

**Metal Mobility in a Stormwater Detention Pond:
Investigating Metal Mobility and Sediment-Water Exchange**

by

Shannon Lynne Vickers

**A thesis submitted in conformity with the requirements for the degree of Master of Science,
Graduate Department of Geography, University of Toronto**

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Abstract

Surface and pore water samples were taken from a stormwater detention pond in Richmond Hill, Ontario, to determine the mobility of sediment-bound cationic metals on a seasonal basis. Analyses of surface waters indicated that the stormwater detention pond behaved as sink for nutrients, except total phosphorus, and trace metals as intended. However, low dissolved oxygen, and very high total phosphorus, chloride, ammonia; and some trace metals make the pond a challenging environment for biota. Occasionally Cu, Fe, and Zn exceeded recommended Provincial Water Quality Objectives. An increase of 50 – 60 % in trace metal concentrations occurred during the winter. Plotting of pore water profiles and diffusive flux calculations indicated an upward flux of trace metals from the sediments that were recycled and precipitated to the sediments as Fe and Mn oxides throughout the summer, fall, and spring. A downward flux of trace metals into the sediments occurred during the winter.

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1.0 INTRODUCTION

It is well recognised that urban runoff contains a wide array of chemicals at concentrations that can cause deleterious effects. Higher pollutant levels are associated with more intensive development such that urban runoff pollutant levels may be comparable to secondary treated wastewater effluent (Scholes et. al., 1998). Nutrients, trace metals, and synthetic organic compounds from runoff can accumulate in the sediments and biota of receiving waters (William et. al, 1995). In terms of natural wetlands, this process of chemical accumulation has led to cleaner water at the expense of wetland ecosystem quality (Shaw et. al., 1997). To avoid these problems with natural wetlands, government policies have promoted the use of stormwater detention ponds as they are considered a compromise between the preservation of existing natural systems and exploitation of the biological and physicochemical processes that remove contaminants from water (Debusk et. al., 1996).

Stormwater detention ponds were originally designed for stormwater quantity mitigation. However, recently developed ponds have been designed for mitigating contaminants within stormwater as well. Hence, polluted urban stormwater is routed through the stormwater detention pond which then acts as a pollution control device by allowing pollutants to settle or decay (Shaw et. al., 1997). It is for this reason that the Ontario Ministry of the Environment has included the implementation of stormwater detention ponds (SDPs) as a best management practice in its mandate to mitigate stormwater runoff in newly developed areas of Ontario (MOEE, 1991a). The construction of SDPs for stormwater management has been viewed as a feasible solution to improve water quality in urban and rural environments (MOEE, 1992). While these SDPs appear to be a cost-effective and reasonable means of dealing with urban runoff, the

expectations of their role as a water treatment option are high. For example, Makos and Hrnčir (1995) state:

“While SDPs efficiently remove many pollutants from urban wastewater streams, SDPs also greatly enhance the environment by providing a habitat for vegetation, fish, birds, and other wildlife.”

Helfield and Diamond (1997) have raised concerns that achieving the objectives of water quality improvement and provision of habitat may not be compatible, and that insufficient attention has been paid to long term fate and effects of chemical loadings into these treatment systems.

Most studies of SDP performance have been carried out over restricted time periods, usually during the summer, during the first few years of operation when accumulated loadings are low, and over a single or restricted range of loading rates (Tanner et. al., 1998). In addition, much of the literature on the implementation and use of SDP's comes from warmer climates, such the southern United States (Debusk et. al., 1996, Dombeck et. al., 1998, Gambrell et. al., 1991, Makos and Hrnčir, 1995, and Tanner et. al., 1998). These short-term studies conducted under conditions optimal for chemical removal are unlikely to provide us with an unbiased assessment of SDP efficiency under ambient conditions.

The major constituents of urban runoff are metals (Makepeace et al., 1995). They originate from a variety of municipal and industrial sources (Marsalek et al., 1997). Metals may exist in a variety of forms that are governed by ambient conditions such as pH and redox potential. Metal mobility is a function of environmental conditions, including those that govern speciation. Therefore, to understand metal mobility in SDP's we must investigate overall SDP performance under ambient conditions as well as factors that influence metal speciation.

The overall goal in this study was to investigate the effectiveness of SDP's for retaining metals. The objectives of this field-based research were:

- to determine the seasonal mobility of trace metals, and;
- to examine factors that influence metal mobility (e.g. salinity, ionic strength, water temperature, position of the redoxcline, Eh, DIC/DOC, POC, and nutrient levels).

These objectives were achieved by conducting field studies at SDP. The sampling program was designed to:

- assess the diffusive flux of metals across the sediment-water interface,
- and to measure metal inputs and outputs across a SDP.

The SDP was located in Harding Park in Richmond Hill, Ontario, Canada. The pond was constructed in 1993 - 1994 and consists of a forebay and a wet detention pond that discharges to wetland before entering German Mills Creek, a tributary of the east Don River.

2.0 LITERATURE REVIEW

2.1 Urban and Stormwater Runoff: Sources of Trace Metals to Stormwater Detention Ponds

Urban soils, sediments, and waters are prone to environmental degradation through excessive inputs of toxic contaminants. These contaminants, including both toxic elements and organic contaminants, originate from municipal and industrial sources. Concentrations of many pollutants in urban stormwater are at least an order of magnitude above background levels (Marsalek et al., 1997). Stormwater discharges are characterised by high flows during or shortly after periods of wet weather or during periods of snowmelt. The discharges contain high concentrations of suspended solids, and significant quantities of nutrients and toxic substances (e.g. trace metals, chlorides from deicing salts, hydrocarbons) (Chambers et al., 1997, and Bodo, 1989). Loadings from stormwater are dependent upon the drainage area and the land use activities in that area (Chambers et al., 1997). Once particles and particle-sorbed chemicals have settled, the sediments themselves may act as a reservoir for trace metals since chemical reactions (i.e. sorption, precipitation, and complexation), flow or wind induced currents and bioturbation may contribute to the flux of trace metals to and from the sediments (Dombeck et al., 1998).

In a summary of stormwater loadings published for the Canadian Great Lakes basin (Marsalek and Schroeter, 1988), the annual loading for inorganics (mostly trace metals) was estimated at $10^2 - 10^5$ kg/yr. Toxic metals commonly found in stormwater runoff that have the potential to affect aquatic life and human health include aluminium, beryllium, mercury, silver, zinc, lead, iron, copper, cadmium, chromium, nickel and manganese (Marsalek et al., 1997, and Makepeace et al., 1995). Such metals originate from automobile operation, abrasion and corrosion of roadways, and roadway maintenance procedures. Significant fractions of trace

metals are found in runoff in the dissolved phase and are generally considered bioavailable (Marsalek et al., 1997).

2.2 Review of the Sources and Uses of Trace Metals Examined in this Study

The following is a review of the sources and uses of the metals that were examined in this study. These trace metals were selected based on their abundance in the Harding Park SDP. The metals examined included barium, copper, iron, manganese, strontium, sodium, and zinc.

2.2.1 Barium, Ba

A silvery-white metal (atomic number 56; atomic weight 137.6; specific gravity 3.5; melting point 725°C; boiling point 1640°C, oxidation state +2) (Adriano, 1986, and Reeves, 1979), barium is the heaviest of the stable alkaline earth elements. The free element oxidises readily in moist air and reacts with water or with dilute acids under evolution of hydrogen gas. The element is used in the form of barium compounds, primarily as barite (BaSO_4), which in turn is produced from high-grade ore (75%-89%), often in association with granite and shale (Adriano, 1986). About 80% of ground and crushed barite sold have been used directly as a weighting agent in oil- and gas-well drilling mud. The remainder of barite, and all witherite (BaS), are used in the manufacture of glass, ceramics, television picture tubes, brick and tile refractories, plastic stabilisers, railroad flares, fireworks, fine chemicals, lubricating oil additives, brake pads, and permanent magnets (Reeves, 1979, and Hildemann et. al., 1991). Barium is also used in the manufacturing processes of sugar refining, paper coating, steel hardening, and as a pigment in paint (Reeves, 1979). Barium containing household and consumer products constitute a minuscule part of barium consumption, but have the greatest toxicological significance. They include rodenticides, insecticides, and depilatories (Reeves, 1979). Recently barium has also been

found to be used in red lipsticks and has also been considered a source of barium to the environment (Rastogi and Pritzl, 1998).

2.2.2 Copper, Cu

Copper (atomic number 29; atomic weight 63.5; density 8.9; melting point 1083.4°C; boiling point 2567°C) is one of the most important metals to humans. It is reddish coloured, takes on a bright metallic luster, is malleable, ductile and a good conductor of heat and electricity (Piscator, 1979, and Adriano, 1986). The principle uses of copper are in the production of wire and its brass and bronze alloys. Copper is alloyed with tin, lead, zinc, nickel, aluminium, and manganese. The electrical industry is one of the major users of Cu in the production of electrical wires and other electrical apparatus. Because of its high thermal conductance and relative inertness, copper is extensively used in containers such as boilers, steam pipes, automobile radiators, and cooking utensils. The metal is widely used in water delivery systems. It is also extensively used in agriculture in the form of fertilisers, bactericides, and fungicides, and as an algacide in water purification. It is used as a feed additive, such as in antibiotics, drugs, and selected chemical compounds, as a growth promoter, and as an agent of disease control in livestock and poultry production (Adriano, 1986, and Piscator, 1979).

2.2.3 Iron, Fe

Iron (atomic number 26; atomic weight 55.8; density 7.9; melting point 1535°C; boiling point 3000°C) is superior to all other elements in magnetic properties. The principle forms of iron are ferrous (Fe^{2+}) and ferric (Fe^{3+}) (Adriano, 1986, and Elinder and Piscator, 1979). Iron undergoes several structural changes when heated or mixed with other metals and these phenomena are the basis for metallurgy. Humans have used iron for several thousand years and production of steel is one of the corner stones of the industrialised world. Steel and iron products

are used in the construction of ships, bridges, railroads, highways, buildings, etc. Large amounts of steel are also used in the production of transportation vehicles and weapons. Iron compounds have a great number of applications though they constitute less than 1% of the total iron consumption. Iron oxides are used as pigments in paints, plastics, etc. Ferrite materials made of iron oxide are utilised in the electronic industry for products such as computer-memory cores. Certain iron salts, mainly ferrous sulphate and ferrous succinate, are frequently used for the treatment and prevention of iron deficiency in humans (Adriano, 1986, and Elinder and Piscator, 1979).

2.2.4 Manganese, Mn

Manganese (atomic number 25, atomic weight 54.938; melting point 1244°C; boiling point 1962°C; density 7.21-7.44 depending on form, oxidation states 0, +1, +2, +3, +4, +5, +6, +7) is a whitish grey metal, harder than iron but very brittle (Adriano, 1986, Piscator, 1979). Since 1939, Mn has been used primarily in the metallurgical industry. As an essential ingredient in steel, it neutralises the harmful effects of sulphur, serves as an anti-oxidant, and provides strength, toughness, and hardness. For these reasons, Mn is used also in the production of alloys of steel, aluminium, and copper. These alloys are used in the electrical industry and for ship propellers. Manganese, or its compounds, is used quite extensively in alkaline batteries, electrical coils, ceramics, matches, welding rods, glass, dyes, paints, and drying industries. Other compounds that contain manganese are dryers for paints, varnishes and oils, fertilisers, disinfectants, and animal food additives. It is also used as a component of anti-knock compounds for internal combustion of engines (Adriano, 1986, and Piscator, 1979).

2.2.5 Sodium, Na

Sodium (atomic number 11; atomic weight 22.99; density 0.97; melting point 97.5°C; boiling point 880 °C; oxidation state +1) has a bright metallic luster that soon dulls as the surface is oxidised. It is a good conductor of heat and electricity however, because it is soft, mechanically weak, and reacts with the atmosphere, it is not used as a structural material. As it is an alkali metal, it commonly occurs as rock salt, NaCl, in enormous salt deposits that were formed by the evaporation of ancient seas. It is mined either by conventional methods or by forcing water into the deposit to form a concentrated salt solution, brine, that is pumped to the surface and evaporated (Gillespie et al., 1989). In this form, NaCl, is applied to roadways as a deicing agent in order to maintain bare pavement throughout the winter in Canada and the northern United States (Buttle and Labadia, 1999, and Mason et al., 1999).

2.2.6 Strontium, Sr

Strontium (atomic number 38; atomic weight 87.62; density 2.6; melting point 770°C; boiling point 1380 °C; oxidation state +2) is a silvery white metal. It tends to be a good conductor of heat, has a high electrical conductivity, and is malleable and ductile. Because it is a soft metal it has no importance as a structural material (Gillespie et al., 1989). Industrial uses of strontium are limited to the manufacture of pyrotechnic devices, the processing of steel and paint, and the refining of sugar. Strontium bromide is often used for x-ray diagnostic work and as a therapeutic agent in reducing gastric hyperacidity (Beliles, 1979).

2.2.7 Zinc, Zn

Zinc (atomic number 29; atomic weight 65.4; density 7.1; melting point 420°C; boiling point 907°C, oxidation state +2) is a crystalline bluish white metal (Adriano, 1986, and Elinder and Piscator, 1979). It is a relatively soft metal and has a strong tendency to react with inorganic

compounds (oxides, sulphates, phosphates) as well as organic ones (Elinder and Piscator, 1979). Zinc ranks fourth among metals of the world in annual consumption, behind Fe, Al, and Cu. The automobile industry accounts for almost one third of United States use and consumption (Adriano, 1986). Zinc is also extensively used as a protective coating on a number of metals to prevent corrosion and in alloys such as brass and bronze. Galvanised metals have a variety of applications in the building, transportation, and appliance industries. Galvanised pipes are commonly used in domestic water delivery systems, and zinc solubilised by corrosion is thought to make some contribution to the zinc concentrations found in wastewater. Zinc and its compounds are ingredients of many household items, including utensils, cosmetics, powders, ointments, antiseptics and astringents, paints, varnishes, linoleum, rubber, and others. They are also used in the manufacture of parchment papers, glass, automobile tires, television screens, dry cell batteries, and electrical apparatus. Other uses include agricultural micronutrient fertilisers, insecticides, hardeners in cement and concrete, and printing and drying textiles. They are also used in the production of adhesives, as a flux in metallurgical operations, and as a wood preservative (Adriano, 1986).

2.3 Water Quality Mitigation and Habitat Generation in Stormwater Detention Ponds

The potential hazard to organisms from exposure to trace metals in the SDP ecosystem (influent, sediment reflux) may be great due to the extreme toxicity of trace metals. However, the impacts of metals on organisms are dependent on numerous mechanisms including the pathway of exposure, the trace metal concentration and physicochemical state (i.e. speciation) in the environment, and the uptake mechanisms. Stormwater detention ponds attract a host of aquatic and aquatic-dependent organisms (Dombeck et. al., 1998). However, the dual purposes and

objectives of stormwater management and water quality mitigation along with those for habitat quality and creation may not be reasonable. Wildlife (both aquatic and terrestrial) that use these systems may be exposed to accumulated contaminants within the stormwater detention pond (Helfield and Diamond, 1997). In addition to threatening the viability of the vegetative community and decreasing the system's capacity to process additional contaminant inputs, contaminants sequestered in vegetation and substrates may bioconcentrate and biomagnify through the aquatic food web. The diversity of biota that may be impacted by chemical contamination include benthic invertebrates, fish, and floating plants in aquatic habitats; and soil invertebrates, insects, plants, mammals, waterfowl, and predatory birds in terrestrial habitats (Pascoe, 1993). Studies of the lower Don River and Keating Channel have cited bioaccumulation of trace metals in fish and wading birds via direct uptake from the water column and ingestion of sediment contaminated particles or biota (MTRCA, 1983).

The mechanisms of metal-ion toxicity have been divided into the following three categories by Nieboer and Richardson (1980): (1) blocking of essential biological functional groups of biomolecules, (2) displacing the essential metal ion in biomolecules, and (3) modifying the active conformation of biomolecules. The overall result of the binding of metal ions to reactive sites, where they are not normally required, is often inhibitory. These effects may result in acute and chronic toxicity impacts in organisms (Dombeck et. al., 1998).

Hence, the dichotomous roles of stormwater detention ponds for water quality mitigation and habitat enhancement ecologically oppose one another as the habitat benefits related to feeding and reproduction by aquatic fauna may be threatened in areas subject to substantial loadings of trace metals (Helfield and Diamond, 1997). In addition, in cases of large and chronic contaminant loadings, the proximity of stormwater detention ponds and other surrounding or connecting

systems (e.g. upland-based wildlife) may allow for impacts to be manifested outside the stormwater detention pond (Catallo, 1993). The ecological consequences of stormwater detention ponds are of great concern since they are designed to accumulate contaminants. These contaminants may then bioconcentrate throughout the aquatic and aquatic-dependent faunal structure, since these pond systems are also designed to be open for habitat establishment (Helfield and Diamond, 1997). In addition, the greatly increased circulation of trace metals through soils, sediments, water, and air and their eventual transfer to the human food chain remains an important environmental issue which may result in some unknown health risks for future generations (Nriagu and Pacyna, 1988).

2.4 Factors Affecting Metal Mobilisation in Stormwater Detention Pond Environments

There are a number of physical and chemical properties of soils and sediments affecting metal mobilisation-immobilisation processes. Physical properties include texture (proportion of sand, silt, and clay), organic matter content, and to some extent the type of clay minerals. Chemical properties include redox potential, pH, salinity, and the presence and solubility of important inorganic chemical components such as carbonates and sulphides. Contaminants can partition themselves between the various solid phases contained within soils and sediments. These phases include phyllosilicate clays, hydrous oxides of iron, aluminium and manganese, and humic materials. The surfaces of these phases are chemically active, which allows charged ions to be adsorbed to their surfaces.

2.4.1 Physical Characteristics

The edges of clays and oxide minerals accept and donate protons and assume negative, neutral, or positive charges. Many metallic cations, such as toxic trace metals, can form strong

complexes with pH-dependent charged mineral surfaces found in soils and sediments, whereas others, such as Ca, Mg and Ba, form weak complexes. Specific adsorption of cations onto mineral surfaces occurs most readily for those metals that hydrolyse in water. The extent of adsorption is dependent on pH and increases to a maximum, as the pH is raised (Bolton and Evans, 1997). Positively charged cations in solution are attracted by electrostatic forces to the negatively charged edges and surfaces of sediment and soil particles (Evans, 1989). Such metals include most of the transition elements and the rare earth elements, in addition to other ions, such as Hg and Pb. The adsorption reaction generally involves the formation of an inner sphere complex between the hydroxo-metal complex and the negatively charged deprotonated surface of oxides, hydroxides, and oxyhydroxides of Al, Mn, and Fe (Evans, 1989).

Humic Materials

Soil and sediment organic matter contains humic materials that are significant to the environment in terms of the storage of trace metals. Humic materials contain functional groups (carboxyls, phenolics, alcohols, methoxyls, carbonyls, ethers, and esters) that can act as complexant organic ligands (Bolton et al., 1996). They are a mixture of poorly degradable decomposition products and by-products of natural organic matter produced by both plants and animals and they account for the bulk of the organic material in natural waters and soils (Snoeyink and Jenkins, 1980). Humic substances are able to combine with, or bind, considerable quantities of metal ions. For example, many metals can be enriched into peat, a type of soil organic matter of a humic nature, from soil waters so that the enrichment of the metal in the peat is up to 10 000 times the concentration in the water (Snoeyink and Jenkins, 1980). Hence, it is the fine-textured soils and sediments containing an appreciable organic matter content that tend to accumulate

contaminants in surface water bodies and thereby act as reservoirs of contaminants (Gambrell, 1994).

2.4.2 Chemical Characteristics

The metals in contaminated soils and sediments are usually in unavailable forms: a) precipitated as metal oxides, hydroxides, and carbonates of low solubility, b) adsorbed to colloidal hydrous oxides of iron and manganese in aerobic, neutral or alkaline pH environments, c) precipitated as highly insoluble sulphides under strongly reducing conditions, and d) complexed with dissolved and insoluble humic materials (Gambrell and Patrick, 1988). However, metals may undergo chemical transformations thereby affecting their mobility and availability. These transformations are a result of changes in the physicochemical properties of the system such as pH, redox potential, and salinity (Gambrell and Patrick, 1988).

pH and Redox

The importance of pH in controlling trace metal partitioning between solid and solution phases has been widely identified. In addition, the oxidation status of soils and sediments has been shown to affect the distribution of some trace metals between bound, unavailable forms and soluble and/or plant-available forms (Gambrell et. al., 1991). As soils are flooded and become anaerobic or reducing, the pH tends to converge toward 7 (neutrality). The pHs of natural wetland soils generally ranges from around 6.5 to 7.5 and favours metal immobilisation. However, upon oxidation, many wetland soils and sediments with a near neutral pH may become sufficiently acid to induce metal release (Gambrell, 1994). Natural waters are, in general, highly dynamic with respect to oxidation-reduction reactions. There is a marked difference in the redox environment between the surface in contact with oxygen in the atmosphere and the bottom waters

at the sediment-water interface. The region in between may also reflect large redox gradients depending upon mixing, diffusion, and the extent of biological activity. Exact measurement of redox environments in natural water systems is probably not as important as understanding and defining the redox gradients and transport mechanisms acting within the system (Leckie and James, 1974). Changing redox environments may also affect trace metals in aquatic systems in the following two ways: (1) by direct changes in the oxidation state of the metal ion, and (2) by redox changes in available and competing ligands or chelates (Leckie and James, 1974). In the study by Gambrell and Patrick (1988), substantial amounts of Cd and Zn were released under moderately acid, oxidising conditions. In a more recent study by Gambrell et al. (1991), under slightly basic, strongly anaerobic environments of marsh sediment, metals were found to be effectively immobilised. Substantial release could occur for some of the metals if the sediments were excavated and placed under upland conditions where they would eventually become oxidised and strongly acidic.

Interactions with Sulphides

Intense redox activity occurs at the sediment-water interface mainly because of the deposition and accumulation of organic matter and the lack of molecular oxygen diffusing down into the sediment interstitial waters, thus creating a large redox gradient. It is well known that high organic sediments generally contain large quantities of reduced material, especially sulphides. Since most trace metal sulphides tend to be rather insoluble, it is clear that interaction in heterogeneous sulphide systems can be important processes whereby trace metals are retained or released from the aqueous phase (Leckie and James, 1974).

Temperature and Chloride

In systems where pH remains relatively constant, particularly in well-buffered systems with high pH values, other environmental factors may become more important sources of variance for metal partitioning, solubility, mobility and potential bioavailability of particle bound metals. Temperature and NaCl (from road salt) have also been found to be key environmental variables influencing trace metal partitioning (Warren and Zimmerman, 1994). Warren and Zimmerman (1994) found that a decrease in water temperature caused decreases in the accumulation of Cd, Cu and Zn in the particulate pool used in the laboratory. In addition, increasing NaCl concentrations decreased concentrations of Cd and Zn associated with the particulate leachable phase and the Cd, Zn, and Cu content in the oxidisable suspended particulate matter (Warren and Zimmerman, 1994). Lumsdon et al. (1995) obtained similar results for Hg, but the observed effect of high Cl⁻ ion concentration on Cd, Pb, and Zn retention was substantially less.

2.5 Pore Water Sampling

Bottom sediments in natural systems are formed by sedimentation of particles from the overlying water column. During this process, water will be trapped and entrained in the sediment, forming the interstitial or pore water (Bufflap and Allen, 1995). Sediment pore water, also referred to as interstitial water, is defined as the water filling the space between sediment particles and not held by surface forces, such as adsorption and capillarity, to sediment particles. Sediment pore water acts as a linking agent between the bottom sediments and the overlying water (Adams, 1994). Within the sediment system, chemical species will tend toward equilibrium between the pore water and solid phase. However, due to diagenetic processes such as precipitation, adsorption, sulphide formation, remobilization, biological degradation, and biological uptake, the

concentrations of chemical species in the pore water and the overlying water will not necessarily be the same (Bufflap and Allen, 1995).

The increasing number of studies of contaminant concentrations in sediment pore water in marine and lacustrine environments reflect the significance of this part of the aquatic environment (Adams, 1994). An important fraction of the substances present in the aquatic environment is reversibly associated with surficial sediments (i.e. acting as reservoir for contaminants and thereby possibly contributing to the pollution of the overlying water column). The study of substance dynamics in surficial sediments is prerequisite to the understanding of their behaviour in whole aquatic systems. Particular aspects to be addressed include the study of sediment-water exchanges, the chemical speciation of substances in surficial sediments, and their diagenetic modelling (Angelidis, 1997).

The toxicity of metals in sediment depends largely upon the extent to which the metals bind to the sediment. Such binding will alter the concentration of metals to which organisms are subjected, resulting in different sediments exhibiting different degrees of toxicity for the same total quantity of metals. These differences in sediment binding capacity can be reconciled by relating organism toxicity to metal concentration in the pore water. Thus, the measure of metals in pore water can provide one indication of the potential toxicity of the sediment with respect to these contaminants (May et. al., 1997). Knowledge of pore water chemical concentrations is also important in dredging operations, as these chemicals will potentially be released into the water column or mobilised after sediment disposal as sediment is removed from the natural environment (Bufflap and Allen, 1995).

Several techniques have been developed for pore water sampling. Table 2.1 summarises the most commonly used methods for sediment pore water sampling and their main advantages

and disadvantages (Mudroch, 1995). This study involved the use of dialysis samplers, the most common of which is known as a “peeper”. The general principle of these samplers involves allowing a volume of deionised, distilled water to come to equilibrium with the sediment pore water in order to determine chemical concentrations (Bufflap and Allen, 1995).

Table 2.1: Advantages and Disadvantages of Techniques Commonly Used for Pore Water Sampling (from Mudroch, 1995)

Method	Advantages	Disadvantages
Squeezing	Simple equipment Portable Inexpensive Sediment composition available	Oxygen contamination CO ₂ degassing that will change pore water composition Temperature-induced changes Pressure-related additions of metabolites
Centrifugation	Simple Sediments composition available Easy to obtain large volumes	Risk of sampling artifacts Pressure artifacts Effects of oxidation and elevated temperatures
Dialysis	Minimal manipulation of sample No induction of interstitial water flow Allows maximal replication Analysis of dissolved gases is possible Temperature- and pressure-related artifacts are avoided	Disturbance of the sediment structure Need scuba divers or submersibles Timing (minimum 12 days) Risks of incomplete equilibration Risks of membrane breakdown
Suction	Simple and easy to use Allows sampling at fairly well-defined depth	Fine particles could be collected (reduction of mesh size may cause clogging) Oxidation effects are hard to prevent

One important problem in the use of dialysis samplers is the production of oxidation artifacts. Dialysis samplers must be deaerated before insertion into anoxic sediments. Another problem is the type of membrane material used. The membrane must be able to exclude sediment particles, allow the chemical species in the pore water to diffuse into the sampler, retain the

dialysis water, and maintain its integrity while in the sediment (Bufflap and Allen, 1995). Due to problems associated with microbial attack, cellulose-based dialysis membranes are not recommended (Adams, 1994).

Other issues that require consideration include the limited volume of sample, length of equilibration time, the need for SCUBA divers for peeper placement, and too many manipulations of the sample and time. The volume of sample obtained is limited and should be considered beforehand for analytical considerations. The equilibration time is dependent on a number of factors such as the porosity of the sediment, the diffusion coefficient of the species of interest, temperature, and the area/volume ratio of the sample compartment (Bufflap and Allen, 1995). Equilibration times may be as long as 20 days (Bufflap and Allen, 1995), or longer for winter pore water sampling (Rosa, 1998). Because most pore water sampling studies have been performed in deep-water locations, the use of peepers normally requires SCUBA divers for their placement and retrieval (Bufflap and Allen, 1995). Too many manipulations of the samples may result in contamination or changes in the sample concentrations due to exposure to various atmospheres and temperatures. Time is critical especially in the case of field measurements where the sampling site and the analytical laboratory are separated geographically. The time elapsed between sampling and analysis may result in significant concentration changes (Angelidis, 1997).

