

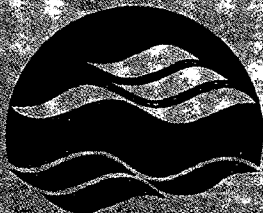
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**FINAL REPORT ON THE EFFECTS OF  
ATMOSPHERIC DEPOSITION OF METALS FROM  
THE SUDBURY SMELTERS ON AQUATIC  
ECOSYSTEMS**

**Borgmann, U., T.B. Reynoldson, F. Rosa and W.P.  
Norwood**

**NWRI Contribution No. 01-023**



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THE SUDBURY SMELTERS ON  
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**Part I: Major ions, nutrients, total metals, benthos, and  
toxicity and bioavailability of metals to benthic invertebrates.**

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## **MANAGEMENT PERSPECTIVE**

This report describes research resulting from 1996 and 1998 field trips to lakes in the Sudbury area to investigate the impacts of atmospherically deposited metals on aquatic ecosystems. The work was initiated to provide scientific data in support of Canada's involvement in international agreements and management of the long range atmospheric transport of metals. Metal contamination from the Sudbury smelters has been well documented in the past, and the biological impacts of acid deposition from these smelters, and recovery following reductions in acid emissions, has been studied extensively. However, the biological impact of metal deposition from the smelters has not previously been investigated in detail.

This report summarizes the level of metal contamination in sediments from 12 circum-neutral (not acid stressed) lakes at various distances from Sudbury, the abundance of benthic invertebrates in these lakes, the toxicity of lake sediments to benthic invertebrates, and the bioaccumulation of metals by amphipods exposed to these sediments. It also demonstrates that toxicity is due to dissolved contaminants in overlying water, and quantifies the amount of metal leached from the sediment into overlying water in laboratory toxicity tests. When compared to previously determined critical concentrations of metals in amphipods and overlying water, these data demonstrate that nickel is the substance responsible for toxicity. This study addresses all four key questions outlined in the Aquatic Effects Technology Evaluation (AETE) program. In addition, the spatial extent of nickel contamination near Sudbury, sufficient to cause toxicity, has been estimated.

These data assist in understanding the impact of atmospherically transported metals, the design and interpretation of Environmental Effects Monitoring programs for mining, and the development and interpretation of chemically based sediment quality guidelines for metals. This study also contributes to ECs involvement in the Metals In The Environment Research Network (MITERN) with other federal departments, universities and industry.

## SOMMAIRE À L'INTENTION DE LA DIRECTION

Ce rapport décrit des recherches résultant de visites de lacs de la région de Sudbury, effectuées en 1996 et en 1998 pour étudier l'impact du dépôt atmosphérique de métaux sur les écosystèmes aquatiques. Cette étude devrait fournir des données scientifiques utiles pour la participation du Canada à des accords internationaux et pour la gestion du transport atmosphérique à grande distance des métaux. On a déjà documenté la contamination par les métaux due aux fours de fusion de Sudbury; des études approfondies ont porté sur l'impact biologique du dépôt acide causé par ces fours et sur le rétablissement qui a suivi les réductions d'émissions acides, mais non sur l'impact biologique du dépôt de métaux dû aux fours.

Ce rapport résume les données sur le niveau de contamination par les métaux des sédiments de 12 lacs à peu près neutres (non stressés par les dépôts acides) à diverses distances de Sudbury, ainsi que celles sur l'abondance des invertébrés benthiques dans ces lacs, la toxicité des sédiments lacustres pour les invertébrés benthiques et la bioaccumulation des métaux chez les amphipodes exposés à ces sédiments. De plus, il démontre que cette toxicité est due à des contaminants dissous dans l'eau sus-jacente, et il présente les résultats d'essais de toxicité en laboratoire qui quantifient les métaux lixiviés de ces sédiments et entraînés dans l'eau sus-jacente. Comparées à des concentrations critiques de métaux déjà mesurées chez des amphipodes et dans l'eau sus-jacente, ces données montrent que le nickel est la substance responsable de la toxicité. Cette étude répond aux quatre questions clés du Programme d'évaluation des techniques de mesure d'impact en milieu aquatique. De plus, on a estimé l'étendue spatiale de la contamination par le nickel dans le voisinage de Sudbury, qui est suffisante pour causer des problèmes de toxicité.

Ces données aident à comprendre l'impact des métaux transportés par voie atmosphérique, la conception et l'interprétation des programmes de suivi des effets sur l'environnement prévus pour les activités minières, ainsi que le développement et l'interprétation des lignes directrices relatives à la qualité des sédiments limitant les métaux, fondées sur leurs caractéristiques chimiques. De plus, on a réalisé cette étude dans le cadre de la participation d'EC au Réseau de recherche sur les métaux dans l'environnement, en collaboration avec d'autres ministères du gouvernement fédéral, des universités et des industries.

## **ABSTRACT**

A collaborative study by members of the former Sediment Assessment and Remediation Project of the Aquatic Ecosystem Restoration Branch of the National Water Research Institute (NWRI) was conducted to address the issue of atmospheric transport of metals from smelters. The objective 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 spatial extent of such effects. In order to specifically address the issue of metal effects, rather than acidification, only survey lakes with circum neutral pH were selected, and the study focused on sediment and benthic invertebrates. Two major field trips were undertaken to the Sudbury area, one in 1996 and another in 1998. Data collected in 1996 were summarized in an Interim Report (Borgmann et al. 1998a). This report summarizes results obtained from the 1998 field trip and interpretation of the combined 1996 and 1998 data.

The study addressed the four key questions posed in the Aquatic Effects Technology Evaluation (AETE) program. 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?

Answers to these questions are:

1. The sediment and water chemistry data clearly show that metals have been deposited in lakes near Sudbury. Both water and sediment metal concentrations decrease rapidly with distance from Sudbury.
2. Metal bioaccumulation by amphipods clearly showed that cadmium, cobalt and nickel were bioavailable and elevated in sediments from Sudbury area lakes. Increased bioavailability was also suggested by increased metals in overlying water in the toxicity tests, coupled with the demonstration that mortality in amphipods was due to a dissolved substance and not the solid

phase of the sediment.

3. The question of biological effects was addressed through a combination of in-situ invertebrate community assessment and toxicity testing. Fingernail clams were absent, and amphipods and tanytarsid midges were reduced in the Sudbury area lakes. Severe sediment toxicity to amphipods and mayflies was detected, and reproduction in oligochaete worms was lower than in reference sediments. This indicates that there are biological impacts in the deep sediments of lakes in the Sudbury area, and these are apparently the result of sediment toxicity.

4. The comparison of metal bioaccumulation with lethal body concentrations in amphipods, and comparison of metals in overlying water with lethal metal concentrations in water, demonstrated that nickel was the primary cause of sediment toxicity in laboratory tests.

The concentration of nickel in Sudbury area sediments resulting in nickel bioaccumulation to toxic levels in amphipods was determined. Since nickel was identified as the toxic agent, this provided a rough estimation of the spatial extent (20 to 27 km from Copper Cliff in a southeasterly direction) of toxic effects in the deep sediments near Sudbury.

## RÉSUMÉ

Des membres de l'ancien projet d'évaluation de l'état et de l'assainissement des sédiments de la Direction de la restauration des écosystèmes aquatiques de l'Institut national de recherche sur les eaux (INRE) ont effectué une étude collaborative en réponse à des préoccupations concernant le transport atmosphérique de métaux libérés par des fours de fusion. L'objectif de cette étude était de déterminer si l'on pouvait démontrer l'existence d'effets biologiques sur les écosystèmes aquatiques et, le cas échéant, d'établir des liens nets entre ces effets et des métaux définis, et en déterminer l'étendue spatiale. Afin d'étudier les effets spécifiques des métaux, à l'exclusion de ceux de l'acidification, on a limité la sélection des lacs à ceux dont le pH est presque neutre, et l'étude a porté principalement sur les sédiments et les invertébrés benthiques. On a effectué deux grandes visites d'étude dans la région de Sudbury, l'une en 1996 et l'autre, en 1998. On a résumé les données collectées en 1996 dans un rapport provisoire (Borgmann et al., 1998a), qui présente un sommaire des résultats de la visite de 1998, ainsi que l'interprétation des données combinées de 1996 et de 1998.

Cette étude portait sur les quatre questions clés du Programme d'évaluation des techniques de mesure d'impact en milieu aquatique :

1. Est-ce que ces contaminants pénètrent dans l'écosystème?
2. Ces contaminants sont-ils biodisponibles?
3. Y a-t-il une réponse mesurable?
4. Est-ce que cette réponse est causée par les contaminants?

On a obtenu les réponses suivantes :

1. Les données sur les sédiments et la chimie de l'eau indiquent clairement qu'il y a des dépôts de métaux dans les lacs du voisinage de Sudbury. Les concentrations de métaux de l'eau et des sédiments diminuent rapidement en fonction de la distance de Sudbury.
2. La bioaccumulation des métaux par les amphipodes indique clairement la présence de concentrations élevées et biodisponibles de cadmium, de cobalt et de nickel dans les sédiments



des lacs de la région de Sudbury. Combinée à la démonstration que la mortalité chez les amphipodes était due aux substances dissoutes et non à la phase solide des sédiments, l'augmentation de la teneur en métaux de l'eau sus-jacente mise en évidence par des essais de toxicité semble indiquer qu'il y a un accroissement de la biodisponibilité.

3. Pour ce qui est des effets biologiques, on combine une évaluation in situ de la communauté des invertébrés à des essais de toxicité. On n'a pas observé de sphaeriidés, et les populations d'amphipodes et de petits tarsidés étaient réduites dans les lacs de la région de Sudbury. On a détecté, par rapport aux sédiments témoins, des signes de forte toxicité des sédiments pour les amphipodes et les éphémères communs, ainsi qu'une diminution de la reproduction des oligochètes, ce qui indique qu'il y a des impacts biologiques dans les sédiments profonds des lacs de la région de Sudbury, qui semblent dus à la toxicité des sédiments.

4. Lors d'essais en laboratoire, on a montré que le nickel est la principale cause de la toxicité des sédiments en comparant la bioaccumulation des métaux à des concentrations corporelles létales chez les amphipodes, et les teneurs en métaux de l'eau sus-jacente à des concentrations létales de métaux dans l'eau.

On a déterminé que la concentration de nickel dans les sédiments de la région de Sudbury causait la bioaccumulation de ce métal à des teneurs toxiques chez les amphipodes. Étant donné qu'il a été établi que le nickel est l'agent toxique responsable, on a pu obtenir une estimation grossière de l'étendue spatiale de ces effets toxiques (vers le sud-est, de 20 à 27 km de Copper Cliff) dans les sédiments profonds du voisinage de Sudbury.

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## 1. INTRODUCTION

During the summer on 1996 a collaborative study by members of the former Sediment Assessment and Remediation 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 spatial extent of such effects. The study area chosen was Sudbury, because of its long history of metal mining and smelting. 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 circum neutral pH were selected, and the study focused on sediment and benthic invertebrates.

Two major field trips were conducted to the same lakes in the Sudbury area, one in 1996 and another in 1998. Data collected in 1996 were summarized in an Interim Report (Borgmann et al. 1998a). Unexpected high mortality due to pH depression occurred in initial toxicity tests conducted with sediments collected in 1996. This necessitated the development of an alternate test method with larger water to sediment volume ratios, resulting in a more stable overlying water quality (Borgmann and Norwood 1999a). This caused delays in completing all the toxicity tests with the 1996 sediments, and prolonged sediment storage times. As a result, a second field trip was conducted in 1998 to collect fresh sediments to verify sediment toxicity and measure metal bioavailability to *Hyalella*. Some types of data were collected only in 1996, and these are not reproduced in this report (Table 1.1). Selected data from the Interim Report are presented

here again, in order to facilitate comparison between 1996 and 1998 data (Table 1.2). In addition, the toxicity of three different nickel-spiked sediments to *Hyaella*, and Ni bioaccumulation, was determined in a separate study (Borgmann et al. 2001) which directly supports the interpretation of data summarized in this report.

**Table 1.1. Data collected from the Sudbury area lakes in 1996 and not summarized in this report.**

Data collected	Location in Interim Report (Borgmann et al. 1998a)
Hydrolab profiles (temperature, pH, conductivity, oxygen) for 1996.	Appendix 1
Trace metals in water by ICAP-OES in 1996.	Table 2.4
Profiles for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in sediments.	Appendix 2
Total metals in surface (0-5 cm) sediments.	Table 3.4
Chronic toxicity test results for <i>Chironomus riparius</i> , <i>Hexagenia</i> sp., <i>Hyaella azteca</i> , and <i>Tubifex tubifex</i> , and metal concentrations measured in the overlying water.	Appendix 3
Metal speciation, metals in porewater, sediment pH and Eh, acid volatile sulfide, and light absorbency characteristics of porewater and sediment extracts.	Chapter 6 and Appendix 4

**Table 1.2. Data collected from the Sudbury area lakes in 1996 and 1998, and summarized in this report.**

Data collected	Location
Hydrolab profiles (temperature, pH, conductivity, oxygen) for 1998.	Appendix 1
Conductivity, dissolved oxygen, temperature, pH, 1996 and 1998 comparisons.	Appendix 2, Table A1
Major ions and DOC, 1996 and 1998 comparisons.	Appendix 2, Table A2
Nutrients, 1996 and 1998 comparisons.	Appendix 2, Table A3
Trace metals in water by ICP-MS in 1998.	Appendix 2, Table A4
Total metals in mini-ponar grab samples from 1996 and 1998.	Appendix 2, Table A5
Benthic Invertebrate abundances, 1996 and 1998 comparisons.	Appendix 2, Table B
Repeat chronic toxicity tests with <i>Chironomus</i> and <i>Hyaella</i> exposures to sediments collected in 1998.	Appendix 2, Tables C1 and C2
Metals in overlying water and metals bioaccumulated by <i>Hyaella</i> in one-week exposures to sediments collected in 1998.	Appendix 2, Tables D and E

In addition to data on bulk chemistry and metal impacts on benthic invertebrates, data were also collected on metal speciation in sediments, porewater, acid volatile sulfides, and light absorption properties of sediment extracts (Jackson and Nguyen, in Borgmann et al. 1998a, Chapter 6 and Appendix 4). Additional information on these and microbiological parameters, and their relationship to sediment toxicity, will be presented in Part II of this report.

Table 1.3. Table of Abbreviations.

Abbreviation	Meaning
B-1	1m above the bottom sediments
1m	1m below the water surface
Alk	alkalinity
Ca	filtered calcium
CaUF	total calcium (un-filtered)
CHLA	total chlorophyll a
CHLAC	chlorophyll a, corrected for pheophytin
Cl	chloride
COND	specific conductance
DIC	dissolved inorganic carbon
DO	dissolved oxygen
DOC	dissolved organic carbon
Epi	epilimnion
Hypo	hypolimnion
K	potassium
Meso	mesolimnion or thermocline
Mg	filtered magnesium
MgUF	total magnesium
Na	sodium
NH <sub>3</sub>	ammonia
NO <sub>3+2</sub>	nitrate plus nitrite
SiO <sub>2</sub>	silica
SO <sub>4</sub>	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. MATERIALS AND METHODS**

### **2.1 Sampling Sites**

Water, sediment and benthic invertebrate samples were collected from 12 lakes (Fig. 2.1) on August 19-26, 1996, and again on August 11-16, 1998, from the same lakes with a trailerable launch. These included four potentially impacted lakes in the immediate Sudbury area (<13 km from the smelter stacks at Copper Cliff), 4 reference lakes at considerable distance (94-154 km) from Sudbury, and 4 lakes at intermediate distance (32-52 km, Table 2.1). All lakes were circum-neutral with pH values of 6.6-8.3 near the surface, although lower values were observed near the bottom. Two sampling depths were selected in each lake, including the deepest location and a site at 10 m depth if the deep site was greater than 10 m. 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.

In addition to the reference lakes indicated above, two "control" sediments were used in the toxicity tests, one from Hamilton Harbour (HH1) and another from Lake Erie (LE303), near Long Point. The Lake Erie sediment is low in metals (Borgmann et al. 1998a). Although the Hamilton Harbour sediment is not a "clean" sediment, it has consistently supported excellent growth and survival of *Hyaella* in our laboratory.

### **2.2 Sediment and water chemistry**

The pH, specific conductance, dissolved oxygen concentration (DO), and temperature were recorded with a HYDROLAB Profiling System, Model DataSonde® 3 (Hydrolab Corp. 1991). Water samples for the determination of trace and major element concentrations were collected 1 m below the surface and 1 m above the bottom using a van Dorn bottle (Rosa et al. 1991) and

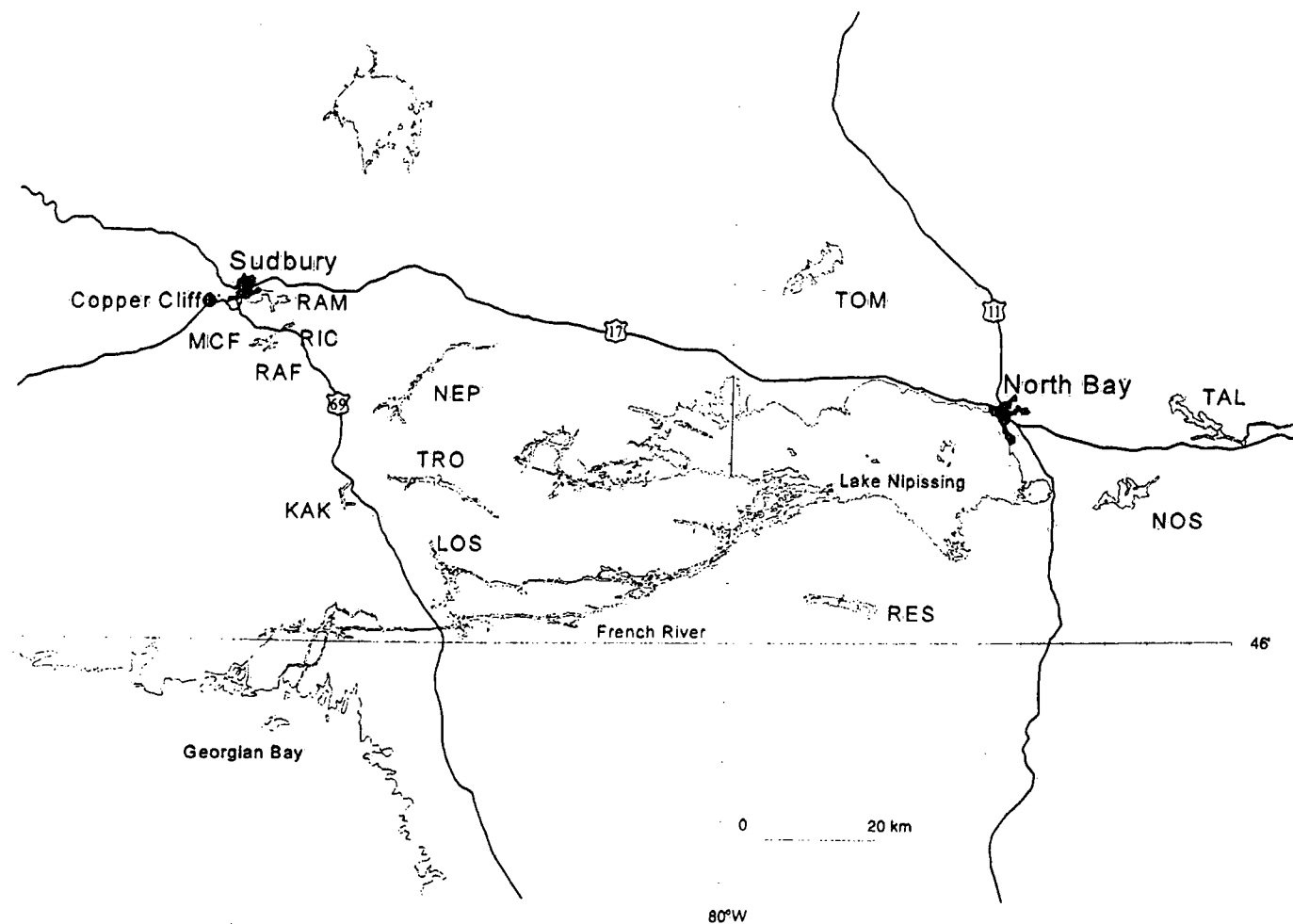


Figure 2.1. Map of the study area with three letter codes indicating study lakes (Table 2.1).

Table 2.1. Study lakes and control sediment collection sites (for toxicity tests), site codes, latitude (Lat.) and longitude (Long.), and distance from the smelter stacks at Copper Cliff.

