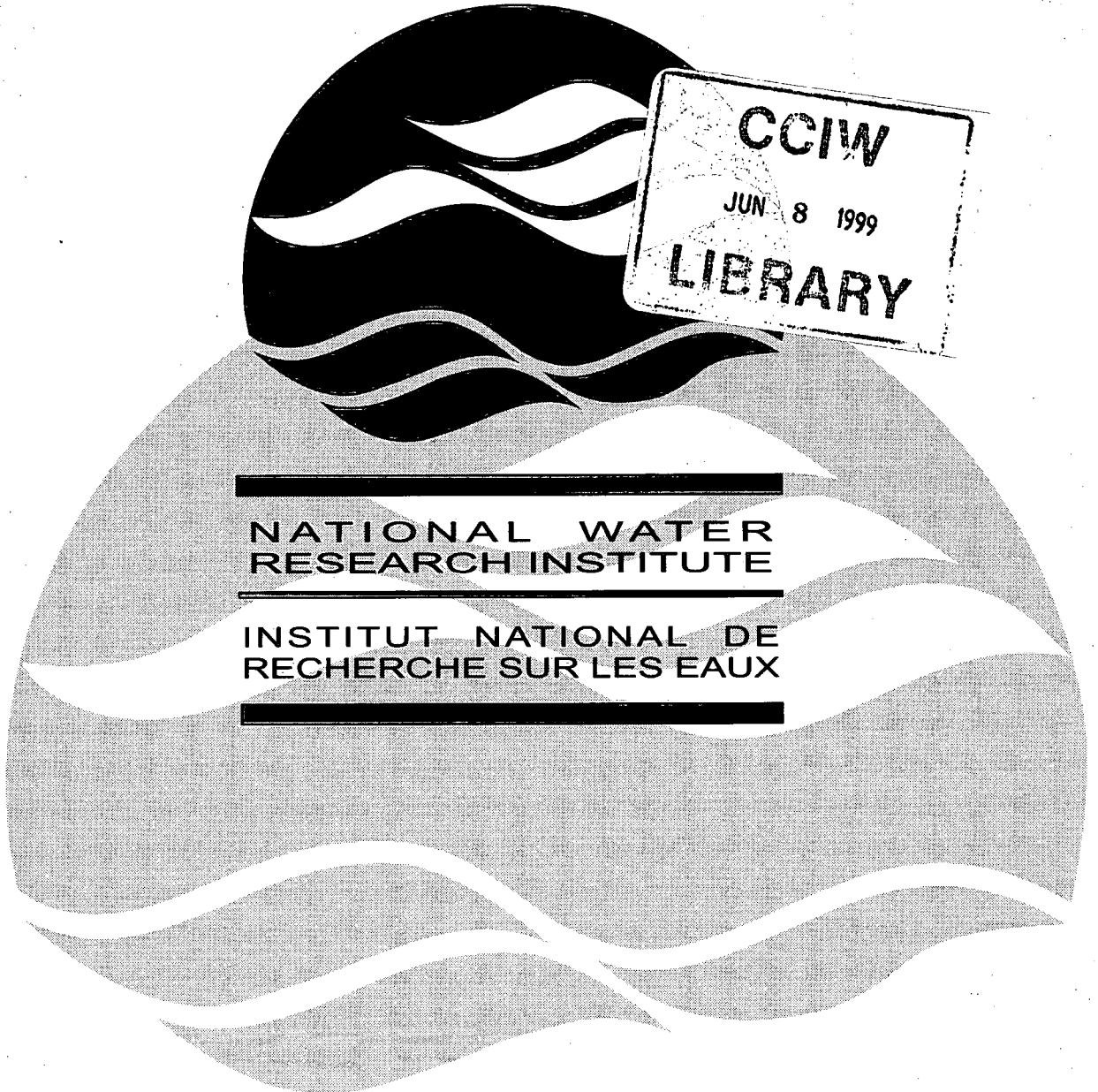


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**IMPACT OF ROAD SALTS ON SMALL URBAN  
PONDS: ROUGE RIVER POND CASE STUDY**

**Mayer, T., Q. Rochfort, U. Borgmann and M. Brown**

**NWRI Contribution No. 99-072**

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ROUGE RIVER POND CASE STUDY**

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## **MANAGEMENT PERSPECTIVE**

A comprehensive study was carried out to investigate the impacts of road salts on the benthic compartment of a small urban detention facility, Rouge River Pond. The Specific objective of the study was to document the porewater chemistry of an aquatic system affected by elevated salt concentrations and to carry out the toxicological assessment of sediment porewater to determine what factors may cause porewater toxicity. The purpose of the present report is to present results of the above study, which may be helpful in the mitigation of impacts of road salts on aquatic systems. This report contributes to the CEPA PSL2 assessment of road salts.

## **SOMMAIRE À L'INTENTION DE LA DIRECTION**

On a effectué une étude détaillée visant à déterminer les impacts des sels de voirie sur le milieu benthique d'une petite installation urbaine de retenue d'eau, le Rouge River Pond. L'étude visait spécifiquement à caractériser la chimie des eaux intersitnelles d'un milieu aquatique affecté par de fortes concentrations de sels et à réaliser l'évaluation toxicologique des eaux intersitnelles des sédiments pour déterminer quels facteurs peuvent les rendre toxiques. Le présent rapport présente les résultats de cette étude, qui pourraient s'avérer utiles en vue de l'atténuation des impacts des sels de voirie sur les milieux aquatiques. Ce rapport contribue à l'évaluation des sels de voirie qui s'inscrit dans le cadre de l'évaluation des substances de la LSIP2 de la LCPE.



## ABSTRACT

A comprehensive study was carried out to investigate the impacts of road salts on the benthic compartment of a small urban detention facility, Rouge River Pond. Although the pond is an engineered water body designed primarily for hydraulic flow management and stormwater treatment, it is representative of many small urban lakes, ponds and wetlands which receive road runoff and are probable high impact areas. Specific objective of the study was to document the porewater chemistry of an aquatic system affected by elevated salt concentrations and to carry out the toxicological assessment of sediment porewater to determine what factors may cause porewater toxicity. To meet the objectives porewater chemistry was determined and geochemical model was formulated to assess the salt impact on metal speciation. Solid phase metal chemistry was also assessed using Tessier's protocol. The benthic invertebrate *Hyalella azteca* was used as a test organism in the toxicity assessment. The results indicate that the sediment porewater which is in a steady state with the overlying water, enriched in inorganic salts, may itself attain high salt concentrations. The computations show that increased chloride levels have important implications on the Cd complexation, augmenting its concentration in porewater. The toxicity tests suggest that the toxicity in porewater is caused by metals rather than high levels of chloride or  $\text{NH}_4\text{-N}$ .

## RÉSUMÉ

On a effectué une étude détaillée visant à déterminer les impacts des sels de voirie sur le milieu benthique d'une petite installation urbaine de retenue d'eau, le Rouge River Pond. Bien que cet étang soit une masse d'eau artificielle conçue principalement pour le contrôle de l'écoulement hydraulique et le traitement des eaux pluviales, il est représentatif de nombreux petits lacs, étangs et milieux humides urbains qui reçoivent les eaux du ruissellement routier et qui sont susceptibles de faire l'objet d'impacts importants. L'étude visait spécifiquement à caractériser la chimie des eaux intersitnelles d'un milieu aquatique affecté par de fortes concentrations de sels et à réaliser l'évaluation toxicologique des eaux intersitnelles des sédiments pour déterminer quels facteurs peuvent les rendre toxiques. Pour atteindre ces objectifs, on a déterminé la chimie des eaux interstitielles et formulé un modèle géochimique visant à évaluer l'impact des sels sur la spéciation des métaux. On a aussi évalué la chimie des métaux en phase solide en appliquant le protocole de Tessier. On a utilisé pour l'évaluation de la toxicité l'invertébré benthique *Hyaella azteca*. Les résultats indiquent que les eaux interstitielles des sédiments qui sont en équilibre avec les eaux sus-jacentes, enrichies en sels inorganiques, peuvent elles-mêmes renfermer de fortes concentrations de sels. Les calculs montrent que les niveaux accrus de chlorure ont des effets marqués sur la complexation du Cd qui se traduisent par une augmentation de la concentration de ce métal dans les eaux interstitielles. Selon les tests de toxicité, la toxicité des eaux interstitielles est attribuable aux métaux plutôt qu'aux fortes concentrations de chlorure ou de  $\text{NH}_4\text{-N}$ .

# **IMPACT OF ROAD SALTS ON SMALL URBAN PONDS: ROUGE RIVER POND CASE STUDY**

## **1. INTRODUCTION**

Increased concern over contamination of surface waters by road salts and adverse effects of this group of contaminants on freshwater organisms lead to inclusion of "Road salts" on the second Priority Substances List (PSL2) under the Canadian Environmental Protection Act (CEPA). The susceptibility of aquatic systems to potential environmental impacts from road salts depends largely on the characteristics of the receiving water bodies. Small urban lakes and streams, wetlands, and man-made lakes which are being developed in urban and suburban areas are particularly vulnerable to degradation.

Presently, detention ponds remain the most widely used form of watershed management and many are operational in Toronto and other urban areas. Although these ponds were designed primarily for hydraulic flow management and stormwater treatment, they have also created wetland habitats for wildlife in urban areas and have become home to many species of plants, mammals, birds, amphibians and fish. These engineered water bodies are vulnerable to the same impacts as many small natural urban lakes.

Although some information exists on the adverse effects of road salts on aquatic organisms (Dickman and Gochbauer, 1978; Bailey, 1979; Crowther and Hynes, 1977) little is known about the effects of road salts on the benthic environment, particularly on porewater chemistry. Data on the toxicity of saline waters to benthic organisms are limited and date back to the 1970s. In view of the fact that the gradual buildup of a saline layer near the bottom of the lake would most impact the benthic environment, information is needed on the effect of salts on the benthic compartment of lentic systems. Sediment porewater chemistry is a particularly important part of this assessment. With this in mind, a study investigating salt impacts on small urban water bodies was initiated.

The Rouge River stormwater detention pond situated in the Rouge River Valley in the Greater Toronto Area, was selected for the investigation, as this pond has been extensively studied by various agencies (Marshall, Macklin, Monahan Ltd. 1993) and earlier investigations indicated elevated salt (NaCl) concentrations in the water column in this pond. Moreover, the pond is of interest because it is located in an area recognized for having significant tree cover, diverse flora and fauna and rare or unusual plant, bird and reptile species. The area has been designated as an ANSI (Area of Natural and Scientific Interest) and as a candidate Carolinian Canada site (Marshall, Macklin, Monahan Ltd. 1993).

