PHYTOACCUMULATION OF HEAVY METALS BY AQUATIC PLANTS

by

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DEDICATION

To:

My Wife

Heba M. Deeb

My Baby

Hanna

My Parents

Gen. Amin and Dr. Nariman

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

AFBR	Anaerobic Fluidized Bed Reactor
ALD	Anoxic Limestone Drain
AMD	Acid Mine Drainage
ANOVA	Analysis of Variance
ANZECC	Australian and New Zealand Environment Conservation Council
AS	Activated Sludge
ASBR	Anaerobic Sequencing Batch Reactor
B	Bog
BAMR	Bureau of Abandoned Mine Reclamation
BCMELP	British Columbia Ministry of Environment, Land, and Protection
BOD	Biological Oxygen Demand
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
C	Concentration
CCME	Canadian Council of Ministers of the Environment
CEC	Cation Exchange Capacity
CLR	Chemical Loading Rate
COD	Chemical Oxygen Demand
CPEO	Center for Public Environment Oversight
CPOM	Coarse Particulate Organic Matter
DNR	Department of Natural Resources
DNT	2-methylbenzene-1,5-diamine
DO	Dissolved oxygen
DOC	Dissolved Organic Compounds
DW	Deepwater marsh
dw	Dry Weight
EC	Environment Canada
EDTA	Ethylene-diamine-tetraacetic acid
EQL	Estimated Quantitation Limit

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FRTR	Federal Remediation Technologies Roundtable
FWS	Free Water Surface
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HRT	Hydraulic Residence Time
INAC	Indian and Northern Affair Canada
MAP	Magnesium Ammonium Phosphate
MSW	Municipal Solid Waste
MSWI	Municipal Solid Waste Incineration
n/a	Not applicable
nd	Not detected
NF	Nanofiltration
NGA	No Guideline Available
NRC	Natural Resources Canada
O&M	Operation and Management
OLC	Open Limestone Channel
OLD	Oxic Limestone Drain
OW	Open water marsh
PAC	Powdered Activated Carbon
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated biphenyl
PCB	Polychlorinated Biphenyl
PCE	Trichloroethylene
PCP	Pentachlorophenol
R	Removal Efficiency
RDX	Cyclotrimethylenetrinitramine
RO	Reverse Osmosis
SBR	Activated Sludge Reactor
SM	Shallow marsh
SS	Shrub swamp
SS	Suspended Solids
SSF	Sub-surface flow

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TCE	Trichloroethylene
TCE	Trichloroethylene
TDS	Total Dissolved Solids
TF	Translocation factor
TKN	Total Kjeldahl Nitrogen
TNT	Trinitrotoluene
TPH	Total Petroleum Hydrocarbon
TSS	Total Suspended Solids
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
VFA	Volatile Fatty Acid
VOC	Volatile Organic Compound
VSS	Volatile Suspended Solids
WCMC	World Conservation Monitoring Centre
WMPP	Wetlands Mapping Protection Program
ha	hectare
DF	Degrees of Freedom
SS	Sum of Squares
MS	Mean of Squares
CV	Coefficient of Variation
NS	No Stem
NF	No Flower
mg	Milligram
kg	Kilogram
L	Liter
cm	centimeter
m	meter

English Symbols

C_{O_2}	Aqueous oxygen concentration (mol/L)
P_{CO_2}	Carbon dioxide partial pressure (atm)

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K_{CO_2}	Equilibrium constant of carbon dioxide dissolving reaction (-)
$[Ca^{+}]$	Concentration of calcium ion (mol/L)
$[H^{+}]$	Concentration of hydrogen ion (mol/L)
$[HCO_3^{-}]$	Concentration of bicarbonate (mol/L)
$[H_{eq}]$	Interfacial (equilibrium) hydrogen ion concentration (mol/L)
A	Spherical limestone mass-specific surface area (cm^2/gm)
a	Interfacial area of calcium carbonate per unit volume (cm^2/cm^3)
$A_{abiotic}$	Pre-exponential factor (4.00×10^5 mol/L/sec)
A_{bio}	Pre-exponential factor (1.09×10^9)
A_c	Cross-sectional area of the reactor (cm^2)
a_H	Hydrogen ion activity
A_{Mn}	Pre-exponential factor
A_{Mn}	Pre-exponential factor (sec^{-1})
C_{Ci}	Initial calcium carbonate concentration (mol/L)
C_{Ct}	Calcium carbonate concentration at time t (mol/L)
C_{Mni}	Initial manganese concentration (mg/L)
C_{Mnt}	Manganese concentration at time t (mg/L)
C	Concentration of element (mg/cm^3)
C*	Irreducible background concentration (mg/L)
C_1	Inflow Concentration (mg/L)
C_2	Outflow Concentration (mg/L)
C_a	Influent concentrations of anions excluding inorganic carbon species and hydroxide
Ca_{dis}	Dissolved calcium ion per area of limestone (mg/cm^2)
C_{bact}	Concentration of *T. ferrooxidans* (dw mg/L)
C_C	Calcium carbonate concentration in the solution (mol/L)
C_e	Target effluent concentration (mg/L)
C_{Fe}	Iron concentration in the solution (mg/L)
C_{Fe+3}	Fe(III) concentration in the system (mol/L)
C_{Fe}^{2+}	Aqueous ferrous iron concentration (mol/L)
C_{Fei}	Initial iron concentration (mg/L)

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C_{Fet}	Iron concentration at time t (mg/L)
C_{H}^{+}	Aqueous hydrogen ion concentration (mol/L)
C_i	Influent concentration (mg/L)
C_{MI}	Initial manganese concentration (mg/L)
C_{Mn}	Manganese concentration in the solution (mg/L)
C_{Mn}^{2+}	Aqueous ferrous iron concentration (mol/L)
CP	Concentration Reduction (%)
C_Z	Initial zinc concentration (mg/L)
D	Calcium ion diffusivity (m^2/sec)
d	Volume mean diameter of limestone particles (cm)
D	Decomposition Rate (mg/d)
d_{50}	Filter material size (m)
df	Degrees of freedom
E	Diffusion/Dispersion coefficient (cm^2/s)
E	Evaporation (m)
$E_{a,abiotic}$	Activation energy (kJ/mol)
$E_{a,bio}$	Activation energy (kJ/mol)
E_h	Redox potential
E_{Mn}	Activation energy of manganese oxidation (kJ/mol)
ET	Evapotranspiration (m)
G_i	Groundwater inflows (m^3/d)
G_o	Groundwater outflows (m^3/d)
h	Water Depth (m)
I_F	Iron concentration in flower tissues (mg/kg)
I_L	Iron concentration in leaf tissues (mg/kg)
I_R	Iron concentration in root tissues (mg/kg)
I_S	Iron concentration in stem tissues (mg/kg)
I_{TO}	Total iron concentration in plant tissues (mg/kg)
J_{in}	Flux-in of mass of the element due to transport (mg/cm^2/s)
J_{out}	Flux-out of mass of the element due to transport (mg cm^{-2} s)
k	First order oxidation/dissolution rate constant (sec^{-1})

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K_1	Equilibrium constant of carbonic acid dissolution reaction
k_1	First order rate constant
K_2	The second dissociation constant of carbonic acid
$k_{abiotic}$	Abiotic rate constant (mol/L/sec)
k_{bio}	Biotic rate constant ($L^3mg^{-1}mol^{-2}sec^{-1}$)
k_C	Calcium carbonate dissolution rate constant (min^{-1})
k_c	First order surface reaction rate constant (cm/sec)
k_{Ca}	Calcium carbonate dissolution rate (sec^{-1})
k_f	Armoring layer mass transfer coefficient (cm/sec)
k_{Fea}	Abiotic iron oxidation first order rate (sec^{-1})
k_{Febio}	Biotic first order iron oxidation rate constant (sec^{-1})
K_H	The Henry's Law constant (mol/L atm.)
K_I	Iron oxidation rate constant (min^{-1})
k_L	Mass transfer rate constant for calcium ion (cm/sec)
k_M	Manganese oxidation rate constant (min^{-1})
K_{Mn}	Manganese oxidation first order rate (sec^{-1})
k_o	Overall dissolution rate constant (cm/sec)
K_{sp}	Calcium carbonate solubility product
K_w	Water ion product
LP	Pollutant Load Reduction (%)
M_F	Manganese concentration in flower tissues (mg/kg)
M_L	Manganese concentration in leaf tissues (mg/kg)
M_M	Maximum concentration of metal that can be accumulated in the wetland plant (mg/kg)
M_p	Concentration of metal in the wetland plant at a given time (mg/kg)
M_R	Manganese concentration in root tissues (mg/kg)
MRe	Modified Reynold's number (-)
M_S	Manganese concentration in stem tissues (mg/kg)
M_{TO}	Total Manganese concentration in plant tissues (mg/kg)
n	Manning's roughness coefficient
N	Number of limestone particles (at least 50)

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°C	Degree Celsius
p	Bed porosity (cm^3/cm^3)
p	Porosity of the medium (m^3/m^3)
P	Precipitation (m)
PC_I	Total iron concentration in plant in mg/kg
PC_M	Total Mn concentration in plant in mg/kg
P_n	Net precipitation (m)
Q	Flow rate (m^3/y)
q	Hydraulic Loading Rate (m/d)
R	Gas constant (kJ/mol/K)
R	Gas constant (kJ/mol/K)
R	Runoff (m^3/d)
rc	Runoff coefficient
reaction	Gain or loss of mass within the element due to reaction (mg/s)
RE_I	Iron overall removal efficiency in season I (%)
RE_{II}	Iron overall removal efficiency in season II (%)
RE_M	Manganese removal efficiency (%)
RE_{MI}	Manganese overall removal efficiency in season I (%)
RE_{MII}	Manganese overall removal efficiency in season II (%)
RE_Z	Zinc removal efficiency (%)
Rg	Gas constant (kJ/mol/K)
S	Channel bed slope (m/m)
s	Sphericity of limestone particles
Sc	Schmidt number (-)
SC_I	Iron concentration in the inlet sediments in mg/kg
SC_M	Mn concentration in the inlet sediments in mg/kg
S_i	Surface inflows (m^3/d)
S_o	Surface outflows (m^3/d)
T	Temperature (K)
t	Time (s)
Tr	Hydraulic Residence Time (d)

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T_a	Temperature in Kelvin (T °C + 273.15)
Te	Temperature (K)
T_t	Time (days)
u	Ionic strength (mg/L)
U	Velocity (cm/s)
V	Volume of wetland water storage (m^3)
W	Mass of specific number limestone particles (g)
W	Width of System (m)
WA	Watershed area (m^2)
WP	Flow Reduction (%)
z	Distance from inlet (cm)
Z_F	Zinc concentration in flower tissues (mg/kg)
Z_i	The charge of species *i* (-)
Z_L	Zinc concentration in leaf tissues (mg/kg)
Z_R	Zinc concentration in root tissues (mg/kg)
Z_S	Zinc concentration in stem tissues (mg/kg)
Z_{TO}	Total zinc concentration in plant tissues (mg/kg)

Greek Symbols

Σ	Summation
α	Alpha
ε	Water Column Void Fraction
τ	Nominal Detention Time (d)
γ	Activity coefficient of the same ion (-)
ΔV	Volume of the differential element of a length $\Delta z = A_c \Delta z$ (cm^3)
ρ	Mass density of high calcium limestone (~2.7g/cm^3)
υ	Kinematic viscosity (cm^2/s)

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ABSTRACT

This study evaluated the use of an integrated system consisting of two passive technologies (constructed wetland and limestone/sandstone filter) for the treatment of landfill leachate. It included both field and laboratory studies.

The effectiveness of constructed wetland for treating landfill leachate was evaluated over two years. Increasing the number of cells in the constructed wetland from 4 to 9 and the level of plant establishment in the second year improved the removal efficiencies for Fe, Mn, ortho-PO_4, TKN, NH_4-N, NO_3-N, COD, TSS and TDS by 29.68, 7.30, 33.3, 33.3, 30.6, 8.00, 26.7, 52.2, 43.5 and 54.1 %, respectively. Although the ten plants (wool grass, soft rush, tweedy's rush, pickerelweed, yellow-green sedge, fowl mannagrass, soft stem bulrush, fringed sedge, reed canary grass and broad leaf cattail) used in the constructed wetland were excellent accumulators of Fe (8690-23725 mg/kg), they did not accumulate high concentrations of Mn (554-3370 mg/kg) due to Mn-Fe antagonism. The roots of the plants accumulated significantly greater concentrations of Fe than the shoots and flowers while the leaves and flowers accumulated significantly greater concentrations of Mn than the roots.

A laboratory experiment, in which two facultative (Woolgrass, Soft stem bulrush) and two obligate (Broadleaf cattails, Soft rush) wetland plants were planted, was used to provide a better understanding of the removal mechanism and the factors affecting removal efficiency. The plant type, time and initial concentrations of heavy metals have significant effects on the removal efficiency of the heavy metals. The Fe, Mn and Zn concentrations in the plant tissues were directly proportional to their initial concentrations in the wastewater. A first-order kinetic model was used to determine Fe, Mn and Zn uptake parameters by wetland plants.

Laboratory experiments were performed to assess the ability of limestone and limestone/sandstone filters to treat landfill leachate. The results showed that the limestone and the limestone/sandstone filters removed 96% and 70% of the Fe and Mn from solution under batch condition in the first 20 and 50 minutes, respectively. The dissolution of $CaCO_3$ and the precipitation of Fe and Mn were affected by temperature and time. As temperature decreased from 20 to 5°C, the removal efficiencies decreased from 99.77 to 94.85 % and from 86.11 to 58.00 % for Fe and Mn, respectively. The Fe and Mn removal rate constants of the limestone filters were higher than those of the limestone/sandstone. The effluent from continuous flow filters contained on average less than 0.66 mg/L of Fe and 0.47 mg/L of Mn. A mathematical model was developed and used to predict the Fe and Mn concentrations in the outlet of a continuous flow limestone/sandstone filter. Two limestone filters were designed and the various dimensions of the filters were calculated.

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CONTRIBUTIONS TO KNOWLEDGE

The contributions of this thesis to knowledge in the field of wastewater treatment can be summarized as follows:

1. The effects of weather, plant maturity and density and water quality on the performance of a constructed surface flow wetland treating landfill leachate and stormwater runoff from an industrial park were documented under Atlantic Canadian condition. The phytoremediation potential of obligate (pickerelweed, yellow-green sedge, fowl mannagrass, soft stem bulrush, fringed sedge and broad-leaved cattail) and facultative (wool grass, soft rush, tweedy's rush and reed canary grass) plant species for the removal and translocation of Fe and Mn in roots, stems, leaves and flowers were documented.

2. Relationships between plant uptake of metal and plant activity (growth) and between metal concentrations in plants and sediments were established. A first-order kinetic model was used to determine iron and manganese specific uptake rate by wetland plants and the maximum concentration that can be accumulated by each plant.

3. A mathematical model was developed to predict the calcium carbonate, iron and manganese concentrations in the outlet of a continuous flow limestone/sandstone filter. The model was capable of predicting calcium carbonate, iron and manganese concentrations.

4. A design procedure for field limestone/sandstone filters was developed.

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1. INTRODUCTION

Landfills are potential threats to groundwater and surface water quality, the primary concern being the production of leachates (Howard, 1997). Leachates are highly toxic and, if discharged directly into water bodies, could impact aquatic life and degrade water quality (Cameron and Koch, 1980). Chemical and biological reactions occur as water percolates through refuse in landfills. The products of the complex combination of ongoing reactions within the refuse are transported by the infiltrating water. Besides the chemical and biological reactions, physical processes such as sorption and dissolution also take place during the passage of water through the waste. The sum total of all these processes and reactions is a leachate with dimensional attributes varying over time (McBean and Rovers, 2000). The leachate generated from the biochemical processes is characterized by very high concentrations of organic and inorganic contaminants. Water percolating through the landfill surface from infiltration will actually dilute contaminants in the leachate, as well as aid in the formation of new leachate (Bagchi, 1990). The temporal variability of leachate quantities and qualities is influenced by features including the meteorology, the cover overlying the refuse, the hydrogeologic conditions in the vicinity of the site, and other characteristics of the refuse such as age, composition, and degree of compaction (McBean and Rovers, 2000). The chemical composition of leachate varies greatly depending on the age of landfill and the events prior the time of sampling (Christensen, et al., 1994). The biodegradability of organic matter in leachate is generally inversely proportional to the molecular weight of the various components of the organic matter; lower molecular weights indicate a higher degree of biodegradability. Chain and deWalle (1977) stated that organic matter in landfill leachates ranges from volatile acids with low molecular weight to refactory fulvic- and humic-like compounds of intermediate and high molecular weights, respectively.

Wetlands are used to treat a variety of wastewaters, including municipal, mine drainage, urban and agricultural storm waters, sludges, leachates, and various industrial effluents. Wetland treatment can take place in natural or constructed wetland sites. Principal categories of constructed wetland systems include densely vegetated overland flows,

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subsurface systems, pond and island systems, and channels with floating plants (Kadlec, 2000). Metals are removed by cation exchange to wetland sediments, precipitation as sulfides and other insoluble salts, and plant uptake. Plant storage is typically predominantly to the roots (Surface, et al., 1993). The anaerobic sediments provide sulfate reduction to sulfide and facilitate chemical precipitation. As a result, removals of metal are reported for operating wetland facilities (Eger, 1994; Dickman and Rygiel, 1996; Mungur et al., 1997; Lytle et al., 1998; Deng et al., 2004; and Mungur et al., 2005). Nonvolatile, nontoxic organics are often lumped as COD or BOD, because they can create oxygen deficiencies in receiving waters. Biological mechanisms include oxidation and anaerobic digestion (Kadlec and Knight, 1996). Reduction of phosphorous, nitrogen compounds and other nutrients requires the longest detention of any of the pollutants (Picard et al., 2005). Nitrogen removal may require active or passive reaeration to promote nitrification. Nitrogen is also stored, but in larger measure is sequentially transformed, ultimately leaving the wetland as dinitrogen or ammonia (Puetpaiboon and Yirong, 2004; and McHale et al., 2005). Phosphorus is stored in new wetland sediments (Paasch et al., 1977; and Rosolen and Anderson, 2000).

In many ways, living plants can be compared to solar driven pumps which can extract and concentrate several elements from their environment (soil and water). All plants have the ability to accumulate heavy metals which are essential for their growth and development. These metals include Mg, Fe, Mn, Zn, Cu, Mo and Ni (Langille and MacLean, 1976). Certain plants also have the ability to accumulate heavy metals which have no known biological function. These include Cd, Cr, Pb, Co, Ag, Se and Hg (Hanna and Grant, 1962; Baker and Brooks, 1989). However, excessive accumulation of these heavy metals can be toxic to most plants. The ability to both tolerate elevated levels of heavy metals and accumulate them in very high concentrations has evolved both independently and together in a number of different plant species (Ernst et al., 1992). Plants distribute metals internally in many different ways: (a) they may localize selected metals mostly in roots and stems, or (b) they may accumulate and store other metals in nontoxic form for latter distribution and use. A mechanism of tolerance or accumulation in some plants apparently involves binding potentially toxic metals at cell walls of roots

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and leaves, away from sensitive sites within the cell or storing them in a vacuolar compartment (Memon et al., 2001). It should be pointed out that wetland plants play an important role in metal removal from metal-polluted water in constructed wetland by metal immobilization in the roots and in the oxygenated rhizosphere (Ye et al., 2001). However, metals accumulate in the leaves and flowers of some plants which are used as food for wetland animals and birds and there is, therefore, the possibility that these plants may be harmful to wildlife (Kamal et al., 2005).

Conventional water treatment systems that remove iron and manganese from wastewater involve the addition of alkaline chemicals (such as lime, sodium hydroxide and sodium carbonate) to the water. Alkali addition causes the pH of the water to increase and the dissolved metals to precipitate out of solution (Ziemkiewicz et al, 1997, and Gazea et al, 1996). These active systems usually have increased costs associated with operation and maintenance, purchase of chemical reagents and disposal of metal laden sludge (Ziemkiewicz et al, 1997, and Gazea et al, 1996). According to Cravotta III and Trahan (1999) and Hedin et al (1994), passive treatment systems that use limestone have become very popular for treating landfill leachates and mine drainage because the systems are inexpensive to construct and maintain and limestone is a cheap source of alkalinity, especially in coal mining regions.

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2. OBJECTIVES

The main aim of this study was to shed some light on the mechanisms of heavy metals removal in constructed wetlands and investigate the effectiveness of combining a constructed wetland with a passive treatment technology for the treatment of landfill leachate. The specific objectives were:

1. To evaluate the performance of a constructed wetland treating landfill leachate:
   (a) determine the overall removal efficiencies of the wetland for heavy metals (Fe and Mn), COD, TSS, TDS, Ortho-phosphate, Ammonium-Nitrogen, TKN, NO_3-N, NO_2-N, DO and pH,
   (b) determine the cell-to-cell removal efficiency for the above parameters,
   (c) determine the rate and concentration of heavy metals uptake by the plants, and
   (d) determine the rate and concentration of heavy metal precipitates.

2. To assess the ability of facultative and obligate wetland plants to remove heavy metals from landfill leachate and to gain a better understanding of the removal mechanism:
   (a) determine the overall removal efficiency of the heavy metals (iron, manganese and zinc) by facultative (wool grass and soft stem bulrush) and obligate (broadleaf cattails and soft rush) wetland plants,
   (b) determine the fractions of heavy metals accumulated in the different parts of each plant species (root, stem, leaves and flower),
   (c) determine the plant heavy metals selectivity, and
   (d) determine the fraction of heavy metals removed by precipitate.

3. To assess the ability of limestone/sandstone filters for the pretreatment of landfill leachate:
   (a) evaluate the effectiveness of limestone and limestone/sandstone filters in removing dissolved iron and manganese from landfill leachate,
   (b) determine the suitability of the treated wastewater for aquatic life in the wetland as measured by its final pH,

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(c) evaluate the effectiveness of limestone and limestone/sandstone filters in removing dissolved iron and manganese from landfill leachate under different temperatures (20, 15, 10 and 5°C),

(d) evaluate the effectiveness of the limestone/sandstone filters in removing dissolved iron and manganese from landfill leachate in continuous system,

(e) develop a mathematical model capable of predicting the wastewater quality of the outlet of limestone/sandstone filters, and

(f) design a field scale limestone/sandstone filters to treat landfill leachate.

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3. SCOPE

This study was carried out in five separate but interrelated stages. The first stage was devoted to the evaluation of the performance of a constructed wetland. Water, plant and soil samples were taken from the wetland cells for heavy metals (Fe and Mn) analyses. Also, COD, TSS, TDS, Ortho-phosphate, Ammonium-Nitrogen, TKN, NO_3-N, NO_2-N, DO and pH analyses were performed on the water samples.

The second stage was devoted to a laboratory experimental work to determine the rate of removal of heavy metals by wetland plants and to determine the fractions of heavy metals stored in the plant parts, and precipitated in the soil. Facultative (wool grass and soft stem bulrush) and obligate (broadleaf cattails and soft rush) wetland plants were used and three different concentrations of heavy metals were studied. The heavy metals contents in the four plants were compared to determine the heavy metal selectivity by plants.

The third stage was dedicated to a laboratory experimental work to determine the effectiveness of limestone and limestone/sandstone filters in removing dissolved iron and manganese from landfill leachate and to determine the suitability of the treated wastewater for aquatic life in the wetland as measured by its final pH. The work was carried out under batch condition at different temperatures and under continuous flow condition at ambient temperature and different ratios of limestone:sandstone and various particle sizes of sandstone.

In the fourth stage, a model was developed capable of predicting the amounts of heavy metals removed from the water using limestone/sandstone filter. The validity of the model was verified using the experimental results. A sensitivity analysis was also carried out on the model.

In the fifth stage, a field scale limestone/sandstone filter was designed.

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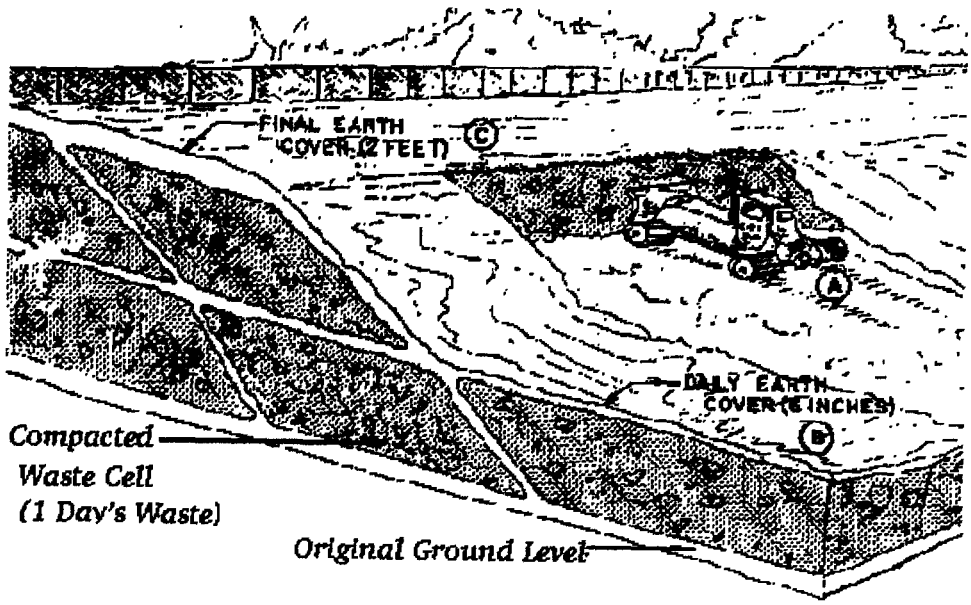
4. LITERATURE REVIEW

4.1 Landfills

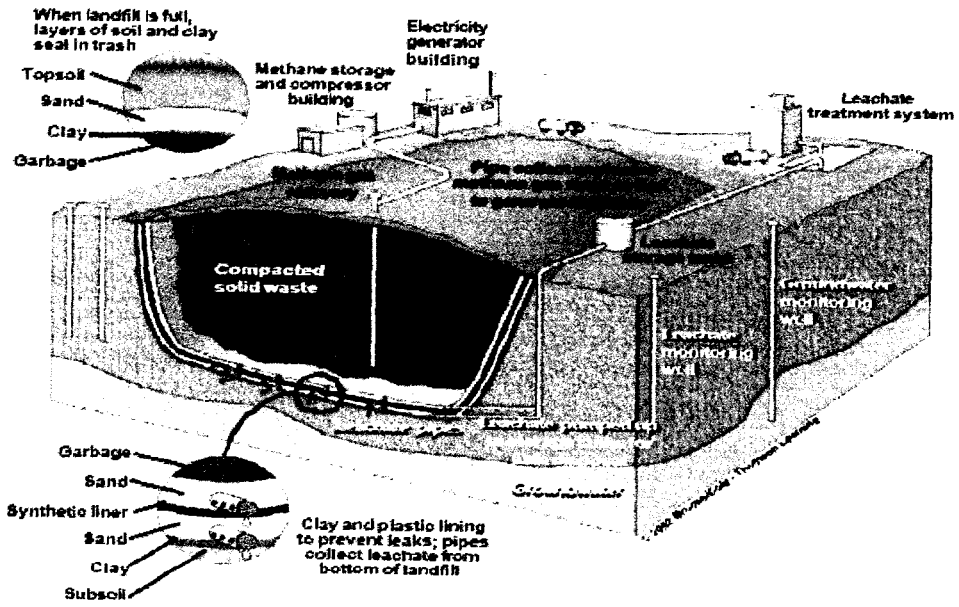
4.1.1 Definition

Landfills are physical facilities used for the disposal of residual solid wastes within the surface soils of the earth. In the past, the term sanitary landfill was used to denote a landfill in which the waste placed in the landfill was covered at the end of each day's operation (Figure 4.1a). Today, sanitary landfill refers to an engineered facility for the disposal of waste designed and operated to minimize public health and environmental impacts (Figure 4.1b). Landfills for the disposal of hazardous wastes are called secure landfills. Landfilling is the process by which residual solid waste is placed in a landfill. It includes monitoring of the incoming waste stream, placement and compaction of the waste and installation of landfill environmental monitoring and control facilities (Tachobanoglous et al., 1993). Historically, landfills have been the most economical and environmentally acceptable method for the disposal of solid wastes in United States, Canada and throughout the world. Even with implementation of waste reduction, recycling, and transformation technologies, disposal of residual solid waste in landfills still remains as important component of an integrated solid waste management strategy (McBean, et al., 1995). However, because of varying nature of the physical, chemical, and biological characteristics of Municipal Solid Waste (MSW) and the many landfilling approaches used, the management of MSW can have a significant adverse impact on those who own or use properties near the waste management location. This can be divided into two periods: (a) the active life when the landfill receives waste, and (b) the post-closure period after the landfill has stopped receiving waste. The active life of an MSW landfill is in the order of 20-30 years because it often requires at least 10 years to bring a new landfill on line (Lee and Jones-Lee, 1993).

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(a) old landfill (Ham, 1979)



(b) engineered landfill (Thomson, 1992)

Figure 4.1. Typical old and engineered landfills.

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4.1.2 Types of Landfills

The principal types of landfills can be classified as: (a) conventional landfills, (b) landfills for milled solid wastes, and (c) Landfills for individual waste constituents.

4.1.2.1 Conventional Landfills

The majority of landfills are designed for municipal solid waste (MSW) and only limited amounts of non-hazardous industrial wastes and sludges from water and wastewater treatment plants can be accepted. In most cases, native soil is used as the intermediate and final cover material. Alternative materials such as compost produced from yard wastes and MSW, foam, old rugs and carpeting, dredging spoils, and demolition wastes have been used in locations where the amount of native soil available for use is limited. Abandoned and or closed landfills in some locations are being reused by excavating the decomposed material to recover the metals and using the decomposed residue as daily cover for the new wastes (Baum, 1993).

In conventional landfills, the stabilization process takes such a long time due to the fact that the waste material has been essentially entombed in the landfill so that substantially no oxygen or moisture is introduced into the landfill (IWM, 1998; and EPA, 1998). The reactions that does take place is primarily anaerobic (without oxygen), which produce harmful and objectionable by-products, such as methane gas, hydrogen sulfide and volatile organic acids (Read et al., 2001). Research involving the mining of wastes from older landfills, especially those with low-permeability caps, has revealed that a significant fraction of the waste mass remains relatively intact, with little evidence of biodegradation within the landfill even after several years (Ham, 1979; and Qasim and Chiang, 1994).

A conventional landfill will potentially generate leachate and landfill gas beyond the current 30 year post-closure monitoring period due to the low but consistent infiltration of storm water. This poses long-term environmental impacts to the landfill area and increased maintenance cost burdens for municipal and private solid waste management

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entities (Wall and Zeiss, 1995). In addition, anaerobic conditions within a landfill results in the production of methane, an explosive and odorless gas and vapor-phase volatile organic compounds (VOCs). Methane 'greenhouse gas' generated in landfills is typically in excess of 45% of the total landfill gases (USEPA, 1998). In some cases, VOCs present in the landfill gas have been identified as a source of groundwater contamination (IWM, 1998). These gases need to be collected and controlled (flare or other end use) to minimize the risks of gas build up and/or fires.

4.1.2.2 Landfills for Shredded Materials

An alternative method of landfilling that is being tried involves shredding of the solid wastes before placement in a landfill. Shredded (or milled) waste can be placed at up to 35 percent greater density than unshredded waste, and without daily cover in some facilities. Because shredded waste can be compacted to a tighter and more uniform surface, a reduced amount of soil cover or some other cover material may be sufficient to control infiltration of water during the fill operation. Among the disadvantages of this method are: (a) the need for shredding facility and (b) the need to operate a conventional landfill section for wastes that cannot be easily shredded. The shredded waste method has potential applications in areas where: (a) landfill area is very expensive, (b) where suitable cover material is not readily available, and (c) precipitation is very low. Shredded waste can also be used to produce compost that can be used as intermediate cover material (Tachobanoglous et al., 1993).

Shredding of waste can greatly affect leachate characteristics. Leachate from shredded waste is more highly contaminated during early stages of waste stabilization and less contaminated during later phases than leachate from unshredded waste (Reinhardt and Ham, 1974; Lu et al., 1985; and Qasim and Chiang, 1994). This higher strength leachate can be attributed to increased surface area and, consequently, increased rates of biodegradation in shredded waste landfills (Lu et al., 1985; and Bookter and Ham, 1982; and Otieno, 1989). Qasim and Chiang (1994) reported that attainment of field capacity (i.e. maximum moisture that can be retained without continuous downward percolation

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by gravity) was delayed for shredded waste landfills, but the rate of pollutant removal, solid waste decomposition, and cumulative mass of pollutants released per unit volume of leachate was significantly increased when compared to unshredded waste fills.

4.1.2.3 Landfills for Individual Waste Constituents

Landfills for individual waste constituent are known as monofills. Combustion ash, asbestos, and other similar wastes, often identified as designated wastes, are typically placed in monofills to isolate them from materials placed in MSW landfills. Because combustion ash contains small amounts of unburned organic material, the production of odors from the reduction of sulfate has been a problem in monofills used for combustion ash and the installation of a gas recovery system is recommended to control odor problems (Tachobanoglous et al., 1993). Municipal Solid Waste Incineration (MSWI) slag/ash and construction/demolition waste, upon reaction with CO_2, form carbonates. After several years, these carbonates dominate the chemistry of the pore water or leachate and play an important role for contaminant fixation even in sulphide-rich mine tailings. They include calcite [$CaCO_3$], cerussite [$PbCO_3$], rhodochrosite [$MnCO_3$], azurite, [$Cu_3(CO_3)_2(OH)_2$], smithsonite, [$ZnCO_3$] and hydrozincite, [$Zn_5(CO_3)_2(OH)_6$] (Al et al., 2000; Carroll et al., 1998; and Jambor et al., 2000). In equilibrium with atmospheric CO_2 (0.035 %), calcite has a pH of about 8.3. For CO_2 concentration of 0.2–2.0 %, which is often found in soils under moderate climates, the pH may be in the range of about 7.0–7.5, while in upper soils containing $CaCO_3$ the pH can be between 7.5 and 8.5 (Rozema et al., 1985; and Sabbas et al., 2001).

High temperatures at the bottom of these types of landfills may affect the stability of the landfill liner system (flexible membrane liner, polymer membrane liner and mineral clay layer). Temperatures above 40 °C may damage the stability of the polymer membrane liner (made of high-density-polyethylene) due to depolymerisation and oxidation (Albano et al., 2001). The most important reactions that cause a temperature increase in the stored bottom ash are the corrosion of iron and aluminium, the hydration of lime (CaO) and the carbonation of portlandite ($Ca(OH)_2$) (Jaros and Huber, 1998, Speiser et al., 2001; Chandler and Hartlen, 1997; and Klein et al., 2001)). Because of the transport of water

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and water vapor along the temperature gradient in the mineral clay layer, the liner may also desiccate and fail to retain leachate (Doll, 1997; and Holzlohner et al., 1999).

4.1.3 Advantages and Disadvantages of Landfills

The advantages and disadvantages of landfills have been summarized by Indian and Northern Affair Canada (INAC, 2002). The advantages are: (a) the initial capital investment is low compared to that of other disposal methods, (b) a landfill is flexible, increased or peak refuse quantities of solid wastes can be disposed of with little additional personnel and equipment, (c) a landfill can receive all types of solid wastes, thus, eliminating the necessity of separate collections, (d) operations can easily be terminated without a great loss in equipment or land, the equipment can be readily used for other municipal functions and the land may be reclaimed for use as parking lots, play grounds, golf courses or airports, (e) a landfill can be established immediately upon the purchase or rental of standard digging and compacting equipment and authorization to use the land, no plant has to be built before operations can begin as the case with other solid waste reduction methods, (f) where land is available, landfill is usually the most economical method of solid waste disposal, (g) landfill is a complete final disposal method as compared to incineration and composting where residue, quenching water and unusable materials remain and require further disposal, and (h) unusual materials and bulky articles do not usually cause difficulties in operations. The disadvantages are: (a) large amounts of land are required, (b) sites located outside of a city are usually under some other governmental jurisdiction, (c) winter operations present certain difficulties, (d) prevention of ground water pollution may be costly, and (e) if the distance to the landfill is very great, the cost of transfer operations may be high.

4.2 Landfill Leachates

Leachate may be defined as liquid that has percolated through solid waste and has extracted dissolved or suspended materials. In most landfills leachate is composed of the liquid that has entered the landfill from external sources, such as surface discharge,

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rainfall, ground water, and water from underground springs and the liquid produced from the decomposition of the wastes (Tchobanoglous et al., 1993 and Clabaugh, 2001).

4.2.1 Leachate Generation

The chemical composition of leachate varies greatly depending on the age of landfill and the events prior to the time of sampling. However, the generation of the landfill leachate is thought to occur in five sequential phases as shown in Figure 4.2 (Christensen et al., 1994). The principle source of both the aerobic and the anaerobic organisms responsible for waste decomposition in these phases is the soil material that is used as a daily and final cover (Barlaz, 1996; and Barlaz et al., 1998). The production of landfill leachate during the individual phases will vary depending on the distribution of the organic components in landfill, the availability of nutrients, the moisture content of waste, moisture routing through the fill, and the degree of initial compaction.

Phase I is the initial adjustment phase, in which the organic biodegradable components in MSW undergo microbial decomposition as they are placed in a landfill and soon after. In this phase, biological decomposition occurs under aerobic conditions, since a certain amount of air is trapped within the landfill.

Phase II is identified as the transition phase in which oxygen is depleted and anaerobic conditions begin to develop. As the landfill becomes anaerobic, nitrate and sulfate, which can serve as electron acceptors in biological conversion reactions, are often reduced to nitrogen gas and hydrogen sulfide. The pH of the leachate starts to drop due to the formation of organic acids and the effect of elevated concentrations of CO_2 within the landfill.

In Phase III, identified as the acid phase, the microbial activity initiated in Phase II accelerates with the production of significant amounts of organic acids in two steps, with lesser amounts of hydrogen gas (Gujer and Zehnder, 1983). The first step involves the

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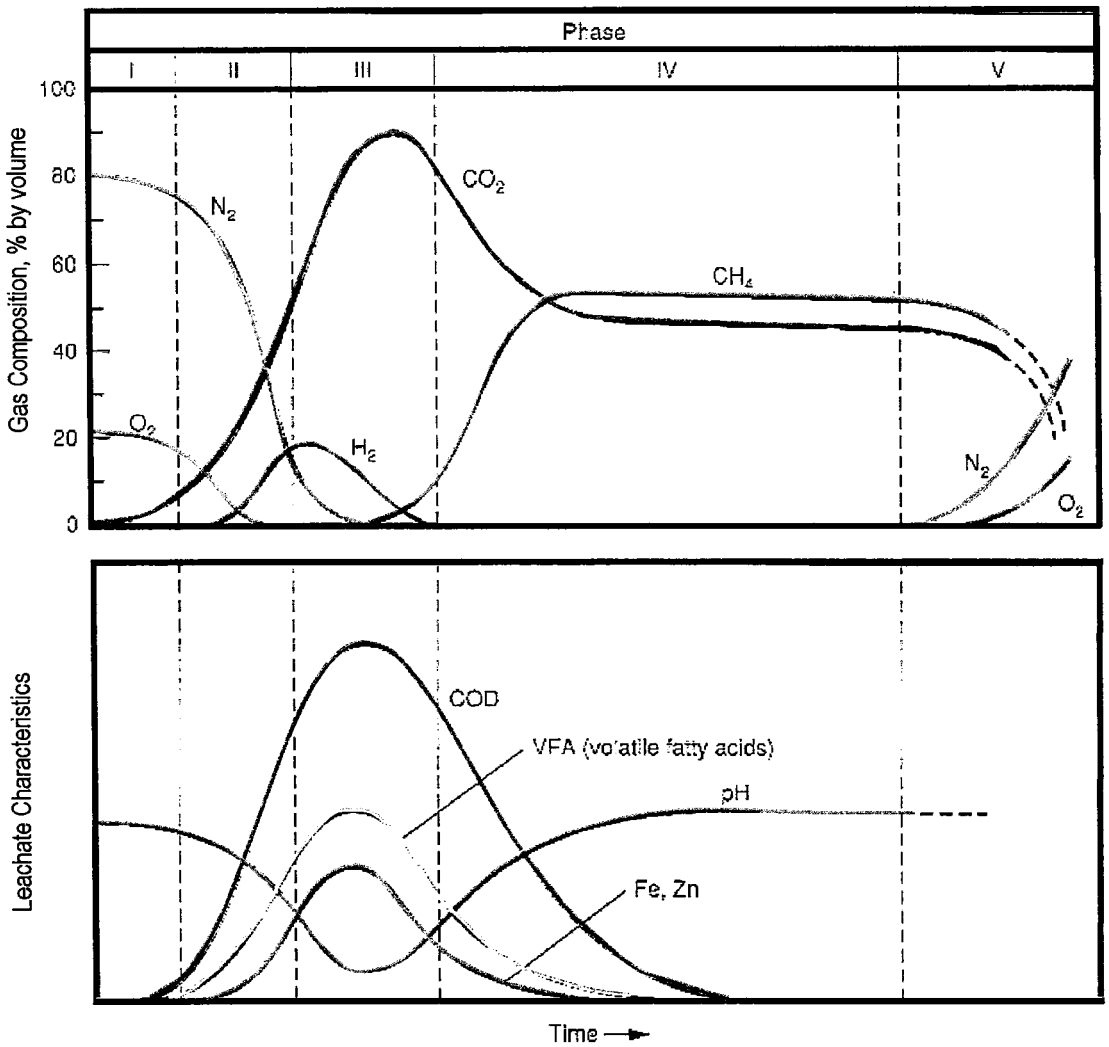


Figure 4.2. Landfill leachate generation phases.

enzymatic hydrolysis of higher-molecular mass compounds (fat and oil, lipids, carbohydrates, and proteins, and nucleic acids) suitable for use by microorganisms as a source of energy and cell carbon. The next step takes place inside the cell, where the hydrolyzed materials are oxidized to organic acids. The conversion of hydrolyzed material to organic acids is referred to as acidogenesis. Organic acids are then further converted into acetic acid (Mah et al., 1977; and DeWalle et al., 1978). The general pathways that micro-organisms use for the breakdown of most types of organic waste are shown in Figure 4.3. The pH of the leachate drops to a value of 5 or lower because if the presence of organic acids and the effect of elevated concentrations of CO_2 within the

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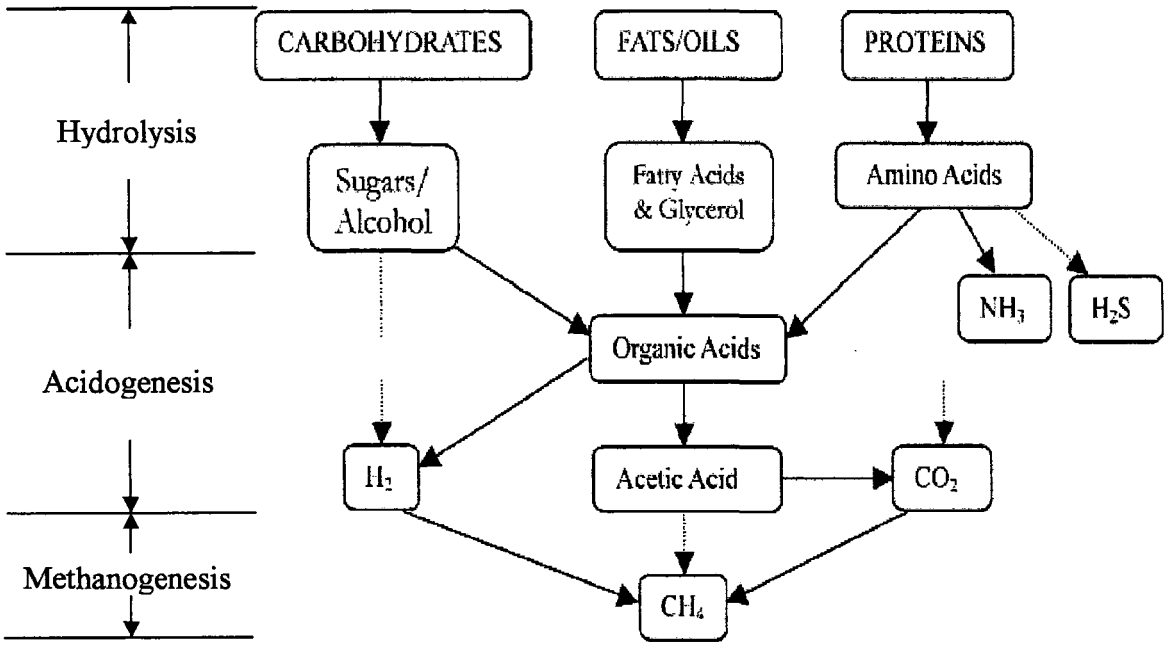


Figure 4.3. Simplified biochemical pathways of landfill leachate (adapted from Zacharof and Butler, 2004).

landfill. The biological oxygen demand (BOD_5), chemical oxygen demand (COD), and the conductivity of the leachate increase significantly due to the dissolution of the organic acids in the leachate. Also, because of the formation and the presence of organic acids, a number of inorganic constituents, principally heavy metals are solubilized.

In Phase IV, identified as the methane fermentation phase, a second group of microorganisms convert the acetic acid and hydrogen gas formed in the acid phase to methane and carbon dioxide and as a result the pH within the landfill rises and the concentration of BOD_5, COD, heavy metals and the conductivity decreased.

Phase V, identified as the maturation phase, occurs after the readily available biodegradable organic materials have been converted to CH_4 and CO_2. As moisture continues to migrate through the waste, portions of the biodegradable material that were previously unavailable will be converted. During the maturation phase, the leachate often contain humic and fulvic acids, which are difficult to process further biologically.

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4.2.2 Leachate Migration

Leachate that escapes from a landfill may migrate through the unsaturated zone and eventually reaches the uppermost aquifer. In some instances, the water table may be located above the base of the landfill, so that only saturated flow and transport from the landfill need to be considered. Once leachate reaches the water table, contaminants may be transported through the saturated zone to a point of discharge (a pumping well, a stream or a lake). The migration of leachate in the subsurface depends on factors such as the volume of the liquid component of the waste, the chemical and physical properties of the leachate constituents, the loading rate, climate, and the chemical and physical properties of the subsurface saturated and unsaturated zones (Islam and Singhal, 2004; Christensen et al., 2001; and USEPA, 1993). Once leachate migrates outside the confines of the landfill, its physiochemical and biochemical character will be altered. The most active physiochemical processes are likely to be dilution, adsorption, exchange reactions, and precipitation, with filtration for particulate matter (Bagchi and Amalendu 1987; Christensen et al., 1994).

4.2.2.1 Physical Processes

Physical processes that control the transport of contaminants in the subsurface include advection, mixing and dilution as a result of dispersion and diffusion, mechanical filtration, physical sorption, multi-phase fluid flow, and fracture flow.

4.2.2.1.1 Advection: it is the process by which solute contaminants are transported by the overall motion of flowing ground water. A non reactive solute will be transported at the same rate and in the same direction as ground water flow (Freeze and Cherry, 1979). Advection transport is chiefly a function of the subsurface hydraulic conductivity distribution, porosity, and hydraulic gradients (Cokca, 1999; Lo et al., 1999; and Munro et al., 1997).

4.2.2.1.2 Hydrodynamic Dispersion: it is a non-steady, irreversible mixing process by which a contaminant plume spreads as it is transported through the subsurface. The

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hydrodynamic dispersion coefficient (cm^2/sec) is often represented by the product of the pore flow velocity (cm/sec) and the dispersivity (cm) neglecting the contribution of the molecular diffusion coefficient. The dispersivity has a longitudinal component (in the flow direction), a vertical component and a horizontal, transverse component. The dispersivity is difficult to measure in field situations, and it has often been used as a calibration parameter accounting for insufficient information on the spatial distribution of the hydraulic conductivity (Christensen et al., 2001). Gelhar et al. (1992) reviewed dispersivity observations from 59 different landfill sites. The high reliability data (from tests with well controlled physics of the system and appropriate data analysis) showed low longitudinal dispersivities in range from 0.4 to 3 m for a scale between 15 and 250 m. Published field injection studies confirmed the lower dispersivities (Adams and Gelhar, 1992; Jensen et al., 1993; and Rugge et al., 1999). The variations in dispersivity reflect the influence of different degrees of aquifer heterogeneity at different sites (Christensen et al., 2001; Aller et al., 1987; Young and Warith, 1990; Islam et al., 2001; and Voudrias, 2002).

4.2.2.1.3 Mechanical Filtration: it removes from ground water contaminants that are larger than the pore spaces of the soil. Thus, the effects of mechanical filtration increase with decreasing pore size within a medium. Filtration occurs over a wide range of particle sizes. The retention of larger particles may effectively reduce the permeability of the soil or aquifer (Koenig et al., 1996; and Radenkova-Yaneva et al., 1995). Reddi et al. (2000) used two kinds of particulate suspensions to permeate the soil samples (one prepared with kaolinite particles, and another prepared with polystyrene micro-spheres) to study the physical clogging of filter drainage layer or subsurface soils. The major finding from this experiment was the increase in particle concentration that led to a faster reduction in permeability. Kaolinite particles in the pore fluid caused higher permeability reductions comparable to those of polystyrene spheres, which are relatively large.

4.2.2.1.4 Physical Sorption: Sorption is the process by which contaminants are removed from solution in ground water and adhere or cling to a solid surface. The distribution of a contaminant between the solution and the solid phase is called partitioning (Oman, 2001,

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Barry, 2002; and Zuairi, 2003). Sorption of non-polar compounds onto soil can be described as a partitioning into the solid organic C of the soil. Physical sorption of leachate onto aquifer material seems to be only of minor significance based on column experiments that showed relative solute velocities of 0.7-1.0 for COD of acid phase as well as CH_4 phase leachate (Hoeks et al., 1979; Farquhar and Sykes, 1982; Kjeldsen and Christensen, 1984; and Kjeldsen, 1986).

4.2.2.1.5 Multiphase Fluid Flow: it occurs because many solvents and oils are highly insoluble in water and may migrate in the subsurface as a separate liquid phase (Berglund, 1998; Nastev et al., 2001; and Gordon et al., 2002). The flow of leachate may physically differ from the flow of groundwater at least with respect to: (a) local water table gradients below and around the landfill, (b) the viscosity of the leachate and (c) the density of the leachate (Christensen et al., 2001). Local water table gradients below and around the landfill will most likely differ from the general gradients because the landfill will usually have a different hydrogeology than the surrounding area (MacFarlane et al., 1983; Kjeldsen, 1993; Duijvenbooden and Kooper, 1981; and Kjeldsen et al., 1998). The viscosity of the leachate may differ from the viscosity of the groundwater. A higher viscosity would theoretically lead to lower flow velocities, which would affect the advection process of the leachate. However, Christensen et al. (1985) and Christensen et al. (2001) reported that the effect of the leachate viscosity was marginal (1-15 % increase relative to water at equal temperatures). Also, Kimmel and Braids (1980) stated that the changes in viscosity due to temperature changes and to changes in solid concentration were insignificant. The density of the leachate is a function of the temperature and the concentration of dissolved solids (Christensen et al., 2001). Leachate with a total dissolved solids concentration of 20,000 mg/L will have a density that is 1% higher than the groundwater density (Kimmel and Braids, 1980). Christensen et al., (1985) measured densities of 13 different leachates and found salt content to contribute to the density increase. Although temperatures elevated by up to 10 °C in leachate plumes have been reported by several researchers (MacFarlane et al., 1983; and Kjeldsen et al., 1998), the effect of 10 °C increase in temperature on the density is insignificant compared to that caused by the dissolved solids content (Kimmel and Braids, 1980).

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4.2.2.1.6 Hydraulic Conductivity: it is a measure of the ability of geologic media to transmit fluids (USGS, 1987) and is a function of the size and arrangement of pores and fractures in the media and the density and viscosity of the fluids. Spatial variations in hydraulic conductivity are referred to as heterogeneities, whereas, a variation in hydraulic conductivity with the direction of measurement is referred to as anisotropy. Variable hydraulic conductivity of the geologic formation may cause ground-water flow velocities to vary spatially (Smith et al., 1992; King et al., 1993; and Jang, 2000).

4.2.2.1.7 Secondary Porosity: it may be caused by the dissolution, regional fracturing of rock, desiccation cracks or fissures in soil. Fractures or macropores respond quickly to rainfall events and other fluid inputs and can transmit water rapidly along unexpected pathways. Secondary porosity can result in localized high concentrations of contaminants at significant distances from the landfill. The relative importance of secondary porosity to hydraulic conductivity of the subsurface depends on the ratio of fracture hydraulic conductivity to intergranular hydraulic conductivity (Kincaid et al., 1984).

4.2.2.2 Chemical Processes

Chemical processes that are important in controlling subsurface transport include: precipitation/dissolution, chemical sorption, redox reactions, hydrolysis, ion exchange, and complexation (Keely, 1989).

4.2.2.2.1 Precipitation/Dissolution: The solubility of a solid controls its equilibrium state. When the soluble concentration of a contaminant in leachate is lower than that of the equilibrium value, the contaminant exists in solution but when its soluble concentration is higher than that of the equilibrium state, precipitation occurs. The precipitation of a dissolved substance may be initiated by changes in pressure, temperature, pH, concentration, or redox potential (Aller et al., 1987). Precipitation of contaminants in the pore space of an aquifer can decrease aquifer porosity. Precipitation and dissolution reactions are especially important processes for trace metal migration in soils (Wu and Li, 1998, Thornton et al., 2000; Islam and Singhal, 2002; and van Berukelen et al., 2004). Fe(II) and Mn (II) removal by precipitation has been

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demonstrated by direct identification of the minerals (Heron et al., 1994; and 1998), and indirectly by minerals saturation-index calculations. Field studies have shown super-saturation with respect to iron sulfide, FeS (Kimmel and Braids, 1980; Nicholson et al., 1983; Kehew and Passero, 1990; and Bjerg et al., 1995) and siderite, $FeCO_3$ (Cherry, 1983; Nicholson et al., 1983; Barker et al., 1986; and Bjerg et al., 1995). Siderite precipitation may especially be important in Fe reducing zones (Heron and Christensen, 1995; Heron et al., 1994; and 1998). If dissolved Fe migrates to oxidized parts of the plume, precipitation of ferrihydrite, $Fe(OH)_3$, may take place and shown by an increased Fe(III) content on the aquifer solids down-gradient from the Fe reducing zone (Heron and Christensen, 1995; and Nicholson et al., 1983). Solubility of the heavy metals Cd, Ni, Zn, Cu, and Pb in leachate plumes may be governed by sulfides or carbonates. Phosphates and hydroxides may also limit metal solubility (Christensen et al., 2001).

4.2.2.2.2 Chemical Adsorption/Desorption: it is the most common mechanism affecting contaminant migration. Like precipitation/dissolution, adsorption/desorption is a reversible process but it generally occurs at a relatively rapid rate. The dominant mechanism of organic sorption is the hydrophobic attraction between carbon content of the porous medium and the contaminants in some aquifers (Schaefer et al., 1991; and Doust and Huang, 1992). There is a direct relationship between the quantity of a substance sorbed on a particle surface and the quantity of the substance suspended in solution (Gau and Chow, 1996; and Gau and Chow, 1998). Divalent metal cations have a high affinity for sorption onto negatively charged sites associated with clay minerals, organic matter, oxides of Fe, Mn, Al and Si, and calcite ($CaCO_3$).

4.2.2.2.3 Oxidation/Reduction (Redox): the reaction involves the transfer of electrons and occurs when the redox potential in leachate is different from that of the soil or aquifer environment. Redox reactions are important processes for inorganic compounds and metallic elements. Together with pH, redox reactions affect the solubility, complexing capacity, and sorptive behavior of constituents, and thus control the presence and mobility of many substances in water (Papadopoulos et al., 1998; Amirbahman et al., 1998; and van Berukelen et al., 2004). The sequence of redox processes strongly affects

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the migration of pollutants leaching from landfills and is the main key to understanding the transformation of reactive pollutants in the plume (Lyngkilde and Christensen, 1992; and Bjerg et al., 1995). Figure 4.4 and Table 4.1 show the sequence of different redox reactions down-gradient of a landfill. Redox zones develop in response to decomposition of organic material and its effects on the behavior of inorganic constituents. The boundaries and extent of these zones are controlled by competing rates of reactions. There may be considerable overlap of redox reaction zones in leachate-contaminated groundwater systems (Baedecker and Back, 1979; and Christensen et al., 1994). In an aquifer with a continuous leachate release, a methanogenic zone evolves close to the landfill within which, and down gradient from it, SO_4^{2-} reduction may take place. Iron reduction takes place further down-gradient as conditions become less reducing. Zones of Mn and NO_3^- reduction have been observed, sometimes overlapping with Fe reducing zone. (Christensen et al., 2001).

4.2.2.2.4 Hydrolysis: it is the chemical breakdown of carbon bonds in organic substances by water and its ionic species H and OH. Hydrolysis is most significant at high temperatures, low pH, and low redox potential. For many biodegradable contaminants, hydrolysis is a slow process compared to biodegradation (Pareek et al., 1998, Meima et al., 2002; and Chen et al., 2003). Half-life values under anoxic conditions ranges from 5-10 days (20 °C) or 30-100 days (10 °C). The volatile fatty acids, which dominate the COD content of acid phase leachate, are relatively easily converted under anaerobic conditions (Hoeks et al., 1979; Soyupak, 1979; and Kjeldsen and Christensen, 1984). For methanogenic leachates, Hoeks et al. (1984) found no measurable COD degradation during experimental retention times of 19-25 days and Kjeldsen (1986) found no degradation for retention times up to 240days.

4.2.2.2.5 Ion Exchange: it originates primarily from exchange sites on layered silicate clays and organic matter that have a permanent negative charge. Cation exchange balances negative charges in order to maintain neutrality. The capacity of soils to exchange cations is called the cation exchange capacity (CEC). CEC is affected by the type and quantity of clay mineral, the organic matter content, and the pH of the soil.

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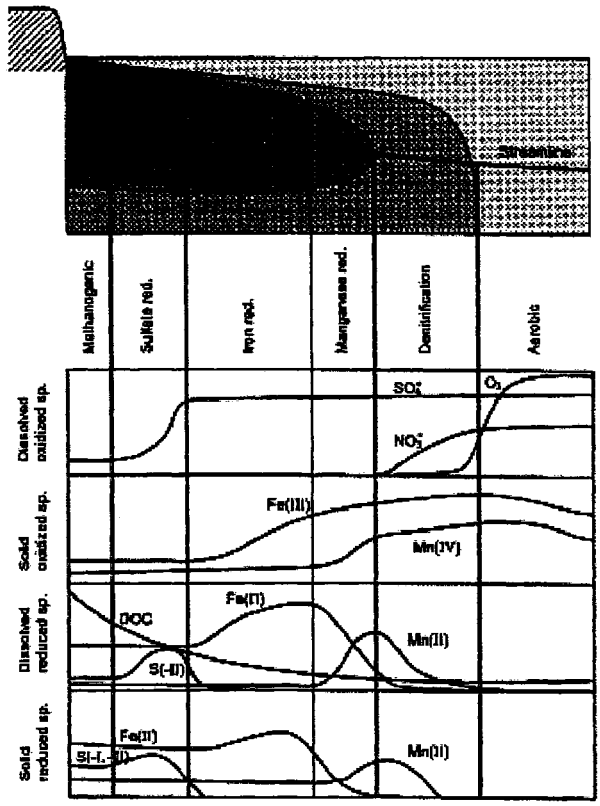


Figure 4.4. Schematic redox zonation in an originally aerobic aquifer downgradient from a landfill, and the distribution of redox-sensitive species along a streamline in the plume.

Table 4.1. Sequence of different redox reaction down gradient of a landfill (adapted from Christensen et al., 1994).

Reactants	Products	ΔG° (kcal/mol)*
Methanogenic processes		
$2CH_2O \rightarrow CH_3COOH$	$CH_4 + CO_2$	-22
$4H_2 + CO_2$	$CH_4 + 2H_2O$	
Sulphate reduction		
$2CH_2O + SO_4^{2-} + H^+$	$2CO_2 + HS + 2H_2O$	-25
Iron (ferric) reduction		
$CH_2O + 4Fe(OH)_3 + 8H^+$	$CO_2 + 4Fe^{2+} + 11H_2O$	-28
Manganese (manganic) reduction		
$CH_2O + 2MnO_2 + 4H^+$	$CO_2 + 2Mn^{2+} + 3H_2O$	-81
Denitrification		
$5CH_2O + 4NO_3^- + 4H^+$	$5CO_2 + 7H_2O + 2N_2$	-114
Aerobic respiration, oxygen reduction		
$CH_2O + O_2$	$CO_2 + H_2O$	-120

* pH = 7

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Major cations in the leachate (Ca, Mg, K, Na) usually dominate the CEC sites, resulting in a little attenuation in soils of trace metals in the leachate. A smaller ion exchange effect for anions is associated with hydrous oxides. Soils typically have more negatively charged clay particles than positively charged hydrous oxides. Therefore, the transport of cations is attenuated more than the transport of anions (Sezer et al., 2003; Tilkens and Svavarsson, 1995; and Christensen et al., 2001). The ion exchange properties of Fe and Mn are expected to be similar to Ca considering their valencies and hydrated ion radii. Significant amounts of Fe (up to 30% of the CEC) have been detected on the cation exchange complex in the anaerobic part of landfill leachate plume (Heron and Christensen, 1995).

4.2.2.2.6 Complexation: it involves reactions of metal ions with inorganic anions or organic ligands. The metal and the ligand bind together to form a new soluble species called a complex. Complexation can either increase the concentration of a constituent in solution by forming soluble complex ions or decrease the concentration by forming a non-soluble ion complex with a solid (Baker et al., 1986; and Mostbauer, 2003). Complexation of Fe^{2+} and Mn^{2+} with organic ligands was identified in field studies by Barker et al. (1986). The authors showed that precipitation of siderite, ferric oxides and manganous carbonate might diminish the amount of organically complexed Fe and Mn. Complexation of Fe and Mn was also indicated in column studies (Knox and Jones, 1979; Hoeks et al., 1984; and Kjeldsen, 1986). Fe was found to be kept in solution by complexation with short chain carboxylic acids (Knox and Jones, 1979). Theis and Singer (1974) showed that complexation of Fe^{2+} in plumes might facilitate its transport down-gradient of the landfill.

4.2.2.3 Biological Processes

Biodegradation of contaminants may result from the enzyme-catalyzed transformation of organic compounds by microbes. Contaminants can be biodegraded to harmless byproducts or to more mobile and/or toxic products. Biodegradation of a compound depends on environmental factors such as redox potential, dissolved oxygen concentration, pH, temperature, presence of other compounds and nutrients, salinity,

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depth below land surface, competition among different types of organisms, and concentrations of compounds and organisms. The transformations that occur in a subsurface system and the fate of biologically reactive substances are difficult to predict because of the complexity of the chemical and biological reactions that may occur (USEPA, 1993; and Qasim and Chiang, 1995). The biochemical processes involve either aerobic or anaerobic microbial population with the latter expected to be most active, since the major part of the degradation takes place under strictly anaerobic conditions (Lyngkilde and Christensen, 1992a). Depending on the composition of the leachate, a sequence of redox zones of increasing redox potential may develop downgradient of a landfill. Zones of methane production, sulphate reduction, ferric reduction, manganic reduction, nitrate reduction, and oxygen reduction will develop if the corresponding electron acceptors are present in the aquifer (Baedecker and Back, 1979; Lyngkilde and Christensen, 1992; and Christensen et al., 1994).

4.2.3 Factor Affecting Leachate Quality

Composition of leachate (Table 4.2) is important in determining its potential effects on the quality of nearby surface water or ground water. Contaminants carried in leachate are dependent on solid waste composition and on the simultaneously occurring physical, chemical and biological activities within the landfill. The control of leachate produced in municipal solid waste landfill is one of the most difficult problems to be solved during landfill management due to the leachate high content in hardly-biodegradable organics as well as inorganics. The factors influence leachate quality include: refuse composition, time, temperature, oxygen, depth, moisture content and preprocess of waste.

4.2.3.1 Refuse Composition

Because of the variation in refuse composition, the quality of municipal leachate varies widely (Lu at al., 1985). In general, quality variation is higher for putrescible wastes than for non-putrescible waste. The waste composition of refuse determines the extent of biological activity within the landfill (Chen and Bowerman, 1974). Rubbish, food and garden wastes, and crop and animal residues contribute to the organic material in

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Table 4.2. Typical chemical composition of landfill leachate (El-Fadel et al., 2002).

Parameters	Concentration Range (mg/L)	Parameters	Concentration Range (mg/L)
Alkalinity (as $CaCO_3$)	0-20850	Nitrogen (ammonia)	0-1250
Aluminum	0.5-85	Nitrogen (nitrate)	0-9.8
Antimony	0-3.19	Nitrogen (nitrite)	0-1.46
Arsenic	0-70.2	Nitrogen (organic)	0-1000
Barium	0-12.5	Nitrogen (Kjeldahl)	0-3320
Beryllium	0-0.36	Nickel	0-7.5
BOD_5	480-72500	Phenol	0.17-6.6
Boron	0.413	Phosphorus (total)	0-234
Cadmium	0-1.16	Phosphate	0.01-154
Calcium	5-4080	pH	1.5-9.5
Chloride	11,375	Potassium	0.16-3370
Chromium	0-22.5	Selenium	0-1.85
COD	0-195000	Silver	0-1.96
Conductivity (μmho/cm)	480-72500	Sodium	0-8000
Copper	0-9.9	Thallium	0-0.32
Cyanide	0-6	Tin	0-0.16
Fluoride	0.1-1.3	TDS	584-55000
Hardness (as $CaCO_3$)	0.1-225000	TSS	140900
Iron	0-420000	TOC	335000
Lead	0-14.2	TVA (as acetic acid)	0-19000
Magnesium	0-115600	Turbidity	40-500
Manganese	0.05-1400	Sulfate	0-1850
Mercury	0-3	Zinc	0-1000
Organic halides	0.320-3.5	Phenols	0-4
Benzene	0.1-0.6	Toluene	0-3.2
Ethyl-benzene	0-4.9		

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leachate, whereas inorganic constituents in leachate are often derived from ash wastes and construction and demolition debris (Pohland and Harper, 1985). Chen and Bowerman (1974) found that increased quantities of paper in solid waste resulted in a decreased rate of waste decomposition. Lignin, the primary component of paper, is resistant to anaerobic decomposition which is the primary means of degradation in landfills.

4.2.3.2 Processing of Waste

Shredding or baling of waste can greatly affect leachate characteristics. Leachate from shredded waste is more highly contaminated during early stages of waste stabilization and less contaminated during later phases than leachate from unshredded waste (Reinhardt and Ham, 1974; Lu et al., 1985; and Qasim and Chiang, 1994). This higher strength leachate from shredded waste can be attributed to increased surface area and consequently increased rates of biodegradation landfills (Lu et al., 1985; Bookter and Ham, 1982; and Otieno, 1989). Attainment of field capacity (maximum moisture that can be retained without continuous downward percolation by gravity) was delayed for shredded waste landfills, but the rates of pollutant removal waste decomposition, and cumulative mass of pollutants released per unit volume of leachate were significantly increased when compared to unshredded waste landfills (Qasim and Chiang, 1994). Unlike shredding, baling results in large volumes of dilute leachate as the waste requires a longer period to stabilize (Qasim and Chiang, 1994). Baling can enhance leachate production by decreasing the elapsed time before leaching, reducing the moisture-retention ability of the waste, and increasing the overall volume of the leachate produced (Lu et al., 1985).

4.2.3.3 Elapsed Time

Leachate quality reaches a peak value after a few years and then gradually declines. For an actual landfill leachate, the quality variation is not as smooth, although distinctive zones of upward and downward trends can be observed if quality variation is plotted with time. All the contaminants do not peak at the same time, and the time versus concentration variation plots of all contaminants from the same landfill may no be similar in shape. McBean et al. (1995) and Lu et al. (1985) reported that leachate quality reach a

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peak after approximately two to three years followed by a gradual decline in ensuing years. Akyurek (1995) stated that leachate from new landfills were high in BOD and COD and then steadily declined leveling off after about 10 years. Chian and DeWalle (1977) reported that all contaminants do not peak at the same time. Due to their initially biodegradable nature, organic compounds decrease more rapidly than inorganics with increasing age of the landfill. Qasim and Chiang (1994) reported that inorganics are removed as a result of washout by infiltrating rainwater, whereas organics decrease in concentration as a result of decomposition and washout.

4.2.3.4 Ambient Temperature

The atmospheric temperature at the landfill site influences leachate quality as the temperature affects both bacterial growth and chemical reactions. Under subzero temperatures, the waste freezes, some chemical reaction are inhibited and the leachable compounds are reduced. Landfill temperature is a largely uncontrollable factor and it has been shown to fluctuate with seasonal ambient temperature (Lu et al., 1985). Each microorganism possesses an optimum growth temperature, and any deviation from that temperature will decrease growth due to enzyme deactivation and cell wall rupture. Solubility of many salts (e.g. $Ca_3(PO_4)_2$ and NaCl) decreases at lower temperatures (Lu et al., 1985).

4.2.3.5 Available Oxygen

The effect of available oxygen is notable for putrescible waste. The quantity of free oxygen in a landfill dictates the type of decomposition (i.e. anaerobic or aerobic). Aerobic decomposition occurs during initial placement of waste, while oxygen is available. Aerobic degradation may continue to occur at, and just below, the surface of the fill (McBean et al., 1995). Chemicals released as a result of aerobic decomposition differ greatly from those produced during anaerobic degradation (Bagchi, 1990). During aerobic decomposition, microorganisms degrade organic matter to CO_2, H_2O, and partially degraded residual organics, producing considerable heat. The anaerobic condition in a landfill develops due to frequent covering of waste with soil (daily/weekly cover) or with fresh waste. The supply of oxygen is depleted as soon as the waste is

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covered (either with soil or more waste). A predominantly anaerobic condition develops in thicker refuse beds. High concentrations of organic acids, ammonia, hydrogen, carbon dioxide, methane, and water are produced during anaerobic degradation (McBean et al., 1995). Phase changes occur in the fill as a result of reductions in the quantity of oxygen in the landfill, a transitional change takes place when oxygen is depleted and an anaerobic environment develops.

4.2.3.6 Depth of Waste

Greater concentrations of constituents are found in leachates from deeper landfills under similar conditions of precipitation and percolation (Qasim and Chiang, 1994). Deeper fills require more water to reach saturation, require a longer time for decomposition, and distribute the leached material over a longer period of time (Qasim and Chiang, 1994; Lu et al., 1985). Water entering the fill will travel down through the waste. As the water percolates through the landfill, it contacts the refuse and leaches chemicals from the waste. Deep landfills offer greater contact time between the liquid and solid phases which increases leachate strength (McBean et al., 1995).

4.2.3.7 Moisture Availability

Water is the most significant factor influencing waste stabilization and leachate quality. Water within the landfill serves as a reactant in the hydrolysis reactions, transports nutrients and enzymes, dissolves metabolites, provides pH buffering, dilutes inhibitory compounds, exposes surface area to microbial attack, and controls microbial cell swelling (Noble and Arnold, 1991). Lu et al. (1985) stated that high water flow rates can flush soluble organics and microbial cells out of the landfill and in such cases microbial activity plays a lesser role in determining leachate quality. Also, high water application rates can remove the majority of waste contaminants early in the life of the fill. Under low flow rate conditions, anaerobic microbial activity is the significant factor governing leachate organic strength (McBean et al., 1995). The quantity of water is important because it directly affects stabilization rates within the landfill. Barlaz et al., 1990, Sulfita et al. (1992) and Miller et al. (1994) noted the important role of moisture in supporting

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methanogenic fermentation of solid waste. Relatively dry landfills (20 to 40 % moisture content) have very slow stabilization rates because there is only a small quantity of water to support biological degradation. Recommended moisture content reported in the literature ranges from a minimum of 25 % (wet basis) to optimum levels of 40 - 70 % (Barlaz et al., 1990; and Chen and Bowerman, 1974).

4.2.4 Factors Affecting Leachate Quantity

Leachate quantity also dependent on weather and operational practices including precipitation, ground water, moisture content and final cover design. The amount of rain and snow falling on a landfill influences leachate quantity significantly. Sometimes landfill base is constructed below the groundwater table and in such cases groundwater intrusion may increase leachate quantity (Christensen et al., 2001). Leachate quantity will increase if the waste releases pore water when squeezed. Unsaturated waste continues to absorb water until it reaches field capacity (a water saturation state) and, therefore, dry waste will reduce leachate formation. However, channeling causes water to flow through without being absorbed by the waste. Co-disposal of sludge or liquid waste in municipal landfills will increase the leachate quantity in a landfill (Safari and Baronian, 2000). Leachate volume is reduced significantly after a landfill is closed and finally covered because: (a) vegetation grown in the topsoil of a final cover reduces infiltratable moisture significantly by evapotranspiration and (b) the low permeability layer reduces percolation. A properly designed final cover will reduce post closure leachate quantity significantly (Hauser et al., 2001).

4.2.5 Leachate Treatment

The potentials methods for the management of landfill leachate are: (a) recirculation of leachate through the landfill, (b) spray irrigation on adjacent grassland, (c) disposal off site to sewer for treatment as an admixture with domestic sewage, (d) physical-chemical treatment, (e) membrane filtration and reverse osmosis, (f) biological treatment, and (g) constructed wetlands. The identification of the preferred option in specific circumstances is a function of the costs, both operating and capital, and the limitation impose on the quality and quantity of discharge.

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4.2.5.1 Recirculation of Leachate through Landfill

Recirculation of leachates through the landfill accelerates stabilization processes of solids wastes and, therefore, enhances gas production (Reinhart et al, 1996). However, problems that may be encountered include: water tables in the waste, high hydraulic gradient above the liner, seepage and geotechnical instabilities (Cossu, R. et al, 2001). Leachate recirculation has important consequences with regard to metal contamination of leachate. The primary removal mechanism for metal in conventionally operated landfills appears to be washout, although limited chemical precipitation may occur. In leachate recirculating landfills, the primary metal removal mechanism appears to be sulfide and hydroxide precipitation. With time, moderate to high molecular weight humic-like substances are formed from waste organic matter in a process similar to soil humification. These substances tend to form strong complexes with heavy metals. In some instances, a remobilization of precipitated metals can result from such complexation once the organic content has been stabilized and oxic conditions are being re-established (Reinhart et al, 1996). However, in areas with high precipitation or during rainy season, recirculation could be a problem as it becomes necessary to discharge and treat part of the leachate.

4.2.5.2 Land Application

The environmental risk associated with landfill leachate is largely attributable to the presence of high ammonium levels that threaten surrounding waters (Lu et al., 1984). Since it is a potential source of ammonia, which poses a significant threat to fresh and marine environments (ANZECC, 1992), removal of ammonium is an essential component of leachate remediation. Commonly used batch treatment processes for the removal of nitrogen from leachate require high energy and capital inputs and can generate large quantities of by-products (Kosson and Ahlert, 1985). In contrast, irrigating with leachate using the plant-soil system to manage excess nitrogen, dissolved salts and water appears to offer a cost-effective, low energy alternative (Burford and Bremner, 1975). Consequently, irrigation of recreational areas such as turf and parkland provides a mechanism for the beneficial reuse of leachate in the urban environment (Revel et al., 1999).

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Irrigation of leachate as a means of in situ bioremediation is limited by the capacity of the system to accommodate added pollutants, particularly nitrogen. Where soil conditions are favourable and leachate nitrogen is in an appropriate form, bacterial denitrification can provide a significant sink of nitrogen (Stevenson, 1982). For in situ denitrification to occur, ammonium (NH_4^+) applied to the soil must first be oxidized (nitrification) to form nitrate (NO_3^-). Conversion of NO_3^- to gaseous N (denitrification) is favoured by high soil moisture (Stevenson, 1982), temperatures of 15–35 °C (Dawson and Murphy, 1972), neutral pH (Crasswell and Martin, 1974), the presence of suitable bacterial populations (Jacobsen and Alexander, 1980), and by the availability of a soluble carbon source (Leffelaar, 1987). Although leachate irrigation aims to promote denitrification, attention must also be given to other environmental concerns. Variation in leachate composition, soil physical and chemical properties, climatic conditions and the tolerance of target plant species will also affect the volume and sustainability of leachate irrigation (Sapari, 1987). Of particular interest is the leachate salinity and sodicity on growth and survival of the turf grass (Lu et al., 1985; and Sapari, 1987). Control of salinity and sodicity must, therefore, form an integral component of any leachate irrigated system. Bowman et al. (2002) suggested that *in situ* bioremediation is sustainable provided that management strategies such as dilution of leachate to reduce solution electrical conductivity to 3.6 dS m^{-1} are adopted.

4.2.5.3 Treatment with Domestic Wastewater

Depending on the location of the landfill and characteristics of the leachates, municipal waste water treatment facilities could be used for leachate treatment. However, it may adversely affect sewage treatment facilities performance since leachate is a highly concentrated wastewater both in terms of inorganic and organic pollutants. Dilution may, therefore, be needed for leachate containing persistent organic compounds (Cossu, et al, 2001). In many cases, pre-treatment is required prior to sewer discharge (Senior, 1995).

Cecen and Aktas (2004) investigated the effluent quality in the co-treatment of sanitary landfill leachate and domestic wastewater and the improving effect of powdered activated carbon (PAC). The volumetric ratio of leachate was varied from 5 to 25% (v/v). Batch

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activated sludge (AS) reactors were fed with leachate and domestic wastewater. Parallel AS + PAC reactors also contained PAC, which was added at the dose of 100-3,500 mg/L. The study revealed that the negative impact of leachate on a municipal wastewater treatment system could be prevented by the addition of PAC. Diamadopoulos et al. (1997) examined the feasibility of biologically treating a combined waste stream of landfill leachate and municipal sewage (9:1 ratio by volume) in a sequencing batch activated sludge reactor (SBR). The combined waste had an average BOD_5 430 mg/L, COD 1090 mg/L, and TKN 133 mg/L (80% of which was in the form of ammonia). The SBR reactor was operating in daily time cycles employing the following sequential operation phases: filling phase, anoxic phase, aeration reaction phase, settling phase, and drain phase. In particular, the anoxic and aeration periods were tailored in order to develop conditions conducive to nitrification and denitrification. The results indicated that successful biotreatment of combined leachate and sewage was possible. The system was capable of achieving a BOD_5 removal efficiency exceeding 95%. Nitrate removal during the anoxic phase was approximately 99% due to denitrification. However, the overall nitrogen removal during a full cycle was about 50%.

4.2.5.4 Physical-Chemical Treatment

Physical-Chemical precipitation is based on the addition of chemicals to remove suspended solids, nitrogen, phosphorus and metals. The main disadvantages of this technology are associated with its operating costs, and the high variability of landfill leachate and sludge produced.

Physical–chemical methods such as nanofiltration, air-stripping and ozonation were used by Marttinen et al. (2002) for COD, ammonium and toxicity removal. About 66% COD and 50% ammonia were removed by nanofiltration. Air-stripping at pH=11 resulted in 89% ammonia removal at 20 °C within 24 h. Ozonation increased the concentration of rapidly biodegradable COD. Physicochemical methods were used in combination with nanofiltration for treatment of landfill leachate by Trebouet et al. (2001). Nanofiltration was found satisfactory for removal of refractory COD from the leachate used.

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The feasibility of selectively precipitating NH_4-N in a landfill leachate as magnesium ammonium phosphate (MAP) was investigated using three combinations of chemicals: $MgCl_2.6H_2O$+-$Na_2HPO_4.12H_2O$, MgO+85%H_3PO_4, and $Ca(H_2PO_4)_2.H_2O$+$MgSO_4.7H_2O$. The results indicated that NH_4-N contained in the leachate could be quickly reduced from 5618 to 112 mg/L within 15 min, when $MgCl_2.6H_2O$ and $Na_2HPO_4.12H_2O$ were applied with a Mg^{2+}:NH_4^+:PO_4 at a mol ratio of 1:1:1. The pH range of the minimum MAP solubility was 8.5-9.0. The experimental results indicate that the settled sludge is quite solid and can be directly dumped at a landfill site even without any further dewatering treatment. However, the high salinity formed in the treated leachate may affect microbial activity in the following biological treatment process (Li et al., 1999)

A landfill leachate was characterized and chemically treated with an organic flocculant (DEC). Maximum removal efficiencies of 79% in COD and 98% in color were achieved. A COD removal of 49% and a maximum color removal of 96% were also obtained by lime slurry addition. The oxygen uptake rate of municipal wastewater that is accepted as a reference value for biological treatability was found as 46 mg/L/h (Pala and Erden, 2004).

4.2.5.5 Membrane Filtration and Reverse Osmosis

Due to the ability of modern high-rejection reverse osmosis membranes to retain both organic and inorganic contaminants dissolved in water at rejection rates of 98-99%, reverse osmosis is also useful for purifying landfill leachate. On the feed-water side of the membrane, the dissolved organic and inorganic contaminants are concentrated in the retentate, whereas the pure water is "pressed" through the membrane. Consequently with the reverse osmosis membrane, a treated water stream (permeate) is generated, which contains very low levels of inorganic and organic contaminants. These meet discharges guideline into river or aquifer and contribute to maintenance of the natural equilibrium of water as this leachate was originally clean rain water. As the reverse osmosis membrane operates like a well-defined barrier, the purification process can be controlled continuously with a high degree of security by a simple and precise measurement of the electric conductivity (Peters, 1998). The membrane process of reverse osmosis offers a

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high operating stability as the startup and shut-down of the respective plants can be carried out in few minutes. Because of the high rejection rate for each type of contaminant dissolved in the feed water, a high flexibility against changes of the concentrations of the compounds in landfill leachate is given and the permeate produced has always the expected high quality. The modular design of reverse osmosis plants allows for a quick increase or decrease of the purification capacity by adding or taking away membrane area. However in addition to requiring highly resistant membranes, the treatment of landfill leachate with reverse osmosis demands the use of open channel module systems that can be cleaned with high efficiency with regard to scaling, fouling and especially bio-fouling (Peters, 1996).

Nanofiltration (NF) has attracted increasing attention during recent years due to the development of new applications. The advantage of NF compared with reverse osmosis (RO) and ultrafiltration (UF) is that it is possible to separate organic substances from some types of salts. It is also possible to separate different kinds of salts due to the negatively charged groups on the membrane (Treboutet et al., 2001; and Meier et al., 2002). NF was utilized to treat a landfill leachate with an extremely high salt content from a waste cell containing mainly ash because of the good separation of cations. Most of the heavy metals, which are multivalent cations, were rejected while the monovalent cations, which are rather harmless substances, passed through the membrane. The retention of cadmium, zinc, lead and chromium was found to be higher than 70%, while the retention of potassium and sodium was less than 10%. Since the transmembrane osmotic pressure was low, due to the low retention of the monovalent ions, the flux was several times higher than for RO membranes (Linde and Jonsson, 1995).

4.2.5.6 Biological Treatment

Gulsen and Turan (2004) investigated the treatability of landfill leachate in an anaerobic fluidized bed reactor (AFBR) with typical sand filter having an average particle size of 0.5 mm and a fixed bed height of 70 cm. The AFBR attained steady state conditions with a COD removal of 90% after 80 days. A biogas production yield of 0.50-0.52 L of biogas per g COD, with a methane (CH_4) content of 75%, was obtained. Ammonia removal

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efficiency appeared to be very low but ammonia inhibition has not occured during the study.

Timur and Ozturk (1999) evaluated anaerobic treatability of municipal landfill leachate using anaerobic sequencing batch reactors (ASBR) at 35 °C. A COD removal efficiency of 85% was achieved. The net daily biomass conversion yield was about 0.1 g VSS per g of COD removed. About 83% of COD removed during the treatment was converted to methane.

A two-stage process, including an anaerobic pretreatment (up-flow anaerobic sludge blanket, UASB) unit and a pre-denitrification activated sludge process, was used for treating leachates from a 5-year old municipal landfill. The results show that 45-50% COD removal could be achieved in the UASB reactor even at temperatures below 10°C. The removal efficiencies for the activated sludge process were up to 90% for COD, over 98% for BOD_7, over 90% for NH_4-N and over 70% for N_{total}. The denitrification efficiency depended on leachate biodegradable COD fraction and COD:N ratio was evaluated (Pelkonen et al., 1999).

High chemical oxygen demand (COD), high ammonium-N content and presence of toxic compounds such as heavy metals result in low removal efficiencies in direct biological treatment of landfill leachate and as a result raw landfill leachate was subjected to pre-treatment by coagulation-flocculation and air stripping of ammonia before biological treatment (Trebouet et al., 2001). Kargi and Pamukoglu (2004) tested pre-treated leachate, which subjected to biological treatment in an aeration tank operated in repeated fed-batch mode in the absence and presence of powdered activated carbon (PAC) as adsorbent. The results clearly indicated that PAC addition improved COD removal significantly as compared to PAC-free biological treatment. Repeated fed-batch treatment also resulted in lower effluent COD and higher COD removal efficiencies as compared to single-cycle operation.

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4.2.5.7 Constructed Wetlands

Field and laboratory studies have been conducted using wetland systems to treat landfill leachates, but with variable results (Surface et al, 1993; Martin and Moshiri, 1994; Urbanc-Bercic, 1994; Mulamoottil, McBean and Rovers, 1998, Liehr et al, 2000 and Cossu et al, 2001). Inconsistent results can be attributed to the variable nature of the leachate and the lack of universally accepted design standards for wetland treatment systems. The constructed wetlands for wastewater treatment can be classified on the bases of vegetation and hydraulic pathways into: horizontal subsurface flow wetlands, horizontal surface flow wetlands, vertical flow wetlands and floating plant based wetlands. Subsurface flow systems (SSF) are the most used due to absence of odors and mosquitoes, simple operation and maintenance, reliable operating conditions and a combination of aerobic and anaerobic processes inside the system. This aerobic-anaerobic environment allows high removal rates of different organic compounds, pathogens and some low-degradable matter. For this reason, over the last several years, different aspects of constructed wetlands have been investigated, including: effects of soil composition and grain-size distribution, removal mechanisms, fate of pollutants, engineering aspects, hydraulic distribution and flow (Paredes, 2004).

4.3 Phytoremediation

4.3.1 Definition and History of Phytoremediation

Phytoremediation is a low-tech, low-cost in-situ emerging cleanup technology for contaminated soils, groundwater, and wastewater. Phytoremediation is defined as the engineered use of green plants, such as grasses, forbs, and woody species, to remove, contain, or render harmless such environmental contaminants as heavy metals, trace elements, organic compounds, and radioactive compounds in soil or water. This definition includes all plant-influenced biological, chemical, and physical processes that aid in the uptake, sequestration, degradation, and metabolism of contaminants, either by plants or by the free-living organisms that constitute the plant's rhizosphere. Phytoremediation takes advantage of the unique and selective uptake capabilities of plant

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root systems, together with the translocation, bioaccumulation, and contaminant storage/degradation abilities of the entire plant body (Schnoor, 1997; Hichman, et al., 1998; Burd et al., 2000; and Modjeski, 2000). According to Hinchman et al. (1998), plant-based soil remediation systems can be viewed as biological, solar-driven, pump-and-treat systems with an extensive, self-extending uptake network (the root system) that enhances the below-ground ecosystem for subsequent productive use.

The technique of using plants to clean up contaminated environments is not new. At the end of the 19th century, *Thlaspi caerulescens* and *Viola calaminaria* were the first plant species documented to accumulate high levels of metals in leaves (Hartman, 1975). In the mid 1930's, researchers discovered that plants of the genus *Astragalus* were capable of accumulating up to 0.6 % selenium in dry shoot biomass (Lasat, 2002). Also in the late 1940's, researchers identified plants able to accumulate up to 1% Ni in shoots (Lasat, 2000). The idea of using plants to extract metals from contaminated soil was reintroduced and developed by Rascio (1977) and Utsunamyia (1980) and Chaney (1983). The first field trial on Zn and Cd phytoextraction was conducted by Baker et al. (1991). In the last decade, extensive research has been conducted to investigate the biology of metal phytoextraction. However, the understanding of the plant mechanisms that allow metal extraction is still emerging (Lasat, 2000).

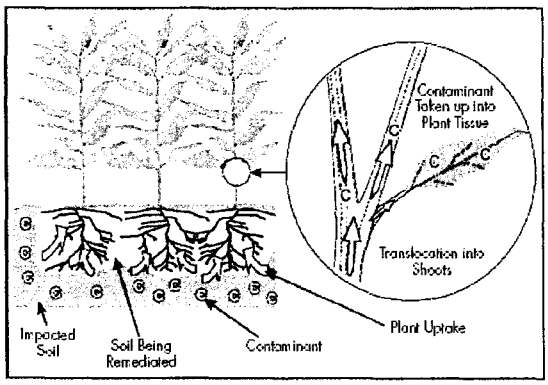
4.3.2 Phytoremediation Techniques

These are six phytoremediation techniques: phytoaccumulation (phytoextraction), rhizofiltration, phytostabilization, phytodegradation, rhizodegradation, and phytovolatilization (Figure 4.5).

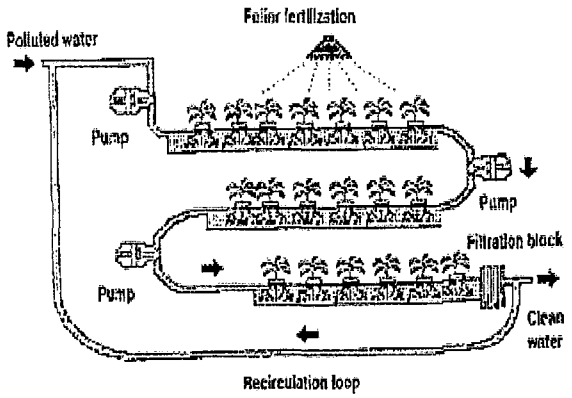
4.3.2.1 Phytoaccumulation (Phytoextraction)

Phytoaccumulation refers to the use of metal-accumulating plants that translocate and concentrate metals from the soil in roots and above ground shoots or leaves. It has also been proposed for extraction of radionuclides from sites with mixed wastes. Phytoextraction offers significant cost advantages over alternative schemes of soil

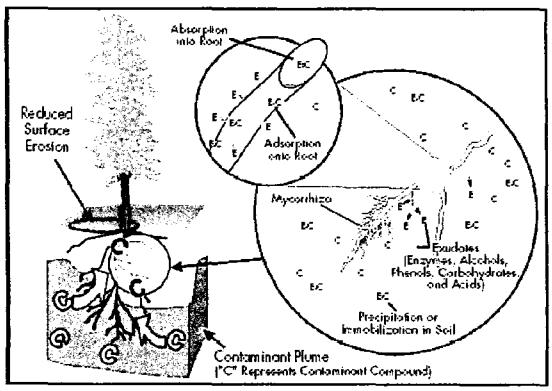
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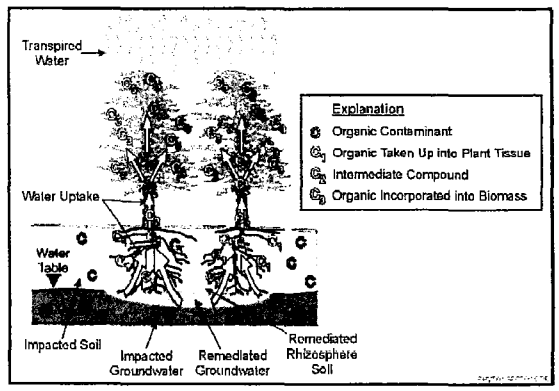
(a) phytoaccumulation (phytoextraction)



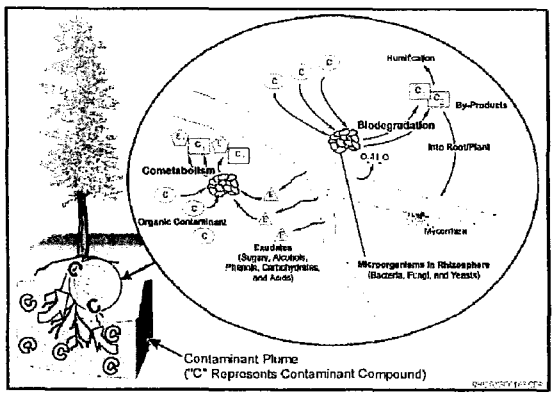
(b) rhizofiltration



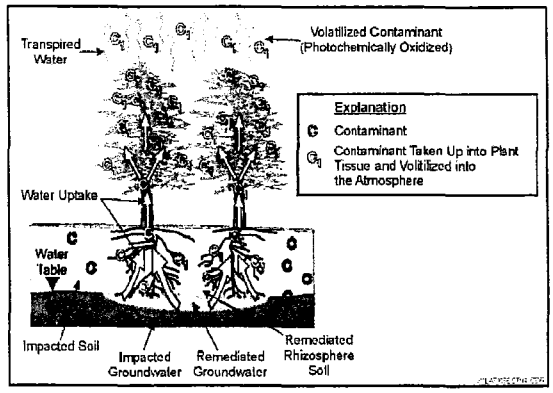
(c) phytostabilization



(d) phytodegradation



(e) rhizodegradation



(f) phytovolatilization

Figure 4.5. Phytoremediation techniques.

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excavation and treatment or disposal (Schnoor, 1997). The harvested materials are incinerated, composted or landfilled, depending on the concentration of metals in the plant shoots and leaves. Many metals can be reclaimed from the ash after incineration. This reduces the amount of hazardous waste as an end product and can also generate revenues. This procedure of planting and harvesting may be repeated as often as necessary in order to bring the contaminant levels down to acceptable limits (Modjeski, 2000). Constituents amenable to Phytoextraction include metals (Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Zn), radionuclides (^{90}Sr, ^{137}Cs, ^{239}Pu, ^{238}U, ^{234}U) and non-metals (B). Organic compounds and subsequent removal of biomass generally has not been examined as a remedial strategy (USEPA, 2000).

Hyperaccumulator plants are found in the *Brassicaceae, Euphorbiaceae, Asteraceae, Lamiaceae,* or *Scrophulariaceae* plant families (Baker, 1995). Examples include: *Brassica juncea* (Indian mustard) - a high-biomass plant that can accumulate Pb, Cr (VI), Cd, Cu, Ni, Zn, ^{90}Sr, B, and Se. It has over 20 times the biomass of *Thlaspi caerulescens*. *Brassicas* can also accumulate metals and the ability to transport lead to the shoots (Kumar et al., 1995). Because potentially toxic levels of metals can accumulate in the aboveground portion of the plant, access to the plants must be controlled and plant debris must be monitored more closely than with other phytoremediation technologies. Thus, care must be taken to restrict access of browsing animals, and harvested plant material must be properly disposed of (EPA, 2000). Soil conditions must be appropriate for plant growth and contaminant migration to the plant, yet not allow leaching of the metals. The pH of the soil may need to be adjusted and/or chelating agents may need to be added to increase plant bioavailability and uptake of metals (Banuelos, 2000; and Lasat, 2000).

4.3.2.2 Rhizofiltration

Rhizofiltration is the adsorption or precipitation of contaminants onto or into the plant roots (Dushenkov, et al., 1995; and Salt et al., 1995). The contaminants are in solution surrounding the root zone. Rhizofiltration is similar to phytoaccumnlation because in both of these methods the contaminants being remediated are heavy metals. The two

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methods differ in their contaminant media. The plants specifically used for rhizofiltration remediate contaminated groundwater, which are unlike phytoaccumnlation plants that address the remediation of contaminated soil (Modjeski, 2000).

Extracted groundwater, surface water, and wastewater can be treated using this technology. Rhizofiltration is generally applicable to low-concentration, high-water-content conditions. This technology does not work well with soil, sediments, or sludge because the contaminant needs to be in solution in order to be sorbed to the plant system (EPA, 2000). Constituents amenable to rhizofiltration include metals (Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cr^{2+}, Cr(VI)) (Dusenkov, et al., 1995) and radionuclides (U, Cs, Sr) (Lasat, et al., 1997).

Dushenkov et al. (1995) stated that terrestrial plants can be grown and used hydroponically in rhizofiltration systems. These plants generally have a greater biomass and longer, faster-growing root systems than aquatic plants. The authors found that 5 dicots (broadleaf crops), 3 monocots (cereals), 11 cool season grasses, and 6 warm season grasses were found to be effective in accumulating Pb in their roots after three days of exposure to 300 mg/L Pb under hydroponic conditions. The dicot Indian mustard (*Brassica juncea*) was also effective in taking up other metals.

Salt, et al. (1995) reported that sunflowers (*Helianthus annuus* L.) removed concentrated Cr^{6+}, Mn, Cd, Ni, Cu, U, Pb, Zn, and Sr in laboratory greenhouse studies. Sunflowers also were more effective than Indian mustard (*Brassica juncea*) and bean (*Phaseolus coccineus*) in removing uranium. Dushenkov et al. (1997) bioaccumulation coefficients for uranium in the sunflowers were much higher for the roots than for the shoots.

Dushenkov et al. (1995) used aquatic plants in wastewater treatment system. The floating aquatic plant milfoil (*Myriophyllum spicatum*), at a biomass density of 0.02 kg/L, rapidly accumulated Ni, Cd, Cu, Zn, and Pb. The plant accumulated up to 0.5% Ni, 0.8% Cd, 1.3% Cu, 1.3% Zn, and 5.5% Pb by weight. Wang, et al. (1996) reported that hydroponically-grown plants concentrated Pb, Cr(VI), Cd, Ni, Zn, and Cu onto their roots

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from wastewater. Raskin et al. (1994) reported that lead had the highest bioaccumulation coefficient and zinc was the lowest.

4.3.2.3 Phytostabilization

Phytostabilization is the use of specific plant species to retain or hold contaminated soils and sediments in place. And it can be used also to immobilize contaminants in the soil and the groundwater (Schnoor, 1997). These plants are able to accomplish this retention by absorbing and accumulating contaminants onto the roots, or by precipitating contaminants within the root zone of the plants (EPA, 1998; Berti and Cunningham, 2000; and Modjeski, 2000). Typically, this technique is used to reestablish vegetation on sites where vegetation is lacking because of high concentrations of metals in surface soils. The reestablished vegetation prevents wind erosion, transport of exposed surface soils, and leaching of soil contamination to the groundwater, thereby decreasing the potential of contaminant migration (Modjeski, 2000).

Phytostabilization occurs through root-zone microbiology and chemistry, and/or alteration of the soil environment or contaminant chemistry. Soil pH may be changed by plant root exudates or through the production of CO_2. Phytostabilization can change metal solubility and mobility or impact the dissociation of organic compounds. The plant-affected soil environment can convert metals from a soluble to an insoluble oxidation state (Salt et al., 1995). Phytostabilization can occur through sorption, precipitation, complexation, or metal valence reduction. Plants can also be used to reduce the erosion of metal-contaminated soil. The root zone is the primary area affecting chemically moderated immobilization or root precipitation (Dusenkov, 2003). Plants can be selected for their root depth; for example, poplars can be used for remediation of soil to a depth of 5 to 10 feet. The impact of the roots may extend deeper into the soil, depending on the transport of root exudates to lower soil depths (USEPA, 2000). Phytostabilization might be most appropriate for heavy-textured soils and soils with high organic matter content. Phytostabilization can be performed after more active soil treatment technologies have been tried. Soil water content, which can affect redox conditions in the soil, must be appropriate for plant growth.

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4.3.2.4 Phytodegradation

Phytodegradation, also known as phytotransformation, is a process in which plants take up and break down contaminants through either metabolic processes within the plant, or externally when the enzymes produced by plant roots are released around the plant root area, and then break down the contaminants into molecular fragments (Shroder et al., 2002; and Modjeski, 2000). These fragments can then be incorporated into new plant tissue (USEPA, 1998).

Various plants may release different enzymes such as nitroreductase, dehalogenase, peroxidase, and others. These enzymes can either detoxify the contaminant, or make the contaminant vulnerable to microbial consumption (Modjeski, 2000). Phytodegradation is implemented typically when treating surface water and groundwater that is contaminated with organic matter or material composed of hydrocarbon chains (Chappell 1997). Phytodegradation bas been implemented at various sites to remediate trichloroethylene contaminants in groundwater (Schnoor 1997). Uptake is dependent on hydrophobicity, solubility, and polarity. Moderately hydrophobic organic compounds are most readily taken up by and translocated within plants. Very soluble compounds (with low sorption) will not be sorbed onto roots or translocated within the plant (Schnoor et al. 1995). Hydrophobic compounds can be bound to root surfaces or partitioned into roots, but cannot be further translocated within the plant. Non-polar molecules with molecular weights <500 will adsorb to the root surfaces, whereas polar molecules will enter the root and be translocated (EPA, 2000).

4.3.2.5 Rhizodegradation

Rhizodegradation is called plant-assisted degradation, rhizosphere biodegradation, or phytostimulation (Modjeski, 2000). Rhizodegradation is the breakdown of an organic contaminant in soil through microbial activity that is enhanced by the presence of the root zone (Corgie et al., 2003). Root-zone biodegradation is the mechanism for implementing rhizodegradation. Root exudates are compounds produced by plants and released from plant roots. They include sugars, amino acids, organic acids, fatty acids, sterols, growth

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factors, nucleotides, flavanones, enzymes, and other compounds (Schnoor et al., 1995). The chemical and physical effects of the exudates and any associated increase in microbial populations might change the soil pH or affect the contaminants in other ways. Rhizodegradation technique can be used to degrade very wide ranges of compounds such as total petroleum hydrocarbon (TPH), polycyclic aromatic hydrocarbons (PAH), BTEX (Benzene, toluene, ethylbenzene, xylenes), pesticides, chlorinatd solvents, PCP (pentachlorophenol), PCBs (polychlorinated biphenyls) and surfactants (EPA, 2000).

Because the rhizosphere extends only about 1 mm from the root and initially the volume of soil occupied by roots is a small fraction of the total soil volume, the soil volume initially affected by the rhizosphere is limited. With time, however, new roots will penetrate more of the soil volume and other roots will decompose the contaminants, resulting in additional exudates to the rhizosphere. Thus, the extent of rhizodegradation will increase with time and with additional root growth. The effect of rhizodegradation might extend slightly deeper than the root zone. If the exudates are water soluble, not strongly sorbed, and not quickly degraded, they may move deeper into the soil. Contaminated groundwater can be affected if it is within the influence of roots (EPA, 2000).

Plants that produce exudates that have been shown to stimulate growth of degrading microorganisms or stimulate co-metabolism will be of more benefit than plants without such directly useful exudates. The type, amount, and effectiveness of exudates and enzymes produced by plant roots will vary between species and even within subspecies or varieties of one species. The following examples for the plants used in the rhizodegradation such as Red mulberry (*Morus rubra* L.), crabapple (*Malus fusca (Raf.) Schneid*), Osage Orange (*Maclura pomifera (Raf.) Schneid*), Spearmint (*Mentha spicata*), Bush bean (*Phaseolus vulgaris* cv. "Tender Green"), and Rice (*Oryza sativa* L.).

4.3.2.6 Phytovolatilization

Phytovolatilization is a process in which plants take up and transpire a contaminant, and then they release the contaminant, or a modified form of the contaminant, to the

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atmosphere (EPA, 1998). This process is most useful in remediating organic contaminants. During the course of this process, many of the contaminants actually pass through the plants, out the leaves and then are volatilized into the atmosphere at very minimal concentrations (Modjeski, 2000).

Phytovolatilization has mainly been applied to ground water, but it can be used for soil, sediments, and sludges. Contaminants could be transformed to less-toxic forms, such as elemental mercury and dimethyl selenite gas (Carvalho and Martin, 2001). Contaminants or metabolites released to the atmosphere might be subject to more effective or rapid natural degradation processes such as photodegradation. Contaminant or hazardous metabolites, such as vinyl chloride formed from trichloroethylene (TCE), might be released into the atmosphere. Hazardous metabolites might also accumulate in vegetation and be passed on in later products such as fruit or lumber. Low levels of metabolites have been found in plant tissue (Newman et al. 1997).

4.3.3 Advantages of Phytoremediation

The advantages of phytoremediation are: (a) it is a cost-effective technology, (b) it is applicable to treat a wide variety of contaminants, (c) it is aesthetically pleasing, (d) it has high public acceptance, (e) it allows reduction in soil erosion, (f) in-situ application avoids excavation, (g) it is a permanent treatment solution and (h) it is proactive treatment solution.

Significant cost saving is one of the biggest advantages of using phytoremedaition technology. Phytoremediation can reduce the cost of clean up of a site to between one-third and one-hundredth of the cost of some existing remediation technologies (Modjeski, 2000; and Robinson et al., 2003). There are a number of reasons for this large reduction in costs of this method. First, the operating costs are significantly lower because the primary energy used to sustain this system is solar energy from the sun. Second, the installation costs are quite low because the installation of phytoremediation systems involves the use of standards and slightly modified agricultural equipment and practices

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(Ensely, 2000). Some common farm equipment used at phytoremediation sites are tractors, tillers, seeding devices, fertilizer applicators and irrigation equipment (Rock 1997). Third, it continues with low levels of maintenance over a period of many years, compared with large-scale costly remediation systems Phytoremediation significantly reduces capital costs by the reduction in the consultant/owner manpower required to design and operate the system (Modjeski, 2000).

In general, it is typically pleasing to the eye to see trees, grasses, and shrubs growing in open spaces. In addition, the trees and vegetation may provide shade, dust control, and the ability to house bird and wildlife habitats (Rock, 1997). There is a widespread agreement from the general public that sites covered in vegetation seem less hazardous than an abandoned lot (Rock, 1997). The common public perception is that when plants or vegetation are growing on a site, the site must be clean. Plants and vegetation can clean up sites with minimal disruption to the local community (Modjeski, 2000). Plants may be maintained in areas that may receive future contamination such as treatment facilities or industrial sites. In such a situation, if a contaminant release should occur, the plants are already in place, acting as extremely effective clean up tools (Susarla et al., 2002).

Since the main component of ecosystem restoration is vegetation, establishing vegetation on a site can reduce soil erosion from wind and water, which can help prevent contaminants from spreading and also can reduce the exposure to humans and animals from contaminants (Chaney and Ryan, 1994). The soils remain in place and are usable following phytoremediation treatment. When using a phytoremediation treatment system less secondary wastes are generated since the soils are not removed. Since there is no excavation necessary, workers are exposed to less risk in handling the material because the material is left in place (Chappell 1997).

Phytoremediation is a permanent treatment solution in which heavy metals can be recovered, and organic contaminants are destroyed. It also permanently decreases the availability, toxicity, and concentrations of contaminants (Modjeski, 2000). Contaminants that have been remediated in laboratory or field tests using phytoremediation include:

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heavy metals such as Cd, Cr (VI), Pb, Co, Cu, Ni, Se, and Zn (Dushenkov, et al., 1995; Kumar et al., 1995; Zayed et al., 1998; Zhu, et al., 1999; and Qian, et al., 1999), radionuclides such as Cs, Sr, and Ur (Lasat et al, 1997; and Dushenkov et al., 2003), chlorinated solvents such as TCE, and PCE (Susarla, et al., 2002), petroleum hydrocarbons such as BTEX (Collins, et al., 2002), polychlorinated biphenyls (PCBs) (Campanella, et al., 2002), poly aromatic hydrocarbons (PAH) (Harvey, et al., 2002), chlorinated pesticides (Chaudhry et al., 2002), explosives such as TNT, DNT, RDX, and HMX (Hughes et al., 1998), nutrients such as nitrates, ammonium, and phosphate (Barber, 1984) and surfactants (Schwitzguebel et al, 2002).

4.3.4 Disadvantages of Phytoremediation

The disadvantages of phytoremediation are: (a) it has slow reaction rates, (b) it is seasonal in nature, (c) it is applicable to shallow low/moderate levels of contaminant concentration, (d) it is unfamiliar to regulators and (e) it requires a large surface area.

Phytoremediation may take several growing seasons to clean up a site effectively. This limitation may not be a factor to consider if the site being remediated is not limited by time constraints. Typically, remediating a site by means of chemical, physical, or mechanical treatment takes a shorter length of time than does phytoremediation (Rock, 1997; and Chaney et al., 1997).

The success of the implementation of phytoremediation on a given site may be seasonal, depending on the plant species chosen, as well as the location of the site in question. Many other climatic factors may influence the effectiveness of a phytoremediation system such as rainfall patterns, and wind duration at various seasons. (Modjeski, 2000).

The contaminant concentration must be sufficiently low enough for the vegetation to be established and thrive for extended periods of time on a given site. If the contaminant concentration is too high, the contaminant will be toxic to the plant species. If it is difficult to establish vegetation on the site, this remediation technology choice is useless

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(Schnoor 1997). Also, in many cases, the depth of contaminant treatment is limited to shallow soils, streams, and groundwater (Susarla, et al., 2002). However, some researchers have found that using trees, rather than small plants and grasses, will enable them to treat much deeper contamination. The tree roots penetrate much more deeply into the ground, which allows for treatment of contaminants at a greater depth (Chaney et al., 1997).

Regulatory standards for phytoremediation have not been developed. Regulators evaluate and approve the proposed phytoremediation applications on a site-by- site basis. The regulators must determine if the specific application meets environmental statutes, regulations, and other requirements that may pertain to that site (Modjeski, 2000). This situation causes regulators unfamiliar with this technology to spend much time in reviewing phytoremediation applications. Also, many regulators know the old ways of remediating sites and may be opposed to exploring new remediation options (Rock 1997). Phytoremediation systems may require large surface areas of land, in order to completely remediate the contaminant (Modjeski, 2000).

4.4 Wetlands

The term wetlands encompass many different habitats including ponds, marshes, swamps, and peatlands. Wetlands may be temporally flooded each day as with tidal marshes, or be filled seasonally with water from melting snow. Plants and animals present in wetlands are from land and water habitats making them highly productive environments. Wetlands function as ecotones, transitions between different habitats, and have characteristics of both aquatic and terrestrial ecosystems (Figure 4.6). Wetlands are found along the shorelines of oceans, lakes, rivers and in local depressions. The water in natural wetlands is derived from tidal flows, lakes, flooding rivers, or connections to groundwater. Wetlands have often been described as the kidneys of the landscape because of the role they play in water and chemical cycles. They filter out sediment and pollution from the surrounding environment so that the water they discharge is cleaner than that which entered the wetland. In this manner, wetlands act as both a sink and a

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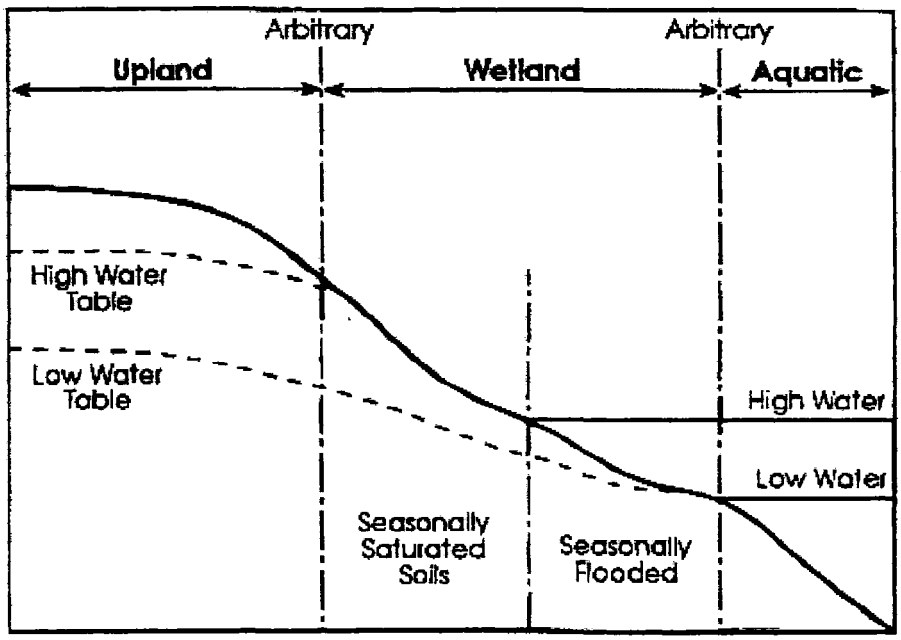


Figure 4.6. Wetlands are transitional areas between uplands and aquatic ecosystems (Kadlec and Knight, 1996).

source, storing and passing on vital resources to their local environment (University of Guelph, 2003 and EPA, 2003). The wetland treatment technology capitalizes on the intrinsic water quality amelioration function of wetlands and is emerging as a cost-effective, environmentally friendly method of treating a variety of wastewaters.

There are two types of wetlands: Natural and Constructed Wetlands. Constructed wetlands are man-made wetlands used to treat non-point source pollution. Natural wetlands are populated by different plant types adapted for growth in water or saturated soil (Figure 4.7). Organization into clear-out groups is difficult because of ambiguous definitions and the unwieldliness and complexity of the classification schemes. Consequently, there are many terms referring to plants growing along the gradient from terrestrial to aquatic habitats: hydrophytes, aquatic macrophytes, vascular hydrophytes, aquatic plants, and vascular aquatic plant (Guntenspergen et al., 1989).

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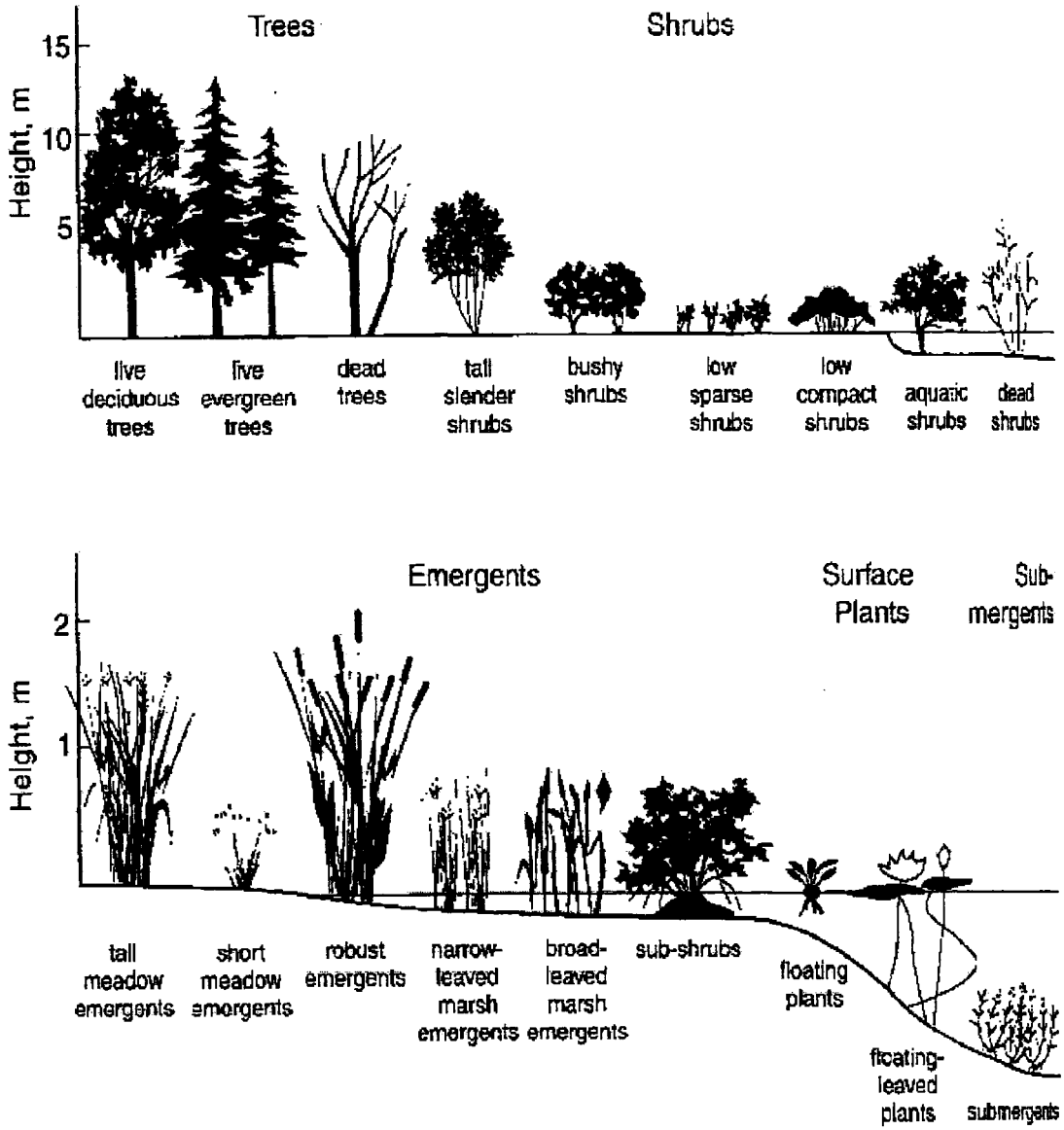


Figure 4.7. Sub forms of vegetation used to classify wetland (Kadlec and Knight, 1996).

4.4.1 Natural Wetlands

Natural wetland ecosystems are variable in nature and support different hydrological and biological regimes. They can be classified based on their location into: (a) fluvial, riverine or riparian wetlands which are freshwater wetlands that border rivers and streams, (b) shore or lacustrine wetlands, which border lakes, (c) freshwater wetlands which are isolated or lacking influence from hydrological features such as oceans, rivers or lakes and are referred to as terminal basin or palustrine systems, (d) marine systems

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wetlands which occur along coastlines, (e) estuarine wetlands which are located in sheltered coastal areas where fresh and salt waters mix, such as salt marshes and mangrove swamps (Ferren et al., 1996). The problem with this classification system is the large amount of overlap existing between the terms, making identification difficult. The more commonly used method of wetland classification places emphasis on a system's hydrological status rather than location. The hydrodynamics of a site (which is defined as the degree of vertical water table fluctuation and rate of lateral groundwater flow) is typically the limiting factor influencing all features in a given wetland (Banner and MacKenzie, 2000). Based on their hydrological status, natural wetlands can be classified into: pocosin, cienega, playa lakes, riverine, prairie potholes, peatlands and swamps and bogs.

4.4.1.1 Pocosin Wetlands

Pocosin (an Algonquin Indian word, literally means "swamp on a hill") are found in ridge and swale topography, in flat areas of the lower coastal plain, in areas of springs and seeps in the upper coastal plain, and in the floodplains of streams. Pocosins (Figure 4.8) contain dense evergreen plant communities, consisting of small broad-leaved evergreen trees (pond pine) and scrub shrubs (fetterbush and inkberry), which can occur either on highly organic soils, such as mucks or peats, or on very poorly drained mineral soils (Richardson and Gibbson, 1999). The soils of pocosins are acidic and low in nutrients and minerals. Pocosins occur in many different shapes and can vary in size from less than an acre to several thousand acres. These wetlands are important to birds and animals such as migratory waterfowl, herons, egrets, and muskrats (Richardson et al., 1981). They

provide very favorable groundwater storage due to the differing permeability properties of their organic layers. Macropores in the upper layers make the soil very permeable, allowing for high retention of rainfall. Conversely, the reduced permeability of the lower layers prohibits the stored rainwater from draining very quickly (Mitchell, 1999). Water movement occurs as seepage at the pocosin's margins that flows to streams or as direct flow to salt marshes in estuarine areas. These two properties make pocosins particularly

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Figure 4.8. Pocosin wetlands.

vulnerable to the adverse effects of stormwater discharges in the many areas of the lower coastal plain that are experiencing development (EPA, 1996).

4.4.1.2 Cienega

Cienega (Figure 4.9) is a term that usually applies to mid-elevation (1,008-2,000 m) wetlands characterized by permanently saturated, highly organic, reducing soils. These warm, temperate habitats were most often termed cienegas by Hispanic (the word cienega comes from the Spanish *cien aqua,* meaning "hundred waters") and later by explorers and settlers, and appear to be distinctive habitats (Hendrickson and Minckley 1984). Cienegas are perpetuated by permanent, scarcely fluctuating sources of water, and are rarely subject to harsh winter conditions. At mid-elevations of in semi-desert grassland, cienegas are usually associated with perennial springs and headwater streams (EPA, 1996).

4.4.1.3 Playa Lakes

The term *playas* generally refers to areas occupied by temporary shallow lakes that have internal drainage, usually in arid to semi-arid regions. They are not a part of an integrated

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Figure 4.9. Cienega wetlands.

surface drainage system, but are related to geologic fracture areas. Playas are shallow (typically less than 1 m deep), circular basins averaging 6.3 hectares in surface area. Playa floors are plate-like with relatively constant water depth throughout much of the basin. Because very few playas are directly associated with groundwater, playas can usually fill only from precipitation and irrigation runoff. Precipitation, ranging from 30-55 cm, is the major input since there are no permanent rivers and streams in the area. Excessive rainfall produces surface runoff in late spring and early fall. Other inputs, such as groundwater from deep aquifers and irrigation water, contribute to the permanence of standing water. Such groundwater input is uncommon because most playas are situated above the regional groundwater table. Most playas are dry during one or more periods of each year, usually late winter, early spring, and late summer. Several wet-dry cycles during one year are not uncommon for a playa and depend on precipitation and irrigation patterns. Soils of the playa are predominantly clays, differing from the loams and sandy loams of the surrounding uplands (Haukos and Smith, 1992). These wetlands are dominated by semi-aquatic sedges, rushes, and grasses (Figure 4.10). Trees are scarce and immediate surroundings are saline as a result of capillarity and evapotranspiration.

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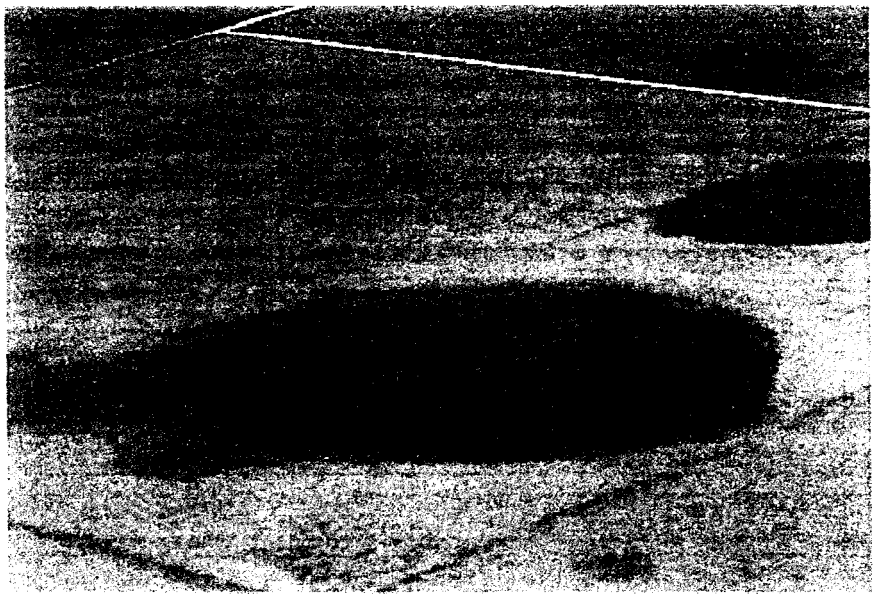


Figure 4.10. Playa lakes

The climate of the region containing most of the playa lakes is mostly semi-arid. Vegetation in dry playas resembles upland vegetation and includes species such as summer cypress, ragweed, and various prairie grasses. Moist and flooded conditions in playas favor vegetation representative of other North American wetlands: barnyard grass, smartweed, bulrush, cattail, spikerush, arrowhead, toothcup, and dock (Haukos and Smith, 1992). Many of these lakes are important migratory bird and songbird habitat.

Since many of the playa watersheds function as cropland and rangeland, their vegetation serves an important purpose, helping to reduce excess nutrients from runoff and thereby improving the quality of surface water. In an area where water is not abundant, any addition to the groundwater will have economic significance, whether it is from irrigation water or recharge. Where playa watersheds receive stormwater discharges, the potential exists for adverse impacts to the playa itself or for degradation of the quality of the local and/or regional groundwater resources (Rucker, 1996). Many have been drained for development or destroyed by upstream pumping of the groundwater sources (Hendrickson and Minckley, 1984).

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4.4.1.4 Riverine (Riparian) Wetland

Riverine or riparian wetlands (Figure 4.11) exist along the margins of rivers, behind natural levees, in oxbows and floodplains (Willems, et al., 1997). Riverine wetlands in arid climates are limited shoreward by desert and riverward by water depth and scouring (Hanson et al., 1994). These wetlands are transitory and develop rapidly only to be removed by channel-straightening floods, or proceed toward an upland community after drying. Like cienegas, riparian lands have been impacted by depletion of base flow sources or by direct diversions upstream (Hawkins, 1993). A number of riparian wetlands exist, but some rely on other water sources such as treated upstream wastewater. The quality of the wastewater discharging to these wetlands plays a more important role in maintaining wetland functions than do the effects of stormwater runoff (EPA, 1996).

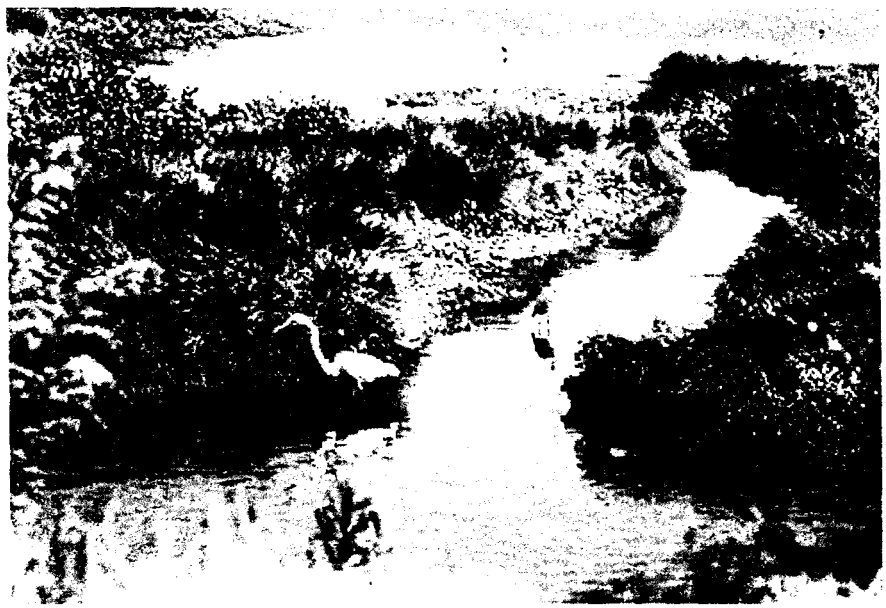


Figure 4.11. Riverine (riparian) wetland.

4.4.1.5 Prairie Potholes

Pothole is defined as a surface depression occurring in glacial sediments (Figure 4.12). Vegetation characteristics include cattails and various species of grasses, sedges, and rushes such as bulrushes. More ephemeral potholes are characterized by meadow grasses and sedges. Prairie potholes are shallow wetlands in a region that is fairly flat to rolling

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Figure 4.12. Prairie potholes.

and can occur at many different elevations (Kreymborg and Forman, 2001). These saucer-shaped depressions have an average depth of about 0.6 to 1.5 m. Their appearance is dependent on the size and shape of the original stagnant ice block that formed them and on the effects of wind-induced wave erosion. Individual potholes can range in size from a few hundred square meters to several thousand square kilometers. Potholes are not usually associated with any regional network of stream channels, but they are related to local and regional groundwater systems. Water input is from groundwater inflow (discharge), direct precipitation, and occasionally from surface inflow from excess storm water or snowmelt runoff. The hydro-periods in wetlands range from temporarily to permanently flood. These differences cause the development of diverse vegetation zones such as wet meadow, shallow marsh, and deep marsh. Prairie potholes lose water through evaporation, transpiration, and seepage to groundwater (Vieux et al., 1996).

4.4.1.6 Peatlands

Peatlands have low topographic relief and have a depth ranging from 1 to 3 meters (Figure 4.13). Peatland soils have partially decomposed remains of plants. The decomposition rate is low because of low oxygen concentrations in saturated soils. Bogs and fens are the predominant types of wetlands found in the peatlands (Mitsch and

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Figure 4.13. Peatlands.

Gosselink, 1993). Water chemistry determines the development of different peatland types. Acidic water with a very low mineral content is typical of bogs, while the fens are characterized by the reverse. These water chemistry differences are related to water origins. Mineralized fen water originates from groundwater, whereas precipitation produces the high-acidity, low-mineral water content of a bog. Peatlands have a hydrogeologic flow system independent of regional groundwater movement (Figure 4.14).

Bogs have acidic, fibrous, spongy, nutrient-poor organic soil (phosphorus and potassium are the limiting factors), whose organic plant material consists mostly of sphagnum moss. Because of their location at or above the local groundwater table, bogs acquire most of their water from precipitation and primarily support the growth of acid-tolerant trees and shrubs such as the tamarack, the black spruce, and the leather-leaf. Depending on the dominant vegetation, bogs can be described as forested, scrub-shrub, or moss-lichen types. They harbor animals and birds such as deer, rabbits, grouse, and owls and are minerals from soil water, exchanging them with hydrogen ions, thereby increasing acidity. The nutrient-deficient environment results in autogenic succession, where plant home to a diverse array of rare plants (DNR, 1998; and Lyon, 1993). The presence of the

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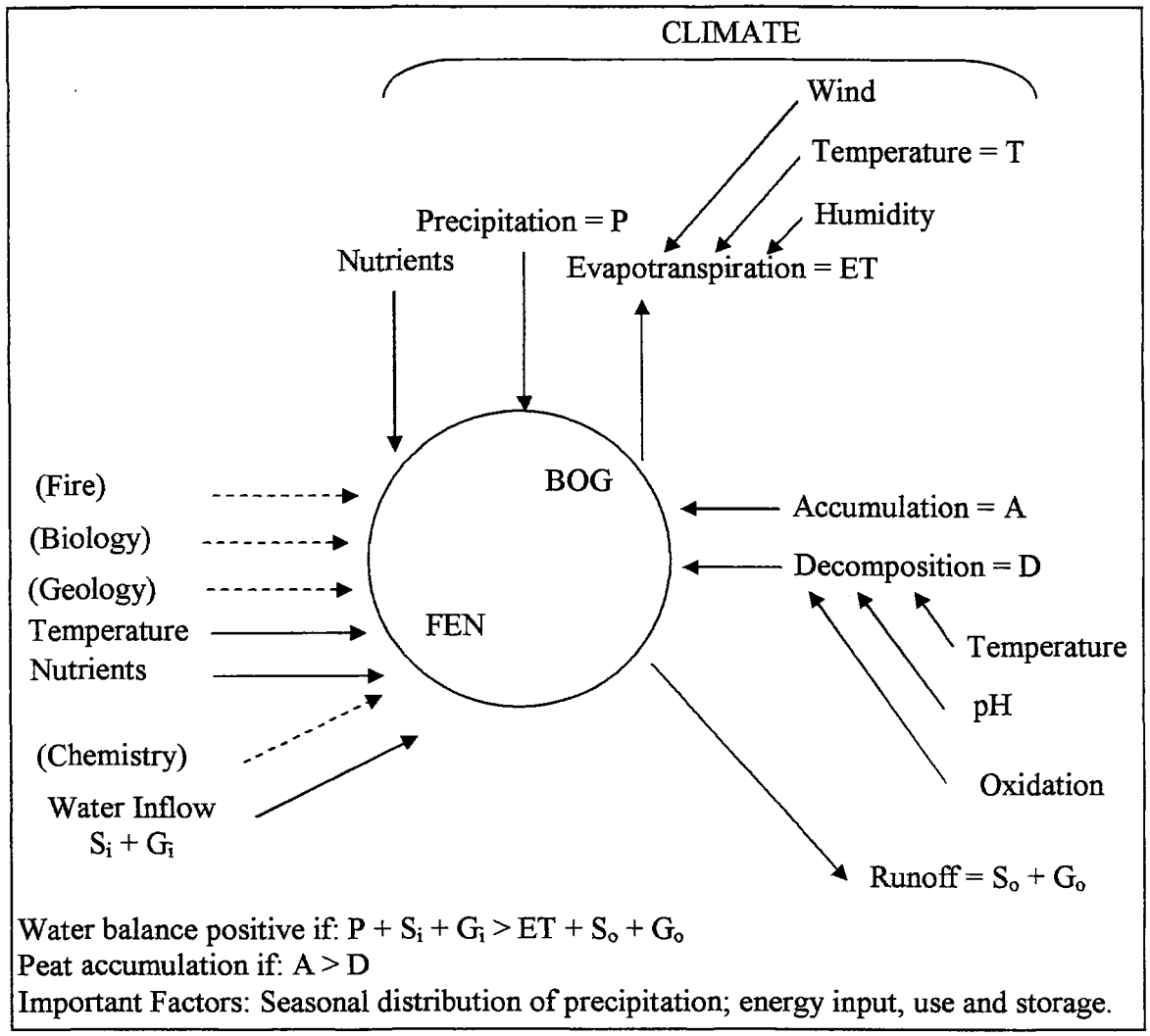


Figure 4.14. Diagram of hydrologic balance and peat accumulation at peatlands (adapted from Tersmae, 1977).

sphagnum also contributes to the acidity of bog waters as it actively removes basic litter is decomposed very slowly. This, occurring over thousands of years, yields the characteristic peat deposits which exist within bogs at depths varying from less than 50 cm over 10 m depending on climate, terrain, and hydrology. Bogs can develop overtime by two different ways: terrestrialization and paludification. Terrestrialization occurs when sphagnum mosses grow over a lake or pond, slowly filling it. Paludification occurs when sphagnum mosses grow over dry land, preventing water from leaving the surface. Bogs tend to develop in shallow, low-lying areas above layers of bedrock (EPA, 2002; Banner and MacKenzie, 2000; and DNR, 1998).