Lake name	Site codes	Lat. (deg)	Long. (deg)	Distance (km)
<u>Sudbury Lakes:</u>				
Ramsey	RAMD	46.4806	80.9758	6
McFarlane	MCF10	46.4233	80.9494	10
	MCFD	46.4136	80.9689	
Raft	RAF10	46.4125	80.9406	11
	RAFD	46.4128	80.9514	
Richard	RICD	46.4378	80.9167	12
<u>Intermediate Lakes:</u>				
Nepewassi	NEPD	46.3333	80.6956	32
Kakakiwaganda	KAK10	46.1917	80.7894	38
	KAKD	46.1900	80.7908	
Trout	TRO10	46.2283	80.6408	43
	TROD	46.2278	80.6169	
Lower Sturgeon	LOS10	46.1269	80.6006	52
	LOSD	46.1353	80.6081	
<u>Reference Lakes:</u>				
Tomiko	TOM10	46.5383	79.8333	94
	TOMD	46.5439	79.8142	
Restoule	RES10	46.0561	79.7953	107
	RESD	46.0569	79.8061	
Nosbonsing	NOS10	46.2167	79.2228	144
	NOSD	46.2183	79.2181	
Talon	TAL10	46.2964	79.0436	154
	TALD	46.3014	79.0647	
<u>Control sediment collection sites:</u>				
Hamilton Harbour (site 1)	HH1	43.2802	79.8728	368
Lake Erie (site 303)	LE303	42.5639	80.0417	443

filtered in the field within a few hours of collection using a Millipore glass filter apparatus with 0.45 micron cellulose acetate filters. Methods of collection, preservation, and analysis for major ions and nutrients were the same for the 1998 as for the 1996 survey reported in Borgmann et al. (1998a). Filtered samples for metal analysis were acidified with "Ultrex" grade HNO<sub>3</sub> (conc.) to a final concentration of 0.4% and shipped to the laboratory as quickly as possible. The samples were stored at 4°C prior to analysis. The concentrations of major elements in water were determined by the National Laboratory for Environmental Testing (NLET) in Burlington,



Ontario according to the methods described by Environment Canada (1995). Trace metals in water were analyzed on a JY 74 inductively coupled argon plasma optical emission system (ICAP-OES) in 1996 and by inductively coupled plasma mass spectrometry (ICP-MS) by NLET in 1998. Only the 1998 metal concentrations in water are presented here. The 1996 metal concentrations are reported in Borgmann et al. (1998a), but are less accurate than the 1998 data because of the much greater sensitivity of the ICP-MS analytical method.

Surface sediment samples for metal analysis were obtained from within the top 5 cm of sediment collected with a box corer in 1996. In addition, in 1996 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 1991) 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. These data are reported in Borgmann et al. (1998a).

Five mini-ponar sediment samples were collected at each sampling site in both 1996 and 1998 and stored separately in polyethylene bags to obtain replicate samples for sediment toxicity and metal bioavailability testing. Samples were stored at 4°C until used. Analyses for total metals were conducted on two different mini-ponar grab samples from each site collected in 1998, and, following publication of the Interim Report (Borgmann et al. 1998a), also on one of the stored replicate mini-ponar grab samples from each site collected in 1996. Sediment samples were freeze dried and ground with 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 re-dissolved 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, centrifuged at 5000 rpm for 30 minutes, and analyzed by ICAP-OES. Recovery of metals from certified reference material (NIST-2704 Buffalo River sediment) was within 10% of the certified values. Samples were then re-analyzed for Cd by graphite furnace atomic absorption spectrophotometry (GFAAS) because ICAP-OES was not sufficiently sensitive for this metal. Analysis of water samples for Cd by GFAAS

provided a check on the accuracy of the GFAAS method for Cd. Agreement between GFAAS and ICP-MS analyses was good for Cd concentrations above 0.1 µg/L (Table A4).

### 2.3 Benthic community structure

In 1996, in-situ benthic invertebrates were collected using a box corer (38 cm x 38 cm x 46 cm) from which 5 core tubes (10 cm deep, 33.2 cm<sup>2</sup> area each) 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 de-calcification. Due to the low numbers of invertebrates obtained from the core tubes, animals were collected by mini-ponar grab sampler (224 cm<sup>2</sup> area per grab) in 1998. Three replicate grabs were collected from each station. These were sieved through a 500 micron mesh screen because of the larger sediment volume collected in 1998. The entire invertebrate samples were identified and counted in both years.

### 2.4 Sediment toxicity and metal bioaccumulation in *Hyaella*

Methods and results from chronic toxicity tests conducted on sediments collected in 1996 with *Chironomus riparius*, *Hexagenia limbata*, *Hyaella azteca*, and *Tubifex tubifex* are reported in Borgmann et al. (1998a). Experiments conducted in 1998 focused primarily on metal bioaccumulation by *Hyaella azteca*.

Amphipods used for bioaccumulation measurements were cultured in dechlorinated Burlington city tap water (from Lake Ontario, hardness 130 mg•L<sup>-1</sup>, alkalinity 90 mg•L<sup>-1</sup>, DOC 2.3 mg•L<sup>-1</sup>, pH 7.8-8.6) as described in Borgmann et al. (1989). Cultures and experimental animals were kept in an incubator at 23°C with a 16 h light:8 h dark photoperiod; the same conditions were used for the experiments. In order to maintain overlying water quality, bioaccumulation and toxicity experiments were conducted in Imhoff settling cones with 15 mL of sediment and 1 L of overlying water using methods described in Borgmann and Norwood (1999a). Sediments and overlying water were gently aerated and allowed to equilibrate for 10-14 days before test animals were added. Fifteen adult (4-6 week old) *Hyaella* were added to each test container and exposed

for one week. This is sufficient time for *Hyalella* metal body concentrations to come to equilibrium; Ni turnover rates are about 0.5/day in *Hyalella* (Borgmann et al. 2001). Oxygen concentrations in the overlying water in the test containers were usually about  $8 \text{ mg} \cdot \text{L}^{-1}$  and always above 7.5. The pH averaged 8.40 (SD 0.19,  $n=122$ ). Two experiments were conducted within two months of sediment collection. Each included one test container with sediment from each site (21 sites) plus two control sediments (Hamilton Harbour and Lake Erie) and an additional container without sediment but with cotton gauze as a substrate. This approaches the maximum number of experimental containers that could be processed in one day. The second experiment was conducted using sediments from a different mini-ponar grab sample from each site. A third experiment, with selected sediments from toxic and non-toxic sites, was conducted with sediments from a third mini-ponar grab and with the addition of caged animals to determine the effect of direct contact with the sediment on metal bioaccumulation. Cages consisted of a 250 mL polypropylene specimen container with the bottom cut out and replaced with a  $200 \mu\text{m}$  mesh nylon screen (Borgmann and Norwood 1999b). A  $5 \times 5 \text{ cm}$  piece of cotton gauze was added to the cage to provide a substrate for the animals.

At the end of the incubation period, a sample of overlying water was filtered through a 0.4 micron polycarbonate membrane filter and preserved with nitric acid. The surviving amphipods were sorted from the sediment by sieving, rinsed in clean water, and placed in 120 mL plastic specimen containers with  $50 \mu\text{M}$  EDTA and cotton gauze for 24 hours to clear their guts. They were then dried at  $60^\circ\text{C}$  for 72 hrs. Groups of four dried amphipods (approx. 0.5-3 mg total dry mass) were digested with 70% nitric acid at room temperature for 6 days, after which 30% hydrogen peroxide was added and digestion allowed to continue for another 24 h. Each sample was then made up to 6 mL with Milli-Q de-ionized water for analysis by inductively coupled plasma mass spectrometry (ICP-MS), or to 0.5-2 mL (depending on tissue mass) for analysis by graphite furnace atomic absorption spectrophotometry (GFAAS). Acid and peroxide volumes were  $25 \mu\text{L}$  and  $20 \mu\text{L}$  per 1 mL of total volume respectively. Digested amphipods and overlying water were analyzed on a Varian SpectraAA 400 graphite furnace atomic absorption spectrophotometer with Zeeman background correction using a partition tube, or by ICP-MS by the National Laboratory for Environmental Testing (NLET) in Burlington, Ontario.

To verify sediment toxicity results from the 1996 samples (Borgmann et al. 1998a), some four-week toxicity tests with young *Hyalella* were repeated in 1998 within 3 months of sediment collection. To determine the effect of sediment storage time, some of the original 1996 sediment samples were also retested, 129 weeks after sediment collection. In addition, one experiment with both sediment exposed and caged animals was also conducted in order to determine the effect of direct sediment exposure on survival and growth. These experiments were conducted under identical conditions to those used for bioaccumulation measurements, except that they lasted four weeks instead of one week and were initiated with 0-1 week old young instead of adults.

### 3. MAJOR IONS AND NUTRIENTS

#### 3.1 Temperature, conductance, pH and dissolved oxygen profiles

All of the lakes studied in 1998 were thermally stratified, as in 1996, and probably at the peak of stable stratification (the greatest temperature difference between surface and bottom). The surface temperature for all the sites was fairly constant (Table A1) with a mean of 22.8°C, which is within one standard deviation (0.4°C) from the 1996 mean temperature. 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 between 4 to 7 m, and 2 to 5 m, respectively, and the remainder of the water column consisting of a cold (5 to 7°C) hypolimnion, with the exception of Lakes Richard and Nosbonsing which had no hypolimnion (Appendix 1). This was similar to 1996 (Borgmann et al. 1998a). Some variability in the thermal structure between years is not uncommon, and can be due to different hydrodynamic conditions induced by variable solar radiation and wind forcing at the water surface.

Conductance, pH, and dissolved oxygen for all the sites, at the surface (1m) and bottom (B-1) were obtained from the Hydrolab profiles data, as for 1996 (Table A1). The surface and bottom conductance at each site was very similar. Concentrations were highest (tenfold) in the four lakes closest to Copper Cliff with the exception of Raft Lake, as was the case in 1996. The depth-

concentration data collected with the Hydrolab Profiling System is reported in Appendix (1). The conductance showed less variability between the surface (1m) and one meter above the bottom (B-1), than oxygen and pH.

### 3.2 Major ions

In addition to re-sampling all the lakes (B-1m depth) for the same parameters as for 1996, major ions at 1m and B-1m in each lake were also collected in 1998. Significantly greater concentrations of cations (Table A2a) were found in Ramsey, McFarlane and Richard Lakes than in the other lakes. Sodium showed the greatest variation in concentration (15 fold) compared to all the other cations measured (3 fold), with the exception of calcium, which showed a 5 fold variation. All the cations showed similar concentrations for the surface and bottom depths, with marginally higher (but not statistically different) concentrations at the surface, except for potassium. Greater than 90% of the major ion concentrations are found in the dissolved phase.

Alkalinity and concentration of most anions (Table A2b) were also very similar between the surface and bottom depths. Chloride showed a greater variation in concentration than the other major ions measured. Trends in chloride and alkalinity were similar to those for the cations (high in Ramsey, McFarlane and Richard Lakes and low in the other lakes). Significantly greater concentrations of  $\text{SO}_4^{-2}$  were found in the lakes closest to Copper Cliff, with statistically significant decreasing trend with distance, as was found in 1996 (Borgmann et al. 1998a). Unlike the other major ions,  $\text{SO}_4^{-2}$  concentrations were relatively high in Raft Lake. Sulfate concentrations appeared to be related more to distance from Sudbury and less to the concentrations of alkalinity and other ions. Concentrations of silica were greater in the deep than in the surface waters. DOC showed no distinct spatial trend, and concentrations in the bottom waters were marginally higher than in the surface waters.

### 3.3 Nutrients and chlorophyll

The concentrations of different forms of chlorophyll, nitrogen and phosphorus in the surface water showed some distinct differences among the lakes sampled, and also with depth (Table A3). The total phosphorus concentration in the surface waters ranged from 0.004 to 0.014 mg/L, and concentrations in the bottom water ranged from 0.007 to 0.04 mg/L. 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 phosphorus forms showed a possible decreasing trend with distance from Copper Cliff. Concentrations of chlorophyll seem to increase with distance from the smelters. The nitrate+nitrite concentrations were highly variable, both among lakes and with depth in individual lakes. In some lakes (e.g. Ramsey and McFarlane) surface concentrations were much higher than in deep water, whereas in others (e.g. Talon) concentrations were higher in deeper water. Concentrations of TKN varied less and showed no distinct spatial or depth differences.

### 3.4 Summary

- 1) All of the lakes studied were thermally stratified, and probably at the peak of stable thermal stratification, as in the 1996 survey.
- 2) The surface and bottom conductance at each site was very similar. Concentrations were highest (tenfold), in the lakes closest to Copper Cliff with the exception of Raft Lake. All the other lakes including Raft had a fairly constant conductance of 30 to 70  $\mu\text{S}/\text{cm}$ .
- 3) Significantly greater concentrations of cations were found in Ramsey, McFarlane and Richard Lakes than in the other lakes. Sodium showed the greatest variation in concentration (15 fold) compared to all the other cations measured (3 fold), with the exception of calcium, which showed a 5 fold variation.
- 4) Trends in chloride and alkalinity were similar to those for the cations. Unlike the other major ions,  $\text{SO}_4^{2-}$  concentrations were relatively high in Raft Lake. Sulfate concentrations appeared to be related more to distance from Sudbury and less to the concentrations of alkalinity and other ions.

- 5) The concentrations of different forms of chlorophyll, nitrogen and phosphorus in the surface water showed some distinct differences among the lakes sampled, and also with depth.
- 6) Concentrations of TKN were relatively constant and showed no distinct spatial or depth differences, among and within lakes.

#### **4. METALS IN WATER AND SEDIMENT**

##### **4.1 Metals in Water and Comparison to Surface Sediment Concentrations**

Metal concentrations in lake water in 1998, measured by ICP-MS, are summarized in Appendix 2, Table A4. Equivalent data for 1996 are presented in Borgmann et al. (1998a), but these are less accurate because the analytical method (ICAP-OES) is much less sensitive. Cadmium concentrations in water in 1998 were also measured by graphite furnace atomic absorption spectrophotometry (GFAAS) because this provided a check on the accuracy of the GFAAS method for Cd. Verification of the accuracy of GFAAS measurements for Cd was needed because Cd in ponar grab samples was measured by this method. Agreement between GFAAS and ICP-MS analyses was good for Cd concentrations above 0.1 µg/L (Table A4). Furthermore, concentrations in unfiltered samples were similar to those in filtered samples, indicating that most of the Cd was dissolved or associated with extremely small particles (<0.4 microns).

Concentrations of some metals in bottom (bottom-1m) water were higher than in surface (1m) water for contaminated lakes near Sudbury. This was observed for Cd, Co, Ni, and Zn (Table A4). For Co in McFarlane and Raft Lakes, and Ni in McFarlane Lake, concentrations in deep water at the deepest station were also higher than at the 10m station. This is consistent with an increasing metal concentration in water with increasing depth. Differences between surface and deep water, and between deep water at the deep and 10m stations, were particularly striking for Mn. High Mn concentrations in water were not, however, restricted to contaminated lakes near Sudbury. High Mn was generally associated with low dissolved oxygen in deep water (Table A1). Concentrations of As, Cr, Cu, Pb, Se and Tl did not generally demonstrate strong gradients with water depth (Table A4).

The relationship between metal concentrations in bottom water in 1988 and distance from Copper Cliff (d) was fitted to the equation

$$\text{Metal concentration} = \text{max} \cdot e^{(-k \cdot d)} + \text{bk}$$

where:

max = maximum concentration at 0 km from smelter, less background

k = constant defining the exponential rate of decrease with distance

d = distance from Copper Cliff (km)

bk = background metal concentration at infinite distance

$D_{0.5}$  = distance at which  $e^{(-k \cdot d)} = 0.5$  and metal concentration =  $0.5 \times \text{max} + \text{bk}$

The trends in dissolved metals were similar to those for metals in surface sediments (Borgmann et al. 1998a), but the estimates of the distance from Copper Cliff at which metal enrichment drops by half ( $D_{0.5}$ ) were slightly lower at 7-9 km, except for Cu which provided an estimate of 14 km (Table 4.1). Unlike the sediment concentrations, however, metal concentrations in deep water were much higher for Ni than for Cu in lakes close to Sudbury (Table A4). The maximum concentration of metal in water was over 400 fold greater than the background for Ni, but only 11 fold greater for Cu (Table 4.1). The ratio of metal in water to metal in sediment decreases with increasing distance from Sudbury for Ni, but increases for Cu. Consequently, the degree of metal enrichment is much more pronounced for Ni in water than for Cu in water, whereas enrichment in the sediments is similar for the two metals (Borgmann et al. 1998a).

## 4.2 Metals in Mini-Ponar Grab Samples

Sediment core sections or surface sediments were not collected in 1998, but one of the ponar grab samples (grab #1) was analyzed for metals. Metal concentrations were substantially different from those determined in the 1996 surface sediment samples, so additional metal analyses were performed on a second mini-ponar collected in 1998, and one of the mini-ponar grabs originally collected in 1996 (Table A5). Metal concentrations in mini-ponar grab samples were highly variable. For Cu and Ni in the contaminated Sudbury Lakes, for example,



Table 4.1. Estimates of max, k, bk and  $r^2$  for metals in deep (bottom-1m) water and surface sediments fitted to the equation  $\text{max} \cdot e^{-(k \cdot d)} + bk$  where d is distance from Copper Cliff (km), and  $D_{0.5}$ , the distance from Copper Cliff at which  $e^{-(k \cdot d)}$  equals 0.5.

Metal	max	k ( $\text{km}^{-1}$ )	$D_{0.5}$ (km)	bk <sup>a</sup>	$r^2$
<u>Metal in water 1 m above bottom in 1998 (<math>\text{nmol} \cdot \text{L}^{-1}</math>):</u>					
Cd	4.7	0.099	7	0.43	0.515
Co	11	(0.075) <sup>a</sup>	9	1.2	0.138
Cu	230	0.048	14	21	0.775
Ni	3050	0.076	9	7	0.968
Zn	230	(0.075) <sup>a</sup>	9	140	0.482
<u>Metal in surface (1-3 cm) sediments in 1996 (<math>\mu\text{mol} \cdot \text{g}^{-1}</math> dry wt.):<sup>b</sup></u>					
Cd	0.041	0.070	10	0.034	0.157
Co	1.7	0.039	18	0.36	0.761
Cu	34	0.064	11	0.60	0.973
Ni	72	0.069	10	0.8	0.946
Zn	1.9	0.029	24	3.9	0.063

a. 0.075 = average k for Cd, Cu, Ni. This was used to estimate max and bk for Co and Zn because all three parameters could not be fitted simultaneously.

b. data from Borgmann et al. (1998a).

concentrations ranged from 2 (Ni, RAJD) to 37 (Ni, MCF10) fold (Table 4.2). This does not appear to be a date-of-sampling effect, since the two grabs collected in 1998 had the greatest difference at several sites (e.g. RAMD, MCFD). The highest concentration of metals in the mini-ponar grab samples were similar to, or slightly lower than, those in the surface grab samples. This suggests that the mini-ponar grab collects a variable mixture of contaminated surface and cleaner subsurface sediment. The surface sediments contained from roughly 1 to 11 times as much metal as the mini-ponar samples from the same site in the same year (1996, Table 4.2). Therefore the surface sediment and core data collected in 1996 provide a better indication of the relationship between sediment contamination and distance from Sudbury than do the mini-ponar data. Furthermore, the variability in the mini-ponar grab metal content can be expected to affect the sediment toxicity and metal bioaccumulation observations. This factor was overlooked in the Interim Report (Borgmann et al. 1998a), and correlations between sediment toxicity (based on mini-ponars) and sediment chemistry (based on surface sediments), as reported in the Interim Report, need to be interpreted with caution.

Table 4.2. Copper and nickel in selected mini-ponar grab samples from Sudbury area sites ( $\mu\text{mol} \cdot \text{g}^{-1}$ ) and comparison to metals in surface grab samples and sediment core sections.

Site	Metal	Mini-ponar grab samples			Surface grab <sup>a</sup>	Core section <sup>a</sup>	Core section
		1996#3	1998#1	1998#2	1996, 0-5 cm	1996, 0-3 cm	1996, 14-20 cm
RAMD	Cu	20.5	6.3	29.0	27.0	27.6	0.8
RAMD	Ni	27.0	7.7	36.3	34.5	31.3	1.2
MCF10	Cu	16.8	4.1	0.7	16.9	-	-
MCF10	Ni	41.4	8.7	1.1	34.3	-	-
MCFD	Cu	28.5	24.7	6.1	18.7	20.8	0.5
MCFD	Ni	47.4	45.9	10.7	99.1	90.4	0.7
RAF10	Cu	2.1	0.6	0.4	11.4	-	-
RAF10	Ni	3.0	0.9	0.8	14.9	-	-
RAFD	Cu	23.2	8.4	7.8	34.4	15.6	0.7
RAFD	Ni	26.8	13.2	12.0	39.1	23.8	0.8
RICD	Cu	2.6	15.8	17.5	27.3	16.1	1.1
RICD	Ni	4.9	31.3	32.7	54.4	33.5	3.5

a. from Borgmann et al. 1998a.

