



CHALMERS UNIVERSITY OF TECHNOLOGY
Department of Sanitary Engineering
Applied Environmental Measurement Techniques

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MASTER THESIS

Metal Removal in a Pilot Scale
Upflow Macrophyte System

MARIA JOY N DAIGO

Master Thesis 1997:3



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ABSTRACT

Heavy metals such as lead, zinc, copper and cadmium are discharged in stormwater at high concentrations. These pollutants, particularly the dissolved species are potentially toxic and can pose an ecological imbalance. To mitigate this problem, several studies on stormwater pollution control have been conducted. One of the emerging technologies which can provide effective, low-cost treatment is the use of constructed wetlands for stormwater management.

In this study, the performance of a pilot scale upflow macrophyte system for metal removal is investigated. The system has a sand-based substrate and is planted with *Phragmites australis*. Results showed that the system exhibited variations in the subsurface profile. High treatment efficiencies were observed at the topmost outlet (0.5 m) for Pb, Cu and Cd; while Zn demonstrated high removal in the 0.1 m depth. Plant maturity was found to influence the performance of the system. In the early stage of plant growth (June), treatment efficiencies of 63%, 56%, 13% and 8% for ionic dissolved Zn, Pb, Cu and Cd were noted respectively. Treatment efficiencies increased significantly in August-September to 81%, 71%, 46% and 25% for ionic dissolved Zn, Pb, Cu and Cd respectively. Likewise, removal efficiencies of total Pb, Zn, Cu and Cd were also significant at 71, 62%, 51% and 48% respectively. Fractionation results showed that removal efficiencies of particle bound and colloidal fractions were high; about 88.3% and 100% for Pb and 73.4% and 90% for Zn. Whereas, Cu and Cd showed significant removal in the ionic dissolved phase at 91.4% and 59% respectively. The effect of retention time on metal removal was also investigated and has shown that 2 hours can attain significant treatment. Ionic dissolved Pb and Cu achieved 100% removal after only 2 hours, while Zn achieved treatment efficiencies at 71%, 60% and 69% for 2, 5 and 10 hours respectively. Cd is more difficult to remove and exhibited an increase in concentration with increasing retention time.

Keywords: Phragmites australis, heavy metals, upflow system, stormwater,

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1. INTRODUCTION

Constructed wetlands for wastewater treatment have recently emerged as a possible alternative to more conventional systems. These systems mimic natural wetlands and are economical, requiring little or no energy for operation. Constructed wetlands combine biological, chemical and physical mechanisms for water quality improvement (Crites, 1992).

The applicability of constructed wetlands for domestic and industrial wastewater treatment is widely recognized. Likewise, the use of this system to manage stormwater is becomingly more popular (Cutbill, 1994; Livingston, 1989). It is now recognized that wetland treatment systems enhance the removal and uptake processes which trap sediment, nutrients, microorganisms and heavy metals as well as enhancing oxygen recovery (Ellis, 1993). A great deal of investigation has been carried out on the applicability of constructed wetlands for nutrient removal (Rogers *et al.*, 1990). However, only a few studies have been conducted on how wetland treatment systems affect trace elements (Crites *et al.*, 1997; Mungur *et al.*, 1997; Kadlec and Knight, 1996).

In urban areas, stormwater is polluted with heavy metals (Morrison *et al.*, 1984) from automobiles, atmospheric deposition, corrosion of building materials, and sewer systems. Metals such as Pb, Zn, Cu and Cd are bound to particles, either in a mineral particulate or dissolved form and are not biodegradable. These pollutants pose an environmental risk when accumulated in water and sediments.

Several investigations have been carried out for the selection of treatment methods for stormwater quality improvement. The use of a stormwater detention pond is widely recognized as a useful method for treating stormwater (Yousef *et al.* 1994). On the other hand, constructed wetlands

offer a promising option for stormwater pollution control (Ellis, 1993). Comparison between natural and constructed wetlands has shown that the latter offers better efficiency in stormwater treatment (Strecker *et al.*, 1992; Livingston, 1989).

Constructed wetlands have a number of basic functional elements which facilitate the treatment of metals found in stormwater. Processes of removal include adsorption, complexation, chemical precipitation, sedimentation, microbially-mediated reactions including oxidation and reduction and plant uptake (Reed *et al.* 1995; Dunbabin and Bowmer, 1990; Chan *et al.*, 1982). Design and hydraulic properties, such as vertical upflow and horizontal format play a significant role in the performance of a constructed wetland. The former is more preferable (Breen and Chick, 1989), since the latter is more susceptible to short-circuiting (Breen and Chick, 1995; Brett, 1989; Bowmer, 1987) and requires an extensive area for operation. In addition, plants in constructed wetlands also influence treatment efficiencies (Brix, 1994). Dunbabin *et al.*, (1988) demonstrated that metal retention of Cd, Cu, and Zn was higher in planted miniature gravel-based substrates than in those without plants. The use of rooted macrophytes has shown promise for removing metals. In this study, the potential of constructed wetlands for metal removal in stormwater, using a pilot scale upflow macrophyte system planted with *Phragmites australis* has been investigated.

2. AIMS AND OBJECTIVES OF THE STUDY

The main objective of this study is to assess the performance of a pilot scale vertical macrophyte system for the removal of Zn, Pb, Cu and Cd from stormwater. Specifically, the study focused on the following investigations:

1. Determination of treatment efficiencies, effective retention time and concentration profiles for Pb, Zn, Cu and Cd in the system.
2. Characterization of Pb, Zn, Cu and Cd partitioning and the removal of defined fractions in the system.

3. BACKGROUND

3.1. Wetland Wastewater Treatment Systems

Low cost and simple technology like wetland systems are attractive alternatives for improving water quality. Contaminant removal processes in these systems rely on the physical, chemical and biological processes found in soils, ponds and marshes. Compared with conventional wastewater treatment processes that are mechanically complex and require consumptive artificial energy for its operation, wetland systems are simple and cost-effective, utilizing solar energy to drive the desired reactions.

Wetlands are considered as a transition zone that is neither terrestrial nor aquatic. Specifically, they are defined as lands having a surface and sub-surface water table or which are saturated for a long enough period to enhance aquatic processes as indicated by hydric soils, hydrophilic vegetation and different kinds of biological activity which are adapted to the wet environment (Tarnocai, 1979). This description applies to a wide range of systems, including marshes, meadows and others. Generally, wetlands are classified as: 1) natural wetlands: without human alteration 2) restored wetlands: reconstructed on former wetland sites 3) created wetlands: constructed on sites where no wetland has existed and primarily to compensate for natural wetlands lost to development 4) constructed wetlands: constructed with the intent of managing water quality.

However, natural, restored and created wetlands are not suitable for wastewater treatment because of their ability to significantly alter the ecology of the system. The resulting changes are often not desirable in terms of the wildlife habitat value, biotic diversity and aesthetics. In addition, flow channels in natural systems may be prone to short circuiting which reduces treatment effectiveness. Constructed wetlands on the other hand, are considered as the only wetland systems that are really satisfactory for

wastewater treatment. Components of constructed wetlands, such as flow paths, water depths, water distribution and vegetation can be designed to be compatible with the influent stream and to produce desired effluent quality.

Constructed wetlands undergo wastewater treatment through their many naturally occurring physical and biogeochemical properties. The complex interaction between substrate, plants and microorganisms is responsible for the processes that remove and transform pollutants into harmless forms (Figure 1). These removal mechanisms include: 1) oxidation 2) reduction 3) volatilization 4) adsorption 5) sedimentation 6) precipitation 7) plant uptake 8) peat formation.

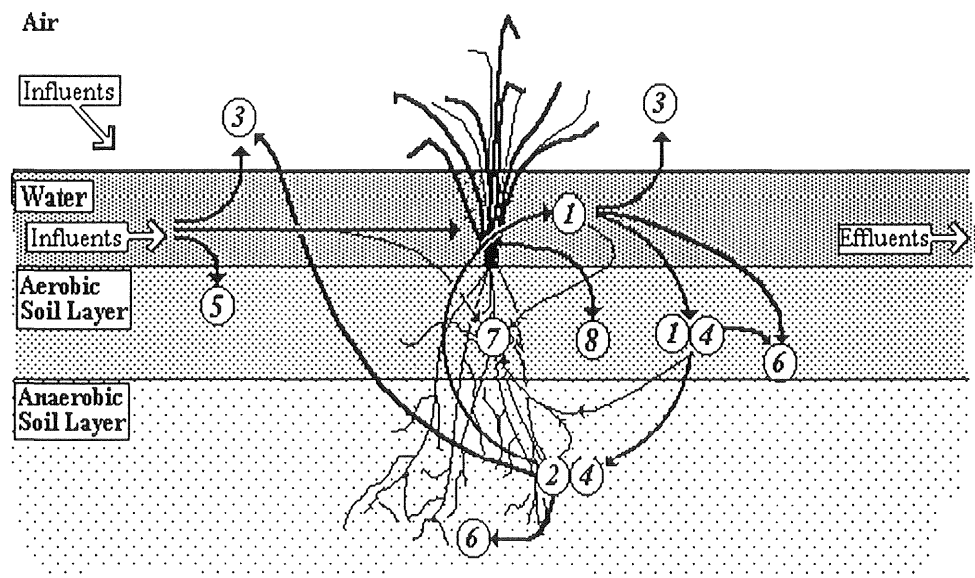


Figure 1. Pollutant Removal Mechanisms of Constructed Wetlands (Kim and Reid, 1997)

3.1.1. Metal Removal

In constructed wetlands, the main pools of metals are found in the substratum, in suspended particulate matter or in colloidal material as free ions or soluble inorganic and organometallic complexes. In the water column, metals occur in a soluble fraction consisting of hydrated ions and complexes, both organic and inorganic.

The removal of metal ions in constructed wetlands depends first of all on the intensity of intrawater body processes, which favor reducing the concentration of free heavy metal ions as the most toxic form. These processes include: adsorption on suspended particles; sedimentation and co-precipitation; complexation with ligands of organic origin; hydrolysis and formation of low soluble compounds; plant uptake and microbially mediated reaction such as reduction and oxidation.

Adsorption

Adsorption, coupled with subsequent sedimentation is the primary removal mechanism of metals (Figure 2). Adsorption occurs when a solid surface attracts and retains a layer of ions or molecules from the solution (Fetter, 1988). Metals are adsorbed in various sediment media such as sulphides, iron and manganese oxyhydrates, particulate organic matter, clays, humic compounds, chloride and hydroxyl ion (Novotny, *et al.*, 1994; Manahan, 1994).

In aerobic sediments the sorption sites are provided by organic carbon, clays and hydrous oxides of iron and manganese. The former is thought to be a very important mechanism in controlling the distribution of metals. The sorption capacity of different sediment particles increases in the order: hydrous manganese oxides > humic acids > hydrous iron oxides > clay

minerals. However, sorption capacity varies for different metals (Taylor *et al.*, 1983). For example, copper and zinc are strongly adsorbed in iron oxide phases.

In anaerobic sediments, iron and manganese oxides are reduced. However, sulphides, become the major complexing ligands. Sulphides, particularly the particulate fraction are found in sediments with sand and gravel texture that do not resemble the anoxic sulfidic sediments (Di Toro, 1990).