## **2. PURPOSE AND OBJECTIVES**

The overall purpose of this study was to assess the impact of road salts on the benthic compartment of an aquatic system. Specific objectives include:

- 1) Characterization of the salt-laden lens in the water column;
- 2) Assessment of the sediment porewater chemistry;
- 3) Characterization of sediment metal chemistry using Tessier's protocol;
- 4) Formulation of a geochemical model;
- 5) Toxicological assessment of sediments, including porewater;

## **3. METHODS OF INVESTIGATION**

### ***Study Area***

The Rouge River stormwater detention pond is located in Scarborough, Ontario, east of Port Union Road and immediately south of Highway 401. The pond receives runoff from a major multilane divided highway (Hwy #401) and Hwy #2 as well as from a large urban catchment. The Rouge Pond is about 300 m long and 20-40 m wide. It consists of two

distinct parts: a sediment forebay (70 m long) and a laminar flow settling pond. The deepest part of this quiescent settling zone is about 3.5 m deep. Sediment and interstitial water (porewater) sampling was carried out in the deep part of the pond, in the vicinity of the pond outlet. The water depth, where the porewater samplers (referred to as peepers) were deployed was about 3.5 m. The investigation was carried out in August of 1998, at which time the temperature, conductivity and dissolved oxygen profiles were also obtained.

### *Porewater Collection and Analysis*

Several dialysis membrane samplers of interstitial water (porewater) were placed in the sediments and allowed to equilibrate with the sediment porewater for two weeks. The samplers were made of acrylic and fitted with a 0.45  $\mu\text{m}$  cellulose acetate membrane (Gelman Scientific, Inc.). Porewater samples were withdrawn from each cell immediately after retrieval using disposable syringes. They were transferred to polystyrene vials which contained appropriate sample preservative. Sampling was completed within 10 minutes of retrieval of peepers from sediments. Separate sets of samples were used for nutrient, metal, chloride, reactive silica ( $\text{RSiO}_2$ ) and sulfide analyses. The samples used for nutrient analyses were stored in vials containing 10  $\mu\text{l}$  of 7%  $\text{H}_2\text{SO}_4$ , and the samples used for metal analyses were preserved with 50  $\mu\text{l}$  of ultrapure Seastar concentrated  $\text{HNO}_3$ . Except for sulphides, further dilution was necessary for all analyses. The porewater samples were analyzed by the National Laboratory for Environmental Testing (NLET) in Burlington for soluble reactive phosphorus (SRP) which includes mostly  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  using an ascorbic acid technique. The acidity in final dilutions prior to SRP determinations was adjusted to yield 0.3%  $\text{H}_2\text{SO}_4$ . Ammonium-nitrogen ( $\text{NH}_4\text{-N}$ ), was determined by an o-tolidine method and includes also the ammonia-N ( $\text{NH}_3\text{-N}$ ). Chloride concentrations were determined using the thiocyanate colorimetric method which is based on the displacement of thiocyanate ion ( $\text{SCN}^-$ ) from mercuric thiocyanate by chloride ion and subsequent reaction of the liberated thiocyanate with ferric ion to form the coloured ferric thiocyanate complex.

Metals (Fe, Mn, Ca, Mg, Na, K, Sr, Ba, Al) were measured with an inductively coupled Ar plasma emission spectrophotometer (ICAP). Porewater samples, used for sulfide analyses, were transferred into vials containing 50  $\mu$ l (2 drops) of 1 M Zn-acetate and preserved with 20  $\mu$ l of 5 N NaOH. Sulfide was determined colorimetrically using the methylene blue method within 1 week in the laboratory.

Alkalinity of porewater samples was determined in the field using standardized  $H_2SO_4$  and a Hach digital titrator. Oxidation-reduction potential (Eh) and pH was determined in porewater immediately after retrieval in the field. A glass combination electrode calibrated against standard buffers (4 and 7) was used for pH measurements and a Pt/Ag/AgCl combination electrode calibrated against standardized (KCl/ $K_4Fe(CN)_6$  /  $K_3Fe(CN)_6$ ) solution was used for Eh measurements.

### *Sediment Collection and Analyses*

Several sediment cores were collected and transported to NWRI for cold storage (4°C). The collected cores were between 15 and 20 cm long. They were sectioned within 24 hours of retrieval and the sediment from the longest core was frozen and subsequently freeze-dried for chemical analysis. Sediment from another core was used for confirmation of pH and Eh values measured on porewater. Water content of sediments was determined in the top 10 cms and loss on ignition (LOI) was determined in the surficial sediments (gravimetrically) after ignition at 550°C in a muffle furnace for two hours. A bulk sediment sample (approximately 4 L) was also collected using a miniponar. The top 10-15 cm of sediment was collected for the toxicity tests and stored at 4°C until exposures began. The sediment used for toxicity tests was centrifuged at 10,000 RPM for 10 minutes to separate the porewater. A total of 500 ml of porewater was collected and split into two sub-samples. One subsample was filtered through a cellulose nitrate filter (45  $\mu$ m), the other subsample was left unfiltered for the toxicity tests.

The sequential extraction of Tessier et al. (1984) was used for partitioning of metals into fractions of different extractability. The extraction employed sequentially: 0.75 M LiCl/0.25 M CsCl in 60% methyl alcohol, 1M Na-acetate, 1M  $NH_2OH.HCl$  in

25% acetic acid, acidified (3 ml of 0.02 M HNO<sub>3</sub>) hydrogen peroxide, and finally *aqua regia*, followed by HF. The concentrations of metals in the extracts were determined by atomic absorption spectrophotometry. Two Lake Ontario sediments with known metal concentrations, each in replicates of two were run with the batch for quality control assurance.

### ***Toxicity Tests***

The benthic invertebrate *Hyaella azteca* was used as a test organism. Static non-renewal toxicity tests were run in replicates of two or three. Sample volume was limited to 125 ml per test flask. Twenty, 0-1 week old *Hyaella* were added to each 250 ml test flask, along with 5 mg ground Tetra-Min® fish food flakes and a 5 x 5 cm piece of cotton gauze as a substrate. The tests were carried out in an incubator at 25°C with a 16 h light/ 8h dark photoperiod. Toxicity tests included dechlorinated tap water used as a control and a reference solution containing 6 g/L of NaCl dissolved in dechlorinated tap water. Toxicity tests were carried out under aerobic conditions for 7 days.

## **4. RESULTS AND DISCUSSION**

### ***Water Column***

High conductivities were measured throughout the water column (Fig. 1). The conductivity increased from 1.65 mmhos/cm at the surface to 9.0 mmhos/cm just above the sediment-water interface. The dissolved oxygen (DO) measurements (1.0 mg/L) in the water column indicated anoxic conditions at a depth of 2.5 m and below (DO of 0.75 mg/L was measured at 3 m depth). The low DO conditions below the chemocline are consistent with the extremely low redox potentials, reported for the deep monimolimnia of meromictic lakes (Wetzel, 1975). The conductivity and DO data indicate chemically induced stratification causing meromixis.

Lakes or ponds which do not undergo complete circulation or where the upper strata do not mix with the lower portion are called meromictic. Sometimes mixing is inhibited by morphometric features, and at other times meromixis is maintained by chemical density gradients. Three types of meromixis have been recognized (Wetzel, 1975): ectogenic meromixis, crenogenic meromixis, and biogenic meromixis. Ectogenic meromixis results from external introduction of salt water into a freshwater body or fresh water into saline water body. In either case the less dense and less saline layer, mixolimnion overlies a stratum of more dense, more saline water, monimolimnion. Ectogenic meromictic lakes include freshwater lakes affected by influxes of marine water, and saline lakes in arid regions or in small depressions receiving infusion of freshwater during wet period or from irrigation. Anthropogenic activities, such as application of de-icing salts may also lead to the formation of ectogenic meromictic lakes. Crenogenic meromixis results from influx of saline water to the lake from submerged saline springs, usually in the deep portion of the basin. Lastly, biogenic meromixis results from an accumulation of salts originating from the decomposition of organic matter in sediments. This type of meromixis is common for lakes with small area and moderate depth in regions which experience long severe winters. As the conditions in the Rouge River Pond are brought about by runoff conveying road salt to the pond, it is clear that the Rouge Pond is an ectogenic meromictic water body.

As the water circulation within the Rouge River Pond, just like in any other water body, is to some degree susceptible to the wind action, design of the pond, particularly surface area and depth, are important factors affecting its efficiency and water quality within the pond. Presently, the wet ponds are designed with a depth between one and two meters, and a length to width ratio greater than 3:1 (Shaw et al., 1997). As the depth of the Rouge River Pond is greater than two meters (3.5 m), physical mixing of the water column by wind may be hindered, and chemical stratification induced by the input of road salts may be enhanced.



## **Sediments**

A sharp decrease in sediment water content was observed as the depth increased. The water content of sediments dropped from 66% at the sediment-water interface to about 20% at 10 cm depth. The organic content (5.53%) of forebay sediments (as determined by LOI) was lower than that of the settling pond sediments (7.10%). The sediment density 2.6 and 2.7 g/cm<sup>3</sup> of the upper sediments (1-2 cm and 10-11 cm, respectively) was consistent with their organic content, indicating that the bulk of sediment was of inorganic character. While meromictic conditions caused by salt water overlying deep water sediments existed at the time of sampling, no distinctive varves were observed.

Sediment accumulation was estimated from the average length of sediment core divided by period of accumulation. Assuming that the original stormwater pond was build around 1955-1960 (W. Snodgrass, personal communication), the average sediment accumulation rate was about 0.5 cm/year.

Overall, only a small population of invertebrates was found in forebay sediments, while none were found in the sediments from the laminar flow settling basin. The population consisted largely of nematodes and chironomids. The total biomass collected was approximately 0.02 g after freeze drying.

The total metal burden of benthic sediments was estimated as a sum of fractions using Tessier's protocol. Tessier et al. (1984) have demonstrated that reactivity and bioavailability of particle-associated heavy metals to aquatic biota depends on their physico-chemical association in sediments. They applied a sequential extraction procedure which is widely used to differentiate between various forms of metals. The procedure consists of five steps and operationally defines five fractions: exchangeable (FR 1), adsorbed or bound to carbonates (FR 2), bound to Fe-Mn oxides (FR 3), bound to organic matter (FR 4) and the residual (FR 5) fraction. The fractionation results for Cd, Cu, Pb, and Zn are presented in Table 1a-1d. Graphical presentation of partitioning of metals among different fractions is shown in Fig. 2. The results show that nearly 11% of Cd was

