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Mechanisms affecting metal retention by surface-flow wetlands in cold temperate climates

Les mécanismes responsables de la rétention des métaux par des marais à écoulement au-dessus de la surface en climat tempéré

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Je dédie cette thèse à ma conjointe Janick. Sans sa patience, sa compréhension et son support moral, ce projet aurait été plus difficile à réaliser. Je dédie aussi cette thèse à ma mère (Geneviève), mon père (Marcel) et mes grands-parents (Roger et Madelaine, Jos et Rose-Aimée) qui m'ont toujours soutenu et appuyé dans mes décisions et surtout, qui m'ont enseigné de ne jamais abandonner et de perseverer malgré les obstacles qui se présentent à nous.

Abstract

Wetlands, whether natural or created, are used as water treatment systems around the world. While extensive research has been conducted in warm climates, there is limited information on the mechanisms affecting the retention of pollutants by surface-flow wetlands in northern climates. In particular, there are serious concerns about the efficiency of metal retention by wetlands built in Canada and other temperate countries.

The mechanisms affecting metal retention by surface-flow wetlands were investigated by relating variations in metal retention to variables such as hydraulic residence time, temperature (i.e. seasonal effects), phytoplankton biomass, photosynthesis and the presence of emergent vegetation.

The importance of hydraulic residence time was investigated at the Monahan surface-flow wetland in Kanata, Ontario. This wetland retained metals best during summer and fall whereas during winter, the metal retention was significantly lower. The first-order removal model predicted Fe and Mn retention in the spring and Zn retention from spring to fall in both years of the study. Hydraulic residence times, greater than 7 days, provided the maximum retention of Fe, Mn, and Zn. However, first-order removal models failed to fit summer, fall and winter data for almost every metal under investigation (Fe, Mn, Cu, As) suggesting that hydraulic residence time (<1-25 days) do not regulate metal retention during these seasons.

The Monahan wetland also affected the partitioning of metals between particulate and dissolved phases thus potentially affecting the bioavailability of metals to downstream systems. On a yearly basis, the wetland showed significant retention of the dissolved phase, but the retention of total Fe and Mn was poor. The wetland transformed dissolved into particulate metals from spring to fall whereas during the winter, dissolved metals were released. Changes in pH, alkalinity and temperature could explain 11% and 40% of the variation in the ratio of dissolved to total Fe and Mn respectively. Furthermore, from spring to late summer, planktonic algal biomass was negatively related to the ratio of dissolved to total Fe and Mn, which suggests the importance of phytoplankton in affecting the partitioning of metal in young plankton-dominated wetlands.

In the Monahan wetland and in an acid mine drainage wetland (Falconbridge) near Sudbury, Ontario, diel changes in metal concentrations followed diel changes in pH and oxygen induced by photosynthesis. During the day, metal concentrations in the water column were low because high pH and oxygen favored the precipitation of Fe and Mn oxides at the sediment-water interface. At night, Fe and Mn oxides were reduced and released to the water column because intense biological respiration decreased oxygen and pH. Diel changes in metal concentrations have to be considered when evaluating the retention performance by surface-flow wetlands.

Finally, the effect of emergent vegetation on the concentration and partitioning of metals in surface sediments of four wetlands was investigated. Surface sediments with and without cattails (*Typha latifolia L.*) had similar total metal concentrations (Fe, Mn, Zn and Cu). The partitioning of metals in shallow vegetated sediments differed from deep unvegetated sediments at the Monahan and Falconbridge wetlands. In contrast, there was no significant difference in the partitioning of metals in surface sediments with or without cattails at the Panel and Riverwalk wetlands. Generally, half of the total metal concentration in sediments was dissolved in the pore water or associated with metal oxides, monosulfides and adsorbed onto organic matter. Zn was an exception as half of the total Zn was associated with the persistent organic fraction. The effect of cattails on the bulk concentration and partitioning of metals may be minimal in surface-flow constructed wetlands.

Résumé

Les marais à écoulement au-dessus de la surface sont de plus en plus utilisés comme systèmes naturels de traitement d'eau. Bien que la recherche sur les mécanismes responsables de la rétention des métaux soit intensive où le climat est chaud et humide, celle-ci est plutôt limitée au Canada où le climat est tempéré et froid. Conséquemment, au Canada et dans d'autres pays situés dans des zones climatiques tempérées, l'efficacité des marais à retenir les métaux est sérieusement questionnée.

Les effets de différentes variables reconnues comme importantes pour la rétention et la transformation des métaux à l'intérieur de marais situés en climat chaud ont été examinées dans des marais situés en climat tempéré. Par exemple, on a examiné l'importance des variables telles le temps de résidence des eaux de surface, la température, la biomasse de phytoplancton, la photosynthèse, et la présence de végétation émergeante sur la rétention des métaux par les marais.

En première partie, j'ai testé un modèle de rétention de premier ordre afin de vérifier l'importance du temps de résidence de l'eau comme variable dans ce modèle. La rétention des métaux était plus efficace pendant l'été et l'automne alors qu'elle a diminué significativement pendant l'hiver. J'ai découvert que le temps de résidence de l'eau est une variable importante pour la rétention du Fe, Mn et du Zn au printemps seulement. Cependant, le temps de résidence de l'eau pouvait prédire la rétention du Zn en été et en automne. Par la suite, la rétention des différents métaux (Fe, Mn, Cu, As) n'était pas celle prédite par le modèle et ce, pendant les trois saisons suivantes. Par conséquent, les modèles de rétention, basés presqu'essentiellement sur des variables physiques et hydrologiques, devraient inclure des variables supplémentaires afin d'améliorer la

performance de rétention des métaux par les marais recevant du drainage urbain et agricole.

Par la suite, j'ai examiné la transformation saisonnière de la partition des métaux dans la colonne d'eau du marais Monahan. Années après années, le marais retenait faiblement les métaux même si les métaux de la fraction dissoute étaient retenus efficacement. La rétention des métaux variait de façon saisonnière et pendant l'hiver, le marais agissait comme source de métaux. Le marais transformait les métaux dissouts en métaux particulaires à partir du printemps jusqu'à l'automne. Pendant l'hiver, le marais était une source de métaux dissouts. Les changement en pH, alcalinité et température pouvaient expliquer 11 et 40% de la variation du rapport en métal dissout sur le métal total du Fe et du Mn respectivement. De plus, la biomasse algale était négativement reliée au rapport du Fe et du Mn dissoût sur le Fe et le Mn total. Les algues ont donc un role important à jouer dans la transformation de la partition du Fer et du Mn dans la colonne d'eau de jeunes marais à écoulement au-dessus de la surface.

J'ai aussi observé que les changements circadiens en pH et en oxygène induits par la photosynthèse avaient un effet direct sur le cycle des métaux dans les marais. Pendant la journée, le pH et les teneurs en oxygène sont au maximum, ce qui favorise la précipitation des oxydes de fer et de manganèse. La nuit venue, les concentrations d'oxygène diminuent rapidement à cause de la forte demande biologique en oxygène, ce qui provoque le relargage du fer et du manganese à l'interface sediment-eau. Ce résultat suggère que l'on doit tenir compte des variations circadiennes lorsque l'on évalue la rétention des métaux dans les marais construits.

Finalement, j'ai examiné si la présence de la quenouille (*Typha latifolia*) avait un effet sur la concentration et la partition des métaux (Fe, Mn, Cu, Zn) dans les sédiments de surface de quatres marais. Lorsque la quenouille était présente, les concentrations en métaux des sédiments étaient semblables aux concentrations mesurées dans les sédiments dénudés de quenouille. De même, la répartition des métaux dans les sédiments de surface n'était pas affectée par la présence de la quenouille aux marais Panel et Riverwalk. Par contre, la répartition des métaux dans les sédiments dénudés et situés en eau profonde étaient différente que les sédiments colonisés par la quenouille en eau peu profonde dans les marais Monahan et Falconbridge. De façon générale, approximativement 50% de la concentration totale en métaux des sédiments était sous la forme dissoute ou adsorbé à la matière organique, aux oxydes métalliques ou au monosulfures. La présence de la quenouille dans les sédiments de marais a donc un effet minimal sur la concentration et la répartition des métaux dans les sédiments de surface.

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Preface

This thesis contains four distinct chapters with an introductory Chapter (Chapter 1) and a conclusion Chapter (Chapter 6). Chapters 2, 3, 4, and 5 were written as individual papers, submitted or accepted for publication. As a result of this format, some repetition is inherent, especially in the "Introduction" and "Method" sections.

This thesis focuses on the effect of hydraulic residence time, phytoplankton biomass, photosynthesis and emergent vegetation on the retention of metals by surface-flow wetlands. In the introductory chapter (Chapter 1), a review of the litterature is presented and the objectives of the study are stated. The core of the thesis is formed of four chapters (Chapter 2–5).

Chapter 2 presents evidence, obtained from inlet-outlet sampling every three days over 2 years, that the first-order removal model is inadequate for predicting the retention of metal in surface-flow wetlands in temperate climates. Chapter 3 presents detailed information on the transformation changes in the dissolved and partitioning fractions of Fe and Mn in a young surface-flow wetland. Chapter 4 presents evidence that photosynthesis significantly affects the concentrations of metals in surface water of wetlands. Chapter 5 shows that the presence of cattails (*Typha latifolia*) does not affect the total concentration and partitioning of metals in surface sediments.

Finally, Chapter 6 synthesizes the information contained in the previous chapters and suggests some design considerations for the creation of wetlands as water treatment systems in northern climates and identifies areas where further research is needed.

Chapter 2 and 3 are in press at *Ecological Engineering*. Chapter 4 was submitted to *Water Science and Technology*. Chapter 5 is in press at *Water, Air, and Soil Pollution*.

Chapter 1

Introduction to wetlands as water treatment systems

1.1 Wetland ecosystems and ecological functions

1.1.1 Definition of wetlands

Wetlands are typical of the Canadian landscape (Shotyk, 1988). Some examples of wetland types are swamps, marshes, bogs or fens depending on existing plants and water conditions. Wetlands have been defined in Canada as "land that is seasonally or permanently covered by shallow water, or in respect of which the water table is close or at the surface, so that the presence of abundant water has led to the formation of hydric soils and has favored the dominance of either hydrophytic or water-tolerant plants" (NWWG, 1988). In general, a broader definition would include wetlands with non-soil substrate such as rock or gravel that are saturated or covered by shallow water at some time during the growing season (Tiner, 1984).

1.1.2 Hydrological functions

Wetlands serve important ecological functions as they act as water buffers between terrestrial and aquatic ecosystems. Wetlands may receive water from underground and/or surface sources where water picks up nutrients through bedrock and soils (minerotrophic wetland) or may receive their water only from precipitation, snow or fog (ombrotrophic wetland) (Johnson, 1985). Depending on the type of wetland, the water budget may differ. For minerotrophic wetlands, we can determine two types of systems. Surface-flow wetlands contain water above the soil surface and subsurface-flow wetlands consist of water infiltrating through the soil or another substrate (Kadlec and Knight, 1996). Transfers of water to and from a wetland follow the same pattern for surface-flow and sub-surface flow wetlands. In treatment wetlands, wastewater additions are normally the dominant flow, but under other circumstances (for example snow melt), other transfers of water can be important. The dynamic overall water budget for a minerotrophic wetland is (Fig 1.1):

$$dV/dt = Q_i - Q_o + Q_c - Q_b - Q_{gw} + Q_{sm} + PA - ETA \tag{1.1}$$

where the change in volume over time (dV/dt) is a function of the surface water inflow rate (Q_i) in $m^3\ d^{-1}$, of the surface water outflow rate (Q_o) in $m^3\ d^{-1}$, of the catchment runoff rate (Q_c) in $m^3\ d^{-1}$, of the bank loss rate (Q_b) in $m^3\ d^{-1}$, of the infiltration to groundwater (Q_{gw}) in $m^3\ d^{-1}$, of the flow rate attributed to snow melt (Q_{sm}) in $m^3\ d^{-1}$, of the precipitation rate (P) in $m^3\ d^{-1}$, of the surface area of the wetland (A) in m^2, and of the evapotranspiration rate (ET) in $m\ d^{-1}$. The parameters defining the water budget or the water mass balance of wetlands are important to measure because chemical mass balances, on which pollutant removal is calculated, can only be built once the water mass balance is accurately defined.

1.1.3 Role of aquatic vegetation in wetland ecosystems

Wetlands are very productive ecosystems and aquatic plants are an important component as the main autotrophic organisms producing oxygen and carbohydrates through photosynthesis. Heterotrophic organisms rely upon the availability of oxygen and carbohydrates produced by autotrophic organisms in order to satisfy their energy requirements through respiration.

The oxygen diffusion in water is slow in comparison to air, which results in oxygen deficiency in sediments when the biological oxygen demand is high. Aquatic macrophytes are morphologically adapted to survive in anoxic sediments. Many species develop specialised tissue (aerenchyma), which allows the transport of oxygen from the leaves via the stem to the roots (Dunbabin et al., 1988; Faulkner and Richardson, 1989). The supply of oxygen to the roots also results in oxygen leaking to the sediments, mostly at the apical meristem (Brix, 1994). Macrophytes also release organic compounds (i.e., carbohydrates) from their roots, which can be utilised for microbial respiration (Pelmont, 1993). Furthermore, macrophytes also provide a physical substrate for the establishment of biofilms and epiphytic algae (Brix, 1994). Epiphyte growth provides food for many invertebrates and fish (Mitsch and Gosselink, 1993).

1.1.4 Role of microbial communities in wetland ecosystems

Microbial communities perform several functions in wetland ecosystems. Some bacteria are autotrophic and produce oxygen and carbohydrates in the water column (Wetzel, 1983; Pelmont, 1993). Microbial communities can also form and dissolve minerals through dissimilatory reactions. Some bacteria are able to dissolve a mineral by using it as a source of energy, as a terminal electron acceptor in respiration, or as a trace element requirement (Ehrlich, 1996). Furthermore, the dissolution of minerals will increase the bioavailabilty of these elements to other organisms (Tessier et al., 1994). For example, iron-reducing bacteria use Fe oxides as an electron acceptor for anaerobic respiration (Lovley and Phillips, 1986). This reaction releases the more bioavailable Fe^{2+} into the pore water and can be assimilated by other bacteria or other organisms. Other essential elements (e.g. Zn, Cu) are also released as free ions because iron oxides are efficient adsorption sites for these metals (Benjamin and Leckie, 1981; Tessier et al., 1985).

Other bacteria can form minerals in the oxidation or reduction of dissolved inorganic species in energy metabolism, in the detoxification of inorganic species, or in active or passive uptake of one or more dissolved inorganic species followed by a conversion into a cellular support or protective structure (Ehrlich, 1996). The formation of minerals usually corresponds to a decrease in the bioavailability of elements. For example, the oxidation of Fe^{2+} into Fe^{3+} by iron oxidative bacteria decreases significantly the bioavailability of iron (Pelmont, 1993). Microbes can also oxidize inorganic species as a means of making them less toxic. For example, bacteria can immobilise toxic metals by fixing them in their cell envelope (Beveridge et al., 1983; Ferris et al., 1986) or precipitating them as sulfides, carbonates or phosphate external to their cells (Ehrlich, 1990).

1.1.5 Metal cycling in wetlands

The cycling of metals in wetlands involves a dynamic exchange at the air-water interface and at the sediment-water interface. The exchange at the air-water interface is limited to wet or dry deposition as most metals are not volatile with the exception of Hg. Figure 1.2 depicts a simplified scheme of a metal cycle. In surface waters, total metal concentrations include the particulate and dissolved fractions. The particulate fraction refers to colloids (> 0.45 μm), inorganic particles, bacteria, phytoplankton and zooplankton whereas the dissolved fraction refers to smaller colloids and free metal ions

(Wetzel, 1983). When metals are introduced to a wetland by surface inflow and atmospheric input, they interact with inorganic and organic particles because metal ions are thermodynamically unstable in surface water. Both organic particles (algae, biological debris) and inorganic particles (e.g., iron and manganese oxides, alumino-silicates) contribute to the binding and transport of dissolved metals. Dissolved metal concentration in water depend upon desorption (1) and adsorption (2) onto suspended inorganic particles or upon algal uptake (3 and 4) (Fig.1.2). The partitioning of metals into algal biomass and their settling is a dominant process, especially in eutrophic systems (Stumm 1992). Settling of organic and inorganic particles (5) is also believed to be the main mechanism of metal removal in surface-flow wetlands (Gilliam et al., 1988). The settling ($g\ d^{-1}$) of particles can be described by the following equation:

$$\text{Settling} = v_s\, A_s\, c_p \tag{1.3}$$

where v_s is the net settling velocity ($m\ d^{-1}$), A_s is the surface area of the sediments (m^2) and c_p the particulate metal concentration ($g\ m^{-3}$). Particles may return to the water column through resuspension (6), which is induced by water turbulence from wind and depends on water depth. In the case of organic particles such as plankton, a significant amount of particulate metals may leave the wetland (7) because plankton has a similar density as water (Fig.1.2).

Once settled onto the sediment surface, metals are affected by a series of redox reactions at the sediment-water interface (Froelich et al., 1979; Tarutis and Unz, 1996). An oxic layer is characterised by the presence of iron and manganese oxides (Fig.1.2).

Trace elements can adsorb onto these oxides in the oxic layer (Tessier et al., 1985) and this sorption process is pH-dependent (Benjamin and Leckie, 1981). The relative thickness of the oxic layer depends on the oxidation and precipitation rates of Fe^{2+} and Mn^{2+} at the sediment-water interface and on the consumption of metal oxides in deeper sediments.

The sub-oxic layer (Fig.1.2) lies below the oxic layer and is marked by a decrease in redox potentials because oxygen is no longer available as an electron acceptor in respiration (Froelich et al., 1979). Nitrate (Sorensen, 1987), manganese oxides (de Vrind et al., 1986; Stone, 1987) and then iron oxides (Lovley and Phillips, 1986) act as a secondary oxidants in the sub-oxic zone. The reduction of manganese and iron oxides into Mn^{2+} and Fe^{2+} results in the release of these ions and other trace metals into the pore water. Newly released metals may diffuse upward or downwards into the sediments. If intense iron and manganese reduction occur, the entire oxic layer may be consumed and therefore, metals diffusing upward will be released to the water column (8) (Fig.1.2). However, if the oxic layer permanently covers the sediments, metals diffusing upward will be reoxidized in the oxic layer. Metals can also diffuse downward to the anoxic layer.

The anoxic layer (Fig.1.2) is characterised by the presence of sulfide, either dissolved or in the form of iron sulfide minerals, generated by the microbial reduction of dissolved sulfate coupled with the anaerobic decomposition of sedimentary organic matter (Widdel, 1988). Lovley and Phillips (1987) found that the presence of microbially reducible iron oxides inhibits sulfate reduction. As a result sulfate reduction can only proceed when the supply of iron oxides becomes depleted. This explains the physical separation of the sub-oxic and anoxic layers. In the anoxic layer, dissolved sulfides react with interstitial Fe^{2+} to form iron monosulfides, which gradually transform into pyrite. The pyritization of iron monosulfides is believed to represent a long-term immobilisation of Fe if the pyrite is not exposed to oxygen. Hydrogen sulfides will also scavenge other metals and lead to their precipitation (Huerta-Diaz et al., 1993).

1.2 Wetlands as wastewater treatment systems

Both natural and created wetlands have been used to treat water from agricultural, municipal and industrial sources (Hammer, 1989). Wood (1995) estimated that there are approximately one thousand created wetlands around the world of which 150 are located in North America (Brix, 1994; Berezowsky, 1996). In Canada, a national survey identified 67 wetlands for treatment of wastewater (Pries, 1994). Most of these wetlands are surface flow facilities receiving municipal effluents.

1.2.1 Advantages of using wetlands for water quality improvement

The high primary production of wetlands leads to the accretion of organic rich sediments and enables wetlands to become major storage sites for organic and inorganic compounds. Furthermore, wetlands can transform many of the common pollutants that occur in wastewater into essential nutrients that can be used for additional biological productivity (Mitsch and Gosselink, 1993). Therefore, wetlands are used for water quality improvement because they are generally viewed as "natural kidneys" (Mitsch and Gosselink, 1993; Kadlec and Knight, 1996).

Also, the use of wetlands for wastewater treatment can be economically advantageous. Wetlands are low-cost alternatives and need little maintenance compared with conventional wastewater treatment plants (WWTP) (Table 1.1). The construction cost for a conventional WWTP is slightly higher than for a created wetland. In fact, the construction costs of wetlands depends mainly on the cost per hectare of a land where the wetland is built. For example, the construction of a wetland on an urban land is much more expensive than one built in an agricultural countryside area. Most importantly, WWTP have significantly higher operation and maintenance costs. For example, Noranda Inc. spent over $11,000,000 in operations and maintenance for seven WWTP in 1998. The money spent each year by Noranda Inc. does not include sludge handling and associated site restoration.

In comparison, wetlands require little maintenance and less highly qualified staff. Only one technician is required to pick up water samples and to verify the functioning of on site equipment. Table 1.2 presents the costs of construction, maintenance and operation costs for recently built wetlands. These data clearly show the economic advantage of using created wetlands for wastewater treatment.

1.3 Are wetlands sources or sinks for metals?

Despite the advantages of using created wetlands for water treatment, there are still uncertainties surrounding the treatment efficiency of these systems. The general assumption is that wetlands are sinks for pollutants and this is determined through chemical mass balances.

1.3.1 Calculating metal retention by wetlands

Chemical mass balances allow the calculation of metal removal by wetlands. There are different approaches to calculate metal retention. The simplest is the mass removal rate "JA" (g d^{-1}) (Kadlec and Knight, 1996):

$$JA = M_i - M_o = Q_iC_i - Q_oC_o \tag{1.4}$$

where M_i and M_o are mass rates at the inlet and outlet of a wetland (g d^{-1}; kg d^{-1}; kg yr^{-1}), Q_i and Q_o are the flow rate at the inlet and outlet in m^3 d^{-1}, and C_i and C_o are metal concentrations at the inlet and outlet in (mg m^{-3}). Mass removal rates do not take into account the effect of the surface area of a wetland. The larger a wetland, the greater the potential to retain metals (Kadlec and Knight, 1996). It is therefore appealing to include a sizing variable in the removal calculation. The specific mass removal rate "J" (kg m^{-2} d^{-1}) measures the quantity of metals removed by a wetland of a specific surface area per time:

$$J = (M_i - M_o)/A = (Q_iC_i - Q_oC_o)/A \tag{1.5}$$

where "A" is the surface area of the water table in m^2. Specific mass removal rates are advantageous because they allow the comparison of removal rates by wetlands of different size. Another way to calculate the removal of metals by wetlands is by using percent concentration reduction (CR) in mg m^{-3}:

$$CR = 100\,(C_i - C_o)/\,C_i \tag{1.6}$$

However, this term is quite ambiguous because dilution or concentration due to rain, evapotranspiration, or other unaccounted flows renders CR an imperfect measure of true removal. Therefore, percent mass removal or treatment efficiency is usually preferred:

$$\text{Treatment efficiency} = 100\,(QC_i - QC_o)/\,QC_i = 100\,(M_i - M_o)/\,M_i \tag{1.7}$$

The rate of pollutant removal in created wetlands can be either dependent or independent of concentration. In the case of metals, removal in a surface-flow wetland follows first-order kinetics (Tarutis et al., 1999). The treatment efficiency and first-order removal are exponentially related if the hydraulic loading rate (Q/A) is held constant:

$$(C_i - C_o/C_i) = 1 - \exp(-k_a A/Q) \tag{1.8}$$

Equation 1.8 allows the calculation of the surface area required to reach a target outlet concentration or to obtain a specific removal if the average inlet concentration of metals, the flow rate and the areal removal rate constant "k_a" (d^{-1}) are known. If the mean water depth is known, then equation 1.8 can be expressed in terms of a volumetric removal (Kadlec and Knight, 1996):

$$(C_i - C_o/C_i) = 1 - \exp(-k_v t) \tag{1.9}$$

where k_v is a first-order volumetric removal constant (d^{-1}) and t is the hydraulic residence time (d). The areal removal model has greater utility because mean depth is difficult to evaluate precisely in wetlands (Kadlec and Knight, 1996). Moreover, the removal of metals such as iron and manganese is primarily due to the deposition of oxidized metal precipitates (Wieder, 1993), which renders the areal removal model more meaningful (Tarutis et al., 1999).

The reaction rate constant "k" depends on temperature as shown in the following equation (Reddy and Burgoon, 1996; Kadlec and Knight, 1996).

$$k = A_v \exp(-E/RT) \tag{1.10}$$

where A_v is the Van't Hoff-Arrhenius coefficient, E is the activation energy ($J\ mol^{-1}\ K^{-1}$), R is the gas constant ($8.314\ J\ Mol^{-1}\ K^{-1}$) and T is temperature in degrees Kelvin. The rate constant will increase along with increasing temperature. Therefore, at high temperatures, wetlands will require lower hydraulic residence times to retain metals than at colder temperatures.

1.3.2 Treatment performance of wetlands in cold climates

In this thesis, cold climate refers to the cold temperate climate where the coldest month has a mean temperature of −3°C and the warmest is above 10°C (Strahler and Strahler, 1992). In cold temperate regions, snow must accumulate for at least one month per year. Such conditions occur in Canada, Alaska, Northern USA, Scandinavia, Eastern Europe, Russia and North Eastern China.

In cold environments such as Canada, created wetlands can be used at temperate latitudes for wastewater treatment, despite the shorter growing season (Maehlum et al., 1995; Wittgren and Maehlum, 1997). However, Wittgren and Maehlum (1997) suggested that the design of cold climate wetlands should differ from a wetland under warmer climate with a longer growing season. However, the data available on treatment performance under northern climates are quite limited (Pries, 1994)

This has led to severe criticisms directed against the use of created wetlands. Brown and Reed (1994) indicated that there is no clear consensus regarding basic hydraulics, engineering designs, type of vegetation, size or pre-treatment procedures. Furthermore, wetlands exposed to wastewater may accumulate levels of pollutants that may represent a risk to wildlife if there is a high degree of exposure to harmful compounds (Helfield and Diamond, 1997). Recently, Gopal (1999) was particularly critical towards the use of wetlands as wastewater treatment systems because we know little about the functioning, the ability to receive wastewater, and the biota of wetlands. In fact, major design variables are exclusively hydrological (Table 1.3), which is surprising since biogeochemical processes are important in productive ecosystems such as wetlands (Mitsch and Gosselink, 1993).

Kadlec and Knight (1996) conducted a survey on the retention performance of constructed wetlands for metals (Fig.1.3). This summary presents a yearly average treatment efficiency of different metals by created wetlands in North America. The treatment efficiency ranged between 40 and 80% for most elements (Mn, Cu, Zn, Ni, Pb, Cd, and Cr). In contrast, some metals (Al, Fe, Hg) are poorly retained by wetlands. Also, there is much variability in treatment efficiency for each metal. This variability can perhaps be explained by the seasonal differences in metal removal and by the difference in the biogeochemical response of each metal to conditions occurring within wetlands. In some cases, wetlands can actually be sources rather than sinks for metals (St-Louis et al., 1994; St-Louis et al., 1996; Kadlec and Knight, 1996). Clearly, more research is required to address the sources of this variation in the retention capabilities of wetlands. The overall objective of this thesis was to address some of the possible causes of variability in metal retention by wetlands.

1.4 Research objectives and thesis organisation

1.4.1 Seasonal importance of hydraulic residence time on metal retention

The hydraulic residence time is considered a key variable in predicting pollutant retention by wetlands. Numerous hydrological studies have been conducted to determine both water residence time values (Wood, 1995) and the accuracy of these values (Johengen and LaRock, 1993; Watt and Marsalek, 1994; Matthews et al., 1997).

According to first-order removal models, the hydraulic residence time and treatment efficiency are exponentially related (Eq. 1.9). This relationship implies that the retention is maximised as the hydraulic residence time increases. However, as water temperature increases over the summer period, the biological activity may have an important impact on metal cycling within wetlands. For example, intense microbial reduction of Fe and Mn oxide may lead to a release of metals in summertime (Vile and Wieder, 1993). The objective of Chapter 2, was to test the first-order removal model on a seasonal basis in a young wetland.

1.4.2 Changes in Fe and Mn partitioning in created wetlands

Mitsch and Gosselink (1993) have described wetlands as transformers of pollutants. In the case of Fe and Mn, the transformation process can be viewed as a change in their partitioning. Few studies have examined the partitioning of Fe and Mn in surface-flow wetlands. Most mass balance studies are based solely on total (dissolved + particulate) concentrations. Information on the partitioning of Fe and Mn is important because of the high binding affinity of more toxic trace metals (i.e. Zn, Cu, Pb, As, Cd) to suspended Fe and Mn oxide particles. Also, it is difficult to evaluate the bioavailabilty of Fe and Mn at the outlet of the wetland treatment system because total metal is a weak predictor of bioavailability (Campbell, 1995).

The partitioning of metals may differ on a seasonal basis. During the growing season, metals are believed to be mostly associated with the particulate fraction because biological productivity is so intense that primary consumers such as bacteria and phytoplankton rapidly take up metals from the water (Kadlec and Knight, 1996). In the fall, algal biomass will decrease when water temperature and solar radiation decreases. As a result, the partitioning of metals in the water column may change in the fall and in the winter when anoxic conditions in sediments lead to a release of dissolved metals. The objective of Chapter 3 was to evaluate the change in the partitioning of metals in a created wetland on a seasonal basis.

1.4.3 Photosynthesis and its role in metal cycling

Constructed wetlands are solar powered ecosystems (Kadlec, 1999). During the day, photosynthesis increases oxygen and pH levels, which favour metal precipitation as oxides. These conditions allow a build up of iron and manganese oxide at the sediment water interface, which decreases the metal concentration in the water column. At night, the oxygen levels decrease rapidly because photosynthesis is stopped and both microbial and aquatic plants consume oxygen. In wetlands, diel changes in oxygen and pH induced by photosynthesis likely induce diel changes in metal concentrations. If such a hypothesis is correct, then diel changes should affect the overall retention of metals by wetlands. However, significant diel changes should be limited to the growing season when photosynthesis is intense. The objective of Chapter 4 was to evaluate if diel changes in oxygen and pH levels induced by photosynthesis affect the concentration of metals in surface water and the overall treatment efficiency of constructed wetlands.

1.4.4 The role of aquatic plants on metal cycling in surface sediments

Aquatic plants are considered essential components of a wetland but their role in metal cycling is not clear (Brix, 1994; Brix, 1997). Sediments colonised by macrophytes may have higher metal concentrations because macrophytes provide mechanical resistance to flow, increase the hydraulic residence time, and facilitate settling of suspended particles (Harlin et al. 1982, Carpenter and Lodge 1986, Stevenson et al. 1988, Brix 1994, Caçador et al. 1996, Brix 1997). Aquatic rooted macrophytes also assimilate metals although most calculations suggest that plant tissue is not a significant sink. Also, there is limited information on the effect of macrophytes on the partitioning of metals in their sediments. The knowledge of metal partitioning in wetlands is important because it gives information on the bioavailability of metals in vegetated sediments, which contain a high diversity and biomass of organisms. The objective of Chapter 5 was to examine if the presence of cattails (*Typha latifolia*), a common aquatic plant of created wetlands, affects the concentration of metals in surface sediments. A second objective was to examine if cattails affect the partitioning and potential bioavailability of metals in sediments.

1.4.5 Design considerations for surface-flow wetlands under cold climates

Chapters 2-5 examine the effect of different variables on the cycling and retention of metals by constructed wetlands under cold temperate climates. These chapters provide new knowledge about the cycling and retention of metals in surface-flow wetlands. Although a generalisation of my results to other surface-flow wetlands should be done cautiously, the objective of Chapter 6 was to provide suggestions for optimal wetland design as well as the research requirements to improve the retention performance of surface-flow wetlands receiving urban and agricultural runoff under cold climates.

Table 1.1 Comparisons of costs (US dollars) associated with the choice of using a conventional water treatment plant and a constructed wetland.

Cost category	**Construction costs ($)**	
Treatment option	*Conventional WWTP*	*Constructed Wetland*
Mobilisation & Administration	95,000	91,000
Earthwork (Cleaning, Grubbing, Excavation)	381,000	1,336,000
Wetland planting	0	309,000
Other Site work (Electrical, Controls, Piping)	728,000	1,720,000
Conventional primary	639,000	0
Conventional Activated Sludge	698,000	0
Sludge handling	687,000	0
Biological Nitrification	476,000	0
Chlorination and outfall	208,000	0
Total	**4,112,000**	**3,456,000**
Operation and Maintenance costs ($/year)		
Personnel	63,000	24,000
Utilities	23,000	5,000
Chemicals	23,000	11,000
Equipment/supplies	47,000	5,000
Total	**156,000**	**45,000**

Modified from Kadlec and Knight 1996

Table 1.2 Costs associated with the construction, operation and maintenance of selected constructed wetlands in Canada (From Goulet 2000)

Constructed Wetland	Construction Cost ($)	Operation and Maintenance cost ($/year)
Monahan (Kanata, Ont)	3,500,000	20,000
Zoo de St-Felicien (Qc)	1,000,000	12,000
St-Henri-de-Taillon (Qc)	1,161,000	12,000

Table 1.3 Optimum values of variables considered in surface flow wetlands design.

Factors	Values
Hydraulic retention time, d	5–14
Max BOD loading rate, kg ha^{-1} d^{-1}	80
Water depth, m	0.1–0.5
Hydraulic loading rate, mm d^{-1}	7–60
Ratio length to width	2:1 to 10:1
Area, ha m^{-3} d^{-1}	0.002–0.014

Modified from Wood 1995

Figure 1.1 Overall water budget of a wetland (modified from Kadlec and Knight 1996). Q refers to water flow and subscript in Q_n refers to various compartments as defined in the text.

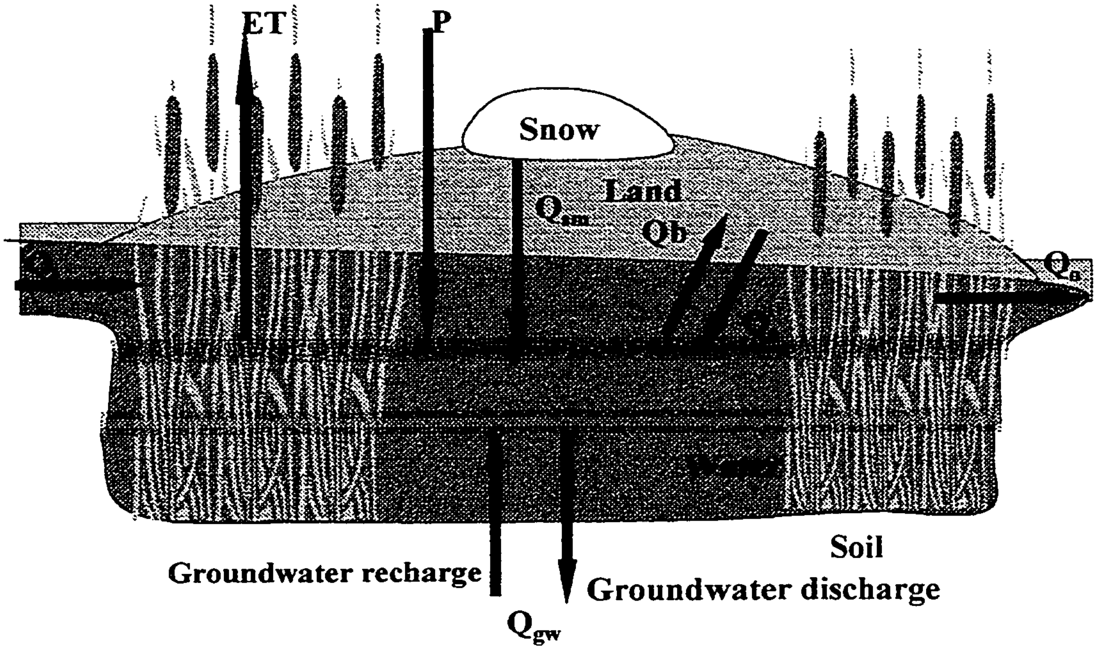

ET
P
Snow
Land
Q_{sm}
Qb
Q_o
Soil
Groundwater recharge
Groundwater discharge
Q_{gw}

Figure 1.2 The cycle of metals in surface-flow constructed wetlands. Width of arrows refers to relative importance of the process. Me^{2+} refers to dissolved metals and PMe^{2+} refers to particulate metals.