## 5. BENTHIC COMMUNITY STRUCTURE

The number of benthic organisms collected at each site was relatively small, even in 1998 after a change in collection methods. Preliminary analysis of the 1996 benthic data are presented in Borgmann et al. (1998a). The 1998 data are summarized and compared with the 1996 data in Appendix 2 (Table B). Phantom midges (Chaoboridae), midges belonging to the Chironomini (including *Chironomus* sp.) and Tanypodinae, and oligochaetes were the most frequently observed organisms over all regions. Their abundance did not correlate with distance from Sudbury (Table B). The frequent absence of Orthocladiinae from sampling sites precludes any interpretation of their abundance with respect to distance from Sudbury, although only 4 individuals were collected within the Sudbury area. Quite marked, however, was the complete absence of fingernail clams (Pisidiidae) from any of the sites in the Sudbury area. Clams were collected at all but one of the sites in both the reference and intermediate lakes. Differences in clam abundance between Sudbury and reference area sites were statistically significant in both 1996 and 1998 ( $P < 0.01$ , Mann-Whitney U test). The only other statistically significant

difference, based on pooled data from both years ( $P < 0.05$ , Mann-Whitney U test), was the absence of midges belonging to the Tanytarsini from all but one of the Sudbury lakes (Table B). The Tanytarsini differences were not quite significant based on 1996 ( $P = 0.0519$ ) or 1998 ( $P = 0.0524$ ) data individually.

Amphipods were also mostly absent from the Sudbury lakes. Only one individual was collected from Richard Lake, but the absence of amphipods from six of the reference and intermediate lakes makes statistical differences of abundance between the three regions not significant (Table B). Most amphipods were *Diporeia hoyi*, a deepwater species, but nine individuals were identified as *Hyaella azteca*, including those from NOS10, NOSD, one individual from TAL10 and the only individual from RICD. *Hyaella* is generally a shallow water species, and it is possible that the individual collected at RICD originated from the shallow nearshore region. *Hyaella* have been reported in the littoral zone of all the Sudbury area lakes sampled in this study (Watson 1992).

## **6. METAL TOXICITY AND BIOACCUMULATION IN *Hyaella***

### **6.1 Chronic toxicity**

Chronic toxicity tests results for tests conducted with four species of benthic invertebrates and sediments collected in 1996 are presented in Borgmann et al. (1998a). A few selected chronic tests were conducted with sediments collected in 1998 to confirm results observed with the 1996 sediments.

Chronic toxicity of sediments collected in 1996 to *Chironomus riparius* did not show any clear relationship with distance from Sudbury, but sediments from two deep stations (NEPD, KAKD) supported less than 50% survival in both replicate samples. Repeat tests with sediments from only the deep stations, collected in 1998, again resulted in low survival in a few tests, but only in one of two replicates from two sites (TROD, grab #2, 53% and LOSD, grab #3, 47%, Appendix 2, Table C1). The other replicate had good survival (80-87%). Furthermore, survival in NEPD

and KAKD sediments collected in 1998 was high (80%). This suggests that the occasional low survival of *Chironomus* is a spurious result not related in a systematic way to distance from Sudbury.

Some chronic toxicity tests with *Hyaella azteca* were also conducted with sediments collected in 1998. At the same time, some of the original test sediments were re-tested to determine the effects of prolonged sediment storage on toxicity. Single-replicate toxicity tests with sediments from MCF10, MCFD and RICD conducted within 11 weeks of sediment collection in 1998 confirmed extreme toxicity in these sediments (0, 7 and 0% survival respectively). Toxicity at sites RAMD, RAF10 and RAFD was tested in three different mini-ponar samples from each site collected in 1998. These also confirmed the high toxicity of Sudbury area sediments, and they also provided information on replicate variability (Appendix 2, Table C2). Unexpected variation sometimes occurred for survival and Ni in overlying water between tests with replicate sediment samples. For example, survival was poor ( $\leq 13\%$ ) in five out of six samples collected at RAMD, but 73% in the sixth sample. In most cases, however, variation in mortality paralleled, and could be explained by, variations in Ni in overlying water. The only exception was the unexplained difference in survival between two replicate tests with mini-ponar sample #2 collected in 1998 at RAFD. Nickel concentration trends in overlying water generally followed Ni in the sediment, suggesting that most of the variation in toxicity was due to variation in Ni in the mini-ponar grab samples. For example, Ni concentrations in overlying water were 19, 40-44, 68, and 160-205  $\mu\text{g/L}$  (Table C2) for sediment concentrations of 454, 706, 773 and 2130  $\mu\text{g/g}$  (Table A5b) for sites RAMD-grab 1, RAFD-grab 1, RAFD-grab 2 and RAMD-grab 2 respectively. All other overlying water concentrations for grabs 1 and 2 from 1998 were below 4  $\mu\text{g/L}$  and corresponding sediment concentrations were below 220  $\mu\text{g/L}$ . The relationship between sediment toxicity and Ni in overlying water was also observed by Borgmann et al. (1998a).

Although metal concentrations in overlying water are not as direct an indicator of metal bioavailability as are body concentrations, they can provide supplemental information and are particularly useful when investigating the potential contribution of Cu to toxicity because of the difficulty in interpreting body concentrations of this metal. In order to relate metal toxicity to

concentration in the overlying water, it is first necessary to demonstrate that toxicity is due to dissolved metal, and not metal attached to the solid phase. This was done in chronic exposure experiments in which some animals were exposed to the solid phase sediment and others were exposed in cages above the sediment in the same containers. The caged animals were exposed to the same overlying water, but did not have access to the sediments themselves. Survival in the cages, although slightly lower on average, correlated well with survival of amphipods exposed directly to the sediment (Fig. 6.1). In particular, there were no cases in which high mortality in the sediment was not also associated with high mortality in the cage. This demonstrates that toxicity was indeed due to a dissolved substance, and that metal concentrations in the overlying water may, therefore, be useful in interpreting toxicity data.

An effect of sediment storage time was also apparent. In general, mortality and Ni in overlying water increased from tests conducted with 1998 sediments (11-26 week storage), to initial tests conducted with 1996 sediments (41-54 week storage), to repeat tests with 1996 sediments (129 week storage, Table C2). Sediments were stored at 4°C in sealed polyethylene bags, but discoloration of sediment next to the bag wall suggests that the bags were not impervious to oxygen, and some oxidation of the sediment may have occurred over time. Oxidation of sulfides in the sediments may have resulted in Ni dissolution and increased Ni bioavailability with storage time.

## **6.2 Metal bioaccumulation by *Hyaella***

Metal bioaccumulation by *Hyaella* was measured in 1-week exposures with adult amphipods because chronic exposures often resulted in complete mortality leaving no survivors for metal analysis in amphipod tissues. Metal concentrations in overlying water were also measured in these tests (Appendix 2, Table D), because of the correlation between Ni in water and toxicity, as indicated above. The increased concentrations of metals in sediments from the Sudbury area lakes resulted in increased bioaccumulation for Cd, Co and Ni in *Hyaella* exposed to these sediments in the lab (Appendix 2, Table E). Bioaccumulation increased rapidly with increasing sediment concentrations, resulting in slopes  $\geq 1$  in log-log plots (Fig. 6.2). On average,

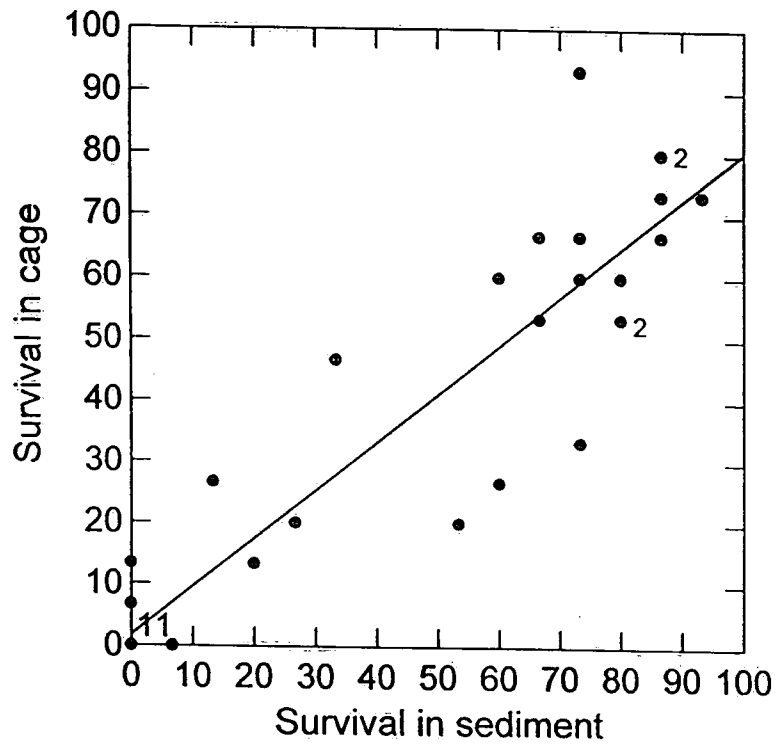


Figure 6.1. Survival of *Hyalella* after four weeks of exposure to overlying water in cages, compared to survival of amphipods exposed directly to the sediment. Numbers beside a data point indicate multiple values. Note there are 11 data points superimposed on the origin.

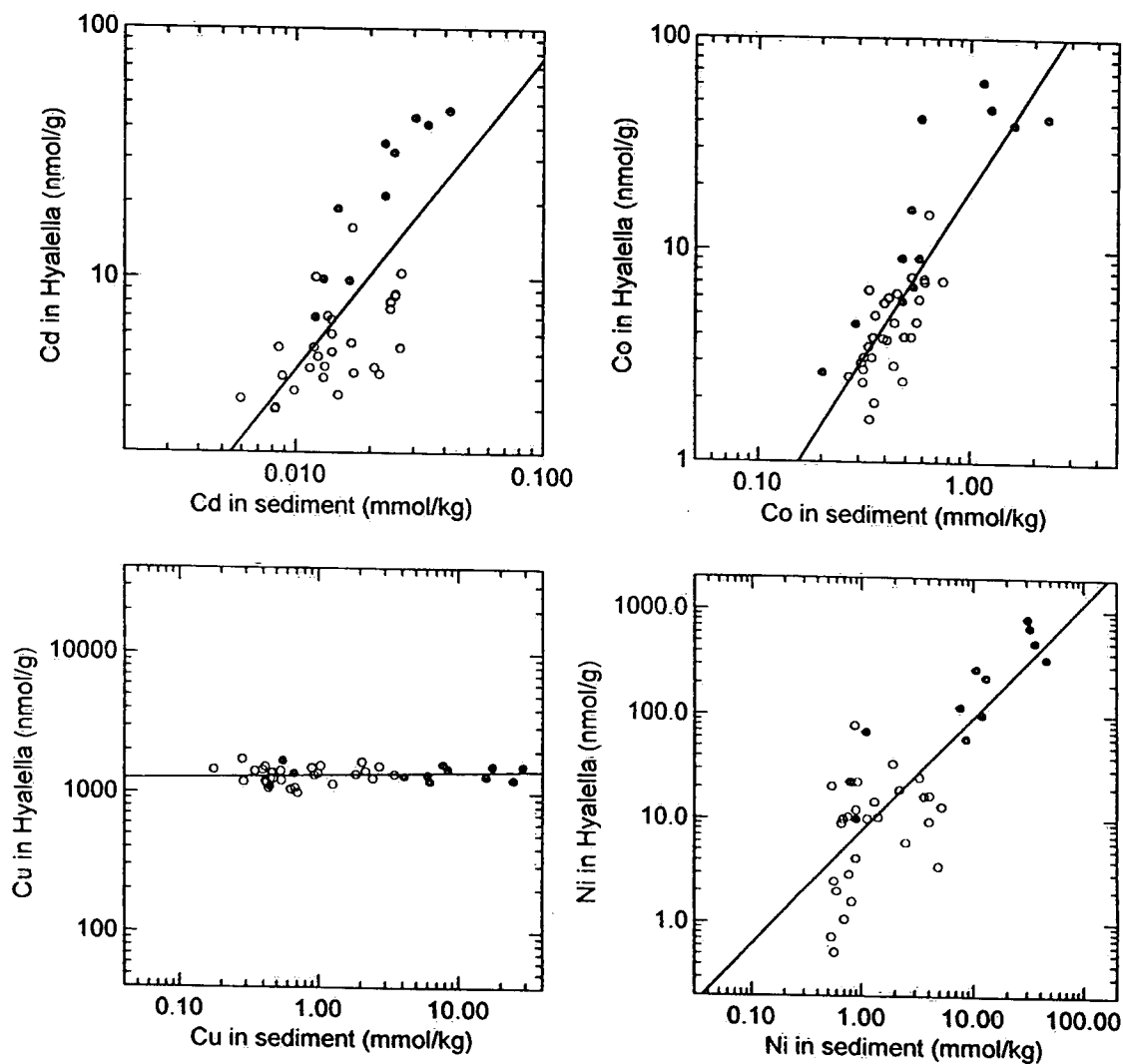


Figure 6.2. Body concentrations of Cd, Co, Cu and Ni in *Hyalella azteca* after one-week exposures to sediments as a function of sediment concentration. Solid symbols represent data for Sudbury area lakes and open symbols are from reference and intermediate lakes.

amphipods exposed to Sudbury area sediments had body concentrations of Ni, Co and Cd that were, respectively, 17, 4.5 and 3.7 fold greater than in amphipods exposed to sediments from reference lakes (Table 6.1). In contrast, As, Cr, Mn, Pb, Se and Tl concentrations in *Hyaletella* did not differ significantly among amphipods exposed to sediments from the Sudbury, reference and intermediate locations, although Mn concentrations were extremely high in some amphipods (e.g. MCFD, Table E). Copper and Zn in *Hyaletella* also did not differ significantly, in spite of the much higher Cu concentrations in Sudbury area sediments. However, Cu and Zn are regulated by *Hyaletella* and body concentrations remain relatively constant until sediment concentrations are high enough to cause toxicity (Borgmann and Norwood 1997a). Copper concentrations in sediment exposed *Hyaletella* were consistently higher than in amphipods not exposed to sediments (gauze controls, Table E), but there was no relationship between Cu in *Hyaletella* and Cu in sediment. Increased bioaccumulation of metals in response to increased sediment concentrations was, therefore, observed for some, but not all, metals.

The cause of sediment toxicity can be determined by comparing metal bioaccumulation to critical body concentrations previously shown to cause toxicity. The maximum amount of metal accumulated by *Hyaletella* in the one-week exposures exceeded the critical body concentrations resulting in 25% mortality in four week exposures (LBC25) for Ni, but not for Cd, Cu, Pb, Tl or Zn (Table 6.1). LBC25s are not yet available for As, Co, Cr, Mn or Se, but the maximum body concentrations of these metals, except Mn, were always below  $60 \text{ nmol} \cdot \text{g}^{-1}$ . This is well below any LBC25 determined so far (Table 6.1). The only metal which can, therefore, clearly be identified as contributing to toxicity in chronic tests with *Hyaletella* exposed to Sudbury area sediments is Ni.

One weakness in the above analysis is the difficulty in interpreting body concentrations of Cu. This metal (and Zn) is regulated by *Hyaletella*, and increases in sediment concentrations do not necessarily result in significant increases in body concentrations until toxicity is relatively severe (e.g. mortality is observed in adults in one week exposures, Borgmann and Norwood 1997a, 1997b). Sudbury area sediments were extremely toxic to young *Hyaletella* exposed for four weeks, but mortality was negligible in the one-week metal bioaccumulation experiments



Table 6.1. Mean metal concentrations in adult *Hyalella* (nmol•g<sup>-1</sup>) exposed for one week to sediments collected by mini-ponar grab samples 1 and 2 from each sampling site in 1998<sup>a</sup>, or exposed to cotton gauze without sediment, and lethal body concentrations in chronic (four-week) toxicity tests.

Site	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Se	Tl	Zn
RAMD	7	28	24	25	1390	670	306	2.1	18	0.6	850
MCF10	20	14	7	24	1350	300	63	0.4	26	0.5	1330
MCFD	14	24	42	26	1300	29600	309	0.5	29	0.3	1090
RAF10	17	6	4	24	1400	150	16	0.3	29	0.4	920
RAFD	13	28	11	26	1560	270	164	1.2	30	0.7	910
RICD	5	43	54	28	1440	410	757	1.8	28	1.2	890
NEPD	11	4	4	24	1500	480	18	0.6	31	0.5	890
KAK10	13	6	4	23	1260	620	15	0.6	23	0.5	960
KAKD	13	6	6	25	1360	1250	18	0.4	28	0.5	900
TRO10	13	8	4	27	1470	410	6	0.8	27	1.3	940
TROD	6	7	7	25	1540	460	9	0.9	28	0.5	950
LOS10	9	4	7	26	1270	2880	12	1.0	18	1.3	930
LOSD	10	5	10	27	1400	1300	11	2.2	20	0.5	930
TOM10	11	13	3	31	1330	730	11	1.3	22	3.0	1050
TOMD	12	5	5	24	1290	360	5	1.2	33	0.7	890
RES10	3	6	6	22	1330	3420	6	0.3	31	1.8	930
RESD	10	5	3	25	1240	500	6	0.6	31	0.5	1260
NOS10	11	4	3	23	1300	470	17	0.3	28	0.5	890
NOSD	12	4	3	24	1340	500	7	0.4	28	0.3	940
TAL10	14	6	3	25	1230	550	5	0.7	21	0.8	1080
TALD	16	4	3	22	1220	1450	41	0.6	23	0.4	890
HH1	12	10	3	26	1940	490	14	1.7	45	2.0	1140
LE303	7	8	5	23	1400	270	25	0.3	26	0.9	940
gauze	11	6	6	23	900	110	10	0.6	26	0.1	890
<u>Enrichment ratio (geometric mean, Sudbury sites/reference sites):</u>											
	1.15	3.7***	4.5***	1.05	1.09	0.93	17***	1.4	0.99	0.77	1.00
<u>Maximum body concentration (gauze corrected):</u>											
	20	43	54	31	1940	29600	757	2	45	3	1330
					(1040)						(440)
<u>Lethal body concentration, LBC25 (gauze corrected):</u>											
	-	270 <sup>b</sup>	> 100 <sup>f</sup>	-	2380 <sup>c</sup>	-	194 <sup>d</sup>	126 <sup>e</sup>	-	290 <sup>b</sup>	4420 <sup>c</sup>
					(1050)						(3080)

a. Mean of two experiments with separate sediment grab samples used in each experiment.

b. Borgmann et al. 1998b.

c. Borgmann and Norwood 1997a, spiked sediment exposure.

d. Borgmann et al. 2001.

e. Borgmann and Norwood 1999b.

f. Norwood and Borgmann, unpublished data.

\*\*\* Significant at P < 0.001.

conducted in 1998. Although Cu bioaccumulation provides no evidence that Cu contributed to toxicity (Table 6.1), it is not possible to state categorically that Cu did not contribute somewhat to total metal toxicity in the chronic studies.

### 6.3 Relationship between toxicity and overlying water concentrations

Comparison of survival in animals exposed directly to sediments, and animals caged above the sediments, has already demonstrated that toxicity is due to a dissolved substance. Further evidence that overlying water is a useful indicator of bioavailable metals is obtained by comparing Ni bioaccumulation in caged animals with bioaccumulation in sediment exposed animals. The same relationship between Ni in *Hyaella* and Ni in water was observed for both groups of animals (Fig. 6.3). Furthermore, the data fit on the same line obtained previously for *Hyaella* exposed to three different sediments spiked with Ni, even though Ni bioavailability on a sediment concentration basis differed between the different sediments (Borgmann et al. 2001).

