIBLIOGRAPHY

ACS Style Manual; Dodd, J. S., Ed.; American Chemical Society: Washington, D.C., 1986.

Alberts, J. J.; Schindler, J. E.; and Miller, R. W. *Science* **1974**, 184, 895-896.

Allard, B. and Arsenie, I. *Water, Air and Soil Pollut.* **1991**, 56, 457-464.

Allison, J. D.; Brown, D. S.; and Novo-Gradac; K. J. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems*: Version 3.0 User's Manual; U.S. Environmental Protection Agency: Athens, 1991; EPA/600/3-91/021.

Anderson, C. E. *Evaluation of Results of Joint Air Force-Weather Bureau Cloud Seeding Trials Conducted During Winter and Spring 1949*; Geophysical Research Papers No. 4. Base Directorate for Geophysical Research. Air Force Cambridge Research Laboratories: Cambridge MA, 1950.

Andersson, A. In *The Biogeochemistry of Mercury in the Environment*; Nriagu, J. O., Ed.; Elsevier/North Holland Biomedical: Amsterdam, 1979, pp 79-112.

Andren, A. W. and Nriagu, J. O. In *The Biogeochemistry of Mercury in the Environment*; Nriagu, J. O., Ed.; Elsevier/North Holland Biomedical: Amsterdam, 1979, pp 1-21.

Ballester, A.; Otero, E.; and González, F. *Hydrometallurgy* **1988**, 21, 127-143.

Bangash, M. A.; Hanif, J.; and Kahn, M. A. *Waste Mgmt.* **1992**, 12, 29-38.

Barkay, T.; Turner, R.; Saouter, E.; and Horn J. *Biodegredation* **1992**, 3, 147-159.

Barnett, M. O.; Turner, R. R.; Harris, L. A.; Henson, T. J.; Melton, R.C.; and Stevenson, R. J. *Abstract of Papers*, Industrial and Engineering Chemistry Division. Special Symposium of the American Chemical Society, Atlanta, GA; American Chemical Society: Washington, D.C., 1994; Abstract 588.

Barnett, M. O. and Turner, R. R. In *Addendum to the East Fork Poplar Creek-Sewer Line Beltway Remedial Investigation Report*; report number DOE/OR/02-1119&D2/A1R1, 1994; Prepared for the U.S. Department of Energy by Science Applications International Corporation, Oak Ridge, Tennessee under contract DE-AC05-91OR21950; ESC.

Barrow N. J. *J. Soil Sci.* **1986**, 37, 295-302.

Barrow N. J. and Cox, V. C. *J. Soil Sci.* **1992a,** 43, 295-304.

Barrow N. J. and Cox, V. C. *J. Soil Sci.* **1992b,** 43, 305-312.

Baas Becking, L. G. M.; Kaplan, I. R.; and Moore, D. *J. Geol.* **1960**, 68, 243-284.

Bell, J. T.; Campbell, D. O.; and Toth, L. M. *Aqueous Iodine Chemistry in LWR Accidents: Review and Assessment.* U.S. Nuclear Regulatory Commission. Office of Nuclear Regulatory Research. Washington, D.C., 1982; NUREG/CR-2493.

Beneš, P. and Havlík, B. In *The Biogeochemistry of Mercury in the Environment*; Nriagu, J. O., Ed.; Elsevier/North Holland Biomedical: Amsterdam, 1979, 175-202.

Bibler, J. P. and Marson, D. B. Technical Report; Westinghouse Savannah River Company. Savannah River Laboratory, 1992; WSRC-RP-92-326

Blinski, H.; Kwokal, Z.; and Branca M. *Wat. Res.* **1992**, 26, 1243-1253.

Bloom, N. S. and Crecelius, E. A. *Marine Chem.* **1987**, 21, 377-390.

Bloomfield, C.; Kelso, W. I.; and Priden, G. *J. Soil Sci.* **1976**, 27, 16-31.

Bohn, H. L.; McNeal B. L.; and O'Connor, G. A. *Soil Chemistry*; Wiley Interscience: New York, 1985.

Brehler, B. In *Handbook of Geochemistry*; Wedepohl, K. H., Ed.; Springer-Verlag: Berlin, 1972, Vol. II, Chapter 53.

Bucher, B.; Davidoff, B.; Amacher, M. C.; Hinz, C.; Iskandar, I. K.; and Selim, H. M. *Soil Sci.* **1989**, 148, 370-379.

Bunzl, K.; Schmidt, W.; and Sansoni, B. *J. Soil Sci.* **1976**, 27, 32-41.

Chilean Iodine Educational Bureau. *Geochemistry of Iodine*; CIEB: New York, 1956.

Chilean Iodine Educational Bureau. *Iodine: Its Properties and Technical Applications*; CIEB: New York, 1951.

Christiansen, J. V. and Carlsen, L. *Iodine in the Environment Revisited: An Evaluation of the Chemical and Physico Chemical Processes Possibly Controlling the Migration Behavior of Iodine in the Terrestrial Environment*; Report of the Chemistry Department, RISØ National Laboratory. Roskilde, Denmark, 1989; RISØ-M-2791.

Clever, H. L.; Johnson, S. A.; and Derrick, M. E. *J. Phys. Chem. Ref. Data* **1985**, 14, 631-680.

Cohen, B. L. *Health Physics* **1985**, 49,279-285.

Coughtrey, P. J.; Jackson, J.; and Thorne, M. C. *Radionuclide Distribution and Transport in Terrestrial and Aquatic Ecosystems: A Compendium of Data*; A. A. Balkema: Rotterdam, 1985; Vol. 6, pp 70-74.

Coughtrey, P. J.; Jackson, J.; and Thorne, M. C. *Radionuclide Distribution and Transport in Terrestrial and Aquatic Ecosystems: A Critical Review of Data*; A. A. Balkema: Rotterdam, 1983; Vol. 3, Chapter 28.

CRC Handbook of Chemistry and Physics, 73rd ed.; Lide, D. R., Ed., CRC: Boca Raton, 1992.

Delfino, J. J. and Crisman, T. L. "Spatial and Temporal Distribution of Mercury in Everglades and Okefenokee Wetland Sediments"; final project report to the U.S. Geological Survey on Grant 14-08-0001-G-2012; University of Florida: Gainsville, FL, 1993.

Diamond, M. L.; Mackay, D.; Cornett, R. J.; and Chant, L. A. *Environ. Sci. Technol.* **1990**, 24, 713-722.

D'Itri, F. M. *The Environmental Mercury Problem*; CRC: Cleveland, 1972, Chapter 1.

Dooley, J. H. "Natural Sources of Mercury in the Kirkwood-Cohansey Aquifer System of the New Jersey Coastal Plain"; New Jersey Geological Survey Report 27; Division of Science and Research. New Jersey Department of Environmental Protection and Energy;Trenton, NJ, 1992.

Dzombak, D. A. and Morel, F. M. *Surface Complexation Modeling: Hydrous Ferric Oxide*. Wiley Interscience: New York, 1990.

Elliott, H. A. and Huang, C. P. *Environ. Internat.* **1979**, 2, 145-155.

Eganhouse, R. P.; Young, D. R.; and Johnson, J. N. *Environ. Sci. Technol.* **1978**, 12, 1151-1157.

Evans, L. J. *Environ. Sci. Technol.* **1989**, 23, 1046-1056.

Fanning, D. S. and Keramidas, V. Z. In *Minerals in Soil Environments*; Dixon, J. B.; Weed, S. B.; and Dinauer, R. C., Eds.; Soil Science Society of America: Madison WI, 1977, Chapter 7.

Farrah, H. and Pickering, W. F. *Water, Air and Soil Pollut.* **1978**, 9, 23-31.

Foust, D. L. "Extraction of Mercury and Mercury Compounds from Contaminated Materials and Solutions"; U.S. Patent #5226545; July 13, 1993

Feick, G.; Horne, R. A.; and Yeaple, D. *Science* **1972**, 175, 1142-1143.

Feldman, C. *Anal. Chem.* **1974**, 46, 99-102.

Fitzgerald, W. F. In *The Biogeochemistry of Mercury in the Environment*; Nriagu, J. O., Ed.; Elsevier/North Holland Biomedical: Amsterdam, 1979, pp 161-174.

Fleischer, M. In *Mercury in the Environment*; Professional Paper 713, U.S. Geological Survey: Washington D.C., 1970, pp 6-13.

Fleming, G. A. In *Applied Soil Trace Elements*; Davies, B. E., Ed.; John Wiley and Sons: New York, 1980, Chapter 6.

Forbes, E. A.; Posner, A. M.; and Quirk, J. P. *J. Colloid Interface Sci.* **1974**, 49, 403-409.

Fuge, R. In *Handbook of Geochemistry*; Wedepohl, K. H., Ed.; Springer-Verlag: Berlin, 1972, Vol. II, Chapter 53.

Gavis J. and Ferguson J. F. *Wat. Res.* **1972**, 6, 989-1008.

Gerritse, R. G. and van Driel, W. *J. Environ. Qual.* **1984**, 13, 197-204.

Glass, G. E.; Sorenson, J. A.; Schmidt, K. W.; and Rapp, G. R. *Environ. Sci. Technol.* **1990**, 24, 1059-1069.

Gill, G. A. and Bruland, K. W. *Environ. Sci. and Technol.* **1990**, 24, 1392-1400.

Gilmour, J. T. *Environ. Lett.* **1971**, 2, 143-152.

Goldberg, S. *Adv. in Agron.* **1991**, 47, 233-329.

Goldschmidt, V. M. *Geochemistry*; Clarendon: Oxford, 1961, pp 602-620.

Hahne, H. C. H. and Kroontje, W. *J. Environ. Qual.* **1973a**, 2, 444-450.

Hahne, H. C. H. and Kroontje, W. *Soil Sci. Soc. Am. Proc.* **1973b,** 37, 838-843.

Hargitai, L. *Sci. Total Environ.* **1989**, 81/82, 643-651.

Helling, C. S.; Chester, G.; and Corey R. B. *Soil Sci. Soc. Am. Proc.* **1964**, 28, 517-520.

Hem, J. D. In *Mercury in the Environment*; Professional Paper No. 713, U.S. Geological Survey: Washington, D.C., 1970, pp 19-24.

Henke, K. R.; Kühnel, V.; Stepan, D. J.; Fraley, R. H.; Robinson, C. M.; Charleton, D. S.; Gust, H. M.; and Bloom, N. S. *Critical Review of Mercury Contamination Issues Relevant to Manometers at Natural Gas Industry Sites*; Gas Research Institute. Environment and Safety Research Department. Gas Research Institute: Chicago, IL, 1993; GRI-93/0117.

Hepler, L. G. and Olofsson, G. *Chem. Rev.* **1975**, 75, 585-602.

Hogg, T. J.; Stewart, J. W. B.; and Bettany, J. R. *J. Environ. Qual.* **1978**, 7, 440-444.

Horvath, G. J.; Harriss, R. C.; and Mattraw, H. C. *Marine Pollution Bulletin* **1972**, 3, 12.

Howard, H. K. *Predicting Movement of Selected Metals in Soil: Application to Disposal Problems*; U. S. Environmental Protection Agency. Risk Reduction Engineering Laboratory. U. S. Government Printing Office: Washington, D.C., 1990; EPA/600/M-89/023.

Huang, P. M. In *The Handbook of Environmental Chemistry*; Hunzinger O., Ed., Springer-Verlag: Berlin, 1980; Vol. 2A, pp. 49-59.

Hurley, J. P.; Krabbenhoft, D. P.; Babiarz, C. L.; and Andren, A. W. In *Environmental Chemistry of Lakes and Reservoirs*; Baker, L. A., Ed.; Advances in Chemistry 237; American Chemical Society: Washington, D.C., 1994.

IT Corporation. *Status Report: Pilot-Scale Thermal Treatment Demonstration-Lower East Fork Poplar Creek;* IT Corporation Project 483138. Report prepared for Martin Marietta Energy Systems, Inc., April 29, 1994.

James, R. O.; Stiglich, P. J.; and Healy, T. W. *Discuss. Faraday Soc.* **1974**, 59, 142-157.

Jeanne, E. A. and Avotins, P. *J. Environ. Qual.* **1975**, 4, 427- 430.

Jeanne, E. A. and Felmy A. R. 1981. *Geochemical Modeling of Trace Elements-A Review.* Department of Energy Draft Document.

Jensen, S. and Jernelöv, A. *Nature* **1969**, 223, 753-754.

Kaiser, G. and Tolg, G. In *The Handbook of Environmental Chemistry*; Hunzinger O., Ed., Springer-Verlag: Berlin, 1980; Vol 3A, pp. 1-58.

Kinniburgh, D. G. and Jackson, M. L. *Soil Sci. Soc. J.*, **1978**, 42, 45-47.

Klusman, R. W. and Matoske, C. P. *Environ. Sci. Technol.* **1983**, 17, 251-256.

Kocher, D. C. *Environ. Internat.* **1981**, 5, 15-31.

Kooner, Z. S.; Smoot, J. L.; and Cox, C. D. 1994. Adsorption of Heavy Metals at the Goethite/Solution Interface. Submitted for Publication.