2.6 Trace Metal Analysis

One of the most commonly requested analyses in environmental chemistry is metal analysis of solid and aqueous samples. The most common procedure for this analysis is to solubilise the elements in question using an acid digestion procedure and analyse the resulting liquid digestate in either an absorption or emission instrument (Kimbrough and Wakakuwa, 1994). When choosing

the analytical instrument the following issues must be considered: sensitivity, cost, simplicity/reliability, dynamic range of concentration, speed, accuracy, precision, utility, waste generation, field portability, ruggedness, and compatibility with existing EPA methods (Pyle et. al., 1996).

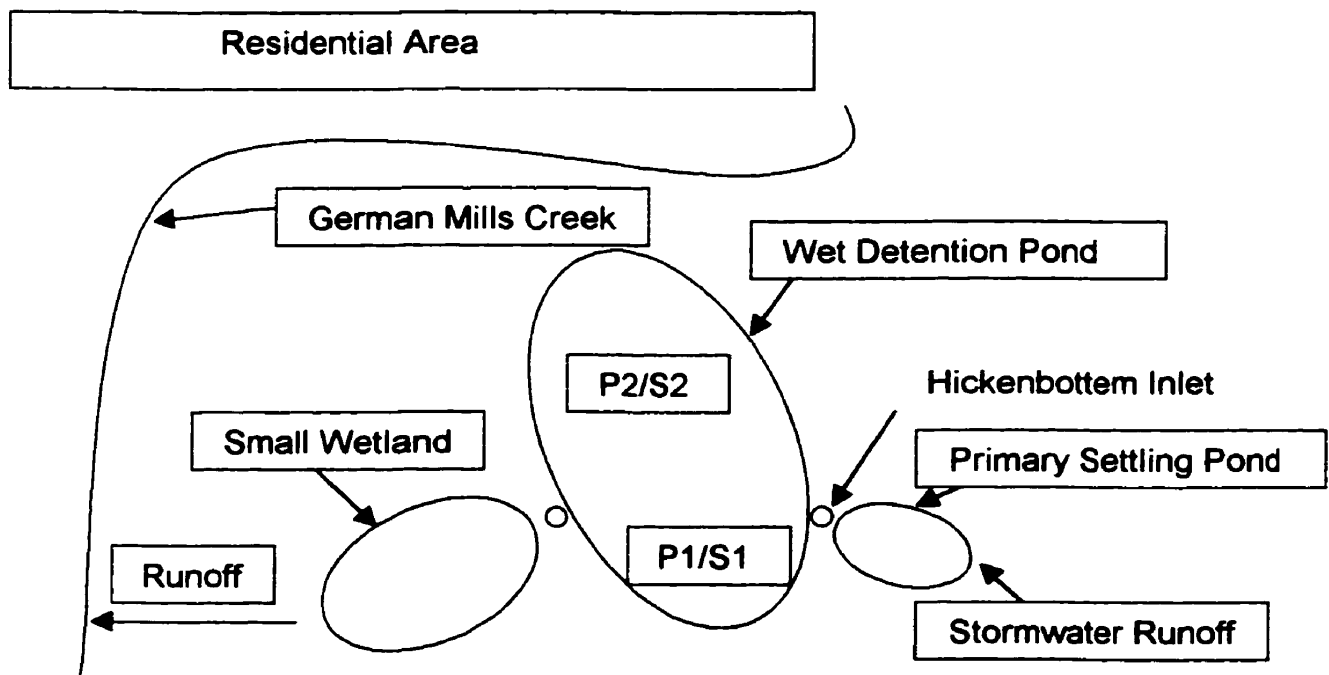
The ICP-OES consistently provides the most precise results for the highest concentration samples. It is a robust technique that a large number of laboratories can apply independently to the same material and obtain very similar results (Kimbrough and Wakakuwa, 1994). Generally, emission technologies are subject to inter-element interferences (Kimbrough and Wakakuwa, 1994). Interferents have the largest impact at lower concentrations where the signal from the analyte is comparable to the signal from the interferent thereby causing a high rate of false negatives and positives (Kimbrough and Wakakuwa, 1994). However, for analysis of water by ICP-OES, ICP-OES is virtually free of inter-element interferences as there are no on-peak spectral interferences at the levels of metals found in water samples (Environment Canada, 1994b).

3.0 METHODS

3.1 Study Site

The stormwater detention pond investigated in this study was constructed in 1994-95. The site is situated in a residential park, Harding Park, in Richmond Hill, Ontario. It was constructed adjacent to the German Mills Creek, located in the west Don River subcatchment area, in order to mitigate stormwater quality in the headwaters region of the Don River system (Figure 3.1). The stormwater discharges into a primary settling pond that reduces the water velocity and encourages settlement of suspended solids. Water then passes through a Hickenbottom inlet into a second, larger wet detention pond. The maximum depth of this pear-shaped pond is 2 to 3 m and the pond has a surface area of about 5 ha. Sediments are fine-grained in the deepest section, and very sandy in the more shallow areas. Water discharges from this wet detention pond into a small wetland of about 1 to 2 ha. This study concentrated on the wet detention pond containing the fine-grained sediments.

Figure 3.1 Diagram of the Harding Park Stormwater Detention Pond



Normal mean monthly precipitation data for Toronto, Ontario obtained through Environment Canada's Greenlane, Atmospheric Services website are found in Table 3.1. This data indicates that the Toronto area, including Richmond Hill, should have expected precipitation to increase throughout the summer of 1998, followed by a slight decrease into the fall and early winter. During the winter precipitation decreases substantially. Beginning in early spring precipitation begins to increase again. However, from personal observation, this did not occur as all of southern Ontario experienced drought-like conditions for the summer of 1998 and increased precipitation was not experienced until the fall.

Table 3.1: Normal Mean Monthly Precipitation (mm) for Toronto, Ontario (Environment Canada, 1999).

Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sept.	Oct.	Nov.	Dec.
55.1	52.6	65.2	65.4	68.0	67.0	71.0	82.5	76.2	63.3	76.1	76.5

3.2 Field Studies

Approximately every four to six weeks, surface water samples were taken from the inflow, outflow and two sites within the main wet detention pond for subsequent analysis. Surface water samples were analysed for trace metals, nutrients (ammonia, nitrate, chloride, and total phosphorus), dissolved inorganic and dissolved organic carbon (DIC/DOC), total particulate carbon (TPC), and suspended solids concentrations. In addition, two pore water peepers were also deployed at each of the two sites centrally located within the SDP. The pore water samples were analysed for trace metals as well as for redox and pH. Water column profiles of pH, redox, conductivity, temperature and dissolved oxygen were taken at the two centrally located sites.

3.3 Peeper Assembly, Installation, and Retrieval (adopted from Rosa and Azcue, 1993)

Rosa and Azcue (1993) provide a thorough explanation of pore water sampling using peepers. The following discussion has been excerpted from their paper. Special attention has to be paid to avoid contamination when cleaning and sampling all sampling equipment and containers for collection of the pore water samples.

A large pre-cleaned plastic bin with lid was filled with doubly distilled water (DDW). Water in the bin was purged with nitrogen gas (N_2) that was bubbled through a rubber tube with an adapted end.

Peepers were soaked in 5% HNO_3 for six days, then rinsed with DDW and placed one peeper at a time in the bin containing the deoxygenated DDW. In order to minimise the trapping of air bubbles in the cells; the peepers were submerged lengthwise and on an angle. The peeper coverplate and pre-cut 0.45 μm dialysis paper (membrane) were submerged in a similar manner. The coverplate, paper and peeper were then aligned and screwed shut. Once all the peepers were assembled they were purged overnight with N_2 before transport into the field.

In the field two peepers per site were inserted perpendicularly into the surficial sediment using a telescoping pole. Approximately half to one third of the peeper was inserted into the sediments. The peepers were left to equilibrate with the sediment pore water and overlying water for approximately three to four weeks.

In the laboratory, sample vials were placed in Styrofoam trays for easy manipulation in the field. The trays were set up in order to provide enough space between sample containers, for easy uncapping, and to clearly show the sample number. Before leaving to go out to the study site, the sample vials, labelled according to peeper number and cell number (plus a few extras), were pre-treated with 10 ul of environmental grade HNO_3 .

Upon retrieval, the peeper was briefly agitated in the water to remove any visible sediment particles adhering to the membrane surface. The positions of the sediment water interface and the redoxcline were noted. The position of the redoxcline was indicated by the red ferric oxyhydroxide staining on the peeper membrane. Pore water was removed from one peeper per site using syringes (one per cell for cells around the sediment-water interface, one for all the cells above the area around the sediment-water interface and another for cells below). The peeper samples were placed in acid washed vials containing 10 µl of environmental grade HNO₃ and stored for subsequent metal analysis. Pore water from the second peeper at each site was removed by syringe, emptied into a beaker, and assessed in the field for pH and Eh.

3.4 Carbon, Suspended Solids, and Nutrients Analysis

3.4.1 Dissolved Inorganic and Organic Carbon in Surface Waters

In the laboratory, surface waters were filtered through 0.45 µm cellulose acetate filters for dissolved inorganic carbon and dissolved organic carbon DIC/DOC analysis at the National Laboratory for Environmental Testing, Environment Canada.

For DIC measurement, the inorganic carbonate is removed by mixing the samples with sulphuric acid (2.4 % v/v) and stripping the carbon dioxide in a heated (95 °C) packed column. The packed column of the stripper is wrapped with an electric heating wire to which 150 watts is applied. In the packed column, the sample is boiled and stripped with oxygen. With oxygen as a carrier gas, the CO₂ released is carried to an infrared detector for quantitation.

For DOC measurement, the inorganic carbonate is first removed from the sample as described above. The liquid from the bottom of the stripper is immediately segmented with oxygen and cooled by being passed through a small-jacketed coil. The solution is de-bubbled, re-

sampled, mixed with a 4% potassium persulphate solution and passed through a continuous UV digester for digestion. After leaving the digester, the hot sample flow is passed through a second stripper, where the carbon dioxide is stripped off into a stream of oxygen. The packed column of the stripper is insulated with asbestos paper. The liquid stream is run to waste and the gas stream is passed to the infrared detector for quantitation (Environment Canada, 1994a).

3.4.2 Total Particulate Carbon (Leco Induction Furnace)

TPC samples were filtered using pre-ashed glass fibre filters and analysed at the University of Guelph, Analytical Services Laboratory. The Leco SC-444 method of carbon determination is based on the combustion and oxidation of C to form CO₂ by burning the sample at 1450°C in a stream of purified O₂. The amount of evolved CO₂ is measured by infrared detection and used to calculate the percentages of C in the sample. In this method, approximately 0.2g of oven-dried sample is analysed (Tabatabai and Bremner, 1970).

3.4.3 Suspended Solid Concentration of Surface Water Samples

Surface water samples were filtered in the laboratory using 0.45 µm pre-weighed membrane filters and the volume of water filtered recorded. Filters were then dried in an oven at 100 °C for 1 hour. The filters were allowed to cool for about 10 minutes before recording their weight again. The filter pre-weight was subtracted from the sample and filter weight in order to determine the amount of suspended solids filtered. The suspended solid weight was then divided by the volume of water filtered to determine the suspended solid concentration in the water.

3.4.4 Ammonium, Nitrate and Nitrite in water

Unfiltered surface water samples were submitted to the University of Guelph, Analytical Services Laboratory for analysis of nitrate (NO_3), nitrite (NO_2), and ammonium (NH_4). A Braun and Leubbe TrAAcs 800 was used to determine the ammonium, nitrate and nitrite concentrations according to the following methods.

The automated method of nitrate analysis is based on the reaction whereby nitrate is reduced to nitrite at pH 7.5 in a copper-cadmium reductor cell. This nitrite (plus any free nitrite) reacts under acidic conditions with sulphanilamide to form a diazo compound that couples with N-1-Naphthylethylenediamine dihydrochloride to form a reddish-purple azo dye which is measured colourimetrically. A dialysis membrane is used in the system to remove any precipitate or original colour from the sample extracts. In this technique, the intensity of the reddish-purple colour in the extracts is compared to that in calibrated standards to determine $\text{NO}_3\text{-N} + \text{NO}_2\text{-N}$ concentrations (mg/L) in the extracts.

$\text{NO}_2\text{-N}$ is determined by repeating the above analysis, using nitrate standards and bypassing the cadmium coil.

The automated method of ammonium analysis utilises the Berthelot reaction in which the formation of a blue coloured compound when the solution of an ammonium salt is added to sodium phenoxide, followed by sodium hypochlorite. A solution of EDTA is added to the sample stream to eliminate the precipitation of the hydroxides of calcium and magnesium. Sodium nitroprusside is added to intensify the blue colour. In this technique, the intensity of the blue colour in the extracts is compared to that in calibrated standards to determine $\text{NH}_4\text{-N}$ concentrations (mg/L) in the extracts.

3.4.5 Total Phosphorus in Surface Water

Total phosphorus content of the pond water was measured at the University of Toronto at Scarborough by Vivian Campbell following the methods of Menzel and Corwin (1965) and Murphy and Riley (1962), which were slightly modified by Smith *et al.*, 1984. Standards were prepared from a concentrated solution of potassium hydrogen orthophosphate. All samples and standards were run in triplicate. Fifty mL of each sample was transferred to 25mm x 20 cm glass culture tubes. Upon addition of potassium persulphate, the tubes were capped with polypropylene lids and were autoclaved for 45 minutes. To each cooled tube, five mL of a mixture of ascorbic acid combined with a premixed solution of ammonium molybdate, potassium antimony tartrate and sulphuric acid was added. After 20 minutes, the absorbances were read using a Spectronic™ Genesys 5 spectrometer at 885 nm. The spectrometer was blanked using ultrapure water. The cuvettes were rinsed several times with each sample prior to reading the absorbances

3.4.6 Chloride in Surface Water

Chloride samples from June and July 1998 were analysed at the University of Toronto at Scarborough by Vivian Campbell. Chloride samples were diluted with ultrapure water to an approximate concentration of 100 ppm prior to analysis with a high performance liquid chromatograph, using a PRPX100 Hamilton™ anion column. To ensure a level baseline the eluent, 4.0mM p-hydroxybenzoic acid with 2.5% methanol adjusted to pH 8.5, was used to equilibrate the instrument for 60 minutes prior to injecting the first sample of each analysis day.

Each analysis day, fresh standards were made by diluting a stock solution of 1000 ppm Cl (made from oven dried NaCl). Concentrations were calculated based on areas of peaks, using

Millennium™ software. Each sample was run in duplicate to ensure that concentrations measured were within a 3% relative standard error.

Samples collected from August 1998 through to May 1999 were submitted to University of Guelph, Analytical Services Laboratory for chloride in water analysis. A Braun and Leubbe TrAAcs 800 was used to determine the chloride in water samples. This automated procedure for the determination of chloride depends on the liberation of thiocyanate from mercuric thiocyanate, by the formation of unionized but soluble mercuric chloride. The liberated thiocyanate, in the presence of ferric ion, forms highly coloured ferric thiocyanate, the concentration of which is proportional to the original chloride concentration.

3.5 Soil/Sediment Analysis

3.5.1 Particle Size Distribution

Sample Preparation:

Sediment samples were submitted to the University of Guelph, Analytical Services Laboratory for particle size distribution according to the method outlined in Manual of Soil Sampling and Methods of Analysis, 1979. The sediment was air-dried and sieved to <2mm. If there were any particles >2mm, their mass and along with the total mass of the sample were recorded. Organic matter was removed by treating the sample with hydrogen peroxide. The sample was dispersed in water with Calgon.

The sample+water+Calgon mixture was poured through a 53 micron sieve into a 1000mL insulated graduated cylinder, washing well. The sand fraction was dried and weighed (retained on the sieve). The silt and clay fractions were separated in the cylinder using a sliding pipette. Each

fraction was dried and weighed. The sand, silt and clay percentages of the organic matter-free soil were then calculated.

For samples containing >10% sand, a nest of sieves was used to separate the sand fraction into the following gradations:

Very Coarse sand	1 000 to 2 000 μm
Coarse sand	500 to 1 000 μm
Medium sand	250 to 500 μm
Fine sand	100 to 250 μm
Very Fine sand	50 to 100 μm

Each fraction was then expressed as a percentage of the total sand fraction.

3.5.2 Cation Exchange Capacity:

The cation exchange capacity of the sediment was determined at the University of Toronto at Scarborough by Vivian Campbell using the method of Evans (1982) by means of saturation with 0.5M barium chloride dihydrate, followed by saturation with 1.0M neutral ammonium acetate. The resulting amount of exchanged barium in solution was determined using a Varian SpectrAA-300 atomic absorption spectrometer.

3.5.3 Extractable Iron

Extractable iron fractions were determined at the University of Toronto at Scarborough by Vivian Campbell using three different reagents. The first, a mixed reagent of dithionite and citrate extracted total organic and inorganic forms of iron, Fe_{DC} . Poorly crystalline iron minerals and organically bound Fe were extracted using acid ammonium oxalate, Fe_{AAO} . Finally, sodium pyrophosphate was used to extract the organically bound iron, Fe_{NAP} . The extracts were diluted as

appropriate and Fe was measured using a Varian SpectrAA-300 atomic absorption spectrometer. The amount of organically bound Fe was considered equivalent to that of Fe_{NAP} . The amount of inorganic, poorly crystalline iron was calculated as $Fe_{AAO} - Fe_{NAP}$ and the inorganic crystalline Fe was determined to be $Fe_{DC} - Fe_{AAO}$ (Evans and Wilson, 1985).

3.5.4 Inorganic, Organic Carbon in Sediments

Sediment samples were submitted to the University of Guelph, Analytical Services Laboratory for analysis. To determine the inorganic carbon content of a sample, approximately 2g of sample is heated in a muffle furnace for five hours at 475 °C to remove the organic carbon. The sample is then analysed in the LECO SC-444 as described above to determine the inorganic C content. Total C in sediments was determined without prior heating of the sample in a muffle furnace and the use of the LECO SC-444 as described above. The organic C content is calculated as the difference between the total and inorganic C values.

3.6 Trace Metal Analysis

Surface water samples for trace metal analysis were filtered through pre-acid washed 0.45µm cellulose acetate filters. Unfiltered/total and filtered/dissolved samples were preserved with 1 ml of 1:1 HNO_3 and refrigerated until analysed. All surface water and peeper samples were analysed for 22 metals according to NLET method 02-2001 (Environment Canada, 1994b) at the National Water Research Institute (NWRI) in Burlington, Ontario. Organically bound metals and metal complexes were converted to metal ions by digesting with hydrochloric acid (HCl). To increase the signal detected by the ICP, the surface water samples were concentrated five times before subsequent acid digestion with HCl. Peeper cell samples were prepared by taking a 1 ml sub-sample and diluting to 10 ml with dilution solution containing DDW, HNO_3 ,

and internal standard. An analytical run consisted of four method blanks, four reference duplicates, two certified references, two DDW, two spiked blanks, 30 to 100 samples, one duplicate sample per 20 samples, and one spiked sample per 20 samples.

Method detection limits were calculated after the method validation, seven sets of analysis, four method blanks per analysis. The standard deviation of the method blanks were calculated and multiplied by two and these method detection limits have been placed in Appendix A (Environment Canada, 1994b).

4.0 Results and Discussion

4.1 Surface Water

The surface waters were profiled for temperature, pH, Eh, dissolved oxygen content, and redox. Surface water profile data was not complete for the entire year, especially during the summer, due to lack of availability of the shared Hydrolab. Surface water samples collected from the inlet, two sites within the pond, and the outlet, were analyzed for total and dissolved metals, as well as chloride, ammonium, nitrate, total phosphorus, total particulate carbon (TPC), and dissolved inorganic and organic carbon (DIC/DOC). Total phosphorus sampling and analysis did not begin until September.

4.1.1 Physical Characteristics

The pH of the wet detention pond ranged from 6.2 to 8.3 with pH tending to decrease with depth (Figures 4.1 and 4.2) during the summer and fall. The values were outside the PWQO range of 6.5 - 8.5 (MOEE, 1994) on only one occasion, during the summer near the bottom of the pond at site P2 when the pH was 6.4. The Don River watershed is located on Wisconsin till and subsequent deposits that overlie either bedrock (limestone and shales) or unconsolidated material deposits from previous ice invasions (Chapman and Putnam, 1966). The limestone and shale bedrock confers high pH to local water systems (approximately 8) (Boyd, unpublished data, as cited in Warren and Zimmerman, 1994). In addition, urban areas are developed with large areas of concrete and alkaline rocks that may also contribute to a more alkaline pH. These near neutral and alkaline pH conditions within the pond favour trace metal immobilisation (Gambrell et al., 1991). Since the pond is so well buffered due to the local geology, even the increasingly oxic conditions that occurred in the surface waters in March and April (Figures 4.1.3 and 4.1.4) did not result in strongly acidic conditions that could induce metal release. Changes in the proton

balance resulting from redox processes can arise from the addition of nitrate or sulphate to the water as in nitrification or sulphur oxidation and thereby increase acidity, while reduction of nitrate and sulphate causes an increase in alkalinity (Schnoor and Stumm, 1985).

Dissolved oxygen ranged from ~ 5 - 15 mg/L and decreased with depth (Figures 4.3 and 4.4). Dissolved oxygen concentrations in the Harding Park pond were similar to the 8 – 11 mg/L measured within the German Mills Creek (MOEE, 1991b). Oxygen concentrations were as low as 1 mg/L during the summer, especially at the deeper locations. Mayer et al. (1999) also measured depleted dissolved oxygen at increased depths in a nearby wet detention pond (1.0 mg/L at a depth of 2.5 m and 0.75 mg/L at a depth of 3 m in August 1998). The oxygen content can be depleted when vascular hydrophytes and macroalgae senesce and die at the end of their growing season in late summer when temperatures are high. Oxygen depletion at the sediment-water interface is the consequence of oxygen uptake during the oxidation of organic matter during bacterial decomposition (Wetzel, 1975). The decrease in DO concentrations result in an increasingly reduced environment that may then induce the mobilisation of Fe and Mn oxides and associated trace metals (Gambrell and Patrick, 1988, and Förstner et al., 1990).

DO concentrations were also low in the winter when the pond was ice covered due to the lack of exchange of oxygen with the atmosphere. However, in March and April the pond became supersaturated (DO > 12 – 13 mg/L). Slight supersaturation results from photosynthetic activity in excess of losses to the atmosphere. Photosynthetic production of organic matter, although reduced, continues throughout the winter, and is often vigorous at the later stages of winter ice-cover (Wetzel, 1975). These increasingly oxic conditions decrease the mobility of Fe and Mn allowing for the complexation of trace metals with Fe and Mn hydroxides (Gambrell and Patrick, 1988, and Förstner et al., 1990).

Figure 4.1: pH at P1

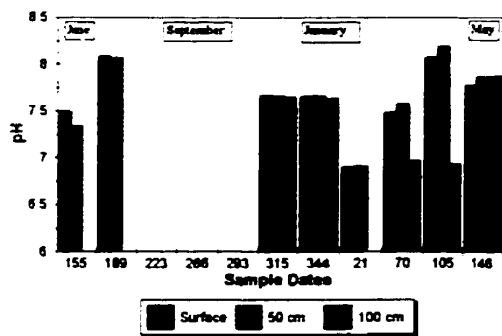


Figure 4.2: pH at P2

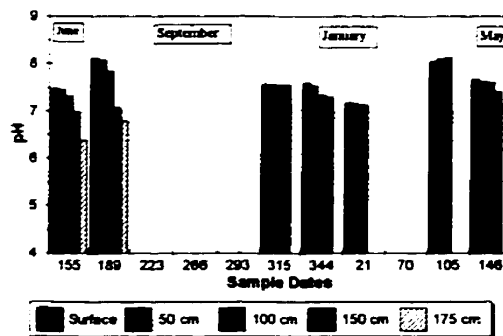


Figure 4.3: Dissolved Oxygen at P1

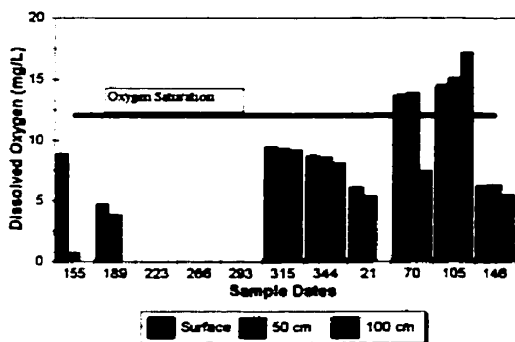


Figure 4.4: Dissolved Oxygen at P2

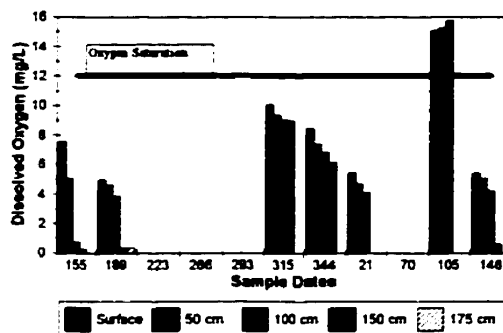


Figure 4.5: Temperature at P1

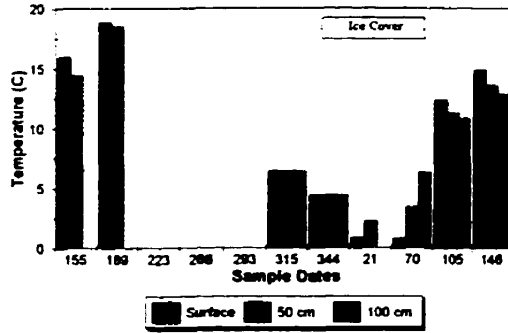


Figure 4.6: Temperature at P2

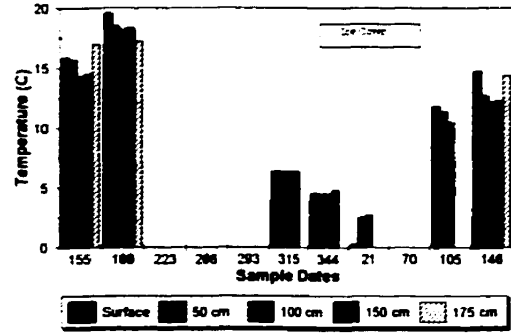


Figure 4.7: Conductance at P1

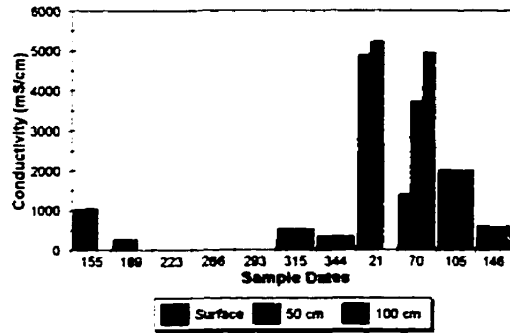
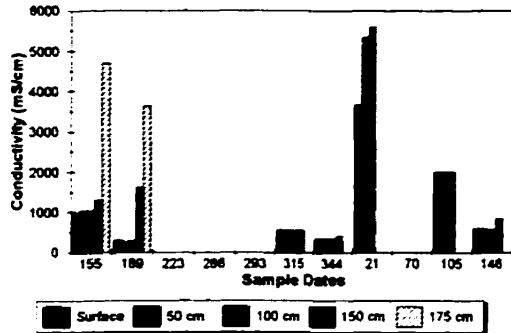


Figure 4.8: Conductance at P2



Temperature was fairly uniform with depth (Figures 4.5 and 4.6). During the summer and fall, temperatures decreased slightly with depth but then increased with depth during winter. Temperature also has an affect on dissolved oxygen concentrations. Increased temperatures such as during the summer decrease the solubility of oxygen in water while decreased temperatures such as throughout the fall and winter increase the solubility of oxygen in water (Wetzell, 1975). DO for the year appear to follow these trends (Figures 4.3 and 4.4). In addition, decreased sorption of metals may be expected at lower temperatures (e.g. during winter months) since the extent of sorption varies positively with temperature (Stumm and Morgan, 1981 as cited in Warren and Zimmerman, 1994). Hence, temperature may impact trace metal mobilisation due to its influence on dissolved oxygen concentrations and on the sorption of metals to particulates.

