

YEARS

ADSORPTION/DESORPTION AND TRANSPORT
OF MERCURY AND ARSENIC IN NEW JERSEY SOILS

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Mercury

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Yujun Yin, Herbert E. Allen and C.P. Huang
Department of Civil and Environmental Engineering
University of Delaware
Newark, DE 19716

Project Manager
Paul F. Sanders, Ph. D.
Division of Science and Research
New Jersey Department of Environmental Protection and Energy
Trenton, NJ 08625

TABLE OF CONTENTS

LIST OF TABLES	v
LIST OF FIGURES.....	vii
ABSTRACT.....	xvi

Chapter

1	INTRODUCTION	1
	References.....	4
2	LITERATURE REVIEW	6
2.1	Origin of Mercury in Soils.....	6
2.2	Aqueous Speciation of Mercury(II) and Methylmercury.....	8
2.3	Adsorption, Desorption and Transformation Reactions of Mercury(II) and Methylmercury in Soils	12
2.3.1	General Theory of Metal Adsorption to and Desorption from Soils.....	12
2.3.2	Adsorption and Desorption of Mercury(II) on Soils	15
2.3.3	Adsorption and Desorption of Methylmercury on Soils	18
2.3.4	Transformation of Mercury(II) and Methylmercury in Soils	19
2.4	Objectives of Research	21
2.5	References.....	22
3	EFFECTS OF pH, CHLORIDE, ORGANIC MATTER, AND CALCIUM(II) ON MERCURY(II) ADSORPTION BY SOILS.....	29
3.1	Abstract.....	29
3.2	Introduction.....	30
3.3	Materials and Methods	32
3.3.1	Materials.....	32
3.3.2	Adsorption Methods.....	32
3.3.3	Mercury Analysis	38

3.4	Results and Discussion	41
3.4.1	Effect of pH.....	41
3.4.2	Effect of Organic Matter	47
3.4.3	Effect of Chloride.....	57
3.4.4	Effect of Calcium	63
3.5	Summary and Conclusions	67
3.6	References.....	69
4	ADSORPTION AND DESORPTION ISOTHERMS OF MERCURY(II) ON SOILS.....	72
4.1	Abstract.....	72
4.2	Introduction.....	73
4.3	Materials and Methods	75
4.3.1	Adsorption Experiments	75
4.3.2	Desorption Experiments.....	76
4.4	Results and Discussion	78
4.4.1	Adsorption Isotherms	78
4.4.2	Effect of Ionic Strength on Adsorption	84
4.4.3	Modeling Adsorption Isotherms	89
4.4.4	Correlations of Adsorption Capacity and Binding Strength with Soil Properties	95
4.4.5	Desorption.....	98
4.5	Summary and Conclusions	104
4.6	References.....	106
5	KINETICS OF MERCURY(II) ADSORPTION AND DESORPTION ON SOILS.....	109
5.1	Abstract.....	109
5.2	Introduction.....	110
5.3	Materials and Methods	111
5.3.1	Kinetic Experiments.....	111
5.3.2	Data Analysis	114
5.4	Results and Discussion	115

5.4.1	Adsorption Kinetics	115
5.4.2	Desorption Kinetics.....	122
5.4.3	Modeling Adsorption and Desorption Kinetics	132
5.5	Summary and Conclusions	138
5.6	References.....	139
6	INTERACTION OF MERCURY(II) WITH SOIL-DERIVED HUMIC SUBSTANCES	142
6.1	Abstract.....	142
6.2	Introduction.....	142
6.3	Materials and Methods	144
6.3.1	Extraction of Humic Substances	144
6.3.2	Free Mercury(II) Determination.....	146
6.3.4	Reagents	146
6.3.5	Potentiometric Titration	147
6.4	Results and Discussion	148
6.4.1	Calibration.....	148
6.4.2	Titration of Humic Substances with Hg.....	154
6.4.3	Modeling the Binding of Hg with Humic Substances.....	157
6.5	Summary and Conclusions	168
6.6	References.....	169
7	ADSORPTION OF METHYLMERCURY BY SOILS: EFFECTS OF pH, CHLORIDE AND CALCIUM.....	173
7.1	Abstract.....	173
7.2	Introduction.....	173
7.3	Materials and Methods	175
7.4	Results and Discussion	176
7.5	Summary and Conclusions	193
7.6	References.....	198
8	PREDICTION OF SOIL-WATER PARTITION OF MERCURY(II) AND METHYLMERCURY AS A FUNCTION OF pH	200
8.1	Abstract.....	200
8.2	Introduction.....	200

8.3 Model Development	203
8.4 Data Collection	207
8.5 Results and Discussion	208
8.5.1 Adsorption of Mercury(II).....	208
8.5.2 Adsorption of Methylmercury.....	218
8.6 Summary and Conclusions	222
8.7 References.....	225
9 SUMMARY AND CONCLUSIONS	228
BIBLIOGRAPHY	233
APPENDIX A: ADSORPTION EDGE	250
APPENDIX B: ADSORPTION ISOTHERMS	272
APPENDIX C: ADSORPTION AND DESORPTION KINETICS	291

LIST OF TABLES

Table 2.1	Aqueous equilibria of Hg(II).....	9
Table 3.1	Soil particle size distribution	34
Table 3.2	Soil pH, CEC, organic C and surface area.....	35
Table 3.3	Soil oxide contents.....	36
Table 3.4	Test of digestion method for determination of Hg	40
Table 3.5	Mass recoveries of Hg from soil and solution phases	40
Table 4.1	Concentrations of dissolved organic carbon in soil suspensions. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	83
Table 4.2	Langmuir and Freundlich constants for adsorption of Hg(II) on fifteen New Jersey soils. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	90
Table 4.3	Gunary constants for adsorption of Hg(II) on fifteen New Jersey soils. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	91
Table 4.4	Model fitting parameters for adsorption of Hg(II) on fifteen New Jersey soils with equations 4.21 and 4.22. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	98
Table 5.1	Model fitting parameters for adsorption and desorption kinetics of Hg(II) on soils.....	135
Table 5.2	Relationships between rate coefficients and soil organic C (SOC) content as well as equilibrium Hg adsorption (q_e). Influent Hg concentration = 8 mg L ⁻¹	136
Table 6.1	Characteristics of humic substance extract.....	145

Table 6.2	Stability constants for Hg(II)	155
Table 6.3	Model fitting parameters.....	164
Table 8.1	Model fitting parameters for adsorption of Hg(II) on soils from a 1 × 10 ⁻⁷ M solution over a pH range of 3 to 10.....	209
Table 8.2	Model fitting parameters for adsorption of methylmercury on soils from a 2 × 10 ⁻⁷ M solution over a pH range of 3 to 10	221

LIST OF FIGURES

Figure 2.1	Hg(II) speciation as a function of pH and Cl ⁻ concentration. Dashed lines refer to the absence of Cl ⁻ ; solid lines denote a Cl ⁻ concentration of 10 ⁻⁴ M.....	10
Figure 2.2	Methylmercury speciation as function of pH and Cl ⁻ concentration. Solid lines refer to the absence of Cl ⁻ ; dashed lines denote a Cl ⁻ concentration of 10 ⁻⁴ M.....	11
Figure 3.1	Schematic of flow injection system.....	39
Figure 3.2	Adsorption of Hg(II) on Washington loam as a function of pH. Soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	42
Figure 3.3	Comparison of Hg(II) adsorption on different properties of soils as a function of pH. Initial Hg(II) concentration = 1 × 10 ⁻⁷ M; soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C. See Table 3.1 for soil identification.....	44
Figure 3.4	Hg(II) speciation as a function of pH and Cl ⁻ concentration. Dashed lines denote the case of Cl ⁻ = 1 × 10 ⁻⁵ M and solid lines denote the case of Cl ⁻ = 1 × 10 ⁻⁶ M.....	46
Figure 3.5	Dissolution of soil organic carbon as a function of solution pH for the Freehold sandy loam (B horizon). Soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	48
Figure 3.6	Effect of dissolved organic carbon on Hg(II) adsorption by Freehold sandy loam (A horizon) at pH 6.5. Initial Hg(II) concentration = 1 × 10 ⁻⁷ M; soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C	49

Figure 3.7a	Comparison of Hg(II) adsorption by Freehold sandy loam (A horizon) with hydrogen peroxide treatment for organic matter removal, addition of organic matter, and no organic matter change as a function of pH. Initial Hg(II) concentration = 1×10^{-7} M; soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C	51
Figure 3.7b	Comparison of Hg(II) adsorption by Rockaway stony loam with hydrogen peroxide treatment for organic matter removal, addition of organic matter, and no organic matter change as a function of pH. Initial Hg(II) concentration = 1×10^{-7} M; soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	52
Figure 3.7c	Comparison of Hg(II) adsorption by Dunellen sandy loam with hydrogen peroxide treatment for organic matter removal, addition of organic matter, and no organic matter change as a function of pH. Initial Hg(II) concentration = 1×10^{-7} M; soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	53
Figure 3.7d	Final concentration of dissolved organic carbon in solution as a function of pH. See Table 3.1 for soil identification. Soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C	54
Figure 3.8a	Adsorption of 1×10^{-7} M Hg(II) on Freehold sandy loam (A horizon) as a function of pH and chloride concentration. Soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	58
Figure 3.8b	Adsorption of 1×10^{-7} M Hg(II) on Dunellen sandy loam as a function of pH and chloride concentration. Soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	59
Figure 3.8c	Adsorption of 1×10^{-7} M Hg(II) on Boonton Union sandy loam as a function of pH and chloride concentration. Soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	60
Figure 3.9	Hg(II) speciation as a function of Cl ⁻ concentration at pH 3	62
Figure 3.10	Comparison of the adsorption of 1×10^{-7} M Hg(II) on Freehold sandy loam (A horizon) in NaNO ₃ and Ca(NO ₃) ₂ . Soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	64

Figure 3.11	Comparison of the adsorption of 1×10^{-7} M Hg(II) on Boonton Union loam in NaNO_3 and $\text{Ca}(\text{NO}_3)_2$. Soil:water = 1 g 100 mL^{-1} ; I = 0.01 M NaNO_3 ; T = $25 \pm 2^\circ\text{C}$	65
Figure 3.12	Comparison of the concentration of dissolved organic C in NaNO_3 and $\text{Ca}(\text{NO}_3)_2$ for Boonton Union loam. Soil:water = 1 g 100 mL^{-1} ; I = 0.01 M; T = $25 \pm 2^\circ\text{C}$	66
Figure 4.1a	S-type adsorption isotherm of Hg(II) on Rockaway stony loam. Solid lines represent model-predicted isotherm (equation 4.21). Soil:water = 0.4 g 40 mL^{-1} ; I = 0.01 NaNO_3 ; T = $25 \pm 2^\circ\text{C}$	79
Figure 4.1b	L-type adsorption isotherm of Hg(II) on fill material from the Delaware River. Solid lines represent model-predicted isotherm (equation 4.21). Soil:water = 0.4 g 40 mL^{-1} ; I = 0.01 NaNO_3 ; T = $25 \pm 2^\circ\text{C}$	80
Figure 4.1c	Adsorption isotherm of Hg(II) on Rockaway sandy loam from which organic matter was removed. Solid lines represent model-predicted isotherm (equation 4.22). Soil:water = 0.4 g 40 mL^{-1} ; I = 0.01 NaNO_3 ; T = $25 \pm 2^\circ\text{C}$	81
Figure 4.2a	Comparison of adsorption isotherms of Hg(II) on Freehold sandy loam (A horizon) in different concentrations of electrolyte. Solid lines represent the model-predicted isotherms in 0.01 M NaNO_3 . Soil:water = 0.4 g 40 mL^{-1} ; I = 0.01 NaNO_3 ; T = $25 \pm 2^\circ\text{C}$	85
Figure 4.2b	Comparison of adsorption isotherms of Hg(II) on Boonton Union loam in different concentrations of electrolyte. Solid lines represent the model predicted isotherms in 0.01 M NaNO_3 . Soil:water = 0.4 g 40 mL^{-1} ; I = 0.01 NaNO_3 ; T = $25 \pm 2^\circ\text{C}$	86
Figure 4.3	Mercury speciation as a function of initial Hg concentration. Solid lines: $\text{Cl}^- = 10^{-5}$ M, pH = 5; dashed line: $\text{Cl}^- = 10^{-6}$ M; pH = 6.5	88
Figure 4.4	Correlation between soil adsorption capacity for Hg and the soil organic carbon content. Regression did not include the three soils having the greatest organic carbon content	97

Figure 4.5a	Desorption isotherms of Hg on Freehold sandy loam (A horizon). Solid lines represent adsorption; dashed lines represent desorption	100
Figure 4.5b	Desorption isotherms of Hg on Boonton Union loam. Solid lines represent adsorption; dashed lines represent desorption.....	101
Figure 4.6	Comparison of Hg desorption from three soils with different properties, Penn silt loam, fill materials from Delaware River, and Rockaway stony loam	103
Figure 5.1	Schematic of kinetic experimental setup. RC: Reaction chamber; WC: water circulator; P: Pump.....	113
Figure 5.2	Effect of stopping flow on the effluent concentration for Hg adsorption on Freehold sandy loam (A horizon) at an influent concentration of 4 mg L ⁻¹	116
Figure 5.3	Kinetics of Hg adsorption on soils at an influent concentration of 8 mg L ⁻¹ . See Table 3.1 for soil identification.....	117
Figure 5.4	Comparison of Hg adsorption kinetics on Freehold sandy loam (A horizon) at different influent concentrations. Solid line refers to an influent concentration of 4 mg L ⁻¹ ; dashed line denotes an influent concentration of 8 mg L ⁻¹	120
Figure 5.5	Fractional Hg adsorption as a function of time square root. Influent Hg concentration = 8 mg L ⁻¹ . See Table 3.1 for soil identification	121
Figure 5.6	Rate of Hg removal from three soils following adsorption at an influent concentration of 8 mg L ⁻¹ . See Table 3.1 for soil identification	123
Figure 5.7	Hg remaining on soils during desorption process following adsorption at an influent concentration of 8 mg L ⁻¹	124
Figure 5.8	Fractional Hg removal as a function of time. See Table 3.1 for soil identification	125
Figure 5.9	Fractional Hg removal as a function of the soil organic C content. Mercury(II) was adsorbed by soils from an 8 mg L ⁻¹ influent.....	128

Figure 5.10	Comparison of Hg remaining and removal profile on Freehold sandy loam (A horizon) for two initial concentrations. Solid lines refer to an initial concentration of $214 \mu\text{g g}^{-1}$; dashed lines denote an initial concentration of $254 \mu\text{g g}^{-1}$	130
Figure 5.11	Comparison of Hg remaining profile on Dunellen sandy loam for two initial concentrations.....	131
Figure 5.12	Comparison of observed and predicted adsorption and desorption kinetics of Hg(II) on Dunellen sandy loam. Solid lines represent predicted values	137
Figure 6.1	Schematic of titration system setup	148
Figure 6.2	Response of iodide electrode to Hg(II) as a function of solution pH. Hg(II) concentration is $9.5 \times 10^{-7} \text{ M}$. The predicted potential values were calculated based on the $K_{\text{Hg-Ag}}$ value and equation 6.11 which were obtained using calibration data at pH 4	150
Figure 6.3	Comparison of measured and predicted potentials as a function of initial Hg concentration. Circles and triangles denotes the measured potential values; solid and dashed lines represent the predicted potential values based on the $K_{\text{Hg-Ag}}$ values and equation 6.11 obtained using calibration data at pH 4.....	153
Figure 6.4	Titration curves of humic substances by Hg(II). Solid lines denote model predictions. The concentration of humic substances is 25.8 mg C L^{-1} , which was extracted from Freehold sandy loam (B horizon).....	156
Figure 6.5	Hg(II) speciation in simulated Hg-humic substances mixture. Total ligand concentration is $1.0 \times 10^{-4} \text{ M}$; proton binding constant $\log K_{\text{H}}$ is 4; and the total Hg(II) concentration is $1.0 \times 10^{-6} \text{ M}$. Dashed lines are for an average Hg binding constant $\log K_{\text{Hg}}$ of 4.5; and solid lines are for $\log K_{\text{Hg}}$ of 8.5	158

Figure 6.6a	Fractions of bound protons and bound Hg over the total ligand concentrations as a function of initial Hg(II) concentration at pH = 4. L sites denote the deprotonated sites on humic substances, and HL sites denote the protonated sites. The concentration of humic substances is 25.8 mg C L ⁻¹ , which was extracted from Freehold sandy loam (B horizon)	165
Figure 6.6b	Fractions of bound protons and bound Hg over the total ligand concentrations as a function of initial Hg(II) concentration at pH = 5. L sites denote the deprotonated sites on humic substances, and HL sites denote the protonated sites. The concentration of humic substances is 25.8 mg C L ⁻¹ , which was extracted from Freehold sandy loam (B horizon)	166
Figure 6.6c	Fractions of bound protons and bound Hg over the total ligand concentrations as a function of initial Hg(II) concentration at pH = 6. L sites denote the deprotonated sites on humic substances, and HL sites denote the protonated sites. The concentration of humic substances is 25.8 mg C L ⁻¹ , which was extracted from Freehold sandy loam (B horizon)	167
Figure 7.1a	Adsorption of 2×10^{-7} M methylmercury on Penn silt loam as a function of pH. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 1°C. Solid lines: no Cl ⁻ addition; dashed lines: 1×10^{-3} M Cl ⁻ addition.....	177
Figure 7.1b	Adsorption of 2×10^{-7} M methylmercury on Freehold sandy loam (A horizon) as a function of pH. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 1°C. Solid lines: no Cl ⁻ addition; dashed lines: 1×10^{-3} M Cl ⁻ addition.....	178
Figure 7.1c	Adsorption of 2×10^{-7} M methylmercury on Freehold sandy loam (B horizon) as a function of pH. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 1°C. Solid lines: no Cl ⁻ addition; dashed lines: 1×10^{-3} M Cl ⁻ addition.....	179

Figure 7.1d	Adsorption of 2×10^{-7} M methylmercury on Rockaway stony loam as a function of pH. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 1°C. Solid lines: no Cl ⁻ addition; dashed lines: 1×10^{-3} M Cl ⁻ addition.....	180
Figure 7.2	Methylmercury speciation as a function of pH and Cl ⁻ . Solid lines: Cl ⁻ = 0; long dashed lines: Cl ⁻ = 1×10^{-6} M; short dashed lines: Cl ⁻ = 1×10^{-5} M; dotted lines: Cl ⁻ = 1×10^{-3} M.....	182
Figure 7.3	Adsorption of 2×10^{-7} M methylmercury on silica as a function of pH. Silica:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 1°C.....	184
Figure 7.4	Effect of dissolved organic matter on adsorption of 2×10^{-7} M methylmercury. Solid:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 1°C. Experimental pH was 7.59 ± 0.08 for silica and 6.49 ± 0.06 for Penn silt loam	186
Figure 7.5a	Effect of Ca ²⁺ on adsorption of 2×10^{-7} M methylmercury on Penn silt loam as a function of pH. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M; T = 25 ± 1°C	188
Figure 7.5b	Effect of Ca ²⁺ on adsorption of 2×10^{-7} M methylmercury on Freehold sandy loam (B horizon) as a function of pH. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M; T = 25 ± 1°C	189
Figure 7.6a	Concentrations of the dissolved organic C in suspensions of Penn silt loam as a function of pH and Ca ²⁺ concentration. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M; T = 25 ± 1°C	191
Figure 7.6b	Concentrations of the dissolved organic C in suspensions of Freehold sandy loam (B horizon) as a function of pH and Ca ²⁺ concentration. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M; T = 25 ± 1°C	192
Figure 7.7a	Comparison of methylmercury adsorption on Penn silt loam from 2×10^{-7} and 1×10^{-6} M solutions. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 1°C. Solid line: 2×10^{-7} M; dashed line: 1×10^{-6} M.....	194

Figure 7.7b	Comparison of methylmercury adsorption on Freehold sandy loam (B horizon) from 2×10^{-7} and 1×10^{-6} M solutions. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 1°C. Solid line: 2×10^{-7} M; dashed line: 1×10^{-6} M	195
Figure 7.7c	Comparison of methylmercury adsorption on Rockaway stony loam from 2×10^{-7} and 1×10^{-6} M solutions. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 1°C. Solid line: 2×10^{-7} M; dashed line: 1×10^{-6} M.....	196
Figure 8.1	Predicted vs. measured soluble Hg(II) concentrations. The predicted values were calculated with equation 8.21 based on the parameters for each soil listed in Table 8.1. Initial Hg concentration = 1×10^{-7} M; soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C	210
Figure 8.2	Correlation between model fitting parameter A (equation 8.21) and the soil organic C content for adsorption of Hg(II) on seven soils listed in Table 8.1. Regression line is forced to pass through the origin.....	212
Figure 8.3	Predicted vs. measured soluble Hg(II) concentrations. The predicted values were calculated with the universal equation 8.25 for adsorption on all soils listed in Table 8.1 at an initial Hg concentration of 1×10^{-7} M over a pH range of 3 to 10. Soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	214
Figure 8.4	Predicted vs. measured soluble Hg(II) concentrations. The predicted values were calculated with the universal equation 8.25 for adsorption on all soils listed in Table 8.1 at an initial Hg concentration of 1×10^{-6} M over a pH range of 3 to 10. Soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	216
Figure 8.5	Predicted vs. measured soluble Hg(II) concentrations. The predicted values were calculated with the universal equation 8.26 for adsorption on all soils listed in Table 8.1 at an initial Hg concentration of 1×10^{-6} M over a pH range of 3 to 10. The K_{HgL} value used in the prediction is 4.78×10^{-3} L μmol ⁻¹ . Soil:water = 1 g 100 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = 25 ± 2°C.....	217

Figure 8.6	Predicted vs. measured soluble methylmercury concentrations. The predicted values were calculated with equation 8.20 based on the parameters listed in Table 8.2 for each soil. Initial Hg concentration = 2×10^{-7} M; soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = $25 \pm 1^\circ\text{C}$	219
Figure 8.7	Correlation between model fitting parameter A (equation 8.20) and the soil organic C content for adsorption of methylmercury on four soils listed in Table 8.2. Regression line is forced to pass through the origin.....	220
Figure 8.8	Predicted vs. measured soluble methylmercury concentrations. The predicted values were calculated with the universal equation 8.28 for methylmercury adsorption on four soils listed in Table 8.2 at an initial Hg concentration of 2×10^{-7} M over a pH range of 3 to 10. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = $25 \pm 1^\circ\text{C}$	223
Figure 8.9	Predicted vs. measured soluble methylmercury concentrations. The predicted values were calculated with the universal equation 8.28 for methylmercury adsorption on four soils listed in Table 8.2 at an initial Hg concentration of 1×10^{-6} M over a pH range of 3 to 10. Soil:water = 0.4 g 40 mL ⁻¹ ; I = 0.01 M NaNO ₃ ; T = $25 \pm 1^\circ\text{C}$	224

ABSTRACT

Adsorption and desorption are two of the primary processes that determine the mobility and bioavailability of heavy metals in soil. In this study, the retention and release reactions of Hg(II) and methylmercury with fifteen New Jersey soils as a function of pH, Cl^- , Ca^{2+} , and Hg loading level were investigated by a batch equilibrium technique. The reaction kinetics was ascertained by a stirred-flow method.

An upside bow shaped curve was observed for adsorption of both types of Hg as a function of pH with maximum adsorption occurring at pH around 3 for Hg(II) and around 6 for methylmercury. Decreases in adsorption at higher pH primarily resulted from the complexation of Hg by soluble organic matter whose concentration increases with pH. A S-shaped adsorption isotherm was followed due to the effect of the soluble organic matter. The binding characteristics of Hg(II) with the soluble organic matter was ascertained by an iodide electrode and the stability constant was calculated for the first time.

The presence of a high concentration (0.003 M) of Ca^{2+} decreased the solubility of organic matter, which resulted in increases in adsorption at high pH for Hg(II) and at low pH for methylmercury. Cl^- has no effect on adsorption at high pH values where hydroxo Hg species are predominant over Hg-Cl species. At lower pH increasing the soil organic matter content decreased the effect of Cl^- on adsorption.

Two time regime kinetics were ascertained for Hg(II) retention to and release from soils. The apparent reaction rate coefficients were calculated and inversely correlated to the soil organic matter content and soil-water partition coefficients of Hg. Organic matter was found to be the most important component responsible for the slow release of Hg from soil.

A model which incorporated the proton competitive binding and soluble organic matter effects was developed to describe soil-water partitioning of both types of Hg. Based on the correlations between model fitting parameters and soil properties, a universal equation was obtained for both Hg(II) and methylmercury. This equation was demonstrated to be able to predict soil-water partitioning of Hg in all tested soils.

Chapter 1

INTRODUCTION

Decades of mining, manufacture and disposal of heavy metals and metal-containing materials have caused serious environmental pollution. Many areas near urban complexes, metalliferous mines and major road systems have been found to contain anomalously high concentrations of these metals (Adriano, 1992; Alloway, 1995). Elevated concentrations of heavy metals have also been identified in a large number of waters and biota (Lindqvist *et al.*, 1991; Kerndorff *et al.*, 1992). The pernicious effects of these metals become more evident with time as their accumulation in food chain continuously increases. Such delayed effects of the chemicals released to the environment was subtly called 'chemical time bombs' (Alloway, 1995).

Mercury is one of the most useful and also most toxic heavy metals. People began to use Hg 3500 years ago (Nriagu, 1979). The early use of Hg was mainly limited to the manufacture of amalgams and medicines. Later on the Hg barometer and thermometer were invented in 1643 and 1720, respectively. By the turn of this century, Hg was mainly used to recover Au and Ag and to make fulminate and vermilion. Beginning from this century, a number of new applications of Hg have been found in industries and in agriculture. The consumption of Hg thus significantly increased. It is estimated that the annual anthropogenic release of Hg on a global basis

was about 3×10^6 kg around the year 1900, and had increased to about three times that amount during the 1970s (Andren and Nriagu, 1979). During last 20 years, Hg applications in agriculture, pharmaceuticals and general laboratory practice have declined. However, the uses in industries and dental fillings are still substantial (Steinnes, 1995). At present, the major Hg consumption areas include agriculture, chloralkali industry, dental preparations, electrical apparatus (batteries and others), general laboratory use, measuring and control apparatus, pharmaceuticals, paints (antifouling and mildew-proofing), and redistilled processes (U.S. Bureau of Mines, 1984).

Occupational Hg poisoning, e.g., in miners, has been documented for centuries (Steinnes, 1995). Mercury environmental pollution, however, was detected and caused increasing concern only during the recent decades. The first known case occurred in Minamata, Japan in the 1950s (Tsu Baki and Iru Kayama, 1977). About 150 people were poisoned by consumption of fish contaminated with high level of Hg released from a chloralkali plant. Later on, several cases of human and wildlife poisoning from methylmercury treated seeds were reported (Lindqvist *et al.*, 1984). Extensive investigation conducted since then has shown that elevated Hg levels in fish were widespread globally (Lindqvist *et al.*, 1991).

Mercury seems not a major problem with respect to phytotoxicity (Adriano, 1986). The levels at which toxicity symptoms are apparent are far above those encountered under normal conditions. However, high concentrations of Hg in soil pose great potential for ground and surface water contamination. Recent studies concerning the cause of mercury contamination of fish have indicated that the soil

system is a significant and sometimes even dominant source of mercury supply to lakes and watercourses (Schlüter, 1993). Although the form of Hg in fish is primarily methylmercury (Stokes *et al.*, 1987), inorganic Hg is generally considered to provide substrate for methylation (Robertson *et al.*, 1987), especially in anoxic environments (Bennett *et al.*, 1985; Gilmour and Henry, 1991).

Whether the Hg applied to soils will be leached to surface and groundwater mainly depends on its retention and release behavior in soils. The purpose of this study was to obtain quantitative information about the behavior of Hg in fifteen New Jersey soils with respect to adsorption, desorption and the reaction kinetics. The results are reported in this thesis. Following this brief introduction, Chapter 2 provides a literature review concerning the source, speciation, and adsorption/desorption behavior of Hg(II) and methylmercury in soils. Chapter 3 discusses the effects of pH, Cl⁻ concentration, background electrolyte, and soil organic matter on Hg(II) adsorption at low initial concentrations of 1×10^{-7} and 1×10^{-6} M. Chapter 4 presents the results on adsorption and desorption isotherms of Hg(II). A model which incorporated the interactions of soluble inorganic Hg with both soil solids and dissolved organic matter is presented to describe the adsorption isotherms. Chapter 5 explores the kinetics of Hg(II) adsorption on and desorption from soils. The relative importance of soil components in determining the reaction rates is addressed. Chapter 6 examines the interaction of Hg(II) with soil-derived organic matter. Chapter 7 shows adsorption of methylmercury as affecting by pH, Cl⁻, and Ca²⁺. Chapter 8 develops models to predict soil-water partitioning of Hg(II) and methylmercury as a function of pH. Chapter 9 summarizes the major findings of this study.

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Chapter 2

LITERATURE REVIEW

2.1 Origin of Mercury in Soils

The natural source of Hg in soils is the parent rocks. The average crustal Hg concentration is about 20 ng g^{-1} (Steinnes, 1995). Igneous rocks generally contain very low levels of Hg (about 10 ng g^{-1}). Some sedimentary rocks, such as sandstones and limestones, contain the same levels of Hg as igneous rocks do, while the concentrations of Hg in shales cover a wide range (Henriques, 1973; Connor and Shacklette 1975). It is believed that one of the important factors responsible for the concentration fluctuation of Hg in shales is the organic matter content (Cameron and Jonasson, 1972; McNeal and Rose, 1974). Rocks formed from volcanic debris or deposited near volcanic areas have more Hg. Rocks deposited in a reducing environment also contain high levels of Hg due to the presence of S (Steinnes, 1995). The major Hg-bearing primary minerals are cinnabar (HgS) and livingstonite (HgSb_4S_7).

Some Hg that is present in soils came from atmospheric deposition. It is generally believed that more than 90% of the total atmospheric Hg are volatile species, in which Hg^0 is the predominant form (Johnson and Braman 1974; Slemr *et al.*, 1981; Iverfeldt and Lindqvist, 1986). Brosset (1981) suggested that Hg^0 is eventually oxidized into water-soluble forms in the atmosphere, which are subsequently

scavenged by wet or dry deposition. Typical concentrations of Hg in precipitation at remote areas are estimated to be of the order of 2 to 10 ng L⁻¹, while levels in more polluted areas may be of the order of 5 times higher (Steinnes, 1995).

Besides the above two sources, a considerable amount of Hg is directly added to soils by human in forms of fertilizers, lime, manures, and sewage sludge (Andersson, 1979). Most commercial fertilizers have a Hg content of less than 50 ng g⁻¹, however, more than 300 ng g⁻¹ Hg was found in P fertilizers (Frank *et al.*, 1976; Andersson, 1977). Manure contains a higher level of Hg (30-360 ng g⁻¹ with a average of 90 ng g⁻¹). The concentration of Hg in lime for agriculture purposes ranges from less than 5 to 20 ng g⁻¹. Sewage sludge contains a wide range of Hg from 0.1 to 55 ng g⁻¹ (Allaway, 1995). It is estimated that the added amount of Hg to soil is typically of the order of 50 mg m² (Steinnes, 1995).

The Hg contents in soils span several orders of magnitude depending on the soil origin and whether it is used for environmental and agricultural purposes. Steinnes (1995) searched literature on the Hg contents in soils of seven countries and reported a concentration range of 5 to 4600 ng g⁻¹ for various kinds of uncontaminated soils. The average concentration for different kinds of soils vary from 20 to 188 ng g⁻¹. Generally, organic soils have higher Hg contents than do mineral soils (John *et al.*, 1975; Frank *et al.*, 1976). In the vicinity of Hg mines and Hg-using industry sites, the soil contents of Hg can be much higher than those contained in uncontaminated soils. For example, 1 to 10 mg kg⁻¹ Hg were found in soils 0.5 km from a chloralkali plant (Bull *et al.*, 1977). The contents of Hg in soils around Hg mines can be as high as 100 mg kg⁻¹ (Lindberg *et al.*, 1979; Morishita *et al.*, 1982).

2.2 Aqueous Speciation of Mercury(II) and Methylmercury

Inorganic mercury may occur in three different valency states in the environment, namely Hg(0), Hg(I), and Hg(II). Under soil redox potential conditions which usually range from -0.4 to 0.8 v, Hg(I) does not occur as a stable species (Schlüter, 1993). Most of the Hg(0) goes to the atmosphere, and only little dissolves in aqueous solution according to Henry's law (Sanemasa, 1975). Hg(II) is therefore the dominant state in soil solution.

Due to the strong Lewis acid nature, Hg(II) rarely occurs as the aquo ionic form under natural conditions. As indicated in Figure 2.1 which is calculated based on the stability constants in Table 2.1 using the MINEQL+ computer program (Schecher and McAvoy; 1991), hydroxo Hg species begin to form at about pH 2 and become predominant at pH greater than 3. In the presence of Cl^- (which is a common ion in soil solution), Hg tends to form stable complexes with Cl^- at low pH, which eventually are replaced with hydroxo Hg species at higher pH. Increases in Cl^- concentration increase the pH value at which hydroxo Hg species become predominant over Hg-Cl complexes.

Under anaerobic conditions where S^{2-} is available, most soluble Hg precipitates together with S^{2-} due to the strong affinity of Hg for S (Fagerström and Jernelöv, 1972) and the extremely low solubility of HgS. In strongly alkaline soils, the soluble HgS_2^{2-} ion will form. If the soil condition changes to aerobic, the HgS precipitate will be physicochemically oxidized to soluble Hg(II) species (Jensen and Jernelöv, 1972, Kromer *et al.*, 1981).

Table 2.1 Aqueous equilibria of Hg(II)

Equilibrium Reactions	Log K^a I = 0.1 M	Log K^a I = 0.01 M	Log K^b I = 0
$\text{Hg}^{2+} + \text{H}_2\text{O} = \text{HgOH}^+ + \text{H}^+$	-3.65	-3.49	
$\text{Hg}^{2+} + 2\text{H}_2\text{O} = \text{Hg}(\text{OH})_2 + 2\text{H}^+$	-6.42	-6.26	
$\text{Hg}^{2+} + 3\text{H}_2\text{O} = \text{Hg}(\text{OH})_3^- + 3\text{H}^+$	-21.10	-21.10	
$\text{Hg}^{2+} + \text{H}_2\text{O} = \text{HgO} + 2\text{H}^+$	-2.81	-2.65	
$\text{Hg}^{2+} + \text{OH}^- + \text{Cl}^- = \text{HgOHCl}$	3.57	-3.87	
$\text{Hg}^{2+} + \text{Cl}^- = \text{HgCl}^+$	6.72	7.02	
$\text{Hg}^{2+} + 2\text{Cl}^- = \text{HgCl}_2$	13.24	13.70	
$\text{Hg}^{2+} + 3\text{Cl}^- = \text{HgCl}_3^-$	14.32	14.78	
$\text{Hg}^{2+} + 4\text{Cl}^- = \text{HgCl}_4^{2-}$	14.93	15.23	
$\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} = \text{CH}_3\text{HgOH} + \text{H}^+$			-4.63
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- = \text{CH}_3\text{HgCl}$			5.25
$\text{CH}_3\text{Hg}^+ + \text{S}^{2-} = \text{CH}_3\text{HgS}^-$			21.02

^aBaes and Mesmer (1976).^bStumm and Morgan (1981).

Perhaps a large fraction of soluble Hg(II) in soils is associated with the dissolved organic matter. Although no direct information on Hg speciation in soil pore water is available, the studies on Hg in river water have indicated that most of the soluble Hg may be present as organic complexes (Peng and Wang, 1982). Moreover, many studies on the origin of Hg in natural lakes have suggested that humic materials transferred Hg from soils to lakes (Surma-Aho *et al.*, 1985).

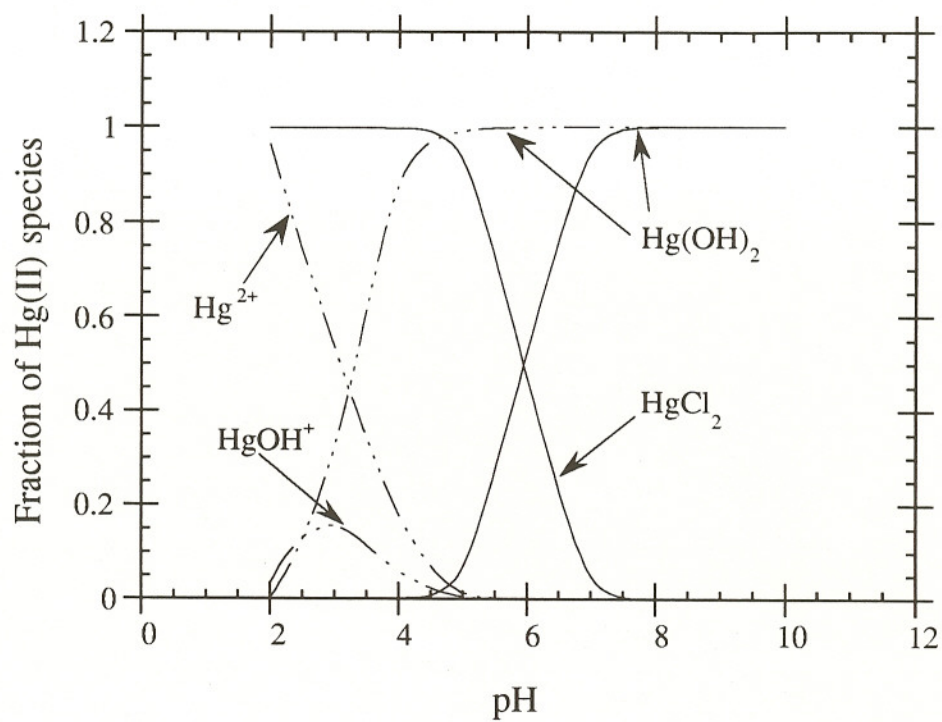


Figure 2.1 Mercury(II) speciation as a function of pH and Cl^- concentration. Dashed lines refer to the absence of Cl^- ; solid lines denote a Cl^- concentration of 10^{-4} M .

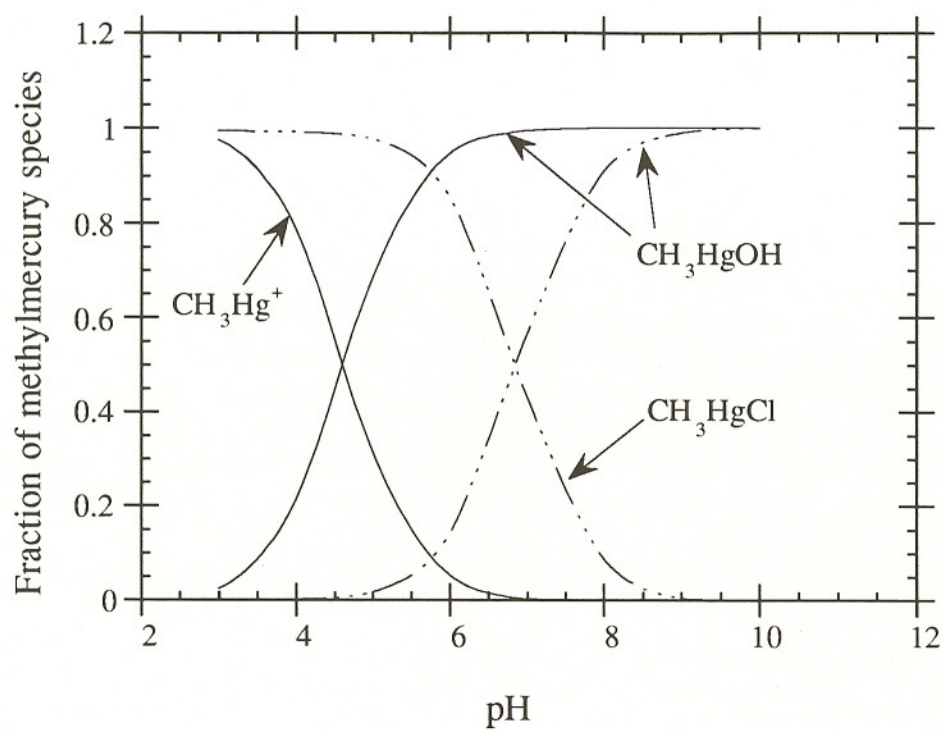


Figure 2.2 Methylmercury speciation as a function of pH and Cl^- concentration. Solid lines refer to the absence of Cl^- ; dashed lines denote a Cl^- concentration of 10^{-4} M.

Methylmercury in aqueous solution acts as a soft acid and has a strong tendency to bind with S^{2-} , OH^- , and Cl^- . In the presence of Cl^- , CH_3HgCl is predominant at low pH (Figure 2.2). Increases in pH result in an increase of the fraction of CH_3HgOH , which eventually becomes the predominant species. In the presence of S^{2-} or organic matter, CH_3Hg^+ will prevail as CH_3HgS complex or bound to the S group of organic matter (Baughman *et al.*, 1973).

2.3 Adsorption, Desorption and Transformation Reactions of Mercury(II) and Methylmercury in Soils

2.3.1 General Theory of Metal Adsorption to and Desorption from Soils

Extensive research has been done to investigate the factors controlling metal retention on and release from soils. Among these factors, pH is one of the most important. For example, Christensen (1989) determined the distribution coefficients for 63 Danish agricultural soils and found that the distribution coefficients correlated very well with soil pH ($r = 0.72$). The pH affects the adsorption of metals from pore water by affecting both soil solid surface charge and soluble metal speciation. Increases in pH weaken proton competitive binding and decrease surface potential, and consequently increase both electrostatic and specific binding of metals to solid surfaces. In addition, increases in pH may result in the formation of hydroxo metal species. The adsorption of metals on solid surfaces has frequently been reported to significantly increase as hydroxo species became predominant (James and Healy, 1972; Tewari and Lee, 1975; Elliott *et al.*, 1986; Huang *et al.*, 1986). James and Healy (1972) suggested that this resulted from the smaller solvation energy of hydroxo metal

species than that of aquo species. Tewari and Lee (1975) further observed that following the adsorption of MOH^+ , M(OH)_2 precipitate, which would not occur in bulk solution, formed on solid surface.

For a given pH value, increasing metal loading results in increases in adsorption. The surface adsorption energy, however, decreases with increasing surface coverage. This results in the fractional adsorption of the added metal to decrease. The adsorption behavior as a function of metal loading can usually be described by equation 2.1 (Sposito, 1985).

$$q(c) = \sum_{i=1}^n \frac{b_i k_i^{\beta_i} c^{\beta_i}}{1 + B_i C_i^{\beta_i}} \quad (2.1)$$

where $q(c)$ is the amount of solute adsorbed, c is the concentration of solute in solution, b_i , B_i , k_i , β_i ($i = 1, \dots, n$) and n are adjustable parameters.

Soil composition is also very important in determining the retention of metals on soils. Some ligands that are present in soil solution at certain environmental conditions, including hydroxide, carbonate, silicate, phosphate, and sulfide, are important to the precipitation of metal ions. Some inorganic ligands, such as Cl^- , and organic ligands can form soluble complexes with metals. The complexation of metals by these ligands could increase, decrease or not change metal adsorption (Vuceta, 1976). This is suggested to mainly depend on the adsorbability of the complexed metal ions (Elliott and Huang, 1979, 1980; Huang and Lin, 1981).

Soil 2:1 clay minerals, such as smectite and vermiculite, bear permanent charge in the interlayer and are important natural ion exchange materials. In surficial soils,

the clay minerals are generally coated with metal oxides (Jenne, 1968) and organic matter (Hart, 1982; Davis, 1984). These soil phases constitute the most important metal-binding components. For example, in a recent study, Lee *et al.* (1996) have shown that organic matter is the most important soil component controlling metal partitioning at fixed pH. The partitioning of Cd(II) to soil can be predicted to a very high degree ($r^2 > 0.92$) by considering the organic matter normalized partition coefficient (K_{om}) as a function of pH. This work suggests that soils are coated by organic matter and that other adsorption phases, such as iron and manganese oxides, serve to store contaminants (Allen and Yin, 1996).

Background electrolyte in pore water can also affect the partition of metals to soil. Zachara *et al.* (1993) investigated Cd(II) adsorption on specimen and soil smectites in sodium and calcium electrolytes and found that ion exchange dominated Cd adsorption at low ionic strength in Na⁺ electrolyte. Increasing Na⁺ concentration to 0.1 M or changing the electrolyte to Ca²⁺ at an ionic strength of 0.003 to 0.006 M suppressed Cd ion exchange.

The retention and release reactions of metals with soil or soil components have been frequently characterized by a fast step followed by a slow step (Sparks, 1989). The fast step usually involves the reaction on solid surfaces, while the slow reaction involves the penetration of metals into the mineral lattice (Kou, 1986; White and Yee, 1986; Bruemmer *et al.*, 1988) or diffuse through intraparticle pores (Avotins, 1975; Sparks *et al.*, 1980).

2.3.2 Adsorption and Desorption of Mercury(II) on Soils

Significant effort has been made to investigate the adsorption behavior of Hg(II) on soils and soil components. A comprehensive review of the early knowledge about Hg in soils was given by Andersson in 1979. Recently, Schuster (1991) reviewed the literature regarding the behavior of Hg in soil with emphasis on complexation and adsorption processes. Another review dealing with the turnover and translocation of natural soil Hg and the Hg deposited from the atmosphere was given by Schlüter (1993). Both soil minerals, especially clay minerals and oxides (Fe, Al and Mn oxides, hydroxides and oxihydroxides), and organic matter have been found to strongly adsorb Hg.

Obukhovskaya (1982) reported that the adsorption of Hg(II) by kaolinite, vermiculite-chlorite, montmorillonite and iron oxide reached equilibrium within 10 to 30 minutes, and the increase in adsorption within one month was insignificant. This suggested that Hg(II) mainly adsorbed on mineral surface and practically did not penetrate into the mineral structure or interlayer. Compared to clay minerals, iron oxide has a higher adsorption capacity. $\text{Hg}(\text{OH})_2(\text{aq})$ seems to play the main role in Hg adsorption on these minerals.

The adsorption capacity sequence of various clay minerals for Hg(II) is different from study to study (Schlüter, 1993). The capacity sequence does not follow the CEC. This might also be an indication that ion exchange does not dominate the adsorption of Hg(II) on clay minerals. Typically, Hg(II) adsorption on clay minerals is highly pH dependent. Obukhovskaya (1982) reported that adsorption of Hg(II) on kaolinite, vermiculite-chlorite, and montmorillonite increased with pH and reached

maximum at pH above 6. Newton (1976) observed that Hg(II) adsorption on bentonite reached a maxima in a pH range of 4 to 5. A further increase in pH decreased adsorption. Varying the concentration of background electrolyte $\text{Ca}(\text{NO}_3)_2$ only slightly affected adsorption.

Mercury(II) adsorption on oxides usually reaches a maximum at low pH, in a range of 3 to 5, and then decreases with increasing pH. Kinniburgh and Jackson (1978) examined the adsorption of Hg(II) on freshly prepared iron hydrous oxide gel and found that adsorption maxima was attained at about pH 5. From pH 5 to 6.5, adsorption remained constant at about 94%. Above pH 6.5 there is a slight decrease in adsorption, for example, from 95% at pH 6.45 to 91.6% at pH 8.6. Similar results were reported by Obukhovskaya (1982). He observed that Hg(II) adsorption on iron hydroxide achieved a maximum value at pH about 6 and then slightly decreased. In a more recent study, Barrow and Cox (1992) reported that the maximum adsorption of Hg(II) by goethite occurred at pH around 4. Further increases in pH decreased adsorption to a small extent.

Manganese oxide also exhibits a large adsorption capacity for Hg(II). Lockwood and Chen (1973) observed that Hg(II) adsorption on MnO_2 remained constant between pH 4 and 10 with decreases in adsorption at both ends of the 2 to 11 pH range used. $\text{Al}(\text{OH})_3$ seems to be a very inefficient Hg(II) adsorbent (Andersson, 1979). Sand exhibits some weak adsorption sites for Hg(II) (McNaughton and James, 1974; Lodénus *et al.*, 1987).

The reason for Hg(II) adsorption maxima on oxides occurring in a low pH range was attributed to the formation of Hg hydroxides. The species $\text{Hg}(\text{OH})_2$ is

believed to bind strongly with solid surfaces via double hydrogen bonding (Forbes *et al.*, 1974; Obuskhovskaya, 1982). No satisfactory explanation for the decreases of Hg(II) adsorption on pure minerals at higher pH has been presented. One possible reason could be the formation of $\text{Hg}(\text{OH})_3^-$. The dispersion of particles at higher pH could also retain some fine colloid ($< 0.45 \mu\text{m}$) - associated Hg in solution.

In the presence of Cl^- in solution, Hg-Cl complexes become predominant at low pH values. Unlike other metals, such as Cu, Pb, Zn, and Cd, whose adsorption on oxides can be enhanced by the presence of Cl^- (Quirk and Posner, 1975; Kinniburgh and Jackson, 1978), the complexation of Hg by Cl^- significantly decreased Hg adsorption (McNaughton and James, 1974; Kinniburgh and Jackson, 1978; Newton *et al.*, 1976; Barrow and Cox, 1992). This probably resulted from the linear configuration of Hg-Cl complexes which makes multidentate ligand bonding to solid surfaces difficult (Kinniburgh and Jackson, 1978). As pH increases to a value where Hg-OH species become predominant over Hg-Cl species, adsorption increases significantly.

The evidence suggests that soil organic matter strongly adsorbs Hg(II). The most important sites on organic matter are $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, and $-\text{SH}$ groups. The amount of $-\text{NH}_2$ and $-\text{SH}$ groups is usually limited, however, their bonding with Hg is very strong (Bowen, 1979; Reimers and Krenkel, 1974). Carboxyl and phenolic groups constitute the majority of the binding sites on organic matter. Duffy *et al.* (1989) compared the binding ability of nine metals (Fe^{3+} , Hg^{2+} , Al^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Mg^{2+} , and Ca^{2+}) with the $-\text{COOH}$ groups of acetate and reported that Fe^{3+} and Hg^{2+} form the most stable complexes with $-\text{COOH}$. The interaction of Hg

with carboxyl groups is believed to involve the formation of metal carboxylates via hydrogen bonding between HgOH^+ and $\text{Hg}(\text{OH})_2$ and $-\text{COOH}$ (Khan *et al.*, 1985).

Higher Hg concentrations are usually found in organic matter-rich soils (McKeague and Kloosterman, 1974). This may be an indication that organic matter has stronger adsorption ability for Hg than soil minerals. Many researchers have investigated the mobility of Hg in soils. It seems that only rather concentrated chlorides or some strong ligands, such as EDTA, can efficiently extract sorbed Hg from soils (Dudas and Pawluk, 1976; Hogg *et al.*, 1978; Harsh and Doner, 1981). However, in most cases, the experiments were conducted using a batch technique or column method, which could underestimate the leachability of Hg in the natural system. In batch desorption, the released solute can not be removed from the system, which could inhibit further release of the solute (Martin and Sparks, 1983). In a column study, considerable diffusion is involved, and consequently the experimental time period may not be long enough to leach out the adsorbed solute. As a matter of fact, transport of Hg from the top layer of soil to a lower layer and from soil to natural water systems have been observed (Lodenius *et al.*, 1983; Lindqvist *et al.*, 1991).

2.3.3 Adsorption and Desorption of Methylmercury on Soils

Little information on the adsorption of organo-mercurials to soils and soil components is available. Reimers and Krenkel (1974) observed that a considerable amount of methylmercury was adsorbed by clay minerals and fine sands with a sequence of illite > montmorillonite > fine sands, whereas no adsorption occurred on kaolinite and coarser sands. The fine sands adsorbed methylmercury only at low Cl^-

concentrations, but at all pH in the range from 5 to 9. This indicates that only CH_3HgOH is adsorbable to the sand surface. Both Cl^- concentration and pH affect the adsorption of methylmercury on illite and montmorillonite. No satisfactory explanation is available for these effects. Inoue and Aomine (1969) reported that phenylmercurials strongly adsorbed to montmorillonite, but they only weakly adsorbed to kaolinite and allophane. The maximum adsorption occurred at pH around 6 and significantly decreased at both higher and lower pH values in the range of 4 to 8. This suggests that cation exchange may dominate the adsorption of phenylmercurials on clay minerals. Unlike inorganic Hg which is strongly adsorbed by all major functional groups of organic matter, methylmercury is only efficiently adsorbed to sulfhydryl groups of organic matter. Amine and carboxyl groups are inefficient in binding with methylmercury (Reimers and Krenkel, 1974). In natural soils, adsorption of organo-mercury seems to be dominant by clay and organic matter (Hogg *et al.*, 1978a, b).

2.3.4 Transformation of Mercury(II) and Methylmercury in Soils

It has been found that some of the inorganic Hg(II) applied to soils can be reduced to Hg^0 or transformed into methylmercury under suitable conditions. Alberts *et al.* (1974) and Miller (1975) suggested that the reduction of Hg(II) to Hg^0 occurs chemically in the presence of humic and fulvic acid catalysts and is favored under slightly alkaline to slightly acid aqueous solutions under aerobic conditions. Skogerboe and Wilson (1981), however, observed that the reduction of Hg(II) to Hg^0 mediated by fulvic acid decreased sharply above pH 4 when the formation of hydroxo Hg species became pronounced. This seems to indicate that only free Hg^{2+} is available for reduction. Other researchers suggested that the reduction of Hg^{2+} to Hg^0

was also mediated by microorganisms as means of detoxification, even under aerobic conditions (Jonasson and Boyle, 1972; Landa, 1979; Waldron, 1980).

The transformation of Hg(II) to methylmercury has been reported by many researchers. Generally, the transformation increased with decreasing particle size (Rogers, 1976). Two pathways, an abiotic chemical process and a biological process, are responsible for the methylation of Hg(II) (Rogers, 1977; Tonomura *et al.*, 1972). The reaction largely depends on the availability of Hg(II). Higher concentrations of Hg(II) favor methylation. However, too high a concentration of Hg(II) could hinder the respective biological and abiological processes. In the presence of S^{2-} , methylation of Hg(II) is reduced by formation of HgS (Bisogni and Lawrence, 1975; Wood, 1984). In most studies, the methylation reaction was found to be very slow. For example, Rogers (1976) reported that no more than 1% of the incubated Hg (as $Hg(NO_3)_2$) was methylated in soil in one week.

The methylmercury formed from Hg(II) in soils or applied directly to soils by mankind can disproportionate into Hg^0 and Hg(II) (Rogers, 1976; Landa, 1979). The mechanisms responsible for demethylation are not well understood (Schlüter, 1993). Demethylation increases with temperature, which favors the microbial activity, and decreases at extreme moisture or dryness that lowers microbial activity (Landa, 1979). This suggests that a biological process may be one of the pathways for demethylation.

2.4 Objectives of Research

From the above literature review, it is clear that different soil components have quite different adsorption ability for Hg(II) and methylmercury. The adsorption ability of the same component for Hg still could be different due to its different origin, which affects the surface characteristics of soil minerals and the functional groups of humic substances. The retention and release behavior of Hg in natural soils, which are mixtures of these components, is even more complicated and depends on the interactions among the soil components themselves and between these components and Hg. This behavior is subject to the simultaneous influences of soil composition and environmental conditions. Accordingly, the objectives of this research were:

- 1) To obtain quantitative information on the adsorption and desorption of Hg(II) and methylmercury on fifteen representative New Jersey soils ranging in texture from sand to silty clay loam.
- 2) To examine the simultaneous effects of pH, Cl^- , soil properties, and the Hg concentration levels on the adsorption reaction.
- 3) To investigate the kinetics of Hg adsorption and desorption on soils and discern the mechanisms controlling the rates of Hg retention on and release from soils.

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Chapter 3

EFFECTS OF pH, CHLORIDE, ORGANIC MATTER, AND CALCIUM(II) ON MERCURY(II) ADSORPTION BY SOILS

3.1 Abstract

The effects of pH, Cl^- , and organic matter on Hg(II) adsorption from 1×10^{-7} and 1×10^{-6} M solutions by fifteen New Jersey soils were examined to understand the factors responsible for Hg(II) partitioning to soils under different environmental conditions. The maximum extent of adsorption ranged from 86% to 98% of the added Hg(II) and occurred in a pH range of 3 to 5 for all soils studied. Increasing the pH above this range significantly decreased the adsorption of the added Hg(II) , for example, from $89 \pm 8\%$ at pH 4.0 to $39 \pm 11\%$ at pH 8.5 for an initial Hg(II) concentration of 1×10^{-7} M. An important factor was the complexation of Hg(II) by the dissolved organic matter whose concentration increased with increasing pH. The presence of high concentration of Ca^{2+} (0.003 M) caused the coagulation of dissolved organic matter, which removed some Hg(II) from solution. The effect of Cl^- on Hg(II) adsorption by soil depended on both pH and the soil organic matter content. At circumneutral and higher pH, the addition of Cl^- did not affect adsorption by any soil. The standard deviation of Hg(II) adsorption for all soils was less than 4% for Cl^- concentrations from about 1×10^{-6} to 1×10^{-2} M. At about pH 3, the effect of Cl^- on Hg(II) adsorption by soil depended on the soil organic matter content. When the Cl^-

concentration increased from about 1×10^{-6} to 1×10^{-2} M, adsorption by the lowest organic matter soil (1.2 g C kg^{-1}) decreased from 93% to 40% for an initial Hg(II) concentration of 1×10^{-7} M, whereas adsorption by the largest organic matter soil (49.9 g C kg^{-1}) decreased only from 95% to 91%.

3.2 Introduction

Adsorption has been recognized as one of the important processes determining the fate of trace metal contaminants in soil. Among the factors controlling the adsorption of trace metal contaminants, pH is one of the most important (Goldberg and Glaubig, 1988; Christensen, 1989; Zachara *et al.*, 1989). Both the surface charge characteristics of soil particles and metal speciation in solution are affected by pH. Because of its strong affinity for Hg(II) (Baes and Mesmer, 1976), Cl^- also could be an important factor affecting the adsorption of Hg(II).

MacNaughton and James (1974) found that Hg(II) adsorption on SiO_2 increased abruptly in the pH range of 2 to 3 when Cl^- was not present in solution. Newton *et al.* (1976) reported that the maximum adsorption of Hg(II) on bentonite clay occurred in a pH range of 4.5 to 5.5 regardless of the initial Hg(II) concentration or the concentration of a $\text{Ca}(\text{NO}_3)_2$ electrolyte. Kinniburgh and Jackson (1978) examined Hg(II) adsorption by freshly prepared iron hydrous oxide gel and reported that from pH 5 to 8.6, more than 90% of the Hg(II) was adsorbed. Adsorption of Hg(II) by goethite was investigated by several researchers. In a recent study, Barrow and Cox (1992a) reported that in the absence of Cl^- , the adsorption maximum was just below pH 4. In all these studies with pure colloids as adsorbents, the addition of Cl^- to

colloidal suspensions significantly reduced Hg(II) adsorption in acidic solutions, and resulted in an increase in the pH at which the adsorption maximum occurred.

Andersson (1979) suggested that in acidic soils (pH < 4.5 to 5), the only effective adsorbents for inorganic Hg(II) are organic substances, whereas in neutral soils, iron oxides and clay minerals become much more effective. Semu *et al.* (1987) studied the effect of pH on Hg(II) adsorption by tropical soils within a pH range of 5 to 8, and observed that the adsorption increased with increasing pH. Barrow and Cox (1992b), however, reported that in the absence of Cl⁻, there was little effect of pH on Hg(II) adsorption between pH 4 to 6. A further increase in the pH resulted in a decrease in adsorption. Little information on the effect of Cl⁻ on Hg(II) adsorption by soils is available. Barrow and Cox (1992b) reported that the addition of Cl⁻ decreased Hg(II) adsorption on a loamy sand soil at low pH, but had little effect at high pH.

Another well-documented factor that significantly affects the adsorption of trace metal contaminants is soil organic matter. Kerndorff and Schnitzer (1980) investigated the adsorption of eleven metals (Hg, Fe, Pb, Cu, Al, Ni, Cr, Zn, Cd, Co, and Mn) by soil humic acid, and reported that among the eleven metals, Hg and Fe exhibited the strongest affinity for humic acid. Trost and Bisque (1970) examined the adsorption capacity of various clay minerals and organic substances, and found that humus-rich materials had a far greater adsorption capacity than did pure clays. Fang (1978) and Landa (1978) also reported similar results. Dissolved organic matter is expected to form very stable complexes with Hg(II). Peng and Wang (1982) reported that most of the Hg in river water may be present as organic complexes. The presence

of organic matter in solution was reported to inhibit the adsorption of Hg(II) on mineral surface (Schuster, 1991).

Often different factors can simultaneously affect the adsorption of trace metal contaminants by soils. The purpose of this study was to investigate the simultaneous effects of pH, Cl⁻, organic matter, and Ca²⁺ on the adsorption behavior of small concentrations of Hg(II).

3.3 Materials and Methods

3.3.1 Materials

All solutions and suspensions were prepared using distilled, deionized water and trace metal analytical-grade reagents. All standard solutions were prepared daily by diluting a 10 mg L⁻¹ Hg(II) stock solution with 1% (v/v) HNO₃, and stabilized by addition of a few drops of 0.1% Na₂Cr₂O₇. Fifteen New Jersey soils, ranging from sand to loam, were used for this study. The soils were ground to pass a 2-mm sieve, and then air dried before use. The characteristics of the soils in terms of particle size distribution, Mn, Fe, and Al oxides, total organic carbon (SOC), cation exchange capacity (CEC), and BET surface area (SA) are given in Table 3.1-3.3 (edited form from Allen *et al.*, 1994).

3.3.2 Adsorption Methods

A batch equilibrium technique was used to perform all adsorption experiments. A mass of 1 ± 0.01 g of each soil was immersed in 100 mL of 0.01 M NaNO₃ (an

indifferent electrolyte) contained in a 125 mL Erlenmeyer flask. Mercury(II) (as $\text{Hg}(\text{NO}_3)_2$) was then added to each soil suspension to make the added $\text{Hg}(\text{II})$ concentration 1×10^{-7} or 1×10^{-6} M. The samples were shaken on a rotatory shaker (Orbit, No. 3590, Lab-Line Instruments, Inc., Melrose Park, IL) at 100 rpm for 24 h at a room temperature of $25 \pm 2^\circ\text{C}$. Preliminary results had shown that $\text{Hg}(\text{II})$ concentrations in solution stabilized within a 24-h reaction period. After 24 h of equilibration, the pH of each sample was determined and was used for data analysis. Following measurement of pH, the samples were filtered using a 10-mL plastic syringe connected to a filter holder containing a $0.45\text{-}\mu\text{m}$ Nuclepore membrane filter (Costar, Cambridge, MA). For each filtration, the syringe was washed twice using the sample solution and the first 10 mL of filtrate was discarded. An aliquot of each filtrate was then analyzed for $\text{Hg}(\text{II})$. Duplicate measurements were made for each filtrate, the average was taken to calculate $\text{Hg}(\text{II})$ concentration. The difference between the initial $\text{Hg}(\text{II})$ concentration and the amount remaining in solution at 24 h was considered to be adsorbed by the soil.

For the adsorption of $\text{Hg}(\text{II})$ as a function of pH, the pH values of the soil samples prepared as described above were adjusted to range from 3 to 10 using 0.1 M HNO_3 or NaOH before the samples were shaken. In addition to the equilibrium soluble $\text{Hg}(\text{II})$ concentrations, the concentrations of soluble organic matter as a function of pH were also determined for seven soils using a Beckman TOC analyzer (Rosemount Inc., Model 915-B).