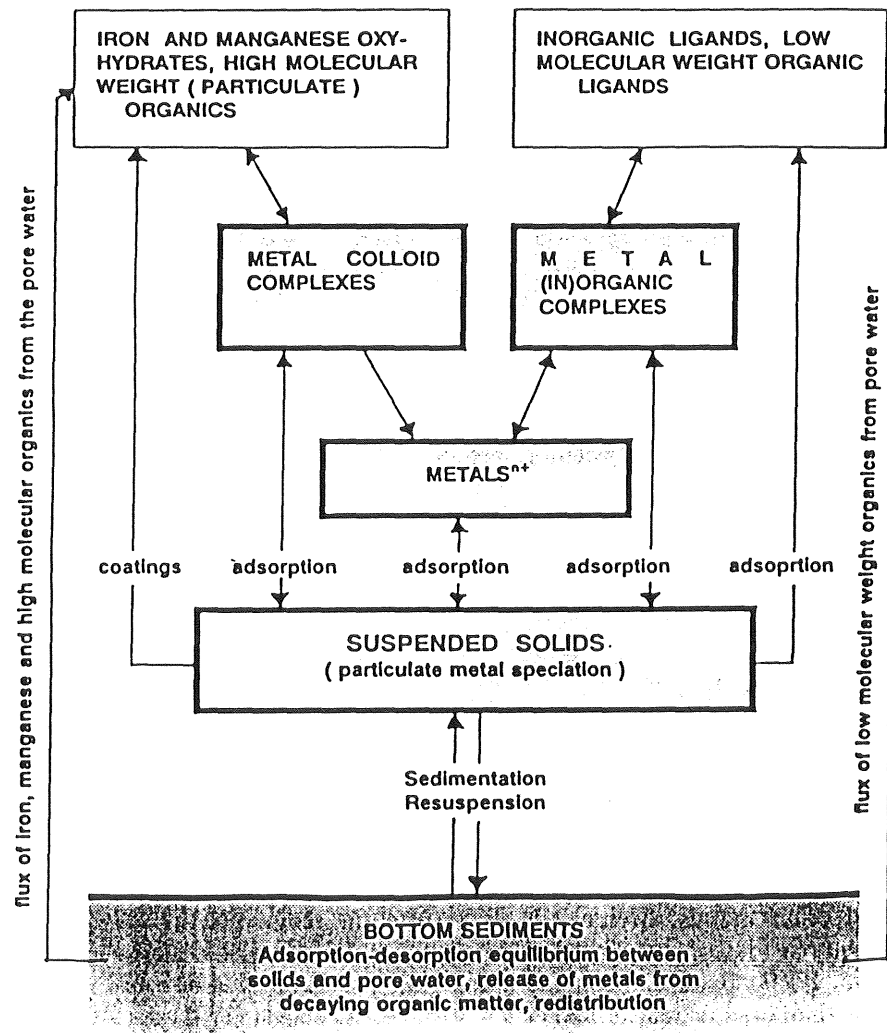


Figure 2 Major Processes and Mechanisms in the Interaction between Dissolved and Solid Metal Species in Sediments (Salomons and Förstner, 1984)

Adsorption of metals in various sediment components depends on the cation-exchange capacity (CEC) or the ability of soil, to sorb cations (Manahan, 1994). Usually, it varies widely among different soils being influenced by pH and salt concentration. At low pH, the dissolution of hydrous metal oxides and carbonates intensifies competition for exchange sites. Zero adsorption is observed at low pH, whereas at high pH, 100% adsorption is achieved. The shift from 0 to complete adsorption is usually within 2 pH units (Salomons and Förstner, 1984). Metals such as Pb, are almost completely adsorbed at pH > 6. Under saline condition, competition for surface binding sites, especially by sodium, calcium and magnesium ions also increases.

Sedimentation

Sedimentation, the major removal pathway for metals adsorbed on particles results in metal fixation in bottom sediments. Metals deposited in the sediments may exist as discrete compounds, ions held by cation-exchange clays, bound to hydrated oxides of iron or manganese, or chelated by insoluble humic substances (Manahan, 1994). This process is enhanced by the ability of wetlands plants to provide quiescent conditions thereby reducing wind turbulence that could disturb the bottom sediments.

Complexation

Metal species that are found in water depends largely on complexation, since the formation of complexes decreases the concentration of free metal ions. The complexed compound consists of one or more atoms or ions bound to other ions or molecules called ligands (Dojlido *et al.*, 1993). Most of the ligands are inorganic complexes such as F⁻, Cl⁻, SO₄²⁻, Cl⁻, PO₄³⁻; While in anoxic conditions, ligands such as S²⁻ or HS⁻ and CO₃²⁻, humic and fulvic acids dominate.

In organic-rich reducing sediments, most metal ions except nickel and vanadium are not retained by the organic fraction. Thus, organic material in constructed wetlands may only play a minor role in long term storage. Nevertheless, organic components may promote the formation of inorganic metal precipitates provided that design optimization to transform organic to inorganic components is considered.

On the other hand, Wildeman and Laudon (1989) postulated that if organic complexing of metals is important, the reason may be to retain the metals in labile forms that can be used directly by bacteria or the products of bacterial growth.

Oxidation-Reduction- Precipitation

Oxidation and reduction processes catalyzed by microbes that occur in aerobic and anaerobic zones, play an important role in precipitating metals such as hydroxides and sulfides. Oxidation occurs in the aerobic water column and in the upper aerobic soil layer. In these aerobic zones, microbes promote the oxidation of trace metals to more insoluble states. In the anoxic environment, sulfate-reducing bacteria promote the formation of hydrogen sulfide. Sulfate reduction decreases the acidity of sulfate contaminated water through the formation of hydrogen sulfide which reacts with metals to form metal-sulfide precipitates. This process may also remove significant amounts of trace metals through adsorption.

Plant Uptake

Nutrient and metal uptake are reported to be primarily through the root system as well as the submerged stem and leaves of wetland plants. This metabolic uptake is widely recognized owing to the nutrient requirements of wetland plants for their growth and reproduction.

For metals, uptake of plants is generally small compared with sediment uptake (Dunbabin *et al.*, 1992). Nevertheless, temporary uptake by plants provides additional capacity for removal (Chan *et al.*, 1982). The distribution of metal uptake into different parts of wetlands plants are reported to be in the order roots > rhizomes > non-green leaves > green leaves (Polprasert *et al.*, 1996; Dunbabin, 1989).

3.1.2. Nutrient Removal

Oxidation, both by physical, chemical and biological processes in the aerobic water column enhances nitrification and the transformation of ammonia to nitrate. On the other hand, chemical and biological reduction in anaerobic zones supports denitrification or the conversion of nitrates to nitrogen. The mechanisms for nutrient removal are nitrification, plant uptake and volatilization (Reed *et al.*, 1995).

3.2. Role of Substrate in Constructed Wetlands

The selection of substrate is important in the successful application of constructed wetlands since it can determine the success or failure of the system. Substrate's physical and chemical properties such as porosity, hydraulic conductivity, bulk density, cation-exchange capacity and redox potential, influence the effectiveness and capacity of constructed wetlands to remove or retain contaminants.

In wastewater purification, the efficiency of soils to remove or retain contaminants is a function of soil-wastewater contact. Sand or gravel soils have high hydraulic conductivity, thus water moves rapidly through it. This is disadvantageous since soil-water contact is diminished. In contrast, fine-textured silty or loamy soils permit more soil-water contact. Mixing sand or gravel with impermeable clay soils can improve soil- water movement.

Cation-exchange capacity measures the soil's capacity to hold cations on exchange sites and varies widely among different soils. In organic soils, H^+ dominates at high organic contents, while metal cations (Ca^{2+} , Mg^{2+} , Na^+) dominate in mineral soils. These factors may play major roles in the retention of specific wastewater components and in pH changes during treatment periods.

3.3. Role of Aquatic Plants in Constructed Wetlands

The role of plants is essential in the purification processes of constructed wetlands. Several studies describe the use of floating plants for metal removal. However, the use of rooted macrophytes has a greater advantage. Macrophytes, the larger aquatic plants growing in wetlands include vascular plants, aquatic mosses, and some larger algae. The most common types are the emergent ones, e.g. the common reed (*Phragmites australis.*), cattail (*Typha schoenoplectus*) bullrush (*Scirpus*), sedges (*Carex*) and other grasses. The common reed offers a number of advantages over other species. Brix, (1994) classified the role of macrophytes in constructed wetlands based on their metabolism (gas transport, oxygen release, plant uptake) and the physical effects the plant tissues give rise to (e.g. erosion control, filtration effect, provision of surface area for attached microorganisms. These are further discussed below.

Gas Transport Mechanism

The gas transport mechanism in wetland plants, wherein atmospheric air is taken in one part of the plant and released back into the atmosphere through another part of the plant may occur through different processes. One is through passive molecular diffusion, following the concentration gradients within the lacunal system (Brix, 1994). This gaseous space serves as an

oxygen conduit from the photosynthetic shoot tissue to the subsurface tissues, where anaerobic processes maintain normal root absorptive functions for nutrient uptake (Bedford et al., 1990) and metal uptake (Dunbabin *et al.*, 1988). Depending on plant species, the extensive internal lacunal system may occupy 60% of the total tissue volume (Brix, 1994). Likewise, oxygen transport is also possible by convective flow of air (either throughflow or non throughflow) through the internal gas spaces of the plants (Armstrong *et al.*, 1990). Convective flow are dependent on the specific porous structures within the plant tissues and differences in water vapour, pressure and temperature between the plant tissues and surrounding air; two processes commonly known as thermal transpiration and humidity induced pressurization (Brix, 1993). Moreover, convective throughflow can also be induced by gradients in wind velocity within a canopy, a process known as venturi-induced convection (Brix, 1994). Unlike the humidity and temperature induced convection, venturi-induced convection can operate in damaged and dead plants and also during night and winter time, when water vapour and temperature gradients are limited (Brix, 1994). *Phragmites australis* displays this mechanism wherein wind blowing across its tall dead culms takes atmospheric air into the underground root system via broken culms close to the ground level.

Wetland plants with a convective through-flow mechanism are believed to have the potential to release more oxygen from their roots, compared to species without convective throughflow (Brix, 1994).

Rhizosphere Oxygenation

Macrophytes release oxygen from their roots into the rhizosphere, a thin film aerobic layer supporting the root hairs (Armstrong and Armstrong, 1990). This mechanism creates aerobic conditions in the anaerobic substrates (Sorrell and Boon, 1992; Barko *et al.*, 1991; Hammer and Bastian, 1989). As a result,

iron (or manganese) is precipitated and an iron plaque or coating is observed (Peeverly, *et al.*, 1995).

Rhizosphere oxygenation is considered important for active root function and also enables the plants to counteract the effects of soluble toxic metals (Peeverly *et al.*, 1995). It is also reported to stimulate the decomposition of organic matter and growth of nitrifying bacteria (Brix, 1994). The rates of oxygen release differ between wetland plant species. Aerobic conditions are required for the oxidation of iron and manganese to hydrous oxides which have a high surface area and adsorptive capacity for metals. This process is dependent on the internal oxygen concentration, the oxygen demand of the surrounding medium and the permeability of the root-walls (Sorrell and Armstrong, 1994).