Conductance ranged from ~ 250 - 1000 mS/cm except during the winter when it peaked at 5000 mS/cm (Figures 4.7 and 4.8). This peak coincided with a peak in chloride and sodium concentrations (Figures 4.10 and 4.25) related to road salting (MOEE, 1983), and elevated concentrations of several metals (eg. dissolved Cu, Ba, Mn, Sr, and Zn) (Figures 4.17, 4.19, 4.23, 4.27, and 4.29).

4.1.2 Suspended Solids

Suspended solids concentrations did not appear to follow a temporal trend (Figure 4.9). Mean suspended solids concentrations were 12 and 22 mg/L in the inlet and S1, respectively. Measured values lie within the mean SS values for the Don River of 12 to 30 mg/L (MOEE, 1991b). Summer SS concentrations may be composed of ~ 25 to 50% particulate carbon associated with biotic growth of algae in the pond (Figure 4.14). However, this is difficult to verify since particulate carbon was analyzed rather than particulate organic carbon.

4.1.3 Chloride and Nutrients

Chloride and Na concentrations were highest in winter and spring when NaCl-based road de-icers are applied (Figure 4.1.10 and 4.1.26). The maximum chloride concentration was almost 1500 mg/L in January, and then dropped to a minimum of ~100 mg/L. Mayer et al. (1996), also measured high concentrations of chloride in the winter (~1000 mg/L) for a detention pond in a mainly residential area of Markham, Ontario. The 12 month average chloride concentration for the Don River ranged from 120 – 250 mg/L from 1983-86 (MOEE, 1991b). Warren and Zimmerman (1994) obtained chloride concentrations within the Don River for the period of October 1990 to February 1991 that ranged from 164 – 1900 mg/L. The Harding Park concentrations are very high in comparison to background concentrations of 5 - 10 mg/L observed for the more pristine Saugeen River Basin (MOEE, 1991b).

Settling or biological processes do not affect chloride concentrations and as such it is a conservative ion impacted more by variations in hydrology. Hence, changes in chloride concentrations are the result of additional inputs of chlorides or dilution from runoff (Wetzell, 1975). Increases in Cl⁻ concentrations from the use of NaCl for snow and ice removal alter the competition for particulate binding sites and promote soluble chloro complexes thereby reducing formation of particulate metal complexes. These results appear to indicate that additions of NaCl due to road salting practices induce increases in the proportion of metals in the dissolved and potentially more bioavailable phase (Figures 4.17, 4.19, 4.23, 4.27, and 4.29) (Warren and Zimmerman, 1994).

The ammonia concentration at the inlet, pond and outlet were similar and frequently above the Provincial Water Quality Objectives of Ontario (PWQO) of 0.02 mg/L (Figure 4.11) (MOEE, 1994). Ammonia is of concern because it is highly toxic to fish and other aquatic biota (MOEE,

1991b) especially when it is present as undissociated NH_4OH . The proportions of NH_4^+ to NH_4OH are dependent upon dissociation dynamics governed by pH. From pH 7 to pH 8, the proportion of NH_4 to NH_4OH changes from 300:1 to 30:1 (Hutchinson, 1957 as cited in Wetzell, 1975). Hence, due to the alkaline pH within the Harding Park pond, NH_4OH may be present in high enough proportions to be exerting a toxic effect upon algae and macrophytes thereby resulting in the low DOC concentrations observed within the pond (Figure 4.16). Concentrations near or above 1 mg/L occurred during ice cover and coincided with depressed dissolved oxygen. Under anoxic conditions, the adsorptive capacity of the sediments is greatly reduced and the result is a marked release of ammonia from the sediments (Wetzell, 1975). Summer and fall ammonia concentrations ranged from <0.02 – 0.7 mg/L. Mayer et al. (1996) reported elevated ammonium concentrations during the winter (0.602 - 1.082 mg/L) in two residential ponds. Ammonia in the German Mills Creek was measured at 0.03 mg/L (MOEE, 1991b) which is also above PWQO.

Total phosphorus concentrations were high and indicative of hypereutrophic conditions (Wetzell, 1975) (Figure 4.12). However, total particulate carbon (Figure 4.14), low DOC (Figure 4.16), and the organic content of 1.75% in the sediments (Table 4.2) are not consistent with hypereutrophic conditions. TP concentrations were highest at ~ 0.25 mg/L in the fall and declined to around 0.07 mg/L in winter and summer. Fall concentrations were likely higher as a result of increased precipitation events that generate runoff from the surrounding residential area. The annual decay of macrophytes at the end of summer and into fall cause a release of phosphorus (Wetzell, 1975). Mayer et al. (1996) reported the same range (0.03 – 0.2 mg/L) for two nearby residential ponds. The average total phosphorus for German Mills Creek was 0.06 mg/L from 1982-86 (MOEE, 1991b). The total phosphorus concentrations of most uncontaminated surface waters are between 0.01 to 0.05 mg/L or 3 to 5 times lower (Wetzell, 1975). Outlet

concentrations were frequently higher than the inlet concentrations indicating that the pond was often a source rather than a sink for phosphorus.

Nitrate concentrations did not vary seasonally (Figure 4.13). Inflow concentrations were usually greater than outflow concentrations indicating that the pond was a net sink for nitrate. Concentrations of around 1 mg/L are high compared to those within the German Mills Creek of 0.4 mg/L (MOEE, 1991b). Concentrations of nitrate range from ~0 to nearly 10 mg/L in unpolluted fresh waters (Wetzell, 1975). Nitrate is an important nutrient for photoautotrophic plants (Wetzell, 1975). Nitrite concentrations in samples were below detection limits (<0.02 mg/L) and concentrations in unpolluted waters are generally very low, in the range of ~0 to 0.01 mg/L (Wetzell, 1975).

Total particulate carbon (TPC) concentrations ranged from 0 – 25 mg/L and 0 – 10 mg/L in the inlet and pond respectively (Figure 4.14). Summer TPC may have increased due to increases in the organic carbon content when algae and aquatic plant growth. This cannot be proven, as TPC does not distinguish between organic and inorganic content. TPC concentrations were generally lower throughout fall, winter and spring than in the summer. However, in November and March, increases in the TPC were observed in the inlet and pond, respectively. The increase in the inlet in November was likely the result of the increased incidence of rainfall events that carried particulate carbon associated with foliage loss in the fall and an influx of carbonates from the surrounding watershed. Total particulate carbon increase in March may have been due to the synthesis of organic matter photosynthetically, although reduced, that continues throughout the winter, and is often vigorous at the later stages of winter ice-cover (Wetzell, 1975).

Dissolved inorganic carbon (DIC) concentrations ranged from 30 - 50 and 10 - 40 mg/L in the inlet and pond, respectively (Figure 4.15 and 4.16). Compounds from abiotic or mineral sources such as carbon dioxide and carbonates contribute to DIC (Gillespie et al., 1989). The origins of DIC within the Harding Park pond are carbonates from the limestone and shale carbonaceous bedrock and till, and also concrete building materials from the local urbanized watershed. Dissolved organic carbon (DOC) concentrations ranged from approximately 5 - 15 mg/L in both the inlet and pond. Organic carbon is derived from biotic sources, e.g. plant and animal matter (Gillespie et al., 1989). The DOC concentrations of swamps may be greater than 30 mg/L (Environment Canada, 1994a). Hence, even though total phosphorus concentrations were very high and indicated that the pond should be hypereutrophic, the low DOC concentration within Harding Park pond was not indicative of this classification.

DOC competes with oxides and sediments for trace metals (Warren, 1994). However, since DOC concentrations were low, trace metals within Harding Park pond were more likely to be associated with Fe and Mn oxides. Neither displayed a temporal pattern. The approximate 10:1 DIC to DOC ratio indicates that the carbon is predominantly inorganic and likely carbonaceous.

Figure 4.9: Suspended Solids at Harding Park for the Inlet and S1

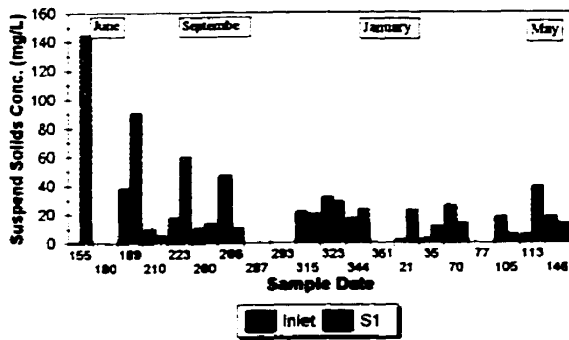


Figure 4.10: Chloride in Surface Waters

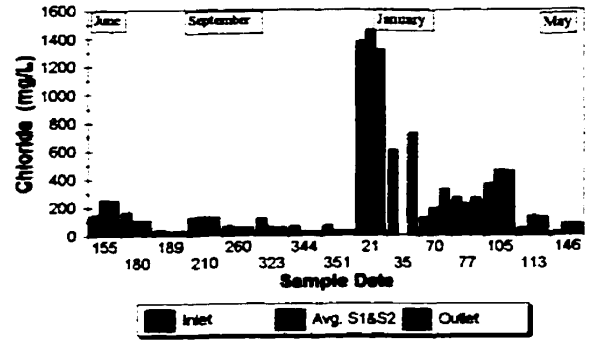


Figure 4.11: Ammonium in Surface Waters

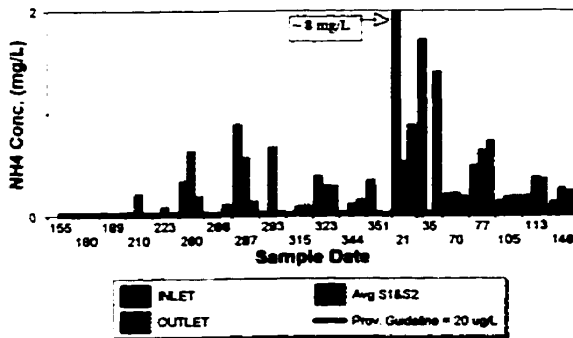


Figure 4.12: Total Phosphorus in Surface Waters

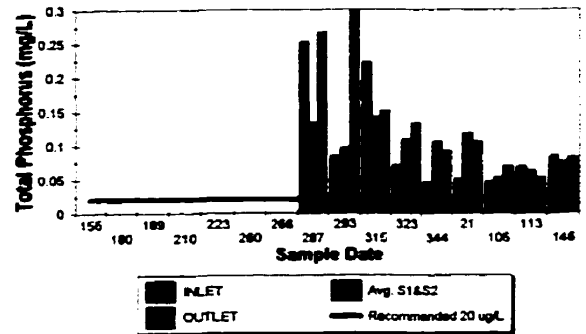


Figure 4.13: Nitrate in Surface Waters

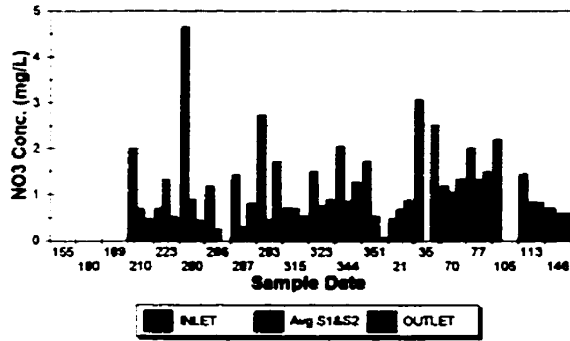


Figure 4.14: Total Particulate Carbon in Surface Waters

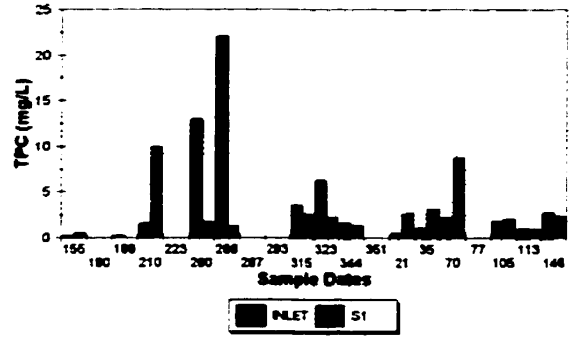


Figure 4.15: Dissolved Inorganic Carbon in Surface Waters at the Inlet & S1

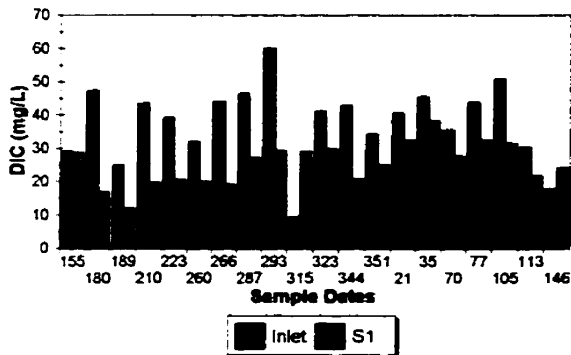
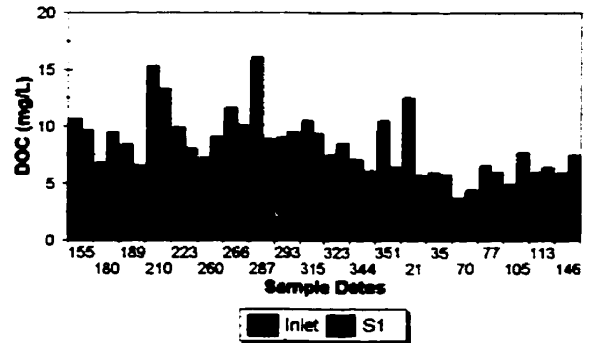


Figure 4.16: Dissolved Organic Carbon in Surface Waters at the Inlet and S1



4.1.4 Trace Metals

4.1.4.1 Relationship to Provincial Water Quality Objectives (PWQO) and other Water Bodies

PWQO were available for only three of the seven metals analyzed: Cu, 5 µg/L, Fe, 300 µg/L, and Zn, 20 µg/L (MOEE, 1994). Total Zn, Cu, and Fe exceeded the guidelines 26, 70 and 80% of the time at the inlet and 16, 21, and 84 % of the time in the outlet, respectively (Figures 4.20, 4.22, and 4.30). Total Cu and Zn in the pond sample sites exceeded the guidelines 20% of the time and coincided with increases in the proportion of these metals in the dissolved phase, while iron exceeded the guideline 73% of the time. The most dramatic exceedances of the guidelines occurred during the winter sample dates.

Metal concentrations found in Harding Park were similar to those of other stormwater detention ponds located in residential areas, and those found within the Don River (Table 4.1). Metal concentrations obtained for highway runoff were higher than those of Harding Park.

Table 4.1: Comparison of Trace Metal Concentrations from Harding Park with other studies, (µg/L).

Trace Metals (µg/L)	Harding Park Detention Pond (min. – max.)	Residential Detention Pond (min.-max.) (Mayer et al., 1996)	East Don River (min. – max.) (MOEE, 1991b)	Higway Runoff (min.-max.) (Marsalek et al., 1997)	PWQO (MOEE, 1994)
Cu	2 – 20	3 - 32	2 – 21	23 – 277	5
Fe	150 – 5000	70 – 9800	260 – 1400	NA	300
Mn	75 – 500	10 – 200	NA	NA	NA
Zn	3 - 50	2 - 80	2 - 120	59 - 775	20

4.1.4.2 Total versus Dissolved Phase and Temporal Trends

Ba, Na, and Sr were 60 - 100%, and Cu and Zn were 20 – 80% in the dissolved phase, while Fe was almost 80 -100% associated with the particulate phase (Figures 4.1.17- 4.1.30). Contrary to expectations, Mn varied from one extreme to the other. The study by Marsalek et al. (1997) found 30 – 45% of the total metal samples to be in the dissolved phase in highway runoff. Dissolved phase metals are of concern since they are bioavailable and thereby more toxic than those in the particulate phases (Hall and Anderson, 1987).

Total concentrations of Cu and Zn tended to decrease over the summer followed by a gradual increase throughout the fall (Figures 4.1.19, 4.1.20, 4.1.29, and 4.1.30). These trends are likely attributed to a very dry summer with minimal loadings that favour gravitational settling of particulate bound metals followed by an increase in rainfall during the fall and hence an influx of street runoff. However, in the summer the DO content decreased resulting in a slightly more reducing environment that causes Cu and Zn to become more mobile. Into the fall, the DO increased creating more oxic conditions, allowing Cu and Zn to become less mobile. The increase of Cu and Zn concentrations into the fall were opposite to expected DO trends due to inputs with increased runoff. Ba and Sr did not seem to follow any seasonal trends in dissolved to particulate distribution. Fe becomes less mobile under oxic conditions as it was transformed to the less soluble ferric complexes. Thus, Fe increased from 88% to 97% particulate phase when DO increased in the fall. Mn, which was expected to behave similarly to Fe, decreased from 70% to 20% in the particulate phase from summer into the fall when the DO increased, the reason for which is uncertain.

A 50 – 60% increase in all total trace metal concentrations, except total Fe which decreased ~40%, was observed during the winter when the pond was ice covered. This coincided

with an increase of metals in the dissolved phase. All metals increased their proportions in the dissolved phase, including Fe even though DO increased: from 85% to 90% dissolved for Ba and Sr, 60% to 90% dissolved for Cu and Zn, 80% to 95% dissolved for Mn, and 10% to 25% dissolved for Fe. Increased % dissolved metals in the winter were likely a function of: a) street scouring of metals from engine, tire, and brake wear on the roads during freeze-thaw events (Marsalek, 1991), b) decreased temperature, and c) increased concentrations Cl^- (Warren and Zimmerman, 1994). Warren and Zimmerman (1994), found an increase in the percentage of metals in the dissolved phase in winter and speculated that it was due to decreased sorption of trace metals on particulates at lower temperatures. Chloride has been found to reduce cationic metal sorption. Increases in Cl^- concentrations were found to decrease the relative partitioning of trace metals to solid phase materials due to the ability of metals to form soluble chloro complexes (O'Shea and Mancey, 1978 as cited in Warren and Zimmerman, 1994). Complexant ligands in solution, such as Cl^- , can compete with the sediment surface complexes for metals thereby reducing the extent to which metals are retained by sediments (Lumsdon et al., 1995). Thus in the Harding Park SDP, which is located within the well buffered system of the Don River watershed, both temperature and NaCl concentrations appear to have a large impact on the partitioning of trace metals between dissolved and particulate phases. An increase in the proportion of dissolved metals could potentially increase the pool of bioavailable metals (Warren and Zimmerman, 1994).

A simple regression exercise was performed to investigate the impact of total Fe concentration on the partitioning of other trace metals within the dissolved or particulate phases. The molar ratios of total Cu: total Fe concentrations were plotted against % dissolved Cu concentration for the inlet, within the pond, and the outlet and a regression analysis performed (Figures 4.31 to 4.33). Regression analyses of these plots was performed to determine the

significance of the relationship between total Cu: Fe to % dissolved Cu and to also produce a mathematical equation that describes the relationship. An r^2 value of 1 signifies a perfect positive relationship between an independent variable and a dependent variable. An r^2 value close to 1 would signify that an increase in the total concentration of a trace metal such as Cu relative to Fe would result in an increased proportion of that trace metal in the dissolved phase. An r^2 value close to -1 signifies a perfect negative relationship whereby an increase in total trace metal concentration relative to total Fe would result in a decrease in the proportion of that trace metal in the dissolved phase (Griffith and Amrhein, 1991). The computed r^2 values for total Cu:Fe and % dissolved Cu were 0.06, 0.021, and 0.004 for the inlet, pond (S1 and S2), and the outlet, respectively. These r^2 values are significantly less than 1 indicating a poor but positive relationship between total Cu:Fe and % dissolved Cu. Hence, an increase in the total concentration of Cu relative to Fe does not have a large impact on the proportion of Cu in the dissolved phase.

Figure 4.17: Dissolved Barium in Surface Waters

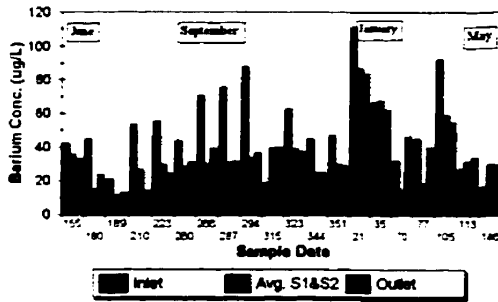


Figure 4.18: Total Barium in Surface Waters

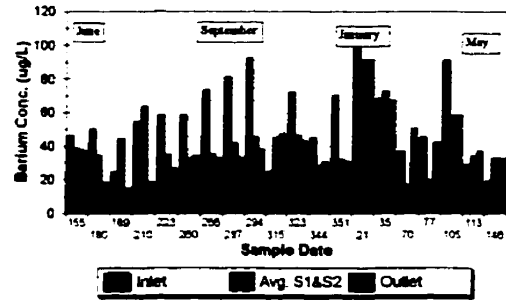


Figure 4.19: Dissolved Copper in Surface Waters

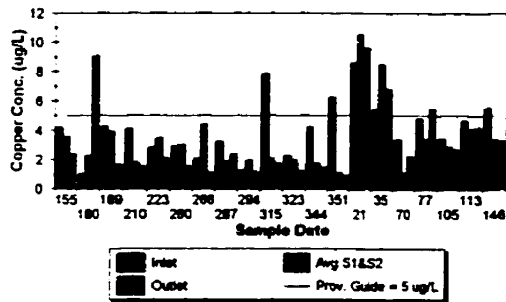


Figure 4.20: Total Copper in Surface Waters

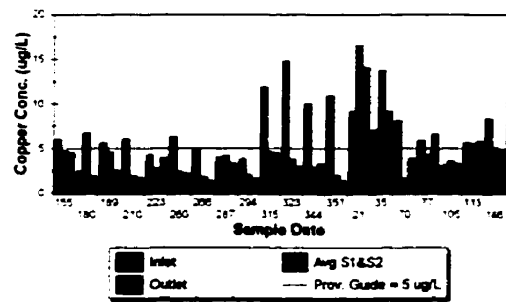


Figure 4.21: Dissolved Iron in Surface Waters

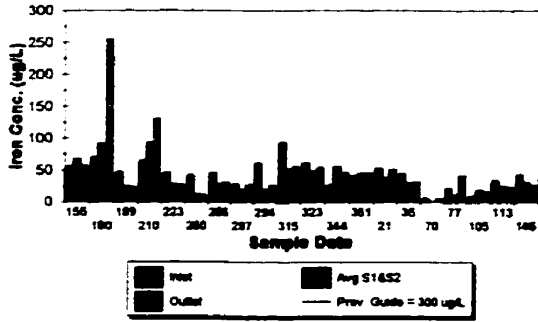


Figure 4.22: Total Iron in Surface Waters

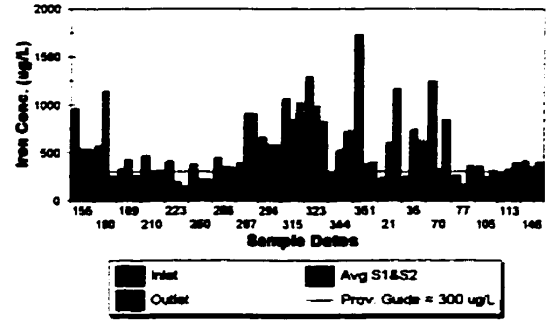


Figure 4.23: Dissolved Manganese in Surface Waters

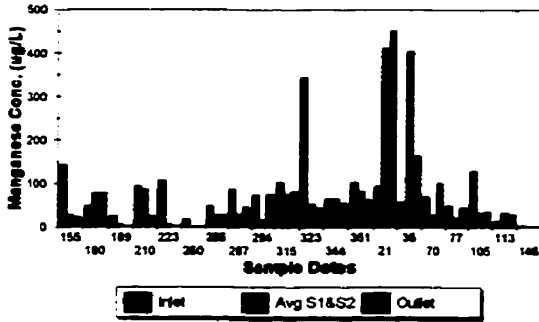


Figure 4.24: Total Manganese in Surface Waters

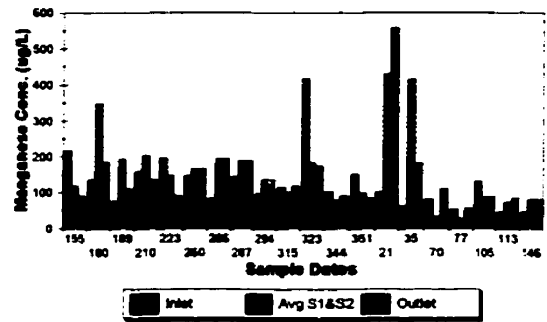


Figure 4.25: Dissolved Sodium in Surface Waters

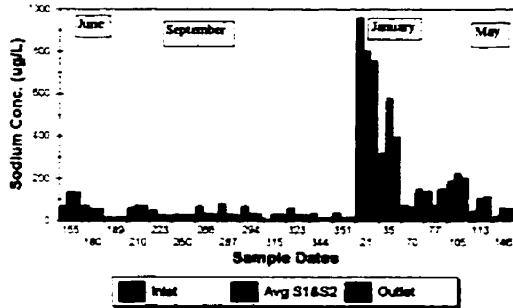


Figure 4.26: Total Sodium in Surface Waters

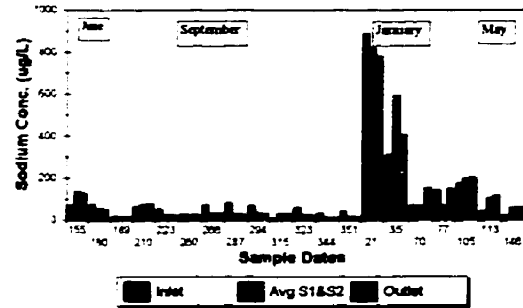


Figure 4.27: Dissolved Strontium in Surface Waters

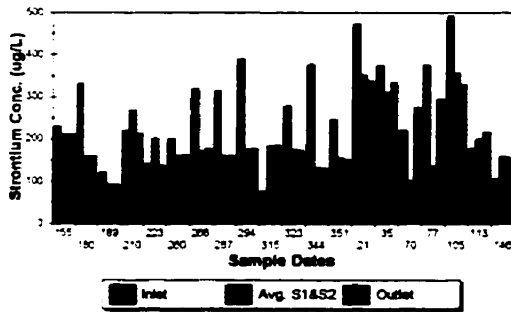


Figure 4.28: Total Strontium in Surface Waters

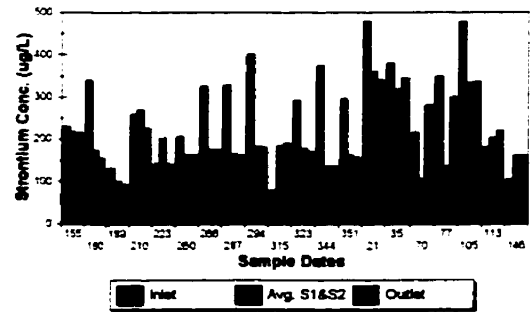


Figure 4.29: Dissolved Zinc in Surface Waters

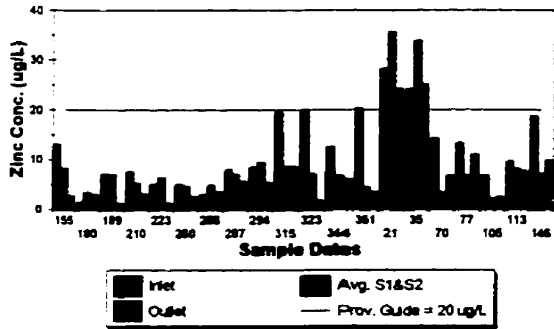
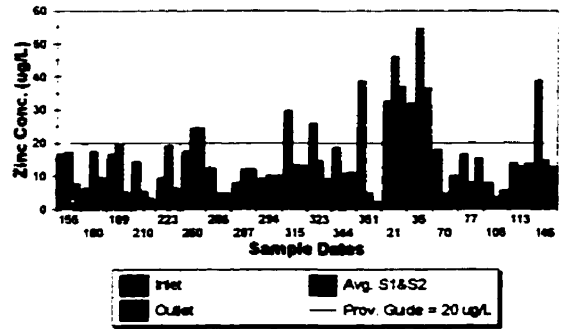
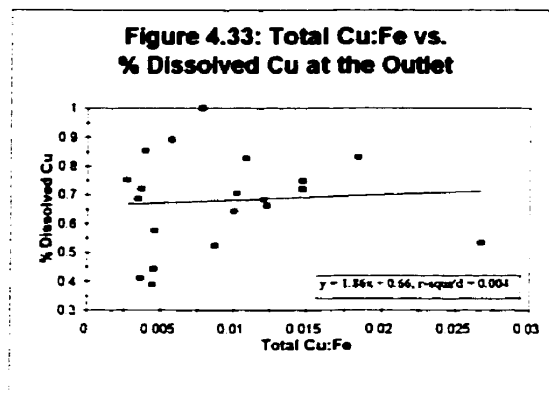
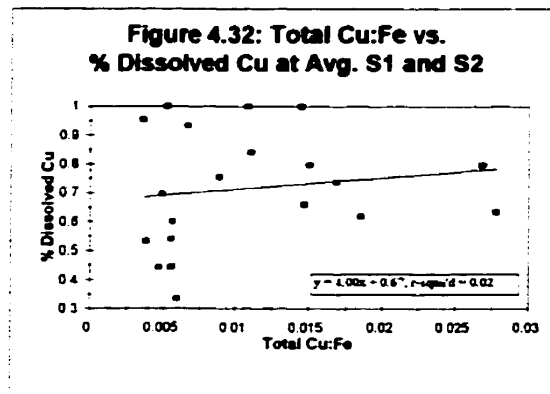
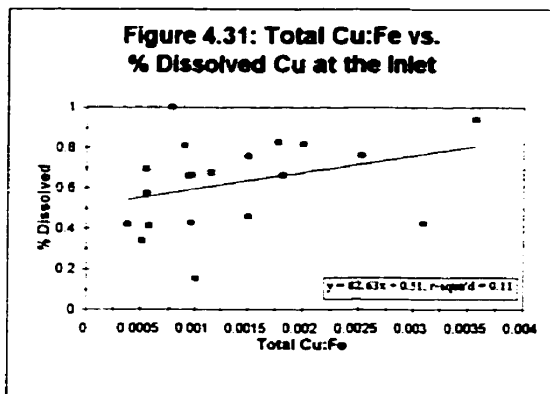


Figure 4.30: Total Zinc in Surface Waters





4.1.4.3 Sink versus Source

To assess whether the SDP was acting as a sink for metals, as intended, trace metal concentrations in the outlet were subtracted from those in the inlet for each sampling time. Total and dissolved trace metal concentrations tended to be higher at the inlet than in the pond or outlet (Figures 4.34 – 4.47). These measurements suggest that the pond was acting as a net sink for metals as intended. Exceptions to this were during the winter and spring when increased NaCl and decreased temperature in the winter favoured trace metal mobilisation, while increased DO in the spring favoured trace metal immobilisation in the dissolved phase due increasingly oxic conditions that would induce metal complexation with Fe and Mn oxides. In addition, increased flows during the winter and spring may have decreased the retention time such that it was insufficient for particle bound metals to settle. The study by Nu Hoai et al. (1998) found that the trap efficiency of an artificial wetland decreased following any medium rainfall. Also, sampling during a major rainfall event resulted in loadings leaving the system to be greater than the load of metals entering the system (Nu Hoai et al., 1998). During the spring the pond behaved as a source of Na as it was still flushing from the pond and inputs from the watershed had decreased. A more accurate analysis would require flow data and more frequent sampling from which mass loadings can be calculated, however these data are unavailable. Loading data would further explain whether the pond behaves as a net sink for trace metals throughout the year or whether large flow volumes at critical times in the year result in the pond behaving as a net source of trace metals.