Table 3.1 Soil particle size distribution

Soil No.	Soil Name†	Particle Size Distribution		
		Sand g kg ⁻¹	Silt g kg ⁻¹	Clay g kg ⁻¹
1	Sassafras sandy loam	450	370	180
2	Lakewood sand	910	30	60
3	Penn silt loam	250	480	270
4	Whippany silty clay loam	490	160	370
5	Washington loam	200	490	310
6	Freehold sandy loam (A horizon)	920	20	60
7	Freehold sandy loam (B horizon)	370	420	210
8	Rockaway stony loam	540	300	160
9	Fill materials from Delaware River	850	50	100
10	Downer loamy sand	870	50	80
11	Boonton Union loam	490	350	160
12	Dunellen sandy loam	560	300	140
13	Birdsboro silt loam	500	320	180
14	Hazen gravelly loam	390	380	230
15	Boonton Bergen loam	600	270	130

†Soil No. 1, 6, 7, 10, 12, and 13 are Typic Hapludults; No. 2 is a Spodic Quartzipsammments; No. 3 and 5 are Ultic Hapludalfs; No. 4 is a Aquic Hapludalfs; No. 8, 11, and 15 are Typic Fragiudalfs; No. 9 is a loamy sand dredged from Delaware River; No. 14 is a Mollic Hapludalfs.

Table 3.2 Soil pH, CEC, organic C and surface area

Soil No.	Soil Name	pH [†]	CEC cmol kg ⁻¹	Organic C [‡] g kg ⁻¹	Surface Area m ² kg ⁻¹
1	Sassafras sandy loam	5.78	3.10	3.5	5310
2	Lakewood sand	4.18	0.90	2.9	1100
3	Penn silt loam	4.67	3.80	7.5	8040
4	Whippany silty clay loam	6.17	9.50	13.3	5980
5	Washington loam	6.03	8.90	16.8	11590
6	Freehold sandy loam (A horizon)	5.22	0.80	1.2	2040
7	Freehold sandy loam (B horizon)	6.44	4.30	13.9	9010
8	Rockaway stony loam	4.69	2.70	28.4	8620
9	Fill materials from Delaware River	4.77	2.30	7.0	2370
10	Downer loamy sand	4.74	2.30	4.6	1150
11	Boonton Union loam	5.14	4.20	49.9	6540
12	Dunellen sandy loam	5.57	4.20	11.0	5210
13	Birdsboro silt loam	5.69	5.30	12.8	7060
14	Hazen gravelly loam	6.02	9.30	18.0	5900
15	Boonton Bergen loam	5.12	4.20	30.7	7200

[†]Determined in 1:1 soil/water.

[‡]Determined by the Walkley-Black wet combustion method (Sims and Heckendorn, 1991).

Table 3.3 Soil oxide contents

Soil No.	Soil Name†	Total Oxides§			Cl ⁻ μmoles L ⁻¹
		Fe g kg ⁻¹	Al g kg ⁻¹	Mn g kg ⁻¹	
1	Sassafras sandy loam	18.70	16.89	0.11	6.42
2	Lakewood sand	45.95	1.70	0.05	2.60
3	Penn silt loam	33.93	33.86	0.49	2.60
4	Whippany silty clay loam	22.96	26.71	0.15	1.78
5	Washington loam	38.86	37.43	0.86	1.89
6	Freehold sandy loam (A horizon)	14.44	6.17	0.27	3.03
7	Freehold sandy loam (B horizon)	10.86	10.63	0.18	2.68
8	Rockaway stony loam	24.75	26.71	0.61	2.35
9	Fill materials from Delaware River	24.75	19.57	0.23	0.97
10	Downer loamy sand	5.27	25.82	0.11	3.51
11	Boonton Union loam	19.82	20.46	1.54	11.92
12	Dunellen sandy loam	34.38	24.93	0.39	2.52
13	Birdsboro silt loam	33.03	19.57	0.49	9.44
14	Hazen gravelly loam	30.12	23.14	0.73	6.27
15	Boonton Bergen loam	26.99	24.03	0.36	1.55

§Determined by extraction with perchloric-nitric acids.

To evaluate the effect of soluble Hg(II) speciation on adsorption, the background concentrations of Cl^- in the soil suspensions were determined. We mixed 1 g of each soil sample with 100 mL of distilled, deionized water in 125-mL Erlenmeyer flasks. The soil suspensions were equilibrated by shaking for 24 h. Soil solution was then separated from solids by filtering through a 0.45 μm filter membrane and the Cl^- concentrations in the supernatants were analyzed by ion chromatography (DIONEX Co. using an ASM-3 column). The results are shown in Table 3.3.

Three soils of different organic matter content, Freehold sandy loam (A horizon), Dunellen sandy loam, and Boonton Union loam, were used to study the effect of Cl^- concentration on Hg(II) adsorption. The Cl^- concentrations were adjusted to range from the background concentration to 10^{-2} M by adding NaCl. The concentration of NaNO_3 was adjusted correspondingly to maintain a constant ionic strength of 0.01 M. The experiments were carried out at a fixed low pH (3), intermediate pH (6.5 - 7), or high pH (8.5 - 10).

The effect of dissolved organic matter on Hg(II) adsorption was studied using organic matter that was extracted with dilute NaOH from Boonton Union loam. We added variable amounts of the organic matter (1.4 mg C L^{-1} - 61.1 mg C L^{-1}) to suspensions of Freehold sandy loam (A horizon) at pH 6.5. We also added the same amount of organic matter (43.7 mg C L^{-1}) to suspensions of Freehold sandy loam (A horizon), Dunellen sandy loam and Rockaway stony loam at variable pH (3 - 10). We also removed organic matter from these three soils by treatment with 30% H_2O_2 following the method of Jackson (1958). The H_2O_2 -treated soils were washed by repetitive mixing with distilled deionized water followed by centrifugation until no

H₂O₂ in supernatants was detected using Quantofix Peroxide test paper, and then were air-dried prior to use. Treatment with H₂O₂ removed 86 to 97% of the organic matter from the three soils. Adsorption of Hg(II) by these organic matter-removed soils was then studied as a function of pH (3 to 10). These experiments were conducted in 0.01 M NaNO₃.

To test the effect of Ca²⁺ on the adsorption of Hg(II), we measured Hg(II) adsorption on two soils, Freehold sandy loam (A horizon) and Boonton Union loam, in Ca(NO₃)₂ instead of NaNO₃. The ionic strength was also maintained at 0.01 M. An initial Hg(II) concentration of 1×10^{-7} M was employed. The tests were conducted at a pH range of 3 to 10.

3.3.3 Mercury Analysis

Mercury was determined by a flow injection analysis (FIA) system combined with atomic absorption spectrophotometric detection (Figure 3.1). The FIA system consisted of an Ismatec pump (Cole-Parmer, No. 7332), a Rheodyne four-way rotary valve with a 500- μ L sample loop, a gas-liquid separator of laboratory design and construction, a gas flow meter, a reaction coil of 450 mm $\times$ 0.5 mm i.d., and an open ended quartz T-tube used as the absorbance cell. All transport tubing was Teflon of 0.5 mm i.d. In this system, Hg(II) was reduced to elemental form by Sn²⁺, and then stripped by N₂ gas to the detection cell where the absorbance of Hg(II) was measured. The linear range for this system was 1 μ g L⁻¹ to 30 μ g L⁻¹ with linear regression coefficient $r^2 = 0.9996$.

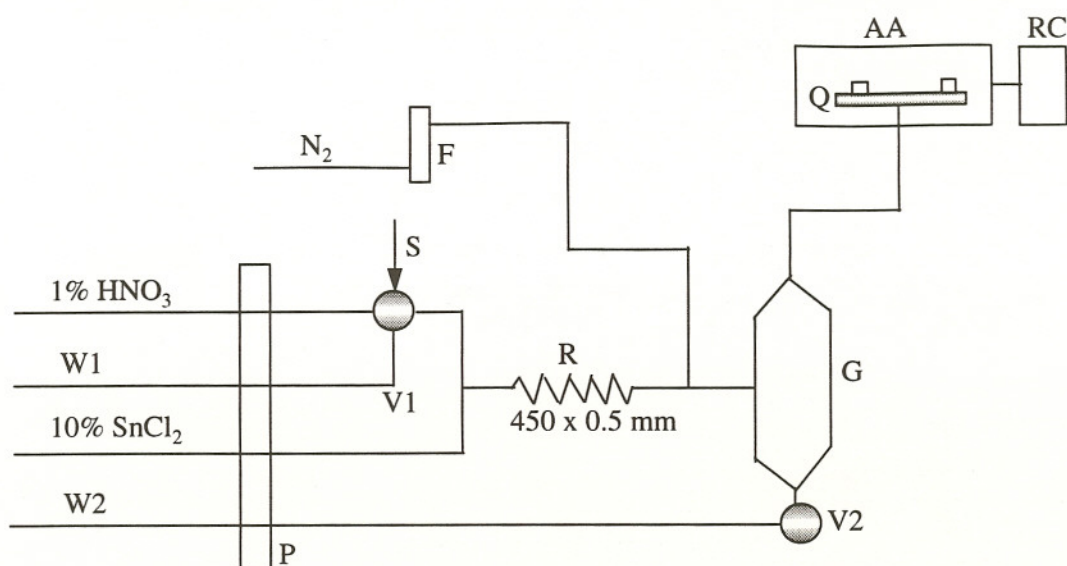


Figure 3.1 Schematic of flow injection system. P: Pump; V1: Six-way valve; V2: Two-way valve; S: Sample injector; R: Reaction coil; Q: Quartz tube; F: Flow meter; RC: Recorder; W1 and W2: Wastes; AA: Atomic absorption spectrophotometer; G: Gas-liquid separator.

Mercury(II) in the solution-phase was determined by FIA followed the digestion of samples according to a modification of the method described by APHA (1992). For the digestion, we placed a 5-mL aliquot of sample into a 10-mL glass vial; gently added 0.5 mL of each of concentrated HNO_3 , H_2SO_4 and HCl ; capped each vial tightly; and placed the vials into a water bath at 80 to 90°C for two hours. After cooling, the samples were analyzed for $\text{Hg}(\text{II})$. The digestion procedure was tested by standard addition using soil extracts as the matrix. Mercury(II) was added to nine soil extracts with dissolved organic C ranging from 16.5 to 98.8 mg organic C L^{-1} to make the final $\text{Hg}(\text{II})$ concentration be 20 $\mu\text{g L}^{-1}$. The mixtures were equilibrated for 24 hours on a reciprocating shaker, and then the $\text{Hg}(\text{II})$ concentrations were determined. The recovery was $91.68 \pm 6.80\%$ (Table 3.4).

Table 3.4 Test of digestion method for determination of Hg

Solution pH	Total Dissolved Organic C (mg L ⁻¹)	Mercury(II) Addition (µg L ⁻¹)	Recovery (%)
3.27	16.54	20	82.98
3.40	15.90	20	96.56
3.69	14.81	20	93.25
4.05	14.12	20	100.32
5.24	17.02	20	96.35
6.05	23.56	20	82.27
6.56	29.57	20	95.43
8.93	75.92	20	83.53
9.70	98.84	20	94.47
Average			91.68
Standard Deviation			6.80

Table 3.5 Mass recoveries of Hg from soil and solution phases

Hg(II) Addition (µg)	pH	Total Mass Recovered (µg)	Recovery (%)
Freehold sandy loam (A horizon), organic matter content: 1.2 g kg ⁻¹			
0		0.25	
10	3.00	8.77	85
10	6.58	8.50	83
10	10.83	8.34	81
5	11.15	4.27	80
Rockaway stony loam, organic matter content: 28.4 g kg ⁻¹			
0		0.29	
10	3.18	8.71	84
10	6.25	8.32	80
10	8.84	8.42	81
5	9.16	4.24	80

3.4 Results and Discussion

Before conducting further adsorption experiments, a mass recovery test was performed to see if any Hg evaporates during adsorption experiments. 1 ± 0.01 g of either Freehold sandy loam (A horizon) or Rockaway stony loam was mixed with 10 μ g or 5 μ g Hg(II) in 100 mL of 0.01 NaNO₃. The pH of each suspension was adjusted to range from 3 to about 11. After 24 hours of equilibration, the solids were separated from solution by filtration through a 0.45 μ m membrane filter. The concentrations of Hg(II) in both solution and solid phases were then analyzed following sample digestion. The solution digestion was performed according to the previously described procedure, and the soil digestion followed the method described in the Methods of Soil Analysis (Page, 1982). The recoveries for both soils of different organic matter content at a variety of pH values are greater than 80% (Table 3.5). The unrecovered mass (15 - 20%) could result from evaporation and/or from irreversible adsorption.

3.4.1 Effect of pH

As expected, the adsorption of Hg(II) by the soils was pH dependent (Figure 3.2). At low pH, Hg(II) was extensively adsorbed by all soils. The maximum adsorption of added Hg(II) occurred in the pH range of 3 to 5 for all soils. After adsorption, the amount of Hg(II) adsorbed ranged from 0.2 to 1.95 mg kg⁻¹ for an initial Hg(II) concentration of 1×10^{-7} M, which was within the concentration range of uncontaminated soils (0.005 - 4.6 mg kg⁻¹) (Steinnes, 1995). For an initial Hg(II) concentration of 1×10^{-6} M, the Hg(II) sorbed ranged from 7.0 to 19.2 mg kg⁻¹, which is above the concentration range of uncontaminated soils. This study mainly focused

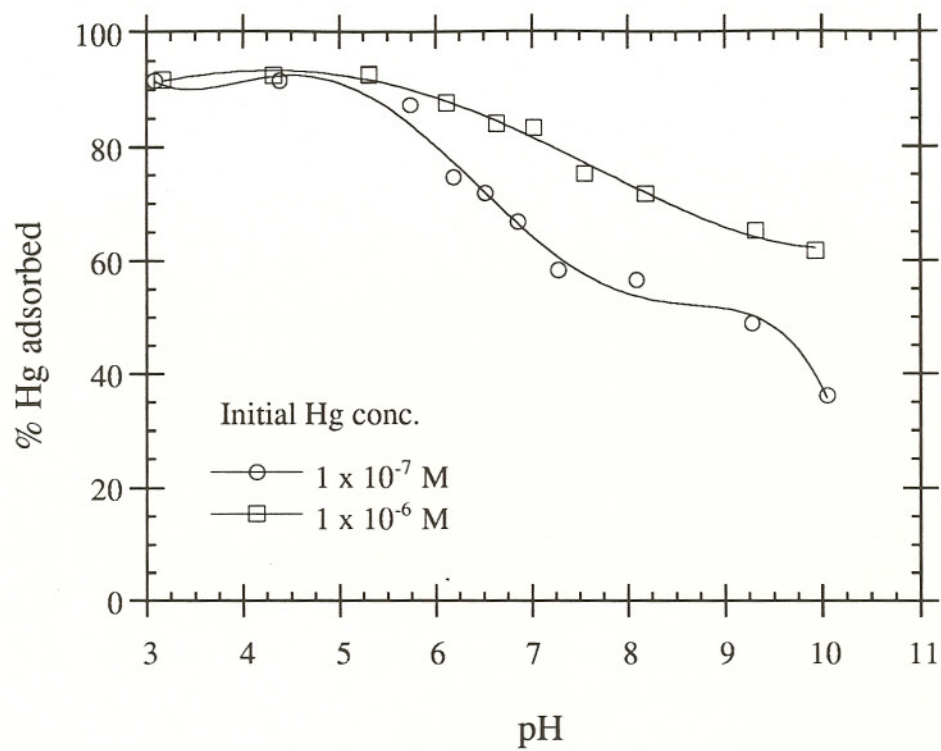


Figure 3.2 Adsorption of Hg(II) on Washington loam as a function of pH. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

on the adsorption of Hg(II) from a 1×10^{-7} M solution to understand the behavior of Hg(II) at natural concentration levels.

At fixed pH, adsorption was related to soil particle size distribution. Freehold sandy loam (A horizon) (No. 6), Lakewood sand (No. 2), fill material from the Delaware River (No. 9), and Downer loamy sand (No. 10) all contained a large portion of sand (850 - 920 g kg⁻¹) and had small organic matter contents (1.2 - 7.0 g C kg⁻¹). The mass of Hg(II) retained on these four soils was small over most of the experimental pH range (Figure 3.3). On the other hand, Sassafras sandy loam (No. 1), which also was a low organic matter soil (3.5 g C kg⁻¹) but contained a larger portion of silt and clay (550 g kg⁻¹), adsorbed more Hg(II) over most of the experimental pH range.

Mercury(II) behaves differently from most other divalent heavy metals in that the extent of adsorption is the greatest in acidic media. For instance, the adsorption of Cd on the same fifteen soils was less than 50% at pH below 4, but increased with increasing pH and reached a maximum of more than 90% at pH above 6.5 to 10 (Allen *et al.*, 1994). Greater adsorption of Hg(II) at low rather than high pH was also reported for pure minerals such as silica, hydrous iron oxide, bentonite, and goethite (MacNaughton and James, 1974; Newton *et al.*, 1976; Kinniburgh and Jackson, 1978; Barrow and Cox, 1992a). As discussed below, the stronger Lewis acid nature of Hg(II) is the major factor responsible for its greater adsorption in acidic media compared with other metals.

In the soil solution of this study, the Cl⁻ concentration ranged from about 1×10^{-6} to 1×10^{-5} M (Table 3.3). The Hg(II) speciation as a function of pH was

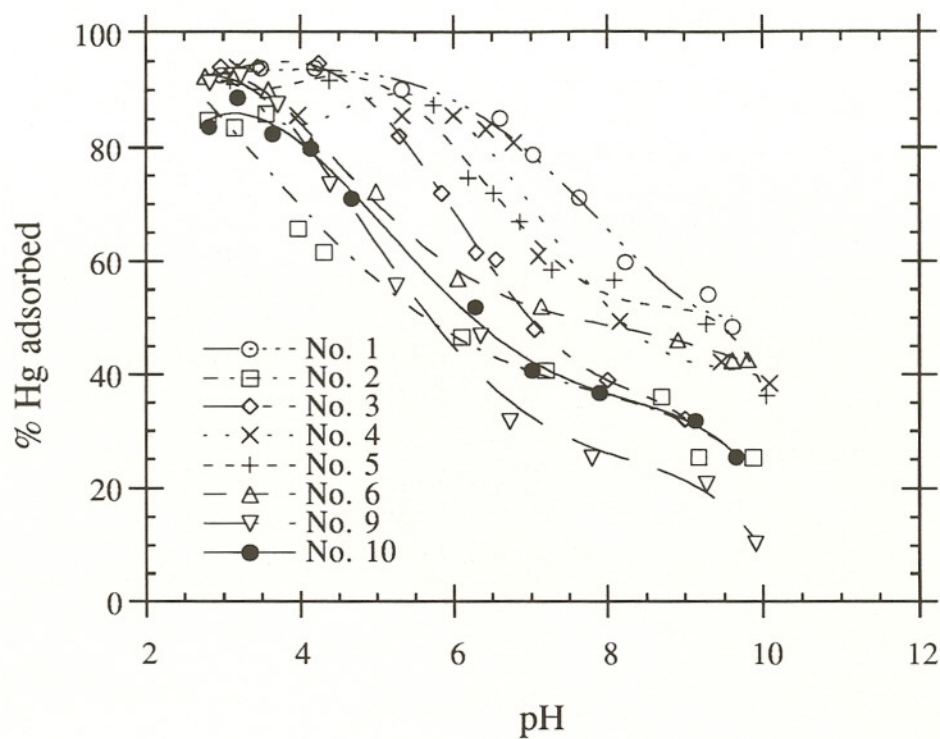


Figure 3.3 Comparison of Hg(II) adsorption on different properties of soils as a function of pH. Initial Hg(II) concentration = 1×10^{-7} M; soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = $25 \pm 2^\circ\text{C}$. See Table 3.1 for soil identification.

calculated and shown in Figure 3.4. Because of the strong Lewis acid characteristics of Hg(II), which has hydrolysis constants of 3.87 for $pK_{OH,1}$ and 2.77 for $pK_{OH,2}$, the proportion of hydroxo-Hg species (including $HgOH^+$, $HgOHCl$, and $Hg(OH)_2$) increased exponentially over a narrow pH range of 3 to 5 (Figure 3.4). The larger the Cl^- concentration, the higher the pH at which the hydroxyl-containing Hg species become predominant over Hg-Cl complexes. As indicated by James and Healy (1972), hydrolysis of the metal could significantly reduce the solvation energy required to overcome for adsorption of metals to solid surfaces. Consequently, the total adsorption energy decreases and adsorption increases when hydrolysis takes place. The occurrence of hydrolysis of Hg(II) at lower pH values could be one reason that caused Hg(II) adsorption to be greater in acidic media.

Due to the strong Lewis acid nature, Hg(II) not only has stronger affinity for OH^- than other metals do, but also is expected to form stronger bond with the surface sites $-O^-$ which can be considered as a base. Therefore, at a fixed low pH value (i.e., $pH < 5$), while the adsorption of other metals on solid surfaces is small due to the competitive binding of H^+ , the adsorption of Hg(II) could be very large because of its stronger binding ability for $-O^-$ than H^+ .

As pH further increased, the adsorption of added Hg(II) significantly decreased, for example, from $89 \pm 8\%$ at pH 4.0 to $39 \pm 11\%$ at pH 8.5 for an initial Hg(II) concentration of 1×10^{-7} M. The existence of adsorption maxima was also observed for the adsorption of Hg(II) by soil components, such as goethite (Barrow and Cox, 1992a), bentonite (Newton *et al.*, 1976), iron hydrous oxide (Kinniburgh and Jackson, 1978), and SiO_2 (MacNaughton and James, 1974), but the extent of the

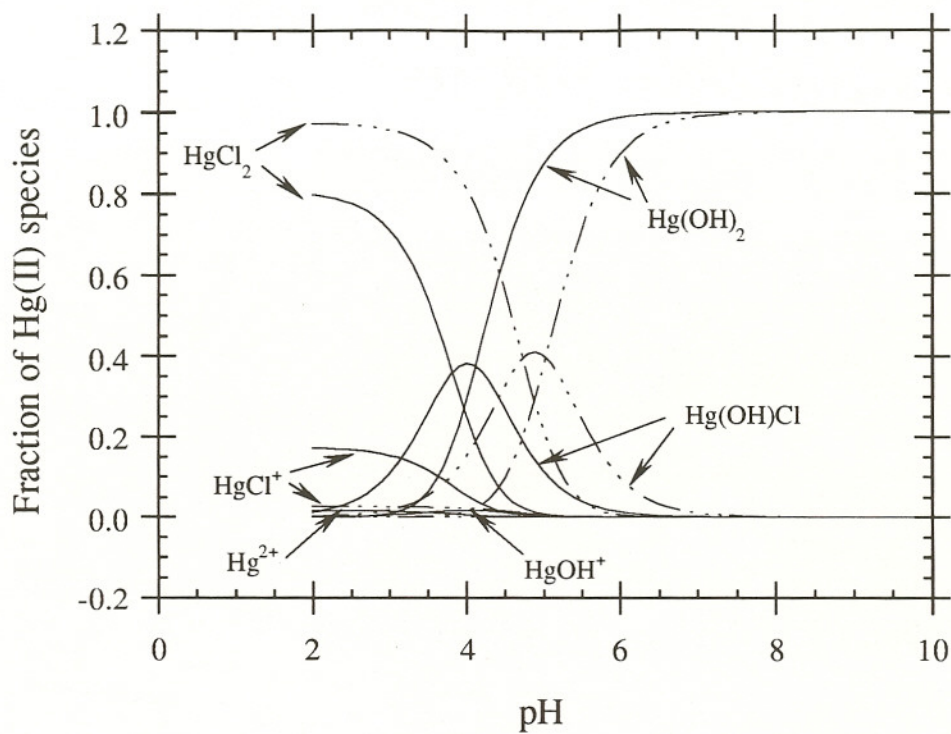


Figure 3.4 Hg(II) speciation as a function of pH and Cl^- concentration. Dashed lines denote the case of $\text{Cl}^- = 1 \times 10^{-5} \text{ M}$ and solid lines denote the case of $\text{Cl}^- = 1 \times 10^{-6} \text{ M}$.

decrease in adsorption by soil components at higher pH was much smaller than that observed in this study. Barrow and Cox (1992a) suggested that the decrease of the concentration of the positively charged species HgOH^+ resulted in the decrease of Hg(II) adsorption by goethite. Some researchers have suggested that the increase of the concentration in Hg(OH)_2 relative to that of Hg(OH)Cl at a pH greater than the pH at which maximum adsorption occurs may be responsible for the decrease in adsorption. At these pH values, the increase in the activity of Hg(OH)Cl as a function of increasing concentration of OH^- is greater than that of Hg(OH)_2 (Kinniburgh and Jackson, 1978; Newton *et al.*, 1976). Any of these reasons could contribute to the decrease in Hg(II) adsorption by soils as pH increased. As shown below, the dissolution of soil organic matter, however, may be the most important factor causing the significant decrease of Hg(II) adsorption by soils at high pH.

3.4.2 Effect of Organic Matter

We noted that the amount of dissolved soil organic matter increased significantly as the solution pH was raised (Figure 3.5). One consequence of the increase in dissolved organic matter is a corresponding decrease in organic-based surface adsorption sites which may contribute to the decrease in Hg(II) adsorption. The complexation of Hg(II) by the dissolved organic matter, however, was probably more important in decreasing the Hg(II) adsorption by soil. We tested this hypothesis by adding organic matter to soil suspensions at both constant pH and variable pH. We found that Hg(II) adsorption at pH 6.5 decreased from approximately 60% to 28% of the added Hg(II) when the added dissolved organic matter increased from 1.4 to 61.1 mg C L⁻¹ (Figure 3.6). When 43.7 mg organic C L⁻¹ was added to soil suspensions at

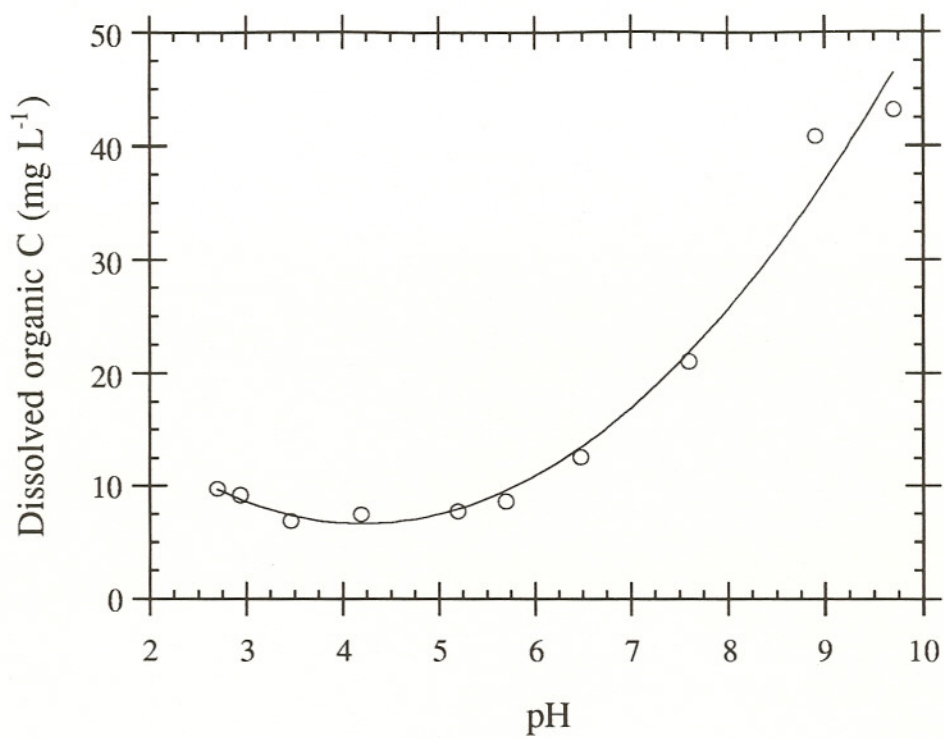


Figure 3.5 Dissolution of soil organic C as a function of solution pH for the Freehold sandy loam (B horizon). Soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

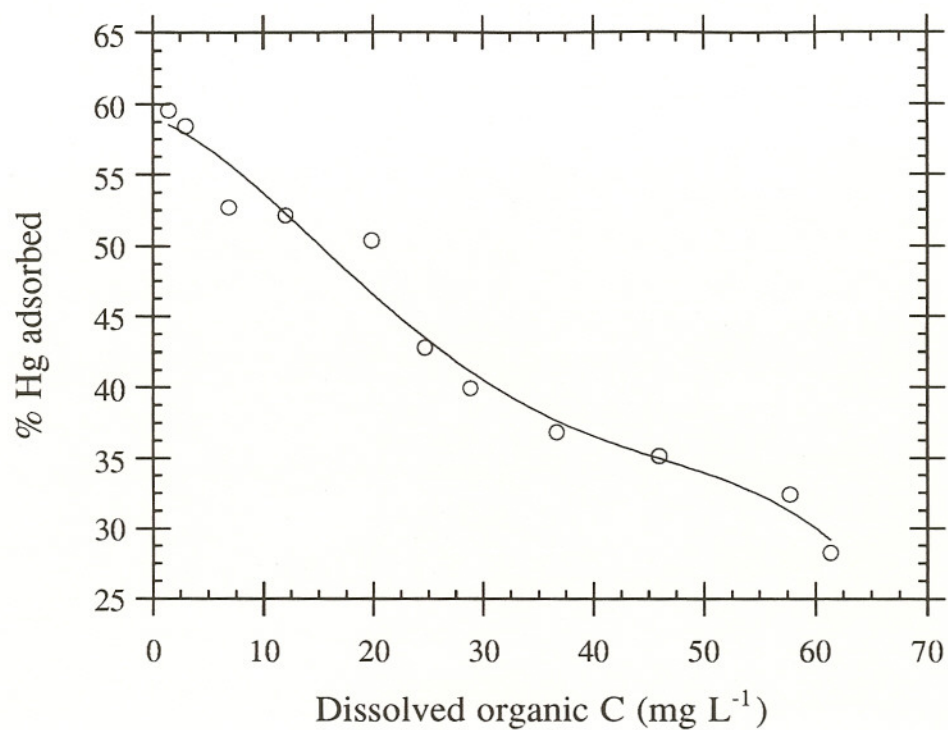


Figure 3.6 Effect of dissolved organic C on Hg(II) adsorption by Freehold sandy loam (A horizon) at pH 6.5. Initial Hg(II) concentration = 1×10^{-7} M; soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = $25 \pm 2^\circ\text{C}$.

pH values ranging from 2.5 to 10, the Hg(II) adsorption generally decreased over most of the pH range for all soils except at very low pH (Figures 3.7a-c). At pH less than 4, more than 50% of the added organic matter was retained by Rockaway sandy loam or precipitated (Figure 3.7d), and Hg(II) adsorption was not affected or only slightly increased (Figure 3.7b). At pH greater than 4, more than 50% of the added organic C remained in solution and Hg(II) adsorption decreased. For Freehold sandy loam (A horizon) and Dunellen sandy loam, only near pH 3 was more than 50% of the added organic C retained by soil particles or precipitated (Figure 3.7d). In this pH region the addition of organic matter had no effect on Hg(II) adsorption (Figures 3.7a, c). At higher pH, more than 50% of the added organic C remained in solution at equilibrium and the adsorption of Hg(II) decreased.

The efficacy of the dissolved organic matter in decreasing Hg(II) adsorption may depend on the amount of Hg(II) present. Barrow and Cox (1992b) also observed that Hg(II) adsorption on a loamy sand soil decreased at higher pH. The extent of the decrease in adsorption in their study, however, was less than we observed for the soils in this study. It is likely that this resulted from the Hg(II) concentration used in their study (greater than 10^{-4} M) being much larger than that in this study (1×10^{-7} and 1×10^{-6} M). For a given amount of dissolved organic matter, at low Hg(II) loading, a large fraction of Hg(II) could be complexed by the dissolved organic matter. Increasing the Hg(II) loading resulted in more inorganic Hg(II) being available for adsorption by soil solids. Because of complexation of Hg(II) by dissolved organic matter, the fraction of the Hg that is in solution at low initial Hg concentrations is greater than that at higher initial Hg concentrations. Comparison of Hg(II) adsorption by soils at two initial concentrations used in this study supported this hypothesis.

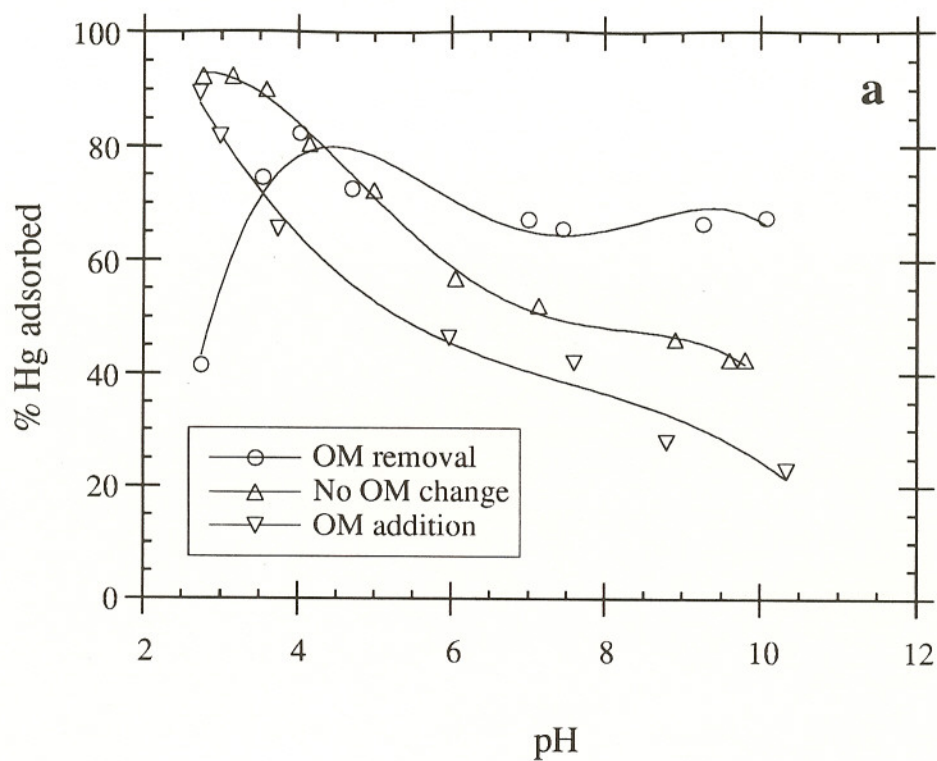


Figure 3.7a Comparison of Hg(II) adsorption by Freehold sandy loam (A horizon) with hydrogen peroxide treatment for organic matter removal, addition of organic matter, and no organic matter change as a function of pH. Initial Hg(II) concentration = 1×10^{-7} M; soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = $25 \pm 2^\circ\text{C}$.

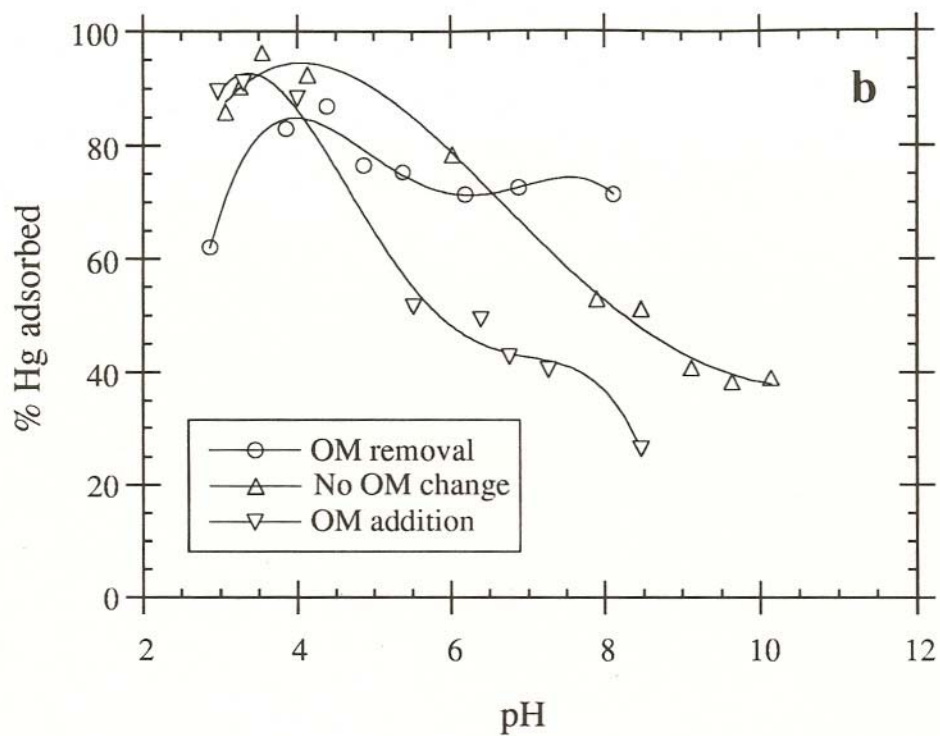


Figure 3.7b Comparison of Hg(II) adsorption by Rockaway stony loam with hydrogen peroxide treatment for organic matter removal, addition of organic matter, and no organic matter change as a function of pH. Initial Hg(II) concentration = 1×10^{-7} M; soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

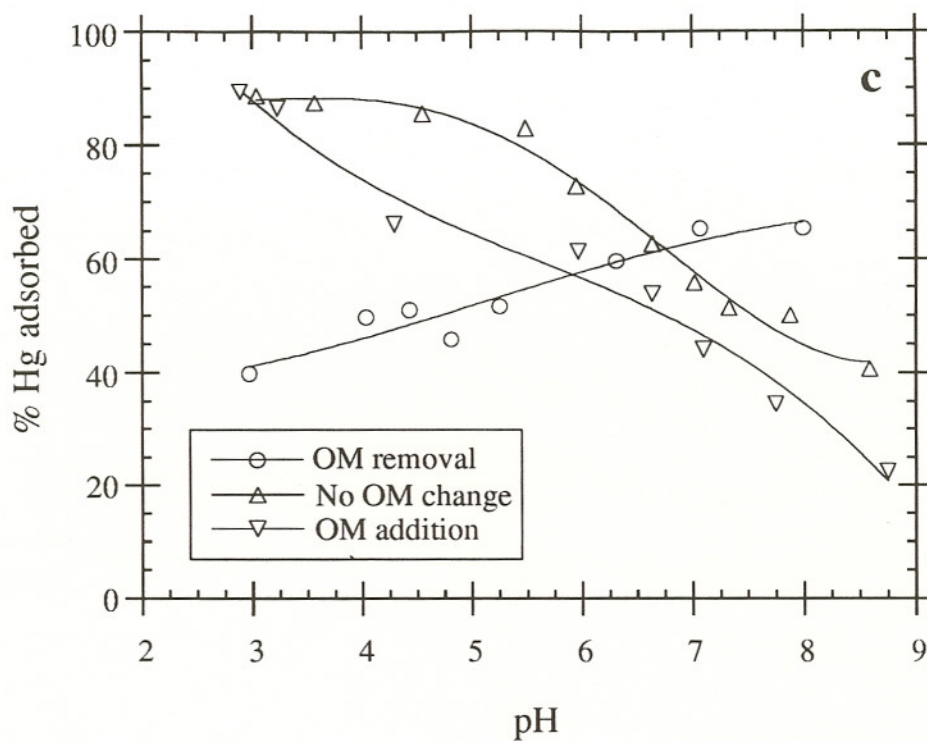


Figure 3.7c Comparison of Hg(II) adsorption by Dunellen sandy loam with hydrogen peroxide treatment for organic matter removal, addition of organic matter, and no organic matter change as a function of pH. Initial Hg(II) concentration = 1×10^{-7} M; soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

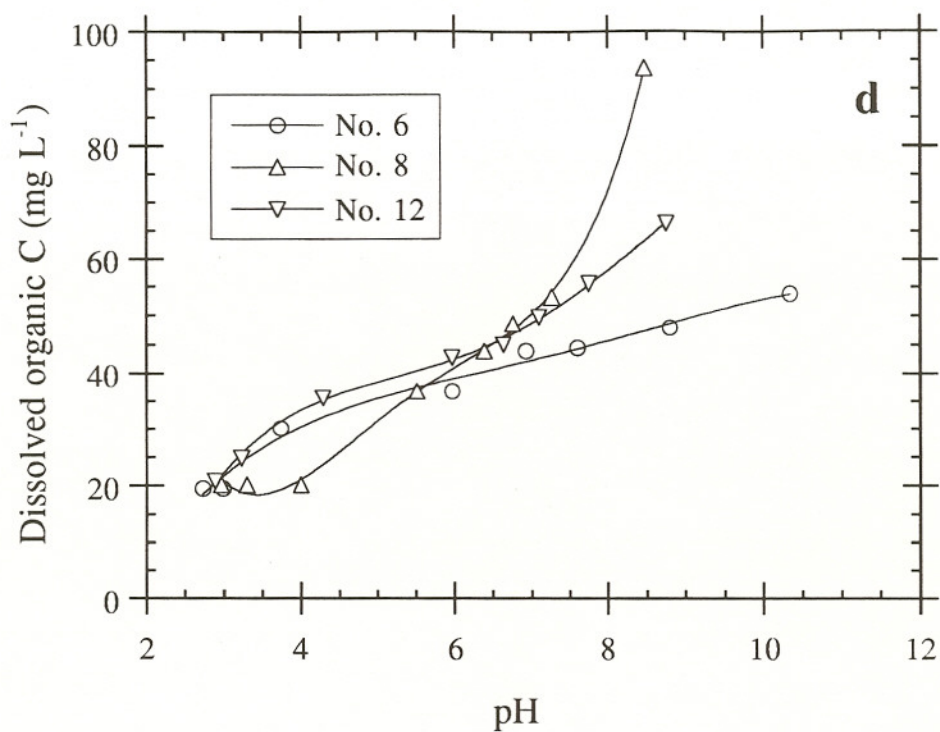


Figure 3.7d Final concentrations of dissolved organic C as a function of pH. See Table 3.1 for soil identification. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

At pH less than 5, the effect of soluble organic matter is small due to its limited quantity. The fractional adsorption of Hg(II) was similar for two initial concentrations or slightly smaller for the higher initial concentration (1×10^{-6} M) (Figure 3.2). Adsorption at these pH values is expected to follow the Langmuir isotherm. Depending on the location of the data points on the Langmuir isotherm, the fractional adsorption for two initial concentration could be the same when both data points are located at the linear portion of the isotherm, or smaller for the higher initial concentration when the data points for two concentrations are located at the different portions of the isotherm. At pH above 5, the dissolved organic matter has significant effect on Hg(II) adsorption. The fractional adsorption of Hg(II) increased as initial Hg concentration increased from 1×10^{-7} to 1×10^{-6} M (Figure 3.2). Further increases in the initial Hg concentration would finally result in decreases in fractional adsorption when the complexation capacity of the dissolved organic matter is exceeded. Details on the effect of the dissolved organic matter on Hg(II) adsorption as a function of the Hg loading level will be discussed in Chapter 4.

The effect of soil organic matter on Hg(II) adsorption was further studied by removal of soil organic matter. When soil was treated by H_2O_2 for the removal of organic matter, the adsorption of Hg(II) was significantly reduced at low pH (Figures 3.7a-c). Two hypotheses seem reasonable for this decrease. First, organic matter generally has stronger affinity for Hg(II) than do soil inorganic components. Removal of organic matter contributed to the decrease of Hg(II) adsorption. Second, when soil organic matter was removed, some inorganic surface areas were exposed. Compared with organic matter, soil inorganic components usually have smaller surface areas (Sparks, 1995). Therefore the total soil surface area was expected to have decreased.

This may have also contributed to the observed decrease of Hg(II) adsorption. After H_2O_2 treatment for the removal of organic matter, for Dunellen sandy loam (No. 12), as pH was increased, the adsorption increased and reached a maximum at pH 7 to 8 (Figure 3.7c). For Freehold surface sandy loam (No. 6) and Rockaway sandy loam (No. 8), the adsorption increased and reached a maximum at about pH 4 (Figures 3.7a, b). Further increases in pH resulted in a decrease in Hg(II) adsorption. The extent of the decrease was much smaller than that for the adsorption of Hg(II) by soils without changes in organic matter. This also suggested that the complexation of Hg(II) by dissolved organic matter was the major factor resulting in Hg(II) adsorption by soils to significantly decrease in alkaline systems.

The difference in pH at which the maximum adsorption of Hg(II) on organic matter-removed soils occurred probably resulted from a difference in soil composition. Two types of components may be responsible for this difference. One is clay minerals. Freehold sandy loam contains 920 g sand kg^{-1} and has a very small CEC (0.8 cmol kg^{-1}). This soil only contains a small amount of clay minerals. Dunellen sandy loam contains almost the same amount of sand (560 g kg^{-1}) as Rockaway sandy loam (540 g kg^{-1}) does, but has a much larger CEC (4.2 cmol kg^{-1}) and smaller organic matter content (11.0 g C kg^{-1}) than Rockaway sandy loam (CEC = 2.7 cmol kg^{-1} ; organic matter = 28.4 g C kg^{-1}). Because soil CEC is largely derived from clay minerals and organic matter (Bohn *et al.*, 1985), the larger CEC in Dunellen sandy loam must have resulted from a larger fraction of clay minerals. The adsorption of Hg(II) on clay minerals has been reported to increase up to pH 8 to 9 (Andersson, 1979). Therefore, a greater clay mineral content in Dunellen sandy loam may have resulted in the maximum adsorption occurring at a higher pH range. Another component possibly

responsible for the difference was iron oxide. Andersson (1979) reported that Hg(II) adsorption by $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ increased with increasing pH up to 6.2 to 8.5. Barrow and Cox (1992a) showed that the adsorption of Hg(II) by goethite reached a maximum at pH about 4, and then only slightly decreased from pH 4 to 7. The Dunellen sandy loam contained more total iron oxide than did the other two soils (Table 3.1). This may have also shifted the maximum adsorption of Hg(II) by Dunellen sandy loam to higher pH.

3.4.3 Effect of Chloride

In this study, we chose three soils of different organic matter content to investigate the effect of Cl^- on Hg(II) adsorption at different pH values. At neutral or higher pH, only a very small amount of Hg-Cl complexes can be formed, and the extent of adsorption largely depends on the balance between the interaction of other forms of Hg(II) with soil surface and the complexation of Hg(II) by dissolved organic matter. An increase in Cl^- concentration was expected to have little effect on adsorption by any of the soils. This was verified by the experimental results (Figures 3.8a-c). At $\text{pH} \geq 6.5$, when Cl^- was increased from about $1 \times 10^{-6} \text{ M}$ to $1 \times 10^{-2} \text{ M}$, there was almost no change in Hg(II) adsorption by any of the three soils. Similar results were reported by Barrow and Cox (1992b) who observed that the adsorption of Hg(II) by a loamy sand was not affected by addition of Cl^- at pH 6.7 to 7.4. They also reported that the addition of Cl^- decreased Hg(II) adsorption at low pH. We found that this was not always the case. The effect of Cl^- on Hg(II) adsorption by soil at low pH depended on the soil organic matter content.

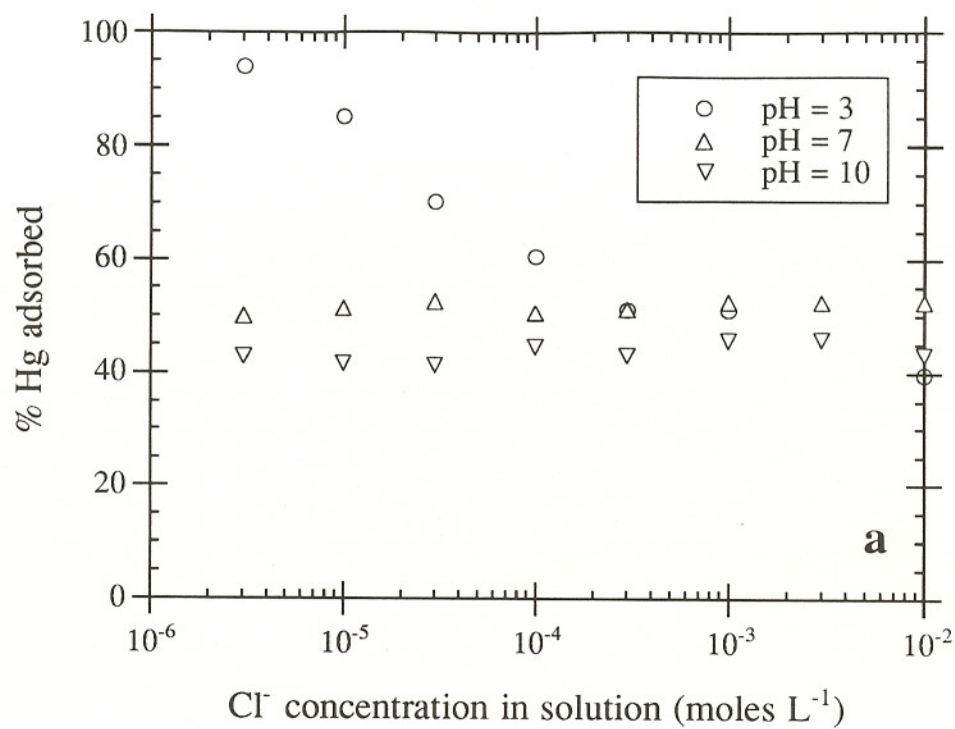


Figure 3.8a Adsorption of 1×10^{-7} M Hg(II) on Freehold sandy loam (A horizon) as a function of pH and chloride concentration. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M; T = $25 \pm 2^\circ\text{C}$.

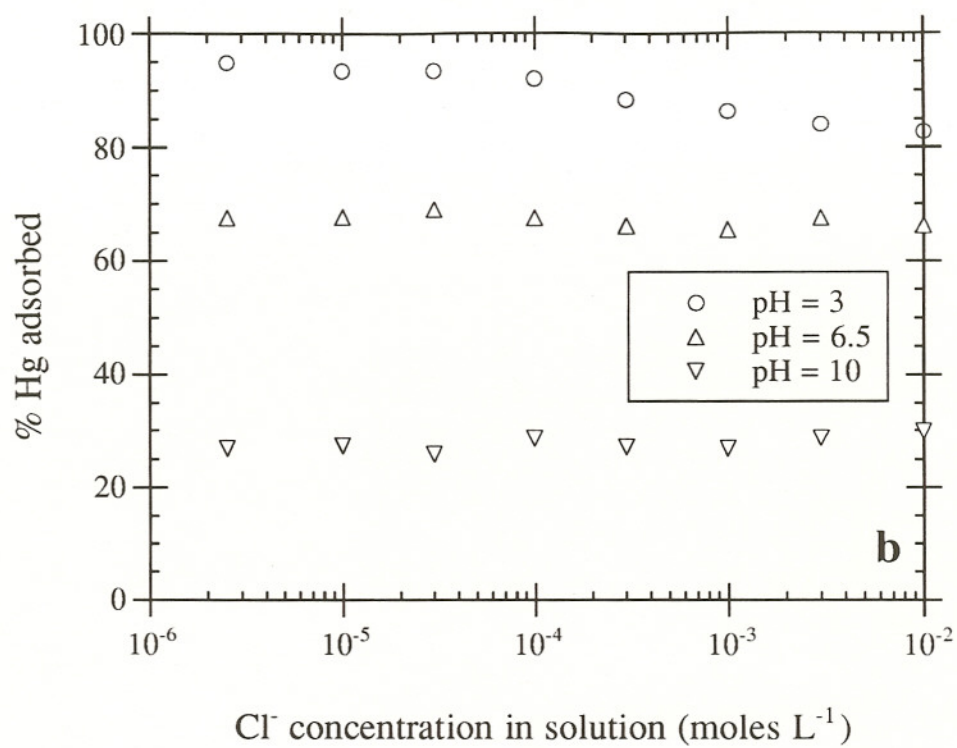


Figure 3.8b Adsorption of 1×10^{-7} M Hg(II) on Dunellen sandy loam as a function of pH and chloride concentration. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M; T = $25 \pm 2^\circ\text{C}$.

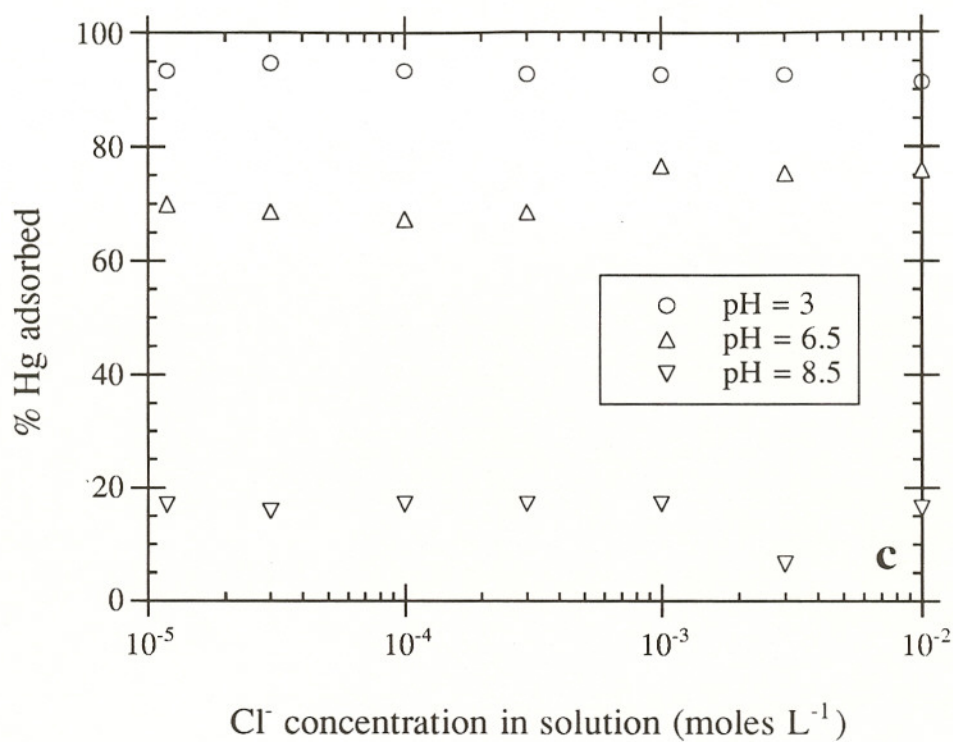


Figure 3.8c Adsorption of 1×10^{-7} M Hg(II) on Boonton Union loam as a function of pH and chloride concentration. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M; T = $25 \pm 2^\circ\text{C}$.

Under acidic conditions, there was a very small amount of dissolved organic matter in the soil solutions. Thus, Hg(II) speciation in different soil solutions was similar. Adsorption largely depended on the interaction of Hg(II) species with different soil surfaces. For the soil with a low organic matter content (1.2 g C kg⁻¹; Freehold sandy loam, A horizon), the addition of Cl⁻ significantly reduced adsorption at pH 3. When Cl⁻ concentration was increased from about 1 × 10⁻⁶ M to 1 × 10⁻² M, adsorption decreased from 93% to 40% of the total added Hg(II). The predominant adsorption sites on this soil were inorganic. In the soil solutions, most of the Hg(II) was calculated to be present as the HgCl₂ complex (Figure 3.9) which is poorly adsorbed by inorganic surfaces (MacNaughton and James, 1974; Newton *et al.*, 1976; Kinniburgh and Jackson, 1978; Barrow and Cox, 1992a). Therefore, as the concentration of Cl⁻ was raised, the fraction of HgCl₂ increased, whereas the fraction of HgCl⁺, Hg²⁺, and Hg(OH)Cl decreased (Figure 3.9), which resulted in the decrease of Hg(II) adsorption (Figure 3.7a).

For the soil of intermediate organic matter content (11.0 g C kg⁻¹; Dunellen sandy loam), the addition of Cl⁻ slightly reduced adsorption. When Cl⁻ concentration was increased from about 1 × 10⁻⁶ M to 1 × 10⁻² M, adsorption decreased from 95% to 81% of the total added Hg(II). For the soil with the largest organic matter content (49.9 g C kg⁻¹; Boonton Union loam), the addition of Cl⁻ had almost no effect on the adsorption of Hg(II). When Cl⁻ was increased from about 1 × 10⁻⁵ M to 1 × 10⁻² M, adsorption decreased only from 95% to 91% of the total added Hg(II). The decrease of the effect of Cl⁻ on Hg(II) adsorption by organic matter probably resulted from the competitive binding of organic matter for Hg(II). Many evidences have suggested that there were different energy of sites on organic matter (Purdue *et al.*, 1984). It is

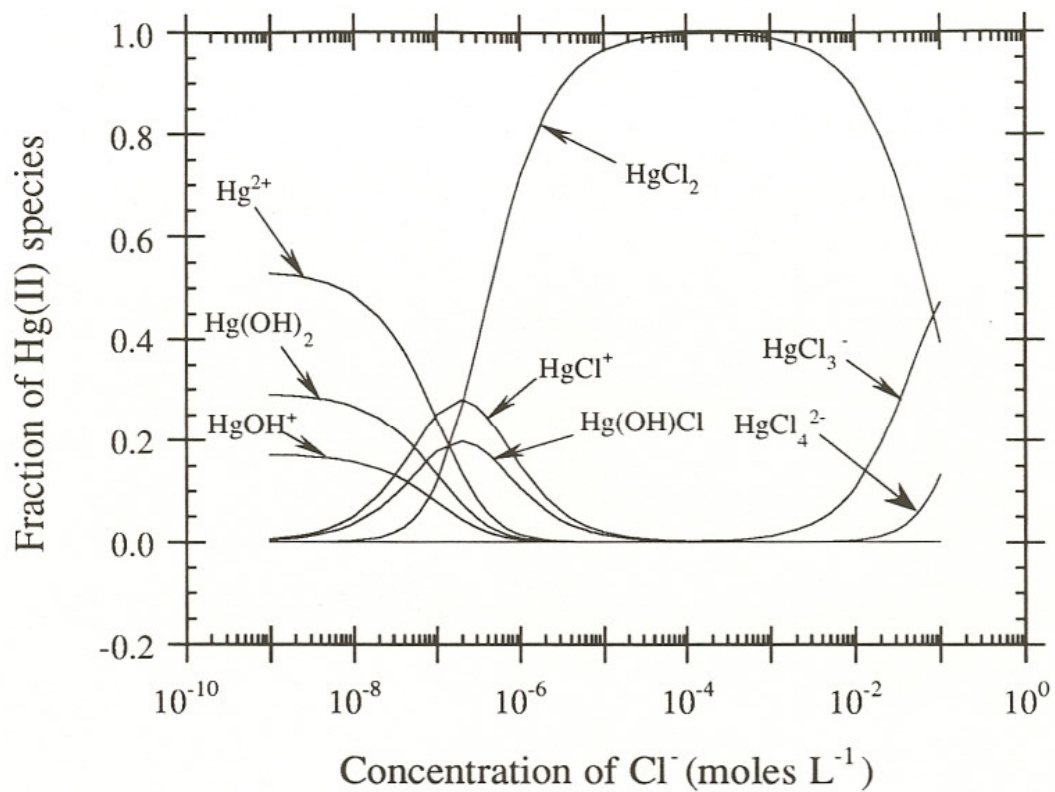


Figure 3.9 Mercury(II) speciation as a function of Cl^- concentration at pH 3

expected that the binding of Hg(II) with some of the sites on organic matter is stronger than that with Cl⁻. For a given Hg(II) concentration, the effect of Cl⁻ on Hg(II) adsorption depends on the concentration of the high energy sites on particulate organic matter. Increases in organic matter content could increase the amount of high energy sites, which adsorb more Hg(II) and eventually decreases the effect of Cl⁻. For a given soil, the binding sites on organic matter are fixed, the effect of a certain amount of Cl⁻ on Hg(II) adsorption may depend on Hg(II) concentration. Increasing Hg(II) concentration could result in more Hg(II) to be available for Cl⁻ binding.

3.4.4 Effect of Calcium

It has been found that background cations can affect heavy metal adsorption to soils via competitive binding for the available binding sites (Zachara *et al.*, 1993). Ca²⁺ is one of the common cations that are present in soil solution. The effect of Ca²⁺ on Hg(II) adsorption was investigated in this study. If there is competitive binding between Ca²⁺ and Hg(II), the adsorption of Hg(II) in Ca(NO₃)₂ (I = 0.01 M) should be smaller than that in NaNO₃, which is an indifferent electrolyte and has been found to exhibit no competitive binding at a concentration level of 0.01 M (Zachara *et al.*, 1993).

As shown in Figures 3.10-3.11, the adsorption of Hg(II) in both electrolytes at pH less than about 4 was similar. At higher pH, Hg(II) adsorption in Ca(NO₃)₂ was even higher than that in NaNO₃. This probably resulted from the coagulation of organic matter by Ca²⁺, which removed some of the dissolved organic matter-associated Hg from solution. Similar results were reported by

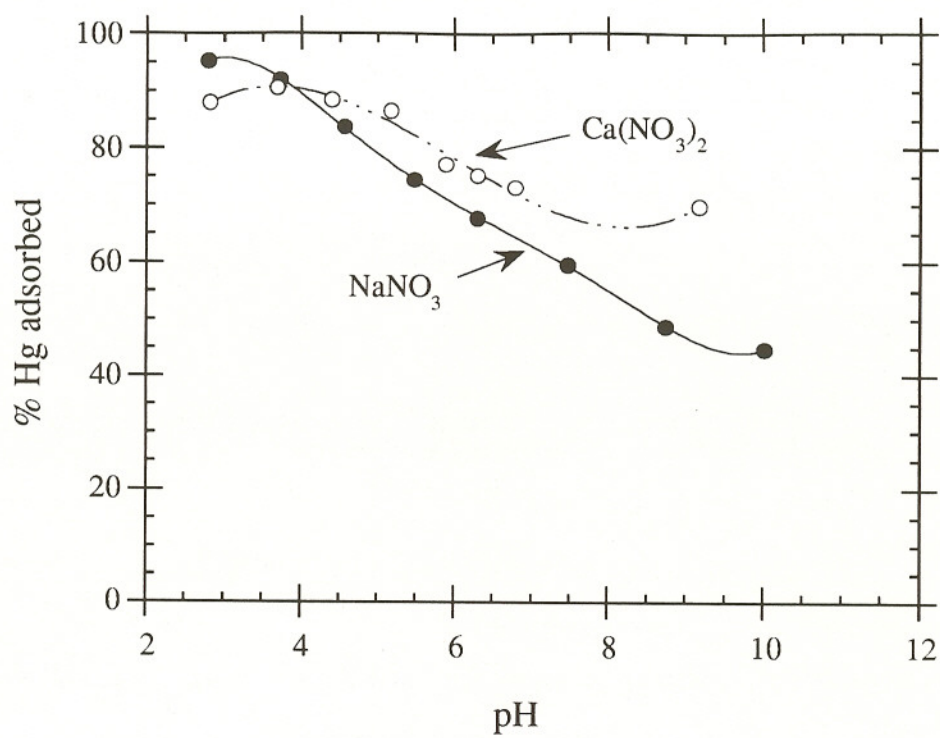


Figure 3.10 Comparison of the adsorption of 1×10^{-7} M Hg(II) on Freehold sandy loam (A horizon) in NaNO_3 and $\text{Ca}(\text{NO}_3)_2$. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M; T = $25 \pm 2^\circ\text{C}$.