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Fens represent a transitional stage between marshes and bogs. They obtain water not only directly from precipitation, but also by surface runoff and groundwater seepage. Fens support diverse plant communities consisting of sedges, grasses, reeds, and some woody vegetation. Both areas contain a vast number of invertebrates, insects, and amphibians (Blodau, 2002).

4.4.1.7 Swamps

Generally, they are found in valleys and valley-side depressions that are periodically flooded (Figure 4.15). They are associated with surface drainage systems and periodically can have standing water. Their size ranges from small depressions of less than an acre to many acres. Trees common to the areas are the white cedar and the red maple. Other swamps, not bordering a river, may contain a mixture of evergreen and deciduous trees. Swamps, which can occur in either freshwater or saltwater floodplains, characteristically contain highly organic, nutrient-rich, black mineral soils which are saturated throughout the year. Standing water can also be found in these systems during wet seasons. However, swamps typically tend to be more waterlogged than wet. They are the only type of wetland dominated by water-tolerant woody plants such as black spruce and alder. Mosses, grasses and ferns also tend to inhabitant these damp systems. The nutrient-rich state of these wetlands provide excellent habitat for frogs, salamanders, songbirds and mammals such as deer and snowshoe hare (DNR, 1998). They serve vital roles in flood protection and nutrient removal, and suffer threat of drainage from agriculture, as their nutrient-rich soils make for ideal farmland (EPA, 2002).

4.4.2 Constructed Wetlands

Constructed wetlands are becoming increasingly common features emerging in landscapes across the globe. Although similar in appearance to natural wetland systems (especially marsh ecosystems), they are usually created in areas that would not naturally support such systems to facilitate contaminant or pollution removal from wastewater or runoff (Hammer, 1992; and Mitsch and Gosselink, 2000). They are designed and constructed to capitalize on the intrinsic water quality amelioration functions of natural

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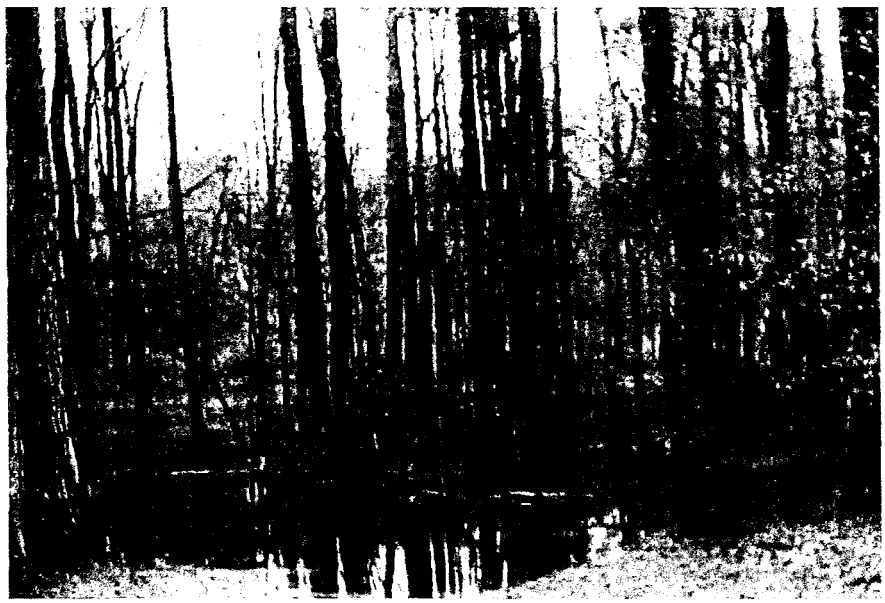


Figure 4.15. Swamps.

wetlands for human use and benefits (Osmund et al., 1995b; and Hammer, 1992). Wetland creation can also encompass wetland enhancement, in which a natural wetland is enhanced (via diversion of flow or the creation of berms) to provide one or more additional functions (Mitsch and Gosselink, 2000; and Osmund et al., 1995a).

Constructed treatment wetlands are being used to treat a variety of wastewaters, including municipal wastewater, stormwater runoff, agricultural runoff, mining drainage, landfill leachate, industrial wastewaters, ammunition, and radionuclides (Davis, 1995). Their increasing popularity can be attributed to several benefits: (a) they are capable of providing removal rates ranging from 60% to over 95% for many pollutants, (b) they are much less costly to build and operate than other conventional treatment facilities as the construction of treatment wetland areas costs anywhere from one half to one tenth the cost of building conventional treatment facilities, (c) they provide important functions such as habitat enhancement, and (d) they are a less intrusive and provide more environmentally sensitive approach to pollution abatement (Tousignant et al., 1999; Hammer, 1992; and Davis, 1995). Some of the disadvantages include: (a) they generally require larger land areas than conventional wastewater treatment systems, which can

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prove disadvantageous in regions where land is scarce or costly, (b) bioremediation and phytoremediation processes require more time than conventional treatments, (c) monitoring can sometimes prove difficult, and (d) the reliability of wetland treatment systems can often be less consistent than that of traditional treatment systems, as nature, can be unpredictable and external factors such as weather and pests often cause sites to display inconsistent contaminant removal rates (FRTR 1998; CPEO, 1998; and Davis, 1998).

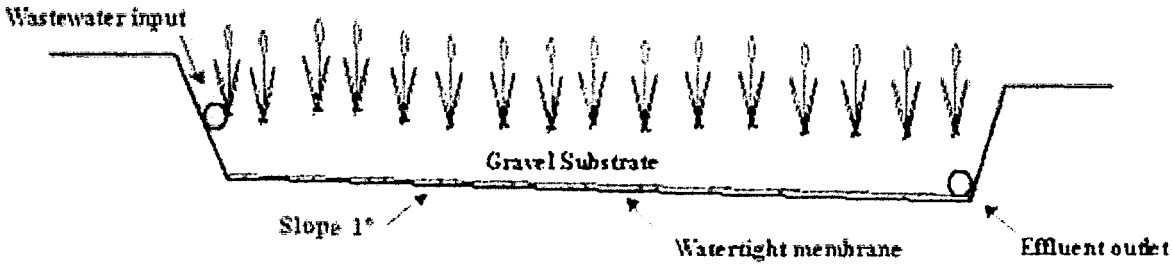
Constructed wetlands are classified as either Free Water Surface (FWS) systems or Subsurface Flow (SSF) systems. Both these systems typically consist of a series of cells or channels lined with impermeable material (such as clay or plastic liners) to limit potential groundwater infiltration. They both support additional substrates composed of soil or stone, which are established with some sort of aquatic vegetation, such as cattails and reeds (*Typha* spp. and *Phragmites* spp.) or water hyacinth (*Eichhornia crassipes*). Wastewaters enter the wetlands via simple gravitational forces or can be more stringently directed and controlled through the use of pumping mechanisms (Liehr et al., 2000).

4.4.2.1 Free Surface Flow Constructed Wetlands

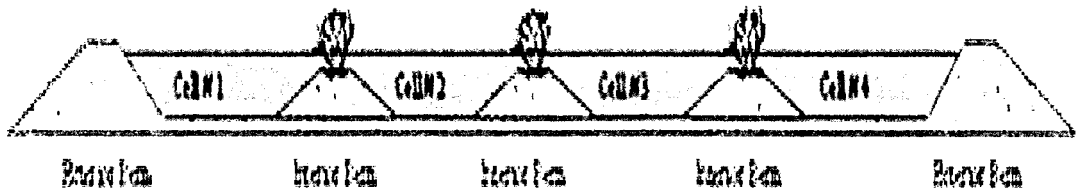
A free water surface (FWS) wetland consists of a shallow basin, soil or other medium to support the roots of vegetation, and a water control structure that maintains a shallow depth of water. The water surface is above the substrate. FWS wetlands look much like natural marshes and can provide wildlife habitat and aesthetic benefits as well as water treatment (Figure 4.16a). In FWS wetlands, the near surface layer is aerobic while the deeper waters and substrate are usually anaerobic.

FWS wetlands have many advantages including: (a) lower and straightforward construction and operating costs, (b) little requirements for mechanical equipment, energy, and skilled operator, (c) superiority in their abilities to remove biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solids (TSS), (d) significant reduction in the levels of nitrogen and phosphorus, metals, persistent

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(a) Cross-section Diagram of Common Sub-Surface Flow Wetland System.



(b) Cross-section diagram of common free water surface wetland system.

Figure 4.16. Constructed wetland.

organics and fecal coliforms, and (e) routine harvest and removal of FWS wetland vegetation is typically unnecessary as phytoremediation represents a relatively secondary removal pathway of contaminants in these systems, hence plant removal does not provide a significant treatment benefit (EPA, 2000c; Davis, 1995; and Liehr et al., 2000). The main disadvantages of FWS systems are: (a) they require a larger land area than other systems, (b) the wastewaters are accessible to humans and animals, hence it may not prove prudent to establish these wetlands in high-use areas such as parks, playgrounds, or similar public facilities, (c) pollutants such as phosphorus, metals, and some persistent organics can become bound in wetland sediments and accumulate over time, and (d) the open water environments of FWS wetlands can attract unwanted pests such as mosquitoes which may ultimately need control (USEPA, 2000c; Davis, 1995; and Liehr et al., 2000).

Emergent macrophytes based wetlands are the most common type of FWS. They consist of a series of channels and/or basins which are lined with an impermeable material (such

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as clay) in order to limit infiltration. A layer of soil is provided on top of the impervious material in which emergent macrophytes (such as cattails and bulrushes) are planted. A slow flow rate is applied so that a shallow depth is maintained (Hamilton et al., 1993).

Settleable solids are removed by sedimentation, which lowers biochemical oxygen demand (BOD) and removes particulate forms of phosphorus and nitrogen from the wastewater. A nutrient rich sludge is then formed on the wetland floor (Davis, 1995). The macrophytes supply oxygen to the sludge zone through their roots, thereby promoting aerobic digestion of the pollutants by microorganisms. Macrophytes also act as physical supports for microorganisms that help remove pollutants (Tousignant et al., 1999; and Davis, 1995).

As the name implies, free floating macrophyte based wetlands make use of floating plants, such as duckweed and water hyacinth, to remove nutrients and control algae in wastewater. A floating barrier grid is used to support the growth of floating macrophytes and to reduce wind effects, which would otherwise cause the plants to drift. It has been claimed that the floating plant mat blocks out sunlight, thereby preventing photosynthesis and inhibiting algae growth (Lemna Corporation, 1994). The plant mat and barrier grid reduce turbulence, allowing suspended solids to settle out more readily. It has been suggested that harvesting be done "periodically", depending on climate, nutrient loading and desired treatment (Tousignant et al., 1999; and Davis, 1995).

4.4.2.2 Subsurface Flow Constructed Wetland

A subsurface flow (SSF) wetland consists of a sealed basin with a porous substrate of rock or gravel. The water level is designed to remain below the top of the substrate (Figure 4.16b). SSF system planted with emergent macrophytes such as reeds (*Phragmites* spp.), Eurasian watermilfoil (*Myriophyllum spicatum*), and duckweeds (*Lemna* spp.). SSF systems are called by several names including vegetated submerged bed; root zone method, microbial rock reed filter, and plant-rock filter systems (Liehr et al., 2000). Because of the hydraulic constraints imposed by the substrate, SSF wetlands are best suited to wastewaters with relatively low solids concentrations and under

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relatively uniform flow conditions. They have been used to reduce 5-day biochemical oxygen demand (BOD_5) from domestic wastewaters from small-scale sources such as individual homes, schools, apartment complexes, commercial establishments, parks, and other recreational facilities (Tousignant et al., 1999).

In horizontal flow SSF wetlands, the medium is kept saturated under a continuous wastewater flow. Oxygen is transferred from the atmosphere into the wetland through the emergent plants (Tousignant et al., 1999). Vertical flow SSF wetlands are operated as a batch process rather than in continuous flow mode. Wastewater is dosed at timed intervals so that the filter is allowed to drain. Consequently, the system is not always saturated and oxygen is more easily transferred from the atmosphere through diffusion. In general, vertical flow SSF wetlands are less common and not as well documented as horizontal flow systems (Tousignant et al., 1999).

The major advantages of SSF wetlands include: (a) the rocky substrates provide greater surface area for microbial reactions and, therefore, SSF wetlands can be smaller in size yet treat larger flow volumes than FWS wetlands, (b) they are often better suited to projects in which the available land area is limited, (c) they are typically more suitable to public areas as contaminated wastewaters are not exposed, and (d) the nature of their substrates and flow regimes allow for better thermal protection and are, therefore, considered to be more effective in colder climates than FWS systems (EPA, 2000). The disadvantages of SSF wetlands are: (a) they are more expensive to construct, maintain and repair, (b) they have problems with clogging and as a result are best suited to wastewaters with relatively low solids concentrations and under relatively uniform flow conditions which often requires the installation of appropriate inlet and outlet structures designed to ensure the uniform distribution and collection of the applied wastewater, (c) as vegetation is the prominent removal mechanism of pollutants in these systems, plants can reach their points of saturation in terms of pollutant absorption, rendering them no longer effective thus requiring costly and time consuming harvesting, (d) they tend to be anoxic, which limits the biological removal of ammonia nitrogen via nitrification unless costly aerators are adopted to mitigate this problem, (e) phosphorus removal rates are

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inferior to that of FWS systems, (f) they have problems associated with the accumulation of pollutants in sediments over time, and (g) they provide less habitat value than FWS (Davis, 1995; Tousignant et al., 1999; and EPA, 2000). The latter is actually advantageous when dealing with substances of high toxicity or treatment systems located in areas where wildlife is not desirable. For example, at the Edmonton Airport in Alberta, Canada, a SSF wetland was created in order to treat runoff contaminated with glycol in de-icing fluid. The creation of habitat in these systems was prohibited as increased birds attracted to the site could have proven problematic to planes utilizing the adjacent runways (Davis, 1995; and EPA, 2000).

4.5 Physical/Chemical/Biological Transformations in Wetlands

The transport and transformation of chemicals in wetland ecosystems involve a great number of interrelated physical, chemical and biological processes which are influenced by the hydrologic conditions in wetland. These processes result not only in changes in the chemical forms of materials but also in the spatial movement within wetlands due to water-sediment exchange, plant uptake and export of organics to the surrounding ecosystem (Atlas and Bartha, 1981) which in turn affect the overall wetland productivity (Mitsch and Gosselink, 1989). The transformations take place in wetlands can be divided into (a) intrasystem cycling through various transformation processes and (b) the exchange of chemicals between a wetland and its surroundings. Although few transformation processes are unique to wetlands, intermittent flooding of these ecosystems causes certain processes to be more dominant in wetlands than in either upland or deep aquatic ecosystems because the soils in wetlands are characterized by waterlogged conditions during part or all of the year, which produce reduced conditions that have clear influence on several biochemical transformations unique to anaerobic conditions (Mitsch and Gosselink, 2000; Craft, 2001; and Bridgham et al., 1998).

4.5.1 Carbon Transformations

The carbon cycle (Figure 4.17) describes the process by which carbon cycles from the atmosphere to plants and animals and back to the atmosphere again. Of the hundreds of

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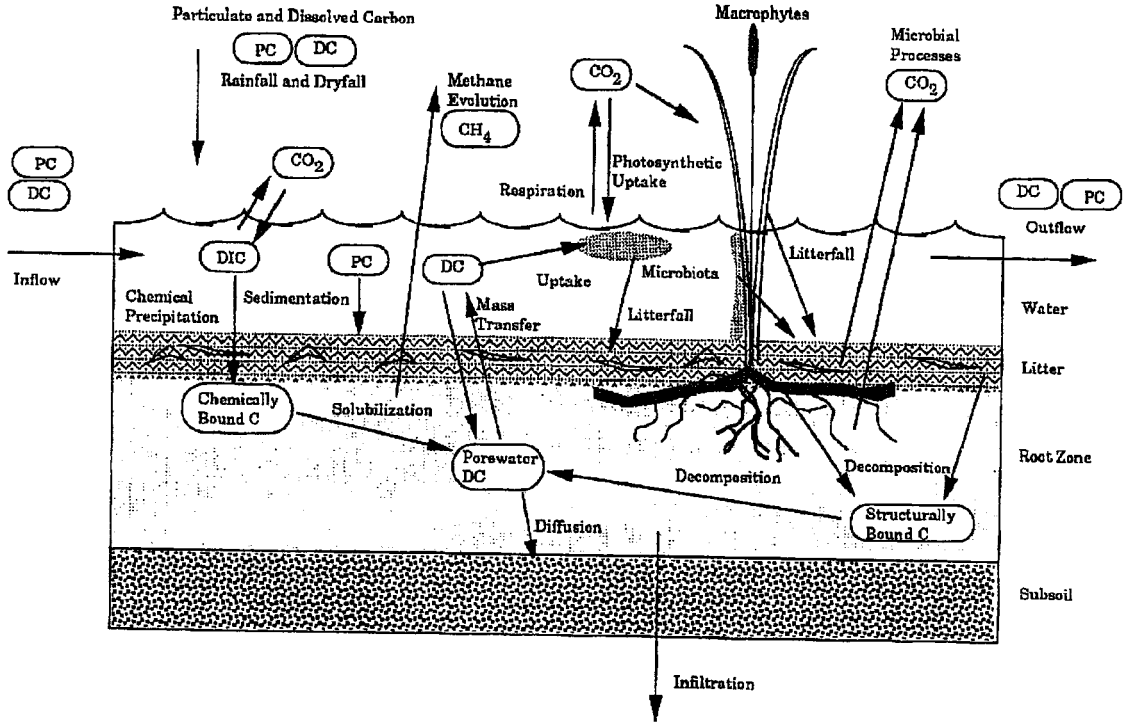


Figure 4.17. Carbon cycle in wetlands.

carbon compounds that may occur in the wetland environment, relatively few are inorganic (carbon dioxide, carbonate, and bicarbonate). Production and consumption of carbon dioxide in the wetland may significantly alter the chemical balance in the water. A variety of cations can precipitate carbonates under certain conditions including Calcite (trigonal-rhomboheral or trigonal-scalenohedral $CaCO_3$ crystals), Aragonite (ortho-rhombic $CaCO_3$ crystals with a needle-like structure), Magnesite ($MgCO_3$), and Dolomite ($CaMg(CO_3)_2$). The most important of which is calcium carbonate ($CaCO_3$). A major process in prephyton-dominated wetlands is chemical precipitation of $CaCO_3$ under conditions of pH created by the algae (Mitsch and Gosselink, 2000).

There is a strong correlation between biomass and carbon content. The carbon content of wetland macrophytes is typically about 41% on a dry weight (dw) basis. The wetland cycle of growth, death, and partial decompositions uses atmospheric carbon and produces gases, dissolved organics, and solids. Decomposition involves the sugars, starches, and low molecular weight celluloses in the dead plant material. Gaseous products include methane and regenerated carbon dioxide. A spectrum of large soluble, organic molecules,

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collectively termed humic substances, is released into the water. The solid residual of plant decomposition is peat or organic sediment, which originated as cellulose and lignin in the plants. These wetland soil organics are broadly classified as fulvic material and humic material. Based upon whether they are acid soluble, base soluble or insoluble (Mitsch and Gosselink, 2000).

Carbon cycles in a wetland system via various physical, chemical and biological processes. Physical processes include: (a) inflow of organic matter from catchment area, (b) aggregation and flocculation of fine particles, (c) settling of particulate matter, and (d) resuspension of particulate matter. Chemical processes include: (a) dissociation and breakdown of compounds and formation of new compounds, (b) adsorption or adhesion of molecules to surface of solids or fluids, (c) desorption, (d) formation of precipitation and insoluble substances as solids, (e) diffusion, and (f) photolysis or degradation of dissolved organic carbon (DOC) by sunlight. Biotic processes and fluxes include: (a) respiration, (b) photosynthesis, (c) consumption (d) death, (e) secretion (organic compounds secreted during photosynthesis such as algal exudates), (f) autolysis or cell breakdown via enzymes, (g) plant transfer (methane in sediments travels through plants and released to atmosphere), (h) excretion by fauna, (i) movement of organisms, and (j) microbial decomposition. Specific decomposition processes include: (a) aerobic decomposition, (b) anaerobic decomposition, (c) methanogenesis (conversion of organic acids to methane and CO_2 by methane-producing bacteria), (d) methane oxidation (methane microbially oxidised and CO_2 produced), and (e) bubbling (escape of methane gas from sediments by bubble formation) (Sommer, 2001; and Mason, 1998).

Biodegradation of organic mater by aerobic respiration is limited by the reduced conditions in wetland soils under aerobic conditions, carbohydrates can be degraded to carbon dioxide:

$$\underset{\text{Carbohydrates}}{C_6H_6O_6} + 6O_2 \longrightarrow 6CO_2 + 6H_2O \qquad (4.1)$$

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Several anaerobic processes in which the organic matter itself is the terminal electron acceptor can degrade organic carbon (Kadlec and Knight, 1996) to form various low-molecular-weight such as lactic acid, alcohols and CO_2 (Braekke and Finer, 1990)

$$\underset{\text{Carbohydrates}}{C_6H_6O_6} \longrightarrow \underset{\text{lactic acid}}{2\ CH_3\ CHOHCOOH} \quad (4.2)$$

$$\underset{\text{Carbohydrates}}{C_6H_{12}O_6} \longrightarrow \underset{\text{ethanol}}{2\ CH_3\ CH_3\ OH + 2\ CO_2} \quad (4.3)$$

Fermentation can be carried out in wetland soils by either facultative or obligate anaerobes and it plays a central role in providing substrates for other anaerobes in sediments in waterlogged soils (Wiebe et al., 1981) by breaking down in which high-molecular-weight carbohydrates low-molecular-weight organic compounds (Valiela, 1984). Methanogenesis occurs when certain bacteria (methanogens) use CO_2 as an electron acceptor for the production of gaseous methane (CH_4), or alternatively, use a low-weight organic compound such as one from a methyl group (Kadlec and Knight, 1996):

$$4\ H_2 + CO_2 \longrightarrow CH_4 + 2\ H_2O \quad (4.4)$$

$$\underset{\text{Acetate}}{CH_3COO^-} + 4\ H_2 \longrightarrow 2\ CH_4 + H_2O + OH^- \quad (4.5)$$

Methanogenic bacteria can use only certain organic substrates for acetate splitting, and in many cases there is evidence that sulfate-reducing bacteria are more effective competitors for the same compounds (Schonheit et al., 1982). Sulfate reducing bacteria also use H_2 as a source of electrons, and they are more efficient in the uptake of H_2 than methanogenesis engaging in CO_2 reduction (Achtnich et al., 1995).

$$\underset{\text{Lactate}}{2\ CH_3CHOHCOO^-} + SO_4^{--} + H^+ \longrightarrow \underset{\text{acetate}}{2\ CH_3COO^-} + 2\ CO_2 + 2\ H_2O + HS^- \quad (4.6)$$

$$\underset{\text{Acetate}}{2\ CH_3COO^-} + SO_4^{--} + 2\ H^+ \longrightarrow 2\ CO_2 + 2\ H_2O + HS^- \quad (4.7)$$

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In most environments, there is little or no overlap between the zone of methanogenesis and the zone of sulfate reduction in sediments. Methanogenesis begins when sulfate is depleted (Kuivila et al., 1989). There are also some other processes happened in the wetland carbon cycling (Kadlec and Knight, 1995) such as nitrate reduction (denitrification) and iron reduction which occur in anaerobic zones as follows:

$$C_6H_{12}O_6 + 4\ NO_3^- \longrightarrow 6\ CO_2 + 6\ H_2O + 2\ N_2 + 4\ e^- \qquad (4.8)$$

$$2\ \underset{\text{Acetate}}{CH_3COO^-} + 8\ Fe^{+++} + 3\ H_2O \longrightarrow 8\ Fe^{+++} + CO_2 + 2\ HCO_3^- + 8\ H^+ \qquad (4.9)$$

4.5.2 Nitrogen Transformations

Nitrogenous compounds are among the principal constituents of concern in wastewater because of (a) their role in eutrophication, (b) their effect on the oxygen content of receiving waters, (c) their toxicity to aquatic invertebrate and vertebrate species, and (d) their beneficial role in the augmentation plant growth which in turn stimulate the production of wildlife (Mitsch and Gosselink, 1993; and Kadlec and Knight, 1996). Although wetlands may remove and store substantial quantities of N, they also potentially release a significant quantity of N to downstream ecosystems. The vast majority of N in wetlands is in organic form, contained either in the vegetation (live plants), plant detritus, macrofauna, microorganisms, soil (soil organic matter or peat) or water (dissolved organic compounds or suspended sediments). Peat accretion potentially affords long-term storage of N in wetlands, although it is a relatively slow process and generally fails to offset high rates of N loading to a wetland. Living components of the wetland also provide storage of N, but subsequently release a large portion of this N during death and decomposition. Plants turn over their stores of N in a matter of months to years, while the turnover time for microorganisms, which may account for up to 5 to 10% of the soil organic matter, is substantially shorter. Turnover rates for soil organic matter (e.g., peat) are commonly measured in terms of decades, centuries or millennia. Nitrogen released from the biota is either recycled within the wetland or exported to downstream waters. Due to the rapid biological uptake of nutrients and extensive

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production of organic matter, wetlands generally export more organic N than inorganic N, even though nutrient inputs are often largely in inorganic form (DeBusk, 1999a). Elemental nitrogen has an atomic weight of 14.01 g/mol with five electrons in the outer electron shell of its atomic structure. Because three electron positions are available in its outer shell, nitrogen can form compounds with varying stability that have oxidation states ranging from +5 to -3. The most important inorganic forms of nitrogen in wetlands are ammonia (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), nitrous oxide (N_2O), and dissolved nitrogen gas (N_2). Nitrogen may also be present in wetlands in many organic forms including urea, amino acids, amines, purines, and pyrimidines (Kadlec and Knight, 1996; and DeBusk, 1999a).

The N cycle in wetlands plays an important role in transport, storage and biological availability of N in the surrounding watershed (DeBusk, 1999a). The N cycle involves in chemical, physical and biological transformations of inorganic compounds to organic compounds and vice versa (Figure 4.18). Some of these processes require energy to proceed, and others release energy, which is used by organisms for growth and survival.

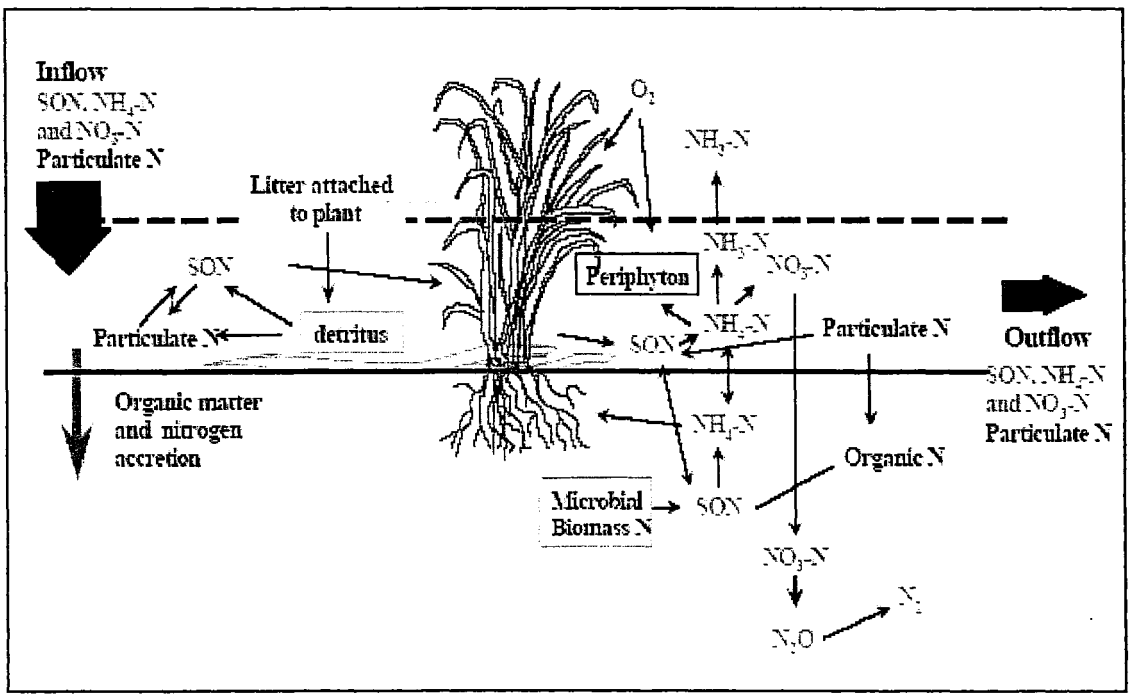


Figure 4.18. An overview of the key physical, chemical and biological processes associated with N cycling in wetlands (Parker, 2003).

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All of these transformations are necessary for wetland ecosystem to function successfully, and most chemical changes are controlled through the production of enzymes and catalysts by the living organisms (Kadlec and Knight, 1996; and Mitsch and Gosselink, 2000). Transformation of nitrogen from one form to another in carried out by five principal mechanisms: (a) ammonification (mineralization), (b) nitrification, (c) denitrification, (d) nitrogen fixation, and (5) nitrogen assimilation.

4.5.2.1 Ammonification (Mineralization)

Ammonification is the biological transformation of organic nitrogen to ammonium and is the first step in mineralization of organic nitrogen (Reddy and Patrick, 1984). This process occurs through microbial breakdown of organic tissues containing amino acids, through excretion of ammonia directly by plants and animals, and by hydrolysis of urea and uric acid (Stevenson and Cole, 1999; and Mitsch and Gooselink, 2000). Ammonium is produced from organic forms through a complex, energy-releasing, multi-step, biochemical process. In some cases, this energy is used by microbes for growth and ammonia is directly incorporated into microbial biomass. A large fraction (up to 100 %) of the organic nitrogen in many wastewaters is readily converted to ammonia (Kadlec and Knight, 1996; and Mitsch and Gooselink, 2000). Ammonium is made up of single, chemically reduced nitrogen atom (oxidation state -3) that has either three or four hydrogen atoms, depending on water temperature and pH:

$$NH_3 \text{ (un-ionized)} + H_2O \longrightarrow NH_4^+ \text{ (ionized)} + OH^- \qquad (4.10)$$

For average environmental conditions of 25°C and a pH of 7, un-ionized ammonia is only 0.6% of the total ammonia percent. At a pH of 9.5 and a temperature of 30°C, the percentage of total ammonia present in the un-ionized form increases to 72%, therefore, the volatility of un-ionized ammonia results in ammonia losses from wetlands (Kadlec and Knight, 1996).

Ammonia nitrogen is important in wetlands because: (a) ammonium is the preferred nutrient form of nitrogen for most wetland plant species and for autotrophic bacteria

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species; (b) ammonium is chemically reduced and, therefore, can be readily oxidized in wetlands resulting in significant oxygen consumption; and (c) un-ionized ammonia is toxic to many forms of aquatic life at low concentrations (Mitsch and Gosselink, 2000). Ammonification (Mineralization) is the key process for producing ammonia in the wetland ecosystems. The typical formulas for the mineralization of simple organic nitrogen such as urea are given as follows:

$$NH_2\,CO\,NH_2 + H_2O \longrightarrow 2NH_3 + CO_2 \qquad (4.11)$$

4.5.2.2 Nitrification

Nitrification is the principal transformation mechanism that reduces the concentration of ammonium nitrogen in many wetland treatment systems by converting ammonium nitrogen to nitrate in a two-step, microbial mediated aerobic process.

$$NH_4^+ + 1.5\,O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + H_2O + 2H^+ \qquad (4.12)$$

$$NO_2^- + 0.5\,O_2 \xrightarrow{\text{Nitrobacter}} NO_3^- \qquad (4.13)$$

Although nitrification will occur if dissolved oxygen above 0.3 mg/L (Reddy and Patrick, 1984), the actual nitrification rate may be controlled by the flux of dissolved oxygen into the system, which typically is mass transfer from atmospheric sources, through water, in wetland treatment system (Kadlec and Knight, 1996). Nitrite is an intermediate oxidation sate of nitrogen (oxidation state +3). Because of this intermediate energetic condition, nitrite is not chemically stable in most wetlands and is generally found at very low concentrations. Detectable levels of nitrite in wetlands frequently indicate incomplete nitrogen assimilation and the presence of anthropogenic nitrogen. Nitrate is the most highly oxidized form of nitrogen (oxidation state +5) found in wetlands. Nitrate can serve as an essential for plant growth, and in excess, nitrate leads to eutrophication of surface water.

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4.5.2.3 Denitrification

The biogeochemical processes that cause nitrogen fixation would ultimately deplete the atmosphere of nitrogen gas if the nitrogen cycle were not closed by the microbial liberation of oxidized nitrogen via the denitrification process (Mitsch and Gosselink, 2000). Denitrification is an energy-requiring reduction process where electrons are added to nitrate or nitrite nitrogen, resulting in the production of nitrogen gas, nitrous oxide (N_2O), or nitric oxide (NO) (Kadlec and Knight, 1996; and Mitsch and Gosselink, 2000). The process is catalyzed exclusive by a diverse group of bacteria that use nitrate or nitrite as terminal electron acceptor in their respiratory processes (Tate, 1995). The most common facultative bacterial groups that accomplish denitrification include *Bacillus, Entrobacter, Micrococcus, Pseudomonas, and Spirillum*.

Theoretically, denitrification does not occur in the presence of dissolved oxygen. However, denitrification has been observed in suspended particles and attached growth treatment systems that have relatively low measured DO concentration. This observation is explained by the presence of microscopic, anoxic zones that are likely to occur in bacterial films and suspended particles (Kadlec and Knight, 1996). Denitrification has been observed in numerous wetland treatment systems which have measurable dissolved oxygen in their surface waters (Phipps and Crumpton, 1994). Oxygen gradients occur between surface water and bottom sediments in wetlands, allowing both aerobic and anaerobic reactions to occur. Nitrate formed by nitrification in wetlands tends to diffuse into anaerobic soil layers where it is effectively denitrified (Reddy and Patrick, 1984) as shown in Equation 4.8.

Gaseous nitrogen may exist as dinitrogen (N_2), nitrous oxide (N_2O), and nitric oxide (NO_2 and N_2O_4). Nitrous oxide is an intermediate product of microbial denitrification. Dinitrogen gas and nitrous oxide are nearly inert for all purpose concerning eutrophication (expect nitrogen fixation) and health of wetland organisms. Dinitrogen gas and nitrous oxide occur in dissolved forms in surface waters in proportion to their partial pressure in the atmosphere. However, dissolved nitrogen gas has a very low biological

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activity compared to its abundance, and concentrations typically vary only in response to temperature changes (Kadlec and Knight, 1996).

4.5.2.4 Nitrogen Fixation

Biological nitrogen fixation is the process by which nitrogen gas in the atmosphere diffuses into solution and is reduced to ammonium nitrogen through the activity of certain organisms in the presence of the enzyme nitrogenase. It may be the source of significant nitrogen for some wetlands (Kadlec and Knight, 1996, Mitsch and Gosselink, 2000). Nitrogen fixation is favored by low oxygen tensions because nitrogenase activity is inhibited by high dissolved oxygen concentration in water (Mitsch and Gooselink, 2000). In wetlands, nitrogen fixation can occur in overlying waters, in aerobic soil layer, in the anaerobic soil layer, in the oxidized rhizosphere of the plants, and on the leaf and stem surface of the plants found under water (Reddy and Graetz, 1988).

All photosynthetic bacteria are apparently capable of nitrogen fixation, as are some aerobic heterotrophs such as *Azotobacter*, some anaerobic bacteria such as *Clostridium*, and many facultative bacteria under anoxic conditions. Algal nitrogen fixers include filamentous, blue-green species in the genera *Anabaena*, *Gloeotrichia*, and *Nostoc*. Also, the aquatic ferns, *Azolla*, and few transitional, wetland vascular plant species in the genera of *Alnus* and *Myrica* have been observed to fix atmospheric nitrogen (Waughman and Bellamy, 1980). Under anaerobic conditions, microbial assemblages in the root zone of *Typha* spp. and *Glyceria borealis* were shown to fix considerable quantities of atmospheric nitrogen (Bristow, 1974).

4.5.2.5 Nitrogen Assimilation

Nitrogen assimilation refers to a variety of biological processes that convert inorganic nitrogen forms into organic compounds that serve as building blocks for cells and tissues. The two forms of nitrogen generally used for assimilation are ammonium and nitrate nitrogen. Because ammonium nitrogen is more reduced energetically than nitrate, it is a preferable source of nitrogen for assimilation. Although ammonia is the preferred

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nitrogen source, nitrate also can be used by some plants species. Nitrate uptake by wetland plants for plant growth is less favored than ammonium uptake under most conditions (Kadlec and Knight, 1996).

4.5.2.6 Physical Processes

A number of processes transport or translocate nitrogen compounds from one point to another in wetlands without resulting in a molecular transformation. These include: (a) particulate settling and resuspension, (b) diffusion of dissolved forms, (c) plant uptake and translocation, (d) litterfall, (e) ammonia volatilization, (f) sorption of soluble nitrogen on substrates, (g) seed release, and (h) organism migrations. (Kadlec and Knight, 1996; and Debusk, 1999a). Dissolved forms of N can be transferred from surface water to soil solution (porewater) and vice versa through the process of diffusion; the driving force behind diffusion is the concentration gradient. A dissolved compound in the soil or water will diffuse from a region of high concentration to regions of lower concentration. Inorganic forms of N (NH_4^+ and NO_3^-) are taken up by plants rooted in the soil or by floating plants and algae. Dead plant tissue (leaves and stems) falling from the live plants are collected at the soil surface to form a litter layer, also known as detritus. Particulate matter (inorganic and/or organic sediment) entrained in the water column settles out, due to the reduced water velocity, shallow water depth and filtering action of emergent vegetation, and collects on the soil surface. The organic matter collected on soil surface is broken down by a variety of microorganisms that utilize organic carbon as a source of energy. Organic N compounds, such as proteins and amino acids, are broken down to smaller organic molecules, both particulate and dissolved, and ultimately to ammonium (NH_4^+), which may be utilized as a nutrient by the microorganisms. Under high-pH conditions in the wetland floodwater, concentration of the un-ionized form of ammonia (NH_3) becomes appreciable compared to NH_4^+, and may be released to the atmosphere as ammonia gas which can lead to substantial N losses for poorly buffered waters with high photosynthetic activity. Retention of N in the soil occurs through the process of cation exchange, whereby the ammonium ion (NH_4^+) is weakly bound to soil particles by electrostatic attraction. Most soil profiles are negatively charged and, therefore, retention of nitrate (NO_3^-) is rare. Partially decomposed plant detritus and other organic matter is

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gradually buried and incorporated into the soil profile. The buried materials represent the portion of organic matter that is more resistant to decomposition. As this material ages, it becomes highly decomposed and compressed forming peat (peat accretion).

4.5.3 Phosphorus Transformations

Phosphorus (P) is an essential nutrient for plants and animals. Elemental phosphorus has an atomic weight of 30.97 g/mol with five electrons in the outer electron shell of its atomic structure. Phosphorus can enter a wetland in several forms. Phosphorus carried in surface water may be in dissolved or particulate (suspended sediment) form, and may exist as organic or inorganic compounds. Organic P compounds are in either dissolved or particulate form, while inorganic P occurs primarily in solution as orthophosphate (HPO_4^{2-}) or as phosphate-containing minerals suspended in the water column (DeBusk, 1999b). The P cycle in wetlands plays an important role in transport, storage and biological availability of P in the surrounding watershed (DeBusk, 1999b).

The overall phosphorus mineral chemistry is very complex and it involves processes such as diffusion, plant uptake, litter fall, sedimentation, decomposition, sorption and peat accretion. (Reddy and D'Angelo, 1994). For the purpose of understanding phosphorus cycling, wetlands may be visualized as consisting of several compartments: water, plants, micro-biota, litter, and soil (Figure 4.19). Naturally occurring inputs of phosphorus are from surface inflows and atmospheric deposition, which consists of both wet- and dry-fall. Outputs may be in surface outflows and in infiltration to groundwater (Kadlec and Knight, 1996). Although wetlands may remove and store substantial quantities of P, they also potentially release a significant amount of P to downstream ecosystems. Most of the P in wetlands is in organic form, contained either in the vegetation (live plants), plant detritus, macrofauna, microorganisms, soil (soil organic matter or peat) or water (dissolved organic compounds or suspended sediments).

Partially decomposed plant detritus and other organic matter is gradually buried and incorporated into the soil profile. The buried material represents the portion of organic matter that is more resistant to decomposition. As this material age, it becomes highly

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decomposed and compressed, forming peat (peat accretion). Peat accretion potentially affords long-term storage of P in wetlands, although it is a relatively slow process and generally fails to offset high rates of P loading to a wetland.

Living components of the wetland also provide storage of P. Inorganic P, primarily orthophosphate (HPO_4^{2-} and $H_2PO_4^-$) is taken up by plants rooted in the soil or floating in the water (including algae). Phosphorus is also incorporated in the tissues of all living organisms and is therefore, present in all wetland biota. Subsequently living components release a large portion of this P during death and decomposition. Organic matter, including plant detritus, organic sediments and peat is broken down by a variety of microorganisms that utilize organic carbon as a source of energy. Organic P compounds are broken down to smaller organic molecules, both particulate and dissolved, and ultimately to orthophosphate, which may be utilized as a nutrient by the microorganisms or diffuse back into the soil or water.

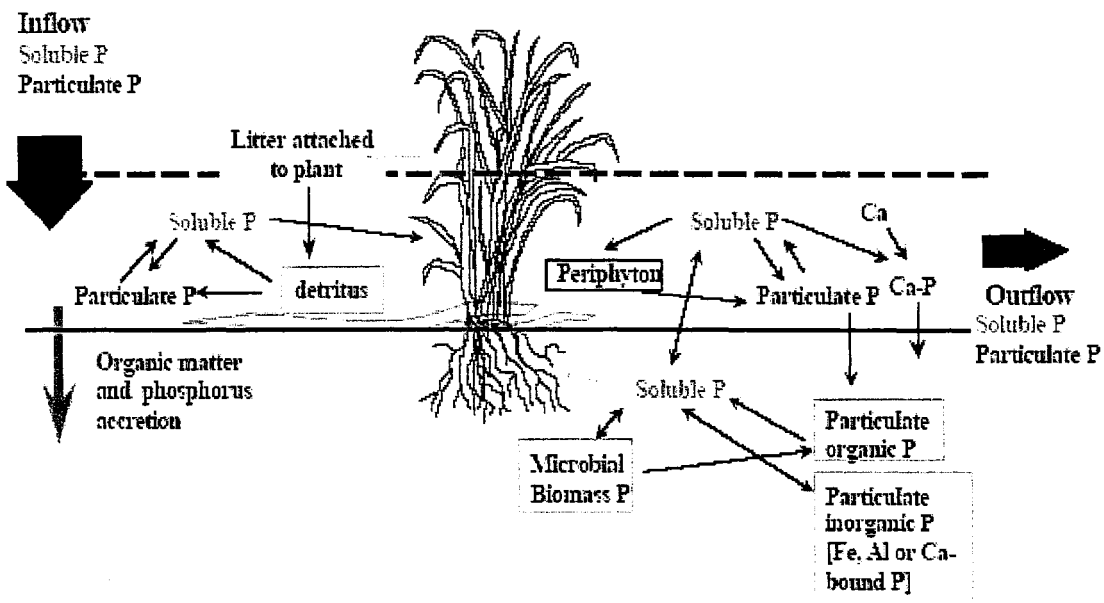


Figure 4.19. An overview of the key physical, chemical and biological processes associated with P cycling in wetlands (Parker, 2003).

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Plants turn over their stores of P in a matter of months to years, while the turnover time for microorganisms, which may account for up to 5 to 10% of the soil organic matter, is substantially shorter. Phosphorus released from the biota is either recycled within the wetland or exported to downstream waters. Due to the rapid biological uptake of nutrients and extensive production of organic matter, wetlands generally export more organic P than inorganic P, even though nutrient inputs are often largely in inorganic form (DeBusk, 1999b).

The phosphorus cycle involves the inter exchange of mineral and organic nutrient forms with the water-soluble phosphate and is being controlled by biological mineralization processes and the dissolution rates from soil mineral fractions. Unique properties of the phosphorus cycle include the observation that phosphorus does not undergo any valence changes in the cycle and there is no gaseous component to the cycle (Tate, 1995).

A variety of cations can precipitate phosphate under certain conditions. Some important mineral precipitations in the wetland environment are (Reddy and D'Angelo, 1994): Apatite (Ca_5 (Cl, F) $(PO_4)_3$), Hydroxylapatite (Ca_5 (OH) $(PO_4)_3$), Variscite (Al (PO_4) $2H_2O$), Strengite (Fe (PO_4) $2H_2O$), Vivianite (Fe_3 $(PO_4)_2$ $8H_2O$) and Wavellite (Al_3 $(OH)_3$ $(PO_4)_2$ $5H_2O$). In acids soils, phosphorus may be fixed by aluminum and iron, if available whereas, in alkaline soils, phosphorus may be fixed by calcium and magnesium. Reducing conditions lead to solubilization of iron minerals and release of phosphorus co-precipitates. If free sulfide is resent due to sulfate-reducing conditions, iron sulfide can form and preclude iron mineralization of phosphorus.

A gaseous form of phosphorus, phosphine (PH_3) has been identified as a potential compound of significance in wetland environments (Gassman and Glindermann, 1993). Phosphine is soluble in water, but has a high vapor pressure (Kadlec and Knight, 1996).

In solution, the principal inorganic species are related by the pH-dependent dissociation series (Freeze and Cherry, 1979):

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$$H_3PO_4 \Leftrightarrow H_2PO_4^- + H^+ \quad (4.14)$$

$$H_2PO_4^- \Leftrightarrow HPO_4^{2-} + H^+ \quad (4.15)$$

$$HPO_4^{2-} \Leftrightarrow PO_4^{3-} + H^+ \quad (4.16)$$

Dissolved forms of P can be transferred from surface water to soil solution (pore water) and vice versa, through the process of diffusion. Dead plant tissue (e.g., leaves and stems) falls from the live plants and collects at the soil surface to form a litter layer. Particulate matter (inorganic and/or organic sediment) entrained in the water column settles out, due to the reduced water velocity, shallow water depth and filtering action of emergent vegetation, and collects on the soil surface. Orthophosphate ion can be adsorbed by clays and iron or aluminum oxides (chemisorption) in the soil. Precipitation of PO_4^{3-} with either iron and aluminum oxides or dissolved calcium forms solid compounds (Fe- and Al-phosphates or Ca-phosphates) in the soil or water column. These phosphate minerals are potentially very stable in the soil, affording long-term storage of phosphorus.

4.5.4 Heavy Metal Transformations

The concentrations of heavy metal ions removed from solution in wetlands is determined by interacting processes of sedimentation and flocculation, absorption, co-precipitation, precipitation, complexation, cation and anion exchange, oxidation/reduction, microbial activities and plant uptake.

4.5.4.1 Sedimentation and Flocculation

The process of sedimentation is closely related to the hydrological flow patterns of the wetlands. In calm waters, particles which are denser than water will settle out (Matagi, et al., 1998). For particles that are light or less dense than water, sedimentation become possible only after floc formation. Particles of clay and organic minerals which have surface electronic charge aggregate to form flocs, which generally settle more rapidly in a wetland than do individual particles (Hakanson and Jansson, 1983). Sedimentation will normally take place after other mechanisms (complexation, precipitation and co-

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precipitation) aggregate heavy metals into particles large enough to sink (Matagi, et al., 1998).

4.5.4.2 Adsorption

In sediments heavy metals are adsorbed to clay and organic matter by electrostatic attraction (Patrick et al., 1990). Once adsorbed on to humic or clay colloids heavy metals will remain as metal atoms, unlike organic pollutants which will ultimately decompose. Their speciation may change with time as the organic molecules binding them decompose or as sediment conditions change. The extent to which metals ions are adsorbed by cation exchange or non-specific adsorption depends on properties of the metals concerned (valence, radius, degree of hydration and co-ordination with oxygen). Other factors are physico-chemical environment (pH and redox status), the nature of the adsorbent medium (permanent and pH-dependent charge complex-forming ligands), and the concentrations and properties of other metals and soluble ligands present (Alloway, 1992). For chemicals such as heavy metals, more than 50% can easily be adsorbed onto particulate matter in the wetland and thus be removed from the water component by sedimentation (Muller, 1988).

4.5.4.3 Co-precipitation

Co-precipitation of heavy metals with secondary minerals, including the hydrous oxides of Fe, Al and Mn is an important adsorptive mechanism in wetland sediments. Cu, Mn, Mo, Ni, V and Zn are co-precipitated in Fe oxides and Co, Fe, Ni, Pb and Zn are co-precipitated in Mn oxides. Precipitation of Fe III is initially in the form of gelatinous stable forms, such as geothite. Ferrihydrite is more likely to be subsequently dissolved again through the decrease in Eh or pH than geothite. Ferrohydrite coprecipitates other ions and as a result of its large surface area acts as a scavenger sorbing both cations, such as heavy metals and anions, especially HPO_4^{2+} or $H_2\ PO^{4+}$ and AsO_4^{3-}. Pyrite (FeS_2) forms in reducing conditions when sulfate become reduced to sulfide, producing H_2S which then reacts with Fe^{2+} to form FeS and FeS_2. The heavy metals normally found co-precipitated with secondary minerals in soil sediments are (Siposito, 1983): Fe oxides (V,

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Mn, Ni, Cu, Zn, Mo), Mn Oxides (Fe, Co, Ni, Zn, Pb), Ca carbonates (V, Mo, Fe, Ni, Co, Cd), and clay minerals (V, Ni, Co, Cr, Zn, Gu, Pb, T, Mn, Fe)

4.5.4.4 Precipitation

Precipitation is one of the major mechanisms by which metals are removed from water in wetlands and deposited in the sediments. The formation of insoluble heavy metal precipitates is one of many aquatic ecosystems. Precipitation depends on the solubility product (K_{sp}) of the metal species involved, pH of the wetland and concentration of metal ions and relevant anions. Precipitation from a saturated solution of a sparingly soluble heavy metal salt may be represented by the dynamic equilibrium:

$$MX_{2(s)} \leftrightarrow M^{2+}_{(aq)} + X^{-}_{(aq)} \tag{4.17}$$

At equilibrium, the rate of removal of metal ions in the form of precipitate equals the rate of their dissolution from the precipitate. The constant governing this equilibrium is described as follow:

$$K_{sp} = [M^{2+}][X^{-}]^2 \tag{4.18}$$

When the values of the concentration of cation and anion are such that their product exceeds K_{sp}, precipitate occurs (Matagi et al., 1998). Under reducing conditions, carbonates, hydroxides and sulfides of metals are precipitated and their precipitation is also pH dependent. More specific for sulfides is that they are insoluble at neutral pH and therefore accumulate in fresh water wetland sediments. For carbonates, the solubility is also influenced by partial pressure of CO_2. The solubility of $PbCO_3$ can be increased several fold in the present of CO_2 (Matagi et al., 1998).

4.5.4.5 Cation and Anion Exchange

Ion exchange can occur between the counter ions balancing the surface charge on the sediment colloids and the ions in the wetland water. Negative charges on the sediment

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colloids are responsible for cation exchange, in which exchange of a hydrogen ion for the metal occurs. The extent to which the sediment constituents can act as cation exchangers is expressed as the cation exchange capacity (CEC). Sediment organic matter has a higher capacity than sediment colloids and plays a very important part in adsorption reactions in most soils even though it is normally present in much smaller amount (1- 10 %) and clays (80 %).

Matagi et al. (1998) stated that the negative charges on the surface of sediment colloids are of two types: (a) permanent charges resulting from the isomorphous substitution of a clay mineral constituent by an ion with a lower valence, and (b) the pH-dependent charges on the oxides of Fe, Al, Mn, Si and organic colloids which are positive at pH below their iso-electric points and negative above their iso-electric points. Hydrous Fe and Al oxides have relatively high iso-electric points (>pH 8) and so tent to be positively charged under most conditions whereas clay and organic colloids are predominantly negatively charged under alkaline conditions.

The commonly quoted relative order of replace ability on the cation exchange complex of metals cations is $Li^{+}=Na^{+}>K^{+}=NH_4^{+}>Rb^{+}>Cs^{+}>Mg_2^{+}>Ca_2^{+}>Sr_2^{+}=Ba_2>La_3^{+}=Al_3^{+}>Tn_4^{+}$. Anion exchange occurs when anions are attracted to positive charges on sediment colloids. Hydrous oxides of Fe and Al are usually positively charged and so tend to be the main sites for anion exchange in sediments. Most sediments have smaller capacities for anion exchange than cation exchange. Some anions such as NO_3^{-} and Cl^{-} are not adsorbed to any marked extent but others such as HPO_4^{2-} and $H_2PO_4^{-}$ are strongly adsorbed. Some organic pesticides, such as phenoxyalkanoic acid herbicides, exist as ions at normal sediment pHs and are adsorbed to a limited extent by hydrous oxides and by H_2 bonding to humic polymers (Matagi et al., 1998).

4.5.4.6 Complexation

Complexation is a reaction whereby heavy metal ions replace one or more coordinated water molecules in the co-ordination sphere with other nucleophilic groups or ligands. Complexation reactions are important regulators of heavy metal ion speciation in water

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and it affects metal reactivity and toxicity (Brezonik, 1994). In wetlands, the ligands are mainly multidentate organic molecules that include humic, tannic and fulvic acids (HA, TA, & FA). Heterogeneous complexants exhibit at least three major distinguishing features (Matagi, et al., 1998): (a) their polyfunctionality, i.e. many complexing sites of different nature present on the same physical structure, (b) their polyelectrolytic character, i.e. possible existence of high electric charge densities due to the presence of large numbers of dissociable functional groups per physical entity, (d) their conformational factors (e.g. reaction on surfaces, formation of aggregates etc.). The ability of dissolved organic matter to form complexes with ions in wetlands is of interest because of the associated biological implications, such as bioavailability and toxicity of heavy metals to living organisms and because of its relevance to efforts of understanding geochemical cycles of metals in the environment.

4.5.4.7 Oxidation/Reduction

The redox state of a heavy metal in solution is an important speciation parameter because it can drastically affect its toxicity, adsorptive behavior and metal transport (Matagi, 1998). The redox state of the heavy metals depends on whether there are anoxic or oxic conditions in the wetlands. Micro-organisms, such as *Thiobacillus* spp catalyse the oxidation of sulfides. In the case of pollution by tailings from metalliferous mining, particles of ore minerals in the soils, such as, PbS, ZnS and $CuFeS_2$ become oxidized, releasing metal cations Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} into the sediment when they are adsorbed. Some organic pollutant molecules on the soil surface will undergo photolytic decomposition due to exposure to UV wavelengths in daylight and hence release the metal originally adsorbed on them. Oxidation of organic pollutants occurs by the action of oxygenase enzymes secreted by microorganisms (Moffet and Zika 1987). Charges in redox potential Eh under reducing conditions allows the metals to precipitate as metal sulfides.

4.5.4.8 Microbial Activities

Micro-organisms remove heavy metals directly from wetlands by two major mechanisms; the first is a metabolism dependent uptake of metals into their cells at low concentrations

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(some toxic metal ions are micronutrients for the micro-organism); the second is bio-sorption which is a non-active adsorption process binding metal ions to the extracellular charged materials or the cell walls.

4.5.4.9 Uptake by Plants

Clemens et al. (2002) summarized the molecular mechanisms proposed to be involved in metal accumulation by plants (Figure 4.20) as follows: (a) metal ions are mobilized by secretion of chelators and by acidification of the rhizosphere, (b) uptake of hydrated metal ions or metal-chelate complexes is mediated by various uptake systems residing in the plasma membrane, metals are chelated and excess metal is sequestered by transport into the vacuole, (c) from the roots, transition metals are transported to the shoot via the xylem, inside the xylem, metals are present as hydrated ions or as metal-chelate complexes, (d) after reaching the apoplast of the leaf, metals are differentially captured by different leaf cell types, move cell-to-cell through plasmodesmata with final storage to occur in trichomes, and (e) uptake into the leaf cells is catalyzed by various transporters and distribution of essential transition metals in the cell is mediated by specific metallochaperones and transporters localized in endomembranes.

4.6 Treatment Wetland Design

Treatment wetland designs attempt to mimic natural wetlands in overall structure with the encouragement of those wetland processes that are considered to contribute to improvement of water quality (Davis, 1995). Mitsch (1992) suggests the following guidelines for creating successful constructed wetlands: (a) simple design, (b) minimal maintenance, (c) use of natural energies such as gravity flow, (d) designing for extreme weather, floods and droughts, (e) integration with the natural topography of the site, (f) avoiding rectangular basins, rigid structures and channels, and (g) giving enough time for the system to establish. The design process of a constructed wetland has physical, chemical and biological features that should be taken into consideration. In order to design a functioning constructed wetland several factors should be taken into account: (a) site conditions, (b) wetland sizing, (c) wetland structure, (d) water hydrology, (e) wetland soil, (f) wetland vegetation, and (g) operation and maintenances plans.

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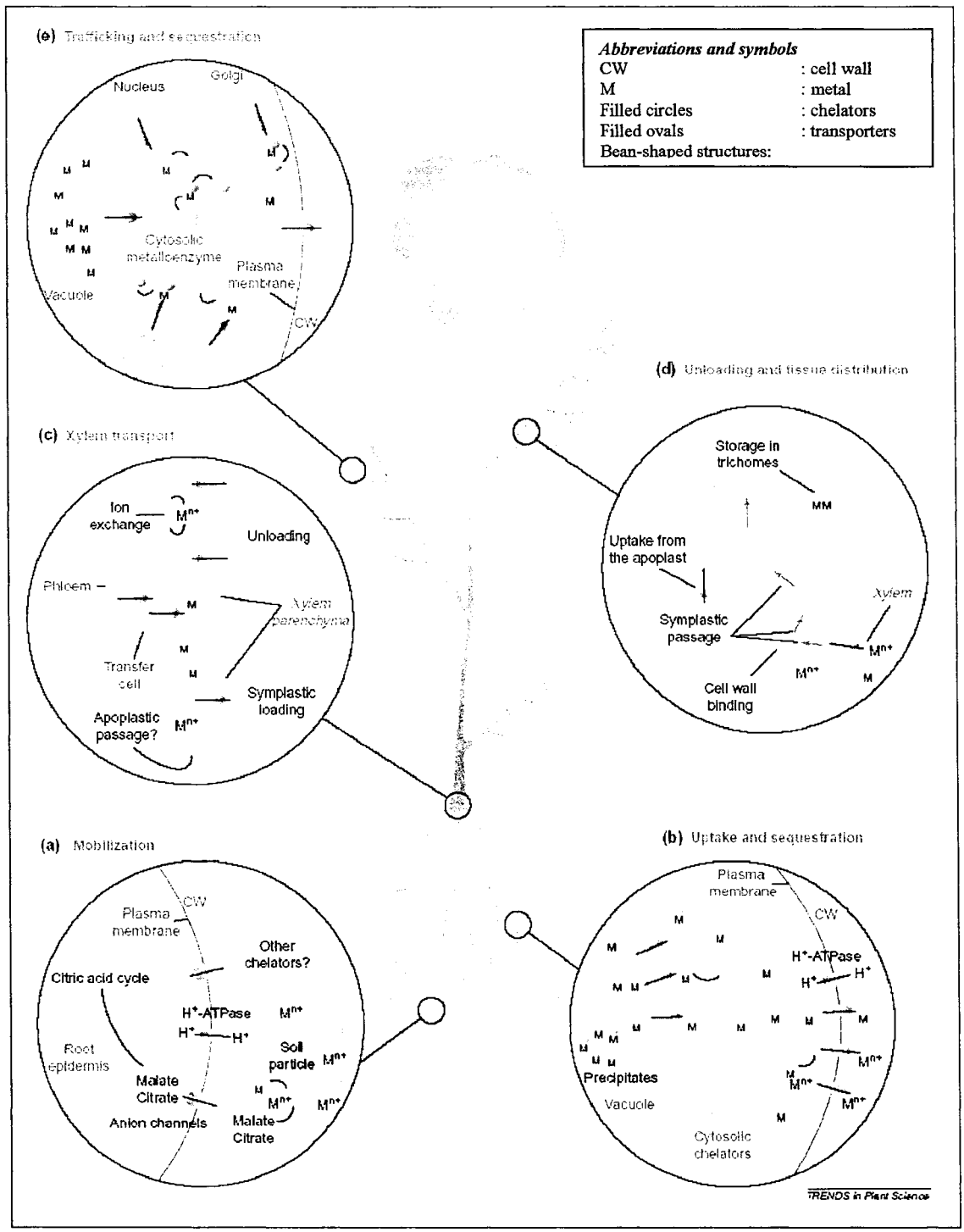


Figure 4.20. Mechanism of metal accumulation by plants (Clemens, et al., 2002).

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4.6.1 Site Conditions

Davis (1995) stated that a site that is well suited for a constructed wetland is one that: (a) is conveniently located to the source of the wastewater, (b) provides adequate space, (c) is gently sloping, so that water can flow through the system by gravity, (d) contains soils that can be sufficiently compacted to minimize seepage to groundwater, (e) is above the water table, (f) is not in a floodplain, (g) does not contain threatened or endangered species, and (h) does not contain archaeological or historic resources. The physical, chemical and biological aspects of a wetland treatment system that should be assessed during development of a wetland treatment system include: climate, site geography and topography, groundwater, and other factors.

4.6.1.1 Climate

Although climate is very difficult factor to control when selecting a specific site for a constructed wetland project, it is an important factor to consider during project planning and alternative selection because it affects the type and size of wetland that will be used. Latitude is the most critical determinant of climate because it determines seasonal temperature ranges (Kadlec and Knight, 1995). According to Ogden (1999), it is important to obtain the following information: (a) monthly average temperatures, (b) precipitation (including 10-year 24-hour storm events), (c) evapotranspiration, (d) soil temperature at 75 cm depth, and (e) solar radiation. Other important climate information that should be taken into account are: atmospheric pressure, vapor pressure, relative humidity, and wind speed. These parameters are used to calculating the runoff characteristics of the site.

4.6.1.2 Geography and Topography

Preliminary site screening of constructed wetlands should look for a relatively leveled ground that is not in a conflicting land use. A candidate site should not include many wet or dry drainage channels because stormwater flows would then need to be redirected. Because piping and pumping can be a significant part or project cost, the site should be

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close to the wastewater source (Kadlec and Knight, 1995). Gravity flow can save considerable capital and operational and maintenance costs. Site appropriateness is improved by the presence of a natural, downhill grade between the source of the wastewater and the constructed wetland (Davis, 1995).

4.6.1.3 Soil

Soils are classified based on a complex array of physical and chemical characteristics. Soil information that might be important during project planning includes the presence of hydric soils; soil texture and composition as a suitable medium for berm construction or for impending leakage to the ground water; depth to seasonal high groundwater; and depth to confining layers of clays or spodic horizons (Kadlec and Knight, 1996). Soil boring information to a depth of 1.5 m at three different sites should be obtained. Soils should be classified as to type and permeability (Ogden, 1999).

4.6.1.4 Groundwater

Infiltration of wastewater to the ground water is important because it affects the wetland water balance and could pose problems under some conditions. Water quality information should be obtained about the underlying aquifer (Ogden, 1999). Groundwater infiltration can be eliminated as a project concern for constructed wetlands by using clay or plastic impervious liner.

4.6.1.5 Others

Other important factors that contribute to the selection of constructed wetland site include: (a) land availability, the site selected should be large enough to accommodate the present requirements and any future expansion, (b) permits and regulations, the appropriate agency(ies) should be contacted to determine the regulatory requirements for a proposed constructed wetland and its discharge, and (c) environmental resources should be taken into account to avoid damaging important resources on the site (Davis, 1995, Kadlec and Knight, 1996; and Tousignant et al., 1999).

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4.6.2 Wetland Sizing

There are many procedures that have been used for estimating land area requirements during treatment wetland design. The easiest are single-number rules (or rule-of-thumb approaches), which have a great appeal because they are quickly applied and easily understood. The other design approach is mass balance design model, which deal with the internal mass balances for water and the pollutant of interest. This approach acknowledges mass conservation for water and the pollutant.

4.6.2.1 Rule of Thumb Approach

The rule of thump approach include: calculating reduction in the concentrations of pollutants, retention time and hydraulic loading rate.

4.6.2.1.1 Percentage Removal and Reduction: It is very easy to compare the amounts of pollutant in the inlet and outlet streams of a wetland and to compute the percentage difference. Removal percentage is for a concentration reduction and is useful only when compared with operating conditions and ecosystem characteristics (Kadlec and Knight, 1996). However, in the case of stormwater wetlands, it may reflect a load reduction instead. These two measures are connected by the alteration in water flow that may occur due to rain, evapotranspiration and leakage:

$$\frac{Q_o C_o}{Q_i C_i} = \frac{Q_o}{Q_i} \cdot \frac{C_o}{C_i} \tag{4.19}$$

$$\left(1 - \frac{LP}{100}\right) = \left(1 - \frac{WP}{100}\right) \cdot \left(1 - \frac{CP}{100}\right) \tag{4.20}$$

Where:

C = pollutant concentration (mg/L)

Q = water flow (m^3/d)

CP = concentration reduction (%)

LP = pollutant load reduction (%)

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WP = flow reduction (%)

If the input to the wetland fluctuates or is subjected to pulses of pollutants, then the interpretation of removal efficiency becomes very difficult. Most treatment wetlands are subject to such events.

4.6.2.1.2 Detention Time: The water detention time can be calculated as follow:

$$\tau = \frac{\varepsilon A h}{Q} \tag{4.21}$$

Where:

A = wetland area (m^2)

h = water depth (m)

ε = water column void fraction

τ = nominal detention time (d)

The activity of the wetland in pollutant removal is associated with the emersed sediments and biota. These reactive surfaces dominate the removal processes for all biologically active substances. As a consequence, the rate of removal is strongly dependent on vegetation density. A bare soil, shallow pond has the minimum efficiency whereas a densely vegetated, fully littered wetland of the same depth has a higher efficiency. If detention time is increased by deeper submergence of these active components, at constant wetland area, further removal activity is typically not proportional to increased depth (Kadlec and Knight, 1996). The overall efficacy of a depth increase depends on three factors: (a) the distribution of the bottom elevations in the wetland, (b) the distribution of biotic material vertically above the wetland bottom and (c) the reactive potential of the materials themselves. In general terms, all emersed surfaces are capable of supporting biological activity, although the time scales of the uptake may differ, and the degree of support may depend on the degree of decomposition of the biomaterial.

4.6.2.1.3 Hydraulic Loading Rate: This single parameter is the most relevant for the sizing of wetland treatment systems. There is another matter of practicality: wetland

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wetted areas are almost always known more accurately than wetland water volumes. Therefore, it is much easier to achieve a specific design wetted area than a design water volume. The relation between detention time and hydraulic loading rate is as follow:

$$q = \frac{\varepsilon h}{\tau} \tag{4.22}$$

Where:

q = hydraulic loading rate (m/d)

ε = volume fraction water in wetland (-)

4.6.2.2 Mass Balance Design Model

This model deals with the internal mass balances for water and pollutants of attention within the wetland and allows mass conservation for water and pollutant. The pollutant interacts with the soil and biota of the ecosystem via transfers to and from those solid compartments. The result is an altered exit concentration, which is to be predicted by the design model. Pollutant concentration profiles in treatment wetlands are typically decreasing with distance and often display exponentially decreasing character. That feature is characteristics of systems described by first-order removal rate equations coupled with plug flow through the system. This may be partially due to the fact that the active ecosystem arranges itself along the gradient from inlet to outlet in treatment wetlands in response to the gradients in waterborne substances, especially nutrients. This model lumps together all the transfers of a substance within the active wetland ecosystem (Kadlec and Knight, 1996).

The wetland ecosystem at any location may be partitioned into pieces (referred to as compartments): above-ground plant parts, roots, litter, biofilms, soils, and water. The rates of movement of a chemical within them form the basis for rational design equations. If all rates are known, it is possible to calculate the interaction between the wetland ecosystem and the chemicals and water passing though it. This wetland design model in its generalized form is as follow (Kadlec and Knight, 1996):

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$$A = -\frac{Q}{k}\ln\left(\frac{C_2 - C^*}{C_1 - C^*}\right) \quad (4.23)$$

Where:

k = rate constant (m/y)

C_1 = inflow concentration (mg/L)

C_2 = outflow concentration (mg/L)

C^* = irreducible background concentration (mg/L)

4.6.3 Wetland Structure

This includes the construction of the wetland cells, liners and flow control system.

4.6.3.1 Cells

Wetlands can be constructed by digging basins, by building up earth embankments (dikes), or by a combination of the two. Dikes should be constructed of soils with adequate fine-grained material that will compact into a relatively stable and impervious embankment. The dikes should be high enough to contain the expected volume plus plenty freeboard to accommodate irregular high flows as well as the increase of litter and sediment over time. Dikes should be sloped no steeper than 2H : 1V and rapped or confined by erosion control fabric on the slopes. If multiple cells are used, divider dikes can be used to separate cells and to produce the desired length-to-width ratios. On steep sites, they can be used to terrace cells (Davis, 1995, Kadlec and Knight, 1996; and Tousignant et al., 1999).

4.6.3.2 Liners

Constructed wetlands should be sealed to prevent possible contamination of groundwater and to avoid groundwater from infiltrating into the wetland. Where on-site soils or clay provide an adequate seal, compaction of these materials may be sufficient to line the wetland. Sites underlain by fractured bedrock, or gravelly or sandy soils have to be sealed

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by some other method. On-site soils can be used if they can be compacted to permeability of $<10^{-6}$ cm/sec. Soils that contain more than 15% clay are suitable (Tousigant et al., 1999). Synthetic liners include asphalt, synthetic butyl rubber, and plastic membranes (0.5 - 10.0 mil high density polyethylene). The liner should be strong, thick, and smooth to prevent root attachment or penetration. If the site soils contain angular stones, sand bedding or geotextile cushions should be placed under the liner to prevent punctures. The liner should be covered with 3 - 4 inches of soil to prevent the roots of the vegetation from penetrating the liner (Davis, 1995).

4.6.3.3 Flow Control Structures

Flow control structures should be simple and easy to adjust. They should allow flexibility so that processes can be optimized initially and adjusted later in response to system changes. 'Multiple inlets must be fully and independently adjustable to ensure an even distribution of flow. Structures should be sized to handle maximum design flows and should be located for easy access and to minimize short circuiting. Boardwalks and piers make access easy and reduce disturbance of the wetland. PVC pipe is recommended. If the wetland will be accessible to the public, or located in an isolated area where it will be vulnerable to vandalism, inlet and outlet structures should be enclosed in lockable concrete structures or manholes to avoid damage or tampering with water level settings. Structures must be protected against damage by animals by installing covers or wire mesh over openings, and enclosing controls, gauges and monitoring devices in pipes or boxes (Davis, 1995).

4.6.4 Wetland Hydrology

Hydrologic conditions affect the soils and nutrients, which in turn influence the character of the biota. The flows and storage volume determine the length of time that water spends in the wetland and, therefore, the chance for interactions between waterborne substances and the wetland ecosystem (Kadlec and Knight, 1996). Hydrologic and hydrogeologic considerations include the characterization of surface water and groundwater. Water may enter into a constructed wetland from various pathways such as precipitation, surface

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flow, groundwater flow and wastewater influent. Improper consideration of these factors may impact the operation and treatment ability of the constructed wetland. If a water balance is not properly computed, the system may dry out during hot dry periods, or may be flooded during wet periods (Tousigant et al., 1999). Hydrologic factors in wetland design pertain to the volume of water, its reliability and extremes, and its movement through the site. Hydrologic considerations include climate and weather, hydroperiod, hydraulic residence time, hydraulic loading rate, groundwater exchanges (infiltration and exfiltration), losses to the atmosphere (evapotranspiration), and overall water balance (Davis, 1995). Climate and weather were discussed before in the site condition section. Hydroperiod is the seasonal pattern of water level fluctuations and is described by the timing, duration, frequency, and depth of inundation. The hydroperiod of a wetland results from the balance of inflow, outflow, and storage. Hydroperiod determines the availability of water throughout the year, the extreme wet and dry conditions that can be expected, the extent of storage and drainage that may be required, and the criteria to be used in designing the water control facilities. Hydraulic loading rate is used to calculate how much contaminant is being received by the system (Davis, 1995; and Tousigant et al., 1999).

Hydraulic residence time is the time that it takes for the waste water to pass through the system. If short-circuiting develops, effective residence time may differ significantly from the calculated residence time. The hydraulic residence time for a constructed wetland system can be determined by the following equation (Tousigant et al., 1999):

$$T = \frac{LWnd}{Q} \tag{4.24}$$

Where:

T = hydraulic residence time (d)

L = length of the system, parallel to flow direction (m)

W = width of the system (m)

n = porosity of the medium (-)

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d = depth of submergence (m)

4.6.5 Wetland Soils

Soils are the product of several physical, chemical and biological modifications of parent materials including bedrock, sedimentary deposits, and metamorphosed sediments and rocks. Wetland soils are typical of other soils, except for the effect of water which modifies soil characteristics by reducing exposure to the atmosphere with subsequent reduction of aerobic conditions. A basic understanding of the physical and chemical properties of wetland soils is vital in the planning, design and operation of wetland treatment systems because these properties influence wetland plant growth and assimilation of some wastewater constituents (Kadlec and Knight, 1996).

Soil properties that should be considered in selecting soils include cation exchange capacity (CEC), pH, electrical conductivity (EC), texture, and soil organic matter. The pH of the soil affects the availability and retention of heavy metals and nutrients. Soil pH should be between 6.5 and 8.5. The EC of a soil affects the ability of plants and microbes to process the waste material flowing into a constructed wetland. Soils with an EC of less than 4 mmho/cm are best as a growth medium. The surface area of the soil particles and the electrical charge on the surfaces of the soil particles account for much of a soil's activity (Kadlec and Knight, 1996). Most soils carry a net negative charge, thus providing electrostatic bonding sites for positively charged ions (cations), such as Ca^{2+}, Mg^{2+}, Fe^{2+}, $A1^{3+}$ and Mn^{2}. These cations on the soil surface can exchange with other cations in the soil solution, so the term cation exchange. CEC measures a soil's capacity to hold positively charged ions and varies widely among different soils. The CEC of a soil that will be used as a planting medium should be greater than 15 meq/100 g of soil. The redox potential of the soil is an important factor in the removal of nitrogen and phosphorus. A reducing substrate must be provided to promote the removal of nitrate and ammonia. The removal of iron and manganese from mine water also requires a reducing environment (Davis, 1995). The soil should provide enough organic matter to fuel plant growth and microbial activity, particularly during startup. Wetlands are often built with infertile site

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soils, and organic amendments, such as compost, leaf litter, or sewage sludge, must be incorporated into the substrate. Soil texture affects root growth and the retention of pollutants. Sandy, coarse-textured soils have a low potential for pollutant retention but little or no restriction on root growth. These soils hold plants well but are low in nutrients (Kadlec and Knight, 1996).

4.6.6 Wetland Vegetation

The function of plants in constructed wetlands is largely to grow and die. Plant growth provides a vegetative mass that deflects flows and provides attachment sites for microbial development whereas death creates litter and releases organic carbon to fuel microbial metabolism. In addition, plants stabilize substrates while enhancing its permeability, and plants add greatly to the aesthetic value of the wetland. A dense stand of vegetation appears to moderate the effects of storms (Kadlec and Knight, 1996).

Not all wetland species are suitable for wastewater treatment since plants for treatment wetlands must be able to tolerate the combination of continuous flooding and exposure to wastewater or stormwater containing relatively high and often variable concentrations of pollutants. For wastewater treatment wetlands, the particular species selected are less important than establishing a dense stand of vegetation. Any species that will grow well can be chosen. For stormwater wetlands, species should be chosen to mimic the communities of emergent plants of nearby natural wetlands. For wastewater and stormwater wetlands, native, local species should be used because they are adapted to the local climate, soils, and surrounding plant and animal communities, and are likely to do well (Davis, 1995).

In wetlands constructed to treat domestic sewage, agricultural wastewaters, and other wastewaters relatively high in organic matter, bulrushes (either softstem or common threesquare) are often used because they are tolerant of high nutrient levels and because they establish readily but are not invasive. Arrowhead and pickerelweed have also been used successfully in agricultural wetlands. Blueflag iris can be planted along wetland edges to provide color. Cattails and common reed have been used frequently because of

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their high tolerances for many types of wastewater, but both have disadvantages. Cattails are invasive. Since cattail tubers are a favorite food of muskrats, cattails are susceptible to damage by muskrats (Davis, 1995; and Kadlec and Knight, 1996).

For agricultural wastewater wetlands, the ammonia tolerances of the species must be considered. Wetland species vary in their ability to tolerate ammonia. Plants may be able to tolerate higher concentrations of ammonia if the plants are slowly acclimated to it. For stormwater wetlands, the goal should be a diverse assemblage of plants. Diverse vegetation is aesthetically pleasing and may be more likely to resist invasive species, to recover from disturbance, and to resist pests than a less diverse stand. The numbers of wildlife attracted to a wetland generally increases as vegetation diversity increases. The State of Maryland guidelines for stormwater wetlands suggest planting two primary species (some combination of arrowhead, common three-square, or softstem bulrush) and three other secondary species to enhance short- and long-term development and to reduce the invasion by undesirable plants such as common reed (Livingston 1989).

Seeds, seedlings, entire plants, or parts of plants (rootstocks, rhizomes, tubers, or cuttings) can be used to establish wetland vegetation. While many wetland plants produce wind-borne seeds, vegetative spread by stolons and runners is common since seeds generally will not sprout under water. Many emergents have rhizomes, rootstocks, or tubers which, although they are primarily food storage organs, can generate new plants (Tousigant et al., 1999).

4.6.7 Operation and Maintenance Plans

Operation and maintenance (O&M) should be described in an O&M plan written during the design of the constructed wetland system. The plan can be updated to reflect specific system characteristics learned during actual operation. The plan should provide a schedule for routine cleaning of distribution systems and weirs, dike mowing and inspection, and system monitoring. The plan should specify those individuals responsible for performing and paying for maintenance. The plan should address (Davis, 1995; and Tousigant et al., 1999): (a) setting of water depth control structures, (b) schedule for

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cleaning and maintaining inlet and outlet structures, valving, and monitoring devices, (c) schedule for inspecting embankments and structures for damage, (d) depth of sediment accumulation before removal is required, (e) operating range of water levels, including acceptable ranges of fluctuation, (f) the supplemental water source to be used to ensure adequate water levels during establishment and operation, (g) wastewater application schedule, if this is part of the system design. An application schedule should be selected that is both convenient and relatively continuous. Short, high-flow discharges to a wetland are more likely to erode or damage established vegetation than lower velocity, more continuous flows, and (h) scheduling discharges to or from the wetland, recycling/redirecting flows, or rotating between cells, if such are part of the design.

4.7 Heavy Metals Removal Systems

Conventional passive wastewater treatment systems that remove iron and manganese from wastewater involve the addition of alkaline chemicals (such as lime, sodium hydroxide and sodium carbonate) to the water which causes the pH of the wastewater to increase and the dissolved metals to precipitate out of solution (Ziemkiewicz et al, 1997, and Gazea et al, 1996). These passive systems usually have increased costs associated with operation and maintenance, the purchase of chemical reagents and the disposal of metal laden sludge (Ziemkiewicz et al, 1997, and Gazea et al, 1996). Active treatment system such as limestone and peat filters have been used successfully to remove heavy elements from wastewater at less cost.

4.7.1 Limestone Filters

Limestone is a sedimentary rock, which is primarily composed of the mineral calcium carbonate ($CaCO_3$). The dissolution of calcium carbonate can increase the pH and the concentrations of alkalinity ($HCO_3^- + OH^-$) in water according to the following equations (Sun, 2000; and Cravotta III and Trahan, 1999):

$$CaCO_{3\,(s)} + 2H_2O \rightarrow Ca^{2+} + H_2CO_3 + 2OH^- \qquad (4.25)$$

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$$CaCO_{3\,(s)} + H_2CO_3 \rightarrow Ca^{2+} + 2\,HCO_3^- \qquad (4.26)$$

The dissolution of calcite depends on factors such as the solution temperature, pH and chemical composition as well as calcite content and the surface area of the sample. The molar solubility of calcite decreases with increases in the pH as shown in Table 4.3 (Bialkowski, 2003). The dissolution rate of calcite also decreases as the temperature decreases. Letterman (1995) conducted experiments to determine the effect of temperature on the rate of calcite dissolution from limestone composed of 94.5 % calcite and found that the dissolution rate of calcite increased from 0.38×10^{-3} to 2.80×10^{-3} cm/s when the temperatures increased from 5 to 25 °C, respectively.

Table 4.3. Solubility of $CaCO_3$ as a function of pH (Bialkowski, 2003).

pH	Molar Solubility
2	170.0
4	1.7
6	2.0×10^{-2}
8	11.0×10^{-3}
10	1.4×10^{-4}
12	7.8×10^{-5}

According to Barton and Karathanasis (1999) and Cravotta (1999), active treatment systems that use limestone have become widespread because limestone is an inexpensive source of alkalinity and limestone systems are relatively easy to construct and maintain. However, in an aerobic environment, treatment of a wastewater contains significant concentrations of heavy metals, with limestone results in the precipitation of metal hydroxides on the surface of the limestone (armoring) which can plug the limestone's void spaces. As a result, the ability of the limestone to dissolve and increase the alkalinity of the wastewater is reduced (Ziemkiewicz et al., 1997).

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4.7.1.1 Types of Limestone Filters

There are types of limestone treatment systems: (a) anoxic limestone drains, (b) oxic limestone drains and (c) open limestone channels.

4.7.1.1.1 Anoxic Limestone Drains: An anoxic limestone drain (ALD) is composed of a trench lined with plastic, filled with crushed limestone, sealed and then covered with soil. The anoxic limestone drain intercepts subsurface flows of wastewater and prevents contact of the wastewater with atmospheric oxygen. By isolating the wastewater from oxygen, the oxidation of metals and armoring of limestone is avoided. Therefore, a settling basin placed between the ALD and an aerobic wetland, in which metals are removed through oxidation and hydrolysis, is employed. The introduction of a settling basin can prolong the service life of the engineered wetland because it is capable of trapping some of the metal hydroxide precipitate (Ulrich, 1999). Berghorn and Hunzeker (2001) stated that the primary purpose of an anoxic limestone drain is to increase the alkalinity of the wastewater. They suggested that at a wastewater retention time in the drain between 14 in 24 h, ALD can contribute 200–300 mg/L of alkalinity in the form of $CaCO_3$.

The chemical reactions occurring in ALD include reactions which increase the alkalinity of water and reactions which decrease the acidity of water (Table 4.4). Depending on natural conditions, acidity may appear as proton, organic or mineral acidity, but most often in various combinations of the three forms. Total acidity is primarily the result of the presence of hydrogen ions and mineral acidity due to the presence of dissolved metals that hydrolyzed in water (Ulrich, 1999).

The increased alkalinity of water passing through the limestone bed is primarily the consequence of reactions increasing the concentrations of bicarbonatic ions (HCO_3^-). In a natural system, the basic reaction generating alkalinity is the reaction between carbonic acid (H_2CO_3) and calcium carbonate ($CaCO_3$). CO_2 comes into the water from air through absorption processes and reacts with water, forming carbonic acid. When water containing H_2CO_3 comes into contact with $CaCO_3$, reactions dissolving limestone begin

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Table 4.4. Chemical reactions in anoxic limestone drain (Blowes et al., 1994; and Donovan et al., 1994).

Alkalinity generating reaction:
$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO^{3-}$
$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + OH^- + HCO_3^-$
$CaCO_3 + SO_4^{2-} + H_2O \rightarrow CaSO_4 + OH^- + HCO_3^-$
$CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2H_2CO_3$
Acidity-lowering reaction:
$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$
$3CaCO_3 + 2Fe^{3+} + 6H_2O \rightarrow 3Ca^{2+} + 2Fe(OH)_3 + 3H_2CO_3$
$3CaCO_3 + 2Al^{3+} + 6H_2O \rightarrow 3Ca^{2+} + 2Al(OH)_3 + 3H_2CO_3$
$CaCO_3 + Fe^{2+} \rightarrow Ca^{2+} + FeCO_3$
$CaCO_3 + Mn^{2+} \rightarrow Ca^{2+} + MnCO_3$

to occur. The content of dissolved CO_2 in water and the $CaCO_3$ dissolution rate are in direct correlation. The higher the partial pressure of CO_2 in the system, the quicker the dissolution of carbonates. The increased concentrations of CO_2 in water directly increase the concentration of HCO_3^- in the system (Ribet et al., 1995; and Assaad and Jordan, 1994).

The acidity of water contaminated with metal ions decreases when passing through the ALD layer due to the neutralization of protonic acidity (dissolution of limestone) and the precipitation of metal ions present in water. The alkalinity-generating reactions and the acidity-reducing reactions occur in a known order which depends on the soluble products of the newly formed compounds (e.g. hydroxides and carbonates). The acidity generated through the hydrolysis of Fe and Al is neutralized by the dissolution of limestone. When the pH value exceeds 4.5, bicarbonates begin to accumulate in considerable quantities. At pH values exceeding 6 (Figure 4.21), the metal ions present in water (Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, Cd^{2+}, Mn^{2+}) begin to precipitate in the form of oxides or hydroxides (Anderson, 1990).

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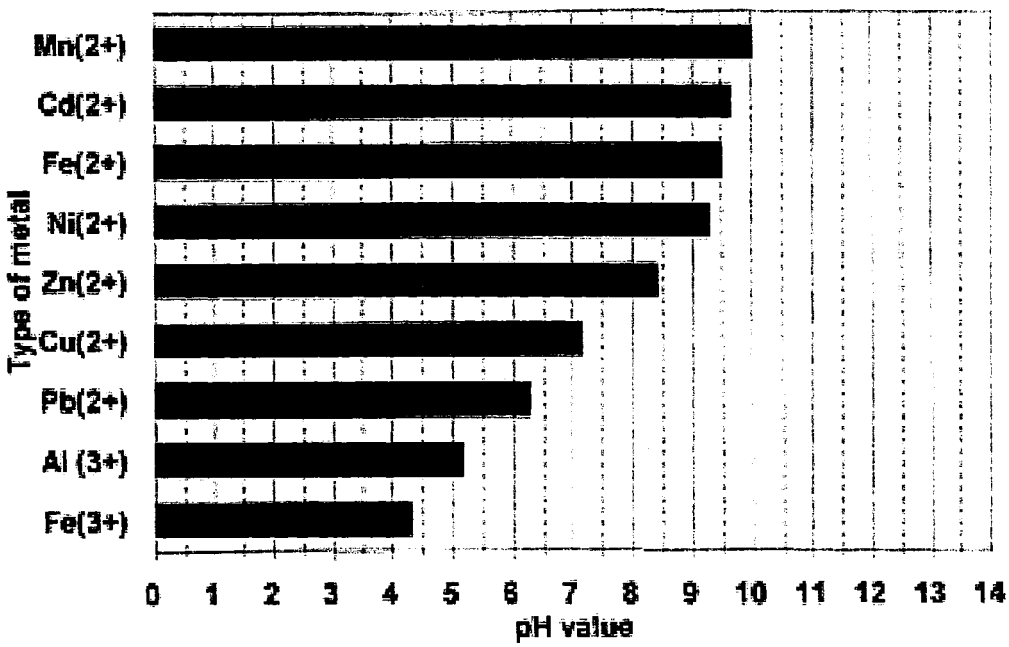


Figure 4.21. Middle pH value for heavy metal precipitation (Ulrich, 1999).

Hedin et al. (1994) evaluated the performances of an anoxic limestone drain (ALD) receiving mine water contaminated with Fe^{2+} (216-279 mg/L) and Mn (41-51 mg/L). The alkalinity increased by an average 248 mg/L, the concentration of Ca increased by 111 mg/L and the concentrations of K, Mg, Mn, and SO_4^{2-} each decreased by an average 17%. Iron, which decreased by 30%, was partially retained within the ALD. By significantly increasing alkalinity concentration in the mine water, the ALD increased metal removal in downstream constructed wetlands. At the rate of calcite solubilization of 2.7 $kgCaCO_3/d$, the theoretical effective lifetime of the ALD was estimated to be in excess of 20 years.

Watzlaf et al. (2000) monitored ten anoxic limestone drains (ALDs), used for treating coal mine drainage, for a decade. Alkalinity concentrations in the effluent of the ten ALDs ranged from 80 - 320 mg/L as CaCO with near maximum levels of alkalinity being reached after approximately 15 hours of detention. The ALDs that received mine water containing less than 1 mg/L of both ferric iron and aluminum continued to produce consistent concentrations of alkalinity. However, the ALDs that received 21 mg/L of aluminum experienced a rapid reduction in permeability and failed within eight months.

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4.7.1.1.2 Oxic limestone Drains: The oxic limestone drain (OLD) is designed to treat water containing appreciable dissolved oxygen and iron that has been oxidized (ferric). Like ALDs, OLDs are designed to promote higher limestone dissolution and hence increase the alkalinity of the wastewater by concentrating the partial pressure of CO_2 (Pco_2). The Pco_2 is increased because the drain is covered, hampering its escape. The limestone dissolves rapidly enough to make the surface an unstable substrate for iron armoring, because the chemical reactions within the drain cause the dissolution of 2 moles of $CaCO_3$ for each mole of $Fe(OH)_3$ produced. The iron hydroxide ($Fe(OH)_3$) and aluminum hydroxide ($Al(OH)_3$) precipitate to some extent within the drain. The drains can be designed for periodic flushing to preclude buildup of these metal hydroxides.

Acid mine drainage (AMD) with a moderate acidity concentration (< 90 mg/L $CaCO_3$), a pH of less than 4.0, and moderately low dissolved iron, manganese, and aluminum concentrations (1 to 5 mg/L) was treated using OLDs (Cravotta, 1998). The drains exhibited decreased iron and aluminum concentrations of up to 95% initially (first 6 months) but manganese concentrations were unaffected. After the initial 6 months, the manganese concentrations were lowered by 50 percent, because of coprecipitation with the $Fe(OH)_3$ facilitated by higher water pH (>5.0). The higher pH was due to increased alkalinity production as the water flowed through the drain. The rate of alkalinity production was greatest initially and decreased as the water traveled through the drain.

Cravotta (1999) constructed three identical experimental OLD (Figure 4.22) in parallel in a horizontal trench (4 m wide, 30 m long and 2 m deep). Each OLD was constructed using corrugated steel culvert pipes with an inside diameter of 0.79 m. The pipes were split lengthwise to form a semicircular trough at the bottom that was lined with vinyl sheeting and filled with 12,700 kg of limestone fragments composed of 97 % calcium carbonate. The vinyl liners were wrapped over the top of the limestone and the drains were backfilled with excavated soil. It was hypothesized that the hydrous oxides of iron and aluminum would not severely inhibit limestone dissolution but would be transported as suspended particles through the drains by the rapid flow of water. Sorption and coprecipitation of Fe^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} were prompted by the

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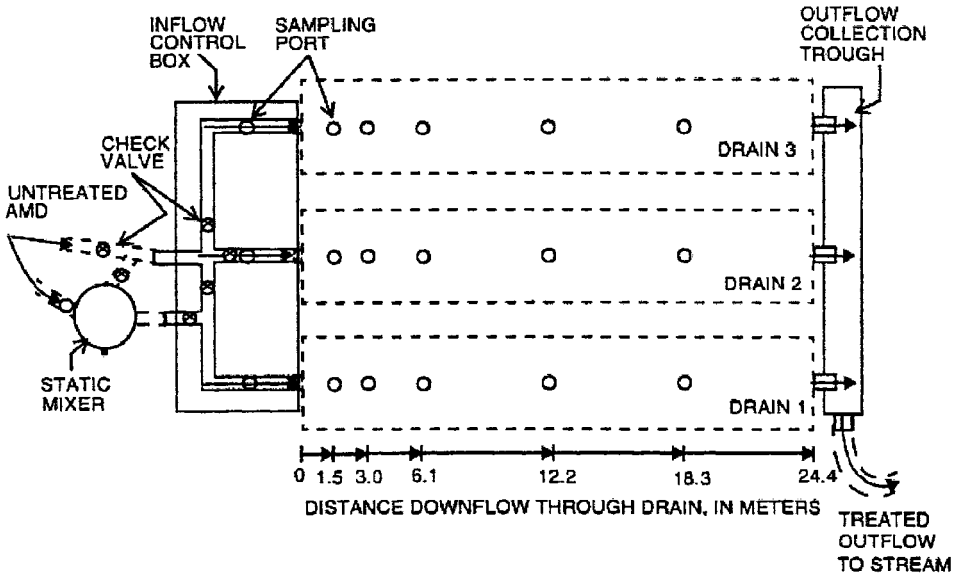


Figure 4.22. Design of the oxic limestone drains (Cravotta, 1999).

accumulated hydrous oxides and elevated pH within the OLDs. The cumulative limestone dissolution rate for the OLDs combined was 4.4 kg/day. Based on this dissolution rate and the total of 38, 200 kg of limestone used in the drains, the OLDs could theoretically function for 24 years.

4.7.1.1.3 Open Limestone Channel: There are two ways to construct open limestone channels (OLCs): (a) creating a drainage ditch that is composed of limestone and then directing wastewater into the ditch, and (b) placing limestone fragments directly into a contaminated stream. When dissolved iron is oxidized, it will precipitate, armoring limestone and creating iron hydroxide sludge. Armoring and plugging of the limestone with metal hydroxides can be minimized by maintaining high flow velocities and turbulence throughout the channel (Berghorn and Hunzeker, 2001). According to Ziemkiewicz et al. (1994), limestone, even if completely armored with iron, will continue to yield some alkalinity. Ziemkiewicz et al. (1996) reported that armored limestone may exhibit 20-33 percent of the $CaCO_3$ solubility of unarmored limestone.

Open limestone channels are relatively simple and inexpensive systems to construct. However, there are some limitations to their use. Neutralization ability of these channels

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is greatly limited by the dissolution rate of armored limestone, atmospheric CO_2 concentrations and contact time (Ziemkiewicz et al., 1994; and Ziemkiewicz et al., 1996). Acidity reduction of up to 5 percent may occur due the formation of the minerals swartzmanite and jarosite, which store acidity (H^+). Limestone dissolves at a rate considerably below 5 percent. Therefore, in order to treat relatively large discharges with considerable acidity concentrations, very long drains (>1000 m) with thousands of tons of limestone would be required.

Carew et al. (2003) used a 2440 m open limestone channel was used to treat AMD. The acidity decreased from an average of 401 mg/l $CaCO_3$ prior to dosing with limestone to an average of 120 mg/l $CaCO_3$ after dosing began. The net acid loading averaged 8.5 tons per month prior to dosing and 1.8 tons after dosing began, a reduction of 79%. Dissolved Iron averaged 39.3 mg/L prior to dosing with limestone and 8.4 mg/L after dosing. Dissolved aluminum, which is particularly harmful to aquatic life, dropped from an average of 32.36 mg/L prior to treatment to an average of 11.5 mg/L after dosing with limestone began.

Ziemkiewicz et al. (1997a) found armored limestone in a series of laboratory experiments to be 50 to 90% as effective as unarmored limestone in neutralizing AMD. Seven OLCs reduced acidity in AMD by 4 to 205 mg/L as $CaCO_3$, at rates of 0.03 to 19.00 mg/L per meter of channel length. The highest removal rates were with channels on slopes of 45 to 60% and for AMD with acidity of 500 to 2600 mg/L as $CaCO_3$.

Ziemkiewicz and Brant (1996) evaluated an OLC (400 m long on a 8% slope) that received 60 L/min of pH 2.7 wastewater (1290 mg/L as $CaCO_3$ acidity) having 622 mg/L Fe, 49 mg/L Mn, and 158 mg/L Al. The effluent pH over a two year period was 2.9 (acidity as $CaCO_3$ was 884 mg/L, 31% decrease), Fe was 210 mg/L (66% removal), Mn was 42 mg/L (14% decrease), and Al was 103 mg/L (35% decrease).

Hellier (1997) used a 15-m long OLC on a 10% slope to treat AMD with a pH of 4.3, (acidity of 162 mg/L as $CaCO_3$) Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L

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(Hellier, 1997). The effluent had a pH of 4.8 (net acidity of 50 mg/L as $CaCO_3$) Fe of 17 mg/L, Mn of 8 mg/L, and Al of 3 mg/L. The OLC removed 72% of the Fe and about 20% of the Mn and Al from the water.

4.7.1.2 Limestone/Sandstone Filters

Limestone is used as a neutralization agent for the remediation of streams polluted by acid mine drainage (AMD). However, under aerobic conditions, metal precipitation on the limestone surface can prevent the limestone from dissolving and creating an alkaline environment. Skousen, et al. (1998), Watzlaf et al. (1994) and Kepler and McCleary (1997) identified the plugging of OLDs with aluminum precipitates as a serious concern for the success of these treatment systems.

In order to improve the functioning of aerobic limestone technologies such as OLDs and OLCs, Xu et al. (1997) and Sasowsky et al. (2000) suggested the use of a mixture of limestone and sandstone. In the presence of a mixture of limestone and sandstone, iron will preferentially precipitate on the sandstone surface. Therefore, limestone can provide a continuous source of neutralization and sandstone can serve as a surface for metal hydroxide precipitation.

Xu et al. (1997) conducted laboratory experiments to investigate the interactions between a simulated acid mine water and a mixture of calcite and quartz sand. In the experiments where calcite was included as part of the solid sample, pH greatly increased and iron was removed from solution in significant quantities because of the precipitation of ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$). Aluminum was also almost completely removed from solution because of $Al(OH)_3$ precipitation. The concentrations of K, Mg and Na did not change significantly throughout the experiments. The dissolution of calcite was responsible for the increase in pH and the increase in Ca concentration. In the experiments where only quartz sand was present, iron was the only species to show significant changes in concentration. The decrease in pH resulted from the reaction shown in Equation (4.28). The author noted that this reaction is not common at low pH values but the high sulphate concentrations present in the mine water accelerated the reaction.

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$$5Fe^{3+} + 12\ H_2O \rightarrow Fe_5HO_8{\cdot}4H_2O + 15H^+ \quad (4.27)$$

Sasowsky et al. (2000) placed gravel sized samples of lithic materials in mesh bags within a culvert in the creek polluted with AMD for 30 days. Quantitative measurements of iron coatings were made before the experiment began and after its completion. The results indicate that quartz-rich samples were more heavily coated with iron precipitate than the carbonate samples. The mixture of sandstone and limestone resulted in a greater iron removal than limestone alone.

4.7.1.3 Construction of Limestone Filters

Construction criteria are determined from the flow rate, channel slope, and acidity concentration. This information will determine the mass of limestone, the cross-sectional area and length of the drain, and ultimately, the in-channel detention time. OLCs also require sufficient slope, hence water velocity, to prevent clogging of the interstitial pore spaces with iron, manganese, and aluminum floc. If the pore spaces are substantially filled with metal floc, the water will flow over the top and be precluded from contacting the armored limestone, greatly attenuating, if not eliminating predicted dissolution rates (Ziemkiewicz et al., 1994). A recommended size of limestone gravel for use in these channels is greater than 4 inches in diameter. Optimal efficiency may be reached with limestone in the 6 to 12 inch diameter range. A channel grade exceeding 10 percent is also recommended to facilitate flushing of the metal floc from the drain, preventing a clogging of the pore spaces. Channels with less than a 9 percent grade were shown to be much less effective than channels with steeper grades (Ziemkiewicz et al., 1996). Because these channels are designed to flush out the metal floc, settling ponds are often constructed at the outlet point. These ponds will allow the metal floc to be concentrated at one point and should permit discharging the compliance water to the receiving stream. However, ponds will require periodic cleaning to maintain efficiency (EPA, 2000).

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4.7.2 Peat Systems

Peat consists of partially decomposing plant material which forms in areas that are moist and poorly oxygenated and where the rate of accumulation of plant material is greater than that of decomposition. Peat is usually a dark brown to black color and has a very soft structure. Peat is a polar material of high organic content with lignin and cellulose as its main components. It has a specific surface area of approximately 200 m^2/g and a porosity between 90-95 %. The physical and chemical properties of peat make it an ideal medium on which purification mechanisms, such as biological degradation, adsorption, complexation and ion exchange, can occur (Warith, 1996; and Murawski, 1994).

According to Murawski (1994), in order to obtain significant metal removal efficiencies with peat: (a) the peat used in construction of a filter should have a high hydraulic conductivity, (b) a complex flow pattern of wastewater through the peat is desirable because it provides a uniform contact time between adsorption sites on the peat and metal ions in the wastewater and a longer retention time which increases the occurrence of exchange reactions, (c) use of peat with higher pH under aerobic conditions, as peat with a pH between 6 and 8 exhibits more efficient metal removal than peat with a low pH because competition exists between hydrogen ions and metal ions for exchange sites on the peat at lower pH and (d) the peat used to construct the filter should have an organic content greater than 90 % for efficient heavy metal removal. Dissanayake and Weerasooriya (1981) suggested that before entering a peat filter, the pH of the waste stream should be adjusted to 4.5 because at this pH nearly all metals found in industrial wastes can be adsorbed. Warith (1996) noted that one factor which affects the lifespan of a peat filter is the rate of decomposition of peat under aerobic environments. Among the standard three types of peat (sphagnum, sedge and woody), sphagnum peat is the most resistant to decay under aerobic conditions.

Warith (1996) conducted batch column experiments to evaluate the potential of a specific peat soil to treat leachate originating from a municipal landfill. The selected peat had a pH of 6.3 (which assists in the adsorption of heavy metals) and a lower nutrient content compared to other peat sources (which reduces its degradation rate). The results

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demonstrated the ability of peat to successfully remove lead and zinc from the landfill leachate. A peat mass of about 20 g was able to reduce the lead concentration in the solution by approximately 95 %, and a peat mass of about 90-100 g was able to reduce the zinc concentration in the solution by 95 %. The concentration of calcium in the leachate solution increased from an initial value of 50 mg/L to a final value of nearly 70 mg/L. This increase was caused by the replacement of calcium ions by heavy metals, which were originally bound to the peat.

Warith (1996) conducted column tests to simulate the continuous flow conditions that would occur in a peat filter. Five columns were packed with 910 g (dry weight) of peat. The leachate solution was applied to the five columns at a rate of 130 ml/day. After the conclusion of the experiment, the peat was removed from each column, cut into four equal slices and analyzed for metal concentrations. The metal ion concentration profiles in the peat columns after the permeation of 2 pore volumes through the filter indicated that the order of preferential adsorption by the first layer of peat was Pb > Zn > Na > Ca.

McLennan and Rock (1988) assessed the ability of *Sphagnum* peat to remove metals from two different landfill leachates at various initial metal concentrations and contact times (1 and 24 hour). Sock solutions of $Al_2(SO_4)_3 \cdot 18H_2O$, $3CdSO_4 \cdot 8H_2O$, $K_2Cr_2O_7 \cdot 8H_2O$, $FeSO_4 \cdot 7H_2O$, $CuSO_4$, $PB(NO_3)_2$, and $ZnSO_4 \cdot 7H_2O$ were prepared so that the concentration of each of the seven metals ranged from 50 to 750 mg/L. The results showed that increased contact time resulted in greater adsorption of metal ions by peat.

4.7.3 Biomass Systems

According to Spinti et al. (1995), there are many advantages of using inactive or dead biomass to remove heavy metals from wastewaters: (a) there is no potential toxic effect of contaminants in the wastewater, (b) non-living biomass does not have to be provided with nutrients, and (c) non-living biomass can be immobilized in a granular or polymeric matrix and used in conventional ion exchange equipment.

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Spinti et al. (1995) formed biomass beads and evaluated their performance in packed columns. The beads were composed of *sphagnum* peat moss immobilized in porous polysulfone. The immobilized biomass beads created were mechanically strong, chemically resistant, easily regenerated and were not harmed by drying. The wastewaters were pumped through a column of biomass beads and metal ions were adsorbed onto the beads until the beads became saturated and breakthrough occurred. The results demonstrated that the initial pH of the packed bed has a strong influence on the beads' capacity to adsorb metal ions. When the beads' capacity to adsorb metal ions was approached, metals with a higher affinity appeared to displace metals with lower affinities. The selectivity of metals was determined to be Fe>Al>Pb>Cu>Cd, Zn>Ca>Mn>Mg>Na. Therefore, *sphagnum* peat moss beads absorb most hazardous metals before calcium, manganese, magnesium and sodium.

Kapoor and Viraraghavan (1998) reported the use of dead A. niger biomass immobilized in polymer polysulfone in the form of spherical beads to remove heavy metals from an industrial wastewater. A packed bed column containing A. niger beads was able to remove approximately 38% copper, 58% lead and 16% zinc at the end of 12 hours from the industrial wastewater containing 0.08, 0.66 and 1.78 mg/L copper, lead and zinc respectively.

Elifantz and Tel-Or (2002) tested the performance of Ludwigia stolonifera biomass (roots, floating roots and leaves) as heavy metal biofilters. Cadmium (Cd) and nickel (Ni) (50 ppm) solutions were filtered through 0.5-1.5 g packed columns with each biomaterial, to determine their metal removal efficiency. Root column was more efficient in removing Ni (as low as 6 ppb in the effluent) than of Cd (as low as to 22 ppb in the effluent). This tendency was also observed upon treatment of a mixed solution of both metals. Floating roots column reduced Cd content to the same level as the root column, but its metal binding capacity was higher (93 mg Cd/g DW in floating roots in comparison to 43 mg Cd/g DW in the roots biofilters). Leaf biomass column demonstrated the best metal binding capacity (128 mg Cd/g DW, and Cd concentration in the effluent was 17 ppb). Pectin content was 5, 8 and 10% W/W in roots, leaves and floating roots biofilters,

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respectively. Evidence for the exchange of the bound heavy metal ions against the discharge of light metal ions such as calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) was noticed.

Skowronski et al. (2001) examined the metal sorption capacity of granulated biosorbent derived from the waste biomass of *Penicillium chrysogenum*. The potential metal sorption abilities of the biosorbent were estimated as the cation-exchange capacity, using a potentiometric titration. The total binding capacity, calculated for the pH range of 3-8 was about 511 μeq/g dry weight. The granular biosorbent was capable of binding Cd, Zn, Cu and Pb. The kinetics of the heavy metal sorption were typical of the microbial biomass. The maximum sorption capacity, calculated from the Langmuir equation for the particular heavy metals, was: 96 mg Pb; 21.5 mg Cd; 13 mg Zn and 11.7 mg Cu (per g dry weight). Optimum pH values for Cd, Zn and Cu sorption were about 7, while for Pb about 6.

4.7.4 Compost

Compost has traditionally been added to soil as an enrichment process. However, because composting has rapidly increased in the past number of years, producers have been encountering difficulties finding markets for their compost. One possible alternative use for compost is as an absorbent for heavy metals in contaminated water bodies. Compost is a combination of organic and inorganic matter. Most of the organic matter is composed of humic substances which have a high molecular weight, are brown/black in color and have a strong ability to absorb complex metal ions from wastewaters. The use of compost will also avoid the depletion of natural resources (Grimes et al., 1999).

Grimes et al. (1999) conducted batch experiments using compost obtained from a facility which received mainly household and garden wastes and used the windrow method of composting to: (a) determine the time taken for the compost to become equilibrated with cadmium, copper, lead and zinc ions, (b) the effect of the initial metal concentrations on the percentage of metals removed from solution, (c) the capacity of compost for the four metal ions, and (d) the effects of pH on metal uptake. After one hour, 97.5 % of lead,

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97.2 % of cadmium, 94.6 % of zinc and 88.0 % of copper were removed from solution by the compost. The capacity of the compost was 60 mg/g for lead, 30 mg/g for copper, 25 mg/g for cadmium and 10 mg/g for zinc. Changing of pH from 2 to 5 had only a small effect on the removal of zinc, cadmium and copper from solution. However, the effect of pH on lead removal was more prominent.

Richman (1997) used a palletized compost medium to trap particulates, absorb organic compounds and heavy metals at shopping centers, restaurants, highways, hospitals, and single retail outlets. That treatment system was reportedly capable of removing up to 90% of the solids, 85% of the oil and greases, and 82-98% of the heavy metals.

Lister and line (2004) found that the biosorptive-capacity of composted paper mill waste (PMW) for the heavy metals [Cd(II), Cu(II), Pb(II) and Zn(II)] was improved by inoculation of sterilized compost with a *Bacillus brevis* strain followed by incubation. This strain was originally isolated from the compost and adsorbed up to 31% of its dry weight of lead and 28% of copper at an initial concentration of 185.2mg/L and 182.3mg/L respectively. Estimated numbers of the bacterium following 21 days growth in the compost at 25°C reached 10^9 cells/g. The modified compost exhibited up to a three-fold increase in capacity for removal of lead and up to a two-fold increase in capacity for removal of copper from aqueous solution.

4.7.5 Peat Wetland Treatment Systems

Murawski (1994) described two successful peat wetland treatment systems constructed to remove heavy metals from acid mine drainage seeping. The main tailings were composed of copper-nickel sulfide mineralized rock and have a pH ranging between 5.4 and 7.5. One system was composed of 6506 m^2 of peat and 9 berms, and the second system was composed of 4647 m^2 of peat and 5 berms. A peat mixture was placed upstream and downstream of each treatment berm as illustrated in Figure 4.23. To ensure that the pH remained alkaline for optimum metal removal, limestone was spread over the top of each berm and on the downstream slope of each berm. To increase the life span of the peat, cattails were planted in both systems. Cattails provide another source of metal removal

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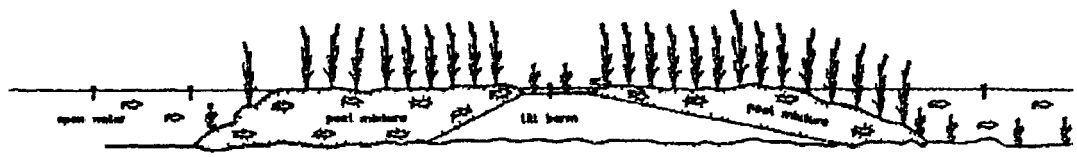


Figure 4.23. Typical peat/wetland treatment berm (Murawski, 1994).

from the wastewater. The peat wetland treatment systems removed 95-99 % of the heavy metals.

Mungur et al. (1997) evaluated the performance of laboratory scale peat-substrate subsurface-flow wetlands in a continuous recirculating mode for the removal of Cu, Pb and Zn from contaminated water. The wetland were planted with *Typha latifolia, Phragmites australis, Schoenoplectus lacustris* and *Iris pseudacorus*. The wetland system was dosed with increasing concentrations (1, 5 and 10mg/l) of Cu, Pb and Zn. Finally a shock load of metals (concentration 20 mg/l) was introduced to simulate a storm event. The removal efficiences and rates for these different doses ranged from 81.7% to 91.8% and 36.6 to 372.7 mg/m^2/d for Cu, 75.8% to 95.3% and 30.8 to 387 mg/m^2/d for Pb and 82.8% to 90.4% and 33.6 to 362.1 mg/m^2/d for Zn respectively. Results for the storm simulation showed that in the time taken for the water level to subside to its original level (just below the substrate surface) at established outlet flow rates, the metal loadings leaving the system remained very low with the wetland system retaining over 99% of the metals. These results indicate the ability of the system to act as an efficient sink for heavy metals.

Wieder et al. (1990) evaluated the potential for constructed wetlands to treat acid coal mine drainage. Six model wetland mesocosms (each 2.4 m × 15 cm) were filled with Sphagnum peat (15 cm deep), planted either with cattails (Typha latifolia) and living Sphagnum, living Sphagnum only, or left as bare peat (2 mesocosms per treatment). The model wetlands were exposed to synthetic acid coal mine drainage (pH 3.5, concentrations of Fe^{2+}, Al^{3+}, Mn^{2+}, Ca^{2+}, and Mg^{2+} of 78.8, 10.0, 5.2, 12.0, and 4.5 mg/L, respectively) at a rate of 90 mL/min, 6 h/d, 5 d/wk, over a 16 week period. Chemical

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analysis of peat at periodic intervals indicated that the model wetlands were net sources of Al^{3+}, Mn^{2+}, Ca^{2+}, and Mg^{2+}, but net sinks for Fe^{2+}.

4.7.6 Overland Flow Systems

Overland flow systems (Figure 4.24) are a land application treatment method in which primary or secondary wastewater is applied at a controlled rate along the upper portions of a sloping vegetated land surface composed of relatively impermeable soil. As a result, infiltration of water is minimized and the water flows down the slope in a thin film. The wastewater is treated by a variety of mechanisms including: filtration, adsorption, ion exchange, precipitation, microbial action and plant uptake. The vegetated surface also maintains maximum contact times between the contaminants in the water and the soil and plants. The water is collected at the bottom of the slope in ditches and may be used for agricultural and reforestation purposes.

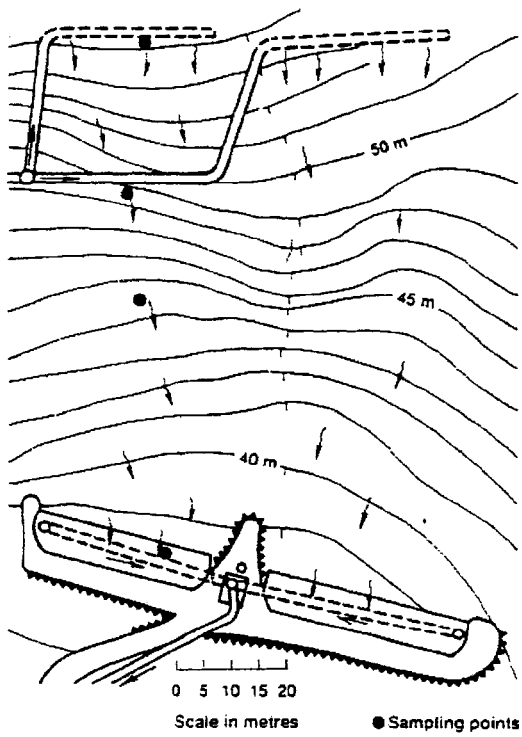


Figure 4.24. Plan view of Salo, Finland overland flow water treatment system (Zirschky and Carlson, 1984).

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Zirschky and Carlson (1984) and Organization of American States (1997) stated that there are many advantages of using an overland flow treatment system: (a) operation of the system is simple because there are few mechanical systems that require observation and maintenance, (b) the influent distribution system is designed to allow half of the slope to be shut down to permit the precipitates to dry and the vegetation to recover, (c) the precipitate does not have to be removed from the slope because it compacts and stabilizes upon drying, (d) the volume of sludge generated for disposal is reduced, and (e) oxidation of metals is achieved without the need for mechanical aeration or the addition of chemicals.

Zirschky and Carlson (1984) reported that groundwater containing high concentrations of iron and manganese was successfully treated using an overland flow system. The overland system provided a large area through which dissolved oxygen concentrations in the groundwater can increase which allowed for the oxidation of iron and manganese. Groundwater with high concentration of carbon dioxide (CO_2) will have its pH increased as it flows across the land surface because of the emission of CO_2 to the atmosphere. Higher pH will result in the precipitation of iron and manganese compounds.

Lee and Peters (1979) studied the factors affecting overland flow treatment of municipal facultative lagoon effluent. These included: amount of wastewater applied, length of application period, slope of treatment area, crop management, and reduction in biochemical oxygen demand, suspended solids, nitrogen, phosphorus, heavy metals and coliforms. Nitrogen reductions of 80 percent or more were achieved at application rates of 2.54 cm in 18 hours for the warmer months of the year and 1.27 cm in 18 hours for the cooler winter months. Phosphorus reduction ranged from 40 to 60% at an application rate of 1.27 cm in 6 hours. However, addition of alum to the wastewater prior to land application enhanced phosphorus reduction to over 80 percent. Runoff concentrations of fecal coliforms were higher than these in the applied wastewater during the summer months. Overland flow systems effectively reduced heavy metals by more than 90 percent.

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Surampalli et al. (1996) evaluated the effects of seasonal variations (summer and winter conditions) on the performance of an existing and successfully operated overland flow wastewater treatment system. The effect of design parameters such as hydraulic and organic loading rates, and the seasonal temperature on performance were investigated. The overland flow system studied consisted of an aerated lagoon, two conventional lagoons, and an overland flow area. The overland flow area was divided into six groups of terraces and the terraces were constructed at a slope of 2% with a length of 341.3 m. The results of the study showed average removal efficiency for BOD_5 and SS in warm weather of 89% and 85%, respectively,. During cold weather, the percent removals for these parameters were 81% and 69%, respectively. No significant ammonia nitrification was observed.

4.7.7 High Surface Area Media

Passive removal of dissolved iron from water can consist of a simple technology where water is discharged over a cascade of steps which allow for aeration and oxidative precipitation of iron oxide minerals. Once an iron oxide mineral surface has been established, the removal of ferrous iron from solution involves the rapid adsorption of Fe^{+2} species to the iron oxide mineral surface followed by surface catalyzed oxidation by dissolved oxygen and surface precipitation as an iron oxide mineral. The reaction occurs rapidly at neutral pH values, but slows dramatically at pH values ≤ 5. The reaction is also irreversible under oxic conditions (Burke and Banwart, 2002).

Best and Aikman (1983) conducted experiments in which they used high surface area media for the treatment of alkaline and ferruginous discharges from an abandoned colliery using a reactor (1 m × 1 m × 2 m) filled with brushwood followed by a tank for the settlement of insoluble iron before the water was discharged to a river. Over a three month period, the filter and the settlement tank successfully removed 82 % of the ferrous iron.

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Jarvis and Younger (2001) evaluated the effectiveness of high surface area media in treating alkaline mine waters for 5 months. Weekly effluent water samples displayed considerable decreases in iron and manganese. The mean influent Fe and Mn concentrations were 1.43 and 0.67 mg/L and the mean effluent Fe and Mn concentrations were 0.40 and 0.50 mg/L. The results suggested that at loading rate of up to 14 g/day, the reactor can successfully remove 85% of the influent iron.

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5. PERFORMANCE EVALUATION OF BURNSIDE CONSTRUCTED TREATMENT WETLAND

5.1 Introduction

Landfills are potential threats to groundwater and surface water quality, the primary concern being the production of leachate (Howard, 1997). The leachate could be highly toxic, and if discharged in directly into water bodies, it could impact aquatic life and degrade water quality (Cameron and Koch, 1980). Chemical and biological reactions occur as infiltrating water percolates through refuse. The products of the complex combination of ongoing reactions within the refuse are transported by the infiltrating water. Besides the chemical and biological reactions, physical processes such as sorption and dissolution also take place during the passage of water through the waste. The sum total of all these processes and reactions is a leachate with dimensional attributes varying over time (McBean and Rovers, 2000). In addition to the leachate generation induced by precipitation, it is also produced as a result of biochemical processes that convert solid materials to liquid form. The leachate generated from the biochemical processes is characterized by very high concentrations of organic and inorganic contaminants. Water percolating through the landfill surface from infiltration will actually dilute contaminants in the leachate, as well as aid in the formation of new leachate (Bagchi, 1990). The percolate water will collect a variety of dissolved organic and inorganic contaminants resulting from the decomposition of refuse. The biodegradability of organic matter in leachate is generally inversely proportional to the molecular weight of the various components of the organic matter; lower molecular weights indicate a higher degree of biodegradability. Chain and deWalle (1977) stated that organic matter in landfill leachates ranges from small, volatile acids with low molecular weight to large, refactory fulvic- and humic-like compounds of intermediate and high molecular weights, respectively. The temporal variability of leachate quantities and qualities is influenced by features including the meteorology, the cover overlying the refuse, the hydrogeologic conditions in the vicinity of the site, and other characteristics of the refuse such as age, composition, and degree of compaction (McBean and Rovers, 2000). The chemical

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composition of leachate varies greatly depending on the age of landfill and the events prior the time of sampling (Christensen et al., 1994).

Wetlands are used to treat a variety of wastewaters, including municipal, mine drainage, urban and agricultural storm water, sludges, leachates, and various industrial effluents. Wetland treatment can take place in natural or constructed wetland sites. Principal categories of constructed wetland systems include densely vegetated overland flows, subsurface systems, pond and island systems, and channels with floating plants (Kadlec, 2000). Metals are removed by cation exchange to wetland sediments, precipitation as sulfides and other insoluble salts, and plant uptake. Plant storage is typically predominantly to the roots (Surface et al., 1993). The anaerobic sediments provide sulfate reduction to sulfide and facilitate chemical precipitation. As a result, good removals of metal are reported for operating wetland facilities (Kadlec, 2000). Nonvolatile, nontoxic organics are often lumped as COD or BOD, because they can create oxygen deficiencies in receiving waters. Mechanisms include oxidation and anaerobic digestion (Kadlec and Knight, 1996). Reduction of phosphorous, nitrogen compounds and other nutrients requires the longest detention of any of the pollutants. Nitrogen removal may require active or passive reaeration to promote nitrification. Nitrogen is also stored, but in larger measure is sequentially transformed, ultimately leaving the wetland as dinitrogen or ammonia. Phosphorus is stored in new wetland sediments.

5.2 Objectives

The main objective of this study was to evaluate the performance of a constructed wetland treating landfill leachate. The specific objectives were:

1. to determine the overall removal efficiency of the wetland for heavy metals (Fe and Mn), COD, TSS, TDS, Ortho-phosphate, Ammonia, TKN, NO_3 and NO_2,
2. to determine the cell-to-cell removal efficiency for the above parameters,
3. to determine the rate and concentration of heavy metals uptake by the plants, and
4. to determine the rate and concentration of heavy metal precipitates.

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5.3 Landfills

A 6.7 hectare refuse disposal area was created in the Burnside Industrial Park, just north of Black Lake (Figure 5.1), in August of 1968. It was used to dispose of incinerator ash, cans, combustibles that could not be taken in at the incinerator, and bulky non-combustibles such as car bodies and refrigeration units (Figure 5.2). It was the only landfill type of operation that involved no open burning and was closed in 1974, with very inconsistent covering. The disposed materials raised the height of the open clay soil to about 8.5 m above the lake level. Scouring on the hillside above the lake, from which an extensive amount of fill had been taken, exposed soil in a harmful position in relation to the lake and surrounding areas.

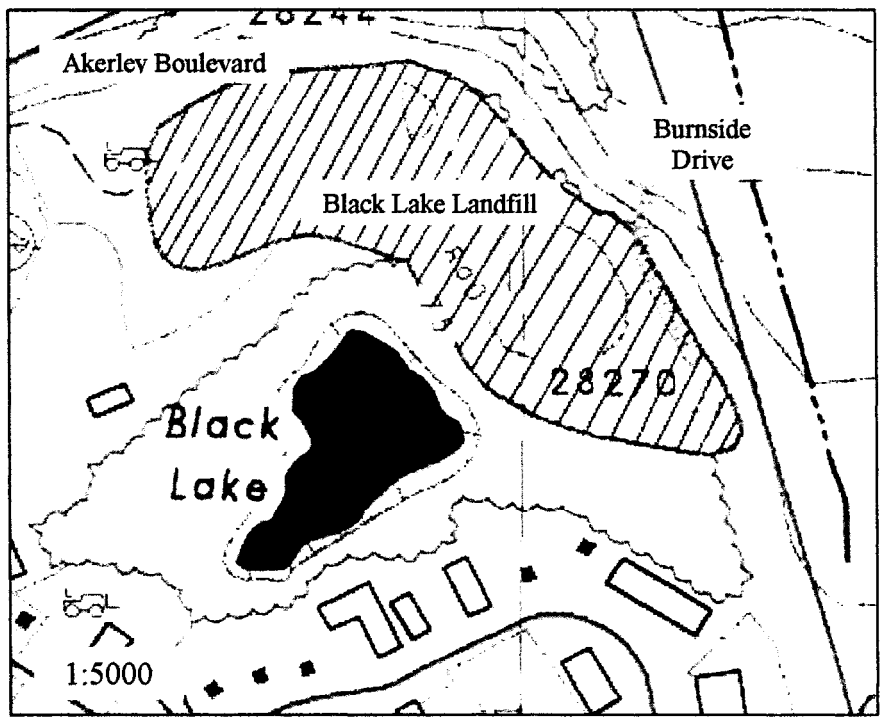


Figure 5.1. Black lake landfill.

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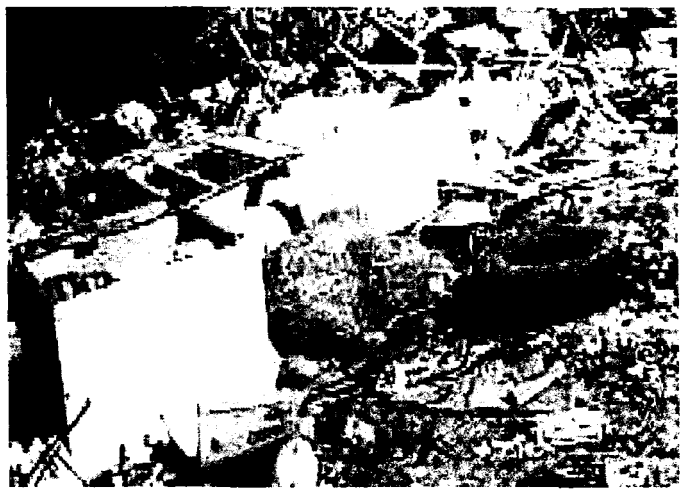




Figure 5.2. Uncovered parts of the Black lake landfill showing autobodies, tires, metal debris, refrigerated units and construction debris.

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The Dartmouth Municipality used another 13.4-acre open waste disposal site, located at the corner of Akerley Boulevard and Burnside Drive (Figure 5.3), as a temporary landfill in 1976. Upon closure in 1977, the waste was covered with 60 cm of soil and later became the Don Bayer's Sports Field (Figure 5.4). The site had accepted municipal, agricultural and industrial wastes, old tires, abandoned cars and demolition wastes. The wastes were reportedly burned to reduce volume.

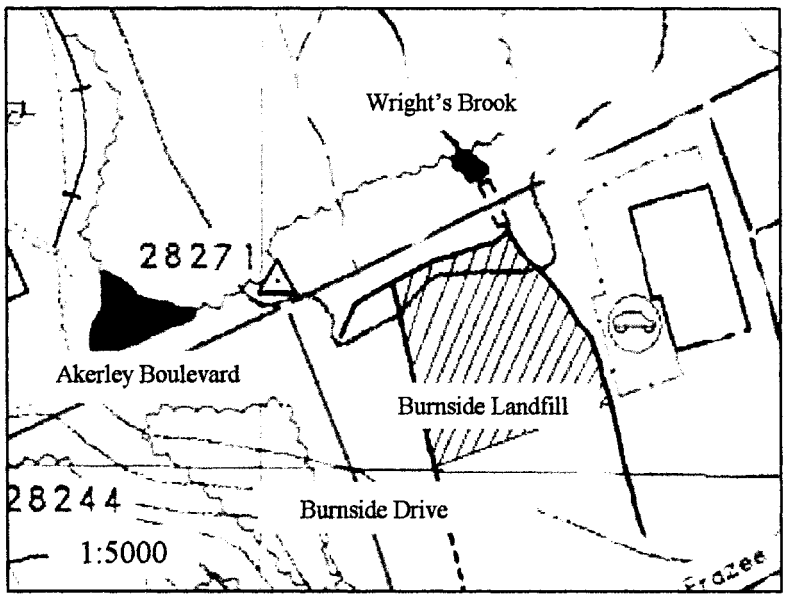


Figure 5.3. Burnside landfill.



Figure 5.4. Don Bayer's sports field.

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The area around Black Lake landfill is steeply sloped to the northeast, and drains first into a dense cattail-dominated natural wetland system and then through a culvert beneath Burnside Drive into the northern ditch of the Don Bayer's Sports Field, which ultimately drains into Wright's Brook. The former Burnside landfill (currently Don Bayer's Sports Field) is also leaching contaminants into the northern ditch and then into the Wright's Brook. Leachate from the former landfill beneath the sports field, as well as urban runoff from an adjacent parking lot discharges into stormwater ditches which surround the former landfill on three sides. All three ditches connect, and discharge via culvert located beneath Akerley Boulevard (Figure 5.5). This discharge is received in a small marshy area, which is connected directly to Wright's Brook (Ghaly and Côté, 2001). The marshy area has been transformed into the engineered wetland since 1999. The Wright's Brook is a natural ecosystem starts at the corner of Akerley Boulevard and Burnside Drive and traverses approximately 4.6 km through forest lands, Enchanted Lake and Flat Lake before discharging into the Bedford Basin as shown in Figure 5.6 (Ghaly and Cote, 2001).