The Harding Park pond appears to be more of an efficient sink for trace metals during the summer when flows are low. It is not entirely clear whether the pond is an efficient sink when flows are high, e.g. March. However, whether the pond is a sink or source appears to be controlled more by water residence time than by complexation with Fe and Mn oxides.

Figure 4.34: Sink vs. Source Assessment of Dissolved Barium

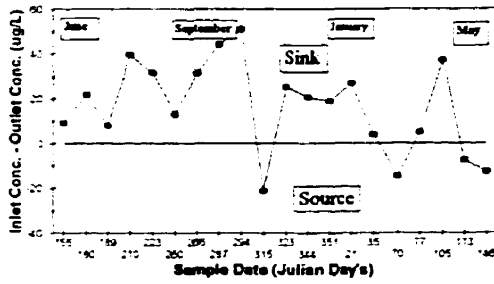


Figure 4.35: Sink vs. Source Assessment for Total Barium

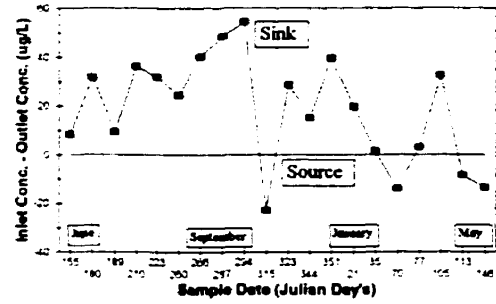


Figure 4.36: Sink vs. Source Assessment for Dissolved Copper

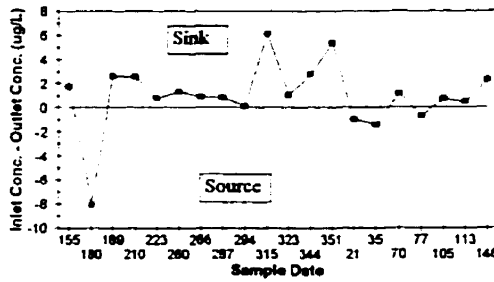


Figure 4.37: Sink vs. Source Assessment for Total Copper

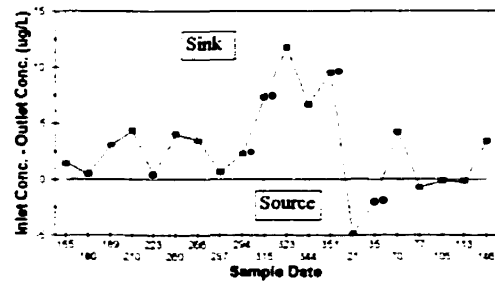


Figure 4.38: Sink vs. Source Assessment of Dissolved Iron

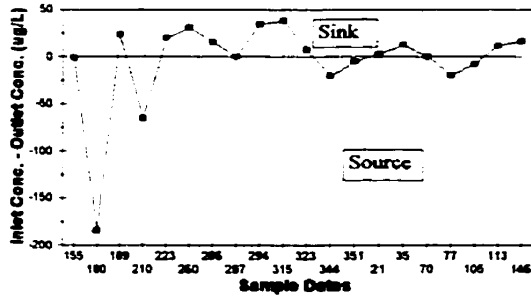


Figure 4.39: Sink vs. Source Assessment of Total Iron

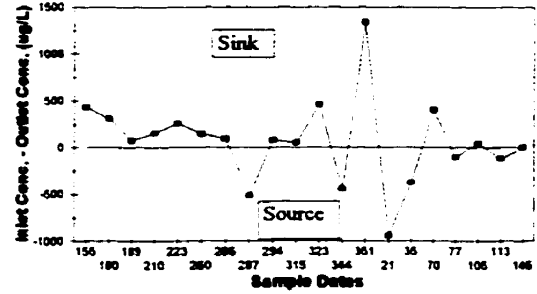


Figure 4.40: Sink vs. Source Assessment of Dissolved Manganese

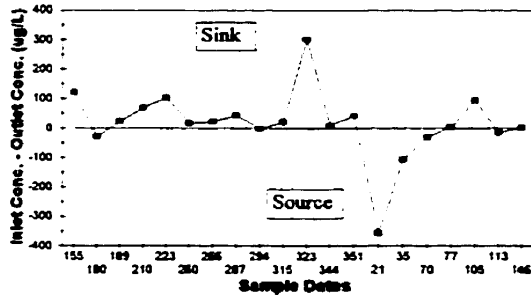


Figure 4.41: Sink vs. Source Assessment of Total Manganese

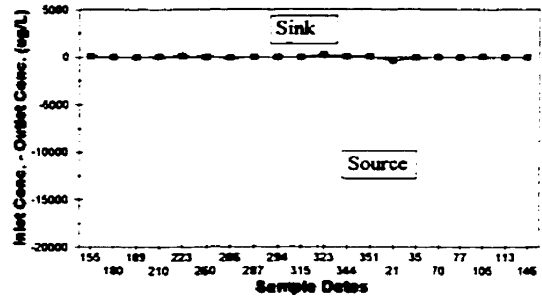


Figure 4.42: Sink vs. Source Assessment of Dissolved Sodium

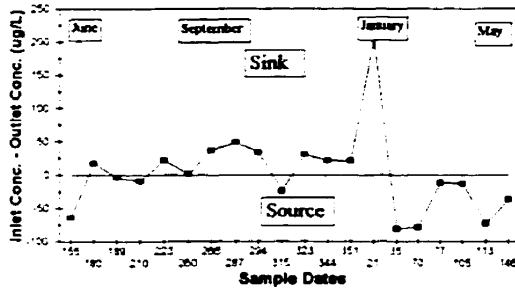


Figure 4.43: Sink vs. Source Assessment of Total Sodium

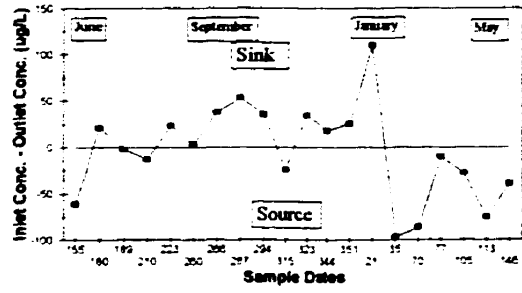


Figure 4.44: Sink vs. Source Assessment of Dissolved Strontium

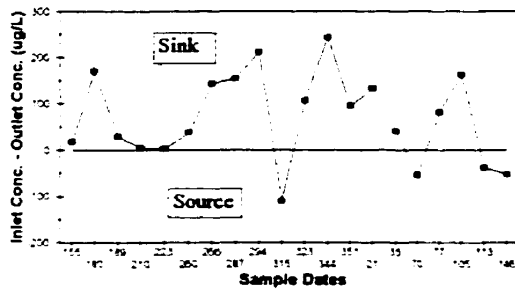


Figure 4.45: Sink vs. Source Assessment of Total Strontium

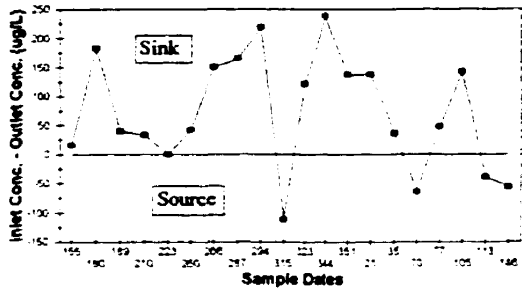


Figure 4.46: Sink vs. Source Assessment of Dissolved Zinc

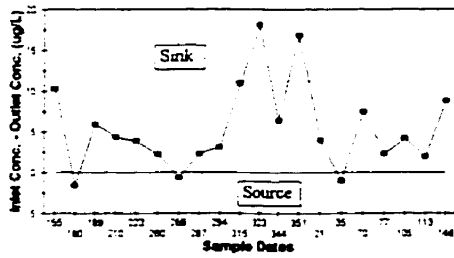
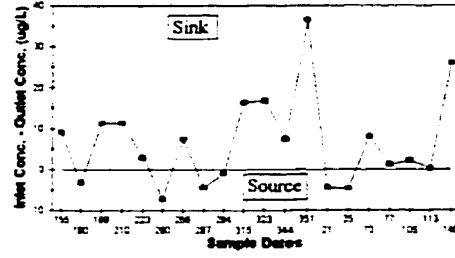


Figure 4.47: Sink vs. Source Assessment of Total Zinc



4.2 Sediment Characterisation and Pore Water Profiles

Sediments were sampled and characterized. Pore water samples were analyzed for trace metals and characterized for redox and pH levels with the use of a platinum electrode. Pore water samples were diluted in order to bring pore water samples to the correct volume required for the analysis by ICP-OES and because concentrations of some metals in sediments (e.g. Fe and Mn) would not have been within the detection limits of the instrument. Because samples were diluted for analysis purposes, Cu and Zn were near detection limits in pore water samples. Detection limits are in Appendix A.

4.2.1 Sediment Characterisation

Sediments within Harding Park stormwater detention pond were comprised of 33.8 % sand, 46.4% silt, and 19.8% clay. The sand composition of the pond sediments may be expected to increase over time due to winter street sanding practices of the town of Richmond Hill, Ontario. A pond studied in Kingston, Ontario found silt (41%) and clay (54%) to dominate in sediment deposits with the remaining 5% as sand (Marsalek, et. al., 1997). Clay minerals found to be present, but not dominant, were smectite, kaolinite, chlorite, clay mica, hydroxy-interlayered vermiculite, and trace amounts of vermiculite. The edges of clays accept and donate protons and due to their prominently negative charges, are important in the retention of trace metals (Bolton and Evans, 1997). The cation exchange capacity was measured as 15 cmol/kg. The sediment contained 643 mg/kg organically bound Fe, 3549 mg/kg inorganic poorly crystalline Fe, and 2035 mg/kg inorganic crystalline Fe.

As indicated in table 4.2, the sediment contained 1.21% organic carbon which was lower than the sediment of the Rouge River detention pond that was found to have an organic carbon content of 7.10% (Mayer et al, 1999). This lower organic carbon content in Harding Park

sediment supports the lower concentrations of particulate carbon (Figure 4.1.14) and DOC (Figure 4.1.16) found in surface waters. The very high concentrations of total phosphorus indicate that the pond could potentially have induced more growth of micro- and macrophytes. During sampling events it was observed that sediments at the sediment-water interface were very black which is indicative of a high organic carbon content at the sediment surface. Below this dark layer, the sediments were a grey/blue colour, indicative of the presence of iron under reduced conditions (Fitzpatrick, 1986). Mixing of these two zones within the sediments may have resulted in an overall lower organic carbon content when sediments were characterised.

Table 4.2. Sediment Characterisation

Sediment Characteristics	Content
Total Carbon	5.00 %
Inorganic Carbon	3.75 %
Organic Carbon	1.75 %
Cation Exchange Capacity	15 cmol/kg
Organically Bound Fe	643 mg/kg
Inorganic Poorly Crystalline Fe	3549 mg/kg
Inorganic Crystalline Fe	2035 mg/kg

Analysis by neutron activation energy (Table 4.3) indicate that Ca, Al, Fe, Mg, and Na were found in the greatest amounts and of the trace metals, Mn, Ba, and Sr were found to have substantial concentrations. No data was reported for either Cu or Zn.

Table 4.3 Data from Neutron Activation Energy Analysis

Major Elements		Trace Metals	
Element	%	Element	ppm
Al	4.88	Ba	544
Ca	11.2	Cu	No data
Fe	2.80	Mn	571
K	1.76	Sr	332
Mg	1.23	Zn	No data
Na	1.22		

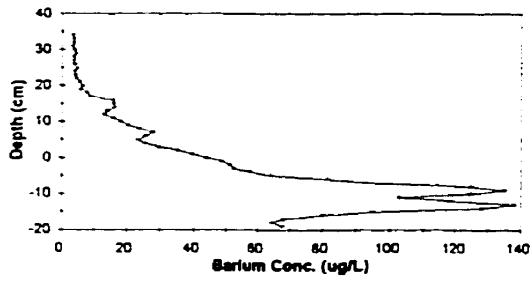
4.2.2 Depth Trends

Throughout most of the year, trace metals in pore water profiles reached a maximum metal concentration near the sediment-water interface that then declined with depth. Pore water profiles for two sampling dates (July 29/98 and March 11/99) are shown, for illustrative purposes (Figures 4.48 – 4.61 and 4.62 - 4.68). Ba, Cu, Sr, Na, and Zn profiles resemble those for Fe and Mn, reaching a maximum concentration at ~10 cm. Pore water profiles for all metals at all sampling dates are in Appendix B. Eh profiles indicate a decrease in redox potential with depth from oxidizing conditions above the sediment water interface to reducing conditions below (Figure 4.69 - 4.80). The pH profiles again indicated a well-buffered system, varying from 8 at the surface to neutrality into the sediments (pH ~ 7.0). For illustrative purposes the pH profile for March 11/99 is shown in Figure 4.81. Since the pH profiles did not change significantly throughout the year, pH profiles at all sampling dates are in Appendix C. Changes in these factors are of importance since Eh and pH control metal mobility.

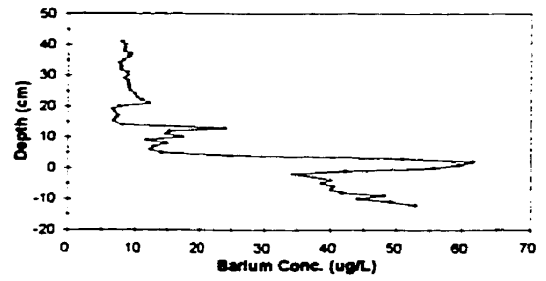
Under strongly oxidizing conditions (e.g. 120 to 225 mV), Fe and Mn are immobilised as they form oxides. Other metals such as Ba, Cu, Sr, Na, and Zn are immobilised due to complexation with Fe and Mn oxides (Förstner et al., 1990, Gambrell and Patrick, 1991, Calmano et al., 1993, and Gambrell, 1994,). Under strongly reducing conditions (e.g. -200 mV), as exhibited by the pond sediments at depth of ~10 to 20 cm within the sediments, metals also become immobilised as they form insoluble complexes with sulphides. Sulphate is transformed to sulphide when the redox potential reaches -75 to -150 mV (Mitsch and Gosselink, 1993). The formation of minerals such as iron and manganese sulphides controls solubility at depth (Davison, 1985 and Förstner et

al., 1990). Between these two zones, manganese is transformed from manganic to manganous compounds at about 225 mV, while iron is transformed from ferric to ferrous forms at about 120 mV (Mitsch and Gosselink, 1993). This suggests a mobilisation of these metals at 120 mV to -75 mV, just below the sediment-water interface, and immobilisation above and below this zone.

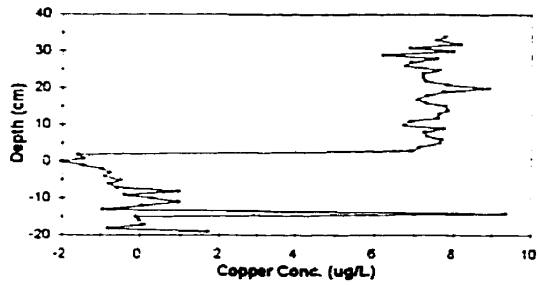
**Figure 4.48: Barium Profile at P1
for July 29/98**



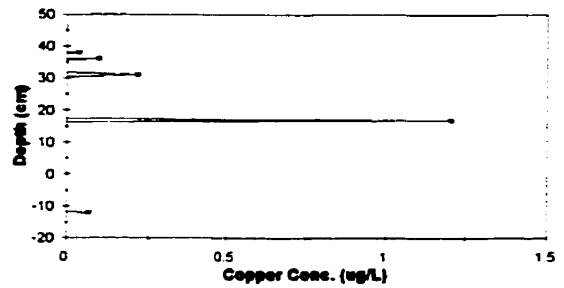
**Figure 4.49: Barium Profile at P2
for July 29/98**



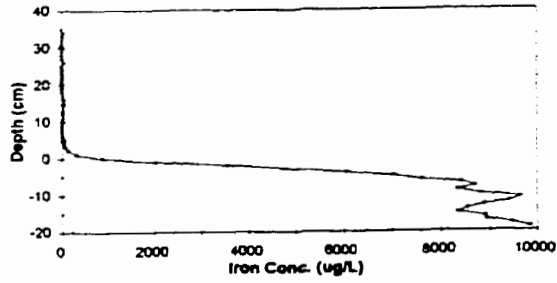
**Figure 4.50: Copper Profile at P1
for July 29/98**



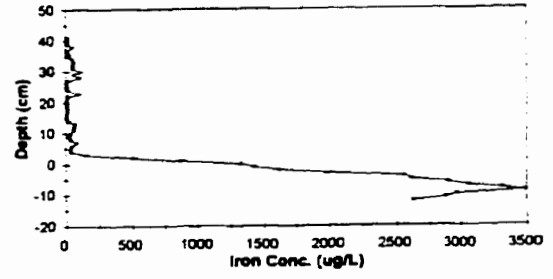
**Figure 4.51: Copper Profile at P2
for July 29/98**



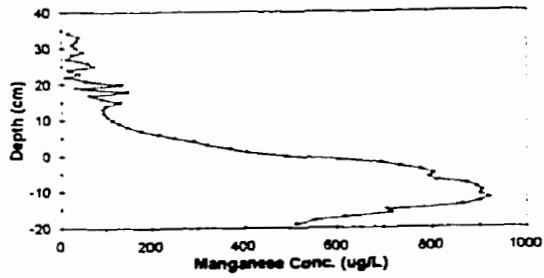
**Figure 4.52: Iron Profile at P1
for July 29/98**



**Figure 4.53: Iron Profile at P2
for July 29/98**



**Figure 4.54: Manganese Profile at P1
for July 29/98**



**Figure 4.55: Manganese Profile at P2
for July 29/98**

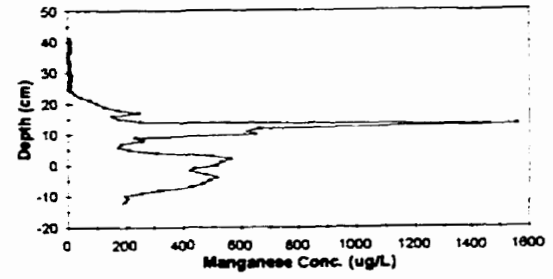


Figure 4.56: Sodium Profile at P1 for July 29/98

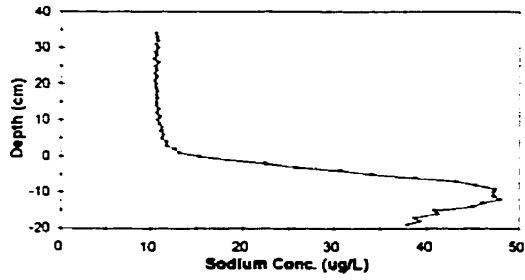


Figure 4.57: Sodium Conc. at P2 for July 29/98

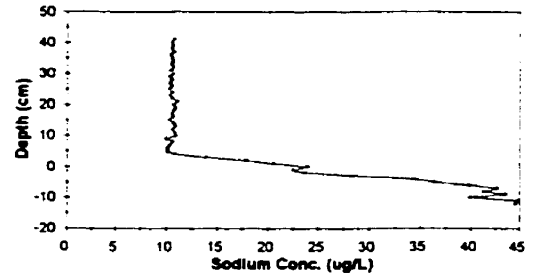


Figure 4.58: Strontium Profile at P1 for July 29/98

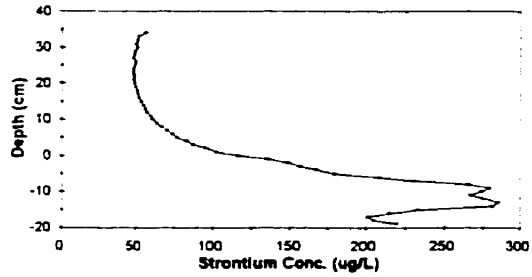
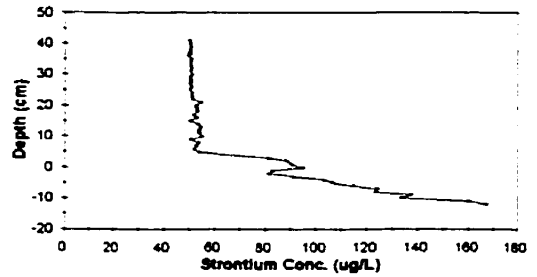
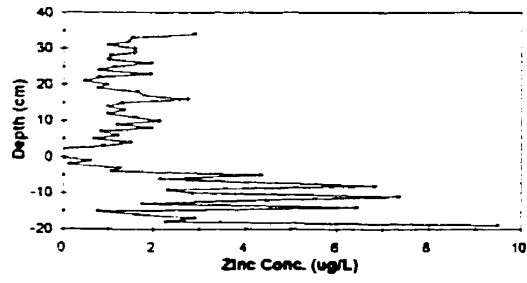


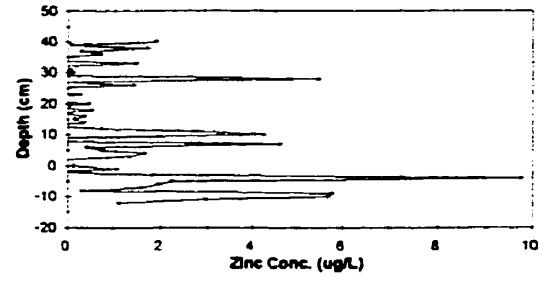
Figure 4.59: Strontium Profile at P2 for July 29/98



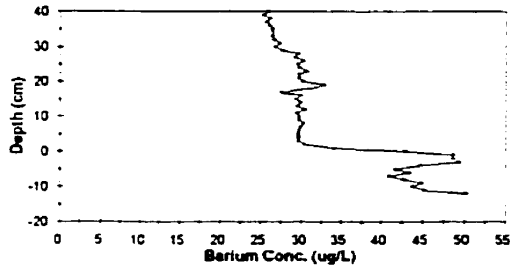
**Figure 4.60: Zinc Profile at P1
for July 29/98**



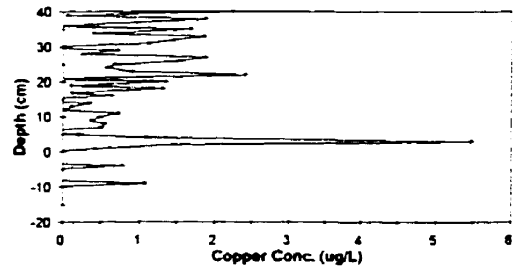
**Figure 4.61: Zinc Profile at P2
for July 29/98**



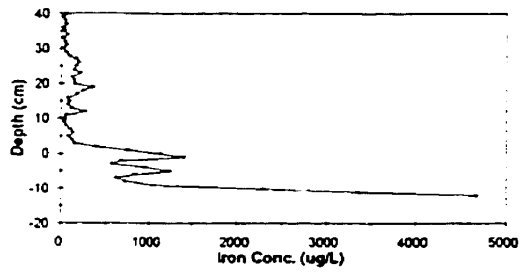
**Figure 4.62: Barium Profile at P1
for March 11/99**



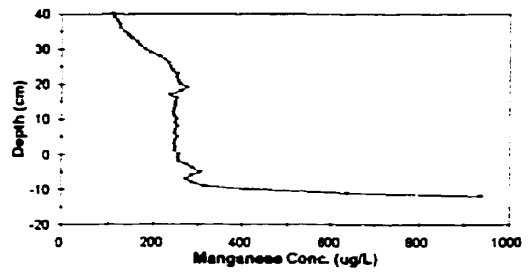
**Figure 4.63: Copper Profile at P1
for March 11/99**



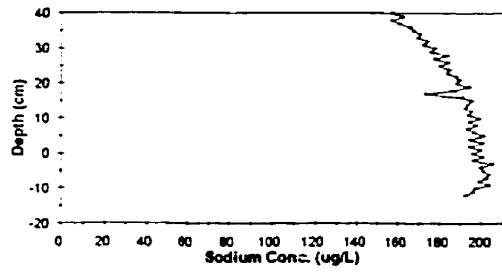
**Figure 4.64: Iron Profile at P1
for March 11/99**