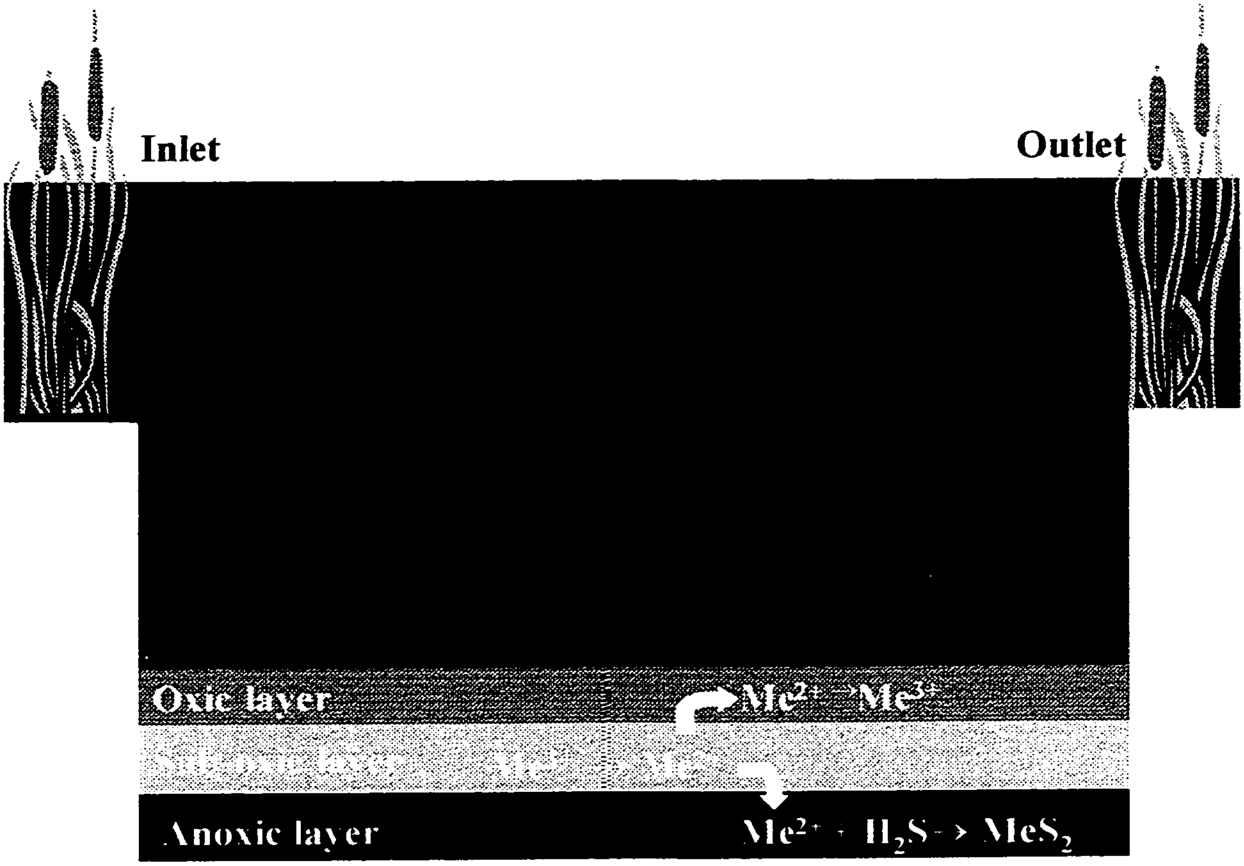
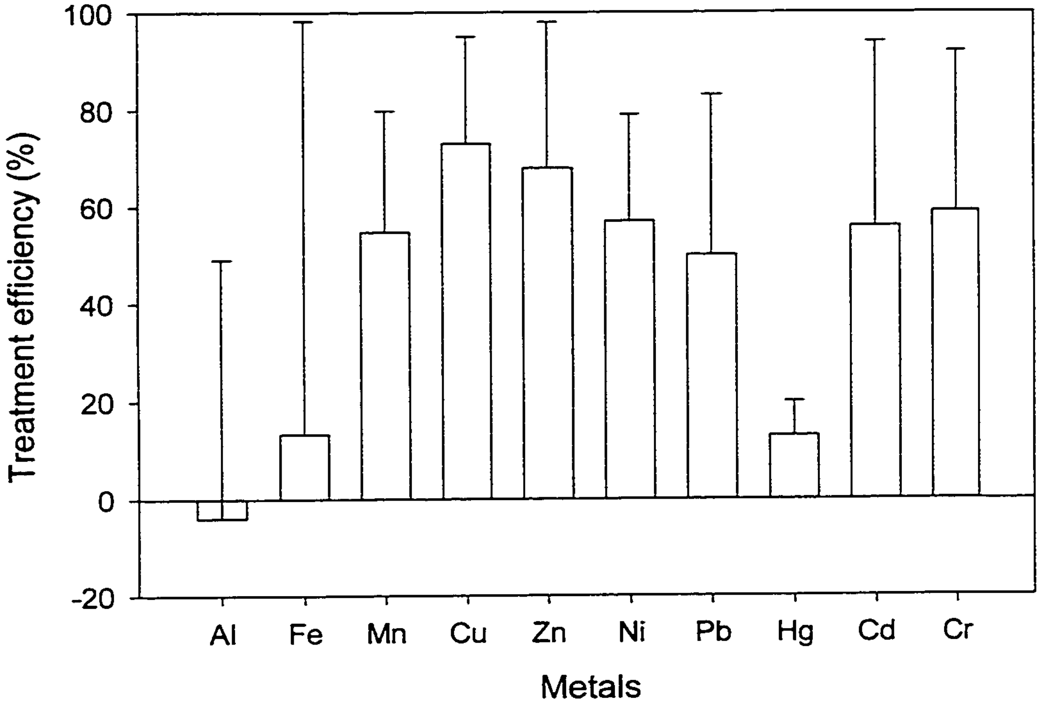

Inlet
Outlet
Oxic layer
$Me^{2+} \rightarrow Me^{3+}$
Suboxic layer
Me → Me
Anoxic layer
$Me^{2+} + H_2S \rightarrow MeS_2$

Figure 1.3 Mean and standard deviation in annual treatment efficiencies of different metals by selected North American created wetlands (N=20) (Modified from Kadlec and Knight 1996)


Treatment efficiency (%)
100
80
60
40
20
0
-20
Al
Fe
Mn
Cu
Zn
Ni
Pb
Hg
Cd
Cr
Metals

Chapter 2

Test of the first–order removal model for metal retention in a young constructed wetland

2.1 Abstract

The first-order removal model is widely used in constructed wetland design. The suitability of this model was tested to predict metal retention in a young constructed wetland receiving agricultural and urban runoff. During two years, flows were measured and water samples for total and dissolved metal analyses were collected every third day at both the inlet and outlet. The wetland retained metals best during summer and fall whereas during winter the retention of metals was significantly lower. The first-order removal model predicted Fe and Mn retention in the spring and dissolved Zn retention from spring to fall in both years. During those periods, hydraulic retention times greater than 7 days provided the maximum retention of Fe, Mn, and dissolved Zn. However, first-order removal models failed to fit summer, fall and winter data for almost every metal under investigation (Fe, Mn, dissolved Cu, dissolved As) suggesting that hydraulic retention times (<1–25 days) did not affect metal retention during these seasons. Since the metal loading to the wetland was low, the input of metals through internal loading may be more significant consequently decreasing the metal retention. Therefore, the first-order removal model is inadequate to predict metal retention on a seasonal basis. Models used to design constructed wetlands must consider seasonal changes that affect biological as well as hydrological variables.

Key words: hydraulic retention time, biological activity, first-order removal model, metals, constructed wetlands, removal efficiency.

2.2 Introduction

Constructed wetlands are increasingly used for the removal of pollutants from wastewater. Municipalities, farms, and industries utilise the retention capacity of wetlands to meet water quality guidelines (Kadlec and Knight, 1996). Unfortunately, effluent concentrations of wetlands are sometimes at levels that may impact aquatic organisms. In some cases, wetlands are even sources of pollutants (St-Louis et al., 1994; St-Louis et al., 1996; Kadlec and Knight, 1996). Constructed wetlands may fail to meet environmental guidelines because they may be poorly designed. This problem arises because of the limited understanding of the variables that affect the cycle of pollutants in wetlands.

In most cases, wetlands are almost exclusively designed based on hydrological and sizing considerations (Wood, 1995). Mathematical models are derived based on steady-state, plug-flow assumptions which combine removal processes and variables affecting those processes into single, first-order removal rate functions. These models take the general form of:

$$C_o = C_i \exp(-K_V t) \tag{2.1}$$

where C_o and C_i are the concentrations exiting and entering the wetland respectively, K_v (d^{-1}) is the volumetric removal rate constant, and t is the hydraulic retention time (d) of the wetland (Kadlec and Knight, 1996). This approach has been widely applied to biochemical oxygen demand, nutrients, and total suspended solids (Dortch, 1996; Kadlec and Knight, 1996).

In theory, the first-order removal model can also be applied to metals because the oxidation of ferrous iron, its precipitation and sedimentation have been shown to be first-order (Stumm and Morgan, 1996). The oxidation of manganese also follows first-order kinetics (Stumm and Morgan, 1996). The precipitation of other metals (e.g., Zn, Cu, As) can also follow first-order kinetics because iron and manganese oxides are important binding sites (Benjamin and Leckie, 1981). Baker et al. (1991) and Flanagan et al. (1994) modelled iron removal in acid mine drainage wetlands using pseudo-first-order kinetic, which were later validated later by Mitsch and Wise (1998). However, the first-order removal model has not been tested for metals in wetlands receiving agricultural and urban wastewater.

According to the first-order removal model, an increase in hydraulic retention time (HRT) results in an increase in the removal of metals by wetlands. During shorter HRT corresponding to storm events or snow melt, the retention of metals reaches very low and even negative values (Stark et al., 1994; Stark et al., 1996). Ideal HRT values are usually around 5 to 14 days (Wile et al., 1985; Watson and Hobson, 1989). Under these conditions, the settling rate of particulate metal on the surface of sediments is optimised.

Few studies have tested first-order removal models on a seasonal basis (Flanagan et al., 1994). Most studies only consider the summer period when biological productivity and removal rate constants are high (e.g., Kadlec, 2000). However, in cold climates such as Canada, there are significant seasonal changes in temperature. The removal of metals is affected by temperature because the volumetric removal rate constant "K_v" increases with temperature:

$$K_v = A_v \exp(-E/RT) \qquad (2.2)$$

where A is the Van't Hoff-Arrhenius coefficient, E is the activation energy (J $mol^{-1} K^{-1}$), R is a gas constant (8.314 J $Mol^{-1} K^{-1}$) and T is temperature in degrees Kelvin (Reddy and Burgoon, 1996). At high temperatures, K_v is high and wetlands should require lower hydraulic residence times to retain metals than at colder temperatures. In the winter, K_v is low because the water temperature is around 4°C and therefore, the HRT required to retain a given amount of metals should be higher.

The first-order removal model only considers HRT but there is increased awareness that other variables need to be included in removal models. Biological variables such as the partitioning of metals into algae and macrophytes and the resuspension and/or resolubilisation of metals are part of so-called autobiotic removal models (Christensen et al., 1994; Lung and Light, 1996; Kadlec, 1997). Algal and macrophyte growth are generally limited by phosphorus in aquatic systems (Wetzel, 1983). Since wastewater from agricultural and urban areas is nutrient rich, primary production increases and metal uptake by algae and macrophytes also increases because of metal requirements for growth. A significant accretion of organic material in sediments will occur over time through die-off. Organic rich sediments have generally low redox values under which a release of metals may occur because of organic matter decomposition or through microbiologically mediated iron and manganese oxide reduction (De Vrind et al., 1986; Lovley and Phillips, 1988; Tarutis and Unz, 1995). In wetlands receiving high nutrient loading, the removal of metals may be impaired.

The objective of this study was to evaluate the first-order removal model for metal retention on a seasonal basis in a temperate constructed wetland receiving urban and agricultural runoff.

2.3 Methods

2.3.1 Study site

The Monahan constructed wetland chosen for this study is located in the city of Kanata, Ontario, Canada ($45^0 16.24$ N $75^0 51.07$ W). This surface-flow wetland was built in 1995 to receive urban and agricultural runoff. Originally, the Monahan Creek drained the area where the wetland was dug out and it continues to feed the wetland. The watershed is principally agricultural land with increasing residential development (Totten Sims Hubicky & Associates, 1997). Five storm water detention ponds, positioned in the drainage basin, precede the wetland. The wetland itself has three consecutive cells (Fig.2.1), which were lined initially with a thick layer of clay to prevent infiltration (Totten Sims Hubicky & Associates, 1997). Cattails (*Typha latifolia*) were planted on the clay substrate and the wetland was flooded for its first year of operation in 1996. The wetland has an average surface area of 31 300 m^2 within a total drainage area of approximately 637 ha (637×10^4 m^2) and an average volume of 5.3×10^4 m^3 with a mean depth of 1.5 m. The inlet and outlet are both gauged and the average water detention time is 12.7 ± 0.8 days. Cell 1, 2, and 3 have a maximum depth of 1.5, 2.0, and 1.5 m respectively. However, shallow zones (< 1 meter) represent as much as 60% of the total surface area of the wetland. Emergent vegetation such as cattails (*Typha latifolia*), water plantain (*Alismaplantago aquatica*), arrowhead (*Sagittaria latifolia*) and sweet flag

(*Acorus calamus*) are established in the littoral zone and represent 20% of the total surface area. Duckweed (*Lemna minor)* is common and mostly found within the emergent vegetation community. Another 30% of the total surface area is dominated by submerged macrophytes such as coontail (*Ceratophyllum demersum*), pectinate pondweed (*Potamogeton pectinatus*), curly pondweed (*Potamogeton crispus*), leafy pondweed (*Potamogeton foliosus*), and horned pondweed (*Zanichellia palustris*). The remaining 50% of the wetland surface area is open water.

2.3.2 Sampling protocol

Duplicate water samples, for both total and dissolved metal measurements, were taken every third day in the early morning at both the inlet and outlet structures. The sampling period extended from April 1997 to March 1999 with some interruptions from November 1997 to February 1998 and from September to October 1998. Winter, spring, summer, and fall periods are indicated in Figure 2.2. The water samples were filtered on site through a 0.45µm nylon polypropylene filter (Chromatographic Specialties Inc.) using a 50 ml syringe (Markson Ltd.) without rubber plunger to prevent metal contamination. Unfiltered water samples were collected for measurements of total metal concentration. Water samples were preserved using 0.5% HNO_3 (Ultra-pure from Seastar Chemical Inc., Vancouver) and kept in new 50 ml Nalgene high-density polyethylene bottles at 4°C until analysis.

2.3.3 Water chemistry

Temperature, pH, alkalinity and dissolved oxygen were measured on each sampling date for both the inlet and outlet. Temperature and dissolved oxygen were recorded using a YSI model 57 oxygen meter. pH was measured in the laboratory using an Orion SA 250 portable pH meter. Alkalinity was measured in the laboratory by Gran titration (Wetzel and Likens, 1991).

Filtered water samples were analysed for Fe, Mn, Cu, Zn, As by ICP-MS (Varian model VG2000) at the Geological Survey of Canada, Ottawa, Ontario. Detection limits were 5 μg/L dissolved Fe, 0.1 $\mu g\ L^{-1}$ for Mn, Cu, and As and 0.5 $\mu g\ L^{-1}$ for Zn. Unfiltered water samples were digested using acid assisted microwave digestion. The digestion was done by adding ultra-pure concentrated nitric acid (10% of the volume of the sample). The microwave digestion lasted 1 h. Total concentrations of Fe and Mn were then measured by ICP-AES (Thermo Instrument Atomscan 25) at the Geology Department of the University of Ottawa. Detection limits were around 10 $\mu g\ L^{-1}$ for Fe and 5 $\mu g\ L^{-1}$ for Mn.

2.3.4 Water budget

A mass balance was done for each season sampled. The water mass balance of the wetland can be described as:

$$I + P = O + ET \tag{2.3}$$

where I corresponds to the amount of water entering the wetland through surface inflow (m^3), P is the quantity of water entering the wetland through precipitation (m^3), O is the quantity of water exiting the wetland through surface outflow, and ET corresponds to the loss of water through evapotranspiration. Infiltration rates were negligible because the wetland was built on a thick clay liner. Outflow rates were calculated using a discharge equation of a free flowing rectangular weir with end contractions:

$$Q = K\,(L - 0.2H)\,H^{1.5} \tag{2.4}$$

where Q is the discharge or flow rate ($m^3\ d^{-1}$), H is the head on the weir (m), L is the crest length of the weir (m), and K is a constant dependent upon units (Grant, 1989). Evapotranspiration was calculated using the Penman estimate (Kadlec and Knight, 1996; Mitsch and Gosselink, 1993). All weather data for the Penman estimate calculation were from the Environment Canada Weather station in Ottawa. Precipitation data were obtained with a rain gauge installed on site (Totten Sims Hubicki & Associates 1997). The inflow through precipitation (P) was calculated by multiplying the surface area of the wetland by the precipitation data. The water storage of the wetland was based on bathymetric calculations (Wetzel and Likens, 1991) and changes in water storage were calculated from the changes in water depth measured twice at the outlet on every sampling day.

2.3.5 Experimental approach

The retention of each metal was calculated based on the total and dissolved fractions. For zinc, copper and arsenic, only the dissolved metal concentration was measured because the total concentration of these elements was below the detection limit of the ICP-AES.

Metal retention was calculated by using the removal efficiency formulas:

$$RE = \frac{(QC_I - QC_o)}{QC_i} \times 100 = \frac{Mass_i - Mass_o}{Mass_i} \times 100 \qquad (2.5)$$

where RE is the treatment efficiency and mass ("i" for inlet and "o" for outlet) is the flow (Q) times the concentration (C) (Wieder, 1993; Dortch, 1996; Kadlec and Knight, 1996; Tarutis et al., 1999). First-order removal and treatment efficiency are exponentially related if hydraulic loading rate is held constant (Tarutis et al., 1999):

$$RE = 1 - \exp(-K_V t) \qquad (2.6)$$

The calculation of treatment efficiency was based on inlet and outlet masses that were averaged over several HRT. Regardless of mixing conditions, approximately three HRTs assures that an entering element is flushed from the wetland (Kadlec and Knight, 1996). Periods of relatively constant flow were selected based on continuous outflow measurements (Totten Sims Hubicky & Associates, 1997, 1998). The flow-weighted average concentration at the inlet and outlet were then calculated, for each period, over a time frame corresponding to three HRT values (Kadlec and Knight, 1996). For each time frame, the average HRT was calculated based on average outflow. Average treatment efficiencies with corresponding average HRT were then plotted for each season to fit the first-order removal model.

In the same manner, retention was also calculated with the area-adjusted formula based on flow-weighed average inlet and outlet.

$$\text{Area-adjusted removal (mg m}^{-2}\text{ d}^{-1}) = (\text{Mass}_i - \text{Mass}_o)Q/A \qquad (2.7)$$

Where Q is the constant flow rate (m^3 d^{-1}) (because $q_i = q_o$) and A is the area of the wetland in m^2.

The calculation of treatment efficiency based on instantaneous inlet and outlet samples does not consider the travel time of metals within the wetland and it does not consider the storage of metals in the water column from a previous event ("parking lot phenomenon"). Averaging over three HRTs fixes these two problems.

In addition, the collection of inlet and outlet water samples on a three days basis over a long time frame allowed the use of time series analysis to identify significant time lags that relate inlet to outlet masses. The time series analysis was done for each metal for the entire sampling period. Finally, treatment efficiency was related to the time since the last rain (or snowmelt) event to evaluate if the storage of metals in the water column affected the retention. An event usually corresponded to over 10 mm of precipitation.

2.3.6 Statistical analysis

All statistical analyses were done using Systat 7.0 for Windows 95. A 2-way repeated measure ANOVA was done on daily retention values to compare seasonal and yearly retention (categorical variables). For each categorical variable, multiple comparisons were done using Bonferroni adjustments.

Non-linear regressions were used to test the goodness of fit of our data to the first order removal model ($y = y_o + a\ (1-\exp(-bx))$). Non-linear regression analyses were done using the Sigma Plot software for Windows 95. For each non-linear regression analysis, power analysis, Kolmogorov-Smirnov tests and Levene's tests were performed using Sigma plot 4.0.

2.4 Results

2.4.1 Water Chemistry

Water chemistry differed between inlet and outlet and varied on a seasonal basis (Table 2.1a). Alkalinity ranged from 2.52 meq L^{-1} at the outlet during summer to up to 5.36 meq L^{-1} at the outlet during the winter. From spring to fall, the alkalinity of the water was higher at the inlet than the outlet. During the winter, the alkalinity between inlet and outlet was similar. In contrast, pH was, on average, 0.3 unit higher at the outlet from spring to fall whereas the opposite trend was observed during the winter (Table 2.1a). The pH ranged from 7.73 at the inlet during summer up to 8.29 at the outlet during the spring. As for dissolved oxygen, it ranged from 7.6 mg L^{-1} at the inlet during summer up to 13.2 mg L^{-1} at the outlet during the spring season. The wetland produced oxygen from spring to fall (Table 2.1a). In the winter, the dissolved oxygen concentration at the outlet was lower than the inlet concentration. Finally, temperature ranged from 0.7°C at the outlet during the winter up to 21.8°C at the outlet during summer. Temperature was 3 degrees higher at the outlet during spring and summer while temperature was similar between inlet and outlet during fall and winter.

Fe concentrations were generally higher at the inlet than the outlet (Table 2.1b). However, the total concentration of Fe at the inlet and outlet was similar during summer. Also, the concentration of dissolved Fe was similar between inlet and outlet during fall and winter. Total Fe concentrations ranged from 209 $\mu g\ L^{-1}$ at the outlet during spring to 470 $\mu g\ L^{-1}$ at the inlet during fall. Dissolved Fe concentrations ranged from 14 $\mu g\ L^{-1}$ at the outlet during spring to 42 $\mu g\ L^{-1}$ at the inlet during spring.

Mn concentrations were generally higher at the inlet than the outlet except during winter when Mn concentrations were higher at the outlet (Table 2.1b). Total Mn concentrations ranged from 58 $\mu g\ L^{-1}$ at the outlet during fall to 153 $\mu g\ L^{-1}$ at the outlet during winter. The concentration of dissolved Mn ranged from 5 $\mu g\ L^{-1}$ at the outlet during fall to 140 $\mu g\ L^{-1}$ at the outlet during winter.

As for other metals, only the dissolved fraction was measured. Zn concentrations were always higher at the inlet than the outlet (Table 2.1b). Zn concentrations ranged from 0.5 $\mu g\ L^{-1}$ at the outlet during summer and fall to 6 $\mu g\ L^{-1}$ at the inlet during winter. Cu concentrations were similar between inlet and outlet for all seasons. The concentration of dissolved Cu ranged from 0.7 $\mu g\ L^{-1}$ at the outlet during summer and fall to 1.2 $\mu g\ L^{-1}$ at the inlet during winter. Finally, As was always higher at the outlet than the inlet (Table 2.1b). The concentration of dissolved As ranged from 0.2 $\mu g\ L^{-1}$ at the inlet during winter to 0.8 $\mu g\ L^{-1}$ at the outlet during summer.

2.4.2 Water budget

The wetland configuration is long and narrow and is divided into three cells; thus it is reasonable to assume that flow through the wetland was near plug-flow (Droste, 1997). In general, the water volume of the Monahan wetland was nearly constant at 53 000 m^3. Heavy rains and snowmelt caused the wetland to overflow its banks in an extreme event in early spring (Fig. 2.2). This resulted in the maximum volume of 57 000 m^3 compared to the average 53 000 m^3, but overall wetland volume fluctuation was minimal.

The seasonal water budget of the Monahan wetland is presented in Table 2.2. Surface inflow and outflow mainly affected the water mass balance of the wetland. Precipitation and evapotranspiration had minimal effects on the change in water storage as compared to surface inflow and outflow (Table 2.2). Difficulties in measuring inflow occurred because of the positioning of the weir. As a result, inflow measurements were assumed to be representative of outflow measurements because of a nearly constant water volume (Fig. 2.2) and of a strong relationship between discharge and water storage ($y = 0.017x + 53 \times 10^3$, R^2=0.80). Infiltration was removed from the mass balance equation because of the presence of a thick clay liner lying on a synthetic sheet at the bottom of the wetland.

2.4.3 Metal retention

Generally, the wetland was a sink for almost every metal under investigation (Fe, Mn, Cu, Zn) except for dissolved As where the wetland was a significant source. During both 1997-98 and 1998-99, metal retention varied seasonally and depended on metal type

(Fig. 2.3–2.4). For total Fe, there was 75% retention in the fall, which was significantly different from other seasons ($p=0.074$) when there was nearly no retention of total Fe (Table 2.3a). For dissolved Fe, the retention in the fall and winter was significantly lower than during spring and summer when the wetland retained around 50% of the dissolved Fe entering the wetland (Table 2.3a). Dissolved Fe retention decreased from spring to fall and there was a net release of dissolved Fe during winter (Fig. 2.3).

Total Mn was poorly retained by the wetland and was released during the spring, summer and winter (Fig. 2.3). For dissolved Mn, there was a significant difference in retention among seasons ($p<0.05$) (Table 2.3a). Dissolved Mn was released during winter and increased from 25% during spring to 75% during fall (Fig. 2.3).

For dissolved As (Fig. 2.4), the wetland was a net source. The As release was significantly different among seasons ($p< 0.05$) As release was higher during summer (-75%) and fall (-100%) as compared to the winter (-45%) and the spring (Table 2.3b). For dissolved Zn (Fig. 2.4), the retention differed significantly among seasons ($p<0.05$) and the retention was greatest during both the summer and fall (~85%). For dissolved Cu (Fig. 2.4), the retention differed among seasons and was the highest (~25%) during summer and fall. For Zn, Cu and As, only the dissolved fraction was measured. It is likely that the retention of total Zn, Cu and As was much lower than the retention of the dissolved fraction as was observed for Fe and Mn.

The calculation of metal retention must consider the travel time of a metal within the wetland. However, time series analyses failed to identify significant time lags between inlet and outlet mass for any of the metals (data not shown).

The parking lot effect (i.e., the storage of a pollutant in the water column that can be displaced during a storm event and result in a significant export) will depend on the total volume of runoff coming into the wetland during an individual event. The catchment runoff coefficient is a measure of water infiltration into the soil; a value near 1.0 corresponds to impermeable soils whereas a value near 0 corresponds to a permeable soil. Typical catchment runoff coefficients for agricultural and urban drainage basin are in the range of 0.3 to 0.4 (Water Environment Federation, 1992). The total runoff volume "V_R" was calculated with the following equation:

$$V_R = C_r \times P \times A \qquad (2.8)$$

Where C_r is the runoff coefficient, P is precipitation (mm) and A is total drainage area (Water Environment Federation, 1992). Precipitation events of at least 10 mm would be equivalent to a runoff volume of 19 000 to 25 000 m^3, which is nearly half the average volume of 53 000m^3. Precipitation events of over 20 mm would result in a complete replacement of the water in the wetland. Regardless of mixing conditions within the wetland, there should be an increase in metal retention with the time since last event if retention follows first-order kinetics. This was only observed in the spring for Total and dissolved Fe, dissolved Mn, dissolved Zn and dissolved Cu (Table 2.4). During summer, fall and winter, no similar trends were detected for any metals (Table 2.4).

2.4.4 First-order removal model

The influence of HRT on zinc retention was similar for the spring, summer and fall seasons. Zinc retention followed the first-order removal model during this period (Fig. 2.5b) and was highest at hydraulic residence times greater than 7 days. However, the first-order removal model failed to fit the winter data (Fig. 2.5a).

In the spring, total and dissolved Fe and Mn retention increased with increasing HRT corresponding to the first-order removal model (Fig.2.6). Generally, HRT of 5 days provided over 50% retention for dissolved Fe and Mn. The retention for total Fe and Mn was not as great (maximum 25% retention). The retention of these metals was best at residence times between 3 to 10 days. For Cu and As, the first-order removal equation failed to fit the data. For Cu, HRT greater than 7 days gave negative retention values where better retention was observed for HRT between 3 and 7 days. For As, the wetland was a source of arsenic at all HRT.

In the summer, the relationship between metal retention and HRT was different (Fig. 2.7). No relationship was observed between Cu retention and HRT and the wetland was a source of Cu at some point in the summer. The same observation can be made for As with the emphasis that the wetland was a significant source. Dissolved Fe and Mn retention decreased with longer HRT values. At HRT values of around 25 days, there was a significant decrease in dissolved Fe and Mn retention. At this point, dissolved Fe and Mn were even released from the wetland. Total Fe and Mn retention also decreased with increasing HRT. However, no significant relationships were observed and retention values were lower than for dissolved Fe and Mn. The highest release of total Fe and Mn was observed when the HRT values were lower than 8 days or greater than 25 days.

In the fall, the HRT had no effect on Fe, Mn, Cu, and As retention (Fig. 2.8).

In the winter, the first-order removal model failed again to fit the data for every metal (Fig. 2.9). The wetland was still, on average, a source of total Fe. For every metal, the wetland acted as an even greater source in comparison with the fall period. In particular, total and dissolved Mn were released over the winter (retention values as negative as –200%). Total and dissolved Fe reached retention values as low as –100%.

2.5 Discussion

In this study, the suitability of the first-order removal model to predict metal retention was tested in a young surface-flow wetland receiving agricultural and urban runoff. According to Kadlec and Knight (1996), the first-order removal model can be applied to surface-flow wetlands only if they satisfy nine assumptions. The Monahan wetland generally satisfied these assumptions (e.g., steady state, no infiltration, no significant atmospheric input, spatial uniformity along the wetland width, plug-flow, rectangular shape, no variations in cross flow direction, precipitation and evapotranspiration are similar, time average and flow weighed concentrations are similar, long term average performance).

At the Monahan wetland, the ability of the first–order removal model to predict metal retention depended on season (Figs. 2.5–2.9). In the spring, Fe^{2+} and Mn^{2+} are oxidised in the water column and settle as oxides with other adsorbed metal (e.g., Zn) at the surface of sediments. This process follows first-order kinetics. Precipitation and sedimentation are also irreversible because the microbial activity is low during spring, which limits metal resolubilisation into the water column. Under such conditions, the amount of metals removed from the water column through this mechanism increases with longer HRT. This enables the oxic layer of the sediments to prevail or increase.

However, during other seasons, first-order removal models did not fit the data for any metal (except Zn) (Fig. 2.7–2.9). The sediments of the Monahan wetland contained Fe, Mn and Cu in a reactive form, which is sensible to biogeochemical changes within the wetland. The establishment of anoxic conditions in the sediments can perhaps explain this result (e.g. Carignan and Lean, 1991). In organic sediments such as those of the Monahan wetland (Chap. 5), the biochemical oxygen demand is high resulting in a quick depletion of oxygen. Under such conditions, a release of Mn and Fe in the overlying water column occurs (Tarutis et al., 1992; Tarutis and Unz, 1995) because iron and manganese reducing bacteria consume Fe and Mn oxides (De Vrind et al., 1986; Lovley and Phillips, 1988). Anoxic conditions occurred mainly during summer, fall and winter (Fortin et al., 2000).

In contrast, hydraulic retention time predicted dissolved Zn retention during spring summer and fall. This is surprising because dissolved Zn retention should be related to the retention of dissolved Fe and Mn since these metals are important adsorption sites for Zn (Benjamin and Leckie, 1981). Instead, Zn cycling is perhaps more regulated by plant biomass. Zn is an essential elements for plant growth (Vymazal, 1995). The sediments of the Monahan wetland contained Zn mostly in resilient organic matter (Chapter 5). Resilient organic matter provides a good long-term sink for Zn because of its long turnover rate. In addition, very low Zn concentrations at the outlet (0.5 $\mu g\ L^{-1}$) can be explained by a high Zn demand by aquatic plants, which is generally measured in large quantities (100 mg kg^{-1}) (Vymazal 1995). As a result, Zn is well retained by the Monahan wetland because it is required in large quantities for plant growth and because of its presence in resilient organic matter. High concentrations of Zn were measured at the outlet (or low retention) only during storm events probably because aquatic plants are less efficient in Zn uptake under high flow conditions. During the winter, intense organic matter decomposition and a potential release of Zn to the water column perhaps explain the incapacity of hydraulic retention time to predict Zn retention.

The failure of the first-order removal models to predict metal retention may also be explained by seasonal changes that favour the development of non-ideal flow patterns during summer and fall, which would deviate from the plug-flow assumption. Wetlands are not exactly plug-flow because they may have a spectrum of flow paths driven by vegetation density (Kadlec, 1994; Werner and Kadlec, 1996; Kadlec, 2000) and wetland morphology (Shaw et al., 1997). In densely vegetated portions of wetlands, the water flow is slow and treatment is high and in poorly vegetated areas of wetlands, the flow is fast and the treatment is low. Non-ideal flow can cause errors in the rate constant estimation and result in the failure of first-order removal models (Kadlec et al., 1993).

The failure of first-order removal model could also be attributed to the overall metal loading to the wetland. Metal loading to the Monahan wetland is low in comparison with other wetlands receiving acid mine drainage (Fennessy and Mitsch, 1989; Wieder, 1993; Kadlec and Knight, 1996; Tarutis et al., 1999). Manyin et al. (1997) found that influent concentration as low as 25 mg Fe L^{-1} provided good retention of Fe. In the Monahan wetland, the average Fe concentration in the water at the inlet was around 0.4 mg L^{-1}. As a result, a release of metals through Fe^{3+} and Mn^{4+} reduction under anoxic conditions in sediments would have a greater impact on metal retention in a wetland receiving modest metal loading.

In this paper, the application of the first-order removal model assumed an asymptotic metal reduction to zero concentration. This assumption is probably invalid for the Monahan wetland. The dissolution of Fe and Mn oxides within anoxic sediments of the Monahan wetland (Fortin et al., 2000) and their subsequent diffusion upward into the water column can cause high background concentrations (Tarutis et al., 1992; Tarutis and Unz, 1995). In another study conducted at the Monahan wetland, Fe and Mn concentrations were as much as six times higher above the sediment-water interface at night than during the day (Chap. 4). If such variations in background concentrations are not considered, K_v (as calculated from Eq. 2.5) will be underestimated (Tarutis et al., 1999). It is difficult to determine an accurate background concentration in wetlands and include such a value in a first–order removal model because the background concentrations of metals can vary on a diel and seasonal basis. The inclusion of a background concentration would not change the relationship between HRT and metal retention.

In light of these results, the first-order removal model is inadequate to predict metal retention for all seasons in wetlands receiving urban and agricultural runoff. Recently, Kadlec (2000) also criticised the first-order removal mainly because the plug-flow assumption is rarely satisfied. Kadlec (2000) suggested the compartmentalisation of wetlands, which is an effective way to force contaminants to travel in a lock step manner (i.e., plug-flow). Alternatively, a system of baffles, coupled with a strategic vegetation planting may increase the predictive power of first-order removal models. These alternatives allow the interception, treatment and disruption of water that tends to travel along higher speed paths to the outlet. However, if compartmentalisation is not possible, other removal models must be considered.

Models need to include biological variables that affect the dynamic of metal precipitation and sedimentation in wetlands receiving urban and agricultural runoff (Christensen et al., 1994; Lung and Light, 1996; Kadlec, 1997). Lung and Light (1996) showed that a model including macrophyte and phytoplankton biomass, suspended solids and total phosphorus could accurately predict Cu removal in wetlands. In wetlands with open water zones, the precipitation of metals may be significantly reduced by the uptake of floating algae, which can potentially transport metals out of the wetland. In Chapter 4, it is shown that phytoplankton biomass was responsible for a significant export of particulate Fe and Mn from the Monahan wetland. These variables are all associated with the productivity of an aquatic system and are of particular relevance to wetlands receiving high nutrient loading (urban and agricultural runoff).

The diffusion of metals from sediments to the water column also needs to be included in removal models. Tarutis and Unz (1995) showed that wetlands release Fe and Mn because of Fe and Mn oxide reduction. Furthermore, this release can also follow diel variations (Wieder, 1994). The release of Fe and Mn increases at night when anoxic conditions arise at the sediment-water interface (Chapter 4).

2.6 Conclusion

This study showed that the suitability of the first-order removal model for metal retention in wetlands depends on the season and the type of metal under investigation. The first-order removal model could accurately predict Fe and Mn retention in the spring. The model could also predict dissolved Zn retention for all seasons except winter. In the summer, fall, and winter, the first-order removal model failed to predict metal retention. This may have occurred because the metal loading to the Monahan wetland is low in comparison to wetlands receiving acid mine drainage where first-order removal models predict metal retention (Baker et al., 1991; Flanagan et al., 1994; Mitsch and Wise, 1998; Tarutis et al., 1999). Another explanation is that vegetation density may have resulted in non-ideal-flow patterns. In addition, export of particulate metal sequestered into phytoplankton or internal loading events may have occurred. Models that consider the seasonal effects on hydrological and biological variables need to be considered in order to better predict metal retention in cold climates.

Table 2.1a Seasonal variation in water chemistry (mean ± standard deviation) at the Monahan wetland from 1997 to 1999.

Variable	Inlet/Outlet	Spring	Summer	Fall	Winter
Alkalinity	In	3.84 ± 0.37	3.91 ± 0.83	3.95 ± 0.71	5.30 ± 0.87
(meq L^{-1})	Out	3.54 ± 0.28	2.52 ± 0.29	3.29 ± 1.64	5.36 ± 1.24
pH	In	7.99 ± 0.17	7.73 ± 0.21	7.80 ± 0.24	7.82 ± 0.13
	Out	8.29 ± 0.20	8.17 ± 0.21	8.14 ± 0.18	7.68 ± 0.17
DO	In	12.1 ± 0.17	7.6 ± 2.4	9.9 ± 2.8	11.1 ± 3.5
(mg L^{-1})	Out	13.2 ± 1.8	9.0 ± 2.1	12.8 ± 1.7	8.6 ± 3.2
Temperature	In	9.8 ± 3.7	18.5 ± 2.9	9.9 ± 6.3	1.9 ± 1.4
(°C)	Out	12.1 ± 3.9	21.8 ± 2.8	10.1 ± 6.6	0.7 ± 1.3

Table 2.1b Seasonal variation in (mean ± standard deviation) metal concentrations ($\mu g\ L^{-1}$) at the Monahan wetland from 1997 to 1999.