Korte, N. E.; Skopp, J.; Fuller, W. H.; Niebla, E. E.; and Alesii, B. A. *Soil Sci.* **1976**, 122, 350-359.

Krenkel P. A.; Reimers R. S.; and Burrows W. D. *Mechanisms of Mercury Transformation in Bottom Sediments, Part I.* Technical Report Number 31, Environmental and Water Resources Engineering Dept., Vanderbilt University, 1973.

Kudo, A.; Mortimer and Hart, J. S. *Can. J. Earth Sci.* **1975**, 12, 1036-1040.

Lange's Handbook of Chemistry, 11th ed.; Dean, J. A., Ed., McGraw-Hill: New York, 1973.

Leckie, J. O. and James, R. O. In *Aqueous Environmental Chemistry of Metals*; Rubin, A. J., Ed.; Ann Arbor Science: Ann Arbor, 1974, pp 1-76.

Leckie, J. O. In *The Importance of Chemical Speciation in Environmental Processes*; Bernhard, Brinckman, and Sadler, Ed.; Springer-Verlag: Berlin, 1986.

Levi-Minzi, R.; Soldatini, G. F.; and Riffaldi, R. *J. Soil Sci.***1976**, 27, 10-15.

Lindberg, S. E. *Atmospheric Environment* **1980**, 14, 227-231.

Lindqvist, O. *Mercury in the Swedish Environment: Recent Research on Causes, Consequences and Corrective Methods*; Kluwer Academic: Dordrecht (Netherlands), 1991.

Lockwood, R. A. and Chen, K. Y. *Environ. Sci. and Technol.* **1974**, 7, 1028-1033.

Lyday, P. A. In *Minerals Yearbook*; U.S. Department of the Interior, U.S. Government Printing Office: Washington, D.C., 1991, pp 741-749.

McLean, J. E. and Bledsoe, B. E. *Behavoir of Metals in Soils*; U. S. Environmental Protection Agency. U. S. Government Printing Office: Washington, D.C., 1992; EPA/540/S-92/018.

MacNaughton, M. G. and James R. O. *J. Colloid Interface Sci.* **1974**, 47, 431-440.

Mantoura, R. F. C.; Dickson, A.; and Riley, J. P. *Estuarine Coastal Mar.Sci.* **1978**, 6, 387-408.

Mierle, G. and Ingram, R. *Water, Air, and Soil Pollut.* **1991**, 349-357.

Mills, W. B.; Porcella, D.B.; Ungs, M. J.; Gherini, S. A.; Summers, K. V.; Mok, L.; Rupp, G. L.; Bowie, G. L.; and Haith, D. A. *Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants in Surface and Groundwater-Parts 1 and 2*; Office of Research and Development. U.S. Environmental Protection Agency, Athens, GA, 1985; EPA/600/6-85/002a.

Moore, J. W. and Ramamoorthy, S. *Heavy Metals in Natural Waters-Applied Monitoring and Impact Assessment*; Springer-Verlag: New York, 1984.

Morel, F. M. M.; Westall, J. C.; O'Melia, C. R.; and Morgan, J. J. *Environ. Sci and Technol.* **1975**, 9, 756-759.

Neal, C. and Truesdale, V. W. *J. Hydrol.* **1976**, 31, 281-291.

Newton, D. W. and Ellis, Jr, R. *J. Environ. Qual.* **1974**, 3, 20-23.

Newton, D. W.; Ellis, Jr., R.; and Paulsen, G. M. *J. Environ. Qual.* **1976**, 5, 251-254.

Nriagu, J. O. In *The Biogeochemistry of Mercury in the Environment*; Nriagu, J. O., Ed.; Elsevier/North Holland Biomedical: Amsterdam, 1979, pp 23-40.

Núñez, C. and Espiell, F. *Metal. Trans.* **1984**, 15B, 13-18.

Núñez, C. and Espiell, F. *Metal. Trans.* **1984** 15B, 229-233.

O'Connor, G. A.; O'Connor, C.; and Cline, G. R. *Soil Sci. Soc. Am. J.* **1984**, 48, 1244-1247.

Oki, S. and Watanabe, M. *Japan Analyst* **1971**, 20, 1204-1206.

Petrucci, R. H. *General Chemistry,* 4th ed.; MacMillan: New York, 1985, pp 1-874.

Pierce, A. P.; Botbol, J. M.; and Learned, R. E. In *Mercury in the Environment*; Professional Paper No. 713, U.S. Geological Survey: Washington, D.C., 1970, pp 14-17.

Pourbaix, M. *Atlas of Electrochemical Equilibria*; Pergamon: Oxford, **1966**

Rai, D. and Zachara, J. M. "Chemical attenuation rates, coefficients and constants in leaching migration. Vol. 1."; research project 2198-1; Electric Power Research Institute: Palo Alto, CA; EA-3356 Vol. 1.

Randle, K. and Hartman, E. H. *Geoderma* **1987**, 40, 281-296.

Rasmussen, R. A.; Khalil, M. A. K.; Gunawardena, R.; and Hoyt, S. D. *J. Geophys. Res.* **1982**, 87, 3086-3090.

Reimers, R. S. and Krenkle, P. A. *J. Wat. Pollut. Control Fed.* **1974**, 46, 352-365.

Reese, Jr, R. G. In *Minerals Yearbook*; U.S. Department of the Interior, U.S. Government Printing Office: Washington, D.C., 1991, pp 989-995.

Robinson, K. G. and Shuman, M. S. *J. Environ. Anal. Chem.* **1989**, 36, 111-123.

Rogers, R. D. *J. Environ. Qual.* **1976**, 5, 454-458.

Rogers, R. D. *J. Environ. Qual.* **1977**, 6, 463-467.

Rogers, R. D. *Soil Sci. Soc. Am. J.* **1979**, 43, 289-291.

Roine, A. *Outokumpu HSC Chemistry for Windows: User's Guide. Version 2.* Outokumpu Research Oy: PORI, Finland, 1994.

Schecher, W. D. and McAvoy, D. C. *MINEQL+: A Chemical Equilibrium Program for Personal Computers*. Proctor and Gamble: Cincinnati, 1991.

Schroeder, W. H. *TrAC* **1989**, 8, 339-342.

Schuster, E. *Water, Air, and Soil Pollut.* **1991**, 56, 667-680.

Shimomura, S.; Nishihara, Y; and Tanase, Y. *Japan Analyst* **1969**, 17, 1148-1149.

Shoesmith, M. A.; Cox, C. D.; Ghosh, M. M.; and Turner, R. R. *Abstract of Papers*, Industrial and Engineering Chemistry Division Special Symposium of the

American Chemical Society, Atlanta, GA; American Chemical Society: Washington, D.C., 1994; Abstract 588.

Snoeyink, V. L. and Jenkins, D. *Water Chemistry*; John Wiley and Sons: New York, 1980.

Sposito, G. *The Chemistry of Soils*; Oxford University: New York, 1989.

Stumm, W. and Morgan, J. J. *Aquatic Chemistry*, 2nd ed.; John Wiley and Sons: New York: 1981.

Stumm, W. and O'Melia, C. R. *J. Am. Water Works Assoc.* 1968, 60, 514-?.

Stumm, W. *Chemistry of the Solid-Water Interface*; Wiley Interscience: New York, 1992.

Takizawa Y. In *The Biogeochemistry of Mercury in the Environment*; Nriagu, J. O., Ed., Elsevier/North Holland Biomedical: Amsterdam, 1979, pp 325-366.

Toran, L. E. and Saunders, J. A. *Evolution of Na-HCO_3-Type Groundwater Near Oak Ridge, Tennessee: Flow Path and Lithologic Controls;* U.S. Department of Energy. Oak Ridge National Laboratory: Oak Ridge, Tennessee, 1992; Y/TS-875/R1.

Turner, R. R. In *Arsenic and Mercury: Workshop on Removal, Recovery, Treatment and Disposal*; U.S. Environmental Protection Agency: Washington, D.C. 1992; EPA/600/R-92/105.

Thanalabasingam, P. and Pickering, W. F. *Environ. Pollut. (Ser. B)* **1986**, 10,115-128.

Ullman, W. J. and Aller, R. C. *Geochem.Cosmochim. Acta*, **1985**, 49, 967-978.

Toxicological Profile for Mercury; U.S. Department of Health and Human Services. Public Health Service. U.S. Government Printing Office: Washington, D.C., 1994, Chapter 3-8.

Informational Brochure for Joyce Kilmer-Slickrock National Wilderness Center; U. S. Department of Agriculture. U. S. Government Printing Office: Washington, D.C. 1994.

Westall, J. and Hohl, H. *Adv. Colloid Interface Sci.* **1980**, 12, 265-294.

Whitehead, D. C. *J. Soil Sci.* **1973a**, 24, 260-270.

Whitehead, D. C. *J.Sci. Fd. Agric.* **1973b**, 24, 574-556.

Whitehead, D. C. *J. Soil Sci.* **1974a**, 25, 461-470.

Whitehead, D. C. *J.Sci. Fd. Agric.* **1974b**, 25, 73-79.

Whitehead, D. C. *J. Soil Sci.* **1978**, 29, 88-94.

Whitehead, D. C. J. *Appl. Ecol.* **1979**, 16, 269-279.

Whitehead, D. C. *J. Soil Sci.* **1981**, 32, 97-102.

Whitehead, D. C. *Environ. Internat.* **1984**, 10, 321-339.

Willet, K. L.; Turner, R. R.; and Beauchamp, J. J. *Haz. Waste Haz. Mat.* **1992**, 9, 275-288.

Wood J. M. In *Polluted Rain* Toribara T. Y.; Miller M. W; and Morrow P.E. Ed.; Plenum: New York, 1980, pp. 223-236.

Xu, H. and Allard, B. *Water, Air, and Soil Pollut.* **1991**, 56, 709-717.

Yamada, M. and Tonomura, K. *J. Ferment. Technol.* **1972**, 50, 159-166.

APPENDICES

APPENDIX A: SUPPLEMENTAL LITERATURE REVIEW

A.1 Background

A.1.1 MERCURY

Mercury, or quicksilver, has been used by humans for centuries. Mercury has been found in the tombs of ancient Egyptians (c. 1550 B.C.), but it is believed that the ancient Chinese were the first to actually utilize mercury ores in dyes and inks (D'Itri, 1972). The first historical record of mercury was made by Aristotle, around 400 B.C., when he mentioned the use of mercury in a religious ceremony (D'Itri, 1972).

Through the ages, mercury has been used as a medicine (in the form of a nutritional supplement, an aphrodisiac, a medicinal ointment and a cure for syphilis and leprosy), an essential element in alchemy, and an ingredient in rouge (D'Itri, 1972). Modern uses are just as varied. Everyone is familiar with the amalgams used in dental fillings, but there are other, less known uses as well. The biggest users of mercury are listed in Table A.1 (Reese, 1991). The electronics industry uses mercury in everything from light bulbs to switches (Nriagu, 1979). The chloralkali industry (generators of chlorine and caustic soda from salt water) has been responsible for some of the greatest mercury releases to the environment since 1950 (Nriagu, 1979). Mercuric chloride is used as a catalyst in the production of polyvinyl chloride and polyvinyl acetate from acetylene (Nriagu, 1979). Mercury compounds are used as

Table A.1: U.S. Industrial Consumption of Refined Mercury Metal, By Use (metric tons). (Reese, 1991)

Mercury Uses	1987	1988	1989	1990	1991
CHEMICAL AND ALLIED PRODUCTS:					
Chlorine and caustic soda manufacture	311	445	381	247	184
Laboratory uses	20	26	18	32	10
Paint	198	197	192	22	6
Other chemical and allied products	59	86	40	33	18
ELECTRICAL AND ELECTRONIC USES:					
Electric lighting	45	31	31	33	29
Wiring devices and switches	131	176	141	70	25
Batteries	533	448	250	106	78
INSTRUMENTS AND RELATED PRODUCTS:					
Measuring and control instruments	59	77	87	108	70
Dental equipment and supplies	56	53	39	44	27
OTHER USES	34	55	35	25	26
TOTAL	1446	1593	1214	720	473

fungicides in paints and antibacterials in pulp and paper industries, soaps and cosmetics (Lindqvist, 1991). Other mercury compounds are used as herbicides and pesticides in agriculture (Lindqvist, 1991).

In more recent times, mercury has received attention because of its toxic effects in humans. Events in Japan in the late 1950's made mercury, particularly methylmercury, a very familiar, albeit sinister, element. A total of 168 people in the towns of Minimata and neighboring Niigata came down with a severe illness, later called "Minimata Disease," due to mercury pollution from a P.V.C. production operation. Methylmercury, which was released into the bay, was being accumulated by fish. The people and cats who ate the fish became severely ill, and 52 people died as a result of methylmercury poisoning (Takizawa, 1979). Congenital damages to human fetuses affected up to 1000 individuals.

