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An Evaluation of Ground Water-Surface Water
Interactions in Saginaw Bay, Lake Huron,
with Implications for Trace Metal Cycling

presented by

Jonathan James Kolak

has been accepted towards fulfillment
of the requirements for

Doctoral degree in Geological Sciences


Major professor

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AN EVALUATION OF GROUND WATER-SURFACE WATER
INTERACTIONS IN SAGINAW BAY, LAKE HURON, WITH
IMPLICATIONS FOR TRACE METAL CYCLING

VOLUME I

By

Jonathan James Kolak

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Geological Sciences

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ABSTRACT

AN EVALUATION OF GROUND WATER-SURFACE WATER INTERACTIONS IN SAGINAW BAY, LAKE HURON, WITH IMPLICATIONS FOR TRACE METAL CYCLING

By

Jonathan James Kolak

A suite of water and sediment samples was collected to characterize the extent of interaction between saline ground water (with solutes derived from Michigan basin brines) and surface water in Saginaw Bay and the Saginaw Lowland Area (SLA). Porewater chemistry in sediment cores from both the bay and SLA indicate the presence of a saline, isotopically light source at depth. Cl:Br ratios indicate formation brine is the source for salinity. Mixing models constrained by Cl- $\delta^{18}\text{O}$ data indicate that porewater chemistry in both areas may be the result of similar multi-stage mixing process(es), but they do not appear to be interacting with the same water masses. 1-D transport simulations indicate that the SLA porewater profiles required approximately 8000 a to develop and that advective transport is an important contributor. Significantly shorter times are needed (<300 a) for bay core porewater profiles; diffusion dominates transport in these cores. A number of samples from the Saginaw Bay watershed also have elevated chloride levels, but Cl:Br ratios indicate that interaction with saline ground water is limited. Agricultural drains appear to be a much more significant source for chloride and bromide to the watershed. However, a number of sediment cores collected from

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riverbeds do indicate the presence of a high-chloride source at depth. The Cl:Br ratios in porewater from these cores are low (generally less than 30) and may reflect the influence of organic matter decomposition.

Sediment cores collected from Saginaw Bay were used to evaluate trace metal loading histories, study metal partitioning and diagenesis, and assess the potential for remobilization due to saline water intrusion. Trace metal mass balances constructed for cadmium and zinc indicate that benthic fluxes could be a significant source for trace metals to the water column. Trace metal partitioning studies, used as a proxy for saline water, indicate that porewater concentrations of cadmium and copper could increase significantly in response to saline water intrusion, however, only the cadmium cycle would be strongly affected by such interaction.

Porewater chemistry in Saginaw Bay, combined with new and historical data regarding porewater chemistry in Lake Michigan, indicate that saline fluids, derived from Michigan basin brines, are interacting with surface sediments on a regional scale. Saline porewater in both Saginaw Bay and Lake Michigan is likely derived from two different geologic formations. A conceptual model for solute transport in the Michigan basin is proposed to account for the presence of saline porewater in sediments. A combination of advection (driven by topography) and diffusion likely accounts for the observed chemistry in the Saginaw Bay area. There exists the potential for topographically-driven flow to transport solutes to Lake Michigan, but advection (as a result of compaction) might also be responsible for the observed porewater chemistry.

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LIST OF

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INTRODU

CHAPTER

Ground-W

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Major

Temp

Discuss

TABLE OF CONTENTS

LIST OF TABLES.....	viii
LIST OF FIGURES	ix
INTRODUCTION	1
CHAPTER I.	
Ground-Water, Large-Lake Interactions in Saginaw Bay, Lake Huron	8
Introduction	9
Geology of the Study Area	13
Methods	16
Sample Collection and Preservation.....	16
Transport Modeling Equations	20
Results	23
Spatial Variations in Chloride Concentrations	23
Major Cations	27
Geochemical Modeling.....	33
Stable Isotopes	40
Spatial Variations in $\delta^{18}\text{O}$ Values	44
Tritium Analyses	49
Discussion.....	51
Fluid Mixing - Chloride:Bromide Ratios and the Source for Salinity	51
Fluid Mixing - Chloride and $\delta^{18}\text{O}$ Constraints.....	57
Transport Modeling and Regional Implications.....	65
Conclusions	73
CHAPTER II.	
Evaluation of Ground Water-Surface Water Interactions in the Saginaw Bay Watershed, Lake Huron	75
Introduction	76
Methods	77
Sampling Plan Design	77
Sample Collection	78
Sample Analysis	83
Results	84
Chloride, Bromide, and Sodium	84
Major Cations	88
Temporal Variations in Water Quality	93
Discussion.....	95

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Solute Sources - Geochemical Modeling	95
Solute Sources - Chloride and Bromide Systematics	100
Solute Sources - River Cores.....	104
Conclusions	111

CHAPTER III.

Evaluation of Trace Metal Loading and Partitioning in Saginaw Bay (Lake Huron) Sediments: Implications for Cycling and Postdepositional Remobilization	113
---	-----

Introduction	114
Methods	121
Sediment Collection	121
Porewater Extraction and Analyses	124
Sediments-Total Metal Extractions	126
Sediments- Sequential Chemical Extractions.....	127
Quality Assurance/Quality Control (QA/QC)	134
Model/parameters Used in Estimating Benthic Fluxes	140
Results	143
Temporal Variations in Metal Loading	143
Organic Carbon Content.....	149
Iron.....	150
Manganese.....	158
Cadmium	164
Copper	167
Zinc.....	172
Discussion.....	176
Diagenetic Controls on Metals - Geochemical Modeling	176
Efficacy of SCEs to Study Metal Mobility in Benthic Sediments	183
Benthic Flux Estimates and Trace Metal Mass Balances.....	195
Potential for Saline Remobilization of Sediment-Bound Metals	204
Conclusions	209

CHAPTER IV.

Regional Significance of Saline Ground-Water Inputs to the Great Lakes: Implications for Chloride Cycling and Michigan Basin Hydrogeology.....	213
---	-----

Introduction	214
Methods	218
Sediment Cores.....	218
Benthic Flux Estimates.....	221
Results and Discussion	223
A Chloride Mass Balance for Saginaw Bay	228
Porewater Chemistry in Lake Michigan Sediments	231
Solute Transport in the Michigan basin.....	236
Conclusions	244

LIST OF REFERENCES	246
--------------------------	-----

APPENDICES

Appendix A: Saginaw Bay sampling Stations/Sediment Core Descriptions	
Figure A-1: Saginaw Bay Sampling Stations.....	267
Table A-1: Saginaw Bay Sampling Stations	268
Table A-2: Bay Cores Collected for Stratigraphic Study.....	269
Table A-3: Gravity Core Descriptions (Porewater Extracted by Hydraulic Squeezer).....	271
Table A-4: Trace Metal Box Core Descriptions	278
Table A-5: Box Core Descriptions.....	284
Appendix B: Saginaw Bay Water Chemistry Data	
Table B-1: Saginaw Bay Water Column Chemistry	301
Table B-2: Saginaw Bay Porewater Chemistry – Geochemical Modeling.....	303
Table B-3: Saginaw Bay Gravity Core Porewater Chemistry.....	304
Table B-4: Ferrous Iron Concentrations in Porewater Samples.....	314
Table B-5: Trace Metal Concentrations in Porewater Samples	315
Appendix C: Terrestrial Core Porewater Chemistry	
Table C-1: Terrestrial Core Porewater Chemistry	322
Appendix D: Saginaw Bay Benthic Sediment Chemistry	
Table D-1: Total Organic Carbon Concentrations in Sediments	325
Table D-2: Total Metal Concentrations in Sediments.....	326
Table D-3: SCE Results for Iron	331
Table D-4: SCE Results for Manganese	333
Table D-5: SCE Results for Cadmium.....	335
Table D-6: SCE Results for Copper	337
Table D-7: SCE Results for Zinc	339
Table D-2: Total Metal Concentrations in Sediments.....	326
Appendix E: Saginaw Bay Watershed – River Chemistry	
Table E-1: Watershed Sampling Events.....	342
Table E-2: Locations of River Sampling Stations.....	343
Table E-3: River Chemistry – RIV I Sampling.....	352
Table E-4: River Chemistry – RIV II Sampling	359
Table E-5: River Chemistry – RIV III Sampling	367
Table E-6: River Chemistry – RIV IV Sampling.....	376
Table E-7: River Chemistry – RIV V Sampling	384

Table 1

Table 2

Table 3

Table 4

Table 5

Table 6

Table 7

Table 8

Table 9

Table 10

Table 11

Table 12

Table 13

Table 14

LIST OF TABLES

Table 1. Average Mineral Saturation Indices Calculated for Saginaw Bay Samples.	37
Table 2. Tritium Levels in Water Column Samples.	50
Table 3. Summary Statistics (Cl, Br, Na) for River Sampling Events.	85
Table 4. Temporal Variations in Water Quality Within the Saginaw Bay Watershed.	94
Table 5. Average Recovery of Trace Metals from SRM 2704 (Buffalo River Sediment) Using Microwave-Nitric Acid Digestion Technique.	136
Table 6. Concentrations of Trace Metals in SCE Procedural Blanks.	138
Table 7. Results of SCE Analysis on Three Sediment Subsplits.	139
Table 8. Comparison Between Total Extractions (Microwave-HNO ₃) and Summation of Sequential Chemical Extractions (Σ SCE).	141
Table 9. Comparison of Geochemical Parameters in Surficial Sediments Between Robbins (1986) and this study.	148
Table 10. WATEQ4F-Calculated Saturation Indices for Major Minerals and Trace Metal-Bearing Phases.	179
Table 11. Results of SCE Analyses on NIST-Certified Standard Reference Materials.	194
Table 12. Estimated benthic flux metal loads to Saginaw Bay. (<i>All entries in units of metric tons/a</i>).	203
Table 13. Use of EX fraction As a Proxy to Simulate the Effect of Saline Porewater on Trace Metal Remobilization from Sediments.	208
Table 14. A Chloride Mass Balance for Saginaw Bay.	227

Figur

Figur

Figur

Figur

Figur

Figur

Figur

Figur

Figur

Figur

Figur

Figur

Figur

Figur

Figur

Figur

LIST OF FIGURES

Figure 1. Temporal variations in dissolved chloride concentrations among the Great Lakes. (<i>Modified from Pringle et al., 1981.</i>).	2
Figure 2. Previously documented occurrences of saline water in near-surface sediments from the Great Lakes' region. (<i>The large oval represents the approximate extent of the Michigan Basin.</i>).	4
Figure 3. Conceptual model of chloride cycling in Saginaw Bay.	6
Figure 4. Distribution of (A) dissolved chloride and (B) $\delta^{18}\text{O}$ in ground water from the Glaciofluvial aquifer. (<i>Modified from Wahrer et al., 1996.</i>).	12
Figure 5. Generalized map showing major bedrock units of the MI RASA study. (<i>Modified from Western Michigan University, 1981, pl.12, and Westjohn et al., 1994.</i>).	14
Figure 6. Map of sampling locations.. . . .	17
Figure 7. Dissolved chloride porewater profiles in (A) terrestrial cores and (B) bay cores.	24
Figure 8. Scatterplots for (A) Ca vs. Cl, (B) Mg vs. Cl, (C) K vs. Cl, and (D) Na vs. Cl in bay-core porewaters. (<i>Regressions based on all porewater samples containing greater than 60mg/L chloride.</i>).	28
Figure 9. Ternary diagram of major cations in water column and porewater samples.	31
Figure 10. Ca vs. Na in bay-core porewaters.	34
Figure 11. Changes in SI values with porewater depth.	39
Figure 12. $\delta^{18}\text{O}$ vs. δD in water column and porewater samples.	43
Figure 13. $\delta^{18}\text{O}$ porewater profiles in (A) terrestrial cores and (B) bay cores.	45
Figure 14. Map of water column stations sampled for tritium analyses.	50
Figure 15. Log Br vs. Log Cl in water column and porewater samples.	53
Figure 16. Mixing relationship between Saginaw Bay water column and formation brine.	55

Fig

Fig

Fig

Fig

Fig

Fig

Fig

Fig

Fig

Fig

Fig

Fig

Fig

Fig

Figures 17. Chloride- $\delta^{18}\text{O}$ mixing curves between a brine and freshwater endmembers.	61
Figure 18. Chloride- $\delta^{18}\text{O}$ mixing curves between a freshwater and brackish/saline endmembers. (<i>Curves I, II, and III are from Figure 17.</i>)	63
Figure 19. 1-D simulation of chloride transport in terrestrial core C.	66
Figure 20. 1-D simulation of chloride transport in bay cores (A) SB24, (B) SB7, (C) SB17 and (D) SB22.	68
Figure 21. 1-D simulation of ^{18}O transport in terrestrial core C.	70
Figure 22. 1-D simulation of ^{18}O transport in bay core SB7.	72
Figure 23. Map of watershed sampling sites.	79
Figure 24. Location of stream gaging stations.	80
Figure 25. Hydrographs for four rivers in the Saginaw Bay watershed. (<i>Roman numerals correspond to sampling events.</i>)	81
Figure 26. Temporal variations in dissolved chloride levels among the Cass, Chippewa, Flint and Kawkawlin rivers.	87
Figure 27. Ternary plot of major cation proportions among river samples.	89
Figure 28. Temporal variations in dissolved calcium levels among the Cass, Chippewa, Flint and Kawkawlin rivers.	91
Figure 29. Temporal variations in dissolved potassium levels among the Cass, Chippewa, Flint and Kawkawlin rivers.	92
Figure 30. Carbonate mineral saturation indices for select RIV III samples.	97
Figure 31. Evaporite mineral saturation indices for select RIV III samples.	98
Figure 32. Quartz and silica saturation indices for select RIV III samples.	99
Figure 33. Cl – Cl:Br relationships among the five watershed sampling events.	101
Figure 34. Cl – Cl:Br relationships among samples from rivers and agricultural drains.	103

Figur

Figur

Figur

Figur

Figur

Figur

Figur

Fig

Fig

Fig

Fig

Fig

Fi

F

F

F

F

Figure 35. Cl – Cl:Br mixing curves for saline ground water and dilute endmembers.	105
Figure 36. Map of 7-27-96 sampling sites. (<i>Inset denotes study area location.</i>).	106
Figure 37. Porewater chemistry from cores collected on 7-27-96.	107
Figure 38. Map of 8-4-96 sampling sites. (<i>Inset denotes study area location.</i>).	109
Figure 39. Porewater chemistry from cores collected on 8-4-96.	110
Figure 40. Map of AOCs in the Great Lakes' region (<i>modified from IJC, 1987.</i>).	115
Figure 41. Map of Saginaw Bay showing (A) sediment sampling sites from Robbins' (1986) study, (B) spatial distribution of calcium in surface sediments and (C) spatial distribution of cadmium in surface sediments (<i>modified from Robbins, 1986.</i>).	119
Figure 42. Map of the stations sampled during the 1994 cruise.	122
Figure 43. Flowchart depicting SCE protocol used in this study.	130
Figure 44. Profiles of total metal concentrations (HNO ₃ digestion) in Saginaw Bay sediments. <i>Sample locations shown at left.</i>	144
Figure 45. Profiles of sediment-organic carbon concentrations in Saginaw Bay cores.	151
Figure 46. Profiles of total and ferrous iron concentrations in porewater from Saginaw Bay cores.	152
Figure 47. SCE results for iron in Saginaw Bay surficial sediments.	154
Figure 48. Changes in iron partitioning with depth in core SB1.	157
Figure 49. Profiles of manganese concentrations in porewater from Saginaw Bay cores.	159
Figure 50. SCE results for manganese in Saginaw Bay surficial sediments.	161
Figure 51. Changes in manganese partitioning with depth in core SB1.	163
Figure 52. Profiles of cadmium concentrations in porewater from Saginaw Bay cores. (<i>Sample locations are depicted at left.</i>).	165
Figure 53. SCE results for cadmium in Saginaw Bay surficial sediments.	166

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure 54. Changes in cadmium partitioning with depth in core SB1.	168
Figure 55. Profiles of copper concentrations in porewater from Saginaw Bay cores. (<i>Sample locations are depicted at left.</i>)	169
Figure 56. SCE results for copper in Saginaw Bay surficial sediments.	171
Figure 57. Changes in copper partitioning with depth in core SB1.	173
Figure 58. Profiles of zinc concentrations in porewater from Saginaw Bay cores. (<i>Sample locations are depicted at left.</i>)	174
Figure 59. SCE results for zinc in Saginaw Bay surficial sediments.	175
Figure 60. Changes in zinc partitioning with depth in core SB1.	177
Figure 61. Profiles of dissolved zinc and silica in porewater from core SB22.	182
Figure 62. Results from SCE analysis of SRM 1566a (Oyster Tissue).	196
Figure 63. Trace metal mass balance for Saginaw Bay.	203
Figure 64. Comparison between profiles of porewater-chloride concentrations (dashed lines) and sediment-metal concentrations (solid lines) in cores SB4 and SB24.	206
Figure 65. 1991-92 and 1999 Lake Michigan sampling stations.	220
Figure 66. Conceptual diagram of inputs considered in chloride mass balance.	224
Figure 67. Porewater-sodium concentrations in 1999 Lake Michigan cores. (<i>Saginaw Bay core SB4 is added for comparison.</i>)	229
Figure 68. Trends in porewater chloride concentrations (<i>Based on data from Callender (1969) and 1991-92 samples.</i>)	230
Figure 69. Cl vs. Cl:Br ratios in Saginaw Bay and Lake Michigan porewaters.	233
Figure 70. K:Cl ratios for Saginaw Bay and Lake Michigan porewaters. (<i>Lake Michigan porewater data from Callender, 1969.</i>)	235
Figure 71. Regional trends in porewater-chloride concentrations with depth.	237
Figure 72. Map of regional bedrock geology underlying study area.	239

Figure 73. Conceptual diagram for modern, regional fluid flow in the Michigan basin. (Base map from Hoaglund, 1996.).	242
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INTRODUCTION

The Great Lakes are a vast freshwater resource, but are nevertheless susceptible to pollution. For example, investigators monitoring Great Lakes' water quality have documented significant increases in dissolved solids concentrations (e.g., chloride; Figure 1) over the past several decades (Beeton, 1970; Bowden et al., 1981; Rockwell et al., 1989). Many of these increases are directly attributable to humans (e.g., road salting practices) (D'Itri, 1992). A number of studies have been conducted to address the fate and pathways by which chemical species (esp. contaminants) are loaded to the Great Lakes' ecosystem (e.g., Edgington and Robbins, 1976; Eisenreich et al., 1989; Shafer and Armstrong, 1991; Sweet et al., 1998). However, one pathway that to date has not been adequately addressed is ground-water transport of solutes and/or contaminants to the Great Lakes (Ground-Water Contamination Task Force, 1985).

One scenario in which ground water could significantly affect hydrochemistry in the Great Lakes' region is through the natural transport of formation brine to the near-surface environment. The Great Lakes are underlain by numerous geologic formations known to contain brine (Mandle and Westjohn, 1989). Some of the Michigan Basin brines have dissolved solids concentrations exceeding 400,000 mg/L (Case, 1945; Wilson and Long, 1993), and are among the most concentrated aqueous fluids on Earth. Thus, introduction of a relatively small amount of brine to the near-surface environment could readily compromise water quality and dramatically affect the cycling of additional chemical species. The presence of saline fluids in near-surface sediments and aquifers

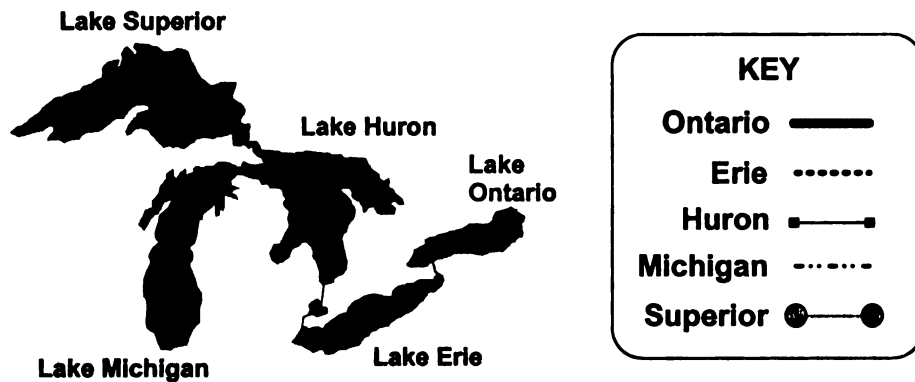
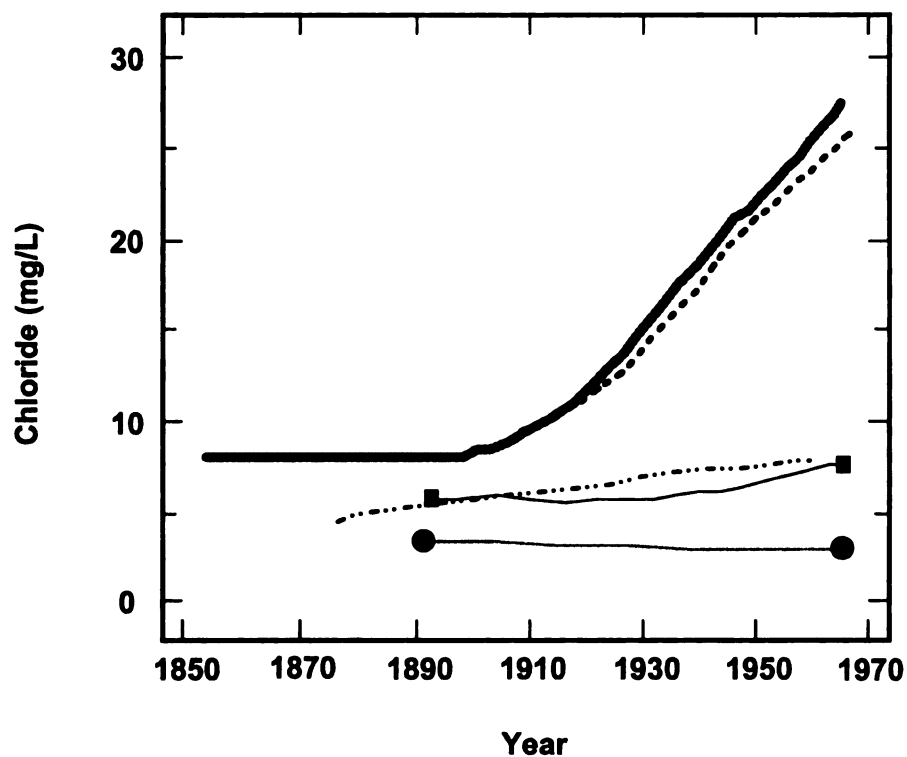


Figure 1. Temporal variations in dissolved chloride concentrations among the Great Lakes. (Modified from Pringle et al., 1981.)

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within the Great Lakes' region has been documented (e.g., Desaulniers et al., 1981; Weaver et al., 1995; Wing et al., 1995; Figure 2), and surface expression of saline water through springs has long been known (Houghton, 1838). Furthermore, in Lake Ontario, Drimmie et al. (1992) have documented chloride concentrations as high as 4,000 mg/L in porewater less than five meters below the sediment-water interface. Studies have also measured ground water discharging up through bottom sediments in Lake Michigan (Cartwright et al., 1979; Cherkauer and McKereghan, 1991), although the influence of this discharge on Lake Michigan's hydrochemistry was not addressed.

Despite the fact that encounters of saline, near-surface water have been documented as far back as 1838, the source for the salinity in many of these instances remains unresolved. While ground water can be a significant contributor to the chemical budget of a lake (e.g., Kenoyer and Anderson, 1989), efforts to link chemical cycling and ground-water flow in the Great Lakes' region have addressed issues on a local or subregional scale. Researchers have generally focused on less geographically extensive studies because either (1) the chemical species of interest (e.g., pesticides or nutrients) have limited areal distribution or are relegated to near-surface aquifers (e.g., Cherkauer et al., 1992), or, (2) a poor understanding of regional ground-water flow paths has hindered modeling efforts (Ground-water Contamination Task Force, 1985). This lack of knowledge regarding regional flow paths has presented a formidable obstacle to researchers, owing to variations in 1) fluid density, 2) hydraulic properties, and, 3) degree of hydraulic communication among bedrock units and overlying glacial sediments (Mandle and Westjohn, 1989; Hoaglund, 1996; Westjohn and Weaver, 1996a). As a

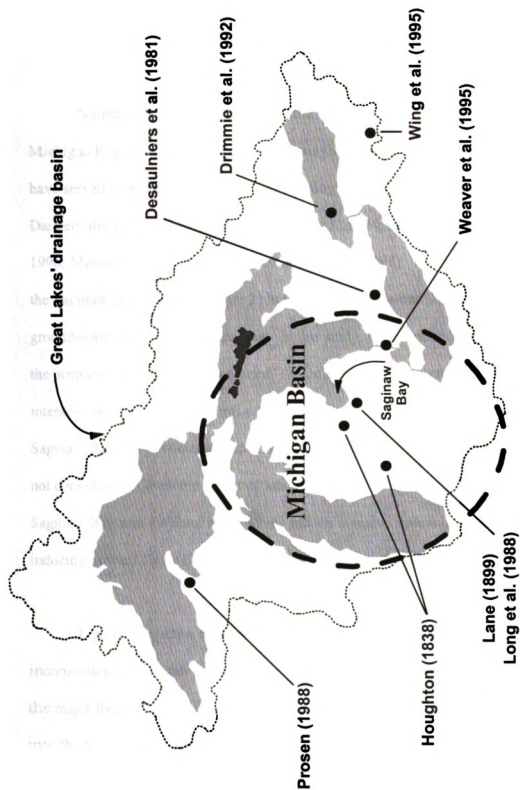


Figure 2. Previously documented occurrences of saline water in near-surface sediments from the Great Lakes' region.
(The large oval represents the approximate extent of the Michigan Basin.)

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result of these complications, the identity of the source for salinity frequently cannot be ascertained (Long et al., 1988; Drimmie et al., 1992).

Numerous studies undertaken by the U.S. Geological Survey –as part of the Michigan Regional Aquifer System Analysis (MI-RASA)– have provided new data that have served to better constrain the hydrogeology of Michigan’s Lower Peninsula (e.g., Dannemiller and Baltusis, 1990; Westjohn et al., 1994; Barton et al., 1996; Ging et al., 1996; Meissner et al., 1996; Westjohn and Weaver, 1998). As a result of these efforts, the Saginaw Bay area (see Figure 2) has emerged as a favorable locale to investigate ground-water, large-lake interactions. In this study, dissolved chloride levels are one of the primary tools used to “fingerprint” the influence of saline ground water and delineate interactions with surface water (i.e., Saginaw Bay). Although chloride cycling in Saginaw Bay has previously been studied (Richardson, 1974), ground-water inputs were not considered. Given the extent of salinization of near-surface ground water in the Saginaw Bay area (Wahrer et al., 1996) and the sizeable hydraulic gradient capable of inducing upward flow (Badalamenti, 1992), these inputs could be substantial.

Figure 3 depicts a conceptual model for chloride cycling in Saginaw Bay that incorporates inputs from ground water. The dashed arrows mark the pathways that are the major focus of this study. For example, ground water may introduce solutes directly into the Saginaw Bay water column by discharging through benthic sediments. Such discharge could also influence trace metal cycling in Saginaw Bay by (1) providing an additional source of trace metals, and/or (2) affecting trace metal diagenesis in benthic

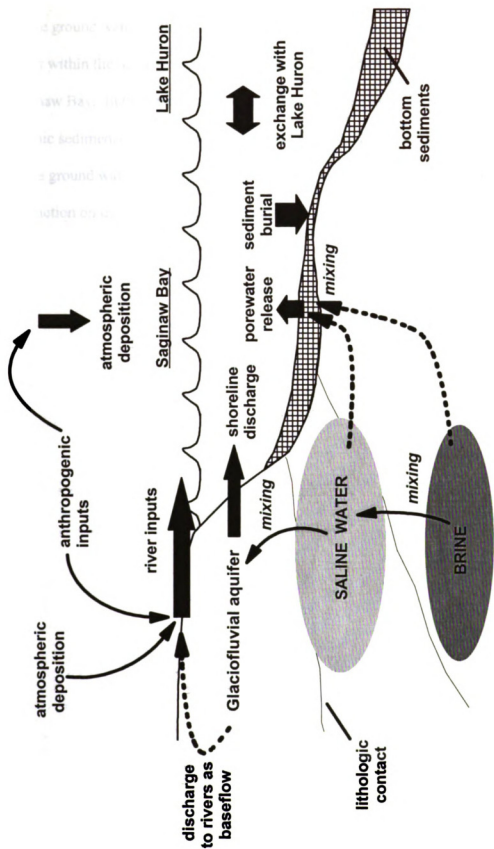


Figure 3. Conceptual diagram of chloride cycling in Saginaw Bay.

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sediments, possibly resulting in enhanced benthic fluxes of metals to the water column. Saline ground water could also affect Saginaw Bay hydrochemistry by discharging to rivers within the Saginaw Bay watershed (i.e., as base flow) with subsequent delivery to Saginaw Bay. In this study, samples of surface waters (bay and river), porewaters, and benthic sediments have been collected to delineate the extent of interaction between saline ground water and surface water, and evaluate the potential significance of such interaction on trace metal cycling in Saginaw Bay.

CHAPTER I.

Ground-water, Large-Lake Interactions in Saginaw Bay, Lake Huron

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INTRODUCTION

The origin and transport of fluids within sedimentary basins have been the focus of numerous studies (Frape and Fritz, 1982; Bethke, 1985; Land and Macpherson, 1992; Wilson and Long, 1993; Person and Garven, 1994; Stueber and Walter, 1994). Although remote from surface waters, brines in sedimentary basins are not isolated from the environment; researchers have documented the upward transport and mixing of formation waters with modern meteoric water in near-surface environments (Tellam, 1995; Weaver et al., 1995). Such interaction could be especially problematic in the Great Lakes' region: a significant portion of this area overlies the Michigan basin, which contains some of the earth's most concentrated fluids (Wilson and Long, 1993; Westjohn and Weaver, 1996a). If transported to the surface on a regional scale, these fluids could significantly affect the hydrogeochemistry of the Great Lakes.

Inadequate knowledge of the regional hydrogeology has limited other studies investigating salinization of near-surface fluids in the Great Lakes' region (e.g., Prosen, 1988; Drimmie et al., 1992). Saginaw Bay, Lake Huron, is a favorable locale to evaluate these potential ground-water/ large-lake interactions because the regional flow paths are better constrained (Vugrinovich, 1986; Mandle and Westjohn, 1989; Wahrer et al., 1996). Furthermore, a number of recent studies have provided more comprehensive information regarding the stratigraphic relations and hydrogeologic properties of the major lithologic units involved (e.g., Westjohn and Weaver, 1996 b&c; Barton et al., 1996). A comparison of hydraulic head between shallow and deep aquifers of Michigan's Lower

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Peninsula indicates that ground water might flow upward from deep aquifers, and that a significant portion of this flow could be focused towards Saginaw Bay (Takacs et al., 1988; Badalamenti, 1992; N. Grannemann, oral communication, 1994). This upward flow of ground water could degrade water quality within Saginaw Bay and the adjacent Saginaw Lowland Area (SLA) because the bedrock units underlying the study area are known to contain brine (Dannemiller and Baltusis, 1990; Ging et al., 1996; Westjohn and Weaver, 1996a).

The existence of saline, near-surface ground water in the SLA has long been known, although the distribution of and source for salinity have not been well documented (Lane, 1899; Twenter and Cummings, 1985). Long et al. (1988) also studied ground-water quality in a portion of the SLA (specifically, Bay County) and found a number of wells containing saline water. Formation waters from the Michigan basin were hypothesized to be the likely source for salinity. Additionally, Long et al. (1988) documented $\delta^{18}\text{O}$ values in the near-surface ground water that are significantly lighter than those typically found in modern meteoric water from the area. These lighter $\delta^{18}\text{O}$ values were interpreted to reflect the presence of water that had been recharged during a much cooler climate (Long et al., 1988). While these conditions (e.g., salinity and light $\delta^{18}\text{O}$ values) were frequently found in conjunction with one another, they were emplaced by different processes and were not necessarily coupled. For example, a few ground-water samples from Bay County that contained light $\delta^{18}\text{O}$ values lacked elevated levels of dissolved solids, and a few samples that were saline had $\delta^{18}\text{O}$ values similar to those measured in local, modern meteoric water (Long et al., 1988).

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The U.S. Geological Survey conducted a more extensive study of the regional ground-water chemistry within Michigan's Lower Peninsula as part of its Regional Aquifer Systems Analysis (RASA) initiative (e.g., Dannemiller and Baltusis, 1990; Ging et al., 1996; Meissner et al., 1996; Wahrer et al., 1996). Collectively, this research documented geochemical evidence supporting the model that solutes derived from brines are mixing with ground water from the glaciofluvial and deeper bedrock aquifers. Such mixing has apparently resulted in a halo, or "anomaly", of elevated chloride concentrations in the shallow ground water surrounding Saginaw Bay (Wahrer et al., 1996; Figure 4a). The MI-RASA study also measured very light $\delta^{18}\text{O}$ values in ground water from the same area (Wahrer et al., 1996; Figure 4b).

Based on the current understanding of ground-water flow within the SLA, it is hypothesized that saline and/or isotopically-light ground water is discharging directly to Saginaw Bay and the surrounding SLA. The fact that levels of dissolved chloride in the Saginaw Bay water column are among the highest reported in the Great Lakes is consistent with this hypothesis (Beeton, 1970; Richardson, 1974). If this hypothesis is correct, then the geochemical and stable isotope signatures of porewater from Saginaw Bay and the SLA should, on a regional scale, be similar to the hydrogeochemistry of ground water in the glaciofluvial aquifer. To test this hypothesis, the geochemistry and stable isotope signature of porewaters obtained from near-surface sediments of the Saginaw Bay area were characterized and compared (i.e., horizontally and vertically) to the regional gradients in ground-water chemistry of the underlying glaciofluvial aquifer.



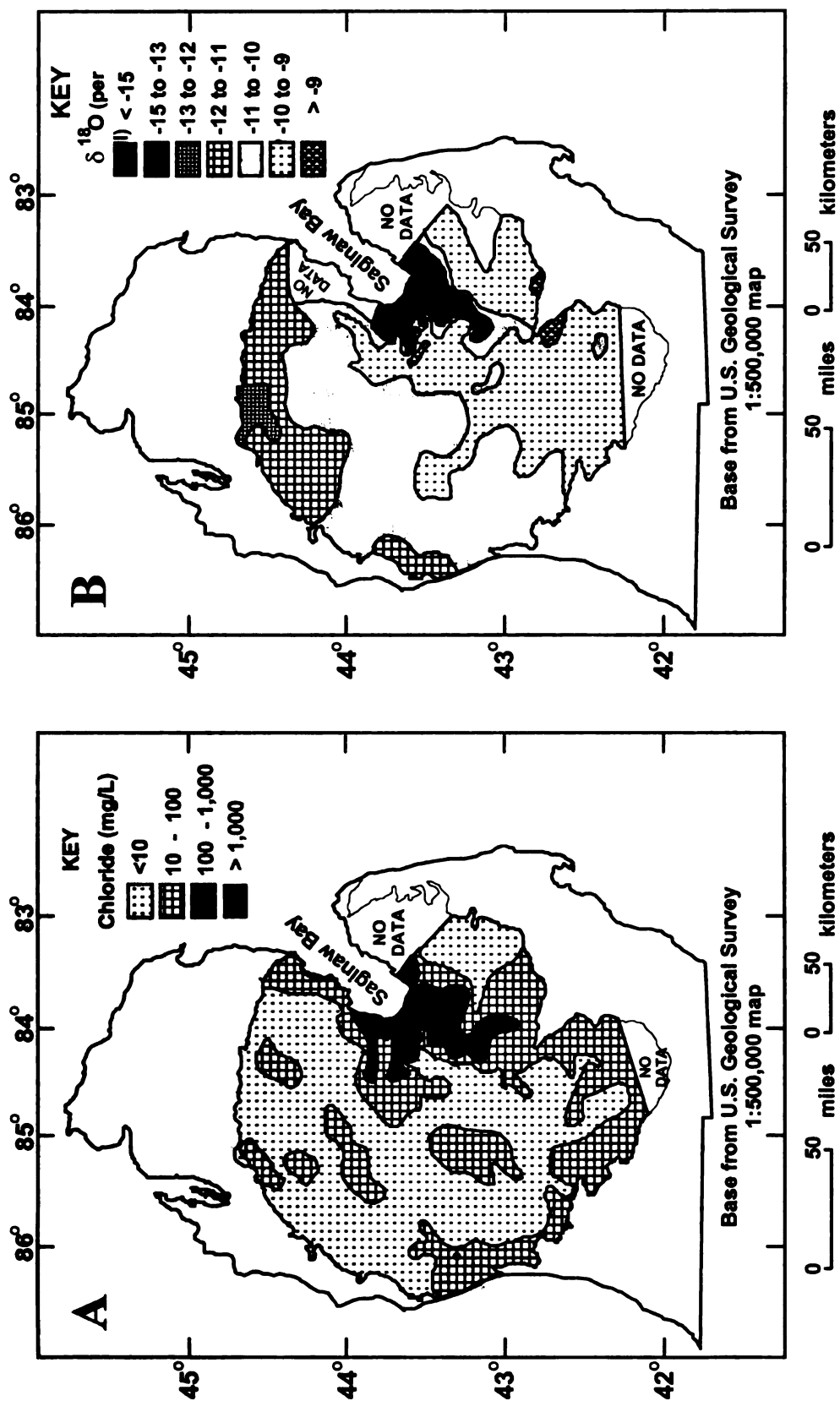


Figure 4. Distribution of (A) dissolved chloride and (B) $\delta^{18}\text{O}$ in ground water from the Glaciofluvial aquifer.
(Modified from Wahrer et al., 1996)

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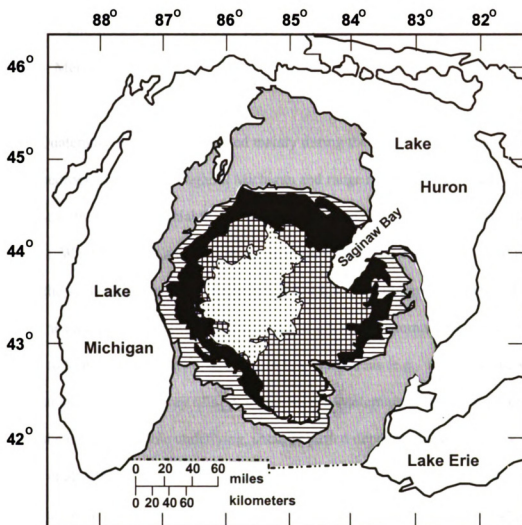
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Furthermore, the dominant transport mechanism was evaluated using one-dimensional (1-D) models to simulate the development of the observed porewater profiles.

Geology of the Study Area

The study area rests atop the Michigan basin, which contains over 5,000 meters of Cambrian to Pleistocene rocks. The Michigan basin is a circular, intracratonic basin which includes Michigan's Lower Peninsula and the eastern portion of the Upper Peninsula and parts of Wisconsin, Illinois, Indiana, Ohio, and Ontario, Canada (Dorr and Eschman, 1970). The stratigraphic relations among the bedrock units of interest are shown in Figure 5. The Mississippian Coldwater shale serves as the lower confining unit, and the contact between this shale and the overlying Marshall aquifer unit delineates the boundary of the Michigan RASA study area. In general, the Marshall aquifer unit consists of relatively permeable sandstones (the lower portion of the Marshall Sandstone, the Napoleon Sandstone, and the Stray Sandstone Member of the Michigan Formation) that are separated by shaly-sandstones and shale, or by an intercalated sequence of dolomite, limestone, shale, shaly-sandstone, and gypsum and/or anhydrite (Westjohn and Weaver, 1996b). The Bayport Limestone and Parma Sandstone [generally] overlie the Michigan Formation, forming a hydraulically-connected, continuous unit that covers most of the basin; these two units form the Parma-Bayport aquifer unit. The Grand River-Saginaw aquifer unit is the uppermost bedrock aquifer unit of the study area and includes all sandstones within the Grand River and Saginaw Formations above the Parma Sandstone. In the west-central portion of the basin, the bedrock sequence is capped by



-  **Jurassic "red beds"**
-  **Pennsylvanian Grand River and Saginaw Formations**
(Includes Upper Mississippian Parma Sandstone and Bayport Limestone)
-  **Mississippian Michigan Formation**
-  **Mississippian Marshall Sandstone**
-  **Mississippian Coldwater Shale and older rocks**

Figure 5. Generalized map showing major bedrock units of the MI RASA study.
(Modified from Western Michigan University, 1981, pl.12, and Westjohn et al., 1994.)

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Jurassic “red beds”, which are predominantly composed of red shale, gypsum, and minor amounts of sandstone. The “red beds” serve as sub-regional confining units (Westjohn et al., 1994; Meissner et al., 1996).

Quaternary sediments, deposited mainly during the Wisconsin ice advances, cap the bedrock sequence throughout Michigan and range in texture from clayey, lacustrine sediments and glacial till to coarse alluvial and outwash deposits (Westjohn et al., 1994). Where outwash and alluvium predominate, as in the northwestern and northern parts of the study area, the glacial sediments are productive aquifers (Wahrer et al., 1996). The alluvium and outwash, or other coarse-grained Quaternary deposits, are grouped to form the glaciofluvial aquifer. In low-lying areas (e.g., the SLA) where proglacial lakebeds and clayey tills predominate, the Quaternary deposits are a confining unit for the more permeable underlying, unconsolidated deposits and sedimentary rock (Wahrer et al., 1996). None of the Quaternary deposits is regionally continuous; the deposits are either aquifers or confining units in relatively small areas. Since the permeable units are discontinuous, regional ground-water flow velocities are likely controlled by the clayey units, resulting in very slow movement of ground water on a regional scale (Takacs et al., 1988). If this reasoning is correct, then the presence of fractures in the clayey units may have a profound effect on solute transport within the study area by creating preferential conduits for flow. Fracture-controlled solute transport has been documented in other systems dominated by argillaceous sediments (Keller and van der Kamp, 1988).

METHODS

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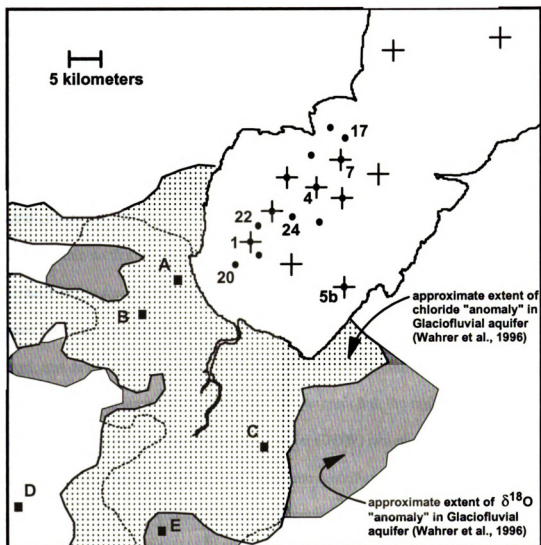
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METHODS

Sample Collection and Preservation

Sediment sampling sites are shown in Figure 6, and comprise both terrestrial cores and bay cores. Terrestrial cores, taken from the SLA, were collected by the U.S. Geological Survey during the summer of 1991 in conjunction with the Michigan RASA study (Long et al., in press). Porewater samples were collected only from the saturated portions of the terrestrial cores. Bay cores were collected from Saginaw Bay in the summer of 1994 during a sampling cruise on-board the R/V *Laurentian*. Coring was limited to the inner portion of Saginaw Bay because the high sand content in sediments from the outer portion of Saginaw Bay precluded the collection of gravity cores.

The terrestrial cores were collected in brass tubes using a hollow stem auger. The ends of the tubes were subsequently covered with plastic caps and sealed with black vinyl tape, then wrapped with plastic film and sealed again with vinyl tape. The sediment samples were then stored at 4° C until the porewater was extracted. The bay cores were collected using a Benthos® gravity-coring device loaded with polycarbonate core liners. Following deployment and retrieval of the coring device, the liners were removed and sectioned into approximately one-foot lengths, the ends of which were stoppered with plastic endcaps and then sealed with black vinyl tape. The one-foot sections were stored at 4° C until the sediments were removed for porewater extraction. Just prior to



KEY

- bay coring locations (SB)
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Figure 6. Map of sampling locations.

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extraction, the foot-long sections were sectioned into smaller segments to provide greater resolution of the porewater chemistry profiles.

In addition to the bay cores, companion water column samples (Figure 6) and box/gravity cores were also collected. These samples were analyzed for major geochemistry and trace metals. All water column samples, and a select number of box cores and gravity cores [designated for use in geochemical modeling] were immediately processed on ship so that measured parameters such as T, pH, and alkalinity were most representative of *in situ* conditions. [No porewater samples from terrestrial cores were processed for use in geochemical modeling.] The box cores and gravity cores were sectioned, and designated intervals (i.e., shallow, intermediate, and deep) were removed for analysis. After the temperature of the sample was recorded, the sediments were transferred to acid-washed, distilled-deionized water (DDW) rinsed polypropylene centrifuge tubes and capped. The samples were then centrifuged at 10,000 rpm for approximately 10 minutes. The supernatant (i.e., porewater) was removed and separated into aliquots for cation, anion, and alkalinity analyses. Cation samples were filtered and acidified to pH < 2 using ultra pure nitric acid. Anion samples were filtered but not acidified. Both cation and anion samples were then refrigerated and brought back to the laboratory for analysis. Alkalinity samples (unfiltered) were immediately measured for pH, and titrated with a dilute acid ($\approx 0.02\text{N H}_2\text{SO}_4$) to pH 4.5.

In the laboratory, porewater was extracted from all terrestrial core and bay core samples by squeezing the sediments in a stainless steel compressor (Manheim, 1966;

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Pucci et al., 1992; R. Drimmie, Univ. of Waterloo, oral communication, 1992). Samples were squeezed for no longer than 24 hours to minimize the potential for evaporative losses. Clean protocols were utilized throughout all stages of sample processing. Water was collected in acid-washed, DDW rinsed syringes and divided into aliquots for major cations, anions and stable isotopes. Extracted fluids were processed according to the following protocols: cation samples were filtered and acidified to $\text{pH} < 2$ using ultra pure nitric acid; anion samples were filtered but unacidified; stable isotope samples were neither filtered nor acidified. Cation and anion samples were stored in acid-washed plastic bottles whereas stable isotope samples were stored in glass scintillation vials. Porewater extracted from the sediment cores was filtered through 0.45 μm Millex® HA filtration units. All porewater samples were stored at 4°C until analysis.

Porewater samples from bay cores were analyzed for chloride and bromide by High Performance Liquid Chromatography (HPLC) using a Dionex® 4000i ion chromatograph equipped with an AS4A column and a suppressed conductivity detector. In samples collected for geochemical modeling (i.e., all water column samples and select box core/gravity core porewater samples), chloride and sulfate concentrations were determined by HPLC at the Environmental Laboratory of the Michigan Department of Environmental Quality (Lansing, MI). Major cation (calcium, magnesium, sodium, and potassium) concentrations in *all samples* were determined using directly coupled plasma atomic emission spectroscopy (DCP-AES). Aliquots of a National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) [*SRM 1643d - Trace Elements in Natural Water*] were analyzed during each run to monitor the accuracy of the

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major cation calibration curves. $\delta^{18}\text{O}$ analyses were conducted using the CO_2 -headspace equilibration technique (at constant T) (Desaulniers et al., 1981; Faure, 1986). The precision of $\delta^{18}\text{O}$ analyses reported in this study is 0.05 ‰ (M. Emmons, oral communication, 1995).

Tritium concentrations in water column and porewater samples were determined using scintillation counting techniques (Kessler, 1988). Prior to counting, the samples were preconcentrated using electrolytic enrichment (Ostlund and Werner, 1962). The overall analytical detection limit is 1 tritium unit (TU), and the precision of an individual analysis is ± 1 TU. 1 TU represents one atom of tritium (^3H) per 10^{18} atoms of hydrogen (^1H) (Faure, 1986).

Transport Modeling Equations

To discern the mechanisms and time frame controlling the vertical gradients in porewater chemistry, the porewater data were modeled using the one-dimensional form of the advection-dispersion equation for solute transport in a saturated, porous medium (Bear, 1972):

$$D \left(\frac{\partial^2 C}{\partial x^2} \right) - v \left(\frac{\partial C}{\partial x} \right) = \frac{\partial C}{\partial t} \quad (1)$$

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where **D** is the coefficient of hydrodynamic dispersion, $\underline{v}$ is the average linear ground water velocity, **C** is the concentration of the constituent of interest, **x** is the distance along the travel path, and **t** represents time. In the Saginaw Bay area, ground water flows [generally] upward toward the surface (Takacs et al., 1988; Hoaglund, 1996). Greatest concentrations of dissolved chloride are encountered at depth and the flux of chloride is therefore also upward (the same direction as flow). When diffusion and flow are in the same direction, the following solution to Equation (1), given by Ogata (1970), is used:

$$C/C_0 = 0.5 * [\text{cerf} \{ (x - \underline{v}t) / 2 (D * t)^{0.5} \}] + \exp(\underline{v}t / D) \text{cerf} \{ (x + \underline{v}t) / 2(D * t)^{0.5} \} \quad (2)$$

where **C** is the concentration along the flow path, **C₀** is the initial concentration, and “**cerf**” is the complementary error function. The initial and boundary conditions for this simulation are as follows (Ogata, 1970):

$$\begin{aligned} \text{(initial)} \quad C(l, 0) = 0, \quad l \geq 0; \quad \text{(boundary)} \quad C(0, t) = C_0, \quad t \geq 0; \\ C(\infty, t) = 0, \quad t \geq 0. \end{aligned}$$

On the other hand, $\delta^{18}\text{O}$ values are greatest at the surface, so diffusion of ^{18}O is considered to be downward (counter to flow) (Desaulniers et al., 1981). As a result, a second analytical solution of Equation 1 was used. A similar approach was employed in a study of chloride and $\delta^{18}\text{O}$ profiles in porewaters from Quaternary sediments in

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southwestern Ontario (Desaulniers et al., 1981). When diffusion is counter to flow, the following solution, given by Al-Niami and Rushton (1977), is used:

$$\frac{C(x,t)}{C_0} = \frac{\sinh(vx/2D) \exp(v(x-L)/2D)}{\sinh(vL/2D)} + \frac{2\pi D}{L^2} \exp\left\{\frac{v(x-L)}{2D} - \frac{v^2 t}{4D}\right\} * \sum_{n=1}^{\infty} \frac{(-1)^n \exp(-Dn^2\pi^2 t/L^2)}{Dn^2\pi^2/L^2 + v^2/4D} * \sin(n\pi x/L) \quad (3)$$

where L is the length of the aquifer along which flow occurs. The initial and boundary conditions for Equation 3 are as follows (Al-Niami and Rushton, 1977):

$$\begin{aligned} \text{(initial)} \quad C(x,0) &= 0, \quad 0 \leq x \leq L; \quad \text{(boundary)} \quad C(0,t) = 0, \quad \text{for all } t; \\ C(L,t) &= C_0, \quad t > 0. \end{aligned}$$

The average linear ground-water velocity used in the simulations was determined from the following equation (Freeze and Cherry, 1979):

$$v = -K I / \phi_e \quad (4)$$

where K is the hydraulic conductivity, I is the hydraulic gradient, and ϕ_e is the effective porosity. The hydraulic gradient in the study area is approximately 0.1525 (N. Grannemann, USGS, Lansing, MI, oral communication, 1994). Values for the porosity of SLA sediments are estimated to be around 0.30 (Long et al., 1988), whereas the average porosity of Saginaw Bay sediments sampled in this study is approximately 0.75

(this study). A range of K values was used in the initial simulations because permeability tests of sediments from terrestrial cores indicated that K values ranged between 10^{-8} and 10^{-9} cm/sec (Long et al., in press). This range of values is similar to hydraulic conductivities generally found in till (Freeze and Cherry, 1979), argillaceous Quaternary deposits in southwestern Ontario (Desaulniers et al., 1981) and clayey Quaternary deposits from the area (Dow Chemical Company, 1986). Calculated average linear ground water flow velocities ranged between 0.00016 and 0.0016 m/a (Long et al., in press). Simulations using a velocity of 0.0016 m/a provided the best agreement with observed profiles (Long et al., in press), and this velocity is used for all profiles simulated herein. The average linear ground-water velocities present in this system are sufficiently small that the amount of mechanical dispersion is negligible and hydrodynamic dispersion can be approximated by the effective molecular diffusion coefficient, D_e (Freeze and Cherry, 1979). Desaulniers et al. (1981) used a value of $0.00946 \text{ m}^2/\text{a}$ to simulate both chloride and $\delta^{18}\text{O}$ profiles; the same value is used in the simulations presented here because of the similarities between the two study areas.

RESULTS

Spatial Variations in Chloride Concentrations

Porewater-chloride concentrations in the terrestrial cores are plotted in Figure 7A. For comparison, the shaded region on the graph represents the range of background chloride concentrations (0 to 50 mg/L). Chloride concentrations in water unaffected by

Depth (meters)

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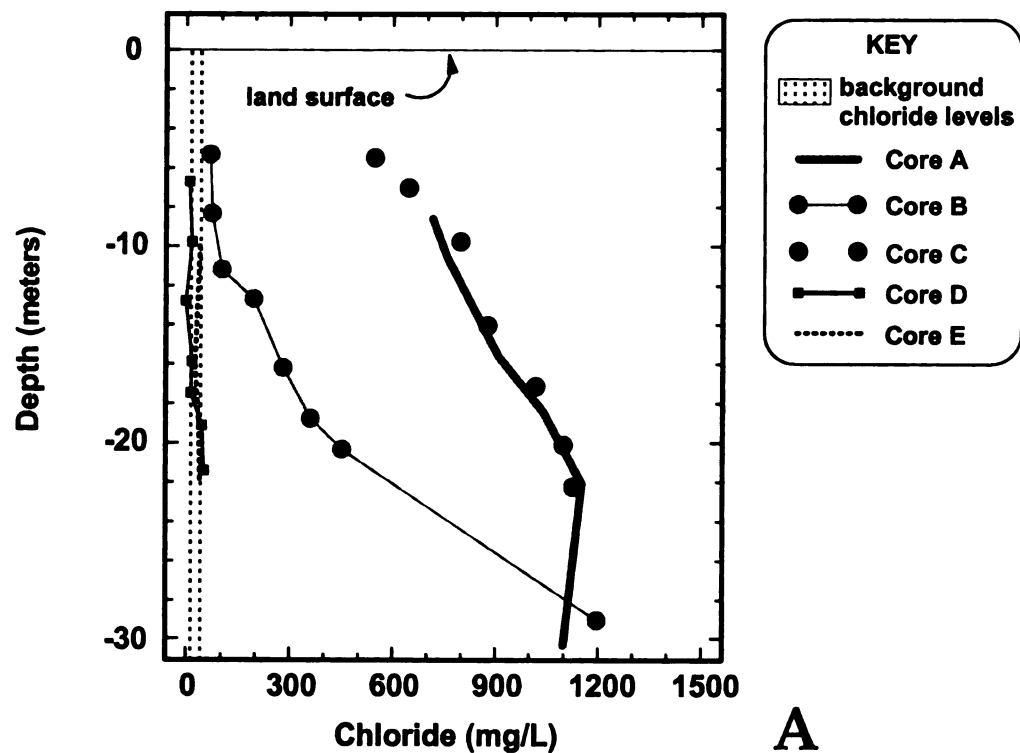
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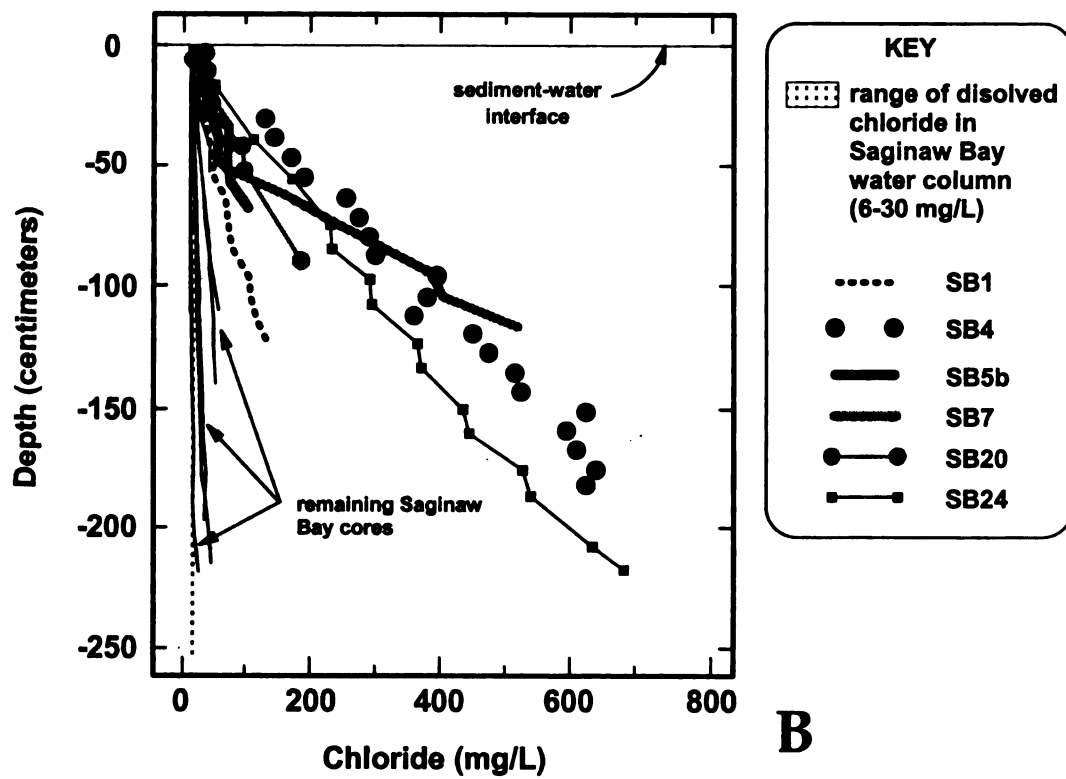
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Depth (centimeters)

FIG. 1



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Figure 7. Dissolved chloride porewater profiles in (A) terrestrial cores and (B) bay cores.

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either anthropogenic inputs or natural salinity sources are generally less than 10 mg/L (Hem, 1989). However, a number of samples from the glaciofluvial aquifer, collected outside the chloride anomaly (Figure 4A) have chloride concentrations between 10 and 100 mg/L (Dannemiller and Baltusis, 1990). Some of these sites are likely receiving chloride from anthropogenic sources such as road salting or septic systems (e.g., Long and Saleem, 1974), making it difficult to estimate a representative background chloride concentration for the study area. Statistical analyses of chloride concentrations in ground-water samples from the glaciofluvial aquifer reveal a significant change in the sample population above 50 mg/L chloride (Long et al., in press). The upper limit of “background” chloride levels in the study area was therefore designated as 50 mg/L chloride.

Chloride concentrations from terrestrial cores A, B, and C greatly exceed the background threshold. The chloride profiles from all three cores indicate that the porewaters are influenced by a high-chloride source at depth, which is in good agreement with regional ground-water chemistry from the RASA study (Meissner et al., 1996; Wahrer et al., 1996). Porewater chloride profiles from cores D and E also show an increase in dissolved chloride concentrations with depth, however, the chloride levels in both cores do not exceed the background threshold. While this finding for cores D and E does not preclude interaction with a high-chloride source, such interaction is apparently of limited extent.

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If saline ground water is moving upward into near-surface sediments, then dissolved chloride concentrations in bay-core porewater samples should also increase with depth. Figure 7B is a plot of vertical chloride profiles from all sediment cores collected in Saginaw Bay. Water column chloride levels in Saginaw Bay (this study) range from 6 to 30 mg/L chloride; this range is depicted as the shaded region on Figure 7B. Nearly every core exhibits increased chloride concentrations with depth; however, in only a few cores (SB1, SB4, SB5b, SB7, SB20 and SB24) do chloride concentrations exceed the background threshold of 50 mg/L chloride. The observed trend in porewater-chloride concentrations supports the model of a high-chloride source present at depth.

The extent to which bay-core porewaters are affected by upward transport of chloride varies widely. This variability could be due to a number of factors such as changes in subcrop lithology, the presence of fractures, or changes in the hydrogeologic properties (e.g., hydraulic conductivity) of the sediments underlying the bay. A study of sediments accumulating in Saginaw Bay (Wood, 1964) found no significant variations in sediment characteristics (e.g., clay content) that could account for the observed differences in porewater-chloride gradients among the bay cores. Porewaters from cores SB4, SB7, and SB24 have the strongest vertical gradients in dissolved chloride. Subcrop lithology might play a role as all three cores appear to overlie the Michigan Formation (Figures 5 and 6); however, there are other cores (e.g., SB17) that also appear to overlie the Michigan Formation, but do not have strong vertical gradients in dissolved chloride. This result indicates that subcrop lithology might not be solely responsible for controlling the degree of interaction between the bay-core porewaters and the chloride source. The

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fact that the core with the strongest chloride gradient, SB7, is in close proximity to a core with a very weak chloride gradient, SB17, suggests that fractures might play a major role in controlling the amount of interaction. That fractures may contribute to saline water transport also seems plausible because the Michigan Formation (which apparently subcrops the sites most strongly affected by saline ground water) is generally regarded as a confining unit (e.g., Mandle and Westjohn, 1989; Hoaglund, 1996). As such, fluid flow through this formation would generally be restricted, except for the influence of fractures. Geophysical studies have shown that Saginaw Bay might be part of a relict graben (Herman et al., 1991), and numerous sets of fractures could have been produced during the formation of the graben. Additionally, fractures could have been formed, or reactivated, during isostatic rebound following glacial loading (Weaver et al., 1995).

Major Cations

Evaluation of major cation concentrations can help elucidate the processes (e.g., mineral dissolution/precipitation) affecting porewater chemistry. As major cation data are not available for terrestrial cores, the remainder of this section will focus solely on Saginaw Bay sediments (i.e., bay cores). Profiles of all major cation concentrations in bay core porewaters (not shown) indicate that concentrations generally increase with depth in the sediment column. Figure 8 depicts scatterplots for each of the major cations versus chloride. With the exception of sodium, major cation concentrations exhibit a high degree of scatter at low (< 60 mg/L) chloride concentrations and appear to vary independent of chloride. Most of these samples are located within 20cm of the

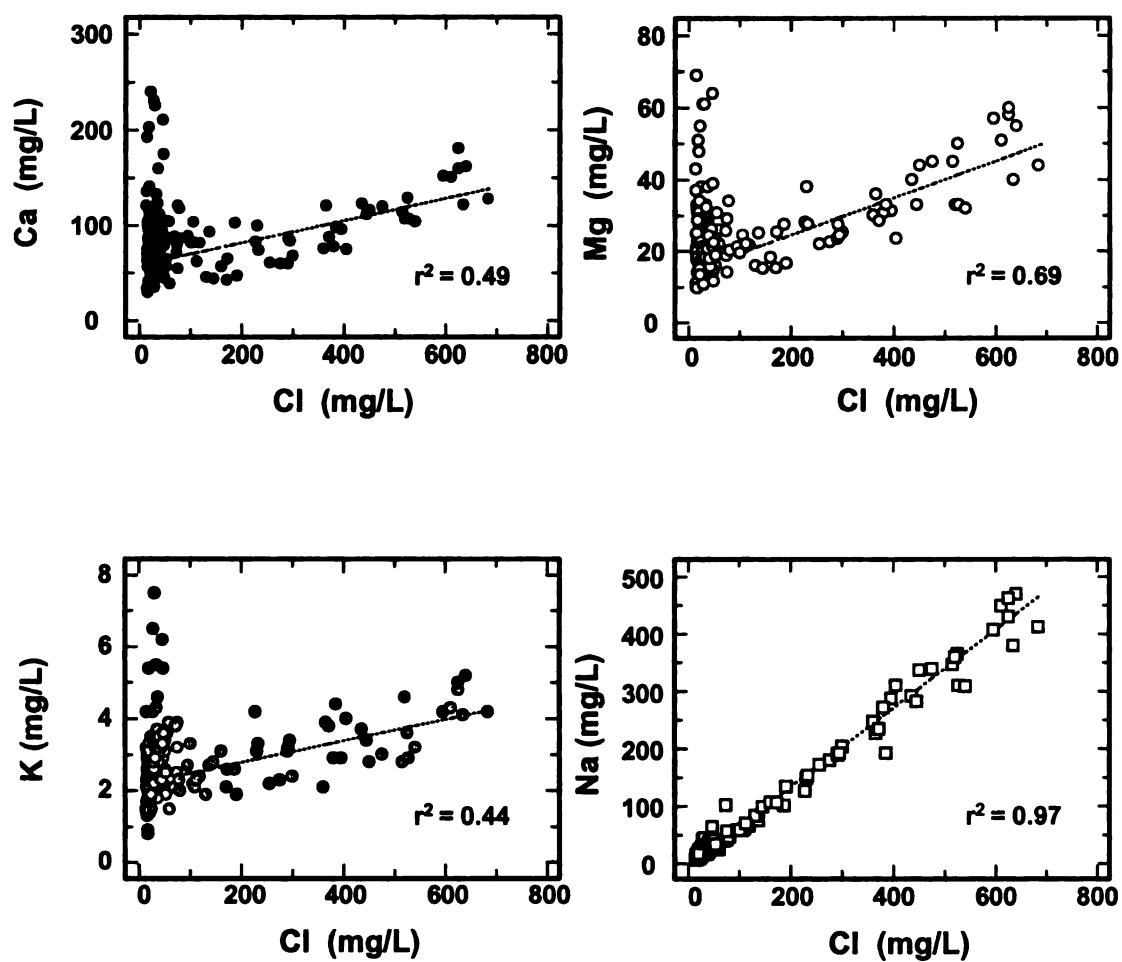


Figure 8. Scatterplots for (A) Ca vs. Cl, (B) Mg vs. Cl, (C) K vs. Cl, and (D) Na vs. Cl in bay core porewater samples. (*Regressions based on all porewater samples containing greater than 60 mg/L chloride.*)

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sediment-water interface, and likely reflect the varying intensity of early diagenetic processes associated with microbial activities (Berner, 1980) and cation exchange (Wilson, 2000).

At greater sediment depths the scatter among major cation concentrations diminishes and all are positively correlated to chloride concentrations. The dashed lines in Figure 8 represent regression lines fit to all samples in which porewater chloride exceeds 60 mg/L; r^2 values for these regression lines are also given in Figure 8. Sodium is most highly correlated to chloride levels, followed by magnesium, calcium and potassium. The positive correlations between all four major cations and chloride might indicate that formation brine –*not halite dissolution*– is the source for chloride. If halite dissolution were the primary chloride source, one should expect that, in the absence of any other significant mineral-water interactions, sodium would be positively correlated to chloride, but the other major cations should be independent of chloride levels. The fact that calcium and potassium are much more poorly correlated to chloride probably indicates that additional processes such as precipitation/dissolution of carbonate minerals (e.g., calcite) and cation exchange (potassium) play a significant role in regulating cation concentrations in the deeper sediments.

Another means of evaluating processes affecting water quality is to plot samples on a Piper diagram (Piper, 1945). The normalized concentrations of cations or anions (in millequivalents) are plotted on ternary diagrams to evaluate the dominant chemical components of water samples and test whether or not samples are affected by simple

mixing or dissolution/precipitation of a single salt (Hem, 1985). Although this technique can be particularly useful when studying regional-scale variations in water quality (e.g., Back, 1961), a major caveat to this approach is that samples with vastly different concentrations of solutes, but *identical proportions* of these solutes, will plot on the same location on the ternary diagram.

Cation data from Saginaw Bay water column and bay-core porewater samples are plotted on a modified Piper diagram in Figure 9. Each apex of the diagram represents 100 per cent of a given cation (e.g., Ca) or group of cations (e.g., Na+K). The bold solid lines connect the midpoints (corresponding to 50% of a given cation) of the triangle's sides, and enclose a field in which each cation contributes less than 50% to the total positive charge in a water sample. Water samples that plot within this field are classified as "no dominant" cation; water samples that plot outside this field are classified according to the cation contributing greater than 50% of the total positive charge (e.g., calcium-dominant) (Piper, 1945).

There is considerable scatter among Saginaw Bay water column samples, but all samples plot within the calcium-dominant field. The scatter likely reflects varying degrees of mixing between the two primary inputs to Saginaw Bay: the Saginaw River and Lake Huron. A number of bay-core porewater samples also plot in the calcium-dominant field, and these exhibit an ever greater degree of scatter than the water column samples. Some of the variation among these porewater samples probably reflects the

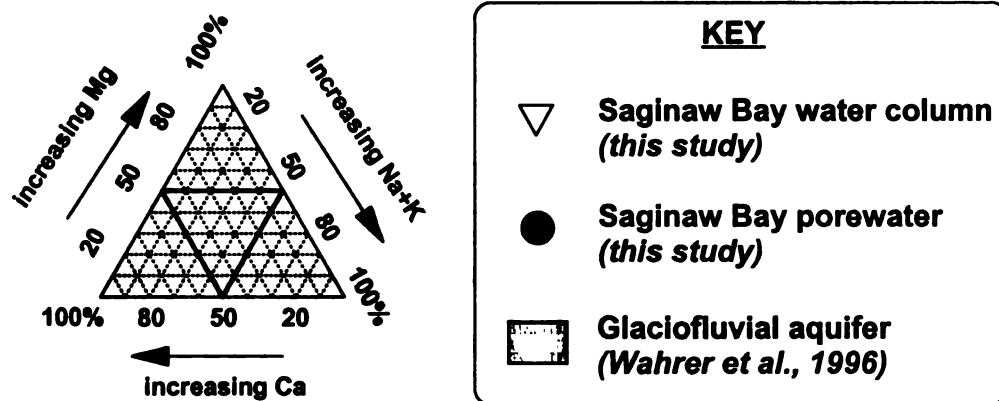
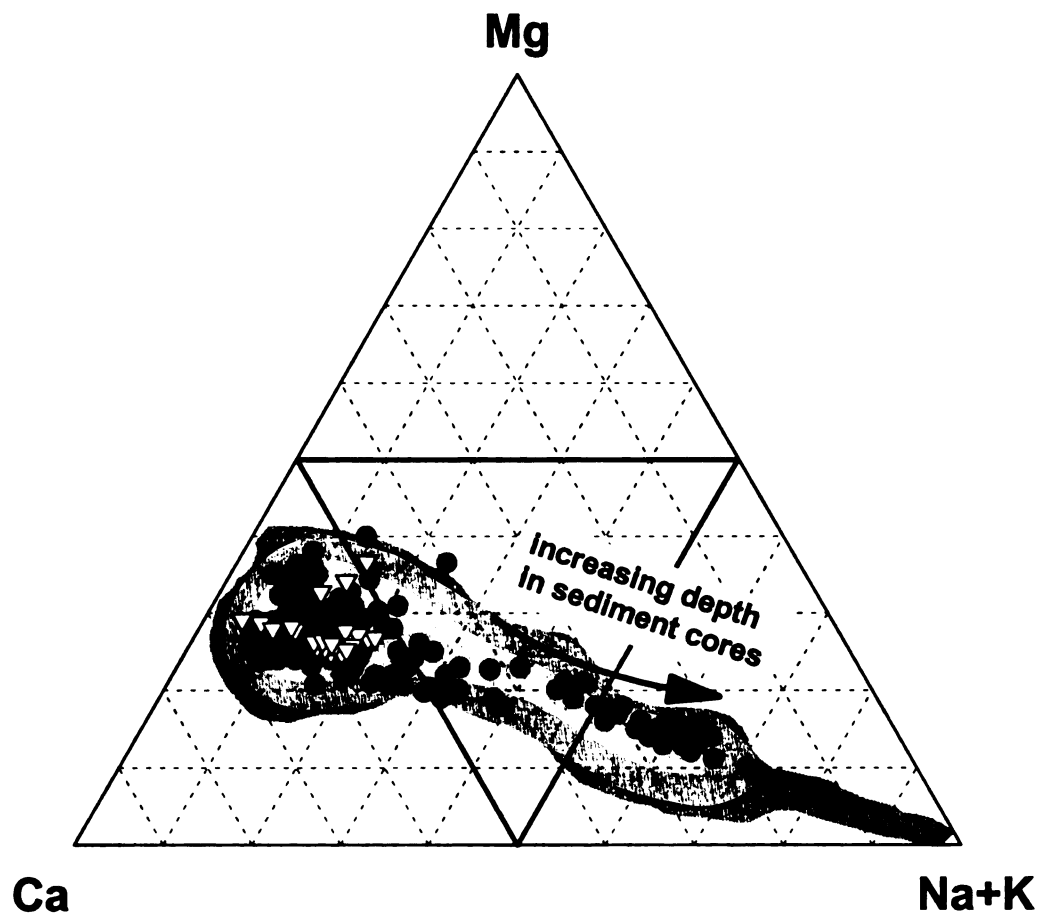


Figure 9. Ternary diagram of major cations in water column, porewater, and ground water samples.

spatial variations in the composition of the water (i.e., Saginaw Bay water column) that is initially incorporated into the sediment column during deposition and burial. However, the fact that water column samples cannot account for the observed variations in shallow porewater chemistry likely indicates that mineral-water interactions associated with early diagenesis have subsequently altered porewater composition.

Compositions of porewater samples collected from deeper sediments (indicated by the curved arrow) generally plot along a trend toward the Na+K apex. The deepest samples plot in the Na+K-dominant field. This trend indicates that mixing with a sodium-rich endmember may be controlling porewater composition at depth. The gray field, representing ground water from the glaciofluvial aquifer (Wahrer et al., 1996), also encompasses all the porewater samples from this study. The porewater samples appear to be following the same trend as the ground water samples, indicating that mixing with more concentrated fluids at depth (e.g., in the glaciofluvial aquifer) might be influencing water quality in the porewater samples.

Another process that might be influencing porewater geochemistry in Saginaw Bay sediments is cation exchange (Wilson, 2000). One can test this scenario by further examining the proportions of the dominant cations in solution. For example, if exchange sites in sediments are regulating sodium and calcium concentrations in water, then the following reaction can be written:

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where the subscript “ex” denotes a cation bound to an exchange site (e.g., Hounslow 1995). Such an approach has previously been employed to evaluate ground-water chemistry in the Saginaw Bay area (Long et al., 1986). Figure 10 shows a scatterplot of calcium versus sodium concentrations (in millimoles/L) in porewater samples. The arrow in the figure indicates the general direction of increasing sediment depth. If cation exchange were the process primarily regulating the concentrations of these two cations, then the samples should plot along the 2 Na:1 Ca line (dashed line in Figure 10). Near the sediment-water interface (i.e., low dissolved sodium concentrations) bay-core porewater samples plot well below the 2:1 stoichiometric line, indicating excess calcium. This excess calcium might be derived from carbonate mineral dissolution in the uppermost portion of the sediment column. At greater depths, Na:Ca ratios in porewater are significantly greater than 2:1 indicating excess sodium. This result supports the model where porewater chemistry is influenced by mixing with a saline endmember at depth, but does not preclude the possibility that carbonate mineral (e.g., calcite) precipitation also contributes; cation exchange does not appear to be regulating sodium and calcium concentrations.

Geochemical Modeling

To further evaluate processes controlling porewater chemistry, selected samples – collected for complete geochemistry – were modeled using WATEQ4F (Ball et al., 1991).

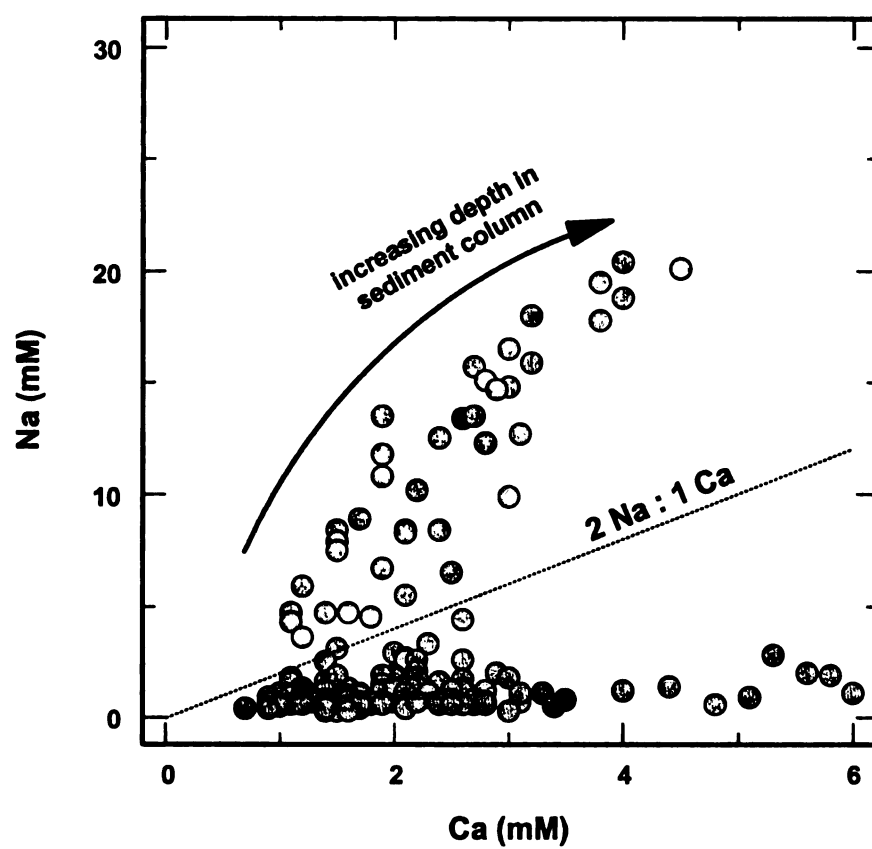


Figure 10. Ca vs. Na in bay core porewaters.

Geochemical modeling can be used to identify mineral phases that might be influencing water chemistry (either by dissolution or precipitation) or to assess changes in the evolution of water chemistry as water moves along a flow path. Results of water analyses are entered into WATEQ4F, and the program calculates elemental speciation and ionic activities and uses these results to determine the saturation index for each mineral of interest. The saturation index (SI) of a mineral phase is calculated according to the following expression:

$$SI = \log (IAP/K_{sp}) \quad (6)$$

where **IAP** is the ion activity product (in the sample) of the ions constituting the mineral phase of interest, and **K_{sp}** is the solubility product (i.e., the value of the thermodynamic equilibrium constant at P,T conditions of interest). Thus a mineral in equilibrium with the aqueous phase (i.e., 100 per cent saturation) would have a SI value of zero. A SI value greater than zero indicates that the aqueous phase is supersaturated with respect to a given mineral, and precipitation of that mineral is thermodynamically favorable. An SI value less than zero indicates that the water sample is undersaturated with respect to a given mineral phase, and dissolution of that mineral is thermodynamically favorable. Calculated SI values are inherently sensitive to the quality of the input data. Given that water is constrained by thermodynamics to continuously remain electrically neutral (e.g., Hem, 1985), the sum of the cations (in milliequivalents) in a water analysis must be

balanced by the sum of the anions (in milliequivalents). In this study, sample analyses with greater than 15% charge imbalance were not used in geochemical modeling.

The minerals of focus in this study are carbonates (aragonite, calcite, dolomite) and evaporites (anhydrite, gypsum, and halite). The results of the geochemical modeling are given in Table 1. The water column samples are separated into two distinct groups, inner bay and outer bay. There are some differences between these two groups, likely the result of varying inputs derived from the two primary sources (i.e., the Saginaw River and Lake Huron). Although both groups are undersaturated with respect to the evaporite minerals and dolomite (d) [a high-order crystalline form of dolomite], the outer bay is slightly undersaturated with respect to aragonite, calcite, and dolomite (c), whereas the inner bay samples are slightly supersaturated with respect to these phases. The outer bay samples are generally more representative of geochemical conditions in Lake Huron (Rockwell et al., 1989). As all bay cores were collected from the inner portion of Saginaw Bay, the inner bay water column samples are a more appropriate point of reference for shallow porewater chemistry.

Bay core porewater samples were split into three groups according to depth in the sediment column (shallow, intermediate, deep). The deep samples were further subdivided into two groups: fresh and brackish. With the exception of a few cores, brackish waters were not encountered and only in deeper sediments. Mean SI values for evaporite minerals indicate that porewaters from shallow sediments are largely

Table 1. Average Mineral Saturation Indices Calculated for Saginaw Bay Samples

WATER COLUMN			BAY CORE POREWATER				
	n :	Inner Bay	Outer Bay	Shallow (0-15 cm)	Intermediate (20-60 cm)	Deep-fresh (70-200 cm)	Deep-brackish (70-200 cm)
Mineral	Formula	SI	SI	SI	SI	SI	SI
Anhydrite	CaSO ₄	-2.8	-3.0	-3.4	-3.6	-3.5	-3.6
Aragonite	CaCO ₃	0.0	-0.3	-0.2	-0.1	-0.2	0.4
Calcite	CaCO ₃	0.2	-0.2	-0.1	0.0	0.0	0.6
Dolomite (d)	(Ca,Mg)(CO ₃) ₂	-0.6	-1.3	-1.0	-0.8	-0.9	0.4
Dolomite (c)	(Ca,Mg)(CO ₃) ₂	0.1	-0.8	-0.4	-0.2	-0.3	1.0
Gypsum	CaSO ₄ ·2H ₂ O	-2.6	-2.8	-3.1	-3.9	-3.2	-3.3
Halite	NaCl	-8.5	-9.1	-8.1	-7.7	-7.8	-5.6

undersaturated with respect to these minerals, and approximately to the same degree as observed in the Saginaw Bay water column. Both shallow porewaters and water column samples are near equilibrium with respect to calcite and aragonite; shallow porewater samples are slightly undersaturated with respect to dolomite.

There does not appear to be a significant difference in mineral SIs among shallow, intermediate, and deep-fresh porewater samples. The intermediate and deep-fresh porewater samples are slightly less undersaturated with respect to halite, owing to modest increases in dissolved sodium and chloride concentrations with depth. On the other hand, SIs determined for the deep-brackish porewater samples differ markedly from the other porewater and water column samples. While the evaporite minerals are still largely undersaturated in the deep-brackish porewaters, the halite SI is approximately two orders of magnitude larger in the deep-brackish porewaters as compared to the other samples. Furthermore, the carbonate minerals are slightly supersaturated in the deep-brackish porewater samples, indicating that these minerals may be precipitating at depth in sediments influenced by the high-chloride source. Figure 11 shows the changes in SIs with porewater depth between a core that has brackish water at depth (SB4) and a core that has fresh water at depth (SB19). The gray lines (dashed and solid) indicate the concentrations of chloride in the porewater samples from these two cores. The data presented in Figure 11 indicate that there is generally no change in mineral saturation indices in cores that are only sparingly influenced by the high-chloride source. Conversely, cores strongly influenced by this chloride source at depth show marked changes in SIs, with the carbonate minerals calcite and dolomite becoming highly

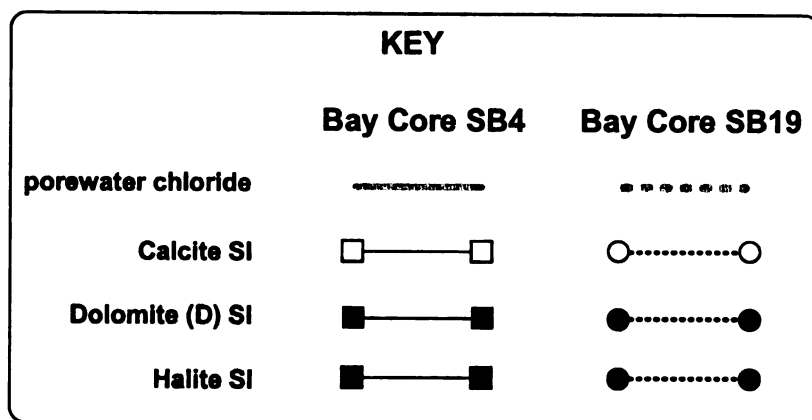
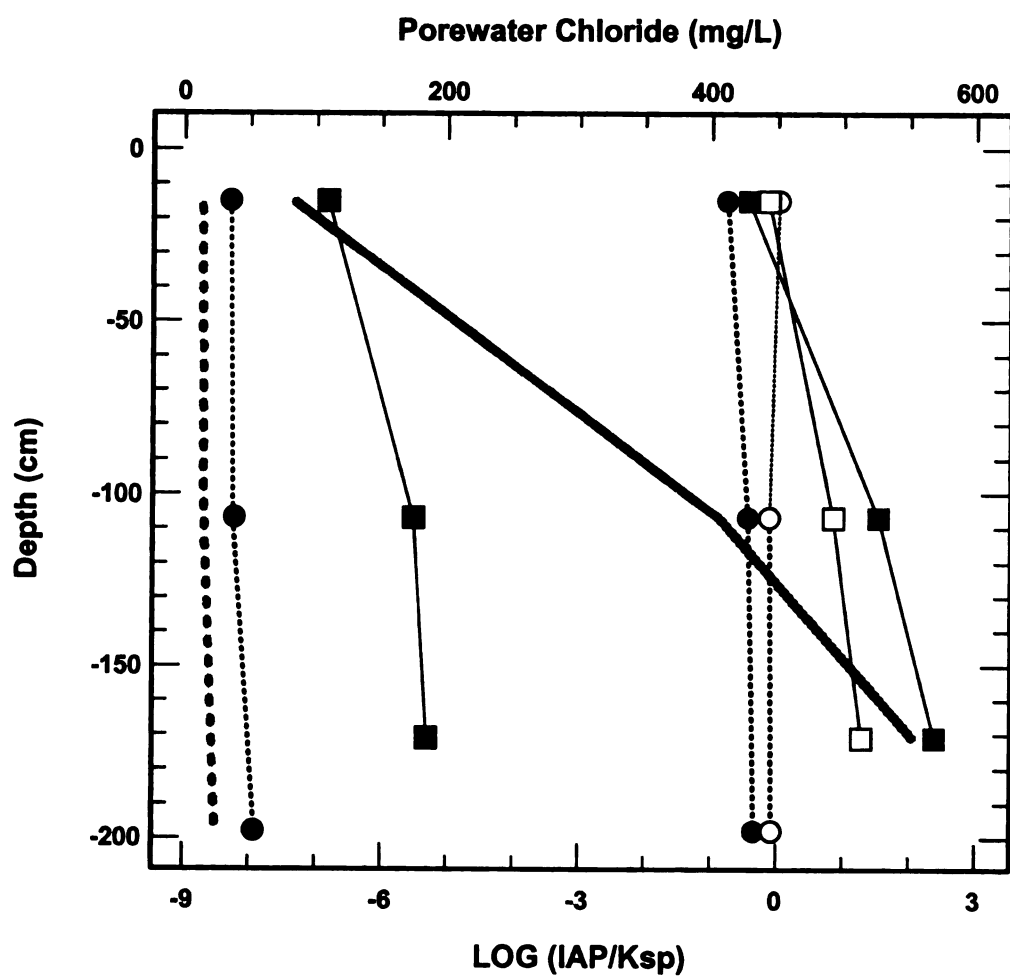


Figure 11. Changes in SI values with porewater depth.

supersaturated at depth. These data indicate that mixing between the surface water and a saline source at depth can have a significant influence on mineral saturation indices, possibly resulting in the precipitation of carbonate minerals at depth in the sediment column.