Variable	Inlet/Outlet	Spring	Summer	Fall	Winter
Total Fe	In	292.2 ± 181.1	229.3 ± 175.0	469.6 ± 367.3	405.4 ± 219.1
	Out	209.8 ± 152.9	225.2 ± 154.3	256.6 ± 123.3	366.0 ± 145.4
Dissolved Fe	In	41.8 ± 14.1	34.5 ± 22.1	17.2 ± 16.4	22.0 ± 15.5
	Out	14.0 ± 10.8	17.3 ± 13.2	17.4 ± 15.1	22.7 ± 12.1
Total Mn	In	67.8 ± 43.0	74.2 ± 48.2	92.4 ± 48.6	109.7 ± 87.9
	Out	64.2 ± 56.8	76.6 ± 58.1	57.8 ± 31.0	153.2 ± 119.6
Dissolved Mn	In	58.4 ± 17.5	65.2 ± 41.2	61.3 ± 32.2	74.3 ± 38.6
	Out	27.3 ± 21.5	23.2 ± 32.0	5.1 ± 2.9	140.7 ± 99.8
Dissolved Zn	In	3.0 ± 1.5	4.2 ± 2.4	3.7 ± 2.4	6.1 ± 3.6
	Out	1.8 ± 1.8	0.5 ± 0.1	0.5 ± 0.2	5.1 ± 3.0
Dissolved Cu	In	1.1 ± 0.2	1.0 ± 0.3	0.9 ± 0.3	1.2 ± 0.4
	Out	1.1 ± 0.3	0.7 ± 0.3	0.7 ± 0.2	1.1 ± 0.5
Dissolved As	In	0.3 ± 0.2	0.5 ± 0.2	0.3 ± 0.1	0.2 ± 0.1
	Out	0.4 ± 0.2	0.8 ± 0.3	0.5 ± 0.2	0.3 ± 0.1

Table 2.2 Seasonal water budget (mean ± standard deviation) of the Monahan wetland.

Period	Inlet loading rate ($m^3\ m^{-2}\ d^{-1}$)	Precipitation ($mm\ d^{-1}$)	ET ($mm\ d^{-1}$)	Outlet loading rate ($m^3\ m^{-2}\ d^{-1}$)
Spring 97	0.49 ± 0.33	6.1 ± 8.0	4.9 ± 1.6	0.49 ± 0.33
Summer 97	0.14 ± 0.12	1.9 ± 4.2	6.0 ± 2.0	0.15 ± 0.12
Fall 97	0.13 ± 0.14	1.6 ± 5.1	2.9 ± 1.2	0.13 ± 0.14
Winter 98	0.13 ± 0.03	--	--	0.13 ± 0.03
Spring 98	0.72 ± 1.27	1.4 ± 3.7	5.2 ± 2.7	0.72 ± 1.27
Summer 98	0.24 ± 0.29	3.4 ± 5.1	6.0 ± 2.1	0.24 ± 0.29
Fall 98	0.10 ± 0.02	2.6 ± 3.2	1.2 ± 3.8	0.10 ± 0.02
Winter 99	1.08 ± 1.30	--	--	1.08 ± 1.30

Table 2.3a. Seasonal mean and standard error of Fe and Mn mass loading at the inlet and outlet with associated area-adjusted removal and treatment efficiency from spring 1997 to winter 98.

Metal	Season	Mass in (g d^{-1})	Mass out (g d^{-1})	Area-adjusted removal (mg m^{-2} d^{-1})	Treatment efficiency (%)
T Fe	Spring	9310 ± 1740	8959 ± 1945	11.12 ± 7.40	4 ± 7^{a}
	Summer	1709 ± 137	1359 ± 79	11.20 ± 7.22	21 ± 7^{a}
	Fall	4949 ± 1004	1379 ± 121	113.84 ± 3.12	72 ± 4^{b}
	Winter	10877 ± 2108	11472 ± 2474	-18.30 ± 5.45	-6 ± 5^{a}
D Fe	Spring	1099 ± 88	441 ± 124	20.83 ± 0.97	60 ± 10^{a}
	Summer	233 ± 14	108 ± 9	3.65 ± 2.40	51 ± 3^{a}
	Fall	74 ± 6	73 ± 6	0.00 ± 7.76	0 ± 7^{b}
	Winter	657 ± 124	629 ± 102	-0.92 ± 5.40	-4± 5^{b}
T Mn	Spring	1486 ± 205	1596 ± 237	-3.48 ± 2.85	-7 ± 3^{ab}
	Summer	379 ± 18	487 ± 38	-3.45 ± 6.29	-28 ± 6^{a}
	Fall	493 ± 52	400 ± 71	2.93 ± 0.96	19 ± 10^{ab}
	Winter	2401 ± 473	3313 ± 563	-27.99 ± 5.64	-38 ± 6^{b}
D Mn	Spring	818 ± 57	622 ± 70	6.22 ± 0.46	24 ± 5^{a}
	Summer	350 ± 18	132 ± 11	6.95 ± 1.55	62 ± 2^{a}
	Fall	251 ± 13	36 ± 4	6.86 ± 0.70	85 ± 1^{b}
	Winter	1847 ± 399	2768 ± 426	-28.27 ± 4.44	-50 ± 5^{c}

Table 2.3b. Seasonal mean and standard error of dissolved Zn, Cu and As mass loading at the inlet and outlet with associated area-adjusted removal and treatment efficiency from spring 1997 to winter 98.

Metal	Season	Mass in (g d^{-1})	Mass out (g d^{-1})	Area-adjusted removal (mg m^{-2} d^{-1})	Treatment efficiency (%)
Zn	Spring	120.5 ± 23.2	109.3 ± 23.8	0.35 ± 2.97	9 ± 3^{a}[1]
	Summer	34.0 ± 2.7	4.3 ± 6.4	0.42 ± 0.82	82 ± 1^{b}
	Fall	15.9 ± 10.6	2.7 ± 2.8	0.95 ± 1.48	87 ± 2^{b}
	Winter	300.5 ± 79.9	240.3 ± 61.1	1.85 ± 1.67	20 ± 11^{a}
Cu	Spring	39.9 ± 8.1	40.9 ± 8.4	-0.03 ± 1.42	-3 ± 11^{a}
	Summer	7.1 ± 8.22	5.3 ± 7.7	0.06 ± 0.37	25 ± 6^{b}
	Fall	4.6 ± 4.0	3.4 ± 3.8	0.04 ± 0.43	25 ± 5^{b}
	Winter	46.1 ± 10.3	42.8 ± 10.1	0.10 ± 4.40	7 ± 4^{a}
As	Spring	5.3 ± 5.8	5.8 ± 5.9	-0.01 ± 1.79	-9 ± 17^{a}
	Summer	2.7 ± 0.2	4.6 ± 3.6	-0.06 ± 0.13	-72 ± 3^{b}
	Fall	1.3 ± 1.3	2.8 ± 3.6	-0.04 ± 0.25	-104 ± 12^{b}
	Winter	6.9 ± 1.7	9.9 ± 2.3	-0.09 ± 0.92	-44 ± 7^{a}

[1] same letters corresponds to similar retention values between seasons for a given metal.

Table 2.4 Mean (± standard deviation) treatment efficiency of metals in relation to time since last event (TSLE) in days (an event corresponds to over 10 mm of precipitation).

Season	TSLE	N	T Fe	D Fe	T Mn	D Mn	D Zn	D Cu
Spring	(0-5)	6	15 ± 4	31 ± 11	1 ± 1	26 ± 3	20 ± 3	7 ± 3
	(5-10)	6	8 ± 28	84 ± 4	-20 ± 31	64 ± 17	68 ± 9	7 ± 11
	(10-20)	10	28 ± 4	83 ± 2	2 ± 5	84 ± 1	72 ± 1	-2 ± 1
	(20>)	6	66 ± 2	74 ± 5	26 ± 7	91 ± 1	55 ± 7	11 ± 2
Summer	(0-5)	35	25 ± 1	54 ± 1	-19 ± 3	70 ± 1	86 ± 1	31 ± 1
	(5-10)	27	3 ± 4	52 ± 1	23 ± 1	68 ± 2	84 ± 1	31 ± 1
	(10-20)	23	13 ± 3	25 ± 2	-50 ± 7	30 ± 4	87 ± 1	37 ± 1
	(20>)	21	-19 ± 3	38 ± 2	-47 ± 3	42 ± 2	84 ± 1	28 ± 1
Fall	(0-5)	20	55 ± 2	-77 ± 11	19 ± 4	88 ± 1	84 ± 1	24 ± 1
	(5-10)	6	48 ± 6	-51 ± 29	20 ± 11	86 ± 3	81 ± 3	21 ± 4
	(10-20)	10	35 ± 2	-13 ± 6	41 ± 3	92 ± 1	77 ± 1	12 ± 2
	(20>)	6	25 ± 6	-9 ± 4	62 ± 4	76 ± 3	71 ± 5	2 ± 7
Winter	(0-5)	6	26 ± 14	10 ± 6	6 ± 32	-1 ± 13	39 ± 12	15 ± 10
	(5-10)	4	33 ± 1	5 ± 1	63 ± 15	-91 ± 6	-2 ± 2	62 ± 1
	(10-20)							
	(20>)	6	-60 ± 37	-68 ± 39	-15 ± 12	-46 ± 5	-1 ± 11	-30 ± 16

Figure 2.1 The Monahan constructed wetland located in the city of Kanata, Ontario. Inlet and outlet sites correspond to the locations where samples were collected.

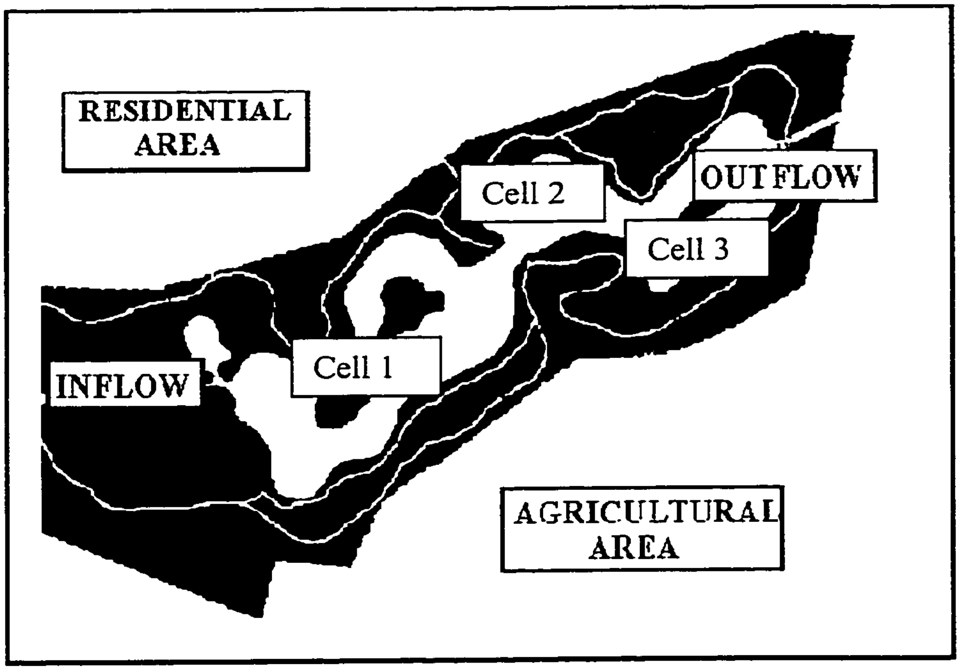
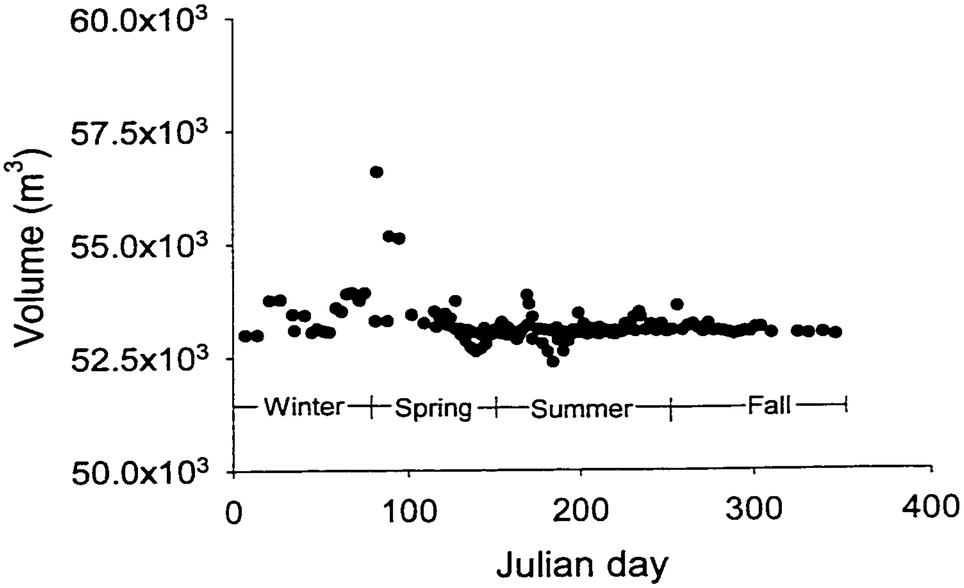

RESIDENTIAL AREA
Cell 2
OUTFLOW
Cell 3
Cell 1
INFLOW
AGRICULTURAL AREA

Figure 2.2 Seasonal variation in water storage of the Monahan wetland for 1997-98 and 1998-99.



60.0x10³
57.5x10³
55.0x10³
52.5x10³
50.0x10³
Volume (m³)
Winter
Spring
Summer
Fall
0
100
200
300
400
Julian day

Figure 2.3 Seasonal mean retention with associated standard deviation for total and dissolved metals (Fe, Mn). Retention = [(inlet mass –outlet mass)/inlet mass] x 100

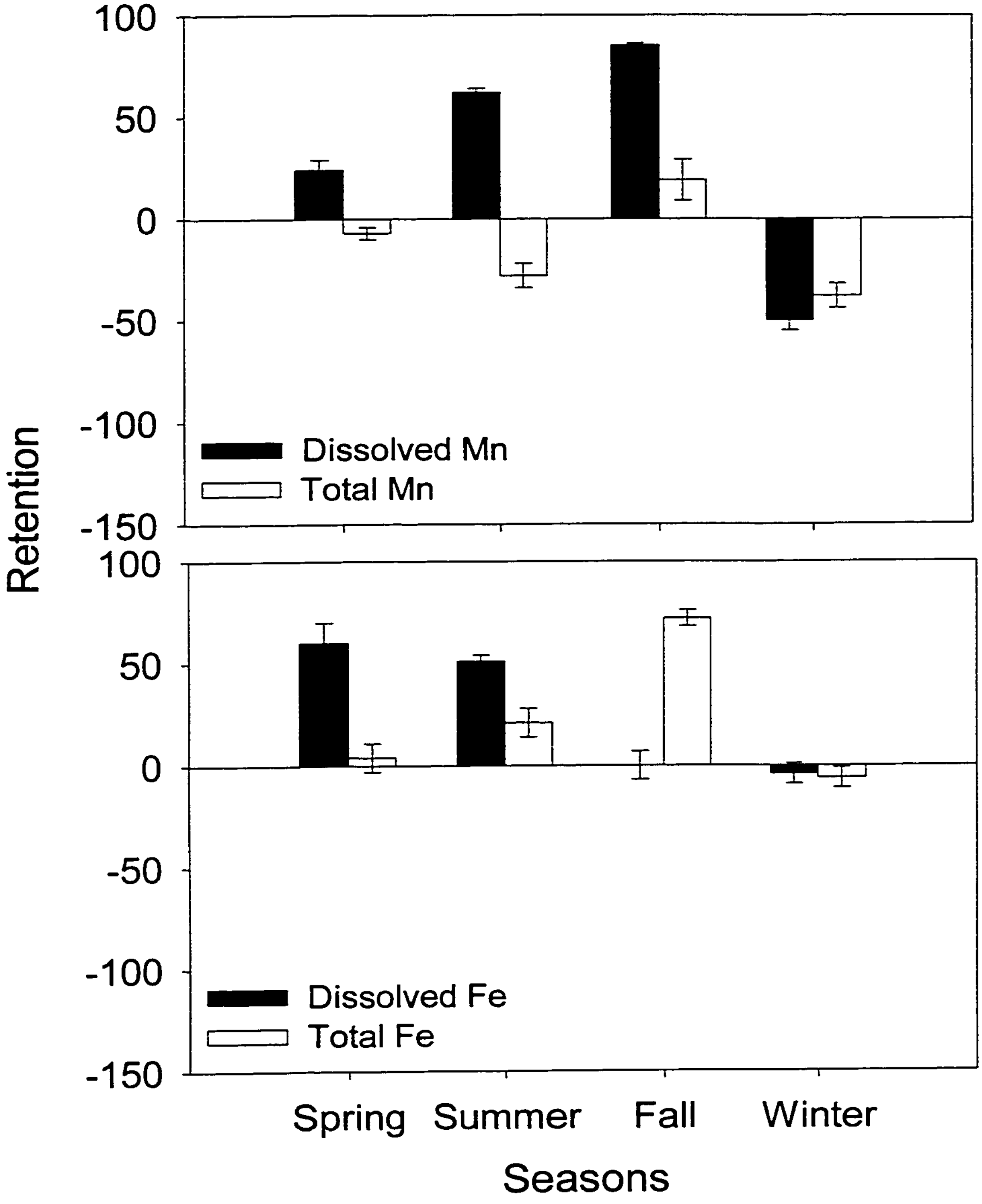

100
50
0
-50
-100
-150
Retention
Dissolved Mn
Total Mn
100
50
0
-50
-100
-150
Dissolved Fe
Total Fe
Spring
Summer
Fall
Winter
Seasons

Figure 2.4 Seasonal mean retention with associated standard deviation of dissolved trace metals (As, Zn, Cu). Retention = [(inlet mass –outlet mass)/inlet] x 100

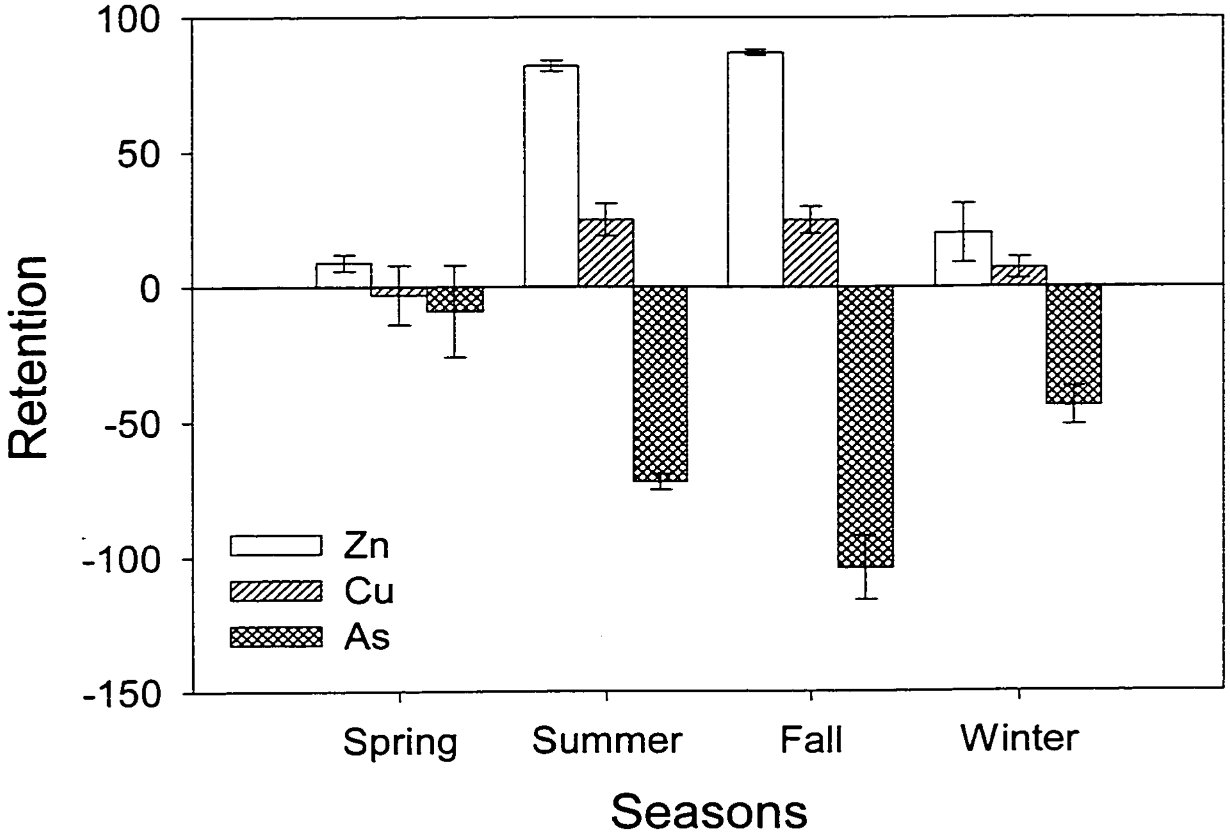

100
50
0
-50
-100
-150
Retention
Zn
Cu
As
Spring
Summer
Fall
Winter
Seasons

Figure 2.5 Influence of hydraulic retention time on dissolved Zn retention for A) winter and B) spring, summer and fall. $y = -3.3 + 85.8\ (1 - e^{0.30x})$ with $R^2 = 0.47$ $p = 0.001$. Error bars are standard deviations.

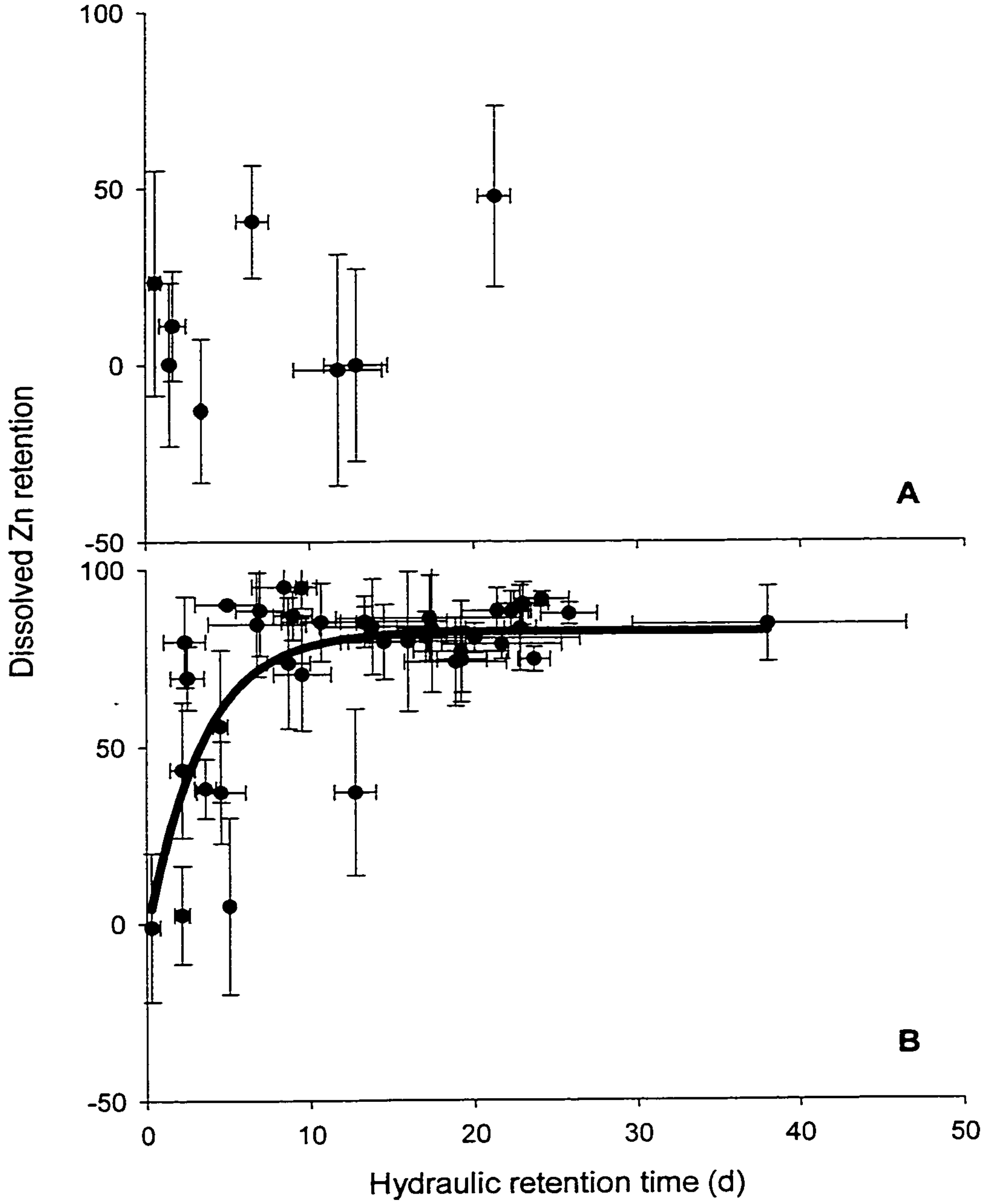

100
50
0
-50
A
100
50
0
-50
B
0
10
20
30
40
50
Dissolved Zn retention
Hydraulic retention time (d)

Figure 2.6 Influence of hydraulic retention time on the retention of dissolved Cu, dissolved As, dissolved Fe ($y = -54.6 + 134.2\ (1-e^{0.51x})$, $R^2=0.77$ $p=0.001$), dissolved Mn ($y = -15.5 + 117.2\ (1-e^{0.14x})$, $R^2=0.55$ $p=0.002$), total Fe ($y = -14.9 + 50.9\ (1-e^{0.20x})$, $R^2=0.21$ $p=0.01$) and total Mn ($y = -74.0 + 117.1\ (1-e^{0.13x})$, $R^2=0.62$ $p=0.009$) in the spring. Error bars are standard deviations.

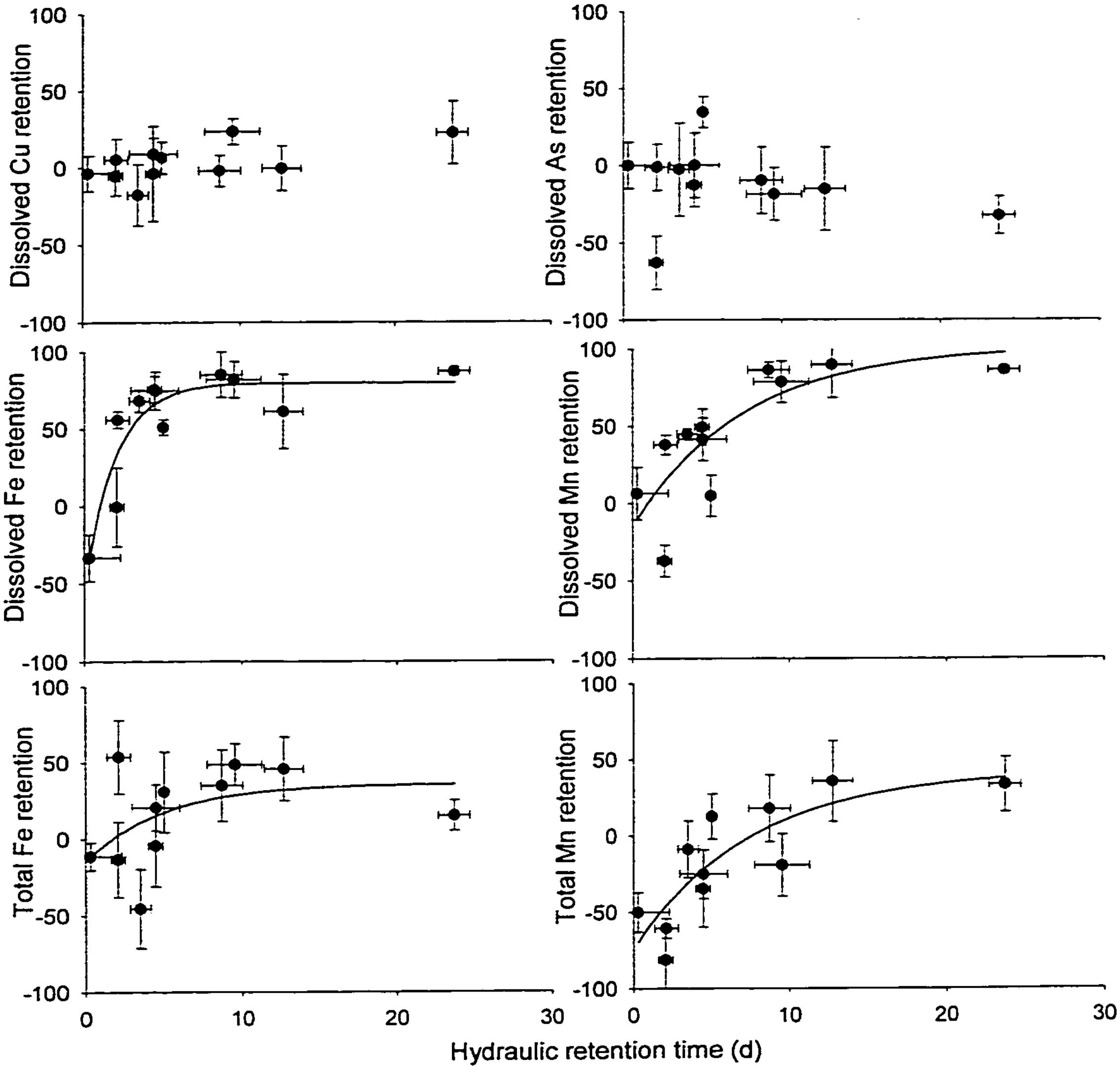

Dissolved Cu retention
Dissolved As retention
Dissolved Fe retention
Dissolved Mn retention
Total Fe retention
Total Mn retention
100
50
0
-50
-100
0
10
20
30
Hydraulic retention time (d)

Figure 2.7 Influence of hydraulic retention time on the retention of dissolved As, dissolved Cu, dissolved Fe, dissolved Mn, total Fe and total Mn in the summer. Error bars are standard deviations.

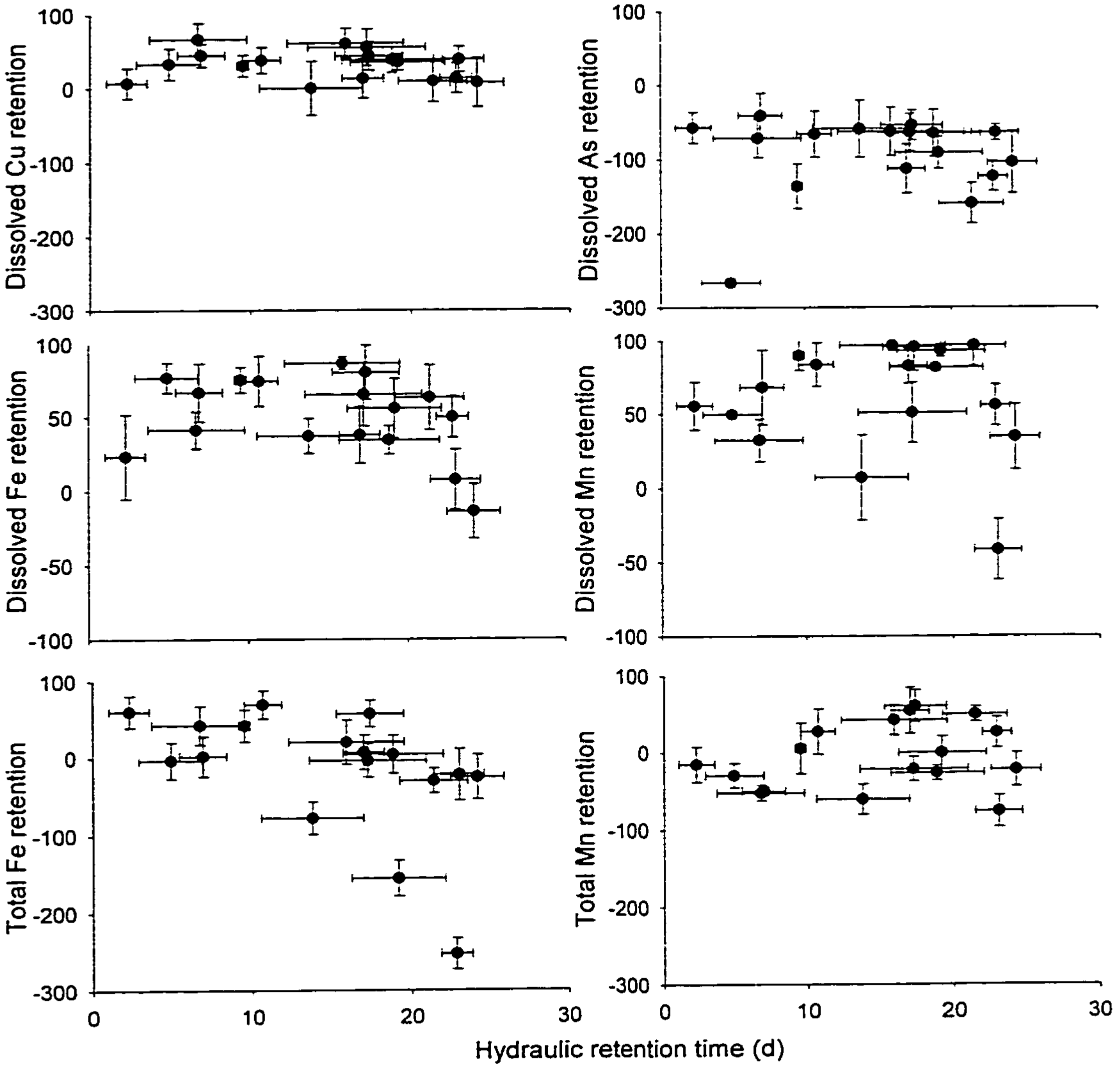

Dissolved Cu retention
Dissolved As retention
Dissolved Fe retention
Dissolved Mn retention
Total Fe retention
Total Mn retention
100
0
-100
-200
-300
50
-50
0
10
20
30
Hydraulic retention time (d)

Figure 2.8 Influence of hydraulic retention time on the retention of dissolved As, dissolved Cu, dissolved Fe, dissolved Mn, total Fe and total Mn in the fall. Error bars are standard deviations.