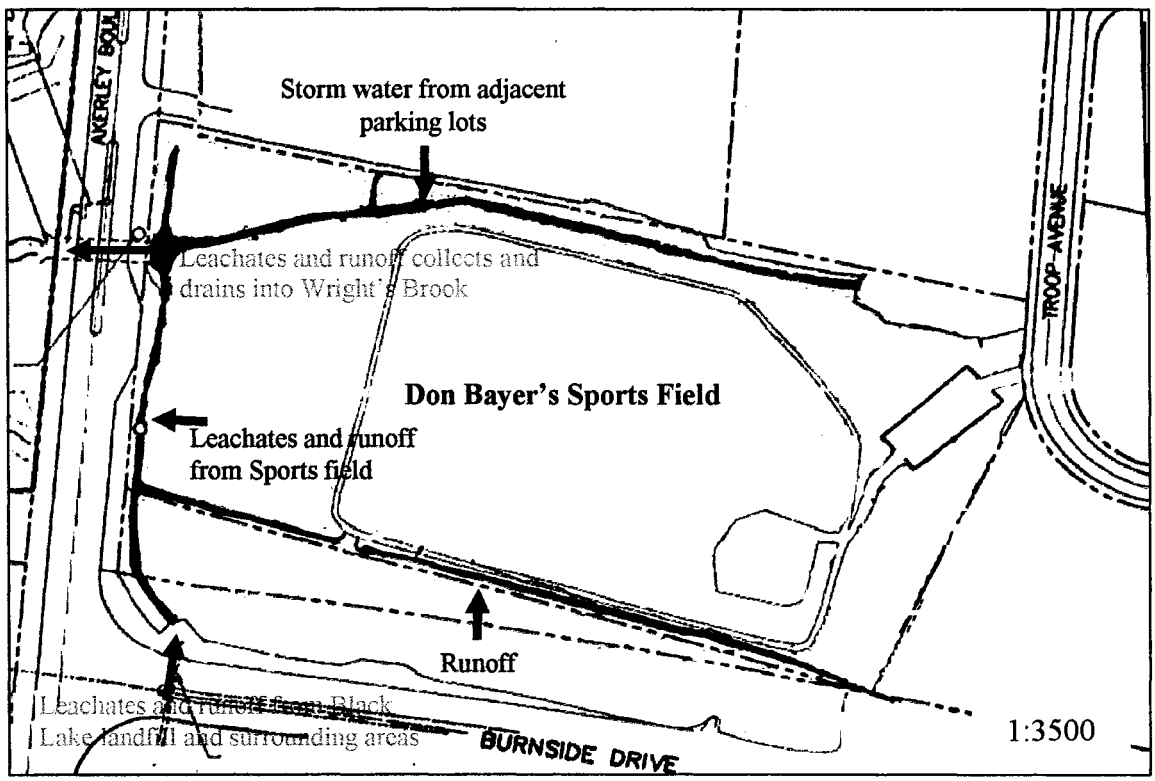


Figure 5.5. Don Bayer's sports field landfill and the ditches connected to the landfills.

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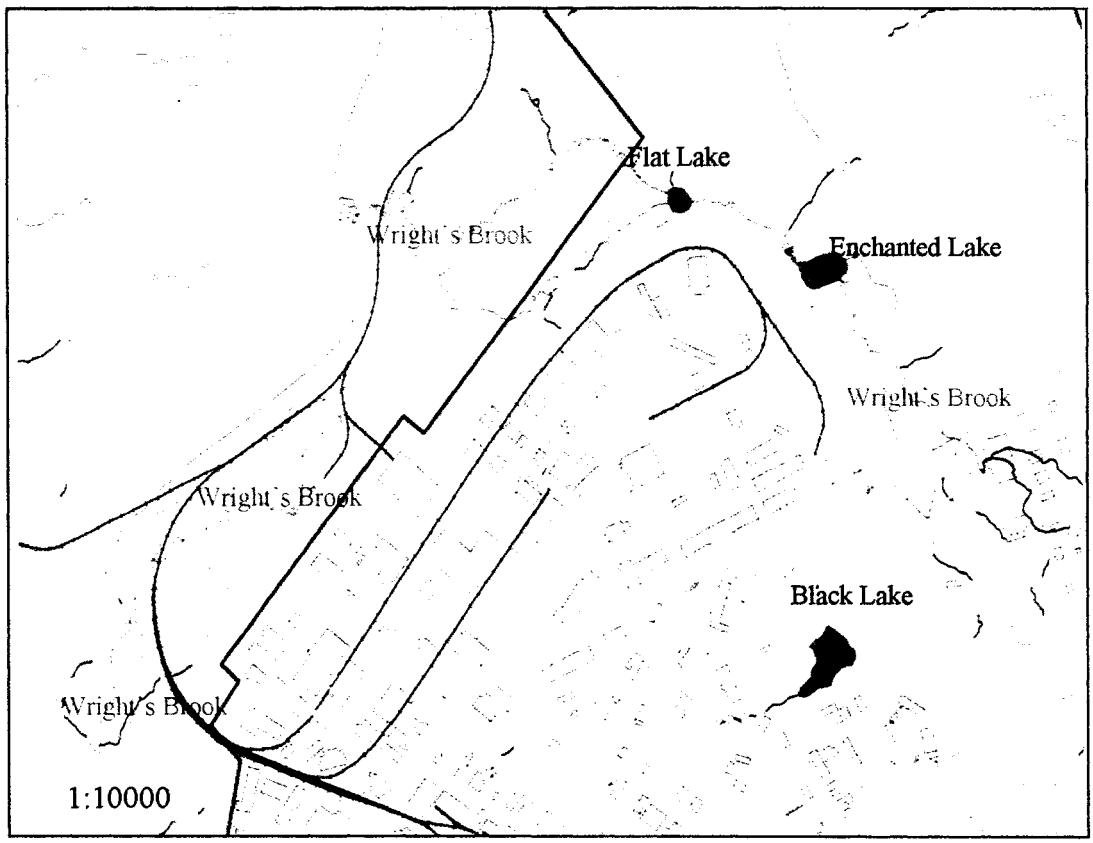


Figure 5.6. Wright's brook.

5.4 Climate Normals

In the Spring of 2003, site investigations along with discussions, maps and schematics offered by Mr. John Sibbald, a Pollution Prevention Coordinator for the Halifax Regional Municipality and Mr. Rick Giffin, a Civil Engineer with CBCL, lead to the discovery of four watershed areas which directly drained into Wright Brook or the constructed treatment wetland system. These watershed areas are referred to herein as watersheds 1, 2, 3, and 4 (Figure 5.7). Watershed 1 currently drains into the Burnside Constructed Treatment Wetland System via a ditch and a culvert under Akerley Boulevard. Watershed 2 drains through a culvert beneath Akerley Boulevard into a dense, cattail-dominated natural wetland system on the corner of Akerley Boulevard and Burnside Drive, then into a ditch adjacent to the Don Bayer Sports Field and finally into the wetland system via a culvert under Akerley boulevard. Watershed 3 encompasses the corner of Akerley Boulevard and Burnside Drive and drains through a culvert under Burnside Drive into a

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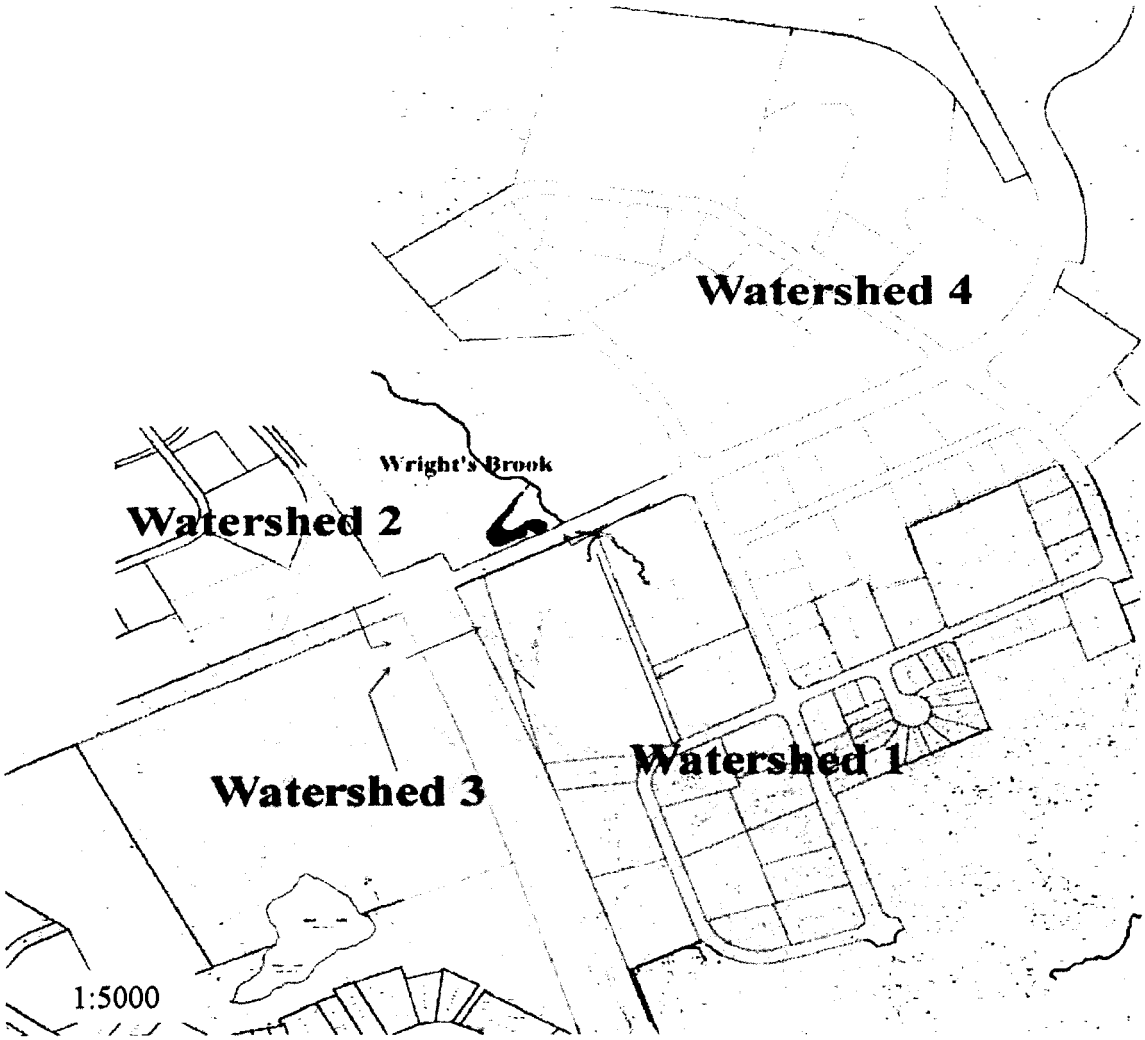


Figure5.7. Wright's brook headwater watersheds.

ditch and finally into wetland via culvert under Akerley Boulevard. Watershed 4 drains directly into the mouth of Wright Brook via a ditch and a culvert beneath Akerley Boulevard and encompasses areas on both the north and south sides of Akerley Boulevard. In order to assess the monthly runoff characteristics of each watershed, the local area climate normals were investigated. The average monthly climate normals for the area for the period of 1971 - 2000 are presented in Table 5.1. The watershed precipitation, evaporation and runoff are presented in Table 5.2. The total monthly runoff for each watershed area is presented in Table 5.3. The tables are complimented with bar graphs (Figures 5.8–5.14) for visual demonstration of the monthly variations of each climate variable. The information presented were obtained from the Shearwater A Weather Station in Dartmouth (Environment Canada, 2003).

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Table 5.1. Average values of the watershed climate normals for the period of 1971 - 2000 (Environment Canada, 2003).

Month	Atmospheric Pressure		Vapor Pressure		Relative Humidity	Saturated Vapor Pressure		Wind Speed	Mean Temperature
	(kPa)	(mm Hg)	(kPa)	(mm Hg)	(%)	(kPa)	(mm Hg)	(km/h)	(°C)
January	100.61	754.68	0.40	3.00	76	0.53	3.95	19	-4.6
February	100.68	755.20	0.38	2.85	74	0.51	3.85	19	-4.9
March	100.66	755.05	0.47	3.53	72	0.65	4.90	19	-1.1
April	100.67	755.13	0.63	4.73	70	0.90	6.75	18	3.8
May	100.92	757.00	0.88	6.60	70	1.26	9.43	15	8.8
June	100.84	756.40	1.24	9.30	70	1.77	13.29	14	13.8
July	100.89	756.78	1.6	12.00	72	2.22	16.67	12	17.5
August	100.98	757.45	1.65	12.38	70	2.35	17.68	12	17.9
September	101.11	758.43	1.34	10.05	67	2.00	15.00	14	14.4
October	101.07	758.13	0.99	7.43	69	1.43	10.76	15	9.3
November	100.88	756.70	0.73	5.48	74	0.99	7.40	17	4.2
December	100.75	755.73	0.5	3.75	78	0.64	4.81	19	-1.8

Table 5.2. Average monthly values of precipitation, evaporation and runoff for Shearwater A, Nova Scotia for the period of 1971 - 2000 (Environment Canada, 2003).

Month	Precipitation (mm/month)			Evaporation (mm/month)	Net Precipitation (mm/month)	Total Runoff** (mm/month)
	Rainfall	Snowfall*	Total			
January	95.5	48.0	143.5	1.5	142.0	66.7
February	69.3	46.0	115.3	1.7	113.6	53.4
March	97.2	32.0	129.2	2.3	126.9	59.6
April	97.9	14.0	111.9	3.3	108.6	51.0
May	110.8	2.0	112.8	3.9	108.9	51.2
June	107.8	0	107.8	5.3	102.5	48.2
July	107.4	0	107.8	5.6	102.2	48.0
August	96.9	0	96.9	6.4	90.5	42.5
September	100.1	0	100.1	6.6	93.5	43.9
October	124.9	2.0	126.9	4.7	122.2	57.4
November	129.0	9.0	138.0	2.9	135.1	63.5
December	117.6	37.0	154.6	1.8	152.8	71.8

* The water equivalent of snowfall is determined by melting the snow that falls into Nipher gauges.
** Total Runoff was calculated using the Rational Formula

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Table 5.3. Average monthly runoff for the four watershed areas for the period of 1971 - 2000.

Month	Watershed Runoff (m^3/d)				Total Runoff (m^3/d)
	1	2	3	4	
January	771.94	65.03	259.71	1029.49	2126.17
February	641.04	53.99	215.67	854.92	1765.63
March	657.89	55.42	221.34	877.39	1812.05
April	616.91	51.96	207.55	822.74	1699.17
May	612.61	51.60	206.10	816.99	1687.31
June	598.90	50.45	201.49	798.72	1649.57
July	558.95	47.08	188.05	745.43	1539.52
August	583.44	49.15	196.29	778.10	1606.98
September	514.75	43.36	173.18	686.49	1417.78
October	709.55	59.77	238.72	946.29	1954.33
November	830.33	69.94	279.35	1107.36	2286.98
December	903.57	76.11	303.99	1205.04	2488.71

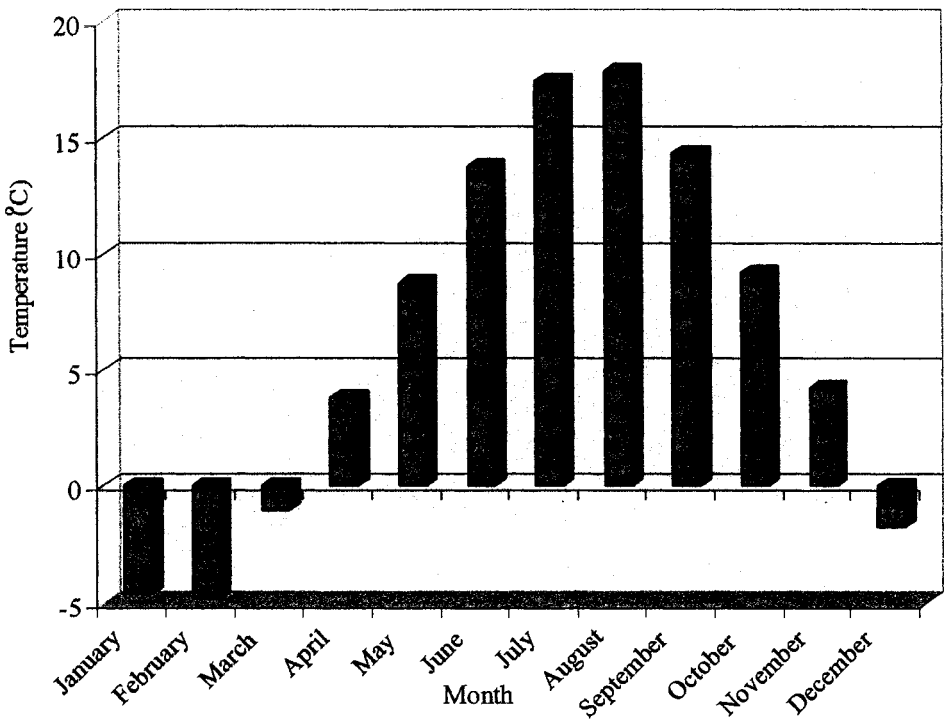


Figure 5.8. Average monthly temperature for the period of 1971 - 2000.

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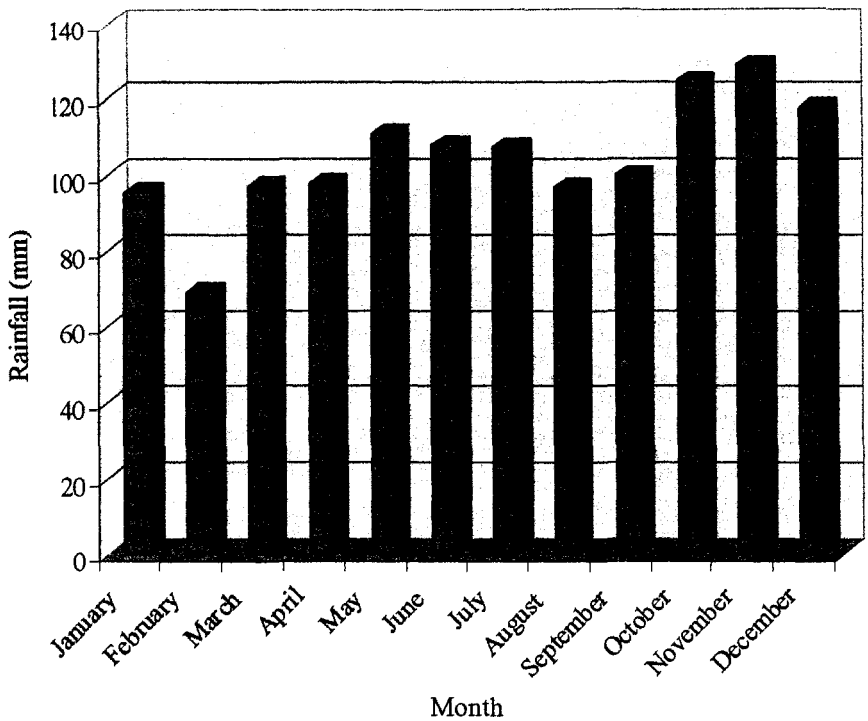


Figure 5.9. Average monthly rainfall for the period of 1971 - 2000.

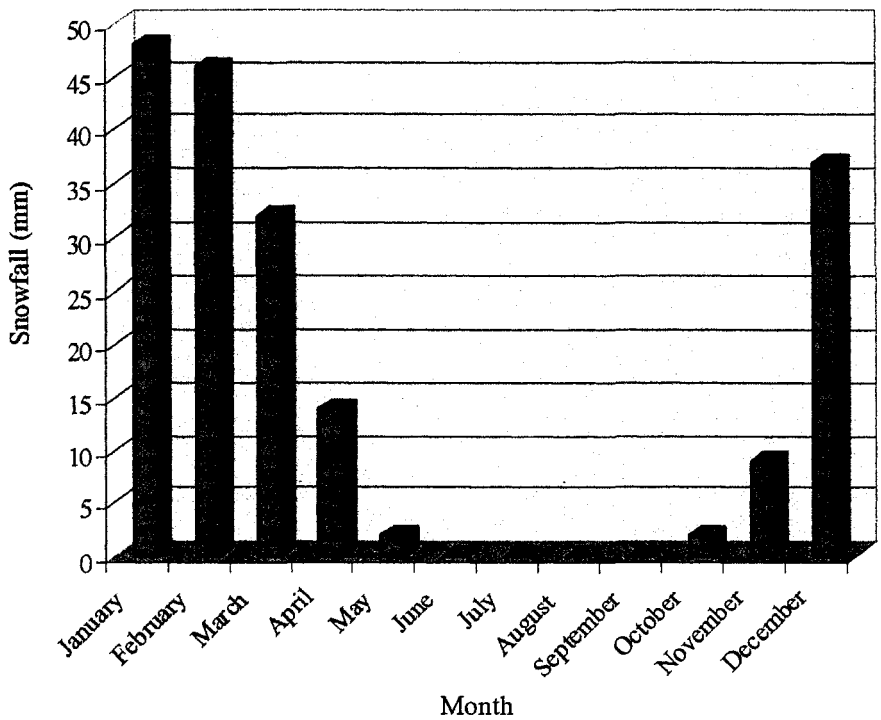


Figure 5.10. Average monthly snowfall for the period of 1971 - 2000.

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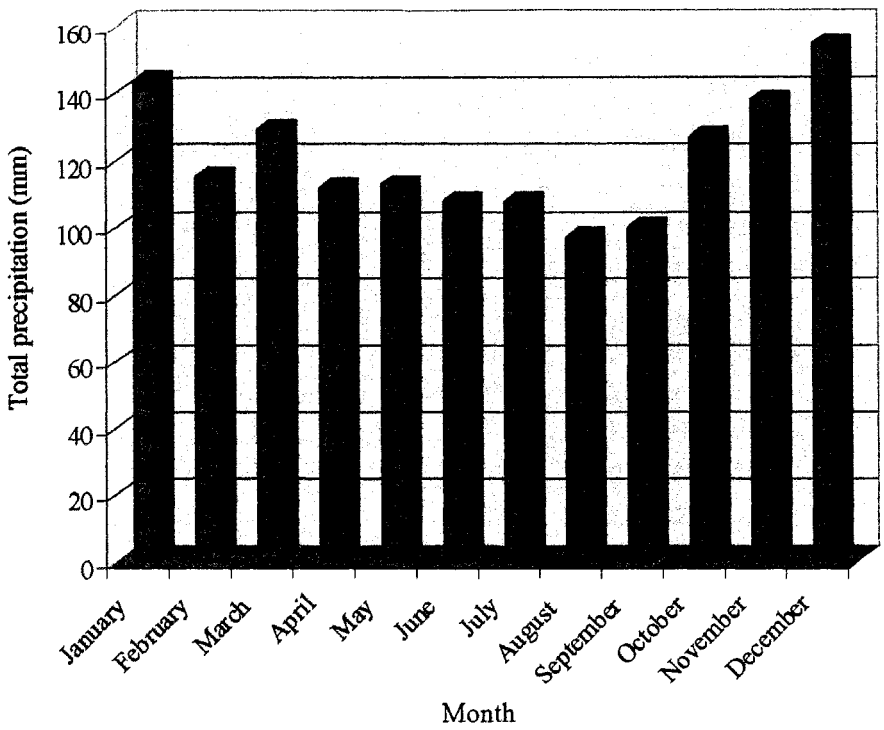


Figure 5.11. Average monthly total precipitation for the period of 1971 - 2000.

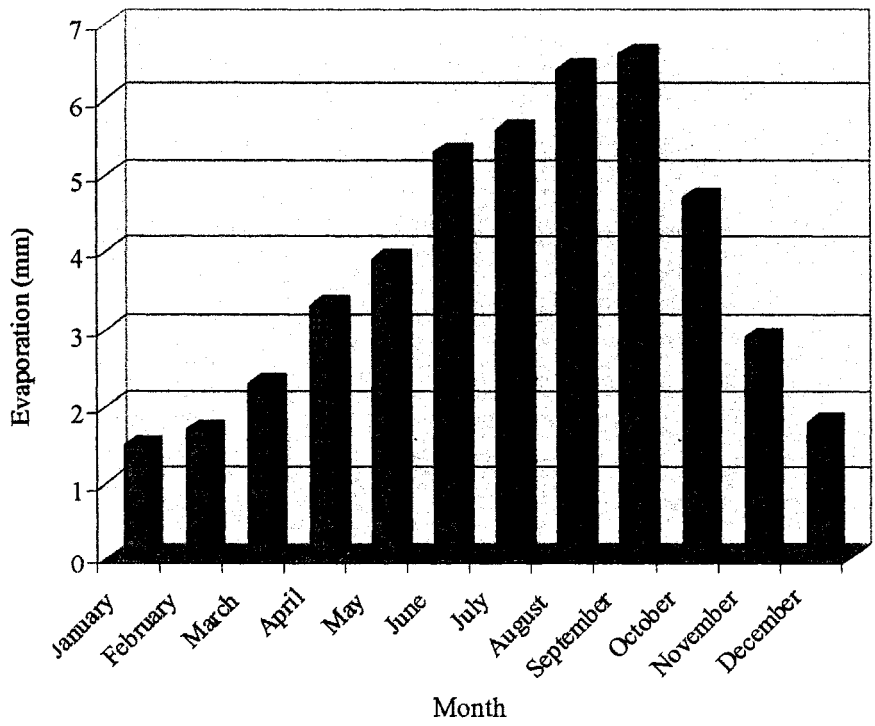


Figure 5.12. Average monthly evaporation for the period of 1971 -2000.

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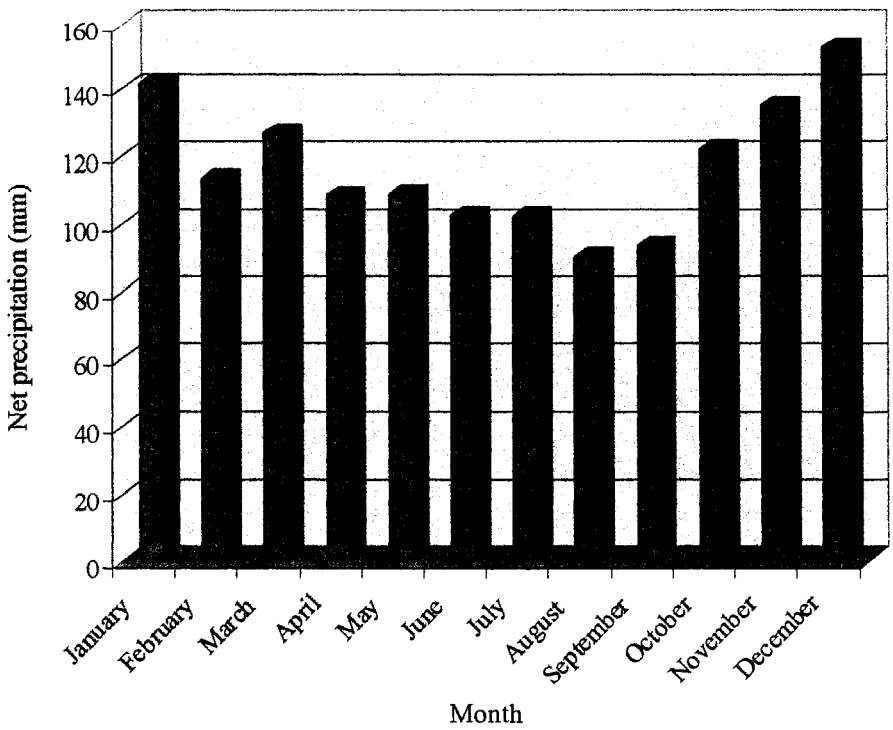


Figure 5.13. Average monthly net precipitation for the period of 1971 - 2000.

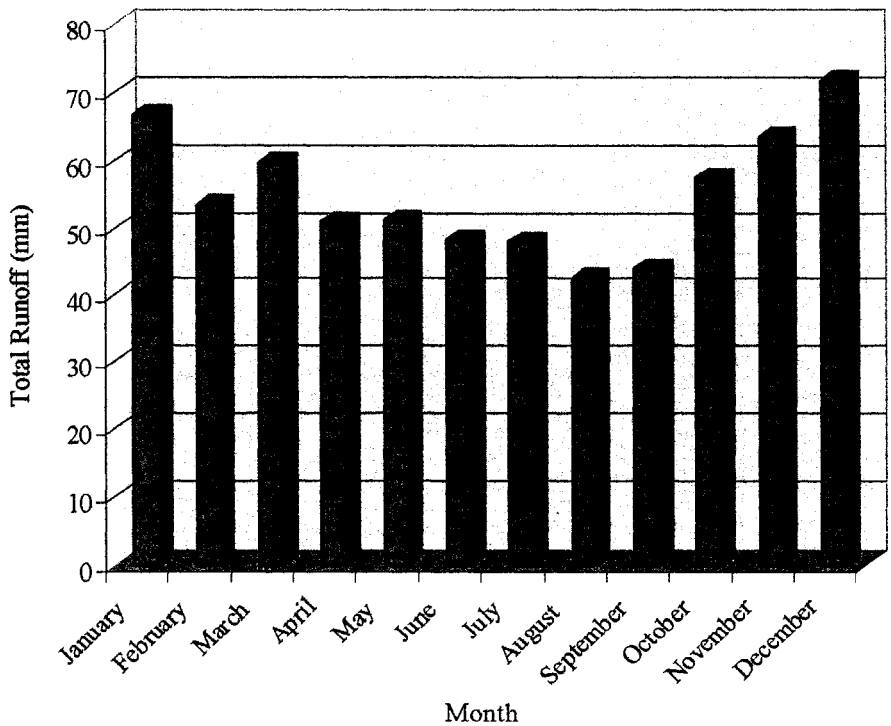


Figure 5.14. Average monthly total runoff for the period of 1971 - 2000.

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The recorded atmospheric pressure ranged from 100.61 kPa (754.7 mm Hg) during January to 101.11 kPa (758.4 mm Hg) during September with an annual average of 100.84 kPa (756.4 mm Hg). The vapor pressure ranged from 0.38 kPa (2.9 mm Hg) during February to 1.65 kPa (12.4 mm Hg) during August with an annual average of 0.90 kPa (6.7 mm Hg). The saturated vapor pressure ranged from 0.514 kPa (3.9 mm Hg) during February to 2.357 kPa (17.7 mm Hg) during August with an annual average of 1.272 kPa (9.5 mm Hg).

The recorded relative humidity varied from 67 % during of September to 78 % during December with an annual average of 72 %. The recorded average wind speeds ranged from 12 km/h for both July and August to 19 km/h for the months of January to March with an annual average of 16.1 km/h. The average high temperature varied from -0.6 °C during February to 22.1 °C during August, while the average low temperature varied from -9.1 °C during February to 13.7 °C during August. The recorded average mean temperatures were -4.85 °C and 17.9 °C for February and August, respectively.

The average rainfall varied from 60 mm/month during February to 130 mm/month during November. The average snowfall (as water equivalent, which was determined by melting the snow that fell into the station's Nipher gauges), varied from 0 cm/month for the months of May through September to 48.9 mm/month during January. The total precipitation (which is the summation of the rainfall and the water equivalent of the snowfall) varied from 9.2 cm/month during September to 15.1 cm/month during December. The recorded average evaporation rates ranged from 0.2 cm/month during January to 0.660 cm/month during September. The net precipitation (which is computed by subtracting evaporation from the total precipitation) varied from 9.2 cm/month during July to 14.9 cm/month during December. The maximum and minimum annual total runoff (calculated using the rational formula) was 7.0 cm/month for December and 4.3 cm/month for July.

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5.5 Watersheds Discharging in the Treatment Wetland

Watershed characteristics were assessed for each watershed area draining into the Wright Brook ecosystem which includes the Burnside Constructed Treatment Wetland System located at the head of the Wright Brook, which was constructed in the fall of 2001. However, for the purpose of clarity, separate runoff calculations were assessed for each watershed area. The average and peak runoff rates for each watershed area were calculated using the following Rational Formula (Burney, 2003):

Runoff = (runoff coefficient) x (precipitation) x (watershed area) (5.1)

A runoff coefficient of 0.47 was used based on the quantity of land designated for different land-use purposes, and the effects of that land on runoff amounts. Based on the climate information obtained from the Shearwater A Weather Station in Dartmouth, the average precipitation volume used in the average runoff calculation was 0.153 mm/h and the peak precipitation volume used in the peak runoff calculation was 39 mm/h.

5.5.1 Watershed 1

Watershed 1, which currently drains into the Burnside Constructed Treatment Wetland System, is approximately 38.69 ha in size. A schematic diagram showing the storm water system serving watershed 1 is illustrated in Figure 5.15. This watershed area supports several commercial buildings and adjoining parking areas as well as ungraded lots currently undergoing development along the more southern and eastern boundaries of the site (Figures 5.16 and 5.17). Drains collecting stormwater from north and south sides of Frazee Avenue, as well as areas surrounding Troop Avenue and Williams Avenue connect at Frazee Avenue and subsequently drain into the stormwater ditch framing the eastern boundary of the Don Bayer Sports Field and ultimately drains into the Wright's Brook through a culvert system (Figure 5.18).

The highest 30 year (1971-2000) average total runoff for watershed 1 was 903.57 m^3/day during December while the lowest total runoff was 514.75 m^3/day during September with

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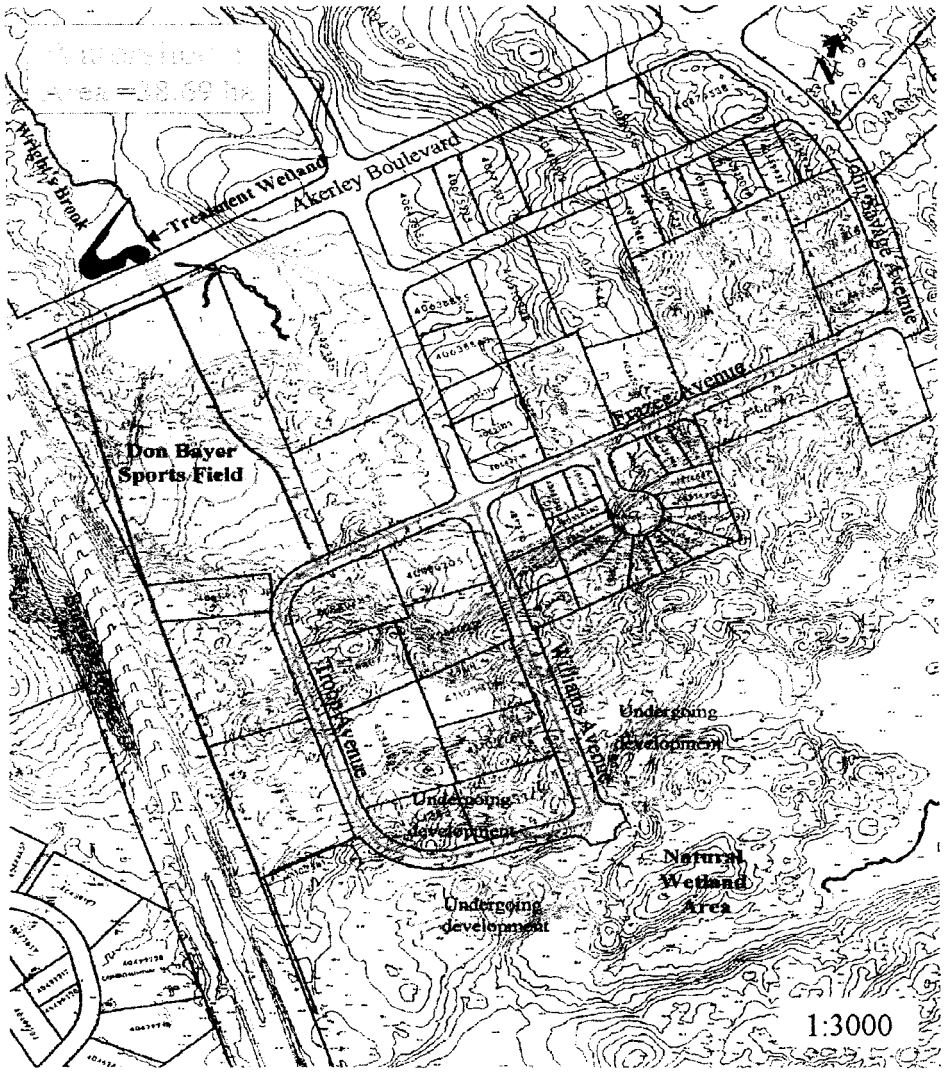


Figure 5.15. Watershed 1.



Figure 5.16. Ditch collecting stormwater from the commercial buildings in watershed 1.

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Figure 5.17. Ditch collecting storm-water from the Don Bayer's sports field.

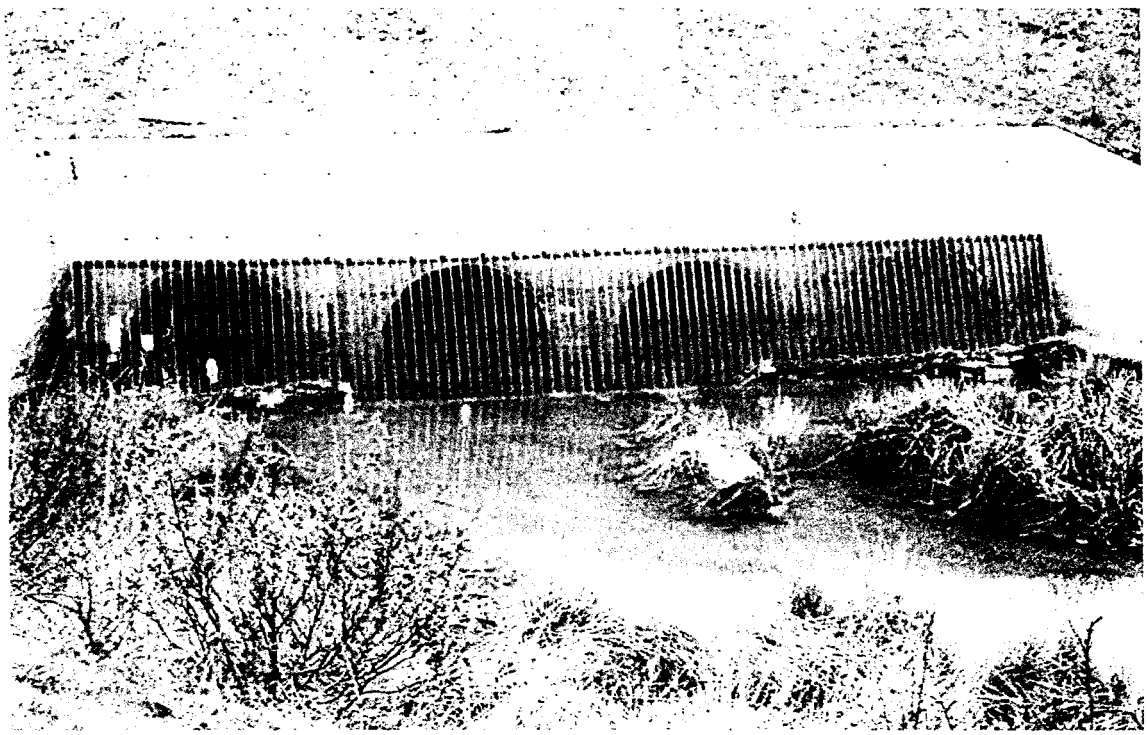


Figure 5.18. Akerley culvert structure.

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an average total runoff of 666.66 m^3/day (Figure 5.19). The water quality analysis of the samples collected from watershed 1 (Table 5.4) indicated that arsenic and iron were above the Canadian Council of Ministers of the Environment (CCME) water quality guidelines for the protection of fresh water life. Also manganese was above the British Columbia Minister of Environment, Lands and Parks (BCMELP) guidelines for the protection of freshwater aquatic life. Using the total runoff (m^3/day) and the concentration (mg/L) of the heavy metals in the water collected from watershed 1, the iron and manganese loads which enters Burnside Constructed Treatment Wetland System were estimated to be 15000 kg/year and 3211.94 kg/year, respectively. No hydrocarbons were detected in samples taken from watershed 1 (Table 5.5).

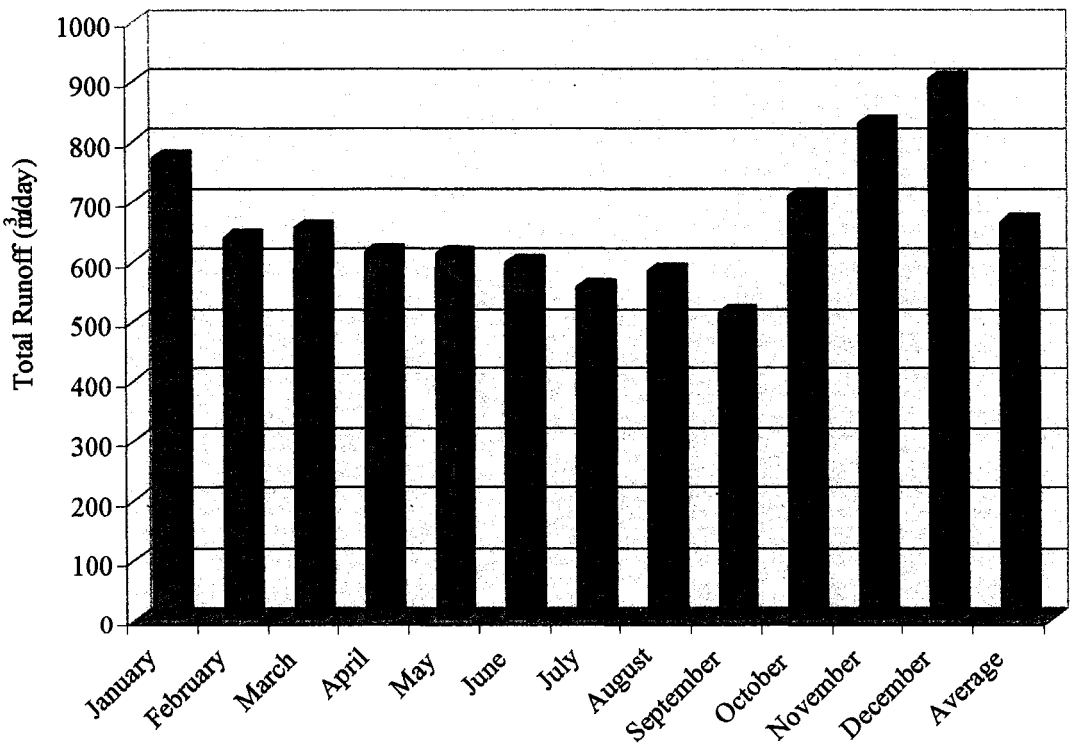


Figure 5.19. 30-year-average monthly runoff for watershed 1 (1971-2000).

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Table 5.4. Results of the water quality analyses for watershed 1.

Parameters	Method	EQL [1]	Units	Guidelines	Measured		
					Summer 2000	Location 1*	Location 2*
Sodium	ICP-OES	0.1	mg/L		62.7	144	38.9
Potassium	ICP-OES	0.1	mg/L		1.8	2.2	1.2
Calcium	ICP-OES	0.1	mg/L		28.23	29.7	16.8
Magnesium	ICP-OES	0.1	mg/L		2.9	3.8	1.8
Alkalinity (as CaCO3)	COBAS	5	mg/L		63	36	26
Sulfate	COBAS	2	mg/L		15	28	26
Chloride	COBAS	1	mg/L		100	230	65
Reactive Silica (as SiO2)	COBAS	0.5	mg/L		5.3	2.9	5
Ortho Phosphate (as P)	COBAS/911	0.01	mg/L		0	1.5	0.16
Nitrite	COBAS	0.01	mg/L	0.6[2]	0	<0.01	<0.01
Nitrate + Nitrite (as N)	COBAS	0.05	mg/L		0	0.07	0.52
Nitrate (as N)	COBAS	0.05	mg/L		0	0.07	0.52
Ammonia (as N)	Auto Color	0.05	mg/L		0.47	<0.05	<0.05
Turbidity	NEPH.	0.1	NTU		25.6	0.9	0.4
Conductance (RCAp)	Electrode	1	uS/cm		534	946	314
pH	Electrode	-	Units		6.7	7.6	7.3
Hardness (as CaCO3)	Calculated	0.1	mg/L		82.4	89.8	49.4
Bicarbonate (as CaCO3)	Calculated	1	mg/L		63	36	26
Carbonate (as CaCO3)	Calculated	1	mg/L		<1	<1	<1
TDS (Calculated)	Calculated	1	mg/L		255	463	173
Cation Sum	Calculated	0.1	meq/L		4.45	8.12	2.71
Anion Sum	Calculated	0.1	meq/L		4.4	7.79	2.93
Ion Balance	Calculated	-	%		0.59	2.04	3.86
Saturation pH @ 4C	Calculated	-	Units		8.65	8.86	9.21
Saturation pH @ 20C	Calculated	-	Units		8.22	8.46	8.81
Aluminum	ICP-MS	10	ug/L	5-100[2]	30	30	20
Antimony	ICP-MS	2	ug/L	20[4]	<2	<2	<2
Arsenic	ICP-MS	2	ug/L	5[2]	6.0	2	3
Barium	ICP-MS	5	ug/L	1000[3]	34	22	12
Beryllium	ICP-MS	2	ug/L	11[4]	<2	<2	<2
Bismuth	ICP-MS	2	ug/L		<2	<2	<2
Boron	ICP-MS	5	ug/L	200[4]	28	13	6
Cadmium	ICP-MS	0.3	ug/L	0.012[2]	<0.3	<0.3	<0.3
Chromium	ICP-MS	2	ug/L	1-8.9[2]	<2	<2	<2
Cobalt	ICP-MS	1	ug/L	0.9[4]	<10	<1	<1
Copper	ICP-MS	2	ug/L	2-4[2]	<20	3	3
Iron	ICP-MS	50	ug/L	300[2]	6600	120	<50
Lead	ICP-MS	0.5	ug/L	1-7[2]	<0.5	<0.5	<0.5
Manganese	ICP-MS	2	ug/L	1000-1500[3]	1800	220	3
Molybdenum	ICP-MS	2	ug/L	73[2]	<2	<2	<2
Nickel	ICP-MS	2	ug/L	25-150[2]	<2	<2	<2
Selenium	ICP-MS	2	ug/L	1[2]	<2	<2	<2
Silver	ICP-MS	0.5	ug/L	0.1[2]	<0.5	<0.5	<0.5
Strontium	ICP-MS	5	ug/L		140	120	85
Thallium	ICP-MS	0.1	ug/L	0.8[2]	<0.1	<0.1	<0.1
Tin	ICP-MS	2	ug/L		<2	<2	<2
Titanium	ICP-MS	2	ug/L		<2	2	<2
Uranium	ICP-MS	0.1	ug/L		<0.1	<0.1	0.1
Vanadium	ICP-MS	2	ug/L		<2	<2	<2
Zinc	ICP-MS	5	ug/L	30[2]	11	7	14
Phosphorus	ICP-OES	0.1	mg/L		<0.1	1.8	0.2
Total Org. Carbon (by UV)	U.V.-ox	0.5	mg/L		1.9	2.7	1.8

* Samples were taken Summer 2003

1 Estimated Quantitation Limit, which is the minimum concentration that can be reliably reported.

2 Canadian Council of Ministers of the Environment water quality guidelines for the protection of fresh water life.

3 British Columbia Minister of Environment, Lands, and Parks Guidelines

4 Ontario Ministry of Environment Environmental Water Quality Objectives

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Table 5.5. Results of the hydrocarbon analyses for watershed 1.

Parameters	Method	EQL[1]	Units	Guidelines[2]	Measured*
Benzene	P&T	0.001	mg/L	0.370	< 0.001
Toluene	P&T	0.001	mg/L	0.002	< 0.001
Ethylbenzene	P&T	0.001	mg/L	0.900	< 0.001
Xylenes	P&T	0.002	mg/L	0.002[3]	< 0.002
C6 - C10 HC {less BTEX}	Calculated	0.010	mg/L	NGA	< 0.010
>C10-C21 (Fuel Range)	GC/FID	0.050	mg/L	NGA	< 0.050
>C21-C32 (Lube Range)	GC/FID	0.100	mg/L	NGA	< 0.100
Modified TPH - Tier 1	Calculated	0.200	mg/L	NGA	< 0.200

* Samples were taken Summer 2003.
1 Estimated Quantitation Limit, which is the minimum concentration that can be reliably reported.
2 Canadian Council of Ministers of the Environment water quality guidelines for the protection of fresh water life.
3 Ontario Minister of Environment Environmental Quality Guidelines.
TPH Total Petroleum Hydrocarbons
NGA No Guideline Available

5.5.2 Watershed 2

A schematic diagram showing the direction of water in watershed 2 is illustrated in Figure 5.20. This relatively small watershed, which is located on the northern side of Akerley Boulevard, is approximately 3.36 ha in size. Watershed 2 drains initially, through a culvert beneath Akerley Boulevard, into a dense, cattail-dominated wetland on the southwestern corner of Akerley Boulevard and Burnside Drive which is often occupied by waterfowl then into the northern storm water ditch of the Don Bayer Sports Field and ultimately into the Burnside Constructed Treatment Wetland System. It received water from the parking lots of two commercial buildings (Figures 5.21 and 5.22).

The highest 30 year (1971-2000) average total runoff for watershed 2 was 76.11 m^3/day during December while the lowest total runoff was 43.36 m^3/day during September (Figure 5.23) with an average total runoff of 56.16 m^3/day. The water quality analyses of the samples collected from watershed 2 (Table 5.6) indicated that no parameters exceeded the specified water quality guidelines. Very low concentrations of hydrocarbons were detected in the water samples collected from watershed 2 (Table 5.7).

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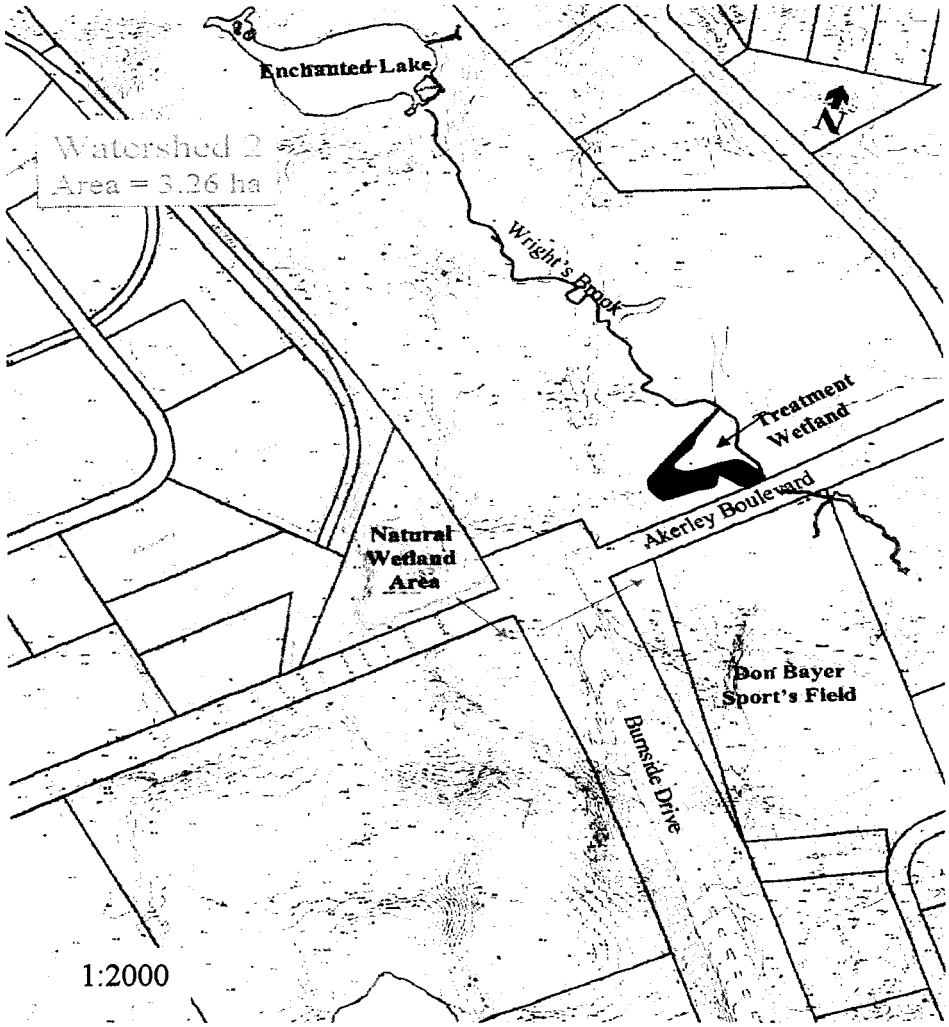


Figure 5.20. Watershed 2.



Figure 5.21. The natural wetland in watershed 2.

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Figure 5.22. Adjacent development in watershed 2.

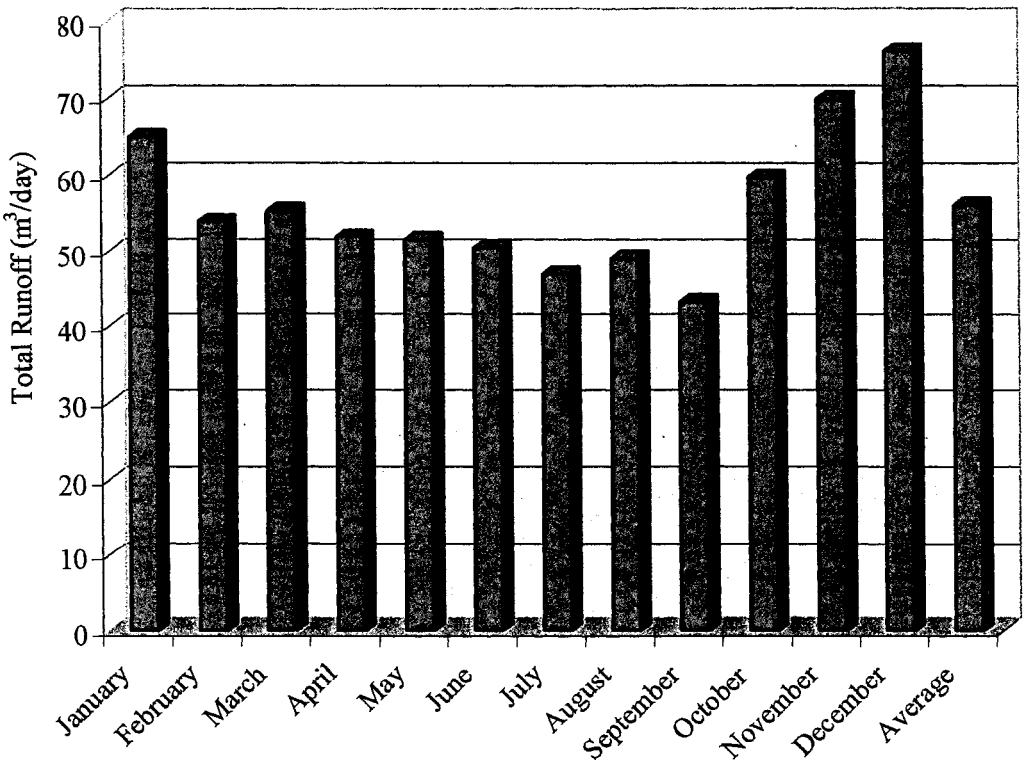


Figure 5.23. 30-year-average monthly runoff for watershed 2 (1971-2000).

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Table 5.6. Results of the water quality analyses for watershed 2.

Parameters	Method	EQL[1]	Units	Guideline	Measured (Summer 2003)	
					May 1	June 15
Sodium	ICP-OES	0.1	mg/L		148	168
Potassium	ICP-OES	0.1	mg/L		13.1	15.6
Calcium	ICP-OES	0.1	mg/L		149	154
Magnesium	ICP-OES	0.1	mg/L		11.4	12.1
Alkalinity (as CaCO3)	COBAS	5	mg/L		330	360
Sulfate	COBAS	2	mg/L		120	130
Chloride	COBAS	1	mg/L		240	240
Reactive Silica (as SiO2)	COBAS	0.5	mg/L		6.9	8.9
Ortho Phosphate (as P)	COBAS/911	0.01	mg/L		<0.02	0.05
Nitrite	COBAS	0.01	mg/L	0.6[2]	<0.01	0.4
Nitrate + Nitrite (as N)	COBAS	0.05	mg/L		0.42	0.15
Nitrate (as N)	COBAS	0.05	mg/L		0.42	0.10
Ammonia (as N)	Auto Color	0.05	mg/L		<0.05	0.05
Turbidity	NEPH.	0.1	NTU		0.2	15
Conductance (RCAp)	Electrode	1	uS/cm		1700	1680
pH	Electrode	-	Units		8.2	7.4
Hardness (as CaCO3)	Calculated	0.1	mg/L		419	434
Bicarbonate (as CaCO3)	Calculated	1	mg/L		325	359
Carbonate (as CaCO3)	Calculated	1	mg/L		5	<1
TDS (Calculated)	Calculated	1	mg/L		888	946
Cation Sum	Calculated	0.1	meq/L		15.2	16.4
Anion Sum	Calculated	0.1	meq/L		15.9	16.7
Ion Balance	Calculated	-	%		2.4	0.70
Saturation pH @ 4C	Calculated	-	Units		7.23	7.18
Saturation pH @ 20C	Calculated	-	Units		6.83	6.18
Aluminum	ICP-MS	10	ug/L	5-100[2]	<100	78
Antimony	ICP-MS	2	ug/L	20[4]	<20	150
Arsenic	ICP-MS	2	ug/L	5[2]	<20	<2
Barium	ICP-MS	5	ug/L	1000[3]	<50	56
Beryllium	ICP-MS	2	ug/L	11[4]	<20	<2
Bismuth	ICP-MS	2	ug/L		<20	<2
Boron	ICP-MS	5	ug/L	200[4]	400	380
Cadmium	ICP-MS	0.3	ug/L	0.012[2]	<3	<0.3
Chromium	ICP-MS	2	ug/L	1-8.9[2]	<20	<2
Cobalt	ICP-MS	1	ug/L	0.9[4]	<10	<1
Copper	ICP-MS	2	ug/L	2-4[2]	<20	<2
Iron	ICP-MS	50	ug/L	300[2]	<500	<50
Lead	ICP-MS	0.5	ug/L	1-7[2]	<5	<5
Manganese	ICP-MS	2	ug/L	1000-1500[3]	<20	72
Molybdenum	ICP-MS	2	ug/L	73[2]	<20	<20
Nickel	ICP-MS	2	ug/L	25-150[2]	<20	<20
Selenium	ICP-MS	2	ug/L	1[2]	<20	<20
Silver	ICP-MS	0.5	ug/L	0.1[2]	<5	<0.5
Strontium	ICP-MS	5	ug/L		670	650
Thallium	ICP-MS	0.1	ug/L	0.8[2]	<1	<0.1
Tin	ICP-MS	2	ug/L		<20	<20
Titanium	ICP-MS	2	ug/L		<20	<20
Uranium	ICP-MS	0.1	ug/L		<1	<1
Vanadium	ICP-MS	2	ug/L		<20	<20
Zinc	ICP-MS	5	ug/L	30[2]	<50	<50
Phosphorus	ICP-OES	0.1	mg/L		<0.1	<0.1
Total Org. Carbon (by UV)	U.V.-ox	0.5	mg/L		2.8	19.4

1 Estimated Quantitation Limit, which is the minimum concentration that can be reliably reported.
2 Canadian Council of Ministers of the Environment Water Quality Guidelines for the Protection of Freshwater Life.
3 British Columbia Minister of Environment, Lands, and Parks Environmental Water Quality Guidelines
4 Ontario Ministry of Environment Environmental Water Quality Objectives

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Table 5.7. Results of the hydrocarbon analyses for watershed 2.

Parameters	Method	EQL[1]	Units	Guidelines[2]	Measured*
Benzene	P&T	0.001	mg/L	0.370	< 0.001
Toluene	P&T	0.001	mg/L	0.002	< 0.001
Ethylbenzene	P&T	0.001	mg/L	0.900	< 0.001
Xylenes	P&T	0.002	mg/L	0.002[3]	< 0.002
C6 - C10 HC {less BTEX}	Calculated	0.010	mg/L	NGA	< 0.01
>C10-C21 (Fuel Range)	GC/FID	0.050	mg/L	NGA	0.110
>C21-C32 (Lube Range)	GC/FID	0.100	mg/L	NGA	0.300
Modified TPH - Tier 1	Calculated	0.200	mg/L	NGA	0.400

* Samples were taken Summer 2003.
1 Estimated Quantitation Limit, which is the minimum concentration that can be reliably reported.
2 Canadian Council of Ministers of the Environment water quality guidelines for the protection of fresh water life.
3 Ontario Minister of Environment Environmental Quality Guidelines.
TPH Total Petroleum Hydrocarbons
NGA No Guideline Available

5.5.3 Watershed 3

A schematic diagram showing the boundaries for watershed 3 is illustrated in Figure 5.24. Watershed 3, which encompasses the southwestern corner of Akerley Boulevard and Burnside Drive, is approximately 13.02 ha in size. The watershed is steeply sloped to the northeast, and drains first into a dense cattail dominated natural wetland system (Figure 5.25) and drain through a culvert beneath Burnside Drive into the northern ditch of the Don Bayer Sports Field, which ultimately drains into the Burnside Constructed Treatment Wetland System. This watershed area includes a decommissioned municipal landfill known as the Black Lake Landfill, which currently serves as a disposal site and storage area for the City of Dartmouth (Figure 5.26).

The highest total runoff for watershed 3 was during December 303.29 m^3/ day while the lowest total runoff was 173.18 m^3/ day (Figure 5.27) with an average total runoff of 224.29 m^3/ day during September. The water quality analyses of the samples collected from watershed 3 (Table 5.8) indicated that aluminum, arsenic, chromium, copper, lead, zinc and iron were highly above the CCME water quality guidelines for the protection of fresh water life. Also manganese was above the BCMELP guidelines for the protection of freshwater aquatic life. Using the total runoff (m^3/day) and the concentration (mg/L) of the heavy metals in the water collected from watershed 3, the loads aluminum, arsenic, chromium, copper, lead, zinc, iron and manganese which enter Burnside Constructed

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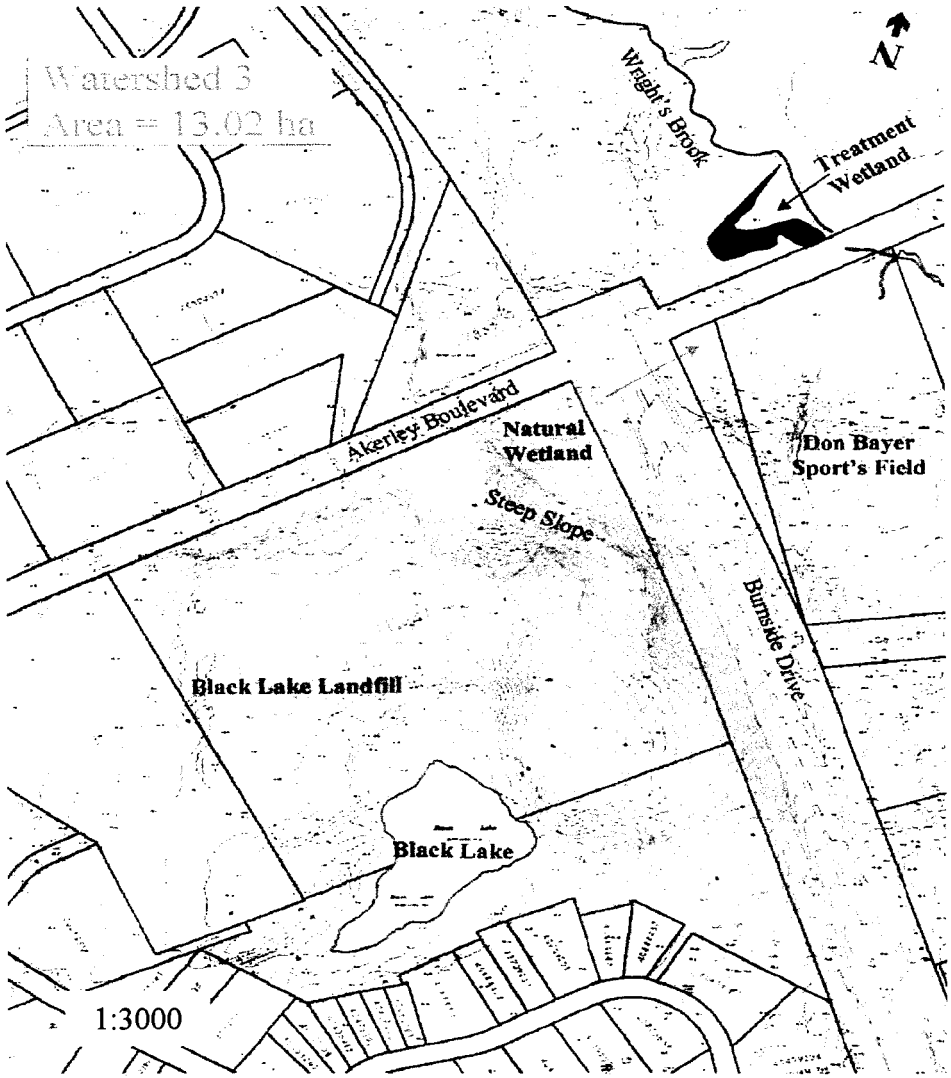


Figure 5.24. Watershed 3.



Figure 5.25. The wetland area in watershed 3.

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Figure 5.26. Piles of old tires, scraps and used asphalt stored by Halifax Regional Municipality on the top of Black lake landfill.

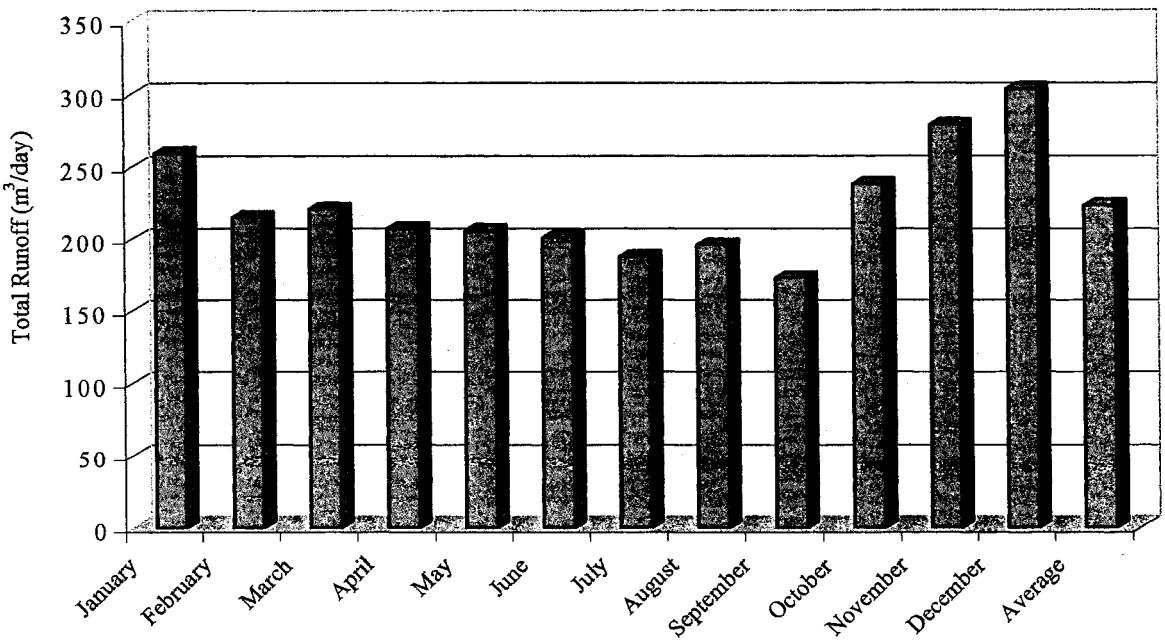


Figure 5.27. 30-year-average monthly runoff for watershed 3 (1971-2000).

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Table 5.8. Results of the water quality analyses for watershed 3.

Parameters	Method	EQL[1]	Units	Guideline	Measured (Summer 2003)	
					May 1	June 15
Sodium	ICP-OES	0.1	mg/L		110	143
Potassium	ICP-OES	0.1	mg/L		13.1	7.9
Calcium	ICP-OES	0.1	mg/L		220	134
Magnesium	ICP-OES	0.1	mg/L		18.9	10.4
Alkalinity (as CaCO3)	COBAS	5	mg/L		200	280
Sulfate	COBAS	2	mg/L		73	66
Chloride	COBAS	1	mg/L		180	190
Reactive Silica (as SiO2)	COBAS	0.5	mg/L		7.8	9.5
Ortho Phosphate (as P)	COBAS/911	0.01	mg/L		<0.02	<0.02
Nitrite	COBAS	0.01	mg/L	0.6[2]	<0.01	<0.01
Nitrate + Nitrite (as N)	COBAS	0.05	mg/L		<0.05	<0.05
Nitrate (as N)	COBAS	0.05	mg/L		<0.05	<0.05
Ammonia (as N)	Auto Color	0.05	mg/L		<0.05	<0.05
Turbidity	NEPH.	0.1	NTU		<1000	978
Conductance (RCAp)	Electrode	1	uS/cm		1240	1300
pH	Electrode	-	Units		8	7.8
Hardness (as CaCO3)	Calculated	0.1	mg/L		627	377
Bicarbonate (as CaCO3)	Calculated	1	mg/L		198	278
Carbonate (as CaCO3)	Calculated	1	mg/L		2	2
TDS (Calculated)	Calculated	1	mg/L		743	729
Cation Sum	Calculated	0.1	meq/L		17.7	14
Anion Sum	Calculated	0.1	meq/L		10.6	12.3
Ion Balance	Calculated	-	%		25	6.21
Saturation pH @ 4C	Calculated	-	Units		7.27	7.34
Saturation pH @ 20C	Calculated	-	Units		6.87	6.94
Aluminum	ICP-MS	10	ug/L	5-100[2]	38000	12000
Antimony	ICP-MS	2	ug/L	20[4]	<20	<20
Arsenic	ICP-MS	2	ug/L	5[2]	24	29
Barium	ICP-MS	5	ug/L	1000[3]	720	400
Beryllium	ICP-MS	2	ug/L	11[4]	<20	<20
Bismuth	ICP-MS	2	ug/L		<20	<20
Boron	ICP-MS	5	ug/L	200[4]	<50	<50
Cadmium	ICP-MS	0.3	ug/L	0.012[2]	<3	<3
Chromium	ICP-MS	2	ug/L	1-8.9[2]	58	20
Cobalt	ICP-MS	1	ug/L	0.9[4]	43	15
Copper	ICP-MS	2	ug/L	2-4[2]	200	41
Iron	ICP-MS	50	ug/L	300[2]	64000	42000
Lead	ICP-MS	0.5	ug/L	1-7[2]	480	51
Manganese	ICP-MS	2	ug/L	1000-1500[3]	18000	14000
Molybdenum	ICP-MS	2	ug/L	73[2]	<20	<20
Nickel	ICP-MS	2	ug/L	25-150[2]	95	30
Selenium	ICP-MS	2	ug/L	1[2]	<20	<20
Silver	ICP-MS	0.5	ug/L	0.1[2]	<5	<5
Strontium	ICP-MS	5	ug/L		570	470
Thallium	ICP-MS	0.1	ug/L	0.8[2]	<1	<1
Tin	ICP-MS	2	ug/L		<20	<20
Titanium	ICP-MS	2	ug/L		310	220
Uranium	ICP-MS	0.1	ug/L		1.5	<1
Vanadium	ICP-MS	2	ug/L		94	35
Zinc	ICP-MS	5	ug/L	30[2]	800	240
Phosphorus	ICP-OES	0.1	mg/L		1.9	0.7
Total Org. Carbon (by UV)	U.V.-ox	0.5	mg/L		<5	<5

1 Estimated Quantitation Limit, which is the minimum concentration that can be reliably reported.
2 Canadian Council of Ministers of the Environment Water Quality Guidelines for the Protection of Freshwater Life.
3 British Columbia Minister of Environment, Lands, and Parks Environmental Water Quality Guidelines
4 Ontario Ministry of Environment Environmental Water Quality Objectives

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Treatment wetland system were 3103.77, 1.96, 4.74, 16.34, 65.34, 39.21, 5227.41, and 1470.21 kg/year respectively. No hydrocarbons were detected in water samples obtained from watershed 3 (Table 5.9).

Table 5.9. Results of the hydrocarbon analysis for watershed 3.

Parameters	Method	EQL[1]	Units	Guidelines[2]	Measured*
Benzene	P&T	0.001	mg/L	0.370	< 0.001
Toluene	P&T	0.001	mg/L	0.002	< 0.001
Ethylbenzene	P&T	0.001	mg/L	0.900	< 0.001
Xylenes	P&T	0.002	mg/L	0.002[3]	< 0.002
C6 - C10 HC {less BTEX}	Calculated	0.010	mg/L	NGA	< 0.010
>C10-C21 (Fuel Range)	GC/FID	0.050	mg/L	NGA	< 0.050
>C21-C32 (Lube Range)	GC/FID	0.100	mg/L	NGA	< 0.100
Modified TPH - Tier 1	Calculated	0.200	mg/L	NGA	< 0.200

* Samples were taken Summer 2003.
1 Estimated Quantitation Limit, which is the minimum concentration that can be reliably reported.
2 Canadian Council of Ministers of the Environment water quality guidelines for the protection of fresh water life.
3 Ontario Minister of Environment Environmental Quality Guidelines.
TPH Total Petroleum Hydrocarbons
NGA No Guideline Available

5.5.4 Watershed 4

A schematic diagram shows the storm water system serving watershed 4 is illustrated in Figure 5.28. Watershed 4, which drains directly into the mouth of Wright Brook via a culvert beneath Akerley Boulevard and encompasses areas on both the north and south sides of Akerley Boulevard, is approximately 51.61 ha in size. All stormwater flows from this watershed into a centrally located stormwater pipe beneath Akerley Boulevard which subsequently discharges into Wright Brook (Figure 5.29). It supports commercially developed areas as well as undeveloped wooded areas, especially along the eastern boundaries of Gloria McCulskey and John Savage Avenues.

The highest 30 year (1971-2000) average total runoff for watershed 4 is 1205.04 m^3/day during December while the lowest total runoff for watershed 4 is 686.5 m^3/day during September (Figure 5.30) with an average total runoff of 889.1 m^3/day. The water quality analyses of the samples collected from watershed 4 (Table 5.10) indicated that aluminum

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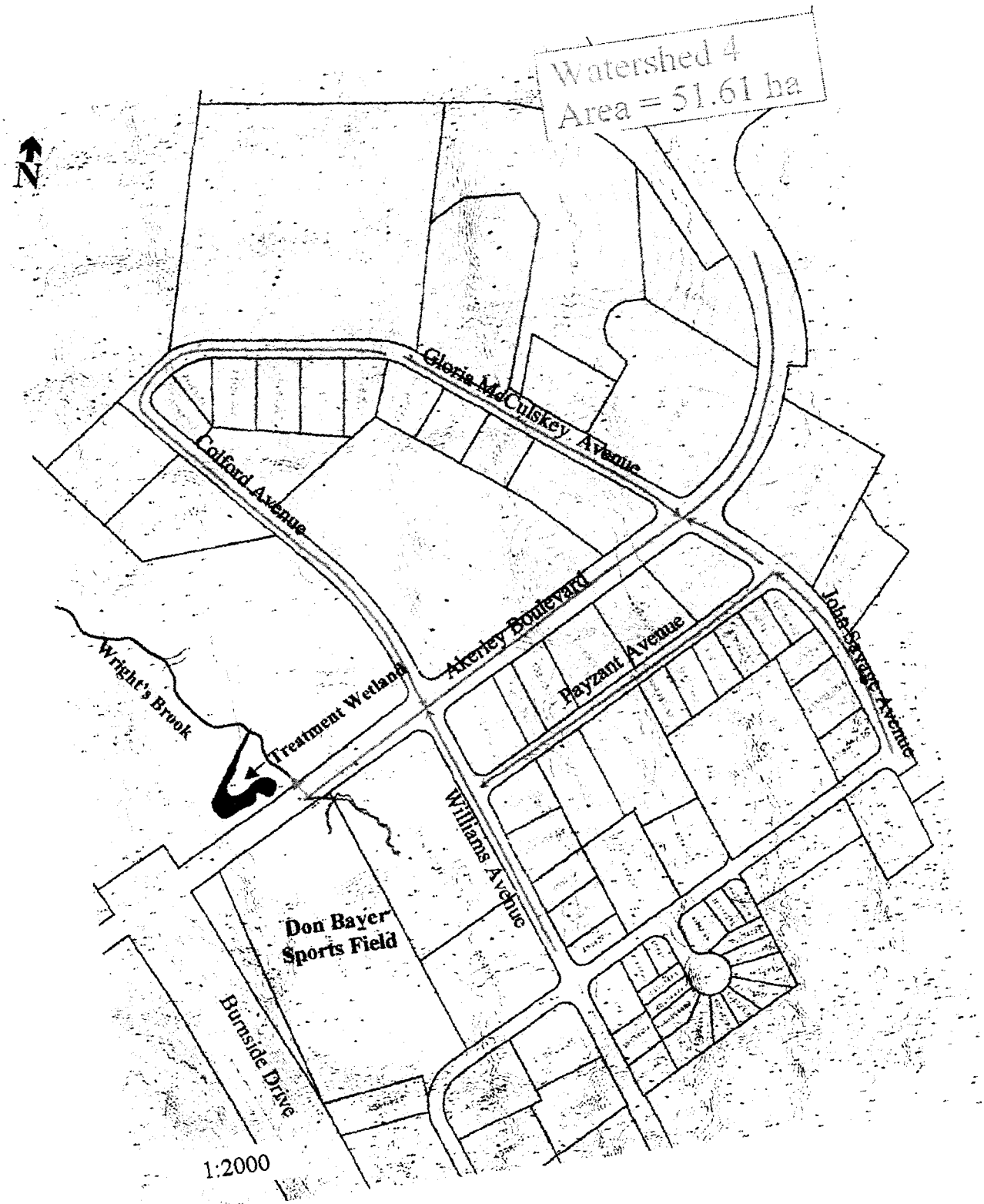


Figure 5.28. Watershed 4.

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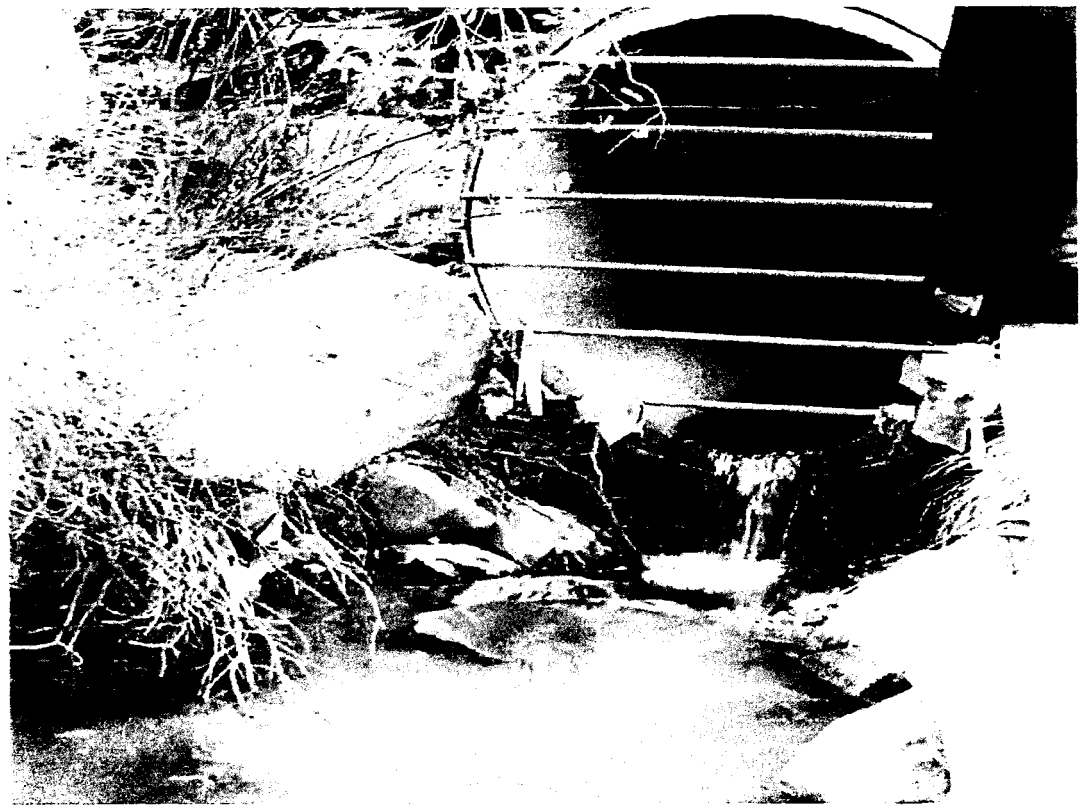


Figure 5.29. Culvert draining stormwater from watershed 4.

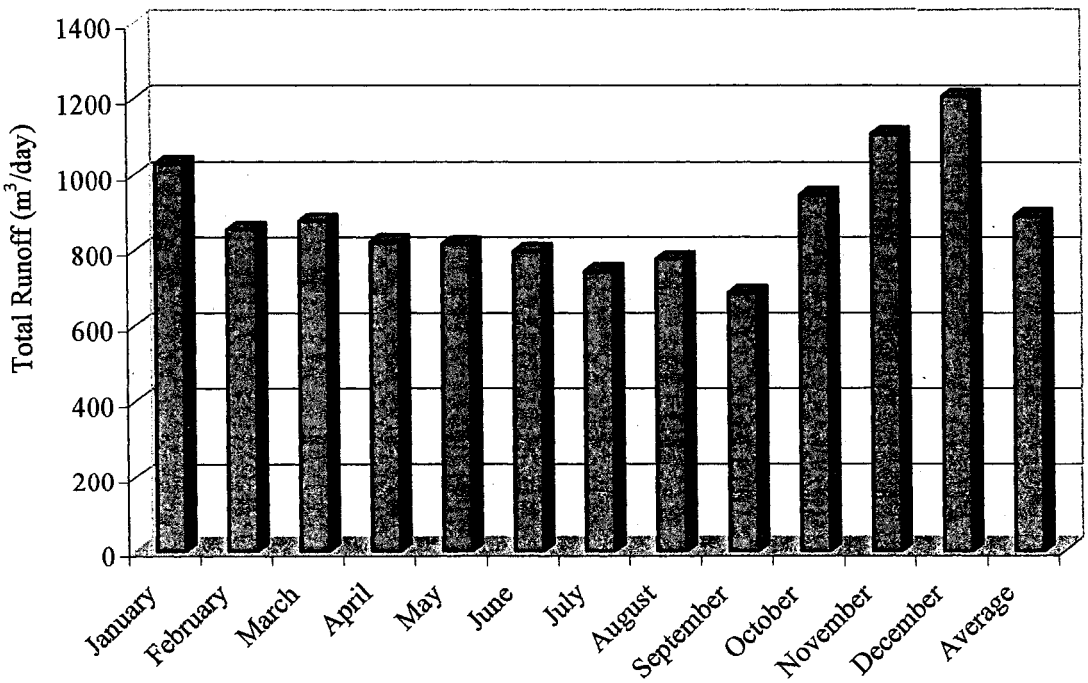


Figure 5.30. 30-year-average monthly runoff for watershed 4 (1971-2000).

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Table 5.10. Results of the water quality analyses for watershed 4.

Parameters	Method	EQL[1]	Units	Guideline	Measured*		
					May 1	May 16**	June 15
Sodium	ICP-OES	0.1	mg/L		140	105	84.4
Potassium	ICP-OES	0.1	mg/L		5.9	3	1.5
Calcium	ICP-OES	0.1	mg/L		72.8	35.4	28.6
Magnesium	ICP-OES	0.1	mg/L		5.6	6.1	2.7
Alkalinity (as CaCO3)	COBAS	5	mg/L		120	34	34
Sulfate	COBAS	2	mg/L		94	19	20
Chloride	COBAS	1	mg/L		220	170	140
Reactive Silica (as SiO2)	COBAS	0.5	mg/L		4.2	5.7	5.6
Ortho Phosphate (as P)	COBAS/911	0.01	mg/L		<0.01	<0.01	<0.01
Nitrite	COBAS	0.01	mg/L	0.6[2]	<0.1	<0.01	<0.01
Nitrate + Nitrite (as N)	COBAS	0.05	mg/L		0.23	0.33	0.37
Nitrate (as N)	COBAS	0.05	mg/L		0.23	0.33	0.37
Ammonia (as N)	Auto Color	0.05	mg/L		<0.05	<0.05	<0.05
Turbidity	NEPH	0.1	NTU		0.7	196	5.6
Conductance (RCAp)	Electrode	1	uS/cm		1190	744	634
pH	Electrode	-	Units		7.5	7.3	7.6
Hardness (as CaCO3)	Calculated	0.1	mg/L		205	114	82.5
Bicarbonate (as CaCO3)	Calculated	1	mg/L		120	34	34
Carbonate (as CaCO3)	Calculated	1	mg/L		<1	<1	<1
TDS (Calculated)	Calculated	1	mg/L		616	366	305
Cation Sum	Calculated	0.1	meq/L		4.3	6.92	5.36
Anion Sum	Calculated	0.1	meq/L		4.22	5.89	5.07
Ion Balance	Calculated	-	%		0.95	7.99	2.80
Saturation pH @ 4C	Calculated	-	Units		9.26	8.8	8.88
Saturation pH @ 20C	Calculated	-	Units		8.86	8.4	8.48
Aluminum	ICP-MS	10	ug/L	5-100[2]	160	7600	110
Antimony	ICP-MS	2	ug/L	20[4]	<2	<2	<2
Arsenic	ICP-MS	2	ug/L	5[2]	2	10	3.0
Barium	ICP-MS	5	ug/L	1000[3]	24	130	32.0
Beryllium	ICP-MS	2	ug/L	11[4]	<2	<2	<2
Bismuth	ICP-MS	2	ug/L		<2	<2	<2
Boron	ICP-MS	5	ug/L	200[4]	5	9	9.0
Cadmium	ICP-MS	0.3	ug/L	0.012[2]	<0.3	0.4	<0.3
Chromium	ICP-MS	2	ug/L	1-8.9[2]	<2	14	<2
Cobalt	ICP-MS	1	ug/L	0.9[4]	<1	8	<1
Copper	ICP-MS	2	ug/L	2-4[2]	4	35	3.0
Iron	ICP-MS	50	ug/L	300[2]	140	14000	400
Lead	ICP-MS	0.5	ug/L	1-7[2]	0.7	38	0.6
Manganese	ICP-MS	2	ug/L	1000-1500[3]	160	920	360
Molybdenum	ICP-MS	2	ug/L	73[2]	<2	<2	<2
Nickel	ICP-MS	2	ug/L	25-150[2]	<2	17	<2
Selenium	ICP-MS	2	ug/L	1[2]	<2	<2	<2
Silver	ICP-MS	0.5	ug/L	0.1[2]	<0.5	<0.5	<0.5
Strontium	ICP-MS	5	ug/L		99	180	140
Thallium	ICP-MS	0.1	ug/L	0.8[2]	<0.1	0.1	
Tin	ICP-MS	2	ug/L		<2	<2	
Titanium	ICP-MS	2	ug/L		4	250	4.0
Uranium	ICP-MS	0.1	ug/L		0.1	0.6	0.2
Vanadium	ICP-MS	2	ug/L		<2	14	<2
Zinc	ICP-MS	5	ug/L	30[2]	13	140	16
Phosphorus	ICP-OES	0.1	mg/L		<0.1	0.7	<0.1
Total Org. Carbon (by UV)	U.V.-ox	0.5	mg/L		2	<5	1.0

* Samples were taken Summer 2003 ** Samples were taken during a storm event.

1 Estimated Quantitation Limit, which is the minimum concentration that can be reliably reported.

2 Canadian Council of Ministers of the Environment water quality guidelines for the protection of fresh water life.

3 British Columbia Minister of Environment, Lands, and Parks Guidelines

4 Ontario Ministry of Environment Environmental Water Quality Objectives

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water life. Using the total runoff and the concentration of the heavy metals in the water collected from watershed 4, the aluminum and copper loads entering mouth of Wright Brook from watershed 4 were 623.07 and 15.577 kg/year, respectively. Due to high turbidity events, which last for 24 hours, the water was analyzed to assess the risk of heavy metal concentration during the event on Wright Brook ecosystem. Aluminum, arsenic, chromium, copper, iron and lead were above the CCME water quality guidelines for the protection of fresh water life. The heavy metal loads entered the Wright Brook during the high turbidity event for iron were 149.366, 0.1067, 0.1494, 0.3734 and 0.4054 kg/24h for iron, arsenic, chromium, copper and lead. No hydrocarbons were detected in water samples obtained from watershed 4 (Table 5.11).

Table 3.11. Results of the hydrocarbon analyses for watershed 4.

Parameters	Method	EQL[1]	Units	Guidelines[2]	Measured*
Benzene	P&T	0.001	mg/L	0.370	< 0.001
Toluene	P&T	0.001	mg/L	0.002	< 0.001
Ethylbenzene	P&T	0.001	mg/L	0.900	< 0.001
Xylenes	P&T	0.002	mg/L	0.002[3]	< 0.002
C6 - C10 HC {less BTEX}	Calculated	0.010	mg/L	NGA	< 0.010
>C10-C21 (Fuel Range)	GC/FID	0.050	mg/L	NGA	< 0.050
>C21-C32 (Lube Range)	GC/FID	0.100	mg/L	NGA	< 0.100
Modified TPH - Tier 1	Calculated	0.200	mg/L	NGA	< 0.200

* Samples were taken Summer 2003.
1 Estimated Quantitation Limit, which is the minimum concentration that can be reliably reported.
2 Canadian Council of Ministers of the Environment water quality guidelines for the protection of fresh water life.
3 Ontario Minister of Environment Environmental Quality Guidelines.
TPH Total Petroleum Hydrocarbons
NGA No Guideline Available

5.6 Burnside Constructed Treatment Wetland

The construction of the engineered wetland began in the late fall of 2001. The initial wetland system was designed to receive stormwater from watershed 1. Four wetland cells totaling an area of approximately 3000m^2 were completed (Figure 5.31). By the end of summer 2003, the wetland treatment system consists of 9 cells (deep open waters) separated by 9 internal berms (vegetated shallow areas) and surrounded by a system of external berms (Figure 5.32). The wetland system consists of several deepwater cells separated by shallow vegetated berms. This design allows for high efficiencies of the

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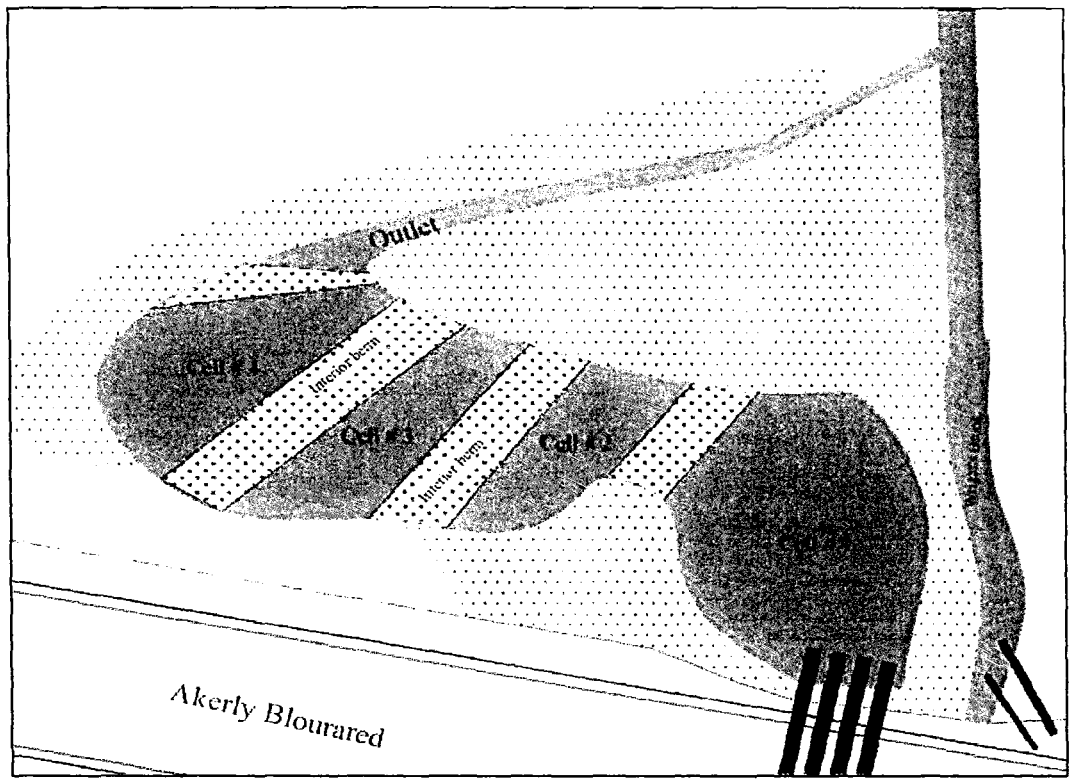


Figure 5.31. Burnside constructed treatment wetland (Summer 2003).

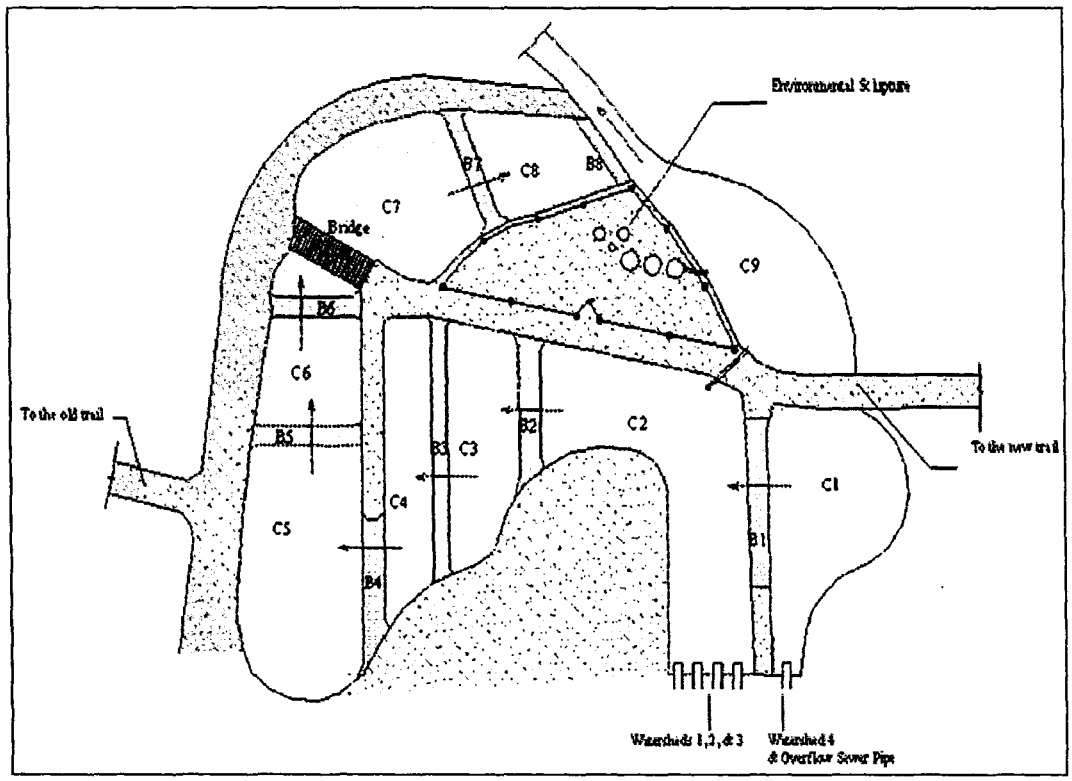


Figure 5.32. Burnside constructed treatment wetland (Summer 2004).

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physical, chemical and biological processes taking place in the wetland. The design also decreases the occurrence of short-circuiting and increases retention time. It was also crucial to design a wetland that is self-sustaining and maintenance-free as possible. The design of the cells was based on the topography of the site. The natural gravitational flow facilitated by the site topography negated the need for pumps that would require electricity and regular maintenance by a professional.

The heavy metal loads received by the engineered treatment wetland, which accommodates stormwaters from Watersheds 1, 2, 3 & 4 are presented in Table 5.12. The total loads of aluminum, arsenic, chromium, copper, iron, lead, manganese and zinc entering Burnside Wetland are 5016.49, 5.93, 8.74, 25.60, 10076.39, 48.86, 1968.66 and 103.11 kg/year with average concentrations of 7.720, 0.009, 0.013, 0.039, 15.508, 0.075, 3.029 and 0.158, respectively.

Table 5.12. Estimated heavy metal loads entering the constructed wetland.

Element	Watershed (kg/year)				Total (kg/year)	Average Concentration (mg/L)*	Guidelines[1] Concentration (mg/L)
	1	2	3	4			
Aluminum	7.31	6.12×10^{-3}	3103.77	1905.41	5016.49	7.720	0.005-0.100
Arsenic	1.46	$\approx 1.00 \times 10^{-3}$	1.96	2.51	5.93	0.009	0.005
Chromium	0.49	$\approx 1.00 \times 10^{-3}$	4.74	3.51	8.74	0.013	0.001-0.009
Copper	0.49	$\approx 1.00 \times 10^{-3}$	16.34	8.77	25.60	0.039	0.002-0.004
Iron	1339.02	$\approx 1.00 \times 10^{-3}$	5227.41	3509.96	10076.39	15.508	0.300
Lead	0.12	$\approx 1.00 \times 10^{-3}$	39.21	9.53	48.86	0.075	0.001-0.007
Manganese	267.80	$\approx 1.00 \times 10^{-3}$	1470.21	230.65	1968.66	3.029	1.000-1.500[2]
Zinc	2.68	$\approx 1.00 \times 10^{-3}$	65.34	35.09	103.11	0.158	0.030

* Calculated on the basis of a total average monthly runoff for the four watersheds of 1779.84 m^3/day

1 Canadian Council of Ministers of the Environment water quality guidelines for the protection of fresh water life.

2 British Columbia Minister of Environment, Lands, and Parks Guidelines.

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5.7 Methodology

Bi-weekly sampling of the site was performed for two consecutive seasons. The first season started in May, 2003 and ended in January 2004 while the second season started in May 2004 and ended October 2004. Water, plant and soil sampling locations are shown in Figures 5.33 and 5.34. Samples from the two seasons were collected on same days and months.

5.7.1 Chemical Water Quality Analyses

For the first season water quality samples were collected from the inlet, cells 1-3 and the outlet. The water qualities of the cells were compared in order to gauge the progress of purification from cell 1 to cell 3.

For the second season, water quality samples were collected from the inlet, cells 1-9 and the outlet. The water qualities of the cells were compared in order to gauge the progress of purification from cell 1 to cell 9 and to determine the cell with the most removal efficiency.

The parameters analyzed included: iron, manganese, phosphorus (orthophosphate), pH, dissolved oxygen (DO), nitrogen (ammonia, nitrate, nitrite and TKN), chemical oxygen demand (COD), total suspended solids (TSS) and total dissolved solids (TDS). The nitrogen, pH, COD, TSS and TDS were analyzed at the Biotechnology Laboratory at Dalhousie University according to American Water Works Association Manual (AWWA, 2002). The iron, manganese, and orthophosphate were analyzed at the Mineral Engineering Laboratory at Dalhousie University according to AWWA (2002).

5.7.2 Plant Tissues Analyses

In the first season, the phytoremediation ability of several plants in the treatment wetland was tested. The species chosen for plant tissues analyses were woolgrass (*Scirpus cyperimus*), soft rush (*Juncus effusus*), tweedy's rush (*Juncus brevicaudatus),* pickerelweed *(Pontederia cordata),* yellow-green sedge *(Carex lurida),* fowl

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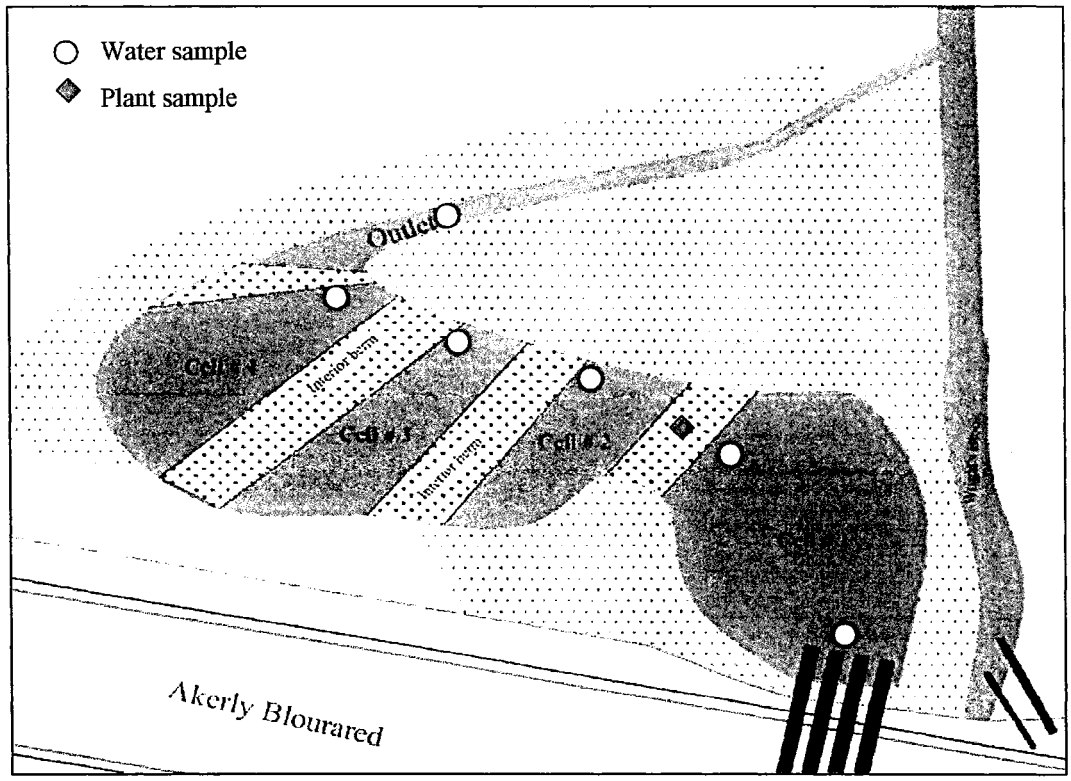


Figure 5.33. Sampling locations for season I.

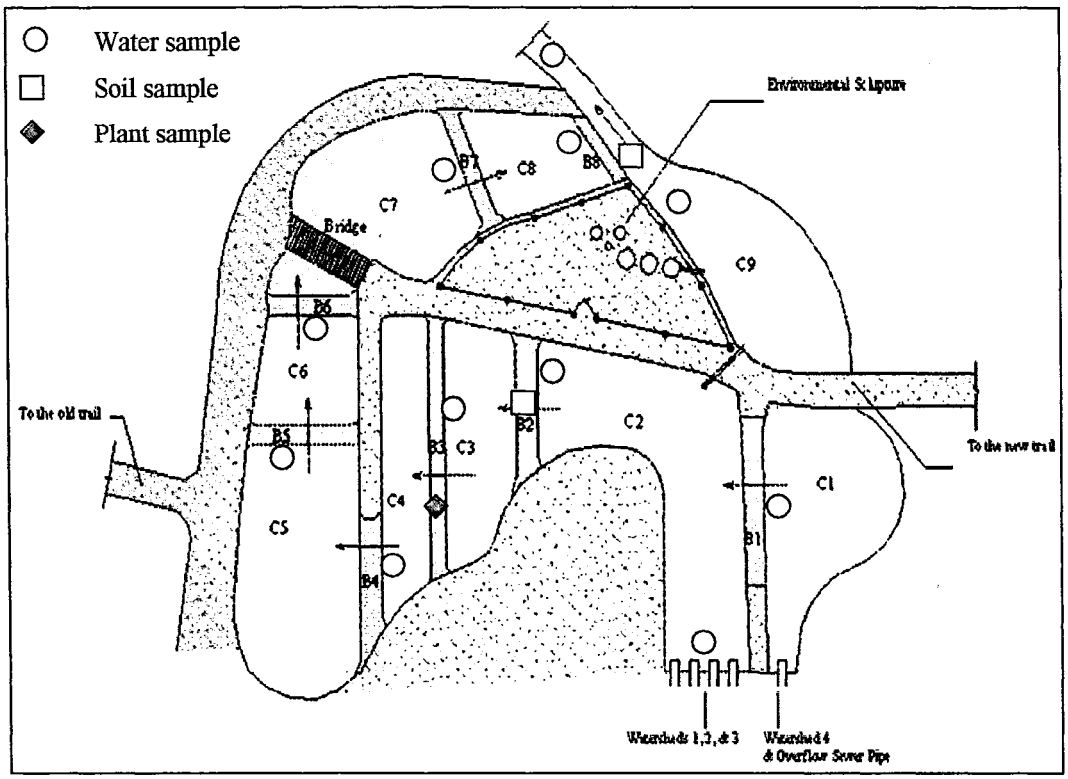


Figure 5.34. Sampling locations for season II.

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mannagrass *(Glyceria striata),* soft stem bulrush *(Scirpus validus)* and fringed sedge (*Carex crinita*). The exotic species reed canary grass (*Phalaris arundinacea*) and aggressive species broad-leaved cattail *(Typha latifolia)* which were also present in the treatment wetland site in abundance were also assessed for their metal hyperaccumulation ability. The plants were sampled at 4 weeks intervals and elemental analyses (iron and manganese) were performed on the plant tissues. Samples of same species were collected from a healthy, local reference site. The reference site for the Burnside treatment wetland was selected by Galbrand (2004) as a result of its fitting classifications and close location (approximately 25 km from the Burnside site in the Waverly Game Sanctuary), marsh A-8 was selected as the control site. Water samples from the site were submitted for fingerprint analysis to establish that the site would be an effective control, as disturbance is not always discernible to the eye.

In the second season, the same plant species of season I were sampled at four week intervals to assess the ability of the plants to remove contaminants from the water during the growing season. The parameters analyzed were iron and manganese.

The collected plant samples were washed thoroughly to remove any soil that may have contained the contaminants of concern as recommended by A&L Canada Laboratories (2002). The plant samples were separated using scissors, into roots, stem, leaves, and flowers. The varies parts were placed into labeled plastic bags, and stored in freezers until the analyses was conducted. The plant samples were dried in a convection oven for 24 hours at 45 °C. After drying, the plants were ground and digested with hydrochloric-nitric-hydrofluric-perchloric acids (30+10+10+5 mL/g sample) in a closed vessel at a temperature of 100°C. The metal analysis was conducted at the Mineral Engineering Laboratory, Dalhousie University. The metal concentrations were determined using an Atomic Absorption Spectometer (Varion SpectrAA, Model Number: 55B, Varion, Mulgrave, Victoria, Australia).

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5.7.3 Soil Analyses

During the second season, soil samples were collected from the inlet and the outlet of the wetland to asses the rate and the amounts of iron and manganese precipitated. The soil samples were dried in a convection oven for 24 hours at 45 °C. After drying, the soil samples were ground and digested with hydrochloric-nitric-hydrofluric-perchloric acids (30+10+10+5 mL/g sample) in a closed vessel at a temperature of 100°C. The metal analysis was conducted at the Mineral Engineering Laboratory, Dalhousie University according to the procedures described by Soil Science Society of America (SSSA, 1986). The metal concentrations were determined using an Atomic Absorption Spectometer (Varion SpectrAA, Model Number: 55B, Varion, Mulgrave, Victoria, Australia).

5.8 Results

5.8.1 Water Quality Analysis

Water samples were taken from the wetland during two successive growing seasons to assess the performance of the wetland. Samples for season one were collected during the period of May 2003 to January 2004, while the samples for season two were taken during the period of May 2004 to November 2004. Sampling was extended to January in season one to assess the performance of the wetland in the winter and to gain a better understanding of the removal mechanisms in the wetland during the sub-zero temperature.

5.8.1.1 Season I (May 2003- January 2004)

5.8.1.1.1 pH: The pH in treatment wetland cells fluctuated between 6.73 and 7.95 (Figure 5.35). The maximum pH in the outlet was 7.95 while the minimum pH in the outlet 6.74 with an average of 7.28.

5.8.1.1.2 Dissolved Oxygen: The dissolved oxygen (DO) concentrations observed in the treatment wetland cells fluctuated between 2.5 and 6.1 mg/L (Figure 5.36). The maximum DO concentration in the outlet was 6.1 mg/L while the minimum DO concentration in the outlet was 3.7 with an average of 4.68 mg/L. The minimum DO

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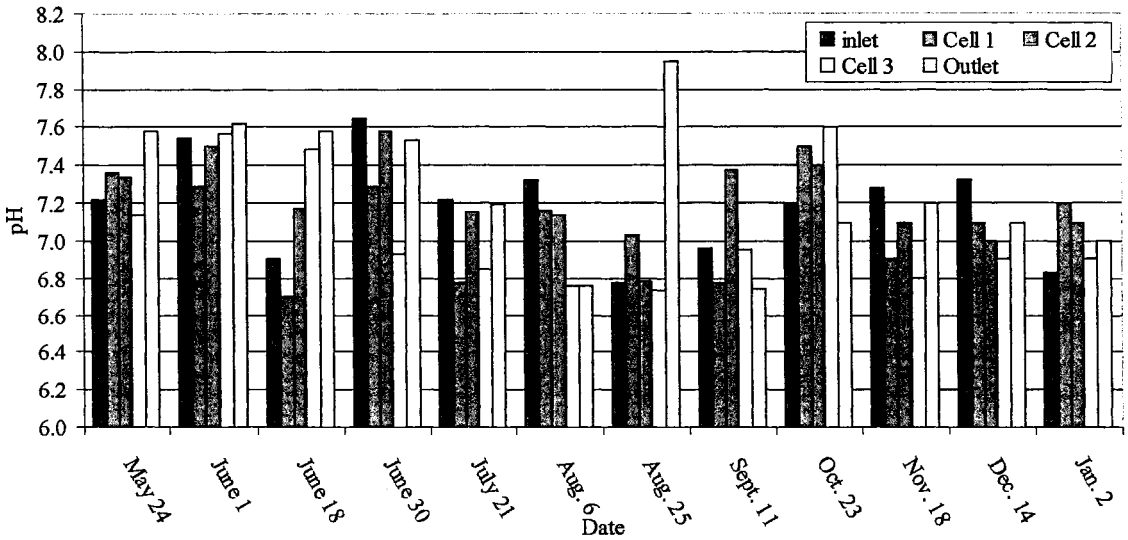


Figure 5.35. pH in the wetland cells (May 2003 – January 2004).

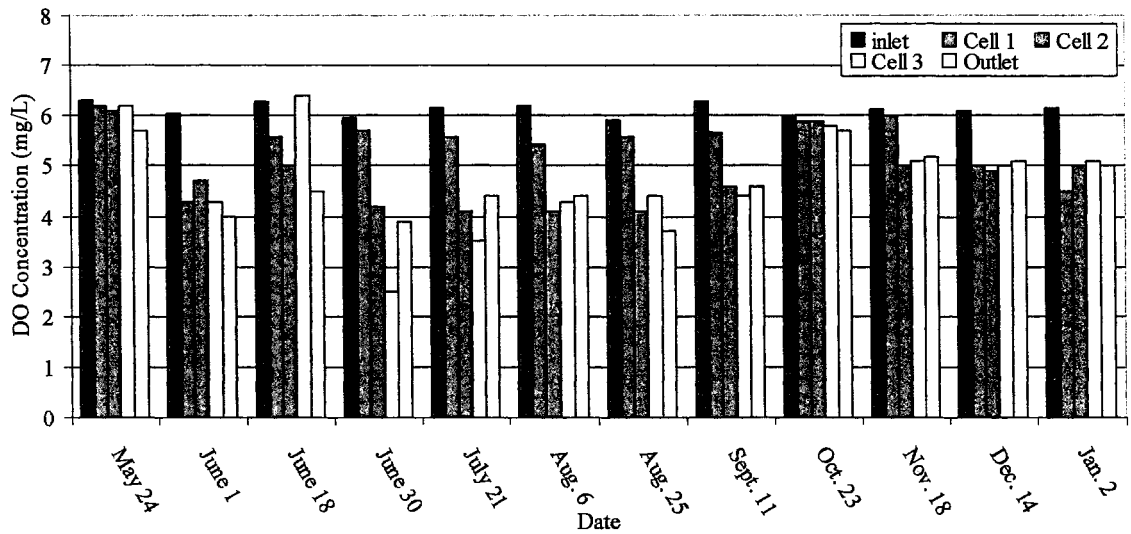


Figure 5.36. Dissolved oxygen concentrations in the wetland cells (May 2003 – January 2004).

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concentration recommended by CCME (2003) guidelines for the protection of freshwater aquatic life is 4.5-9.5 mg/L.

5.8.1.1.3 Orthophosphate: Orthophosphate concentrations in the treatment wetland waters were analyzed in order to identify the cause of the algal blooms occurring in cells 2 and 3 in early May of 2003. The orthophosphate concentrations in the waters of cell 1, 2, 3, and the outlet were minimal, fluctuating between undetectable levels to 0.03 mg/L (Figure 5.37).

5.8.1.1.4 Total Kjeldahl Nitrogen: The Total Kjeldahl Nitrogen (TKN) concentrations in the treatment wetland cells fluctuated during evaluation period between 0.5 and 18.0 mg/L (Figure 5.38). The maximum TKN concentration in the outlet was 6.5 mg/L while the minimum TKN concentration was 0.5 mg/L with an average TKN concentration of 3.76 mg/L.

5.8.1.1.5 Ammonium: The ammonium nitrogen (NH_4) concentrations in the wetland cells fluctuated during the test period between 0 and 3.0 mg/L (Figure 5.39). The maximum NH_4 concentration in the outlet was 1.5 while the minimum NH_4 concentration in the outlet was 0 with an average of 0.24 mg/L.

5.8.1.1.6 Nitrite: The NO_2^- concentrations in the treatment wetland cells fluctuated during the evaluation period between 0 and 0.067 mg/L (Figure 5.40). The maximum NO_2^- concentration in the outlet was 0.067 mg/L while the minimum NO_2^- concentration was 0 mg/L with an average NO_2^- concentration of 0.015 mg/L.

5.8.1.1.7 Nitrate: The NO_3 concentrations in the treatment wetland cells fluctuated during the evaluation period between 1.16 and 8.30 mg/L (Figure 5.41). The maximum NO_3 concentration in the outlet was 7.102 and minimum concentration was 1.35 mg/L with an average of 3.35 mg/L.

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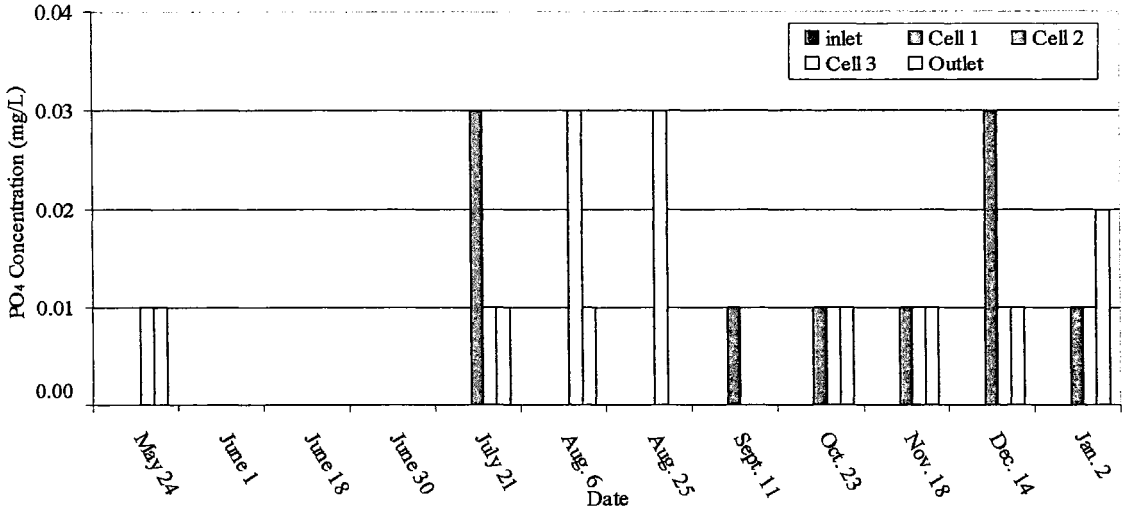


Figure 5.37. Orthophosphate concentration in the wetland cells (May 2003 – January 2004).

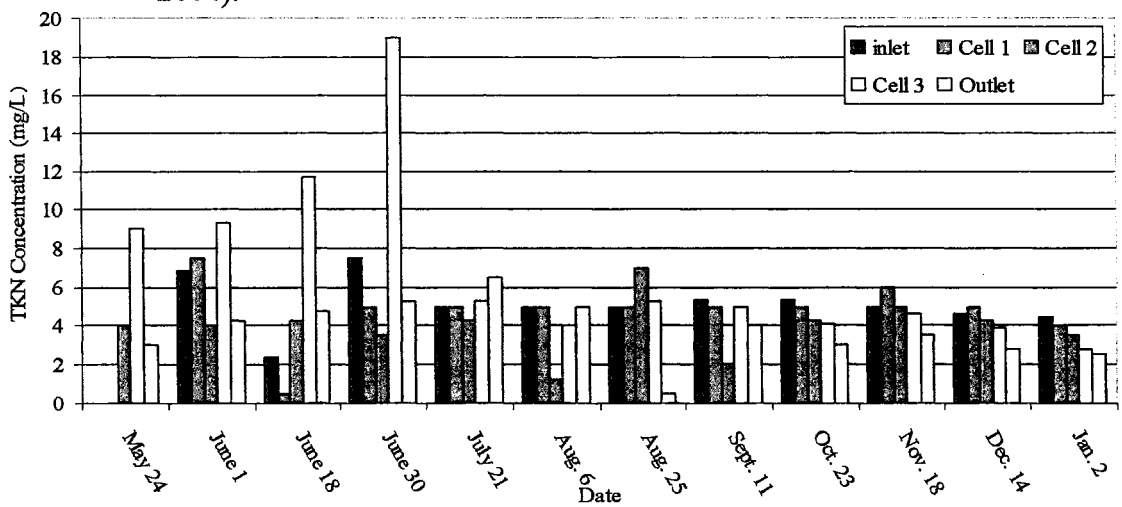


Figure 5.38. TKN concentrations in the wetland cells (May 2003 – January 2004).

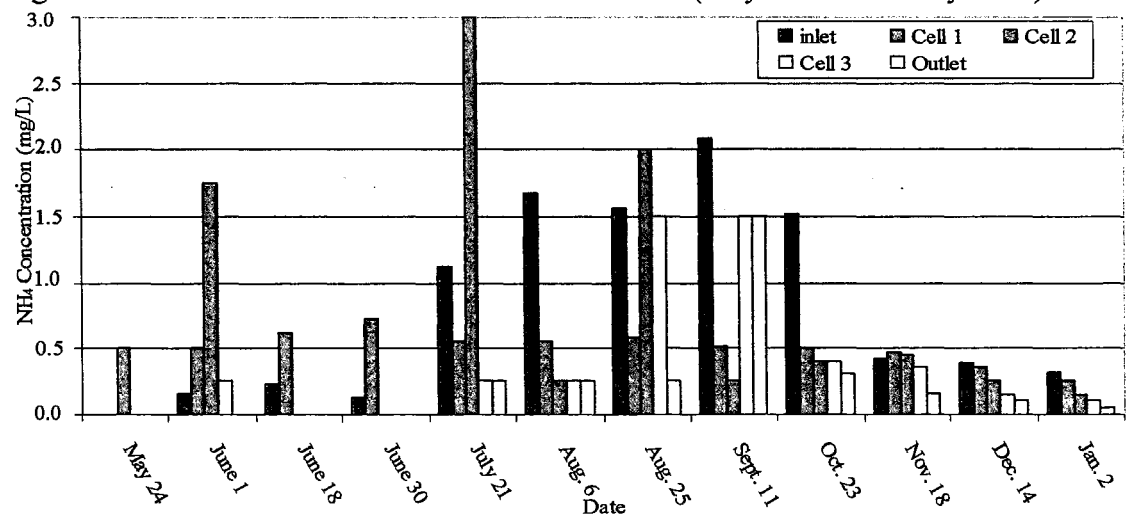


Figure 5.39. Ammonium concentration in the wetland cells (May 2003 – January 2004).

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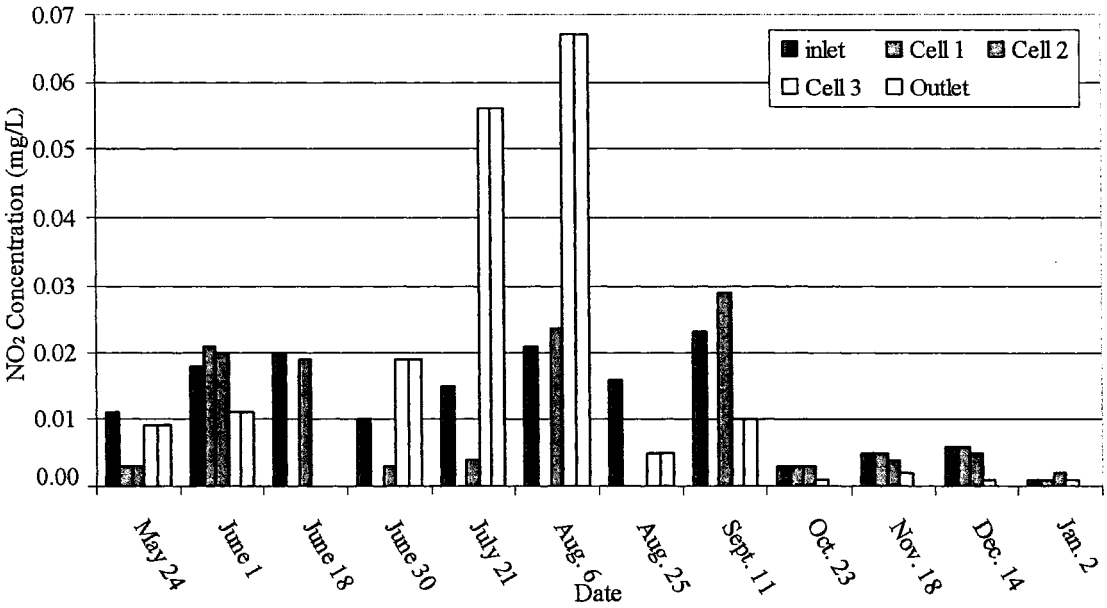


Figure 5.40. Nitrite-nitrogen concentrations in wetland cells (May 2003 – January 2004).

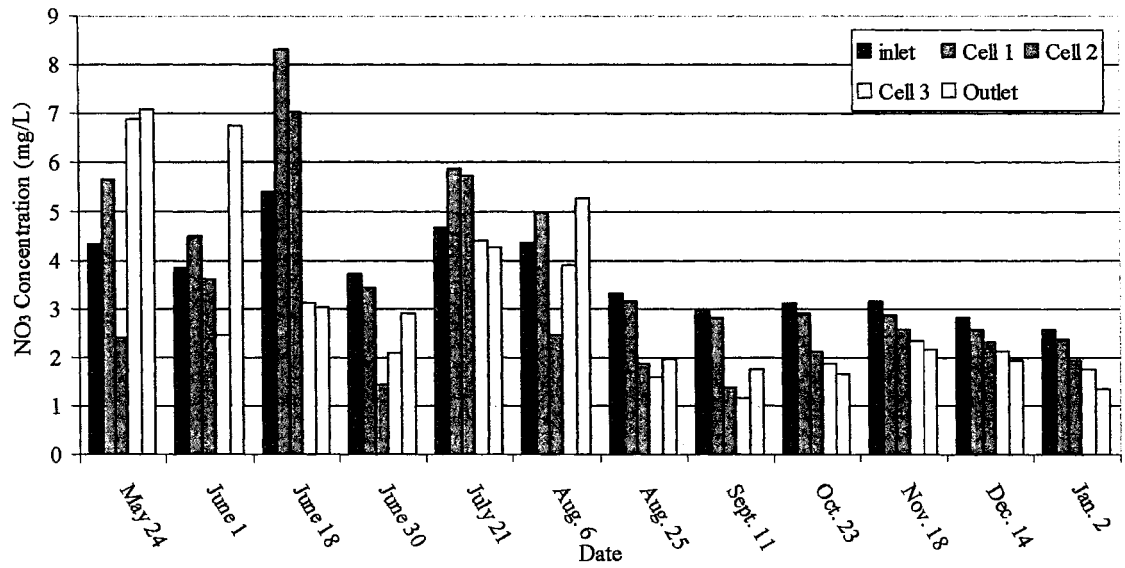


Figure 5.41. Nitrate-nitrogen concentration in the wetland cells (May 2003 – January 2004).

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5.8.1.1.8 Chemical Oxygen Demand: The chemical oxygen demand (COD) concentrations in the treatment wetland cells fluctuated during the evaluation period between 546 and 1209 mg/L (Figure 5.42). The maximum COD concentration in the outlet of the treatment wetland was 1092 mg/L while the minimum COD concentration was 495 mg/L with an average concentration of 797 mg/L.

5.8.1.1.9 Total Suspended Solids: The TSS concentrations in the treatment wetland cells fluctuated during the evaluation period between 260 and 970 mg/L (Figure 5.43). The maximum TSS concentration in the outlet was 893 mg/L while the minimum TSS concentration was 160 mg/L with an average concentration of 451 mg/L.

5.8.1.1.10 Total Dissolved Solids: The TDS concentrations in the treatment wetland fluctuated during the evaluation period between 140 and 883 mg/L (Figure 5.44). The maximum TDS concentration in the outlet was 870 mg/L while the minimum TDS concentration was 135 mg/L with an average concentration of 319 mg/L.

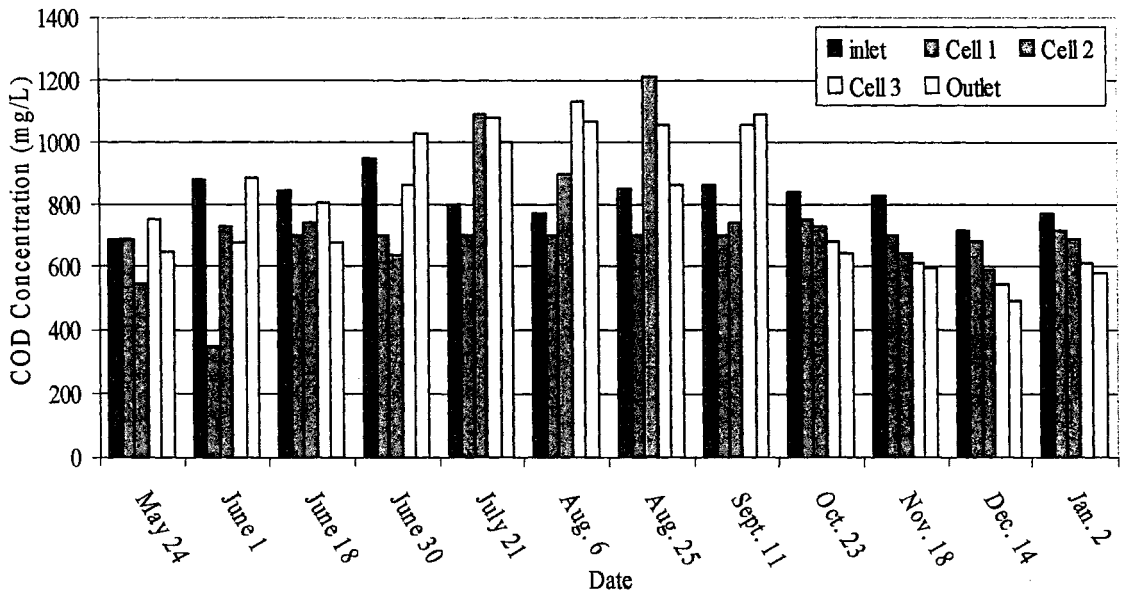


Figure 5.42. Chemical oxygen demand concentrations in the wetland cells (May 2003 – January 2004).

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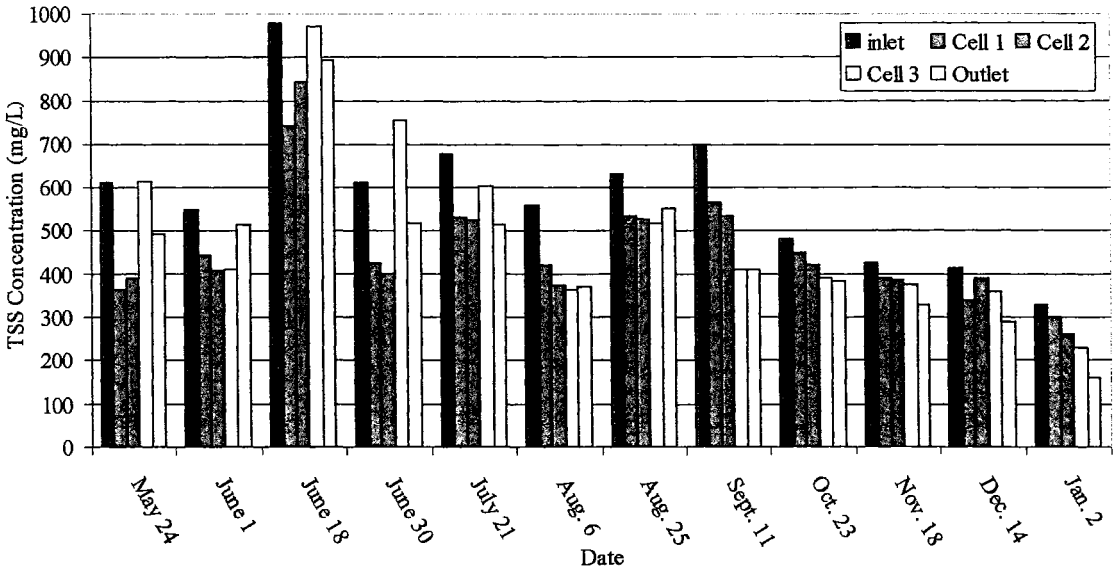


Figure 5.43. Total suspended solids concentrations in the wetland cells (May 2003 – January 2004).

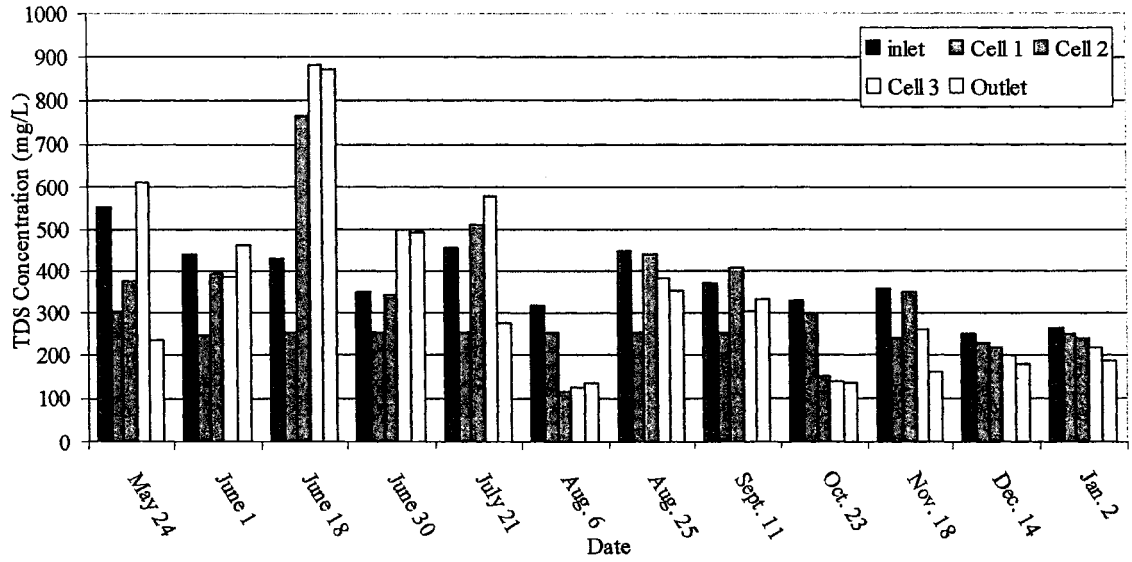


Figure 5.44. Total dissolved solid concentrations in the wetland cells (May 2003 – January 2004).