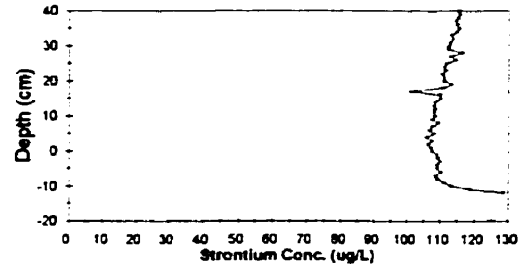
**Figure 4.65: Manganese Profile at P1
for March 11/99**



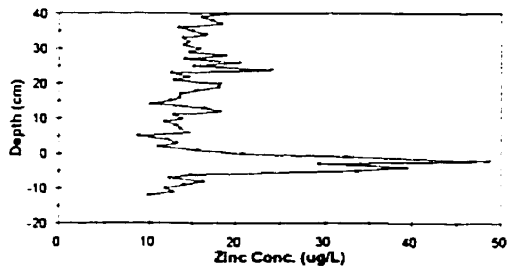
**Figure 4.66: Sodium Profile at P1
for March 11/99**



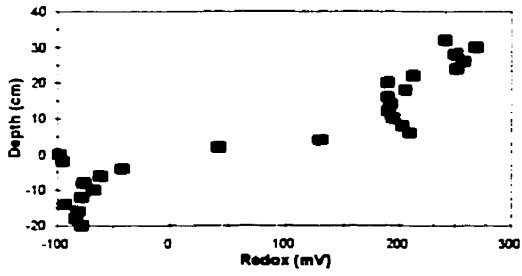
**Figure 4.67: Strontium Profile at P1
for March 11/99**



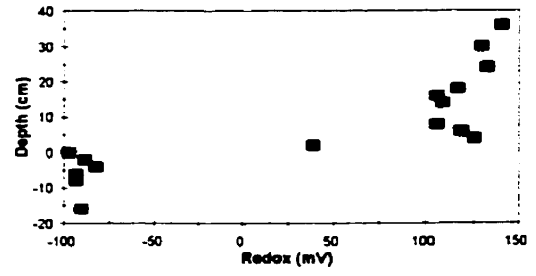
**Figure 4.68: Zinc Profile at P1
for March 11/99**



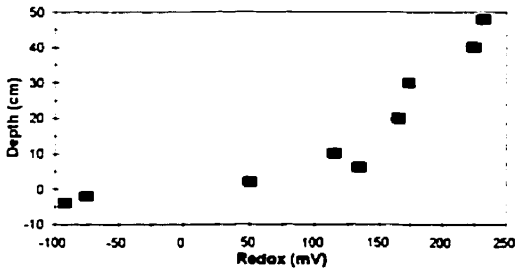
**Figure 4.69: Redox at P1
for June 4/98**



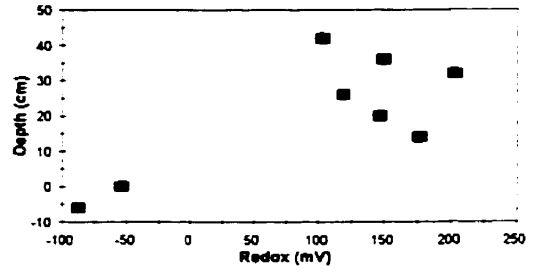
**Figure 4.70: Redox at P2
for June 4/98**



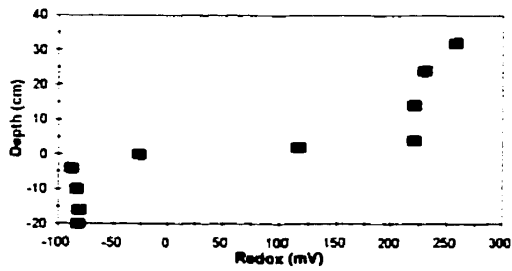
**Figure 4.71: Redox at P2
for June 30/98**



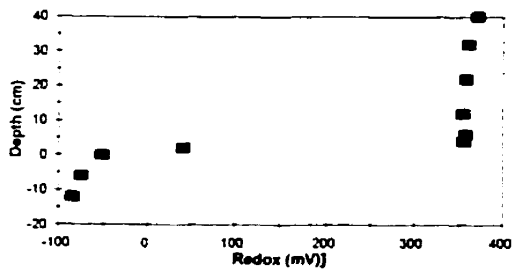
**Figure 4.72: Redox at P2
for July 29/98**



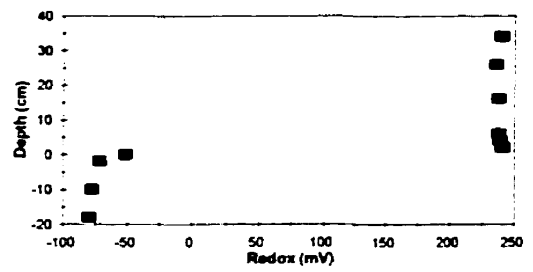
**Figure 4.73: Redox at P1
for Oct 14/98**



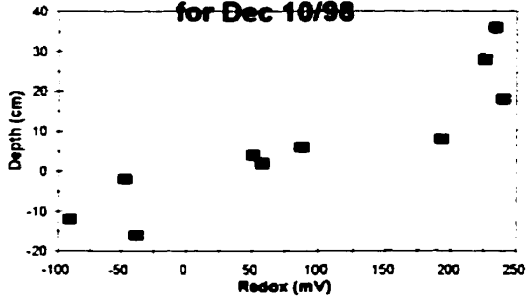
**Figure 4.74: Redox at P1
for Nov 11/98**



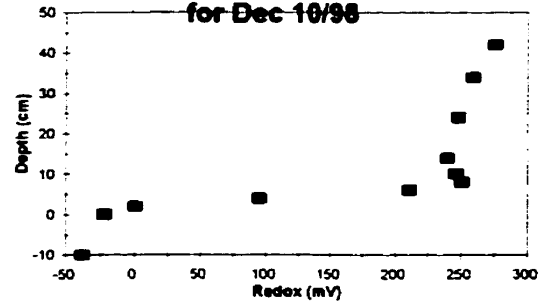
**Figure 4.75: Redox at P2
for Nov 11/98**



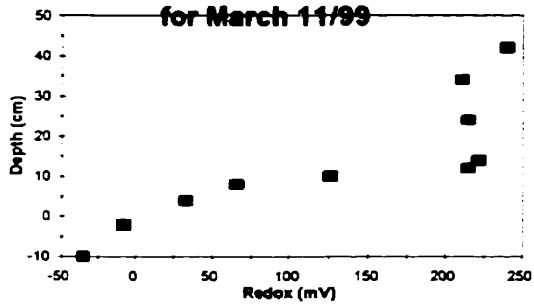
**Figure 4.76: Redox at P1
for Dec 10/98**



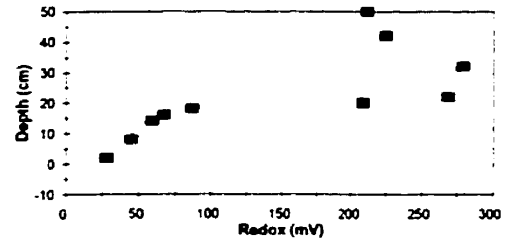
**Figure 4.77: Redox at P2
for Dec 10/98**



**Figure 4.78: Redox Profile at P1
for March 11/99**



**Figure 4.79: Redox Profiles at P1
for April 15/99**



**Figure 4.80: Redox at P1
for May 26/99**

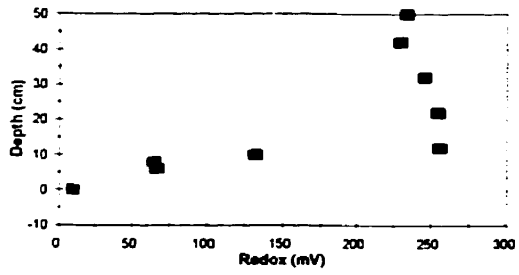
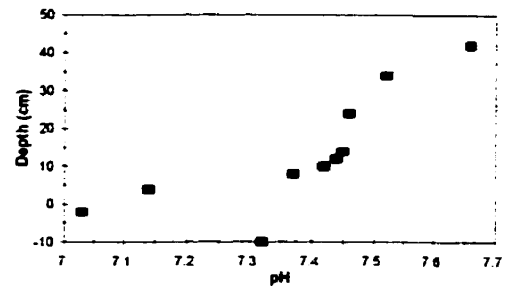


Figure 4.81: pH at P1 for March 11/99



The Mn profiles indicate dissolution beginning at ~10 – 20 cm above the sediment water interface (Figure 4.54 and 4.55) with the reduction of manganese to its more soluble manganous form. This coincides with a decrease in Eh to ~200 mV (Figure 4.72) at ~20 cm above the sediment-water interface. Fe dissolution to its soluble ferric form does not begin until at the sediment-interface (Figures 4.52 and 4.53) which coincides with an Eh of ~50mV at this depth (Figure 4.72). Ba, Sr, and Na pore water profiles also indicate dissolution that coincide with both Mn and Fe dissolution (Figures 4.48 - 4.49, 4.56 – 4.57, and 4.58 – 4.59). Cu and Zn pore water concentrations were close to the detection limits, however, they too generally have similar profiles to Fe and Mn. Hence, Fe and Mn seem to be controlling the solubility of the other trace metals subsequent to their reduction to more soluble forms followed by precipitation as sulphides and carbonates. Many studies, as cited by Davison (1985), have found similar dissolved metal profiles in lake sediments (e.g. Robbins and Callender, 1975, Murray et al., 1978, Crerar et al., 1980, Emerson, 1976, Emerson and Widmer, 1978, and Cook, 1981). Mayer et al. (1999) and Donahoe and Liu (1998) also found similar dissolved trace metal depth trends.

4.2.3 Temporal Trends in Depth Profiles

During the summer DO was depleted in surface waters which resulted in low redox values of 200 mV at ~20-30 cm and 100 mV at ~0-15 cm above the sediment-water interface (Figure 4.72). Dissolution of reduced Fe and Mn oxides occurred higher in the profiles within the water column between 0 to 15 cm and 20 to 30 cm above the sediment-water interface, respectively. Ba, Sr, and Na pore water profiles follow Fe and Mn profiles. Cu and Zn appeared to have increased dissolution throughout the water column possibly due to these reduced conditions. Zn

appears to follow the Fe and Mn profiles more closely than Cu. Again, Cu and Zn profiles were difficult to interpret as their concentrations were close to the instrument detection limits.

However, during the winter when DO had increased (Figure 4.3 - 4.4), low redox values of ~ 200 mV did not occur until ~ 10 cm above the sediment-water interface and ~ 125 mV occurred very close to the sediment-water interface (Figure 4.78). The main dissolution of Fe and Mn occurs ~ 10 cm below the sediment-water interface. Ba, Cu, Sr, and Zn do not appear to be controlled by Fe and Mn above the sediment-water interface. However, at ~ 10 cm below the sediment-water interface, Ba, Cu, Sr, and Zn begin to follow the profiles of Fe and Mn.

The supersaturation of DO (Figure 4.3 - 4.4) that occurred at the end of ice cover in March coincided with trace metal profiles similar to those that occurred in January where Cl^- concentrations were at their maximum (Figure 4.10). Possibly Cl^- concentrations, although decreased, were still exerting an effect on the trace metals in the dissolved phase. It was not until late spring that decreased concentrations of trace metals occurred above the sediment-water interface.

For most of the year, Ba, Cu, Sr, Na, and Zn concentrations appeared to be controlled by Fe and Mn. These metals had similar profiles to Fe and Mn where concentrations reached a maximum that shifted according to changes in the position of the redoxcline caused by changes in DO. During the winter however, Ba, Cu, Sr, Na, and Zn differed from those profiles for Fe and Mn above the sediment-water interface. Hence, immobilisation with Fe and Mn oxides did not appear to be controlling the concentrations of these metals in the water column at this time.

4.2.4 Diffusion Calculations

The diffusive flux for each trace metal was calculated based on the peeper concentration profiles obtained for the year (Figure 4.82 – 4.95). The diffusive flux of each of the trace metals between the sediments and the overlying water column was calculated according to the following equation from Li and Gregory (1974):

$$N = -D_{\text{eff}}(dC/dZ), D_{\text{eff}} = D \cdot k,$$

where N is the flux ($\mu\text{g}/\text{day}\cdot\text{m}^2$), dC is the concentration gradient ($\mu\text{g}/\text{m}^3$), dZ is the path length (m), D is the molecular diffusion coefficient, and k is the diffusivity correction factor (Li and Gregory, 1974). The concentration gradient was taken as the pore water concentration 1 cm above minus 1 cm below the sediment–water interface. Thus, the path length was 2 cm. Specific D values for each metal and according to temperature were taken from Li and Gregory, 1974. The correction factor is a function of sediment porosity and for the Harding Park pond sediments, k was estimated at 0.8 (Diamond, 1999). Diffusive flux calculations were uncertain for Cu due to the proximity of diluted pore water Cu concentrations to the instrument detection limit for Cu.

Positive flux values indicate that the trace metals are diffusing from the overlying water column to the sediments and negative flux values indicate diffusion from the sediments to the water column. Metals that diffuse upwards due to the reduction and dissolution of Fe and Mn, are likely reimmobilised with Fe and Mn oxidized complexes in oxic surface water. This likely results in the metals returning to the sediments in the particulate phase. Hence, a recycling of metals occurs between the zone of dissolution at or below the sediment-water interface at the redoxcline and above where oxidation occurs. Recycling likely increases the residence time of the metals near the sediment–water interface. Immobilisation as metal sulphide complexes occurs

below the Fe and Mn zone of dissolution, and likely enhances the overall status of the pond as a sink.

Trace metals diffused from the sediments into the water 70-100% of the year. During the winter, especially in January and again in March, Ba, Cu, Na, and Zn were diffusing from the water into the sediments (10 – 30% of the time). Metal immobilisation in surface waters was decreased at this time possibly due to the influx of Cl⁻ from road salting applications and to decreased temperatures even though increased DO and the likely complexation with Fe and Mn oxides was expected to decrease the mobility of metals.

Figure 4.82: Diffusive Flux of Barium at P1

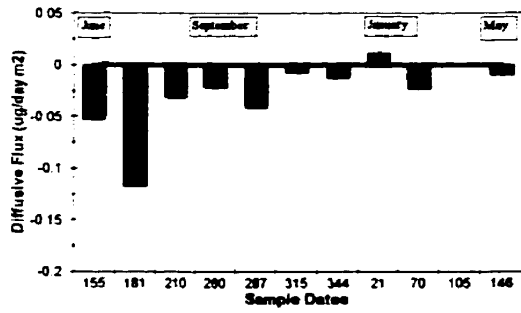


Figure 4.83: Diffusive Flux of Barium at P2

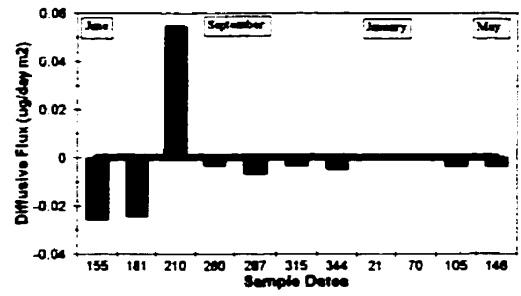


Figure 4.84: Diffusive Flux of Copper at P1

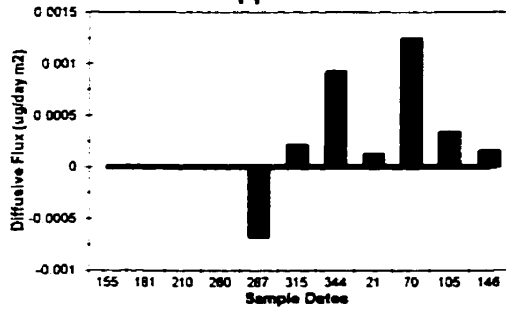


Figure 4.85: Diffusive Flux of Copper at P2

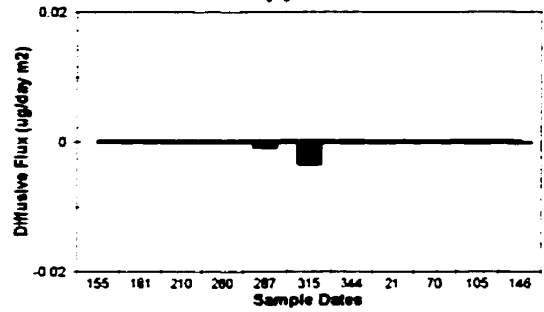


Figure 4.86: Diffusive Flux of Iron at P1

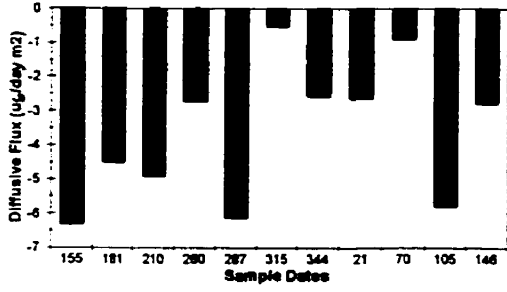


Figure 4.87: Diffusive Flux of Iron at P2

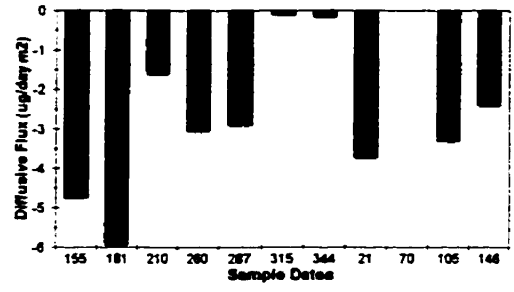


Figure 4.88: Diffusive Flux of Manganese at P1

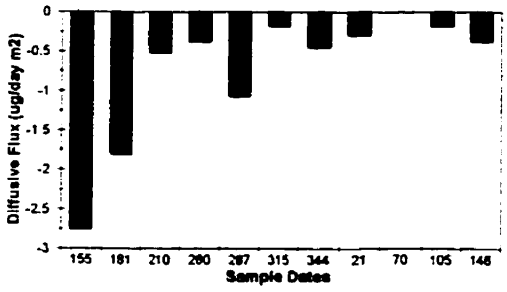


Figure 4.89: Diffusive Flux of Manganese at P2

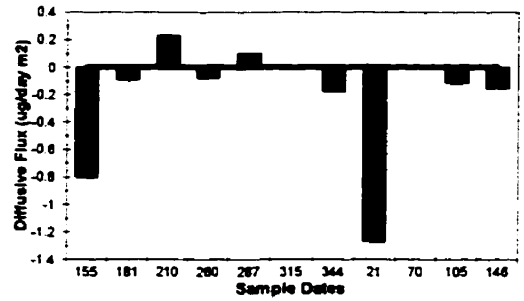


Figure 4.90: Diffusive Flux of Sodium at P1

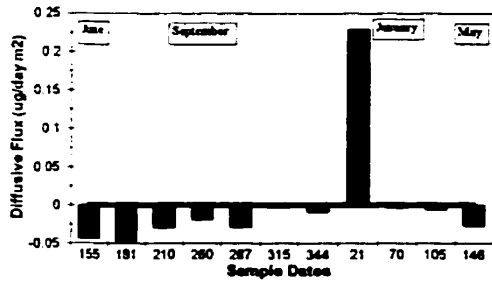


Figure 4.91: Diffusive Flux of Sodium at P2

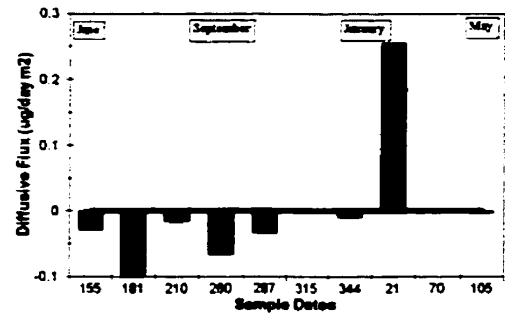


Figure 4.92: Diffusive Flux of Strontium at P1

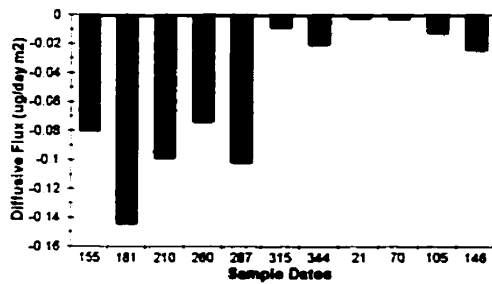


Figure 4.93: Diffusive Flux of Strontium at P2

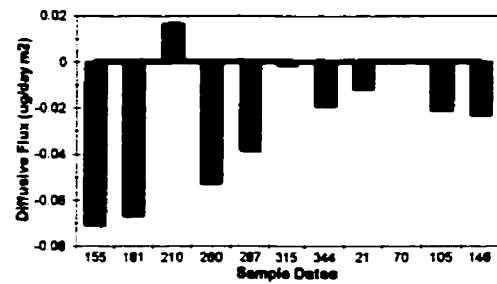


Figure 4.94: Diffusive Flux of Zinc at P1

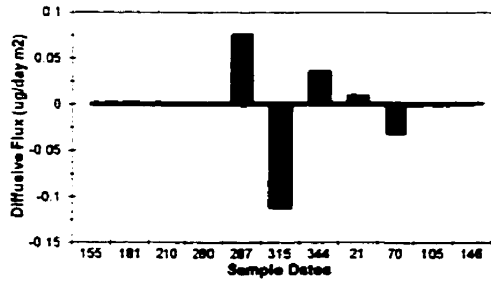
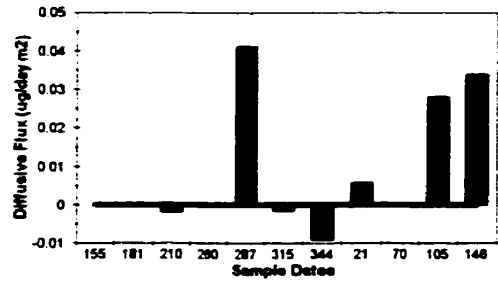


Figure 4.95: Diffusive Flux of Zinc at P2



5.0 Conclusion

The chemical investigation of the Harding Park storm water detention pond was designed to provide information about the seasonal mobility of trace metals and nutrients, and about the factors affecting mobilisation. This investigation revealed that although the pond was hypereutrophic in terms of the total phosphorus, the amount of organic matter within the pond surface waters, as indicated by DOC and organic carbon content within the sediments, were low suggesting possible toxic suppression of biological activity. Throughout most of the year, the pond behaved as a net sink for nitrogen (ammonia and nitrate) and trace metals even though trace metals were predominantly in the dissolved phase. However, the pond appeared to be a net source of total phosphorus. Occasionally trace metal concentrations in surface waters exceeded PWQO's for Cu, Fe, and Zn. Seasonal variations in NaCl from road salt and decreased temperature, appeared to increase the total trace metal concentrations by 50 to 60% and increase the proportion of trace metals in the dissolved phase by 10 to 30%. Due to the increased trace metal mobility in the winter and spring, trace metals could be released from the pond system at this time. There are concerns with regards to the toxicity of Cu and Zn during March and April since the spring is an ecologically significant time for aquatic and aquatic dependent organisms. Throughout most of the year complexation of trace metals with Fe and Mn oxides and gravitational settling were important removal mechanisms of trace metals from the surface waters to the sediments below.

Metal pore water concentrations tended to follow the characteristic profiles of Fe and Mn where concentrations increased to a maximum just below the sediment-water interface, coincident with redox induced dissolution of Fe and Mn oxides. Below this maximum metal concentrations presumably declined due to precipitation with sulphides under very low redox

conditions. Recycling of metals due to their immobilisation with oxidised Fe and Mn compounds likely increased the retention of trace metals in the pond sediments.

Diffusive flux calculations indicated upward fluxes from sediment to water most of the year except during winter when dissolved metal concentrations increased in surface waters. However, the upwardly diffusing metals presumably complexed with Fe and Mn oxide compounds above the sediment-water interface.

Overall, the pond appears to be a net sink for metals and nutrients with the exception of total phosphorus. It is suggested that the extremely high nutrient levels do not support high biological productivity due to toxicity induced by elevated ammonia and some metal concentrations and the transient depletion of DO at depth.

6.0 Recommendations

1. This investigation revealed that there were times during the year when surface water concentrations of trace metals in the Harding Park pond were maintained such that release from the pond system could occur. To better assess the significance of the trace metal release, trace metals should be investigated further in terms of mass loading from the pond to the nearby tributary, German Mills Creek, of the East Don River. A mass balance model for the pond should be implemented so as to establish whether the pond is a sink or source for nutrients and trace metals. This would require more frequent sampling of surface waters, especially during storm events.
2. The exact mechanisms to explain why increased concentrations of trace metals occur in the dissolved phase in the Harding Park pond surface waters during the winter are not fully understood. Hence, a combination of field sampling, mesocosm, and batch experiments

should be used to further investigate the mechanism(s) for increases in dissolved metal concentrations during the winter.

3. Also, even though total phosphorus data indicated that the Harding Park pond should be hypereutrophic, the DOC concentrations in surface waters and organic carbon content in the sediment did not support this classification. To better assess the biological productivity and trophic status of the pond, analysis of surface waters should include particulate organic carbon (POC), chlorophyll A, total phosphorus (TP) and soluble reactive phosphorus (SRP).
4. Ammonia and uptake of Cu and Zn, and transient depletion of DO at depth may have suppressed biological activity within the pond. A Toxicity Identification Evaluation (TIE), as outlined in Wenholz and Crunkilton (1995), should be used to assess the toxicity of the surface waters and pore water in sediments of the Harding Park pond.

References

- Adams, D. D., 1994. Chapter 7: Sediment Pore Water Sampling, *In: Handbook of Techniques for Aquatic Sediments Sampling*, 2nd ed., Mudroch, A., and MacKnight, S. D., Eds., Lewis Publishers, Chelsea, Michigan.
- Adriano, D.C., 1986. Trace Elements in the Terrestrial Environment, Springer-Verlag New York Inc., New York, New York, USA.
- Angelidis, T.N., 1997. Comparison of Sediment Pore Water Sampling for Specific Parameters Using Two Techniques. *Water, Air, and Soil Pollution*, Vol. 99: 179-185.
- Beliles, R.P., 1979. The Lesser Metals, *In: Toxicity of Heavy Metals in the Environment Part 2*, edited by F.W. Oehme, Marcel Dekker, Inc., New York, New York, United States.
- Bodo, B.A., 1989. Heavy Metals in Water and Suspended Particulates from an Urban Basin Impacting Lake Ontario. *Science of the Total Environment*, Vol. 87/88: 329-344.
- Bolton, K.A., and L.J. Evans, 1997. Chapter 26 Contaminant Geochemistry of Urban Sediments and Soils, *In: Environmental Geology of Urban Areas*. 373-382.
- Bolton, K.A., S. Sjöberg, and L.J. Evans, 1996. Proton Binding and Cadmium Complexation Constants for a Soil Humic Acid Using a Quasi-particle Model, *Soil Sciences Society of America Journal*, Vol. 60(4): 1064-1072.
- Boyd, D., Fluvial Sedimentation in a Small Urban River: The Don, University of Toronto, Ontario, Canada, unpublished data.
- Bufflap, S.E., and H.E. Allen, 1995. Sediment Pore Water Collection Methods for Trace Metal Analysis: A Review. *Water Research*, Vol. 29 (1): 165-177.
- Buttle, J.M., and C.F. Labadia, 1999. Deicing Salt Accumulation and Loss in Highway Snowbanks, *Journal of Environmental Quality*, Vol. 28 (1): 155-164.
- Calmano, W., J. Hong, and U. Förstner, 1993. Binding and Mobilisation of Heavy Metals in Contaminated Sediments Affected by pH and Redox Potential, *Water Science and Technology*, Vol. 28 (8-9): 223-235.
- Catallo, W.J., 1993. Ecotoxicology and Wetland Ecosystems: Current Understanding and Future Needs, *Environmental Toxicology and Chemistry*, Vol. 12: 2209-2224.
- Chambers, P.A., M. Allard, S.L. Walker, J. Marsalek, J. Lawrence, M. Servos, J. Busnarda, K.S. Munger, K. Adare, C. Jefferson, R.A. Kent, and M.P. Wong, 1997. Impacts of Municipal Wastewater Effluents on Canadian Waters: a Review. *Water Quality Resources Journal of Canada*, Vol. 32 (2): 659-713.