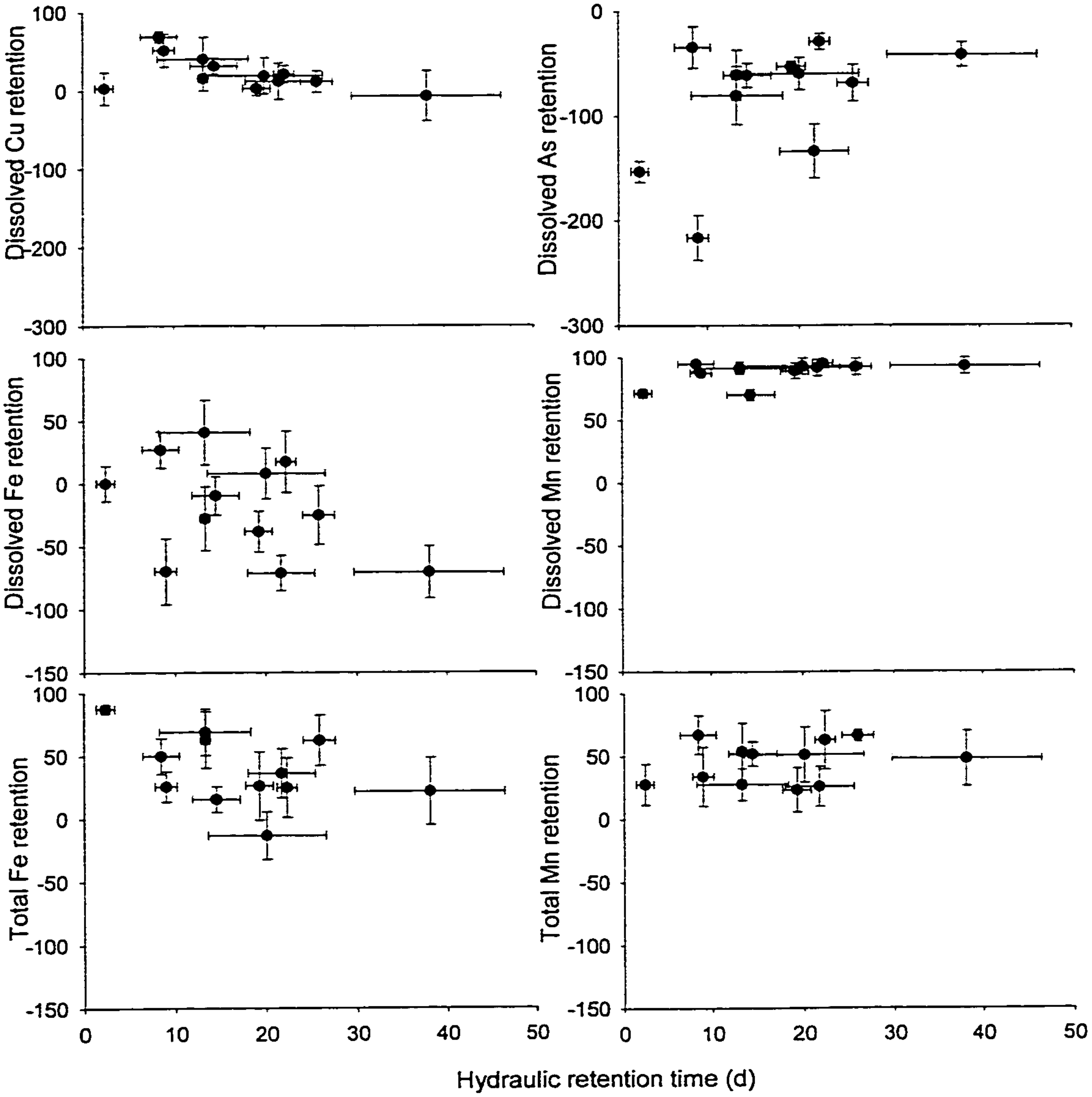
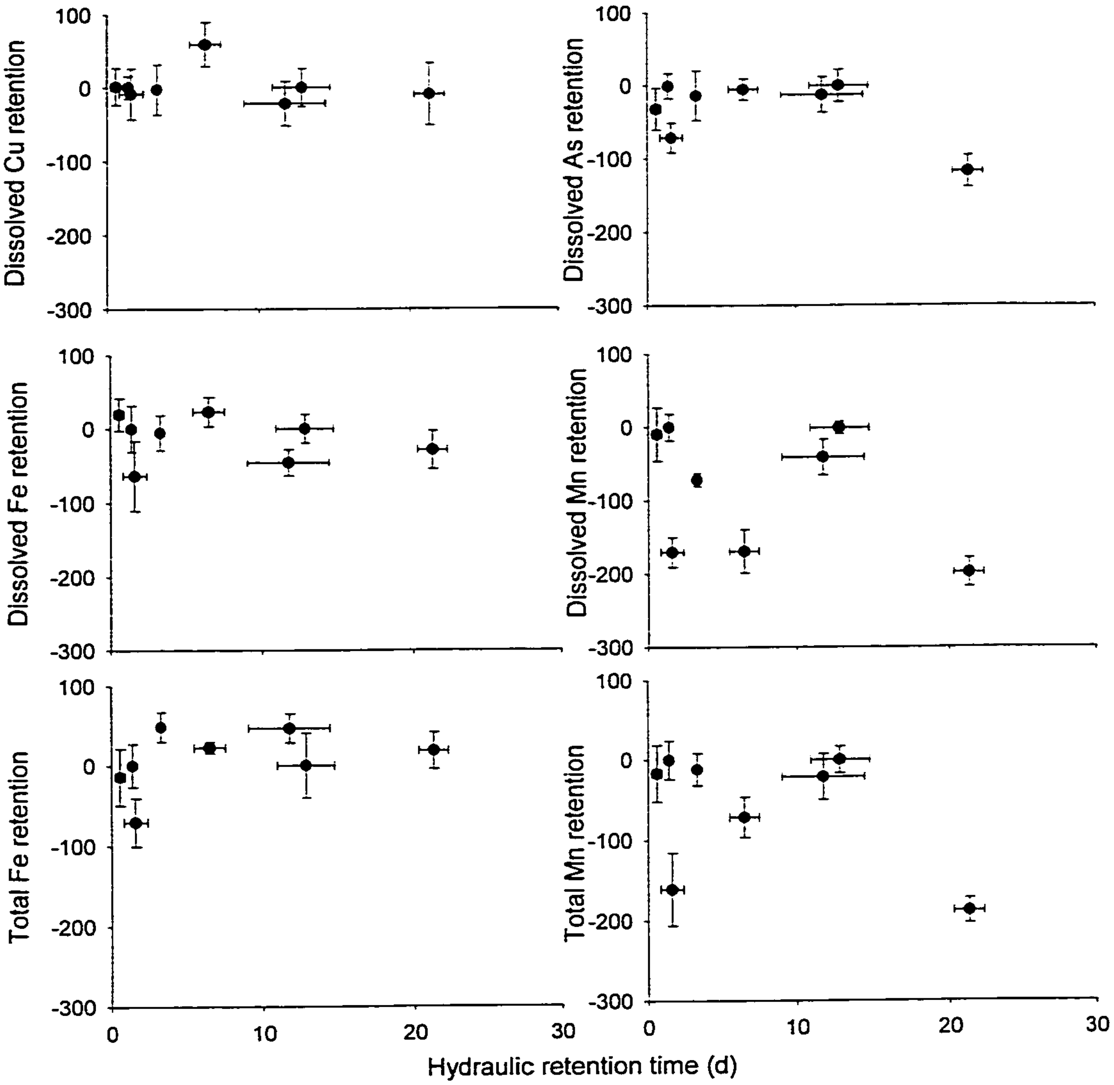

Dissolved Cu retention
Dissolved As retention
Dissolved Fe retention
Dissolved Mn retention
Total Fe retention
Total Mn retention
100
0
-100
-200
-300
50
-50
-150
0
10
20
30
40
50
Hydraulic retention time (d)

Figure 2.9 Influence of hydraulic retention time on the retention of dissolved As, dissolved Cu, dissolved Fe, dissolved Mn, total Fe, and total Mn during the winter. Error bars are standard deviations.


Dissolved Cu retention
Dissolved As retention
Dissolved Fe retention
Dissolved Mn retention
Total Fe retention
Total Mn retention
100
0
-100
-200
-300
0
10
20
30
Hydraulic retention time (d)

Chapter 3

Changes in dissolved and total Fe and Mn in a young constructed wetland: implications for retention performance.

3.1 Abstract

Wetlands are generally considered sinks for Fe and Mn but they may also export and affect the partitioning of these metals. This study was undertaken to evaluate the effect of a young constructed wetland on the retention and transformation of both dissolved and particulate Fe and Mn. Duplicate water samples were collected every three days at the inlet and outlet structures of the Monahan Wetland, Kanata, Ontario, from spring 1997 to the spring of 1999. While on a yearly basis the wetland showed significant retention of the dissolved phase, the retention of total Fe and Mn was poor. There were strong seasonal differences in retention and during the winter, the wetland was a source. The wetland transformed dissolved into particulate Fe and Mn from spring to fall whereas during the winter, dissolved Fe and Mn were released. Changes in pH, alkalinity and temperature could explain 11% and 40% of the outlet variation in the ratio of dissolved to total Fe and Mn respectively. Furthermore, from spring to late summer, planktonic algal biomass was negatively related to the ratio of dissolved to total Fe and Mn implying a role in Fe and Mn transformations in young wetlands where emergent and submerged vegetation have yet to dominate the system.

Key words: Dissolved, Fe, Mn, metal retention, surface-flow wetlands, partitioning, transformation, vegetation.

3.2 Introduction

The behaviour of Fe and Mn in wetlands is governed by a complex and dynamic exchange at the sediment-water interface (Stumm, 1992). Fe and Mn are removed from the water column because Fe^{2+} and Mn^{2+} are oxidized to Fe^{3+} and Mn^{4+} oxides, which precipitate on the surface of sediments (Tarutis and Unz, 1996). Other trace elements can also be removed from the water because Fe and Mn oxides are important adsorption sites (Benjamin and Leckie, 1981; Tessier et al., 1996; Bendell-Young and Harvey, 1992). Under anoxic conditions, Fe and Mn may be released into the water column in the dissolved form (Carignan and Lean, 1991; DeVitre et al., 1994). As a result, the retention capacity of wetlands depends on the relative importance of Fe and Mn precipitation on the surface of sediments over the release of these metals. The factors regulating this cycle need to be understood in order to improve the retention of Fe and Mn by constructed wetlands that are designed for wastewater treatment.

The general assumption that wetlands are sinks for Fe and Mn stems from retention calculations based almost exclusively on total mass (Kadlec and Knight, 1996). The total concentration of metals in water includes the particulate and dissolved fractions. The particulate fraction refers to colloids (> 0.45 μm), planktonic organisms and detritus whereas the dissolved fraction refers to smaller colloids and free metal ions (Wetzel, 1983). In comparison with other aquatic systems, limited information is available on the partitioning of Fe and Mn entering and leaving wetlands. Wetlands may transform dissolved Fe and Mn to the particulate phase and vice versa depending on environmental conditions.

Mitsch and Gosselink (1993) have described wetlands as transformers of pollutants. For Fe and Mn, this transformation can be addressed by examining changes in the dissolved fraction. In organic rich sediments, microbial respiration is particularly intense which leads to a rapid depletion in oxygen. Fe^{3+} and Mn^{4+} oxides are reduced by enzymatic reactions and Fe^{2+} and Mn^{2+} are released into the water column through the oxidation of organic material (DeVrind et al., 1986; Lovley and Phillips, 1988). If Fe and Mn exit the wetland in the dissolved form, the wetland would "transform" particulate into dissolved Fe and Mn.

Once released into the water column, the residence time of Fe and Mn in the dissolved form depends on several factors. First, microbial populations are known to use Fe and Mn for energy requirements (Lovley and Phillips, 1988). In the oxic water column, bacteria can oxidize Fe^{2+} and Mn^{2+} to Fe^{3+} and Mn^{4+} oxides (Ehrlich, 1996). These oxides can aggregate in larger particles that can settle on the surface of sediments (Stumm, 1992; Tarutis and Unz, 1996). Secondly, uptake of dissolved Fe and Mn by algae and plants can occur since wetlands typically support high plant biomass (Vymazal, 1995; Wu and Mitsch, 1998). As a result, the proportion of particulate Fe and Mn in the water increases and therefore, the wetland would "transform" dissolved into particulate metals.

In temperate wetlands, seasonal changes in temperature can influence the transformation processes (Reddy and Burgoon, 1996). During winter time, the low rates of photosynthesis and reduced uptake of Fe and Mn by plants along with high microbial respiration, can lead to anoxic conditions in the sediments and possibly in the water column (Fortin et al., 2000). Under such conditions, a flux of dissolved Fe and Mn from the sediments to the water column is likely (Carignan and Lean, 1991). The release of dissolved Fe and Mn from sediments would lead the wetland to transform particulate into dissolved Fe and Mn.

In this study, I compared seasonal changes in the retention of both dissolved and total Fe and Mn in a young constructed wetland. I examined the seasonal changes in the ratio of dissolved to total Fe and Mn to assess the wetland's potential to affect the partitioning of these metals. These transformations were related to environmental variables (temperature, pH, alkalinity, and algal biomass) that are often hypothesised to affect the partitioning of Fe and Mn in aquatic systems (Morel and Hering, 1993).

3.3 Methods

3.3.1 Study site

See Chapter 2 for description.

3.3.2 Sample collection and water chemistry

From April 24th 1997 to March 30th 1999, duplicate water samples, for both total and dissolved Fe and Mn measurements, were taken every three days in the early morning at both the inlet and outlet. Temperature and dissolved oxygen were measured with a YSI model 57 oxygen meter. Water samples were filtered for dissolved Fe and Mn on site through a 0.45 μm nylon polypropylene filter (Chromatographic Specialties Inc.) using a 50 mL syringe (Markson Ltd.) without rubber plunger to prevent contamination. For measurements of total Fe and Mn concentration, unfiltered water samples were preserved using 0.5% HNO_3 (Ultra-pure from Seastar Chemical Inc., Vancouver) and kept in new 50 mL Nalgene high-density polyethylene bottles at 4°C until analysis. Also, duplicate water samples were taken in 2 L Nalgene jugs for laboratory measurements of pH, dissolved organic carbon (DOC), alkalinity, and chlorophyll a.

pH measurements were done in the lab with a portable Orion SA 250 pH meter . Alkalinity was determined by Gran titration (Wetzel and Likens, 1991). For dissolved organic carbon, the water was filtered through Whatman HA (pore size 0.45 μm) filters and stored at 4°C until analysis with a Hewlett Packard DC-190 TOC analyser. Water samples were filtered through Whatman glass microfiber filters (1.2 μm pore size) for chlorophyll a analysis. Chlorophyll a was extracted using DMSO and acetone (Burnison, 1980) and concentrations were calculated using the equations of Jeffrey and Humphrey (1975).

3.3.3 Fe and Mn analyses

Dissolved Fe and Mn concentrations were measured by ICP-MS (model VG2000) at the Geological Survey of Canada, Ottawa. Detection limits for dissolved Fe and Mn were 5 and 0.1 μg L^{-1} respectively. Water digestion was performed by acid assisted microwave digestion (CEM, 1991). The digestion was done by adding ultra pure concentrated nitric acid (10% of the volume of the sample). The microwave digestion lasted 1 hour. Total concentrations were then measured by IC(A)P-AES (Thermo Instrument Atomscan 25) at the Department of Geology of the University of Ottawa. Detection limits for total Fe and Mn were 10 and 5 μg L^{-1}.

3.3.4 Water budget

Flows were calculated using an equation of a free flowing rectangular weir with end contractions (Grant, 1989):

$$Q = K\,(L - 0.2H)\,H^{1.5} \tag{3.1}$$

Where Q is the discharge or flow rate ($m^3\ d^{-1}$), H is the head on the weir (m), L is the crest length of the weir (m), and K is a constant dependent upon units. Evapotranspiration was calculated using the Penman estimate (Kadlec and Knight, 1996; Mitsch and Gosselink, 1993). The quantity of water loss through evapotranspiration (ET) was then calculated by multiplying the surface area of the wetland by daily evapotranspiration data. All weather data for the Penman estimate calculation were from the Environment Canada Weather station in Ottawa. Precipitation data were obtained with a rain gauge installed on site. The inflow through precipitation (P) was calculated by multiplying the surface area of the wetland by the precipitation data. The water storage of the wetland was based on bathymetric calculations (Wetzel and Likens, 1991) and change in water storage was calculated with the change in water depth of the wetland that was taken on every sampling day.

Difficulties in measuring inflow occurred because of the positioning of the weir. As a result, inflow measurements were assumed to be representative of outflow measurements because of a constant water volume and of a strong relationship between discharge and water storage. Also, precipitation and evapotranspiration had minimal effect on the change in water storage as compared to surface inflow and outflow.

3.3.5 Annual and seasonal retention calculations

For this study, treatment efficiency values (RE), for both dissolved and total, were calculated with the following formula (Wieder, 1993; Dortch, 1996).

$$RE = (M_i - M_o) / M_i = (QC_i - QC_o)/QC_i \qquad (3.2)$$

Where M_i and M_o are inlet and outlet fluxes (Kg d^{-1}), C_i and C_o (μg L^{-1}) are inlet and outlet concentrations, and Q is the water flow rate (m^3 d^{-1}). The flow-weighed average concentration at the inlet and outlet was then calculated over a time frame corresponding to three hydraulic retention time (HRT) values (Kadlec and Knight, 1996). Treatment efficiency was calculated based on inlet and outlet flow-weighed concentrations. From these values, an average daily retention was calculated separately for 1997 and 1998-99. The average seasonal retention was also calculated for five different periods: spring (April 1st-May 30th), early summer (June 1st-July 30th), late summer (August 1st-August 30th), fall (September 1st-December 15th) and winter. (December 16th- March 30th). The summer was divided into two periods because of significant variations in pH. The winter corresponded approximately to the period of ice cover.

The retention data failed to meet the assumptions of the parametric ANOVA, mainly normality of residuals (Wilkes-Shapiro test) and homoscedasticity of variances (Levene's test). Therefore, we performed a three-way Kruskall-Wallis test to test for differences in Fe or Mn retention between years, seasons and metal fraction (dissolved and total) using retention values calculated every third day. Then, we computed the H statistic for each group in the model as the ratio of the sum of squares, divided by the total mean square (Sokal and Rohlf, 1993). This H statistic is then compared to the Chi-square distribution. Bonferroni adjustments were performed on ranked values to examine the differences in the retention between total and dissolved metal within seasons.

3.3.6 Seasonal variability in the ratio of dissolved to total Fe and Mn at the outlet

The ratio of dissolved to total Fe and Mn was calculated for every sampling date at both inlet and outlet. Before any statistical analysis was done, ratio values were arcsine transformed (Sokal and Rohlf, 1993). A Kruskall-Wallis test was done to test for differences in ratios at the outlet between both year and season. A Bonferroni adjustment on ranked values was done to distinguish differences in ratio at the outlet from one season to the other.

Multiple regressions were performed on ratios at the outlet to test for the effect of environmental variables (pH, alkalinity, dissolved organic carbon, dissolved oxygen, and flow rate, chlorophyll a).

3.3.7 Changes in the partitioning of Fe and Mn between the inlet and outlet

The calculation of changes in the partitioning of Fe and Mn based on instantaneous inlet and outlet samples does not consider the travel time of metals within the wetland. One common approach to resolve this problem is to average over three HRT (Kadlec and Knight, 1996). The average outlet ratio of dissolved to total was subtracted from the average inlet ratio. A value near zero corresponds to a conservation of the ratio throughout the wetland (i.e., no transformation). A negative value would correspond to a higher ratio of dissolved to total mass at the outlet whereas a positive value would correspond to a lower ratio at the outlet in comparison with the inlet. T-tests were used to test if seasonal changes in the ratio were significantly different from 0. A Kruskall-Wallis test was used to test for yearly and seasonal differences in the partitioning of Fe and Mn between inlet and outlet. Bonferroni adjustments were done on ranked values to distinguish seasonal differences.

3.4 Results

3.4.1 Environmental variables

Figure 3.1 shows the seasonal trends over the two years for several environmental variables at both the inlet and outlet. The flow ranged from 4500 $m^3 d^{-1}$ (base flow) to a maximum of 45000 $m^3 d^{-1}$ in the spring and during occasional storm events (Table 3.1). Temperature reached a maximum of 27 °C in late summer. Minimum temperature was close to 0 °C as the water flowed under ice cover from mid-December to late March. The outlet temperature was often 1-2 °C over the inlet values. The pH of outlet waters was also higher than at the inlet from spring to fall. The variation in pH was somewhat sigmoidal from spring to fall but decreased steadily to lower values during the winter. Alkalinity was generally lower at the outlet than at the inlet during early and late summer whereas this difference disappeared from fall to spring. Dissolved oxygen increased steadily at both inlet and outlet to reach a maximum of 15 mg L^{-1} in mid summer. Oxygen concentrations were then quite variable from September 1998 to late March of 1999. The wetland was a source of DOC during late summer whereas DOC concentrations were similar between inlet and outlet for other seasons. In both June and

August of 1997, chlorophyll a at the outlet reached a maximum concentration of 53 μg L^{-1} then declined through the fall.

3.4.2 Fe and Mn Retention

At both the inlet and outlet of the wetland, dissolved iron fluxes were at a maximum both during the spring and winter periods whereas total iron fluxes peaked mainly in the spring (Fig. 3.2). The pattern was similar for dissolved and total Mn (Fig. 3.3).

Average retention and associated standard errors for 1997 and 1998-99 are presented in Table 3.2. The treatment efficiency of dissolved Fe was around 75% in the spring and decreased significantly in the early summer to 40% then increasing back to 50% in late summer (Fig. 3.4). The wetland then became a source of dissolved Fe during fall (-43.8±28.6%) and winter (-13.0 ±12.2%). Total Fe was released during late summer (-57.5±29.2%) in contrast to the fall period when the wetland showed the highest total Fe retention (33.2±7.7%).

For almost every season, the wetland retained dissolved Mn better than total Mn with the exception of winter when both dissolved and total Mn were released from the wetland (Fig. 3.5). The wetland retained dissolved Mn efficiently from spring to fall (45 - 95%). In the winter, however, the wetland released dissolved Mn (-117.9±40.2%). Similarly, total Mn retention was similar from spring to fall ranging from –10% to 25% retention. Then, during winter, the wetland was a significant source of total Mn (-94.4 ±32.1%). The high retention of dissolved Mn along with the low retention of total Mn suggests that the wetland released particulate Mn. The same situation was observed for Fe.

A Kruskall-Wallis test showed that the retention of Fe and Mn was similar between years (Table 3.3). However, the retention of both dissolved and total Fe and Mn differed significantly between seasons and this seasonal difference was also different from the first year to the second year.

3.4.3 Seasonal variability in the ratio of dissolved to total Fe and Mn at the outlet in relation to environmental variables

At the outlet, there was a statistically significant difference in the ratio of dissolved to total Fe and Mn between seasons (Table 3.4). The ratio of dissolved to total Fe was higher in the early summer (11.5 ± 0.9%) as compared with the spring (7.8 ± 0.9%) and late summer (6.8 ± 0.8%) (Fig.3.6). For Mn, the ratio of dissolved to total metal reached a maximum during the winter (81.6 ± 3.1%) and decreased significantly to reach the lowest value during late summer (11.1 ± 1.1%).

Alkalinity, pH, and temperature explained a small but significant amount of the variation in the ratio of dissolved to total Fe (R^2 =0.102). DOC, flow rate and dissolved oxygen were not significant variables in multiple regression models. However, chlorophyll a alone, explained 36.8% of the variation in the ratio of dissolved to total Fe (Fig. 3.7). Similarly, alkalinity, pH, and temperature explained 43.9% of the variability in Mn ratios. Chlorophyll a could also explain 28.9% of the variability in Mn ratios at the outlet (Fig. 3.7).

3.4.4 Changes in the partitioning of Fe and Mn between inlet and outlet

Overall, the changes in the partitioning of Fe and Mn between the inlet and outlet were similar between the two years (Table 3.5). However, the changes in Fe and Mn ratios differed significantly between seasons during both years.

The change in the Fe ratio from inlet to outlet was positive in the spring and summer only (Fig. 3.8). This would correspond to a decrease in the dissolved fraction (or an increase in the particulate fraction) from the inlet to the outlet. The change in ratio was highest in the spring (26.3 ± 5%) followed by late summer (15.1 ± 1.9%). During the fall and winter, the change in the Fe ratio from inlet to outlet was not significantly different than zero corresponding to a conservation of this ratio within the wetland.

The change in the Mn ratio was greater than for Fe. From spring to fall, a positive change in the ratio of dissolved to total Mn from the inlet to the outlet was observed. This would correspond to a decrease of the dissolved fraction (or an increase in the particulate fraction) from the inlet to outlet. In the winter, the negative change corresponded to an increase in the dissolved fraction (or a decrease in the particulate fraction) from the inlet to the outlet.

3.5 Discussion

The low retention of Fe and Mn by the Monahan wetland is surprising since wetlands are usually considered sinks for these elements (Kadlec and Knight 1996). The poor retention may be due to the young age of the facility (~3 years old in 1999). Young constructed wetlands are usually plankton dominated (Mitsch et al., 1998). In the young Monahan wetland, phytoplankton growth was important as chlorophyll a ranged from 10 to 60 μg L^{-1}. Algal uptake of Fe and Mn could be a significant mechanism responsible for the export of particulate Fe and Mn from spring to fall. Therefore, our results can be applied to young, plankton dominated, wetlands.

As a wetland ages, emergent and submerged macrophytes take over from phytoplankton by progressively colonising the entire surface area. This succession process depends on the hydrological characteristics of the wetlands, mainly water depth, flow rates, water chemistry, nutrient availability, and sediment characteristics (Fennessy et al. 1994). Once the wetland is dominated by emergent and submerged macrophytes, the transformation dynamic of Fe and Mn may change. In fact, the retention of Fe and Mn may increase because submerged and emergent rooted macrophytes provide a seasonal sink for Fe and Mn through sequestration in plant tissues. Submerged macrophytes may take up Fe and Mn directly from the water by leaf absorption (Denny, 1980). Emergent and submerged vegetation also provide a physical substrate for epiphyton and bacteria that take up metals directly from the water providing an efficient biofilm (Khatiwada and Polprasert, 1999). Finally, the successful colonisation of emergent and submerged vegetation throughout the surface area would reduce flow and increase particulate Fe and Mn deposition (Harlin et al. 1982, Carpenter and Lodge 1986, Stevenson et al. 1988, Gilliam et al. 1988).

The poor retention of Fe and Mn by the wetland could also be due to the relatively low inlet concentrations of these metals. The inlet concentration of the Monahan wetland averaged 0.30 mg L^{-1} for total Fe which is low in comparison to acid mine drainage wetlands, which show good retention (average of 60 mg L^{-1} in the inlet water) (Wieder 1989, Tarutis et al. 1999). A constructed wetland system in South Carolina received similar total iron concentrations (0.24 mg L^{-1}) as the Monahan wetland and also showed low Fe retention (CH2M Hill, 1992). This is in contrast to the conclusion of an experimental mesocosm study, which showed that the lower the loading of Fe, the greater the retention (Manyin et al., 1997). However, the Fe loading to the Monahan and the South Carolina bay wetlands was still much lower than the lowest loading values used in the mesocosm study.

This study showed that the seasonal variation in the partitioning of Fe and Mn was related in part to changes in pH, alkalinity and temperature. These three variables could predict as much as 40% of the variation in the ratio of dissolved to total Mn at the outlet. However, an analogous model for iron removal could only explain 11% of the variability. The variability in Fe and Mn ratios tended to follow pH trends. pH is greatly affected by biological processes such as photosynthesis and respiration (Morel and Hering, 1993). Photosynthesis by algae and macrophytes tend to increase pH and therefore would indirectly affect the partitioning of Fe and Mn. There was an inverse relationship between the ratio (dissolved/total) of Fe ($R^2 = 0.39$) and Mn ($R^2 = 0.29$) and chlorophyll a concentration (Fig. 3.7). The more phytoplankton biomass, the lower the ratio of dissolved to total Fe and Mn and the more Fe and Mn that probably exited the wetland through algal transport. The wetland transformed dissolved Fe and Mn into particulate forms from spring to late summer.

In the fall, pH and chlorophyll a decreased (Fig. 3.1). During this period, chlorophyll a levels reached minimum values suggesting declines in growth rates or die-off. Indeed, during this period, total Fe was well retained by the wetland, which is consistent with a retention of particulate Fe through algal deposition. In addition, a decrease in photosynthesis to respiration ratio probably explain the decrease in pH during fall.

In contrast, the wetland was still transforming dissolved into particulate Mn during the fall. This is surprising since Mn oxides are reduced before Fe oxides in anoxic sediments (Froelich et al., 1979). As a result, the wetland should have transformed particulate into dissolved Mn. However, Mn^{2+} will adsorb onto suspended organic particles in surface water because of its stability along a wide range of pH and redox potentials (Faulkner and Richardson, 1989; Stark et al., 1996).

Finally, during the winter, the presence of an ice cover from mid-December to late March limited the supply of oxygen. As a result, the high biological oxygen demand combined with low oxygen supply to the sediments favour a gradual establishment of anoxic conditions at the sediment-water interface throughout the wetland. Fortin et al. (2000) reported anoxia in the water column during the winter of 1998.

During the winter, the wetland transformed particulate into dissolved Mn but not Fe. The short residence time of dissolved Fe in the water column could explain the conservation of the ratio of dissolved to total Fe within the wetland. Also, the relatively high levels of dissolved Fe of the influent reflecting anoxic conditions in storm water detention ponds prior to the wetland could also explain the conservation of the ratio of dissolved to total Fe within the Monahan wetland.

Other variables may have affected the partitioning of Fe and Mn in surface water of the wetland. In particular, photoreduction of Fe^{3+} to Fe^{2+} has been demonstrated to occur in many aquatic systems (Collienne, 1983; Madsen et al., 1986; McKnight et al., 1988; McKnight and Bencala, 1988) including constructed wetlands (Wieder, 1994).

Although, Wieder (1994) hypothesised that diel changes in Fe^{3+} and Fe^{2+} are more related to microbial Fe^{3+} reduction in sediments than photoreduction in surface water, the latter mechanism could still have a positive effect on the uptake of Fe by algae.

3.6 Conclusions

Measuring the ratio of dissolved to total Fe and Mn in wetland ecosystems is important because it provides information on the biogeochemical cycle of Fe and Mn. Also, measuring the ratio at both the inlet and outlet provides information on the transformation of Fe and Mn within wetlands. In this study, the Monahan wetland retained dissolved Fe and Mn well but retained total Fe and Mn poorly. From spring to late summer, the Monahan wetland was transforming dissolved into particulate Fe and Mn. This transformation process was partly explained by the partitioning of Fe and Mn into planktonic algae. However, as phytoplankton declined during fall and winter, the wetland started to transform particulate into dissolved Fe and Mn likely because of a release of dissolved Fe and Mn from anoxic sediments to the overlying water column. In order to minimise Fe and Mn release in constructed wetlands during the winter period, oxic conditions in the sediments should be maintained. Finally, this study points to the importance of algae in the cycling of Fe and Mn in young plankton dominated wetlands. It may be necessary to control for algal biomass in young constructed wetlands since these organisms provide a significant vector for Fe and Mn release and therefore decrease the overall treatment efficiency.

Table 3.1 Annual and seasonal average flow rates ($m^3\ d^{-1}$) with associated standard deviation at the Monahan surface-flow wetland

Season	Inflow	Outflow	Precipitation	ET
Spring	18150 ± 32400	18280 ± 32370	280 ± 230	160 ± 60
Early summer	8240 ± 9910	8460 ± 9890	180 ± 180	220 ± 60
Late summer	3810 ± 2400	3810 ± 2400	190 ± 180	170 ± 60
Fall	3870 ± 3990	3870 ± 3990	130 ± 240	80 ± 40
Winter	26750 ± 33540	26750 ± 33540	--	--
Annual	11400 ± 22040	11430 ± 21950	200 ± 200	160 ± 70

Table 3.2 Average treatment efficiencies with associated standard error for iron and manganese.

Metal	1997	1998-99
Total Fe	-5.9 ± 9.9	1.4 ± 8.9
Dissolved Fe	15.3 ± 19.9	31.7 ± 6.9
Total Mn	-8.2 ± 5.4	-12.8 ± 11.1
Dissolved Mn	49.0 ± 6.9	22.9 ± 16.0

Table 3.3 Comparisons of Fe and Mn average daily treatment efficiency between fractions, seasons, and year using a Kruskall-Wallis test (H statistic)

Source	Fe (H value)	Mn (H value)	Chi square, 0.05:1
Fraction	34.75***	192.97***	3.84
Season	70.30***	249.00***	3.84
Year	0.34	1.04	3.84
Fraction*Season	113.03***	33.04***	3.84
Fraction*Year	0.38	0.6	3.84
Season*Year	41.97***	0.84	3.84
Fraction*Season*Year	14.57***	35.17***	3.84

*** $p < 0.01$

Table 3.4 Comparisons of the ratio of dissolved to total metals at the outlet using a Kruskall-Wallis test (H value)

Source	Fe (H value)	Mn (H value)	Chi-square (0.05,1)
Season	64.5***	340.46***	3.84
Year	2.71	1.92	3.84
Season*Year	87.76***	89.86***	3.84

***p<0.01

Table 3.5 Comparisons of the change in the ratio of dissolved to total metals between inlet and outlet using a Kruskall-Wallis test.

Source	Fe (H value)	Mn (H value)	Chi square
Season	230.95***	190.45***	3.84
Year	1.92	2.32	3.84
Season*Year	20.76***	22.65***	3.84

***$p<0.01$

Figure 3.1 Seasonal variation of different water chemistry variables collected in early morning at the inlet (○) and the outlet (●) of the Monahan wetland from April 1997 to April 1999. S, Su, Lsu, F, W correspond to spring, early summer, late summer, fall and winter respectively.

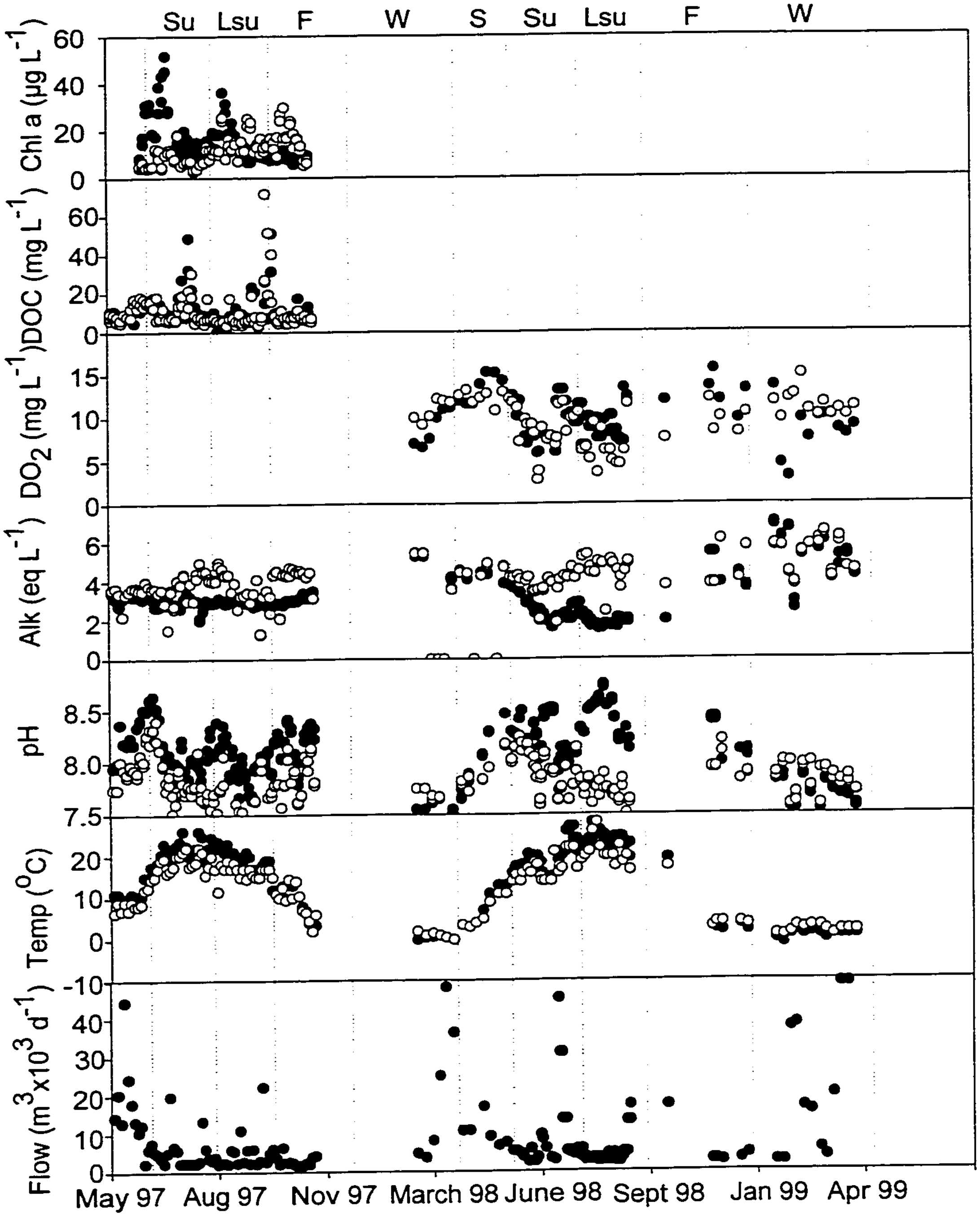

Su
Lsu
F
W
S
Su
Lsu
F
W
Chl a (µg L-1)
60
40
20
0
DOC (mg L-1)
60
40
20
0
DO2 (mg L-1)
15
10
5
0
Alk (eq L-1)
6
4
2
0
pH
8.5
8.0
7.5
Temp (°C)
20
10
0
-10
Flow (m3x103 d-1)
40
30
20
10
0
May 97
Aug 97
Nov 97
March 98
June 98
Sept 98
Jan 99
Apr 99

Figure 3.2 Seasonal Fe fluxes of A) dissolved and B) total at the inlet (○) and at the outlet (●). S, Su, Lsu, F, W correspond to spring, early summer, late summer, fall and winter respectively.

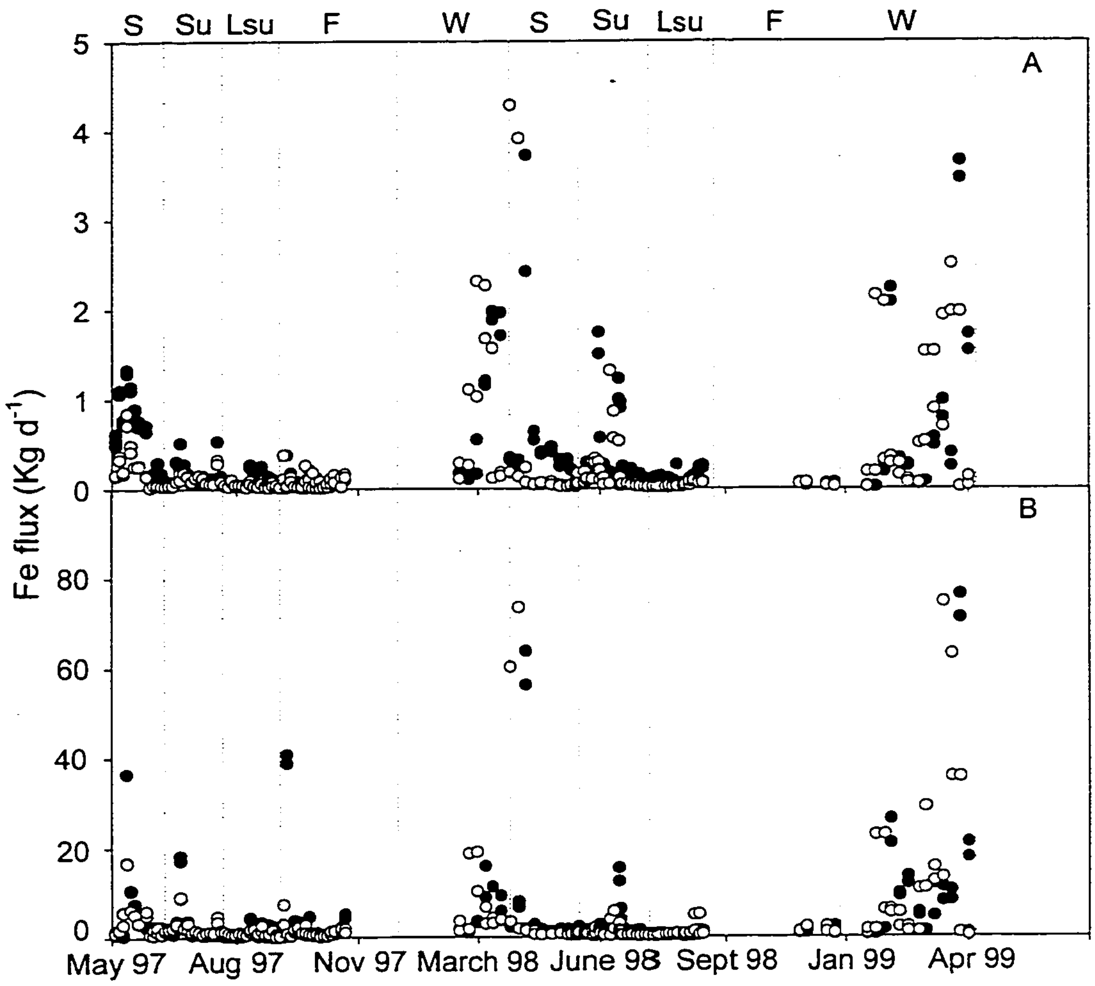

S
Su
Lsu
F
W
S
Su
Lsu
F
W
A
B
Fe flux (Kg d⁻¹)
5
4
3
2
1
0
80
60
40
20
0
May 97
Aug 97
Nov 97
March 98
June 98
Sept 98
Jan 99
Apr 99

Figure 3.3 Seasonal Mn fluxes of A) dissolved and B) total at the inlet (○) and at the outlet (●). S, Su, Lsu, F, W correspond to spring, early summer, late summer, fall and winter respectively.