The results of the geochemical modeling also help to explain some of the cation-chloride trends observed in Figure 8. Sodium is very highly correlated with chloride, whereas the other major cations have much lower correlation coefficients. The lower coefficient for calcium may reflect the fact that carbonate minerals are precipitating at depth in the sediment column (i.e., at high chloride concentrations). Although both calcite and dolomite are supersaturated in these porewaters, the kinetics of dolomite precipitation are very slow and thus removal of magnesium from solution by this mechanism is not as likely. This disparity among crystallization kinetics might explain why calcium is more poorly correlated to chloride concentrations than is magnesium. Potassium concentrations are also poorly correlated to chloride concentrations at depth; cation exchange may be regulating potassium concentrations in solution.

Stable Isotopes

The $\delta^{18}\text{O}$ and δD values in terrestrial-core porewater samples range from -8.8 to -15.8 ‰ and -59.0 to -113.0 ‰, respectively. The lightest values are significantly lighter than what is expected for modern meteoric recharge (Long et al., in press), but are comparable to values documented in ground water from the glaciofluvial aquifer (Wahrer

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et al., 1996). The similarity between the two datasets implies that the glaciofluvial aquifer is simply the source for water to the terrestrial cores, or, that similar processes have affected water in the terrestrial cores and glaciofluvial aquifer. Wahrer et al. (1996) interpreted the lighter isotope values in ground water to reflect the presence of water recharged during cooler conditions (i.e., during glaciation). Such a mechanism has also been proposed for other systems where anomalously-light isotope values have been encountered in ground water (e.g., Desaulniers et al., 1981; Stueber and Walter, 1994; Hendry and Wassenaar, 1999).

Stable isotope values in bay-core porewater samples are much less variable, ranging from -7.2 to -9.0 ‰ (for $\delta^{18}\text{O}$) and -45.3 to -63.3 ‰ (for δD). These values do not appear to reflect the presence of an isotopically-light source. Instead, bay-core porewaters tend to reflect the isotopic composition of the Saginaw Bay water column, which ranges from -7.4 to -8.3 ‰ (for $\delta^{18}\text{O}$) and from -53.1 to -60.0 ‰ (for δD).

One can gain insight into the major processes controlling the isotopic composition of a water sample through joint consideration of $\delta^{18}\text{O}$ and δD values. For example, although $\delta^{18}\text{O}$ and δD values are generally covariant in meteoric water (Craig, 1961), processes such as evaporation, hydrothermal alteration, or freezing can significantly alter its isotopic composition (Faure, 1986; Bottomley et al., 1999). A comparison between $\delta^{18}\text{O}$ and δD values in Saginaw Bay water column, bay-core porewater, and terrestrial-core porewater samples is plotted in Figure 12. Craig (1961) has shown that the isotopic composition of meteoric water could be represented by the following trend:

$$\delta D = 8\delta^{18}O + 10, \quad (7)$$

and this relationship (“Global Meteoric Water Line”; GMWL) is also plotted in Figure 12. Water that is largely derived directly from meteoric water will plot along this trend, whereas water that has undergone significant alteration (e.g., evaporation) will plot off this trend.

Two local meteoric water lines, the Simcoe Line and the Kalamazoo Line, are also plotted on Figure 12. The Simcoe Line represents the stable isotope variation in meteoric water at Simcoe, Ontario, Canada, located approximately 120 miles east of the study area (Desaulniers et al., 1981). The trend for the Simcoe Line is as follows:

$$\delta D = 7.55\delta^{18}O + 12.6 \quad . \quad (8)$$

The Kalamazoo Line represents the $\delta^{18}O$ - δD relationship for meteoric water at Kalamazoo, Michigan, located approximately 110 miles southwest of the study area. The trend for the Kalamazoo Line (Machavaram and Krishnamurthy, 1994; Table 1, unweighted) is as follows:

$$\delta D = 7.21\delta^{18}O + 10.5 \quad . \quad (9)$$

The two local meteoric water lines are included for comparison because local meteoric precipitation can deviate significantly from the GMWL, owing to vapor contributions from Lake Michigan (Machavaram and Krishnamurthy, 1994; 1995). The two local meteoric water lines also serve to constrain the isotopic signature of modern meteoric water input to Saginaw Bay. Water column samples from Saginaw Bay plot off the trends of the Kalamazoo and Simcoe Lines (and even the GMWL), indicating that the

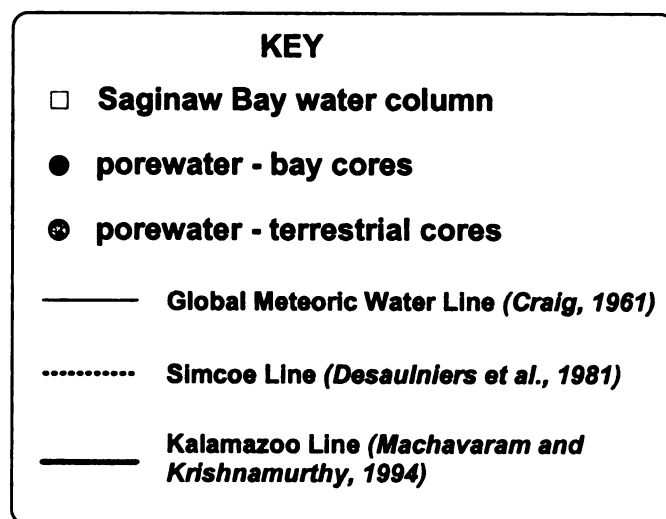
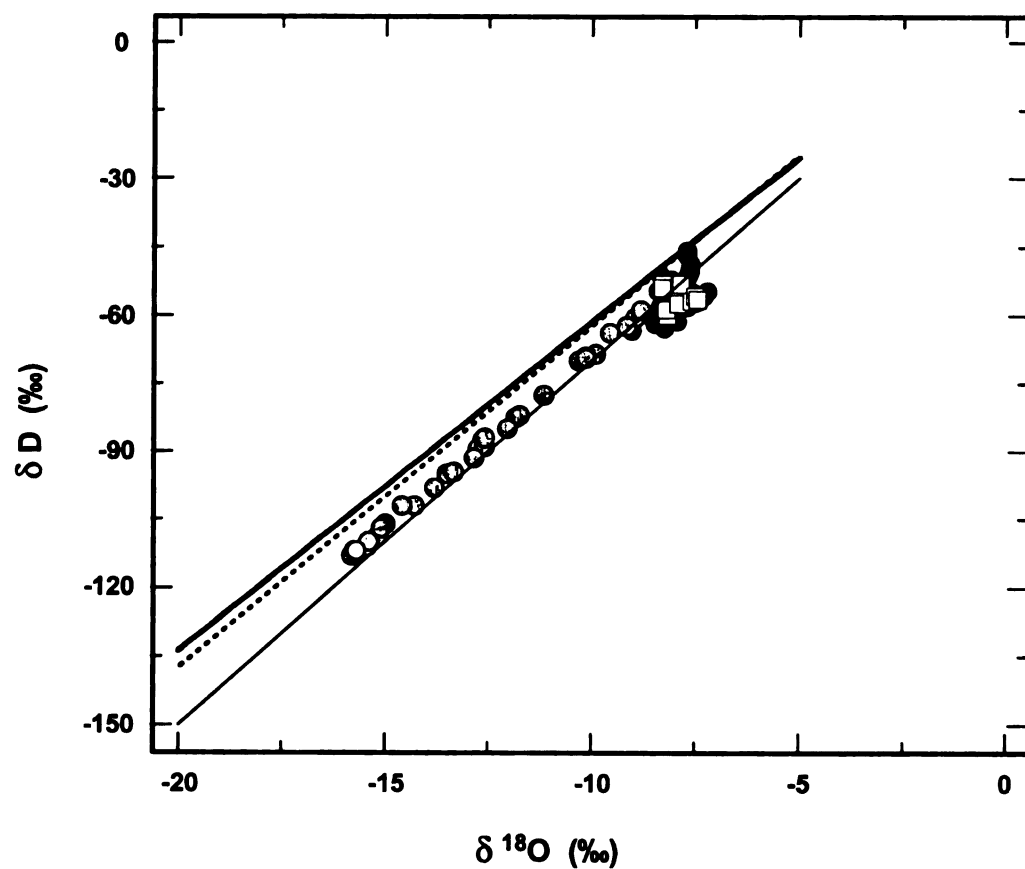


Figure 12. $\delta^{18}\text{O}$ vs. δD in water column and porewater samples.

isotopic signature of the water in Saginaw Bay has been affected by evaporation. Bay-core porewater samples also plot off the local meteoric water lines, likely indicating that the evaporated water column is the primary source for water in Saginaw Bay sediments.

Stable isotope values in terrestrial-core porewater samples plot along a linear trend, but off the Kalamazoo and Simcoe Lines. Instead, the terrestrial-core porewater samples tend to follow the GMWL. The linear trend among these samples likely indicates that porewaters in terrestrial cores are influenced by simple mixing between two endmembers: one similar to modern meteoric water, and one recharged during a much cooler climate.

Spatial Variations in $\delta^{18}\text{O}$ Values

The ability to identify the source for the water using its stable isotope signature is especially important in this setting, where the water and solutes appear to have distinct origins. $\delta^{18}\text{O}$ values measured in terrestrial-core porewater samples are shown in Figure 13A. Background $\delta^{18}\text{O}$ values, representing modern meteoric precipitation, are considered to range between -8.00 and -10.00 ‰ (Long et al., in press), as indicated by the shaded region in Figure 13A. The $\delta^{18}\text{O}$ values measured in terrestrial-core porewater samples correspond to those measured in the local ground water. For example, the $\delta^{18}\text{O}$ values obtained from cores A, B, and C reflect the anomalously light values found in the glaciofluvial aquifer. $\delta^{18}\text{O}$ values in porewater from cores B and C tend to become more

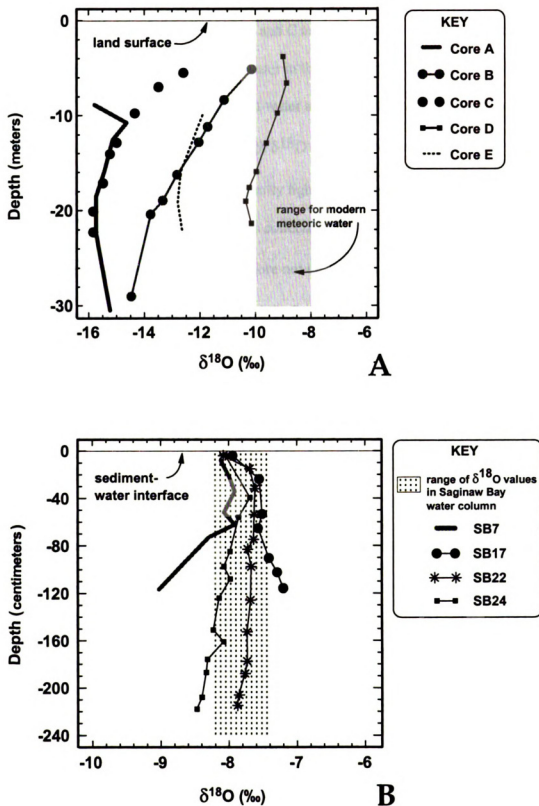


Figure 13. $\delta^{18}\text{O}$ porewater profiles in (A) terrestrial cores and (B) bay cores.

negative with depth and indicate that mixing between two endmembers has occurred. The $\delta^{18}\text{O}$ values measured in cores A, B, and C are significantly lighter than the average values determined for modern meteoric water in the study area. These isotopically-lighter values likely reflect the presence of water at depth that was recharged during much cooler climatic conditions. Although $\delta^{18}\text{O}$ values in porewaters from core D decrease with depth, they are not significantly lighter than $\delta^{18}\text{O}$ values determined for local modern meteoric water. Core D was collected from outside the region of anomalous $\delta^{18}\text{O}$ values and should therefore not be strongly affected by the isotopically-light water that is affecting cores A, B, and C. Porewaters from core E have $\delta^{18}\text{O}$ values that are significantly lighter than modern precipitation. This finding indicates that core E has also been affected by water recharged during a much cooler climate, although to a much lesser degree than terrestrial cores A, B, and C.

While the general distribution of $\delta^{18}\text{O}$ values among the five terrestrial cores upholds the conceptual model for the study area, the presence of lighter $\delta^{18}\text{O}$ values and low chloride concentrations at core E are especially significant. The ground water in the glaciofluvial aquifer beneath core E can be characterized as isotopically-light with low concentrations of dissolved chloride (Figure 4). If porewaters from core E have been derived from the upward flow of ground water, then one should find low chloride concentrations and significantly lighter $\delta^{18}\text{O}$ values (i.e., when compared to modern meteoric water). The fact that both these conditions are met in core E substantiates the

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model and further demonstrates that the conditions of salinity and light $\delta^{18}\text{O}$ values are not directly coupled.

Adjacent to Saginaw Bay, ground water in the glaciofluvial aquifer is (generally) saline and isotopically-light. If Saginaw Bay is influenced by ground-water discharge from the glaciofluvial aquifer, then based on regional ground-water chemistry, porewaters from bay cores should retain a saline, isotopically-lighter signature as a result of such discharge. If such reasoning is correct, then the bay cores with the highest chloride concentrations are also likely to exhibit the lightest $\delta^{18}\text{O}$ values. The bay cores were classified into two groups using porewater-chloride concentrations: those with stronger chloride gradients that greatly exceed background levels (e.g., SB7 and SB24) and those with weaker gradients (e.g., SB17 and SB22). Two cores from each group were chosen for stable isotope analysis.

The $\delta^{18}\text{O}$ values measured in porewaters from the four selected bay cores (SB7, SB17, SB22, and SB24) are plotted versus depth in Figure 13b. The shaded region in the figure represents the range of $\delta^{18}\text{O}$ values measured in the Saginaw Bay water column. Bay-core porewater samples have $\delta^{18}\text{O}$ values similar to those measured in modern meteoric water, although there is a trend of decreasing $\delta^{18}\text{O}$ values with depth in bay core SB7 (and possibly SB24). Common to all four cores is a shift towards lighter $\delta^{18}\text{O}$ values within the top few centimeters of the sediment column. This shift is likely an indication that the uppermost porewater samples have been influenced by the overlying

water column (i.e., a sampling artifact). Gravity coring is known to create such disturbances in the uppermost portion of the sediment cores (Blomqvist, 1985). The lightest $\delta^{18}\text{O}$ value determined for bay core SB7 is significantly lighter than any value measured in the overlying water column at site SB7: samples from the upper, middle, and lower portions of the water column have $\delta^{18}\text{O}$ values of -7.89 ‰, -7.91 ‰, and -7.85 ‰, respectively. When combined with the chloride data (Figure 7b), the $\delta^{18}\text{O}$ profiles indicate that the porewater from core SB7 (and possibly SB24) may be influenced by a saline, isotopically-light source. This result supports current models regarding fluid flow and hydrogeochemistry within the Saginaw Bay area (Hoaglund, 1996; Meissner et al., 1996; Wahrer et al., 1996).

Porewater-chloride concentrations from cores SB17 and SB22 indicate that these cores are not strongly influenced by a saline, isotopically-light source and, therefore, porewaters from these cores should not have $\delta^{18}\text{O}$ values lighter than modern meteoric water. In fact, porewater data from core SB22 show no trend in $\delta^{18}\text{O}$ values with depth, whereas $\delta^{18}\text{O}$ values from core SB17 show an increase with depth. [In the case of the latter, the trend in $\delta^{18}\text{O}$ values appears to be real as it persists throughout the entire core and the overall gradient exceeds the limits of analytical precision.] The trend in $\delta^{18}\text{O}$ values at core SB17 might signify that this location within the bay is interacting (e.g., via a fracture) with an isotopically-heavier water mass at depth, although the data currently available are insufficient to test this hypothesis.

Tritium Analyses

Like stable isotope values, measurements of tritium levels in water can help distinguish between sources of water, particularly between a modern source ($TU > 0$) and significantly older source ($TU \approx 0$) (Faure, 1986). Results of tritium analyses in the Saginaw Bay water column samples are given in Table 2. Three samples, each from a different depth, were collected at each water column sampling station. Locations of the water column stations sampled for tritium are shown in Figure 14.

The results of the analyses show that the water column at each station is fairly well mixed. There is a strong gradient in tritium levels as one proceeds from inner bay (SB4) to the outer bay and open waters of Lake Huron (SB9a and SB11). This gradient could be interpreted to reflect a significant dilution of the Saginaw Bay water column by discharge of old ground water through benthic sediments. However, recent studies of precipitation and stream chemistry in the Lower Peninsula of Michigan (Kim, 1993) have documented tritium levels (~ 15 TU) much lower than those found in the open waters of Lake Huron. The residence time of water in Lake Huron is much greater than in local streams, indicating that Lake Huron is still influenced by tritium inputs associated with precipitation over the past several decades (Faure, 1986; Strachan and Eisenreich, 1987). Thus, the gradient observed between inner and outer Saginaw Bay probably reflects mixing between recently derived meteoric water (e.g., from the Saginaw River/Saginaw Bay watershed) and older water from Lake Huron. Furthermore, the presence of tritium in bay-core porewater samples at levels comparable to those measured in the Saginaw

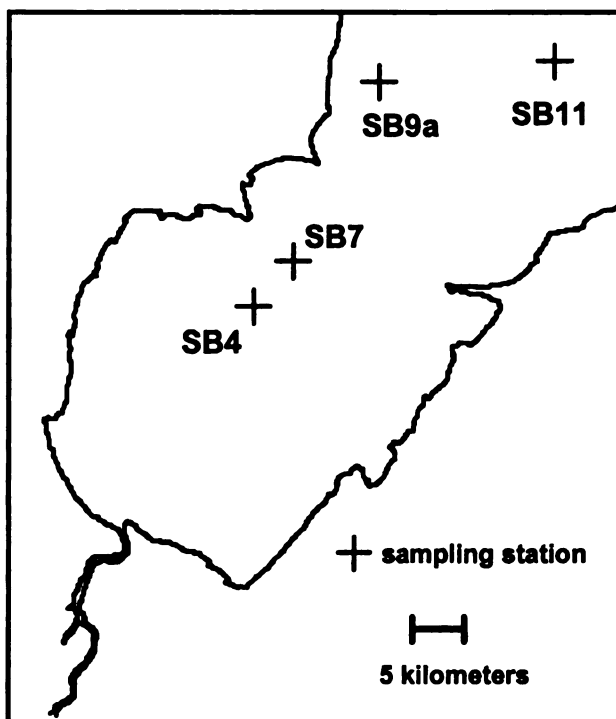


Figure 14. Map of water column stations sampled for tritium analyses.

Table 2. Tritium Levels in Water Column Samples.

SB4	SB4	SB7	SB7
Depth (m)	TU	Depth (m)	TU
-1	47.4	-1	56.3
-4	48.5	-6	54.0
-7	47.3	-11	59.1

SB9a	SB9a	SB11	SB11
Depth (m)	TU	Depth (m)	TU
-1	NA	-1	63.7
-8	61.4	-14	62.3
-15	67.0	-27	67.3

Bay water column (G. Larson, oral communication, 1995) indicates that the water column is the dominant water source to the interstices of benthic sediments. If large amounts of older (e.g., glacial-age) water were discharging through the benthic sediment to produce the observed tritium gradient in the Saginaw Bay water column, then there should be no detectable tritium in the porewater of the benthic sediments.

DISCUSSION

Fluid Mixing – Chloride:Bromide Ratios and the Source for Salinity

The trend of increasing porewater-chloride concentrations with depth in some of the terrestrial and bay cores supports the model of a high-chloride source at depth; however, this chloride source could have been generated by a number of processes (e.g., halite dissolution, mixing with formation brine). Chloride concentrations alone cannot identify the source. The fact that concentrations of all major cations in bay-core porewater samples increase with chloride levels tends to indicate that formation brine, not halite dissolution, is the source for chloride.

One way of discriminating among multiple sources for chloride is to evaluate Cl:Br ratios (Tellam, 1995; Whittemore, 1995). [In this study, the Cl:Br ratio represents the concentration of chloride (in milligrams per liter) divided by the bromide concentration (in milligrams per liter).] The two major chloride sources considered were halite and formation brine from the Michigan basin. These sources have very distinct

Cl:Br ratios because, during halite crystallization, bromide is preferentially partitioned into the solution (i.e., brine). As a result, halite has a Cl:Br ratio which exceeds 3,000 whereas formation brine has a significantly lower Cl:Br ratio (Wilson and Long, 1985). In general, the maximum Cl:Br ratio of formation brine is approximately 300 (the ratio found in seawater), but depending on the amount of halite crystallization, the brine can have a Cl:Br ratio less than 300 (Carpenter, 1978). However, a number of brine samples from the Marshall and Parma-Bayport aquifer units have Cl:Br ratios ranging between 400 and 600. One possible explanation for this discrepancy is that if a brine has formed primarily via halite dissolution, and the system lacked excess halite, then the partitioning of bromide between solid and solution may not have equilibrated, resulting in Cl:Br ratios greater than seawater (Wilson and Long, 1985; Land and Prezbindowski, 1981). While Cl:Br ratios can be used to distinguish between chloride derived from simple halite dissolution and formation brine, these ratios will not provide insight into the process responsible for generating the brine.

Figure 15 shows a plot of log bromide concentrations versus log chloride concentrations. Trend lines for Cl:Br ratios of 100 and 289 (seawater) and 3,000 (halite dissolution) are also plotted on the figure. The shaded area in the figure represents the field where samples affected by halite dissolution (either from natural or anthropogenic processes) would plot. The gray, oblong shape in the figure represents ground-water samples from the glaciofluvial aquifer (Wahrer et al., 1996). The maximum background chloride concentration (50 mg/L chloride; Long et al., in press) is also plotted.

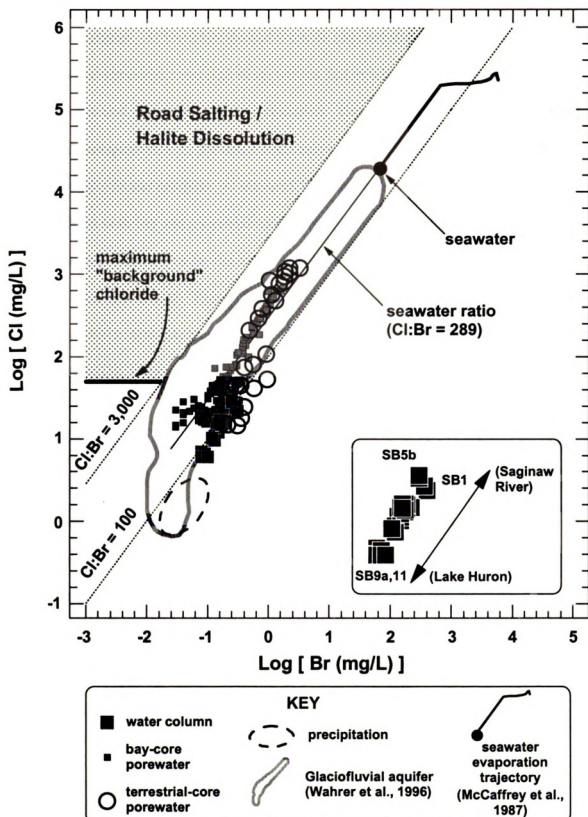


Figure 15. Log Br vs. Log Cl in water column and porewater samples.

Below this background chloride level, there is considerable scatter among the porewater samples. At low chloride and bromide concentrations, porewaters from both bay cores and terrestrial cores plot along a trend that overlaps with the Saginaw Bay water column and, ultimately, local precipitation. This trend likely indicates that mixing with local precipitation (i.e., the dilute endmember) is influencing Cl:Br ratios in the more dilute porewater samples. At elevated TDS levels, Cl:Br ratios in porewater samples from both bay and terrestrial cores parallel the seawater trend. If halite dissolution were the source for the elevated TDS levels, then the samples should plot into the halite dissolution field. That Cl:Br ratios in saline water from the study area generally range from 400 to 600 (Meissner et al., 1996) tends to indicate that formation brine, not halite dissolution, is the source for the chloride.

Cl:Br ratios in ground-water samples from the glaciofluvial aquifer vary widely, although most samples have values less than 600 and have been interpreted to indicate mixing between solutes derived from Michigan basin brines (Cl:Br $\approx$ 400-600) and a dilute endmember (Meissner et al., 1996; Long et al., in press). Nearly all porewater samples from the terrestrial and bay cores also have Cl:Br ratios less than 600. This similarity implies that the terrestrial and bay cores have also been affected by formation brine, but does not eliminate the possibility that the observed Cl:Br ratios could have been produced by a mixture of precipitation and halite dissolution.

To identify the chloride source that is influencing porewater chemistry, Cl:Br ratios are plotted against chloride concentrations in Figure 16. [Only data points from

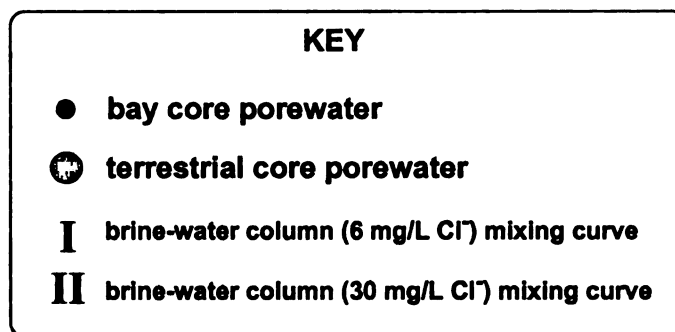
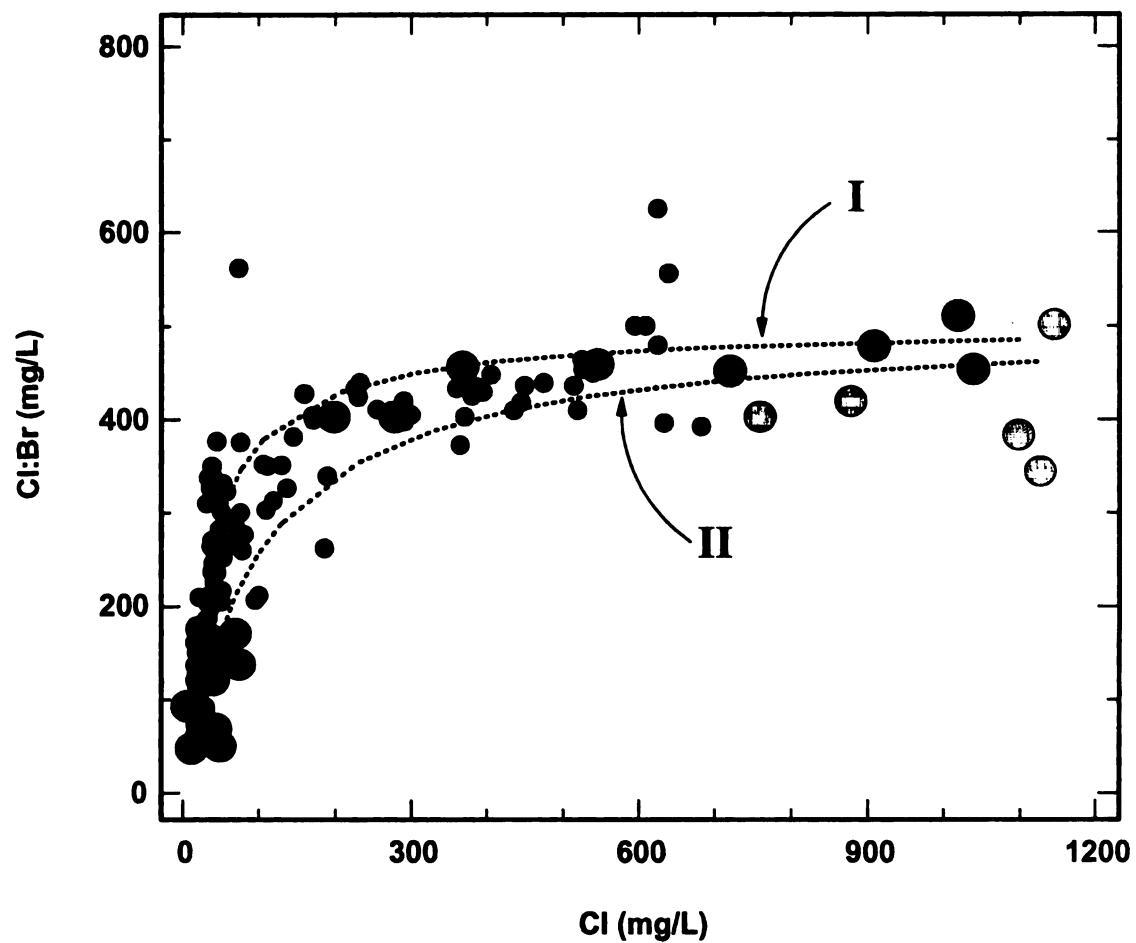


Figure 16. Mixing relationship between Saginaw Bay water column and formation brine.

samples with bromide concentrations greater than the detection limit (0.1 mg/L) are plotted in these diagrams.] Porewater samples from both bay cores and terrestrial cores plot along the same general trend, indicating that they have been affected by a similar chloride source. Initially, the Cl:Br ratios in these samples increase as chloride concentrations increase, but eventually the Cl:Br ratios plateau at a value of approximately 500. If simple halite dissolution were the source for the elevated chloride levels in these samples, then the Cl:Br ratios should continue to increase (up to values near 3,000) as chloride levels increase. The fact that Cl:Br ratios are approximately less than 500 eliminates simple halite dissolution and identifies formation brine as the likely chloride source.

Implicit in Figure 16 is the scenario that mixing between formation brine and a dilute endmember is controlling porewater concentrations of chloride and bromide. To test this model, two mixing curves were generated to simulate these interactions, and these are also plotted on Figure 16. In both scenarios, a formation brine ($[Cl^-]=100,000$ mg/L; Cl:Br = 500) was used as the concentrated endmember. [The formation brine sample is from the Grand River-Saginaw aquifer (Meissner, 1993).] In the case of the bay-core porewaters, the dilute endmember was likely derived from the Saginaw Bay water column, which would have been entrained into pore spaces during sediment deposition. Dissolved chloride levels within the Saginaw Bay water column are variable, ranging from 30 mg/L chloride (Cl:Br = 90) in the inner bay to 6 mg/L chloride (Cl:Br = 70) in the outer portion of the bay. The minimum and maximum water column chloride levels were used as the dilute endmembers in curves I and II, respectively. At low (< 200

mg/L) chloride concentrations, the two mixing curves form an envelope that encloses most of the bay-core porewaters. The few bay-core porewater samples not included in this envelope could be affected by local variations in water column chloride levels not represented by this sampling effort. The two mixing scenarios also adequately describe the chemical compositions of the terrestrial porewaters at low chloride levels. Although a number of these terrestrial porewater samples fall outside the mixing envelope (i.e., below curve II), nearly all are derived from a single core (core D). Compared to the other terrestrial cores, porewater samples from core D have elevated concentrations of bromide, which might be the result of a localized, anthropogenic release of bromide.

At greater (>200 mg/L) chloride concentrations, the two mixing curves reflect the general trend in composition from all porewater samples. The good agreement between the models and field data signifies that the chloride source has a Cl:Br ratio of approximately 500. This value is similar to the Cl:Br ratios found in brines from the Pennsylvanian- and Mississippian-aged units within the study area (Long et al., in press). The results from the mixing models, therefore, indicate that formation brine is the source for the elevated Cl levels encountered in the porewater samples.

Fluid Mixing: Chloride and $\delta^{18}O$ Constraints

Although Cl:Br ratios have proven useful in determining the ultimate source for the elevated solute levels, they do not provide definitive evidence that near-surface sediments in the Saginaw Bay area are *directly* communicating with formation brine.

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The chemical gradients documented in this study may also be the result of a multiple-stage mixing process. For example, initial dilution of formation brine may have coincided with the emplacement of the isotopically-light water (i.e., recharge by subglacial meltwater). The resulting mixture could have subsequently undergone additional mixing/dilution (or a series of dilutions) with modern meteoric water. This multi-stage process has been invoked to explain the presence of saline, isotopically-light ground water elsewhere in the Michigan basin (Weaver et al., 1995), in the Illinois basin (Stueber and Walter, 1994), as well as in the Canadian Shield (Clark et al., 2000). Such a scenario would also support the conceptual model of Long et al. (1988), who postulated that “the cause of salinity distribution [in the Saginaw Bay area] is the slow flushing of water in the argillaceous sediments by recent meteoric water.” Whether or not near-surface sediments in the Saginaw Bay area are directly communicating with formation brine is an important point to resolve. If brines are in direct communication with near-surface sediments, and ground water is moving upward (Badalamenti, 1988; Hoaglund, 1996), then formation brine might eventually reach the surface and discharge directly to Saginaw Bay and/or the surrounding watershed. Such discharge could significantly degrade surface water quality in the Saginaw Bay area.

In this study, possible mixing relationships between brine and freshwater endmembers were further investigated according to the approaches of Wahrer (1993) and Long et al. (in press). Mixing scenarios were simulated using chloride (to constrain the solute source) and $\delta^{18}\text{O}$ (to constrain the solvent [i.e., water] source). The composition of the brine endmember used for modeling in this study is the same as used by Wahrer

(1993) and Long et al. (in press): the brine contains 200,000 mg/L chloride and has a $\delta^{18}\text{O}$ value of 0.0 ‰. [These values are ultimately derived from the data of Clayton et al. (1966).] All three freshwater endmembers used were assigned a chloride concentration of 1 mg/L, however, each had a distinct $\delta^{18}\text{O}$ signature. $\delta^{18}\text{O}$ values of –8 and –10 ‰ were used to bracket the range of values found in mean, modern, meteoric precipitation within the study area (Sheppard et al., 1969; Machavaram and Krishnamurthy, 1994). A $\delta^{18}\text{O}$ value of -20 ‰ was used to represent the isotopically-lightest water documented in the glaciofluvial aquifer (Wahrer et al., 1996).

Chloride concentrations in the mixing scenarios were calculated according to the following relation:

$$\text{Cl}^-_{\text{mixture}} = x * \text{Cl}^-_{\text{brine}} + (1-x) * \text{Cl}^-_{\text{freshwater}} \quad (10)$$

where x is the fraction of brine in the mixture, $\text{Cl}^-_{\text{brine}}$ is 200,000 mg/L, and

$\text{Cl}^-_{\text{freshwater}}$ is 1 mg/L, and $\text{Cl}^-_{\text{mixture}}$ is the final chloride concentration resulting from the mixing of two endmembers. The $\delta^{18}\text{O}$ values in the mixtures were calculated using a slightly different formula, given the variation in density and amount of water in each endmember (Long et al., in press). The $\delta^{18}\text{O}$ values were calculated according to the following relation:

$$\delta^{18}\text{O}_{\text{mixture}} = F * x * \delta^{18}\text{O}_{\text{brine}} + (1-x) * \delta^{18}\text{O}_{\text{freshwater}} \quad (11)$$

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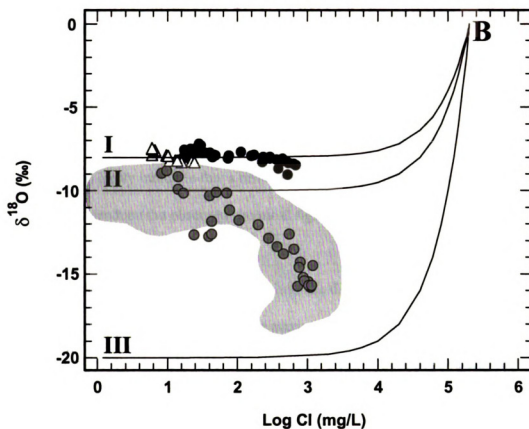
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where F is the ratio of the H_2O weight in brine to its weight in pure water and x is the fraction of brine mixed. A value of 0.70 is used for F in these calculations (Wilson and Long, 1993).

Figure 17 shows the three mixing curves generated using Equations 10 and 11. The combination of the three curves generally brackets all Saginaw Bay water column, bay-core porewater, and terrestrial-core porewater samples. This result supports the idea that mixing between brine and freshwater endmembers is ultimately responsible for producing the geochemical variations observed among these samples. At low dissolved chloride levels, water column and porewater samples appear to overlap, implying that they have a common endmember, possibly modern meteoric water.

The gray field plotted in Figure 17 represents the variations in ground-water chemistry from the Glaciofluvial aquifer (Wahrer, 1993). This field also encompasses the terrestrial-core porewater samples, indicating that these porewaters have been affected by similar mixing processes, and probably are in direct communication with the ground water. Data from Saginaw Bay water column and bay-core porewater samples do not plot within the ground-water field. Implicit in this observation is the scenario that although porewaters from both sets of cores may be affected by a similar process (i.e., transport of solutes derived from formation brine), bay cores and terrestrial cores do not appear to be communicating with the same water mass(es).



KEY	
$\triangle$	Saginaw Bay water column
$\bullet$	porewater - bay cores
$\bullet$	porewater - terrestrial cores
	ground water - Glaciofluvial aquifer (Long et al., in press)
B	brine: 200,000 mg/L Cl^- ; $\delta^{18}\text{O} = 0 \text{ ‰}$
I	freshwater: 1 mg/L Cl^- ; $\delta^{18}\text{O} = -8 \text{ ‰}$
II	freshwater: 1 mg/L Cl^- ; $\delta^{18}\text{O} = -10 \text{ ‰}$
III	freshwater: 1 mg/L Cl^- ; $\delta^{18}\text{O} = -20 \text{ ‰}$

Figure 17. Chloride- $\delta^{18}\text{O}$ mixing curves between a brine and freshwater endmembers.

That neither ground-water nor terrestrial-core porewater data plot along any of the simulated mixing curves is readily apparent in Figure 17. Closer inspection reveals that at elevated chloride levels ($\log [\text{Cl}^-] < 2.6$; $[\text{Cl}^-] < 400 \text{ mg/L}$), bay-core porewaters also begin to deviate significantly from the mixing trend. The fact that none of these sample sets appears to be constrained by any of the mixing trends (or even mimic the shape of the mixing trends) likely indicates that a brine and freshwater endmember *cannot* have *directly* mixed to produce the observed chemical signatures.

As the data in Figure 17 appear to preclude the direct interaction of brine and freshwater, the possibility of a multiple-stage mixing process controlling the observed geochemical and isotopic variations in bay-core and terrestrial-core porewaters was further investigated. A previous study successfully employed a multi-stage mixing model to explain variations in ground-water chemistry from Devonian formations of the Michigan Basin (Weaver et al., 1995). In this study, the brine (from Figure 17) was first mixed with an isotopically-light ($\delta^{18}\text{O} = -20 \text{ ‰}$) freshwater to produce three intermediate waters (brackish, saline, and a less-concentrated brine). The chemical compositions of the three intermediates are listed in Figure 18. Each intermediate was then mixed with modern meteoric freshwater ($[\text{Cl}^-] = 1 \text{ mg/L}$; $\delta^{18}\text{O} = -8 \text{ ‰}$). The mixing between freshwater and intermediates was simulated according to Equations 10 and 11. The value of F used in the $\delta^{18}\text{O}$ calculations varied: a value of 1.0 was used for the brackish and saline waters, and a value of 0.9 (Wilson and Long, 1993) was used for the brine. The mixing curves generated as a result of this secondary dilution are plotted

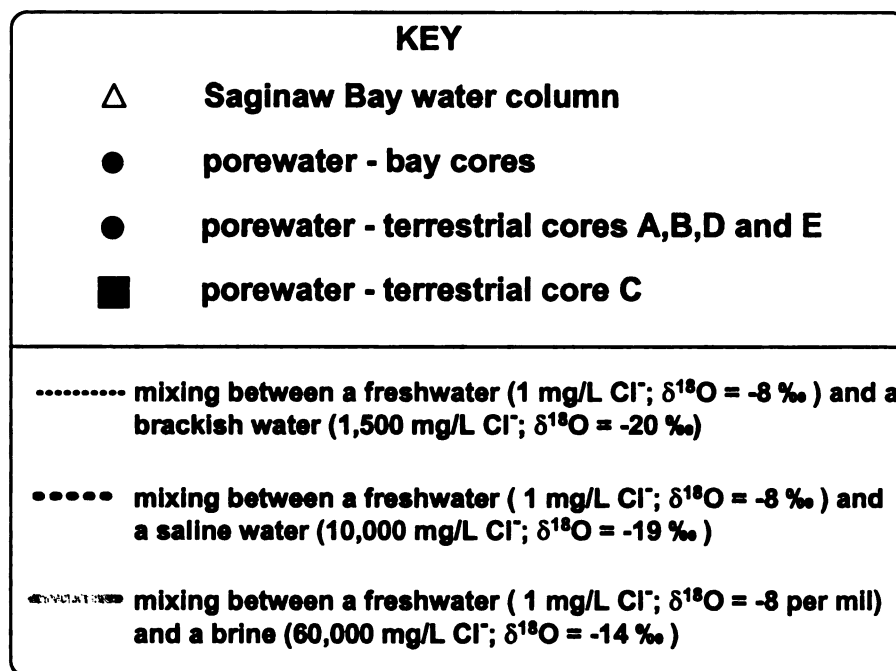
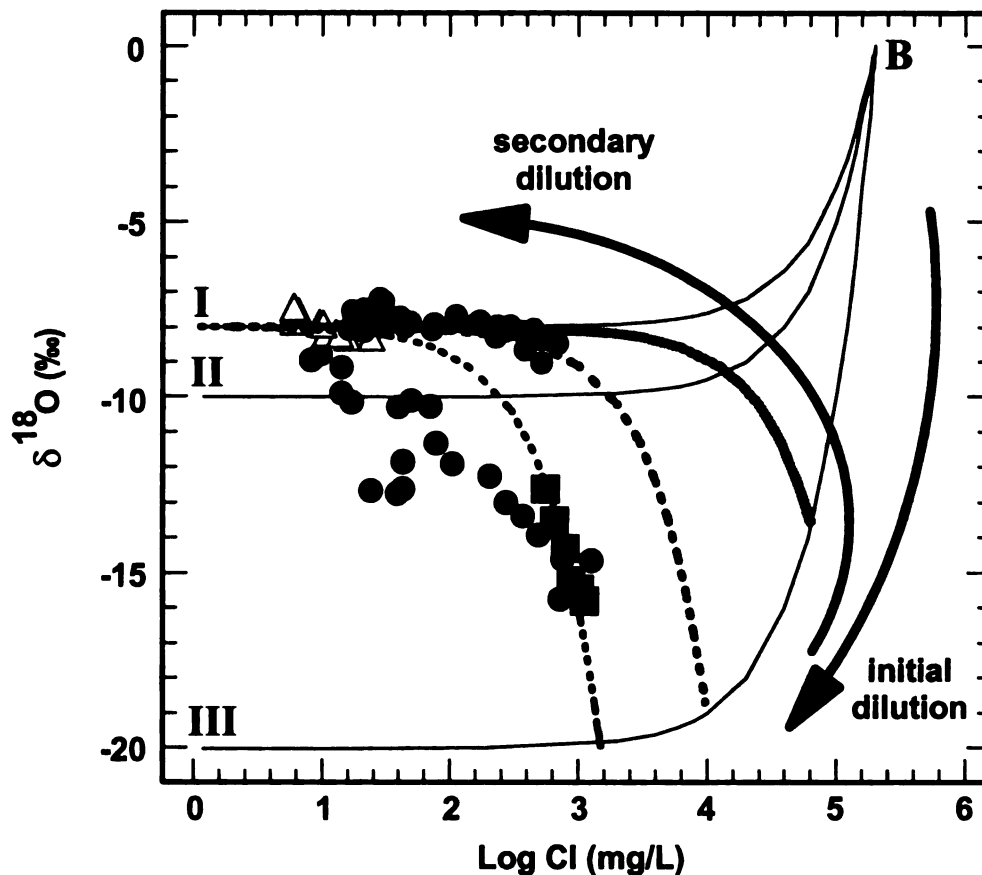


Figure 18. Cl-δ¹⁸O mixing curves between a freshwater and brackish/saline/brine endmembers.
(Curves I, II, and III are from Figure 17.)

on Figure 18. The original mixing trends (curves I, II, and III) from Figure 17 are also plotted for comparison.

Porewaters from terrestrial core C (Figure 18; gray squares) plot precisely along the freshwater-brackish water mixing trend. This finding apparently indicates that the chemical gradients observed in core C are the result of (at least) a two-stage mixing process. Porewaters from the other terrestrial cores do not plot on any of the mixing trends, which may indicate that additional mixing pathways require consideration. In the case of terrestrial core D ($[Cl]_{\max} = 50 \text{ mg/L}$; $\delta^{18}O_{\min} = -10.3 \text{ ‰}$), deeper samples are needed to help further constrain mixing scenarios. Combined, the data from all terrestrial cores indicate that the porewater chemistry cannot be accounted for by a single, homogeneous mixing event.

There is not enough variation among $\delta^{18}O$ values from bay-core porewater to definitively constrain mixing scenarios. The porewaters apparently are best described by a mixing relationship between a freshwater and a saline endmember, although they might also be communicating with an even more concentrated endmember such as a brine. However, given the lack of a $\delta^{18}O$ signature that is significantly lighter than modern meteoric water, one cannot dismiss the possibility that bay core porewater chemistry might simply be described by mixing between modern meteoric water (endmembers I and II) and brine (B). Regardless, the data show that mixing between the freshwater and brackish water endmember cannot account for the observed chemistry. This result is

noteworthy in that it implies that the terrestrial cores and bay cores are not communicating with the same water masses.

Transport Modeling and Regional Implications

Porewater chemistry profiles and Cl:Br mixing curves confirm the influence of the upward transport of brine solutes on water quality. Understanding the time-frame over which these profiles developed is important for assessing the significance of such transport on the geochemical cycling of solutes within the Great Lakes. For example, models simulating chloride mass-balances within the Great Lakes are primarily concerned with short (e.g., decades) timescales (Ownbey and Willeke, 1965). If ground-water transport of brine solutes is capable of significantly affecting porewater chemistry on a similar timescale, then it may be necessary to incorporate this component into mass-balance predictions. Profiles of chloride concentrations and ^{18}O values from the terrestrial and bay cores were modeled to identify the dominant transport process(es) and the timescale(s) over which the profiles developed. These simulations assume that both constituents (i.e., chloride and ^{18}O) are behaving conservatively in this system. If this assumption is correct, then the time frames needed to develop porewater-chloride and porewater- $\delta^{18}\text{O}$ profiles should be similar.

Simulations of porewater-chloride profiles from terrestrial core C are plotted in Figure 19. The maximum porewater-chloride concentration is 1130 mg/L; this value is used as C_0 during the simulations. Simulations using diffusion alone (D only) are shown

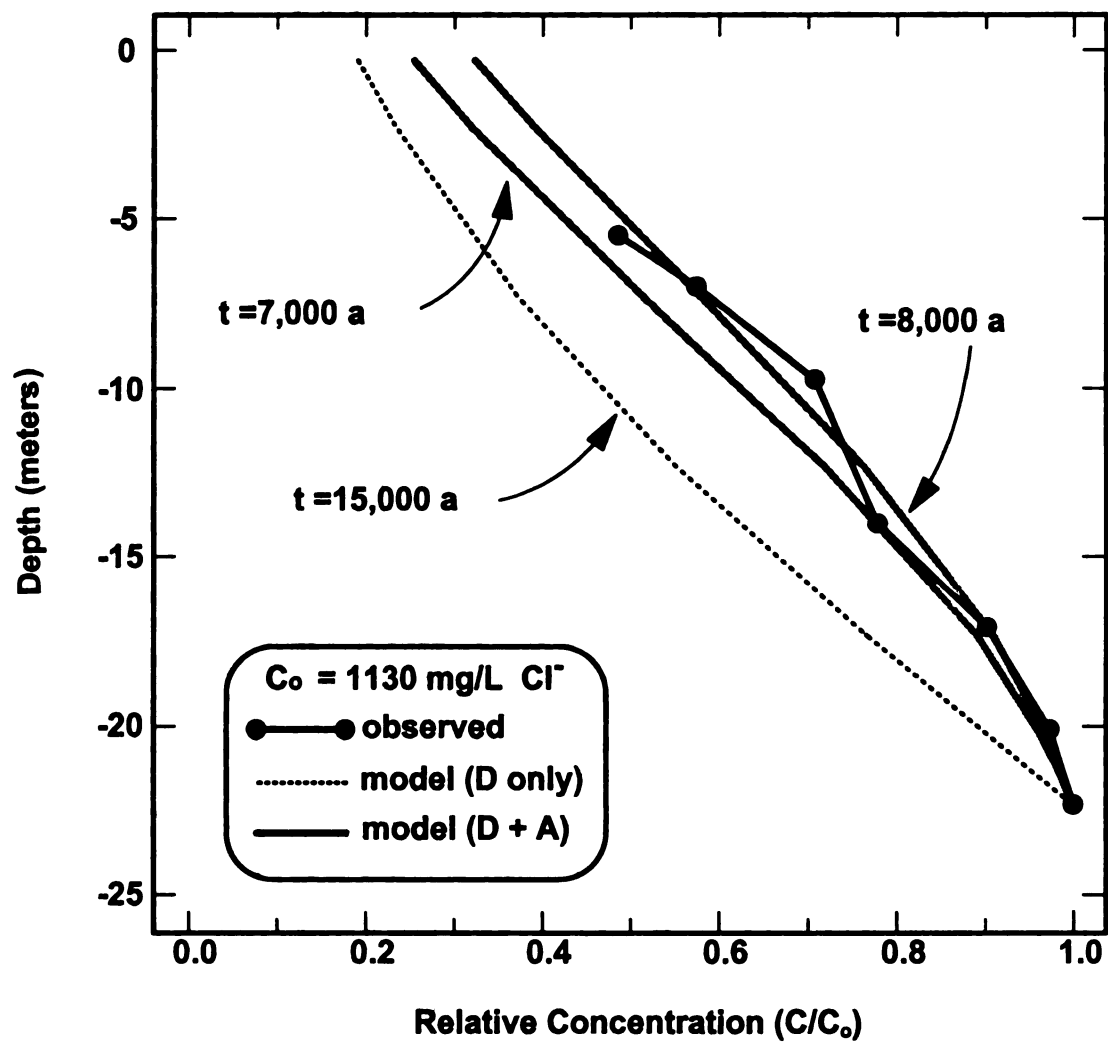
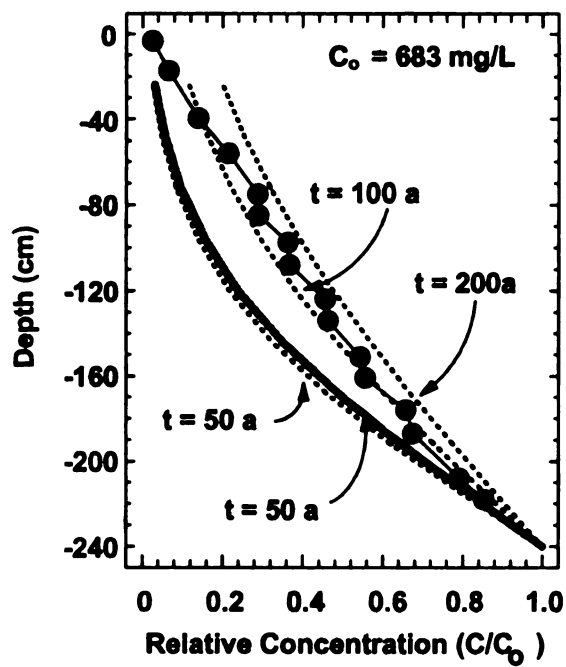


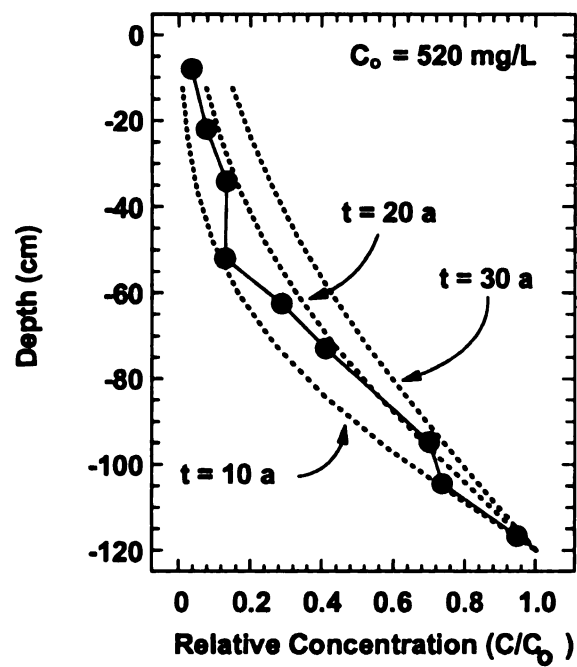
Figure 19. 1-D simulation of chloride transport in terrestrial core C.

as dashed lines whereas the advection-diffusion results (D+A) are shown as solid black lines. The diffusion-only profile, using a time of 15,000 a, predicts lower chloride concentrations than those measured in the porewater. Therefore, in the absence of advection, times in excess of 15,000 a are required to develop a porewater profile similar to the one observed in core C. This region was last free of ice around 13,000 BP with the cessation of the Port Huron advance (Dorr and Eschman, 1970), so the minimum age of the sediments (and hence, maximum age for porewater chemistry to develop) represented in the terrestrial cores is on the order of 13,000 a. Given this time constraint, diffusion alone cannot account for the observed porewater profiles; an advection component is required. Using an average linear velocity of 0.0016 m/a, the simulations best matching the observed data indicate a timespan on the order of 7,000 to 8,000 a is required for the porewater profiles to evolve. This time period is similar to the one that Desaulniers et al. (1981) obtained simulating porewater profiles of dissolved chloride from argillaceous Quaternary deposits in southwestern Ontario.

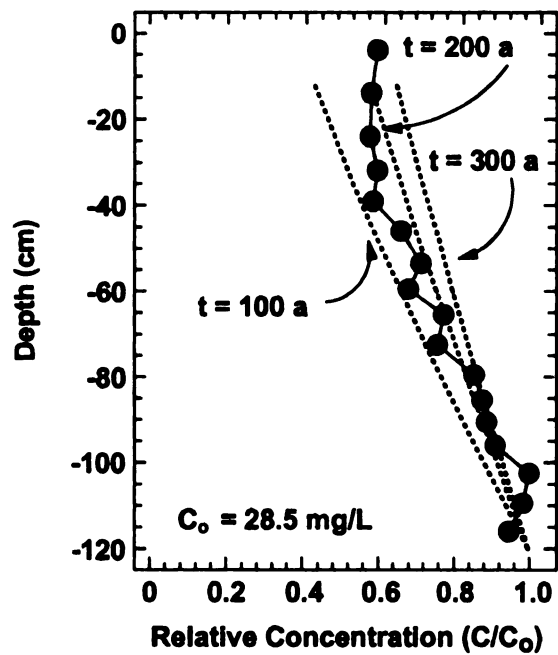
The evolution of porewater chloride profiles from four bay cores (SB7, SB17, SB22, and SB24) are also simulated and these are plotted in Figure 20. The dashed lines represent diffusion-only simulations whereas the solid line represents advection-diffusion simulations. There is little difference between the two models (Figure 20A), implying that chloride transport within the Saginaw Bay sediment column is dominated by diffusion. The times required to generate the chloride profiles vary among the four cores, but all are significantly less than the amount of time required for the profile in terrestrial core C. The difference may indicate that the bay cores have a better hydraulic connection



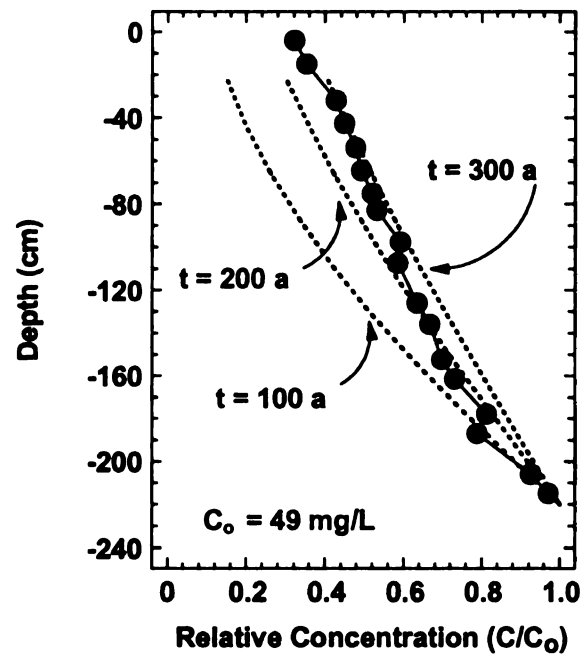
A



B



C



D

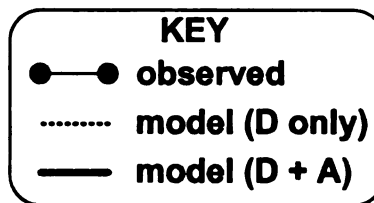


Figure 20. 1-D simulation of chloride transport in bay cores (A) SB24, (B) SB7, (C) SB17 and (D) SB22.

to the chloride source than do the terrestrial cores. A better hydraulic connection may result from the fact that: 1) regional ground-water flow is focused directly into the bay (e.g., Cherkauer and McKereghan, 1991) and there are few flow paths which terminate in the SLA, or, 2) there may be a more extensive fracture network underlying Saginaw Bay, providing a better conduit for solute transport, 3) the lithology underlying terrestrial cores differs from that underlying bay cores, or 4) bay cores are physically closer to their solute source (i.e., the sediment package underlying the bay cores is thinner than the package underlying the bay cores).

The amount of time needed to develop the chloride profile at SB7 is approximately an order of magnitude less than for the other three sites; the simulations for the three remaining sites are in good agreement with one another. Bay core SB7 might be influenced more strongly by the chloride source because of a change in subcrop lithology, but the proximity of site SB7 to SB17 decreases the likelihood of this scenario. The presence of a fracture beneath SB7 could explain the enhanced communication with the chloride source. In addition, there would also be considerable transport of chloride in all directions (i.e. multi-dimensional transport away from SB7), which might explain the chloride profiles observed at SB17 and other sampling sites. The simulations of chloride flux presented here have addressed only one-dimensional (i.e., vertical) transport of solutes.

Figure 21 shows the results from the transport modeling of the $\delta^{18}\text{O}$ profile for terrestrial core C. In the case where diffusion and advection are opposed, a steady-state

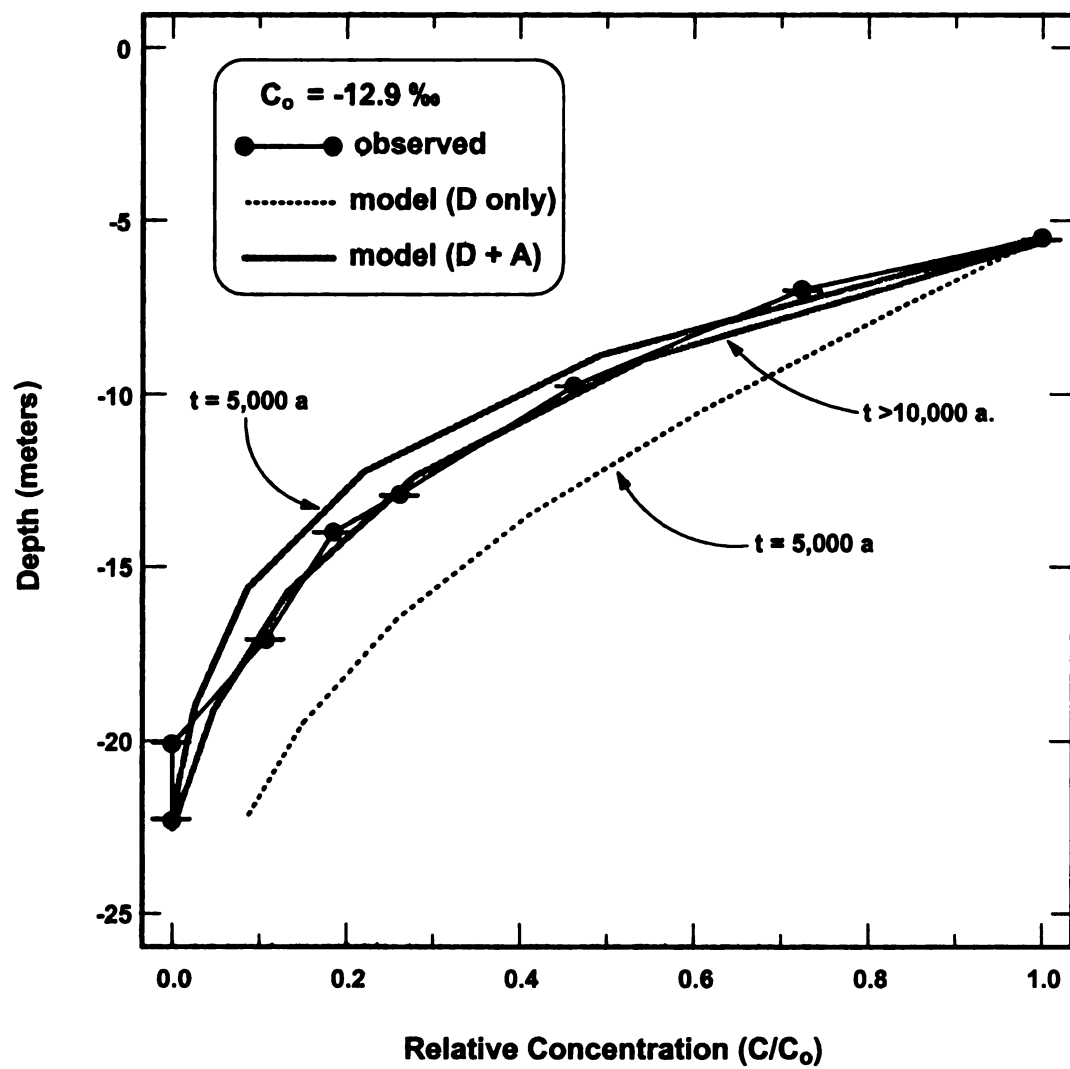


Figure 21. 1-D simulation of ^{18}O transport in terrestrial core C.

between the two transport processes is reached as t becomes large (Al-Niami and Rushton, 1977). The development of a steady-state makes it difficult to specify an upper bound on the time needed for the observed chemical profile to develop. The system modeled in Figure 21 appeared to reach steady-state at 10,000 a, after which there was very little change in the profile. As a result, only a “window” of time, over which the observed profile developed, can be specified. Nevertheless, this “window” (e.g., 5,000 to 10,000+ a) is consistent with the time-frame given by the chloride modeling, and is similar to results obtained by Desaulniers et al. (1981) for $\delta^{18}\text{O}$ profiles in Quaternary sediments from western Ontario.

Only the profile of $\delta^{18}\text{O}$ values from bay core SB7 was modeled; results of the simulations are plotted in Figure 22. The dashed lines on the data points represent the precision (1σ) of the analyses; $\delta^{18}\text{O}$ values from the water column are also included for comparison. The simulations indicate that the porewater profile evolved over a time span between 5 and 15 a. A diffusion-only scenario, not shown, produced similar results, signifying that diffusion is the dominant transport mechanism. Furthermore, the time-span required for the $\delta^{18}\text{O}$ profile to evolve is similar to that needed for the chloride profile to develop. The agreement between models of chloride and $\delta^{18}\text{O}$ in porewater profiles validates the initial assumption that both constituents are behaving conservatively in this system.

These simulations support the conceptual model that, on a regional scale, ground-water flow is focused towards Saginaw Bay and that there is upward transport of saline

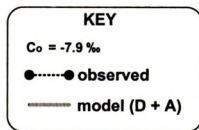
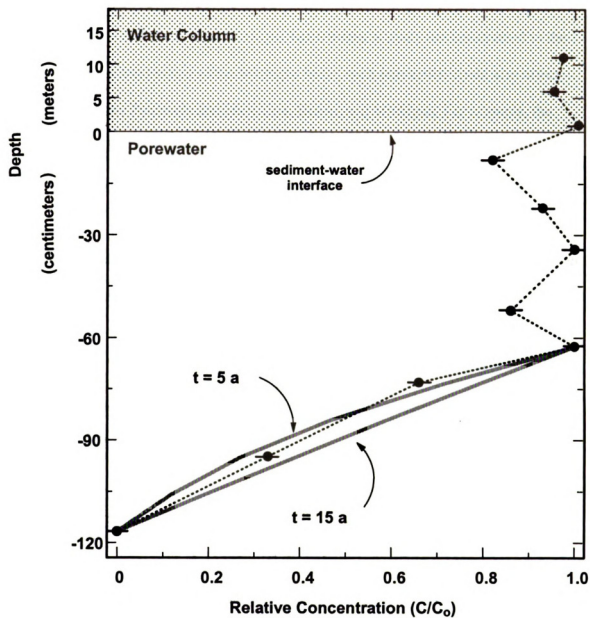


Figure 22. 1-D simulation of ^{18}O transport in bay core SB7.

and/or isotopically-light ground water into Saginaw Bay and the SLA; however, upward transport of solutes derived from Michigan basin brines is likely not constrained to the SLA. Given the areal extent of the Michigan basin, such interaction could also affect Michigan's Upper Peninsula and lakes Erie, Huron, and Michigan. For example, the limited data available on porewater chemistry in Lake Michigan indicate that southern Lake Michigan might also be influenced by a high-chloride source at depth (Callender, 1969; Kolak et al., 1997). Depending on the amount of ground water discharged, Lake Michigan might be even more highly affected by transport of Michigan basin fluids than what has been documented for Saginaw Bay (this study). Preliminary modeling of fluid flow within Michigan's Lower Peninsula indicates that significantly more ground water discharges to Lake Michigan than to Saginaw Bay (Hoaglund, 1996). If this discharge comprises saline ground water or brine, it could have a significant effect on Lake Michigan hydrochemistry.

CONCLUSIONS

Horizontal and vertical patterns in porewater chemistry (e.g., chloride concentrations and $\delta^{18}\text{O}$ values) from Saginaw Bay and SLA sediments are similar to patterns in the regional ground-water chemistry of the glaciofluvial aquifer, and indicate the influence of a high-chloride source at depth. Major cation concentrations in porewaters are also influenced by this source, as calcium, magnesium, sodium, and potassium levels are all positively correlated to porewater chloride concentrations. Mineral precipitation (calcium) and cation exchange (potassium) also affect porewater

cation concentrations. Geochemical modeling (i.e., calculation of mineral saturation indices) of porewater chemistry indicates that the influence of saline water could result in precipitation of calcite and dolomite at depth. Vertical trends in $\delta^{18}\text{O}$ values generally indicate that mixing between modern meteoric water and water recharged during much cooler conditions has occurred. Cl:Br ratios in porewater identify formation brine as the ultimate source for the solutes. Cl- $\delta^{18}\text{O}$ mixing scenarios demonstrate that SLA porewater profiles are not directly communicating with formation brine, but are more likely the result of a multiple (e.g., two-stage) mixing process. Cl- $\delta^{18}\text{O}$ mixing scenarios also appear to indicate that bay cores and terrestrial cores are mixing with different endmembers; bay core porewaters may be communicating directly with formation brine. Transport modeling of porewater chemistry profiles in the SLA cores has demonstrated that the observed profiles could be generated over a period of approximately 8,000 a with an upward advective flux of 0.0016 m/a. Transport modeling of chloride profiles in the Saginaw Bay cores suggest that the profiles are dominated by diffusive transport involving significantly shorter time spans. Within Saginaw Bay, interaction with this saline, isotopically-light ground water is highly variable, and may be controlled by fractures, although subcrop lithology and sediment accumulation rates likely exert some influence. Porewater chemistry from other sites (e.g., Lake Michigan) indicates that transport of Michigan basin fluids to near-surface environments might not be constrained to Saginaw Bay, but might affect the Great Lakes on a much larger scale.

CHAPTER II.

Evaluation of ground water-surface water interactions in the Saginaw Bay Watershed, Lake Huron

INTRODUCTION

Dissolved solids concentrations among the Great Lakes have increased over the last several decades (Ownbey and Willeke, 1965; Beeton, 1970; Rockwell et al., 1989). These increases are largely attributed to elevated solute loading via rivers derived from anthropogenic activities (Tiffany et al., 1969; Diment et al., 1973; Effler et al., 1984). In fact, water quality within numerous watersheds from the Great Lakes basin has degraded (e.g., Grounds et al., 1967; Effler et al., 1984) to the extent that many rivers have been targeted for restoration by the International Joint Commission (IJC, 1987).

One area in which water quality has particularly degraded over recent years is the Saginaw Bay watershed (Tiffany et al., 1969; Richards et al., 1993). Previous studies have evaluated water quality in this watershed, but lacked extensive spatial coverage to determine solute sources (Wood, 1970; Tiffany and Winchester, 1970). One potentially significant source for solutes to this watershed is saline ground water. The glaciofluvial aquifer unit underlying the watershed is known to contain saline water (Wahrer et al., 1996). Discharge of this saline water could significantly affect water quality in the Saginaw Bay watershed.

The primary goals of this study were to evaluate spatial and temporal variations in water quality within the Saginaw Bay Watershed, evaluate the extent of interaction between ground water and surface water in the Saginaw Bay watershed, and determine

whether or not saline ground-water inputs (ultimately derived from Michigan basin brines) were a significant in regulating stream hydrochemistry.

METHODS

Sampling plan design

Five sets of river water samples were collected from the Saginaw Bay watershed over the time frame July 1995 to May 1996. The sampling events were designed to target different hydrologic regimes of the watershed (i.e., hi flow, low flow) and to evaluate temporal variations in solute concentrations associated with seasonal variations in sources (e.g., road salt applications during the winter months). The primary objective of this sampling plan was to target low flow (i.e., baseflow) conditions in the SBW when ground-water inputs would comprise the largest portion of total flow. If the SBW were receiving inputs of saline ground water, these would be most readily detected during low flow conditions, when streams are dominated by ground water inputs. Evaluating spatial variations in hydrochemistry during such events would presumably delineate areas receiving inputs of saline ground water [ultimately derived from Michigan basin brines].

Previous studies of SBW hydrochemistry have noted difficulties in discerning regional trends due to low sampling densities (Tiffany and Winchester, 1969; Wood, 1970; Blumer, 1991). Such efforts are further complicated by the myriad of solute sources and land-use patterns within the SBW (Richards et al., 1993; Pijanowski et al., in

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press). As a result, in this study, approximately 150 to 200 samples were collected from the SBW during each sampling event (Figure 23). The notion was to collect a high-intensity sample set in order to provide synoptic coverage (i.e., a “snapshot”) of the entire watershed at a given time, similar to approaches employed by other researchers (e.g., Flintrop et al., 1996). The samples collected in this study were primarily analyzed for major cations (calcium, magnesium, sodium, and potassium) and anions (chloride and bromide). During one sampling event (RIV III), a select number of stations were sampled for “complete” geochemistry (pH, alkalinity, T, and sulfate). The solutes analyzed generally account for greater than 90% of the charge balance in natural waters (Hem, 1989), and would therefore enable one to geochemically model the stream samples. Such modeling efforts can be used to delineate mineral-water interactions that might be controlling river chemistry (e.g., Phillips, 1988).

Sample collection

Prior to the start of each sampling event, the hydrologic regime of the SBW was monitored for 2-3 weeks until the desired state (e.g., high or low flow) was attained. Stream discharge measurements were later obtained from several U.S. Geological Survey gaging stations located within the watershed (Figure 24) to confirm the watershed’s status. According to these data, sampling events I and III are characterized as summer, low-flow events, II is a summer, high-flow event, IV is a winter, high-flow event, and V is a spring, high-flow event (Figure 25). Sampling events were completed as rapidly as possible (3-4 days) to avoid changes in hydrologic regime during sampling.

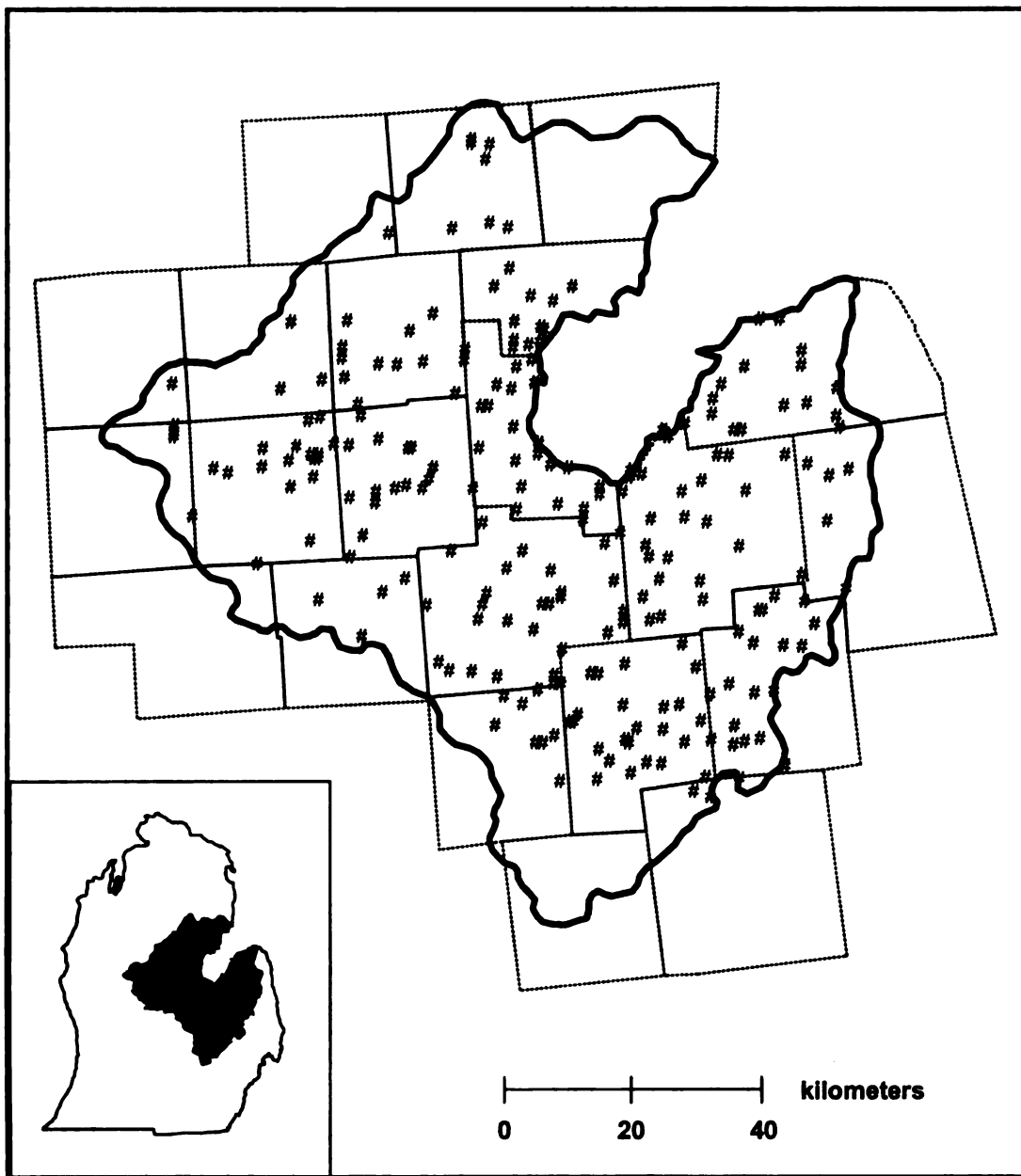


Figure 23. Map of watershed sampling sites.

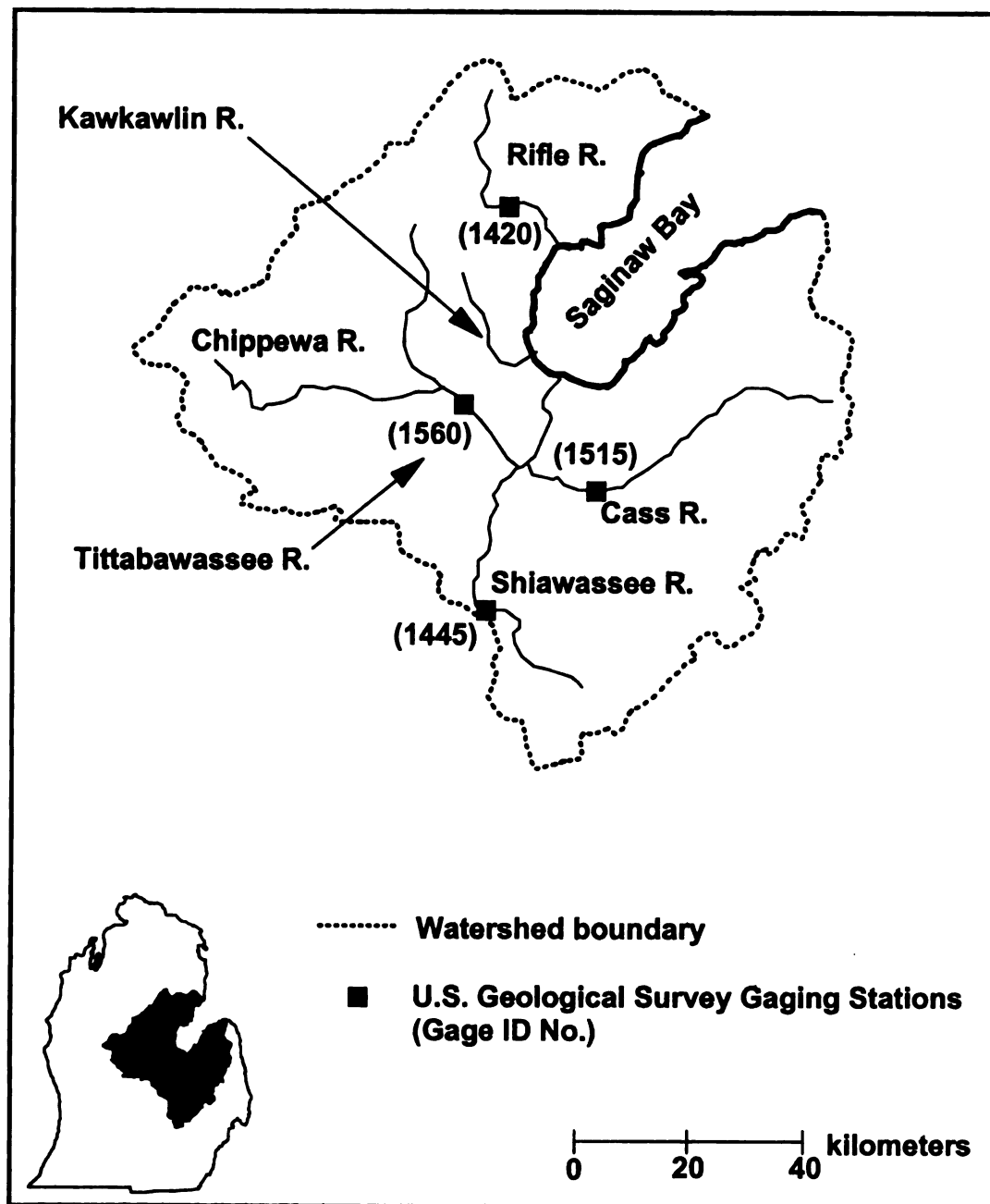


Figure 24. Location of stream gaging stations.

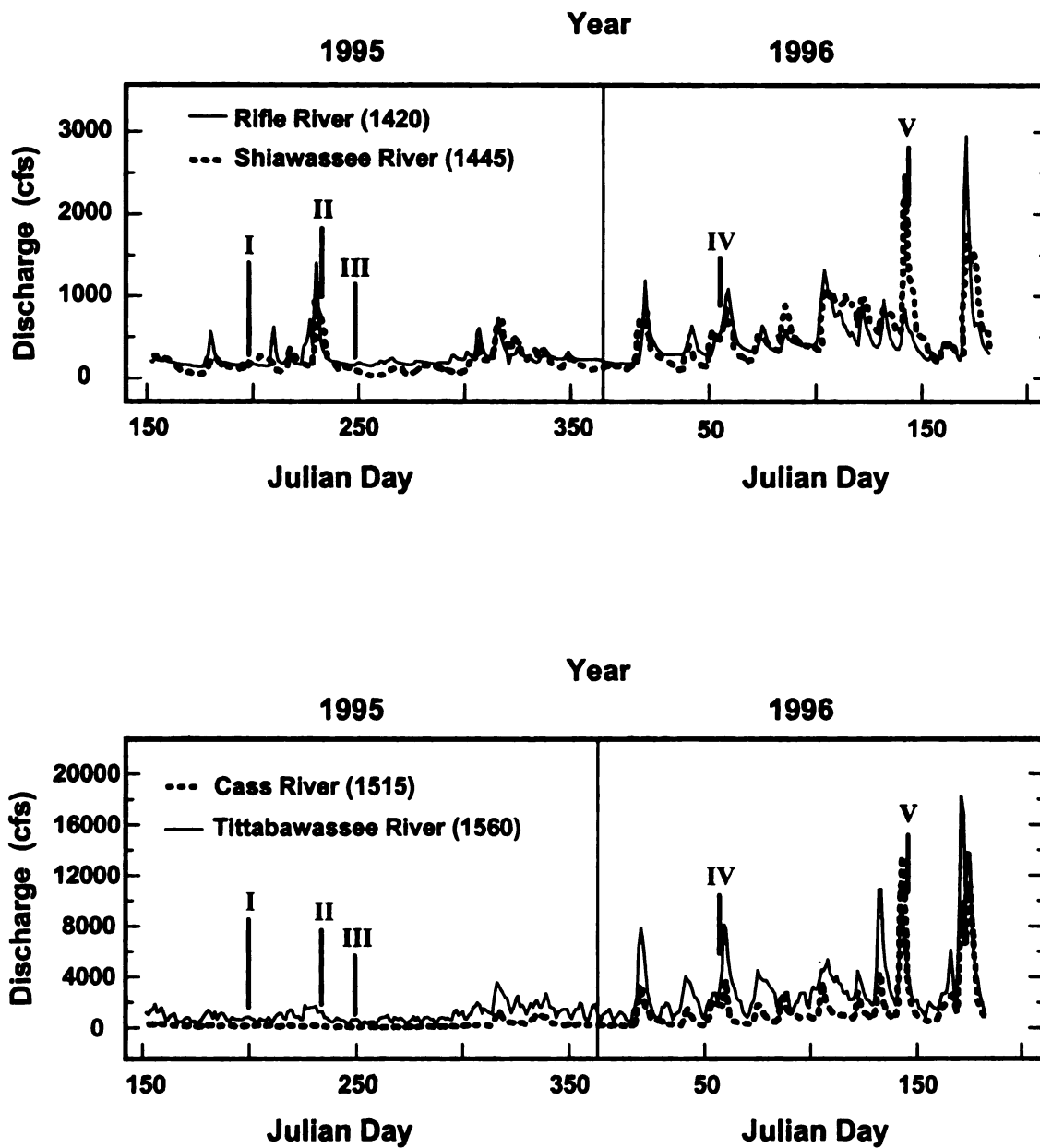


Figure 25. Hydrographs for four rivers in the Saginaw Bay watershed.
(Roman numerals correspond to sampling events.)

Water samples were collected using a clean polyethylene bucket; the bucket was typically deployed from a bridge crossing the stream (on the upstream side). The bucket was rinsed with water 2-3 times at the sampling site prior to sampling to minimize carryover from the previous station. Although point sources undoubtedly contribute to stream hydrochemistry within the SBW, care was taken to avoid point sources in the immediate sampling area in order to obtain a representative sample of stream water. Samples were transferred to acid-washed, distilled-deionized water (DDW) rinsed polyethylene bottles and stored on ice in coolers for transport back to the lab.

Samples were collected solely for major cations and anions and filtered back in the lab; filtration was generally completed within 72 hours after sample collection. Samples were filtered through Millex HA® 0.45 µm disposable filtration units. Samples for anions (chloride and bromide) and silica were filtered and stored unacidified. Samples for major cations (calcium, magnesium, sodium, and potassium) were filtered and then acidified to pH<2 with ultra-pure nitric acid.

Samples collected for geochemical modeling were processed immediately in the field. Temperature was recorded and the pH of the sample measured by pH electrode. The pH electrode was calibrated at each site; pH buffers were equilibrated at the river water temperature prior to calibration. Alkalinity was determined by potentiometric titration using a dilute sulfuric acid solution as the titrant. Aliquots of river water were filtered using Millex HA® 0.45 µm disposable filtration units. One aliquot was collected for anions (Cl, Br) and SiO₂ and stored unacidified. One aliquot was collected for sulfate

analysis and preserved with formaldehyde. Major cation samples were acidified to pH<2 with ultra-pure nitric acid.

Sample Analysis

Calcium, magnesium, and potassium were measured according to standard methods for flame atomic absorption spectrophotometry (flame-AAS). A lanthanum chloride spike was added to samples to control interferences for the calcium and magnesium analyses. Excess sodium was added to control ionization in the potassium analyses. Sodium was measured [on a separate aliquot] by flame atomic emission spectrophotometry; excess potassium was added to control ionization. Standards were prepared fresh daily. Analyzing an aliquot of National Institute of Standards and Technology (NIST) -certified Standard Reference Material (SRM #1643d – Trace Elements in Water) checked the accuracy of the calibration curve. Dissolved silica was measured colorimetrically by the molybdosilicate blue method. Sulfate was measured indirectly by precipitation with BaSO₄ (Gudramovics, 1981); the remaining barium in solution was measured by flame-AAS. Chloride and bromide were measured by ion selective electrode (ISE); an ionic strength adjustor (NaNO₃) was added to each sample aliquot prior to analysis to minimize variations in ionic strength among samples.

RESULTS

Chloride, Bromide, and Sodium

Chloride, bromide and sodium were the only analytes measured in samples collected during the RIV I sampling [the target analyte list was expanded in subsequent sampling events]. These three analytes are therefore the only parameters from which one can draw comparisons among all five sampling events. The summary statistics (e.g., minimum, maximum, mean and median concentrations) for each dataset are presented in Table 3. Within a single sampling event, all three analytes vary widely in concentration: minimum and maximum concentrations differ by one to two orders of magnitude. For example, chloride concentrations from RIV I range from a low of 1.4 mg/L (comparable to the chloride concentration in precipitation) to greater than 200 mg/L. Each dataset contains such a large spread in analyte concentrations that there do not appear to be significant differences among all five sampling events. This seems counterintuitive given that one would expect greater analyte concentrations during low-flow events, and lesser concentrations in high-flow events due to dilution from meteoric water. Previous studies of the SBW have therefore relied on median concentrations to assess temporal hydrochemical changes, owing to the variability within a given sampling event (MDNR, 1988; Richards et al., 1993). However, the median chloride concentration in the RIV V sampling (spring, high flow) is 33 mg/L, which is quite comparable to the median concentration in the summer low-flow events (37 mg/L for RIV I and 42 mg/L for RIV III).

Table 3. Summary Statistics (Cl, Br, Na) for River Sampling Events.