In situ experiments on the quantitative magnitude of oxygen leakage from the roots of wetland plants have been a subject of controversy among the scientific community (Bedford *et al.*, 1991; Sorrel and Armstrong, 1994). This may be attributed to the inhomogeneity of the oxygen release pattern of wetland roots, different techniques used in the experiment as well as seasonal variation (Brix, 1997; Brix, 1994). For *Phragmites australis.*, Lawson (1985), reported a possible oxygen flux from roots up to $4.3 \text{ g m}^{-2} \text{ day}^{-1}$ based on different assumptions of root oxygen release rates, root dimensions, numbers, permeability and others. Using other experimental techniques, *Phragmites australis.* showed different oxygen release rates as low as $0.02 \text{ g m}^{-2} \text{ day}^{-1}$ (Brix, 1990), $1\text{-}2 \text{ g m}^{-2} \text{ day}^{-1}$ (Gries *et al.*, 1990), and as high as $5\text{-}12 \text{ g m}^{-2} \text{ day}^{-1}$ (Armstrong *et al.*, 1990). However, a recent study, based on providing a sink of oxygen released during experiments have shown that the oxygen release rates reported in earlier studies might have been underestimated (Sorrel and Armstrong, 1994).

Physical Effects

The ability of wetland plants to reduce and distribute current water velocities favors sedimentation of suspended solids, reduces the risk of erosion and resuspension and increases the contact time between the water and the plant surface areas (Pettercrew and Kalff, 1992).

Stabilization of the soil surface by wetland plants, through their dense root systems, controls the formation of erosion channels. The filtering effect of the roots, which decompose large debris, prevents the occurrence of clogging, especially in vertical flow. Reduced wind velocities near the soil or water column enhance sedimentation and the removal of suspended solids. Another important role of macrophytes is their insulation ability, made possible by the covering provided by dead plant materials during winter, especially in cold countries.

Biofilms

The stems and leaves of macrophytes submerged in the water column provide a huge surface area for biofilms (Gumbrich, 1993). Roots and rhizomes in the submerged wetland soils also promote a biofilm for attached growth of microorganisms. These biofilms, consisting of dense colonies of photosynthetic algae, bacteria and protozoa are responsible for the majority of microbial processes that occur in wetlands (Brix, 1997).

3.4. Types of Constructed Wetlands

The identification of design criteria for constructed wetlands is essential in assessing the performance of the system. Many studies have been conducted on different types of constructed wetlands that would economically meet specific effluent standards in a wide range of applications. Brix (1994) proposed three classifications of constructed wetlands based on the form of the dominating macrophyte for treating domestic wastewater. These are the free floating, submergent and the rooted emergent systems. Although the first two types are widely used in other continents, the latter has been widely applied in many countries in Europe. In this type, different designs can be used, but the popular ones are based on wastewater flow (Brix and Schierup, 1989). The surface-flow systems, the subsurface-flow and the Max Planck Institute Process systems are discussed below.

3.4.1. Surface-Flow System

This system is the most widely used constructed wetland design displaying the same characteristics as that of natural wetlands (Figure 4). The degradation processes taking place at the submerged-stem water interface, where the biofilms are formed, plays an important role in wastewater purification. The mechanism of removal is the result of water slowly flowing through dense stands of emergent wetland vegetation. The low water velocities and the presence of plants provide stable conditions, which favours sedimentation and filtration. Biofilms on plant surfaces transform pollutants into harmless forms.

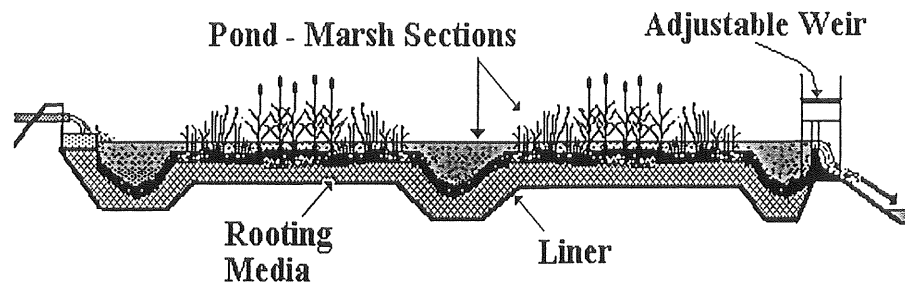


Figure 3. Surface Flow System
(Kim and Reid, 1997)

3.4.2. Subsurface -Flow Systems

Contaminant removal in subsurface-flow systems (SSF) is achieved by biodegradation at the root surfaces, which harbor biofilms. SSF systems usually employ a horizontal or vertical flow regime (Figure 4). In subsurface-horizontal flow systems, rectangular beds planted with emergent macrophytes are used. Wastewater passes horizontally through a substrate, which is soil, gravel or a combination of the two. Kickuth (1977) first constructed this type of system using soil as a substrate. Systems using soil are usually referred to as the 'Rootzone Method'. On the other hand, subsurface-vertical flow systems are characterized by percolating wastewater through the substrate, (typically fine sand) to a drainage system located in the bottom of the bed. Studies conducted on constructed wetland design suggested that the vertical and upscale design might significantly improve wastewater treatment through enhanced contact with the plant root-zone (Mitchell *et al.* 1990; Breen and Chick, 1989).

In systems with a vertical downflow format, it was reported that more than 50% of the root biomass occurred in the top 0.05 m of the profile. However, systems with a vertical upflow format had a more even root density. In addition, the upflow system maximises wastewater rootzone contact by

channeling outflow through the root dense layers (Breen and Chick, 1989; Rogers *et al.*, 1990).

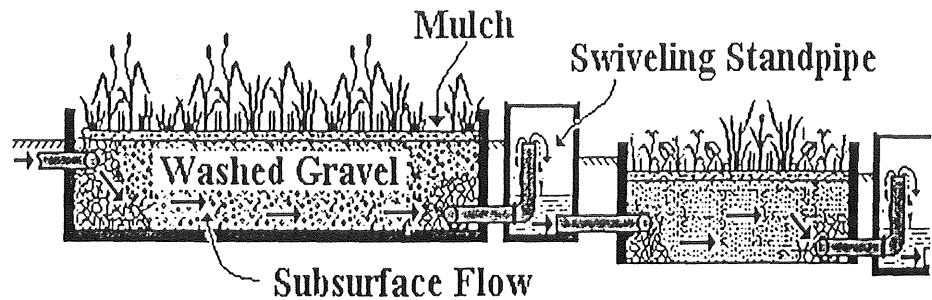


Figure 4 Subsurface Flow System
(Kim and Reid, 1997)

3.4.3. Max Planck Institute Process

A combination of surface-flow and sub-surface flow system is known as the Vertical-Flow Wetland or the Max Planck Institute Process (Figure 5). Seidel, (1967) first developed this combined system, consisting of several beds in each stage, with vertical flow dominating in the first and horizontal flow in the second (beds in series). This intensifies the treatment processes and reduces the surface area requirements (Brix, 1994).

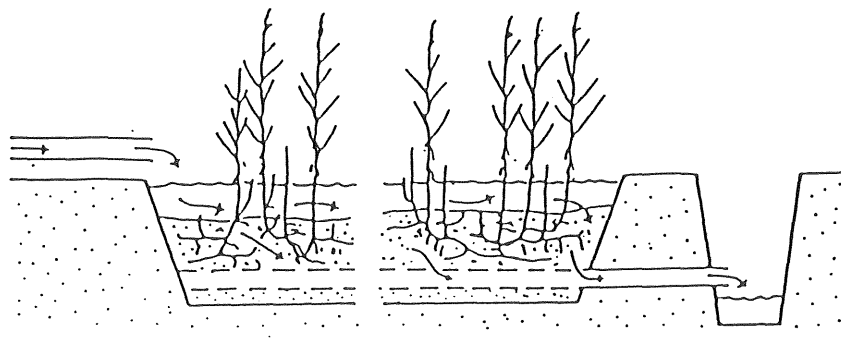


Figure 5. Max Planck Institute Process
(Kim and Reid, 1997)

3.5. STORMWATER

Stormwater flows are sporadic and therefore cause a high degree of variability in stormwater quality. It has been shown to contain high concentrations and loadings of heavy metals in the form of biologically and chemically reactive species (Morrison *et al.*, 1984) which are toxic and therefore pose a threat to the aquatic environment. For this reason, many studies have been conducted on the use of treatment systems that would regulate metals in stormwater.

Over the past years, open stabilization ponds have been considered as the best available method for stormwater treatment (Yousef *et al.*, 1994). However, change in hydraulic regime, nutrient and contaminant cycling and release, and other negative impacts on the receiving waters including thermal enhancement and erosion limit their treatment efficiencies. Other treatment alternatives were also considered such as the use of natural and constructed wetlands for improving stormwater quality. Studies in the US have reported that the latter offers a better efficiency for pollutant removal (Strecker *et al.*, 1992; Livingston, 1989).

3.6. Metal Chemistry in Aquatic Ecosystems

Heavy metals are among the most harmful of the elemental pollutants that are of environmental concern. These elements such as Pb, Cd, Zn and Cu are not biodegradable and therefore considered as persistent. Once discharged into the environment, their potential toxicity is controlled largely by their physico-chemical form.

3.6.1. Cadmium (Cd)

Occurrence

Cadmium exists in the natural environment and is a ubiquitous element in all living things. Its natural sources are from volcanic emissions and vegetation; while the anthropogenic sources are from mining wastes, landfill leachates, fertilizers, sewage sludge and other industrial discharges such as waste incineration, coal, oil combustion and electroplating. (Manahan, 1994). It is also found in plastics, pigments, nickel-cadmium batteries, solders and electronic equipment. Cadmium is rarely found in natural waters at high concentrations. High levels are associated with industrial discharge. (Dojlido *et al.*, 1993).

In natural waters, cadmium exists as Cd^{2+} , $\text{Cd}(\text{OH})_2$ (aq), $\text{Cd}(\text{OH})_3^{-1}$, $\text{Cd}(\text{OH})_4^{2-}$, CdCO_3 and in various other organic and inorganic complexes (Moore, 1991). Adsorption of Cd in sediments depends largely on pH, redox conditions and the presence of complexing agents. Under oxidizing conditions, Cd is mobile and exists as aqueous Cd^{2+} (Fergusson, 1990). The adsorption of Cd in sediments is reported to increase with an increase in pH. Above pH 7, practically all the ions of the metal will be adsorbed. Once incorporated in the sediments, Cd does not redissolve in neutral or alkaline conditions. This is largely attributed to the reduced condition in the sediments, whereby anaerobic decomposition of the sediments produces cadmium sulfide, which is insoluble.

In polluted waters, other species of Cd occur as CdSO_4 and Cd-organic ligand complexes. The binding of Cd with organic material depends on the presence of competing species. The dominant inorganic species of Cd are Cd^{2+} and CdCO_3 . Their occurrence is largely dependent on pH; the former is only found in very alkaline condition, whereas the latter is found at $\text{pH} < 8$. The dominant fate process in freshwater for Cd is sorption to suspended

solids. Co-precipitation with hydrous iron, aluminum-manganese oxides, and carbonate materials also occurs, and periodically dominates the fate processes (Moore, 1991).