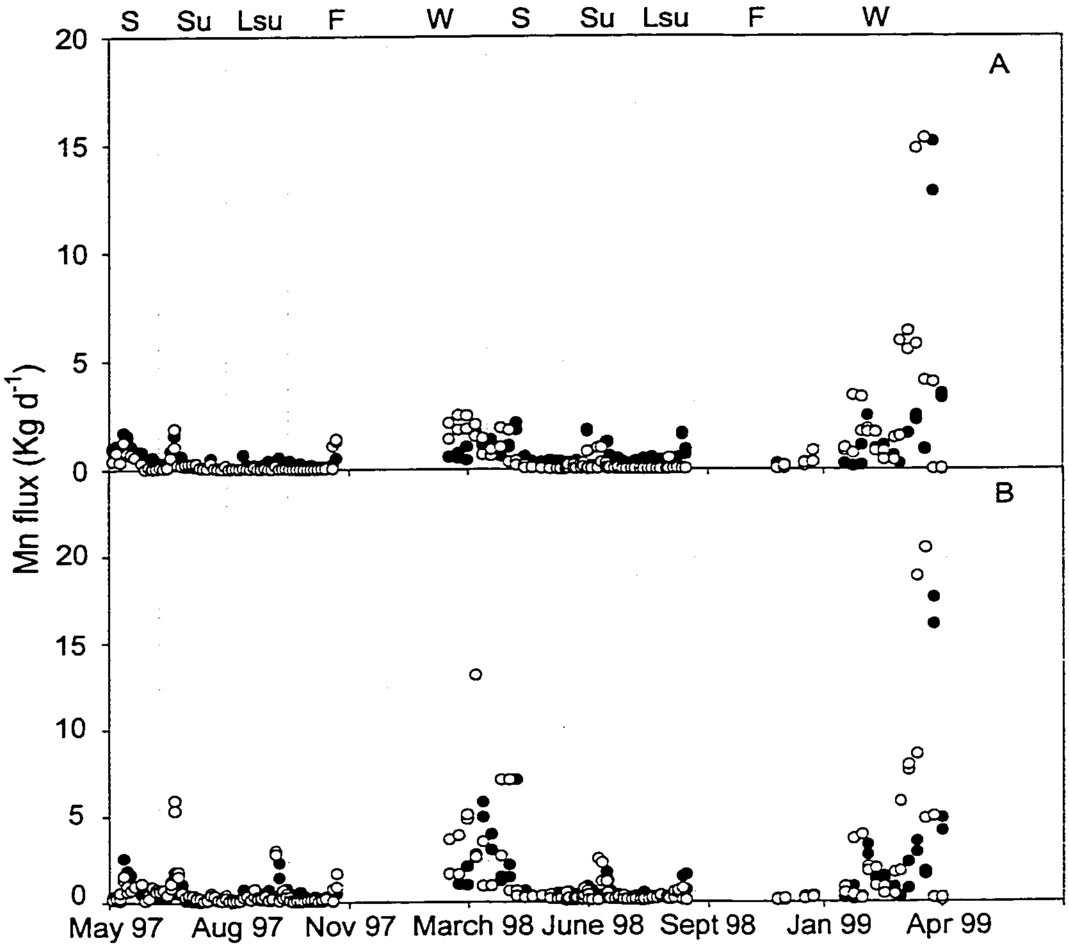

S
Su
Lsu
F
W
S
Su
Lsu
F
W
A
B
Mn flux (Kg d^{-1})
20
15
10
5
0
20
15
10
5
0
May 97
Aug 97
Nov 97
March 98
June 98
Sept 98
Jan 99
Apr 99

Figure 3.4 Seasonal average of daily treatment efficiencies of dissolved and total Fe (with associated standard error) from April 97 to April 99. Retention is calculated with the treatment efficiency formula (Mass in – Mass out) / Mass in.

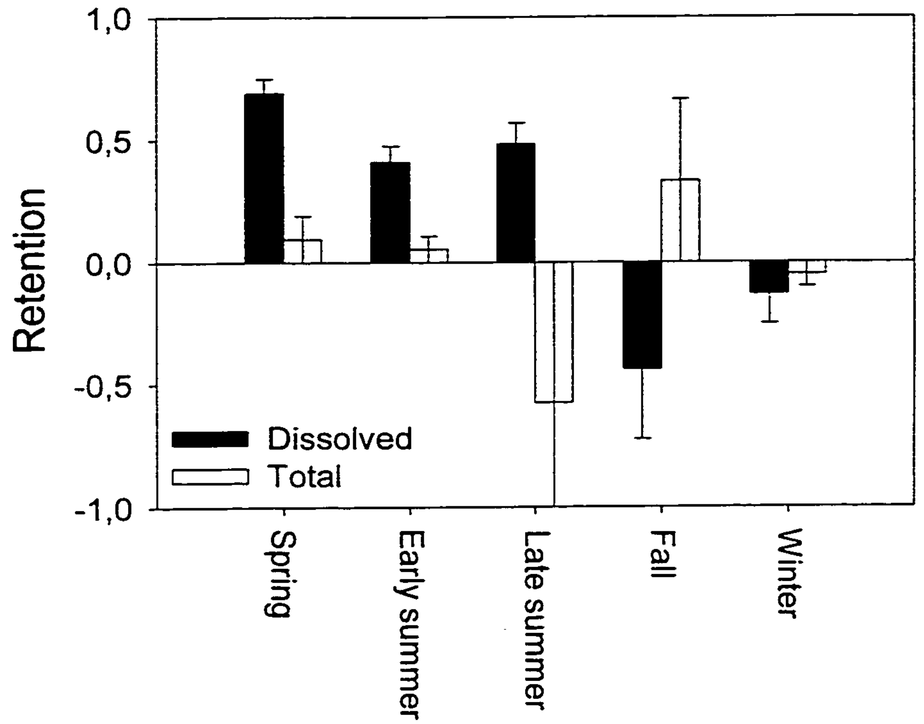

1,0
0,5
0,0
-0,5
-1,0
Retention
Dissolved
Total
Spring
Early summer
Late summer
Fall
Winter

Figure 3.5 Seasonal average of daily treatment efficiencies of dissolved and total Mn (with associated standard error) from April 97 to April 99. Retention is calculated with the treatment efficiency formula (Mass in – Mass out)/Mass in.

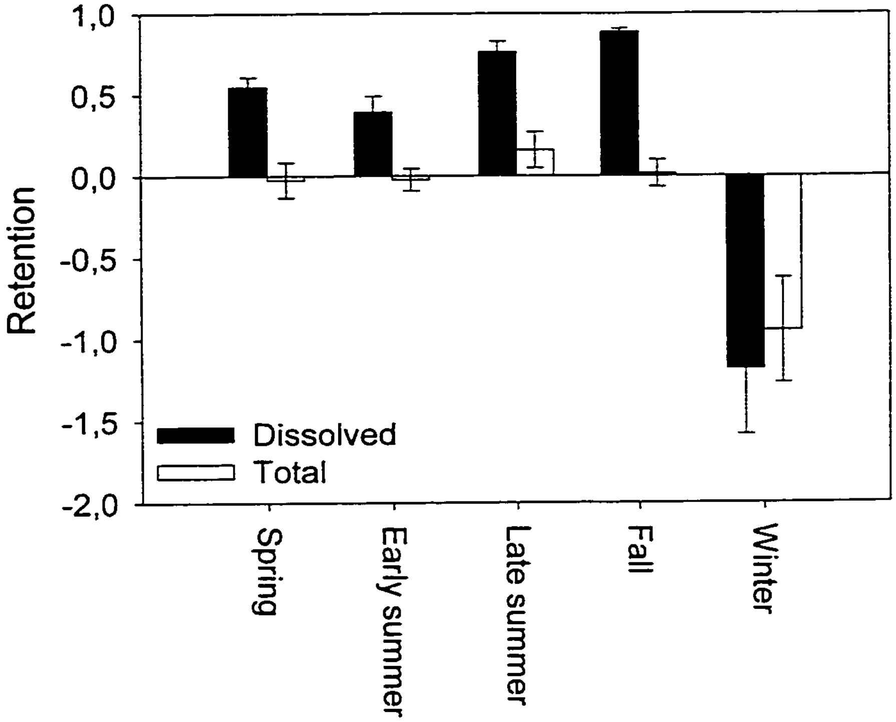

1,0
0,5
0,0
-0,5
-1,0
-1,5
-2,0
Retention
Dissolved
Total
Spring
Early summer
Late summer
Fall
Winter

Figure 3.6 Seasonal variation in ratio of dissolved to total concentration of Fe and Mn at the inlet (○) and the outlet (●). S, Su, Lsu, F, W correspond to spring, early summer, late summer, fall and winter respectively.

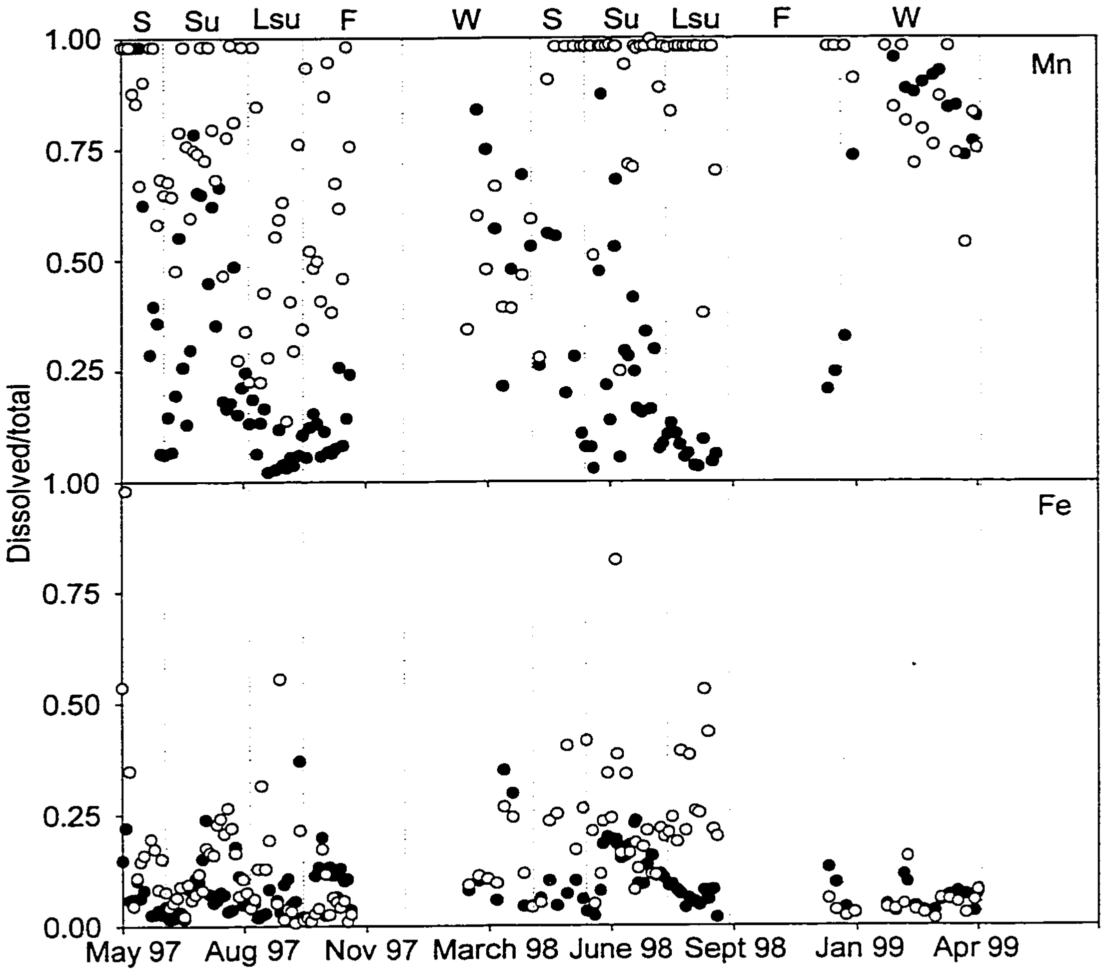

S
Su
Lsu
F
W
S
Su
Lsu
F
W
Mn
Fe
Dissolved/total
1.00
0.75
0.50
0.25
1.00
0.75
0.50
0.25
0.00
May 97
Aug 97
Nov 97
March 98
June 98
Sept 98
Jan 99
Apr 99

Figure 3.7 Ratio of dissolved to total Fe and Mn in relation to chlorophyll a concentration at the outlet. Ratio Fe vs chl a $y = 0.139 - 4.565/x + 48.761/x^2$, $R^2 = 0.386$ and Ratio Mn vs chl a: $y = -0.022 + 4.574/x + 15.1618/x^2$, $R^2 = 0.287$.

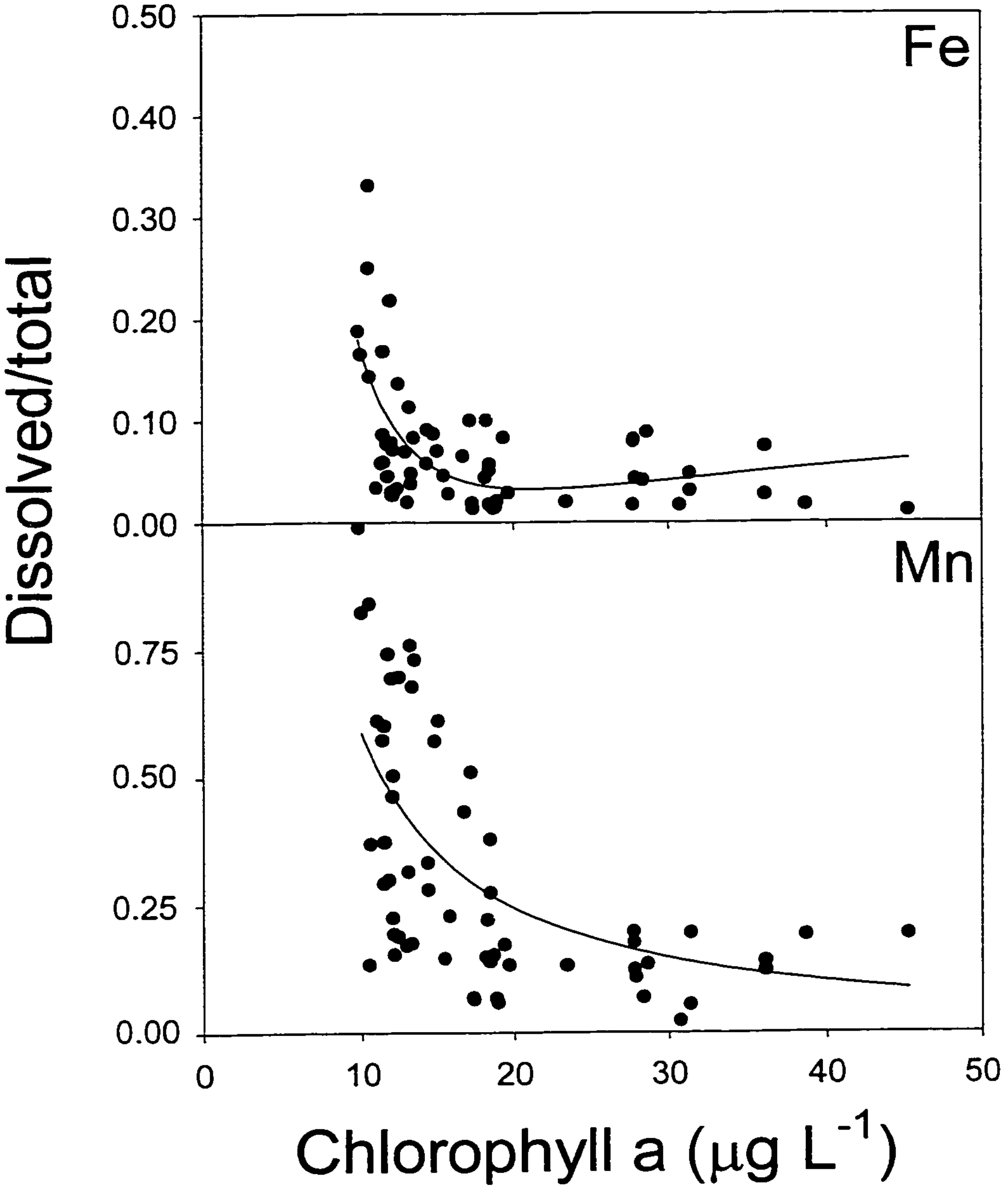
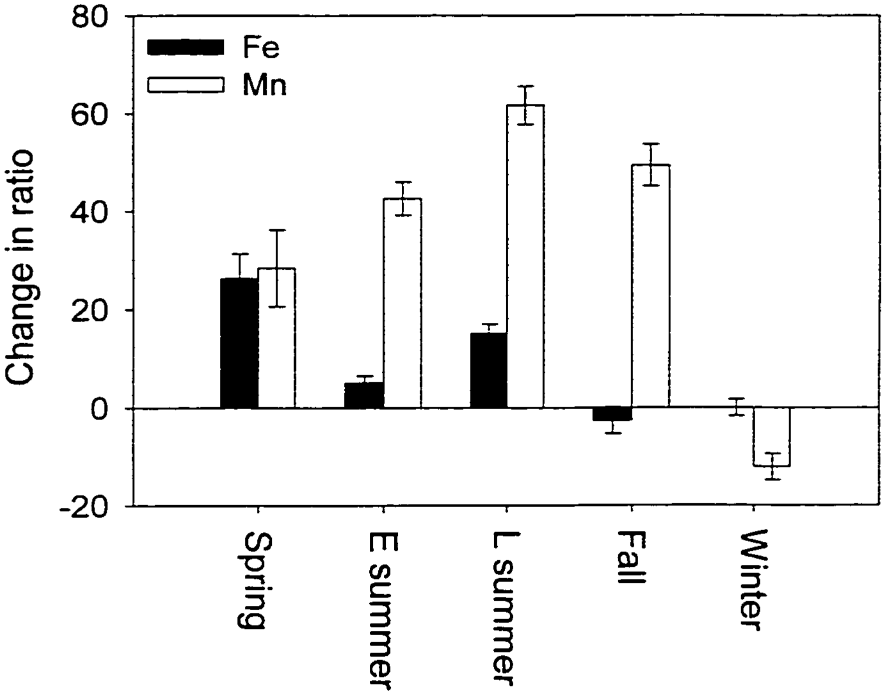

Fe
Mn
Dissolved/total
0.50
0.40
0.30
0.20
0.10
0.00
0.75
0.50
0.25
0.00
0
10
20
30
40
50
Chlorophyll a (μg L^{-1})

Figure 3.8 Seasonal average (with standard error) of daily values of the change (inlet – outlet) in the ratio of dissolved to total concentration from April 97 to April 99.


80
60
40
20
0
-20
Change in ratio
Fe
Mn
Spring
E summer
L summer
Fall
Winter

Chapter 4

Diel changes in metal concentrations in surface-flow wetlands.

4.1 Abstract

Diel changes in metal concentration were examined from spring to late fall at two surface-flow wetlands. The highest concentrations of Fe, Mn and Zn in water were measured at night when oxygen and pH levels were low. In contrast, the lowest concentrations in Fe, Mn and Zn were measured during the day when oxygen and pH levels were high as a result of photosynthesis. Diel changes in Fe and Mn were also seasonally dependent as their amplitude peaked in July. Overall, a multiple regression model indicated that O_2 and pH predict the concentration of total Fe ($R^2 = 0.60$) and total Mn ($R^2 = 0.49$) in the surface water of both wetlands. Other metals (Pb, As, Cu and Ni) did not show as significant diel variations. Diel changes in Fe and Mn concentration also affected the treatment efficiency of Fe and Mn as the wetland retained metals during day and exported metals at night. Therefore, diel changes in metal concentration must be considered when calculating the retention of metals by wetlands.

4.2 Introduction

The calculation of metal retention by constructed wetlands is generally based on the periodic sampling of inlet and outlet water (Wieder, 1993; Kadlec and Knight, 1996). A wetland is effectively retaining metals when the mass of metals leaving is lower than the mass entering (Wieder, 1993). However, this conclusion is frequently based on monthly or at best, weekly collections of water samples. Rarely is retention calculated with more frequent sampling points because it is assumed that a single water sample can be representative of water conditions of a week or more (Wieder, 1994). However, such an assumption may not be valid for many metals and particularly for iron and manganese.

Significant diel changes in metal concentrations can occur in aquatic ecosystems (McKnight and Bencala, 1988; Fuller and Davis, 1989; Bourg and Bertin, 1993; Brick and Moore, 1996). Increases in metal concentrations during the day can be the result of the photoreduction of Fe^{3+} into Fe^{2+}(e.g. Colienne, 1983; Madsen et al., 1986; McKnight et al., 1988; McKnight and Bencala, 1988). Also, the photoreduction of Fe^{3+} can release trace metals adsorbed on metal oxides (McKnight et al. 1988). However, increases in metal concentrations at night have also been observed and cannot be the result of photoreduction (Bourg and Bertin, 1993; Brick and Moore, 1996). In four wetlands, Wieder (1994) observed a decrease in Fe concentration during the day and suggested that oxygenation of surface water by photosynthetic algae and cyanobacteria created conditions under which Fe^{2+}, produced from Fe^{3+} reduction or FeS_2 oxidation, was readily oxidized back to Fe^{3+}.

The solubility of Fe and Mn in water is closely linked to pH and redox potentials. At typical water redox values of 300 mV, Fe^{2+} and Mn^{2+} are oxidized to Fe^{3+} and Mn^{4+}

and precipitate at pH values higher than 5.5 and 7.5 respectively (Faulkner and Richardson, 1989). Photosynthesis will affect the precipitation/dissolution of Fe and Mn by inducing changes in pH and redox potentials (Wetzel, 1983). During daylight, photosynthesis increases pH and redox potentials. At night, biological respiration is intense because aquatic plants consume oxygen along with heterotrophic organisms resulting in a rapid pH and O_2 decrease in the water column.

In this study, I hypothesised that diel changes in O_2 and pH resulting from photosynthesis and respiration would correspond to diel variations in metal concentrations in surface-flow wetlands. I predicted an increase in metal concentrations at night and a decrease in metal concentrations during the day. Secondly, I examined the seasonal differences in diel variations of metals and examined how these variations affected the overall retention of metals in these constructed wetlands.

4.3 Methods

4.3.1 Study sites

The experiments were conducted in two different wetlands. The Monahan wetland, within the city of Kanata, Ontario, Canada ($45^0$16' N, $75^0$51' W), was built in 1995 and completed in 1996 as a stormwater management facility (Table 4.1). The wetland has three consecutive cells, which were lined initially with a thick layer of clay to prevent infiltration. No organic substrate was added to the clay liner and a significant amount of sediments has accumulated since construction.

The Falconbridge wetland is located in the city of Falconbridge, Ontario, Canada (46° 57' N: 80° 80' W). Its construction in 1981 resulted from the flooding of old mine tailings on which cattails quickly established and now represent 70% of the surface area. It was built to treat acid mine drainage originating from a 1200 ha drainage basin (Table 4.1).

4.3.2 Experimental approach

At the Monahan wetland, I conducted diel experiments on a monthly basis (May 19, June 10, July 13, August 16, September 27) during the summer of 1999. At the Falconbridge wetland, I conducted diel experiments on July 22 and October 14. I examined the influence of photosynthesis by comparing diel changes in metal concentrations when photochemical reactions were blocked and when surface sediments were partly exposed to sunlight (because of some macrophyte shading). The experiments were conducted in shallow (~0.5 meter) littoral areas. The dark treatment consisted of a black, opaque and bottom-less chamber, which was deposited onto surface sediments in each wetland the night before the start-up of the experiment. Near the dark treatment, a light treatment was established as a reference site within a cover of cattails (*Typha latifolia*) and floating duckweed (*Lemna minor*) where photosynthesis was not inhibited. At each site and within the dark chamber, duplicate water samples were collected every 4 hours over a 24 hours period using high-density polyethylene tubing fixed 5 cm over the sediment-water interface. Water was pumped into 60 ml HDPE Nalgene bottles using a syringe connected to the tube by a 3-way stopcock. I collected filtered (0.45 μm pore size nylon filter, Chromatographic Specialties) and unfiltered water samples. At the same time, I measured oxygen, temperature, pH and redox using a data-logging hydrosonde (Hydrolab, Austin, TX, USA). I also collected duplicate water samples at the inlet and outlet in the same temporal manner. At the Falconbridge wetland, inlet waters were not collected and I collected water samples in a deep (~1.5 meters) littoral area on July 22 while on October 14, I collected water samples in a shallow (~0.5 meter) littoral area.

4.3.3 Metal analyses

Unfiltered water samples were digested by microwave in ultra pure HNO_3 (10% of the sample volume) and were then analysed for their metal content using an inductively coupled plasma argon emission spectrometer (ICP-AES, Thermo Instrument Atomscan 25) at the Department of Earth Sciences of the University of Ottawa. Filtered water samples were analysed by inductively coupled plasma mass spectrometer (ICP-MS, model VG2000) at the Geological Survey of Canada, Ottawa.

An aliquot of the filtrate of each water sample was immediately analysed *in situ* for Fe^{2+} following the ferrozine method (Stookey, 1970). All glassware was acid cleaned in 10% ultra-pure HNO_3 (Seastar Chemicals Inc.) for one day. Absorbance was measured at 562 nm using a Bausch & Lomb's spectronic 501 single beam spectrophotometer against standard solutions of ferrous sulfate.

4.3.4 Quality assurance and quality control

All water samples were collected using a HDPE syringe, without rubber plunger (Markson Ltd.) to prevent contamination (Hall, 1998). Water was filtered through 0.45 µm pore size polypropylene nylon filters (Chromatographic Specialties). Water samples were preserved with 0.5 ml of ultra-pure concentrated nitric acid (Seastar Chemicals inc., Vancouver, BC). All materials were soaked for several days in ultra-pure distilled water to measure potential contamination (Hall, 1998). The metal content of this water was below ICP-MS detection limits for all elements (Table 4.2).

Two blanks and two standard water samples (Ottawa River water, Geological Survey of Canada) were analysed every 24 samples. Repeat measurements were done randomly at every 24 samples with generally 95% recovery.

4.3.5 Metal retention

Metal retention was calculated every 4 hours using the treatment efficiency formula (Wieder, 1993; Dortch, 1996):

$$\text{Treatment efficiency} = (M_i - M_o)/M_i = (QC_i - QC_o)/QC_i$$

where Q is to the flow rate in $m^3\ d^{-1}$, C_i is to the metal concentration at the inlet, C_o is to the metal concentration at the outlet. Flows were calculated based on daily measurements of the head at the outlet weir using an equation of a free flowing rectangular weir with end contractions (Grant, 1989):

$$Q = K\,(L - 0.2H)\,H^{1.5}$$

where H is the head on the weir (m), L is the crest length of the weir (m), and K is a constant dependent upon units.

4.3.6 Statistical analysis

The statistical analysis was done using Systat 7.0 for Windows 95. Multiple regression analysis was performed to identify variables related to metal concentrations in surface water of both the Monahan and Falconbridge wetlands.

4.4 Results

4.4.1 Dark and sunlight experiments

In the dark experiments at the Monahan wetland, diel changes in Fe concentrations were generally similar from one month to the other (Fig. 4.1). In May, there was an increase in total and dissolved Fe with a decrease in oxygen while pH stayed relatively constant. This trend was observed in June and July. However, in August, total and dissolved Fe peaked at 20h00 and decreased afterwards. In September, total and dissolved Fe remained constant over 24 hours.

In contrast, the effect of pH and O_2 on Fe concentrations in the sunlight experiments varied from one month to the other (Fig. 4.1). In May, the concentration of total and dissolved Fe remained constant along with pH despite a peak in oxygen at noon. In June, total and dissolved Fe showed small diel changes and reached minimum concentrations at 20h00. During the same experiment, pH remained constant and oxygen reached a maximum of 14 mg L^{-1} at 16h00 and a minimum of 5 mg L^{-1} 12 hours later. The most important diel changes in total Fe concentrations were observed in July. Total Fe ranged from 50 μg L^{-1} at 20h00 to 750 μg L^{-1} at 4h00. Simultaneously, oxygen levels reached a maximum of 10 mg L^{-1} at 16h00 and a minimum of 3 mg L-1 at 4h00. pH reached 9.5 at 20h00 and 7.5, 8 hours later. Dissolved Fe concentrations remained constant during the 24 hours. Diel changes were also observed in August, although not these were not as great as in July (Fig. 4.1). Total Fe reached a minimum concentration of 50 μg L^{-1} at 20h00 and a maximum of 450 μg L^{-1} at 4h00. Oxygen levels ranged from 2.5 mg L^{-1} at 4h00 to 15 mgL^{-1} at 16h00 whereas pH remained constant over the 24 hours period. Dissolved Fe also remained constant for 24 hours. In September, total Fe and dissolved Fe also varied on a diel basis (Fig. 4.1). Total Fe ranged from 450 μg L^{-1} at 16h00 to 1500 μg L^{-1} at midnight. Dissolved Fe ranged from 15 μg L^{-1} at 16h00 to 45 μg L^{-1} at 8h00. Simultaneously, oxygen levels ranged between 8 and 10 mg L^{-1} and pH remained constant during the 24 hours.

At the Falconbridge wetland, diel changes in Fe concentrations differed from those observed at the Monahan wetland (Fig. 4.2). In the dark experiment, total and dissolved Fe reached a peak at 20h00 in July and then decreased. At the same time, oxygen levels decreased to near zero and pH remained constant. In October, total and dissolved Fe remained constant in the dark experiment. Oxygen levels remained constant at 5 mg L^{-1} as well as pH.

As for the sunlight experiments, total and dissolved Fe concentrations were lowest at 8h00 and reached a peak at 20h00 (Fig. 4.2). At the same time, oxygen levels reached a maximum of 8 mg L^{-1} at 16h00 and a minimum of 2 mg L^{-1} at 4h00. pH remained constant. In October, total and dissolved Fe concentrations remained constant over the 24 hours along with oxygen and pH.

At the Monahan wetland, seasonal and diel trends in Mn concentrations were similar to those observed for Fe. In the dark experiments, both total and dissolved Mn steadily increased while oxygen decreased near zero and pH remained constant (Fig. 4.3).

In September, however, oxygen levels remained around 5 mg L^{-1}, pH was constant and total and dissolved Mn concentrations increased only between 20h00 and 24h00.

In the sunlight experiments, changes in Mn concentrations followed the diel variations in O_2 and to a lesser extent, pH (Fig. 4.3). The relationship between oxygen, pH and Mn concentration differed between months. In May, total and dissolved Mn concentrations remained constant along with pH despite a diel variation in oxygen. In June, total and dissolved Mn concentrations were minimal at 16h00 and maximal at 4h00. Simultaneously, oxygen was highest at 16h00 and lowest at 4h00. pH remained constant during 24 hours. In July, total and dissolved Mn ranged from 30 and 20 μg L^{-1} at 20h00 to 50 and 45 μg L^{-1} at 4h00 respectively. Simultaneously, oxygen levels ranged from 10 mg L^{-1} at 16h00 to 2.5 mg L^{-1} at 4h00. At the same time, pH reached 9.5 at 16h00 and then declined to 7.5 by midnight. In August, diel changes in Mn concentration, oxygen and pH were not as important as in July but followed the same trend. Finally, in September, diel changes in Mn concentrations were the greatest as total or dissolved Mn ranged from 50 μg L^{-1} at 16h00 to 150 μg L^{-1} at 4h00. Simultaneously, oxygen level ranged between 9 and 10 mg L^{-1} while pH remained constant.

As for trace elements (Table 4.3), there was an increase in dissolved Zn, Cu, Ni and As in dark experiments. Diel changes in most dissolved trace elements (Cu, Ni, As) were small except for dissolved Zn in September and October (Table 4.3). During those times, dissolved Zn increased at night with decreasing O_2 and pH. The dissolved Zn concentration was below the detection limit from May to July.

4.4.2 Diel changes in metal concentrations at the outlet of wetlands

In general, the same diel trends in Fe and Mn observed in the littoral areas of the wetlands were observed at the outlet. At the Monahan wetland, the diel changes in Fe concentrations at the outlet differed between months. In May, total, dissolved and Ferrous Fe remained constant during 24 hours at the outlet despite diel changes in oxygen concentrations (Fig.4.4). In June, total Fe increased from 150 to 250 μg L^{-1} between 24h00 and 4h00 while dissolved oxygen ranged from 4.5 mg L^{-1} at 8h00 to 14 mgL^{-1} at 20h00 and pH remained constant. Dissolved and ferrous iron showed smaller diel changes than the total Fe concentration. In July, total Mn ranged from 50 μg L^{-1} at 20h00 to 500 μg L^{-1} at 4h00 while oxygen levels ranged from 8 mg L^{-1} at 4h00 to 12 mg L^{-1} at 16h00 and pH remained constant. As for dissolved and ferrous Fe, they showed weak diel changes at the outlet over the 24 hours period. In August, diel changes in total Fe were smaller than in July. Total Fe ranged from 200 μg L^{-1} at 16h00 to 400 μg L^{-1} at 24h00 while oxygen ranged from 8 mg L^{-1} at 4h00 to 16 mg L^{-1} at 16h00 and pH remained constant. Again, dissolved and ferrous Fe showed weak diel changes. Finally, total Fe ranged from 120 μg L^{-1} at 20h00 to 220 μg L^{-1} at 12h00 while oxygen and pH remained constant during 24 hours. As for dissolved and ferrous Fe, they remained constant over 24 hours.

At the Falconbridge wetland (Fig. 4.5), diel variations in Fe concentrations at the outlet were much weaker than diel variations observed at the Monahan wetland (Fig. 4.4). In July, total Fe ranged from 250 μg L^{-1} at 20h00 to 300 μg L^{-1} at 8h00 while oxygen ranged from 4 mg L^{-1} at 4h00 to 8 mg L^{-1} at 16h00 and while pH ranged from 6.8 at 4h00 to 7.4 at 20h00 (Fig. 4.5). As for dissolved and ferrous Fe, they also showed weak diel variations at the outlet. In October, total Fe ranged from 120 μg L^{-1} at 16h00 to 280 μg L^{-1} at 4h00 while oxygen ranged from 6.7 mg L^{-1} at 4h00 to 8 mg L^{-1} 16h00 and pH remained constant over 24 hours. As for dissolved and ferrous Fe, they showed weak diel variations at the outlet (Fig. 4.5).

At the Monahan wetland, the diel changes in Mn concentrations at the outlet were different between months. In May, total and dissolved Mn remained constant during 24 hours at the outlet despite diel changes in oxygen concentrations (Fig.4.6). In June, total and dissolved Mn ranged from 60 and 5 μg L^{-1} at 20h00 to 120 and 80 μg L^{-1} at 8h00 while oxygen ranged from 4.4 mg L^{-1} at 8h00 to 14 mg L^{-1} at 20h00 and pH remained constant over 24 hours. In July, total Mn ranged from 20 μg L^{-1} at 16h00 to 55 μg L^{-1} at 4h00 while oxygen levels ranged from 8 mg L^{-1} at 4h00 to 12 mg L^{-1} at 16h00 and pH remained constant. Weak diel changes in dissolved Mn were observed over the 24 hours at the outlet. In August, diel changes in total Mn were less important than in July. Total Mn ranged from 30 μg L^{-1} at 16h00 to 60 μg L^{-1} at 4h00 while oxygen ranged from 8 mg L^{-1} at 4h00 to 16 mg L^{-1} at 16h00 and pH remained constant. Again, dissolved Mn showed small diel changes. Finally, in September, total Mn ranged from 10 μg L^{-1} at 16h00 to 30 μg L^{-1} at 8h00 while oxygen and pH remained constant during 24 hours. As for dissolved Mn, it remained constant over 24 hours.

As for other metals, the outlet reflected the diel trends occurring within littoral areas. Dissolved zinc followed the diel variation in oxygen and pH at the outlet in August and September only when Zn concentrations were above detection limits (Table 4.3). The concentrations of dissolved Cu, Ni and As also varied over 24 hours at the outlet (Table 4.3).

When the entire data set was examined using multiple regression analysis, significant inverse relationships between O_2 and pH, and changes in Fe ($R^2=0.60$) and Mn ($R^2=0.49$) were found. Temperature and redox potential were not significant variables predicting metal concentrations.

4.4.3 The implication on the retention of metals by wetlands

Diel changes in the treatment efficiency are presented in Figure 4.7. The greatest difference between night and day was observed for iron in July. The Fe treatment efficiency reached its lowest value (–185%) at 8h00 and increased to +75% at 20h00. The diel changes in Fe treatment efficiency decreased from August to September.

The diel changes in Mn treatment efficiency showed similar trends to Fe. The greatest difference in Mn treatment efficiency was observed in July when treatment efficiency reached a low of -100% at 4h00 and a maximum of 45% at 12h00. Then, the diel changes in Mn treatment efficiency decreased from August to September.