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5.8.1.1.11 Iron: The iron concentrations observed in the treatment wetland cells during the testing period (May 2003 to January 2004) generally decreased as water flow through the treatment wetland cells (Figure 5.45). However, the concentrations of iron increased in cells 2 and 3 above that of the inlet. This may be due to the flocculation of iron particles which were captured during sampling. The lowest iron concentration observed in the effluent was 0.67 mg/L while the highest was 9.38 mg/L with an average of 4.50 mg/L.

5.8.1.1.12 Manganese: The manganese concentration observed during the testing period (May 2003 – January 2004) decrease as the water flow through the treatment wetland cells (Figure 5.46). The maximum manganese concentration in the outlet was 2.55 mg/L while the minimum was 0.5 mg/L with an average of 1.30 mg/L.

5.8.1.2 Season II (May 2004 – October 2004)

5.8.1.2.1 pH: The pH fluctuated throughout the treatment wetland cells between 6.70 and 7.8 (Figure 5.47). The maximum pH in the outlet was 7.60 while the minimum pH was 6.70 with an average of 7.28.

5.8.1.2.2 Dissolved Oxygen: The DO fluctuated through the treatment wetland cells between 5.7 and 6.3 (Figure 5.48). The maximum DO concentration in the outlet was 6.2 mg/L while the minimum was 5.7 with an average of 6.09 mg/L.

5.8.1.2.3 Orthophosphate: The orthophosphate concentrations in the waters of the inlet, all the cells and the outlet were very low and fluctuating between 0 to 0.02 mg/L (Figure 5.49).

5.8.1.2.4 Total Kjeldahl Nitrogen: The TKN concentrations in the treatment wetland cells fluctuated throughout the evaluation period between 1.37 to 8.23 mg/L (Figure 5.50). The maximum TKN concentration in the outlet was 6.65 mg/L while the minimum TKN concentration was 1.26 mg/L with an average TKN concentration of 2.60 mg/L.

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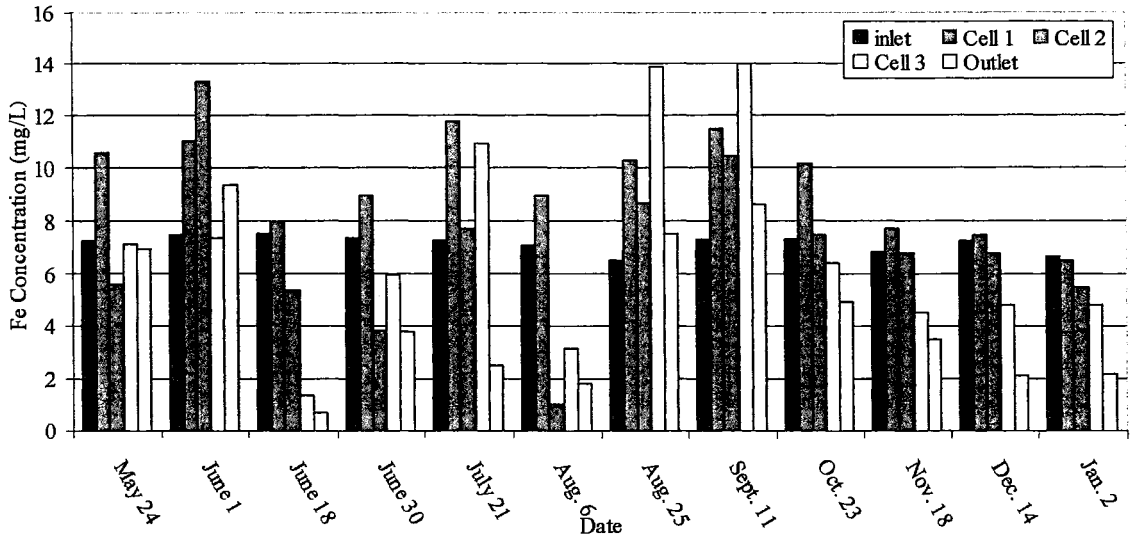


Figure 5.45. Iron concentration in the wetland cells (May 2003-Janusry 2004).

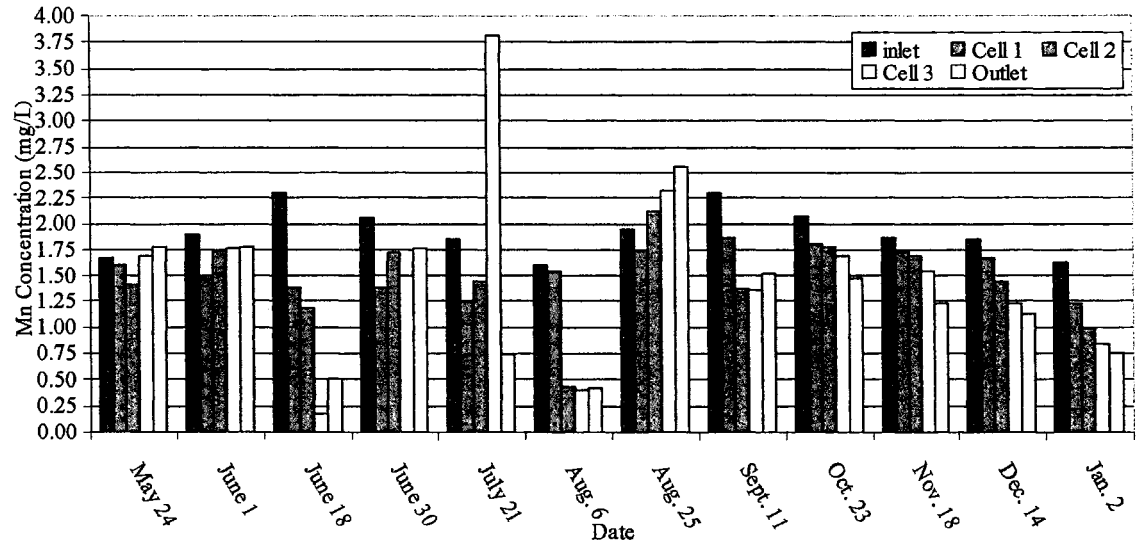


Figure 5.46. Manganese concentration in the wetland cells (May 2003-Janusry 2004).

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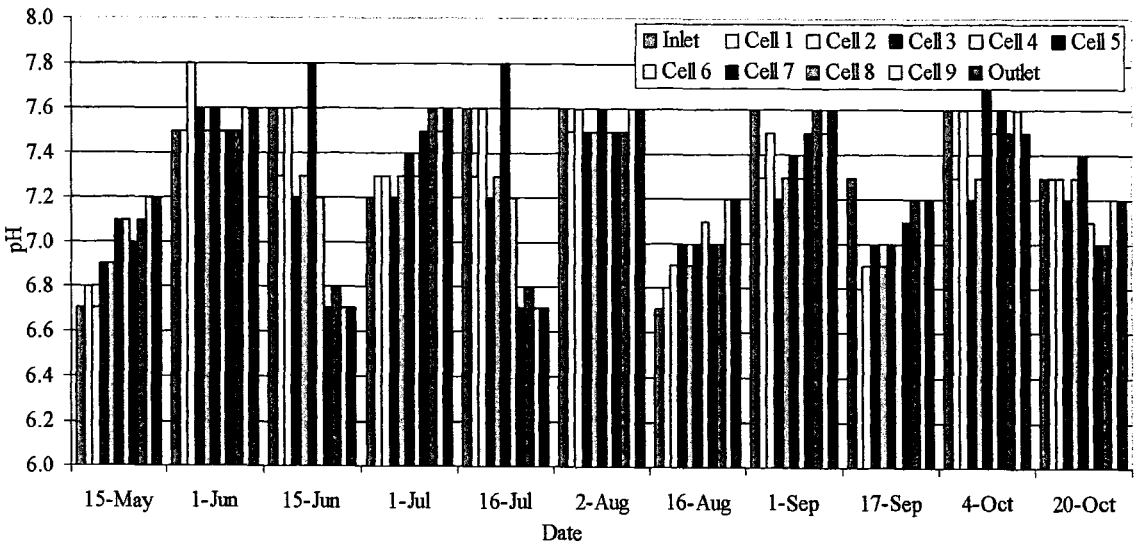


Figure 5.47. pH in the wetland cells (May 2004 – October 2004).

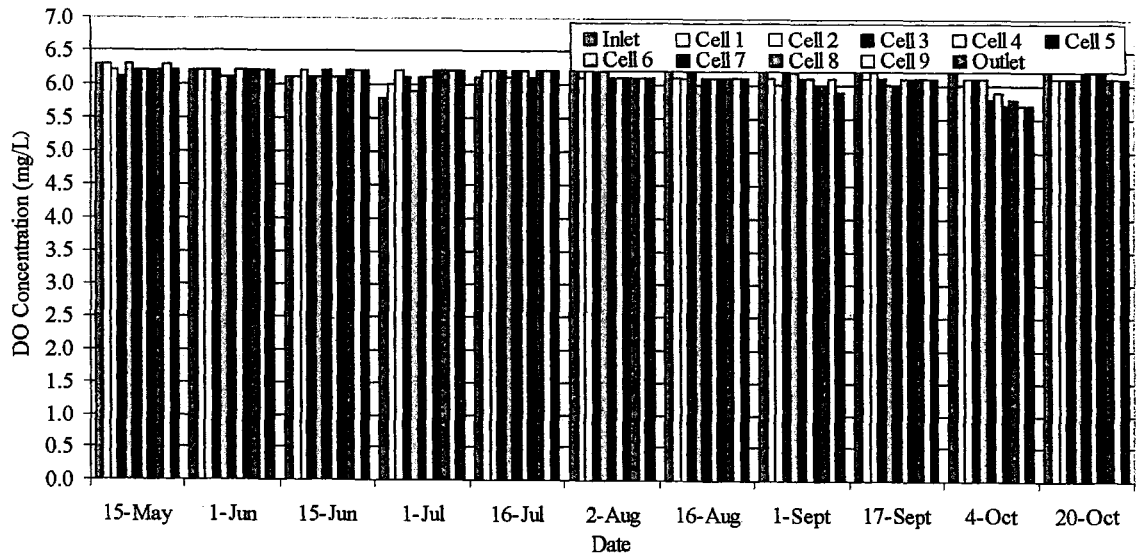


Figure 5.48. Dissolved oxygen concentrations in the wetland cells (May 2004 – October 2004).

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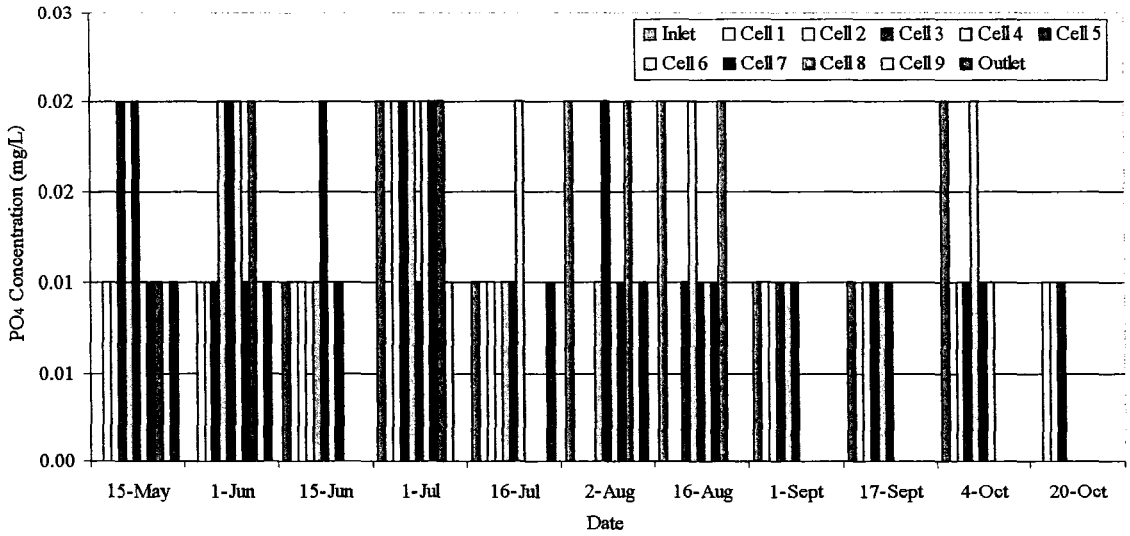


Figure 5.49. Ortho-phosphate concentrations in the wetland cells (May 2004 – October 2004).

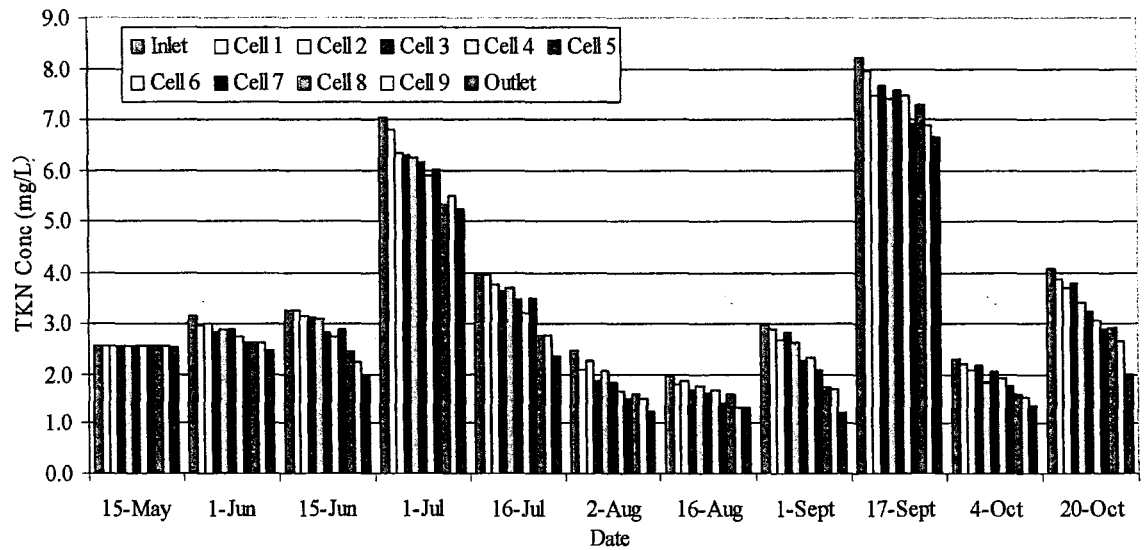


Figure 5.50. Total Kjeldahl nitrogen concentrations in the wetland cells (May 2004 – October 2004).

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5.8.1.2.5 Ammonium: The ammonium concentrations in the wetland cells fluctuated between 0 and 2.60 mg/L during the testing period (Figure 5.51). The maximum NH_4 concentration in the outlet was 2.36 while the minimum NH_4 concentration was 0 with an average of 0.52 mg/L.

5.8.1.2.6 Nitrite: The NO_2 concentrations in the treatment wetland cells fluctuated throughout the evaluation period between 0 to 0.04 mg/L (Figure 5.52). The maximum NO_2^- concentration in the outlet was 0.02 mg/L while the minimum NO_2^- concentration was 0.01 mg/L with an average NO_2^- concentration of 0.01 mg/L.

5.8.1.2.7 Nitrate: The NO_3 concentrations in the treatment wetland cells fluctuated throughout the evaluation period between 1.24 and 4.26 mg/L (Figure 5.53). The maximum NO_3 concentration in the outlet was 3.27 and minimum concentration was 1.03 mg/L with an average of 2.45 mg/L.

5.8.1.2.8 Chemical Oxygen Demand: The COD concentrations in the treatment wetland cells fluctuated throughout the evaluation period between 228 and 992mg/L (Figure 5.54). The maximum COD concentration in the outlet of the treatment wetland was 685 mg/L while the minimum COD concentration was 236 mg/L with an average concentration of 381 mg/L.

5.8.1.2.9 Total Suspended Solids: The TSS concentrations in the treatment wetland cells fluctuated through the evaluation period between 154 and 1185 mg/L (Figure 5.55). The maximum TSS concentration in the outlet of the treatment wetland was 365 mg/L while the minimum TSS concentration was 155 mg/L with an average concentration of 256 mg/L.

5.8.1.2.10 Total Dissolved Solids: The TDS concentrations in the treatment wetland cells fluctuated through the evaluation period between 116 and 685 mg/L (Figure 5.56). The maximum TDS concentration in the outlet of the treatment wetland was 265 mg/L while the minimum TDS concentration was 85 mg/L with an average concentration of

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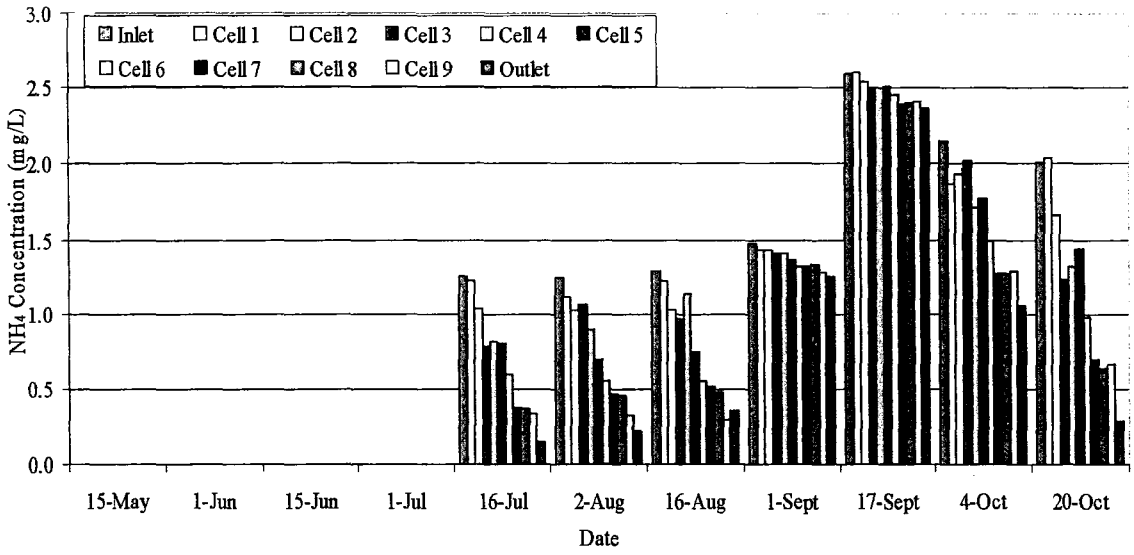


Figure 5.51. Ammonium concentrations in the wetland cells (May 2004 – October 2004).

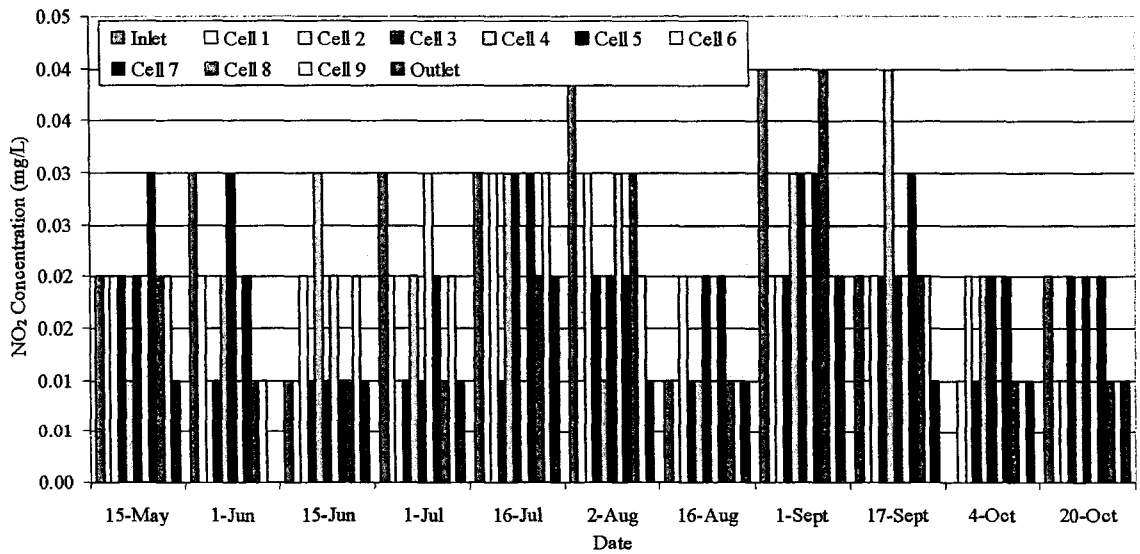


Figure 5.52. Nitrite nitrogen concentrations in the wetland cells (May 2004 – October 2004).

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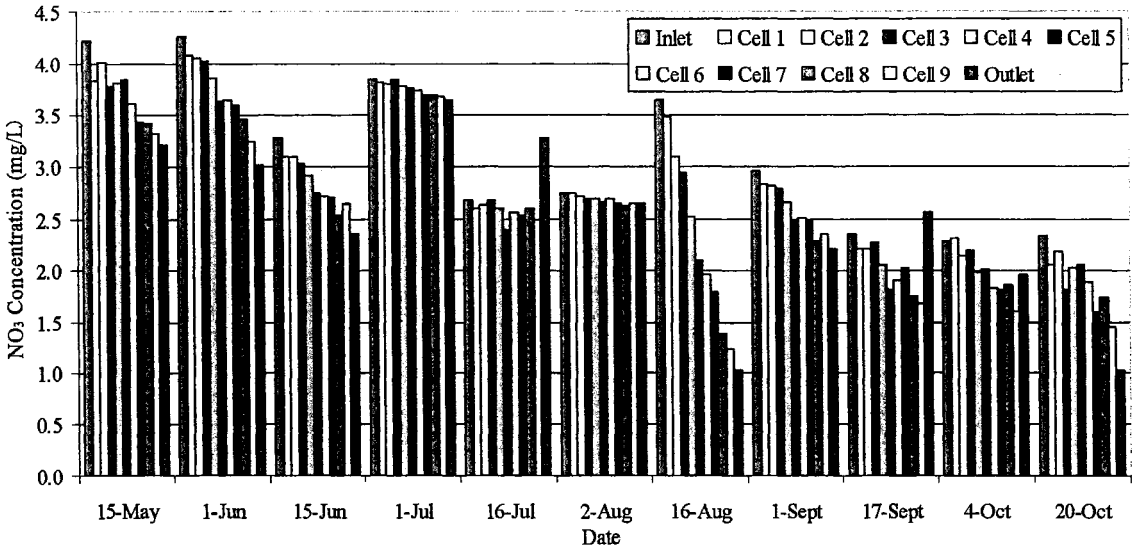


Figure 5.53. Nitrate nitrogen concentrations in the wetland cells (May 2004 – October 2004).

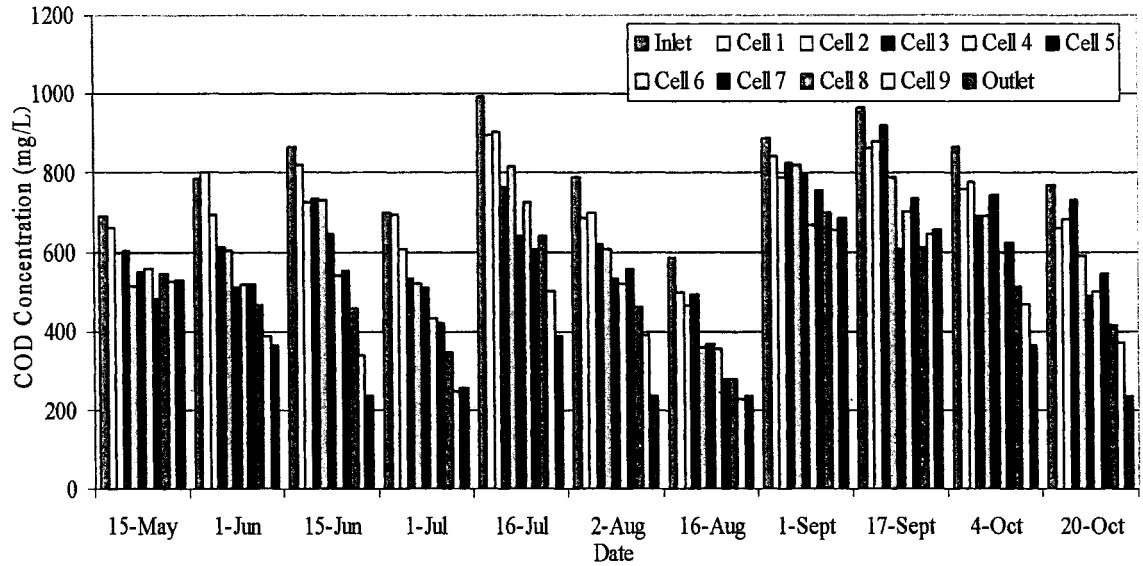


Figure 5.54. Chemical oxygen demand concentrations in the wetland cells (May 2004 – October 2004).

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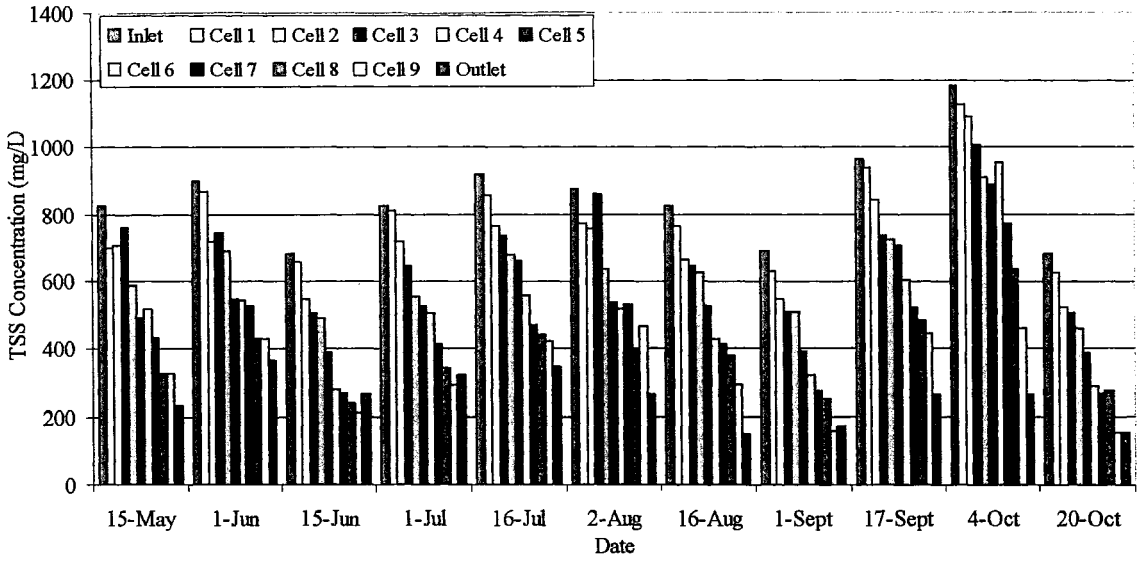


Figure 5.55. Total suspended solids concentrations in the wetland cells (May 2004 – October 2004).

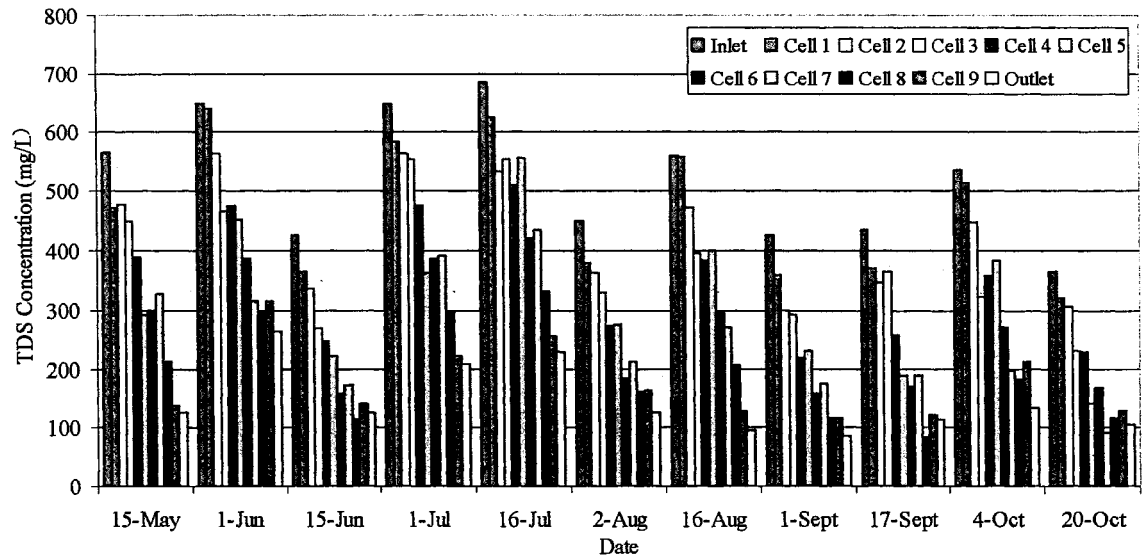


Figure 5.56. Total dissolved solids concentrations in the wetland cells (May 2004 – October 2004).

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146 mg/L.

5.8.1.2.11 Iron: The iron concentrations in the treatment wetland cells fluctuated during the evaluation period between 1.74 and 7.21 mg/L (Figure 5.57). The lowest iron concentration observed in the outlet was 0.96 mg/L whereas; the highest concentration was 3.68 mg/L with an average concentration of 2.27 mg/L.

5.8.1.2.12 Manganese: The manganese concentration generally decreased as the water flowed through the treatment wetland cells (Figure 5.58). The manganese concentrations in the treatment wetland fluctuated during the evaluation period between 1.07 and 2.32 mg/L. The maximum manganese concentration in the outlet was 1.52 mg/L while the minimum manganese concentration was 0.9 mg/L with an average of 1.16 mg/L.

5.8.2 Plant Tissue Analyses

The phytoremediation ability of several plants in the Burnside treatment wetland site was tested. The results of the chemical analyses (iron and manganese) preformed on the sampled plant tissues at the end of the first growing season were compared to those the chemical analyses performed on plant tissues of the same species taken from a control site. In the second season, the plants were sampled on monthly basis to asses the ability of the plants to remove contaminants from the water during the growing season. The iron and manganese concentrations in water were 6.60 and 0.27, and 1.80 and 0.15 mg/L for the treatment wetland and reference wetland, respectively.

5.8.2.1 Season I (October 2003)

5.8.2.1.1 Iron: Generally, the plants obtained from the treatment wetland had higher concentrations of iron in their roots compared to these of the plants obtained from the reference wetland, except for Soft rush and Fowl mannagrass (Figure 5.59). The highest concentration of iron in the roots of the plants sampled from the reference wetland were 7524, 6432, 4572, 4532, 3124, 3062, 2338, 1967, 1827 and 119 mg/kg for Fowl mannagrass, Soft rush, Tweedy rush, Pickerelweed, Wool grass, Soft stem bulrush,

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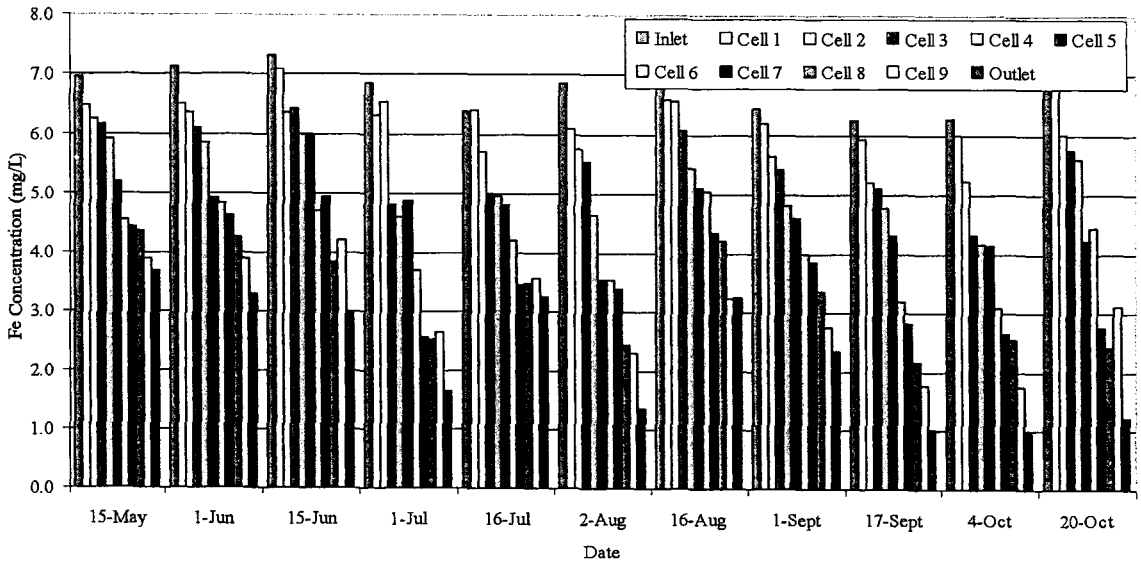


Figure 5.57. Iron concentrations in the wetland cells (May 2004 – October 2004).

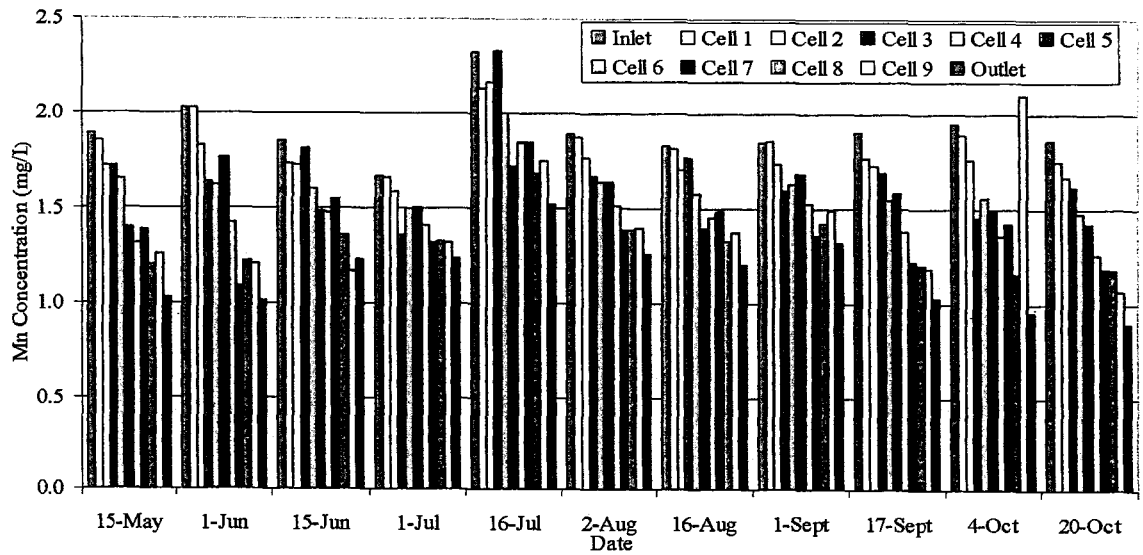


Figure 5.58. Manganese concentrations in the wetland cells (May 2004 – October 2004).

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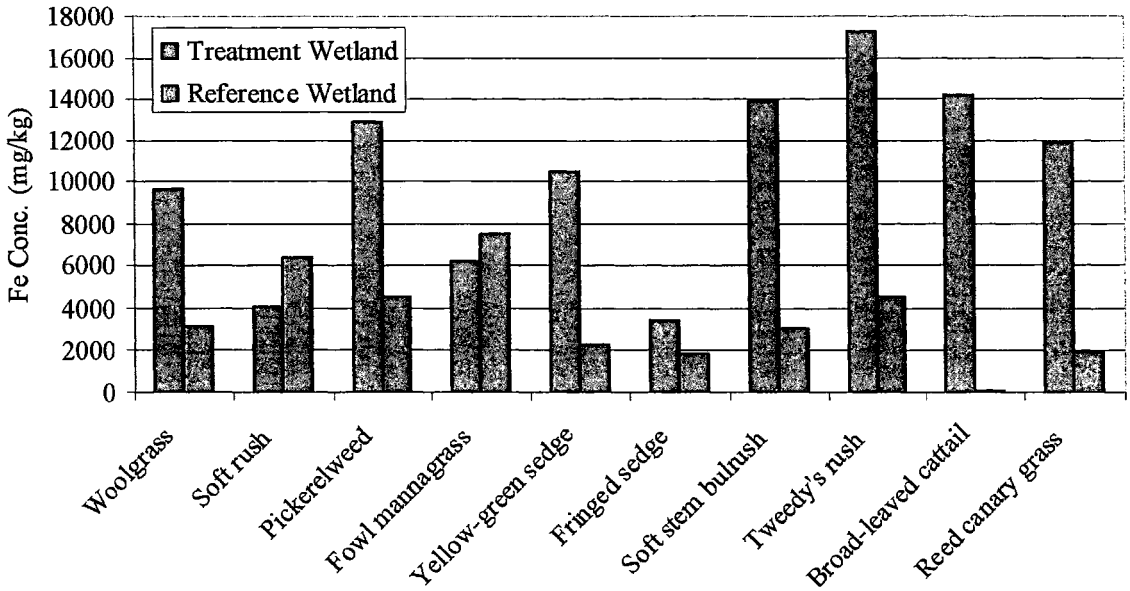


Figure 5.59. Iron concentrations in root tissues (October 2003).

Yellow-green sedge, Reed canary grass, Fringed sedge and Broad leaved cattail, respectively. The highest concentration of iron in the roots of the plants sampled from the treatment wetland were 17302, 14171, 13903, 12868, 11834, 10519, 9620, 6172, 4052 and 3474 mg/kg for Tweedy rush, Broad leaved cattail, Soft stem bulrush, Pickerelweed, Reed canary grass, Yellow-green sedge, Wool grass, Fowl mannagrass, Soft rush and Fringed sedge, respectively.

All plants obtained from the treatment wetland accumulated higher concentrations of iron in their stems compared to those obtained from the reference wetland (Figure 5.60). The highest concentration of iron in the stems of the plants sampled from the reference wetland were 178, 176, 169, 137, 130, 122, 73, 35, 18 and 13 mg/kg for Reed canary, Fringed sedge, Tweedy rush, Pickerelweed, Soft rush, Yellow-green sedge, Wool grass, Fowl mannagrass, Soft stem bulrush and Broad leaved cattail, respectively. The highest concentration of iron in the stems of the plants sampled from the treatment wetland were 813, 461, 302, 260, 245, 173, 160, 129, 116 and 85 mg/kg for Soft stem bulrush, Tweedy's rush, Yellow-green sedge, Wool grass, Reed canary grass, Broad leaved cattail, Soft rush, Fringed sedge, Fowl mannagrass and Pickerelweed, respectively.

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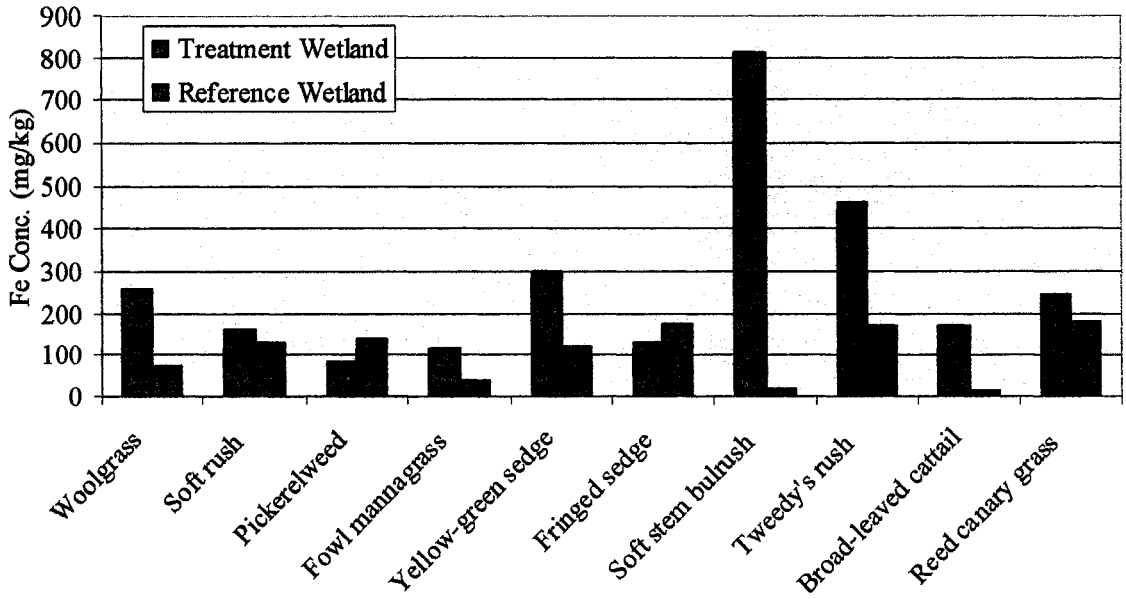


Figure 5.60. Iron concentrations in stem tissues (October 2003).

The accumulation of iron in the plant leaves is shown in Figure 5.61. Wool grass, Pickerelweed, Yellow-green sedge and Reed canary grass accumulated more iron in their leaves in the reference wetland compared to the treatment wetland while Fowl mannagrass, Fringed sedge and Broad leaved cattail accumulated more iron in their leaves in the treatment wetland compared to the reference wetland. The highest concentration of iron in the leaves of the plants sampled from the reference wetland were 1141, 872, 780, 418, 253, 252 and 246 mg/kg for Yellow-green sedge, Reed canary grass, Fringed sedge, Pickerelweed, Broad leaved cattail, Wool grass and Fowl mannagrass, respectively. The highest concentration of iron in the leaves of the plants sampled from the treatment wetland were 5788, 3936, 1002, 809, 775, 221 and 104 mg/kg for Broad leaved cattail, Fringed sedge, Fowl mannagrass, Yellow-green sedge, Reed canary grass, Wool grass and Pickerelweed, respectively.

The iron accumulation in the flowers of the plants is shown in Figure 5.62. Wool grass, Pickerelweed, Yellow-green sedge, Fringed sedge, Soft stem bulrush and Reed canary grass accumulated more iron in their flowers in the reference wetland compared to the treatment wetland while Soft rush, Fowl mannagrass, Tweedy's rush and Broad leaved cattail accumulated more iron in their flowers in the treatment wetland compared to

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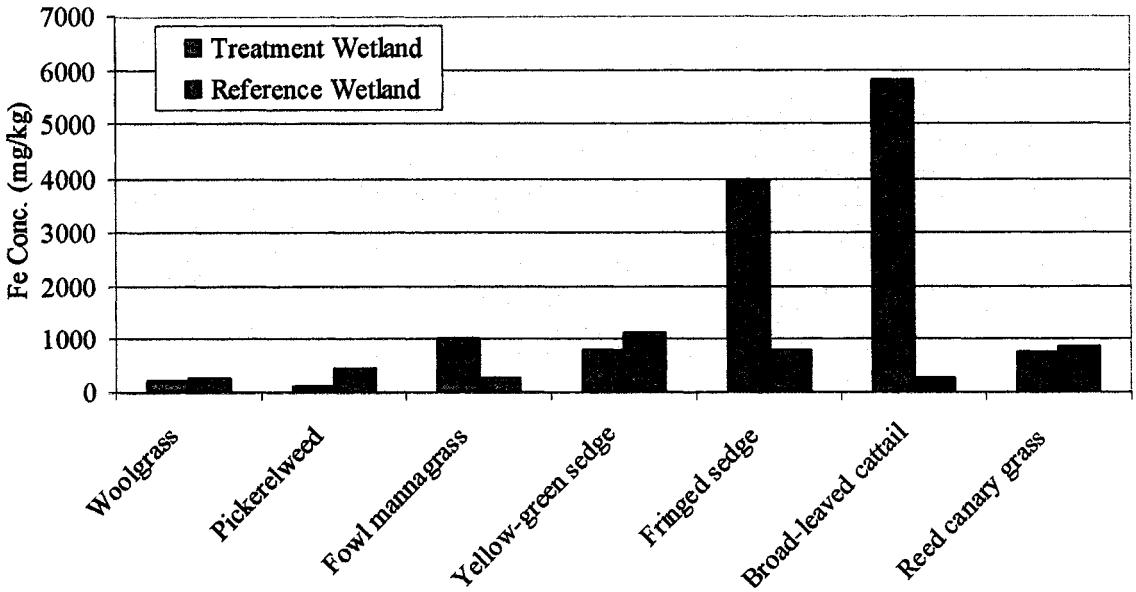


Figure 5.61. Iron concentrations in leaves tissue (October 2003).

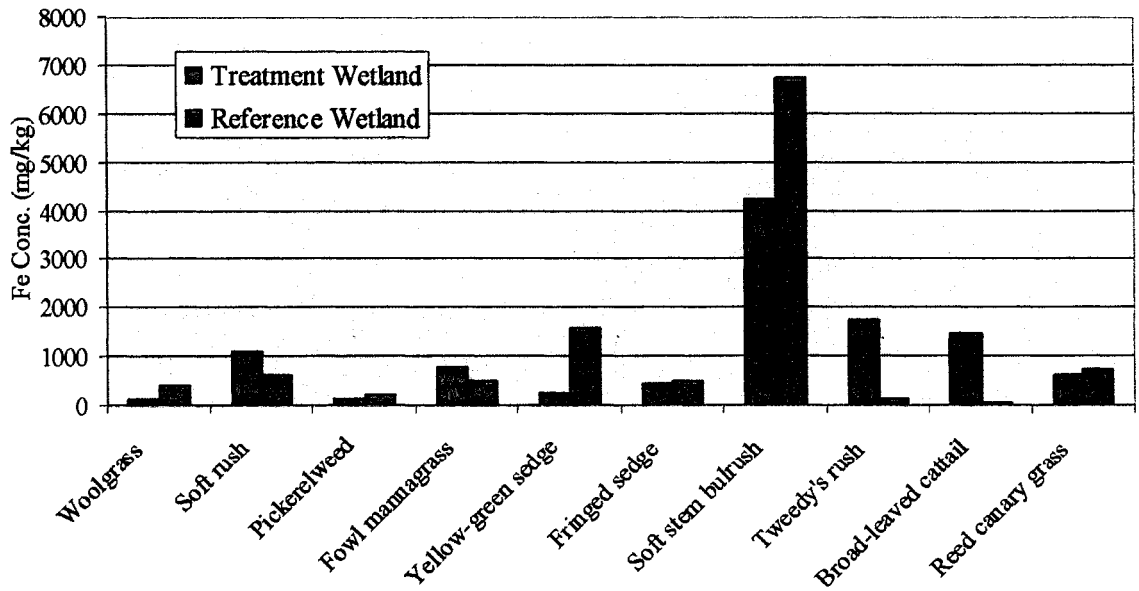


Figure 5.62. Iron concentrations in flower tissues (October 2003).

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the reference wetland. The highest concentration of iron in the flowers of the plants sampled from the reference wetland were 6695, 1564, 739, 596, 471, 466, 415, 184, 138 and 24 mg/kg for Soft stem bulrush, Yellow-green sedge, Reed canary grass, Soft rush, Fowl mannagrass, Fringed sedge, Wool grass, Pickerelweed, Tweedy's rush and Broad leaved cattail, respectively. The highest concentration of iron in the flowers of the plants sampled from the treatment wetland were 4222, 1714, 1466, 1094, 779, 619, 433, 433, 229, 122 and 105 mg/kg for Soft stem bulrush, Tweedy rush, Broad leaved cattail, Soft rush, Fowl mannagrass, Reed canary grass, Fringed sedge, Yellow-green sedge, Pickerelweed and Wool grass, respectively.

Generally, the plants obtained from the treatment wetland had higher total concentrations of iron in their tissues compared to these of the plants obtained from the reference wetland, except for Soft rush and Fowl mannagrass (Figure 5.63). The highest total concentration of iron in the tissues of the plants sampled from the treatment wetland were 21598, 19477, 18938, 13473, 13179, 11859, 10206, 8069, 7972 and 5306 mg/kg for Broad leaved cattail, Tweedy's rush, Soft stem bulrush, Reed canary grass, Pickerelweed, Yellow-green sedge, Wool grass, Fowl mannagrass, Fringed sedge and Soft rush, respectively. The highest total concentration of iron in the tissues of the plants sampled from the reference wetland 9775, 8276, 7158, 5271, 5165, 4879, 3864, 3756, 3249 and 409 mg/kg for Soft stem bulrush, Fowl mannagrass, Soft rush, Pickerelweed, Yellow green sedge, Tweedy's rush, Wool grass, Fringed sedge and Broad leaved cattail, respectively.

5.8.2.1.2 Manganese: Generally, all plants accumulated more manganese in their roots in the treatment wetland compared to the reference wetland, except for Fowl mannagrass and Fringed sedge (Figure 5.64). The highest concentration of manganese in the root of the plants sampled from the reference wetland were 427, 270, 140, 129, 97, 84, 72, 71, 49 and 34 mg/kg for Fringed sedge, Fowl mannagrass, Soft stem bulrush, Pickerelweed, Soft rush, Tweedy's rush, Wool grass, Yellow green sedge, Reed canary grass and Broad leaved cattail, respectively. The highest manganese concentration in the roots of the plants sampled from the treatment wetland were 447, 269, 217, 200, 156, 127, 90, 86, 74

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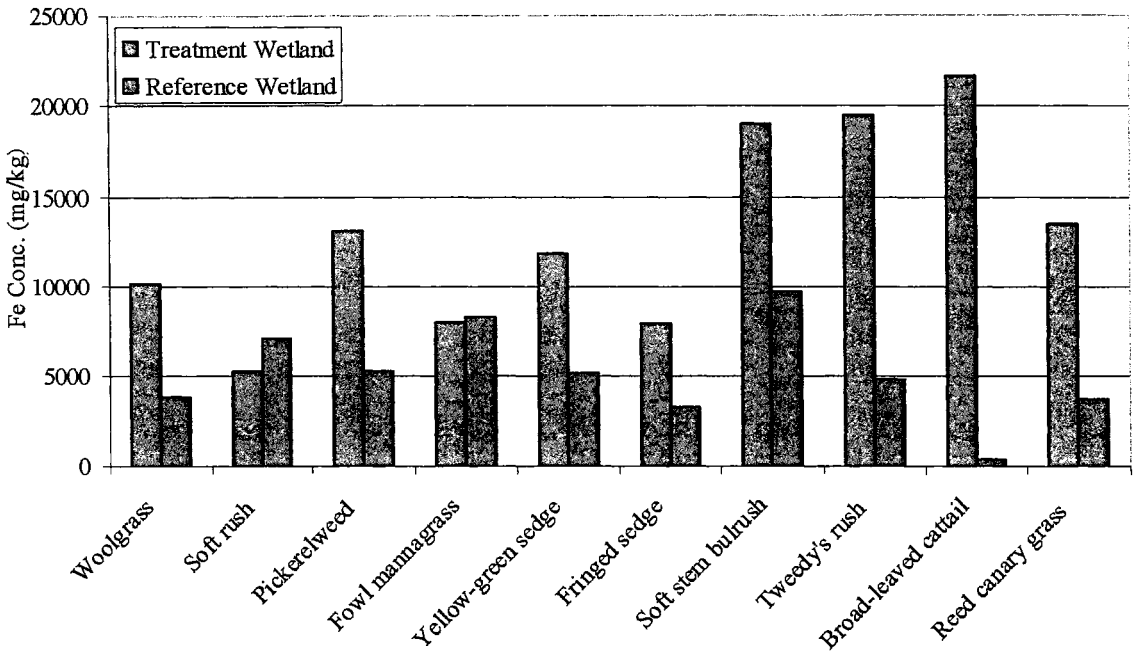


Figure 5.63. Total Iron concentrations in plant tissues (October 2003).

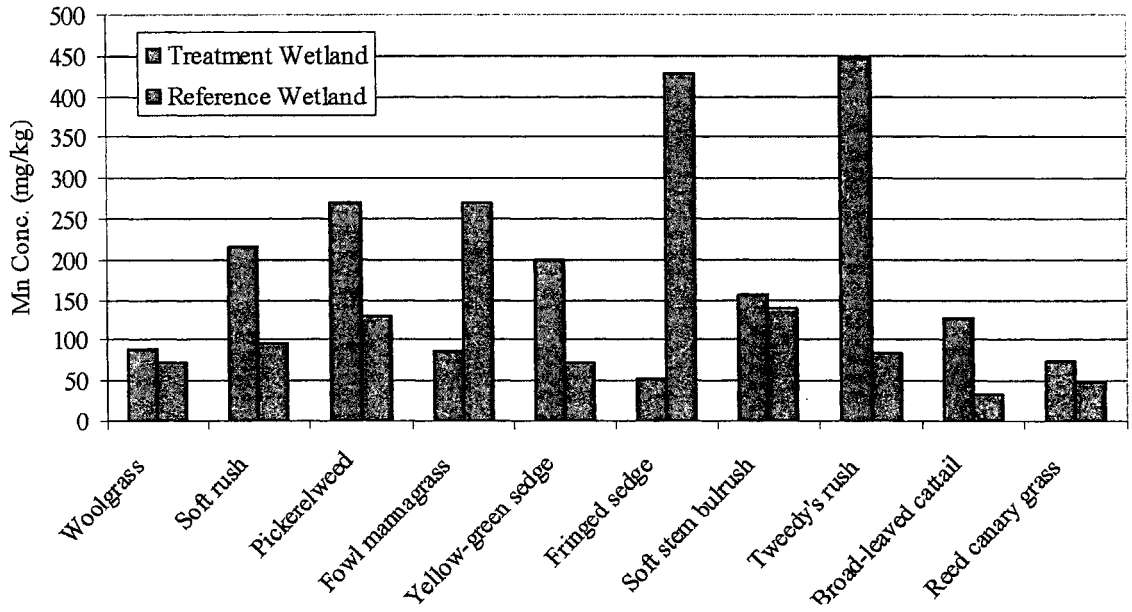


Figure 5.64. Manganese concentrations in root tissues (October 2003).

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and 52 mg/kg for Tweedy rush, Pickerelweed, Soft rush, Yellow green sedge, Soft stem bulrush, Broad leaved cattail, Wool grass, Fowl mannagrass Reed canary grass and Fringed sedge, respectively.

Most plants accumulated more manganese in their stems in the treatment wetland compared to the reference wetland, except for Soft rush, Pickerelweed and Yellow-green sedge (Figure 5.65). The highest concentration of manganese in the stems of the plants sampled from the reference wetland were 313, 308, 210, 129, 103, 88, 83, 49, 44 and 43 mg/kg for Soft rush, Tweedy rush, Yellow-green sedge, Fowl mannagrass, Wool grass, Soft stem bulrush, Pickerelweed, Reed canary grass, Broad leaved cattail and Fringed sedge, respectively. The highest concentrations of manganese in the stems of the plants sampled from the treatment wetland were mg/kg 309, 289, 277, 268, 225, 171, 129, 103, 52 and 44 mg/kg for Fowl mannagrass, wool grass, Broad leaved cattail, Soft stem bulrush, Tweedy's rush, Soft rush, Reed canary grass, Yellow green sedge, Pickerelweed and Fringed sedge, respectively.

Pickerelweed, Fowl mannagrass, Broad leaved cattail and Reed canary grass accumulated more manganese in their leaves in the treatment wetland compared to the reference wetland while Wool grass, Yellow-green sedge and Fringed sedge accumulated more manganese in their leaves in the reference wetland compared to the treatment wetland (Figure 5.66). The highest concentrations of manganese in the leaves of the plants sampled from the reference wetland were 783, 499, 432, 371, 283, 191 and 150 mg/kg for Broad leaved cattail, Fowl mannagrass, Pickerelweed, Yellow green sedge, Reed canary grass, Wool grass and Fringed sedge, respectively. The highest concentration of manganese in the leaves of the plants sampled from the treatment wetland were 1480, 730, 555, 488, 167, 148 and 130 mg/kg for Fowl managrass Broad leaved cattail, Pickerelweed, Reed canary grass, Yellow green sedge, Wool grass and Fringed sedge, respectively.

Generally, most plants accumulated more manganese in their flowers in the treatment wetland compared to the reference wetland, except Wool grass and Soft rush and

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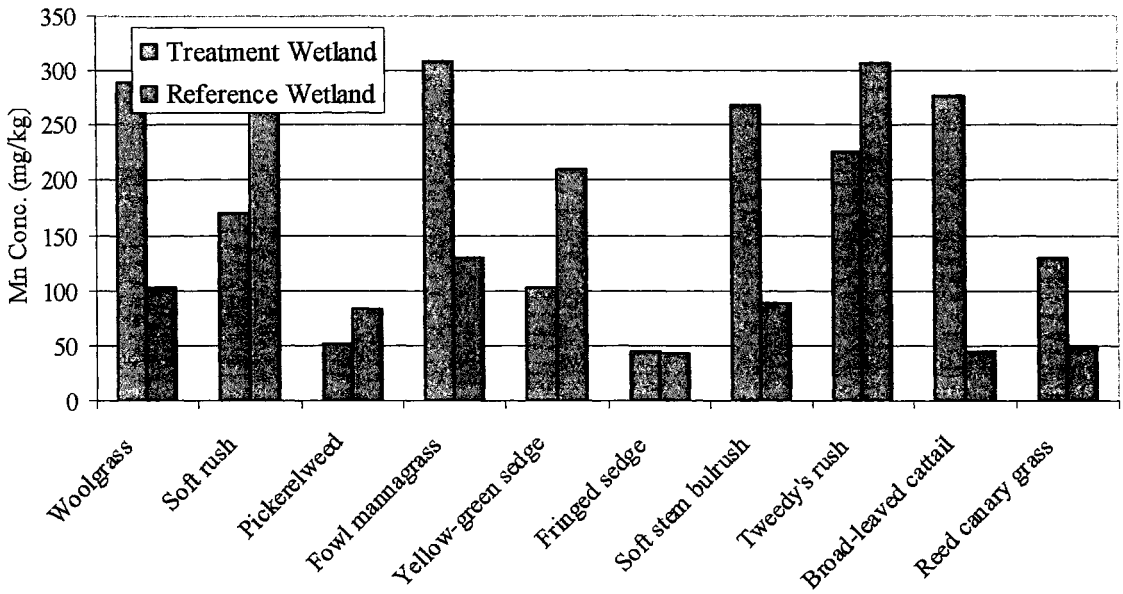


Figure 5.65. Manganese concentrations in stem tissues (October 2003).

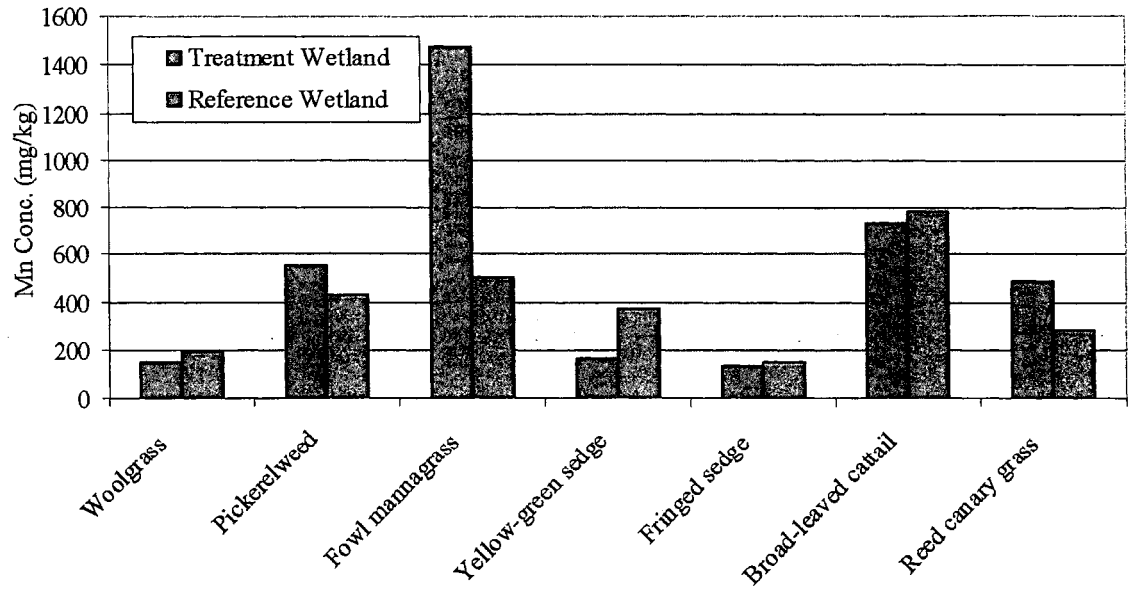


Figure 5.66. Manganese concentrations in leaves tissue (October 2003).

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Pickerelweed (Figure 5.67). The highest concentrations of manganese in the flowers of the plants sampled from the reference wetland were 471, 419, 374, 351, 265, 212, 190, 105, 84 and 79 mg/kg for Soft rush, Soft stem bulrush, Tweedy's rush, Wool grass, Yellow green sedge, Pickerelweed, Fowl mannagrass, Broad leaved cattail, Fringed sedge and Reed canary grass, respectively. The highest concentrations of manganese in the flowers of the plants sampled from the treatment wetland were 778, 467, 443, 412, 392, 386, 249, 230, 198 and 56 mg/kg for Soft stem bulrush, Broad leaved cattail, Tweedy's rush, Soft rush, Yellow green sedge, Fowl mannagrass, Reed canary grass, Fringed sedge, Pickerelweed and Wool grass, respectively.

Generally, all plants accumulated more manganese in their tissues in the treatment wetland compared to the reference wetland, except for Fowl mannagrass, Fringed sedge and Reed canary grass (Figure 5.68). The highest total concentrations of manganese in the tissues of the plants sampled from the treatment wetland were 1999, 1690, 1355, 1115, 1056, 948, 871, 825, 583 and 508 mg/kg for Pickerelweed, Soft stem bulrush, Soft rush, Tweedy's rush, Fringed sedge, Fowl mannagrass, broad leaved cattail, Yellow green sedge, Wool grass and Reed canary grass, respectively. The highest total manganese concentrations in the tissues of the plants sampled from the reference wetland were 1337, 1313, 960, 930, 923, 766, 717, 696, 528 and 183 mg/kg for Fringed sedge, Soft rush, Fowl mannagrass, Soft stem bulrush, Pickerelweed, Tweedy's rush, Wool grass, Yellow green sedge, Reed canary grass and Broad leaved cattail, respectively.

5.8.2.2 Season II (May 2004- October 2004)

5.8.2.2.1 Iron: The iron concentrations in the roots of all the plants sampled from the treatment wetland increased with time during the testing period (May – October 2004) as shown in Figure 5.69. The highest concentrations of iron in the roots observed at the end of the testing period (October 2004) were 18365, 15368, 14037, 13562, 12685, 11250, 9850, 7689, 7235 and 3689 mg/kg for Tweedy's rush, Broad leaved cattail, Soft stem bulrush, Pickerelweed, Reed canary grass, Yellow-green sedge, Wool grass, Fowl mannagrass, Soft rush and Fringed sedge, respectively (Figure 5.70). The average accumulation rates of iron in the roots were 3173, 2716, 2201, 2192, 1982, 1738, 1257,

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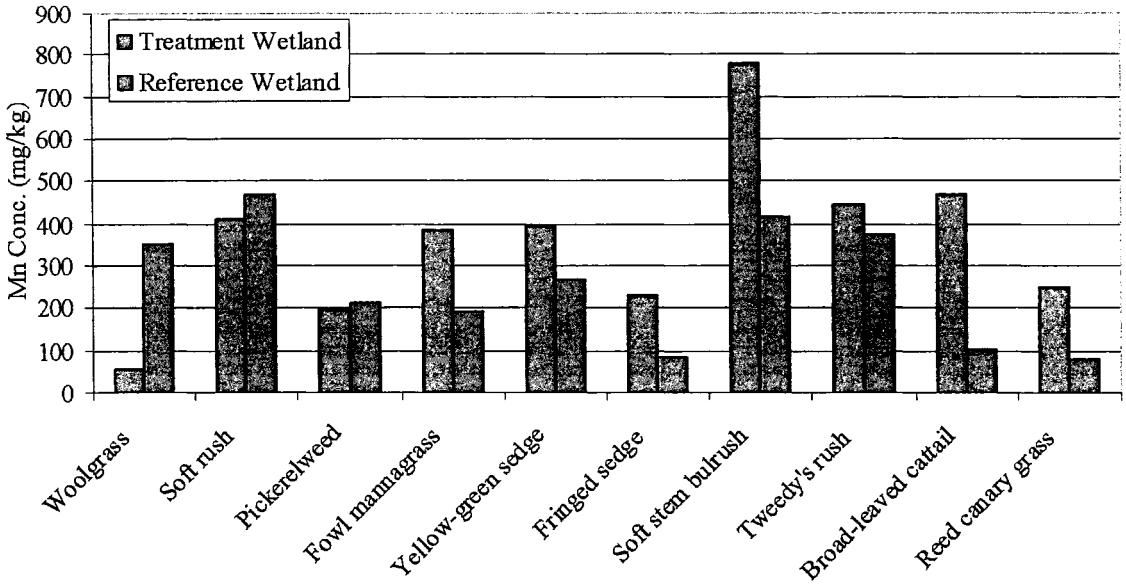


Figure 5.67. Manganese concentrations in flower tissues (October 2003).

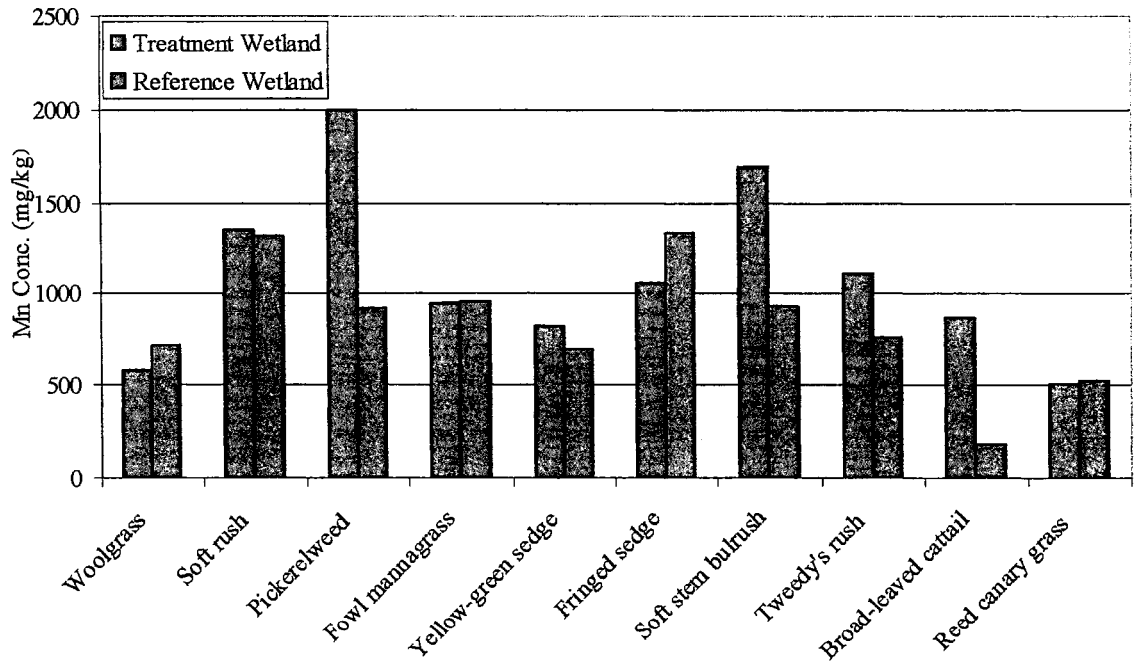


Figure 5.68. Total manganese concentrations in plant tissues (October 2003).

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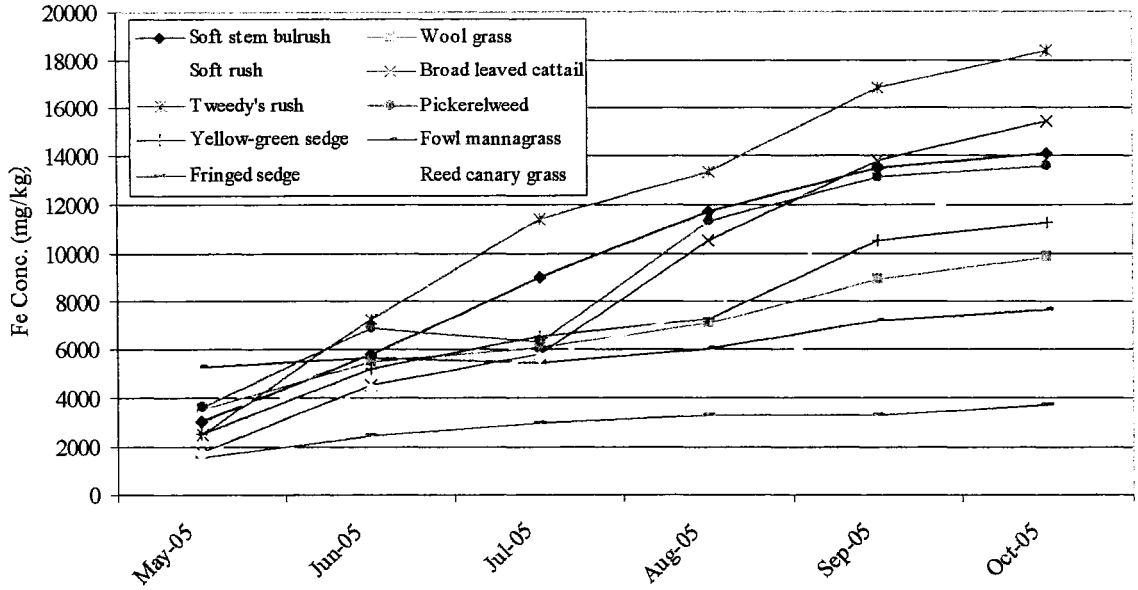


Figure 5.69. Accumulation of iron in plant root tissues (May - October 2004).

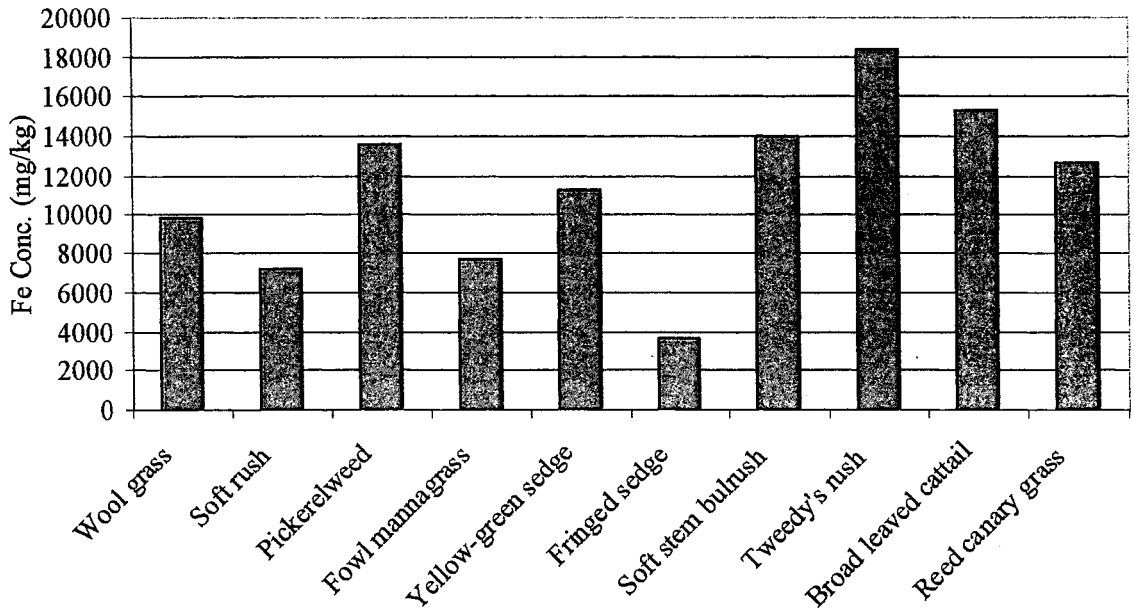


Figure 5.70. Iron concentrations in root tissues (October 2004).

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733, 488 and 431 mg/kg/month for Tweedy's rush, Broad leaved cattail, Reed canary grass, Soft stem bulrush, Pickerelweed, Yellow-green sedge, Wool grass, Soft rush, Fowl mannagrass and Fringed sedge, respectively.

The iron concentrations in the stem of all the plants sampled from the treatment wetland increased with time during the testing period (May – October 2004) as shown in Figure 5.71. The highest concentrations of iron in the stems observed at the end of the testing period (October 2004) were 956, 586, 485, 356, 350, 205, 192, 186, 145 and 129 mg/kg for the Soft stem bulrush followed by Broad leaved cattail, Tweedy's rush, Reed canary grass, Yellow-green sedge, Soft rush, Fringed sedge, Wool grass, Pickerelweed and Fowl mannagrass, respectively (Figure 5.72). The average accumulation rates of iron in the stems were 168, 90, 67, 47, 43, 41, 21, 14, 10 and 7 mg/kg/month for Soft stem bulrush, Broad leaved cattail, Tweedy's rush, Soft rush, Yellow-green sedge, Reed canary grass, Fowl mannagrass, Fringed sedge, Pickerelweed and Wool grass, respectively.

The iron concentrations in the leaves of all the plants sampled from the treatment wetland increased with time during the testing period (May – October 2004) as shown in Figure 5.73. The highest concentrations of iron in the leaves observed at the end of the testing period (October 2004) were 6235, 4360, 1260, 1210, 856, 523 and 354 mg/kg for the Broad leaved cattail, Fringed sedge, Fowl mannagrass, Yellow-green sedge, Reed canary grass, Pickerelweed and Wool grass, respectively (Figure 5.74). The average accumulation rates of iron in the leaves were 1127, 725, 199, 82, 81, 60 and 42 mg/kg/month for Broad leaved cattail, Fringed sedge, Fowl mannagrass, Pickerelweed, Reed canary grass, Yellow-green sedge and Wool grass, respectively.

The iron concentrations in the flowers of all the plants sampled from the treatment wetland increased with time during the testing period (May – October 2004) as shown in Figure 5.75. The highest concentrations of iron in the flowers observed at the end of the testing period (October 2004) were 7550, 1775, 1590, 1536, 1250, 952, 836, 560, 456, 195 mg/kg for the Soft stem bulrush, Tweedy rush, Yellow green sedge, Broad leaved cattail, Soft rush, Fowl mannagrass, Reed canary grass, Fringed sedge, Wool grass and

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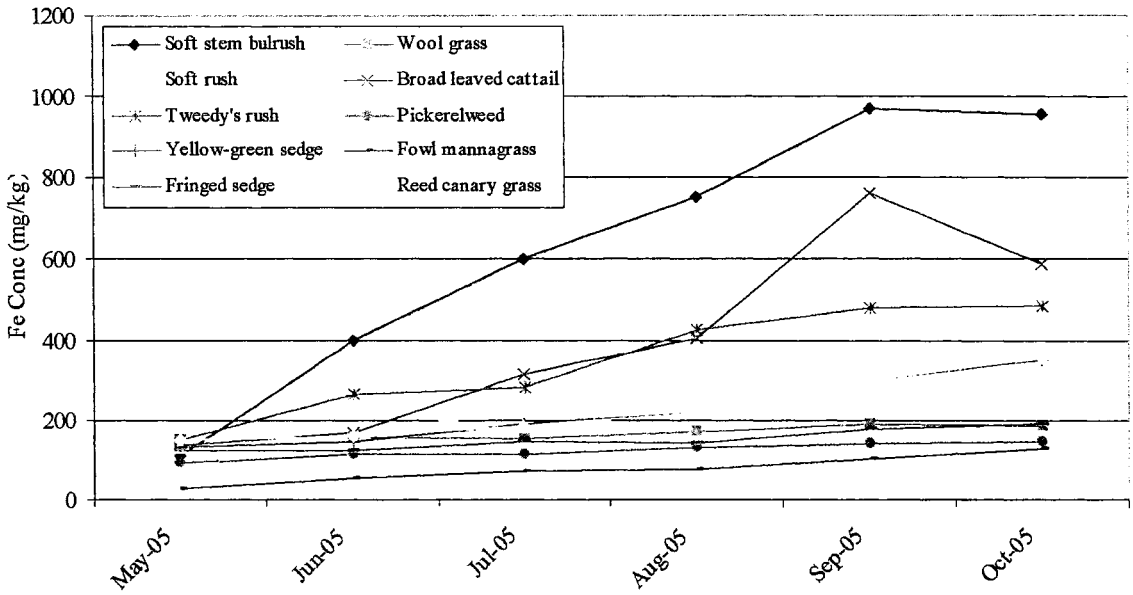


Figure 5.71. Accumulation of iron in plant stem tissues (May - October 2004).

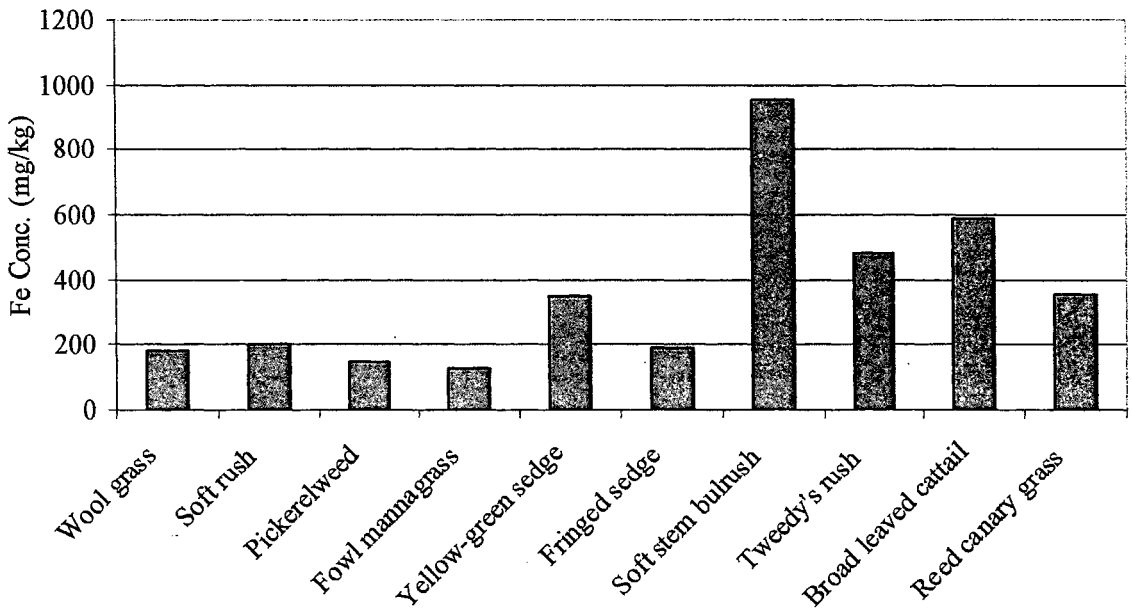


Figure 5.72. Iron concentrations in stem tissues (October 2004).

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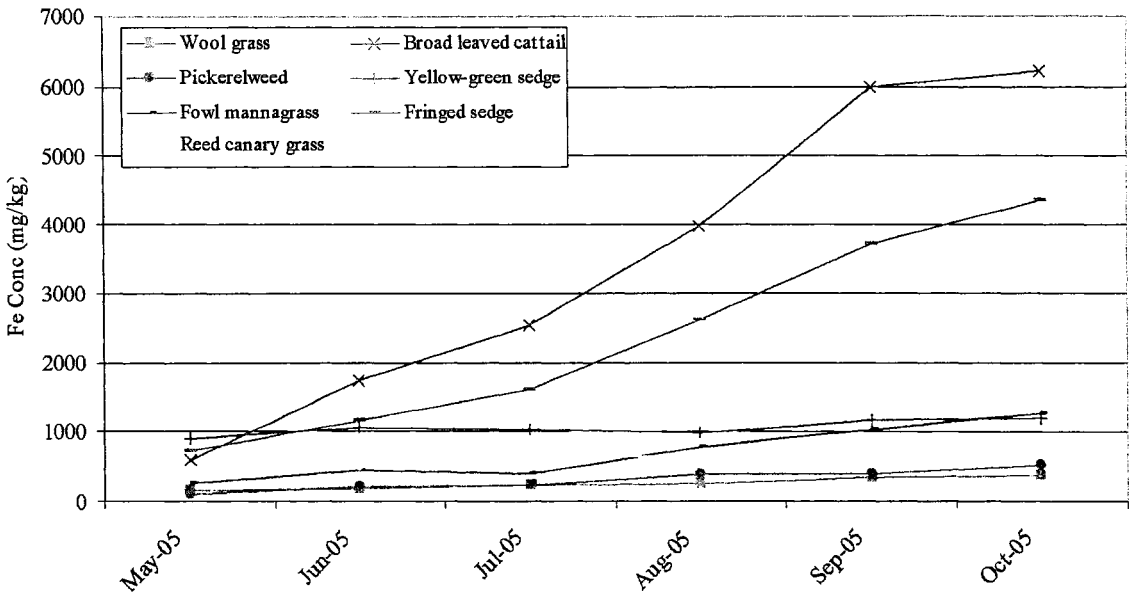


Figure 5.73. Accumulation of iron in plant leaves tissues (May - October 2004).

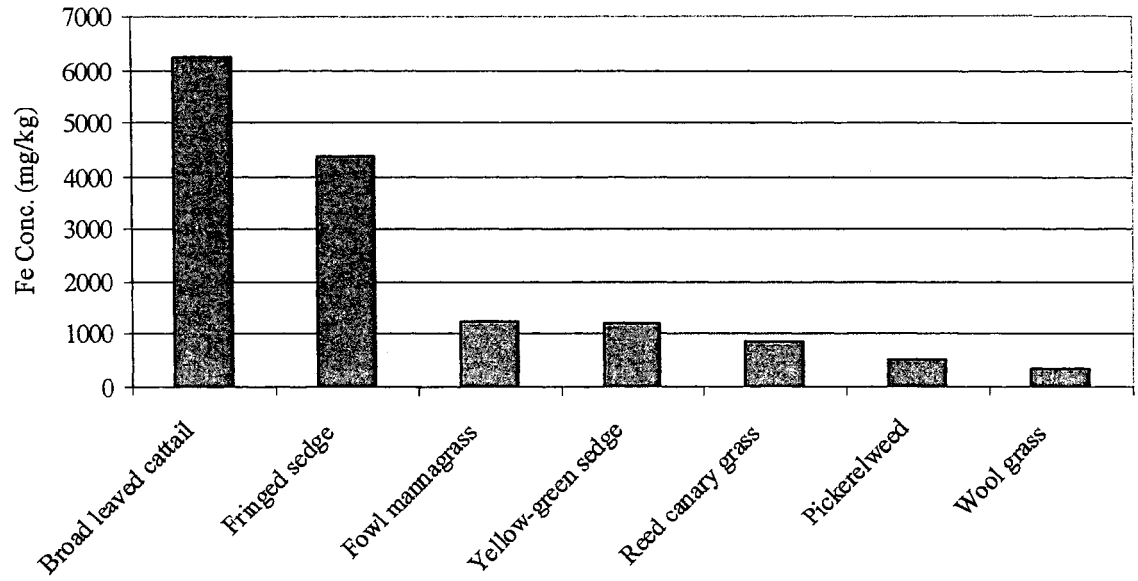


Figure 5.74. Iron concentrations in leaves tissues (October 2004).

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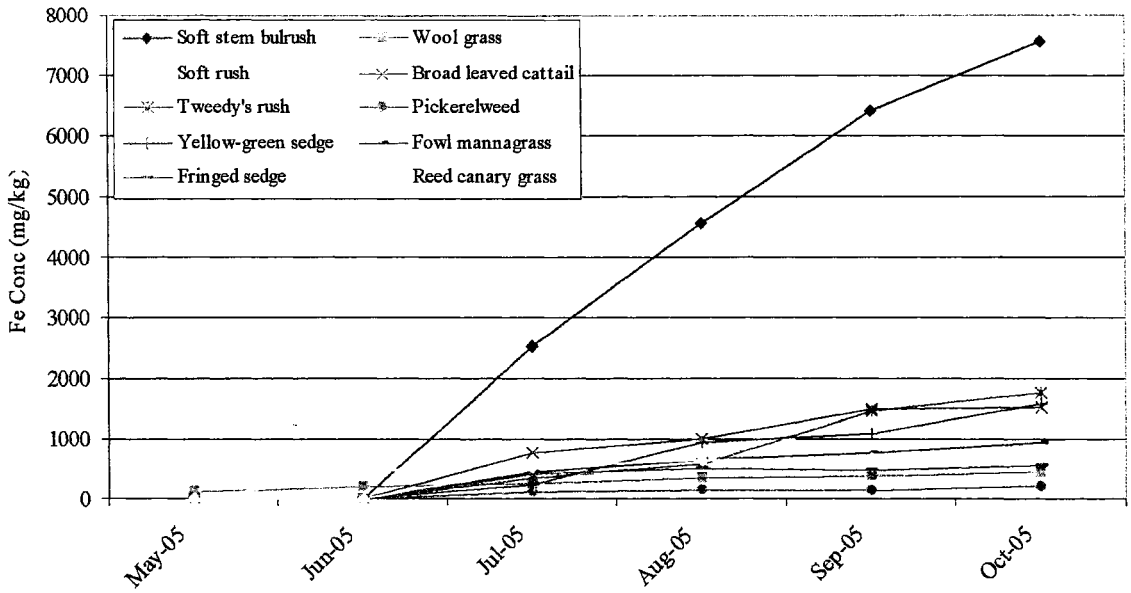


Figure 5.75. Accumulation of iron in plant flowers tissues (May - October 2004).

Pickerelweed, respectively (Figure 5.76). The average accumulation rates of iron in the flowers were 1570, 355, 318, 307, 250, 190, 167, 112, 66 and 39 mg/kg/month for Soft stem bulrush, Tweedy rush, Yellow green sedge, Broad leaved cattail, Soft rush, Fowl mannagrass, Reed canary grass, Fringed sedge, Wool grass and Pickerelweed, respectively.

The highest total concentrations of iron in the plants observed at the end of the testing period (October 2004) were 23725, 22543, 20625, 14733, 14425, 14400, 10846, 10030, 8690 and 8801 mg/kg for Broad leaved cattail, Soft stem bulrush, Tweedy's rush, Reed canary grass, Pickerelweed, Yellow-green sedge, Wool grass, Fowl mannagrass, Fringed sedge and Soft rush, respectively (Figure 5.77).

5.8.2.2.2 Manganese: The manganese concentrations in the roots of all the plants sampled from the treatment wetland increased with time during the testing period (May – October 2004) as shown in Figure 5.78. The highest manganese concentrations in the roots observed at the end of the testing period (October 2004) were 575, 524, 295, 286, 250, 235, 168, 136, 123 and 92 mg/kg for Tweedy's rush, Fringed sedge, Pickerelweed, Fowl mannagrass, Soft rush, Yellow-green sedge, Soft stem bulrush, Broad leaved cattail,

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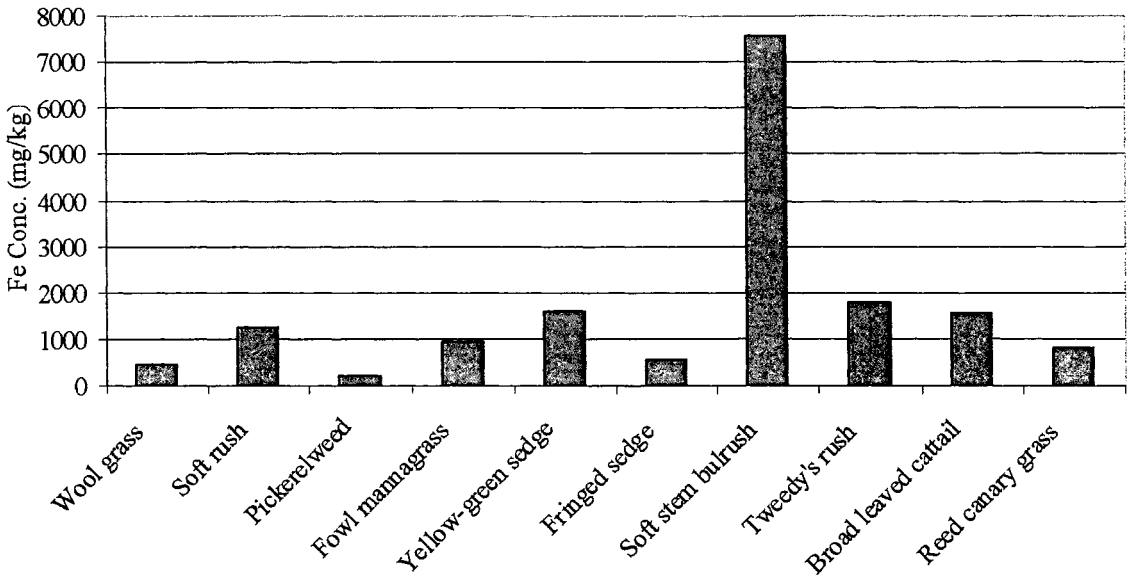


Figure 5.76. Iron concentrations in flowers tissues (October 2004).

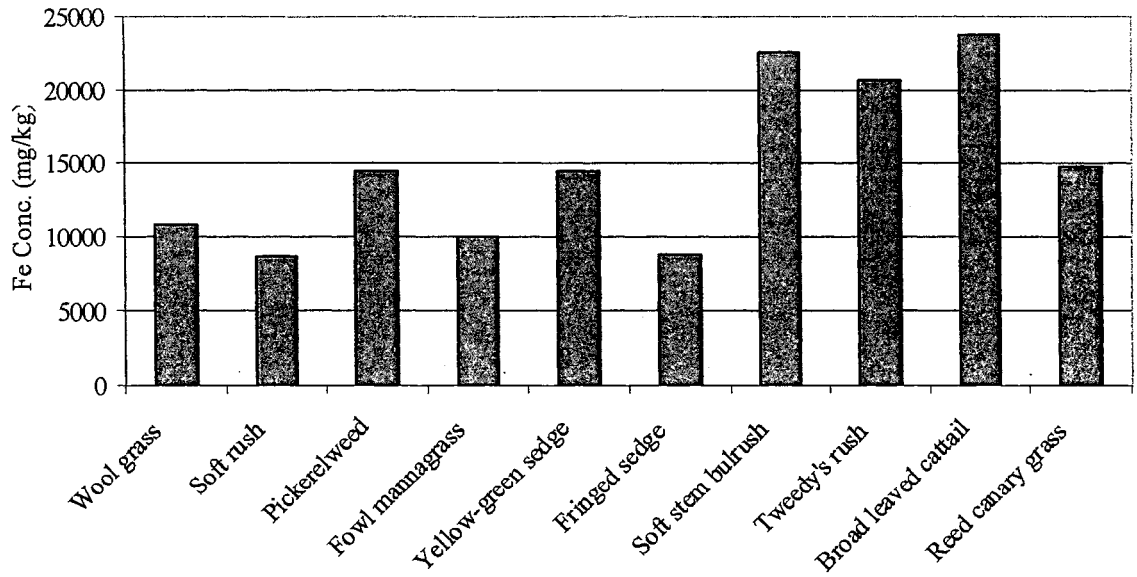


Figure 5.77. Total iron concentrations in plant tissues (October 2004).

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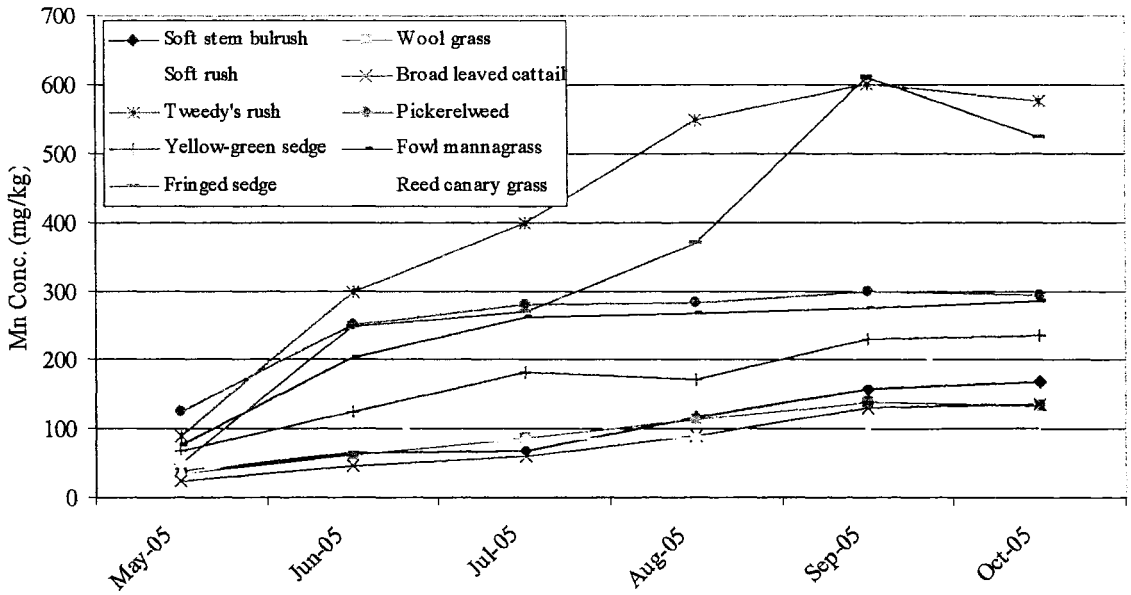


Figure 5.78. Accumulation of manganese in plant roots tissues (May - October 2004).

Wool grass and Reed canary grass, respectively (Figure 5.79). The average accumulation rates of manganese in the roots were 97, 95, 43, 42, 34, 33, 26, 23, 19 and 8 mg/kg/month for Tweedy's rush, Fringed sedge, Soft rush, Fowl mannagrass, Pickerelweed, Yellow-green sedge, Soft stem bulrush, Broad leaved cattail, Wool grass and Reed canary grass, respectively.

The manganese concentrations in the stems of all the plants sampled from the treatment wetland increased with time during the testing period (May – October 2004) as shown in Figure 5.80. The highest concentrations of manganese in the stems observed at the end of the testing period (October 2004) were 386, 375, 365, 356, 356, 325, 253, 153, 96 and 74 mg/kg for Soft rush, Fowl mannagrass, Broad leaved cattail, Wool grass, Tweedy's rush, Soft stem bulrush, Yellow-green sedge, Reed canary grass, Pickerelweed and Fringed sedge, respectively (Figure 5.81). The average accumulation rates of manganese in the stems were 69, 59, 54, 51, 46, 31, 30, 24, 11 and 6 mg/kg/month for Broad leaved cattail, Soft rush, Wool grass, Fowl mannagrass, Soft stem bulrush, Tweedy's rush, Yellow-green sedge, Reed canary grass, Pickerelweed and Fringed sedge, respectively.

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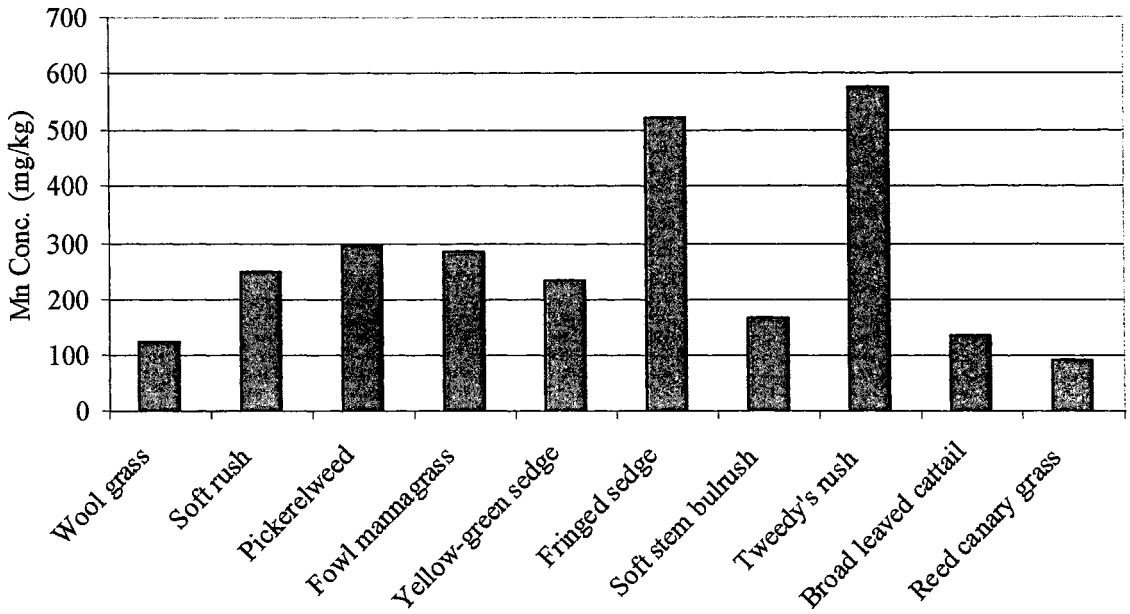


Figure 5.79. Manganese concentrations in root tissues (October 2004).

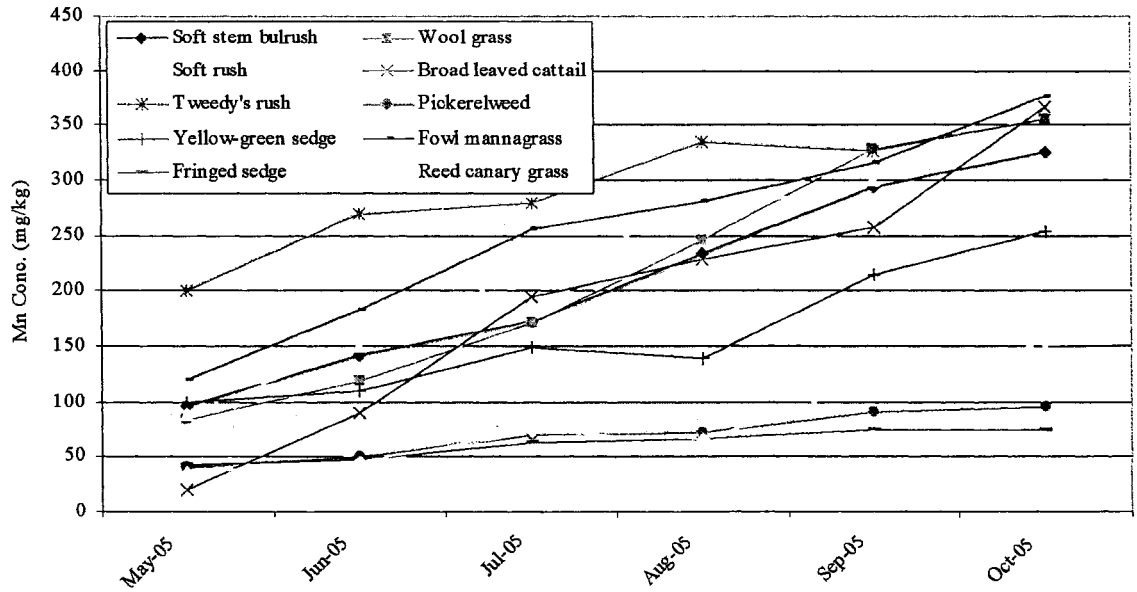


Figure 5.80. Accumulation of manganese in plant stem tissues (May - October 2004).

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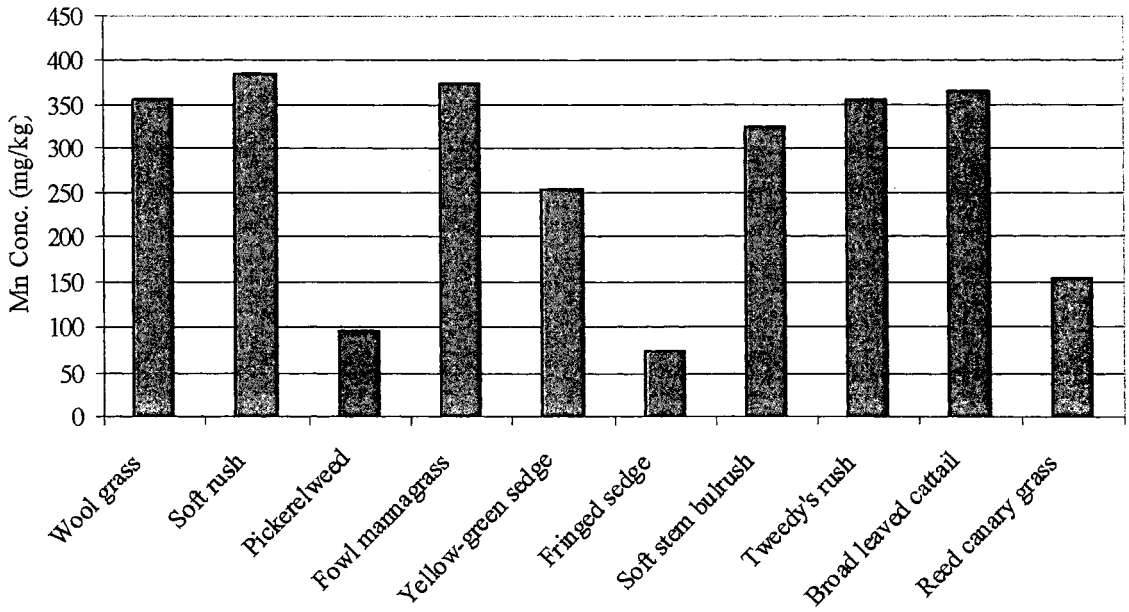


Figure 5.81. Manganese concentrations in stem tissues (October 2004).

The manganese concentrations in the leaves of all the plants sampled from the treatment wetland increased with time during the testing period (May – October 2004) as shown in Figure 5.82. The highest concentrations of manganese in the leaves observed at the end of the testing period (October 2004) were 1586, 793, 685, 589, 389, 325, and 189 mg/kg for Fowl managrass, Broad leaved cattail, Reed canary grass, Pickerelweed, Yellow-green sedge, Wool grass and Fringed sedge, respectively (Figure 5.83). The average accumulation rates of manganese in the leaves were 203, 147, 89, 48, 37, 34 and 13 mg/kg/month for Fowl managrass, Broad leaved cattail, Reed canary grass, Yellow-green sedge, Wool grass, Pickerelweed and Fringed sedge, respectively.

The manganese concentrations in the flowers of all the plants sampled from the treatment wetland increased with time during the testing period (May – October 2004) as shown in Figure 5.84. The highest concentrations of manganese in the flowers observed at the end of the testing period (October 2004) were 823, 536, 521, 489, 425, 425, 395, 265, 265 and 256 mg/kg for Soft stem bulrush, Broad leaved cattail, Soft rush, Tweedy's rush, Wool grass, Yellow-green sedge, Fowl mannagrass, Pickerelweed, Reed canary grass and Fringed sedge, respectively (Figure 5.85). The average accumulation rates of manganese

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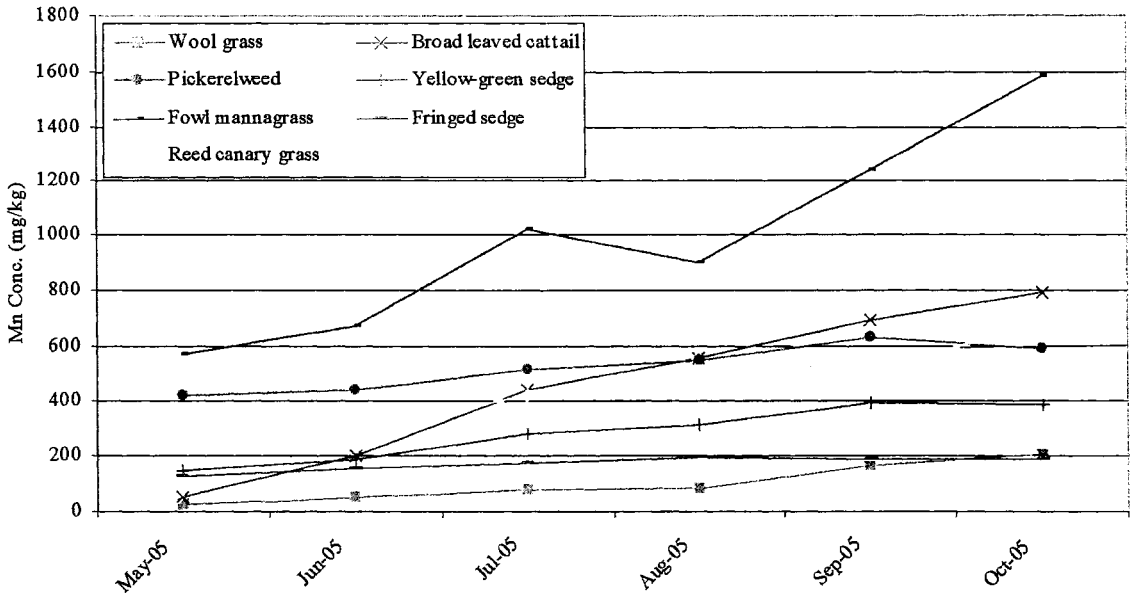


Figure 5.82. Accumulation of manganese in plant leaves tissues (May - October 2004).

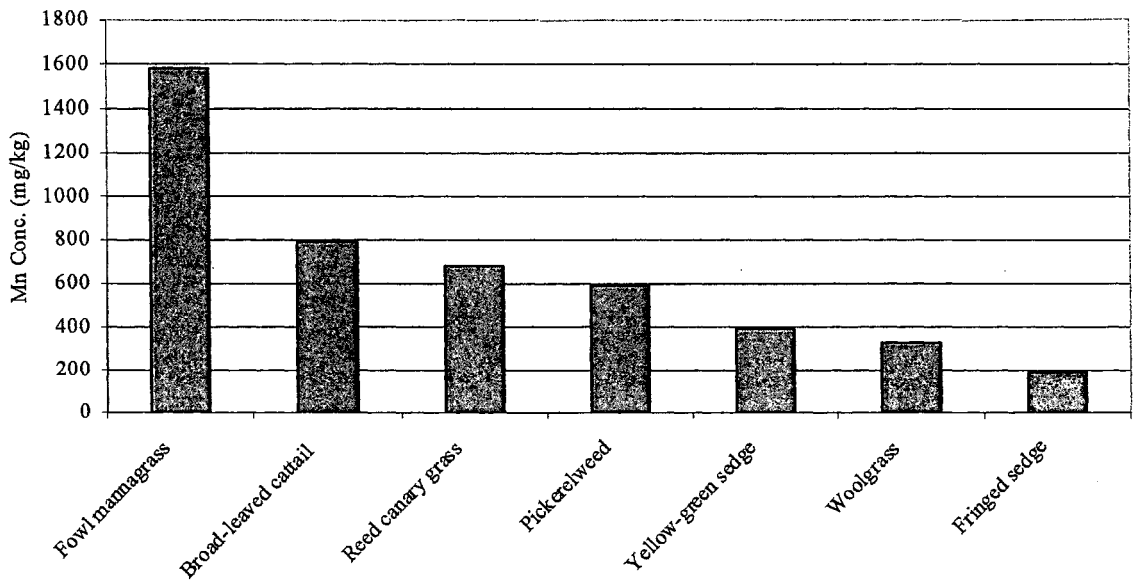


Figure 5.83. Manganese concentrations in leaves tissue (October 2004).

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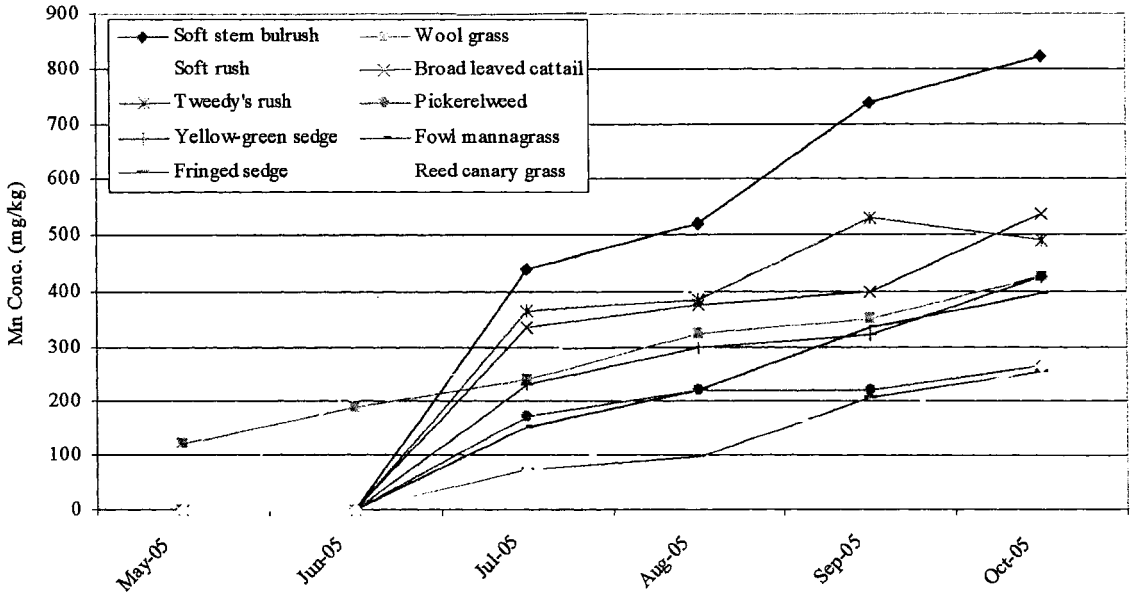


Figure 5.84. Accumulation of manganese in plant flowers tissues (May - October 2004).

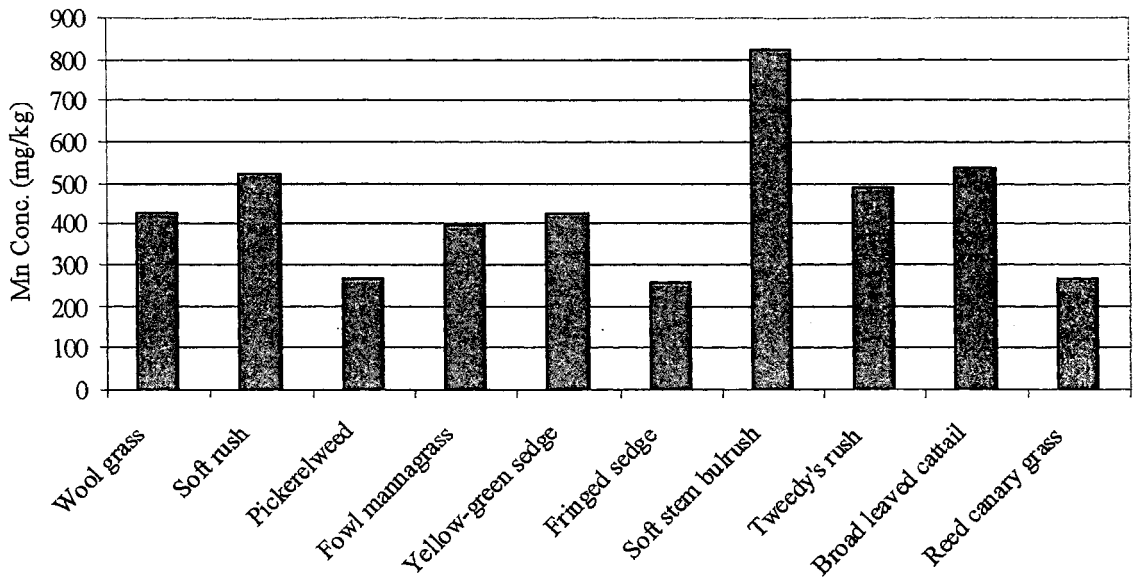


Figure 5.85. Manganese concentrations in flower tissues (October 2004).

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in the flowers were 165, 80, 75, 67, 65, 64, 60, 60, 41 and 30 mg/kg/month for Soft stem bulrush, Fowl mannagrass, Soft rush, Broad leaved cattail, Reed canary grass, Yellow-green sedge, Fringed sedge, Wool grass, Tweedy's rush and Pickerelweed, respectively.

The highest total concentrations of manganese in the plant tissues observed at the end of the testing period (October 2004) were 2642, 1830, 1420, 1316, 1302, 1245, 1229, 1195, 1157 and 1043 mg/kg for Fowl mannagrass, Broad leaved cattail, Tweedy's rush, Soft stem bulrush, Yellow-green sedge, Pickerelweed, Wool grass, Reed canary grass, Soft rush and Fringed sedge, respectively (Figure 5.86).

5.8.3 Soil Analyses

The iron and manganese concentrations in the wetland sediments in season II are shown in Table 5.13. The iron concentrations in the sediments measured during the growing season ranged from 59580 to 61850 and from 40180 to 40850 mg/kg near the inlet and outlet, respectively. The average accumulation rate of iron in the wetland sediments was 454 mg/kg/month. The manganese concentrations measured in the sediments ranged from769 to 850 and from 536 to 589 mg/kg near the inlet and outlet, respectively. The average accumulation rate of manganese in the wetland sediments was 11 mg/kg/month.

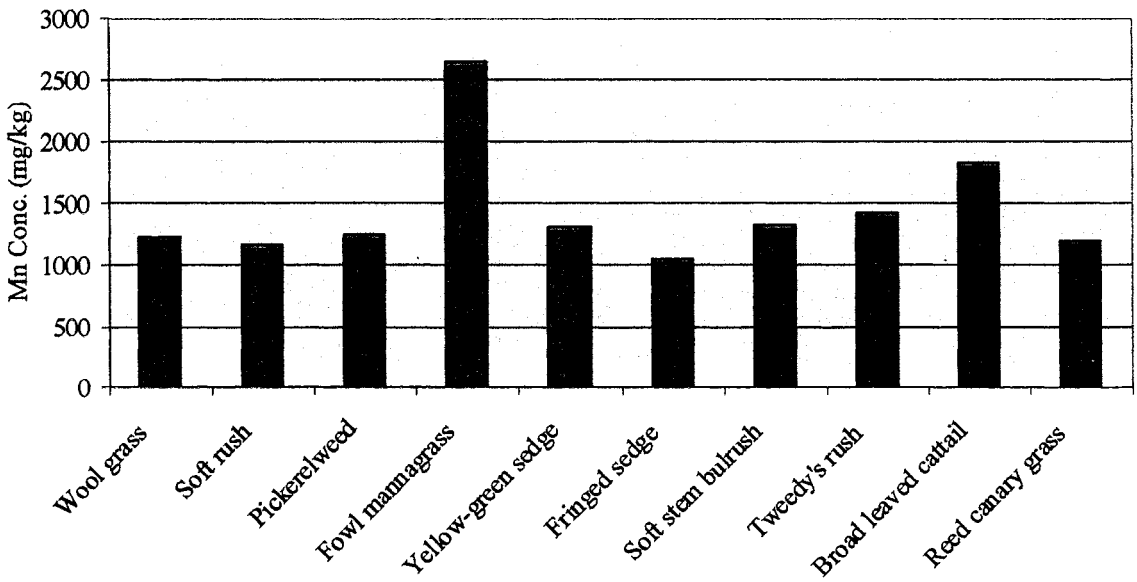


Figure 5.86. Total manganese concentrations in plant tissues (October 2004).

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Table 5.13. Iron and manganese concentrations in the wetland sediments.

Sampling Date	Location	Fe (mg/kg)	Mn (mg/kg)
15-May	Inlet	59580	850
	Outlet	40850	540
15-Jun	Inlet	60250	769
	Outlet	40550	562
16-Jul	Inlet	60035	769
	Outlet	40240	564
16-Aug	Inlet	60690	820
	Outlet	40980	589
17-Sep	Inlet	60890	810
	Outlet	40690	568
20-Oct	Inlet	61850	795
	Outlet	40180	536

5.9 Discussions

5.9.1 General Water Quality Analyses

Constructed wetlands are highly complex systems that separate and transform contaminants by physical, chemical, and biological mechanisms that may occur simultaneously or sequentially as the wastewater flows through the system. The predominant mechanisms and their sequence of reaction are dependent on the external input parameters to the system, the internal interactions, and the characteristics of the wetland. The external input parameters most often of concern include the wastewater quality and quantity and the system hydrological cycle. The two major mechanisms at work in most treatment systems are liquid/solid separations and constituent transformations. Separations typically include gravity separation, filtration, absorption, adsorption, ion exchange, stripping, and leaching. Transformations may be due to chemical reactions, including oxidation/reduction reactions, flocculation, acid/base reactions, precipitation, or biochemical reactions occurring under aerobic, anoxic, or anaerobic conditions. Several parameters were used to asses the water quality of the wetland. These included: pH, dissolved oxygen, orthophosphate, total Kjeldahl nitrogen, ammonium, nitrite, nitrate, chemical oxygen demand, total suspended solids and total dissolved solids. The results of the water quality are presented in Table 5.14.

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Table 5.14. General water quality parameters used in this study.

Water Quality Parameter	Guidelines* (mg/L)	Reference Wetland (mg/L)	Treatment Wetland					
			Inlet (mg/L)		Outlet (mg/L)		Removal Efficiency (%)	
			Season I	Season II	Season I	Season II	Season I	Season II
pH	5.0 – 9.0	6.5	7.18	7.34	7.27	7.28	---	---
Dissolved Oxygen	4.5 – 9.5	6.32	6.13	6.15	4.68	6.09	---	---
Orthophosphate	NGA	<0.01	0.01	0.01	0.006	0.004	40.00	60.00
Total Kjeldahl Nitrogen	NGA	0.41	4.69	3.82	3.76	2.60	19.83	31.94
Ammonium	NGA	0.06	0.79	1.09	0.23	0.25	70.89	52.29
Nitrite	0.06	<0.05	0.012	0.023	0.01	0.01	16.67	56.52
Nitrate	13.00	0.41	3.69	3.15	3.34	2.45	9.49	22.22
Chemical Oxygen Demand	NGA	132	816	807	797	381	2.33	52.79
Total Suspended Solids	NGA	85	580	851	451	255	22.24	70.04
Total Dissolved Solids	NGA	55	381	522	318	146	16.54	72.03

NGA No Guidelines Available
* Canadian Council of Ministers of the Environment Water Quality Guidelines for the Protection of Freshwater Life.

5.9.1.1 pH

According to EPA (1999), the cellulose of the dead plants in the wetland are degraded by cellulolytic bacteria to generate free sugars and other metabolites as follows:

$$\text{Cellulose} \xrightarrow{\text{Cellulotic Bacteria}} \beta\text{-Glucan} \xrightarrow{\text{Cellulotic Bacteria}} \text{Glucose} + \text{Cellodextrin} \qquad (5.2)$$

The wetland soil is under anaerobic conditions and the free sugars are fermented to short chain organic acids as follows (EPA, 1999):

$$C_6H_{12}O_6 + 2H_2O \longrightarrow 2C_2H_4O_2 + 2CO_2 + 8\,H^+ + 8\,e^- \qquad (5.3)$$

The produced carbon dioxide (Equation 5.3) is converted to bicarbonate as shown by the following equations:

$$CO_2 + H_2O \longrightarrow HCO_3^- + H^+ \qquad (5.4)$$

The produced organic acids (Equation 5.3) are suitable substrates to support the growth of sulphate reducing bacteria (SRB) that reduce sulphate to hydrogen sulphide which precipitates metal ions as low solubility metal sulphides as described by the following equations (Southam et al., 1995; and Luptakova and Kusnierova, 2005):

$$10\,H^+ + SO_4^{2-} + 8\,e^- \xrightarrow{\text{SRB}} H_2S + 4\,H_2O \qquad (5.5)$$

$$M^{2+} + H_2S \longrightarrow MS\downarrow + 2\,H^+ \qquad (5.6)$$

Where:

M^{2+}: Divalent metal ion (such as Fe^{2+} or Zn^{2+})

The production of bicarbonate and the consumption of free hydrogen ion in metal precipitation results in an increased pH.

In this study, the pH fluctuated between 6.74 and 7.95 in season I and between 6.70 and 7.60 in season II. There was no apparent trend as the water flow through the cells in season I but there were increases in the pH value as the water flow from cell 1 to cell 9 in most sampling events in season II.

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Aluko et al. (2003) used a constructed wetland to treat landfill leachate and observed a pH of 8.0-8.28 in the effluent. Gschloessl et al. (1998) constructed wetland to treat municipal wastewater and reported a pH of 7.0 - 8.0 in the effluent. Hench et al. (2003) evaluated the efficacy of constructed wetlands for the treatment of domestic wastewater and reported pH of 6.58 in the outlet. In this study, the average pH values in seasons I and II were 7.27 and 7.28, respectively. These pH values were within the range of the CCME (2003) guidelines (5 – 9) for the protection of aquatic life. Exceedances of pH guidelines for the protection of aquatic life have been associated with many adverse effects on the aquatic life in the wetland. However, one of the most significant impacts of pH in water bodies is the effect that it has on the solubility and, thus, the bioavailability of substances such as ammonia (CCME, 1999a; and EPA, 1999).

5.9.1.2 Dissolved Oxygen

Dissolved oxygen is one of the most fundamental parameters in water bodies, as it is essential to the metabolism of all aerobic aquatic organisms. It is added to the water column via photosynthesizing plants and stream flow aeration and consumed from the water, chemical and biochemical oxidation of decaying plants and organisms and the respiration of bacteria, plants and animals (CCME, 1999b).

The DO concentrations in the treatment wetland ranged from 2.5 to 6.7 mg/L in season I and from 5.7 to 6.3 mg/L for season II. The dissolved oxygen concentrations in the treatment wetland waters generally decreased as the water flow through the wetland cells in season I (Figure 5.37) and remained relatively constant in season II (Figure 5.49). This was unexpected as it had been assumed that as the water flow through the cells it would become more oxygenated as a result of the growing vegetation and water purification. The low dissolved oxygen concentrations observed in season I may be explained as a result of the physical oxidation of the abundant iron ochre observed in the site (Lee and Jones-Lee, 2001; and Fripp et al., 2000) and the decomposition of organic pollutants (Mason, 1998) on one hand and the lower plant growth (i.e. less oxygenation) on the other hand.

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The CCME guideline (2003) for dissolved oxygen for the protection of freshwater aquatic life is between 4.5 and 9.0 mg/L for warm water ecosystems such as treatment wetlands. With the exception of the May 24th sampling date, virtually all water samples obtained from the cells in the spring and summer (June – September) of season I had DO below or close to the minimum CCME guidelines limit of 4.5 mg/L. However, the DO concentrations in the cells and the outlet slightly increased above the CCME minimum guidelines limit of 4.5 mg/L as the weather become colder (October – January) and the solubility of O_2 increased (CCME, 1999b). In this study, the dissolved oxygen concentration correlated with water temperature (R^2=0.65) during season I (Figure 5.87) due to the higher level of chemical oxidation and the lower biological activities (wetland was not yet established). However, DO concentration in season II (Figure 5.87) did not drop below the CCME guidelines limit (4.5 mg/L). This was probably due to the higher plant growth which resulted in the oxygenation of water and higher metal uptake by plants which reduced the amount of elements available for chemical oxidation.

5.9.1.3 Orthophosphate

Phosphorus is an essential macronutrient for plant growth as a component of nucleic acids and a universal energy molecule (Lee and Jones-Lee, 2001). However, excess phosphorus triggers eutrophic conditions that causes prolific growth of algal and other aquatic plants. Algal blooms can reduce the amount of light reaching aquatic plants in sediment that may cause the death of these plants. Large amounts of decaying algae and plants result in the consumption of large quantities of oxygen by the bacteria and fungi that break them down. This results in dramatic reduction of oxygen concentration in the water which in turn affects invertebrate predators with high oxygen requirements. The subsequent lack of predators results in critical disruptions in the food chain and increases of nuisance species such as mosquitoes. Algal blooms can also contain toxic strains of blue-green algae which may kill birds, domestic animals, aquatic macroinvertebrates and even humans if consumed (Lee and Jones-Lee, 2001; Sharpley et al., 1994; and Vollenweider, 1968).

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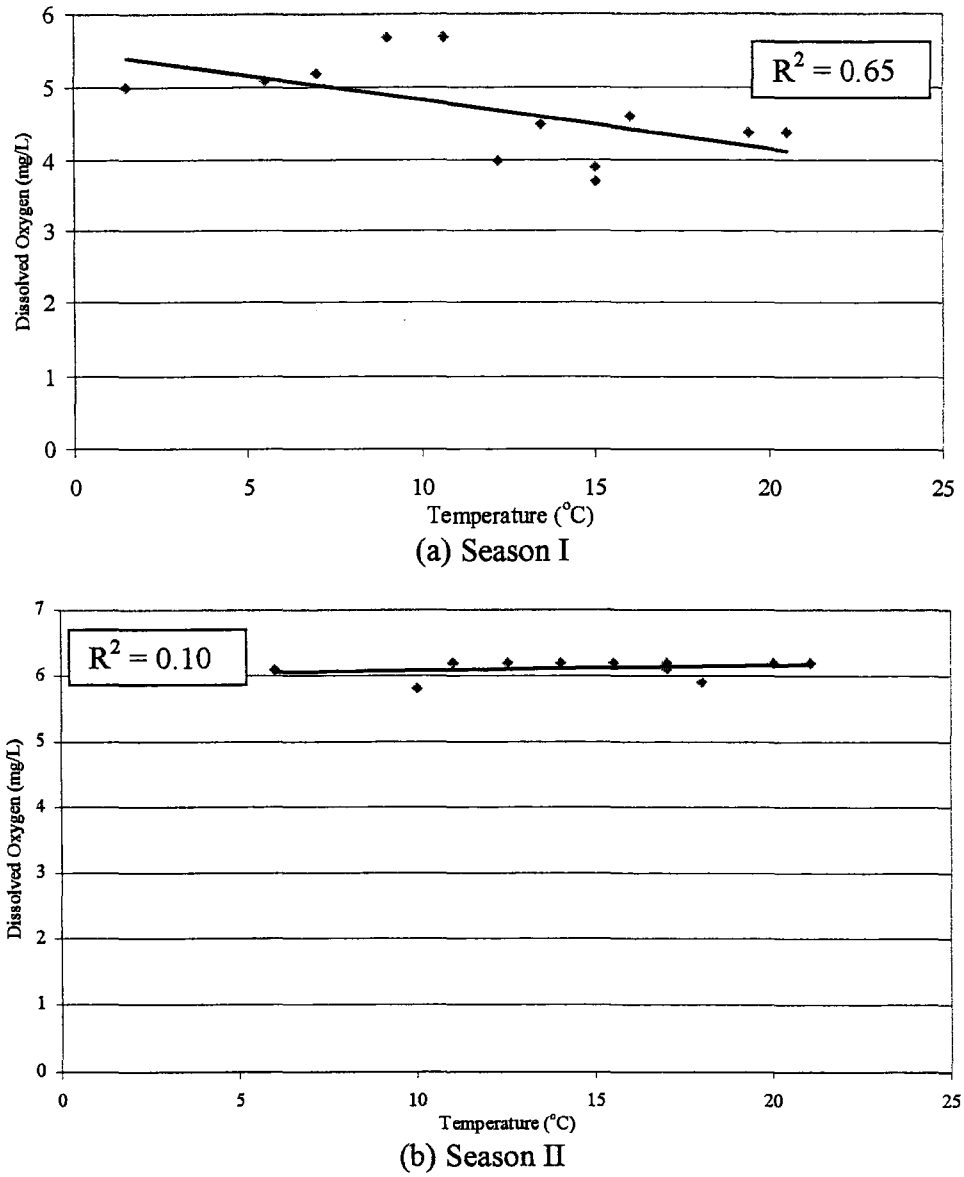
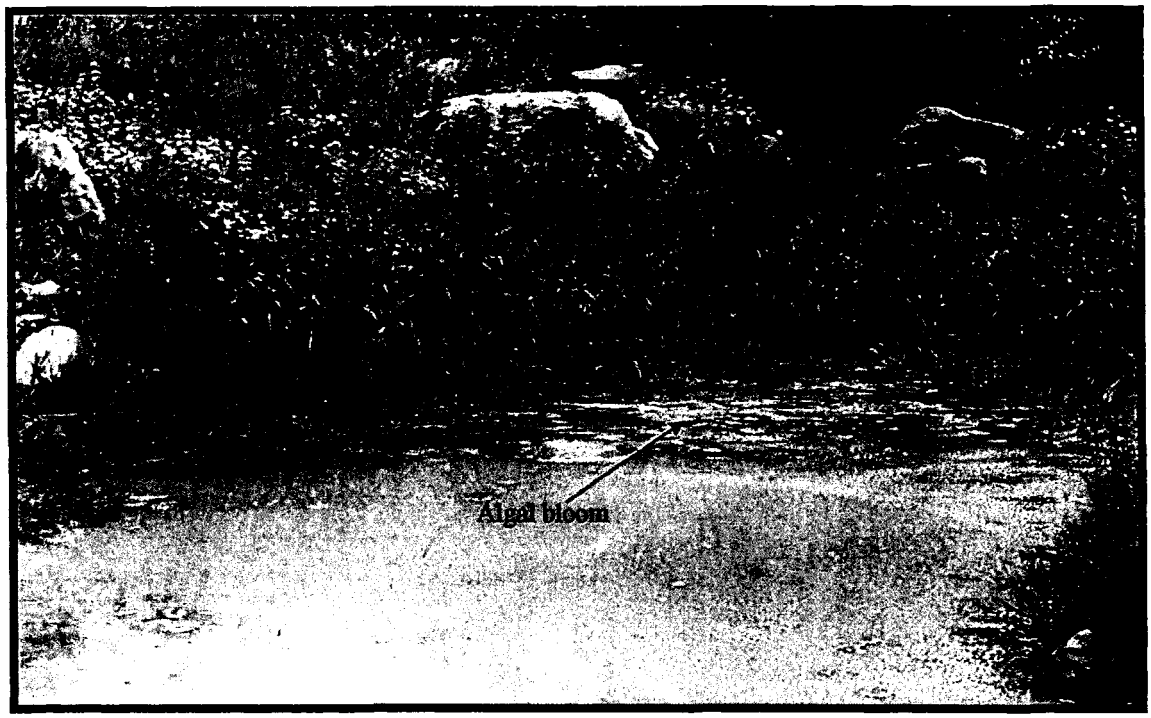


Figure 5.87. Correlation between water temperatures and dissolved oxygen concentration.

Soluble phosphorus, which is available for plant uptake, is called orthophosphate. Orthophosphate concentrations in the treatment wetland waters were analyzed in order to identify the cause of the smaller blooms occurring along the southern edges of Cells 2 and 3 (Figure 5.88). The average PO_4 concentrations in the constructed wetland was 0.006 mg/L which was higher than that of the effluent of the reference wetland (<0.001 mg/L). This may be due to the fact that the reference wetland was very well established

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(a) Cell 2 in season I



(b) Cell 4 in season II

Figure 5.88. Algal blooms.

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whereas the constructed wetland was one year old. Since no algae was observed in cell 1 and some algae blooms appeared in other cells, it is likely that the primary source of the phosphorus is the leaking waters beneath Akerley Boulevard which had higher orthophosphate levels than that of the influent. This loading of phosphorus only occurred in the spring, as the algal blooms disappeared by June. In season II, the orthophosphate was detected in more sampling events than in season I. It is expected that the orthophosphate will be reduced further with time as the vegetation in the constructed wetland become more established over time.