The relative importance of Cu and Ni in contributing to toxicity can now be compared by examining overlying water concentrations. Unlike body concentrations, concentrations of Cu in water are obviously not regulated by *Hyaella*. The four-week LC25 for Cu in water is about 330 nmol•L<sup>-1</sup> (Borgmann et al. 1998b), and the LC25 for Ni in water is about 440 nmol•L<sup>-1</sup> (Borgmann et al. 2001). Copper in overlying water in the chronic toxicity tests ranged from non-detectable to 535 nmol•L<sup>-1</sup>, and Ni ranged from non-detectable to 16500 nmol•L<sup>-1</sup>. Copper exceeded the LC25 in only four of 112 test containers, but Ni measured in these same containers exceeded the LC25 by two-fold or more (Table 6.2). There were no survivors in these four containers. Consequently Cu may have contributed somewhat to overall toxicity in these four containers, but Ni would be expected to be the most toxic component. Overall, complete mortality was observed in 33 containers, and Ni exceeded the LC25 in 29 of these. This leaves only 4 containers with unexplained mortality. Clearly, Ni was responsible for most of the toxicity observed. All containers with >33% survival had Ni concentrations <440 nmol•L<sup>-1</sup>, with the exception of one container which had 80% survival and a Ni concentration of 680 nmol•L<sup>-1</sup>. This was the only case of unexplained survival, possibly due either to an error in

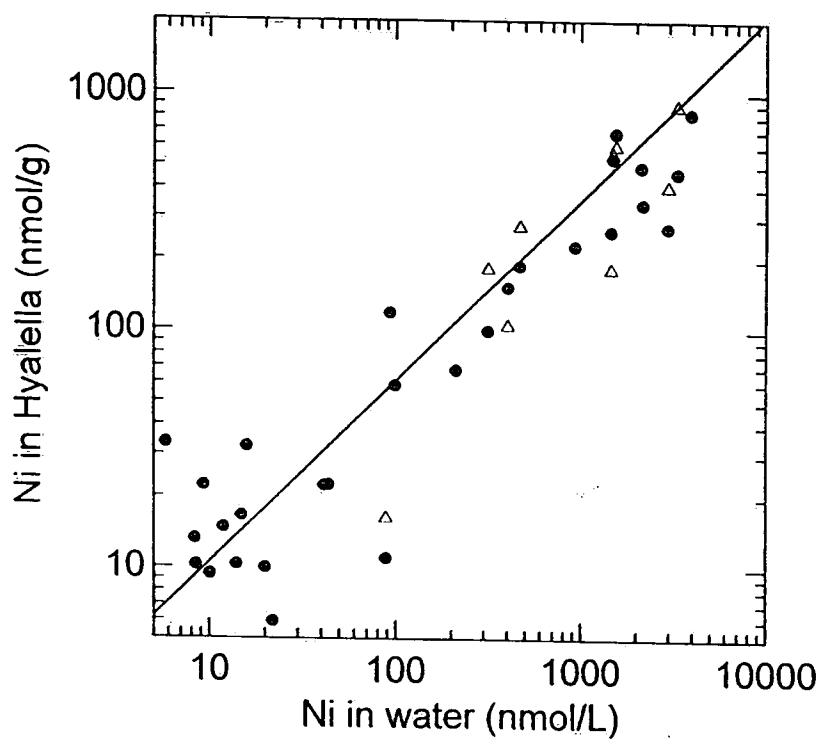


Figure 6.3. Nickel accumulation in sediment-exposed *Hyalella* (●), or amphipods exposed in cages above the sediment (Δ), as a function of Ni in overlying water during one-week bioaccumulation experiments with Sudbury, reference and intermediate area sediments. The line through the points was calculated from experimental data obtained with three different Great-Lakes sediments spiked with Ni (Borgmann et al. 2001).

measured Ni or the presence of an unknown parameter which reduced Ni bioavailability. This suggests that toxicity in the chronic tests with *Hyaella* was primarily due to Ni, with the exception of occasional unexplained mortality which could not be attributed to either Ni or Cu.

Table 6.2. Summary of survival results in all chronic (four-week) toxicity tests conducted with *Hyaella* and the number of times Cu and Ni exceeded the LC25.

Survival (percent)	Frequency of occurrence		
	Total	Cu>330 nmol•L <sup>-1</sup>	Ni>440 nmol•L <sup>-1</sup>
0	33	4 <sup>a</sup>	29
7-27	14	0	4 <sup>b</sup>
>33	65	0	1 <sup>c</sup>
0-100	112	4	34

a. Cu = 331-535 nmol•L<sup>-1</sup>, Ni = 820-16500 nmol•L<sup>-1</sup>  
b. Ni = 800-2300 nmol•L<sup>-1</sup>  
c. Ni = 680 nmol•L<sup>-1</sup>

#### 6.4 Spatial extent of biological impacts

It is difficult to accurately quantify the exact geographical extent of changes in benthic community composition because the data are quite variable, but it is possible to estimate the spatial extent of sediment toxicity as measured in laboratory toxicity tests. Since the cause of sediment toxicity has been identified as Ni, the most direct way of estimating the geographical extent of metal induced toxicity would be to compare Ni bioaccumulation in *Hyaella* with distance from the smelters. This would have been possible if metal bioaccumulation had been measured using surface sediments. Unfortunately, however, bioaccumulation was measured following exposure to sediments collected by mini-ponar grab, and Ni in mini-ponar grab samples from the same site was quite variable (Table 4.2). However, it is possible to compare Ni bioaccumulation with Ni in the sediment (Fig. 6.2), and to estimate sediment concentrations which will cause toxic effects in the Sudbury area. For example, the Ni body concentration causing 25% mortality in four-weeks (LBC50) was 194 nmol•g<sup>-1</sup>, and the effective concentration resulting in a 25% reduction in biomass (i.e. combined effects of growth and mortality, EBC25)

was  $115 \text{ nmol} \cdot \text{g}^{-1}$  for experiments with Ni-spiked sediments conducted in Imhoff settling cones (Borgmann et al. 2001). Using the regression equation off Fig. 6.2, this equates to sediment concentrations of 19.5 (LC25) and 12.1 (EC25)  $\mu\text{mol} \cdot \text{g}^{-1}$ . Using the relationship between Ni in surface sediments ( $\mu\text{mol/g}$ ) and distance from Copper Cliff ( $72 \cdot \exp(-0.069 \cdot d) + 0.8$ , Table 4.1), toxic sediment concentrations would be expected to extend, on average, from the smelter to 20 (LC25) or 27 (EC25) km in a south-easterly direction. This provides an estimate of the approximate geographical extent of sediment toxicity, assuming that bioavailability in surface sediments is similar to that observed in mini-ponar grab samples. This is lower than the previous estimate of 36 km to 25% mortality, calculated from Ni concentrations in overlying water before bioaccumulation data were available (Borgmann et al. 1998a).

## 7. DISCUSSION

The observations made during this study can be summarized by comparison to the four key questions posed in the Aquatic Effects Technology Evaluation (AETE) program (ESG 1999). 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?

An attempt to address these questions was made in an Interim Report based on data collected following the 1996 field trip to Sudbury (Borgmann et al. 1998a). The second field trip in 1998, and laboratory studies on sediments collected during that trip, provided additional data on metals in water, metals in sediments collected by mini-ponar grab samplers, additional data on benthic invertebrate abundances, verification of sediment toxicity at selected sites, and data on metal bioaccumulation by *Hyalella*. The above four questions can now be answered more clearly.

### **7.1. Are contaminants getting in the system?**

The sediment and water chemistry data clearly show that metals have been deposited in lakes near Sudbury. Both water and sediment metal concentrations decrease rapidly with distance from Sudbury (Table 4.1 and Borgmann et al. 1998a). Furthermore, sediment core profiles indicate that only the top sediment layers are heavily contaminated with metals (Borgmann et al. 1998a), implying that contamination occurred following industrialization (i.e. within the last century) and is not natural. However, because of the extremely low sedimentation rates in many of the lakes, surface (0-3 cm) sections may represent sediment accumulated over one or more decades, and are not necessarily indicative of metal deposition within the last few years. It is also important to remember that some of the metals currently entering lakes may come from gradual leaching or erosion of soils that have been contaminated due to past metal emissions. A time lag would be expected between reductions in industrial emissions and decreases in metal concentrations in surface sediments.

### **7.2. Are contaminants bioavailable?**

Bioaccumulation clearly showed that Cd, Co and Ni bioavailability was elevated in sediments from Sudbury area lakes (Fig. 6.2). Increased bioavailability was also suggested by increased metals in overlying water in the toxicity tests, coupled with the demonstration that exposure to overlying water alone resulted in mortality to *Hyaella* that was just as great as exposure to both water and sediment (Fig. 6.1). Therefore, the increased metals in the sediment are bioavailable.

### **7.3. Is there a measurable response?**

This question is addressed through a combination of in-situ community assessment and toxicity testing. Analysis of benthic community composition can demonstrate whether populations in contaminated areas differ from those in reference locations, but this difference is not necessarily due to toxic chemicals. Toxicity testing can demonstrate whether sediments are toxic, but laboratory conditions are rarely identical to exposure conditions in the field. Taken together,

however, changes in benthic composition coupled with a demonstration of sediment toxicity indicate a measurable response due to poor sediment quality.

Benthic community data collected in 1998 supported previous findings from 1996 (Borgmann et al. 1998a). Furthermore, chronic toxicity tests with *Chironomus* and *Hyaella* at selected sites confirmed previous observations based on sediments collected in 1996. Good concordance was observed between the benthic survey and sediment toxicity, demonstrating severe effects to some organisms and non-detectable effects in other species. There were no observed differences in abundance of chironomids belonging to the Chironomini between the three study regions, and no sediment toxicity was detected using *Chironomus*. Severe sediment toxicity was, however, detected using *Hyaella*, and this coincided with an absence of amphipods in Sudbury area sediments with the exception of one *Hyaella* caught in Richard Lake (Table B). Unfortunately, the sporadic abundance of amphipods in the reference and intermediate sediments resulted in a non-significant difference in abundance between the study regions, and mayflies were absent from most sites, but the abundance of Pisidiids and tanytarsid midges matched the toxicity of sediments to *Hyaella* and *Hexagenia*. Although a difference in reproduction among sediments was detected in *Tubifex* (Borgmann et al. 1998a), reproductive inhibition was only partial, and this coincided with the lack of a clear difference in oligochaete abundance between regions (Table B). Consequently both abundance in the field and sediment toxicity demonstrated effects to some, but not all species, and field abundance matched sediment toxicity whenever the same, or closely related species, were examined in the field and laboratory studies. Taken together, in-situ invertebrate abundances and toxicity tests indicate that there are biological impacts in the deep ( $\geq 10$  m) sediments of lakes in the Sudbury area, and these are probably the result of sediment toxicity.

#### **7.4. Are the contaminants causing this response?**

The comparison of metal bioaccumulation with lethal body concentrations (LBC25s, Table 6.1), and comparison of metals in overlying water with LC25s (Table 6.2), demonstrated that Ni was the primary cause of sediment toxicity, thereby answering the final question affirmatively.

Furthermore, identification of the cause of toxicity, and correlation of Ni bioaccumulation in *Hyaella* to Ni in sediments, allowed estimation of the sediment concentration causing Ni bioaccumulation to toxic levels in amphipods. This, in turn, provided a rough estimation of the spatial extent of toxic effects in deep sediments near Sudbury.

## 8. ACKNOWLEDGMENTS

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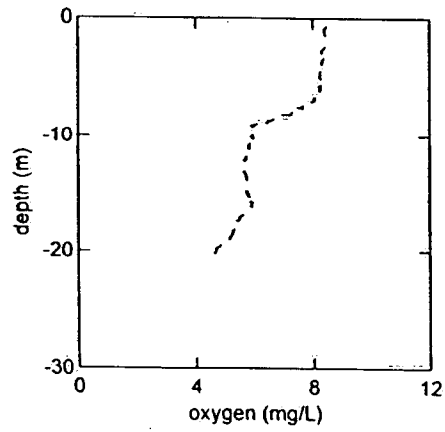
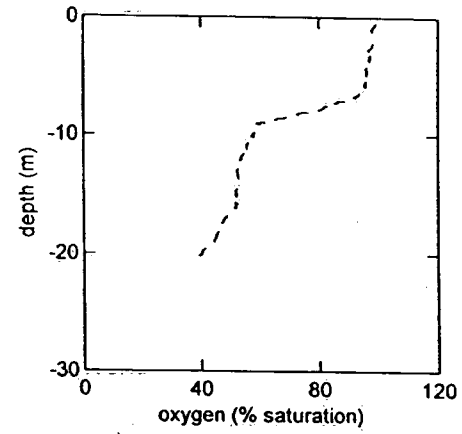
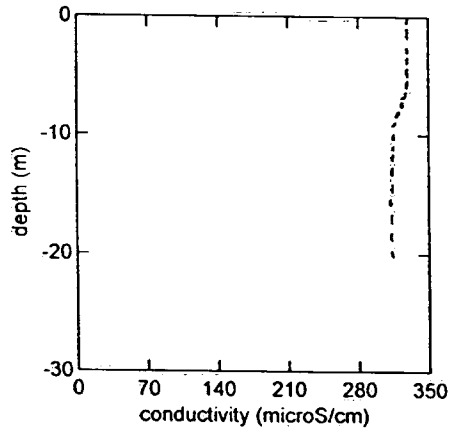
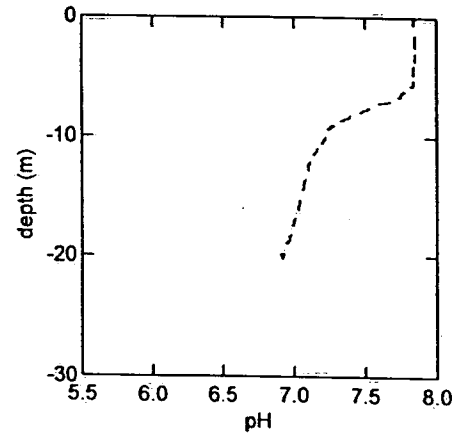
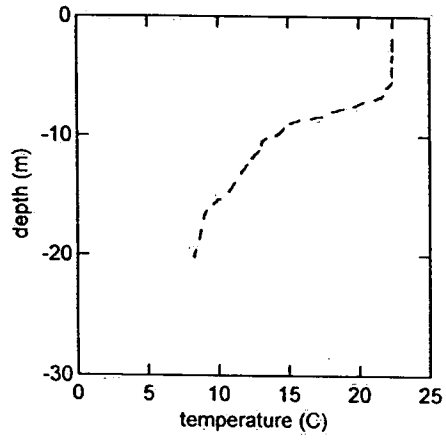
# Appendix 1

Hydrolab (temperature, pH, conductivity, oxygen) profiles for each of the stations sampled in August 1998. 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).

All profiles were measured from top to bottom except the deep profile (dashed line) for Raft Lake, which was measured from bottom to top because of data recording errors on the way down. This profile appears to show a delayed sensor response (histerises), due to a time lag in instrument response and/or sediment clogging of the sensors.

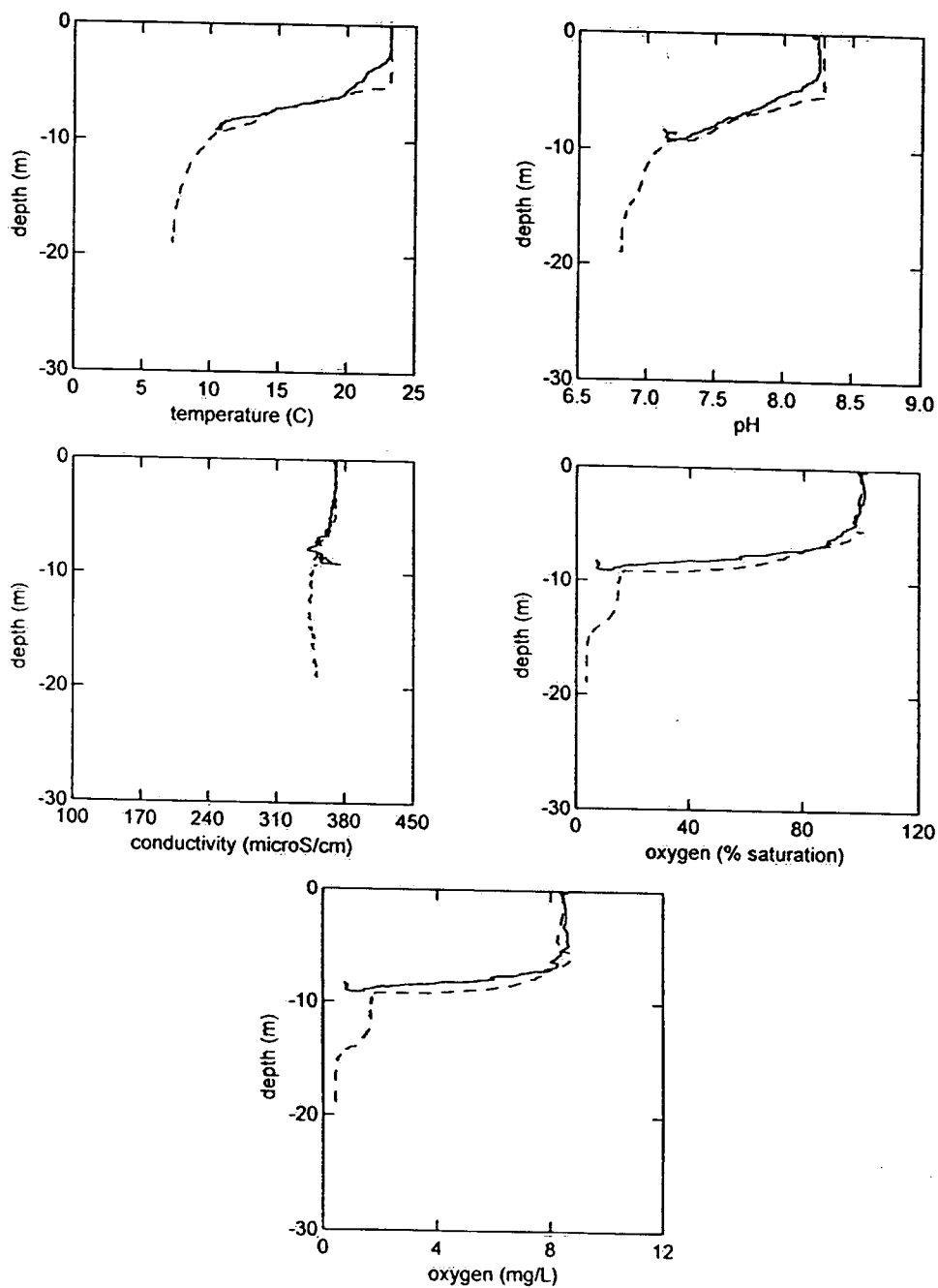
Note the scale change for pH and conductivity for McFarlane lake. All other lakes have the same scales.