Finally, data from Chapter 3 were used to compare the diel variability with the monthly variability in Fe and Mn treatment efficiencies (Fig. 4.8). The box plots indicated high variability in treatment efficiency for Fe in July and August as compared to other months and the winter. The variability in Fe treatment efficiency attributed to diel changes was also higher during July and decreased in August and September. However, the variability due to diel changes in Fe treatment efficiency was generally low compared to the monthly variability.

As for Mn, the highest variability in treatment efficiency occurred in July followed by the winter. Similarly, the variability in Mn treatment efficiency attributed to diel changes was higher in July and decreased in August and September. Overall, the variability attributed to diel changes in Mn treatment efficiency was comparable to the monthly variability.

4.5 Discussions

4.5.1 Importance of photosynthesis in predicting diel changes in metal concentration

In this study, I hypothesised that the diel variations in oxygen and pH induced by photosynthesis would correspond to diel changes in metal concentration in surface-flow wetlands. In particular, I predicted an increase in metal concentrations during the night and a decrease in metal concentrations during the day.

A multiple regression model, which included oxygen and pH as independent variables, predicted Fe and Mn concentrations at the Monahan and Falconbridge wetlands. Photosynthesis and respiration have a significant effect on the concentrations of metals in water because the precipitation-dissolution equilibrium of Fe and Mn is extremely sensitive to fluctuations in pH, oxygen and redox potentials (Faulkner and Richardson, 1989). During the day, photosynthesis produces oxygen, increases pH and redox potentials in the wetland and the sediment-water interface is well oxygenated. Under these conditions, soluble Fe^{2+} and Mn^{2+} are oxidized to Fe^{3+} and Mn^{4+} oxides, which precipitate and build up at the sediment-water interface (Froelich et al., 1979; Tarutis and Unz, 1996). As a result, photosynthesis will keep metal concentrations low during the day.

In the dark experiments, autotrophic organisms did not produce oxygen through photosynthesis and this resulted in a significant decline in dissolved oxygen, pH and redox potentials at the sediment-water interface. The establishment of anoxic conditions at the sediment-water interface led to the reduction of manganic and ferric oxyhydroxides into soluble Fe^{2+} and Mn^{2+}. This translated into a constant increase over time in ferrous Fe, dissolved, total Fe and Mn into the water column. Also, high numbers of Fe reducing bacteria were obtained from these sediments (data not shown) suggesting that iron and manganese reducing bacteria were responsible for the reductive dissolution of Fe and Mn oxides (Lovley and Phillips, 1986; Stone, 1987). The dark experiments demonstrated that the sediments were a source of metals when photosynthesis was stopped.

Fe and Mn oxides are important adsorption sites for trace metals such as Zn, As, Ni, and Cu (Benjamin and Leckie, 1981). The concentrations of these trace metals in water were expected to follow the diel changes in Fe and Mn concentration observed within wetlands. However, even if some diel changes occurred for these metals, the variation was not as striking as for Fe and Mn. In contrast, Fuller and Davis (1989) found diel variations in As at Whitewood Creek, South Dakota perhaps because their concentrations of dissolved As were much greater ($\sim 52\ \mu g\ L^{-1}$) than in the Monahan wetland ($\sim 1\ \mu g\ L^{-1}$). The same explanation may be provided for dissolved Zn, Cu and Ni that bind to metal oxides but were also measured in low concentrations. McKnight et al. (1988) also found weak diel cycles of trace elements in an acidic stream.

My study also showed that diel changes in metal concentration varied from spring to late fall. The diel changes in Fe follow the diel changes in oxygen and pH induced by photosynthesis. Water temperature and solar radiation drive photosynthesis, which peaks in July as did the amplitude of diel changes in Fe and Mn. In August and September, water temperature and solar radiation decline. This decline will decrease photosynthetic rates, which translates into a decrease in the difference in O_2 concentration between day and night. Also, a decline in water temperature leads to more homogenised O_2 profile throughout the water column because the entire water column mixes and the solubility of O_2 in cold water is high (Wetzel, 1983). Diel variations disappeared when the surface water temperature was around 4°C in late October and early May.

In the sunlight experiments, cattails and duckweed prevented sunlight from reaching the sediments, which suggests that photosynthesis was a more important mechanism in regulating Fe changes than sunlight-induced Fe photoreduction. At the Falconbridge wetland, an increase in Fe was measured between 16h00 and 20h00 in July, which corresponded to the time period when surface sediments were exposed to sunlight. Therefore, Fe photoreduction may regulate diel changes in metal concentrations in aquatic systems only when solar radiation reaches the bottom sediments. Photoreduction may induce diel changes in metal concentrations in shallow aquatic systems with good light penetration, that is in systems with low dissolved organic carbon, low planktonic and macrophyte biomass. McKnight and Bencala (1988) first described diel changes in Fe concentration induced by photoreduction in the Snake River in Colorado. The system was a shallow and acidic stream with low dissolved organic carbon.

4.5.2 The implication of diel changes in metal concentration on the retention of metals by wetlands

Diel variations in metal concentrations were much greater in shallow littoral zones than at the outlet of both wetlands, most likely because the outlet water results from surface mixing of pelagic water (where diel variations in metal concentration would not be significant) and littoral water (where diel variations are observed). Deeper water may not mix with surface water in summer because of thermal stratification (Wetzel, 1983). This may explain why the increase in Fe in deep water at the Falconbridge wetland was not measured at the outlet. Shallow littoral zones likely contribute significantly to the treatment efficiency of wetlands.

Generally, the monitoring of surface-flow wetlands is mostly conducted during storm events when wetlands are believed to release a significant amount of pollutants. The monitoring of metal retention by wetlands during dry periods (no rain) is rarely conducted because retention is assumed to be high. This study indicated that this assumption is unlikely because metal concentrations varied significantly over a 24-hours period during dry and sunny periods. Therefore, the time of sampling is critical. Collecting water samples in the afternoon will result in an overestimation of the treatment efficiency and the treatment efficiency will be underestimated if water samples are collected late at night (Fig. 4.7).

Also, diel changes in Fe and Mn concentrations at the outlet of the Monahan wetland occurred over almost five months and this period could be longer in warm climates. As a result, diel changes can significantly affect the yearly treatment efficiency of surface-flow wetlands. However, wetland managers are limited in the number of samples they can collect and need to evaluate the importance of diel variability in treatment efficiency as opposed to the seasonal variability in treatment efficiency in order to measure accurately the retention of metals on a yearly basis. It is important to increase the number of samples during periods of high variability. For Fe, a large percentage of the sampling should be conducted in July and August when the variability in Fe treatment efficiency is high as compared to the winter. As for Mn, a large proportion of the sampling effort should also be directed to the July period followed by the winter period (Fig. 4.8).

Collecting water samples on a 24 hours basis throughout the summer will result in a significant increase in monitoring costs. More accurate retention values could be obtained if integrated water samples over a 24-hour period are taken. Several constructed wetlands are equipped with auto-samplers at both inlet and outlet. Collecting an integrated or composite water sample by sampling at least every 4 hours would be sufficient to obtain a realistic daily average metal concentration. Treatment efficiencies could then be calculated more accurately.

4.6 Conclusions

Constructed wetlands are believed to be efficient sinks for metals. This affirmation stems from mass balance calculations that generally do not consider diel variations in metal concentrations. The results from this study suggest that significant diel variations in metal concentration induced by photosynthesis are likely:

1) if intense photosynthesis results in diel changes in oxygen and pH
2) if dense macrophytes prevent solar radiation from reaching surface sediments
3) if the proportion of shallow to deep water area is high
4) during warm summer months and not during spring, late fall and winter
5) for Fe, Mn and metals that adsorb onto metal oxides such as Zn, As and Pb.

The calculation of retention should be based on integrated samples taken over a 24-hour interval to better evaluate wetlands as sinks or sources for metals.

Table 4.1 Description of the Monahan and Falconbridge wetlands

Parameter	Monahan		Falconbridge	
Age (years)		4		18
Mean depth (m)		1.5		1.75
Water storage (m^3)		53 000		830 000
Drainage area (ha)		637		1200
Yearly average total suspended	In	50.5	In	--
solids (mg L^{-1})	Out	20.3	Out	--
Yearly average Fe (μg L^{-1})	In	360	In	--
	Out	270	Out	530
Yearly average pH	In	7.82	In	--
	Out	8.04	Out	6.89

Table 4.2. Detection limits of total and dissolved metal concentrations (µg L-1) using ICP-AES and ICP-MS.

Metal	ICP-AES (total)	ICP-MS (dissolved)
Fe	30	5.0
Mn	6	0.1
Zn	22	0.5
Cu	8	0.1
As	--	0.1
Ni	70	0.2

Table 4.3 Range in dissolved trace metals (μg L^{-1}), oxygen levels (mg L^{-1}) and pH at the outlet, and in dark and sunlight exposed experiments within the Monahan[1] and Falconbridge[2] wetlands.

	Place	Zn	Cu	Ni	As	Oxygen	pH
May[1]	Dark	0.54-1.03	0.58-0.81	--	0.54-0.68	4.0-10.2	7.2-7.7
(20°C)	Sunlight	0.54-1.08	0.93-1.20	--	0.24-0.41	9.0-18.0	7.6-8.5
	Outlet	0.50-0.52	0.95-1.11	--	0.37-0.56	12.0-17.0	8.1-8.7
June[1]	Dark	0.52-0.96	0.64-0.95	0.75-1.08	1.89-2.25	0.4-6.2	7.6-7.9
(22°C)	Sunlight	0.60-0.92	0.96-1.18	0.64-1.14	1.91-2.12	4.0-14.0	7.9-8.4
	Outlet	0.50-0.56	0.89-1.12	0.84-1.20	1.86-2.37	5.0-14.0	7.8-8.6
July[1]	Dark	0.50-1.29	0.61-0.76	0.55-1.49	0.86-0.91	0.5-5.0	7.4-7.9
(24°C)	Sunlight	0.50-0.79	0.63-0.85	0.46-1.72	0.76-1.04	2.0-11.0	7.5-9.6
	Outlet	0.50-0.55	0.68-0.98	0.46-3.74	1.21-1.85	8.5-11.0	8.4-9.0
July[2]	Dark	--	--	50-60	4.75-10.5	0.5-2.0	7.0-7.3
(24°C)	Sunlight	--	--	40-70	2.50-2.50	2.0-8.0	6.9-7.6
	Outlet	--	--	60-70	2.50-5.50	4.0-8.1	6.7-7.7
Aug.[1]	Dark	0.63-0.91	0.23-0.37	0.99-1.31	0.80-1.14	0.5-2.0	6.9-7.6
(20°C)	Sunlight	0.73-1.15	0.32-0.62	0.73-1.14	0.63-0.68	2.0-14.0	7.4-8.0
	Outlet	0.58-0.82	0.51-0.53	0.68-1.02	0.72-0.81	8.0-15.0	8.2-8.5
Sept.[1]	Dark	0.87-3.55	0.68-0.80	1.49-2.60	0.61-0.76	3.0-6.0	7.2-7.3
(16°C)	Sunlight	0.67-1.75	0.57-0.91	1.71-2.69	0.58-0.74	8.0-11.0	7.5-7.7
	Outlet	0.51-1.38	0.61-1.99	1.13-1.82	0.46-0.56	12.0-13.0	8.1-8.3
Oct.[2]	Dark	2.00-6.00	1.95-3.10	85-100	1.45-1.80	4.5-5.5	7.0-7.1
(7°C)	Sunlight	2.00-6.00	2.30-4.25	110-115	1.50-2.05	6.6-7.6	7.0-7.1
	Outlet	2.00-10.00	2.50-4.90	95-115	1.80-2.85	6.4-7.9	7.0-7.1

Figure 4.1 Seasonal comparisons of diel changes in Fe concentrations (μg L^{-1}), oxygen levels (mg L^{-1}) and pH between dark and sunlight experiments at the Monahan wetland.

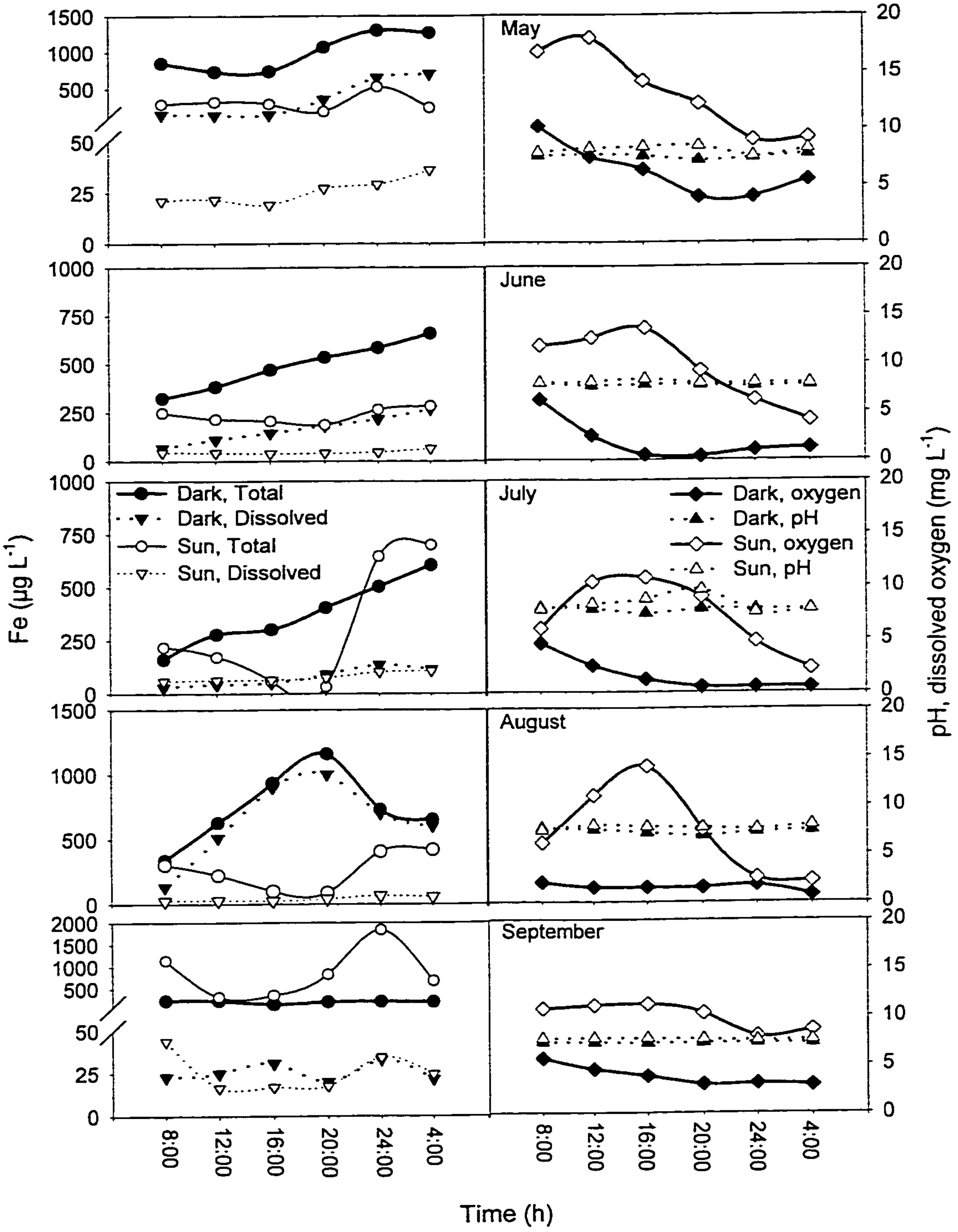

May
June
July
August
September
Dark, Total
Dark, Dissolved
Sun, Total
Sun, Dissolved
Dark, oxygen
Dark, pH
Sun, oxygen
Sun, pH
Fe (µg L-1)
pH, dissolved oxygen (mg L-1)
Time (h)
8:00
12:00
16:00
20:00
24:00
4:00
0
25
50
500
1000
1500
2000
250
750
5
10
15
20

Figure 4.2 Seasonal comparisons of diel changes in Fe concentrations (μg L^{-1}), oxygen levels (mg L^{-1}) and pH between dark and sunlight experiments at the Falconbridge wetland.

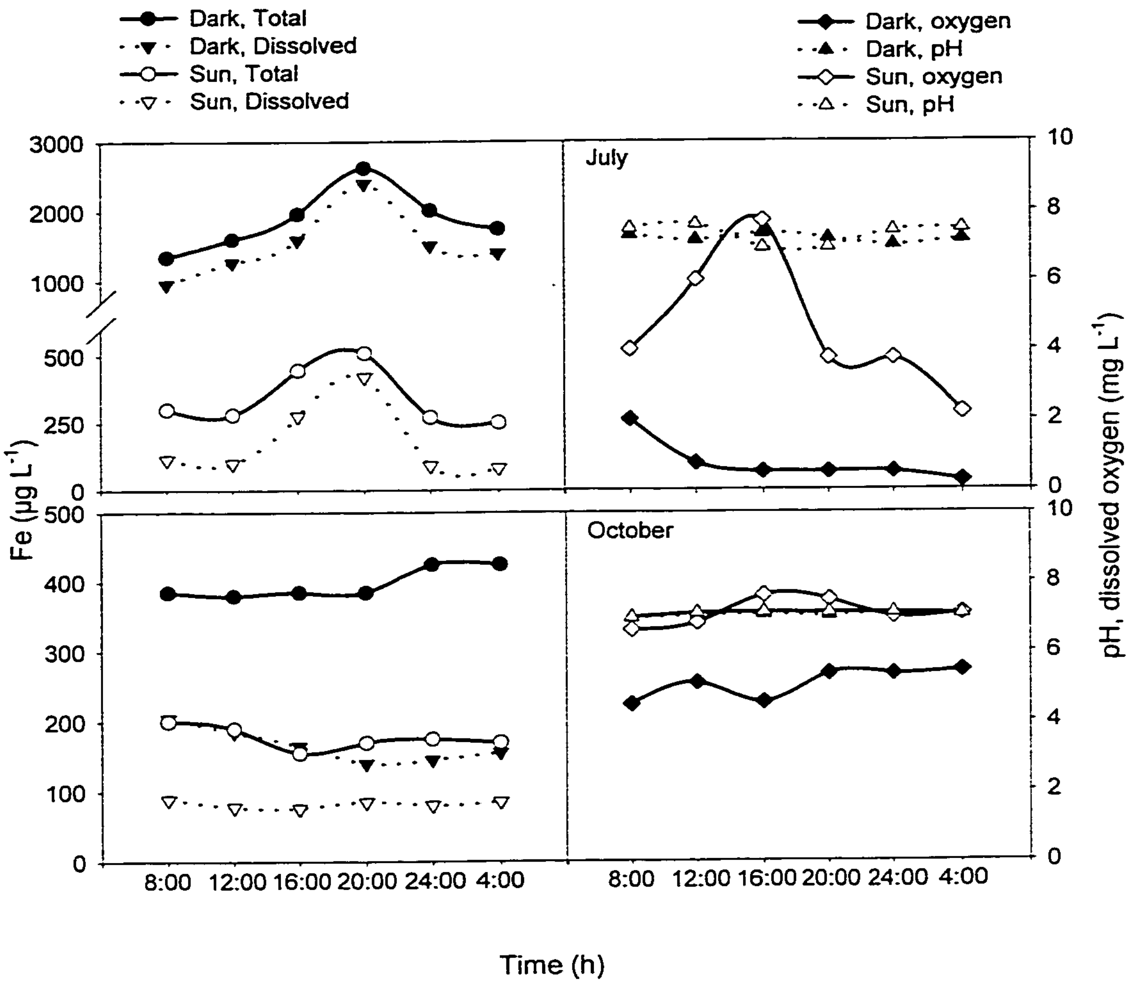

Dark, Total
Dark, Dissolved
Sun, Total
Sun, Dissolved
Dark, oxygen
Dark, pH
Sun, oxygen
Sun, pH
July
October
3000
2000
1000
500
250
0
500
400
300
200
100
0
10
8
6
4
2
0
10
8
6
4
2
0
Fe (µg L-1)
pH, dissolved oxygen (mg L-1)
8:00
12:00
16:00
20:00
24:00
4:00
8:00
12:00
16:00
20:00
24:00
4:00
Time (h)

Figure 4.3 Seasonal comparisons of diel changes in Mn concentrations (μg L^{-1}), oxygen levels (mg L^{-1}) and pH between dark and sunlight experiments at the Monahan wetland

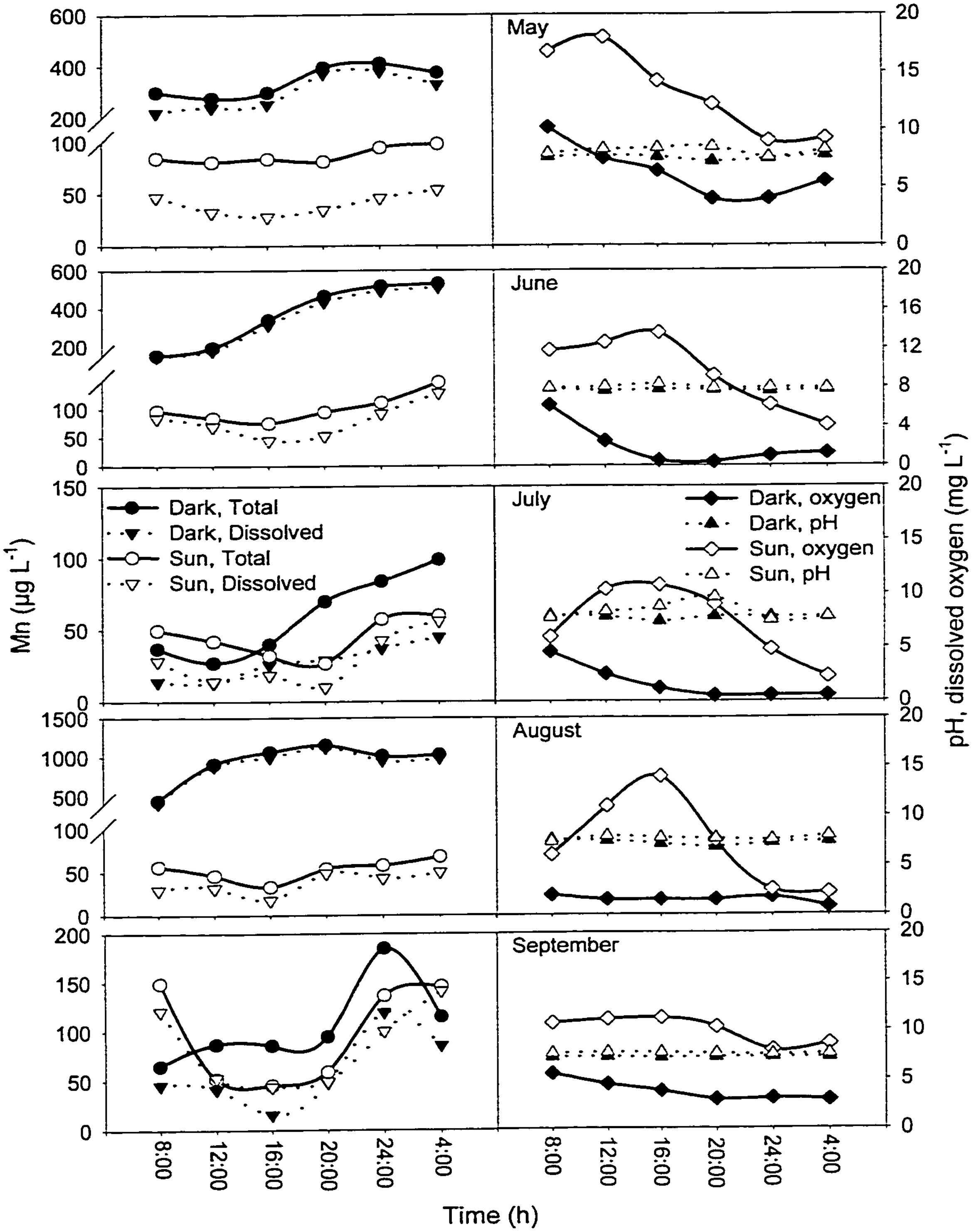

May
June
July
August
September
Dark, Total
Dark, Dissolved
Sun, Total
Sun, Dissolved
Dark, oxygen
Dark, pH
Sun, oxygen
Sun, pH
Mn (µg L-1)
pH, dissolved oxygen (mg L-1)
Time (h)
8:00
12:00
16:00
20:00
24:00
4:00
600
400
200
100
50
0
150
1500
1000
500
20
15
10
5
16
12
8
4

Figure 4.4 Seasonal comparisons of diel variations in Fe concentrations (μg L^{-1}), oxygen levels (mg L^{-1}) and pH at the outlet of the Monahan wetland.

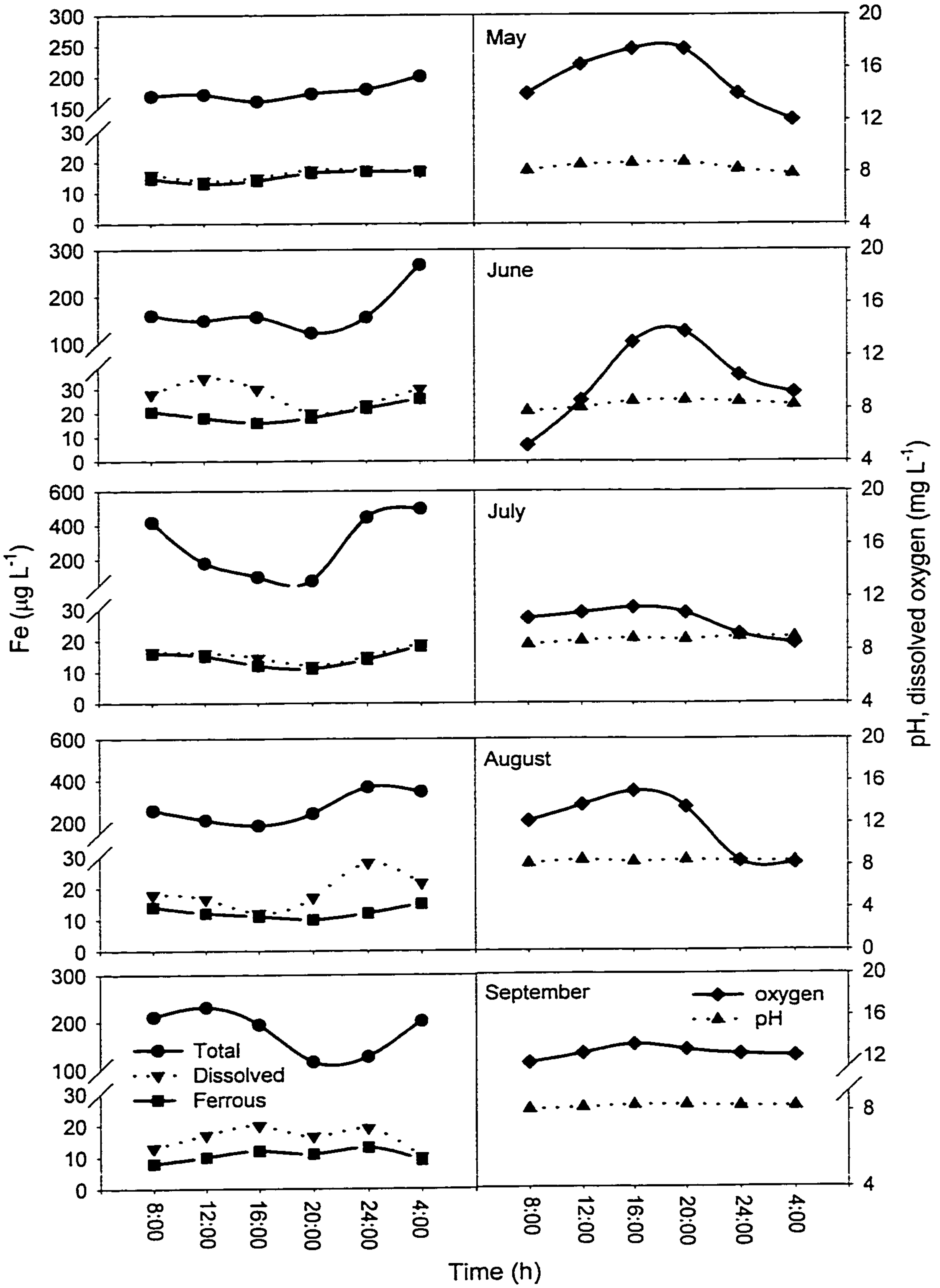

May
June
July
August
September
Fe (µg L-1)
pH, dissolved oxygen (mg L-1)
Time (h)
Total
Dissolved
Ferrous
oxygen
pH
8:00
12:00
16:00
20:00
24:00
4:00
300
250
200
150
30
20
10
0
600
400
100
16
12
8
4

Figure 4.5 Seasonal comparisons of diel changes in Fe concentrations (μg L^{-1}), oxygen levels (mg L^{-1}) and pH at the outlet of the Falconbridge wetland.

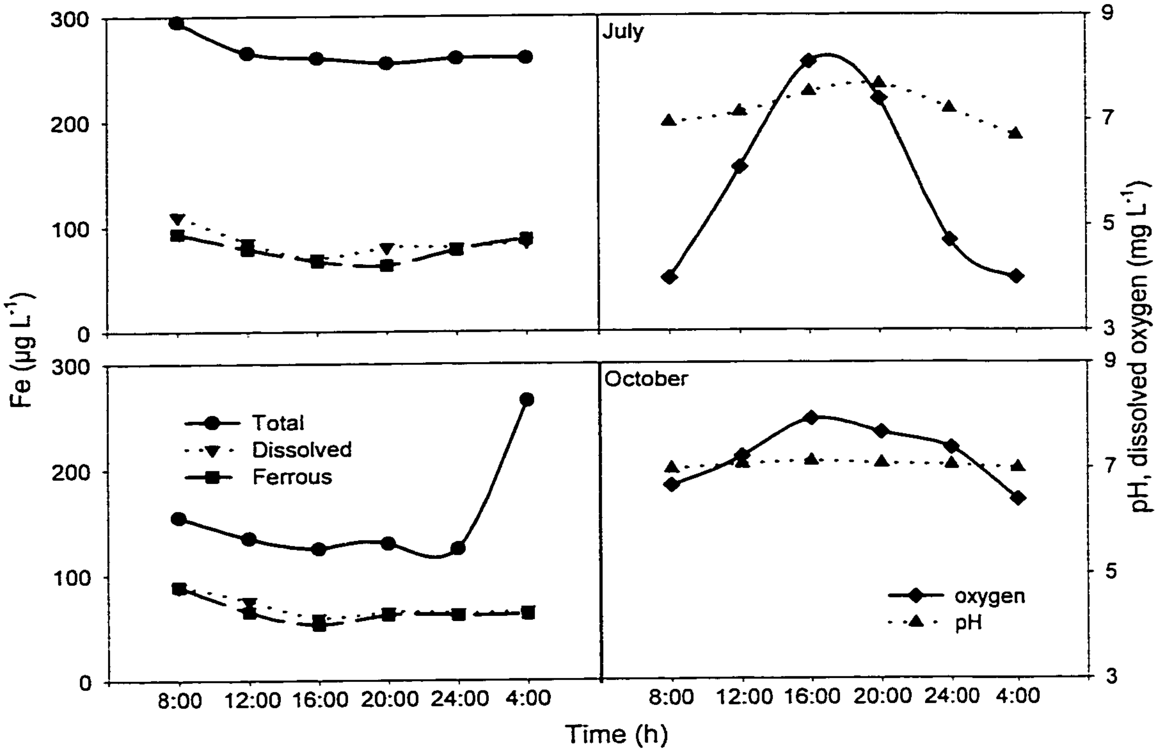

July
October
Fe (µg L⁻¹)
pH, dissolved oxygen (mg L⁻¹)
300
200
100
0
9
7
5
3
Total
Dissolved
Ferrous
oxygen
pH
8:00
12:00
16:00
20:00
24:00
4:00
Time (h)

Figure 4.6 Seasonal comparisons of diel changes in Mn concentrations (μg L^{-1}), oxygen levels (mg L^{-1}) and pH at the outlet of the Monahan wetland.

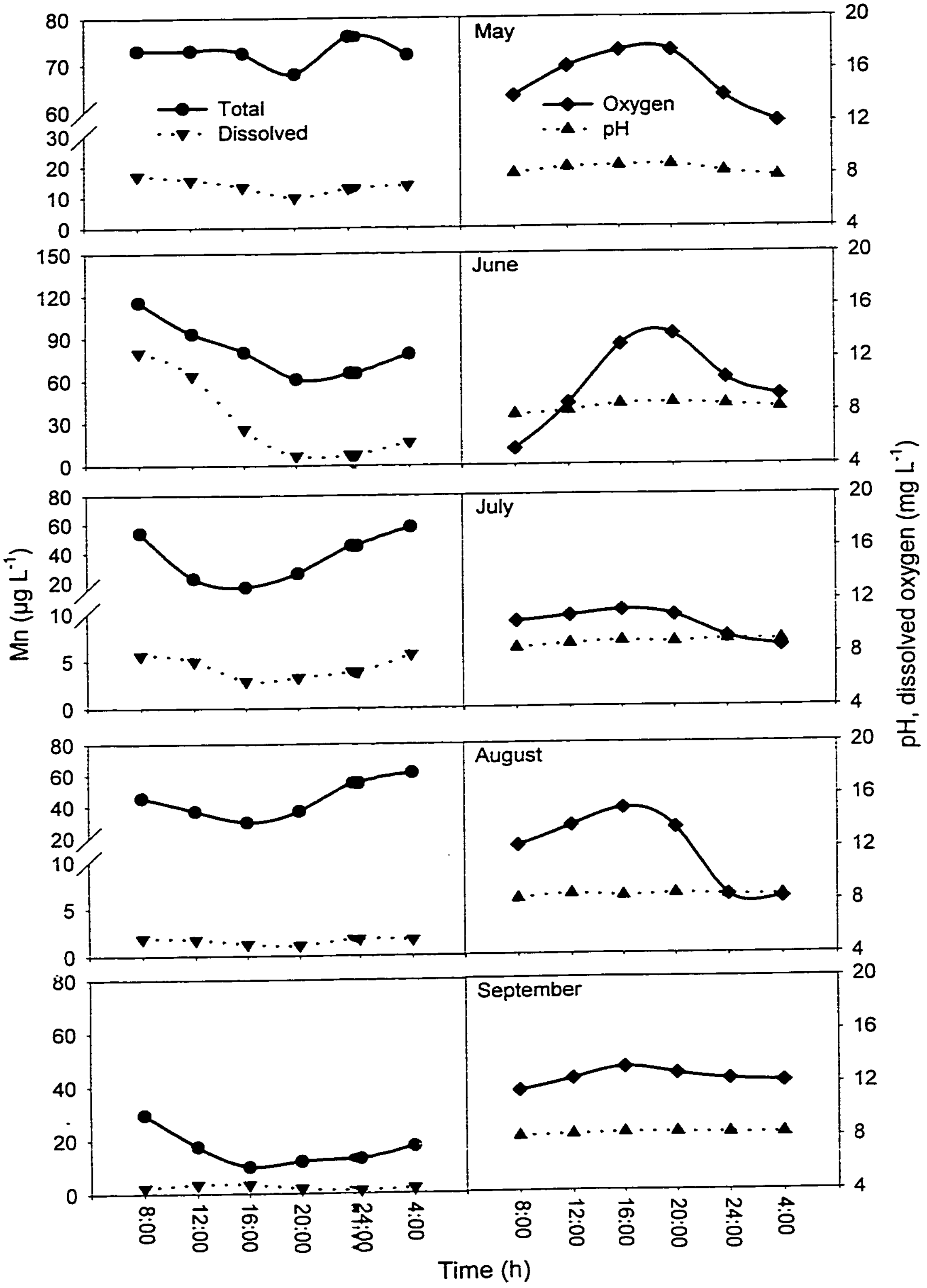

May
June
July
August
September
Total
Dissolved
Oxygen
pH
Mn (µg L-1)
pH, dissolved oxygen (mg L-1)
Time (h)
8:00
12:00
16:00
20:00
24:00
4:00
80
70
60
30
20
10
0
150
120
90
60
30
5
40
4
8
12
16
20

Figure 4.7 Diel change in treatment efficiencies for Fe (bottom) and Mn (Top) at the Monahan surface-flow wetland.