There are no specific water quality guidelines for PO_4 (CCME, 2003). According to Boulton and Brock (1999), low concentrations of orthophosphate are not necessarily reflective of wetland conditions as it is rapidly taken up by aquatic plants and microorganisms. Studies by Burgoon et al. (1989), Maddox and Kingsley (1989), DeBusk et al. (1990), Mitchell et al. (1990) and van Oostrum and Cooper (1990) confirmed that vegetated wetland treatment remove greater percent of phosphorous from wastewater. However, phosphorous removal is typically highly variable in constructed wetlands systems, ranging from 0–98% (Steiner and Freeman, 1989; Watson et al., 1989).

In this study, PO_4 removal efficiency in seasons I and II were 40 and 60 %. This can be attributed to plant uptake because the number of cells and the number of vegetated berms in constructed wetland increased from 4 to 9 in season II. Bacterial uptake also may have occurred because plant rhizospheres support larger populations of bacteria as suggested by Hatano et al. (1993). The presence of oxidized rhizospheres around plant roots also may have increased phosphorous removal by enhancing adsorption reactions that occur under oxic conditions (Wolstenholme and Bayes 1990).

5.9.1.5 Total Kjeldahl Nitrogen

Total Kjeldahl Nitrogen (TKN) is the sum of both ammonia and organic nitrogen. The combination of the organic nitrogen and all forms of inorganic nitrogen (NH_4, NO_3, NO_2) make up total nitrogen. Natural levels of TKN in water bodies are typically less than 2.0

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mg/L (Cameron et al., 2003). Sources of TKN include the decay of organic materials such as plants and aquatic animals wastes. Organic nitrogen readily binds to particulates and is removed by the TSS removal processes (flocculation, sedimentation, filtration, and interception) or through biological transformation to ammonia. The process occurs under aerobic and anaerobic conditions (Mitsch and Gosselink, 1993).

$$NH_2CONH_2 + 2H_2O \longrightarrow 2NH_4^+ + CO_2 + OH^- \qquad (5.7)$$

Once the ammonium is formed, it can be absorbed by plants in the water column, immobilized by ion exchange in the sediments, volatilized as gaseous ammonia, converted back to organic matter by microbes, or nitrified by aerobic microorganisms (Mistch and Gosselink, 2000).

The average TKN concentrations in the outlet of constructed wetland in season I was 3.76 mg/L which was higher than that of the reference wetland (0.41 mg/L). By increasing the number of cells in the second season, the TKN was reduced to 2.60 mg/L (30.85% reduction). It is expected that this will be further reduced with time as the vegetation in the treatment wetland and microbial population become more established.

The TKN decreased as the waters moved through the cells in season I as shown in Figure 5.42. Concentrations of TKN were notably high in cell 3 for the May 24th to June 30th sampling dates. The mostly likely explanation is the algae blooms found in the wetland system during the sampling period. The organic forms of nitrogen measured in TKN analyses include nitrogen that is bound to algae. Commonly, sites which support prolific algae contain elevated levels of TKN (Mason, 1998; and Boulton and Brock, 1999). Algal blooms were developing and decaying in the treatment site during the period when TKN levels in the water samples appeared exceptionally high. In season II, the concentrations of TKN decreased as the water flowed through the wetland cells. However, the inlet TKN concentration was higher in two sampling dates (July 1 and September 17) as shown in Figure 5.54. Based on the weather data for these dates, there was no heavy precipitation prior or during these sampling events but there was, however, an overflow sewage pipe discharging wastewater into the inlet, which may have caused

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the high TKN concentrations in the inlet for these two dates. Sewage wastewater contains high levels of organic and ammonium nitrogen concentrations (EPA, 1993).

Yirong and Puetpaiboon (2004) reported TKN removal efficiency of 49% from a constructed wetland treating wastewater from a seafood-processing factory and. Cameron et al. (2003) reported a TKN removal efficiency of 37 % for a constructed wetland treating municipal lagoon effluents. Poach et al. (2004) TKN removal efficiency of 9-56 % for a constructed wetland treating swine wastewater. In this study, the average outlet TKN removal efficiencies were 19.83 and 31.94 % for seasons I and II, respectively. The TKN removal efficiency of the constructed wetland in season II was comparable to these reported in the literature and it is expected to further improve as the wetland site mature over time. The CCME (2003) currently has not published water quality guidelines for TKN because it is not considered toxic in high concentration levels. However, TKN concentrations above 3 mg/L are considered excessive in natural waters (Cameron et al., 2003).

5.9.1.6 Ammonium-Nitrogen

Ammonium was identified as one of the contaminants of concern in the Burnside landfill leachate effluent. Ammonium is fairly harmless but ammonia can be deadly at high levels to fish. Acute effects of fish exposure to ammonia include convulsions, coma, and death. Chronic effects of exposure to ammonia include damage to gill membranes, preventing fish from carrying on normal respiration, alteration of metabolisms or increases in body pH. Ammonia can cause osmoregulatory damage and is an irritant to delicate tissues such as the internal organs. Even trace amounts of ammonia can stress fish, suppressing the immune system. This can cause a gradual breakdown of fish health, developmental problems, and disease outbreaks (EPA, 1998a).

The average ammonium-nitrogen (NH_4-N) concentrations in the outlet of the constructed wetland in season I was 0.23 mg/L which was higher than that of the reference wetland (0.06 mg/L). Increasing the number of cells in the constructed wetland from 4 to 9 cells in the second season did not affect NH_4-N concentration (0.25 mg/L). This might be due

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to the increase of vegetated areas in the wetland which resulted in increased organic nitrogen that was converted into ammonium. There are no specific ammonium water quality guidelines for the protection of aquatic life (CCME, 2003).

The NH_4-N concentrations in the influent generally decreased as the water flow through the treatment wetland cells in seasons I and II. NH_4-N was actually not detected in 37% of the samples analyzed. The concentrations of NH_4-N did not appear to be particularly affected by rain events. Also, the NH_4-N concentrations in the cells appeared to increase slightly over the course of the summer. The amount of ammonia volatilization in seasons I and II was not significant in this study because the pH values of the wetland systems ranged from 6 to 7. According to Reddy and Patrick (1984) the losses of ammonia through volatilization are considered insignificant if pH is less than 7.5.

Yirong and Puetpaiboon (2004) reported NH_4-N removal efficiency of 52% for a constructed wetland treating wastewater from a seafood-processing factory. Coon (2004) reported an average NH_4-N removal efficiency of 84% for a constructed wetland treating storm water runoff. In this study, the average NH_4-N removal efficiencies in the wetland were 70.89 and 77.06 % for seasons I and II, respectively. These values are comparable to the values reported in the literature.

5.9.1.7 Nitrite-Nitrogen

Nitrite is rapidly oxidizes to nitrate, the presence of excessive nitrite depletes dissolved oxygen in the water column. Nitrite is toxic to fish at low concentrations (Mason, 1998).

The nitrite-nitrogen (NO_2-N) concentrations in the outlet of the constructed wetland in seasons I and II were 0.01 and 0.01 mg/L, respectively. These are slightly lower than that of the reference wetland (0.05 mg/L). The CCME (2003) guidelines for the protection of freshwater aquatic life recommended a maximum NO_2-N concentration of 0.06 mg/L.

Generally, the NO_2-N levels observed in season I were minimal until the July 21st sampling date, when the NO_2-N concentration rose to 0.59 mg/L, which exceeds the

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CCME (2003) Guidelines. There was water stagnation observed in the site that day (Figure 5.89). Nitrite can persist in waters which suffer from oxygen depletion (Mason, 1998). The DO concentration in cell 2 was 4 mg/L which was below the CCME (2003) guidelines. In addition, the NO_2-N concentration in cell 2 and the outlet taken on August 6th were 0.24 mg/L and 0.07 mg/L respectively, which also exceed the CCME (2003) Guideline. The exceedances of nitrite-nitrogen concentrations observed on these days could be due to the heavy rain events occurring previous to and during the day of sampling which could have brought excess nitrite to the wetland as suggested by Bennet (1994). The NO_2-N concentrations in season II were minimal and did not exceed the CCME (2003) guidelines.



Figure 5.89. Stagnation and flocs in cell 3 (Summer 2003).

Machate et al. (1999) reported a NO_2-N removal efficiency of 97% for a constructed wetland used to purify contaminated ground water from a former coke plant site. Lin et al. (2005) reported a NO_2-N removal efficiency of 83-94% for a constructed wetland used to purify aquacultural wastewater. In this study, the average NO_2-N removal efficiency was 56.52%.

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5.9.1.8 Nitrate-Nitrogen

Nitrate is bioavailable for plant uptake and is essential to plant growth (Boulton and Brock, 1999; and Freedman, 2001). Nitrate is virtually harmless, with direct toxic effects to aquatic life typically not observed until concentrations greater than 100 mg/L (Mason, 1998). However, if phosphorus concentrations are sufficient, high nitrate content in waters can increase the severity of eutrophication, which can have chronic effects on aquatic life.

The average nitrate-nitrogen (NO_3-N) concentration in the outlet of the constructed wetland in seasons I was 3.34 mg/L which was higher than that of the reference wetland (0.41 mg/L). Increasing the number of cells from 3 to in season II reduced the concentration of NO_3-N to 2.45 mg/L (26.65% improvement). It is expected that NO_3-N concentrations will be reduced further with time as the vegetation in the constructed wetland become more established over time. The CCME (2003) NO_3-N water quality guideline for the protection of aquatic life is 13.00 mg/L.

Concentrations of NO_3-N generally decreased during the course of the summer as a result of increased nitrate uptake by the matured aquatic vegetation. Also, the NO_3 concentrations decreased as the water flow through the wetland during the fall and the winter. This is most likely because of the low precipitation which increased the retention time.

Machate et al. (1999) a reported NO_3-N removal efficiency of 91% for a constructed wetland used to purify contaminated ground water from a former coke plant site. Ingersoll and Baker (1998) reported a NO_3-N removal efficiency of 95% for a constructed wetland treating wastewater. Baker (1998) reported a NO_3-N removal efficiency of 90 % for a constructed wetland treating highly contaminated wastewater. The average NO_3-N removal efficiencies in seasons I and II were 9.49 and 22.22 %, respectively. However, the NO_3-N removal efficiency of the constructed wetland in season II was improved and it is expected to further improve as the vegetation mature over time.

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5.9.1.8 Chemical Oxygen Demand

Chemical oxygen demand (COD) is a measure of the amount of oxygen required to chemically oxidize reduced minerals and organic matter. The COD was chosen as one of the contaminant of concern because the greater the COD value in water, the more oxygen the influent demands from the water body, which is essential to the metabolism of all aerobic aquatic organisms (Silva et al., 2003; Cusso et al., 2001; and CCME, 1999b).

The average COD concentrations in the outlet of the constructed wetland in season I was 797 mg/L which was higher than that of the reference wetland (132 mg/L). Increasing the number of cells in season II resulted in the reduction of COD to 381 mg/L (52.19% improvement). It is expected that the COD concentrations will be reduced further with time as the vegetation in the treatment wetland become more established. There are no specific CCME (2003) water quality guidelines for COD.

The COD concentrations in all cells remained relatively stable in season I during spring and summer (May – September 2003). However, in the fall and winter (October 2003 – January 2004), the COD concentrations decreased as the water flow through the wetland cells reaching 671 mg/L. The COD concentrations in season II decreased as the water flow through the wetland cells and the overall performance of wetland cells were better than that of season I because: (a) the area of the wetland was increased by 110 %, (b) the number of cells were increased from 4 to 9 which increases in the vegetated areas in the wetland that intercept the solids in the wastewater, and (c) the berms was repaired to increase the retention time and facilitate the flocculation and sedimentation processes which affected the concentrations of COD in the wetland cells.

According to Reddy and D'Angelo (1994) and Wittgren and Maehlum (1997), the primary parameters affecting COD removal in a wetland are the hydraulic, chemical, and microbiological characteristics of the wetland. During water flow, the microorganisms responsible for the degradation of organic matter (whether soluble or suspended) are generally associated with slimes or films that develop on the surfaces of soil particles, vegetation, and litter (Manios et al., 2003). In this study, the constructed wetland system

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consists of several deepwater cells separated by shallow vegetated berms. The vegetation grown in the shallow berms facilitated the formation of slimes and biofilms which resulted in the removal of COD in the treatment wetland.

Lin et al. (2002) reported a COD removal efficiency of 25-55 % for a constructed wetland treating aquaculture wastewater. Lim et al. (2001) reported a COD removal efficiency of 70 – 89 % for a constructed wetland treating storm water runoff. In this study, the average COD removal efficiencies were 2.33 and 52.79 % for seasons I and II, respectively. The COD removal efficiencies in season II was within the range reported in the literature.

5.9.1.9 Total Suspended Solids

Total suspended solids (TSS) include all particles suspended in water that will not pass through a filter of 1.2 μm pore size diameter. The TSS was chosen as one of the contaminants of concern because abundant suspended solids, including clay and silt and fine particles of organic soluble (such as compounds of phytoplankton) and inorganic matter (such as iron particulate), can result in: (a) decreased light penetration in water thereby reducing photosynthesis of water plants, (b) decreased water depth due to sediment build-up, (c) smothering of aquatic vegetation habitat and food, (d) smothering of macro and micro-organisms and the larva and eggs of insects and clogging of fish gills, (e) reduced efficiency of predation by visual hunters, and (f) increased heat absorption by the water, which in turn results in lowering dissolved oxygen concentration, facilitating parasite and disease growth and increasing toxicity of ammonia (Mason, 1998; and Boulton and Brock, 1999).

Total suspended solids are both removed and produced by wetland processes. Mechanisms for suspended solids removal include flocculation/sedimentation and filtration/interception, whereas suspended solids production within the wetland may occur due to death of invertebrates, fragmentation of detritus from plants, production of plankton and microbes within the water column or attached to plant surfaces, and formation of chemical precipitates such as iron oxides. Resuspension of solids may occur

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due to turbulence created by animals, high inflows or winds (EPA, 1999). According to EPA (1999) and Tousignant et al. (1999), suspended solid removal in constructed wetlands is best facilitated through the encouragement of settling by the creation of a settling pond at the head of the wetland. In this study, the constructed wetland system consists of several deepwater cells separated by shallow vegetated berms. The first cell (Cell 1) in the wetland was larger and deeper than the rest of the cells in order to facilitate the settling processes of suspended solids. It was designed to support long retention times in order to allow the suspended solids and other debris to settle out. The increased depth accommodated sediment build up, thereby reducing the need for frequent dredging. Also, the vegetation grown in the shallow berms facilitated the settling of suspended matter by obstructing water flows and physically filtering and trapping the matter as suggested by Davis (1995).

The average TSS concentrations in the outlet of the constructed wetland in season I was 451 mg/L which was higher than that of the reference wetland (85 mg/L). It should be noted that the concentrations of pollutants in the water entering the constructed wetland were much higher than those in the water entering the reference wetland. Also, the reference wetland was very well established whereas the constructed wetland was one year old. There are no specific CCME (2003) water quality guidelines for the protection of aquatic life or recreation water for TSS.

The TSS concentrations in season I in the outlet were gradually reduced over time (August and September 2003). The ineffective facilitation of settling in the first season was due to the frequent breaking of the wetland berms (Figure 5.90) caused by higher flows which caused dramatic reductions in retention times. The TSS concentrations in the wetland outlet were significantly improved through the fall and winter (October 2003 - January 2004) because of small quantity of precipitation which resulted in longer retention time of the water in the wetland. In season II, the TSS concentrations decreased as the water flow through the wetland cells. Increasing the number of cells in the constructed wetland from 4 to 9 cells in the second season increased the vegetated area

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(Figure 5.91) which intercepted the solids and resulted in the reduction of total suspended solids to 225 mg/L (about 50% improvement over season I).



Figure 5.90. Breaks in berm 2 (Spring 2003).



Figure 5.91. Increased vegetation on berm 2 in season II (Summer 2004).

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Karathanasis et al. (2003) reported a TSS removal efficiency of 46-90 % for a constructed wetlands treating storm water runoff. Aluko et al. (2003) reported a TSS removal efficiency of 81 % for a constructed wetland used to treat landfill leachate. Coleman et al. (1999) reported a TSS removal efficiency of 70 % for a small scale constructed wetlands treating wastewater. Worrall et al. (1997) reported a TSS removal efficiency of 80 % for a constructed wetland built to improve water quality of effluent from a pond holding a large collection of captive waterfowl. In this study, the average TSS removal efficiencies in the wetland were 22.24 and 70.04 % for seasons I and II, respectively. Although most of the above mentioned studies reported lower inlet TSS concentrations and the wetlands were more mature than the wetland used in this study, the suspended solids removal efficiency of the constructed wetland in season II was comparable to these studies and it is expected to further improve as the vegetation mature over time.

5.9.1.10 Total Dissolved Solids

Total dissolved solids (TDS) is a measure of the concentration of dissolved constituents in water, which commonly include carbonate, bicarbonate, chloride, sulfate, phosphate, nitrate, calcium, magnesium, sodium, organic ions, and other ions. Certain levels of these ions in water are essential as nutrients for aquatic life. The TDS was chosen as one of the contaminant of concern because changes in TDS concentrations can affect the density of water, reduce water clarity, hinder photosynthesis, and lead to increased water temperatures (Mason, 1998; DeBusk, 1999; and Boulton and Brock, 1999).

The average TDS concentration in the outlet of constructed wetland in season I was 318 mg/L which was higher than that of the reference wetland (55 mg/L). The TDS concentrations in season I (May 2003 – January 2004) in the outlet slightly decreased over time showing a little improvement at the end of the growing season as sites vegetation matured (August and September 2003). The TDS concentrations in the wetland were also slightly improved through the winter (December 2003 – January 2004) due to low precipitation and the colder weather which decreased biochemical reactions inside the landfill resulting in lower TDS concentrations in the wastewater discharged

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into the wetland. Increasing the number of cells in the constructed wetland in the second season resulted in the reduction of TDS to 146 mg/L (about 54% improvement). This occurred because the area of the wetland was increased by 110 %, and the number of cells were increased from 4 to 9. Increasing in the vegetated areas in the wetland, increased the uptake of dissolved solids from the wastewater by the plant roots. There are no specific CCME (2003) water quality guidelines for TDS.

Reicher et al. (2005) reported a TDS removal efficiency of 59 % for a wetland system treating golf course tile drainage. Borin et al (2001) reported a 30 % removal efficiency of TDS from wastewater by a constructed wetland. In this study, the average TDS removal efficiencies were 16.54 and 72.03 % for seasons I and II, respectively. The TDS removal efficiency in the second season was higher than most value reported in the literature and it is expected to improve more as the treatment wetland mature over time.

5.9.2 Heavy Metal Removal

5.9.2.1 Iron

Iron as one of the main chemical constituents in water, is an essential micronutrient element required by both plants and wildlife at significant concentrations (Boulton and Brock, 1999; and Mason, 1998). Iron exists in two forms, soluble ferrous (Fe^{2+}) and insoluble ferric (Fe^{3+}). In most aquatic systems supporting waters with adequate oxygen concentrations, all iron present in the water bodies and other aerobic parts of the system such as the rhizosphere of the sediments will be Fe^{3+} (Boulton and Brock, 1999). At a pH greater than 3.5 with oxygen present, ferrous iron will oxidize to ferric iron as follows:

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^{+}_{(aq)} \longrightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(l)} \qquad (5.8)$$

If oxygen is low, this transformation will not occur until the pH reaches 8.5 (Fripp et al., 2000). Certain microbes (*Thiobacillus-Ferrobacilus* bacteria) can increase the rate of iron oxidation. In surface waters, ferric iron frequently forms iron hydroxide ($Fe(OH)_3$) precipitate as a result of hydroxylation (Fe^{3+} reacting with H_2O molecules) as follows (Colorado School of Mines, 1999):

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$$Fe^{3+}_{(aq)} + 3\ H_2O_{(l)} \longrightarrow Fe(OH)_{3(s)} + 3H^{+}_{(aq)}\ (\text{Acidity}) \qquad (5.9)$$

Iron precipitates such as iron hydroxide and ferric phosphate ($FePO_4$) cause orange staining and the formation of slick orange coagulants commonly referred to as ocher (Boulton and Brock, 1999). In spite of its repellent appearance, Fe^{3+} and its associated compounds are not acutely toxic to wildlife, as they are not readily bioavailable. This is because the primary pathway for most metal uptake by aquatic life is through respiratory organs or via the consumption of other organisms (i.e. aquatic invertebrates) (Boulton and Brock, 1999). The reduced form of iron (Fe^{2+}) is soluble and is, therefore, bioavailable and considered to be extremely toxic to wildlife (Mitsch and Gosselink, 2000).

5.9.2.1.1 Iron Concentrations in Water: The iron concentrations in seasons I and II observed in the outlet effluent did not dropped below the CCME Guideline of 0.3 mg/L for the Protection of Freshwater Aquatic Life (CCME, 2003). The iron concentrations in the water of cells were higher than those in the influent water. This was due to the fact that cell 1 was designed to facilitate the flocculation and sedimentation processes which increased the chances of the formation of iron particulates as shown in Figure 5.92. Generally, the iron concentrations in the water of cell 2 were lower than those in the water of cell 1. However, in 6 out of the 12 of the sampling events, the iron concentrations increased in cell 3 and cell 2 and iron flocs were present in both cells due to the breaks in berms 2 and 3. The cell layouts made it very difficult to access the surface water in cell 3 without stirring the bottom sediments or disturbing the flocs deposited on the vegetation when collecting the samples. Thus, more iron particulate may have been collected in the water samples than was actually present in the surface water before the disturbance.

Generally, the iron concentrations in the water in season II decreased as the water flew through the wetland cells. The results from season II were more consistent than those of season I because: (a) the sampling procedure was changed to avoid the disturbance of the of the flocs from the plant parts and the sediments, (b) the wetland size was increased and the site vegetation was more mature, and (c) the berms were becoming more stable in

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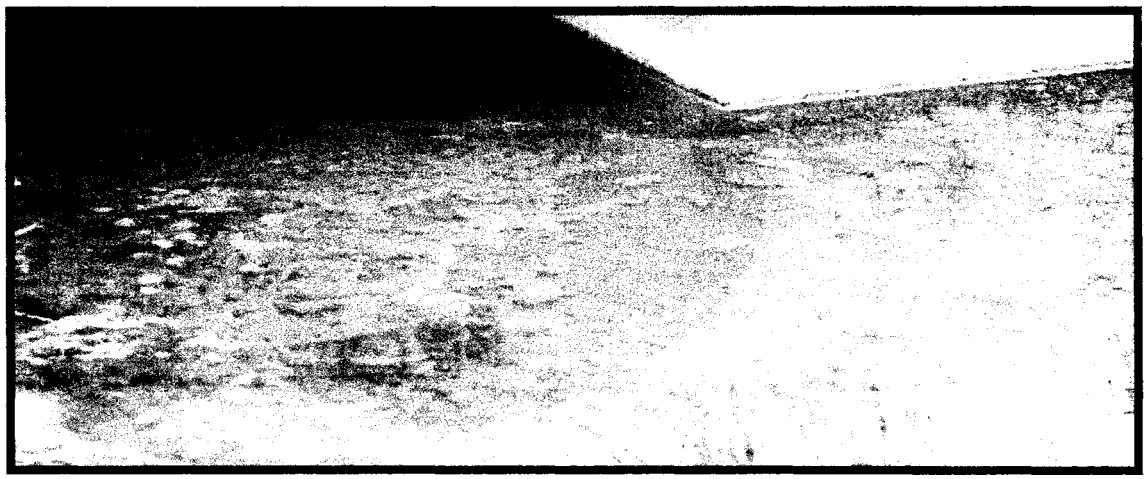


Figure 5.92. Particulate materials in cell 1 (Summer 2003).

season II.

Analysis of variance (ANOVA) was performed on the iron concentrations data in season II using SAS System, 5th Ed. (SAS Institute Inc., Cary, North Carolina). The Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA results (Table 5.15) showed that the date and sample locations have significant effects on the removal efficiency (P = 0.0001). The results also showed significant interactions (P = 0.0001) between these parameters. The results of Duncan's Multiple Range test (Table 5.16) showed that the means of the 11 sample locations (inlet, cells 1-9 and outlet) used in this study were significantly different from one another at a 95% confidence level. However, the sampling dates are divided into four groups based on the weather conditions. The first group included the sampling dates May 15th, June 1st, June 16th and August 16th, the second group included the sampling dates July 16th, September 2nd, and October 20th, the third group included sampling dates July 1st and August 2nd and the fourth group included sampling dates September 16th and October 4th. The average iron concentrations in the water within these groups were not significantly different from one another but the groups were significantly different from one another at a 95 % confidence level. This clearly shows the effect of both temperature and precipitation levels on iron concentration in water.

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Table 5.15. Analysis of variance of the iron concentrations (Season II).

Source	DF	SS	MS	F-Value	P
Total	241	665.24	2.76		
Model	120	651.51	5.42	47.86	0.0001
Sample Location (S)	10	532.77	53.28	469.68	0.0001
Date (D)	10	82.84	8.28	73.04	0.0001
S x D	100	35.89	0.35	3.16	0.0001
Error	121	13.73	0.11		

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 0.98
CV = 7.01%

Table 5.16. Differences in iron concentrations among the sampling dates and sample locations (Season II).

Parameter	Number of Observations	Fe Concentrations (mg/L)	Duncan Grouping
Date			
May 15th	22	5.47	A
June 1st	22	5.46	A
June 16th	22	5.64	A
July 1st	22	4.44	C
July 16th	22	4.83	B
Aug. 2nd	22	4.32	C
Aug. 16th	22	5.37	A
Sept. 2nd	22	4.67	B
Sept 17th	22	4.01	D
Oct. 4th	22	3.88	D
Oct. 20th	22	4.70	B
Sample Location			
Inlet	22	7.12	A
Cell 1	22	6.74	B
Cell 2	22	6.19	C
Cell 3	22	5.78	D
Cell 4	22	5.41	E
Cell 5	22	4.46	F
Cell 6	22	4.32	F
Cell 7	22	3.82	G
Cell 8	22	3.40	H
Cell 9	22	3.15	I
Outlet	22	2.39	J

Means with the same letter are not significantly different from each other at 95% confidence level.

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The overall iron removal efficiency of the system is the sum removal of iron from the system by the chemical and/or biological precipitation and plant uptake. The overall removal efficiencies for the system in season I and II are shown in Tables 5.17 and 5.18. Since the treatment wetland was designed to accommodate both passive and active treatments, the settling pond facilitated settling while removal of iron was facilitated by the established dense, deep rooting vegetation which acted to immobilize the oxidized iron through phytostabilization and extract reduced iron from the deeper anaerobic sediments. The iron overall removal efficiency of season I ranged from -25.40 to 91.09 % with an average of 37.07 %, while that of season II ranged from 47.13 to 82.97 % with an average of 66.75 %. Generally, the overall removal efficiency increased by the end of the season because: (a) the site was more mature by the end of the growing season (August- September 2003) and (b) the precipitation during the fall (September-December 2003) was low, which increased the residence time in the wetland. Higher overall removal efficiency was observed in season II because of increased vegetation which resulted in increased iron uptake by plants, increased filtration capability of the plants for particulate materials and increased amount of oxygen that was introduced into the water and the sediments by the plants which facilitated the oxidation of iron. The iron removal efficiency (Figure 5.93) can be described as a function of time and inlet iron concentration as follows:

$$RE_I = 0.17\,T + 6.65\,C_I \qquad R^2 = 0.51 \qquad (5.10)$$

$$RE_{II} = 0.24\,T + 6.65\,C_I \qquad R^2 = 0.71 \qquad (5.11)$$

Where:

RE_I = Iron overall removal efficiency in season I (%)

RE_{II} = Iron overall removal efficiency in season II (%)

T = Time (days)

C_I = Initial iron concentration (mg/L)

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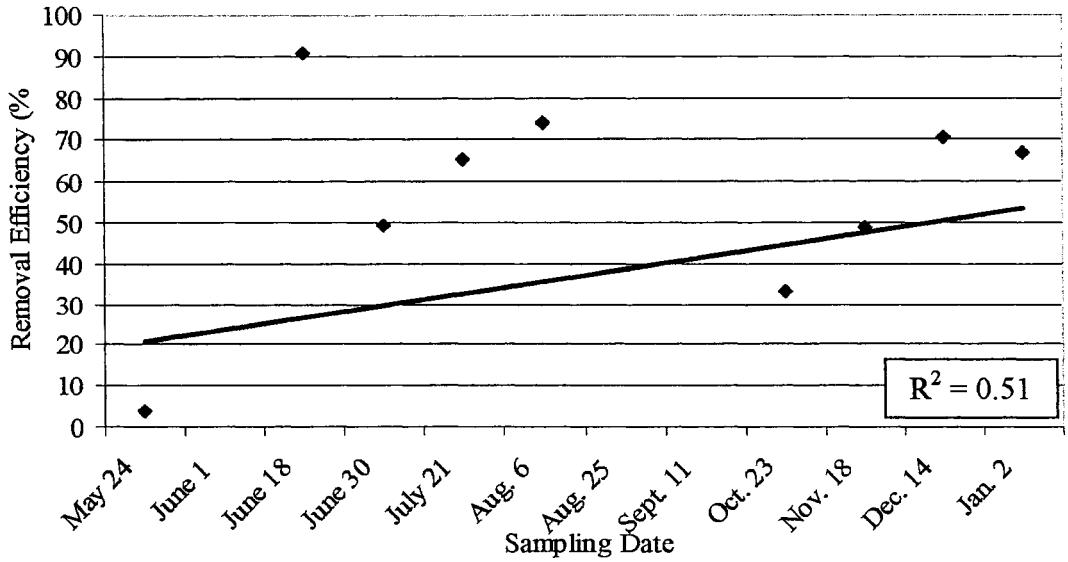
Table 5.17. Iron overall removal efficiencies in season I.

Sampling Date	Concentration (mg/L)		Removal Efficiency (%)
	Inlet	Outlet	
May 24	7.28	7.00	3.85
June 1	7.48	9.38	-25.40
June 18	7.52	0.67	91.09
June 30	7.40	3.75	49.32
July 21	7.28	2.51	65.52
Aug. 6	7.09	1.84	74.05
Aug.25	6.50	7.52	-15.69
Sept. 11	7.33	8.65	-18.00
Oct. 23	7.38	4.90	33.15
Nov. 14	6.84	3.50	48.83
Dec. 14	7.23	2.10	70.95
Jan. 2	6.70	2.20	67.16

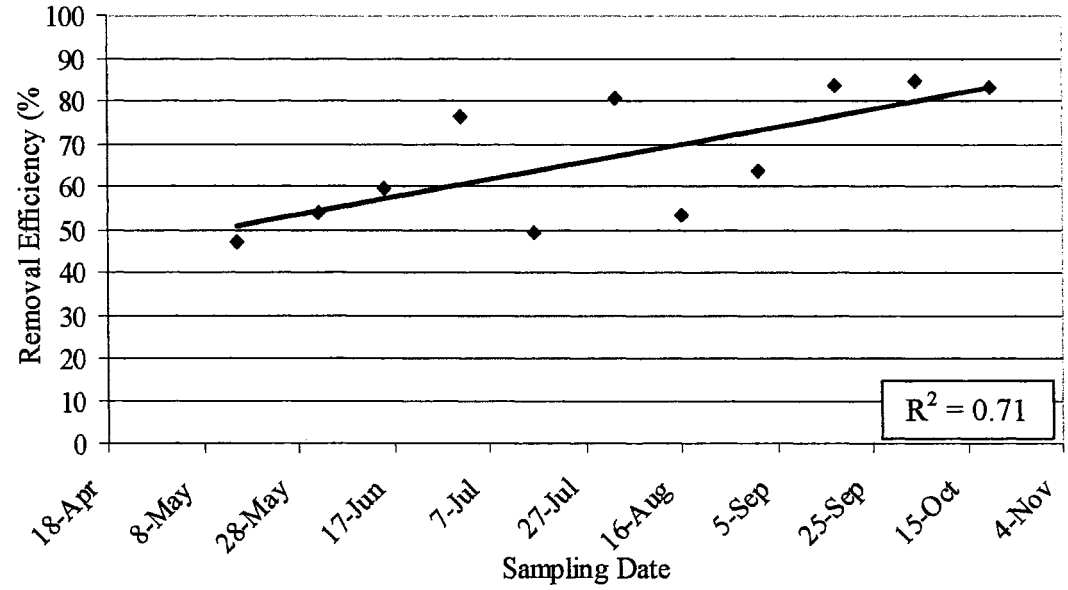
Table 5.18. Iron overall removal efficiencies in season II.

Sampling Date	Concentration (mg/L)		Removal Efficiency (%)
	Inlet	Outlet	
15-May	6.96	3.68	47.13
1-Jun	7.12	3.29	53.79
15-Jun	7.32	2.96	59.56
1-Jul	6.85	1.63	76.20
16-Jul	6.38	3.25	49.05
2-Aug	6.85	1.35	80.29
16-Aug	6.95	3.25	53.24
1-Sep	6.45	2.35	63.56
17-Sep	6.25	1.02	83.68
4-Oct	6.29	0.96	84.74
20-Oct	7.21	1.23	82.94

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(a) Season I.



(b) Season II.

Figure 5.93. Iron overall removal efficiency.

The lower R^2 obtained in season I was due to the artificially higher removal efficiencies in the period of June 18 to August 6 resulting from higher precipitation that diluted the iron concentration. Also, wet and dry events during the period of July 17 to September 5 affected the removal efficiencies in season II during this period resulting in lower R^2.

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Lorion (2001) reported up to 99% iron removal in AMD treatment wetland sites. Ye et al. (2001a) reported up to 91% of iron removal in treatment wetlands designed to treat iron in contaminated wastewaters from coal combustion processes. In a review of constructed wetlands in the USA, Skousen et al. (1994) reported iron removal rates from acid mine drainage ranging from 28 and 99%. However, these figures can be unintentionally deceiving to the reader, as the term removed is typically inclusive of both plant uptake and the forming of particulates. In fact, it is immobilization via oxidative precipitation that generally accounts for the majority of the reported iron removal rates in treatment wetland systems (Henrot and Weider, 1990; and Skousen et al., 1994). According to Henrot and Wieder (1990), Calabrese et al. (1991) and Wieder (1992), about 50 to 70% of total iron removal is via iron hydroxylation (Skousen, 1998). Clearly, when iron precipitates, it is not physically removed from the system, but becomes unavailable to biological components, so in a sense, the harmful toxic metal is removed (Ye et al., 2001a). Ye et al. (2001a) observed that in their wetland systems (which achieved 91% removal of iron), only 0.91% of iron removal was carried out by the wetland plant population. Similarly, in studies conducted by Sencindiver and Bhumbla (1988), Faulkner and Richardson (1989), Mitsch and Wise (1998) and Whiting and Terry (1999), iron accumulation by plants only accounted for less than 1% of the iron removal in several study sites (Ye et al., 2001a).

Given that the pH of the Burnside landfill leachate is neutral, and that substantial orange staining and abundant ochre have been observed in the treatment wetland and Wright's Brook, it is highly likely that the majority of the iron detected in the 2003 and 2004 water quality analyses is non-toxic Fe^{3+} and its associated precipitates. The primary sink for metal particulates consequently becomes bottom sediments as they precipitated by either root-induced changes or physical processes happened in the wetland. Root-induced changes can be many; prominent among them are changes in rhizosphere dissolved oxygen (DO), pH, redox potential (ORP), and exudation of low-molecular weight organic compounds (Marschner et al., 1987). As accumulation occurs and oxygen becomes more depleted in the lower portions of the build up, oxidized iron may be reduced back to its bioavailable dissolved form, where it then can be taken up by vegetation (Mitsch and

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Gosselink, 2000). However, in areas accommodating high loading rates, accumulation will likely overwhelm any removal progress via phytoremediation processes (Ye et al., 2001a). Therefore, most systems receiving high suspended solid loads will need to be physically dredged of their sediment build-up once every few years (Davis, 1995).

5.9.2.1.2 Iron Uptake by Wetland Plants: Water quality analysis is an essential component of any constructed wetland monitoring program. However, this type of assessment only indicates whether or not parameters have increased or decreased, and does not indicate what mechanisms were responsible for any observed changes. The plant tissue analysis indicated that iron concentrations were highest in plant roots for all plant species analyzed. Plant roots remove metals via two mechanisms: absorption and adsorption. Absorption involves the actual uptake of the metal (phytoextraction), whereas adsorption involves the immobilization of the metal via precipitation of the metal onto the roots (phytostabilization).

The precipitation of iron onto the roots occurs because wetland plants translocate oxygen from the aerial portions of the plants to the root and rhizomes which leaks oxygen out of the plant system creating a thin oxidized layer around the surface of the roots known as the rhizosphere (Skousen et al., 1994; Hansel et al, 2002; Matagi et al., 1998; Colmer, 2003; Armstrong et al., 2000; Christensen et al., 1994; Sorrel and Armstrong, 1994; Armstrong and Beckett, 1987; Armstrong, 1979; and Armstrong, 1978). Published estimates of plant oxygen release ranged from 5–45 g O_2/day-m^2 of the total wetland surface area (Reed et al., 1995).

At a pH greater than 3.5 with oxygen present, soluble and bioavailable ferrous oxide is oxidized to insoluble ferric oxide which cannot be readily taken up (or absorbed) by plants. Under these circumstances, a coating of ferric oxide precipitate (or plaque) will accumulate on the outside surface of the roots. According to Mays and Edwards (2000), Taylor and Crowder (1983) and Shutes et al. (1993), this iron coating can account for 32-93% of metal concentration in root tissue analyses. Consequently, some metal concentrations for the roots are quite high when compared to the other plant parts. Since

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the pH of the water in the Burnside treatment wetland is neutral, most of the iron which came in contact with the plant oxygen-rich rhizosphere was likely oxidized, adhered (or adsorbed) to the surface of roots (Figure 5.94), and was subsequently not absorbed by the plant. Therefore, the main mechanism for iron removal by the wetland plants was phytostabilization.



Figure 5.94. Iron precipitation onto the root surface.

The distribution of iron in the tissues of the 10 plants species used in this study and the translocation factor (TF) are shown in Table 5.19. Translocation factor is the sum concentrations of iron in the upper parts divided by the iron concentration in roots.

5.9.2.1.2.1 Broad-leaved cattail (Typha latifolia): Broad-leaved cattail is considered by many researchers as a highly effective hyperaccumulator of metals and nutrients and consequently has seen wide-spread application in the field of wastewater treatment (Mitsch and Gosselink, 2000; Kadlec and Knight, 1996; Ye et al., 2001a; Snyder and Aharrah, 1985, Kleinmann, 1985; Coleman et al., 2001; Younger and Batty, 2002; and Huang et al., 1999). This species was included in the tissue analysis in order to gauge how the phytoremediation ability of the native, non-aggressive species of the site compared in terms of their uptake ability to this notorious hyperaccumulator.

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Of the 10 plant species analyzed, broad-leaved cattail was the highest accumulator of iron. The total iron concentration of Broad-leaved cattail in season I was 21598 mg/kg which increased in season II to 23725 mg/kg (8.96 % increase). This was due to the longer retention time achieved in season II by the addition of more cells. The root contained the highest concentration of iron followed by leaves then flowers and stems. The TF of Broad leaved cattail obtained from the treatment wetland was 0.52 and 0.54 in seasons I and II, respectively. The TF of cattail obtained from the reference wetland was 0.067. The broad-leaved cattail was the most effective iron absorber of all the species analyzed, with the treatment wetland specimen holding 7427 mg/kg of iron in its aerial tissues. Hence, some intrinsic mechanism must be at work to increase the mobility of iron within this species as suggested by Johnson et al. (2002), Romheld and Marschner (1986), Kanazawa et al., (1995), Shen et al. (2002) and Jones (1998).

In treatment wetlands designed to treat pH neutral, metal contaminated waters with an iron concentration of 1.4 mg/L, Ye at al. (2001a) reported iron concentrations of up to 268 mg/kg in above-ground cattail tissues, and 8000 mg/kg in below ground cattail tissues, given a ratio of 1:30. Hansel et al. (2002) reported iron concentration ranging from 15000 to 59000 mg/kg in the roots of Broad-leaved cattail collected from a constructed wetland receiving wastewater from gold mining operation. The iron concentrations observed in this study were 7427 mg/kg in the above-ground tissues and 14171 mg/kg in the below-ground tissues, given a ratio of 1:2. It was also noticed that the specimens analyzed from the control site, which supported a low surface water iron concentration of 0.27 mg/L, had very little metal uptake. It is clear that iron accumulation within broad-leaved cattail plants is dependent on the iron concentration in the wastewater as reported by (Kamal, 2004).

5.9.2.1.2.2 Tweedy's rush (Juncus brevicaudatus): Tweedy's rush is low-growing, inconspicuous rush which was selected as a candidate species because of its ability to spread prolifically throughout the wetland, becoming the dominant plant in the site. Of the 10 plant species analyzed, tweedy's rush was the 2nd highest accumulator of iron. The total iron concentration in tweedy's rush in season I was 19477 mg/kg which increased

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Table 5.19. Iron concentration in plant tissues in mg/kg and the translocation factor for all plants.

Plant Type	Roots		Stems		Leaves		Flowers		Translocation Factor†	
	Season I	Season II	Season I	Season II	Season I	Season II	Season I	Season II	Season I	Season II
Broad leaved cattail	14171	15368	173	586	5788	6235	1466	1536	0.524	0.123
Tweedy's rush	17302	18365	461	485	-----	-----	1714	1775	0.126	0.304
Soft stem bulrush	13903	14037	813	956	-----	-----	4222	7550	0.362	0.101
Pickerelweed	12868	13562	85	145	104	523	122	195	0.024	0.049
Reed canary grass	11834	12685	245	356	775	856	619	836	0.138	0.161
Yellow-green sedge	10519	11250	302	350	809	1210	229	1590	0.127	1.386
Wool grass	9620	9850	260	186	221	354	105	456	0.061	0.201
Fowl mannagrass	6172	7689	116	129	1002	1260	779	952	0.307	0.544
Fringed sedge	3474	3689	129	192	3936	4360	433	560	1.295	0.606
Soft rush	4052	7235	160	205	-----	-----	1094	1250	0.309	0.280

† The sum concentrations of iron in the upper parts divided by the iron concentration in roots.

in season II to 20625 mg/kg (5.56 % increase). The root contained the highest concentration of iron followed by flowers then stems. The TF of tweedy's rush obtained from the treatment wetland was 0.125 and 0.123 in seasons I and II, respectively. The TF of Tweedy's rush obtained from the reference wetland was 0.067. This species is one of the most effective iron phytoremediators in the treatment wetland. However, a review of the literature revealed no specific studies on the metal uptake ability of this particular species.

5.9.2.1.2.3 Soft stem bulrush (Scirpus validus): This species was selected as a candidate based on the reports by Mitchell and Karathanasis (1995) who reported that soft stem bulrush was an effective hyperaccumulator of metals and was more effective at metal removal than cattail.

Of the 10 plant species analyzed, soft stem bulrush was the 3rd highest accumulator of iron. The total iron concentration in soft stem bulrush in season I was 18938 mg/kg which increased in season II to 22543 mg/kg (15.99 % increase). The root contained the highest concentration of iron followed by flowers then stems. The TF of soft stem bulrush obtained from the treatment wetland was 0.36 and 0.61 in seasons I and II, respectively (Table 5.21). The TF of the bulrush obtained from the reference wetland was 2.19. The iron concentrations in the flower of the soft stem bulrush were exceptionally high (4222 mg/kg). The second highest iron concentrations observed in a flower was 1714 mg/kg in the Tweedy's rush flower which is nearly 60% lower. In the samples obtained from the reference wetland, it was the flower and not the roots that had the highest concentrations of iron. Clearly, this plant effectively facilitates iron absorption. Johnson et al. (2002), Romheld and Marschner (1986) and Kanazawa et al. (1995) reported that some plants can regulate metal solubility in the rhizosphere by exuding a variety of organic acids from roots. Although a review of the literature revealed no insight as to which specific mechanisms are utilized by this particular family of plant, it is clear that some mechanism is at play facilitating iron mobilization.

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Soft stem bulrush was used in different studies which include: the determination of radial oxygen loss (Bezharuah and Zhang, 2004), the management of dairy lagoons (Karpiscak et al., 1999), the reduction of total nitrogen and total phosphorus from soil leachate (Fraser et al., 2004) and in removing pesticides (Stearman et al., 2003) but there were no reports up to date indicating the amount of iron concentrations in the soft stem bulrush except for Ahn et al. (2001). These authors investigated the use of flue-gas-desulfurization (FGD) by-products from electric power plant wet scrubbers as liners in wetlands constructed to improve water quality and planted Soft stem bulrush in 20 constructed wetlands. The iron concentration in the liner was 85000 mg/kg and the iron concentration in the top soil was 170 mg/kg. The soft stem bulrush accumulated 400 mg/kg of iron in their above ground tissues and 15000 mg/kg in their below ground tissues. It is clear from the results reported in this study that soft stem bulrush accumulated more iron in their above ground tissues and comparable amount in their below ground tissues to these reported by Ahn et al. (2001).

5.9.2.1.2.4 Pickerelweed (Pontederia cordata): Of the 10 plant species analyzed, pickerelweed was the 4th highest accumulator of iron. The total iron concentration in pickerelweed in season I was 13179 mg/kg which increased to 14425 mg/kg in season II (8.64 % increase). The roots of this plant contained the highest concentration of iron followed by leaves then the flowers and stem. The same trend of the iron concentration was observed in the pickerelweed obtained from the control site. The TF of pickerelweed obtained from the treatment wetland in season I was 0.024 which increased to 0.049 in season II. The TF for pickerelweed obtained from the reference wetland was 0.16.

In addition to being a very aesthetically pleasing species, pickerelweed has contributed significantly to iron removal in the treatment wetland site. However, due to its small biomass, significant number of plants would be required to remove the same amount of metals removed by larger species such as the wool grass or cattail (EPA, 2000b).

Collins et al. (2005) examined concentrations of iron in the roots and shoots of pickerelweed over two seasons in wetland systems designed to remediate water from a coal pile runoff basin. Pickerelweed was able to accumulate iron in the shoots in the range of 27-1504 mg/kg

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and in the roots in the range of 246-3191 mg/kg. There were no other reports in the literature on the amount of iron accumulation in the pickerelweed tissues.

5.9.2.1.2.5 Reed canary grass (Phalaris arundinacea): Reed canary grass is an aggressive species which is the focus of phytoremediation studies because its rapid growth often makes it conducive to contaminant uptake (EPA, 2001; Environment Canada, 2000b; and Davis, 1995). Reed canary grass became self-established in the treatment wetland site and without weeding, would likely become one of the most dominant species. This species was included in order to gauge how the phytoremediation ability of the native, non-aggressive species of the site compared in terms of their uptake ability to this aggressive weed.

Of the 10 plant species analyzed, reed canary grass was the 5th highest accumulator of iron. The total iron concentration in reed canary grass in season I was 13473 mg/kg which increased in season II to 14733 mg/kg (8.55 % increase). The roots contained the highest concentration of iron followed by leaves then flowers and stem. The same trend was observed for the iron concentrations in the reed canary grass obtained from the control site. The TF of reed canary grass obtained from the treatment wetland was 0.138 and 0.161 in seasons I and II, respectively. The TF obtained from the reed canary grass in the reference wetland was 0.909.

Hansel et al. (2002) observed elevated concentrations in analyzed root tissues of reed canary grass in wetlands treating mine tailings. Samecka-Cymerman and Kempers (2001) collected plant samples from impacted sites around a former open cut brown coal mine. The iron concentration in the water was 130 mg/L, the iron concentration in the leaves was 1440 mg/kg for reed canary grass. Their results indicated that the accumulation of iron in plant tissues was affected by the iron concentration in the water.

5.9.2.1.2.6 Yellow-green sedge (Carex lurida): Yellow-green sedge was chosen because the species is renowned for its ability to uptake metals (Sanders et al., 2000; Kastning-Culp et al., 1993; Haberl et al., 1999; and Campbell and Ogden, 1999). In addition,

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yellow-green sedge supports a relatively small biomass. According to the EPA (2000b) and Kamnev and van der Lelie (2000), most plants that hyperaccumulate metals on a significant level are small in size.

Of the 10 plant species analyzed, yellow-green sedge was the 6th highest accumulator of iron. The total iron concentration in yellow-green sedge was 11859 mg/kg in season I and 14400 mg/kg in season II (17.65 % increase). The roots contained the highest concentration of iron followed by leaves then stem and flowers in season I. However, the flowers had higher concentrations of iron in season II than leaves and stem. The results of the iron distribution in the various parts of the yellow-green sedge obtained from the control site were similar to these obtained from season II. The TF of yellow-green sedge obtained from the treatment wetland was 0.127 and 0.280 in seasons I and II, respectively. The TF for yellow green sedge obtained from the reference wetland was 1.21. Although not as successful as some of the other species used, this sedge did accumulate significant amounts of iron and has contributed significantly to iron removal in the treatment wetland site. However, due to its small biomass, significantly more individual plant are required to remove the same amount of metals as removed by larger species such as the wool grass or cattail (EPA, 2000b). A review of the literature revealed no specific studies on the metal uptake ability of this particular species. However, Grove and Stein (2005) used yellow-green sedge in a constructed wetland received wastewater containing butanol.

5.9.2.1.2.7 Wool grass (Scirpus cyperinus): Of the 10 wetland plant species analyzed, wool grass, was the 7th highest accumulator of iron. The total iron concentration in wool grass in season II (10206 mg/kg) was higher than that of season I (10846 mg/kg) by 5.9 %. The roots of wool grass contained the highest concentration of iron followed by leaves then the stem and the flowers. The same was observed of the iron concentrations in the wool grass from the control site. The TF of wool grass obtained from treatment wetland was 0.06 and 0.10 in seasons I and II, respectively. The TF for the wool grass obtained from the reference wetland was 0.24.

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Because wool grass has highly rhizomous roots it had been expected that it would absorb more iron than the cattail which supports less rhizosphere per surface area. Although on a mg/kg basis, the wool grass roots did not fair as well as the cattail roots in terms of metal accumulation, wool grass roots penetrate up to 3 times the depth and support several times the biomass as cattail roots (Campbell and Ogden, 1999) and as such a treatment wetland dominated by wool grass plants is likely to remove more iron overall than a treatment wetland dominated by the same number of cattail plants.

Several researchers (Pullin and Hammer, 1991; Sikora et al., 1995; Huang et al., 2000; Hunt et al., 2002; Szogi et al., 2003 and Hunt et al., 2003) studied the effectiveness of wool grass in removing nitrogen compounds from different wastewater but information on iron removal is very limited. Mays and Edwards (2001) investigated the accumulation of iron in the wool grass collected from two constructed wetlands for the treatment of acid mine drainage. The sediment iron concentration was 430 mg/kg and the wool grass accumulated 327 mg/kg in their shoot and 28660 mg/kg in their roots. These values are much higher than those obtained in the current study.

5.9.2.1.2.8 Fowl mannagrass (Glyceria striata): A review of the literature revealed no information concerning fowl mannagrass's ability to uptake metals. However, Fowl mannagrass was chosen because it has been documented that some species can exude a class of organic compounds termed siderophores (mugenic and avenic acids) capable of enhancing the bioavailability of iron in areas of iron deficiency (Johnson et al., 2002, Jones, 1998; and Roemheld and Awad, 2000).

Of the 10 plant species analyzed, fowl mannagrass was the 8th highest accumulator of iron. The total iron concentration of fowl mannagrass in season I was 8069 mg/kg and in season II was 10030 mg/kg (19.55 % higher). The roots contained the highest concentration of iron followed by leaves then flowers and stem. The same trend was observed of the iron concentrations in the fowl mannagrass obtained from the control site. The TF of fowl mannagrass obtained from the treatment wetland was 0.30 and 0.30 in seasons I and II, respectively. The TF for fowl mannagrass obtained from the reference

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wetland was 0.09. Iron uptake into the aerial portions of this species was limited, indicating that fowl mannagrass does not likely employ the use of sideophores as a major mechanism for iron absorption (Lasat, 2002). There were no reports in the literature on the amount of iron concentrations in the fowl mannagrass tissues.

5.9.2.1.2.9 Fringed sedge (Carex crinita): Of the 10 plant species analyzed, fringed sedge was the 9th highest accumulator of iron. The total iron concentration in fringed sedge was 7972 mg/kg in season I and 8801 mg/kg in season II (9.40 % increase). The leaves contained the highest concentration of iron followed by roots then flowers and stem. Conversely, the iron concentrations were highest in the roots of the fringed sedge obtained from the control site. The TF of fringed sedge obtained from the treatment wetland was 1.29 and 1.39 in seasons I and II, respectively (Table 5.21). The TF of fringed sedge obtained from the reference wetland was 0.77. A review of the literature revealed no specific studies on the metal uptake ability of this particular species.

5.9.2.1.2.10 Soft rush (Juncus effusus): Soft rush has been utilized successfully in several Acid Mine Drainage (AMD) treatment wetlands which treated heavy metals and ammonia (Ye et al., 2001b; Younger and Batty, 2002; Coleman et al., 2001; Treacy and Timpson, 1999; and Mays and Edwards, 2000). It was, therefore, selected as a species to dominate the treatment wetland site because of its phytoremediative potential. However, the results indicated that of the 10 plant species analyzed, soft rush was the least accumulator of iron.

The total iron concentration of soft rush in season II (5306 mg/kg) was higher than season I (8690 mg/kg) by 38.94 %. The roots contained the highest concentration of iron followed by the stem then the flowers. The same trend was observed for iron concentration in the soft rush obtained from the control site. The TF of soft rush obtained from the treatment wetland was 0.30 and 0.20 in seasons I and II, respectively. The TF for soft rush obtained from the reference wetland was 0.11.

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Ye et al. (2001a) and McCorry and Renou (2003) reported that soft rush is one of the most effective iron phytoremediators. Although, this was not the case in the current study, the species should not be discounted as a candidate for application in the field of metal-contaminated wastewater remediation because it has large, deeply penetrating roots (Campbell and Ogden, 1999). Taking its root biomass into account, the species will likely contributes significantly to iron removal in the treatment wetland site as suggested by EPA (2000b).

Ye et al. (2001a) investigated the ability of a constructed wetland to treat metal-contaminated leachate emanating from a coal ash pile. Soft rush was able to accumulate 1217 and 68469 mg/kg in their shoots and roots tissue, respectively. Sanchez et al. (1994) sampled Soft rush as well as sediments from sites near an old lead-zinc mine. The iron concentration in the leaves of soft rush was 86 mg/kg and the total iron concentration in the sediment was 51800 mg/kg. It is clear from the results reported in this study (Table 5.21) that soft rush accumulated less amounts of iron in their above and below ground tissues compared to those reported by Ye et al. (2001b) but higher amounts than those reported by Sanchez et al. (1994).

5.9.2.1.3 Iron Mobility in Wetland Plants: Pugh et al. (2002) stated that plants which accumulate iron concentrations in the range of 400-1000 mg/kg in their tissues are significant accumulator of iron. It is clear from the results obtained from the present study that the plants used were superior accumulators of iron. However, plant species differ widely in their ability to accumulate and translocate heavy metals (Table 5.20). The root tissues accumulate significantly greater concentrations of iron than shoots, indicating high plant availability of the substrate metals as well as its limited mobility once inside the plant. This is consistent with previous studies (Outridge and Noller, 1991; Cardwell et al., 2002; Fitzgerald et al., 2003).

Outridge and Noller (1991) reported that the concentrations of heavy metals in the root tissues of freshwater macrophytes from polluted areas were usually found to contain higher concentrations of most metals compared to the aboveground parts. The reduction

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Table 5.20. Absolute iron mass and percentages in different plant parts.

Plant Type	Roots				Stems				Leaves				Flowers			
	Season I		Season II		Season I		Season II		Season I		Season II		Season I		Season II	
	mg	%	mg	%	mg	%	mg	%	mg	%	mg	%	mg	%	mg	%
Broad-leaved cattail	2409.07	74.25	2612.56	74.35	9.69	0.30	11.48	0.33	752.44	23.19	810.55	23.07	73.30	2.26	79.50	2.26
Tweedy's rush	173.02	94.66	183.65	94.26	4.61	2.52	5.86	3.01	------	------	------	------	5.14	2.81	5.33	2.73
Soft stem bulrush	2433.03	96.57	2456.48	95.45	60.98	2.42	71.70	2.79	------	------	------	------	25.33	1.01	45.30	1.76
Pickerelweed	1930.20	99.08	2034.30	97.29	3.83	0.20	5.81	0.28	6.24	0.32	21.24	1.02	7.93	0.41	29.64	1.42
Reed canary grass	2070.95	95.96	2219.88	95.46	15.93	0.74	22.75	0.98	62.00	2.87	68.48	2.94	9.29	0.43	14.28	0.61
Yellow-green sedge	683.74	94.14	731.25	91.76	4.53	0.62	7.28	0.91	36.41	5.01	54.45	6.83	1.60	0.22	3.92	0.49
Wool grass	673.40	97.46	689.50	95.09	5.46	0.79	7.48	1.03	11.05	1.60	26.15	3.61	1.05	0.15	1.95	0.27
Fowl mannagrass	1018.38	90.08	1268.69	89.66	6.38	0.56	7.98	0.56	90.18	7.98	113.40	8.01	15.58	1.38	25.00	1.77
Fringed sedge	521.10	77.67	553.35	76.21	6.45	0.96	9.30	1.28	137.76	20.53	152.60	21.02	5.63	0.84	10.87	1.50
Soft rush	607.80	96.59	1085.25	97.58	16.00	2.54	19.20	1.73	------	------	------	------	5.47	0.87	7.68	0.69

of metals from aboveground tissues has been suggested as a metal tolerant strategy (Taylor and Crowder, 1983). The elevated metal concentrations in the underground tissues and low translocation to the aboveground tissues in the wetland plants examined in this study might also suggest that they are capable of rather well balanced uptake and translocation of iron under heavily iron-polluted conditions. Gries and Garbe (1989) indicate that a well-balanced and largely independent ion budget is typical of many grass-like species, and is supposed to partly create their wide ecological amplitude. This could be a desirable property, as iron would not pass into the food chain via herbivores, and thus avoid potential risk to the environment.

It should be pointed out that wetland plants play an important role in metal removal from metal-polluted water in constructed wetlands by metal immobilization in the roots and in the oxygenated rhizosphere (Ye et al., 2001a). However, iron accumulates in the leaves and flowers of some plants which are used as food by wetland animals and birds and there is, therefore, the possibility that they may bioaccumulate iron in their bodies. For protection of aquatic life, remedial measures such as limestone filters should be implemented in order to reduce the level of iron in the wetland influent. Furthermore, species able to accumulate relatively high metal concentrations in the aboveground tissues should not be used in constructed wetlands.

5.9.2.1.4 Iron Variation in Wetland Plants Over Time: In season II plant samples were collected monthly to assess the variation of iron concentrations in different plant parts during the season (May – October 2004). Variations in iron concentration levels have been noted in all the species, but these variations were not consistent for all plants (Table 5.21). Some reasons for these discrepancies may include the random choice of roots, stems, leaves or flowers for analysis. Weis et al. (2004) found great variation among leaves within the same plant at any given sampling time, so that results could vary different depending on which leaves were selected from a given plant(s).

All the plant parts investigated in this study varied greatly during the sampling period. Most of the plant parts accumulated more iron in their tissues during the spring than in

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Table 5.21. Iron accumulation in the plant tissues.

Plant	Date	Iron Concentration (mg/kg)				
		Roots	Stems	Leaves	Flowers	Total
Broad leaved cattail						
	15-Jun	2716.0	1127.0	32.0	0.0	3875.0
	16-Jul	1299.0	797.0	147.0	755.0	2998.0
	16-Aug	4710.0	1459.0	89.0	260.0	6518.0
	17-Sep	3280.0	2021.0	354.0	495.0	6150.0
	20-Oct	1578.0	235.00	-174.0	26.0	1665.0
	Average	2716.6	1127.80	89.6	307.2	4241.2
Tweedy's rush						
	15-Jun	4800.0	118.0	NA	0.0	4918.0
	16-Jul	4100.0	16.4	NA	356.0	4472.4
	16-Aug	1900.0	142.6	NA	244.0	2286.6
	17-Sep	3500.0	53.0	NA	870.0	4423.0
	20-Oct	1565.0	6.0	NA	305.0	1876.0
	Average	3173.0	67.2	NA	355.0	3595.2
Soft stem bulrush						
	15-Jun	2740.5	287.0	NA	0.0	3027.5
	16-Jul	3154.5	200.0	NA	2536.0	5890.5
	16-Aug	2690.0	150.0	NA	2024.0	4864.0
	17-Sep	1800.0	220.0	NA	1840.0	3860.0
	20-Oct	577.0	-14.0	NA	1150.0	1713.0
	Average	2192.4	168.6	NA	1510.0	3871.0
Pickerelweed						
	15-Jun	3250.0	97.0	22.0	0.0	3369.0
	16-Jul	-600.0	31.0	-1.2	125.0	-445.2
	16-Aug	5000.0	137.0	18.2	36.0	5191.2
	17-Sep	1800.0	3.8	10.0	-21.0	1792.8
	20-Oct	462.0	142.2	3.0	55.0	662.2
	Average	1982.4	82.2	10.4	39.0	2114.0
Reed Canary Grass						
	15-Jun	2720.0	67.2	10.4	0.0	2797.6
	16-Jul	1244.8	111.8	27.6	520.0	1904.2
	16-Aug	1982.4	22.6	32.0	120.0	2157.0
	17-Sep	3882.8	128.4	83.0	49.0	4143.2
	20-Oct	1175.0	76.0	53.0	147.0	1451.0
	Average	2201.0	81.2	41.2	167.2	2490.6
Yellow-green sedge						
	15-Jun	2640.0	170.0	10.4	0.0	2820.4
	16-Jul	1324.8	-35.6	44.6	229.0	1562.8
	16-Aug	745.2	-44.4	28.0	711.0	1439.8
	17-Sep	3219.6	178.8	85.0	160.0	3643.4
	20-Oct	760.4	31.2	47.0	490.0	1328.6
	Average	1738.0	60.0	43.0	318.0	2159.0

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Table 5.22. Continued.

Plant	Date	Iron Concentration (mg/kg)				
		Roots	Stems	Leaves	Flowers	Total
Wool grass						
	15-Jun	1933.0	41.0	6.0	66.0	2046.0
	16-Jul	580.0	42.0	-5.0	66.0	683.0
	16-Aug	1040.0	32.0	18.0	92.0	1182.0
	17-Sep	1800.0	72.0	18.0	47.0	1937.0
	20-Oct	930.0	22.0	-4.0	59.0	1007.0
	Average	1256.6	41.8	6.6	66.0	1371.0
Fowl mannagrass						
	15-Jun	430.0	175.0	27.0	0.0	632.0
	16-Jul	-230.0	0.0	20.0	450.0	199.4
	16-Aug	550.0	380.6	5.0	202.0	1137.6
	17-Sep	1200.0	260.0	26.0	113.0	1599.0
	20-Oct	489.0	220.0	26.0	187.0	922.0
	Average	487.8	199.0	20.8	190.4	898.0
Soft rush						
	15-Jun	921.0	41.0	NA	440.0	1402.0
	16-Jul	545.0	42.0	NA	202.0	789.0
	16-Aug	195.0	42.0	NA	203.0	440.0
	17-Sep	1540.0	42.0	NA	315.0	1897.0
	20-Oct	465.0	66.0	NA	90.0	621.0
	Average	733.2	46.6	NA	250.0	1029.8
Fringed sedge						
	15-Jun	884.0	434.0	1.0	0.0	1319.0
	16-Jul	580.0	430.0	19.8	420.0	1449.8
	16-Aug	270.0	1000.0	-0.8	71.0	1340.2
	17-Sep	-10.0	1110.0	34.0	-24.3	1109.7
	20-Oct	429.0	650.0	14.0	93.3	1186.3
	Average	430.6	724.8	13.6	112.0	1281.0

the fall. This was supported by Caçador et al. (2000) who studied concentrations of zinc, lead, copper and cadmium in the roots of *S. maritima* and *Halimone portulacoides*. The lowest levels in roots were in January and they increased during the growth period, suggesting that plant activities were responsible for the uptake. Sediment concentrations of these metals were lowest when root levels of activities were highest, suggesting plant uptake from the sediments. In *S. alterniflora*, however, stems accumulated iron rapidly in the spring and then the levels declined in summer and fall (Gleason et al., 1979). The decline was attributed to a growth dilution effect. Iron levels in *A. tripolium*, *Puccinellia maritima* and *Spartina anglica* were also high in the spring and declined in the summer and fall (Leendertse et al., 1996). Concentrations of metals in roots of S. *maritima* were found to vary seasonally, with low levels in the winter and increasing levels during the

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spring and summer growth period (Caçador et al., 2000). Drifmeyer and Redd (1981) noted that standing dead leaves had higher iron concentrations than leaves of live plants.

5.9.2.1.5 Iron in Wetland Sediments: Weis and Weis (2004) stated that wetland sediments are generally considered a sink for metals and, in the anoxic zone, may contain very high concentrations of metals in a reduced state. As such, the bioavailability of the metals is low compared to terrestrial systems with oxidized soils. Since the constructed wetland was intended to accommodate passive treatment, it was decided that the most effective treatment method for this constituent would be to facilitate settling. This was accommodated by a large, settling pond at the beginning of the wetland. Iron removal was also facilitated by establishing dense, deep rooting vegetation which acted to immobilize the oxidized iron through phytostabilization and extract reduced iron from the deeper, anaerobic sediments. The Fe concentration in the sediments of the inlet increased by 4% (from 59580 to 61850 mg/kg) but no increase in the sediment samples obtained from the outlet was observed. A strong correlation was observed between the total iron concentrations in the plant and the inlet sediment iron concentrations as shown Figure 5.95. The correlation equations and coefficients are shown in Table 5.22.

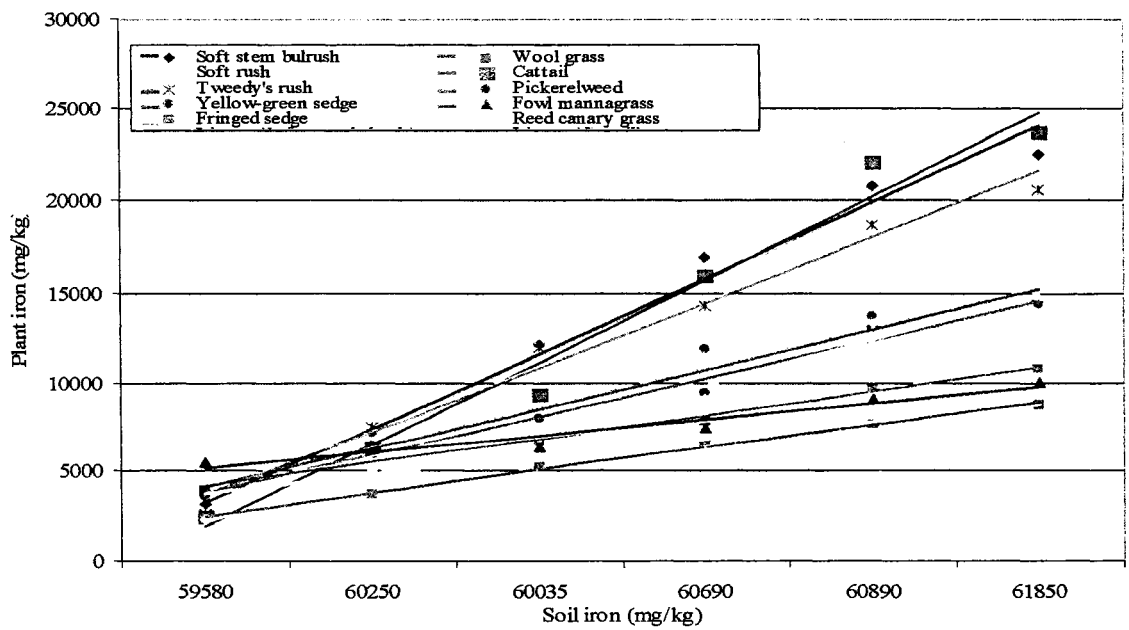


Figure 5.95. Relationship between total iron concentrations in plants and iron concentrations in the inlet sediments.

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Table 5.22. Correlations between iron concentrations in inlet sediments and iron concentrations in plants.

Plant Type	Equation	R^2
Wool grass	$PC_I = 2869.5 + 1338.9\ SC_I$	0.98
Soft rush	$PC_I = 2797.9 + 1016.1\ SC_I$	0.97
Pickerelweed	$PC_I = -1903.5 + 2218.8\ SC_I$	0.93
Fowl mannagrass	$PC_I = 4215.5 + 925.59\ SC_I$	0.98
Yellow-green sedge	$PC_I = 1607.72 + 152.9\ SC_I$	0.98
Fringed sedge	$PC_I = 1193.0 + 1287.5\ SC_I$	0.99
Soft stem bulrush	$PC_I = -906.2 + 4156.6\ SC_I$	0.98
Tweedy's rush	$PC_I = -88.9 + 3591.8\ SC_I$	0.98
Broad-leaved cattail	$PC_I = -2621.3 + 4558.5\ SC_I$	0.98
Reed canary grass	$PC_I = -321.3 + 2543.9\ SC_I$	0.99

PC_I Total iron concentration in plant in mg/kg
SC_I Iron concentration in the inlet sediments in mg/kg

Different forms of iron were observed in the soil profile taken from the wetland sediments. The forms of iron have different availability. Water-soluble metals and exchangeable metals are the most available. Metals precipitated as inorganic compounds, iron complexed with large molecular weight humic materials and iron adsorbed to hydrous oxides are potentially available. Iron precipitated as insoluble sulfide and iron bound within the crystalline lattice of minerals are essentially unavailable (Gambrell, 1994; and Weis and Weis, 2004). This can be clearly seen in the constructed wetland sediments as shown in Figure 5.96. Because of these reducing conditions, the depth to which plant roots can penetrate is limited and this restricts the uptake of contaminants and rhizosphere actions to shallower levels as reported by Williams (2002).

5.9.2.2 Manganese

Manganese (Mn) is a transition metal which is grey, white or silver in colour. It is soft and ductile if pure but usually occurs in compounds and complexes with organic compounds (Sample et al., 1997). Manganese is an essential micronutrient forming a vital part of the enzyme systems that metabolise proteins in all organisms. According to Boulton and Brock (1999) manganese is present in freshwater systems as either soluble,

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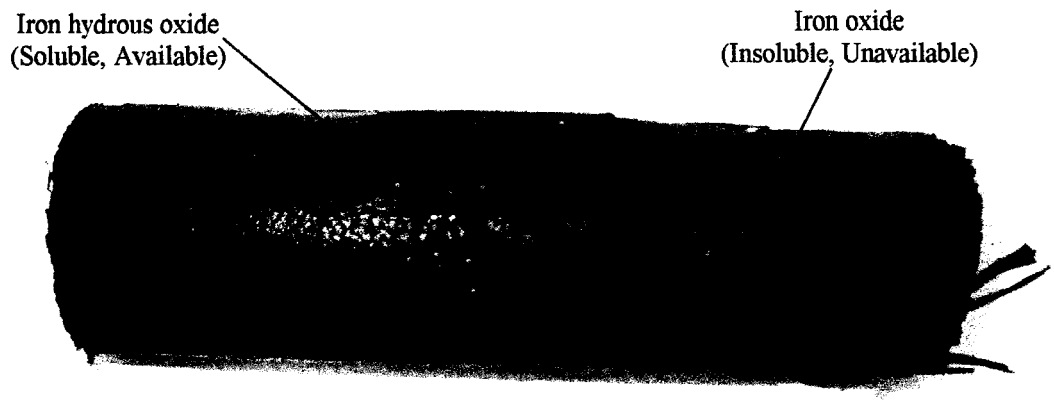


Figure 5.96. Soil profile in the inlet of the constructed wetland.

reduced manganous (Mn^{2+}) or less soluble oxidized manganic (Mn^{4+}). In surface waters, Mn^{2+} frequently forms manganese hydroxide (MnOOH) precipitate as follows (Stiles, 2001):

$$4\,Mn^{2+} + O_2 + 6\,H_2O \longrightarrow 4\,MnOOH_{(s)} + 8\,H^+ \qquad (5.12)$$

Reduced manganese is considered to be the most toxic form of the metal as it is readily bioavailable (BCMELP, 2001). High manganese concentration in freshwater is reported to cause fish gill damage in similar fashion as that of iron. It is also known to cause decreases in white and red blood cells, haemoglobin, and protein concentrations in fish (Sample et al., 1997).

5.9.2.2.1 Manganese Concentrations in Water: In season I, the manganese concentrations in wetland cells decreased as the water flow through the wetland except for two sampling dates (May 24th and August 25th). The increase of manganese concentration on May 24th was due to breaks in the berms which decreased the retention time of the water in the cells, while the increase of manganese concentration on August 25th was due to a rain event which also decreased the retention time of the water in the cells. In season II, the manganese concentrations in wetland cells decreased as the water flow through the wetland during the entire season.

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The CCME (2003) currently does not publish water quality guidelines for manganese. However, the British Columbian Ministry of Environment, Land and Parks (BCMELP, 2001) published acute and chronic manganese guideline for the protection of freshwater aquatic life of 1.914 mg/L and 1.159 mg/L, respectively. The manganese concentrations observed in the outlet effluent exceeded the BCMELP acute guideline on the August 22nd sampling date and exceeded the BCMELP chronic guideline on the May 23rd, June 1st, June 30th, August 25th, September 11th, October 23rd, and November 18th sampling dates. The manganese concentrations observed in the outlet effluent in season II did not exceed the BCMELP (2001) acute guideline of 1.914 mg/L during the entire season but exceeded the BCMELP (2001) chronic guideline of 1.15 mg/L from June 15th to September 1st. Since settling is a major mechanism of manganese removal, two significant factors that likely contributed to the inadequate settling in cells 1 and 2 were the frequent breaks in the vegetated berms and the heavy rain events both of which drastically reduced the retention time. In addition, preliminary wetland sizing calculations indicated that the size of wetland required for treating the manganese received by the treatment system would be about 5 ha, which is substantially larger than the current wetland size of 1.2 ha.

Analysis of variance (ANOVA) was performed on the manganese concentrations data in season II using SAS System, 5th Ed. (SAS Institute Inc., Cary, North Carolina). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA results (Table 5.23) showed that the date and sample locations have significant effects on the removal efficiency ($P = 0.0001$). The results also showed significant interactions ($P = 0.0001$) between these parameters. The results of Duncan's Multiple Range test (Table 5.24) showed that the means of the 11 sampling locations (inlet, cells 1-9 and outlet) were divided into 4 groups. The first group included the inlet and cell 1, the second group included cells 2, 3 and 4, the third group included cells 5-9 and the forth group included the outlet. The average manganese concentrations within each group were not significantly different from one another but the groups were significantly different from one another at a 95% confidence level. These results showed the slow progression from the inlet to the outlet. The sampling dates can also be divided into four groups. The first group included May 15th, June 1st, June 16th, August 2nd,

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Table 5.23. Analysis of variance of the manganese concentrations.

Source	DF	SS	MS	F-Value	P
Total	241	23.27	0.096		
Model	120	21.45	0.178	4.90	0.0001
Sample Location (S)	10	13.62	1.36	90.71	0.0001
Date (D)	10	4.18	0.42	27.86	0.0001
S x D	100	3.64	0.036	2.43	0.0001
Error	121	1.81	0.015		

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 0.92
CV = 7.59%

Table 5.24. Differences among the sampling dates and sample locations (manganese).

Parameter	Number of Observations	Mn Concentrations (mg/L)	Duncan Grouping
Date			
May 15th	22	1.57	B
June 1st	22	1.58	B
June 16th	22	1.60	B
July 1st	22	1.53	C
July 16th	22	1.99	A
Aug. 2nd	22	1.63	B
Aug. 16th	22	1.61	B
Sept. 2nd	22	1.64	B
Sept 17th	22	1.53	C
Oct. 4th	22	1.61	B
Oct. 20th	22	1.44	D
Sample Location			
Inlet	22	2.00	A
Cell 1	22	1.94	A
Cell 2	22	1.83	B
Cell 3	22	1.78	B
Cell 4	22	1.67	C
Cell 5	22	1.48	D
Cell 6	22	1.52	D
Cell 7	22	1.46	D
Cell 8	22	1.38	D
Cell 9	22	1.46	E
Outlet	22	1.22	F

Means with the same letter are not significantly different from each other at 95% confidence level.

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August 16th, September 2nd and October 4th, the second group included July 1st and September 17th, the third group included July 16th and the forth group included October 20th. The manganese concentrations within each group were not significantly different from one another but the groups were significantly different from one another at a 95 % confidence level. These results showed the impact of the weather conditions (temperature and precipitation) on manganese removal.

The overall manganese removal efficiencies for the wetland system in season I and II are shown in Tables 5.25 and 5.26. The overall manganese removal efficiency of the system is the sum removal of manganese from the system by the chemical and/or biological precipitation and plant uptake. The manganese overall removal efficiency of season I ranged from -30.77 to 78.26 % with an average of 32.08 %, while of season II ranged from 25.75 to 51.61 % with an average of 39.38 %. The overall removal efficiency of the treatment wetland was higher at the end of the season because of increased manganese uptake and filtration capability of particulate materials by older plants. The manganese removal efficiencies can be described as a function of time and inlet manganese concentration (Figure 5.97) as follows:

$$RE_{MI} = 0.093\ T + 12.0\ C_{MI} \qquad R^2 = 0.65 \qquad (5.13)$$

$$RE_{MII} = 0.052\ T + 18.4\ C_{MI} \qquad R^2 = 0.82 \qquad (5.14)$$

Where:

RE_{MI} = Manganese overall removal efficiency in season I (%)

RE_{MII} = Manganese overall removal efficiency in season II (%)

T = Time (days)

C_{MI} = Initial manganese concentration (mg/L)

The lower R^2 (0.65) observed in season I was due to the artificially high removal efficiencies observed on June 18, July 21 and August 6 which resulted from higher precipitation that diluted the manganese concentration. Similar results were observed in season II on May 15 and June 1.

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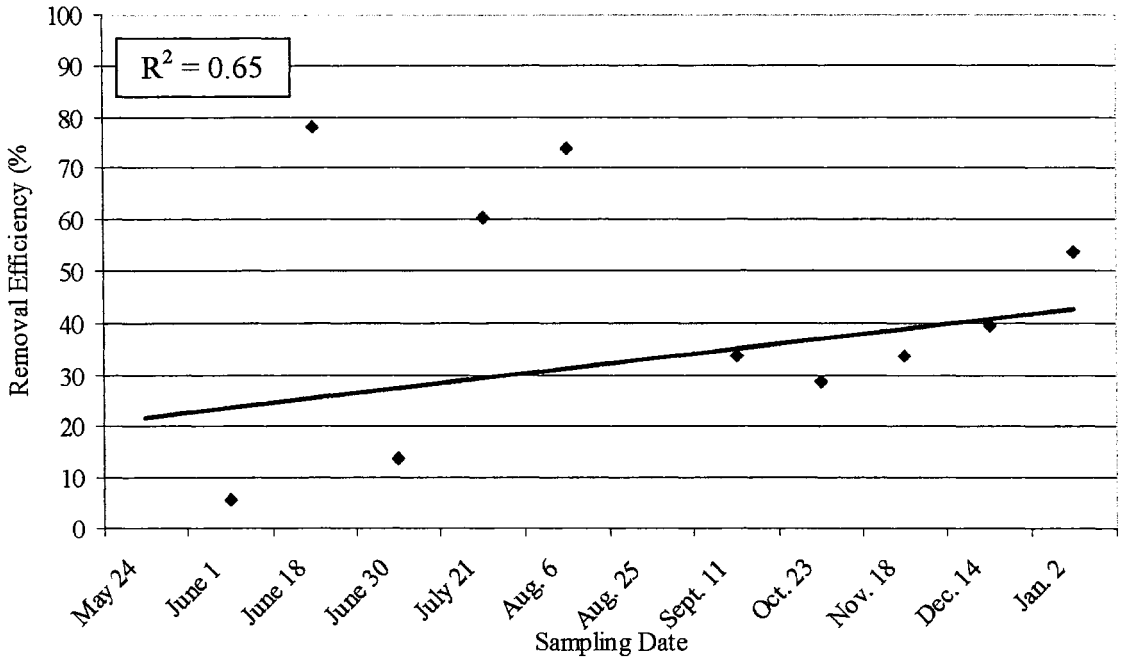
Table 5.25. Manganese overall removal efficiencies in season I.

Sampling Date	Concentration (mg/L)		Removal Efficiency (%)
	Inlet	Outlet	
May 24	1.67	1.78	-6.58
June 1	1.89	1.78	5.82
June 18	2.30	0.50	78.26
June 30	2.05	1.76	14.14
July 21	1.85	0.73	60.54
Aug. 6	1.61	0.42	73.91
Aug.25	1.95	2.55	-30.77
Sept. 11	2.30	1.52	33.91
Oct. 23	2.07	1.48	28.50
Nov. 14	1.86	1.23	33.87
Dec. 14	1.85	1.12	39.46
Jan. 2	1.63	0.75	53.98

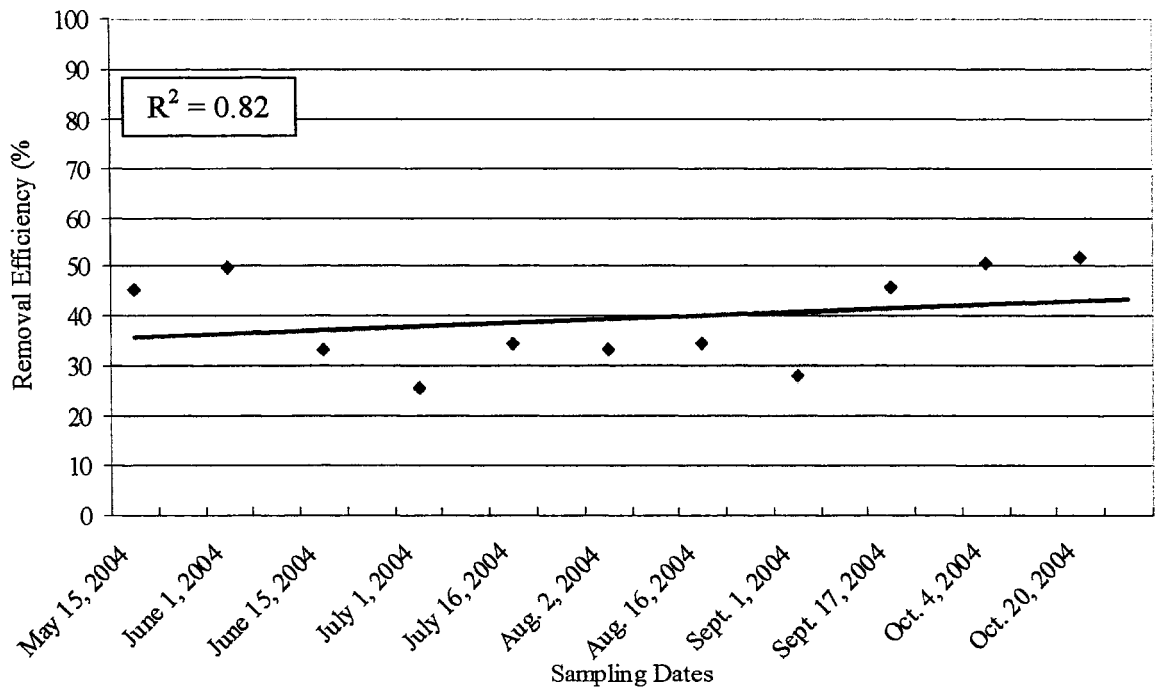
Table 5.26. Manganese overall removal efficiencies in season II.

Sampling Date	Concentration (mg/L)		Removal Efficiency (%)
	Inlet	Outlet	
15-May	1.89	1.03	45.50
1-Jun	2.03	1.02	49.75
15-Jun	1.85	1.23	33.51
1-Jul	1.67	1.24	25.75
16-Jul	2.32	1.52	34.48
2-Aug	1.89	1.26	33.33
16-Aug	1.83	1.20	34.43
1-Sep	1.84	1.32	28.26
17-Sep	1.90	1.03	45.79
4-Oct	1.95	0.96	50.77
20-Oct	1.86	0.90	51.61

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(a) Season I.



(b) Season II.

Figure 5.97. Manganese overall removal efficiency.

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Previous studies (Stillings et al., 1988; Fennessy and Mitsch, 1989; Hedin, 1989; Skousen et al., 1994; and Stark et al., 1994) showed that constructed wetlands are less successful in removing manganese. This is mostly due to the fact that oxidized manganese does not readily form precipitate unless the pH of the water is at least 7, with precipitation most commonly occurring in waters with pHs greater than 10. In addition, manganese oxidation is sensitive to the presence of Fe^{2+}, which can prevent or even reverse manganese oxidation. Some treatment site managers tried to force manganese precipitation (i.e. MnO_2) by increasing the alkalinity of the treatment site via limestone addition (McMillen et al., 1994; and Skousen, 1998). However, this is considered a temporary solution which is difficult to maintain without regular adjustment. Ye et al. (2001a) stated that phytoremediation mechanisms prove relatively insignificant, accounting for approximately 1 to 4% of manganese removal. According to BCMELP (2001), the most effective removal mechanism for manganese in treatment wetland systems is settling, as 90 to 95% of total waterborne manganese binds to particulate matter.

The pH of the water entering the wetland was not acidic (pH=7.28), hence some removal via precipitation has taken place in the wetland. In addition, the facilitation of sedimentation using the settling pond and vegetation seemed to be an effective mean of immobilization in the turbid wetland influent.

5.9.2.2.2 <u>Manganese Uptake by Wetland Plants</u>: Manganese, in its soluble, reduced phase is very bioavailable and is readily and can be absorbed and translocated into aerial plant tissues such as the leaves and flowers (Kabata-Pendias and Pendias, 1992; and Ye et al., 2001a). The results obtained from this study showed that manganese concentrations were higher in flowers and/or leaves (Table 5.27). Fox and Guerinot (1998) reported that at a high manganese supply, the leaves accumulated higher concentrations with time, but small amounts of Mn were translocated from old leaves when young expanding leaves were Mn deficient. Kabata-Pendios and Pendios (1992) reported that the Mn concentration fluctuates greatly within the plant parts and during the growth period. Manchner (1995) reported that the Mn content of plants is not only affected by plant

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characteristics, but also by the pool of available Mn which is highly controlled by soil properties. Foy (1983) stated that Mn tolerance is related to several characteristics and metabolic processes: (a) oxidizing power of plants, possible oxidation of Mn to MnO_2 which is stored as inactive fraction, (b) Mn absorption and translocation rates, (c) complexation of Mn by low molecular weight compounds produced by plant roots or soil microorganisms, (d) Mn entrapment in non-metabolic centers, and (e) interactions with other elements, especially with Ca, Fe, Al, Si and NH_4. The distribution of manganese in the tissues of the 10 plants used in this study and the translocation factor are shown in Table 5.27.

5.9.2.2.2.1 Fowl mannagrass (Glyceria striata): Of the 10 plant species analyzed, fowl mannagrass was the 6th highest accumulator of Mn in season I and the highest in season II. The total Mn concentration in fowl mannagrass was 948 mg/kg in season I and 2642 mg/kg in season II (64.12 % increase). The leaves contained the highest concentration of Mn followed by flowers then stems and roots. The same trend was observed for the Mn concentration in the fowl mannagrass obtained from the reference wetland. The TF of fowl mannagrass obtained from the treatment wetland was 25.29 and 8.23 in seasons I and II, respectively. The TF of fowl mannagrass obtained from the reference wetland was 3.03.

Clearly, the fowl mannagrass contributed significantly to manganese removal in the treatment wetland site. The high concentrations of manganese found in the fowl mannagrass tissues, as compared to the other plants, was because the majority of the fowl mannagrass present in the treatment site was established from seed. Manganese preferentially transports to meristematic tissues, which are the young, expanding tissues in plants. It was expected that the manganese accumulation ability of this plant may decline as its tissues mature over consecutive growing seasons as reported by Kabata-Pendias and Pendias (1992). However, the analyzed mature fowl mannagrass tissues obtained from the constructed wetland in season II did not show any decline. There were no other reports in the literature on the Mn concentrations in the fowl mannagrass tissues.

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Table 5.27. Manganese concentrations in plant tissues in mg/kg and the translocation factor for all plants.

Plant Type	Roots		Stems		Leaves		Flowers		Translocation Factor†	
	Season I	Season II	Season I	Season II	Season I	Season II	Season I	Season II	Season I	Season II
Fowl mannagrass	286	86	375	309	1586	1480	395	386	8.24	25.29
Broad leaved cattail	136	127	365	277	793	730	536	467	12.46	11.61
Tweedy's rush	575	447	356	225	------	------	489	443	1.47	1.49
Soft stem bulrush	168	156	325	268	------	------	823	778	6.83	6.71
Yellow-green sedge	235	200	253	103	389	167	425	392	4.54	3.31
Pickerelweed	295	269	96	52	589	555	265	198	3.22	2.99
Wool grass	132	90	356	289	325	148	425	56	8.38	5.48
Reed canary grass	92	74	153	129	685	488	265	249	11.99	11.70
Soft rush	250	217	386	171	------	------	521	412	3.63	2.69
Fringed sedge	524	52	74	44	189	130	256	230	0.99	7.77

† The sum concentrations of manganese in the upper parts divided by the manganese concentration in roots.

*5.9.2.2.2.2 **Broad-leaved cattail (Typha latifolia)**:* Of the 10 plant species analyzed, broad-leaved cattail was the 7th highest accumulator of Mn in season I and the 2nd highest in season II. The total Mn concentration in broad leaved cattail in season I was 871 mg/kg which increased to 1830 mg/kg in season II (52.40 % increase). This indicates that the accumulation of Mn in this plant may be related to age and maturity of the plant in. One possible explanation for the high manganese concentrations observed in the broad leaved cattail tissues compared to those of the other plant species analyzed may lie in the fact that the vast majority of the cattail present in the treatment site were established mostly from seed. Kabata-Pendias and Pendias (1992) stated that manganese preferentially transports to young, expanding tissues in plants. In this study, the broad leaved cattail tissues analyzed have been all young-new tissues.

The leaves contained the highest concentration of Mn followed by flowers then stems and roots. The TF of broad leaved cattail obtained from the treatment wetland was 11.61 and 12.46 in seasons I and II, respectively. The TF of the broad-leaved cattail obtained from the reference wetland was 27.41. Manganese concentrations observed in the above-ground and below-ground tissues of broad leaved cattail obtained from the treatment wetland were 1474 and 127 mg/kg, respectively. These were lower than these reported by Ye et al. (2001a). The average manganese concentration of the inlet in the treatment wetland tested by Ye et al. (2001a) was 2.5 mg/L whereas the average manganese concentration in the inlet of the treatment wetland was approximately 1.8 mg/L. The board leaved cattail plants obtained from the control site, which supported a low manganese concentration of 0.15 mg/L, had very low manganese concentration (total Mn concentration = 183 mg/kg). Hence it appears that manganese accumulation within broad-leaved cattail plants is correlated with water concentration as reported by Kamal et al. (2004) and Samecka-Cymerman and Kempers (2001).

Sanchez et al. (1994) analyzed broad leaved cattail and sediments obtained from sites near an old lead-zinc mine and reported Mn concentrations of 1950 and 1020 mg/kg in the leaves and the sediment, respectively. Mays and Edwards (2001) investigated the accumulation of Mn in cattail collected from a constructed wetland for the treatment of

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acid mine drainage and found Mn concentrations of 56, 821 and 617 mg/kg in the sediment, the broad leaved cattail shoots and roots, respectively. The manganese distribution in the broad leaved cattail parts used in the present study was similar to that in the broad leaved cattail reported in the literature but with lower concentrations.

5.9.2.2.2.3 Tweedy's rush (Juncus brevicaudatus): Of the 10 plant species analyzed, tweedy's rush was the 3rd highest accumulator of Mn. The total Mn concentration in tweedy's rush in season I was 1115 mg/kg which increased to 1420 mg/kg in season II (21.48 % increase). The roots contained the highest concentration of Mn followed by flowers then stem. The TF of tweedy's rush obtained from the treatment wetland was 1.49 and 1.47 in seasons I and II, respectively. The TF for the tweedy's rush obtained from the reference wetland was 8.11. A review of the literature revealed no specific reports on the manganese uptake ability of the tweedy's rush.

5.9.2.2.2.4 Soft stem bulrush (Scirpus validus): Of the 10 plant species analyzed, soft stem bulrush was the 2nd highest accumulator of Mn in season I and the 4th in season II. The total Mn concentration of soft stem bulrush in season I was 1690 mg/kg which decreased to 1316 mg/kg in season II (22.13 % decrease). The flowers contained the highest concentration of Mn followed by stems then root in the treatment wetland. This indicates that the manganese accumulate by this plant decline with maturity. The TF of soft stem bulrush obtained from the treatment wetland was 6.71 and 6.83 in seasons I and II, respectively. The TF for soft stem bulrush obtained from the reference wetland was 3.62.

Ahn et al. (2001) investigated the use of flue-gas-desulfurization (FGD) by-products from electric power plant wet scrubbers as liners in wetlands constructed to improve water quality and planted with soft stem bulrush. The manganese liner concentration was 130 mg/kg and the manganese top soil concentration was 146 mg/kg. The soft stem bulrush plants accumulated 1543 mg/kg of manganese in their above ground tissues and 596 mg/kg in their below ground tissues. These values are much higher than those accumulated in the soft stem bulrush used in this study. Mitchell and Karathanasis

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(1995) examined the ability of surface flow wetland planted with soft stem bulrush to remove manganese from NaCl-enriched wastewater. However, the amount of manganese in the soft stem bulrush was not determined.

5.9.2.2.2.5 Yellow-green sedge (Carex lurida): Of the 10 plant species analyzed, yellow-green sedge was the 8th highest accumulator of Mn in season I and the 5th in season II. The total Mn concentration in yellow-green sedge was 948 mg/kg in season I and 1302 mg/kg in season II (27.19 % increase). The flowers contained the highest concentration of Mn followed by roots then leaves and stems in season I. However, the flowers had the highest concentration of Mn in season II then leaves, stems and roots. The TF of yellow-green sedge obtained from the treatment wetland was 3.31 and 4.54 in seasons I and II, respectively. The TF of yellow-green sedge obtained from the reference wetland was 11.91. Although, yellow green sedge was not as successful as some of the other species analyzed, this sedge did accumulate high amounts of Mn and contributed significantly to Mn removal in the treatment wetland site. However, due to its small biomass, more individual plants would be required to remove the same amount of metals removed by some of the larger species such as the wool grass or cattail as reported by EPA (2000b). A review of the literature revealed no specific studies on the manganese uptake ability of yellow-green sedge.

5.9.2.2.2.6 Pickerelweed (Pontederia cordata): Of the 10 plant species analyzed, pickerelweed was the highest accumulator of Mn in season I and the 6th in season II. The total Mn concentration in pickerelweed in season I was 1999 mg/kg which decreased to 1245 mg/kg in season II (37.72 % decrease). The leaves of pickerelweed contained the highest concentration of Mn followed by roots then flowers and stem. The same trend was observed for the Mn concentrations in the tissue of the pickerelweed obtained from the reference wetland. The results showed that young plants absorbed more manganese than older mature plants. The TF of pickerelweed obtained from the treatment wetland in season I was 2.99 which increased in season II to 3.22. The TF of pickerelweed obtained from the reference wetland was 5.63. A review of literature revealed no specific reports on the manganese uptake ability of this particular species.

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5.9.2.2.2.7 Wool grass (Scirpus cyperinus): Of the 10 plant species analyzed, wool grass was the 9th highest accumulator of manganese in seasons I and the 7th in season II. The total manganese concentrations in wool grass in season I was 583 mg/kg which increased to 1238 mg/kg in season II (52.91 % increase). The stem contained the highest concentration of Mn in season I followed by leaves then root and flower. The flowers contained the largest Mn concentration in season II followed by stem then leaves and roots. This trend was similar to that observed for the Mn concentrations in the wool grass obtained from the reference wetland. The TF of wool grass obtained from the treatment wetland was 5.48 and 8.38 in seasons I and II, respectively. The TF of the wool grass obtained from reference wetland was 8.96.

Mays and Edwards (2001) investigated the accumulation of Mn in wool grass collected from constructed wetland treating acid mine drainage and found Mn concentrations of 227, 2076 and 2012 mg/kg in the sediment, the wool grass shoots and roots, respectively. The manganese distribution in the wool grass parts in their study was similar to that in wool grass used in this. There were no other reports found in the literature on the amount of manganese concentrations in the wool grass tissues.

5.9.2.2.2.8 Reed canary grass (Phalaris arundinacea): Of the 10 plant species analyzed, reed canary grass was the least accumulator of Mn in season I and the 8th in season II. The total Mn concentration in reed canary grass in season I was 508 mg/kg which increased to 1195 mg/kg in season II (57.49 % increase). The leaves contained the highest concentration of Mn followed by flowers then stems and roots. The same trend of Mn concentration was observed in the reed canary grass obtained from the reference wetland. The TF of reed canary grass obtained from the treatment wetland was 11.70 and 11.99 in seasons I and II, respectively. The TF for reed canary grass obtained from the reference wetland was 8.95.

Samecka-Cymerman and Kempers (2001) collected reed canary grass samples from impacted sites around a former open cut brown coal mine and reported Mn

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concentrations of 1.41 mg/L and 95 mg/kg in the water and the leaves of the reed canary grass, respectively. Culvenor et al. (1986) examined the ability of reed canary grass grown in acid manganiferous soil to accumulate manganese in their tissues and found manganese concentration in the leaves in the range of 179 to 331 mg/kg. The reed canary grass used in this study accumulated more manganese in their leaves tissue than those reported by these authors.

5.9.2.2.2.9 Soft rush (Juncus effusus): Of the 10 plant species analyzed, soft rush was the 3rd accumulator in Mn in season I and the 9th in season II. The total Mn concentration in soft rush was 1355 mg/kg in season I and 1157 mg/kg in season II (14.61 % lower). The flowers contained the highest concentration of Mn followed by the roots and stems in season I whereas in season II, the largest concentration of Mn was accumulated in flowers followed by stems then roots. The trend of Mn distribution in season II was similar to that in the soft rush obtained from the reference wetland. The TF of soft rush obtained from the treatment wetland was 2.68 and 3.63 in seasons I and II, respectively. The TF of soft rush obtained from reference wetland was 8.08.

Ye et al. (2001) investigated the ability of a constructed wetland to treat metal-contaminated leachate from a coal ash pile and reported that Soft rush accumulated 312 and 117 mg/kg in their shoots and roots tissue, respectively. Sanchez et al. (1994) analyzed Soft rush and sediments obtained from sites near an old lead-zinc mine and reported Mn concentrations of 345 and 1140 mg/kg in the leaves and the sediment, respectively. It is clear that soft rush used in the present study accumulated more amounts of Mn in their above and below ground tissues compared to that reported by Ye et al. (2001). The TF of the soft rush used in this study was comparable to the TF reported by Ye et al. (2001) and higher than that reported by Sanchez et al. (1994).

5.9.2.2.2.10 Fringed sedge (Carex crinita): Of the 10 plant species analyzed, fringed sedge was the 5th highest accumulator of Mn in season I and the last in season II. The total Mn concentration of fringed sedge was 1056 mg/kg in season I and 1043 mg/kg in season II (1.23 % lower). The flowers contained the highest concentration of Mn followed by leaves then roots and stem in seasons I. However, the roots contained the

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highest concentration of Mn in season II followed by flowers then leaves and stems. Also, the Mn concentrations were highest in the roots of the fringed sedge obtained from the reference wetland. The TF of fringed sedge obtained from the treatment wetland was 7.77 and 0.99 in seasons I and II, respectively. The TF of fringed sedge obtained from reference wetland was 0.64. A review of the literature revealed no specific studies on the manganese uptake ability of this fringed sedge.

5.9.2.2.3 Manganese Mobility in Wetland Plants: The leaves and flowers tissues accumulated significantly greater concentrations of manganese than the roots, indicating the bioavailability of manganese as well as manganese mobility inside the plant (Table 5.28). Manganese uptake is metabolically controlled (Kabata-Pendias and Pendias, 1992). Generally, Mn is known to be taken up and translocated within plants rapidly (Fox and Guerinot, 1998). Therefore, it is likely that Mn was not binding to insoluble organic ligands either in root tissue or in xylem fluid but occurred in plant fluids and extracts mainly as free cationic forms (Mn^{2+}) as reported by Kabata-Pendias and Pendias (1992). However, its complexing compounds with organic molecules (1000-5000 molecular weight) have been found in phloem exudates (Manchner, 1995). Kabata-Pendias and Pendias (1992) reported a much lower Mn concentration in phloem exudates than in leaf tissues and concluded that a slight transport of Mn through the phloem vessels is responsible for the low concentration of Mn in fruits, seeds, and storage roots.

5.9.2.2.4 Manganese Variation in Wetland Plants Over Time: In season II plant samples were collected monthly to assess the variation of manganese concentrations in different plant parts during the sampling period (May 2004-October 2004). Variations in manganese concentration levels were noted in all the plants analyzed in the present study, but the results were not consistent (Table 5.29). The reason for these discrepancies could be the choice of which part of roots, stems, leaves and flowers are selected for analysis. Weis et al. (2004) found great variations among leaves within the same plant at any given time of sampling and stated that results could be very different depending on which leaf was selected for the analysis.

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Table 5.28. Absolute manganese mass and percentages in different plant parts.

Plant Type	Roots				Stems				Leaves				Flowers			
	Season I		Season II		Season I		Season II		Season I		Season II		Season I		Season II	
	mg	%	mg	%	mg	%	mg	%	mg	%	mg	%	mg	%	mg	%
Fowl mannagrass	47.19	21.60	14.19	8.24	20.63	9.44	17.00	9.87	142.74	65.34	133.20	77.39	7.90	3.62	7.72	4.4
Broad-leaved cattail	23.12	13.33	21.59	13.90	20.44	11.78	15.51	9.99	103.09	59.43	94.90	61.09	26.80	15.45	23.35	15.0
Tweedy's rush	5.75	53.35	4.47	55.53	3.56	33.03	2.25	27.95	------	------	------	------	1.47	13.61	1.33	16.5
Soft stem bulrush	29.40	50.07	27.30	52.43	24.38	41.52	20.10	38.60	------	------	------	------	4.94	8.41	4.67	8.9
Yellow-green sedge	15.28	38.62	13.00	52.41	3.80	9.60	1.55	6.23	17.51	44.26	7.52	30.30	2.98	7.52	2.74	11.0
Pickerelweed	44.25	43.75	40.35	45.41	4.32	4.27	2.34	2.63	35.34	34.94	33.30	37.47	17.23	17.03	12.87	14.4
Wool grass	9.24	24.83	6.30	30.99	7.48	20.09	6.07	29.85	16.25	43.66	7.40	36.40	4.25	11.42	0.56	2.7
Reed canary grass	16.10	18.98	12.95	20.20	9.95	11.72	8.39	13.08	54.80	64.61	39.04	60.90	3.98	4.69	3.74	5.8
Soft rush	37.50	47.65	32.55	62.95	38.60	49.04	17.10	33.07	------	------	------	------	2.61	3.31	2.06	3.9
Fringed sedge	78.60	85.21	7.80	44.47	3.70	4.01	2.20	12.54	6.62	7.17	4.55	25.94	3.33	3.61	2.99	17.0

Table 5.29. Manganese accumulation rates in the plant tissues.

Plant	Date	Manganese Concentration (mg/kg)				
		Roots	Stems	Leaves	Flowers	Total
Fowl mannagrass						
	15-Jun	129.0	99.0	62.0	0.0	290.0
	16-Jul	59.0	350.0	73.0	0.0	482.0
	16-Aug	5.0	-120.0	25.0	64.0	-26.0
	17-Sep	8.0	340.0	35.0	117.0	500.0
	20-Oct	10.0	346.0	60.0	58.0	474.0
	Average	42.2	203.0	51.0	79.6	375.8
Wool grass						
	15-Jun	26.0	26.0	35.0	67.0	154.0
	16-Jul	26.0	26.0	52.0	53.0	157.0
	16-Aug	26.0	6.0	74.0	83.0	189.0
	17-Sep	26.0	84.0	82.0	25.0	217.0
	20-Oct	-7.0	42.0	28.0	74.0	137.0
	Average	19.4	36.8	54.2	60.4	170.8
Broad leaved cattail						
	15-Jun	22.0	147.0	68.0	0.0	237.0
	16-Jul	15.0	237.0	104.0	0.0	356.0
	16-Aug	30.0	115.0	34.0	39.0	218.0
	17-Sep	40.0	135.0	30.0	25.0	230.0
	20-Oct	6.0	103.0	108.0	136.0	353.0
	Average	22.6	147.4	68.8	66.6	305.4
Tweedy's rush						
	15-Jun	211.0	69.0	NA	0.0	280.0
	16-Jul	100.0	10.0	NA	0.0	110.0
	16-Aug	150.0	56.0	NA	21.0	227.0
	17-Sep	50.0	-9.0	NA	144.0	185.0
	20-Oct	-25.0	29.0	NA	-41.0	-37.0
	Average	97.2	31.0	NA	41.3	153.0
Soft stem bulrush						
	15-Jun	26.0	45.0	NA	0.0	71.0
	16-Jul	3.0	31.0	NA	440.0	474.0
	16-Aug	49.0	61.0	NA	80.0	190.0
	17-Sep	40.0	61.0	NA	220.0	321.0
	20-Oct	12.0	31.0	NA	83.0	126.0
	Average	26.0	45.8	NA	164.6	236.4
Yellow-green sedge						
	15-Jun	57.0	36.0	10.4	0.0	103.4
	16-Jul	55.0	98.4	38.6	0.0	192.0
	16-Aug	-10.0	29.6	-9.0	69.0	79.6
	17-Sep	60.0	80.0	75.0	22.0	237.0
	20-Oct	5.0	-5.0	39.0	103.0	142.0
	Average	33.4	47.8	30.8	64.6	150.8

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Table 5.29. (Continued)

Plant	Date	Manganese Concentration (mg/kg)				
		Roots	Stems	Leaves	Flowers	Total
Pickerelweed						
	15-Jun	127.0	20.0	10.4	0.0	157.4
	16-Jul	28.0	75.0	18.6	0.0	121.6
	16-Aug	5.0	37.0	2.2	45.0	89.2
	17-Sep	15.0	78.0	18.7	1.6	113.3
	20-Oct	-5.0	-41.0	5.1	43.3	2.4
	Average	34.0	33.8	11.0	30.0	96.78
Reed Canary Grass						
	15-Jun	28.0	67.2	10.4	0.0	105.6
	16-Jul	4.0	116.8	28.6	0.0	149.4
	16-Aug	2.0	17.6	-7.8	81.0	92.8
	17-Sep	8.0	67.2	51.8	25.0	152.0
	20-Oct	-2.0	176.2	35.0	90.0	299.2
	Average	8.0	89.0	23.6	65.3	185.9
Soft rush						
	15-Jun	43.0	61.0	NA	0.00	104.0
	16-Jul	71.0	71.0	NA	50.00	192.0
	16-Aug	15.0	51.0	NA	137.00	203.0
	17-Sep	10.0	28.0	NA	56.00	94.0
	20-Oct	76.0	86.0	NA	56.00	218.0
	Average	43.0	59.4	NA	74.75	177.2
Fringed sedge						
	15-Jun	200.0	30.0	4.7	0.0	234.7
	16-Jul	20.0	19.0	16.1	0.0	55.1
	16-Aug	100.0	19.0	2.7	23.3	145.0
	17-Sep	240.0	-2.0	8.0	108.6	354.6
	20-Oct	-86.0	-2.0	0.5	49.0	-38.5
	Average	94.8	12.8	6.4	60.3	150.2

Most of the plant parts accumulated more Mn in their tissues during the spring than in the fall. This is in agreement with the finding of Gleason et al. (1979) who noted seasonal variations in manganese accumulation in *S. alterniflora*. Leendertse et al. (1996) reported high manganese levels in *A. tripolium*, *Puccinellia maritima* and Spartina *anglica* in the spring which then declined in the summer and fall due to the growth dilution effect. Caçador et al. (2000) reported that concentrations of metals in roots of *S. maritima* were found to vary seasonally, with low levels in the winter and increasing levels during the spring and summer growth period.

5.9.2.1.5 Manganese in Wetland Sediments: The Mn concentration in the sediments of the inlet remained stable and there was no increase in the manganese concentrations in

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the sediment samples obtained from the outlet was observed. No correlation was observed between the total Mn concentrations in the plant and Mn concentrations in the sediments obtained from the inlet (Figure 5.98). The constructed wetland was intended to accommodate passive treatment in which manganese settling was accommodated in a large settling pond at the beginning of the wetland. Wies and Wies (2004) stated that wetland sediments are generally considered a sink for metals and, in the anoxic zone, may contain very high concentrations of manganese in a reduced state. As such, the bioavailability of the manganese is low compared to terrestrial systems with oxidized soils. Manganese removal was also be facilitated the established dense, deep rooting vegetation that act to immobilize the oxidized manganese through phytostabilization and extract reduced manganese from the deeper, anaerobic sediments.

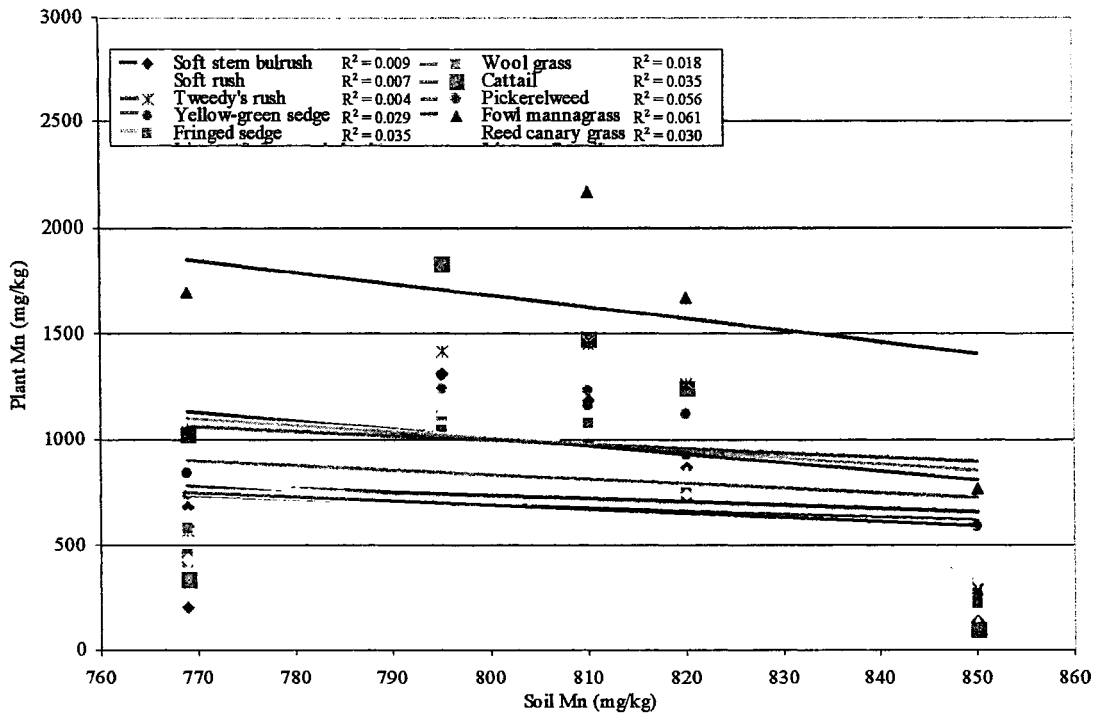


Figure 5.98. Relationship between total manganese concentrations in plants and manganese concentrations in inlet sediments.

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5.9.3 Plant Uptake Kinetic Parameters

5.9.3.1 Uptake Kinetics

The uptake of a metal (in its appropriate ionic form) by an aquatic plant can be expressed by the following first-order kinetic model (Vlyssides and Bouranis, 1998):

$$\frac{d(M_p)}{dt} = k \cdot (M_M - M_p) \tag{5.15}$$

Where:

M_p = Concentration of metal in the wetland plant at a given time (mg/kg)

M_M = Maximum concentration of metal that can be accumulated in the wetland plant during a specific growth period, 150 days (mg/kg)

k = Specific uptake rate (d^{-1})

Equation (5.15) shows that the higher the k-value the faster the metal absorption and hence the more sensitive the wetland plant is to the absorption of particular metal. The k-value is positive if absorption take place and is negative in case of desorption. Equation (5.15) can be integrated using the limits $0 \rightarrow M_p$ and $0 \rightarrow t$ as follows:

$$\int_0^{M_p} \frac{d(M_p)}{M_M - M_p} = \int_0^t k.dt \tag{5.16}$$

On integration, Equation (5.16) can be written as follows:

$$\ln\left(\frac{M_M}{M_M - M_p}\right) = k \cdot t \tag{5.17}$$

Equation (5.17) can also be written in a logarithm form as follows

$$2.3 \log\left(\frac{M_M}{M_M - M_p}\right) = k \cdot t \tag{5.18}$$

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Or $$\log\left(\frac{M_M}{M_M - M_p}\right) = \frac{k\ t}{2.3} \quad (5.19)$$

Equation (5.19) can then be transformed to the following equation:

$$\frac{M_M}{M_M - M_p} = 10^{\frac{kt}{2.3}} \quad (5.20)$$

By substituting r for k/2.3, Equation (5.20) can be rearranged as follows:

$$M_p = M_M\,(1 - 10^{-rt}) \quad (5.21)$$

Equation (5.21) indicates that the concentration of metal in the plant at any time is a function of the maximum concentration that can be accumulated in the plant and the specific uptake rate.

5.9.3.2 Determination of R and M_M

Two kinetic parameters (r and M_M) in Equation (5.21) need to be determined for each plant-metal combination. If the metal concentration in the solution remains stable, which is the case of the constructed wetland, then r and M_M parameters for a wetland plant can be determined. Substituting M_1 for M_p/M_M in Equation (5.21) yields the following equation:

$$M_1 = 1 - 10^{-rt} \quad (5.22)$$

Equation (5.22) can also be rewritten in an exponential form as follows

$$M_1 = 1 - e^{-2.3rt} \quad (5.23)$$

Using Taylor series, a solution for Equation (5.23) is as follows (Stroyan, 1999)

$$M_1 = (2.3\ r\ t)\,[1 - \tfrac{1}{2}(2.3\ r\ t) + 1/6\,(2.3\ r\ t)^2 - 1/24\,(2.3\ r\ t)^3 + \ldots] \quad (5.24)$$

The Taylor series in Equation (5.24) is similar to the following binomial series provided by Thomas (1950):

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$$M_2 = (2.3\ r\ t)\,[1 - \tfrac{1}{2}(2.3\ r\ t) + 1/6\,(2.3\ r\ t)^2 - 1/21.6\,(2.3\ r\ t)^3 + \ldots] \qquad (5.25)$$

The first three terms in the functions M_1 (Equation 5.24) and M_2 (Equation 5.25) are similar and the small residue of the rest of the terms will minimally affect M_1 and M_2. Equation (5.25) follows the following binomial series formula (Stroyan, 1999):

$$(a+x)^n = a^n + n\,a^{n-1}x + \frac{n(n-1)}{2!}\,a^{n-2}x^2 + \frac{n(n-1)(n-2)}{3!}\,a^{n-3}x^3 + \ldots\ldots\ldots \qquad (5.26)$$

In order to transform the right hand side of Equation (5.26) to M_2 series (Equation 5.25), the following conditions were maintained:

$$x = \frac{2.3\,r\,t}{6}$$

$$a = 1$$

$$n = -3$$

Substituting for x, a, and n values in Equation (5.26) yields the following equation:

$$(2.3\,r\,t)\left[1+\frac{2.3\,r\,t}{6}\right]^{-3} =$$

$$(2.3\,r\,t)\left[1^{-3} + \left((-3)\left(1^{-3-1}\right)\left(\frac{2.3\,r\,t}{6}\right)\right) + \left(\left(\frac{-3(-3-1)}{2!}\right)\left(1^{-3-2}\right)\left(\frac{2.3\,r\,t}{6}\right)^2\right) + \ldots\ldots\right] \qquad (5.27)$$

Or $$(2.3\ r\ t)\left[1+\frac{2.3\,r\,t}{6}\right]^{-3} = (2.3\,r\,t)\,[1 - \tfrac{1}{2}(2.3\,r\,t) + 1/6\,(2.3\,r\,t)^2 - 1/21.6\,(2.3\ r\ t)^3 + \ldots] \qquad (5.28)$$

Combining Equation (5.25) and Equation (5.28) can, therefore, yield the following equation:

$$M_2 = (2.3\ r\ t)\left[1+\frac{2.3\,r\,t}{6}\right]^{-3} \qquad (5.29)$$

Since $M_1 = M_p/M_M$ and $M_1 = M_2$, then Equation (5.29) can be rewritten as follows:

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$$M_p = (2.3\ r\ t)\left[1+\frac{2.3\ r\ t}{6}\right]^{-3} M_M \tag{5.30}$$

The linear form for Equation (5.30) is as follows:

$$\left(\frac{t}{M_p}\right)^{1/3} = \frac{1}{(2.3\ r\ M_M)^{1/3}} + \frac{(2.3\ r)^{2/3}\ t}{6\ M_M^{1/3}} \tag{5.31}$$

Equation (5.31) has the following linear form:

$$Y = A + B\ .\ X \tag{5.32}$$

Where:

$$Y = (t/M_p)^{1/3} \tag{5.33}$$

$$X = t \tag{5.34}$$

$$A = (2.3\ r\ M_M)^{-1/3} \tag{5.35}$$

$$B = \frac{(2.3\ r)^{2/3}}{6\ M_M^{1/3}} \tag{5.36}$$

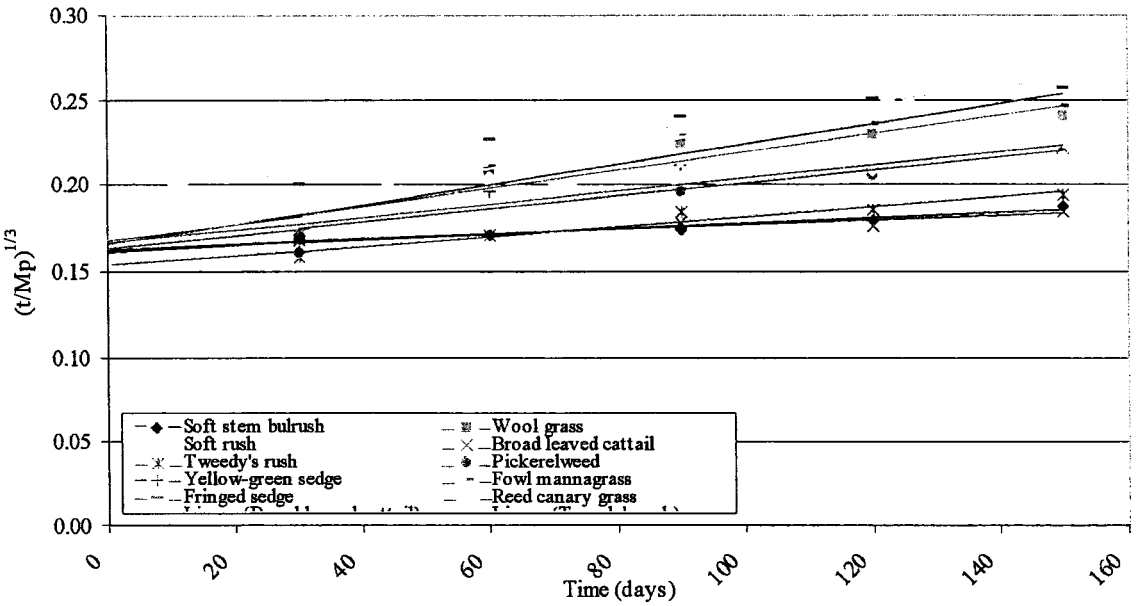
The A and B values can be obtained graphically for various plant-metal combination according to the procedure described by Vlyssides et al. (1997) by plotting $(t/M_p)^{1/3}$ vs. t as shown in Figure 5.99 . The results are shown in Table 5.30. Tables 5.31 and 5.32 present the linear form of Equation (5.31) for iron and manganese uptake by various plants. In order to determine r and M_M in Equation (5.21), Equations (5.35) and (5.36) must be solved simultaneously. Equation (5.35) can be rearranged as follows:

$$r = \frac{1}{2.3\ A^3\ M_M} \tag{5.37}$$

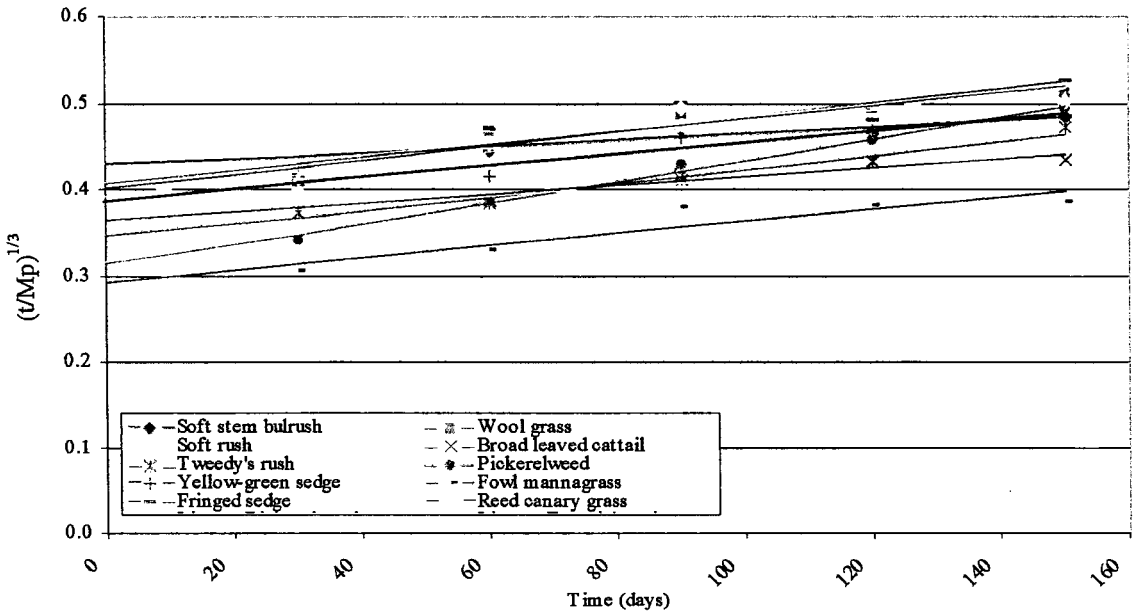
Substituting Equation (5.37) in Equation (5.36) yields the following equation:

$$B = \frac{\left(\frac{2.3}{2.3\ A^3\ M_M}\right)^{2/3}}{6\ M_M^{1/3}} \tag{5.38}$$

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(a) Iron



(b) Manganese

Figure 5.99. Graphical determination of A and B in different wetland plants.

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Table 5.30. Values of A and B in Equation (5.32)

Plant	Iron		Manganese	
	A	B	A	B
Wool grass	0.1662	0.00031	0.4097	0.0012
Soft rush	0.1740	0.00033	0.3933	0.0008
Board leaved cattail	0.1639	0.00020	0.3631	0.0014
Soft stem bulrush	0.1662	0.00021	0.4264	0.0005
Tweedy's rush	0.1529	0.00025	0.3428	0.0015
Yellow-green sedge	0.1659	0.00025	0.3895	0.0013
Reed canary grass	0.1824	0.00023	0.4020	0.0015
Fringed sedge	0.1937	0.00025	0.4005	0.0009
Pickerelweed	0.1633	0.00026	0.3102	0.0008
Fowl mannagrass	0.1647	0.00031	0.2920	0.0016

Table 5.31. Linear form of Equation (5.32) for iron uptake.

Plant	Equation	R^2
Wool grass	$(t/M_p)^{1/3} = 0.1662 + 0.00031\ t$	0.88
Soft rush	$(t/M_p)^{1/3} = 0.1740 + 0.00033\ t$	0.88
Board leaved cattail	$(t/M_p)^{1/3} = 0.1639 + 0.00020\ t$	0.89
Soft stem bulrush	$(t/M_p)^{1/3} = 0.1662 + 0.00021\ t$	0.92
Tweedy's rush	$(t/M_p)^{1/3} = 0.1529 + 0.00025\ t$	0.93
Yellow-green sedge	$(t/M_p)^{1/3} = 0.1659 + 0.00025\ t$	0.83
Reed canary grass	$(t/M_p)^{1/3} = 0.1824 + 0.00023\ t$	0.82
Fringed sedge	$(t/M_p)^{1/3} = 0.1937 + 0.00025\ t$	0.94
Pickerelweed	$(t/M_p)^{1/3} = 0.1633 + 0.00026\ t$	0.86
Fowl mannagrass	$(t/M_p)^{1/3} = 0.1647 + 0.00031\ t$	0.87

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Table 5.32. Linear form of Equation (5.32) for manganese uptake.

Plant	Equation	R^2
Wool grass	$(t/M_p)^{1/3} = 0.4097 + 0.0012\,t$	0.88
Soft rush	$(t/M_p)^{1/3} = 0.3933 + 0.0008\,t$	0.92
Board leaved cattail	$(t/M_p)^{1/3} = 0.3631 + 0.0014\,t$	0.90
Soft stem bulrush	$(t/M_p)^{1/3} = 0.4264 + 0.0005\,t$	0.88
Tweedy's rush	$(t/M_p)^{1/3} = 0.3428 + 0.0015\,t$	0.97
Yellow-green sedge	$(t/M_p)^{1/3} = 0.3895 + 0.0013\,t$	0.91
Reed canary grass	$(t/M_p)^{1/3} = 0.4020 + 0.0015\,t$	0.86
Fringed sedge	$(t/M_p)^{1/3} = 0.4005 + 0.0009\,t$	0.85
Pickerelweed	$(t/M_p)^{1/3} = 0.3102 + 0.0008\,t$	0.99
Fowl mannagrass	$(t/M_p)^{1/3} = 0.2920 + 0.0016\,t$	0.92

Equation (5.38) can be rearranged as follows:

$$B = \frac{(A^{-3} M_M^{-1})^{2/3}}{6 M_M^{1/3}} \tag{5.39}$$

Then, Equation (5.39) can be rewritten as follows:

$$B = \frac{1}{6 A^2 M_M} \tag{5.40}$$

Or

$$M_M = \frac{1}{6 A^2 B} \tag{5.41}$$

By substituting Equation (5.41) in Equation (5.37), the following equation is obtained:

$$r = \frac{1}{2.3 A^3 \left(\frac{1}{6 A^2 B}\right)} \tag{5.42}$$

Equation (5.42) can be rewritten as follows:

$$r = 2.61 \frac{B}{A} \tag{5.43}$$

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By substituting the value of k/2.3 for r in Equation (5.42), the value of k can be determines as follows:

$$k = 4.3839 \frac{B}{A} \qquad (5.44)$$

Equations (5.41) and (5.44) were used to determine the maximum concentrations (M_M) of iron and manganese that can be accumulated by the wetland plants and the specific uptake rates (k), respectively. The results are shown in Table 5.33.

The model results showed that the fastest wetland plant in absorbing iron was wool grass followed by fowl mannagrass then soft rush, tweedy's rush, yellow green sedge, pickerelweed, broad leaved cattail, soft stem bulrush, reed canary grass and fringed sedge with a specific uptake rate (k) of 0.009, 0.009, 0.008, 0.008, 0.008, 0.008, 0.006, 0.006, 0.006 and 0.006 d^{-1}, respectively. The values for manganese specific uptake rate (k) by the wetland plants were 0.012, 0.012, 0.011, 0.009, 0.009, 0.009, 0.008, 0.008, 0.007, 0.005 d^{-1} for pickerelweed, fowl mannagrass, tweedy's rush, soft rush, reed canary grass, fringed sedge, wool grass, yellow green sedge, broad leaved cattail and soft stem bulrush, respectively.

The model also indicated that the maximum concentrations of iron accumulated in the plant during the growth period of 150 days were 31021.4, 28732.1, 24222.3, 24038.3, 21780.7, 19819.8, 19463.7, 18349.7 and 17768.5 mg/kg for broad leaved cattail, soft stem bulrush, tweedy's rush, yellow green sedge, pickerelweed, reed canary grass, fowl mannagrass, wool grass, soft rush and fringed sedge, respectively. The maximum concentrations of manganese accumulated in the plant were 2792.5, 2528.3, 2291.7, 2165.1, 1772.9, 1569.4, 1418.5, 1346.8, 1298.8 and 1289.2 mg/kg for fowl mannagrass, broad leaved cattail, soft stem bulrush, pickerelweed, tweedy's rush, yellow green sedge, wool grass, soft rush, fringed sedge and reed canary grass, respectively.

The predicted maximum concentrations were plotted against the experimental maximum concentrations obtained at the end of the growing season for both iron and manganese as

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Table 5.33. Iron and manganese kinetic uptake parameters (k, M_M) for wetland plants.

Plant	Iron		Manganese	
	k (d^{-1})	M_M (mg/kg)	k (d^{-1})	M_M (mg/kg)
Wool grass	0.009	19463.7	0.014	827.43
Soft rush	0.008	18349.7	0.009	1346.82
Board leaved cattail	0.006	31021.4	0.019	902.82
Soft stem bulrush	0.006	28732.1	0.006	1833.35
Tweedy's rush	0.008	27419.6	0.021	945.53
Yellow-green sedge	0.008	24222.3	0.016	845.06
Reed canary grass	0.006	21780.7	0.018	687.55
Fringed sedge	0.006	17768.5	0.011	1154.52
Pickerelweed	0.008	24038.3	0.012	2165.10
Fowl mannagrass	0.009	19819.8	0.026	1221.69

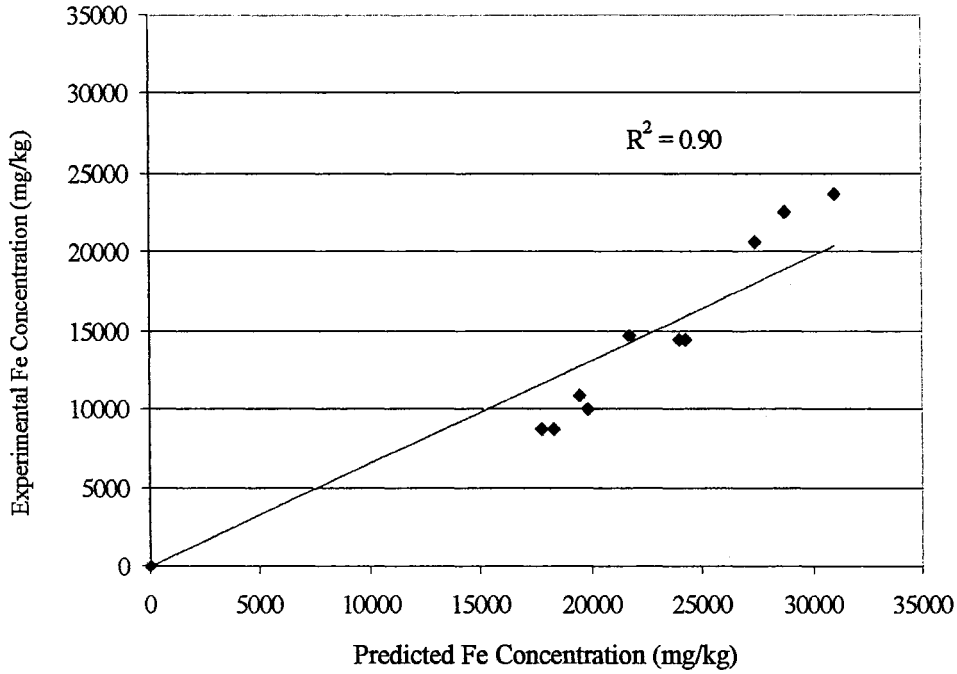
M_M = Maximum accumulated metal concentration at the end of growth season.

shown in Figure 5.100. The results showed that the model is capable of predicting the experimental data with relatively high confidence (R^2 of 0.90 for iron and 0.95 for manganese).