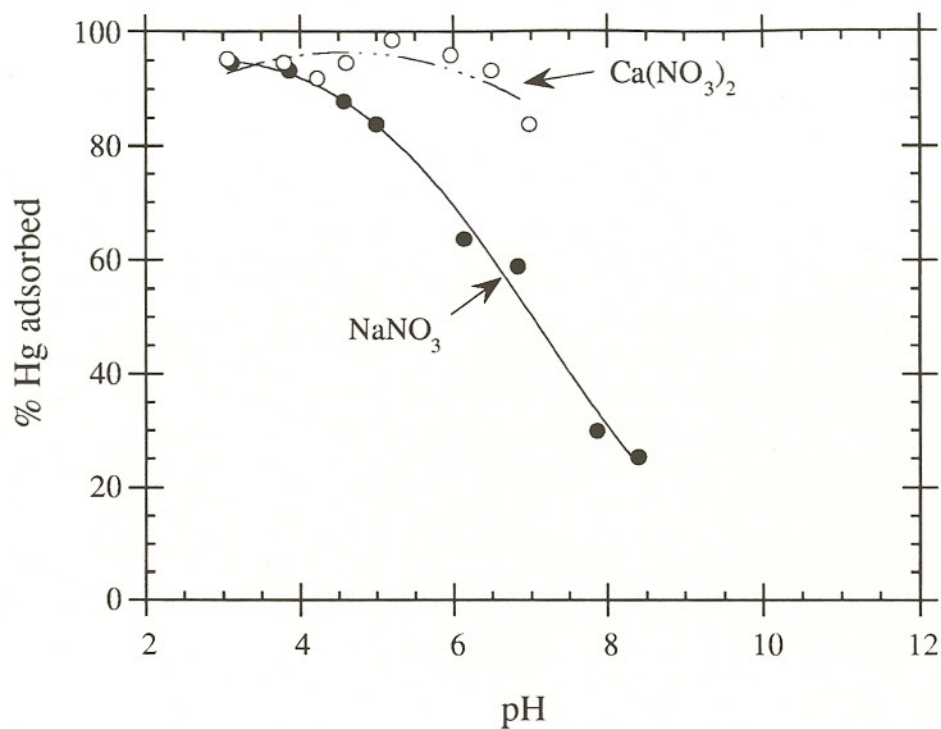


Figure 3.11 Comparison of the adsorption of 1×10^{-7} M Hg(II) on Boonton Union loam in NaNO_3 and $\text{Ca}(\text{NO}_3)_2$. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M; T = $25 \pm 2^\circ\text{C}$.

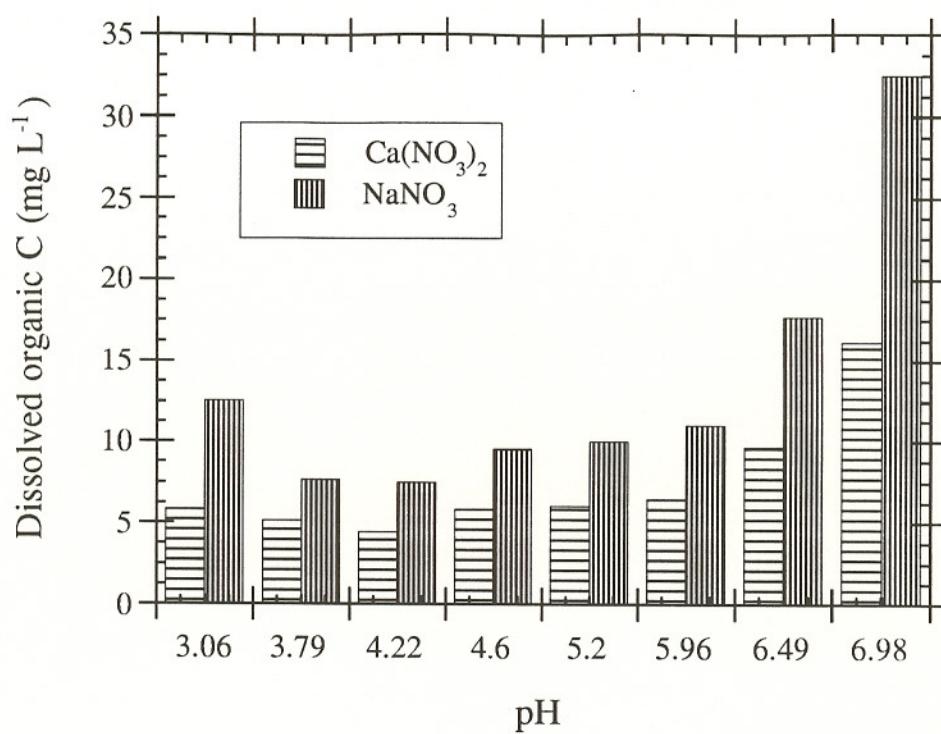


Figure 3.12 Comparison of the concentrations of the dissolved organic C in NaNO₃ and Ca(NO₃)₂ for Boonton Union loam. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M; T = 25 ± 2°C.

Thanabalasingam and Pickering (1985) for the adsorption of Hg(II) on humic acid. They observed that adsorption at pH 3 to 5 was similar for all electrolytes used. As pH further increased, the adsorption in Na⁺ and 1 × 10⁻² NH₄⁺ electrolytes decreased but remained unchanged in 1 × 10⁻² M Ca²⁺ or Mg²⁺ or 1 × 10⁻⁴ M NH₄⁺.

It is speculated that the organic matter coagulated by Ca²⁺ in this study was mainly humic acid, since fulvic acid-metal complexes have been shown to be fairly soluble at a fulvic acid/metal weight ratio of > 2 (which is the case of this study) (Schnitzer and Kerndorff, 1981). This was tested by acidifying the filtrates to pH about 1. No precipitates were found in solution, indicating almost all humic acid being removed from solution. Since there was still dissolved fulvic acid whose concentration increased with increasing pH (Figure 3.12), the complexation of Hg by the fulvic acid may result in the decrease of adsorption. Furthermore, the increasing dispersion of particles at higher pH could also retain some fine colloid (< 0.45 μm) - associated Hg in solution.

3.5 Summary and Conclusions

The adsorption of Hg(II) to soils was highly pH dependent. The maximum adsorption occurred in a pH range of 3 to 5 for all soils studied. Above pH 5, the adsorption significantly decreased. Increasing the pH resulted in an increase of the amount of dissolved organic matter. Because of the complexation of Hg by the dissolved organic matter, adsorption decreased significantly as pH was raised. The importance of the release of organic matter in decreasing Hg(II) adsorption by soil may depend on both Hg(II) loading levels and the environmental conditions which

determine the amount of organic matter that can be dissolved. Consequently, performing studies at environmental Hg(II) levels is very important to understand the behavior of Hg(II) that has already been released to the environment.

The presence of Cl^- in soil had no effect on Hg(II) adsorption by any soil under alkaline conditions because only a small amount of Hg-Cl complexes were present. Under acidic conditions, the effect of Cl^- on Hg adsorption depended on the soil organic matter content and Hg(II) level. For soils with a small organic matter content, the presence of Cl^- could significantly reduce Hg(II) adsorption; for soils with a very large organic matter content, the presence of Cl^- may have almost no effect on Hg(II) adsorption. For a given soil, increasing Hg(II) loading level could result in more Hg(II) available for binding by Cl^- .

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Chapter 4

ADSORPTION AND DESORPTION ISOTHERMS OF MERCURY(II) ON SOILS

4.1 Abstract

Adsorption and desorption isotherms for Hg(II) on the fifteen New Jersey soils are investigated in this chapter. Within an initial Hg solution concentration range of 1.0×10^{-7} to 1.1×10^{-4} M, all soils with a large organic matter content (> 11.0 g C kg⁻¹) had an S-type isotherm, whereas all soils with a low organic matter content (< 7.5 g C kg⁻¹) had an L-type isotherm. Changing the concentration of NaNO₃ background electrolyte had no effect on adsorption, suggesting that adsorption was not dominated by electrostatic interaction. Mercury(II) speciation calculation also indicated that $< 4\%$ of the total Hg could be adsorbed via electrostatic interaction. A model which incorporated the interactions of aqueous Hg with both dissolved organic matter and soil solids was developed to describe the isotherms and to evaluate the adsorption capacities of soils. The adsorption capacity correlated with the soil organic carbon content ($R^2 = 0.92$). The adsorption and desorption isotherms did not follow the same track. Soil organic matter was the most important component responsible for the observed hysteresis. The restricted diffusion of Hg through organic matter was probably the major factor responsible for the hysteresis.

4.2 Introduction

A number of factors, including soil properties, environmental conditions, and the amount of contaminants in soil, affect adsorption (Goldberg and Glaubig, 1988; Christensen, 1989; Sposito, 1989; Zachara *et al.*, 1989; Schuster, 1991; Lee, *et al.*, 1996). Among these factors, the dependence of adsorption on the amount of contaminant present has often been studied in terms of an adsorption isotherm to understand the adsorption process involved and to evaluate soil adsorption capacity. Because of the heterogeneity of soils, adsorption isotherms are typically different for different soils and contaminants. According to the initial slope, adsorption isotherms were classified into four types, i.e., S-type, L-type, H-type and C-type (Giles *et al.*, 1974a, b). The L-type isotherm is frequently observed for the adsorption of heavy metals by soils. It is usually described by either the Langmuir equation or Freundlich equation, or the Langmuir two site equation (Travis and Etnier, 1981). An universal expression of this equation is (Sposito, 1985):

$$q(c) = \sum_{i=1}^n \frac{b_i k_i^{\beta_i} c^{\beta_i}}{1 + B_i C_i^{\beta_i}} \quad (4.1)$$

where $q(c)$ is the amount of solute adsorbed, C is the concentration of solute in the solution, b_i , B_i , k_i , β_i ($i = 1, \dots, n$) and n are adjustable parameters.

It has often been observed that not all of the adsorbed contaminants can be desorbed, i.e., the reactions are not completely reversible (Di Toro *et al.*, 1986; Schultz *et al.*, 1987). This is commonly referred to as adsorption/desorption hysteresis. The extent of hysteresis is governed by both the stability of the surface complexes and the

pathways through which adsorption occurred. The former depends on the Gibbs energy. Generally speaking, inner-sphere complexes in which metal ions bind directly with the surface functional groups are more stable than outer-sphere complexes which are coulombic in nature and have at least one of the metals' coordinated waters interposed between them and the surface functional groups (Sposito, 1984). Physically, metal ions can be adsorbed to the outer-surface of particles and can also diffuse into the particle micropores or penetrate into the mineral structure with aging. The latter two pathways have been frequently reported as the reasons of slow desorption. For example, Bruemmer *et al.* (1988) studied the adsorption/desorption of Ni, Zn, and Cd by goethite and suggested that the diffusion of trace metals into the mineral structure may in part explain the adsorption/desorption irreversibility. Avotins (1975) showed that the desorption of Hg from hydrous ferric oxide was characterized by both a fast and a slow process. They attributed the slow process to the diffusion of Hg from the hydrous ferric oxide interior back to the surface. Dang *et al.* (1994) described Zn desorption from vertisols by a parabolic diffusion model and found that the overall diffusion constant was significantly correlated with organic C content and clay content.

In Chapter 3, we have shown that both particulate and dissolved soil organic matter were important to Hg adsorption from a low concentration (1×10^{-7} M) solution. The amount of dissolved organic matter increased with increasing pH, which significantly decreased Hg adsorption. The purpose of this study was to examine the effect of the amount of Hg present on adsorption and to investigate the factors controlling Hg adsorption and desorption by soil. A model which incorporated the interactions of aqueous Hg with both dissolved organic matter and soil solids was

proposed to describe the adsorption isotherms and to evaluate the adsorption capacities of soils in relation to the soil properties.

4.3 Materials and Methods

4.3.1 Adsorption Experiments

Fifteen New Jersey soils listed in Table 3.1-3.3 were used to perform this study. A batch technique was used to perform all studies. Distilled, deionized water was used to prepare all reagents and soil suspensions. Aliquots of 0.4 g of soil were mixed with 40 mL 0.01 M NaNO_3 in 50-mL glass centrifuge tubes. The soil suspensions were allowed to stand overnight to hydrate before adding Hg. The pH values of the suspensions were then determined and the average was calculated. Upon hydration, Hg(II) was added to each soil suspension from a 40 mg L^{-1} or a 400 mg L^{-1} $\text{Hg(NO}_3)_2$ stock solution which was kept in 0.1 M HNO_3 . The amount of Hg added was varied in order to make the initial Hg solution concentration in the samples range over three orders of magnitude from 1.0×10^{-7} M to 1.1×10^{-4} M (at greater concentrations, precipitation was calculated to occur). The pH of each sample was then adjusted to the above average value calculated for the soil suspensions before addition of Hg by adding 0.1 M NaOH. The centrifuge tubes were capped with Teflon caps and shaken endwise on a reciprocating shaker at 60 strokes per minute for 24 hours at room temperature ($25 \pm 2^\circ\text{C}$). During the shaking, the pH was checked and adjusted if necessary. A preliminary study indicated that the Hg concentrations in solution were stable after 24 hours of shaking. After 24 hours of equilibration, the final pH values of the samples were measured. The pH variation from the initial value

was ± 0.3 pH units. The samples were then centrifuged at 1300 g for 30 min. The Hg concentration in the supernatants were analyzed by the flow injection analysis system. The difference between the initial Hg concentration and the amount remaining in the solution was considered to be adsorbed by soil.

To evaluate the importance of organic matter to Hg adsorption, we compared Hg adsorption on Rockaway stony loam with and without removal of organic matter. The organic matter was removed by treatment of soil with H_2O_2 following the procedure described Chapter 3. The H_2O_2 treatment removed 86% of organic matter from this soil.

In another series of experiments, the effect of the electrolyte concentration on adsorption was studied following the same procedure described above. Two soils with different properties, Freehold sandy loam (A horizon) and Boonton Union loam, were used. For each soil, three sets of 8 soil samples were prepared in 0.001 M NaNO_3 , 0.01 M NaNO_3 , and 0.1 M NaNO_3 . The initial Hg(II) concentrations for each set of samples were adjusted to cover a range of 1.0×10^{-7} to 1.1×10^{-4} M. The pH values of all samples for each soil were adjusted to the pH of the soil-0.01 M NaNO_3 suspension before shaking.

4.3.2 Desorption Experiments

Desorption study was conducted following adsorption for two soils, Freehold sandy loam (A horizon) and Boonton Union loam. Three different adsorbed Hg concentrations were used for each soil. At the end of 24-h adsorption, 3/4 of the supernatant of each sample was replaced by the same volume of 0.01 M NaNO_3 whose

pH had been adjusted to that of the samples. The samples were vortex mixed and then returned to the shaker to shake for an additional 24 h. Following the same procedure as for adsorption, the samples were centrifuged and the Hg concentrations analyzed. The desorption step was repeated four times. The concentration of Hg retained by the soil in the suspension after each desorption step was calculated according to the following equation:

$$q_i = q_{i-1} - (C_i - C_{i-1} / 4) / W \quad (4.2)$$

where q_i is the concentration of Hg remaining in the soil at the end of the i th desorption step ($\mu\text{mol g}^{-1}$); q_{i-1} is the concentration of Hg remaining in the soil at the end of the $(i-1)$ th desorption step ($\mu\text{mol g}^{-1}$); C_i is Hg concentration in the solution at the end of i th step ($\mu\text{mol L}^{-1}$); C_{i-1} is Hg concentration in the solution at the end of the $(i-1)$ th desorption step ($\mu\text{mol L}^{-1}$), and W is the solid concentration in the suspension (g L^{-1}).

Since both pH and soil properties can affect desorption, to further understand the effects of different soil components on Hg desorption, we conducted adsorption and desorption studies at fixed pH 6 for three soils of different properties, Penn silt loam, fill materials from Delaware River, and Rockaway stony loam, following the same procedure as described above. Two initial Hg concentrations, 2.5×10^{-5} and 5×10^{-5} M, were used.

4.4 Results and Discussion

4.4.1 Adsorption Isotherms

Adsorption isotherms for Hg on the fifteen soils were constructed by plotting the amount of Hg adsorbed versus the concentration of Hg remaining in the solution. All soils with an organic carbon content greater than 11.0 g kg^{-1} had an S-type isotherm (Figure 4.1a), whereas all soils with an organic carbon content less than 7.5 g kg^{-1} had an isotherm similar to the L-type isotherm classified by Giles *et al.* (1974a, b) (Figure 4.1b).

The S-type isotherm has rarely been observed for the adsorption of heavy metals. It has only been reported for Cu and Hg adsorption by soils (Sposito, 1989; Barrow and Cox, 1992). The slope of this type of isotherm initially increases with increasing solute concentration, then decreases as surface site coverage increases and eventually becomes zero when surface sites are filled. It is believed that this type of isotherm results from the complexation of metals by dissolved organic matter. As metal concentration exceeds the complexation capacity of dissolved organic matter, adsorption increases greatly (Sposito, 1989). We found that within the experimental Hg concentration range of this study, the shape of adsorption isotherms at the water-soil pH depended on both the amount of dissolved organic matter in the solution and the adsorption capacity of soil for Hg. Generally, in the solutions of soils which had an S-type isotherm, the amount of dissolved organic matter was greater ($\geq 4.0 \text{ mg C L}^{-1}$); whereas in the solutions of soils which had an L-type isotherm, the amount of dissolved organic matter was smaller ($\leq 3.9 \text{ mg C L}^{-1}$) (Table 4.1). This, however,

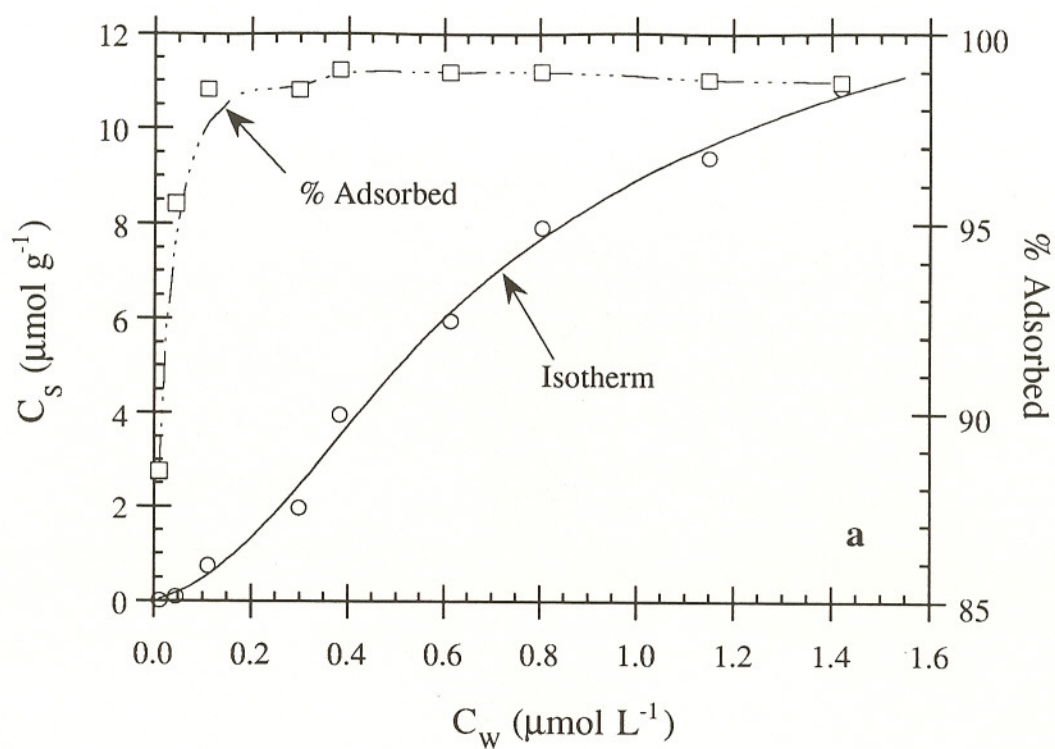


Figure 4.1a S-type adsorption isotherm of Hg(II) on Rockaway stony loam. Solid line represents the model-predicted isotherm (equation 4.21). Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃; T = 25 ± 2°C.

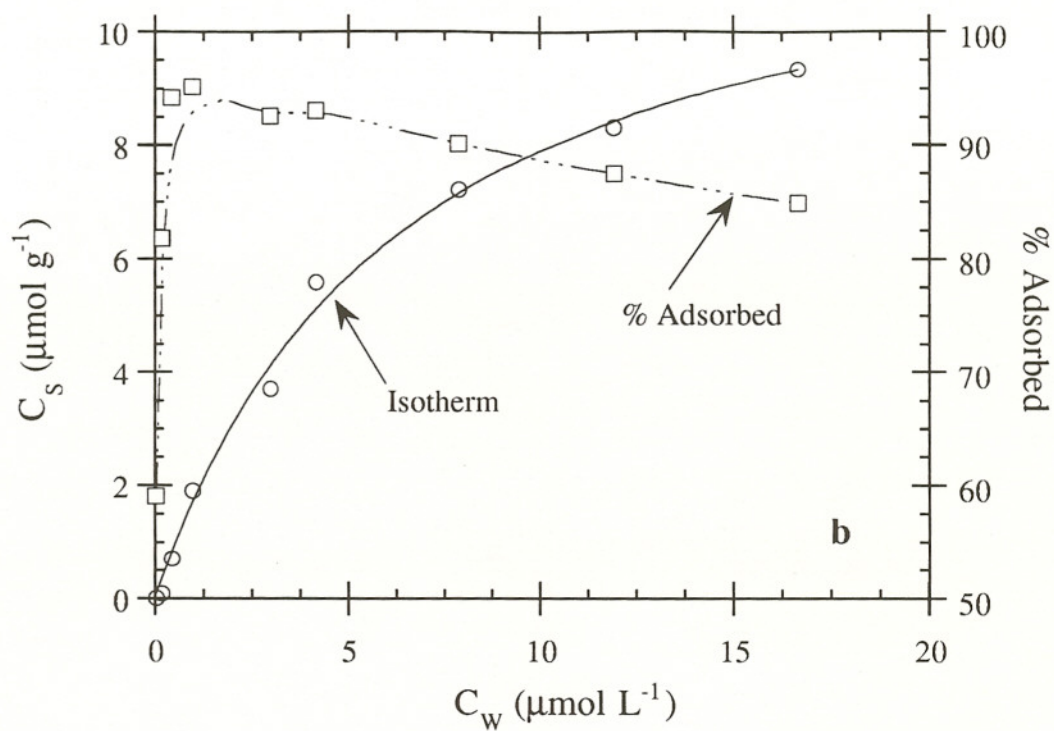


Figure 4.1b L-type adsorption isotherm of Hg(II) on fill material from Delaware River. Solid line represents the model-predicted isotherm (equation 4.22). Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃; T = 25 ± 2°C.

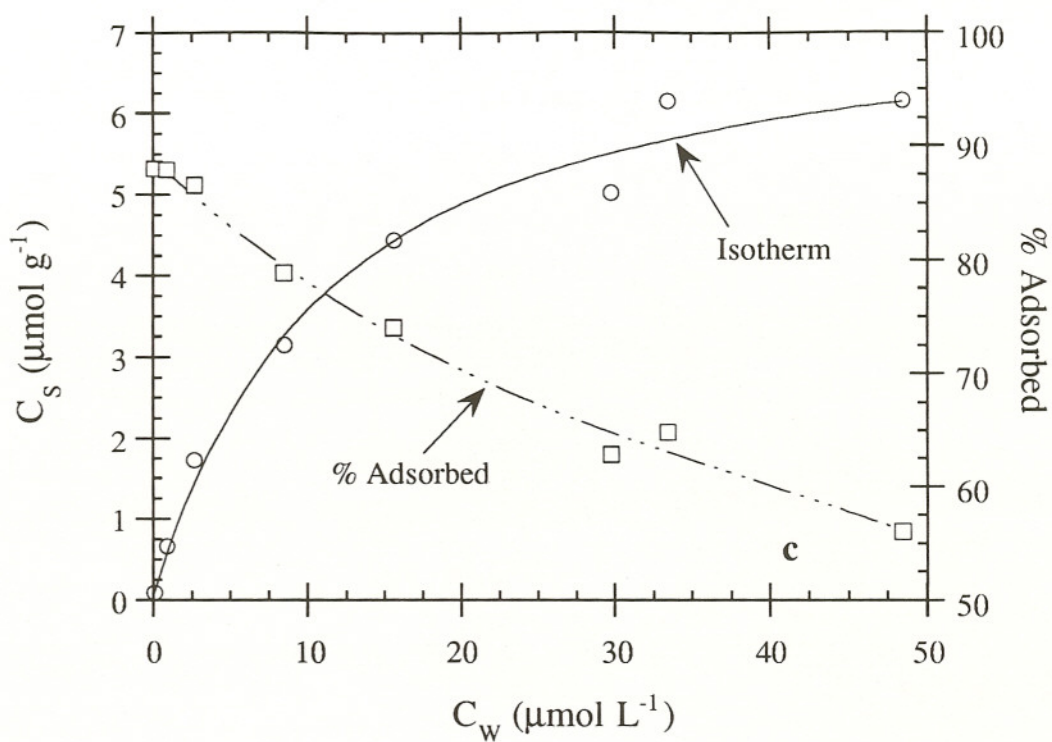


Figure 4.1c Adsorption isotherm of Hg(II) on Rockaway sandy loam from which organic matter was removed. Solid line represents the model-predicted isotherm (equation 4.22). Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃; T = 25 ± 2°C.

was not true for all soils. For example, the isotherm of Rockaway stony loam was S-shaped, but the concentration of dissolved organic matter in the solution of this soil was only 2.2 mg C L^{-1} . On the other hand, fill material from the Delaware River had an L-type isotherm, but the concentration of dissolved organic matter in its solution was 4.1 mg C L^{-1} . This probably resulted from the different adsorption capacity of these two soils for Hg (as shown later). Since dissolved organic matter has a strong adsorption affinity for Hg (Chapter 3; Yin *et al.*, 1996), it was expected that at low Hg concentrations, a large amount of Hg was complexed by dissolved organic matter in the solutions of both soils. As the Hg concentration increased, more Hg became available for adsorption by soil solids. This resulted in increased adsorption. When adsorption reached a critical value, the fractional adsorption (the amount of Hg adsorbed /the total added Hg) began to decrease, which resulted in a decrease in the slope of the isotherm. For Rockaway stony loam (Figure 4.1a), fractional adsorption increased with increasing added Hg until the concentration of the added Hg reached the midpoint ($8 \times 10^{-5} \text{ M}$) of the experimental Hg range, and then it slightly decreased. Therefore, this soil had an S-type isotherm. For fill material from the Delaware River (Figure 4.1b), on the other hand, Hg fractional adsorption increased only when the initial Hg concentration was less than $7.5 \times 10^{-6} \text{ M}$ because of its low adsorption capacity (as shown later). Further increases in the initial Hg concentration resulted in a decrease in the fractional adsorption. As a result, the L-shaped part of the isotherm whose slope decreased with increasing Hg concentration was predominant.

Table 4.1 Concentrations of dissolved organic carbon in soil suspensions.
Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

Soil No.	Soil Name	pH†	Concentration of Dissolved Organic Carbon (mg L ⁻¹)	Type of Isotherm
1	Sassafras sandy loam	6.06	2.2	L
2	Lakewood sand	5.01	3.6	L
3	Penn silt loam	5.17	3.9	L
4	Whippany silty clay loam	6.16	5.3	S
5	Washington loam	6.40	9.1	S
6	Freehold sandy loam (A horizon)	6.26	1.6	L
7	Freehold sandy loam (B horizon)	5.66	7.5	S
8	Rockaway stony loam	5.33	2.2	S
9	Fill materials from Delaware River	5.29	4.1	L
10	Downer loamy sand	4.90	3.5	L
11	Boonton Union loam	5.40	9.1	S
12	Dunellen sandy loam	5.78	4.0	S
13	Birdsboro silt loam	6.20	5.4	S
14	Hazen gravelly loam	6.45	7.0	S
15	Boonton Bergen loam	5.71	10.0	S

†Experimental pH values.

We further studied the effect of organic matter on the adsorption isotherm shape and the soil adsorption capacity by removal of organic matter from Rockaway stony loam as described previously. As shown in Figure 4.1c, when organic matter

was removed, the adsorption capacity of Rockaway stony loam significantly decreased. Because the removal of organic matter significantly decreased the number of binding sites of soil for Hg, we concluded that a large number of adsorption sites on soil come from organic matter. Hg fractional adsorption by this organic matter-removal soil decreased with increasing added Hg concentration within the entire experimental Hg concentration range. Consequently, adsorption took on a L-type isotherm.

4.4.2 Effect of Ionic Strength on Adsorption

Three concentrations of NaNO_3 , 0.001 M, 0.01 M, and 0.1 M, were used as the background electrolyte to evaluate the effect of ionic strength on Hg adsorption as described previously. If adsorption is mainly electrostatic, increases in the concentration of electrolyte would decrease adsorption. As shown in Figure 4.2a,b, adsorption in three different concentrations of NaNO_3 (0.001M, 0.01M and 0.1 M) for two soils were very similar. The variances of the amount of Hg adsorbed at different ionic strength was less than 9.5% for any initial Hg concentration, suggesting Hg adsorption by the soils was not predominated by electrostatic interaction. This was also suggested by the Hg speciation calculation. In the soil suspensions of this study, Hg could be present as soluble species Hg^{2+} , HgOH^+ , HgCl^+ , $\text{Hg}(\text{OH})_2$, HgCl_2 , and HgOHCl , or adsorbed by particles via electrostatic interaction of the positively charged species with negatively charged surface, or adsorbed via chemical reaction between Hg species and the surface functional groups. To evaluate the possibility that adsorption occurred by electrostatic interaction, we calculated Hg speciation by MINEQL⁺ (Schecher and McAvoy, 1991) with consideration of only soluble Hg species and the

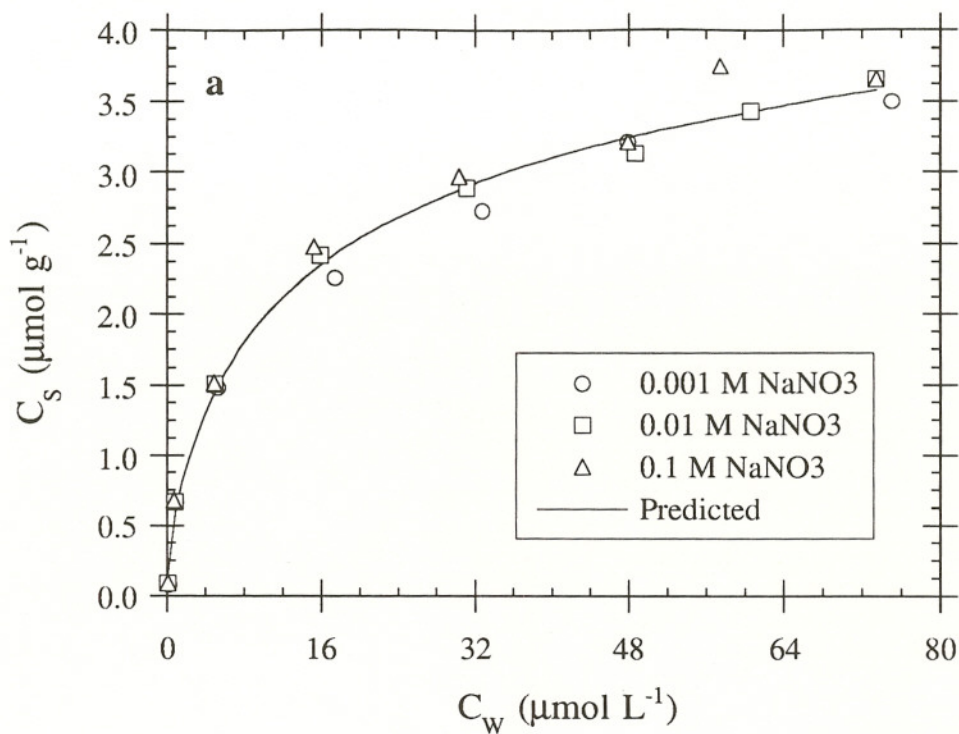


Figure 4.2a Comparison of adsorption isotherms of Hg on Freehold sandy loam (A horizon) in different concentrations of electrolyte. Solid line represents the model-predicted isotherm (equation 4.22) in 0.01 M NaNO₃. Soil:water = 0.4 g 40 mL⁻¹; T = 25 ± 2°C.

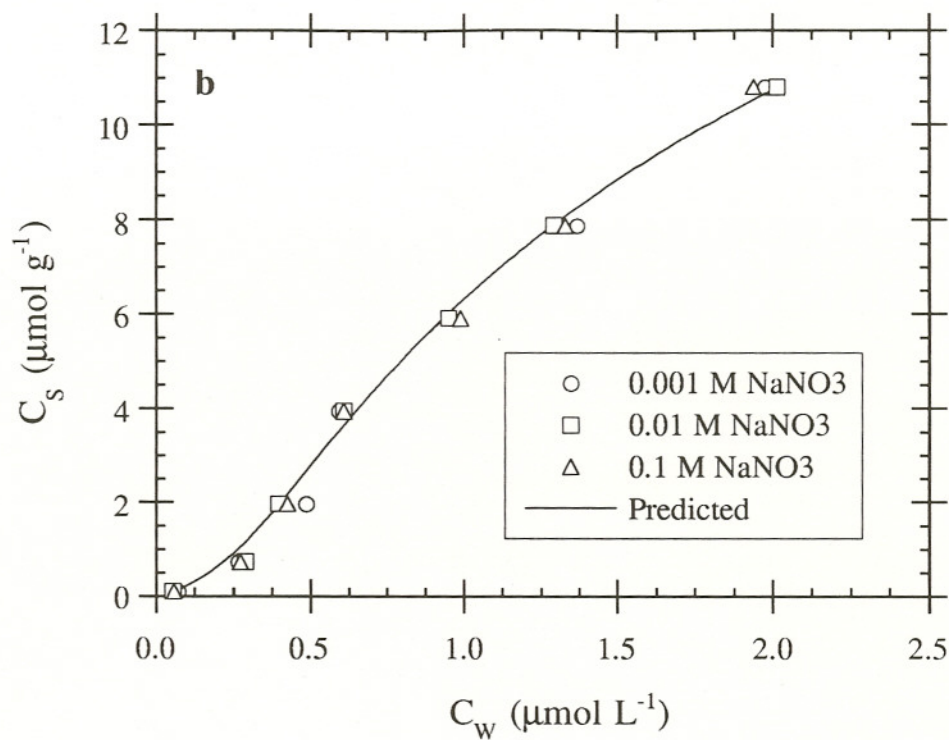


Figure 4.2b Comparison of adsorption isotherms of Hg on Boonton Union loam in different concentrations of electrolyte. Solid line represents the model-predicted isotherm (equation 4.21) in 0.01 M NaNO₃. Soil:water = 0.4 g 40 mL⁻¹; T = 25 ± 2°C.

surface species formed via electrostatic interactions which are expressed by equation 4.3 to 4.5.



The soil surface potential (which was approximated as Zeta potential) is less than 50 mv (Allen, unpublished data), the maximum stability constants ($\log K$) for reaction 4.3 to 4.5 were calculated by equation 4.6, which are 1.69, 0.85, and 0.85 respectively.

$$\Delta G = -nEF = -2.303RT \log K \quad (4.6)$$

where n is the charge of species, E is the surface potential which was taken as 50 mV, F is the Faraday constant, R is the gas constant. In the soil solutions of this study, Cl^- concentrations ranged from 1×10^{-6} to 1×10^{-5} M, and pH ranged from 4.9 to 6.5. The Hg species were calculated as a function of the Hg concentration with solution boundary conditions of pH = 4.9, $Cl^- = 1 \times 10^{-5}$ M and pH = 6.5, $Cl^- = 1 \times 10^{-6}$ M. Using the Davies equation, the thermodynamic constants used were corrected to 0.01 M $NaNO_3$ from those of Baes and Mesmer (1976). As shown in Figure 4.3, the surface species formed via electrostatic interaction for the entire initial Hg concentration range is less than 4%. If the surface potential value is less than 50 mV, the fraction of the electrostatically held surface species would be less. This further

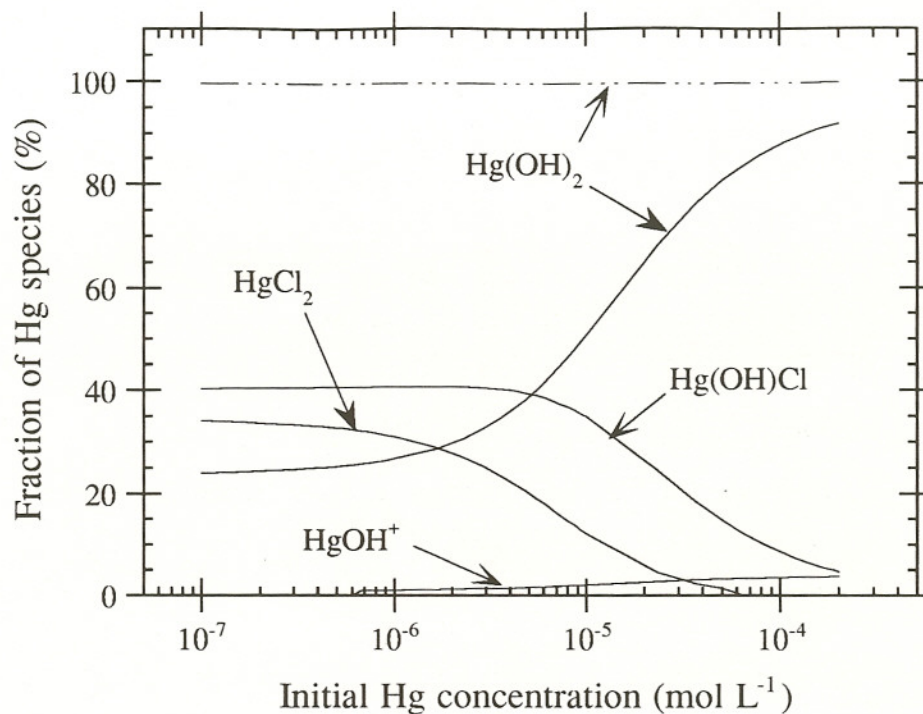


Figure 4.3 Mercury speciation as a function of initial Hg concentration. Solid lines: $\text{Cl}^- = 10^{-5} \text{ M}$, $\text{pH} = 5$; dashed line: $\text{Cl}^- = 10^{-6} \text{ M}$, $\text{pH} = 6.5$.

indicated that electrostatic interaction was not the major driving force responsible for Hg adsorption to soils. Under the currently available experimental results, however, we can not make definite conclusions on the exact nature of adsorption mechanisms.

4.4.3 Modeling Adsorption Isotherms

We first tried to describe adsorption isotherms using the most frequently used equations, the Langmuir equation and Freundlich equation. The non-linear forms of these two equations can be expressed by equation 4.7 and 4.8, respectively.

$$q = \frac{q_{\max} K C}{1 + K C} \quad (4.7)$$

$$q = K_f C^{1/n} \quad (4.8)$$

where q is the Hg adsorbed, $q_{\max}$ is maximum adsorption, K , K_f , and n are constants, and C is soluble Hg concentration. Linear transformation of these two equations has frequently been used to estimate the coefficients. However, the linear transformation tends to increase the variance of the observations at high concentrations for the Langmuir equation, and overweighs the values of low concentrations for the Freundlich equation (Barrow, 1978). In this study, we used a SYSTAT non-linear program (Wilkinson, 1988) to fit the experimental data according to equations 4.7 and 4.8. A Simplex least square minimization method was used in the calculation. As shown in Figures Appendix B.1-B.15, the Langmuir equation can fit all L-type isotherms well with a residual sum of squares (RSS) of < 0.94 (Table 4.2), whereas the Freundlich equation only can only well fit the L-type isotherm of Freehold sandy loam

(A horizon). Both of them poorly described S-type isotherms with RSS > 1.93 for the Langmuir equation and > 2.39 for the Freundlich equation.

Table 4.2 Langmuir and Freundlich constants for adsorption of Hg(II) on fifteen New Jersey soils. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

Soil No.	Langmuir Constants				Freundlich Constants			
	$q_{\max}$ μmol g ⁻¹	K L μmol ⁻¹	RSS μmol g ⁻¹	R^2	K_f L μmol ⁻¹	1/n	RSS μmol g ⁻¹	R^2
1	7.79	0.323	0.94	0.986	2.075	0.382	2.29	0.968
2	10.33	0.185	0.28	0.996	2.044	0.470	2.37	0.968
3	10.99	0.812	0.23	0.998	4.431	0.373	7.39	0.925
4	34.62	0.142	3.94	0.970	4.080	0.859	5.35	0.960
5	54.63	0.070	2.94	0.976	3.446	0.929	3.68	0.972
6	3.73	0.142	0.28	0.990	0.697	0.395	0.43	0.984
7	25.27	0.127	1.93	0.984	2.848	0.772	3.45	0.972
8	39.55	0.274	2.17	0.984	8.387	0.867	2.98	0.978
9	12.80	0.161	0.55	0.994	2.128	0.548	2.81	0.974
10	9.05	0.171	0.47	0.994	1.789	0.444	2.09	0.972
11	162.20	0.036	2.99	0.978	5.568	1.021	3.04	0.978
12	19.52	0.185	3.01	0.972	2.972	0.715	5.63	0.950
13	23.15	0.191	6.19	0.978	3.428	0.763	12.38	0.956
14	2410.90	0.001	3.14	0.976	2.139	1.133	2.39	0.982
15	217.47	0.018	13.88	0.950	3.569	1.064	13.40	0.954

†See Table 3.1 for soil identification.

In order to account for the curvature observed when the linear form of equation 4.7 was plotted as C/q against C , a modification of the Langmuir equation, the Gunary equation, was proposed (Gunary, 1970). The Gunary equation can be expressed as:

$$q = C / (K_1 + K_2 C + K_3 \sqrt{C}) \quad (4.9)$$

where K_1 , K_2 , and K_3 are constants. We used the Gurney equation to fit adsorption isotherms for all soils. As shown in Figures Appendix B.1-B.15, the fits were very good. The RSS values (Table 4.3) for L-type isotherms are close to those obtained by the Langmuir equation. However, the RSS values for S-type isotherms are much smaller than those obtained by either the Langmuir or Freundlich equations.

Table 4.3 Gurney constants for adsorption of Hg(II) on fifteen New Jersey soils. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

Soil No.†	K_1 g L ⁻¹	K_2 g μmol ⁻¹	K_3 g μmol ⁻¹	RSS μmol g ⁻¹	R ²
1	0.196	0.096	0.193	0.56	0.992
2	0.480	0.091	0.034	0.27	0.996
3	0.117	0.093	-0.007	0.23	0.997
4	0.535	0.222	-0.524	1.63	0.988
5	0.886	0.305	-0.866	0.19	0.999
6	0.534	0.175	0.841	0.06	0.998
7	0.726	0.172	-0.482	0.91	0.994
8	0.241	0.211	-0.341	0.87	0.995
9	0.578	0.092	-0.077	0.52	0.995
10	0.477	0.093	0.121	0.41	0.995
11	0.449	0.250	-0.538	0.85	0.993
12	0.604	0.173	-0.418	1.55	0.986
13	0.520	0.171	-0.409	2.03	0.993
14	1.816	0.457	-1.627	0.16	0.998
15	1.072	0.422	-1.193	5.17	0.982

†See Table 3.1 for soil identification.

The Gunary equation is empirical. It does not allow calculation of soil adsorption capacity. In this study, we developed a model in which the reactions of soluble inorganic Hg(II) with both dissolved organic matter and soil solids were considered to describe the adsorption isotherm. The obtained parameters were used to evaluate soil adsorption capacity and binding strength for Hg.

If 1:1 metal-ligand complexation is considered, the reaction between aqueous inorganic Hg and dissolved organic matter can be expressed by the following equations in which charges on chemical species are omitted for simplicity:



$$K_{OM} = \frac{[HgL]}{[Hg][L]} = \frac{[HgL]}{[Hg](C_L - [HgL])} \quad (4.11)$$

$$[HgL] = \frac{K_{OM}[Hg]C_L}{1 + K_{OM}[Hg]} = C_W - [Hg] \quad (4.12)$$

where $[HgL]$ is the concentration of aqueous organically complexed Hg ($\mu\text{mol L}^{-1}$); $[Hg]$ is the concentration of aqueous inorganic Hg ($\mu\text{mol L}^{-1}$); C_W is the total aqueous mercury concentration ($\mu\text{mol L}^{-1}$); $[L]$ is the concentration of free ligand in the solution ($\mu\text{mol L}^{-1}$), C_L is the total ligand concentration in the solution ($\mu\text{mol L}^{-1}$), K_{OM} is the overall stability constant ($\text{L } \mu\text{mol}^{-1}$).

Soil surface sites can be considered as consisting of three types of differently charged sites, $\equiv\text{SOH}_2^+$, $\equiv\text{SOH}$, and $\equiv\text{SO}^-$. At the experimental pH, $\equiv\text{SO}^-$ is

predominant (Allen *et al.*, 1994). The reaction between Hg and $\equiv\text{SO}^-$ can be expressed as:



$$K_S = \frac{[\equiv\text{SOHg}]}{[\text{Hg}][\equiv\text{SO}^-]} \quad (4.14)$$

where K_S is the stability constant ($\text{L } \mu\text{mol}^{-1}$), $[\equiv\text{SO}^-]$ is the density of free surface negative sites ($\mu\text{mol g}^{-1}$), and $[\equiv\text{SOHg}]$ is the concentration of mercury adsorbed by soil ($\mu\text{mol g}^{-1}$), which can be calculated by:

$$[\equiv\text{SOHg}] = (C_T - C_W) / W \quad (4.15)$$

where C_T is the added Hg concentration ($\mu\text{mol L}^{-1}$), and W is the soil concentration in the suspension (g L^{-1}). The density of free $\equiv\text{SO}^-$ can be calculated by:

$$[\equiv\text{SO}^-] = (N_t - [\equiv\text{SOHg}])\alpha_- \quad (4.16)$$

where N_t is Hg adsorption capacity of soil ($\mu\text{mol g}^{-1}$); α_- is the fraction of $\equiv\text{SO}^-$ among the total protonated and deprotonated sites at the experimental pH, which was determined by acid-base titration (Allen *et al.*, 1994).

We define $[\equiv\text{SOHg}] = C_S$, and equation 4.14 is then rewritten as:

$$K_S = \frac{C_S}{[\text{Hg}][\equiv\text{SO}^-]} = \frac{C_S}{[\text{Hg}](N_t - C_S)\alpha_-} \quad (4.17)$$

Equation 4.17 can be rearranged to give:

$$C_S = \frac{K_S [Hg] N_t \alpha_-}{1 + K_S [Hg] \alpha_-} \quad (4.18)$$

From equation 4.12, we have

$$K_{OM} [Hg]^2 + (K_{OM} C_L - K_{OM} C_W + 1) [Hg] - C_W = 0 \quad (4.19)$$

which can be solved for the concentration of aqueous inorganic Hg:

$$[Hg] = \frac{K_{OM} C_W - K_{OM} C_L - 1 + ((K_{OM} C_L + 1 - K_{OM} C_W)^2 + 4 K_{OM} C_W)^{1/2}}{2 K_{OM}} \quad (4.20)$$

Finally we solve for the concentration of sorbed Hg by substituting equation 4.20 to 4.18:

$$C_S = \frac{K_S N_t \alpha_- (K_{OM} C_W - K_{OM} C_L - 1 + ((K_{OM} C_L + 1 - K_{OM} C_W)^2 + 4 K_{OM} C_W)^{1/2})}{2 K_{OM} + K_S \alpha_- (K_{OM} C_W - K_{OM} C_L - 1 + ((K_{OM} C_L + 1 - K_{OM} C_W)^2 + 4 K_{OM} C_W)^{1/2})} \quad (4.21)$$

When $[Hg] \cong C_W$, equation 4.21 is approximated as:

$$C_S = \frac{K_S C_W N_t \alpha_-}{1 + K_S C_W \alpha_-} \quad (4.22)$$

We fitted the L-type and S-type isotherms with equations 4.22 and 4.21, respectively, using the same non-linear regression method described previously. The results are shown in Figures Appendix B.1-B.15 and Table 4.4. It can be seen that the fits are very good. The RSS values are close to those obtained by the Langmuir and Gunary equations for the L-type isotherms. For the S-type isotherms, the RSS values obtained by the model are generally smaller than those obtained by any other equation.

4.4.4 Correlations of Adsorption Capacity and Binding Strength with Soil Properties

The adsorption capacities of the fifteen New Jersey soils for Hg ranged from $3.73 \mu\text{mol g}^{-1}$ to $22.8 \mu\text{mol g}^{-1}$. We analyzed the correlation between adsorption capacity and soil properties, including organic carbon (SOC), Al, Mn, Fe, surface area (SA), and CEC, by a multi-variant regression. The relative importance of these parameters was evaluated according to the standard regression coefficient ($b_{si} = b_i x_i / y_i$, where b_i is the coefficient of the i th variable, x_i is the standard deviation of the i th variable, and y_i is the standard deviation of the dependent variable) (Rosner, 1990). The greater the b_{si} , the more important the parameter. Based on the b_{si} values, the relative importance of these parameters in contributing soil adsorption capacity was SOC ($b_{si} = 0.72$) > CEC ($b_{si} = 0.45$) > SA ($b_{si} = 0.08$) > Mn ($b_{si} = 0.02$) > Fe ($b_{si} = -0.01$) > Al ($b_{si} = -0.11$). Both SOC and SA had significant correlation with soil adsorption capacity. Compared with SA (significant at < 0.05), SOC is more important (significant at < 0.01).

By plotting the adsorption capacity versus the soil organic carbon content, we noticed that the adsorption capacity was highly correlated with SOC except for three data points whose SOC contents were the highest (Figure 4.4). These three data points correspond to soil Nos. 8, 11 and 15. Because of the high adsorption capacities of these three soils, within the experimental initial Hg concentration range we could only observe the initial and middle parts of the S-isotherms. As a result, the estimated adsorption capacity of these three soils may not be accurate (Harter, 1984). When only the remaining 12 soils were considered, a regression coefficient (R^2) of 0.92 was obtained between the adsorption capacity and the soil organic C content. The standard deviation of the predicted value of the adsorption capacity from experimental data was $1.15 \mu\text{mol g}^{-1}$.

We compared the K_S values among the soils that are given in Table 4.4 to evaluate those factors responsible for the difference in the relative binding strength. The log K_S values of soils with a high proportion of sand (including soil Nos. 2, 6, 9, 10) were small ($\log K_S < 5.37$). We determined the relative importance of soil parameters for Hg binding by a multi-variant regression. The sequence obtained for relative importance was SOC ($b_{si} = 0.68$) > SA ($b_{si} = 0.39$) $\cong$ Al ($b_{si} = 0.37$) > Fe ($b_{si} = 0.27$) > CEC ($b_{si} = -0.38$) > Mn ($b_{si} = -0.57$). The correlation of K_S with soil properties that we obtained is only approximate because the K_S values were determined by model fitting which involved four adjustable parameters. More detailed research needs to be conducted to understand the binding strength of Hg on different surfaces.

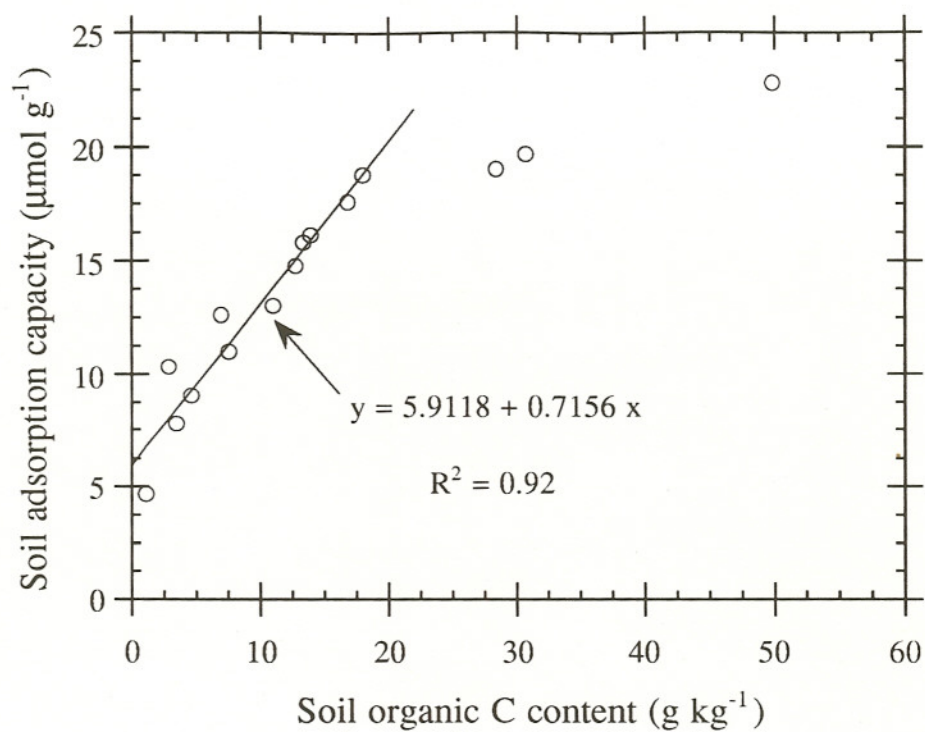


Figure 4.4 Correlation between soil adsorption capacity for Hg and the soil organic carbon content. Regression did not include the three soils having the greatest organic carbon content.

Table 4.4 Model fitting parameters for adsorption of Hg(II) on fifteen New Jersey soils with equations 4.21 and 4.22. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

Soil No.†	$\alpha_{\ddagger}$	Log K_S L mol ⁻¹	N_t μmol g ⁻¹	Log K_{OM} L mol ⁻¹	C_L μmol L ⁻¹	Residual Sum of Squares μmol g ⁻¹	R ²
1	0.975	5.52	7.79			0.94	0.990
2	0.875	5.33	10.33			0.27	0.996
3	0.865	5.97	10.99			0.23	0.998
4	0.990	5.54	17.09	8.24	0.33	0.16	0.998
5	0.990	5.73	17.59	7.00	0.72	0.16	0.998
6	0.985	5.16	3.73			0.28	0.992
7	0.975	5.57	16.11	6.64	0.76	0.90	0.994
8	0.930	6.03	19.03	7.51	0.18	0.63	0.996
9	0.900	5.25	12.80			0.55	0.995
10	0.730	5.37	9.05			0.47	0.995
11	0.975	5.71	22.80	7.78	0.23	0.20	0.998
12	0.975	5.75	13.03	5.69	0.49	0.38	0.996
13	0.980	5.80	14.78	7.28	0.46	0.43	0.998
14	0.990	5.69	18.46	6.76	1.56	0.30	0.998
15	0.985	5.80	19.69	7.17	0.89	1.97	0.995

†See Table 3.1 for soil identification.

‡calculated based on the acid-base titration data of Allen *et al.* (1994).

4.4.5 Desorption

The above results on Hg(II) adsorption suggest that soil organic matter has strong affinity for Hg. Clay content has also been reported to be important to metal persistence in soil (Sparks *et al.*, 1980; Dang *et al.*, 1994). To understand the release behavior of Hg from soil, we chose five soils with organic matter ranging from 1.2 to

49.9 g kg⁻¹ and silt plus clay content from 80 to 750 g kg⁻¹ to conduct desorption experiments as described previously.

Desorption isotherms of Hg for two soils with the lowest and the highest organic matter content, Freehold sandy loam (A horizon) and Boonton Union loam, are shown in Figures 4.5a,b. Adsorption/desorption hysteresis was evident for both soils. The hysteresis for Boonton Union loam was more significant than was that for Freehold sandy loam (A horizon). After 4 steps of desorption, more than 11% of the adsorbed Hg was desorbed from Freehold sandy loam (A horizon), whereas less than 2% of the adsorbed Hg was desorbed from Boonton Union loam. For Freehold sandy loam (A horizon), as the initial Hg concentration in the soil increased from 2.42 to 3.66 $\mu\text{mol g}^{-1}$, desorption increased from 11.9% to 21.2%, implying a large amount of Hg being bound by low energy sites at a higher Hg level. For Boonton Union loam, as the initial Hg concentration in the soil increased from 3.94 to 10.80 $\mu\text{mol g}^{-1}$, desorption decreased from 1.6% to 0.9%. This suggested that at the experimental adsorption level, most of the Hg was bound by high energy sites. Consequently, although the absolute desorption increased (from 0.06 $\mu\text{mol g}^{-1}$ to 0.09 $\mu\text{mol g}^{-1}$) with the increase of the concentration of adsorbed Hg, the fractional desorption decreased.

Since the initial Hg concentrations on Boonton Union loam were higher than those on Freehold sandy loam (A horizon), whereas the fractional desorption was lower, it is obvious that Boonton Union loam had more high energy sites than did Freehold sandy loam (A horizon). These high energy sites could be the sites which form very stable surface complexes with Hg, or they could be the micropores which trapped Hg and require high activation energy to release Hg. Comparing the

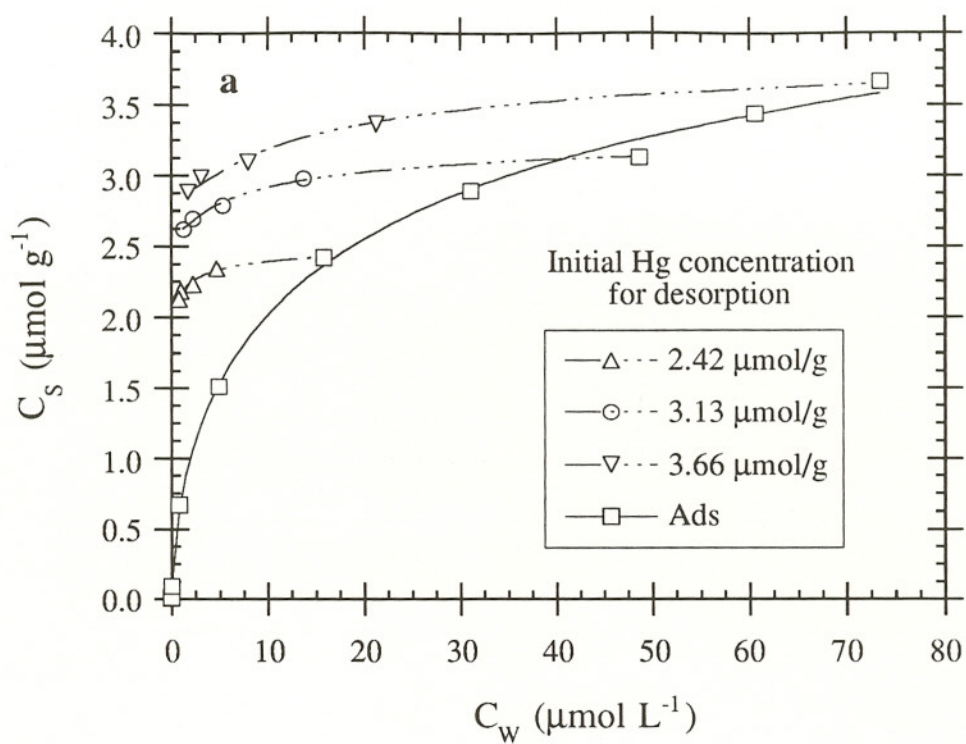


Figure 4.5a Desorption isotherms of Hg on Freehold sandy loam (A horizon). Solid line represents adsorption; dashed lines represent desorption.

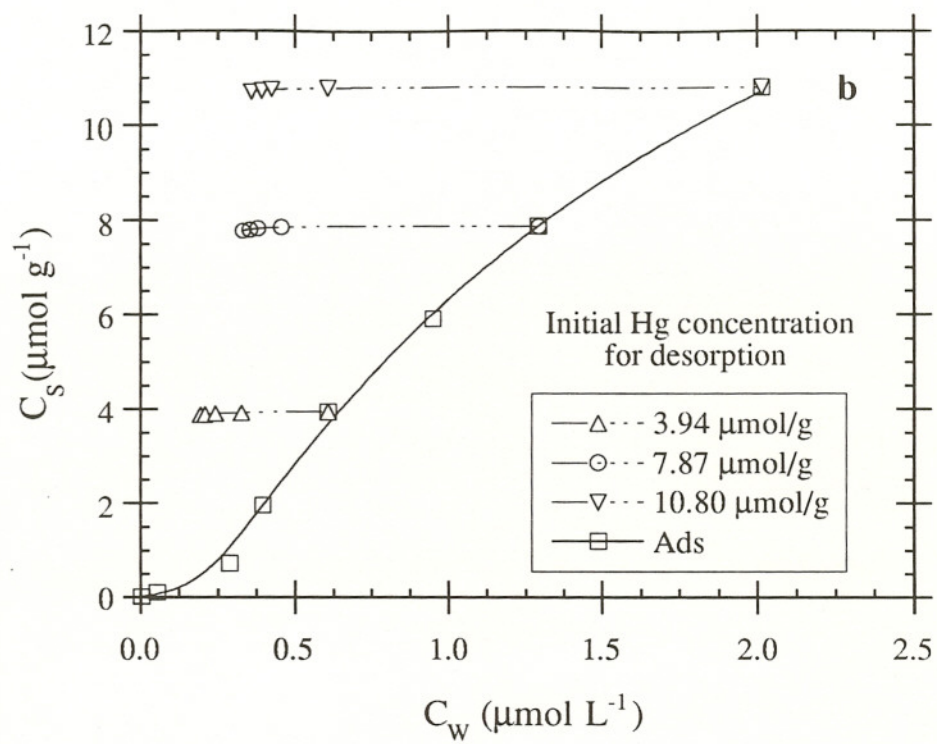


Figure 4.5b Desorption isotherms of Hg on Boonton Union loam. Solid line represents adsorption; dashed lines represent desorption.

composition of Freehold sandy loam (A horizon) with that of Boonton Union loam, the latter soil contains much more silt-clay (510 g kg^{-1}) and organic carbon (49.9 g kg^{-1}) and much less sand (490 g kg^{-1}) than the former soil does (silt-clay: 80 g kg^{-1} ; organic C: 1.2 g kg^{-1} ; sand: 920 g kg^{-1}). The high energy sites are therefore mainly from organic matter and/or silt and clay.

We further investigated the contribution of soil components to the adsorption/desorption hysteresis. Three soils with quite different particle size distribution and organic matter content -- Penn silt loam, Rockaway stony loam, and fill materials from Delaware River -- were employed. The experiments were conducted at fixed pH 6 as described previously. Penn silt loam had much higher silt-clay content (750 g kg^{-1}) and similar organic matter content (7.5 g kg^{-1}) comparing with fill materials from the Delaware River (silt-clay: 150 g kg^{-1} ; organic matter: 7.0 g kg^{-1}). If silt and clay are important to the observed adsorption/desorption hysteresis, the fractional desorption of Hg from Penn silt loam should be much smaller than that from fill materials from the Delaware River. As shown in Figure 4.6, however, the fractional Hg desorption from Penn silt loam was even greater than that from fill materials from the Delaware River for similar initial Hg concentrations on two soils, $2.28 \text{ vs. } 2.23 \text{ } \mu\text{mol g}^{-1}$ and $4.18 \text{ vs. } 4.17 \text{ } \mu\text{mol g}^{-1}$.