## RAM - Ramsey, August 1998



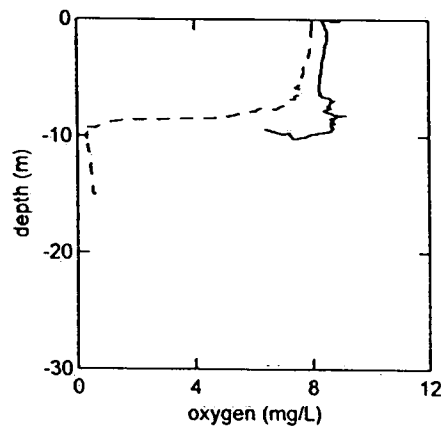
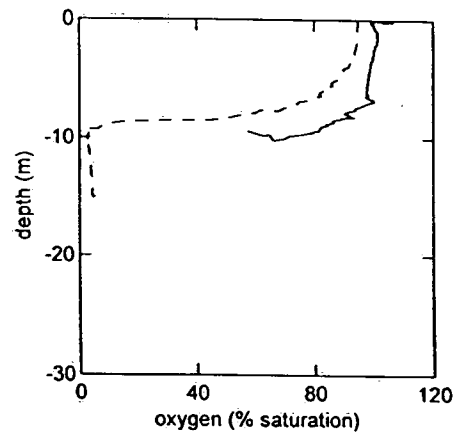
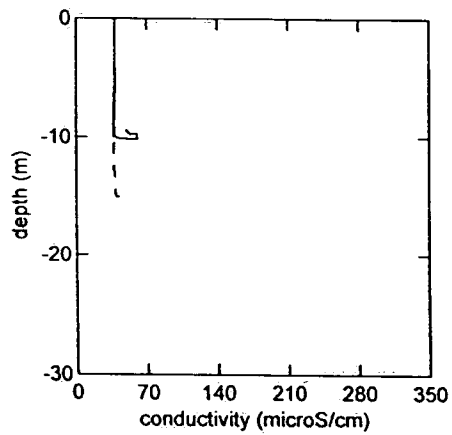
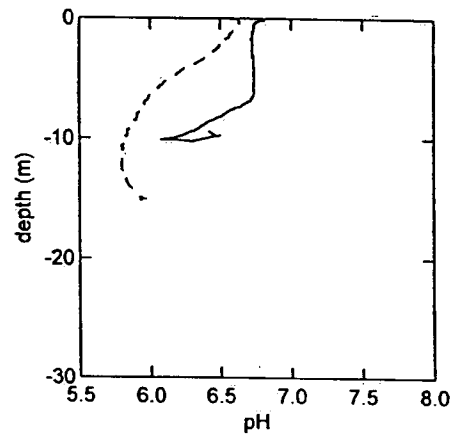
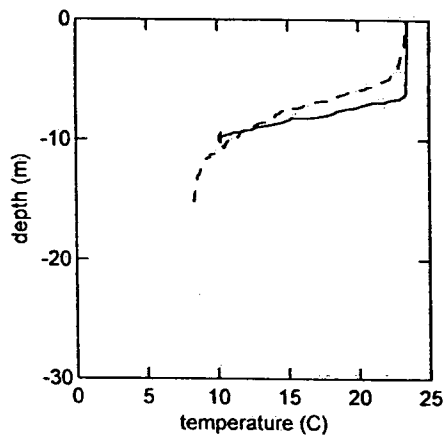
# MCF - McFarlane, August 1998

(note: scale change for pH and conductivity)

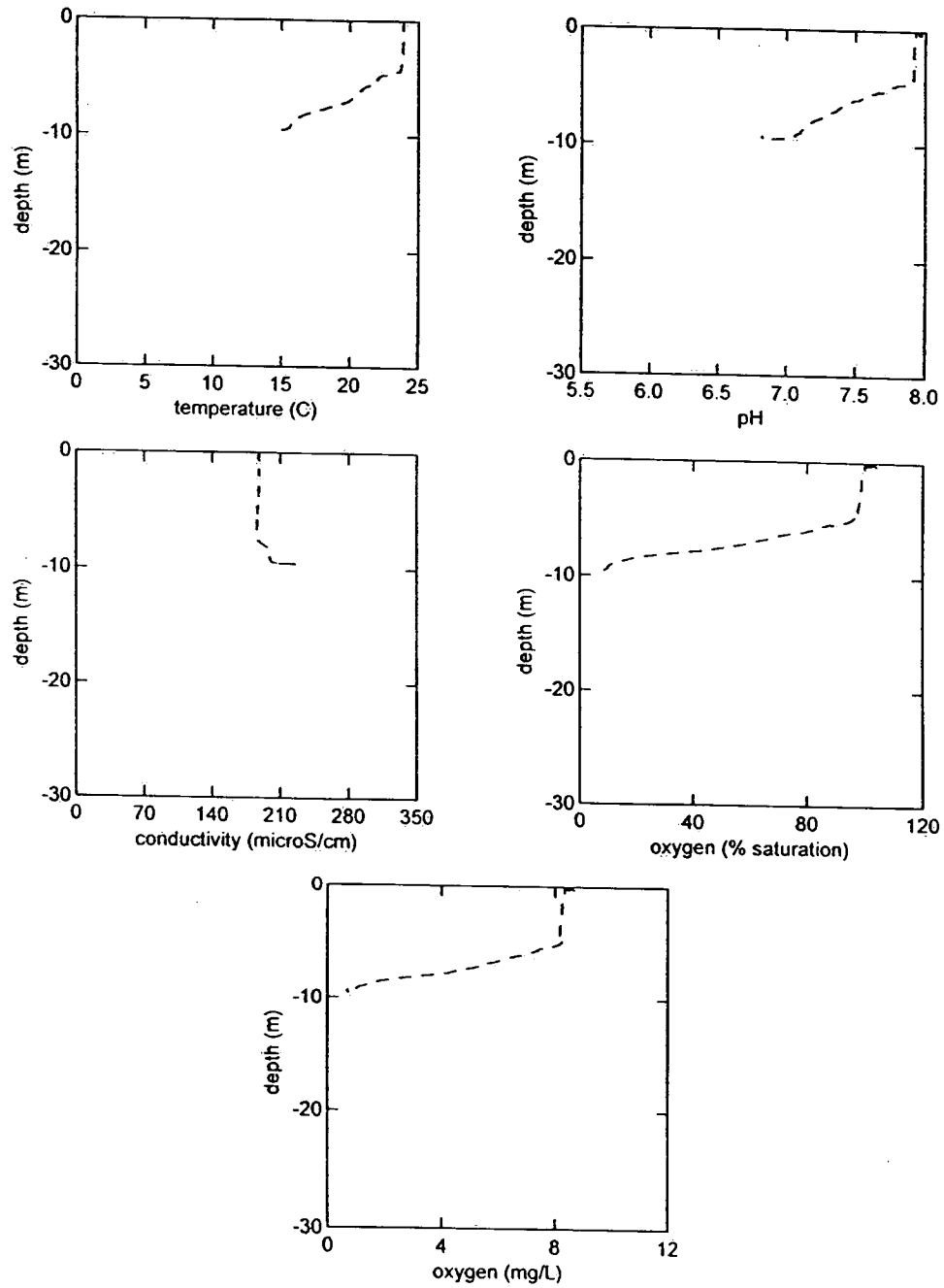


# RAF - Raft, August 1998

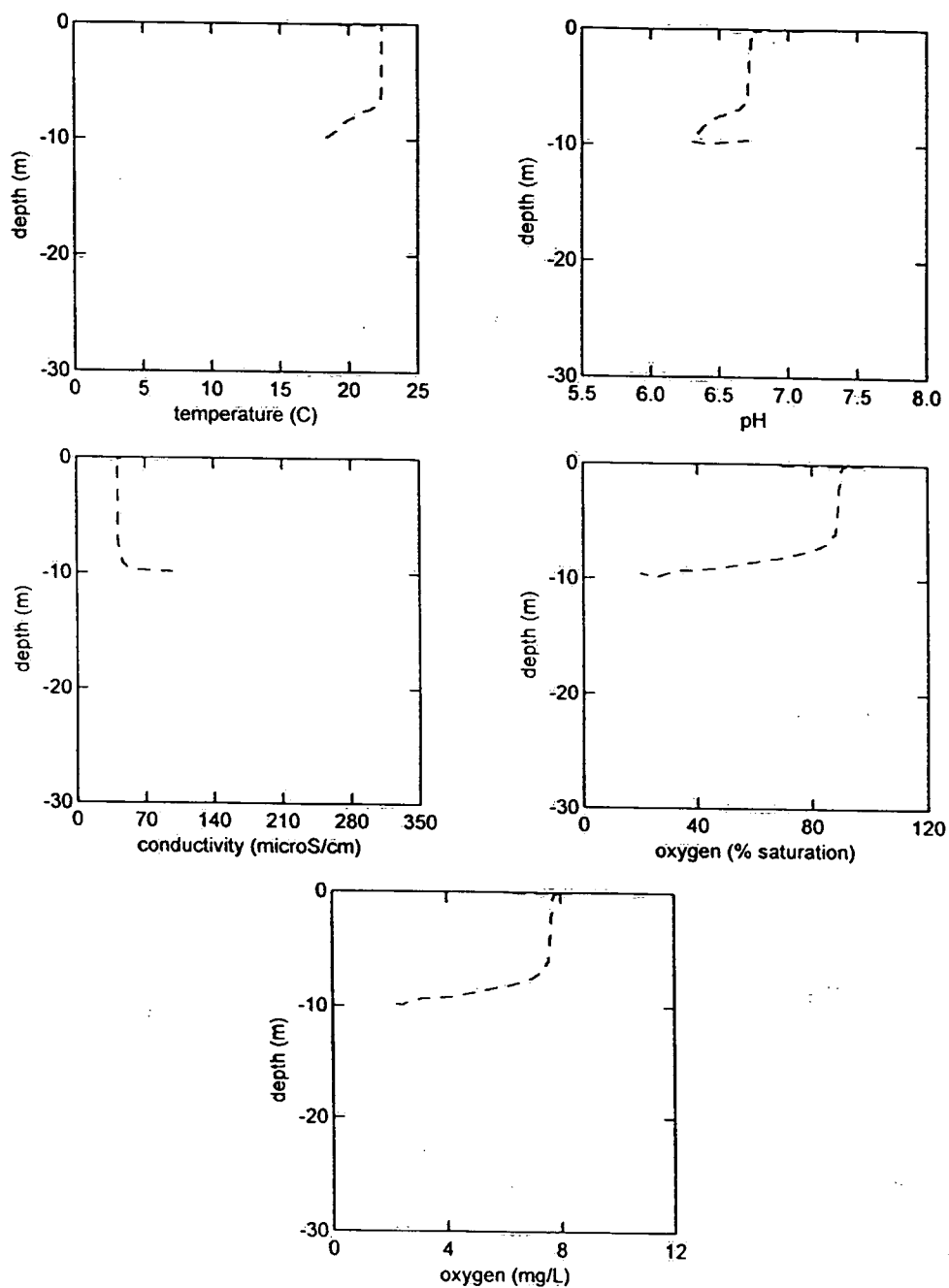
(note: deep station profile from bottom to top)



# RIC - Richard, August 1998

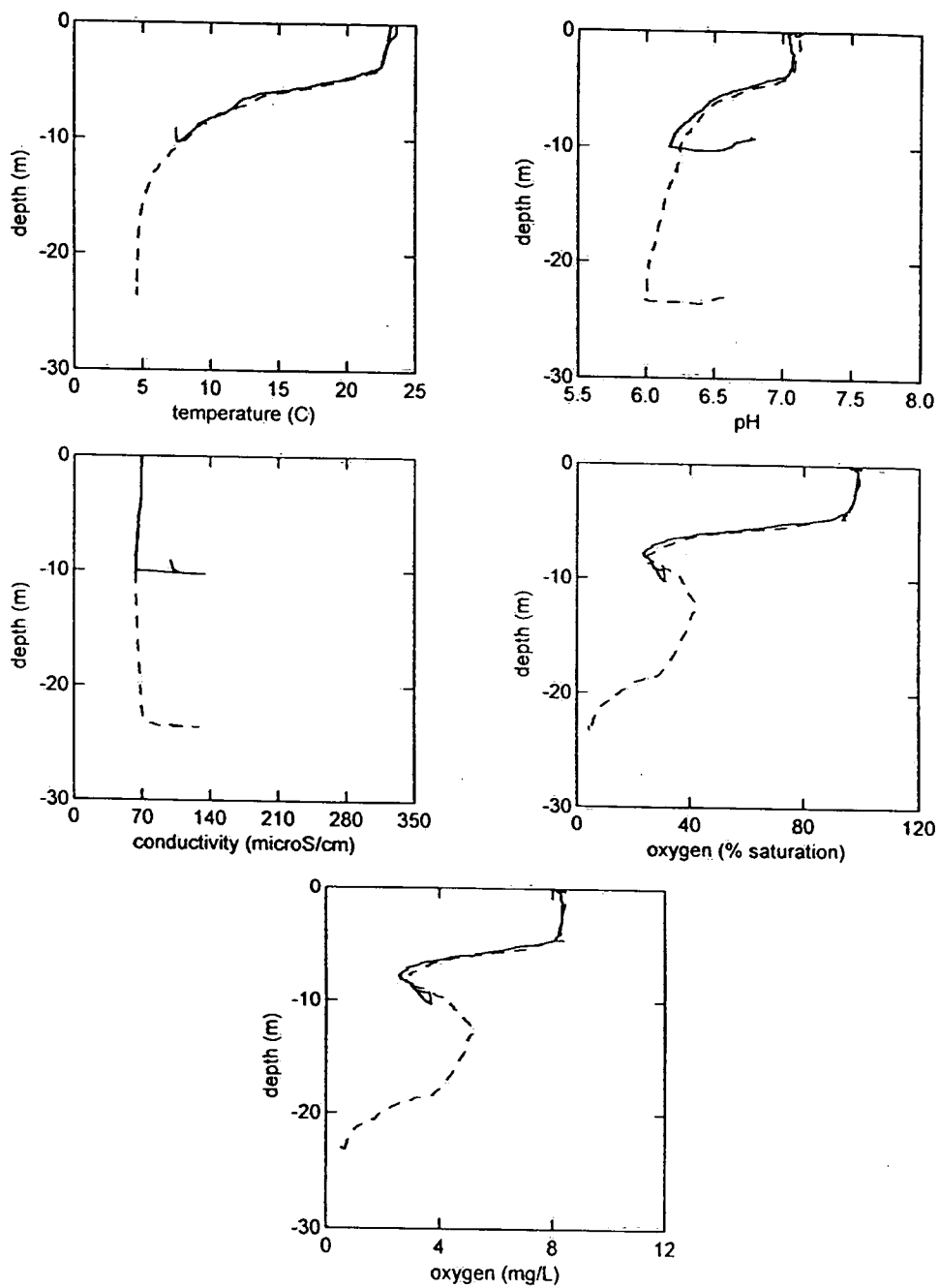


## NEP - Nepewassi, August 1998

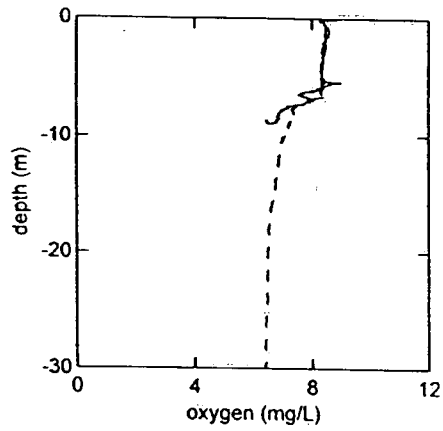
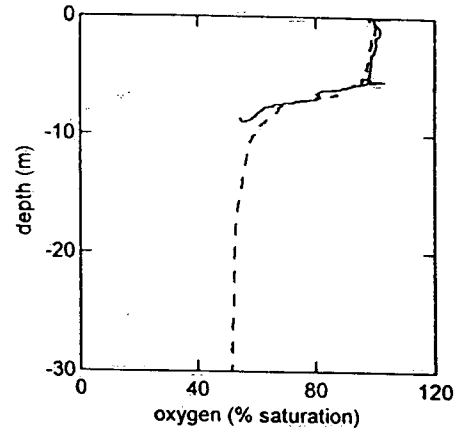
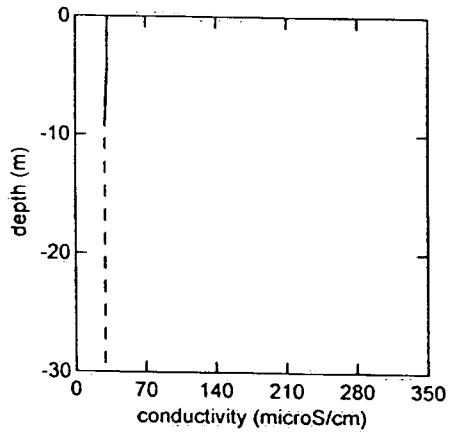
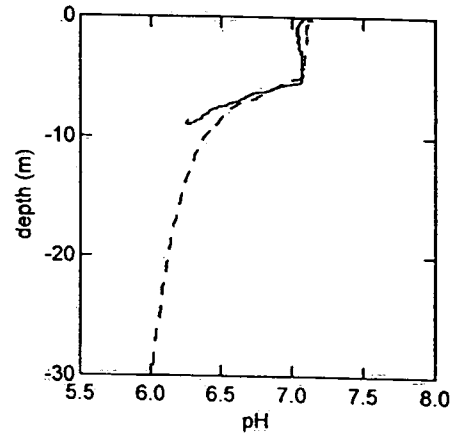
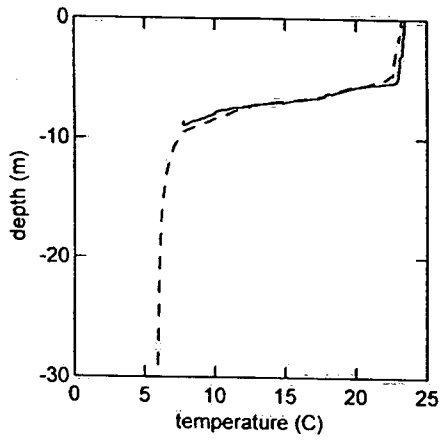




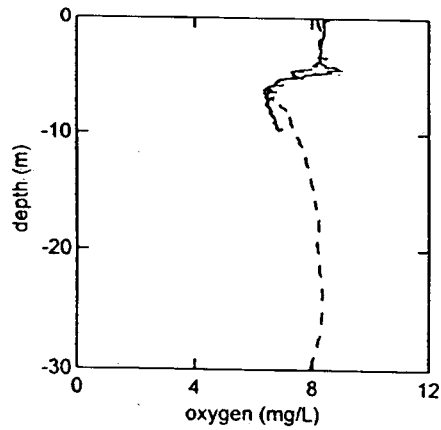
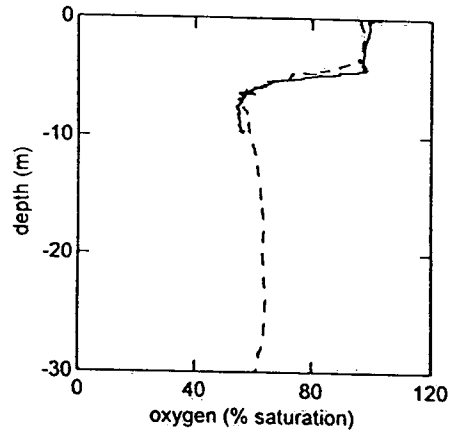
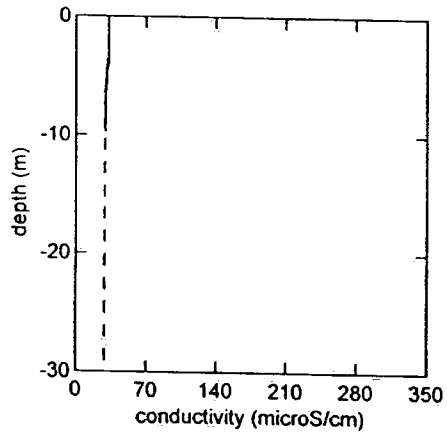
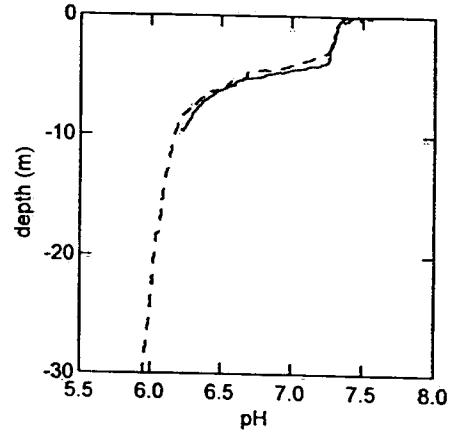
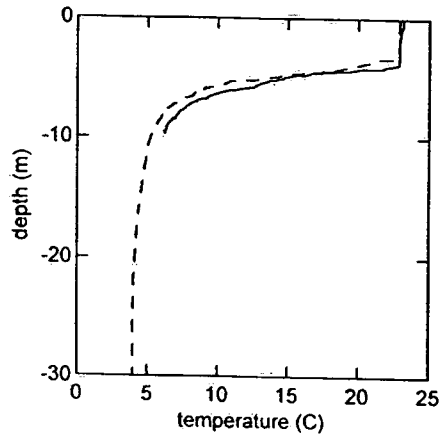
## KAK - Kakakiwaganda, August 1998



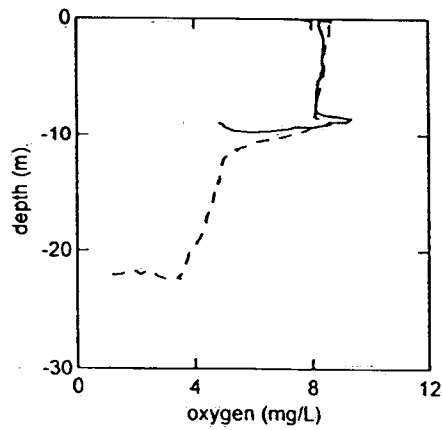
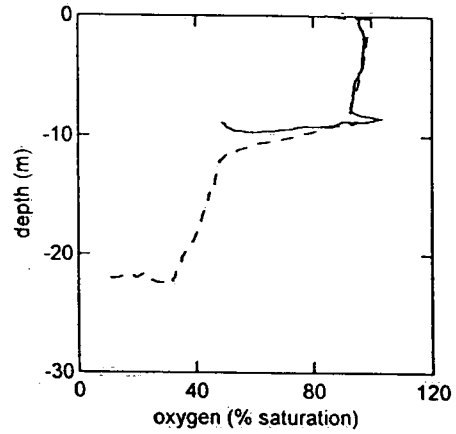
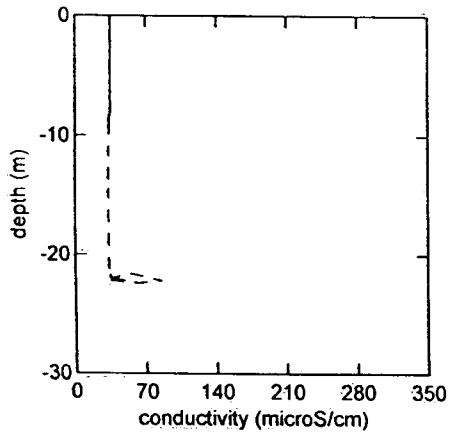
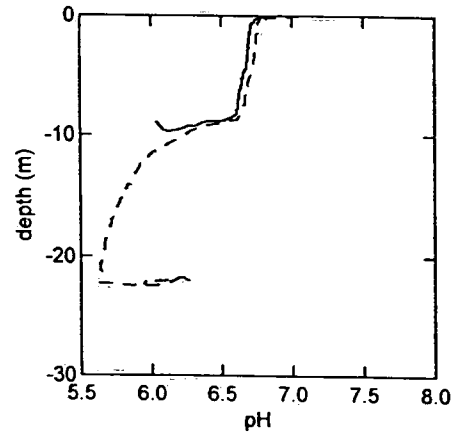
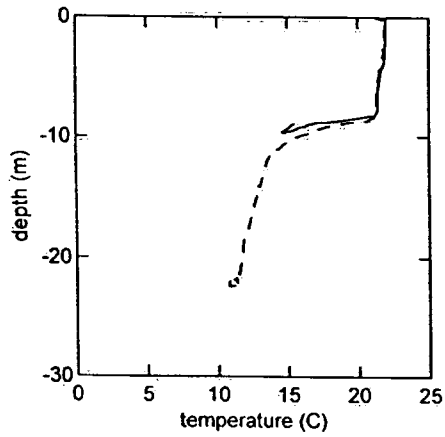
# TRO - Trout, August 1998