Toxicity to Aquatic Plants

Cadmium, specifically the free Cd^{2+} form is very toxic to most plant and animal species (Moore, 1991). The effective concentration $(\text{EC})_{50}$ for the duckweed *Lemna minor* is 0.2 mg/L (Wang, 1986); while only 0.006 mg/L for green alga *Selenastrum capricornutum*.

Bioaccumulation of cadmium in submerged macrophytes is generally low, with an average concentration at 1.3 mg/kg dry weight (Estabrook *et al.*, 1985). However, a high concentration of 342 mg/kg dry weight for the freshwater plant *Lemnaea fluviatilis* has been observed near polluting sources (Harding and Whitton, 1981).

Cadmium uptake is influenced by pH, where uptake is generally high at neutral or basic level (Demon *et al.*, 1988). Freshwater organisms have low tolerance compared to marine organisms. This is attributed to the binding of the free cadmium ion with chloride (Coombs, 1979). In addition, the presence of manganese and iron in water significantly inhibits uptake due to competition for uptake sites (Moore, 1991).

3.6.2. Lead (Pb)

Occurrence

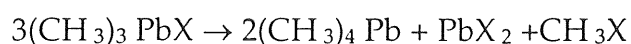
The major source of lead in the aquatic environment is from atmospheric deposition. High concentrations of lead are observed during high rainfall. In surface waters, lead comes from washoff from road surfaces, because much of the lead is in particulate form on roadside dust. Storm runoff carries this pollutant into receiving water bodies.

Manufacturing processes (particularly metals) are also significant sources of Pb, e.g. from paint pigment, mining, coal-fired power plants, use of leaded gasoline in the past and the use of acid car batteries.

Lead exists as Pb^{2+} and Pb^{4+} , the former being the more stable in the aquatic environment. The speciation of Pb in water is dependent on pH, dissolved oxygen and the concentration of organic and inorganic compounds. In freshwaters, Pb forms complexes of low solubility with major anions, such as hydroxides, carbonates, sulfides, and to lesser extent, sulfates (Moore, 1991). It also forms moderately strong chelates when complexed with humic substances.

Under reducing conditions, Pb exists as PbS which is highly insoluble in water. While in highly oxidizing conditions, Pb occurs as Pb^{4+} , PbO_2 and Pb_2O_3 . Pb binds readily with organic ligands such as fulvic acid, humic substances, citrate acetate, glycolate and NTA. This complexation is limited by the presence of competing metals as well as the amount of ligands present. Pb also has a strong affinity with inorganic sorbents such as Fe/Mn oxides. At pH >7, a significant amount of Pb is bound to hydrated Fe_2O_3 (hematite) and is believed to be more important than binding with organics.

Lead-carbonate complexes are only common in surficial sediments while lead-sulfide occurred in anaerobic sediments (Fergusson, 1986). Microorganisms in the sediments play a significant role in the methylation of lead to form $(CH_3)_3 Pb^+$ and other related compounds. This is expressed in the equation:



In surface waters, Pb concentration is highly variable. Typical concentration is <0.05 mg/L (Moore, 1991). High concentrations of Pb are reported in

freshwater sediments especially those receiving industrial or domestic wastes.

Toxicity to Aquatic Plants

Pb is moderately toxic to aquatic plants (Moore, 1991). It acts synergistically with combinations of Cu, Zn and complexation with organic and inorganic ligands reduces its toxicity. Organoleads, particularly tetraethyllead, are reported to be more toxic to aquatic plants than either the methylated derivatives or inorganic compounds (Moore, 1991).

3.6.3. ZINC (Zn)

Occurrence

Zn enters surface waters mainly in discharges from metal treatment plants, chemical plants and foundries and is present in drinking water where the water is conveyed in zinc-coated pipework. Zn is the metal commonly implicated in homeostatic regulation in aquatic organisms. In polluted rivers, zinc varies in the range of 100-500 mg/kg of dry weight of the material (Moore, 1991).

Under aerobic and acidic conditions, Zn^{2+} is the predominant species. At pH 8-11, Zn is in the form of $Zn(OH)_2$, and $Zn(OH)^{3-}/Zn(OH)_4^{2-}$ at pH 11. The formation of ZnS is common under anaerobic conditions regardless of the pH range 1-14.

Zn binds easily with organic ligands such as nitrogen or sulfur atoms. It also shows variable behaviour in binding to suspended particulates, depending on pH and redox conditions and the input of anthropogenically derived zinc (Moore, 1991).

Toxicity to Aquatic Plants

Toxicity of Zn to aquatic plants is very variable, with EC₅₀ (Effect Concentration 50%) ranging from <0.01 to > 100 mg/l (Moore, 1991). The high variability can be explained by the effect of different physicochemical conditions on uptake and the ability of many species to adapt to high zinc levels. In hard or humus water, zinc toxicity is moderated and a greater concentration of zinc can be tolerated (Morrison *et al.*, 1992).

3.6.4. Copper (Cu)

Occurrence

Copper is an essential trace element but considered toxic to plants and algae at high concentrations. Its significant sources are from metal plating, mining and industrial wastes. In addition, copper is also released to surface water from the corrosion of drinking water pipes (Molander, 1992).

Copper is mainly found in two oxidation states, namely Cu (I) and Cu (II). The former is found to be most common in natural waters. However, high concentrations of copper (I), have been found in river waters, and are believed to be due to the ultraviolet radiation (Morrison *et al.*, 1996). Under natural conditions, copper (I) can be reoxidized, but is hindered under reduced condition and increased salinity (Morrison *et al.*, 1996).

In most freshwaters, total copper is detected at low concentrations; although high concentrations are observed in freshwater/saltwater mixing zones due to desorption caused by competition with the chloride ion, and to a lesser degree, by bacterial mediated decomposition of organic matter.

Copper has the ability to bind with inorganic and organic ligands and form stable complexes (Moore, 1991). It has a strong affinity for hydrous iron and manganese oxides, carbonate materials, clays and organic matter in bottom

sediments. In the aquatic environment with neutral pH, most of the inorganic copper in solution does not occur as Cu^{2+} , but instead complexed with carbonate, nitrate and sulfate (Moore, 1991). About 75% of copper is reported to be bound in organic, sulphidic and carbonate fractions. Binding of copper to particles such as clay results in its mobilization; e.g. downstream transport in rivers.

Toxicity to Aquatic Plants

Binding of copper with strong ligands markedly reduced its toxicity. However, weak and moderate ligands such as acetate, succinate, proline and lysine, provided that they occur in sufficient concentrations, can also significantly reduce copper toxicity. This binding is also dependent on pH. The maximum adsorption of copper is observed in the vicinity of pH 8. Copper-carbonates and copper-hydroxides occur at high pH(>7) and are reported to be potentially toxic, but not available for uptake by aquatic organisms (Southart et al., 1996). Generally, the most toxic forms are believed to be Cu^{2+} and Cu OH^+ .

3.7. Speciation of Metals

Bioavailability and toxicity of metal ions in surface water is greatly influenced by their physico-chemical forms or speciation. Florence, (1989) defined metal speciation as the determination of individual physico-chemical forms of an element which together make up its total concentration.

The factors that affect metal speciation include suspended solid types and concentrations, pH, total metal concentrations and dissolved organic carbon concentration and character. Metals discharged in the environment, such as industrial wastes are usually in an insoluble form. Its solubility depends on pH and is often characterised by the formation of complexes with organic material.

As shown in Figure 6, the flux of metals in the aquatic environment is partitioned between particulate, colloidal and dissolved forms (Luoma, S. 1983). Depending on the concentrations and strength of ligands or species that binds with metal ions, further partitioning and speciation may occur. Aquatic organisms are exposed to these different physico-chemical forms, and each form differs in its accessibility to the organisms.

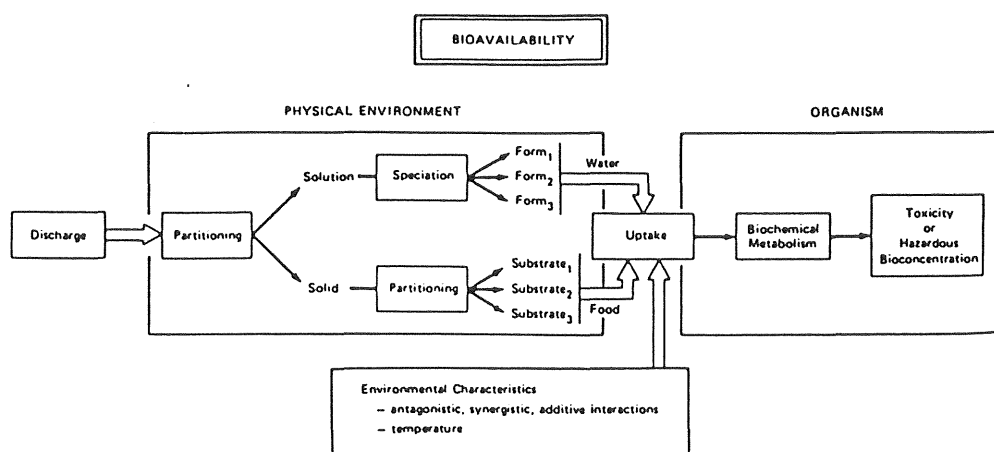


Figure 6. Processes Affecting the Bioavailability and Toxicity of Metals (Luoma, S. 1983)

Morrison, (1989) proposed the possible forms of trace elements (Table 1). The two most toxic forms are the lipid soluble and the simple ionic. The latter is believed to be the most available and toxic to organisms. Examples are the metal ions that are dissolved in sediment solution or weakly adsorbed to sediment particles. In addition, potentially bioavailable metals are those that are precipitated, co-precipitated and complexed, since they can be released

back into solution to restore equilibrium (Dunbabin *et al.*, 1990). Those that are incorporated into mineral lattices are considered essentially unavailable to biota.

Table 1. Possible forms of Metals (*Morrison, 1989*)

Physicochemical Form	Possible ex.	Approx.Dm (nm)
Simple ionic species	Zn (H ₂ O) ₂	0.8
Inorganic complexes	CdCl, PbCO ₃	1
Differing valency states	Cr(III), Cr(IV)	1
Lipid soluble complexes	CH ₃ HgCl	1
Organometallic species	CH ₃ AsO(OH) ₂	2
Weak complexes	Cu fulvate	10-500
Adsorbed on colloidal particles	Cu ₂₊ /humic acid/Fe ₂ O ₃	
Particulate	Metals adsorbed onto or contained within clay particles	>450

The bioavailability of metals in sediments is influenced by increases in acidity, reducing power, salinity and the concentration of either natural or synthetic organic ligands.

Generally, soluble and therefore bioavailable metals dominate in waters and sediments that are acidic; in waters that are low in suspended solids and concentrations of dissolved organic carbon. In addition, the soluble metal fraction is also common in a reduced environment causing the dissolution of hydrous metal oxides with release of any adsorbed or co-precipitated metals.