	RIV I	RIV II	RIV III	RIV IV	RIV V
	summer	summer	summer	winter	spring
	low flow	high flow	low flow	high flow	high flow
Cl (mg/L)					
n	156	182	195	217	193
min	1.4	1.8	1.2	2.2	1.7
max	261	689	911	284	255
mean	47	50	69	35	35
standard deviation	41	63	102	33	24.6
median	37	35	42	26.0	33
geometric mean	34	36	44	26.6	29.3
Br (mg/L)					
n	156	182	195	217	193
min	0.11	0.12	0.05	0.09	0.06
max	2.75	7.36	9.65	4.05	4.73
mean	0.42	0.50	0.61	0.41	0.34
standard deviation	0.38	0.70	1.05	0.40	0.38
median	0.31	0.36	0.34	0.31	0.30
geometric mean	0.34	0.38	0.38	0.33	0.28
Cl/Br (mg/L)					
n	156	182	195	217	193
min	13	14	20	17	28
max	640	198	195	168	225
mean	120	100	118	84	107
standard deviation	83	32	30	25	28
median	106	96	122	83	110
geometric mean	102	94	113	80	103
Na (mg/L)					
n	153	182	195	217	193
min	0.5	0.8	2.4	0.5	0.2
max	156	125	420	150	81
mean	18.9	20.1	30	14.2	13.1
standard deviation	19.5	17.1	40	17.8	10.5
median	13.0	15.1	19.2	8.0	9.7
geometric mean	13.6	15.5	19.7	8.6	10.3

Owing to the variability within a given dataset, drainage basins within the SBW were also evaluated individually. In Figure 26 are plotted the stream chemistry profiles for chloride in the Cass, Chippewa, Flint and Kawkawlin Rivers. Each profile begins with the sample collected furthest upstream, typically at the headwaters, and ends with the sample collected furthest downstream, just before the river terminated at Saginaw Bay (e.g., the Kawkawlin) or joined a larger river such as the Saginaw River (e.g., the Cass and Flint Rivers). Chloride concentrations typically increase downstream in response to anthropogenic pollution (e.g., Flintrop et al., 1996). This behavior is clearly demonstrated in the Flint River, and to a lesser extent in the remaining rivers. The headwaters of the Chippewa River had very high chloride concentrations during the RIV I sampling, but comparable chloride concentrations were not documented in the subsequent low-flow sampling event (RIV III). The Kawkawlin River exhibits the smallest downstream increase, which is to be expected given that there are no major urban centers adjacent to the Kawkawlin, as is the case with the other three rivers. Interestingly, there does not seem to be a significant change in chloride concentrations among the five different datasets, indicating that increased discharge rates did not significantly dilute solute inputs. In fact, the highest chloride concentrations in the Flint River were documented during the RIV IV (winter melt event), likely derived from road salting practices.

Whether these sampling events, compared to historical data, reflect an overall improvement in water quality within the SBW remains uncertain. The chloride concentrations measured in this study are significantly lower than those documented by

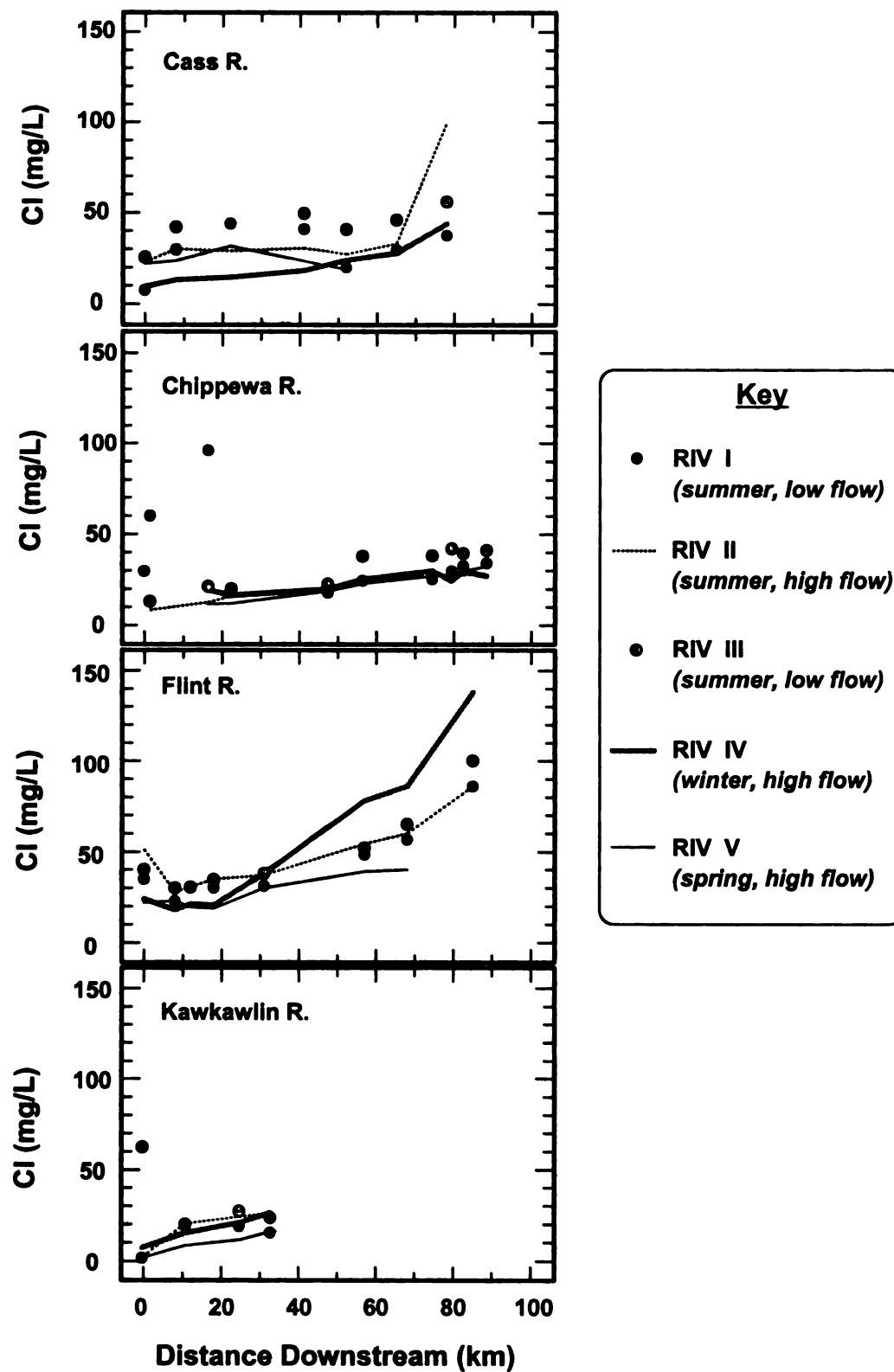


Figure 26. Temporal variations in dissolved chloride levels among the Cass, Chippewa, Flint and Kawkawlin rivers.

Tiffany and Winchester (1969), who repeatedly measured chloride concentrations in excess of 300 mg/L in the Pine River (compared to a maximum of 63 mg/L in this study) and in excess of 200 mg/L in the Saginaw River (compared to a maximum of 85 mg/L in this study). Dissolved chloride concentrations in the Saginaw River (this study) also appear to be lower than those reported by the Michigan Department of Natural Resources (1988). However, data from Blumer (1991) indicate that median chloride concentrations in the Saginaw River show no trend over the interval 1975-89. The median chloride concentrations for the SBW (this study) are comparable to the concentrations reported by Wood (1970). However, elevated chloride concentrations (>40 mg/L) during low-flow conditions are now found over a much larger area of the SBW than in the study by Wood (1970). Collectively, all these studies may indicate that “acute” chloride loading (e.g., possibly from anthropogenic/point sources) has decreased to the present, as a result of water quality regulations; however, diffuse or “chronic” chloride loading may be continuing to spread throughout the watershed, possibly in response to human expansion.

Major Cations

Major cation data for four sampling events (II, III, IV, and V) [calcium, magnesium, and potassium data are not available for RIV I samples] are plotted on the cation portion of a modified a Piper diagram (Figure 27). For ease of interpretation, only data points from the RIV V sampling event are actually plotted, the other three sampling events are represented by fields drawn to encompass the data points. Nearly all the samples from the RIV V event, and most of the samples from the other events plot within

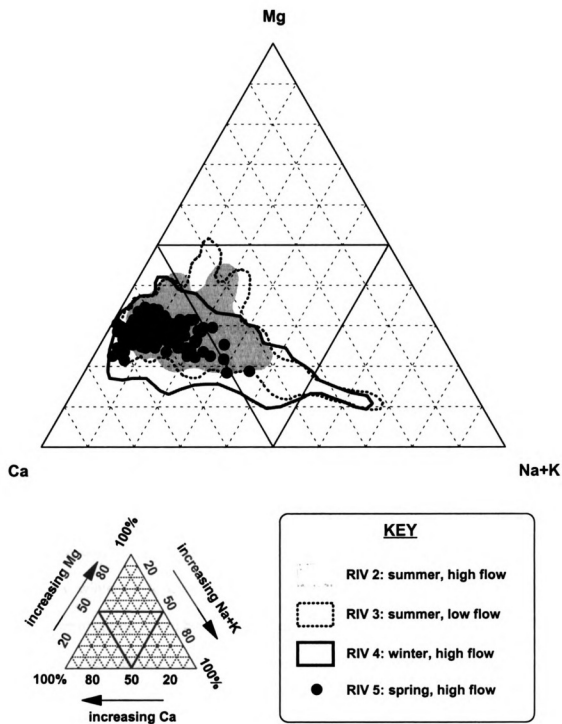


Figure 27. Ternary plot of major cation proportions among river samples.

the Ca-dominant field. These data likely indicate that cation inputs are dominated by carbonate mineral (calcite) dissolution from the glacial material present at the land surface (Phillips, 1988; Long et al., 1988). A few samples from the RIV III and RIV IV events plot within the Na+K field, and there is the appearance of a mixing trend between these and the Ca-dominant samples. The RIV IV samples, collected during a winter melt (high flow) event, likely reflect the influence of road salt (i.e., halite - NaCl) on water chemistry. The mixing trend present in the RIV III data set may reflect the influence of saline ground water from the glaciofluvial aquifer (see Chapter 1; Figure 9) on stream chemistry.

Downstream profiles of cation chemistry were also constructed for calcium and potassium. Whereas chloride showed a general trend of increasing concentrations downstream, calcium does not appear to exhibit such a trend. It is interesting to note that, with the exception of the Kawkawlin River, calcium concentrations are quite comparable between high-flow and low-flow events (Figure 28). Like calcium, potassium concentrations also do not show a distinct trend downstream (Figure 29). However, among the five events, the highest potassium concentrations were measured during RIV IV (high flow, winter), indicating significantly greater solute input during the winter than in the summer or spring. Such behavior has been observed in other studies (Foster, 1978; Flintrop et al., 1996) and may reflect increased flushing of potassium during the winter as a result of reduced biological assimilation and tilling practices.

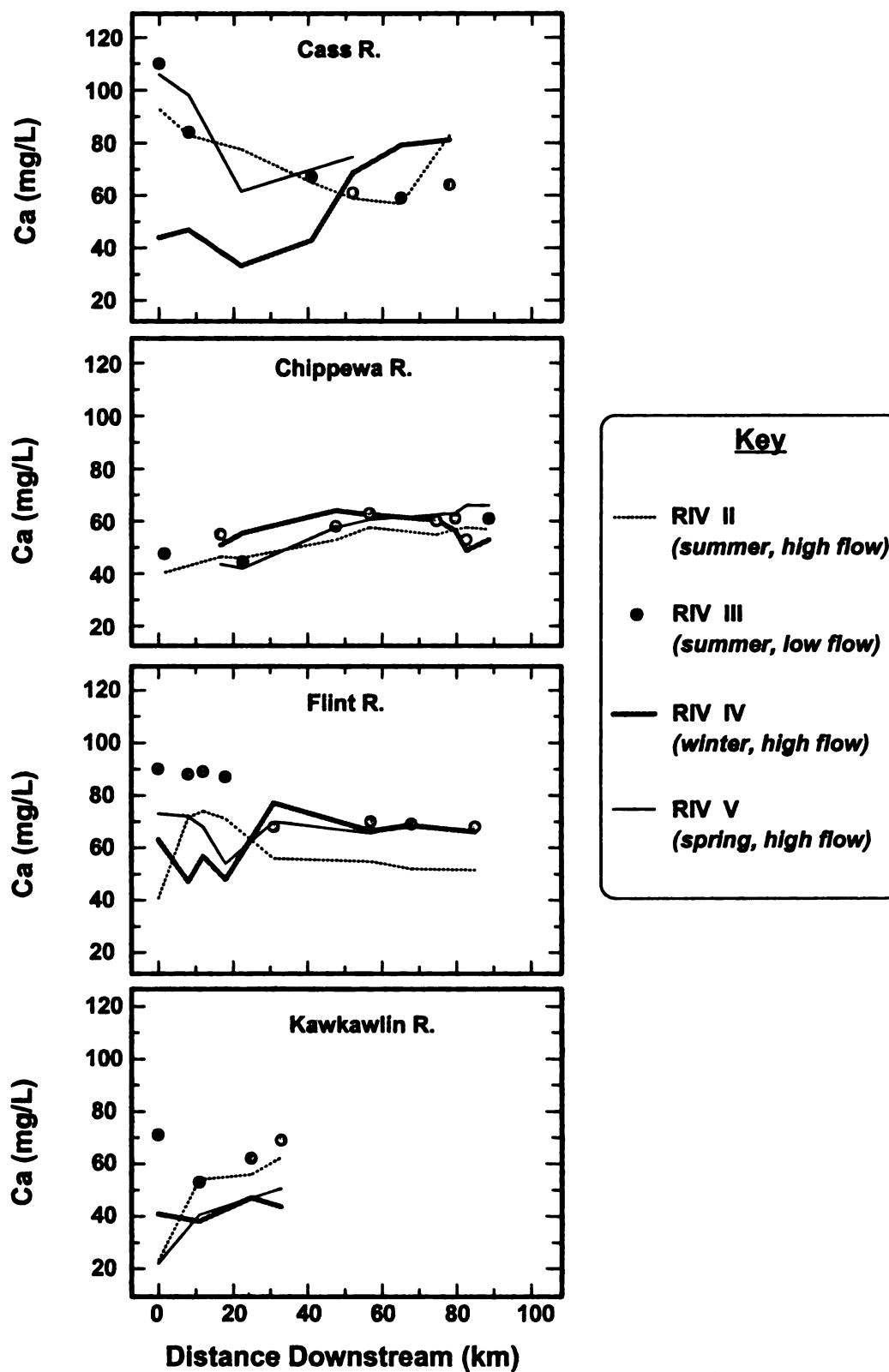


Figure 28. Temporal variations in dissolved calcium levels among the Cass, Chippewa, Flint and Kawkawlin rivers.

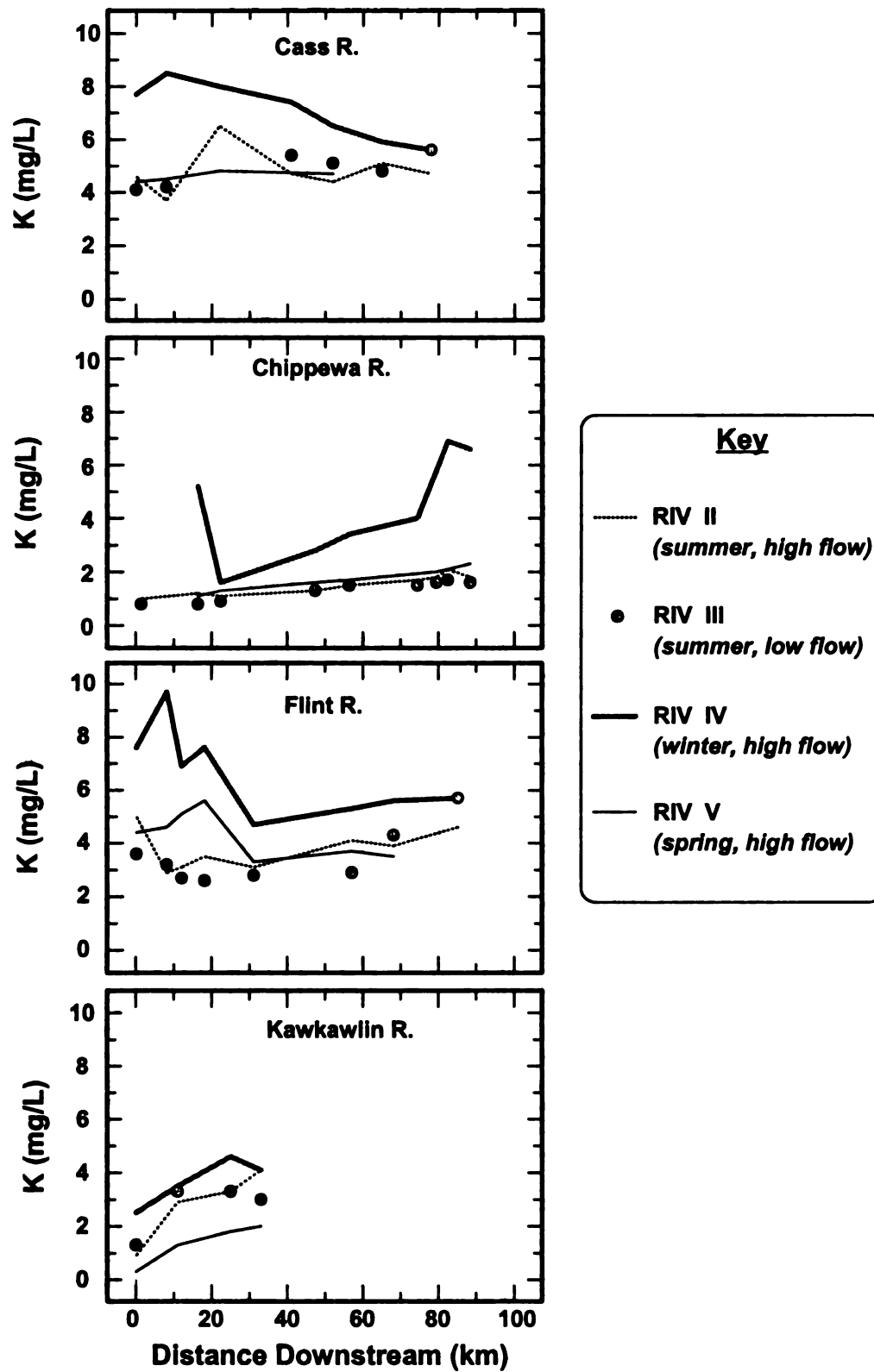


Figure 29. Temporal variations in dissolved potassium levels among the Cass, Chippewa, Flint and Kawkawlin rivers.

Temporal Variations in Water Quality

A number of communities in the SBW obtain their drinking water directly from Saginaw Bay (MDNR, 1988), thus the quality of water in Saginaw Bay is a concern. As the Saginaw River is a prominent source of solutes to Saginaw Bay (e.g., Richardson, 1974) and receives drainage from a majority of the SBW, the current status of water quality in the SBW was addressed. The analytes considered were chloride, sodium, bromide, and sulfate. Analyte concentrations in river samples from the SBW were compared to existing/proposed water quality criteria. Whereas criteria for chloride and sulfate have long been established, sodium has recently been added to the Environmental Protection Agency (EPA)'s Contaminant Candidate List (EPA, 1998). The currently proposed sodium criterion for drinking water is 20 mg/L, although there is some feeling that this value is too low and may cause undue hardship to water treatment facilities (EPA, 1998). High sodium concentrations have been linked to hypertension in schoolchildren (Mattson and Godfrey, 1994). Flury and Papritz (1993) recommend a quality criterion of 1 mg/L for bromide in the environment. Although many questions still exist regarding the bromide toxicology, bromide has shown endocrine-disrupting capabilities in freshwater organisms exposed to concentrations as low as 2 mg/L (Flury and Papritz, 1993).

The results of the water quality assessment are shown in Table 4. In the cases of chloride, sodium, and bromide, at least one site per sampling event exceeded the water quality criterion. This result is noteworthy, as it indicates that regardless of time of year

Table 4. Temporal Variations in Water Quality Within the Saginaw Bay Watershed.

RIV I	RIV II	RIV III	RIV IV	RIV V
summer	summer	summer	winter	spring
low flow	high flow	low flow	high flow	high flow

Chloride (Cl⁻)

Limit: 250 mg/L

Source: EPA Secondary Maximum Contaminant Level

sites exceeding criterion	1	3	9	1	1
% of total	0.6	1.6	4.6	0.5	0.5
max (mg/L)	261	689	911	284	255

Sodium (Na)

Limit: 20 mg/L

Source: EPA Contaminant Candidate List

sites exceeding criterion	42	66	94	42	38
% of total	27.5	36.3	48.2	19.4	19.7
max (mg/L)	156	125	420	150	81

Bromide (Br⁻)

Limit: 1 mg/L

Source: Flury and Papritz (1993)

sites exceeding criterion	12	12	18	6	2
% of total	7.7	6.6	9.2	2.8	1.0
max (mg/L)	2.75	7.36	9.65	4.05	4.73

Sulfate (SO₄)

Limit: 250 mg/L

Source: EPA Secondary Maximum Contaminant Level

sites exceeding criterion	x	x	0	x	x
% of total	x	x	0	x	x
max (mg/L)	x	x	178	x	x

or hydrologic regime (i.e., high flow versus low flow) there is at least some portion of runoff within the Saginaw Bay watershed not in compliance with proposed quality criteria. However, a greater percentage of sites exceed criteria in the summer than in the spring or winter. Nearly 50% of the sites in the SBW exceeded the EPA criterion for sodium during the RIV III sampling event. For chloride and bromide, the percentage of samples not in compliance is generally low (< 5% for chloride, <10% for bromide). No samples exceeded the sulfate criterion, although this assessment is based on a significantly smaller population of samples (n = 38).

DISCUSSION

Solute Sources - Geochemical Modeling

The role of mineral-water interactions in regulating hydrochemistry in the SBW was evaluated using geochemical modeling. Samples collected specifically for modeling (38 samples) during the RIV III sampling were modeled using the WATEQ4F code (Ball et al., 1991). Only samples with less than a 15% charge imbalance were considered in the evaluation of mineral-water interactions. Model output consists of saturation indices (SIs) calculated for each mineral considered (Chapter 1; Equation 6). A mineral in equilibrium with the aqueous phase (i.e., 100 per cent saturation) would have a SI value of zero. A SI value greater than zero indicates that the aqueous phase is supersaturated with respect to a given mineral, and precipitation of that mineral is thermodynamically favorable. An SI value less than zero indicates that the water sample is undersaturated

with respect to a given mineral phase, and dissolution of that mineral is thermodynamically favorable.

A frequency histogram for carbonate mineral SIs is given in Figure 30. In addition to river samples, three samples were collected directly from Saginaw Bay (near the shore) to compare river and bay chemistry. The black bars in the figure represent the bay samples. River samples are generally at equilibrium or supersaturated with respect to calcite and aragonite. Dolomite SIs are more variable, ranging from undersaturated to highly supersaturated. That a number of river samples are supersaturated with respect to carbonates might explain why calcium concentrations do not vary as much as expected between low-flow and high-flow conditions as expected. Although low-flow events are generally fed by water having greater contact time with minerals and thus, a better opportunity for mineral dissolution, calcium concentrations in low-flow events might be constrained by calcite solubility. Figure 31 shows frequency histograms for evaporite mineral SIs. All river and bay samples are highly undersaturated with respect to gypsum and halite. River samples are generally at equilibrium with respect to quartz, and undersaturated with respect to amorphous silica (Figure 32). The bay samples are highly undersaturated with respect to both quartz and amorphous silica. The disparity between bay and river samples likely reflects diatom productivity within Saginaw Bay (Robbins, 1986; Ullman and Aller, 1989).

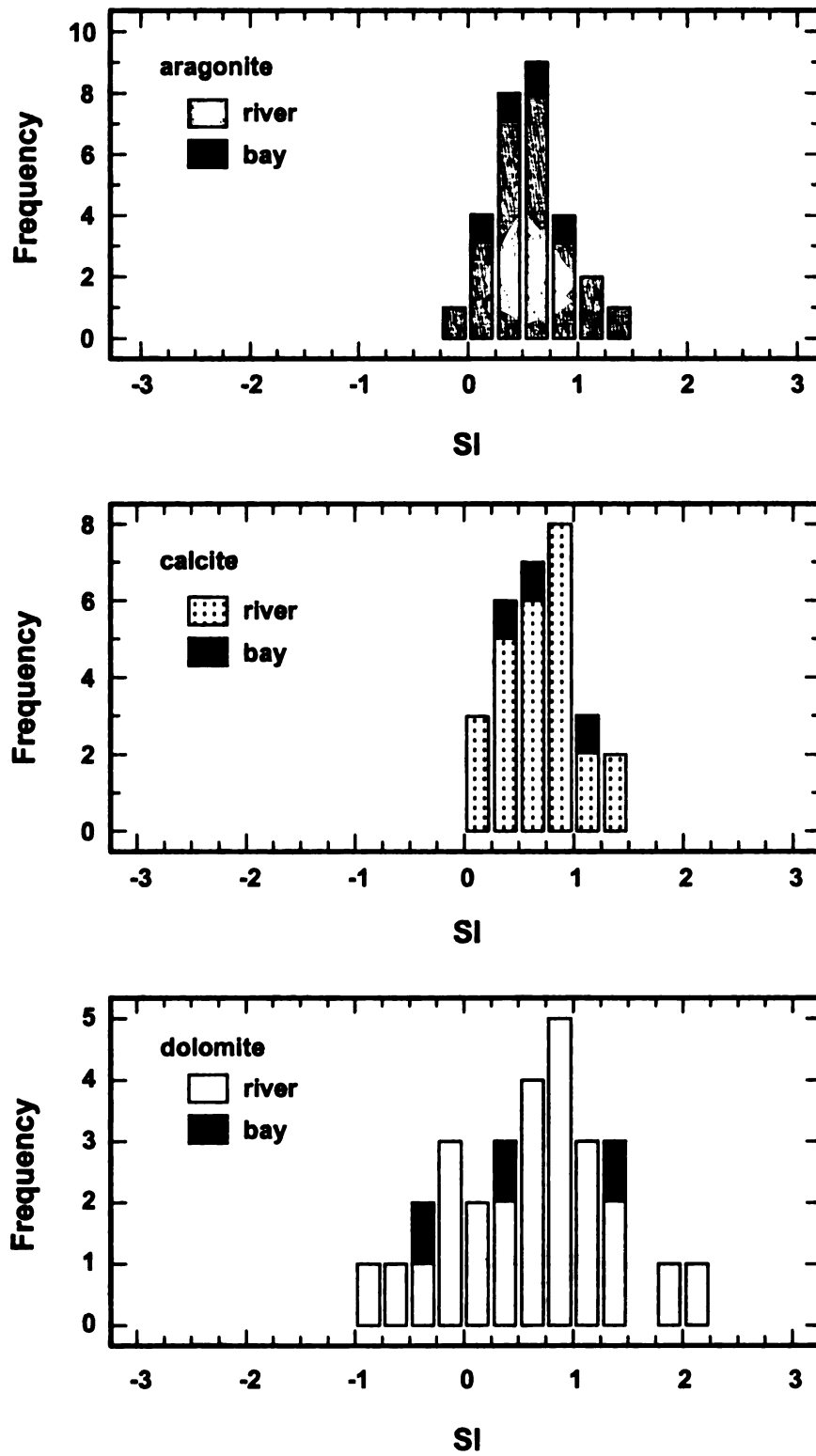


Figure 30. Carbonate mineral saturation indices for select RIV III samples.

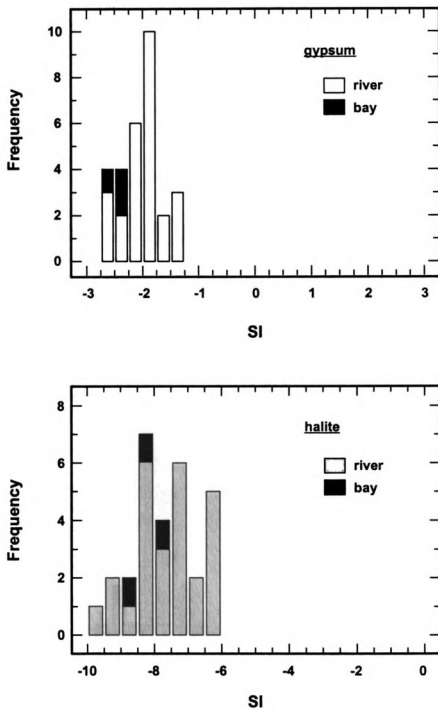


Figure 31. Evaporite mineral saturation indices for select RIV III samples.

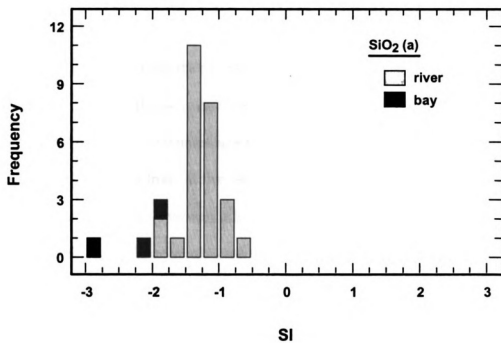
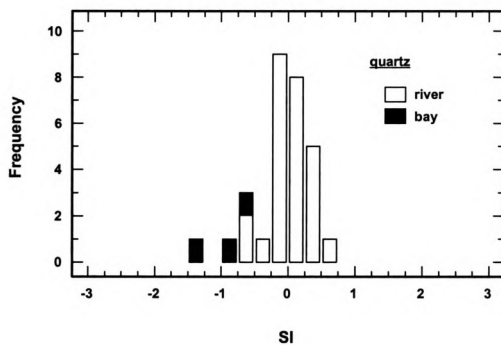


Figure 32. Quartz and silica saturation indices for select RIV III samples.

Solute Sources – Chloride and Bromide Systematics

The primary goal of this study is to ascertain whether or not saline ground water (derived from Michigan basin brines) is contributing solutes to the SBW. Although there are a number of anthropogenic chloride sources (e.g., road salt, septic systems) which confound such assessment, Cl:Br ratios may be useful in delineating chloride sources. Cl:Br ratios have largely been used to determine origins of formation brines (evaporated seawater vs. halite dissolution) (e.g., Stueber and Walter, 1994; Kesler et al., 1995; Chi and Savard, 1997), but have also been successful in delineating solute sources in watersheds (Herczeg et al., 1993). Waters affected by halite dissolution will generally have Cl:Br ratios exceeding 3000 (Wilson and Long, 1985), whereas water influenced by saline ground water in the Michigan basin will generally have a Cl:Br ratio in the range of 400 to 600 (Wahrer, 1993). Figure 33 is a scatterplot of the relationship between chloride and Cl:Br ratios among the samples from all five watershed sampling events. For ease of interpretation, the same data are plotted on both linear and logarithmic axes. A few samples from the RIV I dataset appear to plot within the range of formation brine, but the majority of samples from all five events are well short of this range (Cl:Br values are generally less than 200). That only a few samples appear to have Cl:Br ratios consistent with formation brine would apparently indicate that interaction between surface water and saline ground water in the SBW is limited. However, there are a number of anthropogenic solute sources in the SBW (e.g., urban runoff, agricultural return water) which are known to have similarly low Cl:Br ratios (Vengosh and Pankratov, 1998). In fact, agricultural return waters have been shown to account for as

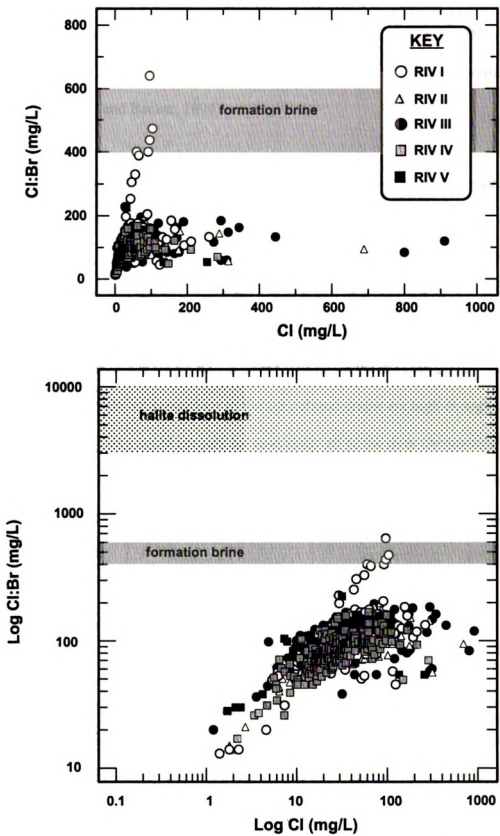


Figure 33. Cl-Cl:Br relationships among the five watershed sampling events.

much as 68% of the total bromide flux in a watershed, overwhelming inputs from atmospheric deposition and industrial discharges (Noling and Becker, 1994). The bromide in these return waters is largely derived from applications of methyl bromide, a soil fumigant (Noling and Becker, 1994).

To further evaluate the potential influence of agricultural return water on stream chemistry, the datasets from two sampling events (one high-flow and one low-flow) were separated into river and agricultural drain samples, and plotted in Figure 34. In both events, the Cl:Br ratio of water in agricultural drains is less than 200, which is comparable to the Cl:Br ratios encountered in nearly all the river samples (except for the small group of samples in the RIV I dataset with Cl:Br ratios greater than 200). Furthermore, the chloride concentrations in the agricultural drains are high enough that simple dilution and mixing could account for essentially all of the river chemistries observed. These data may indicate that regional water chemistry (chloride and bromide) may be dominated by solute inputs to agricultural drains, except in areas of heavy urban influence.

The chemistry of the small group of samples in the RIV I dataset with Cl:Br ratios exceeding 200 appears to be influenced by formation brine. This scenario was further evaluated by simulating mixing between a saline ground water and dilute endmembers. These river samples are generally located in Isabella County; a sample of saline ground water (2100 mg/L chloride, Cl:Br = 583 [Dannemiller and Baltusis, 1990] was used as an endmember. The mean precipitation (n=8 [includes both rain and snow samples];

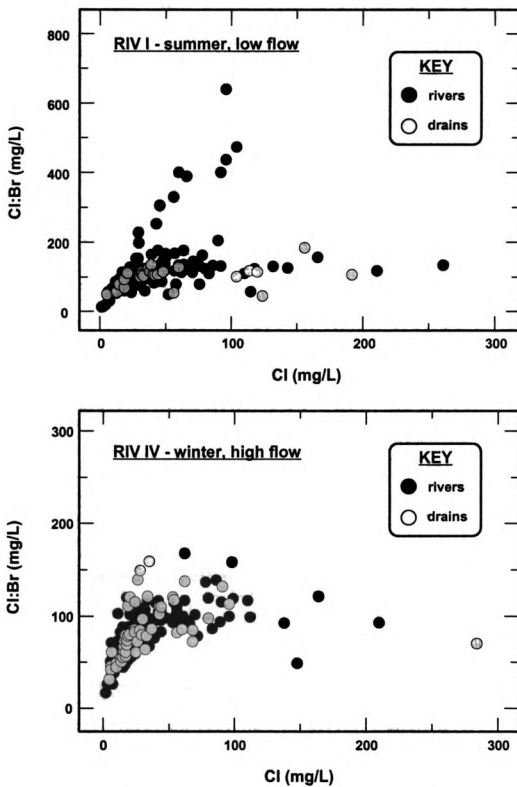


Figure 34. Cl - Cl:Br relationships among samples from rivers and agricultural drains.

mean = 0.8 mg/L chloride, Cl:Br = 67.5) for the SBW and a dilute river water (10 mg/L chloride; Cl:Br = 75) were mixed with the saline ground water. The results from the mixing simulations and the data from the RIV I sampling event are plotted in Figure 35. The two mixing curves generally envelope the high Cl:Br river samples, indicating that these particular samples may be affected by inputs of saline ground water with solutes derived from formation brine.

Solute Sources – River Cores

Of the river samples described in Table 4, one site (9-2) repeatedly exceeded the water quality criterion for chloride and bromide, and likely resulted in the elevated chloride concentrations found downstream in the Salt River. Although the Cl:Br ratio in samples from this site (<100) did not appear to indicate the influence of saline ground water from the glaciofluvial aquifer, a higher resolution sampling event was conducted in the vicinity of this site to identify the solute sources. The locations of stations sampled during this event (7-26-96) are depicted in Figure 36. Two sediment cores were collected, and numerous water column samples were also taken. The results of the chemical analyses (Cl, Cl:Br) for the water column samples are indicated on the figure.

Samples from the McDonald Drain all have very high chloride concentrations, but low Cl:Br ratios. Samples collected to the south of 9-2 generally had much lower chloride concentrations. Profiles of porewater chemistry from the two sediment cores are plotted in Figure 37. Porewater chloride concentrations in core SNJ increase with depth

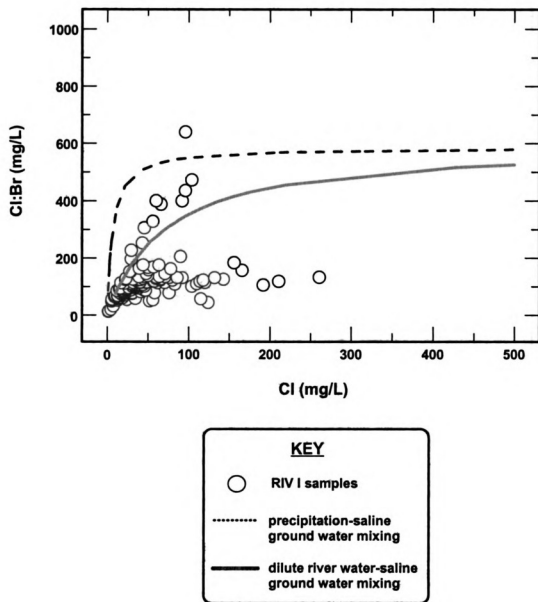


Figure 35. Cl - Cl:Br mixing curves for saline ground water and dilute endmembers.

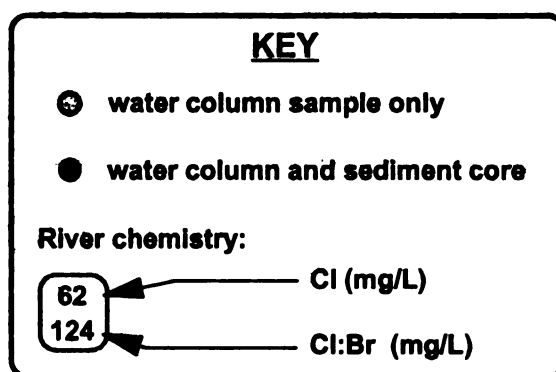
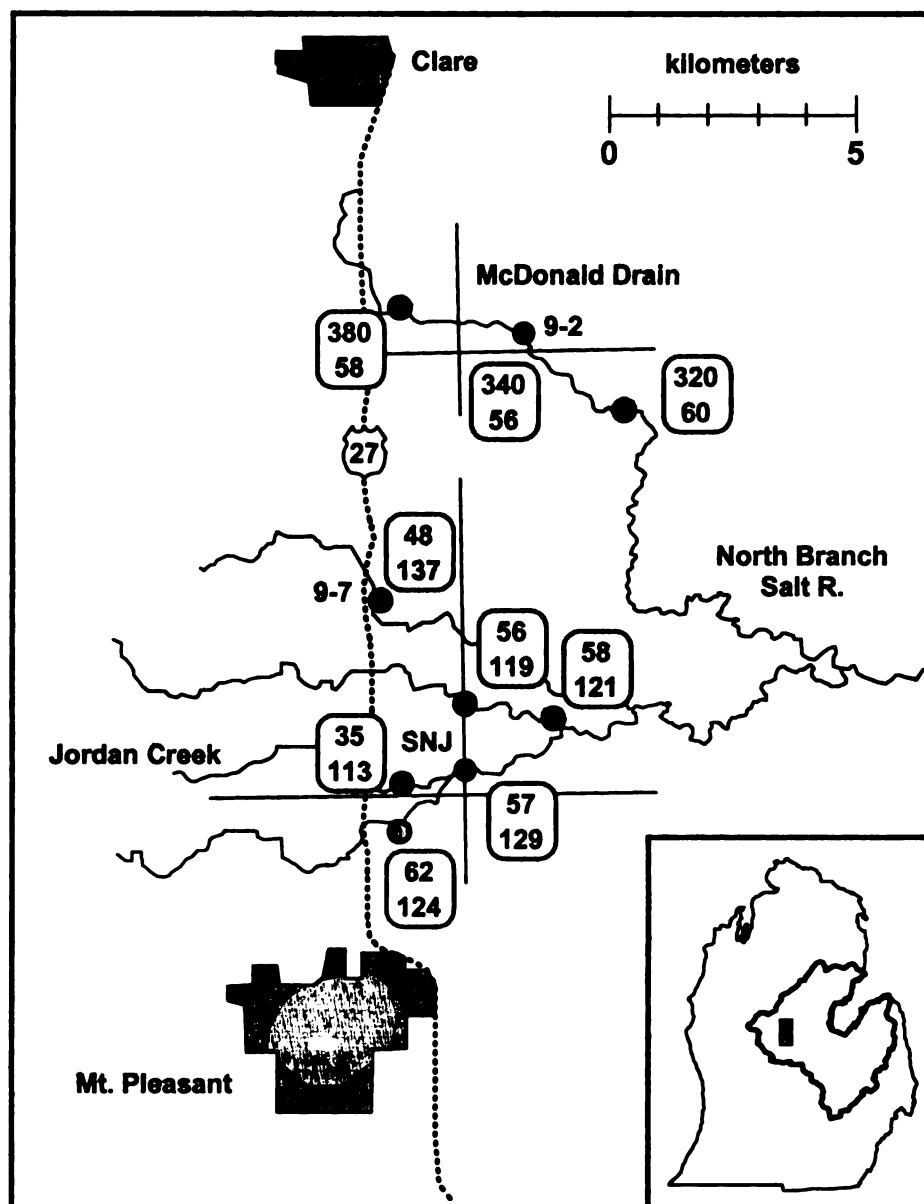


Figure 36. Map of 7-27-96 sampling sites. (Inset denotes study area location.)

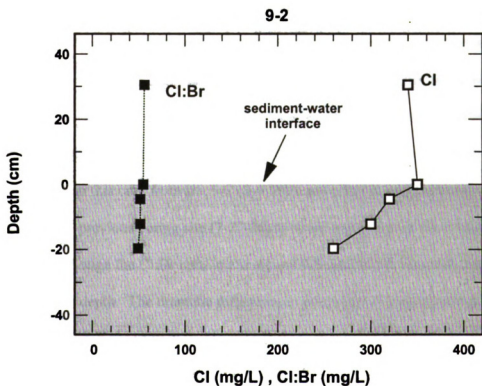
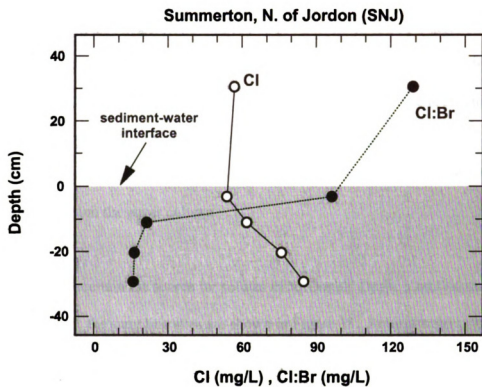


Figure 37. Porewater chemistry from cores collected on 7-27-96.

correspond, indicating a chloride source at depth. One might interpret this to indicate the influence of saline groundwater, but the Cl:Br ratios are extremely low compared to what has been documented in ground water from the Glaciofluvial aquifer (Wahrer, 1993). Perhaps release of bromide associated with organic matter degradation has obscured the Cl:Br ratios in this core (Gerritse and George, 1988). The sediment core from 9-2 has decreasing porewater chloride concentrations with depth, indicating that the riverbed is a sink for chloride from the water column.

To better ascertain the source for solutes in McDonald Drain, a second sampling trip was conducted; the sampling sites are shown in Figure 38. Several water column samples upstream of site 9-2 had elevated chloride concentrations; one site exceeded 900 mg/L chloride. Tributaries to the drain contained significantly more dilute waters; chloride concentrations ranged between 8.6 and 35 mg/L. Several sediment cores were collected in this study and the porewater chemistry profiles from these cores are plotted in Figure 39. Cores GLEM, CSF and SNC do not appear to have significant chloride concentration gradients with depth. Cores SLWI and 9-2 show increasing chloride concentrations with depth. In fact, core 9-2 shows a very strong chloride gradient. It should be noted that this core from site 9-2 (8-4-96) was collected approximately 50 m upstream from the previous coring site (7-27-96) to avoid any potential disturbances to the river bed. Although the Cl:Br ratio in the second 9-2 core is still relatively low, it does increase with depth. The dramatic difference in porewater-chloride profiles between the two cores collected near site 9-2 may indicate fracture-controlled transport of saline ground water to the rivers.

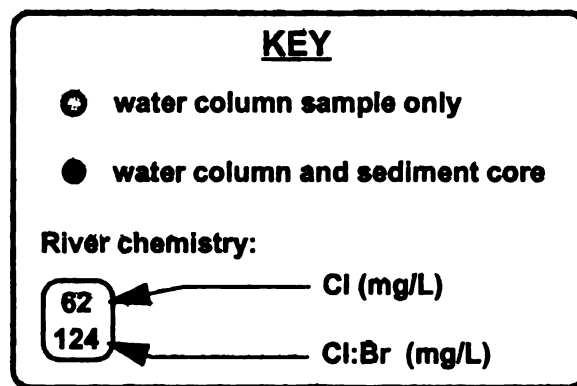
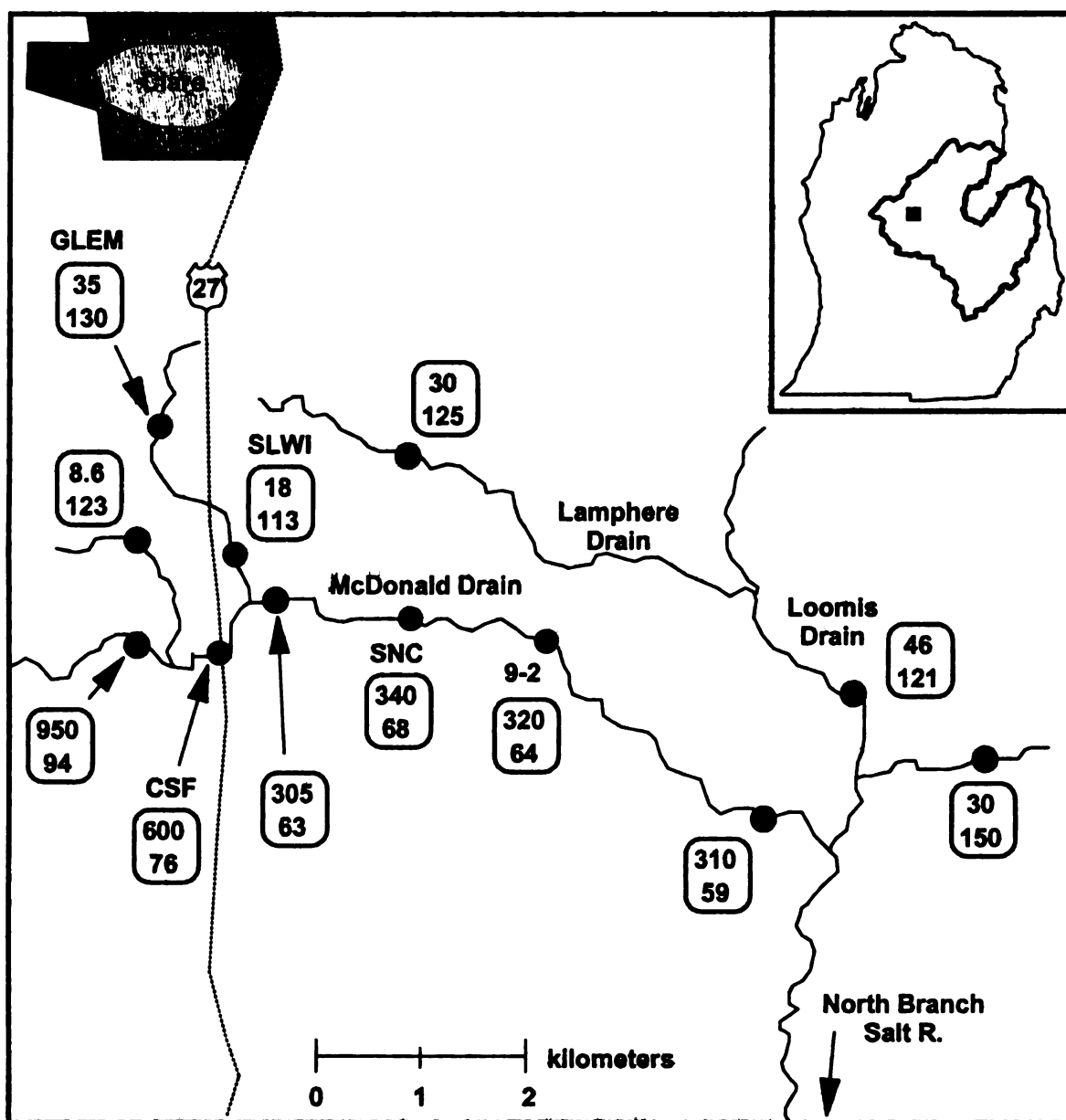


Figure 38. Map of 8-4-96 sampling sites. (Inset denotes study area location.)

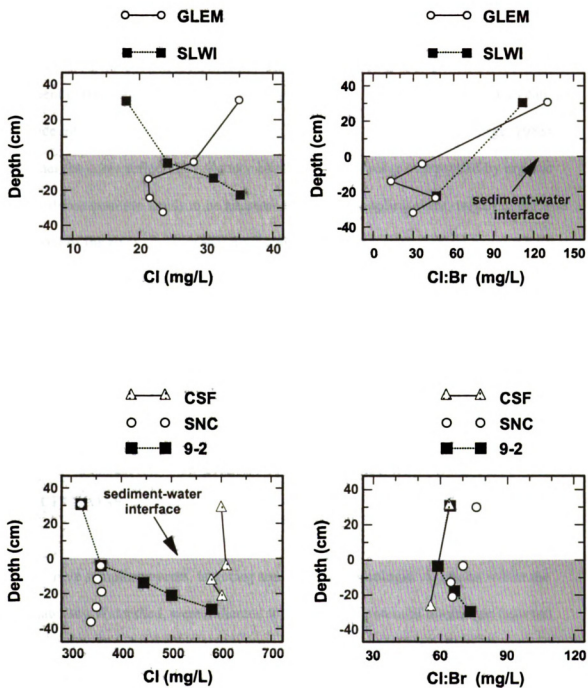


Figure 39. Porewater chemistry from cores collected on 8-4-96.

A number of the sediment cores collected on these two trips indicate that high-chloride sources might be present beneath the river bed, although the low Cl:Br ratios further confound rather than delineate the source for solutes. One possible explanation might be that additional bromide is released from organic matter. A number of the sediment cores contain organic-rich horizons, and organic matter decomposition can produce interstitial waters with Cl:Br ratios as low as 10 (Gerritse and George, 1988). Whether the cores reflect the influence of saline ground water overprinted by organic matter decomposition needs to be addressed. A third sampling event, targeting the area upstream of the river site with 950 mg/L chloride, yielded several creek samples with chloride concentrations exceeding 1000 mg/L. These samples were collected from an area adjacent to an oil field. Oil field brines from the Michigan basin typically have Cl:Br ratios significantly less than 100 (Wilson and Long, 1993; Whittemore, 1995). Thus, in addition to organic matter degradation (Gerritse and George, 1988), one might also attribute the low Cl:Br ratios observed to the influence of oil field brines.

CONCLUSIONS

Five sampling events, targeting seasonal and hydrologic variations within the Saginaw Bay Watershed, were collected to evaluate the potential interaction between saline ground water and surface water. The watershed as a whole did not exhibit strong temporal fluctuations in chloride and bromide concentrations. Locally, strong fluctuations in these solutes were documented, largely attributable to anthropogenic inputs from urban centers. A few sites within the Saginaw Bay Watershed contained

solute levels exceeding water quality guidelines, even during high-flow events.

Carbonate minerals (e.g., calcite) may play a role in regulating stream chemistry. Cl:Br ratios generally indicate that the influence of saline ground water on surface water chemistry is rather limited in extent; return water from agricultural drains may play a large role in regulating Cl:Br ratios in the Saginaw Bay Watershed. One area with persistent high chloride concentrations in stream samples was further investigated. A number of sediment cores collected from this site and the surrounding area contain porewater-chloride gradients that indicate a chloride source beneath the riverbed. Cl:Br ratios in porewater samples from these cores do not necessarily indicate the influence of saline ground water, but may be confounded by additional inputs of bromide from natural sources (e.g., organic matter decomposition).

CHAPTER III.

Evaluation of Trace Metal Loading and Partitioning in Saginaw Bay

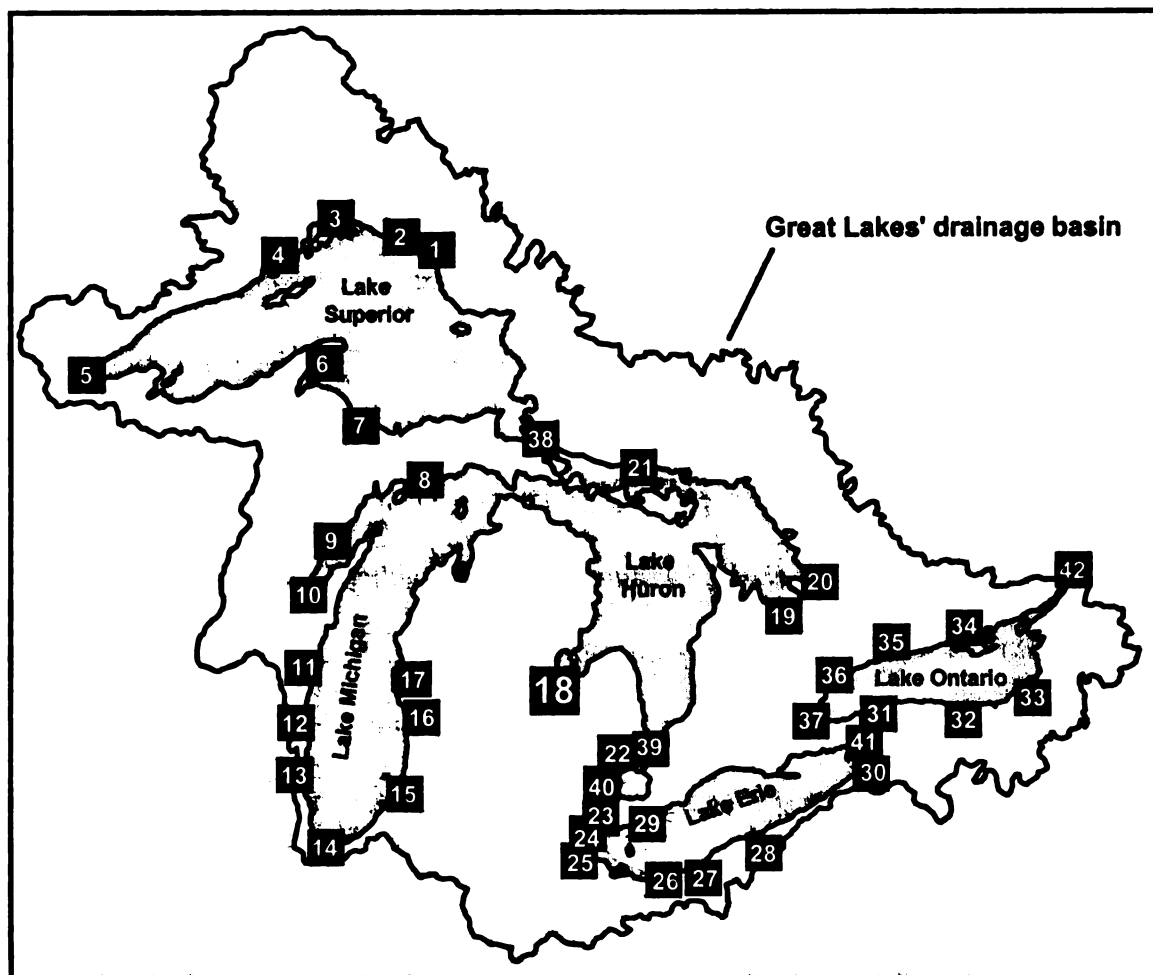
(Lake Huron) Sediments:

Implications for Cycling and Postdepositional Remobilization

INTRODUCTION

Humans have significantly affected trace element cycles by releasing large amounts of metals to the environment through their daily activities (Nriagu and Pacyna, 1988). For example, the Great Lakes' region, which is home to a substantial portion of Canada's and the United States' populace [30% and 20%, respectively; Hartig and Thomas (1988)], has been subjected to considerable, anthropogenic loads of such highly toxic metals as cadmium (e.g., Heft, 1993), arsenic, lead (e.g., Edgington and Robbins, 1976), and mercury (e.g., Sitarz, 1996). As population and industrial expansion has continued, the public has historically held the perception that the Great Lakes were so vast as to have an essentially infinite capacity to absorb such anthropogenic inputs (Thomas and Hartig, 1987). However, research over the past three decades has shown that the Great Lakes are capable of absorbing only so much, and that this finite "loading capacity" has already been exceeded for several metals in Lakes Erie, Michigan, and Ontario (Nriagu, 1986). In fact, trace metals such as copper, chromium, and zinc, which are beneficial to organisms at low concentrations, have been loaded to the Great Lakes to such a degree that some portions of the Great Lakes' ecosystem are experiencing deleterious effects (Ellenburger et al., 1994).

In order to focus remediation efforts on the most heavily contaminated sites, the International Joint Commission (IJC), a binational organization representing the governments of Canada and the United States, has identified 42 areas of concern (AOCs) throughout the Great Lakes' region (Figure 40). These AOCs are sites where water



LAKE SUPERIOR

- 1 Peninsula Harbor
- 2 Jackfish Bay
- 3 Nipigon Bay
- 4 Thunder Bay
- 5 St. Louis R.
- 6 Torch Lake
- 7 Deer Lake

LAKE ERIE

- 22 Clinton R.
- 23 Rouge R.
- 24 Raisin R.
- 25 Maumee R.
- 26 Black R.
- 27 Cuyahoga R.
- 28 Ashtabula R.
- 29 Wheatley Harbour

LAKE MICHIGAN

- 8 Manistique R.
- 9 Menominee R.
- 10 Fox R. and Southern Green Bay
- 11 Sheboygan
- 12 Milwaukee Estuary
- 13 Waukegan Harbor
- 14 Grand Calumet R. and Indiana Harbor Ship Canal
- 15 Kalamazoo R.
- 16 Muskegon Lake
- 17 White Lake

LAKE ONTARIO

- 30 Buffalo R.
- 31 Eighteen mile Creek
- 32 Rochester Embayment
- 33 Oswego R.
- 34 Bay of Quinte
- 35 Port Hope
- 36 Toronto Waterfront
- 37 Hamilton Harbour

LAKE HURON

18 Saginaw River/ Saginaw Bay

- 19 Collingwood Harbor
- 20 Penetang Bay to Sturgeon Bay
- 21 Spanish R. Mouth

CONNECTING CHANNELS

- 38 St. Marys R.
- 39 St. Clair R.
- 40 Detroit R.
- 41 Niagara R.
- 42 St. Lawrence R.

Figure 40. Map of AOCs in the Great Lakes' region (*modified from IJC, 1987*).

quality has been significantly degraded to the point that it is no longer suitable for its originally designated use (e.g., drinking water, recreation, fisheries), or where the health of aquatic life has been compromised (Hartig and Thomas, 1988). The quality of benthic sediments is a major consideration in guiding remediation efforts because benthic sediments are recognized as an important component of the aquatic ecosystem (Park and Jaffe, 1996). As such, sediment quality can be a vital indicator of the overall health and quality of water and biota.

Recent studies of benthic sediment chemistry have documented that metal loadings to the Great Lakes have decreased over the past several years (e.g., Heft, 1993; Sitarz, 1996; Kolak et al., 1998), apparently implying that environmental quality within the Great Lakes' region is improving. Although an important sink for trace metals, benthic sediments are subjected to a suite of postdepositional processes associated with early diagenesis (e.g., bioturbation, mineral dissolution, changes in redox state). These processes act in concert to effect changes in particle surfaces or in metal speciation that can subsequently remobilize surface-bound metals from sediments, facilitating their release to the overlying water column (Shaw et al., 1990). Thus, despite recent decreases in metal loadings, the Great Lakes remain at risk of recontamination from sediment-associated metals (Hartig and Thomas, 1988).

The Saginaw Bay/Saginaw River system has been designated as an AOC (see #18; Figure 40), due in large part to the contaminant loads that the system has received from nearby urban and industrial centers. Cadmium, copper and zinc are among the

metals of concern in water and sediments from the Saginaw Bay/River system (Hartig and Thomas, 1988). The large burden of metals contained in the benthic sediments of Saginaw Bay might be toxic to benthic organisms and could potentially be remobilized by a number of processes, including early diagenesis and tidal/storm-related sediment resuspension. Furthermore, human activities such as dredging, although necessary to maintain viable waterways, can effect the release of sediment-bound metals to the Saginaw Bay water column. The Saginaw Bay navigation channel is among the most heavily dredged locations in the Great Lakes (MDNR, 1988), and will require such maintenance in the future, thus posing a continual threat to the health of aquatic organisms.

Although most of the AOCs within the Great Lakes' region must contend with these factors, the Saginaw Bay system is further complicated, perhaps uniquely so, by the potential influence of regional, saline ground-water discharge on trace metal cycling. Porewater-chloride concentrations exceeding 600 mg/L less than two meters below the sediment-water interface have recently been documented in Saginaw Bay (Kolak et al., 1999). These high chloride concentrations derive from a source at depth and appear to be related to a phenomenon that has salinized water in a number of wells from the area surrounding Saginaw Bay. This saline groundwater could be a source of metals to Saginaw Bay, as trace-metal solubility is generally greater in saline than in fresh water, due to the formation of chloro-metal complexes (e.g., Long and Angino, 1977; Runde et al., 1999). Drimmie et al. (1992) have documented elevated concentrations of metals in Lake Ontario sediments that have been similarly affected by saline water encroachment.

Saline groundwater discharge could also remobilize metals from sediments by liberating metals from exchange sites or complexing metals [released to solution by diagenetic processes], thereby giving rise to a flux of trace metals to the Saginaw Bay water column. Thus, the chemistry of and factors controlling trace metal distributions within benthic sediments must be understood in order to more fully assess the potential for trace metal remobilization from Saginaw Bay sediments.

Robbins (1986) conducted the first extensive study of trace-metal distributions in Saginaw Bay (Figure 41A). The study evaluated spatial variations in trace metal concentrations [and compare these concentrations to the Great Lakes], used sediment chronologies to determine metal-loading and sediment-mixing rates, and made a preliminary assessment of the factors controlling the distribution of trace metals within Saginaw Bay sediments. Additionally, porewater samples were collected to determine benthic fluxes for nutrients, although none were collected to study trace metal cycling. Robbins (1986) documented the presence of an extensive mud deposit, oriented approximately coincident with bathymetric contours, that generally contained the greatest concentrations of trace metals. Within this deposit, zinc and copper were most highly correlated to the distribution of iron in sediments. Cadmium was best correlated to calcium and magnesium distributions (i.e., carbonates) (Figure 41B&C). In general, all trace elements were present in lower concentrations than in open lake sediments, partially due to “dilution” by coarser sediments (e.g., silts).

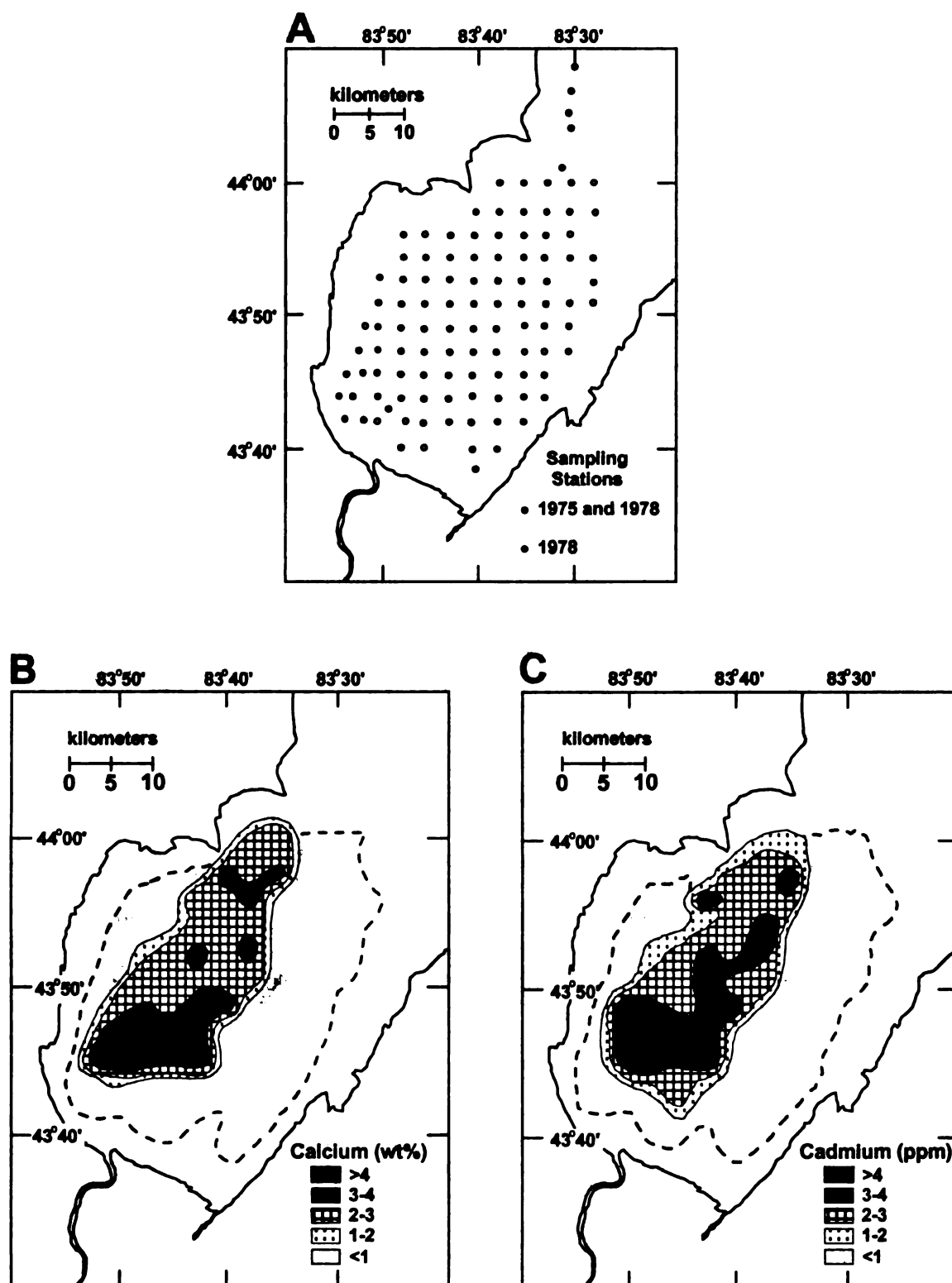


Figure 41. Map of Saginaw Bay showing (A) sediment sampling sites from Robbins' (1986) study, (B) spatial distribution of calcium in surface sediments and (C) spatial distribution of cadmium in surface sediments (*modified from Robbins, 1986*).

The findings of the Robbins' (1986) study relied on total sediment-metal concentrations, which although useful in providing insight into loading histories, are not necessarily good indicators of the risk of exposure to biota. Depending on the physicochemical conditions present in a given environment, the amount of metal available to organisms may range from 0-100% of the total sediment-metal concentration (Forstner, 1993). Robbins (1986) recognized this limitation, stating that the relatively low concentrations in the Saginaw Bay sediments did not necessarily imply a reduced potential for the transfer of elements up the food chain. Studying metal partitioning within sediments is more useful than total metal concentrations in delineating diagenetic processes and evaluating the potential for remobilization of metals (McKee et al., 1989a). For example, Robbins and Callender (1975) found that profiles of total manganese were misleading, and that the high surficial manganese concentrations in Lake Michigan sediments were the result of early diagenetic processes rather than anthropogenic pollution. Only by identifying and quantifying the various forms of the metal present in the sediment, the mechanisms affecting metal availability, and the influence of physicochemical conditions on the partitioning of metals between water and sediment can one attain an understanding of the ultimate fate of metals in sediments (Kersten and Forstner, 1987).

In order to assess the current state of environmental quality in Saginaw Bay the objectives of this study were to: 1) evaluate trace metal concentrations and temporal trends in metal loading to Saginaw Bay sediments and compare these to previously documented results; 2) investigate metal partitioning in sediments to understand the

bioavailability of the associated metals; 3) estimate benthic fluxes of metals; 4) use geochemical modeling to evaluate major processes controlling porewater chemistry; and, 5) evaluate the potential for enhanced metal remobilization from sediments as a result of saline water encroachment.

METHODS

Sediment collection

In the summer of 1994, sediment box cores were collected from Saginaw Bay during a sampling cruise aboard the *R/V Laurentian*. The box core deployed in this cruise measured 70 x 40 x 30 cm. Following retrieval, the box coring device was inspected on ship to ensure that it contained relatively undisturbed sediment. A sediment box core was considered undisturbed if the overlying water was free of suspended matter and if the sediment surface was level. After inspection, polycarbonate core liners (7 cm i.d.) were inserted into the undisturbed box core to collect subsamples for porewater and sediment analyses. The liners were inserted under vacuum to avoid sediment compaction and towards the center of the box core to avoid any disturbed sediment along the edges of the box core. Subcores were immediately sealed with endcaps to avoid contamination; the endcaps were not removed until the subcores could be sectioned.

The locations of the box coring stations are depicted in Figure 42. Most of the sampling stations targeted the extensive mud deposit previously documented by Robbins

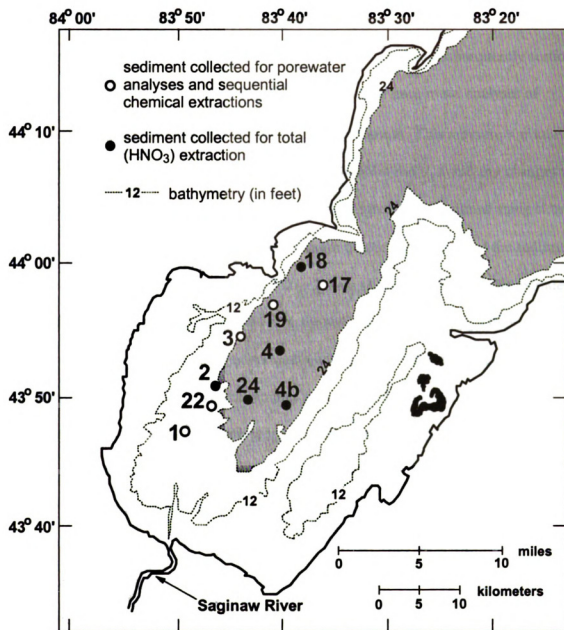


Figure 42. Map of the stations sampled during the 1994 cruise.

(1986). Sites marked with filled circles indicate locations from which sediment cores collected and sectioned (under air) for total metal analyses. Sites marked with open circles denote locations from which sediments were collected and subsequently sectioned under an inert atmosphere [a glove bag filled with N₂] for trace metal analyses of porewaters and sequential chemical extractions of sediments. This measure was taken to prevent oxidation of reduced species in porewater samples and to avoid any changes to metal partitioning within the sediment. All sediment cores were sectioned using clean techniques (e.g., only acid-cleaned Teflon® and/or plastic parts contacted the sediment). The sediment cores were sectioned into 1.0 or 2.0 cm slices using a hydraulic extruder. Thinner slices generally were collected near the sediment-water interface to permit greater resolution of recent changes in metal loading; thicker slices were collected from the deeper sediments. All sediment samples were stored in acid-washed, distilled-deionized water (DDW) -rinsed polypropylene centrifuge tubes. Sediment cores taken for porewater/sequential chemical extraction analyses were immediately sectioned after collection whereas cores taken for total metal analyses generally were sectioned a few hours after collection. Samples collected for total metal analyses were immediately frozen and stored in that manner until extraction; samples collected for porewater/sequential chemical extraction analyses underwent further processing [described in following section].

As organic matter will likely have a strong influence on metal partitioning in the sediments, the organic carbon content was determined for all sediments chosen for analysis by sequential chemical extractions. Organic carbon content was determined

using a wet chemical technique whereby the organic matter in a sediment was oxidized by a chromium(VI)-containing solution, and back-titrated with ferrous sulfate (Gaudette et al., 1974).

Porewater extraction and analyses

Sediment samples designated for porewater/sequential chemical extraction analyses were sectioned under a glove bag filled with N₂, stored in acid-washed, DDW-rinsed polypropylene centrifuge tubes and tightly capped. The centrifuge tubes were removed from the glove bag and centrifuged at 10,000 rpm for 10 minutes. The supernatant (i.e., porewater) was removed from each tube under an N₂-filled glove bag using acid-cleaned syringes. The porewater samples were filtered through acid-cleaned 0.4 µm Nuclepore® polycarbonate membrane filters into polypropylene sample bottles [while still under the glove bag]. The fluids were acidified to pH < 2 using ultrapure nitric acid and refrigerated at 4°C until analysis. Porewater blanks were also processed to monitor for contamination.

Dissolved trace metal concentrations in the porewater samples were determined using inductively-coupled plasma/mass spectrometry (ICP-MS). The ICP-MS was calibrated using certified standards, and an internal standard was used to correct for variations in the ICP-MS signal. The calibration was externally checked using a National Institute of Standards and Technology (NIST)-certified standard reference material (SRM): Trace Elements in Water (SRM #1643c). Three replicates of each sample were

analyzed; an analysis was considered to fail if the relative standard deviation (RSD) of the mean of the three replicates exceeded 15%. Total iron concentrations in the porewater samples were determined by flame atomic absorption spectrometry using similar protocols for precision and accuracy.

At selected sampling stations, subcores were also collected to measure ferrous iron (Fe^{2+}) concentrations in porewater. The ferrous iron concentrations were determined colorimetrically using ferrozine, according to the procedures developed by Stookey (1970) and Murray and Gill (1978). Porewater samples for ferrous iron were collected using a special core liner with regularly-spaced, threaded holes. Initially, the holes were filled with special plugs, and the liner was inserted into the box core. The entire subcore was removed from the box core, capped on both ends with pistons, and placed in a mechanical squeezer. The plugs were removed and acid-cleaned polycarbonate prefilters were inserted into the ports to prevent the loss of mud due to squeezing. The sampling ports were then capped with t-valves. As squeezing began, approximately 1-2 ml of porewater was allowed drip from each of the ports to purge the system. Acid-washed, DDW-rinsed Luer-lok® syringes were then attached to the t-valves and used to collect the porewater. After squeezing, the t-valves were closed to cap the syringes and the entire valve/syringe assemblies were removed from the core and placed in a glove bag filled with N_2 (to prevent oxidation of the ferrous iron). The samples were filtered, fixed with ferrozine, and removed from the glove bag. The color was allowed to develop for a few minutes, after which the samples were analyzed using a spectrophotometer.

Sediments - Total metal extractions

Sediments collected for total metal analyses were extracted using a microwave-nitric acid (HNO₃) digestion technique (Hewitt and Reynolds, 1990). Sediment samples were thawed, homogenized in the centrifuge tube using a Teflon® policeman, and an aliquot of wet sediment was placed on a clean watch glass and dried in a convection oven at 50°C for 24 hrs. Wet weights and dry weights were recorded to determine water content of samples. After drying, sediments were ground with a ceramic mortar and pestle and a 0.5g aliquot of dried, ground sediment was weighed into the Teflon® digestion vessels. 10ml of trace metal grade nitric acid were added to the sediment, and the vessels were capped and digested in a CEM-81d Microwave Digestion System. After digestion, samples were allowed to cool, and 90ml of DDW was added. The digestates were stirred with a Teflon® policeman and filtered through a 0.4 µm Nuclepore® polycarbonate membrane filters into acid-cleaned polypropylene bottles. Blanks were processed during each digestion run to monitor for potential sources of contamination.

Digestates were analyzed for Fe, Mn, As, Cd, Cu, and Zn. Fe, Mn and Zn concentrations were determined by flame atomic absorption spectrophotometry (AAS). As, Cd, and Cu concentrations were determined by graphite furnace atomic absorption spectrophotometry (GFAAS) using a heated graphite analyzer (HGA) and L'vov platforms (L'vov et al., 1977). Calibration standards and blanks were prepared daily under a Class 100 hood; certified atomic absorption standards were used to make the

calibration standards. Each calibration was externally checked for accuracy by analyzing an aliquot of SRM 1643d (Trace Elements in Water).

Sediments - Sequential Chemical Extractions

Sediments accumulating in aquatic systems are complex mixtures of numerous solid phases (e.g., silicates, organic matter, carbonates, etc.). The sediment phases sufficiently labile to readily participate in biologically mediated reactions comprise the hydromorphic fraction of the sediment (McKee et al., 1989b). The hydromorphic fraction of the sediment is generally considered to include clays (exchangeable sites), carbonates, Fe, Mn-oxides, organic matter and sulfides. Tessier et al. (1979) developed a protocol for extracting trace metals associated with sediments, targeting the individual phases comprising the sediment. In this protocol, often referred to as sequential chemical extraction (SCE), the sediment is subjected to a sequence of successively harsher reagents designed to liberate metals from increasingly refractory phases.

In this study, sediments were leached using a modified version of the original Tessier procedure. The first modification was the separation of the Mn- and Fe-oxide extraction into two discrete steps. Tessier et al. (1989) first implemented this modification in a study of zinc partitioning within oxic lake sediments: the researchers wanted to distinguish between Mn- and Fe-oxides because of the tendency of zinc to be associated with Fe-oxides. The second modification involved the type of reagent used to attack organic matter. The original Tessier method used hydrogen peroxide to liberate

metals associated with organic matter; however, hydrogen peroxide is also known to attack sulfides (e.g., pyrite). In this study, an attempt was made to distinguish between metals associated with organic matter and those associated with sulfides by using sodium hypochlorite, which is more selective for organic matter than hydrogen peroxide (Papp et al., 1991; Ellis, 1999). After this extraction was completed, samples were then leached with hydrogen peroxide to dissolve any sulfides present. Whereas Papp et al. (1991) used a hydrochloric acid wash ($\text{pH} = 2$) to remove any metals that might have precipitated after the hypochlorite extraction, this study followed the original procedure outlined in Tessier et al. (1979) and used 3.2 M NH_4OAc (ammonium acetate) to prevent adsorption of metals after extraction.

The SCE procedure utilized in this study also differed from the original Tessier et al. (1979) procedure in that an HF-assisted digestion was not used to extract metals associated with primary and secondary minerals (i.e., silicates). Instead, the microwave- HNO_3 digestion technique was used as the final extraction step. This extraction does not liberate lattice-bound metals associated with silicates and thus cannot be considered a true “total” extraction, but rather a “near-total” extraction. Use of HF in the final extraction step is useful if one wants to ascertain the lithologic/geologic fraction of metals in sediments, which may prove useful in provenance studies. However, according to Tessier et al. (1979): “these [lattice-bound] metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature.” These lattice-bound metals are also not readily bioavailable, and as such, are not within the primary focus of this study. A similar approach has been employed in previous

studies of metal partitioning in sediments (e.g., Wallman et al., 1993). Furthermore, the use of the microwave-HNO₃ digestion as the final extraction step allows direct comparison of SCE data with other published “near-total” metal concentrations data for Saginaw Bay sediments (Robbins, 1986) and the Great Lakes (e.g., Kemp et al., 1978; Heft, 1993; Kolak et al., 1998).

A flowchart describing the SCE procedure used in this study is given in Figure 43. Sediments were thawed in their centrifuge tubes. Once thawed, the tubes were placed in a glove bag filled with N₂ where they were opened and the sediment was homogenized using a Teflon® policeman. [Although the porewater had previously been extracted from these sediments, enough water remained such that the sediments were still moist when thawed. This fact is important because drying sediments (even air-drying, but especially oven-drying) can profoundly affect metal partitioning within the sediment (Rapin et al., 1986).] Approximately 1.0 g of wet, homogenized sediment was weighed into a tared, acid-washed centrifuge tube. Another aliquot of wet, homogenized sediment was taken to determine water content.

The *exchangeable (EX)* fraction [metals bound to exchange sites, mostly on clays, but can include other minerals and organic matter] was extracted using magnesium chloride (pH 7). The EX fraction is considered to represent the most readily bioavailable fraction of metals in sediments (Kersten and Forstner, 1987). In unpolluted sediments, the EX fraction usually constitutes only a very small proportion of the total metal content whereas in polluted sediments, the EX fraction can represent a significant portion of the

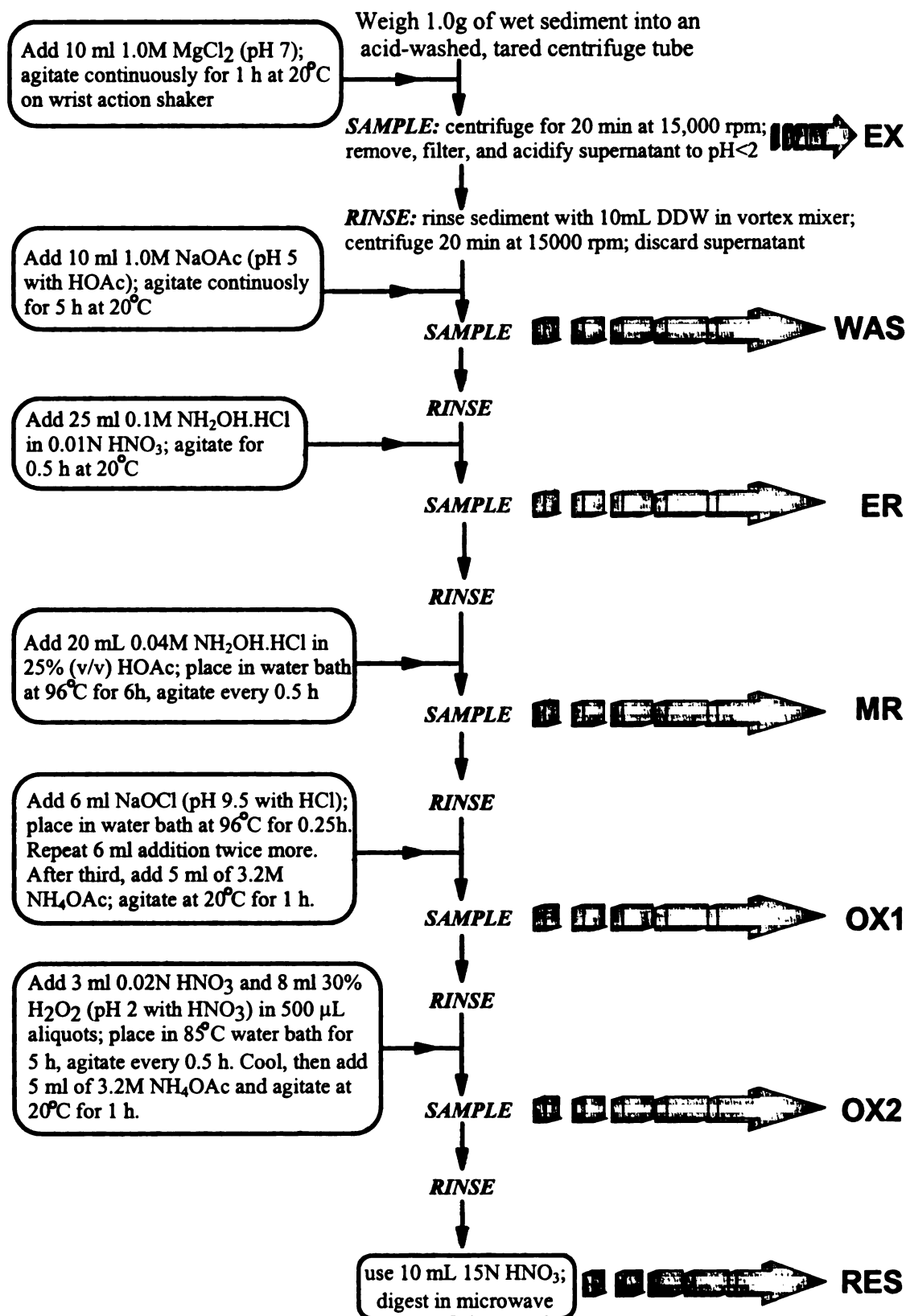


Figure 43. Flowchart depicting sequential chemical extraction method used to study metal partitioning in Saginaw Bay sediments.

total metal content. For example, the EX fraction can contain 20% of the total cadmium in polluted sediment (Kersten and Forstner, 1987). The significance of the EX fraction also varies from metal to metal, as even in polluted sediments the EX fraction rarely contains more than 1% of the total lead and copper in the sediment (Kersten and Forstner, 1987).

Metals associated with carbonates and specifically-adsorbed metals were extracted with sodium acetate (pH 5 with acetic acid) in the *weakly acid soluble (WAS)* fraction. A solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (hydroxylamine hydrochloride) in dilute HNO_3 was used to extract *easily reducible (ER)* phases such as Mn-oxides [although some Fe-oxides are also extracted during this step (Tessier et al., 1989)]. A more concentrated solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in acetic acid was used to extract the *moderately reducible (MR)* phase, which primarily targets Fe-oxides, although even some Mn-oxides remaining from the ER extraction are also attacked (Tessier et al., 1989). These first four steps were carried out under a glove bag filled with N_2 to prevent oxidation of sediments and repartitioning of metals. Rapin et al. (1986) studied extraction procedures on metal partitioning in anoxic sediments and found that exposing samples to an oxidizing atmosphere can produce significantly different and, hence, erroneous results.

Metals associated with organic matter were then extracted with the *first oxidizable (OX1)* extraction step using NaOCl (sodium hypochlorite). After the OX1 extraction had been completed (i.e., after 18 ml of NaOCl had been added to the sediment), but prior to removal of the leachate, 5 ml of 3.2M NH_4OAc were added to

prevent readsorption of metals onto the sediment. Tessier et al. (1979) used the NH_4OAc in conjunction with 20% (v/v) HNO_3 . In this study, the HNO_3 was omitted so that it would not attack the sulfide phases. Metals primarily associated with sulfides were extracted in the *second oxidizable (OX2)* extraction step. Again, 5 ml of 3.2M NH_4OAc were added after extraction to prevent readsorption of metals onto the sediment. The remaining metals, associated with the *residual fraction (RES)*, were extracted using the microwave- HNO_3 technique.

Leachates were removed from the sediment by centrifuging for 20 min at 15,000 rpm; the supernatant was then removed using PTFE tubing attached to plastic syringes. The supernatant was then filtered through 0.4 μm Nuclepore® polycarbonate membrane filters, and acidified to $\text{pH} < 2$ with ultrapure HNO_3 and stored at 4°C until analysis. The concentrations of metals in the leachates were determined using a combination of flame-AAS (iron, manganese and zinc) and GFAAS (cadmium and copper). Calibration solutions were prepared fresh daily. Calibration standards were made up using the same matrix as the particular leachate to be analyzed in order to account for any potential interference. In general, the matrices used in this study did not significantly suppress the metal absorption signal, although there were difficulties in quantifying cadmium concentrations in the OX1 leachate, possibly due to the formation of chloro-cadmium complexes.