A.1.2 IODINE

Iodine was discovered relatively recently by the Frenchman, Bernard Courtois, in 1811. Because the French were isolated by allied forces during the Napoleonic wars, they were forced to produce their own potassium nitrate (necessary for the production of gunpowder). Calcium nitrate, produced in nitre beds, was converted first to sodium nitrate using soda ash from the ashes of seaweed, and then to potassium nitrate using potash from wood ashes. Courtois noticed that the copper vats in which the first conversion took place were quickly corroded by a reaction between the copper and an unknown substance in the soda ash. The substance could be

precipitated as a black powder using sulfuric acid and, when heated, evolved as a violet vapor. Courtois isolated some of this compound and gave it to J. L. Guy-Lussac, who, recognizing it was a new element, named the substance "iode," from the Greek word meaning violet-colored (Chilean Iodine Educational Bureau, 1951).

Iodine was later investigated because it is an essential nutrient for animals, including humans. People deficient in iodine develop enlarged thyroid glands, a condition commonly called goitre (Chilean Iodine Education Bureau, 1951). Attempts to understand the natural distribution and cycle of iodide were undertaken to improve human health. Still later, out of concern for human health, iodine again received attention. The isotope ^{129}I ($t_{1/2}$ = $1.56x10^7$ years) is a long-lived byproduct of nuclear energy production, weapons testing, and fuel reprocessing (Bell, et al., 1982; Kocher, 1981). In the event of a nuclear accident, iodine (as ^{129}I) could be released into the environment; because iodine accumulates in the thyroid, a seemingly insignificant uptake could result in a long-term, internal radiation dose in humans. This toxic potential created considerable interest in the transport and fate of iodine during the infancy of the nuclear era.

Iodine has many modern uses. According to Lyday (1991), the primary uses of iodine are as animal feed supplements, catalysts, inks and colorants, pharmeceuticals, photographic chemicals, sanitary and industrial disinfectants and stabilizers; smaller quantities are used in the production of batteries, high-purity metals, motor fuels, iodized salt and lubricants.

A.2 Current Issues

Approximately 24 million pounds of mercury was used in the production of nuclear weapons at the United States Department of Energy's (USDOE) Oak Ridge Reservation during the 1950's and 1960's. Historically, 23, 194, and 108 metric tons of mercury have been released to air, soil, and water; as a result, over 500,000 m^3 of the 640 acre East Fork Poplar Creek (EFPC) floodplain are contaminated, with mercury concentrations up to 3000 mg/kg.

A.3 Environmental Concentrations

Mercury and iodine occur in all environmental media. Concentrations of each element in each compartment are due to both natural and anthropogenic sources. The distribution and transport of each element among the various compartments of the biosphere have been studied to identify exposure and assess risk associated with human and ecological interactions with the various compartments (Kocher, 1981; Andren and Nriagu, 1979). Figures A.1 and A.2 illustrate the cycles of mercury and iodine, respectively in the biosphere.

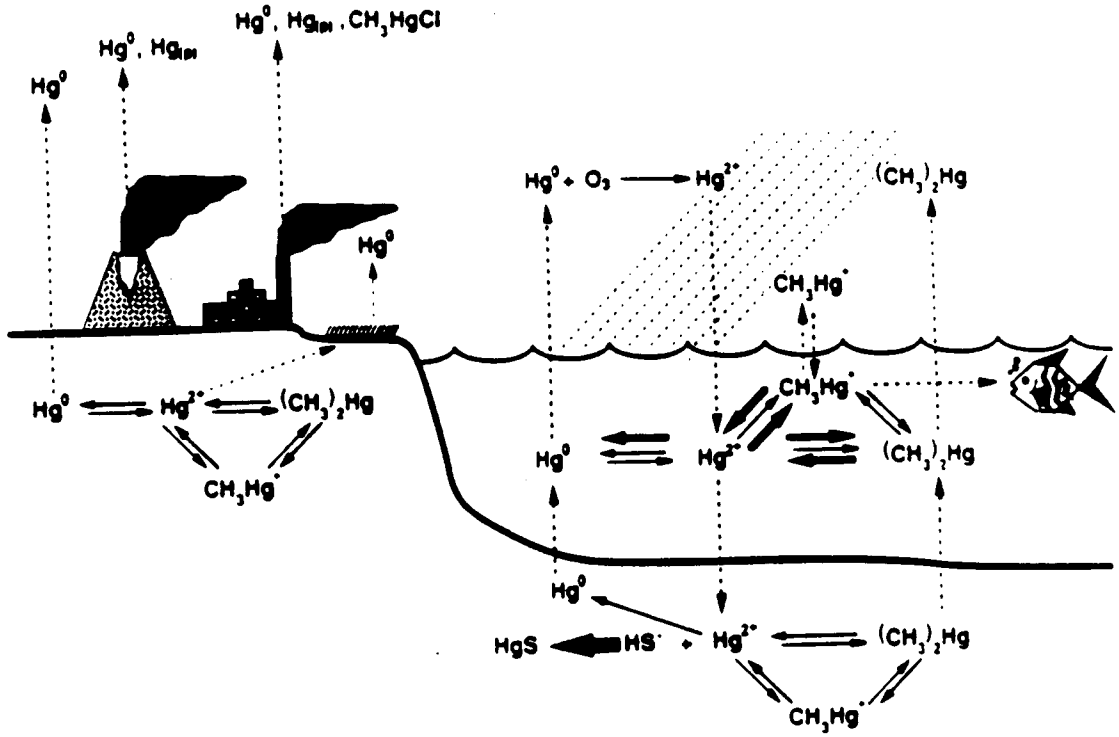


Figure A.1 Mercury Cycle in the Biosphere.
(Barkay et al., 1992)

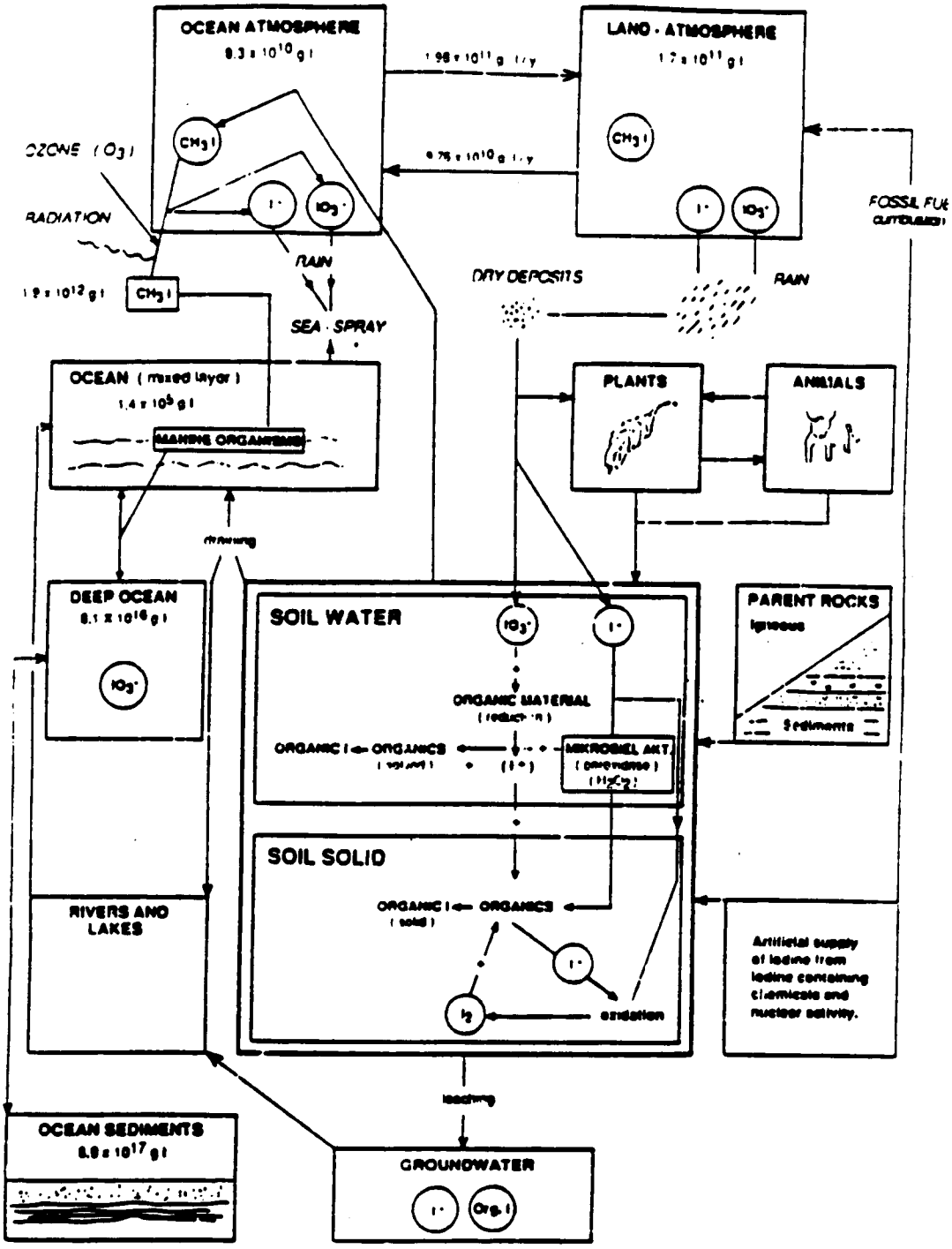


Figure A.2: Iodine Cycle in the Biosphere.
(Christiansen and Carlsen, 1989)

A.3.1 Natural Sources of Mercury

A.3.1.1 *Rocks:*

Mercury is present in the three major types of rocks at concentrations that are typically less than 200 ppb (see Table A.1) (Fleischer, 1970). Igneous rocks contain an average of 100 ppb, with some exceptions, such as those rocks from the Crimea and Donnets Basin in the former Soviet Union, where mercury concentrations can exceed several hundred ppb. Sedimentary and metamorphic rocks average about 50 ppb of mercury, but many shales, coals, clays, and schists can greatly exceed this average (Fleischer, 1970). As an example, certain coals that are found in mineral deposits of high mercury content (i.e. the region in the Crimea) have mercury concentrations of 300,000 ppb.

A.3.1.2 *Soils:*

Since soils are composed in part of fragments of the parent material over which they lay, the mercury content of a particular soil will depend on the soil's parent material (Fleischer, 1970). However, there are additional factors that may increase or decrease the concentration of mercury in soil. Soils that contain organic matter may form strong complexes with ionic mercury or elemental mercury vapor, and hold it in the soil (Rogers, 1979; Klusman and Matoske, 1983), or the organic material may act to reduce ionic mercury to the elemental form and enhance its ability to volatilize (Alberts et al., 1974; Allard and Arsenie, 1991). Exposure to organic matter and plant and microbial systems can result in either an increase mercury content (due to bioaccumulation) or a decrease in mercury content due to biotic methylation (Yamada

Table A.2: Concentration of Mercury in Select Rocks.
(Compiled from Fleischer, 1970)

Sample Location	Concentration Range (μg/kg)
IGNEOUS:	
California	4-11
Washington	4-12
South Africa	200-780
Australia	1,230-1,480
Crimea	0-500,000
Donnets Basin (former U.S.S.R.)	60-30,600
Viet Nam	9000
GRANITIC:	
Rhode Island	29-340
Colorado	15-41
Germany	58-100
Tadzhikistan	10-75
northern Caucasus	60-200
Yenisei Range	5-180
Yakutia	2-80
METAMORPHIC:	
Quebec	18
Vermont	2.5-2,535
Russia	25-100
Kola Peninsula	70-600
northern Caucasus	60

and Tonomura, 1972), abiotic methylation (Rogers, 1976; Rogers, 1977), or chemical reduction and volatilization (Turner, 1992). Finally, atmospheric exposure can result in deposition or removal (through evaporation or resuspension) of mercury (Lindqvist, 1991). Table A.2 illustrates the range of mercury concentrations in several soils.

A.3.1.3 *Air:*

Due to its low vapor pressure, elemental mercury is volatile, and a considerable fraction of the mercury present throughout the world is found in the atmosphere (see Table A.3) (Lindqvist, 1991). Most (95%) of this atmospheric mercury is present as gaseous, elemental mercury, but about five percent is associated with particulate matter (Lindqvist, 1991). Median background concentrations are in the 2 to 9 ng/m^3 range (Kaiser and Tolg, 1980), but higher concentrations will be found over mercury-containing ores and near volcanos, geysers, thermal fluids (Kaiser and Tolg, 1980).

A.3.1.4 *Water:*

Naturally-occurring mercury found in aquatic systems is the result of direct precipitation or runoff. Concentrations in solution will depend on the chemical form of the metal and the complexing ligands available (Gilmour, 1971). In solution, mercury is easily complexed by humic and fulvic acids, as well as chloride and sulfide ligands (Schuster, 1991). Mercury also shows a strong affinity for particulate matter, especially organic matter (Elliott and Huang, 1979); this increases the transportability of mercury to sediments.