3.7.1. Metal Uptake and Metabolism

The biological uptake of different metal species is determined by processes occurring at the environmental interface of the organisms (Luoma, 1983). These include: 1) the characteristics of the interface itself 2) the reactivity of each metal form with the biological interface 3) the presence of other metals or major cations which may antagonise or stimulate metal uptake 4) temperature which affects the rate of biological or chemical reactions; and 5)

the physiological state of the organism or biological factors involved in metal metabolism.

The uptake of trace metals depends on the biochemical metabolism of the organisms. The first step in any metabolic pathway is the transport of the metal across the intracellular membranes and tissues of organisms. The mechanisms for crossing these compartments are through facilitated and active diffusion, active transport or endocytosis (Figure 7).

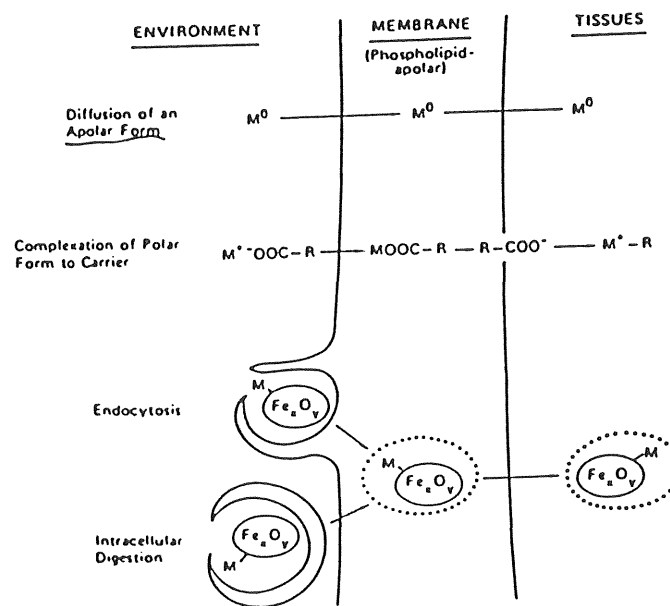


Figure 7. Transport of Metals into Biological Tissues
(Luoma, S. 1983)

Kinetic characteristics show that most trace metals are observed to undergo metabolic transport via diffusion facilitated by carrier molecules impregnated in the environmental interface of the organism (Coombs, 1980). Different mechanisms could influence this carrier-facilitated uptake of metal species. This could include the transport via carriers specific for nutritionally essential cations (e.g. Zn), nutrients (amino acids and proteins) and metal complexes. In addition, non-specific complexation of metal forms with carrier molecules

could result in accidental transport across the interface. In other cases, immobilization at the external interface might occur if the carrier-metal complex cannot pass through membrane.

Another mode of metal uptake is through passive diffusion of metals with reduced polarity. This could occur via pores, which have been observed in membranes. Digestive processes also play a role in determining metal uptake through enzymatic cleavage of proteins, which could facilitate metal assimilation if metals are transported with amino acids.

3.7.2. Biological Response on Metal Uptake

The way that a metal is metabolized ultimately affects the response of the organism. Toxicity of metals occurs when an organism is unable to cope with additional metal concentrations by direct usage, storage and excretion (Morrison, 1989). This response is counteracted by detoxification or the ability of organisms to transform toxic metal forms, aided by the formation of metal-specific binding proteins within tissues (Harrison, F. 1983). These proteins prevent metal ion diffusion which would certainly cause damage to various enzymes and proteins that are important for biological reactions (Morrison *et al.*, 1989). The formation of detoxifying agents is induced by elevated exposures, however it may also cause damage to cells. When the capacity of cell to detoxify is exceeded, deleterious effects on the organisms might occur. Signs of intracellular metal toxicity may include ultrastructural deformities as well as reductions in cell division rate (Morisson, 1989).

4. EXPERIMENTAL

4.1. Sampling Area

Samples were taken from two stormwater detention ponds in Järnbrott, located 5 Km south of Göteborg city center. Both ponds were constructed to investigate the possibility of improving stormwater quality for different conditions, such as rain events, summer and winter variations. The two ponds vary in size. The small pond has a surface area of about 350 m² and a volume of about 420 m³. The larger pond has a surface area of about 5,200 m² and 6000 m³ volume. Pollutant loads such as heavy metals are carried into the ponds mainly from highway runoff.

Water samples were also collected in Kvillebäcken, a small urban river located northwest of Göteborg. The river receives discharges from surface water outfalls (SWOs) and combined sewer overflows (CSOs) containing significant loads of heavy metals (Wei and Morrison, 1993).

4.2. Materials and Methods

The experiments were carried out in a plexiglass column measuring 6 cm wide and 50 cm deep. It has a volume of about 600 ml and is characterised by an up-flow hydraulic format emulating a vertical subsurface constructed wetland. Holes were bored in the plexiglass column and porous frits were tightly inserted on hollow glass rods, then sealed with epoxy glue. Each frit was placed in the middle of the column and each glass rod was lined with polyethylene. The column was filled with sand (median grain diameter, d_{50} of 1 mm and 40% calculated porosity). A single shoot of *Phragmites australis* with an initial weight of 14.6 g was planted on June 3, 1997. The column was filled with water and supplied daily for 3 weeks by 5mg l⁻¹ of NH₃ for system

stability and plant growth. The experiment was kept in a glasshouse to maintain an ambient condition.

To eliminate any external contamination, the system was first backwashed with ultrapure water several times and then with stormwater about 3x the volume of the column. Filtered and unfiltered Influent was introduced to the bottom of the column *via* a central tube. A loading rate of 2 ml min⁻¹ allowed a theoretical retention time of 5 hours which was determined based on the formula:

$$Q=V/T$$

where Q is the flow rate expressed in ml min⁻¹, V is the volume of the column and T is the retention time. For the experiments, 5-hour retention time was used to allow column-wastewater contact. The same retention time was used for the same column, (Farahbakhzad and Morrison, 1997) and have shown effective removal for ammonia. On the other hand, different retention times (2, 5, 10 hours) were also used to investigate an effective retention time for metal removal.

Effluent was collected at the topmost sampling port (0.5 m). However, for profile differentiation, the column was sampled at depths 0.5, 0.4, 0.3, 0.2, 0.1 m within the 6 m profile (Figure 8).

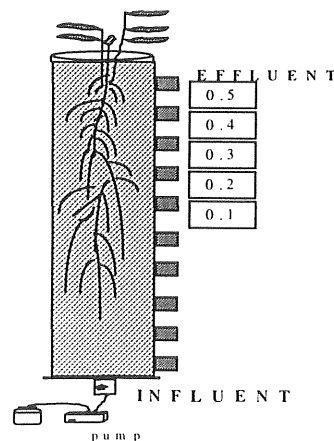


Figure 8. Experimental Column

4.3. Metal Analysis

Effluent wastewater samples were collected and directly analysed with Differential Pulse Anodic Stripping Voltammetry (DPASV) in 0.03 M sodium acetate at pH 4.7 for the analysis of ionic dissolved Pb, Zn, Cu and Cd. Total metal content was measured with DPASV after photolytic oxidation for 3 hours of 20 ml sample in a UV-digester. About 50 µl of concentrated suprapur HNO₃ was added before digestion in order to dissolve all metal-organic complexes in the sample.

Metal fractionation was conducted using a filtration scheme, separating the colloidal, particle bound and ionic dissolved forms in the sample. Filtration of the samples was conducted using a 0.45µm cellulose acetate filter to separate the dissolved and particle bound fractions. The colloidal phase consists of particles that are associated with particles small enough to pass a 0.45 µm filter, while the particle bound fraction consists of particles that are sufficiently large to be separated by filtration.

4.4. Measurement Techniques

DPASV is an excellent technique for measuring very small concentrations of metal ion in solution. This technique is primarily used for analyses at concentrations ranging from 10⁻⁵ to as low as 10⁻¹⁰ M (Braun, 1983). DPASV measures metals in a biologically available or ASV-labile form which correspond to metals which are dissolved in the water and completely surrounded by water molecules (Morrison *et al.*, 1989). However, metals that are lipid soluble are bound and therefore not easily dissociated. They are not detected by this method.

DPASV is an electroanalytical method, which is based on the measurement of a current that develops in an electrochemical cell under conditions of

complete polarization. The use of a microelectrode, for example the hanging mercury drop electrode (HMDE) is used for the analysis due to its desirable properties, which include the immediate formation of amalgams with the metals being analyzed. A differential pulse enhances the electrochemical signal, which is desired.

DPASV can perform multi-elemental analysis. The resultant voltammogram produces distinct peaks for the various elements in the water sample. The element peaks are in the order of the reduction potential of the given metal. As the applied voltage proceeds in a positive direction, the various metals are reduced. The peak area is proportional to the concentration. The concentrations of different elements can be determined through interpolation with a standard calibration curve.

Apparatus

Differential Pulse Anodic Stripping Voltammetry, Metrohm VA-processor

UV Digester, Metrohm 75

5. RESULTS and DISCUSSION

5.1. Concentration Profiles

Concentration profiles for metals at different column depths give an overview of the distribution of metals as well as the treatment performance of the system. Profile investigations of ionic dissolved Zn, Pb, Cu and Cd were conducted at different depths of the column (0.5, 0.4, 0.3, 0.2, and 0.1 m.) The results showed that removals vary depending on the metal species and depths within the sub-surface profile.

Lead

As shown in Figure 9, the concentration profile for ionic Pb showed a decreasing trend from the lower section (0.1 m) towards the higher section (0.5 m) of the column. Concentration of ionic Pb in the sample decreased from $15.3 \mu\text{g l}^{-1}$ to $5.3 \mu\text{g l}^{-1}$, with a significant decrease in the first 0.1m and a gradual decrease throughout the column. Similar studies conducted on a sub-surface flow wetland, reported that most metal removal (>80%) occurs within the top 0.2 m (Eger and Lapakko, 1989). This suggests that adsorption sites are greater in this zone. Pb easily binds with organic and inorganic sorbents such as humics and hydrous iron oxides. *Phragmites australis*. has the ability to form an iron plaque on its roots (Crowder and St-Cyr. 1991), which consists mainly of iron oxides.

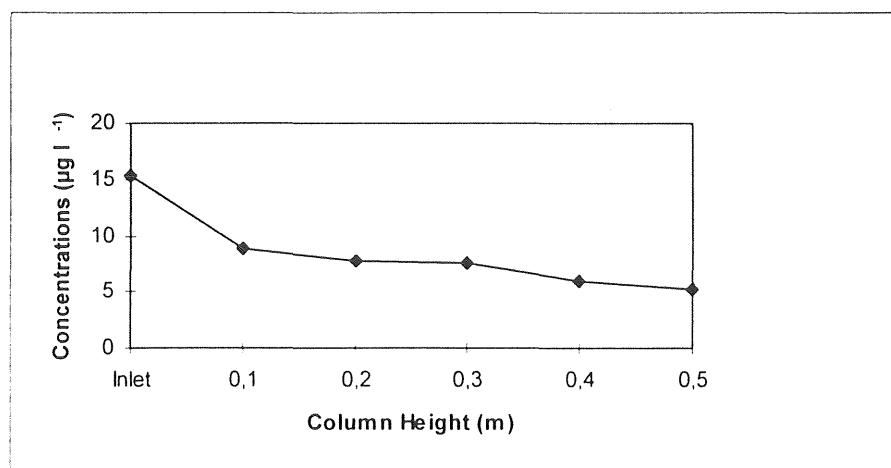


Figure 9 Concentration Profile for Ionic Pb

Copper

The concentrations of ionic Cu as profiled in Figure 10, demonstrated fluctuations at varying depths of the column. Removal was high at the topmost sampling port, where the inlet concentration was reduced from 49 $\mu\text{g l}^{-1}$ to 10.1 $\mu\text{g l}^{-1}$. This shows that Cu uptake is very active at this depth which could be due to the presence of organic materials present in the substrates and rootzone. The fluctuations and low removals at column depth between 0.1 and 0.4 m, probably attributed to the competitive interactions with other species for the similar types of binding sites (Malchamer and Wilderman, 1992). For example Zn and Cu are known to compete with organic ligands. On the other hand, short-circuiting of water flow could have occurred, and possibly affect treatment efficiencies (Mungur, *et al.*, 1997).