**Table 1a. Partitioning of cadmium in sediments from the Rouge River Pond**

| <b>SAMPLE DEPTH (cm)</b> | <b>FR 1<br/>µg/g</b> | <b>FR 2<br/>µg/g</b> | <b>FR 3<br/>µg/g</b> | <b>FR 4<br/>µg/g</b> | <b>FR 5<br/>µg/g</b> | <b>TOTAL Cd<br/>µg/g</b> |
|--------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|--------------------------|
| RP 0-1                   | 0.37                 | 1.10                 | 1.13                 | 0.22                 | 0.83                 | 3.66                     |
| RP 1-2                   | 0.46                 | 1.15                 | 1.42                 | 0.27                 | 0.74                 | 4.04                     |
| RP 2-3                   | 0.36                 | 1.16                 | 1.56                 | 0.34                 | 0.74                 | 4.16                     |
| RP 3-4                   | 0.51                 | 1.23                 | 1.47                 | 0.34                 | 0.79                 | 4.33                     |
| RP 4-5                   | 0.67                 | 1.22                 | 1.33                 | 0.31                 | 0.90                 | 4.43                     |
| RP 5-6                   | 0.41                 | 1.23                 | 1.19                 | 0.28                 | 0.76                 | 3.87                     |
| RP 6-7                   | 0.39                 | 1.11                 | 1.19                 | 0.29                 | 0.82                 | 3.81                     |
| RP 7-8                   | 0.46                 | 1.03                 | 1.12                 | 0.32                 | 0.86                 | 3.80                     |
| RP 8-9                   | 0.38                 | 1.17                 | 1.28                 | 0.29                 | 0.82                 | 3.95                     |
| RP 9-10                  | 0.31                 | 1.11                 | 1.20                 | 0.31                 | 0.87                 | 3.81                     |
| RP 10-11                 | 0.44                 | 1.24                 | 1.18                 | 0.38                 | 0.88                 | 4.12                     |
| RP 11-12                 | 0.43                 | 1.34                 | 1.10                 | 0.36                 | 0.81                 | 4.04                     |
| RP 12-13                 | 0.34                 | 1.06                 | 1.15                 | 0.23                 | 0.80                 | 3.58                     |
| RP 13-14                 | 0.36                 | 1.04                 | 1.00                 | 0.25                 | 0.84                 | 3.50                     |
| RP 14-15                 | 0.37                 | 1.09                 | 1.01                 | 0.31                 | 0.81                 | 3.59                     |

FR 1 exchangeable metals (Me)  
 FR 2 Me bound to carbonates  
 FR 3 Me bound to Fe - Mn oxides  
 FR 4 organically bound Me  
 FR 5 residual Me (bound to primary & secondary minerals)

| <b>SAMPLE DEPTH (cm)</b> | <b>FR 1<br/>% of T</b> | <b>FR 2<br/>% of T</b> | <b>FR 3<br/>% of T</b> | <b>FR 4<br/>% of T</b> | <b>FR 5<br/>% of T</b> | <b>TOTAL Cd<br/>% of T</b> |
|--------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|----------------------------|
| RP 0-1                   | 10.13                  | 30.06                  | 31.01                  | 6.01                   | 22.78                  | 100                        |
| RP 1-2                   | 11.46                  | 28.37                  | 35.24                  | 6.59                   | 18.34                  | 100                        |
| RP 2-3                   | 8.64                   | 27.86                  | 37.60                  | 8.08                   | 17.83                  | 100                        |
| RP 3-4                   | 11.76                  | 28.34                  | 33.96                  | 7.75                   | 18.18                  | 100                        |
| RP 4-5                   | 15.14                  | 27.42                  | 30.03                  | 7.05                   | 20.37                  | 100                        |
| RP 5-6                   | 10.48                  | 31.74                  | 30.84                  | 7.19                   | 19.76                  | 100                        |
| RP 6-7                   | 10.33                  | 29.18                  | 31.31                  | 7.60                   | 21.58                  | 100                        |
| RP 7-8                   | 12.20                  | 27.13                  | 29.57                  | 8.54                   | 22.56                  | 100                        |
| RP 8-9                   | 9.68                   | 29.62                  | 32.55                  | 7.33                   | 20.82                  | 100                        |
| RP 9-10                  | 8.21                   | 29.18                  | 31.61                  | 8.21                   | 22.80                  | 100                        |
| RP 10-11                 | 10.67                  | 30.06                  | 28.65                  | 9.27                   | 21.35                  | 100                        |
| RP 11-12                 | 10.60                  | 33.24                  | 27.22                  | 8.88                   | 20.06                  | 100                        |
| RP 12-13                 | 9.39                   | 29.77                  | 32.04                  | 6.47                   | 22.33                  | 100                        |
| RP 13-14                 | 10.26                  | 29.80                  | 28.48                  | 7.28                   | 24.17                  | 100                        |
| RP 14-15                 | 10.32                  | 30.32                  | 28.06                  | 8.71                   | 22.58                  | 100                        |
| average                  | 10.62                  | 29.47                  | 31.21                  | 7.66                   | 21.03                  | 100                        |

**Table 1b. Partitioning of copper in sediments from the Rouge River Pond**

| <b>SAMPLE DEPTH (cm)</b> | <b>FR 1<br/>µg/g</b> | <b>FR 2<br/>µg/g</b> | <b>FR 3<br/>µg/g</b> | <b>FR 4<br/>µg/g</b> | <b>FR 5<br/>µg/g</b> | <b>TOTAL Cu<br/>µg/g</b> |
|--------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|--------------------------|
| RP 0-1                   | 3.5                  | 4.2                  | 14.3                 | 35.6                 | 13.5                 | 71                       |
| RP 1-2                   | 4.0                  | 3.9                  | 19.8                 | 67.3                 | 19.9                 | 115                      |
| RP 2-3                   | 4.0                  | 3.6                  | 18.9                 | 82.3                 | 23.1                 | 132                      |
| RP 3-4                   | 4.0                  | 3.9                  | 17.7                 | 72.5                 | 20.3                 | 118                      |
| RP 4-5                   | 4.0                  | 4.0                  | 17.6                 | 56.4                 | 17.7                 | 100                      |
| RP 5-6                   | 4.0                  | 4.0                  | 13.2                 | 33.4                 | 13.0                 | 68                       |
| RP 6-7                   | 4.1                  | 4.2                  | 12.5                 | 22.9                 | 12.2                 | 56                       |
| RP 7-8                   | 4.1                  | 4.3                  | 13.1                 | 23.0                 | 12.4                 | 57                       |
| RP 8-9                   | 4.3                  | 4.1                  | 14.3                 | 23.1                 | 16.3                 | 62                       |
| RP 9-10                  | 4.3                  | 3.9                  | 15.3                 | 30.1                 | 15.2                 | 69                       |
| RP 10-11                 | 4.3                  | 4.0                  | 17.3                 | 31.5                 | 18.1                 | 75                       |
| RP 11-12                 | 4.2                  | 4.2                  | 12.8                 | 29.0                 | 14.0                 | 64                       |
| RP 12-13                 | 4.3                  | 4.5                  | 12.0                 | 20.1                 | 12.1                 | 53                       |
| RP 13-14                 | 4.5                  | 4.6                  | 10.1                 | 14.9                 | 10.1                 | 44                       |
| RP 14-15                 | 4.5                  | 4.4                  | 9.6                  | 15.8                 | 9.6                  | 44                       |

**FR 1** exchangeable metals (Me)  
**FR 2** Me bound to carbonates  
**FR 3** Me bound to Fe - Mn oxides  
**FR 4** organically bound Me  
**FR 5** residual Me (bound to primary & secondary minerals)

| <b>SAMPLE DEPTH (cm)</b> | <b>FR 1<br/>% of T</b> | <b>FR 2<br/>% of T</b> | <b>FR 3<br/>% of T</b> | <b>FR 4<br/>% of T</b> | <b>FR 5<br/>% of T</b> | <b>TOTAL Cu<br/>% of T</b> |
|--------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|----------------------------|
| RP 0-1                   | 5.0                    | 5.9                    | 20.2                   | 50.1                   | 18.9                   | 100                        |
| RP 1-2                   | 3.4                    | 3.4                    | 17.3                   | 58.6                   | 17.3                   | 100                        |
| RP 2-3                   | 3.0                    | 2.8                    | 14.3                   | 62.4                   | 17.5                   | 100                        |
| RP 3-4                   | 3.3                    | 3.3                    | 15.0                   | 61.3                   | 17.1                   | 100                        |
| RP 4-5                   | 4.0                    | 4.0                    | 17.6                   | 56.6                   | 17.7                   | 100                        |
| RP 5-6                   | 5.9                    | 5.9                    | 19.6                   | 49.3                   | 19.2                   | 100                        |
| RP 6-7                   | 7.3                    | 7.5                    | 22.4                   | 40.9                   | 21.8                   | 100                        |
| RP 7-8                   | 7.2                    | 7.6                    | 23.0                   | 40.4                   | 21.8                   | 100                        |
| RP 8-9                   | 6.9                    | 6.5                    | 23.0                   | 37.3                   | 26.3                   | 100                        |
| RP 9-10                  | 6.2                    | 5.6                    | 22.2                   | 43.8                   | 22.2                   | 100                        |
| RP 10-11                 | 5.7                    | 5.3                    | 23.0                   | 41.9                   | 24.0                   | 100                        |
| RP 11-12                 | 6.5                    | 6.5                    | 20.0                   | 45.2                   | 21.9                   | 100                        |
| RP 12-13                 | 8.1                    | 8.5                    | 22.6                   | 37.9                   | 22.8                   | 100                        |
| RP 13-14                 | 10.1                   | 10.3                   | 23.0                   | 33.8                   | 22.9                   | 100                        |
| RP 14-15                 | 10.2                   | 9.9                    | 21.9                   | 36.1                   | 21.9                   | 100                        |
| average                  | 6.2                    | 6.2                    | 20.3                   | 46.4                   | 20.9                   | 100                        |

**Table 1c. Partitioning of zinc in sediments from the Rouge River Pond**

| SAMPLE     | FR 1 | FR 2 | FR 3 | FR 4 | FR 5 | TOTAL Zn |
|------------|------|------|------|------|------|----------|
| DEPTH (cm) | µg/g | µg/g | µg/g | µg/g | µg/g | µg/g     |
| RP 0-1     | 1.17 | -    | 132  | 78   | 54   | 265      |
| RP 1-2     | 4.02 | 136  | 237  | 97   | 59   | 533      |
| RP 2-3     | 3.34 | 151  | 237  | 85   | 61   | 538      |
| RP 3-4     | 2.62 | 144  | 239  | 77   | 58   | 519      |
| RP 4-5     | 2.13 | 142  | 195  | 74   | 55   | 468      |
| RP 5-6     | 1.17 | 101  | 141  | 58   | 50   | 352      |
| RP 6-7     | 0.84 | 68   | 103  | 44   | 52   | 268      |
| RP 7-8     | 0.91 | 82   | 99   | 40   | 50   | 273      |
| RP 8-9     | 0.58 | 85   | 120  | 43   | 61   | 309      |
| RP 9-10    | 0.40 | 39   | 176  | 55   | 57   | 328      |
| RP 10-11   | 1.45 | 64   | 144  | 52   | 62   | 324      |
| RP 11-12   | 1.94 | 90   | 113  | 47   | 50   | 302      |
| RP 12-13   | 0.97 | 54   | 86   | 42   | 57   | 239      |
| RP 13-14   | 0.18 | 22   | 43   | 27   | 51   | 143      |
| RP 14-15   | 0.18 | 15   | 43   | 27   | 49   | 134      |