Background concentrations of mercury in fresh waters can vary greatly. Fitzgerald (1979) summarized the work of several researchers, and his results have

Table A.3: Concentration of Mercury in Select Soils.
(Compiled from Fleischer, 1970)

Sample Location	Concentration Range (μg/kg)
California	20-200
British Colombia	10-2500
Germany	30-290
Sweden	60*
Africa	23*
Eastern Europe	40-5800
Donnets Basin	< 50-10000
Kerch Peninsula	< 100-3000
Kerch-Taman area	240-1900
Viet Nam	20-1000

* single measurement

Table A.4: Mercury in Air and Volcanic Emanations.
(Compiled from Fleischer, 1970)

Sample Location	Concentration Range (ng/m^3)
AIR:	
Pacific Ocean	0.6-0.7
California (Winter)	1-25
California (Summer)	1.5-50
California and Arizona, background	1.6
Chicago	7.2
Kamchatka	3-39
Moscow and Tula	80-300
Over a copper deposit	12-30
Over a mercury deposit	12-57.5
VOLCANIC EMANATIONS:	
Air of vent breccias of mud volcanoes	300-700
Gases of mud volcanoes	700-2,000
Gases, Mendeleev and Sheveluch Volcanoes	300-4,000
Gasses from hot springs	10,000-18,000
Condensates from fumeroles and volcanic emanations	0.2-72
Waters from hot springs	0.5-4

been tabulated in Table A.4. These results show that the mercury concentration in freshwaters can vary from sub-nanogram per liter levels to greater than microgram per liter levels near sewage discharges, polluted sites, or mercury deposits.

Mercury in ocean waters seems to vary less. Fitzgerald's (1979) summary (Table A.4) indicates the average mercury concentration to be approximately 10 ng/L in the open ocean and approximately 20 ng/L in coastal waters.

A.3.1.5 *Sediments:*

Pierce et al (1970), have tabulated typical mercury concentrations in stream sediments from sites across the U. S. (Table A.5). Because of the high organic content and anaerobic conditions, sediments are the primary sink for mercury in the environment (Lindqvist,1991). Under anaerobic conditions, the formation of insoluble mercuric sulfide is favored. The strong association of mercury with insoluble organics also results in a long retention time for mercury in sediments. Anaerobic microorganisms found in sediments are capable of converting inorganic mercury to organic methyl mercury (Jensen and Jernolöv, 1969), but little mercury in surface sediments is available for methylation (Delfino et al., 1993).

A.3.2 Anthropogenic Sources of Mercury

Mercury can also be accumulated by man from use in many industrial and technological applications. Land disposal of sludges (Lindqvist, 1991), emissions from power plants (Lindberg, 1980), industrial discharges to water (Morel et al., 1975), and the use of herbicides and pesticides (Nriagu, 1979), along with the

Table A.5: Concentration of Mercury in Natural Waters.
(Compiled from Fitzgerald, 1979)

Region	Hg Concentration (ng/L)	
	range	mean
FRESH WATERS:		
Central Italy	10 - 50	--
Sweden	--	50
Britian	--	9
N. W. Canada	50 - 500	--
Great Lakes	130 - 180	--
Arizona	--	10
Alaska	210 - 470	340
Virgina	4 - 12	8
OPEN OCEAN WATERS:		
N. E. Atlantic	<3 - 142	36
S.E. Atlantic	10 - 54	35
N.W. Atlantic	2 - 20	8
W. Atlantic	2 - 400	
N.E. Pacific	12 - 37	24
N.W. Pacific	0 - 23	11
Japan Sea	3.6 - 5.6	5.0
New Zealand to Ross Sea	50 -150	98
World Ocean	0.5 - 127	47
COASTAL WATERS:		
Iceland	13 -18	14
Britain	11 - 21	16
Irish Sea	25 - 50	32
S.E. Atlantic	5 - 300	62

Table A.6: Concentration of Mercury in Sediments.
(Compiled from Pierce et al., 1970)

Region	Hg concentration (μg/g)	
	range	mean
Edna Mountains, NV	40 - 2,200	77
Bob Marshall Wilderness area, MT	10 - 220	36
Gulf of Mexico	70 - 220	110
Ventana primative area, CA	10 - 290	80
Uncompahgre primative area, CO	10 - 700	100
Blue Range primative area, AZ and NM	10 - 1,200	50
San Rafael Wilderness, CA	10 - >4,000	60
Taylor Mountains, AK	60 - 3,000	190
	80 - 10,000	360
Sierra Cuchillo, NM	10 - 48	19

increase in excavation that accompanies an increasing population (Horvath et al., 1972), can cause large increases in the amount of mercury cycling through the biosphere. As Table A.6 indicates, most of this mercury finds it way into sediments (Gavis and Ferguson, 1972) where it accumulates due to extremely long residence times (Nriagu, 1979).

A.3.3 Natural Sources of Iodine

A.3.3.1 *Rocks:*

Iodine is present in the three major types of rocks, and typical concentrations depend on the rock type (Table A.7). Coughtrey et al (1983) noted that most rocks contain very little iodine. They summarized average concentrations in different types of parent material and concluded that an average concentration of 0.5 μg/g can be assumed for most parent material with the exception of coals and shales, which may contain 2 to 5 μg/g. The Chilean Iodine Educational Bureau (1956) also measured iodine concentrations in rocks. They found that igneous rocks contained significantly less iodine than metamorphic or sedimentary rocks. Whitehead (1984) analyzed several different types of rocks from the U. K. He found that clays and sandstones contained less iodine than limestone and shale, or igneous rocks. Whitehead's average iodine concentrations for different parent materials are greater than those of the Chilean Iodine Educational Bureau (1956) and Coughtrey et al (1983). This is possibly due to the fact that Whitehead includes in his analysis the associated till of the parent material which may contain weathering produces or wet- or dry-deposited

Table A.7: Average Residence Times for Mercury in Different Compartments. (Nriagu, 1979)

Compartment	Residence Time
Atmosphere	11 days
Oceans	2100 years
Sediments	2.5×10^8 years
Soils	1000 years

Table A.8: Iodine Concentration in Parent Material (ppm).

Parent Material	CIEB (1956)	Coughtrey, et al (1983)	Whitehead (1979)
Igneous Rock	0.521	0.5	10.6
Sedimentary Rock	1.545	0.3	---
Shales	2.180	2.2	9.8
Sandstones	1.743	1.7	3.7
Limestones	1.179	1.2	13.0
Metamorphic Rock	1.612	---	---
Clay	---	---	5.2
Coal	---	6.0	---

materials, a source of iodide that can be particularly significant in costal areas such as the U. K.

A.3.3.2 *Soils:*

Depending on the composition, a soil may contain more iodine than the parent material, or may reflect the concentration of the parent material (see Table A.8). Although the Chilean Iodine Educational Bureau (1956) found that igneous rocks contained significantly less iodine than sedimentary or metamorphic rocks, soils derived from igneous rocks contained higher concentrations of iodine than soils derived from sedimentary or metamorphic rocks. Christensen and Carlsen (1989) concluded that this difference is due to accumulation of iodine during the sedimentation process.

It has been suggested (Coughtrey et al, 1983; Whitehead, 1973a-b, 1974b; Christensen and Carlsen, 1989; Cohen, 1985) that the organic fraction of soils is the main repository of iodine because iodine associated with the mineral fractions of soils generally reflects the iodine concentration of parent materials. Plants and organisms that typically constitute the organic fraction of soils tend to bioaccumulate iodine, and the decomposition of these compounds results in an increase in soil iodine content. Plants also serve as a surface for wet and dry deposition from the atmosphere (foliar absorption), so their decomposition can increase the content of iodine in soils (Whitehead, 1984).

It is important to note that some (Whitehead, 1974a, 1978) have *not* noticed a correlation between organic matter content and iodine content. Whitehead concludes

Table A.9: Iodine in Soils.
(Coughtrey et al., 1983)

Soil Type	Concentration (μg/g, dry weight)
general, total	5.0
general	5.0
general	0.6 - 8
general, soil solution	0.01
podzolic humus to peat bog humus	0.50 - 9.30
Russian podzols	2.5
Norweigian podzols	6.49
Russian fluvioglacial and old sand to loess-like loams	0.16
arable and grassland soils	3

that this discrepancy is due to the age of the soils used. In the case where little retention of iodine was noted, the soils were less than 50 years old. This time is much less than is necessary for a significant increase in iodine content (650 years to double iodine concentration).

Whitehead (1973a, 1974a-b, 1978) suggested that iodide adsorbs to sesquioxides (Fe_2O_3 and Al_2O_3). He found that, at pH < 6, a high correlation exists between the iodide content in soils and the concentration of free Fe_2O_3 and Al_2O_3. At pH > 6, however, iodide adsorption appears to be negligible. Neal and Truesdale (1976) saw little iodide adsorption to ferric hydroxides, but did observe significant iodate adsorption under similar conditions. Since the pH values for their solutions were not given, it may be assumed that their solutions were significantly basic (pH > 6) to diminish iodide adsorption. Ullman and Aller (1985) suggested that iron oxides play an important role in the enrichment of marine sediments with iodide. They propose that microorganisms oxidize I^- to IO_3^-; the iodate is then scavenged by iron oxides and transported to sediments where it is reduced back to I^-.

Karelina (1961) and Goldschmidt (1954) have suggested a correlation between distance from the sea and iodine concentration, due primarily to wet and dry deposition. Whitehead (1984) proposed that soils very close to the sea will contain higher concentrations of iodine than those soils far-removed from the ocean, due only to atmospheric transport of sea spray or marine alluvium; he found no correlation between distance from the sea and iodine content of soils. Cohen (1985) also rejected Goldschmidt's and Karelina's proposition, except for those soils very near the coast

where sea spray could increase iodine concentrations, by citing several anomalous examples.

Whitehead (1981) measured volatilization of iodine from soils and soil components. He found that in most of the soils, volatilization was negligible; however, in some soils volatilization accounted for up to 10% of the iodide added. Of soil components, only sand increased the volatilization of iodine, possibly by converting the iodide to hydrogen iodide or by reduction to elemental iodine. Organic matter was most effective at reducing volatilization. He concluded that soils with pH above 5 and organic matter content greater than 2.5% will not induce any appreciable volatilization.

A.3.3.4 *Air:*

Concentrations of iodine in the atmosphere are listed in Table A.9. Microbial production of methyl iodide is believed to be the major route of transport of iodine into the atmosphere (Rasmussen et al., 1982). Based on the available information, Whitehead (1984) suggests that the average global atmospheric iodine concentration is probably in the range of 10 to 20 ng/m^3, with gaseous iodine exceeding particulate iodine by a factor of 2 to 6.

A.3.3.5 *Water:*

Seawater is the largest worldwide source of iodine (see Table A.10), with average concentrations of 45 to 60 μg/L (Fuge, 1972). Some sea plants also have the ability to bioaccumulate iodine, and the decay of these plants results in high iodine concentrations in marine sediment.

Table A.10: Iodine in the Atmosphere.
(Compiled by Whitehead, 1984)

Region	Gaseous (ng/m^3)		Particulate (ng/m^3)	Total (ng/m^3)
Hawaii	8.1± 3.5		2.5± 0.9	10.6
Antarctica (coastal)	2.2± 0.6		0.9± 0.4	3.1
Antarctica (inland)	2.7± 0.8		0.5± 0.1	3.2
Cambridge, MA	13.9± 2.8		6.9± 4.4	20.8
	organic	inorganic		
Arizona	5	11	1.3	17.3
Bermuda	28	17	3.7	48.7
Kansas	12	5	2.9	19.9
N.W. Territories, Canada	3	0.4	0.2	3.6

Table A.11: Iodine in Waters of the Pacific Ocean.
(Compiled by Fuge, 1972)

Depth (m)	Iodide (μg/L)		Iodate (μg/L)		Total Iodine (μg/L)	
	> 15°C	< 15°C	> 15°C	< 15°C	> 15°C	< 15°C
0 - 100	9.4	4.3	33.5	41.0	42.9	45.3
100 - 200	6.0	3.7	39.0	44.4	44.9	48.1
200 - 500	3.2	2.9	45.9	45.9	49.1	48.9
500 - 1000	3.2	2.4	47.3	52.0	50.5	54.4
1000 - 2000	2.8	1.9	51.5	51.9	54.3	53.8
>2000	1.8	2.0	52.4	52.0	54.2	54.1

Iodine in groundwater depends on the age of the water and the extent of interaction with soils, rocks, sediments, and sea water (Whitehead, 1984). Concentrations of iodine in groundwaters are tabulated in Table A.11. The variation in concentrations results from the intrusion of sea water, the enrichment of groundwaters by geothermal activity, and the infiltration of iodine from anthropogenic sources (Fuge, 1972). In general, iodine concentrations in groundwater are less than 100 μg/L and in waters unaffected by seawater, the iodine concentrations can be expected to be much less (Fuge, 1972).

As Table A.11 shows, iodine concentrations in surface waters typically fall in the range of 0.5 to 20 μg/L, and in waters unaffected by human activities, this concentration can be less than 2 μg/L (Neal and Truesdale, 1976). In addition to anthropogenic sources, iodine content can be influenced by surface runoff and groundwater infiltration (Whitehead, 1984).