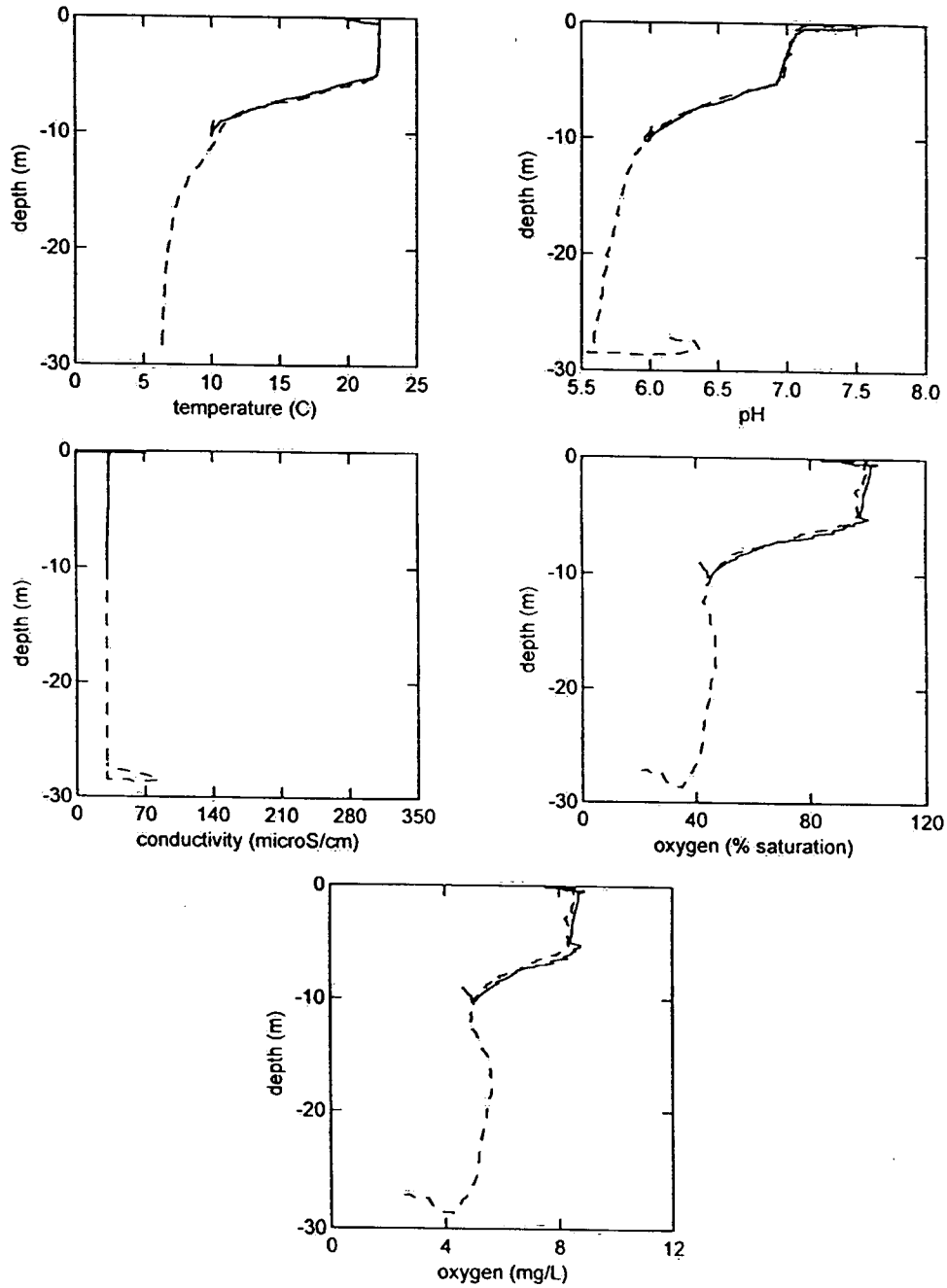
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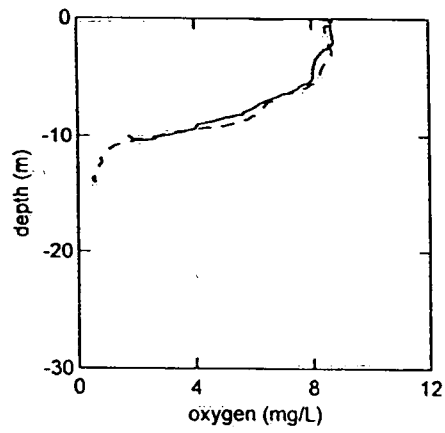
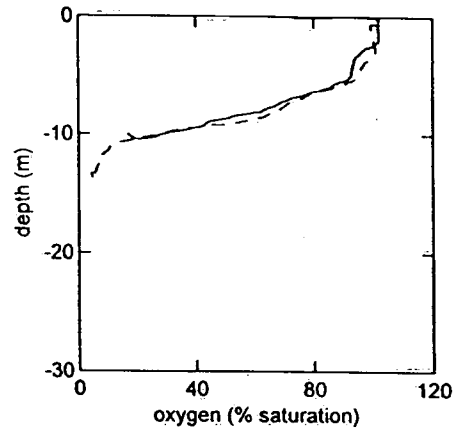
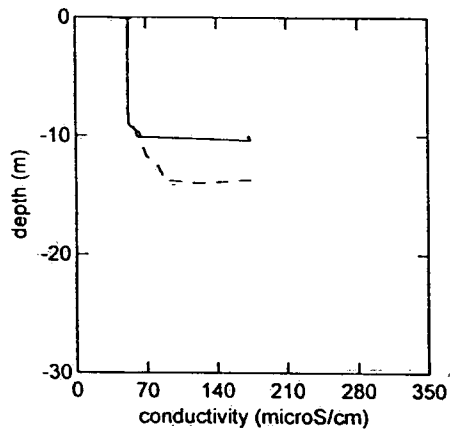
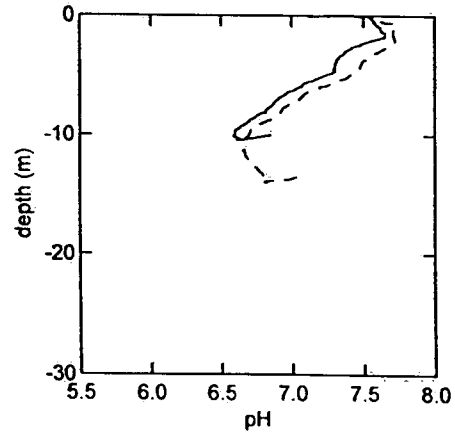
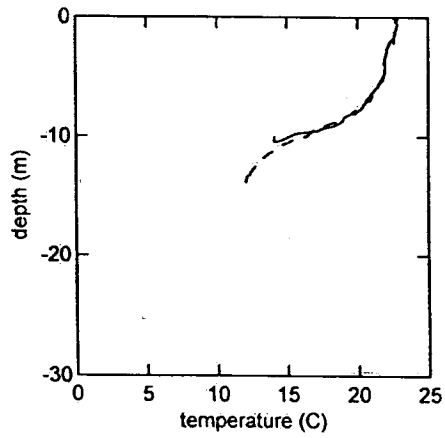
# TOM - Tomiko, August 1998



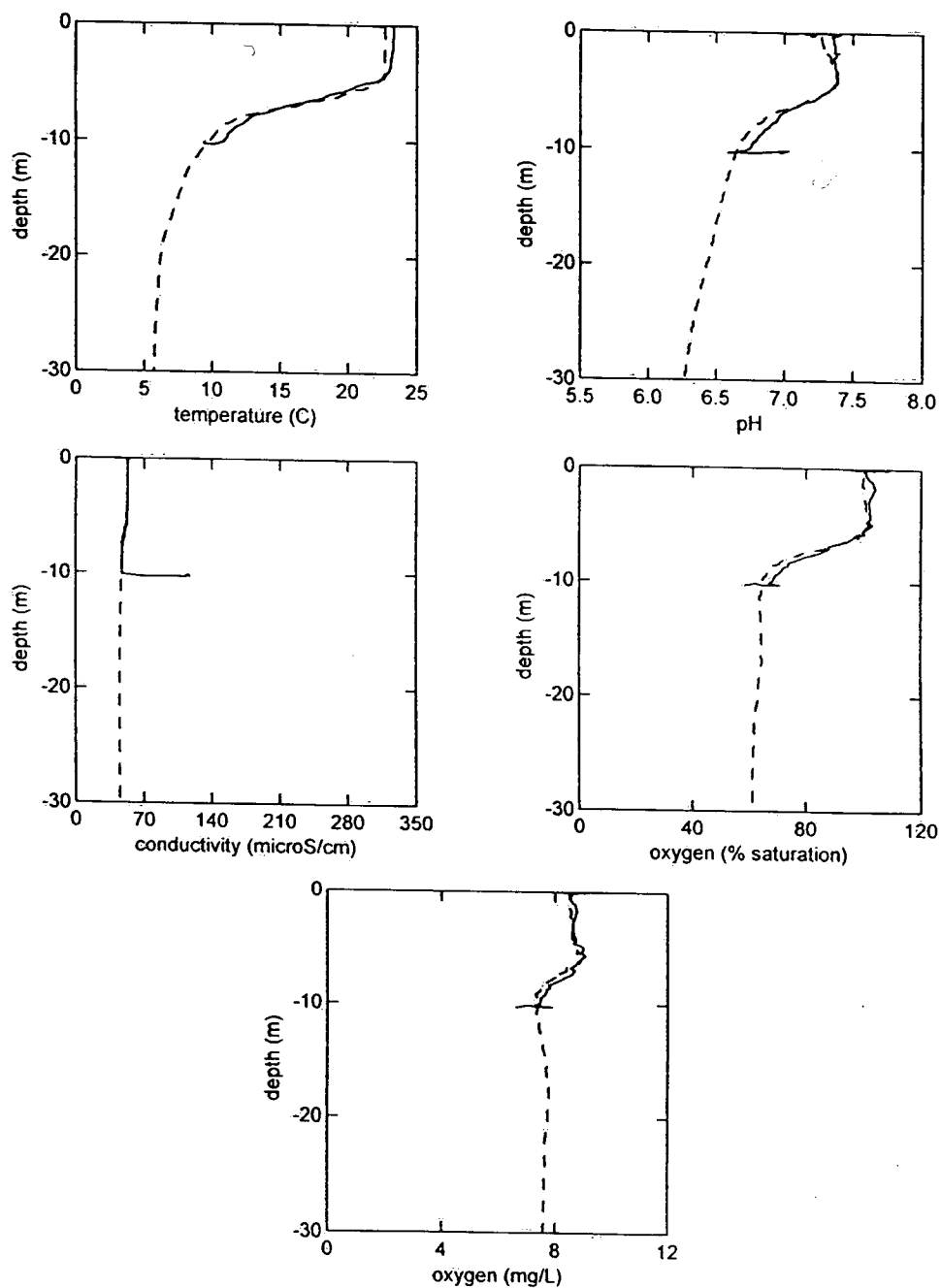
## RES - Restoule, August 1998



## NOS - Nosbonsing, August 1998



## TAL - Talon, August 1998



## Appendix 2

Summary tables of data collected in 1998 and comparison to data collected in 1996 (Borgmann et al. 1998a).

Table	Contents
A1	Temperature, conductivity, pH, dissolved oxygen, 1996 and 1998 comparisons.
A2	Major ions and DOC, 1996 and 1998 comparisons.
A3	Nutrients, 1996 and 1998 comparisons.
A4	Trace metals in water by ICP-MS in 1998.
A5	Trace metals in 3 mini-ponar grabs, one from 1996 and 2 from 1998.
B	Benthic invertebrates collected, 1996 and 1998 comparisons.
C1	Repeat toxicity tests with <i>Chironomus</i> in 1998, deep stations only.
C2	Repeat chronic toxicity tests with <i>Hyaella</i> in 1998 (including retests with some 1996 sediments).
D	Metals in overlying water in 1998 bioaccumulation tests with <i>Hyaella</i> .
E	Metal bioaccumulation in <i>Hyaella</i> exposed to 1998 sediments.



Table A1. Maximum depth (max D), temperature (Temp), conductivity (Cond), pH, and dissolved oxygen (DO) measured with a Hydrolab profiler at 1 m below the surface (1m), 1 m above the bottom (B-1m), and at the bottom at each sampling site in 1996 and 1998.

Site	km	max D Bottom	max D Bottom	Temp 1m	Temp 1m	Temp B-1m	Temp B-1m	Cond 1m	Cond 1m	Cond B-1m	Cond B-1m	pH 1m	pH 1m	pH B-1m	pH B-1m	DO 1m	DO 1m	DO B-1m	DO B-1m	DO Bottom	DO Bottom
		1996	1998	1996	1998	1996	1998	1996	1998	1996	1998	1996	1998	1996	1998	1996	1998	1996	1998	1996	1998
		m	m	C	C	C	C	uS/cm	uS/cm	uS/cm	uS/cm					mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
RAMD	6	20.6	20.2	22.2	22.4	7.2	8.5	308	329	299	313	7.54	7.85	7.01	6.95	8.27	8.39	6.69	5.08	6.45	4.65
MCF10	10	10	9.1	22.4	23.2	9.3	12.1	325	371	300	351	7.37	8.25	7.17	7.46	8.06	8.49	6.76	5.32	0.07	1.42
MCFD	10	20	19.0	22.2	23.2	6.7	7.4	325	371	303	351	7.73	8.29	6.74	6.82	8.32	8.43	0.83	0.42	0.51	0.42
RAF10	11	10	10.2	22.6	23.4	10.6	12.3	42	39	40	37	7.01	6.74	6.89	6.34	8.15	8.53	9.96	8.66	9.96	7.44
RAFD	11	15	15.1	23.0	23.4	7.5	8.5	42	38	42	39	7.10	6.59	6.47	5.87	8.21	7.98	5.78	0.50	4.40	0.54
RICD	12	9	9.6	22.5	23.9	20.2	16.1	170	188	169	199	7.46	7.92	7.20	7.12	8.19	8.31	6.09	1.67	3.72	0.83
NEPD	32		9.9		22.4		19.4		42		46		6.73		6.35		7.73		4.68		2.42
KAK10	38		10.3		23.4		8.7		69		64		7.05		6.20		8.29		3.23		3.71
KAKD	38	24	23.6	22.1	23.0	5.6	4.6	66	69	69	70	7.12	7.12	6.13	6.01	8.07	8.43	2.62	0.74	1.65	0.56
TRO10	43		8.9		23.4		10.0		32		30		7.03		6.41		8.57		6.87		6.66
TROD	43	46	48.2	23.2	23.1	5.7	5.8	33	32	32	29	7.06	7.10	5.78	5.86	8.31	8.49	5.76	5.94	5.74	5.91
LOS10	52	10	9.7	22.7	23.0	5.5	6.6	35	33	32	29	7.11	7.32	6.44	6.28	8.16	8.43	7.83	6.72	7.98	6.84
LOSD	52	46	44.5	22.9	22.9	4.5	3.9	35	33	32	30	7.16	7.33	6.11	5.79	8.30	8.28	8.79	4.85	4.28	4.17
TOM10	94	10	9.7	22.6	22.0	16.0	17.8	34	35	33	33	6.85	6.71	6.36	6.50	8.52	8.34	6.67	9.19	6.14	6.15
TOMD	94	23	22.4	22.5	21.9	9.2	11.5	34	35	31	33	6.89	6.76	5.71	5.65	8.42	8.63	5.07	3.57	4.87	3.51
RES10	107	10	10.3	21.7	22.3	10.9	10.5	33	33	32	32	6.85	7.06	6.34	6.06	8.24	8.69	6.64	5.46	6.33	4.95
RESD	107	28	28.7	21.8	22.3	6.1	6.4	33	33	33	31	6.74	7.04	5.72	5.59	8.14	8.57	6.20	4.55	6.02	4.26
NOS10	144	10	10.4	22.2	22.7	17.6	17.1	52	52	62	59	7.23	7.62	6.56	6.62	8.18	8.68	3.20	3.68	1.55	2.23
NOSD	144	14	14.0	22.2	22.6	12.2	12.4	52	52	82	85	7.18	7.70	6.48	6.77	8.10	8.48	0.46	0.64	0.34	0.58
TAL10	154	11	10.3	23.1	23.3	10.3	11.3	50	53	46	48	7.48	7.37	6.88	6.79	8.50	8.65	7.56	7.59	7.65	7.89
TALD	154	36	40.0	22.5	22.7	5.7	5.6	51	53	45	45	7.47	7.29	6.10	6.15	8.60	8.51	7.57	7.04	7.55	6.96

Table A2a. Concentrations of cations in filtered water samples collected by van Dorn sampler at 1 m below the surface (1m) and 1 m above the bottom (B-1m) at each sampling site in 1998. Analyses were conducted by NLET except for additional measurements of filtered (F) and unfiltered (UF) Ca and Mg conducted by ICAP-OES.

Site	km	Ca	CaF	CaUF	Ca	CaF	CaUF	Mg	MgF	MgUF	Mg	MgF	MgUF	Na	Na	K	K
		1m	1m	1m	B-1m	B-1m	B-1m	1m	1m	1m	B-1m	B-1m	B-1m	1m	B-1m	1m	B-1m
		1998	1998	1998	1998	1998	1998	1998	1998	1998	1998	1998	1998	1998	1998	1998	1998
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
RAMD	6	15.6	16.6	16.9	15.4	16.0	21.0	4.69	4.89	4.94	4.59	4.79	5.46	39.7	38.5	1.46	1.51
MCF10	10	17.3	17.9	18.0	17.2	17.1	17.4	5.46	5.72	5.67	5.37	5.49	5.47	46.4	45.1	1.65	1.72
MCFD	10	17.3	17.6	17.7	16.6	17.0	17.3	5.47	5.56	5.65	5.24	5.31	5.42	46.5	43.7	1.64	1.65
RAF10	11	3.63	5.18	5.49	3.65	3.94	4.22	1.21	2.40	2.51	1.21	1.34	1.38	1.14	1.13	0.56	0.52
RAFD	11	3.62	3.88	4.12	3.63	4.01	4.26	1.22	1.32	1.39	1.21	1.34	1.42	1.16	1.16	0.53	0.45
RICD	12	9.73	11.1	10.4	9.86	10.4	10.3	3.07	3.38	3.23	3.08	3.19	3.24	21.6	21.5	1.01	1.01
NEPD	32	4.09	4.54	4.86	4.26	4.81	5.14	1.79	2.01	2.11	1.86	2.14	2.25	1.19	1.17	0.60	0.62
KAK10	38	4.68	4.85	5.32	4.44	4.70	5.15	2.13	2.27	2.42	2.04	2.13	2.35	5.55	5.20	0.64	0.60
KAKD	38	4.61	4.93	5.21	4.93	6.20	5.55	2.11	2.25	2.21	2.23	2.50	2.28	5.52	5.44	0.56	0.65
TRO10	43	2.99	3.50	3.58	2.96	3.88	3.68	1.30	1.51	1.55	1.27	1.49	1.59	0.96	0.93	0.38	0.44
TROD	43	3.00	3.62	3.71	2.97	5.46	4.53	1.30	1.50	1.66	1.28	1.89	1.74	0.95	0.93	0.56	0.51
LOS10	52	3.12	(21.9) <sup>a</sup>	3.40	2.93	3.69	3.28	1.41	4.34	1.52	1.33	1.60	1.45	0.98	0.93	0.50	0.59
LOSD	52	3.15	3.48	3.61	3.11	3.63	3.47	1.42	1.54	1.58	1.37	1.62	1.51	1.02	0.94	0.53	0.52
TOM10	94	3.17	4.72	5.27	3.19	5.01	5.02	0.91	1.35	1.55	0.91	1.45	1.63	2.12	2.15	0.52	0.43
TOMD	94	3.16	4.99	5.33	3.07	4.89	7.25	0.91	1.45	1.58	0.89	1.45	2.13	2.12	1.99	0.50	0.51
RES10	107	2.98	3.29	3.29	2.93	3.23	3.28	0.82	0.90	0.88	0.79	0.87	0.89	2.03	1.91	0.53	0.59
RESD	107	2.97	3.29	3.24	2.92	3.31	3.25	0.81	0.93	0.95	0.79	0.94	0.91	2.02	1.85	0.61	0.61
NOS10	144	5.30	5.74	6.11	5.50	6.05	6.37	1.71	1.85	2.02	1.74	1.89	2.04	2.17	2.17	0.90	1.00
NOSD	144	5.35	5.63	6.23	6.00	6.94	7.18	1.71	1.88	1.98	1.78	2.01	2.15	2.19	2.11	0.97	1.10
TAL10	154	4.87	5.34	5.82	4.42	4.89	5.16	1.45	1.53	1.68	1.30	1.42	1.52	2.95	2.85	1.01	0.95
TALD	154	4.87	5.34	5.63	4.29	4.67	4.93	1.44	1.56	1.69	1.25	1.41	1.49	2.97	2.78	0.99	0.90

a. Numbers in parentheses are outliers and probably erroneous.