FR 1 exchangeable metals (Me)  
 FR 2 Me bound to carbonates  
 FR 3 Me bound to Fe - Mn oxides  
 FR 4 organically bound Me  
 FR 5 residual Me (bound to primary & secondary minerals)

| SAMPLE     | FR 1   | FR 2   | FR 3   | FR 4   | FR 5   | TOTAL Zn |
|------------|--------|--------|--------|--------|--------|----------|
| DEPTH (cm) | % of T | % of T | % of T | % of T | % of T | % of T   |
| RP 0-1     |        |        |        |        |        |          |
| RP 1-2     | 0.8    | 25.5   | 44.5   | 18.2   | 11.1   | 100      |
| RP 2-3     | 0.6    | 28.1   | 44.0   | 15.9   | 11.4   | 100      |
| RP 3-4     | 0.5    | 27.7   | 46.0   | 14.8   | 11.1   | 100      |
| RP 4-5     | 0.5    | 30.3   | 41.7   | 15.8   | 11.7   | 100      |
| RP 5-6     | 0.3    | 28.8   | 40.1   | 16.6   | 14.2   | 100      |
| RP 6-7     | 0.3    | 25.3   | 38.6   | 16.3   | 19.4   | 100      |
| RP 7-8     | 0.3    | 30.1   | 36.5   | 14.7   | 18.4   | 100      |
| RP 8-9     | 0.2    | 27.5   | 38.7   | 13.8   | 19.7   | 100      |
| RP 9-10    | 0.1    | 11.9   | 53.7   | 16.8   | 17.5   | 100      |
| RP 10-11   | 0.4    | 19.7   | 44.3   | 16.2   | 19.3   | 100      |
| RP 11-12   | 0.6    | 29.8   | 37.5   | 15.5   | 16.6   | 100      |
| RP 12-13   | 0.4    | 22.5   | 36.0   | 17.5   | 23.7   | 100      |
| RP 13-14   | 0.1    | 15.2   | 30.0   | 18.6   | 36.0   | 100      |
| RP 14-15   | 0.1    | 11.1   | 32.1   | 19.9   | 36.8   | 100      |
| average    | 0.4    | 23.8   | 40.3   | 16.5   | 19.1   | 100      |

**Table 1d. Partitioning of lead in sediments from the Rouge River Pond**

| SAMPLE<br>DEPTH (cm) | FR 1<br>µg/g | FR 2<br>µg/g | FR 3<br>µg/g | FR 4<br>µg/g | FR 5<br>µg/g | TOTAL Pb<br>µg/g |
|----------------------|--------------|--------------|--------------|--------------|--------------|------------------|
| RP 0-1               | n.d.         | 8.5          | 48.7         | n.d.         | 17.7         | 74.9             |
| RP 1-2               | n.d.         | 9.2          | 56.9         | n.d.         | 18.2         | 84.3             |
| RP 2-3               | n.d.         | 5.9          | 67.8         | 3.1          | 24.1         | 100.9            |
| RP 3-4               | n.d.         | 9.0          | 71.8         | 3.1          | 20.5         | 104.4            |
| RP 4-5               | n.d.         | 9.9          | 62.8         | n.d.         | 19.8         | 92.6             |
| RP 5-6               | n.d.         | 5.2          | 44.9         | n.d.         | 14.6         | 64.7             |
| RP 6-7               | n.d.         | 7.1          | 40.4         | n.d.         | 11.8         | 59.3             |
| RP 7-8               | n.d.         | 10.6         | 44.2         | n.d.         | 15.4         | 70.2             |
| RP 8-9               | n.d.         | 9.7          | 51.5         | n.d.         | 15.6         | 76.8             |
| RP 9-10              | n.d.         | n.d.         | 66.8         | 0.0          | 16.8         | 83.6             |
| RP 10-11             | n.d.         | 12.8         | 55.7         | n.d.         | 17.0         | 85.5             |
| RP 11-12             | n.d.         | 14.2         | 40.2         | n.d.         | 12.5         | 66.8             |
| RP 12-13             | n.d.         | 14.2         | 37.3         | n.d.         | 13.7         | 65.2             |
| RP 13-14             | n.d.         | 11.8         | 26.0         | n.d.         | 12.0         | 49.8             |
| RP 14-15             | n.d.         | 10.6         | 19.6         | n.d.         | 12.0         | 42.3             |

FR 1 exchangeable metals (Me)  
 FR 2 Me bound to carbonates  
 FR 3 Me bound to Fe - Mn oxides  
 FR 4 organically bound Me  
 FR 5 residual Me (bound to primary & secondary minerals)

| SAMPLE<br>DEPTH (cm) | FR 1<br>% of T | FR 2<br>% of T | FR 3<br>% of T | FR 4<br>% of T | FR 5<br>% of T | TOTAL Pb<br>% of T |
|----------------------|----------------|----------------|----------------|----------------|----------------|--------------------|
| RP 0-1               | 0.0            | 11.4           | 65.0           | 0.0            | 23.7           | 100                |
| RP 1-2               | 0.0            | 10.9           | 67.5           |                | 21.6           | 100                |
| RP 2-3               | 0.0            | 5.9            | 67.2           | 3.0            | 23.9           | 100                |
| RP 3-4               | 0.0            | 8.6            | 68.8           | 2.9            | 19.7           | 100                |
| RP 4-5               | 0.0            | 10.7           | 67.9           | 0.0            | 21.4           | 100                |
| RP 5-6               | 0.0            | 8.0            | 69.3           | 0.0            | 22.6           | 100                |
| RP 6-7               | 0.0            | 12.0           | 68.1           | 0.0            | 19.9           | 100                |
| RP 7-8               | 0.0            | 15.2           | 63.0           | 0.0            | 21.9           | 100                |
| RP 8-9               | 0.0            | 12.6           | 67.1           | 0.0            | 20.3           | 100                |
| RP 9-10              | 0.0            |                | 79.9           | 0.0            | 20.1           | 100                |
| RP 10-11             | 0.0            | 14.9           | 65.2           | 0.0            | 19.9           | 100                |
| RP 11-12             | 0.0            | 21.2           | 60.1           | 0.0            | 18.7           | 100                |
| RP 12-13             | 0.0            | 21.7           | 57.2           | 0.0            | 21.0           | 100                |
| RP 13-14             | 0.0            | 23.7           | 52.1           | 0.0            | 24.2           | 100                |
| RP 14-15             | 0.0            | 25.1           | 46.4           | 0.0            | 28.5           | 100                |
| average              | 0.0            | 18.4           | 83.3           | 3.4            | 29.0           |                    |

present in exchangeable fraction. No other heavy metal was so abundant in this fraction. Organically-bound Cd constituted the lowest fraction of the total Cd (8%). The remaining Cd was nearly evenly distributed between carbonate, Fe-Mn oxides and residual fractions. The relatively high proportion of exchangeable Cd probably reflects the complexing of Cd with chloride which is attributable to high chloride concentrations in sediment porewater. The highest fraction of Cu (46%) was found to be bound to organic matter, followed by equal portions (~20%) distributed between Fe-Mn oxides and residual fractions. Exchangeable and carbonate-bound fractions each accounted for 6% of total Cu. No detectable concentrations of Pb were found in the exchangeable fraction. Pb was distributed among remaining four fractions with the largest proportion of Pb (83%) bound to the Fe-Mn oxides, followed by the residual fraction. Only a small part of Pb (~3%) was organically bound. Barely detectable concentrations of Zn were present in the exchangeable fraction. The largest percentage of Zn (40%) was associated with Fe and Mn oxides. The rest of the Zn was nearly evenly distributed among the remaining three fractions. The metal partitioning in Rouge River Pond sediments was similar to that found in other sediments by Forstner (1993), Levy et al. (1992), and Tessier et al. (1980).

The summary of total metal concentrations are presented in Table 2. Cd, Cu, Pb and Zn show a marked enrichment in the upper 5 cm, where their concentrations (Table 2) are higher than the background levels of Lake Ontario sediments (1.8, 66, 70, 164  $\mu\text{g/g}$ , respectively, unpublished data) and those reported for surficial sediments from Toronto detention ponds in residential and open space catchments. They are just slightly lower than the concentrations reported for sediments from Col. S. Smith Pond, which is located in an industrial catchment and receives runoff from a multilane highway (Mayer et al. 1996). Road runoff is likely the main source of heavy metals entering the Rouge River Pond. The heavy metals come from road infrastructure itself and from vehicular traffic, e.g. tire wear (Cd, Pb, Zn), engine wear (Fe, Mn, Cu) and brake wear (Cu, Pb).

**Table 2. Total metal concentrations in sediments from Rouge River Pond**

| <b>SAMPLE<br/>DEPTH (cm)</b> | <b>Cd<br/>µg/g</b> | <b>Fe<br/>mg/g</b> | <b>Cu<br/>µg/g</b> | <b>Mn<br/>µg/g</b> | <b>Zn<br/>µg/g</b> | <b>Pb<br/>µg/g</b> |
|------------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| RP 0-1                       | 3.66               | 24.16              | 71.0               | 530.8              | 265.3              | 74.9               |
| RP 1-2                       | 4.04               | 25.98              | 114.8              | 505.9              | 532.7              | 84.3               |
| RP 2-3                       | 4.16               | 27.10              | 131.9              | 468.3              | 538.2              | 100.9              |
| RP 3-4                       | 4.33               | 25.50              | 118.3              | 530.0              | 519.5              | 104.4              |
| RP 4-5                       | 4.43               | 25.49              | 99.6               | 541.6              | 467.6              | 92.6               |
| RP 5-6                       | 3.87               | 25.19              | 67.6               | 558.2              | 351.6              | 64.7               |
| RP 6-7                       | 3.81               | 24.76              | 55.9               | 615.4              | 267.6              | 59.3               |
| RP 7-8                       | 3.80               | 23.46              | 56.9               | 583.7              | 272.7              | 70.2               |
| RP 8-9                       | 3.95               | 22.65              | 62.0               | 562.2              | 309.4              | 76.8               |
| RP 9-10                      | 3.81               | 23.13              | 68.7               | 539.8              | 327.7              | 83.6               |
| RP 10-11                     | 4.12               | 23.78              | 75.2               | 517.7              | 323.8              | 85.5               |
| RP 11-12                     | 4.04               | 19.97              | 64.1               | 471.4              | 301.8              | 66.8               |
| RP 12-13                     | 3.58               | 23.27              | 53.0               | 526.3              | 239.4              | 65.2               |
| RP 13-14                     | 3.50               | 22.98              | 44.2               | 562.5              | 142.5              | 49.8               |
| RP 14-15                     | 3.59               | 22.52              | 43.8               | 546.3              | 134.3              | 42.3               |

### *Porewater*

The porewater profiles of major dissolved constituents are presented in Fig. 3. The concentrations of Cl decrease gradually from about 3 g/L at the sediment water interface to about 1.5 g/L at 35 cm. A corresponding decline was observed in Na concentrations, which decrease from about 2 g/L at the interface to about 1 g/L at 35 cm depth. High concentrations of NH<sub>4</sub>-N (Fig. 3) were measured in porewater. The NH<sub>4</sub>-N concentrations are much higher than those in the water column of the meromictic prairie lake, Waldsea Lake, reported by Hammer (1984). They are also substantially higher than porewater concentrations reported for Lake Erie (2.7-5.4 mg/L, Azcue and Rosa, 1996, Matisoff et al. 1980). At the pH and temperature measured in the porewater only about 0.5% of the total NH<sub>4</sub>-N is present in unionized form (NH<sub>3</sub>-N). Presently, there are no Water Quality Guidelines for ammonia, however ammonia is one of the 25 substances included on the PSL2 of CEPA. Alkalinity increased with depth from about 550 mg/L

