NATIONAL WATER RESEARCH INSTITUTE

INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX

INTERIM REPORT ON THE EFFECTS OF ATMOSPHERIC DEPOSITION OF METALS FROM THE SUDBURY SMELTERS ON AQUATIC BENTHIC ECOSYSTEMS

U. Borgmann, T.A. Jackson, T.B. Reynoldson and F. Rosa

INTERIM REPORT ON THE EFFECTS OF ATMOSPHERIC DEPOSITION OF METALS FROM THE SUDBURY SMELTERS ON AQUATIC BENTHIC ECOSYSTEMS

U. Borgmann, T.A. Jackson, T.B. Reynoldson and F. Rosa

Aquatic Ecosystem Restoration Branch
National Water Research Institute
Environment Canada
BURLINGTON, Ontario L7R 4A6

MANAGEMENT PERSPECTIVE

This is part of Environment Canada's Action Plan (Conserving Canada's Ecosystems). It deals with the issue of the effects of atmospheric transport of metals from smelters: does this impact the biota; how can this be quantified; how far are the effects felt (local, regional or trans-boundary); and can the effects be clearly demonstrated to be caused by specific metals?

This report summarizes data collected to date as part of an ongoing study. The degree of contamination from the smelters at Sudbury, including sediment enrichment factors for various metals and how far this contamination extends, has been quantified. Biological impact in the form of absence of selected sensitive benthic invertebrates in lakes near Sudbury, and severe toxicity of sediments collected from these lakes, has also been demonstrated. Information on the geochemical form of metals, and how these correlate with sediment toxicity, has also been obtained.

Direct quantification of the bioavailability of metals will be determined by measuring metal accumulation in benthic invertebrates exposed to sediments collected from lakes near Sudbury. Studies are also planned in which non-toxic sediments are spiked with metals to determine the relationships between metal bioaccumulation and toxicity under conditions where the toxic agent is known. Critical body concentrations at which toxicity first appears in the spiked sediment experiments will be compared to metal accumulation following exposure to Sudbury area sediments in order to identify the toxic agent. This should establish a direct cause and effect relationship between biological impacts and the metals responsible for those impacts. The effects of metal contamination on indigenous microbial communities in sediments will also be examined. This may shed light on the processes and feedback cycles involved in the degradation of benthic communities by metal poisoning.

N.B. The Management Perspective is being translated into French.

EXECUTIVE SUMMARY

During the summer of 1996, a collaborative study by members of the Sediment Assessment and Restoratoin Project, National Water Research Institute (NWRI) was initiated in order to assess the effects of atmospheric transport of metals from the smelters at Sudbury. The objective of the study was to determine whether effects of metals on aquatic ecosystems could be demonstrated, whether such effects could clearly be linked to specific metals or metal species, and to determine the spatial extent of such effects and the roles of metal speciation and bioavaliability and related environmental factors. Twelve lakes were selected; four contaminated lakes in the immediate vicinity of Sudbury (<13 km from the smelter stacks at Copper Cliff); four reference lakes at considerable distances (94-154 km) from Sudbury; and four lakes at intermediate distances (32-52 km). Two sampling sites were selected in each lake, the deepest location and a site at a depth of 10 m if the deep site was greater than 10 m. In order to address specifically the issue of metal effects as distinct from acidification, only lakes with circumneutral pH (6.7-7.7 in the surface waters) were selected, and the study focused on sediments and benthic invertebrates. Metals are readily sorbed and accumulated by particulate matter, with the result that metal concentrations in sediments are much higher than those in the water column. Consequently, benthic invertebrates living in these sediments should be among the most sensitive indicators of adverse metal effects in lakes. This report summarizes data collected so far, in the course of this study. The investigation is continuing, and the conclusions are provisional pending completion of the study.

All of the lakes studied were thermally stratified, and probably at the peak of stable stratification at the time of sampling. All the lakes had a similar and fairly constant conductivity of 35-50 μS/cm, except for three of the lakes closest to Copper Cliff which had a conductivity of 300 μS/cm. The concentrations of different forms of carbon, nitrogen and phosphorus in the bottom water showed no distinct differences among the lakes sampled, with the possible exception of total Kjeldahl nitrogen. Strong, and statistically significant, decreasing trends in the concentrations of sulphate (5-fold), nickel (100-fold) and copper (15-fold) were observed in the deep waters as a function of distance from Sudbury. A statistically significant correlation between water and sediment concentrations of copper and nickel was also observed. This

suggests that de-sorption and molecular diffusion from the bottom sediments may be the main processes controlling the concentrations of soluble metal species in the water column.

A well defined sediment profile, with higher concentrations in the surface sediments (<5 cm) and lower concentrations in the deep (>10 cm) was observed for several metals (Cd, Co, Cu, Ni, Zn) in the deep stations in the lakes close to Sudbury. These profiles were much less pronounced in the reference lakes. A strong lead profile was seen in every lake, regardless of distance from Copper Cliff. Chromium concentrations did not vary with depth. Loss on ignition, total carbon, iron and manganese often varied only moderately with depth, although some lakes did have strong profiles for iron and especially manganese. The enrichment factor (EF = surface (0-3 cm)/deep (16-20 cm) sediment concentration) for several metals demonstrated an exponential drop with distance from Sudbury, approaching a value of 1.0 near the reference lakes. Maximum enrichment factors (EF at 0 km from Copper Cliff) were about 40-fold for Cd, Cu and Ni, 7-fold for Co, and 3-fold for Zn. The distance to a 50% drop in excess (surface-deep) metal in the surface sediments was about 15 km for Cu, Ni and Co, 25 km for Cd, and about 50 km for Zn.

Sampling of *in situ* benthic invertebrates revealed phantom midges (*Chaoborus* spp), chironomids (including *Chironomus* spp.), and oligochaetes in many of the lakes, regardless of the distance from Copper Cliff. However, amphipods (*Diporeia hoyi*), bivalves (fingernail clams), and two chironimids (*Micropsectra* spp. and *Tanytarsus* spp.) were notably absent from the lakes closest to Sudbury. The response of the *in situ* community-to-site characteristics was assessed using species level ordination analysis. There is a possible relationship between both Ni concentration and total metal concentration and abundance, taxa, and the ordination axes. However, there is considerable variation in the reference sites. Ordination of 19 taxa was used to try and discriminate response patterns in the community. There may be effects at the community level, but when analyzed at the species level they are no greater than those associated with normal variation. The variation among the reference lakes makes discrimination of community level effects difficult. There appear to be two major response gradients; one associated with depth and depth related variables (e.g., temperature, particle size), and a second related to metal concentration.

Chronic toxicity tests, with sediments collected from the study sites, revealed no clear relationship between survival or growth of *Chironomus riparius* and distance from Copper Cliff. This is consistent with the presence of *Chironomus* sp. in benthos samples from lakes near Sudbury. However, survival and growth of mayflies (*Hexagenia* sp.) and amphipods (*Hyalella azteca*) in sediments collected from lakes within 12 km of Copper Cliff were substantially poorer than in intermediate and reference lakes. Complete mortality was observed for *Hyalella* exposed to sediments from three of the six sites near Sudbury. This is consistent with the absence of amphipods in benthos samples collected from these lakes. Reproduction of oligochaetes (*Tubifex tubifex*) was also lower in the Sudbury area sediments, although effects were less dramatic than for mayflies or amphipods. Sediment toxicity to *Hexagenia* and *Hyalella* correlated closely with the measured Ni in the overlying water during the toxicity test, with one exception: *Hexagenia* growth, where positive, was related to loss on ignition (possibly related to food quality). Using observed relationships between water and Ni in the sediment, and Ni in the sediment and distance from Copper Cliff, it is possible to compute predicted mean *Hyalella* mortality rates as a function of distance from Copper Cliff. The predicted distance to a mean mortality of 50% in a four-week toxicity test, relative to the reference lakes, is 25 km, 25% mortality is predicted at 36 km, and 10% at 49 km. However, these predicted mortality rates must be interpreted with caution, because they are based on extrapolation beyond the range over which precise data are available.

Sequential extraction of sediments with solvents ranging from mild to rigorous (CaCl$_2$, NaAc/HAc, NH$_2$OH•HCl/HNO$_3$, hot H$_2$O$_2$/NH$_4$acetate/HNO$_3$, and citrate/dithionite solutions, in that order) showed that most of the extractable Cu and Ni are strongly bound to organic matter and possibly sulfide, whereas little Cu or Ni is bound to Fe and Mn oxides and oxyhydroxides. Small but measurable quantities of weakly sorbed, exchangeable (CaCl$_2$-extractable) Cu and Ni (presumably the most readily bioavailable species) are also present. Concentrations of most solvent-extractable Cu and Ni species in the sediments, as well as Cu and Ni levels in the pore water, decline exponentially with distance from Sudbury, levelling off over distances on the order of ~50-100 km. However, the percentages of weakly sorbed, exchangeable Cu and Ni species in the total solvent-extractable Cu and Ni pools increase progressively with distance from the smelter. The survival of *Hyalella* tended to decrease with an increase in total solvent-extractable Cu and Ni in sediments. This relationship was most evident at the 10-meter sites, but was largely

masked unless the survival data were normalized with respect to lake water hardness. The toxicity data for *Hexagenia* larvae also correlated with extractable Cu and Ni. Survival of *Chironomus* showed a "V" shaped pattern when plotted against the sum of solvent extractable Cu and Ni, but only for the deep stations. The ratio of large (>500 μm) to small (<500 μm) *Tubifex tubifex* young correlated with extractable Cu and Ni, but was also significantly related to spectral properties of sedimentary humic matter, implying interrelations between bioavailability of metals and characteristics of the humic matter. The total production of young by *T. tubifex* also correlated, to some extent, with extractable Cu and Ni, but the toxic effect may have been ameliorated by sulfide.

The work completed to date clearly demonstrates the level of contamination, especially by Cu and Ni, in the lakes selected for this study, confirms that contamination is recent (in the surface and not in deeper and older sediments), and quantifies the magnitude of enrichment and the rate at which this contamination decreases with distance from Sudbury. Furthermore, results of both *in situ* benthic invertebrate community structure and sediment toxicity tests suggest that sediments in lakes near Sudbury are less able to support a number of sensitive species, including amphipods, bivalves and mayflies. However, further research is needed to quantify the bioavailability of metals to the biota. Comparison of water and sediment concentrations, and comparison of $CaCl_2$-extractable and total extractable metals, suggests that, while total bioavailable Cu and Ni are most likely higher in lakes near Sudbury, bioavailability is not directly proportional to total metal in the sediments. Direct estimates of bioavailable metal through measurement of the amount of metal actually accumulated in the tissues of benthic organisms still need to be made. Additional research is also required to clearly identify the toxic agent(s) in Sudbury area sediments. A number of toxicity measures correlate with Ni and Cu in water and sediments, but correlations do not prove cause and effect. Studies are needed with metal-spiked sediments to obtain relationships between metal bioaccumulation and toxicity under conditions where the toxic agent is known. Comparison of the critical body concentrations at which toxicity first appears with metal accumulation following exposure to Sudbury area sediments may help identify the toxic agent.

N.B. The Executive Summary is being translated into French.

TABLE OF CONTENTS

1. INTRODUCTION

The ore mined at Sudbury, Northern Ontario is an important source of nickel and copper. Minor quantities of palladium, platinum, gold, silver, selenium, and tellurium have been extracted from it as well (Lindgren, 1933; Bateman, 1950). Thus, the mining and smelting operations conducted by the INCO and Falconbridge companies at Sudbury are of considerable economic significance to Canada. The smelters, however, are major regional sources of air pollution, whose effects on surrounding terrestrial and aquatic ecosystems is a cause for concern (Anonymous, 1978; Chan *et al.*, 1983). The principal point source of pollution is the INCO smelter, which is vented by a tall (381 m) "superstack." The Falconbridge smelter, with its shorter (93 m) chimney, could have a disproportionately large local effect, but the INCO smelter presumably has the dominant effect over relatively long distances as well as the greater total effect. Analysis of particulate matter and gases discharged by the INCO smelter in 1996 showed that the smelter emits particles containing a wide range of heavy metals - chiefly copper, nickel, and palladium accompanied by minor amounts of many other elements - which are mainly in the form of oxides and sulphates (T.C. Burnett, verbal communication), along with vapour consisting mainly of SO_2 with lesser quantities of H_2SO_4 and nitrogen oxides (unpublished survey data from INCO; T.C. Burnett, personal communication). The principal heavy metal in the particulate fraction of the 1996 emissions was copper (Cu), whose mole concentration exceeded that of nickel (Ni), the second most abundant metal, by a factor of 4.30. Owing to the SO_2, H_2SO_4, and nitrogen oxides in the smelter emissions, acidification as well as heavy metal contamination is a significant issue here. Any comprehensive assessment of toxic effects of the emissions must take SO_2 and other components of the vapour phase as well as the heavy metals into account (Linzon, 1958; Dreisinger and McGovern, 1969, 1970; McGovern and Balsillie, 1975; Anonymous, 1978).

During the summer of 1996, a collaborative study by members of the Sediment Assessment and Restoration Project of the Aquatic Ecosystem Restoration Branch of the National Water Research Institute (NWRI), was initiated in order to address the issue of atmospheric transport of metals from smelters. The objective of the study was to determine if biological effects on aquatic ecosystems could be demonstrated; if such effects could clearly be linked to specific metals; and to determine the spacial extent of such effects. The study area chosen was Sudbury, because of

its long history of metal mining and smelting and because of the proximity of this site to NWRI. This report summarizes data collected so far as part of this study, and includes appendices of chemical and physical data at the study sites. This study is continuing, and the conclusions are not final. A more detailed interpretation of the data must await additional measurements (e.g., metal bioavailability).

An extensive literature base already exists on environmental research conducted in the Sudbury region (e.g., Gunn, 1995). Much of this research, however, has been focused on the effects of acidification, and most of the emphasis in biological studies has been on plankton and fish. Metals are known to adsorb onto particulate matter and then settle into the sediments. Metal concentrations in sediments are, therefore, much higher than those in the water column. Consequently, it might be expected that benthic invertebrates living in these sediments should be among the best indicators of adverse metal effects in lakes. However, relatively little research on benthos and/or sediment toxicity has been reported in the Sudbury area.

In order to specifically address the issue of metal effects, rather than acidification, only survey lakes with circumneutral pH were selected, and the study focused on sediment and benthic invertebrates. Lakes were selected from an inventory of lakes and accompanying pH and water chemistry data provided by W. Keller (Ontario Ministry of Northern Development and Mines) and sampled between August 19 and 26, 1996 with the Department of Fisheries and Oceans launch Petrel. Twelve lakes were selected, four potentially impacted lakes in the immediate Sudbury area (<13 km from the smelter stacks at Copper Cliff), four reference lakes at considerable distances (94-154 km) from Sudbury, and four lakes at intermediate distance (32-52 km, Table 1.1, Figure 1.1). Two sampling depths were selected in each lake, the deepest location (site codes ending in D), and a site at 10 m depth if the deep site was greater than 10 m (site codes ending in 10). Only a single (deep) site was chosen for Ramsey Lake. This lake is within the City of Sudbury and sediment contamination by metals is not necessarily entirely due to atmospheric deposition. This site was included since it was very close to the site of emissions, known to be heavily contaminated, and might show effects even if the other lakes did not (i.e., it might serve as a positive control, if needed). All the lakes had circumneutral pH (6.7-7.7) in the surface waters, although pH in the deep water was lower (5.7-7.2, Appendix 1). In addition,

toxicity tests included controls using sediments from Hamilton Harbour or Lake Erie. These sediments had been used previously and were known to support good survival and/or growth of benthic invertebrates in the laboratory.

TABLE 1.1. Study lakes and control sediment collection sites (for toxicity tests), site codes, latitude (Lat.) and longitude (Long.), distance from the smelter stacks at Copper Cliff, and depth.

| Lake name	Site codes	Lat. (deg)	Long. (deg)	Distance (km)	Depth (m)
Sudbury Lakes:					
Ramsey	RAMD	46.4806	80.9758	6	21
McFarlane	MCF10	46.4233	80.9494	10	10
	MCFD	46.4136	80.9689		20
Raft	RAF10	46.4125	80.9406	11	10
	RAFD	46.4128	80.9514		15
Richard	RICD	46.4378	80.9167	12	9
Intermediate Lakes:					
Nepewassi	NEPD	46.3333	80.6956	32	9
Kakakiwaganda	KAK10	46.1917	80.7894	38	10
	KAKD	46.1900	80.7908		24
Trout	TRO10	46.2283	80.6408	43	10
	TROD	46.2278	80.6169		46
Lower Sturgeon	LOS10	46.1269	80.6006	52	10
	LOSD	46.1353	80.6081		46
Reference Lakes:					
Tomiko	TOM10	46.5383	79.8333	94	10
	TOMD	46.5439	79.8142		23
Restoule	RES10	46.0561	79.7953	107	10
	RESD	46.0569	79.8061		28
Nosbonsing	NOS10	46.2167	79.2228	144	10
	NOSD	46.2183	79.2181		14
Talon	TAL10	46.2964	79.0436	154	10
	TALD	46.3014	79.0647		40
Control sediment collection sites:					
Hamilton Harbour (site 1)	HH1	43.2802	79.8728	368	12
Lake Erie (site 303)	LE303	42.5639	80.0417	443	25
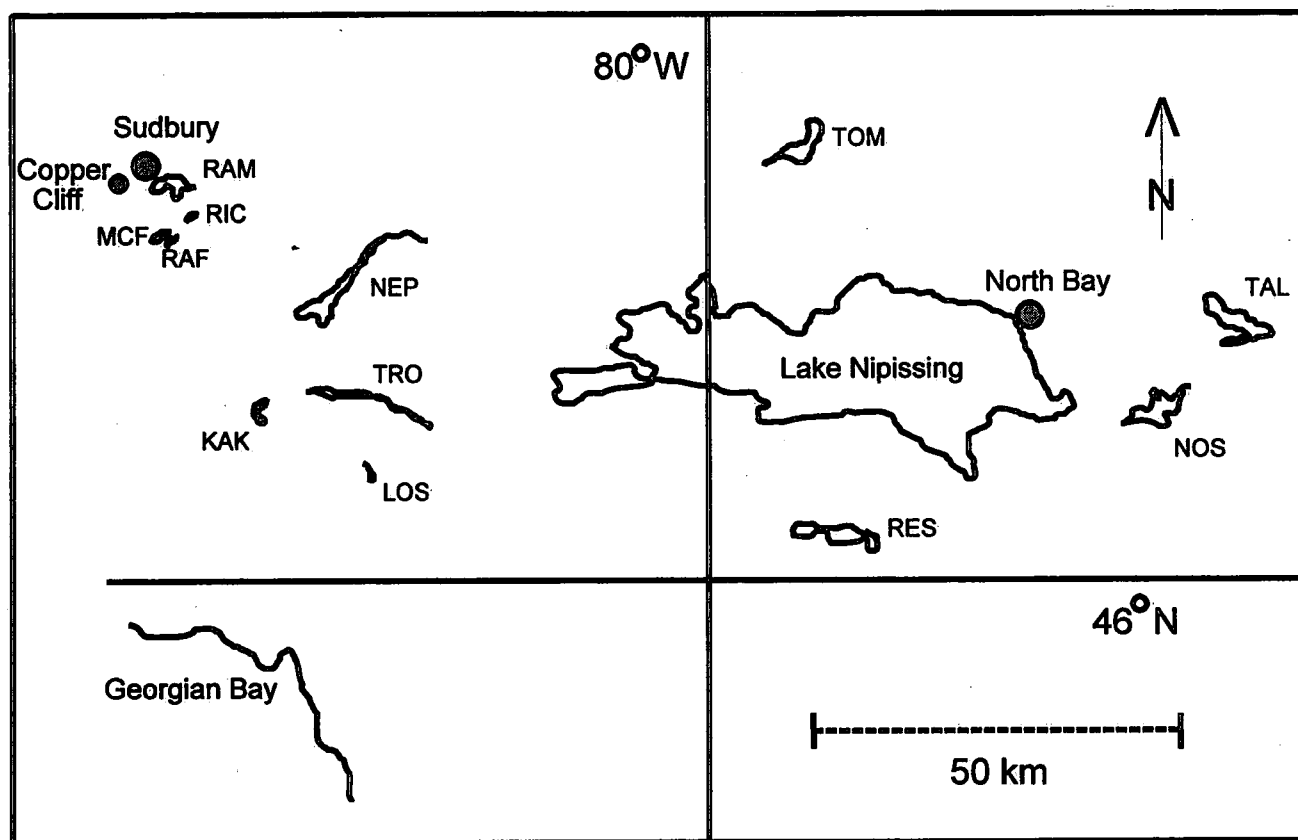
Figure 1.1. Map of the study area including the location of the smelter stack at Copper Cliff. Study lakes are indicated by a 3 letter code corresponding to lake names in Table 1.

TABLE 1.2.   Table of Notations

B-1	1 m above the bottom sediments
1 m	1 m below the water surface
Cl	chloride
COND	specific conductance
DIC	dissolved inorganic carbon
DO	dissolved oxygen
DOC	dissolved organic carbon
Epi	epilimnion
Hypo	hypolimnion
Meso	mesolimnion or thermocline
NH_3	ammonia
NO_{3+2}	nitrate plus nitrite
SiO_2	silica
SO4	sulphate
SRP	soluble reactive phosphorous
TDC	total dissolved carbon
TKN	total Kjeldahl nitrogen
Temp	temperature (°C)
TPF	total filtered phosphorous
TPUF	total phosphorous
TPP	total particulate phosphorous

2.   WATER CHEMISTRY

2.1   Sampling and Analytical Methods

In the twelve lakes sampled, a continuous surface-to-bottom depth profile of pH, specific conductance (COND), dissolved oxygen concentration (DO), and temperature was recorded by a HYDROLAB Profiling System, Model DataSonde$_R$ 3. There were a maximum of two stations in each lake: a shallow station (10 m or less) and another at the the deepest sounding (Table 1.1). Water samples for the determination of nutrient, and trace and major element concentrations were collected 1 m above the bottom sediments, using a van Dorn bottle (Rosa *et al.*, 1991).

The water samples collected for the determination of the concentrations of nutrients and major and trace elements were filtered and then divided into different subsamples. These subsamples were stabilized with various preservatives such as HNO_3 (conc.) for subsamples for the determination of trace and major elements, and H_2SO_4 for subsamples for the determination of chemical forms of phosphorus. Total filtered and unfiltered phosphorus (TPF and TPUF, respectively), and dissolved organic and inorganic carbon (DOC and DIC, respectively) were determined by the methods described by Environment Canada (1995a). The concentration of total particulate phosphorus (TPP) was calculated as the difference between that of TPUF and TPF. The concentration of total dissolved carbon (TDC) was calculated by summing that of DOC and DIC. Total nitrogen (TN) was calculated as total Kjeldahl nitrogen (TKN) plus nitrate (NO_3^-) and nitrite (NO_2^-). Total inorganic nitrogen (TIN) was calculated as ($NO_3^- + NO_2^-$) plus ammonia (NH_3^+). By this method, TIN levels may be overestimated by the contribution of NO_2^- which in most lakes is negligible compared to NO_3^-, based on the findings of Molot and Dillon (1991).

The concentrations of total and dissolved major and trace elements in the water samples (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Tl and Zn) were determined according to the methods described by Environment Canada (1995b). Prior to the determination of the elements, the water samples were filtered in the field within a few hours of collection using a Millipore glass filter apparatus with 0.45 micron (pore size) cellulose acetate filters. Filtered samples were acidified with "Ultrex" grade HNO_3 (conc.) to a final concentration of 0.4% and shipped to the laboratory. The samples were stored at 4°C prior to analysis. In addition to major and trace elements, the concentrations of SO_4^{2-}, SiO_2 and Cl^- were also determined in all collected samples.

2.2   Water Temperature

All of the lakes studied were thermally stratified and were probably at the peak of stable stratification (the greatest temperature difference between surface and bottom). The surface temperature at all the sites was fairly constant (Figure 2.1) with a mean of 22.4°C, and a standard deviation of 0.4°C, (Table 2.1). The thermal layers at the deep sites (D), and some of the shallow sites, were typical of well stratified northern lakes, with epilimnion and thermocline thickness
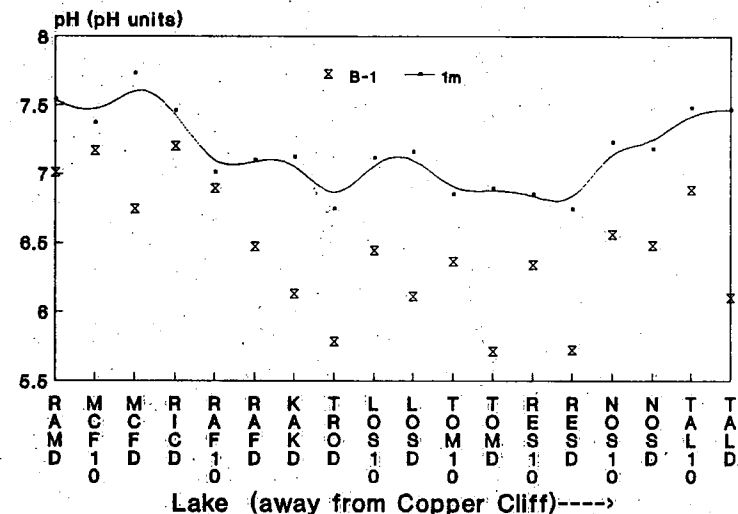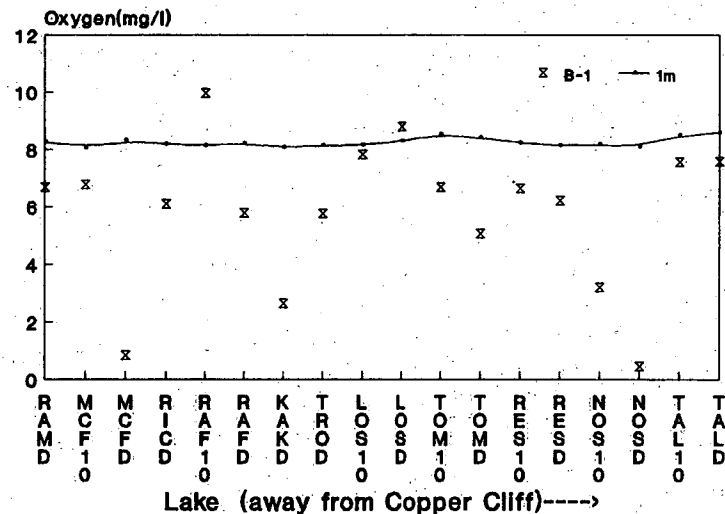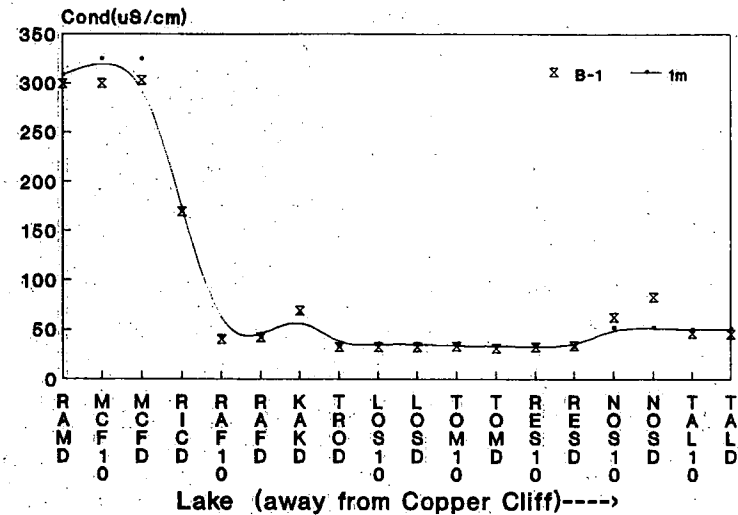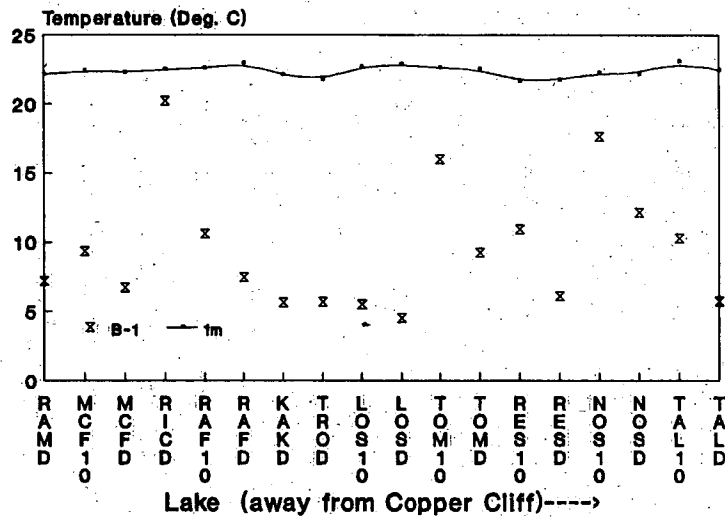
Temperature (Deg. C)

25
20
15
10
5
0

X B-1 — 1m

Lake (away from Copper Cliff)---->

R M M R R R K T L L T T R R N N T T
A C C I A A A R O O O O E E O O A A
M F F C F F K O S S M M S S S S L L
D 1 D D 1 D D D 1 D 1 D 1 D 1 D 1 D
  0   0   0   0   0   0   0

Cond(uS/cm)

350
300
250
200
150
100
50
0

X B-1 — 1m

Lake (away from Copper Cliff)---->

Oxygen(mg/l)

12
10
8
6
4
2
0

X B-1 — 1m

Lake (away from Copper Cliff)---->

pH (pH units)

8
7.5
7
6.5
6
5.5

X B-1 — 1m

Lake (away from Copper Cliff)---->

Figure 2.1. Temperature, specific conductance, dissolved oxygen concentration and pH, at one meter below surface (•) and one meter above the bottom (×), at each site in the study lakes. Data were obtained from the Hydrolab profiles (See Appendix 1).

between 4-7 m, and 2-5 m, respectively, and the remainder of the water column consisting of a cold (5-7°C) hypolimnion, with the exception of Lakes RIC and NOS which had no hypolimnion (Table 2.2). Some variability in the thermal structure is not uncommon, owing to differences in depth, different hydrodynamic conditions induced by variable solar radiation and wind forcing at the water surface, and of course the surface area and orientation of the main axis to prevailing winds, which also play an important role.

2.3   Conductance, pH, and Dissolved Oxygen Concentrations

Conductance, pH, and dissolved oxygen measurements for all the sites, at the surface (1 m) and bottom (B-1) were obtained from the Hydrolab profiles data, (Table 2.1). The surface and bottom conductivities at each site are very similar (Figure 2.1). Conductivities are highest (10-fold) in the four lakes closest to Copper Cliff with the exception of Raft Lake; all the other lakes, including Raft, have a fairly constant conductivity of 35-50 μS/cm. Surface oxygen concentrations and pH values fall in the ranges 8.0-9.0 mg/L, and 7.0-7.5, respectively. The lowest oxygen concentrations (<1.0 mg/L)in the bottom water, were found at the deep site of lakes MCF and NOS, (Table 2.2). The depth-concentration data collected with the Hydrolab Profiling System are reported in Appendix 1. The conductivity showed less variability between the surface (1 m) and 1 m above the bottom (B-1) than did oxygen and pH (Figure 2.1).

2.4   Nutrients and Major Ions

The concentrations of different forms of carbon, nitrogen, and phosphorus in the bottom water show no distinct differences among the lakes sampled (Figure 2.2), with the possible exception of TKN, which seems to decrease with increasing distance from Copper Cliff. The range of total phosphorus concentrations in the bottom waters were 0.007-0.029 mg/L (Table 2.3). These concentrations are much higher than those found in nutrient limited central Ontario lakes (less than 0.01 mg/L) according to Molot and Dillon (1991). The concentrations of the different
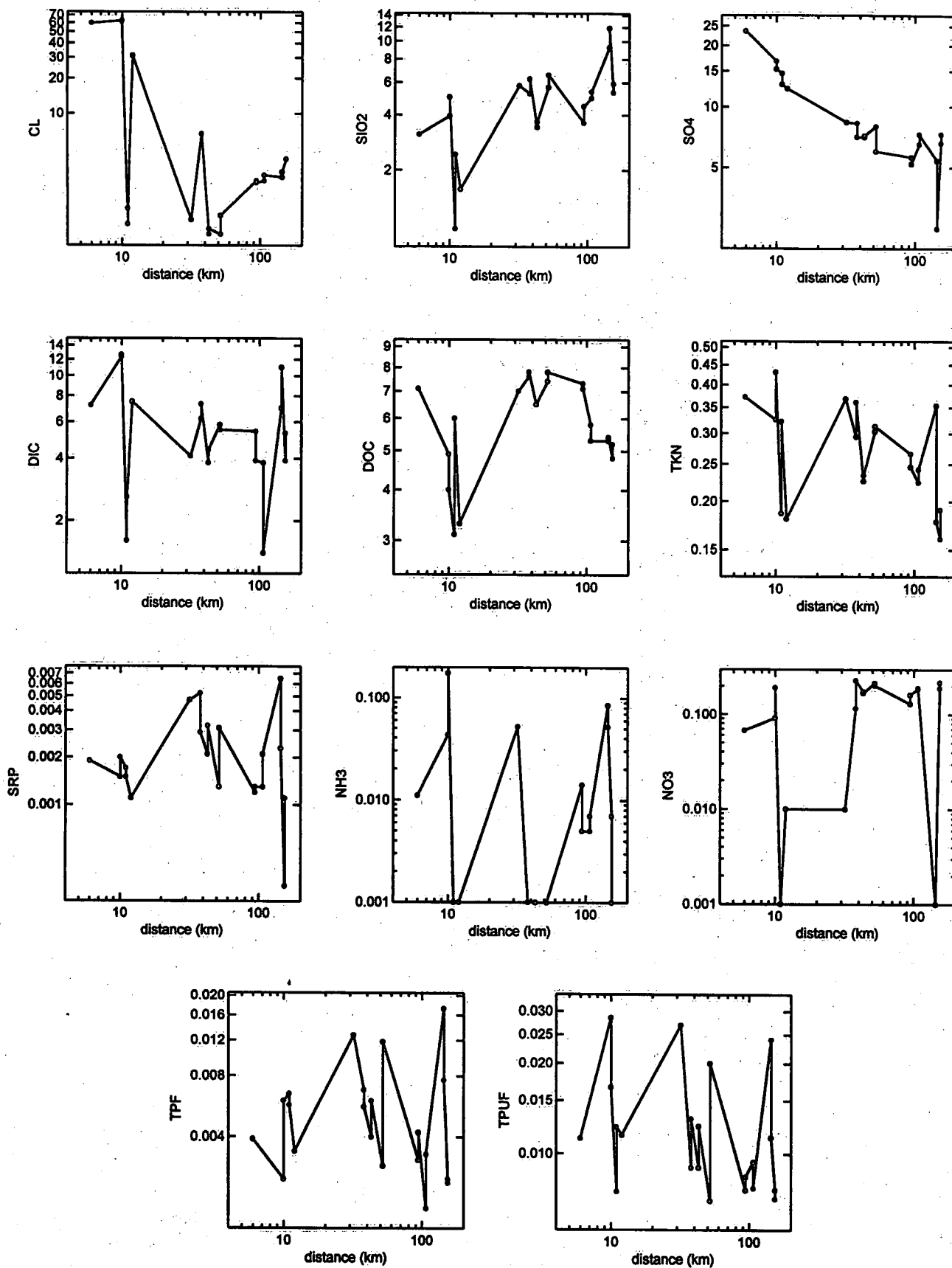
Figure 2.2. Concentration of major ions and nutrients as a function of distance from Copper Cliff. See Table 2.3 for details.

TABLE 2.1. Temperature, pH, conductivity and dissolved oxygen (percent saturation and mg/L) at each site and distance from Copper Cliff.

Lake/site	Distance (km)	Temp (°C)	pH	Cond (μS/cm)	Sat (%)	DO (mg/L)
Summary data, 1 meter above bottom						
RAMD	6	7.2	7.01	299	57	6.69
MCF10	10	9.3	7.17	300	61	6.76
MCFD	10	6.7	6.74	303	7	0.83
RAF10	11	10.6	6.89	40	92	9.96
RAFD	11	7.5	6.47	42	50	5.78
RICD	12	20.2	7.20	169	70	6.09
KAKD	38	5.6	6.13	69	22	2.62
TROD	43	5.7	5.78	32	47	5.76
LOS10	52	5.5	6.44	32	64	7.83
LOSD	52	4.5	6.11	32	70	8.79
TOM10	94	16.0	6.36	33	70	6.67
TOMD	94	9.2	5.71	31	46	5.07
RES10	107	10.9	6.34	32	62	6.64
RESD	107	6.1	5.72	33	52	6.20
NOS10	144	17.6	6.56	62	35	3.20
NOSD	144	12.2	6.48	82	5	0.46
TAL10	154	10.3	6.88	46	70	7.56
TALD	154	5.7	6.10	45	62	7.57
Mean		9.5	6.45	93	52	5.80
SD		4.4	0.46	98	22	2.48
Summary data, 1 meter below surface						
RAMD	6	22.2	7.54	308	98	8.27
MCF10	10	22.4	7.37	325	96	8.06
MCFD	10	22.2	7.73	325	99	8.32
RAF10	11	22.6	7.01	42	97	8.15
RAFD	11	23.0	7.10	42	99	8.21
RICD	12	21.7	6.74	33	96	8.14
KAKD	38	22.1	7.12	66	96	8.07
TROD	43	22.5	6.89	34	101	8.42
LOS10	52	22.7	7.11	35	98	8.16
LOSD	52	22.9	7.16	35	100	8.30
TOM10	94	22.5	7.47	51	103	8.60
TOMD	94	22.6	6.85	34	102	8.52
RES10	107	21.7	6.85	33	97	8.24
RESD	107	21.8	6.74	33	96	8.14
NOS10	144	22.2	7.23	52	97	8.18
NOSD	144	22.2	7.18	52	96	8.10
TAL10	154	22.5	7.46	170	98	8.19
TALD	154	23.1	7.48	50	103	8.50
Mean		22.4	7.17	95	98	8.25
SD		0.4	0.28	105	2	0.16

ERRATA: The data for RICD, TROD, TOM10, TOMD, TAL10 and TALD at 1 meter below the surface have been inadvertently exchanged in Table 2.1. The correct values are given below.

Table 2.1. Temperature, pH, conductivity and dissolved oxygen (percent saturation and mg/L) at each site and distance from Copper Cliff.

| Lake/site	Distance (km)	Temp (°C)	pH	Cond (μS/cm)	Sat (%)	DO (mg/L)
Summary data, 1 meter above bottom						
RAMD	6	7.2	7.01	299	57	6.69
MCF10	10	9.3	7.17	300	61	6.76
MCFD	10	6.7	6.74	303	7	0.83
RAF10	11	10.6	6.89	40	92	9.96
RAFD	11	7.5	6.47	42	50	5.78
RICD	12	20.2	7.20	169	70	6.09
KAKD	38	5.6	6.13	69	22	2.62
TROD	43	5.7	5.78	32	47	5.76
LOS10	52	5.5	6.44	32	64	7.83
LOSD	52	4.5	6.11	32	70	8.79
TOM10	94	16.0	6.36	33	70	6.67
TOMD	94	9.2	5.71	31	46	5.07
RES10	107	10.9	6.34	32	62	6.64
RESD	107	6.1	5.72	33	52	6.20
NOS10	144	17.6	6.56	62	35	3.20
NOSD	144	12.2	6.48	82	5	0.46
TAL10	154	10.3	6.88	46	70	7.56
TALD	154	5.7	6.10	45	62	7.57
Mean		9.5	6.45	93	52	5.80
SD		4.4	0.46	98	22	2.48
Summary data, 1 meter below surface						
RAMD	6	22.2	7.54	308	98	8.27
MCF10	10	22.4	7.37	325	96	8.06
MCFD	10	22.2	7.73	325	99	8.32
RAF10	11	22.6	7.01	42	97	8.15
RAFD	11	23.0	7.10	42	99	8.21
RICD	12	22.5	7.46	170	98	8.19
KAKD	38	22.1	7.12	66	96	8.07
TROD	43	23.2	7.06	33	101	8.31
LOS10	52	22.7	7.11	35	98	8.16
LOSD	52	22.9	7.16	35	100	8.30
TOM10	94	22.6	6.85	34	102	8.52
TOMD	94	22.5	6.89	34	101	8.42
RES10	107	21.7	6.85	33	97	8.24
RESD	107	21.8	6.74	33	96	8.14
NOS10	144	22.2	7.23	52	97	8.18
NOSD	144	22.2	7.18	52	96	8.10
TAL10	154	23.1	7.48	50	103	8.50
TALD	154	22.5	7.47	51	103	8.60
Mean		22.5	7.19	95	98	8.26
SD		0.4	0.27	105	2	0.15
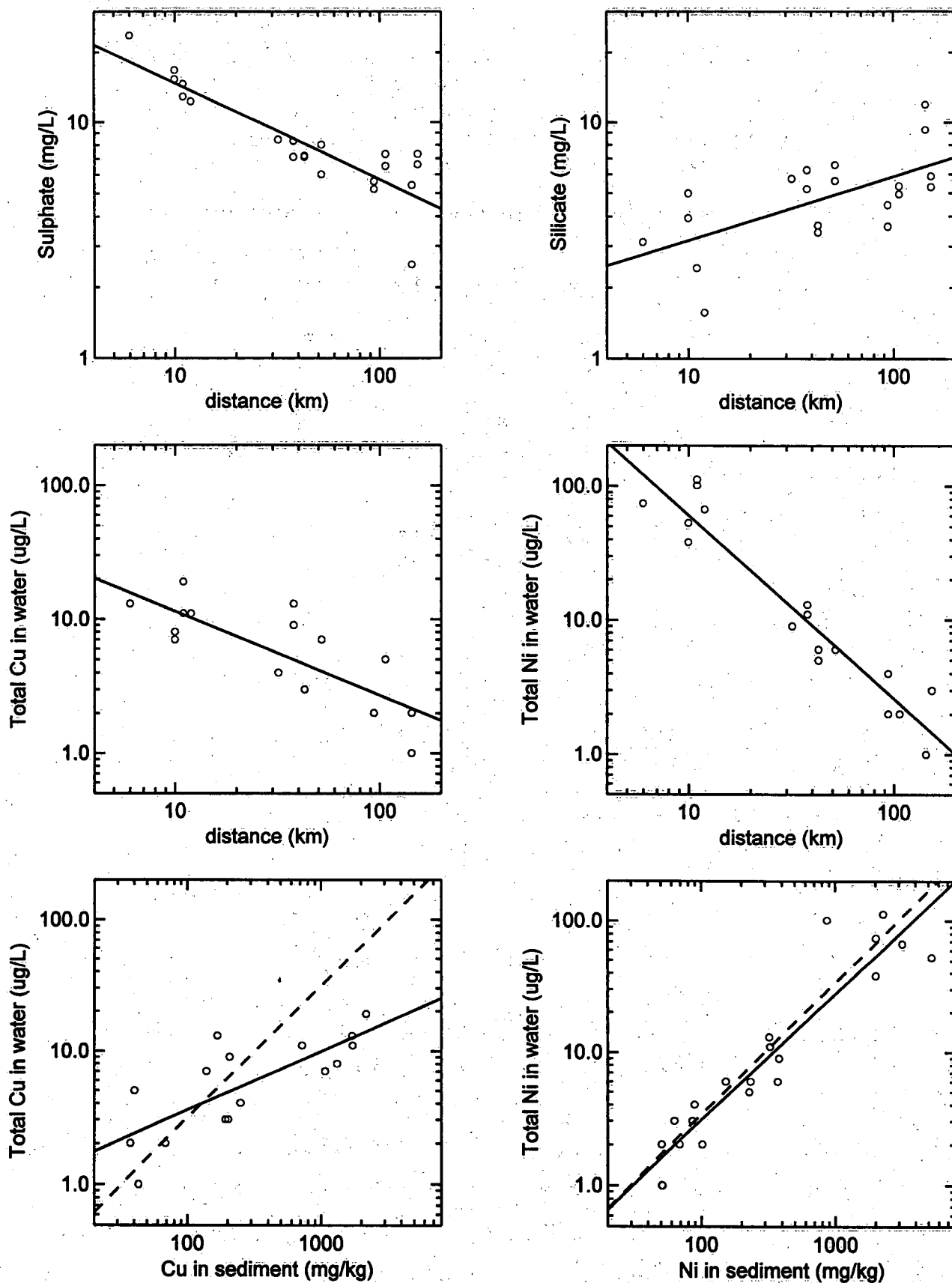
Figure 2.3. Sulphate, silicate, Cu and Ni in water as a function of distance from Copper Cliff or Cu or Ni in sediment. Dashed lines have a slope of 1.0.

TABLE 2.2. Water depth at the bottom of the epilimnion [e] and top of the hypolimnion [h], total water column sounding depth [s], thickness of the epi-, meso- and hypolimnion, and dissolved oxygen concentration at the sediment-water interface (SWI) and 1 meter off the bottom (B-1) at each site and distance from Copper Cliff.

Lake/site	Distance (km)	[e] (m)	[h] (m)	[s] (m)	DO-SWI (mg/L)	DO-B-1 (mg/L)	Epi (m)	Meso (m)	Hypo (m)
RAMD	6	7.8	11.3	20.6	6.45	6.69	7.8	3.5	9.3
MCF10	10	5.6	8.0	10.0	0.07	6.76	5.6	2.4	2.0
MCFD	10	5.5	10.3	19.6	0.51	0.83	5.5	4.8	9.3
RAF10	11	5.5	9.9	9.9	9.96	9.96	5.5	4.4	0.0
RAFD	11	6.1	9.9	15.3	4.40	5.78	6.1	3.8	5.4
RICD	12	7.4	9.0	9.0	3.72	6.09	7.4	1.6	0.0
KAKD	38	5.1	7.2	23.6	1.65	2.62	5.1	2.1	16.4
TROD	43	4.6	9.0	46.3	5.74	5.76	4.6	4.4	37.3
LOS10	52	4.1	6.6	9.8	7.98	7.83	4.1	2.5	3.2
LOSD	52	4.0	6.7	46.3	4.28	8.79	4.0	2.7	39.6
TOM10	94	7.3	9.9	9.9	6.14	6.67	7.3	2.6	0.0
TOMD	94	6.1	11.7	22.6	4.87	5.07	6.1	5.6	10.9
RES10	107	3.9	10.4	10.4	6.33	6.64	3.9	6.5	0.0
RESD	107	4.1	9.3	28.3	6.02	6.20	4.1	5.2	19.0
NOS10	144	8.1	10.3	10.3	1.55	3.20	8.1	2.2	0.0
NOSD	144	9.0	13.5	13.5	0.34	0.46	9.0	4.5	0.0
TAL10	154	4.7	11.0	11.0	7.65	7.56	4.7	6.3	0.0
TALD	154	4.7	9.2	36.1	7.55	7.57	4.7	4.5	26.9
Mean	69.1	5.8	9.6	19.6	4.73	5.80	5.8	3.9	10.0
SD	54.2	1.5	1.7	12.0	2.83	2.48	1.5	1.5	12.6

phosphorus forms show a possible increasing trend with log distance from Copper Cliff. Greater than 70% of the total phosphorus is in the particulate fraction.

Significantly greater concentrations of SO_4^{2-} were found in the lakes closest to Copper Cliff, with statistically significant decreasing trend with distance (Figure 2.3). Sulphate shows a clearer and greater decrease in concentration with distance away from the smelters than all the other elements measured with the exception of nickel and copper. Decreasing trends with distance are also shown by Cl, and DIC, but these parameters are not as highly correlated with distance, as SO_4^{2-}.

TABLE 2.3. Chloride, silicate, sulphate, dissolved inorganic carbon, dissolved organic carbon, total dissolved carbon, total Kjeldahl nitrogen, soluble reactive phosphorus, ammonia, nitrate plus nitrite, total dissolved (filtered) phosphorus, total particulate phosphorus, and total phosphorus (unfiltered) at 1 meter off the bottom at each site and distance from Copper Cliff.

Lake	Distance (km)	Cl	SiO$_2$	SO$_4$	DIC	DOC	TDC	TKN	SRP	NH$_3$	NO$_{3+2}$	TPF	TPP	TPUF
Deep station														
RAMD	6	59.6	3.1	23.6	7.2	7.1	14.3	0.372	0.0019	0.011	0.067	0.0039	0.0073	0.0112
MCFD	10	61.8	5.0	15.3	12.6	4.0	16.6	0.431	0.0020	0.176	0.192	0.0060	0.0106	0.0166
RAFD	11	1.1	2.4	12.9	2.6	6.0	8.6	0.322	0.0015	ND	ND	0.0057	0.0065	0.0122
RICD	12	31.2	1.6	12.3	7.5	3.3	10.8	0.180	0.0011	ND	0.010	0.0034	0.0081	0.0115
NEPD	32	1.2	5.8	8.4	4.1	7.0	11.1	0.368	0.0047	0.052	0.010	0.0127	0.0142	0.0269
KAKD	38	6.6	6.3	7.1	7.3	7.8	15.1	0.361	0.0029	ND	0.230	0.0056	0.0074	0.0130
TROD	43	1.0	3.7	7.2	4.4	6.5	10.9	0.234	0.0032	ND	0.168	0.0060	0.0063	0.0123
LOSD	52	1.3	6.6	6.0	5.5	7.8	13.3	0.313	0.0031	ND	0.202	0.0118	0.0082	0.0200
TOMD	94	2.5	4.5	5.2	3.9	7.1	11.0	0.246	0.0013	0.005	0.162	0.0042	0.0042	0.0084
RESD	107	2.9	5.3	7.3	1.4	5.3	6.7	0.242	0.0021	0.007	0.190	0.0033	0.0044	0.0077
NOSD	144	3.1	11.9	2.5	11.0	5.4	16.4	0.177	0.0023	0.052	ND	0.0076	0.0037	0.0113
TALD	154	4.0	5.9	7.3	5.3	5.2	10.5	0.190	0.0011	ND	0.218	0.0024	0.0047	0.0071
Shallow station														
MCF10	10	62.4	3.9	16.7	12.3	4.9	17.2	0.325	0.0015	0.043	0.091	0.0025	0.0260	0.0285
RAF10	11	1.5	1.0	14.6	1.6	3.1	4.7	0.186	0.0017	ND	ND	0.0065	0.0010	0.0075
KAK10	38	6.6	5.2	8.3	6.2	7.6	13.8	0.294	0.0052	ND	0.116	0.0068	0.0022	0.0090
TRO10	43	0.9	3.4	7.1	3.8	6.5	10.3	0.226	0.0021	ND	0.175	0.0040	0.0050	0.0090
LOS10	52	0.9	5.6	8.0	5.8	7.4	13.2	0.304	0.0013	ND	0.215	0.0029	0.0041	0.0070
TOM10	94	2.6	3.6	5.6	5.4	7.3	12.7	0.266	0.0012	0.014	0.130	0.0031	0.0045	0.0076
RES10	107	2.6	4.9	6.5	3.8	5.8	9.6	0.224	0.0013	0.005	0.186	0.0018	0.0076	0.0094
NOS10	144	2.8	9.3	5.4	7.0	5.3	12.3	0.354	0.0065	0.085	ND	0.0172	0.0069	0.0241
TAL10	154	4.0	5.3	6.6	3.9	4.8	8.7	0.160	0.0003	0.007	0.190	0.0025	0.0051	0.0076

ND= Not Detected

Total Concentrations in Water (ug/l)
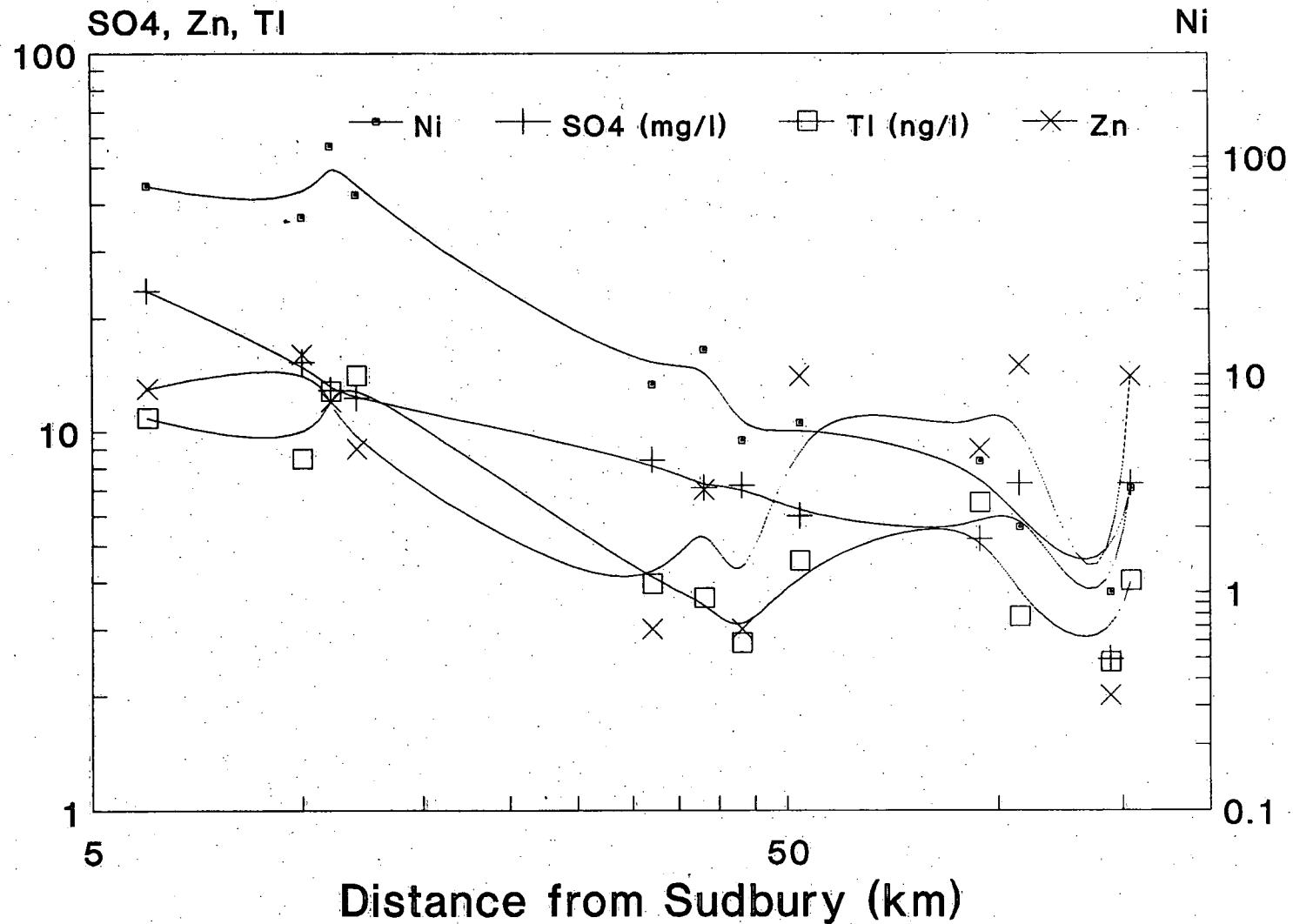
Figure 2.4. Nickel (μg/l), sulfate (mg/l), thallium (ng/l) and zinc (μg/l), concentrations in water at one meter above the bottom. Data points have been fitted with a smoothed curve.