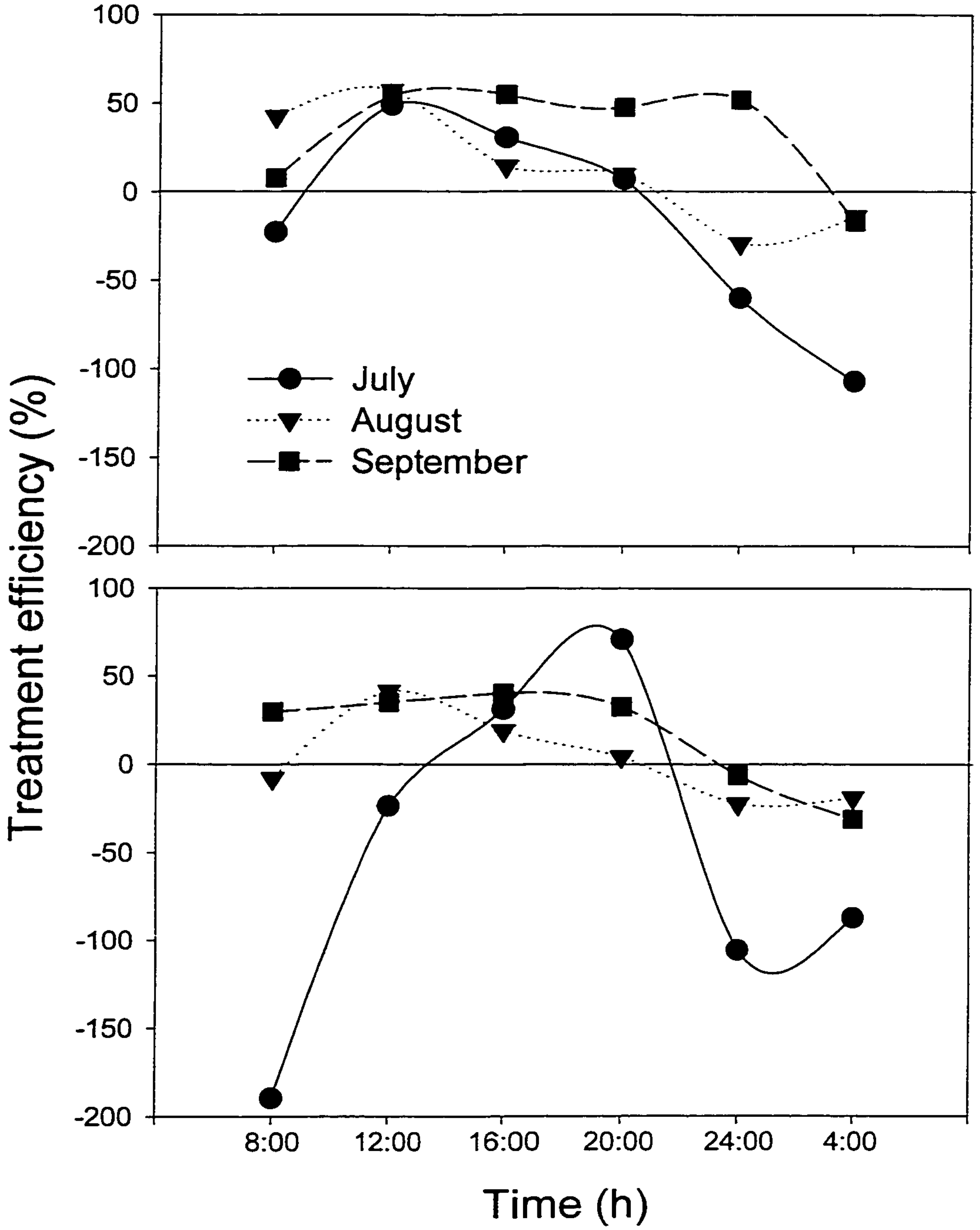
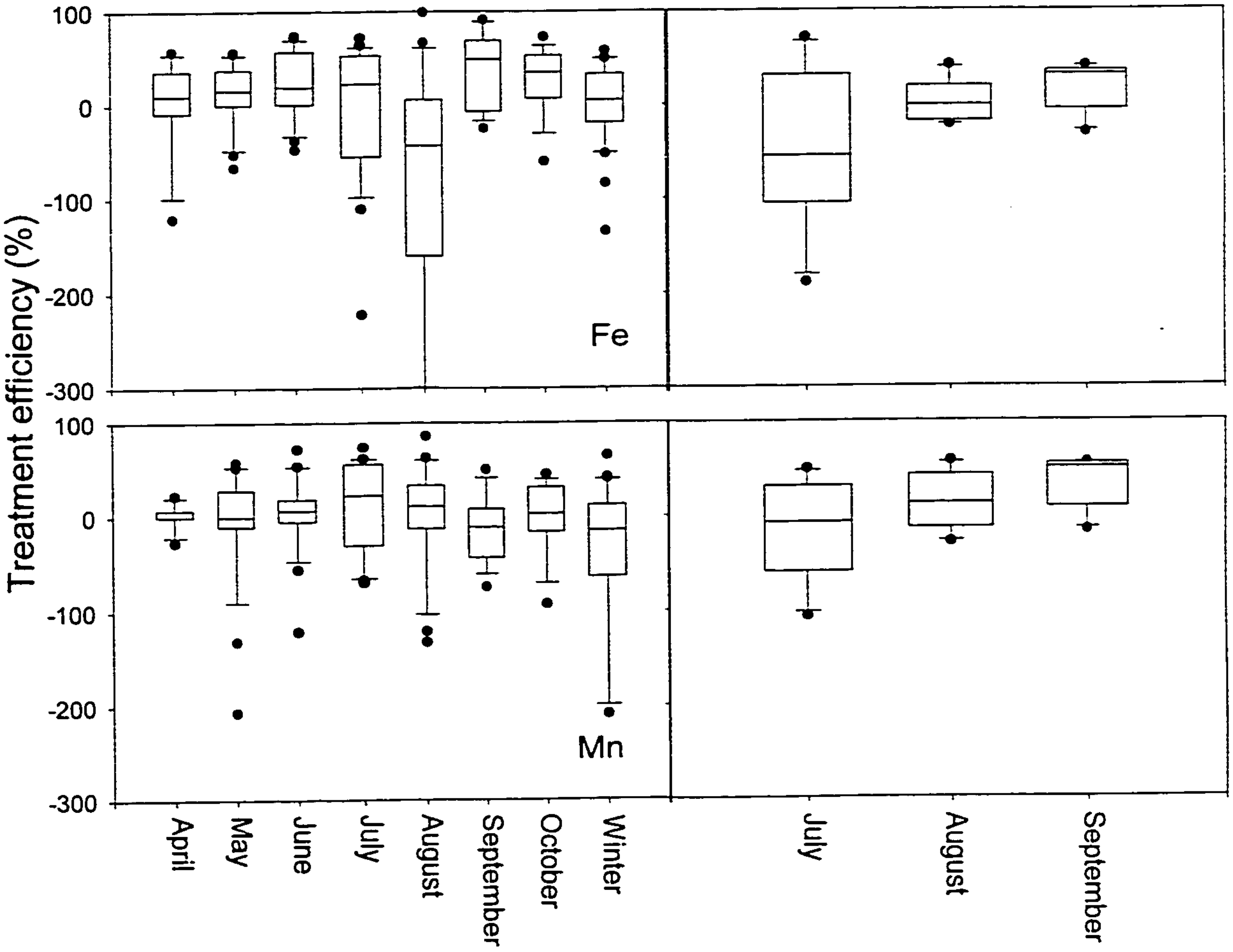

Treatment efficiency (%)
100
50
0
-50
-100
-150
-200
July
August
September
8:00
12:00
16:00
20:00
24:00
4:00
Time (h)

Figure 4.8 Box plots of monthly variability in treatment efficiencies from 1997 to 1999 (left) and diel variability in treatment efficiency (right) during diel experiments in 1999. The top and bottom of the box is drawn at the upper and lower quartile. The line inside the box represent the median value. The vertical lines drawn from the top and bottom of the box reaches the farthest observation within 1.5 interquartile range. Dots correspond to outliers situated over 1.5 interquartile range from the top or bottom of the box.


Treatment efficiency (%)
100
0
-100
-200
-300
Fe
Mn
April
May
June
July
August
September
October
Winter
July
August
September

Chapter 5

The effect of cattails (*Typha latifolia L.)* on total metal concentrations and partitioning in surface sediments of surface-flow constructed wetlands

5.1 Abstract

The concentration and partitioning of metals in vegetated and unvegetated surface sediments were compared among four surface-flow wetlands designed for wastewater treatment. In wetlands with a significant depth gradient (Monahan and Falconbridge), the highest concentrations of metals were found in deeper unvegetated sediments. When the effect of depth was removed, surface sediments with and without cattails (*Typha latifolia L.*) had similar concentrations of metals (Fe, Mn, Zn and Cu). However, vegetated sediments of all four wetlands had higher organic content ($p<0.01$). Furthermore, the redox potential was significantly lower ($p<0.01$) in vegetated sediments for 3 out of 4 wetlands. Vegetated and unvegetated sediments were also compared based on geochemical fractions (reactive, silicate, persistent organic and pyritic). Generally, half of the total metal concentration in sediments was associated with the reactive fraction (metal oxides, monosulfides and adsorbed onto organic matter). Zn was an exception as half of the total Zn was associated with the persistent organic fraction. Generally, there was no significant difference in the partitioning of metals in surface sediments with or without cattails at all four constructed wetlands. The effect of cattails on the bulk concentration and partitioning of metals may be minimal in surface-flow constructed wetlands.

Key words: aquatic plants, metals, geochemical partitioning, surface-flow wetland, surface sediments, *Typha latifolia L*

5.2 Introduction

Wetlands are believed to be natural sinks for metals. The retention of metals is possible through particulate deposition at the sediment-water interface (Gilliam et al., 1988). However, the deposition of suspended particles may not be a homogenous process throughout a wetland because of the presence of a depth gradient which can lead to variations in metal content, organic content, pH, redox potential and cation exchange capacity of the sediments (Reese and Moorhead, 1996; Havens, 1997).

This variation in biogeochemical conditions in sediments may also be explained by the presence of macrophytes along the depth gradient. Emergent macrophytes tend to colonise shallow or littoral areas leaving deeper areas as open water. Fennessy et al. (1994) showed that the deposition of particles was higher in open water areas where water flow was not restricted. Preferential flow paths developed around dense cattail stands and carried the majority of the water flow and hence the suspended particle load. The deposition of particulate metals and hence the resulting concentration of metals in surface sediments may differ from vegetated to open water areas (Caçador et al., 1996; Kadlec, 2000). As such, the percent coverage of a wetland by rooted aquatic plants could be important for the retention of metals by wetlands.

Some studies show higher concentrations of metals in vegetated sediments (Kostka and Luther III, 1995; Doyle and Otte, 1997) while others demonstrate the opposite effect (Otte et al., 1995; Caçador et al., 1996). At the Des Plaines River wetlands, Brueske and Barrett (1994) showed that vegetation affected sedimentation rates depending on hydraulic loading rates. Vegetation patterns did not affect sediment deposition rates in the high-load basin, but vegetation affected sediment deposition rates in a low-load basin.

Several studies have looked at the possible contribution of submerged and emergent macrophytes to the overall budget of metals in rivers and lakes (Brix and Lyngby, 1983; Peverly, 1985; St-Cyr et al., 1994). For example, St-Cyr and Campbell (1996) showed that metal concentrations were higher in sediments than in the roots, which suggests that the adjacent sediment is the main sink for metals. However, vegetated beds are efficient traps for organic matter (Coquery and Welbourn, 1995) and particulate metals (Fennessy et al. 1994, Brueske and Barrett 1994). For lakes, a mass-balance study showed that macrophyte beds retained particulate metals on a yearly basis (Jackson et al., 1994). Also, macrophytes are believed to have significant effects on the biogeochemistry of sediments (Wigand et al., 1997).

Macrophytes are essential components of wetlands through their role in stabilising and oxidising surface sediments (Dunbabin et al., 1988; Brix, 1994). Macrophytes supply oxygen through their roots, which enables metal oxide formation in reducing sediments (Dunbabin et al., 1988; Brix, 1994; St-Cyr and Campbell, 1996). As a result, vegetated sediments may show a different metal profile in the sediments (Breen and Chick, 1995). Under reducing conditions, metal sulfides precipitate resulting in long term immobilisation of metals in sediments (e.g. DiToro et al., 1992). In less reducing conditions, metals are precipitated as oxides or adsorb onto organic material. Since the oxygen supply brought by macrophytes increases the redox potential, the speciation of metals may differ in vegetated sediments as compared with unvegetated sediments.

In this study, the main objective was to evaluate the effect of the presence of cattails on the concentration of metals in recently deposed sediments (0-2 cm). I hypothesised that the concentration of metals in surface sediments should differ between vegetated and unvegetated sediments. As well, I hypothesised that the partitioning of metal in surface sediments should differ with the presence of cattails since they provide oxygen from root leakage (Dunbabin et al. 1988). We tested these hypotheses on four wetlands: two wetlands received low metal loading and the other two wetlands received high metal loading.

5.3 Methods

5.3.1 Study sites

The four wetlands chosen were all surface-flow wetlands with open water areas and areas covered with aquatic plants, principally cattails (*Typha latifolia L.*). For all wetlands, a relatively large amount of sediment had accumulated since their creation. The wetlands vary in age and size (Table 5.1).

The Monahan wetland is located in the city of Kanata, Ontario, Canada ($45^0 16'$ N, $75^0 51'$ W). It was built in 1995 and completed in 1996 as a storm water management facility. The wetland was designed to maintain water velocities under 0.5 m s^{-1}. The wetland itself has three consecutive cells, which were lined initially with a thick layer of clay to prevent infiltration. No organic substrate was added on the clay liner. This facility receives relatively high total phosphorus concentrations (~0.17 mg/L) from urban and agricultural runoff.

The Riverwalk wetland is situated in the city of Nepean, Ontario, Canada (45° 27' N, 75° 42'W) and drains a small residential area (Table 5.1). It was built in 1990 to minimise the impact of urban development on the water quality of the Rideau River. A layer of sand and silt underlies the wetland. The wetland contains two cells. The first cell has shallow water (~0.5 m) and is dominated by cattail stands with open water zones. The second cell is a deep water (~1.5 m) impoundment colonised by submerged macrophytes.

The Falconbridge wetland is located in the city of Falconbridge, Ontario, Canada (46° 57' N: 80° 80' W). It was built to treat acid mine drainage in 1981. The wetland sits on old mine tailings. It is the largest of the four wetlands studied with a total surface area of 200 ha of which 70% is covered by cattails.

The Panel wetland is located approximately 25 km Northeast of the city of Elliot Lake, Ontario, Canada (4600N 7800E). This wetland has a total surface area of 14.5 ha of which 60% of the surface area is dominated by cattails. During the initial operation of the Panel uranium mine (1957 to 1961), tailings were spilled in the Western part of the wetland and they now form part of the substrate. A dam was built in 1979 in order to control the inflow to the wetland. The average water flow through the wetland is approximately 4.4 x 10^{-3} m^3 s^{-1}. The wetland currently receives runoff from exposed tailings, which contribute to the metal rich receiving waters (Davé, 1993).

5.3.2 Sediment sampling

Sediment samples were collected during the summer of 1997 in the Monahan wetland. Sediment samples were collected the following year, for the three other wetlands. For each wetland, ten samples of surface sediments (0-2 cm) were collected randomly within vegetated sediments and ten other samples were collected within unvegetated sediments. For wetlands with a cross-sectional water depth gradient (Falconbridge and Monahan), there were no shallow areas where cattails were absent.

Therefore, unvegetated sediments were collected in deep water (~1 m). Samples were collected with a Kaja-Brinkhurst gravity corer with a Plexiglas tube of a diameter of 3 inches. We measured pH, redox and temperature at the sediment-water interface of each sediment core. We measured pH with an Orion portable pH meter using an Orion epoxy body sure-flow electrode. An epoxy body platinum redox electrode was used for redox measurements. Sediment samples were stored in high-density polyethylene containers and kept at 4°C in a cooler. Upon return to the laboratory, sediment samples were frozen.

5.3.3 Sample preparation

All sediment samples were freeze dried for 24 hours or more depending on the water content of the sediments. We homogenised and ground the sediments until in a powder-like state and passed the sample through a coarse mesh (pore size 5 mm) to remove stones and wood chips.

5.3.4 Total concentration of metals in sediments

Sediment digestion was performed by acid assisted microwave digestion following EPA method 5081. Blanks and standards were included within each run of 12 samples for quality assurance and control. A lake sediment standard (Lksd-2) from the Canadian Centre for Mineral and Energy and Technology was used within each run. Approximately 0.5 g of sediment were digested in ultra pure concentrated HNO_3 (Seastar Chemicals inc.) under pressure conditions of 120 PSI for 10 minutes. Extracted solutions were centrifuged for 10 minutes at 10 000 rpm and were then diluted in ultra pure distilled water. Samples were analysed for total metal concentration using an ICP-AES at the Geology Department of the University of Ottawa.

5.3.5 Sequential extraction

The method of Huerta-Diaz and Morse (1990) was used for sequential extraction. Sequential extraction was performed on three sediment samples per zone and per wetland instead of ten per zone per wetland for the determination of total concentration. I used 0.5 g of sediment and exposed it to a first acid attack with 1 M HCl, which extracts free metals in the pore water, metals adsorbed and associated with oxides, monosulfides, adsorbed to organic matter. Then sediments were digested with 10 M HF and 5 g of boric acid to extract metals associated with the silicate fraction of the sediments. Sediment samples were then exposed to concentrated H_2SO_4 to extract metals associated with organic matter that persisted through the 1 M HCl step. These extracts were filtered through 0.2 μm polycarbonate filters to obtain a clear sample. Ultra pure distilled water spiked with H_2SO_4 was filtered as well to measure potential contamination associated with the filtration process. Finally, I exposed the sediment samples to a concentrated HNO_3 digestion, which extracts the metals associated with the pyrite fraction.

5.3.6 Organic matter

The percentage of organic matter in sediments was estimated by loss on ignition (LOI). A sub-sample of 1.0 g of each freeze-dried sediment sample was ashed for 2.5 hours at 550°C in a muffle furnace (Greenberg et al., 1989). The dried samples were then weighed.

5.3.7 Statistical analysis

All statistical analyses were performed with Systat 7.0 for Windows 95. Differences in redox potential, organic content and metal concentrations between vegetated and unvegetated sediments were tested using one way model II parametric analysis of variances (ANOVA). Assumptions of the parametric ANOVA were tested with Wilkes-Shapiro test for normality of residuals, with Levene's test for homoscedasticity and with autocorrelation plots for independence among residuals.

For the Monahan and Falconbridge wetlands, linear regression analysis was done to test for the relationship between metal concentration in sediments and depth of the water column. In the case of significant relationships, the residuals of the regressions were used in ANOVAs to compare vegetated and unvegetated sediments.

Comparisons of the proportion of metals in the different sediment fractions between vegetated and unvegetated sediments for each wetland was done using a three-way model III factorial non-parametric ANOVA (Kruskall-Wallis test) to determine the effect of the presence of the vegetation on the partitioning of metals among wetlands. An arcsine transformation of the proportions of metals associated with each fraction was done since proportions are not normally distributed (Sokal and Rohlf, 1993).

5.4 Results

5.4.1 Metal concentration in sediments

Surface sediments of the four constructed wetlands showed a wide range of metal concentrations (Fig. 5.1). Concentrations of Fe in the Panel wetlands were 10 times higher than for the Riverwalk pond that had the lowest concentrations of Fe of all the wetlands. However, the total concentration of Mn was highest in the Riverwalk wetland (Fig. 5.1). Finally, Cu and Zn were highest in the Falconbridge wetland.

For the Monahan and Falconbridge wetlands, the total concentrations of Fe, Mn, Cu, Zn in the sediments and the depth of the water column were linearly related (Fig. 5.2). Metal concentration increased with increasing depth of the water column. Therefore, to remove the effect of water depth, residuals of the total metal concentration versus depth regressions were used to test for the effect of cattails on the metal concentration in sediments. For the Riverwalk and Panel wetlands, there were no significant differences between sites with respect to depth so the total concentrations were used for comparison between vegetated and unvegetated sediments. For wetlands with depth gradients, the residual values of Fe, Mn, Zn, Cu concentrations were similar between vegetated and unvegetated sediments. The metal concentrations in surface sediments were similar between vegetated and unvegetated sediments at the Panel and Riverwalk wetlands (Fig. 5.1). However, the Panel wetland had Cu concentrations significantly higher in unvegetated sediments as was also the case for Mn in unvegetated sediments of the Riverwalk pond (Fig. 5.1).

5.4.2 Organic material and redox in sediments

The organic content was significantly different between vegetated and unvegetated zones in all four wetlands (Fig. 5.3). Vegetated sediments had significantly higher organic content in each case (from 5 to 15% increases in organic content). Redox potentials were significantly lower in vegetated sediments of the Monahan, the Falconbridge, and the Riverwalk wetlands. However, there was no difference in redox potential between vegetated and unvegetated sediments in the Panel wetland (Fig. 5.3). The redox potentials in vegetated sediments also differed from one wetland to another. In particular, the Falconbridge and the Riverwalk wetlands had redox potentials below –100 mV.

5.4.3 Partitioning of metals in sediments

The partitioning of metals was different in each wetland (Fig. 5.4). Generally, Fe, Mn and Cu were mainly associated with the reactive fraction which refers to metals associated with oxides, monosulfides or adsorbed onto organic matter. In contrast, Zn was mainly associated with the persistent organic fraction.

There was no difference in the partitioning of metals between vegetated and unvegetated sediments of the Panel wetland (Fig. 5.4). More than 50% of metals extracted from the sediments were associated with oxides, monosulfides or adsorbed onto organic matter (reactive fraction). The partitioning of Zn in sediments was different from other metals since half of the zinc extracted from sediments was present in persistent organic matter (persistent organic fraction).

At the Monahan wetland, the partitioning of metals differed between shallow vegetated and deep unvegetated sediments except for Cu (Fig. 5.4). Approximately 80% of total Cu was associated with oxides, monosulfides or adsorbed onto organic matter in both zones. A higher proportion of Fe and Mn was associated with the persistent organic fraction in the vegetated sediments (10%) as compared with deeper, unvegetated sediments (2%). The difference in the partitioning of Zn stemmed from a higher proportion associated with the silicate fraction (40%) in unvegetated and deeper sediments whereas 40% of Zn was associated with persistent organic mater in the vegetated sediments.

At the Falconbridge wetland, the partitioning of metals between shallow vegetated and deep unvegetated sediments was different for Mn but not for Fe, Zn and Cu. The proportion of Mn associated with the reactive fraction was approximately 50% in shallow vegetated sediments as opposed to only 10% in deeper unvegetated sediments. Furthermore, the proportion of Mn associated with the persistent organic and pyritic fractions was greater in deep unvegetated sediments than in shallow vegetated sediments. For all other metals, the partitioning was similar between shallow vegetated and deep unvegetated sediments. Over 75% of total Cu was associated with oxides, monosulfides or adsorbed onto organic matter. As for other metals, 45% of total Fe and 60% of total Zn in sediments was associated with oxides, monosulfides or adsorbed onto organic matter. A significant proportion of Fe (45%) and Zn (20%) was also associated with the pyritic fraction.

At the Riverwalk wetland, the partitioning of metals was similar between vegetated and unvegetated sediments with the exception of Zn. In vegetated sediments, 75% of extracted Zn was present in persistent organic matter as opposed to only 25% in unvegetated sediments. Furthermore, the proportion of associated with the pyritic fraction was more important in the unvegetated zone reaching 40% of the total concentration as opposed to only 15% in vegetated sediments. As for other metals, 50% of total Fe, 70% of total Mn and 75% of total Cu were associated with oxides, monosulfides or adsorbed onto organic matter.

5.5 Discussion

5.5.1 Metal concentration in sediments

Many factors, aside from the presence of vegetation, can contribute to the accumulation of metals in surface sediments. In the Monahan and Falconbridge wetlands, the concentration of metals was significantly related to depth of the water column (Fig. 5.2). This may be the result of sediment focusing defined as a process whereby water turbulence moves sedimented material from shallower to deeper zones of an impoundment. Such a phenomenon has been described in lakes (e.g., Blais and Kalff, 1995) but may also occur in surface-flow wetlands since they can resemble shallow lakes. Rates of net sediment accumulation are greatest in deeper water because wind- and wave-induced resuspension of particles is reduced (Bloesch, 1982; Dillon and Evans, 1982). Also, an increase in water depth increases the hydraulic retention time, slows water velocity, and increases sediment retention in constructed wetlands (Nichols, 1983). In wetlands with significant water depth gradients, the effect of depth has to be taken into account in order to test for the effect of vegetation.

The hypothesis that cattails play a direct role in metal retention was not supported in any of the four wetlands. This was unexpected as macrophyte beds are known to increase metal deposition. However, in all four wetlands studied, cattails did not cover the entire surface area. Flow paths may have developed around dense vegetation and carried the majority of the metal load resulting in higher metal concentration in open water sediments (Fennessy et al., 1994). In this study, however, vegetated sediments had similar concentrations of metals than unvegetated sediments in the Riverwalk and Panel wetlands. Similar results were obtained for the Falconbridge and Monahan wetlands when the effect of water depth was taken into account. In two boreal lakes, Kahkonen et al. (1997) also measured similar concentrations of metals in vegetated and unvegetated surface sediments.

A few recent studies also suggest that macrophytes do not contribute significantly to the retention of pollutants in constructed wetlands (Dombeck et al., 1998; Mitsch and Wise, 1998; Maehlum and Stalnacke, 1999). Mitsch and Wise (1998) showed that there was no apparent difference in metal retention between sediments with or without cattails in a surface-flow constructed wetland in Ohio. They calculated that cattails stored less than 0.1% of the annual inflow of iron to their surface-flow constructed wetland. Dombeck et al. (1998) showed that annual vegetation harvesting (mainly cattails) accounted for no more than 5% of annual metal retention. Also, ponds without cattails have been found to retain fecal coliforms as well as ponds with vegetation (Ansola et al., 1995). This is because the major retention mechanism of metals in surface-flow wetlands is through deposition of particulate metals onto surface sediments (Harlin et al., 1982; Carpenter and Lodge, 1986; Stevenson et al., 1988; Gilliam et al., 1988; Kadlec, 2000).

Macrophytes are then excluded from the retention mechanism since most of the plant uptake of nutrients and metals is from the sediment porewater and not from the overlying water column (Reddy et al., 1999). In addition, the metal content of plants is generally lower than that of sediments (Brix and Lyngby, 1983; Peverly, 1985; St-Cyr et al., 1994). The sediment compartment of wetlands appears to be a more important sink for metals than macrophytes.

However, there are studies that have shown a difference in metal concentrations between vegetated and unvegetated sediments (Otte et al., 1995; Kostka and Luther III, 1995; Caçador et al., 1996; Christensen, 1997; Doyle and Otte, 1997). A direct comparison of my study with these studies is difficult since metal concentrations within the root zone and within the bulk sediments were compared by analysing sediment profiles of about 20 cm in depth. These studies were not designed to test for the effect of macrophyte beds on metal deposition onto surface sediments but rather to examine the effect of oxygen supply through root leakage on the concentration profile of metals in sediments. In most cases, there was a metal enrichment in the rootzone as compared with nearby bulk sediment. However, one study by Otte et al. (1995) showed the opposite situation. There was higher Fe concentrations in the bulk sediments than in the rhizosphere of the plants. They attributed this result to differences in redox potentials. If redox potentials in bulk sediments are highly negative (below –100 mV), an important accumulation of Fe monosulfide in the bulk sediments can occur leading to higher Fe concentrations.

The wetlands chosen in the present study ranged from 4 to 38 years old. The age of the wetland may have affected the deposition of metals onto vegetated surface sediments. First, plant biomass and density increases as wetlands age (Mitsch and Gosselink, 1993; Mitsch et al. 1998). Therefore, as cattail beds increase in biomass and density, their capacity to decrease water currents and subsequently increase metal deposition should increase with the age of the wetland. However, there was no difference in the concentration of metals between vegetated and unvegetated sediments, and this difference occurred at both the Panel and Riverwalk wetlands even if the cattail density was higher for the older Panel wetland (unpublished data).

5.5.2 Metal partitioning in sediments

The partitioning of metals in vegetated surface sediments differed from unvegetated sediments at the Falconbridge and the Monahan wetlands. In these wetlands, the unvegetated sediments came from deeper water, which alone could explain the difference in the partitioning of metals. Accumulation of organic material and other inorganic particles like silicates and iron oxides in deeper water could lead to a different partitioning of metals. The two wetlands with no cross-sectional depth gradient (Panel and Riverwalk) showed similar partitioning in the two sediment zones.

I hypothesised that cattails would have an effect on the partitioning of metals in surface sediments. However, cattails generally did not affect the partitioning of metals in surface sediments (first two cm) of the surface-flow wetlands. One explanation is that diffusion of O_2 from cattail roots is limited. The oxidized layer around the roots of cattails is usually of the order of millimetres and depends on redox potential in the nearby sediments (Brix, 1994; Peverly et al., 1995). Also, the root biomass of cattails is low in comparison to other aquatic plants like *Juncus roemerianus* or *Spartina* spp. (Vymazal, 1995; Kvet and Westlake, 1998). The supply of oxygen is perhaps insufficient to alter reducing conditions occurring in the nearby surface sediments especially if they have high organic content.

The organic content of sediments was elevated especially in vegetated zones. These zones were an important source of organic matter to wetlands. Ansola et al. (1995) showed that ponds without cattails retained organic matter less efficiently than ponds with cattails. The vegetated sediments of all the constructed wetlands in this study had higher organic content (Fig. 5.3) suggesting that cattail beds enhance organic matter deposition onto surface sediments. Also, cattails contribute to the organic pool through senescence in the fall.

The rate of organic matter oxidation by microbial populations affects the partitioning of metals in surface sediments (Ehrlich, 1996). Microbial populations oxidize organic matter for energy requirements. If microbial respiration is intense (which can be indirectly measured by the redox state in sediments), bacteria will use oxygen, then nitrate, manganese and iron oxide, and sulfate as electron acceptors (Froelich et al., 1979). As a result, a change in redox potential, mediated by microbial respiration, will change the partitioning of metals in sediments. For example, most metals in the pore water will precipitate as metal oxides or will adsorb onto organic matter at redox potentials higher than 100 mV. From 100 mV to –100 mV metal oxides are reduced resulting in a release of dissolved metal in the pore water. These metals can still adsorb onto organic matter if adsorption sites are available. Below –100 mV, metals will be associated with monosulfides but also adsorbed onto organic matter (Froelich et al., 1979).

The redox potential of surface sediments differed between vegetated and unvegetated sediments of every wetland except for the Panel wetland. Therefore, a difference in the partitioning between vegetated and unvegetated sediments was expected in these wetlands. We also expected vegetated sediments to have higher redox potentials because of oxygen leaking from plant roots. However, surface sediments of all four wetlands had lower redox potentials (below –100 mV) in sediments with rooted cattails. This suggests that the oxidising capacity of plants has a minimal effect on the partitioning of metals as compared with microbial respiration in sediments.

The similarity in metal partitioning between vegetated and unvegetated sediments can perhaps be attributed to the choice of sequential extraction. The extraction method does not distinguish between dissolved metals, monosulfides or metals adsorbed onto organic radicals and Fe and Mn oxides, which perhaps explains the similarity in metal partitioning between vegetated and unvegetated sediments. For example, the vegetated sediments of the Falconbridge and Riverwalk wetlands with low redox potentials (< -100 mV) favour metal sulifide formation as opposed to unvegetated sediments with redox potentials higher than –100 mV which favor Fe and Mn oxide reduction. A difference in partitioning between vegetated and unvegetated sediments should have been detected. However, because the 1M HCl leachate is not specific to metal sulfides, I cannot compare the reactive fraction between vegetated and unvegetated sediments.

The partitioning of metals between vegetated and unvegetated surface sediments was generally similar for all wetlands suggesting that this similarity will be maintained as a wetland ages. However, the partitioning of metals in a wetland may change with age. Machemer and Wildeman (1992) demonstrated that the retention of metals in young wetlands relied on the presence of organic substrate as opposed to sulfate reduction in older wetlands. As a result, older wetlands like the Falconbridge and Panel wetlands should have more metals associated with metal monosulfides and the Riverwalk and Monahan wetlands should have more metals associated with organic matter. The sequential extraction does not distinguish between metals associated with monosulfides and metals adsorbed onto organic adsorption sites. However, the sequential extraction showed that the Falconbridge and Riverwalk wetlands had a significant proportion of metals associated with pyrite (~15 to 50%). The formation of pyrite is controlled by ferrous iron and hydrogen sulfide and therefore is a slow process as compared with metal sulfide co-precipitation (Schoonen and Barnes, 1991). As a result, time is needed in order to increase the pyrite fraction in the sediments, which could explain why the youngest wetland (Monahan) had a lower proportion of metals associated with pyrite than the older Falconbridge and Riverwalk wetlands. In the case of the old Panel wetland, redox potentials higher than –100 mV were measured in surface sediments, which would inhibit pyrite formation, but the latter probably occurred deeper in the sediments.

5.6 Conclusion

The presence of cattails in four surface-flow wetlands did not appear to affect concentration and partitioning of metals in surface sediments. Differences in metal concentration and partitioning were mainly due to differences in water column depth. However, sediments with rooted cattails had higher organic content than denuded sediments. Therefore, cattails likely supply a significant amount of organic substrate that fuels microbial activity. This study suggests that the effect of cattail beds on net metal deposition onto surface sediments of surface-flow constructed wetlands is minimal.

Table 5.1 Some physical and chemical variables of the four wetlands

Variables		Monahan	Riverwalk	Panel	Falconbridge
Age (years)		4	9	38	18
Mean depth (m)		1.5	0.5	0.19	1.5
Water storage (m^3)		53 000	5000	24 210	830 000
Drainage area (ha)		637	2.5	49	1200
TSS (mg L^{-1})	In	50.5	1400	--	--
	Out	20.3	10	--	--
Fe (mg L^{-1})	In	0.36	--	15	--
	Out	0.27	--	0.3	0.53
pH	In	7.82	--	6.32	--
	Out	8.04	--	7.12	6.89

Figure 5.1 Total concentrations of Fe, Mn, Zn, and Cu with associated standard deviation in vegetated and unvegetated surface sediments (0-2cm). The asterix (*) denotes significant differences between vegetated and unvegetated sediments (p<0.01).

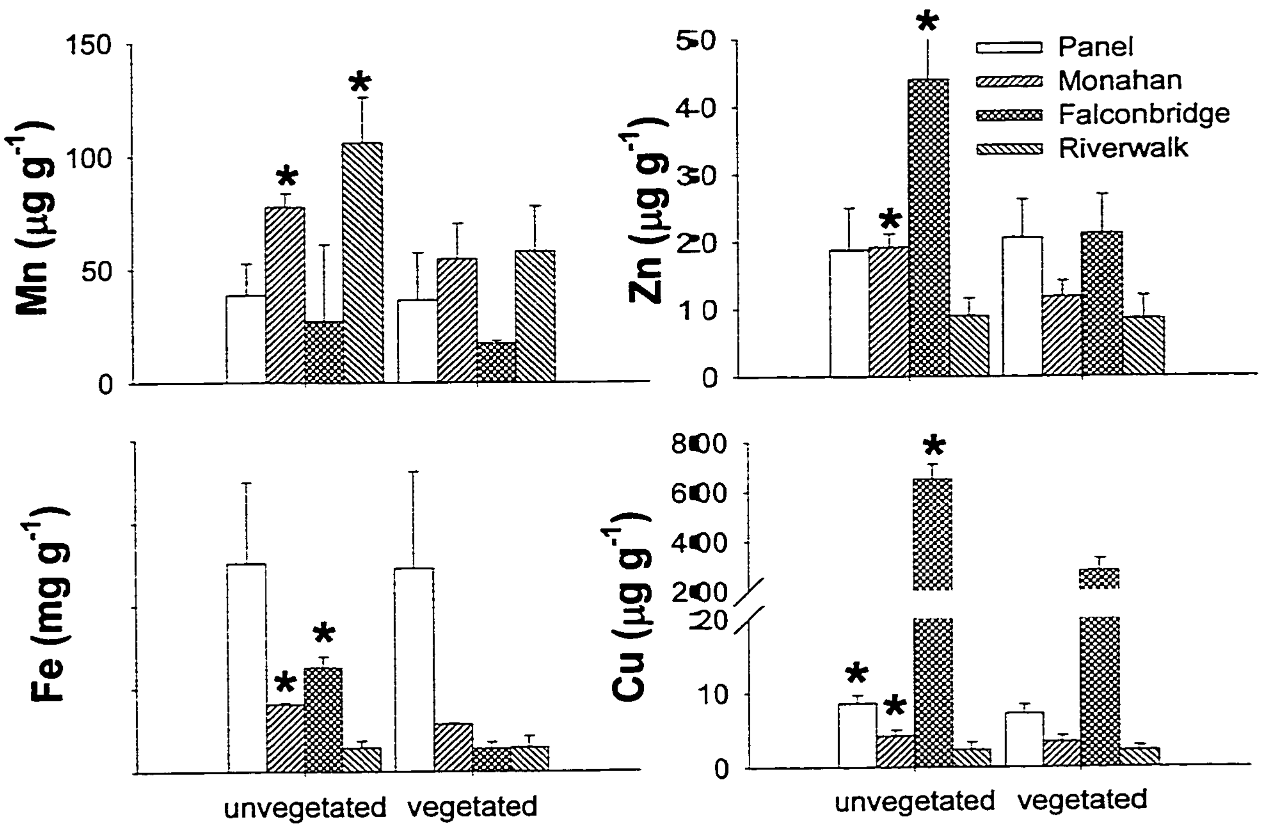

Mn (µg g^{-1})
150
100
50
0
*
*
Zn (µg g^{-1})
50
40
30
20
10
0
*
*
Panel
Monahan
Falconbridge
Riverwalk
Fe (mg g^{-1})
*
*
Cu (µg g^{-1})
800
600
400
200
20
10
0
*
*
*
unvegetated
vegetated
unvegetated
vegetated

Figure 5.2 Concentration of Fe, Mn, Zn and Cu in surface sediments (0-2cm) in relation to water column depth for the Monahan (●), and the Falconbridge (▼) wetlands.