**Table 3. Concentrations of metals and sulfide in sediment porewater in Rouge River Pond**

| Depth<br>(cm) | Al<br>mg/L | Ba<br>mg/L | Cd<br>(mg/L) | Cu<br>(mg/L) | K<br>(mg/L) | Sr<br>(mg/L) | Pb<br>(mg/L) | Zn<br>(mg/L) | sulfide (S <sup>2-</sup> )<br>(mg/L) |
|---------------|------------|------------|--------------|--------------|-------------|--------------|--------------|--------------|--------------------------------------|
| -5            | 0.07       | 1.05       | 0.007        |              | 9.2         | 1.53         | 0.026        | 0.045        | 0.047                                |
| -4            | 0.06       | 1.12       | 0.007        | 0.027        | 8.9         | 1.60         | <0.005       | 0.025        | 0.039                                |
| -3            | 0.06       | 1.16       | 0.008        | 0.018        | 9.5         | 1.63         | 0.011        | 0.024        | 0.038                                |
| -2            | 0.06       | 1.03       | 0.008        | 0.006        | 9.0         | 1.58         | <0.005       | 0.018        | 0.040                                |
| -1            | 0.05       | 0.878      | 0.008        | 0.004        | 9.9         | 1.57         | 0.007        | 0.017        | 0.034                                |
| 0             | 0.04       | 0.714      | 0.008        | 0.005        | 9.9         | 1.49         | <0.005       | 0.029        | 0.032                                |
| 1             | 0.04       | 0.683      | 0.007        | 0.005        | 10.5        | 1.41         | 0.009        | 0.019        | 0.029                                |
| 2             | 0.05       | 0.730      | 0.007        | 0.008        | 10.4        | 1.38         | <0.005       | 0.031        | 0.042                                |
| 3             | 0.04       | 0.752      | 0.007        | 0.007        | 11.0        | 1.36         | 0.006        | 0.039        | 0.031                                |
| 4             | 0.03       | 0.757      | 0.007        | 0.007        | 10.2        | 1.32         | 0.009        | 0.015        | 0.021                                |
| 5             | 0.05       | 0.766      | 0.008        | 0.009        | 10.9        | 1.32         | 0.009        | 0.018        | 0.017                                |
| 6             | 0.06       | 0.787      | 0.008        | 0.007        | 10.4        | 1.33         | <0.005       |              | 0.016                                |
| 7             | 0.04       | 0.725      | 0.007        | 0.005        | 9.9         | 1.21         | 0.006        | 0.017        | 0.003                                |
| 8             |            |            |              |              |             |              |              |              | 0.016                                |
| 9             |            | 0.826      | 0.009        | 0.006        | 10.2        | 1.31         | 0.006        | 0.028        | 0.015                                |
| 10            | 0.06       | 0.887      | 0.010        | 0.008        | 11.3        | 1.39         | 0.008        | 0.033        | 0.005                                |
| 11            | 0.10       | 0.869      | 0.010        | 0.007        | 10.9        | 1.39         | 0.006        | 0.022        | 0.005                                |
| 12            | 0.04       | 0.839      | 0.010        | 0.011        | 11.4        | 1.40         | 0.009        | 0.024        | 0.003                                |
| 13            | 0.07       | 0.818      | 0.010        | 0.005        | 11.0        | 1.40         | 0.012        | 0.019        | 0.000                                |
| 14            | 0.04       | 0.823      | 0.009        | 0.006        | 11.8        | 1.45         | 0.011        | 0.020        | 0.003                                |
| 15            |            |            | 0.010        |              |             |              |              |              | 0.000                                |
| 16            | 0.04       | 0.800      | 0.010        | 0.008        | 11.4        | 1.45         | 0.008        | 0.030        | 0.014                                |
| 17            | 0.05       | 0.597      | 0.007        | 0.008        | 8.8         | 1.11         | <0.005       | 0.049        | 0.002                                |
| 18            | 0.05       | 0.776      | 0.010        | 0.007        | 11.2        | 1.45         | 0.009        | 0.032        | 0.002                                |
| 19            | 0.05       | 0.767      | 0.010        | 0.006        | 11.8        | 1.45         | 0.005        | 0.020        | 0.003                                |
| 20            | 0.05       | 0.773      | 0.010        | 0.005        | 11.4        | 1.46         | 0.005        | 0.032        | 0.007                                |
| 21            | 0.05       | 0.736      | 0.009        | 0.005        | 11.2        | 1.38         | 0.007        | 0.025        | 0.005                                |
| 22            | 0.02       | 0.810      | 0.010        | 0.006        | 11.4        | 1.49         | <0.005       | 0.020        | 0.008                                |
| 23            |            | 0.832      | 0.011        | 0.008        | 11.9        | 1.50         | 0.012        | 0.024        |                                      |
| 24            | 0.01       | 0.793      | 0.009        | 0.007        | 10.4        | 1.40         | <0.005       | 0.015        |                                      |
| 25            | 0.03       | 0.774      | 0.009        | 0.007        | 10.2        | 1.34         | 0.005        | 0.016        | 0.005                                |
| 26            | 0.05       | 0.895      | 0.011        | 0.007        | 11.2        | 1.52         | 0.01         | 0.060        | 0.016                                |
| 27            | 0.04       | 0.883      | 0.011        | 0.005        | 11.2        | 1.49         | <0.005       | 0.018        |                                      |
| 28            | 0.03       | 0.911      | 0.010        | 0.008        | 10.9        | 1.53         | <0.005       | 0.029        | 0.003                                |
| 29            | 0.05       | 0.770      | 0.008        | 0.005        | 9.7         | 1.31         | <0.005       | 0.015        | 0.005                                |
| 30            | 0.02       | 0.757      | 0.008        | 0.005        | 9.2         | 1.30         | <0.005       | 0.015        | 0.013                                |
| 31            | 0.07       | 0.787      | 0.009        | 0.007        | 10.2        | 1.41         | <0.005       | 0.020        | 0.011                                |
| 32            | 0.03       | 0.789      | 0.010        | 0.008        | 10.2        | 1.49         | 0.007        | 0.039        | 0.027                                |
| 33            | 0.09       | 0.739      | 0.010        | 0.007        | 10.4        | 1.48         | <0.005       | 0.022        |                                      |
| 34            | 0.03       | 0.733      | 0.011        | 0.009        | 9.8         | 1.51         | 0.008        | 0.022        |                                      |
| 35            |            | 0.716      | 0.012        | 0.012        | 10.2        | 1.54         | 0.012        |              |                                      |



CaCO<sub>3</sub> at the interface to just over 900 mg/L in deeper porewater. Corresponding increases with depth were observed for the Ca and Mg concentrations (Fig. 3). A small increase in pH (from 6.9 to 7.2) with depth was also noted. Slight variation (between -65 and -80 mV) was observed in the Eh values, but there was no consistent increasing or decreasing trend.

A marginal decline in sulfide concentrations from the sediment-water interface downward was observed. In general, the sulfide concentrations were very low (0.002-0.032 mg/L, Table 3). While the concentrations of Cu, Zn, and Cd, in porewater are low and Pb is barely detectable (Table 3), very high concentrations of Fe and Mn were observed in the porewater (Fig. 3). The Fe and Mn concentrations are substantially higher than those observed in Lake Erie porewater (Rosa and Azcue, 1996) or those reported by Carignan and Nriagu (1985) in porewater from two Sudbury area lakes. High concentrations of Fe in porewater probably result from a large pool (20%) of hydroxylamine hydrochloride reducible Fe, FR 3 in sediments. The Fe concentrations increased with depth from about 50 mg/L to nearly 100 mg/L. Concentrations of Fe 4-12 mg/L were reported for Lake Erie porewater (Rosa and Azcue, 1996), while Fe concentrations up to 22.5 mg/L were reported by Carignan and Nriagu (1985). While the levels of Cu, Pb and Zn were all below the toxicity criteria for *Hyalella*, Cd concentrations did exceed the toxicity criteria (Table 4).

**Table 4. Water Quality and Toxicity Criteria. All values are in µg/L.**

| Metal | 1978 Water Quality Agreement<br>and 1984 Ontario Provincial<br>Water Quality Objectives | 1-week LC50 for<br><i>Hyalella</i> | 4-week LC25 |
|-------|---|------------------------------------|-------------|
| Fe    | 300   | NA                                 | NA          |
| Cd    | 0.2   | 7.6                                | 0.4         |
| Cu    | 5   | 140                                | 21          |
| Pb    | 25  | 120                                | 9           |
| Zn    | 30  | 400                                | 110         |
| Mn    | NA  | NA                                 | NA*         |

\*Mn LC25 possibly >500 µg/L- preliminary data (Borgmann).

### ***Geochemical Model***

The chemical form of metals is a major factor in their geochemical behavior, transport, bioavailability, and toxicity (Chau and Wong, 1976). The mobility and bioavailability of dissolved metals is greater than those of particulate metals. The metal in dissolved form consists of the free metal ( $Me^{r+}$ ) and metal complexed by the ligands in solution (Nriagu and Gaillard, 1984). Its concentration in porewater can be expressed as:

$$Me_{diss} = Me^{r+} + \sum_j \sum_n \alpha_j C_{j,n}$$

where  $\alpha_j$  is number of metal ions in the  $j$ th species and  $C_{j,n}$  is the concentration of  $j$ th complex (Nriagu and Gaillard, 1984). The  $C_{j,n}$  is a function of the metal and  $j$ th ligand concentrations and the association constant. As seen from the equation above, complexation by inorganic ligands increases the concentration of metals in solution and plays an important role in dissolved metal speciation (Stumm and Morgan, 1981).

The speciation of metals in porewater was determined using the geochemical speciation program MINTQA2 (Alison et al., 1992). The metal binding ligands considered in the model were  $OH^-$ ,  $Cl^-$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $PO_4^{3-}$ . The same program was used to assess the degree of saturation of porewater with respect to potential mineral phases controlling the concentrations of heavy metals in porewater.

Input consisted of the measured concentrations of Cl, Fe, Ca, Mg, Na, K, Al, Mn, Ba, Sr,  $NH_4$  and  $RSiO_2$ . SRP values were used for the  $PO_4$ -P. Concentrations of trace metals Cd, Cu, Zn and Pb were also included in the input. Measured alkalinity was entered as mg/L  $CaCO_3$ . Measured Eh and pH and temperature measured in the field, 16°C were used in calculations.