There are a number of procedural problems inherent in SCEs that limit the efficacy with which SCEs can be used to study metal cycling. If these limitations are

taken into account, SCEs can be used to produce meaningful data regarding the reactivity of metals in sediments. One of the biggest drawbacks is the lack of specificity of a particular reagent for its target fraction (Kheboian and Bauer, 1987). For example, in addition to targeting carbonates, the weakly acid soluble (WAS) fraction has been shown to liberate metals from acid volatile sulfides (AVS) (e.g., FeS) prior to the sulfide extraction step (Wallman et al., 1993). As a result, the individual extraction steps do not represent a specific phase of the sediment, but rather, they are only operationally defined. Thus, SCEs may not provide information about the specific source of the metal, but they are still useful in determining the relative lability of a metal of interest within the sediment. Another factor mitigating the applicability of SCEs is that the concentrations of metals in the leachable fractions do not necessarily correspond to the amount of metals available to benthic organisms, owing to grain-size variations or selectivity problems (Luoma, 1983; Forstner, 1993). Still another limitation is the underlying assumption that the removal of a major phase in the sediment also includes the removal of associated trace metals. A number of studies have shown this to be a tenuous assumption due to the potential for metals to readsorb or repartition during extraction (Kheboian and Bauer, 1987). Furthermore, there apparently is no storage method that completely preserves sediment metal partitioning (other than processing sediments right away), however, freezing the samples and processing them under a reducing atmosphere (i.e., nitrogen-filled glove bag), as was done in this study, is the best alternative (Rapin et al., 1986). Regardless of these limitations, studying metal partitioning within sediments using SCEs is useful because they show relative variations in metal reactivity (irrespective of method

used) and provide insight into diagenetic processes affecting postdepositional behavior of metals (Forstner, 1993).

Quality Assurance/Quality Control (QA/QC)

A number of studies have demonstrated that trace metal analyses can be significantly compromised if one does not properly minimize contact between the samples and sources of contamination (e.g., Rossman and Barres, 1988; Boutron, 1990; Krabbenhoft and Babiarz, 1992). Precautions were taken during this study to ensure that the samples were as representative as possible of the conditions within the sediment column and not compromised by processing techniques. For example, only plastic and/or Teflon® parts were allowed to directly contact the sediments. Any such part contacting the sediments was first acid-washed in 10% v/v HCl for 24h at 20°C and then rinsed and soaked in DDW for an additional 24h and dried. All tools and sample bottles were stored double-bagged in plastic bags that had also been acid-washed and DDW-rinsed.

Quality control for total metal extractions in this study was taken from the guidelines (of a previous study of trace metals in Great Lakes' sediments) set forth in the quality assurance project plan developed in conjunction with the U.S. Environmental Protection Agency (Long et al., 1995; Sitarz, 1996). For every core that was extracted, one aliquot of NIST-SRM #2704 (Buffalo River Sediment) was digested and analyzed to check the accuracy of the extraction. Sediment extractions were deemed acceptable if the amount of metal recovered, R , fell within the range of 70% - 120% of the certified value

for the SRM. Results for the average recoveries are shown in Table 5. Values of R generally are within 90% of the certified values. Lower recoveries likely reflect the fact that a significant portion of certain elements (especially iron) are occluded within silicate lattices and are thus resistant to attack by the nitric acid. [In determining certified values of metal concentrations in the Buffalo River Sediment, NIST utilized analytical techniques (e.g., instrumental neutron activation analysis) that were able to quantify metals within silicate lattices).]

Precision of the microwave-HNO₃ digestion technique was checked by leaching multiple aliquots (i.e., subsplits) from the same sample (5% of the total samples were checked in this manner). These aliquots almost always yielded agreement to within 5% of their mean concentration. Three replicate analyses were conducted on each sample to check the precision of the GFAAS analyses. A sample result was considered acceptable if the relative standard deviation (RSD) of the mean concentration was less than 15%. It should be noted that for most samples, the RSD values were less than 5%.

Reproducibility of GFAAS analyses was "spot-checked" by re-analyzing 10% of the samples from each core; cores were flagged and completely re-analyzed if the spot-check results differed from original values by greater than 15%. The method detection limit (MDL) for the digestion procedure was defined as 3 times the standard deviation of 7 replicate analyses of a representative blank (Glaser et al., 1981). Blanks, which were processed during every digestion, were assumed to fail when values greater than the MDL were found.

Table 5. Average Recovery of trace metals from SRM 2704 (Buffalo River Sediment) Using a Microwave-Nitric Acid Digestion Technique.

	n	Average Concentration	Standard Deviation	Certified Value	Average R (% of recovery)
Fe (mg/g)	4	35.2	1.1	41.1	85.6
Mn (µg/g)	4	514.	14.	555.	92.6
As (µg/g)	4	18.9	3.0	23.4	80.9
Cd (µg/g)	4	3.43	0.29	3.45	99.3
Cu (µg/g)	4	87.6	4.3	98.6	88.9
Zn (µg/g)	4	429.	17.	438.	98.0

A modified version of the QA/QC procedures used in monitoring the microwave- HNO_3 metal extractions was also implemented to monitor the precision and accuracy of SCEs. For example, blanks were processed during each suite of extracted samples (and for every extraction step) to monitor for contamination from reagents and/or labware. The mean values for the blanks for each metal and each extraction step are listed in Table 6. In most cases, the blanks contained very low concentrations of the analytes of interest relative to the amount of metals extracted from the sediment. A number of blanks had concentrations that were not detectable (ND) (i.e., they yielded an instrument signal less than that of the calibration blank). Only the OX1 extraction (for cadmium) appeared to have a significant contamination problem. The apparent high concentration of cadmium in the OX1 blanks indicates that either the reagent itself was contaminated, or that the reagent had a sufficiently strong matrix effect that the GFAAS calibration was unable to adequately compensate for it.

Precision of the SCEs was checked by independently analyzing three subsplits of sediment sample SB22-20. The subsplits were analyzed for iron, manganese, cadmium, copper, and zinc to check reproducibility of the extractions (Table 7). The precision of the extractions generally was good, yielding RSD values less than 15%. SCEs of metals present at low concentrations or at analytical detection limits (e.g., cadmium) had poorer precision. A sample with higher metal concentrations (e.g., nearer the sediment-water interface) would have been better suited for such analysis, although there often was not enough material in the surficial samples for the desired number of subsplits.

Table 6. Concentrations of Trace Metals in SCE Procedural Blanks.

	Fe (mg/L)	Mn (mg/L)	Cd (µg/L)	Cu (µg/L)	Zn (mg/L)
EX	0.1	ND	0.8	0.06	0.23
WAS	ND	ND	1.9	0.03	0.42
ER	0.1	ND	ND	ND	0.03
MR	0.2	ND	0.4	5	0.06
OX1	0.1	0.03	19.4	0.02	ND
OX2	0.1	ND	0.1	0.02	0.06
RES	ND	0.03	ND	0.02	0.02

ND: not detectable

Table 7. Results of SCE Analyses on Three Sediment Subsplits.

Fe	EX (mg/g)	WAS (mg/g)	ER (mg/g)	MR (mg/g)	OX1 (mg/g)	OX2 (mg/g)
SB22-20A	0.03	0.73	0.22	1.57	0.04	0.14
SB22-20B	0.02	0.68	0.22	1.60	0.05	0.15
SB22-20C	0.02	0.69	0.21	1.51	0.05	0.14
mean:	0.02	0.70	0.22	1.56	0.05	0.14
RSD(%):	15.1	3.7	2.3	3.1	6.6	3.4

Mn	EX (µg/g)	WAS (µg/g)	ER (µg/g)	MR (µg/g)	OX1 (µg/g)	OX2 (µg/g)
SB22-20A	60.3	42.8	21.2	6.5	ND	ND
SB22-20B	60.7	44.5	22.4	7.5	ND	ND
SB22-20C	60.7	44.0	21.4	7.2	ND	ND
mean:	60.6	43.8	21.7	7.1	---	---
RSD(%):	0.4	2.0	2.8	7.0	---	---

Cd	EX (µg/g)	WAS (µg/g)	ER (µg/g)	MR (µg/g)	OX1 (µg/g)	OX2 (µg/g)
SB22-20A	0.01	-0.00	ND	0.02	ND	0.01
SB22-20B	0.00	0.02	ND	0.02	ND	-0.00
SB22-20C	0.01	0.01	ND	0.02	ND	0.01
mean:	0.01	0.01	---	0.02	---	0.01
RSD(%):	36.6	102.6	---	8.8	---	110.2

Cu	EX (µg/g)	WAS (µg/g)	ER (µg/g)	MR (µg/g)	OX1 (µg/g)	OX2 (µg/g)
SB22-20A	0.1	ND	0.6	0.5	0.6	ND
SB22-20B	ND	ND	0.5	0.4	0.6	ND
SB22-20C	ND	-0.0	0.4	0.4	0.6	ND
mean:	---	---	0.5	0.5	0.6	---
RSD(%):	---	---	15.1	17.9	3.9	---

Zn	EX (µg/g)	WAS (µg/g)	ER (µg/g)	MR (µg/g)	OX1 (µg/g)	OX2 (µg/g)
SB22-20A	0.3	ND	4.9	5.2	ND	0.3
SB22-20B	ND	ND	4.8	5.3	ND	ND
SB22-20C	0.3	ND	4.8	5.1	ND	ND
mean:	0.26	---	4.8	5.2	---	---
RSD(%):	1.4	---	1.0	1.9	---	---

ND: not detectable

In theory, the sum of the metals (Σ SCE) extracted during all the extraction steps in the SCE should be equivalent to the amount of metals liberated during a single microwave-HNO₃ extraction. To test this, two subsplits each of three samples from core SB1 were collected. One subsplit was extracted by SCE and the other was extracted by the microwave-HNO₃ technique. The results of this comparison are given in Table 8. The “Total” column represents the microwave-HNO₃ extraction, and the recovery, expressed as a percent, is the ratio of the Σ SCE:Total. The recoveries for the Σ SCE were generally very good, within 15% of values obtained by the microwave-HNO₃ extraction.

Model/parameters used in estimating benthic fluxes

Profiles of trace metal concentrations (cadmium, copper, and zinc) in porewater samples indicated a flux of metals from benthic sediments to the overlying water column. These benthic fluxes were estimated using Fick’s First Law of Diffusion (Berner, 1980):

$$J_i = -\phi D_{BS}(\delta C_i/\delta x) \quad (12),$$

where J_i is the diffusive flux of the species of interest into or out of benthic sediment (mg metal/cm²-a), ϕ is the porosity of the sediment, D_{BS} is the diffusion coefficient for the species of interest through the Bulk Sediment (cm²/a), and $\delta C_i/\delta x$ is the change in

Table 8. Comparison Between Total Extractions (Microwave-HNO₃) and Summation of Sequential Chemical Extractions (Σ SCE).

Fe	Total (mg/g)	ΣSCE (mg/g)	Recovery (%)
SB1-1	26.2	28.6	109.1
SB1-4	26.2	22.1	84.4
SB1-24	21.1	21.6	102.5

Mn	Total (μ g/g)	ΣSCE (μ g/g)	Recovery (%)
SB1-1	673	748	111.1
SB1-4	600	537	89.5
SB1-24	408	400	98.0

Cd	Total (μ g/g)	ΣSCE (μ g/g)	Recovery (%)
SB1-1	1.11	1.27	114.0
SB1-4	1.33	1.15	86.6
SB1-24	0.93	1.1	118.1

Cu	Total (μ g/g)	ΣSCE (μ g/g)	Recovery (%)
SB1-1	30.8	48.7	158.3
SB1-4	40.1	42.0	104.8
SB1-24	25.8	29.0	112.6

Zn	Total (μ g/g)	ΣSCE (μ g/g)	Recovery (%)
SB1-1	182	181	99.7
SB1-4	195	151	77.5
SB1-24	101	87	85.8

concentration of the metal of interest, C_i , (in mg/cm^3) with respect to sediment depth, x , (cm). Use of this equation is limited to systems where the solute profiles are at steady state and the effects of sedimentation are negligible compared to diffusive transport over the lengths and time scales considered. Previous attempts to model porewater profiles within Saginaw Bay acknowledged the likely existence of non-steady state conditions, but found that steady-state models adequately approximated vertical gradients in porewater chemistry (Ullman and Aller, 1989). Similar applications of steady state conditions have also been successfully used to estimate benthic metal fluxes elsewhere in the Great Lakes (McKee et al., 1989a). Values of D_{BS} were calculated using self-diffusion coefficients listed in Li and Gregory (1974). These coefficients were corrected for temperature variations using the Stokes-Einstein relation and subsequently modified to account for the tortuosity of Saginaw Bay sediments. Bottom temperatures at the time of sampling varied from 19.5 to 24.1°C; D_{BS} values were only calculated for the 19.5°C scenario, thus providing conservative estimates of benthic fluxes. Values of D_{BS} used in this study are as follows: cadmium ($122 \text{ cm}^2/\text{a}$), copper ($124 \text{ cm}^2/\text{a}$), and zinc ($121 \text{ cm}^2/\text{a}$).

The form of Fick's First Law in Equation (12) does not incorporate the influence of advection, wave action or bioturbation on benthic fluxes. Kolak et al. (1999) found that transport of chloride through the benthic sediments of Saginaw Bay is dominated by diffusion, and thus the influence of advection on benthic metal fluxes is probably negligible. Burrowing organisms in Saginaw Bay are capable of extensively mixing sediments to 10cm depth (Robbins, 1986), thus bioturbation could significantly affect benthic metal fluxes. Ullman and Aller (1989) attempted to account for this effect by

incorporating faunal abundance (of chironomid larvae) and burrow geometry into their benthic flux calculations, but generally found that benthic fluxes were similar between bioturbated and non-bioturbated scenarios. In this study, the effects of wave action/current stirring on benthic fluxes are neglected. Ullman and Aller (1989) used a similar approach as have other researchers working in relatively shallow-water systems (e.g., Widerlund, 1996).

RESULTS

Temporal variations in metal loading

One of the goals of this study was to evaluate temporal variations in metal loading to determine whether or not trace metal loading was decreasing to the present day. All ten cores collected were used to evaluate temporal variations in metal loading; metal profiles from the five cores that were only digested by HNO_3 (i.e., not subjected to SCE) are shown in Figure 44.

Total iron concentrations (including ΣSCEs) in surficial sediments range from 17.1 to 29.4 mg Fe/g dry wt. sediment. Most cores have a buried iron maximum at 3-4 cm depth, although the maximum iron concentration in core SB1 is found at the sediment-water interface. The average background iron concentration (excluding the

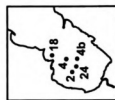
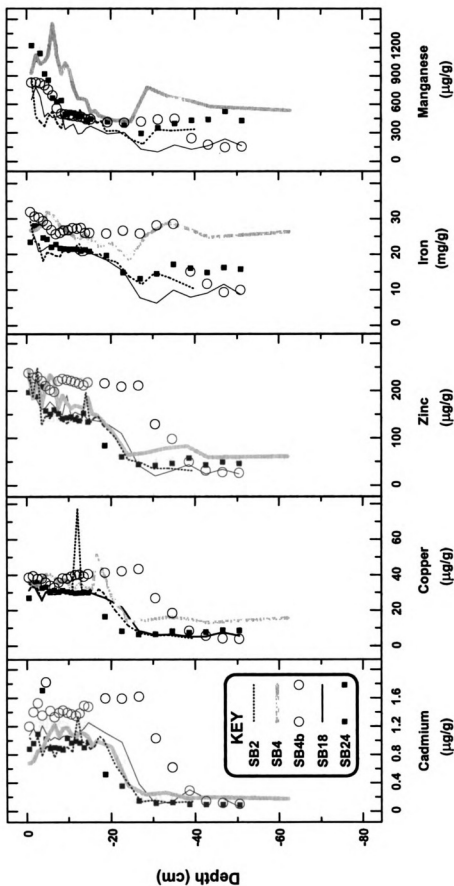


Figure 44. Profiles of total metal concentrations (HNO₃ digestion) in Saginaw Bay sediments. Sample locations are shown at left.

SCE-analyzed cores, due to limited sampling at depth) ranges from 8.8 to 26.5 mg Fe /g dry wt. sediment. The cores with the highest background concentrations, SB4 and SB24, are located in the middle of the primary depocenter in Saginaw Bay, and may represent larger accumulations of anthropogenically-affected sediment.

Total manganese concentrations in sediments are generally enriched at the sediment-water interface (SWI) and decrease with depth. This type of profile has been reported for numerous sites in the Great Lakes, including Lake Michigan (Robbins and Callender, 1975), Lake Huron (Kemp et al., 1978), and selected stations within Lake Superior (Kemp et al., 1978). At these stations, manganese cycling is apparently following the model of Robbins and Callender (1975) where manganese is liberated from sediments at depth, diffuses upward and accumulates primarily at the SWI. In this study, surficial concentrations of manganese range from 643 to 1222 $\mu\text{g Mn/ g dry wt. sediment}$ (mean = 901 $\mu\text{g Mn/ g dry wt. sediment}$). Background concentrations of total manganese range from 156 to 642 $\mu\text{g Mn/ g dry wt. sediment}$.

Profiles of total cadmium concentrations in sediment cores generally indicate the presence of buried maxima, implying that loading is decreasing to the present. Surficial cadmium concentrations range from 0.67 to 1.83 $\mu\text{g Cd/ g dry wt. sediment}$. These values are comparable to cadmium concentrations in sediments from the depositional basins of the Great Lakes (Heft, 1993). Although there is no strong spatial trend to the data, it is noteworthy that the two stations sampled closest to the mouth of the Saginaw River, SB1 and SB22, have the highest surficial cadmium concentrations. Unlike iron

and manganese, all cores have relatively similar background cadmium concentrations, ranging from 0.05 to 0.20 $\mu\text{g Cd/ g dry wt. sediment}$. These background cadmium concentrations are lower than values reported for Lake Huron [0.2-1.8 $\mu\text{g/g}$; Kemp et al. (1978), Mudroch et al. (1988)] and other sites in the Great Lakes (Mudroch et al., 1988; Heft, 1993).

Concentrations of total copper in surficial sediments range from 27.0 to 48.7 $\mu\text{g Cu/ g dry wt. sediment}$. SB1 has the highest surficial copper concentration. Excluding this site, there is little variation among surficial copper concentrations throughout the bay. Background copper concentrations range from 3.3 to 15.6 $\mu\text{g Cu/ g dry wt. sediment}$. Copper concentration profiles from all cores contain buried maxima. Several cores (SB1, SB2, SB4b, and SB17) also show trends of increasing copper concentrations in the uppermost portion of the sediment column, but there does not appear to be a bay-wide gradient in loading. Although surficial copper concentrations in Saginaw Bay are slightly lower than values reported for the lakes Michigan and Ontario, the ratios of surficial:background concentrations are significantly greater in Saginaw Bay, indicating a higher degree of anthropogenic enrichment.

Zinc concentrations are much more variable in surficial sediments from Saginaw Bay, ranging from 93 to 245 $\mu\text{g Zn/ g dry wt. sediment}$. Surficial zinc concentrations are generally greater in sediments from inner bay cores than in outer bay cores. However, the highest surficial concentrations are recorded in the middle of the depocenter, *not* nearest the mouth of the Saginaw River. Background concentrations of zinc in bay

sediments range from 17 to 61 $\mu\text{g Zn/g dry wt. sediment}$. Unlike cadmium and copper, zinc concentrations appear to be increasing to the present in *most* of the cores. Zinc concentrations in cores SB4, SB4b, and SB18 *peak* in the surficial samples. Combined, these results apparently indicate that zinc loading to the entire bay has continued to increase to the present day.

The combination of postdepositional remobilization and bioturbation may have potentially obscured recent trends in trace metal loading, thus compromising the interpretations mentioned above (Farmer, 1991). A comparison between data from this study and the study by Robbins (1986), as given in Table 9, might provide additional support for the earlier interpretations of metal loading. The 1986 study has much better spatial coverage of the bay, comprising a wider variety of physicochemical and sedimentological settings than documented in this study. Thus, variations in mean trace metal concentrations cannot be directly compared between the two studies. Likewise, the smaller standard deviations about the mean associated with data from this study probably reflect the fact that samples in this study were collected from a smaller, less variable portion of Saginaw Bay.

As the highest metal concentrations are generally found in the main depocenter (sampled in both studies), one could compare the maximum trace metal concentrations documented to ascertain dominant patterns in loading over the past several years. Maximum levels of cadmium in surficial sediments have declined sharply over the interval 1986-1994, which may reflect a reduction in loading to the bay. Maximum iron and

Table 9. Comparison of Geochemical Parameters in Surficial Sediments Between Robbins (1986) and This Study.

	<i>data from Robbins (1986)</i>					<i>data from this study</i>				
	n	Min	Max	Mean	Stdev	n	Min	Max	Mean	Stdev
TOC (wt. %)	28	0.32	5.21	3.47	1.14	5	2.28	3.36	2.91	0.47
Fe (mg/g)	35	3.1	34.3	23.8	6.9	10	17.1	32.0	24.1	5.0
Mn (µg/g)	46	20	964	496	298	10	614	1223	816	183
Cd (µg/g)	33	0.17	4.32	2.40	1.22	10	0.67	1.83	1.11	0.30
Cu (µg/g)	45	0.72	49.7	25.5	15.9	10	26.9	48.7	33.7	6.6
Zn (µg/g)	45	5	188	96	56	10	93	245	173	61

copper concentrations in surficial sediments are essentially the same between the two studies. The maximum manganese and zinc concentrations in this study are markedly greater than those measured in 1986, again implying that loading has increased to the present.

Organic carbon content

Organic matter cycling associated with early diagenesis in sediments can strongly influence trace metal behavior (Berner, 1980; Widerlund, 1996). As such, the five sediment cores collected to evaluate trace metal partitioning (by SCE) were also subsampled for total organic carbon (TOC) analyses. TOC concentrations in the surficial sediments of these five cores range from 2.28 to 3.36 wt.%. These concentrations are comparable to levels reported in Robbins (1986). Interestingly, surficial organic carbon concentrations in both studies are lower than concentrations reported for surficial sediments from Lake Huron (Kemp et al., 1978). This result is perplexing when one considers that Saginaw Bay has the highest rate of productivity (phytoplankton) within the Great Lakes' region, and is an important *source* of biomass to Lake Huron (Stoermer and Theriot, 1985). Taken together, these findings tend to support the notion that despite inputs of organic matter from the Saginaw River and from *in situ* production, fluvial inputs of detrital material dilute sediments accumulating in Saginaw Bay (Robbins, 1986), resulting in lower TOC levels.

Vertical profiles of the TOC content (expressed as wt. %) determined for the five sediment cores are shown in Figure 45. The cores are generally enriched in organic carbon near the sediment-water interface, and the TOC levels decrease with increasing sediment depth. The organic carbon profile from core SB3 has a buried maximum (~ 3 cm below the sediment-water interface) which could either reflect a trend of declining organic matter input to the present or the effects of bioturbation/resuspension on the sediment column. At depth, organic carbon concentrations among the cores range from 0.60 to 1.90 wt. %. Cores SB17, SB19, and SB22 all appear to reach background TOC levels at approximately 35-40 cm depth in the sediment column. Samples analyzed from cores SB1 and SB3 were not deep enough to provide an estimate of background TOC concentrations.

Iron

Although iron is generally insoluble in aqueous systems, microbial activities in benthic sediments can dramatically increase the mobility of iron by modifying the local environment (i.e., redox potential) and by incorporating iron into metabolic pathways (i.e., iron reduction) (e.g., Berner, 1980). Vertical profiles of dissolved, porewater-iron concentrations from six cores are presented in Figure 46. Due to the limited volume obtained, porewater samples extracted from the subcores intended for SCE analyses were only analyzed for total iron. However, at some stations [where time permitted] a duplicate subcore was collected, and this duplicate was squeezed on ship and the porewater analyzed for ferrous iron. Sites SB3 and SB4b have both types of data

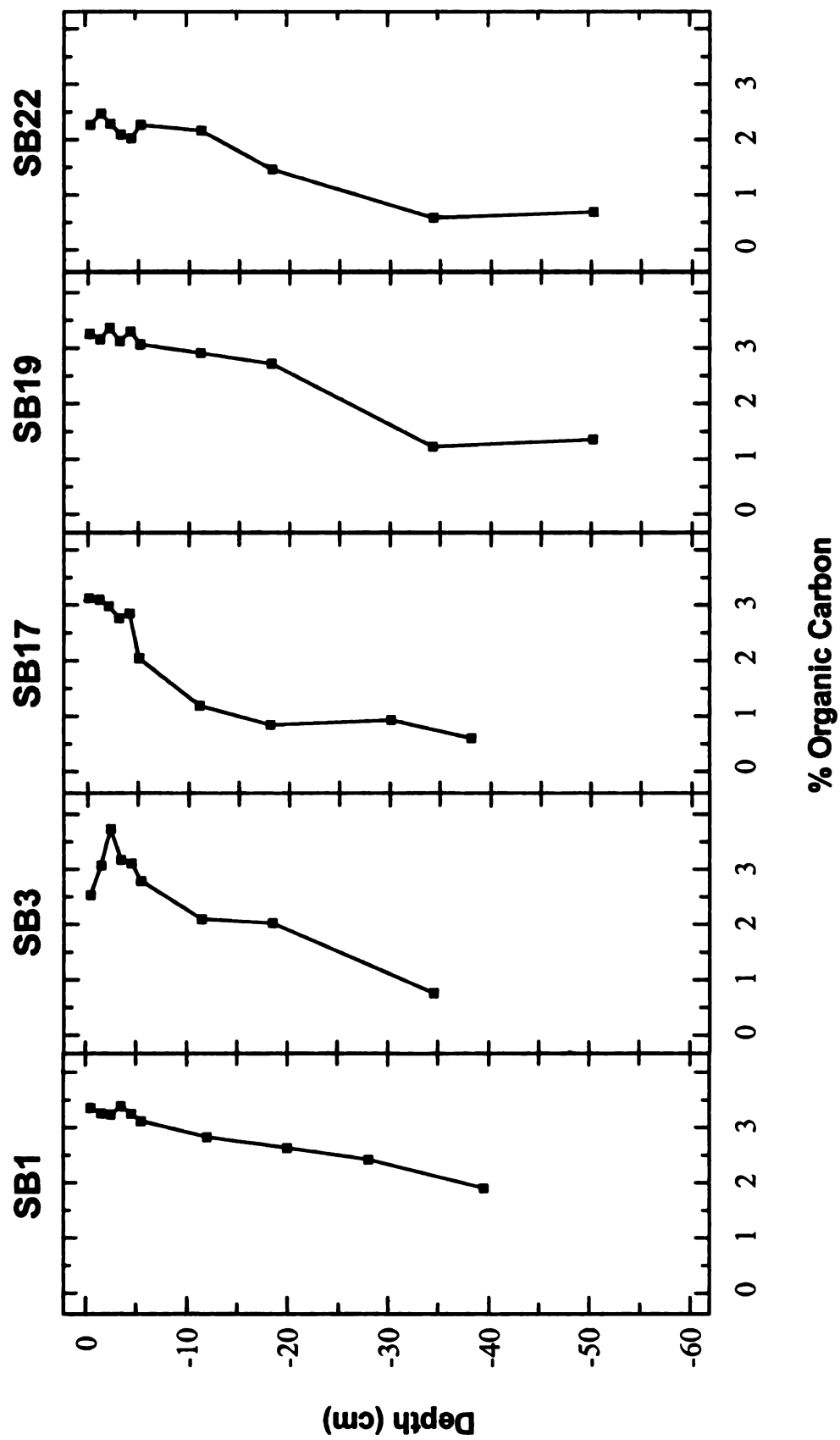


Figure 45. Profiles of organic carbon concentrations in Saginaw Bay sediment cores.

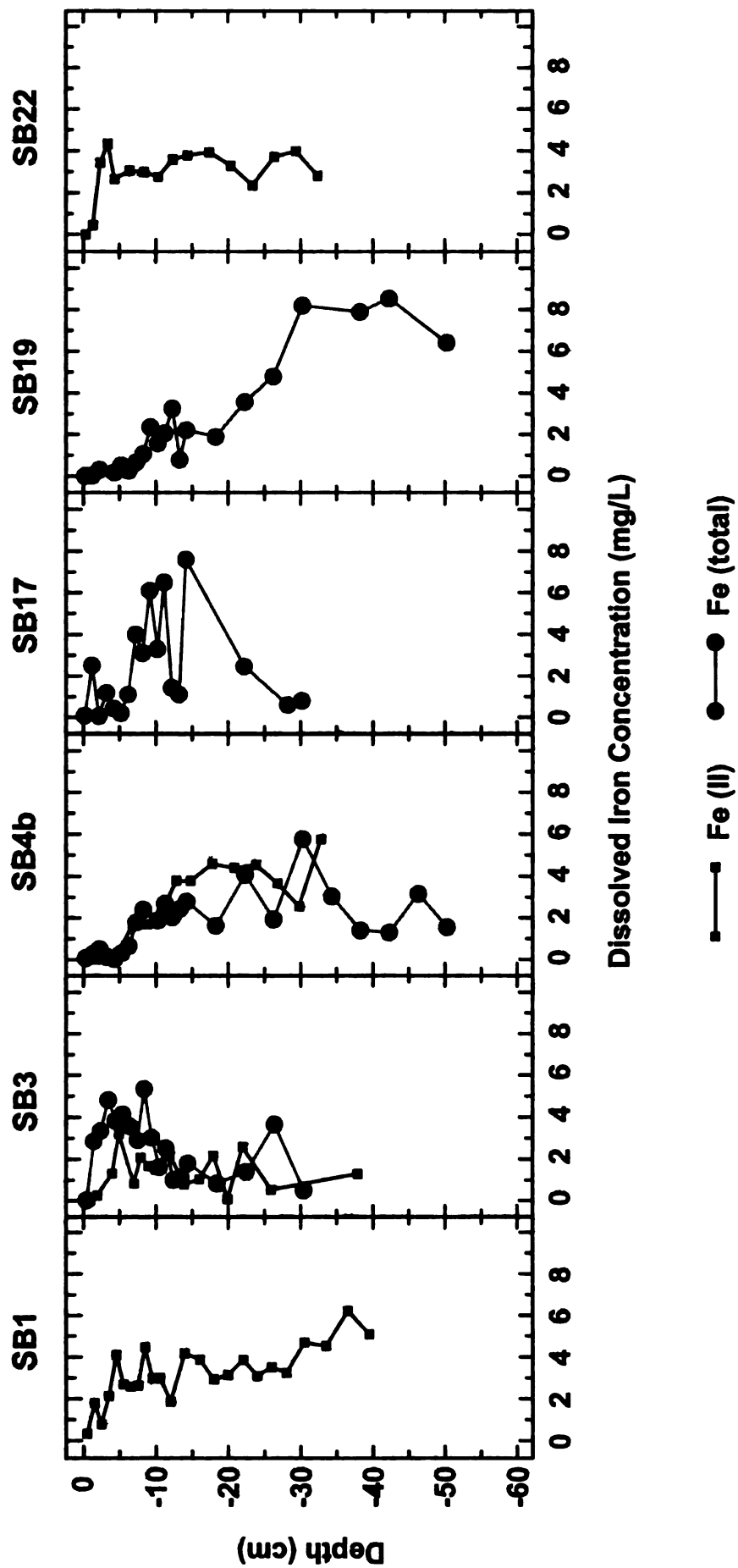
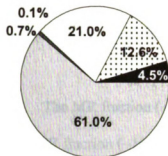


Figure 46. Profiles of total and ferrous iron concentrations in porewater from Saginaw Bay cores.

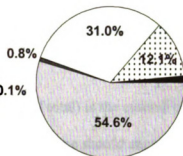
available, and the shapes of the total iron and ferrous iron profiles generally mimic one another, indicating that total iron may be used as a proxy for ferrous iron in porewater. The maximum total iron concentration recorded among these cores is 8.5 mg/L from SB19 (43 cm depth); the maximum ferrous iron concentration recorded is 6.2 mg/L at SB1 (37 cm depth). All cores have essentially no dissolved iron in porewater near the sediment-water interface, indicating oxic conditions are present. However, just a few centimeters below the sediment-water interface, ferrous iron is detectable in porewater, and dissolved iron concentrations generally continue to increase with depth. The porewater iron concentrations from SB3 apparently decline between 20 and 40 cm below the sediment-water interface, possibly indicating that sulfate reduction is occurring and that iron sulfides are precipitating. Sharp declines in porewater iron concentrations in SB4b, SB17, and SB22 may reflect localized incidences of sulfate-reduction.

Figure 47 shows the results of the SCE analyses for iron in Saginaw Bay sediments. The pie charts indicate that iron present in surficial sediments is largely partitioned into the RES fraction. The results are fairly consistent among the five cores studied: the mean concentration of iron in the RES fraction is approximately 60 +/- 5 % of the total iron concentration. The fact that such a large proportion of the total iron resides in the RES fraction raises the question as to whether this is real or an artifact of the SCEs. Tessier et al. (1980, 1996) have interpreted the iron present in the RES fraction as detrital. However, Kersten and Forstner (1987) hypothesized that the $\text{NH}_2\text{OH}.\text{HCl}$ used in the ER and MR extractions is sensitive to carbonate content in sediments due to the very poor buffering capacity of the 0.01 N HNO_3 . Assuming that

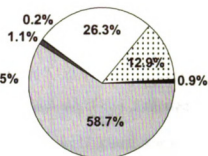
SB1-1
 $\Sigma Fe_{SCE} = 28.6 \text{ mg/g}$



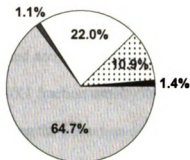
SB3-1
 $\Sigma Fe_{SCE} = 17.1 \text{ mg/g}$



SB17-1
 $\Sigma Fe_{SCE} = 18.2 \text{ mg/g}$



SB19-1
 $\Sigma Fe_{SCE} = 23.0 \text{ mg/g}$



SB22-1
 $\Sigma Fe_{SCE} = 19.9 \text{ mg/g}$

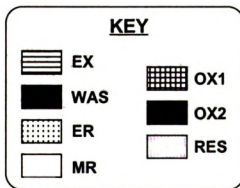
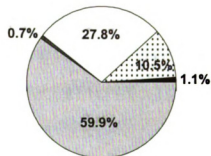


Figure 47. SCE results for iron in Saginaw Bay surficial sediments.

one does not have complete dissolution of carbonates during the WAS step, iron oxides might not be fully liberated during the ER and MR extractions, and probably would not be degraded until the RES extraction. Furthermore, the hydroxylamine-hydrochloride reagent used in the extractions apparently does not attack goethite (Fortin et al., 1993), which might also explain the large pool of iron present in the RES fraction.

The MR fraction (~ 30% of total) is the second largest reservoir of iron, followed by the ER fraction (~10% of total). One should expect more iron to be liberated during the MR extraction as this step was designated to primarily attack iron-oxides (Tessier et al., 1989). However, the substantial amount of iron released during the ER extraction (which is supposed to target Mn-oxides) likely demonstrates the premature dissolution of iron oxides (or possible liberation of acid volatile sulfides), underscoring the argument regarding lack of specificity among the reagents used in SCEs. The remaining four fractions combined account for only 10% of the total iron present in the sediment. Of these four, the OX1 fraction usually had no detectable iron, implying that little to no iron was released during the extraction of the organic matter. The OX2 fraction generally contributed only a trace amount of iron, indicating that iron-bearing sulfide phases are present but that these are not significant sources of iron in the sediment. In general, iron is partitioned within surficial sediments from Saginaw Bay according to the following manner: RES >> MR > ER > WAS > OX2 > EX, OX1 .

Changes in metal partitioning with depth in the sediment core can provide insight into how diagenetic processes affect metal cycling (McKee et al., 1989b). All five cores

studied generally have comparable vertical profiles (i.e., the dominant fractions and major trends with depth are similar among each of the five cores). Core SB1 was chosen to represent all five cores studied because this site likely has the highest sedimentation rate and shallowest mixing depth [based on data from Robbins (1986)] and thus may have the best-preserved metal loading profile of the five cores.

Figure 48 shows vertical profiles depicting how iron is partitioned in the sediment column at site SB1. The total iron concentration profile (Σ SCE) is also included for comparison. There is a big decrease in total iron with depth just below the sediment-water interface, and this decrease is reflected in profiles of iron from the RES, MR, and ER phases. The presence of iron in the MR and ER phases –presumably as iron oxides– at depth in the sediment column is somewhat perplexing, given the reducing environment also present at depth (as evidenced by ferrous iron concentrations in porewater). Given the instability of iron oxides in such an environment, this result calls into question the appropriateness of the Tessier method for use on anoxic sediments (Ellis, 1999). If one assumes the method is correct, then the results above (iron associated with the ER and MR phases) may indicate that the iron oxides, initially deposited under oxic conditions, have not had time to equilibrate (i.e., dissolve) in response to the change in redox state (i.e., a kinetic effect). Interestingly, the amount of iron associated with the WAS fraction increases slightly with depth just below the sediment-water interface, possibly indicating the transformation of iron from one phase to another that is more susceptible to attack by weak acids (e.g., siderite). Solutions used in SCEs are more aggressive towards phases

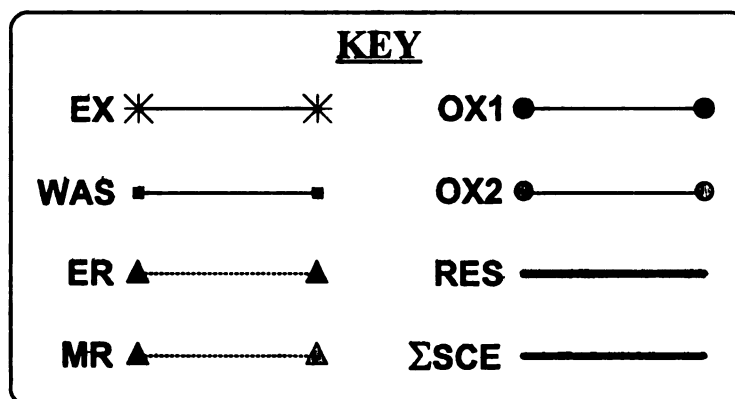
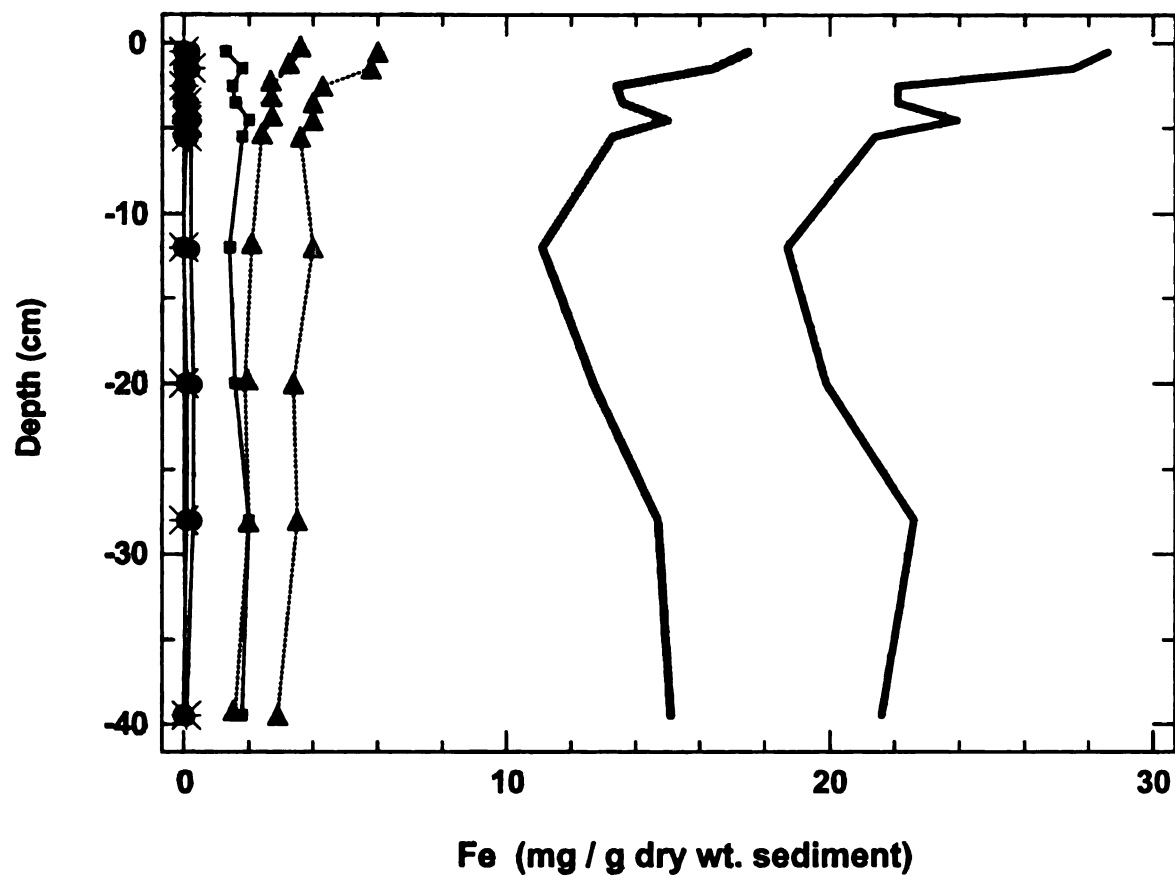


Figure 48. Changes in iron partitioning with depth in core SB1.

containing reduced iron; sediments containing these phases would exhibit release of iron prior to the ER and MR extractions (Tessier et al., 1996).

Manganese

Figure 49 shows concentration profiles of dissolved manganese in porewater. The shapes of these profiles vary widely among the cores studied. Three cores (SB3, SB4b and SB17) have elevated porewater-manganese concentrations near the sediment-water interface, and manganese concentrations decrease with depth. Cores SB19 and SB22 have buried maxima in porewater manganese. Core SB1 shows no readily observable trend in porewater-manganese concentrations with depth, although slightly greater manganese concentrations are found in the uppermost (0-10 cm) and bottom-most (30-40 cm) portions of the core.

Despite the variation among the porewater profiles, most of the cores studied – with core SB4b the exception– generally conform to the conceptual model of manganese cycling put forth by Robbins and Callender (1975). In attempting to derive a mathematical expression to account for dissolved manganese profiles in Lake Michigan sediments, Robbins and Callender (1975) described four distinct zones in the sediment column: the sediment-water interface (SWI), the neutral zone (0-4 cm below the SWI), the dissolution zone (4-8 cm below the SWI) and the equilibrium zone (>8 cm below the SWI). Each zone has a specific role in the diagenetic cycling of manganese. For example, the greatest release of manganese from the solid phase to porewater occurs in

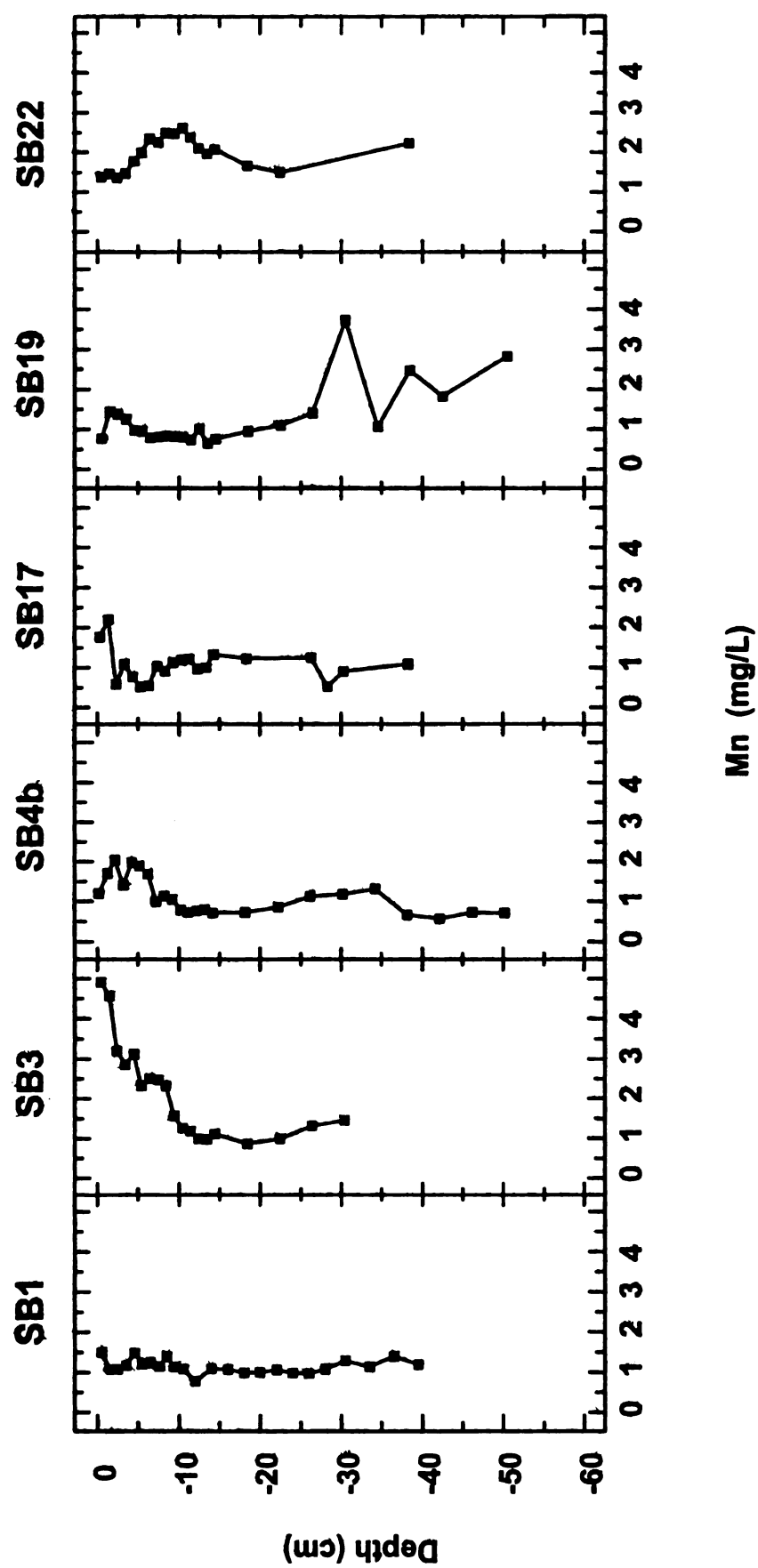


Figure 49. Profiles of manganese concentrations in porewater from Saginaw Bay cores.

the dissolution zone, resulting in a porewater maximum. Manganese diffusing upward passes through the neutral zone, where the slight release of manganese from solids is balanced by precipitation, until the SWI is reached. The SWI is a zone of net accumulation of manganese in the solid phase, as the oxic conditions present readily precipitate manganese oxides from porewater. Manganese diffusing downward from the dissolution zone passes through the equilibrium zone where manganese oxide dissolution is minimal, and manganese concentrations in porewater are constrained by the solubilities of other mineral phases (e.g., rhodochrosite, MnCO_3). The porewater profiles in the Saginaw Bay cores indicate that, according to the model of Robbins and Callender (1975), an authigenic phase (e.g., MnCO_3) may be largely controlling manganese porewater concentrations at depth, and diagenetic precipitation of manganese oxyhydroxides may be controlling porewater concentrations in the shallower (0-5 cm) sediments.

The partitioning of manganese in surficial sediments, shown in Figure 50, varies much more from core to core than does iron. Generally, the WAS fraction contains the largest amount of manganese, accounting for approximately 40% of the total manganese extracted during the SCEs. The EX fraction alone generally accounts for 30% of the total manganese extracted, whereas the ER and MR fractions combined only account 25% of the total manganese. These results are somewhat surprising given that the ER and, to a lesser degree, the MR fractions are specifically designed to target manganese oxides. In a study of metal partitioning in river sediments, Tessier et al. (1980) also found a significant portion of manganese was liberated during the EX and WAS extractions.

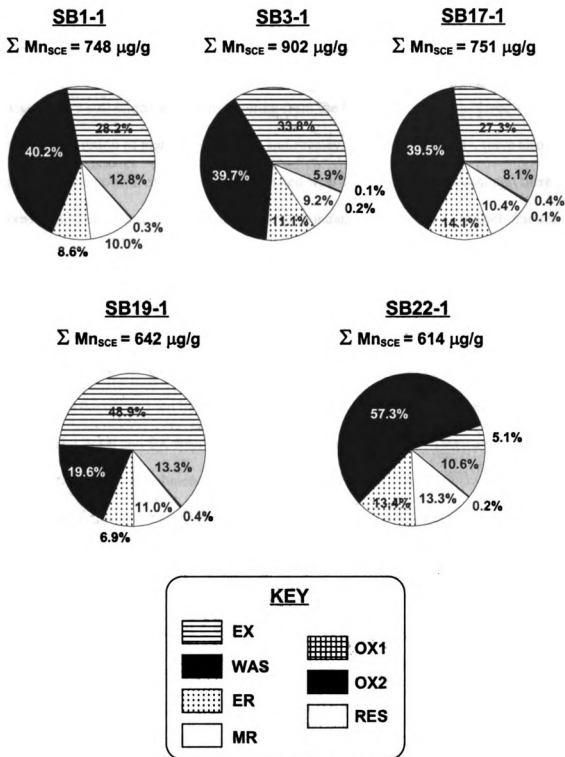


Figure 50. SCE Results for manganese in Saginaw Bay surficial sediments.

They interpreted their results to indicate that the manganese was present in reduced form (Mn^{2+}). Manganese present in this form is highly susceptible to remobilization due to increases in salinity (Tessier et al., 1980); such behavior has been observed in the Gulf of Mexico, where suspended sediments entering from the Mississippi River undergo extensive desorption of manganese (Trefry and Presley, 1976). In this study, there also exists a sizeable portion of manganese associated with the RES fraction. Although there is some variation from core to core, the general abundance of manganese in each fraction decreases according to the following order: WAS > EX > ER,MR > RES >> OX1, OX2.

Figure 51 depicts changes in how manganese is partitioned with depth in sediment core SB1. The total manganese concentration (ΣSCE) decreases sharply with depth, mostly within the upper 5 cm of the sediment column, and then remains relatively constant. The WAS and EX fractions most closely mimic this trend. There also appears to be a slight surficial enrichment of manganese in the RES, ER, and MR fractions. Below 20 cm depth, the amount of manganese contained in the EX and RES fractions are nearly identical. Unlike iron, the dominant *extraction* phase for manganese does change with depth in some of the sediment cores. For example, in cores SB3 and SB17, the WAS fraction is dominant in the uppermost sample, but below this sample the EX fraction dominates. In the upper 35cm of core SB22, the most manganese is liberated during the WAS extraction. At depths greater than 35cm, a larger proportion of the total manganese is tied up with the EX phase than the WAS phase. Throughout the entire SB1 core, the most manganese is liberated during the WAS extraction. However, throughout the entire SB19 core, the EX fraction contains the largest proportion of manganese.

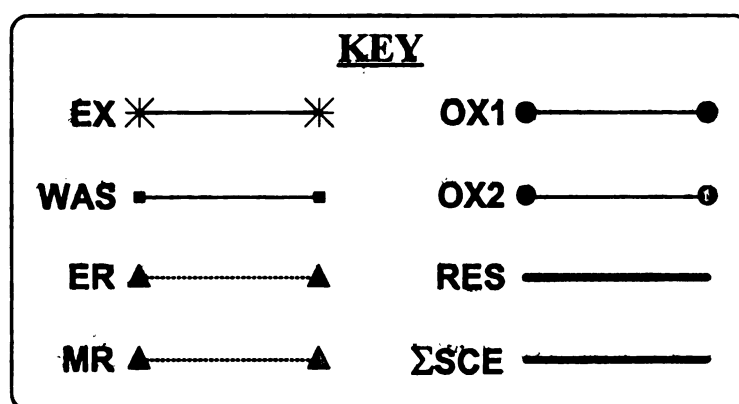
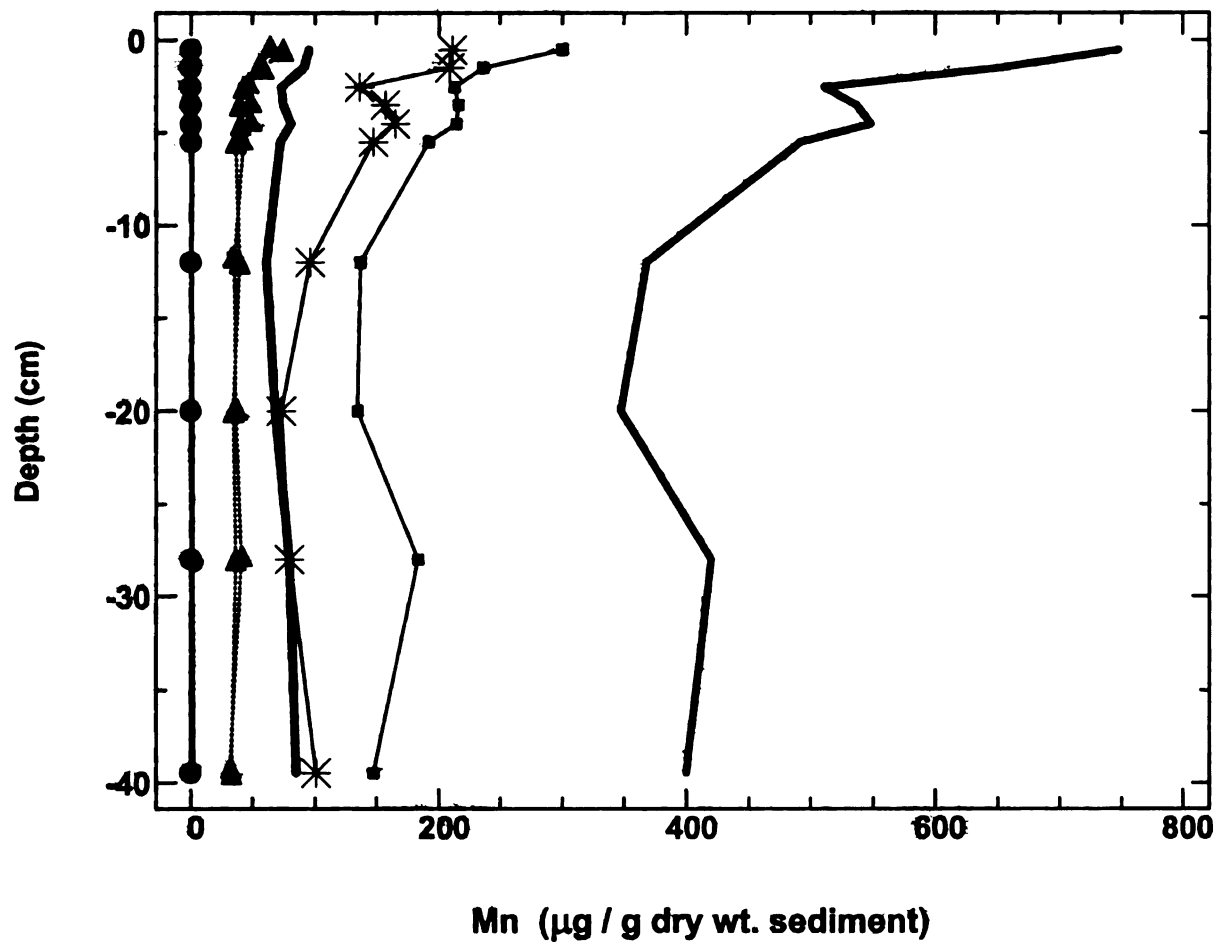


Figure 51. Changes in manganese partitioning with depth in core SB-1.

Cadmium

Profiles of porewater cadmium concentrations in Saginaw Bay sediments are shown in Figure 52. These porewater concentrations are significantly greater than those reported for the water column in Saginaw Bay [$< 0.1 \mu\text{g/L}$; Dolan and Bierman (1982)] as well as in the Great Lakes [3-10 ng/L; Nriagu et al. (1996)], implying that Saginaw Bay sediments could give rise to a significant benthic flux of cadmium to the overlying water column. In cores SB1 and SB22, the maximum cadmium concentrations occur just below the SWI and decrease with depth. The four remaining cores have buried porewater maxima and cadmium concentrations generally increase with depth. The presence of cadmium in porewater tends to preclude the occurrence of sulfate reduction at depth in cores SB3, SB4b, SB17 and SB19, as any dissolved sulfide resulting from that reaction would readily scavenge cadmium from porewater.

The results of the SCE analyses for cadmium in surficial sediments are shown in Figure 53. The manner in which cadmium is partitioned is quite diverse among the five sites, much more so than that observed for either iron or manganese. Generally, the WAS fraction contains the largest proportion of the total cadmium, although in SB17, the RES and WAS fractions contain comparable amounts of cadmium. Assuming the WAS fraction primarily targets metals sequestered in carbonates, these results tend to support the previous work by Robbins (1986) where the spatial distribution of cadmium was most strongly correlated to “calcium-family” elements (i.e., carbonates). Core SB22 deviates from this trend in that the OX2 fraction is dominant, accounting for 52.1% of the total

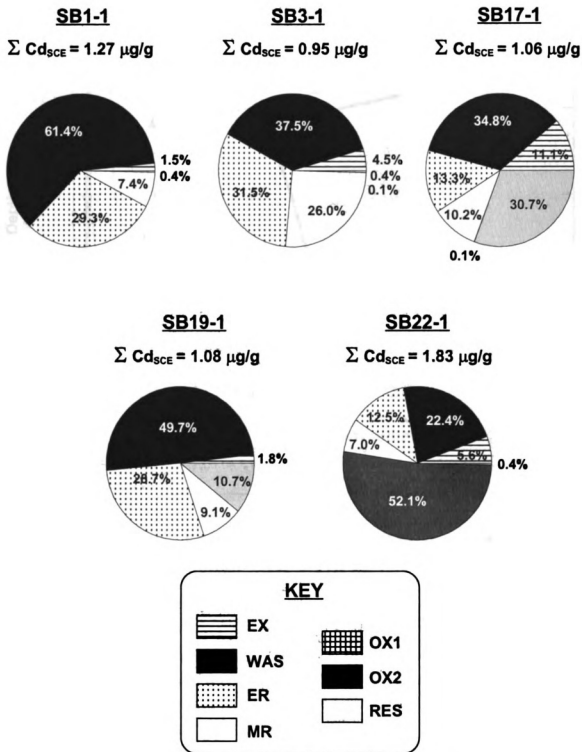


Figure 53. SCE results for cadmium in Saginaw Bay surficial sediments.

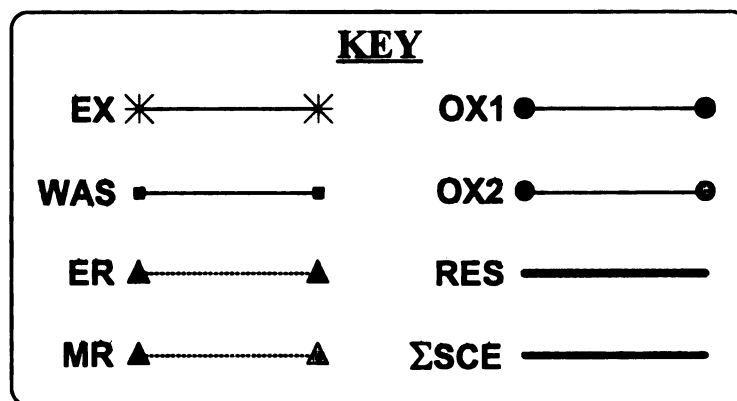
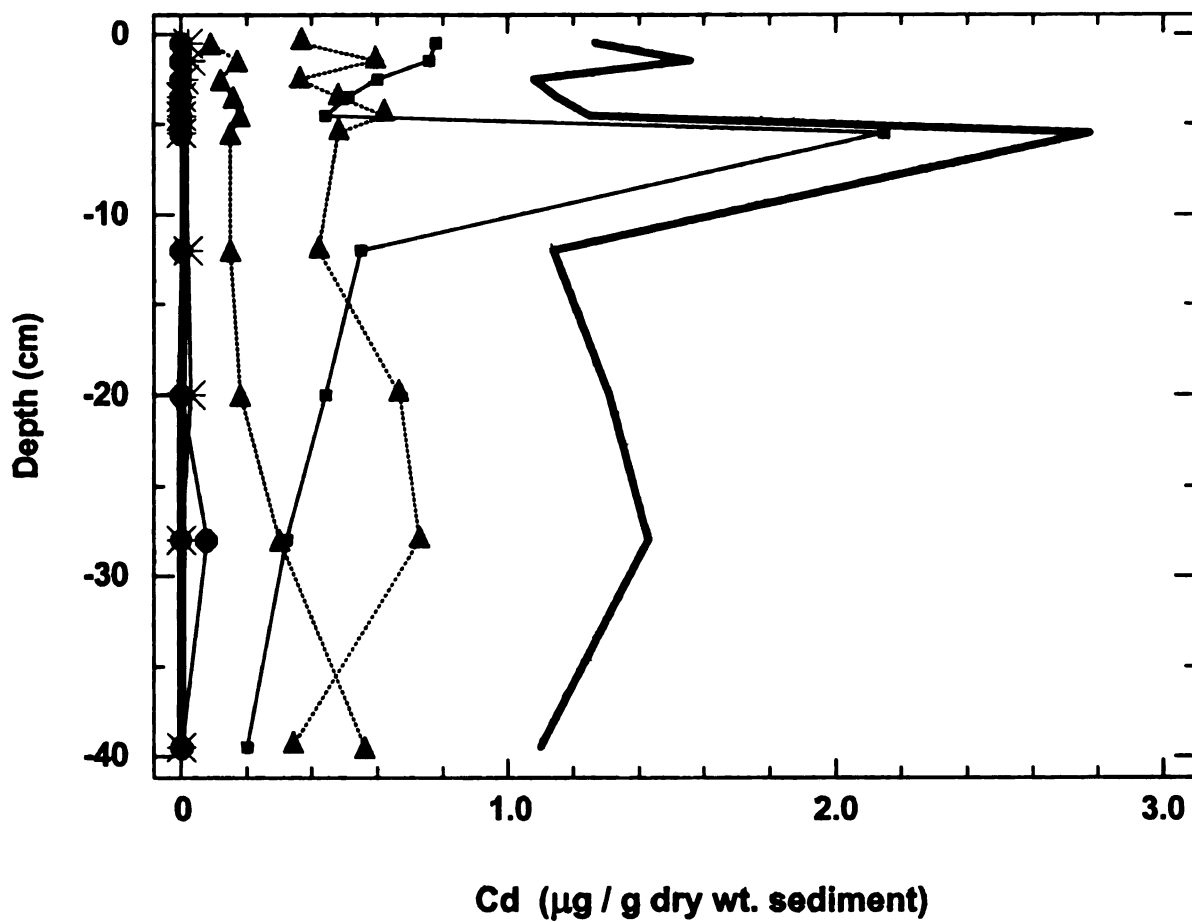


Figure 54. Changes in cadmium partitioning with depth in core SB-1.

cadmium. The phases with which cadmium is most heavily associated, arranged in decreasing order, are as follows: WAS > ER > MR > EX, RES > OX1, OX2.

Unlike iron and manganese, cadmium partitioning in Saginaw Bay sediments is not dominated by one fraction throughout the entire core. The results of the SCE analysis on core SB1, depicted in Figure 54, show that the WAS fraction is dominant from the SWI to approximately 15 cm depth in the sediment column, but below this depth the ER fraction is dominant. At the very base of the core, (~40 cm depth) cadmium is most strongly associated with the MR fraction. Cores SB17 and SB19 show a similar progression, but the RES fraction, not the MR, dominates at the base of the two cores. In core SB22, most cadmium is associated with the OX2 phase at the surface, the WAS and ER phases dominate the middle section of the core, and the OX2 fraction dominates at the base. In general, as depth increases, a greater proportion of cadmium is tied up in increasingly refractory phases.

Copper

Porewater profiles of dissolved copper concentrations are shown in Figure 55. Although each profile contains multiple peaks, the overall trend in each profile is that copper concentrations generally increase with depth. This trend mimics very well the shape of the porewater dissolved iron profiles, possibly indicating that copper release is tied to the diagenetic cycling of iron. In all cores, porewater-copper concentrations just below the SWI are greater than copper concentrations previously reported for the

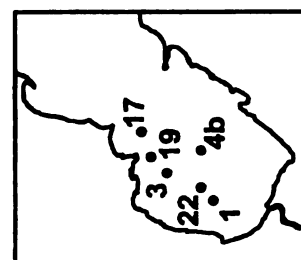
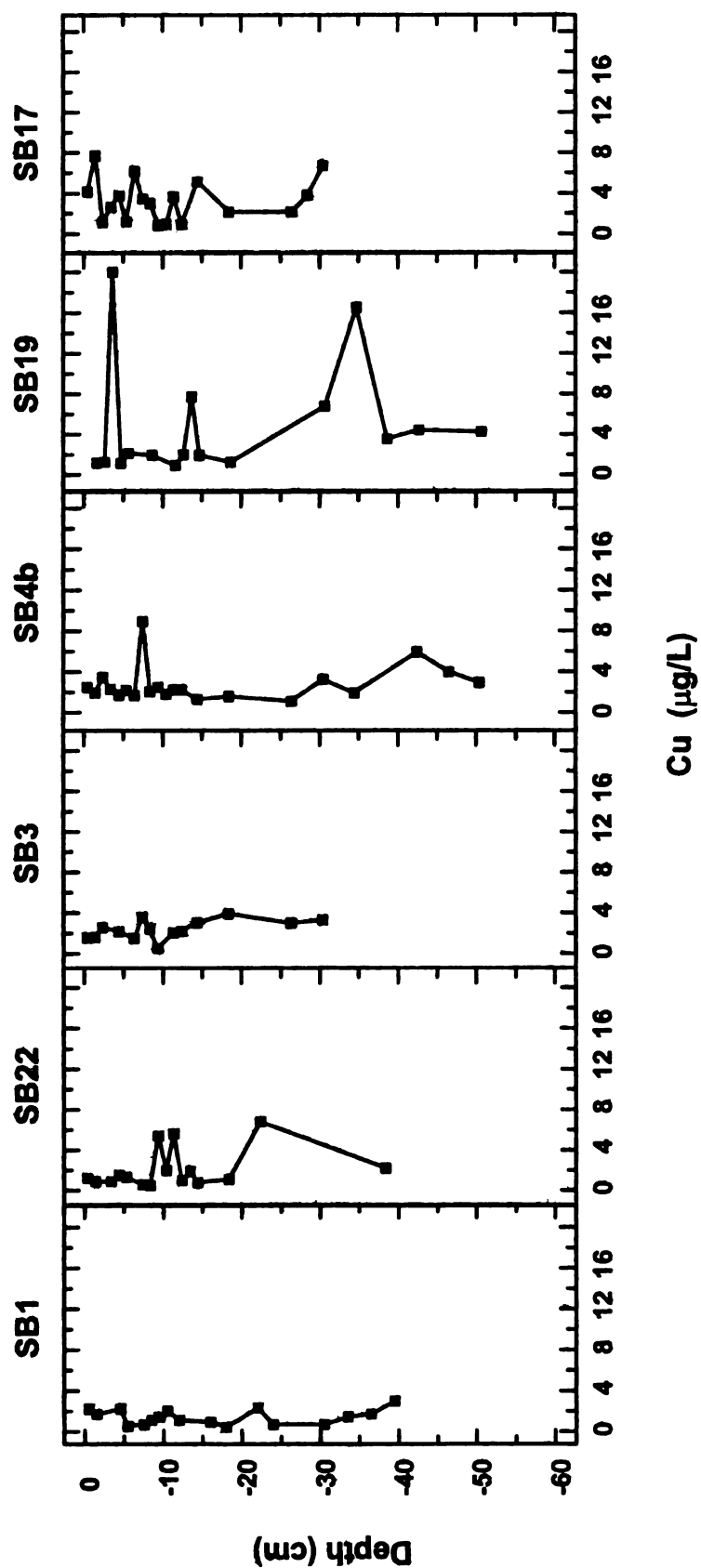


Figure 55. Profiles of dissolved copper concentrations in porewater from Saginaw Bay benthic sediments. (Sample locations are depicted at left.)

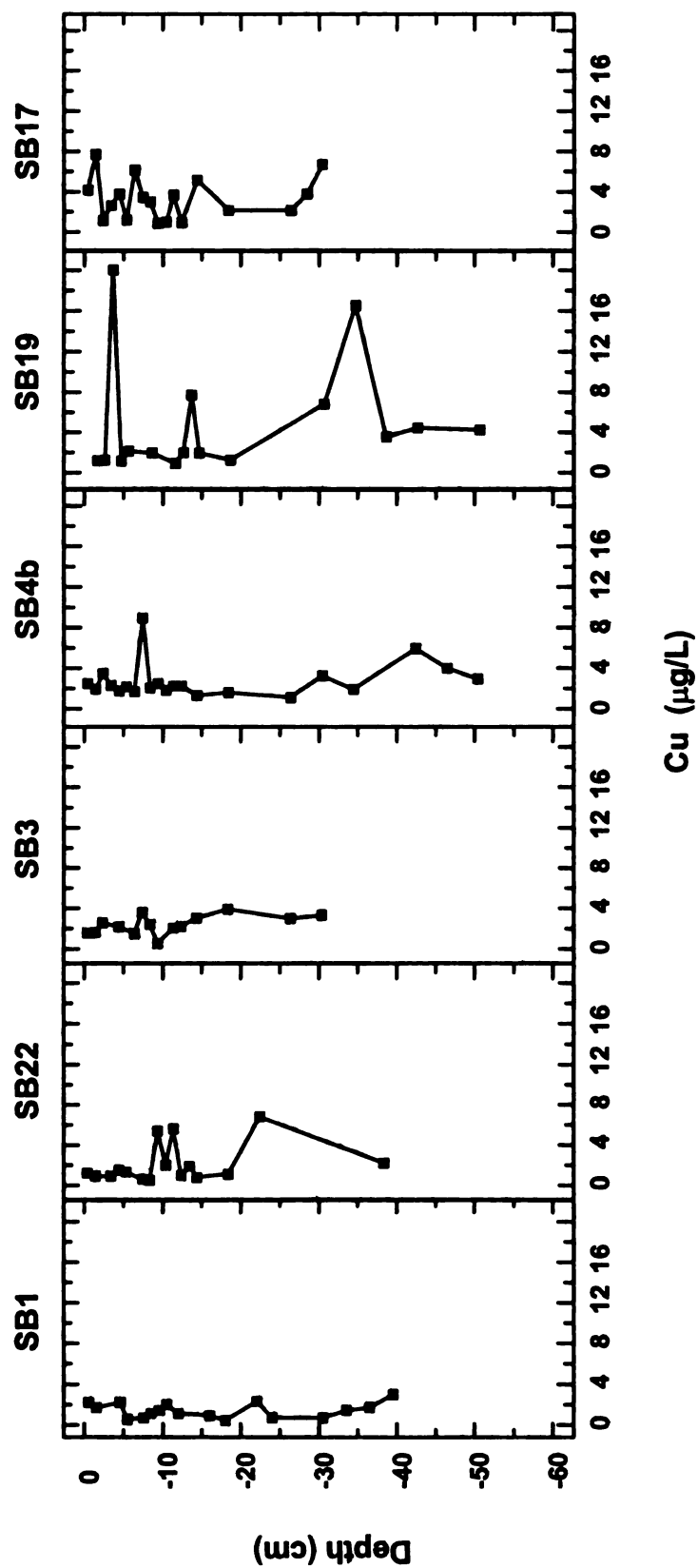


Figure 55. Profiles of dissolved copper concentrations in porewater from Saginaw Bay benthic sediments. (Sample locations are depicted at left.)

Saginaw Bay/River system (Dolan and Bierman, 1982; Moll et al., 1995), indicating that there is a benthic flux of copper from sediments to the overlying water column. Cores SB17 and SB19 have the greatest porewater copper concentrations near the SWI, but the greatest sediment-copper concentration is found at SB1. Cadmium concentrations in Saginaw Bay are greatest near the mouth of the Saginaw River, where the highest porewater concentrations are likewise found. Copper does not follow this pattern, and may be responding to other factors rather than a pollution gradient –perhaps the influence of Lake Huron on the outer portion of Saginaw Bay?

Copper partitioning within surficial sediments generally does not vary much among the cores studied (Figure 56). In all cases, copper is most commonly associated with the ER fraction. This result is somewhat surprising, as one would expect that, given copper's affinity for organic matter, most of the copper would have been liberated during the OX1 extraction. For example, Fischer et al. (1986) performed SCEs [different from the Tessier et al. (1979) procedure] on marine sediment traps and found that 56-84% of the copper flux was associated with organic material. In most cores from this study, the OX1 fraction is the next most abundant copper source. There also is a fair amount of copper (12-32% of the total) associated with the RES fraction. Combined, the EX and WAS phases -which supposedly represent the most labile, available forms of copper- generally account for less than 6% of the total copper in sediments. In core SB17, a significant amount of the total copper (28%) was liberated during the WAS extraction, implying that SB17 has the most abundant source of highly labile copper of the cores

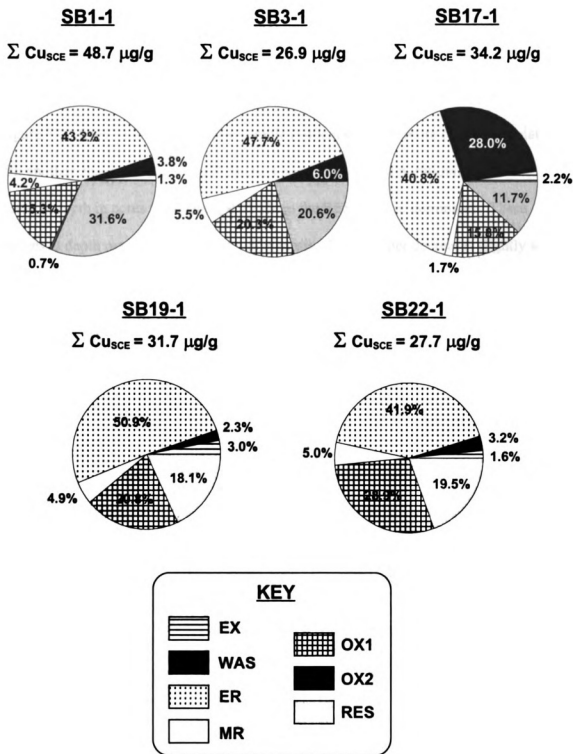


Figure 56. SCE results for copper in Saginaw Bay surficial sediments.

studied. The general order of abundance for copper is as follows: ER > OX1 > RES > MR, WAS > EX > OX2.

Downcore, copper is most strongly associated with the ER fraction in core SB1 (Figure 57). Only in the bottom-most sample (~40cm depth) is more copper associated with another phase (OX1). The ER fraction dominates copper partitioning in other cores, except at depth in cores SB22 and SB17 where the RES fraction dominates. These changes at depth may be influenced by diagenesis. Total copper decreases slightly with depth, as does copper in the ER, RES, and MR phases. Interestingly, copper content in the OX1 phase appears to increase with sediment depth.

Zinc

Profiles of porewater zinc concentrations, shown in Figure 58, are characterized by a series of spikes, mostly relegated to the upper 10 cm of the sediment column, superimposed upon a general trend of increasing zinc concentrations with depth. Porewater zinc concentrations are significantly greater than those previously documented for the Saginaw Bay/River system (Dolan and Bierman, 1982; Moll et al., 1995), indicating that there may be a substantial benthic flux of zinc to the overlying water column.

Partitioning of zinc in surficial sediments, shown in Figure 59, is essentially invariant among the five cores studied. The WAS, ER, MR, and RES fractions combined

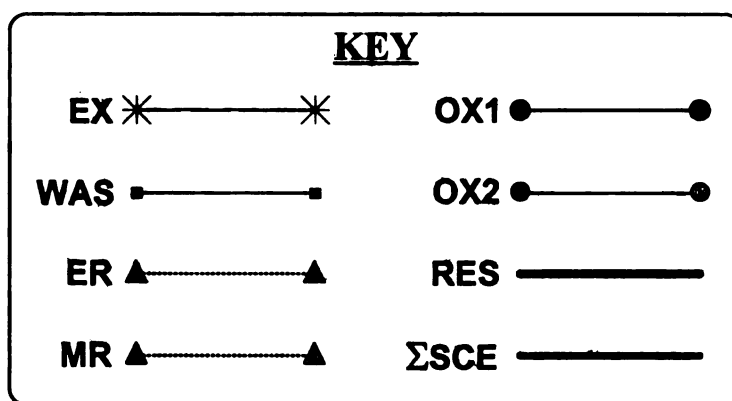
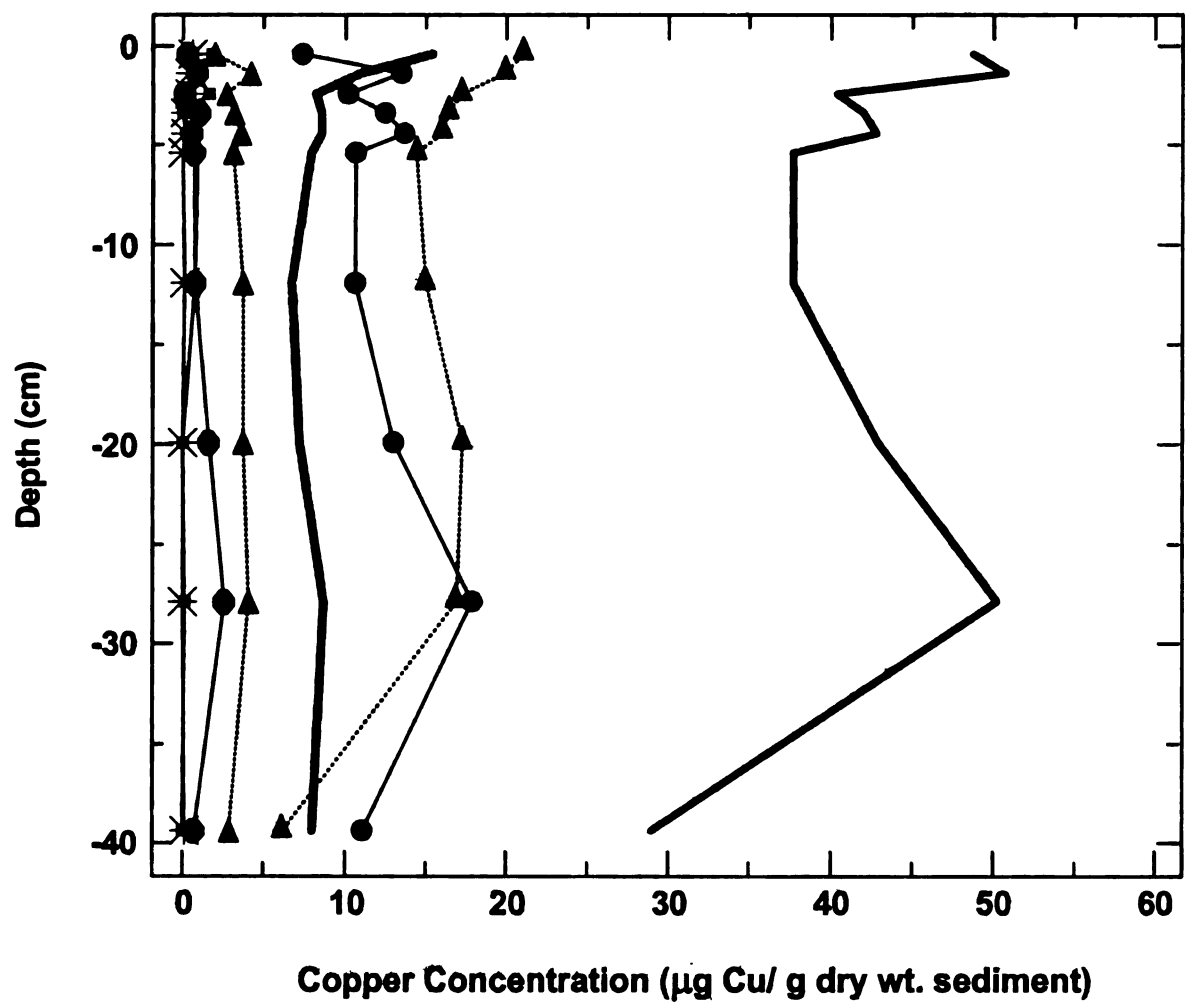


Figure 57. Changes in copper partitioning with depth in core SB-1.

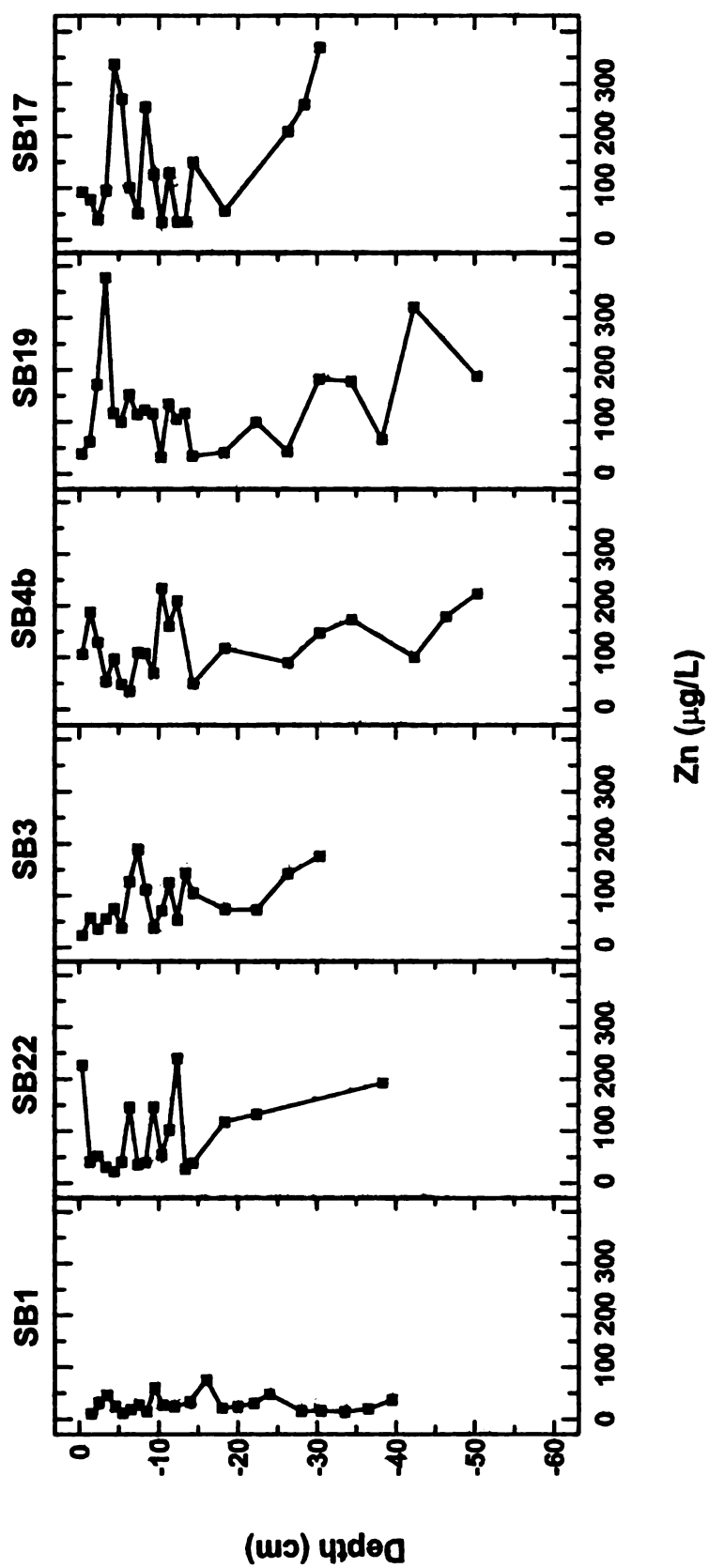


Figure 58. Profiles of dissolved zinc concentrations in porewater from Saginaw Bay benthic sediments. (Sample locations are depicted at left.)

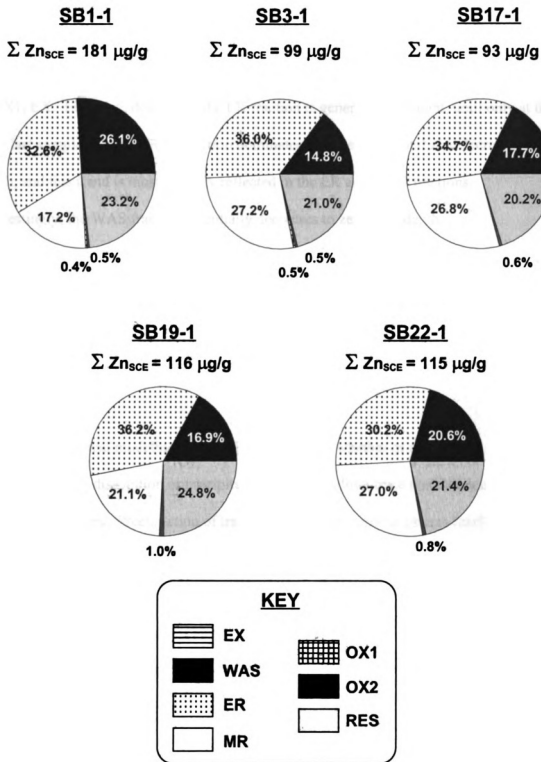


Figure 59. SCE results for zinc partitioning in Saginaw Bay surficial sediments.

account for greater than 99% of the total zinc. Zinc is most commonly associated with the ER phase, accounting for approximately 30-36% of the total zinc in the sediment. Zinc is partitioned among the extraction phases as follows: ER > WAS,MR,RES >> OX2 > OX1, EX. Likewise, down core the ER fraction is generally dominant, until only at the very last sample when the RES fraction dominates (Figure 60). Total zinc decreases with depth, and this trend is most strongly reflected in the ER and WAS fractions. Interestingly, the WAS fraction essentially decreases to zero with depth.

DISCUSSION

Diagenetic Controls on Metals - Geochemical Modeling

Geochemical modeling can provide insight into whether or not mineral-water interactions (e.g., dissolution or precipitation) are controlling trace metal concentrations in interstitial waters. Precipitation of trace metals as pure mineral phases (excluding sulfides) generally does not occur in nature, although trace metal concentrations in the interstitial waters of sediments can become significantly elevated such that precipitation is thermodynamically favorable (Stumm, 1992). Instead, trace metal concentrations are generally regulated by coprecipitation of trace metals with iron- or manganese-bearing phases, or incorporated into the lattices of other minerals (e.g., calcite) as contaminants (Robbins and Callender, 1975; Berner, 1980; Stumm, 1992).