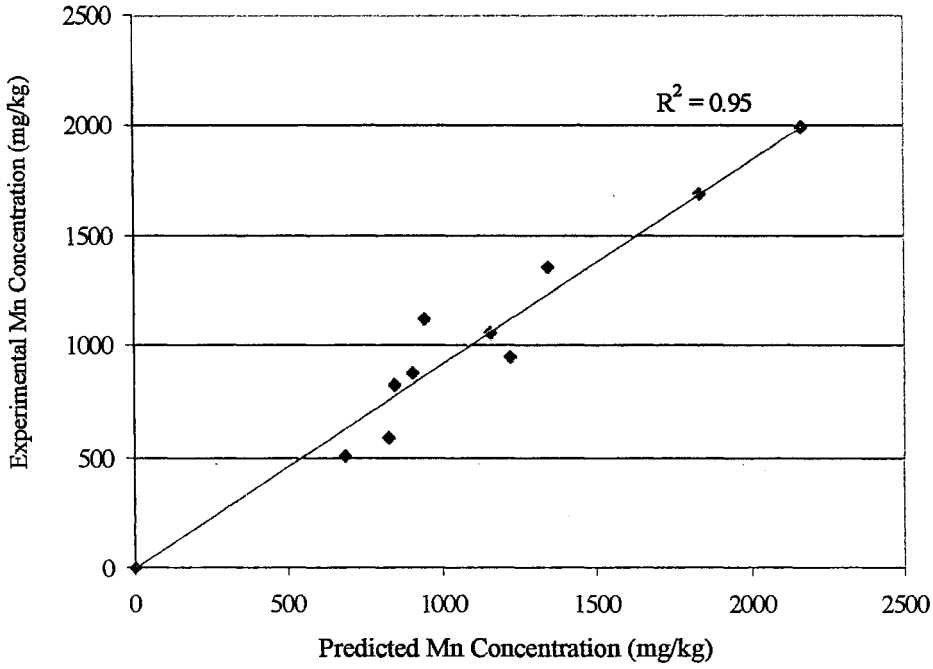
5.10 Conclusions

1. The water pH in the constructed wetland fluctuated around 7 as a result of the fluctuation in precipitation and generation of organic substances in the wetland which acted as buffer.
   (a) The pH fluctuated between 6.7 and 7.9 in season I and between 6.7 and 7.6 in season II.
   (b) There were increases in the pH value as the water flow from cell 1 to cell 9 because of sulfate reducing bacteria.
   (c) The pH values observed during seasons I and II were within the pH limits (5.0 to 9.0) of the CCME (2003) guidelines for the protection of freshwater aquatic life.

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(a) Iron



(b) Manganese

Figure 5.100. Maximum predicted and experimental concentrations of iron and manganese accumulated in wetland plants at the end of the growth season.

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2. The DO concentration in the water of the constructed wetland was affected by the organic and inorganic pollutants discharged into the wetland, water temperature and plant growth and maturity.
   (a) The DO concentrations fluctuated between 2.5 and 6.1 mg/L in season I and between 5.7 and 6.3 mg/L in season II.
   (b) The DO concentrations generally decreased as the water flowed through the wetland cells in season I and remained relatively constant in season II.
   (c) The DO concentrations observed during seasons I and II in the constructed wetland water were within the range (4.5 and 9) set up by the CCME (2003) guidelines for the protection of freshwater aquatic life. However, it dropped below the CCME guidelines limit of 4.5 mg/L in the outlet during the months of June-August of season I due to high water temperature.
3. The water quality of outlet of the constructed wetland improved significantly over time.
   (a) The reduction in othro-PO_4, TKN, NH_4-N, NO_2-N, NO_3-N, COD, TSS, TDS, Fe and Mn in season II were 60.00, 31.94, 52.29, 56.52, 22.22, 52.79, 70.04, 72.03, 66.74 and 39.38 %, respectively.
   (b) Increasing the number of cells in the constructed wetland from 4 cells in season I to 9 cells in season II improved the removal efficiencies of the constructed wetland for ortho-PO_4, TKN, NH_4-N, NO_3-N, COD, TSS, TDS, Fe and Mn by 33.3, 33.3, 30.6, 8.00, 26.7, 52.2, 43.5, 54.1, 44.44 and 18.52 %, respectively.
   (c) The concentrations of Mn, NO_3-N and NO_2-N in the constructed wetland outlet water were below those reported in the guidelines published by CCME (2003) for the protection of freshwater life.
4. The iron removal efficiency of the constructed wetland water was affected by the amount of flocs presented in the wastewater, the site vegetation, the plant maturity and rain events.
   (a) The average iron overall removal efficiency increased over time during the growth season.
   (b) The average iron overall removal efficiency for seasons I and II was 37.07 and 66.75 %, respectively.

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(c) The majority of the iron detected in seasons I and II water quality analyses was non-toxic (Fe^{3+} and its associated precipitates).

(d) The primary sink for iron particulates (precipitated by either root-induced changes or the physical processes happening in the wetland) in the constructed wetland was the sediment.

5. The plants species differed widely in their ability to accumulate and translocate iron.
   (a) The iron concentrations in all plant parts increased with time during the growth season.
   (b) The root tissues of the plants accumulated significantly greater concentrations of iron than the shoots and flowers.
   (c) Broad leaved cattail accumulated the highest total concentrations of iron followed by Soft stem bulrush, Tweedy's rush, Reed canary grass, Pickerelweed, Yellow-green sedge, Wool grass, Fowl mannagrass, Fringed sedge and Soft rush.
6. The sediment pond was effective in removing iron.
   (a) The Fe concentration in the sediment pond (inlet) increased by 4% (from 59580 to 61850 mg/kg) but no increases were observed in the outlet sediment.
   (b) Different forms of iron were observed in the soil profile taken from the inlet sediment.
   (c) A strong correlation was observed between the iron concentrations in the plant parts and those in the sediment.
7. The manganese removal efficiency from the constructed wetland water was affected by rain event, plant density and maturity, and manganese and iron concentrations in the wastewater.
   (a) The average overall manganese removal efficiencies for seasons I and II were 32.08 and 39.38 %, respectively.
   (b) The overall manganese removal efficiencies increased with time during the growth season.
8. Plant species differed widely in their ability to accumulate and translocate manganese
   (a) The leaves and flowers tissues accumulated significantly greater concentrations of manganese than the roots, indicating high manganese mobility inside the plant.

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(b) Fowl mannagrass accumulated the highest total concentrations of manganese followed by Broad leaved cattail, Tweedy's rush, Soft stem bulrush, Yellow-green sedge, Pickerelweed, Wool grass, Reed canary grass, Soft rush and Fringed sedge.

(c) The plants used in the constructed wetland did not accumulate high concentrations of manganese due to Mn-Fe antagonism.

(d) The plants that accumulated higher levels of iron did not necessarily do the same for manganese.

9. The Mn concentrations in the inlet and outlet sediments remained unchanged.

10. A first-order kinetic model was developed and used to determine iron and manganese specific uptake rates by wetland plants and the maximum concentration that can be accumulated by each plant by the end of the growth season.

(a) The model was capable of predicting the experimental data with a relatively high confidence (R^2 of 0.90 and 0.95 for iron and manganese, respectively).

(b) The model showed that the fastest wetland plant in absorbing iron was wool grass followed by fowl mannagrass then soft rush, tweedy's rush, yellow green sedge, pickerelweed, broad leaved cattail, soft stem bulrush, reed canary grass and fringed sedge, while the fastest wetland plant in absorbing manganese was pickerelweed followed by fowl mannagrass, tweedy's rush, soft rush, reed canary grass, fringed sedge, wool grass, yellow green sedge, broad leaved cattail and soft stem bulrush.

(c) The model also indicated that the highest maximum concentration of iron accumulated in the plant was in broad leaved cattail followed by soft stem bulrush, tweedy's rush, yellow green sedge, pickerelweed, reed canary grass, fowl mannagrass, wool grass, soft rush and fringed sedge, while the highest maximum manganese concentration was in fowl mannagrass followed by broad leaved cattail, soft stem bulrush, pickerelweed, tweedy's rush, yellow green sedge, wool grass, soft rush, fringed sedge and reed canary grass, respectively.

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5.11 Recommendations

1. The sediment pond of the constructed wetland will need to be physically dredged of its sediment build-up once every few years to remove the iron from the sediments.
2. The berms should be properly fixed and widened to increase the vegetation areas of the constructed wetland.
3. A model scale wetland should be used to investigate the iron and manganese removal mechanisms in wetlands.
4. The leaves and flowers of the plants investigated in the present study are used as food by wetland animals and birds and there is the possibility that they may bioaccumulate iron and manganese in their bodies. For the protection of aquatic life, a remedial measure such as limestone filter must be implemented in order to reduce the level of iron and manganese in the wetland influent.

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6. HEAVY METAL UPTAKE BY FACULTATIVE AND OBLIGATE WETLAND PLANTS UNDER LABORATORY CONDITIONS

6.1 Introduction

In many ways, living plants can be compared to solar driven pumps which can extract and concentrate several elements from their environment. From soil and water, all plants have the ability to accumulate heavy metals which are essential for their growth and development. These metals include Mg, Fe, Mn, Zn, Cu, Mo and Ni (Langille and MacLean, 1976). Certain plants also have the ability to accumulate heavy metals which have no known biological function. These include Cd, Cr, Pb, Co, Ag, Se and Hg (Hanna and Grant, 1962; Baker and Brooks, 1989). However, excessive accumulation of these heavy metals can be toxic to most plants. The ability to both tolerate elevated levels of heavy metals and accumulate them in very high concentrations has evolved both independently and together in a number of different plant species (Ernst et al., 1992). Plants distribute metals internally in many different ways. They may localize selected metals mostly in roots and stems, or they may accumulate and store other metals in nontoxic form for latter distribution and use. A mechanism of tolerance or accumulation in some plants apparently involves binding potentially toxic metals at cell walls of roots and leaves, away from sensitive sites within the cell or storing them in a vacuolar compartment (Memon et al., 2001).

In wetlands, several processes combine to provide the overall treatment. These include: sedimentation and filtration of solids, (b) gasification of volatile substances, (c) chemical precipitation, (d) ion exchange, and (e) plant uptake of metals. However, the vegetation is extremely important for the nutrient transformations and transfers, because it plays a key role in the cycling and temporary storage of many substances. It is, therefore, important to understand the uptake and storage of metals in various parts of the wetland plants. There are two categories of wetland plants: (a) obligate wetland plants which are found in wetlands 99% of the time, and (b) facultative wetland plants which are found in wetlands 67-99% of the time.

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6.2 Objectives

The aim of this study was to assess the performance of selective facultative and obligate wetland plants for heavy metal removal from landfill leachate in order to gain better understanding of the removal mechanism. The specific objectives were:

1. to investigate the effect of initial concentrations of heavy metals (Fe, Mn and Zn) on the overall removal efficiency of these metals by obligate and facultative wetland plants,
2. to determine the translocation of heavy metals in the different parts of each plant species (root, stem, leaves and flower),
3. to determine the plant heavy metals selectivity, and
4. to determine the fraction of heavy metals removed by precipitate in relation to initial metal concentrations.

6.3 Experimental Apparatus

The experimental setup shown in Figure 6.1 consists of holding tanks, a lighting system, an aeration system, and a temperature monitoring system.

6.3.1 Holding Tanks

Four boxes were constructed from 2.5 cm thick plywood material and used in this experiment, one box for each plant species. Each box (60 x 120 x 80 cm) was divided into three compartments: the first compartment was used as a control and received tap water, the second compartment received leachate with contaminants concentrations similar to those received by the wetland and the third compartment received leachate with contaminants concentrations similar to concentrations reported in the literature as the highest tolerance levels for these four plants.

6.3.2 Lighting System

The light was provided by an artificial lighting system (625 hectolux/7200 cm^2) and was similar to the natural light required for wetland plants. Each lighting unit consists of eight light bulbs (six 34 watts cool white fluorescent bulbs and two Gro-lux 40 watts bulbs) of

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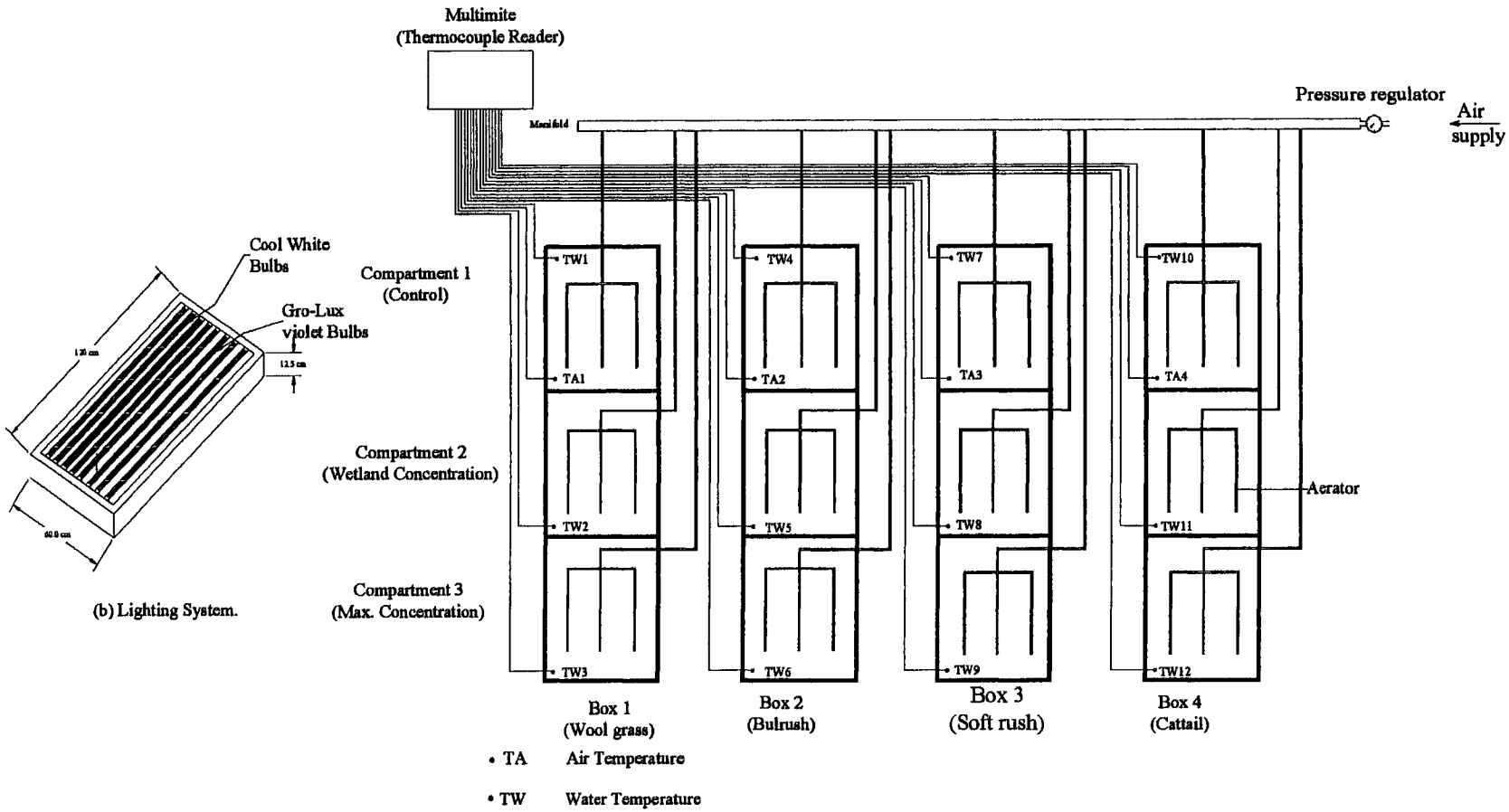


Figure 6.1. Experimental Apparatus.

122 cm in length. The lighting system was placed on the top of each box using wooden supports in such a way that it gave a space of 140 cm clearance between the light bulbs and the water surface in the box. This space was chosen to achieve a good air circulation, provide the heat and light that were required for plant growth. The lights were controlled by a timer, which was set to provide the required number of hours of light per box per day (16 h/d) and to maintain a temperature difference between the soil and the above ground part at 15°C (Mills, 2003).

6.3.3 Aeration System

An aeration unit was installed in the bottom of each compartment to provide oxygen for the plants. The air flew from the main laboratory supply to a manifold with twelve outlets. Each outlet was connected to a pressure regulator (Model 129121/510, ARO, Bryan, Ohio), which was connected to an aerator located in each compartment. Each aerator consists of a main tube (26.5 cm long) with three perforated stainless steel laterals (30 cm in length and 0.6 cm in diameter) coming off it at right angles to the main. Tygon tubing of 0.75 cm outside diameter was used to connect the main air supply, manifold and aeration unit. The pressure regulator was adjusted at 0.068 atm. during the whole experimental period to give the aeration rate of 7 cm^3/min, which is required for the plants survival.

6.3.4 Temperature Monitoring System

The water and the ambient air temperature were monitored during the experimental period. Twelve thermocouples (TW1-TW12) were used to measure the water temperature, one for each compartment. Four thermocouples (TA1-TA4) were used to measure the ambient air temperature above the water surface in each wooden box. The thermocouples were connected to a thermoelectric device (Multimite, Thermoelectric, Brampton, Ontario) for temperature monitoring.

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6.4 Selected Wetlands Plants

Two facultative (wool grass and soft rush) and two obligate (broad-leaved cattails and soft stem bulrush) wetlands plant species were used in the study (Figure 6.2). The selection of these plants was based on their dominance in the constructed wetland. Both soft rush and soft stem bulrush have been listed in many references as both obligate and facultative wetland plants. The selection also took into consideration the aggressive nature of plants (broad-leaved cattail) and the slow growth (wool grass, soft rush and soft stem bulrush). These wetlands plants were obtained from Environmental Concern Inc., St. Michaels, Maryland, USA in order to avoid high initial concentration of heavy metals in their tissues. Complete descriptions of these four plants can be found in Appendix A.

6.5 Experimental Procedures

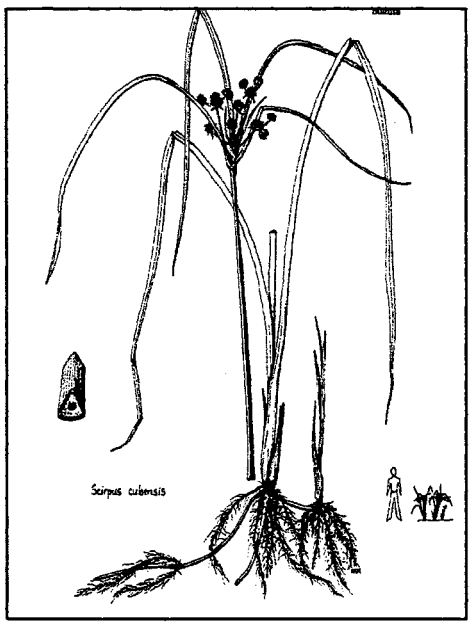
6.5.1 Contaminant Preparation

Three contaminants were investigated in this study (Fe, Mn and Zn). These contaminants were added as ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2.6H_2O$), manganous sulfate ($MnSO_4.H_2O$), and zinc nitrate ($Zn(NO_3)_2.6H_2O$). These compounds were purchased as reagent grade chemicals from Fisher Scientific, Ottawa, Ontario. The concentrations of the individual heavy metals were chosen to simulate their concentrations in the influent of the constructed wetland (Ghaly and Cote, 2001) and the highest tolerance reported in the literature (Snowden and Wheeler, 1993; and Ye et al., 2001) as shown in Table 6.1. Calculations were based on the individual elements versus their compound forms (i.e. Fe versus Ferrous ammonium sulfate). The reagents were dissolved in distilled water to achieve the appropriate contaminants level. The final concentrations of heavy metal used in this experiment are presented in Table 6.2.

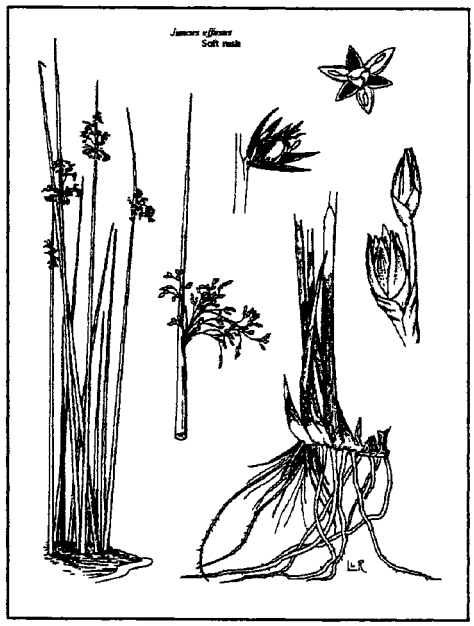
6.5.2 Experimental Protocol

Each compartment (30 x 60 x 80 cm) was filled with 10 cm large gravel (1.25 cm average nominal size) layer to facilitate the collection of drainage water. A drainage tube was placed vertically in each compartment to drain the water at the end of each batch. The drainage tube was 35.5 cm in length with holes in the lower 10 cm end. The drainage

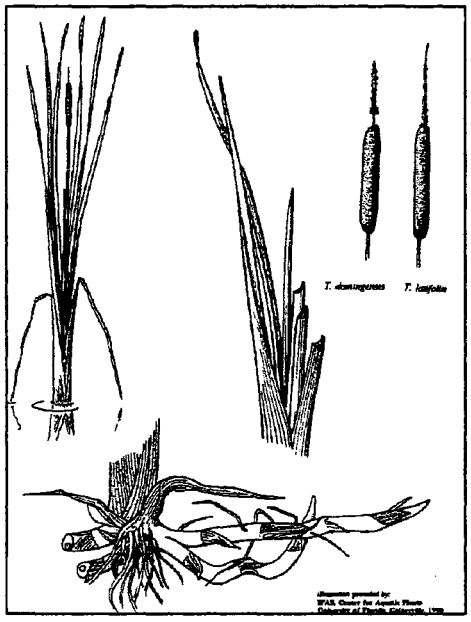
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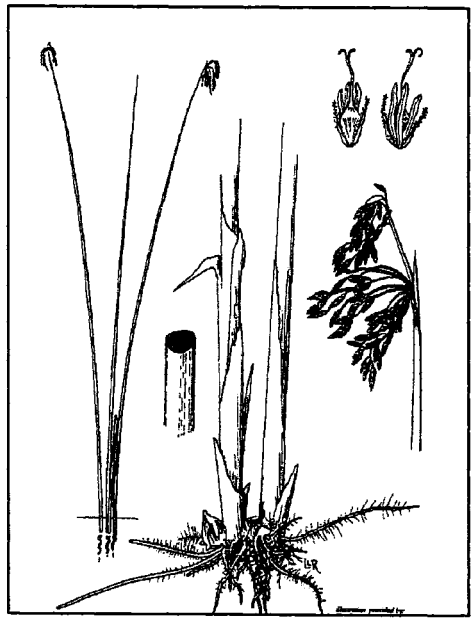
(a) Wool grass



(b) Soft rush



(c) Broad-leaved cattail



(d) Soft stem bulrush

Figure 6.2. Plant species used in the experiments.

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Table 6.1. Contaminants concentration applied to the system.

Contaminants	Wetland Influent (mg/L)	Maximum Tolerance* (mg/L)	Reference
Iron	6.60	100.00	Snowden and Wheeler (1993)
Manganese	1.80	15.00	Ye et al. (2001)
Zinc	0.006	0.390	Ye et al. (2001)

* Maximum concentration reported in the literature.

Table 6.2. Concentrations of elements (mg/L) present in the contaminated water.

Element	Source				Total	
	Water	Fertilizer	Reagents added to simulate		Wetland influent	Maximum tolerance
			wetland influent	maximum tolerance		
Nutrients						
Potassium	----	163.40	------	------	163.40	163.40
Nitrogen	----	163.40	3.34	50.33	166.74	213.73
Phosphorus	----	163.40	------	------	163.40	163.40
EDTA	----	8.17	------	------	8.17	8.17
Boron	----	0.16	------	------	0.16	0.16
Sulfur	----	------	8.60	123.23	8.60	123.21
Heavy Metals						
Iron	0.3	0.82	6.60	100.00	7.72	101.12
Manganese	----	0.41	1.80	15.00	2.21	15.41
Copper	----	0.41	------	------	0.41	0.41
Zinc	----	0.41	0.07	0.39	0.48	0.80

tube was connected to a wet vacuum pump (Bulldog 700, Shop-Vac Canada Ltd., Burlington, Ontario) to ensure complete drainage of water before introducing the next

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batch of contaminated water. The soil was used as a supporting media for the plants and was placed into each compartment in layers approximately 10 cm thick and lightly compacted to remove excessive voids within the soil structure. Each compartment received about 30 L of contaminated water. One box (three compartments) was used for each plant species. About 8 plants (20-30 cm tall) of each plant were placed in each of the three compartments in the holding tank assigned for that plant. The plants were left for 4 weeks to adapt to the laboratory conditions. The following start up procedure for growing wetland plants in closed system was similar to that proposed by Mills (2003):

Week 1: The water level in each compartment was maintained below the root system of the plants with keeping the soil around the root system moist all the time. The plants were sprayed with insecticide Malathion 500EC (The Solaris Group, Mississauga, Ontario) every week to control the spread of aphids in the system. The dilution rate recommended by the manufacture was followed (2.5 ml of Malathion were mixed in 1 L of water). The plants were supplied with fertilizer 20-20-20 Plant-Prod (Plant Products Co. Ltd., Brampton,, Ontario) as recommended by the manufacture (817 mg of fertilizer per 1 L of water). The composition of fertilizer and the calculated amounts of various nutrients added to the system (mg/L) are shown in Table 6.3.

Table 6.3. Nutrients concentrations in fertilizer and the system.

Element*	Concentration in fertilizer (%)**	Concentration in the system (mg/L)
Nitrogen	20.00	163.40
Potassium	20.00	163.40
Phosphorus	20.00	163.40
EDTA***	1.00	8.17
Iron	0.10	0.82
Manganese	0.05	0.41
Copper	0.05	0.41
Zinc	0.05	0.41
Boron	0.02	0.16

* Iron, Copper, Manganese, and Zinc is present as a chelated metal complex of tetrasodium ethylenediaminetetraacetate

** On weight basis

*** EthyleneDiamineTetraAcetate

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Week 2: The water level was maintained below the roots system and the plants were sprayed by the insecticide to control aphids in the system.

Week 3: The water level was maintained at the soil surface and the plants were sprayed with the insecticide. The plants were supplied with the fertilizer to maintain the plant nutrient requirements throughout the adaptation period.

Week 4: The water level was raised to the final water level, which was used during the entire period of the experiment and the plants were sprayed with the insecticides.

After the startup period of 4 weeks, the experiment was run for 72 days. The contaminated water was changed every 9 days to simulate the retention time of the water in the constructed wetland. The fertilizer was added to each compartment every two weeks and the insecticide was sprayed on a weekly basis. Temperature readings were taken every day for the water and the ambient air during the experimental period. The growth of the individual plant was also observed on a daily basis.

6.5.3 Sampling and Analyses

Water samples of 100 mL were collected from all compartments at 3-day intervals. Before sampling, water was added to bring water level to its initial value before the start of the period in order to maintain constant volume of contaminated water during the experiment. The samples were withdrawn using 25 mL wide tip pipette and analyzed for Fe, Mn, and Zn. Soil samples of 50 g were collected from the middle of each compartment (nonrhizosphere) at the end of each period (after day 9) and were analyzed for Fe, Mn, and Zn. Plant samples (root, stem, leaf, and flower) were collected at 9 days intervals and were analyzed for the presence of heavy metals. The plant and soil samples were dried in a convection oven for 24 hours at 45 °C. After drying, the plants were ground and digested with hydrochloric-nitric-hydrofluric-perchloric acids (30+10+10+5 mL/g sample) in a closed vessel at a temperature of 100 °C. The heavy metals were determined using Atomic Absorption Spectometer (Varion SpectrAA, Model Number: 55B, Varion, Mulgrave, Victoria, Australia).

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6.6 Results

6.6.1 Iron

The initial concentrations of iron in the wastewater, soil and plant tissues of the compartments receiving the control, wetland influent and tolerance concentration are shown in Table 6.4. The final concentration of iron after each 9-day retention period and the removal rate depended on the initial concentrations and the type of plant used.

6.6.1.1 Soft Stem Bulrush

The iron concentrations in the wastewater of the soft stem bulrush compartments are shown in Figure 6.3. The iron concentrations in the wastewater decreased by the end of the 9-day retention period to 0.05-0.10, 1.09-2.05 and 1.81-10.8 mg/L given an overall removal efficiencies of 91-96, 73-86 and 89-98 % for the compartments receiving the control, wetland influent and tolerance concentrations, respectively.

The iron concentrations in soil of the soft stem bulrush compartments are shown in Figure 6.4. The initial concentration of iron in the soil was 40407 mg/kg which decreased to 39890 and 39532 mg/kg by the end of the experiment (72 days) in the compartments receiving the control and wetland influent, indicating removal of iron from soil at average rates of 7.18 and 12.15 mg/kg/day, respectively. The concentration of iron in the soil of the compartment that received the tolerance concentration increased from 40407 mg/kg to 46528 mg/kg by the end of the experiment, indicating addition of iron (from wastewater) to the soil by precipitation at an average rate of 85.01 mg/kg/day.

The concentrations of iron in plant tissues of soft stem bulrush are shown in Figure 6.5. The initial concentrations of iron in the roots, leaves and flowers of the plants were 2423 mg/kg, 13 mg/kg and 3869 mg/kg which increased by the end of the experiment (72 days) to 3062, 8482 and 15290 mg/kg, to 18, 415 and 813 mg/kg, and to 4222, 5459 and 6695 mg/kg in the compartments receiving the control, wetland influent and tolerance concentrations, respectively.

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Table 6.4. Initial concentrations of iron in the water, soil and plant tissues.

Source	Soft stem bulrush			Wool grass			Soft rush			Cattail		
	C	W	T	C	W	T	C	W	T	C	W	T
Water (mg/L)	1.12	7.72	101.12	1.12	7.72	101.12	1.12	7.72	101.12	1.12	7.72	101.12
Soil (mg/kg)	40407	40407	40407	40509	40509	40509	40635	40635	40635	40209	40209	40209
	(298.4)	(111.02)	(409.41)	(296.41)	(311.83	(41.72)	(323.14)	(166.87)	(156.27)	(59.39)	(28.99)	(31.11)
Plant Tissues (mg/kg)												
Roots	2423	2423	2423	1533	1533	1533	2479	2479	2479	288	288	288
	(41.01)	(79.90)	(1.41)	(132.94)	(44.55)	(88.39)	(15.56)	(24.75)	(116.67)	(15.56)	(11.46)	(11.67)
Stem	NS	NS	NS	26	26	26	NS	NS	NS	NS	NS	NS
				(1.41)	(1.41)	(0.71)						
Leaves	13	13	13	102	102	102	69	69	69	113	113	113
	(0.71)	(0.71)	(0.10)	(4.24)	(23.33)	(7.78)	(0.26)	(2.12)	(2.83)	(14.14)	(27.58)	(12.73)
Flower	3869	3869	3869	28	28	28	335	335	335	NF	NF	NF
	(2.32)	(64.35)	(90.51)	(2.35)	(0.71)	(3.21)	(28.28)	(21.21)	(7.07)			

() Standard deviation
C Control
W Wetland Influent
T Tolerance Concentration
NS No Stem
NF No Flower

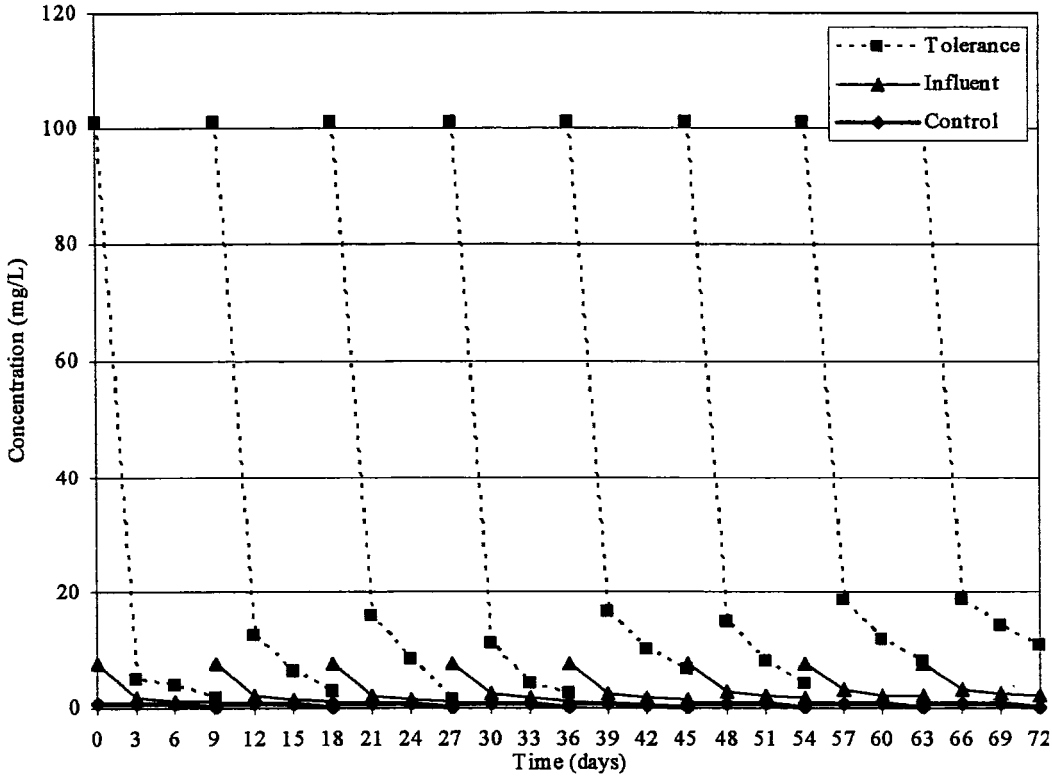


Figure 6.3. Iron concentration in the wastewater of the soft stem bulrush compartments.

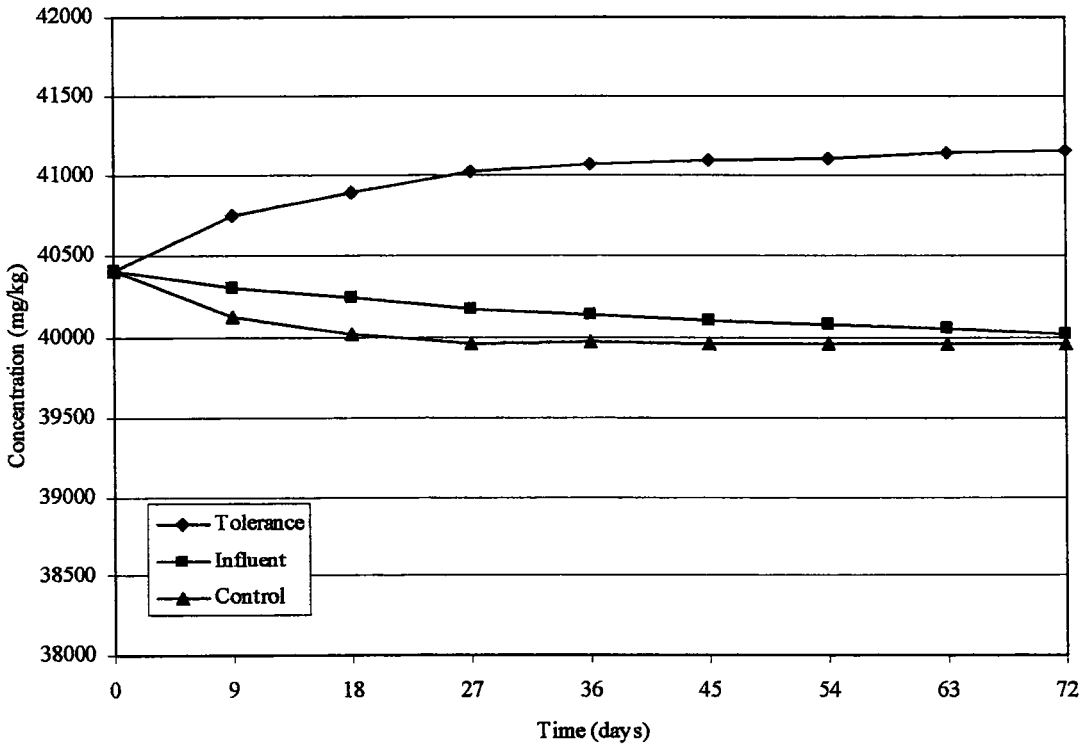
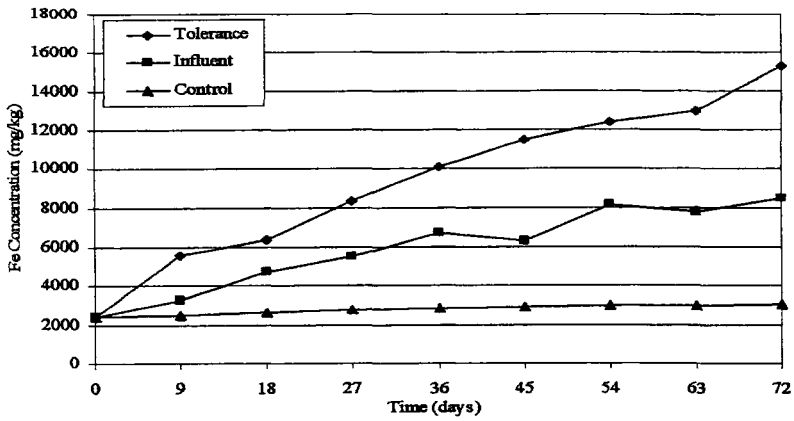
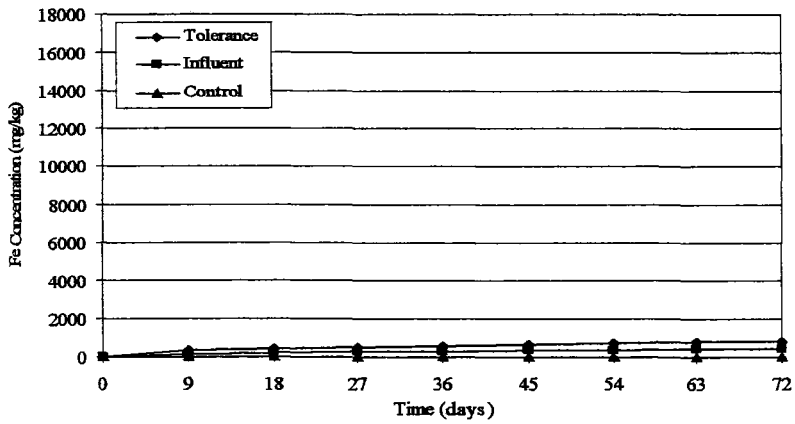


Figure 6.4. Iron concentration in soil of the soft stem bulrush compartments.

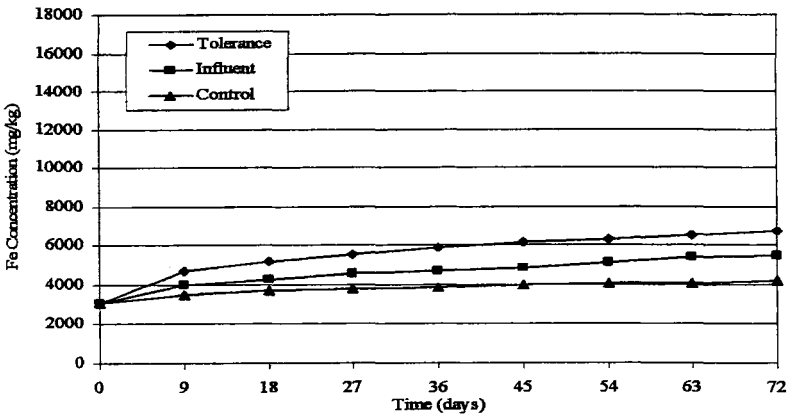
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(a) Roots



(b) Leaves



(c) Flowers

Figure 6.5. Iron concentrations in various parts of the soft stem bulrush.

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6.6.1.2 Wool Grass

The iron concentrations in the wastewater of the wool grass compartments are shown in Figure 6.6. The concentration of iron in the wastewater decreased by the end of each 9-day retention period to 0.35-0.63, 0.86–2.20 and 4.00-25.80 mg/L given an overall removal efficiency of 45-69, 71-89 and 74-96 % for the control, wetland influent and tolerance concentration, respectively.

The iron concentrations in the soil of the wool grass compartments are shown in Figure 6.7. The initial concentration of iron in the soil was 40509 which decreased to 40050 mg/kg in the compartment receiving the control mg/kg by the end of the experiment (72 days) indicating removal of iron from the soil at an average rate of 6.38 mg/kg/day. The concentrations of iron in soils of the compartments that received the wetland influent and tolerance concentration increased from 40509 mg/kg to 41269 and 47395 mg/kg by the end of the experiment indicating addition of iron (from wastewater) to soil by precipitation at average rates of 10.55 and 95.64 mg/kg/day, respectively.

The concentrations of iron in plant tissues of wool grass are shown in Figure 6.8. The initial concentrations of iron in the roots, stems, leaves and flowers of the plants were 1533 mg/kg, 26 mg/kg, 102 mg/kg and 28 mg/kg which increased by the end of the experiment (72 days) to 4220, 6372 and 9620 mg/kg, to 88, 167 and 260 mg/kg, to 181, 232 and 252 mg/kg, and to 105, 260 and 416 mg/kg in the compartments receiving the control, wetland influent and tolerance concentration, respectively.

6.6.1.3 Soft Rush

The iron concentrations in the wastewater of the soft rush compartments are shown in Figure 6.9. The iron concentration in the wastewater decreased by the end of the 9-day retention period to 0.10-0.17, 0.19–1.30 and 1.26-2.50 mg/L given an overall removal efficiency of 79-91, 83-98 and 98-99 % for the control, wetland influent and tolerance concentration, respectively.

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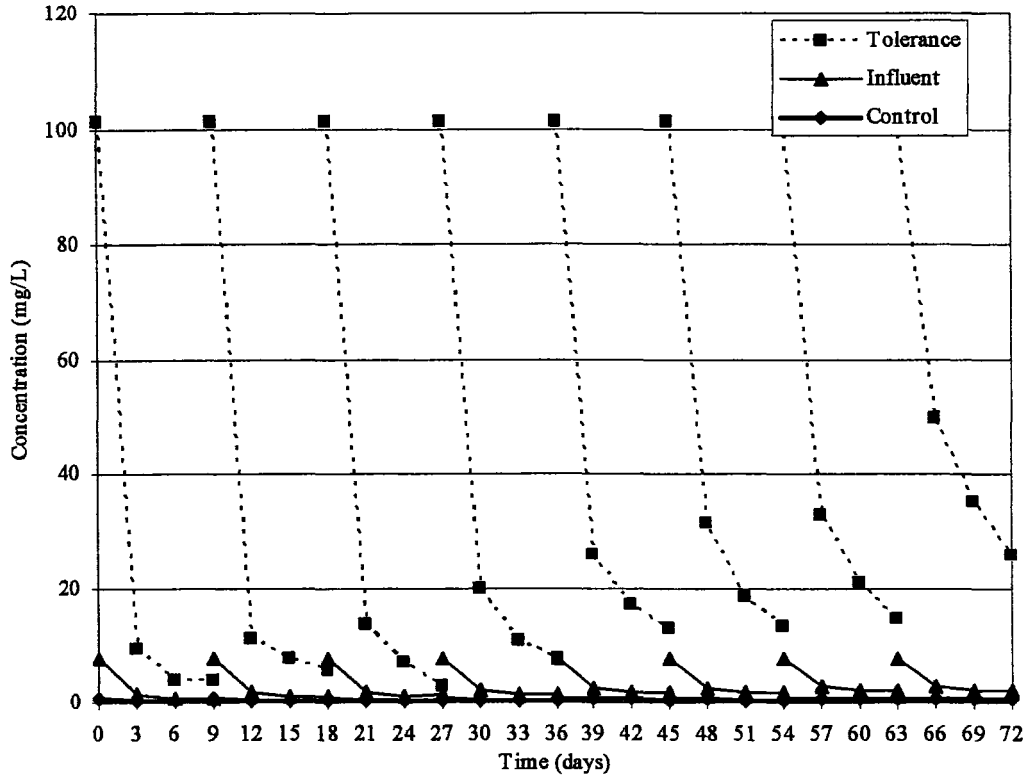


Figure 6.6. Iron concentrations in the wastewater in the wool grass compartments.

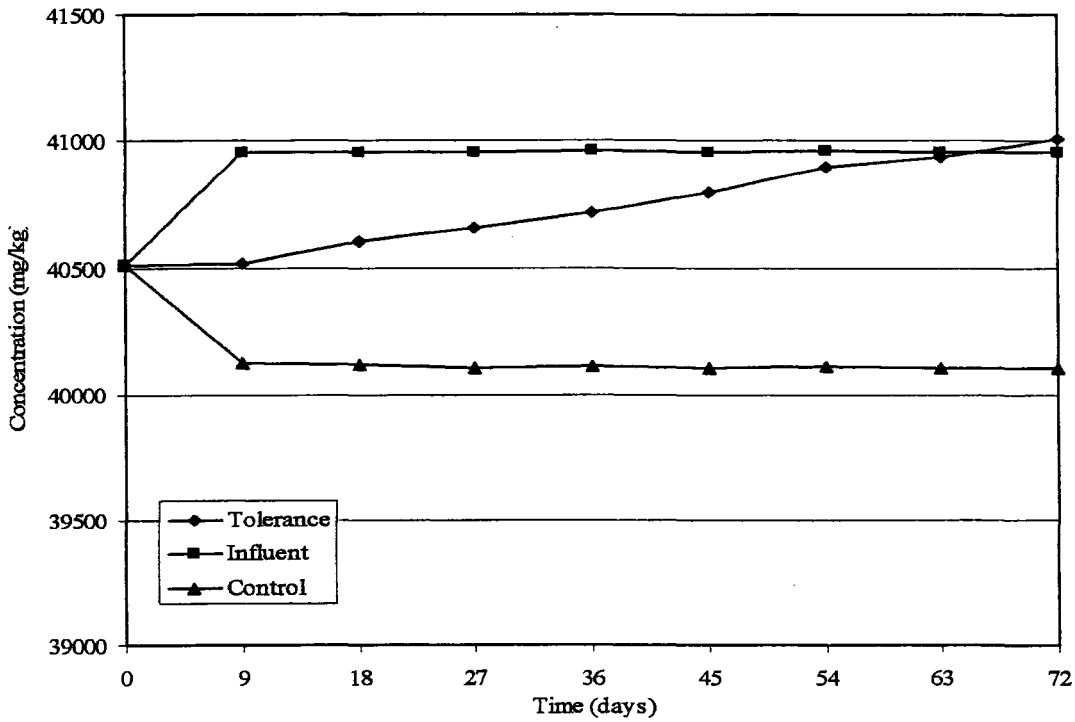
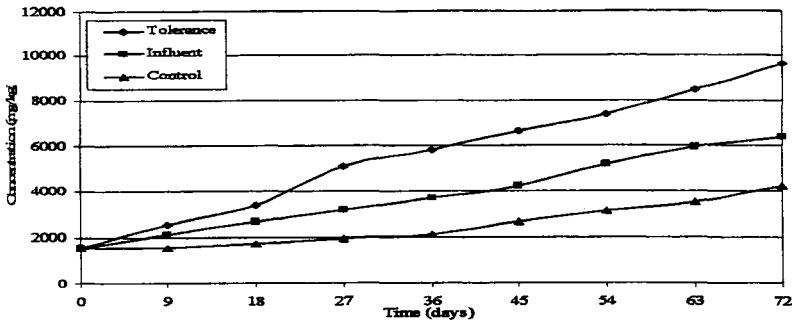
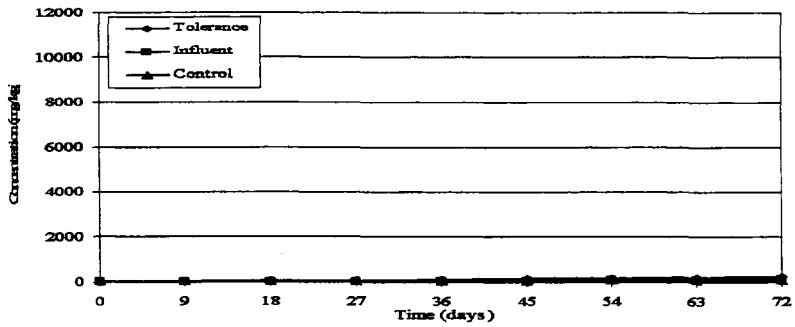


Figure 6.7. Iron concentrations in the soil in the wool grass compartments.

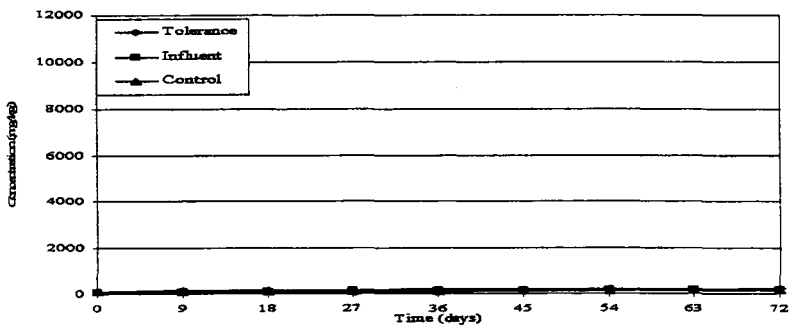
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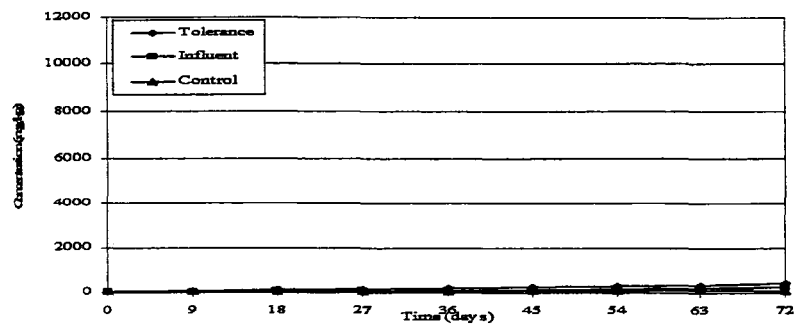
(a) Roots



(b) Stem



(c) Leaves



(d) Flowers

Figure 6.8. Iron concentrations in the various parts of the wool grass.

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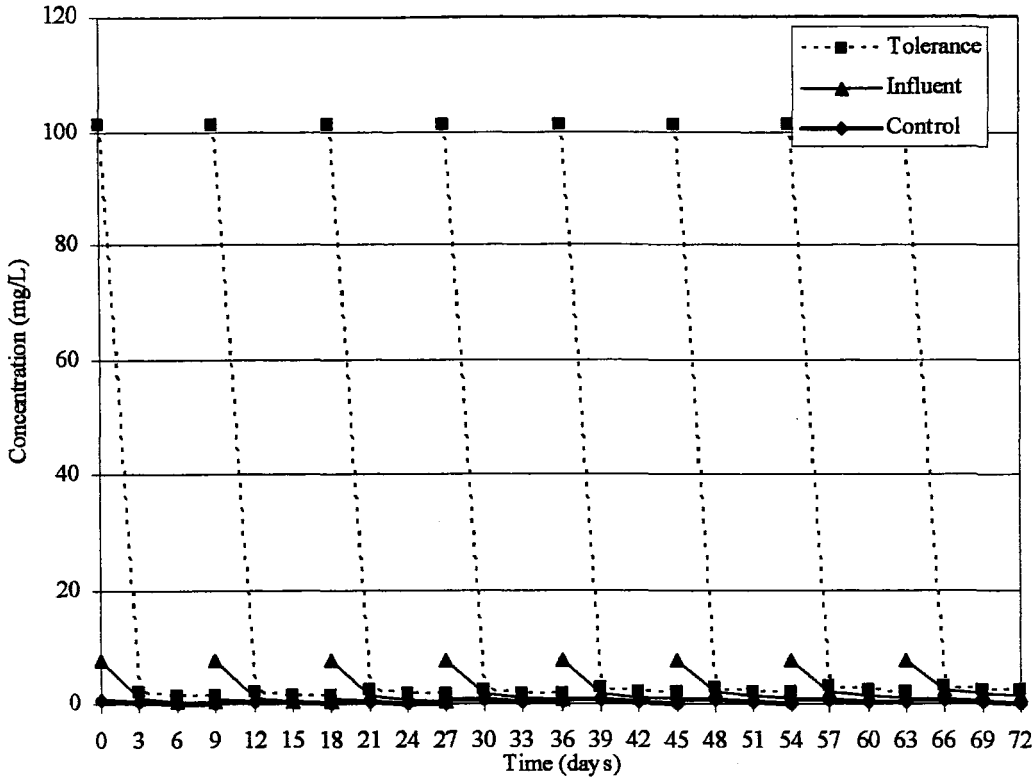


Figure 6.9. Iron concentration in the wastewater of the soft rush compartments.

The iron concentrations in the soil of the soft rush compartments are shown in Figure 6.10. The initial concentration of iron in the soil was 40635 mg/kg which decreased to 40016 mg/kg in the compartment receiving the control by the end of the experiment (72 days) indicating removal of iron from soil at an average rate of 8.59 mg/kg/day. The concentrations of iron in soil of the compartments receiving wetland influent and tolerance concentration increased from 40635 mg/kg to 41006 and 48187 mg/kg by the end of the experiment (72 days) indicating addition of iron (from wastewater) to the soil by precipitation at average rates of 5.15 and 104.88 mg/kg/day, respectively.

The concentrations of iron in plant tissues of soft rush are shown in Figure 6.11. The initial concentrations of iron in the roots, leaves and flowers of the plants were 2479, 69 and 335 mg/kg which increased by the end of the experiment (72 days) to 3840, 5242 and 6432 mg/ kg, to 130, 145 and 160 mg/kg, and to 596, 845 and 1094 mg/kg in the compartments receiving the control, wetland influent and tolerance concentration, respectively.

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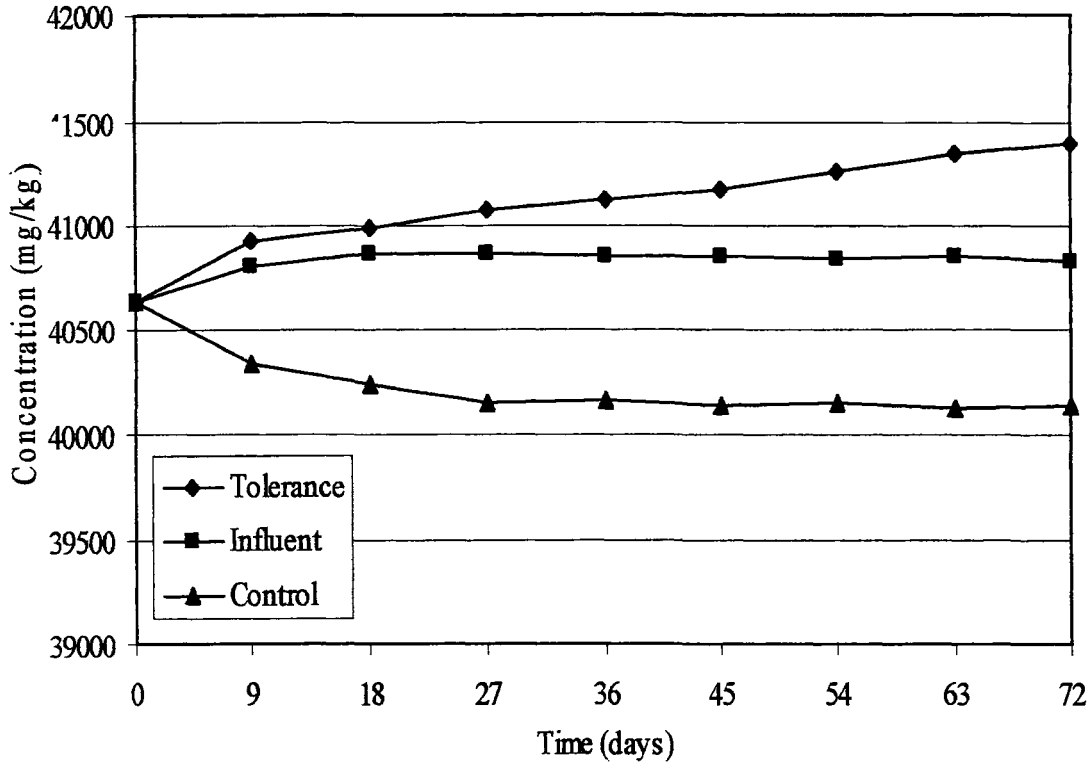


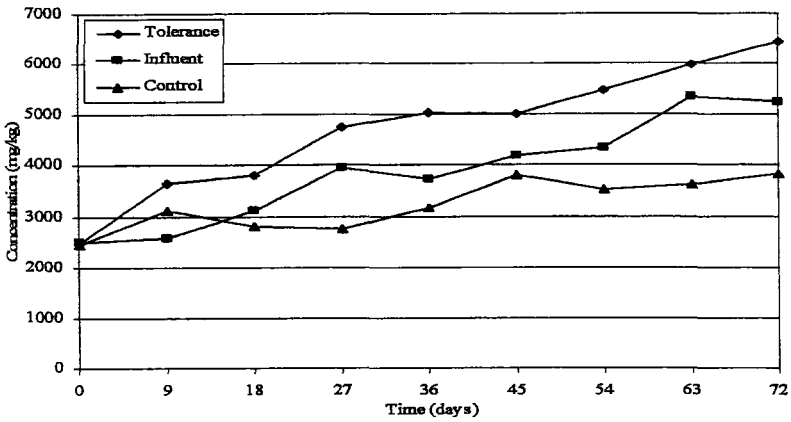
Figure 6.10. Iron concentration in the soil of the soft rush compartments.

6.6.1.4 Cattail

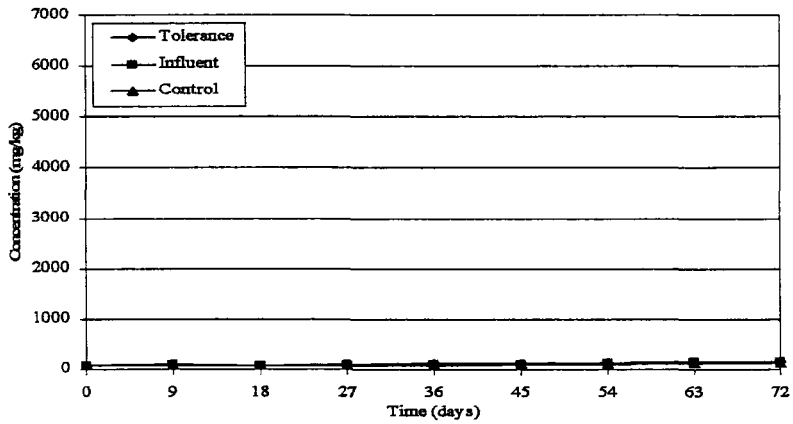
The iron concentrations in the wastewater of the cattail compartments are shown in Figure 6.12. The iron concentration in the wastewater decreased by the end of each 9-day retention period to 0.39-0.54, 0.86–2.17 and 1.26-2.66 mg/L for the control, wetland influent and tolerance concentration, given an overall removal efficiency of 34-77, 72-89 and 97-98 % for the control, wetland and maximum compartments, respectively.

Figure 6.13 shows the iron concentrations in the soil of the cattail compartments. The initial concentrations of iron in the soil was 40209 mg/kg which decreased to 39623 and 39138 mg/kg by the end of the experiment (72 days) in the compartments receiving the control and wetland influent, indicating removal of iron from soil at average rates of 8.14 and 14.88 mg/kg/day, respectively. The concentration of iron in the soil of the compartment that received tolerance concentration increased from 40209 mg/kg by the

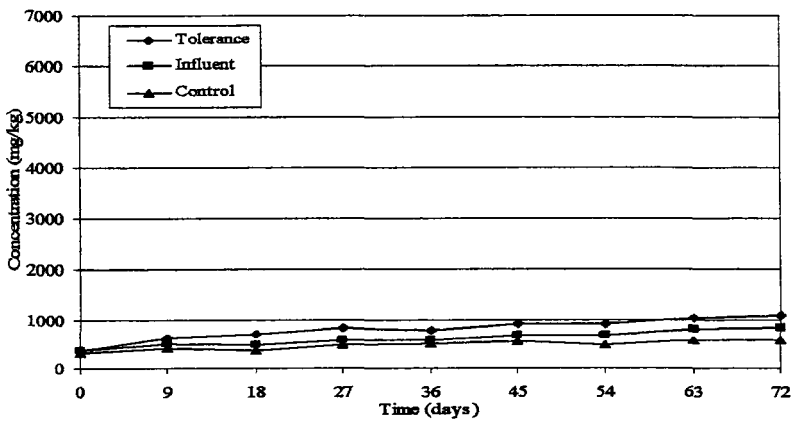
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(a) Roots



(b) Leaves



(c) Flowers

Figure 6.11. Iron concentrations in the various parts of the soft rush.

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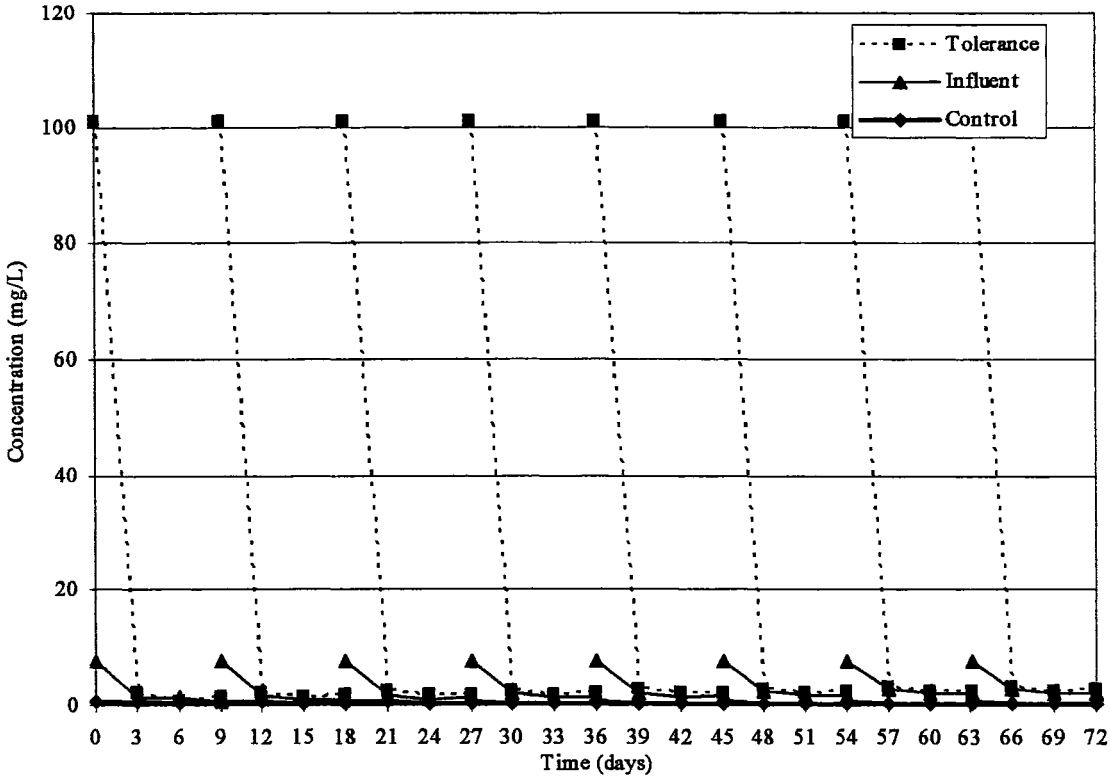


Figure 6.12. Iron concentrations in the wastewater of the cattail compartments.

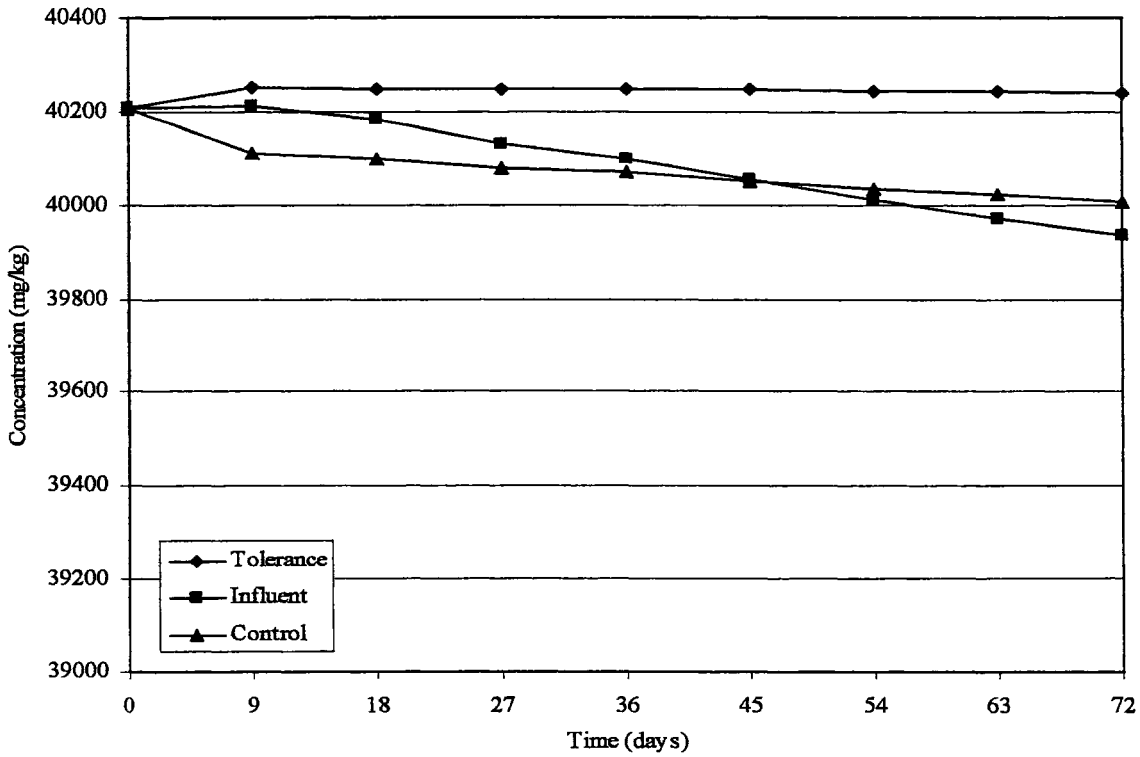


Figure 6.13. Iron concentrations in the soil of the cattail compartments.

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end of the experiment to 45146 mg/kg indicating addition of iron from the wastewater to soil by precipitation at an average rate of 68.57 mg/kg/day.

Figure 6.14 shows the concentrations of iron in plant tissues of cattail. The initial concentrations of iron in the roots and leaves of the cattail plants were 288 mg/kg and 113 mg/kg which increased by the end of the experiment to 2680, 7145 and 14171 mg/kg and to 820, 2980 and 5788 mg/kg in the compartments receiving the control, wetland influent and tolerance concentration, respectively.

6.6.2 Manganese

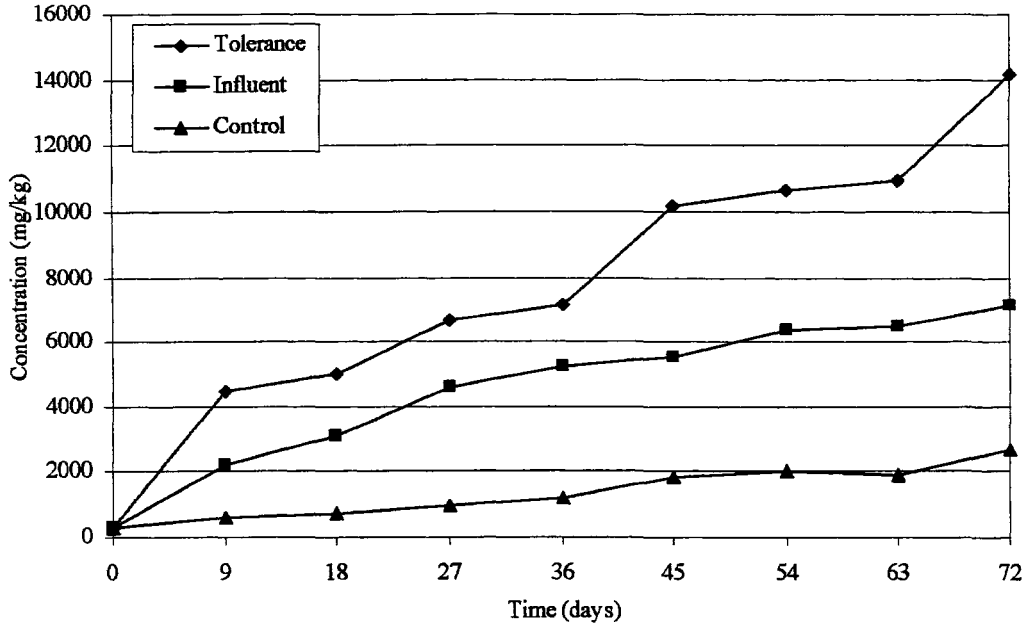
The initial concentrations of manganese in the wastewater, soil and plant tissues of the compartments receiving the control, wetland influent and tolerance concentration are shown in Table 6.5. The final concentration of manganese after the 9-day period and the removal rate depended on the initial concentrations and the type of plant used.

6.6.2.1 Soft Stem Bulrush

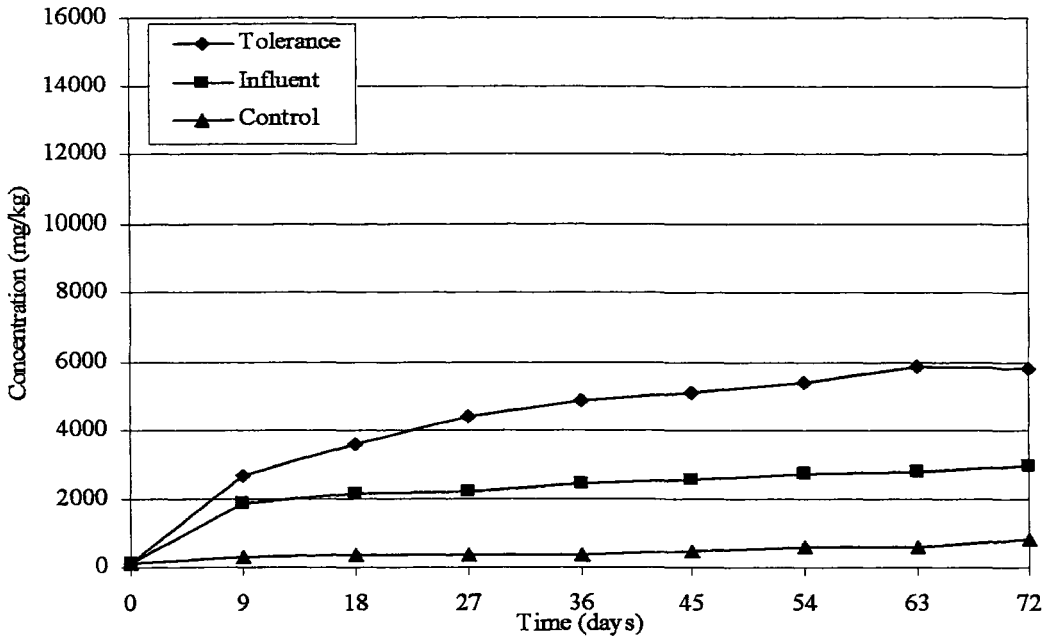
Figure 6.15 shows the manganese concentrations in the wastewater of the soft stem bulrush compartments. The manganese concentration in the wastewater decreased by the end of the 9-day retention period to 0.03-0.25, 0.20-0.27 and 0.36-2.74 mg/L given an overall removal efficiency of 38-92, 87-91 and 82-98 % for control, wetland influent and tolerance concentration, respectively.

The manganese concentrations in the soil of the soft stem bulrush compartments are shown in Figure 6.16. The initial concentration of manganese in the soil was 483 mg/kg which increased to 454, 639 and 1721 mg/kg by the end of the experiment (72 days) in the compartments receiving the control, wetland influent and tolerance concentration, indicating addition of manganese (from wastewater) to the soil by precipitation at average rates of 0.70, 2.17 and 17.19 mg/kg/day in the compartments receiving the control and wetland influent and tolerance concentration, respectively.

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(a) Roots



(b) Leaves

Figure 6.14. Iron concentrations in the various parts of the cattail.

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Table 6.5. Initial concentrations of manganese in the water, soil and plant tissues.

Source	Soft stem bulrush			Wool grass			Soft rush			Cattail		
	C	W	T	C	W	T	C	W	T	C	W	T
Water (mg/L)	0.41	2.21	15.41	0.41	2.21	15.41	0.41	2.21	15.41	0.41	2.21	15.41
Soil (mg/kg)	483 (23.33)	483 (19.09)	483 (4.24)	493 (0.71)	493 (4.95)	493 (5.01)	512 (7.71)	512 (7.78)	512 (0.10)	504 (13.43)	504 (0.71)	504 (2.82)
Plant Tissues (mg/kg)												
Roots	62 (11.31)	62 (0.29)	62 (2.83)	39 (2.12)	39 (8.49)	39 (6.36)	65 (2.12)	65 (2.23)	65 (0.45)	24 (2.12)	24 (1.41)	24 (0.19)
Stem	NS	NS	NS	28 (3.54)	28 (7.07)	28 (1.41)	NS	NS	NS	NS	NS	NS
Leaves	84 (4.24)	84 (6.36)	84 (2.83)	46 (4.95)	46 (5.66)	46 (0.75)	81 (9.09)	81 (7.78)	81 (2.83)	250 (7.78)	250 (3.54)	250 (10.61)
Flower	239 (12.73)	239 (18.38)	239 (0.71)	20 (0.72)	20 (3.45)	20 (3.54)	275 (7.09)	275 (7.89)	275 (2.31)	NF	NF	NF

( ) Standard Deviation
C Control
W Wetland Influent
T Tolerance Concentration
NS No Stem
NF No Flower

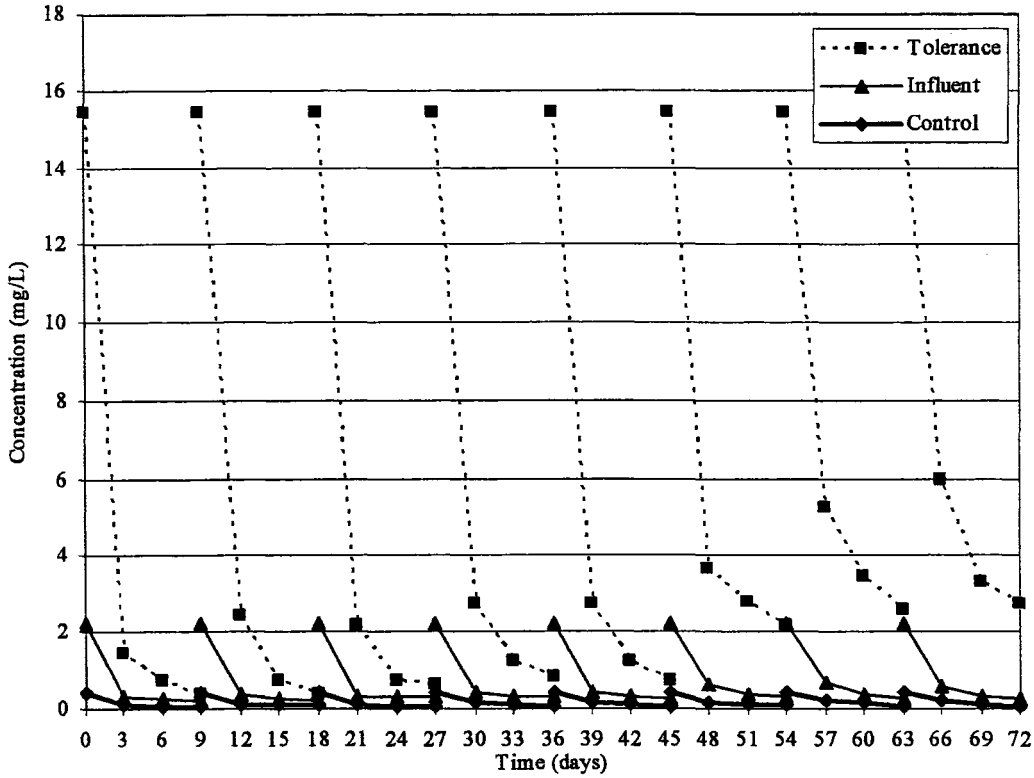


Figure 6.15. Manganese concentration in the wastewater of the soft stem bulrush compartments.

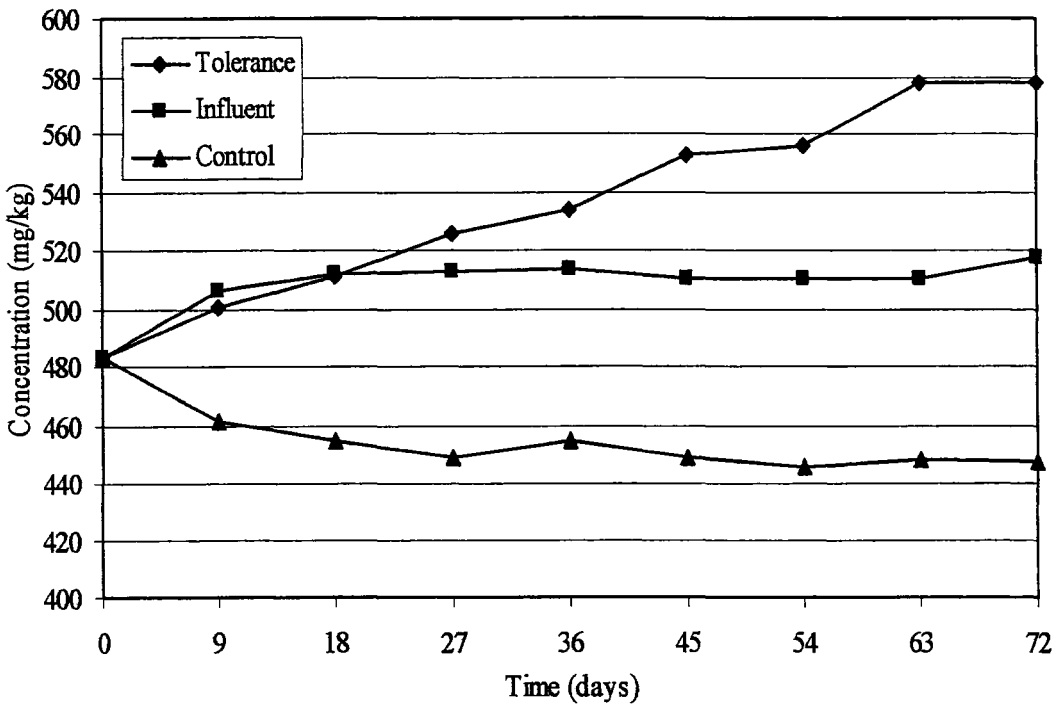


Figure 6.16. Manganese concentration in soil of the soft stem bulrush compartments.

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The concentrations of manganese in plant tissues of soft stem bulrush are shown in Figure 6.17. The initial concentrations of manganese in the roots, leaves and flowers of the plants were 62 mg/kg, 84 mg/kg and 239 mg/kg which increased by the end of the experiment (72 days) to 140, 148 and 156 mg/kg, to 150, 210 and 268 mg/kg, and to 419, 599 and 788 mg/kg in the compartments receiving the control, wetland influent and tolerance concentration, respectively.

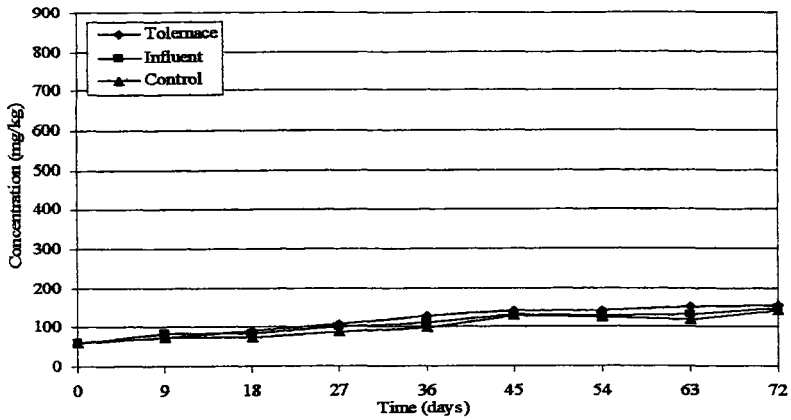
6.6.2.2 Wool Grass

The manganese concentrations in the wastewater of the wool grass compartments are shown in Figure 6.18. The concentration of manganese in the wastewater decreased by the end of the 9-day retention period to 0.10-0.16, 0.10–0.18 and 0.91-1.55 mg/L given an overall removal efficiency of 12-76, 92-95 and 89-94 % for the control, wetland influent and tolerance concentration, respectively.

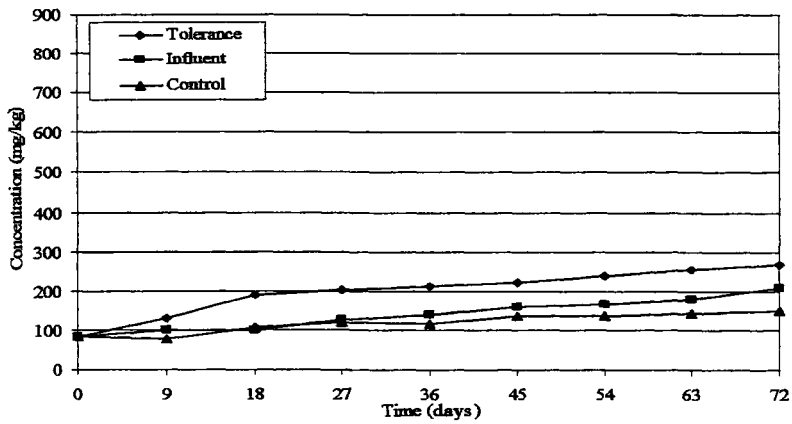
The manganese concentrations in soil of the wool grass compartments are shown in Figure 6.19. The initial concentration of manganese in the soil was 493 mg/kg which decreased to 481 mg/kg by the end of the experiment (72 days) in the compartment receiving the control, indicating removal of manganese from the soil at an average rate of 0.17 mg/kg/day. The concentrations of manganese in soils of the compartments that received the wetland influent and tolerance concentration increased from 493 mg/kg to 645 and 1627 mg/kg by the end of the experiment indicating addition of manganese (from wastewater) to soil by precipitation at average rates of 2.11 and 15.75 mg/kg/day, respectively.

Figure 6.20 shows the concentrations of manganese in plant tissues of wool grass. The initial concentrations of manganese in the roots, stems, leaves and flowers of the plants were 39 mg/kg, 28 mg/kg, 46 mg/kg and 20 mg/kg which increased by the end of the experiment (72 days) to 63, 81 and 90 mg/kg, to 103, 196 and 289 mg/kg, to 148, 170 and 191 mg/kg, and 56, 204 and 351 mg/kg in the compartments receiving the control, wetland influent and tolerance concentration, respectively.

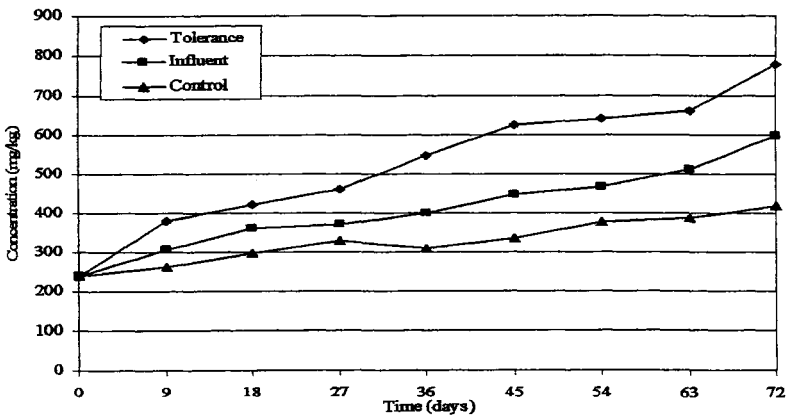
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(a) Roots



(b) Leaves



(c) Flowers

Figure 6.17. Manganese concentrations in the various parts of the soft stem bulrush.

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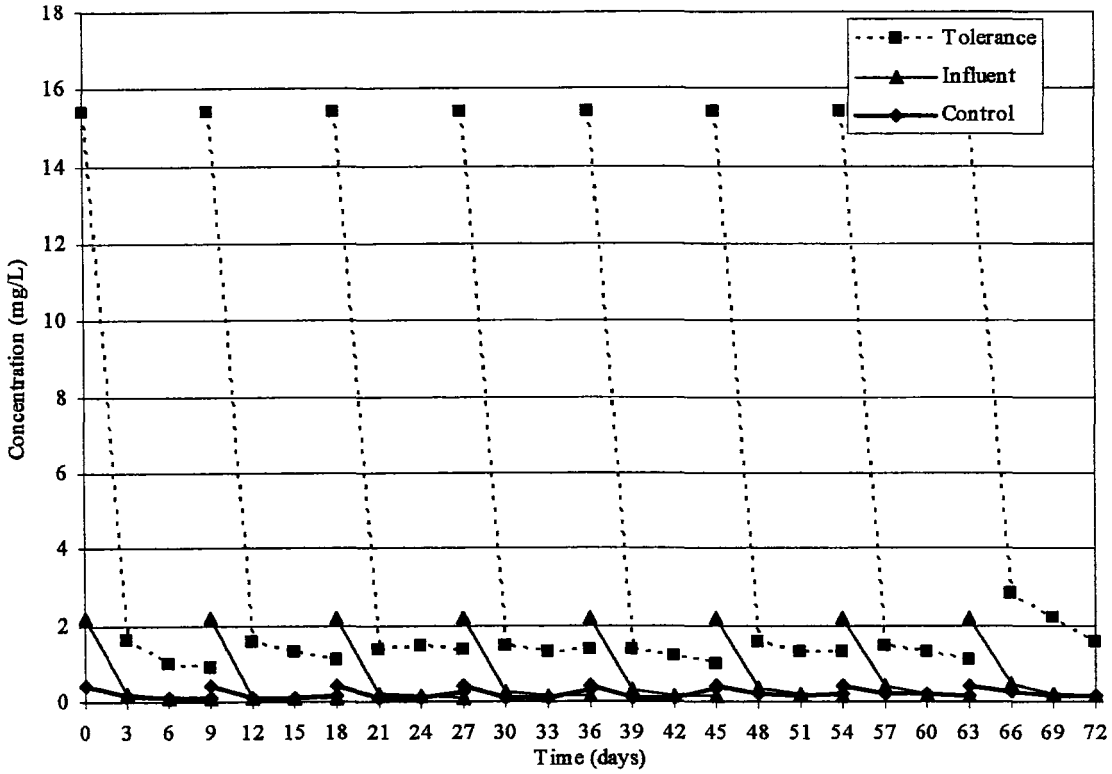


Figure 6.18. Manganese concentrations in the wastewater of the wool grass compartments.

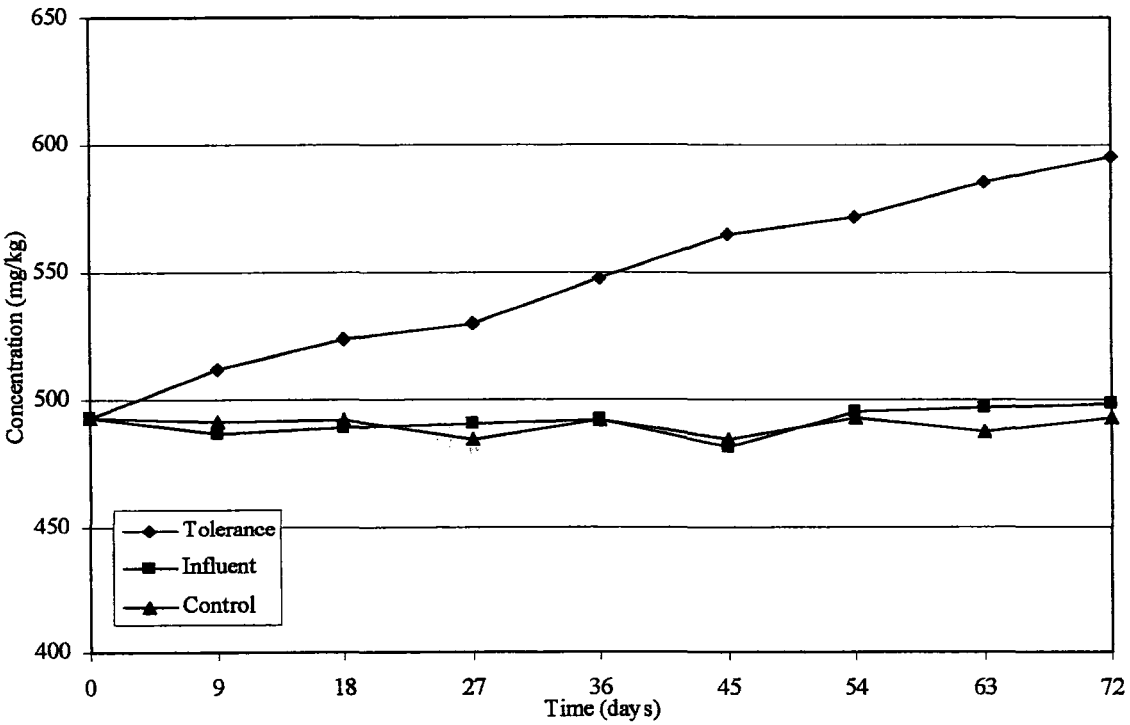
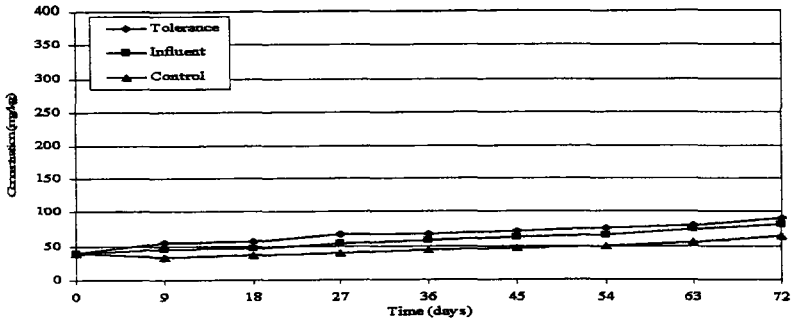
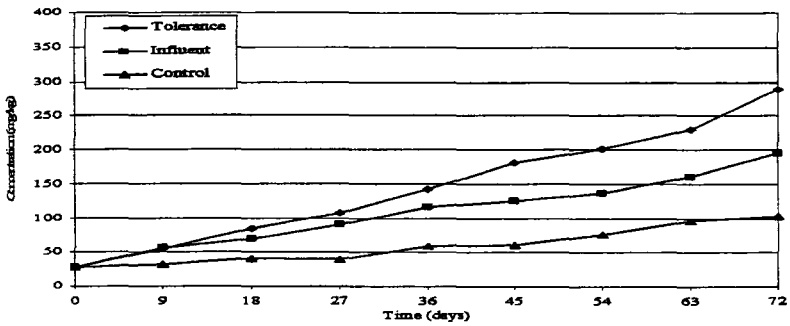


Figure 6.19. Manganese concentrations in the soil of the wool grass compartments.

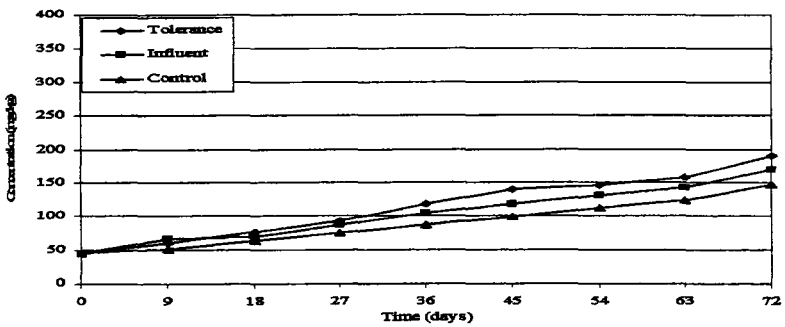
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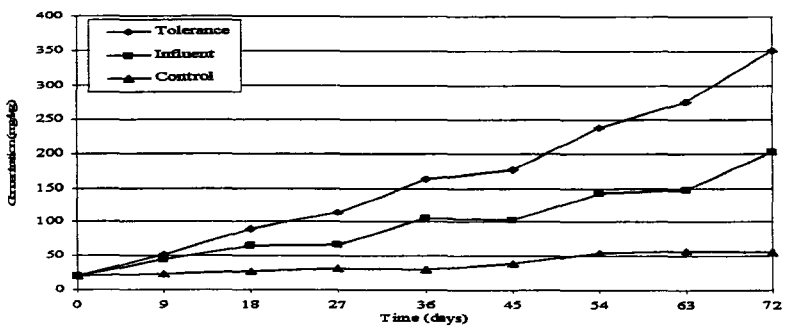
(a) Roots



(b) Stem



(c) Leaves



(d) Flowers

Figure 6.20. Manganese concentrations in the various parts of the wool grass.

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6.6.2.3 Soft Rush

The manganese concentrations in the wastewater of the soft rush compartments are shown in Figure 6.21. The manganese concentration in the wastewater decreased by the end of the 9-day retention period to 0.01-0.28, 0.07–0.21 and 0.23-0.73 mg/L given an overall removal efficiency of 32-98, 90-97 and 95-98 % for the control, wetland influent and tolerance concentration, respectively.

The manganese concentrations in the soil of the soft rush compartments are shown in Figure 6.22. The initial concentration of manganese in soil was 512 mg/kg which increased to 530, 635 and 1654 mg/kg in the compartments receiving the control, wetland influent and tolerance concentration by the end of the experiment (72 days), indicating addition of manganese (from wastewater) to the soil by precipitation at average rates of 0.25, 1.71 and 15.86 mg/kg/day, respectively.

The concentrations of manganese in plant tissues of soft rush are shown in Figure 6.23. The initial concentrations of manganese in the roots, leaves and flowers of the plants were 65 mg/kg, 81 mg/kg, and 275 mg/kg which increased by the end of the experiment (72 days) to 97, 157 and 217 mg/kg, to 171, 242 and 313 mg/kg, and to 421, 446 and 471 mg/kg in the compartments receiving the control, wetland influent and tolerance concentration, respectively.

6.6.2.4 Cattail

The manganese concentrations in the wastewater of the cattail compartments are shown in Figure 6.24. The manganese concentration in the wastewater decreased by the end of the 9-day retention period to 0.1-0.13, 0.13–0.35 and 0.24-0.64 mg/L for the control, wetland influent and tolerance concentration, given an overall removal efficiency of 67-76, 84-95 and 95-98 % for the control, wetland and maximum compartments, respectively.

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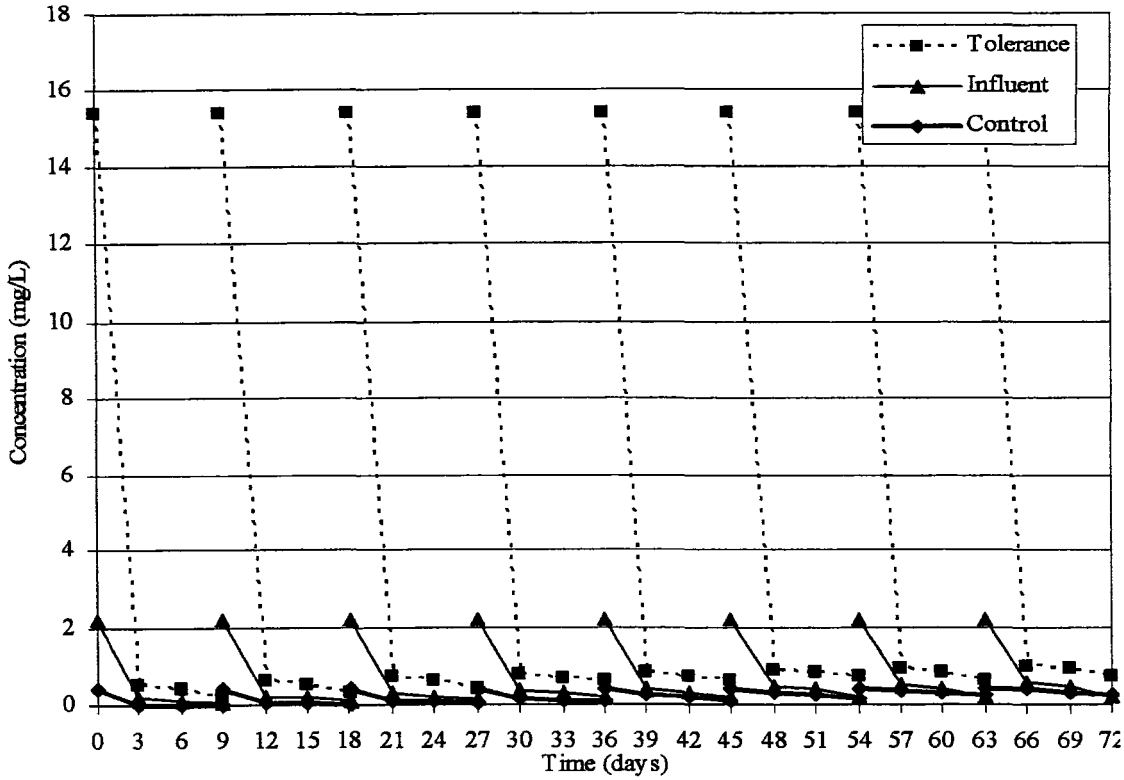


Figure 6.21. Manganese concentration in the wastewater of the soft rush compartments.

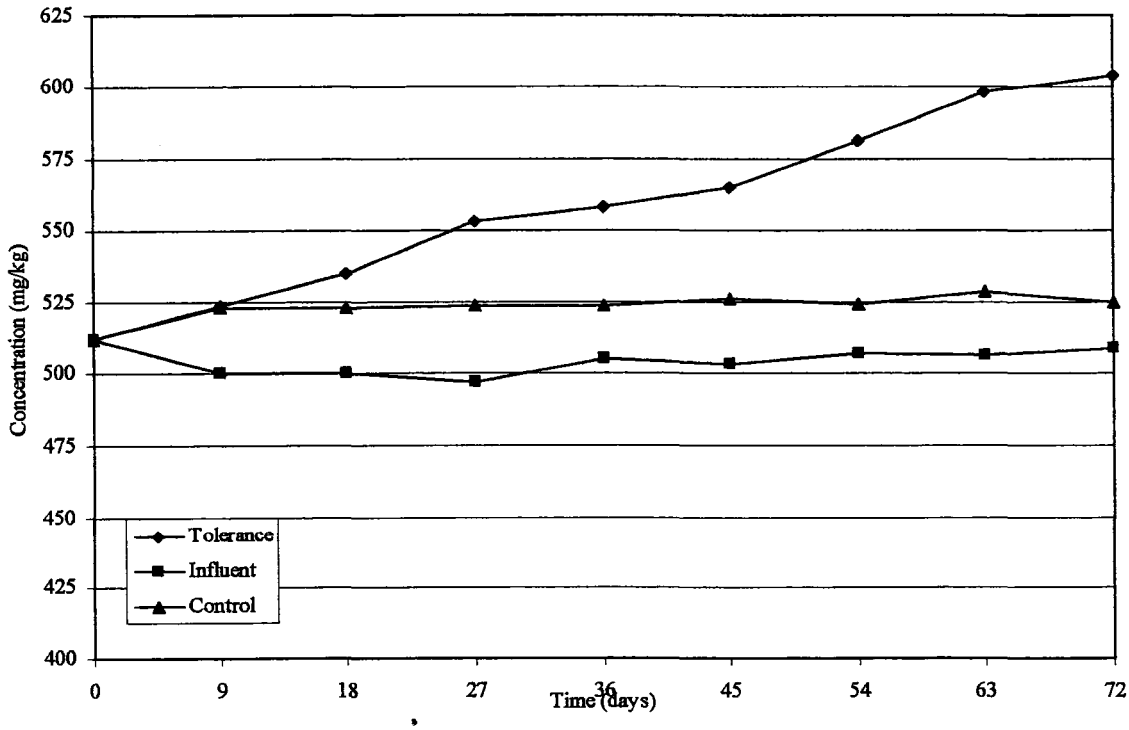
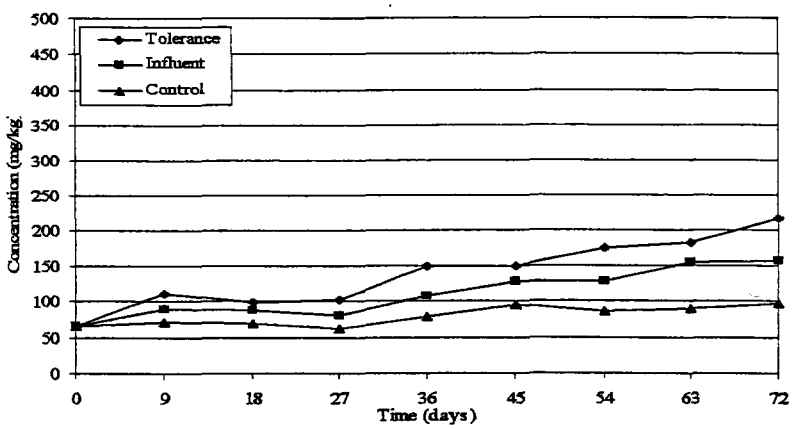
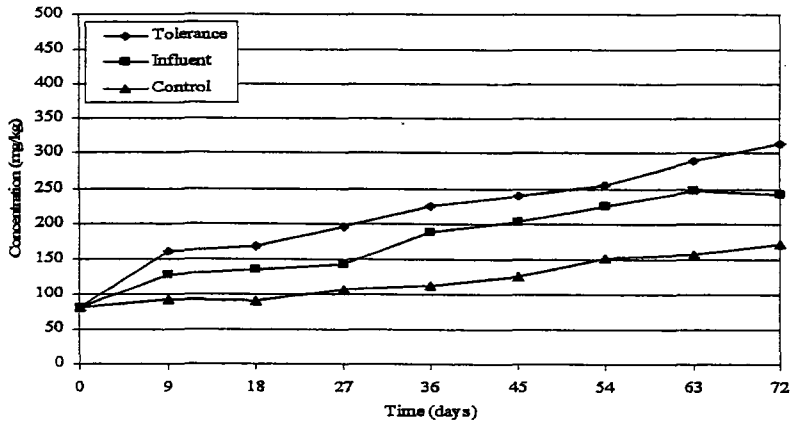


Figure 6.22. Manganese concentration in the soil of the soft rush compartments.

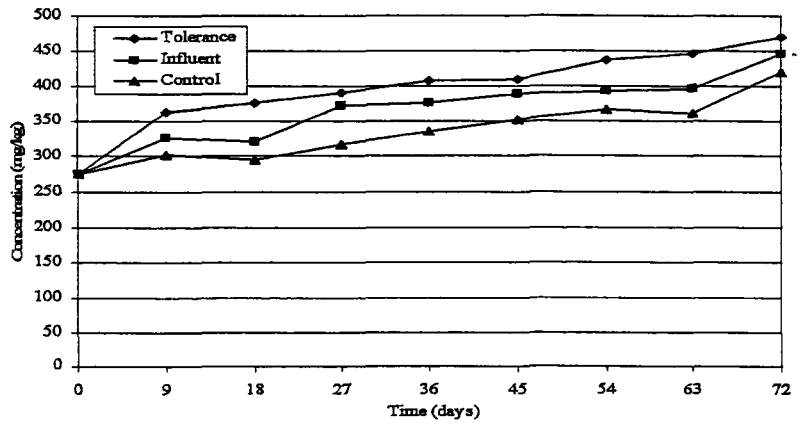
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(a) Roots



(b) Leaves



(c) Flowers

Figure 6.23. Manganese concentration in the various parts of the soft rush.

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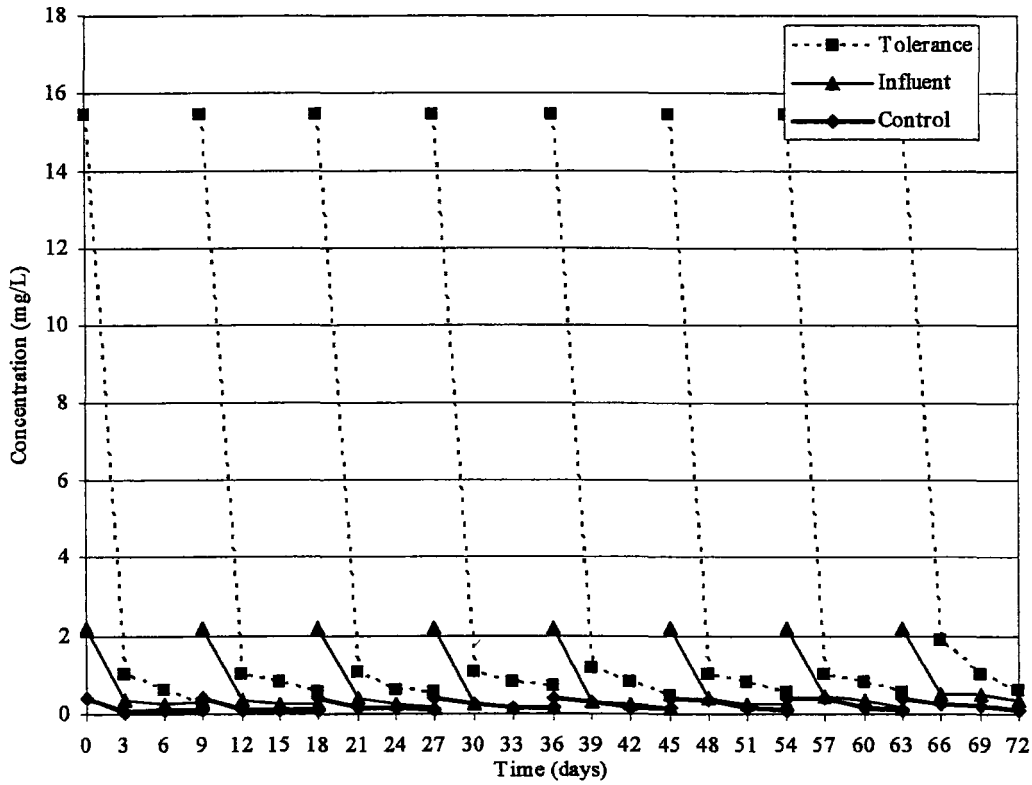


Figure 6.24. Manganese concentrations in the wastewater of the cattail compartments.

The manganese concentrations in the soil of the cattail compartments are shown in Figure 6.25. The initial concentration of manganese in the soil was 504 mg/kg which decreased to 476 mg/kg by the end of the experiment (72 days) in the compartment receiving the control, indicating removal of manganese from soil at an average rate of 0.36 mg/kg/day. The concentrations of manganese in the soil of the compartments that received wetland influent and tolerance concentrations increased from 502 mg/kg by the end of the experiment (72 days) to 586 and 1603 mg/kg indicating addition of manganese from the wastewater to soil by precipitation at an average rate of 1.17 and 15.29 mg/kg/day.

The concentration of manganese in plant tissues of cattail are shown in Figure 6.26. The initial concentration of manganese in the roots and leaves of the cattail plants were 24 mg/kg and 250 mg/kg which increased by the end of the experiment (72 days) to 34, 81 and 127 mg/kg and 730, 757 and 783 mg/kg in the compartments receiving the control, wetland influent and tolerance concentrations, respectively.

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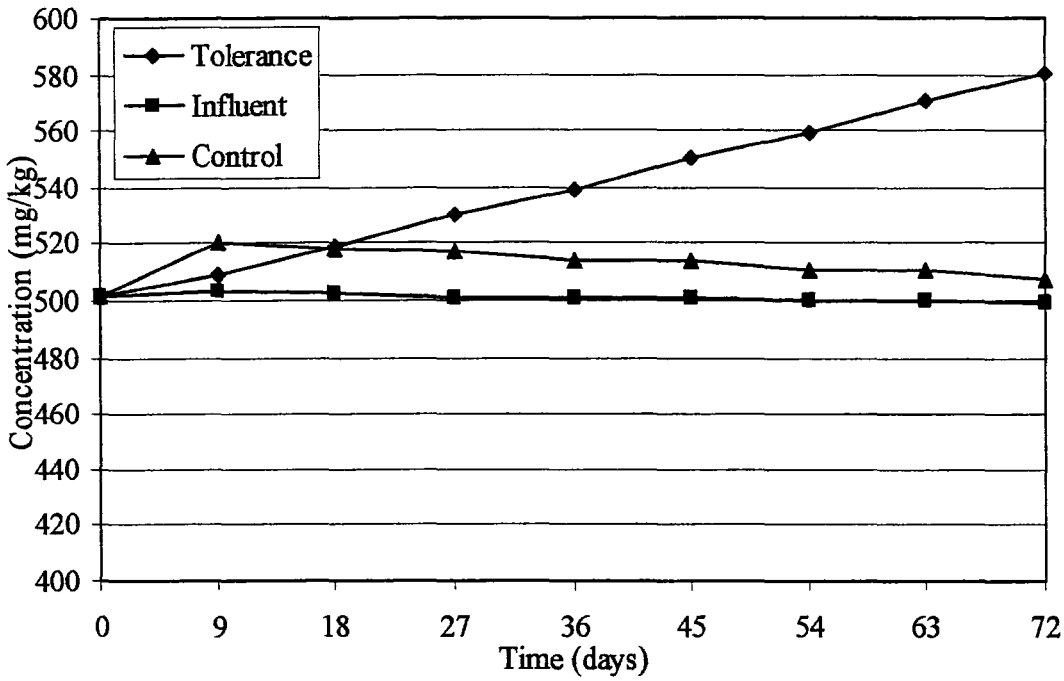


Figure 6.25. Manganese concentrations in the soil of the cattail compartments.

6.6.3 Zinc

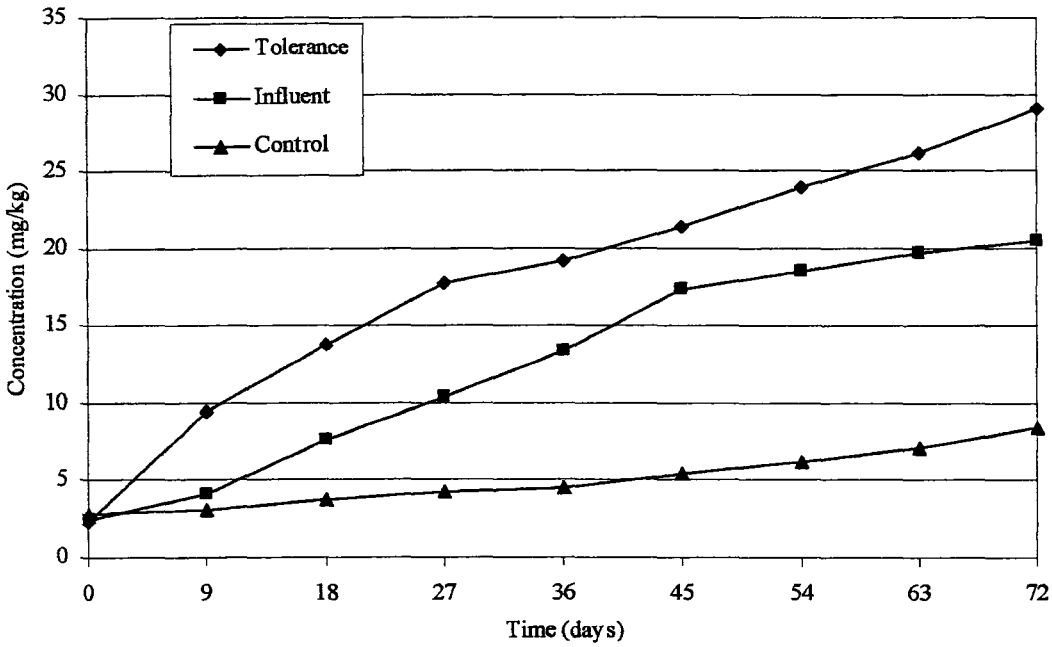
The initial concentrations of zinc in the wastewater, soil and plant tissues of the compartments receiving the control, wetland influent and tolerance concentration are shown in Table 6.6. The final concentration of zinc after the 9-day period and the removal rate depended on the initial concentrations and the type of plant used.

6.6.3.1 Soft Stem Bulrush

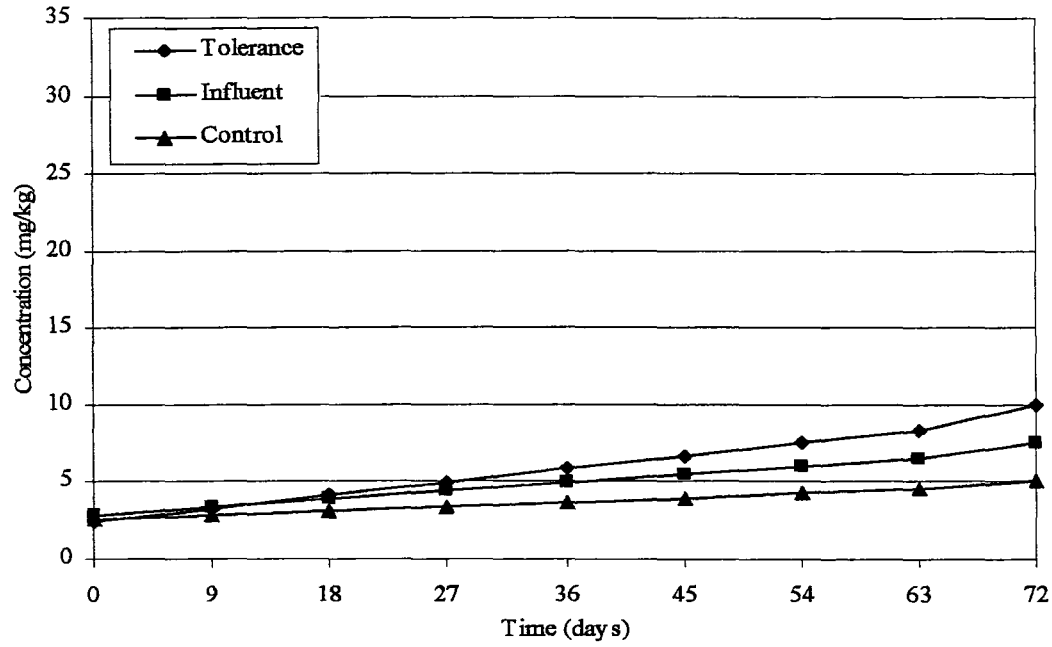
The zinc concentrations in the wastewater of soft stem bulrush compartment are shown in Figure 6.27. The zinc concentration in the wastewater decreased by the end of the 9-day retention period to 0.059-0.187, 0.128-0.257 and 0.130-0.267 mg/L given an overall removal efficiency of 54-86, 46-73 and 66-84 % for control, wetland influent and tolerance concentration, respectively.

The zinc concentrations in the soil of the soft stem bulrush compartment are shown in Figure 6.28. The initial concentration of zinc in the soil was 97 mg/kg which increased by

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(a) Roots



(b) Leaves

Figure 6.26. Manganese concentrations in the various parts of cattail.

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Table 6.6. Initial concentrations of zinc in the water, soil and plant tissues.

Source	Soft stem bulrush			Wool grass			Soft rush			Cattail		
	C	W	T	C	W	T	C	W	T	C	W	T
Water (mg/L)	0.41	0.48	0.79	0.41	0.48	0.79	0.41	0.48	0.79	0.41	0.48	0.79
Soil (mg/kg)	97 (0.71)	97 (3.54)	97 (3.45)	106 (2.12)	106 (1.41)	106 (0.72)	103 (0.40)	103 (1.41)	103 (0.71)	104 (3.53)	104 (3.53)	104 (0.20)
Plant Tissues (mg/kg)												
Roots	19 (1.41)	19 (0.72)	19 (0.73)	3.8 (0.26)	3.8 (0.69)	3.8 (0.94)	5.7 (0.01)	5.7 (0.13)	5.7 (0.50)	2.6 (0.23)	2.6 (0.05)	2.6 (0.19)
Stem	NS	NS	NS	2.2 (0.62)	2.2 (0.12)	2.2 (0.09)	NS	NS	NS	NS	NS	NS
Leaves	1.2 (0.12)	1.2 (0.02)	1.2 (0.09)	2.9 (0.14)	2.9 (0.12)	2.9 (0.02)	7.2 (1.34)	7.2 (0.42)	7.2 (0.92)	2.6 (0.02)	2.6 (0.19)	2.6 (0.16)
Flower	24 (2.12)	24 (0.21)	24 (2.16)	10.7 (0.37)	10.7 (1.25)	10.7 (1.22)	23.7 (1.65)	23.7 (1.89)	23.7 (0.23)	NF	NF	NF

( ) Standard Deviation
C Control
W Wetland Influent
T Tolerance Concentration
NS No Stem
NF No Flower

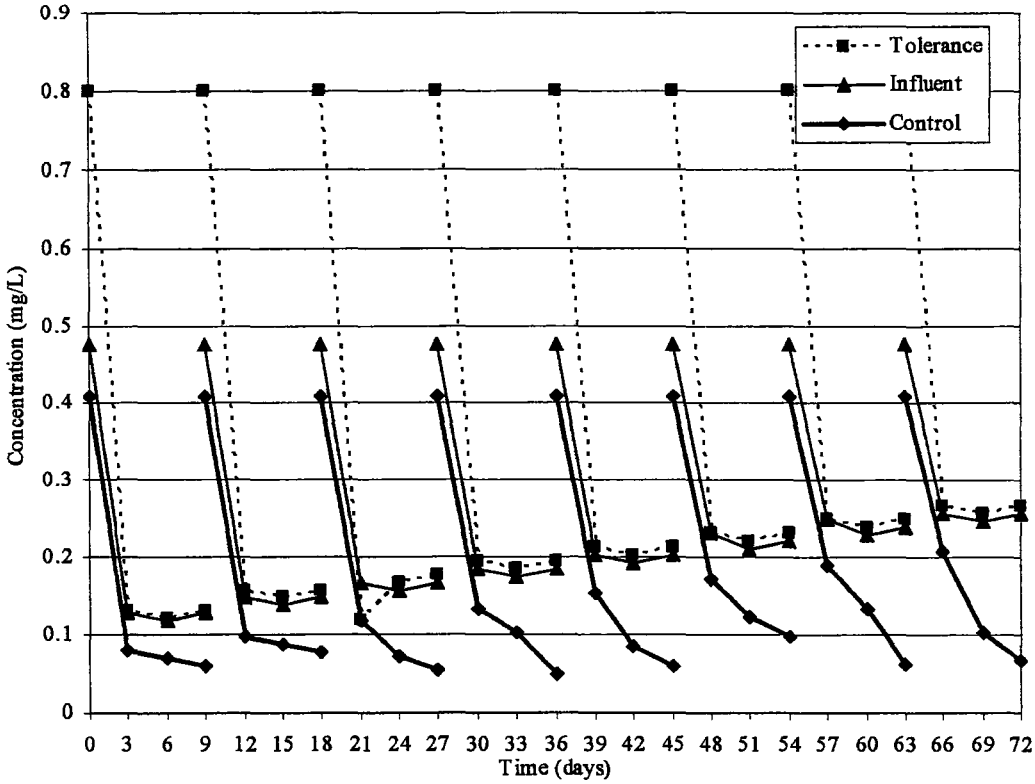


Figure 6.27. Zinc concentration in the wastewater of the soft stem bulrush compartments.

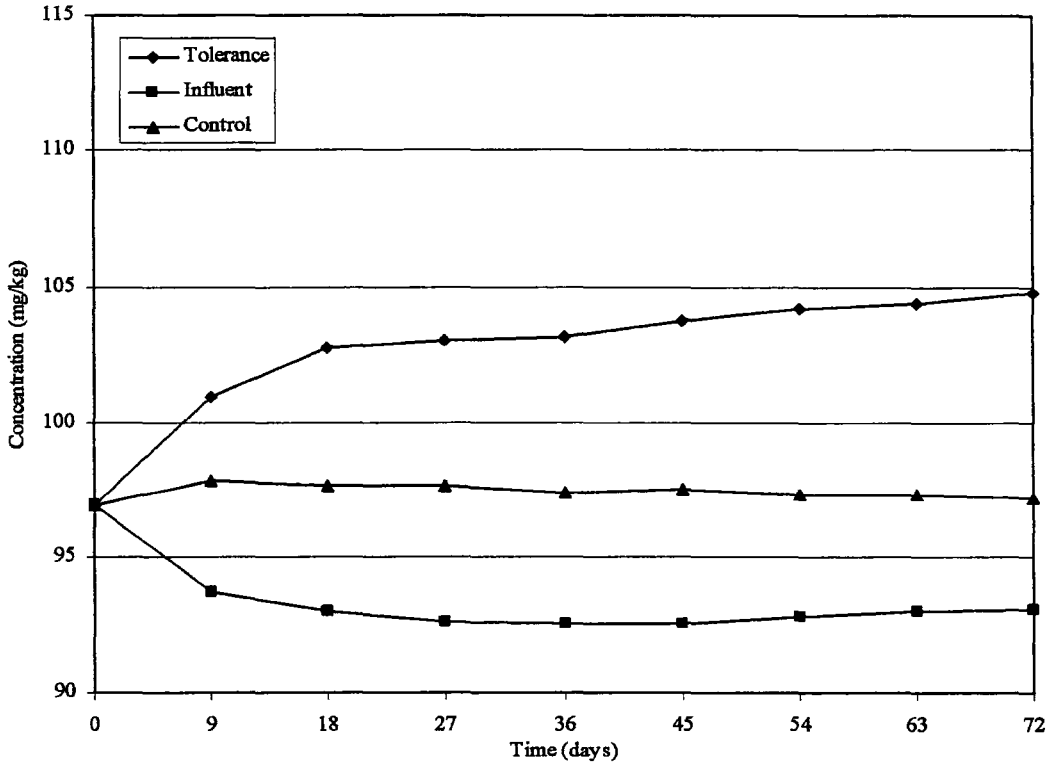


Figure 6.28. The zinc concentration in the soil of the soft stem bulrush compartments.

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the end of the experiment (72 days) to 124, 111 and 144 mg/kg in the compartments that received the control, wetland influent and tolerance concentration, indicating addition of zinc (from wastewater) to the soil by precipitation at an average rate of 0.38, 0.19 and 0.65 mg/kg/day, respectively.

The concentrations of zinc in plant tissues of soft stem bulrush are shown in Figure 6.29. The initial concentrations of zinc in the roots, leaves and flowers of the plants were 19 mg/kg, 1.2 mg/kg and 24 mg/kg which increased by the end of the experiment (72 days) to 27, 36 and 45 mg/kg, to 4, 6 and 9 mg/kg, and to 55, 110 and 167 mg/kg in the compartments receiving the control, wetland influent and tolerance concentration, respectively.

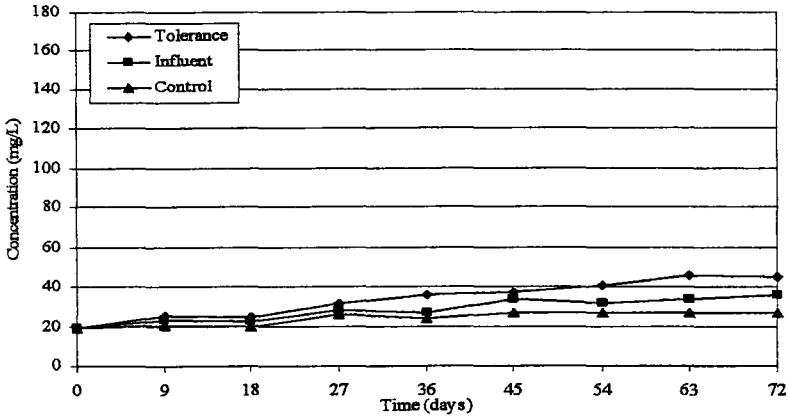
6.6.3.2 Wool Grass

The zinc concentrations in the wastewater of the wool grass compartments are shown in Figure 6.30. The concentration of zinc in the wastewater decreased by the end of the 9-day retention period to 0.015-0.133, 0.086-0.217 and 0.158-0.307 mg/L given an overall removal efficiency of 65-96, 57-82 and 62-80 % for the control, wetland influent and tolerance concentration, respectively.

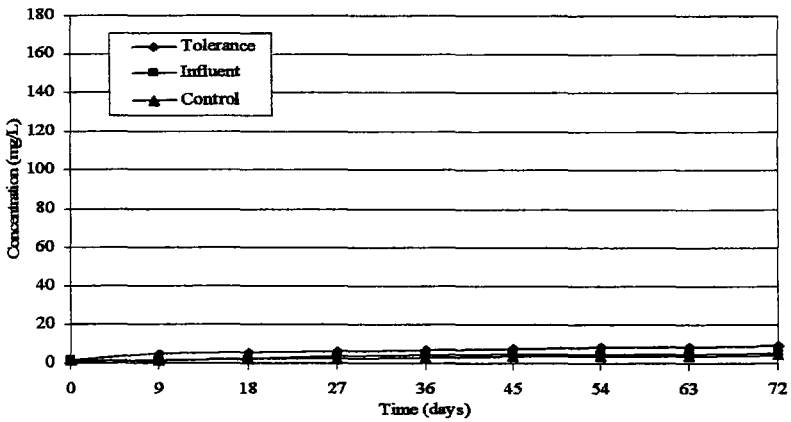
The zinc concentrations in the soil of the wool grass compartments are shown in Figure 6.31. The initial concentration of zinc in the soil was 106 mg/kg which increased by the end of the experiment (72 days) to 132, 135 and 153 mg/kg in the compartments that received the control, wetland influent and tolerance concentration indicating addition of zinc (from wastewater) to the soil by precipitation at an average rate of 0.361, 0.403 and 0.652 mg/kg/day, respectively.

Figure 6.32 shows the concentrations of zinc in plant tissues of wool grass. The initial concentrations of zinc in the roots, stems, leaves and flowers of the plants were 3.8 mg/kg, 2.2 mg/kg, 2.9 mg/kg and 10.7 mg/kg which increased by the end of the experiment (72 days) to 10.1, 12.0 and 13.0 mg/kg, to 5.0, 5.5 and 6.0 mg/kg, to 8.0, 11.5 and 15.0 mg/kg, and to 26.9, 44.0 and 66.0 mg/kg in the compartments receiving the control, wetland influent and tolerance concentration, respectively.

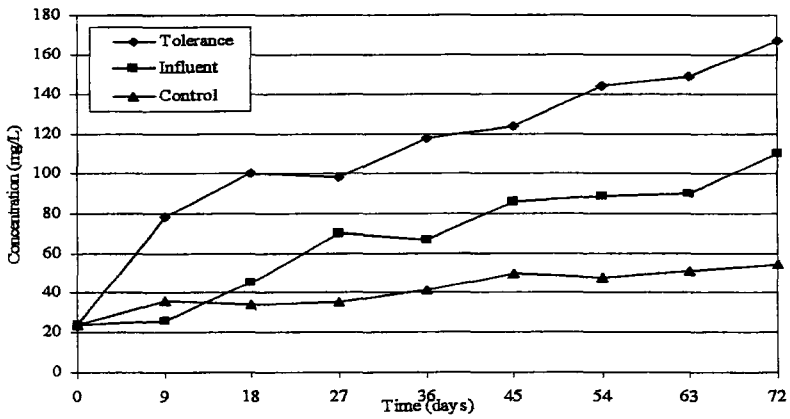
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(a) Roots



(b) Leaves



(c) Flowers

Figure 6.29. Zinc concentration in the various parts of the soft stem bulrush.

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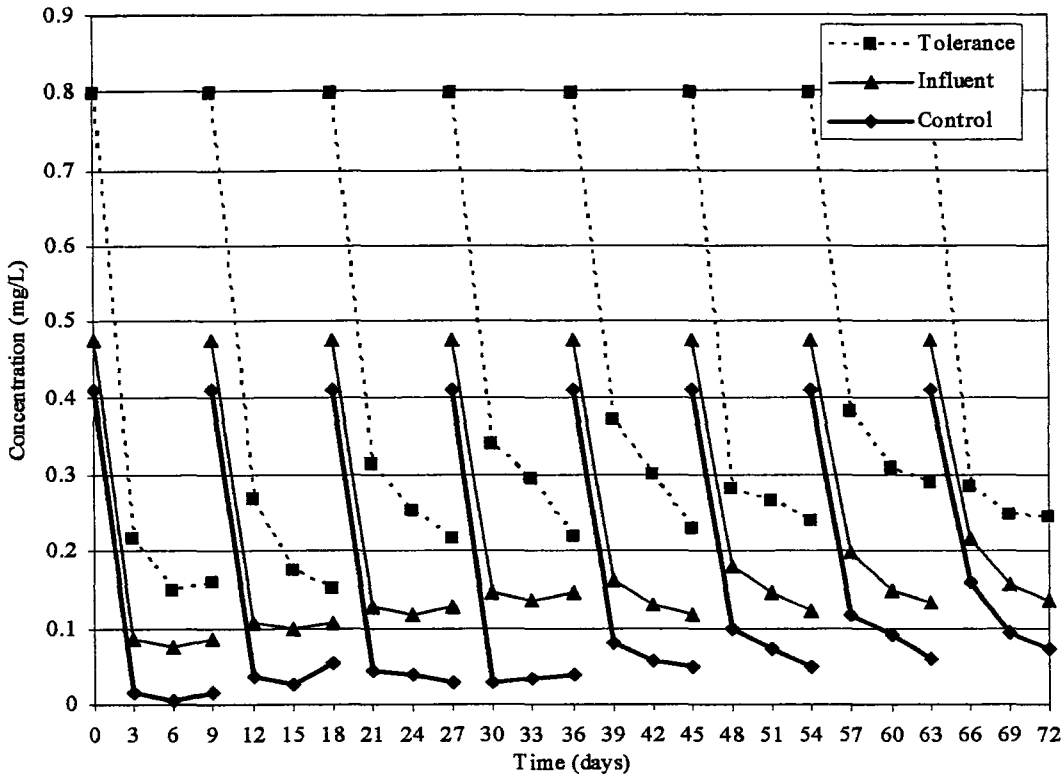


Figure 6.30. Zinc concentrations in the wastewater of the wool grass compartments.