The correlation between distance and SO_4^{2-} (0.51), is statistically significant at the 5% level of significance. Silicate shows a tendency to increase with distance from Copper Cliff (Figure 2.3), but the trend is not statistically significant. Other nutrients show a variable pattern of spatial distributions and do not reveal any trends with respect to distance from the smelters (Figure 2.2).

2.5 Trace Elements

The effect of smelting operations in the Sudbury Basin on the metal loadings to the Sudbury area lakes is clearly revealed by results shown in Table 2.4. The lake water concentration of nine metals (Table 2.4), sampled in two sites in each lake within the study area, shows considerable decrease in metal concentrations from the severely polluted areas (Sudbury lakes) to the "reference" lakes, especially for Ni, Tl and Zn (Figure 2.4), and also Cu (Figure 2.3). The greatest decrease (100-fold) was observed in the concentration of nickel, followed by copper, which showed a 15-fold decrease. In contrast, the concentration of Cd was below detection limit for all sites, with the exception of three sites where the Cd levels were at the detection limit. Concentrations of Cr were very low and fairly constant (2-3 μg/L) for all the sites. The same spatial pattern was observed for Hg (see Section 6).

Regression analyses relating the total thallium and copper concentrations in water to the total nickel content showed significant positive correlations (Figure 2.5), which may indicate the possibility of these elements originating from a similar source. Moreover, the concentrations of Ni and Cu in the surficial (0-1 cm) sediments are well correlated (Figure 2.5). Statistically significant positive correlations between water and sediment concentration of Cu and Ni were also found (Figure 2.3). This may be a result of desorption and molecular diffusion transferring soluble metal species from the contaminated sediments leading to the release of the metals to the water column above. Nickel in water was directly proportional to Ni in sediment, but the Cu concentrations in water increased more slowly than sediment Cu concentrations (Figure 2.3). This may be due to the higher binding capacity of Cu to organic matter, compared with Ni (see Section 6.3.6). The strong relationship between Ni in sediment and Ni in water is only seen if

Sediment Concentrations [ug/g] (0-1cm)

Cu (Thousands)

Cu=0.81Ni-12 [r^2=0.93, n=11]

NI

Total Concentrations in Water (B-1)

Cu(ug/l)

Cu=0.13Ni+3.5 [r^2=.84, n=9]

Ni(ug/l)
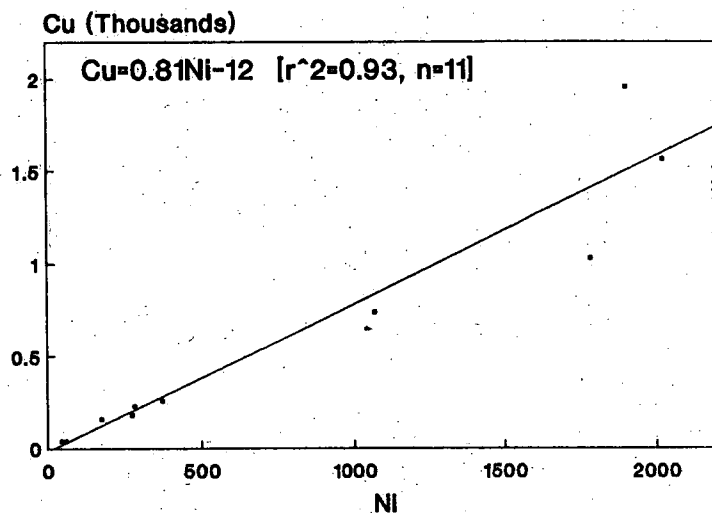
Total Concentrations in Water (B-1)

Tl(ng/l)

Tl=.09Ni+4 [r^2=.8, n=9]

Ni(ug/l)

Total Concentrations in Water (B-1)

SIO2(mg/l)

Ni(ug/l)
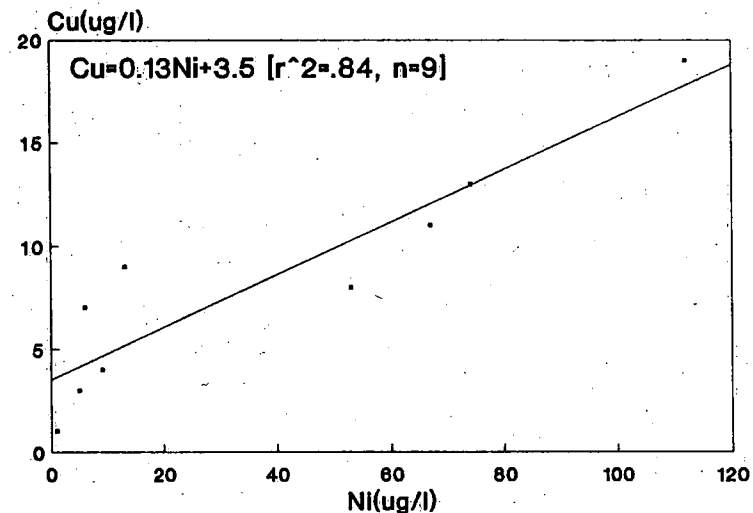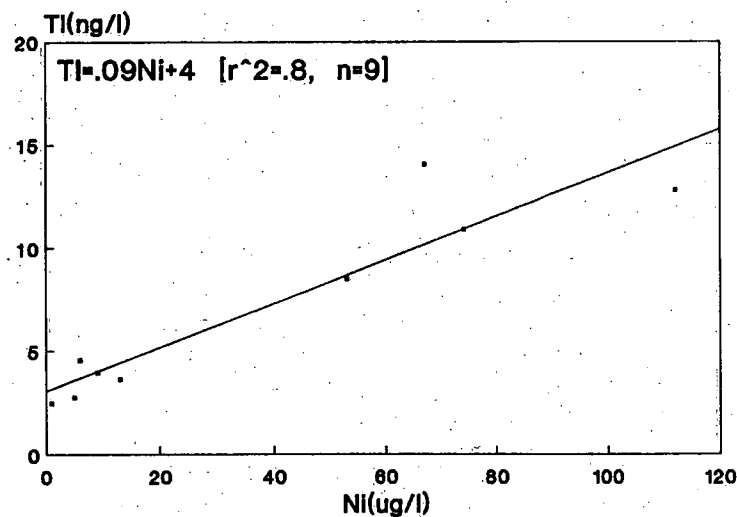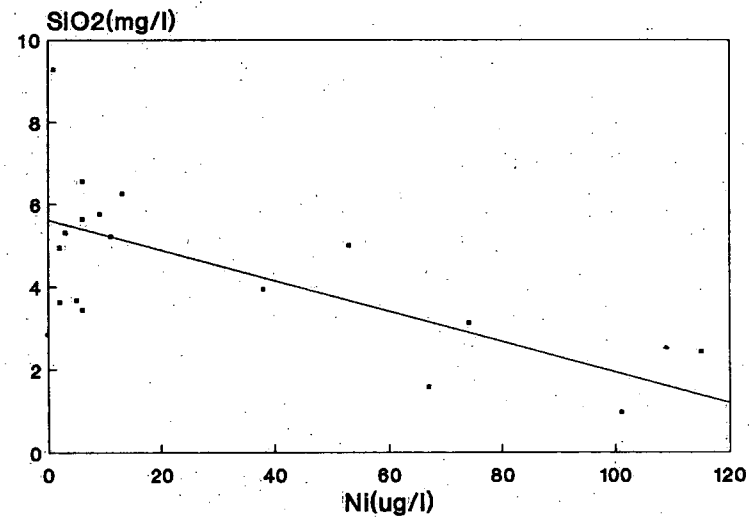
Figure 2.5. Concentration plots of different elements (copper, thallium and silica) with nickel, both in surficial sediments and in water. Correlations and line equations are shown for statistically significant (p<.01) relationships only.

TABLE 2.4. Total metal concentrations (μg/L except for Tl) in water 1 meter off the bottom at each station and distance from Copper Cliff. Copper concentrations in parentheses are anomalously high when compared to the other stations from the same lake and might be due to contamination.

Lake	Distance (km)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Tl (ng/L)
Deep station										
RAMD	6	ND	3	13	60	81	74	ND	13	11
MCFD	10	3	2	8	26	857	53	1	16	8
RAFD	11	ND	3	19	239	252	112	1	12	13
RICD	12	ND	3	11	105	146	67	ND	9	14
NEPD	32	ND	3	4	784	604	9	ND	3	4
KAKD	38	ND	3	9	1100	859	13	ND	7	4
TROD	43	ND	3	3	91	9	5	2	3	3
LOSD	52	ND	3	7	1387	238	6	2	14	5
TOMD	94	ND	3	(63)	249	24	4	ND	9	6
RESD	107	ND	3	(20)	155	34	2	ND	15	3
NOSD	144	ND	2	1	4241	1012	1	ND	2	2
TALD	154	ND	3	(20)	171	9	3	ND	14	4
Shallow station										
MCF10	10	3	3	9	59	140	38	2	12	5
RAF10	11	ND	3	11	84	16	101	1	13	18
KAK10	38	ND	3	13	91	20	11	ND	33	4
TRO10	43	ND	3	3	90	13	6	ND	4	2
LOS10	52	ND	3	(132)	131	8	6	1	15	4
TOM10	94	ND	4	2	88	22	2	ND	4	4
RES10	107	ND	3	5	75	14	2	1	5	2
NOS10	144	3	3	2	349	869	1	ND	4	5
TAL10	154	ND	3	(166)	84	5	3	32	34	3

ND = Not Detected

data for all lakes are compared; no such relationship is observed when the Sudbury area lakes are examined separately.

2.6 Summary of Water Chemistry Observations

1) All of the lakes studied were thermally stratified, and probably at the peak of stable stratification.

2) The surface and bottom conductivities at each site were very similar. Conductivity is highest (tenfold), in the four lakes closest to Copper Cliff with the exception of Raft Lake. All the other lakes, including Raft, have a fairly constant conductivity of 35-50 μS/cm.

3) The concentrations of different forms of carbon, nitrogen, and phosphorus in the bottom water show no significant differences among the lakes sampled, with the possible exception of TKN.

4) Significantly greater concentrations of SO_4^{2-} were found in the lakes closest to Copper Cliff, with statistically significant decreasing trend with distance from Sudbury. Sulphate shows the clearest and greatest decrease in concentration with distance of all the elements measured with the exception of nickel and copper.

5) The greatest decrease (100-fold) was observed in the concentration of nickel, followed by copper with a 15-fold concentration decrease.

6) A statistically significant correlation between water and sediment concentration of copper and nickel also exists. This correlation suggests that de-sorption and molecular diffusion may be the main processes transferring soluble metal species from the contaminated sediments to the water column above.

3. SEDIMENT BULK CHEMISTRY

3.1 Methods

Surface sediment samples for metal analysis were obtained from within the top 5 cm of sediment collected with a box corer. In addition, at the deep stations only, a 20-cm sediment core was taken using a Technical Operations Corer (modified combination of Kajak-Brinkhurst and Benthos Gravity Corers) and carefully sectioned using a hydraulic extruder (Mudroch and MacKnight, 1994) into 1-cm intervals for the first 10 cm, and 2-cm intervals for the next 10 cm, to obtain a sediment profile of metal concentrations. Sediment samples were freeze-dried and ground in a mortar and pestle before analysis for total metals. A 0.5 g subsample was digested with concentrated nitric (5 mL) and hydrofluoric (3 mL) acid in teflon beakers on a hotplate at 95°C and evaporated to dryness. Residues were redissolved in hydrogen peroxide (30%, 1 mL)

and nitric acid (0.4 M, 5 mL) and gently heated for 1 h. Samples were then cooled, diluted to 50 mL with 0.4 M nitric acid and centrifuged at 5000 rpm for 30 minutes. Metals were analyzed on a Jy 74 inductively coupled argon plasma optical emission system (ICAP-OES). Recovery of metals from certified reference material (NIST-2704 Buffalo River sediment) was within 10% of the certified values.

Particle size was determined by sieving to remove sand and gravel (62.4 micron mesh). The material passing through the sieve was suspended in a dispersant solution and analyzed on a Sedigraph analyzer for particle size (silt >3.91 microns> clay). Organic and inorganic carbon were measured by infrared analysis of combusted carbon from dried sediment samples using a LECO-12 Carbon Determinator.

3.2   Sediment Metal Profiles

A well defined sediment profile, with higher concentrations in the surface sediments (<5 cm) and lower concentrations in the deep sediments (>10 cm) was observed for several metals (Cd, Co, Cu, Ni, Zn) in many of the deep stations, especially in the lakes close to Sudbury (Appendix 2). These profiles were much less pronounced in sediments of the reference lakes. A strong lead profile was seen in every lake, regardless of distance from Copper Cliff. The depth of maximum change in metal concentrations was similar for each of these metals within a lake, but varied between lakes. Chromium concentrations did not vary with depth. Loss on ignition, total carbon, iron and manganese often varied only moderately with depth, although some lakes did have strong profiles for iron and especially manganese (e.g., McFarlane Lake, Appendix 2).

In order to examine metal concentrations with distance from Sudbury, the average surface (mean of the 0-1, 1-2, and 2-3 cm depths) and average deep (mean of 14-16, 16-18 and 18-20 cm depths) metal concentrations were calculated (Table 3.1). For surface manganese at site MCFD and surface iron at site RESD, where one of the measurements was over range, the median is reported instead of the mean. Surface and deep metal concentrations were then plotted as a function of distance from Copper Cliff (Figure 3.1). Smooth solid curves drawn through the

TABLE 3.1. Mean metal concentrations in surface (0-3 cm) and deep (14-20 cm) sediments of the deep water sites in each lake and distance from Copper Cliff.

Site	Distance (km)	Cd (µg/g)	Co (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Mn (µg/g)	Ni (µg/g)	Pb (µg/g)	Zn (µg/g)	LOI (%)	TC (%)
Surface sediment mean concentration												
RAMD	6	4.94	95	94	1753	4.20	904	1838	143	303	10.7	5.56
MCFD	10	18.15	198	62	1325	4.97	41090	5307	99	1107	20.8	9.86
RAFD	11	3.60	51	69	989	3.81	420	1399	100	182	17.4	9.66
RICD	12	4.86	75	64	1023	2.79	432	1968	57	228	14.7	8.03
NEPD	32	2.91	37	98	222	4.25	870	353	56	275	18.1	9.23
KAKD	38	3.69	38	71	190	6.25	1673	299	70	280	23.0	10.93
TROD	43	6.65	55	67	259	7.54	5767	386	189	395	21.7	10.69
LOSD	52	4.01	41	79	141	4.12	1247	177	152	294	21.0	9.75
TOMD	94	2.26	22	42	28	3.15	1152	35	19	148	27.9	13.34
RESD	107	7.42	25	50	55	7.59	5694	57	137	369	18.0	9.95
NOSD	144	2.31	18	81	39	6.36	984	49	30	174	18.7	8.25
TALD	154	4.76	25	106	39	9.90	4626	57	49	390	15.2	6.11
Deep sediment mean concentration												
RAMD	6	0	18	96	48	3.08	448	72	0	99	12.7	4.80
MCFD	10	1.11	23	66	34	3.15	1446	43	0	149	28.1	15.03
RAFD	11	0.01	20	74	44	2.56	529	45	0	85	18.1	9.85
RICD	12	0.50	14	64	73	2.00	368	205	0	89	26.0	15.49
NEPD	32	0.30	29	131	41	4.94	722	73	0	166	14.0	6.10
KAKD	38	0.62	24	83	42	3.66	974	58	18	166	20.7	10.04
TROD	43	0.22	22	67	34	3.38	2335	33	0	132	28.6	14.05
LOSD	52	0	31	74	32	3.32	1366	34	0	140	29.5	14.72
TOMD	94	1.44	23	68	21	3.26	989	29	0	137	30.6	14.56
RESD	107	1.25	16	53	33	4.02	1472	23	0	168	27.3	12.84
NOSD	144	1.00	19	90	34	4.67	626	48	4	161	9.5	5.19
TALD	154	2.59	26	120	29	7.97	2788	53	0	181	15.9	7.08

plots represent linear regressions of log(concentration) against distance from Copper Cliff (the lines are curved because distance is plotted on a log scale for clearer presentation). The surface concentrations of Co, Cu and Ni decreased with distance from Copper Cliff, while the deep concentrations remained relatively constant. The surface concentrations of Cd and Zn decreased slightly with distance from Copper Cliff, and the deep sediments increased somewhat. For all
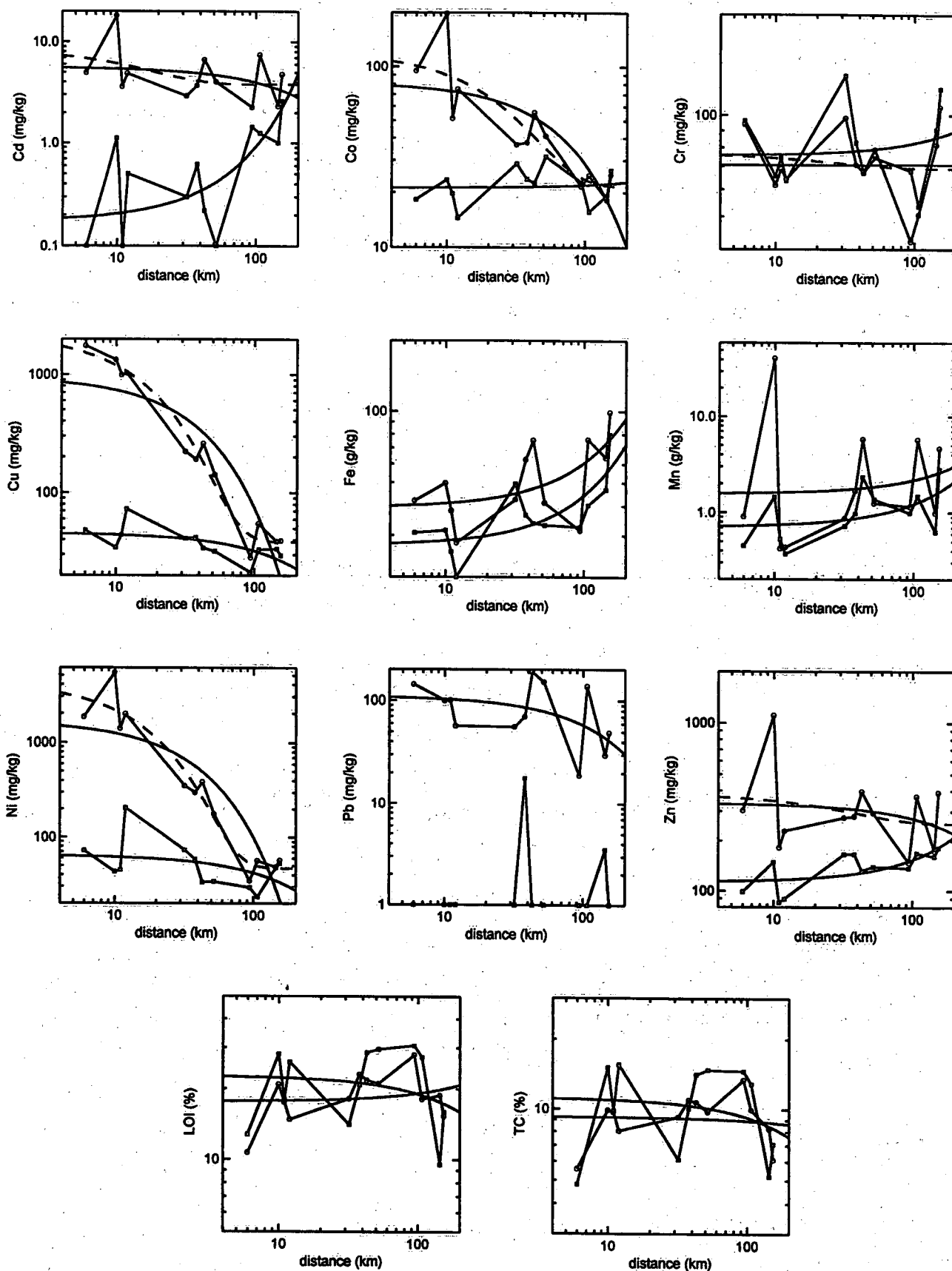
Figure 3.1. Metal concentrations in surface (0-3 cm) and deep (14-20 cm) sediments as a function of distance from Copper Cliff. Solid lines are linear regressions of log[metal] against distance. Dashed lines are given by equation 1 in the text.

21

five of these metals the surface and deep sediment concentrations converged at the reference sites. Surface concentrations of Pb decreased slightly with distance, but were always much higher than the deep sediments. The surface concentrations of Fe and Mn were generally slightly higher than the deep concentrations, and both surface and deep sediment concentrations increased with distance from Copper Cliff, possibly due to a gradual shift in surface geology. The concentrations of Cr, loss on ignition, and total carbon showed no consistent trend, either with depth or with distance from Copper Cliff.

For Cd, Co, Cr, Cu, Ni and Zn the surface data were fitted to the equation

$$\log(\text{surface metal concentration}) = \log(\text{background} + 10^{A + B*d}) \tag{1}$$

where d is distance from Copper Cliff and A and B are constants. Equation 1 (dashed lines in Figure 3.1) provides a much better fit to surface metal concentrations than a linear regression of log[metal] against distance, and can be used to predict approximate metal concentrations in surface sediments without reference to deep sediments, if necessary. This equation could not be fitted successfully to Fe, Mn or Pb surface concentrations. Background metal concentrations predicted from equation 1 are summarized in Table 3.2 and compared to observed deep sediment concentrations. Background metal concentrations predicted in this way were similar to the deep sediment concentrations for all of the metals except Cd and Zn, the 2 metals for which concentrations in the deep sediments increased with distance from Copper Cliff.

For Cd, Co, Cu, Ni and Zn, which showed significant enrichment in surface sediments near Sudbury, the enrichment factor (EF = surface/deep concentration) was calculated and fitted to the equation

$$\log(\text{EF}) = \log(1 + 10^{a + b*d}) \tag{2}$$

where d is distance from Copper Cliff and a and b are constants; 10^{a} is the maximum EF (EF_{max}) obtained at d=0 and -log(2)/b is the distance over which EF-1 drops by 50% ($D_{0.5}$). The EF values are plotted against distance from Copper Cliff and the fitted equation is shown by the

dashed curve in Figure 3.2. Maximum enrichment factors for Cu and Ni were about 40-fold, and the distance to a 50% drop in excess (surface-deep) metal in the surface sediments ($D_{0.5}$) was about 15 km (Table 3.3). The EF_{max} was lower for Co, but the $D_{0.5}$ was similar. The EF_{max} for Cd was similar to that for Cu and Ni, but had wide confidence limits because of considerable scatter in the data due to the very low measured Cd concentrations in the deep sediments. The predicted $D_{0.5}$ for Cd was slightly higher than for Co, Cu or Ni, but the confidence limits overlap.

TABLE 3.2. Background metal concentration predicted for surface (0-3 cm) sediment concentrations using equation 1 (Bk_{pred}), estimates of A, B and R^2 from equation 1, and the observed concentration in the deep (14-20 cm) sediments (Bk_{obs}).

Metal	Bk_{pred} (95% confidence limits)	A	B	R^2	Bk_{obs} (range)
Cd	3.79 (1.40-6.18)	0.67	-0.0303	0.157	0.42 (0-1.11)
Co	21 (10-33)	2.00	-0.0168	0.761	21 (14-29)
Cr	69 (41-96)	0.89	-0.0157	0.015	86 (64-131)
Cu	38 (25-51)	3.34	-0.0278	0.973	47 (34-73)
Ni	47 (22-72)	3.63	-0.0301	0.946	83 (43-205)
Zn	253 (25-480)	2.10	-0.0128	0.063	126 (85-166)

Zinc was enriched much less than the other metals (EF_{max} = 2.3) and its $D_{0.5}$ was considerably greater (Table 3.3). This metal did not, therefore, fit the general pattern for the other metals, in which a 50% drop in excess metal was observed for every 15 km increase in distance from Copper Cliff.
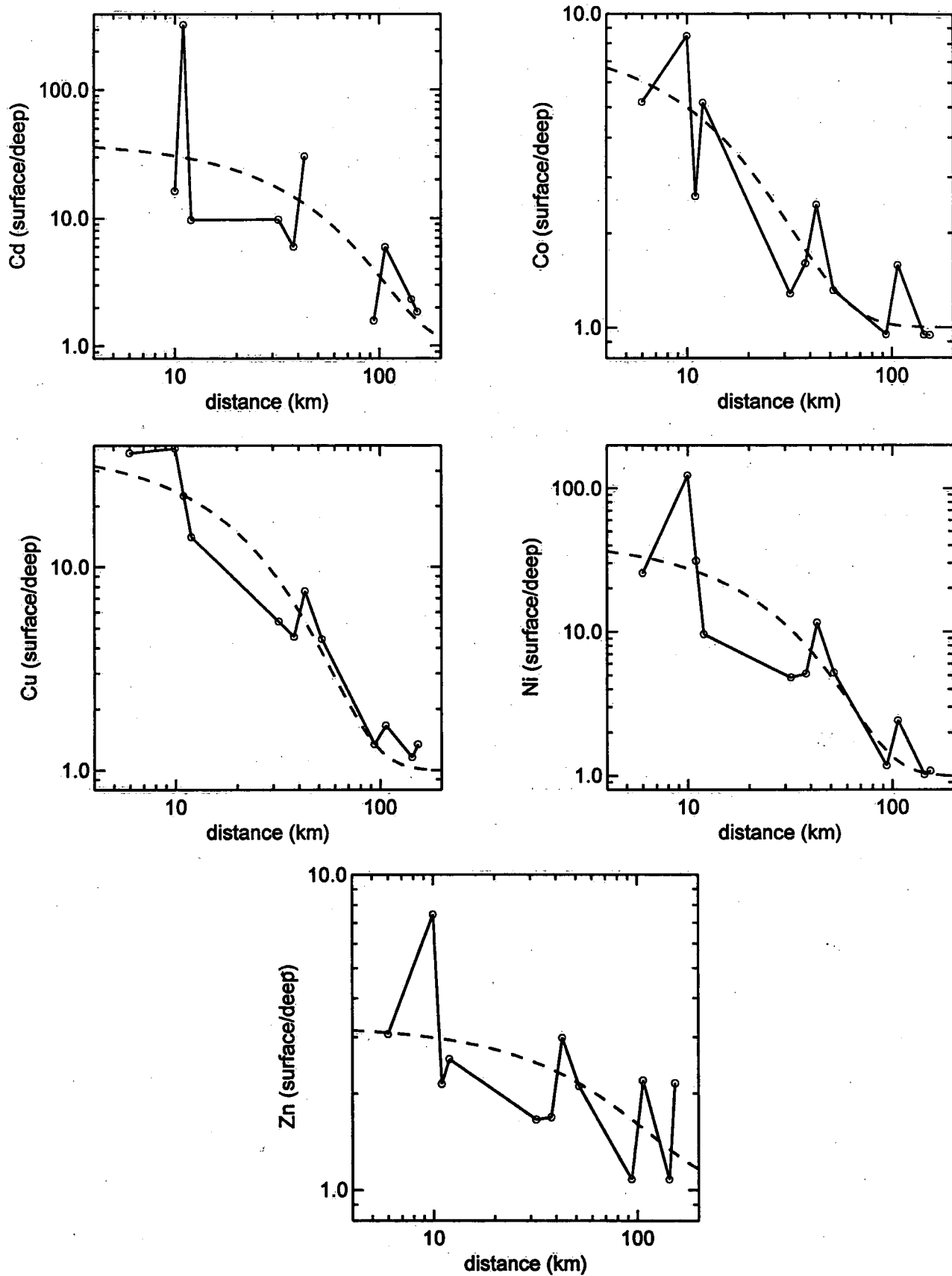
Figure 3.2. Ratio of metal concentration in surface to deep sediments (enrichment factor) as a function of distance from Copper Cliff. Dashed lines are given by equation 2 in the text.

TABLE 3.3. The maximum enrichment factor (EF_{max} = surface/deep sediment concentrations at 0 km from Copper Cliff) and the increase in distance required for excess metal (EF-1) to drop by 50% ($D_{0.5}$). The predicted EF at any given distance (d, km) from Copper Cliff can be computed from $1 + EF_{max} \times 10^{(-log(2) \times d / D_{0.5})}$.

Metal	EF_{max} (95% confidence limits)	$D_{0.5}$ (95% confidence limits)	R^2
Cd	39 (8.6-174)	25 (13-1115)	0.530
Co	6.7 (3.2-14)	12 (7-35)	0.786
Cu	37 (23-61)	14 (10-21)	0.936
Ni	43 (16-112)	15 (9-41)	0.799
Zn	2.3 (1.1-4.7)	53 (24-infinity)	0.335

3.3 Surficial Sediments, Grab Samples, and Particle Size

The particle size distribution of the surface sediment samples was relatively uniform, consisting of 50-75% clay with the remainder being silt. The only exception was sediment from RAF10 which contained 41% sand. Sediment from TRO10 also contained a small amount of sand (2%).

Metal concentrations in the surface grab samples were very similar to the mean metal concentrations in the top 3 cm of the sediment profiles (Tables 3.1 and 3.4). In most cases, metal concentrations in the surface sediments from the 10 m and deep stations were similar (Table 3.4). The major exceptions were MCF and RAF, where the deep sediments contained higher concentrations of Co, Cu, Ni, Pb and Zn than the 10 m sediments. The sediments from RAF10 contained fewer small particles than those from RAFD, so their lower metal concentrations are, perhaps, not surprising. The grain size distribution of MCF10 and MCFD sediments were, however, similar. In contrast, at sites >30 km from Sudbury, sediments from the 10 m site contained similar concentrations of Cu and similar or higher concentrations of Ni than the deep sediments. Sediment focusing, therefore, seemed to be minimal in lakes >30 km from Sudbury.

TABLE 3.4. Particle size distribution, loss on ignition (LOI), organic carbon (OC), inorganic carbon (IC) and metal concentrations in surface grab samples from each site and distance from Copper Cliff. HH1 and LE303 are control sediments from Hamilton Harbour and Lake Erie known to be non-toxic.

Site	Distance (km)	Sand (%)	Silt (%)	Clay (%)	LOI (%)	OC (%)	IC (%)	Co ($\mu g/g$)	Cr ($\mu g/g$)	Cu ($\mu g/g$)	Fe (%)	Mn ($\mu g/g$)	Ni ($\mu g/g$)	Pb ($\mu g/g$)	Zn ($\mu g/g$)
RAMD	6	0	35.2	64.8	12.0	3.47	0.32	89	105	1716	4.07	770	2027	99	271
MCF10	10	0	49.7	50.3	13.0	3.77	0.12	113	95	1077	3.06	1259	2016	37	440
MCFD	10	0	42.7	57.3	28.1	4.80	0.14	213	54	1190	4.11	81650	5818	81	1096
RAF10	11	41.1	30.1	28.8	4.9	7.89	0.08	56	86	725	3.52	977	874	19	117
RAFD	11	0	46.5	53.5	23.5	8.02	0.08	89	86	2187	3.66	637	2293	178	221
RICD	12	0	49.5	50.5	15.6	4.80	0.29	113	87	1732	3.10	561	3193	74	354
NEPD	32	0	25.2	74.8	23.9	6.55	0.13	26	100	251	3.42	875	383	28	249
KAK10	38	0	30.9	69.1	19.1	5.03	0.29	22	78	169	3.18	1164	328	25	274
KAKD	38	0	38.0	62.0	24.3	6.92	0.03	26	83	208	5.10	1566	323	40	271
TRO10	43	2.1	46.9	51.0	26.1	7.56	0.22	29	52	194	4.70	5794	374	107	250
TROD	43	0	31.9	68.1	29.7	8.72	0.16	35	81	204	7.02	2247	229	116	273
LOS10	52	0	43.4	56.6	17.2	5.33	0.24	33	82	86	6.10	11580	235	37	308
LOSD	52	0	25.7	74.3	27.6	7.51	0.06	22	96	140	4.28	1962	154	78	265
TOM10	94	0	43.7	56.3	27.0	8.83	0.04	19	98	69	5.35	3822	102	77	456
TOMD	94	0	47.4	52.6	23.0	7.60	0.09	29	82	65	3.60	1383	90	71	298
RES10	107	0	40.9	59.1	61.9	6.73	0.21	27	59	41	9.53	13420	69	38	378
RESD	107	0	40.0	60.0	29.5	7.40	2.12	9	47	43	6.42	3046	51	90	303
NOS10	144	0	45.9	54.1	18.4	5.37	0.16	10	106	38	4.32	862	52	<2.5	172
NOSD	144	0	50.3	49.7	19.7	5.42	0.14	10	96	43	4.82	956	51	5	162
TAL10	154	0	36.5	63.5	16.7	4.90	0.20	13	107	46	8.41	7111	86	33	435
TALD	154	0	42.4	57.6	18.1	5.13	0.06	13	113	42	6.24	2880	63	16	386
HH1	368	-	-	-	11.8	3.09	2.13	12	119	101	4.54	1722	47	113	1235
LE303	443	-	-	-	3.0	0.40	3.66	3	34	25	2.19	682	19	<2.5	69

4. BENTHIC COMMUNITY STRUCTURE

4.1 Methods and General Observations

In situ benthic invertebrate communities were sampled in each of the lakes and compared to metal concentrations and other potential modifying factors. Animals were collected using a box

26

corer (38 x 38 x 46 cm) from which 5 core tubes (10 cm deep by 6.5 cm diameter) of sediment were sampled, sieved through a 250 micron mesh and fixed in 5% formalin. The samples were transferred to 70% ethanol after several days to prevent decalcification. A listing of the more common taxa is given in Table 4.1. Phantom midges (*Chaoborus* spp), chironomids, and oligochaetes were found in many of the lakes, regardless of the distance from Copper Cliff. Bivalves (fingernail clams) were found in all of the intermediate and reference lakes, and at most sites, but were notably absent from the lakes closest to Sudbury. Amphipods (*Diporeia hoyi*) were found in 5 out of 8 intermediate or reference lakes (6 out of 15 sites), and were also absent from the Sudbury lakes. Two of the chironimods (*Micropsectra* and *Tanytarsus*) were likewise absent from the lakes closest to Copper Cliff, whereas *Chaoborus flavicans* was found only in the lakes near Sudbury (Table 4.1).

4.2   Community Structure Response Using Species Level Ordination Analysis

Data have been examined based on total abundance, number of taxa (species), and using ordination summaries at the lowest taxonomic level (usually species). Thirty-three taxa have been identified, 17 of these only occur at one of the 21 sites (Table 4.2). The most common (frequently occurring) and abundant (numerically dominant) taxa are *Chironomus* spp (14 sites), *Chaoborus* (12 sites) and *Endochironomus* spp (12 sites). There is no relationship between abundance, number of taxa or the ordination axes with distance from Sudbury (Figure 4.1), based on either correlation or ANOVA. There is a possible relationship between both Ni concentration and total metal concentration and abundance, taxa and the ordination axes (Figure 4.2). However, there is considerable variation in the low concentration (reference) sites. There are statistically significant relationships ($P < 0.05$) between, taxa and lead, axis 1 scores and nickel and zinc, axis 3 scores and lead. There are also significant relationships between abundance and axis 3 with temperature and TOC.

27
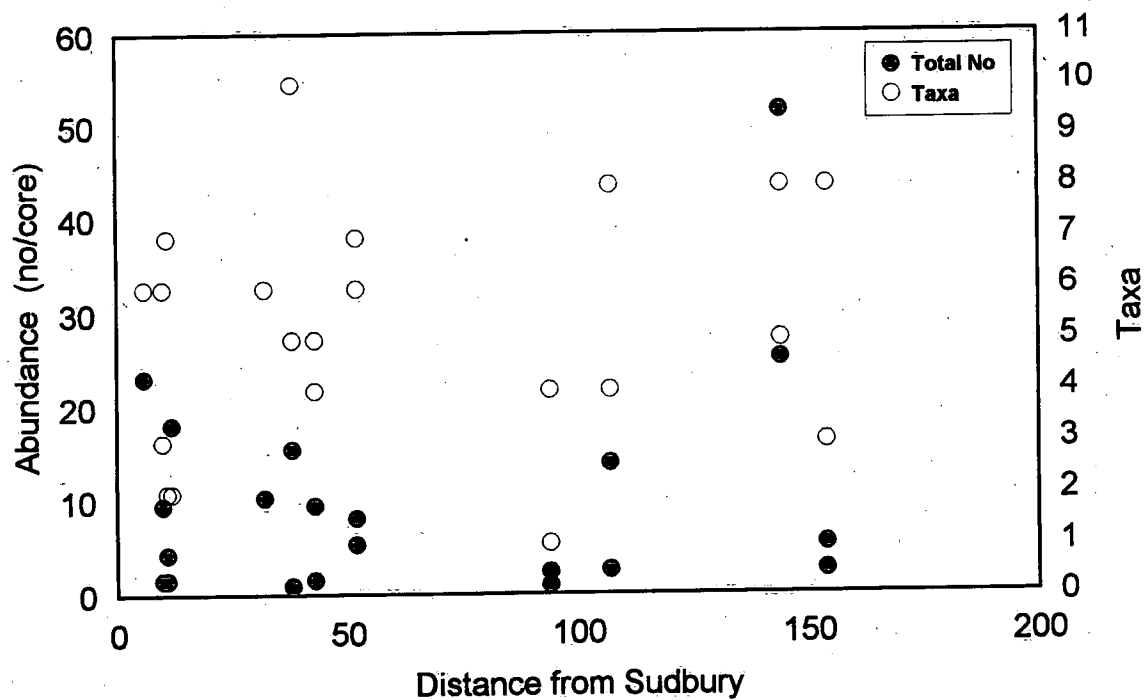
Figure 4.1. Abundance and number of taxa as a function of distance from Copper Cliff.
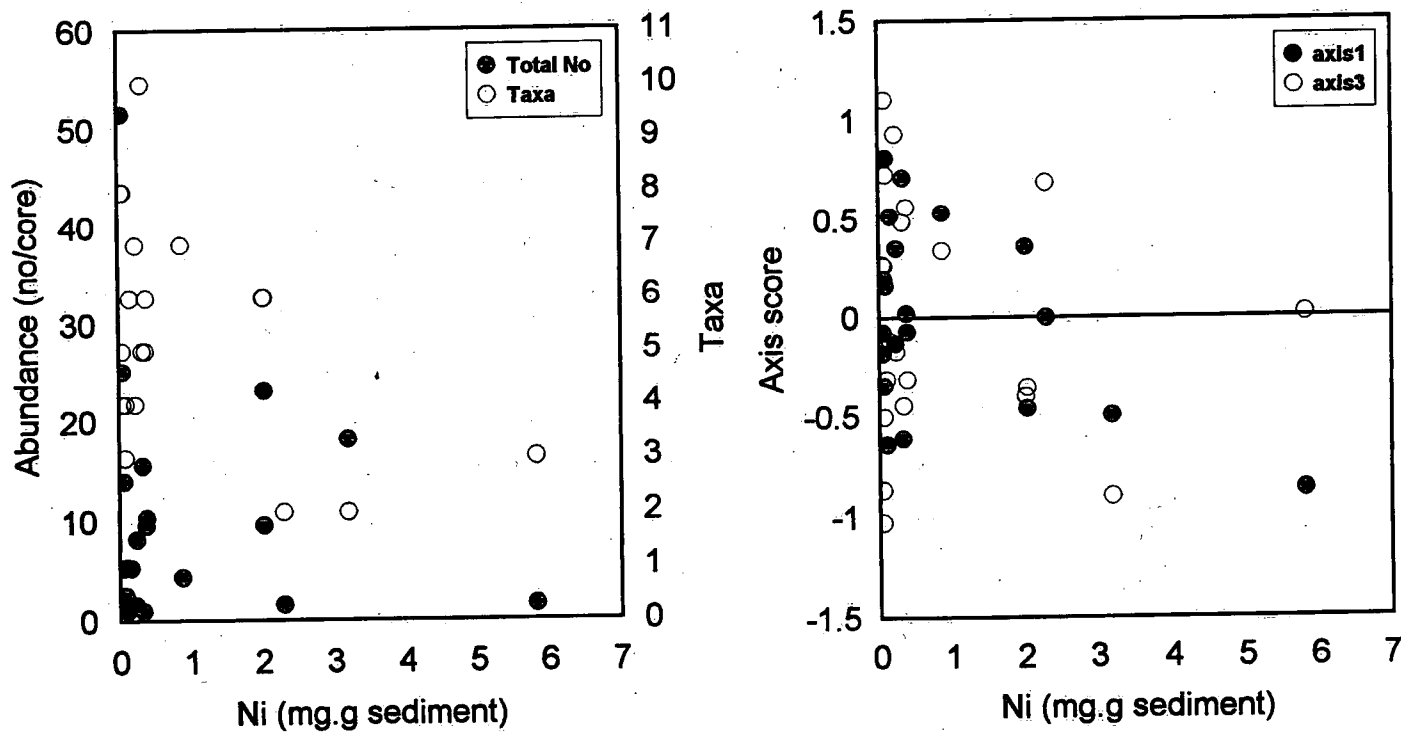
Figure 4.2. Abundance, number of taxa and ordination axes scores as a function of Ni concentration in sediments.

TABLE 4.1. Mean abundance (number per replicate) of major (found at more than 2 sites) taxa in 5 replicate samples of 5.5 cm diameter by 10 cm deep sediment cores collected from each sampling site, distance from Copper Cliff (km), and water depth at the sampling site.

Site	km	Depth (m)	Midges Cf	Cp	Chironomids Cs	Es	Hs	Ps	Ms	Ts	Am. Dh	Bivalves Mp	Pis	Ss	Oligo. o+	o-
RAMD	6	20.6		1.6	0.4	0.4									20.4	0.2
MCF10	10	10	0.6	0.4	6.0	0.2		1.6								0.6
MCFD	10	19.6	0.8	0.4	0.2											
RAF10	11	9.9		0.2	0.2	0.8	0.6	0.2								
RAFD	11	15.3	0.4			1.2										
RICD	12	9		1.2	17.0											
NEPD	32	8.9		7.4	0.4									0.4		0.4	1.6
KAK10	38	9.9			0.2		0.6	0.4		2.6	0.8	1.2				0.2
KAKD	38	23.6		0.2		0.2				0.2						0.2
TRO10	43	10.9					4.0			0.4	0.2		3.6			
TROD	43	46.3			0.2	0.2	0.2						1.0			
LOS10	52	9.8					2.0		0.6	0.6	2.8	1.8				
LOSD	52	46.3			3.0	0.8					0.2	0.6			0.6	
TOM10	94	9.9								1.0						
TOMD	94	22.6				0.6		0.2						1.0	0.6	
RES10	107	10.4		2.6	0.2		2.8	0.4		0.8	3.2			3.8		
RESD	107	28.3		0.2	1.2	0.4								0.8		
NOS10	144	10.3		14.2	25.2			2.0					2.4		0.6	5.6
NOSD	144	13.5		20.4	3.4								0.2		1.0	
TAL10	154	11				0.6							1.8		0.2	
TALD	154	39.6			1.2	1.8	0.2			1.0	0.2		0.6			

Group	Code	Taxon
Phantom midge	Cf	*Chaoborus flavicans*
	Cp	*Chaoborus punctipennis*
Chironomids	Cs	*Chironomus* spp
	Es	*Endochironomus* spp
	Hs	*Heterotrissocladius* spp
	Ps	*Procladius (Holotanypus)* spp
	Ms	*Micropsectra* spp
	Ts	*Tanytarsus* spp
Amphipods	Dh	*Diporeia hoy*i
Bivalves	Mp	*Musculium partumeium*
	Pis	*Pisidium* spp
	Ss	*Sphaerium* spp
Immature oligochaetes	o+	with hair chaetae
	o-	without hair chaetae

TABLE 4.2. Taxa present at the sampling sites, overall abundance (mean individuals per replicate summed over all sites), occurrence (number of sites where found), and strength of the relation between each taxon on the major ordination axes.

Taxa	Abundance	Occurrence	Ordination "r"
Tanytarsus spp	5.6	6	0.6757
Musculium partumeium	3.6	3	0.6673
Chaoborus	50.6	12	0.6523
Chironomus spp	58.8	14	0.6122
Pisidium casertanum	7.0	4	0.5962
Heterotrissocladius spp	9.8	6	0.5827
Endochironomus spp	7.2	11	0.5822
Diporeia hoyi	7.4	6	0.5266
Sphaerium striatum	4.6	2	0.4924
Zalutschia tatrica group	8.8	1	0.4825
Procladius (Holotanypus) spp	6.2	5	0.4762
Micropsectra spp	2.2	4	0.4663
Immatures with hair chaetae	23.8	7	0.4539
Stictochironomus spp	1.4	1	0.4485
Pisidium nitidum	3.0	3	0.4444
Aulodrilus pigueti	0.8	2	0.4321
Limnodrilus hoffmeisteri	1.2	2	0.4007
Immatures without hair chaetae	8.4	6	0.3083
Sphaerium simile	1.0	1	0.2551
Paracladopelma galaptera	0.8	1	not included
Tribelos spp	0.6	1	not included
Atractides spp	0.2	1	not included
Cryptochironomus spp	0.2	1	not included
Djalmabatista pulcher	0.2	1	not included
Huitfeldtia spp	0.2	1	not included
Hydra cauliculata	0.2	1	not included
Laversia spp	0.2	1	not included
Neotiphys spp	0.2	1	not included
Parakiefferiella spp	0.2	1	not included
Probezzia spp	0.2	1	not included
Pseudofeltria spp	0.2	1	not included
Tubifex tubifex	0.2	1	not included
Uncinais uncinata	0.2	1	not included
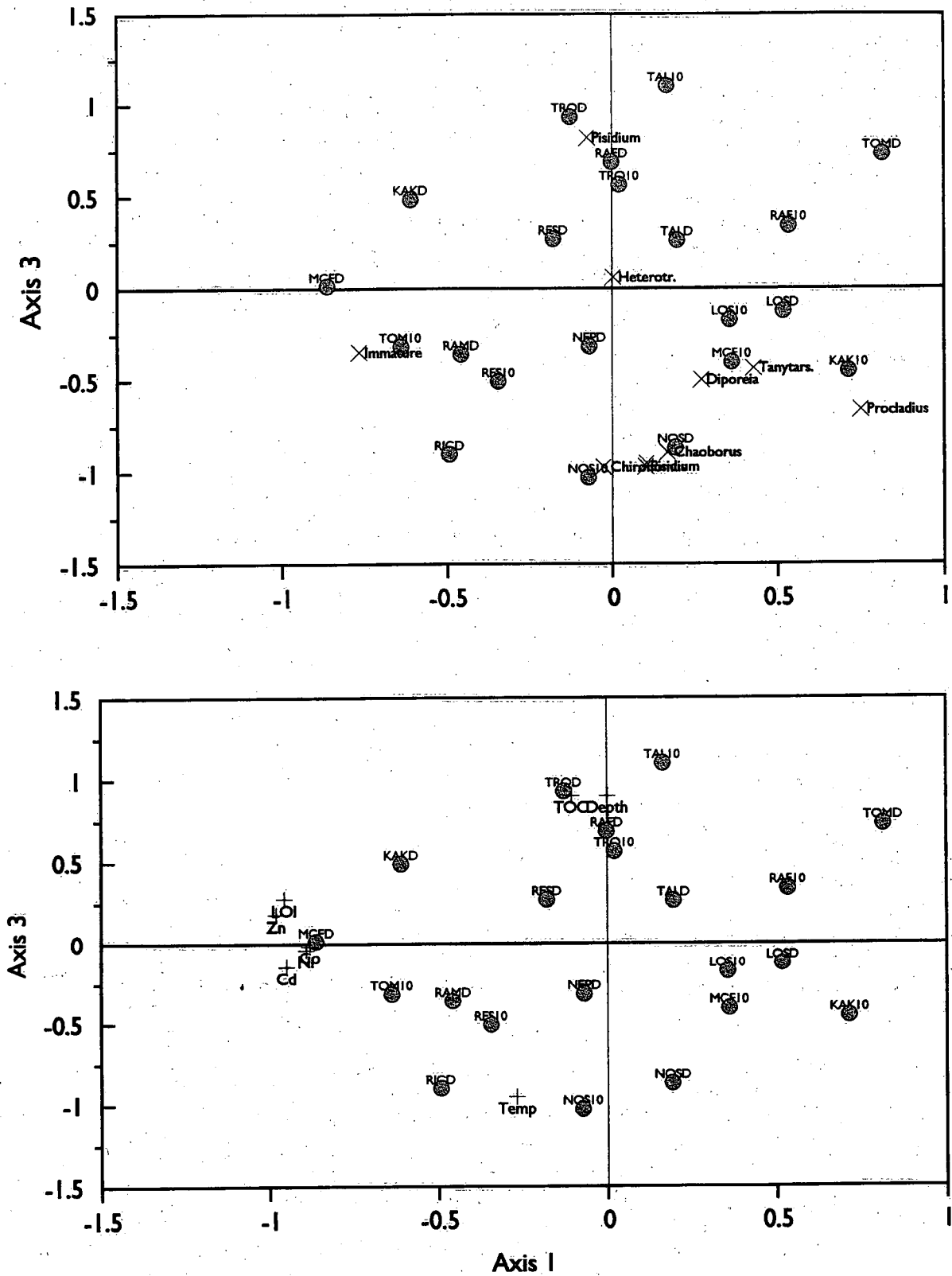
Figure 4.3. Position of individual sites, species and selected environmental variables in ordination space.

Ordination of 19 taxa was used to try and discriminate response patterns in the community. Three ordination axes (stress = 0.174) were required (as mentioned above) to explain the observed variation. Taxa contributing most to the new axes were: *Tanytarsus*, *Musculium*, *Chaoborus*, and *Chironomus* (Figure 4.3). The environmental variables most correlated with the ordination structure were temperature and zinc (P < 0.05), nickel, cobalt, cadmium, TOC and LOI (Figure 4.3). There appear to be two community responses. First, along a depth temperature gradient (axis 3) influencing *Chironomus*, *Chaoborus* and *Pisidium*. Second along a metals LOI gradient (axis 1) affecting worms, *Diporeia* and *Procladius*. However, examination of the distribution of these species with either metal concentrations or depth showed no statistical relationship.

In summary, there may be effects at the community level, but when analyzed at the species level they are no greater than those associated with normal variation. The variation in the reference lakes makes discrimination of community level effects difficult. There appear to be two major response gradients, one associated with depth and depth related variables (e.g., temperature, particle size), the second related to metal concentration.