Compared with Penn silt loam and fill materials from the Delaware River, Rockaway stony loam has intermediate silt-clay content (460 g kg^{-1}) but much greater organic matter content (28.4 g kg^{-1}). The fractional desorption of Hg from Rockaway stony loam was smaller than those from other two soils (Figure 4.6), even at higher

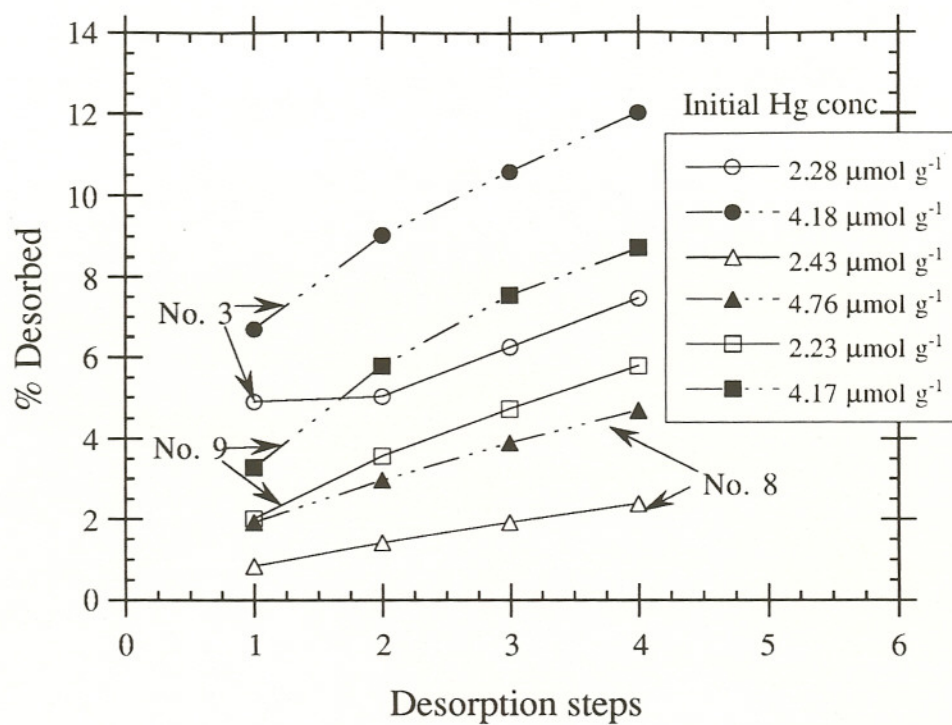


Figure 4.6 Comparison of Hg desorption from three soils with different properties, Penn silt loam, fill materials from Delaware River, and Rockaway stony loam.

initial concentrations (2.43 vs. 2.28 and 2.23 $\mu\text{mol g}^{-1}$ and 4.76 vs. 4.18 and 4.17 $\mu\text{mol g}^{-1}$).

All of the above results suggest that organic matter was the most important component responsible for the observed adsorption/desorption hysteresis. Although we are unable to make definite conclusions on the mechanisms of the adsorption/desorption hysteresis based on the available results, it is likely that restricted diffusion of Hg through organic matter was the major factor responsible for the observed hysteresis. A similar mechanism has been proposed to explain the persistence of organic compounds in the environment (Nkedi-Kizza et al., 1989; Bouchard et al., 1988). In addition, the binding of Hg to the S-containing (-S) groups on organic matter might also contribute to the adsorption/desorption hysteresis because the binding of -S with Hg is very strong (Reimers and Krenkel, 1974).

4.5 Summary and Conclusions

The shape of adsorption isotherms of Hg largely depended on the soil organic matter content. Within the experimental initial Hg concentration range, which covered three orders of magnitude (1.0×10^{-7} M to 1.1×10^{-4} M), all soils with organic carbon content greater than 11.0 g kg^{-1} had an S-type isotherm, whereas all soils with organic carbon content less than 7.4 g kg^{-1} had an L-type isotherm. Organic matter affected the adsorption isotherm by affecting the amount of Hg complexed by dissolved organic matter and affecting the adsorption capacity of soil for Hg. The S-type isotherm can be described by a model developed in this study which considered the interaction of Hg(II) with both dissolved organic matter and soil solids. The

adsorption capacity of soil for Hg obtained via model fitting was correlated with the organic matter content ($R^2 = 0.92$).

Adsorption of Hg(II) was not affected by the concentration of background electrolyte NaNO₃, suggesting that the adsorption was not dominated by electrostatic interaction. Mercury(II) speciation calculations also indicated that <4% of the total Hg could be adsorbed via electrostatic interaction.

Adsorption and desorption isotherms did not follow the same track. Organic matter was found to be the most important soil component responsible for the observed adsorption/desorption hysteresis. The restricted diffusion of Hg through organic matter was probably the major factor responsible for the hysteresis.

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Chapter 5

KINETICS OF MERCURY(II) ADSORPTION AND DESORPTION ON SOILS

5.1 Abstract

Adsorption and desorption kinetics of Hg(II) at pH 6 were investigated using a stirred-flow reactor to discern the mechanisms controlling the retention and release reaction rates of Hg on soil. Adsorption was very fast at the beginning for all soils. After 2 min, the Hg adsorbed ranged from 96 to 180 $\mu\text{g g}^{-1}$ for an influent concentration of 8 mg L^{-1} , and accounted for 4 to 38% of the total Hg adsorbed within 5 h. As the soil organic matter and silt and clay contents increased, so did adsorption of Hg and the time required for attainment of equilibrium. Mercury desorption was characterized by a fast phase followed by a slow phase. Not all adsorbed Hg was readily released. Organic matter was found to be the major component responsible for Hg persistence in soil. Lower initial Hg concentrations in soil resulted in higher fractions that were resistant to desorption, implying that Hg preferentially bound to high energy sites. Apparent adsorption and desorption rate coefficients were determined using a one-site kinetic model. Both rate coefficients were inversely correlated with the soil organic C content.

5.2 Introduction

Equilibrium reactions between Hg(II) and soils have been extensively studied (Chapter 3 and 4; Yin *et al.*, 1996a, b; Schuster, 1991; Barrow and Cox, 1992). Little, however, has appeared in the literature concerning the kinetics of these reactions. Due to the mobility of soil solution, the retention and release reactions of soluble contaminants with soil, in most cases, are time-dependent rather than instantaneous equilibrium processes. A knowledge of the reaction rates is therefore necessary in order to predict the transport and fate of contaminants in soil and provide cost-effective soil remediation strategies.

The reactions of contaminants with soil involve both chemical reaction and diffusion processes. Diffusion has often been reported to be the rate limiting step (Sparks, 1989). Both penetration into the mineral lattice (Kou, 1986; White and Yee, 1986; Bruemmer *et al.*, 1988) and diffusion through intraparticle pores (Avotins, 1975, Sparks *et al.*, 1980) have been suggested to be responsible for the slow reactions of metals with soils or soil components. These diffusion processes were often considered as the cause of the observed adsorption/desorption hysteresis which increases with time of aging (Ainsworth *et al.*, 1994). Some researchers suggested that hysteresis resulted from the binding of metals to different sites. Di Toro *et al.* (1986) modeled the adsorption/desorption of Co and Ni on montmorillonite and quartz by assuming the adsorbed chemical to be the sum of a reversibly sorbed component and a resistant component. Amacher *et al.* (1988, 1990) proposed a multi-reaction model to describe the reactions of several metals with soils. They assumed that adsorption/desorption processes involved three concurrent reactions with three different kinds of sites on

soils, i.e., a rapid and reversible reaction, a slow and reversible reaction, and an irreversible reaction.

In most cases, kinetic information has been obtained using either batch or miscible displacement techniques. Both methods suffer from pronounced diffusion effects (Ogwada and Sparks, 1985).

The purpose of this study was to examine the rates of Hg retention to and release from soils and to understand the mechanisms controlling the reaction rates. In this study, we used a stirred-flow method to perform experiments. The soil suspension in the reaction chamber was well mixed (Seyfried *et al*, 1989) and diffusion was significantly reduced (Amacher, 1991). The desorbed solute was continuously removed from the reactor, the further release of Hg was therefore not prohibited by the soluble Hg as was observed in batch experiments (Martin and Sparks, 1983). We investigated Hg adsorption/desorption kinetics on four soils with different properties. We also removed organic matter from soils to evaluate the importance of soil components and porosity in determining the reaction rates. Apparent Hg adsorption and desorption rate coefficients were determined using a one-site kinetic model.

5.3 Materials and Methods

5.3.1 Kinetic Experiments

Four soils, Freehold sandy loam (A horizon), Sassafras sandy loam, Dunellen sandy loam, and Rockaway stony loam, listed in Tables 3.1-3.3 were used to perform studies. The stirred-flow reaction chamber (Figure 5.1) used was a modification of

that developed by Carski and Sparks (1985). It was made of Plexiglas and consisted of two units, a reaction cell (6.7 cm^3) with an inlet side port near the bottom, and a cover with an outlet port on the top. The reaction cell was thread sealed by the cover. A 25-cm diameter, $0.45\text{-}\mu\text{m}$ pore size Nuclepore membrane filter (Costar, Cambridge, MA) was fitted just below the outlet port of the cover to retain the soil in the chamber. Both influent and effluent were transported by 0.89 mm i.d. Teflon tubing. For adsorption studies, 0.3 g soil samples and a Teflon-coated magnetic stirrer were placed into the reaction cell. The soil was wetted with 0.5 mL of 0.01 M NaNO_3 and allowed to hydrate for 1 hour. The reaction cell was then filled with 8 mg L^{-1} or 4 mg L^{-1} Hg influent (prepared in 0.01 M NaNO_3 at pH 6) and sealed with the cover. The same influent solution was then pumped into the chamber using an Ismatec pump (Cole Parmer, No. 7332) at a rate of 1 mL min^{-1} , and the effluent was collected with an automatic fraction collector after the first 2 minutes and then at 5-min intervals. Hg concentrations in the effluent samples were then determined by a cold vapor Hg analyzer (Perkin Elmer MHS 10) coupled with an atomic absorption spectrophotometer (Perkin Elmer Zeeman model 5000). The adsorption experiment was continued until equilibrium, which was judged by equivalence of influent and effluent concentrations, was achieved. Following adsorption, desorption was initialized by passing 0.01 M NaNO_3 (pH = 6) through the chamber.

To account for the dilution effect and the amount of Hg adsorbed by the reaction chamber, we measured blank curves for adsorption and desorption without soil in the chamber following the same procedure as described above. 23% of the input Hg was initially adsorbed by the reactor for an influent Hg concentration of 8 mg L^{-1} , and 38% for an influent concentration of 4 mg L^{-1} . The reactor was saturated in

30 minutes and 60 minutes for an influent Hg concentration of 8 mg L^{-1} and 4 mg L^{-1} , respectively. Duplicate experiments were run and the variance of effluent concentrations at each time point was less than 6%.

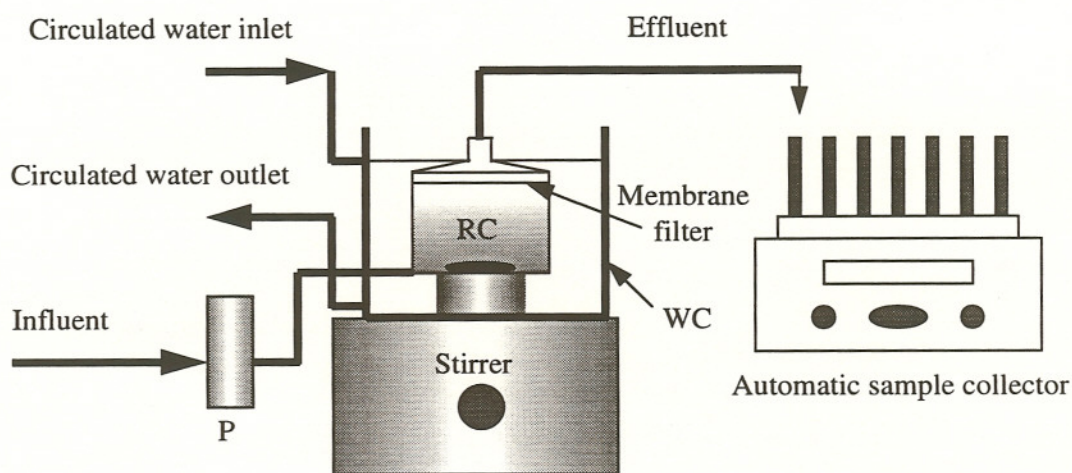


Figure 5.1 Schematic of kinetic experimental setup. RC: Reaction chamber; WC: water circulator; P: Pump.

The flow rate was monitored during the entire experiment, and the change of the flow rate was less than 5%. A magnetic stirrer was used to ensure adequate mixing in the reaction chamber, and the stirring speed was maintained at a minimum to reduce abrasion of the soil. After each run either with or without soil present, the transport tubing was washed by passing 15% HNO_3 followed by distilled deionized water, and the reaction chamber was cleaned by soaking in 15% HNO_3 overnight followed by washing with distilled deionized water.

5.3.2 Data Analysis

The amount of Hg adsorbed or released from soil can be calculated from the difference in solution concentrations with and without soil in the reaction chamber (Schnabel and Fitting, 1988; Sparks, 1989). The adsorbed or released quantity is the sum of the concentration differences in both effluents and the solutions in the chamber with and without soil. For adsorption, it can be expressed as:

$$q_a(t_i) = \frac{\sum[(\bar{C}_{ib} - \bar{C}_{is}) J \Delta t_i / V] + [C_b(t_i) - C_s(t_i)]}{W} \quad (5.1)$$

in which $q_a(t_i)$ is the cumulative adsorption at time t_i , $\mu\text{g g}^{-1}$; J is flow rate; L min^{-1} ; Δt_i is sampling time interval, min; $\bar{C}_i$ is the effluent concentration for the i th sampling period, $\mu\text{g L}^{-1}$; $C(t_i)$ is the concentration in the chamber at time t_i , $\mu\text{g L}^{-1}$; V is the volume of the reaction chamber, L; and W is the soil concentration in the chamber, g L^{-1} . Subscripts s and b refer to the cases with and without soil in the chamber, respectively.

The quantity desorbed is given by:

$$q_d(t_i) = \frac{\sum[(\bar{C}_{is} - \bar{C}_{ib}) J \Delta t_i / V] + [C_s(t_i) - C_b(t_i)]}{W} \quad (5.2)$$

where $q_d(t_i)$ is the cumulative desorption at time t_i , $\mu\text{g g}^{-1}$.

For equations 5.1 and 5.2, effluent Hg concentrations can be determined directly. The concentration in the chamber at the end of a specific sampling period,

however, needs to be estimated. This was approximated by averaging the effluent concentrations for that time period and the succeeding one.

5.4 Results and Discussion

5.4.1 Adsorption Kinetics

Before running complete adsorption and desorption kinetic experiments, we conducted a preliminary study following the method of Bar-Tal *et al.* (1990) to ascertain whether the reactions of Hg with soil were instantaneous or kinetically controlled. The assumption of this method is that if a non-equilibrium condition exists in the reaction chamber, stopping the flow of adsorptive for a sufficient time period before equilibrium is established should result in a noticeable drop in effluent concentration when flow is restarted. If the reaction is instantaneous, the plot of effluent concentrations versus time should be continuous. As shown in Figure 5.2, a sharp drop in effluent concentration for Hg adsorption on Freehold sandy loam (A horizon) was observed after stopping the flow for 30 min. This indicated that the reaction of Hg with soil was time dependent, rather than instantaneous.

Kinetics of Hg adsorption on four soils at an influent concentration of 8 mg L^{-1} are shown in Figure 5.3. Adsorption was initially very fast. At the end of the first 2 min, the adsorbed Hg was $96 \text{ } \mu\text{g g}^{-1}$ on Freehold sandy loam (A horizon), $153 \text{ } \mu\text{g g}^{-1}$ on Sassafras sandy loam, $180 \text{ } \mu\text{g g}^{-1}$ on Dunellen sandy loam, and $176 \text{ } \mu\text{g g}^{-1}$ on Rockaway stony loam, which respectively accounted for 38%, 12%, 5%, and 4% of the total Hg adsorbed by these soils within 5 h. The time required to reach equilibrium

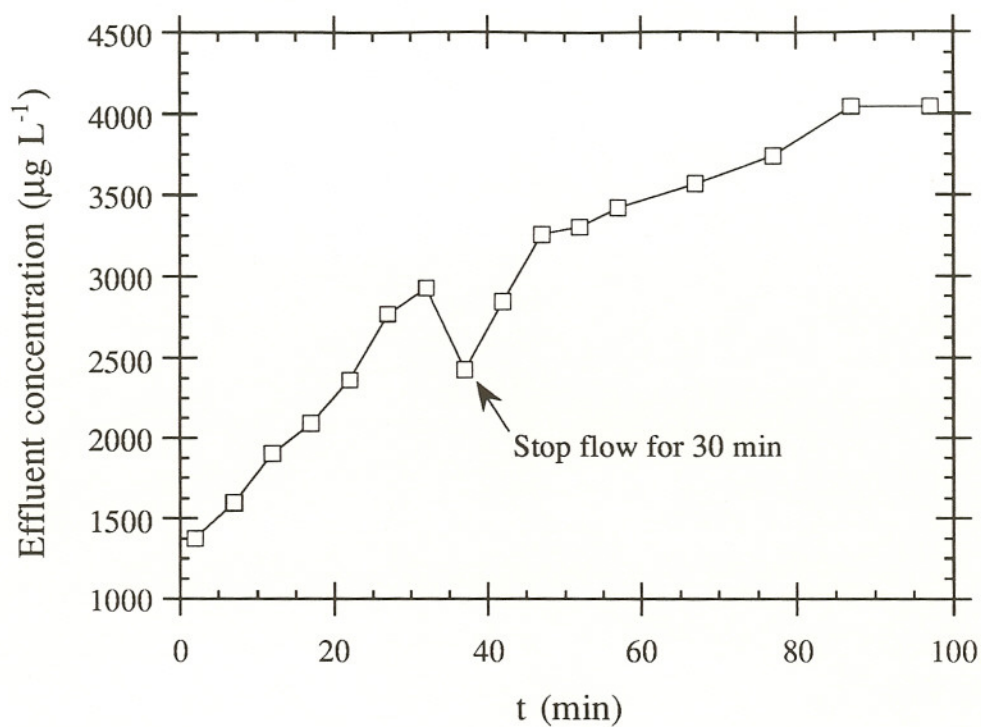


Figure 5.2 Effect of stopping flow on the effluent concentration for Hg(II) adsorption on Freehold sandy loam (A horizon) at an influent concentration of 4 mg L^{-1} .

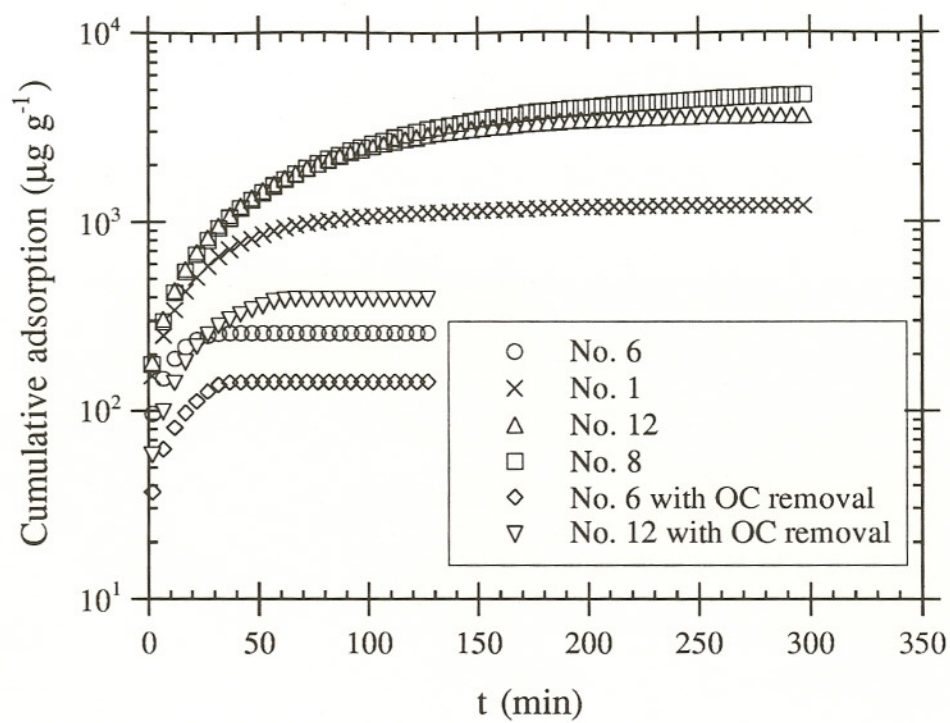


Figure 5.3 Kinetics of Hg adsorption on soils at an influent concentration of 8 mg L^{-1} . See Table 3.1 for soil identification.

depended on soil properties. Generally, the higher the soil organic matter content, the longer the time needed for the reaction to reach equilibrium. For example, the adsorption of Hg on Freehold sandy loam (A horizon), which contained a very small amount of organic C, did not significantly increase after 60 min, while adsorption on Dunellen sandy loam kept increasing until equilibrium was achieved at about 5 h. For Rockaway stony loam, which had a similar particle size distribution as Dunellen sandy loam did, adsorption equilibrium was not achieved even within 5 h. This probably resulted from the higher organic C content of Rockaway stony loam.

Higher soil organic C (SOC) content also resulted in higher adsorption. For example, for an influent concentration of 8 mg L^{-1} , the equilibrium adsorption was $257 \text{ } \mu\text{g g}^{-1}$ for Freehold sandy loam (A horizon) (SOC: 1.2 g kg^{-1}), $1216 \text{ } \mu\text{g g}^{-1}$ for Sassafras sandy loam (SOC: 3.5 g kg^{-1}), and $3610 \text{ } \mu\text{g g}^{-1}$ for Dunellen sandy loam (SOC: 11.0 g kg^{-1}). Similar results were observed in a previous study (Chapter 4; Yin *et al.*, 1996b). The amount of Hg adsorbed at equilibrium measured in the previous study, however, is smaller than that determined in this study for the same aqueous Hg concentration of 8 mg L^{-1} , e.g., $257 \text{ } \mu\text{g g}^{-1}$ vs. $640 \text{ } \mu\text{g g}^{-1}$ for Freehold sandy loam (A horizon) and $1216 \text{ } \mu\text{g g}^{-1}$ vs. $1600 \text{ } \mu\text{g g}^{-1}$ for Sassafras sandy loam. This difference probably resulted from the different soil:water ratios used in two studies, $0.3 \text{ g } 6.7 \text{ mL}^{-1}$ vs. $0.4 \text{ g } 40 \text{ mL}^{-1}$. Di Toro *et al.* (1986) also reported that increasing the solid:water ratio decreased adsorption.

It is speculated that soil particle size may also be important to the reaction rate. This hypothesis was tested by removal of organic C from Freehold sandy loam (A horizon) and Dunellen sandy loam. The organic C was removed following the method

described in Chapter 3. If micropore diffusion contributed to the slow reaction rate, it will take a longer time for adsorption to reach equilibrium on Dunellen sandy loam than on Freehold sandy loam (A horizon) after removal of organic C from both soils, because the former soil contains much more silt and clay which have more micropores than does sand. As shown in Figure 5.3, after removal of organic C, Dunellen sandy loam adsorbed more Hg and required longer time for reaction to reach equilibrium than Freehold sandy loam (A horizon) did. This suggests that micropore diffusion was probably involved in the adsorption.

The effect of influent Hg concentration on the reaction was tested on Freehold sandy loam (A horizon) and Dunellen sandy loam. The results are represented in Figure 5.4. A decrease in influent concentration decreased adsorption, indicating that the reaction was reversible or partially reversible. The decrease in influent concentration also resulted in an increase in the equilibrium time. The influent Hg concentrations used in this study resulted in the soil being nearly saturated (Chapter 4). It is expected that for a lower Hg influent concentration level, the effect of influent concentration on the adsorption kinetics would be more significant. The dependence of the adsorption rate on the influent Hg concentration suggests that diffusion was probably involved in the reaction. Diffusion has frequently been reported to be the rate limiting step for metal adsorption and desorption (Sparks *et al.*, 1980; Jardine and Sparks, 1983; Bruemmer, *et al.*, 1988). Diffusion controlled processes often follow parabolic kinetics, which are characterized by a linear relationship between fractional adsorption (q/q_{∞} , where q is the solute adsorbed at time t , and q_{∞} is the solute adsorbed at equilibrium) and $t^{1/2}$. As shown in Figure 5.5, plots of Hg fractional

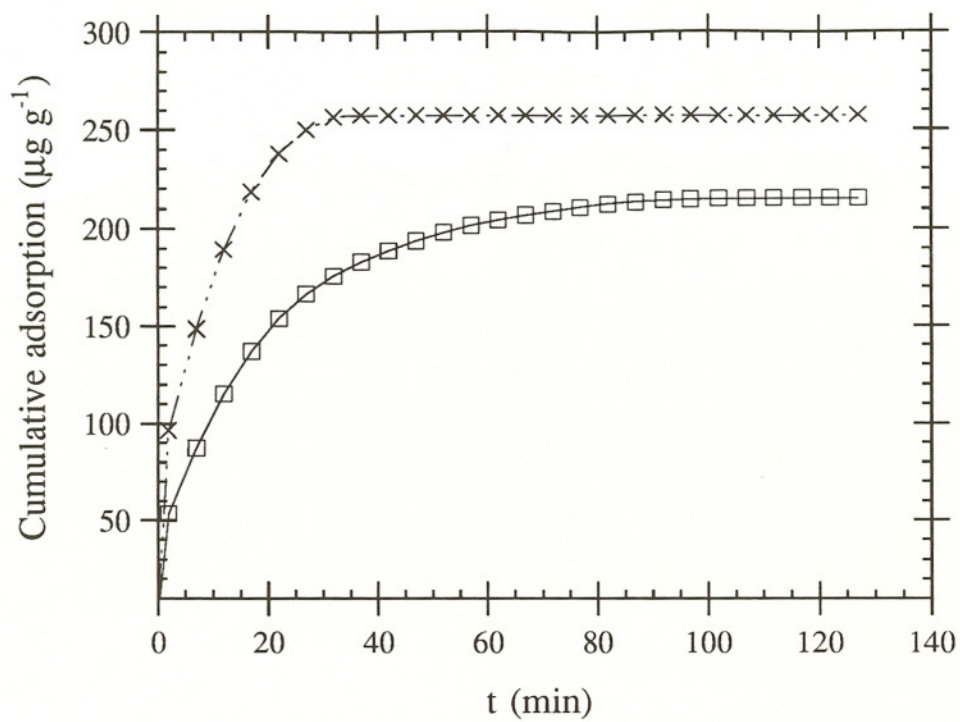


Figure 5.4 Comparison of Hg adsorption kinetics on Freehold sandy loam (A horizon) at different influent concentrations. Solid line refers to an influent concentration of 4 mg L^{-1} ; dashed line denotes an influent concentration of 8 mg L^{-1} .

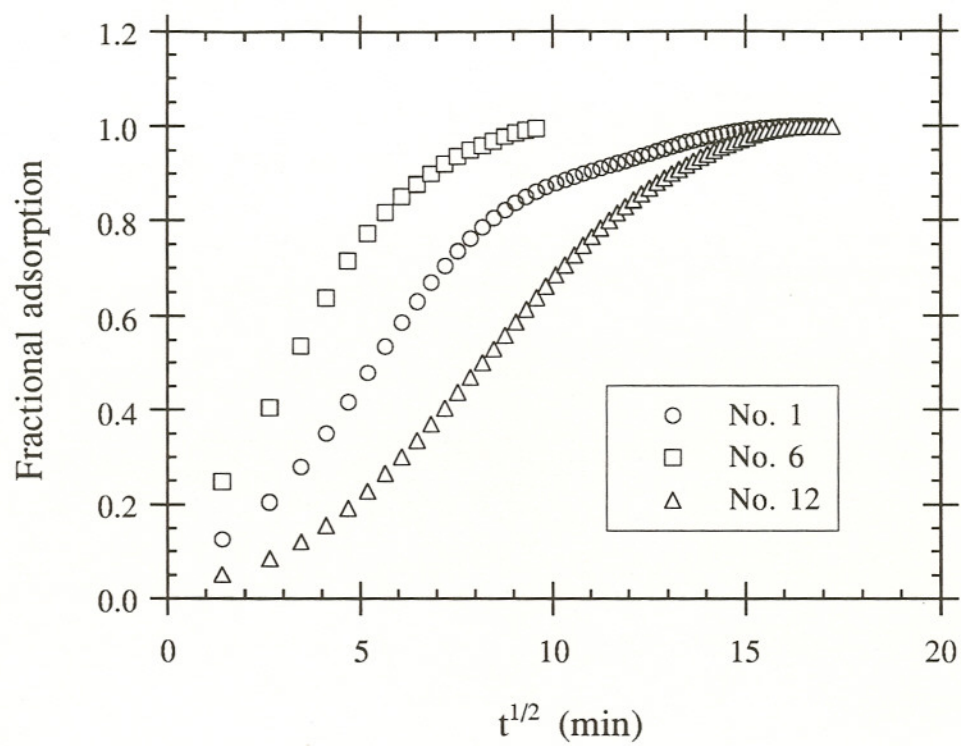


Figure 5.5 Fractional Hg adsorption as a function of $t^{1/2}$. See Table 3.1 for soil identification.

adsorption versus $t^{1/2}$ for all soils studied are curvilinear, implying that parabolic diffusion was not predominant for the reactions of this study.

5.4.2 Desorption Kinetics

Desorption experiments were initialized by introducing 0.01 M NaNO_3 to the reaction chamber after adsorption equilibrium had been attained. As shown in Figure 5.6, Hg removal rate profiles on all soils were characterized by two desorption regimes, a fast regime followed by a slow regime. The fast desorption regime occurred during the first 100 min, and the desorption rate related to the initial Hg concentration in soil. After 8 h of desorption, the desorption rate was less than $0.6 \mu\text{g g}^{-1} \text{min}^{-1}$ for all soils. However, $2000 \mu\text{g g}^{-1}$ Hg still remained on the Dunellen sandy loam, $446 \mu\text{g g}^{-1}$ on the Sassafras sandy loam, and $50 \mu\text{g g}^{-1}$ on the Freehold sandy loam (A horizon) (Figure 5.7). The fractional removal (q/q_0) profiles for all soils are similar in shape, but the quantity is different (Figure 5.8). At the end of 8 h of desorption, 79% of the Hg retained was released from the Freehold sandy loam (A horizon), 62% from the Sassafras sandy loam, and 43% from the Dunellen sandy loam.

The fractional Hg release from soils within 8 h in this study was much greater than that obtained for 96 h using the batch desorption method in Chapter 3. For example, after 96 h of batch desorption, 12% to 21% of the 2.42 to $3.66 \mu\text{mol g}^{-1}$ adsorbed Hg was released from the Freehold sandy loam (A horizon) (Chapter 3). After 8 h of desorption using the stirred-flow technique, however, 79% of the adsorbed Hg ($1.29 \mu\text{mol g}^{-1}$) was released from the same soil. For a higher initial concentration, a greater fraction of the Hg is expected to be released using the stirred-flow method

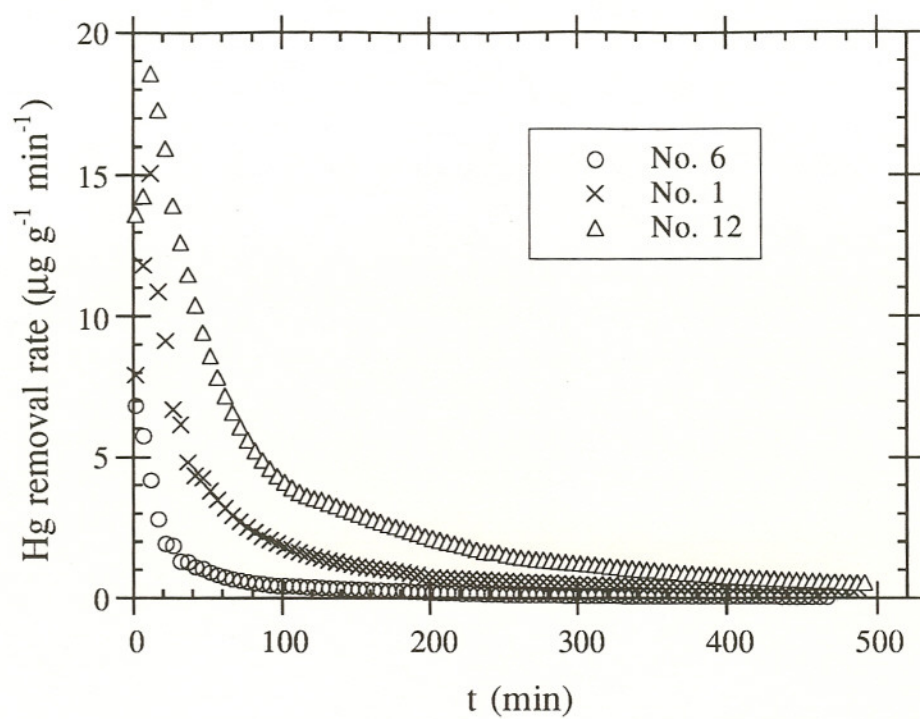


Figure 5.6 Rate of Hg removal from three soils following adsorption at an influent concentration of 8 mg L^{-1} . See Table 3.1 for soil identification.

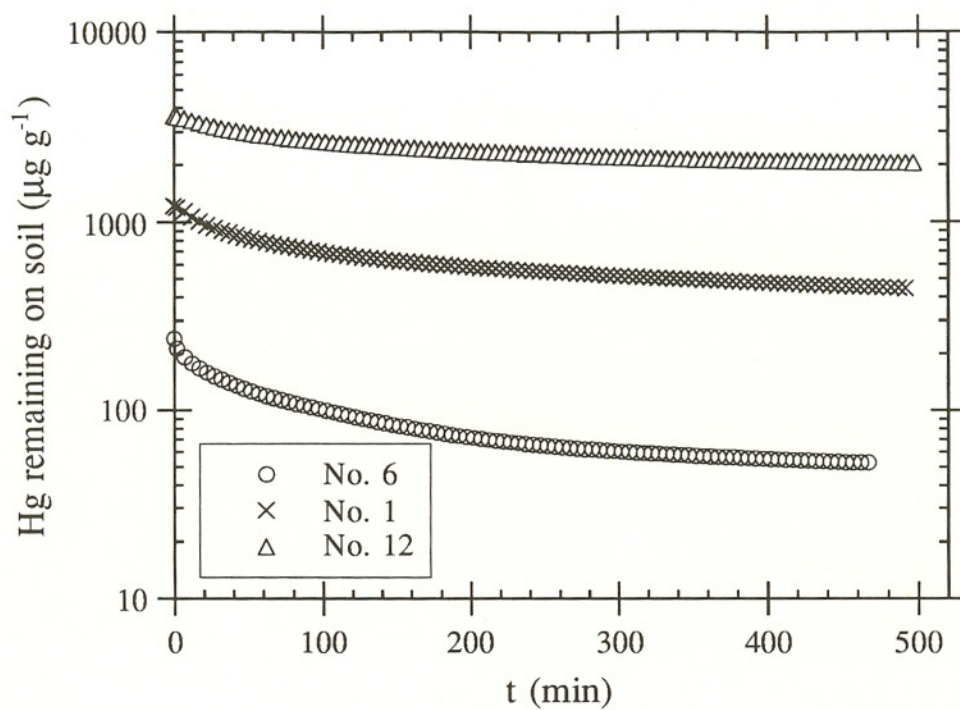


Figure 5.7 Hg remaining on soils during desorption process following adsorption at an influent concentration of 8 mg L^{-1} .

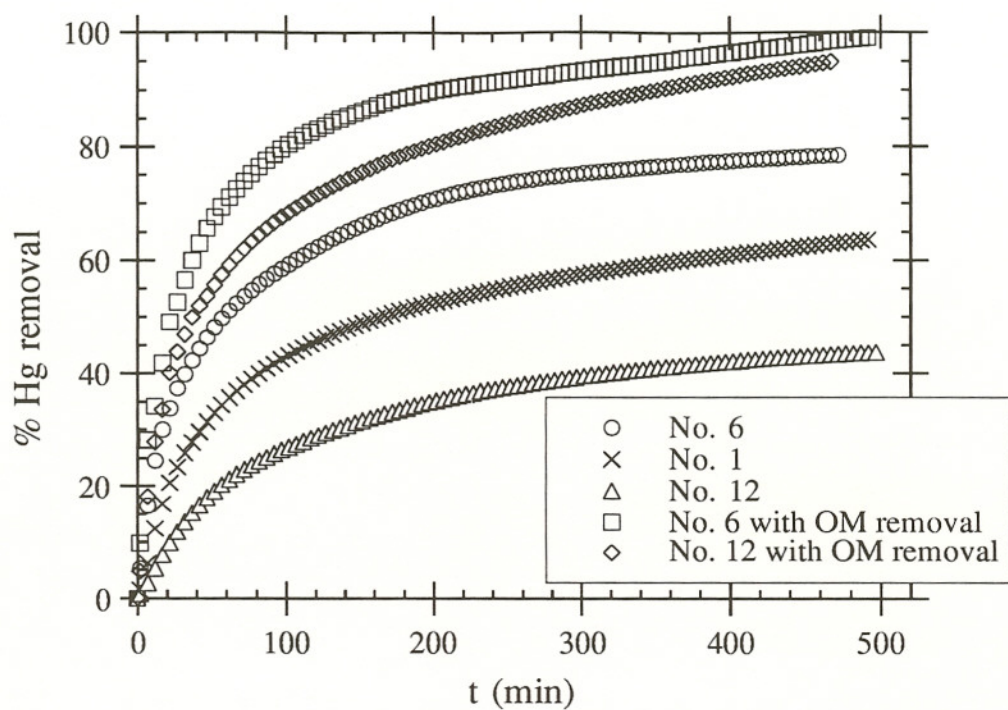


Figure 5.8 Fractional Hg removal as a function of time. See Table 3.1 for soil identification.

(details about the effect of the initial concentration on the fractional Hg release will be discussed later in this section) . The smaller fractional Hg release in batch desorption experiments can be attributed to the backward reaction caused by the released Hg.

One well-documented factor responsible for the persistence of metals in soil or soil components is diffusion into the mineral lattice (Kou, 1986; White and Yee 1986; Bruemmer *et al.*, 1988) or into intraparticle pores (Avotins, 1975, Sparks *et al.*, 1980). We speculated that the interaction of metals with soil organic matter might also contribute to the observed adsorption/desorption hysteresis. Although few attempts have been made to study the importance of soil organic matter to metal persistence in soil, it has been reported that restricted diffusion in organic matter was responsible for the persistence of many organic chemicals in soil (Bouchard *et al.*, 1988; Nkedi-Kizza *et al.*, 1989; Carroll *et al.*, 1994). To ascertain the soil components responsible for Hg persistence in soil, we compared Hg desorption from Freehold sandy loam (A horizon) and Dunellen sandy loam with and without removal of organic matter.

After removal of organic matter, the predominant portion of the Freehold sandy loam (A horizon) was sand, whereas there was nearly 50% silt and clay in the Dunellen sandy loam. If the interaction of Hg with soil organic matter is responsible for the observed hysteresis, then the removal of organic matter should significantly increase Hg fractional release. If diffusion through intra or/and inter mineral micropores is responsible for Hg slow release, then Hg fractional release should be much higher for Freehold sandy loam (A horizon) than for Dunellen sandy loam after removal of organic matter. As shown in Figure 5.8, removal of organic C significantly increased fractional release of Hg from both soils. At the end of 8-h desorption, the

fractional release from Dunellen sandy loam (SOC removal) was 95%, which was slightly lower than the 99% from Freehold sandy loam (A horizon). This suggested that organic matter was the major component responsible for Hg persistence in soil. Diffusion through mineral micropores may contribute to hysteresis, but the contribution was much smaller than that by organic matter. This was probably because the experimental time period was not long enough for Hg to penetrate into the mineral structure, and the diffusion within mineral micropores may also be significantly reduced by continuous stirring.

Comparison of Hg desorption on Sassafras sandy loam and Dunellen sandy loam also suggested that organic matter was the most important component responsible for Hg persistence in soil. As shown in Table 3.1 and Table 3.2, Sassafras sandy loam has a similar surface area and higher silt and clay content than does Dunellen sandy loam, however, Hg fractional desorption from this soil was much higher (62%) than that from Dunellen sandy loam (42%) (Figure 5.7). This probably resulted from the higher organic matter content in Dunellen sandy loam.

We plotted the fraction of Hg remaining ($F = (q_{\infty} - q_d)/q_{\infty}$) in soil after 8 h of desorption versus the soil organic C (SOC) content, and found that the F values proportionally increased with SOC. Upon log transformation of SOC values, a linear correlation between F and log SOC was obtained (Figure 5.9). The regression equation is: Fractional Hg remaining (F) = $0.18 + 0.36 \log \text{SOC}$ with a regression coefficient of 0.998.

We speculated that the slow release resulted from Hg preferentially bonding to high energy sites. Because these high energy sites have limited adsorption capacity,

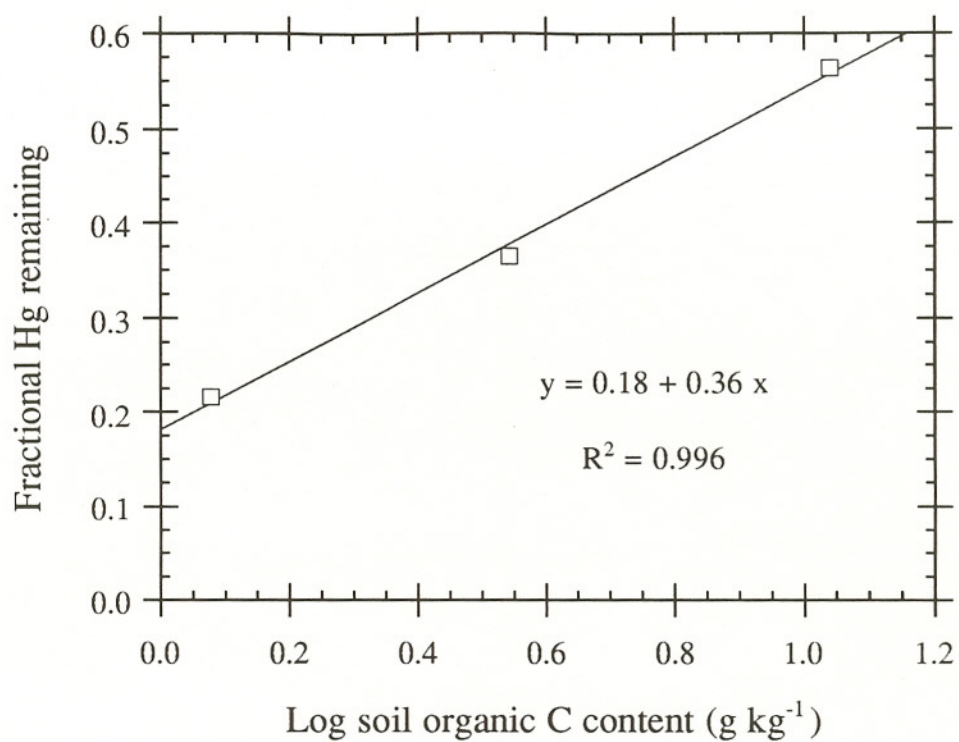


Figure 5.9 Fractional Hg remaining on soils after 8 h of desorption as a function of the soil organic C content. Mercury(II) was adsorbed by soils from an 8 mg L⁻¹ influent.

lower concentration may result in higher fractional adsorption to these high energy sites, and consequently cause lower fraction of release from soil. This hypothesis was tested on Freehold sandy loam (A horizon). As shown in Figure 5.10, 60% Hg retained was released within nearly 2 h for an initial concentration of $254 \mu\text{g g}^{-1}$, whereas 55% Hg retained was released for an initial concentration of $214 \mu\text{g g}^{-1}$. Figure 5.10 also indicated that after 50 min of desorption, the Hg remaining on the soil for two initial concentrations was almost the same. This can only be explained by the preferential distribution of adsorbed Hg among soil sites. Although the initial concentrations were different, the amount of Hg adsorbed on high energy sites could be similar. As a result, after the Hg on the low energy sites was quickly released, the Hg remaining on soil (high energy sites) was similar for different initial concentrations.

A similar result was observed for Dunellen sandy loam. The desorption study was conducted following adsorption from 4 mg L^{-1} and 8 mg L^{-1} influents. Since adsorption equilibrium was only reached for the 8 mg L^{-1} influent but not for the 4 mg L^{-1} influent within the experimental time period, the fractional desorption from the soil for two initial concentrations (3611 vs. $2825 \mu\text{g g}^{-1}$) is not comparable. Comparison of Hg remaining in the soil for two initial concentrations as a function of time, however, allows us to understand the reaction processes involved. As shown in Figure 5.11, after nearly 6 h of desorption, the Hg remaining in the soil for two initial concentration is very close (2122 vs. $2048 \mu\text{g g}^{-1}$), although the initial concentration difference is large ($786 \mu\text{g g}^{-1}$).

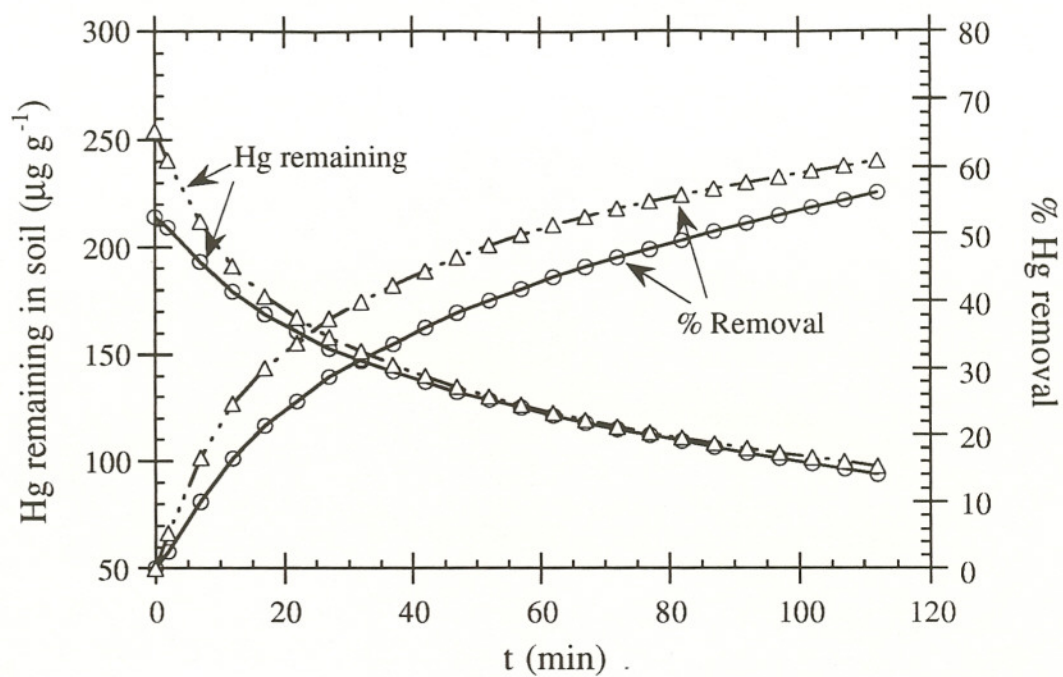


Figure 5.10 Comparison of Hg remaining and removal profile on Freehold sandy loam (A horizon) for two initial concentrations. Solid lines refer to an initial concentration of $214 \mu\text{g g}^{-1}$; dashed lines denote an initial concentration of $254 \mu\text{g g}^{-1}$.

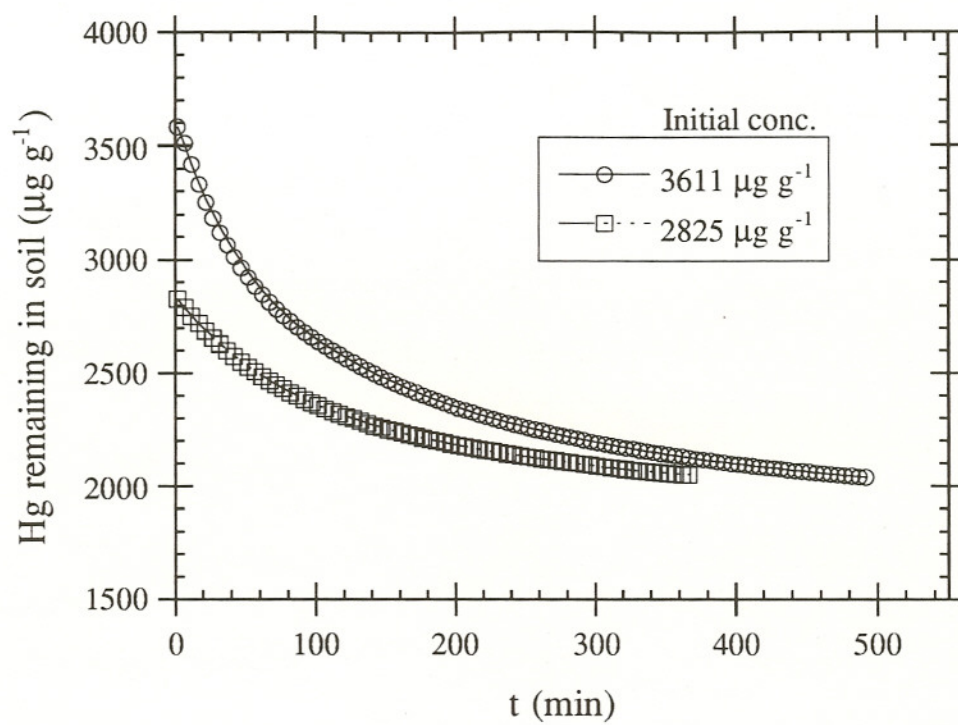


Figure 5.11 Comparison of Hg remaining profile on Dunellen sandy loam for two initial concentrations.

5.4.3 Modeling Adsorption and Desorption Kinetics

A number of models have been postulated to describe metal adsorption and desorption kinetics. Many attempts focused on one-site kinetic equations (Travis and Etnier, 1981). The rate coefficient obtained using these equations is usually an apparent coefficient that changes with flow rate and initial solute concentration. In some cases, a deviation of experimental data from the simple one-site kinetic equations was observed. Accordingly, two-site or two-region models, with two classes of sites either in series or parallel, were proposed to describe non-equilibrium adsorption (Selim *et al.*, 1976; Nkedi-Kizza *et al.*, 1989). Selim and co-workers (Amacher *et al.*, 1990; Selim, 1992) also proposed a multireaction model, with adsorption sites ranging from 3 to 5 types, to simulate metal adsorption on soils. Because this model involves so many adjustable parameters, its usefulness is limited.

In many cases, the reaction kinetics can be described equally well by different models (Sparks, 1989). The model fitting alone therefore does not allow one to make a conclusion on the reaction mechanisms. Due to the heterogeneous nature of soil, there is a virtual continuum of sites on the soil. For simplicity, we assume that there is one type of sites on soils in this study. The apparent average rate coefficient for the reaction of Hg with soil solids was calculated based on the model developed below.

The adsorption reaction between Hg and soil surface sites can be expressed as:



The reaction rate is defined by equation 5.4:

$$\frac{dq_a}{dt} = k_a (q_\infty - q) C - k_{-a} q_a \quad (5.4)$$

where dq_a/dt is the reaction rate ($\mu\text{g g}^{-1} \text{ min}^{-1}$); k_a is the forward rate coefficient ($\text{L } \mu\text{g}^{-1} \text{ min}^{-1}$); q_a is the concentration of Hg adsorbed by soil at time t ($\mu\text{g g}^{-1}$); C is the soluble Hg concentration in the reaction chamber at time t ($\mu\text{g L}^{-1}$), k_{-a} is the reverse rate coefficient (min^{-1}); and q_∞ is the concentration of Hg adsorbed at equilibrium ($\mu\text{g g}^{-1}$).

In equation 5.4, the quantity of q and C are dependent each other and each is a function of time. The correlation between q and C is unknown, which makes integration of equation 5.4 difficult. A finite difference method (Bear and Verruijt, 1990) was therefore used to solve this equation. The derivatives in equation 5.4 can be replaced by the finite difference form:

$$\frac{q_{a(t+\Delta t)} - q_{a(t)}}{\Delta t} = k_a (q_\infty - q_{a(t)}) C_t - k_{-a} q_{a(t)} \quad (5.5)$$

where subscripts t and $t+\Delta t$ indicate the quantities at time t and $t+\Delta t$. Rearrangement of equation 5.5 gives:

$$q_{a(t+\Delta t)} = k_a (q_\infty - q_{a(t)}) C_t \Delta t - k_{-a} q_{a(t)} \Delta t + q_{a(t)} \quad (5.6)$$

The desorption reaction of Hg from the soil can be expressed as:



$$\frac{d(q_0 - q_d)}{dt} = -k_d (q_0 - q_d) + k_{-d} q_d C \quad (5.8)$$

where $d(q_0 - q_d)/dt$ is the desorption rate ($\mu\text{g g}^{-1} \text{min}^{-1}$); q_d is Hg concentration released from the soil at time t ($\mu\text{g g}^{-1}$); k_d is the desorption rate coefficient (min^{-1}); k_{-d} is the reverse rate coefficient; and q_0 is the desorbable Hg concentration on the soil at the beginning. At $t = 0$, $q_d = 0$, and the reverse reaction rate is zero.

Similarly, by applying finite difference method to equation 5.8, following expression was obtained:

$$\frac{q_{d(t)} - q_{d(t+\Delta t)}}{\Delta t} = -k_d(q_0 - q_{d(t)}) + k_{-d}q_{d(t)} C_t \quad (5.9)$$

where subscripts t and $t+\Delta t$ indicate the quantities at time t and $t+\Delta t$. Rearranging equation 5.9 to give:

$$q_{d(t+\Delta t)} = q_{d(t)} + k_d(q_0 - q_{d(t)})\Delta t - k_{-d}q_{d(t)} C_t \Delta t \quad (5.10)$$

Equations 5.6 and 5.10 were used to fit adsorption and desorption kinetic data, respectively. Parameters were determined with a non-linear multi-variant program (Wilkinson, 1988). The program begins with an estimation of the values of the parameters and then keeps optimizing their values until the residual sum of squares no longer decreases significantly. A preliminary fitting exercise indicated that under the experimental conditions, the reverse reactions during both adsorption and desorption experiments were insignificant. Equations 5.6 and 5.10 are therefore simplified as 5.11 and 5.12, respectively.

Table 5.1 Model fitting parameters for adsorption and desorption kinetics of Hg(II) on soils

Soil No.	Influent Hg Conc. $\mu\text{g L}^{-1}$	Adsorption				
		q_{∞} $\mu\text{g g}^{-1}$	SE [†]	k_a $\text{L } \mu\text{g}^{-1} \text{ min}^{-1}$	SE	RMS [‡] $\mu\text{g g}^{-1}$
1	8000	1176	11	6.09e-6	4.97e-7	0.46
6	4000	210	2	2.57e-5	2.74e-6	0.46
	8000	255	1	1.99e-5	4.05e-7	0.09
8	8000	5100	64	3.06e-6	3.22e-7	1.64
12	4000	2930	32	1.06e-5	1.22e-6	1.40
	8000	3610	50	5.56e-6	7.47e-7	1.85

Soil No.	Influent Hg Conc. $\mu\text{g L}^{-1}$	Desorption				
		q_0 $\mu\text{g g}^{-1}$	SE	k_d min^{-1}	SE	RMS [‡] $\mu\text{g g}^{-1}$
1	8000	780	8	1.16e-2	4.92e-4	0.40
6	4000	126	4	2.28e-2	1.52e-3	0.16
	8000	205	2	1.65e-2	8.70e-4	0.32
12	8000	1585	14	9.26e-3	2.24e-4	0.29

[†] SE is standard deviation of the estimated parameter.

[‡] RMS is the root mean square which is defined by $[\text{RSS}/(n-p)]^{0.5}$, where RSS is residual sum of squares; n is the number of data points; and p is the number of parameters.

$$q_{a(t+\Delta t)} = k_a (q_{\infty} - q_{a(t)}) C_t \Delta t + q_{a(t)} \quad (5.11)$$

$$q_{d(t+\Delta t)} = q_{d(t)} + k_d (q_0 - q_{d(t)}) \Delta t \quad (5.12)$$

We used equation 5.11 and 5.12 to describe the kinetics of Hg(II) adsorption and desorption on soils. The model fitting results are summarized in Table 5.1. The small values of standard deviation (SE) for estimated parameters and the magnitude of root mean squares (RMS) indicated that the fit of experimental data was good. An example is shown in Figure 5.12.

As indicated in Table 5.1, the amount of Hg that could be released from soils (q_o) is much smaller than the total retained Hg (q_∞), suggesting that not all adsorbed Hg can be readily desorbed. Both k_a and k_d obtained for an influent concentration of 8 mg L⁻¹ were found to inversely correlate with the soil organic C content. By plotting log k_a and log k_d versus log SOC, linear relationships were obtained as indicated in Table 5.2. The regression coefficients (r^2) for both regressions are ≥ 0.88 .

Table 5.2 Relationships between rate coefficients obtained for an influent Hg concentration of 8 mg L⁻¹ and soil organic C (SOC) content.

	Log k_a (min ⁻¹)				Log k_d (min ⁻¹)			
	Intercept	Slope	r^2	SD [†]	Intercept	Slope	r^2	SD
Log SOC (g kg ⁻¹)	-4.76	-0.53	0.88	0.17	-1.77	-0.26	0.98	0.03

[†]Standard deviation of predicted values.

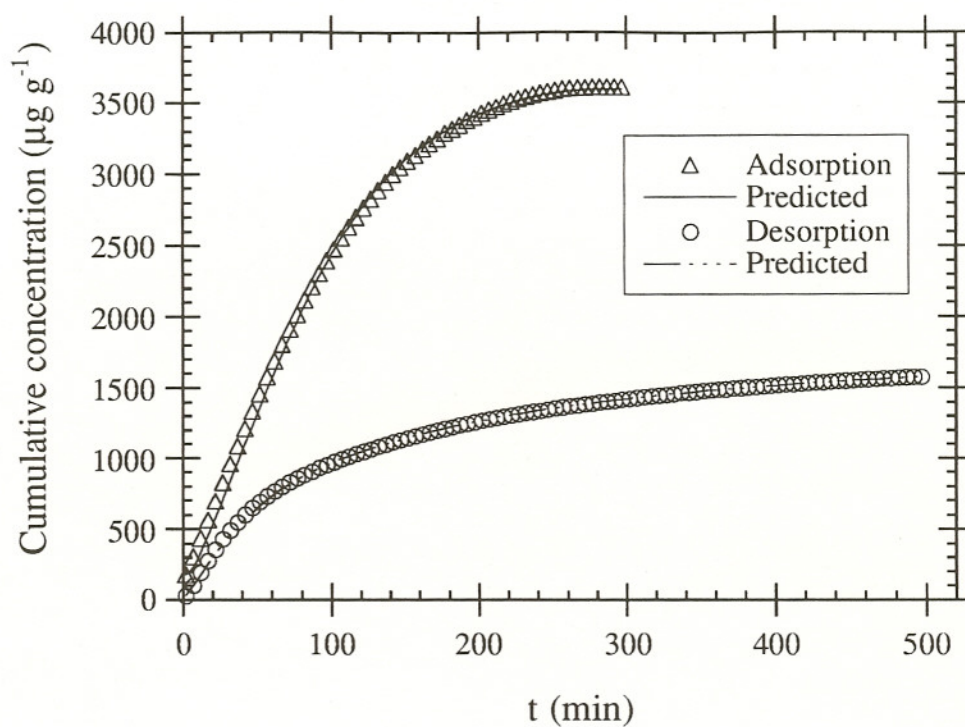


Figure 5.12 Comparison of the observed and predicted adsorption and desorption kinetics of Hg(II) on Dunellen sandy loam. Solid lines represent predicted values.

5.5 Summary and Conclusions

Mercury(II) adsorption and desorption on soils were kinetically controlled and not completely reversible. Adsorption was initially very fast. At the end of the first 2 min, the adsorbed Hg was 96 - 180 $\mu\text{g g}^{-1}$, which accounted for 4 - 38% of the total Hg that was adsorbed within 5 h. Soils with higher organic matter and higher silt and clay contents had greater adsorption of Hg and took a longer time to reach equilibrium. Hg desorption was characterized by a biphasic pattern, a slow desorption followed an initial fast phase. The fractional Hg release depended on soil properties. Among the soil components, organic matter is the major component responsible for Hg persistence in soil. Low initial Hg concentration in soil resulted in a higher resistant fraction, which is a result of Hg preferential bonding to the high energy sites.

Kinetics of Hg adsorption to and desorption from soils can be described by a one-site kinetic model. Both apparent adsorption and desorption rate coefficients were found to inversely relate to the soil organic C content. Linear relationships between $\log(k_a \text{ or } k_d)$ and $\log \text{SOC}$ were obtained with regression coefficients $r^2 \geq 0.88$.

An implication of the results is that the application of Hg to a low organic matter sandy soil could eventually result in groundwater contamination. On the other hand, the contamination of a high organic matter soil with Hg, especially for low concentration of Hg and after long contact time, may not pose serious groundwater problem. However, the decontamination of the latter soil using some methods, such as in-situ washing with water, may not be effective.

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Chapter 6

INTERACTION OF MERCURY(II) WITH SOIL-DERIVED HUMIC SUBSTANCES

6.1 Abstract

The complexation of Hg(II) with soil-derived humic substances was investigated using an iodide selective electrode. Humic substances were titrated with Hg(II) at fixed pH values of 4, 5, and 6. The binding behavior was successfully described with a multiligand distribution model which incorporated proton competitive binding and ionic strength effects. The parameters obtained from three titration curves at different pH were very similar with a Hg binding constant of 4.69 ± 0.19 . Less Hg(II) was bound by humic substances at lower pH due to the competitive binding of protons.

6.2 Introduction

The fate and toxicity of heavy metals in both aquatic and terrestrial environments are governed by many factors. Among these factors, soluble humic substances often play a key role because of their strong complexation affinity for heavy metals (Sposito, 1986; Stevenson and Fitch, 1986). Studies on fresh water have shown that substantial amounts of Cu, and lesser amounts of Pb, Cd, and Zn, are associated with soluble organic matter (Florence, 1977; Cox *et al.*, 1984). Binding to

organic matter generally reduced metal toxicity because in most cases, the free metal ion, rather than all forms of metal, is correlated to toxicity (Sunda *et al.*, 1978; Anderson *et al.*, 1978; Allen *et al.*, 1980). Heavy metals in soil solution are also partly present as organically complexed species (Camerlynck *et al.*, 1982; Sunders, 1982). In previous chapters, we have shown that organic matter is the most important soil component controlling Hg(II) retention on and release from soils. An increase in dissolved organic matter significantly decreased Hg adsorption, which was attributed to the complexation of Hg(II) by the dissolved organic matter.

In order to accurately predict the fate and toxicity of heavy metals in the environment, a knowledge of metal speciation in solution is necessary. The speciation information can be obtained by calculation using computer programs, such as MINEQL⁺ (Schecher and McAvoy, 1991) or MINTEQA2 (Allison *et al.*, 1990), based on total concentrations and the stability constants of a metal with ligands. Extensive research has been conducted to determine the stability constants of metals with humic substances using a variety of methods, such as ultrafiltration, ion-exchange, equilibrium dialysis, ion selective electrode potentiometry, lanthanide ion probe spectroscopy, and fluorescence spectroscopy (Schnitzer and Skinner, 1967; Shuman, 1977; Tuschall and Brezonik, 1983; Dobbs *et al.*, 1989a, b; Grimm *et al.*, 1991). In attempts to describe the binding characteristics, a number of models have been proposed. Representative of these models are the one-site or two-site Scatchard equation (Scatchard, 1949), the simple mixture model (Mattigod and Sposito, 1979), the normal distribution model (Perdue and Lytle, 1983), and the discrete pK's models with or without incorporation of the electrostatic energy term (Tipping and Hurley, 1992; Tipping, 1993; Westall *et al.*, 1995). Almost any of these models can

satisfactorily describe the data in simple systems, but no model has been proven to be the best with respect to natural systems.

Due to the difficulty in differentiating inorganically complexed and organically complexed Hg, few efforts have been made to determine the stability constants of Hg(II) and humic substances. Tipping (1993) modeled the interaction of Hg(II) with humic acids using the data of Kerndorff and Schnitzer (1980). In the study of Kerndorff and Schnitzer, however, the authors separated free Hg from bound Hg by centrifugation. Because of the presence of dissolved organic matter in aqueous phase, the free Hg determined by the authors actually was real free Hg(II) plus dissolved organic matter-complexed Hg.

This study was conducted to investigate the binding of Hg(II) with soil-derived humic substances using an iodide electrode to monitor the Hg concentration. We titrated humic substances with Hg(II) at fixed pH values of 4, 5, and 6. A continuous multiligand distribution model, which incorporated proton competitive binding and ionic strength effects, was used to describe the binding characteristics.