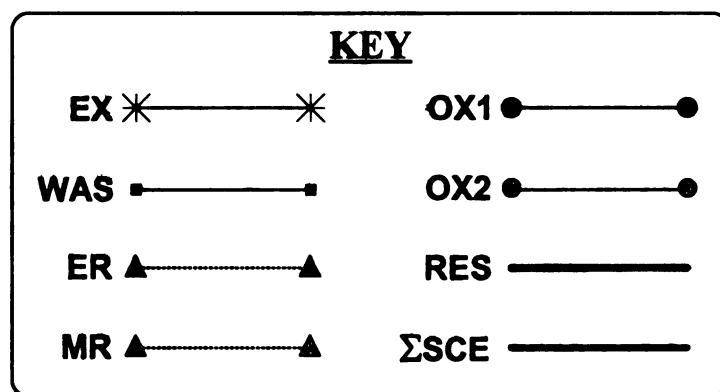
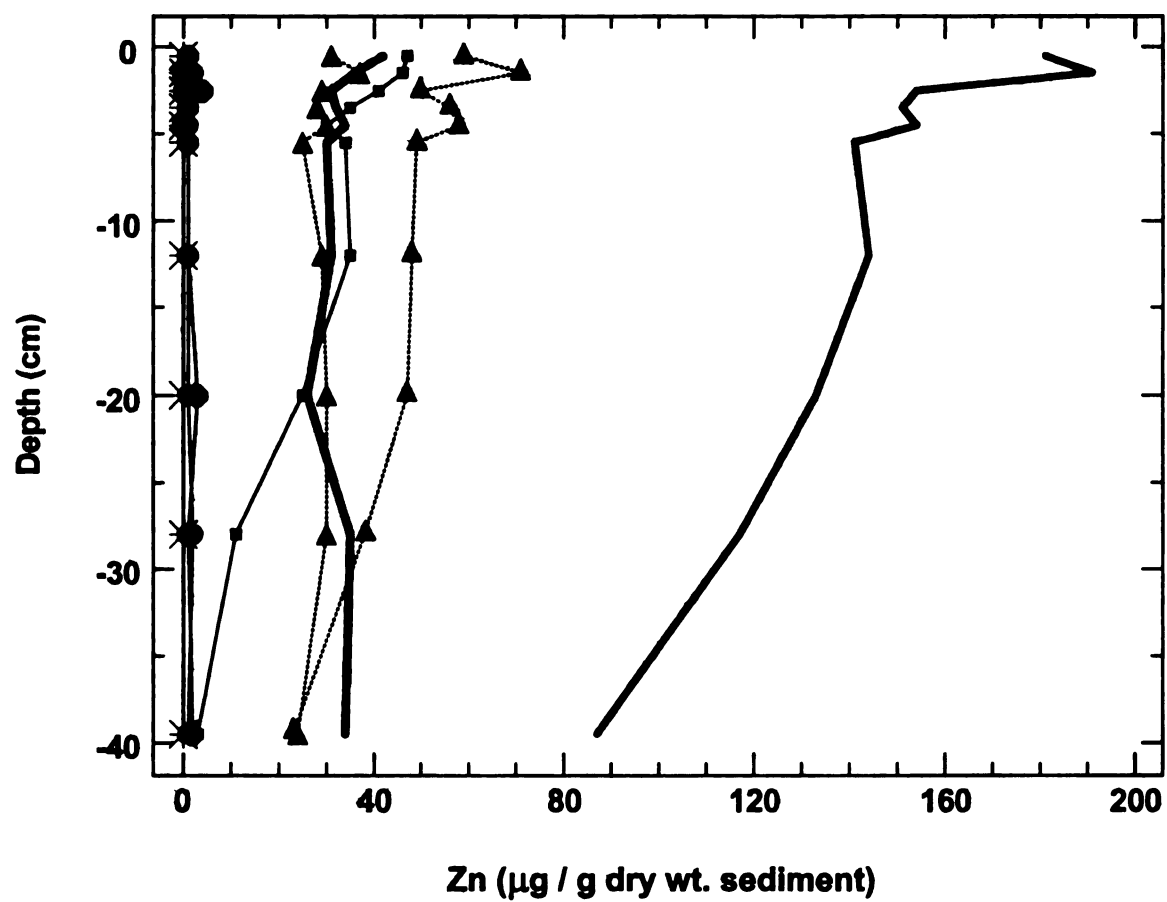


Figure 60. Changes in zinc partitioning with depth in core SB1.

Table 10 shows the saturation indices (SIs) calculated for various mineral phases using the computer code, WATEQ4F (Ball and Nordstrom, 1991) (see Chapter 1, page 35, Equation 6). A SI with a value at or near zero indicates that a mineral is in equilibrium with the aqueous phase. SI values less than zero indicate that the aqueous phase indicate that dissolution of a mineral is favored, whereas SI values greater than zero indicate that precipitation of a mineral phase is thermodynamically favorable. Sulfide minerals were not considered in this modeling effort, as sulfide concentrations were not measured in the porewater samples. Metal sulfides could play an important role in regulating trace metal concentrations (e.g., cadmium), as metal sulfides are generally only sparingly soluble (Gobeil et al., 1997). It should also be noted that iron and manganese oxyhydroxides are not considered in the WATEQ4F calculations; diagenetically-formed iron and manganese oxyhydroxides have very high binding affinities for trace metals, and can regulate trace metal concentrations in interstitial waters (Tessier et al., 1996).

The porewater samples in Table 10 are generally at equilibrium or slightly supersaturated with respect to siderite, indicating that this mineral may control ferrous iron concentrations in porewater. The presence of siderite in sediments could account for the iron liberated during the WAS extraction step. Ullman and Aller (1989) also found siderite precipitation to be thermodynamically favored in their study of Saginaw Bay porewater chemistry. Depending on the equilibrium constant used, porewater samples in

Table 10. WATEQ4F-Calculated Saturation Indices for Major Minerals and Trace Metal-Bearing Phases.

		Core	SB3-PC1	SB4b-PC1	SB17-BCG-1	SB17-BCG-2	SB17-BCG-3	SB19-PC1	SB22-PC1
		Depth (cm)	-15 cm	-15 cm	-2.5 cm	-14.5 cm	-26.5 cm	-15 cm	-8 cm
	Mineral	Formula							
	Calcite	CaCO ₃	.033	-0.004	-0.142	-0.309	-0.301	0.026	-0.199
	Aragonite	CaCO ₃	-.112	-0.149	-0.290	-0.457	-0.448	-0.122	-0.347
	Dolomite (d)	CaMg(CO ₃) ₂	-0.652	-0.673	-1.123	-1.455	-1.437	-0.766	-1.259
	Quartz	SiO ₂	.272	0.231	0.236	0.531	0.457	0.104	0.401
	Amorphous Silica	SiO ₂ (a)	-1.009	-1.044	-1.069	-0.774	-0.848	-1.201	-0.904
Fe	Siderite (d)	FeCO ₃	.188	0.420	-0.930	-0.114	0.149	0.246	0.358
	Siderite (c)	FeCO ₃	.616	0.855	-0.524	0.292	0.555	0.652	0.764
Mn	Rhodochrosite (d)	MnCO ₃	-0.093	-0.156	-0.262	-0.073	-0.134	-0.275	0.157
	Rhodochrosite (c)	MnCO ₃	0.640	0.581	0.458	0.647	0.587	0.446	0.878
Cd	Otavite	CdCO ₃	-1.501	-2.113	-1.684	-0.415	-2.286	-2.165	-2.398
	Malachite		-3.385	-3.481	-4.263	-2.959	-3.766	-3.945	-5.088
	Azurite		-5.971	-6.264	-7.600	-5.533	-6.631	-6.766	-8.531
		Cu(OH) ₂	-2.922	-2.803	-3.106	-2.566	-3.082	-3.305	-3.826
Zn	Smithsonite	ZnCO ₃	-1.727	-1.436	-2.090	-1.647	-1.531	-2.268	-2.272
		Zn(OH) ₂ (e)	-3.133	-2.560	-2.821	-2.602	-2.711	-3.714	-3.619
	?	ZnSiO ₃ (a)	1.609	2.207	1.671	2.185	2.002	0.645	1.038

this study are either slightly supersaturated or at equilibrium with respect to rhodochrosite. This result is also in agreement with the findings of Ullman and Aller (1989). Precipitation of rhodochrosite could explain why a substantial amount of manganese is liberated from sediment during the WAS extraction. The large portion of manganese associated with the EX phase might indicate that adsorption onto sediments also regulates porewater-manganese concentrations. Adsorption of manganese onto solids may be a significant control on porewater-manganese concentrations just below the sediment-water interface (Wang and van Cappellen, 1996). In this study, manganese concentrations in the EX phase are greatest just below the sediment-water, and decrease sharply with depth; this pattern is consistent with the model of manganese cycling proposed by Wang and van Cappellen (1996).

In most cases, the porewater samples are highly undersaturated with respect to mineral phases where trace metals are the primary cation (e.g., otavite, malachite and smithsonite), thus mineral precipitation does not appear to be a major control on trace metal concentrations in porewater. This finding is in agreement with results from other studies in the Great Lakes' region, where Matisoff et al. (1980) found that zinc- and cadmium-carbonates were not controlling porewater chemistry in Lake Erie. Instead, Matisoff et al. (1980) proposed that adsorption and/or precipitation of sulfides or mixed minerals were more likely to regulate zinc and cadmium levels in porewater. Calcite precipitation could thus be regulating cadmium levels in porewater, as CdCO_3 tends to coprecipitate with CaCO_3 , owing to similar ionic radii between Cd^{2+} and Ca^{2+} (Shafer

and Armstrong, 1991). Such regulation would explain why generally the most sediment-bound cadmium is liberated during the WAS extraction.

It is noteworthy that one mineral phase, ZnSiO_3 [probably amorphous; Willey (1977)], is apparently supersaturated with respect to all porewater samples modeled. Matisoff et al. (1980) did not consider this phase in their study of Lake Erie. Tessier et al. (1989) did investigate ZnSiO_3 as a possible control on porewater chemistry in small lakes from the Great Lakes' region, but dismissed this possibility when porewaters were found to be highly undersaturated with respect to this phase. These acidic lakes had abundant levels of zinc in the interstitial waters, but very low levels of dissolved silica (Tessier et al., 1989). Willey (1977) has shown that silica levels exceeding $70 \mu\text{M}$ are needed to precipitate ZnSiO_3 . In Saginaw Bay, however, high diatom productivity and accumulation in sediments results in significantly elevated interstitial silica concentrations (Robbins, 1986). In this study, silica concentrations exceeding $300 \mu\text{M}$ have been documented; previous studies of Saginaw Bay have documented comparable levels of dissolved silica in porewater (Robbins, 1986; Ullman and Aller, 1989).

All porewater samples in this study are slightly supersaturated with respect to quartz, but highly undersaturated with respect to amorphous silica (e.g., diatom tests), indicating that continued dissolution of diatom tests is favorable. Profiles of dissolved zinc and silica concentrations in porewater from the upper portion of core SB22 (Figure 61) generally show that increases in dissolved silica correspond to decreases in levels of dissolved zinc. Likewise, sudden drops in dissolved silica levels are correlated to abrupt

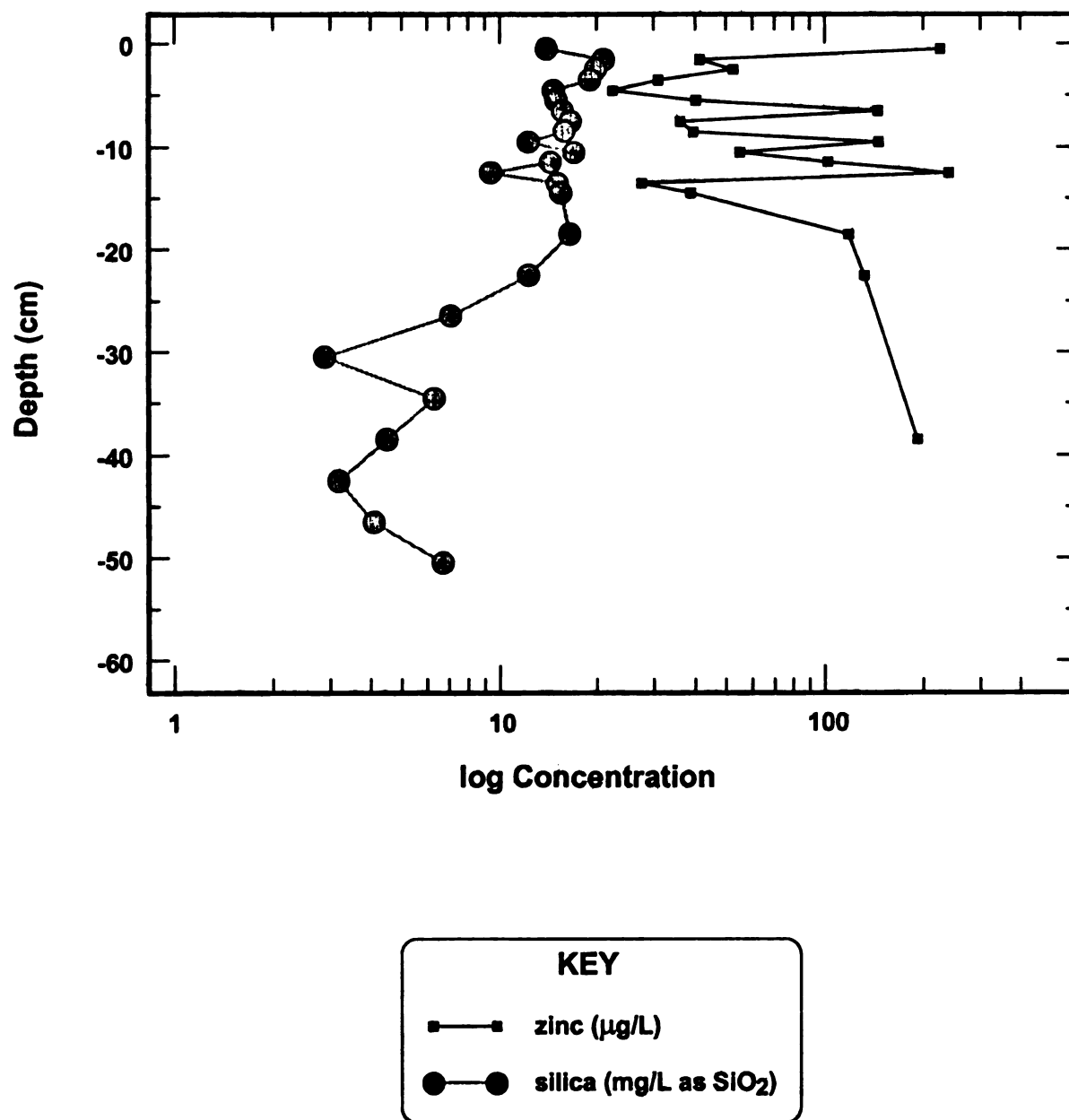


Figure 61. Profiles of dissolved zinc and silica in porewater from core SB22.

increases in porewater zinc. These observations support the idea of ZnSiO_3 precipitation as a control on porewater zinc levels. Furthermore, precipitation of ZnSiO_3 would explain why a substantial amount of zinc in Saginaw Bay sediments is associated with the WAS phase: Willey (1977) was able to dissolve the ZnSiO_3 precipitate in an acetic acid solution, similar to the one used in the WAS extraction. That porewaters appear to be significantly supersaturated with respect to ZnSiO_3 might reflect that much of the dissolved zinc is complexed by DOM and not present as the free ion in solution. This mechanism requires additional study in the future, as it has significant ramifications for zinc cycling in Saginaw Bay: declines in diatom productivity in the Saginaw Bay water column might indirectly result in increased fluxes of zinc from benthic sediments.

Efficacy of SCEs to study metal mobility in benthic sediments

The SCE results and geochemical modeling output presented thus far have yielded some insight into the postdepositional changes in trace metal partitioning within benthic sediments, and identified mechanisms that may be regulating trace metal behavior. Given the multitude of processes typically occurring within benthic sediments (Berner, 1980) and the lack of specificity of SCE reagents for an individual phase, information gained from SCEs is relegated to identifying the dominant process(es) controlling trace metal partitioning rather than delineating the complete geochemical cycle.

There are two large reservoirs/sources for trace metals in Saginaw Bay sediments, the roles of which apparently have not been resolved by the SCEs. First, a very large proportion of the total iron in sediments ($> 60\%$) is associated with the RES fraction. What is the identity of this iron reservoir [can it be considered biologically available?], and can this phase also account for the other trace metals liberated during the RES extraction? Secondly, what is the role of organic matter in trace metal partitioning in Saginaw Bay sediments? Most of the trace metals are extracted from sediment samples prior to the OX1 extraction. As the OX1 phase supposedly targets organic matter, the results of the SCEs would tend to indicate that metals associated with organic matter constitute only a minor portion of the total metal burden in sediments. Resolving these issues will go a long way towards addressing the suitability of SCEs to study trace metal partitioning in anaerobic sediments – a matter that has been raised in previous studies (e.g., Wallman et al., 1993; Ellis, 1999).

Given the aggressive nature of the reagent used in the RES extraction (15N HNO_3), the fact that most of the iron in Saginaw Bay sediments is released during this treatment apparently indicates that this iron is not present in a highly labile form, and would not be as readily bioavailable as other forms of iron (e.g., iron bound to exchange sites, or amorphous iron oxyhydroxides). Generally, iron liberated in the final extraction step has been attributed to silicate lattices (Tessier et al., 1979). However, the RES step in the original Tessier method used a HF-HClO_4 mixture, which will dissolve silicates, whereas this study utilized HNO_3 , which does not dissolve silicate lattices. Can the iron in the RES phase (this study) be attributed to some other source of iron, or is it merely an

artifact of the SCE procedure (e.g., incomplete dissolution of iron oxyhydroxides, oxides, or sulfides), indicating a shortcoming in the method?

In more recent studies of metal partitioning in sediments (e.g., Tessier et al., 1989), the MR extraction step was modified from the original Tessier et al. (1979) procedure: the concentration of the hydroxylamine hydrochloride solution was increased from 0.04M to 0.5M, and the volume of solution used was increased from 20ml to 30ml. The changes were made to insure sufficient reagent was present for complete reduction of iron-rich particles in sediment (Tessier et al., 1989). This modification was not discovered until *after* the samples in this study had already been extracted according to the procedure outlined in Figure 43. As a result, some of the RES-associated iron might be derived from incomplete dissolution of iron oxides (or sulfides) in the MR extraction (or OX2 extraction) due to insufficient amount of reagent.

One way to test this scenario would be to characterize the mineralogy in sediments before and after the RES extraction. Two samples from core SB17 (SB17-5 and SB17-16) were mounted on slides for x-ray diffraction (XRD) analysis [using a Cu-K α source] to determine to sediment mineralogy prior to and proceeding the RES extraction. Owing to the amount of material needed to prepare the slide, sample SB17-5 was mounted immediately following OX2 extraction and used to represent “pre”-RES mineralogy, whereas SB17-16 was subjected to the RES treatment and then mounted on a slide (thus representing “post”-RES mineralogy). In both “pre” and “post” samples, feldspars, quartz, mica (muscovite?), chlorite and kaolinite could be identified. These

minerals are typically found in Saginaw Bay sediments (Wood, 1964; Wilson, 2000). It is noteworthy that neither calcite nor dolomite is detected in either sample. These two minerals are quite abundant in Saginaw Bay sediments (Wood, 1964; Wilson, 2000). Given that the WAS extraction supposedly targets carbonate phases, the lack of these two minerals in the XRD slides would tend to indicate that the SCE procedure had successfully dissolved these minerals from the sediments.

No iron-bearing mineral [that could reasonably account for the significant amount of iron released during the RES extraction] was identified in the “pre” sample. Two possible explanations for this apparent lack of a suitable iron source are: (1) the iron in sediments immediately prior to RES extraction is present in an amorphous form and, therefore, would not yield an XRD pattern, or, (2) the iron is present in crystalline form, but in such low concentration that it is not detectable by the instrument. XRD detection limits will vary slightly from mineral to mineral, but are generally on the order of a couple weight percent. Furthermore, the slides prepared in this study were random grain mounts (as opposed to oriented mounts), thus detection limits might be slightly greater.

Theoretically, amorphous iron-bearing phases (e.g., iron oxyhydroxides - FeOOH) should have largely been removed during the ER and MR extractions and should not be present in the sample by the time the RES step is reached. In previous experiments where sediments were spiked with known quantities of FeOOH, approximately 77% of the total iron added was recovered during the extraction step that targeted iron oxides (fraction F3; Shannon and White, 1991). Both the MR (this study)

and F3 (Shannon and White, 1991) extractions utilized the same reagent concentration and reagent volume and can thus be considered equivalent treatments. Some of the added iron was recovered in a subsequent extraction step (fraction F4; Shannon and White, 1991), corresponding to the OX2 fraction (this study). This “delayed” recovery was not interpreted as incomplete dissolution of FeOOH during the MR extraction, but was attributed to the fact that the anoxic conditions in the sediments may have resulted in either the reprecipitation of FeOOH as FeS, or the sorption of reduced Fe to organic matter. Regardless of the exact mechanism, 100% of the added FeOOH was recovered prior to the final extraction step (F5; Shannon and White, 1991). The results of the experiment by Shannon and White (1991) tend to indicate that the iron released during RES extraction (this study) is not derived from amorphous iron oxyhydroxides.

Is it possible that a trace amount of crystalline iron oxides (or sulfides) (i.e., present at low enough levels so as to evade detection by XRD) might persist through the SCE steps up until the RES extraction? Iron sulfides are generally absent from Saginaw Bay sediments (Wood, 1958) and are, therefore, not a likely source for iron. Iron oxides such as magnetite and hematite have been documented in Saginaw Bay sediments (Wood, 1964) and could be plausible sources for iron. Researchers have documented difficulties in accurately detecting and quantifying iron oxides in sediments when present in low concentrations (Bish and Post, 1993; Phillips et al., 1993). CuK α radiation sources (as used in this study) have even poorer detection limits for iron oxides than do other sources (e.g., FeK α) (Bish and Post, 1993). These findings indicate that iron oxides

may be present, but not detectable, in the XRD samples. If this is true, could these oxides persist through the SCE procedure up until the RES extraction?

Recently, Ellis (1999) tested the effectiveness of the Tessier procedure (the same modifications as employed in this current study) to extract pure mineral phases, and found that the greatest release of iron from magnetite occurred during the MR extraction (~85% of the *extracted* iron). This result indicates that the Tessier method successfully targeted magnetite. However, further evaluation of the data in Ellis (1999; Table 3F-1) shows that the *total recovery* of iron is very low: only 2% of the magnetite was recovered during the extraction procedure [a RES extraction was not conducted in the experiments by Ellis (1999)]. Assuming a similar recovery for hematite is encountered, the iron associated with the RES phase (this study) might be derived from iron oxides that have resisted chemical attack by the reagent used in the MR step.

The iron content in the RES fraction of Saginaw Bay sediments (this study) ranges from 3.9 to 17.5 mg Fe/g dry wt. sediment. If all this iron were derived from hematite, concentrations of this mineral in Saginaw Bay sediments would range between 0.56 to 2.50 percent by weight. A similar magnetite content would be necessary to account for all the iron (0.54 to 2.42 percent magnetite by weight). These iron oxide contents are quite reasonable: data by Wood (1964) indicate that iron oxide minerals are generally present in Saginaw Bay sediments in concentrations of 0.4 to 2.0 percent by weight. Sediment cores with the lowest iron concentration in the RES fraction, cores SB3 and SB17, also appear to overlie zones mapped out by Wood (1964; Figure 6) that

are relatively depleted with respect to heavy minerals. Thus, the distribution of heavy minerals (i.e., iron oxides) could be responsible for the iron extracted in the RES fraction.

The ramifications of this interpretation on the effectiveness of the Tessier procedure are not entirely clear. Tessier et al. (1980) explicitly state that the Fe-Mn oxide extraction step in the original (1979) procedure (steps ER and MR in this study) targets both amorphous iron hydroxides as well as “crystalline solids such as hematite, goethite, birnessite, etc.” However, Tessier et al. (1989) later modified the MR extraction step, increasing the reagent strength by an order of magnitude in order to “insure sufficient amounts of reagent” for the extraction of “iron-rich particles”. The data from Ellis (1999) and the results of this study tend to indicate that the original Tessier procedure is ineffective at dissolving crystalline iron oxides. Whether or not the modified extraction step is more effective at removing iron oxides remains unresolved. However, a study comparing the original Tessier procedure with an analogous method used by the Geological Survey of Canada (GSC) found that the GSC method liberated more iron prior to the final (RES) extraction than the original Tessier method (Hall and Pelchat, 1999). This result was interpreted to indicate that the original Tessier method was not as effective at extracting crystalline and poorly-crystalline forms of iron as the GSC method. This matter needs to be further explored in the future: if the modified Tessier step is equally ineffective at extracting crystalline iron oxides, then the iron liberated during the MR step – previously attributed to both amorphous and crystalline iron oxides – is largely representative of iron in an amorphous form. Furthermore, if crystalline iron oxides are not removed until the RES extraction, can one consider this

pool of iron biologically unavailable? Ferric iron reduction by microorganisms is an important process in freshwater sediments, but ferric iron in crystalline oxides such as hematite and magnetite is not microbially reducible (Lovley and Phillips, 1987; Phillips et al., 1993).

In addition to the questions regarding the ability of the Tessier procedure to accurately characterize iron partitioning within Saginaw Bay sediments, there also exists some uncertainty as to whether or not this method has adequately delineated the influence of organic matter on trace metal partitioning. The SCE phase that supposedly comprises the organic fraction of the sediment, OX1, is essentially a negligible contributor to the total budgets of iron, manganese, cadmium and zinc in Saginaw Bay sediments. Only in the case of copper is the OX1 fraction a significant contributor to the total metal content, but even in this instance, the OX1 fraction comprises only 20 to 30% of the total copper in sediments. Fischer et al. (1986) found a much greater proportion of copper associated with organic matter in benthic marine sediments (56-84% of the total), but this information was obtained using a vastly different SCE protocol. Nevertheless, the results obtained in this study are perplexing, given that biological particles generally regulate metal loading in lakes (Sigg, 1985). For example, it has been shown that settling seston scavenge zinc and cadmium from the Lake Michigan water column (Parker et al., 1982). More recent work in Lake Michigan has demonstrated that diatom fluxes to sediments comprise the dominant vector for metal accumulation in benthic sediments, accounting for 74%, 67%, and 82% of the total annual fluxes of cadmium, copper and zinc, respectively (Shafer and Armstrong, 1991).

At first glance, the SCE results from this study would apparently indicate that these mechanisms are not nearly as prominent in Saginaw Bay as in Lake Michigan. This is a rather dubious interpretation, considering that the high level of productivity within Saginaw Bay results in a significant flux of diatoms to the sediment column, as evidenced by high levels of dissolved silica in porewaters (Robbins, 1986). Furthermore, the fact that Saginaw Bay is significantly shallower than Lake Michigan means that settling particles undergo much less recycling in the water column. Recycling of settling particulates by organisms dramatically reduces the carbon content of suspended matter before it is finally incorporated into sediments (Baker et al., 1991). This process also affects the cycling of trace metals and organic contaminants by releasing a significant portion of these analytes to the water column (Hamilton-Taylor et al., 1984; Baker et al., 1991; Nriagu et al., 1996). Thus, given that there is less opportunity for such cycling to occur within the Saginaw Bay water column, one might expect that organic matter-associated metals should comprise the dominant fraction of the total metal burden in sediments.

The fact that (apparently) such a small proportion of the total metal burden in Saginaw Bay sediments is associated with the organic fraction might lead one to question the effectiveness and specificity of the Tessier method for extracting metals associated with organic matter. Previous studies have investigated these issues, and shown that the Tessier method is fairly selective for organic matter, based on total carbon analyses of sediments after each extraction step (Tessier et al., 1979; Shannon and White, 1991).

However, this approach does not directly quantify the amount of organic-associated *metals* remaining in the sediment. Rather, the underlying assumption is that characterizing the state of the “organic pool” (i.e., total carbon content) will indirectly provide information regarding the behavior of the associated metals. Previous studies have already demonstrated the potential for trace metals to repartition during the SCE (Kheboian and Bauer, 1987), thus, such an indirect approach may not be valid. Furthermore, measurements of total carbon content may be obscured, as multiple reagents used in the SCE procedure (WAS and MR) contain organic ions; analyses of sediment following the WAS extraction have yielded total carbon contents greater than the initial starting material (Shannon and White, 1991). Thus, given the intimate association between organic and amorphous iron/manganese oxyhydroxide coatings in sediments (Tessier et al., 1996), it is conceivable that one could extract organics and associated metals in conjunction with the oxyhydroxides (i.e., during the ER and MR extraction steps), but that this loss of organic matter would be overwhelmed by the residual organics derived from the reagents.

This study sought a more direct method by which to monitor the selectivity of the Tessier method for extracting organic-associated metals. Thus, in addition to the Saginaw Bay sediments, aliquots of two NIST-certified SRMs, SRM 1566a (Oyster Tissue) and SRM 2704 (Buffalo River Sediment), were also subjected to the SCE procedure. The Buffalo River Sediment SRM provided an additional natural sediment matrix for comparison with the Saginaw Bay sediments, whereas the Oyster Tissue SRM served as a “pure” organic matrix in order to test the selectivity of the SCE procedure.

The results of the SCE analyses on these two SRMs are given in Table 11. The recovery of trace metals from these two SRMs is fairly good: only iron (both), manganese (oyster) and cadmium (oyster) recoveries are not within 20% of certified values. It should be noted that the extractions were initially conducted in centrifuge tubes (as were all the other SCEs on Saginaw Bay benthic sediments), and subsequently transferred to Teflon® digestion vessels for the final extraction. The sediment SRM could easily be transferred whereas the oyster tissue sample could not: the oyster tissue had formed a gelatinous residue over the course of the extractions that could not be completely removed from the tube, and thus some material was lost in the transfer. Even after the microwave digestion step, the oyster tissue residue was not completely degraded, which might account for the generally lower recoveries.

The SCE results for the Buffalo River sediment are quite similar to those for Saginaw Bay sediments in that the OX1 fraction generally comprises a relatively small portion of the total metal budget. Likewise, of the metals studied, copper is most heavily associated with the OX1 fraction (~26% of the total extractable copper). These results apparently indicate that only a minor portion of the metals in Buffalo River sediment is associated with the organic fraction. However, a similar distribution of trace metals among SCE phases is also observed for the oyster tissue: the OX1 fraction constitutes a minor portion of the total metal budget, and OX1 fraction contributes most to the total copper content (~22% of the total). The results from the oyster tissue extractions are especially perplexing, given that the matrix is presumably all organic matter.

Table 11. Results of SCE Analyses on NIST-Certified Standard Reference Materials.

SRM 1566a: Oyster Tissue

Fraction	Fe (mg/g)	Mn (µg/g)	Cd (µg/g)	Cu (µg/g)	Zn (µg/g)	Fe (mg/g)	Mn (µg/g)	Cd (µg/g)	Cu (µg/g)	Zn (µg/g)
EX	0.01	6	1.6	6.7	408	0.0	51	1.6	1.2	29
WAS	0.01	2	0.8	7.4	213	0.7	98	0.9	1.6	119
ER	0.00	0	0.0	5.8	33	3.1	113	0.4	29.8	79
MR	0.15	0	0.1	15.4	83	6.1	64	0.3	6.8	74
OX1	0.00	ND	BDL	12.1	7	0.0	1	BDL	22.8	17
OX2	0.00	0	0.0	5.2	2	0.3	4	0.00	6.4	5
RES	0.14	2	0.0	1.4	6	21.1	126	0.7	18.8	95
Σ-phases	0.31	9.6	2.5	54.0	751	31.3	457	3.9	87.2	417

SRM 2704: Buffalo River Sediment

Certified Value	0.539 +/- 0.015	12.3 +/- 1.5	4.15 +/- 0.38	66.3 +/- 4.3	830 +/- 57	41.1 +/- 0.1	555 +/- 19	3.45 +/- 0.22	98.6 +/- 5.0	438 +/- 12
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BDL: below detection limit

ND: not detectable

Figure 62 shows the amount of copper and zinc, respectively, extracted from the oyster tissue during each step, and plots the cumulative fraction (the sum of the metal extracted through a given step normalized by the total metal extracted at the conclusion of the procedure) of metal extracted throughout the course of the procedure. A curve representing the “theoretical yield” is plotted for comparison; this curve is a conceptual model of metal release during the SCE procedure based on the assumption that organic matter is not attacked until the OX1 step. Both metals shown in the figure indicate that most of the extractable copper and zinc in the oyster tissue is already liberated before the OX1 extraction step is encountered, but this does not necessarily indicate premature degradation of organic matter. Some of the metals liberated in the early steps could be released from exchange sites; the EX extraction targets exchange sites on *both* minerals and organic matter (Tessier et al., 1979). The sample handling (i.e., freeze-drying) may also have affected partitioning and rendered metals more susceptible to extraction (Rapin et al., 1986). Nonetheless, these results indicate that one must exercise caution when attempting to study metal partitioning using SCEs. The data presented herein underscore the need for a more thorough characterization of organic matter (both dissolved and particulate) in order to more accurately predict sediment-metal binding capacities (e.g., Tessier et al., 1996) and model controls on porewater chemistry.

Benthic Flux Estimates and Trace Metal Mass Balances

Studies of metal cycling in aquatic ecosystems have shown that benthic fluxes of trace metals from sediments can comprise a substantial source of metals to the overlying

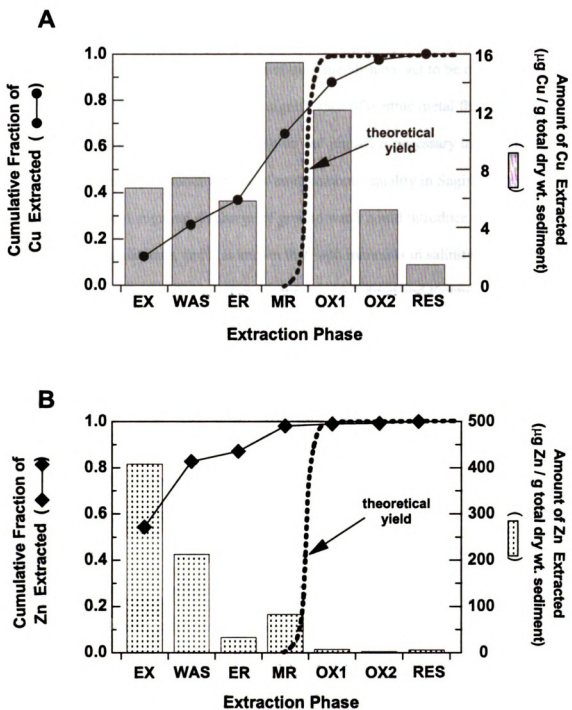


Figure 62. Results from SCE analysis of SRM 1566a (Oyster Tissue).

water column (McKee et al., 1989a; van den Berg et al., 1999; Yu et al., 2000). Although mass-balance modeling has previously been used to study metal cycling in Saginaw Bay (Dolan and Bierman, 1982), benthic fluxes of trace metals have yet to be incorporated into such efforts. An understanding of the significance of benthic metal fluxes relative to other metal inputs (e.g., atmospheric deposition and runoff) is necessary in order to characterize accurately the current status of environmental quality in Saginaw Bay. Furthermore, focused, regional discharge of ground water could introduce saline water into Saginaw Bay sediments, and it is known that such increases in salinity can augment remobilization and release of metals from sediments (Adediran and Kramer, 1987; Calmano et al., 1992). The need to assess the potential degradation of environmental quality within Saginaw Bay associated with such regional discharge provides additional impetus for quantitation of benthic metal fluxes.

In this study, the average, annual benthic fluxes for the trace metals cadmium, copper and zinc are estimated at the five stations for which porewater chemistry data are available. Trace metal fluxes are calculated according to Fick's First Law (Equation 12), using the appropriate bulk-sediment diffusion coefficients. The benthic fluxes are determined at the lowest temperature documented; fluxes are slightly greater (~10%) at the highest temperature recorded during sampling. The term, $\delta C_i / \delta x$, is the slope between the depth of the maximum trace metal concentration in porewater ($C_{i \text{ max}}$ at x_{max}) and the trace metal concentration in the water column ($x = 0$). Concentrations of dissolved trace metals in the water column are taken from previous measurements of the Saginaw Bay/River system (Dolan and Bierman, 1982; Moll et al., 1995). The water

column concentrations for cadmium and zinc are approximately an order of magnitude greater than values reported for open waters in the Great Lakes (Nriagu et al., 1996) indicating that there may still be considerable inputs of these metals to the Saginaw Bay/River system. The copper concentrations previously reported by Dolan and Bierman (1982) and Moll et al. (1995) in the Saginaw River/Bay system are comparable to concentrations in the open waters of the Great Lakes.

All sediment cores yield negative benthic fluxes for cadmium and zinc, implying metals are being released *from* the sediment *to* the water column. In the case of copper, one core – SB22 – has a *positive* benthic flux, indicating that transfer is from the water column to the sediment. It should be noted that zinc fluxes are blank-corrected; copper and cadmium were not detected in the blanks. To estimate the average annual load of metals to Saginaw Bay released from benthic sediments, the benthic fluxes were extrapolated over the primary depocenter in Saginaw Bay, an area of approximately 600 km² in extent [i.e., the SW-NE trending mud accumulation described by Robbins (1986)]. Fluxes were not extrapolated across the entire bay as the limited number of samples would not be representative of bay-wide conditions, based on the spatial geochemical patterns documented in Robbins (1986). Annual loads of cadmium, copper, and zinc released from benthic sediments are approximately 1100, 50, and 37000 kg/a, respectively. Although cadmium and copper loads are relatively small compared to total annual metal loadings determined by Robbins (1986), zinc loads may comprise a significant proportion of the total zinc input to Saginaw Bay.

These estimated metal loads must be tempered by the realization that they are derived from a “snap shot” – a one-time sampling event. Although this dataset may be spatially representative of the Saginaw Bay depocenter, extrapolating such estimates over the course of an entire year may not be representative of the temporal dynamics of the system. For example, output from a previous mass-balance model of trace metals in Saginaw Bay indicated an annual accumulation of zinc into the sediments (Dolan and Bierman, 1982). However, the model output also indicated that zinc fluxes could range from + 5000 kg/day (into the sediment) to – 5000 kg/day (out of the sediment). This model was hampered by a lack of direct measurements on sediment and porewater chemistry, and the erratic nature of the daily sediment fluxes likely indicated that the model was poorly constrained with respect to the chemical dynamics of benthic sediments. Nevertheless, these model results underscore the potential pitfalls of the estimates presented here regarding annual releases of metal from benthic sediments.

One additional caveat to the estimates presented above is that the potential effect of dissolved organic matter (DOM) on porewater chemistry has not been taken into account. The benthic fluxes were estimated according to the concentration of the free metal ion in solution, which was calculated using the computer code WATEQ4F (Ball and Nordstrom, 1991). In general, the percent free cadmium, copper and zinc in solution were 90%, 5% and 55%, of the total dissolved metal concentration, respectively. DOM concentrations in these porewater samples are not available, and, generally, a substantial proportion of dissolved metals in porewater are associated with organic ligands (van den Berg and Dharmvnaaj, 1984). Complexation of porewater copper with DOM is a

probable control on the molecular diffusion of copper in porewaters (Elderfield, 1981; Widerlund, 1996). If this mechanism is applicable to all metals in this study, the effect would be to diminish benthic fluxes, as the velocity of organically-complexed metals is one to two orders of magnitude slower than that of the free metal ion in solution (Elderfield, 1981).

In this study, diffusive transport of organically-complexed metals was simulated according to the approach of Widerlund (1996) in order to estimate the mitigating effect of DOM on benthic metal fluxes. In natural systems, the diffusion coefficient for the organically-complexed metal will vary widely, depending on the molecular weight of the DOM. The value used in this study represents an average of diffusion coefficients reported for DOM over the range of 1000 to 10000 daltons (Widerlund, 1996). The entire amount of the calculated free trace metal ions (according to the WATEQ4F output) is assumed to be complexed by DOM. Previous studies have shown that greater than 90% of the dissolved zinc in interstitial waters is complexed by DOM (van den Berg and Dharmmvanij, 1984). The load of organically-complexed zinc released from the Saginaw Bay depocenter is approximately 11500 kg zinc/a; copper and cadmium fluxes are not as significantly affected. Even after accounting for the blank, %free and possible influence of DOM, the benthic fluxes calculated for zinc are substantial, especially when compared to the previously determined sediment accumulation rate for zinc over the *entire bay* – 86 metric tons/a (Robbins, 1986).

A mass-balance model was constructed to evaluate the influence of benthic fluxes on metal cycling in Saginaw Bay. The primary inputs considered in a previous mass balance were tributaries (i.e., the Saginaw River) and atmospheric deposition (Dolan and Bierman, 1982). This study sought to update estimates of metal loads derived from these inputs based on more recent measurements (e.g., MDNR, 1988; Moll et al., 1995; Sweet et al., 1998). In addition, the mass balance constructed in this study includes inputs from water exchange with Lake Huron as well as from benthic fluxes of metals to the Saginaw Bay water column.

Atmospheric deposition rates of metals to Saginaw Bay were taken from the Integrated Atmospheric Deposition Network (IADN) in Sweet et al. (1998). Atmospheric deposition rates of cadmium did not vary much among the IADN stations whereas copper and zinc varied over twofold and threefold, respectively. The most conservative deposition rates were used in the mass balance; the larger deposition rates do not significantly affect the results. Atmospheric fluxes of cadmium, copper and zinc to Saginaw Bay are estimated at 1.3, 5.5, and 17.8 metric tons/a, respectively. These new fluxes are comparable to previous estimates (Dolan and Bierman, 1982).

Tributary inputs were calculated by approximating mean total (dissolved plus particulate) metal concentrations from Moll et al. (1995). Cadmium was not considered in that study, thus, concentrations were estimated from water column concentrations near the mouth of the Niagara River (Nriagu et al., 1996), a river similarly degraded by anthropogenic activities. The tributary inputs for cadmium, copper and zinc to Saginaw

Bay are calculated to be 0.2, 21, and 93.7 metric tons/a, respectively. These tributary fluxes for cadmium and zinc are significantly lower than those determined by Dolan and Bierman (1982).

Given the large volume of water exchanged annually between Lake Huron and Saginaw Bay (Richardson, 1974), Lake Huron could be a significant source of trace metals to Saginaw Bay. Concentrations of metals in Lake Huron were estimated from measurements of the open waters of the Great Lakes (Nriagu et al., 1996). The average cadmium, copper, and zinc concentrations in Lake Huron used in the mass balance are 1, 900, and 100 ng/L, respectively. The rate of water exchange between Lake Huron and Saginaw Bay was taken from Richardson (1974). The annual input of the metals cadmium, copper and zinc from Lake Huron to Saginaw Bay is 0.2, 180, and 20 metric tons/a, respectively.

The results of the mass balance are shown in Figure 63. The percent contribution derived from benthic fluxes to the Saginaw Bay water column are given in Table 12. Benthic fluxes of cadmium and zinc comprise a significant portion of the total inputs to Saginaw Bay, whereas benthic fluxes of copper apparently represent a negligible input. Copper input to Saginaw Bay is dominated by exchange with Lake Huron. Copper is present in the Great Lakes water column at much greater levels than the other metals, probably owing to the high affinity that copper has, relative to the other metals, for complexing with DOM. Zinc loading is dominated by tributary input, but benthic zinc fluxes are comparable inputs from atmospheric deposition and Lake Huron. Benthic

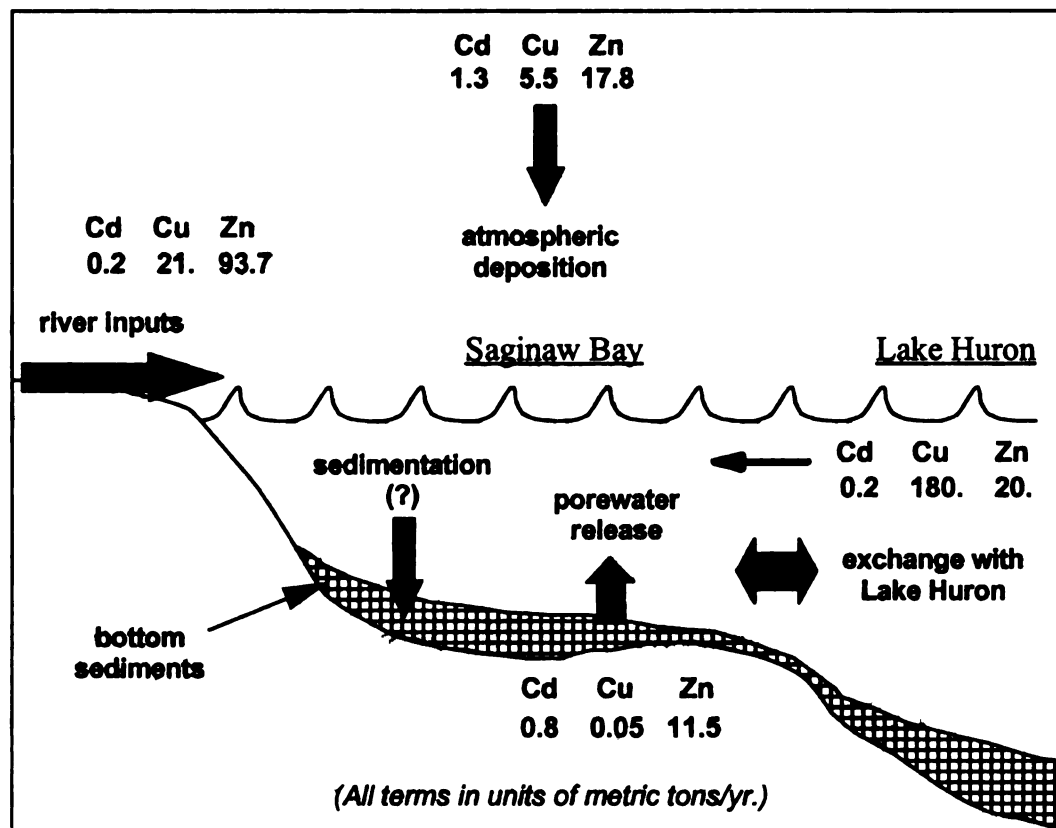


Figure 63. Trace metal mass balance for Saginaw Bay.

Table 12. Estimated Benthic Flux Metal Loads to Saginaw Bay.
(All entries in units of metric tons/yr.)

Metal	Σ_{inputs}	Benthic Flux	% of Total
Cd	2.4	0.8	33. %
Cu	206.55	0.05	0.02 %
Zn	143.	11.5	8. %

cadmium fluxes account for nearly one third of the total load to the Saginaw Bay water column; atmospheric deposition is apparently the largest single source for cadmium. The crudeness of this mass balance is acknowledged: the simplifying assumptions and extrapolations made in lieu of direct measurements understandably limit the accuracy of the calculated loading rates. Furthermore, in several of the cores used in the benthic flux estimates, $C_i \text{ max}$ occurs at 1 to 2 cm below the sediment-water interface. At this shallow depth, diffusion will likely dissipate the porewater-trace metal gradient in only a matter of days. Unless additional metals are released from sediment occurs and at a sufficient rate –not evaluated in this study– the benthic flux of metals from the sediment to the water column will rapidly decrease to zero. Thus, it is probably more appropriate to express the benthic flux term *per diem* rather than *per annum*. This change does not necessarily affect the relative significance of benthic fluxes in the trace metal mass balance (Table 12), but constrains the temporal duration of this particular input. Despite these limitations, this model clearly demonstrates that benthic fluxes of cadmium and zinc *could be* a substantial source of metals to the Saginaw Bay water column.

Potential for saline remobilization of sediment-bound metals

Regional discharge of saline ground water to Saginaw Bay could significantly increase benthic metal fluxes and alter metal cycling within the bay. For example, solubilities of cadmium, copper and zinc are augmented by the formation of chloro-metal complexes (Long and Angino, 1977). Increases in the ionic strength of porewater as a result of saline discharge could also remobilize metals from sediments as additional

major cations (e.g., sodium) outcompete trace metals for exchange sites (Puls et al., 1991; Turner, 1996). Furthermore, increases in porewater salinity will reduce formation constants for metal-DOM complexes, enhancing the diffusive velocity of trace metals and increasing benthic releases of metals to the water column (Vandenburg and Dharmvanij, 1984). Saline-water enhanced release of sediment-bound metals to Saginaw Bay could be especially problematic, given that the bulk of the anthropogenic metal burden resides in the uppermost portion of the sediment column, where present porewater-chloride concentrations are generally low (Figure 64). Chloride concentrations exceeding 20,000 mg/L have been documented in near-surface ground water from the Saginaw Lowland Area (SLA) (Wahrer et al., 1996), and it is conceivable that water with a similar chemistry is discharging into Saginaw Bay. Thus, in the future, the combination of diffusive transport of chloride (upward) and sediment burial will expose anthropogenic sediment-bound metals to more concentrated pore fluids. The amount of metals potentially released by this interaction, and the significance of such release on benthic metal fluxes requires further consideration.

The results from the SCEs of benthic sediments may help resolve these questions. The fluid used in the EX extraction, which is essentially a magnesium-chloride brine, may be useful as a proxy for the saline ground water entering Saginaw Bay. The chloride concentration and ionic strength of solution used in the EX extraction (~70,000 mg/L and 3.0, respectively) are significantly greater than what has been recorded thus far in Saginaw Bay porewater (~700 mg/L and 0.003, respectively), but comparable to the most concentrated fluid documented by Wahrer et al. (1996) in the glaciofluvial aquifer

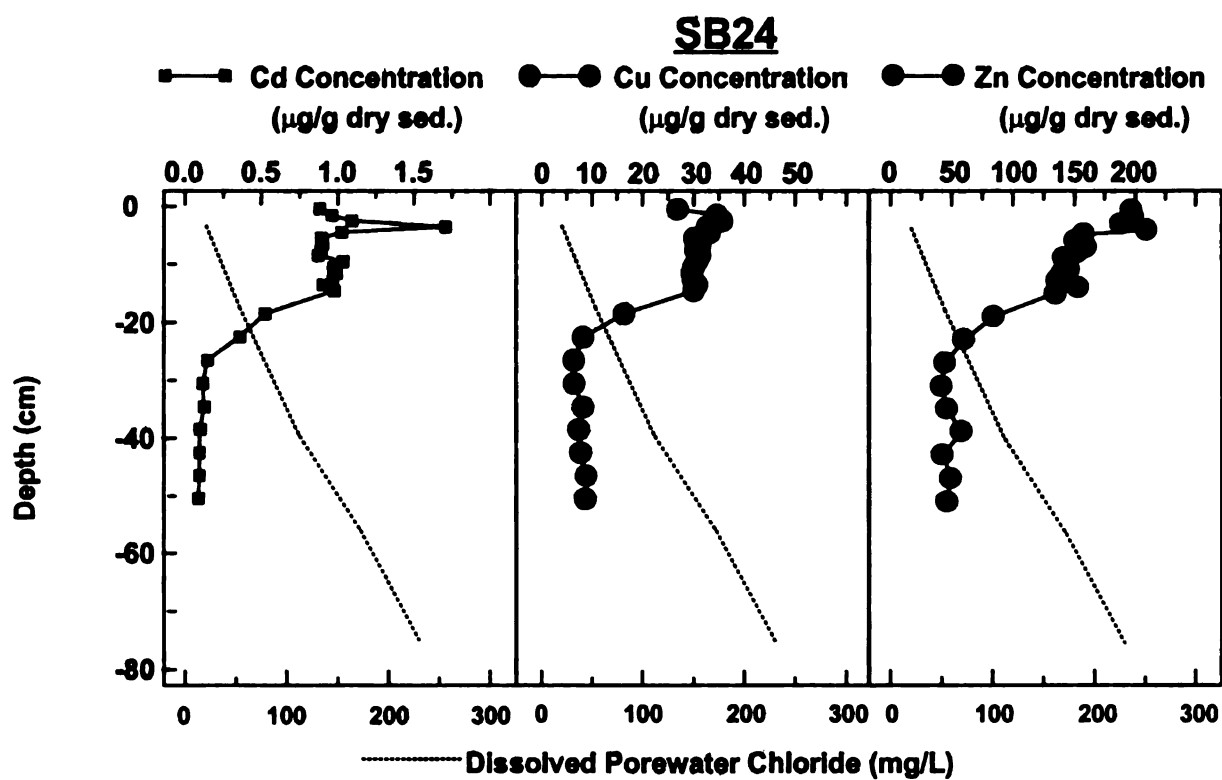
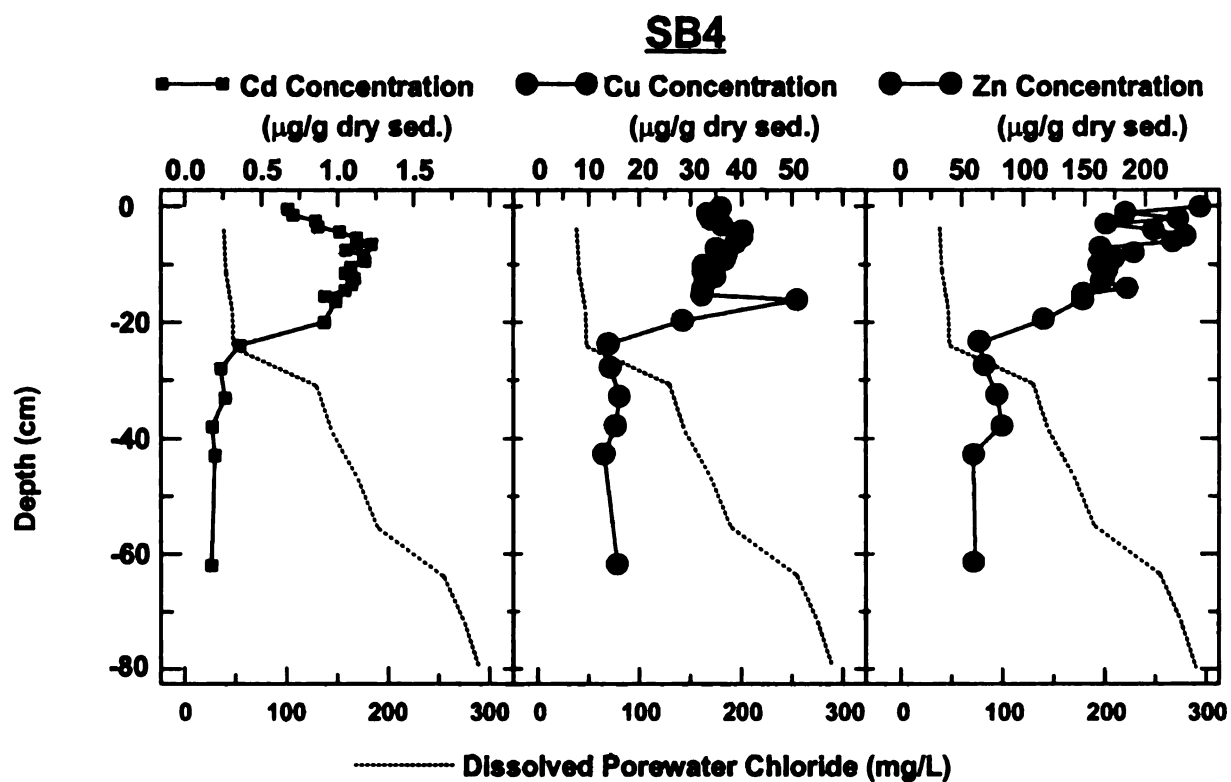


Figure 64. Comparison between profiles of porewater-chloride concentrations (dashed lines) and sediment-metal concentrations (solid lines) in cores SB4 and SB24.

(>20,000 mg/L and 1.8). Thus, the concentration of metals measured in the EX fraction might provide an upper-bound estimate of metals that could naturally be released to saline porewater.

Table 13 shows the projected concentrations of cadmium, copper, and zinc in porewater, using the EX fraction as a proxy to simulate the exposure of Saginaw Bay sediments to saline porewater. These projected porewater concentrations are based on trace metal concentrations measured in the EX fluid, normalized to the initial porosity of the sediment sample. The amount of metal extracted from the surficial sediments during the EX step corresponds to porewater concentrations as high as 38 µg/L Cd and 274 µg/L Cu; there was no detectable zinc in all but one of the EX extraction solutions. The projected cadmium and copper concentrations listed in Table 13 are generally much larger than what was actually measured in the porewaters, indicating that sediment exposed to higher salinities would release additional metals to porewater. The data in Table 13 apparently indicate that there would be no significant release of zinc to porewater. However, this result might also be an artifact from the analyses: the low sensitivity of the flame-AAS analyses for zinc, combined with the high background of the method blanks, may be responsible for the essentially negligible blank-corrected zinc concentrations. Manganese releases to porewater (not shown) were also substantial, as demonstrated by the large portion of manganese associated with the EX fraction (Figure 50). Simulated porewater manganese concentrations generally ranged from 100-300 mg/L.

Table 13. Use of the EX Fraction as a Proxy to Simulate the Effect of Saline Porewater on Trace Metal Remobilization from Sediments

Sample	Depth (cm)	<i>Projected Concentrations in Porewater</i>		
		Cd (µg/L)	Cu (µg/L)	Zn (µg/L)
SB22-1	-0.5	29	126	0
SB22-2	-1.5	16	0	0
SB22-3	-2.5	16	62	0
SB22-4	-3.5	10	73	1415
SB22-5	-4.5	11	19	0
SB22-6	-5.5	9	0	0
SB22-12	-11.5	1	53	0
SB22-16	-18.5	18	61	0
SB22-20	-34.5	3	30	0
SB22-24	-50.5	4	0	0
SB19-1	-0.5	5	274	0
SB19-2	-1.5	38	49	0
SB19-3	-2.5	5	0	0
SB19-4	-3.5	10	0	0
SB19-5	-4.5	0	73	0
SB19-6	-5.5	0	0	0
SB19-12	-11.5	0	23	0
SB19-16	-18.5	0	182	0
SB19-20	-34.5	0	87	0
SB19-24	-50.5	0	87	0

Assuming the EX extraction is a suitable proxy for saline ground water from the SLA, the projected trace metal concentrations in porewaters are used to estimate benthic fluxes of metals to Saginaw Bay. No benthic fluxes for zinc could be calculated, as there was no detectable zinc in the EX extraction. The benthic fluxes for cadmium and copper, as a result of saline ground-water discharge to Saginaw Bay sediments, are estimated at 3.9 and 21.5 metric tons/a, respectively. In both instances, benthic metal fluxes influenced by saline water are significantly greater than in the current freshwater condition. The benthic copper flux actually increases by over two orders of magnitude, whereas the benthic cadmium flux increases by a factor of five. Despite the dramatic increase in benthic copper flux, the influence of this flux on the total load of copper to the Saginaw Bay water column is relatively small, resulting only in approximately a 10% increase. The annual load of cadmium to the water column, however, would nearly double as a result of the new benthic flux. Thus, although saline ground water discharge to Saginaw Bay sediments might liberate substantially more copper than cadmium, it would appear that only the cadmium cycle in Saginaw Bay would be strongly affected.

CONCLUSIONS

Trace metal loading histories recorded in Saginaw Bay benthic sediments (sampled in 1994) show that surficial sediments are enriched in manganese and zinc relative to deeper sediments. Histories for iron, cadmium and copper generally contain buried maxima and may indicate that loading has decreased to the present. A comparison of metal concentrations in surficial sediments from this study and a previous one (1986)

indicates a dramatic reduction in cadmium levels in recent sediments, whereas manganese and zinc have undergone marked increases; iron and copper levels are comparable between the two studies.

Metal partitioning in benthic sediments was studied using a sequential chemical extraction procedure modified from the original Tessier method. Results from these extractions were used in conjunction with geochemical modeling results for porewater chemistry to evaluate major processes controlling trace metal diagenesis. Iron partitioning is relatively uniform among the cores studied; the RES fraction contains the largest portion of the total iron present. Manganese is largely associated with the EX and WAS fractions, implying that oxyhydroxides are not the dominant form of manganese in sediments. Profiles of porewater manganese and total manganese in sediments indicate significant remobilization of manganese is occurring; such postdepositional remobilization is consistent with previously proposed models of manganese diagenesis. Porewater concentrations of cadmium, copper and zinc indicate significant remobilization of these metals occurs in surficial sediments. Although phase associations vary widely among cadmium, copper, and zinc, sequential chemical extraction data indicate that all three metals undergo significant changes in partitioning as a result of early diagenesis. As depth in the sediment column increases, each of these metals becomes increasingly associated with more refractory phases. Carbonate mineral precipitation may be important in regulating iron and manganese levels in porewater, whereas pure carbonate phases do not appear to be a viable control on porewater concentrations of cadmium,

copper and zinc. Zinc concentrations in porewater may be regulated by precipitation with silica as an amorphous phase.

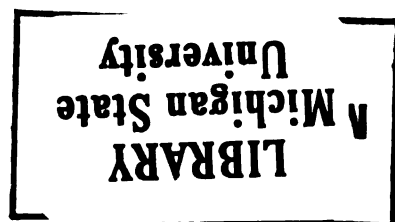
The sequential extraction procedure used in this study did not adequately resolve the distribution of iron in sediments, apparently the result of the inability of the procedure to extract crystalline iron oxides (e.g., Fe_3O_4). Although iron present in such forms may not be biologically available, this result contradicts the partitioning scheme originally proposed by Tessier et al. (1979). The selectivity of this sequential chemical extraction procedure for organic matter was tested using a certified, natural organic matrix. Trace metals associated with this matrix were generally liberated well before the target extraction step, indicating that sequential chemical extractions may underestimate the importance of metal-organic associations in sediments due to the premature release of metals. The results of this study indicate that the sequential chemical extraction “phases” require more definitive characterization in order to yield tenable assessments of trace metal partitioning in sediments.

Profiles of dissolved trace metal concentrations in porewaters indicate benthic releases of cadmium, copper and zinc to the overlying Saginaw Bay water column. A trace metal mass balance was constructed to evaluate the significance of benthic fluxes on trace metal loading: benthic fluxes of cadmium and zinc comprise substantial portions of the annual inputs to the Saginaw Bay water column. Data from the sequential chemical extraction procedure were used to simulate regional discharge of saline groundwater to Saginaw Bay. The results of this simulation indicate that saline ground

water could substantially increase benthic fluxes of cadmium and copper, but that only the cadmium cycle would be strongly impacted by this release.

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AN EVALUATION OF GROUND WATER-SURFACE WATER
INTERACTIONS IN SAGINAW BAY, LAKE HURON, WITH
IMPLICATIONS FOR TRACE METAL CYCLING

VOLUME II

By

Jonathan James Kolak

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Geological Sciences

2000

CHAPTER IV.

Regional significance of saline ground-water inputs to the Great Lakes:

Implications for chloride cycling and Michigan basin hydrogeology

INTRODUCTION

Water quality in the Great Lakes has been monitored for a number of years, and the observed build-up in dissolved solids levels has prompted concerns regarding chemical inputs to the lakes (e.g., Beeton, 1970). One chemical that has been the focus of numerous studies is chloride (Ownbey and Willeke, 1965; Tiffany et al., 1969; Rumer et al., 1974; Bowden et al., 1981; Rockwell et al., 1989). Increases in dissolved chloride levels have been primarily attributed to releases from municipal water treatment facilities and the use of salt (e.g., halite) as a road-deicing agent (Sonzogni et al., 1983; D'Itri, 1992). Researchers have used mass balances to study chloride cycling in the Great Lakes (Tiffany and Winchester, 1969; Richardson, 1974; Sonzogni et al., 1983), but none of these mass balances has included chloride inputs from ground water. This potentially significant source for solutes has been largely neglected due to the difficulties in quantifying regional ground-water inputs to the Great Lakes (Cherkauer et al., 1992). As a result, lake sediments have generally been considered as *chemical sinks*, rather than *chemical sources* (Tiffany and Winchester, 1969; Lerman and Weiler, 1970), except in instances where early diagenesis promotes a benthic flux of chemicals (e.g., metals) from sediment to the water column (e.g., Robbins, 1986; McKee et al., 1989a). More recent studies of porewater chemistry in the Great Lakes' region have documented significantly elevated chloride concentrations within a few meters of the sediment-water interface (Drimmie et al., 1992; Kolak et al., 1999), thus demonstrating the need to reconsider the role of ground-water, large lake interactions in chemical cycling.

Studies of ground-water quality in Michigan have shown that transport of saline water may be occurring on a regional scale. In addition to Saginaw Bay (Kolak et al., 1999) and the surrounding Saginaw Lowlands (Long et al., 1988), a number of shallow (<100m depth) wells in the Michigan Lowlands also contain groundwater with elevated total dissolved solids levels (Lane, 1899; Dannemiller and Baltusis, 1990). Although the distribution of saline groundwater in the Michigan Lowlands is not as well defined as it is in the Saginaw Lowlands (Ging et al., 1996; Meissner et al., 1996; Wahrer et al., 1996), the cause of the salinity in the Michigan Lowlands may be similar to the mechanism inferred for the Saginaw Lowlands (i.e., migration of fluids out of the Michigan Basin). If this hypothesis were correct, then near-surface groundwater quality in both areas would appear to be a function of basin-scale hydrogeology.

The ability to quantify ground water transport on a regional scale and combine this knowledge with geochemical data is paramount to the understanding of chemical cycling in the Great Lakes. For example, Cartwright et al. (1979) have documented upward fluxes of ground water in southern Lake Michigan sediments, and estimated that direct ground-water discharge comprises approximately 10% of the total hydrologic input to Lake Michigan. Although this may appear to be a “minor” contribution, studies of ground-water, lake interactions on a smaller scale have shown that, at comparable hydrologic inputs, ground water can be the dominant source for solutes to a lake (e.g., Kenoyer and Anderson, 1989). However, Cartwright et al. (1979) did not record companion measurements of water chemistry, and thus an estimate of the effect of this discharge on solute loading to Lake Michigan cannot be made. Conversely, Callender

(1969) has detected the saline water in Lake Michigan sediments, although transport of this water was not addressed. Cherkauer et al. (1992) have successfully linked geochemical data with a ground-water flow model to evaluate the effect of ground-water discharge from the Door Peninsula to bays located along the western Lake Michigan coastline; the chloride flux resulting from such discharge readily overwhelmed chloride inputs derived from atmospheric deposition. However, Cherkauer et al. (1992) could not construct a mass balance to evaluate the significance of these inputs on Lake Michigan owing to “the variation of hydrogeologic conditions around the lake’s perimeter.”

The need to assess present and predict future quality and availability of ground water in Michigan has provided the impetus for a regional study of the geology, geochemistry, and hydrogeology of the Michigan basin as part of the U.S. Geological Survey Regional Aquifer System Analysis (RASA) initiative (e.g., Mandle and Westjohn, 1989; Westjohn et al., 1994; Ging et al., 1996; Wahrer et al., 1996). One of the major products of this research effort is the development of a regional ground-water flow model (Hoaglund, 1996). Model simulations have shown that ground-water flow tends to be focused toward low-lying areas, such as the Saginaw and Michigan Lowlands. However, the rate of ground-water discharge to Saginaw Bay is relatively small ($\sim 1.13 \text{ m}^3/\text{s}$, ~ 40 cfs; Hoaglund, 1996); the rate of discharge to Lake Michigan is significantly greater. The model output also enables the construction of a revised chloride mass balance for Saginaw Bay, one in which ground water inputs are incorporated. The fact that significantly more ground water (possibly saline?) may be discharged to Lake Michigan

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also underscores the need for a more thorough characterization of porewater chemistry and the source for solutes in Lake Michigan sediments.

The potential regional-scale transport of solutes derived from formation brines is an important process to identify. Jessop and Majorowicz (1994) assert that there is little topographic drive for fluid flow in the Michigan basin. Furthermore, borehole temperature residuals, when corrected for the local geothermal gradient, show no significant redistribution of heat that could be attributed to fluid flow (Speece et al., 1985). These results tend to imply that Michigan basin brines are largely stagnant and transport of brine solutes is extremely limited, as has been found for other intracratonic basins (Pinti et al., 1997). If this scenario is applicable to the Michigan basin, then how does one explain the porewater chemistry observed in Saginaw Bay (Chapter 1) and in Lake Michigan (Callender, 1969)? By investigating the spatial variations in porewater chemistry and identifying the source for solutes in porewaters from Saginaw Bay and Lake Michigan, can one infer the major process controlling fluid flow within the Michigan basin in order to account for the distribution of near-surface saline water?

The overall goal of this study was to evaluate ground-water, large-lake interactions between the Michigan basin and the Great Lakes (Saginaw Bay and Lake Michigan). Lee et al. (1980) injected a chloride tracer into lake sediments to study the seepage flux through the sediment-water interface and evaluate ground-water, lake interactions. In this study, porewater chemistry (e.g., chloride) was used as a “natural tracer” for saline water in order to elucidate ground-water, lake interactions.

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Geochemical data was integrated with output from a regional-scale ground-water flow model (Hoaglund, 1996) to estimate solute fluxes to Saginaw Bay and evaluate the influence of ground water on lake hydrochemistry. Porewater chemistry in Lake Michigan sediments was studied to ascertain the source for solutes and identify potential contributions from saline ground water. Results from Saginaw Bay and Lake Michigan were then combined to develop a conceptual model accounting for the distribution of saline water in near-surface sediments.

METHODS

Sediment cores

The porewater chemistry data presented in this study were obtained from four different sets of sediment cores. One set of gravity cores was collected from Saginaw Bay in 1994 aboard the R/V *Laurentian* (see Chapter 1). Three sets of sediment cores were used to evaluate spatial variations in porewater chemistry of Lake Michigan sediments. One Lake Michigan data set is from Callender (1969). The 1969 study focused primarily on sediment geochemistry, however, porewater chemistry data were also collected and subsequently published in order to evaluate mineral-water equilibria (e.g., carbonates). As a result, this expansive data set also provides a substantial amount of information regarding porewater chloride concentrations. At some sampling stations, there appear to be significant gradients in porewater chloride concentrations ($Cl_{\max} \sim 400$ mg/L), indicating a high-chloride source at depth. Callender (1969) postulated that

clay membrane filtration might have played a role in generating the elevated chloride levels, but did not specifically resolve this issue, as it was outside the original scope of the study. Bromide concentrations were not measured in the 1969 study, and Cl:Br ratios thus cannot be used to evaluate salinity sources.

To supplement the data from Callender (1969), a suite of box cores collected from Lake Michigan in 1991 and 1992 aboard the R/V *Lake Guardian* (Heft, 1993) were analyzed for interstitial concentrations of chloride and bromide. The 1991 and 1992 box cores do show increasing porewater chloride concentrations with depth, but are generally much shorter than the Callender (1969) cores and thus do not record porewater with significantly elevated chloride levels ($\text{Cl}_{\text{max}} \sim 40\text{mg/L}$). As a result, a third set of Lake Michigan sediment cores was recently collected. In 1999, a suite of gravity cores was collected from Lake Michigan aboard the R/V *Lake Guardian*; stations from both the 1969 and 1991-92 data sets were re-occupied in order to provide a uniform data set. At the time of this writing, porewater sodium concentrations are the only data available from the 1999 cores.

The 1991-92 and the 1999 Lake Michigan sediment sampling stations are shown in Figure 65. A number of these stations occupy sites that are part of the Environmental Protection Agency's (EPA) monitoring network for Lake Michigan; the equivalent EPA station identification labels are also given. Samples from the 1991-92 cruises were initially stored in centrifuge tubes and frozen. For this study, the 1991-92 samples were thawed overnight at room temperature, and centrifuged for 10 minutes at 10,000 rpm.

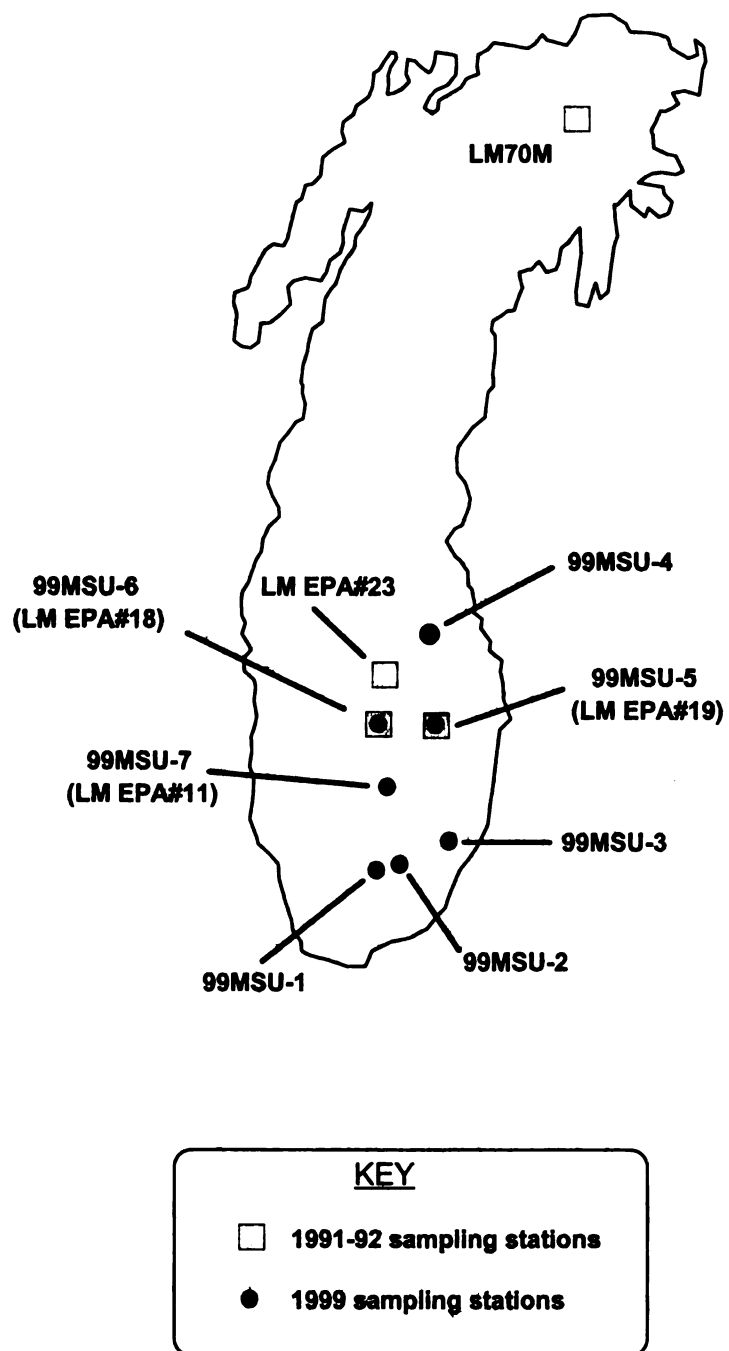


Figure 65. 1991-92 and 1999 Lake Michigan sampling stations.

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The supernatant (i.e., porewater) was decanted and filtered through Millex-HA® 0.45µm disposable filters and stored in precleaned polypropylene bottles. Dissolved chloride and bromide concentrations were determined using High Performance Liquid Chromatography (HPLC) on a Dionex 4000I ion chromatograph equipped with an AS4A column and suppressed conductivity detector. The 1999 Lake Michigan cores were squeezed in a stainless steel compressor, and the extracted porewaters were processed according to the same protocols used in the 1994 Saginaw Bay study (see Methods; Chapter 1). Porewater sodium concentrations were determined via atomic emission spectrophotometry with an air-acetylene flame. Excess potassium was added to samples immediately prior to analysis to mask interferences. Calibration accuracy was externally checked by analyzing aliquots of NIST-certified SRM 1643d (Trace Elements in Water).

Benthic Flux estimates

Porewater-chloride profiles from Saginaw Bay sediments generally show increasing chloride concentrations with depth, indicating that the flux of chloride is upward from the sediments into the water column (Chapter 1). The diffusive flux of porewater chloride to the water column was calculated using Fick's First Law (e.g. Berner, 1980):

$$F = -\Theta * D_e * dC/dz, \quad (13)$$

where F is the flux of solute of interest (mg/m²/s), Θ is the porosity of the sediments, D_e is the effective molecular diffusion coefficient, and dC/dz is the porewater-chloride

concentration gradient with depth in the sediment. An average value of 0.9 was used to represent the porosity of Saginaw Bay sediments. A value of $1.62 \times 10^{-5} \text{ cm}^2/\text{sec}$ was used for D_e in flux calculations; this value is comparable to those reported by other studies investigating chloride diffusion in lacustrine sediments (Lerman and Weiler, 1970; Effler et al., 1990). Porewater-chloride concentrations in Saginaw Bay sediments generally increase linearly with depth (Chapter 1). The porewater-chloride gradient, dC/dz , was therefore determined from the slope of a linear regression between chloride concentration and depth.

A number of processes including adsorption, sediment burial and compaction can significantly affect porewater-solute transport (Morse, 1974; Berner, 1980). Tidal pumping of Saginaw Bay sediments likely is another significant influence on porewater fluxes, especially owing to the strength of seiche activity within Saginaw Bay (Allender and Green, 1976). Bioturbation will also affect solute exchange between sediments and the Saginaw Bay water column; benthic organisms are known to mix Saginaw Bay sediments as deep as 10 cm below the sediment-water interface (Robbins, 1986). All these processes combined will likely increase the efficacy with which chloride is released to the water column and thus, the calculated diffusive fluxes are considered to be conservative estimates of the amount of chloride released into the water column.

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RESULTS AND DISCUSSION

A Chloride Mass Balance for Saginaw Bay

A chloride mass balance was constructed in order to quantitatively evaluate the significance of saline (i.e., derived from formation brine) ground-water inputs on Saginaw Bay hydrochemistry. The bold arrows in Figure 66 denote the chloride inputs that were considered in the mass balance. Note that indirect ground-water input of chloride (i.e., ground-water discharge to rivers as baseflow) was not quantified in this study. Although there is certainly some contribution of saline ground water to baseflow (Chapter 2), the ability to resolve this input is obscured by additional natural and anthropogenic contributions of chloride. As a result, the total chloride load derived from saline ground water in this mass balance is a conservative estimate.

Ground-water flow is generally focused towards Saginaw Bay (Mandle and Westjohn, 1989; Hoaglund, 1996), as has been documented at other coastal embayments (Cherkauer and McKereghan, 1991; Millham and Howes, 1994). However, the rate of ground-water discharge to Saginaw Bay is relatively low – approximately 40 cfs ($\sim 1.13 \text{ m}^3/\text{s}$) – likely due to the presence of glaciolacustrine sediments with low hydraulic conductivities (Hoaglund, 1996). 1-D simulations of porewater-chloride profiles in Saginaw Bay sediments (Chapter 1) also indicate that advection rates are very small, as chloride transport appears to be diffusion-dominated.

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Assigning a chloride concentration to this shoreline discharge that is representative of local ground water is an arduous task. Chloride concentrations in the glaciofluvial aquifer from the Saginaw Lowland Area (SLA) [defined here as the area immediately adjacent to Saginaw Bay: ~ 43-44.5°N, 83-84.5°W] range from 1 to 2,600 mg/L (Wahrer et al., 1996). Such elevated concentrations of chloride in ground water are frequently the result of anthropogenic activities (Hem, 1985). In this area, however, studies have documented that Michigan basin brine is mixing with water from the bedrock and near-surface aquifers and that this process is largely responsible for the elevated chloride concentrations reported (Long et al., 1988; Wahrer et al., 1996). The mean concentration of chloride in the glaciofluvial aquifer in the SLA is 430 mg/L (n=69), but is heavily influenced by the more concentrated samples. As a result, the median chloride concentration in this data set (180 mg/L) was used in the mass balance calculations. Given the median chloride concentration and the flow-model output, the daily chloride flux to Saginaw Bay derived from shoreline discharge is estimated at 17,570 kg/day.

An additional input of chloride derived from saline ground water is the benthic flux (i.e., “porewater release”; Figure 66) from the sediment to the Saginaw Bay water column. Results from Chapter 1 indicate that the elevated chloride levels in Saginaw Bay sediments are ultimately derived from formation brine, but were likely emplaced by transport of saline ground water. Porewater-chloride concentration gradients in Saginaw Bay sediments range from 1.0×10^{-4} to 4.7×10^{-3} mg/cm³/cm. From these gradients, an average benthic chloride flux of 23,540 kg/day was calculated using Fick’s First Law.

This estimate should be considered conservative as it represents only the inner portion of Saginaw Bay; similar porewater chloride gradients may be present in the outer bay, but previous attempts to core this portion of Saginaw Bay were unsuccessful.

The results of the mass balance calculations are shown in Table 14. The estimates of average river chemistry and daily discharge rate were compiled from data collected by the Water Resources Division of the U.S. Geological Survey. The exchange of water with Lake Huron constitutes the dominant (~70% of the total) chloride input to Saginaw Bay. The Saginaw River is the next most significant source for chloride, accounting for approximately 28% of the total daily load. The chloride loading rate from the Saginaw River is approximately half the loading rate reported in Richardson (1974), although monitoring efforts of chloride concentration in the Saginaw River have documented a significant decline in recent years (MDNR, 1988).

The cumulative influence of ground-water discharge (shoreline discharge plus benthic flux) on the Saginaw Bay water column is relatively small, accounting for approximately 1% of the total daily chloride load. The results from Richardson (1974) indicate that there may be a significant degree of uncertainty associated with the estimated rate of exchange between Saginaw Bay and Lake Huron. Although future modifications to this rate of exchange will probably not alter the fact that Lake Huron is the dominant source for chloride, such modifications could affect the relative significance of ground-water inputs. A more refined estimate of this exchange is therefore necessary to better constrain

Table 14. A Chloride Mass Balance for Saginaw Bay

Input	Period of Record	Mean Daily Discharge (m³/s)	Mean Chloride Concentration (mg/L)	Mean Daily Chloride Load (kg)	% of Total
Atmospheric					
Direct deposition (wet + dry)	1982-1984 **	-	-	2000	0.05
Exchange					
Lake Huron	-	6371.5***	5.5 †	3.03x10 ⁶	70.47
River					
Saginaw R.	WY 1991-1993*	198.2	70.	1.20x10 ⁶	27.91
Kawkawlin R.	WY 1976-1982*	1.8	70.	10,886.	0.25
Pigeon R.	WY 1987-1993*	2.7	49.	11,431.	0.27
Ground Water					
Shoreline discharge	-	1.13	180. (median)	17,570.	0.41
Porewater flux	-	-	-	23,540.	0.55
TOTAL	-	-	-	4.30x10⁶	
Sub-watersheds					
Chippewa R.	WY 1991-	11.2	25.	24,192.	0.56
Shiawassee R.	WY 1989-	18.0	42.	65,318.	1.52

* source: USGS-WRD

** source: MDNR (1988)

*** source: Richardson (1974)

† source: Rockwell et al. (1989)

hydrological and geochemical mass balances for Saginaw Bay. Nevertheless, it is noteworthy that the cumulative ground-water chloride flux exceeds chloride fluxes for several sub-basins (e.g., the Chippewa, Kawkawlin, and Pigeon Rivers) within the Saginaw Bay Watershed (Table 14).

Porewater chemistry in Lake Michigan sediments

Figure 67 shows profiles of porewater-sodium concentrations in the 1999 Lake Michigan cores. The profile from site SB4 from Saginaw Bay is also added for comparison; site SB4 has the highest porewater sodium concentration (470 mg/L) among the Saginaw Bay cores (Chapter 1). All 1999 Lake Michigan cores show increasing porewater sodium concentrations with depth, implying that the entire southern portion of Lake Michigan might be affected by a high-solute source at depth. Core 99MSU1 shows a dramatic increase in porewater sodium concentrations less than one meter below the sediment water interface. This site was collected during an attempt to reoccupy station S1-29 (Callender, 1969); the results from this study confirm the presence of the high sodium waters originally documented by Callender.

Not all cores from Lake Michigan show such increases in dissolved solids levels with depth. Combining the data from Callender (1969) and the 1991-1992 Lake Michigan cores reveals that porewater chloride concentrations decrease with depth at a number of locations (white circles; Figure 68). Of the cores with porewater chloride concentrations that decrease with depth, only one is found in southern Lake Michigan;

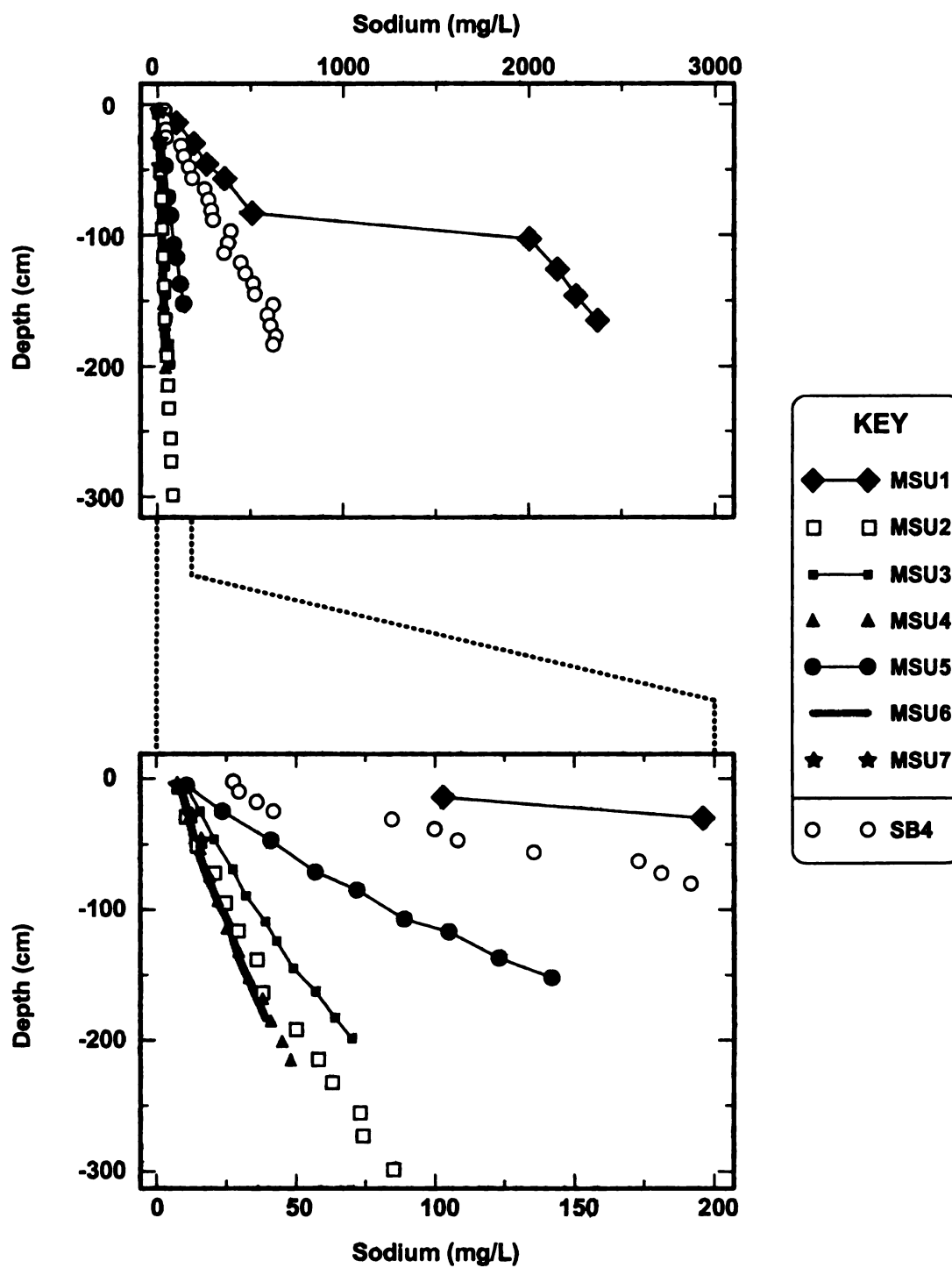


Figure 67. Porewater-sodium concentrations in 1999 Lake Michigan cores.
(Saginaw Bay core SB4 is added for comparison.)