5. SEDIMENT TOXICITY

5.1 Methods

At each sampling site, five mini-ponar sediment samples were collected to obtain replicate samples for sediment toxicity testing. Samples were stored at 4°C until analyzed. Four toxicity tests were conducted, a 10-day survival and growth test with *Chironomus riparius*, a 21-day survival and growth test with *Hexagenia limbata*, a 28-day survival and growth test with *Hyalella azteca*, and a 28-day survival and reproduction test with *Tubifex tubifex*. Methods, except for sediment and water volumes and number of animals per container (see below) followed Day *et al.* (1995) and Borgmann and Norwood (1993). Each separate experiment was conducted with one species and sediment samples from one replicate ponar grab from each sampling site (21 sites) plus two control sediments (Hamilton Harbour and Lake Erie). This was the maximum number of experimental containers that could be processed in one day. A second experiment was

conducted with each species using sediments from a second ponar grab, and a third experiment was conducted with sediment from a third ponar grab for *Hyalella*. Experiments were conducted at 23°C with dechlorinated Burlington City tap water (originating from Lake Ontario, hardness 130 mg/L, alkalinity 90 mg/L, DOC 2.3 mg/L, pH 7.8-8.6) overlying the test sediments.

In initial static bioassays, conducted in beakers with a sediment to water ratio of 1:4, the pH quickly dropped to around 4 in most of the test containers, resulting in high or complete mortality of *Hexagenia* and *Hyalella* in all test sediments except for controls, including Sudbury area, intermediate, and reference sediments. It is assumed that, under aeration, sulfide in sediments from these regions probably became oxidized and resulted in the acidification of the overlying water. This does not occur with sediments from the Great Lakes, and required modification of the test procedure. The rate of drop in the pH was recorded for each of the sediments. Sediments from the most rapidly acidifying containers were then mixed with water in various sediment to water ratios. Mixtures of 1.5% sediment by volume or less resulted in minimal change in overlying water quality; pH values consistently remained above 7.5. All further toxicity tests were, therefore, conducted in polycarbonate Imhoff settling cones, plugged with a #4 silicone rubber stopper. Fifteen mL of sediment and 1 L of overlying water was added to each cone. This resulted in a sediment depth of about 2.4 cm and circular surface of 3.1 cm diameter.

Experiments with varying numbers of *Chironomus* and *Hyalella* were conducted to check for density effects due to the decreased volume of sediment used in the cones. No reductions in survival or growth could be detected even at the highest density tested (15 *Chironomus* or 30 *Hyalella* per container). For all subsequent tests, 15 *Chironomus*, 15 *Hyalella*, 2 *Hexagenia*, or 2 *Tubifex* were added per test chamber. Survival, growth and reproduction for all species in control sediments were comparable to previous test results in beakers.

5.2   Sediment Toxicity and Distance from Copper Cliff

No relationship could be detected between survival or growth of *Chironomus riparius* and distance from Copper Cliff (Figure 5.1, Appendix 3). Survival was variable from site to site, usually ranging from 40 to 100%. Final animal size was between 1 and 4 mg (wet weight). No differences could be detected between Sudbury area, intermediate, or reference sediments. Although sediments from some sites did appear to be toxic (e.g., NEPD), this did not appear to be related to proximity to Copper Cliff.

All *Hexagenia* in the toxicity tests survived except for 1 out of 4 animals in each of RAMD, MCF10, and RICD sediments, and 1 animal in each replicate (2/4 animals overall) of the MFD sediments (Figure 5.1, Appendix 3). All *Hexagenia* exposed to sediments within 12 km of Copper Cliff grew less than those exposed to any other sediment. ANOVA on log transformed growth rates by sediment group (Sudbury, intermediate, reference and control) followed by the Tukey test indicated significantly lower (P<0.001) growth in the Sudbury area sediments than all others, and no significant differences between the other groups.

Sediments collected from lakes within 12 km of Copper Cliff also appeared to be toxic to *Hyalella azteca* (Figure 5.1, Appendix 3). Survival and growth were variable in sediments from intermediate and reference sites, and even between replicates of sediment collected from the same site. In contrast, survival and growth were consistently low in sediments collected near Sudbury. The mean survival at each site averaged across replicates was always greater than 41% at all intermediate and reference sites and in the control sediments, but always less than 32% at any site within 12 km of Copper Cliff (Table 5.1). The mean survival (transformed to log mortality rates) and growth (log final size) were both significantly lower in the Sudbury group of lakes than in either the intermediate or reference lakes, or in control sediments (ANOVA with Tukey test, P<0.01). This is identical to the results obtained with *Hexagenia*. Sediments from RAMD, MCFD, and RICD always resulted in 100% mortality (Table 5.1). Furthermore, at the MCF and RAF sites, sediments from the deep station were more toxic than those from the 10 m station. This is consistent with the higher metal concentrations in the sediments from the deep site of these two lakes (Table 3.4).
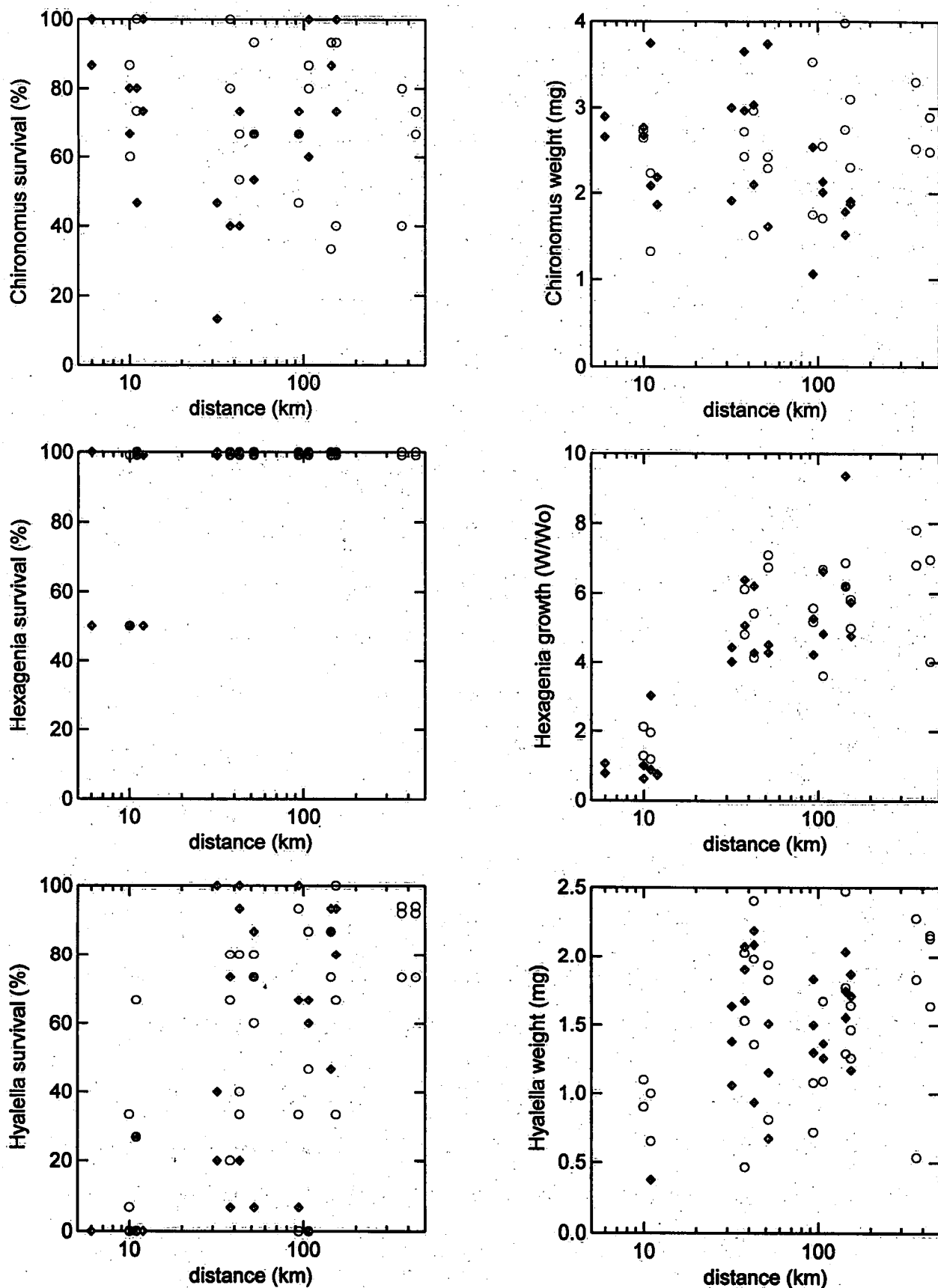
Figure 5.1. Survival and growth (final weight or final/initial weight) of Chironomus, Hexagenia and Hyalella as a function of distance from Copper Cliff, including control sediments. Open circles and solid diamonds are data for 10 m and deep stations respectively.

35

TABLE 5.1. Survival of *Hyalella azteca* as a function of distance from Copper Cliff and station depth (10 m or maximum depth).

Lake	Distance (km)	Percent survival (range)	
		10 m	deep
RAM	6	-	0 (0-0)
MCF	10	13 (0-33)	0 (0-0)
RAF	11	31 (0-67)	9 (0-27)
RIC	12	-	0 (0-0)
NEP	32	-	53 (20-100)
KAK	38	56 (20-80)	51 (7-73)
TRO	43	51 (33-80)	72 (20-100)
LOS	52	71 (60-80)	56 (7-87)
TOM	94	42 (0-93)	60 (7-100)
RES	107	44 (0-87)	42 (0-67)
NOS	144	82 (73-87)	76 (47-93)
TAL	154	67 (33-100)	84 (80-93)
HH1	368	-	87 (73-93)
LE303	443	-	87 (73-93)

Most of the *Tubifex tubifex* survived the toxicity tests. Reproduction was observed in all sediments with both adults surviving. The total number of live young produced was lower in the Sudbury area sediments (P<0.01) and lower in control sediments (P<0.05) than in intermediate or reference sediments (ANOVA with Tukey test). Reproduction in control and Sudbury area sediments was not significantly different (Figure 5.2, Appendix 3). The same general trend was observed for large young retained on a 500 µm screen as for small young passing through the screen, but the total number of young was more sensitive at discriminating between the sediment groups statistically that either large or small young. There were no significant differences among the sediment groups for either empty or full cocoons, except that there were fewer empty cocoons in the control sediments than in the intermediate or reference sediments (P<0.05).
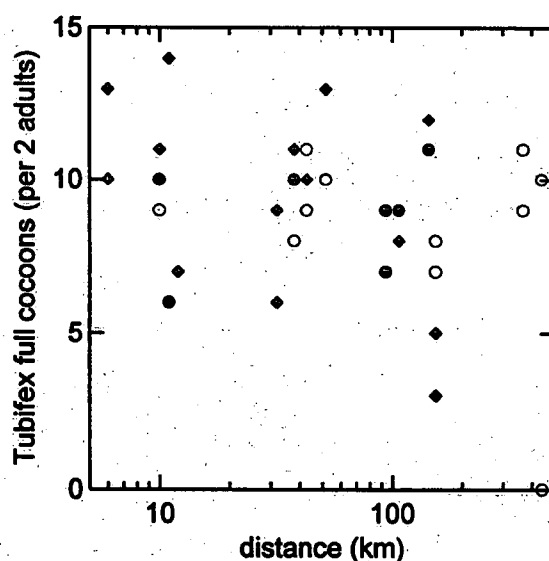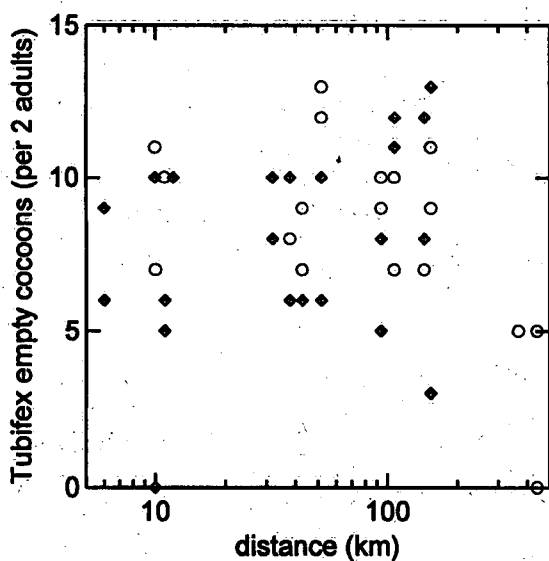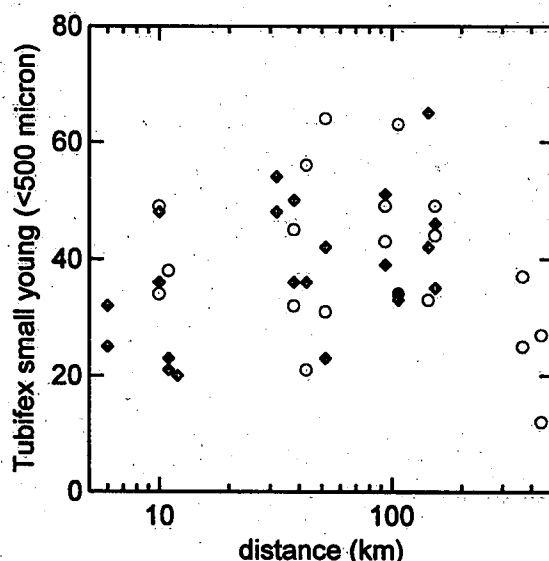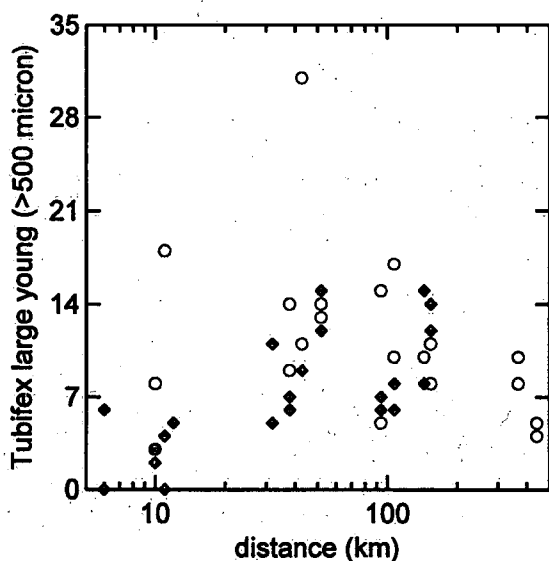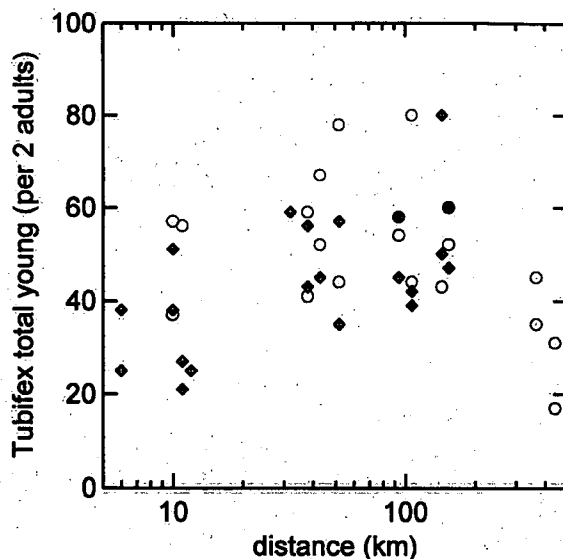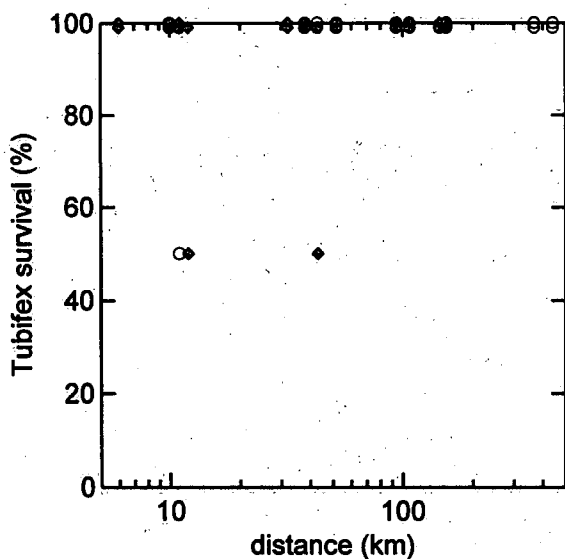
Figure 5.2. Survival, total, large and small young, and empty and full cocoons produced by Tubifex as a function of distance from Copper Cliff, including control sediments. Open circles and solid diamonds are data for 10 m and deep stations respectively.

37

Overall, the toxicity tests results were in good agreement with observations on benthic community structure. There was no observed toxicity to *Chironomus* (Figure 5.1) and abundance of this genus was not limited by proximity to Copper Cliff (Table 4.1). Similarly, *Tubifex* toxicity tests showed only minor reproductive effects in sediments from Sudbury area lakes (Figure 5.2) and oligochaetes were found in two lakes close to Copper Cliff (Table 4.1). Toxicity to the amphipod *Hyalella* was high in Sudbury area sediments (Figure 5.1) and no amphipods were found within 12 km of Copper Cliff (Table 4.1). Furthermore, toxicity to *Hyalella* was higher in sediments collected from the deep stations than at the 10 m stations, suggesting that shallower sediments could be less toxic still. *Hyalella* are, in fact, found in shallow water in all four of the lakes close to Copper Cliff (Watson 1992), in spite of the absence of amphipods in benthos samples from the deep sediments. No mayflies were found at any of the sites sampled, so toxicity to *Hexagenia* in Sudbury area sediments (Figure 5.1) cannot be compared to abundance in the field. However, two genera of Chironomids (*Micropsectra* and *Tanytarsus*) and bivalves were absent from lakes within 12 km of Copper Cliff (Table 4.1), in accordance with the high toxicity of these sediments to *Hexagenia* and *Hyalella*.

A closer examination of the toxicity test data for those parameters which demonstrated a clear difference between the Sudbury area and the other sites suggests that sediments from the Sudbury area can be divided into two groups. Tests with sediments from RICD, MCFD and RAMD resulted in no *Hexagenia* growth (decrease in body weight) and no survival of *Hyalella* (Table 5.2). Sediments from sites RAFD, MCF10 and RAF10 supported slight growth of *Hexagenia*, and some survival of *Hyalella*. Sediment toxicity to *Hexagenia* and *Hyalella* correlates closely with the measured Ni in the overlying water, with one exception; *Hexagenia* growth, if positive $(W/W_0>1)$, was related to loss on ignition. Nickel concentrations in the overlying water exceeded the one week LC50 in waterborne toxicity tests (unpublished data) in all Sudbury area sediments except RAF10, but Cu in water was always well below the one week LC50. This suggests that Ni is more likely the toxic agent than Cu. However, this cannot be concluded definitively because dissolved organic matter originating from the sediment might decrease the toxicity of waterborne Ni, and Cu in the sediment might also contribute to toxicity (i.e., via ingestion). The growth of *Hexagenia*, if positive, is probably affected by food quality, as suggested by the correlation to LOI, and this confounds the toxicity-chemistry relationship. Reproduction by

Tubifex, on the other hand, does not fit into the same pattern as toxicity to *Hexagenia* and *Hyalella*. Reproduction was higher in MCFD sediments and lower in RAFD sediments than expected if RICD, MCFD and RAMD sediments are more toxic than RAFD, MCF10 and RAF10 sediments. *Tubifex*, therefore, appears to respond slightly differently from the other species.

TABLE 5.2. Sediment loss on ignition (LOI), mean Cu and Ni concentration in bioassay water and in sediments, and toxicity to *Hexagenia*, *Hyalella*, and *Tubifex*. Sites are ordered from highest to lowest Ni in the bioassay water.

Site	LOI (%)	Cu in water (μg/L)	Cu in sediment (μg/g)	Ni in water (μg/L)	Ni in sediment (μg/g)	*Hexagenia* growth (W/W$_o$)	*Hyalella* survival (%)	*Hyalella* weight (mg)	*Tubifex* young produced
RICD	16	10	1732	726	3193	0.74	0	-	13
MCFD	28	7	1190	506	5818	0.81	0	-	45
RAMD	12	15	1716	245	2027	0.91	0	-	32
RAFD	24	8	2187	213	2293	1.95	9	0.38	24
MCF10	13	7	1077	123	2016	1.70	13	1.00	47
RAF10	5	7	725	37	874	1.56	31	0.83	43
NEPD-TALD	17-62	0-8	38-251	0-21	51-383	4.22-7.77	42-84	0.90-1.91	41-65

1 week LC50 to *Hyalella* in
waterborne toxicity tests: 140   70

It is possible to use the data in Table 5.2 to compute predicted mean *Hyalella* mortality rates as a function of distance from Copper Cliff under the assumption that mortality is proportional to Ni in the overlying water during the toxicity test. Mortality rates can be computed from

$$m = m' + m'' = m' + a'' \text{ (Ni in water)}^n \qquad (3)$$

where m = -log(fraction of animals surviving)/time in weeks, m' is the control or reference mortality rate, m'' is the mortality rate correlated to Ni in the toxicity test water, and a'' and n are constants. Using the mean survival in the reference sediments (61.94%) to compute m', this

gives estimates of 0.485, 0.384 and 0.172/wk for m" for survival rates of 9, 13, and 31% after four weeks respectively. Additionally, an approximate minimum mortality rate can be estimated for the lowest Ni concentration giving 0% survival by assuming that 0.5 animals survived out of 45 (3 replicates of 15 animals each). This gives an m" of 1.005/wk at Ni = 245 μg/L. Log-log regression of m" against Ni in water gives

$$\log(m") = 0.786 \log(\text{Ni in water}) - 2.02 \tag{4}$$

with an R^2 of 0.87. A similar regression of m" against Ni in sediment gives an R^2 of only 0.64. This is lower, as expected if metal bioavailability from sediments is more variable than from overlying water. For sediments from the six sites near Sudbury, a log-log regression of Ni in toxicity test water against Ni in sediment gives

$$\log(\text{Ni in water}) = 1.623 \log(\text{Ni in sediment}) - 3.126 \tag{5}$$

with an R^2 of 0.83. Combining equations 3-5 with equation 1 for Ni in surface sediments as a function of distance from Copper Cliff, using the coefficients in Table 3.2, allows computation of average percent survival expected as a function of distance from Copper Cliff. The predicted survival, relative to the reference lakes (i.e., survival/0.6194), is 9% at 10 km, 51% at 25 km, 90% at 50 km and 98% at 100 km from Copper Cliff. Alternatively, the predicted distance to a survival of 50% in four weeks is 25 km, 75% is 36 km and 90% is 49 km, relative to the reference lakes. The average survival in the intermediate lakes (56.39%), divided by mean survival in the reference lakes (61.94%) was 91%, in approximate agreement with the predicted survival at a distance of 50 km. However, this difference was not sufficient to be statistically significant. These are average mortalities since survival in sediments from any given lake will depend to some degree of local geochemistry and other parameters affecting total Ni and Ni bioavailability. These estimates are based on the assumption that survival is correlated to Ni in the toxicity-test water. This should not be taken to imply that Ni is necessarily the cause of toxicity. Furthermore, prediction of mortality rates at distances in excess of 12 km from Copper Cliff must be interpreted with extreme caution, because these are based on extrapolation of equations 3-4 beyond the range over which reliable data were available.

6. METAL SPECIATION IN RELATION TO SEDIMENT TOXICITY
T.A. Jackson and N. Nguyen

6.1. Approach to the Problem, and its Scientific Rationale

The biological uptake, bioaccumulation, and adverse or beneficial biological effects of heavy metals in aquatic environments depend on the relative bioavailability of different forms of the metals and the concentrations of these bioavailable forms in different compartments of the water and surficial bottom sediments. The bioavailability, bioaccumulation, and biological effects of metals are functions of metal speciation and the binding and release of metals by complexing agents and sorbents in the environment. These processes, in turn, are controlled or affected by a wide range of physical, chemical, and biological factors, including sulfides, iron and manganese oxyhydroxides, clay minerals, humic substances, labile organic matter, pH, dissolved salts, water hardness and alkalinity, Eh, dissolved O_2, primary productivity, and a complex assortment of microbial activities and other specific biological processes, as well as the fundamental properties of the metals themselves (ionization potentials, electronegativity, etc.). Hence, biological consequences of heavy metal pollution, such as bioaccumulation of the metals and various toxic effects (including inhibition of enzymes and impairment of growth, reproduction, and other vital functions, as well as death), in aquatic environments are likely to be much more significantly correlated with the concentrations of bioavailable forms of the metals and the environmental and biological variables which affect bioavailability than with the total concentrations of the metals in the water and sediments. Furthermore, fine-grained sediments, which bind and accumulate heavy metals introduced into aquatic environments, are the chief repositories and secondary sources of these metals in bodies of water. Consequently, the authors are investigating the forms and bioavailability, as well as total concentrations, of heavy metals in fine-grained contaminated bottom sediments in relation to sediment properties, environmental variables, and toxic effects of the sediment-bound pollutants on benthic microbes and animals. As the geographical extent of the ecological damage caused by the pollution is a matter of serious concern, the authors are also comparing lake sites located at different distances from the INCO smelter.

6.2. Materials and Methods

Sediment samples consisted of triplicate specimens of the top 5 cm of sediment from each site. The sediment samples were collected with a box corer and then transferred to plastic bags with exclusion of air. The sediments consisted of mud varying in colour from very dark brownish grey (nearly black) to greyish brown. One of the subsamples from each site was immediately frozen, and the other two were stored at 4°C. Analysis of material kept at 4°C began shortly after the samples were brought back from the field. Only a brief outline of the laboratory techniques will be given here. More detailed descriptions of the methods can be made available on request. Samples stored in their native state at 4°C were used for all analyses listed below except where otherwise indicated. The analyses were done in duplicate.

The pH and Eh of the sediment were measured using a pH meter, and the moisture content was estimated by measuring loss of weight on heating at 105°C. Pore water was separated from the solids by centrifuging weighed sediment samples and collecting the supernatants. Humic matter in the pore water specimens was analyzed by UV-visible spectrophotometry, and the Cu, Zn, Cd, Hg, Pb, Ni, Cr, Fe, and Mn concentrations of the water were determined by atomic absorption spectrophotometry (AAS) following stabilization of the samples with suitable preservatives (BrCl for Hg, and HNO_3 for all other metals); the Hg analyses were performed by cold vapour AAS preceded by reduction of Hg(II) to Hg(0) by $SnCl_2$. The spun-down solid fraction of the sediment was rinsed with N_2-purged water and then subjected to sequential solvent extractions to isolate different operationally defined forms of heavy metals using methods similar to those of Gupta and Chen (1975), Tessier *et al.* (1979), Jackson (1988), and Jackson *et al.* (1995). The solvents and solvent mixtures, listed in the order in which they were used (with the theoretically expected, though as yet ill-defined, nature of the metal species in brackets) were as follows:

1. N_2-purged 0.5 M $CaCl_2$ [weakly sorbed, "exchangeable" species; regarded as readily bioavailable];

2. N_2-purged Na acetate/acetic acid (NaAc/HAc) at pH 5 [carbonate-bound species and some oxide- and oxyhydroxide-bound species, possibly accompanied by some fulvic acid

complexes; more strongly bound than the $CaCl_2$-extractable fraction but could be relatively bioavailable];

3. N_2-purged $NH_2OH \cdot HCl/HNO_3$ at pH 1.7 [strongly bound by easily reduced "amorphous" Mn and Fe oxides and oxyhydroxides owing to "specific sorption" and coprecipitation; this fraction may include some humic complexes solubilized during extraction];

4. hot H_2O_2/NH_4 acetate (Ac)/HNO_3 [strongly bound by organic matter and sulfides];

5. citrate/dithionite [strongly bound by less easily reduced, more crystalline Fe and Mn oxides and oxyhydroxides].

All extracts were analyzed for Cu, Zn, Cd, Hg, Ni, Cr, and Pb; in addition, extracts 3, 4, and 5 were analyzed for Fe and Mn. Metal content was determined by AAS techniques and calculated as extractable metal per unit dry weight of sediment (Appendix 4). Fractions 1 and 2 - especially 1 - are assumed to be much more readily available to organisms than fractions 3, 4, and 5. In any case, this is probably true of single-celled organisms, such as bacteria and algae, which take up substances from their surroundings solely by absorbing dissolved substances through the cell membrane. All of the extractable fractions could be largely or completely available to benthic animals that ingest sediment particles (Jackson *et al.*, 1995).

On completion of the analyses of sediment samples stored at 4°C, frozen samples were thawed and subjected to additional analyses. Percent loss on ignition was measured, and humic matter was extracted under N_2 with N_2-purged 0.1 M NaOH (Jackson, 1988), whereupon the extracts were subjected to UV-visible spectrophotometry (Schnitzer and Khan, 1972; Pennanen, 1975; Salfeld, 1975; Chen *et al.*, 1977; Aiken *et al.*, 1985) followed by determination of Cu, Ni, and Fe content. (Note: Loss on ignition, though commonly used as an estimate of the organic content of sediments, is an ambiguous and unreliable parameter, because dehydroxylation of clay minerals and oxyhydroxides may affect the results; consequently, organic C is probably a more satisfactory parameter, although it, too, has limitations, as different kinds of organic matter differ in C content.) Total nonvolatile sulfide was determined by digesting sediment samples with hot N_2-purged 6 M HCl to volatilize the sulfide as H_2S and then trapping the gaseous sulfide by bubbling it through N_2-purged Zn acetate solution to convert it to ZnS, reacting the ZnS with

other reagents to form a coloured aqueous complex, and measuring the concentration of the complex in solution by colorimetry.

6.3. Results and Tentative Interpretations

6.3.1. Variations in the concentrations of heavy metal fractions in sediments with distance from the smelter

As would be expected, the total solvent-extractable Cu and Ni fractions in the surface sediments, together with the concentrations of Cu and Ni in pore water, show a sharp exponential decline with distance from the INCO smelter, reaching background levels at distances on the order of ~50-100 km (Figure 6.1, A-D). The NaAc/HAc-, $H_2O_2/NH_4Ac/HNO_3$-, and NaOH-extractable fractions display essentially the same trend (Appendix 4), as do the total Cu and Ni concentrations in the sediments and the SO_4^{2-} content of the water (Figures 2.3 and 3.1). These results are not at all surprising, as Cu, Ni, and oxidized S compounds are the major contaminants emanating from the smelter (unpublished INCO survey data; T.C. Burnett, personal communication). The observed trends clearly reflect a progressive decline in the deposition rates of airborne pollutants with distance from the principal source of pollution.

Similarly, $CaCl_2$-extractable Cu and Ni, the most loosely bound and hence, presumably, the most readily bioavailable Cu and Ni fractions, tend to vary inversely with distance from the smelter. However, the correlation between $CaCl_2$-extractable Cu and distance (Figure 6.2A) is relatively weak owing to an exceptionally large amount of seemingly random scatter, and the range of $CaCl_2$-extractable Cu concentrations is rather small (~0.3-0.9 µg/g at the deep sites). Much of the variation in the $CaCl_2$-extractable Cu data is probably attributable to local variations in environmental factors (as discussed more fully below), whereas relatively little of it is due to the decrease in the rate of Cu deposition with distance from the smelter. $CaCl_2$-extractable Ni shows much less random scatter and generally closer agreement with the major Cu and Ni fractions (see above) than $CaCl_2$-extractable Cu does, besides being two orders of magnitude more abundant (Figure 6.2B). Nevertheless, it is anomalous in one respect: Among the four lakes situated within 12 km of the smelter, the $CaCl_2$-extractable Ni content of sediments in the lake closest to

44
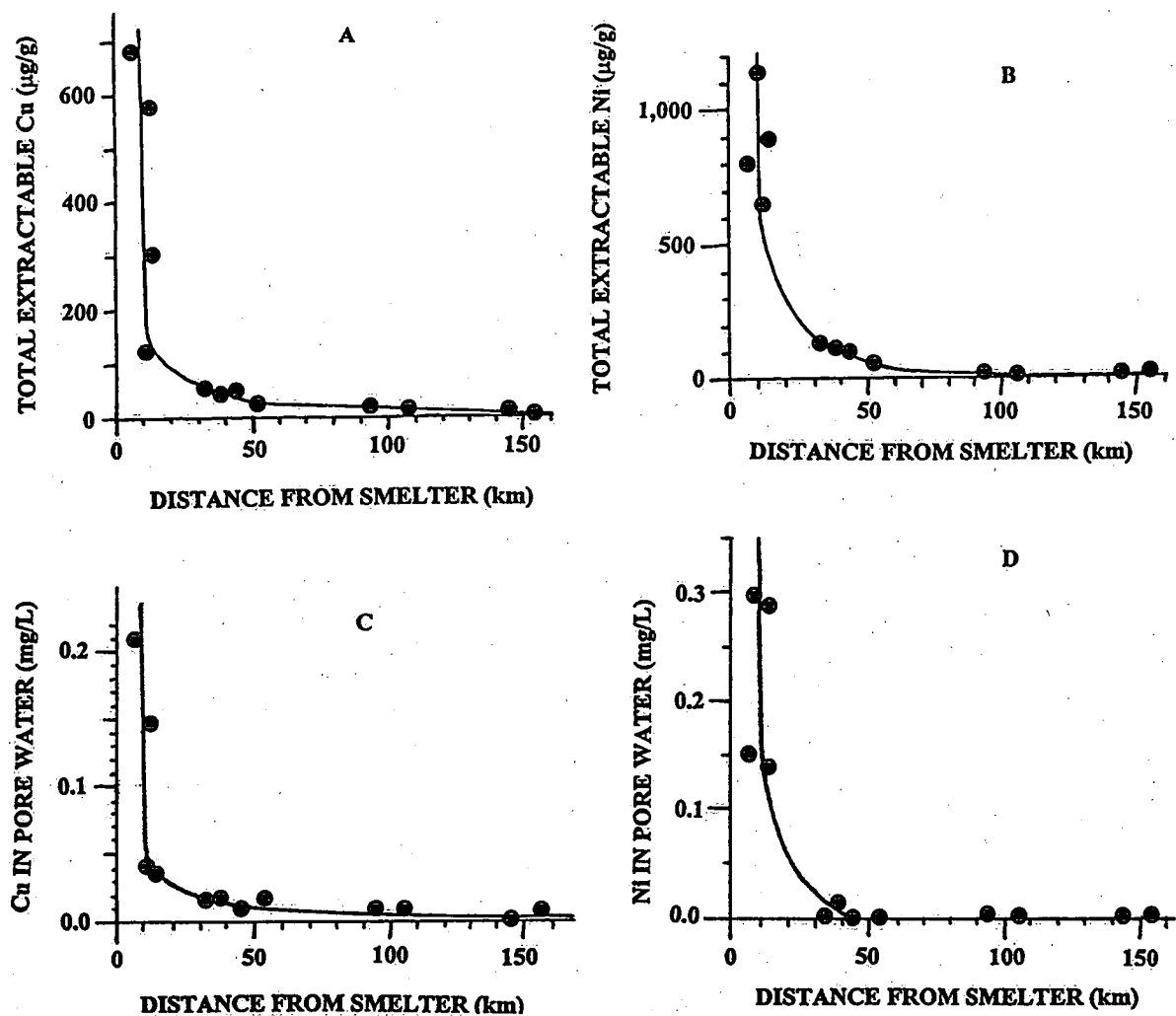
Figure 6.1. The total solvent-extractable Cu and Ni content of sediments from deep sites (A and B, respectively), and the concentrations of Cu and Ni in the sediments' pore water (C and D, respectively), plotted against distance from the smelter.
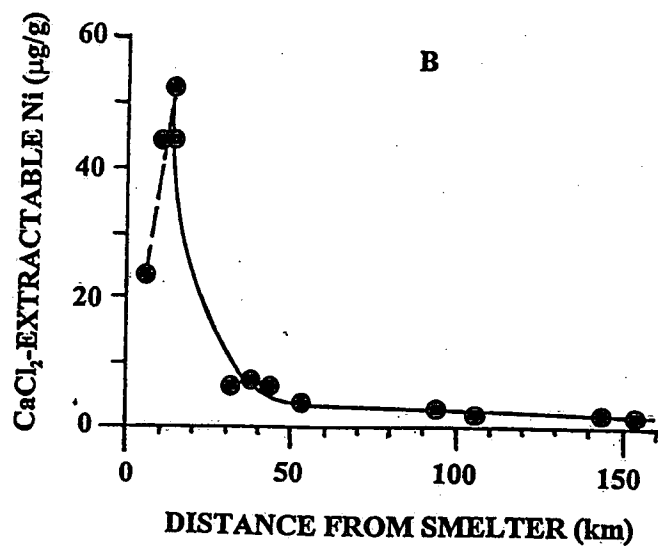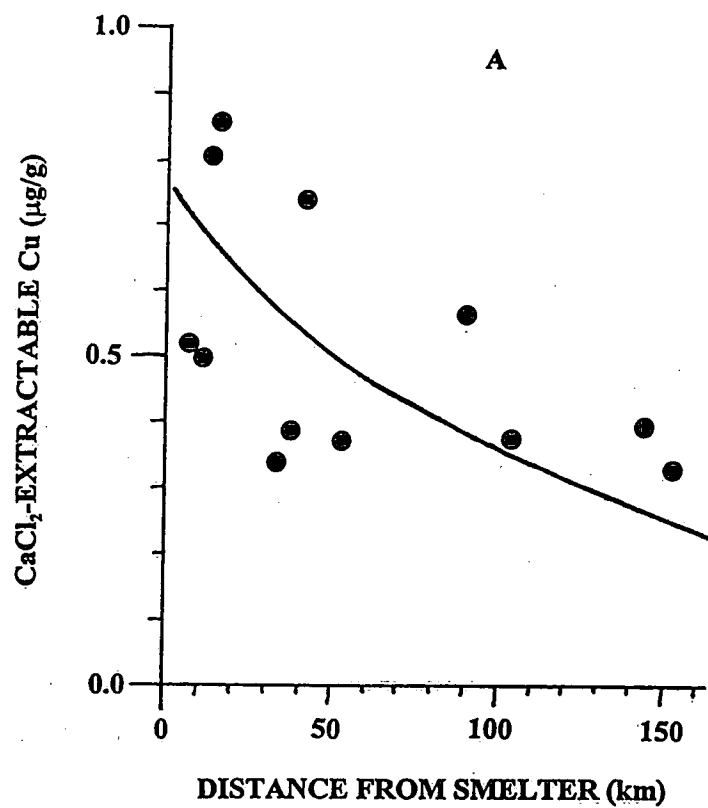
Figure 6.2. The concentrations of $CaCl_2$-extractable Cu and Ni (A and B, respectively) in sediments from deep sites plotted against distance from the smelter.

the smelter is aberrantly low; consequently, with increasing distance from the smelter the $CaCl_2$-extractable Ni concentration first rises sharply to form a maximum ~11-12 km from the smelter before plunging to uniformly low values further away. Evidently variation in the $CaCl_2$-extractable Cu or Ni content of sediment with distance from the smelter is a function of both the gross rate of metal deposition (which declines progressively outward from the smelter, establishing the basic trend) and the net effect of local environmental conditions on metal binding (a more complex and patchy process which modifies the trend, partly obscuring it in the case of Cu).

In contrast to the major extractable Cu and Ni fractions, the corresponding fractions of Hg, Cd, Zn, Pb, and Cr did not vary systematically with respect to distance from the smelter (Appendix 4). This undoubtedly reflects the fact that these metals, unlike Cu and Ni, are quantitatively negligible as smelter contaminants. (Moreover, what little Hg is discharged from the smelters is probably to a large extent dispersed in the atmosphere as $Hg(0)$ gas as well as particulate $Hg(II)$ and is transported far away.) From this point on, therefore, we will focus on the principal heavy metal pollutants, Cu and Ni, and say nothing further about the other heavy metals.

6.3.2. The partitioning of Cu and Ni among different solvent-extractable sediment fractions

In bottom sediments at all sampling sites, by far the greatest proportion of the sequentially extracted Cu or Ni is in the $H_2O_2/NH_4Ac/HNO_3$-extractable fraction, although measurable quantities of the metals were found in all or most of the other fractions as well (Figure 6.3, A-D). The NaOH-extractable Cu and Ni fractions are comparable in magnitude to the $H_2O_2/NH_4Ac/HNO_3$-extractable fractions (Appendix 4), as would be expected if the organic matter consisted chiefly of humic substances. Evidently the bulk of the sediment-bound Cu and Ni species are strongly bound to organic matter and sulfides, and most of it is in the form of humic complexes. The organic-and-sulfide fraction, being resistant to mobilization by mild extractants such as 0.5 M $CaCl_2$, is probably not readily available for uptake by organisms, with the possible exception of benthic animals that ingest sediment particles and may subsequently solubilize bound metals during digestion and absorb them through the gut wall (Jackson *et al.*, 1995). By
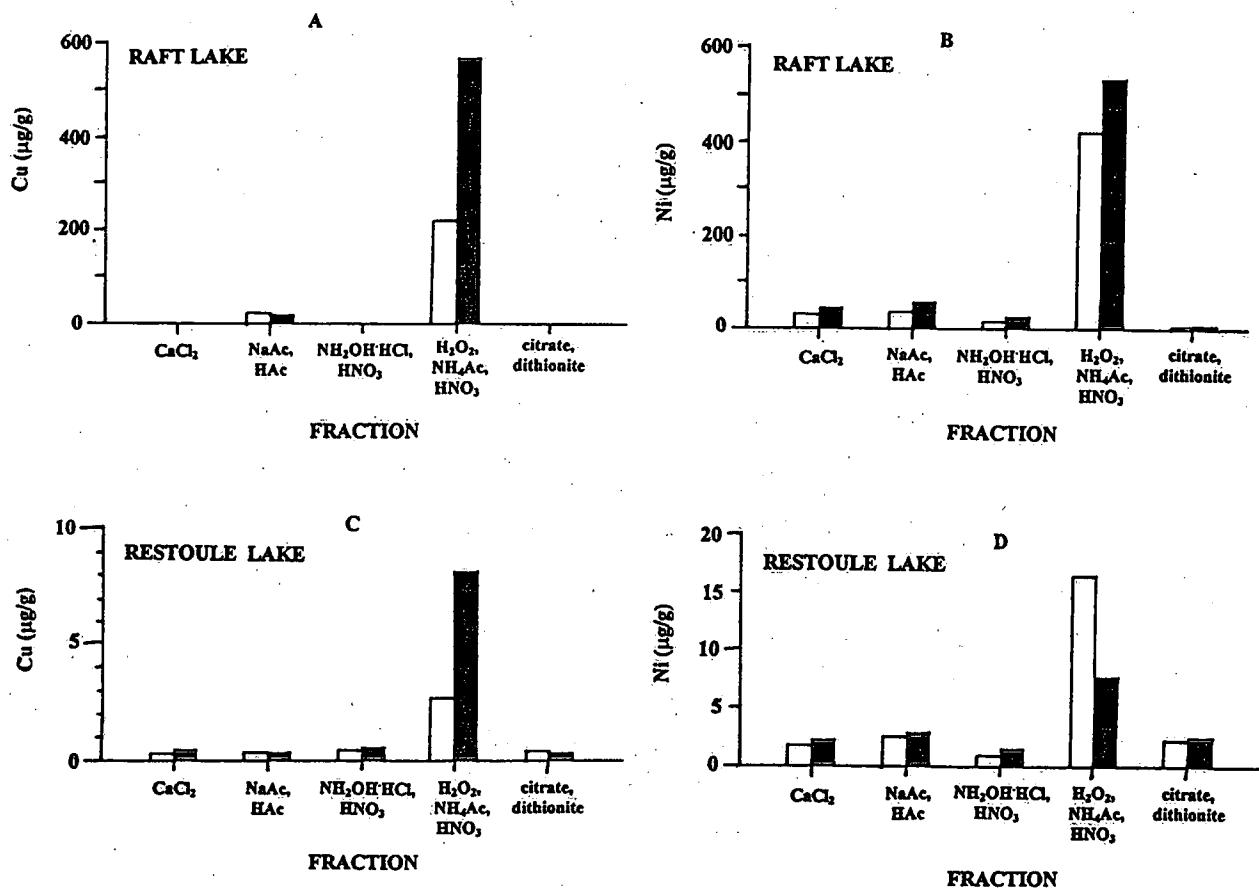
Figure 6.3. The concentrations of different solvent-extractable Cu and Ni fractions in sediments from the deep sites (black bars) and 10 m sites (white bars) of Raft Lake (A and B) and Restoule Lake (C and D).

comparison, very little Cu or Ni appears to be associated with Fe and Mn oxides and oxyhydroxides. This distribution is consistent with the Eh values [oxidation-reduction potentials] and sulfide concentrations of the sediments (Appendix 4). The Eh values were invariably negative, indicating that reducing conditions prevailed in the sediments at all of the sampling sites, even though the bottom water contained abundant dissolved O_2 (Figure 2.1), and all samples contained measurable quantities of sulfide. (In sediments from the deep sites, sulfide gave a highly significant inverse correlation with Eh, as would be expected [Appendix 4].) The small amounts of oxide- and oxyhydroxide-bound Cu and Ni (possibly including NaAc/HAc- as well as NH_2OH·HCl/HNO_3- and citrate/dithionite-extractable species) may well be localized in a thin oxidized zone at the sediment-water interface (the interface between the zones of oxidizing and reducing conditions). The weakly sorbed $CaCl_2$-extractable Cu and Ni fractions are probably distributed amongst cation exchange sites of organic (mainly humic) matter, oxyhydroxides, and clay minerals. These fractions, however, make up no more than a small proportion of the total Cu and Ni or even the total solvent-extractable Cu and Ni although the proportion tends to increase with distance from the smelter (compare Figures 6.3A & 6.3B with Figures 6.3C & 6.3D, respectively; also, see next section). Judging from the distribution of the metals amongst the different solvent-extractable fractions (Figure 6.3, A-D), along with well established general principles (Jackson, 1998), it is probable that the Cu and Ni associated with organic matter, oxyhydroxides, and <u>edge</u> faces of clay are, in large part, strongly bound by "surface complexation" ("specific sorption") and are not easily dissociated and taken up by organisms - except, perhaps, inside the intestines of deposit-feeding benthic animals, as mentioned above (Jackson et al., 1995). Besides, much of the Cu and Ni associated with oxyhydroxides and FeS may be inaccessible to organisms because the metals were sealed inside these mineral deposits through coprecipitation.

6.3.3. Effects of smelter emissions on Cu and Ni speciation and related environmental factors

We have seen that the concentrations of the major solvent-extractable Cu and Ni species in the sediments, the total Cu and Ni concentrations in the sediments and pore water, and the SO_4^{2-} content of the lake water decrease progressively, as would be expected, with increasing distance

from the smelter. In contrast, the percentages of the total solvent-extractable Cu and Ni fractions which are in the form of $CaCl_2$-extractable species (hereafter designated $%CaCl_2$-Cu and $%CaCl_2$-Ni for brevity) <u>increase</u> with distance from the smelter (Figure 6.4, A & B). Thus, the proportion of weakly bound, easily desorbed metal species to more strongly bound species (in other words, the relative bioavailability of the metals) tends to be lowest in the most severely polluted lakes (the ones closest to the smelter) and highest in the least polluted lakes (the ones farthest away), suggesting that the harmful biological effects of the pollutants have been mitigated to some extent by environmental changes caused directly or indirectly by the pollutants themselves.

As uncritical use of compound variables can lead to misinterpretations and errors, it is necessary to digress briefly at this point to ponder the actual meaning of the observed variations in $%CaCl_2$-Cu and $%CaCl_2$-Ni. The $%CaCl_2$-Cu and -Ni values were obtained by multiplying the $CaCl_2$-extractable Cu and Ni concentrations by 100 and dividing by the corresponding total solvent-extractable Cu and Ni concentrations, respectively; therefore, the variations in these values are to a greater or lesser extent attributable to the previously described variations in the total extractable Cu and Ni data (Figure 6.1, A & B), especially the H_2O_2/NH_4Ac/HNO_3-extractable species, which make up the dominant extractable fractions. Since total extractable Cu and Ni decrease with distance from the smelter, their reciprocals automatically show equal but opposite trends; and since the total extractable metal concentrations vary over a much wider range of values than the $CaCl_2$-extractable fractions, their variations are largely responsible for the observed variations in the percentage $CaCl_2$-extractable metal data. Thus, it is primarily because the total solvent-extractable Cu and Ni concentrations <u>decrease</u> with distance from the smelter that the $%CaCl_2$-Cu and -Ni values <u>increase</u>. Nevertheless, the trends showing that $%CaCl_2$-Cu and -Ni increase with distance are not to be dismissed as mathematical artefacts created by questionable use of compound variables: They have physical meaning and reveal real information about metal binding and bioavailability. (If the sedimentary environments and the forms of the sediment-bound metals were constant throughout the field area, all the $%CaCl_2$-Cu and $%CaCl_2$-Ni values would be the same within the bounds of analytical error, and the curves shown in Figure 6.2 would be horizontal. As that was not the case, it follows that not only the total extractable Cu and Ni but also the factors that determine the relative bioavailability of the
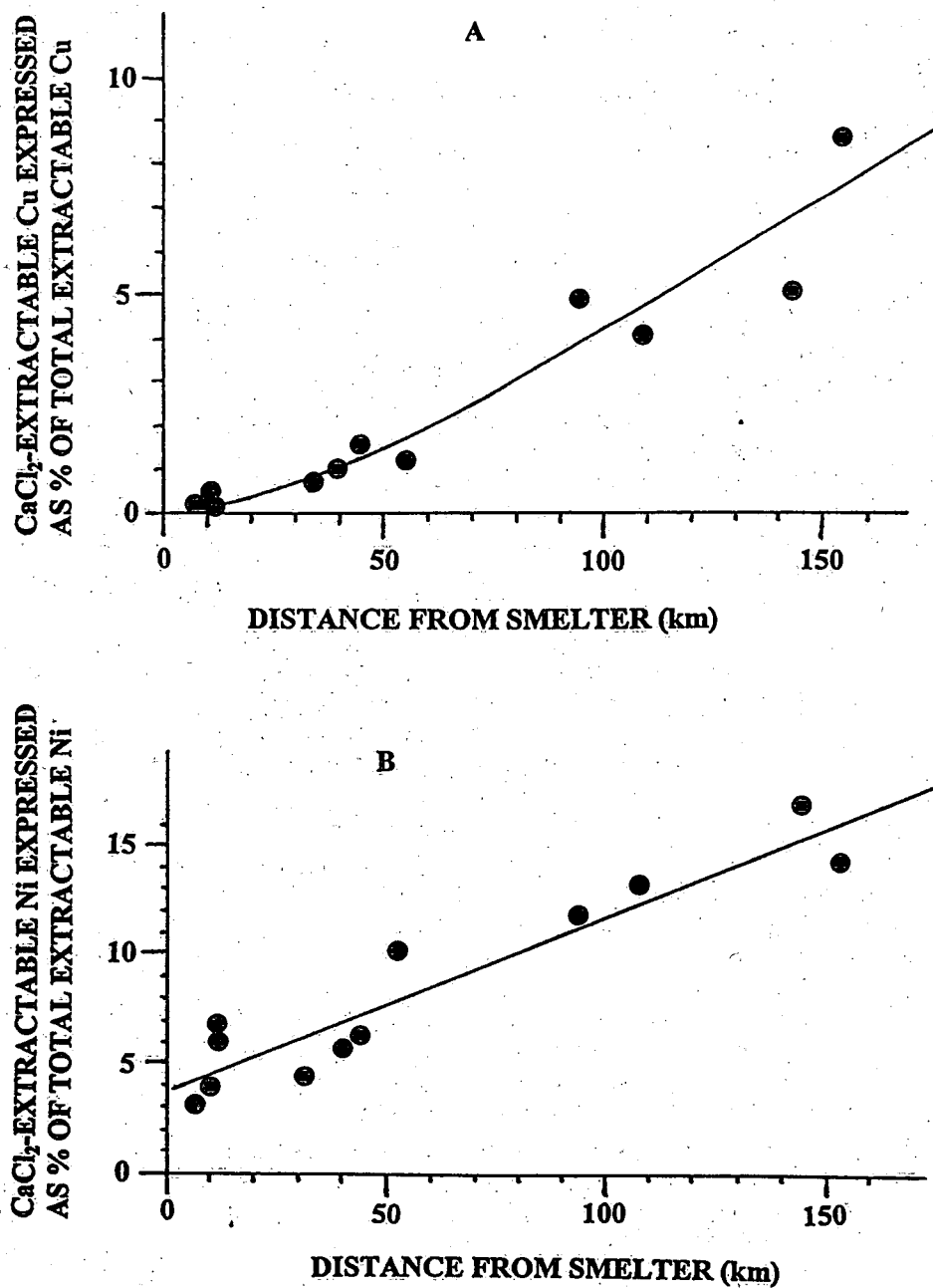
Figure 6.4. The percentages of the total solvent-extractable Cu and Ni in deep-site sediments that are in the form of CaCl$_2$-extractable species plotted against distance from the smelter (A and B, respectively).