The output files for each depth were recorded and average percentage values for each dissolved species were calculated from all depths. The computation results show that chloro complexes accounted for the highest percentage of the dissolved Cd (56%),

followed by carbonate complexes (26%). 17% of dissolved Cd was present as a free ion. The principal dissolved Cu and Pb species were carbonates (89%, 95%, respectively), the remaining Cu was nearly evenly split between the free Cu and hydroxy complex  $\text{Cu}(\text{OH})_2$ , while Pb was evenly split between free Pb and  $\text{PbCl}^+$ . Slightly more than half of Zn (59%) was present in carbonate complexes, about 39% of dissolved Zn was present as free  $\text{Zn}^{2+}$  and only a minute fraction (2%) was present as  $\text{ZnCl}^+$ . The thermodynamic computations show that  $\text{CuCO}_3$  and  $\text{PbCO}_3$  complexes predominate in Cu and Pb systems affected by road salts. Carbonates are also important complexes in Zn system, while chloro complexes are the most stable species in Cd(II) systems with elevated chloride concentrations. In general, carbonate complexes increased slightly with depth, while an opposite trend was observed for the free metal ions and chloro complexes. The computation shows that the increased chloride levels have important implications on the Cd complexation, augmenting its concentration in porewater.

Porewater composition is a sensitive indicator of chemical reactions and equilibria between solid phases and dissolved species (Matisoff et al., 1980). The precipitation/dissolution of mineral phases depends on the degree of porewater saturation with respect to potential mineral phases controlling the concentrations of heavy metals in porewater. The degree of porewater saturation with respect to a mineral phase is measured by the saturation index (SI), through which the actual ion activity product (IAP) may be compared with the solubility constant ( $K_{sp}$ ) of the solid phase ( $\text{SI} = \log \text{IAP}/K_{sp}$ ). The SI values were calculated by MINTEQA2. Values of  $\text{SI} > 0$ ,  $= 0$  and  $< 0$  indicate that the  $\text{IAP} > K_{sp}$ ,  $\text{IAP} = K_{sp}$ , and  $\text{IAP} < K_{sp}$ , and the porewater is supersaturated, saturated and undersaturated, respectively, with respect to the mineral phase considered. Solubility constants of potential authigenic mineral phases from the MINTEQA2 data base used in calculation are shown in Table 5.

Concentration of Fe in anoxic porewater appears to be controlled by siderite (Fig. 4). As seen in Fig. 4 porewater is supersaturated with respect to siderite by about two orders of magnitude over the entire porewater profile. It is also supersaturated with respect to vivianite. These phases would therefore be expected to precipitate in sediments.

The calculated SI values of cerrussite and smithsonite (Fig. 4), the Pb and Zn carbonates show that porewater is undersaturated with respect to these phases and they would not be expected to control the concentrations of these metals in porewater. The SI value of otavite is near equilibrium at the sediment-water interface and becomes slightly supersaturated with depth. This phase would be expected to control the Cd concentration in porewater.

**Table 5. Solubility constants of potential authigenic mineral phases used for MINTEQA2 calculations.**

| Mineral       | Formula   | log $K_{sp}$ | Reference         |
|---------------|---|--------------|-------------------|
| Calcite       | CaCO <sub>3</sub>   | -8.47        | MINTEQA2 database |
| Dolomite      | CaMgCO <sub>3</sub>   | -17.00       | MINTEQA2 database |
| Siderite      | FeCO <sub>3</sub>   | -10.55       | MINTEQA2 database |
| Rhodochrosite | MnCO <sub>3</sub>   | -10.41       | MINTEQA2 database |
| Magnesite     | MgCO <sub>3</sub>   | -8.03        | MINTEQA2 database |
| Nesquehonite  | MgCO <sub>3</sub> · 3H <sub>2</sub> O                               | -5.62        | MINTEQA2 database |
| Smithsonite   | ZnCO <sub>3</sub>   | -10.00       | MINTEQA2 database |
| Otavite       | CdCO <sub>3</sub>   | -13.74       | MINTEQA2 database |
| Cerrussite    | PbCO <sub>3</sub>   | -13.13       | MINTEQA2 database |
| Vivianite     | Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> · 8H <sub>2</sub> O | -26.40       | MINTEQA2 database |
| Strengite     | FePO <sub>4</sub> · 2H <sub>2</sub> O                               | -36.00       | MINTEQA2 database |
| Gibbsite      | Al(OH) <sub>3</sub>   | 8.77         | MINTEQA2 database |

The geochemical model suggests that porewater is slightly undersaturated with respect to dolomite, near the sediment surface, but saturation increases with depth. However porewater is supersaturated with respect to calcite and rhodochrosite (Mn carbonate). Slight supersaturation with respect to calcite in hard waters is apparently not uncommon (Matisoff et al. 1980). While the interstitial waters were supersaturated with respect to iron minerals such as goethite (log  $K_{sp}$ =0.50) and lepidocrocite (log  $K_{sp}$ =1.37), it is unlikely that these minerals would form in anoxic sediments. Both mineral phases are alteration products of iron bearing minerals which form under oxidizing conditions.

### ***Toxicological Assessment***

Ideally, *in situ* toxicity tests would provide the best assessment of sediment toxicity. However, this is not feasible, as toxicity tests follow strict protocols, which are only viable under the laboratory conditions. *Hyaella* was used as a test organism, as this amphipod is a common test species for sediment toxicity assessment (Borgmann and Borgmann, 1997). The attempt of the toxicity tests was to assess the importance of NaCl toxicity versus toxicity of other porewater constituents to benthic organisms. While the tested unfiltered porewater and the reference solution, containing 6 g/L of NaCl had similar chloride concentrations and conductivity (11,300 and 11,400  $\mu\text{mhos/cm}$ , respectively) noticeable differences were observed in their toxicity. The final live count of *Hyaella* showed a 100% survival of tested organisms in the reference solution, while 0% survival was observed in undiluted porewater (Fig. 5). The LC50 of aerated filtered and unfiltered porewater was estimated using the Trimmed Spearman/Karber Method. LC50 of unfiltered porewater was 11% with a 95% confidence interval between 9% and 16%. Filtering the porewater reduced toxicity to an LC50 of 29%, with 95% confidence limits between 22% and 39%. The chemical analyses of both samples indicated similar pH,  $\text{NH}_4^+\text{-N}$  and chloride concentrations which was expected, as chlorides and ammonium salts are highly soluble. The main differences between the filtered and unfiltered porewater were the higher concentrations of Fe in unfiltered samples. The filtered samples had nearly 50 times lower Fe concentrations than unfiltered samples. The thermodynamic computation indicates that 99% of Fe and 81% of Mn in porewater is present as free species  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ . These species of metals are highly toxic to aquatic organisms. Moreover, Cd concentrations in porewater exceeded the WQA toxicity criteria (Table 4). Thus, it seems that the toxicity in porewater is probably caused by metals rather than NaCl, however more toxicity testing needs to be done to systematically identify the factors causing porewater toxicity. Wenholz and Crunkilton (1995) used toxicity identification evaluation (TIE) procedures to assess the toxicity of sediment porewater from a stormwater detention pond in Madison Wisconsin. A similar approach could be adopted in future toxicity tests.

## 5. CONCLUSIONS AND RECOMMENDATIONS

### *Conclusions*

Chemical and toxicological investigation of the Rouge River Pond was carried out to fill a paucity of information on the effect of road salts on the chemistry and toxicity of sediment porewater. The investigation revealed that sediment porewater which is in a steady state with the overlying water, enriched in inorganic salts, may itself attain high salt concentrations. At the sediment-water interface concentrations of Cl higher than 3g/L and Na about 2g/L were measured in porewater. A gradual decrease was observed for both ions, however even at the depth of 40 cm below the water-sediment interface the Cl concentrations were about 1.5 g/L. The porewater was considerably enriched in  $\text{NH}_4\text{-N}$ , Fe and Mn. High levels of Fe in porewater result probably from a large pool (20%) of hydroxylamine hydrochloride reducible Fe (FR 3) in sediments.

The metal speciation reveals that nearly all the Fe (99%) and most of Mn (81%) in porewater is present as free species  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ , the free species of metals being the most toxic to aquatic organisms. The thermodynamic calculations indicate that chloro complexes are the most stable species in the Cd(II) systems with elevated chloride concentrations. Thus, the fact that Cd concentrations in porewater exceeded the toxicity criteria may be due to Cd complexation by Cl ligands.

Toxicity tests using the benthic organism *Hyalella* suggest that the toxicity in porewater is caused by metals rather than high levels of chloride or  $\text{NH}_4\text{-N}$ .

### *Recommendations*

The present study revealed substantial accumulation of salts in sediment porewater. To better assess the impacts of road salts on the surface waters, additional work is needed to document the chloride levels in water immediately overlying benthic sediments in small urban lakes and ponds in the winter, as these are the aquatic systems most vulnerable to

degradation. Additional toxicity tests using a TIE approach should be carried out to more specifically isolate the factors causing porewater toxicity in salt-enriched systems. Additional toxicity tests should include other test organisms such as *Daphnia magna* and *Ceriodaphnia dubia*. Furthermore, endpoints other than acute mortality should be used for the toxicity tests to evaluate the toxic impacts on aquatic organisms.