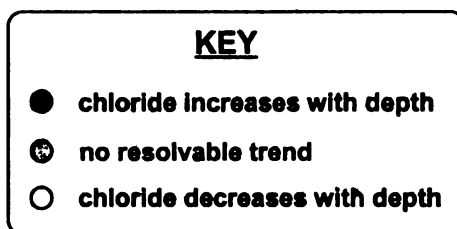
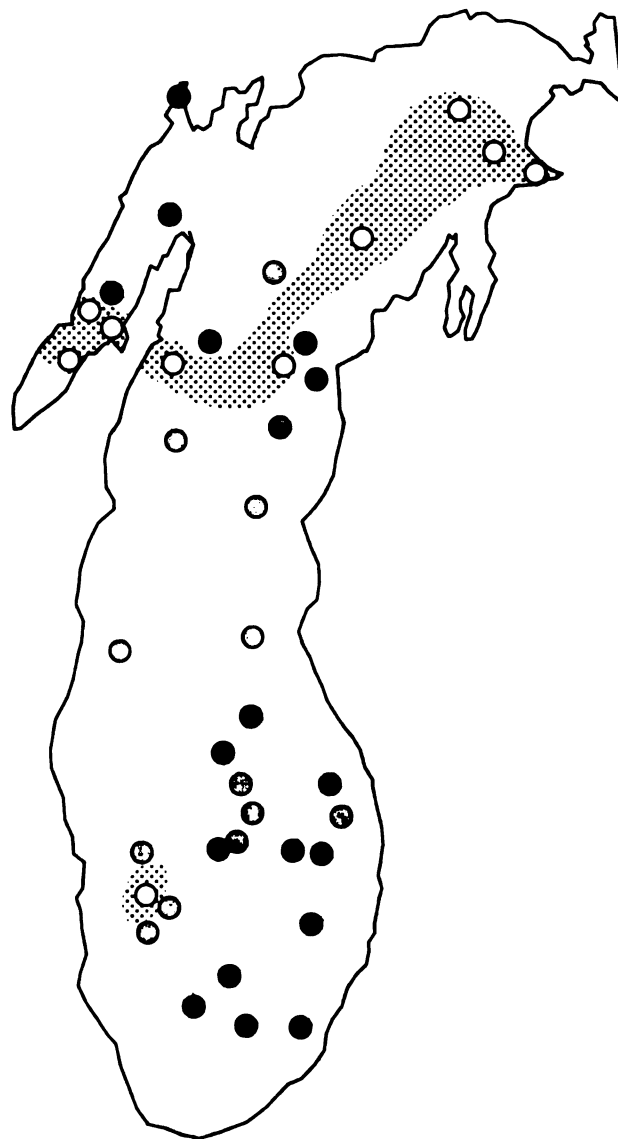


Figure 68. Trends in porewater chloride concentrations. *(Based on data from Callender(1969) and 1991-92 samples).*

the remaining cores are found in the northern portion of Lake Michigan. This trend of decreasing chloride concentrations with depth is interpreted to reflect the influence of anthropogenic inputs of chloride to the Great Lakes (Lerman and Weiler, 1970). Given that the average chloride concentrations among the Great Lakes have increased over the last 100 years as a result of anthropogenic activities (e.g., use of road deicers, and municipal and industrial discharges) (Lerman and Weiler, 1970; Rockwell et al., 1989), the major pathway by which chloride from these sources could enter the porewaters is via the overlying water column. Therefore, if anthropogenic inputs were the primary source for chloride to porewaters, then maximum chloride concentrations should occur near the sediment-water interface and subsequently decrease with depth.

A number of sediment cores indicated in Figure 68 show no resolvable trend (gray circles). This classification is not meant to imply that porewater chemistry does not change with depth. Rather, there is generally sufficient scatter in the porewater chloride profiles of these cores so as to preclude delineation of any trend with depth.

Source for elevated solute levels in Lake Michigan porewaters

Although these results demonstrate porewater chemistry – especially in southern Lake Michigan – has been influenced by saline ground water, they do not necessarily imply the influence of Michigan Basin brines. If the elevated dissolved solids levels concentrations are ultimately derived from Michigan Basin brine, then the porewaters should retain a geochemical signature that reflects brine input. In addition to Michigan

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basin brine, another potential source for chloride that warrants consideration is the dissolution of evaporite minerals, particularly halite (NaCl). Ground-water dissolution and transport of solutes derived from halite could significantly influence porewater chemistry.

Cl:Br ratios are frequently used to distinguish between brine and halite as sources for chloride because both ions are relatively conservative in solution (Whittemore, 1995; Land and Macpherson, 1992). The Cl:Br ratio (mg/L) in a solution that has congruently dissolved halite will be around 3,000 (Carpenter, 1978; Wilson and Long, 1985); brines will have a Cl:Br ratio significantly less than 3,000. Typical values of Cl:Br ratios from Michigan Basin brines, including those in the Pennsylvanian and Mississippian units, range between 400 and 600 (Long et al., 1988; Ging et al., 1996; Meissner et al., 1996). However, brines from the upper Devonian (e.g., Traverse Group) also warrant consideration, as the Devonian-aged formations appear to comprise a significant portion of the bedrock geology underlying Lake Michigan (Wold et al., 1981). Cl:Br ratios in brines from the Traverse Group range approximately from 70 to 230 (Wilson and Long, 1993).

Cl:Br ratios in porewater from Saginaw Bay sediments initially increase with increasing chloride concentrations and plateau at a value of approximately 500 (Figure 69), signifying that brine from Pennsylvanian- and/or Mississippian-aged units is the likely source for salinity. If simple halite dissolution were the source for chloride, then the Cl:Br ratios would continue to increase to a much higher value. Of all the Lake

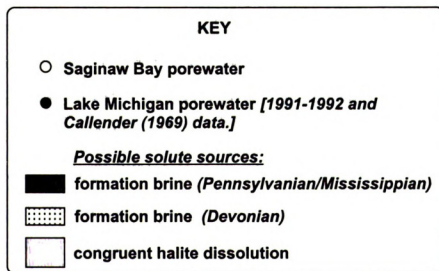
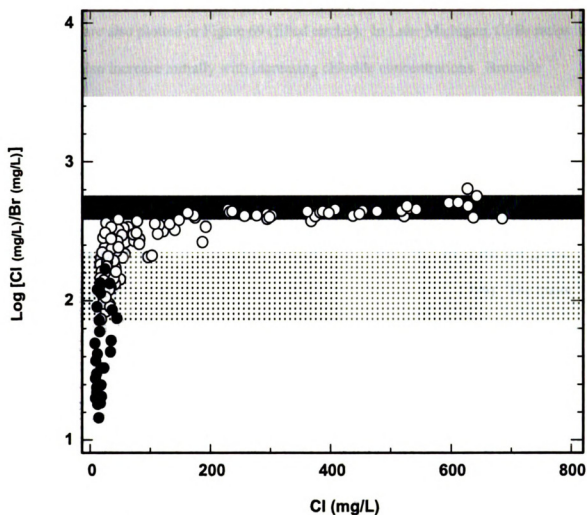


Figure 69. Cl vs. Cl:Br ratios in Saginaw Bay and Lake Michigan porewaters.

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Michigan samples, bromide data are only available for the 1991-1992 sediment cores. These data are also plotted in Figure 69 (filled circles). In Lake Michigan, Cl:Br ratios in porewater also increase initially with increasing chloride concentrations. Bromide concentrations from deeper (i.e., higher salinity) porewater samples are currently unavailable, hindering identification of the chloride source.

Alternatively, K:Cl (mg/L) ratios were used to evaluate the source for salinity, because potassium behavior is relatively conservative at chloride concentrations greater than 50 mg/L (Ging et al., 1996; Meissner et al., 1996; Wahrer et al., 1996). The major process affecting potassium concentrations in near-surface groundwater in the Michigan Basin is mixing between brine and meteoric water (Long et al., in press). Potassium concentrations in porewater are available for both the 1991-1992 and the Callender (1969) Lake Michigan cores; both of these data sets are plotted as filled circles on Figure 70. At high chloride concentrations, K:Cl ratios in the porewaters of Lake Michigan are similar to those in Saginaw Bay as well as in near-surface groundwater impacted by brine (gray-shaded area; Figure 70). This similarity among K:Cl ratios indicates that brine is also the source for the salinity in the Lake Michigan porewaters. The notion that both Lake Michigan and Saginaw Bay are affected by Michigan basin brines is supported by studies that have (1) documented the potential for upward flow of groundwater from Pennsylvanian, Mississippian, and Devonian units, (Mandle and Westjohn, 1989; Hoaglund, 1996) and (2) measured upward advective fluxes in porewaters from southern Lake Michigan sediments (Cartwright et al., 1979).

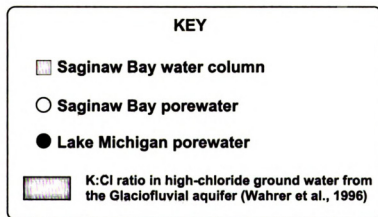
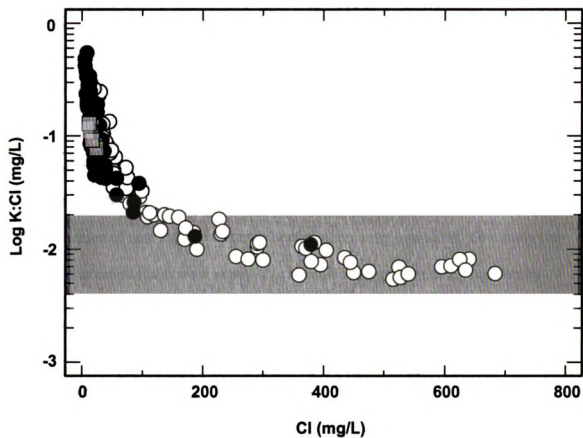


Figure 70. K:Cl ratios for Saginaw Bay and Lake Michigan porewater samples. (*Lake Michigan porewater data from Callender, 1969.*)

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Solute transport in the Michigan Basin

Given that porewater chemistry in sediments from both Saginaw Bay and Lake Michigan appears to have been influenced by inputs of saline water, what can one infer regarding solute transport in the Michigan basin? These porewater data and results from previous studies of ground-water geochemistry in the Michigan basin (e.g., Lane, 1899; Long et al., 1988; Weaver et al., 1995; Meissner et al., 1996; Wahrer et al., 1996) indicate that salinization of near-surface waters is occurring on a regional scale. One study has proposed that saline fluids were expelled as a result of flushing of basin aquifers by recharge from ice loading (Panno and Bourcier, 1990). Glacial loading would certainly have reversed flow and induced recharge into the bedrock aquifers that could have mixed with brines (Weaver et al., 1995; Hoaglund, 1996; Clark et al., 2000). However, rather than ice loading *directly* resulting in the expulsion of saline/isotopically-light water, it may also be that the *removal* of the hydraulic head (in response to ablation of the ice load) has resulted in the discharge of saline water—along the same pathways once preferentially recharged by the glacier—to the areas vacated by the ice (i.e., the Saginaw Lowland Area). Given the latter scenario, one could argue that the observed porewater chemistry in the Saginaw Bay area and southern Lake Michigan is merely the result of a “relict” hydrologic system, and that the Michigan basin is still attempting to equilibrate to the perturbation resulting from the ice loading.

Another possible explanation for the spatial distribution of saline water is that, given that these saline fluids are generally found adjacent to low-lying areas (Figure 71),

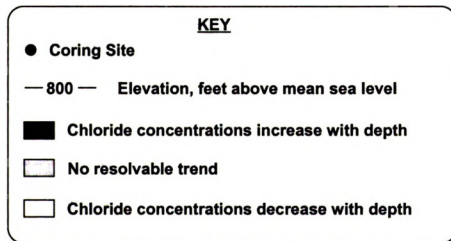
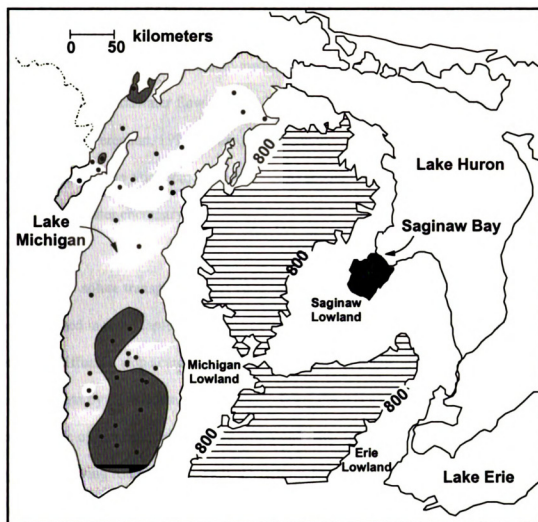
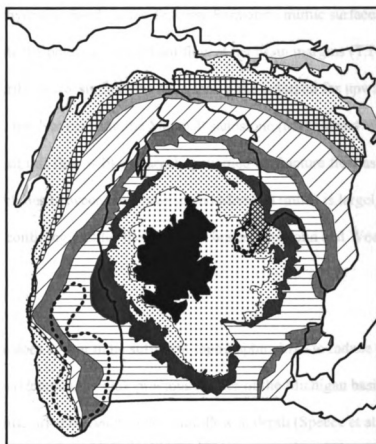


Figure 71. Regional trends in porewater-chloride concentrations with depth.

ground-water flow might be driven by topography. Topography can be an effective driving force, influencing fluid flow as deep as 5 km below the ground surface (Hitchon, 1969; Bachu, 1995). Furthermore, embayments and low-lying areas are known to locally focus near-surface groundwater flow into the Great Lakes (Mandle and Westjohn, 1989; Cherkauer and McKereghan, 1991). The question remains, is there sufficient topography to drive fluid flow in the Michigan basin in order to account for the observed spatial variations in porewater chemistry?

Although solute transport has not yet been simulated for the porewater chemistry profiles presented in this chapter, the shape of the porewater profiles (especially MSU-1) indicates that diffusion alone cannot account for the vertical solute gradients. Furthermore, data by Cartwright et al. (1979) indicate there is a significant hydraulic gradient capable of inducing upward flow of groundwater into Lake Michigan. Resolving the driving forces for such advective transport may be especially problematic, given that the highly saline Lake Michigan porewaters appear to overlie even deeper geologic strata, namely the upper Devonian (e.g., Traverse Formation) (Figure 72). [The bedrock geology presented in this figure represents a compilation of maps by Cvancara and Melik (1961), Wold et al. (1981), and Westjohn et al. (1994).] The influence of topography on fluid flow in deeper formations, such as the Traverse Formation (upper Devonian), is poorly understood. [Resolution of the drive for solute transport is further confounded by the fact that Cartwright et al. (1979) show that Mississippian formations



KEY



Areas of elevated porewater chloride in lake sediments

Jurassic "red beds"	Upper Devonian
Pennsylvanian & Upper Mississippian Parma Sandstone and Bayport Limestone	Middle Devonian
Mississippian Michigan Formation	Lower Devonian
Mississippian Marshall Sandstone	Upper Silurian
Lower Mississippian	Lower/Middle Silurian
	Upper Ordovician

Figure 72. Map of regional bedrock geology underlying study area.

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underlie the cores influenced by saline water.] However, calculations show that the equivalent freshwater hydraulic heads in the Traverse Formation mimic surface topography and indicate the potential for upward flow at the basin margins (T.P. Wilson, unpublished data). Furthermore, simulations have shown the potential for upward transport of fluid from the Traverse into the Marshall sandstone (Mandle and Westjohn, 1989); however, most of this flow is likely largely governed by fracture flow as the Coldwater shale –which lies between the Traverse and Marshall units– is largely considered a regional confining unit for the Michigan basin (Westjohn and Weaver, 1998).

Although there does appear to be sufficient topographic drive to induce regional flow in surficial layers (Hoaglund, 1996), previous studies of the Michigan basin tend to indicate that there is little drive or evidence for fluid flow at depth (Speece et al., 1985; Jessop and Majorowicz, 1994). Thus, despite the *potential* for upward flow (e.g., from the Traverse), the regional topography may not be sufficiently capable of transporting solutes (derived from formation brine) to account for the observed spatial variations in porewater chemistry. Furthermore, recent modeling efforts of fluid flow in the Michigan basin have shown that while topography does appear to exert a considerable influence on the glaciofluvial and Saginaw aquifer units, this influence is largely dampened out prior to reaching the Marshall aquifer unit, owing to the relative impermeability of the overlying confining units (e.g., the Michigan Formation) (Hoaglund, 1996). Preliminary analysis of flow-path travel times also indicates that flow paths which dip into bedrock units (and subsequently terminate in the glaciofluvial aquifer) are sufficiently long that

such travel paths are unable to generate the observed variations in near-surface water chemistry within a reasonable amount of time (i.e., since the last glacial advance) (Hoaglund, 1996).

Assuming topography is an insufficient driving force, what other mechanism could provide the impetus for advective transport of saline water into Lake Michigan? One possible explanation is that fluid displacement is driven by compaction (e.g., Bethke, 1985). Compaction-driven flow may be a plausible mechanism, as Wilson and Long (1993) hypothesized that brines in the Devonian strata were derived from the residual seawater squeezed from the deeper Silurian-aged salts during their compaction. If true, this process may have generated sufficient drive for fluid flow into Lake Michigan. Deformation of Salina salt beds (Silurian-aged) in response to glacial loading may also contribute to such advective fluid transport (White, 1992).

Figure 73 is a conceptual diagram for fluid flow in the Michigan basin constructed in an attempt to account for observed spatial variations in porewater chemistry. It should be noted that the arrows in this figure are not intended to denote specific flow paths, but rather indicate the likely solute transport process. Although both arrows A and B could account for the presence of saline water in the Saginaw Lowland Area, modeling results from Hoaglund (1996) tend to indicate that arrow A [advective transport only in the glaciofluvial aquifer; diffusive transport between the Saginaw and glaciofluvial aquifers] is more likely than B [advective transport between the Saginaw and glaciofluvial aquifers] (e.g., based on travel times). However, there does seem to be

x

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[☐ classical multiplier unit
☐ shadow multiplier unit]

x

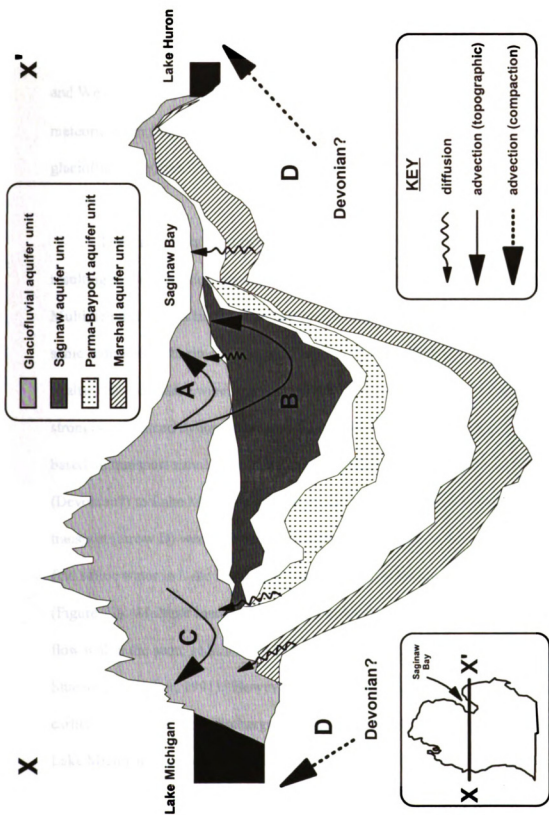


Figure 73. Conceptual diagram for regional fluid flow in the Michigan basin.
 (Base map from Hoaglund, 1996.)

some evidence that suggests arrow B is plausible. First, just west of the Saginaw Lowland area there is fresh water in the upper portion of the Saginaw aquifer (Westjohn and Weaver, 1996), and the stable isotope signature (i.e., $\delta^{18}\text{O}$) is comparable to modern meteoric water (Meissner et al., 1996), indicating recharge of recent water from the glaciofluvial aquifer.

There may be at least two different flow regimes within the Michigan basin resulting in the expulsion/transport of saline water to near-surface environments. Multiple mechanisms have previously been employed to account for fluid flow within the same sedimentary basin, such as the Illinois basin (e.g., Bethke, 1985; Stueber and Walter, 1991). Saline water transport in the uppermost layers and glacial deposits may be strongly influenced by topography, although diffusion also appears to play a major role, based on transport simulations (Chapter 1). Saline water transport from deeper units (Devonian?) to Lake Michigan may originate from compaction-driven flow. If such transport (arrow D) were occurring within Devonian-aged units, one might also expect to find saline water in Lake Huron and Lake St. Clair sediments where these units subcrop (Figure 72). Multiple mechanisms have previously been employed to account for fluid flow within the same sedimentary basin, such as the Illinois basin (e.g., Bethke, 1985; Stueber and Walter, 1991). However, one cannot rule out the possibility (mentioned earlier) that the apparent discharge of saline ground water in Saginaw Bay and southern Lake Michigan is merely the result of the continuing response of the Michigan basin to the perturbation from ice loading/removal. One could test this scenario by evaluating the $\delta^{18}\text{O}$ signature of the saline porewater from Lake Michigan. If the saline water contains

4.500

1.200

1.100

1.100

1.100

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1.100

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1.100

a modern meteoric signature, this could be interpreted as mixing between brine (transported by compaction-driven flow) and modern water. If the saline water contains a $\delta^{18}\text{O}$ signature that is significantly lighter than modern meteoric water, then one could argue that the observed porewater chemistry is the result of the fact that the Michigan basin has not yet reached equilibrium with the ice loading/removal perturbation.

Fractures likely exert a significant influence on the degree of communication/interaction between aquifer units at all levels within the basin. This factor is acknowledged in the modeling efforts of Hoaglund (1996) and Mandle and Westjohn (1989), and could account for the spatial variations in porewater chloride concentrations in Saginaw Bay sediments (Chapter 1). Furthermore, fracture flow likely accounts for the presence of documented saline springs (Houghton, 1838). These fractures could have developed in both the glaciofluvial sediments as well as the bedrock aquifer units, as a result of isostatic rebound stemming from load release due to glacial ablation resulted in reactivation of fractures. This mechanism was employed to account for the occurrence and distribution of saline water in near surface bedrock in the Erie Lowlands area (Weaver et al., 1995).

CONCLUSIONS

Recent development of a regional-scale ground-water flow model permits construction of a refined chloride mass balance model for Saginaw Bay. This model enables quantitative assessment of the effect of ground-water, large lake interactions on

hydrochemical cycling. Direct ground water input of chloride to Saginaw Bay accounts for approximately 1% of the total daily chloride load. Porewater chemistry in Lake Michigan sediments indicates that a similar process is occurring there. The most strongly affected area is southern Lake Michigan. The combination of Cl:Br and K:Cl ratios tend to indicate that the source for salinity in Lake Michigan porewaters is derived from formation brine. A conceptual model is presented to account for the regional occurrences of saline water in lake sediments. It is proposed that the Saginaw Lowland Area is affected by a combination of advection and diffusion, the advective component originating from topographically-controlled flow. The source for salinity in Lake Michigan sediments appears to be the Devonian-aged units; advective solute transport, originating from compaction-driven flow, may account for the presence of salinity in these sediments.

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APPENDICES

APPENDIX A.

Saginaw Bay Sampling Stations/Sediment Core Descriptions

Figure A-1: Saginaw Bay Sampling Stations

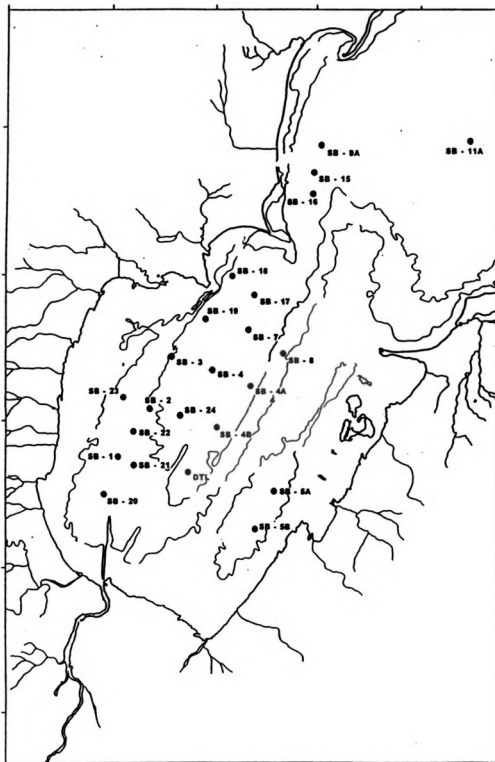


Table A-1: Saginaw Bay Sampling Stations

Site	Latitude (decimal degrees)	Longitude (decimal degrees)	Water Depth (m)	Comment
SB1	43.79383	83.84167	8	
SB2	43.84717	83.77167	7	
SB3	43.90767	83.73750	7	
SB4	43.89167	83.67500	8	
SB4a	43.86733	83.60117	9	
SB4b	43.82667	83.66433	9	
SB5a	43.75333	83.57633	5	no samples taken
SB5b	43.71117	83.60483	4	
SB7	43.93833	83.61500	12	
SB8	43.91083	83.55833	6	water column only
SB9a	44.14833	83.49383	16	water column only
SB11a	44.15333	83.25567	28	water column only
SB15	44.11683	83.50050	17	no samples taken
SB16	44.08433	83.50067	14	no samples taken
SB17	44.97833	83.60500	12	
SB18	44.00000	83.63417	8	
SB19	43.95000	83.68333	8	
SB20	43.75050	83.83467	6	
SB21	43.78333	83.80000	6	
SB22	43.81717	83.80000	6	
SB23	43.85100	83.81667	4	no samples taken
SB24	43.83400	83.71750	7	
DTL	43.77500	83.71500	7	water column only

Table A-2. Bay Cores Collected for Stratigraphic Study

Sample	Depth Interval (cm)	Unit	Description
SB2	0-187	silt-clay	lighter brown clay layer from 136-147 cm; lighter brown clay from 51-79 cm; shell fragments near base
	187-197(base)	clay	root fragments
SB4	0-186	silt-clay	lighter brown clay from 170-186 cm (and some shell fragments); small wood fragments at base; clay layer from 80-112 cm
	186-205(base)	clay	shell fragments; 7-13-95 removed small wood fragments (SB4-S1) and shells (SB4-S2) at the contact for possible AMS dating
SB4 (bottom 57")	64-154	silt-clay	shell fragments near base; lots shells at base; clay layer from 66-90 cm
	154-203(base)	clay	small wood fragments(?); shell fragments
SB4b	0-20	clay	x
	20-40	silt	x
	40-85	clay	siltier near base
	85-122(base)	silt	2 cm thick wood layer at 90 cm; pebbles; 0.2 cm thick gray clay @108 cm; 7-13-95 removed wood layer from one of the two split halves for possible 14C dating (SB4b-S1)
SB5b	0-5	sand	x
	5-60(base)	silty clay	organics in top 5 cm; 2 cm thick sand lens @32 cm; occasional pebbles and stones (not enough organics for a date)
SB7-PC2	0-57	silt	organic; coarser near base; sand layer(<0.25 cm) at base 7-13-95, 5 cm thick section (52-57) removed from both halves of split core for possible 14C dating; organic matter is disseminated; the entire section (0-57) appears to have similar organic content (SB7-PC2-S1)
	57-123(base)	silty clay	occasional pebbles; small shell fragments and root fragments throughout

Table A-2. (cont'd)

Sample	Depth Interval (cm)	Unit	Description
SB17-PC2	0-19	sandy silt	organic
	19-55	sandy silt	1cm thick sand layer at 46 cm; wood fragment at 48 cm
	55-64	silty clay	7-13-95, 3cm thick segment removed from just above unconformity (61-64) from one of the two split halves, organics are disseminated (SB17-PC2-S1)
	64-115(base)	silty clay	mottled; shell fragments throughout; clay layer at 90 cm; large shell at base
SB19	0-170(base)	silt-clay	organic rich at top; wood mass at base (removed for dating), GJL has this in his possession
SB19-PC3 (bottom 75" of 89")	36-164	silt-clay	shell fragments near base; lighter brown clay layer 157-164 cm
	164-188(base)	clay	a few root fragments
SB20-PC2	0-14	silt	charcoal clast at base; organic
	14-30	sandy silt	banded at top
	30-56	silt-clay	some banding
	56-63	sandy silt	dk. gray near top; gray near base
	63-77(base)	sandy silt	organics near top
SB21-PC1	0-145	silt-clay	organic rich at top; clay layer at 41-56 cm; very organic rich at base (from 126-145 cm) 7-13-95, 9 cm thick interval of organic rich sediment (disseminated organics) removed for 14C dating from one of the two split halves (145-163)
	145-163(base)	silt-clay	organic fragments; snail shell; stone
SB22-PC1	0-176	silt-clay	sand lens (<0.25 cm) at 79 cm; organic rich base
	176-201(base)	silt-clay	sandy near base; organic specks near top
SB24-PC2	0-204	silt-clay	stone at 72 cm; 3 cm thick dark band at 159 cm; organic rich base; 7-13-95, removed section from (195-203) from one of two split halves for 14C dating; layer A (dark brown) (194-198); layer B (brown) (198-204); GJL thinks organics may have leached from B to A, so we obtained a mixture of both; contact between A and B appears gradational
	204-218(base)	silt-clay	wood fragments near top

[illegible]

**Table A-3. Gravity Core Descriptions
(Porewater Extracted by Hydraulic Squeezer)**

Sample	Interval (cm)	Mean Depth (cm)	Unit	Description
SB1-GC-1	0-28	-14	silt	chocolate brown soup w/black streaks
SB1-GC-2a	28-38	-33	silt	firmer dk. gray mud
SB1-GC-2b	40.5-51.0	-45.75	silt	dk. gray mud
SB1-GC-2c	53.0-59.0	-56	silt	same
SB1-GC-3a	59-68	-63.5	silt	same
SB1-GC-3b	68-80.5	-74.25	silt	same
SB1-GC-3c	80.5-89.5	-85	sandy silt	dk. gray mud; coarser (some sand present)
SB1-GC-4a	92-101	-96.5	clay	lt. gray sandy clay; OM fragments
SB1-GC-4b	101-110	-105.5	clay	same; OM fragments
SB1-GC-4c	110-119	-114.5	clay	lt. blue-gray sandy clay (less sand than layer above); firmer
SB1-GC-5a	120-130	-125		
SB2-GC-1a	0-9	-4.5	silt	chocolaty brown soup w/black streaks
SB2-GC-1b	23-33	-28	silt	dark gray silt w/black streaks
SB2-GC-2a	33-42.5	-37.75	silt	dk. gray silty mud
SB2-GC-2b	42.5-53.5	-48	silt	dk. gray mud; firmer
SB2-GC-3a	65-76	-70.5	clay(?)	dk. gray mud; firmer; clay-rich(?)
SB2-GC-4a	98-108	-103		
SB2-GC-4b	108-119	-113.5		
SB2-GC-5a	129			
SB3-GC-1	0-28	-14	silt	dk. gray silty mud
SB3-GC-2a	28-39	-33.5	silt	dk. gray mud; firmer
SB3-GC-2b	39-49	-44	silt	dk. gray mud; firmer; silty
SB3-GC-3a	58-69	-63.5	silt	dk. gray mud
SB3-GC-3b	69-80	-74.5	silt	gray mud; silty
SB3-GC-4a	97-107	-102	silty sand	firm, black, muddy sand; OM fragments (roots & chunks)
SB3-GC-4b	107-116	-111.5	silty sand	firm, gray, muddy sand; less OM visible (no big chunks)

Table A-3. (cont'd)

Sample	Interval (cm)	Depth (cm)	Unit	Description
SB4-GC-1a	0-8	-4	silt	very wet, muddy on top
SB4-GC-1b	8-15	-11.5	silt	very wet
SB4-GC-1c	15-22	-18.5	silt	wet
SB4-GC-1d	22-27	-24.5	silt	wet
SB4-GC-2a	27-35	-31	silt	moist
SB4-GC-2b	35-43	-39	silt	moist
SB4-GC-2c	43-51	-47	silt	moist
SB4-GC-2d	51-60	-55.5	silt	moist
SB4-GC-3a	60-68	-64	silt	less moist
SB4-GC-3b	68-76	-72	silt	less moist
SB4-GC-3c	76-84	-80	silt	less moist
SB4-GC-3d	84-91	-87.5	silt	x
SB4-GC-4a	91-101	-96	silt	x
SB4-GC-4b	101-109	-105	silt	soft mud
SB4-GC-4c	109-116	-112.5	silt	x
SB4-GC-5a	116-124	-120	silt	brown mud w/large black streak
SB4-GC-5b	124-132	-128	silt	dk. brown mud; lt.brown/black streaks
SB4-GC5c	132-140	-136	silt	dk. brown mud w/ lt. brown mottling
SB4-GC-5d	140-148	-144	silt	x
SB4-GC-6a	148-156	-152	silt	dk. brown mud w/ lighter brown areas
SB4-GC-6b	156-164	-160	silt	dk. brown mud w/ lighter brown areas
SB4-GC-6c	164-172	-168	silt	x
SB4-GC-6d	172-180	-176	silt	x
SB4-GC-6e	180-185	-182.5	silt	x
SB4a-GC-1a	0-8	-4	sandy silt	chocolaty brown soup, grading to dk. gray sandy mud; pebbles
SB4a-GC-1b	8-15	-11.5	silty sand	dk. brown muddy sand
SB4a-GC-2a	15-25	-20	clay	gray/lt. gray, firm, dry sandy clay; large pebbles; shells; root fragments
SB4a-GC-2b	25-36	-30.5	clay	firm, gray sandy clay w/pebbles; root fragments; orange-brown mottling
SB4a-GC-3a	37-48	-42.5	clay	gray sandy clay w/orange-brown mottling; very firm; pebbles
SB4a-GC-3b	48-58	-53	clay	same

Table A-3. (cont'd)

Sample	Interval (cm)	Mean Depth (cm)	Unit	Description
SB4b-GC-1	0-27	-13.5	silt	dk. gray mud w/black streaks
SB4b-GC-2a	27-34	-30.5	silt	dk. gray silty mud
SB4b-GC-2b	37-47	-42	silt	same
SB4b-GC-3a	57-67	-62	silt	same
SB4b-GC-3b	67-77.5	-72.25	silt/clay	dk. brown; transition to clay band(?); sand content increasing to base; muddy sand at base
SB4b-GC-4a	87.5-96.5	-92	clay	blue-gray, v. firm sandy clay; OM fragments; quartz pebbles
SB4b-GC-5a	105.5-115.5	-110.5	clay	gray clay; coarser (sand present)
SB5b-GC-1a	0-7	-3.5	sand/clay	sandy top; bottom ~ 1 cm is clay
SB5b-GC-1b	7-14	-10.5	clay	clay
SB5b-GC-1c	14-21	-17.5	clay	clay
SB5b-GC-2a	21-28	-24.5	clay	clay
SB5b-GC-2b	28-35	-31.5	clay	dry clay
SB5b-GC-2c	35-44	-39.5	clay	clay
SB5b-GC-3a	44-51	-47.5	clay	clay
SB5b-GC-3b	51-55	-53	clay	clay; one root
SB5b-GC-3c	55-60	-57.5	clay	x
SB7-GC-1	0-16	-8	silt	dk. brown mud
SB7-GC-2a	16-27	-22	silt	dk. gray mud; firmer
SB7-GC-2b	27-41.5	-34.25	silt	same
SB7-GC-3a	47-57	-52	clay?	gray clay band(?); sandy at base
SB7-GC-3b	57-68	-62.5	silt/clay	dk. gray silty clay changing to v. <i>firm</i> lt. gray clay w/ OM fragments
SB7-GC-3c	68-78	-73	clay	lt. gray, firm clay; root fragments
SB7-GC-4a	80-90	-85	clay	extremely firm, brown clay
SB7-GC-4b	90-99.5	-94.75	clay	same; sandier towards base
SB7-GC-4c	99.5-109.5	-104.5	clay	same
SB7-GC-5a	111.75- 121.75	-116.75	clay	same
SB7-GC-5b	121.75- 131.25	-126.5	clay	same; less sandy

Table A-3. (cont'd)

Sample	Interval (cm)	Mean Depth (cm)	Unit	Description
SB17-GC-1a	0-8	-4	silt	mostly brown
SB17-GC-1b	8-20	-14	silt	x
SB17-GC-2a	20-28	-24	sandy silt	watery, sandy
SB17-GC-2b	28-36	-32		x
SB17-GC-2c	36-42	-39		x
SB17-GC-3a	42-50	-46		x
SB17-GC-3b	50-57	-53.5		x
SB17-GC-3c	57-62	-59.5		x
SB17-GC-4a	62-69	-65.5	clay	white stuff in sediment.
SB17-GC-4b	69-76	-72.5	clay	white stuff (some); drier, clayey
SB17-GC-4c	76-83	-79.5	clay	very dry clay
SB17-GC-4d	83-88	-85.5	clay	x
SB17-GC-5a	88-93	-90.5	clay	dry clay
SB17-GC-5b	93-99	-96	clay	x
SB17-GC-5c	99-106	-102.5	clay	x
SB17-GC-5d	106-113	-109.5	clay	x
SB17-GC-5e	113-119	-116	clay	x
SB19-GC-1	0-30.5	-15.25	silt	chocolaty brown, silty mud
SB19-GC-2	30.5-61.0	-45.75	silt	same; firmer; can feel some sand
SB19-GC-3	61.0-91.5	-76.25	silt	dk. brown silty mud (no sand)
SB19-GC-4	91.5-122.0	-106.75		x
SB19-GC-5a	122-137.5	-129.75	silt	same
SB19-GC-5b	137.5-152.5	-145		x
SB19-GC-6a	152.5-168	-160.25	silt	same
SB19-GC-6b	168-183	-175.5	silt	same; firmer
SB19-GC-7a	183-198	-190.5	silt	same
SB19-GC-7b	198-213.5	-205.75	clay	blue-gray clay; v. firm; large (2.5 cm dia.) pebbles; large WOOD fragments
SB19-GC-8	213.5-223.5	-218.5		x

Table A-3. (cont'd)

Sample	Interval (cm)	Mean Depth (cm)	Unit	Description
SB20-GC-1	0-13	-6.5	silt	dk. brown soup w/black streaks
SB20-GC-2a	13-22	-17.5	silt	dk. gray mud; firmer
SB20-GC-2b	23-32	-27.5	silt	lt. gray mud
SB20-GC-3a	38-47.5	-42.5	silt	same; slightly firmer
SB20-GC-3b	47.5-57.5	-52.5	silt	same
SB20-GC-4a	57.5-67	-62.25	clay	firm gray clay; PEAT at base (67 cm); GJL has this entire section for possible 14C dating
SB20-GC-5a	85-95	-90	clay	lt. gray clay; firm
SB21-GC-1	0-14	7	silt	chocolaty brown soup w/dark streaks
SB21-GC-2	19-29	24	silt	dk. gray mud with some sand
SB21-GC-3	39-50	44.5	silt	dk. gray mud; no sand felt
SB21-GC-4a	51-61	56	silt	dk. gray silty clay
SB21-GC-4b	61-71	66	silt	same; slightly. firmer
SB21-GC-5a	79-88	83.5	silt	dk. gray clay
SB21-GC-5b	88-98	93	silt	same
SB21-GC-6a	109-119	114	silt	dk. gray clay; firmer; drier
SB21-GC-6b	119-129	124	silt	same
SB21-GC-7a	135-146	140.5	silt	dk. gray silt/clay; firmer; coarser
SB21-GC-7b	146-164		clay	dk. gray clay; sandy lens at 150 cm, PEAT beneath it; pebbles at base of section; 7-13-95 very well defined organic horizon (151-154) removed for 14C dating, labeled as SB21-SQ- S1; this sample is better than the sample from the SB21 stratigraphy core, which comprises finely disseminated organics

Table A-3. (cont'd)

Sample	Interval (cm)	Mean Depth (cm)	Unit	Description
SB22-GC-1	0-8	-4	silt	dk. brown mud w/ dk. gray streaks
SB22-GC-2	10-20	-15	silt	silty, dk. gray mud
SB22-GC-3a	27-37	-32	clay(?)	firmer (clay?); silty; dk. gray
SB22-GC-3b	37-48	-42.75	clay(?)	same
SB22-GC-4a	49-59	-54	silt	gray mud; finer-grained
SB22-GC-4b	59-70	-64.5	silt	gray clay
SB22-GC-5a	71-79	-75	silt	gray clay; firmer
SB22-GC-5b	79-87	-83	silt	same
SB22-GC-6a	93-102.5	-97.75	silt	gray clay; firmer; drier
SB22-GC-6b	102.5-112.5	-107.5	silt	dk. gray clay; drier, firmer
SB22-GC-7a	121-131	-126	silt	dk. gray mud; firmer
SB22-GC-7b	131-141	-136	silt	same
SB22-GC-8a	148-157	-152.5	silt	dk. gray clay; very firm
SB22-GC-8b	157-166	-161.5	silt	same
SB22-GC-9a	174-182	-178	silt	dk. gray clay; firmer
SB22-GC-9b	182-192	-187	clay	transition from dk. gray (top) to light gray (like fireplace ashes); bottom clay is very firm and dry/crumby
SB22-GC-10a	201-211	-206	clay	lt. gray clay; very firm; flecks of OM, small pebbles present
SB22-GC-10b	211-219	-215	clay	lt. gray clay; v. firm; OM fragments

Table A-3. (cont'd)

Sample	Interval (cm)	Mean Depth (cm)	Unit	Description
SB24-GC-1	0-6.5	-3.25	silt	chocolaty brown soupy mud
SB24-GC-2	6.5-28	-17.25	silt	dk. gray mud; slightly. firmer
SB24-GC-3	28-51	-39.5	silt	same
SB24-GC-4	51-61	-56	silt	dk. gray mud; much firmer
SB24-GC-5a	70-80	-75	clay(?)	lt. gray mud; firmer, drier (clay?)
SB24-GC-5b	80-90	-85	silt	dk. gray mud
SB24-GC-6a	92-103	-97.5	silt	dk. gray mud; firmer, drier
SB24-GC-6b	103-113	-108	silt	same
SB24-GC-7a	119-129	-124	silt	same
SB24-GC-7b	129-139	-134	silt	same
SB24-GC-8a	146-156	-151	silt	same
SB24-GC-8b	156-166	-161	silt	same
SB24-GC-9a	171-181	-176	silt	same
SB24-GC-9b	181-193	-187	silt	same
SB24-GC-10a	203-213	-208	silt	same
SB24-GC-10b	213-223	-218	silt	lt. brown mud; v. <i>firm</i> , dry

Table A-4. Trace Metal Box Core Descriptions

Core: SB1-BC-1D

(Collected for porewater/trace metals and sequential extractions)

Sample #	Thickness (cm)	Interval	Depth (cm)	Description
1	1	0-1.0	-0.5	fluffy, brownish mud
2	1	1.0-2.0	-1.5	slightly firmer (less soupy) brown mud
3	1	2.0-3.0	-2.5	slightly firmer (less soupy) brown mud; able to stand on its own
4	1	3.0-4.0	-3.5	same stuff, a little firmer; orange and black streaks, maybe
5	1	4.0-5.0	-4.5	essentially same, a little firmer; no hint of streaks
6	1	5.0-6.0	-5.5	more of the same
7	1	6.0-7.0	-6.5	same
8	1	7.0-8.0	-7.5	same
9	1	8.0-9.0	-8.5	same, a little firmer
10	1	9.0-10.0	-9.5	same
11	1	10.0-11.0	-10.5	same
12	2	11.0-13.0	-12	same
13	2	13.0-15.0	-14	same
14	2	15.0-17.0	-16	same
15	2	17.0-19.0	-18	same
16	2	19.0-21.0	-20	same
17	2	21.0-23.0	-22	dark gray
18	2	23.0-25.0	-24	getting sticky
19	2	25.0-27.0	-26	same
20	2	27.0-29.0	-28	same
21	3	29.0-32.0	-30.5	same
22	3	32.0-35.0	-33.5	same
23	3	35.0-38.0	-36.5	same
24	3	38.0-41.0	-39.5	same

Table A-4. (cont'd)

Core: SB3-BC-3D

(Collected for porewater/trace metals and sequential extractions)

Sample #	Thickness (cm)	Depth Interval	Depth (cm)	Description
1	1	0-1.0	-0.5	soupy brown fluff
2	1	1.0-2.0	-1.5	soupy brown, changing to gray at base
3	1	2.0-3.0	-2.5	gray clay; some dk. streaks at base
4	1	3.0-4.0	-3.5	same
5	1	4.0-5.0	-4.5	slightly firmer
6	1	5.0-6.0	-5.5	same
7	1	6.0-7.0	-6.5	slightly firmer; possible tan streaks
8	1	7.0-8.0	-7.5	same; tan streaks
9	1	8.0-9.0	-8.5	firmer, brown color
10	1	9.0-10.0	-9.5	darker brown; pastier
11	1	10.0-11.0	-10.5	dk. brown/lt. brown; gas pockets;clumpy
12	1	11.0-12.0	-11.5	same; little firmer
13	1	12.0-13.0	-12.5	same; little firmer; tan color at base
14	1	13.0-14.0	-13.5	mix of dark and light brown
15	1	14.0-15.0	-14.5	dark brown, homogeneous
skipped	3 (discarded)	15.0-18.0		same, little drier
16	1	18.0-19.0	-18.5	dark brown, drier, clumpy
skipped	3 (discarded)	19.0-22.0		dark brown clay, firmer
17	1	22.0-23.0	-22.5	same
skipped	3 (discarded)	23.0-26.0		dark brown to light brown at base
18	1	26.0-27.0	-26.5	light brown to dark brown
skipped	3 (discarded)	27.0-30.0		little firmer, light brown
19	1	30.0-31.0	-30.5	same
skipped	3 (discarded)	31.0-34.0		same; possible light brown patches
20	1	34.0-35.0	-34.5	same
skipped	3 (discarded)	35.0-38.0		few black streaks; soft base
21	1	38.0-39.0	-38.5	dark gray; very firm surface
skipped	3 (discarded)	39.0-42.0		lighter brown; fairly dry clay
22	1	42.0-43.0	-42.5	same
skipped	3 (discarded)	43.0-46.0		same
23	1	46.0-47.0	-46.5	same
skipped	3 (discarded)	47.0-50.0		same
24	1	50.0-51.0	-50.5	same

Table A-4. (cont'd)

Core: SB4b-BC-1D

(Collected for porewater/trace metals and sequential extractions)

Sample #	Thickness (cm)	Depth Interval	Depth (cm)	Description
1	1	0-1.0	-0.5	very wet, brown mud
2	1	1.0-2.0	-1.5	wet brown mud
3	1	2.0-3.0	-2.5	same; slightly firmer
4	1	3.0-4.0	-3.5	same
5	1	4.0-5.0	-4.5	same
6	1	5.0-6.0	-5.5	same
7	1	6.0-7.0	-6.5	same, changing to darker
8	1	7.0-8.0	-7.5	same, firmer at base; tan streaks(?)
9	1	8.0-9.0	-8.5	dk. brown material w/ a few tan streaks
10	1	9.0-10.0	-9.5	same
11	1	10.0-11.0	-10.5	same
12	1	11.0-12.0	-11.5	same
13	1	12.0-13.0	-12.5	essentially the same, a little firmer
14	1	13.0-14.0	-13.5	same, tan less frequent at base
15	1	14.0-15.0	-14.5	same
skip	3 (discarded)	15.0-18.0		same, tan streaks; darker at bottom
16	1	18.0-19.0	-18.5	dark brown-tan streaks; firmer at base
skip	3 (discarded)	19.0-22.0		same, w/tan patches
17	1	22.0-23.0	-22.5	firmer, dark brown
skip	3 (discarded)	23.0-26.0		same
18	1	26.0-27.0	-26.5	same
skip	3 (discarded)	27.0-30.0		same
19	1	30.0-31.0	-30.5	same
skip	3 (discarded)	31.0-34.0		firmer clay; dark brown
20	1	34.0-35.0	-34.5	same, firm clay
skip	3 (discarded)	35.0-38.0		same
21	1	38.0-39.0	-38.5	same clay, a little firmer
skip	3 (discarded)	39.0-42.0		same
22	1	42.0-43.0	-42.5	same
skip	3 (discarded)	43.0-46.0		same
23	1	46.0-47.0	-46.5	same, but drier; clumpier
skip	3 (discarded)	47.0-50.0		same
24	1	50.0-51.0	-50.5	same

Table A-4. (cont'd)

Core: SB17-BC-1D

(Collected for porewater/trace metals and sequential extractions)

Sample #	Thickness (cm)	Depth Interval	Depth (cm)	Description
1	1	0-1.0	-0.5	brown, fluffy material; very wet
2	1	1.0-2.0	-1.5	firmer, light brown material
3	1	2.0-3.0	-2.5	firmer, brown; lt. brown/tan streaks
4	1	3.0-4.0	-3.5	firmer; numerous tan streaks
5	1	4.0-5.0	-4.5	same
6	1	5.0-6.0	-5.5	mostly gray w/ a little brown
7	1	6.0-7.0	-6.5	same
8	1	7.0-8.0	-7.5	same
9	1	8.0-9.0	-8.5	same, less brown
10	1	9.0-10.0	-9.5	same, very little brown
11	1	10.0-11.0	-10.5	same
12	1	11.0-12.0	-11.5	same dark gray w/brown streaks
13	1	12.0-13.0	-12.5	same, w/plant material
14	1	13.0-14.0	-13.5	dark gray, w/plant material
15	1	14.0-15.0	-14.5	dark gray, no plant matter
skipped	3 (discarded)	15.0-18.0		same
16	1	18.0-19.0	-18.5	same, firmer
skipped	3 (discarded)	19.0-22.0		same, firmer; drier at base
17	1	22.0-23.0	-22.5	mix of brown and dark brown; chunk of (organic?) in sediment
skipped	3 (discarded)	23.0-26.0		brown clay
18	1	26.0-27.0	-26.5	same, firmer
skipped	1 (discarded)	27.0-28.0		same
19	1	28.0-29.0	-28.5	brown clay; sandy @base
skipped	1 (discarded)	29.0-30.0		same
20	1	30.0-31.0	-30.5	very sandy clay
skipped	1 (discarded)	31.0-32.0		same
21	1	32.0-33.0	-32.5	same, firmer, sandier
skipped	2 (discarded)	33.0-35.0		same
22	1	35.0-36.0	-35.5	same
skipped	2 (discarded)	36.0-38.0		same
23	1	38.0-39.0	-38.5	same

Table A-4. (cont'd)

Core: SB19-BC-1D

(Collected for porewater/trace metals and sequential extractions)

Sample #	Thickness (cm)	Depth Interval	Depth (cm)	Description
1	1	0-1.0	-0.5	very soupy brown material
2	1	1.0-2.0	-1.5	same material, only firmer
3	1	2.0-3.0	-2.5	same; slightly firmer
4	1	3.0-4.0	-3.5	slightly firmer; brown/dark brown
5	1	4.0-5.0	-4.5	same consistency; more dark streaks
6	1	5.0-6.0	-5.5	firmer, dk. brown mud w/tan splotches
7	1	6.0-7.0	-6.5	same
8	1	7.0-8.0	-7.5	same, but slightly firmer
9	1	8.0-9.0	-8.5	firmer; frequent tan/lt. brown splotches
10	1	9.0-10.0	-9.5	same
11	1	10.0-11.0	-10.5	same, but less light brown material
12	1	11.0-12.0	-11.5	same
13	1	12.0-13.0	-12.5	same, slightly firmer
14	1	13.0-14.0	-13.5	same
15	1	14.0-15.0	-14.5	same, less light brown
skipped	3 (discarded)	15.0-18.0		dark brown mud
16	1	18.0-19.0	-18.5	same, perhaps a little sandier
skipped	3 (discarded)	19.0-22.0		same
17	1	22.0-23.0	-22.5	same
skipped	3 (discarded)	23.0-26.0		clayey; dark gray/brown
18	1	26.0-27.0	-26.5	firmer, dark gray clay
skipped	3 (discarded)	27.0-30.0		same
19	1	30.0-31.0	-30.5	same
skipped	3 (discarded)	31.0-34.0		same
20	1	34.0-35.0	-34.5	same
skipped	3 (discarded)	35.0-38.0		same
21	1	38.0-39.0	-38.5	same
skipped	3 (discarded)	39.0-42.0		same
22	1	42.0-43.0	-42.5	same
skipped	3 (discarded)	43.0-46.0		same
23		46.0-47.0	-46.5	same
skipped	3 (discarded)	47.0-50.0		same
24		50.0-51.0	-50.5	same

Table A-4. (cont'd)

Core: SB22-BC-1D

(Collected for porewater/trace metals and sequential extractions)

Sample #	Thickness (cm)	Depth Interval	Depth (cm)	Description
1	1	0-1.0	-0.5	very soupy brown mud
2	1	1.0-2.0	-1.5	firmer brown mud
3	1	2.0-3.0	-2.5	firmer, dark brown/lt. brown mud
4	1	3.0-4.0	-3.5	same
5	1	4.0-5.0	-4.5	same
6	1	5.0-6.0	-5.5	same
7	1	6.0-7.0	-6.5	same
8	1	7.0-8.0	-7.5	same, slightly firmer
9	1	8.0-9.0	-8.5	same
10	1	9.0-10.0	-9.5	same
11	1	10.0-11.0	-10.5	same, slightly firmer
12	1	11.0-12.0	-11.5	same, clumpier
13	1	12.0-13.0	-12.5	same
14	1	13.0-14.0	-13.5	same
15	1	14.0-15.0	-14.5	same
skipped	3 (discarded)	15.0-18.0		same
16	1	18.0-19.0	-18.5	same
skipped	3 (discarded)	19.0-22.0		same
17	1	22.0-23.0	-22.5	same
skipped	3 (discarded)	23.0-26.0		same
18	1	26.0-27.0	-26.5	same
skipped	3 (discarded)	27.0-30.0		same
19	1	30.0-31.0	-30.5	lighter brown, firmer, drier clay
skipped	3 (discarded)	31.0-34.0		same
20	1	34.0-35.0	-34.5	same
skipped	3 (discarded)	35.0-38.0		same
21	1	38.0-39.0	-38.5	same
skipped	3 (discarded)	39.0-42.0		same
22	1	42.0-43.0	-42.5	same
skipped	3 (discarded)	43.0-46.0		same
23		46.0-47.0	-46.5	same
skipped	3 (discarded)	47.0-50.0		same
24		50.0-51.0	-50.5	same

Table A-5. Box Core Descriptions

Core: SB1-BC-1A

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	2	0-2	-1	tan, soupy mud w/critters; dark black streaks
2	2	2-4	-3	dark, tan mud-firmer; brown and black streaks; brown changing to gray
3	2	4-6	-5	firmer; black streaks
4	2	6-8	-7	brown to dark gray mud w/black spots: red worm
5	2	8-10	-9	mostly gray: some brown; spots: red worm
6	2	10-12	-11	gray w/ black streaks; same texture
7	2	12-14	-13	gray w/ black streaks; much firmer and sticky
8	2	14-16	-15	gray with black streaks
9	2	16-18	-17	gray with black streaks
10	2	18-20	-19	dark gray; no black streaks, texture is very firm and sticky
11	2	20-22	-21	dark gray, slight tan stripes; firm
12	2	22-24	-23	dark gray, firm
13	2	24-26	-25	dark gray and brown
14	2	26-28	-27	dark gray and brown
15	2	28-30	-29	dark gray w/brown streaks; firm

Table A-5. (cont'd)**Core: SB1-BC-1C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	0.5	0-0.5	-0.25	lt. brown, very wet; flocculent; some critters, watery
2	0.5	0.5-1.0	-0.75	lt. brown, soupy; gray streaks
3	0.5	1.0-1.5	-1.25	lt. to dk. brown w/black streaks, still somewhat watery
4	1	1.5-2.5	-2	lt. to dk. brown w/black streaks, still watery
5	1	2.5-3.5	-3	lt. gray w/black streaks and small lt. brown specks; firmer (less watery)
6	1	3.5-4.5	-4	lt. to dk. gray w/ black and brown streaks, firmer texture
7	1	4.5-5.5	-5	lt. to dk. gray w/ black streaks
8	1	5.5-6.5	-6	med. to dk. brown
9	1	6.5-7.5	-7	med. to dk. brown
10	1	7.5-8.5	-8	small fracture (w/water); dark brown
11	1	8.5-9.5	-9	more water-filled fractures; mostly dark brown w/ lt. brown streaks
12	1	9.5-10.5	-10	mostly dark brown; no fractures
13	1	10.5-11.5	-11	mostly dark brown
14	1	11.5-12.5	-12	mostly dark brown
15	1	12.5-13.5	-13	50/50 lt. to dk. brown
16	1	13.5-14.5	-14	50/50 lt. to dk. brown
17	1	14.5-15.5	-15	dark brown, firmer
18	1	15.5-16.5	-16	dark brown w/ black streak; numerous air pockets
19	1	16.5-17.5	-17	dark brown w/ black streak; numerous air pockets
20	1	17.5-18.5	-18	dark brown w/ black streak; numerous air pockets
21	1	18.5-19.5	-19	dk. brown; numerous air pockets
skip	2 (discarded)	19.5-21.5		
22	1	21.5-22.5	-22	dk. brown; numerous air pockets
skip	3 (discarded)	22.5-25.5		
23	1	25.5-26.5	-26	dk. brown; numerous air pockets
skip	3 (discarded)	26.5-29.5		
24	1	29.5-30.5	-30	dk. gray/brown; numerous air pockets

Table A-5. (cont'd)**Core: SB2-BC-C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	water included just above sediment-water interface; worms, tan w/gray streaks
2	1	1.0-2.0	-1.5	tan w/ gray streaks, no worms
3	1	2.0-3.0	-2.5	tan w/ gray streaks, no worms; silty; white shells present, sandy
4	1	3.0-4.0	-3.5	firmer; tan w/ gray streaks
5	1	4.0-5.0	-4.5	light to medium gray; firmer dark gray streaks
6	1	5.0-6.0	-5.5	lt. to med. gray; firmer dark gray streaks; gas pockets
7	1	6.0-7.0	-6.5	lt. to med. gray; firmer dark gray streaks; continue to see gas pockets
8	1	7.0-8.0	-7.5	light/med. gray; firmer dk. gray streaks; gas pockets
9	1	8.0-9.0	-8.5	same
10	1	9.0-10.0	-9.5	same
11	1.5	10.0-11.5	-10.75	light to medium gray; firmer dark gray streaks; gas pockets
12	1	11.5-12.5	-12	same
13	1	12.5-13.5	-13	same
14	1	13.5-14.5	-14	gas pockets; more dark gray material at base
15	1	14.5-15.5	-15	medium gray; gas pockets
16	1	15.5-16.5	-16	medium gray; gas pockets; sand particles
17	1	16.5-17.5	-17	medium gray; gas pockets; sand particles
18	1	17.5-18.5	-18	medium gray; gas pockets; sand still present
skip	2 (discard)	18.5-20.5		
19	1	20.5-21.5	-21	dk. gray; gas pockets; sandy, much firmer
skip	2 (discard)	21.5-23.5		
20	1	23.5-24.5	-24	dark gray; gas pockets; sandy, much firmer
skip	2 (discard)	24.5-26.5		
21	1	26.5-27.5	-27	dk. gray; gas pockets; sandy, v. thick
skip	2 (discard)	27.5-29.5		
22	1	29.5-30.5	-30	dk. gray; gas pockets; sandy, v. thick
skip	2.5 (discard)	30.5-33.0		
23	1	33.0-34.0	-33.5	dk. gray; few gas pockets; sandy, v. thick
skip	5 (discard)	34.0-39.0		
24	1	39.0-40.0	-39.5	dk. gray; few gas pockets; sandy

Table A-5. (cont'd)**Core: SB3-BC-3C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	wet, brown mud
2	1	1.0-2.0	-1.5	wet, brown mud; changing to gray mud
3	1	2.0-3.0	-2.5	grayish mud, slightly firmer
4	1	3.0-4.0	-3.5	gray w/ small black spots
5	1	4.0-5.0	-4.5	gray w/reddish brown streaks
6	1	5.0-6.0	-5.5	firmer, gray w/reddish brown streaks
7	1	6.0-7.0	-6.5	gray w/red streaks, changing to darker gray
8	1	7.0-8.0	-7.5	dark gray w/reddish streaks; getting stickier
9	1	8.0-9.0	-8.5	dark gray w/reddish streaks
10	1	9.0-10.0	-9.5	dk. gray w/red streaks, changing to lt. gray
11	1	10.0-11.0	-10.5	gray w/dark gray streaks
12	1	11.0-12.0	-11.5	gray w/dark gray streaks
13	1	12.0-13.0	-12.5	gray clay
14	1	13.0-14.0	-13.5	gray clay
15	1	14.0-15.0	-14.5	gray w/dark gray streaks
skip	3 (discarded)	15.0-18.0		
16	1	18.0-19.0	-18.5	dark gray
skip	3 (discarded)	19.0-22.0		gray clay w/dark streaks
17	1	22.0-23.0	-22.5	gray clay w/dark streaks
skip	3 (discarded)	23.0-26.0		gray clay w/dark streaks
18	1	26.0-27.0	-26.5	gray clay w/dark streaks; white shell
skip	3 (discarded)	27.0-30.0		gray w/dk. gray streaks; shell fragments
19		30.0-31.0	-30.5	gray w/dark streaks, sandy
skip	3 (discarded)	31.0-34.0		stiff gray clay; small sand; shell
20		34.0-35.0	-34.5	stiff gray clay; small sand
skip	3 (discarded)	35.0-38.0		stiff gray clay; small sand
21		38.0-39.0	-38.5	gray, sandier; shells present
skip	3 (discarded)	39.0-42.0		sandy gray clay
22		42.0-43.0	-42.5	sandy gray clay
skip	3 (discarded)	43.0-46.0		sandy gray clay
23		46.0-47.0	-46.5	gray clay; no sand
skip	3 (discarded)	47.0-50.0		gray clay, very little sand
24		50.0-51.0	-50.5	gray clay, slightly sandy

Table A-5. (cont'd)**Core: SB3-BC-3E**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	very soupy, brown mud
2	1	1.0-2.0	-1.5	brown to gray soupy mud
3	1	2.0-3.0	-2.5	grayish clay w/red-brown streaks
4	1	3.0-4.0	-3.5	gray w/brown and black streaks; firmer
5	1	4.0-5.0	-4.5	less brown, more black
6	1	5.0-6.0	-5.5	gray w/brown and black
7	1	6.0-7.0	-6.5	gray w/brown and black
8	1	7.0-8.0	-7.5	more gray, fewer brown and black streaks
9	1	8.0-9.0	-8.5	gray clay
10	1	9.0-10.0	-9.5	gray clay
11	1	10.0-11.0	-10.5	brown and black streaks
12	1	11.0-12.0	-11.5	brown and black streaks
13	1	12.0-13.0	-12.5	dark gray w/brown streaks
14	1	13.0-14.0	-13.5	dark gray clay
15	1	14.0-15.0	-14.5	dark gray clay
skip	3 (discarded)	15.0-18.0		dark gray clay
16	1	18.0-19.0	-18.5	dark gray clay
skip	3 (discarded)	19.0-22.0		dark gray clay; some sand
17	1	22.0-23.0	-22.5	dark gray clay with some sand
skip	3 (discarded)	23.0-26.0		dark gray clay with some sand
18	1	26.0-27.0	-26.5	dark gray clay with some sand
skip	3 (discarded)	27.0-30.0		dark gray clay with some sand
19	1	30.0-31.0	-30.5	dark gray clay; more sand
skip	3 (discarded)	31.0-34.0		dark gray clay; more sand
20	1	34.0-35.0	-34.5	dark gray clay; more sand; twig present
skip	3 (discarded)	35.0-38.0		dark gray clay; less sand
21	1	38.0-39.0	-38.5	dark gray clay; less sand

Table A-5. (cont'd)**Core: SB4-BC-C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	surface water; light brown tan
2	1	1.0-2.0	-1.5	wet, brown; dark spots; tiny white shell fragments
3	1	2.0-3.0	-2.5	wet, brown w/black streaks
4	1	3.0-4.0	-3.5	less wet, brown w/black streaks
5	1	4.0-5.0	-4.5	firmer; less brown, more black
6	1	5.0-6.0	-5.5	mostly black mud, little brown
7	1	6.0-7.0	-6.5	more black, less brown
8	1	7.0-8.0	-7.5	dark gray; gas pockets (probably worm holes); some sand
9	1	8.0-9.0	-8.5	dark gray; red-brown streaks
10	1	9.0-10.0	-9.5	dk. gray; red-brown streaks; firm @base
11	1	10.0-11.0	-10.5	dark gray; red-brown streaks; red worm
12	1	11.0-12.0	-11.5	dark gray; brown patches
13	1	12.0-13.0	-12.5	dk. gray; brown patches, black streaks
14	1	13.0-14.0	-13.5	gray w/red-brown spots; no streaks
15	1	14.0-15.0	-14.5	dark gray; brown spots
16	1	15.0-16.0	-15.5	mostly dark gray, little brown
17	1	16.0-17.0	-16.5	slightly dark gray, no brown on bottom
skip	2 (discarded)	17.0-19.0		slightly dark gray, no brown on bottom
18	2	19.0-21.0	-20	firmer; silty
skip	2 (discarded)	21.0-23.0		firmer; silty
19	2	23.0-25.0	-24	dark gray, silty
skip	2 (discarded)	25.0-27.0		dark gray, silty
20	2	27.0-29.0	-28	dark gray; possibly clay
skip	3 (discarded)	29.0-32.0		dark gray
21	2	32.0-34.0	-33	wetter, less firm; dark gray
skip	3 (discarded)	34.0-37.0		not as wet, less firm; dark gray
22	2	37.0-39.0	-38	wetter, less firm; dark gray
skip	3 (discarded)	39.0-42.0		firmer
23	2	42.0-44.0	-43	dark gray, firmer
skip	17 (discarded)	44.0-61.0		dark gray, firmer
24	2	61.0-63.0	-62	dark gray

Table A-5. (cont'd)**Core: SB4b-BC-C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	light brown soupy mud; critters on top
2	1	1.0-2.0	-1.5	light brown, less soupy; black spots
3	1	2.0-3.0	-2.5	tan to light brown mud
4	1	3.0-4.0	-3.5	gray w/brown streaks
5	1	4.0-5.0	-4.5	gray w/brown and black spots
6	1	5.0-6.0	-5.5	gray worm holes; brown and black spots
7	1	6.0-7.0	-6.5	gray worm holes; brown and black spots
8	1	7.0-8.0	-7.5	gray w/more black
9	1	8.0-9.0	-8.5	gray w/more black
10	1	9.0-10.0	-9.5	more brown than black
11	1	10.0-11.0	-10.5	darker gray w/brown and black
12	1	11.0-12.0	-11.5	darker gray w/brown and black
13	1	12.0-13.0	-12.5	more black, less brown
14	1	13.0-14.0	-13.5	dark gray, little brown
15	1	14.0-15.0	-14.5	dark gray, little brown
skip	3 (discarded)	15.0-18.0		
16	1	18.0-19.0	-18.5	dark gray, little brown
skip	3 (discarded)	19.0-22.0		
17	1	22.0-23.0	-22.5	all dark gray
skip	3 (discarded)	23.0-26.0		
18	1	26.0-27.0	-26.5	more sticky, all dark gray streaks
skip	3 (discarded)	27.0-30.0		
19	1	30.0-31.0	-30.5	stickier; dk. gray w/ black streaks
skip	3 (discarded)	31.0-34.0		stickier; dk. gray w/ black streaks
20	1	34.0-35.0	-34.5	dark gray w/fewer black streaks
skip	3 (discarded)	35.0-38.0		dark gray w/fewer black streaks
21	1	38.0-39.0	-38.5	same
skip	3 (discarded)	39.0-42.0		same
22	1	42.0-43.0	-42.5	same, w/small amount of sand
skip	3 (discarded)	43.0-46.0		same, w/more black
23	1	46.0-47.0	-46.5	dark gray sticky mud w/ a pebble
skip	3 (discarded)	47.0-50.0		same
24	1	50.0-51.0	-50.5	same

Table A-5. (cont'd)**Core: SB7-BC-C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	soupy brown to tan
2	1	1.0-2.0	-1.5	same w/black streaks
3	1	2.0-3.0	-2.5	tan to gray; still soupy
4	1	3.0-4.0	-3.5	gray w/red-brown spots; worms
5	1	4.0-5.0	-4.5	gray soupy w/brown spots
6	1	5.0-6.0	-5.5	same w/black streaks
7	1	6.0-7.0	-6.5	same
8	1	7.0-8.0	-7.5	same; slightly firmer
9	1	8.0-9.0	-8.5	same; more red/brown
10	1	9.0-10.0	-9.5	same
11	1	10.0-11.0	-10.5	same; more plant material
12	1	11.0-12.0	-11.5	same; still plant material
13	1	12.0-13.0	-12.5	same; darker toward bottom
14	1	13.0-14.0	-13.5	dk. gray w/round spots and plant material
15	1	14.0-15.0	-14.5	same
skip	3 (discard)	15.0-18.0		mostly dark gray w/lighter gray streaks
16	1	18.0-19.0	-18.5	same, w/plant material
skip	3 (discard)	19.0-22.0		dark gray; firmer
17	1	22.0-23.0	-22.5	same
skip	3 (discard)	23.0-26.0		same
18	1	26.0-27.0	-26.5	dk. gray w/lt. gray streaks; much stickier
skip	3 (discard)	27.0-30.0		same; gas pockets
19	1	30.0-31.0	-30.5	same
skip	3 (discard)	31.0-34.0		more gas pockets; dark gray and light gray streaks
20	1	34.0-35.0	-34.5	more dark than light
skip	3 (discard)	35.0-38.0		mostly dark; gas pockets
21	1	38.0-39.0	-38.5	same; a lot stickier
skip	3 (discard)	39.0-42.0		same
22	1	42.0-43.0	-42.5	very clayey
skip	3 (discard)	43.0-46.0		same
23	1	46.0-47.0	-46.5	same
skip	3 (discard)	47.0-50.0		same
24	1	50.0-51.0	-50.5	same

Table A-5. (cont'd)**Core: SB7-GC-C**

Sample #	Thickness (cm)	Depth Interval	Depth (cm)	Description
1	1	0-1.0	-0.5	soupy brown mud
2	1	1.0-2.0	-1.5	brown clay; few black and red streaks near base
3	1	2.0-3.0	-2.5	brown and gray w/red streaks
4	1	3.0-4.0	-3.5	same
5	1	4.0-5.0	-4.5	same
6	1	5.0-6.0	-5.5	gray clay w/large reddish spot; few dark streaks
7	1	6.0-7.0	-6.5	same
8	1	7.0-8.0	-7.5	gray w/rust pockets
9	1	8.0-9.0	-8.5	same
10	1	9.0-10.0	-9.5	same
11	1	10.0-11.0	-10.5	same, w/tiny amount of sand
12	1	11.0-12.0	-11.5	same
13	1	12.0-13.0	-12.5	same
14	1	13.0-14.0	-13.5	same
15	1	14.0-15.0	-14.5	dark gray w/light brown spots
skip	3 (discarded)	15.0-18.0		same
16	1	18.0-19.0	-18.5	same
skip	3 (discarded)	19.0-22.0		same
17	1	22.0-23.0	-22.5	same
skip	3 (discarded)	23.0-26.0		same
18	1	26.0-27.0	-26.5	same
skip	3 (discarded)	27.0-30.0		same
19	1	30.0-31.0	-30.5	same
skip	3 (discarded)	31.0-34.0		same
20	1	34.0-35.0	-34.5	same
skip	3 (discarded)	35.0-38.0		same
21	1	38.0-39.0	-38.5	same; black streaks at base
skip	3 (discarded)	39.0-42.0		same
22	1	42.0-43.0	-42.5	same
skip	3 (discarded)	43.0-46.0		same
23	1	46.0-47.0	-46.5	same
skip	3 (discarded)	47.0-50.0		same
24	1	50.0-51.0	-50.5	same

Table A-5. (cont'd)**Core: SB17-BC-C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	brown, little sand; black spots
2	1	1.0-2.0	-1.5	brown w/ red and gray streaks @base
3	1	2.0-3.0	-2.5	same
4	1	3.0-4.0	-3.5	brown; little red, more gray
5	1	4.0-5.0	-4.5	same
6	1	5.0-6.0	-5.5	brown w/red and black
7	1	6.0-7.0	-6.5	dark gray w/brown and red
8	1	7.0-8.0	-7.5	same
9	1	8.0-9.0	-8.5	dark gray w/brown spots
10	1	9.0-10.0	-9.5	same; worm went down in
11	1	10.0-11.0	-10.5	dark gray, less brown
12	1	11.0-12.0	-11.5	same; tiny root; worm popped up again
13	1	12.0-13.0	-12.5	same, w/tiny plant pieces; finally got worm
14	1	13.0-14.0	-13.5	sandy, dark gray w/brown spots; still plant material
15	1	14.0-15.0	-14.5	same; less brown; worm included
skip	3 (discarded)	15.0-18.0		same w/black streaks
16	1	18.0-19.0	-18.5	same; firmer
skip	3 (discarded)	19.0-22.0		same
17	1	22.0-23.0	-22.5	same; w/many black streaks; plant material
skip	3 (discarded)	23.0-26.0		same w/clay ball
18	1	26.0-27.0	-26.5	same, no black
skip	1 (discarded)	27.0-28.0		same
19	1	28.0-29.0	-28.5	dark gray, sandy; w/wood chunk
skip	1 (discarded)	29.0-30.0		same
20	1	30.0-31.0	-30.5	same, w/pebble
skip	1 (discarded)	31.0-32.0		same
21	1	32.0-33.0	-32.5	same
skip	2 (discarded)	33.0-35.0		same
22	1	35.0-36.0	-35.5	same, w/wood bits
skip	2 (discarded)	36.0-38.0		same, w/wood
23	1	38.0-39.0	-38.5	same
skip	2 (discarded)	39.0-41.0		same
24	1	41.0-42.0	-41.5	same

Table A-5. (cont'd)**Core: SB18-BC-C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	brown soupy mud w/black specks
2	1	1.0-2.0	-1.5	same; some critters
3	1	2.0-3.0	-2.5	same, w/rusty spots
4	1	3.0-4.0	-3.5	brown mud w/black and rust streaks
5	1	4.0-5.0	-4.5	same, small white specks
6	1	5.0-6.0	-5.5	same
7	1	6.0-7.0	-6.5	brown, rusty, more black
8	1	7.0-8.0	-7.5	same; dark rust spot
9	1	8.0-9.0	-8.5	same; with root
10	1	9.0-10.0	-9.5	same, a little sandy
11	1	10.0-11.0	-10.5	same, one big gas pocket
12	1	11.0-12.0	-11.5	same
13	1	12.0-13.0	-12.5	same colors; red worm
14	1	13.0-14.0	-13.5	mostly dark gray, firmer
15	1	14.0-15.0	-14.5	dark gray, rust streaks
skip	3 (discarded)	15.0-18.0		same
16	1	18.0-19.0	-18.5	mostly dark gray
skip	3 (discarded)	19.0-22.0		same
17	1	22.0-23.0	-22.5	same
skip	3 (discarded)	23.0-26.0		same, w/pebble
18	1	26.0-27.0	-26.5	dark gray, very sandy
skip	3 (discarded)	27.0-30.0		same
19	1	30.0-31.0	-30.5	firmer, w/lots of sand
skip	3 (discarded)	31.0-34.0		same
20	1	34.0-35.0	-34.5	same
skip	3 (discarded)	35.0-38.0		same
21	1	38.0-39.0	-38.5	same
skip	3 (discarded)	39.0-42.0		same
22	1	42.0-43.0	-42.5	same
skip	3 (discarded)	43.0-46.0		same
23		46.0-47.0	-46.5	same
skip	3 (discarded)	47.0-50.0		same
24		50.0-51.0	-50.5	same

Table A-5. (cont'd)**Core: SB19-BC-C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	soupy, dark brown; black streaks
2	1	1.0-2.0	-1.5	same w/red streak; twig
3	1	2.0-3.0	-2.5	brown w/black and red streaks
4	1	3.0-4.0	-3.5	same w/more black
5	1	4.0-5.0	-4.5	dark gray w/brown
6	1	5.0-6.0	-5.5	same
7	1	6.0-7.0	-6.5	dark gray w/brown spot
8	1	7.0-8.0	-7.5	dark gray w/rust pockets
9	1	8.0-9.0	-8.5	same
10	1	9.0-10.0	-9.5	same-less rust pockets
11	1	10.0-11.0	-10.5	same
12	1	11.0-12.0	-11.5	dark gray; one rust spot
13	1	12.0-13.0	-12.5	mostly dark gray; little rust
14	1	13.0-14.0	-13.5	all dark gray
15	1	14.0-15.0	-14.5	all dark gray
skip	3 (discarded)	15.0-18.0		same w/worm
16	1	18.0-19.0	-18.5	same
skip	3 (discarded)	19.0-22.0		same
17	1	22.0-23.0	-22.5	same
skip	3 (discarded)	23.0-26.0		same
18	1	26.0-27.0	-26.5	same w/hint of black streaks
skip	3 (discarded)	27.0-30.0		tan and black streaks
19	1	30.0-31.0	-30.5	gray w/black streaks
skip	3 (discarded)	31.0-34.0		same
20	1	34.0-35.0	-34.5	same but firmer (clayey)
skip	3 (discarded)	35.0-38.0		black streaks present
21	1	38.0-39.0	-38.5	same
skip	3 (discarded)	39.0-42.0		same
22	1	42.0-43.0	-42.5	same
skip	3 (discarded)	43.0-46.0		same
23	1	46.0-47.0	-46.5	same
skip	3 (discarded)	47.0-50.0		same
24	1	50.0-51.0	-50.5	same

Table A-5. (cont'd)**Core: SB20-BC-C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	brown mud w/silt and fine sand
2	1	1.0-2.0	-1.5	same
3	1	2.0-3.0	-2.5	gray and brown silty mud
4	1	3.0-4.0	-3.5	same
5	1	4.0-5.0	-4.5	same, w/rust-colored splotches
6	1	5.0-6.0	-5.5	same (w/out rust color)
7	1	6.0-7.0	-6.5	mainly gray silty mud
8	1	7.0-8.0	-7.5	gray, w/few black streaks
9	1	8.0-9.0	-8.5	gray and black w/rusty blotch
10	1	9.0-10.0	-9.5	same
11	1	10.0-11.0	-10.5	same
12	1	11.0-12.0	-11.5	same
13	1	12.0-13.0	-12.5	gray and brown w/roots
14	1	13.0-14.0	-13.5	gray w/ a little brown
15	1	14.0-15.0	-14.5	same
skip	3 (discarded)	15.0-18.0		same, w/wood
16	1	18.0-19.0	-18.5	stickier and sandier
skip	3 (discarded)	19.0-22.0		same
17	1	22.0-23.0	-22.5	tanner, drier
skip	3 (discarded)	23.0-26.0		same
18	1	26.0-27.0	-26.5	same, very dry; pebble present
skip	3 (discarded)	27.0-30.0		
19	1	30.0-31.0	-30.5	very sticky (dry), gray clay
skip	3 (discarded)	31.0-34.0		same
20	1	34.0-35.0	-34.5	same
skip	3 (discarded)	35.0-38.0		same
21	1	38.0-39.0	-38.5	same
skip	3 (discarded)	39.0-42.0		same
22	1	42.0-43.0	-42.5	same
skip	3 (discarded)	43.0-46.0		same
23		46.0-47.0	-46.5	same
skip	3 (discarded)	47.0-50.0		same
24		50.0-51.0	-50.5	same

Table A-5. (cont'd)**Core: SB21-BC-C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	brown and gray soupy mud
2	1	1.0-2.0	-1.5	more gray; firmer
3	1	2.0-3.0	-2.5	mostly gray; plant material, tan
4	1	3.0-4.0	-3.5	mostly gray; black spots, some brown
5	1	4.0-5.0	-4.5	same, darker gray
6	1	5.0-6.0	-5.5	same, w/less brown
7	1	6.0-7.0	-6.5	same, w/no brown
8	1	7.0-8.0	-7.5	dark gray
9	1	8.0-9.0	-8.5	same
10	1	9.0-10.0	-9.5	same, w/piece of shell
11	1	10.0-11.0	-10.5	dark gray and stickier
12	1	11.0-12.0	-11.5	same
13	1	12.0-13.0	-12.5	same, w/worm
14	1	13.0-14.0	-13.5	same, w/twig
15	1	14.0-15.0	-14.5	same
skip	2 (discarded)	15.0-17.0		same
16	1	17.0-18.0	-17.5	same
skip	2 (discarded)	18.0-20.0		same, w/black streaks
17	1	20.0-21.0	-20.5	same, w/black and tan streaks
skip	2 (discarded)	21.0-23.0		same, but firmer
18	1	23.0-24.0	-23.5	dark gray, w/black streaks
skip	2 (discarded)	24.0-26.0		same
19	1	26.0-27.0	-26.5	same, but silty
skip	2 (discarded)	27.0-29.0		same, firm
20	1	29.0-30.0	-29.5	same, very sticky
skip	2 (discarded)	30.0-32.0		same
21	1	32.0-33.0	-32.5	one edge very soft (soupy), more silty; same; no black streak
skip	2 (discarded)	33.0-35.0		same
22	1	35.0-36.0	-35.5	same
skip	2 (discarded)	36.0-38.0		same
23		38.0-39.0	-38.5	same, very sticky

Table A-5. (cont'd)**Core: SB22-BC-C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	very soupy tan w/gray and rust streaks; root
2	1	1.0-2.0	-1.5	same, more gray
3	1	2.0-3.0	-2.5	mostly gray w/little brown
4	1	3.0-4.0	-3.5	same w/black streaks
5	1	4.0-5.0	-4.5	same, v. little tan
6	1	5.0-6.0	-5.5	all dark gray w/black streaks
7	1	6.0-7.0	-6.5	dark gray
8	1	7.0-8.0	-7.5	same
9	1	8.0-9.0	-8.5	same, white shell fragments
10	1	9.0-10.0	-9.5	same, no shells
11	1	10.0-11.0	-10.5	mostly gray, firmer; plant material
12	1	11.0-12.0	-11.5	same w/black streak
13	1	12.0-13.0	-12.5	dark gray
14	1	13.0-14.0	-13.5	same
15	1	14.0-15.0	-14.5	same, w/black streak
skip	3 (discarded)	15.0-18.0		same
16	1	18.0-19.0	-18.5	same
skip	3 (discarded)	19.0-22.0		same
17	1	22.0-23.0	-22.5	stickier; gray w/light and dark streaks
skip	3 (discarded)	23.0-26.0		same; fewer dark streaks
18	1	26.0-27.0	-26.5	same
skip	3 (discarded)	27.0-30.0		sticky on sides, soupy towards center
19	1	30.0-31.0	-30.5	very sticky, completely dark gray
skip	3 (discarded)	31.0-34.0		same
20	1	34.0-35.0	-34.5	wetter
skip	3 (discarded)	35.0-38.0		same
21	1	38.0-39.0	-38.5	same
skip	3 (discarded)	39.0-42.0		very thick
22	1	42.0-43.0	-42.5	very thick, almost dry
skip	3 (discarded)	43.0-46.0		same
23		46.0-47.0	-46.5	one soft corner; the rest-same
skip	3 (discarded)	47.0-50.0		same, w/pebble
24		50.0-51.0	-50.5	same, no pebble

Table A-5. (cont'd)**Core: SB24-BC-C**

Sample #	Thickness (cm)	Interval (cm)	Depth (cm)	Description
1	1	0-1.0	-0.5	brown, soupy mud w/dark gray streaks
2	1	1.0-2.0	-1.5	same, w/more gray
3	1	2.0-3.0	-2.5	mostly dark gray, some brown
4	1	3.0-4.0	-3.5	same
5	1	4.0-5.0	-4.5	same
6	1	5.0-6.0	-5.5	same, w/plant piece
7	1	6.0-7.0	-6.5	same, w/plant piece
8	1	7.0-8.0	-7.5	same, w/less brown; no plant piece
9	1	8.0-9.0	-8.5	same
10	1	9.0-10.0	-9.5	same; darker gray streaks
11	1	10.0-11.0	-10.5	same and firmer
12	1	11.0-12.0	-11.5	same dark gray; little brown spots
13	1	12.0-13.0	-12.5	same
14	1	13.0-14.0	-13.5	same
15	1	14.0-15.0	-14.5	same, getting sticky
skip	3 (discarded)	15.0-18.0		same; big shell
16	1	18.0-19.0	-18.5	dark gray
skip	3 (discarded)	19.0-22.0		same, w/black streaks
17	1	22.0-23.0	-22.5	same, w/piece of wood
skip	3 (discarded)	23.0-26.0		dark gray
18	1	26.0-27.0	-26.5	same
skip	3 (discarded)	27.0-30.0		same
19	1	30.0-31.0	-30.5	same, dark gray
skip	3 (discarded)	31.0-34.0		same
20	1	34.0-35.0	-34.5	same
skip	3 (discarded)	35.0-38.0		same, but stickier
21	1	38.0-39.0	-38.5	same
skip	3 (discarded)	39.0-42.0		same
22	1	42.0-43.0	-42.5	same
skip	3 (discarded)	43.0-46.0		same, w/plant material
23		46.0-47.0	-46.5	same
skip	3 (discarded)	47.0-50.0		same
24		50.0-51.0	-50.5	same

APPENDIX B.