A.3.4 Anthropogenic Sources of Iodine:

Unlike mercury, natural sources of iodine are responsible for the majority of iodine in the biosphere (Christiansen and Carlsen, 1989). Whitehead (1984) calculated the average annual load of iodine to the environment from fossil fuel combustion to be $4x10^5$ kg/year, or less than 0.1% of the amount of iodine exchanged between the atmosphere and all earth surfaces. There are, however, several routes by which iodine can enter the biosphere due to human activities. In addition to nuclear fuel processing and weapons testing, iodine enters the biosphere through the use of

Table A.12: Iodine in Natural Waters.
(Compiled by Fuge, 1972)

Region	Range (μg/L)	Mean (μg/L)
RIVER WATER:		
Japan	--	2.2
U.S.S.R.	3.3 - 42.4	11.0
Moscow region	4 - 18	--
Opole region, Poland	1.23 - 9.79	--
Saale River, Germany	--	4.54
Potomac River, Washington	--	2.2
LAKE WATER:		
Central Kazakhstan	--	160
Central Kazakhstan	--	680
THERMAL/MINERAL SPRINGS:		
Japan (average)		730
Saratoga Springs, NY	310 - 3760	1270
Beppu spa, Japan	30 - 290	96
Shirahama, Japan	123 - 158	140
Obama, Japan	210 - 329	277
SUBSURFACE BRINES/FORMATION WATER:		
Oklahoma	23 - 1400	370
Mississippi/Alabama	2 - 65	--
California	21 - 23	
Poland		199
Japan		132
Michigan		40
California	25 - 29	27
W. Canada	< 1 - 39	15

pesticides, herbicides and fungicides (Lyday, 1991). The former practice of cloud seeding (using substances to condense water vapor and bring about precipitation) used silver iodide as nucleation substrate (Anderson, 1950). In addition, petroleum brines from oil drilling often contain elevated concentrations of iodide (Goldschmidt, 1961). All of these practices can potentially increase the content of iodine in the environment.

A.4 Properties of Mercury

Mercury is a member of the group IIB elements, and shares a few characteristics with the other group IIB elements, Zinc (Zn) and Cadmium (Cd), such as an ability to easily form a large variety of complex ions and low melting and boiling points (Petrucci, 1985). Mercury differs from the lighter elements of group IIB because of relativistic effects that affect only the more massive sixth period elements. These effects give mercury a unique set of physical and chemical properties (Petrucci, 1985).

A.4.1 Physical Properties:

Several researchers (Henke et al, 1993; Nriagu, 1979; U.S. Department of Health and Human Services, 1994) have compiled thorough lists of physical properties of elemental mercury (Table A.12) and other mercury compounds (Table A.13).

Table A.13: Physical Properties of Mercury.
(Compiled from Henke et al., 1993; Andren and Nriagu, 1979; and others)

Atomic Number	80
Atomic Radius	1.5 Å
Atomic Volume	14.81 cm^3/g-atom
Atomic Weight	200.59 amu
Boiling Point	356.9°C
Melting Point (Freezing Point)	-38.87°C
Conductivity	0.022 cal/sec/cm^3°C
Compressibility	$4x10^{-6}$ cm^3 @ 20°C from 99 to 493 atm
Critical Density	3.56 g/cm^3
Critical Pressure	732 atm
Critical Temperature	1677°C
Density	13.546 g/cm^3 @ 20°C
Electronegativity	1.92
Heat Capacity	0.0332 cal/g @ 20°C
Heat of Fusion	2.7 cal/g
Heat of Vaporization	14.67 cal/g-atom @ 25°C
Odor	none
Resistivity	$9.58x10^{-6}$ ohm/cm @ 20°C
Specific Gravity	13.546 @ 20°C
Specific Heat	0.0333 cal/g/°C
Surface Tension	480 dynes/cm @ 20°C
Vapor Pressure	$2x10^{-3}$ mm Hg @ 25°C
Viscosity	1.554 cp @ 20°C

Table A.14: Physical Properties of Select Mercury Compounds.
(Compiled from Henke et al., 1993;
U.S.Department of Health and Human Services, 1994)

Compound	Formula	M.W.	B.P.	M.P.	ρ	V_P
		amu	°C	°C	g/mL	mm Hg
Mercuric Chloride	$HgCl_2$	271.5	302	276	5.44	0.1
Mercuric Oxide	HgO	216.6	--	500[d]	11.1	--
Mercuric Sulfide	HgS	232.7	--	583.5[s]	8.1	--
Mercurous Chloride	Hg_2Cl_2	472.1	400 - 500[s]	none	7.15	--
Methylmercuric Chloride	CH_3HgCl	251.1	--	170	4.063	0.0085
Phenylmercuric Acetate	$C_6H_5HgCH_3COO$	336.8	--	149	--	$9x10^{-6}$
Mercuric Acetate	$Hg(CH_3COO)_2$	318.7	--	179	3.28	--

M.W. = molecular weight
B.P. = boiling point
M.P. = melting point
ρ = density
V_P = vapor pressure
[s] = sublimes
[d] = decomposes

Elemental mercury has several physical properties that affect its environmental transport and fate. Elemental mercury is quite dense, is a liquid at room temperature, and has a low saturation vapor pressure. In addition, because of a high surface tension, elemental mercury has a propensity to break up into small beads, which further enhances its ability to volatilize and disperse. Turner (1992) asserts that these four physical properties control the initial transport of elemental mercury in soils. A spill of liquid mercury will result in the formation of small beads which, because of their density and liquid nature can penetrate deep into the soil pores. Once trapped in soil pores, elemental mercury vapor will volatilize into the soil gas or the atmosphere due to elemental mercury's low vapor pressure.

The physical properties of mercury compounds are different from those of elemental mercury. Physical properties such as density, melting point, and boiling point are greatly dependant on the compound considered. Additionally, most physical properties are dependant on temperature. Henke et al. (1993) note that, for a temperature range of -30 to 60°C, saturation vapor pressure varies over three orders of magnitude and viscosity varies by a factor of about 1.5.

A.4.2 Chemical Properties:

Perhaps the most important chemical property of mercury is valency. Mercury can exist in any one of three valence states. Under reduced conditions, elemental mercury is prominent. In an oxidized environment, either of the two oxidized forms are thermodynamically possible; however mercurous mercury (Hg(I)) is unstable in

nature, and disproportionates to mercuric mercury (Hg(II)) and elemental mercury according to the following reaction:

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg^o \qquad \text{(A.1)}$$

Solubility is also an important chemical property of mercury compounds, and the type of solvent will affect the solubility of mercury. Water solubility of mercury is of primary concern for fate and transport reasons, but mercury solubility in other solvents can also be of interest from the standpoint of fate and transport or for decontamination purposes. The effect of solvent type is illustrated in Table A.15. Because mercury is hydrophobic, it is more soluble in polar solvents than in water.

The chemical form of mercury also influences solubility. While mercuric sulfide is relatively insoluble in water, mercuric chloride is quite soluble. Table A.15 illustrates the importance of chemical form and solvent in determining the solubility of a particular mercury compound.

A.5 Properties of Iodine

Iodine, element 53, is the least common of the group VIIB nonmetal elements. Commonly called the halogens (salt formers), the elements of this group (F, Cl, Br, and I) are characterized by high ionization energies (difficult to lose electrons) and large, negative electron affinities (electrons are gained easily), resulting in highly

Table A.15: Solubility of Mercury and Some Mercury Compounds.
(Compiled from Henke et al., 1993 and CRC Handbook, 1992)

Compound	Solvent	Solubility
		(μg/L)
Hg^{o}	Water	60-80
Hg^{o}	Nitric Acid	"soluble"
Hg^{o}	Dioxane	7,000
Hg^{o}	Benzene	2,000
HgI_2	Water	60,000
Hg_2I_2	Water	0.2
$HgBr_2$	Water	6,200,000
Hg_2Br_2	Water	40
Hg_2O	Water	insoluble
Hg_2Cl_2	Water	2,000
HgO	Water	53,000
$HgCl_2$	Water	66,000,000
HgS	Water	10
Hg_2S	Water	insoluble

electronegative nonmetals. However, the detailed chemistry of iodine cannot be deduced from general halogen chemistry. The chemistry of the particular system will determine iodine behavior (Bell et al., 1982).

A.5.1 Physical Properties

Several of the physical properties of iodine have been compiled into Table A.16. Iodine is the only halogen that is a solid at room temperature, and its properties approach those of metals (Brehler, 1972). Compounds of iodine are typically poor conductors (with the exception of AgI and CuI) (Chilean Iodine Educational Bureau, 1951). Elemental iodine has a significant vapor pressure, even at room temperatures, causing a violet vapor to form above crystals or solutions of iodine (Chilean Iodine Educational Bureau, 1951).

Iodine has only one stable isotope, ^{127}I; there are however, 23 other known isotopes of iodine, ranging from ^{117}I to ^{139}I. The aforementioned ^{129}I ($t_{1/2}$ = 1.7 x 10^7 yr), in addition to being a byproduct of nuclear fuel reprocessing, is produced naturally through spontaneous fission of natural uranium and through reactions with xenon in the upper atmosphere (Fuge, 1972). ^{131}I ($t_{1/2}$ = 8.4 d) is a commonly-used medicinal isotope. Of the 24 known isotopes of iodine, 18 have half-lives of less than one day (Fuge, 1972).

Table A.16: Physical and Chemical Properties of Iodine.
(Compiled from CRC Handbook, 1992 and others)

Atomic Number	53
Atomic Radius	2.2 Å
Atomic Weight	126.9 amu
Boiling Point	184°C
Melting Point	113.6°C
Conductivity	0.9×10^{-5} @ 140°C cal/sec/cm^3°C
Color	
solid	blackish, bluish
liquid	black
vapor	violet
Electronegativity	2.5 (Pauling)
Specific Gravity	4.93 @ 20°C
Dielectric Constant	12.0
Vapor Pressure	1 mm Hg @ 40°C
Refractive Index	3.34
Solubility	
@ 20°C	0.29 mg/L
@ 100°C	4.00 mg/L
@ 300°C	misible
Oxidation States	-1, +1, +3, +5, +7

A.5.2 Chemical Properties

Elemental iodine, much like mercurous mercury, is unstable in the environment, and prefers to convert either to the reduced form (I^- or iodide) or the oxidized form (IO_3^- or iodate) (Bell et al., 1982). Iodine is very chemically active, and can react with all elements except sulfur, selenium and the noble gases (Chilean Iodine Educational Bureau, 1951). Iodide compounds are typically unstable, except for compounds of cadmium, mercury, and silver, which can form a variety of complex molecules. In addition, several organic iodine compounds can form, such as methyl iodide, which plays a large part in environmental transport.

Iodine is fairly soluble, and most iodide salts (with the exception of copper, silver, mercury, thallium, lead, and palladium) are soluble (Chilean Iodine Educational Bureau, 1951). Many iodide salts are also soluble in organic solvents and non-aqueous liquids, such as acetone, furfural, liquid sulfur dioxide and anhydrous ammonia (Chilean Iodine Educational Bureau, 1951).

A.6 Soil Chemistry

A.6.1 Soil Composition

Soil is actually a composite of several different chemical phases: (1) inorganic, (2) organic including biological, (3) gaseous, and (4) aqueous (Sposito, 1989). Although important, the effect of soil gas on mercury mobility will not be discussed here.

Of the two solid phases in soils, the inorganic fraction comprises the largest fraction by mass. The inorganic fraction of a soil is typically greater than 95% of the soil, and is composed of various elements, depending on the location. Perhaps the most important inorganic component of soils is the clay fraction, because it is the inorganic fraction that accurately reflects the soil's chemistry (Bohn et al., 1985). The clay fraction is defined as those particles in a soil that have a diameter of less than 1 μm but greater than 1 nm (Bohn et al., 1985). They are important because they tend to coat the surfaces of other particles, are finely dispersed, and have a large specific surface area resulting in a large adsorption capacity (Kooner et al., submitted for publication).

Oxides and hydroxides of silica, aluminum and iron are the most common inorganic constituent of soils (Table A.17). Together, these three elements typically compose more than 95% of a soil (Bohn et al., 1985). In addition, oxygen is the most abundant anion in soils; other important anions like carbonate, phosphate, nitrate, and sulfate contain oxygen, and their negative charge is a result of the oxygen atom. The only other inorganic ligand that typically has environmental significance is sulfide, which is unstable in aerobic soils (Bohn et al., 1985).