6.3 Materials and Methods

6.3.1 Extraction of Humic Substances

Humic substances were extracted from Freehold sandy loam (B horizon, Typic Hapludults). To avoid formation of Hg-Cl complexes during titration, we removed Cl⁻ from soil by washing soil samples before extracting humic substances. 1 g samples of soil were initially mixed with 30 mL of 0.01 M NaNO₃ in 35-mL centrifuge tubes.

We added NaNO_3 to replace electrostatically-adsorbed Cl^- on the particle surface with NO_3^- . The pH of each suspension was adjusted to 4 which resulted in dissolution of only a very small amount of soil humic substances (Chapter 3). The tubes were then shaken on a reciprocating shaker at 60 strokes per minute for 12 h at room temperature ($25 \pm 2^\circ\text{C}$). After shaking, the suspensions were centrifuged for 30 minutes at $1300 \times g$ and the supernatants were discarded. The soil samples were then washed three times with distilled, deionized water followed by centrifugation. Humic substances were then extracted by shaking the water-washed soil samples in $3.0 \times 10^{-3} \text{ M NaOH}$ solution for 12 hours. The extract was separated from soil solids by centrifugation followed by filtration through a $0.45 \mu\text{m}$ membrane filter, and then stored in a refrigerator at 4°C in a foil covered bottle. Characteristics of the humic substance extract are listed in Table 6.1. The total organic carbon was determined by a Beckman TOC analyzer (Rosemount Inc., Model 915-B). The residual Cl^- concentration was determined by ion chromatography (DIONEX Co. using an ASM-3 column), and cation concentrations were determined by atomic absorption spectrophotometry (Perkin Elmer Zeeman model 5000).

Table 6.1 Characteristics of humic substance extract

pH	TOC mg L^{-1}	Cl^- mol L^{-1}	Na^+ mol L^{-1}	Ca^{2+} mol L^{-1}	Mg^{2+} mol L^{-1}
8.5	103	$< 10^{-6}$	1.8×10^{-3}	4.6×10^{-5}	1.0×10^{-4}

6.3.2 Free Mercury(II) Determination

An Orion iodide electrode (Model 94-53) coupled with an Orion double junction reference electrode (Model 90-02) was used to determine free Hg(II). This iodide electrode can respond to Hg(II) as low as 10^{-8} M. The mechanism is not fully understood. It was suggested that it involves the reaction of Hg^{2+} with the AgI membrane to release Ag^+ at the electrode membrane and solution interface (as discussed later) (Orion Research Inc., 1970). The electrode senses to the released Ag^+ and an potential therefore develops across the membrane. The reaction in this situation is very similar to that which occurs at the electrode surface when the iodide electrode is used to determine I^- , where silver is dissolved from the electrode surface by I^- . The magnitude of the potential depends on the concentration of the released Ag ion, which, in the present case, further depends on the Hg(II) concentration.

6.3.4 Reagents

Distilled, deionized water was used to prepare all reagents. A 400 mg L^{-1} Hg(II) stock solution was prepared by dissolving $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (Fisher Scientific, Certified A.C.S. grade) in 0.1 M trace metal grade HNO_3 solution (Fisher Scientific). From the 400 mg L^{-1} stock solution, 4 mg L^{-1} , 40 mg L^{-1} , and 200 mg L^{-1} Hg(II) stock solutions were further prepared by dilution with 0.1 M HNO_3 . All four concentrations of stock solutions were used as titrants. 5 M NaNO_3 (Fisher Scientific, Certified A.C.S. grade) stock solution was used to maintain ionic strength. Solution pH was adjusted with 0.1 M NaOH (J. T. Baker) and 0.1 M HNO_3 .

6.3.5 Potentiometric Titration

Titration were performed in a 250-mL double-walled glass cell (Figure 6.1) at fixed pH values of 4, 5, and 6. The temperature was maintained at $25 \pm 0.1^\circ\text{C}$ by circulating water controlled by an isotemp refrigerated circulator (Fisher Scientific, Model 9100) between the double walls. For each titration, 25 mL of humic substance extract was mixed with 75 mL of distilled, deionized water and 2 mL of 5 M NaNO_3 background electrolyte to make a humic substance concentration of about 25.8 mg C L^{-1} and an ionic strength of 0.1 M. The pH of the solution was then adjusted to the desired value using 0.1 M HNO_3 and 0.1 M NaOH . The iodide working electrode and the double junction reference electrode were then inserted into the solution and allowed 10 minutes to equilibrate before beginning the titration. The titration was then initialized by dispensing 50 μL increments of the appropriate concentration of Hg titrant into the solution with a micropipet (Brinkman Instruments). After each addition, 5 minutes were allowed for equilibration. During the entire titration, the solution pH was monitored by an Orion combination pH electrode (Model 91-05) and maintained constant by adding 0.1 M NaOH with a microburet (Gilmont Instruments, GS-1200A). A Teflon-coated magnetic stirrer was used to ensure adequate mixing in the reaction chamber, and the stirring speed was maintained to a minimum to avoid turbulence. The pH and potential were recorded by an automatic Dual Titration System (Tanager Scientific Systems, IDG-8800) coupled with a microcomputer.

After each titration, the iodide electrode was restored by repolishing the membrane surface using Orion polishing strips (No. 94-82-01) and then dipping in 10^{-3} M NaI solution for 15 seconds followed by thorough washing with distilled,

deionized water. The recovery of the electrode was judged by a stable potential reading of 145 ± 2 mv in 10^{-7} M Hg(II) solution at pH 5. The reaction cell was cleaned by soaking in 15% HNO_3 solution overnight followed by rinsing with distilled, deionized water.

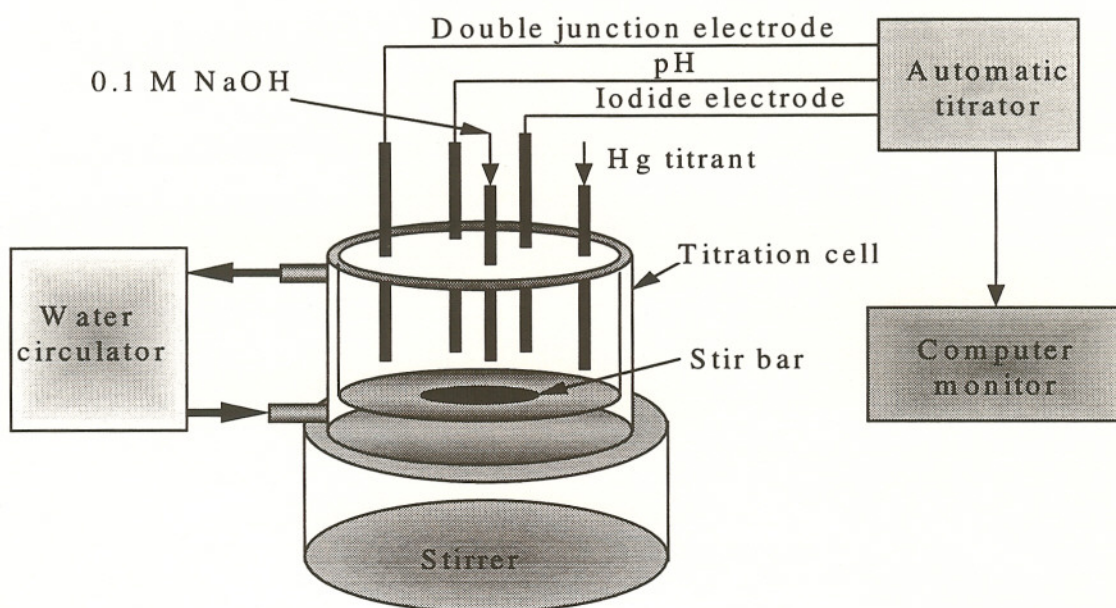


Figure 6.1 Schematic of titration system setup.

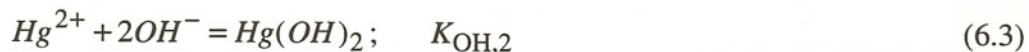
6.4 Results and Discussion

6.4.1 Calibration

We speculated that increases in pH would reduce the response of the electrode to Hg(II) because $\text{Hg}(\text{OH})_2$ (aq) comprises a greater proportion of the Hg(II). This

was tested by varying pH while maintaining Hg(II) concentration in 0.1 M NaNO₃ at 9.5×10^{-7} M. As shown in Figure 6.2, the potential reading slightly decreased from pH 3 to 6 and then significantly decreased as pH further increased. Based on this result, the titration of humic substances with Hg(II) was only performed at pH ≤ 6 . Three pH values, 4, 5, and 6, were chosen for the titration. The Hg(II) calibration curve at each fixed pH was determined in 0.1 M NaNO₃. The regression coefficients for all calibration curves, potential versus log total added mercury concentration in the solution, are greater than 0.999. The linear range is from about 5×10^{-8} M to more than 10^{-5} M for pH 4 and 5, but only from about 5×10^{-8} M to 1×10^{-6} M for pH 6.

Assuming Hg²⁺ reacted with the electrode surface membrane as described by equation 6.1, the local increase of Ag⁺ concentration was detected by the electrode. This mechanism is similar to that proposed by Budimir *et al.* (1989) for the determination of CN⁻ by an iodide electrode, in which the local increase of I⁻ concentration by the reaction of CN⁻ with AgI membrane was detected by the electrode. The concentration of the released Ag⁺ at the electrode surface was controlled by reactions 6.1 - 6.3.



where $K_{\text{Hg-Ag}}$, $K_{\text{OH},1}$, and $K_{\text{OH},2}$ are the stability constants for the reactions. The values of $K_{\text{OH},1}$ and $K_{\text{OH},2}$ are 10.35 and 21.58 for an ionic strength of 0.1 M NaNO₃

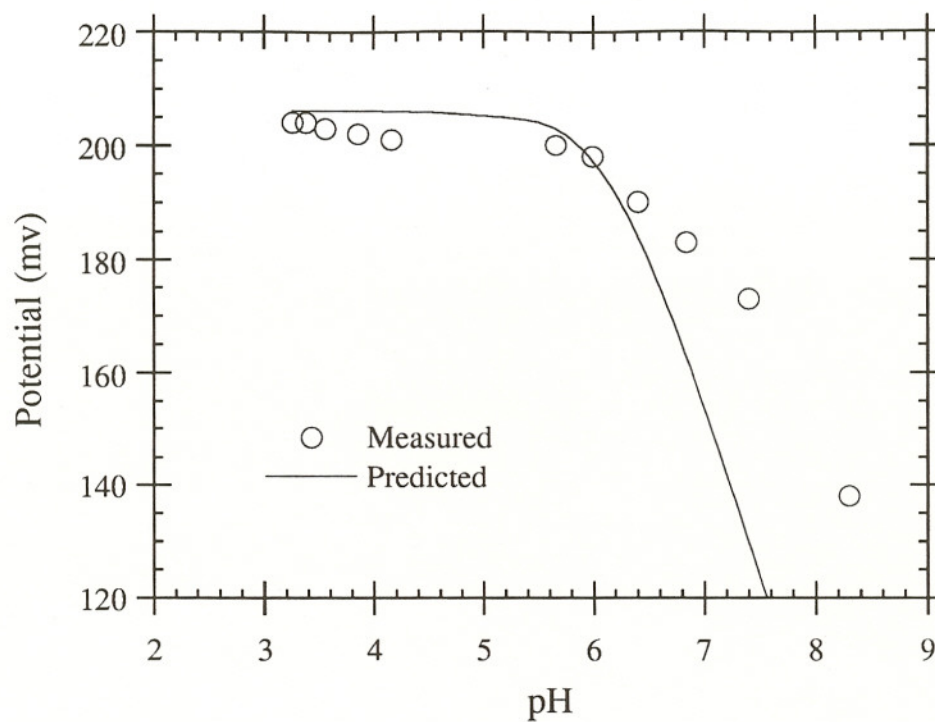


Figure 6.2 Response of iodide electrode to Hg(II) as a function of solution pH. Hg(II) concentration is 9.5×10^{-7} M. The predicted potential values were calculated based on the $K_{\text{Hg-Ag}}$ value and equation 6.11 which were obtained using calibration data at pH 4.

(Baes and Mesmer, 1976). The local total Hg concentration at the electrode surface (T_{Hg}), which equals to the concentration in the bulk solution, is:

$$T_{\text{Hg}} = [\text{Hg}^{2+}]_s + [\text{HgOH}^+]_s + [\text{Hg}(\text{OH})_2]_s + [\text{HgI}^+]_s \quad (6.4)$$

where [] indicates concentration, and the subscript, s, indicates the concentrations at the electrode surface. The concentrations on the right hand side of equation 6.4 can be expressed as functions of concentrations of Hg^{2+} and OH^- :

$$[\text{HgOH}^+]_s = K_{\text{OH},1} [\text{Hg}^{2+}]_s [\text{OH}^-] \quad (6.5)$$

$$[\text{Hg}(\text{OH})_2]_s = K_{\text{OH},2} [\text{Hg}^{2+}]_s [\text{OH}^-]^2 \quad (6.6)$$

$$[\text{HgI}^+]_s = [\text{Ag}^+]_s = K_{\text{Hg-Ag}}^{1/2} [\text{Hg}^{2+}]_s^{1/2} \quad (6.7)$$

Substitution of equations 6.5 and 6.7 into 6.4 yields:

$$\begin{aligned} (1 + K_{\text{OH},1}[\text{OH}^-] + K_{\text{OH},2}[\text{OH}^-]^2)[\text{Hg}^{2+}]_s \\ + K_{\text{Hg-Ag}}^{1/2} [\text{Hg}^{2+}]_s^{1/2} - T_{\text{Hg}} = 0 \end{aligned} \quad (6.8)$$

Solving equation 6.8 gives:

$$\begin{aligned} [\text{Hg}^{2+}]_s^{1/2} \\ = \frac{-K_{\text{Hg-Ag}}^{1/2} + (K_{\text{Hg-Ag}} + 4(1 + K_{\text{OH},1}[\text{OH}^-] + K_{\text{OH},2}[\text{OH}^-]^2)T_{\text{Hg}})^{1/2}}{2(1 + K_{\text{OH},1}[\text{OH}^-] + K_{\text{OH},2}[\text{OH}^-]^2)} \end{aligned} \quad (6.9)$$

The equilibrium concentration of Ag^+ at the electrode surface can then be calculated by substitution of equation 6.9 into 6.7.

$$[Ag^+]_s = \frac{-K_{Hg-Ag}^{1/2} + (K_{Hg-Ag} + 4(1 + K_{OH,1}[OH^-] + K_{OH,2}[OH^-]^2)T_{Hg})^{1/2}}{2(1 + K_{OH,1}[OH^-] + K_{OH,2}[OH^-]^2)} K_{Hg-Ag}^{1/2} \quad (6.10)$$

According to the Nernst equation, $\log [Ag^+]$ is linearly correlated with potential. Based on the calibration curve at pH 4, K_{Hg-Ag} was determined by solving equation 6.10 by a trial and error method until the regression coefficient for $\log [Ag^+]$ and the potential reached 0.9999, approximately unity. A K_{Hg-Ag} value of 1.21 was obtained. The correlation equation of $\log [Ag^+]$ ($\mu\text{mol L}^{-1}$) with potential (E: mV) is:

$$E = 574.08 + 61.09 \log [Ag^+]_s \quad (6.11)$$

Based on the obtained K_{Hg-Ag} value, the equilibrium concentrations of Ag^+ at the electrode surface at pH 5 and 6 were calculated using equation 6.10 for each initial Hg(II) concentration. The potential values were then calculated using equation 6.11. As shown in Figure 6.3, the calculated and measured potential values for a given initial Hg(II) concentration at pH 5 and 6 agree very well, implying that the hypothesized mechanism by which Ag^+ is released is probably valid. The potential at each pH value for the test shown in Figure 6.1 was also calculated. The agreement of the measured and predicted potential values is very good at pH less than 6.5. At pH greater than 6.5, the calculation indicated that only a small amount of Ag^+ can be released and it exponentially decreases with increasing pH. Therefore, the predicted

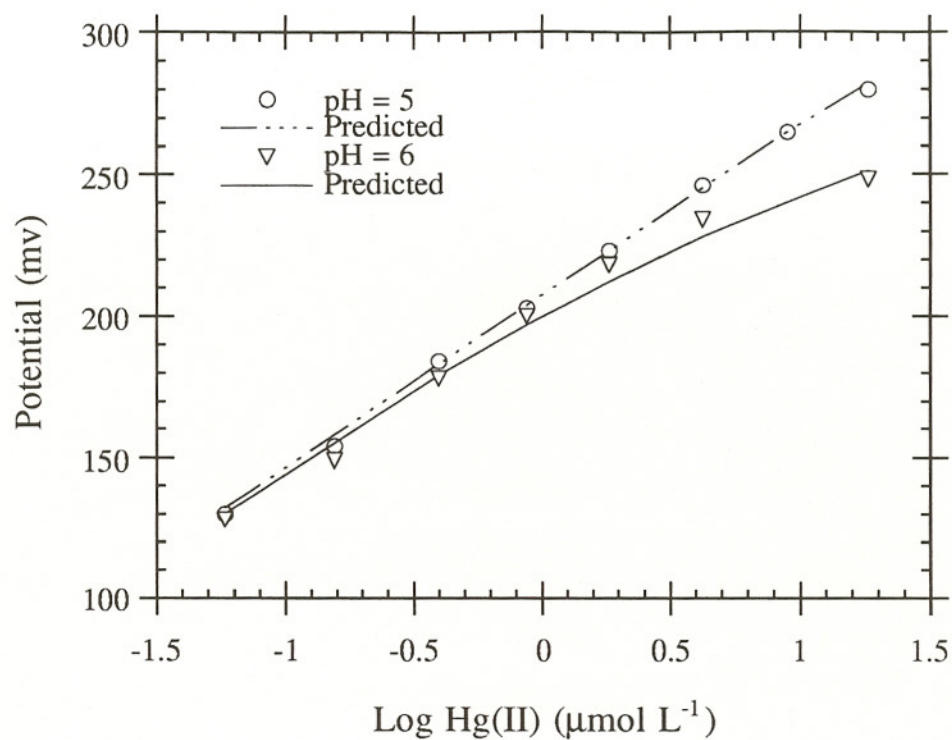


Figure 6.3 Comparison of measured and predicted potentials as a function of initial Hg concentration. Circles and triangles denote the measured potential values; solid and dashed lines represent the predicted potential values based on the $K_{\text{Hg-Ag}}$ value and equation 6.11 obtained using calibration data at pH 4.

potential sharply decreased as pH increased. Due to the interference of the background ions and the Ag^+ that has already been released to solution during the experiment, the measured potential values are higher than the predicted at pH greater than 6.5.

6.4.2 Titration of Humic Substances with Hg

Before the titration of humic substances with Hg(II) , we tested the iodide electrode by titrating Hg(II) with EDTA to ensure conformity of our results with the literature values. We titrated 100 mL of 9.8×10^{-7} M Hg(II) with an increment additions of 100 μL of 10^{-4} M EDTA. After each addition of EDTA, the free Hg(II) was measured with the iodide electrode and also calculated with the MINEQL⁺ computer program (Schecher and McAvoy, 1991) based on the stability constants shown in Table 6.2. The measured free Hg(II) concentrations agreed well with the calculated ones. The ratio of the measured to the calculated values is 0.95 ± 0.07 .

Titration of humic substances by Hg(II) were carried out at three fixed pH values (4, 5, and 6) as previously described. The amount of added Hg(II) increased from about 1×10^{-7} M to 2×10^{-5} M. Only those data points whose free Hg(II) concentrations were within the linear range of the calibration curve were used for analysis. To ensure that all the Hg(II) disappeared from the solution was bound by humic substance rather than vaporized, we analyzed the total Hg(II) concentration in the solution by cold vapor atomic absorbance spectrophotometry (Perkin Elmer MHS-10 coupled with Perkin Elmer 5000 atomic absorbance spectrophotometer) at the end of the titration. The concentration of Hg in the background solution (including

all of the reagents but without addition of Hg) was also analyzed, and less than 1×10^{-8} M of Hg was found. The recovery of added Hg(II) was $96.5 \pm 0.9\%$.

Table 6.2 Stability constants for Hg(II)

Equilibrium Reaction	Log K (I = 0.1 M)
$\text{Hg}^{2+} + \text{H}_2\text{O} = \text{HgOH}^+ + \text{H}^+$	-3.65 ^a
$\text{Hg}^{2+} + 2\text{H}_2\text{O} = \text{Hg}(\text{OH})_2 + 2\text{H}^+$	-6.42 ^a
$\text{Hg}^{2+} + \text{EDTA}^{4-} = \text{HgEDTA}^{2-}$	21.50 ^b
$\text{Hg}^{2+} + \text{H}^+ + \text{EDTA}^{4-} = \text{HgHEDTA}^-$	24.70 ^b

^aFrom Baes and Mesmer (1976).

^bFrom Martell and Smith (1993).

Figure 6.4 shows the titration curves, bound Hg versus free Hg(II), at three pH values. The fraction of added Hg(II) bound by humic substances increased with pH. Based on the results of this study, we can not make any definite conclusions on the binding mechanisms. Due to the strong Lewis acid characteristics of Hg, whose hydrolysis constants are 3.65 for $\text{p}K_{\text{OH},1}$ and 6.42 for $\text{p}K_{\text{OH},2}$ at an ionic strength of 0.1 M, hydroxo-Hg species were calculated to be dominant among the free Hg(II) species at pH above 3. Khan *et al.* (1985) suggested that hydroxo-Hg species were important for Hg binding to organic matter via hydrogen bonding. We tested the involvement of soluble Hg hydroxides in the binding by comparison of the calculated and experimental results. Based on the results of this study, we calculated Hg speciation assuming a total ligand concentration for Hg binding of 1×10^{-4} M, an

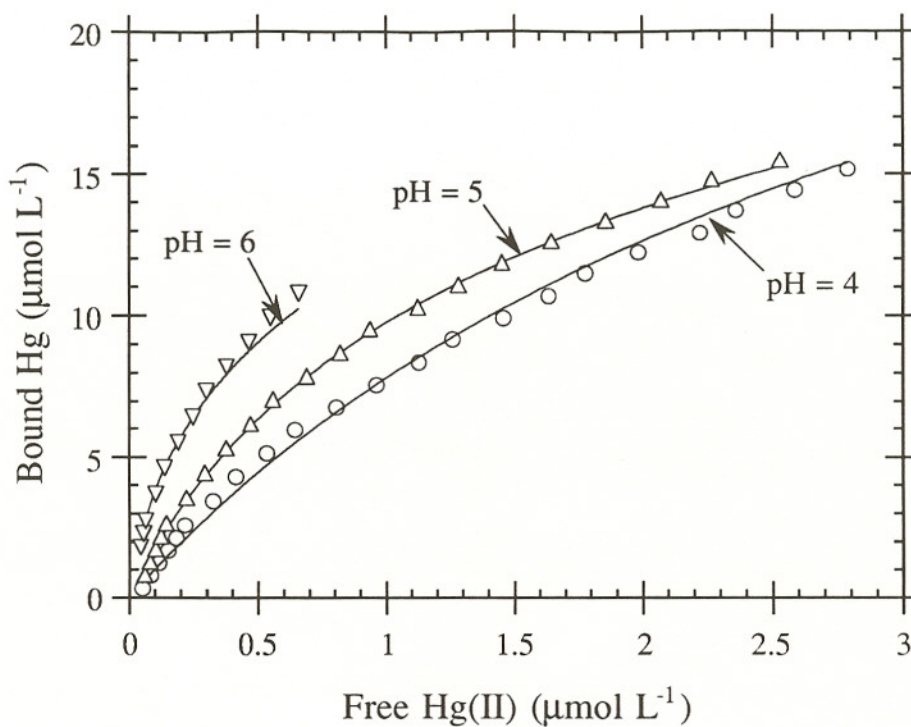


Figure 6.4 Titration curves of humic substances by Hg(II). Solid lines denote model predictions. The concentration of humic substances was 25.8 mg C L⁻¹, which was extracted from Freehold sandy loam (B horizon).

average proton binding constant ($\log K_H$) of 4, and an average Hg binding constant ($\log K_{Hg}$) of 4.5 to 8.5. Only the binding of free Hg^{2+} ion with humic substances was considered. As shown in Figure 6.5, increases in pH increased the fraction of free Hg(II) and decreased the fraction of bound Hg. Higher $\log K_{Hg}$ values resulted in more bound Hg. However, even for a $\log K_{Hg}$ value of 8.5, the fraction of bound Hg at pH 6 is only 7.6%, while almost 100% of Hg(II) is bound at pH less than 4. This is in conflict with the experimental results that the bound Hg increased as pH increased from 4 to 6. This inconsistency between the experimental and these calculated results suggested that the hydroxo-Hg species were involved in the binding.

6.4.3 Modeling the Binding of Hg with Humic Substances

A number of models have been proposed to describe the binding of metals with humic substances. Basically, these models can be divided into two types. One type is the one site or two site reaction models which are represented by the Scatchard equations (Scatchard, 1949). The other type is the multi-site discrete or continuous distribution models (Mattigod and Sposito, 1979; Perdue and Lytle, 1983; Tipping and Hurley, 1992; Tipping, 1993; Westall *et al.*, 1995). As indicated by Perdue and Lytle (1983), the Scatchard equations over-simplifies the complexity of humic substances. The stability constants obtained by either Scatchard one site or two site equation vary with the metal/ligand concentration ratio, and consequently are not capable of predicting metal speciation. This is even more evident when there is competitive binding of other ligands with humic substances for metals. For example, mercury can be strongly bound by humic substances and also by Cl^- . It is expected that some of the binding sites on humic substances have stronger affinity for Hg than Cl^- , and some do

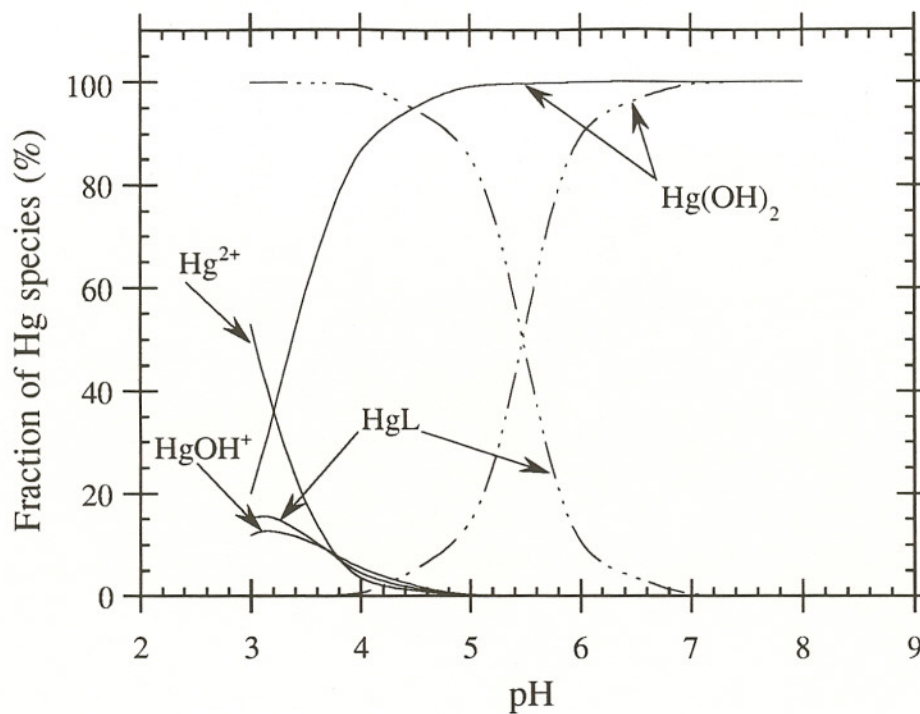


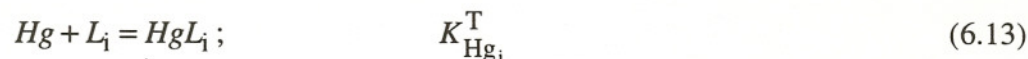
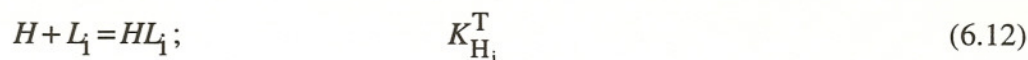
Figure 6.5 Hg(II) speciation in simulated Hg-humic substances mixture. Total ligand concentration is 1.0×10^{-4} M; proton binding constant $\log K_H$ is 4; and the total Hg(II) concentration is 1.0×10^{-6} M. Dashed lines are for an average Hg binding constant $\log K_{Hg}$ of 4.5; and solid lines are for $\log K_{Hg}$ of 8.5.

not. For given concentrations of organic matter and Cl^- , at low Hg concentration, the majority of the Hg would be complexed by the high energy sites on humic substances. When these high energy sites are saturated, the complexation of Hg by Cl^- becomes predominant. This kind of behavior can not be predicted based on one or two site models.

Sposito's model (Mattigod and Sposito, 1979) is based on the assumption that humic or fulvic acid can be simulated with a mixture of selected simple ligands displaying similar properties to the sites on humic or fulvic acids. Due to the difficulty in selecting the simulating ligands, we did not use this model in this study. In Tipping's model V, only the major proton-dissociating groups were considered, and the groups containing N and S were ignored (Tipping and Hurley, 1992). It is assumed that there are two types of sites. Within each type, there are four different groups which are present in equal amounts. This model may not be suitable for Hg binding because it has been shown that Hg very strongly bonds to $-\text{NH}_2$ and $-\text{SH}$ groups and less strongly bonds to carboxyl groups (Bowen, 1979; Reimers and Krenkel, 1974). Consequently, the functional groups containing N and S could be very important for Hg binding. Furthermore, the unique property of this model is that it incorporates an electrostatic energy term into the model. However, almost all free Hg is present as neutral $\text{Hg}(\text{OH})_2(\text{aq})$ species in natural systems. In a recent study, Westall *et al.* (1995) modeled $\text{Co}(\text{II})$ binding to humic acid by a discrete log K spectrum model. They assumed that there were four binding sites on humic acid and the log K s for the binding of proton with these sites were arbitrarily set as 4, 6, 8, and 10. The binding of $\text{Co}(\text{II})$ with these four sites were modeled based on both acid-base titration data and the $\text{Co}(\text{II})$ -humic acid reaction results.

Based on the earlier work of Posner (1966), Perdue and Lytle (1983) proposed a Gaussian distribution model to describe the distribution of metal binding sites in humic substances. This model predicts that the binding of a metal with humic substances begins with very strong ligands at low metal/humic substances values and gradually shifts to weaker ligands at high metal/humic substance ratios (Perdue, 1988). It reflects the complex nature of the humic substances. Only two parameters, the mean $\log K$ and the standard deviation of the range of $\log K$, are required. Recently, Susetyo *et al.* (1990) further incorporated proton competitive binding and ionic strength effects into this model, and showed that the stability constant obtained was independent of humic substance concentration, metal concentration, pH, and ionic strength. This model has been incorporated into MINTEQA2 for chemical speciation calculation (Allison *et al.*, 1991). In this study, we used this model to describe the binding of Hg with humic substances.

In this model, 1:1 Hg-ligand complexation was assumed for simplicity. The binding of the i th ligand with protons and Hg can be expressed as:



in which the charges have not been considered. The corresponding thermodynamic constants for proton ($K_{H_i}^T$) and Hg ($K_{Hg_i}^T$) binding are:

$$K_{H_i}^T = \frac{\{H\}\{L_i\}}{\{HL_i\}} = \frac{[H][L_i]}{[HL_i]} \frac{\gamma_H \gamma_{L_i}}{\gamma_{HL_i}} = \frac{[H][L_i]}{[HL_i]} \Gamma_{H_i} \quad (6.14)$$

$$K_{Hg_i}^T = \frac{\{Hg\}\{L_i\}}{\{HgL_i\}} = \frac{[Hg][L_i]}{[HgL_i]} \frac{\gamma_{Hg}\gamma_{L_i}}{\gamma_{HgL_i}} = \frac{[Hg][L_i]}{[HgL_i]} \Gamma_{Hg_i} \quad (6.15)$$

where braces { } and square brackets [] denote activities and concentrations, respectively; γ is an activity coefficient; and Γ is the activity coefficient ratio. Based on the mass balance for the i th ligand, we have:

$$[HL_i] = C_i - [L_i] - [HgL_i] \quad (6.16)$$

where C_i is the total concentration of the i th ligand. Substitution of equations 6.14 and 6.15 into 6.16 yields:

$$[L_i] = \frac{C_i}{1 + \frac{K_{Hg_i}^T}{\Gamma_{Hg_i}}[Hg] + \frac{K_{H_i}^T}{\Gamma_{H_i}}[H]} \quad (6.17)$$

The concentration of Hg bound by the i th ligand is then calculated by substitution of equation 6.17 into 6.15:

$$[HgL_i] = \frac{\frac{K_{Hg_i}^T}{\Gamma_{Hg_i}}[Hg]C_i}{1 + \frac{K_{Hg_i}^T}{\Gamma_{Hg_i}}[Hg] + \frac{K_{H_i}^T}{\Gamma_{H_i}}[H]} \quad (6.18)$$

Assuming that the relative concentration of each ligand is normally distributed relative to the pK_i of the ligand and can be expressed by the Gaussian error function (Perdue and Lytle, 1983), then

$$\frac{C_i}{C_L} = \frac{1}{\sigma(2\pi)^{1/2}} e^{-(\mu_{Hg} - \log K_{Hg_i})^2 / 2\sigma^2} d \log K_{Hg} \quad (6.19)$$

where μ_{Hg} is the mean value of all $\log K_{Hg}$ values, and σ is the standard deviation of the $\log K_{Hg}$ values. Substituting equation 6.19 into 6.18 and summing up for all ligands, the total Hg bound by humic substances is:

$$\begin{aligned} \Sigma[Hg L_i] = C_{Hg} - [Hg] = \\ \frac{C_L}{\sigma(2\pi)^{1/2}} \int_{-\infty}^{+\infty} \frac{\frac{K_{Hg_i}^T}{\Gamma_{Hg_i}} [Hg]}{1 + \frac{K_{Hg_i}^T}{\Gamma_{Hg_i}} [Hg] + \frac{K_{H_i}^T}{\Gamma_{H_i}} [H]} e^{-(\mu_{Hg} - \log K_{Hg_i})^2 / 2\sigma^2} d \log K_{Hg} \quad (6.20) \end{aligned}$$

where C_{Hg} is the total Hg concentration ($\mu\text{mol L}^{-1}$). For each addition of Hg, the concentration of free Hg was experimentally determined, and this was further used to calculate the amount of bound Hg. The values of C_L , μ_{Hg} , K_{Hg}^T , and σ were estimated by a non-linear regression method to fit the experimental data by equation 6.20 with an integration range of $\mu_{Hg} \pm 4\sigma$. The FGMIN computer program developed by Perdue (1993) was used to perform the fitting procedure. The activity coefficients were calculated using the Davies equation (Stumm and Morgan, 1981). A value of -2.8 was used as the average charge of humic substance anion. This value was determined via model fitting by Susetyo *et al.* (1990) and was used to successfully model Eu^{3+} and Cu^{2+} binding by humic substances (Susetyo *et al.*, 1990; Grimm *et al.*, 1991). With this value, the binding of Hg with humic substances was successfully described in this study (as discussed later).

The goodness of the fit of experimental data with equation 6.20 was judged by the residual sum of squares, which was calculated by equation 6.21:

$$RSS = \sum_{i=1}^n \frac{(Y_p - Y_e)^2}{Y_e} \quad (6.21)$$

where n is the number of data points used in modeling, Y_e and Y_p are the concentrations of complexed metal experimentally determined and model predicted, respectively.

The binding of Hg(II) with humic substances was modeled by equation 6.20. When Hg^{2+} was considered as the sole binding species, the μ_{Hg} values obtained for the best fit of the titration data increased by a factor of about 2 for an increase of each pH unit. This further indicates that the Hg^{2+} species was not the dominant species for Hg binding to humic substances at the experimental pH because theoretically the binding constants for a given Hg species with humic substances should be same at different pH values. Since at the experimental pH range of 4 to 6, almost all free Hg(II) was present as $\text{Hg}(\text{OH})_2(\text{aq})$ (93% at pH 4; 99.4% at pH 5; 99.9% at pH 6), we speculated that the $\text{Hg}(\text{OH})_2(\text{aq})$ species was probably the dominant species for Hg(II) binding to humic substances. When only $\text{Hg}(\text{OH})_2(\text{aq})$ was considered for modeling, the parameters that best fit each titration curve are very similar. For the binding of given metal and humic substances, the values of C_L , σ , and μ_H should be constants. When a fixed set of C_L , σ , and μ_H values (C_L : $2.6 \mu\text{mol mg}^{-1} \text{ C}$; σ : 1.5; μ_H : 3.8 L mol^{-1}) that best describes all titration curves (Figure 6.4) was used, a value of $4.69 \pm 0.19 \text{ L mol}^{-1}$ was obtained for μ_{Hg} (Table 6.3). The residual sum of squares for all curves are less than $0.0009 \mu\text{mol mg}^{-1}$. The slightly higher μ_{Hg} value for pH 4 is

probably because more aquo Hg^{2+} is involved in the reaction, and its binding constant may be higher than that of hydroxo Hg species.

Table 6.3 Model fitting parameters

pH	C_L $\mu\text{mol mg}^{-1} \text{ C}$	σ	μ_H L mol^{-1}	μ_{Hg} L mol^{-1}	RRS $\mu\text{mol mg}^{-1} \text{ C}$
4	2.6	1.5	3.8	4.88	0.0009
5	2.6	1.5	3.8	4.52	0.0003
6	2.6	1.5	3.8	4.51	0.0004
Average $\pm$ SD [†]				4.69 $\pm$ 0.19	

[†]Standard deviation.

The difference in three titration curves shown in Figure 6.4 mainly resulted from the competitive binding of protons. This effect is illustrated in Figures 6.6a-c, which were generated by model calculation based on the obtained parameters and initial Hg concentrations. Before addition of Hg(II) to the solution, 30% of the ligands was bound by protons at pH 4, 15% at pH 5, and 4% at pH 6. As Hg(II) binding increased, both the concentrations of free ligands and bound protons decreased. For a given Hg(II) total concentration in solution, the amount of bound protons increased with decreasing pH, which resulted in corresponding decreases in Hg binding. It is expected that the effect of pH on Hg(II) binding would be negligible when the Hg(II) concentration is so high relative to the total ligand concentration that all bound protons are replaced by Hg. Consequently, the binding capacity of humic substances for Hg at different pH values is the same.

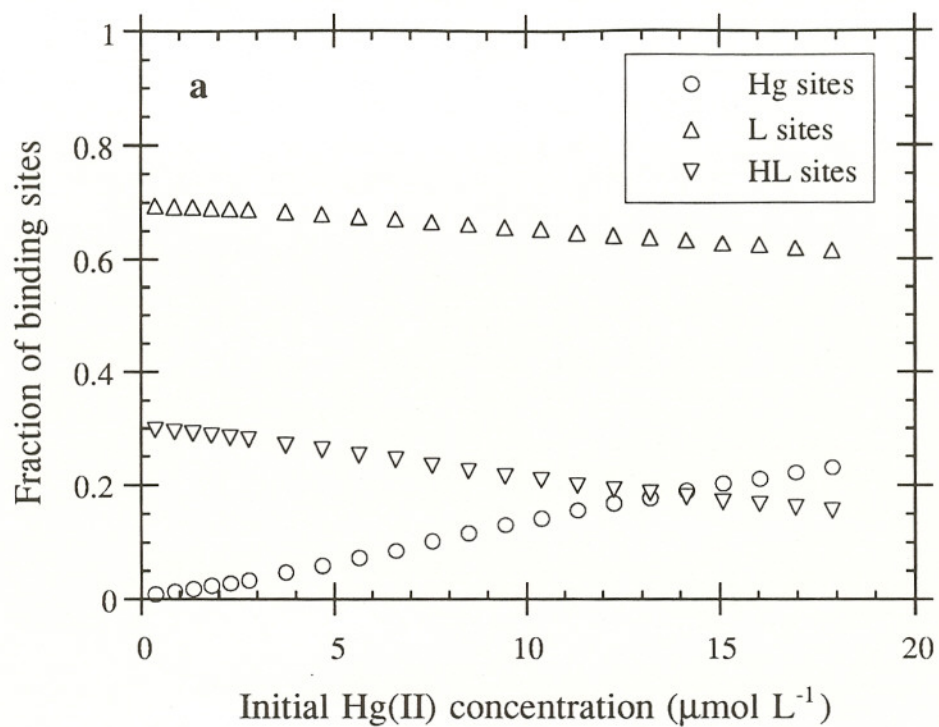


Figure 6.6a Fractions of bound protons and bound Hg over the total ligand concentration as a function of initial Hg(II) concentration at pH 4. L sites denote the deprotonated sites on humic substances, and HL sites denote the protonated sites. The concentration of humic substances was 25.8 mg C L^{-1} , which was extracted from Freehold sandy loam (B horizon).

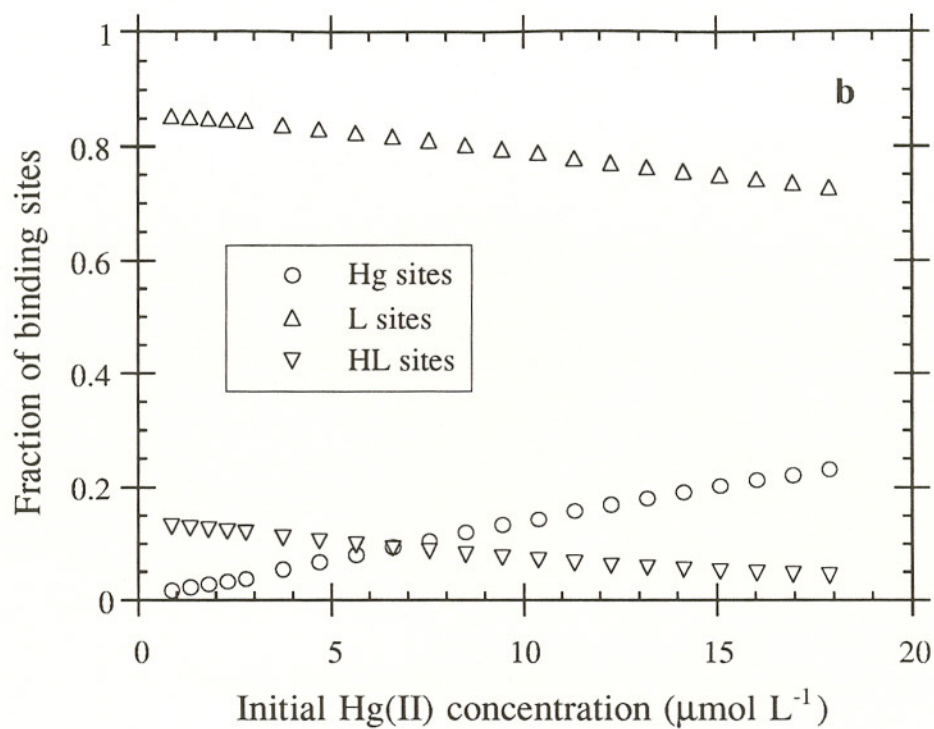


Figure 6.6b Fractions of bound protons and bound Hg over the total ligand concentration as a function of initial Hg(II) concentration at pH 5. L sites denote the deprotonated sites on humic substances, and HL sites denote the protonated sites. The concentration of humic substances was 25.8 mg C L⁻¹, which was extracted from Freehold sandy loam (B horizon).

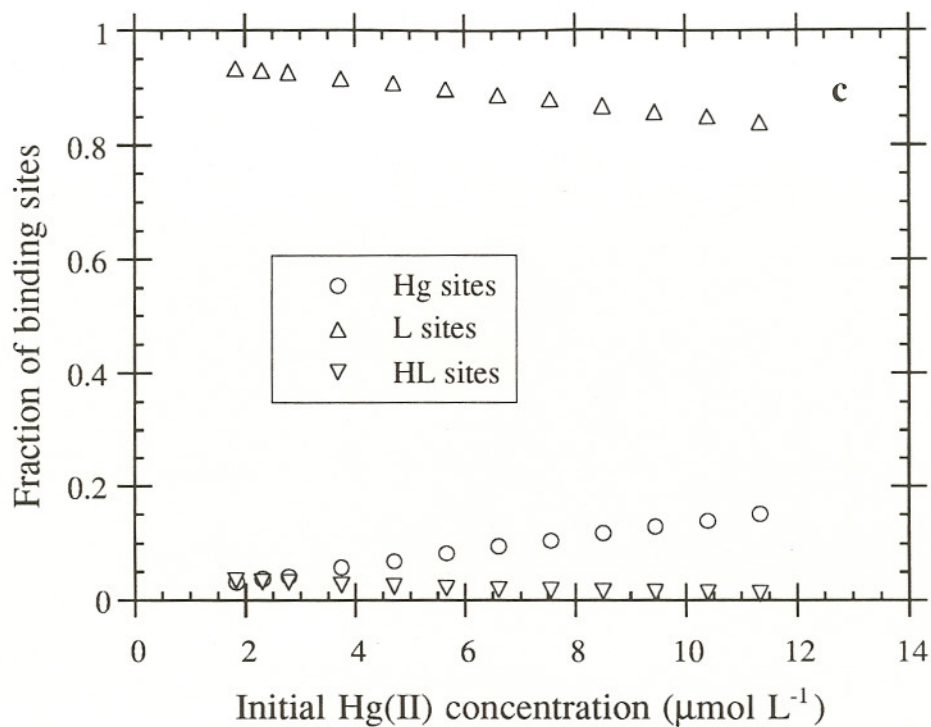


Figure 6.6c Fractions of bound protons and bound Hg over the total ligand concentration as a function of initial Hg(II) concentration at pH 6. L sites denote the deprotonated sites on humic substances, and HL sites denote the protonated sites. The concentration of humic substances was 25.8 mg C L^{-1} , which was extracted from Freehold sandy loam (B horizon).

The estimated binding capacity of humic substances for Hg ($C_L = 1.5 \text{ mmol g}^{-1}$ humic substances assuming 57% C content in humic substances) is much smaller than the reported density of proton exchange sites on soil humic substances (5.7 - 14.2 mmol g^{-1}) (Schnitzer and Khan, 1972). A similar result was observed by Susetyo *et al.* (1990). They reported a density of 0.6 mmol g^{-1} Suwannee River humic substance for binding Eu(III), which is also much smaller than the reported density of proton exchange sites for aquatic humic substances (5 - 14.8 mmol g^{-1}) (Borggaard, 1974; Perdue *et al.*, 1980; Thurman and Malcolm, 1983). This is probably an indication that not all proton exchange sites were involved in binding or/and one Hg(II) or Eu(III) ion bound to more than one proton exchange site.

6.5 Summary and Conclusions

The binding of Hg(II) with humic substances at pH values 4, 5, and 6 was investigated with an iodide electrode. Hg(II) was found to be strongly bound by humic substances at all three pH values. A smaller fraction of Hg(II) was bound at lower pH values due to competitive proton binding.

The binding characteristics of Hg(II) with humic substances was successfully described by the Gaussian distribution model. By incorporating proton competitive binding and ionic strength effects into the model, a stability constant which is independent of the experimental conditions was obtained. Not only aquo Hg^{2+} , but also hydroxo-Hg species were probably involved in the binding. At the experimental pH values (which is similar to those in natural systems), $\text{Hg}(\text{OH})_2(\text{aq})$ probably is the major species determining Hg(II) binding behavior.

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Chapter 7

ADSORPTION OF METHYLMERCURY BY SOILS: EFFECTS OF pH, CHLORIDE, AND CALCIUM

7.1 Abstract

Adsorption of methylmercury on soils as a function of pH, Cl^- , and Ca^{2+} was investigated. Four soils of different properties and an initial Hg concentration of 2×10^{-7} M or 1×10^{-6} M were employed. The experiments were conducted at a pH range of 3 to 10. Adsorption as a function of pH followed a upside bow shape with maximum adsorption at pH about 5 to 6. A higher initial Hg concentration resulted in higher adsorption. Addition of 1×10^{-3} M Cl^- decreased adsorption at $\text{pH} < 7$. The presence of high concentration of Ca^{2+} (0.003 M), however, increased adsorption at $\text{pH} < 6$. Both aqueous speciation and surface charge controlled adsorption. Soluble organic ligands, whose concentration was affected by pH and possibly multi-valent cations, played an important role in determining soil-water partitioning of methylmercury.

7.2 Introduction

Methylmercury has been recognized as the most toxic Hg species (Steinnes, 1995). Methylmercury in soils mainly originated from direct input by mankind in forms of fertilizer and sludge, and from transformation of inorganic Hg(II) (Rogers,

1977; Tonomura *et al.*, 1972). Whether methylmercury in soil is toxic to plants or will cause surface and groundwater contamination largely depends on its adsorption/desorption behavior, which determines the amount of soluble methylmercury available for plant uptake and/or transport to surface and groundwater.

Little information on the adsorption of methylmercury on soils and soil components is available. Hogg *et al.* (1978) compared adsorption of three Hg species, methylmercuric chloride (MMC), phenyl mercuric acetate (PMA), and HgCl_2 , on two soils with different chemical and physical properties, and reported that adsorption capacity increased in the order of $\text{MMC} < \text{PMA} < \text{HgCl}_2$. Among soil components, organic matter and clays seem dominant for methylmercury adsorption. A similar result was observed by Reimers and Krenkel (1974). They reported that a considerable amount of methylmercury was adsorbed by clay minerals and fine sands with a sequence of illite > montmorillonite > fine sands, whereas no adsorption occurred on kaolinite and coarser sands. Unlike inorganic Hg which is strongly adsorbed by all major functional groups of organic matter (Reimers and Krenkel, 1974; Bowen, 1974; Duffy *et al.*, 1989), methylmercury is only efficiently adsorbed to sulfhydryl groups of organic matter. Amine and carboxyl groups are inefficient in binding with methylmercury (Reimers and Krenkel, 1974).

The purpose of this study was to examine environmental factors influencing methylmercury adsorption on soils. One factor examined is pH, which affects both soil surface charge and aqueous speciation. Another factor is Cl^- , which is usually present in soil solution at significant level and has strong affinity for methylmercury ion. The third factor is Ca^{2+} , one of the representative interfering divalent cations that

are present in soil solution. The simultaneous effects of these factors on methylmercury retention on and release from soils were investigated.

7.3 Materials and Methods

Four soils, Freehold sandy loam (A horizon), Freehold sandy loam (B horizon), Penn silt loam, and Rockaway stony loam, were used to conduct experiments. Selected properties of the soils were listed in Tables 3.1-3.3.

Adsorption of methylmercury on the four soils as a function of pH was investigated according to the following procedure. 0.4 g soil sample was mixed with 40 mL of 0.01 M NaNO_3 in 50-mL glass centrifuge tubes. 0.2 mL of 4×10^{-5} or 2×10^{-4} M methylmercury stock solution (prepared from 1 M CH_3HgOH solution, Aldrich) was then added to each soil suspension to make the final Hg concentration 2×10^{-7} or 1×10^{-6} M. The pH of each suspension was then adjusted to cover a range of 3 to 10 using 0.1 M HNO_3 or 0.1 M NaOH . The centrifuge tubes were capped with Teflon caps and shaken for 24 hours at a rate of 50 strokes per minute on a reciprocating shaker (Fisher Scientific, Model 224) at $25 \pm 1^\circ\text{C}$. After equilibration, the soil was separated from solution by centrifugation for 25 minutes at 1300 g. The concentrations of methylmercury in the supernatants were then determined by cold vapor atomic absorbance spectrophotometry (Perkin Elmer MHS-10 coupled with Perkin Elmer AA-5000) using NaBH_4 as the reducing agent. Sodium borohydride can cleave the C-Hg bond and release Hg(II) for reduction (Goulden and Anthony, 1980; Oda and Ingle, 1981). The amount of methylmercury adsorbed was calculated as the difference of the initial Hg concentration and that remaining in the solution after

equilibration. Following the same procedure described above, adsorption of 2×10^{-7} M methylmercury on pure SiO_2 (Davison Chemical, Mesh size: 28 - 200 μm) as a function of pH was investigated to understand adsorption mechanisms.

The effect of Cl^- on methylmercury adsorption was investigated with the addition of 1×10^{-3} M Cl^- (from NaCl) to each soil suspension. An initial methylmercury concentration of 2×10^{-7} M was used and the same procedure described above was followed. The concentration of NaNO_3 was adjusted to maintain a constant ionic strength of 0.01 M. The effect of Ca^{2+} on methylmercury adsorption was examined for two soils, Penn silt loam and Freehold sandy loam (B horizon), as a function of pH. Two Ca^{2+} concentrations, 1.0×10^{-4} M and 3.3×10^{-3} M, were employed, and the ionic strength was kept as 0.01 M by adjusting the concentration of NaNO_3 .

To evaluate the effect of dissolved organic matter (DOM) on adsorption, we added DOM extract to suspensions of silica or Penn silt loam. DOM was extracted from Rockaway stony loam with dilute NaOH . The initial methylmercury concentration was 2×10^{-7} M and the concentrations of added DOM ranged from 0 to 50 mg L^{-1} . The experiments were conducted at constant pH of 7.59 ± 0.08 for silica and 6.49 ± 0.06 for Penn silt loam at an ionic strength of 0.01 M NaNO_3 .

7.4 Results and Discussion

Adsorption of methylmercury from a 2×10^{-7} M solution as a function of pH is shown in Figures 7.1a-d. Maximum adsorption occurred at pH around 6 for all soils. Adsorption increased from 15 - 41% at pH 3.5 to 42 - 73% at pH 6.0 and then

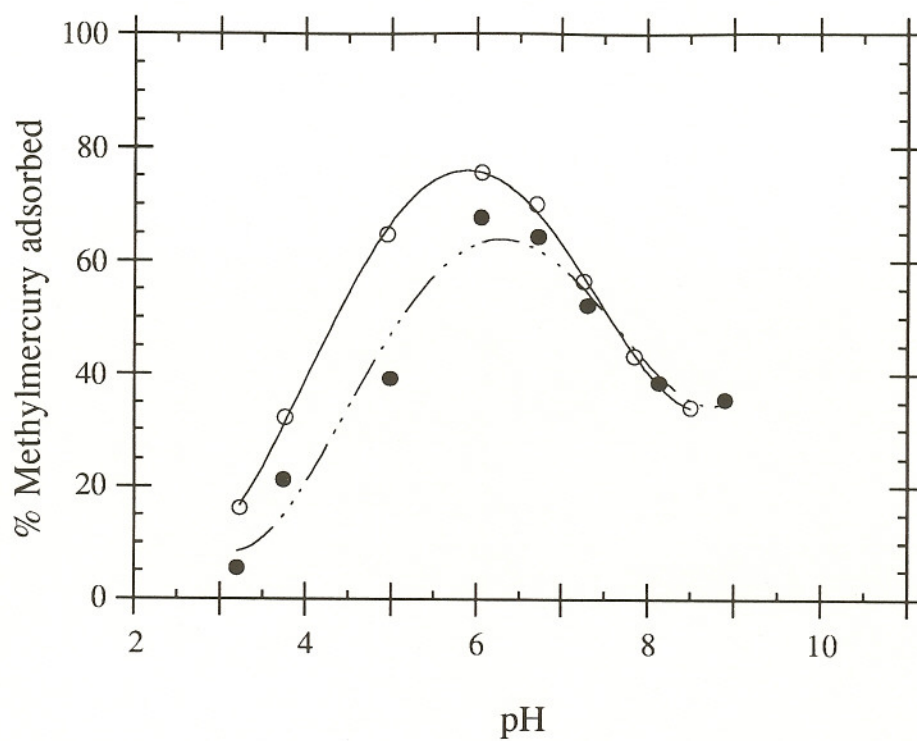


Figure 7.1a Adsorption of $2 \times 10^{-7} \text{ M}$ methylmercury on Penn silt loam as a function of pH. Soil:water = $0.4 \text{ g } 40 \text{ mL}^{-1}$; $I = 0.01 \text{ M NaNO}_3$; $T = 25 \pm 1^\circ\text{C}$. Solid line: no Cl^- addition; dashed line: $1 \times 10^{-3} \text{ M Cl}^-$ addition.

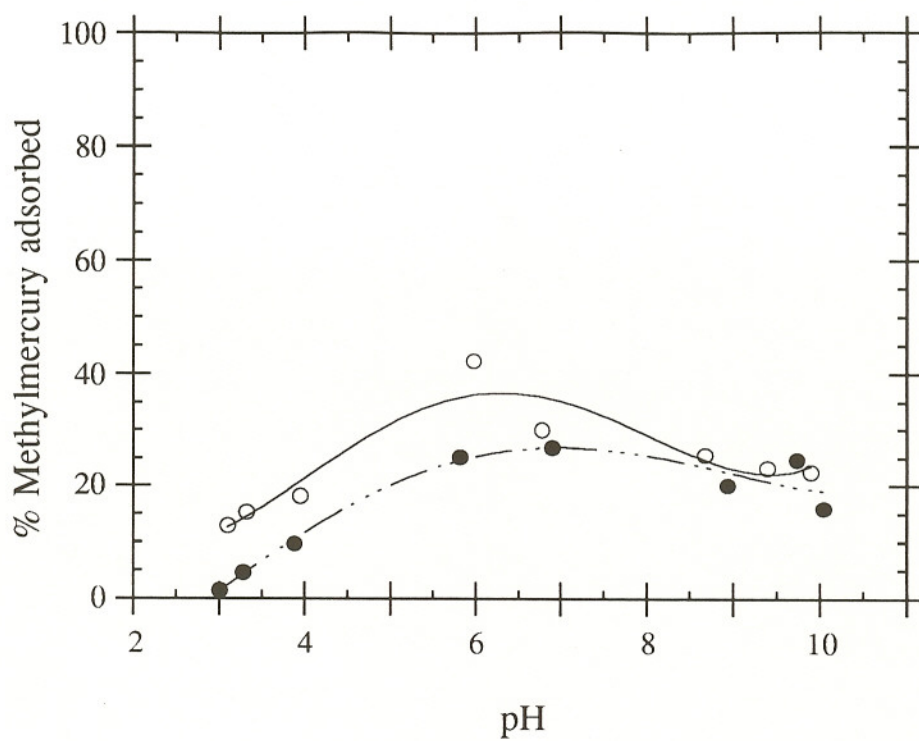


Figure 7.1b Adsorption of $2 \times 10^{-7} \text{ M}$ methylmercury on Freehold sandy loam (A horizon) as a function of pH. Soil:water = $0.4 \text{ g } 40 \text{ mL}^{-1}$; $I = 0.01 \text{ M NaNO}_3$; $T = 25 \pm 1^\circ\text{C}$. Solid line: no Cl^- addition; dashed line: $1 \times 10^{-3} \text{ M Cl}^-$ addition.

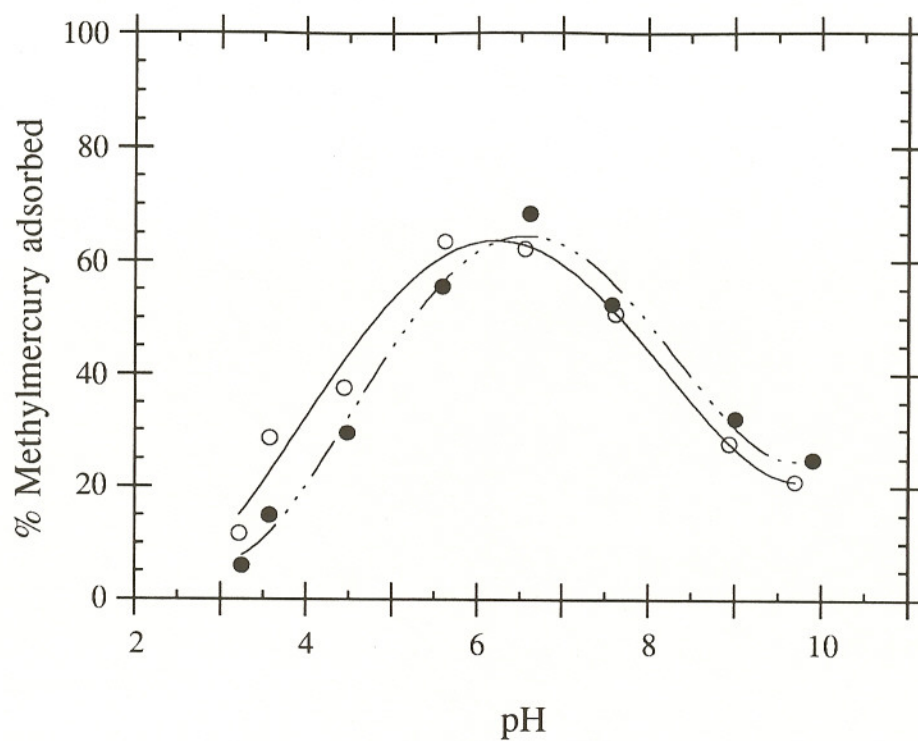


Figure 7.1c Adsorption of $2 \times 10^{-7} \text{ M}$ methylmercury on Freehold sandy loam (B horizon) as a function of pH. Soil:water = $0.4 \text{ g } 40 \text{ mL}^{-1}$; $I = 0.01 \text{ M NaNO}_3$; $T = 25 \pm 1^\circ\text{C}$. Solid line: no Cl^- addition; dashed line: $1 \times 10^{-3} \text{ M Cl}^-$ addition.

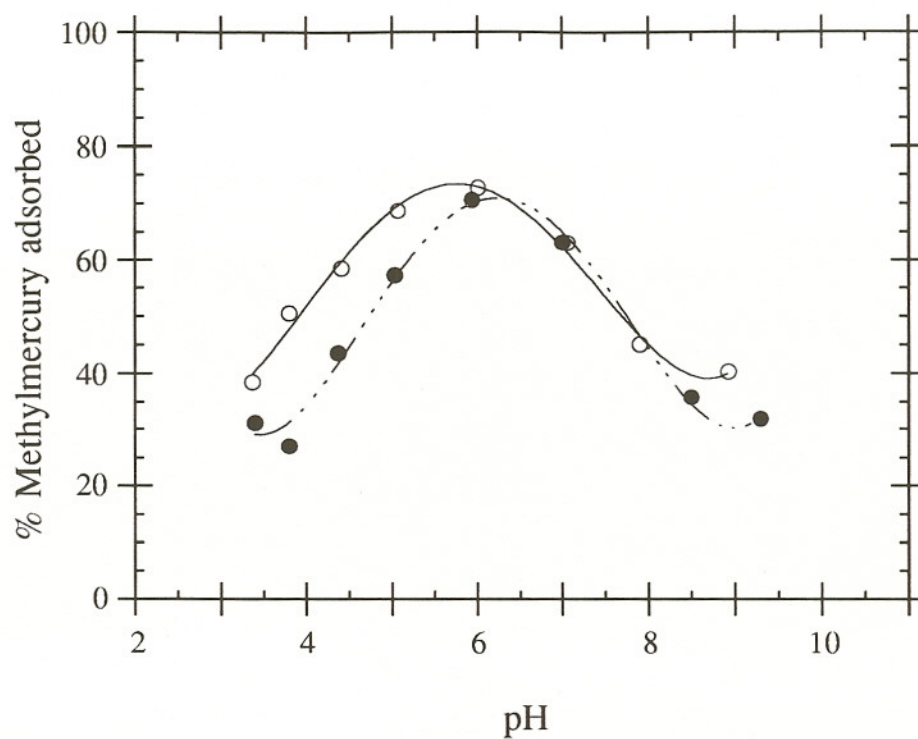


Figure 7.1d Adsorption of 2×10^{-7} M methylmercury on Rockaway stony loam as a function of pH. Soil:water = $0.4 \text{ g } 40 \text{ mL}^{-1}$; $I = 0.01 \text{ M NaNO}_3$; $T = 25 \pm 1^\circ\text{C}$. Solid line: no Cl^- addition; dashed line: $1 \times 10^{-3} \text{ M Cl}^-$ addition.

decreased to 25 - 41% at pH 8.5. Both higher silt and clay contents and organic matter content resulted in greater adsorption. Freehold sandy loam (A horizon) has the lowest organic matter content (1.2 g C kg⁻¹) and silt plus clay content. (80 g kg⁻¹). The maximum adsorption of methylmercury on this soil is only 42%. Penn silt loam also contains a very small amount of organic matter (7.5 g C kg⁻¹), but has very high silt plus clay content (750 g kg⁻¹). The maximum adsorption of methylmercury on this soil is 73%, which is similar to that on the Rockaway stony loam, a very high organic matter soil (28.4 g C kg⁻¹).