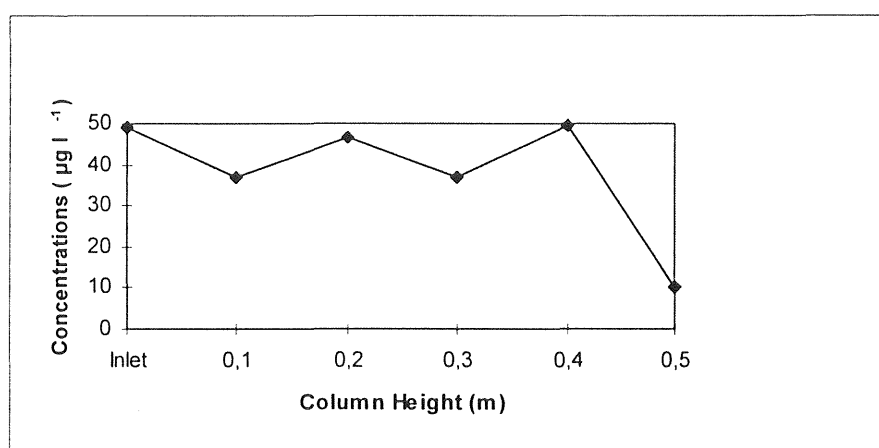


Figure 10 Concentration Profile for Ionic Copper

Zinc

The concentration profile for Zn, showed that removal was more effective as the depth decreases in height (Figure 11). The initial concentration of 14 $\mu\text{g l}^{-1}$ was reduced to 3.1 $\mu\text{g l}^{-1}$ at 0.1m sample. Since Zn in water is predominantly present as soluble bioavailable metal ion or weak complex, binding with organic ligands at the topmost outlet as exhibited by Pb and Cu would be minimal. In this case, plant uptake might be significant. Zn is more readily accumulated by plants than Cu and Pb (Mungur *et al.*, 1997; Sawidis *et al.*, 1995).

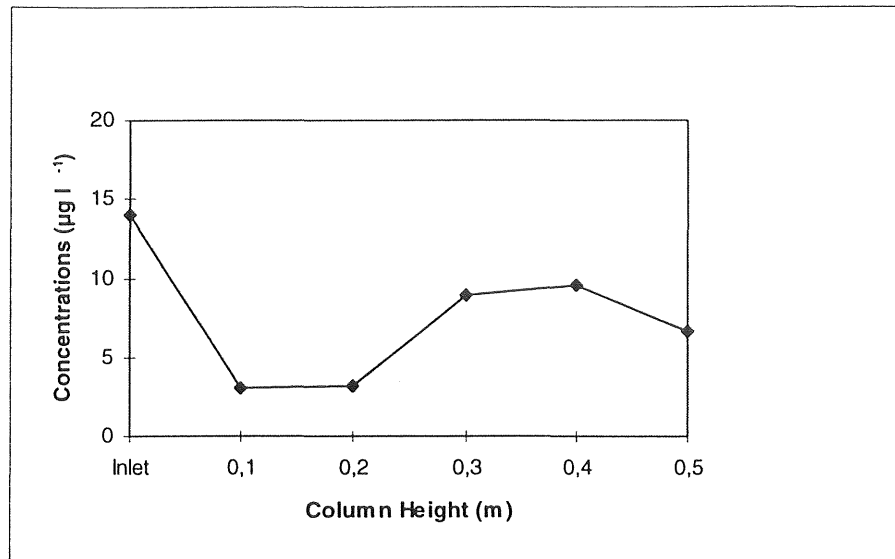


Figure 11 Concentration Profiles for Ionic Zn

Cadmium

Cd, as profiled in Figure 12, showed that it is difficult to remove in the column. Effluent concentrations mostly exceeded the inlet concentration and could be attributed to trace levels in the column from previous experiments. This might have increased Cd concentration in the column. On the other hand, speciation could also play a role, by transforming organic or particulate Cd to the ionic form.

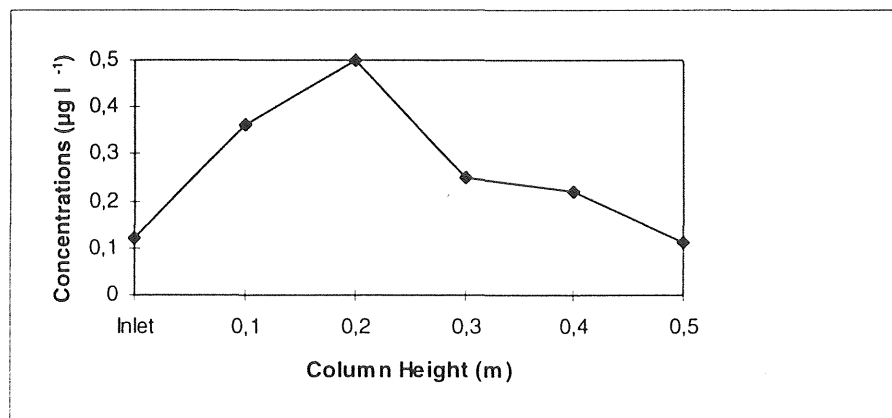


Figure 12 Concentration Profile for Cadmium

5.2. Partitioning

Lead

Preferential uptake in the column of colloidal and particle bound Pb was observed (Figure 13). The colloidal form, with an initial concentration of $11.6 \mu\text{g l}^{-1}$ was ultimately removed from the outflow. Pb is known to bind with the smallest fraction in the sediments (Mudroch and Duncan, 1986). Likewise, high removal of particle bound Pb was also observed, from $37 \mu\text{g l}^{-1}$ to $4.3 \mu\text{g l}^{-1}$. The removal mechanism is probably through direct filtration. The presence of organic and inorganic ligands in the column offers attractive binding sites, making Pb strongly bound and therefore not bioavailable. The particle bound fraction would be easily filtered, and once deposited in the column substrate, it may exhibit little remobilization. Pb species in the column could be in the form of PbCO_3 , PbS or bound with Fe/Mn oxides and ammonia. However, the presence of these binding sites also depends on the condition in the column and is influenced by pH, redox condition and the presence of competing species (Fergusson, 1990). Pb is rarely found as a free metal ion, as demonstrated by the low concentration in the influent; while removal or plant uptake was also low, from $1.5 \mu\text{g l}^{-1}$ to $1.4 \mu\text{g l}^{-1}$. The preference of uptake in the column followed, in decreasing order; colloidal > particle bound > ionic dissolved.

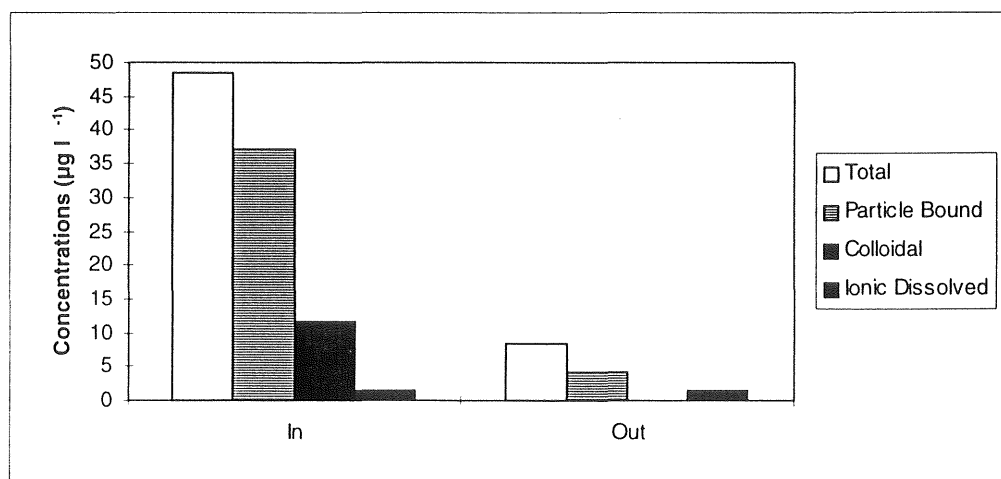


Figure 13. Removal of Pb Fractions in the Planted Column

Copper

As shown in Figure 14, the tendency of Cu to bind with organic and inorganic substances was evident. About 59% of the particle bound fraction was retained in the column (based on the inlet concentration of $45.3 \mu\text{g l}^{-1}$). Similarly, the colloidal fraction retained in the column was fairly significant at 38% (based on the inlet concentration of $37.8 \mu\text{g l}^{-1}$). Cu adsorption and complexation seemed to occur. Cu is strongly concentrated on iron oxide phases (Manahan, 1994). On the other hand, competition with other metals (e.g. Pb and Zn) for binding sites, probably limited Cu uptake. Pb is more readily bound, while zinc also complexes with hydrous and manganese oxides in sediments. Column uptake of the ionic dissolved fraction was higher compared with ionic dissolved Pb. Observed influent and effluent concentrations were $25.6 \mu\text{g l}^{-1}$ and $19.3 \mu\text{g l}^{-1}$ respectively. The preference of Cu uptake in the column followed in decreasing order, particle bound > colloidal > ionic dissolved.