The solid organic phase of soils is relatively small, but may have a large effect on mercury adsorption, since mercury is very hydrophobic. Typically, soils consist of less than 5% organic matter by mass, but arid soils may contain less than 1% and poorly drained soils (peat) may approach 100% (Sposito, 1989). The relative

Table A.17: Composition of Average Igneous Rocks and of Three Surface Soils of Increasing Maturity (%). (Bohn et al., 1985)

	Average of Igneous Rocks	Barnes Loam (S. Dakota)	Cecil Sandy Clay Loam (N. Carolina)	Colombiana Clay (Costa Rica)
SiO_2	60	77	80	26
Al_2O_3	16	13	13	49
Fe_2O_3	7	4	5	20
TiO_2	1	0.6	1	3
MnO	0.1	0.2	0.3	0.4
CaO	5	2	0.2	0.3
MgO	4	1	<0.1	0.7
K_2O	3	2	0.6	0.1
Na_2O	4	1	0.2	0.3
P_2O_5	0.3	0.2	0.2	0.4
SO_3	0.1	0.1	--	0.3
Total	100.5	100.9	100.6	100.4

importance of factors that determine organic matter content in soils is (Bohn et al., 1985):

climate > vegetation > topography > parent material > degree of weathering

Organics in soils are typically made up of decomposing organic matter or organisms such as microorganisms, worms, plants, etc. Decomposed insoluble organics are lumped into one broad category called humics. Humics, like clays, have a tendency to coat the surface of larger soil particles, altering the character of the surface (Bohn et al., 1985).

Weathering (the process of transforming parent material (rocks) of a soil surface to a more stable state) results in the release of numerous solutes into the aqueous phase of the soil matrix (Bohn et al., 1985). Once dissolved, the solute can adsorb onto other solids, recrystallize to form a precipitate, be taken up by plants or other organisms, complex with other ions, or remain in solution (Sposito, 1989). Decomposition of organics will also result in the release of organic acids into the aqueous fraction of the soil matrix. These acids will mobilize hydrophobic compounds such as mercury due to high formation constants and low affinity for surfaces (Stumm, 1992).

A.6.2 Charge Development

Most soil particles display an overall negative surface charge. This negative charge is typically the result of some combination of the following processes (Stumm, 1992):

A.6.2.1 *Isomorphic Substitution*:

Substitution of one ion of a given valence for another ion of a different valence but similar size in the crystal lattice of a mineral will cause the overall charge on the particle to change. The crystallographic differences in clay minerals are illustrative of this type of permanent charge development.

A.6.2.2. *Adsorption of Hydrophobic Substances*:

Certain compounds, especially organic polymers, can be "adsorbed" by soil particles due to the hydrophobic nature of segments of the polymer chain. These polymers contain ionizable functional groups that can redefine the surface charge of a particle by coating the surface (Figure A.3). If coated, the surface charge depends primarily on the characteristics of the coating polymer.

A.6.2.3. *Chemical Reactions at the Surface*:

The surfaces of soil particles contain functional groups that can undergo chemical reaction. When a solute becomes covalently bound to a surface (termed an inner-sphere surface complex, Figure A.4) or merely electrostatically associated with the surface (called an outer-sphere surface complex, Figure A.4), the resulting compound can alter the original charge of the surface. Figure A.5 illustrates a number of possible surface-solute interactions.

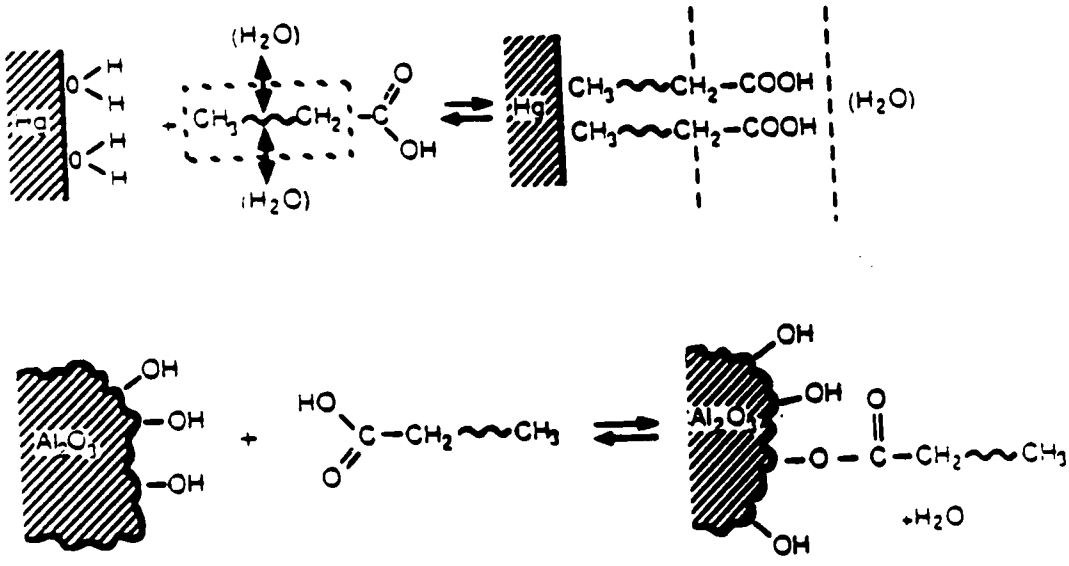


Figure A.3: Adsorption of Organics Affecting Particle Charge.
(Stumm, 1992)

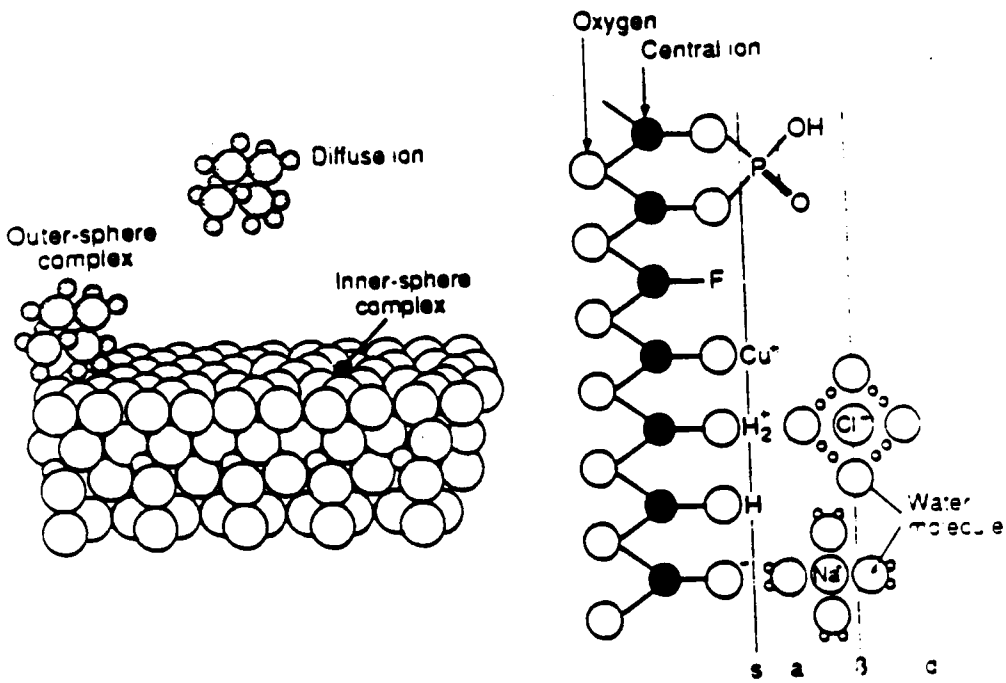


Figure A.4: Inner- and Outer-Sphere Surface Complexes.
(Stumm, 1992)

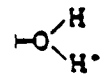
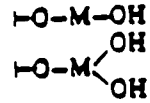
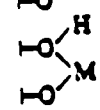
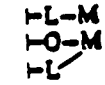
Surface reactions	Surface species
Proton/Surface Reactions	
$SOH_2^+ = SOH + H^+$	$\vdash O-H$
$SOH = SO^- + H^+$	$\vdash O^-$
Metal/Surface Reactions (Inner-Sphere)	
$SOH_2^+ + M = SOM + 2H^+$	
$SOH + M = SOM + H^+$	$\vdash O-M$
$SO^- + M = SOM$	
$SOH + H_2O + M = SOMOH + 2H^+$	$\vdash O-M-OH$
$SOH + 2H_2O + M = SOM(OH)_2 + 3H^+$	
$(SOH)_2 + M = (SO)_2M + 2H^+$	
$(SOH)_2 + M = S_2OOHM + H^+$	
Ligand/Surface Reactions (Inner-Sphere)	
$SOH_2^+ + L = SL + H_2O$	$\vdash L$
$SOH + H^+ + L = SL + H_2O$	$\vdash LH$
$SOH + 2H^+ + L = SLH + H_2O$	$\vdash\!\!> L$
$(SOH)_2 + 2H^+ + L = S_2L + 2H_2O$	$\vdash\!\!\geqslant L$
$(SOH)_2 + 3H^+ + L = S_2L + 3H_2O$	
Mixed Ligand (Ternary) Reactions (Inner-Sphere)	
$SOH + ML = SOML + H^+$	$\vdash O-M-L$
$SOH + ML = SLM + OH^-$	$\vdash L-M$
$(SOH)_2 + ML = SOMLS + H_2O$	
Ion Pair Reactions (Outer-Sphere)	
$SOH + M = SO^- - M + H^+$	$\vdash O^- - -M$
$SOH + H_2O + M = SO^- - MOH + 2H^+$	$\vdash O^- - -MOH$
$SOH + H^+ + L = SOH_2^+ - L$	$\vdash OH_2^+ - -L$
$SOH + 2H^+ + L = SOH_2^+ - LH$	$\vdash OH_2^+ - -LH$
Exchange Reactions	
$SO^- - Na^+ + M = SO^- - M + Na^+$	$\vdash O^- - -M$
$SO^- - Na^+ + M = SOM + Na^+$	$\vdash O-M$
$SOH_2^+ - SO_4^{2-} + L = SOH_2^+ - L + SO_4^{2-}$	$\vdash OH_2^+ - -L$
$SOH_2^+ - SO_4^{2-} + L = SL + SO_4^{2-} + H_2O$	$\vdash L$

Figure A.5: Possible Surface Complexation Reactions.
(Leckie, 1986)

APPENDIX B: CALCULATIONS

The following adjustments were made to convert pCi/mL (spectrometry output) to $\mu g/L$ or $\mu g/g$:

Initial and Equilibrium Suspension Concentrations:

$$\left(\frac{\mu g}{L}\right) = \left(\frac{pCi}{mL}\right) \cdot \frac{\mu Ci}{10^6\ pCi} \cdot \frac{1}{SA} \cdot \frac{1000\ mL}{L} \qquad \text{(B.1)}$$

where SA = specific activity of the isotope ($\mu Ci/\mu g$)

Filtrate Concentration:

$$\left(\frac{\mu g}{L}\right) = \left(\frac{pCi}{mL}\right) \cdot \left(\frac{\mu Ci}{10^6\ pCi}\right) \cdot \left(\frac{1}{SA}\right) \cdot \left(\frac{1000\ mL}{L}\right) \cdot d \qquad \text{(B.2)}$$

where d = dilution factor = 2 for filtrate

Solids Concentration:

$$\left(\frac{\mu g}{g}\right) = \left(\frac{pCi}{mL}\right)\left(\frac{\mu Ci}{10^6\ pCi}\right)\left(\frac{1}{SA}\right)\left(\frac{1000\ mL}{L}\right)\left(\frac{1}{\rho}\right)d \qquad \text{(B.3)}$$

where d = dilution factor = 0.333 for solids
ρ = suspension concentration = 1 g/L

Mass balances were calculated at two points in the experiment using the radiochemical activities of the individual compartments. The first mass balance (MB1) was determined by comparing suspension activity before (IA) and after (EA) the 18 hour equilibration period:

$$MB1\ (\%) = (\frac{EA}{IA}) \times 100 \qquad \textbf{(B.4)}$$

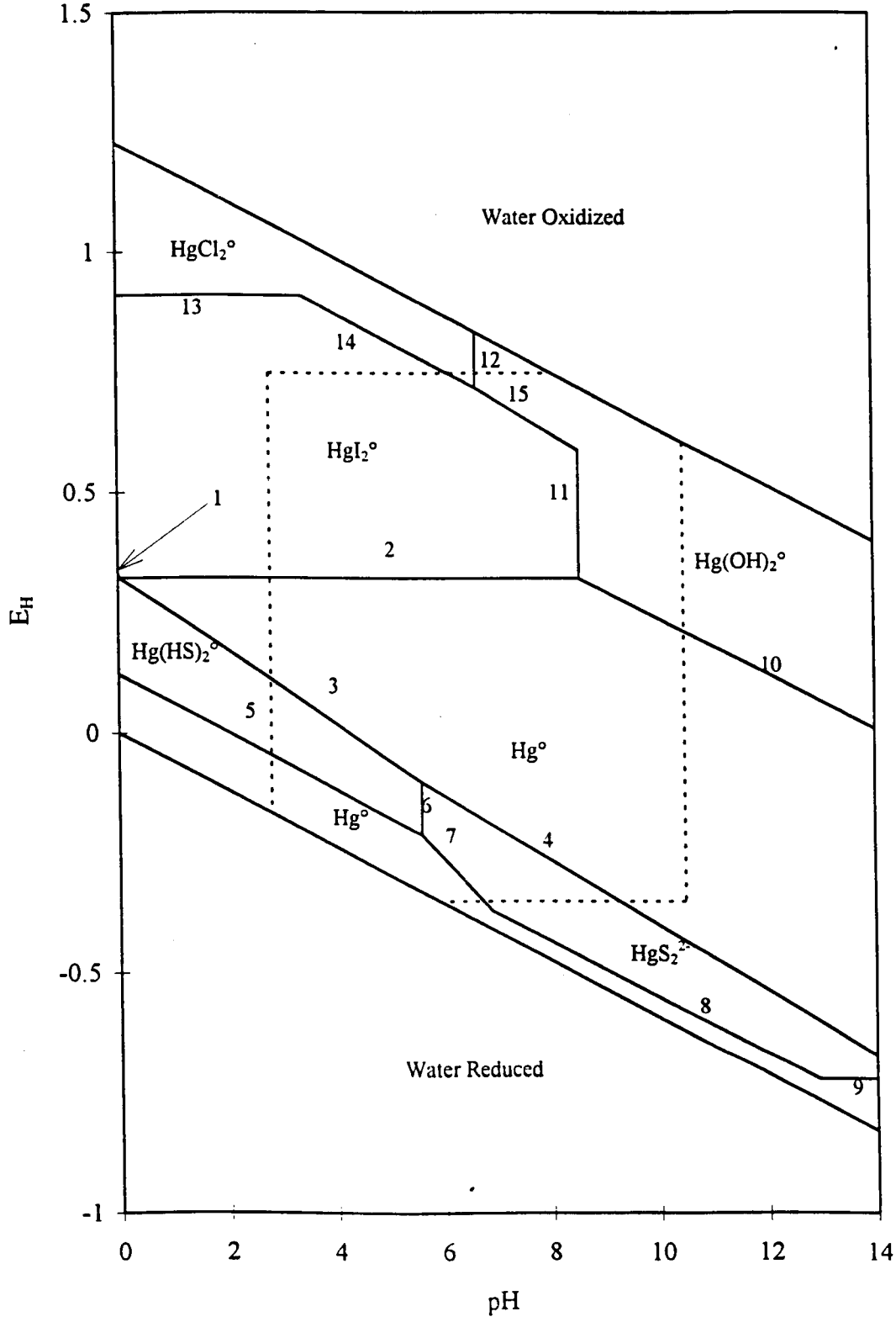
A second mass balance was computed after filtration by comparing the sum of the individual filtrate (F) and solids (S) activity to the equilibrium suspension activity:

$$MB2 = (\frac{S/3 + 2F}{EA}) \times 100 \qquad \textbf{(B.5)}$$

Adsorption percentages were computed from solids and equilibrium suspension activities:

$$\%\ Ads = (\frac{S/3}{EA}) \times 100 \qquad \textbf{(B.6)}$$

APPENDIX C: INFORMATION ON CONSTRUCTION OF E_H-pH DIAGRAM


1.5
1
0.5
0
-0.5
-1
E_H
0
2
4
6
8
10
12
14
pH
Water Oxidized
Water Reduced
$HgCl_2°$
$HgI_2°$
$Hg(OH)_2°$
$Hg(HS)_2°$
Hg°
Hg°
HgS_2^{2-}
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

Information on individual lines for E_H-pH diagram.

1. $HgI_2^\circ + 2\ SO_4^{2-} + 16\ H^+ + 14\ e^- \rightleftharpoons Hg(HS)_2^\circ + 2\ I^- + 8\ H_2O$
   $\Delta G^\circ_{rxn} = -110.6$ kcal/mol
   $p\in^\circ = 5.82$
   $E_H = 0.343 - 0.674\ pH$

2. $HgI_2^\circ + 2\ e^- \rightleftharpoons Hg^\circ + 2\ I^-$
   $\Delta G^\circ_{rxn} = 2.61$ kcal/mol
   $p\in^\circ = 2.04$
   $E_H = 0.12$

3. $Hg^\circ + 2\ SO_4^{2-} + 16\ H^+ + 12\ e^- \rightleftharpoons Hg(HS)_2^\circ + 8\ H_2O$
   $\Delta G^\circ_{rxn} = -113.2$ kcal/mol
   $p\in^\circ = 6.94$
   $E_H = 0.38 - 0.079\ pH$

4. $Hg^\circ + 2\ SO_4^{2-} + 16\ H^+ + 14\ e^- \rightleftharpoons HgS_2^{2-} + 8\ H_2O$
   $\Delta G^\circ_{rxn} = -98.40$ kcal/mol
   $p\in^\circ = 5.17$
   $E_H = 0.28 - 0.67\ pH$

5. $Hg(HS)_2^\circ \rightleftharpoons HgS_2^{2-} + 2\ H^+$
   $\Delta G^\circ_{rxn} = 14.80$ kcal/mol
   $K_{eq} = 10^{-10.88}$
   $pK_a = 5.44$

6. $Hg(HS)_2^\circ + 2\ e^- + 2\ H^+ \rightleftharpoons Hg^\circ + 2\ H_2S$
   $\Delta G^\circ_{rxn} = 2.57$ kcal/mol
   $p\in^\circ = -0.95$
   $E_H = 0.12 - 0.59\ pH$

7. $HgS_2^{2-} + 2\ e^- + 4\ H^+ \rightleftharpoons Hg^\circ + 2\ S^{2-}$
   $S^{2-} = \beta_2[H_2S]/[H^+]^2$
   $\Delta G^\circ_{rxn} = 41.85$ kcal/mol
   $p\in^\circ = -15.4$
   $E_H = 0.44 - 0.120\ pH$

8. $HgS_2^{2-} + 2\ e^- + 2\ H^+ \rightleftharpoons Hg^\circ + 2\ S^{2-}$

$S^{2-} = K_1[HS^-]/[H^+]$

$\Delta G^\circ_{rxn} = 41.85$ kcal/mol

$p\in^\circ = -15.4$

$E_H = 0.031 - pH$

9. $HgS_2^{2-} + 2\ e^- + 2\ H^+ \rightleftharpoons Hg^\circ + 2\ S^{2-}$

$\Delta G^\circ_{rxn} = 41.85$ kcal/mol

$p\in^\circ = -15.4$

$E_H = -0.73$

10. $Hg(OH)_2^\circ + 2\ e^- + 2\ H^+ \rightleftharpoons Hg^\circ + 2\ H_2O$

$\Delta G^\circ_{rxn} = -38.40$ kcal/mol

$p\in^\circ = 14.13$

$E_H = 0.834 - 0.59\ pH$

11. $HgI_2^\circ + OH^- \rightleftharpoons Hg(OH)_2^\circ + 2\ I^-$

$\Delta G^\circ_{rxn} = 2.84$ kcal/mol

$K_{eq} = 10^{-2.085}$

$pK_a = 8.64$

12. $HgCl_2^\circ + 2\ OH^- \rightleftharpoons Hg(OH)_2^\circ + 2\ Cl^-$

$\Delta G^\circ_{rxn} = -11.85$ kcal/mol

$K_{eq} = 10^{8.73}$

$pK_a = 6.34$

13. $HgCl_2^\circ + I_2^\circ + 2\ e^- \rightleftharpoons HgI_2^\circ + 2\ Cl^-$

$\Delta G^\circ_{rxn} = 43.24$ kcal/mol

$p\in^\circ = 15.92$

$E_H = 0.91$

14. $HgCl_2^\circ + 2\ IO_3^- + 10\ e^- + 12\ H^+ \rightleftharpoons HgI_2^\circ + 2\ H_2O + 2\ Cl^-$

$\Delta G^\circ_{rxn} = -318.20$ kcal/mol

$p\in^\circ = 23.42$

$E_H = 1.34 - 0.071\ pH$

15. $Hg(OH)_2^\circ + 2\ IO_3^- + 12\ e^- + 14\ H^+ \rightleftharpoons HgI_2^\circ + 2\ H_2O$

$\Delta G^\circ_{rxn} = -344.51$ kcal/mol

$p\in^\circ = 21.14$

$E_H = 1.18 - 0.069\ pH$

APPENDIX D: EXPERIMENTAL DATA

MB1 Data for Mercury-Illite Suspensions.

I = 0 µg/L		I = 500 µg/L		I = 1.5 mg/L		I = 50 mg/L	
pH	MB1	pH	MB1	pH	MB1	pH	MB1
(a) Hg = 40 µg/L							
9.53	94.79	9.85	71.52	9.33	101.83	10.09	96.22
9.09	40.87	8.99	72.15	7.69	98.00	9.07	93.12
8.41	51.77	8.86	76.42	7.55	100.20	8.69	99.35
8.12	46.75	7.40	87.31	7.27	93.33	8.17	96.08
7.55	56.78	6.91	75.53	7.06	101.35	7.69	94.59
7.28	71.14	6.29	91.40	7.16	102.22	7.46	93.26
7.16	68.18	4.48	86.19	6.76	103.41	7.24	96.25
6.89	68.15			6.48	99.41	6.91	96.87
6.64	70.66			5.93	104.42	6.66	96.05
6.17	71.81			4.98	105.74	6.24	95.83
5.14	80.71			3.94	102.79	5.43	94.70
4.09	87.27					4.19	93.63
(b) Hg = 100 µg/L							
9.27	78.87	9.24	93.62	8.87	96.78	8.70	97.90
8.62	56.00	8.55	92.17	8.19	97.06	8.34	97.14
7.89	90.02	7.65	95.27	7.44	101.29	7.55	97.75
7.16	88.73	7.24	96.01	7.08	96.95	7.26	94.32
6.88	86.23	7.10	84.59	6.94	88.10	7.04	
6.66	83.26	6.89	91.42	6.76	92.22	6.85	
6.25	86.33	6.61	99.40	6.64	96.21	6.76	96.10
5.97	79.60	5.96	99.39	6.43	99.44	6.62	97.68
4.88	86.10	5.56	98.68	5.30	96.29	5.87	97.51
		4.49	95.14	4.68	97.60	5.27	98.03
		3.92	93.97	4.21	99.72	4.40	98.16
				3.79	96.64	3.88	97.97
(c) Hg = 200 µg/L							
8.58	87.62	9.86	93.85	9.88	92.34	8.33	96.69
8.69	91.49	9.39	90.44	9.38	91.69	8.00	95.80
8.57	94.71	8.84	99.03	8.91	93.84	7.39	97.13
8.30	82.69	8.47	93.71	8.28	96.41	7.00	99.73
7.62	96.23	7.54	96.40	7.52	94.69	6.59	98.32
7.36	93.08	7.32	98.74	7.23	97.59	6.22	97.56
7.16	86.33	7.12	97.42	7.03	93.96	5.37	98.15
7.02	89.52	6.94	100.34	6.68	95.72	4.24	98.04
6.72	95.48	6.08	100.85	6.64	97.40	3.97	99.11
6.03	93.62	5.18	94.88	5.92	94.53		
4.84	94.68	4.31	96.84	4.90	96.73		
				4.25	95.42		

MB2 Data for Mercury-Illite Suspensions.

I = 0 µg/L		I = 500 µg/L		I = 1.5 mg/L		I = 50 mg/L	
pH	MB2	pH	MB2	pH	MB2	pH	MB2
(a) Hg = 40 µg/L							
9.53	78.77	9.85	99.11	9.33	97.47	10.09	87.84
9.09	85.72	8.99	97.23	7.69	85.82	9.07	97.57
8.41	89.41	8.86	96.19	7.55	90.48	8.69	95.79
8.12	88.82	7.40	101.40	7.27	97.02	8.17	92.51
7.55	87.27	6.91	99.84	7.06	96.84	7.69	93.02
7.28	84.82	6.29	99.10	7.16	93.04	7.46	100.58
7.16	85.58	4.48	101.34	6.76	94.71	7.24	99.46
6.89	86.88			6.48	97.56	6.91	103.41
6.64	84.99			5.93	94.24	6.66	101.39
6.17	89.97			4.98	81.00	6.24	102.15
5.14	82.23			3.94	96.21	5.43	104.31
4.09	86.70					4.19	104.24
(b) Hg = 100 µg/L							
9.27	82.81	9.24	91.74	8.87	88.26	8.70	96.26
8.62	60.55	8.55	97.59	8.19	93.22	8.34	97.70
7.89	56.17	7.65	87.33	7.44	88.10	7.55	89.89
7.16	57.77	7.24	87.34	7.08	88.62	7.26	98.83
6.88	59.60	7.10	88.01	6.94	89.87	7.04	98.45
6.66	50.60	6.89	86.86	6.76	89.48	6.85	97.21
6.25	52.13	6.61	88.29	6.64	91.33	6.76	100.72
5.97	43.35	5.96	88.47	6.43	89.98	6.62	99.86
4.88	54.51	5.56	85.84	5.30	91.54	5.87	100.15
		4.49	82.24	4.68	90.90	5.27	100.72
		3.92	95.55	4.21	91.70	4.40	100.67
				3.79	94.01	3.88	98.38
(c) Hg = 200 µg/L							
8.58	90.58	9.86	87.90	9.88	96.04	8.33	96.97
8.69	85.12	9.39	86.27	9.38	89.35	8.00	98.08
8.57	86.06	8.84	86.97	8.91	90.29	7.39	100.52
8.30	91.29	8.47	88.72	8.28	90.87	7.00	100.36
7.62	72.79	7.54	88.87	7.52	93.96	6.59	99.37
7.36	78.82	7.32	87.11	7.23	92.44	6.22	98.53
7.16	83.72	7.12	91.37	7.03	94.27	5.37	100.09
7.02	75.04	6.94	89.04	6.68	91.72	4.24	98.51
6.72	67.99	6.08	89.52	6.64	90.35	3.97	96.67
6.03	78.47	5.18	96.20	5.92	93.14		
4.84	76.62	4.31	91.61	4.90	89.82		
				4.25	90.97		

Distribution Coefficients (L/kg)
for Mercury-Illite Suspensions.