Table A2b. Alkalinity (Alk), concentrations of anions, and dissolved organic carbon (DOC) in filtered water samples collected by van Dorn sampler at 1 m below the surface (1m) and 1 m above the bottom (B-1m) at each sampling site in 1996 and 1998.

Site	km	Alk	Alk	Cl	Cl	Cl	SO4	SO4	SO4	SiO2	SiO2	SiO2	DOC	DOC	DOC
		1m	B-1m	1m	B-1m	B-1m	1m	B-1m	B-1m	1m	B-1m	B-1m	1m	B-1m	B-1m
		1998	1998	1998	1996	1998	1998	1996	1998	1998	1996	1998	1998	1996	1998
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
RAMD	6	28.4	27.4	65.5	59.6	63.9	20.2	23.6	19.9	1.52	3.1	3.09	4.1	7.1	3.7
MCF10	10	34.9	35.7	73.8	62.4	71.7	18.8	16.7	18.0	0.92	3.9	2.70	4.5	4.9	4.4
MCFD	10	33.5	35.9	74.2	61.8	71.5	18.4	15.3	16.3	0.92	5.0	4.21	4.7	4.0	4.0
RAF10	11	3.40	3.50	0.59	1.5	0.62	13.1	14.6	13.8	0.72	1.0	1.17	2.8	3.1	3.4
RAFD	11	3.20	4.70	0.92	1.1	0.64	13.4	12.9	12.8	0.72	2.4	2.82	3.0	6.0	3.3
RICD	12	24.2	28.6	35.9	31.2	35.8	8.0	12.3	6.2	0.46	1.6	1.67	3.2	3.3	3.4
NEPD	32	9.10	10.6	0.69	1.2	0.73	8.7	8.4	7.9	1.34	5.8	2.73	5.8	7.0	6.0
KAK10	38	9.50	9.00	7.97	6.6	7.59	9.3	8.3	8.8	0.80	5.2	3.81	6.4	7.6	6.0
KAKD	38	10.7	14.6	7.92	6.6	7.90	9.0	7.1	8.4	0.80	6.3	4.79	6.8	7.8	7.2
TRO10	43	5.40	4.90	0.61	0.9	0.60	7.1	7.1	7.0	0.98	3.4	2.60	6.0	6.5	5.2
TROD	43	6.80	6.00	0.59	1.0	0.61	7.1	7.2	7.1	0.99	3.7	2.90	5.9	6.5	5.5
LOS10	52	5.90	5.10	0.53	0.9	0.60	7.9	8.0	7.5	0.30	5.6	3.75	6.7	7.4	6.8
LOSD	52	6.00	5.60	0.64	1.3	0.72	7.5	6.0	7.2	0.30	6.6	4.62	6.7	7.8	6.9
TOM10	94	4.80	4.80	3.12	2.6	3.09	6.4	5.6	6.2	1.96	3.6	2.00	6.7	7.3	6.9
TOMD	94	5.40	3.30	3.06	2.5	2.83	6.2	5.2	6.2	1.98	4.5	3.32	7.3	7.1	6.6
RES10	107	4.70	4.30	2.70	2.6	2.52	6.2	6.5	6.1	1.21	4.9	3.43	5.5	5.8	5.3
RESD	107	4.50	3.00	2.77	2.9	2.41	6.2	7.3	6.0	1.22	5.3	4.15	5.2	5.3	5.0
NOS10	144	17.2	15.8	2.66	2.8	2.65	5.8	5.4	5.6	4.35	9.3	5.91	4.7	5.3	4.4
NOSD	144	17.1	18.4	2.65	3.1	2.70	5.6	2.5	6.3	4.32	11.9	10.50	4.5	5.4	6.1
TAL10	154	12.9	9.30	4.12	4.0	4.11	6.4	6.6	6.6	3.05	5.3	4.05	4.7	4.8	4.4
TALD	154	12.6	9.50	4.15	4.0	3.99	6.5	7.3	6.4	3.04	5.9	4.64	4.9	5.2	4.3

Table A3. Soluble reactive phosphorus (SRP), total unfiltered phosphorus (TPUF), nitrate + nitrite (NO<sub>3</sub>/2), ammonia (NH<sub>3</sub>), total Kjeldahl nitrogen (TKN) and uncorrected (CHLA) and pheophytin corrected (CHLAC) chlorophyll a in filtered water samples collected by van Dorn sampler at 1 m below the surface (1m) and 1 m above the bottom (B-1m) at each sampling site in 1996 and 1998.

Site	km	SRP			TPUF			NO <sub>3</sub> /2			NH <sub>3</sub>			TKN			CHLA	CHLAC
		1m	B-1m	B-1m	1m	B-1m	B-1m	1m	B-1m	B-1m	1m	B-1m	B-1m	1m	B-1m	B-1m	1m	1m
		1998	1996	1998	1998	1996	1998	1998	1996	1998	1998	1996	1998	1998	1996	1998	1998	1998
		ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
RAMD	6	1.8	1.9	16.0	8.0	11.2	23.4	334	67	216	14	11	25	319	372	259	0.3	0.4
MCF10	10	1.8	1.5	1.1	10.5	28.5	27.0	286	91	62	7	43	9	273	325	251	1.1	1.0
MCFD	10	1.8	2.0	5.5	8.1	16.6	24.0	442	192	196	6	176	241	298	431	485	2.0	2.4
RAF10	11	1.6	1.7	1.1	11.2	7.5	10.6	<10	<10	26	5	<5	12	177	186	160	0.3	<0.1
RAFD	11	1.4	1.5	1.8	4.0	12.2	21.8	23	<10	35	6	<5	87	161	322	233	0.3	0.2
RICD	12	1.0	1.1	7.0	11.6	11.5	40.7	131	10	15	5	<5	76	188	180	249	0.5	0.4
NEPD	32	0.9	4.7	3.8	14.3	26.9	13.3	25	10	19	10	52	115	283	368	379	5.3	4.3
KAK10	38	1.0	5.2	2.0	13.9	9.0	7.8	147	116	179	6	<5	12	301	294	273	1.3	1.6
KAKD	38	1.0	2.9	4.6	8.7	13.0	29.6	242	230	437	<5	<5	89	304	361	372	1.2	1.2
TRO10	43	0.5	2.1	1.9	5.1	9.0	7.1	345	175	1230	8	<5	11	247	226	280	0.8	0.4
TROD	43	0.4	3.2	1.5	7.8	12.3	9.2	465	168	<10	6	<5	26	266	234	237	1.6	1.6
LOS10	52	1.0	1.3	0.7	8.2	7.0	11.4	45	215	278	6	<5	6	318	304	311	1.2	1.0
LOSD	52	1.2	3.1	7.9	4.1	20.0	17.7	49	202	259	8	<5	10	318	313	284	1.0	1.2
TOM10	94	0.7	1.2	1.0	5.3	7.6	5.5	174	130	188	11	14	14	261	266	263	2.6	2.6
TOMD	94	0.4	1.3	1.8	6.3	8.4	4.3	<10	162	147	12	5	20	263	246	250	2.0	1.6
RES10	107	1.2	1.3	1.9	6.1	9.4	6.7	103	186	232	9	5	12	262	224	227	1.2	1.2
RESD	107	0.9	2.1	2.4	6.4	7.7	8.7	46	190	270	8	7	18	265	242	256	2.8	2.0
NOS10	144	0.9	6.5	3.1	11.4	24.1	13.8	<10	<10	<10	20	85	25	248	354	251	2.4	2.8
NOSD	144	1.6	2.3	(25.6) <sup>a</sup>	12.2	11.3	(342)	<10	<10	<10	9	52	(672)	274	177	(957)	3.6	3.5
TAL10	154	0.7	0.3	0.8	7.0	7.6	4.4	68	190	303	<5	7	7	213	160	179	2.2	2.3
TALD	154	0.4	1.1	1.2	5.1	7.1	6.1	67	218	289	8	<5	7	226	190	161	2.0	1.2

a. Numbers in parentheses are outliers and probably erroneous.

Table A4a. Trace metal concentrations measured by ICP-MS in filtered water samples collected by van Dorn sampler at 1 m below the surface (1m) and 1 m above the bottom (B-1m) at each sampling site in 1998. Also shown are comparative measurements of Cd measured by graphite furnace atomic absorption spectrophotometry in filtered (Cd-G) and unfiltered (Cd-GUF) water samples.

Site	km	As 1m 1998 ug/L	As B-1m 1998 ug/L	Cd 1m 1998 ug/L	Cd-G 1m 1998 ug/L	Cd-GUF 1m 1998 ug/L	Cd B-1m 1998 ug/L	Cd-G B-1m 1998 ug/L	Cd-GUF B-1m 1998 ug/L	Co 1m 1998 ug/L	Co B-1m 1998 ug/L	Cr 1m 1998 ug/L	Cr B-1m 1998 ug/L
RAMD	6	1.59	1.84	0.118	0.077	0.211	0.170	0.166	0.062	0.024	0.035	0.33	0.23
MCF10	10		1.44		0.023	0.060	0.315	0.256	0.291		0.036		0.22
MCFD	10	1.57	1.20	0.052	0.042	0.006	0.214	0.239	0.159	0.029	0.115	0.27	0.18
RAF10	11	0.99	0.92	0.170	0.172	0.127	0.436	0.434	0.200	0.029	0.485	0.16	0.14
RAFD	11	0.95	1.10	0.224	0.159	0.076	0.378	0.359	0.106	0.021	4.57	0.15	0.05
RJCD	12	0.94	2.49	0.061	0.014	0.019	0.124	0.099	0.116	0.018	4.02	0.20	0.12
NEPD	32	1.01	1.16	0.050	ND	0.017	0.100	0.052	ND	0.026	0.212	0.31	0.25
KAK10	38	0.76	0.63	0.002	ND	ND	0.034	0.018	ND	0.021	0.051	0.32	0.32
KAKD	38	0.75	1.14	0.026	0.019	ND	0.052	0.017	ND	0.020	1.209	0.36	0.58
TRO10	43				0.003	0.008		0.084	0.041				
TROD	43	0.59	0.39	0.048	ND	0.013	0.055	0.008	ND	0.020	0.060	0.29	0.19
LOS10	52	0.46	0.21	0.042	0.039	ND	0.033	0.028	ND	0.021	0.041	0.37	0.35
LOSD	52	0.66	0.83	0.070	0.023	ND	0.057	ND	ND	0.030	0.205	0.40	0.48
TOM10	94	0.70		0.027	0.021	0.154		ND	0.015	0.026		0.43	
TOMD	94	0.40	0.57	0.117	0.123	0.019	0.101	0.082	ND	0.024	0.123	0.37	0.50
RES10	107	0.34	0.51	0.049	ND	0.022	0.060	ND	0.017	0.014	0.030	0.35	0.33
RESD	107	0.84	0.43	0.130	0.084	0.109	0.178	0.142		0.015	0.051	0.35	0.52
NOS10	144	0.15		0.015	0.008	ND		0.072	ND	0.013		0.20	
NOSD	144	0.29	0.92	0.053	0.076	ND	0.099	0.107	ND	0.014	0.423	0.30	0.23
TAL10	154	0.24	0.56	0.011	0.005	ND	0.032	0.014	ND	0.012	0.021	0.23	0.38
TALD	154		0.09		0.160	ND	0.007	0.012	ND		0.020		0.29

Table A4b. Trace metal concentrations measured by ICP-MS in filtered water samples collected by van Dorn sampler at 1 m below the surface (1m) and 1 m above the bottom (B-1m) at each sampling site in 1998.

Site	km	Cu	Cu	Mn	Mn	Ni	Ni	Pb	Pb	Se	Se	Tl	Tl	Zn	Zn
		1m	B-1m	1m	B-1m	1m	B-1m	1m	B-1m	1m	B-1m	1m	B-1m	1m	B-1m
		1998	1998	1998	1998	1998	1998	1998	1998	1998	1998	1998	1998	1998	1998
		ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
RAMD	6	11.19	16.0	4.77	14	65.8	87.2	0.39	0.47	0.93	1.09	0.065	0.087	7.63	16.5
MCF10	10		6.46		53		49.4		0.30		0.27		0.058		18.9
MCFD	10	8.46	7.23	1.77	1310	34.5	104	0.45	0.55	0.95	1.18	0.064	0.059	6.13	18.5
RAF10	11	10.1	15.7	2.12	48	93.6	127	ND	0.00	1.29	0.38	0.026	0.029	13.3	19.9
RAFD	11	8.25	16.9	1.19	402	91.2	129	ND	0.18	0.06	0.08	0.026	0.039	12.4	18.5
RICD	12	7.24	5.96	0.70	1340	24.0	85.5	0.24	0.40	0.24	1.13	0.061	0.067	3.95	9.53
NEPD	32	3.66	3.43	0.91	462	5.95	8.07	ND	0.02	0.12	ND	0.026	0.021	8.93	6.73
KAK10	38	3.39	3.55	1.48	85	8.12	11.3	0.17	0.10	0.17	0.06	0.044	0.043	4.54	7.63
KAKD	38	3.98	3.70	1.02	904	7.78	12.2	0.13	0.14	0.38	0.05	0.041	0.035	8.03	11.8
TRO10	43														
TROD	43	2.41	6.66	2.09	9.6	4.23	4.37	0.04	0.37	0.09	4.92	0.010	0.007	6.13	12.5
LOS10	52	3.94	1.61	0.93	9.2	3.76	3.78	0.11	0.01	0.11	ND	0.019	0.012	4.56	8.83
LOSD	52	3.45	2.26	1.76	197	3.50	4.06	0.17	0.38	ND	0.15	0.012	0.037	8.03	12.2
TOM10	94	1.18		2.92		0.97		0.07		ND		0.027		7.83	
TOMD	94	5.13	2.07	3.81	127	1.37	1.41	0.08	0.31	3.18	0.25	0.030	0.026	8.63	14.2
RES10	107	1.30	1.22	1.08	29	0.33	0.44	0.11	0.09	ND	0.56	0.055	0.025	5.67	11.7
RESD	107	1.74	1.23	1.20	88	0.51	0.42	0.08	0.21	0.18	0.32	0.023	0.023	8.73	9.33
NOS10	144	0.77		0.78		0.15		0.02		0.47		0.018		4.02	
NOSD	144	1.12	3.68	0.71	1520	0.23	0.48	0.08	0.27	0.02	1.34	0.023	0.020	5.08	7.83
TAL10	154	0.79	0.80	0.54	4.7	0.32	0.34	0.04	0.03	ND	0.05	0.030	0.036	2.42	8.43
TALD	154		0.81		4.0		0.27		0.05		0.32		0.028		5.56

Table A5a. Trace metals measured by graphite furnace atomic absorption spectrophotometry (Cd) or ICAP-OES (all other metals) in dried sediment samples collected by ponar grab at each sampling site in 1996 and 1998.

Site	km	Cd	Cd	Cd	Co	Co	Co	Cr	Cr	Cr	Cu	Cu	Cu	Fe	Fe	Fe
		grab#3	grab#1	grab#2	grab#3	grab#1	grab#2	grab#3	grab#1	grab#2	grab#3	grab#1	grab#2	grab#3	grab#1	grab#2
		1996	1998	1998	1996	1998	1998	1996	1998	1998	1996	1998	1998	1996	1998	1998
		ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	mg/g	mg/g	mg/g
RAMD	6	2.43	1.46	4.72	71	28	94	96	83	82	1300	400	1840	42.6	34.9	58.3
MCF10	10	5.40	1.86	1.67	117	28	34	83	63	74	1070	262	42	28.6	28.5	45.0
MCFD	10	8.82	9.03	2.83	142	137	35	78	67	70	1810	1570	385	37.5	62.5	38.6
RAF10	11	0.42	0.19	1.35	18	12	17	44	62	79	135	35	28	18.6	19.6	76.6
RAFD	11	4.99	2.59	2.60	54	31	32	72	65	67	1470	536	496	35.2	33.2	44.1
RJCD	12	1.41	3.44	3.85	38	68	74	111	64	67	165	1000	1120	37.1	32.7	41.6
NEPD	32	6.37	1.29		105	27	29	90	92	107	137	138	66	27.6	40.6	50.4
KAK10	38	2.00	1.58	0.96	31	33	19	90	86	66	120	80	118	38.1	40.6	41.4
KAKD	38	2.63	1.48	2.74	32	23	27	81	73	82	238	59	30	42.5	41.9	56.5
TRO10	43	3.14	2.85	2.73	33	29	31	51	48	53	127	156	131	39.5	28.7	38.8
TROD	43	1.77	0.99	3.02	32	20	44	73	58	67	54	26	173	35.1	32.9	54.2
LOS10	52	2.29	1.58	1.11	32	36	36	64	72	73	142	27	222	42.1	41.7	63.9
LOSD	52	2.07	0.67	1.52	36	25	38	79	73	71	94	43	18	36.6	36.7	56.9
TOM10	94	3.02	1.36	1.91	38	21	19	85	78	65	69	18	11	50.5	29.4	43.4
TOMD	94	1.39	1.68	5.06	25	20	34	63	68	79	42	28	57	30.6	32.1	38.8
RES10	107	2.54	2.47	2.87	23	26	32	53	53	52	39	29	29	46.9	55.1	63.7
RESD	107	1.73	2.35	2.99	32	19	23	52	48	45	27	40	34	48.7	43.5	49.6
NOS10	144	1.71	0.93	1.39	20	18	26	98	90	97	39	34	63	52.3	40.3	49.1
NOSD	144	0.76	0.92	1.34	16	16	20	81	82	90	41	30	22	41.8	45.2	55.9
TAL10	154	1.68	1.58	1.90	25	21	24	95	90	90	33	30	26	79.7	66.6	83.4
TALD	154	2.89	1.94	1.46	28	20	21	101	91	96	31	45	25	67.4	48.6	68.5

Table A5b. Trace metals measured by ICAP-OES in dried sediment samples collected by ponar grab at each sampling site in 1996 and 1998.

Site	km	Mg	Mg	Mg	Mn	Mn	Mn	Ni	Ni	Ni	Pb	Pb	Pb	Zn	Zn	Zn
		grab#3	grab#1	grab#2	grab#3	grab#1	grab#2	grab#3	grab#1	grab#2	grab#3	grab#1	grab#2	grab#3	grab#1	grab#2
		1996	1998	1998	1996	1998	1998	1996	1998	1998	1996	1998	1998	1996	1998	1998
		mg/g	mg/g	mg/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
RAMD	6	8.95	5.80	9.69	487	355	508	1590	454	2130	95	27	143	192	114	258
MCF10	10	8.93	6.31	2.15	764	468	1020	2430	509	65	83	17	79	492	163	180
MCFD	10	7.37	5.88	7.93	3400	6900	588	2780	2700	631	150	150	14	554	451	185
RAF10	11	5.47	6.49	11.6	324	322	702	178	53	46	<2.5	<2.5	10	47	54	146
RAFD	11	7.31	7.06	7.97	363	341	389	1570	773	706	138	52	40	142	137	129
RICD	12	9.64	6.83	7.78	701	305	344	289	1840	1920	30	56	63	249	196	240
NEPD	32	8.17	8.27	10.8	593	547	711	240	215	129	84	28	<2.5	353	220	190
KAK10	38	9.99	10.1	8.00	1200	1660	359	189	147	195	28	18	<2.5	204	196	72
KAKD	38	8.89	7.58	9.88	885	870	1850	263	77	54	134	59	12	302	174	154
TRO10	43	4.30	4.57	5.11	1940	972	1400	220	287	238	79	92	78	232	246	248
TROD	43	9.19	2.12	5.50	2380	711	1160	99	32	239	14	17	132	228	103	272
LOS10	52	4.91	3.81	8.32	896	2150	1070	173	67	308	97	<2.5	115	230	197	264
LOSD	52	9.01	7.40	9.14	906	975	2100	115	33	48	93	<2.5	<2.5	212	127	194
TOM10	94	8.00	3.41	7.81	3410	1110	1550	90	41	32	62	<2.5	<2.5	389	158	195
TOMD	94	5.87	5.48	7.57	960	855	1180	44	43	83	39	34	97	172	177	298
RES10	107	4.72	5.38	5.37	1490	2860	3740	45	33	39	91	24	<2.5	268	265	251
RESD	107	4.90	4.26	4.75	5240	1270	1740	40	35	40	24	57	59	250	208	228
NOS10	144	11.4	4.73	10.2	610	550	656	52	48	113	30	23	<2.5	2	129	170
NOSD	144	10.6	7.08	12.6	494	641	760	44	46	44	37	37	9	131	126	142
TAL10	154	10.5	9.82	11.5	4860	1400	2180	58	48	53	37	19	10	288	217	260
TALD	154	11.2	9.72	16.6	5780	1150	1090	67	53	51	58	64	19	441	308	196



Table B. Total number of benthic invertebrates counted within each taxonomic group (rare organisms found at only a few sites excluded) in 1996 (sum of 5 cores of 6.5 cm diameter, total area 166 cm<sup>2</sup>) and 1998 (sum of 3 ponar grabs, total area 672 cm<sup>2</sup>).