Cu and Ni vary systematically with distance from the source of pollution. Furthermore, the solubility of Cu and Ni salts in water was not a limiting factor: According to information from the *Handbook of Chemistry and Physics*, $CaCl_2$ extraction would, in theory, have removed all the Cu and Ni, even from the most metal-rich sediments, if the metals had been in the form of Cu(II) and Ni(II) chlorides and sulphates and had not been bound by specific sorption sites on the sediment particles.) Thus, %$CaCl_2$-Cu and -Ni are useful measures of bioavailability, but to interpret their variations properly, one must know the relative contributions made by the simple variables of which they are composed. In the present case, it would seem that the differences between the values obtained for different lakes are due mainly to variations in the concentrations of the more strongly bound (less bioavailable) forms of Cu and Ni (notably $H_2O_2/NH_4Ac/HNO_3$-extractable Cu and Ni) rather than variations in the concentrations of $CaCl_2$-extractable (relatively bioavailable) Cu and Ni species: Thus, the progressive increase in the percentage of $CaCl_2$-extractable Cu and Ni species with distance from the smelter is attributable to a drop in the abundance of strongly bound, relatively unavailable metal species; it was not caused by an increase in the abundance of weakly bound, readily available species. This interpretation leads to the conclusion that the sedimentary Cu and Ni in the lakes closest to the smelter have the highest proportions of strongly bound metal species owing either to environmental changes caused by smelter pollutants or to special properties of the smelter particles that settle out closest to the source, or both.

Now let us consider possible reasons for the observed trends. One is that the coarsest particles in the smelter plumes settle out closest to their source, whilst the finest ones are transported farthest. This hypothesis is based on the premise that many of the Cu- and Ni-bearing smelter particles that settled out have remained intact in the sediments and that Cu and Ni are less readily dissolved from the coarser particles than from the finer ones by relatively mild reagents like 0.5 M $CaCl_2$, owing, perhaps, to the greater specific surface of finer particles, entrapment of Cu and Ni inside the larger particles, and the well known fact that metal cations in larger mineral particles are generally less soluble than metal cations in smaller particles of the same material because they are more strongly bound by the anions to which they coordinated (Blaedel and Meloche, 1963). Possibly the electron microscopic examination and energy dispersive X-ray microanalysis of selected sediment samples, which is currently underway, will help to resolve this

question. Another possibility, which is consistent with a body of indirect chemical evidence, is that the smelter emissions alter local environmental conditions, biological activities, and biogeochemical processes in ways that influence the forms of the metals, lowering their bioavailability. The following lines of chemical evidence are particularly telling: The concentrations of SO_4^{2-} in bottom water (Figures 2.3 and 2.4) and the Mn/Fe ratios of sediment pore water at deep sites (Figure 6.5A) are exceptionally high in the four lakes closest to the smelter, and Fe levels in the deep-site pore water of these same lakes are very low (Appendix 4), whereas lakes further away have relatively SO_4^{2-}-poor bottom water and Fe-rich pore water with low Mn/Fe ratios. The abundance of SO_4^{2-} (one of the principal pollutants from the smelter) probably stimulates the growth of SO_4^{2-}-reducing bacteria, resulting in precipitation of Fe as FeS accompanied by immobilization of Cu and Ni owing to coprecipitation and sorption by FeS and binding by thiols. This could account for the relative abundance of the less bioavailable forms of Cu and Ni in the immediate vicinity of the smelter. The high Mn/Fe ratios in the pore water are consistent with this theory, as reducing conditions and sulfide production promote solubilization of Mn whilst removing dissolved Fe (Jackson and Bistricki, 1995). The sulfide data (Appendix 4) are not consistent with this interpretation, as they are independent of distance from the smelter, but this does not rule out the possibility that SO_4^{2-}-reducing bacteria are most active, and are exerting specific effects on metal availability (e.g., by producing certain metal-sequestering thiols), in the SO_4^{2-}-enriched environments with high Mn/Fe ratios situated closest to the smelter.

Other varieties of microbial activity besides SO_4^{2-} reduction could play direct and indirect roles in controlling metal bioavailability. If microbial activities and other biological processes in the lakes of the study area tend to promote mobilization of sediment-bound Cu and Ni (for instance, by producing complexing agents and acids and by liberating the metals from decomposing remains of aquatic and benthic organisms), thereby enhancing their bioavailability, then inhibition of microbes and other organisms by toxic smelter emissions could cause the bioavailability of Cu and Ni to be relatively low near the smelter and higher farther away. (Of course, organisms may immobilize heavy metals as well as mobilizing them under both oxidizing and reducing conditions, as occurs, for example, when microbes mediate precipitation of highly insoluble metal-binding agents such as FeOOH and MnOOH and, as mentioned above, FeS. Many
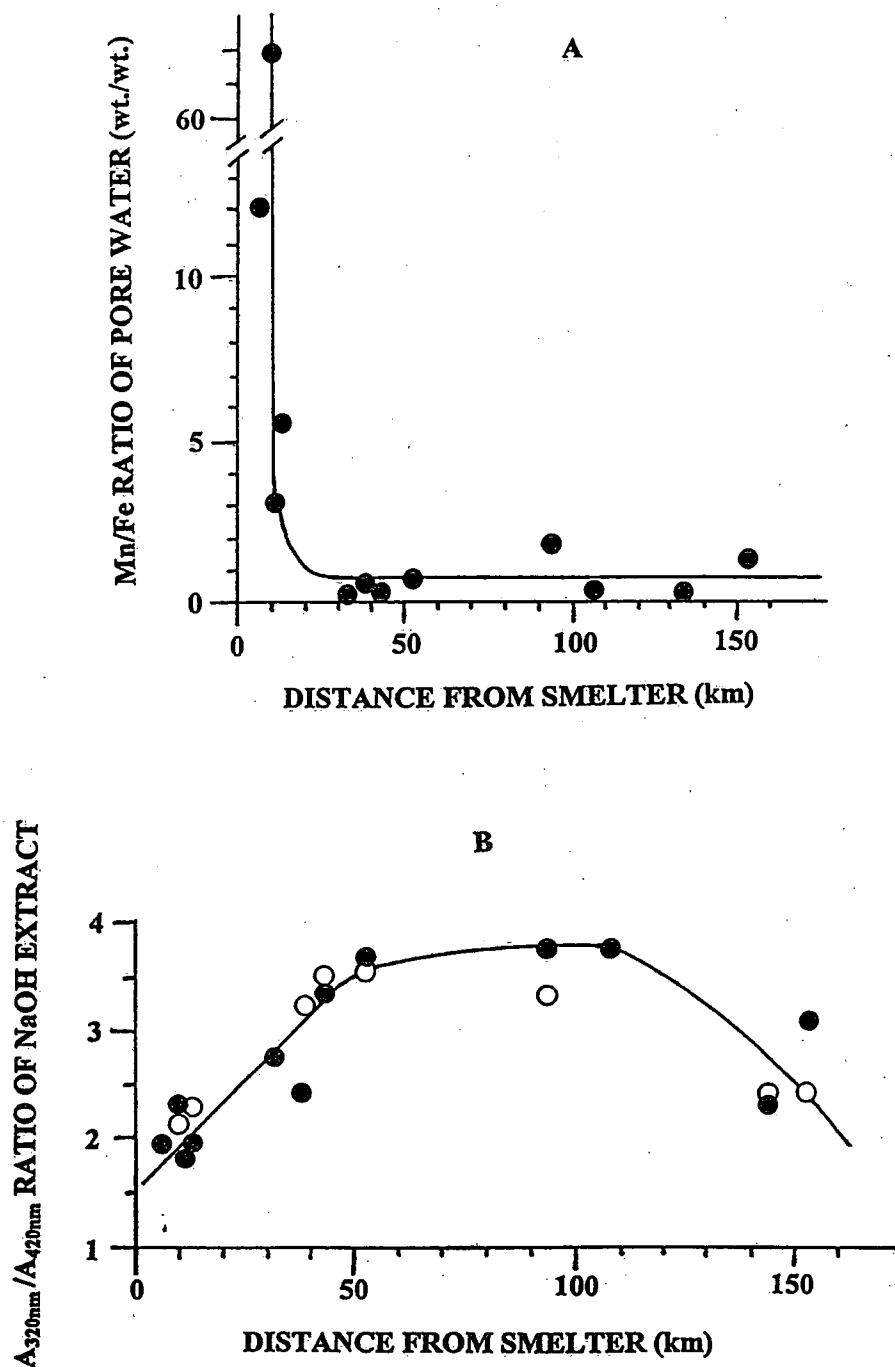
Figure 6.5. Variations in the Mn/Fe ratio of sediment pore water (A) and the A_{320nm}/A_{420nm} ratio of NaOH-extractable sedimentary humic matter (B) with respect to distance from the smelter. Explanation of symbols: deep sites, ● ; 10 m sites, o.

processes may occur simultaneously, and the <u>net</u> effect may vary with environmental conditions, owing in part to ecological succession in the microbial community.)

The nature of the sedimentary humic matter may also be an important factor in bioavailability, and it is linked to the Mn/Fe ratio and other chemical parameters that are affected by the smelter emissions. Unexpectedly, certain spectral properties of the sedimentary humic matter were found to vary systematically as a function of distance from the smelter. Thus, with increasing distance, the UV-visible absorbance ratio A_{320nm}/A_{420nm} of the NaOH-extractable fraction of the sediment rises, levels off, and then comes back down (Figure 6.5B). ("A" stands for absorbance at the wavelength indicated by the subscript.) The A_{465nm}/A_{665nm} ratio (usually called E_4/E_6 in the literature) shows a similar pattern of variation but with much more scatter (not shown). Note that the highest A_{320nm}/A_{420nm} values (the ones that make the "plateau" in the curve) represent the four lakes whose waters are poorest in dissolved Ca (W. Keller, unpublished data); the possible significance of Ca is discussed in another section (see below). These observations are of considerable interest, as absorbance ratios such as these reflect inherent characteristics of the humic substances (properties such as molecular size, structure, and composition, which depend on the nature of the starting material and the environment of formation) but are independent of the concentration of humic matter. (The ratios are also known to vary with ambient pH, but the pH in this case was presumably constant, as all the humic extracts were dissolved in 0.1 M NaOH.) In general, the absorbance ratios decrease with increasing molecular size (i.e., increasing degree of "humic acid," as opposed to "fulvic acid," character) and increasing degree of humification (i.e., maturity), and humic matter formed in aquatic environments tends to have higher values of these ratios than humic matter generated in soil (Schnitzer and Khan, 1972; Pennanen, 1975; Chen, 1977; Aiken *et al.*, 1985). The observed relationship, therefore, between A_{320nm}/A_{420nm} ratio and distance from the smelter suggests that pollutants in the smelter emissions have a marked effect on the processes which determine the properties of the sedimentary humic matter.

A possible explanation for the change in A_{320nm}/A_{420nm} values with distance from the smelter is that the proportion of autochthonous humic substances to allochthonous ones increases away from the smelter because of the corresponding decrease in the severity of pollution (Figure 6.1) and

consequent abatement of inhibitory effects of the pollutants on biological activities in the lakes. (The autochthonous component of the humic matter in lakes is formed *in situ* from decomposing remains of aquatic organisms [notably phytoplankton], whereas the allochthonous component, which is quantitatively important in Boreal forest lakes such as those of Northern Ontario, is formed in soil from remains of terrestrial organisms [mostly forest vegetation] and transported into the lakes by streams and runoff.) The observed effect could result from inhibition of the organisms whose decomposing remains comprise the raw material of humic matter or the microbes that decompose the labile organic matter and produce the humic matter, or both. If this interpretation is correct, environmental conditions in the lakes are essentially normal at a distance of 50 km or more from the smelter insofar as the overall production of aquatic biomass and its partial conversion to humic matter by microbial activity are concerned, although particularly sensitive species could still be adversely affected. Another possible reason for the apparent effect of smelter emissions on the A_{320nm}/A_{420nm} ratio is that the spectral properties of the humic matter were altered by the complexing of large quantities of metals in the most severely polluted lakes in the vicinity of the smelter; humic matter is known to be subject to "auxochrome" effects of this nature caused by variations in their chemical environment. This idea could be tested experimentally at some future time.

Thus, there are several possible causes of the observed effect, and more information is needed to find the correct explanation. Furthermore, we do not yet understand why the curve comes back down beyond a distance of 100 km. This probably represents natural variation in the local source material or conditions of humification and is irrelevant to the smelter problem. Evidence to be presented further on (see below) suggests that the observed geographical variation in the properties of humic matter affects the bioavailability of the metals owing to related variation in the stability of metal-humic complexes. In any case, the fact that most of the extractable Cu and Ni are strongly bound by organic matter and sulfide (Figure 6.3), and the firmly established generalization that humic substances play major roles in the binding, release, and biological uptake of metals in natural environments (roles which vary with the properties of the humic matter), are sufficient grounds for suspecting that the nature of the humic matter as well as its abundance in the lakes of the study area has an important bearing on the question of bioavailability.

In brief, the findings illustrated in Figures 6.4 and 6.5 are of interest because they suggest that the smelter emissions affect freshwater ecosystems in the vicinity of Sudbury not only by introducing potentially toxic heavy metals and sulphur compounds into them but also by influencing the forms and bioavailability of the metals by alteration of aquatic and sedimentary environments.

6.3.4. Effects of Cu and Ni species and other factors on benthic animals

Results of the toxicity tests with benthic invertebrates (young of the crustacean *Hyalella*, larvae of the insect genera *Chironomus* and *Hexagenia*, and adults of the oligochaete *Tubifex tubifex*, Section 5) were compared with metal speciation data and related measurements. As the Cu and Ni fractions of the sediments are essentially covariant, their relationships with the results of the bioassays are similar, but Cu was found to give somewhat better correlations in some cases, whereas Ni or the sum of the mole concentrations of Cu and Ni gave the best results in other cases. The study revealed not only that toxicity varied as functions of site-dependent chemical characteristics of the sediments and associated lake water but also that the different kinds of experimental animals responded in quite different ways to the contaminated sediments to which they were exposed even though all of these creatures habitually feed on sediment particles and must therefore have ingested portions of the contaminated sediments (although perhaps not precisely the same kinds of particles, as they discriminate to a greater or lesser extent between different edible sediment components). The diverse results of the toxicity bioassays serve to remind us that a bioassay performed on a culture of a single test species is of limited value in the assessment of toxic effects of pollutants on complex natural communities composed of vast numbers of species interacting with each other in numerous direct and indirect ways. Laboratory bioassays may yield useful information, as in the present case, but their limitations must be kept clearly in mind. Ideally, it would be preferable to combine such tests with comprehensive in-depth investigation of the effects of pollutants on entire ecosystems under field conditions.

6.3.4.1. Effects of pollutants on *Hyalella*. Measurements of percentage survival of *Hyalella* on exposure to the lake sediments (Figure 5.1, Appendix 3) were plotted against the total solvent-extractable Cu and Ni concentrations in the sediments. For sediments from the "10 m" sites, the result was a weak inverse correlation (Figure 6.6A, Appendix 5). However, the weakness of the relationship is due mainly to the fact that percentage survival was abnormally low in the presence of sediments from Restoule Lake and Tomiko Lake, whose waters have the lowest Ca and Mg content (i.e., the lowest degree of hardness) (W. Keller, unpublished data). When the percentage survival data were normalized with respect to water hardness (expressed as the sum of the mole concentrations of Ca and Mg), the correlation improved dramatically, becoming highly significant, and the data for Restoule Lake and Tomiko Lake were no longer aberrant (Figure 6.6B). (Essentially the same trend emerged when the survival/hardness ratio was plotted against $CaCl_2$-extractable Cu, but the correlation was not as strong (Appendix 5); and there was no meaningful correlation at all between survival/hardness ratio and NaAc/HAc-extractable Cu.) The data for sediment samples from "deep" sites yielded similar results to those representing 10 m sites, except that the survival/hardness ratio was anomalously high in the case of Tomiko Lake and Trout Lake for reasons that we cannot, at present, explain (not shown). (Note that the apparent effect of water hardness was not a direct effect of lake water chemistry on the bioassay results, as all the bioassays were performed on sediment samples immersed in Lake Ontario water of uniform composition rather than water from the sampling sites. Instead, the observed effect is attributable to related characteristics of the sediments; for instance, a possible explanation would be the presence of carbonate minerals, or relatively high concentrations of sorbed Ca^{2+}, Mg^{2+}, and HCO_3^- ions, in sediments from lakes containing relatively hard water. Further analysis of the sediments, including X-ray diffraction analysis, along with closer scrutiny of the geological formations in the drainage basins of the lakes, is needed to test this idea.)

Although the cause-and-effect relations remain to be determined, the correlation between the bioassay results and geochemical data (Figure 6.6) are consistent with poisoning of *Hyalella* by the solvent-extractable Cu and Ni fractions, possibly including the strongly sorbed H_2O_2/NH_4Ac/HNO_3-extractable Cu and Ni species which comprise the principal solvent-extractable Cu and Ni fractions. If this tentative interpretation is correct, the apparent availability of these relatively refractory forms of the metals and the absence of a preferential effect of the

58
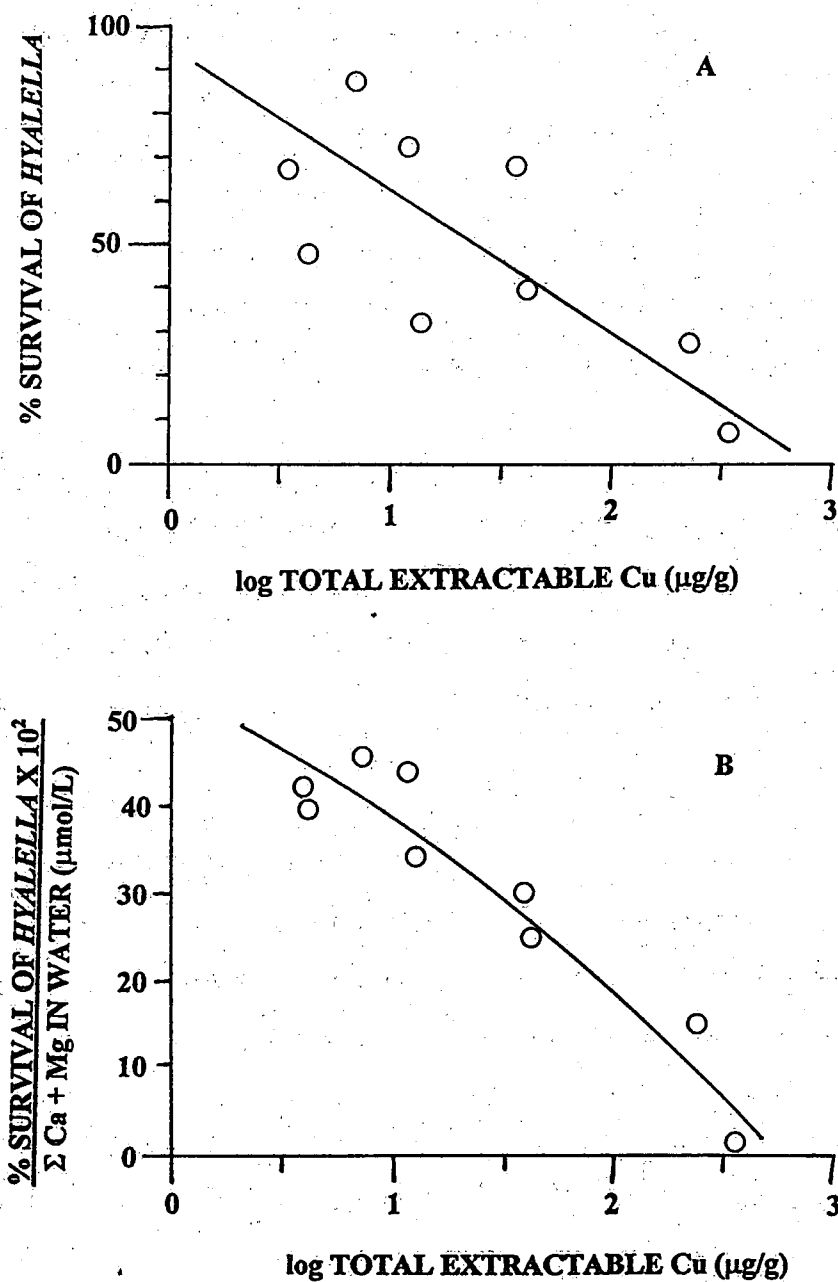
Figure 6.6. Apparent effects of total solvent-extractable Cu in sediments from 10 m sites on *Hyalella* survival with and without correction for variations in the combined Ca and Mg content (hardness) of the water. The diagrams show % survival of *Hyalella* and % survival of *Hyalella* normalized with respect to Ca + Mg (A and B, respectively) plotted against the extractable Cu content of the sediment. The Ca and Mg data, which represent water samples collected in 1981, were furnished by W. Keller (Ontario Ministry of the Environment).

more loosely sorbed species probably reflect the fact that the organisms ingest entire sediment particles. Observations suggest that even the more strongly bound metals can be solubilized by the organisms' digestive juices and then absorbed through the wall of the gut (Jackson *et al.*, 1995). Nevertheless, the ameliorating effect of water hardness suggests that Ca and Mg salts interfere with metal uptake (as reported by others in the literature). Alternatively, it is possible that toxicity to *Hyalella* is caused by dissolved Ni; the correlation between survival and Ni in the bioassay water was also very close (Table 5.2, Appendix 5).

6.3.4.2. Effects of pollutants on *Chironomus* larvae. *Chironomus* gave radically different bioassay results than *Hyalella*, implying a fundamental qualitative difference in its response to the toxic contaminants. The percentage survival data for *Chironomus* populations exposed to sediments from the 10 m sites showed no correlation with extractable Cu or Ni (Appendix 5), and the results were independent of water hardness. However, a plot of percentage survival against total solvent-extractable Cu + Ni for the deep sites revealed a well defined V-shaped pattern of variation formed by the junction of two opposing trends (Figure 6.7). Surprisingly, this means that percentage survival was highest closest to the smelter (where extractable Cu and Ni levels in the sediments were highest) and farthest away from it (where extractable Cu and Ni were least abundant), the minimum percentage survival (i.e., maximum toxicity) occurring at intermediate distances (where extractable Cu and Ni concentrations were intermediate). As with *Hyalella*, the correlation of toxic effects with the total extractable metal fractions and the apparent lack of discrimination between weakly bound and strongly bound metal species may be related to the animal's habit of swallowing and digesting sediment particles. In this case, however, water hardness plays no role in mitigating the apparent toxicity of the metals to *Chironomus*. (Note that Cu or Ni alone gave essentially the same result, but Cu + Ni gave the best trends, indicating that both metals may contribute to the observed effect. Also note that survival of *Hyalella* correlated with the Ni content of bioassay water (Appendix 5).)

If the unexpected V-shaped pattern of variation seen in Figure 6.7 is indeed caused by emissions of from the smelter, and is not an artifact, then this implies that the contaminants from the smelter include not only heavy metals such as Cu which have toxic effects on the organisms but
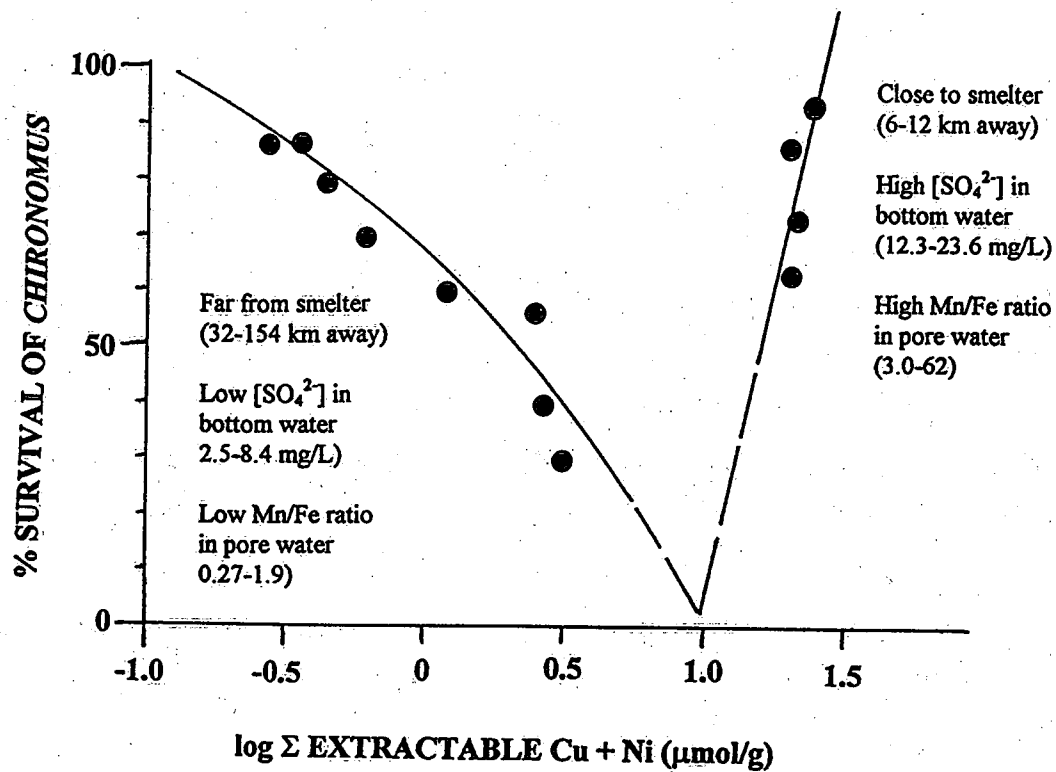
Figure 6.7. Apparent effects of total solvent-extractable Cu and Ni in sediments from deep sites on *Chironomus*. The diagram shows % survival of *Chironomus* plotted against the sum of the total mole concentrations of extractable Cu and Ni.

also constituents which, to some extent, ameliorate those effects in the immediate vicinity of the smelter. Possibly the Cu in the particles that settle out closest to the smelter are less readily available to the *Chironomus* than the Cu in the particles that settle out further away, although this is obviously not the case where *Hyalella* is concerned. As discussed in Section 3.3 (above), there is independent evidence that the bioavailability of Cu and Ni is lowest in the lakes closest to the smelter and increases with distance from it. Again, there could, in theory, be a number of reasons for suppression of biological uptake of Cu and Ni and consequent abatement of toxicity near the smelter; among them are preferential deposition of coarser, less readily solubilized metal-bearing particles closer to the smelter, inhibition of sedimentary bacteria that enhance bioavailability, and direct or indirect detoxifying effects of certain smelter products such as SO_4^{2-}, which is most abundant in lake waters nearest the smelter (Figure 2.3). Sulphate could, perhaps, indirectly interfere with the biological uptake of Cu and Ni by stimulating the activities of SO_4^{2-} reducing bacteria, causing enhanced production of sulfides, which bind heavy metals such as Cu strongly, diminishing their bioavailability. Although our total sulfide data do not support this hypothesis, they do not necessarily rule out the possibility that SO_4^{2-}-reducing bacteria play a role in suppressing metal bioavailability in the lakes closest to the smelter. Whatever the detoxification mechanism for *Chironomus* in the vicinity of the smelter, it is ineffectual for *Hyalella*. Furthermore, certain distinctive characteristics of the sedimentary environment at the deep sites which are not present at the 10 m sites must contribute in some way to the outcome (suggesting a role for sulfide, thiols, or other products of relatively reducing environments). More information is needed to explain the observed results.

6.3.4.3. Effects of pollutants on *Hexagenia*. The relative growth of *Hexagenia* (the ratio of final weight to initial weight) is inversely related to the total solvent-extractable Ni and Cu content of the sediment, and the data for both the deep and the 10 m sites conform to the same trend. However, the plot shows considerable scatter. Normalizing the relative growth measurements with respect to water hardness improves the correlation somewhat, though not dramatically, and Ni (or Ni + Cu) gave somewhat better results than Cu (Figure 6.8A, Appendix 5).
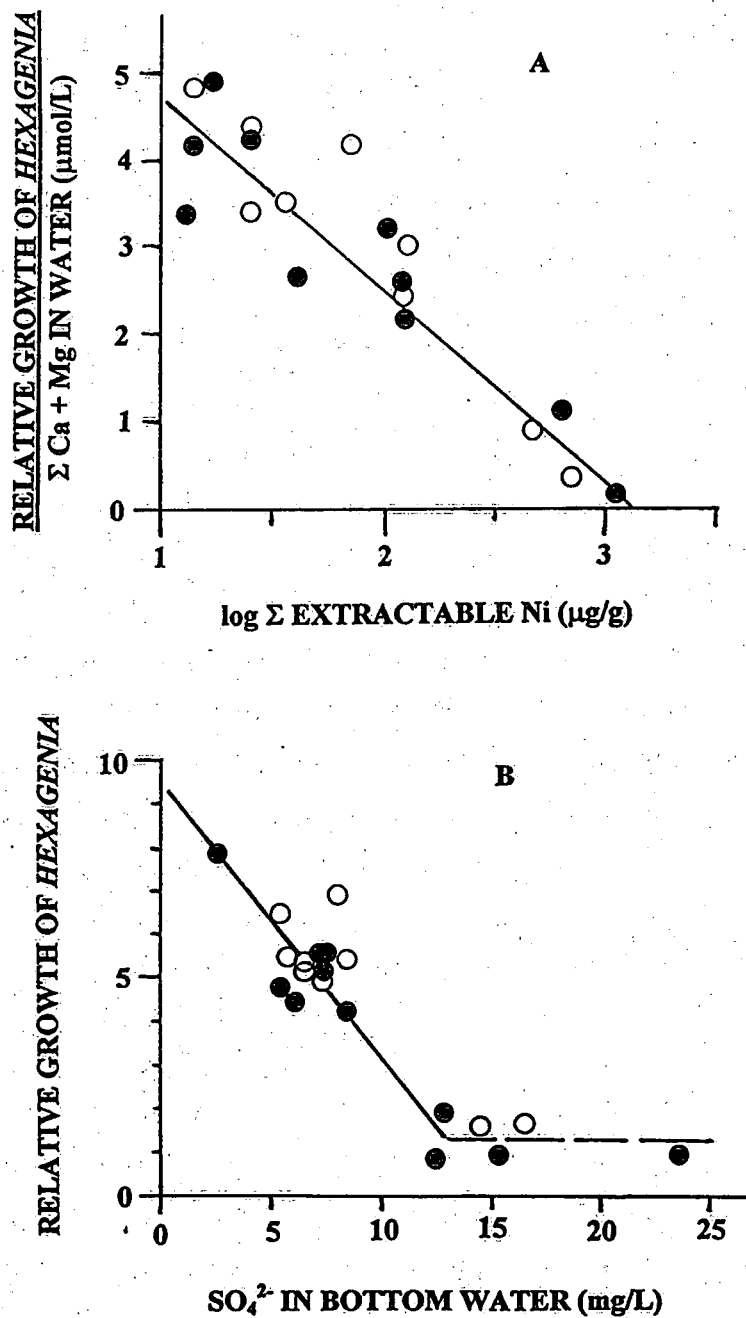
Figure 6.8. Apparent effects of total solvent-extractable Ni in sediments and SO_4^{2-} in bottom water on *Hexagenia* exposed to sediments from deep sites and 10 m sites. The diagrams show (A) relative growth of *Hexagenia* (normalized with respect to the Ca and Mg content (hardness) of the water) plotted against the extractable Ni content of the sediment, and (B) relative growth of *Hexagenia* (not normalized) plotted against the SO_4^{2-} level of the water. Explanation of symbols: deep sites, ● ; 10 m sites, ○.

A comparable but more significant curve was obtained by plotting relative growth of *Hexagenia* against the SO_4^{2-} content of the bottom water (Figure 6.8B). In this plot, relative growth decreases in linear fashion with increasing SO_4^{2-} down to a minimum value greater than zero at a critical value of SO_4^{2-}, whereupon it levels off abruptly, remaining constant with further increase in SO_4^{2-}. This correlation should probably not be construed as indicating a toxic effect of SO_4^{2-}, as SO_4^{2-} ions are relatively harmless. A more plausible explanation is that SO_4^{2-} is strongly covariant with certain toxic metal species. This interpretation is consistent with the fact that SO_4^{2-} is most abundant in the lakes closest to the smelter, where the concentrations of smelter-derived metals are also highest.

6.3.4.4. Effects of pollutants on *Tubifex tubifex*. The ratio of large (>500 μm) to small (<500 μm) *Tubifex tubifex* young (hereafter called the L/S ratio) after incubation of the adult worms with sediments from deep sites gave an inverse correlation with the total solvent-extractable Cu and Ni content of the sediment and positive correlations with the A_{465nm}/A_{665nm} and A_{320nm}/A_{420nm} ratios of the humic matter extracted from the sediment with NaOH. Normalization of the L/S ratio with respect to water hardness improved the correlations slightly (Figure 6.9, A-C). All of these relationships, though apparently significant, are characterized by considerable dispersion, and they do not appear to differ greatly from one another in significance. The data for the 10 m sites did not show significant correlations and hence are not included in Figure 6.9.

The most straightforward interpretation of the results would seem to be that bioavailable Cu and Ni and other pollutants from the smelter tended to impair the growth of young worms, causing a drop in the proportion of relatively large individuals, but that other pollution-related factors too - including variations in the nature of the humic matter (which is itself subject to alteration by the pollutants) - contributed in large part to the observed variance of the L/S ratio. However, the correlations between L/S ratio and spectral properties of humic matter cannot be evaluated properly without more information. They could represent an actual effect of humic matter (such as variation of the bioavailability of Cu as a function of the molecular properties of the humic matter), but they could merely mean, instead, that the growth of the worms and the absorbance ratios of the humic matter are independent of each other but correlate significantly because both
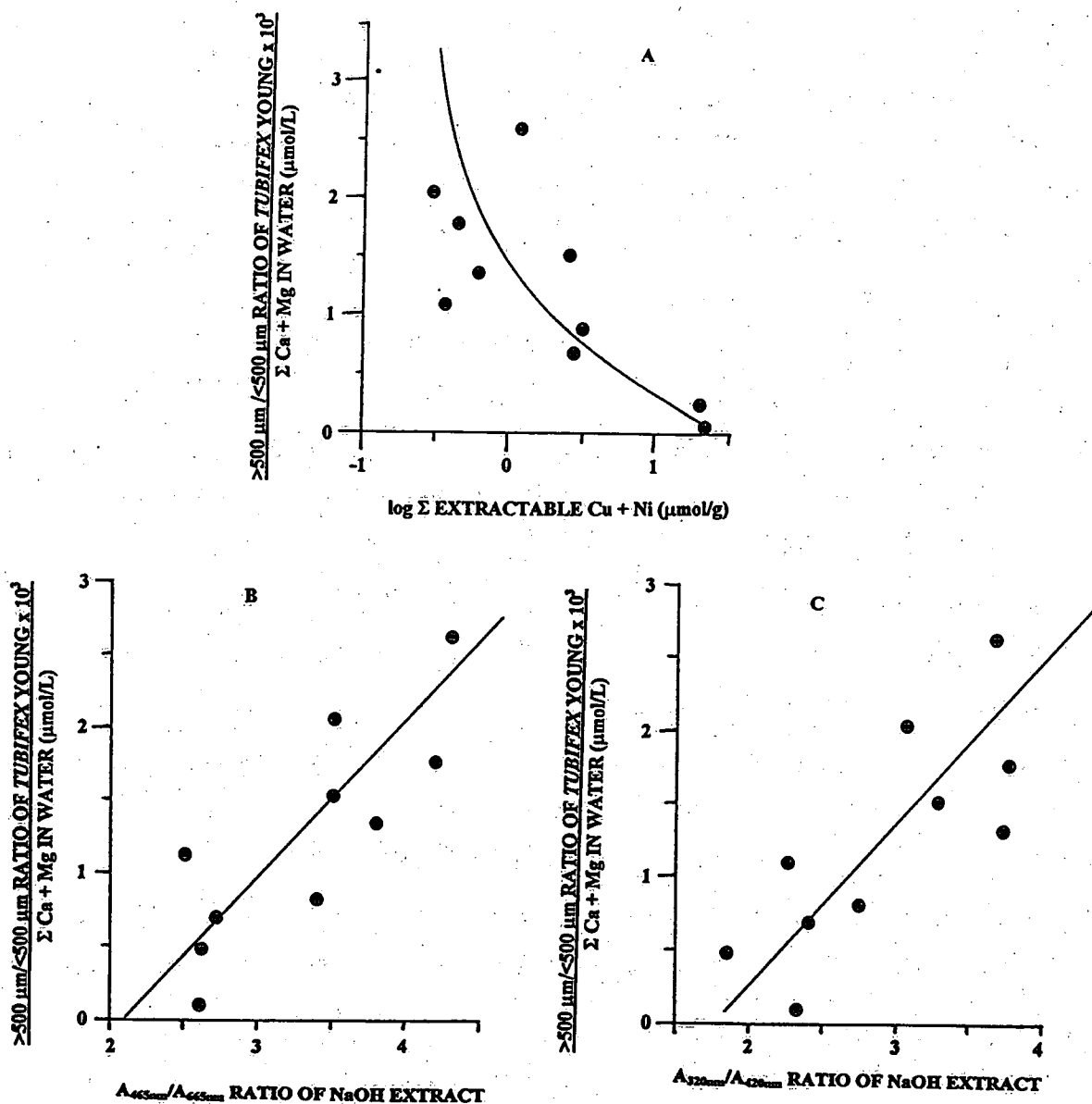
Figure 6.9. Apparent effects of deep-site sediment composition on the ratio of large (>500 mm) to small (<500 mm) *Tubifex* young (normalized with respect to the combined Ca and Mg content (hardness) of the water). The diagrams show the adjusted size ratio plotted against the sum of the total mole concentrations of extractable Cu and Ni in the sediments (A) and against the A_{465nm}/A_{665nm} and A_{320nm}/A_{420nm} ratios of the NaOH-extractable humic matter in the sediments (B and C, respectively).

65

are affected by the Cu and Ni and other pollutants. It is possible, of course, that the L/S ratio is a function of both the abundance of bioavailable Cu and Ni species and the properties of the humic matter, (in particular, those properties which determine the molecules' metal-binding and - releasing abilities). The Cu and Ni may alter the nature of the humic matter indirectly by poisoning the microbes which produce humic matter or the organisms whose remains comprise the raw materials for the humic matter (the autochthonous component of it, in any case), or both.

The total yield of *Tubifex tubifex* young (the sum of <500 μm and >500 μm young) from all sites gave a negative correlation with extractable Cu (Figure 6.10A) and somewhat less satisfactory negative correlations with extractable Ni and the sum of the extractable Cu and Ni fractions (Appendix 5). However, the relationship loses most of its significance if the data for the four lakes closest to the smelter are omitted, suggesting that the metals exerted significant toxic effects only at the extremely high concentrations found in the immediate vicinity of the smelter. In contrast, the samples from all sites showed a significant complex relationship between *T. tubifex* young and the A_{320nm}/A_{420nm} ratio of NaOH-extractable sedimentary humic matter (Figure 6.10B). In the presence of sediment from the 10 m sites, the total number of *T. tubifex* young tended to increase progressively and gradually with increasing A_{320nm}/A_{420nm} ratio, whereas in the presence of sediment from the deep sites, the number of young increased sharply with rising A_{320nm}/A_{420nm} ratio in the range of the lowest ratio values (~1.8-2.4) but then peaked and declined gradually with further increase in the ratio (Figure 6.10B). These trends are, to some extent, linked to smelter emissions, as the sediments from the four lakes closest to the smelter all possess humic matter characterized by low A_{320nm}/A_{420nm} ratios (~1.8-2.4) and a tendency to become less toxic to *T. tubifex* young with increasing A_{320nm}/A_{420nm} ratio; but they are not consistently related to distance from the smelter, as sediment samples from certain lakes relatively far from the smelter (e.g., Nosbonsing Lake) are also distinguished by low ratios (~2.3-2.4). The relationships shown in Figures 6.10A and 6.10B are consistent with a direct biological effect of the humic matter as opposed to a mere correlation reflecting effects of pollutants on both the organisms and the nature of the humic matter. However, the reproductive success of *T. tubifex* is also linked to the sulfide content of the sediments from the deep sites. Thus, the total yield of *T. tubifex* young increases with rising sulfide concentration and then abruptly levels off (Figure 6.10C). This relationship suggests that sulfide helps to protect the worms against metal
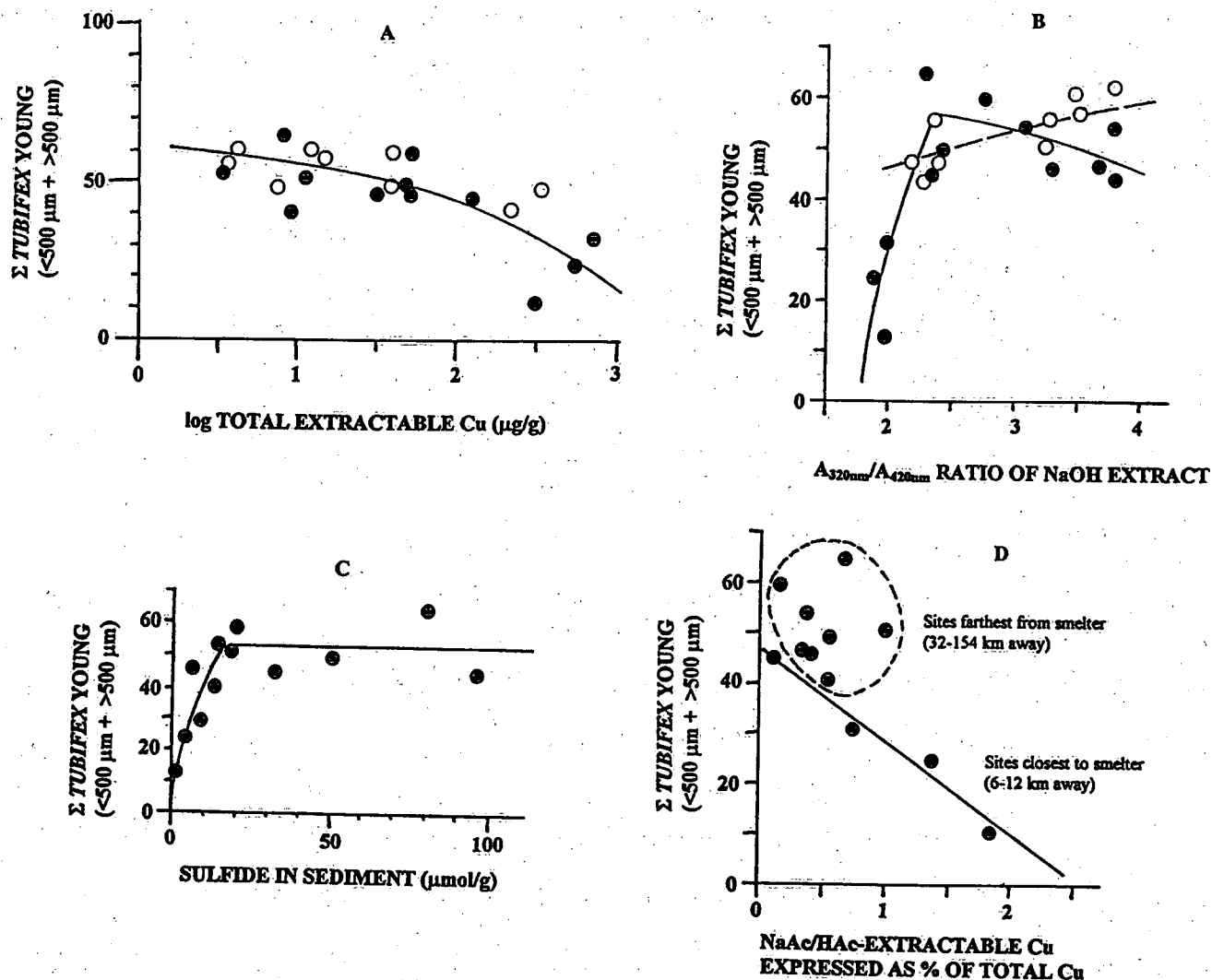
Figure 6.10. Relationships between the total number of *Tubifex* young produced by adults exposed to sediments and certain physicochemical characteristics of the sediments. The diagrams show the sum of large (> 500 mm) and small (< 500 mm) *Tubifex* young plotted against (A) the total solvent-extractable Cu content of the sediment, (B) the A_{320nm}/A_{420nm} ratio of NaOH-extractable sedimentary humic matter, (C) the sulfide content of the sediment, and (D) the percentage of NaAc/HAc-extractable species in the total Cu pool in the sediment. Explanation of symbols: deep sites, ● ; 10 m sites, o.

67

poisoning by immobilizing the metals, making them less bioavailable. In short, the available evidence reveals that production of *T. tubifex* young varies as a function of the extractable heavy metal (especially Cu) and sulfide concentrations in the sediments and also the molecular properties of the associated humic matter. Obviously, all of these variables are interrelated, but further work is needed to elucidate the cause-and-effect relations. Possibly more than one factor determines the net effect of the sediments on reproduction in *T. tubifex*. For instance, bioavailable Cu may poison *T. tubifex* directly but may also exert an indirect effect by poisoning the organisms that produce humic matter *in situ*, thereby altering the properties and hence the metal-binding capabilities of the humic matter, with the result that the average bioavailability and toxicity of the sediment-bound metal species are altered. Thus, there could be a complex system of direct and indirect feedback processes. More will be said about relations between the bioavailability of Cu and the nature of the humic matter in another section (see below).

One other interesting relationship emerged from the study of *T. tubifex* reproduction. A plot of the total yield of young worms against the percentage of the total sedimentary Cu pool that was in the form of NaAc/HAc-extractable species (percentage NaAc/HAc-Cu) gave a highly significant inverse linear correlation for the deep sites in the four lakes closest to the smelter - and only those sites (Figure 6.10D). In contrast, production of young in sediments from the deep sites of lakes further away from the smelter was entirely independent of percentage NaAc/HAc-Cu, the points representing these lakes forming a separate cluster lying above the regression line for the four lakes closest to the smelter (Figure 6.10D). These results suggest that the sediment constituents or environments in the lakes closest to the smelter differ markedly from those of the other lakes and that these inherent differences affect the binding, release, and bioavailability of Cu. Moreover, the results suggest some sort of link between the spectral properties of the humic matter and the bioavailability of Cu insofar as bioavailability is represented by the NaAc/HAc-extractable Cu fraction (see Figure 6.10B). (Incidentally, note that it is important not to confuse the "bioavailability" of Cu [percentage of "bioavailable" Cu species in the total Cu pool] with the concentration of "bioavailable" Cu species [mass of "bioavailable" Cu species per unit mass of sediment].)

6.3.5. Variation of spectral properties of humic matter with abundance of solvent-extractable Cu species in sediments: a means of quantifying toxic effects of Cu on aquatic ecosystems?

A plot of the A_{320nm}/A_{420nm} ratio of NaOH-extractable humic matter against the total solvent-extractable Cu concentration in sediment samples from deep sites and 10 m sites is shown in Figure 6.11A. (Since the variation in the concentration of extractable Cu in the sediment depends almost entirely on the rate of deposition of airborne contaminants and hence on distance from the smelter (Figure 6.1), it is logical to express the absorbance ratio as a function of extractable Cu rather than the other way round.) Not surprisingly, a virtually identical result was obtained by substituting $H_2O_2/NH_4Ac/HNO_3$-extractable Cu (the principal extractable fraction) for the total extractable Cu in the plot.

Clearly there is a highly significant but complex relationship between the A_{320nm}/A_{420nm} ratio and the abundance of extractable Cu, and the data for the deep and 10 m sites conform to the same curve (Figure 6.11A). The A_{320nm}/A_{420nm} ratio is lowest (implying that the average molecular size of the humic matter is largest) at the highest concentration of extractable Cu (686 µg/g) (i.e., in the most severely contaminated environment) and rises gradually and steadily with decreasing extractable Cu (from right to left in the plot) down to a Cu concentration of ~50 µg/g; at that point there is an abrupt break in the slope of the curve, and the ratio increases at a much steeper angle (almost vertically) to form a large peak (signifying that the average molecular size drops to a minimum) with further decrease in Cu but then declines at an equally steep angle as the Cu level falls to ≤10 µg/g. The lakes represented by the A_{320nm}/A_{420nm} maximum have at least one feature in common: They are all characterized by water of relatively low Ca content (~3-4 mg/L), whereas the other lakes (those for which data are currently available) have water with higher Ca concentrations (~5-15 mg/L) (W. Keller, unpublished data). Note that this differentiation is based solely on Ca concentration, not on total hardness (the sum of the Ca and Mg concentrations).

The progressive increase in the A_{320nm}/A_{420nm} ratio with decreasing extractable Cu within the Cu concentration range ~10-686 µg/g may be interpreted as signifying that with decreasing severity of pollution there is a corresponding abatement of the toxic effects of the pollutants on aquatic organisms and the sedimentary microbes that mediate the decomposition of their remains and the conversion of decomposition products into autochthonous humic matter. This hypothesis is
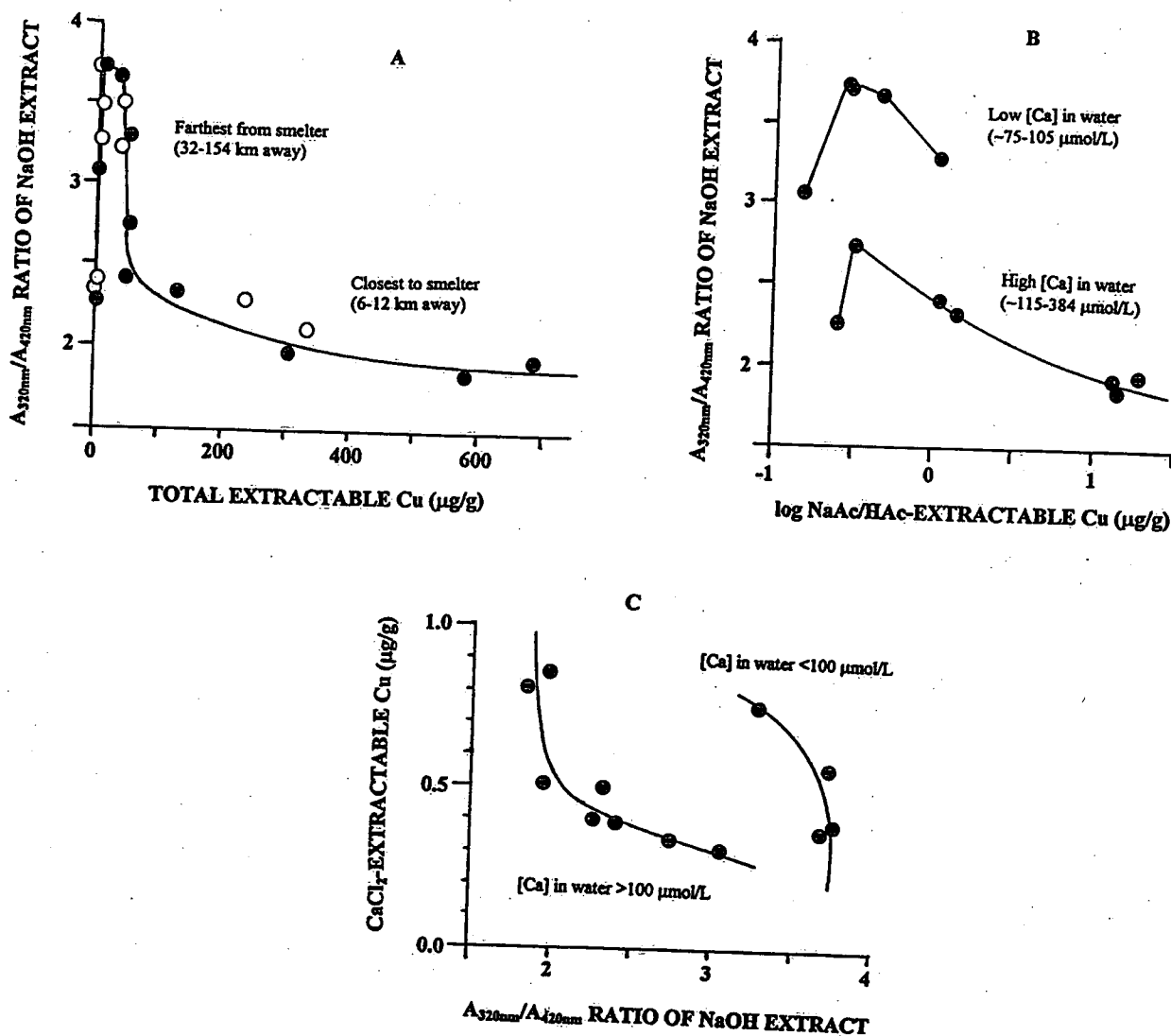
Figure 6.11. Relationships between Cu speciation and spectral properties of humic matter in the sediments. The diagrams show the A_{320nm}/A_{420nm} ratio of NaOH-extractable humic matter plotted against the total extractable Cu and NaAc/HAc-extractable Cu concentrations (A and B, respectively), and the CaCl$_2$-extractable Cu concentration plotted against the A_{320nm}/A_{420nm} ratio (C). Explanation of symbols: deep sites, ● ; 10 m sites, ○.

consistent with the general observation that humic matter of aquatic origin tends to have higher absorbance ratios than humic matter of terrestrial origin (the allochthonous component of aquatic humic matter). Another theoretically possible explanation of the change in the spectral properties with decreasing Cu is that it demonstrates diminishing effects of complexed Cu and other metals on the characteristic light-absorbing ability of the humic matter. (For instance, aggregation of humic acid molecules to form larger units owing to the bridging action of divalent and polyvalent metal cations could lower the A_{320nm}/A_{420nm} ratio) The marked difference between the spectral properties of humic substances in Ca-rich and Ca-poor environments may result from the tendency of Ca^{2+} and other polyvalent ions to immobilize humic acids, creating relatively large aggregates by flocculating molecules of humic acid or linking them to one another through bridging mechanisms. As the A_{320nm}/A_{420nm} ratio of humic matter tends to decrease with increasing molecular size, an enlarged chromophore complex consisting of smaller humic acid units "cemented" together in this manner by shared metal cations could well have a lower overall A_{320nm}/A_{420nm} ratio than any of its component parts. More research is needed to test these working hypotheses and to examine their possible relevance to the bioavailability and toxicity of heavy metals.