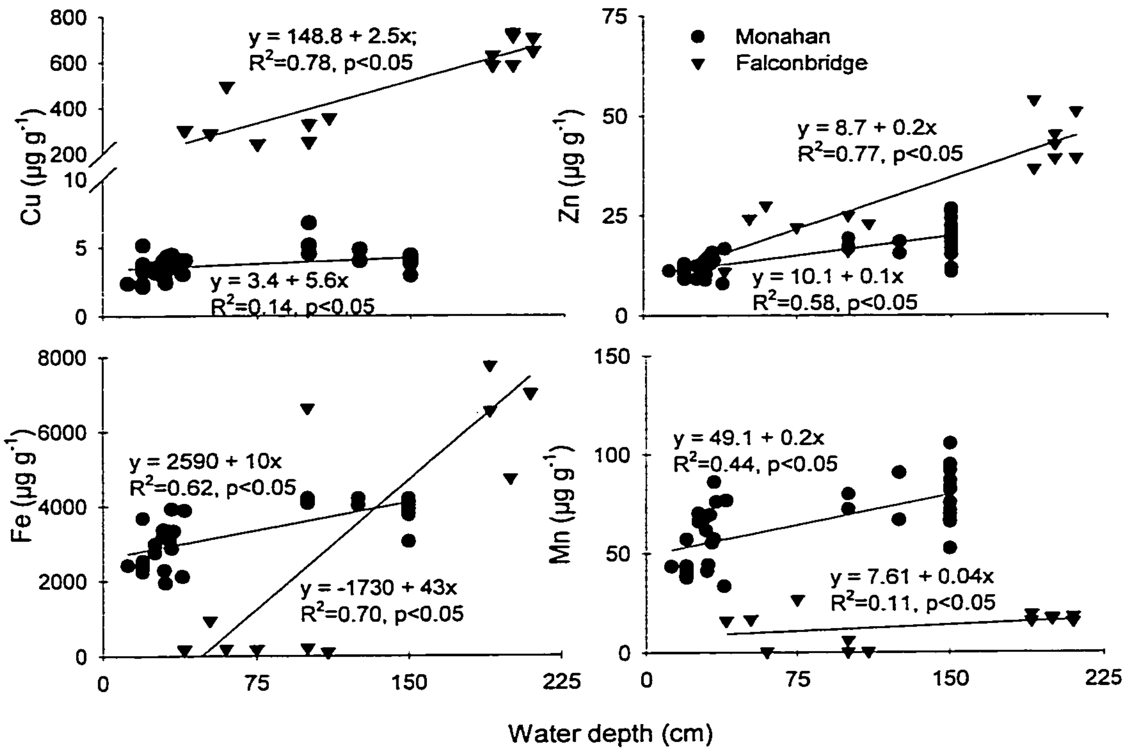

800
600
400
200
10
5
0
Cu (µg g-1)
y = 148.8 + 2.5x;
R2=0.78, p<0.05
y = 3.4 + 5.6x
R2=0.14, p<0.05
75
50
25
0
Zn (µg g-1)
● Monahan
▼ Falconbridge
y = 8.7 + 0.2x
R2=0.77, p<0.05
y = 10.1 + 0.1x
R2=0.58, p<0.05
8000
6000
4000
2000
0
Fe (µg g-1)
y = 2590 + 10x
R2=0.62, p<0.05
y = -1730 + 43x
R2=0.70, p<0.05
150
100
50
0
Mn (µg g-1)
y = 49.1 + 0.2x
R2=0.44, p<0.05
y = 7.61 + 0.04x
R2=0.11, p<0.05
0
75
150
225
0
75
150
225
Water depth (cm)

Figure 5.3 Average redox potential (lower panel) and percentage of organic matter as loss on ignition (upper panel) with associated standard errors in vegetated and unvegetated surface sediments (0-2cm) of four constructed wetlands. The asterix (*) denotes significant differences between vegetated and unvegetated sediments ($p<0.01$).

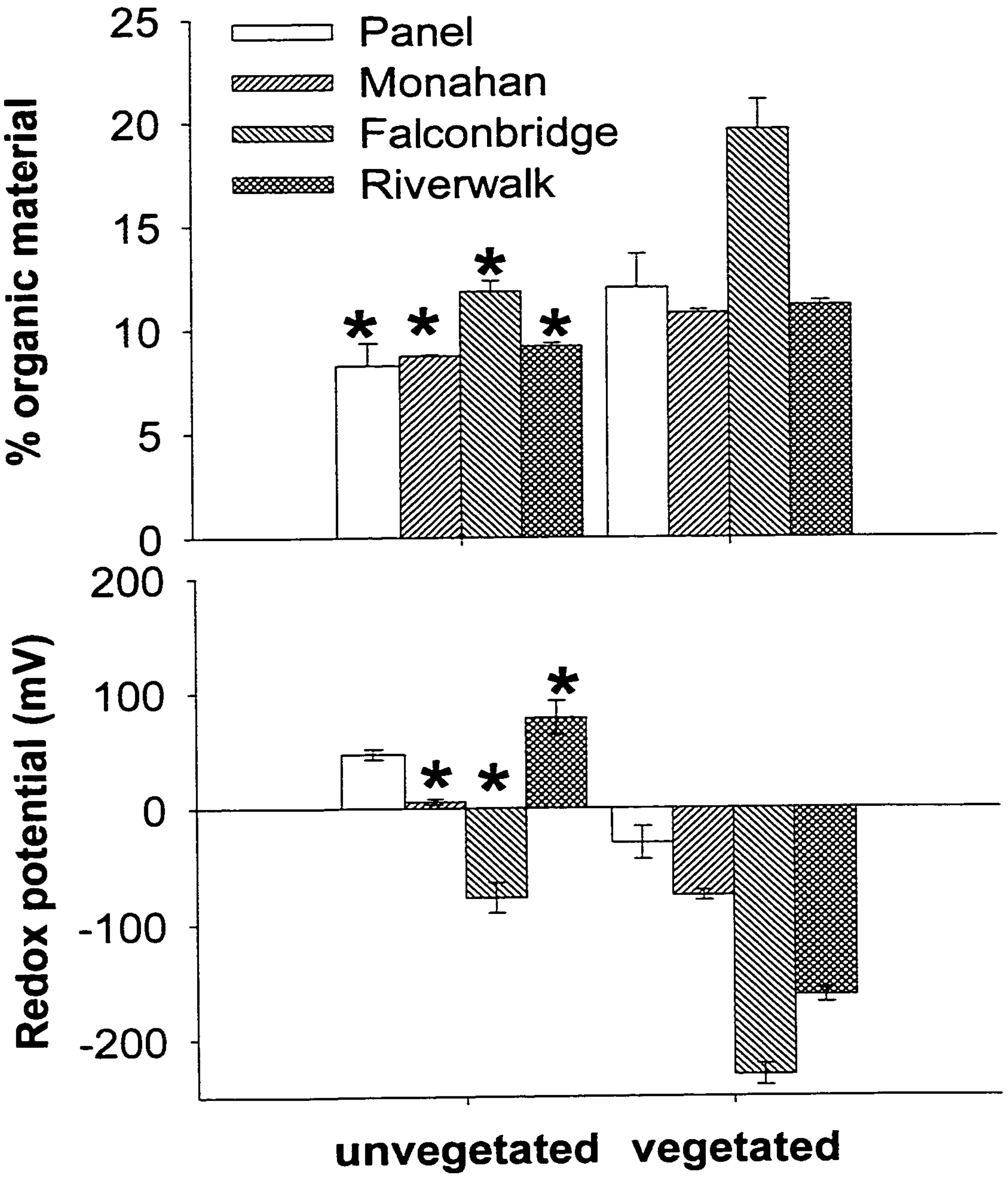
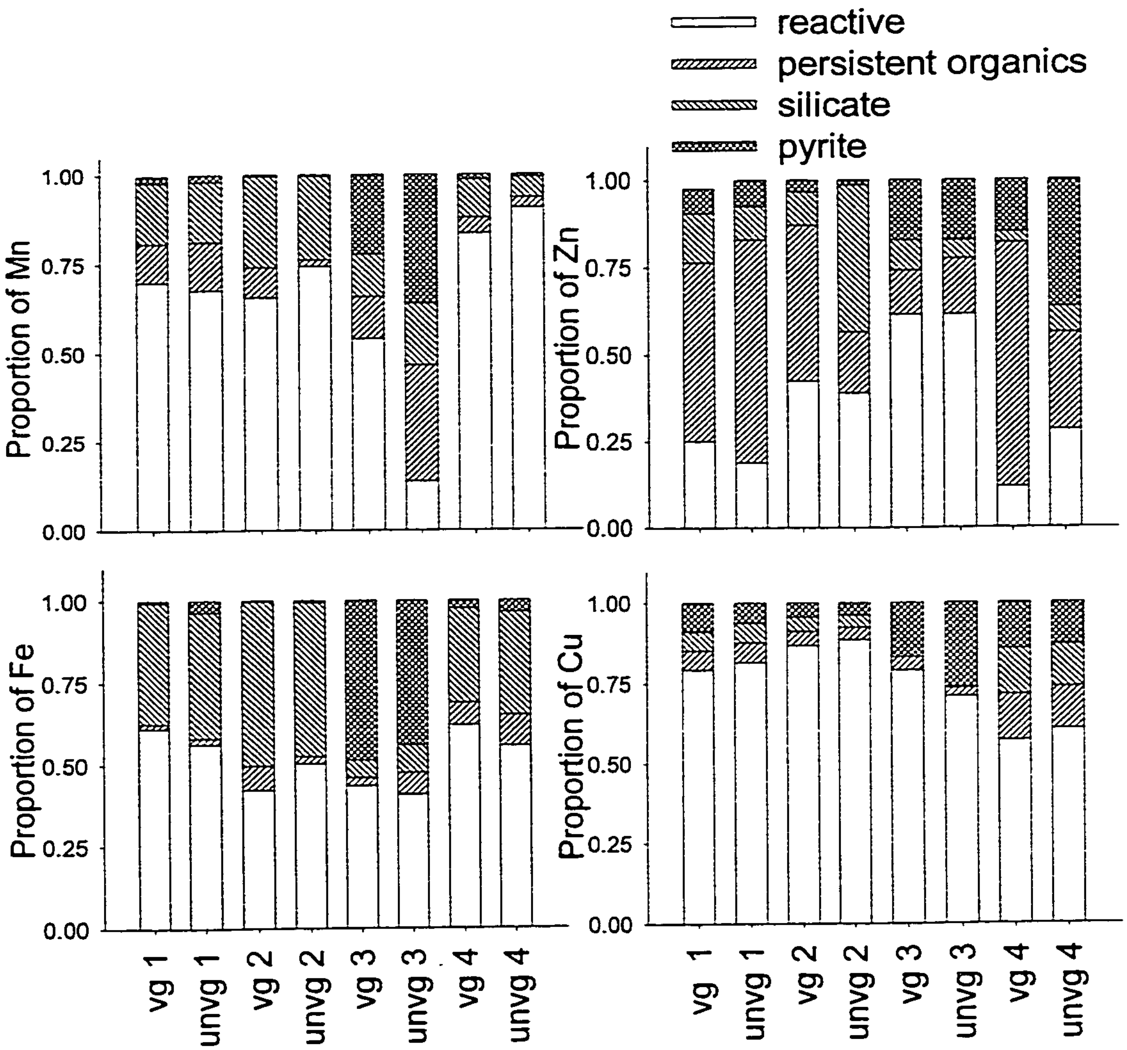

Panel
Monahan
Falconbridge
Riverwalk
% organic material
25
20
15
10
5
0
*
*
*
*
Redox potential (mV)
200
100
0
-100
-200
*
*
*
unvegetated
vegetated

Figure 5.4 Proportion of Fe, Mn, Zn, and Cu associated with different fractions in unvegetated (unvg) and vegetated (vg) surface sediments (0–2cm) of the 1) Panel 2) Monahan 3) Falconbridge and 4) Riverwalk wetlands.


reactive
persistent organics
silicate
pyrite
Proportion of Mn
Proportion of Zn
Proportion of Fe
Proportion of Cu
0.00
0.25
0.50
0.75
1.00
vg 1
unvg 1
vg 2
unvg 2
vg 3
unvg 3
vg 4
unvg 4

Chapter 6

General conclusion and design considerations for the use of surface-flow wetlands as water treatment systems under cold climates.

6.1 Summary of research findings

In Canada, surface-flow wetlands increasingly are used as water treatment systems despite the limited data available on treatment performance under northern climates (Pries, 1994). Wetlands are assumed to behave as sinks for pollutants (Mitsch and Gosselink, 1993). In Chapter 1, Fig. 1.3 showed that there is a great deal of variation in treatment efficiency. Under cold temperate climates, much of this variation may be related to seasonal changes that affect internal mechanisms responsible for metal retention. Therefore, the main goal of my thesis was to identify the factors and processes that control metal cycling in surface-flow wetlands and to examine how these processes vary on a seasonal basis under cold temperate climates.

Generally, surface-flow wetlands are designed so that the hydraulic residence time is long enough to allow the settling of particulate metals, which is believed to be the main mechanism responsible for metal retention (Gilliam et al., 1988). The removal of metals is assumed to follow first-order kinetics (Tarutis et al., 1999). In Chapter 2, I showed that the first-order removal model predicted metal retention only during a short period of the year, usually during spring. For the remainder of the year, the first-order removal model did not fit the data. The first-order removal model is inadequate to describe the retention of metals in a young wetland receiving agricultural and urban runoff. There is a need to consider seasonal changes and other variables that significantly affect the retention of metals.

The influence of planktonic algal biomass on the metal cycling in surface-flow wetlands deserves a closer examination in order to evaluate its role in the metal retention process. This is particularly important in young wetlands that are plankton dominated

(Mitsch et al., 1998) because emergent and submerged vegetation have yet to take over. Phytoplankton biomass was closely related to the changes in the ratio of dissolved to total Fe and Mn leaving the Monahan wetland (Chapter 3). The particulate metal fraction increased in the wetland because dissolved metal partitioned into algae. This process resulted in an export of particulate metals from the wetland during summer. During the winter, the ratio of dissolved to total metal was higher at the outlet than the inlet, which suggests a transformation of particulate into dissolved metals probably because anoxic sediments released dissolved metals.

Photosynthesis by algae and other aquatic plants may also affect indirectly the cycling of metals. Changes in oxygen and pH could explain 60 and 40% of the variability in Fe and Mn concentrations respectively (Chapter 4). Significant diel changes in Fe, Mn and to a lesser extent Zn, Cu, Ni and As were observed particularly during summer. As a result, the calculation of metal retention by surface-flow wetlands must consider the time at which water samples are collected.

Finally, I examined if the presence of emergent vegetation affects the metal concentration and partitioning in surface sediments. Cattails did not affect the concentration of metals in surface sediments (Chapter 5), suggesting that cattails have a minor impact on the net deposition of metals. However, cattails did contribute to increases in the organic content of surface sediments, which lead to lower redox potentials. Cattails may then affect indirectly the partitioning of metals by supplying an organic substrate for microbial respiration, which is responsible for mineral formation and dissolution in sediments (Ehrlich, 1996). However, I did not detect significant differences in the partitioning of metals in sediments with and without cattails in four different surface-flow wetlands.

The findings of this thesis provide new knowledge about the cycling and retention of metals in surface-flow wetlands. Although a generalisation of my results to other young surface-flow wetlands should be done cautiously, the goal of this chapter is to integrate the findings with the general knowledge of metal cycling and retention. This exercise will lead to suggestions about optimal wetland design as well as suggestions for further research in order to improve the performance of surface-flow wetlands for water treatment under cold climates.

6.2 Design considerations

6.2.1 Sizing wetlands for metal removal

The rate of pollutant removal in surface-flow wetlands can be either dependent (first-order) or independent of concentration (zero-order). In the case of metals, removal in surface-flow wetlands is concentration dependent and follows first-order kinetics (Tarutis et al., 1999). Particularly, the treatment efficiency $((C_i-C_o)/C_i)$ and first-order removal are exponentially related if the hydraulic loading rate (Q/A) is held constant:

$$((C_i-C_o)/C_i) = 1-\exp(k_aA/Q) \qquad (6.1)$$

Equation 6.1 allows the calculation of the surface area required to reach a target outlet concentration if the average inlet concentration of metals and the areal removal rate constant are known.

I tested the first-order removal model by relating treatment efficiencies to hydraulic retention time and discovered a relationship only during the spring (Chapter 2). During the spring, the cold water has high oxygen levels, which favours the oxidation of Fe^{2+} and Mn^{2+} and their precipitation at the sediment-water interface. The precipitation of Fe and Mn oxides should follow first-order kinetics if the hydraulic residence time is long enough to allow particles to settle. However, the first-order removal model could not predict metal removal for the remainder of the year.

Recently, Kadlec (2000) criticised the first-order removal model because plug-flow is largely an assumption. Most wetlands are not plug-flow nor completely mixed (Kadlec, 1994) because they have a spectrum of flow paths driven by vegetation density (Kadlec, 2000) and wetland morphology (Shaw et al., 1997), along which water moves at different speeds. As a result, in densely vegetated areas of wetlands, the water flow is slow and treatment is high and in poorly vegetated areas, the flow is fast and the treatment is low. Non-ideal flow can cause large errors in the estimation of rate constants and result in the failure of first-order removal models (Kadlec et al., 1993). Furthermore, the spectrum of flow path within wetlands varies seasonally because of changes in the distribution of macrophytes. Overall, it is essential to consider seasonal changes in the residence time distribution in the design of treatment wetlands.

In wetlands receiving urban and agricultural runoff, high primary production occurs because of nutrient rich waters. As a result, the sizing of a wetland based on first-order removal models may be difficult when biological variables are significantly affecting the cycling of metals. First, metals may rapidly partition into planktonic algal biomass and leave the wetland especially in young wetlands when emergent and submerged macrophytes have not substantially colonised the open water zones. Second, submerged macrophytes cause hydraulic resistance, which translates into non-ideal flow paths within wetlands. Finally, the high organic content in sediments provides abundant organic substrate that is utilised by bacteria for energy requirements (Pelmont, 1993). Intense microbial oxidation of the organic substrate in sediments by bacteria could lead to the entire consumption of the oxic layer when bacteria use Fe and Mn oxides as electron acceptors instead of oxygen in anoxic sediments (Tarutis an Unz, 1996). The disappearance of the oxic layer leads to the release of metals to the pore water and their diffusion into the water column (e.g., Carignan and Lean, 1991). Metal removal in productive wetlands is not irreversible when sediments become anoxic and therefore, metal removal is no longer first-order.

6.2.2 Biotic removal models for the design of created wetlands

Few studies have attempted to integrate biogeochemical variables in removal models (Christensen et al., 1994; Kadlec, 1997). Kadlec (1997) presented a phosphorus removal model based on "first-order biomass-based" rather than solely on the simple first-order removal model:

$$Q\ dC/dy = -K_N\ N_{max}\ [(C\text{-}Co)/((C\text{-}Co)+s)] \qquad (6.2)$$

Where Q is the flow rate ($m^3\ s^{-1}$), C is the concentration of total phosphorus, Co is the target concentration and s the half saturation concentration (the concentration of P at which the total biomass is half its maximum value, N_{max}) and K_N is the autobiotic rate constant, $g\ m^{-2}\ y^{-1}$. K_N can be obtained through the following equation:

$$K_N = [X_n m(1-\beta)] \tag{6.3}$$

Where X_n is the P concentration in biomass, m is the biomass death rate constant yr^{-1}, and β is the fraction of P returned to the water.

Kadlec (1997) argued that the first-order biomass based model was more appealing because of its simplicity (only five parameters). Kadlec's model shows that neither sorption nor biomass expansion contribute to the removal of phosphorus. The autobiotic model provides an intermediate alternative between the one parameter first-order removal model and the ecosystem compartment model proposed by Christensen et al. (1994).

The ecosystem compartment model for phosphorus removal was tested on four wetlands situated in the watershed of the Des Plaines River, Ohio (Christensen et al., 1994). The model was built on five sub-models: hydrology, sediment, primary production, macrophyte and phosphorus. Hydrology is only one out of five components of the model predicting phosphorus retention. Christensen et al. (1994) identified sedimentation as the major mechanism responsible for P retention in the Des Plaines wetlands. Similarly, the settling of particles is also believed to be the main metal removal mechanism in surface-flow wetlands (Gilliam et al., 1988). The settling (St) of particles can be expressed as a first-order reaction rate:

$$St = K_s \, V \, c \tag{6.4}$$

Where V is the water volume (m^3) and c the concentration of particulate metals and k_s is the first-order rate constant (s^{-1}). K_s can be expressed as:

$$K_s = v_s / D = [\alpha \frac{g}{18} \frac{(\rho_s - \rho_w)}{\mu} d^2]/D \qquad (6.5)$$

where v_s is the net settling velocity (cm s^{-1}), D is depth of the water column (m). The net settling velocity can be calculated with Stoke's law where α is a dimensionless form factor reflecting the effect of the particle's shape on settling velocity (for a sphere, it is 1.0), g is the acceleration due to gravity (cm s^{-1}), ρ_s and ρ_w are densities of the particle and water respectively (g cm^{-3}) μ is the dynamic viscosity (g cm^{-1} s^{-1}), and d is the particle diameter (Chapra, 1997).

It is important to consider the composition of settling particles. Inorganic and dead organic material settle because their density is higher than water (Eq. 6.5). In comparison, algal cells maintain their density close to that of water, which allows them to remain suspended in water (Wetzel, 1983). Therefore, the settling rate may be over-estimated when phytoplankton represents a large fraction of suspended material in the water column of wetlands.

Sigg et al. (1987) showed that the partitioning of metals in algae and their subsequent deposition onto bottom sediments was a major retention mechanism in lakes. Lakes are sinks for algal biomass because their long hydraulic residence times maximise algal deposition and minimise the algal export. However, in young wetlands or wetland emulating mashes, the hydraulic residence time is much shorter, which results in a significant export of metals partitioned into algal biomass (Chapter 3).

The age of a wetland and the nutrient loading are likely important parameters in the treatment performance of wetlands. The export of phytoplankton from constructed wetlands should be important in young wetlands where submerged and emergent plants have yet to take over phytoplankton as the dominant vegetation. The young age of a wetland treatment ecosystem combined with high nutrient loading coming from urban and agricultural runoff should increase the export of metal partitioned into phytoplankton biomass. As a wetland ages, the export of particulate metals should decline as submerged and emergent plants invade the wetland. Once completely established, the settling rate of particulate metals should increase because of a decline in phytoplankton biomass and a significant reduction in wave and wind-resuspension due to macrophytes colonisation.

The settling of particulate metals at the sediment-water interface results in an accumulation of metals in sediments. The change in metal concentration in sediments over time is expressed by the following equation:

$$dSM/dt = St\,(t) + MA_{decay}(t) - Dm_{res}(t) - M_{uptake}(t) \tag{6.6}$$

where St is the settling rate ($\mu g\ m^{-2}\ d^{-1}$) , MA_{decay} is metal concentration from plant decay ($\mu g\ m^{-2}\ d^{-1}$), Dm_{res} is the release rate of metals from the sediment to the water column ($\mu g\ m^{-2}\ d^{-1}$) and M_{uptake} is the metal uptake rate by rooted macrophytes ($\mu g\ m^{-2}\ d^{-1}$) (Christensen et al., 1994). The effect of decaying cattails on the concentration of surface sediments can be assumed to be minimal. My data suggest that the presence of cattails do not contribute significantly to the metal content of surface sediments because the concentrations in the first two centimetres of both vegetated and unvegetated sediments were similar in all four wetlands that we sampled. As well, Mitsch and Wise (1998) showed that there was no apparent difference in metal concentrations between sediments with or without cattails in a surface-flow constructed wetland in Ohio.

Similarly, the effect of metal uptake by macrophytes (M_{uptake}) on the concentration of metals in sediments should be negligible. A few recent studies suggest that macrophytes do not contribute significantly to the retention of pollutants in constructed wetlands (Dombeck et al., 1998; Mitsch and Wise, 1998; Maehlum and Stalnacke, 1999). The change in metal concentration in sediment should then simplify to:

$$dSM/dt = St(t) - Dm_{res}(t) \qquad (6.7)$$

According to equation 6.7 the long term accumulation or removal of metals depends on the relative importance of both the settling rate of particulate metals and the release of metals from the sediments. I have already discussed the variables that affect the settling rate of particles previously in this Chapter. On the other hand, the conditions under which metals are released to the water column are not as well known.

First, sediment resuspension has received some attention and can be calculated if the wind velocity, the mean water depth, the fetch and the wave height and period are known (Chapra, 1997). Secondly, dissolved metals are also released to the water column when surface sediments become anoxic (Wetzel, 1983). Under these conditions, dissolved metals can diffuse out of the sediments to the water column because the oxic zone was consumed. The oxic zone is mainly constituted of Fe and Mn oxides that are consumed through dissimilatory Fe and Mn reduction when oxygen and nitrate are depleted in surface sediments (Tarutis and Unz, 1996). In addition, the release of metals from the sediment to the water column was probably underestimated in most wetland studies because diel changes in metal concentrations at the sediment-water interface have been overlooked (Chapter 4). In chapter 4, I showed an increase in Fe, Mn and Zn concentrations into the water column over night because pH and oxygen decreased. In contrast, high pH and oxygen levels during the day favor the precipitation of Fe and Mn oxides at the sediment-water interface.

Overall, an accurate estimation of the long-term burial of metals relies on an accurate estimate of the two parameters in equation 6.7. An accurate settling rate S(t) should be obtained by measuring the fraction of total suspended solids represented by phytoplankton. Finally, an accurate release rate of metals to the water column (D_{mes}) should be obtained by measuring sediment resuspension and by measuring Fe^{3+} and Mn^{4+} bacterial reduction, which is influenced by diel changes in oxygen and pH at the sediment-water interface.

6.2.3 Season

Temperature affects the rate of many biogeochemical processes related to pollutant retention by surface-flow wetlands and its inclusion in biotic removal models is essential. This is even more important in Northern created wetlands, where the temperature of surface waters typically varies between 0-30°C.

The Van't Hoff-Arrhenius equation (see equation 2.2 in Chapter 2) predicts an increase in the reaction rate constant with an increase in temperature within the 0-30°C range (Reddy and Burgoon, 1996; Chapra, 1997). An appealing approach is using the

Van't Hoff-Arrhenius equation to relate changes in temperature with changes in the removal rate constant (Reddy and Burgoon, 1996). Based on this equation, the removal rate constant increases with an increase in temperature. This leads to the general belief that removal should be high during warm season. However, high temperature does not necessarily leads to high removal as suggested by the Van't Hoff-Arrhenius equation.

The use of the removal rate constant in the Van't Hoff-Arrhenius equation is incorrect because the reaction rate constant does not necessarily translate into a removal rate constant. Many biogeochemical processes promote metal releases from wetlands. For example, the uptake of metals by phytoplankton increases with temperature, but algae may leave the wetland and therefore, the removal rate constant decreases with increasing temperature. At the Monahan wetland, the retention of Fe decreased steadily from spring to late summer because phytoplankton biomass was increasingly exported as temperature and solar radiation increased during summer. Also, dissimilatory Fe and Mn reduction, that are biologically mediated, increases with an increase in temperature. The reduction of Fe and Mn oxides result in a release of these metals to the water column and therefore, the removal rate constant decreases with increasing temperature.

There is some concern that constructed wetlands cannot operate efficiently at low temperature (Kadlec and Knight, 1996). The retention of metals by the Monahan wetland was indeed low during winter. However, the decrease in retention was probably not directly related to a decrease in temperature. The release of metals by the Monahan wetland occurred because of anoxic conditions in sediments (Fortin et al., 2000; Chapter 3). This result suggests that bacterial populations were still active during the winter.

The effects of temperature on microbial growth and reduction rates have been studied in cold climate sediments, such as the Arctic and Antarctic (Pelmont, 1993; Isaksen and Jogersen, 1996; Sageman et al., 1998). Sageman et al. (1998) showed growth of sulfate reducing bacteria from Arctic sediments. The same studies concluded that sulfate reduction rates were more dependent on substrate supply than temperature. At the Monahan wetland, the number of sulfate reducing bacteria was higher during the winter than during the summer (Fortin et al., 2000). Sulfate reducing bacteria have the capacity to increase their numbers in cold temperature to compensate for lower activity per cell (Batal, 1989; Fortin et al. 2000). Similarly, Fe and Mn reducing bacteria likely increased their numbers during winter at the Monahan wetland.

6.3 Design recommendations

Christensen et al. (1994) identified sedimentation as the main removal mechanism in surface-flow wetlands. As discussed in section 6.2, the sedimentation of metals depends on the settling rate of particles and also on the release of metals from the sediments.

The design of surface-flow wetlands should consider the variables that affect the settling of particulate metals. As discussed earlier, the settling of particulate metals may decrease significantly if algal biomass represents a great proportion of the particulate metal fraction. As a wetland ages, the vegetation switches from planktonic plants to submerged and emergent macrophytes. Therefore, the establishment of submerged and emergent vegetation, which limit algal growth and the export of metals should be promoted. The advantages of introducing emergent and submerged macrophyte in surface-flow wetlands are several. First, macrophytes can outcompete phytoplankton for light resulting in a significant decrease of the particulate metal export through algal biomass. Second, submerged macrophytes may serve as a physical substrate for epiphyton and bacteria growth that take up metals directly from the water, which would result in an efficient biofilm (Khatiwada and Polprasert, 1999). Third, the presence of macrophytes should shade the sediments, which would limit the release of metals during the day because of Fe^{3+} photoreduction at the sediment-water interface (Chapter 4). Finally, the presence of rooted macrophytes reduces the amount of deposited sediments that can be resuspended by wave and current action and exported from a wetland (Ward et al., 1984; Stevenson et al., 1988). Therefore, the variables affecting the establishment of macrophytes should be considered in the design of surface-flow wetlands.

The establishment of emergent and submerged macrophytes depends on water depth, flow rate, nutrient availability, and sediment characteristics (Fennessy et al., 1994). Water depth determines if the wetland will be dominated by emergent or submerged macrophytes. Both submerged and emergent vegetation limit phytoplankton growth. In practice, the dominance of macrophytes versus phytoplankton can be difficult to predict in shallow systems (Moss et al. 1996).

Water depth also affects diel changes in metal concentrations induced by photosynthesis as they occurred predominantly in shallow water (<0.5 m). Diel changes were responsible for a significant over-estimation of metal retention at the Monahan wetland. A deep wetland would then limit diel changes in metal concentrations leaving the wetland. Therefore, a typical maximum depth of 1.5 m would be appropriate for surface-flow wetlands. In 1.5 m, diel changes in metal concentrations induced by photosynthesis were not observed at the Monahan or the Falconbridge wetlands (Chapter 4). Furthermore, diel changes in metal concentrations should be minimal if submerged macrophytes shade surface sediments, thus preventing Fe^{3+} photoreduction.

Anoxic conditions occurred at 1.5 m at the Monahan wetland near the inlet (Goulet pers. comm.). The establishment of anoxic conditions can result in a net release of dissolved metals from the sediments to the water column. Deep metal rich water should be isolated from surface water during the growing season because of some thermal stractification. However, deep metal rich water may leave a wetland if it is a young ecosystem deprived of emergent and submerged vegetation where the whole column mixes because of wind induced turbulence. As a wetland ages, mixing of the water column decrease because of submerged macrophyte colonisation. Submerged macrophytes should also supply enough oxygen in deep water to favor oxidation and prevent the establishment of anoxic conditions.

However, in nutrient rich wetlands, the aeration of bottom sediments may be necessary (Kadlec and Knight, 1996). Aeration would inhibit diel changes in metal concentration induced by photosynthesis and respiration, allow the build up of an oxic layer on top of sediments preventing the release of metals to the water column. However, aeration systems may be expensive and would require maintenance. In some cases, it may be easier to control for phosphorus loading, which is usually the limiting factor to primary production in aquatic systems (Wetzel, 1983).

Surface-flow wetlands situated in cold temperate climates are exposed to low temperatures and ice can cover surface-flow wetlands from 3 to 4 months. The ice cover can act as a barrier to oxygen transport from the atmosphere to the water column. The decrease in metal retention during the winter is likely more related to anoxia than low temperature. It may be necessary to prevent anoxic conditions during the winter in order to increase metal retention.

As autobiotic removal models are still not considered, wetland treatment systems are mainly designed based on the first-order removal model despite its inadequacies (Kadlec, 2000). Internal hydraulics should be considered when using the first-order removal. The first-order removal model may be applicable only when homogeneous flow occurs within wetlands. Vegetation should be spread evenly over the surface area of the wetland, which would result in ideal flow (Bastian and Benforado, 1988). However, ideal flow is unlikely in surface-flow wetlands because of their bathymetry and the usual uneven distribution of aquatic vegetation. It may be necessary to intercept, treat and disrupt the water that tends to travel along higher speed paths to the outlet (Kadlec, 2000). The compartmentalisation of wetlands can do this (Matthews et al., 1997). A system of baffles forces the whole water mass to take the same path resulting in a unique hydraulic residence time value. If the system of baffles is coupled with strategic placement of vegetation, treatment may be increased significantly and should follow first-order removal models. Finally, the wetland should be designed in order to avoid short-circuiting. This could greatly be minimised by the creation of a water storage basin prior to the wetland in order to avoid flushout events and ensure that flow is relatively constant all year round.

6.4 Research needs

This thesis addressed several mechanisms involved in the cycling and retention of metals in surface-flow wetlands. This led to some design considerations for surface-flow wetlands receiving agricultural and urban runoff. However, much research remains to be done especially under cold temperate climate.

First, it is important to evaluate the long-term potential of constructed wetlands to retain metals. Long-term studies are few and originate mainly from the USA (e.g. Houghton Lake project in Kadlec and Knight 1996). There is also a need to evaluate the effect of age on the treatment efficiency of metals. Kadlec and Knight (1996) suggest that a wetland needs approximately three years to reach its full treatment potential but this may not be the case for wetlands situated in cold temperate climates.

Furthermore, simple first-order removal models are not appropriate to design surface-flow wetlands unless compartmentalisation is done (Kadlec, 2000). More complex models are needed, which should integrate more internal detail than is provided by inlet-outlet measurements. A better understanding of internal hydraulics appears essential for the improvement of treatment wetland modelling.

Also, removal models should integrate biogeochemical mechanisms. I showed that diel changes in metal concentrations significantly affected the retention of metals but also affected the overall variability in metal retention on a yearly basis. Therefore, it is necessary to address under which conditions diel variations occur. For example, the effect of water depth and the presence of submerged macrophytes in relation to diel changes in metal concentrations need further examination. Also, few studies have yet to consider phytoplankton as a significant carrier of metals especially in young wetlands where submerged and emergent vegetation have yet to establish. The effect of submerged macrophyte beds on the retention of metals should also be studied further. As submerged macrophytes are sedentary, they may remove metals directly from the water or provide a physical substrate for the growth of a biofilm of bacteria and epiphytes, which should remove metals directly from the water. Few studies have addressed this mechanism (Khatiwada and Polprasert, 1999). Furthermore, a metal budget should be done in the fall to identify to what extent metals are released during macrophyte senescence compared with the removal done during the summer. Jackson et al., (1994) showed that macrophyte beds were significant sinks for metals on a yearly basis even if some release of particulate metals occurred during senescence. Finally, all these studies should be done on a seasonal basis as temperature affects significantly the retention mechanisms.

7.0 References

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8.0 Appendices

8.1 Appendix I : Description of symbols

Symbol	Description
A	Surface area (m^2)
A_s	Surface area of sediments (m^2)
A_v	Van't Hoff-Arrhenius coefficient
C	Concentration (µg L^{-1}, mg L^{-1})
C_I	Inlet concentration (µg L^{-1}, mg L^{-1})
C_o	Outlet concentration (µg L^{-1}, mg L^{-1})
C_p	Concentration of particulate metals (µg L^{-1}, mg L^{-1})
D	Water depth (m)
d	Particle diameter (cm)
Dm_{res}	Release of metals from sediments to the water column (µg m^{-2} d^{-1})
E	Activation energy (J mol^{-1} K^{-1})
ES	Early summer season
ET	Evapotranspiration rate (mm d^{-1})
F	Fall period (d)
G	Accelaration due to gravity (9.8 m s^{-2})
H	Head of a weir (m)
I	Inlet
JA	Mass removal rate (Kg d^{-1})
J	Specific mass removal rate (Kg m^{-2} d^{-1})
K	Removal rate constant (d^{-1})

Symbol	Description
K_a	Areal removal rate constant (d^{-1})
K_N	Autobiotic rate constant (g m^{-2} d^{-1})
K_s	First-order rate constant (s^{-1})
K_v	Volumetric removal rate constant (d^{-1})
L	Crest length of a weir (m)
LS	Late summer period (d)
M	Mass rate (Kg d^{-1})
MA_{decay}	Metal concentration from plant decay (μg m^{-2} d^{-1})
M_i	Inlet mass rate (Kg d^{-1})
M_o	Outlet mass rate (Kg d^{-1})
M_{uptake}	Metal uptake rate by rooted macrophyte (μg m^{-2} d^{-1})
N_{max}	Total maximum biomass
O	Outlet
P	Precipitation rate (mm d^{-1})
Q	Surface water flow rate (m^3 d^{-1})
Q_b	Bank loss rate (m^3 d^{-1})
Q_c	Catchment runoff rate (m^3 d^{-1})
Q_{gw}	Groundwater flow rate (m^3 d^{-1})
Qi	Surface water inflow rate (m^3 d^{-1})

Symbol	Description
Q_o	Surface outflow rate ($m^3\ d^{-1}$)
Q_{sm}	Water flow rate attributed to snowmelt ($m^3\ d^{-1}$)
q	Hydraulic loading rate ($m\ d^{-1}$)
R	Gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$)
S	Spring period
s	Half saturation concentration of phophosphorus in total maximum biomass
St	Settling rate ($g\ m^{-2}\ d^{-1}$)
Su	Summer period
t	Hydraulic retention time (d)
T	Temperature (°C)
V	Water storage, volume of water (m^3)
v_s	Net settling velocity ($m\ s^{-1}$)
X_n	Concentration of an element in biomass ($\mu g\ g^{-1}$)
α	A dimensionless form factor reflecting the effect of a particle shape on settling velocity
β	Fraction of phosphorus returned to the water column
μ	Dynamic viscosity ($g\ cm^{-1}\ s^{-1}$)
ρ_w	Water density ($g\ cm^{-3}$)
ρ_s	Density of a particle ($g\ cm^{-3}$)