Saginaw Bay Water Chemistry Data

Table B-1. Saginaw Bay Water Column Chemistry

Sample	Depth (m)	$\delta^{18}\text{O}$ (per mil)	δD (per mil)	^3H (in TU)	T (°C)	pH	SiO ₂ (mg/L)
SB1-surface	-1	-8.24	-53.6	x	17.1	8.20	0.45
SB1-middle	-4	-8.28	-53.1	x	17.1	8.22	0.47
SB1-bottom	-7	-8.29	-54.0	x	17.1	8.20	0.38
SB2-surface	-1	x	x	x	17.1	8.21	0.44
SB2-middle	-4	x	x	x	17.1	8.22	0.41
SB2-bottom	-7	x	x	x	17.1	8.13	0.41
DTL1-surface	-1	x	x	x	16.8	8.38	0.19
DTL1-middle	-3.5	x	x	x	16.8	8.35	0.16
DTL1-bottom	-6	x	x	x	16.8	8.35	0.24
SB3-surface	-1	x	x	x	16.3	8.09	0.46
SB3-middle	-3.5	x	x	x	16.3	8.04	0.44
SB3-bottom	-6	x	x	x	16.3	8.08	0.50
SB4-surface	-1	-8.18	-59.4	47.4	16.3	8.21	0.31
SB4-middle	-4	-8.18	-60.0	48.5	16.3	8.27	0.22
SB4-bottom	-7	-8.20	-58.7	47.3	16.3	8.21	0.30
SB4a-surface	-1	x	x	x	16.3?	8.37	0.21
SB4a-middle	-4.5	x	x	x	16.3?	8.34	0.24
SB4a-bottom	-8	x	x	x	xxx	xxx	0.21
SB5b-surface	-1	x	x	x	18?	8.27	0.73
SB5b-bottom	-3	x	x	x	18?	8.24	0.69
SB7-surface	-1	-7.89	-55.5	56.3	16?	8.16	0.50
SB7-middle	-6	-7.91	-57.5	54.0	16?	8.18	0.40
SB7-bottom	-11	-7.85	-53.2	59.1	16?	8.09	0.40
SB7-field blank	xxx	x	x	3.5	xxx	xxx	-0.10
SB8-surface	-1	x	x	x	16?	8.22	0.24
SB8-bottom	-5	x	x	x	16?	8.26	0.22
SB9a-surface	-1	x	x	?	15?	8.06	0.59
SB9a-middle	-8	x	x	61.4	15?	8.06	0.54
SB9a-bottom	-15	x	x	67.0	15?	7.98	0.70
SB11a-surface	-1	-7.59	-56.9	63.7	15?	8.01	0.51
SB11a-middle	-14	-7.51	-55.8	62.3	15?	7.69	0.59
SB11a-bottom	-27	-7.45	-56.5	67.3	15?	7.96	0.62

Table B-1. (cont'd)

Sample	Mg (mg/L)	Ca (mg/L)	K (mg/L)	Na (mg/L)	Alkalinity (mg/L HCO ₃ ⁻)	SO ₄ (mg/L)	Cl (mg/L)	Br (mg/L)
SB1-surface	11.9	38.9	1.8	16.0	145	22	22.0	0.31
SB1-middle	12.0	39.5	1.9	15.7	153	14	15.8	0.20
SB1-bottom	12.1	39.0	1.9	16.2	142	20	24.2	0.29
SB2-surface	9.1	30.7	1.5	10.5	105	10	15.6	0.18
SB2-middle	9.2	30.8	1.5	10.5	133	17	15.8	0.18
SB2-bottom	9.2	30.4	1.5	10.9	114	17	15.4	0.18
DTL1-surface	9.7	35.3	1.6	6.6	115	16	14.5	0.17
DTL1-middle	9.6	34.6	1.5	6.2	114	13	12.0	0.15
DTL1-bottom	9.6	34.6	1.5	5.8	115	18	16.6	0.18
SB3-surface	8.8	29.5	1.4	9.2	109	16	13.4	0.15
SB3-middle	8.8	29.4	1.4	9.1	111	16	13.3	0.15
SB3-bottom	8.9	29.3	1.4	9.3	117	16	13.2	0.14
SB4-surface	9.1	35.5	1.4	10.6	118	16	12.9	0.15
SB4-middle	9.0	34.7	1.4	8.8	120	15	10.8	0.13
SB4-bottom	9.2	35.0	1.4	9.8	117	15	13.8	0.15
SB4a-surface	9.6	36.3	1.6	11.5	121	17	16.9	0.17
SB4a-middle	9.4	35.8	1.6	9.9	125	16	15.8	0.15
SB4a-bottom	9.5	36.2	1.6	11.9	-	17	16.9	0.16
SB5b-surface	13.4	49.5	2.6	17.3	151	22	28.5	0.25
SB5b-bottom	13.9	49.6	2.6	17.2	156	24	30.0	0.25
SB7-surface	8.8	19.2	1.1	6.0	91	15	9.6	0.13
SB7-middle	8.9	22.5	1.2	6.0	106	14	10.2	0.12
SB7-bottom	5.6	15.8	0.7	3.3	107	9	6.0	0.08
SB7-fieldblank	0.4	0.1	0.0	0.0	-	<2	1.3	0.02
SB8-surface	9.4	34.4	1.5	10.4	96	17	15.0	0.17
SB8-bottom	9.5	35.0	1.6	11.9	118	16	15.5	0.16
SB9a-surface	7.0	26.1	0.9	6.4	98	12	7.0	0.08
SB9a-middle	7.0	25.7	1.0	6.9	94	14	6.2	0.08
SB9a-bottom	6.9	25.2	1.0	7.4	90	11	6.0	0.08
SB11a-surface	7.0	25.7	0.9	2.5	97	12	6.6	0.09
SB11a-middle	6.8	25.5	0.8	3.4	90	12	6.0	0.09
SB11a-bottom	6.7	25.3	0.8	1.4	93	13	6.0	0.10

Table B-2. Saginaw Bay Porewater Chemistry – Geochemical Modeling

(All concentrations in mg/L.)

Sample	Depth (cm)	T (°C)	pH	SiO ₂	Mg	Ca	K	Na	Alkalinity (HCO ₃ ⁻)	SO ₄	Cl
SB1-BCC-4	-2	23.0	7.61	-	-	-	-	-	157	4	20
SB1-BCC-11	-9	23.0	7.40	-	-	-	-	-	185	4	15
SB1-BCC-18	-16	23.0	7.35	-	-	-	-	-	223	<2	16
SB1-BCC-22	-22	23.0	7.49	-	-	-	-	-	235	<2	18
SB3-PC-1	-15	23.0	7.30	17.0	12.1	42	2.9	10.1	258	<2	14
SB4-PC-1	-15	23.0	7.31	16.3	15.2	48	2.1	67	235	4	84
SB4-PC-4	-107	23.0	7.65	15.8	37.9	119	3.5	318	583	2	406
SB4-PC-6	-171	23.0	7.98	15.3	44.8	145	3.8	388	665	<2	552
SB4b-PC-1	-15	24.1	7.50	18.2	15.6	44	5.7	18.2	201	<2	24
SB4b-PC-3	-76	24.1	7.64	7.9	14.3	42	2.8	30.7	203	10	50
SB7-BCG-1	-2.5	20.8	7.59	11.0	12.2	44	2.3	9.7	223	4	14
SB7-BCG-2	-27.5	20.8	7.19	16.8	13.1	46	3.1	29.4	243	3	48
SB7-BCG-3	-52.5	20.8	7.31	20.8	15.8	53	3.4	67	322	<2	84
SB17-BCG-1	-2.5	19.5	7.65	8.3	10.3	36	2.3	8.7	140	14	16
SB17-BCG-2	-14.5	19.5	7.44	17.7	10.9	38	2.9	9.9	145	2	13
SB17-BCG-3	-26.5	19.5	7.32	14.9	11.8	41	2.9	9.8	185	<2	19
SB18-PC-1	-15	19.5	7.43	12.0	9.6	34	2.3	9.4	172	6	13
SB18-PC-2	-30	19.5	7.57	10.8	13.4	40	1.9	10.5	227	<2	14
SB19-PC-1	-15	19.5	7.26	14.6	20.1	67	2.4	13.3	304	<2	14
SB19-PC-4	-107	19.5	7.36	10.9	15.3	48	1.6	13.6	231	<2	15
SB19-PC-7	-198	19.5	7.42	8.8	15.9	48	1.9	18.4	222	<2	24.2
SB20-BCG-1	-2.5	19.5	7.58	11.4	16.3	57	2.6	12.8	295	<2	20
SB20-BCG-2	-22.5	19.5	8.08	5.9	9.7	39	2.8	14.8	185	<2	28
SB20-BCG-3	-42.5	19.5	7.85	6.3	11.1	44	2.8	25.9	212	<2	50
SB22-PC-1	-8	19.5	7.27	13.1	12.5	46	3.2	11.1	244	8	15
SB22-PC-5	-81	19.5	7.30	11.3	13.9	48	2.0	18.8	261	<2	27
SB24-PC-1	-10	19.5	7.23	10.4	9.9	34	1.7	14.9	171	5	23
SB24-PC-4	-71	19.5	7.27	11.5	18.0	54	1.4	118	243	<2	200
SB24-PC-8	-165	19.5	7.60	6.5	27.5	82	2.4	273	322	2	440

Table B-3. Saginaw Bay Gravity Core Porewater Chemistry*(All concentrations in mg/L.)*

Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br
SB1-GC-1	-14.00	9.2	21.1	113	3.1	13.7	22.5	0.09
SB1-GC-2a	-33.00	10.4	14.6	57	2.6	20.3	39.2	0.15
SB1-GC-2b	-45.75	12.9	11.7	47	2.1	24.7	49	0.19
SB1-GC-2c	-56.00	12.7	16.0	65	1.9	31.0	53	0.21
SB1-GC-3a	-63.50	6.9	20.0	89	2.1	40	69	0.24
SB1-GC-3b	-74.25	4.5	18.7	80	2.5	43	73	0.27
SB1-GC-3c	-85.00	7.7	20.2	86	2.0	48	80	0.29
SB1-GC-4a	-96.50	3.8	24.6	104	2.2	59	106	0.30
SB1-GC-4b	-105.50	5.9	21.2	82	2.1	61	109	0.36
SB1-GC-4c	-114.50	4.0	21.8	82	2.4	66	119	0.38
SB1-GC-5a	-125.00	2.2	25.1	93	2.7	76	137	0.42
Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br
SB2-GC-1a	-4.5	15.2	25	64	2.3	8	15.1	0.09
SB2-GC-1b	-28	10.6	21	60	0.8	8	17.3	0.10
SB2-GC-2a	-37.75	9.8	26	60	1.5	9	21.3	0.15
SB2-GC-2b	-48	6.4	21	55	1.5	10	22.5	0.16
SB2-GC-3a	-70.5	3.7	38	107	1.5	14	24.7	QNS
SB2-GC-3b	-82	2.7	29	76	1.5	13	24.7	0.08
SB2-GC-4b	-113.5	2.7	27	102	2.3	18	26.8	0.18
SB2-GC-5b	-147	2.4	28	95	2.3	19	31.0	0.10
SB2-GC-6b	-178	3.2	33	133	3.1	26	33.9	<.05
SB2-GC-7a	-187	4.2	31	112	3.1	28	39.5	0.16
SB2-GC-7b	-197	3.9	29	103	3.1	28	38.0	0.16

Table B-3. (cont'd)

(All concentrations in mg/L.)

Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br
SB3-GC-1	-14.0	11.4	21.0	64	1.6	9.1	16.5	0.07
SB3-GC-2a	-33.5	6.5	20.1	63	1.5	11.0	15.8	0.09
SB3-GC-2b	-44.0	6.3	18.4	56	1.3	10.2	16.1	0.10
SB3-GC-3a	-63.5	7.5	19.7	70	1.4	13.1	15.4	0.09
SB3-GC-3b	-74.5	5.3	20.9	75	1.7	13.3	15.1	0.11
SB3-GC-4b	-111.5	3.3	17.6	67	1.3	16.5	15.7	0.04

Table B-3. (cont'd)*(All concentrations in mg/L.)*

Sample	Depth (cm)	Si	Mg	Ca	K	Na	Cl	Br
SB4-GC-1a	-4	8.5	16.5	55	3.2	27.5	38.5	0.11
SB4-GC-1b	-11.5	8.8	15.0	47	3.3	29.7	40.5	0.12
SB4-GC-1c	-18.5	3.5	14.3	46	2.9	35.8	47	0.15
SB4-GC-1d	-24.5	5.6	14.8	45	2.2	42	48	0.17
SB4-GC-2a	-31	6.7	16.0	46	1.9	84	130	0.37
SB4-GC-2b	-39	8.1	15.2	44	2.8	100	145	0.38
SB4-GC-2c	-47	8.5	15.3	43	2.1	108	170	0.42
SB4-GC-2d	-55.5	11.8	16.7	47	1.9	135	190	0.56
SB4-GC-3a	-64	10.0	22.1	61	2.2	173	255	0.62
SB4-GC-3b	-72	9.0	22.6	60	2.3	181	275	0.67
SB4-GC-3c	-80	4.8	23.5	60	3.1	192	290	0.69
SB4-GC-3d	-87.5	5.5	25.4	68	2.4	204	300	0.74
SB4-GC-4a	-96	2.2	31.3	96	2.9	288	395	0.92
SB4-GC-4b	-105	4.0	30.8	78	2.9	272	380	0.89
SB4-GC-4c	-112.5	7.4	30.0	76	2.1	248	360	0.83
SB4-GC-5a	-120	3.5	44	116	2.8	337	450	1.03
SB4-GC-5b	-128	4.1	45	120	3.0	339	475	1.08
SB4-GC-5c	-136	5.1	45	114	2.8	347	515	1.18
SB4-GC-5d	-144	3.0	50	129	3.6	366	525	1.13
SB4-GC-6a	-152	1.9	58	160	4.8	431	625	1.30
SB4-GC-6b	-160	5.9	57	152	4.2	408	595	1.19
SB4-GC-6c	-168	4.6	51	151	4.3	449	610	1.22
SB4-GC-6d	-176	5.1	55	162	5.2	470	640	1.15
SB4-GC-6e	-182.5	3.4	60	181	5.0	463	625	1.00

Table B-3. (cont'd)*(All concentrations in mg/L.)*

Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br
SB4a-GC-1a	-4	10.9	27.3	113	2.8	16.4	20.5	0.04
SB4a-GC-1b	-11.5	7.8	28.9	109	2.9	17.6	21	0.04
SB4a-GC-2a	-20	4.3	61	231	6.5	43	28.3	0.04
SB4a-GC-2b	-30.5	3.4	61	226	7.5	46	30.5	0.06
SB4a-GC-3a	-42.5	4.6	64	211	6.2	65	46	0.14
SB4a-GC-3b	-53	-	-	-	-	-	45	0.12
Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br
SB4b-GC-1	-13.5	10.4	17.0	68	3.5	15.4	23.6	0.06
Sb4b-GC-2a	-30.5	-	26.0	51	2.5	15.0	25.5	0.07
SB4b-GC-2b	-42	10.3	11.7	35	2.4	16.5	29.1	0.14
Sb4b-GC-3a	-62	-	29.0	87	1.8	26.0	36	0.18
SB4b-GC-3b	-72.25	4.8	27.7	89	2.8	32	38	0.14
SB4b-GC-4a	-92	2.7	18.8	57	3.2	37	48	0.18
SB4b-GC-5a	-110.5	-	22	39	1.5	26	59	0.22
Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br
SB5b-GC-1a	-3.5	5.7	26	123	2.3	17	36	0.11
SB5b-GC-1b	-10.5	6.5	28.0	123	5.5	26.2	34	0.10
SB5b-GC-1c	-17.5	3.6	38	160	4.6	27	37	0.14
SB5b-GC-2a	-24.5	3.3	39	175	5.4	32	47	0.18
SB5b-GC-2b	-31.5	6.1	21	105	3.1	30	51	0.17
SB5b-GC-2c	-39.5	-	26	104	3.9	32	58	0.18
SB5b-GC-3a	-47.5	-	-	-	4.6	45	58	0.20
SB5b-GC-3b	-53	3.1	29	121	3.9	42	75	0.25
SB5b-GC-3c	-57.5	7.2	34	118	2.3	47	78	0.30

Table B-3. (cont'd)

(All concentrations in mg/L; stable isotope values in per mil.)

Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br	δ¹⁸O	δ D
SB7-GC-1	-8	10.8	21.1	66	3.0	15.5	22	0.1	-8.12	-57.8
SB7-GC-2a	-22	16.9	17.1	59	3.2	43	44	0.2	-7.99	-53.7
SB7-GC-2b	-34	13.2	14.2	55	3.2	57	75	0.2	-7.91	-53.8
SB7-GC-3a	-52	7.9	25.7	72	3.8	103	73	0.1	-8.07	-56.9
SB7-GC-3b	-63	10.5	18.3	57	3.1	108	160	0.4	-7.91	-58.4
SB7-GC-3c	-73	6.9	28.1	83	4.2	127	227	0.5	-8.29	-58.4
SB7-GC-4b	-95	5.7	33	98	4.4	193	385	0.9	-8.66	-59.8
SB7-GC-4c	-105	2.3	23.6	75	4.0	311	405	0.9	-	-
SB7-GC-5	-117	-	33	107	4.6	360	520	1.2	-9.03	-63.3

Table B-3. (cont'd)*(All concentrations in mg/L; stable isotope values in ‰.)*

Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br	δ¹⁸O	δ D
SB17-GC-1a	-4	13.3	24	70	1.7	9.0	18.0	0.12	-7.94	-61.4
SB17-GC-1b	-14	9.8	31	84	2.0	10.0	17.5	0.09	-	-
SB17-GC-2a	-24	6.5	22	58	0.9	8.0	17.4	0.08	-7.55	-55.4
SB17-GC-2b	-32	3.9	23	58	1.8	9.0	18.0	0.08	-	-
SB17-GC-2c	-39	5.4	24	61	1.5	10	17.7	0.10	-	-
SB17-GC-3a	-46	3.9	32	84	1.6	13	19.9	0.07	-	-
SB17-GC-3b	-53.5	2.8	28	73	1.4	13	21.5	0.09	-7.51	-57.3
SB17-GC-3c	-59.5	5.2	24	86	1.5	11	20.5	0.13	-	-
SB17-GC-4a	-65.5	3.6	31	94	1.8	21	23.3	0.15	-7.57	-55.1
SB17-GC-4b	-72.5	3.3	25	76	2.1	17	22.8	0.13	-	-
SB17-GC-4c	-79.5	2.6	27	79	3.2	30	25.7	0.17	-	-
SB17-GC-4d	-85.5	2.0	28	81	3.2	15	26.4	0.16	-	-
SB17-GC-5a	-90.5	-	27	64	2.1	23	26.7	0.16	-7.41	-56.9
SB17-GC-5b	-96	3.2	18	49	4.2	19	27.4	0.15	-	-
SB17-GC-5c	-102.5	-	24	67	2.3	22	30.1	0.17	-7.29	-55.7
SB17-GC-5d	-109.5	2.9	-	-	-	-	29.6	0.32	-	-
SB17-GC-5e	-116	-	18	46	2	22	28.5	0.17	-7.20	-54.8

Table B-3. (cont'd)*(All concentrations in mg/L.)*

Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br
SB18-GC-1	-5	9.7	37	136	3.2	11.9	14.7	0.03
SB18-GC-2a	-15	4.9	69	193	4.2	14.9	15.6	<.02
SB18-GC-2b	-24.5	6.5	33	100	2.6	12.8	15.9	<.02
SB18-GC-3a	-34.75	4.7	32	87	2.4	15.5	16.8	<.02
SB18-GC-3b	-44.25	3.4	51	203	2.7	19.9	18.8	<.02
SB18-GC-4a	-57.5	2.5	55	240	2.5	25.8	22.6	0.03
SB18-GC-4b	-67	6.7	34	92	3.0	25.6	21.6	0.1
SB18-GC-4c	-77	7.0	31	83	2.5	24.6	20.4	QNS
Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br
SB19-GC-1	-15.25	6.6	20.1	67	2.9	13.3	15.8	0.13
SB19-GC-2	-45.75	10.0	11.1	34	2.1	10.1	15.3	0.19
SB19-GC-3	-76.25	5.5	9.7	29.8	1.7	8.6	16.4	0.22
SB19-GC-4	-106.8	6.8	14.1	41	1.8	10.9	17.6	0.22
SB19-GC-5a	-129.8	3.5	13.8	41	2.4	12.9	18.6	0.16
SB19-GC-5b	-145	5.7	16.5	55	1.9	14.4	19.3	0.20
SB19-GC-6a	-160.3	5.2	16.7	57	2.2	15.8	21.3	0.25
SB19-GC-6b	-175.5	4.5	15.4	50	2.1	17.5	21.7	0.24
SB19-GC-7a	-190.5	2.1	18.5	63	3.3	19.5	20.0	0.27
SB19-GC-7b	-205.8	7.9	15.9	48	1.9	22.0	24.2	0.29
SB19-GC-8	-218.5	0.9	10.8	36	2.2	21.0	29.5	0.33

Table B-3. (cont'd)*(All concentrations in mg/L.)*

Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br
SB20-1	-6.5	11.0	17.6	73	2.8	15.0	21.1	0.19
SB20-2a	-17.5	16.5	16.9	73	3.7	19.0	35	0.24
SB20-2b	-27.5	9.4	15.7	67	3.4	24.9	42	0.28
SB20-3a	-42.5	6.7	21.3	89	2.7	59	95	0.46
SB20-3b	-52.5	3.7	19.5	82	3.3	59	100	0.47
SB20-5a	-90	3.0	27.6	103	2.6	102	186	0.71
Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br
SB21-1	-7	12.5	18.5	83	2.5	12.6	18.0	0.14
SB21-2	-24	7.6	29.2	95	2.6	14.5	22.0	0.14
SB21-3	-44.5	5.1	25.5	93	3.4	19.9	29.0	0.16
SB21-4a	-56	3.7	32.4	101	4.3	27.1	34.0	0.18
SB21-4b	-66	4.5	26.2	77	3.0	24.6	38.0	0.18
SB21-5a	-83.5	3.3	23.9	78	2.3	25.6	45	0.14
SB21-5b	-93	5.0	26.2	95	3.3	30.0	45	0.19
SB21-6a	-114	4.8	23.7	88	2.6	29.1	52	0.24
SB21-6b	-124	3.7	23.5	84	3.4	32	51	0.25
SB21-7a	-140.5	4.3	30.7	105	3.6	38	55	0.21

Table B-3. (cont'd)*(All concentrations in mg/L; stable isotope values in ‰.)*

Sample	Depth (cm)	SiO ₂	Mg	Ca	K	Na	Cl	Br	δ ¹⁸ O	δ D
SB22-1	-4	9.7	25.2	104	3.1	13.3	16.1	0.08	-8.08	-52.4
SB22-2	-15	7.8	28.7	96	2.8	15.4	17.7	0.11	-7.69	-45.9
SB22-3a	-32	6.8	15.1	50	2.5	13.5	21.4	0.20	-7.62	-49.0
SB22-3b	-42.75	5.3	13.4	46	2.7	14.1	22.5	0.21	-	-
SB22-4a	-54	3.3	22.6	66	2.8	17.2	23.9	0.21	-7.63	-50.1
SB22-4b	-64.5	3.5	17.9	55	2.7	17.0	24.6	0.21	-	-
SB22-5a	-75	3.9	18.8	57	2.5	19.3	26.0	0.15	-7.64	-50.6
SB22-5b	-83	2.5	21.4	64	2.7	20.4	26.6	0.15	-7.73	-57.5
SB22-6a	-97.75	4.8	20.0	68	2.6	23.5	29.6	0.20	-7.67	-51.4
SB22-6b	-107.5	4.9	20.4	80	2.8	25.2	29.2	0.23	-	-
SB22-7a	-126	4.3	18.6	76	2.9	28.0	32	0.20	-7.68	-47.0
SB22-7b	-136	3.5	18.3	79	3.2	28.0	33	0.21	-	-
SB22-8a	-152.5	3.7	21.5	88	3.4	32	35	0.26	-7.73	-52.8
SB22-8b	-161.5	4.2	20.7	85	3.2	32	37	0.25	-	-
SB22-9a	-178	2.8	17.9	77	3.3	35	41	0.18	-7.73	-
SB22-9b	-187	3.2	24.4	96	3.5	38	39	0.23	-7.76	-
SB22-10a	-206	7.2	21.4	78	3.3	43	46	0.32	-7.86	-
SB22-10b	-215	2.7	22.5	79	3.6	42	49	0.34	-7.88	-

Table B-3. (cont'd)*(All concentrations in mg/L; stable isotope values in ‰.)*

Sample	Depth (cm)	SiO₂	Mg	Ca	K	Na	Cl	Br	δ¹⁸O	δ D
SB24-1	-3.25	5.1	47.9	141	5.4	18.2	20	<.05	-8.05	-56.0
SB24-2	-17.25	7.2	18.9	57	2.5	34	53	0.16	-	-
SB24-3	-39.5	5.0	22.2	62	2.3	71	112	0.32	-7.69	-58.1
SB24-4a	-56	3.8	25.4	65	2.6	107	172	0.43	-7.85	-55.1
SB24-5a	-75	2.9	38	100	3.1	150	230	0.54	-	-
SB24-5b	-85	2.9	27.7	74	3.3	154	233	0.53	-7.98	-61.1
SB24-6a	-97.5	4.3	27.5	86	3.2	190	291	0.73	-8.07	-55.3
SB24-6b	-108	2.8	24.5	84	3.4	193	294	0.73	-7.98	-57.1
SB24-7a	-124	2.7	36	121	3.9	227	365	0.98	-8.14	-53.0
SB24-7b	-134	2.6	28.6	88	3.8	235	371	0.92	-	-
SB24-8a	-151	3.6	40	123	3.7	292	435	1.06	-8.23	-62.9
SB24-8b	-161	3.4	33	112	3.4	283	445	1.06	-8.08	-56.9
SB24-9a	-176	4.3	33	107	2.9	311	527	1.16	-8.32	-51.5
SB24-9b	-187	3.2	32	104	3.2	309	540	1.20	-8.34	-58.0
SB24-10a	-208	3.6	40	122	4.1	380	634	1.60	-8.40	-54.7
SB24-10b	-218	4.1	44	128	4.2	413	683	1.74	-8.47	-61.8

Table B-4. Ferrous Iron Concentrations in Porewater Samples

SB1 Depth (cm)	SB1 Fe(II) (mg/L)	SB3 Depth (cm)	SB3 Fe(II) (mg/L)	SB4b Depth (cm)	SB4b Fe(II) (mg/L)	SB22 Depth (cm)	SB22 Fe(II) (mg/L)
-1	0.01	-1	-0.01	-1	0.01	-1	0.00
-2	0.03	-2	0.26	-2	0.00	-2	0.45
-3	0.10	-4	1.32	-3	0.01	-3	3.43
-4	0.41	-5	3.19	-4	0.09	-4	4.32
-5	0.37	-7	0.84	-5	0.33	-5	2.64
-6	0.35	-8	2.07	-7	1.67	-7	3.06
-7	0.42	-9	1.68	-9	1.70	-9	2.98
-9	0.11	-10	1.50	-11	2.21	-11	2.75
-10	0.38	-12	2.18	-13	3.78	-13	3.57
-14	1.56	-14	0.78	-15	3.78	-15	3.77
-16	1.58	-16	1.04	-18	4.59	-18	3.92
-18	0.31	-18	2.15	-21	4.40	-21	3.28
-20	0.24	-20	0.08	-24	4.53	-24	2.34
-22	0.73	-22	2.57	-27	3.65	-27	3.70
-24	0.43	-26	0.53	-30	2.56	-30	3.98
-26	0.51	-38	1.29	-33	5.76	-33	2.79
-28	0.43	-	-	-	-	-	-
-30	0.23	-	-	-	-	-	-
-34	1.06	-	-	-	-	-	-
-38	0.01	-	-	-	-	-	-
-42	0.59	-	-	-	-	-	-

Table B-5. Trace Metal Concentrations in Porewater Samples**Core: SB1-BC-1D***[Shaded values denote concentrations with RSD values exceeding 15 per cent.]*

Sample #	Depth (cm)	Mn (mg/L)	Cd (µg/L)	Cu (µg/L)	Zn (µg/L)	Ba (µg/L)	Sr (µg/L)
1	-0.5	1.5	1.1	2.2	94	34.6	165
2	-1.5	1.1	0.1	1.7	10.5	30.1	135
3	-2.5	1.1	6.3	1.1	31.4	32.2	136
4	-3.5	1.2	0.1	15.4	46	27.0	136
5	-4.5	1.5	0.3	2.2	23.7	29.9	156
6	-5.5	1.2	0.1	0.5	11.8	23.9	135
7	-6.5	1.3	0.2	0.9	18.6	21.4	142
8	-7.5	1.2	0.2	0.7	26.9	22.4	137
9	-8.5	1.4	0.1	1.1	14.3	27.0	150
10	-9.5	1.1	0.4	1.4	60	25.6	142
11	-10.5	1.1	0.2	2.0	26.7	26.9	143
12	-12	0.8	0.2	1.1	23.0	24.9	127
13	-14	1.1	0.8	0.5	32.5	27.2	163
14	-16	1.1	0.2	0.9	75	33.9	171
15	-18	1.0	0.1	0.4	21.1	28.5	182
16	-20	1.0	0.1	0.5	24.1	30.9	194
17	-22	1.1	0.1	2.3	29.7	31.0	214
18	-24	1.0	0.1	0.7	48	32.1	219
19	-26	1.0	0.1	1.6	156	29.5	224
20	-28	1.1	0.1	0.4	15.2	35.4	271
21	-30.5	1.3	0.0	0.7	16.0	32.7	304
22	-33.5	1.1	0.1	1.4	13.6	30.9	269
23	-36.5	1.4	0.2	1.7	19.0	32.5	328
24	-39.5	1.2	0.1	3.0	36.5	30.0	275

Table B-5. (cont'd)**Core: SB3-BC-1D***[Shaded values denote concentrations with RSD values exceeding 15 per cent.]*

Sample #	Depth (cm)	Mn (mg/L)	Cd (µg/L)	Cu (µg/L)	Zn (µg/L)	Ba (µg/L)	Sr (µg/L)
1	-0.5	4.9	0.1	1.5	23.1	46	202
2	-1.5	4.6	0.2	1.6	57	38.7	201
3	-2.5	3.2	0.2	2.6	35.5	33.2	167
4	-3.5	2.9	0.1	1.0	55	26.2	140
5	-4.5	3.1	0.4	2.2	74	29.3	138
6	-5.5	2.3	0.1	1.0	37.4	22.9	105
7	-6.5	2.5	0.2	1.5	126	27.0	134
8	-7.5	2.5	0.2	3.6	189	36.2	148
9	-8.5	2.3	0.4	2.4	111	30.7	145
10	-9.5	1.6	0.1	0.6	37.5	24.8	116
11	-10.5	1.3	0.2	0.6	71	21.0	110
12	-11.5	1.2	1.7	2.1	125	28.1	106
13	-12.5	1.0	0.1	2.2	53	26.2	104
14	-13.5	1.0	0.3	2.6	143	32.2	112
15	-14.5	1.1	1.4	3.1	105	28.6	115
16	-18.5	0.9	0.1	3.9	73	23.1	102
17	-22.5	1.0	0.1	1.7	73	26.0	114
18	-26.5	1.3	2.9	3.0	142	31.9	140
19	-30.5	1.5	3.0	3.3	176	38.2	163

Table B-5. (cont'd)**Core: SB4b-BC-1D***[Shaded values denote concentrations with RSD values exceeding 15 per cent.]*

Sample #	Depth (cm)	Mn (mg/L)	Cd (µg/L)	Cu (µg/L)	Zn (µg/L)	Ba (µg/L)	Sr (µg/L)
1	-0.5	1.2	0.2	2.5	106	35.9	184
2	-1.5	1.7	0.2	1.9	188	36.8	200
3	-2.5	2.0	0.2	3.4	129	40	233
4	-3.5	1.4	0.1	2.3	54	33.6	212
5	-4.5	2.0	0.1	1.8	97	40	231
6	-5.5	1.9	0.2	2.2	48	33.6	219
7	-6.5	1.7	0.3	1.7	35.2	29	182
8	-7.5	1.0	0.2	9.0	109	26.3	150
9	-8.5	1.1	0.2	2.1	107	25.8	138
10	-9.5	1.1	0.2	2.5	70	49	123
11	-10.5	0.8	0.2	1.8	233	23.2	110
12	-11.5	0.7	0.3	2.2	160	33.2	104
13	-12.5	0.8	0.2	2.2	209	26.7	110
14	-13.5	0.8	0.8	13.3	329	28.9	126
15	-14.5	0.7	0.3	1.3	50	28.7	112
16	-18.5	0.7	0.8	1.6	118	27.5	129
17	-22.5	0.9	3.0	5.8	359	30.5	135
18	-26.5	1.1	0.2	1.1	90	34.3	193
19	-30.5	1.2	0.5	3.2	148	35.2	190
20	-34.5	1.3	0.1	1.9	173	43	210
21	-38.5	0.7	0.8	9.8	436	44	110
22	-42.5	0.6	0.4	5.9	101	26.5	104
23	-46.5	0.7	0.3	4.0	179	44	114
24	-50.5	0.7	0.2	3.0	223	38.4	114
Field	Blank	0.0	0.1	1.7	85	4.6	0.8

Table B-5. (cont'd)**Core: SB17-BC-1D***[Shaded values denote concentrations with RSD values exceeding 15 per cent.]*

Sample #	Depth (cm)	Mn (mg/L)	Cd (µg/L)	Cu (µg/L)	Zn (µg/L)	Ba (µg/L)	Sr (µg/L)
1	-0.5	1.8	0.2	4.1	92	34.5	141
2	-1.5	2.2	0.1	7.7	78	25.5	140
3	-2.5	0.6	0.1	1.2	40	23.0	131
4	-3.5	1.1	0.1	2.7	95	25.7	132
5	-4.5	0.8	0.1	3.7	338	26.6	125
6	-5.5	0.5	0.1	1.2	270	28.3	124
7	-6.5	0.6	0.1	6.2	100	36.8	103
8	-7.5	1.0	0.2	3.5	52	28.9	115
9	-8.5	0.9	0.1	3.0	255	35.5	108
10	-9.5	1.1	0.2	0.9	126	22.8	114
11	-10.5	1.2	0.5	1.0	34.5	31.0	124
12	-11.5	1.2	0.1	3.6	129	25.2	113
13	-12.5	1.0	0.0	1.0	34.7	25.8	99
14	-13.5	1.0	0.1	1.0	34.8	32.3	106
15	-14.5	1.3	24.1	5.2	149	55.9	110
16	-18.5	1.2	0.2	2.2	56	33.9	110
17	-22.5	-	-	-	-	-	-
18	-26.5	1.2	0.3	2.1	209	38.9	131
19	-28.5	0.5	0.4	3.8	261	50	101
20	-30.5	0.9	2.3	6.7	369	49	129
21	-32.5	-	-	-	-	-	-
22	-35.5	-	-	-	-	-	-
23	-38.5	1.1	1.5	18.0	547	91	139
24	-	-	-	-	-	-	-

Table B-5. (cont'd)**Core: SB19-BC-1D***[Shaded values denote concentrations with RSD values exceeding 15 per cent.]*

Sample #	Depth (cm)	Mn (mg/L)	Cd (µg/L)	Cu (µg/L)	Zn (µg/L)	Ba (µg/L)	Sr (µg/L)
1	-0.5	0.8	0.2	1.0	38.7	35.4	161
2	-1.5	1.4	0.2	1.2	62	33.8	148
3	-2.5	1.4	0.3	1.3	172	31.6	155
4	-3.5	1.3	0.7	20.1	378	93	186
5	-4.5	1.0	0.1	1.2	117	29.2	128
6	-5.5	1.0	0.1	2.1	99	26.0	122
7	-6.5	0.8	0.1	0.9	152	27.8	109
8	-7.5	0.8	6.5	1.8	115	29.5	112
9	-8.5	0.8	0.2	2.0	123	32.8	113
10	-9.5	0.8	0.9	1.8	116	30.1	117
11	-10.5	0.8	0.1	1.1	32.3	31.4	113
12	-11.5	0.7	0.1	0.9	134	25.1	110
13	-12.5	1.0	0.2	2.0	105	35.3	119
14	-13.5	0.7	0.2	7.7	116	28.5	98
15	-14.5	0.8	0.3	2.0	34.5	24.0	104
16	-18.5	0.9	0.3	1.3	41	31.1	127
17	-22.5	1.1	1.3	1.2	99	30.8	134
18	-26.5	1.4	0.2	1.0	44	30.0	160
19	-30.5	3.7	0.8	6.8	182	141	423
20	-34.5	1.1	1.3	16.5	178	41	124
21	-38.5	2.5	1.2	3.6	66	38.8	229
22	-42.5	1.8	0.5	4.4	320	351	167
23	-46.5	-	-	-	-	-	-
24	-50.5	2.8	0.5	4.3	188	50	217

Table B-5. (cont'd)**Core: SB22-BC-1D***[Shaded values denote concentrations with RSD values exceeding 15 per cent.]*

Sample #	Depth (cm)	Mn (mg/L)	Cd (µg/L)	Cu (µg/L)	Zn (µg/L)	Ba (µg/L)	Sr (µg/L)
1	-0.5	1.4	3.4	1.2	226	30.8	132
2	-1.5	1.5	0.3	0.9	41	25.0	113
3	-2.5	1.4	0.3	0.6	52	25.9	116
4	-3.5	1.5	0.2	0.9	30.9	26.4	107
5	-4.5	1.8	0.1	1.5	22.3	28.7	113
6	-5.5	2.0	0.1	1.3	40	28.7	121
7	-6.5	2.3	0.3	1.3	145	28.5	137
8	-7.5	2.3	0.2	0.6	36.1	19.8	125
9	-8.5	2.5	0.1	0.5	39.6	25.0	147
10	-9.5	2.5	0.2	5.4	146	52.1	149
11	-10.5	2.6	0.1	2.0	55	36.1	165
12	-11.5	2.4	0.2	5.6	103	32.4	165
13	-12.5	2.1	0.0	1.0	239	31.7	161
14	-13.5	2.0	0.1	1.9	27.4	34.2	154
15	-14.5	2.1	0.0	0.8	38.8	33.7	173
16	-18.5	1.7	0.1	1.1	118	37.6	169
17	-22.5	1.5	0.1	6.8	132	39.0	160
18	-26.5	-	-	-	-	-	-
19	-30.5	-	-	-	-	-	-
20	-34.5	-	-	-	-	-	-
21	-38.5	2.2	0.1	2.2	192	63	212
22	-42.5	-	-	-	-	-	-
23	-46.5	-	-	-	-	-	-
24	-50.5	-	-	-	-	-	-
Field	Blank	0.0	0.0	1.3	32.4	1.2	0.2

APPENDIX C.

Terrestrial Core Porewater Chemistry

Table C-1. Terrestrial Core Porewater Chemistry*(Depth in meters below land surface.)*

	Depth (m)	Cl (mg/L)	Br (mg/L)	Cl/Br	del O (‰)	del D (‰)
Core A (Schwab)	-8.8	720	1.6	450	-15.75	-112
	-10.7	760	1.9	400	-14.60	-102
	-12.5	-	-	-	-15.10	-107
	-15.9	910	1.9	479	-15.40	-110
	-18.6	1040	2.3	452	-15.70	-112
	-22.3	1150	2.3	500	-15.70	-112
	-30.5	-	-	-	-15.20	-
Core B (Wegner)	-5.2	70	0.42	167	-10.15	-69.5
	-8.4	77	0.57	135	-11.15	-77.5
	-11.3	105	0.94	-	-11.75	-82
	-12.8	200	0.50	400	-12.05	-85
	-16.7	280	0.70	400	-12.85	-91.5
	-18.9	370	0.81	457	-13.35	-94.5
	-20.4	460	1.40	-	-13.80	-98
	-29	1200	1.00	1200	-14.5	-
Core C (Roedel)	-5.5	550	1.2	458	-12.60	-87
	-7	650	0.5	1300	-13.50	-95
	-9.8	800	1.1	-	-14.30	-102
	-12.9	-	-	-	-15.00	-106
	-14	880	2.1	419	-15.20	-109
	-17.1	1020	2.0	510	-15.45	-111
	-20.1	1100	2.9	379	-15.80	-113
	-22.3	1130	3.3	342	-15.80	-113

Table C-1. (cont'd)

(Depth in meters below land surface.)

	Depth (m)	Cl (mg/L)	Br (mg/L)	Cl/Br	del O (‰)	del D (‰)
Core D (Houlihan)	-3.7	8.3	0.09	92	-8.95	-60.5
	-6.7	9.8	0.01	980	-8.80	-59
	-9.8	14	0.23	-	-9.15	-62.5
	-12.8	-	-	-	-9.55	-64
	-15.9	14	0.32	44	-9.90	-68.5
	-17.5	17	0.36	47	-10.15	-69
	-19.1	40	0.6	67	-10.30	-70
	-21.3	50	1	50	-10.1	-
Core E (Burt)	-9.9	43	0.31	139	-11.85	-82.5
	-13	-	-	-	-	-
	-16	24	0.42	57	-12.65	-87.5
	-19.1	39	0.25	156	-12.75	-89.5
	-22.1	43	0.36	119	-12.60	-89

APPENDIX D.

Saginaw Bay Benthic Sediment Chemistry

Table D-1. Total Organic Carbon Concentrations in Sediments

Sample	Depth (cm)	TOC (wt. %)	Sample	Depth (cm)	TOC (wt. %)	Sample	Depth (cm)	TOC (wt. %)
SB1-1	-0.5	3.36	SB3-1	-0.5	2.55	SB17-1	-0.5	3.12
SB1-2	-1.5	3.26	SB3-2	-1.5	3.09	SB17-2	-1.5	3.10
SB1-3	-2.5	3.24	SB3-3	-2.5	3.75	SB17-3	-2.5	2.98
SB1-4	-3.5	3.39	SB3-4	-3.5	3.19	SB17-4	-3.5	2.76
SB1-5	-4.5	3.25	SB3-5	-4.5	3.13	SB17-5	-4.5	2.85
SB1-6	-5.5	3.12	SB3-6	-5.5	2.81	SB17-6	-5.5	2.04
SB1-12	-12	2.83	SB3-12	-12	2.11	SB17-12	-11.5	1.19
SB1-16	-20	2.63	SB3-16	-19	2.04	SB17-16	-18.5	0.84
SB1-20	-28	2.42	SB3-20	-35	0.78	SB17-20	-30.5	0.93
SB1-24	-40	1.90	-	-	-	SB17-23	-38.5	0.60
Sample	Depth (cm)	TOC (wt%)	Sample	Depth (cm)	TOC (wt%)			
SB19-1	-0.5	3.25	SB22-1	-0.5	2.28			
SB19-2	-1.5	3.16	SB22-2	-1.5	2.49			
SB19-3	-2.5	3.36	SB22-3	-2.5	2.31			
SB19-4	-3.5	3.13	SB22-4	-3.5	2.11			
SB19-5	-4.5	3.30	SB22-5	-4.5	2.04			
SB19-6	-5.5	3.07	SB22-6	-5.5	2.28			
SB19-12	-12	2.91	SB22-12	-12	2.18			
SB19-16	-19	2.72	SB22-16	-19	1.48			
SB19-20	-35	1.22	SB22-20A	-35	0.60			
SB19-24	-51	1.35	SB22-24	-51	0.71			

Table D-2. Total Metal Concentrations in Sediments

Core: SB2-BC2

(Shaded values indicate analyses with RSD values greater than 15 per cent.)

Sample	Depth (cm)	Fe (mg/g)	Mn (µg/g)	Cd (µg/g)	Cu (µg/g)	Zn (µg/g)	As (µg/g)
1	-0.5	29.4	883	1.04	35.4	239	7.4
2	-1.5	23.7	470	0.97	33.3	188	5.5
3A	-2.5	22.9	419	1.04	32.3	249	7.5
4	-3.5	18.1	368	0.79	25.5	128	4.9
5	-4.5	20.5	470	0.91	30.3	147	5.7
6	-5.5	20.1	524	0.94	29.2	142	5.3
7	-6.5	19.5	409	0.76	29.0	156	4.4
8	-7.5	19.4	344	0.92	29.3	142	4.7
9	-8.5	21.5	528	0.91	30.2	136	4.9
10	-9.5	20.5	435	0.91	29.5	131	4.9
11	-10.75	21.1	460	0.85	30.9	140	4.8
12	-12	23.1	538	1.34	77.1	148	5.4
13	-13	21.0	447	0.98	30.0	135	4.6
14	-14	20.3	383	0.96	29.5	197	4.6
15	-15	20.8	462	0.88	31.8	132	4.5
16A	-16	19.8	406	0.92	29.1	143	4.1
17	-17	20.1	424	1.06	32.0	145	5.1
18	-18	18.8	320	1.01	30.0	127	6.2
19	-21	17.8	322	0.64	19.8	101	7.5
20	-24	13.7	234	0.39	11.4	55	7.3
21	-27	11.6	180	0.13	7.0	49	6.3
22	-30	14.8	333	0.16	5.8	35	6.2
23	-33.5	13.4	324	0.12	6.0	36	6.5
24	-39.5	10.2	338	0.14	4.3	31	x

Table D-2. (cont'd)

Core: SB4-BCC

(Shaded values indicate analyses with RSD values greater than 15 per cent.)

Sample	Depth (cm)	Fe (mg/g)	Mn (µg/g)	Cd (µg/g)	Cu (µg/g)	Zn (µg/g)	As (µg/g)
1	-0.5	26.6	928	0.67	36.0	245	6.6
2	-1.5	26.6	1121	0.71	33.4	184	6.9
3	-2.5	27.4	1025	0.86	34.1	227	7.8
4	-3.5	28.2	1058	0.87	36.3	168	7.9
5	-4.5	32.0	1115	1.01	40.3	207	8.7
6A	-5.5	31.2	1456	1.12	40.3	233	9.5
7	-6.5	30.0	1115	1.22	39.0	223	8.4
8	-7.5	27.8	916	1.06	35.1	163	8.3
9	-8.5	27.4	1038	1.17	37.2	191	8.1
10	-9.5	26.4	960	1.18	36.8	175	8.2
11	-10.5	25.3	769	1.09	32.6	162	7.0
12	-11.5	24.0	661	1.05	32.5	169	5.8
13	-12.5	24.6	656	1.11	35.0	167	5.9
14	-13.5	25.8	644	1.09	32.9	164	6.0
15	-14.5	23.7	516	1.05	32.5	186	5.1
16	-15.5	24.5	534	0.92	32.3	151	5.4
17	-16.5	22.2	483	0.99	51.0	150	5.0
18	-20	23.1	432	0.91	28.5	117	5.0
19	-24	18.5	421	0.36	13.9	64	4.7
20	-28	25.3	779	0.24	14.4	69	6.1
21A	-33	29.0	682	0.26	16.1	79	5.5
22	-38	27.3	637	0.18	15.3	83	4.5
23	-43	24.8	576	0.20	13.1	59	4.8
24	-62	26.3	535	0.18	15.6	61	4.5

Table D-2. (cont'd)

Core: SB4b-BCD

*(***Originally collected for SCE, but was only digested for totals because sediment was refrigerated, not frozen.)*

Sample	Depth (cm)	Fe (mg/g)	Mn (µg/g)	Cd (µg/g)	Cu (µg/g)	Zn (µg/g)	As (µg/g)
1	-0.5	32.0	829	1.20	38.5	238	8.0
2	-1.5	30.7	832	1.40	39.4	227	8.0
3	-2.5	30.4	823	1.53	37.9	231	7.7
4A	-3.5	29.4	801	1.36	38.0	221	7.7
5	-4.5	28.3	754	1.82	35.9	211	7.5
6	-5.5	26.8	693	1.42	34.1	202	7.1
7	-6.5	25.7	560	1.33	32.9	198	6.2
8	-7.5	26.1	502	1.39	35.8	221	6.0
9	-8.5	26.7	495	1.43	38.2	226	6.8
10	-9.5	26.9	486	1.39	38.0	223	7.0
11	-10.5	27.4	478	1.37	39.2	221	6.5
12	-11.5	27.2	473	1.35	40.1	219	6.6
13	-12.5	27.5	468	1.38	40.2	216	6.4
14	-13.5	26.0	444	1.49	39.2	212	5.9
15	-14.5	26.1	446	1.48	40.6	218	6.1
16	-18.5	25.9	413	1.60	41.4	216	5.8
17	-22.5	26.7	408	1.59	42.2	209	6.1
18	-26.5	25.9	419	1.62	43.5	212	5.9
19	-30.5	28.2	442	1.03	26.9	130	5.3
20A	-34.5	28.6	448	0.62	18.6	98	4.6
21	-38.5	15.2	244	0.29	8.5	50	4.5
22	-42.5	11.7	177	0.14	5.8	32	3.4
23	-46.5	9.4	150	0.12	4.2	28	2.3
24	-50.5	10.0	156	0.10	3.9	26	2.2

Table D-2. (cont'd)

Core: SB18-BCC

Sample	Depth (cm)	Fe (mg/g)	Mn (µg/g)	Cd (µg/g)	Cu (µg/g)	Zn (µg/g)	As (µg/g)
1	-0.5	23.1	643	1.07	31.3	205	6.5
2	-1.5	25.1	779	1.18	35.2	197	7.4
3A	-2.5	20.8	684	1.03	29.9	178	6.1
4	-3.5	21.1	467	1.21	26.0	161	5.0
5	-4.5	22.1	509	1.11	30.2	164	5.5
6	-5.5	22.6	460	1.00	31.9	177	5.8
7	-6.5	22.7	468	1.05	30.9	167	6.1
8	-7.5	22.2	495	1.01	30.1	158	7.5
9	-8.5	20.7	333	1.06	30.0	149	5.1
10	-9.5	21.3	368	1.07	30.0	191	5.3
11	-10.5	21.5	389	1.05	30.6	147	5.3
12	-11.5	20.2	289	1.13	30.2	155	5.2
13	-12.5	19.6	295	1.12	29.0	150	5.3
14	-13.5	19.7	348	1.17	28.8	149	5.2
15	-14.5	20.4	372	1.25	30.4	139	5.6
16	-18.5	18.4	288	1.11	27.1	134	5.0
17	-22.5	15.3	305	0.98	21.9	110	4.7
18A	-26.5	7.8	129	0.38	8.4	42	2.4
19	-30.5	6.2	101	0.10	6.1	20	1.8
20	-34.5	10.0	172	0.14	6.4	31	3.9
21	-38.5	7.9	127	0.30	5.2	44	3.3
22	-42.5	9.0	165	0.18	5.2	24	3.2
23	-46.5	11.6	236	0.18	7.5	34	3.3
24	-50.5	8.8	164	0.06	5.6	24	2.7

Table D-2. (cont'd)

Core: SB24-BCC

Sample	Depth (cm)	Fe (mg/g)	Mn (µg/g)	Cd (µg/g)	Cu (µg/g)	Zn (µg/g)	As (µg/g)
1	-0.5	23.4	1223	0.88	27.0	197	8.8
2	-1.5	28.1	1078	0.96	34.6	198	7.9
3	-2.5	28.0	1138	1.09	35.6	188	7.7
4A	-3.5	24.7	923	1.71	32.6	209	6.9
5	-4.5	24.2	853	1.02	33.2	158	6.5
6	-5.5	21.9	666	0.89	30.2	151	5.8
7	-6.5	22.8	627	0.90	31.4	160	5.7
8	-7.5	21.7	639	0.89	30.4	152	5.4
9	-8.5	21.5	493	0.87	31.3	141	6.0
10	-9.5	21.5	513	1.03	30.6	143	5.8
11	-10.5	21.4	509	0.97	30.1	145	5.4
12	-11.5	21.4	469	0.99	29.7	140	5.3
13	-12.5	20.9	475	0.97	29.9	137	5.2
14	-13.5	21.3	433	0.90	30.6	152	5.4
15	-14.5	20.8	445	0.98	30.0	134	5.5
16A	-18.5	19.7	419	0.52	16.4	84	5.0
17	-22.5	14.9	383	0.36	8.3	61	4.2
18	-26.5	13.1	295	0.15	6.4	44	3.4
19	-30.5	14.5	352	0.12	6.5	42	4.4
20	-34.5	17.2	398	0.13	8.2	46	5.1
21	-38.5	16.1	432	0.10	7.5	58	4.7
22	-42.5	14.9	441	0.09	7.8	43	5.3
23	-46.5	16.3	526	0.09	8.9	49	4.3
24	-50.5	15.8	429	0.09	8.7	46	5.0

Table D-3. SCE Results for Iron

Sample	Depth (cm)	EX mg/g	WAS mg/g	ER mg/g	MR mg/g	OX1 mg/g	OX2 mg/g	RES mg/g	TOTAL mg/g
SB1-1	-0.5	0.0	1.3	3.6	6.0	0.0	0.2	17.5	28.6
SB1-2	-1.5	0.2	1.8	3.2	5.8	0.0	0.2	16.4	27.5
SB1-3	-2.5	0.0	1.5	2.7	4.3	0.0	0.1	13.4	22.1
SB1-4	-3.5	0.1	1.6	2.7	4.0	0.0	0.2	13.6	22.1
SB1-5	-4.5	0.1	2.0	2.7	4.0	0.0	0.2	15.0	23.9
SB1-6	-5.5	0.1	1.8	2.4	3.6	0.0	0.2	13.3	21.4
SB1-12	-12	0.0	1.4	2.1	4.0	0.0	0.2	11.1	18.7
SB1-16	-20	0.0	1.6	1.9	3.4	0.1	0.3	12.7	19.9
SB1-20	-28	0.0	2.0	2.0	3.5	0.1	0.3	14.7	22.6
SB1-24	-39.5	0.1	1.8	1.6	2.9	0.0	0.1	15.1	21.6
SB3-1	-0.5	0.0	0.3	2.1	5.3	0.0	0.1	9.4	17.1
SB3-2	-1.5	0.0	0.8	2.4	4.8	0.0	0.1	9.6	17.7
SB3-3	-2.5	0.2	1.5	2.5	5.3	0.0	0.2	-	-
SB3-4	-3.5	0.2	1.4	2.6	5.1	0.0	0.2	9.9	19.4
SB3-5	-4.5	0.0	1.0	3.0	5.1	0.0	0.2	-	-
SB3-6	-5.5	0.1	1.0	2.4	4.5	0.0	0.2	10.9	19.2
SB3-12	-11.5	0.0	0.7	1.9	3.9	0.0	0.1	-	-
SB3-16	-18.5	0.0	0.9	1.8	3.8	0.0	0.1	-	-
SB3-20	-34.5	0.0	0.4	0.8	2.4	0.0	0.1	-	-
SB17-1	-0.5	0.0	0.2	2.3	4.8	0.0	0.2	10.7	18.2
SB17-2	-1.5	0.1	0.5	1.8	4.2	0.0	0.2	11.9	18.7
SB17-3	-2.5	0.0	0.5	2.1	4.2	0.0	0.2	12.0	19.1
SB17-4	-3.5	0.1	0.6	1.7	3.9	0.0	0.2	7.5	14.1
SB17-5	-4.5	0.1	-	2.2	4.0	0.0	0.2	-	-
SB17-6	-5.5	0.1	0.8	2.0	3.6	0.0	0.2	10.7	17.5
SB17-12	-11.5	0.2	0.6	0.9	1.8	0.0	0.1	5.4	9.0
SB17-16	-18.5	0.1	0.5	0.7	1.5	0.0	0.1	3.9	6.8
SB17-20	-30.5	0.1	0.5	0.7	1.6	0.0	0.1	4.7	7.7
SB17-23	-38.5	0.0	0.5	0.6	1.5	0.0	0.1	4.0	6.7

Table D-3. (cont'd)

Sample	Depth (cm)	EX mg/g	WAS mg/g	ER mg/g	MR mg/g	OX1 mg/g	OX2 mg/g	RES mg/g	TOTAL mg/g
SB19-1	-0.5	0.0	0.3	2.5	5.0	0.0	0.2	14.8	23.0
SB19-2	-1.5	0.0	0.3	2.1	4.8	0.0	0.2	13.5	21.0
SB19-3	-2.5	0.0	0.5	2.3	4.7	0.0	0.2	16.9	24.8
SB19-4	-3.5	0.0	0.5	2.4	4.8	0.0	0.2	15.9	23.8
SB19-5	-4.5	0.1	0.7	2.3	4.9	0.0	0.2	14.2	22.4
SB19-6	-5.5	0.1	0.7	2.1	4.3	0.0	0.3	12.8	20.2
SB19-12	-11.5	0.2	1.2	2.0	3.8	0.0	0.3	12.6	20.1
SB19-16	-18.5	0.3	1.1	1.7	3.3	ND	0.2	13.2	19.9
SB19-20	-34.5	0.1	0.7	1.0	2.0	0.0	0.1	8.7	12.7
SB19-24	-50.5	0.2	1.2	1.4	2.2	0.0	0.1	11.9	17.1
SB22-1	-0.5	0.0	0.2	2.1	5.5	0.0	0.1	11.9	19.9
SB22-2	-1.5	0.0	0.7	2.0	4.3	BDL	0.1	11.3	18.5
SB22-3	-2.5	0.1	0.9	2.0	4.0	BDL	0.1	-	-
SB22-4	-3.5	0.0	0.8	2.0	3.8	0.0	0.1	8.1	14.9
SB22-5	-4.5	0.0	0.9	1.9	4.0	0.0	0.1	-	-
SB22-6	-5.5	0.0	0.9	2.1	4.1	0.0	0.1	12.5	19.7
SB22-12	-11.5	0.0	0.7	1.5	2.8	BDL	0.1	8.0	13.1
SB22-16	-18.5	0.0	0.9	1.6	3.1	0.0	0.1	9.3	15.0
SB22-20A	-34.5	0.0	0.7	0.9	1.6	0.0	0.1	5.5	8.9
SB22-24	-50.5	0.0	0.8	1.0	1.5	0.1	0.1	6.4	9.9

Table D-4. SCE Results for Manganese

Sample	Depth (cm)	EX µg/g	WAS µg/g	ER µg/g	MR µg/g	OX1 µg/g	OX2 µg/g	RES µg/g	TOTAL µg/g
SB1-1	-0.5	211	300	64	74	BDL	2	95	748
SB1-2	-1.5	209	236	55	58	BDL	2	91	652
SB1-3	-2.5	136	213	46	42	BDL	1	73	511
SB1-4	-3.5	157	216	49	39	BDL	2	74	537
SB1-5	-4.5	165	214	48	40	BDL	1	81	549
SB1-6	-5.5	147	192	42	36	BDL	2	72	492
SB1-12	-12	96	137	35	39	ND	1	61	368
SB1-16	-20	73	134	36	34	ND	2	68	347
SB1-20	-28	79	183	41	36	BDL	2	79	420
SB1-24	-39.5	101	147	31	33	BDL	2	85	400
SB3-1	-0.5	305	358	100	83	2	1	53	902
SB3-2	-1.5	317	225	68	59	2	1	53	726
SB3-3	-2.5	386	215	58	57	2	1	-	-
SB3-4	-3.5	396	181	53	53	3	1	54	741
SB3-5	-4.5	357	240	86	57	2	1	*	-
SB3-6	-5.5	303	143	62	49	2	1	59	619
SB3-12	-11.5	111	88	36	42	2	1	-	-
SB3-16	-18.5	104	80	32	40	2	1	-	-
SB3-20	-34.5	47	56	22	23	1	0	-	-
SB17-1	-0.5	205	297	106	78	1	3	61	751
SB17-2	-1.5	202	105	42	54	1	3	68	475
SB17-3	-2.5	194	73	31	54	1	3	69	426
SB17-4	-3.5	156	51	21	46	0	3	45	322
SB17-5	-4.5	164	-	27	46	1	3	-	-
SB17-6	-5.5	137	51	23	42	0	2	61	318
SB17-12	-11.5	71	21	13	18	0	1	33	156
SB17-16	-18.5	56	12	9	15	0	1	26	120
SB17-20	-30.5	61	16	10	16	-1	1	29	133
SB17-23	-38.5	42	15	10	15	0	1	26	109

Table D-4. (cont'd)

Sample	Depth (cm)	EX µg/g	WAS µg/g	ER µg/g	MR µg/g	OX1 µg/g	OX2 µg/g	RES µg/g	TOTAL µg/g
SB19-1	-0.5	314	126	44	70	ND	3	85	642
SB19-2	-1.5	188	181	43	68	ND	2	75	558
SB19-3	-2.5	224	84	34	59	ND	2	95	499
SB19-4	-3.5	185	87	36	60	ND	2	88	457
SB19-5	-4.5	178	57	29	60	ND	2	82	409
SB19-6	-5.5	165	52	27	52	ND	2	72	370
SB19-12	-11.5	126	49	26	40	ND	2	68	311
SB19-16	-18.5	131	43	24	34	ND	2	75	309
SB19-20	-34.5	102	28	16	22	ND	1	52	220
SB19-24	-50.5	155	52	26	24	ND	2	71	330
SB22-1	-0.5	32	352	82	82	ND	1	65	614
SB22-2	-1.5	151	144	57	48	0	1	62	462
SB22-3	-2.5	137	122	45	41	BDL	1	-	-
SB22-4	-3.5	97	162	47	40	BDL	1	47	394
SB22-5	-4.5	120	149	42	39	BDL	1	-	-
SB22-6	-5.5	128	169	53	40	0	1	68	460
SB22-12	-11.5	99	103	28	28	BDL	1	45	303
SB22-16	-18.5	39	130	30	30	ND	1	55	286
SB22-20A	-34.5	60	43	21	17	BDL	0	37	179
SB22-24	-50.5	83	72	29	20	BDL	ND	39	242

Table D-5. SCE Results for Cadmium

Sample	Depth (cm)	EX µg/g	WAS µg/g	ER µg/g	MR µg/g	OX1 µg/g	OX2 µg/g	RES µg/g	TOTAL µg/g
SB1-1	-0.5	0.02	0.78	0.37	0.09	ND	ND	0.00	1.27
SB1-2	-1.5	0.03	0.76	0.59	0.17	BDL	ND	0.01	1.56
SB1-3	-2.5	0.01	0.60	0.36	0.12	BDL	ND	0.00	1.08
SB1-4	-3.5	ND	0.51	0.48	0.16	BDL	ND	0.00	1.15
SB1-5	-4.5	BDL	0.44	0.62	0.18	BDL	ND	0.01	1.25
SB1-6	-5.5	BDL	2.15	0.48	0.15	BDL	ND	0.01	2.78
SB1-12	-12	0.02	0.55	0.42	0.15	BDL	ND	0.01	1.14
SB1-16	-20	0.03	0.44	0.67	0.18	ND	ND	0.00	1.31
SB1-20	-28	ND	0.32	0.73	0.30	BDL	0.08	0.00	1.43
SB1-24	-39.5	ND	0.20	0.34	0.56	BDL	0.00	0.00	1.10
SB3-1	-0.5	0.04	0.36	0.30	0.25	BDL	0.00	0.00	0.95
SB3-2	-1.5	0.02	0.40	0.39	0.25	BDL	0.00	0.02	1.07
SB3-3	-2.5	ND	0.13	0.79	0.34	BDL	0.00	-	-
SB3-4	-3.5	0.02	0.29	0.58	0.33	BDL	0.01	0.00	1.23
SB3-5	-4.5	0.24	0.44	0.32	0.27	BDL	0.00	-	-
SB3-6	-5.5	0.08	0.16	0.46	0.30	BDL	0.00	0.01	1.02
SB3-12	-11.5	0.08	0.33	0.40	0.32	BDL	0.00	-	-
SB3-16	-18.5	0.02	0.29	0.48	0.31	BDL	0.00	-	-
SB3-20	-34.5	0.07	0.04	-	-	BDL	0.00	-	-
SB17-1	-0.5	0.12	0.37	0.14	0.11	BDL	0.00	0.32	1.06
SB17-2	-1.5	0.01	0.35	0.18	0.17	BDL	0.00	0.16	0.86
SB17-3	-2.5	ND	0.50	0.26	0.11	BDL	0.00	0.08	0.95
SB17-4	-3.5	ND	0.45	0.24	0.16	BDL	0.00	0.13	0.99
SB17-5	-4.5	ND	-	0.29	0.12	BDL	0.00	-	-
SB17-6	-5.5	ND	0.35	0.28	0.12	BDL	0.00	0.16	0.91
SB17-12	-11.5	ND	0.16	0.23	0.10	BDL	0.00	0.09	0.58
SB17-16	-18.5	ND	0.16	0.16	0.07	BDL	0.00	0.07	0.46
SB17-20	-30.5	ND	0.01	ND	0.00	BDL	0.00	0.07	0.08
SB17-23	-38.5	BDL	0.01	ND	0.01	BDL	0.00	0.01	0.03

Table D-5. (cont'd)

Sample	Depth	EX	WAS	ER	MR	OX1	OX2	RES	TOTAL
	(cm)	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
SB19-1	-0.5	0.02	0.54	0.31	0.10	BDL	0.00	0.12	1.08
SB19-2	-1.5	0.13	0.52	0.18	0.09	BDL	0.00	0.07	1.00
SB19-3	-2.5	0.02	0.46	0.29	0.09	ND	0.00	0.02	0.87
SB19-4	-3.5	0.04	0.48	0.01	0.11	ND	0.00	0.03	0.67
SB19-5	-4.5	BDL	0.59	0.34	0.12	BDL	0.00	0.02	1.07
SB19-6	-5.5	0.00	0.50	0.33	0.14	BDL	0.00	0.08	1.05
SB19-12	-11.5	ND	0.38	0.47	0.13	ND	0.00	0.13	1.10
SB19-16	-18.5	0.00	0.22	0.62	0.16	BDL	0.00	0.23	1.23
SB19-20	-34.5	BDL	0.00	ND	0.03	BDL	0.00	0.02	0.04
SB19-24	-50.5	BDL	0.03	0.02	0.03	BDL	0.00	0.07	0.15
SB22-1	-0.5	0.10	0.41	0.23	0.13	BDL	0.95	0.01	1.83
SB22-2	-1.5	0.06	0.44	0.39	0.16	BDL	BDL	0.04	1.08
SB22-3	-2.5	0.06	0.39	0.55	0.22	BDL	BDL	-	-
SB22-4	-3.5	0.04	0.43	0.38	0.23	ND	0.50	0.10	1.68
SB22-5	-4.5	0.04	0.38	0.37	0.22	BDL	BDL	-	-
SB22-6	-5.5	0.03	0.48	0.38	0.25	BDL	0.05	0.03	1.22
SB22-12	-11.5	0.00	0.21	0.33	0.20	BDL	BDL	0.08	0.83
SB22-16	-18.5	0.06	0.36	0.19	0.12	ND	0.29	0.23	1.25
SB22-20A	-34.5	0.00	BDL	ND	0.00	ND	0.06	0.01	0.08
SB22-24	-50.5	0.01	ND	ND	0.03	ND	ND	0.02	0.06

Table D-6. SCE Results for Copper

Sample	Depth (cm)	EX µg/g	WAS µg/g	ER µg/g	MR µg/g	OX1 µg/g	OX2 µg/g	RES µg/g	TOTAL µg/g
SB1-1	-0.5	0.6	1.8	21.0	2.0	7.4	0.3	15.4	48.7
SB1-2	-1.5	0.4	0.8	19.9	4.2	13.5	0.9	11.0	50.7
SB1-3	-2.5	0.4	1.6	17.2	2.7	10.2	0.1	8.2	40.4
SB1-4	-3.5	0.1	0.0	16.4	3.2	12.5	1.1	8.6	42.0
SB1-5	-4.5	0.2	0.2	16.0	3.6	13.7	0.6	8.6	42.8
SB1-6	-5.5	0.0	0.9	14.4	3.1	10.7	0.7	7.9	37.7
SB1-12	-12	0.1	0.8	15.0	3.7	10.6	0.8	6.7	37.7
SB1-16	-20	0.0	0.0	17.3	3.7	13.0	1.6	7.2	42.9
SB1-20	-28	0.0	0.1	16.9	4.1	17.9	2.6	8.7	50.2
SB1-24	-39.5	0.1	ND	6.2	2.9	11.1	0.7	8.0	29.0
SB3-1	-0.5	0.0	1.6	12.9	1.5	5.5	-0.2	5.6	26.9
SB3-2	-1.5	0.0	0.6	14.3	1.5	7.3	0.2	7.0	30.8
SB3-3	-2.5	0.0	0.2	14.7	2.3	10.0	1.1	-	-
SB3-4	-3.5	0.0	0.6	14.5	2.4	8.7	0.7	6.9	33.8
SB3-5	-4.5	0.0	0.9	16.7	1.7	10.1	0.3	-	-
SB3-6	-5.5	0.0	0.4	13.1	2.1	9.4	0.3	7.5	32.8
SB3-12	-11.5	0.0	0.3	10.8	2.2	8.4	0.7	-	-
SB3-16	-18.5	0.0	5.3	10.4	2.4	8.1	0.7	-	-
SB3-20	-34.5	0.0	3.7	1.7	0.5	1.2	-	-	-
SB17-1	-0.5	0.8	9.6	14.0	0.6	5.4	BDL	4.0	34.2
SB17-2	-1.5	0.2	7.5	12.5	0.7	5.6	0.0	4.9	31.5
SB17-3	-2.5	0.2	1.0	13.7	1.0	5.6	BDL	5.8	27.5
SB17-4	-3.5	0.5	0.5	11.0	1.3	7.3	0.2	4.1	24.9
SB17-5	-4.5	0.5	-	13.4	1.6	7.3	0.3	-	-
SB17-6	-5.5	0.6	0.2	11.5	1.2	6.7	0.3	4.6	25.0
SB17-12	-11.5	0.4	ND	4.4	1.0	3.1	0.5	3.0	12.4
SB17-16	-18.5	0.3	ND	3.5	0.9	2.5	BDL	2.8	10.1
SB17-20	-30.5	0.5	ND	1.4	0.4	0.9	BDL	1.2	4.5
SB17-23	-38.5	0.1	ND	1.2	0.5	0.6	BDL	0.9	3.3

Table D-6. (cont'd)

Sample	Depth (cm)	EX µg/g	WAS µg/g	ER µg/g	MR µg/g	OX1 µg/g	OX2 µg/g	RES µg/g	TOTAL µg/g
SB19-1	-0.5	1.0	0.7	16.2	1.5	6.6	BDL	5.7	31.7
SB19-2	-1.5	0.2	1.2	15.1	1.2	6.9	BDL	5.5	30.0
SB19-3	-2.5	0.0	ND	15.5	1.2	6.0	BDL	8.0	30.8
SB19-4	-3.5	BDL	ND	16.4	1.5	5.7	BDL	6.7	30.2
SB19-5	-4.5	0.3	0.5	16.0	1.6	7.9	0.3	15.5	42.0
SB19-6	-5.5	BDL	0.6	13.8	2.1	7.8	0.2	4.2	28.7
SB19-12	-11.5	0.1	0.7	13.2	2.4	9.3	BDL	4.5	30.2
SB19-16	-18.5	0.6	ND	11.5	2.8	8.7	0.6	5.6	29.8
SB19-20	-34.5	0.3	ND	1.5	1.0	0.7	BDL	1.8	5.3
SB19-24	-50.5	0.3	0.2	2.3	1.1	1.0	BDL	3.0	8.0
SB22-1	-0.5	0.4	0.9	11.6	1.4	8.0	BDL	5.4	27.7
SB22-2	-1.5	BDL	0.4	13.2	2.2	10.5	BDL	5.7	31.9
SB22-3	-2.5	0.2	0.4	12.6	2.9	9.9	0.2	-	-
SB22-4	-3.5	0.3	0.4	11.4	2.6	9.6	0.3	4.5	29.0
SB22-5	-4.5	0.1	0.4	10.6	3.2	10.1	BDL	-	-
SB22-6	-5.5	0.0	0.7	11.4	2.4	11.6	0.3	6.0	32.4
SB22-12	-11.5	0.2	0.1	7.3	1.9	7.2	0.3	4.3	21.2
SB22-16	-18.5	0.2	0.3	10.0	1.6	6.2	0.1	4.4	22.8
SB22-20A	-34.5	0.1	BDL	0.6	0.5	0.6	ND	1.6	3.4
SB22-24	-50.5	BDL	0.0	0.0	0.8	1.4	ND	1.8	4.0

Table D-6. SCE Results for Zinc

Sample	Depth (cm)	EX µg/g	WAS µg/g	ER µg/g	MR µg/g	OX1 µg/g	OX2 µg/g	RES µg/g	TOTAL µg/g
SB1-1	-0.5	ND	47	59	31	1	1	42	181
SB1-2	-1.5	ND	46	71	37	2	ND	36	191
SB1-3	-2.5	ND	41	50	29	ND	4	31	154
SB1-4	-3.5	ND	35	56	28	1	1	32	151
SB1-5	-4.5	ND	30	58	30	1	0	34	154
SB1-6	-5.5	ND	34	49	25	1	1	30	141
SB1-12	-12	ND	35	48	29	1	1	31	144
SB1-16	-20	ND	25	47	30	1	3	26	133
SB1-20	-28	ND	11	38	30	2	1	35	117
SB1-24	-39.5	ND	3	23	24	1	2	34	87
SB3-1	-0.5	ND	15	36	27	0	0	21	99
SB3-2	-1.5	ND	16	41	28	0	1	24	110
SB3-3	-2.5	ND	11	57	34	1	0	-	-
SB3-4	-3.5	ND	17	48	31	1	0	23	120
SB3-5	-4.5	ND	20	41	31	1	1	-	-
SB3-6	-5.5	ND	15	42	29	1	1	25	115
SB3-12	-11.5	ND	14	37	27	1	0	-	-
SB3-16	-18.5	ND	11	37	25	1	0	-	-
SB3-20	-34.5	ND	ND	6	7	BDL	ND	-	-
SB17-1	-0.5	BDL	16	32	25	0	1	19	93
SB17-2	-1.5	BDL	24	27	24	1	1	23	100
SB17-3	-2.5	BDL	30	34	24	0	2	24	112
SB17-4	-3.5	BDL	27	31	24	1	0	14	97
SB17-5	-4.5	BDL	-	38	25	0	2	-	-
SB17-6	-5.5	BDL	20	35	23	0	2	20	99
SB17-12	-11.5	BDL	8	22	14	ND	ND	10	53
SB17-16	-18.5	BDL	6	16	8	ND	ND	7	36
SB17-20	-30.5	BDL	ND	6	5	ND	ND	5	16
SB17-23	-38.5	BDL	ND	12	4	ND	ND	4	20

Table D-6. (cont'd)

Sample	Depth (cm)	EX µg/g	WAS µg/g	ER µg/g	MR µg/g	OX1 µg/g	OX2 µg/g	RES µg/g	TOTAL µg/g
SB19-1	-0.5	BDL	20	42	24	ND	1	29	116
SB19-2	-1.5	BDL	22	34	24	ND	1	26	107
SB19-3	-2.5	BDL	18	39	23	2	0	36	117
SB19-4	-3.5	BDL	19	41	25	1	1	28	115
SB19-5	-4.5	BDL	27	40	26	0	1	26	119
SB19-6	-5.5	BDL	23	37	26	13	1	27	125
SB19-12	-11.5	BDL	23	44	24	1	2	25	119
SB19-16	-18.5	BDL	4	40	24	ND	1	26	95
SB19-20	-34.5	BDL	ND	8	7	ND	BDL	10	24
SB19-24	-50.5	BDL	ND	8	8	ND	BDL	17	33
SB22-1	-0.5	BDL	24	35	31	ND	1	25	115
SB22-2	-1.5	BDL	23	42	29	ND	0	21	115
SB22-3	-2.5	BDL	19	45	28	ND	0	-	-
SB22-4	-3.5	5.0	20	42	27	ND	1	15	110
SB22-5	-4.5	BDL	21	41	28	ND	1	-	-
SB22-6	-5.5	BDL	25	42	30	ND	2	24	123
SB22-12	-11.5	BDL	14	33	21	ND	1	15	84
SB22-16	-18.5	BDL	13	23	18	ND	1	17	72
SB22-20A	-34.5	BDL	BDL	5	5	ND	0	5	16
SB22-24	-50.5	BDL	ND	4	6	ND	BDL	8	17

APPENDIX E.

Saginaw Bay Watershed – River Chemistry

Table E-1. Watershed Sampling Events

Data Set	Collection Dates	Watershed Status	Comment	Samples
RIV I	10-11 July 1995	low flow	post-drought sampling	156
RIV II	20-21 July 1995	hi flow	collected after heavy rainfall	182
RIV III	1-5 September 1995	low flow	post-drought sampling; (36 sites sampled for geochemical modeling)	195
RIV IV	21-25 February 1996	hi flow	mid-winter thaw	217
RIV V	23-25 May 1996	hi flow	spring flood/heavy rain	193

Table E-2. Locations of River Sampling Stations*(Shaded entries indicate USGS gaging stations.)*

Site ID	LAT	LONG	Site	Drainage Basin
BLUFF	43.7564	84.5392	Bluff Cr.	Tittabawassee
DTL	43.6753	84.7081	Spring Cr.	Tittabawassee
T	43.6753	84.3833	Tittabawassee @Sanford	Tittabawassee
X	43.6700	84.6836	South Br Salt R.	Tittabawassee
1-1	44.3721	84.1061	Bailer Cr.	Rifle
1-1a	44.3775	84.1056	Prior Cr.	Rifle
1-2	44.1796	84.0746	Rifle @Skidway Lake	Rifle
1-3	44.0733	84.0203	Rifle N of Sterling	Rifle
1-3a	44.1648	84.0078	Mansfield Cr.	Rifle
1-4	44.0149	83.8243	Old Channel (Rifle R)	Saginaw Bay
1-5	44.3342	84.0636	Rifle N of Selkirk	Rifle
1-5a	44.3675	84.0517	drain	Rifle
2-1	44.0331	84.0678	North Br Pine R.	Pine
2-2	44.0056	83.9587	Pine @Standish	Pine
2-3	43.9853	83.8875	Pine @Pine River	Pine
2-4	43.9450	84.0210	South Br Pine R.	Pine
3-1	43.8844	84.0256	White Feather Cr.	Saginaw Bay
3-1a	43.9050	84.0210	Budd Drain	Saginaw Bay
3-2	43.8944	83.9379	White Feather Cr.	Saginaw Bay
3-2a	43.8581	83.9658	Pinconning R @Pinconning	Saginaw Bay
3-2b	43.8944	83.9713	drain	Saginaw Bay
3-3	43.9320	83.9330	Saganing R.	Saginaw Bay
3-lake	43.9220	83.9250	Saginaw Bay	-
4-1	43.8069	84.0864	Erickson Drain	Saginaw Bay
4-2	43.7969	84.0461	Erickson Drain	Saginaw Bay
4-2a	43.8010	83.9640	Tebo Drain	Saginaw Bay
4-3	43.8442	84.0264	Pinconning R	Saginaw Bay
5-1	43.8925	84.1856	Watson Drain	Kawkawlin

Table E-2. (cont'd)*(Shaded entries indicate USGS gaging stations.)*

Site ID	LAT	LONG	Site	Drainage Basin
5-1a	43.8636	84.1864	Watson Drain	Kawkawlin
5-2	43.7925	84.2272	Kawkawlin Cr.	Kawkawlin
5-3	43.7544	84.1447	North Br Kawkawlin R.	Kawkawlin
5-3a	43.7544	84.1225	Renner Drain	Kawkawlin
5-4	43.6674	84.1670	Davis Drain	Kawkawlin
5-5	43.7041	84.0477	North Br Kawkawlin R.	Kawkawlin
5-6	43.6675	83.9701	North Br Kawkawlin R.	Kawkawlin
5-7	43.6386	83.9778	Kawkawlin R. @KawkawlinOilField	Kawkawlin
5-8	43.6299	84.0503	Kawkawlin R. north of Auburn	Kawkawlin
5-lake	43.6683	83.9030	Saginaw Bay	-
6-1	44.1754	84.4018	West Br Tittabawassee	Tittabawassee
6-2	44.1758	84.2003	Spring Cr.	Tittabawassee
6-3	43.9778	84.2767	Molasses R.	Tittabawassee
6-4	43.8722	84.3197	Tittabawassee R.@Wixom Lake	Tittabawassee
6-4a	43.9450	84.3630	Larrabee Cr.	Tittabawassee
6-4b	43.8700	84.4080	Little Cedar R.	Tittabawassee
6-5	43.6256	84.3152	Tittabawassee R. west of Midland	Tittabawassee
6-6	43.5706	84.1946	Tittabawassee S of Midland	Tittabawassee
6-7	43.5674	84.0324	Squaconning Cr.	Saginaw River
6-8	43.5099	84.0508	Armon Drain	Saginaw River
6-9	43.4165	84.0459	Tittabawassee	Tittabawassee
7-1a	43.9874	84.7400	Mostellar Cr.	Tittabawassee
7-1b	43.9872	84.7463	Jose Cr.	Tittabawassee
7-2	43.9819	84.5553	Howland Cr.	Tittabawassee
7-3	43.9244	84.5853	North Br Tobacco R.	Tittabawassee
7-4	43.8300	84.7881	South Br Tobacco R.	Tittabawassee

Table E-2. (cont'd)*(Shaded entries indicate USGS gaging stations.)*

Site ID	LAT	LONG	Site	Drainage Basin
7-5	43.8447	84.6564	South Br Tobacco R.	Tittabawassee
7-6	43.8764	84.4728	Tobacco @Beaverton	Tittabawassee
7-7	43.8536	84.5853	South Br Tobacco R.	Tittabawassee
7-7a	43.8978	84.5844	Middle Br Tobacco R.	Tittabawassee
8-1	43.8581	85.1389	North Br Chippewa R.	Tittabawassee
8-2	43.7408	85.1450	Chippewa @Barryton	Tittabawassee
8-2a	43.7619	85.1478	North Br Chippewa R.	Tittabawassee
8-2b	43.7461	85.1472	West Br Chippewa R.	Tittabawassee
8-3	43.6622	85.0306	Chippewa @Drew	Tittabawassee
8-4	43.6458	84.9775	Chippewa @Isabella	Tittabawassee
8-4a	43.6540	84.8680	North Br Chippewa R.	Tittabawassee
8-4b	43.6970	84.8570	North Br Chippewa R.	Tittabawassee
8-5	43.6011	84.7856	Chippewa @Mt. Pleasant	Tittabawassee
8-6	43.6272	84.7084	Chippewa E of Mt. Pleasant	Tittabawassee
8-7	43.5846	84.5081	Chippewa	Tittabawassee
8-8	43.5812	84.4481	Chippewa	Tittabawassee
8-9	43.5881	84.4099	Chippewa	Tittabawassee
8-10	43.6014	84.3308	Chippewa	Tittabawassee
9-1	43.6647	84.7878	Jordan Cr.	Tittabawassee
9-1a	43.6690	84.6966	Lewis Drain	Tittabawassee
9-1b	43.6690	84.6910	Jordan Cr.	Tittabawassee
9-2	43.7569	84.7064	McDonald Drain	Tittabawassee
9-2a	43.7570	84.6690	drain	Tittabawassee
9-2a'	43.7569	84.6700	Loomis Drain	Tittabawassee
9-3	43.6783	84.6875	North Br Salt R.	Tittabawassee
9-3a	43.6700	84.6917	South Br Salt R.	Tittabawassee
9-3a'	43.6700	84.6828	South Br Salt R.	Tittabawassee
9-4	43.6922	84.6275	drain	Tittabawassee

Table E-2. (cont'd)

Site ID	LAT	LONG	Site	Drainage Basin
9-5	43.6906	84.5883	Salt R.	Tittabawassee
9-6	43.7056	84.4881	Salt R.	Tittabawassee
9-7	43.6983	84.7550	Spring Creek	Tittabawassee
10-1	43.7858	84.5442	Bliss Drain	Tittabawassee
10-1a	43.7856	84.5442	Howe Drain	Tittabawassee
10-2	43.6767	84.3950	Salt @Sanford	Tittabawassee
12-1	43.5533	85.1055	Pine R.	Tittabawassee
12-2	43.4346	84.9061	Pine R.	Tittabawassee
12-3	43.3351	84.7108	Pine W of Alma	Tittabawassee
12-4	43.4299	84.5980	Pine @St. Louis	Tittabawassee
12-5	43.5645	84.3696	Pine @Gordonville	Tittabawassee
13-1	43.4736	84.7274	Salt Cr.	Tittabawassee
13-2	43.5739	84.5881	Salt Cr.	Tittabawassee
14-1	43.4811	84.5600	Little Salt Cr.	Tittabawassee
14-2	43.5538	84.5088	Little Salt Cr.	Tittabawassee
15-1	43.3792	84.1012	Swan Cr.	Shiawassee
15-2	43.4313	84.2698	Whitmore Drain	Tittabawassee
15-3	43.4920	84.1690	Flemming Drain	Shiawassee
17-1	43.3429	84.5080	Beaver Drain	Shiawassee
17-2	43.3722	84.4301	Beaver Cr.	Shiawassee
17-3	43.3190	84.1694	Beaver Cr.	Shiawassee
18-1	43.2430	84.5829	Bad R.	Shiawassee
18-2	43.3072	84.3694	Bad R.	Shiawassee
18-3	43.2984	84.1890	Bad R.	Shiawassee
19-1	43.1728	84.3461	drain	Shiawassee
19-2	43.1515	84.3058	Lano Cr.	Shiawassee
19-3	43.1420	84.2420	Griffus Cr.	Shiawassee

Table E-2. (cont'd)*(Shaded entries indicate USGS gaging stations.)*

Site ID	LAT	LONG	Site	Drainage Basin
19-4	43.2614	84.2087	Potato Cr.	Shiawassee
20-1	42.8760	83.8673	Jones Cr.	Shiawassee
20-2	42.8787	83.9860	Threemile Cr.	Shiawassee
20-3	42.9690	84.0557	Shiawassee near Corunna	Shiawassee
20-4	43.0135	84.1807	Shiawassee @Owosso	Shiawassee
20-5	43.1293	84.1620	Mickles Cr.	Shiawassee
20-6	43.2547	84.1065	Shiawassee N of Chesaning	Shiawassee
20-7	43.0864	84.1397	Sixmile Cr.	Shiawassee
20-8	43.2317	84.0344	Fairchild Cr.	Shiawassee
21-1	42.8950	83.6578	Seaver Drain	Flint
21-1a	42.9003	83.6986	Swartz Cr.	Flint
21-2	42.8855	83.7542	Indian Cr.	Flint
21-2a	42.9150	83.8192	Kimball Drain	Flint
21-3	42.9425	83.8580	West Br Flint R.	Flint
21-4	42.9878	83.7283	West Br Flint R.	Flint
21-5	42.9528	83.7489	Swartz Cr.	Flint
21-5a	42.9569	83.7636	Howland Drain	Flint
22-1	43.0242	83.9100	Misteguay Cr.	Flint
22-1a	43.0136	83.9322	Crawford Drain	Flint
22-1b	43.0082	83.9303	Misteguay Cr.	Flint
22-2	42.9783	83.9878	Rush Cr.	Flint
22-2a	42.9718	84.0331	drain	Shiawassee
22-3	43.1010	83.9582	Misteguay Cr.	Flint
22-3a	43.1181	83.9789	Northwood Cr.	Flint
22-3b	43.1011	83.9767	Onlon Drain	Flint
22-4	43.0931	84.0267	Porter Cr.	Flint
22-4a	43.0619	84.0897	Kinsman Drain	Flint
22-5	43.2911	83.9914	Misteguay Cr.	Flint
22-6	43.2910	83.9710	Pattee Cr.	Flint

Table E-2. (cont'd)*(Shaded entries indicate USGS gaging stations.)*

Site ID	LAT	LONG	Site	Drainage Basin
22-7	43.1750	83.9430	drain	Flint
23-1	42.8302	83.5615	Thread Cr.	Flint
23-2	42.8625	83.5152	Thread Cr.	Flint
23-3	42.9410	83.5763	Thread Cr.	Flint
23-4	42.9757	83.6393	Thread Cr.	Flint
23-5	43.0243	83.6282	Gilkey Cr.	Flint
24-1	42.8127	83.4725	Duck Cr.	Flint
24-2	42.8462	83.4150	Kearsley Cr.	Flint
24-3	42.9947	83.5170	Kearsley Cr.	Flint
24-4	43.0498	83.4855	Black Cr.	Flint
24-5	43.0323	83.5855	Kearsley Cr.	Flint
25-1	42.9475	83.4947	Hasler Inlet	Flint
25-2	42.9689	83.4111	drain	Flint
25-3	43.0686	83.4206	Hasler Cr.	Flint
26-1	42.8693	83.2685	South Br Flint R.	Flint
26-2	42.9325	83.4206	Mill Cr.	Flint
26-2a	42.9353	83.3797	drain	Flint
26-3	42.9340	83.3315	South Br Farmers Cr.	Flint
26-4	43.0432	83.2852	South Br Flint R.	Flint
26-5	43.0445	83.3372	Farmers Cr. @Lapeer	Flint
26-6	43.1603	83.3333	South Br Flint R.	Flint
27-1	43.1442	83.1722	Bottom Cr.	Flint
27-1a	43.1872	83.1350	Cedar Cr.	Flint
27-1b	43.2413	83.1629	Elm Cr.	Flint
27-2	43.1482	83.2333	Gravel Cr.	Flint
27-3	43.3087	83.1628	Indian Cr.	Flint

Table E-2. (cont'd)*(Shaded entries indicate USGS gaging stations.)*

Site ID	LAT	LONG	Site	Drainage Basin
27-4	43.2602	83.2463	Indian Cr.	Flint
27-4a	43.2358	83.2925	Indian Cr.	Flint
27-4b	43.2358	83.3036	Squaw Cr.	Flint
27-5	43.1887	83.3687	North Br Flint R.	Flint
27-6	43.1105	83.5225	Flint @Rt. 15	Flint
27-6a	43.1697	83.5614	Butternut Cr.	Flint
27-7	43.0392	83.7690	Flint @Flint	Flint
27-8	43.1158	83.8598	Flint @Flushing	Flint
27-8a	43.1333	83.7522	Brent Run	Flint
27-8b	43.1172	83.8356	Armstrong Cr.	Flint
27-9	43.2062	83.7987	Pine Run	Flint
27-10	43.2344	83.7439	Silver Creek Drain	Flint
27-11	43.2587	83.7357	Horton Graham Drain	Shiawassee
27-12	43.2978	83.9340	Flint @E Fry Road	Flint
27-13	43.3073	83.9340	Birch R.	Flint
28-1	43.2708	83.0238	South Br Cass R.	Cass
28-2	43.4300	83.0665	North Br White Cr.	Cass
28-3	43.5445	82.9757	Middle Br Cass R.	Cass
28-4	43.5323	83.0442	South Br Cass R.	Cass
28-5	43.7237	82.9330	North Br Cass R.	Cass
28-6	43.6643	82.9997	North Br Cass R.	Cass
28-7	43.6428	82.9997	South Fork	Cass
28-8	43.5675	83.1128	South Br Cass R.	Cass
28-9	43.5848	83.1767	Cass @Cass City	Cass
28-10	43.5135	83.3093	White Cr.	Cass
28-10a	43.3894	83.3446	Phelps Lake Drain	Cass
28-11	43.4500	83.4410	Cass @Wahjamega	Cass
28-12	43.2683	83.4817	Millington Cr.	Cass
28-12a	43.3100	83.4817	Goodings Cr.	Cass

Table E-2. (cont'd)*(Shaded entries indicate USGS gaging stations.)*

Site ID	LAT	LONG	Site	Drainage Basin
28-14	43.3222	83.6152	Millington Cr.	Cass
28-15	43.3707	83.5818	Cass @Vassar	Cass
28-16	43.3288	83.7598	Cass @Frankenmuth	Cass
28-16a	43.2869	83.6725	Perry Cr.	Cass
28-17	43.3652	83.9563	Cass W of Bridgeport	Cass
28-18	43.2358	83.6188	Perry Cr.	Cass
28-18a	43.2293	83.6522	Dead Cr.	Cass
29-1	43.7022	83.1000	Pigeon R.	Pigeon
29-2	43.7022	83.1740	Huron Drain	Pigeon
29-3	43.5997	83.3612	Columbian Drain	Saginaw Bay
29-3a	43.6564	83.3056	Brookfield Drain	Saginaw Bay
29-3b	43.6564	83.3389	Carlton Drain	Saginaw Bay
29-3c	43.5997	83.4000	Bach Drain	Saginaw Bay
29-4	43.7008	83.3946	State Drain	Saginaw Bay
29-4a	43.8019	83.2889	Pigeon @Pigeon	Pigeon
29-4b	43.7680	83.3690	Shebeon Cr.	Saginaw Bay
29-4c	43.7368	83.3946	Gettel Drain	Saginaw Bay
29-5	43.9380	83.2427	Pigeon	Pigeon
29-6	43.8283	83.1000	Bad Axe Cr.	Pinnebog
29-7	43.7882	83.1000	Silver Cr.	Pinnebog
29-lake	43.9704	83.2149	Saginaw Bay	-
30-1	43.5283	83.5132	Allen Drain	Saginaw Bay
30-2	43.5477	83.4557	Wiscoggin Drain	Saginaw Bay
30-3	43.6792	83.4940	Wiscoggin Drain	Saginaw Bay
30-4	43.6672	83.5650	Allen Drain	Saginaw Bay
30-lake	43.6892	83.5450	Saginaw Bay	-
31-1	43.4663	83.5113	drain	Saginaw Bay
31-1a	43.4664	83.5225	drain	Saginaw Bay
31-2	43.4650	83.6282	Northwest Drain	Saginaw Bay
31-3	43.4435	83.7320	Watercourse Drain	Quanicassee

Table E-2. (cont'd)

Site ID	LAT	LONG	Site	Drainage Basin
31-4	43.5297	83.7802	Redy Drain	Quanicassee
31-4a	43.5378	83.7078	drain	Saginaw Bay
31-4b	43.5525	83.7802	drain	Quanicassee
31-5	43.5660	83.6773	Northwest Drain	Quanicassee
31-5a	43.5378	83.7153	drain	Quanicassee
31-5b	43.5360	83.7113	drain	Quanicassee
31-6	43.5808	83.6792	Quanicassee R.	Quanicassee
31-6b	43.5760	83.6780	Quanicassee R.	Quanicassee
32-1	43.3813	83.6407	Sheboygan R.	Quanicassee
32-1a	43.5677	83.6428	Tinglan Drain	Quanicassee
32-1b	43.3813	83.6385	Richville Drain	Quanicassee
32-2	43.4178	83.7820	Blumfield Cr.	Saginaw River
32-3	43.4757	83.8407	Cheboyganing Cr.	Saginaw River
32-3a	43.5018	83.8407	Trombley Drain	Saginaw River
32-4	43.5199	83.9170	Saginaw R.	Saginaw River
32-5	43.6403	83.8483	Saginaw R.	Saginaw River
32-6	43.4083	83.6486	drain	Saginaw Bay

Table E-3. River Chemistry - RIV I sampling*(All concentrations in mg/L.)*

SITE	Cl	Br	Na
BLUFF	-	-	-
DTL	-	-	-
T	-	-	-
X	-	-	-
1-1	17.5	0.19	6.5
1-1a	-	-	-
1-2	12	0.14	6.5
1-3	14.8	0.16	8.0
1-3a	-	-	-
1-4	16	0.17	8.0
1-5	6.2	0.11	4.0
1-5a	5.4	0.11	5.0
2-1	110	1.00	35.0
2-2	83	0.76	23.5
2-3	80	0.65	25.5
2-4	-	-	-
3-1	57	0.34	14.5
3-1a	-	-	-
3-2	63.5	0.36	19.0
3-2a	90	0.44	24.5
3-2b	-	-	-
3-3	-	-	-
3-lake	-	-	-
4-1	156	0.85	61
4-2	32.2	0.30	8.5
4-2a	-	-	-
4-3	47.8	0.33	12.0
5-1	56	1.05	6.0
5-1a	13	0.23	5.0
5-2	1.8	0.13	0.5
5-3	19	0.23	5.0
5-3a	-	-	-
5-4	48	0.42	28.0
5-5	19	0.23	6.0
5-6	15.5	0.25	5.5

Table E-3. (cont'd)**RIV I***(All concentrations in mg/L.)*

SITE	Cl	Br	Na
5-7	65	0.53	24.5
5-8	66	0.52	25.0
5-lake	-	-	-
6-1	1.4	0.11	3.5
6-2	10	0.16	6.0
6-3	2.3	0.17	5.0
6-4	12.5	0.24	7.5
6-4a	-	-	-
6-4b	-	-	-
6-5	47	0.54	25.5
6-6	166	1.06	73
6-7	18.5	0.23	6.0
6-8	104	1.03	41.0
6-9	261	1.96	99
7-1a	96	0.15	-
7-1b	20.9	0.23	7.5
7-2	10.2	0.15	8.5
7-3	8.9	0.14	5.0
7-4	43	0.17	6.5
7-5	92	0.23	12.0
7-6	56	0.17	8.0
7-7	104	0.22	12.0
7-7a	66	0.17	6.5
8-1	45.7	0.15	7.0
8-2	60	0.15	6.5
8-2a	12.3	0.18	7.0
8-2b	29.5	0.13	3.0
8-3	96	0.22	-
8-4	18	0.25	12.0
8-4a	-	-	-
8-4b	-	-	-
8-5	18	0.27	8.5
8-6	24.5	0.28	14.0
8-7	25	0.32	15.0
8-8	29.8	0.27	16.0
8-9	32.5	0.3	16.0
8-10	34.1	0.34	18.5
9-1	28.5	0.26	12.5

Table E-3. (cont'd)

RIV I
(All concentrations in mg/L.)