A plot of the A_{320nm}/A_{420nm} values against the concentration of NaAc/HAc-extractable Cu for samples from deep sites (Figure 6.11B) yielded comparable results but with an even more obvious distinction between Ca-rich and Ca-poor lakes. In this case, the high-Ca and low-Ca lakes can be represented by two parallel curves, each of which forms a peak at a Cu concentration of ~0.3 mg/kg. It is noteworthy that these curves are almost identical in shape and that their peaks coincide almost exactly, though the curve for Ca-poor lakes is displaced upward with respect to the curve for Ca-rich lakes owing to the systematically higher A_{320nm}/A_{420nm} values of the humic matter in Ca-poor lakes.

The plot shown in Figure 6.11C reveals that there is a very significant inverse relation between $CaCl_2$-extractable Cu and the A_{320nm}/A_{420nm} ratio of humic matter in sediments from the deep sites. The points in the plot resolve themselves into two separate and distinct trends: one for Ca-rich lakes and the other for Ca-poor lakes. In this case, it seemed logical to represent $CaCl_2$-Cu as a function of A_{320nm}/A_{420nm} rather than the other way around, as $CaCl_2$-extractable Cu represents only a small proportion of the total solvent-extractable Cu and is not strongly covariant with the

major Cu fractions, which are apparently the ones which influence the properties of the humic matter. Unlike the principal extractable Cu fractions (and, indeed, the A_{320nm}/A_{420nm} ratio as well), CaCl$_2$-extractable Cu correlates rather poorly with distance from the smelter (Figure 6.2A). A reasonable working hypothesis to explain the relationships demonstrated in Figure 6.11C would be as follows: (1) the "exchangeable," highly bioavailable fraction of Cu is mostly sorbed to cation exchange sites (e.g., -COOH groups) of humic matter; (2) the variation in the CaCl$_2$-extractable Cu level with respect to A_{320nm}/A_{420nm} indicates that the number of cation exchange sites per unit quantity of humic matter varies with the properties (e.g., average molecular size) of the humic matter; (3) these properties, in turn, are influenced by the toxic effects of Cu and other pollutants from the smelter, and are further modified by Ca^{2+} ions in the environment. In brief, bioavailable forms of Cu and other pollutants from the smelter alter the properties of the sedimentary humic matter owing to their toxic effects on local biological communities, including microbes that decompose organic matter, and, in so doing, modify its metal-binding and -releasing functions, thereby changing the bioavailability and toxicity of the Cu and other metals.

6.3.6. Relations between "bioavailability"of Cu, properties of humic matter, and composition of pore water

6.3.6.1 Variation of the "bioavailability" of Cu with spectral properties of humic matter. Among the sediments deposited at deep and 10 m lake sites located 6-52 km from the smelter, the percentage of the total Cu pool that was extractable with CaCl$_2$ (percentage CaCl$_2$-Cu) showed a well defined positive linear correlation with the A_{320nm}/A_{420nm} ratio of the NaOH-extractable humic matter (Figure 6.12A), suggesting that the number of cation exchange sites (e.g., -COOH groups) belonging to humic acids increases with decreasing molecular size. This is a reasonable interpretation, as lower molecular weight humic substances (fulvic acids) are known to have more -COOH groups per unit of mass than higher molecular weight ones (humic acids). In contrast, the percentage CaCl$_2$-Cu values for sampling sites much farther away (94-154 km) from the smelter are considerably higher than any of the percentage CaCl$_2$-Cu values for sites within 52 km of the smelter, even though the A_{320nm}/A_{420nm} ratios of the two groups largely overlap; and, with the exception of the sample representing the deep site in Tomiko Lake, which has an anomalously high percentage CaCl$_2$-Cu value with respect to the others in this group, they

Figure 6.12. Relationships between Cu speciation and spectral properties of humic matter in the sediments. The diagrams show the percentage of $CaCl_2$-extractable species in the total Cu pool in the sediment plotted against the A_{320nm}/A_{420nm} ratio of NaOH-extractable humic matter (A) and the percentage of NaAc/HAc-extractable species in the total Cu plotted against the A_{320nm}/A_{420nm} ratios of NaOH-extractable humic matter (B) and pore water (C). Explanation of symbols: deep sites, ● ; 10 m sites, ○. TOM = Tomiko Lake.

vary <u>inversely</u> with respect to A_{320nm}/A_{420nm} ratio. The clear separation of the points in the plot into two distinct populations based on distance from the smelter may imply an important difference in the nature of the humic substances represented by these two groups, and hence a significant systematic difference in the relative bioavailability of the Cu bound to their ligands. If this hypothesis is correct, a higher proportion of the Cu complexed by humic matter in lakes 94-154 km from the source of pollution is readily dissociated from the binding sites, and hence is readily available for biological uptake, than is the case with humic matter in lakes only 6-52 km away. The anomalously high percentage $CaCl_2$-Cu value of the sediment from the deep site in Tomiko Lake is of interest, as Tomiko Lake is the only lake situated in a predominantly deciduous forest. This anomaly could conceivably reflect the unique character of the source material from which the allochthonous component of the humic matter in Tomiko Lake was formed; but without additional analytical data (which we may eventually obtain) to confirm it, speculation about its significance would be premature, especially since no such anomaly was detected in the sediment sample from the 10 m site of Tomiko Lake.

The percentage of the total Cu that was extractable with NaAc/HAc (percentage NaAc/HAc-Cu) also varied as a complex function of the A_{320nm}/A_{420nm} ratio of the NaOH-extractable humic matter, but the pattern of variation was very different than was the case with percentage $CaCl_2$-Cu. With rising A_{320nm}/A_{420nm} ratio, the percentage NaAc/HAc value decreased sharply to a minimum and then increased (Figure 6.12B). Essentially the same pattern of variation was observed when percentage NaAc/HAc-Cu was plotted against the A_{320nm}/A_{420nm} ratio of the pore water (Figure 6.12C), implying that the humic fraction dissolved or dispersed in the pore water is essentially similar in molecular structure and composition to the bulk of the humic matter in the sediment. More research is needed to explain these relationships, but the results suggest that the NaAc/HAc-extractable Cu fraction is associated with humic matter and that the proportion of the sediment-bound Cu in this form varies with the nature of the humic substances. In any case, the results imply a profound inherent difference between the $CaCl_2$-Cu and NaAc/HAc-Cu fractions, probably reflecting a major difference in the nature of the metal-binding sites from which the two fractions were extracted.

6.3.6.2. Relationships between the "bioavailability" of Cu and the Mn/Fe ratio of pore water. Oxidation and reduction play crucial roles in regulating the speciation, bioavailability, and toxicity of heavy metals owing to phenomena such as: (1) involvement of oxidation and reduction in the decomposition of biological remains and accompanying production of humic matter, nonhumic complexing agents, and H_2S, a complex assortment of interrelated processes that lead to both mobilization and immobilization of metals; (2) the creation and destruction of the common metal-scavenging colloidal minerals MnOOH, FeOOH, and FeS, attended by the binding and release, respectively, of metals; and (3) the oxidation and reduction of certain metals themselves, such as Cr, whose toxicity is a function of oxidation state. Consequently, any data revealing links between oxidation-reduction reactions and the speciation and bioavailability of metals in natural environments merit serious attention.

Our work yielded evidence that the formation of bioavailable Cu species in the lakes of the study area correlates with at least one environmental parameter linked to oxidation-reduction reactions: the Mn/Fe ratio of the pore water. Unfortunately, the parameter is somewhat ambiguous in the present case, as it is independent of sediment Eh and sulfide content (Appendix 4). Nevertheless, the Mn/Fe ratios of natural waters and sediments are generally regarded as being sensitive to oxidation-reduction potential and dissolved O_2 concentration. Under O_2-poor, anoxic, or reducing conditions, in both the presence and the absence of free sulfide, the Mn/Fe ratio of water tends to be relatively high because Mn is more soluble than Fe, whereas the Mn/Fe ratio of sediment or the oxyhydroxide fraction of the sediment tends to be relatively low for the same reason (Jackson, 1988; Jackson and Bistricki, 1995). As we have already established an empirical connection between Cu speciation and the nature of the sedimentary humic matter (Figures 6.11 and 6.12), humic matter, too, will have to be taken into account in our final synthesis of our results (see next section). Further research, including experiments, will be needed to sort out the questions of cause and effect as opposed to mere correlation. Meanwhile, let us see how the data representing the bioavailability of Cu are related to the Mn/Fe ratio of pore water.

Among sediments from deep sites, the percentage of the total Cu that is extractable with $CaCl_2$ (percentage $CaCl_2$-Cu) was found to vary as a bimodal function of the Mn/Fe ratio of the sediment's pore water (Figure 6.13A). Thus, with increasing Mn/Fe ratio the percentage $CaCl_2$-
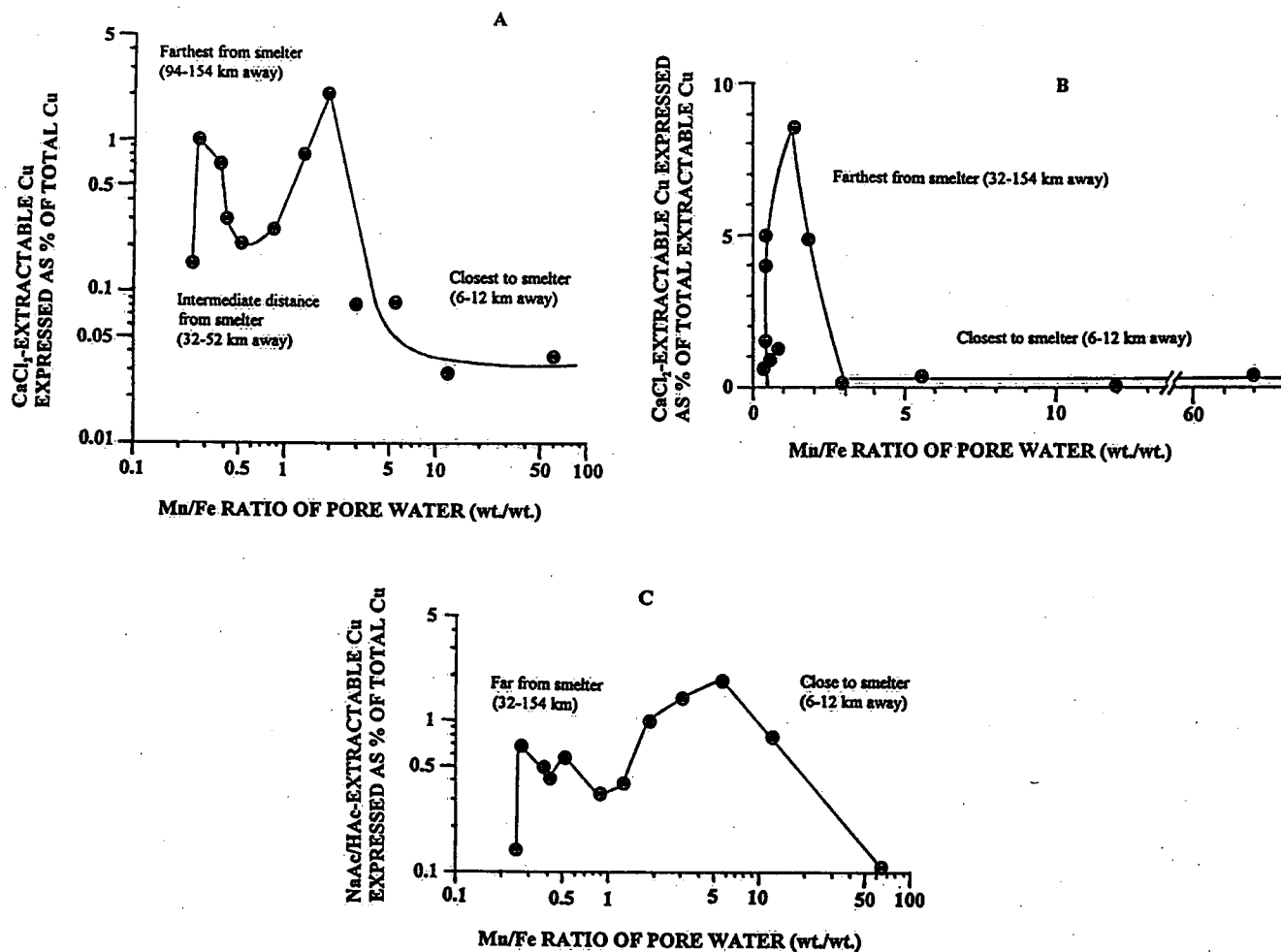
Figure 6.13. Relationships between Cu speciation and the Mn/Fe ratio of pore water in sediments from deep sites. The diagrams show the percentages of $CaCl_2$-extractable species in the total Cu pool and total solvent-extractable Cu fraction (A and B, respectively), and the percentage of NaAc/HAc-extractable species in the total Cu pool (C), plotted against Mn/Fe ratio. Note that "A" and "C" are log-log plots.

Cu rises to a maximum, decreases to a minimum, rises to a second maximum, and decreases again, tapering off to the lowest values of all at the highest Mn/Fe levels. The region of lowest percentage $CaCl_2$-Cu values and highest Mn/Fe ratios on the right side of Figure 6.13A represents the four sampling sites closest to the smelter (6-12 km away from it), whilst the two peaks, which make up the region of highest percentage $CaCl_2$-Cu and lowest Mn/Fe ratio, represent the more distant sites (32-154 km from the smelter). It could also be pointed out that the tops of the two peaks, which comprise the region of highest percentage $CaCl_2$-Cu values, are formed by the data for the four sites farthest from the smelter (94-154 km away), and the zone of intermediate percentage $CaCl_2$-Cu values (comprising the minimum between the two peaks and the left side of the base of the first peak) represents the four sites located at intermediate distances (32-52 km) from the smelter. The percentage of the total solvent-extractable Cu that is in the $CaCl_2$-extractable fraction gave a comparable pattern of variation, except that there was only a single peak at low Mn/Fe values (Figure 6.13B). As demonstrated previously (Figure 6.4), the percentage of $CaCl_2$-extractable Cu in the total extractable fraction tends to increase progressively with distance from the smelter in accordance with a simple regression line, though its relationship with the Mn/Fe ratio, which tends to decrease exponentially with distance from the smelter (Figure 6.5A), is complex. The percentage of the total Cu that is extractable with NaAc/HAc (percentage NaAc/HAc-Cu) varies in a roughly similar manner to the percentage $CaCl_2$-Cu with respect to the Mn/Fe ratio, although the relationship is different in certain details (Figure 6.13C). Comparable patterns of variation were obtained for Ni (not shown).

On the premise that the Mn/Fe ratio of pore water is a function of oxidation-reduction reactions despite the fact that it does not correlate with overall sediment Eh (and temporarily setting aside the involvement of humic matter), the patterns of variation illustrated in Figure 6.13 can, to some extent, be interpreted in terms of known effects of oxidation and reduction on heavy metal mobility and bioavailability. Thus, the association of the lowest percentage $CaCl_2$-Cu values with the highest Mn/Fe ratios (Figure 6.13A), together with the fact that these data represent the lakes that lie closest to the smelter and hence are most heavily contaminated with SO_4^{2-} (Figure 2.3), suggests exceptionally intense activity of SO_4^{2-} reducing bacteria accompanied by immobilization of both Fe and Cu by sulfide generated by the bacteria, even though the percentage $CaCl_2$-Cu values are independent of the total nonvolatile sulfide content of the sediment. (Possibly the role

of inorganic sulfide is masked by effects of thiols and other organic complexing agents present under reducing conditions.) Regarding the data for lakes farther away from the smelter, the formation of two percentage $CaCl_2$-Cu peaks in succession with rising Mn/Fe ratio could be explained by invoking alternating effects of increasingly anoxic conditions: relatively high percentage $CaCl_2$-Cu values owing to reduction and solubilization of oxyhydroxides with concomitant release of sorbed and coprecipitated Cu under moderately reducing conditions, and lower percentage $CaCl_2$-Cu values under more highly reducing conditions owing to immobilization of Cu by sulfide or thiols. Without more information, however, we cannot explain why there should be two peaks rather than just one. Possibly they represent the same basic principles but different sets of conditions and different assemblages of interacting species.

6.3.6.3. Variations of the spectral properties of humic matter with the Mn/Fe ratio of pore water. Finally, we found interesting relationships between spectral properties of pore water and the Mn/Fe ratio of the water (Figure 6.14, A & B). Our results strikingly illustrate the uniqueness of the humic substances and sedimentary environments in the four lakes closest to the smelter (within 12 km of it) as well as the dependence of the properties of the humic matter on its environment of formation or deposition.

With increasing Mn/Fe ratio, the A_{320nm}/A_{420nm} ratios of pore water samples from both deep and 10 m sites decrease sharply to a minimum value and then rise again very gradually (Figure 6.14A). Thus, a plot of A_{320nm}/A_{420nm} ratio against Mn/Fe ratio forms a distorted U-shaped pattern with a nearly vertical left limb (representing the highest A_{320nm}/A_{420nm} ratios and lowest Mn/Fe ratios) joined to a nearly horizontal right limb (representing the lowest A_{320nm}/A_{420nm} ratios and highest Mn/Fe ratios). The data for the four lakes closest to the smelter are confined to the right-hand limb owing to the consistently high Mn/Fe ratios and low A_{320nm}/A_{420nm} ratios of pore water from these lakes. The data for lakes farther away (32-154 km) from the smelter are distributed along both limbs of the curve, but the subset of data representing the deep sites of those lakes are restricted to the left-hand limb owing to the relatively low Mn/Fe ratios and high A_{320nm}/A_{420nm} ratios of pore water from those sites.
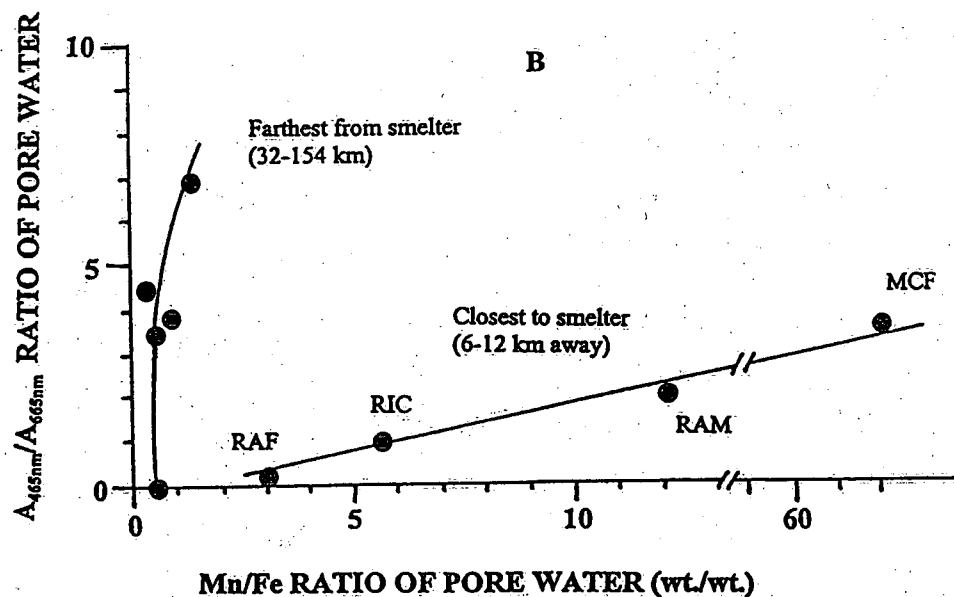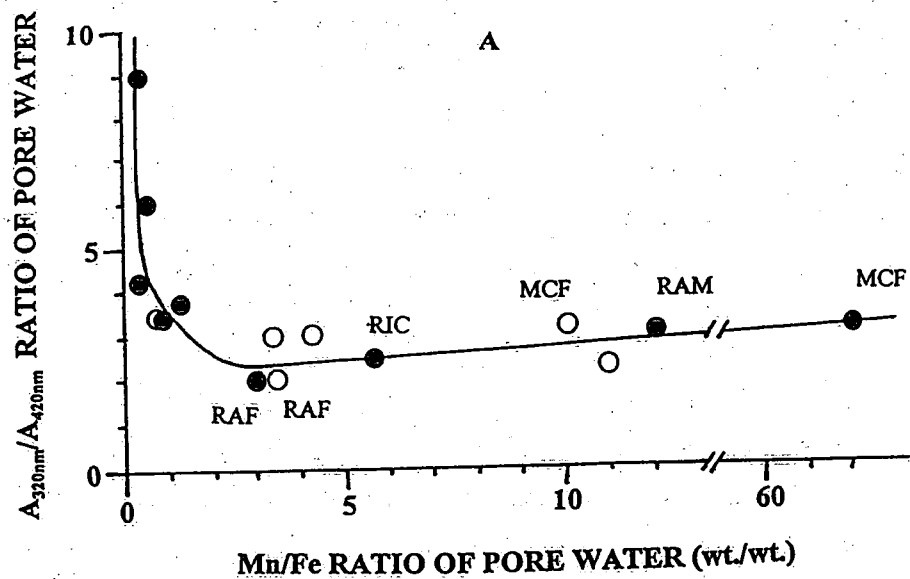
Figure 6.14. The A_{320nm}/A_{420nm} ratio and A_{465nm}/A_{665nm} ratio of sediment pore water (A and B, respectively) plotted against the Mn/Fe ratio of the pore water. Explanation of symbols: deep sites, ● ; 10 m sites, ○. The abbreviations stand for lake names: RAM = Ramsay; MCF = McFarlane; RAF = Raft; RIC = Richard.

A plot of A_{465nm}/A_{665nm} ratios for deep sites against the corresponding Mn/Fe ratio values gave a somewhat different result (Figure 6.14B). (The data for 10 m sites did not conform to the observed pattern of variation and did not show a consistent pattern of any description; consequently, they are not shown.) In this case, there is a clear-cut separation between the four lake sites closest to the smelter (6-12 km away) and the lakes farthest from it (32-154 km away), although each of the two groups shows a significant positive correlation between A_{465nm}/A_{665nm} ratio and Mn/Fe ratio. The ranges of A_{465nm}/A_{665nm} values for the two groups of samples overlap widely, although the samples from lakes relatively far from the smelter have a higher mean A_{465nm}/A_{665nm} ratio than the samples from the four lakes closest to the smelter; but, as mentioned above, the samples from the group of lakes closest to the smelter all have higher Mn/Fe ratios than any of the samples from lakes farther away, with the result that the plot resolves itself into two curves instead of a single one. (It could also be represented as a single complex curve in which A_{465nm}/A_{665nm} ratio rises abruptly with increasing Mn/Fe ratio, forms a peak, plunges to minimum, and then increases again gradually.) Taken at face value, the pair of curves in Figure 6.14B could be interpreted as follows: (1) As conditions become more reducing (i.e., as the Mn/Fe ratio rises), the autochthonous humic matter becomes less mature and hence has a higher degree of "fulvic acid" character (a higher A_{465nm}/A_{665nm} ratio), as would be anticipated; and (2) the humic matter in the lakes closest to the smelter displays this tendency to a much lesser degree than the humic matter in the lakes farther away because it has an anomalously high proportion of allochthonous components (which have characteristically low A_{465nm}/A_{665nm} ratios), owing to inhibition of the lacustrine organisms (mainly phytoplankton and bacteria) that form the autochthonous component of the sedimentary humic matter (see above).

In summary, the relationships shown in Figure 6.14, A & B appear to demonstrate well defined interrelated effects of the smelter emissions on the sedimentary environment (in particular, on oxidation-reduction reactions in the sediment) and the molecular properties of the sedimentary humic matter. According to our data, these effects extend at least as far as 12 km from the smelter but not as far as 32 km.

6.4. Summary of Results and Tentative Interpretations

- Concentrations of most solvent-extractable Cu and Ni species in the sediments, as well as Cu and Ni levels in the pore water, decline exponentially with distance from the INCO smelter, levelling off over distances on the order of ~50-100 km; but the concentrations of the other metals investigated (Cd, Zn, Pb, Cr, and Hg) do not vary as functions of distance from the smelter. In short, Cu and Ni are the principal airborne heavy metals deposited in the lakes from the particulate phase of the smelter emissions, and their rates of loading decrease away from the source of pollution.

- Sequential extraction of sediments with solvents ranging from mild to rigorous (solutions of $CaCl_2$, NaAc/HAc, $NH_2OH\cdot HCl/HNO_3$, hot $H_2O_2/NH_4Ac/HNO_3$, and citrate/dithionite, in that order) showed that most of the extractable Cu and Ni are strongly bound to organic matter and possibly sulfide, whereas little Cu or Ni is bound to Fe and Mn oxides and oxyhydroxides; this is consistent with the observation that all of the sediments have moderately to strongly reducing environments, although they are overlain by O_2-rich water. Small but measurable quantities of weakly sorbed, exchangeable ($CaCl_2$-extractable) Cu and Ni (presumably the most readily bioavailable species) are also present.

- The percentages of weakly sorbed, exchangeable Cu and Ni species in the total solvent-extractable Cu and Ni pools, respectively, increase progressively with distance from the smelter. Thus, although the concentrations of Cu and Ni in the sediments decrease with distance from the smelter, the proportions of highly bioavailable Cu and Ni actually increase. Molecular peculiarities of sedimentary humic matter as represented by certain spectral properties (UV-visible absorbance ratios) also vary systematically with distance from the smelter. These trends are probably interrelated. They are tentatively ascribed to toxic effects of smelter emissions on the organisms that produce humic matter, the principal metal-binding agent in the lakes of the field area. According to this theory, the pollutants (e.g., bioavailable forms of Cu and Ni) influence the properties of humic matter in the lake sediments by inhibiting the organisms that create the humic matter, and, since the binding and release of

81

the metals by humic matter in large part determines the bioavailability of the metals, this, in turn, affects the bioavailability of the metals.

- With increasing concentrations of extractable Cu species in the contaminated sediments, benthic invertebrates exposed to the sediments are subject to increasingly severe toxic effects (and comparable results were obtained for extractable Ni). In the laboratory bioassays, however, different kinds of animals were affected in quite different ways, even though all the test species have comparable feeding habits to the extent that all of them ingest sediment particles of one kind or another:

  - The percentage survival of *Hyalella* young tended to decrease with an increase in total solvent-extractable Cu and Ni in sediments from deep and 10 m sites, but because percentage survival was especially low in lakes whose water was relatively soft (poor in Ca and Mg), the inverse relation with Cu was largely masked unless the percentage survival data were normalized with respect to lake water hardness. In striking contrast to this result, percentage survival of *Chironomus* larvae was highest in deep-water sediments with the highest <u>and</u> lowest extractable Cu and Ni concentrations, falling to its lowest levels at intermediate metal concentrations, and this pattern of variation was seen only in the presence of sediments from the deep sites; moreover, percentage survival was independent of water hardness (Ca and Mg content). Thus, *Chironomus*, if poisoned by certain constituents of the smelter emissions (e.g., Cu and Ni), is also protected by a detoxifying effect of at least one component of the emissions (possibly SO_4^{2-} owing to its conversion to sulfide by SO_4^{2-}-reducing bacteria?) in the immediate vicinity of the smelter. These results illustrate the limitations as well as the usefulness of experimental toxicity bioassays employing single species. Such tests should, whenever possible, be accompanied by investigations of the effects of pollutants on entire natural communities, and they should involve numerous different kinds of test organisms. Furthermore, the fact that the toxic effects correlated with the total solvent-extractable Cu or Ni or Cu + Ni pool rather than the supposedly most bioavailable Cu and Ni species (in particular, the $CaCl_2$-extractable fraction) suggests that sediment-consuming animals take up strongly as well as weakly bound metals from the sediments because they habitually ingest whole

particles of sediment instead of merely absorbing dissolved nutrients from lake water through their cell membranes, as do the phytoplankton. According to this interpretation, both weakly and strongly bound Cu and Ni fractions of ingested sediment particles are indiscriminately released into solution during digestion and then absorbed through the gut wall. Alternatively, it is possible that toxicity in the case of *Hyalella* is caused largely by dissolved Ni in the overlying bioassay water (Table 5.2, Appendix 5).

- The toxicity data for *Hexagenia* larvae suggest that extractable Cu and Ni tend to inhibit larval growth. The toxicity of Cu and Ni is only slightly worse in lakes with lower dissolved Ca and Mg levels. The toxic effect of the metals, even when the bioassay data are normalized with respect to water hardness, is less pronounced than is the case with *Hyalella*.

- The growth rate of *Tubifex tubifex* young as represented by the ratio of large (>500 μm) to small (<500 μm) individuals had a tendency to be retarded by extractable Cu and Ni but was also significantly related to spectral properties of sedimentary humic matter, implying interrelations between bioavailability of metals and characteristics of the humic matter. The total production of young by *T. tubifex* (the sum of all >500 μm and <500 μm individuals produced) was also inhibited to some extent by extractable Cu and Ni, but the toxic effect may have been ameliorated by sulfide - presumably owing to immobilization of Cu and Ni; in addition, total production of young varied as a complex function of spectral properties of humic matter, the samples from the lakes closest to the smelter forming a different trend than the samples from the lakes located farther away. Moreover, the lakes closest to the smelter showed a strong inverse correlation between number of young and percentage of NaAc/HAc-extractable species in the total Cu pool of the sediment, whereas the data for the lakes farther away showed no correlation whatsoever between the two variables. Although the processes represented by these various relationships remain to be elucidated, the results suggest that environmental alteration by smelter emissions in the most heavily polluted lakes has a marked effect on metal speciation and bioavailability, owing at least in part to modification of the properties of sedimentary humic matter.

- Examination of analytical data representing extractable Cu fractions, comparative bioavailability of Cu, and spectral properties of humic matter in the sediments, as well as the Mn/Fe ratio of pore water and the Ca content of lake water, revealed a number of complex relationships that are consistent with the following tentative interpretations: (1) The relative bioavailability of Cu in the lakes of the field area is largely dependent on the binding and release of Cu by sedimentary humic matter, and both the strongly bound and weakly bound Cu fractions are probably associated, for the most part, with humic matter. (2) Cu and, we may assume, other pollutants from the smelter have influenced the properties of the sedimentary humic matter, especially in the lakes closest to the smelter; the pollutants may have altered the proportion of autochthonous to allochthonous humic substances and hence the average molecular size of the humic matter by poisoning the organisms that produce the autochthonous components (i.e., the organisms whose remains constitute the raw material of the autochthonous fraction and the microbes that decompose and humify it). Consequently, (3) the pollutants have altered the metal-binding and -releasing ability of the humic matter, thereby affecting the bioavailability of the metals in such a way that the percentage of weakly sorbed, exchangeable, presumably bioavailable species in the total Cu pool of the sediments increases with distance from the smelter even though the concentrations of most solvent-extractable Cu species decrease. (4) These processes are modified by spatially varying environmental factors, including the Ca content of the lake water and oxidation-reduction reactions such as bacterial reduction of smelter-derived SO_4^{2-} in the sediments.

In conclusion, it is necessary to emphasize that the interpretations of biogeochemical and ecotoxicological processes offered in this interim report are merely working hypotheses that remain to be tested by further work. At the present stage of the project, it would be premature to draw any definite conclusions about these processes, and we are not yet in a position to differentiate, with confidence, between cause-and-effect relations and mere correlations.

7.   SUMMARY AND FURTHER RESEARCH NEEDS

This report describes data collected so far as part of a continuing project to assess the impact of atmospheric deposition of metals from the Sudbury smelters on aquatic ecosystems. The work completed to date, and studies which still need to be done, can be conveniently summarized by comparison to the four questions outlined in the Aquatic Effects Technology Evaluation (AETE) program (AETE, 1997). The AETE program was designed to review appropriate technologies for assessing the impacts of mine effluents on the aquatic environment. Although the present study deals with atmospheric inputs of metals rather than effluents per se, the same questions apply. These are:

1. Are contaminants getting into the system?
2. Are contaminants bioavailable?
3. Is there a measurable response?
4. Are the contaminants causing this response?

7.1.   Are Metals Getting Into Aquatic Ecosystems?

The answer to this question is clearly "yes". The contamination of aquatic ecosystems near Sudbury by metals has been known for some time (e.g., Nriagu *et al.*, 1982). The present study demonstrates the level of contamination, especially by Cu and Ni, in the lakes selected for this study, confirms that contamination is recent and in the surface sediments, not in deeper and older sediments (Table 3.1, Figure 3.2), and quantifies the magnitude of enrichment and the rate at which this contamination decreases with distance from Sudbury (Table 3.3).

7.2.   Are These Metals Bioavailable?

Further research is required to address this question. Clearly, the elevated concentrations of Cu and Ni in sediments near Sudbury are reflected in increased concentrations in lake water (Figure

2.3), increased concentrations in the overlying bioassay water during toxicity tests with sediments from these lakes (Table 5.2), and increased concentrations of the most readily extractable and presumably most bioavailable forms of these metals in the sediments (CaCl$_2$-extractable, Figure 6.2). However, although the total CaCl$_2$-extractable Cu and Ni concentrations are highest in sediments from lakes near Sudbury, the relative bioavailability (percent of total metal which is extractable by CaCl$_2$) is lowest here (Figure 6.4). Similarly, Cu concentrations in lake water increase more gradually than concentrations in sediments, suggesting a lower relative bioavailability of Cu in the most contaminated sediments (Figure 2.3). (In contrast, Ni concentrations in lake water are almost directly proportional to Ni concentrations in sediments. [Figure 2.3]) These data suggest that, while total bioavailable Cu and Ni are most likely higher in lakes near Sudbury, bioavailability is not directly proportional to total metal in the sediments. Additional research which still needs to be conducted includes direct analysis of bioavailable metal through measurement of the amount of metal actually accumulated in the tissues of benthic organisms.

7.3. Is There a Measurable Biological Response?

The answer to this question is "yes". Results of both *in situ* benthic community structure and sediment toxicity tests suggest that sediments in lakes near Sudbury are less able to support a number of sensitive species, including amphipods (Table 4.1, Figure 5.1), bivalves (Table 4.1), and mayflies (Figure 5.1). Some insects, such as phantom midges (Table 4.1) and chironomids of the genus *Chironomus* (Table 4.1, Figure 5.1) appear to be relatively unaffected. The biological effects of proximity to Sudbury are clearly species specific.

7.4. Are the Metals Causing This Response?

Additional research is needed to address this very important question. A number of interesting correlations have been observed, including the correlation between sediment toxicity to *Hyalella* and *Hexagenia* and Ni in the bioassay water (Table 5.2, Appendix 5), sediment toxicity and total

extractable Cu and Ni (Figures 6.6 - 6.9), and reproduction of *Tubifex* and sulfide and spectral properties of humic matter (Figures 6.9 - 6.10). These are, however, only correlations and not proof of cause and effect. Sediment toxicity to *Hyalella*, *Hexagenia* and *Tubifex* correlates to some extent with each of Cu or Ni expressed as $CaCl_2$-extractable, total extractable, total in sediment, dissolved in porewater, dissolved in bioassay water, or dissolved in lake water, although the correlations with dissolved metal are somewhat better for Ni than for Cu (Appendix 5). The identity and toxic fraction of the metal responsible for biological effects is, therefore, not clear. Additional research needed includes studies with metal-spiked control (i.e., non-toxic prior to spiking) sediments to obtain relationships between metal bioaccumulation and toxicity under conditions where the toxic agent is know. Comparison of the critical body concentrations at which toxicity first appears with metal accumulation following exposure to Sudbury area sediments (see section 7.2 above) may help identify the toxic agent. This approach has been used previously to identify zinc as the toxic agent in sediments from Manitouwadge Lake (Borgmann and Norwood, 1997). Identification of the toxic agent, and a clearer understanding of the toxic fraction, will allow a much better interpretation of the biological significance of the chemical contamination observed in aquatic ecosystems impacted by the Sudbury smelters. It is possible, for example, to derive a relationship between chronic survival of *Hyalella* after four weeks exposure to sediments and proximity to the smelters at Copper Cliff, based on the relationship between toxicity and Ni in the bioassay water (Table 5.2, equations 3-5). Such a relationship would carry much more weight and have much greater predictive capacity if it was based on a true cause and effect relationship.

8. ACKNOWLEDGEMENTS

distribution measurements and carbon analyzes were performed by J. Dalton. Major ion and nutrient analysis were performed by the National Laboratory for Environmental Testing. The Ca and Mn data for lake water, as well as pH data used to make the initial selection of study lakes, were provided by W. Keller (Ontario Ministry of Northern Development and Mines). Bathymetric maps of lakes near Sudbury were supplied by K. Laws (Ontario Ministry of Natural Resources). Unpublished analytical data for smelter emissions were furnished by T.C. Burnett (INCO). The word processing was done by D. Crabtree.

9. REFERENCES

AETE. 1997. Aquatic Effects Technology Evaluation (AETE) Program, Background Document, Canada Centre for Mineral and Energy Technology (CANMET), Ottawa, ON.

Aiken, G.R., McKnight, D.M., Wershaw, R.L. and MacCarthy, P. 1985. Humic Substances in Soil, Sediment, and Water. John Wiley & Sons (Wiley-Interscience), New York, Chichester, Brisbane, Toronto, Singapore.

Anonymous. 1978. Extensive monitoring of lakes in the greater Sudbury area, 1974-1976. Report of the Ontario Ministry of the Environment (Water Resources Assessment, Northeastern Region).

Bateman, A.M. 1950. Economic Mineral Deposits, 2nd edition. John Wiley & Sons, New York and London.

Blaedel, W.J. and Meloche, V.W. 1963. Elementary quantitative analysis - theory and practice (2nd edition). Harper & Row, New York, Evanston, London.

Borgmann, U. and W.P. Norwood. 1997. Identification of the toxic agent in metal-contaminated sediments from Manitouwadge Lake, Ontario, using toxicity-accumulation relationships in *Hyalella azteca*. Can. J. Fish. Aquat. Sci. 54: 1055-1063.

Borgmann, U. and W.P. Norwood. 1993. Spacial and temporal variability in toxicity of Hamilton Harbour sediments: Evaluation of *Hyalella azteca* 4 week chronic toxicity test. J. Great Lakes Res. 19: 72-82.

Chan, W.H., Vet, R.J., Lusis, M.A. and Skelton, G.B. 1983. Airborne particulate size distribution measurements in nickel smelter plumes. Atmospheric Environment 17: 1173-1181.

Chen, Y., Senesi, N. and Schnitzer, M. 1977. Information provided on humic substances by E_4/E_6 ratios. Soil Science Society of America Journal 41: 352-358.

Day, K.E., Dutka, B.J., Kwan, K.K., Batista, N., Reynoldson, T.B. and Metcalfe-Smith, J.L. 1995. Correlations between solid-phase microbial screening assays, whole-sediment toxicity tests with macroinvertebrates and *in situ* benthic community structure. J. Great Lakes Res. 21: 192-206.

Dreisinger, B.R. and McGovern, P.C. 1969. Sulphur dioxide levels and resultant injury to vegetation in the Sudbury area during the 1968 season. Report, Ontario Department of Mines.

Dreisinger, B.R. and McGovern, P.C. 1970. Sulphur dioxide levels and resultant injury to vegetation in the Sudbury area during the 1969 season. Report, Ontario Department of Energy & Resources Management, Sudbury, Ontario.

Environment Canada. 1995a. Manual of Analytical Methods, Vol 1. Major Ions and Nutrients. Ecosystem Sciences & Evaluation Directorate, Eco-Health Branch, Ottawa, Ont.

Environment Canada. 1995b. Manual of Analytical Methods, Vol 2. Trace Metals. Ecosystem Sciences & Evaluation Directorate, Eco-Health Branch, Ottawa, Ont.

Gunn, J.M. 1995. Restoration and Recovery of an Industrial Region. Springer-Verlag, New York.

Gupta, S.K. and Chen, K.Y. 1975. Partitioning of trace metals in selective chemical fractions of nearshore sediments. Environmental Letters 10: 129-158.

Jackson, T.A. 1988. The mercury problem in recently formed reservoirs of northern Manitoba (Canada): effects of impoundment and other factors on the production of methyl mercury by microorganisms in sediments. Can. J. Fish. Aquat. Sci. 45: 97-121.

Jackson, T.A. 1998. The biogeochemical and ecological significance of interactions between colloidal minerals and trace elements. In: Rae, J.E. and Parker, A. (editors), Environmental Interactions of Clay Minerals. Springer-Verlag, Berlin. (In press.)

Jackson, T.A. and Bistricki, T. 1995. Selective scavenging of copper, zinc, lead, and arsenic by iron and manganese oxyhydroxide coatings on plankton in lakes polluted with mine and smelter wastes: results of energy dispersive X-ray micro-analysis. Journal of Geochemical Exploration 52: 97-125.

Jackson, T.A., Klaverkamp, J.F. and Dutton, M.D. 1993. Heavy metal speciation and its biological consequences in a group of lakes polluted by a smelter, Flin Flon, Manitoba, Canada. Applied Geochem., Suppl. Issue No. 2, pp. 285-289.

Jackson, T.A., Reynoldson, T.B., Zhou, K., Nguyen, N., Rosa, F. and Mudroch, A. 1995. Selective toxic effects of heavy metals on reproductive activities of the oligochaete *Tubifex tubifex* in lake sediments polluted with mine tailings. In: Wilken, R.-D., Förstner, U., and Knöchel, A. (editors), Heavy Metals in the Environment, vol. 2 (Proc. Internat. Conf., Hamburg, Germany, Sept., 1995), pp. 13-16. CEP Consultants Ltd., Edinburgh, Scotland.

Lindgren, W. 1933. Mineral Deposits. 4th edition. McGraw-Hill, New York and London.

Linzon, S.N. 1958. The influence of smelter fumes on the growth of white pine in the Sudbury region. Report published jointly by Ontario Department of Lands and Forests and Ontario Department of Mines, Toronto, Ontario.

McGovern, P.C. and Balsillie, D. 1975. Effects of sulphur dioxide and heavy metals on vegetation in the Sudbury area (1974). Report of the Ontario Ministry of the Environment, Northeast Region.

Molot, L.A. and Dillon, P.J. 1991. Nitrogen/phosphorus ratios and the prediction of chlorophyll in phosphorus limited lakes in Central Ontario. Can. J. Fish. Aquat. Sci. 48: 140-145.

Mudroch, A. and MacKnight, S.D. 1994. CRC Handbook of Techniques for Aquatic Sediments Sampling. CRC Press, Boca Ratan.

Nriagu, J.O., Wong, H.K.T. and Coker, R.D. 1982. Deposition and chemistry of pollutant metals in lakes around the smelters at Sudbury, Ontario. Environ. Sci. Technol. 16: 551-560.

Pennanen, V. 1975. Humus fractions and their distribution in some lakes in Finland. In Povoledo, D. and Golterman, H.L. (editors), Humic Substances - Their Structure and Function in the Biosphere (Proc. Internat. Meeting, Nieuwersluis, The Netherlands, 29-31 May, 1972), pp. 207-215. Centre for Agricultural Publishing and Documentation, Wageningen, The Netherlands.

Rosa, F., Bloesch, J. and Rathke, D. E. 1991. Sampling the settling and suspended particulate matter (SPM). In: Handbook of techniques for aquatic sediment sampling, Chapter 5; A. Mudroch and S. MacKnight (editors), CRC Incorporated, publishers.

Salfeld, J.C. 1975. Ultraviolet and visible absorption spectra of humic systems. In: Povoledo, D. and Golterman, H.L. (editors), Humic Substances - Their Structure and Function in the Biosphere (Proc. Internat. Meeting, Nieuwersluis, The Netherlands, 29-31 May, 1972), pp. 269-280. Centre for Agricultural Publishing and Documentation, Wageningen, The Netherlands.

Schnitzer, M. and Khan, S.U. 1972. Humic Substances in the Environment. Marcel Dekker, New York.

Tessier, A., Campbell, P.G.C. and Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry 51: 844-851.

Watson, G. 1992. Factors affecting the distribution of the freshwater amphipod *Hyalella azteca* in Sudbury area lakes. Undergraduate Thesis, Laurentian University, Sudbury.

Appendix 1

Hydrolab (temperature, pH, conductivity, oxygen) profiles for each of the stations sampled. The profiles for the 10 m station (solid lines) and the deep station (dashed lines) are shown in the same figure for lakes greater than 10 m in depth. Sudden changes in the conductivity and pH at the bottom of some of the profiles occurs when the probe touches the bottom. Profiles are plotted from 0 to 30 m only. There was very little change in any parameter below 30 m in those stations deeper than 30 m (TROD and TALD).