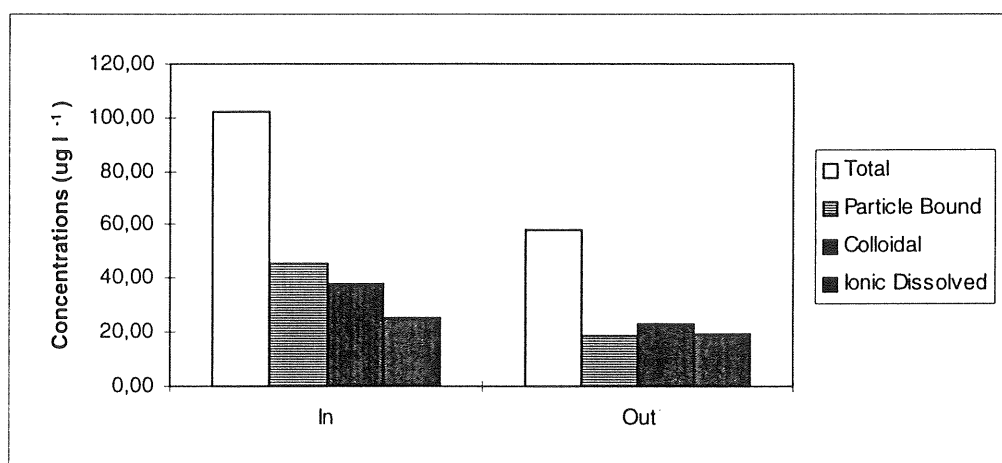


Figure 14 Removal of Cu Fractions in the Planted Column

Zinc

As shown in Figure 15, a high concentration of particle bound and colloidal fraction can be observed in the influent. This represents most of the total Zn concentration. The results exhibited that most of the particle bound and colloidal fractions were retained in the column. Percentage removal efficiency

obtained for the colloidal fraction was 90%, (based on an inlet concentration of $368\mu\text{g l}^{-1}$); and 73.4% for particle bound,(based on an inlet concentration of $511\mu\text{g l}^{-1}$). Likewise, percentage removal efficiency for the ionic dissolved phase was also high at 79%, although the influent concentration was rather low at $7.9\mu\text{g l}^{-1}$. Zn has been found to accumulate in shoots rather than in rhizomes (Pevery *et al.*, 1995). The preference of Zinc uptake followed in decreasing order; colloidal > ionic dissolved > particle bound.

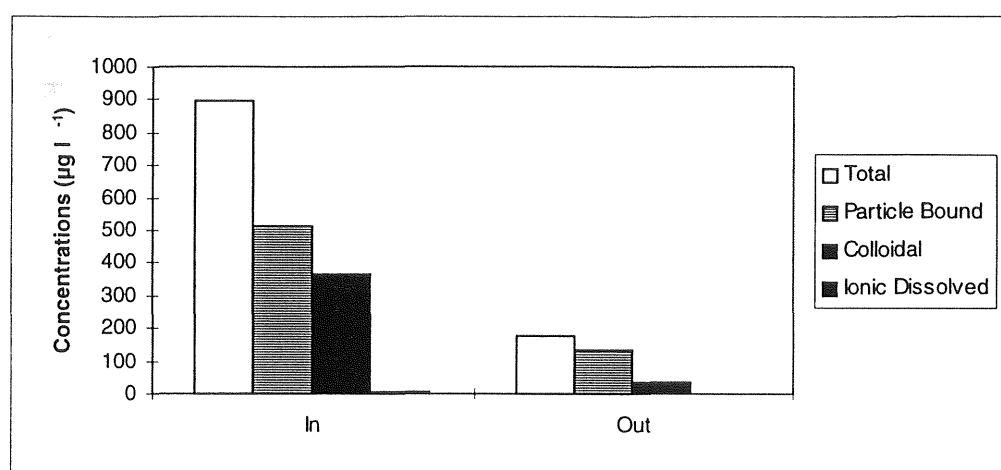


Figure 15 Removal of Zn Fractions in the Planted Column

Cadmium

The ionic dissolved fraction accounted for most of the total Cd concentration in the influent (Figure 16). Moreover, retention of this fraction was significantly high at 91.4%, (based on the inlet concentration of $0.91\mu\text{g l}^{-1}$). This signifies that Cd is mostly taken up in its ionic dissolved form. Only a small percentage of the colloidal fraction was retained in the column from $0.43\mu\text{g l}^{-1}$ to $0.38\mu\text{g l}^{-1}$, probably due to weak adsorption of Cd. Negative removal was observed for the particle bound fraction. This can also be attributed to Cd weak adsorptive capacity and potential mobility. High mobility of cadmium in sediments was documented (Fergusson and Kim, 1991). Its release from the sediment is high compared with Cu, Pb and Zn (Modak *et al.*, 1992). On the other hand, trace levels of Cd mobilized in the substrates and roots might have been released in the water solution and

could have added to the increase in the concentration of the particle bound fraction.

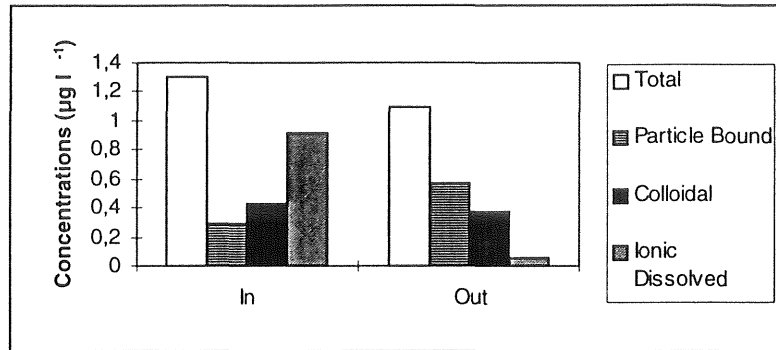


Figure 16. Removal of Cd Fractions in the Planted Column

5.3. Treatment Efficiencies

The results obtained for the samples indicate the ability of the system to act as an efficient sink for heavy metals. The performance of the column in metal uptake is demonstrated by the result shown in Figure 17. Treatment during the early stage of plant growth (June) was relatively low compared with the treatment achieved after 2-3 months (August-September). This means that system age or maturity influence metal uptake. The role of the plant seemed to enhance metal uptake. The column was only planted in June, in this case, roots and rhizomes of *Phragmites australis* which provide surface areas for microbial growth only started to develop. Metals are known to adsorb to these surfaces, and thus become bound. The mean treatment efficiencies obtained in June for Zn and Pb were 63% and 56% respectively. Low removal can be observed for Cd and Cu at 13% and 8.33% respectively. In some cases, negative removals were found for Cd and Cu, probably due to external contamination during the analysis. Thus, these values were not included in the results. On the other hand, the high values obtained could possibly be due to speciation in the column.

Metal uptake was high in the month of August and September. Mean treatment efficiencies obtained for Zn, Pb, Cd and Cu increased to 81%, 71%, 46% and 25% respectively. Increased surface areas from roots and rhizomes could have increased the adsorption of metals, as well as the ability of roots to detoxify and transport metals in their above ground tissues.

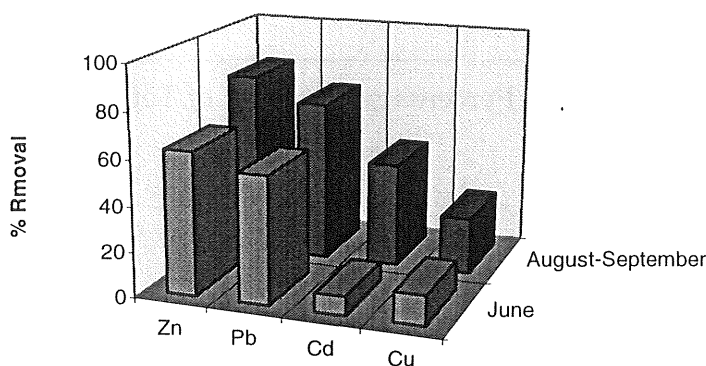


Figure. 17 Treatment Efficiencies of Ionic Dissolved Zn, Pb, Cd & Cu

Uptake of total metals was investigated in August to September (Figure 18). The results exhibited high preference of Pb uptake in the column followed by Zn, Cu and Cd. The mean treatment efficiencies obtained were 71%, 62%, 51% and 48% for total Pb, Zn, Cu and Cd respectively. The preference of uptake for Pb and Zn showed that these two metals are readily bound in the column substrates. Giblin *et al.*, (1980) found that sediments retained 50-100% of Pb and 20-45% of Zn. Studies conducted on a subsurface flow laboratory scale wetland, reported high removal efficiencies for total Zn, Pb, and Cu at 99.5%, 99.7% and 99.5% respectively (Gersberg *et al.*, 1985, Mungur *et al.*,1997), although no speciation studies were carried out.

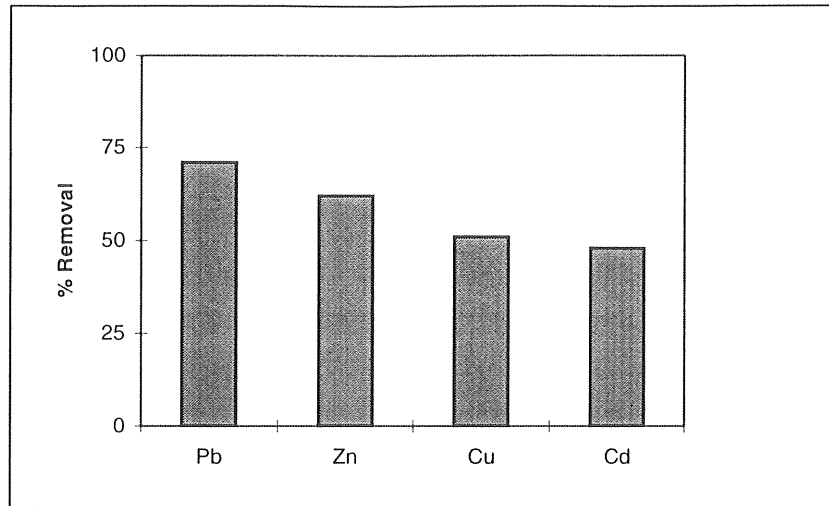


Figure 18. Percentage Removal of Total Metals

5.4. Retention Time

Different retention times (2, 5 and 10 hours) was used to determine how the concentrations of Pb, Cu, Zn and Cd vary with time. The results, as profiled in Figure 19, showed that cadmium removal was effective after 5 hours, although the amount removed was only 10% of the initial concentration. Negative removal can be observed after 2 and 10 hours. Inefficient treatment at 2-hours could possibly be attributed to short column-wastewater contact which could limit plant uptake, adsorption in the roots and substrate. The concentration peak after 10 hours could be due to desorption in the sediments and subsequent release to water owing to Cd mobility.

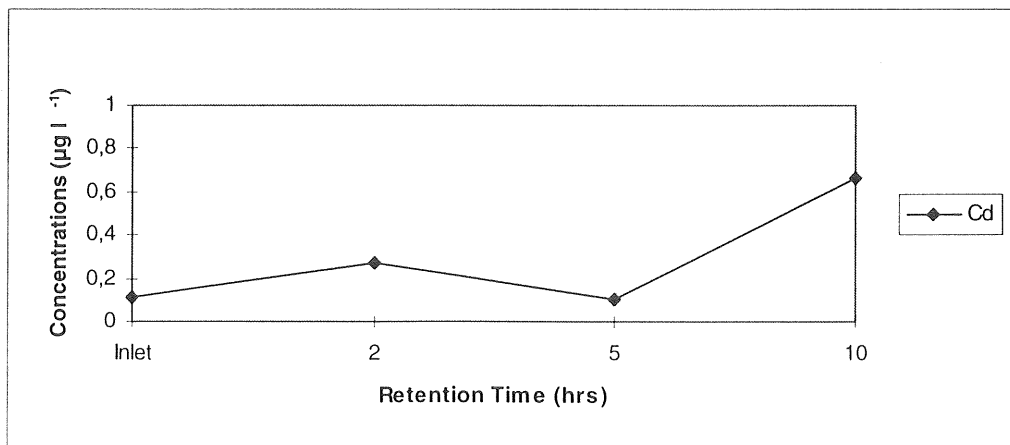


Figure 19. Concentrations of Ionic Dissolved Cadmium at Different Retention Time

Pb and Cu achieved 100% removal in the water sample after only 2 hours (Figure 20). Aside from the ability of these two metals to adsorb rapidly in surfaces, another possibility of this effective removal could be due to the low concentrations in the influent.