SITE	Cl	Br	Na
9-1a	-	-	-
9-1b	-	-	-
9-2	124	2.75	83
9-2a	-	-	-
9-2a'	-	-	-
9-3	45.7	0.34	24.0
9-3a	60	0.45	31.0
9-3a'	-	-	-
9-4	120	1.05	51
9-5	132	1.01	60
9-6	118	0.96	58
9-7	23	0.18	14.0
10-1	21	0.19	4.5
10-1a	-	-	-
10-2	49.5	0.36	22.5
12-1	6.3	0.12	4.0
12-2	13.3	0.22	7.0
12-3	23.2	0.33	9.5
12-4	41	0.5	16.0
12-5	45	0.52	15.5
13-1	15.8	0.19	8.5
13-2	25.7	0.28	11.5
14-1	34.3	0.58	12.0
14-2	58	0.74	15.5
15-1	92	0.7	40.0
15-2	-	-	-
15-3	-	-	-
17-1	60	0.47	12.5
17-2	70.5	0.62	14.5
17-3	58	0.49	15.5
18-1	34.5	0.28	12.0
18-2	64	0.47	19.0
18-3	71	0.49	16.0
19-1	18.5	0.27	14.5

Table E-3. (cont'd)**RIV I**
(All concentrations in mg/L.)

SITE	Cl	Br	Na
19-2	19.8	0.24	7.5
19-3	18.5	0.31	6.0
19-4	76	0.97	37.5
20-1	23.4	0.25	11.0
20-2	29	0.19	10.0
20-3	36	0.29	21.5
20-4	50	0.3	28.5
20-5	39.4	0.24	20.0
20-6	44	0.25	24.5
20-7	-	-	-
20-8	-	-	-
21-1	-	-	-
21-1a	-	-	-
21-2	143	1.14	55
21-2a	-	-	-
21-3	40.5	0.35	24.5
21-4	80	0.65	40.5
21-5	-	-	-
21-5a	-	-	-
22-1	-	-	-
22-1a	-	-	-
22-1b	-	-	-
22-2	-	-	-
22-2a	-	-	-
22-3	50.5	0.32	16.0
22-3a	-	-	-
22-3b	-	-	-
22-4	-	-	-
22-4a	-	-	-
22-5	-	-	-
22-6	-	-	-
22-7	-	-	-
23-1	39.4	0.37	19.5
23-2	52.2	1.05	13.5
23-3	34.6	0.36	17.5
23-4	62.2	0.55	31.5
23-5	211	1.79	156

Table E-3. (cont'd)**RIV I***(All concentrations in mg/L.)*

SITE	Cl	Br	Na
24-1	24.2	0.27	6.0
24-2	24	0.44	10.5
24-3	38.6	0.41	19.0
24-4	38.4	0.37	12.0
24-5	45.6	0.45	23.5
25-1	23.4	0.28	9.0
25-2	-	-	-
25-3	23.6	0.27	8.5
26-1	37.6	0.4	7.5
26-2	-	-	-
26-2a	-	-	-
26-3	13.1	0.19	5.5
26-4	20	0.27	9.5
26-5	19.4	0.25	11.5
26-6	24.6	0.3	15.0
27-1	-	-	-
27-1a	-	-	-
27-1b	-	-	-
27-2	12.2	0.19	5.0
27-3	35	0.37	18.5
27-4	23	0.25	13.0
27-4a	-	-	-
27-4b	-	-	-
27-5	30.3	0.4	11.0
27-6	31.2	0.33	12.0
27-6a	-	-	-
27-7	48.5	0.42	21.0
27-8	56.6	0.48	26.5
27-8a	-	-	-
27-8b	-	-	-
27-9	78	0.48	33.0
27-10	-	-	-
27-11	192	1.81	55
27-12	86	0.65	39.5
27-13	115	2.01	43.5
28-1	32	0.28	10.5
28-2	31	0.39	9.0

Table E-3. (cont'd)**RIV I***(All concentrations in mg/L.)*

SITE	Cl	Br	Na
28-3	27	0.36	26.0
28-4	27.6	0.18	21.5
28-5	7.4	0.24	4.5
28-6	29.6	0.15	11.5
28-7	17	0.15	4.0
28-8	-	-	-
28-9	44	0.34	15.0
28-10	22.4	0.18	10.0
28-10a	-	-	-
28-11	41	0.36	19.0
28-12	4.6	0.23	8.0
28-12a	-	-	-
28-14	18	0.21	8.5
28-15	20	0.24	13.0
28-16	29.5	0.33	16.0
28-16a	-	-	-
28-17	37.5	0.33	12.5
28-18	31.3	0.25	11.0
28-18a	-	-	-
29-1	26.5	0.28	-
29-2	18.5	0.2	5.5
29-3	14.8	0.19	9.0
29-3a	-	-	-
29-3b	-	-	-
29-3c	-	-	-
29-4	40.5	0.38	17.5
29-4a	-	-	-
29-4b	-	-	-
29-4c	-	-	-
29-5	38.5	0.31	16.5
29-6	-	-	-
29-7	-	-	-
29-lake	-	-	-
30-1	31	0.31	9.5
30-2	33	0.32	13.0
30-3	42	0.4	14.0
30-4	38	0.33	18.0

Table E-3. (cont'd)

RIV I
(All concentrations in mg/L.)

SITE	Cl	Br	Na
30-lake	-	-	-
31-1	37	0.3	6.5
31-1a	-	-	-
31-2	44	0.41	13.5
31-3	32	0.28	7.5
31-4	114	0.97	69
31-4a	-	-	-
31-4b	-	-	-
31-5	39	0.29	19.5
31-5a	-	-	-
31-5b	-	-	-
31-6	41	0.33	20.5
31-6b	-	-	-
32-1	42	0.42	15.0
32-1a	-	-	-
32-1b	-	-	-
32-2	76	0.58	28.5
32-3	71	0.53	26.5
32-3a	-	-	-
32-4	-	-	-
32-5	-	-	-
32-6	-	-	-

Table E-4. River Chemistry - RIV II sampling*(All concentrations in mg/L.)*

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
BLUFF	-	-	-	-	-	-	-
DTL	-	-	-	-	-	-	-
T	-	-	-	-	-	-	-
X	-	-	-	-	-	-	-
1-1	16.3	0.2	8.2	63.6	17.8	2.2	2.2
1-1a	-	-	-	-	-	-	-
1-2	11.4	0.18	8.0	65.6	15.0	2.0	3.0
1-3	13.8	0.2	9.0	62.4	16.2	2.1	2.8
1-3a	-	-	-	-	-	-	-
1-4	12.9	0.18	8.4	61.6	14.4	2.2	2.6
1-5	6.4	0.15	4.4	61.2	15.6	1.1	3.6
1-5a	9.8	0.17	6.6	62.8	19.6	2.3	3.9
2-1	93	0.9	43.6	64.8	16.0	1.9	3.2
2-2	76	0.72	33.8	66.8	21.0	3.1	2.5
2-3	87	0.78	39.2	68.0	21.6	3.7	2.3
2-4	-	-	-	-	-	-	-
3-1	61	0.36	27.6	106	28.8	5.4	3.3
3-1a	-	-	-	-	-	-	-
3-2	65.9	0.39	27.8	86.8	31.0	5.0	3.0
3-2a	70	0.41	26.0	110	35.0	6.2	3.1
3-2b	-	-	-	-	-	-	-
3-3	48.5	0.34	21.2	76.8	23.8	5.8	2.7
3-lake	-	-	-	-	-	-	-
4-1	53	0.34	19.4	108	31.6	6.5	5.8
4-2	39	0.28	12.2	110	30.2	5.9	2.3
4-2a	44	0.33	16.8	113	31.6	5.9	4.8
4-3	57.7	0.37	15.8	119	35.8	5.9	5.0
5-1	13.9	0.21	7.2	48.4	11.8	2.1	4.5
5-1a	21.5	0.24	7.0	60.8	15.4	1.8	4.1
5-2	1.9	0.14	0.8	22.8	7.0	0.9	1.1
5-3	20.3	0.25	7.2	54.0	14.8	2.9	2.9

Table E-4. (cont'd)

RIV II
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
5-3a	-	-	-	-	-	-	-
5-4	68	0.63	40.4	83.2	19.4	3.7	3.1
5-5	24.2	0.29	7.6	56.0	16.2	3.3	3.3
5-6	26.2	0.37	10.0	62.4	15.4	4.1	8.1
5-7	54.5	0.45	22.2	101	27.0	4.4	4.0
5-8	64	0.54	27.4	95.2	27.0	4.3	3.8
5-lake	-	-	-	-	-	-	-
6-1	1.8	0.12	3.2	48.8	15.2	0.6	3.6
6-2	11.3	0.2	7.4	79.2	22.2	1.3	3.4
6-3	2.7	0.13	3.4	43.2	11.0	0.9	2.1
6-4	-	-	-	-	-	-	-
6-4a	101	1.32	36.0	91.2	22.8	2.6	3.8
6-4b	80.5	1.08	35.4	102	21.2	2.9	2.8
6-5	17.8	0.24	11.2	44.4	16.0	1.1	2.4
6-6	96	1.02	49.0	66.0	20.0	3.0	2.0
6-7	45	0.37	8.4	110	28.4	4.7	3.4
6-8	76	0.62	38.2	106	17.8	8.1	-
6-9	114	1.21	57.4	65.6	19.8	3.2	2.7
7-1a	7	0.14	3.4	48.4	16.6	0.7	3.3
7-1b	20.4	0.22	9.8	62.8	19.4	0.7	2.4
7-2	10.3	0.15	9.6	76.8	23.6	1.9	3.8
7-3	8.6	0.14	5.6	59.2	18.2	0.8	3.9
7-4	10.2	0.15	7.8	56.0	19.2	1.0	4.2
7-5	21.2	0.22	14.6	66.8	21.4	1.4	4.3
7-6	14.1	0.17	9.8	59.6	18.4	1.5	-
7-7	20.2	0.21	13.6	66.8	19.8	1.5	3.0
7-7a	12.4	0.16	7.4	65.6	21.2	1.1	3.2
8-1	6.4	0.16	6.0	36.4	11.2	0.8	3.0
8-2	8.4	0.18	5.2	40.4	15.0	1.0	2.5
8-2a	-	-	-	-	-	-	-
8-2b	-	-	-	-	-	-	-
8-3	12.7	0.23	7.0	46.4	15.8	1.2	3.4

Table E-4. (cont'd)

RIV II
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
8-4	15.8	0.26	8.2	46.0	17.4	1.1	-
8-4a	17.9	0.23	8.6	78.8	24.4	2.8	4.0
8-4b	-	-	-	-	-	-	-
8-5	19.2	0.27	9.4	52.8	19.2	1.3	-
8-6	24.5	0.28	13.0	57.6	19.4	1.5	3.3
8-7	27.5	0.3	15.4	54.8	18.8	1.7	2.0
8-8	27.2	0.3	14.0	56.8	19.4	1.8	2.1
8-9	27.9	0.3	14.2	57.6	20.0	2.1	2.4
8-10	28.2	0.32	14.8	56.8	19.8	1.8	2.4
9-1	30	0.3	13.2	105	31.4	5.5	3.5
9-1a	-	-	-	-	-	-	-
9-1b	-	-	-	-	-	-	-
9-2	314	5.63	118.0	124	39.4	6.8	1.3
9-2a	56.3	0.5	22.2	104	23.6	4.3	-
9-2a'	-	-	-	-	-	-	-
9-3	84	0.75	41.6	113	32.0	12.1	3.1
9-3a	60	0.52	27.6	109	34.0	13.3	3.4
9-3a'	-	-	-	-	-	-	-
9-4	120	1.12	48.4	116	32.4	5.5	2.0
9-5	114	1.02	47.2	104	29.8	8.9	2.4
9-6	112	0.98	45.2	96.4	29.8	9.1	1.9
9-7	39	0.39	22.0	103	30.2	5.0	2.5
10-1	53	0.74	10.8	82.4	17.4	5.6	2.1
10-1a	56	0.78	10.8	83.6	17.4	5.5	6.1
10-2	142	1.3	63.2	96.0	29.2	7.3	2.3
12-1	42.5	0.35	19.6	72.0	23.2	4.8	6.8
12-2	15.8	0.2	6.8	63.6	20.0	1.4	4.4
12-3	19.9	0.28	8.6	69.6	20.6	1.7	4.4
12-4	30.5	0.4	12.4	68.4	20.8	2.4	1.0
12-5	39.3	0.44	16.4	68.4	20.2	2.8	3.1
13-1	23.2	0.27	8.8	90.8	25.0	2.4	3.3
13-2	38	0.39	15.0	87.6	25.4	3.8	2.9
14-1	32.8	0.36	12.0	70.4	21.4	2.5	4.0

Table E-4. (cont'd)

RIV II
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
14-2	61	0.66	16.6	86.	25.4	9.7	3.5
15-1	52.5	0.43	14.6	89.	24.8	5.3	3.8
15-2	-	-	-	-	-	-	-
15-3	-	-	-	-	-	-	-
17-1	67	0.64	17.0	99.	28.6	5.6	1.3
17-2	54	0.52	10.6	94.	26.4	4.8	3.1
17-3	66	0.63	18.2	67.	20.0	7.5	2.6
18-1	50	0.43	15.2	116.	33.6	7.1	3.4
18-2	62	0.61	20.8	60.	18.6	5.8	2.2
18-3	72	0.75	15.6	72.	24.4	5.3	1.7
19-1	18.5	0.2	18.8	45.	22.0	6.8	3.5
19-2	27.3	0.28	9.2	93.	32.6	3.7	3.3
19-3	23.3	0.27	6.8	92.	30.6	3.5	4.0
19-4	33.8	0.33	15.6	51.	14.6	4.0	1.3
20-1	29	0.34	12.0	84.4	30.4	5.1	3.3
20-2	23.9	0.27	8.2	88.4	29.6	3.4	3.8
20-3	28.1	0.3	12.6	57.2	19.8	3.8	2.5
20-4	29.8	0.33	13.0	54.4	20.0	3.8	0.9
20-5	27.6	0.29	11.8	52.8	19.0	3.9	3.0
20-6	30.5	0.32	12.2	53.2	18.8	4.3	1.8
20-7	-	-	-	-	-	-	-
20-8	52.3	0.41	23.4	65.2	29.5	5.2	-
21-1	42	0.44	24.2	51.6	21.6	5.1	2.7
21-1a	-	-	-	-	-	-	-
21-2	74	0.58	38.4	71.2	18.6	4.7	1.3
21-2a	-	-	-	-	-	-	-
21-3	41.9	0.36	20.2	85.6	32.8	4.7	3.6
21-4	64	0.47	31.4	62.8	21.8	3.8	2.0
21-5	-	-	-	-	-	-	-
21-5a	-	-	-	-	-	-	-
22-1	689	7.36	33.0	103	39.0	16.4	0.1
22-1a	-	-	-	-	-	-	-

Table E-4. (cont'd)

RIV II
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO ₂
22-1b	-	-	-	-	-	-	-
22-2	35.5	0.24	36.0	89.2	36.6	3.4	3.8
22-2a	-	-	-	-	-	-	-
22-3	83	0.42	38.4	65.6	19.6	8.2	-
22-3a	-	-	-	-	-	-	-
22-3b	-	-	-	-	-	-	-
22-4	33	0.21	12.4	74.8	38.6	4.9	3.2
22-4a	-	-	-	-	-	-	-
22-5	92	0.56	32.8	97.6	37.8	7.5	1.7
22-6	53	0.32	24.4	57.6	35.8	5.0	-
22-7	86	0.49	34.8	54.8	17.2	8.7	-
23-1	44	0.3	19.6	44.4	27.6	1.6	-
23-2	42	0.65	10.6	63.2	20.8	3.4	6.3
23-3	42.5	0.4	17.8	60.8	25.6	2.0	4.6
23-4	64	0.5	28.2	64.4	25.2	2.7	3.4
23-5	180	1.19	88.0	85.2	27.6	4.7	2.3
24-1	29.5	0.3	6.6	95.6	30.0	1.7	2.8
24-2	33	0.46	11.6	70.4	24.2	2.0	4.8
24-3	49	0.38	22.4	65.6	21.8	3.4	3.6
24-4	46	0.28	16.4	59.6	23.8	5.5	2.1
24-5	53.5	0.39	24.8	66.0	24.2	3.1	5.0
25-1	30	0.28	10.4	103	33.6	3.0	4.4
25-2	26.8	0.25	4.4	67.2	20.2	5.6	1.2
25-3	30.3	0.27	16.0	82.4	27.4	4.3	3.9
26-1	69	0.48	22.8	79.6	31.4	2.9	4.8
26-2	10.9	0.13	5.2	58.8	22.6	1.8	4.4
26-2a	15.2	0.22	7.2	48.0	28.0	1.1	3.2
26-3	20.5	0.29	7.0	68.8	28.2	3.2	6.1
26-4	25.9	0.32	9.8	64.0	24.4	2.6	3.4
26-5	26.7	0.3	12.0	54.0	25.0	2.6	2.7
26-6	29.9	0.29	14.2	68.0	21.0	2.8	1.4

Table E-4. (cont'd)**RIV II**
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
27-1	17.2	0.22	5.8	76.4	28.0	2.1	3.7
27-1a	23	0.3	10.2	74.0	29.8	2.3	5.1
27-1b	-	-	-	-	-	-	-
27-2	39	0.38	12.6	84.4	40.4	5.5	2.4
27-3	51.5	0.46	29.6	40.4	30.6	5.0	4.9
27-4	27.8	0.35	11.0	71.6	32.6	2.9	3.3
27-4a	30.9	0.38	12.2	74.0	32.0	3.1	3.0
27-4b	-	-	-	-	-	-	-
27-5	35	0.47	11.6	71.2	28.4	3.5	3.0
27-6	37	0.43	16.2	56.0	26.0	3.1	-
27-6a	32.5	0.34	18.0	60.0	25.4	2.1	4.7
27-7	54.5	0.4	25.6	54.8	26.2	4.1	1.3
27-8	60	0.4	29.8	52.0	24.2	3.9	1.5
27-8a	-	-	-	-	-	-	-
27-8b	-	-	-	-	-	-	-
27-9	72	0.39	30.8	55.2	23.0	3.4	2.3
27-10	-	-	-	-	-	-	-
27-11	176	1.94	48.2	74.4	28.2	4.3	1.9
27-12	86	0.52	43.0	51.6	21.2	4.6	1.3
27-13	289	2.01	125.0	58.4	22.0	7.9	1.7
28-1	-	-	-	-	-	-	-
28-2	38	0.35	4.6	47.2	18.6	2.3	-
28-3	49	0.43	27.6	84.0	30.0	8.5	2.9
28-4	44	0.40	25.8	57.2	40.2	7.6	1.8
28-5	22.9	0.24	8.6	92.8	27.0	4.6	1.7
28-6	30	0.30	14.4	82.8	27.6	3.7	1.2
28-7	17.2	0.22	5.6	90.0	28.8	3.2	1.9
28-8	-	-	-	-	-	-	-
28-9	28.9	0.33	14.0	77.6	27.6	6.5	2.4
28-10	21.2	0.29	9.8	65.2	27.0	5.4	2.3
28-10a	35	0.39	8.4	79.2	29.8	2.9	-
28-11	30.5	0.37	16.8	64.8	27.2	4.7	1.8

Table E-4. (cont'd)

RIV II
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
28-12	29	0.36	11.2	92.0	41.8	5.3	3.3
28-12a	-	-	-	-	-	-	-
28-14	25.5	0.33	15.2	65.2	29.2	3.7	3.3
28-15	27.2	0.36	16.2	58.8	26.2	4.4	0.8
28-16	33.1	0.4	19.2	56.8	24.0	5.1	0.7
28-16a	31.5	0.43	14.2	80.8	31.0	4.2	2.9
28-17	100	0.8	60.6	82.8	28.0	4.7	2.4
28-18	28.2	0.28	11.0	88.4	30.0	2.8	2.7
28-18a	32.2	0.3	25.2	70.8	24.8	2.4	3.7
29-1	30.3	0.31	10.8	99.6	37.2	4.4	3.7
29-2	18.6	0.23	7.0	86.0	33.6	2.4	-
29-3	27.5	0.35	13.6	86.8	22.0	8.0	-
29-3a	30	0.39	7.2	60.0	23.6	8.1	4.4
29-3b	52	0.73	20.4	125	37.2	4.0	6.3
29-3c	-	-	-	-	-	-	-
29-4	52	0.54	20.4	54.4	32.4	5.1	1.8
29-4a	36	0.35	14.2	78.4	27.4	7.1	-
29-4b	-	-	-	-	-	-	-
29-4c	-	-	-	-	-	-	-
29-5	34	0.34	16.0	72.4	27.8	5.5	-
29-6	-	-	-	-	-	-	-
29-7	-	-	-	-	-	-	-
29-lake	-	-	-	-	-	-	-
30-1	42	0.46	13.2	66.0	27.6	6.3	1.1
30-2	26.5	0.32	20.8	79.2	26.0	6.8	3.5
30-3	55	0.59	29.8	62.8	30.6	6.2	-
30-4	54	0.53	21.2	47.6	28.4	4.4	0.5
30-lake	-	-	-	-	-	-	-
31-1	-	-	-	-	-	-	-
31-1a	25	0.29	6.4	74.8	24.4	2.0	1.8
31-2	58	0.56	20.2	103	39.2	2.8	4.2

Table E-4. (cont'd)**RIV II**
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
31-3	46	0.45	29.6	113	36.6	5.6	-
31-4	-	-	-	-	-	-	-
31-4a	-	-	-	-	-	-	-
31-4b	-	-	-	-	-	-	-
31-5	50	0.50	22.8	62	30.6	3.7	1.5
31-5a	-	-	-	-	-	-	-
31-5b	-	-	-	-	-	-	-
31-6	50	0.44	20.4	41	21.2	4.6	0.3
31-6b	54	0.49	20.4	44	24.2	4.8	-
32-1	-	-	-	-	-	-	-
32-1a	-	-	-	-	-	-	-
32-1b	-	-	-	-	-	-	-
32-2	162	0.90	58	68	38.4	8.8	0.7
32-3	51	0.37	19.0	100	33.8	4.3	2.6
32-3a	-	-	-	-	-	-	-
32-4	44	0.38	31.0	48	20.0	3.3	1.8
32-5	60	0.51	36.0	48	19.0	3.8	1.8
32-6	80	0.64	36.0	69	35.2	3.3	-

Table E-5. River Chemistry - RIV III sampling

(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO ₂	T (°C)	pH	Alk HCO ₃ ⁻	SO ₄
bluff	-	-	-	-	-	-	-	-	-	-	
dtl	-	-	-	-	-	-	-	-	-	-	
T	-	-	-	-	-	-	-	-	-	-	
X	-	-	-	-	-	-	-	-	-	-	
1-1	18.2	0.17	8.1	74	21.0	1.9	1.9	14.0	-	-	
1-1a	-	-	-	-	-	-	-	-	-	-	
1-2	11.2	0.14	7.8	64	16.8	1.0	2.3	15.0	-	-	
1-3	15	0.17	12.0	63	16.6	1.1	3.2	16.0	-	-	
1-3a	6.1	0.10	5.4	63	18.0	1.2	2.8	-	-	-	
1-4	15	0.17	9.0	64	16.8	1.3	1.6	18.0	-	-	
1-5	5.3	0.11	3.9	65	16.6	0.7	4.3		-	-	
1-5a	-	-	-	-	-	-	-	14.0	8.11	190	
2-1	88	0.81	37.5	90	24.6	1.6	5.0	14.0	7.69	292.0	-
2-2	70	0.63	27.6	79	24.6	3.8	1.8	16.5	-	-	-
2-3	-	-	-	-	-	-	-	18.0	7.95	-	-
2-4	72	0.37	24.9	80	26.0	11.0	1.7	16.0	-		
3-1	67	0.41	31.2	96	31.6	7.0	1.2	19.0	-		
3-1a	42	0.31	19.8	92	28.2	5.8	1.7	16.0	7.87	279	
3-2	-	-	-	-	-	-	-	-	-	-	-
3-2a	274	2.36	113	103	33.2	7.5	2.1	-	-		
3-2b	108	0.68	47.4	105	30.6	5.8	3.2	-	-		
3-3	114	0.81	53	75	29.4	5.4	1.1	19.0	-		
3-lake	19.8	0.22	15.3	27.0	12.6	2.6	0.7	23.5	8.57	95	
4-1	445	3.36	204	169	43.8	7.8	6.9	16.0	-		
4-2	43.8	0.81	13.8	101	36.8	7.8	3.4	18.0	-		
4-2a	294	1.60	123	100	21.4	5.6	2.4	22.0	-		
4-3	38	0.26	16.5	127	47.2	4.0	2.7	22.0	7.74	284.0	
5-1	76	1.41	8.4	96	19.6	3.8	4.7	-	-		
5-1a	4.8	0.11	3.3	68	15.6	2.0	2.4	16.0	7.82	231.0	

Table E-5. (cont'd)

RIV III
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO ₂	T (°C)	pH	Alk HCO ₃ ⁻	SO ₄
5-2	62.4	0.51	29.7	71	17.8	1.3	3.2	16.0	-	-	
5-3	20	0.17	6.0	53	14.4	3.3	0.5	18.0	-	-	
5-3a	96.8	0.60	22.2	175	47.6	5.8	6.2	-	-	-	
5-4	74	0.46	46.2	70	17.0	3.2	3.7	14.1	-	-	
5-5	27	0.21	7.5	62	17.0	3.3	4.2	17.5	-	-	-
5-6	23.5	0.34	8.1	69	18.6	3.0	10.4	17.7	7.35	281.0	
5-7	75.6	0.53	28.8	86	31.6	4.5	1.8	21.5	-	-	-
5-8	90	0.59	34.8	89	29.4	4.5	1.9	21.2	8.14	309	
5-lake	33	0.27	18.6	33.5	13.0	2.1	0.1	19.0	-	-	-
6-1	1.2	0.06	2.7	54	14.4	0.5	5.3	13.0	7.78	191	
6-2	9.9	0.13	5.7	82	22.2	1.1	4.4	14.0	-	-	-
6-3	3.6	0.10	6.6	50	11.0	1.0	2.6	17.0	-	-	-
6-4	-	-	-	-	-	-	-	-	-	-	-
6-4a	43	0.34	6.9	85	26.4	3.8	5.1	16.0	-	-	-
6-4b	120	1.66	53	92	26.2	3.2	3.0	20.0	-	-	-
6-5	32.4	0.30	16.5	51	16.6	1.3	3.2	18.5	-	-	-
6-6	172	1.07	81	73	20.4	3.0	3.0	21.3	8.47	213.0	
6-7	49.4	0.35	13.5	50	31.0	2.3	0.8	21.8	-	-	-
6-8	108	0.84	63	145	28.2	9.1	5.9	22.8	-	-	-
6-9	190	1.05	78	73	20.0	2.5	2.4	20.1	7.94	235	
7-1a	4.9	0.05	2.4	52	15.6	0.5	4.9	18.0	8.26	207	
7-1b	28.4	0.23	8.4	66	19.2	0.7	3.9	-	-	-	-
7-2	11.5	0.22	9.3	77	23.8	1.6	3.8	18.0	-	-	-
7-3	9	0.14	4.8	65	18.2	0.8	3.5	16.0	-	-	-
7-4	10	0.1	6.6	61	18.0	0.8	2.9	16.0	-	-	-
7-5	26.4	0.19	14.4	68	20.0	1.4	2.9	18.5	-	-	-
7-6	19.8	0.15	10.2	65	19.6	1.2	2.2	21.0	-	-	-
7-7	25.6	0.2	14.4	66	20.0	1.3	2.7	19.0	-	-	-
7-7a	16	0.13	6.6	72	21.2	1.0	4.0	18.0	-	-	-
8-1	8	0.11	5.4	39.0	11.0	0.5	6.9	-	-	-	-

Table E-5. (cont'd)

RIV III
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO ₂	T (°C)	pH	Alk HCO ₃ ⁻	SO ₄
8-2	13	0.12	5.4	47.5	14.8	0.8	3.8	-	-	-	-
8-2a	-	-	-	-	-	-	-	-	-	-	-
8-2b	-	-	-	-	-	-	-	-	-	-	-
8-3	21.2	0.19	53	55	17.2	0.8	4.9	-	-	-	-
8-4	20	0.18	7.2	44.5	15.6	0.9	3.6	-	-	-	-
8-4a	22.6	0.18	9.9	80	26.8	2.2	2.1	18.0	-	-	-
8-4b	17.6	0.16	7.2	81	25.2	2.0	2.7	19.0	-	-	-
8-5	22.6	0.18	7.8	58	18.6	1.3	3.1	-	-	-	-
8-6	38	0.25	15.9	63	19.2	1.5	3.0	-	-	-	-
8-7	38.2	0.24	15.9	60	19.2	1.5	2.3	-	-	-	-
8-8	42	0.29	18.0	61	19.6	1.6	2.5	-	-	-	-
8-9	39.4	0.29	16.5	53	20.0	1.7	1.8	-	-	-	-
8-10	41.2	0.32	17.1	61	20.6	1.6	2.1	-	-	-	-
9-1	34.2	0.25	13.5	107	34.4	3.3	4.7	18.0	-	-	-
9-1a	72	0.72	42.9	121	40.2	4.8	2.1	-	-	-	-
9-1b	68	0.76	47.4	123	41.6	6.4	1.9	-	-	-	-
9-2	310	5.21	85	111	36.6	5.6	2.0	16.5	8.05	284.0	
9-2a	53	0.41	18.6	104	26.0	3.3	3.1	-	-	-	-
9-2a'	-	-	-	-	-	-	-	-	-	-	-
9-3	136	1.11	75	119	41.8	6.4	1.3	18.0	-	-	-
9-3a	72	0.48	37.8	116	41.6	6.6	2.5	18.5	-	-	-
9-3a'	-	-	-	-	-	-	-	-	-	-	-
9-4	144	1.72	64	114	33.2	3.9	0.6	-	-	-	-
9-5	178	2.10	76	109	36.0	4.9	0.6	19.0	7.75	228	
9-6	165	2.05	73	103	36.2	5.1	0.4	19.0	-	-	-
9-7	35	0.21	15	101	32.6	3.9	3.2	-	-	-	-
10-1	35.4	0.24	16.8	79	17.2	1.3	4.1	17.0	7.51	307	
10-1a	-	-	-	-	-	-	-	-	-	-	-
10-2	-	-	-	-	-	-	-	-	-	-	-

Table E-5. (cont'd)

RIV III
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO ₂	T (°C)	pH	Alk HCO ₃ ⁻	SO ₄ ²⁻
12-1	11	0.10	4.2	71	22.8	0.9	5.6	18.2	-	-	-
12-2	19.8	0.21	6.9	70	22.6	1.0	4.0	21.7	8.71	303.0	
12-3	31	0.30	8.7	74	22.2	1.3	2.9	20.5	-	-	-
12-4	53	0.52	20.4	83	24.0	2.7	3.6	24.1	8.12	311	
12-5	53	0.47	18.0	75	23.2	2.6	3.4	-	-	-	-
13-1	22.2	0.17	6.3	78	26.0	1.7	4.2	19.1	-	-	-
13-2	33.6	0.27	11.1	82	27.4	12.5	3.2	-	-	-	-
14-1	66	0.50	19.5	84	31.0	7.7	5.2	24.4	-	-	-
14-2	83	0.77	22.5	69	28.2	9.3	1.9	-	-	-	-
15-1	80	0.57	24.9	68	25.8	5.3	0.3	20.8	-	-	-
15-2	-	-	-	-	-	-	-	-	-	-	-
15-3	108	0.96	39.0	69	28.6	3.8	3.6	-	-	-	-
17-1	83	0.67	18.6	75	32.4	7.3	2.2	20.0	-	-	-
17-2	100	0.82	19.2	61	33.2	5.6	4.5	19.7	-	-	-
17-3	72	0.52	14.4	76	21.2	7.7	2.7	18.4	-	-	-
18-1	28.5	0.27	11.7	111	34.4	8.5	3.9	18.6	8.14	412	
18-2	69	0.59	38.7	90	28.6	6.5	2.4	21.6	7.92	265	
18-3	85	0.69	23.7	75	26.0	5.1	0.6	19.3	8.04	246	
19-1	28.4	0.20	21.9	54	22.0	9.1	5.9	21.1	-	-	-
19-2	23.9	0.21	9.6	85	33.8	3.2	1.7	19.6	8.01	333	
19-3	27.8	0.20	6.3	96	31.4	3.0	5.9	18.3	-	-	-
19-4	92.4	0.91	46.5	69	27.4	4.3	0.8	17.5	-	-	-
20-1	33	0.30	9.6	103	39.4	4.6	1.2	17.2	-	-	-
20-2	21	0.20	11.1	91	33.0	2.3	4.0	15.3	7.65	347.0	
20-3	34.6	0.33	19.2	66	25.4	2.5	2.5	20.5	-	-	-
20-4	58	0.44	30.6	70	25.4	3.4	3.3	20.1	-	-	-
20-5	44.4	0.34	22.5	70	25.6	2.9	3.9	18.8	7.99	235	
20-6	44	0.37	23.4	67	25.6	2.9	3.4	20.3	-	-	-
20-7	31.2	0.26	21.0	59	41.2	3.6	1.3	17.0	-	-	-
20-8	-	-	-	-	-	-	-	-	-	-	-

Table E-5. (cont'd)**RIV III***(All concentrations in mg/L.)*

SITE	Cl	Br	Na	Ca	Mg	K	SiO ₂	T (°C)	pH	Alk HCO ₃ ⁻	SO ₄
21-1	-	-	-	-	-	-	-	-	-	-	-
21-1a	34.4	0.32	19.8	60	23.8	2.0	2.0	20.0	-	-	-
21-2	114	0.92	59	113	34.4	5.4	5.0	18.0	-	-	-
21-2a	32	0.84	32.7	99	46.4	2.4	5.0	14.3	-	-	-
21-3	39.6	0.35	32.1	84	45.2	3.0	2.8	16.8	-	-	-
21-4	64	0.51	39.0	69	26.8	2.6	1.8	20.0	-	-	-
21-5	39	0.33	21.6	62	24.4	2.1	2.0	19.1	-	-	-
21-5a	172	1.32	53	155	37.6	4.9	5.4	17.9	-	-	-
22-1	57.4	0.38	33.3	51	35.8	3.4	1.9	20.1	-	-	-
22-1a	84	0.65	89	43.5	35.8	10.8	5.3	18.5	-	-	-
22-1b	-	-	-	-	-	-	-	-	-	-	-
22-2	51.8	0.39	33.6	118	40.2	2.6	3.3	13.4	-	-	-
22-2a	-	-	-	-	-	-	-	-	-	-	-
22-3	49.6	0.39	30.0	75	38.6	4.9	0.9	18.2	-	-	-
22-3a	50	0.39	26.7	53	28.4	5.8	0.1	21.0	-	-	-
22-3b	33.6	0.28	15.9	57	45.0	3.7	1.0	18.2	-	-	-
22-4	28.8	0.24	12.0	85	39.8	4.1	4.1	18.0	-	-	-
22-4a	40	0.39	20.4	86	41.0	9.8	3.8	16.8	-	-	-
22-5	104	0.76	46.5	123	59.6	7.7	0.6	19.0	-	-	-
22-6	104	0.66	58	72	24.8	6.5	1.7	21.7	-	-	-
22-7	-	-	-	-	-	-	-	-	-	-	-
23-1	44	0.29	24.6	57	26.2	1.7	2.8	25.9	-	-	-
23-2	800	9.65	92	136	52	13.4	7.4	20.0	-	-	-
23-3	50	0.32	25.5	75	28.6	2.0	4.0	17.5	-	-	-
23-4	120	0.68	68	72	30.8	2.8	1.9	19.0	-	-	-
23-5	344	2.12	113	76	23.8	6.4	2.9	19.8	8.12	208	-
24-1	30.8	0.24	6.6	98	31.4	1.5	3.2	18.0	-	-	-
24-2	33	0.39	12	80	25.8	1.8	4.6	22.0	-	-	-
24-3	52	0.41	28.8	68	26.2	2.2	4.2	18.9	-	-	-
24-4	-	-	-	-	-	-	-	-	-	-	-

Table E-5. (cont'd)

RIV III
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO ₂	T (°C)	pH	Alk HCO ₃ ⁻	SO ₄
24-5	-	-	-	-	-	-	-	-	-	-	-
25-1	30.4	0.26	12	101	32.2	2.8	8.4	19.0	-	-	-
25-2	-	-	-	-	-	-	-	-	-	-	-
25-3	-	-	-	-	-	-	-	-	-	-	-
26-1	66	0.46	26.1	101	34.8	2.4	4.5	21.8	-	-	-
26-2	8.8	0.13	5.1	77	24.2	1.7	4.2	20.7	-	-	-
26-2a	21.2	0.25	12.6	64	26.4	2.1	4.2	21.0	-	-	-
26-3	12.4	0.2	4.9	94	33.6	1.8	4.7	18.0	-	-	-
26-4	26	0.31	11.7	84	31.4	1.8	3.8	22.9	-	-	-
26-5	27	0.29	16.5	68	28.0	2.1	2.4	23.0	-	-	-
26-6	34.4	0.35	21.6	82	29.6	2.4	2.6	20.0	-	-	-
27-1	15.2	0.18	5.4	87	28.8	1.1	4.7	16.7	-	-	-
27-1a	15.8	0.20	10.5	87	32.8	1.7	2.7	22.5	-	-	-
27-1b	24.5	0.24	18.9	85	29.8	5.1	1.5	-	-	-	-
27-2	14	0.22	5.7	60	20.8	1.2	2.9	25.4	8.10	234	
27-3	40	0.33	33.3	90	29.2	3.6	3.7	18.5	-	-	-
27-4	30	0.29	13.2	88	35.8	3.2	2.2	19.5	-	-	-
27-4a	30.4	0.30	13.5	89	36.0	2.7	3.5	19.8	-	-	-
27-4b	31.5	0.27	12.8	82	33.4	2.9	2.6	19.3	-	-	-
27-5	34.4	0.36	14.1	87	32.2	2.6	2.9	19.4	7.93	304	
27-6	38	0.37	18.0	68	26.8	2.8	1.4	24.0	-	-	-
27-6a	42	0.33	24.6	74	28.0	2.2	6.8	16.9	-	-	-
27-7	52	0.43	27.6	70	27.0	2.9	1.6	22.9	-	-	-
27-8	65	0.50	38.1	69	25.2	4.3	1.2	22.3	-	-	-
27-8a	88	0.55	48.6	87	25.8	2.5	2.3	19.1	-	-	-
27-8b	44	0.28	28.2	73	24.2	3.3	2.5	19.4	-	-	-
27-9	84	0.54	42.9	80	29.6	3.3	1.9	18.2	7.82	252	
27-10	-	-	-	-	-	-	-	-	-	-	-
27-11	294	5.03	81	106	35.4	3.5	1.7	18.2	7.70	164	
27-12	100	0.69	56	68	24.6	5.7	1.0	17.8	8.85	252.0	

Table E-5. (cont'd)

RIV III
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO ₂	T (°C)	pH	Alk HCO ₃ ⁻	SO ₄
27-13	911	7.64	420	131	38.6	9.0	0.7	18.9	-	-	-
28-1	43	0.29	14.4	137	47.0	8.7	2.1	21.5	-	-	-
28-2	39	0.29	12.9	101	46.8	4.9	3.5	19.2	8.02	325	
28-3	88	0.65	54	94	33.0	7.5	1.8	17.9	-	-	-
28-4	80	0.53	51	78	44.0	6.9	1.6	19.2	-	-	-
28-5	25.6	0.18	6.9	110	26.4	4.1	2.7	18.7	7.88	339	
28-6	42	0.29	20.7	84	26.2	4.2	3.1	17.2	-	-	-
28-7	19.9	0.17	4.5	105	27.6	2.5	1.6	20.0	-	-	-
28-8	-	-	-	-	-	-	-	-	-	-	-
28-9	-	-	-	-	-	-	-	-	-	-	-
28-10	25.8	0.23	10.8	78	30.4	4.6	1.8	17.5	-	-	-
28-10a	23.4	0.22	9.3	97	32.0	2.6	3.2	17.0	-	-	-
28-11	49.4	0.40	30.0	67	26.4	5.4	0.2	22.6	-	-	-
28-12	59	0.48	21.6	107	43.4	5.8	4.2	17.6	-	-	-
28-12a	24.6	0.25	13.8	66	26.4	2.3	3.3	23.0	-	-	-
28-14	33.6	0.32	17.7	78	29.4	3.6	3.5	19.1	-	-	-
28-15	40.8	0.37	21.3	61	25.6	5.1	0	23.0	-	-	-
28-16	46	0.39	27.3	59	25.4	4.8	3.4	24.8	8.13	219	
28-16a	31.4	0.29	14.1	89	31.6	3.2	0.2	18.9	-	-	-
28-17	56	0.46	22.5	64	25.2	5.6	0.6	23.0	-	-	-
28-18	31.8	0.26	12.3	94	28.4	2.4	4.3	21.9	-	-	-
28-18a	72	0.42	48.0	90	24.2	2.4	3.5	20.3	-	-	-
29-1	34.2	0.28	11.1	115	39.6	3.6	3.5	15.0	-	-	-
29-2	24	0.19	6.9	112	35.4	2.6	3.3	23.8	-	-	-
29-3	-	-	-	-	-	-	-	-	-	-	-
29-3a	44.2	0.38	10.8	41.5	23.0	12.2	0.3	20.5	-	-	-
29-3b	90	0.91	29.7	94	40.0	8.8	1.1	17.3	-	-	-
29-3c	-	-	-	-	-	-	-	-	-	-	-
29-4	76	0.63	30.9	52	33.4	6.2	0.8	-	-	-	-

Table E-5. (cont'd)**RIV III***(All concentrations in mg/L.)*

SITE	Cl	Br	Na	Ca	Mg	K	SiO ₂	T (°C)	pH	Alk HCO ₃ ⁻	SO ₄
29-4a	42.2	0.31	16.5	84	30.6	6.0	1.9	19.8	-	-	-
29-4b	-	-	-	-	-	-	-	-	-	-	-
29-4c	-	-	-	-	-	-	-	-	-	-	-
29-5	58	0.43	29.1	103	33.8	5.9	1.7	18.2	8.05	262	
29-6	-	-	-	-	-	-	-	-	-	-	-
29-7	-	-	-	-	-	-	-	-	-	-	-
29-Philp Park (lake)	9.8	0.11	3.6	28.5	7.4	1.0	0.4	20.2	8.38	91.0	
30-1	56	0.45	18.6	72	29.0	6.7	2.4	19.2	-	-	-
30-2	29.8	0.24	20.1	88	26.6	6.7	2.9	19.8	-	-	-
30-3	68	0.53	34.2	67	31.8	6.9	0	19.5	-	-	-
30-4	35.8	0.25	16.2	31.0	15.0	2.2	0.2	21.6	-	-	-
30-lake	-	-	-	-	-	-	-	-	-	-	-
31-1	-	-	-	-	-	-	-	-	-	-	-
31-1a	33	0.24	5.1	92	22.2	2.7	2.6	19.0	-	-	-
31-2	-	-	-	-	-	-	-	-	-	-	-
31-3	85	0.63	25.2	100	42.2	3.7	4.0	18.3	-	-	-
31-4	82	0.59	22.8	131	35.6	13.4	4.7	14.9	-	-	-
31-4a	80	0.55	93	65	32.2	6.6	4.2	23.2	8.09	210	
31-4b	-	-	-	-	-	-	-	-	-	-	-
31-5	52	0.37	21.3	47	21.0	3.6	0.2	20.3	-	-	-
31-5a	84	0.62	27.6	69	35.8	9.1	0.2	23.5	-	-	-
31-5b	-	-	-	-	-	-	-	-	-	-	-
31-6	28.6	0.22	12.3	33	13.0	2.4	0.2	20.5	-	-	-
31-6b	-	-	-	-	-	-	-	-	-	-	-
32-1	-	-	-	-	-	-	-	-	-	-	-
32-1a	-	-	-	-	-	-	-	-	-	-	-

Table E-5. (cont'd)

RIV III

(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂	T (°C)	pH	Alk HCO₃⁻	SO₄
32-1b	-	-	-	-	-	-	-	-	-	-	-
32-2	124	0.92	87	117	39.0	18.2	3.4	22.0	-	-	-
32-3	68	0.43	25.8	98	36.4	4.3	2.3	22.0	-	-	-
32-3a	-	-	-	-	-	-	-	-	-	-	-
32-4	-	-	-	-	-	-	-	-	-	-	-
32-5	85	0.66	51	66	20.4	3.9	2.7	22.5	7.98	231	
32-6	314	2.14	199	72	21.0	11.9	4.1	19.5	-	-	-

Table E-6. River Chemistry - RIV IV sampling*(All concentrations in mg/L.)*

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
BLUFF	54	0.47	25.5	31.	5.6	6.0	4.43
DTL	-	-	-	-	-	-	-
T	17.8	0.23	10.0	62.	17.2	2.2	1.39
X	-	-	-	-	-	-	-
1-1	18.0	0.15	6.5	40.	12.0	6.0	2.71
1-1a	6.4	0.09	3.5	54.	17.2	1.4	5.5
1-2	22.5	0.25	12.0	56.	15.6	2.0	4.65
1-3	20.5	0.20	12.0	53.	15.6	2.3	4.56
1-3a	28.0	0.30	12.0	91.	24.0	1.2	4.59
1-4	-	-	-	-	-	-	-
1-5	13.2	0.16	6.5	53.	16.4	3.0	4.65
1-5a	16.9	0.22	9.5	57.	16.4	1.1	5.12
2-1	62	0.64	31.5	40.	10.0	2.3	4.37
2-2	42	0.40	7.5	55.	14.8	2.1	4.37
2-3	44	0.46	19.0	43.	11.2	4.6	3.15
2-4	20.0	0.24	7.0	40.	5.6	11.2	5.98
3-1	20.3	0.20	7.5	29.	8.0	5.4	2.13
3-1a	20.1	0.24	7.0	42.	8.0	5.8	2.74
3-2	27.0	0.27	12.0	28.	7.6	4.4	1.88
3-2a	25.2	0.25	13.0	27.	7.6	5.7	1.8
3-2b	-	-	-	-	-	-	-
3-3	42	0.36	19.5	53.	16.4	3.2	3.23
3-lake	-	-	-	-	-	-	-
4-1	28.3	0.19	9.5	40.	10.8	5.0	2.71
4-2	18.9	0.17	6.5	33.	10.0	6.5	2.38
4-2a	24.0	0.29	11.0	32.	8.8	6.1	2.1
4-3	21.8	0.29	8.5	30.	8.4	6.7	2.02
5-1	10.3	0.21	3.5	43.	12.4	1.1	4.53
5-1a	13.6	0.25	4.0	43.	11.6	2.2	3.82
5-2	7.3	0.28	2.0	41.	12.4	2.5	4.59

Table E-6. (cont'd)**RIV IV**
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
5-3	15.2	0.34	4.5	38.	11.2	3.5	3.51
5-3a	-	-	-	-	-	-	-
5-4	56	0.68	31.0	65.	16.8	3.2	3.84
5-5	21.0	0.24	7.0	47.	14.4	4.6	3.26
5-6	26.2	0.33	10.5	44.	12.8	4.1	2.63
5-7	18.8	0.23	6.5	26.	7.6	5.0	1.1
5-8	27.9	0.29	11.0	30.	8.4	4.1	
5-lake	-	-	-	-	-	-	-
6-1	3.4	0.13	2.5	53.	16.0	0.5	5.48
6-2	16.7	0.35	6.5	69.	18.0	5.5	4.65
6-3	3.8	0.14	1.0	37.	9.2	1.0	4.37
6-4	-	-	-	-	-	-	-
6-4a	148	3.04	57.0	81.	16.4	2.2	2.82
6-4b	-	-	-	-	-	-	-
6-5	31.0	0.36	13.5	59.	16.0	3.2	4.04
6-6	72	0.92	23.5	57.	16.0	10.1	2.99
6-7	32.0	0.35	8.0	32.	8.8	11.2	1.6
6-8	23.9	0.28	2.5	30.	7.2	7.9	1.33
6-9	110	0.94	50.0	70.	18.4	4.0	3.98
7-1a	2.2	0.13	1.0	60.	18.0	0.5	4.29
7-1b	6.1	0.18	2.5	56.	16.4	0.6	5.31
7-2	27.3	0.25	6.0	49.	15.2	4.3	3.32
7-3	8.5	0.16	3.5	61.	19.2	1.2	5
7-4	13.0	0.19	8.0	64.	18.8	0.9	4.92
7-5	32.0	0.30	20.0	64.	18.8	3.4	4.23
7-6	19.2	0.23	11.5	75.	22.0	1.7	5.14
7-7	20.8	0.25	12.0	67.	21.2	3.8	4.29
7-7a	12.2	0.27	4.5	55.	16.8	3.9	3.57
8-1	-	-	-	-	-	-	-
8-2	-	-	-	-	-	-	-

Table E-6. (cont'd)

RIV IV
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
8-2a	-	-	-	-	-	-	-
8-2b	-	-	-	-	-	-	-
8-3	19.4	0.25	6.5	51.	16.8	5.2	3.98
8-4	16.4	0.27	7.0	56.	18.0	1.6	4.42
8-4a	17.8	0.28	3.5	38.	13.6	13.7	1.93
8-4b	13.8	0.25	2.5	37.	10.8	10.7	1.96
8-5	19.9	0.30	7.5	64.	20.0	2.8	3.7
8-6	25.0	0.39	10.5	62.	19.6	3.4	3.82
8-7	29.9	0.40	12.0	60.	18.8	4.0	3.54
8-8	24.3	0.41	10.5	56.	17.2	5.8	3.18
8-9	29.5	0.41	10.0	49.	14.4	6.9	2.74
8-10	27.0	0.34	11.0	53.	16.0	6.6	3.1
9-1	13.5	0.21	3.0	34.	11.2	10.4	1.57
9-1a	16.5	0.21	4.5	19.6	5.6	15.6	1.66
9-1b	52.	0.54	8.0	26.	4.0	35.2	3.05
9-2	68.	0.80	26.5	40.	12.4	7.8	1.55
9-2a	18.8	0.24	3.5	34.	10.4	9.9	1.49
9-2a'	-	-	-	-	-	-	-
9-3	34.0	0.40	11.0	28.	10.8	15.8	1.35
9-3a	37.0	0.38	7.0	24.	10.0	24.8	1.33
9-3a'	35.0	0.37	8.0	25.	9.2	20.6	1.38
9-4	60.	0.70	23.5	66.	19.2	5.7	2.32
9-5	89.	0.95	41.0	101.	29.2	4.1	4.01
9-6	70.	0.69	32.5	82.	23.6	4.2	3.01
9-7	17.0	0.28	4.5	22.	8.4	8.8	1.41
10-1	20.0	0.25	5.5	39.	11.2	2.9	2.54
10-1a	16.1	0.22	3.0	39.	10.8	5.6	2.16
10-2	112.	1.13	52.5	100.	28.0	3.5	4.09
12-1	18.3	0.25	8.0	63.	21.6	3.3	4.45
12-2	16.3	0.24	6.5	65.	22.0	2.1	4.81

Table E-6. (cont'd)**RIV IV**
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
12-3	22.3	0.30	7.5	69.	19.6	2.8	4.62
12-4	42.	0.44	16.5	67.	20.0	4.4	3.48
12-5	63.	0.66	26.5	68.	19.2	4.8	3.18
13-1	19.9	0.24	5.5	87.	22.8	3.6	3.46
13-2	27.8	0.27	7.0	54.	16.0	8.9	2.63
14-1	30.0	0.28	5.5	67.	18.0	8.0	2.21
14-2	34.0	0.39	7.5	50.	14.0	8.4	2.43
15-1	39.0	0.41	12.5	41.	12.8	10.0	1.91
15-2	54.	0.46	17.0	48.	12.8	12.7	1.57
15-3	43.	0.39	7.0	50.	15.2	15.6	1.93
17-1	37.0	0.43	10.0	50.	13.2	12.2	2.1
17-2	34.0	0.37	6.5	41.	11.6	13.7	1.8
17-3	35.0	0.42	8.5	41.	11.6	11.9	1.8
18-1	27.3	0.36	6.0	76.	24.4	7.2	2.46
18-2	31.0	0.41	10.5	38.	11.6	8.0	1.46
18-3	32.0	0.39	12.0	36.	10.8	7.6	1.63
19-1	15.8	0.23	3.0	30.	11.6	7.1	1.91
19-2	14.5	0.25	2.0	31.	10.8	6.7	2.18
19-3	15.5	0.26	3.0	43.	12.8	7.4	1.57
19-4	29.0	0.37	9.0	43.	14.0	7.1	1.88
20-1	32.0	0.42	9.5	68.	25.6	5.3	2.93
20-2	22.2	0.31	5.5	68.	25.6	4.3	2.96
20-3	35.0	0.52	15.0	64.	24.8	3.9	3.01
20-4	61.	0.61	31.5	65.	23.2	5.3	3.23
20-5	43.	0.42	21.5	56.	21.6	5.1	2.71
20-6	55.	0.55	27.5	57.	21.2	5.0	25.09
20-7	16.1	0.19	2.0	26.	8.0	7.9	1.82
20-8	26.0	0.31	6.0	31.	10.4	10.5	1.77
21-1	80.	0.82	43.0	46.	17.2	5.2	1.38
21-1a	43.	0.42	18.0	66.	27.6	4.0	2.63
21-2	83.	0.96	39.0	69.	22.4	4.4	2.49

Table E-6. (cont'd)

RIV IV
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
21-2a	43.	0.42	13.0	71.	24.4	3.9	3.04
21-3	33.0	0.35	18.0	68.	30.4	3.2	2.16
21-4	80.	0.67	38.5	58.	22.8	4.5	2.27
21-5	62.	0.53	28.5	62.	24.0	4.2	2.32
21-5a	96.	0.85	46.0	56.	19.6	3.7	2.4
22-1	90.	0.78	43.5	52.	18.0	6.0	2.38
22-1a	20.5	0.17	4.0	38.	12.8	3.9	2.13
22-1b	40.	0.35	15.5	68.	24.4	5.9	2.71
22-2	35.0	0.36	11.0	47.	16.4	7.8	2.32
22-2a	-	-	-	-	-	-	-
22-3	33.0	0.36	13.0	38.	13.6	6.1	2.16
22-3a	14.8	0.19	3.0	32.	12.4	7.0	1.88
22-3b	18.4	0.25	3.0	30.	10.8	6.5	1.85
22-4	17.4	0.25	3.0	36.	12.4	6.7	1.96
22-4a	29.5	0.37	2.0	28.	10.0	10.5	1.69
22-5	60.	0.63	28.0	67.	25.2	4.5	0
22-6	57.	0.59	24.0	29.	10.0	10.6	1.33
22-7	44.	0.40	17.5	26.	8.8	8.1	1.44
23-1	48.	0.49	20.0	60.	27.6	1.9	3.21
23-2	39.0	0.51	8.5	52.	19.6	3.7	2.18
23-3	53.	0.57	20.5	63.	22.0	3.4	3.18
23-4	96.	0.96	44.0	62.	21.6	4.2	2.71
23-5	210.	2.26	102.0	69.	23.2	5.2	2.82
24-1	21.5	0.19	4.5	92.	29.6	2.1	4.66
24-2	44.	0.42	12.5	52.	18.8	4.8	2.97
24-3	-	-	-	-	-	-	-
24-4	42.	0.42	17.0	59.	21.6	5.5	1.11
24-5	56.	0.51	28.5	60.	21.2	4.0	2.91
25-1	23.0	0.32	5.5	74.	23.2	3.8	2.83
25-2	33.0	0.42	17.5	46.	16.8	7.8	2.55
25-3	36.0	0.37	12.5	57.	22.0	5.1	2.94

Table E-6. (cont'd)**RIV IV**
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
26-1	66.	0.72	20.5	105.	38.4	2.5	5.21
26-2	18.0	0.22	5.5	63.	24.4	2.6	4.63
26-2a	17.9	0.26	4.5	58.	23.6	3.5	3.94
26-3	24.0	0.35	5.5	55.	21.2	4.7	3.33
26-4	25.3	0.40	7.5	59.	22.8	3.5	3.66
26-5	30.0	0.43	11.0	64.	28.0	3.1	3.55
26-6	34.0	0.29	18.0	64.	25.2	4.2	3.63
27-1	11.3	0.11	3.0	68.	22.0	3.6	3.55
27-1a	15.0	0.17	5.0	41.	16.8	7.5	2.94
27-1b	19.5	0.22	6.0	43.	15.2	11.8	2.25
27-2	7.4	0.13	3.0	65.	24.4	1.1	4.66
27-3	24.0	0.28	9.5	63.	20.4	7.6	
27-4	17.9	0.23	5.5	47.	17.6	9.7	2.55
27-4a	21.2	0.38	7.0	57.	20.4	6.9	2.88
27-4b	20.7	0.30	5.0	48.	16.4	6.4	3.02
27-5	20.5	0.25	5.5	48.	19.6	7.6	2.33
27-6	38.0	0.40	16.5	77.	30.4	4.7	2.74
27-6a	36.0	0.38	15.5	61.	22.4	3.5	3.85
27-7	78.	0.57	38.5	66.	26.0	5.3	2.72
27-8	86.	0.62	44.5	68.	26.8	5.6	2.99
27-8a	164.	1.35	95.5	57.	18.4	3.9	2.74
27-8b	62.	0.37	35.5	57.	19.6	4.0	2.85
27-9	98.	0.62	53.0	52.	19.2	5.7	2.47
27-10	35.0	0.22	18.0	41.	15.6	6.9	2.77
27-11	68.	0.94	27.5	65.	20.4	5.1	2.8
27-12	138.	1.49	80.5	66.	26.8	5.7	2.05
27-13	99.	0.83	51.0	52.	17.6	6.6	2.44
28-1	23.2	0.22	8.5	42.	15.2	11.6	2.16
28-2	-	-	-	-	-	-	-
28-3	10.9	0.15	2.0	24.	8.8	9.5	1.25

Table E-6. (cont'd)**RIV IV**
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
28-4	15.7	0.23	4.5	24.	8.8	9.7	1.33
28-5	9.4	0.18	1.5	44.	12.4	7.7	1.61
28-6	13.1	0.23	3.0	47.	13.6	8.5	1.97
28-7	12.5	0.24	3.0	42.	14.8	9.1	1.89
28-8	18.0	0.23	11.0	135.	20.4	1.8	3.58
28-9	14.5	0.21	4.0	33.	13.6	8.0	1.39
28-10	16.8	0.22	3.5	40.	12.4	9.1	1.75
28-10a	17.1	0.28	3.5	62.	21.2	6.7	2.99
28-11	18.2	0.31	5.5	43.	16.4	7.4	1.66
28-12	10.3	0.22	2.0	30.	13.6	5.2	2.19
28-12a	16.8	0.32	6.0	59.	28.0	3.6	0.92
28-14	18.8	0.36	5.5	42.	16.8	9.1	2.74
28-15	24.0	0.39	9.0	68.	22.0	6.5	2.72
28-16	27.8	0.40	12.5	79.	25.6	5.9	2.22
28-16a	18.7	0.27	6.0	42.	15.2	10.9	3.38
28-17	44.	0.53	21.5	81.	26.0	5.6	3.1
28-18	22.9	0.26	8.0	75.	24.8	4.7	3.6
28-18a	30.0	0.34	14.5	64.	22.0	5.0	3.3
29-1	8.4	0.13	2.5	0.4	4.4	5.0	1.44
29-2	5.9	0.13	1.0	23.	8.0	9.2	1.33
29-3	5.9	0.14	1.0	23.	8.8	5.1	1.22
29-3a	9.8	0.22	1.5	28.	10.8	14.2	1.94
29-3b	4.7	0.15	0.5	19.2	8.8	3.8	1.19
29-3c	14.9	0.27	2.5	25.	9.2	5.2	1.47
29-4	10.3	0.23	2.5	31.	11.2	5.8	1.66
29-4a	27.0	0.40	9.0	88.	26.8	4.5	2.88
29-4b	16.3	0.26	5.0	35.	12.4	7.8	1.66
29-4c	15.5	0.25	5.0	30.	10.0	5.9	1.58
29-5	36.0	0.47	13.0	88.	26.8	5.5	2.72

Table E-6. (cont'd)

RIV IV
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
29-6	5.6	0.11	0.5	20.0	6.8	6.9	1.11
29-7	8.5	0.22	2.0	25.	8.8	5.6	0.03
29-Philp Park	-	-	-	-	-	-	-
30-1	13.7	0.27	2.5	42.	14.8	6.6	1.72
30-2	17.0	0.30	3.5	42.	12.8	5.4	1.94
30-3	25.0	0.41	5.5	38.	13.2	8.3	1.66
30-4	32.0	0.50	13.0	51.	17.2	4.5	2
30-lake	-	-	-	-	-	-	-
31-1	26.0	0.36	3.0	72.	25.6	9.8	2.97
31-1a	28.0	0.33	3.0	74.	23.2	9.4	2.74
31-2	17.4	0.22	4.0	36.	12.4	6.1	1.69
31-3	6.7	0.11	0.5	16.8	7.2	3.5	2.56
31-4	16.0	0.24	6.5	15.2	6.8	7.5	1.25
31-4a	284.	4.05	150.0	52.	15.6	6.8	0.89
31-4b	62.	0.45	30.5	28.	6.0	9.5	2.02
31-5	34.0	0.28	15.5	42.	14.4	7.5	2.33
31-5a	53.	0.44	19.0	47.	15.6	8.1	1.89
31-5b	24.2	0.21	8.5	35.	12.4	5.6	1.66
31-6	-	-	-	-	-	-	-
31-6b	-	-	-	-	-	-	-
32-1	25.5	0.24	5.5	48.	17.6	12.2	1.61
32-1a	30.0	0.31	11.0	48.	16.4	6.3	2.3
32-1b	26.5	0.19	8.0	49.	13.6	6.3	2.3
32-2	27.2	0.28	11.5	32.	13.2	5.6	2.22
32-3	54.	0.56	26.5	40.	15.2	6.5	1.66
32-3a	91.	0.69	45.5	43.	9.6	4.9	1.61
32-4	56.	0.53	30.5	44.	8.4	11.2	1.86
32-5	-	-	-	-	-	-	-
32-6	-	-	-	-	-	-	-

Table E-7. River Chemistry - RIV V sampling*(All concentrations in mg/L.)*

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
BLUFF	-	-	-	-	-	-	-
DTL	52.	0.41	26.9	101.	35.5	4.7	0.63
T	14.9	0.15	8	49.	12	1.9	2.62
X	52.	0.43	23.6	100.	33	5.1	1.16
1-1	-	-	-	-	-	-	-
1-1a	4.2	0.11	6.5	53.	14.5	1.1	4.09
1-2	11.4	0.17	8.1	62.	15.5	1.4	3.05
1-3	11.9	0.16	8	58.	14.5	1.4	2.7
1-3a	-	-	-	-	-	-	-
1-4	15.5	0.17	8.8	59.	14.5	1.6	2.7
1-5	-	-	-	-	-	-	-
1-5a	-	-	-	-	-	-	-
2-1	30.0	0.30	17.6	34.	9	1.4	2.04
2-2	39.3	0.37	21	53.	14	2.3	2.72
2-3	36.0	0.29	17.3	69.	21	3.1	2.25
2-4	26.2	0.19	9.6	75.	20.5	5.4	3.06
3-1	32.6	0.26	14.4	80.	23.5	2.8	2.53
3-1a	20.6	0.16	7.6	64.	17.5	3.2	3.24
3-2	35.5	0.27	14.9	80.	24	2.8	2.7
3-2a	49.	0.36	17.4	94.	30	3.5	2.04
3-2b	33.0	0.30	13.9	80.	23.5	2.9	2.7
3-3	21.8	0.20	10.5	61.	16	3.3	3.48
3-lake	34.5	0.28	15	64.	17.5	3	0.53
4-1	20.8	0.19	9.8	73.	20	2.5	2.67
4-2	25.1	0.23	10.6	83.	23	3.5	1.49
4-2a	41.	0.32	15.6	93.	27	3.9	1.37
4-3	32.0	0.24	10.1	85.	25	4	2.34
5-1	7.9	0.08	4.7	42.	10.5	2.2	2.27
5-1a	8.9	0.12	3.9	48.	12.5	1.4	3.22
5-2	1.7	0.06	0.2	22.	6	0.3	0.64
5-3	8.4	0.15	3.8	41.	11	1.3	2.04

Table E-7. (cont'd)

RIV V
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
5-3a	-	-	-	-	-	-	-
5-4	56.	0.50	31.7	75.	18.5	2.5	2.51
5-5	11.5	0.13	5.1	47.	13	1.8	1.94
5-6	15.9	0.17	6.6	51.	14	2	0.88
5-7	-	-	-	-	-	-	-
5-8	-	-	-	-	-	-	-
5-lake	-	-	-	-	-	-	-
6-1	2.1	0.07	2.9	48.	14	0.4	4.31
6-2	12.1	0.19	8.3	75.	21.5	0.9	3.22
6-3	2.4	0.08	0.6	28.	7.5	0.7	2.18
6-4	-	-	-	-	-	-	-
6-4a	134.	2.49	57.3	85.	19	2	2.08
6-4b	18.5	0.22	9.2	57.	13.5	1.4	3.88
6-5	52.	0.52	25.9	53.	14.5	1.7	2.56
6-6	47.	0.49	21.8	68.	17.5	2.6	2.91
6-7	58.	0.46	20.7	99.	29	2.7	1.59
6-8	59.	0.43	22.9	90.	29.5	2.8	1.07
6-9	49.	0.33	22.7	62.	16.5	2.4	2.7
7-1a	7.3	0.07	2.9	49.	16	0.7	3.24
7-1b	23.9	0.23	10.2	60.	19.5	0.7	4.62
7-2	14.2	0.15	7.8	67.	19	2	3.17
7-3	9.1	0.11	4.7	60.	18	1	4.14
7-4	11.1	0.17	7.7	56.	17.5	0.8	3.43
7-5	26.2	0.25	14.4	68.	21	1.4	3.15
7-6	14.3	0.19	9.3	64.	17	1.8	3.46
7-7	-	-	-	-	-	1.8	3.2
7-7a	12.7	0.17	7.2	69.	20.5	1.6	3.62
8-1	-	-	-	-	-	-	-
8-2	-	-	-	-	-	-	-
8-2a	-	-	-	-	-	-	-
8-2b	-	-	-	-	-	-	-
8-3	11.7	0.18	6.4	44.	15	1.1	2.52

Table E-7. (cont'd)

RIV V
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
8-4	12.0	0.19	6.2	42.	14	1.3	2.16
8-4a	20.3	0.26	8.3	88.	25	3	2.57
8-4ab	17.9	0.22	7.4	84.	23.5	2.4	2.39
8-5	18.6	0.25	8.5	58.	18	1.6	2.54
8-6	23.0	0.27	11.3	61.	18.5	1.7	2.61
8-7	-	-	-	-	-	-	-
8-8	28.0	0.31	13.2	63.	18.5	2	2.72
8-9	29.8	0.32	12.7	66.	19.5	2.1	2.72
8-10	32.3	0.34	13.4	66.	19	2.3	2.77
9-1	36.0	0.35	13.4	102.	32	4.9	2.39
9-1a	50.	0.41	23.7	102.	32.5	5.2	1.19
9-1b	-	-	-	-	-	-	-
9-2	255.	4.73	80.5	128.	35	5.5	2.59
9-2a	42.	0.36	10.1	85.	21	3.2	2.34
9-2a'	54.	0.49	20.3	104.	26.5	3.3	2.27
9-3	68.	0.56	30	100.	33	5.1	1.35
9-3a	-	-	-	-	-	-	-
9-3a'	-	-	-	-	-	-	-
9-4	81.	0.75	28.7	102.	28	3.8	2.14
9-5	58.	0.64	26.6	91.	27	3.9	2
9-6	56.	0.58	25.5	92.	26.5	3.9	2.45
9-7	33.5	0.30	17.1	97.	30.5	4.2	3.38
10-1	21.2	0.29	6.5	58.	14.5	2.1	3.92
10-1a	18.8	0.26	4.2	71.	16.5	1.9	3.49
10-2	54.	0.60	24.5	81.	23	3.2	2.79
12-1	-	-	-	-	-	-	-
12-2	16.0	0.17	8.1	64.	0	1.3	3.4
12-3	22.0	0.26	8.7	71.	20.5	1.9	4.14
12-4	26.5	0.31	10.1	73.	20	3.1	4.46
12-5	32.0	0.35	11.3	80.	20.5	3.2	3.98

Table E-7. (cont'd)

RIV V
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
13-1	20.0	0.23	6.1	84.	21.5	3.5	3.26
13-2	32.0	0.32	10.5	86.	23	3.2	2.95
14-1	34.0	0.35	5.8	89.	23.5	4.1	1.19
14-2	48.	0.48	11.5	84.	23.5	4.1	2.3
15-1	40.	0.35	11.8	82.	22.5	4	3.4
15-2	50.	0.40	13.3	91.	25	4.4	2.36
15-3	40.	0.33	8.5	90.	27	2.6	2.5
17-1	46.	0.37	8.9	96.	26	3.3	3.02
17-2	44.	0.66	6.7	99.	26	3.3	3.11
17-3	42.	0.38	6.8	90.	24	4.7	3.42
18-1	21.8	0.19	3.8	53.	17	8.8	3.15
18-2	42.	0.38	7.6	84.	23.5	4.5	3.24
18-3	37.0	0.29	5.6	78.	24.5	3.8	3.24
19-1	29.2	0.23	7.2	79.	24.5	2.6	3.29
19-2	34.0	0.28	6.3	100.	27.5	2.6	2.95
19-3	36.5	0.29	6.6	94.	25.5	2.6	2.59
19-4	14.7	0.16	4.3	46.	13.5	3.2	3.65
20-1	27.2	0.26	10.5	68.	23.5	4.6	3.42
20-2	20.4	0.24	7.2	74.	24	3.5	3.67
20-3	30.0	0.32	14.6	66.	21.5	3.6	3.08
20-4	42.	0.41	21.9	71.	22.5	3.7	3.22
20-5	33.9	0.31	15.9	70.	23	3.6	3.02
20-6	-	-	-	-	-	-	-
20-7	33.2	0.29	6.4	82.	28.5	2	2.81
20-8	-	-	-	-	-	-	-
21-1	43.	0.36	23	47.	18	3.6	2.12
21-1a	42.	0.38	20.3	63.	23	2.5	2.09
21-2	52.	0.43	27.8	70.	21.5	3.7	3.42
21-2a	29	0.26	11	62.	21	4.2	3.47
21-3	48	0.41	21.8	93.	29.5	3.5	3.67
21-4	46	0.37	27	65.	22	3.7	2.99

Table E-7. (cont'd)

RIV V
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
21-5	45	0.38	25.2	63.	22	3.5	2.57
21-5a	42	0.36	22.2	63.	23.5	3	3.2
22-1	46	0.33	21.3	72.	22	3.9	3.42
22-1a	35	0.28	14.2	53.	15.5	5.5	3.17
22-1b	-	-	-	-	-	-	-
22-2	50	0.34	22.1	61.	18.5	6.3	3.08
22-2a	62	0.41	7.1	66.	19	5.7	4.39
22-3	40	0.33	16.4	75.	23.5	3.5	3.44
22-3a	35	0.29	6.3	85.	25	2.8	2.75
22-3b	49	0.34	13.5	91.	31.5	2.8	2.52
22-4	32.2	0.23	7.6	90.	29	2.4	3.02
22-4a	22.2	0.19	5.6	78.	26	2.6	2.45
22-5	-	-	-	-	-	-	-
22-6	-	-	-	-	-	-	-
22-7	39	0.31	14	77.	23.5	3.6	3.44
23-1	54	0.41	26.3	61.	22	1.8	2.14
23-2	31	0.36	10	55.	16.5	2.7	2.39
23-3	46	0.41	23.1	67.	20.5	2.4	3.85
23-4	56	0.45	28.9	71.	21	2.9	3.92
23-5	106	0.78	55.2	90.	29	2.9	3.33
24-1			6.7	91.	26	1.4	4.21
24-2	-	-	-	-	-	-	-
24-3	45	0.28	18	64.	18.5	2.8	3.6
24-4	40	0.30	15.4	61.	17	5	1.55
24-5	37	0.30	18.5	63.	18.5	3.4	3.13
25-1	20.2	0.22	7.9	80.	23	4.1	3.7
25-2	30.4	0.30	7.1	75.	24.5	7.2	2.83
25-3	26	0.33	12.6	71.	22	4.2	2.39
26-1	58	0.62	21.6	88.	30	2	4.34
26-2	13.5	0.17	6.8	64.	19.5	1.7	2.98
26-2a	17.8	0.22	8	69.	24.5	1.4	3.47

Table E-7. (cont'd)**RIV V***(All concentrations in mg/L.)*

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
26-3	25	0.30	9.4	66.	21.5	3.2	3.06
26-4	27	0.31	10.9	82.	25.5	2.2	4.67
26-5	25.9	0.29	12.6	66.	22	2.7	2.27
26-6	24	0.32	13.1	71.	22.5	2.8	3.39
27-1	11	0.15	4.3	79.	22	2.2	4.36
27-1a	18.2	0.23	7.9	67.	21.5	3.7	3.9
27-1b	35.1	0.36	11.6	102.	28.5	6.3	4.67
27-2	8.9	0.12	4.3	61.	18.5	1	3.49
27-3	22	0.24	9.2	73.	20	4.4	3.42
27-4	23	0.25	8.5	72.	20.5	4.6	4.82
27-4a	19.5	0.23	6.8	68.	18.5	5.1	4.98
27-4b	18	0.25	5.6	51.	14	5	3.7
27-5	18.9	0.24	6	54.	14.5	5.6	4.16
27-6	30	0.33	13.4	70.	21.5	3.3	1.86
27-6a	32	0.36	16.4	59.	17	3.1	3.6
27-7	39	0.33	18.8	66.	20	3.7	2.29
27-8	40	0.33	19.8	70.	21.5	3.5	2.06
27-8a	104	0.82	61.1	71.	18	3.2	3.57
27-8b	37	0.27	24.6	75.	20	2.9	3.54
27-9	50	0.35	25.8	77.	20.5	3.6	4.18
27-10	42	0.30	18.6	79.	24	4.9	4.77
27-11	61	0.52	29.6	80.	20	3.4	4.13
27-12	-	-	-	-	-	-	-
27-13	-	-	-	-	-	-	-
28-1	36	0.28	8.8	96.	26	5.3	3.6
28-2	48	0.35	9.3	106.	31	4.1	3.44
28-3	25	0.21	6.1	98.	23.5	4.9	3.6
28-4	38	0.30	9.8	109.	29.5	5.8	3.62
28-5	22	0.18	4.4	106.	20	4.4	2.75
28-6	23.5	0.21	6.6	98.	19	4.5	2.88
28-7	11.3	0.11	2.3	63.	13.5	3.5	2.93

Table E-7. (cont'd)

RIV V
(All concentrations in mg/L.)

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
28-8	31	0.27	8.1	99.	25.5	5.6	3.67
28-9	31.5	0.14	2.8	62.	13	4.8	3.37
28-10	22.5	0.23	6	84.	21	4.2	3.83
28-10a	18.2	0.19	6.6	75.	20	3.8	3.24
28-11	-	-	-	-	-	-	-
28-12	-	-	-	-	-	-	-
28-12a	12.5	0.21	6.3	50.	18	3.5	0.99
28-14	17.1	0.23	6.6	61.	17.5	3.4	3.39
28-15	18.9	0.24	5.6	75.	17.5	4.7	3.57
28-16	-	-	-	-	-	-	-
28-16a	17.5	0.31	10	82.	21	5.1	3.65
28-17	-	-	-	-	-	-	-
28-18	22.8	0.24	9.5	72.	17	3.4	3.16
28-18a	23.1	0.25	12.4	67.	16.5	3.4	4.23
29-1	30.5	0.31	5.9	98.	25	4.8	3.65
29-2	31	0.28	5.3	104.	26	3.4	2.85
29-3	26.5	0.25	5.6	99.	20	3.8	2.88
29-3a	38	0.32	6.8	96.	22.5	5.1	3.03
29-3b	48	0.38	6.3	107.	26	1.8	2.27
29-3c	-	-	-	-	-	-	-
29-4	44	0.33	7.1	106.	26.5	2.9	2.88
29-4a	34	0.26	7.4	102.	24	4.9	3.16
29-4b	56	0.40	10.1	135.	31.5	3.9	2.24
29-4c	74	0.52	11.1	139.	38.5	2.7	1.78
29-5	36	0.25	8.2	101.	23	4.9	3.11
29-6	-	-	-	-	-	-	-
29-7	33	0.22	9.7	103.	19.5	4	2.37
29-lake	14.4	0.13	6.8	37.	9	1.6	0.4
30-1	30.2	0.25	4.9	91.	21	4.7	2.93
30-2	-	-	-	-	-	-	-
30-3	42	0.33	7.1	102.	25	3.8	3.01

Table E-7. (cont'd)**RIV V***(All concentrations in mg/L.)*

SITE	Cl	Br	Na	Ca	Mg	K	SiO₂
30-4	48.	0.35	10.5	108.	25.5	3.9	2.9
30-lake	36.	0.27	9.2	62.	18	3.4	0.04
31-1	61.	0.42	2.2	97.	24.5	1.6	4.2
31-1a	40.	0.29	5.8	102.	28	2.2	3.9
31-2	48.	0.35	7.1	110.	32	2.3	2.4
31-3	-	-	-	-	-	-	-
31-4	-	-	-	-	-	-	-
31-4a	80.	0.51	46.8	121.	30	4.2	4.4
31-4b	-	-	-	-	-	-	-
31-5	49.	0.34	9.3	107.	26	4.9	3.4
31-5a	-	-	-	-	-	-	-
31-5b	-	-	-	-	-	-	-
31-6	48.	0.31	9.2	106.	25.5	4.8	3.3
31-6b	-	-	-	-	-	-	-
32-1	63.	0.41	6.5	117.	33.5	4.0	2.4
32-1a	58.	0.39	11.9	108.	29	1.7	2.1
32-1b	56.	0.40	9.8	113.	31	2.3	2.7
32-2	-	-	-	-	-	-	-
32-3	-	-	-	-	-	-	-
32-3a	-	-	-	-	-	-	-
32-4	-	-	-	-	-	-	-
32-5	28.	0.19	11.7	54.	13	5.0	3.1
32-6	-	-	-	-	-	-	-

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