Both solution chemistry and soil surface charge controlled soil-water partitioning of methylmercury. In solution phase, the following equilibria (Stumm and Morgan, 1981) determined methylmercury speciation in the presence of dissolved organic ligands:



Based on the stability constants and Cl⁻ concentrations (1 × 10⁻⁶ M to 1 × 10⁻⁵ M) determined by ion chromatography (DIONEX Co. using an ASM-3 column), we calculated methylmercury speciation in the solutions of this study using the MINEQL⁺ computer program (Schecher and McAvoy, 1991). As shown in Figure 7.2, at pH around 3, major species are CH₃Hg⁺ and CH₃HgCl. Due to the high positive surface potential at low pH, CH₃Hg⁺ is expected to be poorly adsorbed. CH₃HgCl has also been reported to be weakly adsorbed by inorganic surfaces and most organic functional groups (Reimers and Krenkel, 1974). Consequently, adsorption at low pH values was

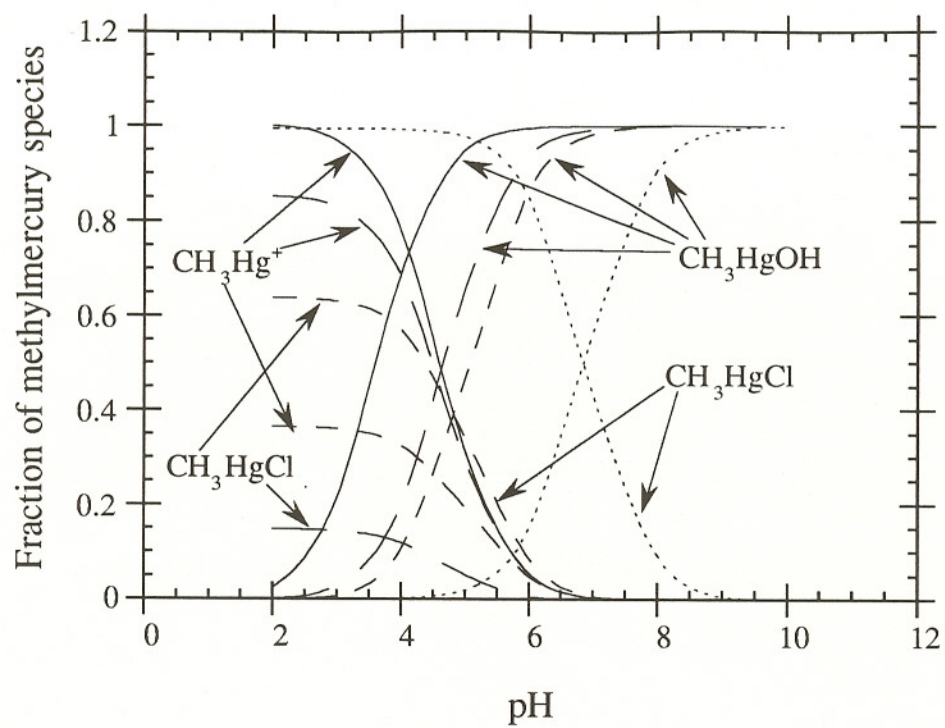


Figure 7.2 Methylmercury speciation as a function of pH and Cl^- . Solid lines: $\text{Cl}^- = 0$; long dashed lines: $\text{Cl}^- = 1 \times 10^{-6} \text{ M}$; short dashed lines: $\text{Cl}^- = 1 \times 10^{-5} \text{ M}$; dotted lines: $\text{Cl}^- = 1 \times 10^{-3} \text{ M}$.

small. As pH increased, the surface potential became more negative, which may result in increases in adsorption of CH_3Hg^+ to surfaces. Consequently, adsorption increased. At pH greater than 6, adsorption decreased. There are two possibilities for the decreases of adsorption at higher pH values. One is that only CH_3Hg^+ was strongly adsorbed to solid surfaces. When the hydroxo methylmercury species CH_3HgOH became predominant and the concentration of CH_3Hg^+ became very small at pH above 6, adsorption started to decrease. The other possibility is that some soluble ligands formed complexes with methylmercury and decreased adsorption.

We tested the first possibility by conducting adsorption experiments with pure silica as the adsorbent. The results are shown in Figure 7.3. Silica has a very low zero point of charge of 2 to 3 (Li and Bruyn, 1966; James and Healy, 1972). If only CH_3Hg^+ can be strongly adsorbed by the silica surface, adsorption should abruptly increase at pH above 3 when proton competitive binding for available surface sites significantly decreased, and then decrease at a certain pH value where CH_3HgOH became more stable relative to surface- CH_3Hg^+ complexes. In contradiction to this hypothesis, adsorption increased at pH above 3 and reached maximum of about 92% at pH about 6.5 when almost all soluble methylmercury became CH_3HgOH (Figure 7.2), and then remained high adsorption until pH 9.6. This clearly suggests that CH_3HgOH can be equally or even more strongly adsorbed than is CH_3Hg^+ . The decreases in adsorption of methylmercury by soils at pH above 6 were therefore not likely caused by the dominance of CH_3HgOH in the aqueous phase.

In Chapter 3, we showed that increasing pH resulted in increases in dissolved organic matter. The complexation of Hg(II) by the dissolved organic matter caused

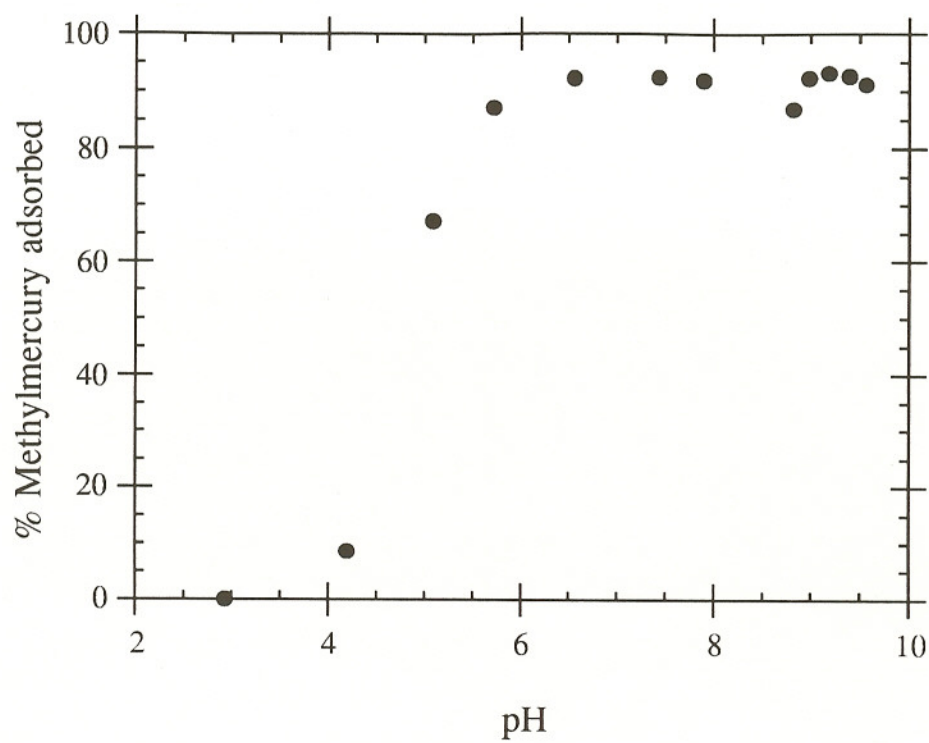


Figure 7.3 Adsorption of 2×10^{-7} M methylmercury on silica as a function of pH. Silica:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 1°C.

adsorption to significantly decrease with increasing pH. Similarly, we speculated that increases of dissolved organic matter with pH resulted in decreases of adsorption of methylmercury by soils. We tested this hypothesis by adding dissolved organic matter to silica or Penn silt loam suspensions at fixed pH as described previously. As shown in Figure 7.4, when the added dissolved organic C increased from 0 to 50 mg L⁻¹, adsorption of methylmercury decreased from 90% to 70% of the added methylmercury on silica and from 67% to 22% on Penn silt loam. These results indicate that the dissolved organic matter formed unadsorbable complexes with methylmercury, which decreased adsorption.

When 1×10^{-3} M Cl⁻ was added to soil suspensions, adsorption decreased at pH less than 7 (Figures 7.1a-d) because of the competitive binding of Cl⁻ and soil surfaces for methylmercury. At pH above 7, hydroxo methylmercury species CH₃HgOH became predominant (Figure 7.2). Consequently, adsorption did not change with addition of Cl⁻. At pH less than 5, almost all aqueous methylmercury was calculated to be present as CH₃HgCl in the presence of 1×10^{-3} M Cl⁻ in solution. However, adsorption continuously increased from pH 3 to 5. Again, this indicated the competitive binding of protons and methylmercury for the available surface sites. Increases in pH weakened proton binding and increased methylmercury binding. At pH around 3, addition of 1×10^{-3} M Cl⁻ decreased methylmercury adsorption on Freehold sandy loam (A or B horizon) and Penn silt loam to about 0 - 5%. However, adsorption on Rockaway stony loam at pH 3 in the presence of 1×10^{-3} M Cl⁻ was more than 25%. This possibly because Rockaway stony loam contains more organic matter which has greater fractional high energy sites.

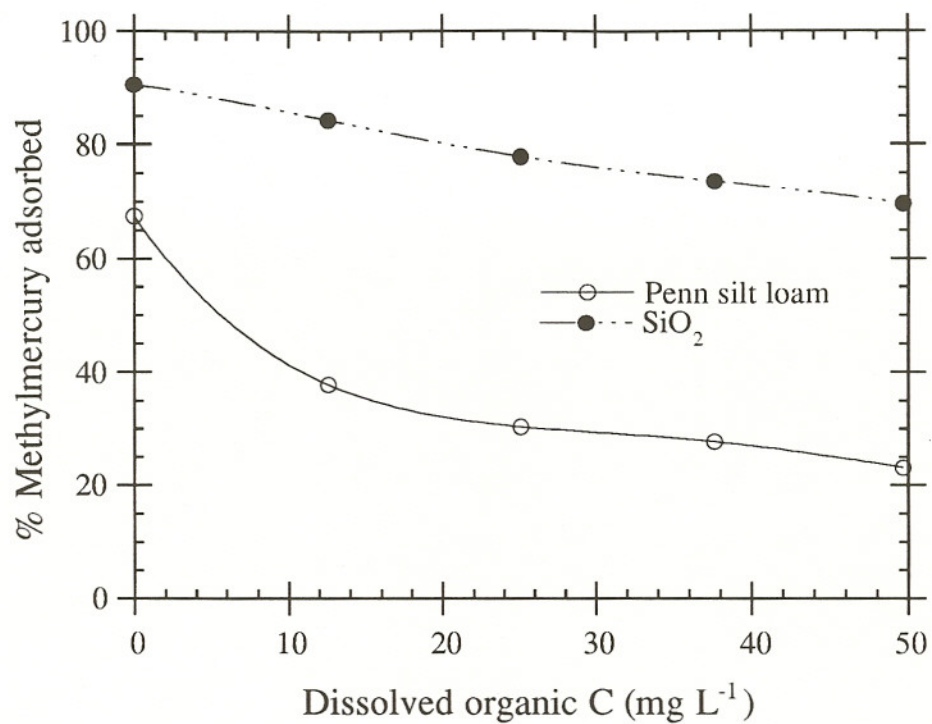


Figure 7.4 Effect of dissolved organic matter on adsorption of 2×10^{-7} M methylmercury. Solid:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = $25 \pm 1^\circ\text{C}$. Experimental pH was 7.59 ± 0.08 for silica and 6.49 ± 0.06 for Penn silt loam.

Besides pH and Cl^- , the background electrolyte has frequently been reported to affect the partition of metals to soil. Zachara *et al.* (1993) investigated Cd(II) adsorption on specimen and soil smectites in sodium and calcium electrolytes and found that ion exchange dominated Cd adsorption at low ionic strength in Na^+ electrolyte. Increasing Na^+ concentration to 0.1 M or changing the electrolyte to Ca^{2+} at an ionic strength of 0.003 to 0.006 M suppressed Cd ion exchange. In Chapter 3, we compared Hg(II) adsorption on soils in NaNO_3 and $\text{Ca}(\text{NO}_3)_2$ electrolytes (ionic strength = 0.01 M) at a range of pH, and found that adsorption in both electrolytes was similar at low pH, but more Hg was adsorbed from the Ca^{2+} electrolyte at higher pH (> 5). Higher Hg adsorption from the Ca^{2+} electrolyte mainly resulted from a smaller extent of dissolution of organic matter, which consequently reduced the effect of dissolved organic matter on Hg adsorption. Similar results were reported by Thanabalasingam (1985) for the adsorption of Hg(II) on humic acid. They observed that adsorption at pH 3 to 5 was similar for all electrolytes used. As pH further increased, adsorption in Na^+ and 0.01 M NH_4^+ electrolytes decreased but remained unchanged in 0.01 M Ca^{2+} or Mg^{2+} or 0.0001 M NH_4^+ .

In this study, we investigated the effect of Ca^{2+} on methylmercury adsorption at a pH range of 3 to 10 as previously described. As shown in Figures 7.5a, b, adsorption in the presence of 1×10^{-4} M Ca^{2+} was no different from that when 0.01 M NaNO_3 was the sole electrolyte. However, when the NaNO_3 electrolyte was replaced with $\text{Ca}(\text{NO}_3)_2$ and the ionic strength was still maintained at 0.01 M, adsorption increased at $\text{pH} < 6$ but maintained constant at higher pH values.

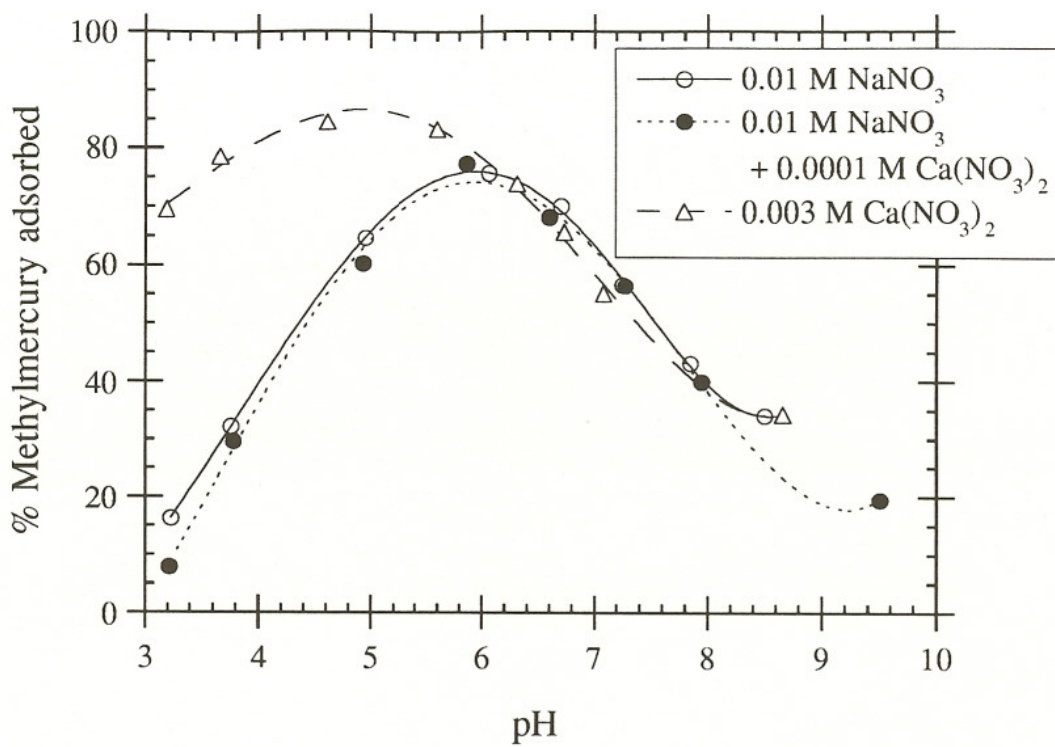


Figure 7.5a Effect of Ca^{2+} on adsorption of 2×10^{-7} M methylmercury on Penn sil loam as a function of pH. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M; T = $25 \pm 1^\circ\text{C}$.

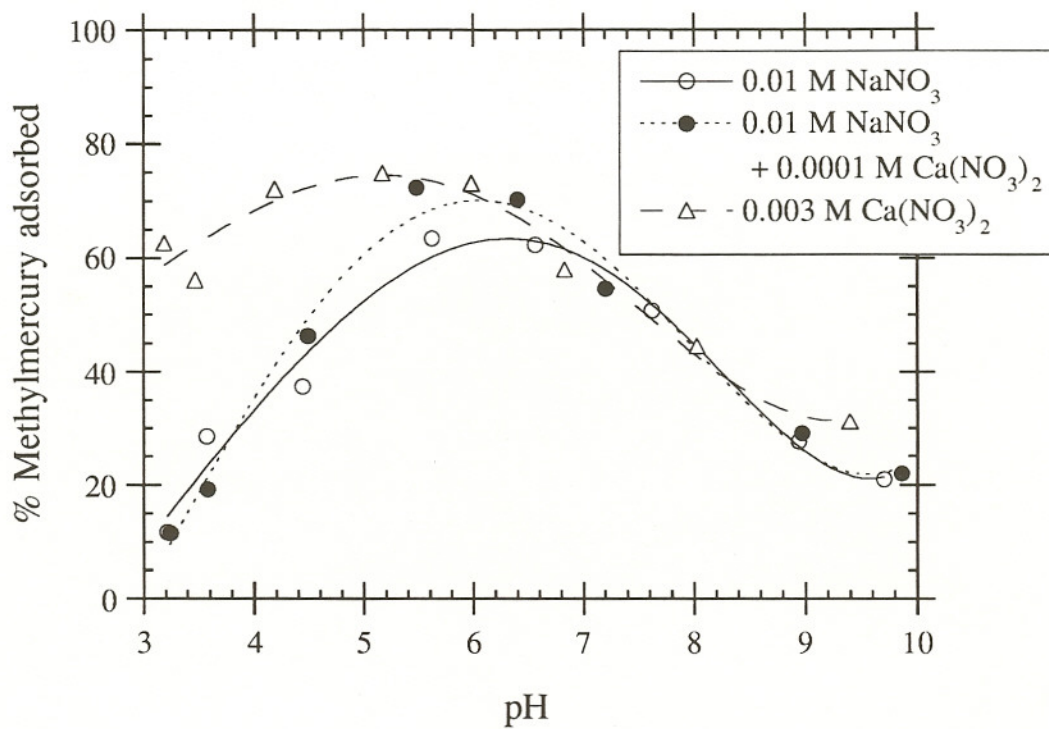


Figure 7.5b Effect of Ca^{2+} on adsorption of 2×10^{-7} M methylmercury on Freehold sandy loam (B horizon) as a function of pH. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M; T = $25 \pm 1^\circ\text{C}$.

We measured the concentrations of the dissolved organic matter and the results are shown in Figures 7.6a, b. The concentrations of the dissolved organic matter in both 0.01 M NaNO_3 and 0.01 M NaNO_3 plus 0.0001 M $\text{Ca(NO}_3)_2$ were similar. The higher Ca^{2+} concentration (0.003 M), however, caused significant decreases in the concentrations of the dissolved organic matter at any fixed pH value above 6. Ca^{2+} could reduce dissolution of organic matter by either coagulation or complexation in which Ca^{2+} served as a bridge between solid surfaces and organic matter (Schnitzer 1986). Unlike adsorption of Hg(II) (Chapter 3), decreases of the dissolved organic matter in 0.003 M $\text{Ca(NO}_3)_2$ did not change methylmercury adsorption at pH above 6. This probably resulted from preferential dissolution (independent of electrolyte) of S-containing organic functional groups, which have been reported to be the only efficient groups on organic matter for binding methylmercury (Reimers and Krenkel 1974).

Based on the results of this study, we are unable to make a definite conclusion on the mechanisms by which adsorption of methylmercury increased in 0.003 M $\text{Ca(NO}_3)_2$ at $\text{pH} < 6$. One possible reason could be that a significant amount of soluble methylmercury was associated with the dissolved S-containing organic functional groups at $\text{pH} < 6$. When Ca^{2+} was present at a high concentration (0.003 M), Ca^{2+} caused the solubility of the S-containing organic groups to significantly decrease at low pH values, which eventually resulted in increases in adsorption. If this is the case, for a given electrolyte, increasing the initial Hg concentration would result in an increase in the fractional adsorption due to the limited capacity of soluble ligands. Because the amount of dissolved organic matter at low pH was much smaller

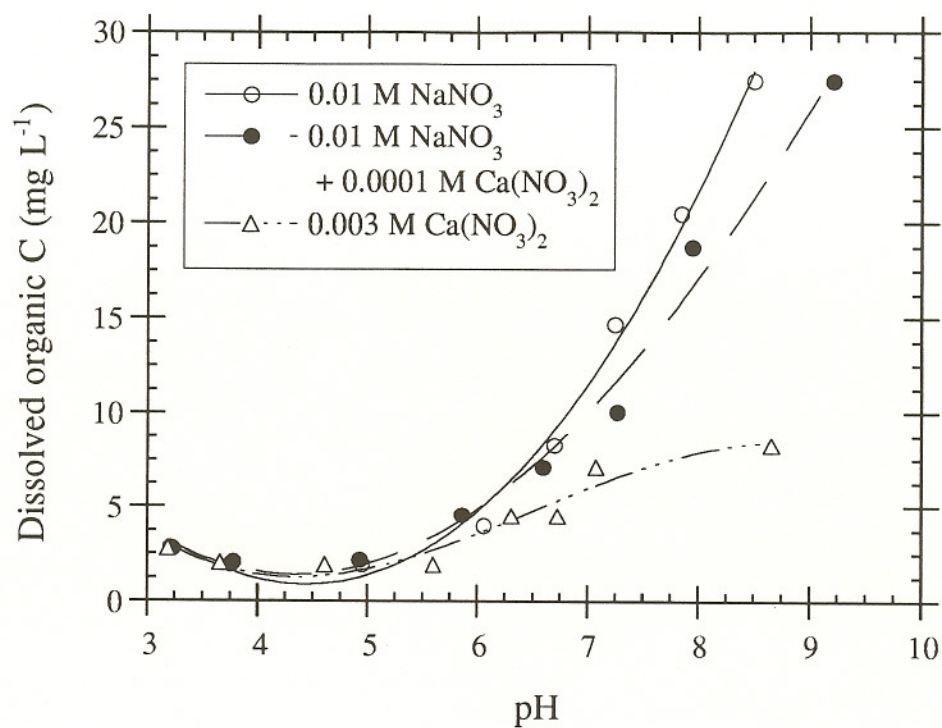


Figure 7.6a Concentrations of the dissolved organic C in suspensions of Penn silt loam as a function of pH and Ca^{2+} concentration. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M; T = 25 ± 1°C.

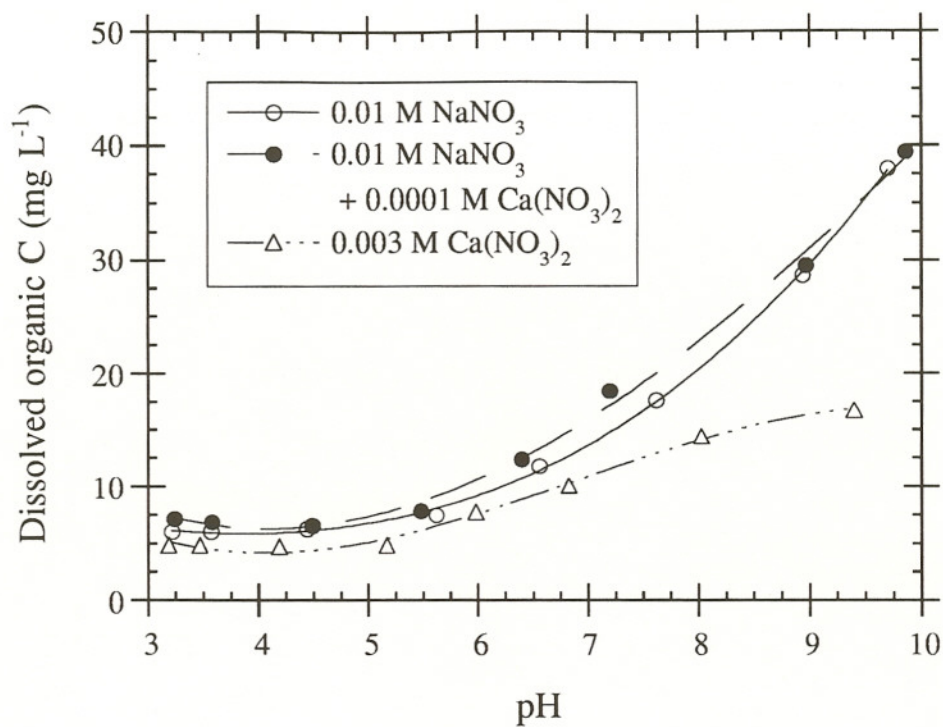


Figure 7.6b Concentrations of the dissolved organic C in suspensions of Freehold sandy loam (B horizon) as a function of pH and Ca^{2+} concentration. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M; T = 25 ± 1°C.

than that at high pH values, increasing the initial Hg concentration would increase adsorption to a greater extent at low pH than that at high pH values.

We tested the above hypothesis by conducting adsorption experiments at a higher initial methylmercury concentration of 1×10^{-6} M. As shown in Figures 7.7a-c, increasing the initial Hg concentration from 2×10^{-7} to 1×10^{-6} M increased adsorption over almost the entire pH range employed in this study. As expected, adsorption increased to a greater extent at $\text{pH} < 6$ than that at higher pH values. For Rockaway stony loam, adsorption from a 1×10^{-6} M solution was even smaller than that from a 2×10^{-7} M solution at pH above 8. This probably resulted from the larger concentrations of the dissolved organic matter ($> 40 \text{ mg L}^{-1}$) in the solutions of Rockaway stony loam at pH above 8.

7.5 Summary and Conclusions

Adsorption of methylmercury followed an upside bow shape as a function of pH. Maximum adsorption occurred at pH around 6. Both larger silt plus clay content and organic matter content resulted in greater adsorption. Smaller adsorption at $\text{pH} < 6$ mainly resulted from the competitive binding of protons for available surface sites and the competitive binding of soluble ligands (Cl^- and organic ligands) for methylmercury. Decreases in adsorption at higher pH values, however, mainly resulted from the complexation of methylmercury by soluble organic ligands whose concentration increased with pH. Addition of Cl^- decreased adsorption at low pH where CH_3HgCl was dominant over CH_3HgOH , and did not change adsorption at higher pH when CH_3HgOH became predominant. The presence of a low

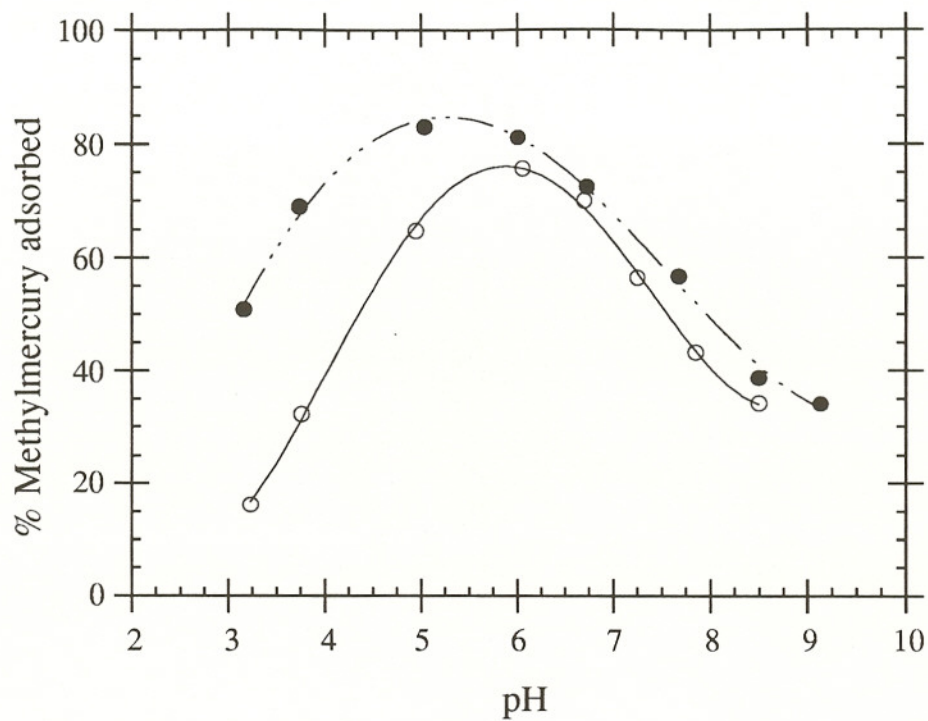


Figure 7.7a Comparison of methylmercury adsorption on Penn silt loam from 2×10^{-7} and 1×10^{-6} M solutions. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 1°C. Solid line: 2×10^{-7} M; dashed line: 1×10^{-6} M.

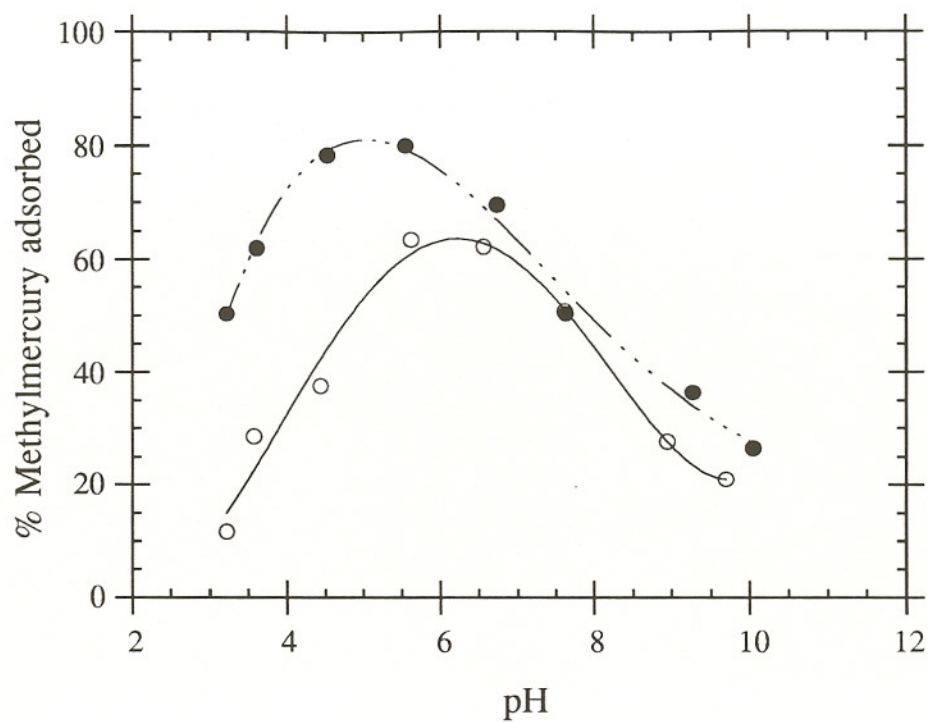


Figure 7.7b Comparison of methylmercury adsorption on Freehold sandy loam (B horizon) from 2×10^{-7} and 1×10^{-6} M solutions. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 1°C. Solid line: 2×10^{-7} M; dashed line: 1×10^{-6} M.

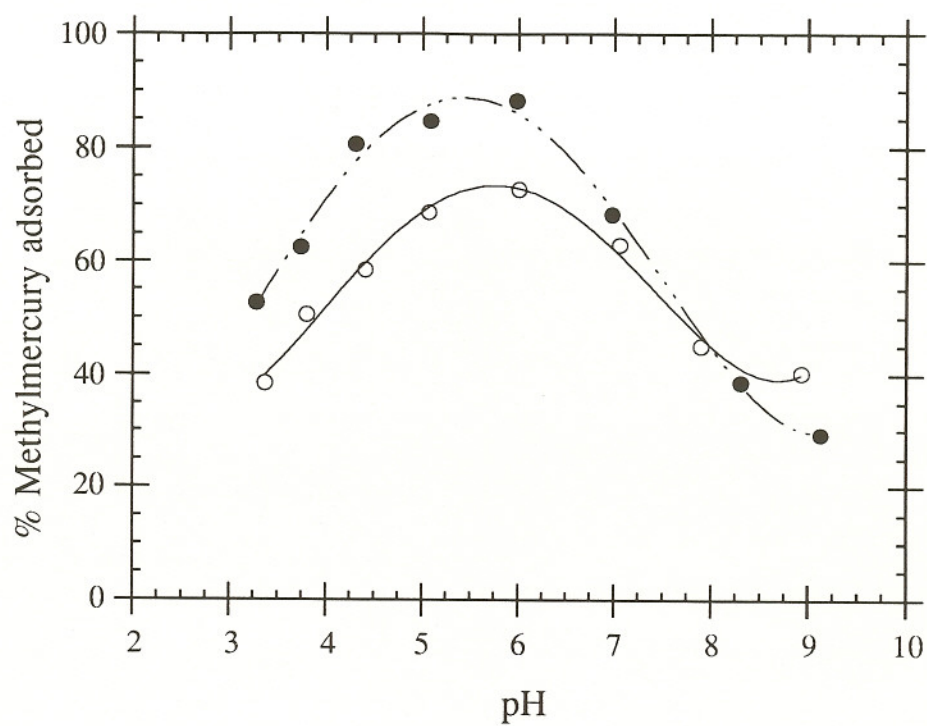


Figure 7.7c Comparison of methylmercury adsorption on Rockaway stony loam from 2×10^{-7} and 1×10^{-6} M solutions. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 1°C. Solid line: 2×10^{-7} M; dashed line: 1×10^{-6} M.

concentration of Ca^{2+} ($\leq 1 \times 10^{-4}$ M) had no effect on methylmercury adsorption. However, a high concentration of Ca^{2+} caused adsorption to increase at $\text{pH} < 6$, but had no effect at higher pH. This probably resulted from the preferential decrease in the solubility of the S-containing organic functional group, an efficient methylmercury binding group, caused by Ca^{2+} at $\text{pH} < 6$.

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Chapter 8

PREDICTION OF SOIL-WATER PARTITION OF MERCURY(II) AND METHYLMERCURY AS A FUNCTION OF pH

8.1 Abstract

In this chapter, we presented a model describing soil-water partitioning of Hg(II) and methylmercury as function of pH. The model was derived based on the interactions of mercury with both soil solid surfaces and the dissolved organic matter. The competitive binding of protons for the available sites on both solids and the dissolved organic matter were considered. The model predicted concentration values agree very well with those measured for each soil with a regression coefficient $R^2 \geq 0.911$ and the residual mean square ≤ 0.0036 . Based on the parameters obtained by the model fitting for each soil, a universal equation was derived by correlating the model fitting parameters with the soil properties. With the universal equation, adsorption of Hg(II) and methylmercury on all tested soils over a pH range of 3 to 10 was described.

8.2 Introduction

Partitioning of metals in soils is subject to the effects of many processes, adsorption, desorption, precipitation, and co-precipitation (Sposito, 1981; Sparks, 1995). For trace metals, their solution activities in soils are usually below those levels at which precipitation occurs (Barrow *et al.*, 1981; Medrano and Jurinak, 1975; Hem,

1972). Partition of trace metals in soils is therefore generally described in terms of adsorption/desorption. Both empirical and theoretical models have been developed to describe adsorption of trace metals on soils and soil components. Among the empirical models, the Langmuir and Freundlich equations have been most frequently used. The basic limitation of these models is that they can not account for the effects of ionic strength, pH, and soluble ligands on adsorption.

To account for the competitive binding of protons with metal species for surface sites, Huang *et al.* proposed a modified Langmuir equation in which the proton competing constant was incorporated (Huang, 1984; Huang *et al.*, 1984). They reported that the modified Langmuir equation described metal adsorption very well over a wide pH range. This model does not account for the effects of soluble ligands on adsorption.

A number of surface complexation models have also been developed to describe adsorption as a function of pH. The basis of these models is the constant capacity model which was developed based on the double layer theory (Schindler *et al.*, 1976; Stumm *et al.*, 1976). Modification of this model resulted in the development of four related models, including the triple layer model, the Stern variable surface charge-variable surface potential (VSC-VSP) model, and the one-pK model (Goldberg, 1992). Among these modified models, the triple layer model (Davis and Leckie, 1978, 1980; Hayes and Leckie, 1986, 1987), which incorporates ionic strength into the model, has been most frequently used. The surface complexation models were developed from well defined pure mineral-water systems. They have been used to successfully describe adsorption of metals on soil colloids.

The application of these models to soil, a heterogeneous system consisting of various kinds of minerals and organic matter, is still under study. The use of these models requires a knowledge of the total binding sites on a soil and the surface protonation and deprotonation constants. These parameters, together with the stability constants for metal binding to soil surfaces obtained by model fitting, are generally soil specific.

In attempt to obtain a generalized equation to predict metal partitioning in soil on a large number of soils basis, researchers tried to correlate adsorption with soil properties and pH. For example, Schulte and Beese (1994) divided 16 soils used in their study into three groups based on the soil buffered pH range, and showed that by normalization of the amount of Cd adsorbed with soil specific surface area, adsorption isotherms on all soils in each group could be described by a generalized equation. Christensen (1989) correlated partition coefficients of Cd with pH for 63 soils and reported a regression coefficient R^2 of 0.63. More recently, Lee *et al.* (1996) demonstrated that soil-water partition coefficients of Cd correlated with soil organic matter content very well at fixed pH. After normalizing the partition coefficients with soil organic matter content, an excellent correlation between the normalized partition coefficients and pH ($R^2 = 0.92$) was obtained.

As shown in previous studies (Chapters 3-7; Yin *et al.*, 1996a-d), adsorption of Hg(II) and methylmercury is not only governed by the reaction of Hg with the particulate phase, but also significantly affected by the soluble organic matter. Dissolution of organic matter depends on the content of SOC in soil, the pH, and soil inorganic components that bind with organic matter. The interactions of Hg with soluble organic matter and both particulate inorganic components and organic matter

make modeling of Hg adsorption on soils very complicated. No simple correlation between Hg partition coefficients with soil properties was found. In this chapter, we developed a model, which incorporated the interactions of Hg with both the particulate phase and dissolved organic matter, to describe adsorption of Hg(II) and methylmercury on soils as a function of pH. One site was assumed each for the particulate phase and the dissolved organic matter. Competitive binding of protons for the available sites on both particulates and the dissolved organic matter was considered.

8.3 Model Development

It has been frequently reported that the interactions of metals with natural material, such as organic matter, at low pH values can be well described by consideration of aquo metal ions M^{2+} alone (Dobbs *et al.*, 1989a, b; Grimm *et al.*, 1991). At higher pH, however, hydroxo metal species need to be considered in order to fit the experimental data (Tipping, 1993; Westall *et al.*, 1995). For mercury, we have previously demonstrated that the aquo Hg species is not the only species that can bind to the soluble organic matter and soil surfaces at high pH (Chapter 6, 7; Yin *et al.*, 1996d). In this study, we assume that both aquo mercury species and hydroxo mercury species ($HgOH^+$, $Hg(OH)_2$, and CH_3HgOH) react with soil solids and the soluble organic matter. The effect of Cl^- on adsorption is neglected due to its small concentration ($< 10^{-5}$ M). The binding constants for all Hg species are assumed to be equal. A similar assumption was made by Tipping (1993, 1994b) in modeling metal binding by humic substances with the model WHAM. He assumed that both aquo metal ions (M^{2+}) and MOH^+ are involved in the reaction, and the equilibrium

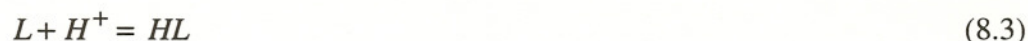
constants for both species have the same value. With this assumption, he successfully modeled the binding of many metals with humic substances.

Assume that Hg reacts with both solid surfaces and the dissolved organic matter to form 1:1 complexes. The reaction between Hg and the dissolved organic matter can be expressed as:



$$K_{HgL} = \frac{[HgL]}{[Hg][L]} = \frac{C_w - [Hg]}{[Hg][L]} \quad (8.2)$$

where L is the organic ligand, Hg is the soluble Hg unbound by organic ligand, HgL is the Hg bound by organic ligand, $[]$ denotes concentration ($\mu\text{mol L}^{-1}$), K_{HgL} is the stability constant for Hg binding with ligand ($\text{L } \mu\text{mol}^{-1}$), and C_w is the total aqueous mercury concentration ($\mu\text{mol L}^{-1}$). The protonation reaction of L is:



$$K_{HL} = \frac{[HL]}{[H^+][L]} \quad (8.4)$$

where HL is protonated ligand and K_{HL} is the stability constant for proton binding ($\text{L } \mu\text{mol}^{-1}$). The total concentration of dissolved organic ligand which is represented by DOC ($\mu\text{mol C L}^{-1}$) is:

$$DOC = [L] + [HL] + [HgL] \quad (8.5)$$

Since the initial mercury concentrations used for the adsorption edge study ($\leq 1 \times 10^{-6}$ M) was 100 more times less than *DOC* concentrations ($> 1 \times 10^{-4}$ M), the term $[HgL]$ in equation 8.5 can be neglected, which yields:

$$TOC \cong [L] + [HL] \quad (8.6)$$

Substitute equations 8.2 and 8.4 into 8.6 and rearrange, we have:

$$[Hg] = \frac{C_w}{1 + K_{HgL} \frac{DOC}{1 + K_{HL}[H^+]}} \quad (8.7)$$

The reaction of Hg with solid surface can be expressed as :



$$K_{\equiv SOHg} = \frac{[\equiv SOHg]}{[\equiv SO^-][Hg]} \quad (8.9)$$

where $\equiv SO^-$ is the surface binding site, $\equiv SOHg$ is the Hg adsorbed by the surface, and $K_{\equiv SOHg}$ is the binding constant of Hg with solid surface ($L \mu mol^{-1}$). The protonation reaction of the surface site is:



$$K_{\equiv SOH} = \frac{[\equiv SOH]}{[\equiv SO^-][H^+]} \quad (8.11)$$

where $\equiv\text{SOH}$ is the protonated surface site and $K_{\equiv\text{SOH}}$ is the proton binding constant ($\text{L } \mu\text{mol}^{-1}$). The total surface site density Γ_t ($\mu\text{mol L}^{-1}$) is:

$$\Gamma_t = [\equiv\text{SO}^-] + [\equiv\text{SOH}] + [\equiv\text{SOHg}] \quad (8.12)$$

The third term in equation 8.12 can be neglected compared to the total surface binding sites due to low mercury loading. This gives:

$$\Gamma_t \cong [\equiv\text{SO}^-] + [\equiv\text{SOH}] \quad (8.13)$$

Substitute equations 8.9 and 8.11 into 8.13 and rearrange, we have:

$$[\equiv\text{SOHg}] = \frac{K_{\equiv\text{SOHg}}\Gamma_t[\text{Hg}]}{1 + K_{\equiv\text{SOH}}[\text{H}^+]} \quad (8.14)$$

Substitution of equation 8.7 into 8.14 yields:

$$[\equiv\text{SOHg}] = \frac{K_{\equiv\text{SOHg}}\Gamma_t C_w}{(1 + K_{\equiv\text{SOH}}[\text{H}^+])(1 + K_{\text{HgL}} \frac{\text{DOC}}{1 + K_{\text{HL}}[\text{H}^+]})} \quad (8.15)$$

In equation 8.15, there are three variables, C_w , $[\text{H}^+]$, and DOC . All of them can be experimentally determined. The dependent variable $[\equiv\text{SOHg}]$ can be calculated by equation 8.16:

$$[\equiv\text{SOHg}] = T_{\text{Hg}} - C_w \quad (8.16)$$

where T_{Hg} is the initial mercury concentration. Substitution of equation 8.16 into 8.15 yields:

$$T_{\text{Hg}} - C_w = \frac{K_{\equiv\text{SOHg}}\Gamma_t C_w}{(1 + K_{\equiv\text{SOH}}[H^+])(1 + K_{\text{HgL}} \frac{DOC}{1 + K_{\text{HL}}[H^+]})} \quad (8.17)$$

By rearranging equation 8.17, we have:

$$C_w = \frac{1 + K_{\text{HL}}[H^+] + K_{\text{HgL}}DOC}{1 + K_{\text{HL}}[H^+] + K_{\text{HgL}}DOC + K_{\equiv\text{SOHg}}\Gamma_t \frac{1 + K_{\text{HL}}[H^+]}{1 + K_{\equiv\text{SOH}}[H^+]}} T_{\text{Hg}} \quad (8.18)$$

The dependent variable C_w in equation 8.18 will be minimized during a non-linear least square regression based on the known quantity T_{Hg} and the experimentally determined DOC and $[H^+]$. We further define the product of two constants $K_{\equiv\text{SOHg}}$ and Γ_t as A , i.e.,

$$K_{\equiv\text{SOHg}}\Gamma_t = A \quad (8.19)$$

Substitution of equation 8.19 into 8.17 yields:

$$C_w = \frac{1 + K_{\text{HL}}[H^+] + K_{\text{HgL}}DOC}{1 + K_{\text{HL}}[H^+] + K_{\text{HgL}}DOC + A \frac{1 + K_{\text{HL}}[H^+]}{1 + K_{\equiv\text{SOH}}[H^+]}} T_{\text{Hg}} \quad (8.20)$$

8.4 Data Collection

We tested the model developed above with the adsorption edge data of Hg(II) (Table A.1-A.2) and methylmercury (Table A.3-A.4). Seven soils, Penn silt loam, Washington loam, Whippany silty clay loam, Freehold sandy loam (B horizon), Downer loamy sand, Boonton Union loam and Dunellen sandy loam, were chosen for

Hg(II), and four soils, Penn silt loam, Freehold sandy loam (A horizon), Freehold sandy loam (B horizon), and Rockaway stony loam, for methylmercury. Two initial concentrations, 1×10^{-7} and 1×10^{-6} M for Hg(II) and 2×10^{-7} and 1×10^{-6} M for methylmercury, were employed for the test. The experimental procedures and data collection for Hg(II) and methylmercury adsorption were described in Chapter 3 and Chapter 7, respectively. The initial mercury concentrations and the equilibrium concentrations of the total soluble organic C and aqueous mercury in soil suspensions at each pH value were used for model fitting.

8.5 Results and Discussion

8.5.1 Adsorption of Mercury(II)

We first tried to fit experimental data for adsorption of Hg(II) with equation 8.20. Preliminary fitting exercises indicated that under the experimental conditions, the competitive binding of protons with Hg(II) for the available solid surface sites can be neglected. Equation 8.20 can therefore be simplified as:

$$C_w = \frac{1 + K_{HL}[H^+] + K_{HgL}DOC}{1 + K_{HL}[H^+] + K_{HgL}DOC + A(1 + K_{HL}[H^+])} T_{Hg} \quad (8.21)$$

Adsorption data for Hg(II) on each soil as a function of pH for an initial concentration of 1×10^{-7} M was then fitted with equation 8.21. The model fitting parameters are listed in Table 8.1.

Table 8.1 Model fitting parameters for adsorption of Hg(II) on soils from a 1×10^{-7} M solution over a pH range of 3 to 10†

Soil No.	Soil Name	A	$K_{HL}^{\ddagger}$	$K_{HgL}^{\ddagger}$ ($\times 10^{-3}$)	R^2 §	RMS^*
3	Penn silt loam	8.38	0.20	13.50	0.981	0.0015
4	Whippany silty clay loam	11.13	0.30	14.30	0.981	0.0017
5	Washington loam	12.00	0.31	9.23	0.975	0.0019
7	Freehold sandy loam (B horizon)	10.01	0.41	5.14	0.979	0.0005
10	Downer loamy sand	4.33	0.30	5.86	0.911	0.0036
11	Boonton Union loam	41.36	0.41	13.50	0.943	0.0015
12	Dunellen sandy loam	7.44	0.29	15.20	0.979	0.0005
Average			0.32	10.96		0.0016

†Experimental data was fitted by equation 8.21.

‡In the unit of $L \mu mol^{-1}$.

§Regression coefficient for the predicted vs. measured soluble Hg concentrations.

*Residual mean square in $\mu mol L^{-1}$.

The predicted soluble Hg concentrations (C_w) agree very well with the observed for each soil with a regression coefficient (R^2) of ≥ 0.911 (Table 8.1). The residual mean square (RMS), which was calculated by equation 8.22, ranges from 0.0005 to 0.0036. The equality of the predicted and measured values is showed in Figure 8.1.

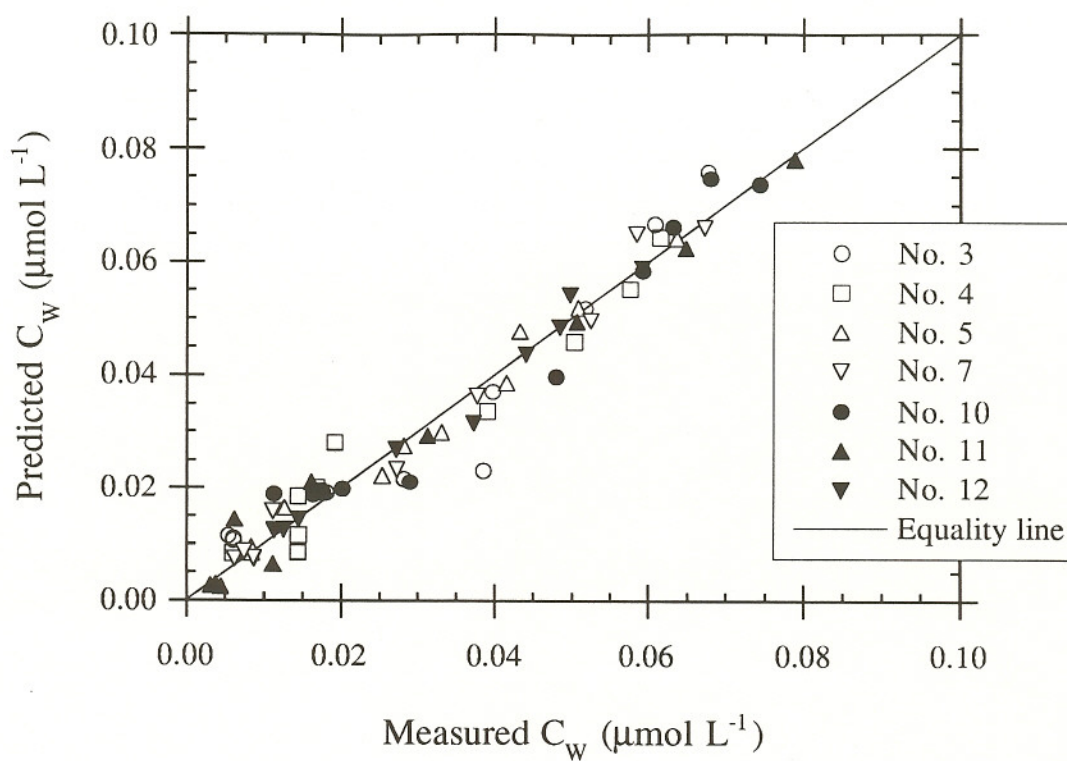


Figure 8.1 Predicted vs. measured soluble Hg(II) concentrations. The predicted values were calculated with equation 8.21 based on the parameters for each soil listed in Table 8.1. Initial Hg concentration = 1×10^{-7} M; soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = $25 \pm 2^\circ\text{C}$.

$$RMS = \sum_{i=1}^n \frac{(Y_p - Y_e)^2}{n Y_e} \quad (8.22)$$

where n is the number of data points used in the calculation and Y_e and Y_p are the concentrations of soluble Hg experimentally determined and predicted, respectively.

We plotted the values of A obtained by model fitting against soil properties, including CEC, surface area, and organic C content, and found that A correlates very well with soil organic C content with a regression coefficient R^2 of 0.986 (Figure 8.2). Based on equation 8.19, the value of A depends on the soil binding capacity and the binding strength for Hg. In Chapter 4, we found that soil adsorption capacity of Hg(II) correlated well with soil organic C content (Figure 4.4). In Chapter 5, it was demonstrated that soil organic matter was the major component responsible for Hg persistence in soil. The persistence of Hg in soil most likely resulted from Hg binding (or trapping) to high energy sites. These high energy sites could be those that form a very strong chemical bond with Hg, or the micropores in which Hg was trapped and requires high activation energy to diffuse out. Based on the findings in Chapters 4 and 5, it is no surprise that the values of A correlate well with soil organic C content.

By forcing the regression line to pass through the origin (Figure 8.2), we obtained following correlation between the parameter A and the soil organic C content:

$$A = 0.81 SOC \quad (8.23)$$

where SOC is the soil organic C content. Substitution of equation 8.23 into 8.20 yields:

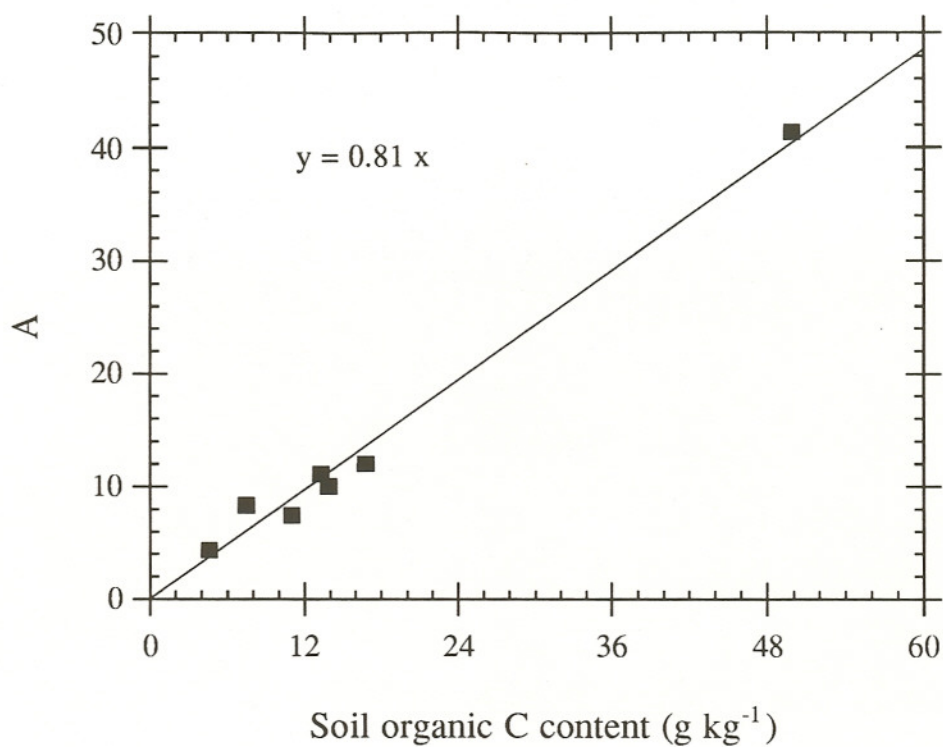


Figure 8.2 Correlation between model fitting parameter A (equation 8.21) and the soil organic C content for adsorption of Hg(II) on seven soils listed in Table 8.1. Regression line is forced to pass through the origin.

$$C_w = \frac{1 + K_{HL}[H^+] + K_{HgL} DOC}{1 + K_{HL}[H^+] + K_{HgL} DOC + 0.81 SOC (1 + K_{HL}[H^+])} T_{Hg} \quad (8.24)$$

Based on the model fitting parameters for each soil that is listed in Table 8.1, the average values for K_{HL} and K_{HgL} are calculated to be $0.32 \text{ L } \mu\text{mol}^{-1}$ and $1.096 \times 10^{-2} \text{ L } \mu\text{mol}^{-1}$, respectively. Substitution of these average values into equation 8.24 yields the universal equation 8.25:

$$C_w = \frac{1 + 0.32[H^+] + 1.096 \times 10^{-2} DOC}{1 + 0.32[H^+] + 1.096 \times 10^{-2} DOC + 0.81 SOC (1 + 0.32[H^+])} T_{Hg} \quad (8.25)$$

We used equation 8.25 to predict the equilibrium aqueous Hg concentrations (C_w) for adsorption of Hg(II) on all soils listed in Table 8.1 at an initial concentration of 1×10^{-7} based on the experimentally determined DOC and pH values. The predicted and measured C_w values agree well with a correlation coefficient R^2 of 0.915 and RMS value of 0.0019. The equality of the predicted and measured values is showed in Figure 8.3.

Because the composition (e.g., humic acid /fulvic acid ratio) of both particulate and soluble organic matter could vary with soils, the stability constant of Hg with organic matter could correspondingly vary with soils. The change of stability constants from humic acid to fulvic acid has been demonstrated by Tipping (1994a) for many metals. Besides soil organic matter, other solid phases might also contribute the adsorption of Hg. Consequently, the approximation of $K_{\equiv SOHg} \Gamma_t (A)$ in equation 8.25 by $0.81 SOC$ could cause an estimate error. All these factors might contribute to

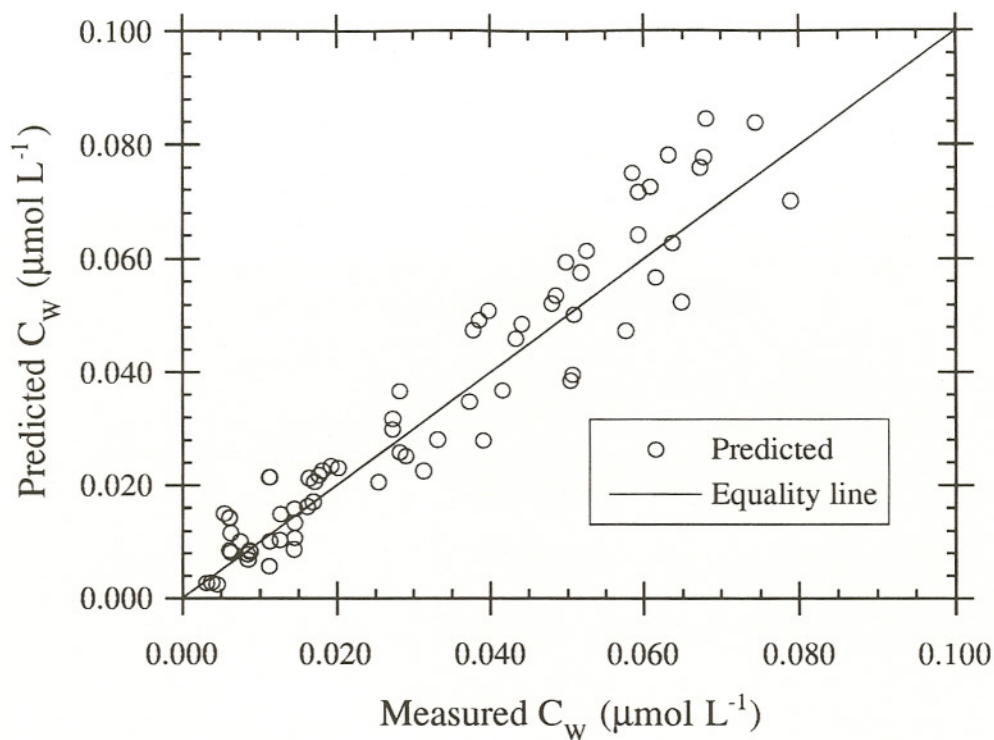


Figure 8.3 Predicted vs. measured soluble Hg(II) concentrations. The predicted values were calculated with the universal equation 8.25 for adsorption on all soils listed in Table 8.1 at an initial Hg concentration of 1×10^{-7} M over a pH range of 3 to 10. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = $25 \pm 2^\circ\text{C}$.

the greater extent of scatter of the predicted C_w values from those measured (Figure 8.3) compared with that shown in Figure 8.1.

When we used the universal equation 8.25 to predict the soluble Hg concentrations (C_w) for adsorption at a higher initial concentration of 1×10^{-6} M, the C_w values were over-estimated (Figure 8.4). This probably resulted from the assumption that there is one type of sites on soluble organic matter. Consequently, the average stability constant K_{HgL} for low Hg concentrations would be higher than that for higher concentrations. Therefore, when we used the K_{HgL} value obtained for a low initial Hg concentration (1×10^{-7} M) to calculate the C_w values for a higher initial Hg concentration (1×10^{-6} M), the C_w was over-estimated.

If we use the average value 0.32 for K_{HL} in equation 8.24 and consider K_{HgL} as an adjustable parameter, equation 8.26 is obtained:

$$C_w = \frac{1 + 0.32[H^+] + K_{\text{HgL}} \text{DOC}}{1 + 0.32[H^+] + K_{\text{HgL}} \text{DOC} + 0.81 \text{SOC} (1 + 0.32[H^+])} T_{\text{Hg}} \quad (8.26)$$

We used equation 8.26 to fit the experimental data for adsorption of Hg(II) from an 1×10^{-6} M solution. As shown in Figure 8.5, the predicted and measured soluble Hg concentrations agree much better than that shown in Figure 8.4. The regression coefficient (R^2) for these two sets of values is 0.80 and the *RMS* value is 0.037. As expected, the K_{HgL} value obtained for a 1×10^{-6} M initial concentration (4.78×10^{-3}) is smaller than that for a 1×10^{-7} M initial concentration (10.96×10^{-3}).

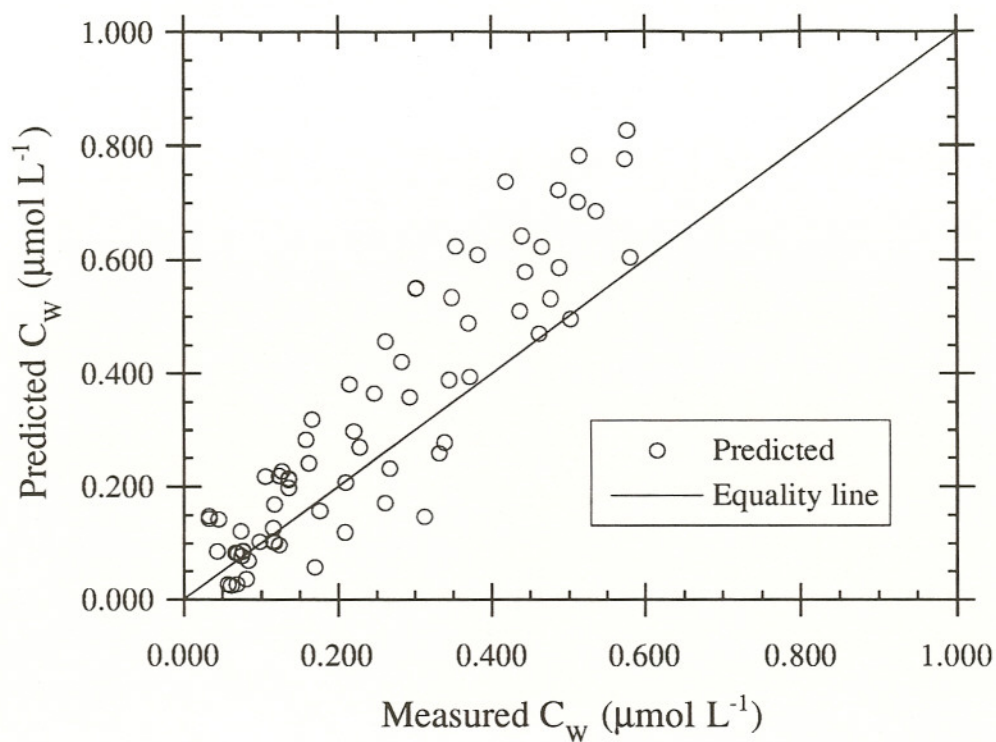


Figure 8.4 Predicted vs. measured soluble Hg(II) concentrations. The predicted values were calculated with the universal equation 8.25 for adsorption on all soils listed in Table 8.1 at an initial Hg concentration of 1×10^{-6} M over a pH range of 3 to 10. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = $25 \pm 2^\circ\text{C}$.