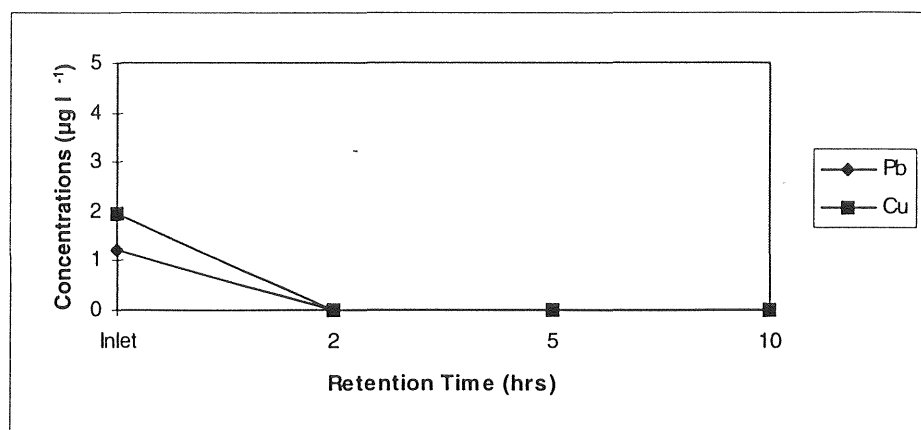


Figure 20 Concentrations of Ionic Dissolved Cu and Pb at Different Retention Time

Zinc demonstrated small differences in removal through time (Figure 21). However, it can be noted that removal was high after only 2 hours compared with 5 and 10 hours results. Removal efficiencies for 2, 5 and 10 hours were found to be 71%, 60% and 69% respectively.

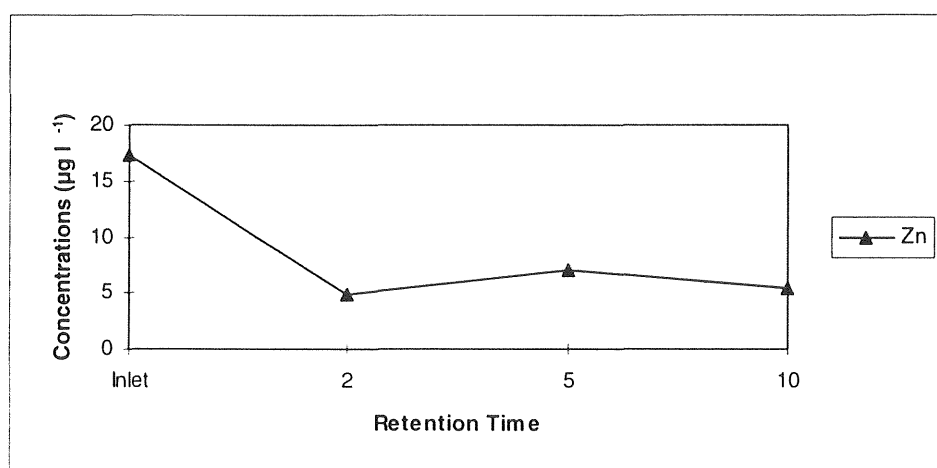


Figure 21 Concentrations of Ionic Dissolved Zn at Different Retention Time

Removal of metals is therefore effective at relatively low retention times. Studies of NH_4^+ removal in similar column (Farahbakshad Personal Communication) demonstrate that nutrient root uptake increases slowly with time. Rapid removal and occasional release tend to demonstrate that metals are initially and rapidly removed by physico-chemical processes, transfer to roots being a slow process.

6. Conclusion

Metal removals in an upflow macrophyte system confirm the ability of constructed wetlands to serve as an efficient sink for metals. Results have shown that uptake of ionic dissolved metals in the system followed the order: $Zn > Pb > Cu > Cd$. The uptake of ionic dissolved species varied depending on the maturity of the system. High removals were observed when the system became matured. For total metals, removal in the column followed the order: $Pb > Zn > Cu > Cd$. This signifies that high removal efficiencies observed for Zn and Pb can be due to their high adsorption with the organic and inorganic fractions in the substrates, complemented by plant uptake. Removals of particle bound and colloidal fraction were obvious for Zn and Pb attesting the high adsorption capacity of these metal species. While competition for binding sites might have lowered the removal efficiencies of Cu and Cd in the system.

Variation of concentrations in the column profiles could probably be attributed to the density and distribution of roots. High treatment efficiencies were observed for Pb, Cu and Cd at 0.5 m depth, while Zn removal was most effective at 0.1 m depth.

Assessment of effective retention time showed that significant removal can be attained after 2 hours for Pb, Zn and Cu. While Cd is more difficult to remove and therefore needs longer retention time. The rapid or initial removal followed by subsequent release of metals seemed to imply that the major removal mechanism for metals is attributed to the physico-chemical processes undergoing in the system. Transfer of metals to the roots, might be a slow process.

7. Recommendation

This study is a preliminary assessment on the performance of a pilot scale macrophyte system for metal removal. Results have shown that the system has the ability to remove Zn, Pb, Cu and Cd from stormwater. However, metal removal mechanisms should be fully understood so that the system can be optimised and more confidence can be given in predicting system performance. In lieu of this, assessment on the role of substrate and plants in metal removal should be investigated. The determination of the fate of individual species, whether they adsorb to sand through filtration, or onto/into the roots will give a better understanding on the treatment processes of the system. In addition, a closer look at shorter retention times should also be assessed. It may be, that metals could rapidly be removed in a storm event with a very short detention time, using *Phragmites australis* in gravel, with large volumes and metals gradually adsorb into the roots.

8. References

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APPENDIX

I. Concentration Profiles of Ionic Dissolved Zn, Pb, Cu and Cd

	Pb (ug/l)				
Influent	15,28	9,85	14,00	2,06	3,58
Effluent (0.1)	8,78	6,49	9,50	2,15	1,87
Effluent (0.2)	7,81	7,91	8,94	1,12	1,87
Effluent (0.3)	7,46	2,29	3,18	xxx	2,14
Effluent (0.4)	5,97	1,57	3,11	1,51	3,76
Effluent (0.5)	5,29	1,5	1,71	1,46	3,12

	Cu (ug/l)			
Influent	49	49,50	33,01	23,50
Effluent (0.1)	36,7	21,01	36,37	139,40
Effluent (0.2)	46,5	36,77	37,82	128,47
Effluent (0.3)	37,13	46,49	27,96	96,88
Effluent (0.4)	49,5	37,13	25,07	91,95
Effluent (0.5)	10,1	49,45	24,77	29,01

	Zn (ug/l)			
Influent	14	324,20	38,18	16,38
Effluent (0.1)	3,11	105,00	21,72	4,47
Effluent (0.2)	3,18	102,85	17,40	5,53
Effluent (0.3)	8,94	377,51	17,30	4,69
Effluent (0.4)	9,5	231,23	21,00	6,39
Effluent (0.5)	6,61	159,76	10,15	2,56

	Cd (ug/l)	
Influent	0,34	0,12
Effluent (0.1)	0,50	0,36
Effluent (0.2)	0,58	0,5
Effluent (0.3)	1,09	0,25
Effluent (0.4)	1,11	0,22
Effluent (0.5)	3,18	0,11

II. Partitioning

Cd (ug/l)	In	Out	% Removal
Particle Bound	0,29	0,57	
Colloidal	0,43	0,38	11,63
Ionic Dissolved	0,91	0,06	93,41
Total	1,30	1,10	15,38

Pb (ug/l)	In	Out	% Removal
Particle Bound	36,9	4,3	88,3
Colloidal	11,6	0,0	100,0
Ionic Dissolved	1,5	1,4	6,7
Total	48,5	8,3	82,9

Cu (ug/l)	In	Out	% Removal
Particle Bound	45,3	18,7	58,7
Colloidal	37,8	23,4	38,1
Ionic Dissolved	25,6	19,3	24,6
Total	102,0	58,0	43,1

Zn (ug/l)	In	Out	% Removal
Particle Bound	511,0	135,7	73,4
Colloidal	368,0	37,2	89,9
Ionic Dissolved	7,9	2,2	72,2
Total	897,0	179,0	80,0

III Treatment Efficiencies for Ionic Dissolved Metals

A. June

Pb (ug/l)					
Influent	15,28	9,85	3,58	2,06	14
Effluent	5,29	1,5	3,12	1,46	1,71
% Removal	65,37	84,7	12,84	29,1	87,7

Zn (ug/l)					
Influent	324,18	222,76	38,18	16,38	14
Effluent	159,76	88,97	10,15	2,56	6,61
% Removal	51	60	73,4	84,4	53

Cu (ug/l)			
Influent	33,01	12	16
Effluent	24,77	11,21	14,8
% Removal	25	79,5	8

Cd (ug/l)	
Influent	0,12
Effluent	0,11
% Removal	8,33

B. August-September

Pb(ug/l)					
Influent	2,51	0,73	6,8	10,4	4,9
Effluent	0,97	0,25	1,6	4,4	0,5
% Removal	62	66	77	58	90

Zn(ug/l)					
Influent	3,6	88	58,3	7,9	12,6
Effluent	2	9,3	1,5	2,2	1,24
% Removal	44	89	97	72	90

Cu (ug/l)	
Influent	26
Effluent	19,3
% Removal	25

Cd (ug/l)		
Influent	0,3	0,4
Effluent	0,1	0,3
% Removal	67	25

IV. Treatment Efficiencies for Total Metals

August-September

Pb (ug/l)							
Influent	31,89	2,56	27,5	91,6	48,5	13,6	24,5
Effluent	7,9	1,47	3,4	24,4	8,3	2,3	12,5
% Removal	75	43	88	73	83	83	49

Zn (ug/l)							
Influent	606,2	330,3	163,5	208	224	220,15	
Effluent	120	195,3	42	77,25	44,75	147,65	
% Removal	80	41	74	62,8	80	33	

Cu (ug/l)				
Influent	151	260	252	102
Effluent	87	92,32	147	43
% Removal	42	65	42	58

Cd (ug/l)					
Influent	0,72	1,13	0,7	0,3	0,56
Effluent	0,56	0,47	0,38	0,06	0,35
% Removal	22	58	46	80	38

V. Retention Time

	Heavy Metals (ug/l)			
	Cd	Pb	Zn	Cu
Influent	0,11	1,2	17,3	1,97
After 2-hour	0,27	0	4,95	0
After 5-hour	0,1	0	7	0
After 10-hour	0,66	0	5,44	0

Please refer to the following pages for corrections:

1) Page i Abstract

Cu and Cd showed significant removal in the ionic dissolved phase at 93.4% and 24.6%; instead of 91.4% and 59%.

2) Page i Abstract

Treatment efficiencies increased significantly in August and September to 81%, 71% 46% and 25% for ionic dissolved Zn, Pb, Cd and Cu; instead of Cu and Cd.

3.) Page 38 Cadmium

Moreover, retention of this fraction was significantly high at 93.4%; instead of 91.4%.