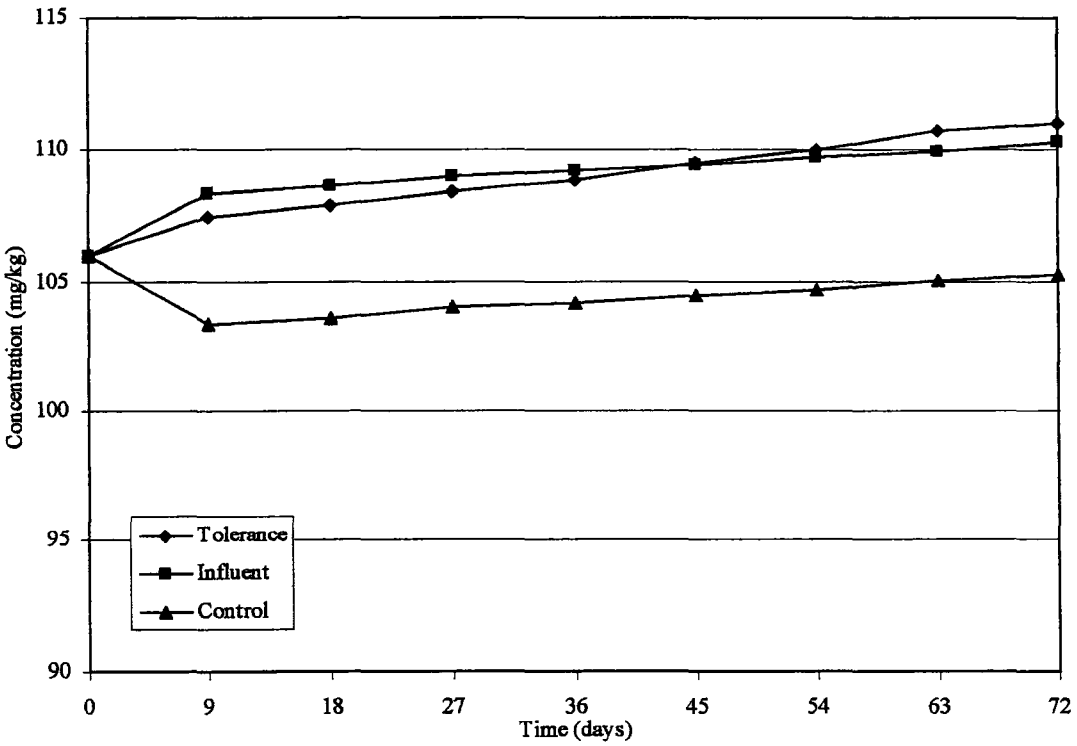
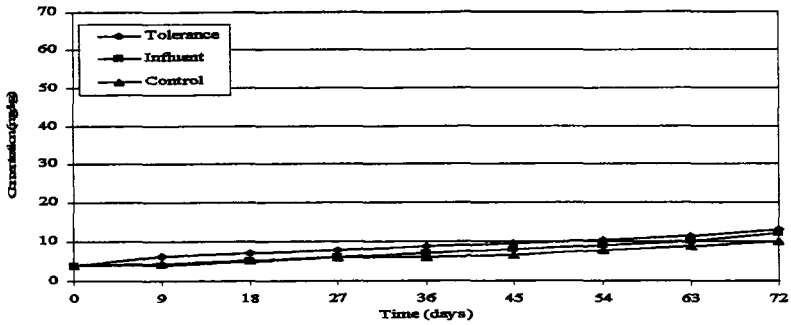
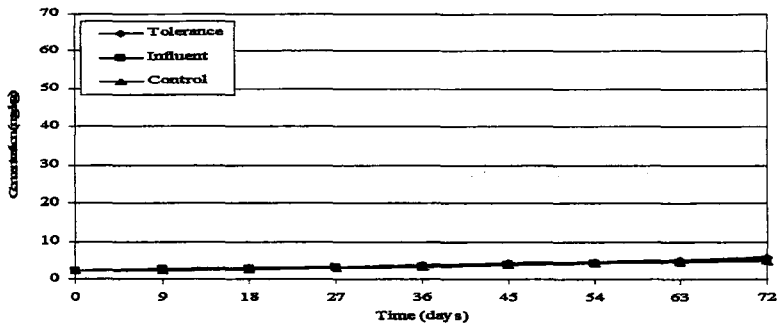


Figure 5.31. Zinc concentrations in the soil of the wool grass compartments.

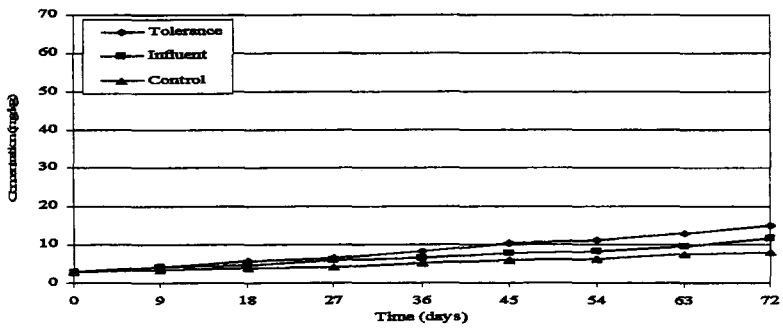
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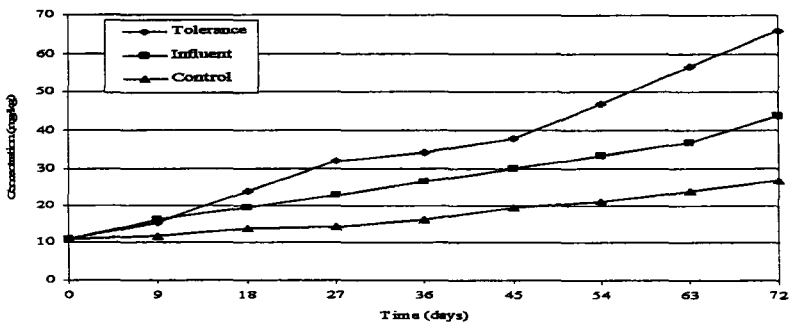
(a) Roots



(b) Stem



(c) Leaves



(d) Flowers

Figure 6.32. Zinc concentrations in the various parts of the wool grass.

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6.6.3.3 Soft rush

The zinc concentrations in the wastewater of the soft rush compartments are shown in Figure 6.33. The zinc concentration in the wastewater decreased by the end of the 9-day retention period to 0.005-0.127, 0.037-0.157 and 0.055-0.157 mg/L given an overall removal efficiency of 68-99, 67-92 and 80-93 % for the control, wetland influent and tolerance concentration, respectively.

The zinc concentrations in the soil of the soft rush compartments are shown in Figure 6.34. The initial concentration of zinc in the soil was 103 mg/kg which increased by the end of the experiment (72 days) to 128, 128 and 155 mg/kg in the compartments that received the control, wetland influent and tolerance concentration, indicating addition of zinc (from wastewater) to the soil by precipitation at an average rate of 0.347, 0.347 and 0.722 mg/kg/day, respectively.

The concentrations of zinc in the plant tissues of soft rush are shown in Figure 6.35. The initial concentrations of zinc in the roots, leaves and flowers of the plants were 5.7 mg/kg, 7.2 mg/kg, and 23.7 mg/kg which increased by the end of the experiment (72 days) to 11.0, 14.5 and 18 mg/ kg, to 18.0, 23.5 and 29.0 mg/kg, and to 49, 64 and 79 mg/kg in the compartments receiving the control, wetland influent and tolerance concentration, respectively.

6.6.3.4 Cattail

The zinc concentrations in the wastewater of the cattail compartments are shown in Figure 6.36. The zinc concentration in the wastewater decreased by the end of the 9-day retention period to 0.046-0.187, 0.231-0.367 and 0.270-0.427 mg/L for the control, wetland influent and tolerance concentration, given an overall removal efficiency of 54-89, 23-51 and 47-66 % for the control, wetland and maximum compartments, respectively.

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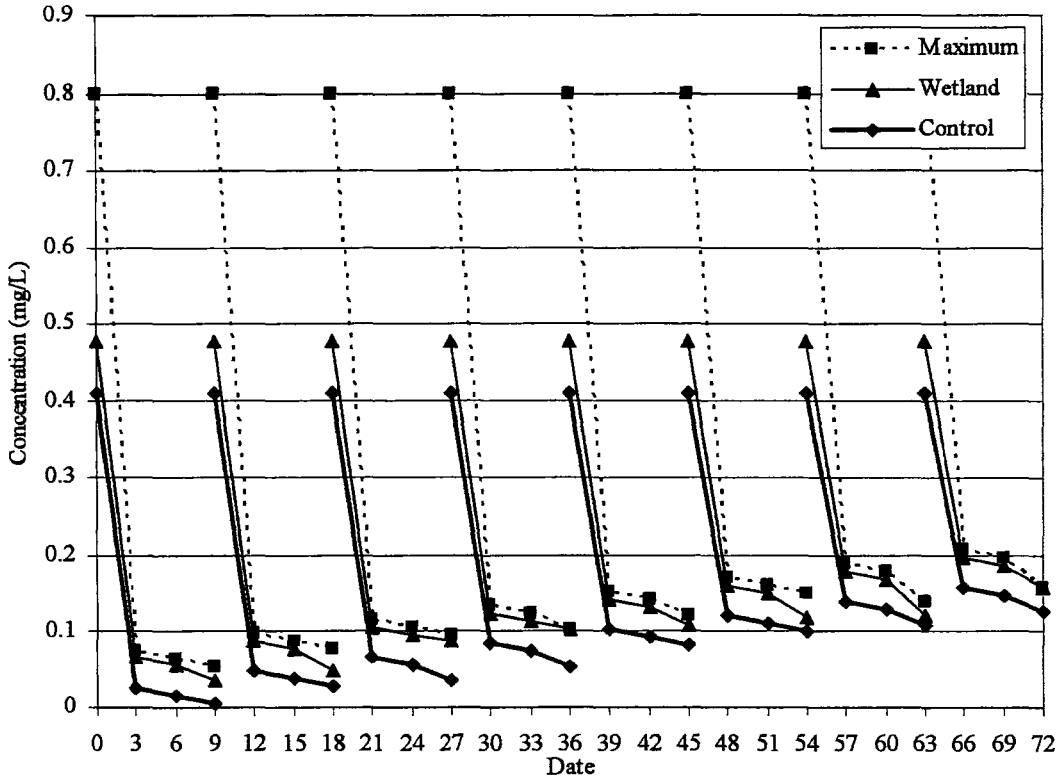


Figure 6.33. Zinc concentrations in the wastewater of the soft rush compartments.

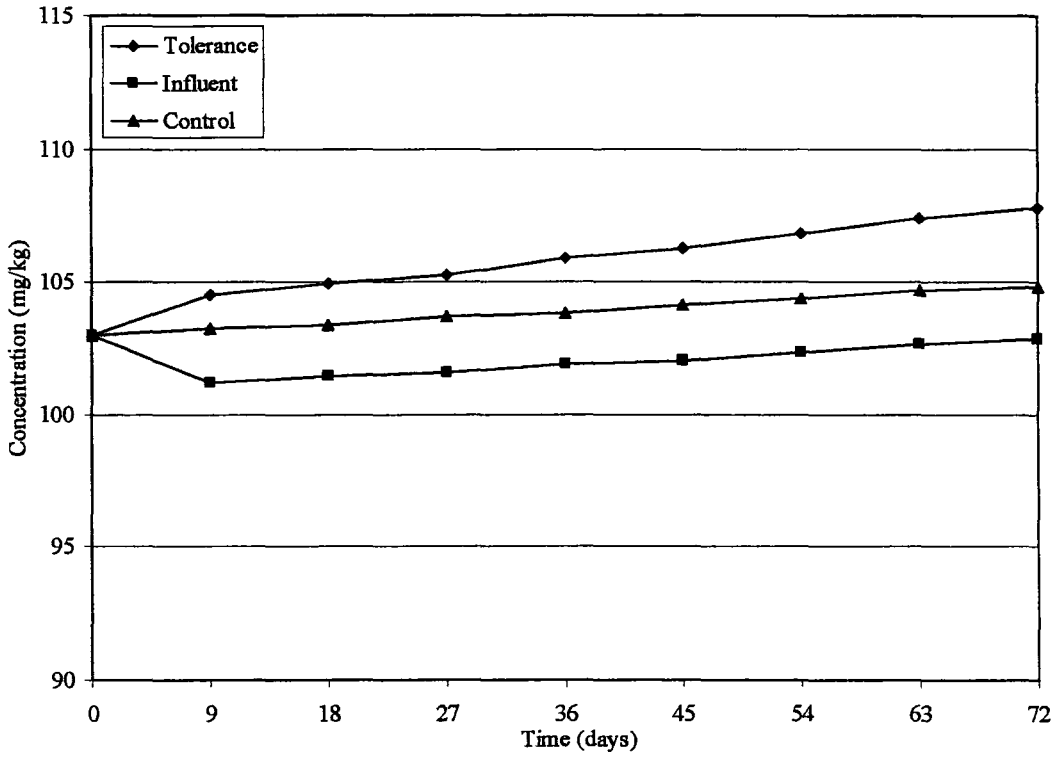
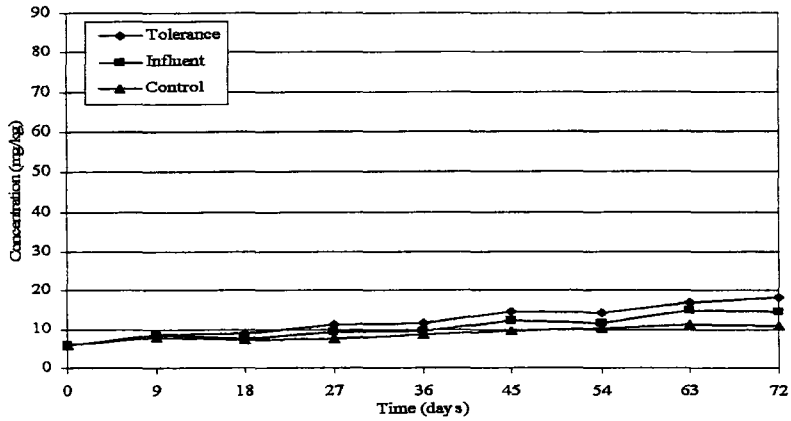
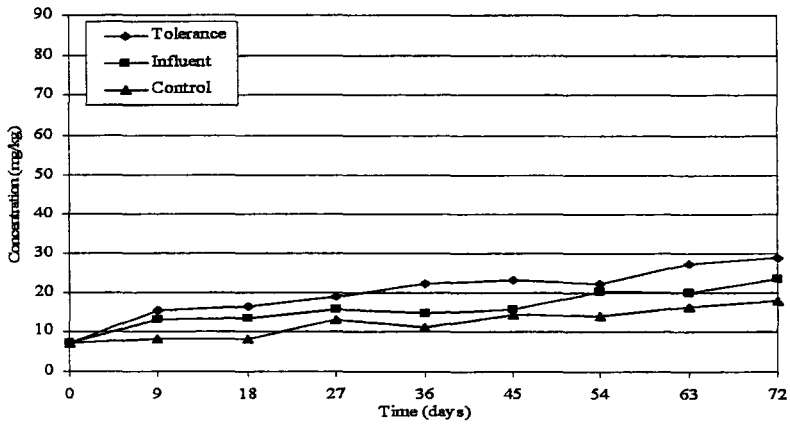


Figure 6.34. Zinc concentrations in the soil of the soft rush compartments.

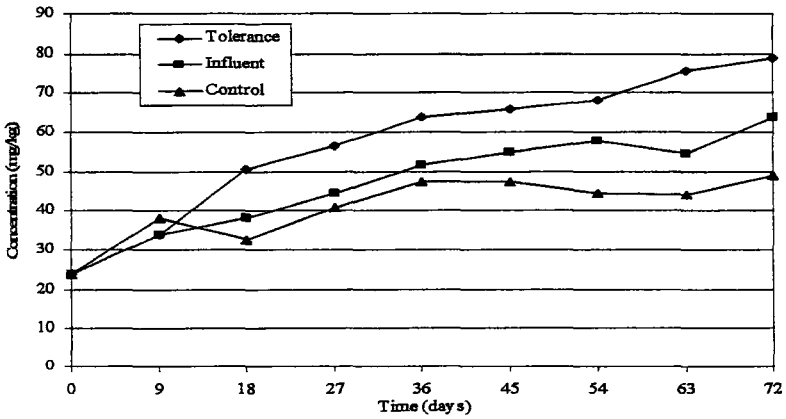
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(a) Roots



(b) Leaves



(c) Flowers

Figure 6.35. Zinc concentrations in the various parts of the soft rush.

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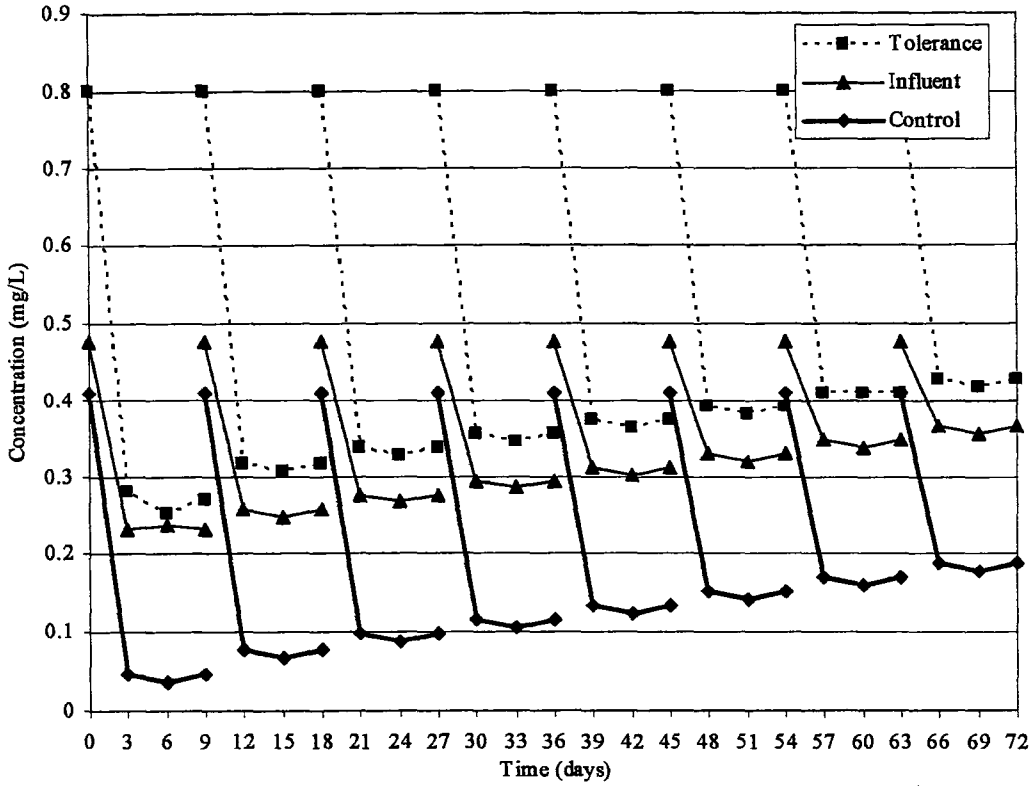


Figure 6.36. Zinc concentration in the wastewater of the cattail compartments.

The zinc concentrations in the soil of the cattail compartments are shown in Figure 6.37. The initial concentration of zinc in the soil was 104 mg/kg which increased by the end of the experiment to 130, 109 and 134 mg/kg, indicating addition of zinc (from wastewater) to the soil by precipitation at an average rate of 0.361, 0.069 and 0.417 mg/kg/day in the compartments that received the control, wetland influent and tolerance concentration, respectively.

Figure 6.38 shows the concentrations of zinc in plant tissues of soft rush. The initial concentrations of zinc in the roots and leaves of the cattail plants were 2.5 mg/kg and 2.6 mg/kg which increased by the end of the experiment to 8.4, 20.5 and 29.0 mg/kg and 5.0, 7.5 and 10.0 mg/kg in the compartments receiving the control, wetland influent and tolerance concentration, respectively.

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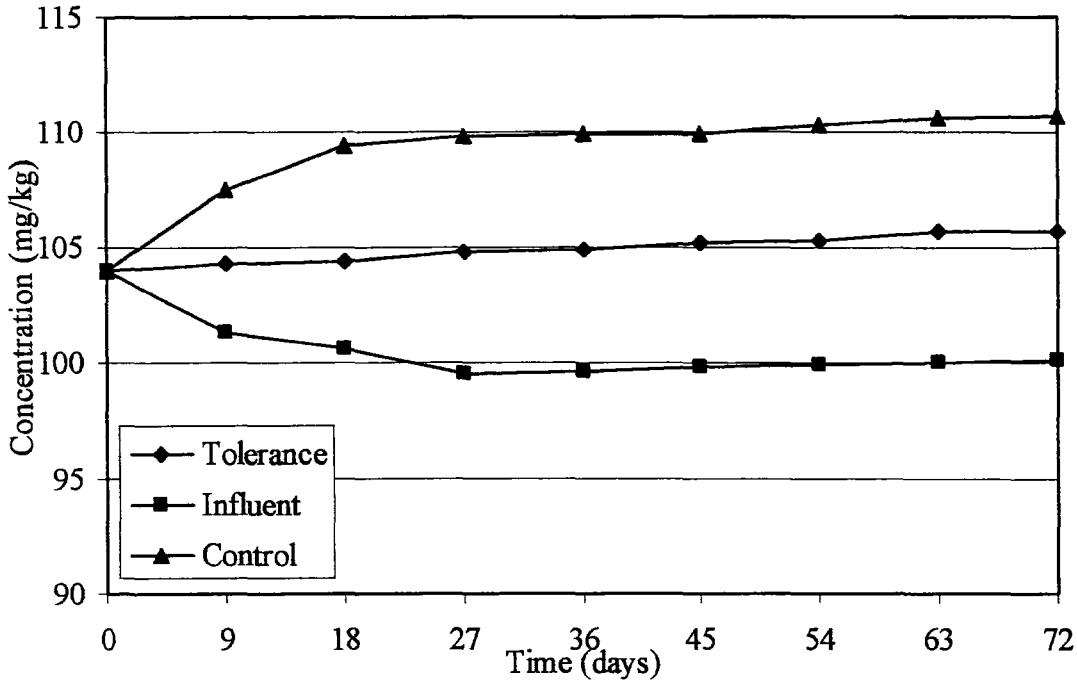


Figure 6.37. Zinc concentration in the soil in the cattail compartments.

6.7 Discussion

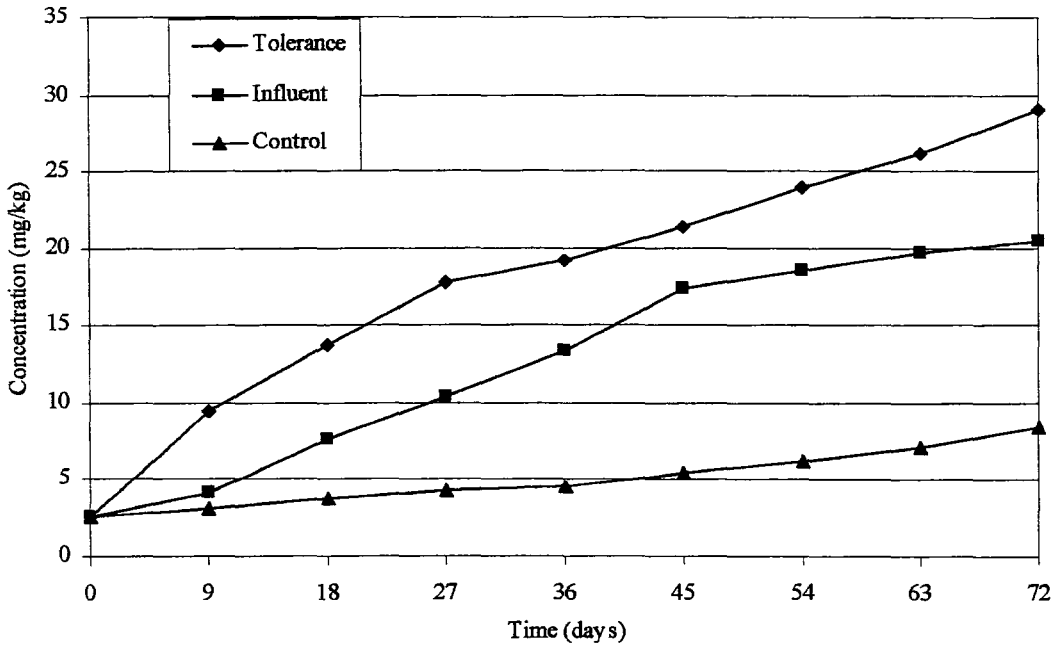
6.7.1 Iron

6.7.1.1 Overall Iron Removal Efficiency

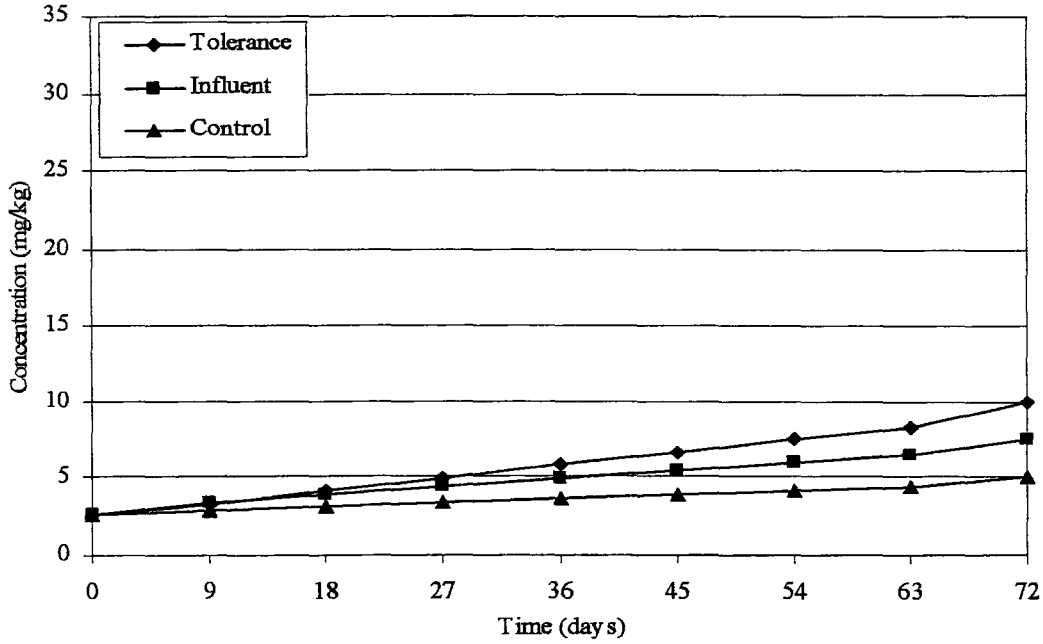
The concentrations of iron in the various compartments at the end of each period are shown in Table 6.7. The removal efficiencies for the various compartment of the system are shown in Table 6.8. The overall iron removal efficiency of the system is the sum removal of iron from the system by the chemical and/or biological precipitation and plant uptake.

Analysis of variance (ANOVA) was performed on the removal efficiency data using SAS System, 5th Ed. (SAS Institute Inc., Cary, North Carolina). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA results (Table 6.9) showed that the plant type, time and iron concentration have significant effects on the removal efficiency ($P = 0.0001$). The results also showed

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(a) Roots



(b) Leaves

Figure 6.38. Zinc concentration in the various parts of the cattail.

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Table 6.7. Iron concentration in the wastewater.

Time	Tolerance concentration				Wetland Influent				Control			
	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail
9	1.81 (0.13)	4.00 (0.26)	1.26 (0.09)	1.26 (0.08)	1.09 (0.08)	0.86 (0.06)	0.19 (0.01)	0.86 (0.06)	0.05 (0.003)	0.35 (0.025)	0.10 (0.006)	0.54 (0.035)
18	2.90 (0.17)	5.40 (0.29)	1.53 (0.09)	1.59 (0.09)	1.18 (0.07)	1.13 (0.07)	0.40 (0.020	1.10 (0.06)	0.09 (0.005)	0.44 (0.026)	0.10 (0.005)	0.32 (0.017)
27	1.55 (0.10)	2.70 (0.16)	1.60 (0.10)	1.77 (0.10)	1.20 (0.08)	1.31 (0.08)	0.50 (0.03)	1.28 (0.08)	0.07 (0.004)	0.41 (0.027)	0.12 (0.007)	0.39 (0.023)
36	2.50 (0.13)	7.70 (0.36)	1.70 (0.09)	1.95 (0.09)	1.20 (0.06)	1.49 (0.08)	0.70 (0.04)	1.46 (0.07)	0.08 (0.004)	0.44 (0.022)	0.23 (0.011)	0.39 (0.018)
45	6.60 (0.39)	12.70 (0.75)	2.00 (0.12)	2.13 (0.13)	1.50 (0.09)	1.67 (0.10)	1.00 (0.06)	1.64 (0.10)	0.08 (0.005)	0.48 (0.028)	0.10 (0.006)	0.23 (0.014)
54	4.00 (0.20)	13.10 (0.71)	2.15 (0.11)	2.31 (0.13)	1.60 (0.08)	1.85 (0.09)	1.13 (0.06)	1.82 (0.10)	0.07 (0.004)	0.46 (0.023)	0.14 (0.008)	0.30 (0.016)
63	8.00 (0.47)	14.50 (0.85)	2.20 (0.13)	2.49 (0.15)	2.00 (0.12)	2.03 (0.12)	1.20 (0.07)	2.00 (0.12)	0.08 (0.005)	0.56 (0.033)	0.18 (0.011)	0.36 (0.021)
72	10.80 (0.51)	25.80 (1.40)	2.50 (0.12)	2.66 (.014)	2.05 (0.10)	2.20 (0.12)	1.30 (0.06)	2.17 (0.12)	0.10 (0.005)	0.63 (0.030)	0.17 (0.009)	0.39 (0.021)

The values are the average of 3 replicates with a coefficient of variation in the range of 0.5-2.0%

Initial Tolerance Concentration = 101.12 mg/L

Initial Wetland Influent Concentration = 7.72 mg/L

Initial Control Concentration = 1.12 mg/L

( ) Standard deviation

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Table 6.8. Iron removal efficiencies.

Time	Tolerance concentration				Wetland Influent				Control			
	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail
9	98.20	96.04	98.75	98.75	85.87	88.85	97.53	88.85	95.52	68.66	91.04	51.65
18	97.13	94.65	98.48	98.42	84.70	85.35	94.81	85.74	91.94	60.60	91.04	71.35
27	98.46	97.32	98.41	98.24	84.44	83.02	93.52	83.41	93.73	62.93	89.25	65.08
36	97.52	92.38	98.31	98.07	84.44	80.69	90.92	81.08	92.83	60.60	79.40	65.08
45	93.47	87.44	98.02	97.89	80.56	78.35	87.04	78.74	92.83	57.02	91.04	79.40
54	96.04	87.04	97.87	97.71	79.26	76.02	85.35	76.41	93.73	58.81	87.46	73.14
63	92.08	85.66	97.82	97.53	74.08	73.69	84.44	74.08	92.83	49.86	83.88	67.77
72	89.31	74.48	97.52	97.36	73.43	71.49	83.15	71.88	91.04	43.59	84.78	65.08

Table 6.9. Analysis of variance of the iron removal efficiency.

Source	DF	SS	MS	F-Value	P
Total	191	34817.96	182.29		
Model	95	34571.08	363.91	141.51	0.0001
Plant Type (P)	3	8688.86	2896.28	1126.25	0.0001
Time (T)	7	2143.21	306.17	119.06	0.0001
Concentration (C)	2	12989.54	6494.77	2525.55	0.0001
P x T	21	1096.96	52.22	20.31	0.0001
P x C	6	7711.42	1285.24	499.78	0.0001
T x C	14	810.17	57.87	22.50	0.0001
P x T x C	42	1131.19	26.93	20.47	0.0001
Error	96	246.87	2.57		

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
$R^2 = 0.99$
CV = 1.91%

significant interactions (P = 0.0001) between the parameters. The results of Duncan's Multiple Range test (Table 6.10) showed that the four plants used in this study (soft stem bulrush, wool grass, soft rush and cattail) were significantly different from one another in their ability to remove iron and the three levels of iron concentrations in the wastewater were significantly different from one another at a 95% confidence level. The average removal efficiencies during the periods 1 and 2, 2 and 3 and 4 and 5 were not significantly different from one another. The iron removal efficiencies (RE_I) for the four plants can be described as a function of time and initial iron concentration as follows:

Soft stem bulrush

$$RE_I = 0.0863\ C_I + 12.8\ T - 0.571\ T^2 + 0.00985\ T^3 - 0.000580\ T^4 \qquad R^2 = 0.95 \qquad (6.1)$$

Wool grass

$$RE_I = 0.2700\ C_I + 10.3\ T - 0.471\ T^2 + 0.00821\ T^3 - 0.000049\ T^4 \qquad R^2 = 0.85 \qquad (6.2)$$

Soft rush

$$RE_I = 0.1140\ C_I + 13.2\ T - 0.600\ T^2 + 0.01040\ T^3 - 0.000062\ T^4 \qquad R^2 = 0.96 \qquad (6.3)$$

Cattail

$$RE_I = 0.275\ C_I + 9.49\ T - 0.411\ T^2 + 0.00705\ T^3 - 0.000042\ T^4 \qquad R^2 = 0.90 \qquad (6.4)$$

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Table 6.10. Differences among the plant type, periods and initial iron concentration.

Parameter	Number of Observations	Iron Removal Efficiency	Duncan Grouping
Plant Type			
Soft stem bulrush	48	89.03	A
Wool grass	48	74.32	B
Soft rush	48	91.17	C
Cattail	48	80.72	D
Periods (days)			
1 (1-8)	24	87.61	A
2 (9-17)	24	87.18	A B
3 (18-26)	24	86.57	B
4 (27-35)	24	84.36	C
5 (36-44)	24	84.25	C
6 (45-53)	24	83.08	D
7 (54-62)	24	80.00	E
8 (63-72)	24	77.46	F
Concentration (mg/L)			
Tolerance	64	94.98	A
Wetland Influent	64	81.65	B
Control	64	75.41	C

Means with the same letter are not significantly different from each other at 95% confidence level.

Where:

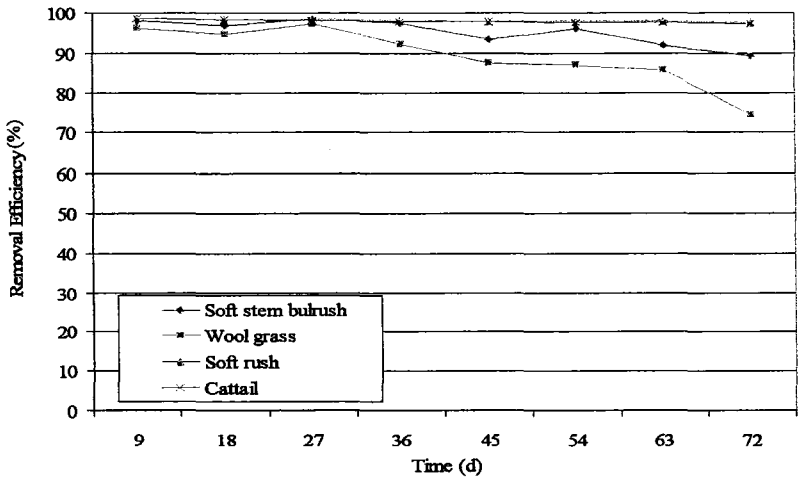
RE_I = Iron removal efficiency (%)

T = Time (d)

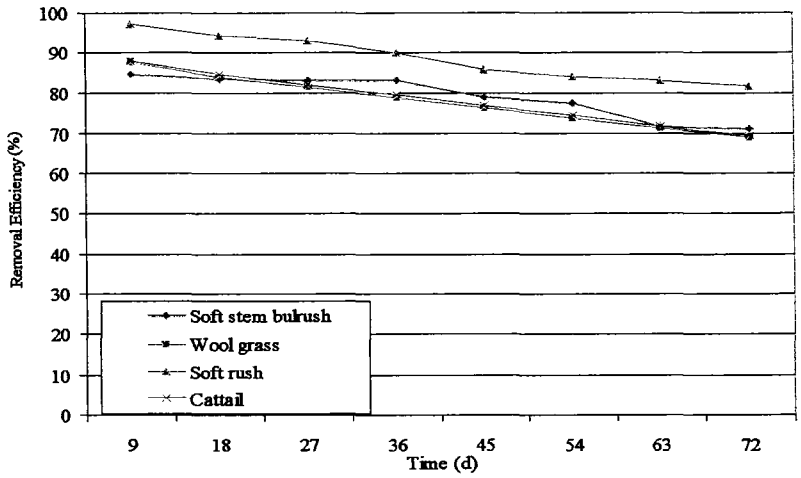
C_I = Initial iron concentration (mg/L)

These equations are valid for the time between 0 and 72 days and initial iron concentrations between 0.817 and 101.117 mg/L. The overall iron removal efficiency the compartments receiving the tolerance concentration during the first period were 98, 96, 98 and 98 % which decreased to 89, 74, 97 and 97% during the last period (after 72 days) of the experiment for soft stem bulrush, wool grass, soft rush and cattail, respectively (Figure 6.39). The overall iron removal efficiencies the compartments receiving the wetland influent during the first period were 86, 79, 98 and 89 % which decreased to 73, 71, 83 and 89% during the last period of the experiment (after 72 days) for soft stem

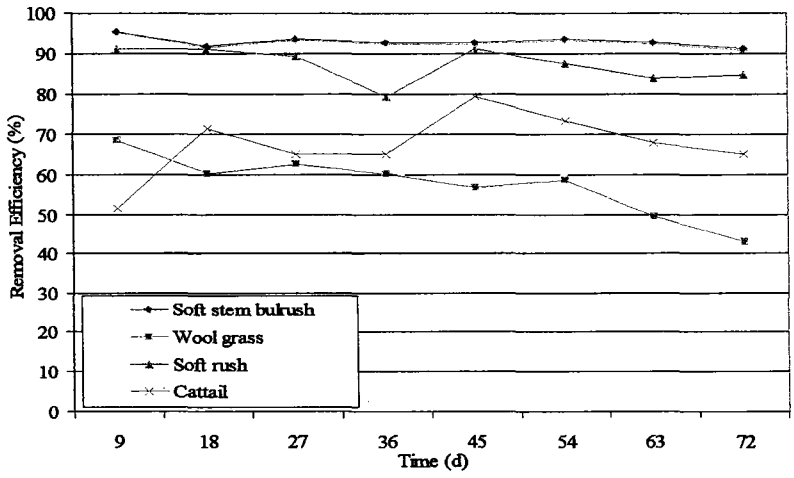
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(a) Tolerance Concentration



(b) Wetland Influent



(c) Control

Figure 6.39. Removal efficiency trends for the four plants.

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bulrush, wool grass, soft rush and cattail, respectively. The overall iron removal efficiency of the compartments receiving wetland influent were less than the overall removal efficiency for compartments receiving the tolerance concentration for the four plants. This is because: (a) the plant uptake of iron is a function of initial concentration as reported by Kamal et al. (2004) and (b) the siderophores, synthesized by the growth promoting bacteria found in the rhizosphere, solubilized the iron in the soil in the vicinity of the root system at a rate much faster than the diffusion iron rate as reported by Davison (1988) and Kloepper et al. (1989). Kirk (2002) reported that solubilization by acidification due to the siderophores accounted for at least 80% of the minerals taken up in both the unfertilized and fertilized soil.

Beneficial free-living soil bacteria are generally referred to as plant growth-promoting rhizobacteria and are found in association with the roots of many plants (Glick et al., 2002). High concentrations of bacteria around the roots (i.e., in the rhizosphere) presumably occurs because of the presence of high levels of nutrients (especially small molecules such as amino acids, sugars and organic acids) that are exuded from the roots of most plants, and can then be used to support bacterial growth and metabolism (Whipp, 1990; and Glick, 2003). Siderophores production can be stimulated by the presence of heavy metals. Since most siderophores also show a significant affinity for bivalent heavy metal ions, they affect the bioavailability of the heavy metals (van der Lelie et al., 2000; and Huyer and Page, 1988).

Lorion (2001) reports iron removal of up to 99% by plants in treatment wetland sites. Ye et al. (2001) reported iron removal of up to 91% in treatment wetlands designed to treat iron in contaminated wastewaters from coal combustion processes. Skousen et al. (1994) reported iron removal from acid mine drainage ranging from 28 to 99 %. The term "removed" typically accounts for both plant uptake and forming of particulate. Immobilization via oxidative precipitation accounts for the majority of the reported iron removal rates in treatment wetland systems (Wieder, 1988; Perry and Kleinmann, 1991; Bordoie et al., 1993; and Calabrese et al., 1991). According to Calabrese et al. (1991) and Wieder (1992), about 50 to 70% of total iron removal is via iron hydroxylation.

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6.7.1.2 Iron Plant Uptake and Mobility

The bioavailable iron in the current system was made of two portions: (a) the iron in the water from fertilizers and reagents and (b) the iron that already existed in the soil (phytoavailable portion). Schulte (2004) stated that the phytoavailable portion of iron in soil ranges from 5-10% of the total iron content in the soil. Therefore, the total plant uptake of iron may include that in water plus some of the phytoavailable in the soil. The results showed that the iron concentration in the plant tissues is directly proportional to the initial iron concentration in the wastewater. Due to the high affinity of the four plants for iron, the plants in the compartments receiving the control and wetland influent utilized some of the phytoavailable iron found in the soil as shown Table 6.11.

The iron accumulations in various plant tissues are shown in Tables 6.12 and 6.13. Cumulatively, the highest iron accumulated in the total plant tissues was in cattail with concentrations of 19194, 9847 and 3339 mg/kg and the lowest was in soft rush with iron concentrations of 4808, 3281 and 1745 mg/kg in the compartments receiving tolerance concentration, wetland influent and control, respectively. The highest amount of iron accumulated in the root tissues was in cattail with concentrations of 13501, 7019 and 2612 mg/kg and the lowest was in soft rush with concentrations of 3964, 2728 and 1383 mg/kg in compartments receiving the tolerance concentration, wetland influent and control, respectively. The highest amount of iron accumulated in the leaf tissues was in cattail with concentrations of 5693, 2828 and 727 mg/kg and the lowest was in soft rush with concentrations of 95, 73 and 61 mg/kg in compartments receiving the tolerance concentration, wetland influent and control, respectively. The highest amount of iron accumulated in the flower tissues was in soft stem bulrush with concentrations of 3639, 2494 and 1038 mg/kg and the lowest was in wool grass with concentrations of 379, 231 and 87 mg/kg in compartments receiving the tolerance concentration, wetland influent and control, respectively.

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Table 6.11. Sources of the iron assimilated by plants.

Iron Concentration	Plant	Total Uptake+		From Water		From Soil	
		mg/kg	(mg)	(mg)	(%)	(mg)	(%)
Control							
	Soft stem bulrush	7302	1229 (71.61)	177 (9.62)	14.4	1052 (61.98)	85.6
	Wool grass	4594	836.8 (49.30)	81.1 (4.77)	9.69	755.7 (44.53)	90.31
	Soft rush	4566	1720.8 (100.06)	159 (8.03)	9.24	1561.8 (92.02)	90.76
	Cattail	3500	4308.4 (254.91)	108.3 (6.96)	2.5	4200.7 (247.52)	97.5
Wetland Influent							
	Soft stem bulrush	14356	9740 (536.57)	1497 (88.21)	15.37	8243 (448.36)	84.63
	Wool grass	7030	1380.8 (81.79)	1475.9 (86.96)	106.88	95.1 (5.17)	-6.88
	Soft rush	6232	3348.3 (189.64)	1659 (97.75)	49.55	1689.3 (91.88)	50.45
	Cattail	10125	12488 (685.97)	1482 (87.32)	11.87	11006 (598.64)	88.13
Tolerance Concentration							
	Soft stem bulrush	22798	17327.2 (916.20)	23124 (1257.78)	133.45	5796.8 (341.58)	-33.45
	Wool grass	10547	2281.6 (18.70)	21619.2 (1175.93)	947.55	19409.6 (1143.722)	-847.55
	Soft rush	7686	4862.3 (179.09)	23817 (1295.47)	489.82	18954 (1116.88)	-389.82
	Cattail	19959	24282 (1322.26)	23783 (1293.63)	97.94	498 (29.34)	2.05

The values are the average of 3 replicates with a coefficient of variation in the range of 0.6-2.0%

\+ Total iron accumulation after 72 days

( ) Standard deviation

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Table 6.12. Iron concentration in mg/kg in facultative wetland plant tissues.

Time	Soft stem bulrush									Wool grass											
	Roots			Leaves			Flowers			Roots			Stem			Leaves			Flowers		
	T	W	C	T	W	C	T	W	C	T	W	C	T	W	C	T	W	C	T	W	C
0	3320	1750	2200	13	14	12	3056	2965	3184	1658	1596	1345	26	29	25	129	107	71	36	29	18
9	5560	3279	2452	340	160	15	4670	4000	3530	2542	2126	1543	52	39	30	160	129	72	78	54	27
18	6350	4730	2600	450	220	16	5200	4260	3700	3427	2657	1740	78	49	35	167	146	80	120	80	37
27	8340	5490	2730	531	256	16	5560	4520	3810	5090	3188	1938	104	60	41	183	153	90	175	98	47
36	10080	6740	2800	592	296	17	5890	4710	3880	5830	3718	2136	130	82	46	194	167	103	204	131	46
45	11540	6270	2860	654	346	17	6150	4860	3960	6640	4249	2680	156	99	51	205	178	125	237	135	66
54	12400	8100	2930	725	388	18	6270	5120	4030	7370	5200	3150	182	118	67	218	199	142	288	183	84
63	13020	7766	2975	780	405	18	6480	5370	4092	8450	5970	3550	208	142	83	230	201	150	330	225	110
72	15290	8482	3062	813	415	18	6695	5459	4222	9620	6372	4220	260	166	88	252	232	181	415	260	105

T Tolerance Concentration
W Wetland Influent
C Control

Table 6.13. Iron concentration in mg/kg in obligate wetland plant tissues.

Time	Soft rush									Cattail					
	Roots			Leaves			Flowers			Roots			Leaves		
	T	W	C	T	W	C	T	W	C	T	W	C	T	W	C
0	2468	2514	2457	65	72	69	345	365	295	670	126	68	95	152	93
9	3650	2570	3110	88	90	88	626	500	403	4460	2230	620	2650	1840	300
18	3800	3120	2811	86	88	82	710	472	362	5020	3110	690	3600	2140	330
27	4740	3950	2750	107	99	77	846	591	494	6660	4600	960	4400	2200	330
36	5030	3726	3166	119	107	87	800	578	520	7147	5220	1200	4860	2410	360
45	5000	4200	3800	130	112	103	920	690	556	10190	5540	1850	5120	2540	480
54	5460	4332	3520	137	120	111	916	685	496	10659	6360	2000	5400	2740	600
63	5970	5330	3620	148	141	116	1040	804	588	10950	6480	1920	5860	2760	580
72	6432	5242	3840	160	145	130	1094	845	596	14171	7145	2680	5788	2980	820

T Tolerance Concentration
W Wetland Influent
C Control

Analysis of variance (ANOVA) was performed on the total iron accumulate data using SAS System, 5th Ed. (SAS Institute Inc., Cary, North Carolina). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA analysis (Table 6.14) showed that the plant type and iron concentration have significant effects on the plant uptake (P = 0.0001). The analysis also showed significant interactions (P = 0.0001) between the parameters on the plant uptake. The results of Duncan's Multiple Range test (Table 6.15) showed that, the four plants used in this study (soft stem bulrush, wool grass, soft rush and cattail) were significantly different from one another in their ability to accumulate iron and the three levels of iron concentrations in the wastewater were significantly different from one another at a 95% confidence level. The iron accumulation in the tissues of the four plants can be described as a function of initial iron concentration and time by the following equations:

Soft stem bulrush

$$I_R = 78.10\,T + 424.00\,C_I - 3.55\,C_I^{\,2} \qquad R^2 = 0.93 \qquad (6.5)$$

$$I_L = 2.87\,T + 22.4\,C_I - 0.179\,C_I^{\,2} \qquad R^2 = 0.89 \qquad (6.6)$$

$$I_F = 56.90\,T + 378.00\,C_I - 3.39\,C_I^{\,2} \qquad R^2 = 0.94 \qquad (6.7)$$

$$I_{TO} = 138.00\,T + 824.00\,C_I - 7.12\,C_I^{\,2} \qquad R^2 = 0.98 \qquad (6.8)$$

Table 6.14. Analysis of variance of the iron accumulation in plant tissues.

Source	DF	SS	MS	F-Value	P
Total	23	1344437517	58453805		
Model	11	1340933352	121903032	417.5	0.0001
Plant Type (P)	2	442051159	221025579	756.9	0.0001
Concentration (C)	3	615293689	205097896	702.4	0.0001
P x C	6	283588502	47264750	161.9	0.0001
Error	12	3504166	292014		

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 0.99
CV = 7.46%

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Table 6.15. Differences among the plant type and initial iron concentration.

Parameter	Number of Observations	Total Iron in Plant Tissues	Duncan Grouping
Plant Type			
Soft stem bulrush	6	9791.3	A
Wool grass	6	1526.2	B
Soft rush	6	3421.0	C
Cattail	6	14226.2	D
Iron Concentration (mg/L)			
Tolerance	8	12612.3	A
Wetland Influent	8	7003.2	B
Control	8	2107.9	C

Means with the same letter are not significantly different from each other at 95% confidence level.

Wool grass

$I_R = 69.20\ T + 191.00\ C_I - 1.59\ C_I^2$ $R^2 = 0.99$ (6.9)

$I_S = 1.72\ T + 3.92\ C_I - 0.025\ C_I^2$ $R^2 = 0.89$ (6.10)

$I_L = 2.12\ T + 13.2\ C_I - 0.119\ C_I^2$ $R^2 = 0.99$ (6.11)

$I_F = 2.48\ T + 5.50\ C_I - 0.0427\ C_I^2$ $R^2 = 0.82$ (6.12)

$I_{TO} = 75.5\ T + 213.00\ C_I - 1.77\ C_I^2$ $R^2 = 0.98$ (6.13)

Soft rush

$I_R = 55.00\ T + 278.00\ C_I - 2.48\ C_I^2$ $R^2 = 0.97$ (6.14)

$I_L = 1.62\ T + 7.44\ C_I - 0.0679\ C_I^2$ $R^2 = 0.96$ (6.15)

$I_F = 8.84\ T + 42.70\ C_I - 0.375\ C_I^2$ $R^2 = 0.98$ (6.16)

$I_{TO} = 66.0\ T + 328.00\ C_I - 2.93\ C_I^2$ $R^2 = 0.99$ (6.17)

Cattail

$I_R = 68.9\ T + 265.00\ C_I - 2.11\ C_I^2$ $R^2 = 0.90$ (6.18)

$I_L = 23.9\ T + 175.00\ C_I - 1.40\ C_I^2$ $R^2 = 0.89$ (6.19)

$I_{TO} = 92.8\ T + 440\ C_I - 3.51\ C_I^2$ $R^2 = 0.92$ (6.20)

Where:

I = Iron concentration in tissues (mg/kg)

R = Roots

S = Stem

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$_{L}$ = Leaves

$_{F}$ = Flowers

$_{TO}$ = Total

Sanchez et al. (1994) sampled Aquatic moss (*Brachythecium rivulare*), Soft rush (*Juncus effusus*), and Board leaf cattail (*Typha latifolia*) as well as sediments from sites near an old lead-zinc mine. The iron concentrations in the leaves were 2370, 86 and 515 mg/kg and the total iron concentrations in the sediment were 33600, 51800 and 55000 mg/kg for the aquatic moss, soft rush and board leaf cattail, respectively. Their results indicated that the concentration of iron in plant tissues was plant specific and was not related to the iron concentration in the sediments.

Samecka-Cymerman and Kempers (2001) collected plant samples from impacted sites around a former open cut brown coal mine. The iron concentration in the water was 9 mg/L, and the iron concentrations in the leaves were 612, 2100 and 1360 mg/kg for *Phyragmites australis, Potamogeton natans* and *Iris pseudoacorus*, respectively. In another site where the iron concentration in water was 130 mg/L, the iron concentrations in the leaves were 841, 974, 995 and 2150 mg/kg for *Phragmites austrlis, Juncus bulbosus, Phalaris arundinacea*, and *Carex remota*, respectively. Their results indicated that the accumulation of iron in plant tissues was affected by the iron concentration in the water.

It is clear from the results obtained from the present study that the four plants used were superior accumulators of iron. However, plant species differ widely in their ability to accumulate and translocate heavy metals. The root tissues accumulate significantly greater concentrations of iron than shoots as it is shown in Table 6.16, indicating high plant availability of the substrate metals as well as its limited mobility once inside the plant. This is consistent with pervious studies (Outridge and Noller, 1991; cardwell et al., 2002; Fitzgerald et al., 2003). Outridge and Noller (1991) reported that the concentrations of heavy metals in the root tissues of freshwater macrophytes from polluted areas were usually found to contain higher concentrations of most metals compared to the

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Table 6.16. Iron uptake and distribution in plant tissues.

	Total Uptake* (mg)	Iron Distribution				Translocation Factor +
		Root (mg)	Stem (mg)	Leaves (mg)	Flowers (mg)	
Soft stem bulrush						
Tolerance	17327.2 (916.20)	16760.0 (1185.1)	NA	480.0 (33.9)	87.2 (6.17)	0.033
Wetland Influent	9740.0 (536.60)	9440.0 (667.5)	NA	240.0 (16.9)	60.0 (4.24)	0.031
Control	1229 (71.61)	3368.2 (234.5)	NA	10.4 (1.3)	50.6 (2.31)	0.018
Wool grass						
Tolerance	2280.8 (18.70)	2229.6 (157.7)	12.8 (0.91)	28.8 (2.1)	8.8 (0.62)	0.016
Wetland Influent	1380.8 (81.79)	1337.6 (94.6)	7.2 (0.51)	29.6 (2.1)	4.8 (0.34)	0.026
Control	836.8 (49.30)	886.2 (52.1)	4.4 (0.21)	23.5 (1.9)	2.0 (0.14)	0.033
Soft rush						
Tolerance	4794.4 (179.09)	4756.8 (336.3)	NA	7.2 (0.51)	29.6 (2.09)	0.007
Wetland Influent	3348.0 (189.64)	3273.6 (231.5)	NA	58.4 (4.12)	16.0 (1.13)	0.022
Control	1720.8 (100.06)	2649.6 (141.6)	NA	5.2 (0.12)	11.3 (0.56)	0.006
Cattail						
Tolerance	24282.4 (1322.26)	18361.6 (1298.4)	NA	5920.8 (418.6)	NA	0.320
Wetland Influent	12128.0 (685.97)	9545.6 (674.9)	NA	2941.6 (208.0)	NA	0.310
Control	4308.4 (254.91)	3580.5 (250.6)	NA	809.4 (60.1)	NA	0.226

The values are the average of 8 replicates with a coefficient of variation in the range of 1-5%

* Total iron accumulation after 72 days

\+ Translocation factor: concentration of iron in the above ground tissues divided by below ground tissues.

NA Not applicable

aboveground parts. The exclusion of metals from aboveground tissues has been suggested as a metal tolerant strategy by *T. latifolia* (Taylor and Crowder, 1983). The elevated metal concentrations in the underground tissues and low translocation to the aboveground tissues in the wetland plants examined might also suggest that they are capable of rather well balanced uptake and translocation of iron under heavily iron-polluted conditions. Gries and Garbe (1989) indicate that a well-balanced and largely independent ion budget is typical of many grass-line species, and is supposed to partly create their wide ecological amplitude. In the view of toxicology, this could be a desirable property, as iron would not be passed into the food chain via herbivores, and thus avoid potential risk to the environment.

Wetland plants play an important role in metal removal from metal-polluted water in constructed wetland by metal immobilization in the roots and in the oxygenated rhizosphere as indicated by Ye et al. (2001). However, iron accumulates in the leaves and flowers of some plants which are used as food by wetland animal and birds and there is, therefore, the possibility that they may bioaccumulate iron in their bodies. For protection of aquatic life a remedial measure such as a limestone filter must be implemented in order to reduce the level of iron in the wetland influent. Furthermore, species able to accumulate relatively high metal concentrations in the above ground tissues should not be used in constructed wetland.

6.7.1.3 Iron Uptake Kinetic Parameters

As indicated in the previous chapter, the uptake of dissolved iron by wetland plant can be expressed by a first-order kinetic model (Equation 5.15). The concentration of metal in the plant at any time is a function of the maximum concentration of metal that can accumulate in the plant and specific uptake rate as shown in Equation (5.20). In order to determine the specific uptake rate (k) and the maximum iron uptake (M_M) that can be accumulated during the experimental period (72 days) for each plant-iron concentration combination, the values of A and B in the linear form of this equation (Equations 5.31 and 5.32) are first obtained graphically for various plant-iron concentration combination according to the procedure described by Vlyssides et al. (1997) by plotting $(t/M_p)^{1/3}$ vs t

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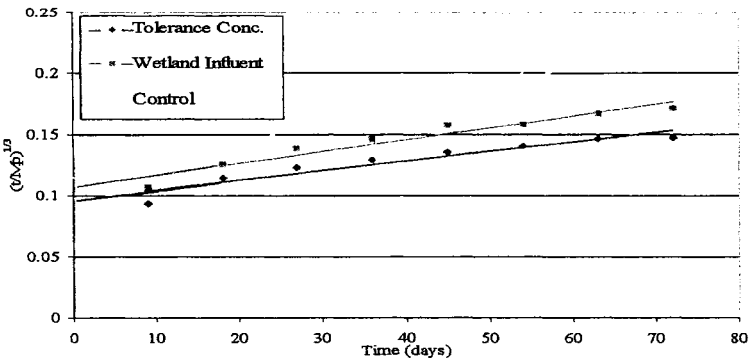
in Equation (5.31) as shown in Figure 6.40. The results are shown in Table 6.17. Table 6.18 presents the linear form of Equation (5.31) for iron uptake by various plants in different iron concentrations. Equations (5.41) and (5.44) were then used to determine the maximum concentrations (M_M) of iron that can be accumulated by the wetland plants and the specific uptake rates (k), respectively. The results are shown in Table 6.19.

The specific iron uptake rate (k) was 0.021, 0.027 and 0.031 d^{-1}, 0.036, 0.041 and 0.052 d^{-1} and 0.035, 0.041, 0.058 d^{-1} for wool grass, soft rush and soft stem bulrush in the compartment receiving tolerance concentration, wetland influent and control, respectively. The results showed that the specific iron uptake rate was affected by the initial iron concentration as shown in Figure 6.41. Vlyssides et al. (2001) reported that the specific uptake rates of metal are affected by the initial metal concentrations. It also appears from the results that the broad leaved cattail did not show any sign of iron toxicity since the specific iron uptake rate (k) increased from 0.019 to 0.032 d^{-1} as the iron concentration increased from 0.817 to 101.117 mg/L. The other three plants used in the study showed signs of toxicity because the k value of each plant decreased when iron concentration increased above 0.817 mg/L.

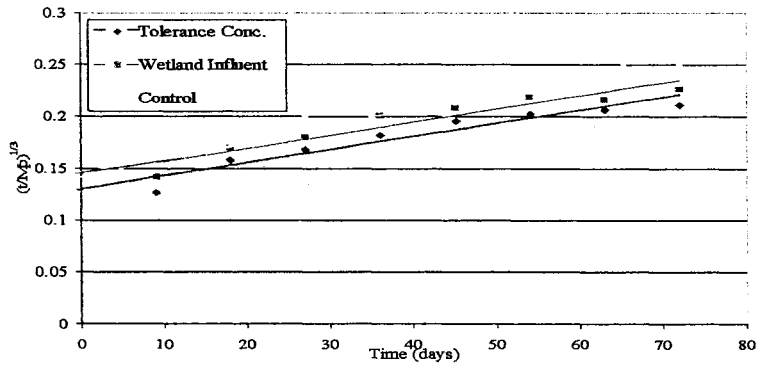
The relationship between Fe initial concentration and specific uptake rate can be described by the equations shown in Table 6.20. The equations for wool grass, soft stem bulrush and soft rush show the effect of iron toxicity on plant uptake rate within the range of 0.817-101.117 mg/L. Reported Fe concentrations for the occurrence of Fe toxicity vary widely between 1 to 1,000 mg Fe/L (Dobermann and Fairhurst, 2000). In Figure 6.41, the first portions of all Fe specific uptake curves are similar. Therefore, the first part of the Fe specific uptake curves for wool grass, soft stem bulrush and soft rush can be described by an equation similar to that used for cattail as shown in Table 6.20. However, in order to accurately describe the mechanism of toxicity, the initial iron concentration in the solution should be varied within the range of 0 to 1 mg/L.

The model also indicated that the highest concentration of iron (21781.20 mg/kg) accumulated by the end of experimental period (72 days) was in the soft stem bulrush

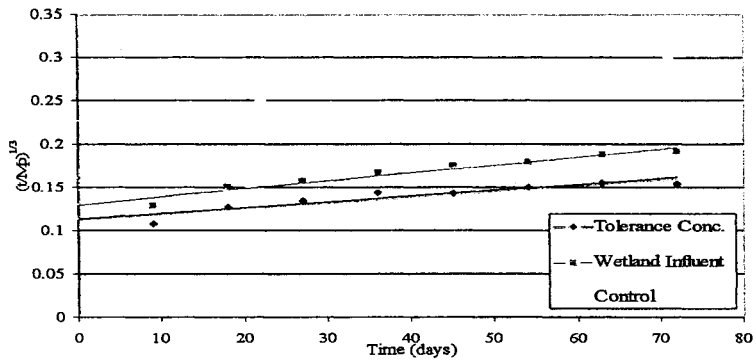
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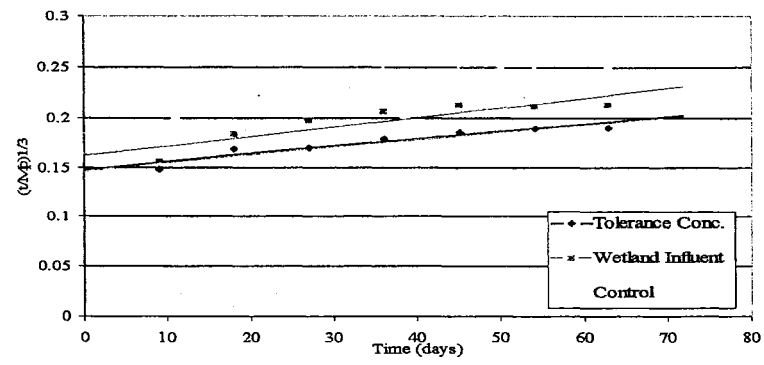
(a) Soft stem bulrush



(b) Soft rush



(c) Board leaved cattail



(d) Wool grass

Figure 6.40. Graphical determination of A and B for iron in plants at different initial concentrations.

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Table. 6.17. Values of A and B in Equation (5.31).

Plant	Concentration	A	B
Broad leaved cattail			
	Tolerance Conc.	0.1129	0.0007
	Wetland Influent	0.1306	0.0009
	Control	0.2273	0.0010
Wool grass			
	Tolerance Conc.	0.1487	0.0007
	Wetland Influent	0.1628	0.0010
	Control	0.1852	0.0013
Soft stem bulrush			
	Tolerance Conc.	0.0978	0.0008
	Wetland Influent	0.1067	0.0010
	Control	0.1131	0.0015
Soft rush			
	Tolerance Conc.	0.1036	0.0012
	Wetland Influent	0.1446	0.0012
	Control	0.1421	0.0017

Table 6.18. Linear form of Equation (5.31) for iron uptake.

Plant	Concentration	Equation	R^2
Broad leaved cattail			
	Tolerance Conc.	$(t/M_p)^{1/3} = 0.1129 + 0.0007\ t$	0.86
	Wetland Influent	$(t/M_p)^{1/3} = 0.1306 + 0.0009\ t$	0.95
	Control	$(t/M_p)^{1/3} = 0.2273 + 0.0010\ t$	0.80
Wool grass			
	Tolerance Conc.	$(t/M_p)^{1/3} = 0.1487 + 0.0007\ t$	0.90
	Wetland Influent	$(t/M_p)^{1/3} = 0.1628 + 0.0010\ t$	0.82
	Control	$(t/M_p)^{1/3} = 0.1852 + 0.0013\ t$	0.80
Soft stem bulrush			
	Tolerance Conc.	$(t/M_p)^{1/3} = 0.0978 + 0.0008\ t$	0.92
	Wetland Influent	$(t/M_p)^{1/3} = 0.1067 + 0.0010\ t$	0.94
	Control	$(t/M_p)^{1/3} = 0.1131 + 0.0015\ t$	0.96
Soft rush			
	Tolerance Conc.	$(t/M_p)^{1/3} = 0.1306 + 0.0012\ t$	0.92
	Wetland Influent	$(t/M_p)^{1/3} = 0.1446 + 0.0012\ t$	0.90
	Control	$(t/M_p)^{1/3} = 0.1421 + 0.0017\ t$	0.91

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Table 6.19. Iron kinetic uptake parameters (k, M_M) for wetland plants.

Plant	Concentration	k (d^{-1})	M_M (mg/kg)
Broad leaved cattail			
	Tolerance Conc.	0.032	18679.40
	Wetland Influent	0.026	10857.25
	Control	0.019	3225.89
Wool grass			
	Tolerance Conc.	0.021	10767.84
	Wetland Influent	0.027	6288.39
	Control	0.031	3737.86
Soft stem bulrush			
	Tolerance Conc.	0.035	21781.16
	Wetland Influent	0.041	14639.21
	Control	0.058	8686.25
Soft rush			
	Tolerance Conc.	0.036	8142.94
	Wetland Influent	0.041	6642.49
	Control	0.052	4855.25

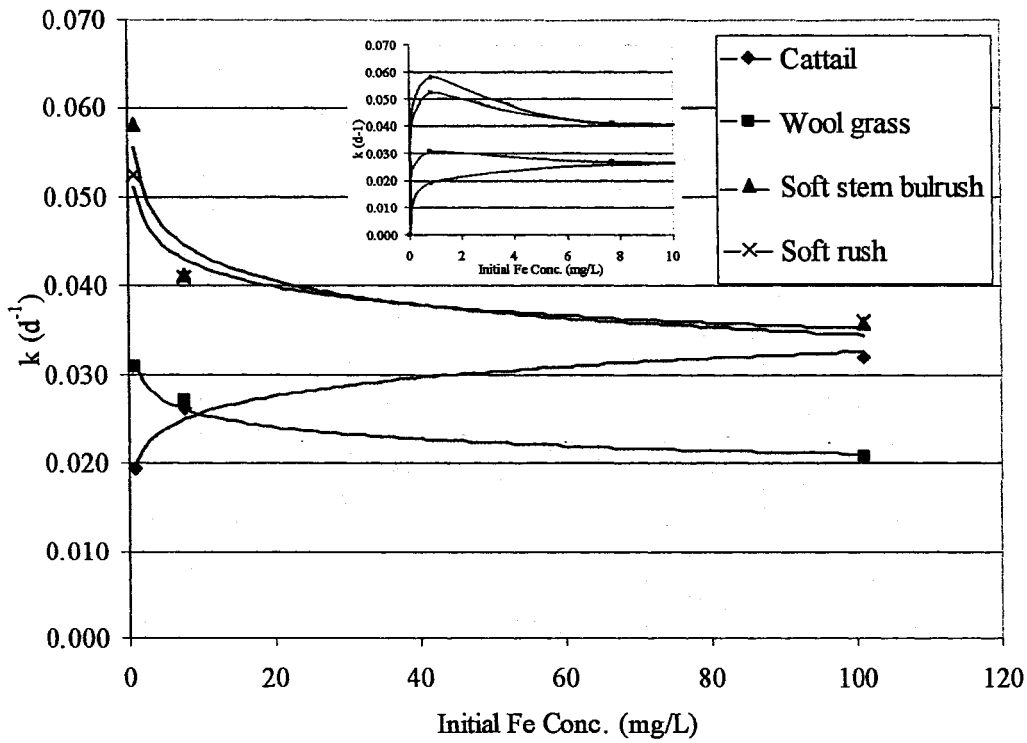


Figure 6.41. Effect of initial iron concentrations on the specific uptake rate for each plant.

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Table 6.20. The relationship between specific uptake rate and initial iron concentrations.

Plant	k (d^{-1})			
	0 - 0.817 mg/L		0.817 - 101.117 mg/L	
Broad leaved cattail	$k = 0.0201\ C_i^{0.1045}$	$R^2 = 0.98$	$k = 0.0201\ C_i^{0.1045}$	$R^2 = 0.98$
Wool grass	$k = 0.0350\ C_i^{0.6360}$	$R^2 = 0.99$	$k = 0.0308\ C_i^{-0.0834}$	$R^2 = 0.98$
Soft stem bulrush	$k = 0.0604\ C_i^{0.6952}$	$R^2 = 0.99$	$k = 0.0546\ C_i^{-0.0992}$	$R^2 = 0.92$
Soft rush	$k = 0.0503\ C_i^{0.7066}$	$R^2 = 0.99$	$k = 0.0503\ C_i^{-0.0774}$	$R^2 = 0.93$

C_i Initial iron concentration

in the compartment receiving tolerance concentration while the lowest concentration of iron (3225.89 mg/kg) was accumulated in the broad leaved cattail in the control compartment. The maximum concentration of iron that can be accumulated in plants was also affected by the initial iron concentration as shown in Figure 6.42. The relationships can be described by the equations shown in Table 6.21. The intercept values in these equations are the initial values of the iron concentration in these plants before the start of the experiment. The predicted maximum concentrations were plotted against the experimental maximum concentrations obtained at the end of the experiment for iron as shown in Figure 6.43. The results showed that the model is capable of predicting the experimental data with relatively high confidence (R^2 of 0.98).

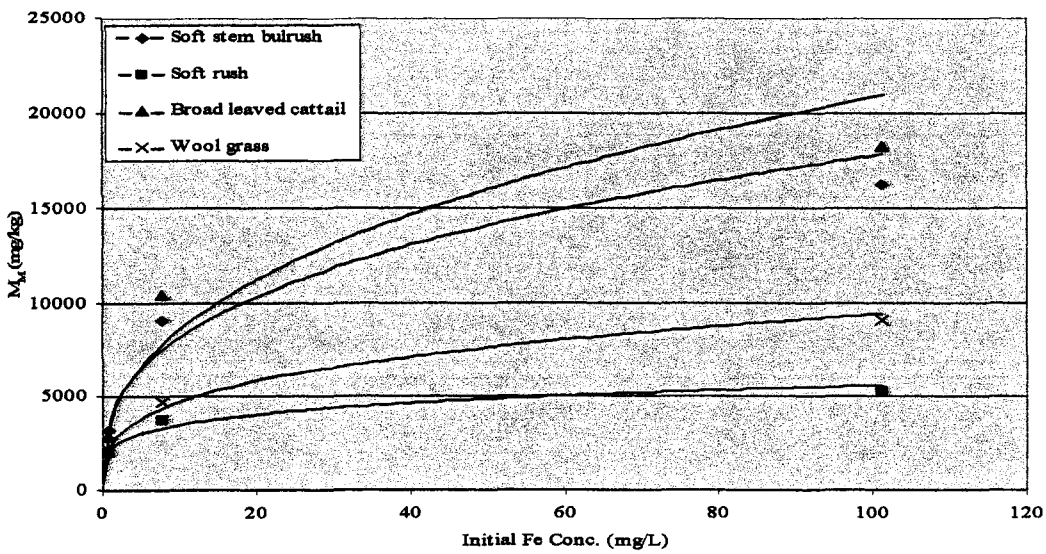


Figure 6.42. Effect of initial iron concentrations on the maximum iron concentration for each plant.

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Table 6.21. The relationship between maximum iron concentration and initial iron concentrations.

Plant	Equation	R^2
Broad leaved cattail	$M_M = 401 + 3567\ C_i^{0.3834}$	0.93
Wool grass	$M_M = 1690 + 2351\ C_i^{0.3018}$	0.99
Soft stem bulrush	$M_M = 5492 + 3793\ C_i^{0.3354}$	0.96
Soft rush	$M_M = 2883 + 2196\ C_i^{0.2018}$	0.99

C_i Initial iron concentration
M_M Maximum iron concentration accumulated by the end of the experimental period (72 days)

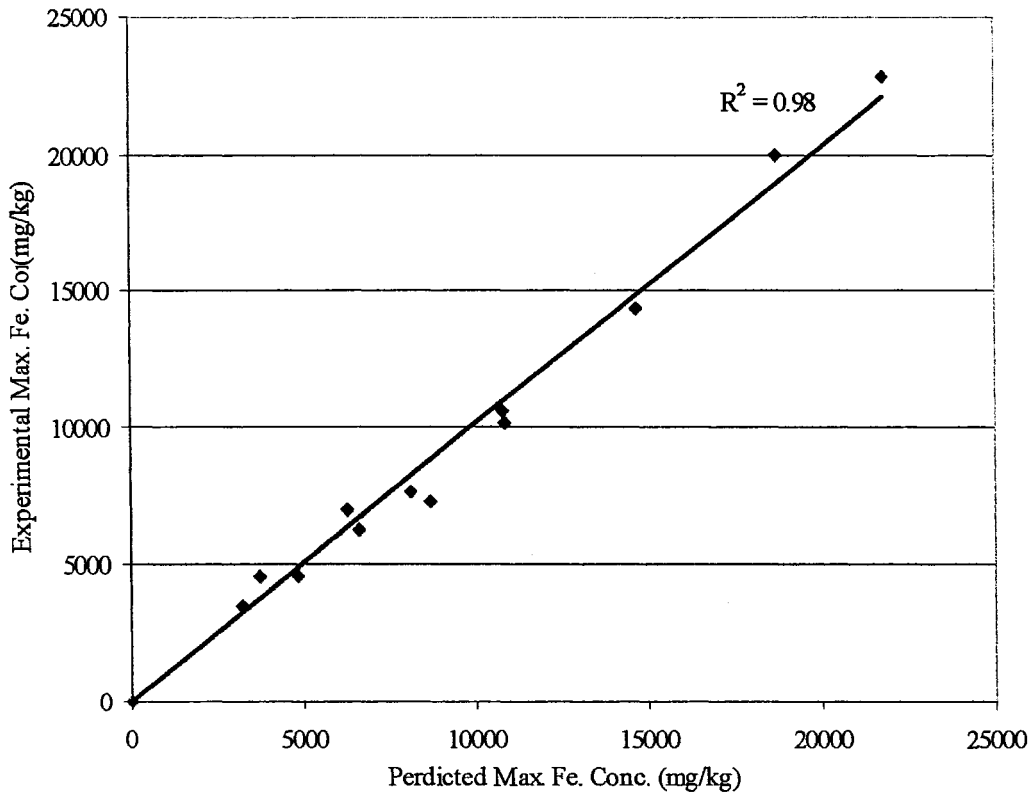


Figure 6.43. Maximum predicted and experimental concentrations of iron accumulated in wetland plants by the end of the experimental period (72 days).

Table 6.22 present the iron kinetic uptake parameters (k and M_M) for wetland plants of laboratory and the field wetlands. The plants tested in the constructed wetland had slower specific uptake rate than those tested in the laboratory. This may be due to the constant (day and night) higher temperature and light duration maintained in the laboratory compared to fluctuating and the lower and inconsistent temperature in the field. However,

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the plants in the constructed wetland accumulated higher concentrations of iron (approximately 2-3 folds) in their tissues than the plants in the laboratory. This was because the testing period in the constructed wetland (150days) was longer than that in the laboratory (72 days).

Table 6.22. Iron kinetic uptake parameters (k, M_M) for wetland plants in the laboratory and field wetlands.

Plant	k (d^{-1})		M_M (mg/kg)	
	Laboratory	Field	Laboratory	Field
Broad leaved cattail	0.030	0.006	10857.2	31021.4
Wool grass	0.027	0.009	6288.3	19463.7
Soft stem bulrush	0.041	0.006	14639.2	28732.1
Soft rush	0.036	0.008	6642.4	18349.7

M_M Maximum iron accumulated by wetland plant by the end of the experimental period (72 days for laboratory and 150 days for field)

6.7.2 Manganese

6.7.2.1 Manganese Overall Removal Efficiency

The concentrations of manganese in the various compartments at the end of each period are shown in Table 6.23. The removal efficiencies for the various compartments of the system are shown in Table 6.24. The overall removal efficiency of the system is the sum removal of manganese from the system by the chemical and/or biological precipitation and plant uptake.

Analysis of variance (ANOVA) was performed on the removal efficiency data using SAS System, 5th Ed. (SAS Institute Inc., Cary, North Carolina). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA results (Table 6.25) showed that the plant type, time and Mn initial concentration have significant effects on the removal efficiency (P = 0.0001). The results also showed significant interactions (P = 0.0001) between the parameters. The results of Duncan's Multiple Range test (Table 6.26) showed that the four plants used in this study

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Table 6.23. Manganese concentration in the wastewater.

Time	Tolerance concentration				Wetland Influent				Control			
	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail
9	0.36 (0.03)	0.91 (0.06)	0.23 (0.02)	0.24 (0.02)	0.20 (0.01)	0.10 (0.01)	0.07 (0.005)	0.32 (0.02)	0.03 (0.002)	0.10 (0.002)	0.10 (0.001)	0.10 (0.007)
18	0.36 (0.02)	1.10 (0.07)	0.33 (0.02)	0.55 (0.04)	0.21 (0.01)	0.10 (0.01)	0.12 (0.01)	0.28 (0.02)	0.05 (0.003)	0.18 (0.012)	0.02 (0.001)	0.10 (0.006)
27	0.63 (0.03)	1.37 (0.08)	0.43 (0.03)	0.55 (0.03)	0.30 (0.02)	0.10 (0.01)	0.14 (0.01)	0.13 (0.01)	0.08 (0.005)	0.24 (0.014)	0.04 (0.002)	0.11 (0.007)
36	0.80 (0.06)	1.37 (0.10)	0.63 (0.05)	0.73 (0.06)	0.29 (0.02)	0.14 (0.01)	0.21 (0.01)	0.18 (0.01)	0.13 (0.010)	0.30 (0.024)	0.08 (0.006)	0.13 (0.010)
45	0.70 (0.05)	1.01 (0.07)	0.65 (0.05)	0.46 (0.03)	0.26 (0.02)	0.16 (0.01)	0.20 (0.02)	0.13 (0.01)	0.15 (0.010)	0.36 (0.025)	0.11 (0.007)	0.13 (0.095)
54	2.19 (0.11)	1.28 (0.06)	0.73 (0.04)	0.55 (0.03)	0.30 (0.02)	0.15 (0.01)	0.21 (0.01)	0.28 (0.01)	0.20 (0.010)	0.18 (0.009)	0.15 (0.007)	0.11 (0.005)
63	2.58 (0.17)	1.10 (0.07)	0.63 (0.04)	0.55 (0.04)	0.26 (0.02)	0.16 (0.01)	0.20 (0.01)	0.13 (0.01)	0.20 (0.013)	0.17 (0.011)	0.24 (0.015)	0.12 (0.007)
72	2.74 (0.16)	1.55 (0.09)	0.73 (0.04)	0.64 (0.04)	0.27 (0.02)	0.18 (0.01)	0.21 (0.01)	0.35 (0.02)	0.25 (0.015)	0.16 (0.009)	0.28 (0.017)	0.12 (0.007)

The values are the average of 3 replicates with a coefficient of variation in the range of 1.0-6.0%
Initial Tolerance Concentration = 15.41 mg/L
Initial Wetland Influent Concentration = 2.21 mg/L
Initial Control Concentration = 0.41 mg/L
( ) Standard deviation

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Table 6.24. Manganese removal efficiencies (%).

Time	Tolerance concentration				Wetland Influent				Control			
	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail
9	97.66	94.09	98.51	98.44	90.94	95.47	96.83	85.51	92.65	75.55	97.56	75.55
18	97.66	92.86	97.86	96.43	90.49	95.47	94.56	97.32	87.78	55.99	95.11	75.55
27	95.91	91.11	97.21	96.43	86.41	95.47	93.66	94.11	80.44	41.32	90.22	72.37
36	94.81	91.11	95.91	95.26	86.87	93.66	90.49	91.85	68.22	26.65	80.44	67.97
45	95.45	93.45	95.78	97.01	88.23	92.75	90.94	94.11	63.32	11.98	73.11	97.23
54	85.78	91.69	95.26	96.43	86.41	93.21	90.49	87.32	51.10	55.01	63.33	73.35
63	83.25	92.86	95.91	96.43	88.23	92.76	90.94	94.12	51.10	58.43	41.32	71.64
72	82.22	89.94	95.26	95.85	87.78	91.85	90.49	84.16	38.88	61.61	31.54	71.64

Table 6.25. Analysis of variance of the manganese removal efficiency.

Source	DF	SS	MS	F-Value	P
Total	191	67075.38	351.18		
Model	95	66831.56	703.49	276.99	0.0001
Plant Type (P)	3	2552.19	850.73	334.97	0.0001
Time (T)	7	4719.77	674.25	265.48	0.0001
Concentration (C)	2	36853.10	18426.55	7255.27	0.0001
P x T	21	5011.22	238.63	93.96	0.0001
P x C	6	4693.16	782.19	307.98	0.0001
T x C	14	5121.54	365.82	144.04	0.0001
P x T x C	42	7880.57	187.63	73.88	0.0001
Error	96	243.82	2.54		

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 0.99
CV = 1.91%

Table 6.26. Differences among the plant type, periods and initial manganese concentration.

Parameter	Number of Observations	Mn Removal Efficiency	Duncan Grouping
Plant Type			
Soft stem bulrush	48	81.36	A
Wool grass	48	77.07	B
Soft rush	48	86.19	C
Cattail	48	85.45	D
Periods (days)			
1 (1-8)	24	91.14	A
2 (9-17)	24	88.42	B
3 (18-26)	24	85.65	C
4 (27-35)	24	80.94	D
5 (36-44)	24	79.29	E F
6 (45-53)	24	80.07	D E
7 (54-62)	24	78.83	F
8 (63-72)	24	75.79	G
Concentration (mg/L)			
Tolerance	64	93.93	A
Wetland Influent	64	90.61	B
Control	64	63.02	C

Means with the same letter are not significantly different from each other at a 95% confidence level.

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(soft stem bulrush, wool grass, soft rush and cattail) were significantly different from one another in their ability to remove manganese and the three levels of initial manganese concentrations in the wastewater were significantly different from one another at a 95% confidence level. However, the average removal efficiency during the periods 4, 5 and 6 were not significantly different from one another at a 95% confidence level. The manganese removal efficiencies for the four plants can be described as a function of time and initial manganese concentration (within the ranges studied) as follows:

Soft stem bulrush

$$RE_M = 0.153\ C_M + 12.8\ T - 0.572\ T^2 + 0.0096\ T^3 - 0.000055\ T^4 \quad R^2 = 0.86 \qquad (6.21)$$

Wool grass

$$RE_M = 0.141\ C_M + 13.4\ T - 0.603\ T^2 + 0.0103\ T^3 - 0.000061\ T^4 \quad R^2 = 0.85 \qquad (6.22)$$

Soft rush

$$RE_M = 0.148\ C_M + 11.9\ T - 0.535\ T^2 + 0.0093\ T^3 - 0.000055\ T^4 \quad R^2 = 0.92 \qquad (6.23)$$

Cattail

$$RE_M = 0.207\ C_M + 12.9\ T - 0.631\ T^2 + 0.0116\ T^3 - 0.000071\ T^4 \quad R^2 = 0.80 \qquad (6.24)$$

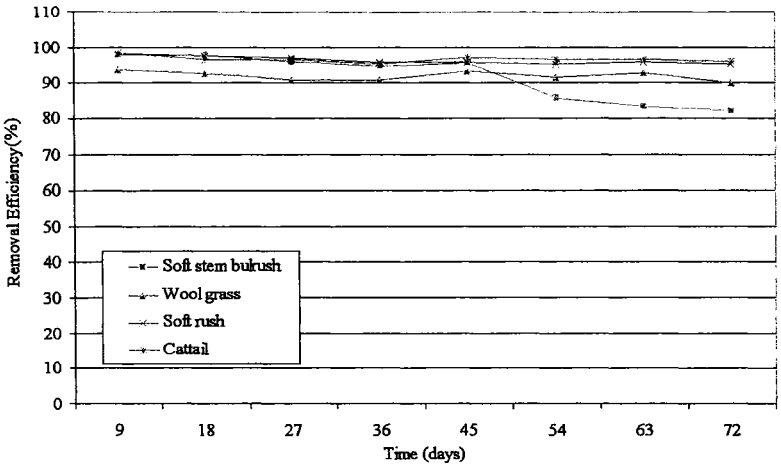
Where:

RE_M = Manganese removal efficiency (%)

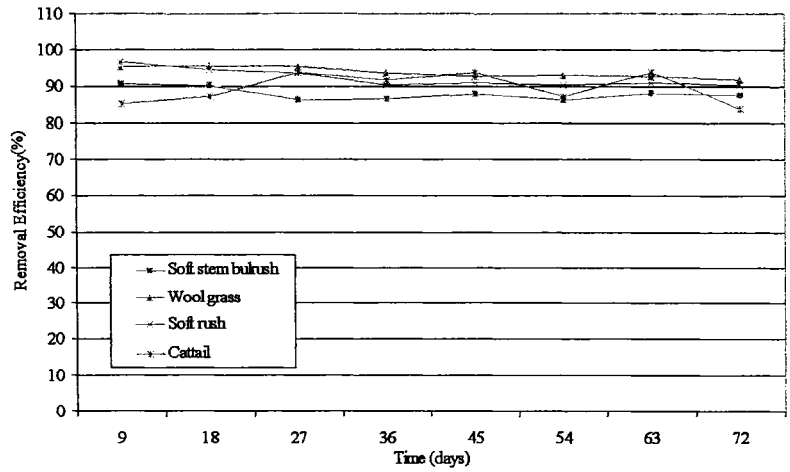
C_M = Initial manganese concentration (mg/L)

The overall manganese removal efficiencies of the system during the first period in the compartments receiving the tolerance concentration were 97.66, 94.09, 98.50 and 98.44 % which decreased to 82.21, 89.94, 95.26 and 95.84% by the last period (after 72 days) of the experiment for soft stem bulrush, wool grass, soft rush and cattail, respectively (Figure 6.44). The overall manganese removal efficiencies of the system during the first period in the compartments receiving the wetland influent concentration were 90.94, 95.47, 96.83 and 85.51 % which decreased to 87.77, 91.85, 90.49 and 84.15% during the last period of the experiment (after 72 days) for soft stem bulrush, wool grass, soft rush and cattail, respectively. The compartments receiving wetland influent had overall manganese removal efficiencies lower than those of the compartments receiving the

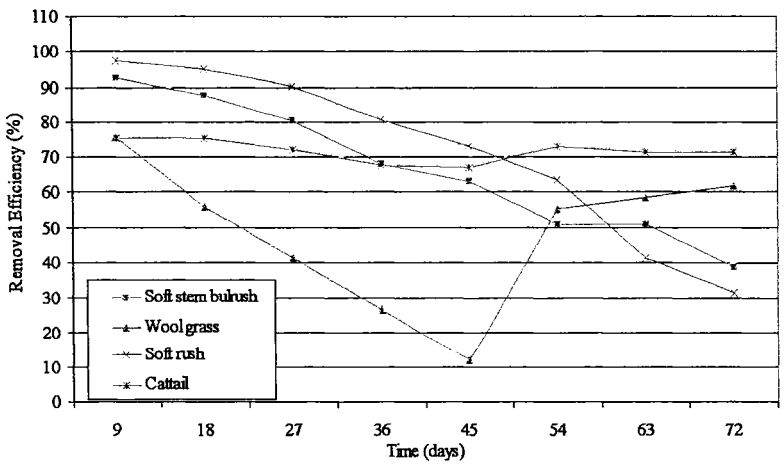
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(a) Tolerance Concentration



(b) Wetland Influent



(c) Control

Figure 6.44. Manganese removal efficiency trends for the four plants.

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tolerance concentration for soft stem bulrush, soft rush and cattail.

Previous studies (Stillings et al., 1988; Fennessy and Mitsch, 1989; Hedin, 1989; Skousen et al., 1994; and Stark et al., 1994) showed that constructed wetlands are less successful in removing manganese. This is mostly due to the fact that oxidized manganese does not readily form precipitate unless the pH of water is at least 7.0, with precipitation most commonly occurring in waters with pHs greater than 10.0. In addition, manganese oxidation is sensitive to the presence of Fe^{2+} which can prevent or even reverse manganese oxidation (Skousen, 1998). Phytoremediation mechanisms prove relatively insignificant, accounting for approximately 1 – 4 % of manganese removal (Ye et al., 2001). In the current study, the pH of the wastewaters in this experiment is not acidic, hence some removal via precipitation may be accommodated in the system. Some treatment site managers try to force manganese precipitation (i.e. MnO_2) by increasing the alkalinity of the treatment site via limestone addition. However, the most effective removal mechanism for manganese in treatment wetland systems is settling, as 90 to 95% of total waterborne manganese binds to particulate matter (BCMELP, 2001).

6.7.2.2 Manganese Plant Uptake and Mobility

The bioavailable manganese in the system is made of two portions: (a) the manganese in the water from fertilizers and reagents and (b) the manganese that already existed in the soil (phytoavailable portion). Therefore, the total plant uptake of manganese may include that in water plus some of the phytoavailable in the soil. Due to the high affinity of the four plants for utilizing manganese, some plants in the compartments receiving the control and wetland influent utilized manganese from the phytoavailable portion of the manganese found in the soil. The results (Table 6.27) showed that the manganese concentration in the plant tissues is directly proportional to the initial manganese concentration in the wastewater.

The manganese accumulations in various plant tissues are shown in Tables 6.28 and 6.29. Cumulatively, the highest manganese accumulated in the total plant tissues was in soft stem bulrush with concentrations of 1202, 957 and 709 mg/kg and the lowest was in wool

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Table 6.27. Sources of the manganese assimilated by plants.

Mn Concentration	Plant	Total Uptake+		From Water		From Soil	
		(mg/kg)	(mg)†	(mg)	(%)	(mg)	(%)
Control							
	Soft stem bulrush	709	144.8 (10.24)	65.4 (4.62)	45.17	79.4 (5.61)	54.83
	Wool grass	370	40.8 (2.62)	47.4 (3.35)	117.32	-6.6 (0.47)	-17.32
	Soft rush	689	131.4 (9.29)	70.2 (4.96)	53.42	61.2 (4.33)	46.58
	Cattail	776	544.6 (32.09)	70.5 (4.99)	12.95	474.1 (33.52)	87.05
Wetland Influent							
	Soft stem bulrush	957	210.4 (14.88)	468.0 (33.09)	222.43	-257.6 (18.21)	-122.43
	Wool grass	649	52.5 (4.12)	497.5 (35.17)	947.61	-445.0 (31.47)	-847.61
	Soft rush	845	290.8 (16.49)	489.0 (34.57)	209.60	-255.8 (18.09)	-109.64
	Cattail	838	607.2 (35.78)	476.2 (33.67)	78.42	131.0 (9.26)	21.57
Tolerance Concentration							
	Soft stem bulrush	1202	258.4 (18.27)	3387.0 (239.49)	1310.75	-3128.6 (221.23)	-1210.75
	Wool grass	921	81.5 (4.09)	3326.0 (240.94)	4080.98	-3338.0 (236.03)	-4802.87
	Soft rush	1001	372.6 (26.34)	3567.0 (252.22)	957.32	-3194.4 (225.87)	857.32
	Cattail	910	678.8 (43.63)	3570.0 (252.43)	525.92	-2891.2 (204.44)	-425.92

The values are the average of 3 replicates with a coefficient of variation in the range of 1.5-6.7%

\+ Total iron accumulation after 72 days

( ) Standard deviation

† Calculated from plant weight

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Table 6.28. Manganese concentration in mg/kg in wetland plant tissues.

	Bulrush									Wool grass											
	Roots			Leaves			Flowers			Roots			Stem			Leaves			Flowers		
Time	T	W	C	T	W	C	T	W	C	T	W	C	T	W	C	T	W	C	T	W	C
0	58	62	65	88	75	90	240	220	257	48	40	30	26	38	23	45	54	39	15	25	19
9	73	85	74	130	99	77	380	307	260	55	45	33	55	55	31	61	66	51	52	44	23
18	91	83	74	190	100	105	424	360	298	57	46	36	84	69	41	77	70	63	89	64	27
27	107	102	86	203	127	119	460	371	329	66	53	39	108	90	39	93	87	75	113	66	31
36	126	110	99	213	138	115	549	400	310	67	58	43	142	116	58	118	105	87	164	104	30
45	141	133	128	221	158	135	625	449	336	71	62	47	181	125	60	140	118	99	177	102	39
54	141	126	124	240	167	135	643	467	379	76	66	48	201	136	76	146	131	111	239	144	55
63	150	132	118	257	180	142	660	514	386	80	74	56	230	160	97	158	143	123	276	148	57
72	156	148	140	268	210	150	778	599	419	90	81	63	289	196	103	191	169	148	351	203	56

T Tolerance Concentration
W Wetland Influent
C Control

Table 6.29. Manganese concentration in mg/kg in wetland plant tissues.

	Soft rush									Cattail					
Time	Roots			Leaves			Flowers			Roots			Leaves		
	T	W	C	T	W	C	T	W	C	T	W	C	T	W	C
0	65	68	62	85	92	67	275	286	265	24	26	21	265	245	239
9	111	89	71	160	128	92	364	326	303	48	38	27	464	358	408
18	99	88	70	167	135	90	377	322	295	47	38	24	549	400	451
27	103	80	62	196	142	107	392	373	317	62	37	24	592	467	403
36	150	108	78	226	188	113	408	376	335	70	50	31	620	472	457
45	149	128	95	239	203	125	410	390	352	83	69	28	635	550	512
54	175	127	85	254	226	152	438	393	368	103	70	33	686	632	566
63	183	156	89	290	248	157	446	397	362	110	78	41	710	643	621
72	217	157	97	313	242	171	471	446	421	127	81	46	783	757	730

T Tolerance Concentration
W Wetland Influent
C Control

grass with manganese concentrations of 921, 649 and 370 mg/kg for the compartments receiving tolerance concentration, wetland influent and control, respectively. The highest amount of manganese accumulated in the root tissues was in soft rush with concentrations of 217, 157 and 97 mg/kg and the lowest was in wool grass with concentrations of 90, 81 and 63 mg/kg for compartments receiving the tolerance concentration, wetland influent and control, respectively. The highest amount of manganese accumulated in the leaf tissues was in cattail with concentrations of 783, 757 and 730 mg/kg and the lowest was in wool grass with concentrations of 191, 169 and 148 mg/kg in compartments receiving the tolerance concentration, wetland influent and control, respectively. The highest amount of manganese accumulated in the flower tissues was in soft stem bulrush with concentrations of 778, 599 and 419 mg/kg and the lowest was in wool grass with concentrations of 351, 203 and 56 mg/kg in compartments receiving the tolerance concentration, wetland influent and control, respectively.

Analysis of variance (ANOVA) was performed on the total manganese accumulation data using SAS System, 5th Ed. (SAS Institute Inc., Cary, North Carolina). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA analysis (Table 6.30) showed that the plant type and the initial manganese concentration have significant effects on the plant uptake ($P = 0.0001$). There were significant interactions ($P = 0.0001$) between the parameters. The results of Duncan's Multiple Range test (Table 6.31) showed that the four plants used in this study (soft stem bulrush, wool grass, soft rush and cattail) were significantly different from one another in their utility to accumulate manganese and the three levels of the initial manganese concentrations in the water were significantly different from one another at a 95% confidence level. The manganese accumulation in the tissues of the four plants as a function of initial manganese concentration and time can be described by the following equations:

Soft stem bulrush

$$M_R = 1.80\ T + 6.69\ C_M - 0.0611\ C_M^2 \qquad R^2 = 0.93 \qquad (6.25)$$

$$M_L = 2.25\ T + 8.73\ C_M - 0.0746\ C_M^2 \qquad R^2 = 0.90 \qquad (6.26)$$

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Table 6.30. Analysis of variance of the manganese accumulation in plant tissues.

Source	DF	SS	MS	F-Value	P
Total	23	1192725.75	51857.64		
Model	11	118676.12	107887.38	217.05	0.0001
Plant Type (P)	2	74287.28	37143.64	74.73	0.0001
Concentration (C)	3	1086547.82	362182.61	728.66	0.0001
P x C	6	25926.03	4321.00	8.69	0.0008
Error	12	5964.75			

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 0.99
CV = 7.65%

Table 6.31. Differences among the plant type and initial manganese concentration.

Parameter	Number of Observations	Total Mn in Plant Tissues	Duncan Grouping
Plant Type			
Soft stem bulrush	6	214.78	A
Wool grass	6	56.82	B
Soft rush	6	258.06	C
Cattail	6	636.48	D
Iron Concentration (mg/L)			
Tolerance	8	361.16	A
Wetland Influent	8	288.45	B
Control	8	224.99	C

Means with the same letter are not significantly different from each other at a 95% confidence level.

$$M_F = 6.31\ T + 27.9\ C_M - 0.2460\ C_M^2 \qquad R^2 = 0.90 \qquad (6.27)$$

$$M_{TO} = 10.20\ T + 43.3\ C_M - 0.3810\ C_M^2 \qquad R^2 = 0.92 \qquad (6.28)$$

Wool grass

$$M_R = 0.778\ T + 0.45\ C_M - 0.0402\ C_M^2 \qquad R^2 = 0.95 \qquad (6.29)$$

$$M_S = 1.94\ T + 5.12\ C_M - 0.0432\ C_M^2 \qquad R^2 = 0.90 \qquad (6.30)$$

$$M_L = 1.95\ T + 4.95\ C_M - 0.0440\ C_M^2 \qquad R^2 = 0.98 \qquad (6.31)$$

$$M_F = 1.80\ T + 4.30\ C_M - 0.0328\ C_M^2 \qquad R^2 = 0.82 \qquad (6.32)$$

$$M_{TO} = 6.48\ T + 18.8\ C_M - 0.1610\ C_M^2 \qquad R^2 = 0.90 \qquad (6.33)$$

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Soft rush

$M_R = 1.55\ T + 7.94\ C_M - 0.0704\ C_M^2$ $R^2 = 0.85$ (6.34)

$M_L = 2.53\ T + 12.20\ C_M - 0.1090\ C_M^2$ $R^2 = 0.92$ (6.35)

$M_F = 4.75\ T + 29.50\ C_M - 0.2070\ C_M^2$ $R^2 = 0.91$ (6.36)

$M_F = 8.83\ T + 49.70\ C_M - 0.4490\ C_M^2$ $R^2 = 0.93$ (6.37)

Cattail

$M_R = 0.801\ T + 3.47\ C_M - 0.0298\ C_M^2$ $R^2 = 0.85$ (6.38)

$M_L = 0.808\ T + 28.30\ C_M - 0.2530\ C_M^2$ $R^2 = 0.92$ (6.39)

$M_F = 9.600\ T + 31.70\ C_M - 0.2830\ C_M^2$ $R^2 = 0.95$ (6.40)

Where:

M = Manganese concentration in tissues (mg/kg)

Fox and Guerinot (1998) reported that at a high manganese supply, the leaves accumulated higher concentrations with age, and small amounts of Mn were translocated from old leaves when young expanding leaves were Mn deficient. Thus, Mn appeared to have a low mobility when the supply to the plant was limited. Kabata-Pendios and Pendios (1992) reported that the Mn concentration fluctuates greatly within the plant parts and within the vegetative period. Manchner (1995) stated that the Mn content of plants is not only affected by plant characteristics, but also by the pool of available Mn which is highly controlled by soil properties.

Peltier, et al. (2003) collected common reeds (*Phragmites*) grown along the edge of the waterline of a metal-contaminated wetland having manganese concentration of 0.96 mg/L and found that the concentrations of manganese were 1027, 138 and 46 mg/kg in roots, stem and leaves, respectively. Sanchez et al. (1994) sampled Aquatic moss (*Brachythecium rivulare*), Soft rush (*Juncus effusus*), and Board leaf cattail (*Typha latifolia*) from different sites near an old lead-zinc mine and found the total manganese concentrations in the sediment were 860, 1850 and 1020 mg/kg and the manganese concentrations in the leaves were 1850, 345 and 1950 mg/kg for moss, soft rush and

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board leaf cattail, respectively. Samecka-Cymerman and Kempers (2001) collected plant samples from 9 different impacted sites around former open cut brown coal mine. The manganese concentration in the leaves of the various plant samples (*Phyragmites australis, Potamogeton natans, Iris pseudoacorus, Juncus effusus, Drepanocladus aduncus, Juncus bulbosus, Phalaris arundinacea, Carex remota* and *Calamagrostis epigeios*) increased with the increase of manganese concentration in the water. Kabata-Pendios and Pendios (1992) suggested that because Mn seems to be easily taken up by plants when it occurs in soluble forms in soils, the Mn content of plants should be a direct function of the soluble Mn pool in soils.

It appears from the results obtained from the present study that the four plants used were inferior accumulators of manganese to the plants used in other studies. One reason for this inferiority is the interaction between the iron and manganese as reported by Kabata-Pendias and Pendia (1992). Fe and Mn are interrelated in their metabolic functions.

The leaves accumulate significantly greater concentrations of metals than roots (Table 6.32), indicating high plant availability of the substrate metals as well as manganese mobility once inside the plant. Generally, Mn is known to be taken up and translocated within plants rapidly. Therefore, it is unlikely that Mn is binding to insoluble organic ligands either in root tissue or in xylem fluid (Fox and Guerinot, 1998). Manganese is reported to occur in plant fluids and extracts mainly as free cationic forms and is likely to be transported as Mn^{2+}. However, its complexing compounds with organic molecules of 1000 to 5000 molecular weights have been found in phloem exudates (Manchner, 1995). Van Goor (1974) reported a much lower Mn concentration in phloem exudates than in leaf tissues and concluded that a slight transport of Mn through the phloem vessels is responsible for the low concentration of Mn in fruits, seeds, and storage roots.

6.7.2.3 Manganese Uptake Kinetic Parameters

The uptake of dissolved manganese by wetland plant can be expressed by a first-order kinetic model (Equation 5.15). In order to determine the specific manganese uptake rate

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Table 6.32. Manganese uptake and distribution in plant tissues.

	Total Uptake* (mg)	Manganese Distribution				**Translocation Factor +**
		Root (mg)	Stem (mg)	Leaves (mg)	Flowers (mg)	
Soft stem bulrush						
Tolerance	258.4 (18.27)	137.6 (9.73)	NA	108.0 (7.64)	12.9 (0.91)	0.87
Wetland Influent	210 (14.88)	120.8 (8.54)	NA	80.8 (5.71)	9.0 (0.64)	0.74
Control	144.8 (10.24)	119.0 (5.4)	NA	58.5 (3.89)	6.5 (0.23)	0.54
Wool grass						
Tolerance	81.5 (4.09)	19.5 (0.17)	14.7 (1.04)	35.0 (2.47)	8.0 (0.57)	2.95
Wetland Influent	52.5 (4.12)	11.4 (0.81)	8.8 (0.62)	27.8 (1.96)	4.2 (0.31)	3.57
Control	40.8 (2.62)	9.5 (1.20)	4.9 (0.53)	25.16 (2.12)	1.2 (0.12)	3.29
Soft rush						
Tolerance	372.6 (26.34)	182.4 (12.89)	NA	182.4 (12.0)	7.6 (0.53)	1.04
Wetland Influent	290.8 (16.49)	107.0 (7.55)	NA	120.0 (8.49)	64.0 (4.52)	1.72
Control	131.4 (9.29)	46.3 (4.28)	NA	92.5 (7.89)	6.3 (0.31)	2.13
Cattail						
Tolerance	678.8 (43.63)	140.1 (9.91)	NA	538.7 (38.09)	NA	3.85
Wetland Influent	607.2 (35.78)	74.8 (5.28)	NA	532.5 (37.65)	NA	7.11
Control	544.6 (32.09)	46.0 (1.02)	NA	503.7 (10.23)	NA	10.95

The values are the average of 8 replicates with a coefficient of variation in the range of 2-6%

* Total iron accumulation after 72 days

\+ Translocation factor: concentration of iron in the above ground tissues divided by below ground tissues.

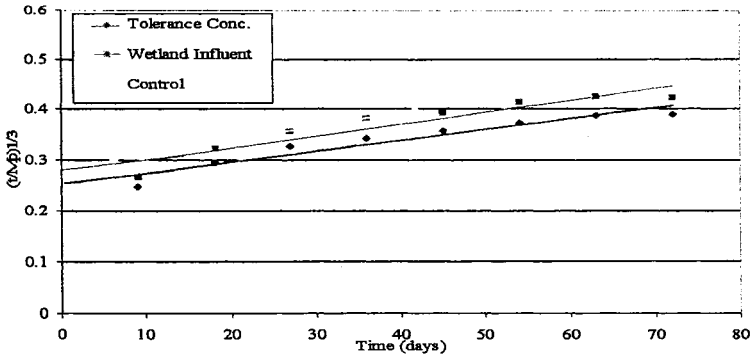
NA Not applicable

(k) and maximum manganese uptake (M_M) that can be accumulated in the plant by the end of the experimental period (72 days) in Equation (5.20) for each plant-manganese concentration combination, the values of A and B obtained graphically for various plant-manganese combination according to the procedure described by Vlyssides et al. (1997) by plotting $(t/M_p)^{1/3}$ vs. t in Equation (5.31) as shown in Figure 6.45. The results are shown in Table 6.33. Table 6.34 presents the linear form of Equation (5.31) for manganese uptake by various plants in different manganese concentrations. Equations (5.41) and (5.44) were used to determine the maximum concentrations (M_M) of manganese that can be accumulated by the wetland plants and the specific uptake rates (k), respectively. The results are shown in Table 6.35.

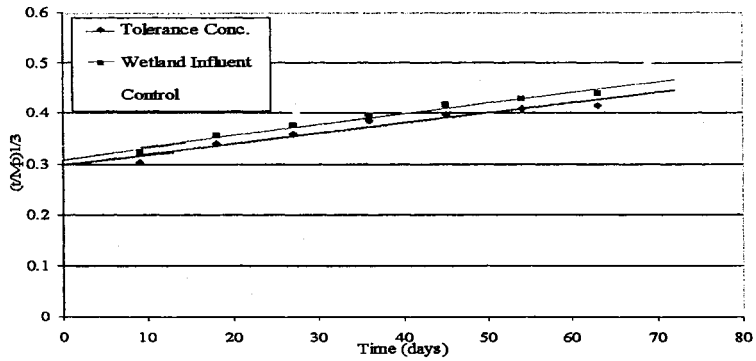
The specific uptake rate (k) of 0.019, 0.029 and 0.032 d^{-1}, 0.022, 0.029 and 0.031 d^{-1}, 0.032, 0.038 and 0.035 d^{-1} and 0.044, 0.044, 0.050 d^{-1} for wool grass, soft rush, soft stem bulrush and broad-leaved cattail in the compartments receiving tolerance concentration, wetland influent and control, respectively. The resulted showed that specific manganese uptake rate is affected by the initial manganese concentrations as shown in Figure 6.46. The plant used in this study showed signs of toxicity as the k value of each plant decreased with manganese concentrations above 0.409 mg/L. The relationship between Mn initial concentration and specific uptake rate can be described the equations shown in Table 6.36. The equations for all the plants used show the effect of manganese toxicity on plant uptake rate within the range of 0.409-15.409 mg/L. Bould et al. (1983) reported that manganese concentrations for the toxicity vary widely between 0.5 to 200 mg/L. The equations used to describe the first portions of the curves shown in Figure 6.46 were based on two initial manganese concentrations (0 and 0.409 mg/L), in order to precisely describe the mechanism of toxicity and the initial Mn concentration in the solution which will have a toxicity effect on the plants more experiments should be preformed on the range form 0 to 0.409 mg/L.

The model also indicated that the maximum concentrations of manganese (1177.02 mg/kg) accumulated by the end of the experimental period was in soft stem bulrush in the

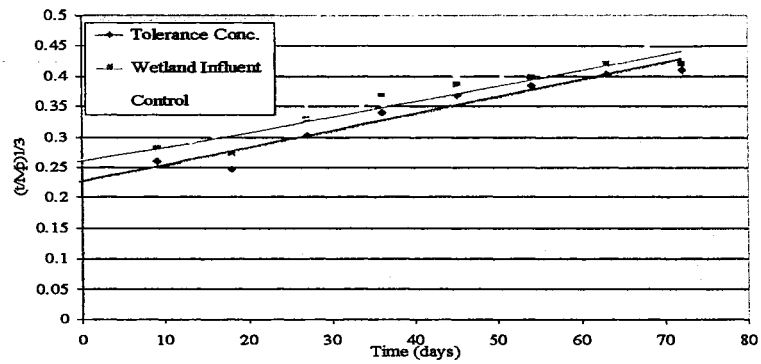
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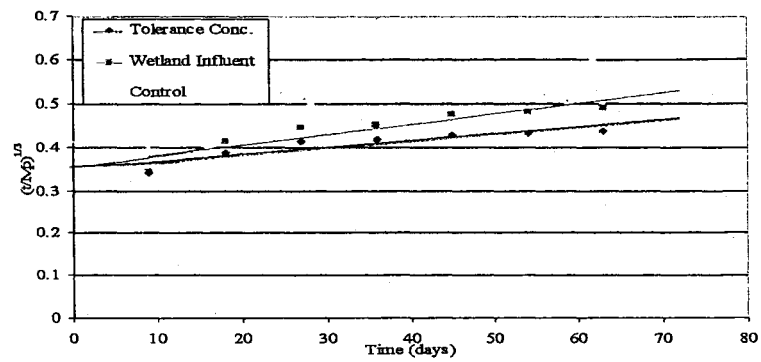
(a) Soft stem bulrush



(b) Soft rush



(c) Board leaved cattail



(d) Wool grass

Figure 6.45. Graphical determination of A and B for manganese in wetland plants in different initial concentrations.

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Table. 6.33. Values of A and B in Equation (5.31).

Plant	Concentration	A	B
Broad leaved cattail			
	Maximum	0.2262	0.0028
	Wetland	0.2574	0.0026
	Control	0.2532	0.0029
Wool grass			
	Maximum	0.3526	0.0016
	Wetland	0.3611	0.0024
	Control	0.4162	0.0030
Soft stem bulrush			
	Maximum	0.2537	0.0022
	Wetland	0.2749	0.0024
	Control	0.2824	0.0028
Soft rush			
	Maximum	0.2988	0.0020
	Wetland	0.3137	0.0021
	Control	0.3347	0.0024

Table 6.34. Linear form of Equation (5.31) for manganese uptake.

Plant	Concentration	Equation	R^2
Broad leaved cattail			
	Maximum	$(t/M_p)^{1/3} = 0.2262 + 0.0028\,t$	0.94
	Wetland	$(t/M_p)^{1/3} = 0.2574 + 0.0026\,t$	0.92
	Control	$(t/M_p)^{1/3} = 0.2532 + 0.0029\,t$	0.90
Wool grass			
	Maximum	$(t/M_p)^{1/3} = 0.3526 + 0.0016\,t$	0.82
	Wetland	$(t/M_p)^{1/3} = 0.3611 + 0.0024\,t$	0.84
	Control	$(t/M_p)^{1/3} = 0.4162 + 0.0030\,t$	0.82
Soft stem bulrush			
	Maximum	$(t/M_p)^{1/3} = 0.2537 + 0.0022\,t$	0.92
	Wetland	$(t/M_p)^{1/3} = 0.2749 + 0.0024\,t$	0.90
	Control	$(t/M_p)^{1/3} = 0.2824 + 0.0028\,t$	0.93
Soft rush			
	Maximum	$(t/M_p)^{1/3} = 0.2988 + 0.0020\,t$	0.92
	Wetland	$(t/M_p)^{1/3} = 0.3137 + 0.0021\,t$	0.90
	Control	$(t/M_p)^{1/3} = 0.3347 + 0.0024\,t$	0.91

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Table 6.35. Manganese kinetic uptake parameters (k, M_M) for wetland plants.

Plant	Concentration	k (d^{-1})	M_M (mg/kg)
Broad leaved cattail			
	Maximum	0.035	1163.34
	Wetland	0.044	967.52
	Control	0.050	896.44
Wool grass			
	Maximum	0.019	837.85
	Wetland	0.029	532.57
	Control	0.032	320.72
Soft stem bulrush			
	Maximum	0.032	1177.02
	Wetland	0.038	918.94
	Control	0.043	746.38
Soft rush			
	Maximum	0.022	933.37
	Wetland	0.029	806.49
	Control	0.031	619.19

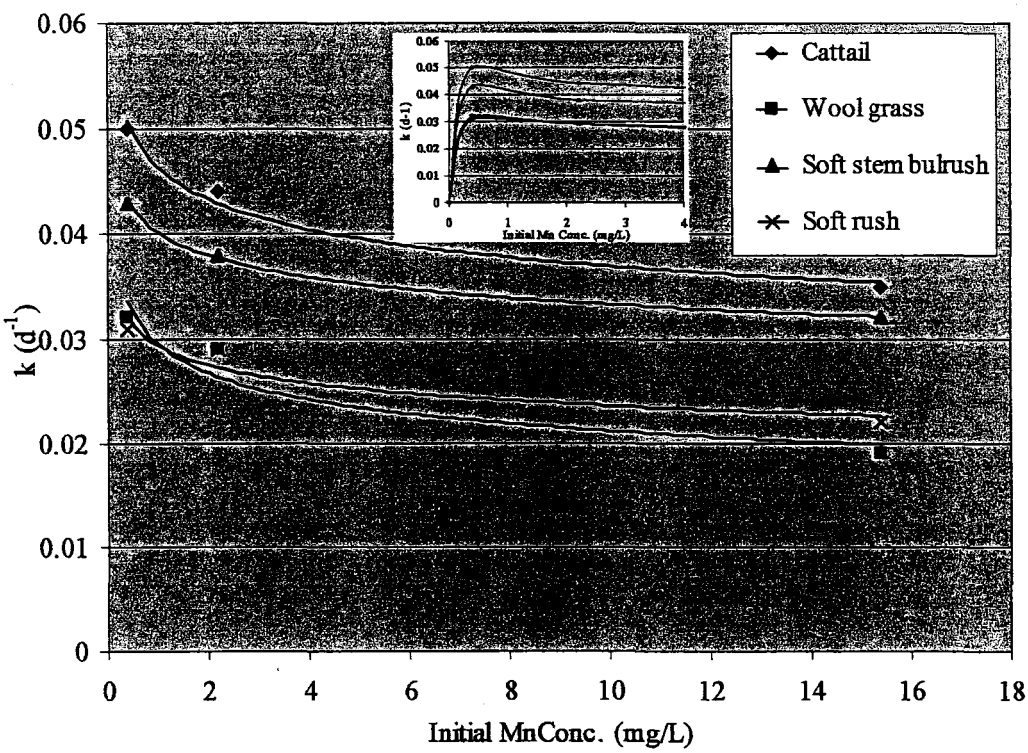


Figure 6.46. Effect of initial manganese concentrations on the specific uptake rate for each plant.

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Table 6.36. The relationship between specific uptake rate and initial manganese concentrations.

Plant	k (d^{-1})			
	0 – 0.409 mg/L		0.409 – 15.409 mg/L	
Broad leaved cattail	$k = 0.0975\ C_i^{0.7473}$	$R^2 = 0.99$	$k = 0.0464\ C_i^{-0.0988}$	$R^2 = 0.99$
Wool grass	$k = 0.0825\ C_i^{0.7291}$	$R^2 = 0.99$	$k = 0.0402\ C_i^{-0.0816}$	$R^2 = 0.99$
Soft stem bulrush	$k = 0.0574\ C_i^{0.6898}$	$R^2 = 0.99$	$k = 0.0294\ C_i^{-0.0957}$	$R^2 = 0.91$
Soft rush	$k = 0.0595\ C_i^{0.6936}$	$R^2 = 0.99$	$k = 0.0296\ C_i^{-0.1455}$	$R^2 = 0.91$

C_i initial manganese concentration

compartment receiving tolerance concentration while the lowest concentration of manganese (320.72 mg/kg) was accumulated in the wool grass in control compartment. The maximum concentration of manganese that can be accumulated in plants is also affected by the initial manganese concentration as shown in Figure 6.47. The relationships can be described by the equations shown in Table 6.37. The intercept values in these equations are the initial values of manganese concentration in these plants before the start of the experiment. The predicted maximum concentrations were plotted against the experimental maximum concentrations obtained at the end of the experiment as shown in Figure 6.48. The results showed that the model is capable of predicting the experimental data with relatively high confidence (R^2=0.90).

Table 6.38 present the manganese kinetic uptake parameters (k and M_M) for wetland plants under laboratory and field conditions. The plants tested in the constructed wetland had slower specific manganese uptake rate than those tested in the laboratory. This may be, as mentioned before, due to the constant temperature found in the laboratory compared to the temperature variations in the field. However, the plants in the constructed wetland accumulated similar concentrations of manganese in their tissues to those in the laboratory plants except for wool grass which accumulated higher concentration in the constructed wetland compared to that accumulated in the laboratory.

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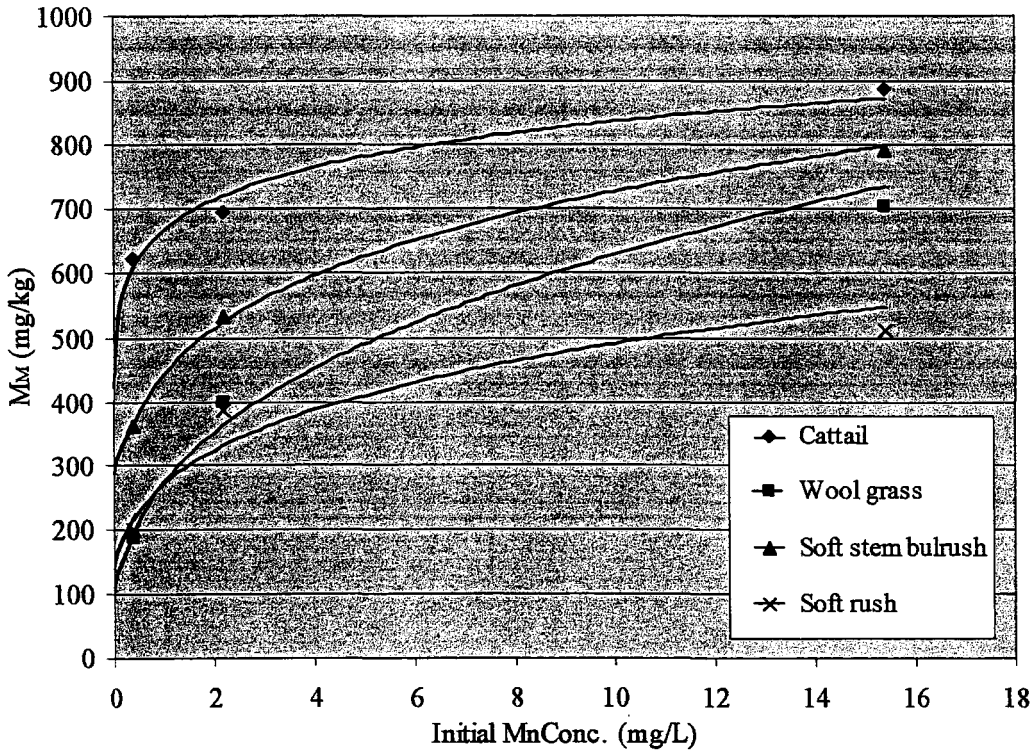


Figure 6.47. Effect of initial manganese concentrations on the maximum iron concentration for each plant.

Table 6.37. The relationship between maximum manganese concentration and initial iron concentrations.

Plant	Equation	R^2
Broad leaved cattail	$M_M = 274 + 666.25\ C_i^{0.0991}$	0.96
Wool grass	$M_M = 133 + 272.96\ C_i^{0.3628}$	0.99
Soft stem bulrush	$M_M = 385 + 442.35\ C_i^{0.2159}$	0.99
Soft rush	$M_M = 421 + 270.53\ C_i^{0.2588}$	0.93

C_i initial manganese concentration
M_M Maximum manganese concentration accumulated by the end of the experiment (72 days)

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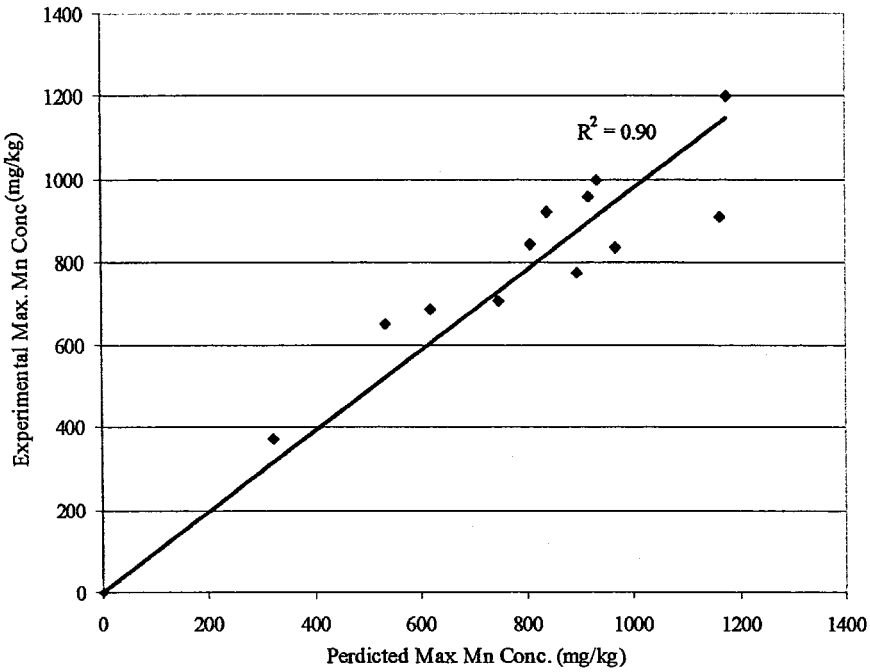


Figure 6.48. Maximum predicted and experimental concentrations of manganese accumulated in wetland plants.

Table 6.38. Manganese kinetic uptake parameters (k, M_M) for wetland plants in the laboratory and constructed wetland.

Plant	k (d^{-1})		M_M (mg/kg)	
	Laboratory	Constructed Wetland	Laboratory	Constructed Wetland
Broad leaved cattail	0.044	0.019	967.52	902.82
Wool grass	0.029	0.014	532.57	827.43
Soft stem bulrush	0.038	0.006	1833.35	1833.35
Soft rush	0.031	0.009	1346.82	1346.82

6.7.3 Zinc

Zn plays essential metabolic roles in the plant, the most significant of which is its activity as component of a variety of enzymes such as dehydrogenases, proteinases, peptidases, and phosphohydrolases. The basic functions in plants are related to metabolism of carbohydrates, proteins, and phosphate and also to auxins, RNA, and ribosome formations (Coleman, 1992). Zn is believed to stimulate the resistance of the plants to dry

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and hot weather and also to bacterial and fungal diseases (Kabata-Pendios and Pendios, 1992).

The form in which Zn is absorbed by roots has not been precisely defined. However, there is general agreement on the predominating uptake of both hydrated Zn and Zn^{2+}. Several other complex ions and Zn-organic chelates may be absorbed. Several studies (Weinberg, 1977, Gaillard, 1994; Van Cappellen and Gaillard, 1996) suggest that Zn generally is bound to soluble low molecular weight proteins; however, the formation of Zn-phytate and other insoluble Zn complexes were also reported. Tinker (1981) reported that the portion of Zn bound in complexes with a negative charge constitutes more than half of the total metal present in the plant. Some authors (Hacisalihoglu and Kochain, 2003; Hacisalihoglu, et al., 2001; Hacisalihoglu, 2002) regard Zn as highly mobile.

Zinc is a ubiquitous contaminant that imposes a hazard to a host of plants and animals, many aquatic organisms are particularly sensitive to this element. Although it is not a redox active species within soil or aquatic environments, oxidation and reduction reactions may nevertheless affect zinc partitioning. Retention of zinc can be modified by changes in substrate chemistry (Bostick et al., 2001). Zinc sorbs strongly to iron (Stahl and James, 1991) and manganese (hydr)oxides (Zasoski and Burau, 1988) in aerated systems and to sulfide (Kornicker and Morse, 1991; and Huerta-Diaz et al., 1998) and carbonate (Morse, 1986; Zachara et al., 1991; and Zachara et al., 1991) phases in anoxic environments. Thus, changes in redox status may shift Zn partitioning. For example, reductive dissolution of iron and manganese (hydr)oxides under suboxic conditions releases Zn into the aqueous phase; persistence of sub- or anoxic conditions may then lead to a repartitioning of Zn into sulfide or carbonate solids.

6.7.3.1 Zinc Overall Removal Efficiency

The concentrations of zinc in the various compartments at the end of each period are shown in Table 6.39. The removal efficiencies for the various compartments are shown in Table 6.40. The overall removal efficiency of the system is the sum removal of zinc by the chemical and/or biological precipitation and plant uptake.

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Table 6.39. Zinc concentration in the wastewater (mg/L).

Time	Tolerance Concentration				Wetland Influent				Control			
	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail
9	0.13 (0.009)	0.16 (0.011)	0.06 (0.003)	0.27 (0.019)	0.13 (0.009)	0.09 (0.006)	0.04 (0.003)	0.23 (0.016)	0.06 (0.004)	0.02 (0.001)	0.01 (0.001)	0.05 (0.003)
18	0.16 (0.010)	0.15 (0.009)	0.08 (0.005)	0.32 (0.020)	0.15 (0.009)	0.11 (0.007)	0.05 (0.003)	0.26 (0.017)	0.08 (0.005)	0.06 (0.004)	0.03 (0.002)	0.08 (0.005)
27	0.18 (0.010)	0.22 (0.012)	0.10 (0.006)	0.34 (0.019)	0.17 (0.009)	0.13 (0.007)	0.09 (0.005)	0.28 (0.016)	0.05 (0.003)	0.03 (0.002)	0.04 (0.002)	0.10 (0.006)
36	0.20 (0.015)	0.22 (0.017)	0.11 (0.008)	0.36 (0.027)	0.19 (0.014)	0.15 (0.011)	0.11 (0.008)	0.30 (0.023)	0.05 (0.004)	0.04 (0.003)	0.06 (0.004)	0.12 (0.009)
45	0.21 (0.015)	0.23 (0.016)	0.12 (0.009)	0.37 (0.026)	0.20 (0.014)	0.12 (0.008)	0.11 (0.008)	0.31 (0.022)	0.06 (0.004)	0.05 (0.003)	0.08 (0.006)	0.13 (0.009)
54	0.23 (0.011)	0.24 (0.012)	0.15 (0.008)	0.39 (0.019)	0.22 (0.011)	0.12 (0.006)	0.12 (0.006)	0.33 (0.017)	0.10 (0.004)	0.05 (0.002)	0.10 (0.005)	0.15 (0.008)
63	0.25 (0.016)	0.29 (0.018)	0.14 (0.009)	0.41 (0.026)	0.24 (0.015)	0.13 (0.009)	0.12 (0.008)	0.35 (0.022)	0.06 (0.004)	0.06 (0.004)	0.11 (0.007)	0.17 (0.011)
72	0.27 (0.016)	0.24 (0.014)	0.16 (0.009)	0.43 (0.025)	0.26 (0.015)	0.14 (0.008)	0.16 (0.009)	0.37 (0.021)	0.07 (0.004)	0.07 (0.004)	0.13 (0.007)	0.19 (0.011)

The values are the average of 3 replicates with a coefficient of variation in the range of 0.5-5.0%
Initial Tolerance Concentration = 0.79 mg/L
Initial Wetland Influent Concentration = 0.49 mg/L
Initial Control Concentration = 0.41 mg/L
( ) Standard deviation

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Table 6.40. Zinc removal efficiencies (%).

	Tolerance				Wetland Influent				Control			
Time	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail	Bulrush	Wool grass	Soft rush	Cattail
9	99.16	98.97	99.64	98.25	94.21	96.11	98.33	89.54	85.57	96.33	98.78	88.75
18	98.97	99.01	99.49	97.94	93.30	95.11	97.74	88.32	80.93	86.55	93.15	80.93
27	98.85	98.59	99.37	97.81	92.44	94.25	96.06	87.46	86.80	92.67	90.95	76.28
36	98.73	98.57	99.32	97.70	91.63	93.44	95.25	86.65	88.26	90.22	86.55	71.88
45	98.62	98.51	99.20	97.58	90.81	94.70	95.02	85.83	85.33	88.02	79.71	67.48
54	98.50	98.44	99.02	97.46	90.00	94.48	94.57	85.02	76.28	88.02	75.31	63.08
63	98.38	98.12	99.10	97.35	89.18	93.98	94.43	84.20	84.84	85.33	73.35	58.68
72	98.27	98.42	98.98	97.23	88.37	93.84	92.89	83.39	83.62	82.15	68.95	54.28

Analysis of variance (ANOVA) was performed on the zinc removal efficiency data using SAS System, 5th Ed. (SAS Institute Inc., Cary, North Carolina). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA results (Table 6.41) showed that the plant type, time and initial zinc concentration have significant effects on the removal efficiency (P = 0.0001). There were significant interactions (P = 0.0001) between the parameters. The results of Duncan's Multiple Range test (Table 6.42) showed that the four plants used in this study (soft stem bulrush, wool grass, soft rush and cattail) were significantly different from one another in their ability to remove zinc and the three levels of the initial zinc concentrations were significantly different from one another at a 95% confidence level. However, the average removal efficiency during the periods 2 and 3 and 6 and 7 were not significantly different from one another at a 95 % confidence level. The zinc removal efficiencies for the four plants can be described as a function of time and initial zinc concentration (within the ranges studied) as follows:

Soft stem bulrush

$$RE_Z = 0.0215\ C_Z + 11.4\ T - 0.511\ T^2 + 0.00872\ T^3 - 0.000051\ T^4 \qquad R^2 = 0.82 \qquad (6.41)$$

Wool grass

$$RE_Z = -\ 0.0744\ C_Z + 12.8\ T - 0.583\ T^2 + 0.0102\ T^3 - 0.000060\ T^4 \qquad R^2 = 0.91 \qquad (6.42)$$

Soft rush

$$RE_Z = 0.0466\ C_Z + 13.7\ T - 0.631\ T^2 + 0.01100\ T^3 - 0.000065\ T^4 \qquad R^2 = 0.94 \qquad (6.43)$$

Cattail

$$RE_Z = 0.0051\ C_Z + 9.95\ T - 0.467\ T^2 + 0.00813\ T^3 - 0.000048\ T^4 \qquad R^2 = 0.81 \qquad (6.44)$$

Where:

RE_Z = Zinc removal efficiency (%)

C_Z = Initial zinc concentration (mg/L)

The zinc overall removal efficiency of the system during the first period were 99.16, 98.97, 99.64 and 98.25 % which decreased to 98.27, 98.42, 98.98 and 97.23 % by the last period (after 72 days) of the experiment in the compartments receiving the tolerance concentration for soft stem bulrush, wool grass, soft rush and cattail, respectively (Figure

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Table 6.41. Analysis of variance of the zinc removal efficiency.