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## **FIGURES**

### Rouge Pond Scarborough

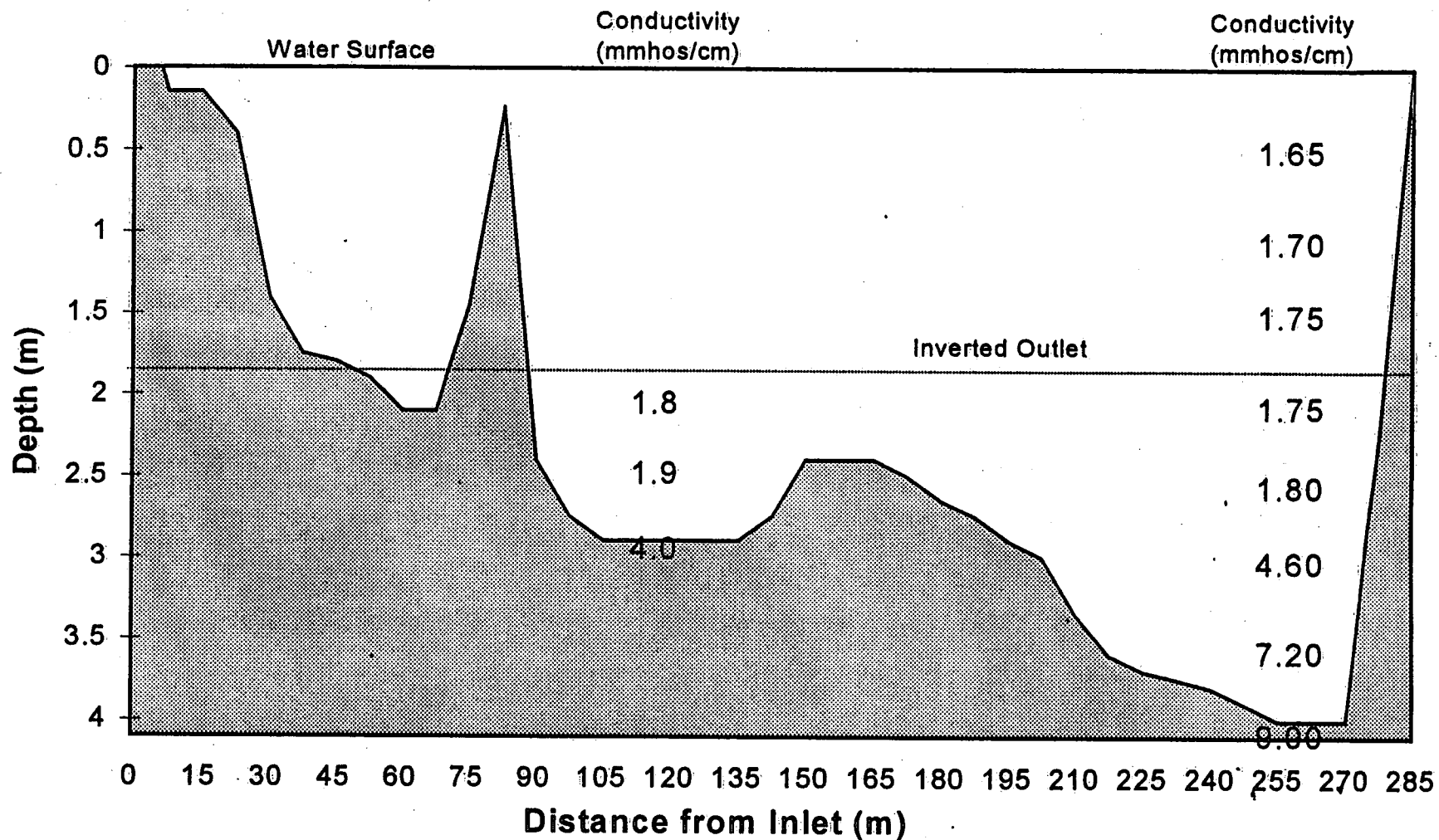


Fig. 1: Profile of Rouge River Pond

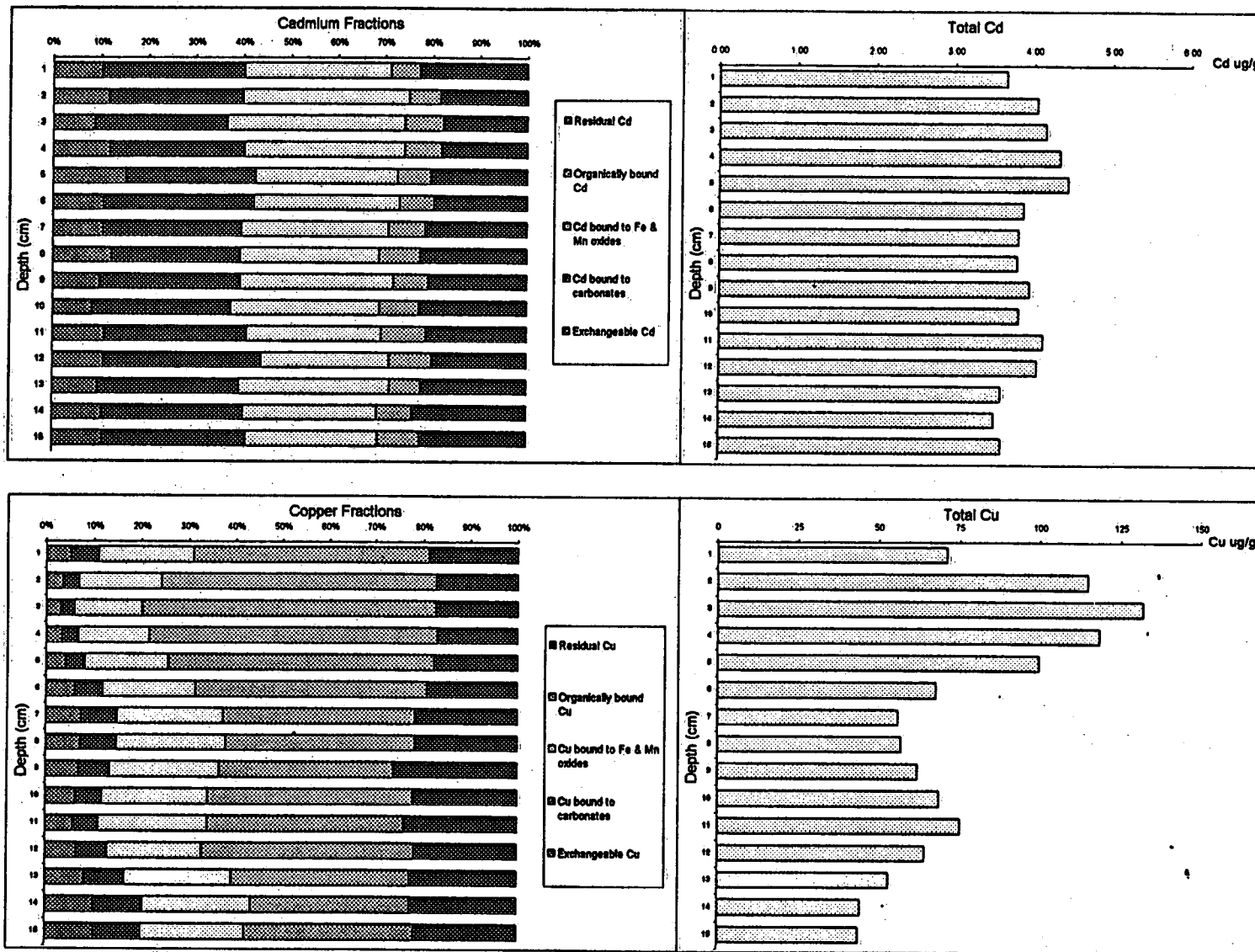


Fig. 2: Partitioning and Total Concentrations of Cd and Cu in Sediments from the Rouge River Pond

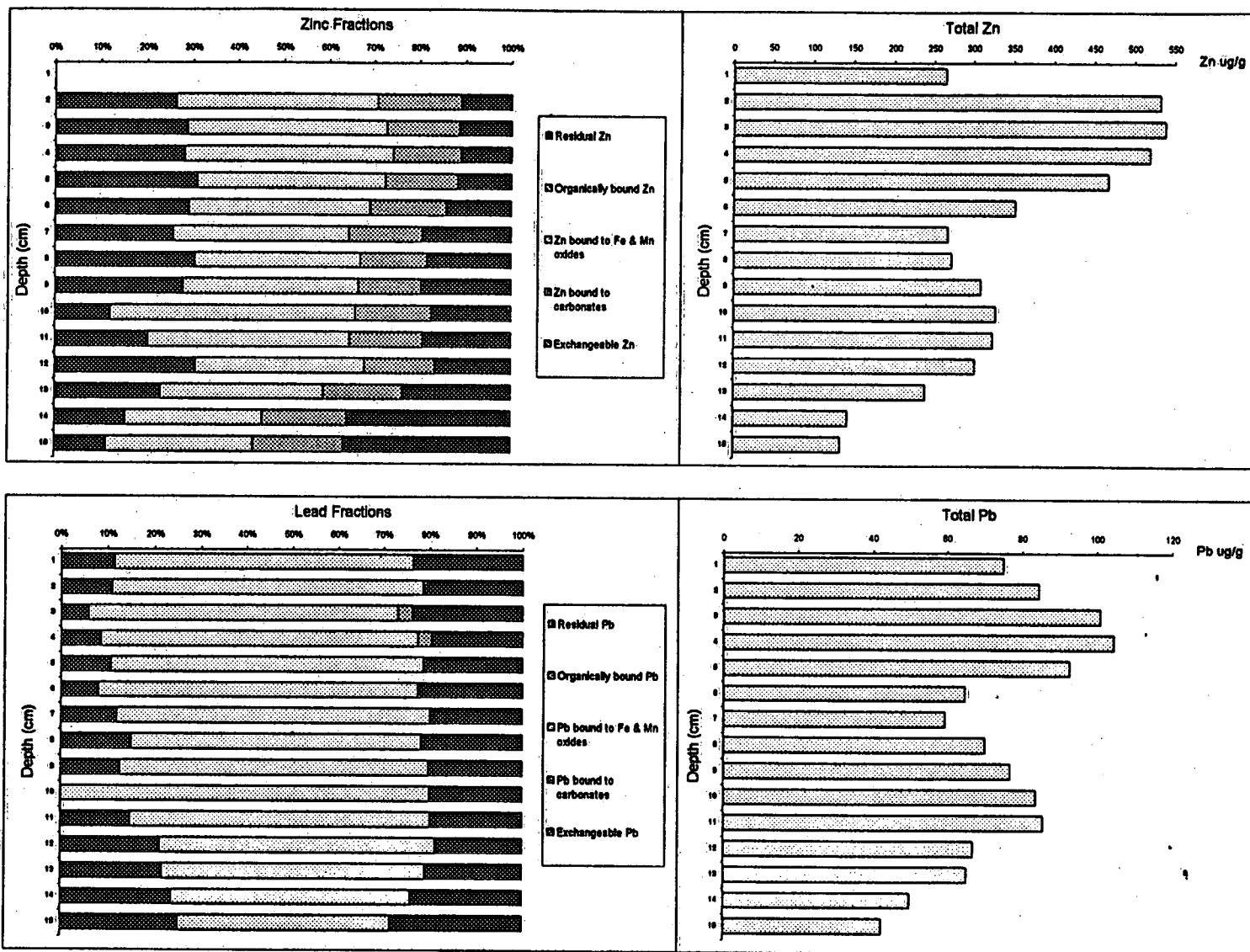


Fig. 2 Cont: Partitioning and Total Concentrations of Zn and Pb in Sediments from the Rouge River Pond