- Chapman, L.J., and D.F. Putnam, 1984. The Physiography of Southern Ontario, Ontario Geological Survey, Special Volume 2.
- Cook, R.B., 1981. The Biogeochemistry of Sulfur in Two Small Lakes, Ph.D. thesis, Columbia University, 234 p.
- Crerar, D.A., R.K. Cormick, and H.L. Barnes, 1980. Geochemistry of Manganese: An Overview, *In: Geology and Geochemistry of Manganese, Vol. I General Problems* edited by I.M. Varentov and G. Graselly, Academiai Kiado, Budapest.
- Davison, W., 1985. Chapter 2: Conceptual Models for Transport at a Redox Boundary, *In: Chemical Processes in Lakes*, edited by W. Stumm, John Wiley & Sons, Inc., New York, New York, USA.
- Debusk, T.A, R.B. Laughlin Jr., and L.N. Schwartz, 1996. Retention and Compartmentalisation of Lead and Cadmium in Wetland Microcosms, *Water Resources*, Vol. 30 (11): 2707-2716.
- Diamond, M, 1999. Personal Communication, Faculty of Department of Geography, University of Toronto.
- Dombeck, G.D., M.W. Perry, and J.T. Phinney, 1998. Mass Balance on Water Column Trace Metals in a Free-Surface-Flow-Constructed Wetland in Sacramento, California. *Ecological Engineering*, Vol. 10: 313-339.
- Donahoe, R.J., and C. Liu, 1998. Pore Water Geochemistry Near the Sediment-Water Interface of a Zoned, Freshwater Wetland in the Southeastern United States, *Environmental Geology*, Vol. 33 (2/3): 143-153.
- Elinder, C.G., and M. Piscator, 1979. Chapter 27 Iron and Chapter 42 Zinc, *In: Handbook on the Toxicology of Metals*, edited by L. Friberg, G.F. Nordberg, and V.B. Vouk, Elsevier/North-Holland Inc., New York, New York, USA.
- Emerson, S., 1976. Early Diagenesis in Anaerobic Lake Sediments: Chemical Equilibria in Interstitial Waters, *Geochimica Cosmochimica Acta*, Vol. 40: 925-932.
- Emerson, S., and G. Widmer, 1978. Early Diagenesis in Anaerobic Lake Sediments II, Thermodynamic and Kinetic Factors Controlling the Formation of Iron Phosphate, *Geochimica Cosmochimica Acta*, Vol. 42: 1307-1315.
- Environment Canada, 1994a. Method 01-1020: Method for the Analysis of Dissolved Organic and Inorganic Carbon in Precipitation, Surface, and Ground Water by Automated UV Digestion and Infrared Detection, National Laboratory for Environmental Testing (NLET), National Water Research Institute (NWRI), Burlington, Ontario, Canada.

Environment Canada, 1994b. Method 02-2001: Method for the Analysis of Metals in Surface, Ground, and Precipitation Waters by Automated Inductively Coupled Argon Plasma Emission Spectrometry with Ultrasonic Nebulisation and Preconcentration, NLET, NWRI, Burlington, Ontario, Canada.

Environment Canada, 1999. Normal Mean Monthly Precipitation (mm) for Toronto, Ontario, Environment Canada Greenlane, Atmospheric Services Website.

Evans, L.J., 1989. Chemistry of Metal Retention by Soils, *Environmental Science and Technology*, Vol. 23 (9): 1046-1056.

Evans, L., 1982. Cation exchange capacities and surface areas of humic gleysolic Ap. horizons from Southwest Ontario. *Canadian Journal of Soil Science*, Vol.65: 489-496.

Evans, L.J., and W.G. Wilson, 1985. Extractable Fe, Al, Si and C in B horizons or Podzolic and Brunisolic soils from Ontario, *Canadian Journal of Soil Science*, Vol. 65: 489-496.

Fitzpatrick, E.A., 1986. An Introduction to Soil Science: Second Edition, John Wiley & Sons, Inc., New York, New York, USA.

Förstner, U., W. Ahlf, W. Calmano, M. Kersten, and J. Schoer, 1990. Assessment of Metal Mobility in Sludges and Solid Wastes, *In: Metal Speciation in the Environment*, edited by J.A.C. Broekaert, Ş. Güçer, and F. Adams, Springer-Verlag, New York, USA.

Gambrell, R.P., 1994. Trace and Toxic Metals in Wetlands - A Review, *Journal of Environmental Quality*, Vol. 23 (5): 883-891.

Gambrell, R.P., J.B. Wiesepape, W.H. Patrick, Jr., M.C. Duff, 1991. The Effects of pH, Redox, and Salinity on Metal Release from a Contaminated Sediment. *Water, Air, and Soil Pollution*, Vol. 57-58: 359-367.

Gambrell, R.P., and W.H. Patrick, Jr., 1988. Chapter 27: The Influence of Redox Potential on the Environmental Chemistry of Contaminants in Soils and Sediments, *In: The Ecology and Management of Wetlands Volume 1*, edited by D.D. Hook, Timber Press, Portland, Oregon, USA.

Gillespie, R.J., D.A. Humphreys, N.C. Baird, and E.A. Robinson, 1989. Chemistry: Second Edition, Allyn and Bacon, Inc., Massachusetts, United States.

Griffith, D.A., and C.G. Amrhein, 1991. Statistical Analysis for Geographers, Practice-Hall, Inc., New Jersey, USA.

Hall, K.J., and B.C. Anderson, 1987. The Toxicity and Chemical Composition of Urban Stormwater Runoff, *Canadian Journal of Civil Engineering*, Vol. 15:98-106.

- Helfield, J.M., and M.L. Diamond, 1997. Use of Constructed Wetlands for Urban Stream Restoration: A Critical Analysis, *Environmental Management*, Vol. 21 (3): 329-341.
- Hildemann, L.M., G.R. Markowski, and G.R. Cass, 1991. Chemical Composition of Emissions from Urban Sources of Fine Organic Aerosol, *Environmental Science and Technology*, Vol. 24 (4): 744-759.
- Kimbrough, D. E., and J. Wakakuwa, 1994. Interlaboratory Comparison of Instruments Used for the Determination of Elements in Acid Digestates of Solids. *Analyst*, Vol. 119:383-388.
- Leckie, J. O., and R.O. James, 1974. Chapter 1: Control Mechanisms for Trace Metals in Natural Waters *In: Aqueous-Environmental Chemistry of Metals*, edited by A.J. Rubin, 1-76.
- Li, Y. H., and S. Gregory, 1974. Diffusion of Ions in Sea Water and in Deep Sea Sediments, *Geochimica et Cosmochimica Acta*, Vol. 38: 703-714.
- Lumsdon, D.G., L.J. Evans, and K.A. Bolton, 1995. The Influence of pH and Chloride on the Retention of Cadmium, Lead, Mercury, and Zinc by Soils, *Journal of Soil Contamination*, Vol. 4 (2): 137-150.
- Makepeace, D.K., D.W. Smith, and S.J. Stanley, 1995. Urban Stormwater Quality: Summary of Contaminant Data. *Critical Reviews Environmental Science and Technology*, Vol.25 (2): 93-139.
- Makos, J.D., and D.C. Hrcir, 1995. Chemistry of Cr (VI) in a Constructed Wetland. *Environmental Science and Technology*, Vol. 29 (9): 2414-2419.
- Marsalek, J., B. Brownlee, T. Mayer, S. Lawal, and G.A. Larkin, 1997. Heavy Metals and PAHs in Stormwater Runoff from the Skyway Bridge, Burlington, Ontario, *Water Quality Research Journal of Canada*, Vol. 32. (4): 815-827.
- Marsalek, J., and Schroeter, 1988. Annual Loadings of Toxic Contaminants in Urban Runoff from the Canadian Great Lakes Basin, *Water Pollution Research Journal of Canada*, Vol. 23 (3): 360-378.
- Mason, C.F., S.A. Norton, I.J. Fernandez, and L.E. Katz, 1999. Deconstruction of the Chemical Effects of Road Salt on Stream Water Chemistry, *Journal of Environmental Quality*, Vol. 28 (1): 82-91.
- May, T.W., R.H. Wiedmeyer, W.G. Brumbaugh, and C.J. Schmitt, 1997. The Determination of Metals in Sediment Pore Waters and in 1N HCl-Extracted Sediments by ICP-MS, *Atomic Spectroscopy*, Vol. 18 (5): 133-139.
- Mayer, T., J. Marsalek, and E. D. Reyes, 1996. Nutrients and Metal Contaminants Status of Urban Stormwater Ponds, *Journal of Lake and Reservoir Management*, Vol. 12 (3): 348-363.

Mayer, T., Q. Rochfort, U. Borgmann, and M. Brown, 1999. **Impact of Road Salts on Small Urban Ponds: Rouge River Pond Case Study**, National Water Research Institute Contribution No. 99-072.

McKeague, J.A., 1979. Manual of Soil Sampling and Methods of Analysis, 2nd edition, Canadian Soil Survey Committee.

Menzell, D.W. and N. Corwin, 1965. The measurement of total phosphorus in sea water based on the liberation of organically bound fractions by persulfate oxidation. *Limnology and Oceanography*, Vol. 10: 280-282.

Mitsch, W.J., and J.G. Gosselink, 1993. Wetlands, Wan Nostrand Reinhold Company, New York.

MOEE, 1994. Water Management Policies, Guidelines, Provincial Quality Objectives of the Ministry of Environment and Energy, Queen's Printer for Ontario.

MOEE, 1992. Constructed Wetlands for Stormwater Management: A Review. Prepared by Mark E. Taylor & Associates, Queen's Printer for Ontario.

MOEE, 1991a. Stormwater Quality Best Management Practices. Prepared by Marshall Macklin Monaghan Limited in association with LGL Limited and Loiederman Associates Inc., Queen's Printer for Ontario.

MOEE, 1991b. Analysis of Water Quality Data for the Don River – Supporting Document #5: Strategy for Improvement of Don River Water Quality. Prepared by Beak Consultants Limited and Paul Theil Associates Ltd., Queen's Printer for Ontario.

MOEE, 1983. Toronto Area Watershed Management Strategy Study: Interim Report on Toronto Area Water Quality, Toronto, Ontario, Canada.

MTRCA (Metropolitan Toronto and Region Conservation Authority) (1983). Appendix E: Biological Studies, Keating Channel Environmental Assessment, Toronto, Ontario.

Mudroch, A., and S.D. MacKnight, 1995. Chapter 4: Description of Equipment for Sediment Pore Water Sampling, *In: Manual of Aquatic Sediment Sampling*, Lewis Publishers, Chelsea, Michigan, USA, 81-111.

Murphy, J. and J.P. Riley, 1962. A modified single solution for the determination of phosphate in natural waters. *Anal. Chim. Acta*. 27:31-36.

Murray, J.W., V. Grundmanis, and W.M. Smethie, 1978. Interstitial Water Chemistry in the Sdeiments of Saanich Inlet, *Geochimica Cosmochimica Acta*, Vol. 42: 1011-1020.

Nieboer, E., and D. H. S. Richardson, 1980. The Replacement of the Nondescript Term 'heavy metals' by a Biologically and Chemically Significant Classification of Metal Ions. *Environmental Pollution*, Vol. B1: 3-26.

Nriagu, J.O., and J.M. Pacyna, 1988. Quantitative Assessment of Worldwide Contamination of Air, Water and Soils by Trace Metals, *Nature*, Vol. 333 (12): 134-139.

Nu Hoai, V.N., H.E. Farrah, G.A. Lawrance, G.L. Orr, 1998. Efficiency of a Small Artificial Wetland with an Industrial Urban Catchment, *Science of the Total Environment*, Vol. 214: 221-237.

O'Shea, T.A., and K.H. Mancy, 1978. The Effect of pH and Hardness Metal Ions on the Competitive Interaction between Trace Metal Ions and Inorganic and Organic Complexing Agents Found in Natural Waters, *Water Research*, Vol. 12:703-711.

Pascoe, G.A., 1993. Wetland Risk Assessment (Annual Review), *Environmental Toxicology and Chemistry*, Vol. 12: 2293-2307.

Pettersson, T.J.R., 1998. Water Quality Improvement in a Small Stormwater Detention Pond, *Water Science and Technology*, Vol. 38 (10): 115-122.

Piscator, M., 1979. Chapter 24 Copper and Chapter 29 Manganese, *In: Handbook on the Toxicology of Metals*, edited by L. Friberg, G.F. Nordberg, and V.B. Vouk, Elsevier/North-Holland Inc., New York, New York, USA.

Pyle, S. M., and J.M. Nocerino, 1996. Comparison of AAS, ICP-AES, PSA, and XRF in Determining Lead and Cadmium in Soil, *Environmental Science and Technology*, Vol. 30 (1): 204-213.

Rastogi, S.C., and G. Pritzl, 1998. Red Lipstick: A Source of Barium to Humans and the Environment, *Bulletin of Environmental Contamination and Toxicology*, Vol. 60: 507-510.

Reeves, A.L., 1979. Chapter 18 Barium, *In: Handbook on the Toxicology of Metals*, edited by L. Friberg, G.F. Nordberg, and V.B. Vouk, Elsevier/North-Holland Inc., New York, New York, USA.

Robbins, J.A, and E. Callender, 1975. Diagenesis of Manganese in Lake Michigan Sediments, *American Journal of Science*, Vol. 275: 512-519.

Rosa, F., and J.M. Azcue, 1993. Peeper Methodology, NWRI Contribution No. 93-33, Environment Canada.

Schnoor, J.L., and W. Stumm, 1985. Chapter 14: Acidification of Aquatic and Terrestrial Systems, In: Chemical Processes in Lakes, edited by W. Stumm, John Wiley & Sons, Inc., New York, New York, USA.

Scholes, L., R.B.E. Shutes, D.M. Revitt, M. Forshaw, D. Purchase, 1998. The Treatment of Metals in Urban Runoff by Constructed Wetlands, *Science of the Total Environment*, Vol. 214: 211-219.

Shaw, J.K.E., W.E. Watt, J. Marsalek, B.C. Anderson, and A.A. Crowder, 1997. Flow Pattern Characterisation in an Urban Stormwater Detention Pond and Implications for Water Quality, *Water Quality Research Journal of Canada*, Vol. 32 (1): 53-71.

Smith, V.H., F.H. Rigler, O. Choulik, M. Diamond, S. Griesbach and D. Skraba, 1984. Effects of phosphorus fertilisation on phytoplankton biomass and phosphorus retention in subarctic Quebec lakes, *Verh. Internat. Verein. Limnol.*, Vol. 22: 673-687.

Snoeyink, V.L., and D. Jenkins, 1980. Chap. Five : Coordination Chemistry, Section 5.7.3. Metal Ion Association with Humic Substances, In: Water Chemistry, John Wiley & Sons, Toronto, Ontario.

Stumm, W., and J.J. Morgan, 1981. Aquatic Chemistry, 2nd edition, John Wiley & Sons, Inc., New York, New York, USA.

Tanner, C.C., J.P.S. Sukias, and M.P. Upsdell, 1998. Relationships between Loading Rates and Pollutant Removal during Maturation of Gravel-Bed Constructed Wetlands, *Journal of Environmental Quality*, Vol. 27 (2): 448-458.

Tabatabai, M.A., and J.M. Bremner, 1970. Use of the Leco Automatic 70-second Carbon Analyser for Total Carbon Analysis of Soils, *Soil Science Society of America Journal*, Vol. 34: 608-610.

Warren, L.A., 1994. Trace Metal Complexation by Suspended Particulates in an Urban River, Ph.D. Thesis, University of Toronto, Ontario, Canada.

Warren, L.A., and P. Zimmerman, 1994. The Influence of Temperature and NaCl on Cadmium, Copper and Zinc Partitioning among Suspended Particulate and Dissolved Phases in an Urban River, *Water Resources*, Vol. 28 (9): 1921-1931.

Wenholz, M., and R. Crunkilton, 1995. Use of Toxicity Identification Evaluation Procedure in the Assessment of Sediment Pore Water Toxicity from an Urban Stormwater Retention Pond in Madison, Wisconsin, *Bulletin of Environmental Contamination and Toxicology*, Vol. 54: 676-682.

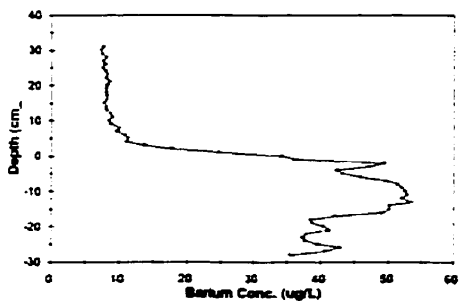
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Appendix A: Detection Limits for ICP-OES

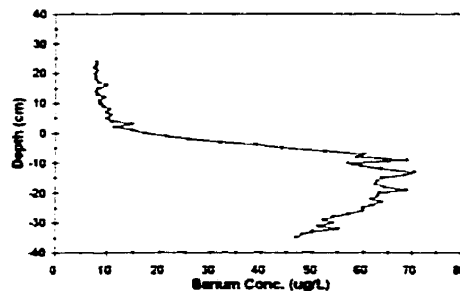
Parameter	Method Detection Limit (mg/L)	Upper Limit (mg/L)
Barium	0.001	0.5
Copper	0.002	0.2
Iron	0.0004	2
Manganese	0.001	0.5
Strontium	0.001	1
Zinc	0.002	0.2

Appendix B: Trace Metal Pore Water Profiles

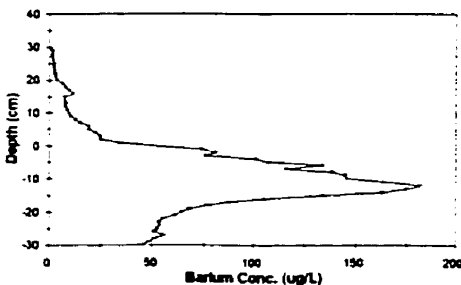
Barium Profiles at P1 for June 4/98



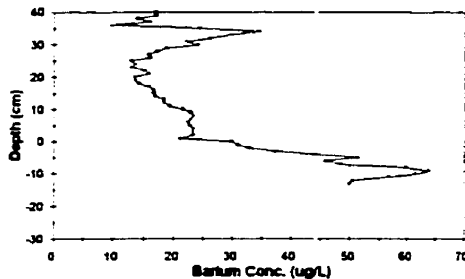
Barium Profile at P2 for June 4/98



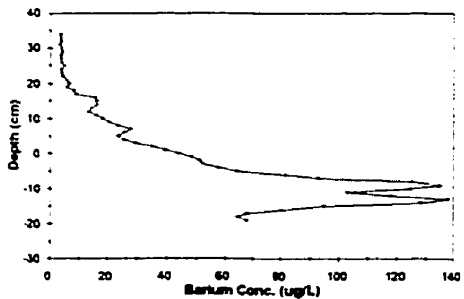
Barium Profile at P1 for June 30/98



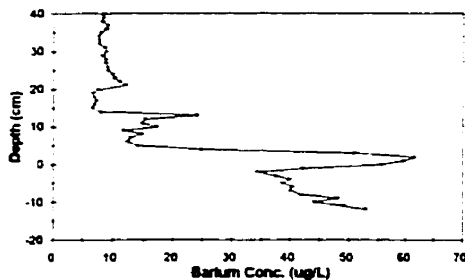
Barium Profile at P2 for June 30/98



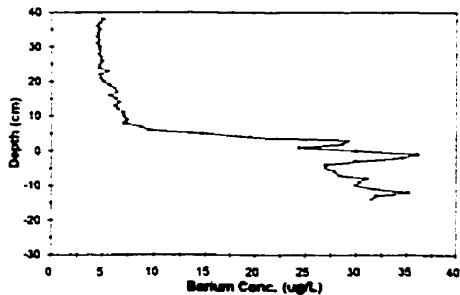
Barium Profile at P1 for July 29/98



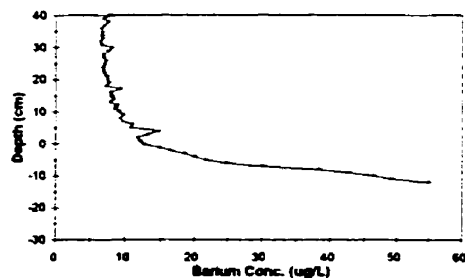
Barium Profile at P2 for July 29/98



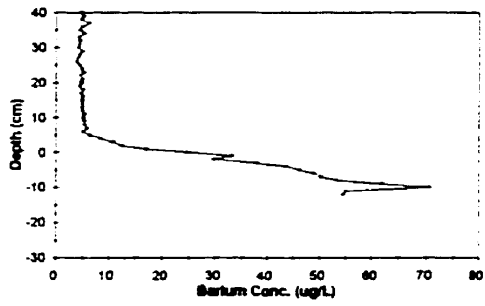
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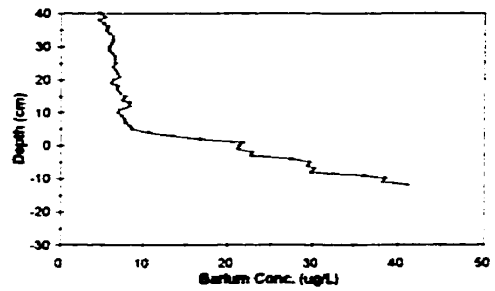
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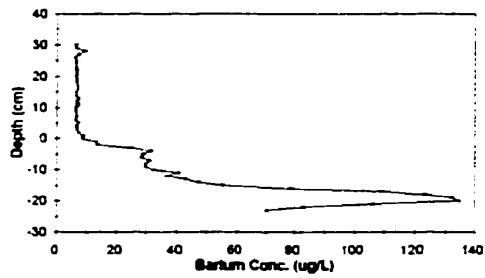
Barium Profile at P1 for Oct 14/98



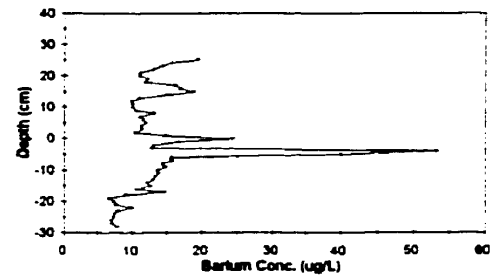
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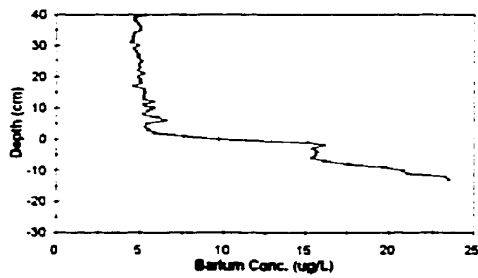
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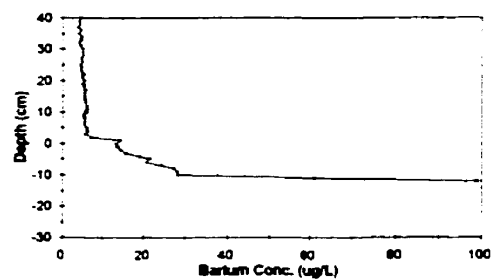
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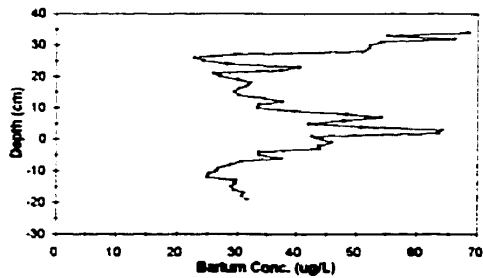
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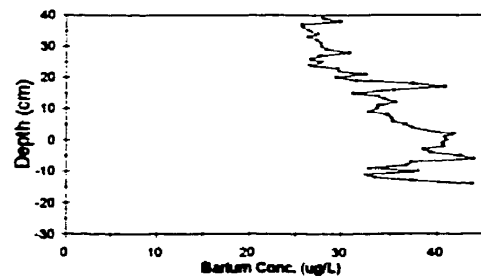
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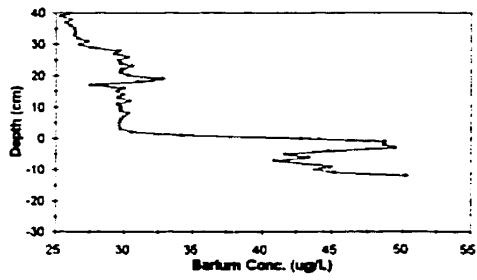
Barium Profile at P1 for Jan 21/99



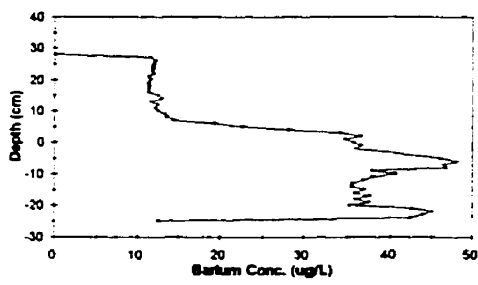
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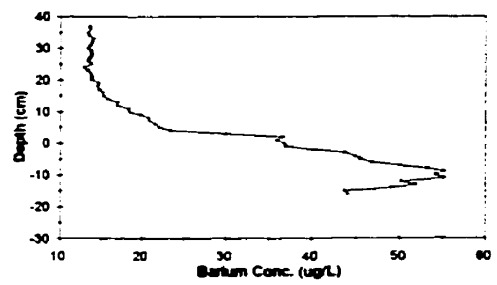
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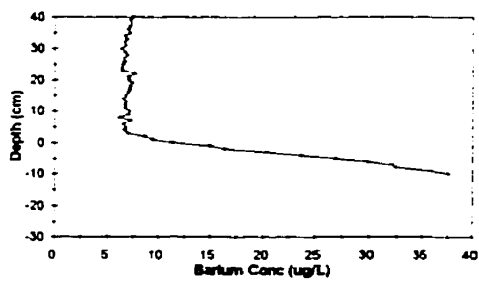
Barium Profile at P1 for April 15/99