RAM
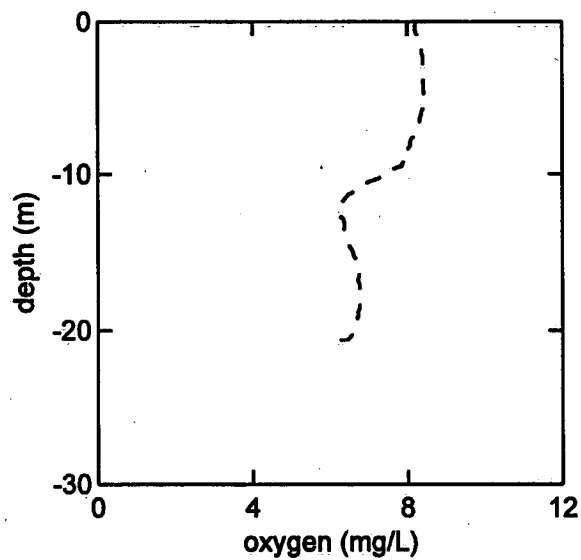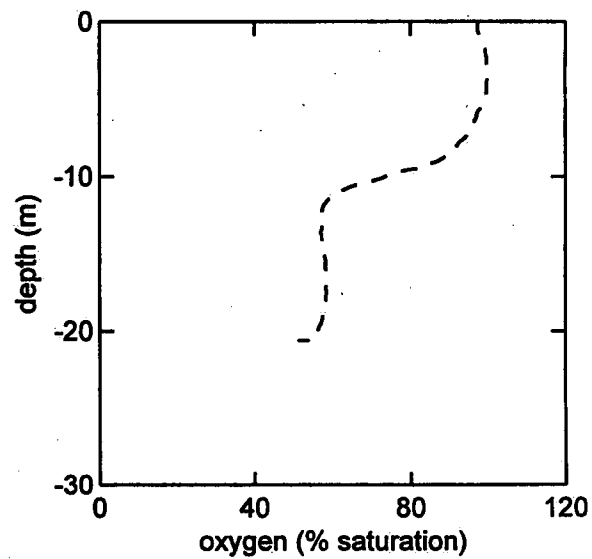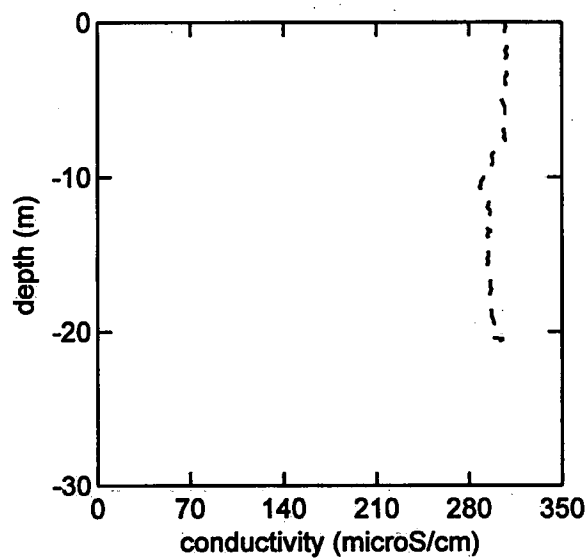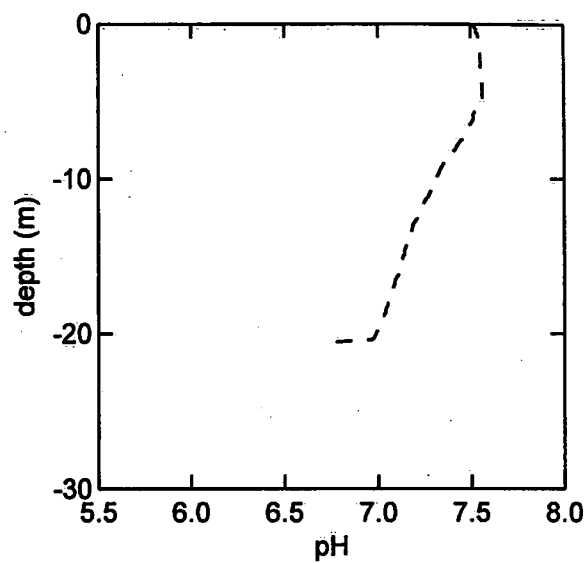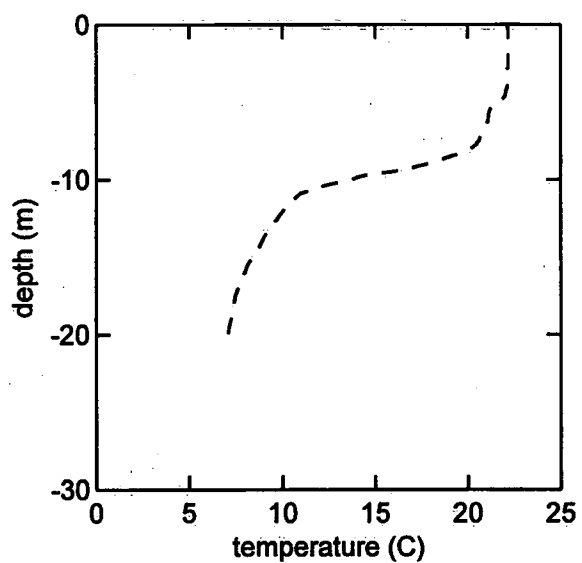
MCF
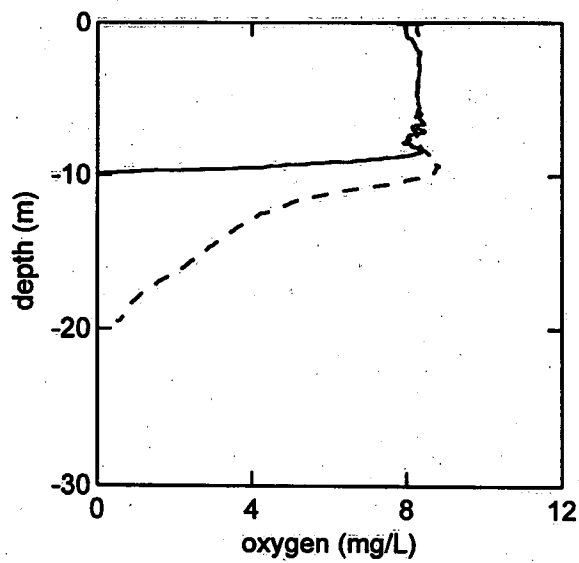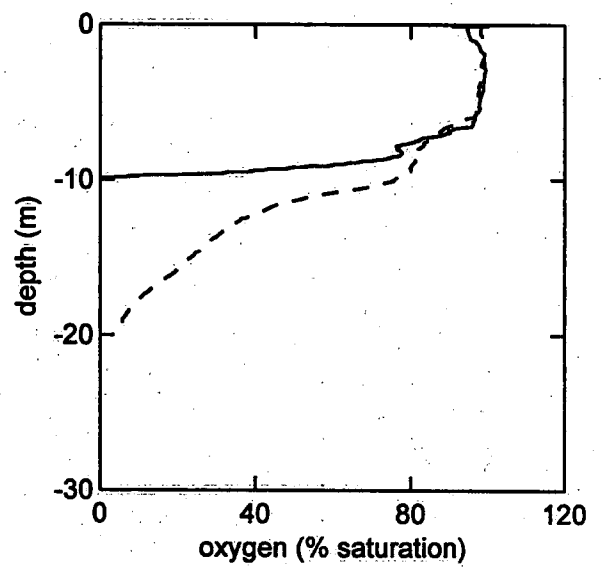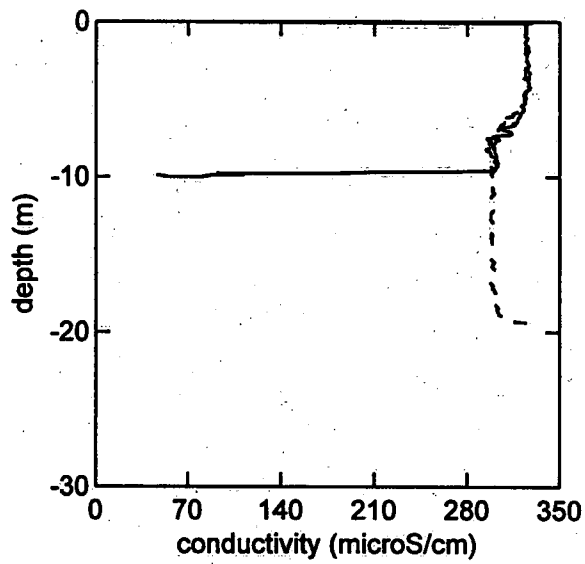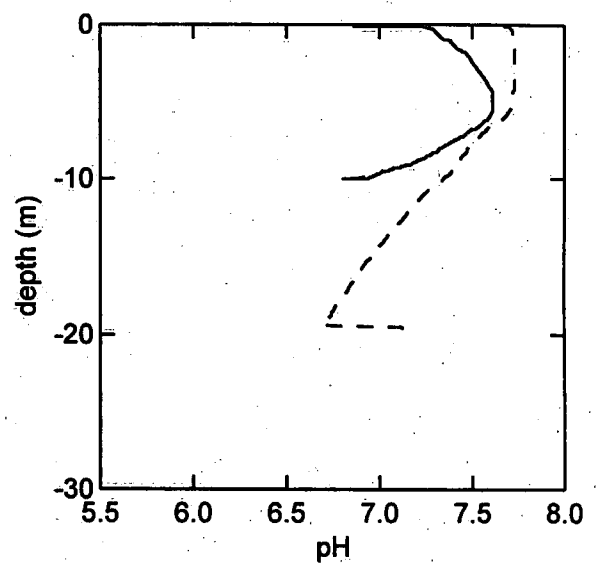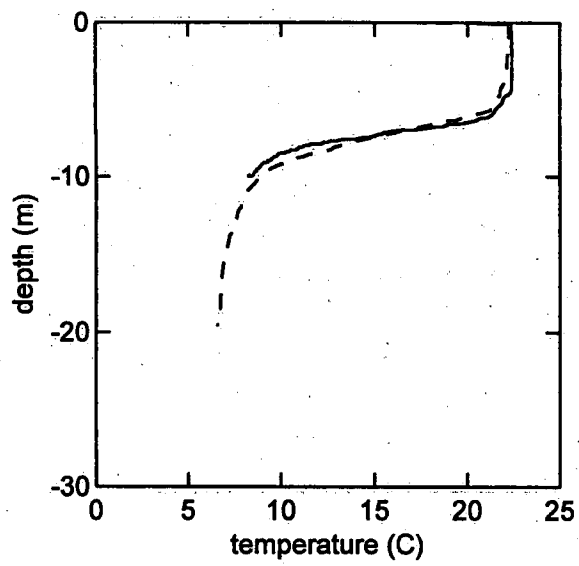
RAF
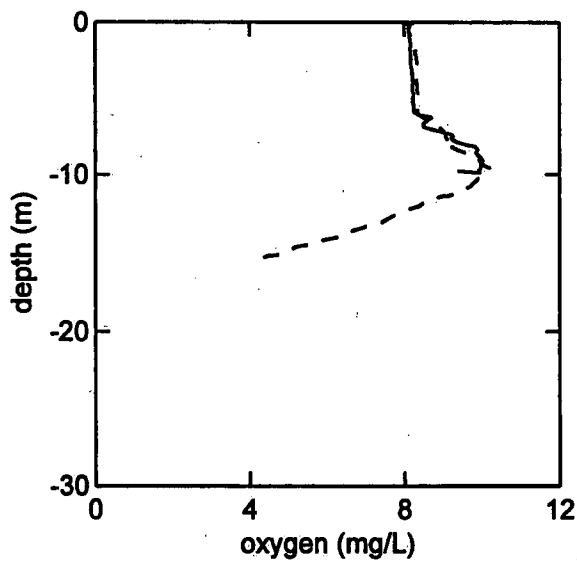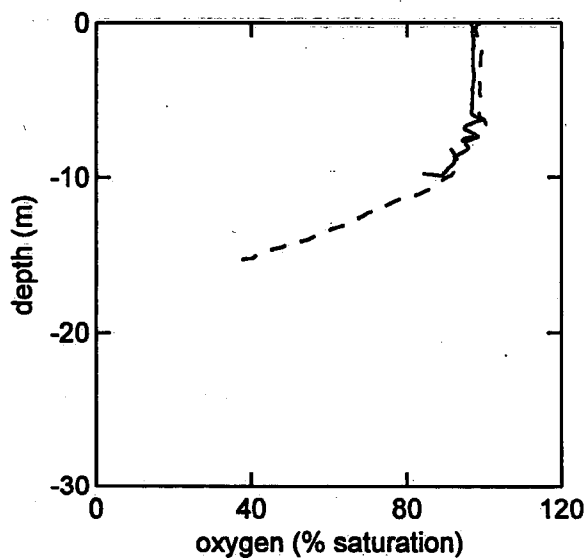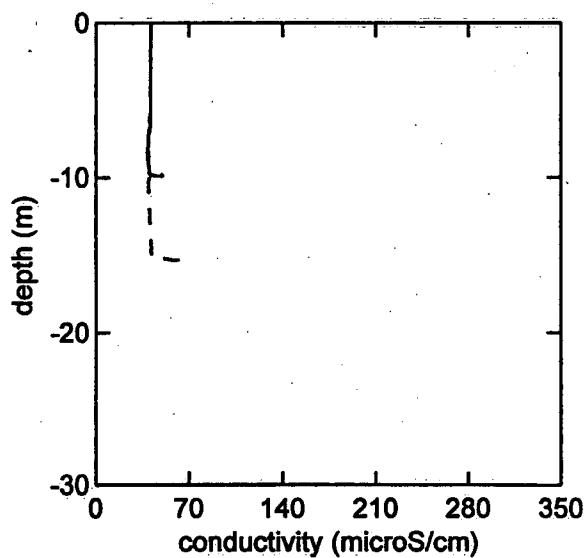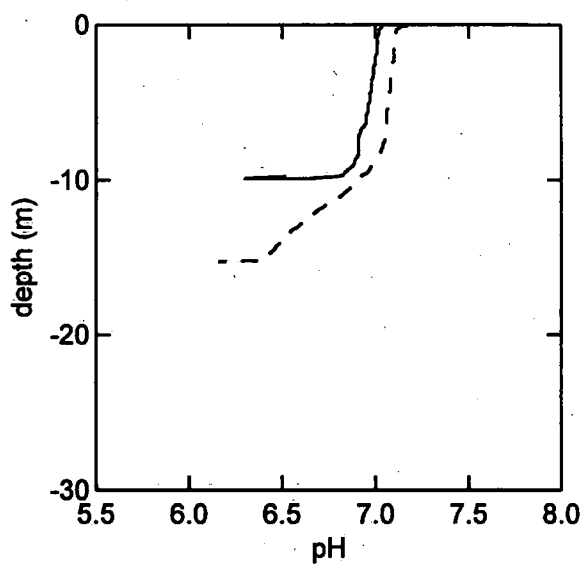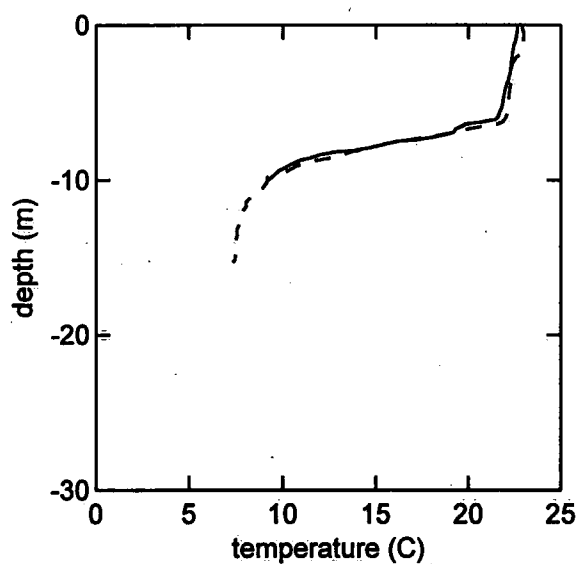
RIC
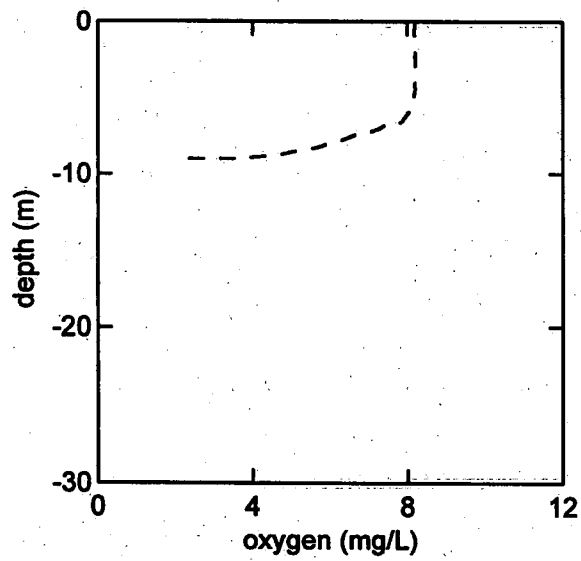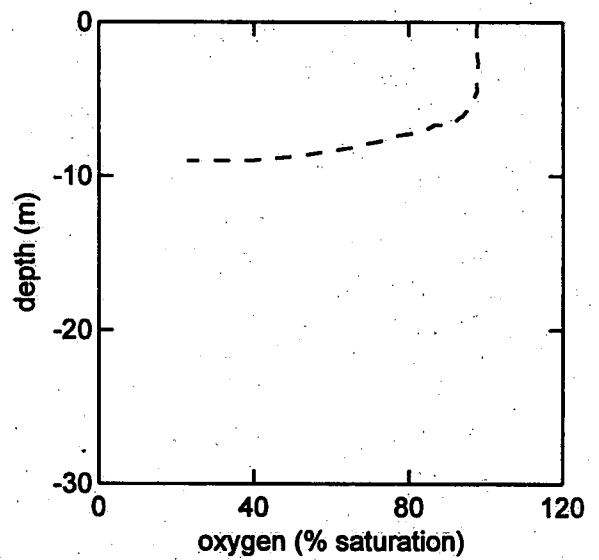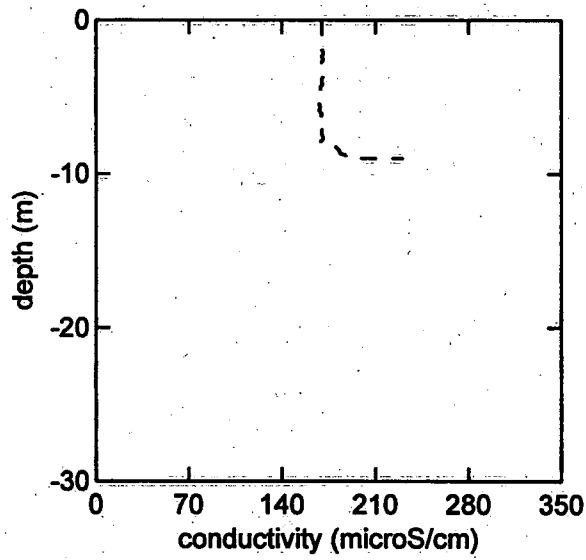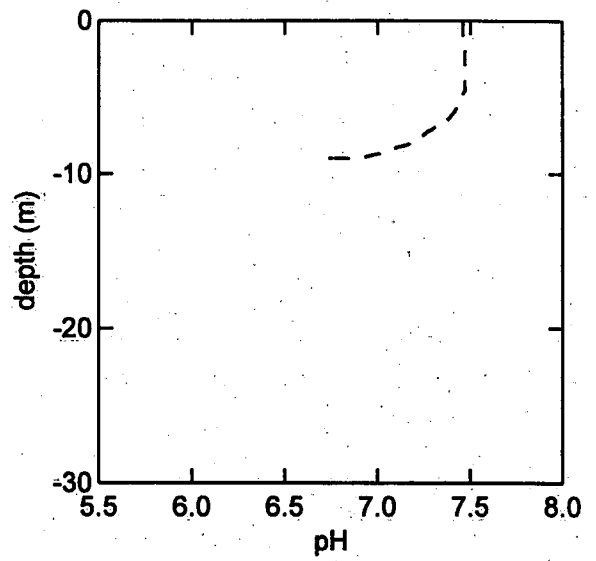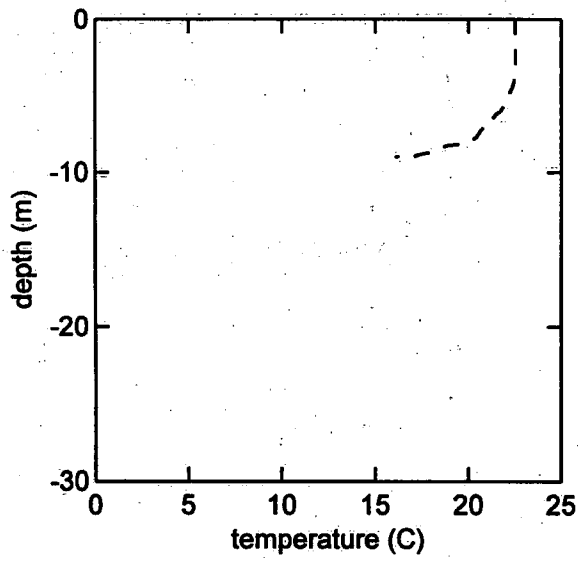
KAK
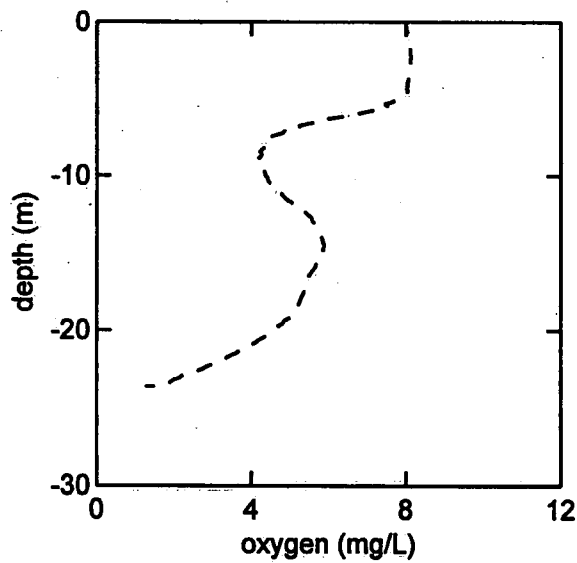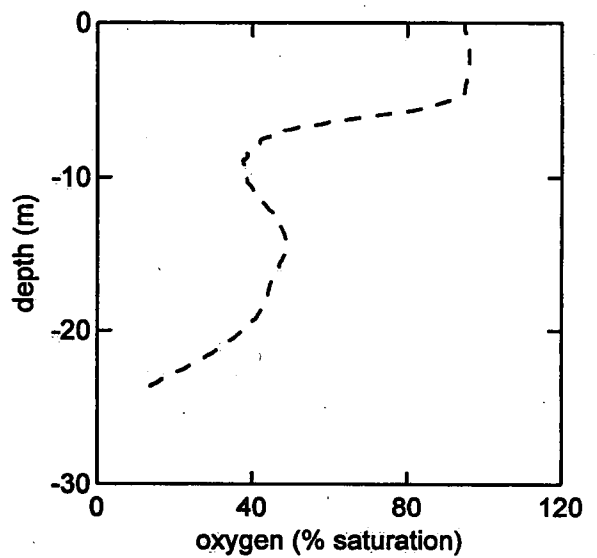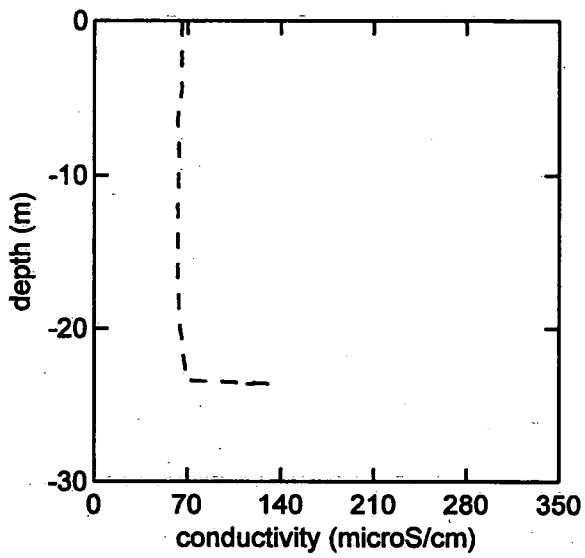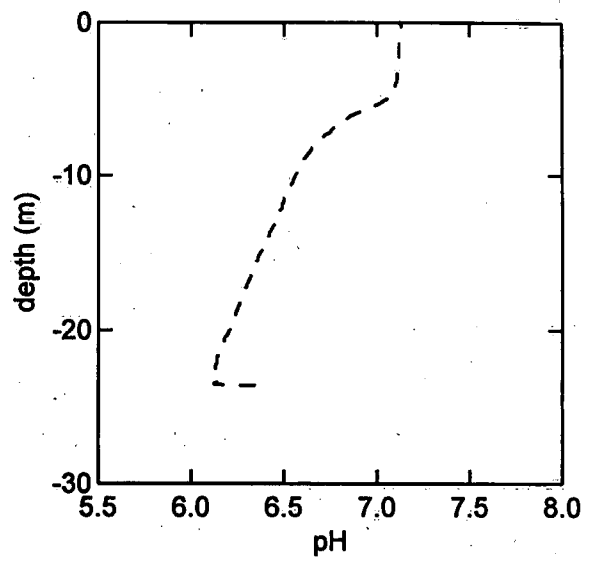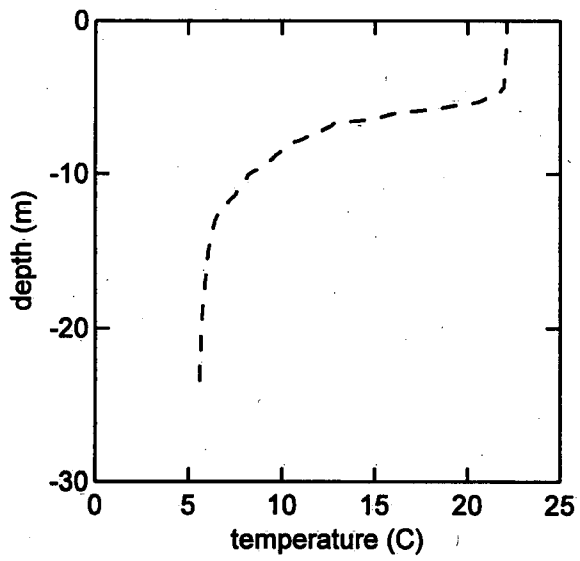
TRO
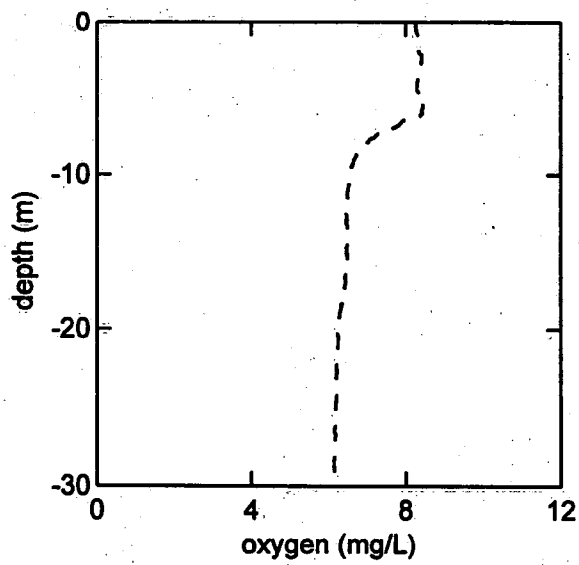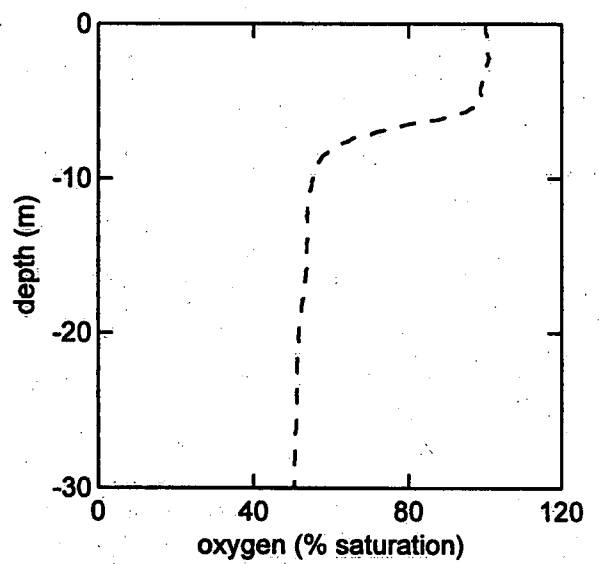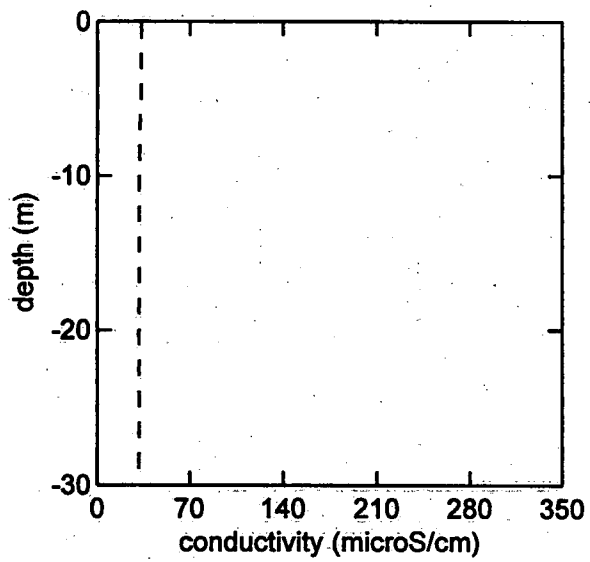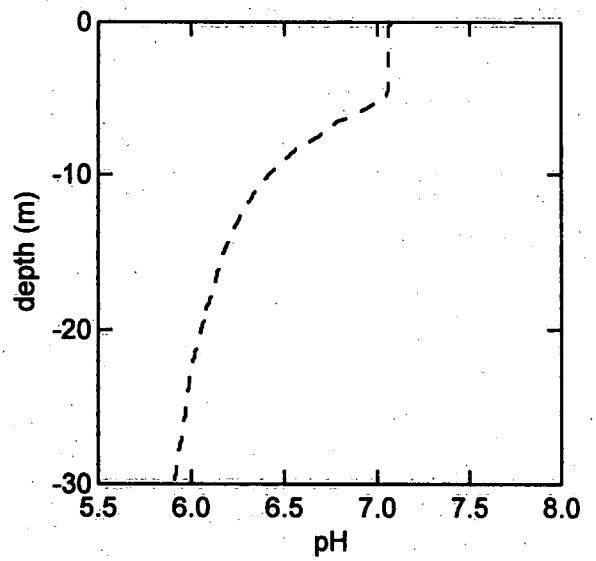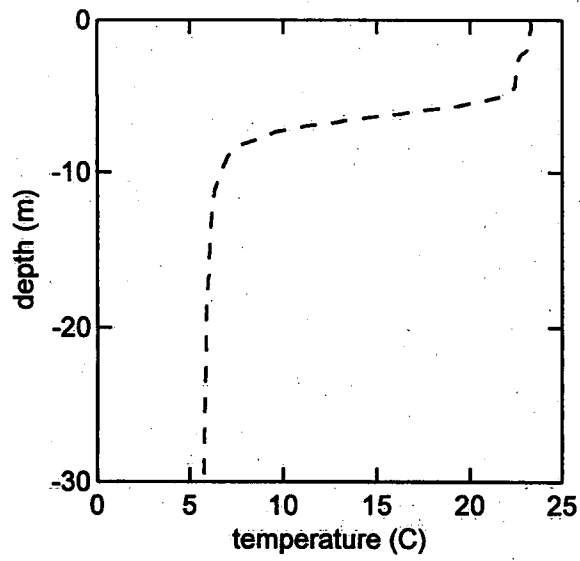
LOS
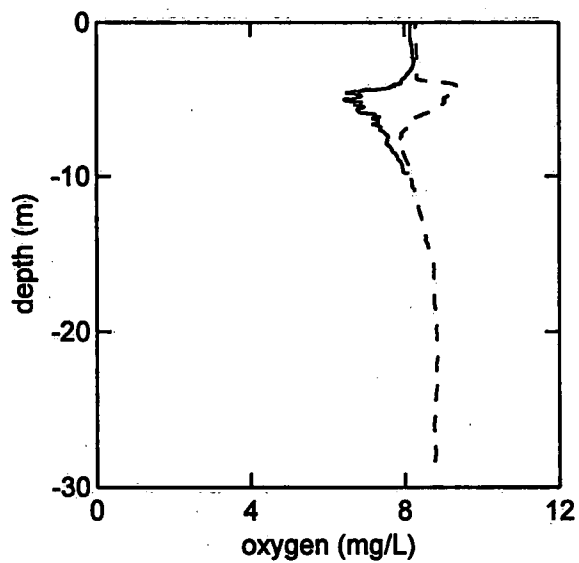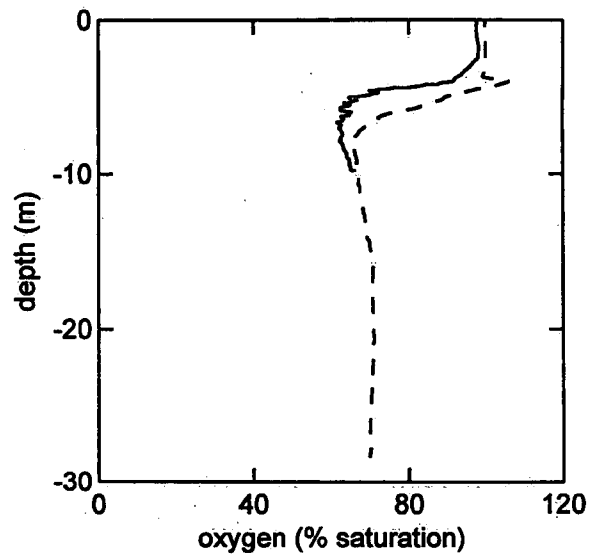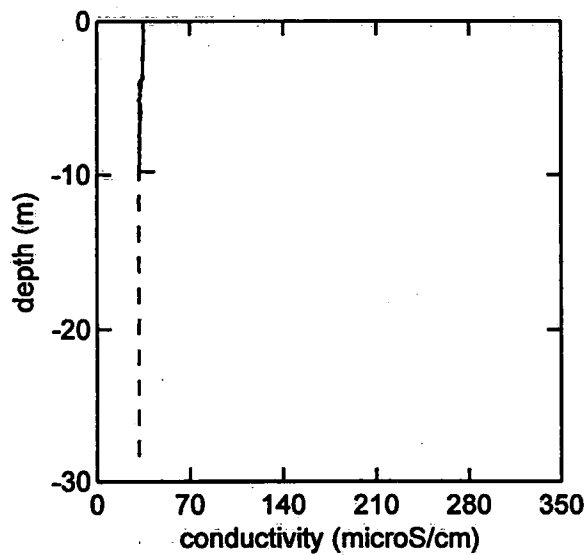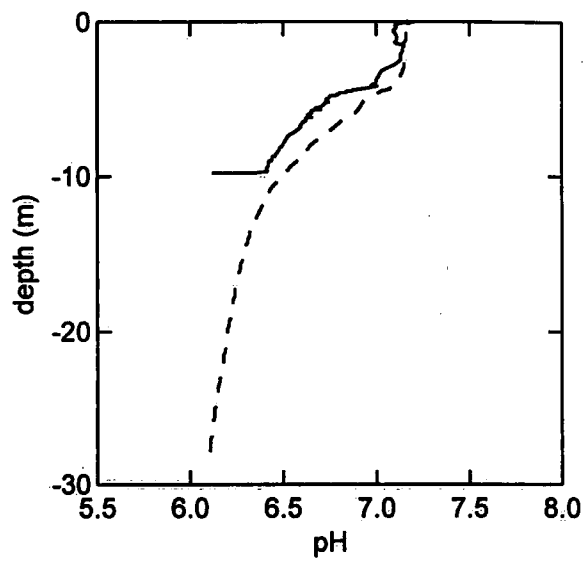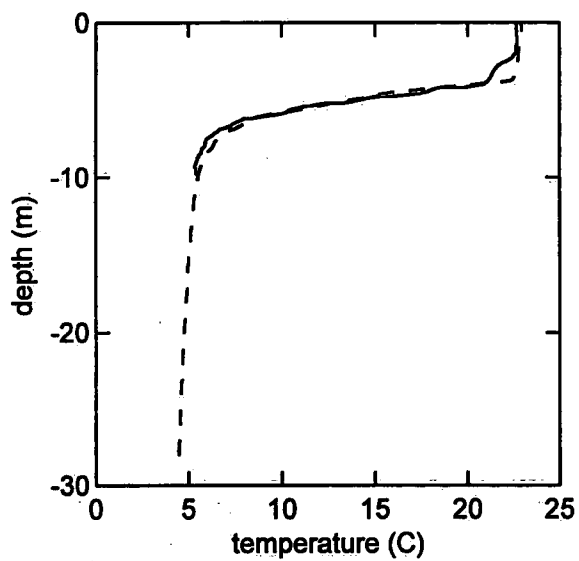
TOM
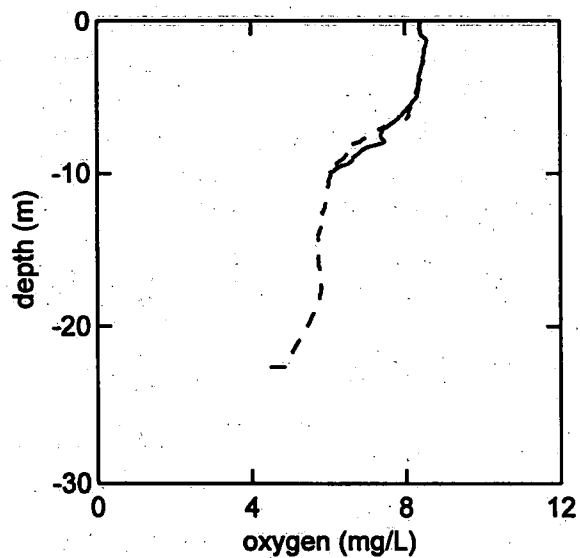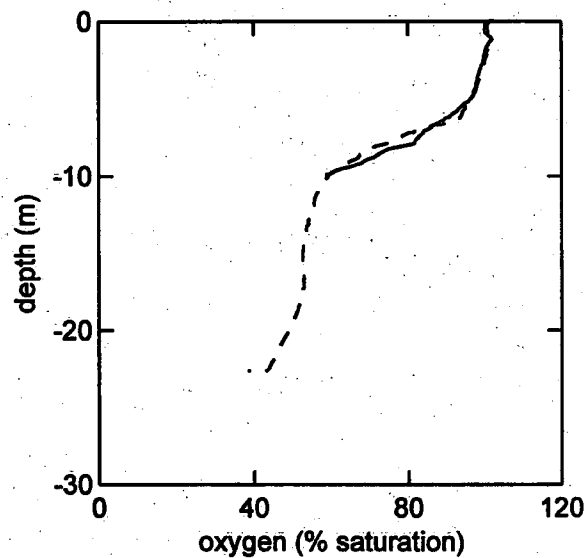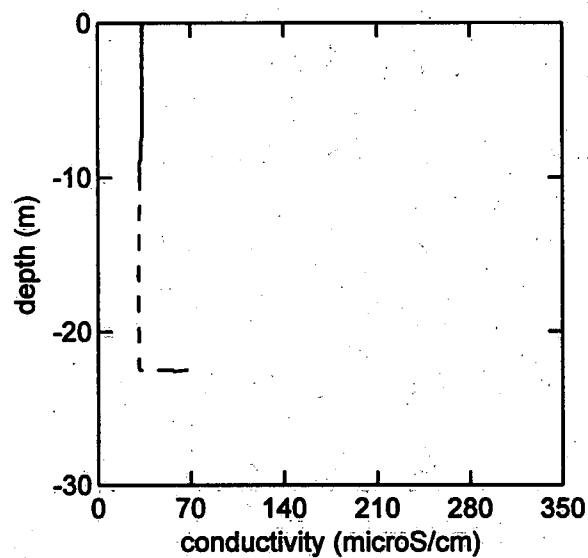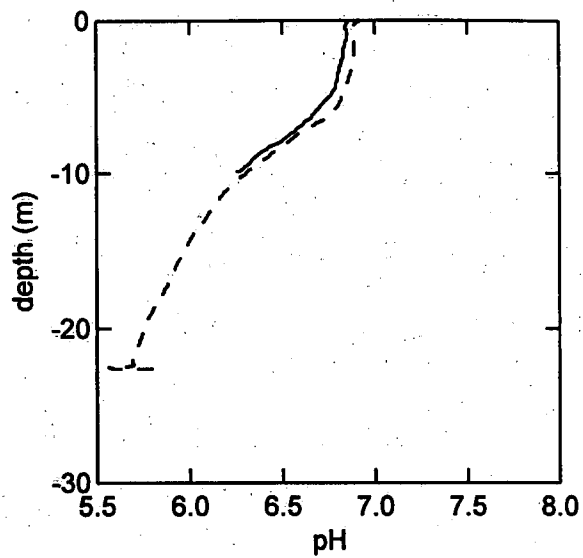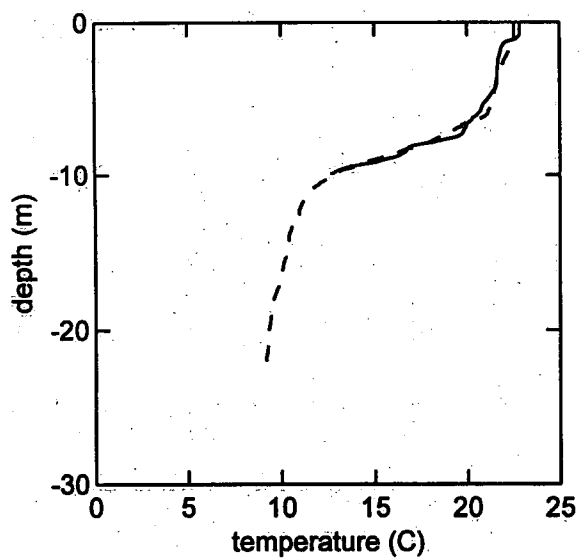
RES
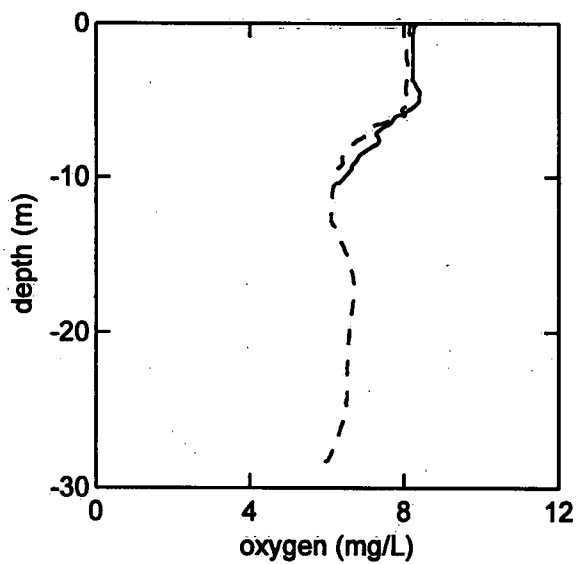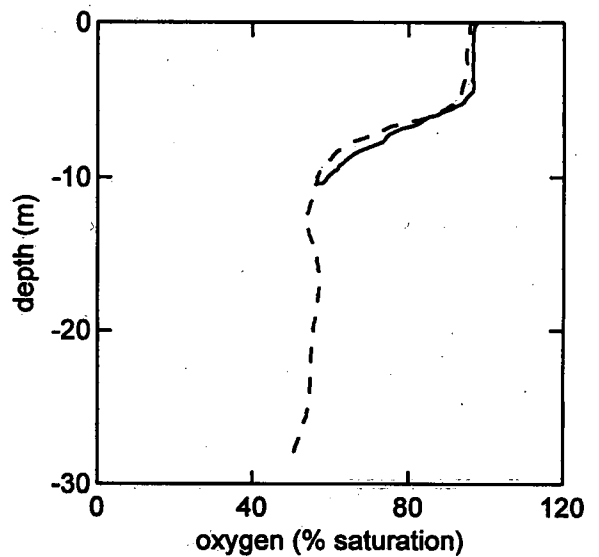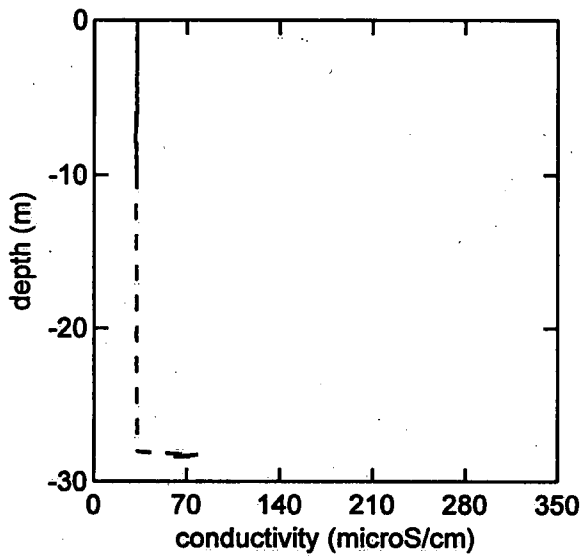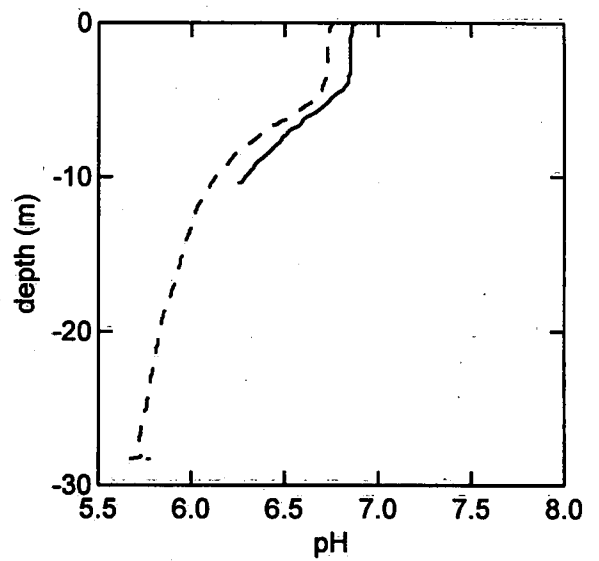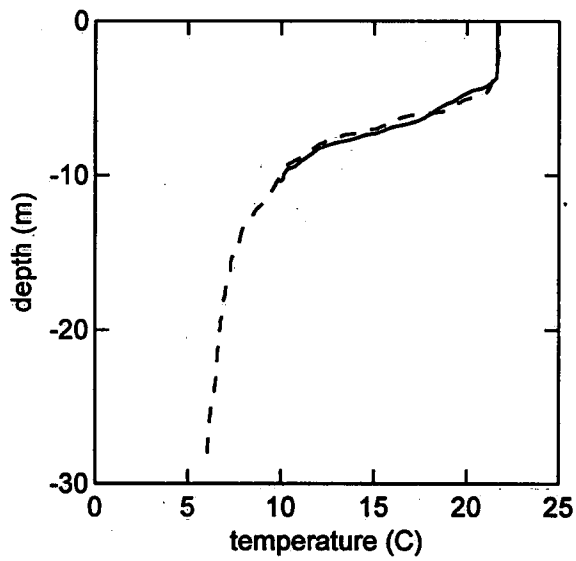
NOS
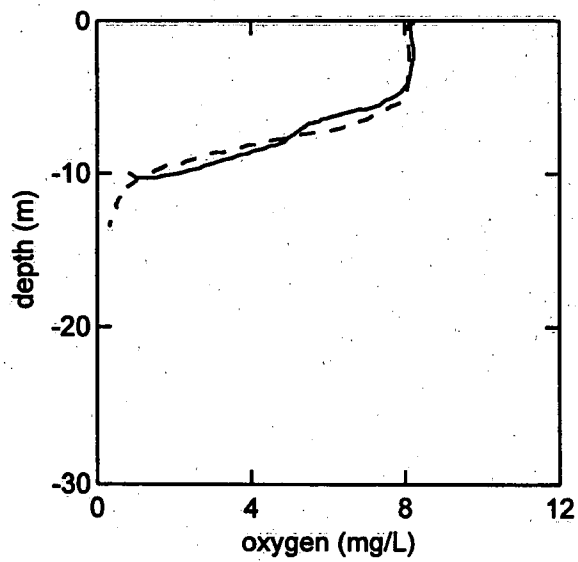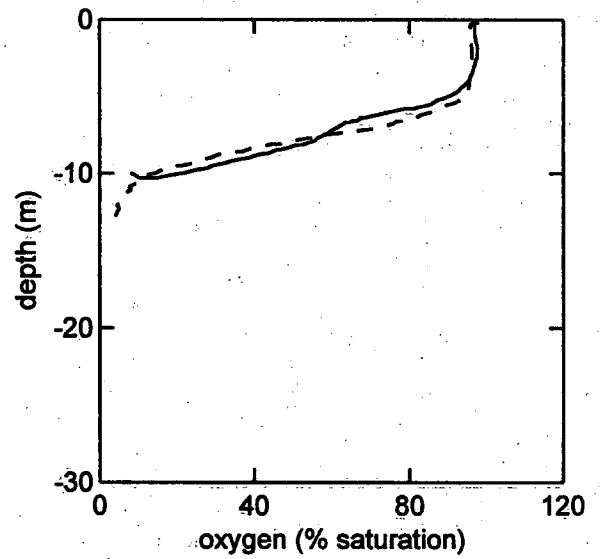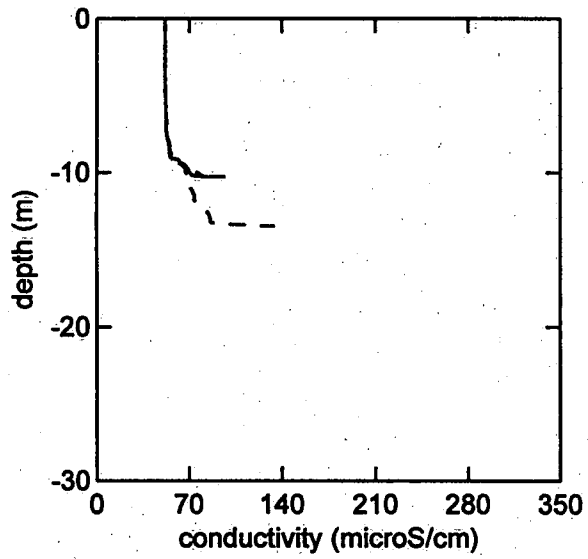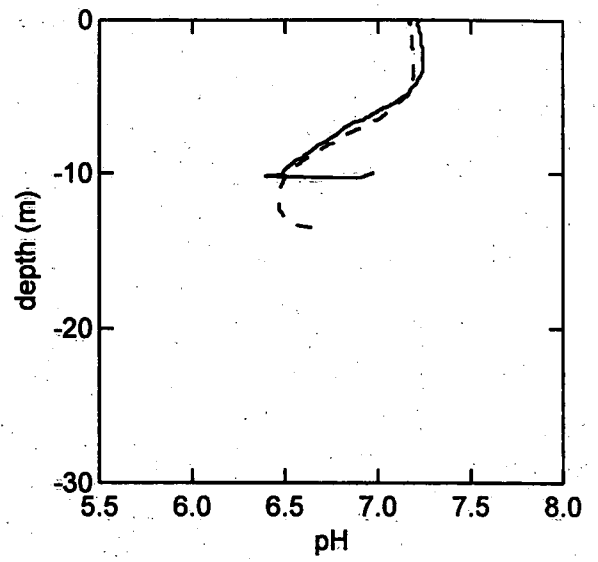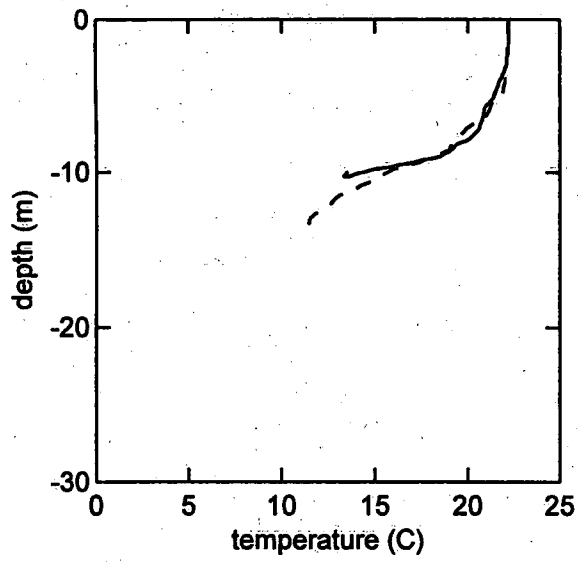
TAL
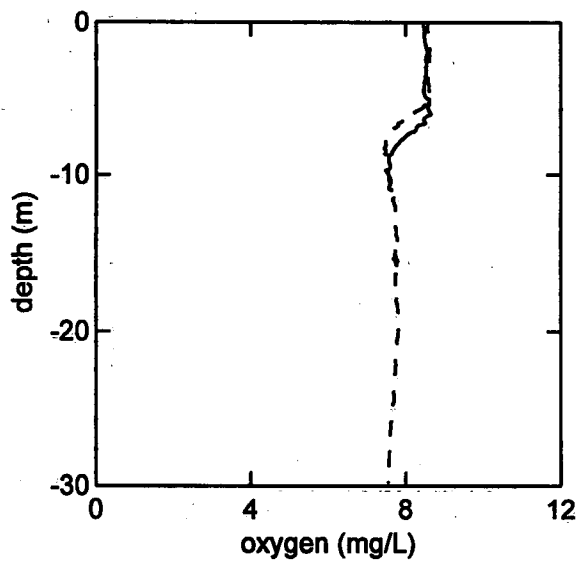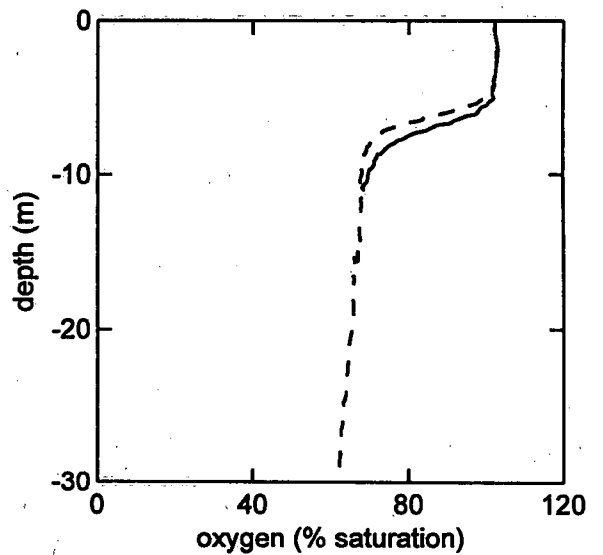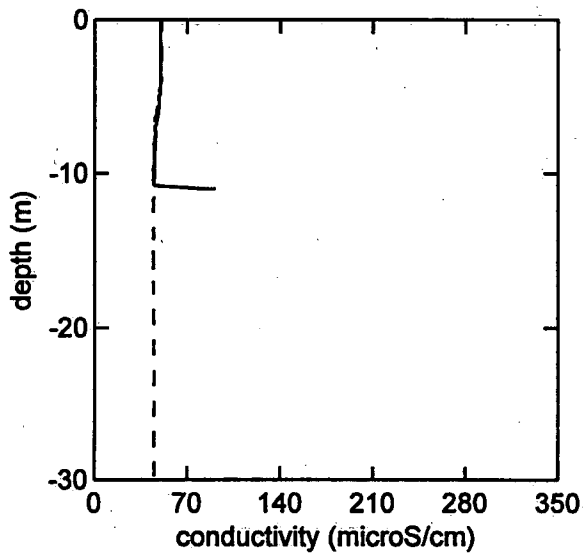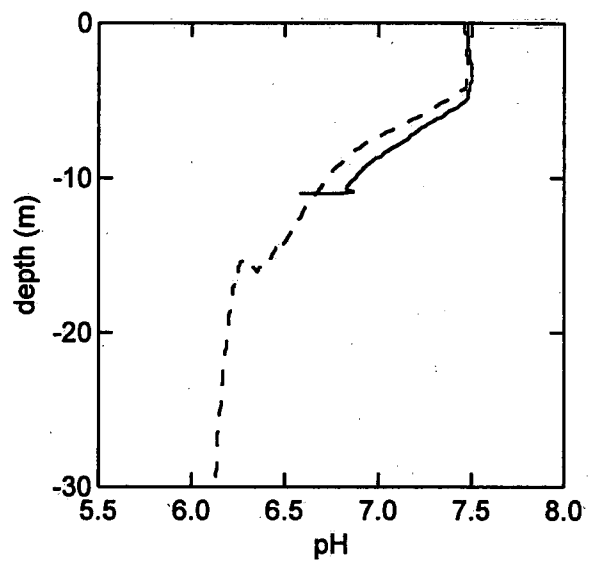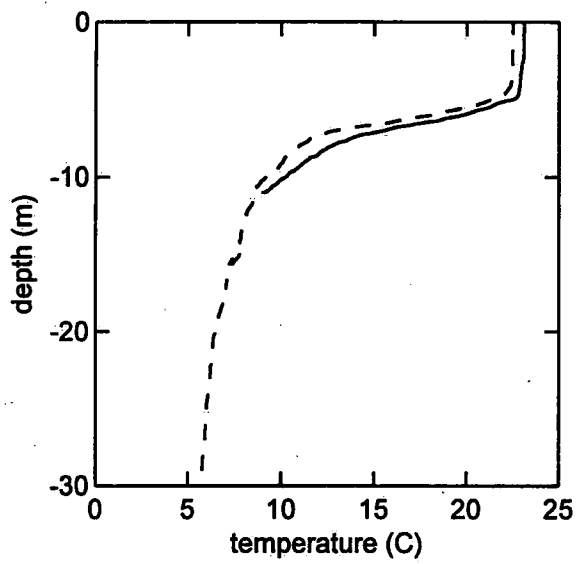
Appendix 2

Sediment profiles for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, loss on ignition (LOI) and total carbon (TC) from the deep station in each of the lakes sampled. Sediment cores were sectioned every cm from 1-10 cm and every 2 cm from 10-20 cm. Data are shown plotted by lake and summarized in table format by metal.

RAMD

MCFD

RICD

RAFD

NEPD

KAKD

TROD

LOSD

TOMD

RESD

NOSD

TALD

Metal Concentrations, Loss on Ignition (LOI) and Total Carbon (TC) in Sediment Profiles from the deep station in lakes at various distances from Copper Cliff.