Site	km	Chaoboridae		Chironomini		Orthoclaadiinae		Tanypodinae		Tanytarsini		Amphipoda			Pisidiidae		Oligochaeta	
		1996	1998	1996	1998	1996	1998	1996	1998	1996	1998	Diporeia hoyi	Hyaella azteca		1996	1998	1996	1998
RAMD	6	8		4	1			1									103	1170
MCF10	10	5	24	31	59	1		8									3	9
MCFD	10	6	5	2	30				3									1
RAF10	11	1	5	9	22	3		8	2		3							
RAFD	11	2	2	6	1													1
RICD	12	6	52	85	48				2				1					21
NEPD	32	37	95	2	16				1						2	5	11	8
KAK10	38		1	4	4	44	58	3	9	15	29	4	3			13	1	3
KAKD	38	1	1	1	2					1							1	
TRO10	43			7	17	20	15		1	2	7	1	3		18	11		2
TROD	43			2	14	1									5	2		11
LOS10	52		5		16	10			1	6	5	14	15			14		6
LOSD	52			19	16							1				4	4	12
TOM10	94							3	5	5						4		
TOMD	94		4	3	4				1	1					5	11	3	1
RES10	107	13	4	1	1	14		2		4	1	16	6		19	9	1	1
RESD	107	1	4	8	15						4				4	2		2
NOS10	144	71	169	126	96			10	3					4	12	11	39	34
NOSD	144	102	116	17	26				1		1			3	1	6	6	8
TAL10	154		12	3	2		40				31		2	1	9	36	1	5
TALD	154			15	6	1	2			5	1	1	1		3			1

Table C1. Toxicity test results for Chironomus (10 day test) conducted with sediments from ponar grabs #2 and 3 from deep stations only in 1998. Two replicates with control sediments from Hamilton Harbour (HH1) and Lake Erie (LE303) are also included.

Site	km	Grab #	Percent Survival	Final weight (mg)
RAMD	6	3	100	2.86
MCFD	10	3	87	3.25
RAFD	11	3	87	3.54
RICD	12	2	87	1.50
RICD	12	3	93	2.64
NEPD	32	3	80	3.23
KAKD	38	3	80	3.63
TROD	43	2	53	3.86
TROD	43	3	80	4.13
LOSD	52	2	87	3.73
LOSD	52	3	47	5.46
TOMD	94	2	80	3.38
TOMD	94	3	93	2.43
RES D	107	2	73	3.22
RES D	107	3	100	2.79
NOSD	144	2	87	2.44
NOSD	144	3	80	4.04
TALD	154	2	100	2.57
TALD	154	3	93	2.54
HH1	368		93	4.14
HH1	368		80	3.72
LE303	443		87	2.75
LE303	443		87	2.43

Table C2. Survival and mean final wet weight of *Hyaella* exposed to sediments collected in 1996 and 1998 from selected sampling sites for chronic (4-week) tests conducted in late 1998 and early 1999, along with dissolved organic carbon (DOC), alkalinity (Alk), and Ni in overlying water and Ni measured in *Hyaella*. Duplicate data for the same site and grab number represent replicate tests.

Site	km	Sediment collection date	Experiment completion date	Grab #	Survival in sediment (%)	Survival in cage (%)	Wet weight in sediment	Wet weight in cage	DOC	Alk	Cu in water (ug/L)	Ni in water (ug/L)	Ni in <i>Hyaella</i> in sediment (nmol/g)	Ni in <i>Hyaella</i> in cage (nmol/g)
RAMD	6	960820	990317	1	0	0								
RAMD	6	960820	990317	2	0	0			5.1	64	6.6	283		
RAMD	6	960820	990317	2	0				5.9	45	21	567		
RAMD	6	980811	990317	1	13	27	0.15	0.38	4.7	43	24	970		
RAMD	6	980811	990317	2	0	0			4.9	55	ND	19	281	129
RAMD	6	980811	990317	2	0				3.7	43	ND	160		
RAMD	6	980811	981203	3	73	93	1.25	0.47	2.6	51	ND	205		
MCF10	10	980811	981203	3	0	0					4.4	8.5	30	56
MCFD	10	980811	981203	3	7	0	0.10				8.1	132		
RAF10	11	960820	990317	1	0	13		0.10	3.9	40	9.2	64		56
RAF10	11	960820	990317	2	0	0			4.3	48	14	67		
RAF10	11	960820	990317	2	0				3.1	51	9.0	95		
RAF10	11	980811	990317	1	60	60	1.74	0.69	3.1	51	ND	ND	7	9
RAF10	11	980811	990317	2	60	27	1.17	0.50	3.3	48	ND	0.9	82	11
RAF10	11	980811	990317	2	93		1.45		2.3	64	1.6	3.4	26	
RAF10	11	980811	981203	3	80	60	0.68	0.40			3.2	4.4	10	29
RAFD	11	960820	990317	1	0	0			3.7	37	6.4	285		
RAFD	11	960820	990317	2	0	0			3.8	40	14	266		
RAFD	11	960820	990317	2	0				3.0	37	28	554		
RAFD	11	980811	990317	1	0	7		0.20	4.6	41	ND	68		779
RAFD	11	980811	990317	2	0	0			4.7	43	ND	44		
RAFD	11	980811	990317	2	80		1.75		2.5	55	ND	40	16	
RAFD	11	980811	981203	3	73	33	0.56	0.40			3.8	14	45	42
RICD	12	980811	981203	3	0	0					19	216		
NEPD	32	960820	990317	1	67	53	1.36	0.49	3.5	38	3.1	1.2	12	17
NEPD	32	960820	990317	2	80	53	1.73	0.58	4.3	52	ND	5.0	6	20
NEPD	32	960820	990317	2	80		1.63		4.7	49	ND	1.3	12	
NEPD	32	980811	990317	1	80	53	1.53	0.41	4.8	46	3.4	1.2	13	24
NEPD	32	980811	990317	2	87	80	1.09	0.60	3.6	52	1.2	ND	10	8
NEPD	32	980811	990317	2	80		1.60		2.2	61	1.7	0.6	ND	
NEPD	32	980811	981203	3	27	20	0.78	0.37			2.8	2.2		
KAKD	38	960820	990317	1	0	0			6.0	22	ND	41		
KAKD	38	960820	990317	2	0	0			3.6	12	ND	166		
KAKD	38	960820	990317	2	20		0.37		2.8	38	ND	137	330	
KAKD	38	980811	990317	1	87	67	0.89	0.84	3.8	41	1.5	0.6	9	14
KAKD	38	980811	990317	2	67	67	0.86	0.74	3.5	36	ND	3.0	17	43
KAKD	38	980811	990317	2	80		1.96		2.3	44	1.4	0.8	15	
KAKD	38	980811	981203	3	87	80	0.94	0.47			3.3	7.9	29	190
TALD	154	980811	981203	3	73	60	0.97	0.27			1.1	0.7	4	23
HH1	368		990317		73	67	1.32	0.70	3.5	76	ND	0.3	50	11
HH1	368		981203		20	13	1.50	0.40			3.5	1.5	9	
LE303	443		990317		87	73	2.09	0.66	2.8	87	ND	1.4	14	11
LE303	443		981203		93	73	0.83	0.64			2.1	1.0	6	15
GAUZE			990317		33	47	0.58	0.53	5.3	69	ND	0.6	7	12
GAUZE			981203		53	20	0.46	0.30			1.2	ND	8	13

Table D. Metal concentrations in overlying water (ug/L) at the end of 7-day exposures of adult *Hyalella* to sediments collected by ponar grab at each sampling site in 1998. Analyses were done by ICP-MS (grab #2), GFAAS (Ni in grabs #1 and 3) or ICAP-OES (Mn in grab #1). All experiments were completed within three months of sediment collection.

Site	km	Grab #	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Se	Tl	Zn
RAMD	6	1						ND	5.5				
RAMD	6	2	9.85	0.161	0.20	0.23	13.44	1.5	125	0.19	0.42	0.08	5.7
RAMD	6	3							3.7				
MCF10	10	1						14	5.9				
MCF10	10	2	3.76	0.052	0.06	0.22	3.80	0.6	13	0.24	0.35	0.06	1.0
MCF10	10	3							88				
MCFD	10	1						1961	127				
MCFD	10	2	3.15	0.444	6.45	0.19	7.85	2860	174	1.26	0.52	0.06	12.5
MCFD	10	3							86				
RAF10	11	1						ND	ND				
RAF10	11	2	1.87	0.006	0.04	0.17	2.36	0.0	2.6	0.19	0.17	0.04	1.4
RAF10	11	3							28				
RAFD	11	1						21	55				
RAFD	11	2	3.29	0.083	0.05	0.24	3.73	0.7	19	1.87	0.36	0.06	7.7
RAFD	11	3							24				
RICD	12	1						17	230				
RICD	12	2		0.110				ND	91				
RICD	12	3							195				
NEPD	32	1						77	0.1				
NEPD	32	2	0.95	0.011	0.04	0.20	0.79	0.2	ND	0.17	0.47	0.04	0.4
NEPD	32	3							0.1				
KAK10	38	1						156	1.3				
KAK10	38	2	0.91	0.007	0.05	0.32	0.76	0.3	ND	0.21	0.07	0.04	4.0
KAKD	38	1						236	ND				
KAKD	38	2	1.47	0.025	0.09	0.15	1.72	4.8	2.4	0.34	0.10	0.05	1.7
KAKD	38	3							5.2				
TRO10	43	1						18	ND				
TRO10	43	2	1.37	0.004	0.03	0.26	1.26	1.1	0.6	0.21	0.39	0.06	1.2
TROD	43	1						67	ND				
TROD	43	2	2.22	0.004	0.04	0.18	1.55	0.3	0.9	0.17	0.06	0.05	0.5
LOS10	52	1						434	ND				
LOS10	52	2	1.21	ND	0.22	0.13	0.79	225	0.1	0.18	ND	0.04	0.2
LOSD	52	1						244	ND				
LOSD	52	2	4.36	0.019	0.38	0.20	1.37	78	0.5	0.33	0.15	0.05	ND

See next page for sites >90 km from Sudbury.

Table D (cont'd). Metal concentrations in overlying water (ug/L) at the end of 7-day exposures of adult *Hyaella* to sediments collected by ponar grab at each sampling site in 1998. Analyses were done by ICP-MS (grab #2), GFAAS (Ni in grabs #1 and 3) or ICAP-OES (Mn in grab #1). All experiments were completed within three months of sediment collection.

Site	km	Grab #	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Se	Tl	Zn
TOM10	94	1						87	ND				
TOM10	94	2	1.41	0.012	0.05	0.34	0.70	0.7	ND	0.20	ND	0.12	0.8
TOMD	94	1						7.0	ND				
TOMD	94	2	1.59	0.010	0.06	0.21	0.95	0.4	0.5	0.26	0.11	0.06	3.4
RES10	107	1						313	ND				
RES10	107	2	1.30	0.026	0.19	0.24	1.09	528	ND	0.17	0.55	0.10	ND
RESD	107	1						78	ND				
RESD	107	2	1.19	0.004	0.05	0.25	0.68	0.4	ND	0.22	0.09	0.05	1.4
NOS10	144	1						76	ND				
NOS10	144	2	0.70	0.003	0.02	0.11	0.85	ND	0.3	0.19	0.17	0.04	1.5
NOSD	144	1						66	11				
NOSD	144	2	0.94	0.016	0.05	0.14	1.32	0.7	0.8	0.21	ND	0.05	4.8
NOSD	144	3							ND				
TAL10	154	1						32	ND				
TAL10	154	2	0.48	0.001	0.03	0.19	0.55	0.2	ND	0.18	0.09	0.05	ND
TALD	154	1						151	0.6				
TALD	154	2	1.01	0.001	0.00	0.20	0.61	0.4	ND	0.20	ND	0.04	1.3
TALD	154	3											
HH1	368	1*							ND				
HH1	368	2	2.08	0.025	0.06	0.23	3.13	0.5	1.2	0.29	0.75	0.11	13.6
HH1	368	3							0.5				
LE303	443	1*							ND				
LE303	443	2	1.23	0.002	0.02	0.17	2.57	0.1	0.9	0.21	ND	0.07	0.1
LE303	443	3							0.2				
GAUZE		1*						ND	ND				
GAUZE		2	0.68	0.001	0.06	0.17	0.59	ND	0.7	0.18	ND	0.05	0.9
GAUZE		3							ND				

a. Numbers under "Grab #" for HH1, LE303 and Gauze refer to measurements taken from these controls at the same time as the corresponding grab samples for the other stations, but from the same batch of control sediment or gauze.

Table E. Metal concentrations in *Hyalella* (nmol/g) at the end of 7-day exposures of adult *Hyalella* to sediments collected by ponar grab at each sampling site in 1998, and Ni in *Hyalella* exposed in cages over sediments (Ni-cage). Analyses were done by ICP-MS (grab #1 and 2) or GFAAS (Ni in grab #3). All experiments were completed within three months of sediment collection.

Site	km	Grab #	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Se	Tl	Zn	Ni-cage
RAMD	6	1	7.3	9.9	9.1	28	1213	214	118	0.4	29	0.3	839	
RAMD	6	2	6.7	46.9	39.1	22	1563	1116	494	3.7	8	0.9	854	
RAMD	6	3							4					2
MCF10	10	1	15.8	9.8	5.7	20	1316	311	59	0.5	27	0.4	928	
MCF10	10	2	24.7	18.9	9.1	28	1375	294	68	0.3	24	0.6	1737	
MCF10	10	3							537					559
MCFD	10	1	16.5	15.2	42.0	26	1247	17604	344	0.8	40	0.2	1327	
MCFD	10	2	12.3	31.9	41.5	26	1348	41543	274	0.3	17	0.4	852	407
MCFD	10	3							263					182
RAF10	11	1	17.3	5.1	2.6	26	1694	170	10	0.3	31	0.4	929	
RAF10	11	2	16.8	7.0	4.5	23	1108	130	23	33.1	27	0.5	901	
RAF10	11	3							188					275
RAFD	11	1	15.4	34.6	15.5	25	1502	408	228	1.8	25	0.9	900	
RAFD	11	2	11.4	21.3	6.7	27	1612	139	99	0.6	36	0.5	913	182
RAFD	11	3							152					104
RICD	12	1	3.4	44.0	61.9	24	1310	480	830	1.9	31	1.2	881	
RICD	12	2	7.2	41.3	46.3	31	1564	344	685	1.7	26	1.2	896	601
RICD	12	3							467					887
NEPD	32	1	8.1	4.4	6.3	23	1436	844	16	0.7	29	0.5	935	
NEPD	32	2	12.9	4.5	2.4	25	1567	119	19	0.5	33	0.5	850	
NEPD	32	3							2					6
KAK10	38	1	11.6	6.0	4.6	22	1156	964	6	0.3	26	0.6	921	
KAK10	38	2	13.7	5.3	2.7	25	1364	272	25	0.9	19	0.5	1009	
KAKD	38	1	8.5	4.4	5.6	22	1335	1926	14	0.2	32	0.5	914	
KAKD	38	2	17.0	8.1	6.3	28	1392	580	22	0.6	24	0.4	882	
KAKD	38	3							11					16
TRO10	43	1	10.5	8.5	3.9	25	1269	614	3	0.8	28	1.6	961	
TRO10	43	2	14.9	7.6	3.9	28	1671	203	9	0.8	26	0.9	922	
TROD	43	1	8.8	4.1	6.5	25	1533	543	1	0.3	25	0.4	1016	
TROD	43	2	4.2	10.5	7.1	25	1557	375	17	1.4	31	0.6	875	
LOS10	52	1	8.9	5.1	7.1	25	1174	2319	10	0.1	26	1.8	926	
LOS10	52	2	8.9	3.5	7.3	27	1361	3441	13	1.8	11	0.8	938	
LOSD	52	1	4.3	3.3	6.0	23	1085	1595	1	1.1	24	0.4	964	
LOSD	52	2	14.9	7.1	14.7	32	1725	1006	22	3.3	15	0.7	905	

See next page for sites >90 km from Sudbury.

Table E (cont'd). Metal concentrations in *Hyalella* (nmol/g) at the end of 7-day exposures of adult *Hyalella* to sediments collected by ponar grab at each sampling site in 1998, and Ni in *Hyalella* exposed in cages over sediments (Ni-cage). Analyses were done by ICP-MS (grab #1 and 2) or GFAAS (Ni in grab #3). All experiments were completed within three months of sediment collection.

Site	km	Grab #	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Se	Tl	Zn	Ni-cage
TOM10	94	1	3.4	10.1	3.9	27	1195	983	1	0.2	34	3.4	929	
TOM10	94	2	19.2	15.9	3.1	36	1456	468	20	2.5	9	2.6	1168	
TOMD	94	1	9.3	3.4	3.5	21	1070	335	ND	0.6	30	0.6	843	
TOMD	94	2	13.8	6.1	5.9	27	1508	394	10	1.8	36	0.8	938	
RES10	107	1	2.2	4.1	4.6	23	1268	1962	2	0.2	35	1.7	919	
RES10	107	2	3.5	8.6	7.4	21	1384	4874	9	0.4	26	1.9	936	
RESD	107	1	7.5	4.4	2.4	22	1056	804	2	0.6	33	0.5	905	
RESD	107	2	13.1	5.3	3.8	28	1432	198	10	0.5	28	0.5	1624	
NOS10	144	1	11.8	3.0	2.9	24	1223	766	2	0.1	33	0.6	936	
NOS10	144	2	9.4	4.9	2.8	22	1378	183	33	0.5	23	0.4	844	
NOSD	144	1	13.0	3.0	2.5	25	1250	834	3	0.5	32	0.3	955	
NOSD	144	2	10.9	5.3	3.1	22	1430	170	10	0.3	24	0.4	926	
NOSD	144	3							ND					
TAL10	154	1	13.0	6.8	1.9	25	1265	543	ND	0.3	25	0.8	928	2
TAL10	154	2	15.6	5.5	3.8	26	1202	561	12	1.2	17	0.7	1226	
TALD	154	1	12.3	4.2	1.6	24	997	1691	4	0.3	20	0.3	880	
TALD	154	2	19.2	4.0	4.9	20	1451	1202	78	1.0	27	0.4	907	
TALD	154	3							ND					6
HH1	368	1 <sup>a</sup>	9.5	8.4	2.8	23	1638	592	17	2.3	41	2.7	1176	
HH1	368	2	13.6	12.6	2.9	28	2232	385	10	1.0	49	1.2	1106	
HH1	368	3							13					3
LE303	443	1 <sup>a</sup>	11.4	6.1	5.0	24	1386	386	17	0.5	29	0.8	978	
LE303	443	2	1.8	9.9	4.7	23	1410	160	32	0.2	24	0.9	895	
LE303	443	3							11					7
GAUZE		1 <sup>a</sup>	3.1	3.3	6.3	24	827	119	6	0.8	31	0.1	900	
GAUZE		2	18.1	8.1	5.6	22	979	99	15	0.4	21	0.1	877	
GAUZE		3							2					1

a. Numbers under "Grab #" for HH1, LE303 and Gauze refer to measurements taken from amphipods exposed to these controls at the same time as the corresponding grab samples for the other stations, but using the same batch of control sediment or gauze.

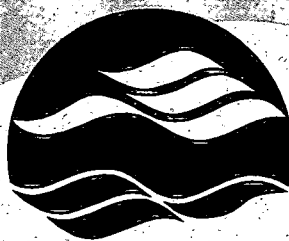
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