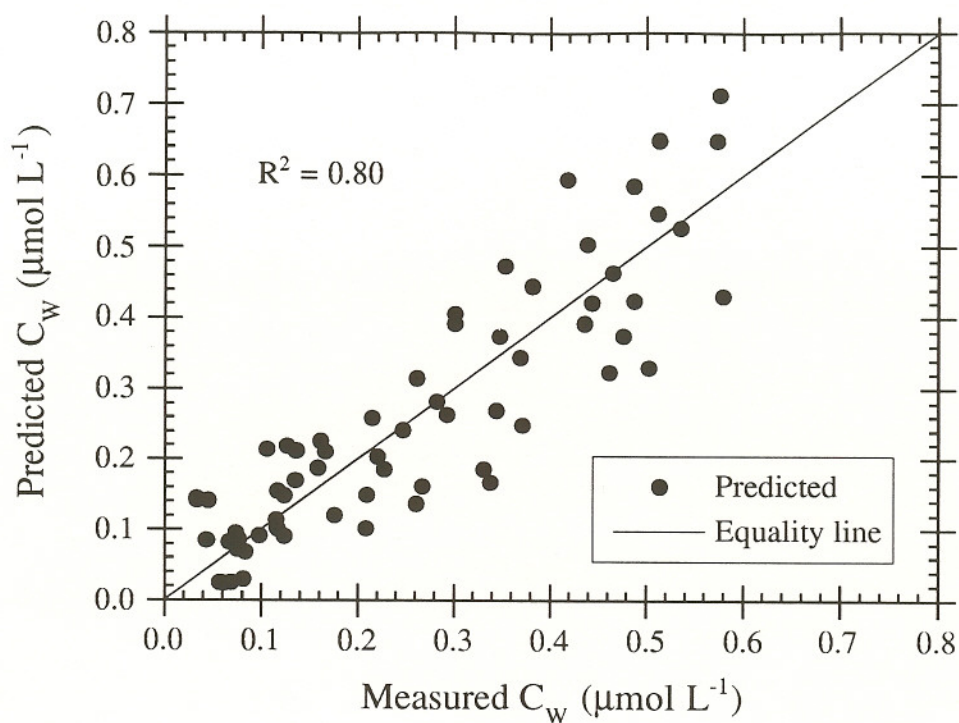


Figure 8.5 Predicted vs. measured soluble Hg(II) concentrations. The predicted values were calculated with the equation 8.26 for adsorption on all soils listed in Table 8.1 at an initial Hg concentration of 1×10^{-6} M over a pH range of 3 to 10. The K_{HgL} value used in the prediction is 4.78×10^{-3} L μmol^{-1} . Soil:water = 1 g 100 mL $^{-1}$; I = 0.01 M NaNO₃; T = $25 \pm 2^\circ\text{C}$.

Assume that the total binding sites on per mg organic C is $2.6 \mu\text{mol}$ (Chapter 6), the average stability constant ($\log K_{\text{HgL}}$) for Hg binding to soluble organic matter (Table 8.1) on organic matter bases was then calculated to be 5.54 for the $1 \times 10^{-7} \text{ M}$ initial concentration. The average $\log K_{\text{HgL}}$ value obtained in this study is greater than that determined in Chapter 6 (4.69). Again, this probably resulted from the low Hg concentration used in this study and the assumption of one site binding.

8.5.2 Adsorption of Methylmercury

We first modeled adsorption of methylmercury from a $2 \times 10^{-7} \text{ M}$ solution over a pH range of 3 to 10 with equation 8.20. The model fitting parameters are listed in Table 8.2. The predicted and measured soluble Hg concentrations agree very well for all soils with a R^2 of ≥ 0.934 and $RMS \leq 0.001$. The equality of the predicted and measured values is shown in Figure 8.6.

In a similar way as we did for Hg(II) , we correlated the values of A in Table 8.2 with soil properties, and obtained a good linear relationship between A and the soil organic C content with a regression coefficient of 0.997 (Figure 8.7). By forcing the regression line to pass through the origin, following regression equation was obtained:

$$A = 8.88 \text{ SOC} \quad (8.27)$$

By substituting equation 8.27 into 8.20 and replacing the constants K_{HL} , K_{HgL} , and $K_{\text{=SOH}}$ with the average values listed in Table 8.2, we obtained the universal equation 8.28:

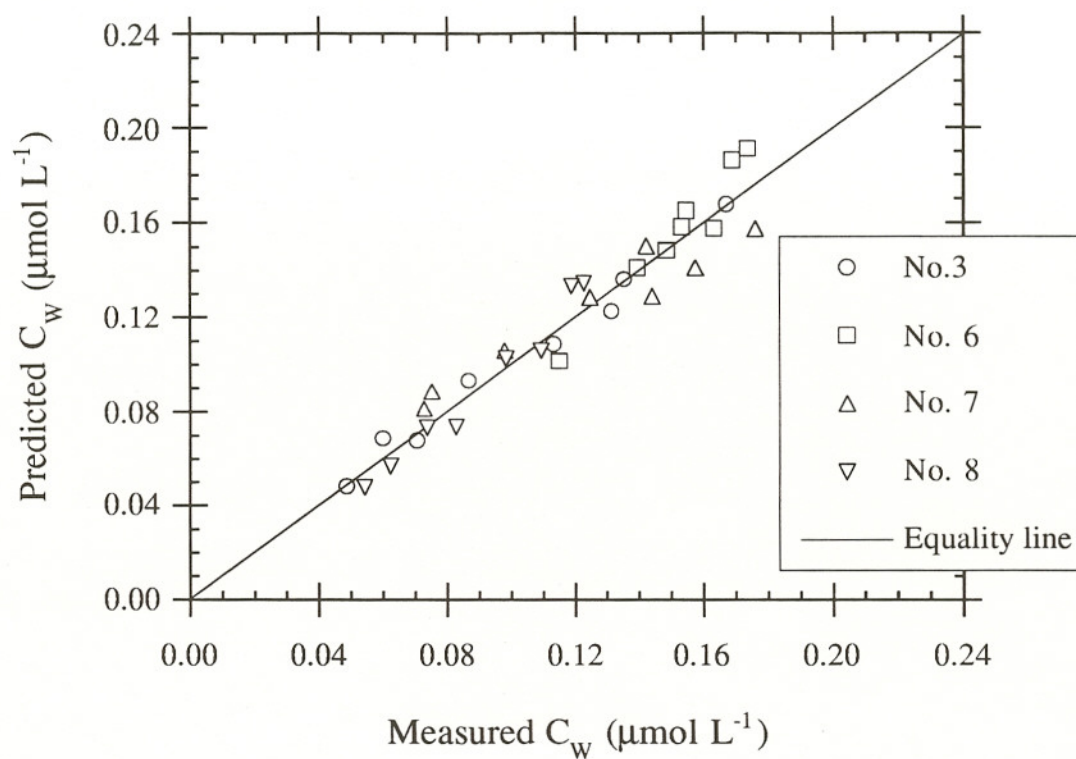


Figure 8.6 Predicted vs. measured soluble methylmercury concentrations. The predicted values were calculated with equation 8.20 based on the parameters listed in Table 8.2 for each soil. Initial Hg concentration = 2×10^{-7} M; soil:water = 0.4 g 40 mL $^{-1}$; I = 0.01 M NaNO₃; T = $25 \pm 1^\circ\text{C}$.

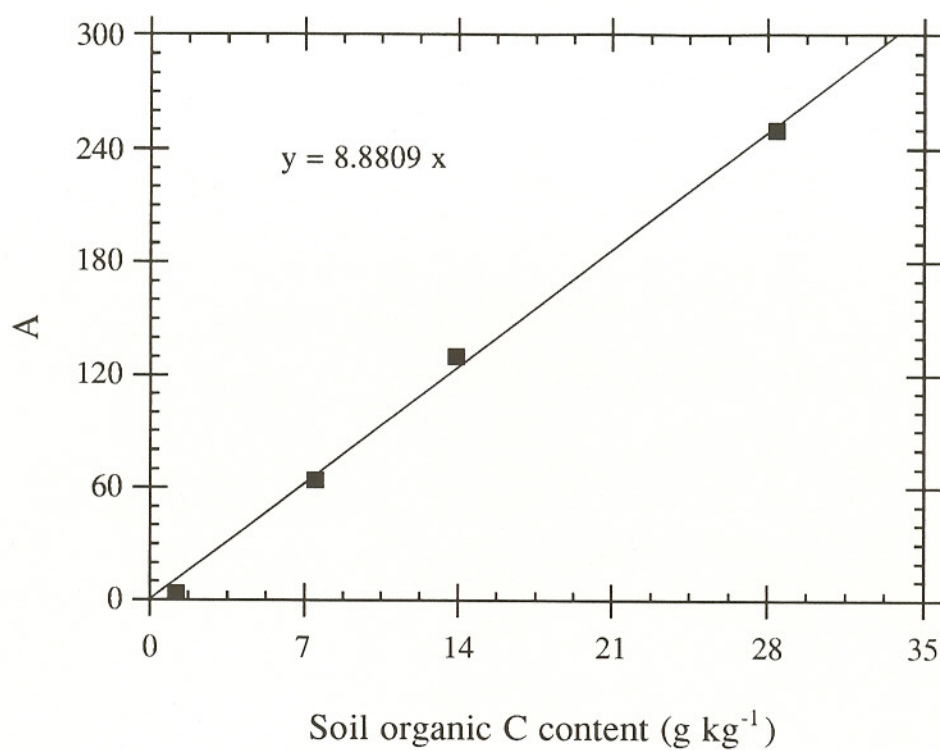


Figure 8.7 Correlation between model fitting parameter A (equation 8.20) and the soil organic C content for adsorption of methylmercury on four soils listed in Table 8.2. Regression line is forced to pass through the origin.

$$C_w = \frac{1 + 0.0586[H^+] + 0.0746 DOC}{1 + 0.0586[H^+] + 0.0746 DOC + 8.88 SOC \frac{1 + 0.0746[H^+]}{1 + 0.0366[H^+]}} T_{Hg} \quad (8.28)$$

Table 8.2 Model fitting parameters for adsorption of methylmercury on soils from a 2×10^{-7} M solution over a pH range of 3 to 10†

Soil No.	Soil Name	A	$K_{\equiv SOH}^\ddagger$	$K_{HL}^\ddagger$ ($\times 10^{-2}$)	$K_{HgL}^\ddagger$ ($\times 10^{-2}$)	R ² §	RMS*
3	Penn silt loam	64.0	0.3934	3.57	4.42	0.982	0.0003
6	Freehold sandy loam (A horizon)	3.5	0.1000	8.00	6.90	0.944	0.0006
7	Freehold sandy loam (B horizon)	130.0	0.2242	3.00	9.91	0.934	0.0010
8	Rockaway stony loam	250.0	0.5222	8.86	8.60	0.973	0.0006
Average			0.3099	5.86	7.46		0.0006

†Experimental data was fitted by equation 8.20.

‡In the unit of $L \mu mol^{-1}$.

§Regression coefficient for the predicted vs. measured soluble Hg concentrations.

*Residual mean square in $\mu mol L^{-1}$.

We used equation 8.28 to predict the equilibrium aqueous mercury concentrations (C_w) for adsorption of methylmercury on all tested soils listed in Table 8.2 at an initial concentration of 2×10^{-7} M based on the measured *DOC* and pH

values. The equality of the predicted and measured C_w values is shown in Figure 8.8. The regression coefficient (R^2) for two sets of values is 0.720 and the *RMS* value is 0.0040. Again, when we used the universal equation 8.28 to predict the soluble Hg concentrations (C_w) for adsorption at a higher initial concentration of 1×10^{-6} M, the C_w values were over-estimated (Figure 8.9). The regression coefficient for the predicted and measured C_w values is 0.610 and the *RMS* value is 0.0984.

8.6 Summary and Conclusions

This study demonstrated that adsorption of Hg(II) and methylmercury by soils can be described by a model which incorporated the interactions of Hg with both soil solids and dissolved organic matter. The dependency of the concentration of the dissolved organic matter on pH as well as the competitive binding of protons for available sites has been considered in order to model Hg adsorption as a function of pH. The facts that the model fitting parameter *A* correlates well with the soil organic C content and that Hg adsorption can be predicted reasonably well with the average stability constants for all soils indicate that soil organic matter is the most important component for Hg binding. The model developed in this study is suitable for the description of Hg adsorption from low concentration solutions, which is the case usually occurred in the field. To predict soil-water partitioning of Hg at wide (from very low to high) loading levels, a more complicated model, which accounts for Hg binding to low to high affinity of sites on both soil particulates and the soluble organic matter, needs to be developed.

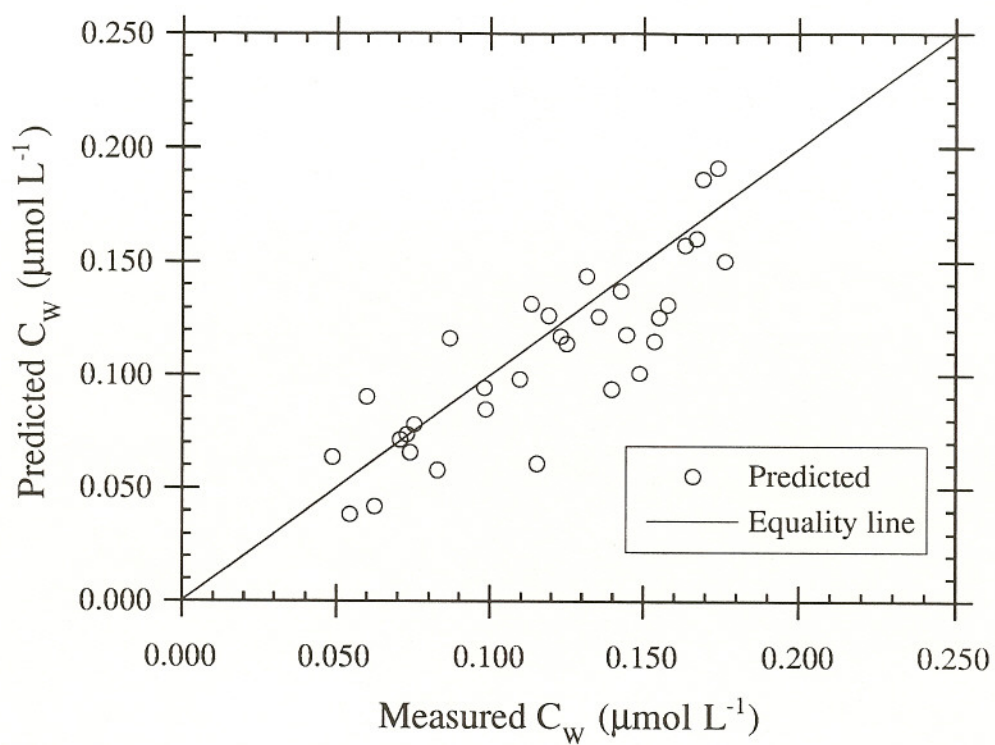


Figure 8.8 Predicted vs. measured soluble methylmercury concentrations. The predicted values were calculated with the universal equation 8.28 for methylmercury adsorption on four soils listed in Table 8.2 at an initial Hg concentration of 2×10^{-7} M over a pH range of 3 to 10. Soil:water = 0.4 g 40 mL $^{-1}$; I = 0.01 M NaNO₃; T = $25 \pm 1^\circ\text{C}$.

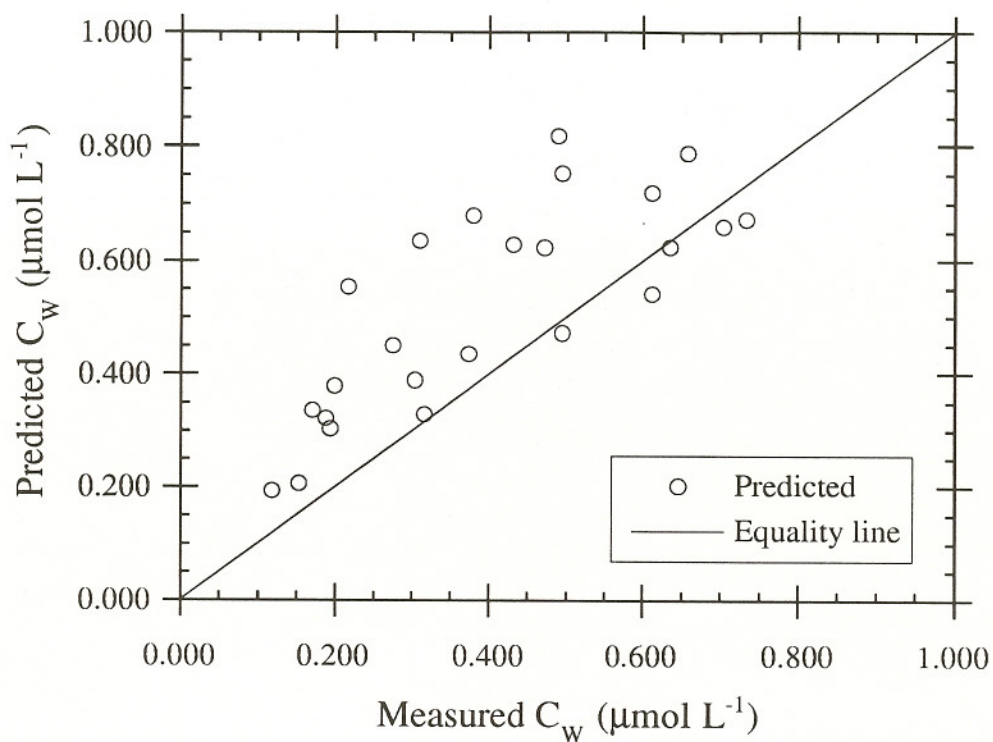


Figure 8.9 Predicted vs. measured soluble methylmercury concentrations. The predicted values were calculated with the universal equation 8.28 for methylmercury adsorption on four soils listed in Table 8.2 at an initial Hg concentration of 1×10^{-6} M over a pH range of 3 to 10. Soil:water = 0.4 g 40 mL $^{-1}$; I = 0.01 M NaNO₃; T = $25 \pm 1^\circ\text{C}$.

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Chapter 9

SUMMARY AND CONCLUSIONS

Retention and release reactions of heavy metals at the solid-solution interface greatly influence their mobility and bioavailability in soils. In this study, adsorption and desorption of Hg(II) and methylmercury on fifteen New Jersey soils were investigated. The simultaneous effects of pH, Cl^- , Ca^{2+} , and soluble organic matter on the surface reactions of both types of mercury were examined. A stirred-flow technique was used to ascertain reaction kinetics of Hg(II) on soils. The binding of Hg(II) with soluble organic matter was characterized potentiometrically. Finally, a model, which incorporated the reactions of Hg with both soil solids and soluble organic matter and the proton competitive binding effect, was developed to predict soil-water partitioning of Hg(II) and methylmercury.

As expected, adsorption of both Hg(II) and methylmercury is highly pH dependent. The adsorption edge for both types of Hg followed an upside bow shape as a function of pH. Maximum adsorption occurred at pH around 4 for Hg(II) and around 6 for methylmercury. The occurrence of maximum adsorption at different pH value for two types of Hg resulted from the stronger acidic nature of Hg(II) than methylmercury.

Increasing pH above 5 considerably increased the solubility of soil organic matter. The complexation of Hg by the dissolved organic matter resulted in significant

decreases in adsorption of both Hg(II) and methylmercury at high pH values. This finding has not been reported in the literature. Part of the reason is because researchers usually use high initial metal concentrations, which suppresses the effect of the dissolved organic matter. It is expected that at natural concentration levels, the mobility of heavy metals, especially those which can form strong complexes with soluble organic matter, would increase with pH.

Due to the effect of the dissolved organic matter, adsorption of Hg at low loading levels was quite different from that at high loading levels at fixed pH. Fractional adsorption initially increased with Hg loading as more free Hg became available for surface binding, and then decreased when the capacity of soluble organic matter was exceeded and surface coverage further increased. Consequently, adsorption isotherms followed a S-shape. The adsorption capacities of soils were found to correlate with soil organic matter contents. This suggests that the surficial adsorption sites of the soils used in this study are mainly from organic matter, which may coated on soil minerals. A similar finding was reported by Lee *et al.* (1996) in studying Cd(II) adsorption on the same soils.

In the presence of a small concentration of Ca^{2+} (1×10^{-4} M) in solution, adsorption of Hg did not change. A high concentration of Ca^{2+} (0.003 M), however, caused adsorption to increase at higher pH values (> 5) for Hg(II) and at lower pH values (< 6) for methylmercury. Calcium(II) interfered with Hg adsorption, not by competitive binding for available surface sites, but by affecting the solubility of soil organic matter. The solubility of soil organic matter was not affected by a low concentration of Ca^{2+} , but was decreased by a high concentration of Ca^{2+} , especially

at pH above 5. For Hg(II), which forms very stable complexes with all major functional groups on soluble organic matter, the decreases of the dissolved organic matter at pH above 5 increased adsorption. At pH less than 5, adsorption of Hg(II) was large in all electrolytes. For methylmercury, which only efficiently binds to S-containing groups on organic matter, the decreases of the total soluble organic matter had no effect on adsorption at pH > 6, but increased adsorption at lower pH values. This probably resulted from the preferential dissolution of S-containing groups at high pH, which was not affected by Ca^{2+} . The interference of Ca^{2+} on Hg adsorption found in this study would be expected to be true for other divalent cations that have similar properties to Ca^{2+} .

The presence of Cl^- in soil solution would have no effect on Hg adsorption at a pH value above which hydroxo Hg species are predominant over Hg-Cl species. At lower pH values, Cl^- could affect Hg adsorption. This effect, however, depends on soil organic matter content and the Hg loading level. For a given Hg concentration, the effect of Cl^- on adsorption would decrease as soil organic matter content increases. Increases in Hg loading level would eventually saturate the high energy sites on organic matter, and the additional Hg would bind with Cl^- .

Both Hg(II) retention to and release from soils were characterized by two time regimes, a fast step followed by a slow step. The higher the soil organic matter content, the longer the time required for attainment of equilibrium. An increase in the influent concentration decreased the time required for the adsorption reaction to reach equilibrium. The adsorption and desorption reaction kinetics were described with a one-site kinetic model. The apparent reaction rate coefficients for both processes were

calculated. Both coefficients were found to inversely correlate with the soil organic matter content.

Both batch equilibrium and kinetic (using stirred-flow method) desorption studies indicate that not all adsorbed Hg could be readily released. Among the soil components, organic matter was found to be the most important one responsible for Hg persistence in soil. Smaller adsorption resulted in less fractional desorption, implying that Hg preferentially bound to high energy sites. These high energy sites could be physical sites in which Hg was entrapped and requires high activation energy to diffuse out, or they could be chemically strong binding sites, such as -S containing groups on soil organic matter.

Comparing the desorption results obtained by a batch equilibrium method and a stirred-flow technique, the fractional release of Hg by the former method was much smaller than that by the latter method, even within a longer desorption time period. This suggests that the released Hg could inhibit the further desorption reaction in batch desorption experiments. Consequently, the results obtained by batch desorption studies would underestimate the potential of the mobility of contaminants in soils. To better assess the mobility and transport of contaminants in soils, kinetic flow techniques are recommended.

Information on the binding of Hg(II) with soluble organic matter was gleaned with an iodide electrode. For the first time, the stability constant for the interaction of Hg(II) and natural organic matter was determined by differentiating inorganic and organically complexed Hg. Less Hg was bound by humic substances at lower pH due to the competitive binding of protons. The binding characteristics were described with

a Gaussian continuous distribution model. The parameters obtained from titration curves at three pH values of 4, 5, and 6 are very similar. The calculated stability constant for Hg(II) binding with soluble organic matter is 4.69 ± 0.19 .

As indicated in several chapters, soluble organic matter greatly affected Hg retention to and release from soils. To model Hg partitioning in soil, the interaction of Hg with soluble organic matter has to be considered. By incorporating the soluble organic matter and proton competitive binding effects into a model, adsorption of Hg(II) and methylmercury as a function of pH was well described for each soil. Again, the soil adsorption capacity and binding strength for Hg were found to correlate with the soil organic matter content. Based on these correlations and the average values of the stability constants for Hg and proton binding for each soil, adsorption of Hg(II) and methylmercury on all tested soils over a pH range of 3 to 10 were described. The regression coefficients (R^2) for the predicted and measured concentration values were 0.908 for Hg(II) and 0.820 for methylmercury. The method developed in this study should apply to the modeling of the partitioning of other metals in soils at low concentrations. In order to describe soil-water partitioning of heavy metals as a function of pH over a wide range of initial concentrations, a more complicated model, which accounts for Hg binding to low to high affinity of sites on both soil particulates and the soluble organic matter, needs to be developed.

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APPENDIX A

ADSORPTION EDGE

Table A.1 Adsorption edge data for Hg(II) on fifteen New Jersey soils. Initial Hg(II) concentration = 1×10^{-7} M; soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

Birdsboro silt loam		Boonton Bergen loam		Boonton Union loam		
pH	% ads	pH	% ads	pH	% ads	DOC†
3.01	87.93	2.87	97.63	3.15	95.53	13.12
3.61	89.78	3.54	97.63	3.41	96.86	17.65
4.84	84.80	4.29	96.44	3.97	96.24	7.45
5.56	82.28	4.99	88.12	4.86	88.78	9.72
6.03	73.43	5.99	78.65	5.56	93.76	10.01
6.59	61.96	6.49	66.82	6.05	83.78	10.85
6.91	51.88	6.80	46.03	6.30	68.65	15.38
7.24	49.42	7.90	31.20	7.04	49.13	32.37
7.74	44.29	8.28	27.76	8.15	34.96	53.89
8.11	39.29	9.27	24.15	8.75	20.89	116.29

Downer loamy sand			Dunellen sandy loam			Fill materials from Delaware River	
pH	% ads	DOC†	pH	% ads	DOC†	pH	% ads
2.82	83.58	5.26	3.04	88.64	3.60	2.83	91.17
3.19	88.67	5.26	3.57	87.35	3.88	3.23	92.43
3.64	82.32	3.60	4.55	85.44	4.71	3.71	87.36
4.14	79.79	3.60	5.49	82.88	3.32	4.39	73.35
4.67	70.94	2.49	5.95	72.73	4.71	5.25	55.60
6.28	51.86	4.43	6.64	62.62	4.99	6.35	46.79
7.02	40.61	10.80	7.02	55.75	9.41	6.73	31.61
7.90	36.69	15.51	7.33	51.33	11.63	7.80	25.25
9.13	31.78	24.37	7.88	50.03	14.96	9.28	20.59
9.66	25.44	22.99	8.59	40.58	18.56	9.91	10.20

Freehold sandy loam (A horizon)		Freehold sandy loam (B horizon)			Hazen gravelly loam	
pH	% ads	pH	% ads	DOC†	pH	% ads
2.77	92.30	2.70	93.77	9.72	2.99	93.49
3.15	92.31	2.94	91.25	9.16	4.09	94.66
3.59	89.93	3.46	91.28	6.89	5.40	85.80
4.15	80.44	4.19	92.52	7.45	5.91	80.47
4.99	72.16	5.20	88.77	7.74	6.67	69.77
6.05	56.76	5.70	72.66	8.59	7.14	66.25
7.14	52.04	6.48	62.16	12.55	7.85	57.28
8.91	46.08	7.60	47.33	21.05	9.20	48.41
9.61	42.46	8.90	41.39	40.83	9.83	43.08
9.81	42.51	9.70	32.54	43.19	10.27	37.67

Table A.1 Continued

Lakewood sand		Penn silt loam			Rockaway stony loam	
pH	% ads	pH	% ads	DOC†	pH	% ads
2.81	84.63	2.97	93.91	2.82	3.07	85.92
3.15	83.44	3.45	93.92	2.30	3.26	90.35
3.56	85.80	4.24	94.56	1.97	3.55	96.22
3.97	65.64	5.29	81.91	2.53	4.14	92.44
4.31	61.53	5.84	71.78	4.54	6.02	78.32
6.10	46.57	6.29	61.38	7.05	7.90	53.00
7.20	40.66	6.55	60.17	7.12	8.47	51.13
8.70	36.01	7.05	48.04	9.21	9.12	40.67
9.18	25.40	8.00	39.02	18.80	9.64	38.19
9.88	25.38	9.00	32.07	25.38	10.14	38.97

Sassafras sandy loam		Washington loam			Whippany silty clay loam		
pH	% ads	pH	% ads	DOC†	pH	% ads	DOC†
2.97	92.55	3.09	91.51	1.68	3.19	93.93	2.98
3.49	93.78	4.38	91.55	2.72	3.97	85.51	1.17
4.19	93.75	5.74	87.28	2.72	5.33	85.45	0.91
5.32	90.01	6.19	74.56	3.76	6.00	85.48	1.68
6.60	85.01	6.52	71.76	5.05	6.42	83.05	1.68
7.03	78.66	6.86	66.82	5.57	6.78	80.73	2.98
7.63	71.10	7.28	58.32	8.68	7.10	60.81	4.01
8.23	59.78	8.09	56.55	13.08	8.16	49.42	7.12
9.30	54.16	9.28	48.95	15.67	9.47	42.20	10.74
9.61	48.47	10.05	36.13	27.06	10.09	38.34	16.18

†Dissolved organic C concentration in mg L⁻¹.

Table A.2 Adsorption edge data for Hg(II) on fifteen New Jersey soils. Initial Hg(II) concentration = 1×10^{-6} M; soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

Birdsboro silt loam		Boonton Bergen loam		Boonton Union loam		
pH	% ads	pH	% ads	pH	% ads	DOC†
3.15	87.44	2.98	94.55	3.17	93.86	13.12
3.78	91.63	3.63	94.54	3.46	94.26	17.65
4.68	86.96	4.37	94.47	3.88	93.11	7.50
5.39	79.07	4.95	90.58	4.44	91.87	8.00
5.95	70.37	5.78	87.47	4.86	83.03	9.72
6.61	67.40	6.29	85.26	5.81	68.66	11.00
7.15	65.34	7.42	65.64	6.56	66.09	19.50
7.58	65.59	8.63	54.21	7.14	62.72	32.00
8.29	59.55	9.34	46.47	7.86	49.57	48.00
9.41	51.37	9.90	42.51	8.53	41.84	75.00

Downer loamy sand			Dunellen sandy loam			Fill materials from Delaware River	
pH	% ads	DOC†	pH	% ads	DOC†	pH	% ads
2.86	86.38	5.26	3.03	88.30	3.60	2.86	91.86
3.22	86.40	5.00	3.59	88.36	3.87	3.31	90.81
3.68	89.41	3.60	4.44	88.40	4.70	3.78	84.26
4.07	87.30	3.50	5.05	73.84	4.00	4.39	61.64
4.44	83.83	2.90	5.78	66.77	4.00	4.80	56.12
5.93	56.26	4.90	6.64	65.46	6.20	6.25	50.41
6.69	55.97	7.50	7.15	62.93	9.50	6.71	40.42
7.22	51.14	11.00	7.69	55.49	14.00	7.15	37.33
7.78	42.49	15.00	8.24	53.33	17.00	7.63	38.61
8.46	42.21	21.00	9.41	48.60	24.70	8.80	32.42

Freehold sandy loam (A horizon)		Freehold sandy loam (B horizon)			Hazen gravelly loam	
pH	% ads	pH	% ads	DOC†	pH	% ads
2.80	86.70	2.73	93.02	9.72	3.14	82.75
3.19	88.69	2.95	93.30	9.16	4.49	82.86
3.66	91.37	3.46	92.36	6.89	5.53	77.18
4.36	89.32	4.20	90.16	7.45	6.29	68.98
5.56	87.90	4.85	82.36	7.50	6.88	66.20
6.41	81.20	5.29	73.20	7.80	7.46	65.08
7.02	76.84	6.41	53.67	12.50	8.14	65.94
7.14	73.25	7.00	52.23	15.00	9.19	63.16
7.49	68.58	7.37	51.08	18.70	9.64	59.62
8.68	63.15	8.14	46.24	29.20	10.28	53.12

Table A.2 Continued

Lakewood sand		Penn silt loam			Rockaway stony loam	
pH	% ads	pH	% ads	DOC†	pH	% ads
2.85	87.60	3.03	95.48	2.82	3.17	95.15
3.27	88.82	3.53	96.69	2.30	3.32	95.28
3.64	87.28	4.10	96.67	1.98	3.61	95.72
4.08	75.65	4.75	88.28	2.00	4.07	96.39
4.66	64.98	5.10	86.44	2.20	5.66	57.77
6.27	59.63	5.92	70.64	4.10	6.86	42.61
7.07	56.46	6.68	69.76	8.50	7.42	42.33
7.83	51.35	7.15	64.59	11.50	8.02	42.14
8.97	49.90	8.05	58.04	20.00	8.51	42.02
9.83	45.38	8.78	48.48	26.00	9.07	41.65

Sassafras sandy loam		Washington loam			Whippany silty clay loam		
pH	% ads	pH	% ads	DOC†	pH	% ads	DOC†
2.97	92.60	3.17	91.66	1.68	3.22	95.66	2.97
3.51	95.65	4.32	92.49	2.72	3.92	92.35	1.16
4.29	96.10	5.31	92.62	2.80	4.88	87.59	1.00
5.14	92.19	6.12	87.62	4.30	5.63	79.06	1.00
5.76	86.82	6.64	84.13	5.80	6.46	79.01	2.50
6.55	81.53	7.03	83.36	6.85	6.97	77.16	3.80
7.49	69.10	7.56	75.22	8.50	7.31	77.91	4.50
7.80	64.01	8.19	71.66	11.00	8.24	78.44	7.00
9.31	63.13	9.32	65.13	18.00	9.20	73.74	10.00
9.49	58.04	9.93	61.70	25.00	9.95	69.79	15.00

†Dissolved organic C concentration in mg L⁻¹.

Table A.3 Adsorption edge data for methylmercury on four New Jersey soils. Initial Hg concentration = 2×10^{-7} M; soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 1°C.

Freehold sandy loam (A horizon)			Freehold sandy loam (B horizon)		
pH	% ads	DOC†	pH	% ads	DOC†
3.10	12.87	0.14	3.22	11.68	5.96
3.32	15.26	0.14	3.57	28.62	6.02
3.95	18.12	0.14	4.44	37.45	6.25
5.98	42.22	0.43	5.62	63.45	7.41
6.78	30.05	1.30	6.56	62.26	11.78
8.68	25.52	1.60	7.62	50.81	17.59
9.40	23.13	2.18	8.94	27.66	28.65
9.90	22.42	2.76	9.70	20.98	37.95

Penn silt loam			Rockaway stony loam		
pH	% ads	DOC†	pH	% ads	DOC†
3.23	16.21	2.76	3.37	38.40	7.12
3.76	32.20	1.94	3.80	50.57	4.50
4.95	64.64	1.94	4.41	58.44	3.63
6.06	75.62	3.98	5.07	68.70	4.21
6.70	70.01	8.29	6.01	72.75	7.70
7.25	56.53	14.66	7.06	62.97	19.34
7.85	43.17	20.50	7.90	45.08	39.12
8.50	34.11	27.48	8.93	40.30	70.09

†Dissolved organic C concentration in mg L⁻¹.

Table A.4 Adsorption edge data for methylmercury on three New Jersey soils. Initial Hg concentration = 1×10^{-6} M; soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 1°C.

Freehold sandy loam (B horizon)			Penn silt loam		
pH	% ads	DOC†	pH	% ads	DOC†
3.22	50.34	5.96	3.16	50.93	2.76
3.61	61.98	6.02	3.74	68.97	1.94
4.53	78.28	6.25	5.04	82.94	1.94
5.55	80.01	7.41	6.01	81.19	3.98
6.74	69.55	12.00	6.73	72.46	8.29
7.63	50.34	17.59	7.68	56.75	18.00
9.27	36.38	33.00	8.50	38.70	27.50
10.05	26.48	41.00	9.13	34.05	40.00

Rockaway stony loam		
pH	% ads	DOC†
3.28	52.67	8.00
3.74	62.57	4.50
4.31	80.61	3.63
5.09	84.68	4.21
5.99	88.18	7.70
6.98	68.39	19.34
8.31	38.70	48.00
9.13	29.39	79.00

†Dissolved organic C concentration in mg L⁻¹.

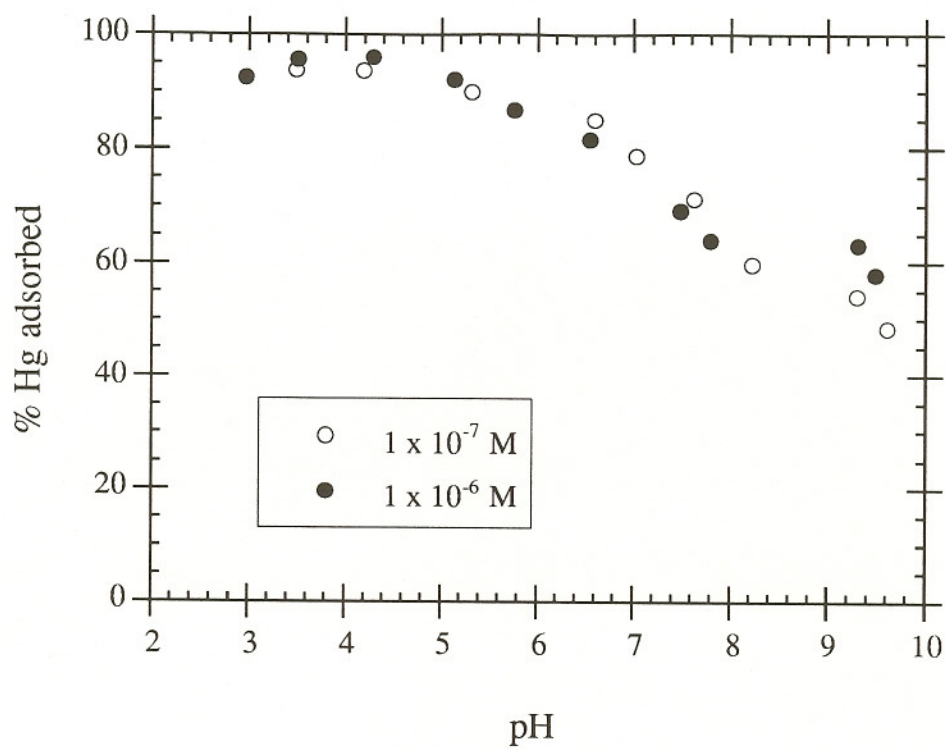


Figure A.1 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Sassafras sandy loam. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

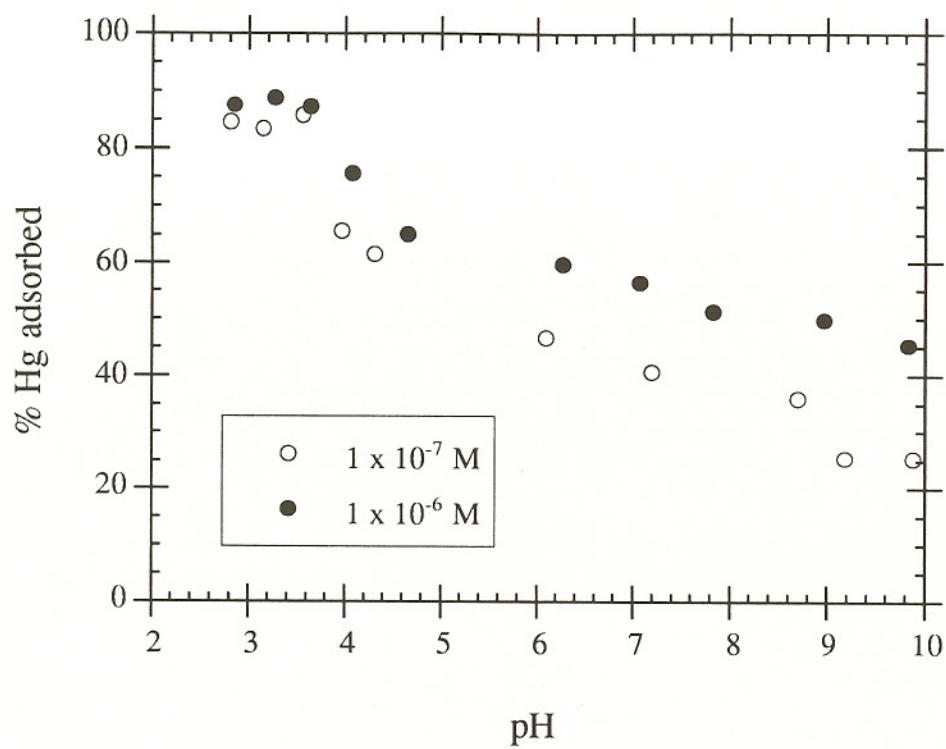


Figure A.2 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Lakewood sand. Soil : Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

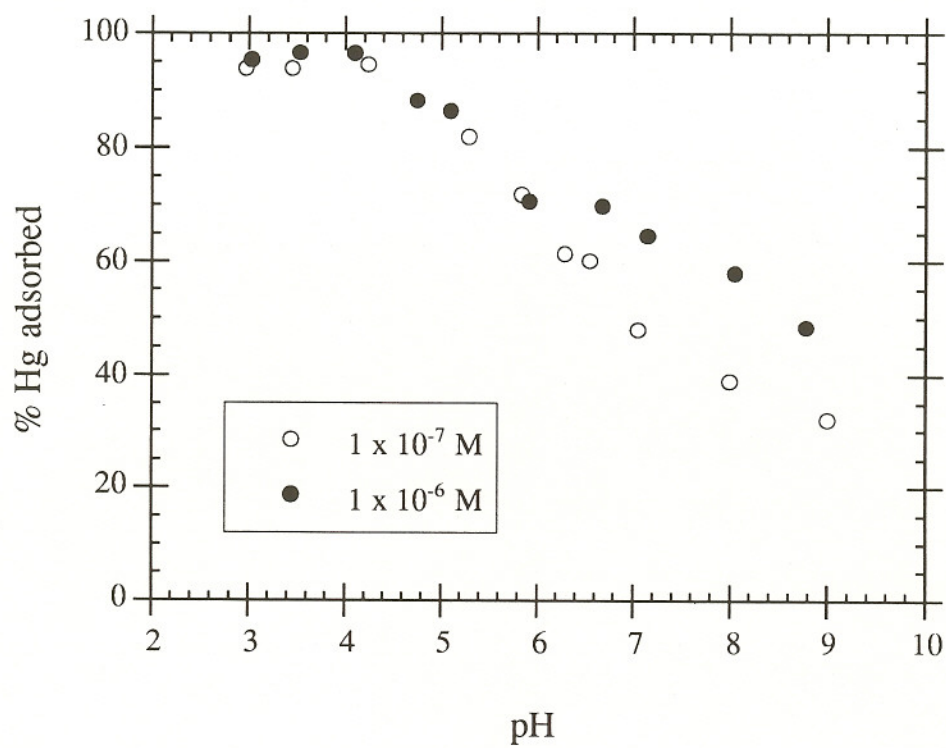


Figure A.3 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Penn silt loam. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

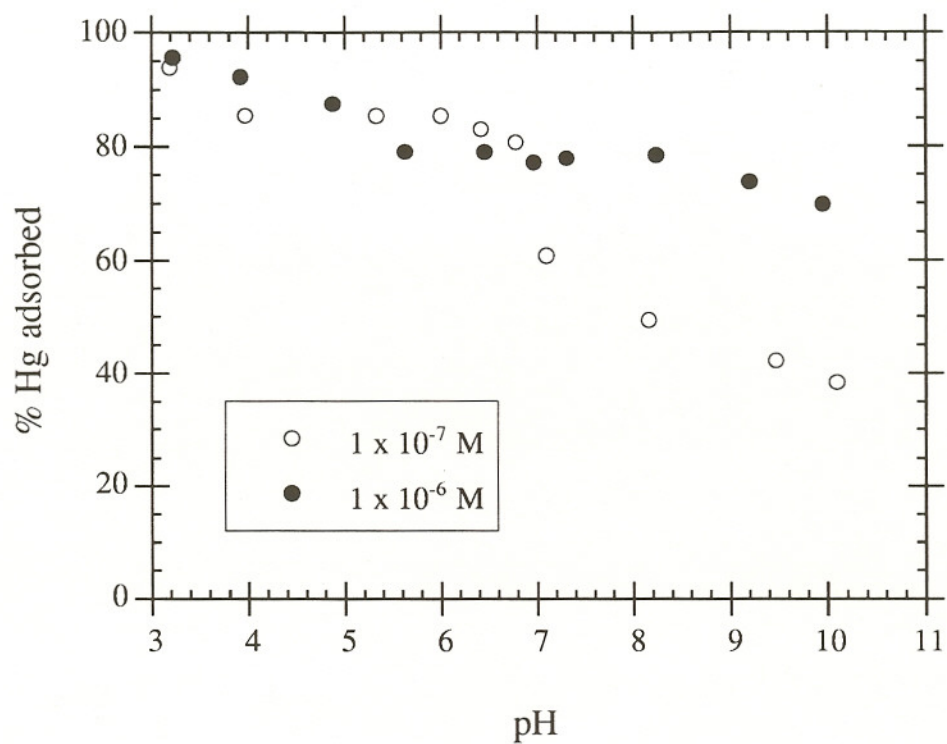


Figure A.4 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Whippany silty loam. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

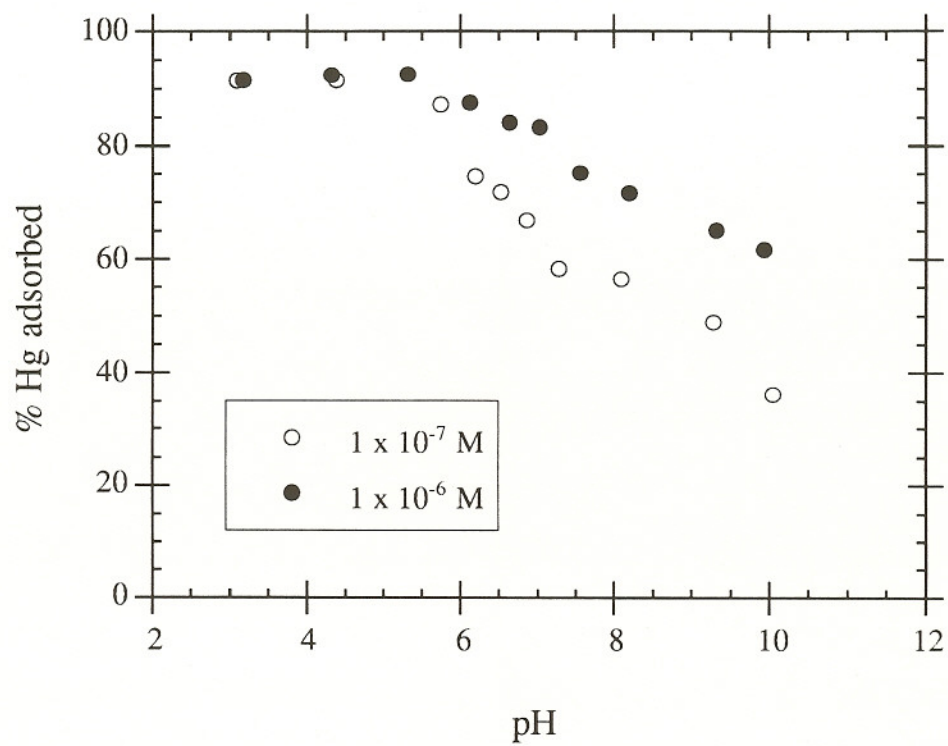


Figure A.5 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Washington loam. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

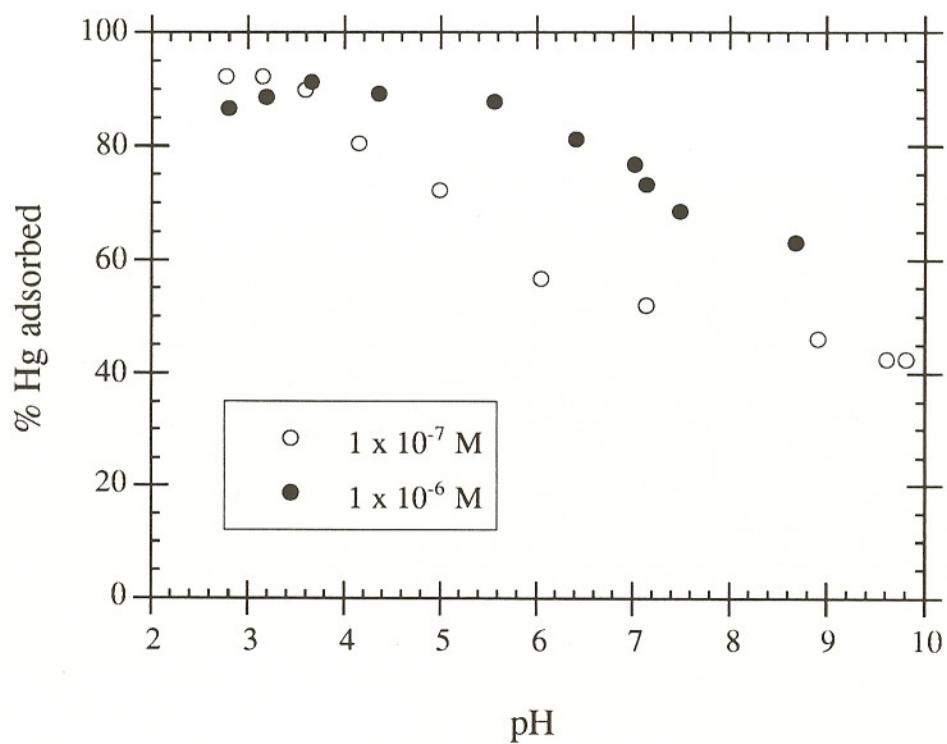


Figure A.6 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Freehold sandy loam (A horizon). Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

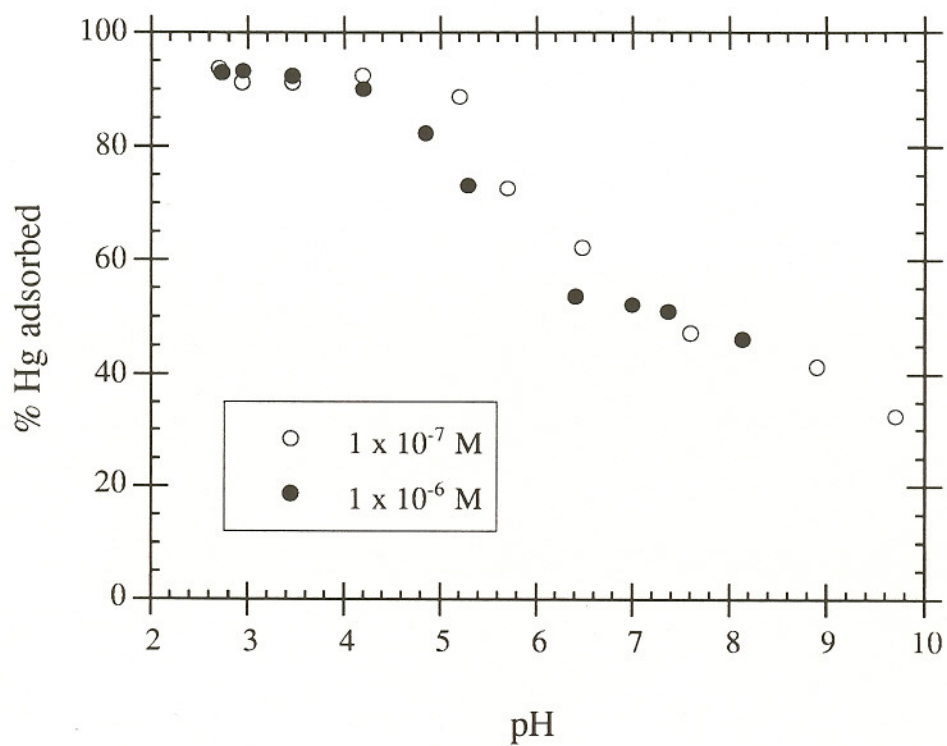


Figure A.7 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Freehold sandy loam (B horizon). Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

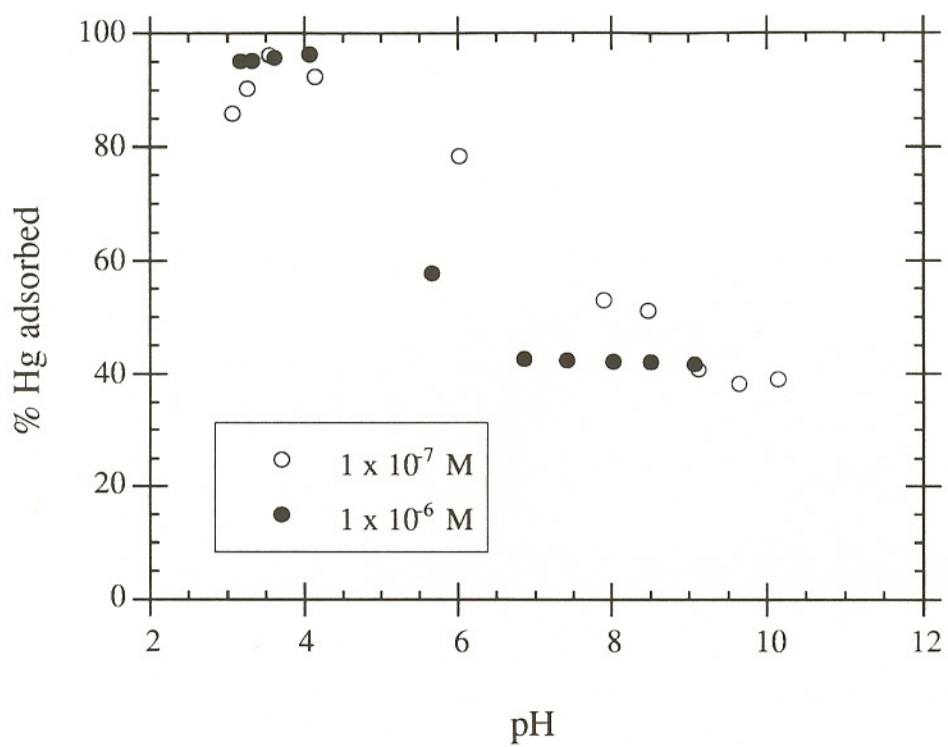


Figure A.8 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Rockaway stony loam. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

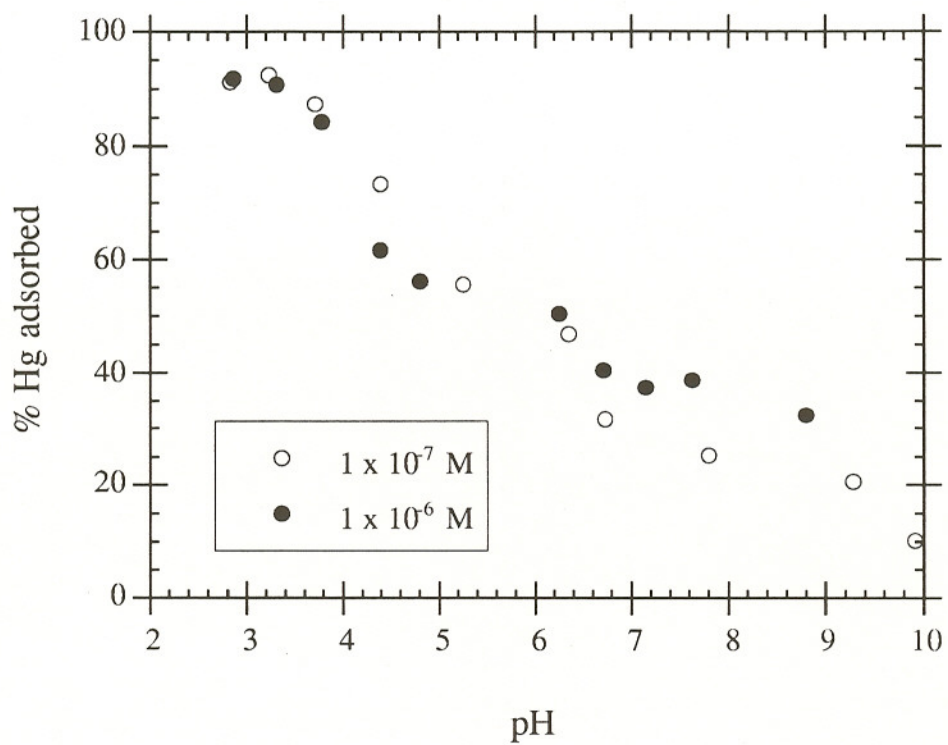


Figure A.9 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on fill material from Delaware River. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 $\pm$ 2°C.