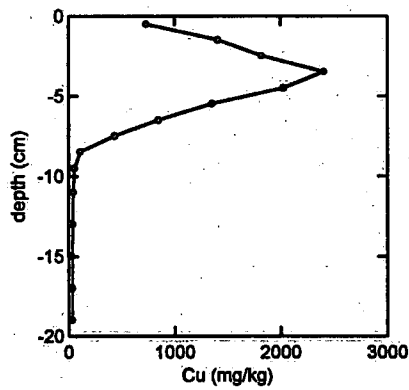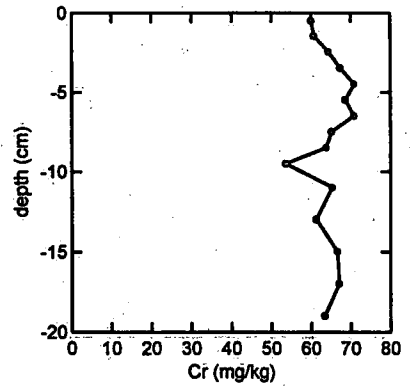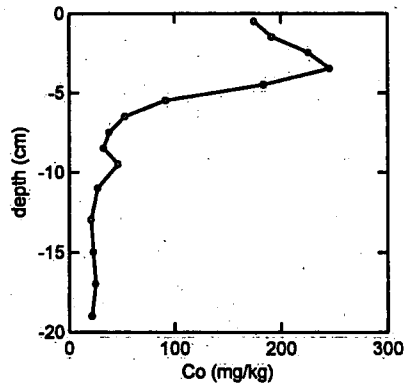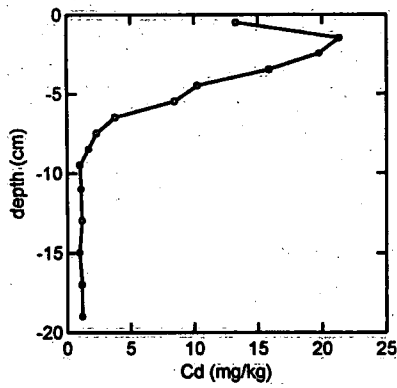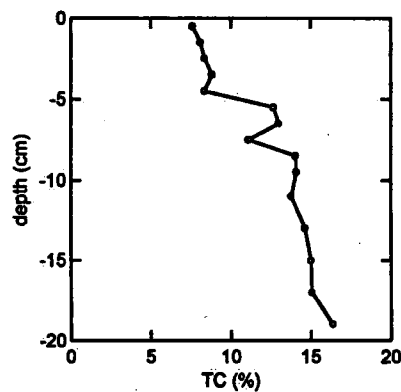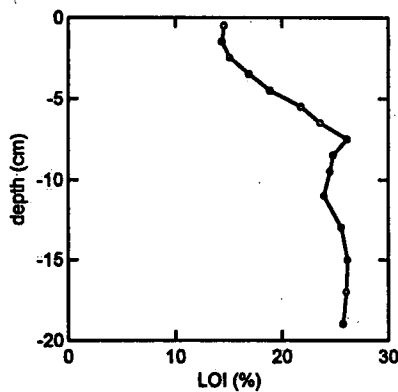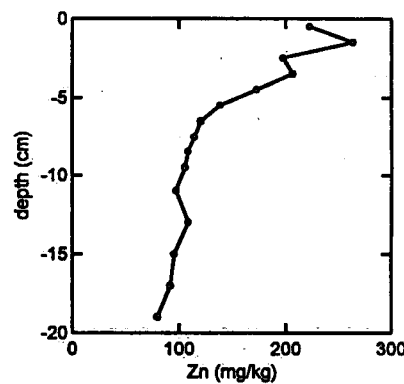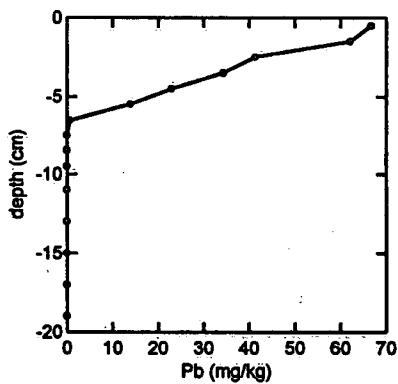|	RAMD	MCFD	RAFD	RICD	NEPD	KAKD	TROD	LOSD	TOMD	RESD	NOSD	TALD
km	6	10	11	12	32	38	43	52	94	107	144	154
depth	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd
cm	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
0-1	6.5	13.3	5.6	7.4	5.0	4.3	10.7	7.0	3.9	12.3	2.8	5.9
1-2	4.9	21.4	3.2	4.3	2.1	3.4	4.6	2.6	1.6	5.3	2.1	4.2
2-3	3.4	19.8	2.0	2.8	1.7	3.4	4.7	2.4	1.3	4.6	2.0	4.2
3-4	3.5	15.9	0.4	2.6	1.2	2.7	3.4	0.7	1.2	4.3	2.3	3.9
4-5	3.6	10.3	0	2.1	0.9	2.5	2.3	0	1.2	4.1	1.8	3.8
5-6	3.3	8.5	0	1.5	0	2.3	0.4	0	1.2	3.8	2.0	3.9
6-7	2.8	3.8	0	1.1	0	2.8	0.6	0	1.6	3.3	2.2	3.9
7-8	3.6	2.4	0	0.5	0	3.4	0.3	0	1.4	3.1	1.8	3.4
8-9	1.0	1.7	0.6	0.8	3.5	3.6	0.6	0.3	1.8	2.1	1.9	3.0
9-10	0.9	1.0	0.1	0.2	0	3.2	0	0	1.5	1.9	1.7	2.3
10-12	0	1.1	0.3	0.2	0	2.5	0	0	1.4	1.4	1.4	2.3
12-14	0	1.2	0.1	0	0.6	2.0	0	0	1.3	1.7	1.2	2.0
14-16	0	1.0	0	0.8	0.6	1.2	0	0	1.6	1.3	1.0	2.5
16-18	0	1.2	0	0.7	0.3	0.7	0.3	0	1.3	1.3	0.9	2.6
18-20	0	1.2	0	0.1	0	0	0.4	0	1.4	1.2	1.1	2.8
detection limit = 3.4												
	Co	Co	Co	Co	Co	Co	Co	Co	Co	Co	Co	Co
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
0-1	106	175	72	76	35	39	56	34	26	29	18	26
1-2	99	192	51	89	38	36	54	47	20	20	18	24
2-3	79	226	31	59	37	38	56	42	19	25	19	24
3-4	76	246	22	61	33	34	32	32	17	29	19	27
4-5	85	184	13	46	31	32	34	54	18	25	19	28
5-6	78	92	18	32	28	32	19	26	21	27	18	28
6-7	77	53	18	26	29	39	20	27	21	30	19	25
7-8	97	38	16	23	31	42	18	30	22	27	19	26
8-9	44	33	18	19	34	46	21	30	23	25	18	23
9-10	24	47	20	19	30	46	25	29	25	20	18	23
10-12	18	27	19	18	31	38	29	29	23	16	19	24
12-14	21	21	20	16	31	28	20	28	22	16	18	25
14-16	20	23	20	16	30	26	19	31	24	17	20	25
16-18	18	25	19	15	27	24	22	28	21	16	20	26
18-20	17	22	20	12	29	21	26	35	23	14	18	28
detection limit = 0.9												
	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
0-1	95	60	66	57	98	71	65	80	2	45	78	105
1-2	94	61	71	71	92	71	70	80	63	50	81	107
2-3	93	65	70	66	104	71	66	77	62	56	86	105
3-4	102	67	76	70	110	74	61	84	59	54	86	107
4-5	95	71	51	66	113	71	62	89	63	50	89	110
5-6	90	69	70	66	125	73	61	77	67	52	82	105
6-7	72	71	72	67	139	71	70	81	69	53	83	102
7-8	99	65	65	67	143	72	66	85	64	52	84	103
8-9	99	64	75	67	141	71	74	87	68	49	80	105
9-10	86	54	78	69	136	76	60	81	67	52	82	104
10-12	86	65	76	68	138	77	69	82	71	52	89	107
12-14	94	61	73	68	140	68	64	70	69	53	87	111
14-16	98	67	75	67	133	77	62	78	72	55	93	116
16-18	95	67	75	66	128	88	67	71	65	57	91	120
18-20	96	63	74	58	133	83	72	74	67	48	88	123
detection limit = 0.9												
	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
0-1	1955	735	1561	1028	254	180	227	158	39	38	37	37
1-2	1954	1414	995	1197	242	180	277	168	23	54	38	40
2-3	1349	1825	410	845	169	211	272	97	22	72	42	41
3-4	1329	2408	150	687	73	211	153	38	19	65	41	42
4-5	1577	2032	58	476	58	176	52	31	22	60	42	46
5-6	1448	1356	63	293	42	191	34	32	21	49	42	45
6-7	1520	848	55	189	43	263	40	35	22	40	44	41
7-8	1788	438	35	151	45	312	35	33	19	34	40	41
8-9	524	113	37	114	50	331	39	33	20	32	39	37
9-10	165	58	44	112	45	333	30	31	23	35	40	29
10-12	78	47	40	99	43	279	36	31	22	29	40	27
12-14	121	39	38	78	44	111	32	33	21	32	37	27
14-16	69	34	43	91	41	50	33	35	21	32	39	29
16-18	40	34	44	73	39	42	34	28	21	40	33	30
18-20	34	35	45	54	43	34	35	33	22	27	29	29
detection limit = 1.0												

Metal Concentrations, Loss on Ignition (LOI) and Total Carbon (TC) in Sediment Profiles from the deep station in lakes at various distances from Copper Cliff.

	RAMD	MCFD	RAFD	RICD	NEPD	KAKD	TROD	LOSD	TOMD	RESD	NOSD	TALD
km	6	10	11	12	32	38	43	52	94	107	144	154
depth cm	**Fe %**	**Fe %**	**Fe %**	**Fe %**	**Fe %**	**Fe %**	**Fe %**	**Fe %**	**Fe %**	**Fe %**	**Fe %**	**Fe %**
0-1	3.69	5.20	4.07	2.54	4.56	6.72	11.10	3.91	3.21	over	7.11	10.14
1-2	4.27	5.17	4.00	3.22	3.92	5.99	5.25	4.11	3.11	7.59	5.93	10.32
2-3	4.63	4.53	3.36	2.61	4.27	6.03	6.26	4.35	3.12	5.30	6.05	9.25
3-4	4.73	6.97	2.93	2.81	4.33	4.97	4.53	3.86	2.95	5.19	5.62	8.03
4-5	4.82	6.93	1.94	2.64	4.30	4.45	4.64	3.88	2.95	4.66	5.82	8.21
5-6	4.64	5.56	2.44	2.41	4.40	4.63	3.34	3.42	3.14	4.95	5.81	8.26
6-7	4.06	4.17	2.58	2.26	4.89	4.74	3.64	3.46	3.24	4.99	6.49	7.92
7-8	5.11	3.39	2.25	2.24	5.10	4.99	3.33	3.62	3.06	4.78	5.81	7.30
8-9	3.84	3.11	2.50	2.43	5.20	5.54	3.51	3.76	3.28	4.26	5.49	6.61
9-10	3.17	3.16	2.62	2.23	4.93	5.23	3.09	3.53	3.15	4.53	5.39	5.86
10-12	2.87	3.31	2.53	2.26	5.13	4.22	3.54	3.49	3.09	4.11	5.14	6.13
12-14	3.06	2.93	2.53	2.11	5.06	3.89	3.10	3.08	3.28	4.23	4.73	6.58
14-16	3.11	3.14	2.59	2.03	4.91	3.65	3.20	3.41	3.42	4.38	4.88	7.49
16-18	3.01	3.19	2.52	2.11	4.89	3.64	3.35	3.24	3.14	4.32	4.79	7.94
18-20	3.11	3.12	2.56	1.86	5.02	3.68	3.60	3.31	3.22	3.37	4.34	8.48
detection limit = 1.2 mg/kg												
	Mn mg/kg	**Mn mg/kg**	**Mn mg/kg**	**Mn mg/kg**	**Mn mg/kg**	**Mn mg/kg**	**Mn mg/kg**	**Mn mg/kg**	**Mn mg/kg**	**Mn mg/kg**	**Mn mg/kg**	**Mn mg/kg**
0-1	1059	2568	445	432	947	1996	8841	1428	1145	10130	1128	6170
1-2	912	over	409	451	827	1567	4526	1202	1187	4314	916	4052
2-3	742	41090	406	412	836	1457	3934	1112	1123	2637	908	3655
3-4	577	19730	425	454	781	1305	3017	1040	1078	2301	845	3363
4-5	503	8550	344	431	777	1265	2879	1155	1050	2014	832	3687
5-6	433	4039	431	444	735	1191	2686	1236	1024	1860	819	3609
6-7	387	3158	460	477	709	1149	2955	1188	1012	1883	897	3508
7-8	429	2627	426	474	724	1071	2634	1074	1002	1948	848	3255
8-9	467	2900	466	480	723	1011	2650	1087	1014	1916	840	2704
9-10	445	2884	508	449	704	1043	2414	1103	998	1933	833	2197
10-12	427	2852	508	457	720	982	2444	1121	995	1761	723	2135
12-14	445	2018	512	423	718	942	2175	1241	1018	1686	637	2439
14-16	451	1495	518	395	723	973	2385	1360	1039	1581	648	2880
16-18	447	1504	523	376	712	1013	2432	1306	978	1516	629	2674
18-20	446	1338	545	333	731	935	2187	1432	950	1319	600	2809
detection limit = 0.2												
	Ni mg/kg	**Ni mg/kg**	**Ni mg/kg**	**Ni mg/kg**	**Ni mg/kg**	**Ni mg/kg**	**Ni mg/kg**	**Ni mg/kg**	**Ni mg/kg**	**Ni mg/kg**	**Ni mg/kg**	**Ni mg/kg**
0-1	1903	4067	2022	1784	373	274	281	175	48	46	46	58
1-2	1986	6341	1511	2449	398	280	419	225	29	55	48	55
2-3	1626	5513	663	1672	289	342	459	131	27	68	51	58
3-4	1681	5145	239	1786	156	300	214	54	24	72	53	60
4-5	1945	3690	89	1285	122	269	71	48	26	61	53	66
5-6	1766	1905	81	950	90	287	41	38	27	50	51	67
6-7	1844	1021	64	702	82	364	48	40	29	39	52	63
7-8	2397	500	41	546	86	439	41	40	28	30	52	65
8-9	745	159	47	403	88	472	42	42	29	26	49	55
9-10	240	92	52	390	77	505	36	38	30	26	52	47
10-12	116	76	46	321	80	392	39	38	31	24	53	46
12-14	170	59	46	248	78	137	33	33	29	24	48	47
14-16	99	45	51	263	77	71	32	37	32	24	51	51
16-18	63	46	42	216	71	58	33	34	28	24	49	53
18-20	54	38	42	136	72	46	36	30	29	22	43	55
detection limit = 2.0												
	Pb mg/kg	**Pb mg/kg**	**Pb mg/kg**	**Pb mg/kg**	**Pb mg/kg**	**Pb mg/kg**	**Pb mg/kg**	**Pb mg/kg**	**Pb mg/kg**	**Pb mg/kg**	**Pb mg/kg**	**Pb mg/kg**
0-1	158	66	156	67	65	64	189	162	46	108	36	45
1-2	165	128	99	62	68	71	190	185	11	132	23	52
2-3	105	104	47	41	35	74	189	108	0	172	30	50
3-4	98	197	13	34	6	97	115	35	0	162	30	67
4-5	120	149	0	23	0	92	46	1	0	134	32	80
5-6	110	103	0	14	0	110	6	0	0	100	40	81
6-7	120	63	0	1	0	153	2	0	0	65	44	73
7-8	148	42	0	0	0	229	0	0	0	50	41	68
8-9	26	22	0	0	0	149	0	0	0	28	43	43
9-10	0	5	0	0	0	165	0	0	0	17	36	2
10-12	0	0	0	0	0	135	0	0	0	4	33	0
12-14	0	0	0	0	0	60	0	0	0	0	17	0
14-16	0	0	0	0	0	35	0	0	0	0	17	0
16-18	0	0	0	0	0	18	0	0	0	0	2	0
18-20	0	0	0	0	0	0	0	0	0	0	0	0
detection limit = 2.5												

Metal Concentrations, Loss on Ignition (LOI) and Total Carbon (TC) in Sediment Profiles from the deep station in lakes at various distances from Copper Cliff.

km	RAMD 6	MCFD 10	RAFD 11	RICD 12	NEPD 32	KAKD 38	TROD 43	LOSD 52	TOMD 94	RESD 107	NOSD 144	TALD 154
depth cm	Zn mg/kg	Zn mg/kg	Zn mg/kg	Zn mg/kg	Zn mg/kg	Zn mg/kg	Zn mg/kg	Zn mg/kg	Zn mg/kg	Zn mg/kg	Zn mg/kg	Zn mg/kg
0-1	353	955	221	223	273	285	385	290	186	300	169	381
1-2	314	1222	192	264	291	273	406	329	136	381	172	389
2-3	241	1143	132	198	260	282	394	262	122	425	181	399
3-4	231	861	105	207	221	278	300	197	122	383	181	410
4-5	248	590	104	173	206	272	197	166	132	326	188	402
5-6	222	342	69	139	179	272	128	124	137	306	181	391
6-7	220	255	86	121	179	302	133	146	144	251	193	355
7-8	266	195	84	115	183	319	129	166	137	226	186	333
8-9	144	154	72	109	189	323	153	160	146	188	177	270
9-10	103	121	82	106	173	303	137	166	146	177	179	202
10-12	94	170	92	98	176	280	154	172	146	160	181	168
12-14	103	149	87	109	179	216	127	153	147	174	164	162
14-16	101	149	84	96	173	174	125	164	149	174	167	178
16-18	98	149	85	92	163	180	125	127	130	186	163	176
18-20	97	148	86	80	161	144	147	128	134	145	154	190
detection limit = 0.9												
	LOI %	LOI %	LOI %	LOI %	LOI %	LOI %	LOI %	LOI %	LOI %	LOI %	LOI %	LOI %
0-1	12.2	N/A	18.6	14.6	18.7	26.1	24.2	21.9	27.1	4.0	20.3	15.8
1-2	10.5	20.8	17.1	14.4	18.1	22.4	17.6	20.2	28.7	30.7	18.5	15.4
2-3	9.3	19.3	16.6	15.1	17.5	20.5	23.3	20.9	27.9	19.4	17.4	14.6
3-4	9.1	17.6	16.2	17.0	17.1	17.6	23.7	19.6	27.3	18.1	15.3	13.9
4-5	8.4	16.9	17.2	18.9	17.8	17.3	25.1	22.0	26.5	20.6	15.3	13.6
5-6	7.6	16.8	17.7	21.8	16.0	17.5	25.8	28.7	25.5	22.7	15.7	13.4
6-7	10.7	16.4	17.9	23.6	14.1	19.0	27.8	27.2	26.4	21.2	16.0	13.3
7-8	11.1	18.7	17.6	26.2	13.4	17.7	27.2	23.6	27.3	22.5	14.1	13.0
8-9	13.3	23.9	17.4	24.9	13.0	18.3	26.9	22.7	27.2	23.9	13.7	12.8
9-10	13.2	27.7	17.4	24.6	14.6	20.1	25.9	26.8	27.3	25.7	12.4	11.5
10-12	13.2	30.3	16.3	24.0	13.4	21.6	25.0	23.6	29.7	26.1	10.3	11.1
12-14	12.6	30.0	17.3	25.6	12.7	21.4	26.6	27.7	30.1	26.5	10.2	13.6
14-16	12.7	27.9	18.0	26.2	13.5	21.0	29.6	28.1	29.7	27.4	8.4	16.2
16-18	12.3	27.7	17.9	26.1	14.3	21.3	29.9	29.1	31.1	27.4	10.0	16.0
18-20	13.2	28.8	18.3	25.8	14.2	19.8	26.2	31.4	31.1	27.2	10.2	15.4
	TC %	TC %	TC %	TC %	TC %	TC %	TC %	TC %	TC %	TC %	TC %	TC %
0-1	6.38	11.93	9.80	7.62	9.53	12.15	12.13	9.13	11.89	10.35	9.73	6.66
1-2	5.34	9.67	9.36	8.11	9.39	10.98	10.98	9.81	14.16	9.92	7.39	5.91
2-3	4.97	7.99	9.83	8.37	8.78	9.65	8.97	10.30	13.96	9.57	7.64	5.77
3-4	4.09	7.67	9.26	8.83	8.93	9.39	11.96	9.31	14.27	9.94	7.78	5.62
4-5	3.61	7.31	9.05	8.36	8.31	9.99	12.14	11.14	13.58	9.75	8.26	5.69
5-6	3.92	7.51	9.04	12.69	6.61	8.81	12.64	13.12	12.84	9.97	8.42	5.89
6-7	3.59	8.44	10.28	13.01	5.58	8.71	12.93	12.39	12.21	10.34	7.37	5.61
7-8	4.66	10.19	9.54	11.11	5.16	8.58	13.19	11.14	13.82	11.17	7.68	5.18
8-9	4.86	12.81	9.45	14.07	6.56	8.78	12.95	11.04	13.52	11.12	7.38	5.06
9-10	4.97	15.15	10.18	14.12	5.21	10.91	14.39	12.41	13.43	12.15	6.78	4.89
10-12	4.05	15.28	9.12	13.79	5.65	11.41	12.84	11.71	13.72	12.96	6.96	4.58
12-14	4.38	16.91	10.37	14.66	6.23	10.81	13.47	14.32	14.34	13.14	5.41	5.78
14-16	4.94	14.87	10.39	15.02	6.77	10.75	14.28	14.02	14.34	12.79	4.24	7.56
16-18	4.83	14.75	9.78	15.07	5.82	10.36	15.39	15.14	15.22	12.94	5.24	6.76
18-20	4.63	15.46	9.37	16.38	5.72	9.01	12.49	15.01	14.12	12.78	6.10	6.91

Appendix 3

Toxicity test results for *Chironomus riparius*, *Hexagenia* sp., *Hyalella azteca*, and *Tubifex tubifex*, and metal concentrations measured in the overlying water at the end of the exposure period for each replicate test container. Replicate (Rep) numbers refer to separate sediment grab samples from each site (i.e., replicate 2 for each species refers to the same sediment sample from that site). Toxicity was measured for different replicates in different experiments (1 replicate per experiment), but all replicates for any one species were tested in the same experiment.

Toxicity test results for Chironomus (10 day test).

Replicate, site, distance from Copper Cliff, survival, final weight, and metal concentrations in bioassay water.

Rep	Site	km	No	N	Percent Survival	Final weight (mg)	Co ug/L	Cu ug/L	Mn ug/L	Ni ug/L	Pb ug/L	V ug/L	Zn ug/L
1	RAMD	6	15	13	87	2.89	nd	23	283	264	nd	51	nd
2	RAMD	6	15	15	100	2.65	<9	44	602	404	<25	<2	<9
1	MCF10	10	15	9	60	2.73	nd	12	98	95	21	17	nd
2	MCF10	10	15	13	87	2.64	<9	<10	198	88	<25	<2	<9
1	MCFD	10	15	12	80	2.77	21	24	12500	390	11	44	11
2	MCFD	10	15	10	67	2.67	<9	<10	9661	524	<25	<2	22
1	RAF10	11	16	16	100	2.23	nd	nd	539	nd	nd	45	nd
2	RAF10	11	15	11	73	1.32	<9	<10	6	20	37	<2	<9
1	RAFD	11	15	7	47	3.74	nd	9	41	176	29	44	nd
2	RAFD	11	15	12	80	2.08	<9	<10	40	261	78	<2	<9
1	RICD	12	17	17	100	2.18	nd	16	19	351	nd	51	nd
2	RICD	12	15	11	73	1.86	<9	<10	74	1361	<25	<2	47
1	NEPD	32	15	2	13	3.00	nd	3	6	nd	33	51	5
2	NEPD	32	15	7	47	1.91	<9	<10	7	<20	33	<2	<9
1	KAK10	38	15	15	100	2.72	2	4	14	nd	15	50	nd
2	KAK10	38	15	12	80	2.43	<9	<10	55	10	33	<2	<9
1	KAKD	38	15	6	40	3.65	nd	4	471	nd	11	52	nd
2	KAKD	38	15	6	40	2.97	<9	<10	1079	22	<25	<2	<9
1	TRO10	43	15	8	53	2.96	nd	7	nd	38	nd	49	nd
2	TRO10	43	15	10	67	1.51	<9	<10	38	<20	<25	<2	<9
1	TROD	43	15	6	40	3.03	nd	3	35	nd	42	44	nd
2	TROD	43	15	11	73	2.10	<9	<10	46	30	<25	<2	<9
1	LOS10	52	15	14	93	2.42	nd	nd	14	nd	nd	45	nd
2	LOS10	52	15	10	67	2.29	<9	<10	230	<20	<25	<2	<9
1	LOSD	52	15	8	53	3.74	nd	4	339	nd	72	nd	nd
2	LOSD	52	15	10	67	1.61	<9	<10	501	<20	<25	<2	<9
1	TOM10	94	15	7	47	3.53	nd	4	236	3	22	51	nd
2	TOM10	94	15	10	67	1.75	<9	<10	39	<20	44	<2	<9
1	TOMD	94	15	11	73	2.54	nd	3	58	nd	17	45	nd
2	TOMD	94	15	10	67	1.06	<9	<10	129	<20	<25	<2	14
1	RES10	107	15	13	87	2.55	nd	nd	20	nd	nd	44	nd
2	RES10	107	15	12	80	1.71	<9	<10	76	<20	<25	<2	<9
1	RESD	107	15	15	100	2.13	nd	3	50	35	55	51	nd
2	RESD	107	15	9	60	2.01	<9	<10	8	<20	<25	<2	<9
1	NOS10	144	15	5	33	3.98	nd	4	nd	nd	24	49	nd
2	NOS10	144	15	14	93	2.74	<9	<10	78	<20	<25	<2	<9
1	NOSD	144	15	13	87	1.78	nd	3	nd	nd	23	43	nd
2	NOSD	144	15	13	87	1.52	<9	<10	97	<20	<25	<2	<9
1	TAL10	154	15	14	93	2.30	nd	1	67	nd	nd	42	nd
2	TAL10	154	15	6	40	3.10	<9	<10	105	10	<25	<2	<9
1	TALD	154	15	15	100	1.91							
2	TALD	154	15	11	73	1.87	<9	<10	965	<20	<25	<2	<9
1	HH1	368	15	6	40	3.30	nd	3	9	nd	nd	47	2
2	HH1	368	15	12	80	2.52	<9	<10	13	<20	26	<2	14
1	LE303	443	15	10	67	2.48	nd	4	6	nd	19	53	2
2	LE303	443	15	11	73	2.89	<9	<10	8	<20	<25	<2	<9

Toxicity test results for Hexagenia (21 day test).

Replicate, site, distance from Copper Cliff, survival, growth, and metal concentrations in bioassay water.

Rep	Site	km	No	N	Percent Survival	initial	final	initial/ final	Co ug/L	Cu ug/L	Mn ug/L	Ni ug/L	Pb ug/L	V ug/L	Zn ug/L
						Wet weight (mg)									
2	RAMD	6	2	2	100	4.3	3.3	0.8	<9	13	234	<20	34	<2	17
3	RAMD	6	2	1	50	7.6	8.0	1.05	<9	13	2	172	87	<2	<9
2	MCF10	10	2	1	50	7.3	9.3	1.28	<9	13	125	141	<25	<2	<9
3	MCF10	10	2	2	100	9.2	19.4	2.12	<9	10	425	241	57	<2	11
2	MCFD	10	2	1	50	5.4	5.4	1.00	<9	12	12100	<20	<25	<2	<9
3	MCFD	10	2	1	50	8.9	5.5	0.62	37	<10	7357	994	<25	<2	66
2	RAF10	11	2	2	100	4.0	7.8	1.95	<9	17	<2	56	<25	<2	<9
3	RAF10	11	2	2	100	7.4	8.7	1.18	<9	<10	4877	<20	<25	<2	<9
2	RAFD	11	2	2	100	5.1	4.5	0.88	<9	12	104	486	<25	<2	<9
3	RAFD	11	2	2	100	6.6	19.8	3.02	<9	10	<2	65	<25	<2	<9
2	RICD	12	2	1	50	5.1	3.7	0.73	<9	34	21	70	<25	<2	16
3	RICD	12	2	2	100	6.7	5.1	0.75	<9	<10	60	811	<25	<2	<9
2	NEPD	32	2	2	100	5.4	23.7	4.43	<9	10	5	<20	<25	<2	11
3	NEPD	32	2	2	100	8.6	34.3	4.01	<9	<10	<2	<20	<25	<2	<9
2	KAK10	38	2	2	100	5.5	33.6	6.12	<9	<10	<2	<20	<25	<2	<9
3	KAK10	38	2	2	100	6.8	32.7	4.80	<9	<10	31	<20	<25	<2	<9
2	KAKD	38	2	2	100	5.2	26.1	5.06	<9	<10	450	62	<25	<2	25
3	KAKD	38	2	2	100	5.4	34.2	6.38	<9	<10	1267	<20	49	<2	<9
2	TRO10	43	2	2	100	4.5	24.1	5.42	<9	<10	<2	<20	<25	<2	<9
3	TRO10	43	2	2	100	6.7	27.5	4.14	<9	<10	205	<20	<25	<2	<9
2	TROD	43	2	2	100	5.5	33.8	6.21	<9	<10	<2	<20	<25	<2	<9
3	TROD	43	2	2	100	7.2	30.8	4.27	<9	58	<2	<20	<25	<2	<9
2	LOS10	52	2	2	100	4.4	30.9	7.09	<9	<10	<2	<20	<25	<2	<9
3	LOS10	52	2	2	100	6.3	42.2	6.74	<9	<10	571	<20	<25	<2	<9
2	LOSD	52	2	2	100	5.1	22.8	4.51	<9	<10	927	<20	<25	<2	<9
3	LOSD	52	2	2	100	7.2	30.6	4.28	<9	<10	390	<20	48	<2	<9
2	TOM10	94	2	2	100	4.5	25.1	5.57	<9	<10	37	<20	<25	<2	<9
3	TOM10	94	2	2	100	7.5	38.5	5.17	<9	<10	2	<20	<25	<2	15
2	TOMD	94	2	2	100	4.7	24.5	5.27	<9	<10	<2	<20	<25	<2	<9
3	TOMD	94	2	2	100	7.0	29.6	4.22	<9	<10	10	<20	<25	<2	<9
2	RES10	107	2	2	100	5.6	37.1	6.68	<9	<10	<2	<20	<25	<2	<9
3	RES10	107	2	2	100	7.9	28.3	3.61	<9	<10	6	<20	<25	<2	11
2	RESD	107	2	2	100	4.3	28.2	6.63	<9	<10	<2	<20	<25	<2	<9
3	RESD	107	2	2	100	7.3	35.0	4.82	<9	<10	110	<20	<25	<2	<9
2	NOS10	144	2	2	100	5.0	34.0	6.87	<9	<10	<2	<20	<25	<2	<9
3	NOS10	144	2	2	100	7.9	49.0	6.20	<9	15	6	<20	<25	<2	10
2	NOSD	144	2	2	100	4.3	39.8	9.35	<9	<10	<2	<20	<25	<2	<9
3	NOSD	144	2	2	100	6.8	41.8	6.19	<9	<10	562	<20	<25	<2	<9
2	TAL10	154	2	2	100	4.8	27.7	5.83	<9	<10	<2	<20	<25	<2	<9
3	TAL10	154	2	2	100	7.4	36.7	4.99	<9	51	6	<20	<25	<2	<9
2	TALD	154	2	2	100	5.7	32.5	5.74	<9	<10	1129	<20	41	<2	<9
3	TALD	154	2	2	100	6.9	32.6	4.75	<9	<10	5	35	<25	<2	<9
2	HH1	368	2	2	100	6.2	48.0	7.80	<9	<10	<2	<20	40	<2	<9
3	HH1	368	2	2	100	6.2	41.9	6.81	<9	<10	3	<20	<25	<2	<9
2	LE303	443	2	2	100	5.1	35.2	6.97	<9	<10	<2	<20	<25	<2	<9
3	LE303	443	2	2	100	11.1	44.4	4.02	<9	<10	<2	<20	<25	<2	<9

Toxicity test results for Hyalella (28 day test).
Replicate, site, distance from Copper Cliff, survival, final weight, and metal concentrations in bioassay water.

Rep	Site	km	No	N	Percent Survival	Final weight (mg)	Co ug/L	Cu ug/L	Mn ug/L	Ni ug/L	Pb ug/L	V ug/L	Zn ug/L
1	RAMD	6	15	0	0		0	19	504	141	69	68	0
2	RAMD	6	15	0	0		2	10	130	223	0	36	3
3	RAMD	6	15	0	0		0	13	0	149	13	41	17
1	MCF10	10	15	1	7	1.10	0	5	330	108	16	76	0
2	MCF10	10	15	5	33	0.90	0	8	22	13	20	53	1
3	MCF10	10	15	0	0		0	1	4	4	0	0	1
1	MCFD	10	15	0	0		15	18	14400	362	0	65	8
2	MCFD	10	15	0	0		7	5	6959	196	39	39	8
3	MCFD	10	15	0	0		0	4	7536	229	0	41	12
1	RAF10	11	15	0	0		0	34	104	48	49	65	0
2	RAF10	11	15	4	27	0.65	0	11	0	15	27	24	0
3	RAF10	11	15	10	67	1.00	0	11	2	14	0	31	3
1	RAFD	11	15	0	0		13	21	132	230	50	70	0
2	RAFD	11	15	0	0		0	3	1	78	8	37	0
3	RAFD	11	15	4	27	0.38	0	11	0	47	0	32	3
1	RICD	12	15	0	0		4	17	22	370	28	69	0
2	RICD	12	15	0	0		0	4	81	770	47	57	5
3	RICD	12	15	0	0		0	11	0	185	41	38	5
1	NEPD	32	15	3	20	1.06	7	19	0	17	23	68	0
2	NEPD	32	15	15	100	1.38	0	1	0	0	0	39	0
3	NEPD	32	15	6	40	1.63	0	5	0	0	36	36	0
1	KAK10	38	15	3	20	2.03	2	4	0	0	23	67	0
2	KAK10	38	15	12	80	0.47	0	1	0	0	0	37	2
3	KAK10	38	15	10	67	1.53	0	5	0	0	0	34	0
1	KAKD	38	15	1	7	1.90	11	2	789	12	8	70	0
2	KAKD	38	15	11	73	1.67	1	2	677	17	0	33	0
3	KAKD	38	15	11	73	2.07	0	6	0	0	3	31	2
1	TRO10	43	15	6	40	2.40	1	2	0	0	0	65	0
2	TRO10	43	15	12	80	1.36	0	0	0	0	0	37	0
3	TRO10	43	15	5	33	1.98	0	1	0	3	0	36	2
1	TROD	43	15	3	20	2.19	9	2	320	0	4	32	0
2	TROD	43	17	17	100	0.94	3	0	0	0	3	34	3
3	TROD	43	15	14	93	2.09	0	2	0	2	0	36	3
1	LOS10	52	15	12	80	1.82	0	2	0	0	10	68	0
2	LOS10	52	15	11	73	0.81	0	0	26	0	0	35	0
3	LOS10	52	15	9	60	1.93	0	0	0	0	0	12	3
1	LOSD	52	15	1	7	0.67	3	1	699	0	20	30	0
2	LOSD	52	15	13	87	1.51	0	0	251	0	10	34	0
3	LOSD	52	15	11	73	1.15	0	3	0	0	0	31	2
1	TOM10	94	15	0	0		0	0	0	0	0	62	0
2	TOM10	94	15	14	93	0.71	2	0	0	0	3	29	0
3	TOM10	94	15	5	33	1.08	0	2	0	0	0	10	2
1	TOMD	94	17	17	100	1.50	2	9	0	0	54	62	0
2	TOMD	94	15	1	7	1.30	0	0	0	0	33	54	0
3	TOMD	94	15	10	67	1.83	0	3	0	1	40	31	5
1	RES10	107	15	0	0		0	1	17	0	13	61	0
2	RES10	107	15	13	87	1.09	0	2	0	0	23	49	0
3	RES10	107	15	7	47	1.67	0	4	0	0	20	35	2
1	RESD	107	15	0	0		0	13	0	18	24	30	0
2	RESD	107	15	10	67	1.26	1	1	0	5	3	33	0
3	RESD	107	15	9	60	1.37	0	4	0	0	46	34	2
1	NOS10	144	15	13	87	1.77	0	8	0	11	21	63	0
2	NOS10	144	15	13	87	1.29	0	0	0	0	14	39	0
3	NOS10	144	15	11	73	2.47	0	4	0	0	13	35	0
1	NOSD	144	15	7	47	2.04	0	1	0	0	18	29	0
2	NOSD	144	15	14	93	1.74	0	3	0	0	78	50	0
3	NOSD	144	15	13	87	1.55	0	13	10	0	41	43	26
1	TAL10	154	15	10	67	1.46	14	3	0	0	7	28	0
2	TAL10	154	15	15	100	1.64	0	3	0	0	26	54	0
3	TAL10	154	15	5	33	1.26	0	0	0	0	0	33	2
1	TALD	154	15	12	80	1.17	0	13	383	11	0	63	0
2	TALD	154	15	12	80	1.87	0	0	1	0	0	33	2
3	TALD	154	15	14	93	1.71	0	0	0	0	12	34	2
1	HH1	368	15	14	93	2.28	1	7	0	9	0	69	0
2	HH1	368	15	11	73	0.54	0	2	0	0	31	54	0
3	HH1	368	15	14	93	1.83	0	7	0	0	7	42	7
1	LE303	443	15	11	73	2.15	2	4	0	12	26	73	0
2	LE303	443	15	14	93	1.64	0	5	0	1	59	0	0
3	LE303	443	15	14	93	2.13	0	9	0	0	15	40	2

Toxicity test results for Tubifex (28 day test).
Replicate, site, distance from Copper Cliff, survival, young and cocoons produced, and metal concentrations in bioassay water.

Rep	Site	km	No	N	Percent Survival	young >500um	young <500um	cocoons empty	cocoons full	Co ug/L	Cu ug/L	Mn ug/L	Ni ug/L	Pb ug/L	V ug/L	Zn ug/L
2	RAMD	6	2	2	100	6	32	9	13	<9	<10	473	534	<25	<2	<9
3	RAMD	6	2	2	100	0	25	6	10	<9	<10	127	241	<25	<2	<9
2	MCF10	10	2	2	100	8	49	11	9	<9	<10	<2	151	<25	<2	<9
3	MCF10	10	2	2	100	3	34	7	10	<9	10	66	186	<25	<2	<9
2	MCFD	10	2	2	100	3	48	0	10	<9	<10	11260	855	<25	<2	22
3	MCFD	10	2	2	100	2	36	10	11	<9	<10	9350	758	<25	<2	<9
2	RAF10	11	2	1	50	3	27	6	9	<9	<10	<2	106	<25	<2	<9
3	RAF10	11	2	2	100	18	38	10	6	<9	<10	<2	60	<25	<2	<9
2	RAFD	11	2	2	100	0	21	5	6	<9	<10	32	350	<25	<2	<9
3	RAFD	11	2	2	100	4	23	6	14	<9	10	37	128	<25	<2	<9
2	RICD	12	2	1	50	0	0	0	0	<9	10	148	1810	<25	<2	73
3	RICD	12	2	2	100	5	20	10	7	<9	<10	10	523	<25	<2	<9
2	NEPD	32	2	2	100	11	48	8	9	<9	<10	<2	<20	<25	<2	<9
3	NEPD	32	2	2	100	5	54	10	6	<9	<10	<2	<20	<25	<2	<9
2	KAK10	38	2	2	100	14	45	8	8	<9	<10	<2	<20	<25	<2	<9
3	KAK10	38	2	2	100	9	32	8	10	<9	<10	9	<20	<25	<2	<9
2	KAKD	38	2	2	100	7	36	6	10	<9	<10	780	64	<25	<2	<9
3	KAKD	38	2	2	100	6	50	10	11	<9	<10	686	<20	<25	<2	<9
2	TRO10	43	2	2	100	11	56	7	11	<9	<10	9	<20	<25	<2	<9
3	TRO10	43	2	2	100	31	21	9	9	<9	<10	478	<20	<25	<2	<9
2	TROD	43	2	1	50	9	37	6	10	<9	<10	<2	<20	<25	<2	<9
3	TROD	43	2	2	100	9	36	6	10	<9	<10	<2	21	<25	<2	<9
2	LOS10	52	2	2	100	13	31	13	10	<9	<10	<2	<20	<25	<2	<9
3	LOS10	52	2	2	100	14	64	12	10	<9	<10	618	<20	<25	<2	<9
2	LOSD	52	2	2	100	15	42	10	13	<9	<10	251	<20	<25	<2	<9
3	LOSD	52	2	2	100	12	23	6	13	<9	<10	7	<20	54	<2	<9
2	TOM10	94	2	2	100	15	43	10	9	<9	<10	<2	<20	<25	<2	<9
3	TOM10	94	2	2	100	5	49	9	7	<9	<10	190	<20	<25	<2	<9
2	TOMD	94	2	2	100	7	51	8	9	<9	<10	50	<20	<25	<2	<9
3	TOMD	94	2	2	100	6	39	5	7	<9	<10	57	<20	<25	<2	<9
2	RES10	107	2	2	100	17	63	7	9	<9	<10	965	<20	<25	<2	<9
3	RES10	107	2	2	100	10	34	10	9	<9	<10	11	<20	<25	<2	<9
2	RESD	107	2	2	100	8	34	12	9	<9	<10	<2	<20	<25	<2	<9
3	RESD	107	2	2	100	6	33	11	8	<9	16	869	<20	<25	<2	<9
2	NOS10	144	2	4	200	11	40	8	9	<9	<10	<2	<20	<25	<2	<9
3	NOS10	144	2	2	100	10	33	7	11	<9	<10	<2	<20	<25	<2	<9
2	NOSD	144	2	2	100	15	65	12	11	<9	<10	<2	<20	<25	<2	<9
3	NOSD	144	2	2	100	8	42	8	12	<9	<10	<2	<20	95	<2	<9
2	TAL10	154	2	2	100	11	49	11	7	<9	<10	<2	<20	<25	<2	<9
3	TAL10	154	2	2	100	8	44	9	8	<9	<10	304	<20	<25	<2	<9
2	TALD	154	2	2	100	14	46	3	5	<9	<10	371	<20	<25	<2	<9
3	TALD	154	2	2	100	12	35	13	3	<9	<10	2912	<20	<25	<2	<9
2	HH1	368	2	2	100	8	37	5	9	<9	<10	<2	<20	<25	<2	<9
3	HH1	368	2	2	100	10	25	5	11	<9	<10	<2	<20	<25	<2	<9
2	LE303	443	2	2	100	5	12	0	0	<9	12	<2	<20	<25	<2	<9
3	LE303	443	2	2	100	4	27	5	10	<9	<10	<2	<20	34	<2	<9

Appendix 4

Data on sediments, sediment extracts, and sediment pore water including metal concentrations, UV-visible absorbance, pH and Eh and acid volatile sulfide (Jackson and Nguyen). Concentrations of sediment constituents are expressed on the basis of oven-dry (105°C) weight. Site codes are described in Table 1.1.

METAL CONCENTRATIONS IN SEDIMENT PORE WATER

Site	Cd ug/L	Cr mg/L	Cu mg/L	Fe mg/L	Hg ug/L	Mn mg/L	Ni mg/L	Pb mg/L	Zn mg/L
RAMD	0.06	0.07	0.21	0.33	0.08	3.9	0.14	0.04	2.54
	0.13	0.11	0.21	0.34	0.04	3.9	0.16	0.06	2.63
MCF10	0.06	0.2	0.08	0.54	0.05	6.75	0.31	ND	0.93
	0.05	0.2	0.04	0.81	0.05	6.77	0.23	ND	0.9
MCFD	0.05	0.13	0.04	0.6	0.04	36.8	0.32	ND	1.86
	0.05	0.1	0.04	0.59	0.03	36.7	0.28	ND	2.25
RAF10	0.56	0.15	0.19	2.67	0.06	9.64	0.59	0.01	2.74
	0.55	0.1	0.23	2.92	0.06	9.51	0.59	0.01	2.65
RAFD	0.4	0.06	0.18	0.38	0.08	1.2	0.29	0.02	1.75
	0.44	0.1	0.11	0.48	0.07	1.32	0.29	0.02	1.87
RICD	0.07	0.06	0.03	0.19	0.06	1	0.13	0.01	2.63
	0.07	0.11	0.04	0.15	0.05	0.9	0.14	0.01	2.59
NEPD	0.03	0.16	0.01	9.58	0.05	2.63	ND	ND	2.17
	0.03	0.16	0.02	9.99	0.05	2.23	ND	ND	2.29
KAK10	0.05	0.1	0.05	8.27	0.39	5.21	0.01	0.04	2.46
	0.02	0.1	0.01	6.1	0.38	4.98	0.01	0.03	1.63
KAKD	0.06	0.15	0.01	8.4	0.39	4.11	ND	0.02	1.14
	0.05	0.11	0.02	8.2	0.39	4.31	ND	0.02	0.9
TRO10	0.02	0.1	0.03	0.37	0.06	4.36	ND	0.06	2.15
	0.03	0.1	0.03	0.42	0.05	4.56	ND	0.07	2.84
TROD	0.02	0.1	0.01	6	0.08	2.52	ND	0.01	1.72
	0.04	0.14	0.01	6.3	0.07	2.46	ND	0.01	1.42
LOS10	0.04	0.21	0.01	1.76	0.08	5.42	ND	0.04	2.34
	0.04	0.18	0.01	1.68	0.07	5.78	ND	0.05	3.13
LOSD	0.04	0.11	0.02	4	0.16	3.66	ND	0.11	1.84
	0.04	0.09	0.02	4.2	0.13	3.59	ND	0.11	2.88
TOM10	0.07	0.14	0.15	8.92	0.38	2.59	ND	0.17	2.48
	0.07	0.17	0.1	8.95	0.37	2.58	ND	0.1	2.19
TOMD	0.06	0.08	0.01	4.41	0.39	9.71	ND	0.02	3.12
	0.06	0.11	0.01	6.24	0.38	10	ND	0.04	3.22
RES10	0.06	0.08	0.01	12	0.11	3.18	ND	0.04	2.38
	0.06	0.08	0.01	12.5	0.1	3.16	ND	0.04	2.38
RESD	0.06	0.11	0.01	13.3	0.12	5.08	ND	0.1	3.14
	0.06	0.13	0.01	14.5	0.12	5.16	ND	0.1	2.6
NOS10	0.02	0.1	ND	3.45	0.06	1.46	ND	ND	1.29
	0.05	0.11	ND	4.66	0.07	1.5	ND	ND	1.84
NOSD	0.03	0.08	ND	5.61	0.09	1.28	ND	ND	1.18
	0.02	0.09	ND	4.19	0.09	1.27	ND	ND	1.13
TAL10	0.06	0.06	0.01	2.67	0.37	12.9	ND	0.01	1.76
	0.05	0.05	0.02	3.9	0.37	13.8	ND	0.02	1.71
TALD	0.01	0.12	0.01	10.1	0.38	12.9	ND	0.13	2.38
	0.02	0.15	0.01	10.1	0.37	13.3	ND	0.13	2.37

ULTRAVIOLET AND VISIBLE ABSORBANCE VALUES OF SEDIMENT PORE WATER AT SELECTED WAVELENGTHS IN THE RANGE 320 - 700 nm

Site	320nm	400nm	420nm	465nm	500nm	600nm	665nm	700nm
RAMD	0.053	0.023	0.018	0.01	0.007	0.005	0.005	0.005
	0.054	0.023	0.018	0.009	0.005	0.004	0.004	0.004
MCF10	0.104	0.043	0.032	0.018	0.012	0.005	0.006	0.006
	0.101	0.042	0.032	0.018	0.012	0.005	0.005	0.005
MCFD	0.413	0.173	0.134	0.083	0.062	0.032	0.025	0.024
	0.409	0.17	0.134	0.084	0.063	0.032	0.026	0.024
RAF10	0.002	0.002	0.001	0	0	0	0	0
	0.001	0.001	0	0	0	0	0	0
RAFD	0.004	0.003	0.003	0.002	0.001	0.003	0.004	0.006
	0.003	0.002	0.001	0	0	0.001	0.003	0.004
RICD	0.034	0.019	0.015	0.009	0.007	0.005	0.007	0.007
	0.035	0.018	0.014	0.008	0.008	0.005	0.005	0.006
NEPD	0.048	0.017	0.012	0.005	0.003	0.001	0.001	0.001
	0.049	0.016	0.011	0.004	0.002	0.001	0.001	0.001
KAK10	0.291	0.107	0.081	0.043	0.028	0.009	0.006	0.005
	0.296	0.115	0.089	0.049	0.034	0.014	0.011	0.01
KAKD	0.067	0.016	0.011	0.006	0.004	0.002	0.002	0.002
	0.066	0.016	0.011	0.008	0.004	0.002	0.002	0.002
TRO10	0.188	0.1	0.085	0.055	0.039	0.019	0.016	0.014
	0.188	0.101	0.086	0.055	0.038	0.02	0.016	0.014
TROD	0.018	0.005	0.002	0	0	0	0.001	0.001
	0.018	0.006	0.002	0	0	0	0.001	0.001
LOS10	0.621	0.258	0.207	0.127	0.091	0.04	0.03	0.026
	0.62	0.257	0.206	0.127	0.091	0.04	0.03	0.026
LOSD	0.648	0.242	0.19	0.111	0.08	0.036	0.029	0.024
	0.647	0.241	0.19	0.111	0.079	0.036	0.028	0.024
TAL10	0.755	0.352	0.257	0.152	0.095	0.071	0.016	0.01
	0.763	0.357	0.253	0.153	0.092	0.071	0.015	0.01
TALD	0.641	0.231	0.17	0.09	0.06	0.018	0.013	0.011
	0.641	0.231	0.169	0.09	0.06	0.018	0.013	0.01

THE pH AND Eh VALUES OF THE SEDIMENTS

Site	pH	Eh (mV)
RAMD	6.57	-108.7
	6.58	-109.6
MCF10	6.74	-155.9
	6.73	-149.8
MCFD	7.18	-233
	7.16	-238.9
RAF10	6.71	-157.8
	6.74	-151.8
RAFD	6.28	-118.2
	6.29	-112.5
RICD	6.48	-109.4
	6.49	-108.5
NEPD	7.03	-147.9
	7.02	-149.8
KAK10	6.9	-137.4
	6.89	-138.1
KAKD	6.74	-188.9
	6.78	-187.8
TRO10	6.49	-27.1
	6.5	-26.5
TROD	6.81	-151.1
	6.8	-150.8
LOS10	6.49	-13.4
	6.5	-12.1
LOSD	6.52	-77.5
	6.53	-78.1
TOM10	6.53	-92.8
	6.55	-93.9
TOMD	7.03	-104.9
	7.06	-106
RES10	6.37	-26
	6.38	-25.8
RESD	6.25	-120.7
	6.29	-120.9
NOS10	7.1	-230.9
	7.13	-231.8
NOSD	7.22	-200.8
	7.24	-203
TAL10	7.1	-334.5
	7.12	-340
TALD	7.2	-127.9
	7.22	-130.4

THE TOTAL ORGANIC CONTENT OF THE SEDIMENT

Site	% LOSS ON IGNITION
RAMD	8.51
MCF10	7.45
MCFD	17.31
RAF10	7.02
RAFD	14.04
RICD	9.52
NEPD	9.33
KAK10	10.89
KAKD	15.19
TRO10	15.38
TROD	10.98
LOS10	10.26
LOSD	11.54
TOM10	16.67
TOMD	14.29
RES10	10
RESD	10.91
NOS10	10.43
NOSD	11.11
TAL10	7.69
TALD	9.91