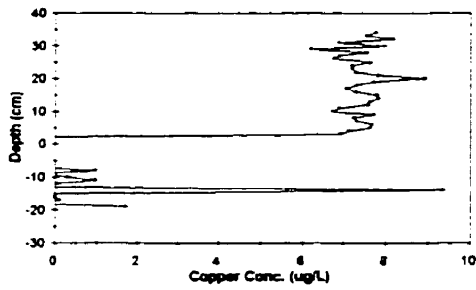
Barium Profile at P2 for April 15/99



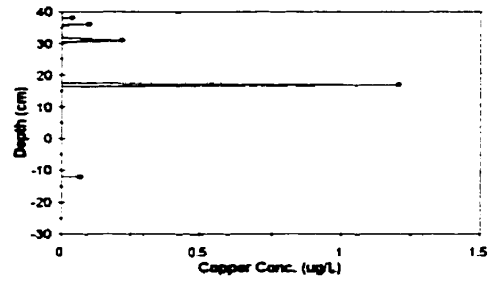
Barium Profile at P1 for May 26/99



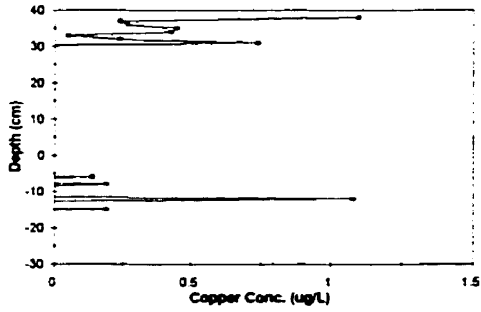
Copper Profile at P1 for July 29/98



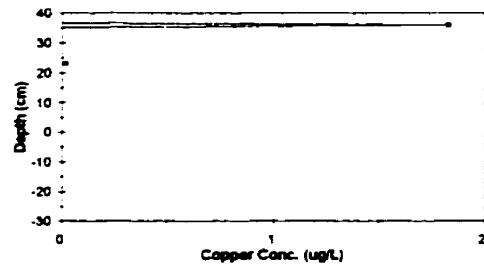
Copper Profile at P2 for July 29/98



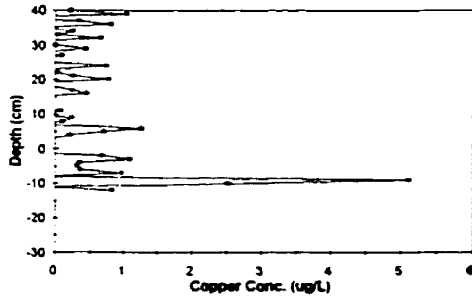
Copper Profile at P1 for Sept 17/98



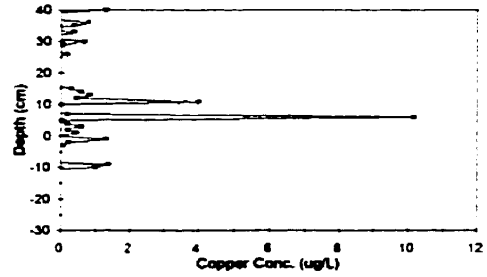
Copper Profile at P2 for Sept 17/98



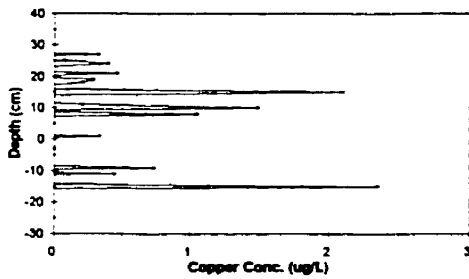
Copper Profile at P1 for Oct 14/98



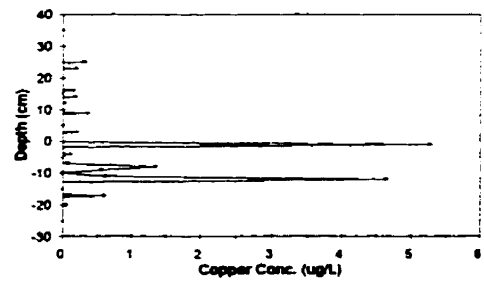
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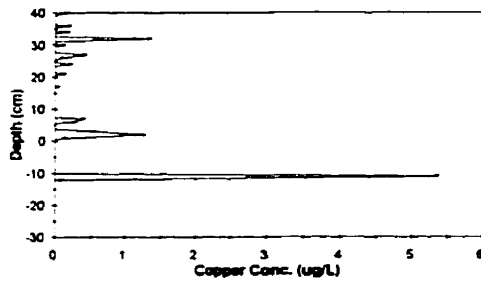
Copper Profile at P1 for Nov 11/98



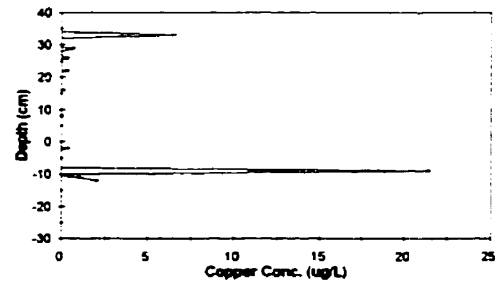
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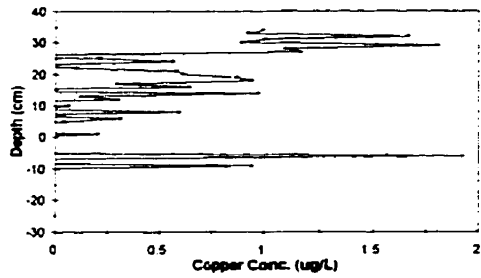
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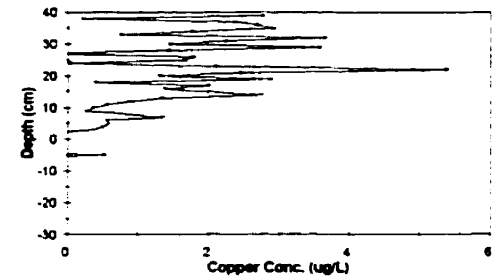
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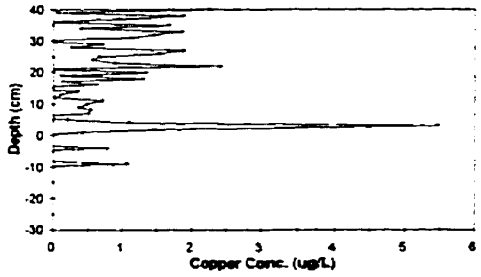
Copper Profile at P1 for Jan 21/99



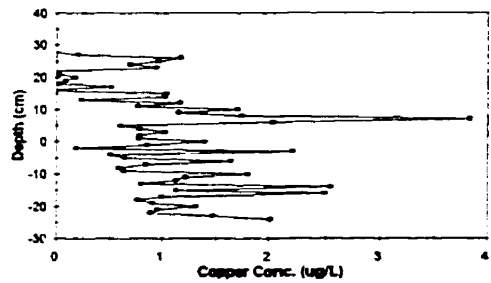
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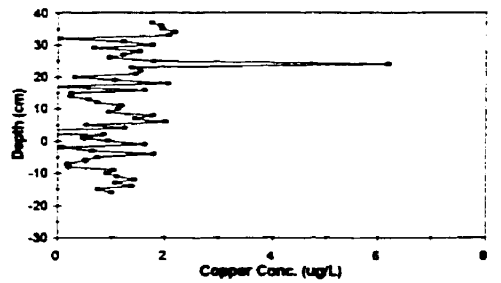
Copper Profile at P1 for March 11/99



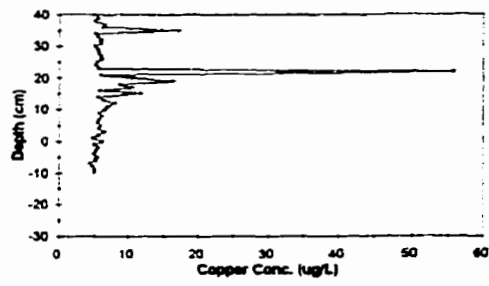
Copper Profile at P1 for April 15/99



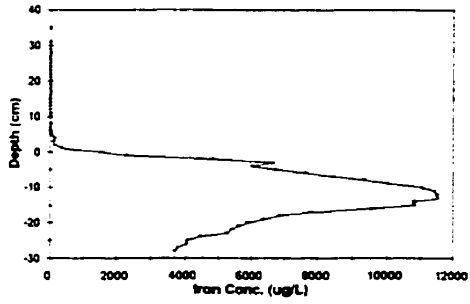
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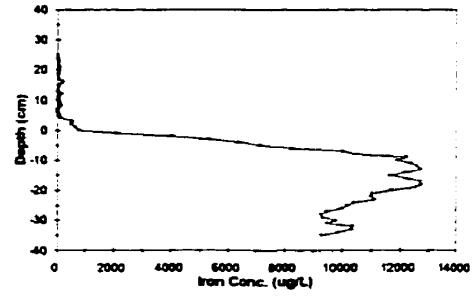
Copper Profile at P1 for May 26/99



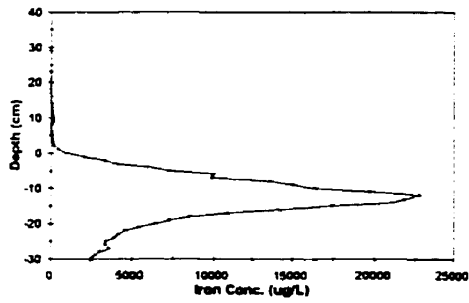
Iron Profile at P1 for June 4/98



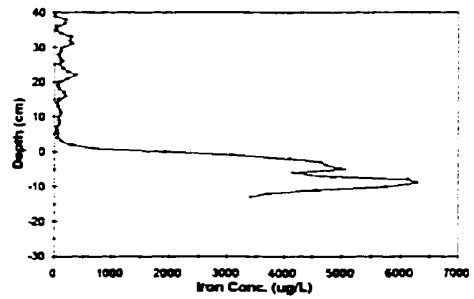
Iron Profiles at P2 for June 4/98



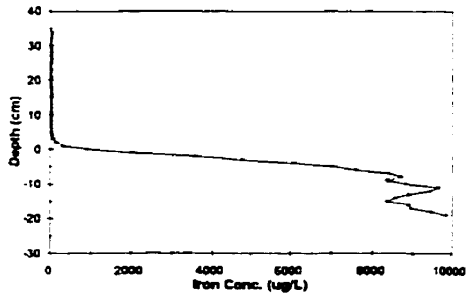
Iron Profile at P1 for June 30/98



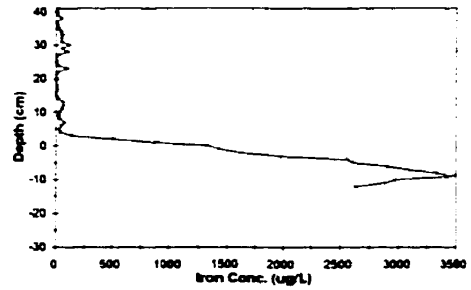
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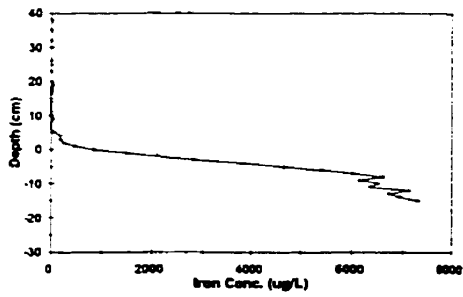
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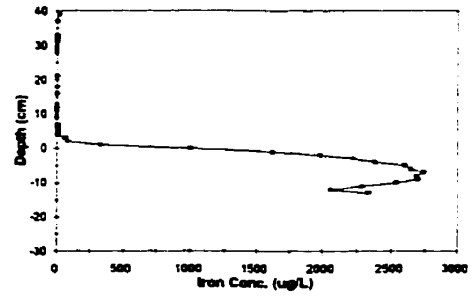
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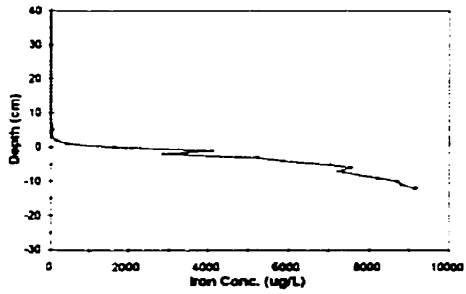
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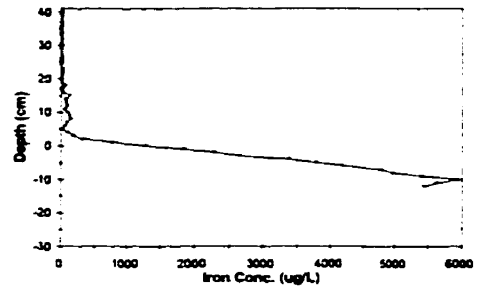
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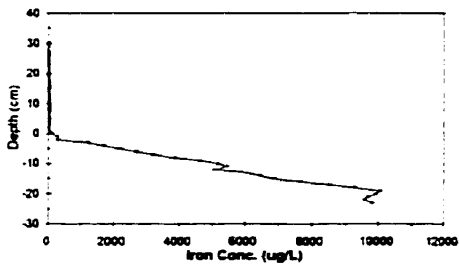
Iron Profile at P1 for Oct 14/98



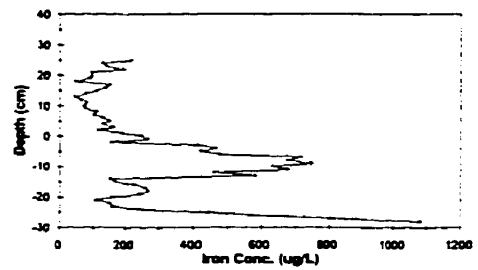
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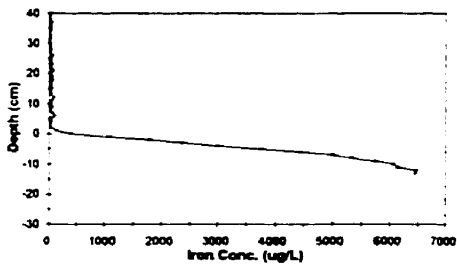
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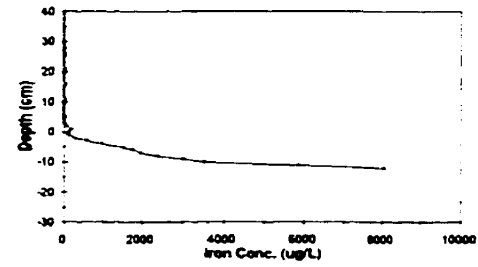
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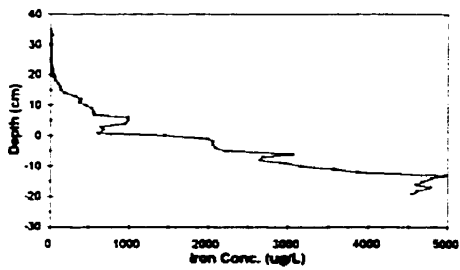
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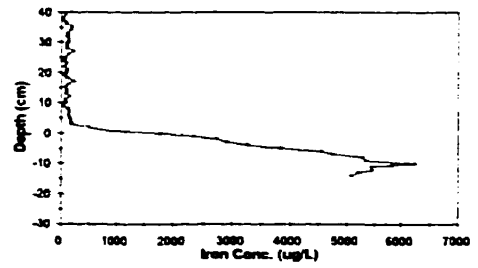
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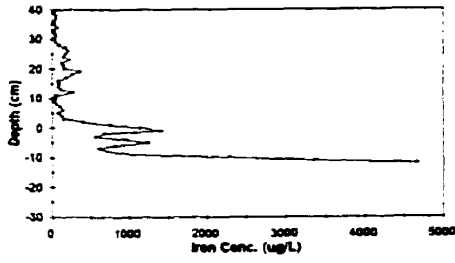
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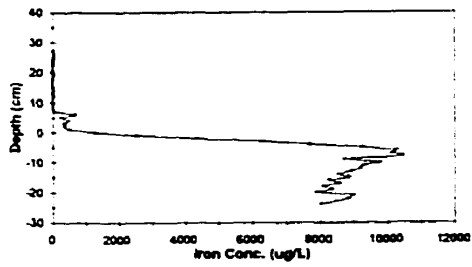
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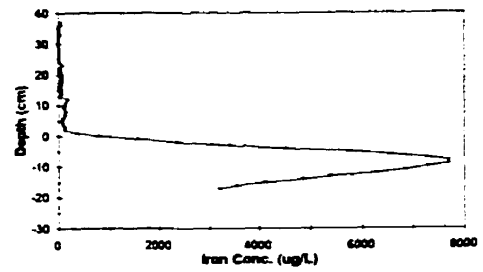
Iron Profile at P1 for March 11/99



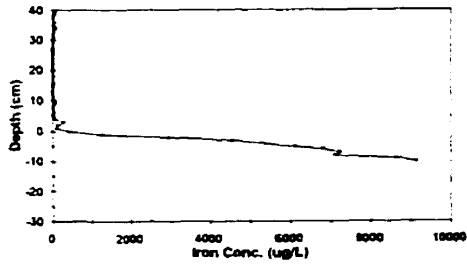
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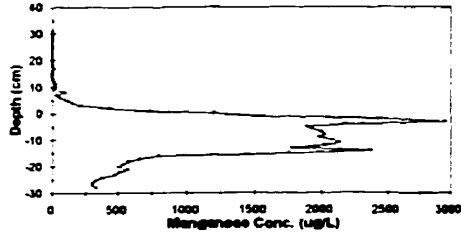
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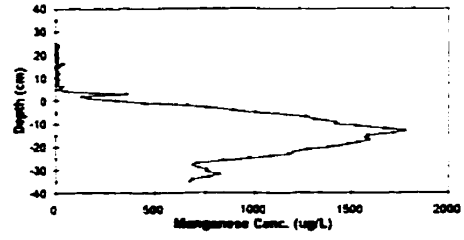
Iron Profile at P1 for May 26/99



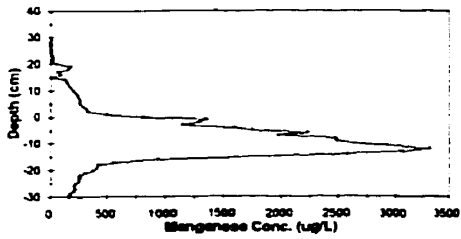
Manganese Profile at P1 for June 4/98



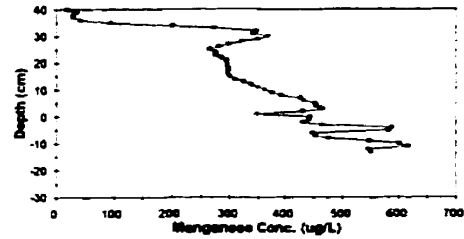
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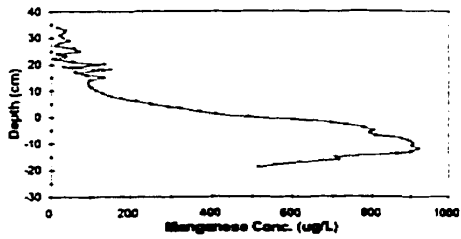
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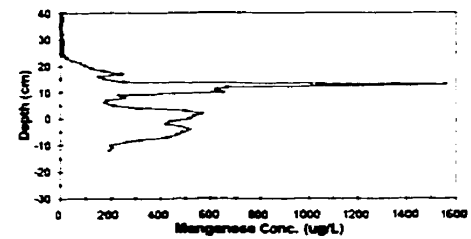
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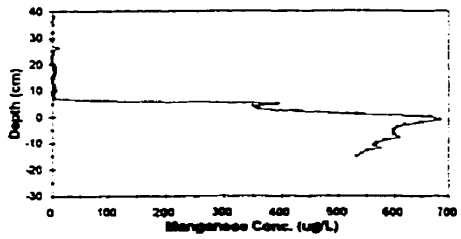
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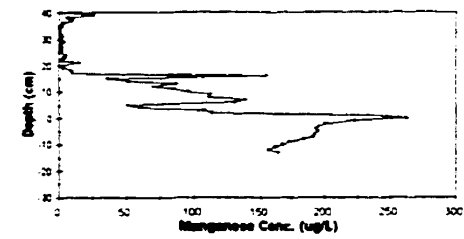
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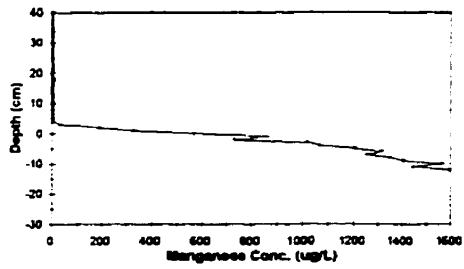
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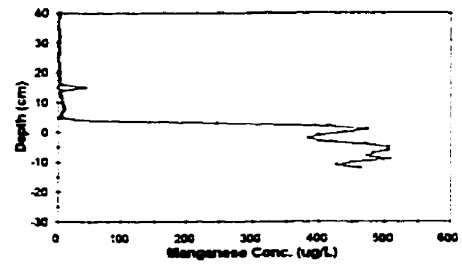
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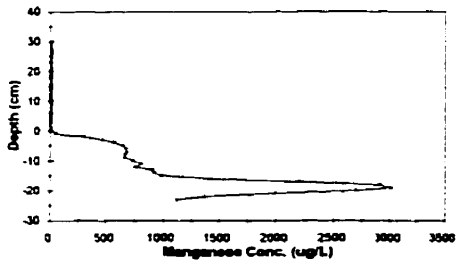
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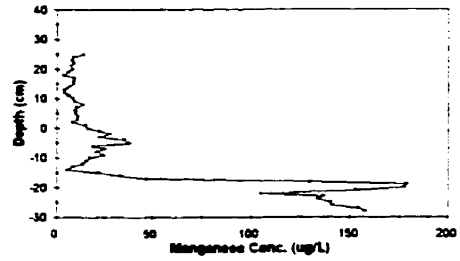
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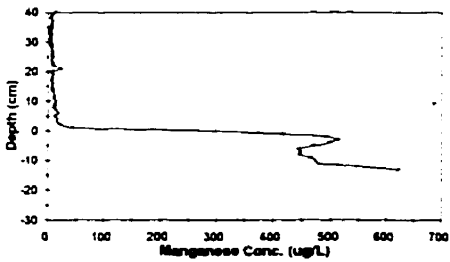
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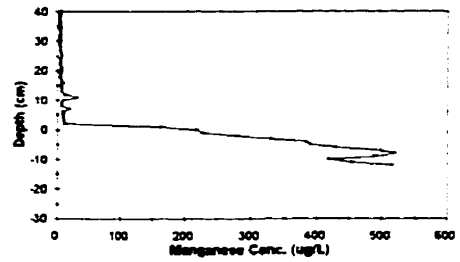
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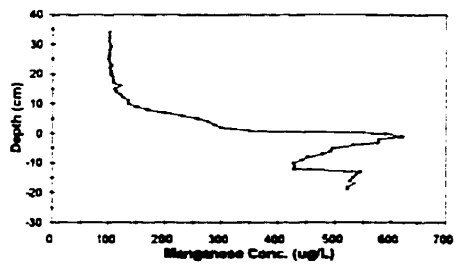
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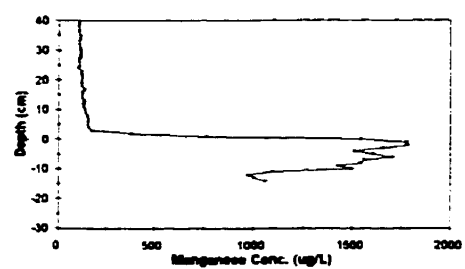
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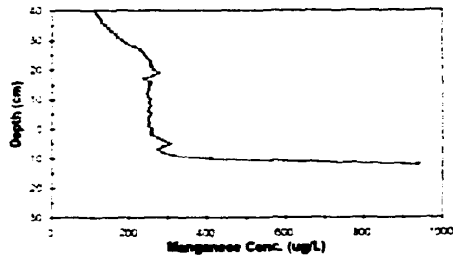
Manganese Profile at P1 for Jan. 21/99



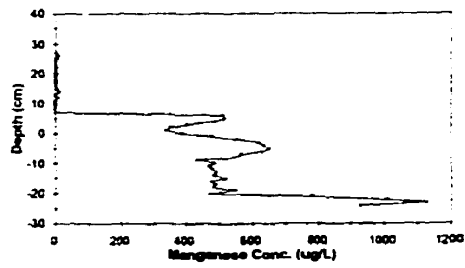
Manganese Profile at P2 for Jan. 21/99



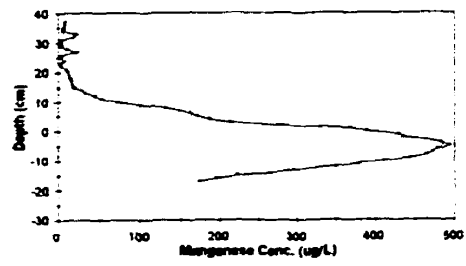
Manganese Profile at P1 for Mar 11/99



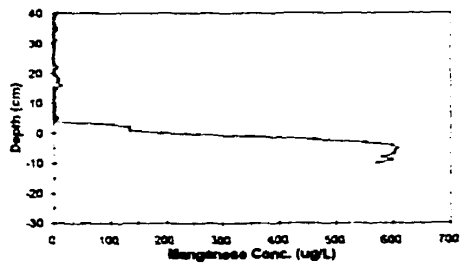
Manganese Profile at P1 for Apr 15/99



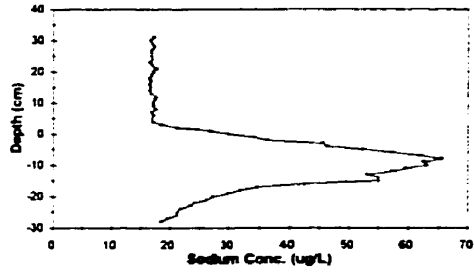
Manganese Profile at P2 for Apr 15/99



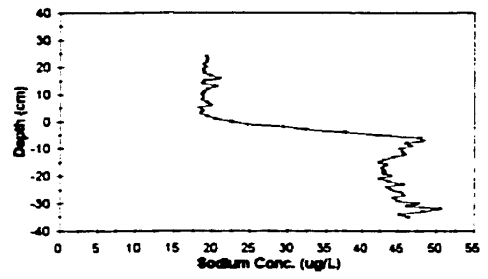
Manganese Profile at P1 for May 26/99



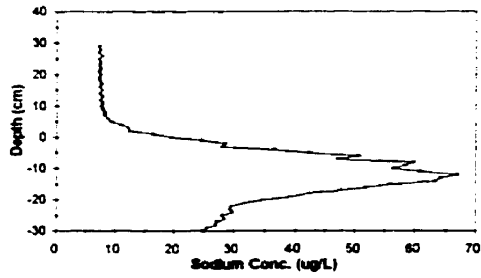
Sodium Profile at P1 for June 4/98



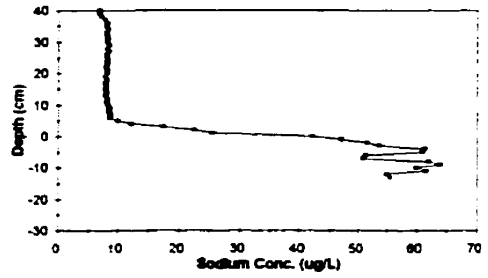
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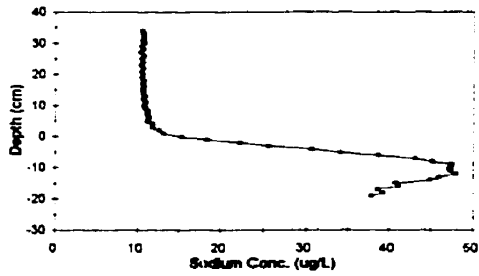
Sodium Profile at P1 for June 30/98



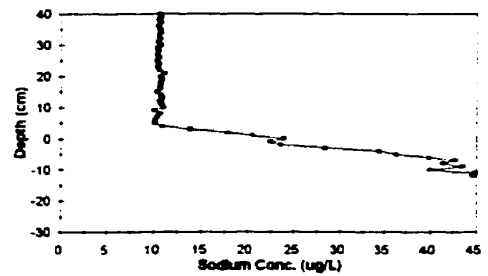
Sodium Profile at P2 for June 30/98



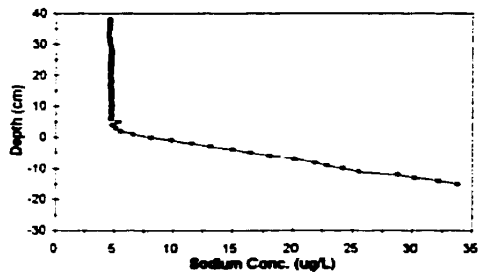
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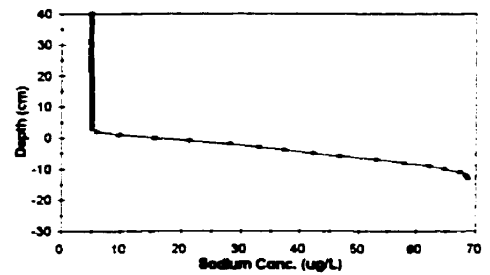
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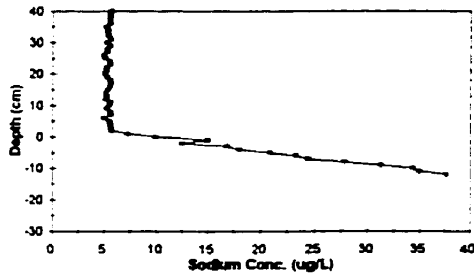
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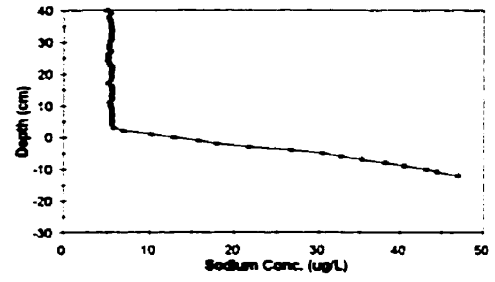
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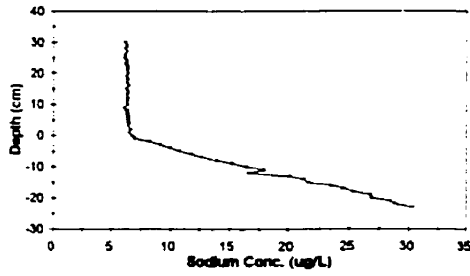
Sodium Profile at P1 for Oct 14/98