I = 0 µg/L		I = 500 µg/L		I = 1.5 mg/L		I = 50 mg/L	
pH	K_D	pH	K_D	pH	K_D	pH	K_D
(a) Hg = 40 µg/L							
9.53	864.98	9.85	802.36	9.33	328.28	10.09	201.82
9.09	3329.60	8.99	812.11	7.69	328.70	9.07	134.50
8.41	6319.59	8.86	664.92	7.55	236.55	8.69	130.16
8.12	4430.43	7.40	293.61	7.27	327.80	8.17	136.26
7.55	7317.67	6.91	252.52	7.06	420.49	7.69	123.92
7.28	7952.29	6.29	231.84	7.16	305.23	7.46	111.74
7.16	6946.85	4.48	140.46	6.76	275.03	7.24	115.20
6.89	9853.05			6.48	293.99	6.91	103.89
6.64	14686.62			5.93	272.74	6.66	101.19
6.17	13452.97			4.98	127.51	6.24	104.11
5.14	14530.35			3.94	172.34	5.43	88.50
4.09	53927.36					4.19	126.62
(b) Hg = 100 µg/L							
9.27	1245.75	9.24	343.02	8.87	201.78	8.70	84.71
8.62	3425.67	8.55	323.52	8.19	189.71	8.34	72.84
7.89	20115.97	7.65	181.48	7.44	71.37	7.55	89.51
7.16	9185.65	7.24	62.90	7.08	58.18	7.26	88.50
6.88	1272.93	7.10	68.79	6.94	59.97	7.04	106.13
6.66	2085.64	6.89	49.30	6.76	58.45	6.85	96.42
6.25	1549.15	6.61	51.14	6.64	58.58	6.76	77.32
5.97	1773.37	5.96	67.27	6.43	56.19	6.62	71.99
4.88	2584.89	5.56	75.47	5.30	69.46	5.87	83.89
4.54	7037.45	4.49	90.67	4.68	71.46	5.27	92.03
3.87	3601.91	3.92	64.83	4.21	86.97	4.40	92.54
				3.79	83.56	3.88	111.44
(c) Hg = 200 µg/L							
8.58	712.41	9.86	433.96	9.88	211.00	8.33	71.41
8.69	736.55	9.39	369.55	9.38	178.86	8.00	71.11
8.57	659.14	8.84	250.93	8.91	145.43	7.39	62.97
8.30	669.79	8.47	199.09	8.28	129.32	7.00	52.96
7.62	803.77	7.54	109.44	7.52	90.14	6.59	59.00
7.36	969.41	7.32	91.93	7.23	79.17	6.22	60.36
7.16	970.00	7.12	82.99	7.03	86.69	5.37	75.87
7.02	937.96	6.94	83.72	6.68	86.17	4.24	89.97
6.72	1041.37	6.08	72.64	6.64	79.50	3.97	90.41
6.03	1885.05	5.18	63.03	5.92	62.97		
4.84	2383.24	4.31	60.64	4.90	65.27		
				4.25	62.11		

MB1 Data for Mercury-Illite-NOM Suspensions.

I = 0 µg/L		I = 500 µg/L		I = 1.5 mg/L		I = 50 mg/L	
pH	MB1	pH	MB1	pH	MB1	pH	MB1
(a) Hg = 40 µg/L							
10.24	76.13	10.19	69.68	10.01	73.29	10.11	68.81
10.07	77.31	10.07	72.85	9.56	74.27	9.56	86.71
9.54	81.11	9.48	73.50	8.92	81.03	8.99	92.57
8.88	75.40	8.68	79.21	7.59	94.30	7.67	94.48
7.60	84.45	7.43	86.11	7.27	92.76	7.38	97.49
7.26	85.11	7.12	91.39	6.94	98.43	6.97	98.42
6.89	92.61	6.74	89.48	6.64	100.99	6.71	102.32
6.60	83.50	6.29	92.44	6.07	100.16	6.24	97.82
5.94	84.42	5.31	92.31	5.00	99.58	5.23	98.39
4.93	92.21	4.45	93.25	4.25	96.60	4.34	96.77
4.21	90.43						
3.93	92.48						
(b) Hg = 100 µg/L							
9.86	68.47	9.76	71.13	9.73	70.04	9.75	90.88
9.22	77.00	9.12	71.68	8.93	80.28	9.05	96.80
8.50	75.94	8.38	74.86	8.23	90.63	8.13	100.64
7.77	82.93	7.61	86.74	7.78	95.60	7.81	97.28
7.22	83.01	7.17	93.16	7.36	94.44	7.41	99.61
7.12	80.43	6.84	94.21	6.91	97.84	7.12	97.45
6.83	86.42	6.54	93.35	6.63	95.93	6.76	102.51
6.49	85.46	6.04	94.93	6.11	93.56	6.27	99.17
5.93	86.87	4.96	96.22	4.96	95.21	5.28	99.93
4.81	88.81	4.20	95.40	4.25	96.53		
4.15	88.11						
(c) Hg = 200 µg/L							
10.00	85.86	9.96	78.92	9.92	79.25	10.10	83.49
9.47	90.01	9.46	84.94	9.32	74.08	9.47	94.54
8.39	84.57	8.32	87.16	8.29	87.48	8.57	97.97
8.00	88.88	8.05	90.33	7.89	92.58	8.19	97.42
7.17	86.89	7.21	97.17	7.20	96.05	7.36	98.19
6.30	94.77	6.19	96.25	6.40	96.60	6.52	98.42
5.16	88.11	5.24	98.74	5.15	97.22	5.41	98.67
4.80	86.91	4.80	98.66	4.77	93.03	4.92	97.28
3.71	94.02	4.25	96.15	4.29	95.99	4.34	97.60

MB2 Data for Mercury-Illite-NOM Suspensions.

I = 0 µg/L		I = 500 µg/L		I = 1.5 mg/L		I = 50 mg/L	
pH	MB2	pH	MB2	pH	MB2	pH	MB2
(a) Hg = 40 µg/L							
10.24	101.40	10.19	103.40	10.01	93.17	10.11	99.63
10.07	102.84	10.07	93.90	9.56	85.16	9.56	103.32
9.54	100.48	9.48	91.35	8.92	86.32	8.99	100.12
8.88	99.96	8.68	99.23	7.59	95.41	7.67	103.60
7.60	98.62	7.43	96.62	7.27	100.80	7.38	100.24
7.26	92.39	7.12	95.69	6.94	96.38	6.97	103.21
6.89	91.60	6.74	100.54	6.64	99.14	6.71	98.90
6.60	95.60	6.29	94.77	6.07	97.22	6.24	103.05
5.94	91.10	5.31	89.10	5.00	97.32	5.23	104.36
4.93	99.56	4.45	94.79	4.25	96.99	4.34	100.56
4.21	107.77						
3.93	102.34						
(b) Hg = 100 µg/L							
9.86	86.65	9.76	80.80	9.73	72.14	9.75	94.17
9.22	78.99	9.12	86.20	8.93	73.23	9.05	98.57
8.50	66.93	8.38	86.71	8.23	79.27	8.13	92.50
7.77	61.37	7.61	88.31	7.78	87.37	7.81	101.69
7.22	57.88	7.17	93.85	7.36	93.14	7.41	92.61
7.12	66.90	6.84	94.45	6.91	90.37	7.12	95.63
6.83	62.53	6.54	97.97	6.63	94.08	6.76	92.00
6.49	94.26	6.04	98.02	6.11	92.30	6.27	95.85
5.93	88.81	4.96	95.53	4.96	95.30	5.28	95.71
4.81	93.66	4.20	98.74	4.25	95.03		
4.15	91.44						
(c) Hg = 200 µg/L							
10.00	85.86	9.96	91.97	9.92	78.47	10.10	95.31
9.47	90.01	9.46	87.70	9.32	87.87	9.47	97.99
8.39	84.57	8.32	95.31	8.29	90.90	8.57	100.41
8.00	88.88	8.05	91.98	7.89	92.91	8.19	98.62
7.17	86.89	7.21	92.26	7.20	95.01	7.36	99.01
6.30	94.77	6.19	96.22	6.40	93.66	6.52	84.80
5.16	88.11	5.24	92.50	5.15	94.87	5.41	85.64
4.80	86.91	4.80	93.21	4.77	96.50	4.92	100.72
3.71	94.02	4.25	91.00	4.29	99.54	4.34	99.08

Distribution Coefficients (L/kg)
for Mercury-Illite-NOM Suspensions.

I = 0 µg/L		I = 500 µg/L		I = 1.5 mg/L		I = 50 mg/L	
pH	K_D	pH	K_D	pH	K_D	pH	K_D
(a) Hg = 40 µg/L							
10.24	2039.89	10.19	3237.91	10.01	1953.75	10.11	1188.13
10.07	2164.29	10.07	3510.59	9.56	2236.53	9.56	626.35
9.54	1956.32	9.48	2632.76	8.92	1095.04	8.99	398.15
8.88	1683.51	8.68	1200.55	7.59	290.18	7.67	235.11
7.60	1797.69	7.43	506.53	7.27	286.73	7.38	244.98
7.26	2017.02	7.12	419.13	6.94	247.31	6.97	213.90
6.89	2685.00	6.74	336.52	6.64	231.47	6.71	188.71
6.60	3878.09	6.29	282.99	6.07	230.83	6.24	158.30
5.94	9542.40	5.31	233.91	5.00	244.44	5.23	159.33
4.93	13943.24	4.45	237.01	4.25	222.96	4.34	185.57
4.21	20224.75						
3.93	15508.26						
(b) Hg = 100 µg/L							
9.86	1611.02	9.76	1684.61	9.73	1234.36	9.75	254.55
9.22	1435.71	9.12	1460.41	8.93	542.74	9.05	127.74
8.50	1060.36	8.38	992.96	8.23	283.94	8.13	107.21
7.77	1830.60	7.61	423.61	7.78	221.87	7.81	108.12
7.22	3162.11	7.17	286.65	7.36	183.55	7.41	83.53
7.12	3937.15	6.84	260.62	6.91	167.92	7.12	96.97
6.83	5830.09	6.54	226.51	6.63	169.83	6.76	99.31
6.49	14642.84	6.04	182.30	6.11	134.76	6.27	105.82
5.93	10708.73	4.96	138.65	4.96	121.67	5.28	99.74
4.81	21594.13	4.20	123.81	4.25	121.39		
4.15	14936.06						
(c) Hg = 200 µg/L							
10.00	3192.62	9.96	2938.45	9.92	2736.33	10.10	298.96
9.47	3204.14	9.46	3284.71	9.32	2346.34	9.47	152.42
8.39	4154.52	8.32	1340.61	8.29	573.34	8.57	124.83
8.00	4758.63	8.05	831.89	7.89	293.45	8.19	99.86
7.17	8733.07	7.21	300.30	7.20	160.83	7.36	83.76
6.30	13865.93	6.19	162.88	6.40	117.53	6.52	80.49
5.16	19527.99	5.24	130.67	5.15	96.17	5.41	82.03
4.80	undef.	4.80	133.79	4.77	96.79	4.92	77.74
3.71	22921.53	4.25	106.05	4.29	141.63	4.34	90.19

VITA

William Patrick Hamilton was born in Ft. Riley, Kansas on October 30, 1967. He attended elementary school in the St. Louis, Missouri area, and graduated from Chaminade College Preparatory School in May, 1982. He attended St. Louis University High School and graduated in May of 1986.

The following September he enrolled at Vanderbilt University in Nashville, Tennessee. He received a Bachlor of Science degree in Mathematics (May, 1990) and a Bachlor of Engineering degree in Civil Engineering (July, 1992).

The following January, he entered the University of Tennessee in Knoxville, Tennessee. He conducted his research at Oak Ridge National Laboratory and in May, 1995 he received a Masters of Science degree in Environmental Engineering.

Mr. Hamilton has published one article in the *Journal of Water, Air, and Soil Pollution*, entitled "Effect of pH and iodide on the adsorption of mercury(II) by illite." He has also presented his work in an oral presentation before the Division of Environmental Chemistry at the 207th National Meeting of the American Chemical Society (San Diego, CA) and at the Southeastern Regional Meeting of the Geological Society of America, and as a general poster for the 4th International Conference on Mercury as a Global Pollutant (Whistler, B.C.).

Mr. Hamilton is currently living in Nashville, Tennessee, where he is pursuing a Doctoral degree in Environmental Engineering at Vanderbilt University.

May, 1995