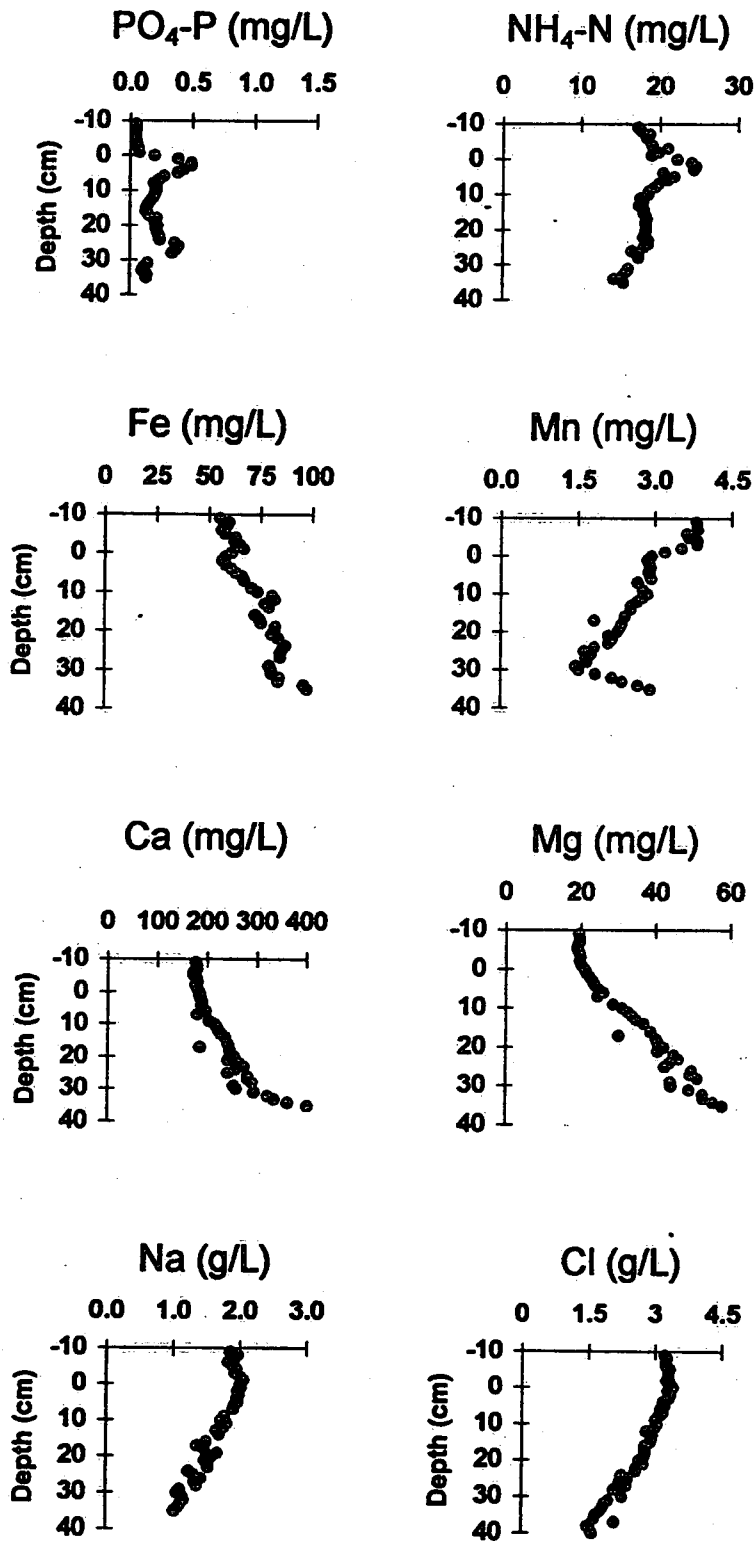


Fig.3 Porewater profiles for major dissolved constituents

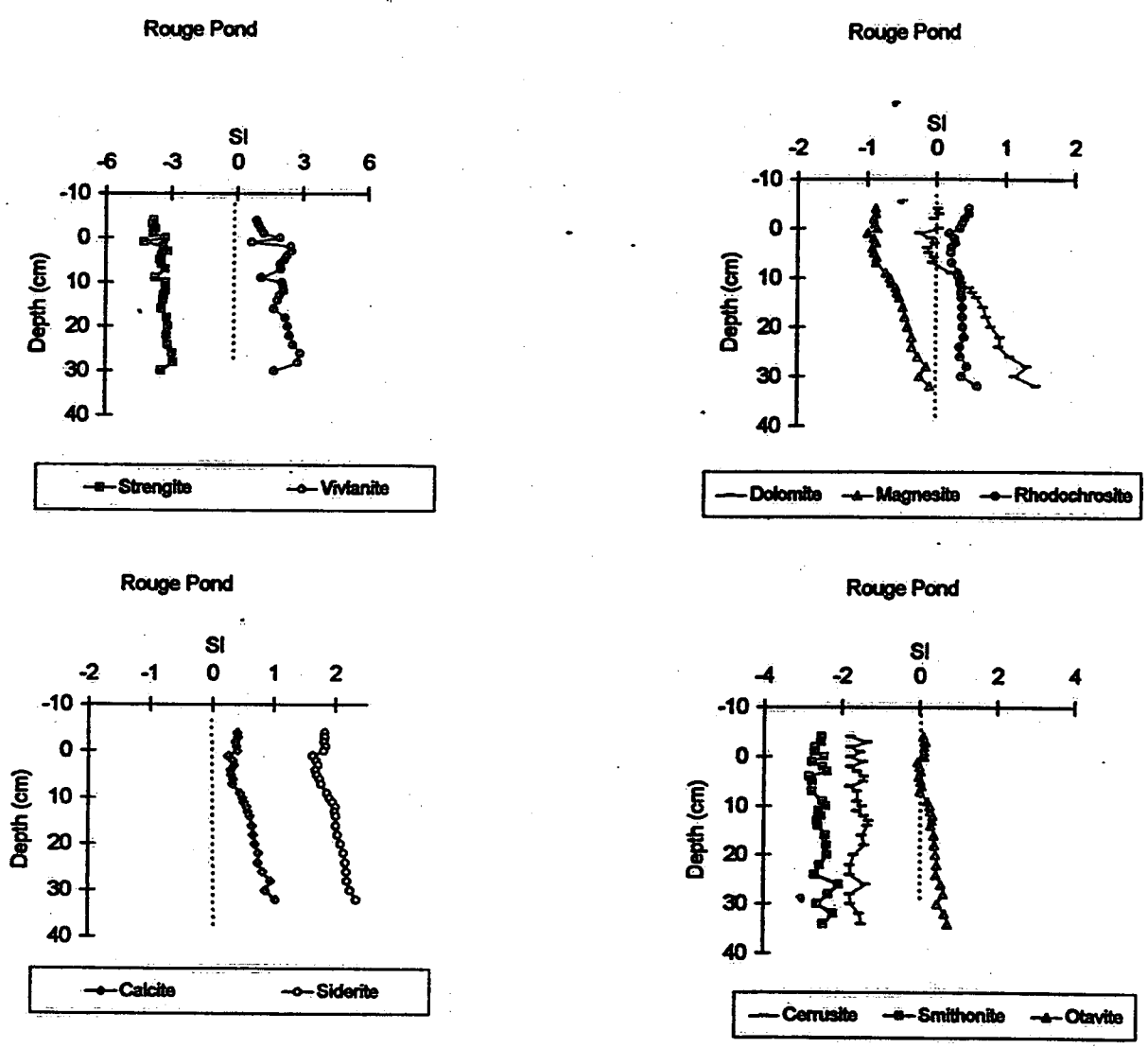


Fig. 4 Saturation indices for various minerals

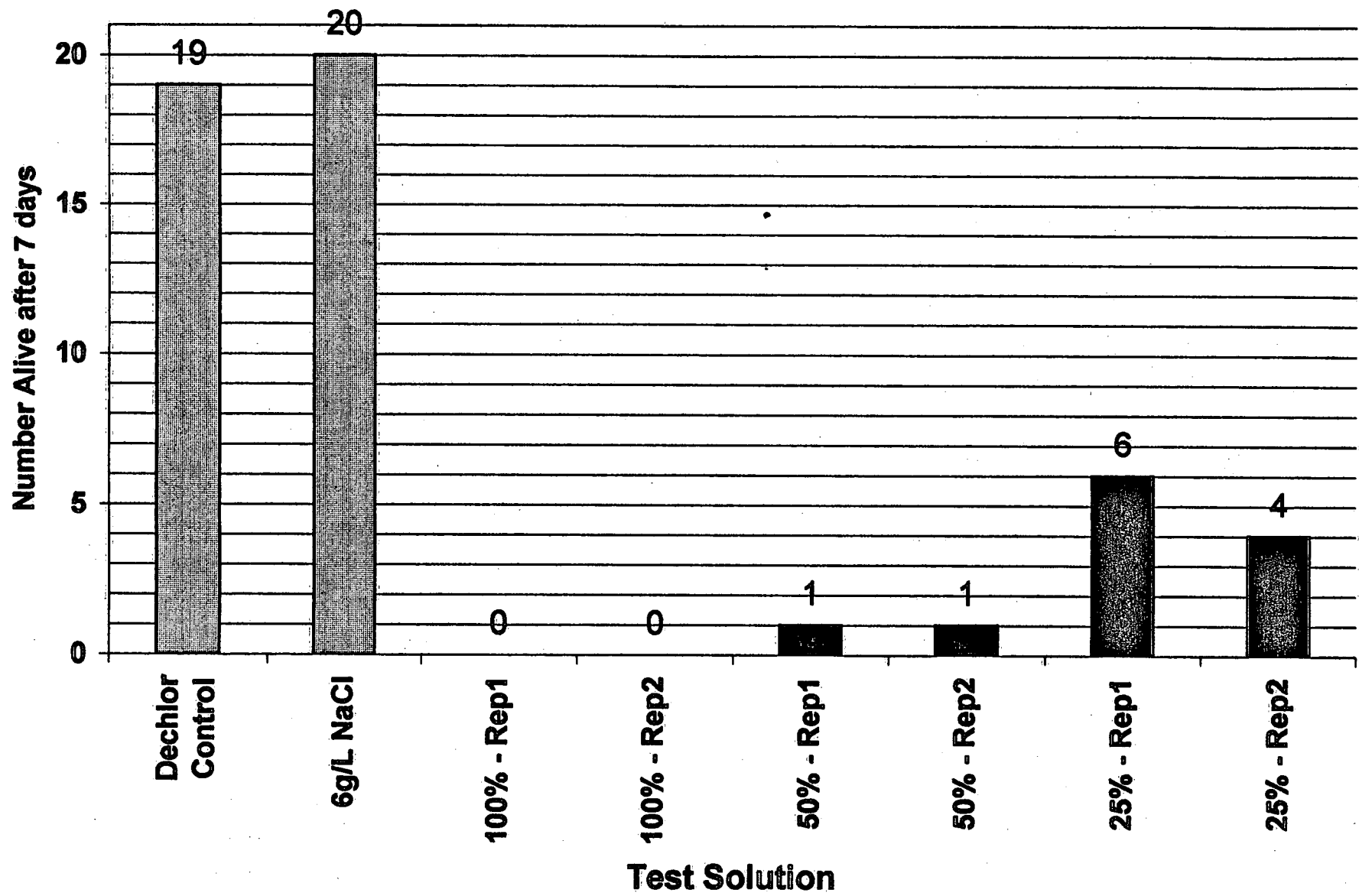
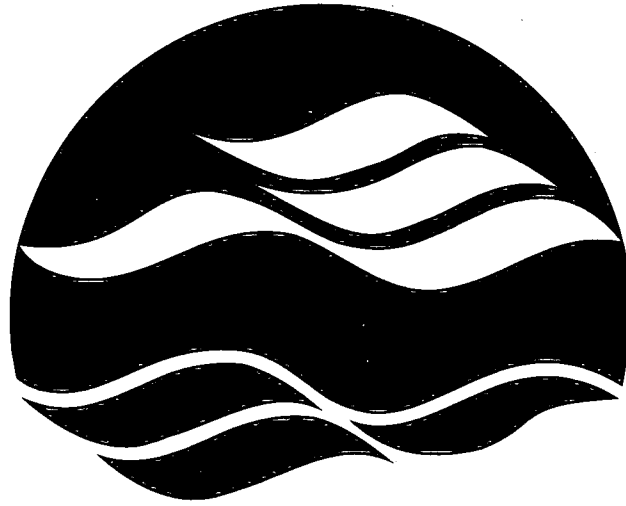


Fig. 5 Toxicity test results showing the survival of *Hyalella*





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