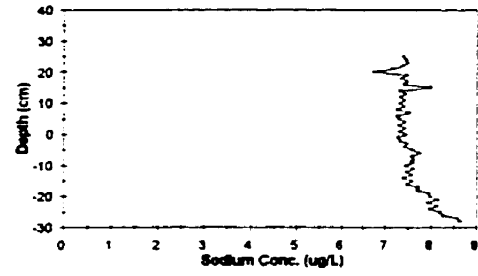
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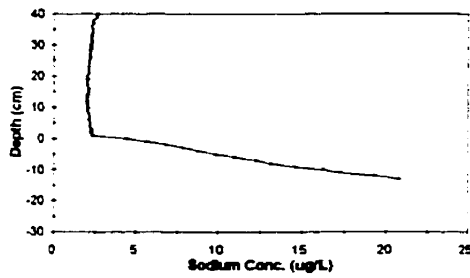
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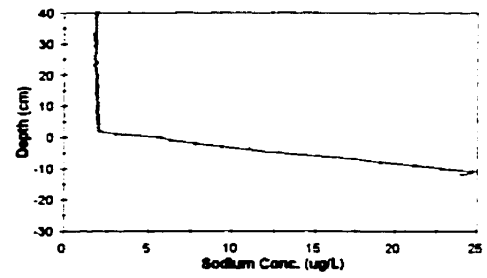
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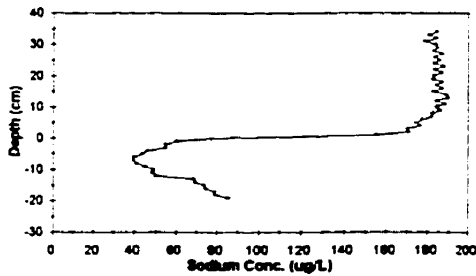
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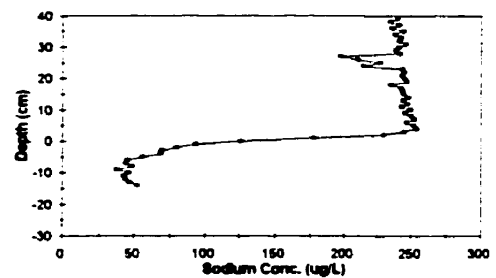
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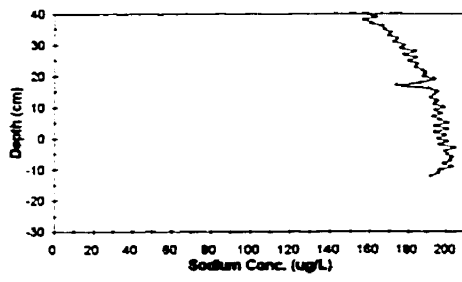
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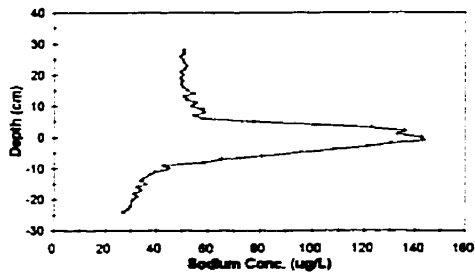
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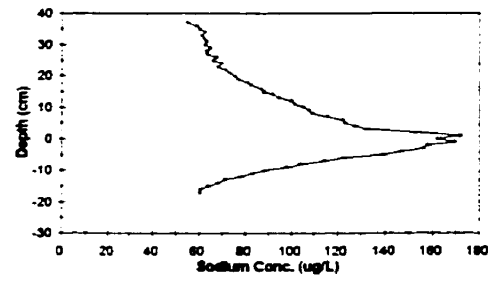
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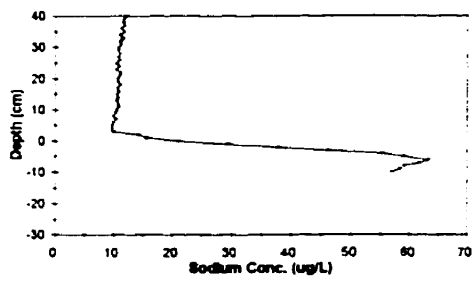
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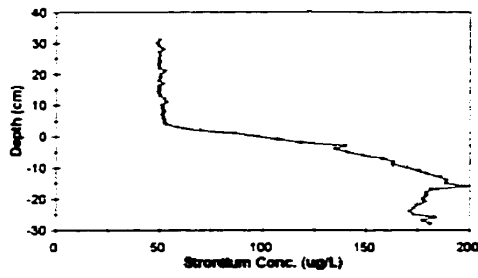
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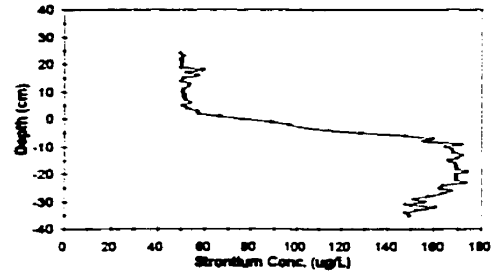
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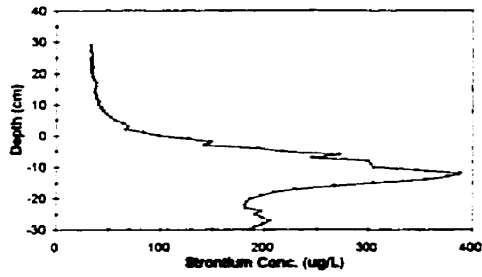
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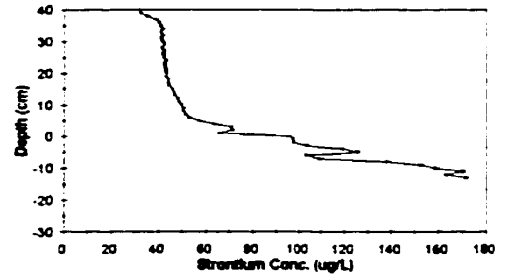
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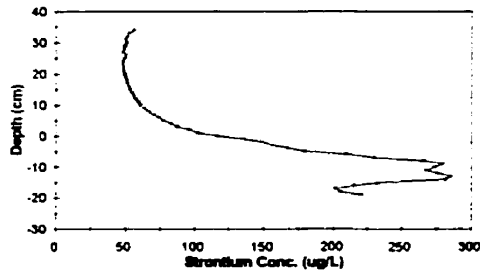
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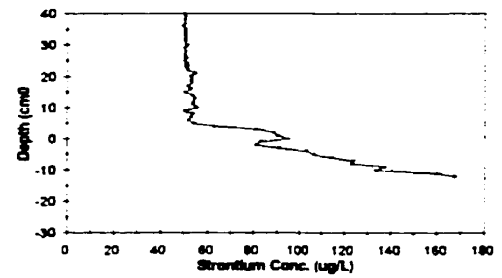
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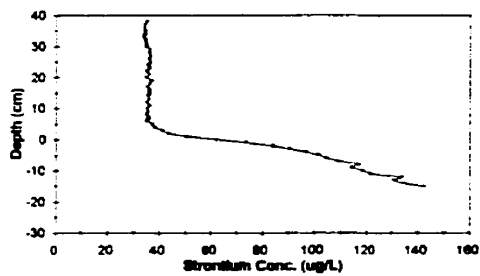
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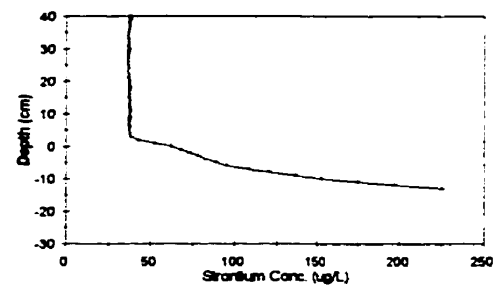
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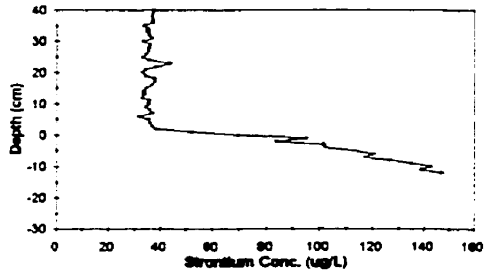
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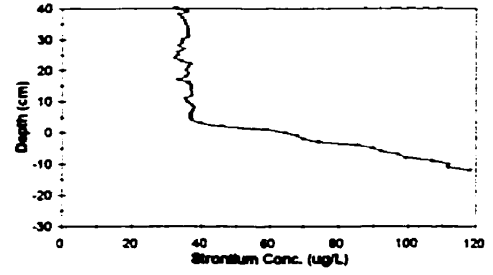
Strontium Profile at P2 for Sept 17/98



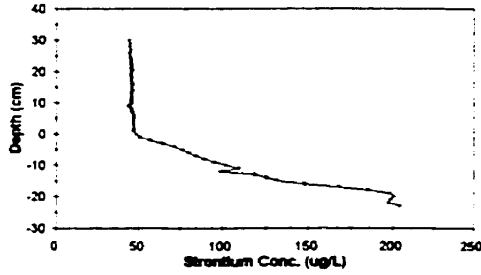
Strontium Profile at P1 for Oct 14/98



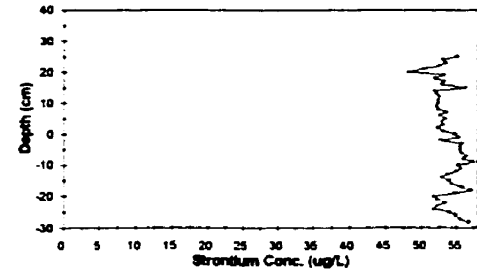
Strontium Profile at P2 for Oct 14/98



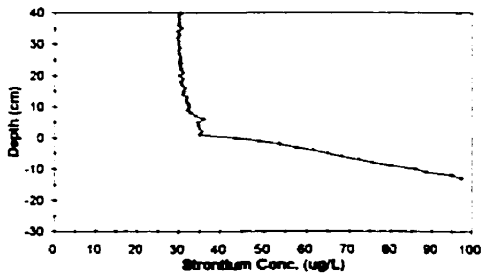
Strontium Profile at P1 for Nov 11/98



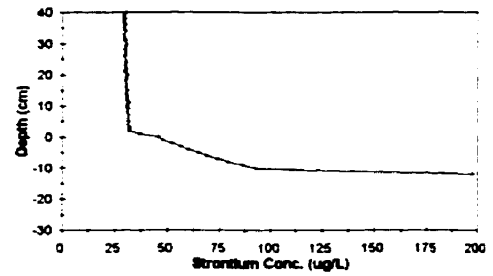
Strontium Profile at P2 for Nov 11/98



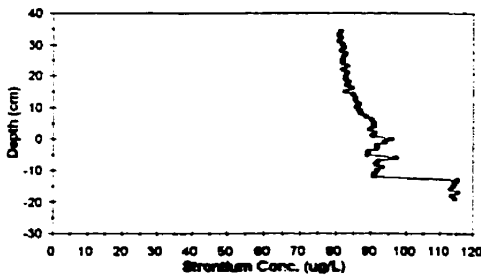
Strontium Profile at P1 for Dec 10/98



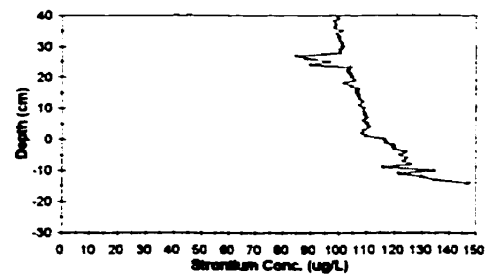
Strontium Profile at P2 for Dec 10/98



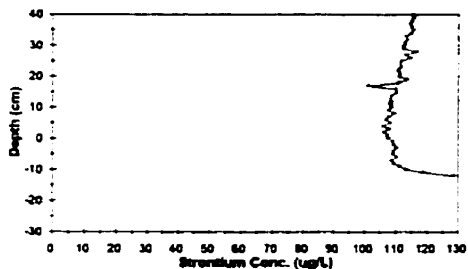
Strontium Profile at P1 for Jan 21/99



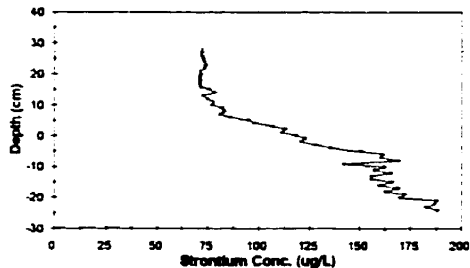
Strontium Profile at P2 for Jan 21/99



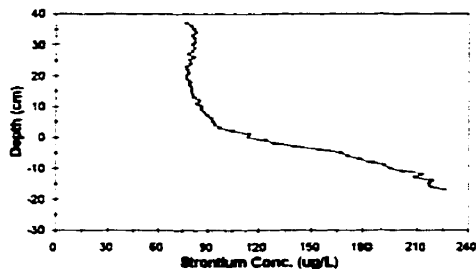
Strontium Profile at P1 for Mar 11/99



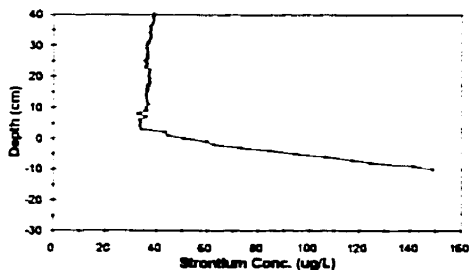
Strontium Profile at P1 for Apr 15/99



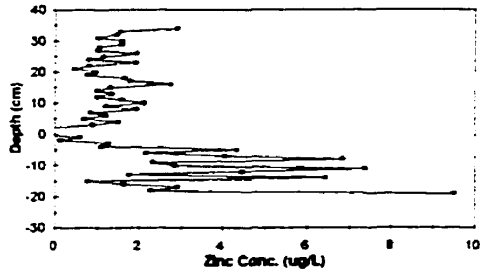
Strontium Profile at P2 for Apr 15/99



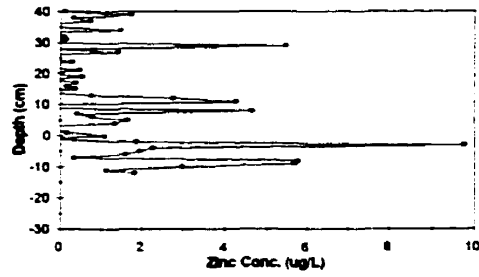
Strontium Profile at P1 for May 26/99



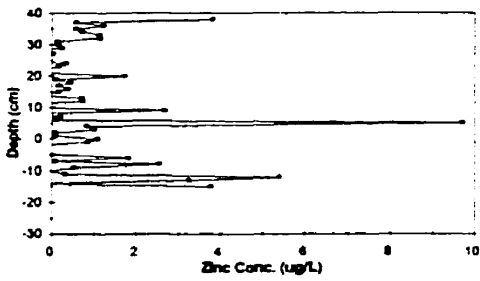
Zinc Profile at P1 for July 29/98



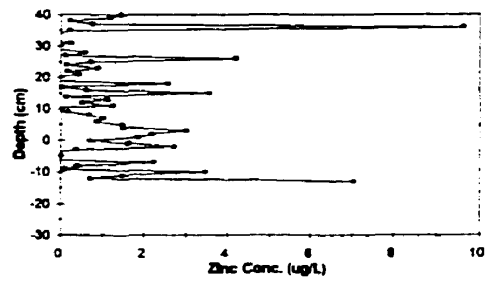
Zinc Profile at P2 for July 29/98



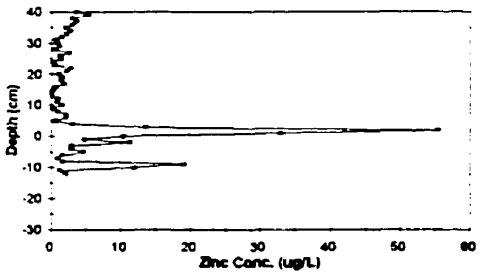
Zinc Profile at P2 for Sept 17/98



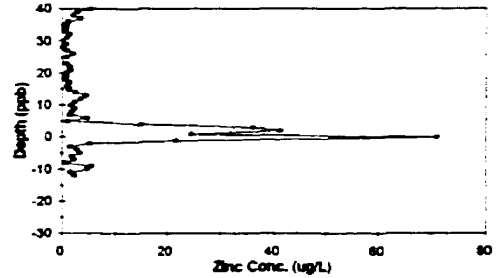
Zinc Profile at P2 for Sept 17/98



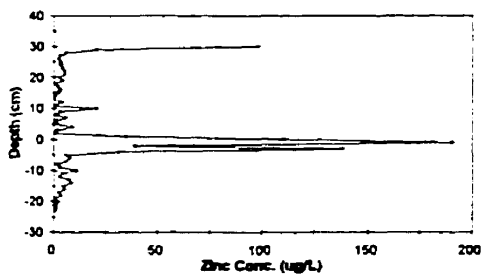
Zinc Profile at P1 for Oct 14/98



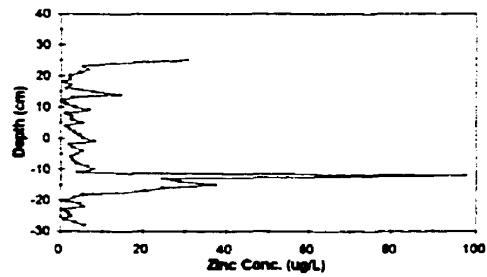
Zinc Profile at P2 for Oct 14/98



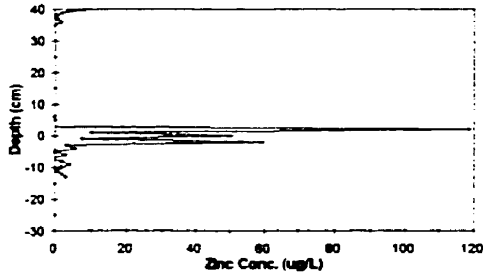
Zinc Profile at P1 for Nov 11/98



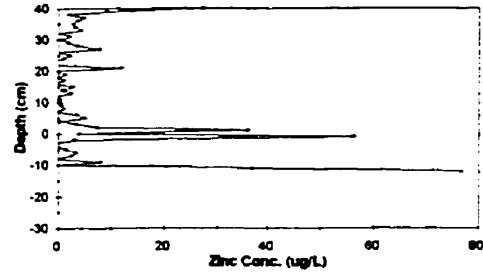
Zinc Profile at P2 for Nov 11/98



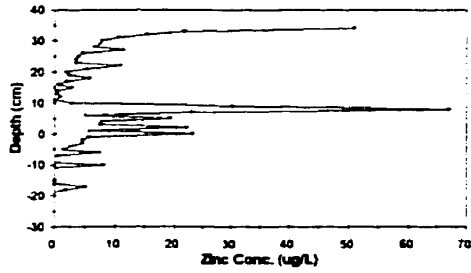
Zinc Profile at P1 for Dec 10/98



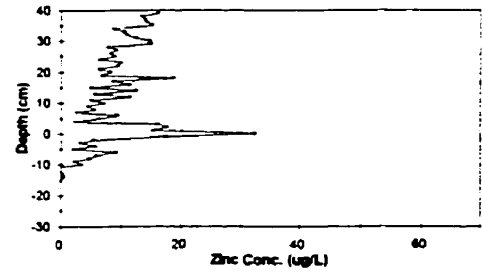
Zinc Profile at P2 for Dec 10/98



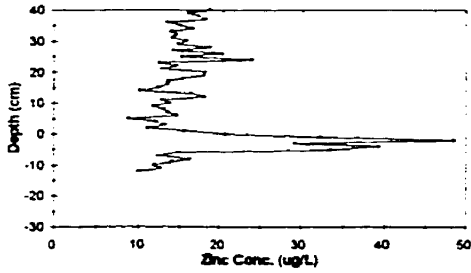
Zinc Profile at P1 for Jan 21/99



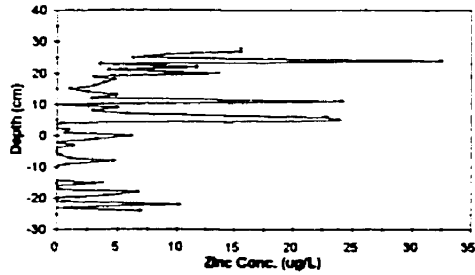
Zinc Profile at P2 for Jan 21/99



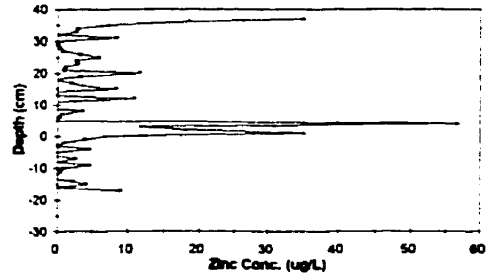
Zinc Profile at P1 for March 11/99



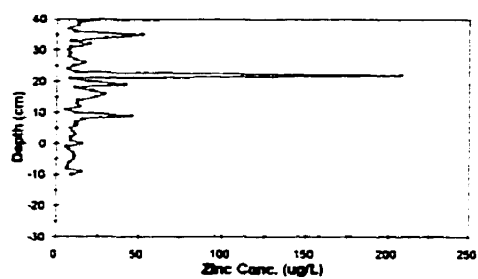
Zinc Profile at P1 for April 15/99



Zinc Profile at P2 for April 15/99

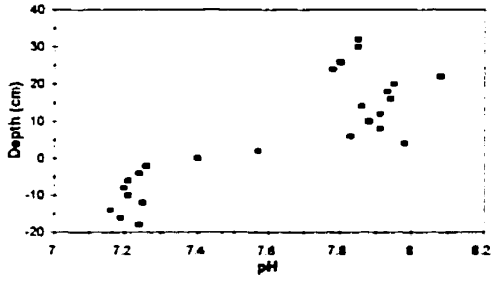


Zinc Profile at P1 for May 26/99

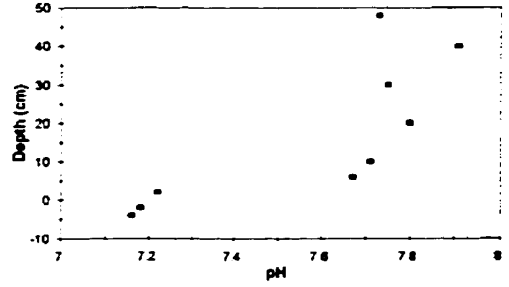


Appendix C: pH in Pore Water Profiles

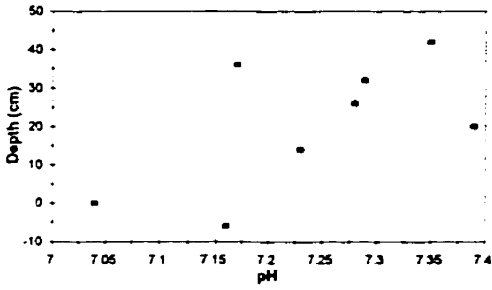
pH at P1 for June 4/98



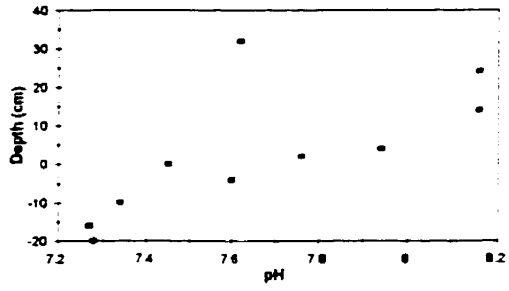
pH at P2 for June 30/98



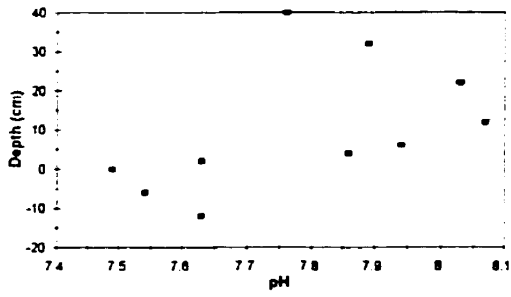
pH at P2 for July 29/98



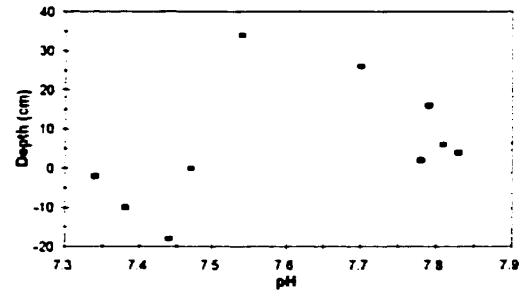
pH for October 14/98



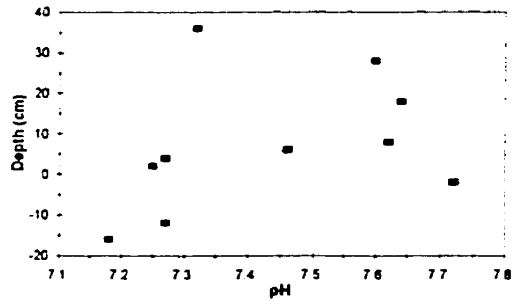
pH at P1 for November 11/98



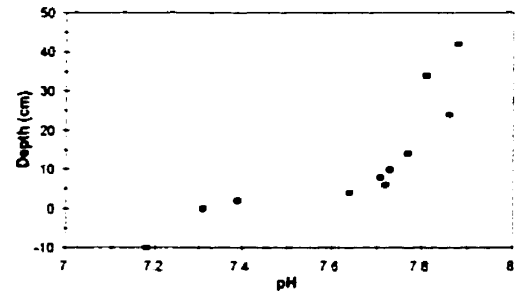
pH at P2 for November 11/98



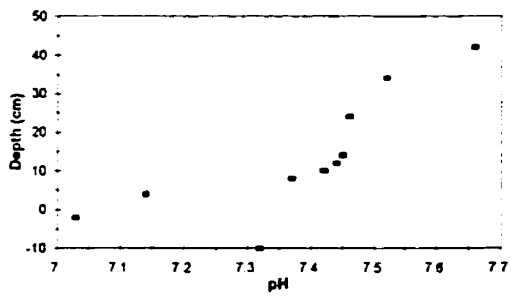
pH at P1 for December 10/98



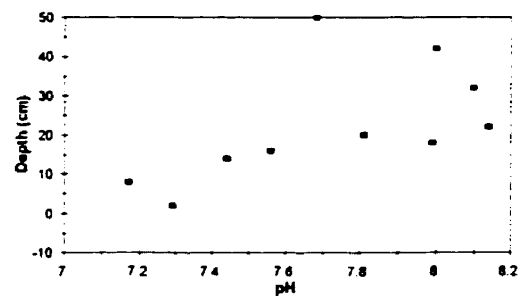
pH at P2 for December 10/98



pH at P1 for March 11/99



pH at P1 for April 15/99



pH at P1 for May 26/99