CONCENTRATIONS OF CaCl$_2$ - EXTRACTABLE METAL SPECIES IN THE SEDIMENTS

Site	Cd ug/kg	Cr mg/kg	Cu mg/kg	Hg ug/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
RAMD	2.11	0.91	0.51	0.18	21.59	2.79	4.06
	2.13	1.14	0.51	0.21	24.64	2.79	5.08
MCF10	0.52	1.54	0.58	0.19	31.89	2.89	6.38
	0.69	1.54	0.58	0.2	36.83	2.89	6.96
MCFD	ND	3.01	0.49	0.27	49.65	4.43	1.47
	ND	3.98	0.49	0.51	38.83	3.93	1.47
RAF10	2.96	0.86	0.55	0.14	32.15	2.02	4.59
	3.39	1.19	0.55	0.15	29.04	2.2	4.04
RAFD	4.8	0.91	0.65	0.27	34.49	3.88	6.16
	5.75	1.26	0.96	0.33	53.08	3.88	6.79
RICD	4.56	1.28	0.79	0.21	48.78	3.05	10.06
	4.57	1.37	0.91	0.25	55.65	3.34	12.16
NEPD	0.19	1.96	0.33	0.28	5.99	3.33	3.66
	0.19	2.06	0.33	0.29	5.66	3.66	3.33
KAK10	3.13	1.57	0.43	0.29	6.09	2.61	2.61
	4.16	1.71	0.39	0.31	5.22	2.61	1.74
KAKD	ND	1.51	0.38	0.26	6.05	3.4	1.14
	ND	1.81	0.38	0.27	6.8	3.4	1.13
TRO10	0.48	1.87	0.59	0.21	10.75	3.98	12.74
	0.48	1.99	0.59	0.55	10.76	3.98	11.76
TROD	0.13	1.9	0.64	0.29	6.37	3.82	2.55
	0.13	1.78	0.85	0.39	6.79	4.24	2.55
LOS10	2.55	1.44	0.29	0.22	6.44	2.94	10.84
	2.55	1.61	0.29	0.25	6.46	3.22	10.57
LOSD	1.87	2.13	0.37	0.32	4.11	4.11	7.84
	2.57	2.24	0.37	0.33	4.48	4.11	7.48
TOM10	0.59	2.51	0.57	0.29	2.66	3.79	5.34
	0.68	2.29	0.57	0.29	2.67	3.81	6.45
TOMD	0.37	2.69	0.56	0.25	2.99	3.37	4.86
	0.37	2.65	0.56	0.29	2.99	3.37	4.86
RES10	0.37	2.32	0.31	0.17	1.85	3.39	2.78
	0.34	2.29	0.31	0.2	1.86	3.09	2.79
RESD	0.34	3.47	0.38	0.19	2.27	3.78	4.91
	0.49	3.06	0.38	0.25	2.27	3.78	4.54
NOS10	0.12	2.05	0.37	0.19	2.32	3.86	1.93
	0.12	2.63	0.37	0.23	2.32	3.86	1.93
NOSD	ND	2.19	0.47	0.17	1.89	3.17	1.89
	ND	2.18	0.32	0.19	1.9	3.17	1.27
TAL10	ND	1.7	0.33	0.21	2.01	3.01	3.35
	ND	1.67	0.33	0.21	2.01	3.34	3.68
TALD	0.12	1.69	0.31	0.18	1.84	2.76	4.29
	0.13	1.86	0.31	0.19	1.84	2.76	3.82

CONCENTRATION OF NaAc/HAc - EXTRACTABLE METAL SPECIES IN THE SEDIMENTS

Site	Cd mg/kg	Cr mg/kg	Cu mg/kg	Hg ug/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
RAMD	0.51	0.3	10.36	0.3	39.11	7.67	4.65
	0.53	0.3	16.12	0.31	42.34	7.92	5.89
MCF10	0.67	0.26	0.75	0.33	81.92	5.13	21.75
	0.58	0.26	0.67	0.33	82.47	5.05	14.99
MCFD	0.44	0.29	1.57	0.47	288.6	2.56	18.09
	0.59	0.29	1.23	0.47	296.71	2.46	11.4
RAF10	0.46	0.29	18.51	0.21	34.17	4.06	2.76
	0.49	0.24	15.5	0.21	36.25	4.5	3.05
RAFD	0.81	0.52	13.42	0.28	54.44	15.13	4.38
	0.87	0.52	14.16	0.28	57.53	15.25	5.39
RICD	0.88	0.18	17.13	0.25	60.09	10.09	8.63
	0.94	0.18	20.22	0.25	62.55	10	8.69
NEPD	0.39	0.33	0.33	0.36	10.09	3.93	3.06
	0.37	0.33	0.3	0.36	10.02	3.99	3.03
KAK10	0.34	0.38	0.35	0.27	9.99	2.46	4.38
	0.35	0.35	0.29	0.27	9.74	2.49	4.55
KAKD	0.3	0.23	1.02	0.39	17.58	1.21	0.3
	0.26	0.26	1.13	0.39	16.69	1.25	0.3
TRO10	0.79	0.59	1.47	0.2	13.99	7.41	10.27
	0.84	0.64	1.4	0.11	14.09	6.82	10.01
TROD	0.34	0.68	1.06	0.73	14.59	3.52	4.12
	0.34	0.55	1.06	0.73	13.8	2.97	3.95
LOS10	0.7	0.23	0.35	0.28	7.16	1.11	8.75
	0.76	0.23	0.38	0.28	7.38	1	9.64
LOSD	0.29	0.34	0.41	0.44	3.85	6.21	4.59
	0.29	0.34	0.49	0.44	3.88	6.57	4.56
TOM10	0.38	0.53	0.27	0.11	2.77	6.53	6.64
	0.38	0.42	0.3	0.11	2.67	6.48	6.48
TOMD	0.29	0.34	0.29	0.47	4.41	4.86	13.05
	0.37	0.3	0.29	0.47	4.49	5.24	13.01
RES10	0.59	0.28	0.31	0.36	2.56	1.92	6.02
	0.59	0.34	0.28	0.36	2.57	1.92	5.63
RESD	0.49	0.57	0.26	0.45	2.91	9.87	10.46
	0.49	0.42	0.3	0.45	2.91	10.16	10.13
NOS10	0.15	0.35	0.31	0.44	2.09	1.62	2.01
	0.15	0.31	0.27	0.44	2.12	1.62	2.08
NOSD	0.22	0.32	0.28	0.45	1.55	2.03	2.97
	0.13	0.32	0.25	0.45	1.61	2.03	2.19
TAL10	0.3	0.33	0.23	0.63	3.88	1.67	9.64
	0.33	0.33	0.27	0.63	4.25	1.74	13.51
TALD	0.37	0.31	0.15	0.92	2.61	1.59	6.96
	0.28	0.31	0.15	0.92	2.12	1.47	4.89

CONCENTRATIONS OF NH$_2$OH·HCl/HNO$_3$ - EXTRACTABLE METAL SPECIES IN THE SEDIMENTS

Site	Cd ug/kg	Cr mg/kg	Cu mg/kg	Fe mg/kg	Hg mg/kg	Mn mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
RAMD	98.5	0.03	0.31	207.7	0.12	31.2	12.78	0.94	5.3
	82.3	0.03	0.31	197.2	0.19	28.4	11.55	0.94	4.68
MCF10	127.1	0.07	0.36	308.5	0.8	36.7	22.8	0.36	16.03
	96.6	0.07	0.36	344.5	0.8	46.3	23.16	0.36	14.96
MCFD	13.7	0.06	0.59	649.8	2.01	204.1	197.5	0.6	12.68
	19.8	0.06	0.59	650.4	2.1	204.1	216.8	0.6	15.7
RAF10	95.9	0.02	0.23	166.7	0.28	13.8	9.71	0.23	2.93
	99.3	0.02	0.23	176.7	0.28	13.9	9.93	0.23	2.71
RAFD	113.3	0.08	0.39	243.3	0.42	6.8	13.1	1.19	3.93
	131.9	0.11	0.39	273.9	0.37	8.3	12.74	1.19	3.98
RICD	159.9	0.07	0.37	218.4	0.15	12.4	16.11	0.75	7.12
	139.5	0.07	0.37	236.9	0.24	15.3	16.81	0.75	7.85
NEPD	77.3	0.08	ND	442.7	0.46	33.1	3.68	0.41	6.55
	79.3	0.08	ND	434.1	0.99	26.6	3.68	0.41	6.14
KAK10	81.1	0.04	0.36	354.5	0.05	52	2.85	0.36	6.76
	77.9	0.04	0.36	364.2	0.05	54.8	2.85	0.36	6.41
KAKD	31.3	0.05	0.46	827.5	0.04	34.9	6.04	0.46	6.04
	22.3	0.05	0.46	898.5	0.04	39.5	5.58	0.46	4.65
TRO10	203.7	0.09	0.49	178.8	2.21	148.7	3.91	0.98	12.72
	186	0.09	0.49	179	2.1	144.5	3.92	0.98	12.24
TROD	53.7	0.16	ND	718.8	2.53	42.2	4.17	1.04	7.31
	52.5	0.16	ND	695.6	3.07	41.3	4.17	1.04	7.3
LOS10	175.4	0.04	0.36	162.7	0.99	122.3	3.25	0.36	14.43
	174.2	0.04	0.36	170.6	0.99	122.3	3.59	0.36	15.83
LOSD	74.9	0.05	ND	357.5	1.54	38.6	1.38	0.46	6.42
	68.1	0.05	ND	351.9	1.54	36.8	1.38	0.46	5.97
TOM10	79.3	0.05	ND	453.8	0.62	42.9	0.94	0.47	8.43
	78.9	0.05	ND	451.1	0.62	42.6	1.39	0.47	8.39
TOMD	51.9	0.14	0.46	435.9	1.07	128.6	1.38	0.69	12.86
	57.7	0.13	0.46	449.3	1.07	126.3	1.38	0.46	12.86
RES10	136.4	0.04	0.38	180.3	0.87	125.5	1.14	0.76	13.39
	154.3	0.04	0.38	116.7	0.87	126.8	0.76	0.76	11.03
RESD	129.3	0.05	0.46	359.9	1.28	144.3	1.39	1.39	13
	81	0.05	0.46	392.4	1.28	92.9	1.86	1.39	14.84
NOS10	19	0.05	ND	582.8	1.29	22.8	0.95	0.95	2.85
	27.2	0.05	ND	575.7	1.08	20.9	0.95	0.95	4.27
NOSD	35.8	0.12	ND	457.2	2.31	16.7	0.78	0.39	3.49
	25.3	0.12	ND	463.4	2.2	16	0.78	0.39	3.11
TAL10	29.5	0.08	ND	563.2	0.79	121.2	0.82	0.41	12.33
	33.4	0.04	ND	565.5	0.79	120	0.82	0.41	13.55
TALD	54.2	0.08	0.19	466.9	0.89	118.2	1.13	0.38	6.8
	39.4	0.08	0.19	471	0.89	118.6	1.13	0.38	7.93

CONCENTRATIONS OF H$_2$O$_2$/NH$_4$Ac/HNO$_3$-EXTRACTABLE METAL SPECIES IN THE SEDIMENTS

Site	Cd mg/kg	Cr mg/kg	Cu mg/kg	Fe mg/kg	Hg ug/kg	Mn mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
RAMD	2.99	18.00	805.97	785.07	0.91	86.57	743.28	42.54	79.49
	2.09	12.70	537.31	373.13	0.48	35.82	674.63	57.97	69.34
MCF10	1.36	4.77	341.33	112.00	0.15	202.67	469.33	26.85	74.99
	2.40	6.77	320.00	112.00	0.47	258.67	573.33	27.89	84.61
MCFD	5.02	0.62	123.08	24.62	0.79	12476.92	233.85	4.86	53.57
	5.45	0.55	123.08	120.00	0.76	13821.54	304.62	4.86	63.42
RAF10	2.15	5.24	253.16	478.48	0.49	427.85	255.70	24.48	61.22
	2.03	5.52	265.82	443.04	0.49	455.70	582.28	32.05	80.33
RAFD	2.34	9.19	562.50	1168.75	1.14	3965.62	562.50	54.63	74.09
	2.81	7.94	565.63	1168.75	0.93	3468.75	506.25	62.93	72.03
RICD	2.10	5.77	280.52	57.14	1.03	909.09	675.32	41.25	82.49
	2.16	6.91	285.71	96.10	0.83	1402.60	696.10	43.82	84.83
NEPD	0.85	12.23	53.52	383.10	1.32	163.38	101.41	21.92	73.38
	0.93	12.11	53.52	276.06	1.32	61.97	118.31	26.25	74.06
KAK10	0.99	8.09	35.82	191.04	0.16	501.49	92.54	20.03	89.34
	1.19	9.85	38.81	158.21	0.22	522.39	101.49	22.00	90.29
KAKD	0.86	7.65	46.04	5611.51	0.42	618.71	83.45	11.68	69.53
	0.78	9.27	43.17	4549.64	0.41	486.33	83.45	18.07	68.03
TRO10	1.61	7.75	36.11	30.56	0.33	966.67	77.78	34.36	82.03
	1.75	9.11	38.89	22.22	0.28	861.11	80.56	42.67	87.67
TROD	1.09	13.44	45.61	642.11	0.51	361.40	73.68	55.58	93.19
	1.09	13.89	49.12	582.46	0.56	435.09	77.19	57.93	95.61
LOS10	0.86	5.20	8.57	74.29	1.34	885.71	42.86	11.46	86.54
	1.02	8.44	12.70	200.00	3.99	1523.81	60.32	12.98	98.16
LOSD	0.79	13.00	27.27	224.24	0.7	1424.24	30.30	47.33	79.88
	0.88	11.33	33.33	333.33	0.96	1424.24	30.30	50.94	80.03
TOM10	12.06	10.83	12.70	301.59	0.37	31.75	6.35	47.65	83.33
	1.27	9.56	11.27	695.77	0.35	45.07	5.63	33.86	76.06
TOMD	2.55	8.64	8.70	162.32	0.34	579.71	14.49	32.78	98.67
	1.89	7.25	11.11	30.56	0.38	569.44	13.89	33.39	99.58
RES10	1.51	10.90	2.74	24.66	1.52	808.22	13.70	12.62	96.25
	1.51	12.11	2.70	51.35	1.61	835.14	18.92	12.78	95.08
RESD	1.22	5.22	10.17	227.12	4.15	94.92	6.78	59.53	90.51
	1.25	4.84	5.97	110.45	4.16	59.70	8.96	53.79	85.52
NOS10	0.56	10.06	5.63	236.62	0.49	253.52	19.72	13.58	58.56
	0.63	11.66	6.25	290.63	0.53	281.25	31.25	17.41	64.13
NOSD	0.27	7.32	5.41	181.08	0.47	16.22	8.11	8.78	48.81
	0.31	7.83	8.45	290.14	0.75	14.08	5.63	9.97	51.94
TAL10	1.05	10.66	2.63	39.47	9.88	247.37	10.53	14.55	91.18
	1.35	10.68	2.60	90.91	9.88	187.01	20.78	17.51	94.99
TALD	0.53	12.76	2.94	52.94	3.04	461.76	5.88	6.65	80.53
	0.44	12.32	2.47	41.98	4.03	451.85	4.94	6.50	72.67

CONCENTRATIONS OF CITRATE/DITHIONITE-EXTRACTABLE METAL SPECIES IN THE SEDIMENTS

Site	Cd ug/kg	Cr mg/kg	Cu mg/kg	Fe mg/kg	Hg ug/kg	Mn mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
RAMD	13.60	0.44	0.29	533.72	37.30	1.31	4.87	1.42	0.41
	12.83	0.46	0.26	571.84	37.33	1.39	5.46	1.34	0.38
MCF10	9.78	0.36	0.30	626.35	137.53	2.32	7.42	1.03	0.63
	10.27	0.46	0.30	629.66	84.71	3.12	6.59	1.06	0.56
MCFD	16.40	1.40	0.56	2719.10	131.69	195.45	320.22	0.73	26.69
	18.93	1.40	0.62	2859.55	228.43	199.38	303.37	0.73	27.02
RAF10	10.13	0.26	0.21	684.87	11.71	3.72	2.50	0.63	0.21
	9.68	0.20	0.21	629.92	28.46	3.13	2.46	0.61	0.23
RAFD	18.25	0.16	0.33	1540.17	90.37	10.67	3.58	1.29	0.74
	17.30	0.16	0.33	1570.37	90.63	8.22	4.37	1.22	0.37
RICD	17.32	0.46	0.38	686.41	37.14	1.36	20.00	1.15	0.66
	19.95	0.50	0.38	900.09	37.06	1.70	20.82	1.39	0.73
NEPD	19.14	0.48	0.42	780.21	29.99	2.25	3.16	0.91	0.57
	19.68	0.53	0.42	1023.79	30.00	2.28	3.39	0.84	0.57
KAK10	14.05	0.17	0.33	1080.36	94.98	2.58	4.11	1.36	0.27
	15.46	0.43	0.36	1298.01	120.60	2.45	2.81	1.46	0.63
KAKD	14.64	0.39	0.35	1529.16	113.61	3.15	3.20	0.99	0.52
	16.35	0.39	0.39	1561.08	172.71	3.42	3.37	0.95	0.48
TRO10	25.56	0.41	0.46	1981.78	111.53	28.93	3.60	2.32	0.87
	25.39	0.42	0.46	2120.59	76.36	30.67	3.82	2.37	0.91
TROD	23.79	0.58	0.44	2650.49	64.08	7.18	3.25	1.70	0.73
	25.50	0.63	0.44	2846.06	70.30	7.18	3.30	1.75	0.78
LOS10	16.91	0.27	0.23	1617.45	7.36	39.36	2.28	0.87	0.67
	15.63	0.23	0.23	1673.64	7.34	50.24	2.31	1.21	0.70
LOSD	21.84	0.43	0.51	995.73	32.76	4.49	2.82	1.41	0.34
	22.71	0.21	0.51	960.51	32.44	3.84	2.82	1.66	0.55
TOM10	22.18	0.41	0.31	1010.89	54.00	2.44	2.57	1.00	0.48
	19.78	0.48	0.30	1054.23	53.77	2.43	2.73	1.00	0.61
TOMD	14.27	0.88	0.38	1944.44	52.56	20.94	2.86	1.28	1.15
	13.80	0.74	0.38	1931.62	52.95	19.32	2.78	1.45	1.28
RES10	21.15	0.34	0.35	1000.88	109.35	48.91	2.23	1.10	1.59
	18.61	0.31	0.39	988.53	109.16	49.81	2.44	1.20	1.62
RESD	23.50	0.34	0.35	1559.40	41.39	10.28	2.46	1.12	0.86
	27.10	0.28	0.35	1268.61	41.34	9.71	2.42	1.21	0.91
NOS10	20.26	0.62	0.49	922.74	56.37	1.90	2.69	0.75	0.53
	23.58	0.61	0.49	807.95	56.37	1.94	2.65	0.88	0.53
NOSD	17.30	0.41	0.36	803.62	39.82	1.45	2.21	0.65	0.43
	16.46	0.64	0.36	813.74	40.18	1.59	2.39	0.72	0.47
TAL10	19.04	0.72	0.38	4206.50	51.31	35.53	2.41	1.49	1.53
	20.78	0.52	0.38	4137.54	51.26	47.34	2.48	1.49	1.57
TALD	17.10	0.83	0.28	3848.99	31.43	33.89	2.00	0.91	0.91
	18.84	0.61	0.28	3796.85	31.35	33.59	2.03	1.05	1.16

CONCENTRATIONS OF NaOH - EXTRACTABLE METAL SPECIES IN THE SEDIMENTS

Site	Cu mg/kg	Fe mg/kg	Ni mg/kg
RAMD	357.89	957.89	206.58
	378.95	1015.79	207.63
MCF10	51.60	4422.22	74.57
	47.65	4382.72	56.05
MCFD	217.50	979.17	549.58
	180.83	927.08	486.67
RAF10	91.53	586.49	46.13
	99.46	551.35	45.23
RAFD	441.74	950.00	325.22
	490.00	1139.13	340.87
RICD	187.37	6996.49	206.67
	235.79	7101.75	287.72
NEPD	43.88	2392.54	62.09
	42.99	2556.72	64.78
KAK10	41.85	3718.46	59.69
	40.31	3630.77	59.38
KAKD	76.92	833.85	110.77
	65.85	829.23	75.08
TRO10	178.28	843.10	201.03
	224.14	989.66	279.66
TROD	18.04	9647.06	34.51
	88.24	17905.88	92.16
LOS10	24.64	6842.03	66.38
	26.38	6891.30	67.83
LOSD	44.62	6726.15	51.69
	49.54	7564.62	52.62
TOM10	18.46	11123.08	36.92
	88.08	19700.00	102.31
TOMD	20.00	14841.79	39.40
	17.91	13110.45	38.21
RES10	14.78	15205.80	27.25
	13.04	21681.16	30.43
RESD	20.36	22800.00	31.64
	16.36	27527.27	33.82
NOS10	11.08	1380.00	28.00
	11.38	1372.31	25.23
NOSD	13.33	1850.00	23.94
	13.03	1843.94	21.82
TAL10	12.47	4922.08	21.04
	11.95	5105.19	22.60
TALD	13.67	6275.95	18.48
	13.16	6713.92	21.77

ULTRAVIOLET AND VISIBLE ABSORBANCE VALUES OF NaOH EXTRACTS OF THE SEDIMENTS MEASURED AT SELECTED WAVELENGTHS IN THE RANGE 320 - 665 nm

Site	320nm	420nm	465nm	665nm
RAMD	0.469	0.233	0.139	0.059
	0.441	0.235	0.144	0.064
MCF10	0.903	0.505	0.314	0.097
	0.903	0.363	0.223	0.055
MCFD	0.364	0.158	0.095	0.037
	0.419	0.18	0.109	0.041
RAF10	0.261	0.118	0.067	0.027
	0.256	0.11	0.063	0.025
RAFD	0.485	0.263	0.151	0.059
	0.553	0.302	0.175	0.068
RICD	0.903	0.563	0.354	0.115
	0.903	0.393	0.243	0.062
NEPD	0.903	0.328	0.214	0.061
	0.849	0.311	0.207	0.062
KAK10	0.759	0.239	0.148	0.04
	0.774	0.236	0.147	0.039
KAKD	0.484	0.21	0.132	0.048
	0.403	0.16	0.093	0.034
TRO10	0.487	0.14	0.09	0.026
	0.605	0.17	0.108	0.029
TROD	0.654	0.211	0.14	0.041
	0.721	0.207	0.123	0.034
LOS10	0.759	0.217	0.13	0.031
	0.721	0.208	0.126	0.032
LOSD	0.668	0.184	0.112	0.027
	0.799	0.215	0.13	0.029
TOM10	0.701	0.226	0.149	0.044
	0.779	0.226	0.132	0.035
TOMD	0.699	0.188	0.122	0.032
	0.611	0.164	0.107	0.029
RES10	0.789	0.216	0.129	0.033
	0.903	0.236	0.135	0.029
RESD	0.747	0.203	0.123	0.032
	0.903	0.238	0.136	0.03
NOS10	0.234	0.095	0.061	0.024
	0.218	0.09	0.058	0.024
NOSD	0.278	0.122	0.077	0.03
	0.293	0.13	0.083	0.033
TAL10	0.432	0.186	0.114	0.04
	0.349	0.148	0.086	0.032
TALD	0.723	0.236	0.148	0.042
	0.683	0.222	0.14	0.04

CONCENTRATIONS OF HUMIC MATTER IN THE SEDIMENTS EXPRESSED AS ULTRAVIOLET AND VISIBLE ABSORBANCE VALUES OF NaOH EXTRACTS PER UNIT DRY WEIGHT OF SEDIMENT

Site	A_{320nm}/g	A_{420nm}/g	A_{465nm}/g	A_{665nm}/g
RAMD	246.84	122.63	73.16	31.05
	232.11	123.68	75.79	33.68
MCF10	445.93	249.38	155.06	47.90
	445.93	179.26	110.12	27.16
MCFD	303.33	131.67	79.17	30.83
	349.17	150.00	90.83	34.17
RAF10	94.05	42.52	24.14	9.73
	92.25	39.64	22.70	9.01
RAFD	421.74	228.70	131.30	51.30
	480.87	262.61	152.17	59.13
RICD	633.68	395.09	248.42	80.70
	633.68	275.79	170.53	43.51
NEPD	539.10	195.82	127.76	36.42
	506.87	185.67	123.58	37.01
KAK10	467.08	147.08	91.08	24.62
	476.31	145.23	90.46	24.00
KAKD	297.85	129.23	81.23	29.54
	248.00	98.46	57.23	20.92
TRO10	671.72	193.10	124.14	35.86
	834.48	234.48	148.97	40.00
TROD	1538.82	496.47	329.41	96.47
	1696.47	487.06	289.41	80.00
LOS10	880.00	251.59	150.72	35.94
	835.94	241.16	146.09	37.10
LOSD	822.15	226.46	137.85	33.23
	983.38	264.62	160.00	35.69
TOM10	1617.69	521.54	343.85	101.54
	1797.69	521.54	304.62	80.77
TOMD	1251.94	336.72	218.51	57.31
	1094.33	293.73	191.64	51.94
RES10	1372.17	375.65	224.35	57.39
	1570.43	410.43	234.78	50.43
RESD	1629.82	442.91	268.36	69.82
	1970.18	519.27	296.73	65.45
NOS10	288.00	116.92	75.08	29.54
	268.31	110.77	71.38	29.54
NOSD	336.97	147.88	93.33	36.36
	355.15	157.58	100.61	40.00
TAL10	224.42	96.62	59.22	20.78
	181.30	76.88	44.68	16.62
TALD	1098.23	358.48	224.81	63.80
	1037.47	337.22	212.66	60.76

CONCENTRATIONS OF SULFIDE ("ACID-VOLATILISED SULFIDE",OR AVS) IN SEDIMENTS

SITE	DRY WEIGHT (g)	AVS (umoles/ml)	AVS (umoles/g)
RAMD	0.65	5.76	8.84
	0.65	6.35	9.75
MCF10	0.67	26.85	40.32
	0.67	25.40	38.14
MCFD	0.41	41.06	100.64
	0.41	37.53	91.99
RAF10	1.10	0.21	0.20
	1.10	0.21	0.19
RAFD	0.36	1.13	3.10
	0.36	1.12	3.08
RICD	0.53	0.76	1.44
	0.53	0.85	1.60
NEPD	0.58	11.61	19.98
	0.58	11.59	19.94
KAK10	0.61	8.93	14.74
	0.61	8.98	14.82
KAKD	0.53	26.62	50.04
	0.53	27.04	50.64
TRO10	0.50	5.39	10.82
	0.50	5.39	10.81
TROD	0.50	16.25	32.24
	0.51	16.47	32.42
LOS10	0.68	0.44	0.64
	0.68	0.45	0.65
LOSD	0.49	2.70	5.55
	0.49	2.73	5.61
TOM10	0.45	12.06	26.92
	0.45	12.14	27.09
TOMD	0.55	9.80	17.92
	0.55	10.08	18.44
RES10	0.58	0.98	1.68
	0.58	1.00	1.72
RESD	0.46	6.09	13.27
	0.46	6.10	13.29
NOS10	0.60	32.93	54.70
	0.60	33.25	55.23
NOSD	0.56	44.49	79.59
	0.56	44.61	79.80
TAL10	0.74	7.84	10.54
	0.74	7.36	9.89
TALD	0.84	11.11	13.29
	0.84	11.21	13.41

Appendix 5

Chironomus survival and growth, Hexagenia growth, Hyalella survival and growth, and Tubifex reproduction plotted as a function of Cu or Ni expressed as metal extractable with $CaCl_2$ (the most easily dissociated metal), total extractable metal (sum of 5 sequential extractions), total metal in sediment, pore water metal, metal in the water at the end of the toxicity tests, and metal in lake water collected 1 m off the bottom at the time of sediment collection. Also shown are the same biological responses plotted against the difference between total extractable (sum of Cu, Ni, Pb and Zn in the 5 sequential extractions) or total metal (sum of Cu, Ni, Pb and Zn in sediment) and acid volatile sulfide.

Chironomus survival
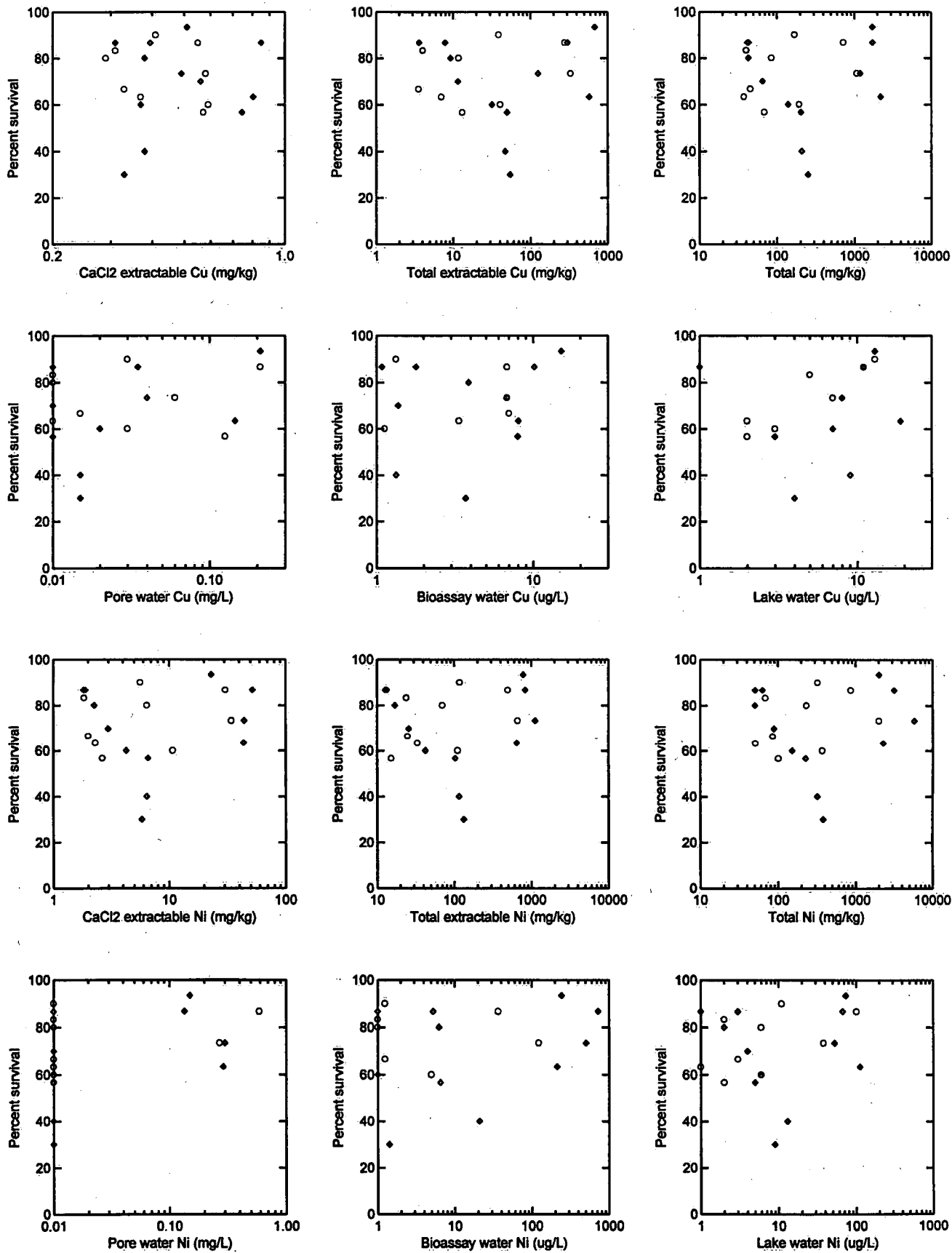
Chironomus growth
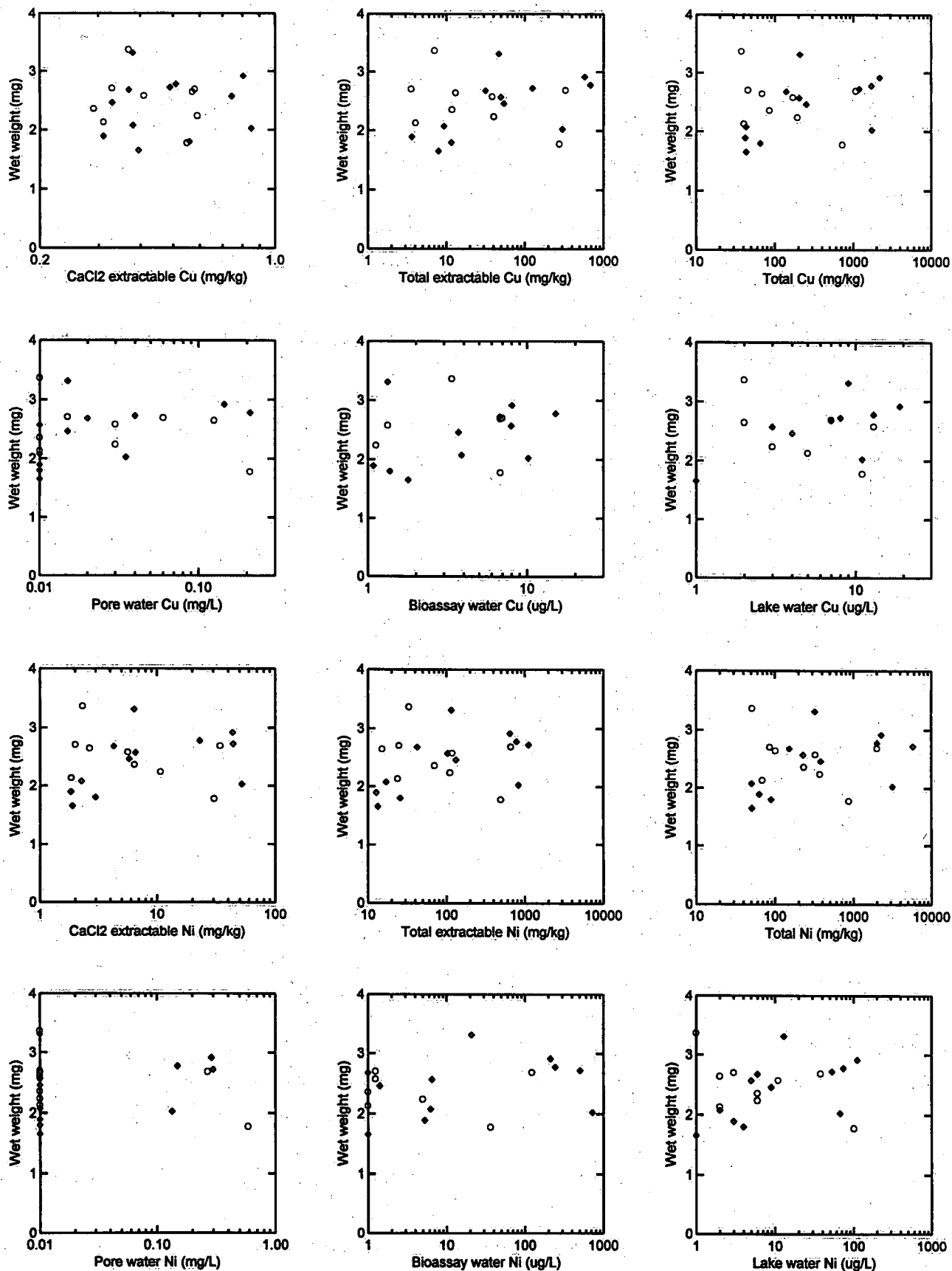
Hexagenia growth
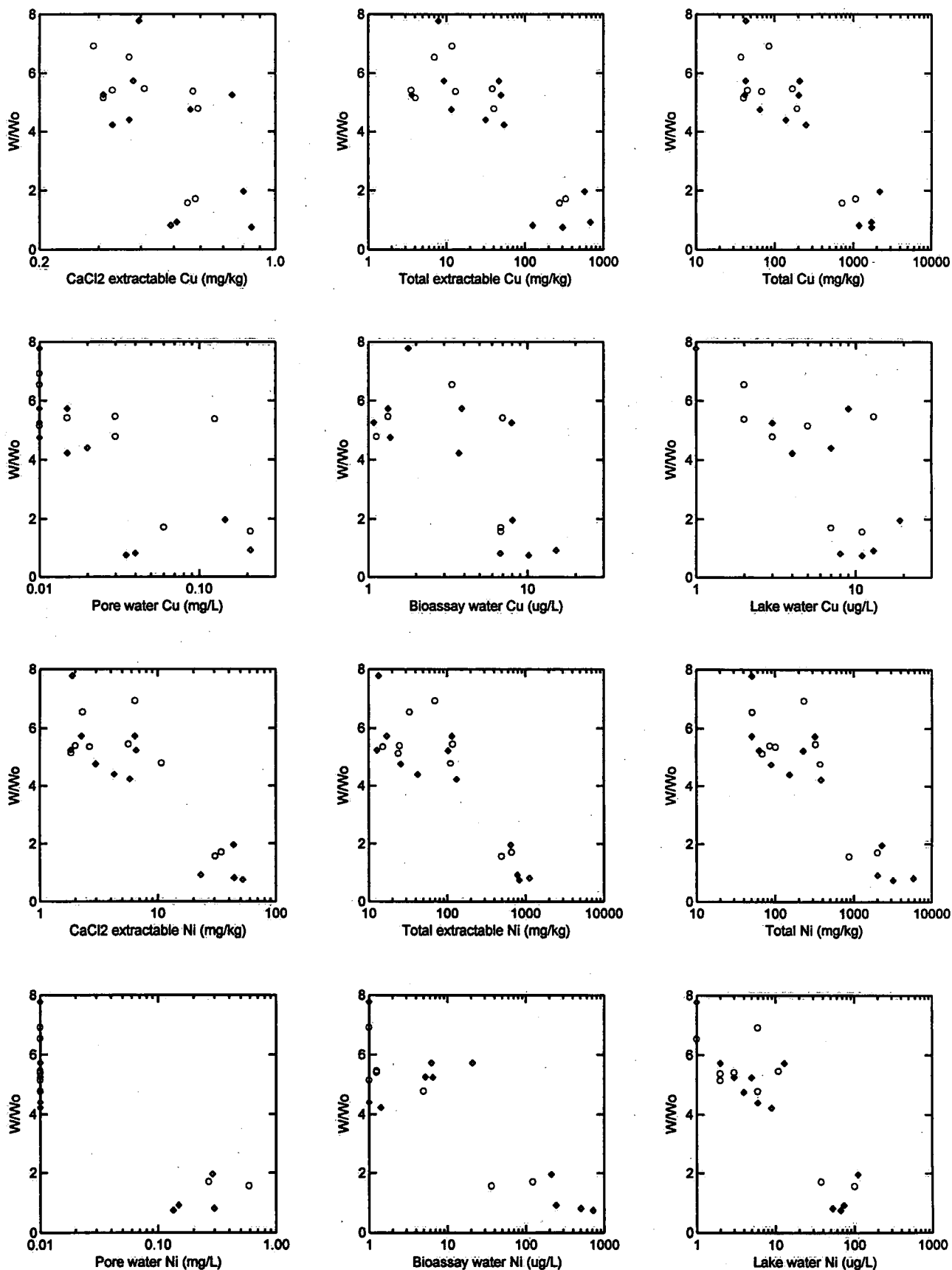
Hyalella survival
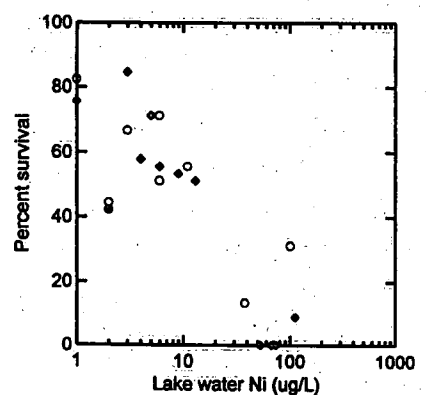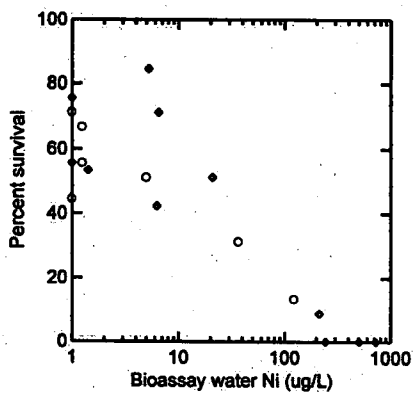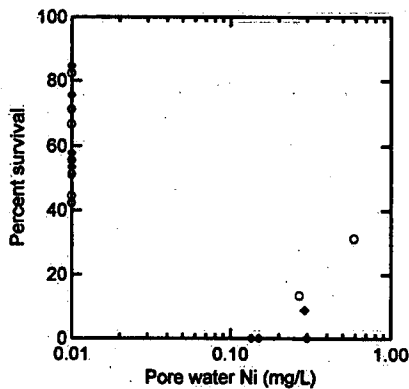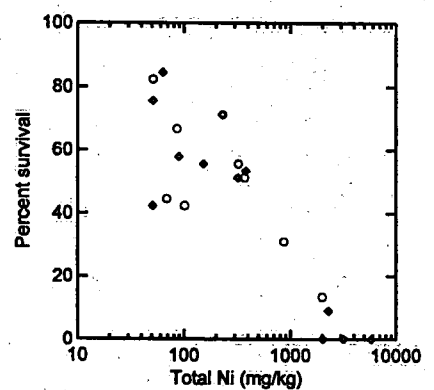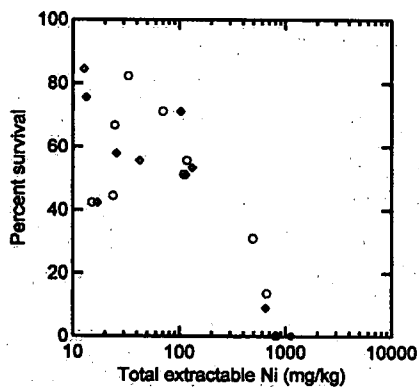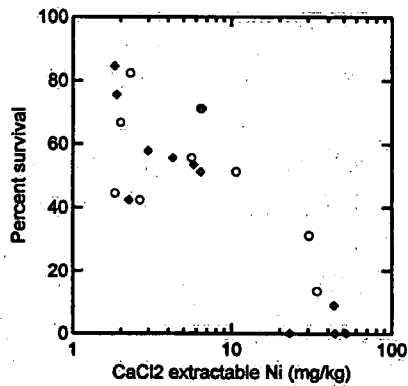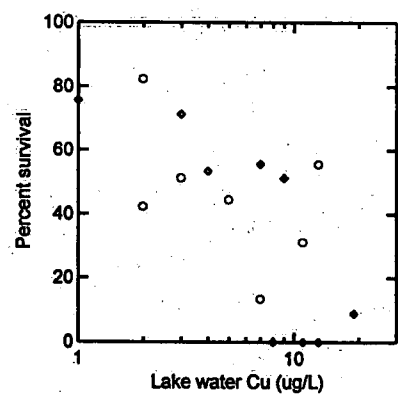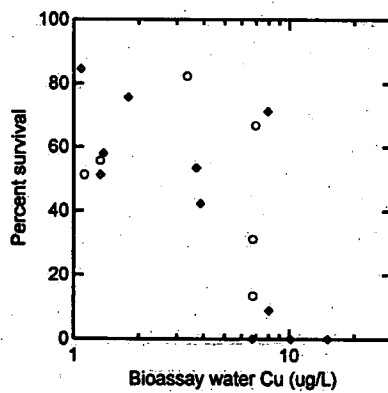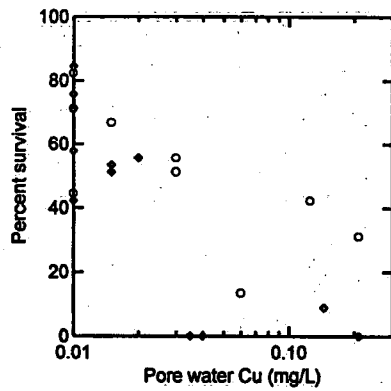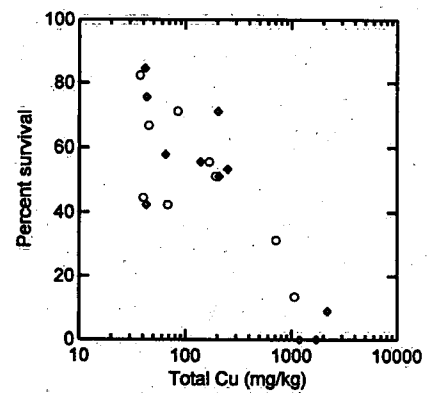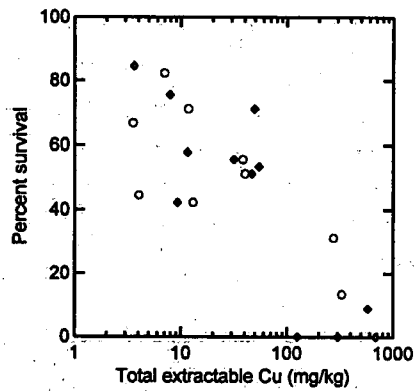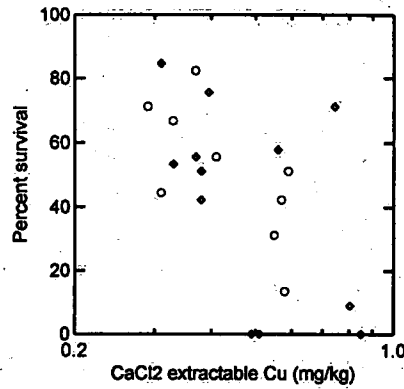
Hyalella growth
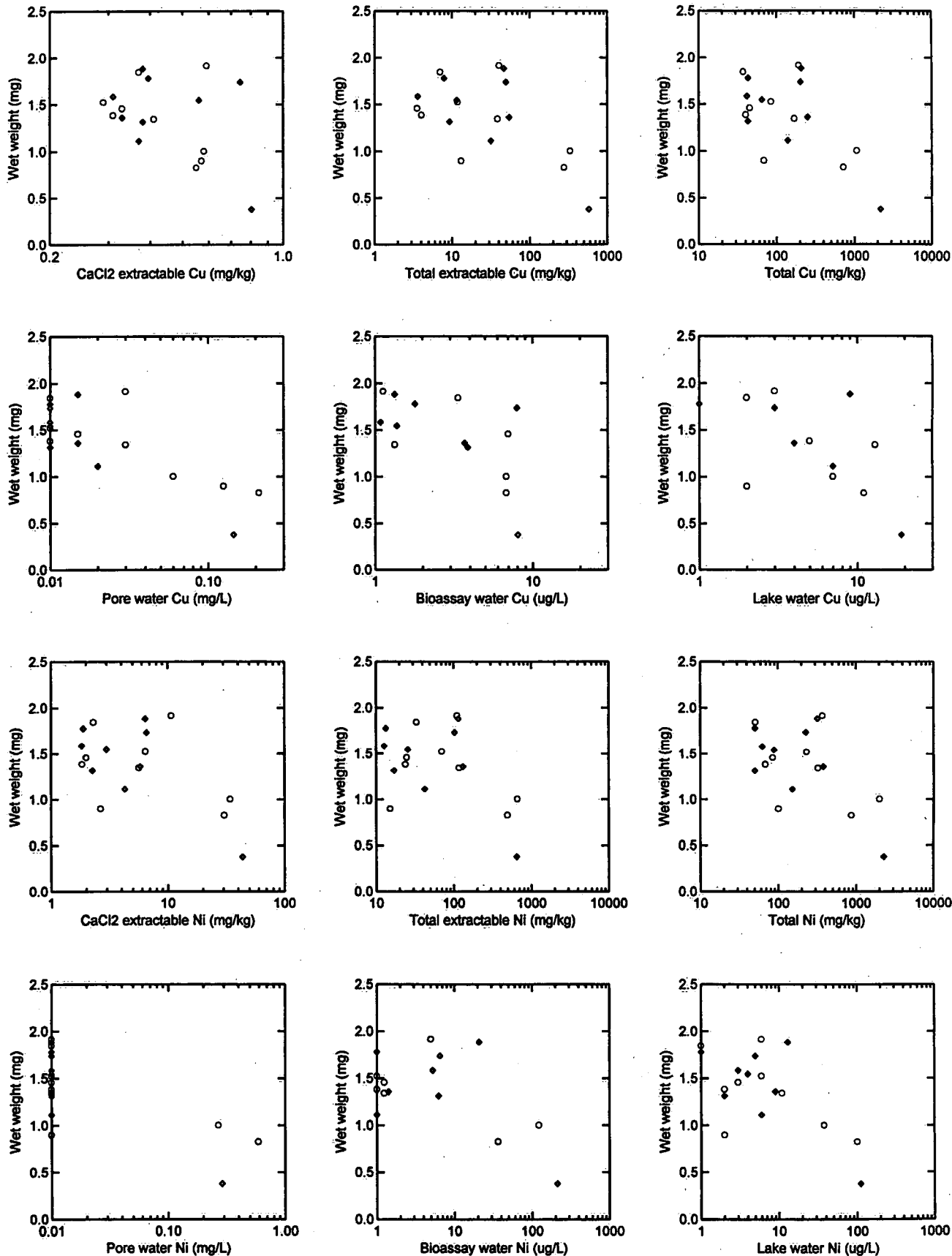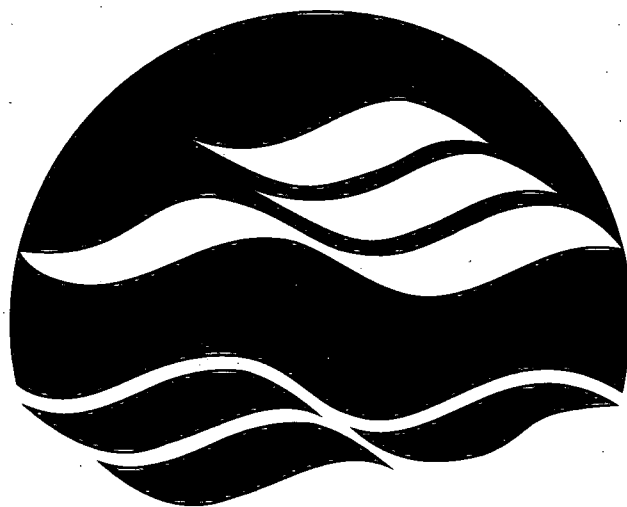
Tubifex reproduction
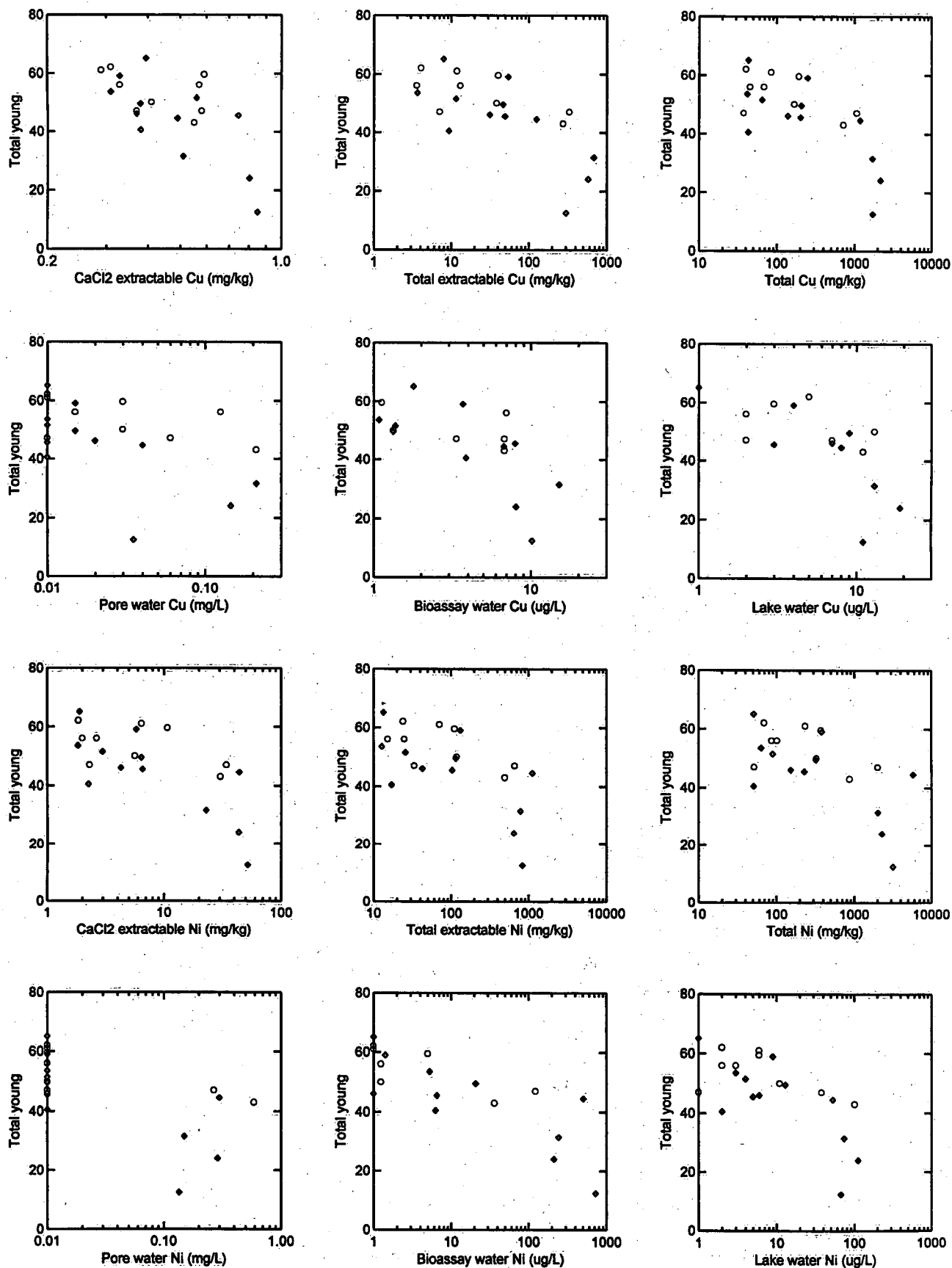
Response vs metal-AVS

NATIONAL WATER RESEARCH INSTITUTE

INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX

Environment Environnement
Canada Canada

Canada