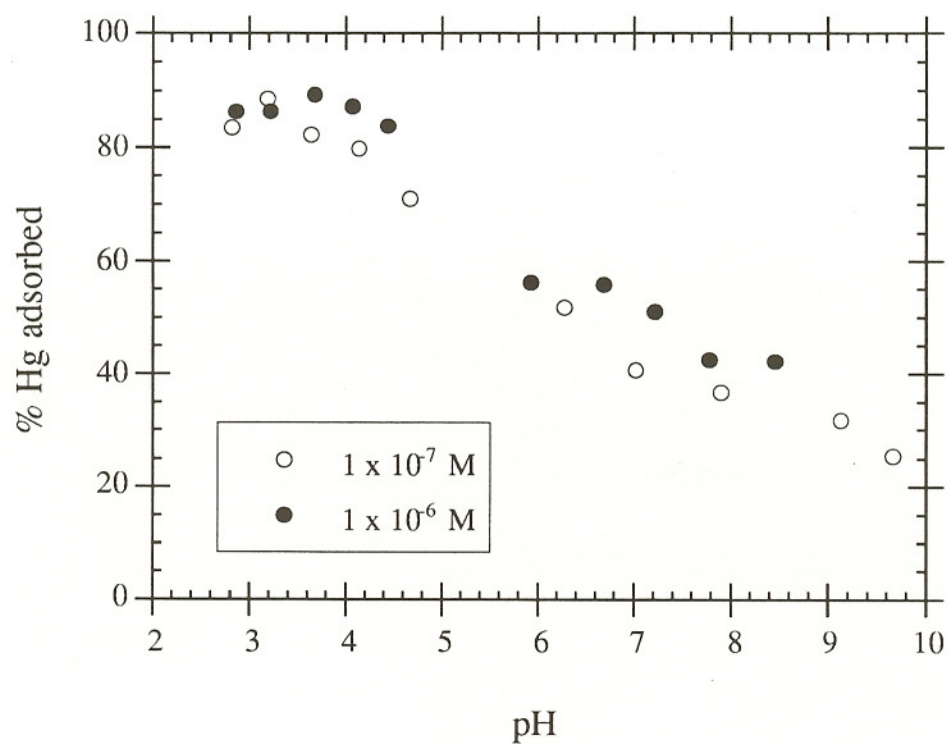


Figure A.10 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Downer loamy sand. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

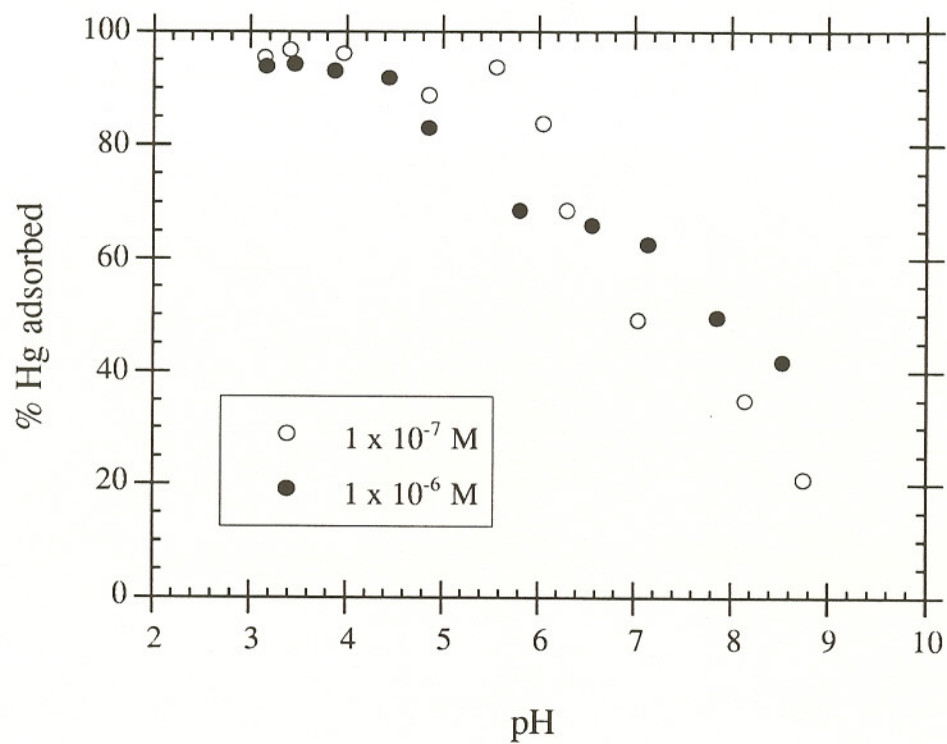


Figure A.11 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Boonton Union loam. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

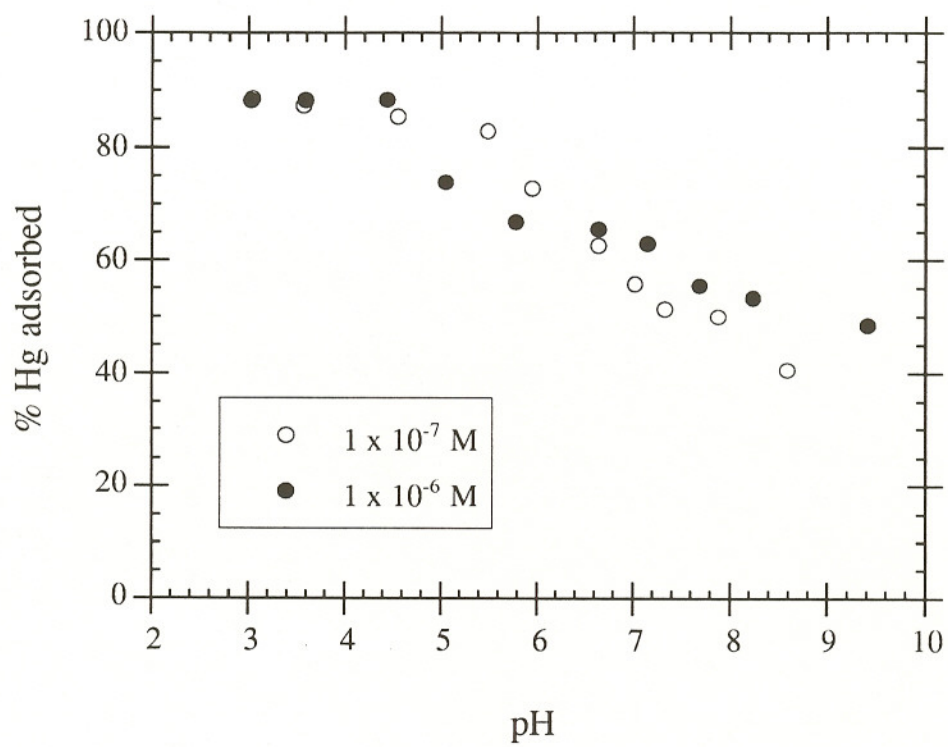


Figure A.12 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Dunellen sandy loam. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

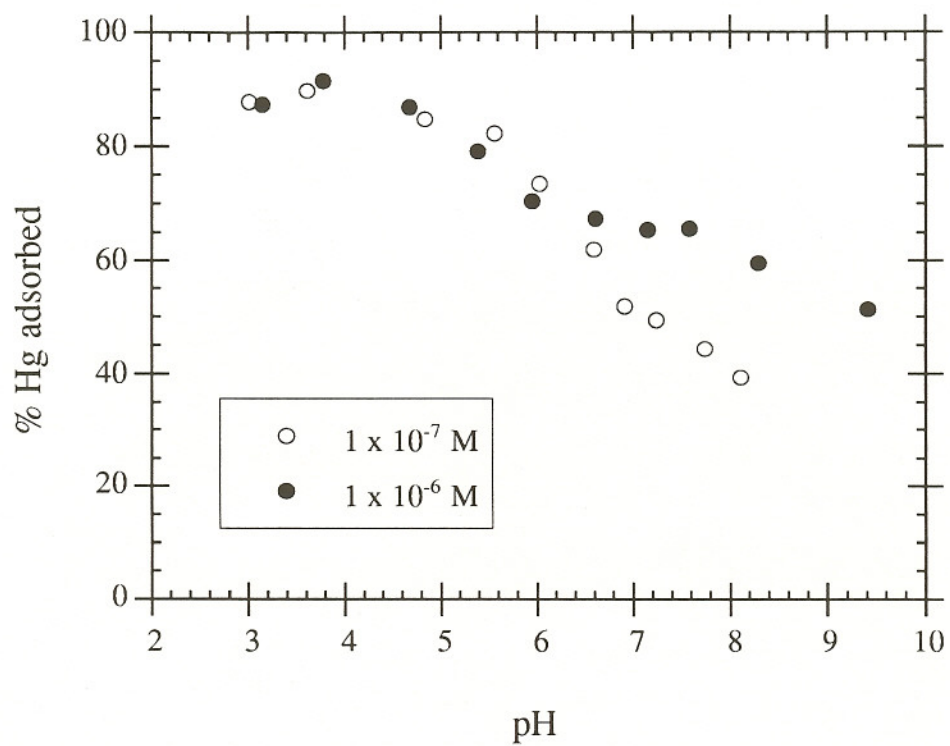


Figure A.13 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Birdsboro silt loam. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

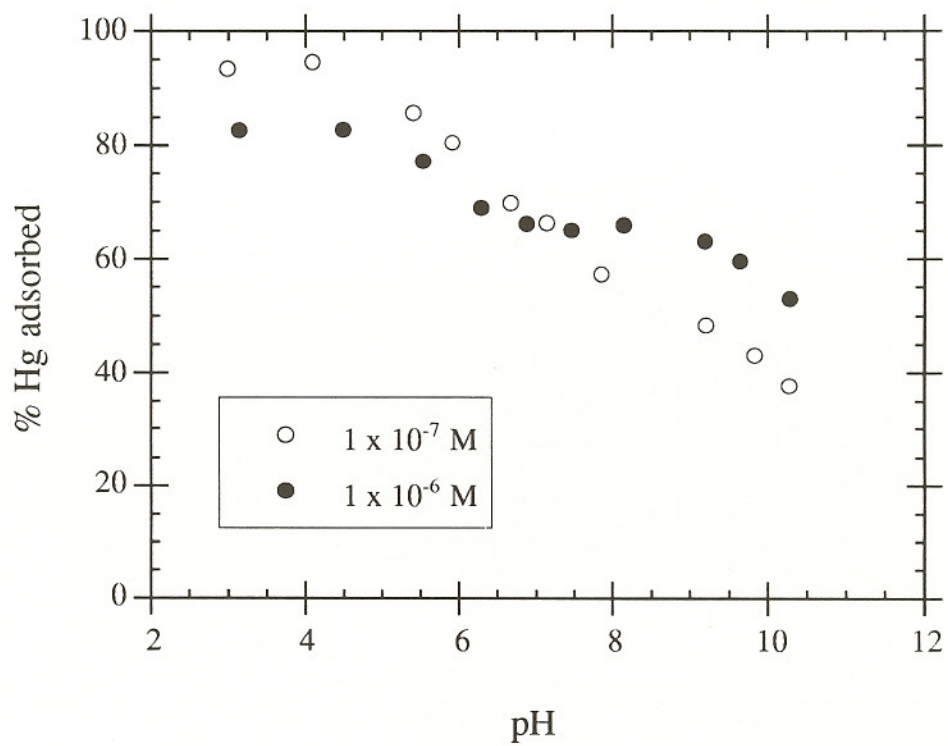


Figure A.14 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Hazen gravelly loam. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

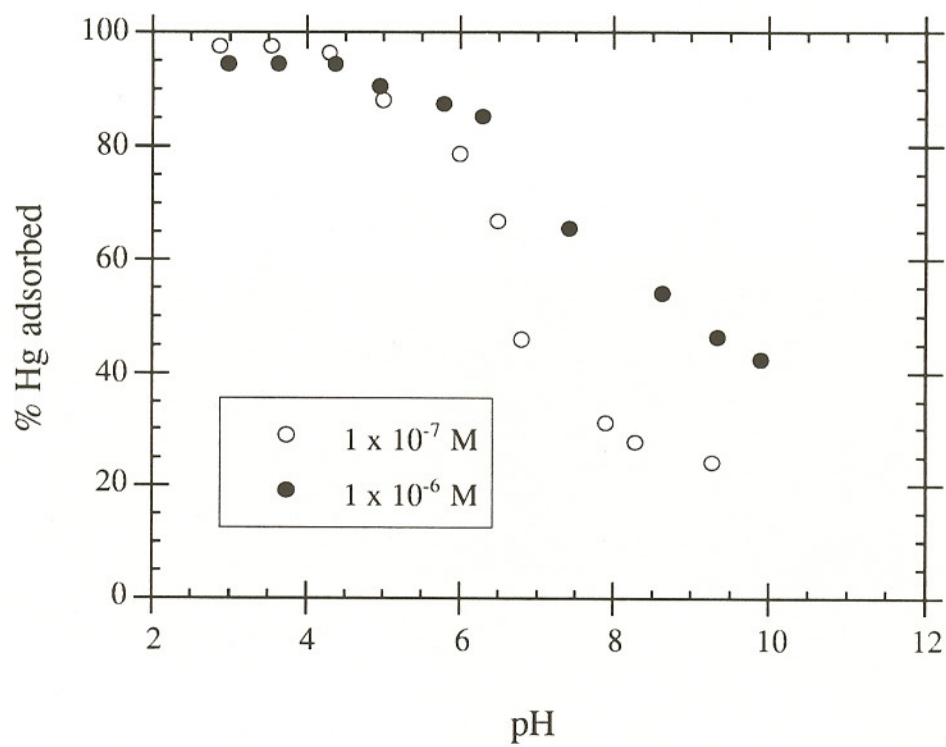


Figure A.15 Adsorption of 1×10^{-7} and 1×10^{-6} M Hg(II) on Boonton Bergen loam. Soil:water = 1 g 100 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C.

APPENDIX B

ADSORPTION ISOTHERM

Table B.1 Adsorption isotherm data for Hg(II) on fifteen New Jersey soils
Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

Birdsboro silt loam pH = 6.20		Boonton Bergen loam pH = 5.71		Boonton Union loam pH = 5.40	
C _w (μmol L ⁻¹)	C _s (μmol g ⁻¹)	C _w (μmol L ⁻¹)	C _s (μmol g ⁻¹)	C _w (μmol L ⁻¹)	C _s (μmol g ⁻¹)
0.018	0.008	0.012	0.009	0.006	0.009
0.097	0.040	0.066	0.043	0.056	0.044
0.157	0.084	0.137	0.086	0.107	0.189
0.202	0.180	0.216	0.178	0.177	0.382
0.237	0.376	0.296	0.370	0.207	0.579
0.317	0.568	0.342	0.566	0.289	0.721
0.403	0.760	0.426	0.757	0.395	1.961
0.426	0.957	0.600	0.940	0.608	3.939
0.661	1.934	0.920	1.908	0.950	5.905
0.973	3.903	1.201	3.880	1.293	7.871
1.482	5.852	1.330	5.867	2.015	10.799
2.167	7.783	1.901	7.810		
3.800	9.620	2.622	9.738		
4.396	10.560	2.679	10.732		
5.598	11.440	3.194	11.681		

Downer loamy sand pH = 4.90		Dunellen sandy loam pH = 5.78		Fill materials from Del. River pH = 5.29	
C _w (μmol L ⁻¹)	C _s (μmol g ⁻¹)	C _w (μmol L ⁻¹)	C _s (μmol g ⁻¹)	C _w (μmol L ⁻¹)	C _s (μmol g ⁻¹)
0.028	0.007	0.025	0.009	0.041	0.006
0.180	0.082	0.227	0.092	0.182	0.082
0.365	0.713	0.519	0.680	0.436	0.706
1.355	1.865	0.831	1.808	0.975	1.903
4.286	3.571	1.086	3.611	2.987	3.701
7.146	5.285	1.730	5.417	4.172	5.583
16.430	6.357	2.998	7.230	7.875	7.213
23.801	7.120	4.076	8.591	11.919	8.308
30.930	7.907	6.078	9.961	16.672	9.333

Table B.1 Continued

Freehold sandy loam (A horizon) pH = 6.26		Freehold sandy loam (B horizon) pH = 5.66		Hazen gravelly loam pH = 6.45	
C_w ($\mu\text{mol L}^{-1}$)	C_s ($\mu\text{mol g}^{-1}$)	C_w ($\mu\text{mol L}^{-1}$)	C_s ($\mu\text{mol g}^{-1}$)	C_w ($\mu\text{mol L}^{-1}$)	C_s ($\mu\text{mol g}^{-1}$)
0.020	0.008	0.033	0.007	0.029	0.007
0.150	0.085	0.092	0.041	0.213	0.079
0.407	0.709	0.276	0.172	0.638	0.686
0.822	1.918	0.405	0.359	1.078	1.892
1.457	3.854	0.723	0.528	1.803	3.820
2.504	5.750	0.798	0.670	2.259	5.774
2.844	7.716	4.934	1.507	2.935	7.707
4.336	9.066	15.797	2.420	3.331	9.167
5.829	10.417	31.125	2.888	4.361	10.564
		48.690	3.131		
		60.655	3.435		
		73.417	3.658		
Lakewood sand pH = 5.01		Penn silt loam pH = 5.17		Rockaway stony loam pH = 5.33	
C_w ($\mu\text{mol L}^{-1}$)	C_s ($\mu\text{mol g}^{-1}$)	C_w ($\mu\text{mol L}^{-1}$)	C_s ($\mu\text{mol g}^{-1}$)	C_w ($\mu\text{mol L}^{-1}$)	C_s ($\mu\text{mol g}^{-1}$)
0.149	0.085	0.040	0.096	0.012	0.009
0.476	0.702	0.088	0.741	0.045	0.096
1.054	1.895	0.262	1.974	0.111	0.739
3.060	3.694	0.654	3.935	0.299	1.970
5.861	5.414	1.566	5.843	0.384	3.962
10.890	6.911	2.697	7.730	0.614	5.939
18.376	7.662	5.153	8.985	0.804	7.920
23.366	8.663	11.609	9.839	1.150	9.385
				1.420	10.858

Table B.1 Continued

Sassafras sandy loam pH = 6.06		Washington loam pH = 6.40		Whippany silty clay loam pH = 6.16	
C_w ($\mu\text{mol L}^{-1}$)	C_s ($\mu\text{mol g}^{-1}$)	C_w ($\mu\text{mol L}^{-1}$)	C_s ($\mu\text{mol g}^{-1}$)	C_w ($\mu\text{mol L}^{-1}$)	C_s ($\mu\text{mol g}^{-1}$)
0.013	0.009	0.027	0.007	0.020	0.008
0.144	0.086	0.194	0.081	0.209	0.079
0.258	0.724	0.389	0.711	0.436	0.706
0.840	1.916	0.755	1.925	0.555	1.945
2.497	3.750	1.140	3.886	0.833	3.917
8.563	5.144	1.627	5.837	1.230	5.877
16.653	6.335	2.097	7.790	1.905	7.810
26.159	6.884	2.694	9.231	2.499	9.250
33.054	7.695	3.665	10.634	3.331	10.667

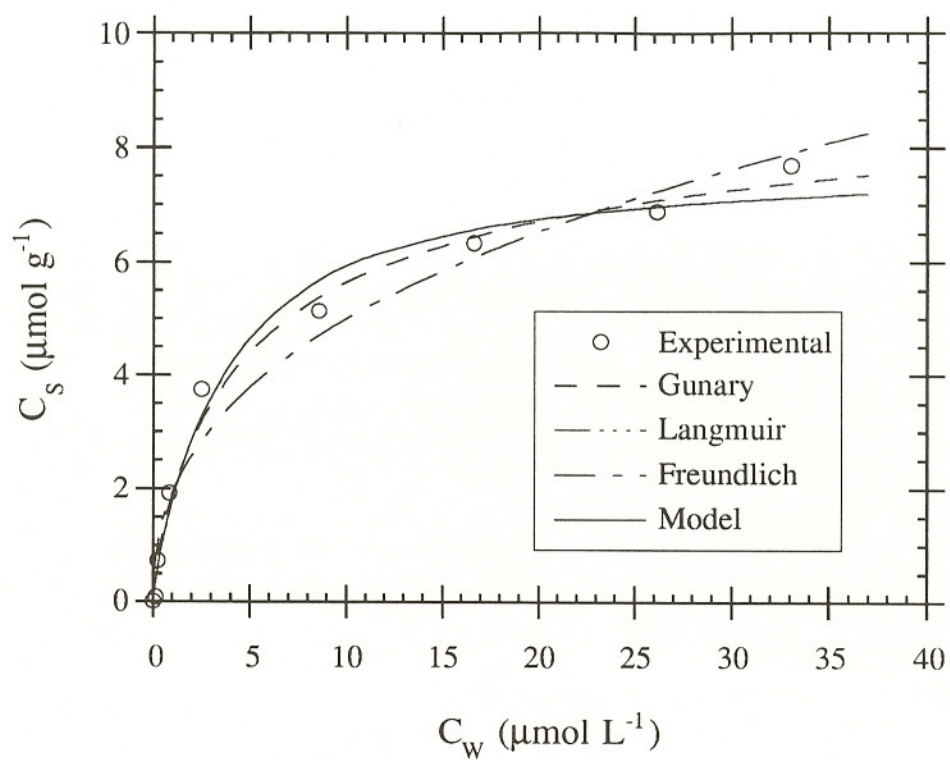


Figure B.1 Adsorption isotherm of Hg(II) on Sassafras sandy loam. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.22.

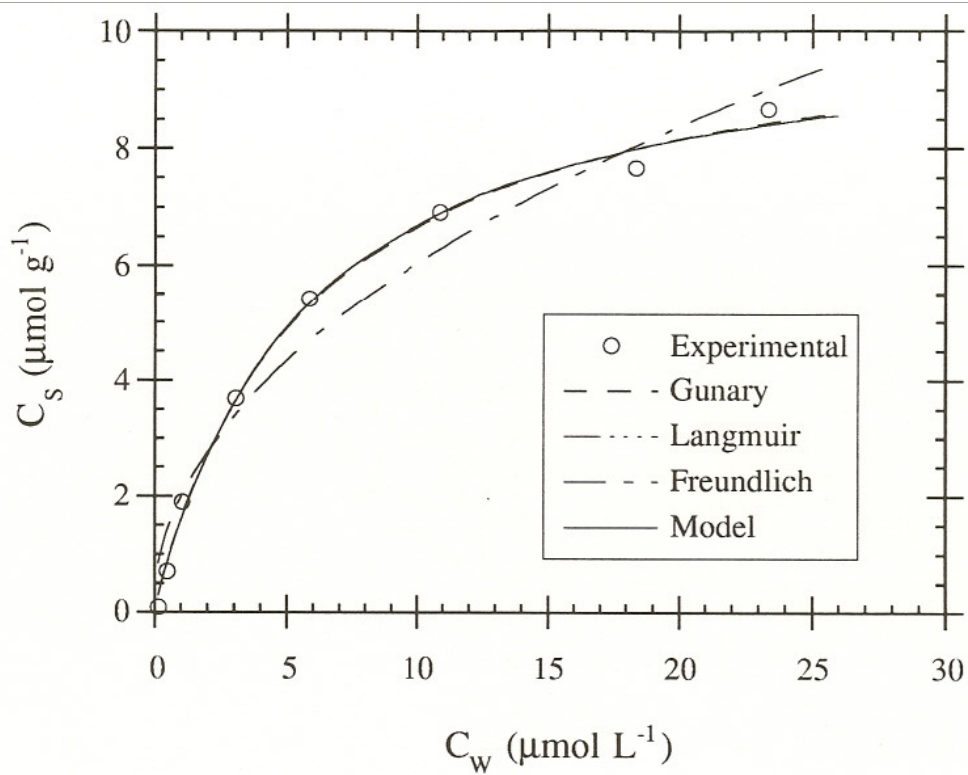


Figure B.2 Adsorption isotherm of Hg(II) on Lakewood sand. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.22.

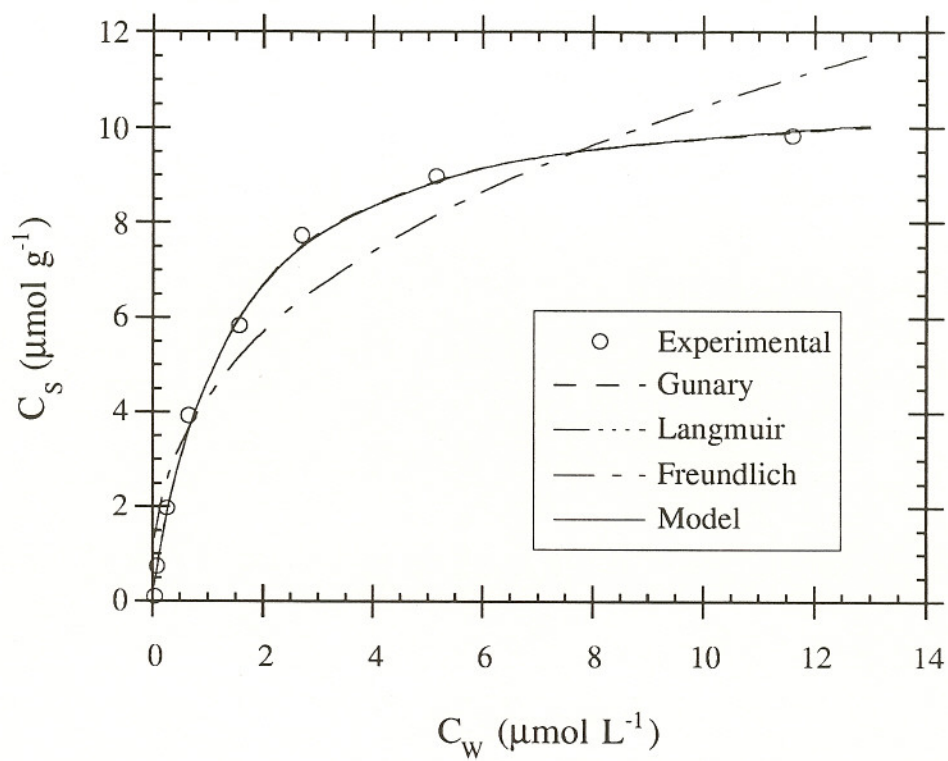


Figure B.3 Adsorption isotherm of Hg(II) on Penn silt loam. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.22.

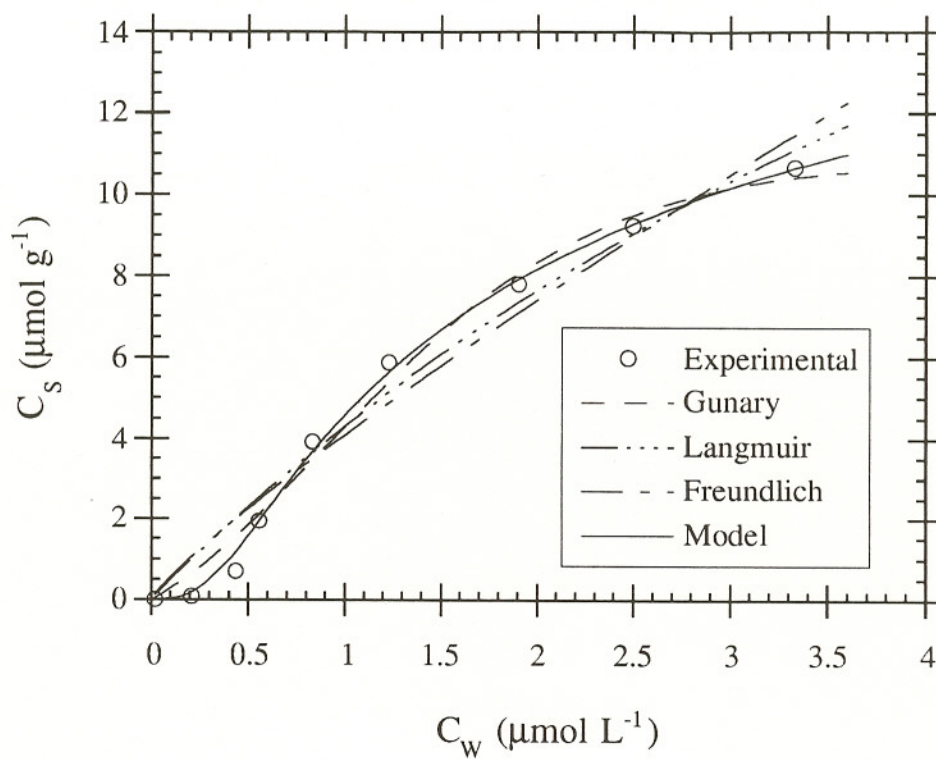


Figure B.4 Adsorption isotherm of Hg(II) on Whippany silty loam. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.21.

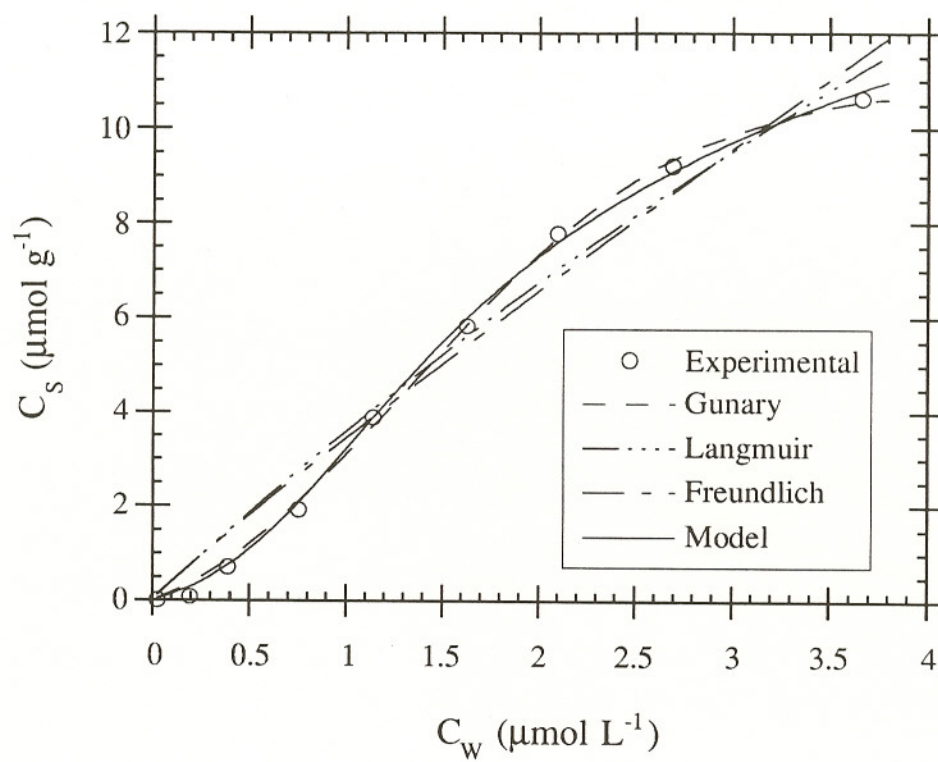


Figure B.5 Adsorption isotherm of Hg(II) on Washington loam. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.21.

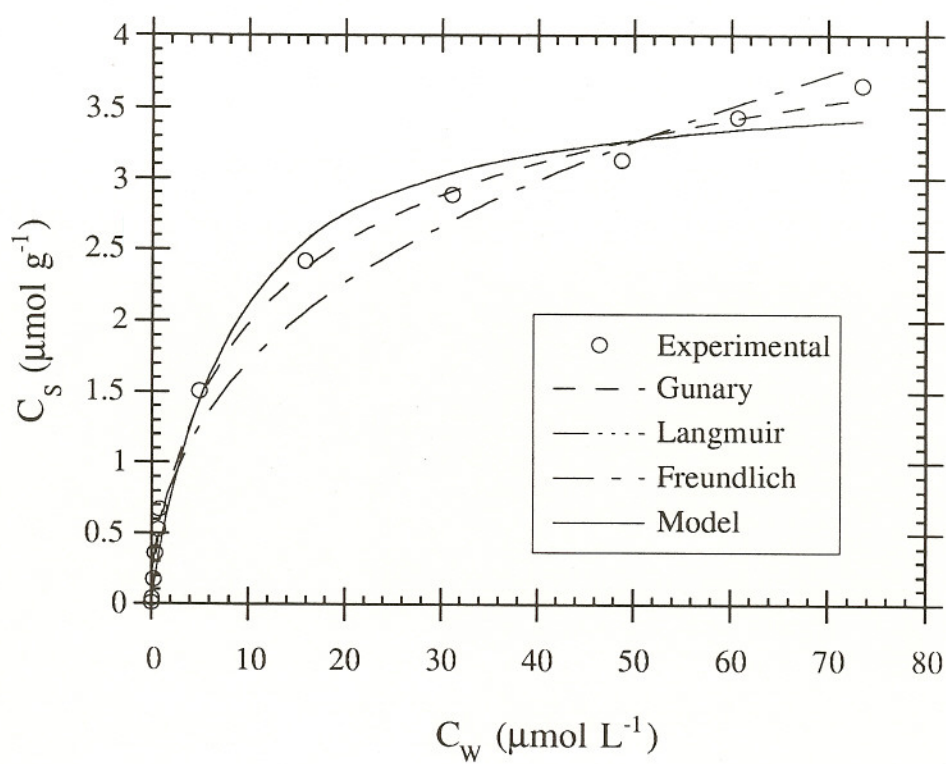


Figure B.6 Adsorption isotherm of Hg(II) on Freehold sandy loam (A horizon). Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.22.

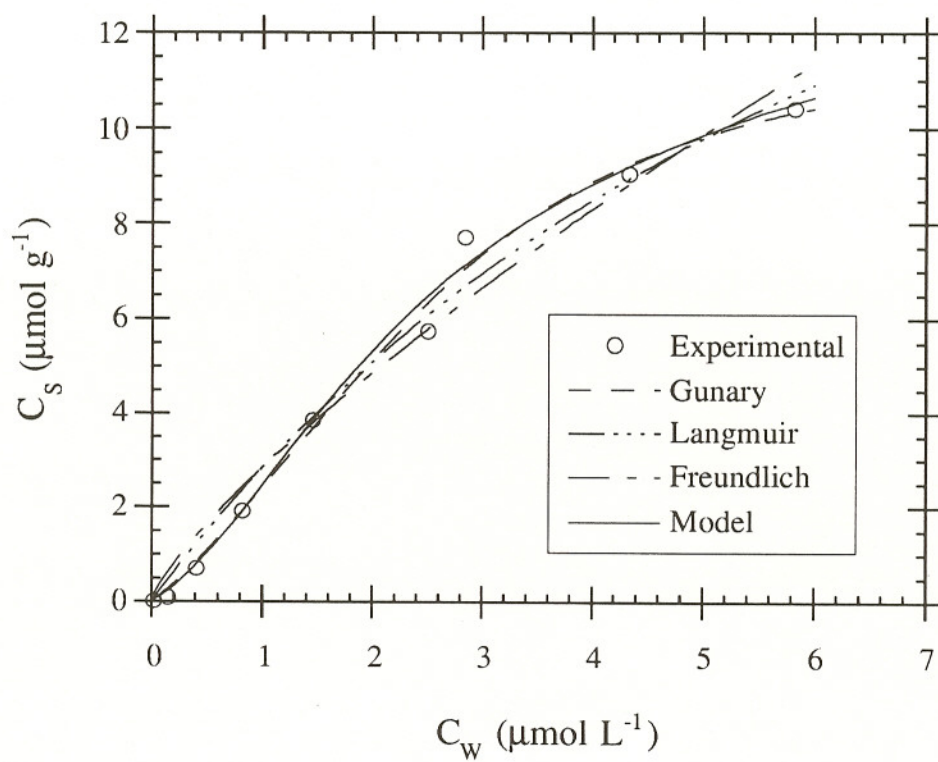


Figure B.7 Adsorption isotherm of Hg(II) on Freehold sandy loam (B horizon). Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.21.

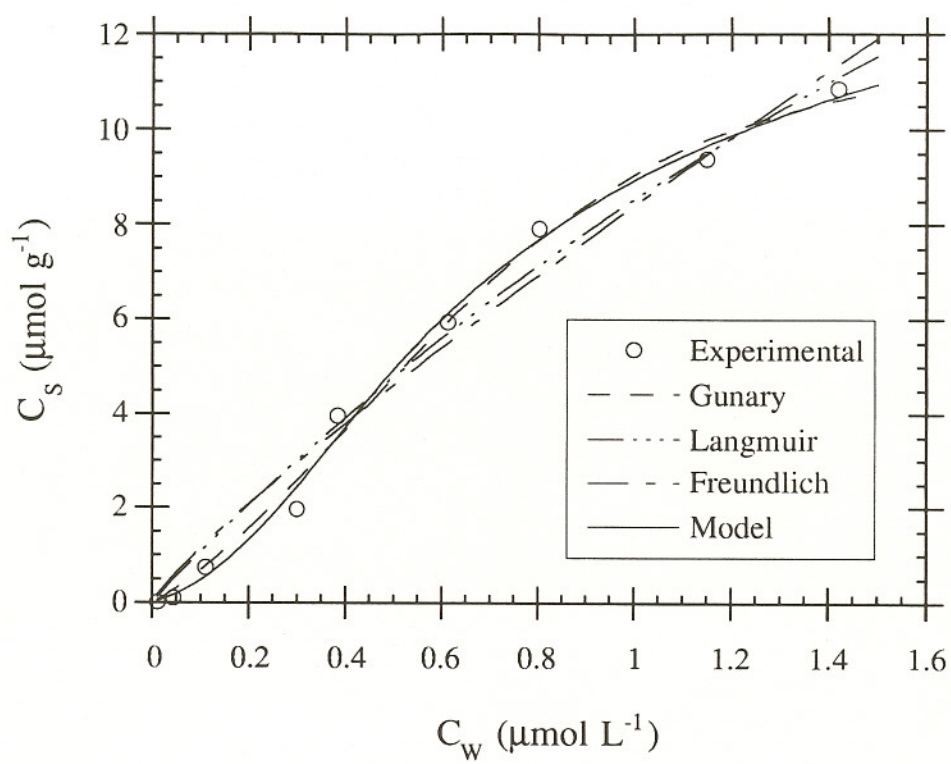


Figure B.8 Adsorption isotherm of Hg(II) on Rockaway stony loam. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.21.

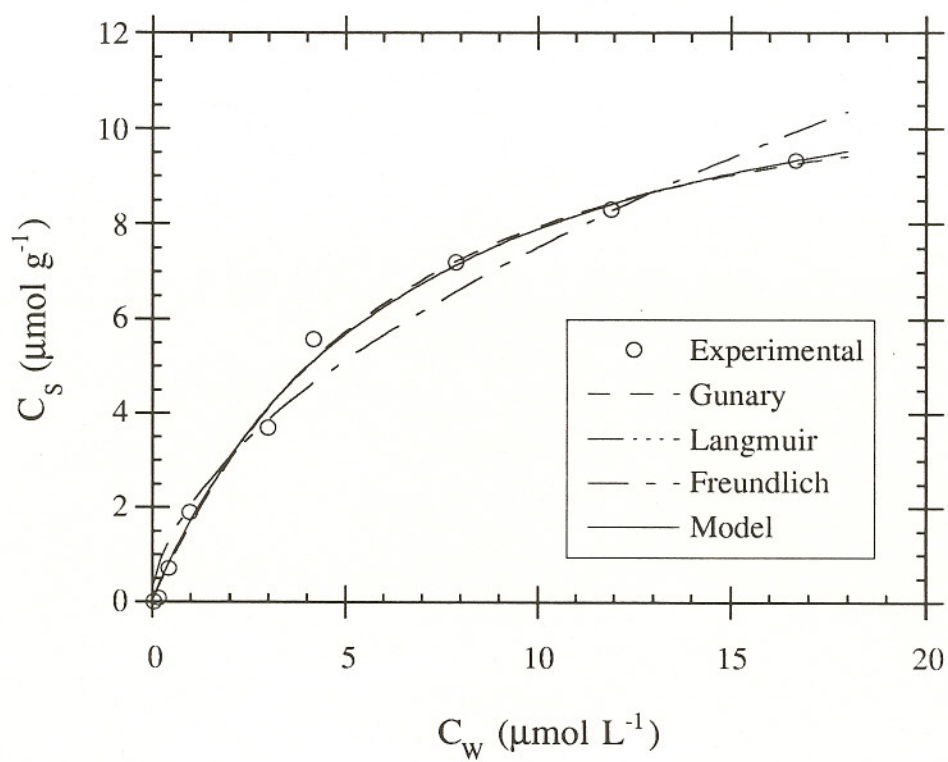


Figure B.9 Adsorption isotherm of Hg(II) on fill material from the Delaware River. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.22.

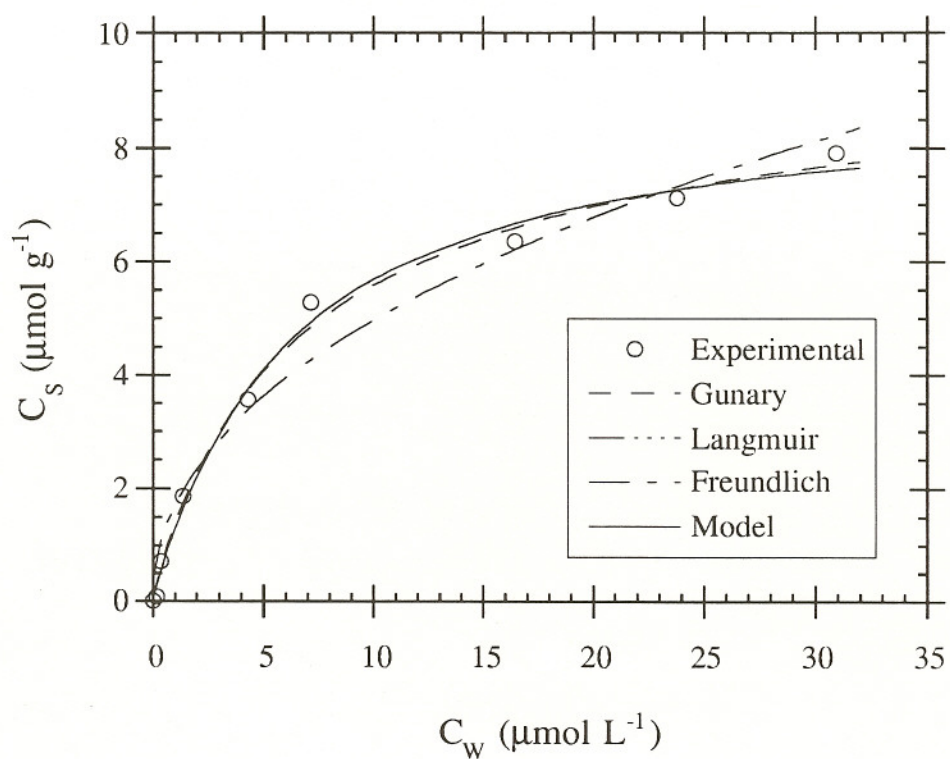


Figure B.10 Adsorption isotherm of Hg(II) on Downer loamy sand. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.22.

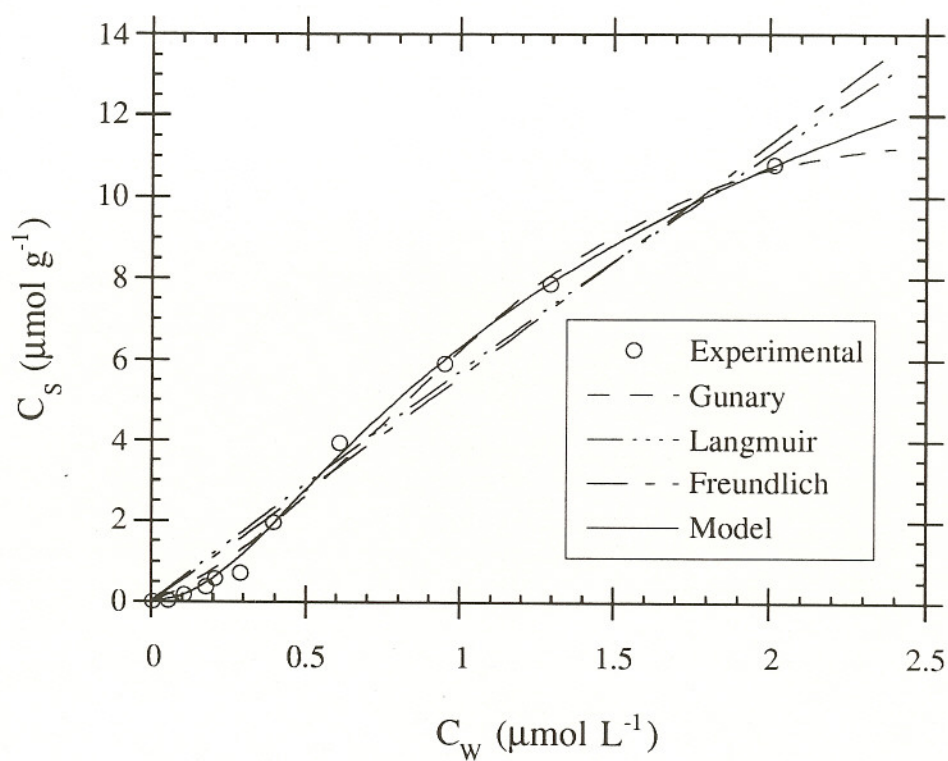


Figure B.11 Adsorption isotherm of Hg(II) on Boonton Union loam. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.21.

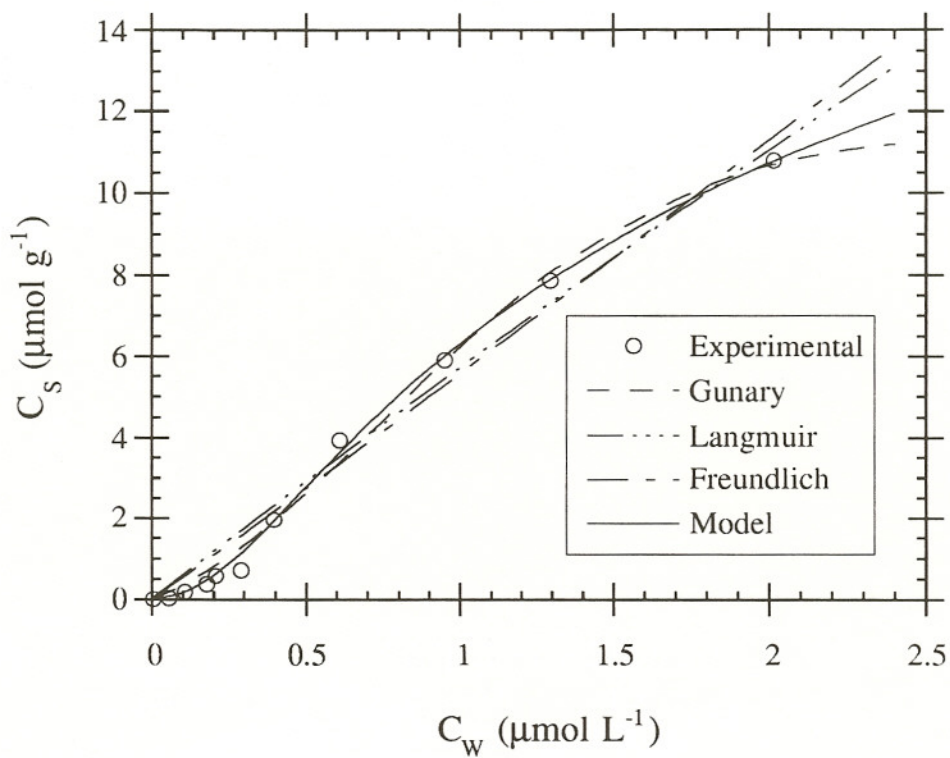


Figure B.12 Adsorption isotherm of Hg(II) on Dunellen sandy loam. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.21.

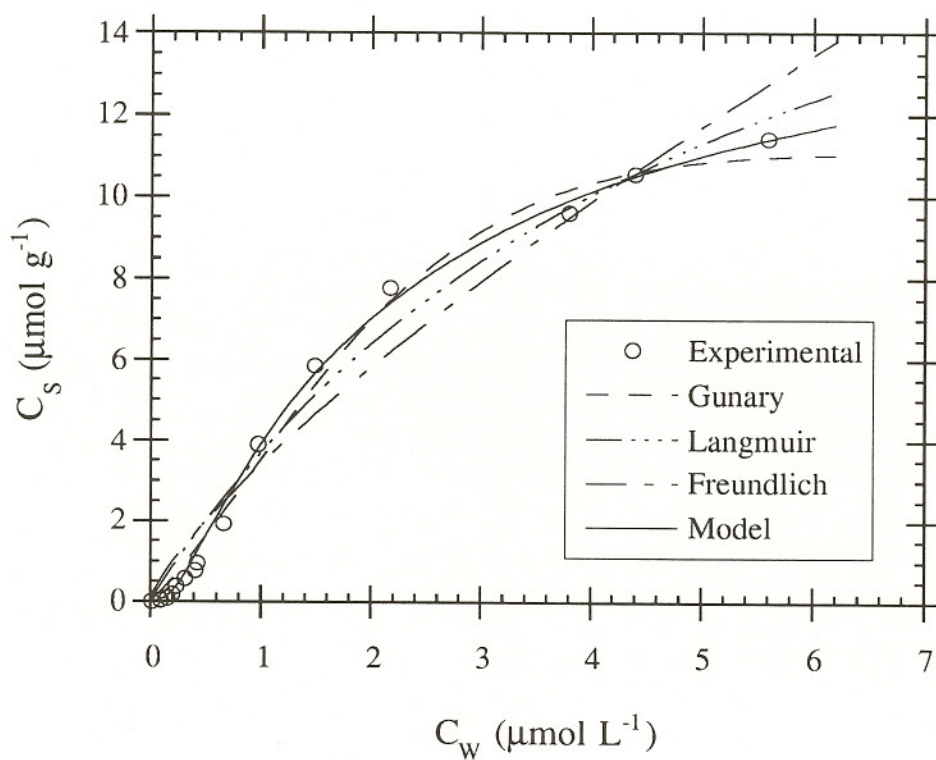


Figure B.13 Adsorption isotherm of Hg(II) on Birdsboro silt loam. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.21.

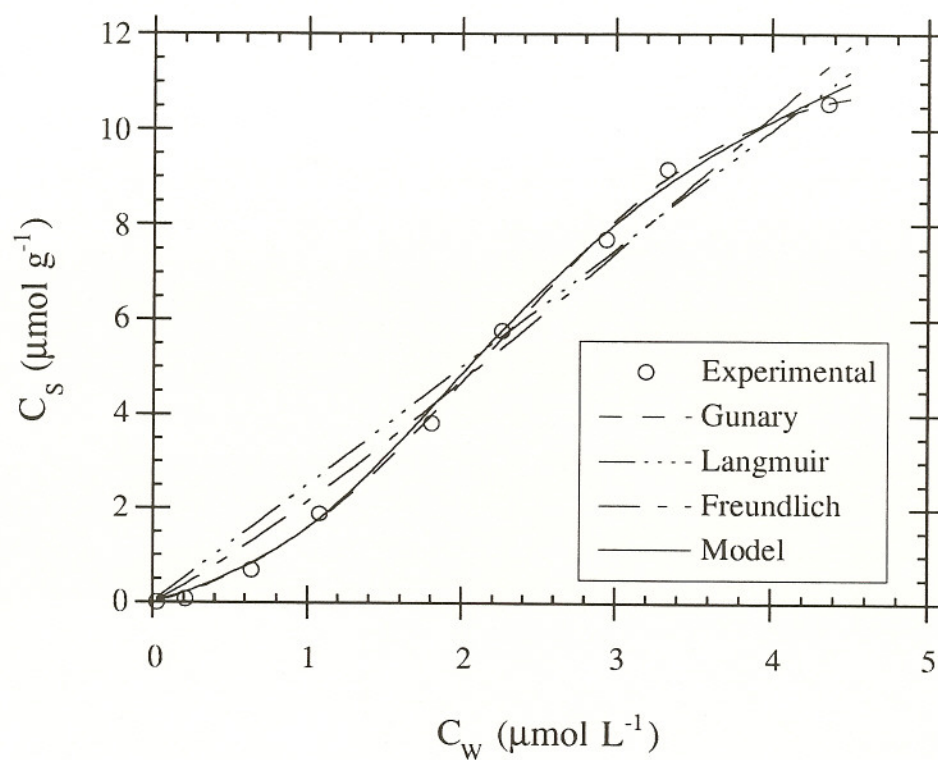


Figure B.14 Adsorption isotherm of Hg(II) on Hazen gravelly loam. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.21.

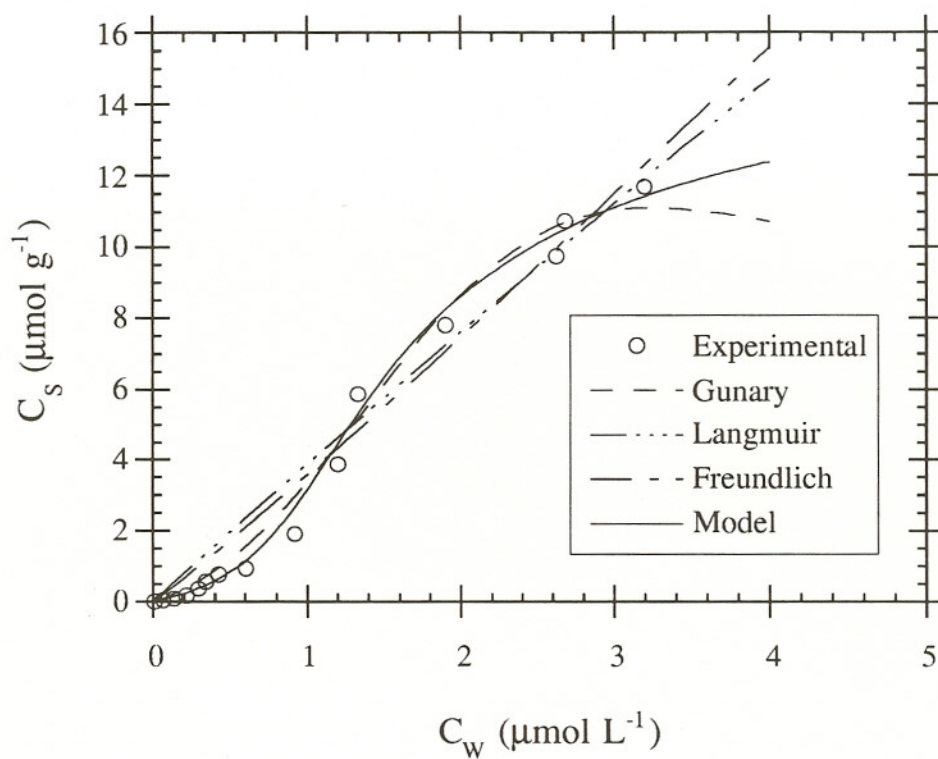


Figure B.15 Adsorption isotherm of Hg(II) on Boonton Bergen loam. Soil:water = 0.4 g 40 mL⁻¹; I = 0.01 NaNO₃ M; T = 25 ± 2°C. Model refers to equation 4.21.

APPENDIX C

ADSORPTION AND DESORPTION KINETICS

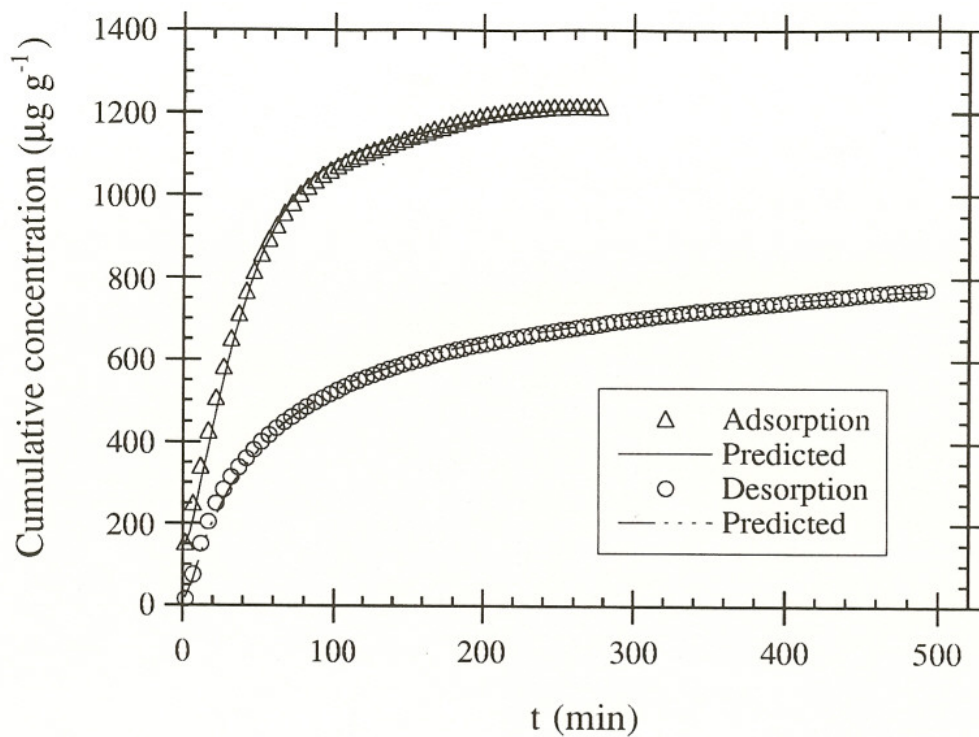


Figure C.1 Kinetics of Hg(II) adsorption to and desorption from Sassafras sand loam. Influent Hg concentration = 8 mg L^{-1} . The predicted values were calculated with equations 5.11 and 5.12 for adsorption and desorption respectively.

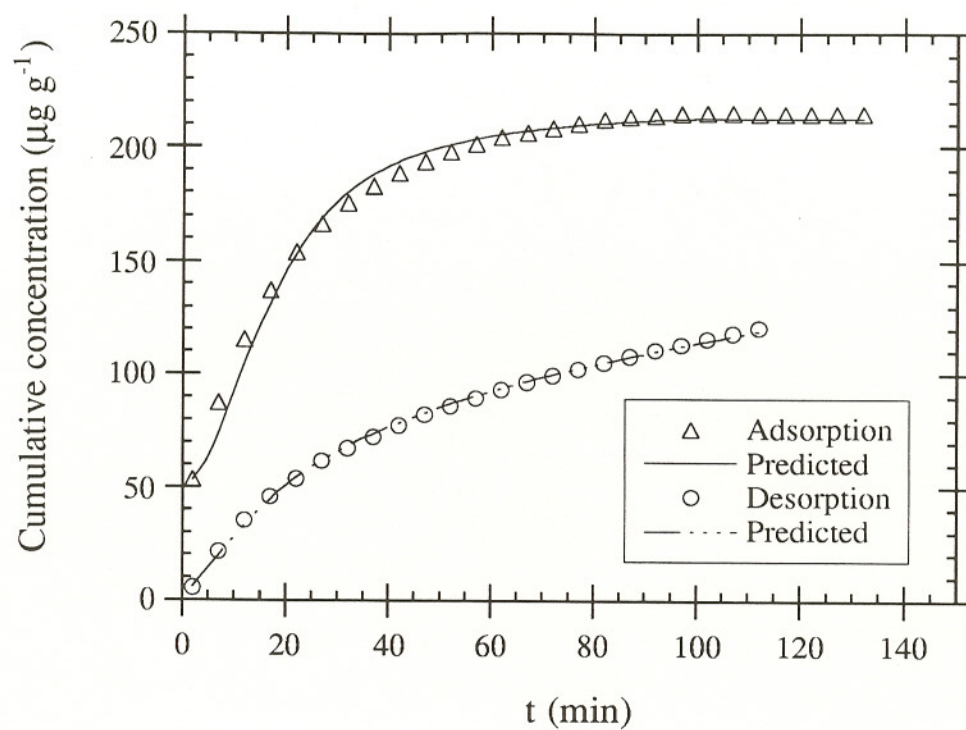


Figure C.2 Kinetics of Hg(II) adsorption to and desorption from Freehold sandy loam (A horizon). Influent Hg concentration = 4 mg L^{-1} . The predicted values were calculated with equations 5.11 and 5.12 for adsorption and desorption, respectively.

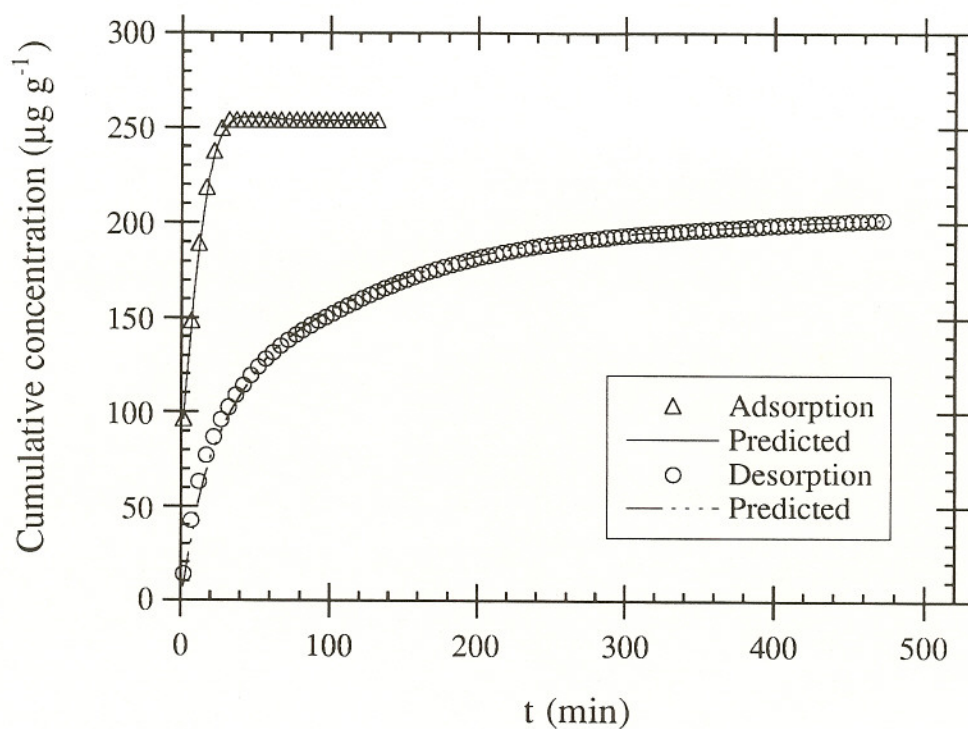


Figure C.3 Kinetics of Hg(II) adsorption to and desorption from Freehold sandy loam (A horizon). Influent Hg concentration = 8 mg L^{-1} . The predicted values were calculated with equations 5.11 and 5.12 for adsorption and desorption, respectively.

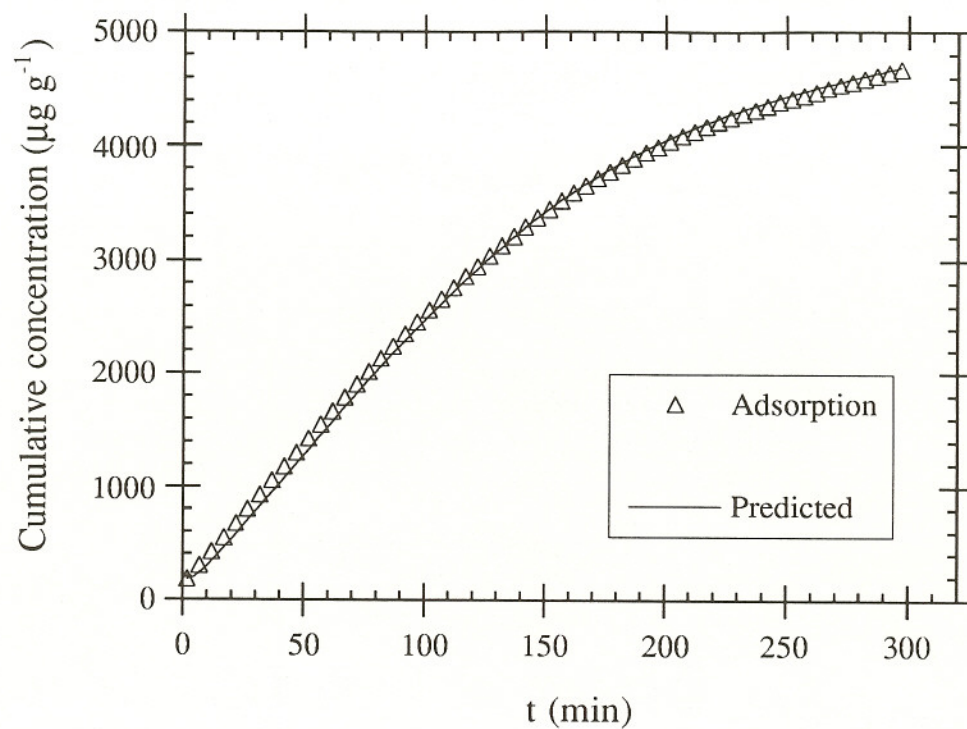


Figure C.4 Kinetics of Hg(II) adsorption to Rockaway stony loam. Influent Hg concentration = 8 mg L^{-1} . The predicted values were calculated with equations 5.11.

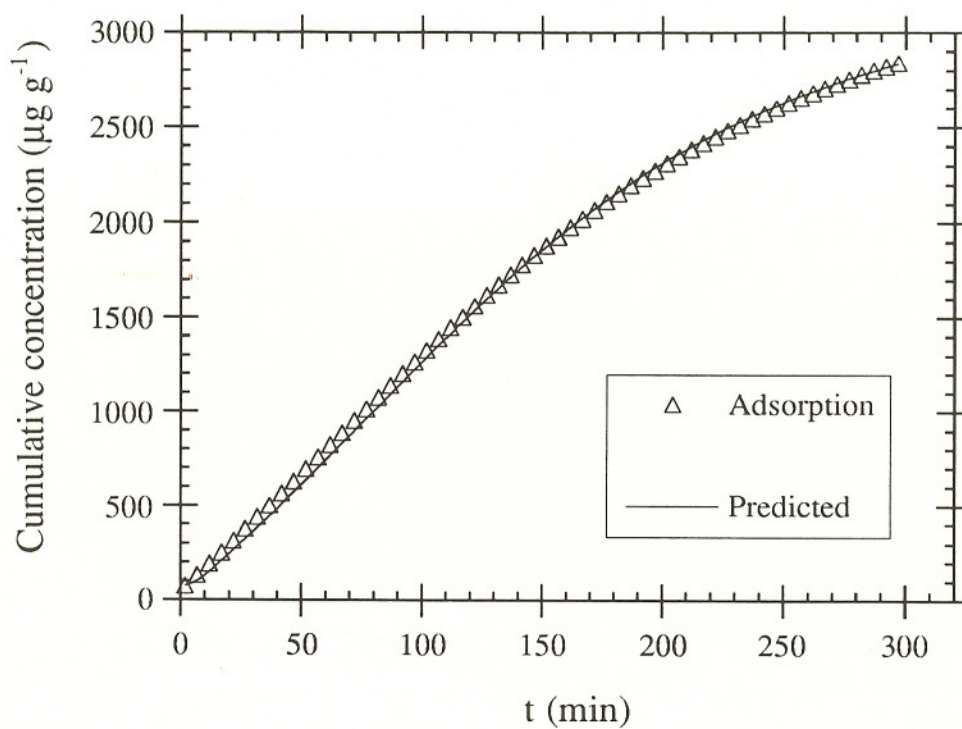


Figure C.5 Kinetics of Hg(II) adsorption to Dunellen sandy loam. Influent Hg concentration = 4 mg L^{-1} . The predicted values were calculated with equations 5.11.

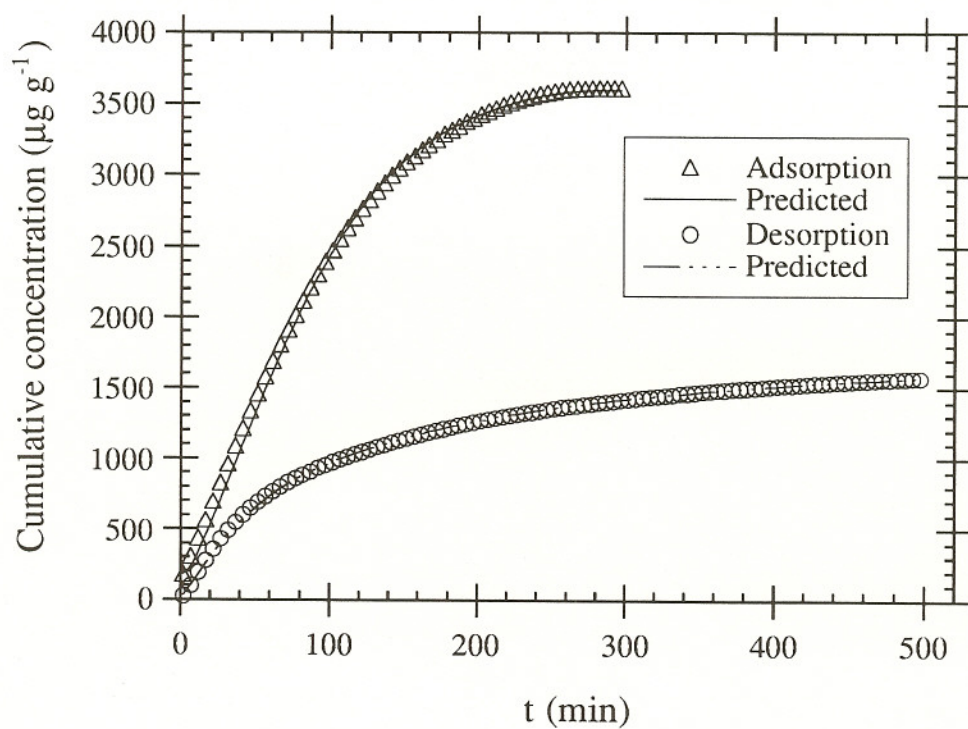


Figure C.6 Kinetics of Hg(II) adsorption to and desorption from Dunellen sandy loam. Influent Hg concentration = 8 mg L^{-1} . The predicted values were calculated with equations 5.11 and 5.12 for adsorption and desorption, respectively.