Source	DF	SS	MS	F-Value	P
Total	191	19018.58	99.57		
Model	95	18951.51	199.49	285.51	0.0001
Plant Type (P)	3	2644.68	881.56	1261.70	0.0001
Time (T)	7	1492.78	231.26	305.21	0.0001
Concentration (C)	2	10290.56	5145.28	7363.99	0.0001
P x T	21	541.00	25.76	36.87	0.0001
P x C	6	1570.04	261.67	374.51	0.0001
T x C	14	1451.72	103.69	148.41	0.0001
P x T x C	42	960.73	22.87	32.74	0.0001
Error	96	67.08	0.69		

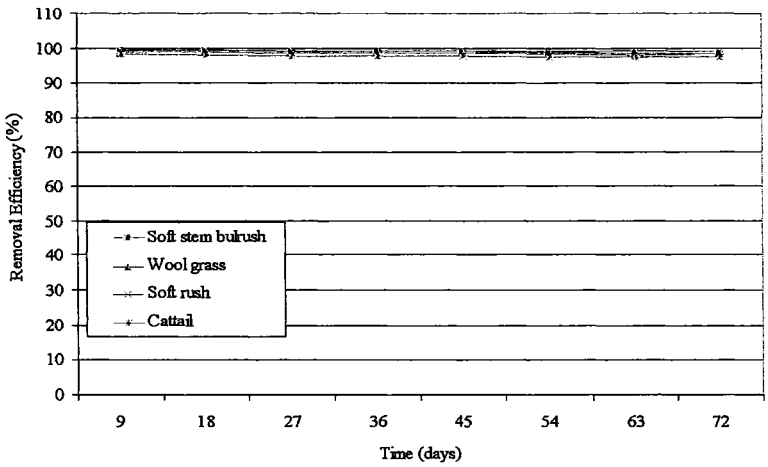
DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 0.99
CV = 0.92%

Table 6.42. Differences among the plant type, periods and initial zinc concentration.

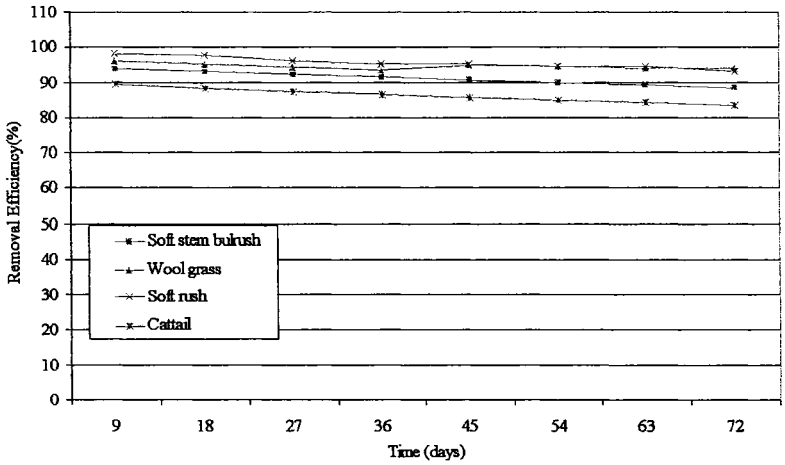
Parameter	Number of Observations	Zn Removal Efficiency	Duncan Grouping
Plant Type			
Soft stem bulrush	48	90.90	A
Wool grass	48	93.61	B
Soft rush	48	92.39	C
Cattail	48	84.02	D
Periods (days)			
1 (1-8)	24	95.07	A
2 (9-17)	24	92.24	B
3 (18-26)	24	92.32	B
4 (27-35)	24	91.04	C
5 (36-44)	24	89.57	D
6 (45-53)	24	87.93	E
7 (54-62)	24	87.53	E
8 (63-72)	24	86.14	F
Concentration (mg/L)			
Tolerance	64	98.48	A
Wetland Influent	64	91.52	B
Control	64	80.69	C

Means with the same letter are not significantly different from each other at a 95% confidence level.

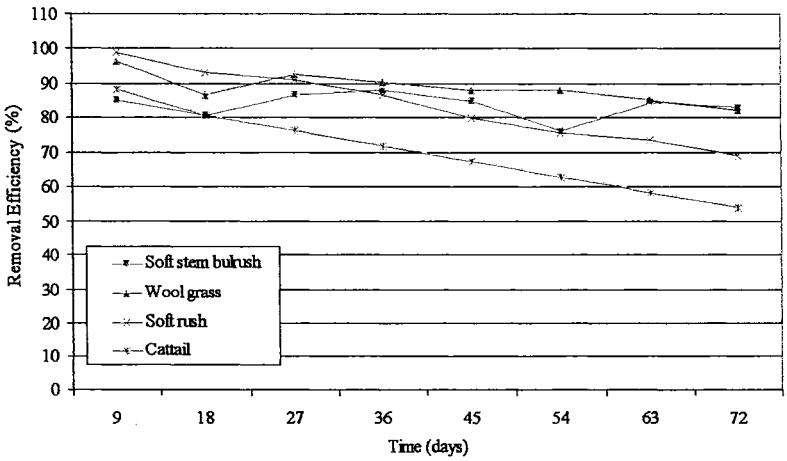
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(a) Tolerance Concentration



(b) Wetland Influent



(c) Control

Figure 6.49. Zinc removal efficiency trends for the four plants.

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6.49). The overall zinc removal efficiency of the system during the first period were 94.21, 96.11, 98.33 and 89.54 % which decreased to 88.37, 93.84, 92.89 and 83.39 % during the last period of the experiment in the compartments receiving the wetland influent concentration for soft stem bulrush, wool grass, soft rush and cattail, respectively.

The overall zinc removal efficiency of the compartments receiving wetland influent was less than the overall removal efficiency for compartments receiving the tolerance concentration for soft stem bulrush, soft rush and cattail. This is because (a) the plant uptake of zinc is a function of initial concentration as reported by Kamal et al. (2004) and (b) the siderophores, synthesized by the growth promoting bacteria found in the rhizosphere, solubilized the zinc in the soil in the vicinity of the root system at a rate much faster than the diffusion rate. Kirk (2002) reported that solubilization by acidification due to the siderophores accounted for at least 80% of the minerals taken up in both the unfertilized and fertilized soil.

Song et al. (2002) tested thirteen lab-scale constructed wetlands to treat synthetic, slightly basic, mine water containing 300 µg/L Zn. The average removal efficiency for zinc was 72%. A lower zinc removal efficiency of 55% was also observed due to Fe/Mn coprecipitation. O'Sullivan et al. (2003) monitored two experimental-scale treatment wetlands used to treat alkaline mine seepage with elevated zinc levels (2.0 mg/L) over a two-year period and reported successful (maximum) removal of zinc (98%). Nelson et al. (2004), Shutes et al. (2001) and Lorin (2001) reported zinc removal efficiencies of 77%. The removal efficiency of zinc in this study was in good agreement with those reported in the literature.

6.7.3.2 Zinc Plant Uptake and Mobility

The bioavailable zinc in the system is made of two portions: (a) the dissolved zinc in the water from fertilizers and reagents and (b) the zinc that already existed in the soil (phytoavailable portion). Therefore, the total plant uptake of zinc may include that in water plus some of the phytoavailable in the soil. The results (Table 6.43) showed that the zinc concentration in the plant tissues is directly proportional to the initial zinc concentration in the wastewater.

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Table 6.43. Pathways of zinc removal in the system.

Mn Concentration	Plant	Total Removal[+] (mg)	Plant Uptake		Precipitation	
			(mg)	(%)	(mg)	(%)
Control						
	Soft stem bulrush	82.4 (5.83)	10.8 (0.76)	13.11	71.5 (5.06)	86.77
	Wool grass	87.0 (5.59)	3.7 (0.26)	4.25	83.3 (5.89)	95.75
	Soft rush	81.8 (5.78)	17.5 (1.23)	21.40	64.3 (4.54)	78.60
	Cattail	68.9 (4.06)	10.6 (0.74)	15.38	58.3 (4.12)	84.62
Wetland Influent						
	Soft stem bulrush	67.8 (4.79)	30.3 (2.14)	44.69	37.5 (2.65)	55.31
	Wool grass	85.0 (6.67)	3.3 (0.23)	3.88	81.7 (5.77)	96.12
	Soft rush	90.6 (6.41)	65.3 (4.61)	72.08	25.3 (1.78)	27.92
	Cattail	41.6 (2.45)	29.3 (2.07)	70.40	11.9 (0.84)	29.60
Tolerance Concentration						
	Soft stem bulrush	143.1 (10.12)	45.9 (3.25)	32.08	97.3 (6.88)	67.99
	Wool grass	139.3 (8.21)	6.6 (0.46)	4.74	132.7 (9.38)	95.26
	Soft rush	164.6 (11.62)	32.8 (2.31)	19.93	131.8 (9.31)	80.07
	Cattail	100.00 (6.43)	60.7 (4.29)	57.59	44.6 (3.15)	42.41

The values are the average of 3 replicates with a coefficient of variation in the range of 2.0-8.0%

\+ Total manganese removal after 72 days

( ) Standard deviation

The accumulation of zinc in various plant tissues are shown in Tables 6.44 and 6.45. The highest amount of zinc accumulated in the root tissues was in soft stem bulrush with concentrations of 45, 38 and 27 mg/kg and the lowest was in wool grass with concentrations of 13, 12 and 10 mg/kg in the compartments receiving the tolerance concentration, wetland influent and control, respectively. The highest amount of zinc accumulated in the leaf tissues was in soft rush with concentrations of 29, 24 and 18 mg/kg and the lowest was in soft stem bulrush with concentrations of 9, 6 and 4 mg/kg in the compartments receiving the tolerance concentration, wetland influent and control, respectively. The highest amount of zinc accumulated in the flower tissues was in soft stem bulrush with concentrations of 167, 100 and 55 mg/kg and the lowest was in wool grass with concentrations of 66, 44 and 27 mg/kg in the compartments receiving the tolerance concentration, wetland influent and control, respectively. Cumulatively, the highest zinc accumulated in the total plant tissues was in soft stem bulrush with concentrations of 221, 152 and 86 mg/kg and the lowest was in cattail with zinc concentrations of 39, 28 and 13 mg/kg in the compartments receiving tolerance concentration, wetland influent and control, respectively.

Analysis of variance (ANOVA) was performed on the total zinc accumulation data using SAS System, 5th Ed. (SAS Institute Inc., Cary, North Carolina). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA analysis (Table 6.46) showed that the plant type and the initial zinc concentration have significant effects on zinc accumulation ($P = 0.0001$). There were significant interactions ($P = 0.0001$) between the parameters. The results of Duncan's Multiple Range test (Table 6.47) showed that the four plants used in this study (soft stem bulrush, wool grass, soft rush and cattail) were significantly different from one another in their utility to accumulate zinc and the three levels of initial zinc concentrations were significantly different from one another at a 95% confidence level. The zinc accumulation in the tissues of the four plants as a function of initial zinc concentration and time can be described by the following equations:

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Table 6.44. Zinc concentration in mg/kg in wetland plant tissues.

	Bulrush									Wool grass											
	Roots			Leaves			Flowers			Roots			Stem			Leaves			Flowers		
Time	M	W	C	M	W	C	M	W	C	M	W	C	M	W	C	M	W	C	M	W	C
0	18.0	18.0	21.0	1.1	1.2	1.4	21.0	24.0	27.0	5.2	2.9	3.5	2.6	2.4	1.7	2.9	3.1	2.7	9.0	12.5	10.2
9	25.0	23.4	20.3	5.1	1.5	1.1	78.6	25.9	35.7	6.1	3.9	4.3	2.9	2.7	2.3	4.2	4.0	3.3	15.3	16.0	11.5
18	24.8	22.5	19.5	5.9	2.4	2.0	100.0	45.5	34.0	6.9	4.9	5.2	3.2	3.1	2.6	5.6	4.7	3.9	24.0	19.5	13.8
27	31.6	28.0	25.9	6.2	3.8	2.4	98.2	70.1	35.4	7.8	5.9	6.0	3.4	3.4	3.0	6.5	5.9	4.1	32.0	23.0	14.1
36	35.6	27.0	24.0	7.0	4.2	2.7	117.5	67.0	41.0	8.7	6.9	6.0	3.8	3.7	3.5	8.3	6.5	5.1	34.3	26.5	16.0
45	37.0	33.7	26.8	7.5	4.8	3.4	124.0	85.9	50.2	9.5	8.0	6.3	4.4	4.1	3.9	10.3	7.8	6.0	38.0	30.0	19.4
54	41.0	31.5	26.7	8.2	4.8	3.4	144.0	88.5	48.0	10.4	9.0	7.7	4.7	4.5	4.4	11.0	8.2	6.2	47.0	33.5	21.3
63	46.0	33.8	26.4	8.3	4.9	3.6	148.8	90.3	51.5	11.3	10.0	8.8	5.1	4.8	4.6	12.8	9.6	7.4	56.9	37.0	24.0
72	45.0	36.0	27.0	9.0	6.0	4.0	167.0	110.0	55.0	13.0	12.0	10.1	6.0	5.5	5.0	15.0	11.5	8.0	66.0	44.0	26.9

T Tolerance Concentration
W Wetland Influent
C Control

Table 6.45. Zinc concentration in mg/kg in wetland plant tissues.

	Soft rush									Cattail					
	Roots			Leaves			Flowers			Roots			Leaves		
Time	M	W	C	M	W	C	M	W	C	M	W	C	M	W	C
0	6.5	5.6	5.8	8.5	7.8	5.3	24.0	21.0	26.0	2.3	2.5	2.9	2.4	2.9	2.6
9	8.6	8.6	7.8	15.3	13.0	8.2	34.0	33.8	38.0	9.4	4.1	3.1	3.2	3.4	2.9
18	9.1	7.6	7.2	16.4	13.5	8.2	50.5	38.0	32.7	13.8	7.7	3.7	4.1	3.9	3.1
27	11.2	9.4	7.6	18.9	15.5	13.0	56.3	44.4	40.9	17.7	10.4	4.3	4.9	4.4	3.4
36	11.6	9.6	8.7	22.3	14.8	11.2	64.0	51.5	47.4	19.2	13.4	4.5	5.8	4.9	3.7
45	14.5	12.1	9.6	23.0	15.8	14.2	66.0	54.9	47.4	21.4	17.4	5.5	6.6	5.5	3.9
54	14.2	11.5	10.1	22.2	20.2	14.1	68.0	57.8	44.5	24.0	18.5	6.3	7.5	6.0	4.2
63	16.7	14.7	11.1	27.3	20.0	16.4	75.5	54.4	43.9	26.2	19.7	7.1	8.3	6.5	4.5
72	18.0	14.5	11.0	29.0	23.5	18.0	79.0	64.0	49.0	29.0	20.5	8.4	10.0	7.5	5.0

T Tolerance Concentration
W Wetland Influent
C Control

Table 6.46. Analysis of variance of the zinc accumulation in plant tissues.

Source	DF	SS	MS	F-Value	P
Total	23	11416.73	496.38		
Model	11	11349.18	1031.74	183.29	0.0001
Plant Type (P)	2	3369.55	1684.78	299.31	0.0001
Concentration (C)	3	4516.76	1505.59	267.48	0.0001
P x C	6	3462.87	577.15	102.53	0.0001
Error	12	67.55	5.63		

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 0.99
CV = 8.56%

Table 6.47. Differences among the plant type and initial zinc concentration.

Parameter	Number of Observations	Total Zn in Plant Tissues	Duncan Grouping
Plant Type			
Soft stem bulrush	6	30.45	A
Wool grass	6	4.76	B
Soft rush	6	40.46	C
Cattail	6	35.21	D
Iron Concentration (mg/L)			
Tolerance	8	38.33	A
Wetland Influent	8	33.66	B
Control	8	11.18	C

Means with the same letter are not significantly different from each other at 95% confidence level.

Soft stem bulrush

$$Z_R = 0.399\,T + 2.07\,C_Z - 0.0185\,C_Z^2 \qquad R^2 = 0.87 \qquad (6.45)$$

$$Z_L = 0.066\,T + 0.187\,C_Z - 0.0185\,C_Z^2 \qquad R^2 = 0.91 \qquad (6.46)$$

$$Z_F = 1.07\,T + 3.97\,C_Z - 0.0322\,C_Z^2 \qquad R^2 = 0.88 \qquad (6.47)$$

$$Z_{TO} = 1.54\,T + 86.00\,C_Z - 0.0522\,C_Z^2 \qquad R^2 = 0.88 \qquad (6.48)$$

Wool grass

$$Z_R = 0.131\,T + 0.364\,C_Z - 0.00322\,C_Z^2 \qquad R^2 = 0.90 \qquad (6.49)$$

$$Z_S = 0.0639\,T + 0.223\,C_Z - 0.00204\,C_Z^2 \qquad R^2 = 0.99 \qquad (6.50)$$

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$Z_L = 0.125\ T + 0.327\ C_Z - 0.00284\ C_Z^2$ $R^2 = 0.92$ (6.51)

$Z_F = 0.460\ T + 1.40\ C_Z - 0.0120\ C_Z^2$ $R^2 = 0.87$ (6.52)

$Z_{TO} = 0.780\ T + 2.32\ C_Z - 0.0201\ C_Z^2$ $R^2 = 0.91$ (6.53)

Soft rush

$Z_R = 0.163\ T + 0.670\ C_Z - 0.00601\ C_Z^2$ $R^2 = 0.90$ (6.54)

$Z_L = 0.247\ T + 1.02\ C_Z - 0.00897\ C_Z^2$ $R^2 = 0.91$ (6.55)

$Z_F = 0.736\ T + 3.03\ C_Z - 0.0270\ C_Z^2$ $R^2 = 0.85$ (6.56)

$Z_{TO} = 1.15\ T + 4.72\ C_Z - 0.0420\ C_Z^2$ $R^2 = 0.90$ (6.57)

Cattail

$Z_R = 0.184\ T + 0.808\ C_Z - 0.00686\ C_Z^2$ $R^2 = 0.88$ (6.58)

$Z_L = 0.077\ T + 0.316\ C_Z - 0.00282\ C_Z^2$ $R^2 = 0.88$ (6.59)

$Z_{TO} = 0.261\ T + 1.12\ C_Z - 0.00968\ C_Z^2$ $R^2 = 0.90$ (6.60)

Where:

Z = Zinc concentration in tissues (mg/kg)

Peltier et al. (2003) collected common reeds (*Phragmites*) which grew along the edge of the waterline of a metal-contaminated wetland and found that the concentration of total zinc in water was 8.30 mg/L while the concentrations of zinc in roots, stem and leaves were 362, 30 and 58 mg/kg, respectively. Sanchez et al. (1994) sampled Aquatic moss (*Brachythecium rivulare*), Soft rush (*Juncus effusus*) and Broad leaf cattail (*Typha latifolia*) from different sites near an old lead-zinc mine and found that the total zinc concentrations in the sediment were 405, 3080 and 8750 mg/kg while the zinc concentrations in the leaves were 4570, 290 and 300 mg/kg for the aquatic moss, soft rush and board leaf cattail, respectively. Kumar et al. (1995) tested *B. juncea* cultivar 182921 grown for 14 days in sand/perlite mixture supplemented with 100 mg/L Zn supplied as $Zn(NO_3)_2.6H_2O$ and found the zinc concentration at the shoot at the end of the experiment was 1723 mg/kg. Samecka-Cymerman and Kempers (2001) collected plant samples (*Phyragmites australis, Potamogeton natans, Iris pseudoacorus, Juncus effusus, Drepanocladus aduncus, Juncus bulbosus, Phalaris arundinacea, Carex remota,* and *Calamagrostis epigeios*) from 9 different contaminated sites around former open cut

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brown coal mine and found that concentrations of the zinc in the leaves of the plants increased with the increase in the zinc concentrations in the wastewater.

It appears from the results obtained from the present study that the four plants used were inferior accumulators of zinc compared to the plants reported in the literature. The reasons of this inferiority may be due to (a) the amount of zinc found in the water or sediments was higher than the amount of zinc supplied to the plants used in this experiment and (b) the Zn-Fe antagonism. Kabata-Pendios and Pendios (1992) stated that soluble forms of Zn are readily available to plants and the uptake of Zn has been reported to be linear with concentration in the nutrient solution and in soils. Also, Zn-Fe antagonism is widely known. There are two possible mechanisms of this interaction (a) the competition between Zn^{2+} and Fe^{2+} in the uptake processes and the interference in chelation processes during the uptake and translocation of Fe from roots to tops and (b) Fe decreases Zn absorption (Cohen et al., 1998).

Zinc showed mixed results (Table 6.48) between high mobility and low mobility in the wetland plants used in the experiments. In wool grass and soft rush, the leaf tissues accumulated significantly greater concentrations of metals than roots, indicating high zinc mobility once inside the plant. Conversely, in soft stems bulrush and cattail, the root tissues accumulate significantly greater concentrations of metals than shoots, indicating high plant availability of zinc as well as its limited mobility once inside the plant. The rate of Zn absorption differed greatly among plant species. In the literature, disagreement exists to whether Zn uptake is active or passive metabolically. Moore (1972) and Loneragan (1975) suggest that Zn uptake is mostly metabolically controlled but it can also be a part of a non-metabolic process. Kochain (1991) reported that fractions of Zn bound to light organic compounds in xylem fluids and in other plant-tissue extracts may suggest its high mobility in the plant. Tinker (1981) reported that the portion of Zn bound in complexes with a negative charge constitutes more than half of the total metal present in the plant. Hacisalihoglu and Kochain (2003), Hacisalihoglu et al. (2001) and Hacisalihoglu (2002) regard Zn as highly mobile, while Scheffer et al. (1999) and Ylaranta et al. (1995) consider Zn to have intermediate mobility.

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Table 6.48. Zinc uptake and distribution in plant tissues.

Concentration	Total Uptake* (mg)	Zinc Distribution‡				Translocation Factor +
		Root (mg)	Stem (mg)	Leaves (mg)	Flowers (mg)	
Soft stem bulrush						
Tolerance	45.9 (3.25)	37.6 (2.6)	NA	4.8 (0.34)	3.5 (0.25)	0.22
Wetland Influent	30.3 (2.14)	25.2 (1.7)	NA	3.0 (0.21)	2.1 (0.15)	0.20
Control	10.8 (0.76)	10.8 (2.0)	NA	2.0 (0.15)	1.1 (0.12)	0.29
Wool grass						
Tolerance	6.6 (0.46)	2.2 (0.15)	0.19 (0.01)	2.9 (0.20)	1.4 (0.09)	2.36
Wetland Influent	5.5 (0.23)	2.5 (0.18)	0.17 (0.01)	2.0 (0.14)	0.7 (0.05)	1.15
Control	3.7 (0.26)	1.8 (0.03)	0.15 (0.02)	1.5 (0.09)	0.5 (0.03)	1.19
Soft rush						
Tolerance	32.8 (2.31)	13.8 (0.9)	NA	16.8 (1.18)	2.2 (0.15)	1.38
Wetland Influent	25.3 (4.61)	10.8 (0.8)	NA	12.8 (0.91)	1.7 (0.12)	1.34
Control	17.5 (1.23)	8.3 (0.5)	NA	9.9 (0.51)	1.3 (0.05)	1.35
Cattail						
Tolerance	44.6 (4.29)	36.7 (2.5)	NA	6.5 (0.3)	NA	0.17
Wetland Influent	29.3 (2.07)	25.6 (1.7)	NA	4.8 (0.2)	NA	0.18
Control	10.6 (0.74)	10.0 (0.2)	NA	3.1 (0.1)	NA	0.31

‡ The values are the average of 8 replicates with a coefficient of variation in the range of 2-6%

* Total iron accumulation after 72 days

\+ Translocation factor: concentration of iron in the above ground tissues divided by below ground tissues.

NA Not applicable

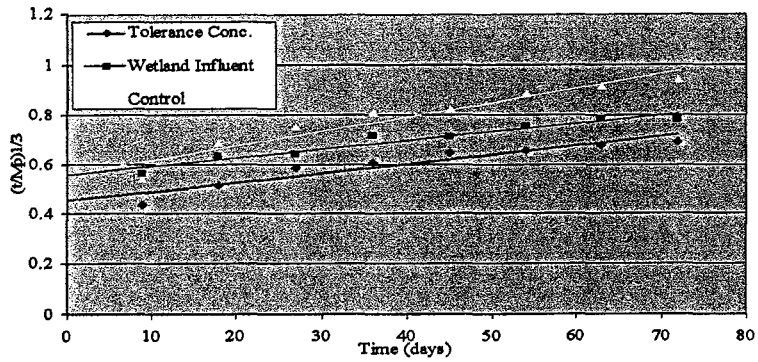
6.7.3.3 Zinc Uptake Kinetic Parameters

The uptake of dissolved zinc by wetland plants can be expressed by a first-order kinetic model (Equation 5.15). The concentration of zinc in plant at any time is a function of the maximum concentration of metal that can accumulate in the plant and specific uptake rate as shown in Equation (5.20). To determine the specific uptake rate (k) and maximum iron uptake (M_M) in Equation (5.20), the values of A and B were obtained graphically for various plant-zinc concentration combinations according to the procedure described by Vlyssides et al. (1997) by plotting $(t/M_p)^{1/3}$ vs. t in Equation (5.31) as shown in Figure 6.50. The results are shown in Table 6.49. Table 6.50 presents the linear form of Equation (5.31) for zinc uptake by various plants in different initial zinc concentrations. Equations (5.41) and (5.44) were then used to determine the maximum concentrations (M_M) of zinc that can be accumulated by the wetland plants at the end of the experimental period (72 days) and the specific uptake rates (k), respectively. The results are shown in Table 6.51.

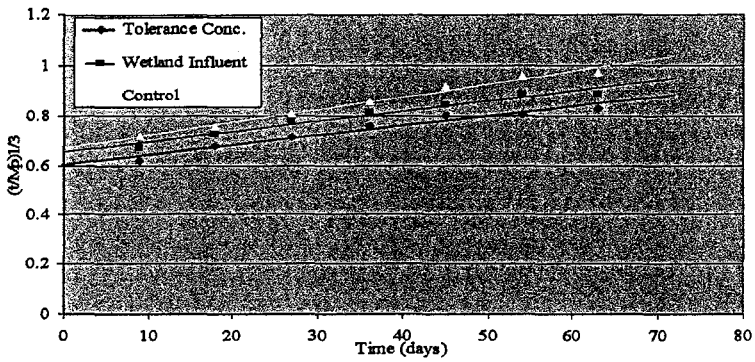
The specific zinc uptake rate was 0.018, 0.025 and 0.033 d^{-1}, 0.027, 0.028 and 0.032 d^{-1}, 0.025, 0.033 and 0.037 d^{-1} and 0.027, 0.036, 0.045 d^{-1} for broad leaved cattail, soft rush, wool grass and soft stem bulrush in the compartments receiving tolerance concentration, wetland influent and control, respectively. The results showed that the specific zinc uptake rate was affected by the initial zinc concentration as shown in Figure 6.51. Vlyssides et al. (2001) reported that the specific metal uptake rates are affected by the initial metal concentrations in the solution. It also appears from the results that all plants used in this study showed signs of toxicity because the k value of each plant decreased when zinc concentration increased above 0.409 mg/L.

The relationship between Zn initial concentration and k can be described by the equations shown in Table 6.52. Rout and Das (2003) reported that Zn concentrations for the incidence of Zn toxicity can be as low as 0.2 mg/L. The first portions of all Zn specific uptake curves (the range of 0-0.35 mg/L) are similar and can be described by equations similar to those used for iron uptake. However, further investigation should be done on the initial zinc concentration in range of 0 - 0.4 in order to accurately establish the Zn toxicity limit.

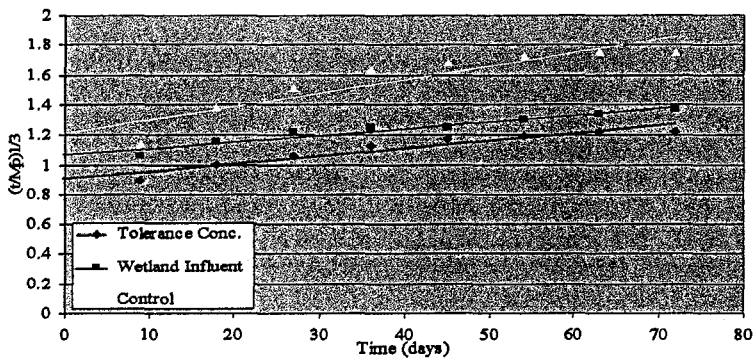
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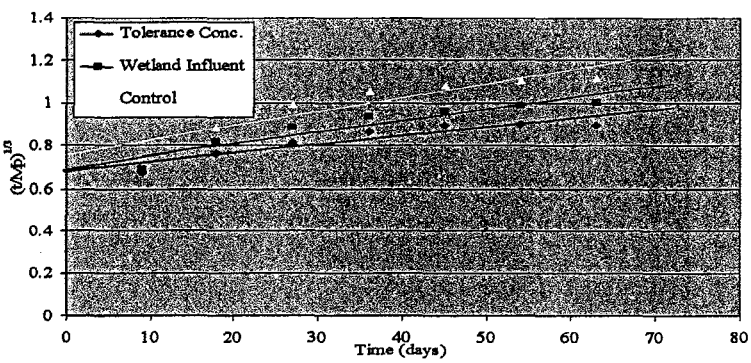
(a) Soft stem bulrush



(b) Soft rush



(c) Board leaved cattail



(d) Wool grass

Figure 6.50. Graphical determination of A and B for zinc in plants at different initial concentrations.

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Table. 6.49. Values of A and B in Equation (5.31).

Plant	Concentration	A	B
Broad leaved cattail			
	Maximum	0.9044	0.0051
	Wetland	1.0668	0.0044
	Control	1.2114	0.0090
Wool grass			
	Maximum	0.6886	0.0040
	Wetland	0.7091	0.0054
	Control	0.7668	0.0065
Soft stem bulrush			
	Maximum	0.4500	0.0037
	Wetland	0.5580	0.0035
	Control	0.5600	0.0058
Soft rush			
	Maximum	0.6049	0.0039
	Wetland	0.6554	0.0041
	Control	0.6767	0.0050

Table 6.50. Linear form of Equation (5.31) for zinc uptake.

Plant	Concentration	Equation	R^2
Broad leaved cattail			
	Maximum	$(t/M_p)^{1/3} = 0.9044 + 0.0051\ t$	0.91
	Wetland	$(t/M_p)^{1/3} = 1.0668 + 0.0044\ t$	0.94
	Control	$(t/M_p)^{1/3} = 1.2114 + 0.0090\ t$	0.85
Wool grass			
	Maximum	$(t/M_p)^{1/3} = 0.6886 + 0.0040\ t$	0.86
	Wetland	$(t/M_p)^{1/3} = 0.7091 + 0.0054\ t$	0.89
	Control	$(t/M_p)^{1/3} = 0.7668 + 0.0065\ t$	0.86
Soft stem bulrush			
	Maximum	$(t/M_p)^{1/3} = 0.4500 + 0.0037\ t$	0.90
	Wetland	$(t/M_p)^{1/3} = 0.5580 + 0.0035\ t$	0.93
	Control	$(t/M_p)^{1/3} = 0.5600 + 0.0058\ t$	0.92
Soft rush			
	Maximum	$(t/M_p)^{1/3} = 0.6049 + 0.0039\ t$	0.95
	Wetland	$(t/M_p)^{1/3} = 0.6554 + 0.0041\ t$	0.96
	Control	$(t/M_p)^{1/3} = 0.6767 + 0.0050\ t$	0.98

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Table 6.51. Zinc kinetic uptake parameters (k, M_M) for wetland plants.

Plant	Concentration	k (d^{-1})	M_M (mg/kg)
Broad leaved cattail			
	Maximum	0.018	39.95
	Wetland	0.025	33.28
	Control	0.033	12.62
Wool grass			
	Maximum	0.025	87.87
	Wetland	0.033	61.38
	Control	0.037	43.61
Soft stem bulrush			
	Maximum	0.027	222.45
	Wetland	0.036	152.94
	Control	0.045	91.63
Soft rush			
	Maximum	0.027	116.79
	Wetland	0.028	94.64
	Control	0.032	72.79

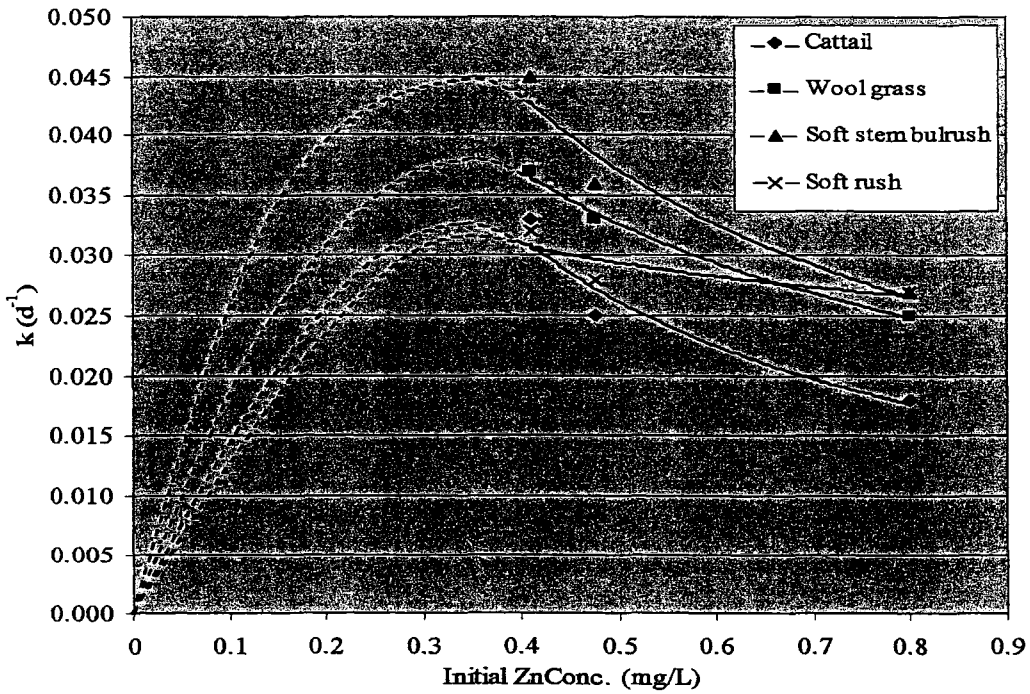


Figure 6.51. Effect of initial zinc concentrations on the specific uptake rate for each plant.

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Table 6.52. The relationship between specific uptake rate and initial zinc concentrations.

Plant	k (d^{-1})	
	0 – 409 mg/L	0.409 - 0.799 mg/L
Broad leaved cattail	$k = 0.0616\ C_i^{0.6973}$ $R^2 = 0.99$	$k = 0.0146\ C_i^{-0.8357}$ $R^2 = 0.94$
Wool grass	$k = 0.0699\ C_i^{0.7111}$ $R^2 = 0.99$	$k = 0.0219\ C_i^{-0.5728}$ $R^2 = 0.99$
Soft stem bulrush	$k = 0.0868\ C_i^{0.7346}$ $R^2 = 0.99$	$k = 0.0227\ C_i^{-0.7096}$ $R^2 = 0.95$
Soft rush	$k = 0.0595\ C_i^{0.6936}$ $R^2 = 0.99$	$k = 0.0146\ C_i^{-0.2067}$ $R^2 = 0.85$

C_i initial zinc concentration

The results also indicated that the maximum concentrations of zinc accumulated in the plant was 222.45 mg/kg for soft stem bulrush in the compartment receiving tolerance concentration while the lowest zinc accumulated in the plant was 12.62 mg/kg for broad leaved cattail in control compartment. The maximum concentration of zinc that can be accumulated in plants was also affected by the initial zinc concentration as shown in Figure 6.52.The relationships can be described by the equations shown in Table 6.53. The intercept values in these equations are the initial values of zinc concentration in these plants before the start of the experiment. The predicted maximum concentrations were plotted against the experimental maximum concentrations obtained at the end of the experiment for zinc as shown in Figure 6.53. The results showed that the model is capable of predicting the experimental data with relatively high confidence (R^2 of 0.99).

Table 6.53. The relationship between maximum zinc concentration and initial zinc concentrations.

Plant	Equation	R^2
Broad leaved cattail	$M_M = 5.20 + 59.88\ C_i^{1.37}$	0.82
Wool grass	$M_M = 19.73 + 111.66\ C_i^{0.96}$	0.99
Soft stem bulrush	$M_M = 44.23 + 301.90\ C_i^{0.63}$	0.99
Soft rush	$M_M = 36.66 + 137.70\ C_i^{1.17}$	0.99

C_i initial zinc concentration
M_M Maximum accumulated zinc in plant tissues by the end of the experiment (72 days)

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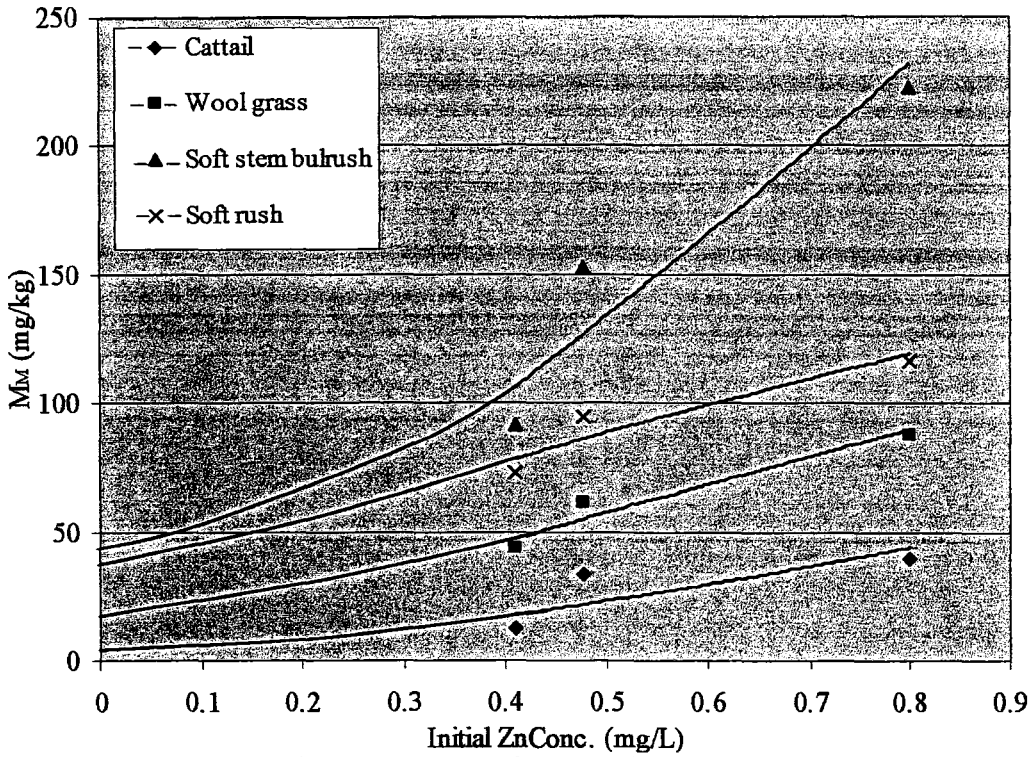


Figure 6.52. Effect of initial zinc concentrations on the maximum zinc concentration for each plant.

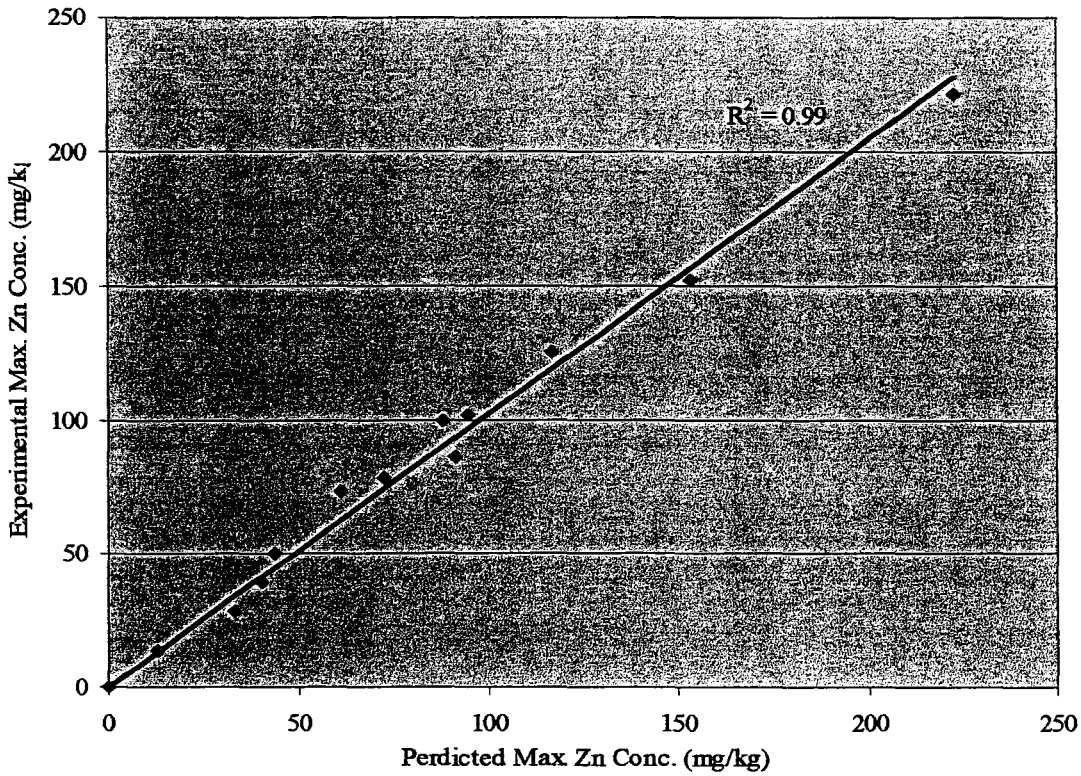


Figure 6.53. Maximum predicted and experimental concentrations of zinc accumulated in wetland plants.

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6.7.4 Plant Selectivity to Heavy Metals

The selectivity for heavy metal for all plants was iron, manganese and zinc (Table 5.54). The selectivity of plant for iron was soft stem bulrush, cattail, wool grass and soft rush while for manganese and zinc was soft stem bulrush, soft rush, wool grass and cattail, respectively.

Table 5.54. Plant accumulation of heavy metals.

Plant	Accumulation (mg/kg)		
	Iron	Manganese	Zinc
Soft stem bulrush	22798	1202	43.2
Wool grass	10547	921	19.7
Soft rush	7686	1001	39.0
Cattail	19959	910	4.7

6.8 Conclusions

1. It is clear from the results obtained from the present study that the four plants used were superior accumulators of iron but inferior accumulators of manganese and zinc.
2. The plant type, time and initial concentrations of heavy metals have significant effects on the plant uptake and the removal efficiency of these metals.
   (a) The four plants used in this study (soft stem bulrush, wool grass, soft rush and cattail) were significantly different from one another in their ability to remove iron, manganese and zinc from the wastewater.
   (b) The iron, manganese and zinc concentrations in the plant tissues were directly proportional to their initial concentrations in the wastewater.
   (c) Due to the high affinity of the four plants for iron and manganese, the plants in the compartments receiving the control and wetland influent utilized some of the phytoavailable portions found in the soil. No zinc was removed from the soil by the plants

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(d) The highest amounts of iron, manganese and zinc accumulated in the total plant tissues were in cattail, soft stem bulrush and soft stem bulrush and the lowest amounts were in soft rush, wool grass and cattail, respectively.

3. Plant species differ widely in their ability to translocate and accumulate heavy metals in various tissues.
   (a) The roots accumulated significantly greater concentrations of iron than the shoots indicating high plant availability of the iron as well as its limited mobility once inside the plant. The highest amount of iron accumulated in the root tissues was in cattail and the lowest amount was in soft rush.
   (b) The leaves accumulate significantly greater concentrations of manganese than the roots, indicating high plant availability of manganese and mobility once inside the plant. The highest amounts of manganese accumulated in the leaf tissues was in cattail and the lowest amount was in wool grass.
   (c) In wool grass and soft rush, the leaf tissues accumulated significantly greater concentrations of zinc than the roots while in soft stems bulrush and cattail, the root tissues accumulated significantly greater concentrations of zinc than the shoots. The highest amount of zinc accumulated in the flower tissues was in soft stem bulrush and the lowest amount was in wool grass.
4. The maximum concentrations of iron, manganese and zinc that can be accumulated at the end of the experimental period (72 days) in plants are affected by their initial concentrations.
5. Cattail did not show any sign of iron toxicity while the other three plants showed signs of toxicity. All four plants used in this study showed signs of Mn and Zn toxicity.
6. A first-order kinetic model was used to determine iron, manganese and zinc uptake by wetland plants. The model was capable of predicting the experimental data with a relatively high confidence (R^2 of 0.98, 0.90 and 0.99 for Fe, Mn and Zn, respectively).
7. The selectivity for heavy metal for all plants was iron, manganese and then zinc.

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6.9 Recommendations

1. In order to precisely determine the contribution of the phytoavailable iron, manganese and zinc in the soil of those accumulated in the plant tissues, Fe, Mn and Zn isotopes should be used as the initial metals concentration in the solution.

2. In order to accurately describe the mechanism and establish the limits of Fe, Mn and Zn toxicity in the wetland plants, the initial concentration of these metals in the solution should be investigated within the range of 0 to 0.817, 0 to 0.409 and 0 to 0.4 mg/L for Fe, Mn and Zn, respectively.

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7. TREATMENT OF LANDFILL LEACHATE USING AEROBIC LIMESTONE/SANDSTONE FILTERS

7.1 Introduction

Landfill leachate is generated when water from rain and snow percolates through the waste material in a landfill. Contaminants in leachate include organic matter, heavy metals and mineral oils. Leachate is one of the main environmental concerns associated with landfill management because it has the potential to damage the quality of both the ground and surface waters (Aziz et al, 2004). In 2000, a 4000 m^2 surface flow constructed wetland was established in the Burnside Industrial Park, Dartmouth, Nova Scotia to treat landfill leachate from the Burnside and Black Lake former landfills, located at the east and west corners of Akerley Boulevard and Burnside Drive, respectively, in order to protect natural waterways such as Wright's Brook, Enchanted Lake and Flat Lake (Ghaly and Côté, 2001). The water entering the wetland contained an abundance of heavy metals, specifically iron and manganese. The average concentrations of iron and manganese in the water entering the wetland were 6.600 mg/L and 1.8 mg/L, respectively. The Canadian Water Quality Guidelines for the Protection of Aquatic Life (CCME, 2002) sets allowable limits for iron and manganese to 0.3 mg/L and 0.2 mg/L, respectively. To date, the constructed wetland has not been able to produce an outlet water quality that meets these standards. Furthermore, some of the wetland plants accumulated high concentrations of these elements in their flowers and leaves which were might be used as food by wildlife. Therefore, the aim of this study was to use a passive technology to partially treat the wastewater before it enters the wetland to reduce the influent concentrations of Fe and Mn.

Conventional water treatment systems that remove iron and manganese from wastewater involve the addition of alkaline chemicals (such as lime, sodium hydroxide and sodium carbonate) to the water. Alkali addition causes the pH of the water to increase and the dissolved metals to precipitate out of solution (Ziemkiewicz et al, 1997, and Gazea et al, 1996). These active systems usually have increased costs associated with operation and

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maintenance, purchase of chemical reagents and disposal of metal laden sludge (Ziemkiewicz et al, 1997, and Gazea et al, 1996). According to Cravotta III and Trahan (1999) and Hedin et al (1994), passive treatment systems that use limestone have become very popular for treating landfill leachates and mine drainage because the systems are inexpensive to construct and maintain and limestone is a cheap source of alkalinity, especially in coal mining regions.

7.2 Objectives

The aim of this study was to develop a passive technology, consisting of filters composed of a mixture of limestone and sandstone rocks, for the pretreatment of landfill leachates before they enter the wetland system. The specific objectives were:

1. To evaluate the effectiveness of limestone and limestone/sandstone filters in removing dissolved iron and manganese from landfill leachate under batch conditions.
   (a) to evaluate the impact of sandstone/limestone ratio on the removal efficiency of Fe and Mn
   (b) to evaluate the impact of temperature (20, 15, 10 and 5°C) on the effectiveness of limestone and limestone/sandstone filters in removing Fe and Mn.
   (c) to determine the suitability of the treated wastewater for aquatic life in the wetland as measured by its final pH.
   (d) to determine the specific removal rate for Fe and Mn under various conditions
2. To evaluate the effectiveness of the limestone/sandstone filters in removing dissolved iron and manganese from landfill leachate under continuous operation.
3. To develop a mathematical model capable of predicting the wastewater quality of the outlet of limestone/sandstone filters.
4. To design a field scale limestone/sandstone filters to treat landfill leachate.

7.3 Experimental Apparatus

7.3.1 Tank Batch Experiment

The experimental setup shown in Figure 7.1 consisted of six holding tanks each equipped with an aeration system. Three boxes, constructed from 2.5 cm thick plywood, were used

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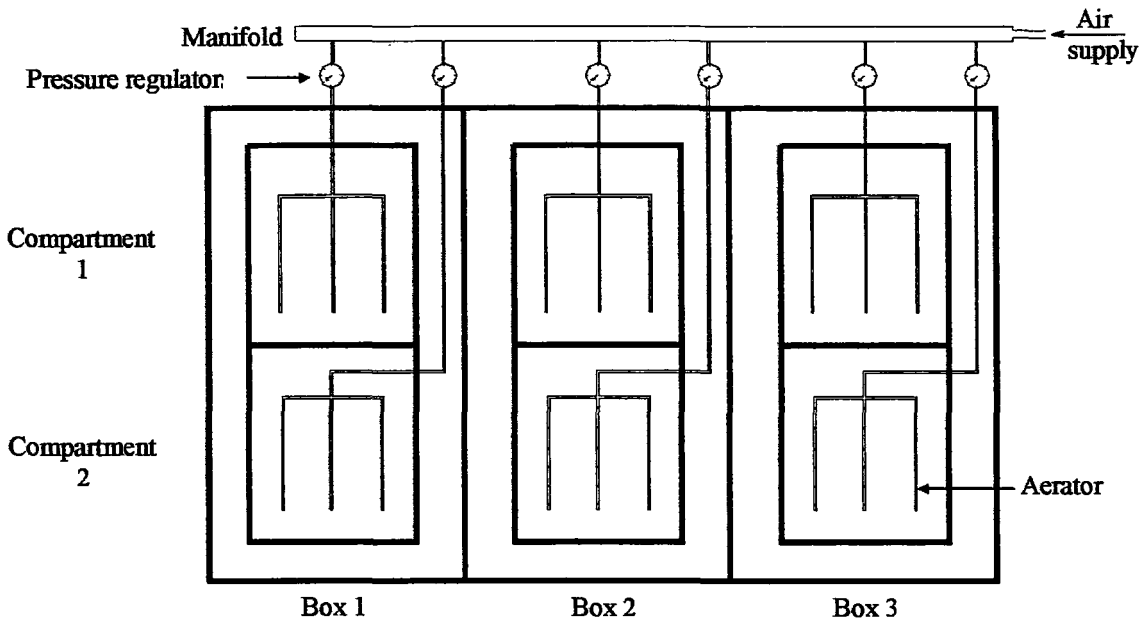


Figure 7.1. Tank experimental setup.

in this experiment. Each box had dimensions of 60 x 120 x 80 cm and housed two holding tanks (compartments), each had dimensions of 38 x 45 x 40 cm. One tank (compartment 1) in each box received limestone, while the other tank (compartment 2) received a mixture of limestone and sandstone of 1:1 ratio. The main precipitation reaction for iron and manganese is oxidation. Therefore, an aeration unit was installed in the bottom of each holding tank to provide oxygen. The air was provided from the main laboratory air supply to a manifold with six outlets. Each outlet was connected to a pressure regulator (Model 129121/510, ARO, Bryan, Ohio), which was connected to the aerator located in each holding tank. Each aerator consisted of a main tube (26.5 cm long) with three perforated stainless steel laterals (30 cm in length and 0.6 cm in diameter) coming off it at right angles to the main. Tygon tubing of 0.75 cm outside diameter was used to connect the main air supply, manifold and aeration unit.

7.3.2 Beaker Batch Experiment

The experimental setup shown in Figure 7.2 consisted of six holding beakers each was equipped with an aeration system. Each beaker had a 12.5 cm diameter and a 15 cm

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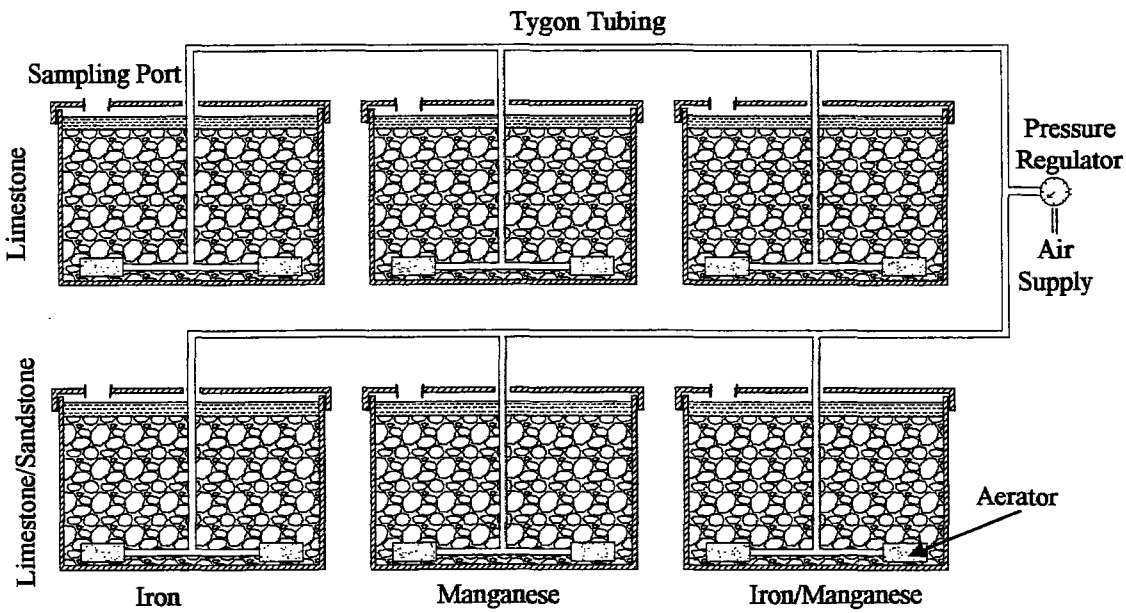


Figure 7.2. Beaker experimental setup.

height. Three beakers received limestone while the other three beakers received a mixture of limestone and sandstone of 1:1 ratio. An aeration unit was installed at the bottom of each beaker. The air was provided from the main laboratory air supply to a manifold with six outlets. Each outlet was connected to a pressure regulator (Model 129121/510, ARO, Bryan, Ohio), which was connected to the aerator located in each holding beaker. Tygon tubing of 0.75 cm outside diameter was used to connect the main air supply, manifold and aeration unit.

7.3.3 Continuous Flow Experiment

The continuous flow experimental setup shown in Figure 7.3 consisted of four reactors, four feeding tanks and peristaltic pump. Four tanks of a 10 cm diameter and a 30 cm height each were used. Two reactors received a mixture of limestone and sandstone of 1:1 ratio while the other two reactors received a mixture of limestone and sandstone of 1:2 ratio. Variable speed modular peristaltic pump with Masterflex® precision tubing (Digi-Staltic, Masterflex®, Model No. 7525-30, with Head Model No. 7024-20, and Tubing No. 6404-24, Barnant Company, Division of Cole-Parmer Instrument Co.,

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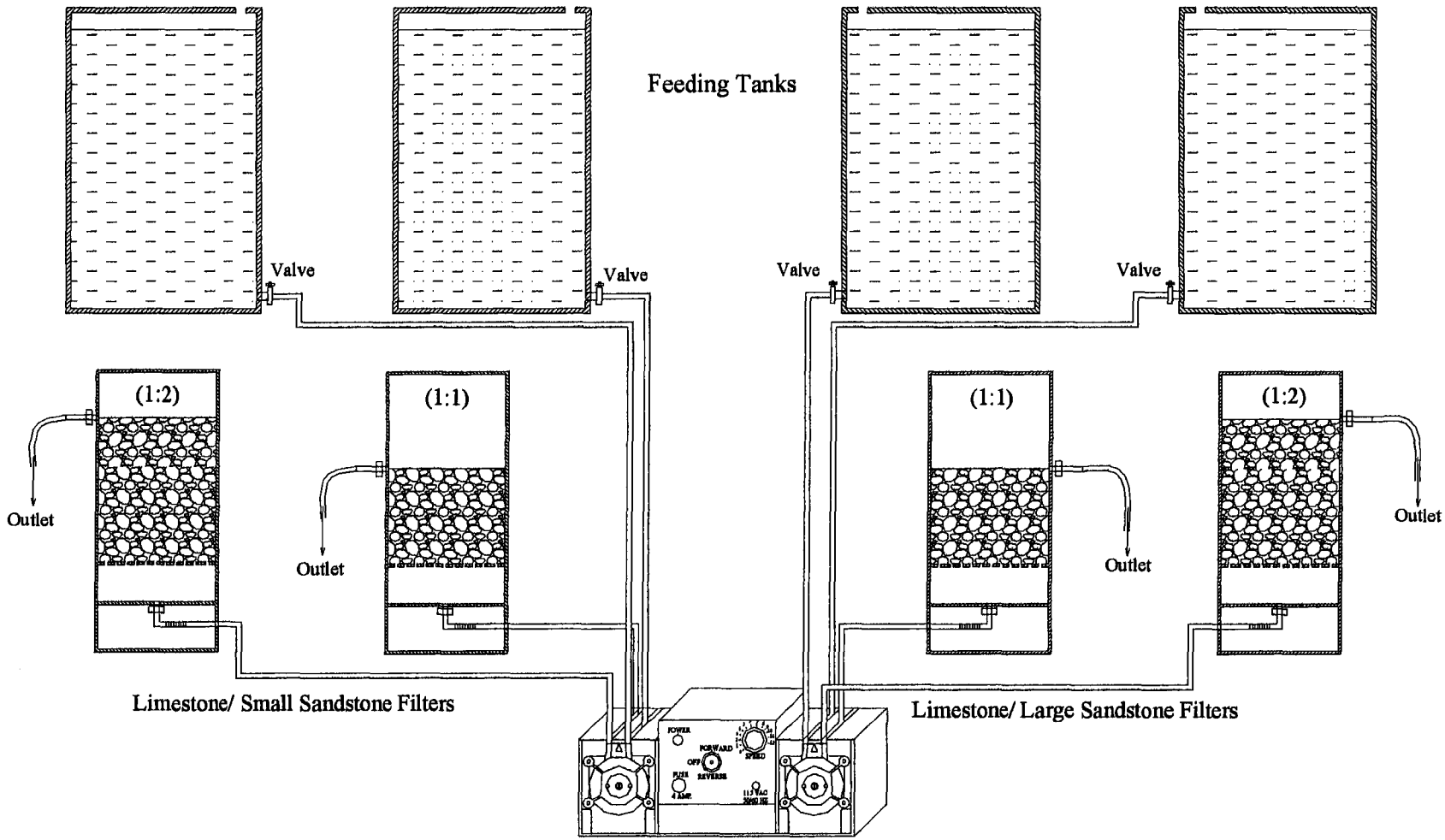


Figure 7.3. Continuous flow experimental setup.

Barrington, Illinois, USA) was used to pump the synthetic wastewater from the feeding tanks to the holding tanks. Tygon tubing of 0.75 cm outside diameter was used to connect the main air supply, manifold and aeration unit.

7.4 Preparation of Synthetic Wastewater

The two heavy metals investigated in this study were iron and manganese. Contaminated water solutions were prepared using ferrous ammonium sulfate hexahydrate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$), and manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$). They were purchased as reagent grade chemicals from Fisher Scientific, Ottawa, Ontario. Each chemical was dissolved in tap water which produced solutions with an iron concentration of 6.60 mg/L and a manganese concentration of 1.8 mg/L as shown in Table 7.1.

Table 7.1. Concentrations of elements present in the synthetic landfill leachate.

Element	Synthetic Landfill Leachate (mg/L)
Tap Water	
Aluminum	0.069
Arsenic	<0.002
Chloride	7.000
Copper (Total)	0.010
Fluoride	0.060
Lead (μg/L)	<0.500
Mercury	<0.050
Nitrate-Nitrogen	0.060
Sodium	8.000
Sulfate	11.800
Zinc (Total)	0.072
Regent Added	
Iron	6.60
Manganese	1.80

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7.5 Experimental Procedures

7.5.1 Tank Batch Experiment

One tank in each box was filled with limestone (30 kg) while the second tank was filled with a mixture of limestone (15 kg) and sandstone (15kg), both to a height of 15 cm. The void space in the filter material was determined to be 0.53. Therefore, the filter material occupied a volume of approximately 12 L. 13.5 L of iron solution (6.60 mg/L) were poured into each tank in the first box, 13.5 L of manganese solution (1.8 mg/L) were poured into each tank in the second box and 13.5 L of solution containing 6.6 mg/L of iron and 1.8 mg/L of manganese were poured into each tank in the third box. The pressure regulator on the aeration system was adjusted to 0.068 atm during the experiment to provide an aeration rate of 7 cm^3/min.

The experiment was carried out for 7 days. Water samples of 10 mL were collected from all boxes at 0, 2, 4, 6, 8, 12, and 24 hours. The samples were stored in the freezer immediately to slow the oxidation reaction and were then analyzed for iron and manganese using a spectrophotometer (Model DR/2500, HACH Company, Loveland, CO, USA). The FerroVer® Method (Method 8008) was used to measure iron and the Periodate Oxidation Method (Method 8034)was used to measure manganese. The pH of the samples was also measured using a pH meter (Model 805MP, Fisher Scientific, Montreal, Quebec, Canada). Three replicates were used for each sample. Every 24 hours, the filters were drained and 13.5 L of fresh synthetic wastewater was applied.

7.5.2 Beaker Batch Experiments

Three beakers were filled with limestone (2.024 kg) while the other three beakers were filled with a mixture of limestone (1.012 kg) and sandstone (1.012 kg), each to a height of 15 cm. A 0.9 L iron solution (6.6 mg/L) was poured into each of the first set of two beakers, a 0.9 L manganese solution (1.8 mg/L) was poured into each of the second set of two beakers and a 0.9 L iron/manganese solution (6.6 mg/L and 1.8 mg/L) was poured

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into each of the third set of two beakers. The pressure regulator on the aeration system was adjusted to provide an aeration rate of 7 cm^3/min.

The experiment was conducted for 3 hours under four different temperatures (5, 10, 15 and 20°C). Water samples of 5 mL were collected from all beakers at times of 2.5, 5, 7.5, 10, 20, 30, 40, 50, 60, 80, 100, 120, 150, 180 minutes and were then stored in the freezer immediately to slow the iron oxidation reactions. The samples were analyzed for iron and manganese using a spectrophotometer (Model DR/2500, HACH Company, Loveland, CO, USA). The FerroVer® Method (Method 8008) was used to measure total iron and the Periodate Oxidation Method (Method 8034) was used to measure manganese. The pH of the samples was also measured using a pH meter (Model 805MP, Fisher Scientific, Montreal, Quebec, Canada). The experiment was replicated three times.

7.5.3 Continuous Flow Experiments

Two reactors were filled with a mixture of limestone (0.657 kg) and small particles (approximately 0.63 cm maximum nominal diameter) of sandstone (0.657 kg), both to a height of 10.5 cm. The other two reactors were filled with a mixture of limestone (0.657 kg) and larger particles (approximately 1.27 cm maximum nominal diameter) of sandstone (1.314 kg). The synthetic wastewater, a mixture of iron (6.6 mg/L) and manganese (1.8 mg/L) was fed into each of the two reactor sets (ratios 1:1 and 1:2 of limestone and sandstone) at two rates 2.79 and 2.67 L/h. The flow rates were chosen to provide a 20 min retention time.

The experiment was conducted for 3 months. Water samples of 50 mL were collected from all reactors on a daily basis. The samples were stored in the freezer immediately to slow the iron oxidation reactions and were then analyzed for iron and manganese using a spectrophotometer (Model DR/2500, HACH Company, Loveland, CO, USA). The FerroVer® Method (Method 8008) was used to measure total iron and the Periodate Oxidation Method (Method 8034) was used to measure manganese. The pH of the samples was also measured using a pH meter (Model 805MP, Fisher Scientific, Montreal, Quebec, Canada).

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7.6 Results

7.6.1 Tank Batch Experiment

Tables 7.2– 7.4 show the measured concentrations of iron and manganese, their percent removal and the pH of the water for each of the seven days of the experiment. Figures 7.4 – 7.9 present the changes in the pH and the iron and manganese concentrations in the wastewater over time. Figure 7.10 shows the precipitation of iron on the limestone.

7.6.1.1 Iron

The iron concentrations in the water samples obtained from the limestone and limestone/sandstone filters after 24 hours ranged from 0.00 mg/L to 0.50 mg/L and from 0.00 mg/L to 0.45 mg/L, respectively. About 95.35 % and 96.32 % of the iron were removed from solution after 2 hours by the limestone and the limestone/sandstone filters, respectively. Extending the retention time to 24 hours resulted in a total iron removal of 99.69 % and 98.95 % by the limestone and limestone/sandstone filters, respectively.

Removal of iron from the solutions containing iron and manganese was similar to that of the solutions containing iron alone for both the limestone and the limestone/sandstone filters. The iron concentration in the water samples obtained from the limestone and limestone/sandstone filters after 24 hours ranged from 0.00 mg/L to 0.35 mg/L and from 0.00 mg/L to 0.40 mg/L, respectively. About 95.67 % of the iron was removed from solution by both the limestone and limestone/sandstone filters after 2 hours. Extending the retention time to 24 hours resulted in a total iron removal of 99.57 % and 99.78 % by the limestone and limestone/sandstone, respectively.

7.6.1.2 Manganese

The manganese concentrations in the water samples obtained from the limestone and limestone/sandstone filters after 24 hours ranged from 0.0 to 1.0 mg/L and 0.4 to 1.4 mg/L, respectively. About 44.44 % and 22.22 % of the manganese were removed from

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Table 7.2. Fe concentrations and pH of the Fe containing wastewater treated in limestone and limestone/sandstone filters under batch conditions at ambient temperature.

Time		Limestone			Limestone/Sandstone		
Day	Hours	Concentration (mg/L)	Removal (%)	pH	Concentration (mg/L)	Removal (%)	pH
	2	0.35	94.70	7.15	0.40	93.94	7.45
	4	0.15	97.73	7.36	0.25	96.21	7.50
1	6	0.10	98.48	7.55	0.15	97.73	7.51
	8	0.10	98.48	7.63	0.15	97.73	7.53
	12	0.05	99.24	7.72	0.15	97.73	7.67
	24	0.05	99.24	7.74	0.05	99.24	7.82
	2	0.35	94.70	7.45	0.45	93.18	7.39
	4	0.10	98.48	7.46	0.20	96.97	7.43
2	6	0.10	98.48	7.48	0.15	97.73	7.48
	8	0.00	100.00	7.48	0.10	98.48	7.55
	12	0.00	100.00	7.60	0.10	98.48	7.60
	24	0.00	100.00	7.62	0.00	100.00	7.67
	2	0.25	96.21	7.34	0.20	96.97	7.48
	4	0.15	97.73	7.39	0.20	96.97	7.49
3	6	0.10	98.48	7.45	0.10	98.48	7.51
	8	0.10	98.48	7.46	0.05	99.24	7.55
	12	0.10	98.48	7.46	0.05	99.24	7.55
	24	0.00	100.00	7.50	0.00	100.00	7.58
	2	0.35	94.70	7.05	0.25	96.21	7.50
	4	0.10	98.48	7.48	0.25	96.21	7.46
4	6	0.10	98.48	7.53	0.15	97.73	7.48
	8	0.10	98.48	7.55	0.15	97.73	7.60
	12	0.05	99.24	7.62	0.10	98.48	7.63
	24	0.05	99.24	7.63	0.00	100.00	7.63
	2	0.25	96.21	7.46	0.15	97.73	7.51
	4	0.20	96.97	7.47	0.10	98.48	7.51
5	6	0.10	98.48	7.47	0.05	99.24	7.53
	8	0.10	98.48	7.49	0.05	99.24	7.54
	12	0.10	98.48	7.51	0.00	100.00	7.59
	24	0.05	99.24	7.51	0.00	100.00	7.59
	2	0.25	96.21	7.46	0.25	96.21	7.34
	4	0.15	97.73	7.51	0.15	97.73	7.44
6	6	0.10	98.48	7.54	0.10	98.48	7.46
	8	0.05	99.24	7.61	0.05	99.24	7.53
	12	0.05	99.24	7.61	0.05	99.24	7.56
	24	0.00	100.00	7.66	0.00	100.00	7.61
	2	0.20	96.97	7.25	0.20	96.97	7.32
	4	0.20	96.97	7.53	0.15	97.73	7.49
7	6	0.15	97.73	7.61	0.10	98.48	7.54
	8	0.15	97.73	7.64	0.10	98.48	7.59
	12	0.10	98.48	7.71	0.10	98.48	7.66
	24	0.00	100.00	7.71	0.00	100.00	7.68

Initial Fe concentration = 6.6 mg/L
Initial pH = 6.1

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Table 7.3. Mn Concentrations and pH of the Mn containing wastewater treated in limestone and limestone/sandstone filters under batch conditions at ambient temperature.

Time		Limestone			Limestone/Sandstone		
Day	Hours	Concentration (mg/L)	Removal (%)	pH	Concentration (mg/L)	Removal (%)	pH
	2	0.0	100.00	7.46	0.4	77.78	7.46
	4	0.1	94.44	7.53	0.6	66.67	7.46
1	6	0.1	94.44	7.55	0.4	77.78	7.55
	8	0.2	88.89	7.57	0.4	77.78	7.60
	12	0.6	66.67	7.62	0.5	72.22	7.62
	24	0.3	83.33	7.63	0.4	77.78	7.62
	2	0.9	50.00	7.34	1.1	38.89	7.12
	4	0.6	66.67	7.36	0.9	50.00	7.29
2	6	0.7	61.11	7.39	1.1	38.89	7.29
	8	0.9	50.00	7.39	0.9	50.00	7.31
	12	0.9	50.00	7.39	1.1	38.89	7.41
	24	0.8	55.56	7.41	0.7	61.11	7.53
	2	1.0	44.44	7.34	1.4	22.22	7.63
	4	0.8	55.56	7.51	1.2	33.33	7.39
3	6	0.6	66.67	7.52	0.8	55.56	7.49
	8	0.6	66.67	7.55	1.0	44.44	7.53
	12	0.8	55.56	7.57	1.0	44.44	7.55
	24	0.8	55.56	7.60	1.0	44.44	7.57
	2	0.6	66.67	7.45	0.4	77.78	7.43
	4	0.6	66.67	7.46	0.6	66.67	7.41
4	6	0.6	66.67	7.46	0.8	55.56	7.43
	8	0.6	66.67	7.46	0.4	77.78	7.43
	12	0.4	77.78	7.48	0.4	77.78	7.45
	24	0.4	77.78	7.50	0.4	77.78	7.48
	2	1.2	33.33	7.37	0.8	55.56	7.20
	4	0.8	55.56	7.46	0.9	50.00	7.34
5	6	0.8	55.56	7.47	1.0	44.44	7.39
	8	0.6	66.67	7.47	0.8	55.56	7.42
	12	0.5	72.22	7.48	1.0	44.44	7.42
	24	0.5	72.22	7.49	0.5	72.22	7.49
	2	0.6	66.67	7.25	0.8	55.56	7.29
	4	0.6	66.67	7.37	0.8	55.56	7.31
6	6	0.6	66.67	7.39	0.4	77.78	7.34
	8	0.2	88.89	7.42	0.6	66.67	7.41
	12	0.4	77.78	7.49	0.6	66.67	7.41
	24	0.6	66.67	7.53	0.6	66.67	7.47
	2	0.5	72.22	7.27	1.0	44.44	7.17
	4	0.8	55.56	7.29	0.5	72.22	7.31
7	6	0.8	55.56	7.42	0.8	55.56	7.32
	8	0.5	72.22	7.46	1.0	44.44	7.37
	12	0.5	72.22	7.56	0.8	55.56	7.49
	24	0.5	72.22	7.64	1.0	44.44	7.56

Initial Mn concentration = 1.8 mg/L
Initial pH = 6.71

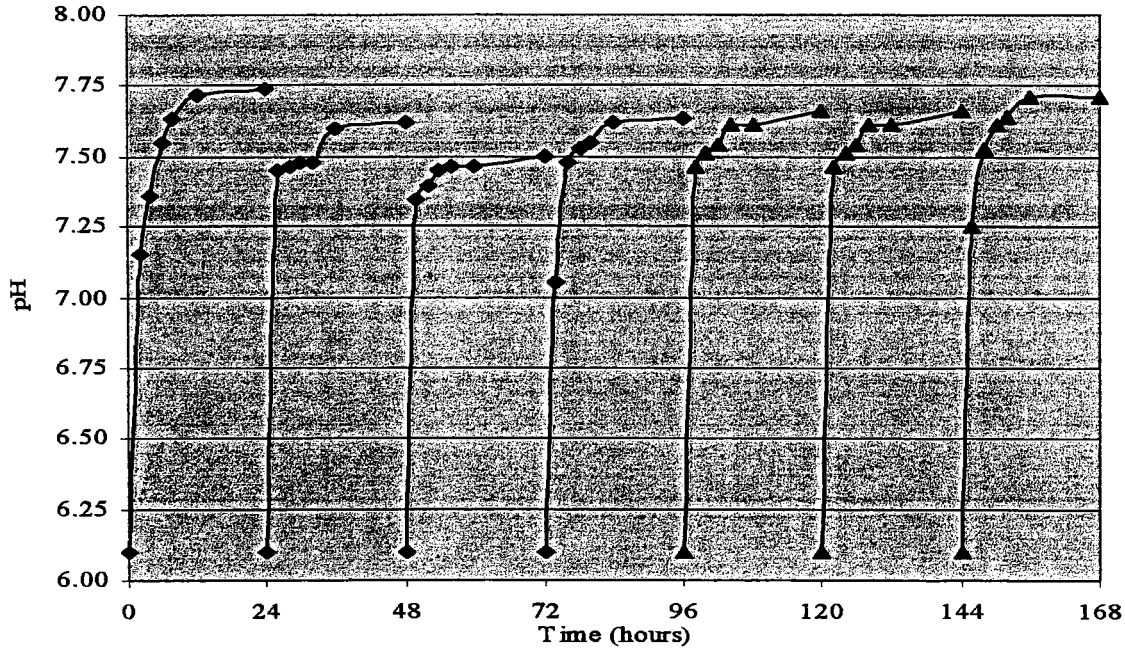
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Table 7.4. Fe and Mn concentrations and pH of the Fe and Mn containing wastewater treated in limestone and filters under batch conditions at ambient temperature.

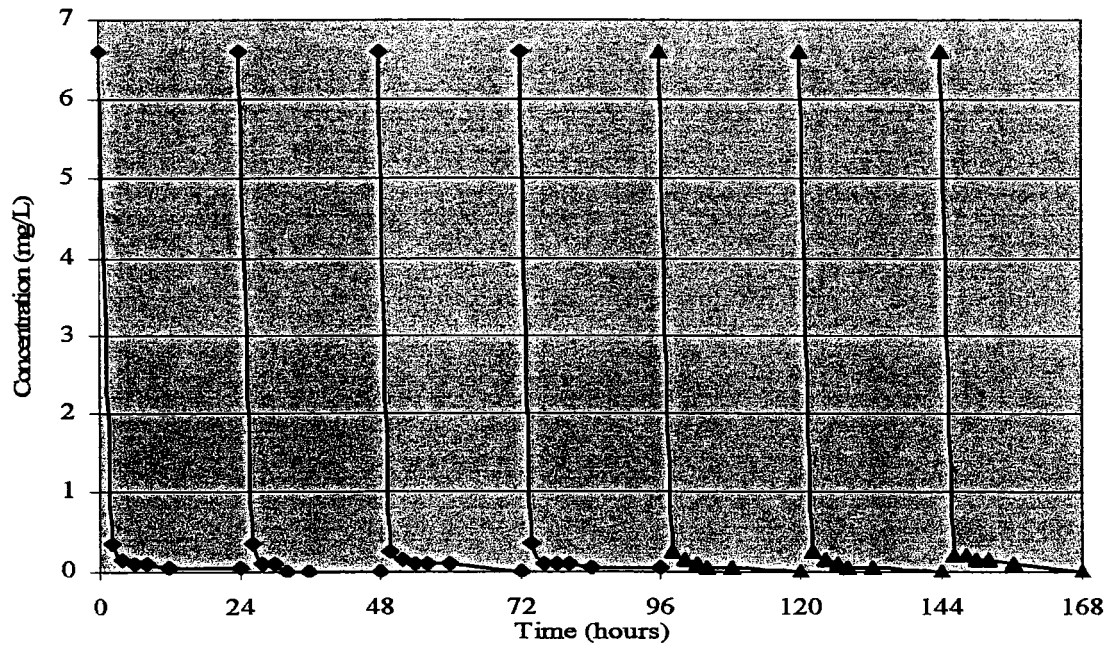
Time		Limestone					Limestone/Sandstone				
Day	Hours	Concentration (mg/L)		Removal (%)		pH	Concentration (mg/L)		Removal (%)		pH
		Fe	Mn	Fe	Mn		Fe	Mn	Fe	Mn	
1	2	0.35	0.6	94.70	66.67	7.10	0.40	0.6	93.94	66.67	7.34
	4	0.30	0.5	95.45	72.22	7.31	0.30	0.4	95.45	77.78	7.34
	6	0.30	0.3	95.45	83.33	7.51	0.20	0.4	96.97	77.78	7.46
	8	0.25	0.5	96.21	72.22	7.60	0.20	0.6	96.97	66.67	7.46
	12	0.15	0.3	97.73	83.33	7.62	0.15	0.3	97.73	83.33	7.51
	24	0.00	0.5	100.00	72.22	7.63	0.10	0.6	98.48	66.67	7.53
2	2	0.35	1.1	94.70	38.89	7.41	0.40	1.4	93.94	22.22	7.31
	4	0.15	0.6	97.73	66.67	7.41	0.30	0.9	95.45	50.00	7.31
	6	0.10	0.8	98.48	55.56	7.43	0.05	1.4	99.24	22.22	7.38
	8	0.00	0.6	100.00	66.67	7.43	0.05	1.4	99.24	22.22	7.48
	12	0.00	0.6	100.00	66.67	7.50	0.00	0.7	100.00	61.11	7.48
	24	0.00	0.4	100.00	77.78	7.51	0.00	0.3	100.00	83.33	7.50
3	2	0.30	1.2	95.45	33.33	7.53	0.05	1.0	99.24	44.44	7.38
	4	0.05	1.0	99.24	44.44	7.41	0.05	0.80	99.24	55.56	7.39
	6	0.05	1.1	99.24	38.89	7.43	0.00	0.4	100.00	77.78	7.41
	8	0.05	0.8	99.24	55.56	7.46	0.00	0.6	100.00	66.67	7.45
	12	0.05	0.8	99.24	55.56	7.48	0.00	0.6	100.00	66.67	7.46
	24	0.00	0.4	100.00	77.78	7.51	0.00	0.4	100.00	77.78	7.51
4	2	0.30	0.4	95.45	77.78	7.45	0.25	1.0	96.21	44.44	7.46
	4	0.25	0.5	96.21	72.22	7.39	0.10	0.8	98.48	55.56	7.41
	6	0.20	0.6	96.97	66.67	7.45	0.10	0.8	98.48	55.56	7.46
	8	0.15	0.8	97.73	55.56	7.49	0.00	0.6	100.00	66.67	7.46
	12	0.10	0.2	98.48	88.89	7.51	0.00	0.4	100.00	77.78	7.53
	24	0.05	0.4	99.24	77.78	7.58	0.00	0.6	100.00	66.67	7.69
5	2	0.25	1.3	96.21	27.78	7.39	0.40	1.2	93.94	33.33	7.31
	4	0.20	1.4	96.97	22.22	7.41	0.30	1.0	95.45	44.44	7.32
	6	0.10	1.0	98.48	44.44	7.42	0.10	1.3	98.48	27.78	7.36
	8	0.10	0.9	98.48	50.00	7.47	0.05	0.8	99.24	55.56	7.41
	12	0.10	0.9	98.48	50.00	7.47	0.05	0.3	99.24	83.33	7.46
	24	0.10	0.8	98.48	55.56	7.47	0.00	0.8	100.00	55.56	7.47
6	2	0.25	1.2	96.21	33.33	7.41	0.30	0.8	95.45	55.56	7.19
	4	0.15	0.6	97.73	66.67	7.42	0.15	1.0	97.73	44.44	7.25
	6	0.10	0.4	98.48	77.78	7.47	0.15	0.6	97.73	66.67	7.36
	8	0.10	0.4	98.48	77.78	7.47	0.05	0.6	99.24	66.67	7.37
	12	0.10	0.4	98.48	77.78	7.47	0.00	0.8	100.00	55.56	7.37
	24	0.05	0.4	99.24	77.78	7.56	0.00	0.6	100.00	66.67	7.39
7	2	0.20	1.0	96.97	44.44	7.37	0.20	0.8	96.97	55.56	7.24
	4	0.10	0.8	98.48	55.56	7.41	0.10	1.0	98.48	44.44	7.41
	6	0.10	1.0	98.48	44.44	7.41	0.05	1.0	99.24	44.44	7.44
	8	0.05	0.8	99.24	55.56	7.46	0.05	0.5	99.24	72.22	7.53
	12	0.00	1.0	100.00	44.44	7.59	0.00	0.9	100.00	50.00	7.58
	24	0.00	0.7	100.00	61.11	7.63	0.00	0.8	100.00	55.56	7.61

Initial Fe concentration = 6.6 mg/L
Initial Mn concentration = 1.8 mg/L
Initial pH = 6.1

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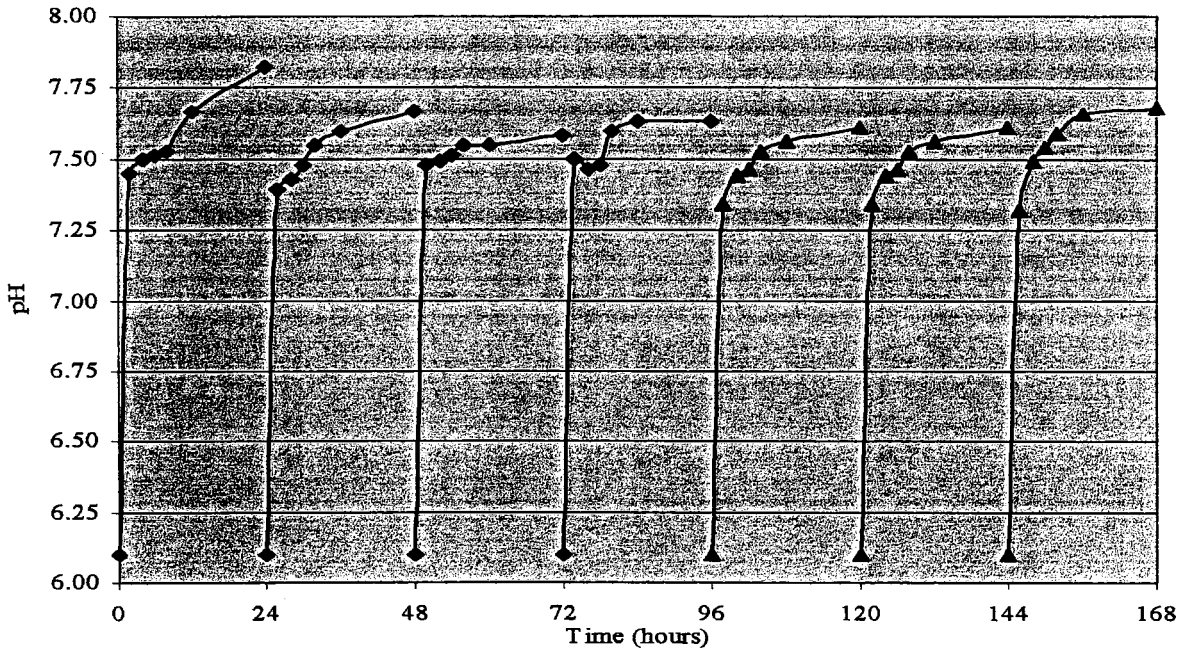
(a) pH



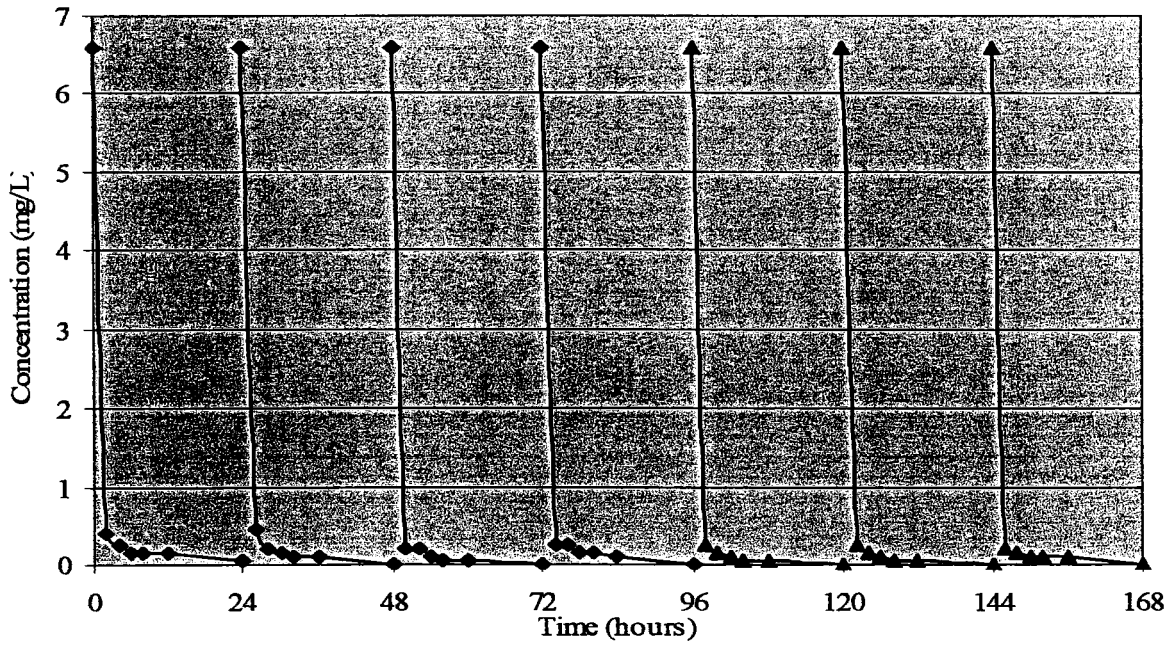
(b) Iron

Figure 7.4. pH and Fe concentration of water samples obtained from the limestone filter treating Fe containing wastewater under batch conditions at ambient temperature.

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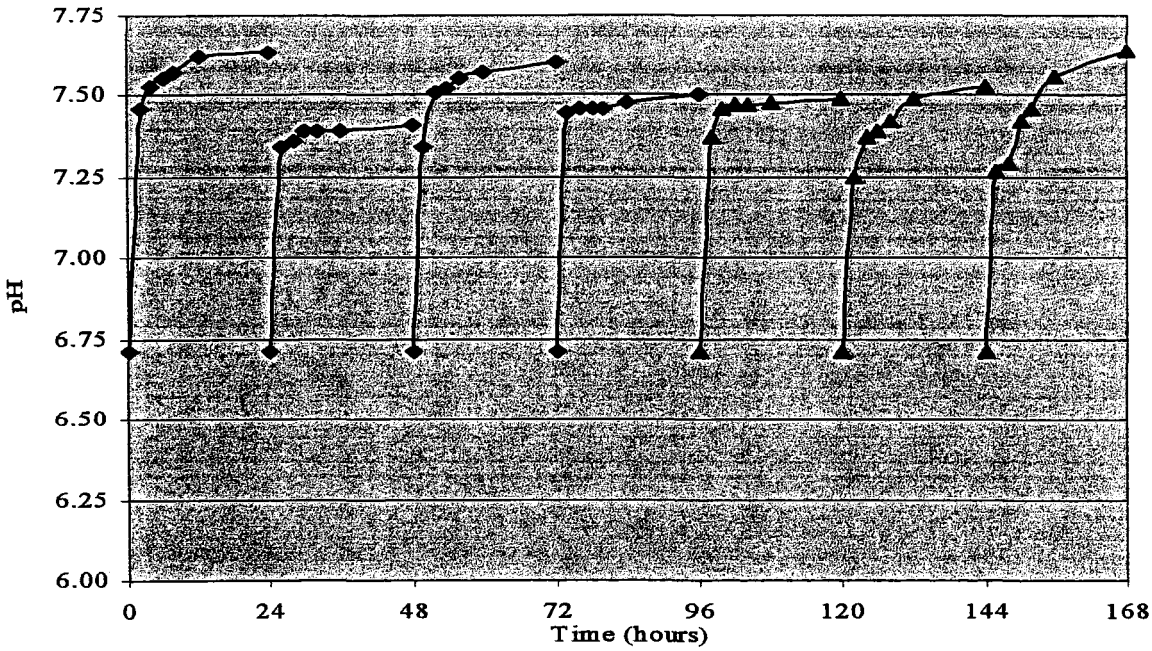
(a) pH



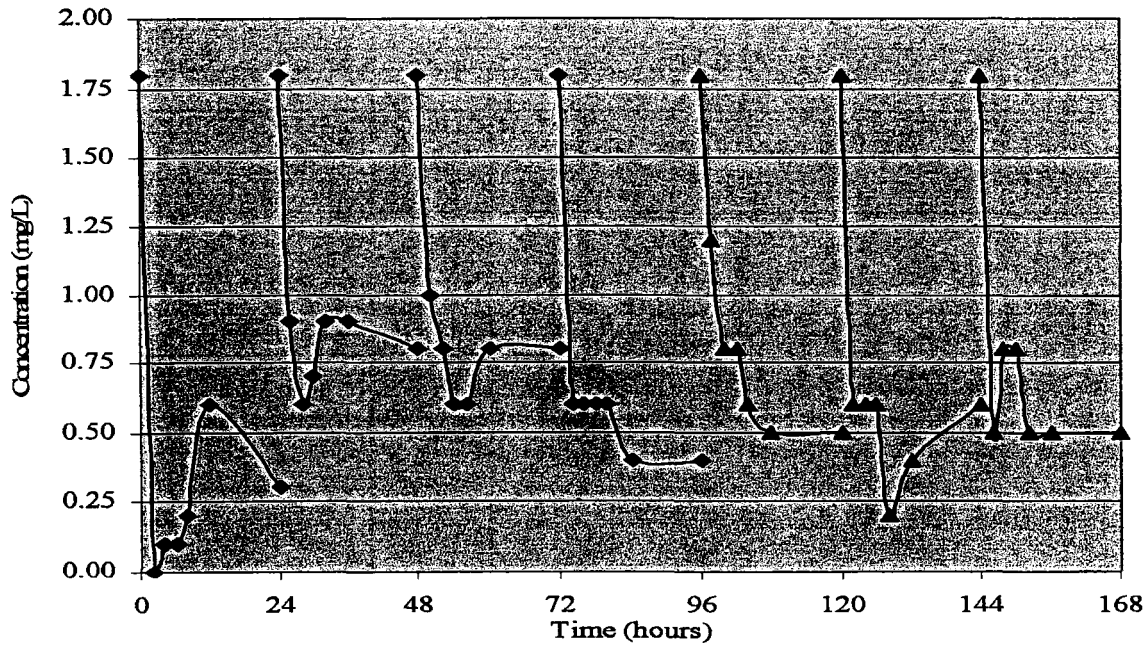
(a) Iron

Figure 7.5. pH and Fe concentration of water samples obtained from the limestone /sandstone filters treating Fe containing wastewater under batch conditions at ambient temperature.

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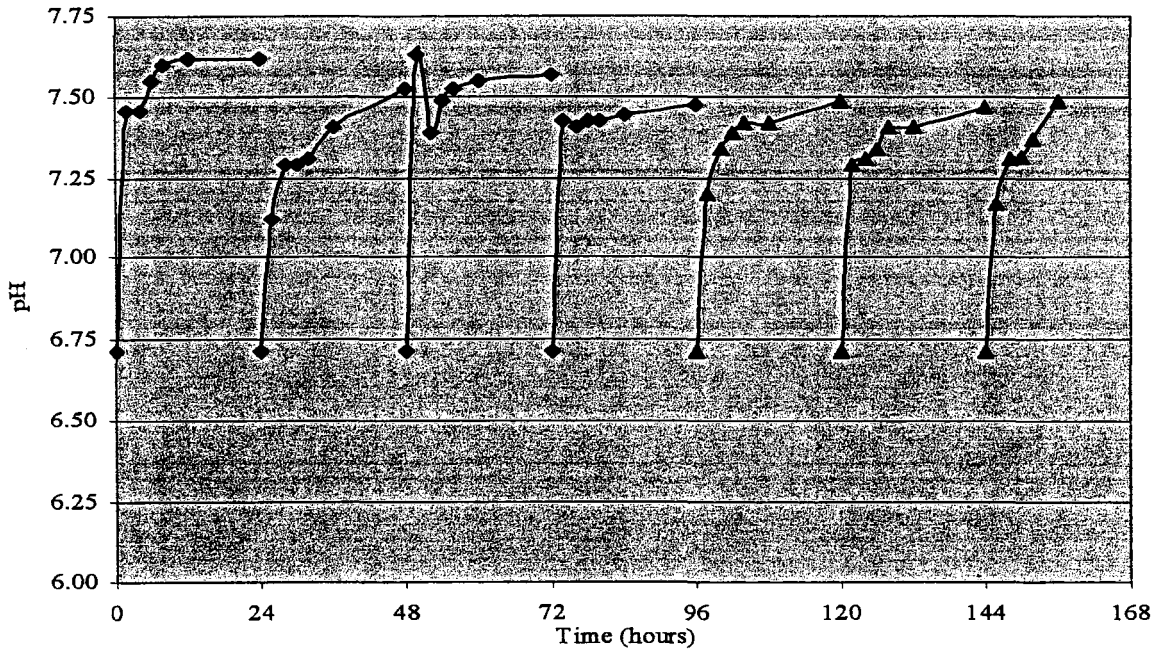
(a) pH



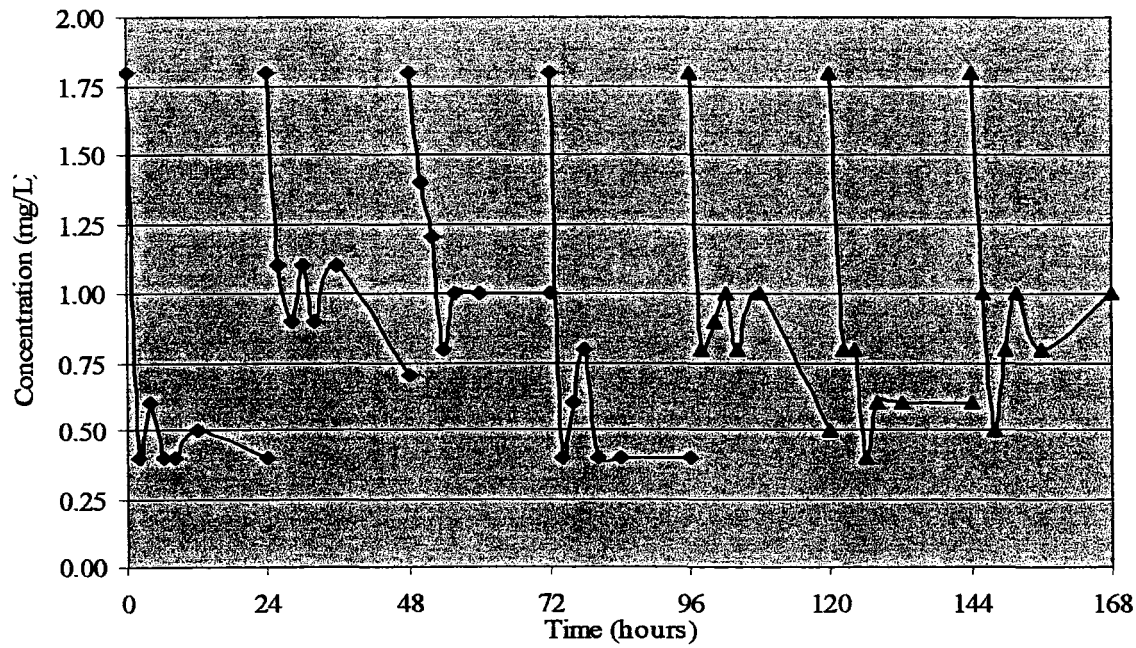
(b) Manganese

Figure 7.6. pH and Mn concentration of water samples obtained from the limestone filter treating Mn containing wastewater under batch conditions at ambient temperature.

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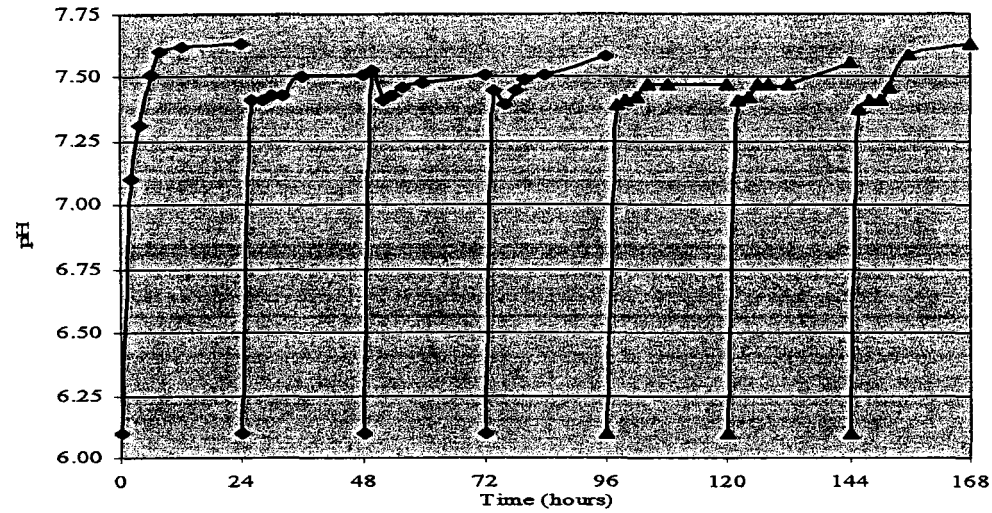
(a) pH



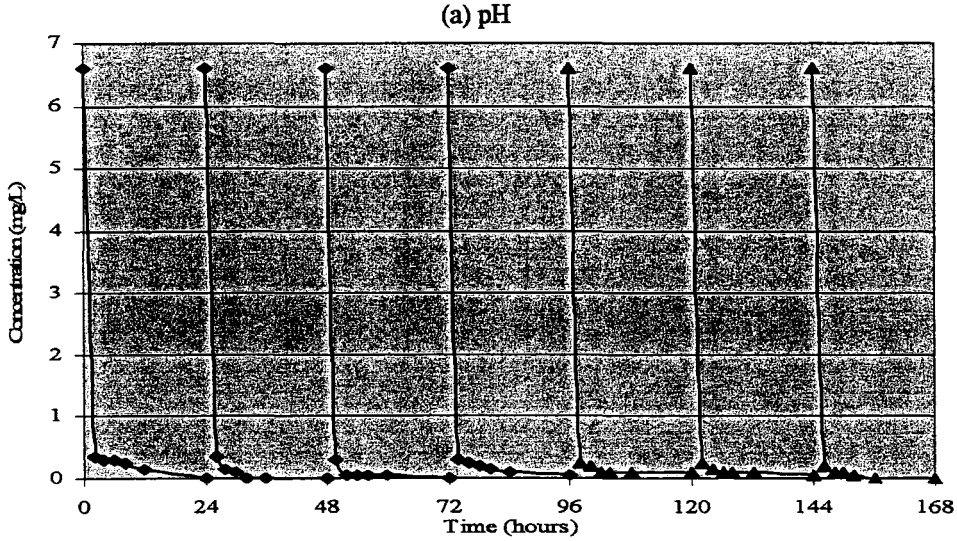
(b) Manganese

Figure 7.7. pH and Mn concentration of water samples obtained from the limestone /sandstone filter treating Mn containing wastewater under batch conditions at ambient temperature.

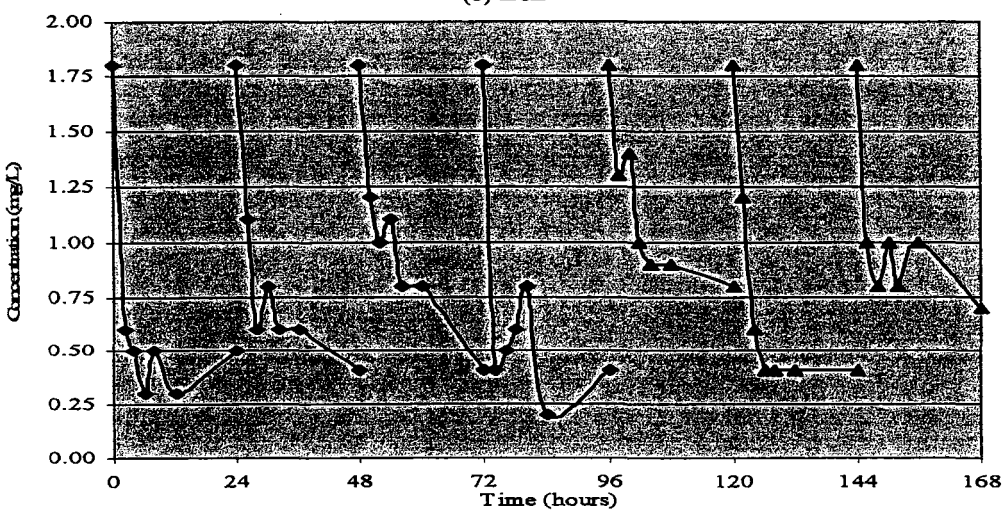
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(a) pH



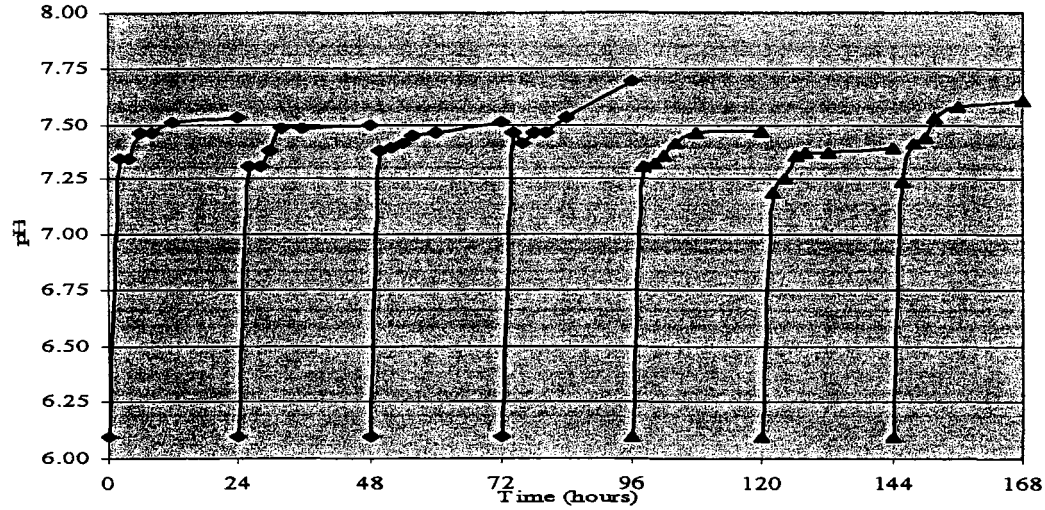
(b) Iron



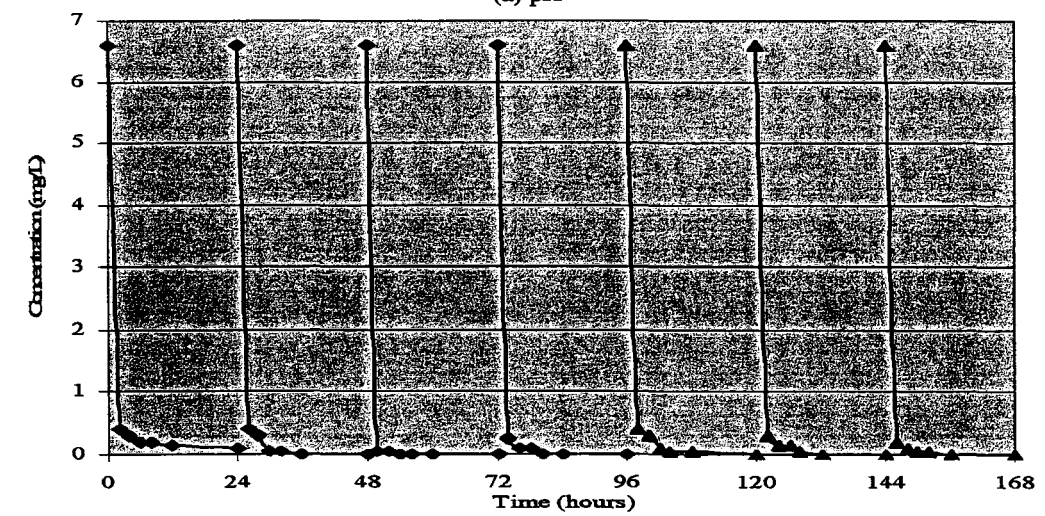
(c) Manganese

Figure 7.8. pH, Fe and Mn concentrations of water samples obtained from the limestone filter treating Fe and Mn containing wastewater under batch conditions at ambient temperature.

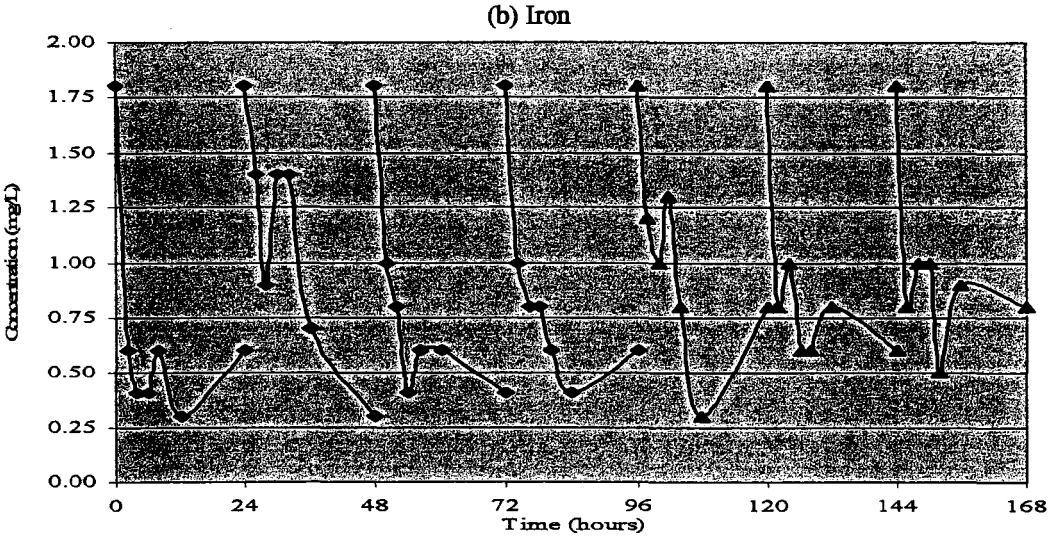
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(a) pH



(b) Iron



(c) Manganese

Figure 7.9. pH, Fe and Mn concentrations of water samples obtained from the limestone /sandstone filter treating Fe and Mn containing wastewater under batch conditions at ambient temperature.

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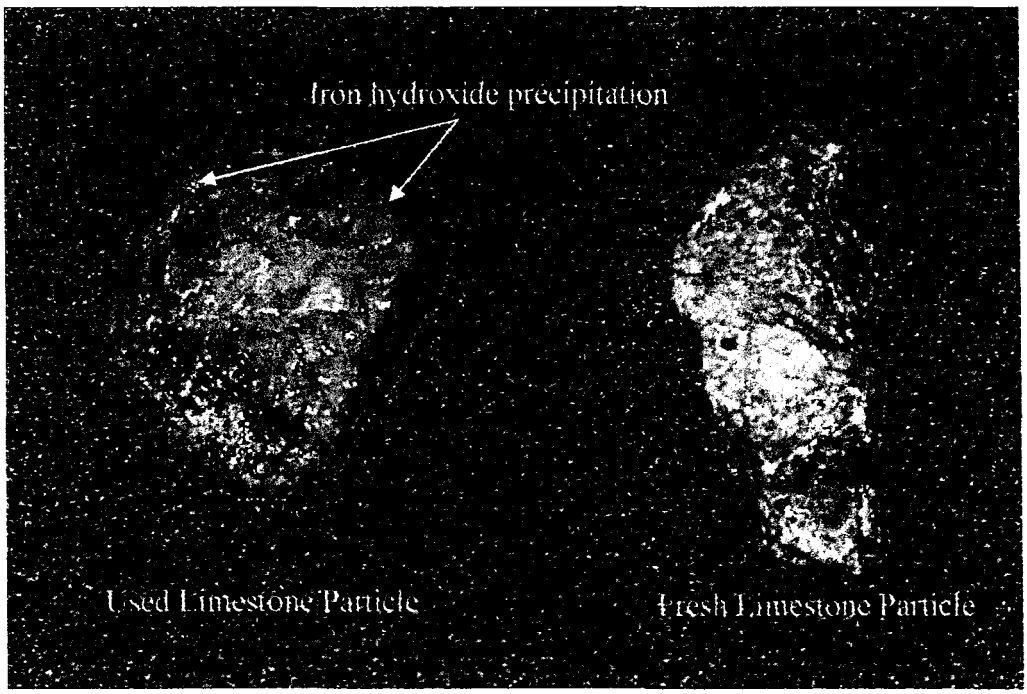


Figure 7.10. Iron precipitation on limestone particles from limestone filter.

solution by the limestone and the limestone/sandstone filters, respectively.

The removal of manganese from the solutions containing both iron and manganese was not similar to that of solutions containing manganese alone for both the limestone and the limestone/sandstone filters. The manganese concentrations in the water samples obtained from the limestone and the limestone/sandstone filters after 24 hours were higher (ranged from 0.3 mg/L to 1.4 mg/L). About 22.22 % of the manganese was removed from solution by the limestone and limestone/sandstone filters.

7.6.1.3 pH

The initial pH of the iron solution was 6.1 which increased to 7.1 - 7.8 over time during the experiment. The initial pH of the manganese solution was 6.7 which increased to 7.1 - 7.6. The initial pH of the iron/manganese solution was 6.1 which increased to 7.1 - 7.7. The highest pH level (pH = 7.8) was found in the iron solution sample obtained from the limestone/sandstone filter while the lowest (pH = 7.4) was found in the manganese solution sample obtained from the limestone/sandstone filter.

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7.6.2 Beaker Batch Experiment

Tables 7.5 – 7.10 show the measured concentrations of iron and manganese, their percent removal and the pH. Figures 7.11 – 7.16 present the changes in the pH and the iron and manganese concentrations in the wastewater over time.

7.6.2.1 Iron

The iron concentrations in the water samples obtained from the limestone filters after 3 hours were 0.02, 0.07, 0.23 and 0.23 mg/L with average total removal efficiencies of 99.77, 98.94, 96.52 and 96.52 % for the temperatures of 20, 15, 10 and 5 °C, respectively. The iron concentrations in the water samples obtained from for the limestone/sandstone filters after 3 hours were 0.05, 0.07, 0.23 and 0.34 mg/L with average removal efficiencies of 99.32, 98.94, 96.52 and 94.85 % for the temperatures of 20, 15, 10 and 5 °C, respectively. About 96.29, 97.49, 91.21 and 62.42 % of the iron was removed from solution by the limestone filters and about 90.68, 88.48, 83.33 and 61.67 % of the iron were removed from the solution by the limestone/sandstone filters after 20 minuets for the temperatures of 20, 15, 10 and 5 °C, respectively.

Removal of iron from the solution containing iron and manganese was similar to that of the solution containing iron alone for both the limestone and the limestone/sandstone filters. The iron concentrations in the water samples obtained from the limestone filters after 3 hours were 0.02, 0.06, 0.23 and 0.33 mg/L with average total removal efficiencies of 99.70, 98.99, 96.52 and 95.00 % for the temperatures of 20, 15, 10 and 5 °C, respectively. The iron concentrations in the water samples obtained from limestone/sandstone filters were 0.02, 0.05, 0.24 and 0.26 mg/L with average removal efficiencies of 99.70, 99.00, 97.12 and 96.01 % for the temperatures of 20, 15, 10 and 5 °C, respectively. About 90.15, 84.09, 74.85 and 58.64 % of the iron were removed from solution by the limestone filters and about 90.15, 86.21, 77.27 and 62.42 % of the iron were removed from the solution by the limestone/sandstone filters after 20 minutes for the temperatures of 20, 15, 10 and 5 °C, respectively.

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Table 7.5. Iron concentrations and pH of the Fe containing wastewater treated in beaker-limestone filters under batch condition at different temperatures.

Time	20 °C			15 °C			10 °C			5 °C		
	Concentration (mg/L)	Removal (%)	pH	Concentration (mg/L)	Removal (%)	pH	Concentration (mg/L)	Removal (%)	pH	Concentration (mg/L)	Removal (%)	pH
0	6.60		6.10	6.60		6.10	6.60		6.10	6.60		6.10
2.5	3.00	54.55	7.30	4.27	35.30	7.48	4.51	31.67	7.48	5.48	16.97	7.45
5	1.27	80.76	7.43	2.14	67.58	7.55	2.62	60.30	7.62	4.49	31.97	7.72
7.5	0.43	93.48	7.45	1.32	80.00	7.55	1.68	74.55	7.68	3.96	40.00	7.73
10	0.30	95.45	7.49	0.60	90.91	7.55	0.96	85.45	7.68	3.45	47.73	7.73
20	0.25	96.29	7.40	0.47	92.88	7.49	0.58	91.21	7.69	2.48	62.42	7.78
30	0.20	96.97	7.44	0.33	95.00	7.54	0.54	91.82	7.69	1.80	72.73	7.78
40	0.19	97.12	7.46	0.34	94.85	7.54	0.40	93.94	7.68	1.42	78.48	7.78
50	0.16	97.58	7.46	0.33	95.00	7.54	0.45	93.18	7.71	1.20	81.82	7.80
60	0.14	97.88	7.43	0.33	95.00	7.54	0.43	93.48	7.66	0.96	85.45	7.73
80	0.12	98.18	7.31	0.33	95.00	7.49	0.43	93.48	7.64	0.80	87.88	7.76
100	0.09	98.64	7.46	0.26	96.06	7.53	0.43	93.48	7.69	0.60	90.91	7.76
120	0.07	99.02	7.45	0.20	96.97	7.59	0.33	95.00	7.69	0.50	92.42	7.76
150	0.05	99.32	7.43	0.03	99.55	7.55	0.17	97.42	7.69	0.30	95.45	7.78
180	0.02	99.77	7.51	0.07	98.94	7.58	0.23	96.52	7.69	0.23	96.52	7.76

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Table 7.7. Iron and manganese concentrations and pH of the Fe and Mn containing wastewater treated in beaker-limestone filters under batch condition at different temperatures.

Time	20 °C					15 °C					10 °C					5 °C				
	Fe		Mn		pH	Fe		Mn		pH	Fe		Mn		pH	Fe		Mn		pH
	C	R	C	R		C	R	C	R		C	R	C	R		C	R	C	R	
0	6.60		1.80		6.10	6.60		1.80		6.10	6.60		1.80		6.10	6.60		1.80		6.10
2.5	3.46	47.58	1.65	8.56	7.05	4.78	27.58	1.72	4.22	7.24	5.28	20.00	1.71	5.17	7.30	5.48	16.97	1.70	5.67	7.46
5	2.09	68.33	1.57	12.78	7.05	3.27	50.45	1.64	8.67	7.28	4.51	31.67	1.65	8.39	7.39	4.73	28.33	1.72	4.44	7.57
7.5	1.59	75.91	1.47	18.44	7.07	2.46	62.73	1.58	12.44	7.32	3.29	50.15	1.62	9.94	7.47	4.15	37.12	1.67	7.11	7.61
10	1.46	77.88	1.40	22.22	7.14	1.83	72.27	1.49	17.00	7.26	2.60	60.61	1.56	13.17	7.47	3.71	43.79	1.64	8.89	7.69
20	0.65	90.15	1.00	44.44	7.23	1.05	84.09	1.04	42.00	7.28	1.66	74.85	1.22	32.33	7.47	2.73	58.64	1.34	25.61	7.75
30	0.52	92.12	0.90	50.00	7.19	0.73	88.94	0.95	47.28	7.32	1.15	82.58	1.10	38.72	7.53	2.22	66.36	1.16	35.56	7.80
40	0.37	94.39	0.80	55.56	7.30	0.56	91.52	0.88	51.11	7.46	0.83	87.42	0.98	45.39	7.61	1.60	75.76	1.06	41.28	7.75
50	0.25	96.21	0.80	55.56	7.19	0.44	93.33	0.84	53.61	7.41	0.78	88.18	0.95	47.33	7.56	1.34	79.70	1.04	42.22	7.75
60	0.12	98.18	0.80	55.56	7.26	0.40	93.94	0.88	51.11	7.48	0.66	90.00	0.94	47.61	7.63	1.12	83.03	1.00	44.44	7.75
80	0.11	98.33	0.80	55.56	7.22	0.33	95.00	0.72	60.00	7.49	0.60	90.91	0.87	51.44	7.65	0.88	86.67	0.92	48.89	7.72
100	0.08	98.79	0.60	66.67	7.24	0.26	96.06	0.65	63.78	7.42	0.49	92.58	0.78	56.56	7.59	0.78	88.18	0.84	53.33	7.73
120	0.04	99.39	0.60	66.67	7.28	0.20	96.97	0.70	61.33	7.46	0.40	93.94	0.75	58.50	7.61	0.66	90.00	0.81	55.28	7.71
150	0.04	99.39	0.60	66.67	7.32	0.07	98.94	0.57	68.33	7.48	0.22	96.67	0.66	63.61	7.61	0.44	93.33	0.75	58.50	7.69
180	0.02	99.70	0.40	77.78	7.20	0.06	98.94	0.48	73.61	7.48	0.23	96.52	0.56	68.89	7.56	0.33	94.85	0.64	64.44	7.68

C Concentration (mg/L)
R Removal Efficiency (%)

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Table 7.8. Iron and manganese concentrations and pH of the Fe and Mn containing wastewater treated in beaker-limestone/sandstone filters under batch condition at different temperatures.

Time	20 °C					15 °C					10 °C					5 °C				
	Fe		Mn		pH	Fe		Mn		pH	Fe		Mn		pH	Fe		Mn		pH
	C	R	C	R		C	R	C	R		C	R	C	R		C	R	C	R	
0	6.60		1.80		6.10	6.60		1.80		6.10	6.60		1.80		6.10	6.60		1.80		6.10
2.5	3.85	41.67	1.74	3.22	7.30	4.56	30.91	1.60	11.39	7.48	5.28	20.00	1.64	8.67	7.48	5.70	13.64	1.79	0.67	7.63
5	2.51	61.97	1.61	10.83	7.43	3.52	46.67	1.56	13.33	7.55	4.26	35.45	1.65	8.61	7.63	4.80	27.27	1.76	2.22	7.71
7.5	1.89	71.36	1.49	17.22	7.45	2.59	60.76	1.39	22.94	7.55	3.54	46.36	1.55	14.06	7.64	4.22	36.06	1.70	5.78	7.76
10	1.46	77.88	1.30	27.78	7.49	2.02	69.39	1.36	24.44	7.55	2.72	58.79	1.44	20.00	7.69	3.67	44.39	1.65	8.61	7.80
20	0.65	90.15	1.20	33.33	7.40	0.91	86.21	1.27	29.67	7.49	1.50	77.27	1.36	24.22	7.68	2.48	62.42	1.52	15.33	7.81
30	0.52	92.12	0.90	50.00	7.44	0.65	90.15	1.10	38.89	7.54	0.93	85.91	1.27	29.67	7.68	1.80	72.73	1.47	18.50	7.80
40	0.46	93.03	0.80	55.56	7.46	0.54	91.82	0.92	49.06	7.54	0.67	89.85	1.14	36.67	7.68	1.42	78.48	1.41	21.67	7.76
50	0.25	96.21	0.80	55.56	7.46	0.40	93.94	0.91	49.72	7.54	0.59	91.06	1.07	40.44	7.69	1.20	81.82	1.36	24.44	7.77
60	0.12	98.18	0.70	61.11	7.43	0.33	95.00	0.84	53.33	7.54	0.53	91.97	1.02	43.33	7.68	1.07	83.79	1.29	28.39	7.76
80	0.11	98.33	0.60	66.67	7.31	0.33	95.00	0.76	57.78	7.49	0.43	93.48	0.90	50.00	7.61	0.80	87.88	1.27	29.33	7.73
100	0.08	98.79	0.60	66.67	7.46	0.30	95.45	0.71	60.83	7.53	0.43	93.48	0.82	54.50	7.68	0.67	89.85	1.07	40.78	7.75
120	0.04	99.39	0.50	72.22	7.45	0.15	97.73	0.64	64.44	7.59	0.35	94.70	0.72	60.00	7.72	0.54	91.82	0.88	51.11	7.77
150	0.04	99.39	0.50	72.22	7.43	0.03	99.55	0.58	67.83	7.55	0.22	96.67	0.67	62.78	7.65	0.37	94.39	0.81	55.11	7.76
180	0.02	99.70	0.40	77.78	7.51	0.05	99.00	0.50	72.28	7.58	0.24	96.40	0.62	65.61	7.69	0.26	96.01	0.76	58.00	7.76

C Concentration (mg/L)
R Removal Efficiency (%)

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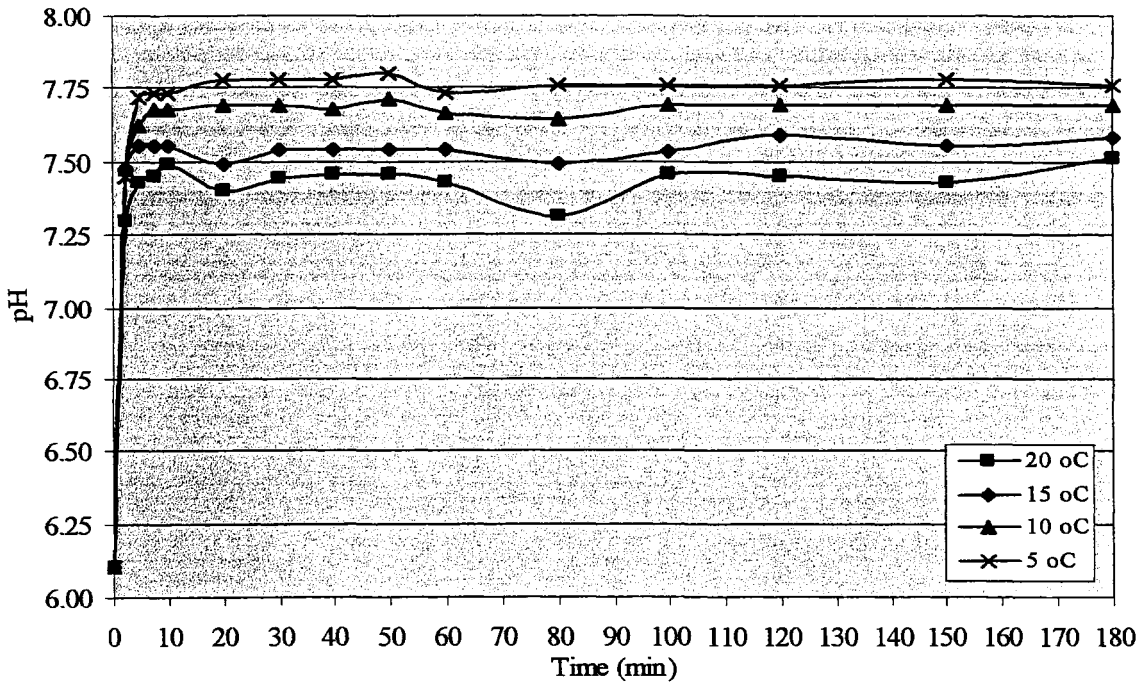
Table 7.9. Manganese concentrations and pH of the Mn containing wastewater treated in beaker-limestone filters under batch condition at different temperatures.

Time	20 °C			15 °C			10 °C			5 °C		
	Concentration (mg/L)	Removal (%)	pH	Concentration (mg/L)	Removal (%)	pH	Concentration (mg/L)	Removal (%)	pH	Concentration (mg/L)	Removal (%)	pH
0	1.80		6.70	1.80		6.70	1.80		6.70	1.80		6.70
2.5	1.49	17.44	7.14	1.60	11.39	7.22	1.64	8.67	7.36	1.70	5.67	7.61
5	1.24	31.11	7.23	1.38	23.44	7.42	1.38	23.44	7.57	1.53	15.06	7.72
7.5	1.03	42.61	7.29	1.15	36.22	7.44	1.23	31.50	7.58	1.42	21.11	7.75
10	0.70	61.11	7.14	0.88	51.11	7.40	1.02	43.61	7.55	1.25	30.50	7.78
20	0.55	69.44	7.23	0.62	65.44	7.42	0.73	59.39	7.60	0.98	45.61	7.79
30	0.50	72.22	7.19	0.56	69.11	7.48	0.63	64.78	7.62	0.88	51.33	7.79
40	0.50	72.22	7.30	0.45	74.83	7.46	0.58	67.78	7.68	0.75	58.39	7.82
50	0.40	77.78	7.19	0.45	74.83	7.41	0.51	71.44	7.62	0.72	60.00	7.80
60	0.40	77.78	7.26	0.44	75.56	7.48	0.50	72.11	7.65	0.71	60.61	7.80
80	0.40	77.78	7.22	0.42	76.50	7.49	0.47	73.83	7.65	0.62	65.56	7.78
100	0.40	77.78	7.24	0.42	76.50	7.42	0.47	74.17	7.65	0.61	66.22	7.79
120	0.35	80.56	7.28	0.41	77.17	7.46	0.39	78.17	7.62	0.58	67.67	7.83
150	0.25	86.11	7.32	0.42	76.83	7.48	0.36	80.22	7.67	0.55	69.39	7.78
180	0.25	86.11	7.19	0.40	77.78	7.48	0.34	80.89	7.68	0.56	68.89	7.78

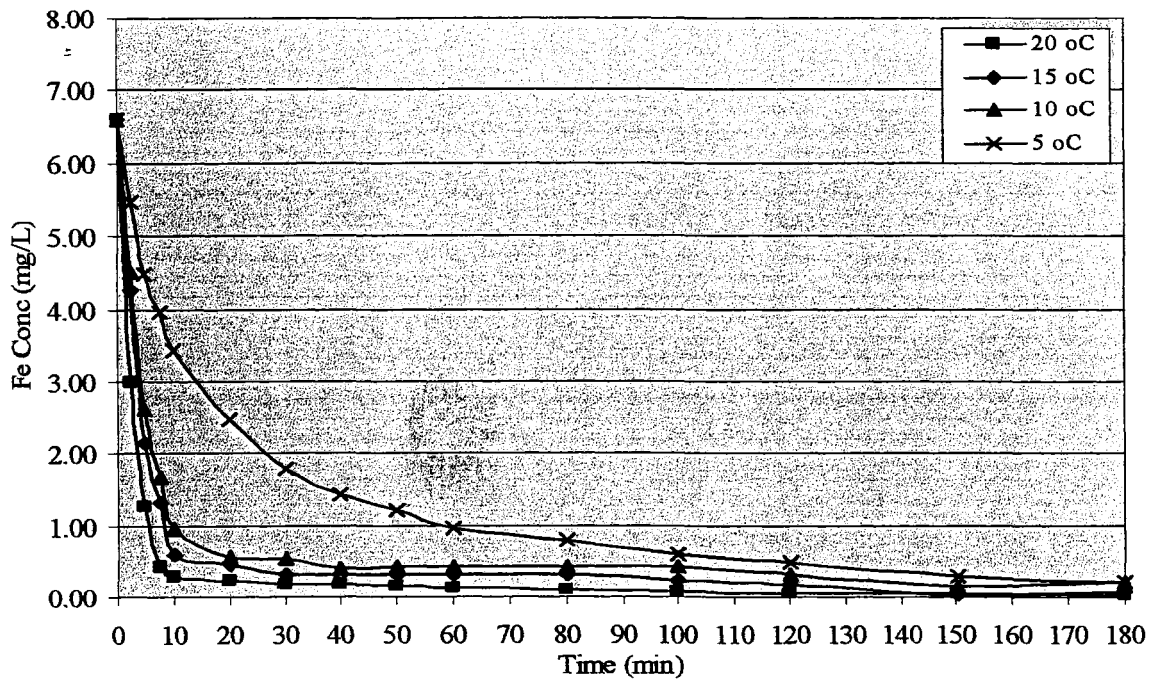
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Table 7.10. Manganese concentrations and pH of the Mn containing wastewater treated in beaker-limestone/sandstone filters under batch condition at different temperatures.

Time	20 °C			15 °C			10 °C			5 °C		
	Concentration (mg/L)	Removal (%)	pH	Concentration (mg/L)	Removal (%)	pH	Concentration (mg/L)	Removal (%)	pH	Concentration (mg/L)	Removal (%)	pH
0	1.80		6.70	1.80		6.70	1.80		6.70	1.80		6.70
2.5	1.49	17.44	7.03	1.60	11.39	7.33	1.64	8.67	7.25	1.70	5.67	7.65
5	1.24	31.11	7.17	1.38	23.44	7.46	1.38	23.44	7.64	1.53	15.06	7.72
7.5	1.03	42.61	7.20	1.23	31.78	7.48	1.28	28.89	7.62	1.42	21.11	7.76
10	0.85	52.78	7.26	1.06	41.28	7.41	1.10	38.83	7.60	1.29	28.61	7.76
20	0.70	61.11	7.28	0.81	55.00	7.42	0.90	50.06	7.57	1.05	41.61	7.77
30	0.65	63.89	7.32	0.72	60.00	7.49	0.76	57.78	7.64	0.88	51.33	7.83
40	0.65	63.89	7.30	0.70	60.94	7.48	0.73	59.22	7.65	0.80	55.56	7.80
50	0.50	72.22	7.30	0.57	68.33	7.49	0.65	63.78	7.68	0.74	58.83	7.78
60	0.50	72.22	7.34	0.59	67.28	7.49	0.63	64.83	7.65	0.70	61.33	7.77
80	0.50	72.22	7.33	0.54	70.11	7.49	0.58	68.00	7.68	0.65	64.11	7.78
100	0.50	72.22	7.31	0.53	70.44	7.48	0.60	66.94	7.66	0.64	64.44	7.76
120	0.40	77.78	7.31	0.45	75.06	7.49	0.54	70.11	7.68	0.65	64.11	7.76
150	0.40	77.78	7.33	0.44	75.56	7.50	0.53	70.83	7.70	0.63	64.83	7.80
180	0.40	77.78	7.25	0.46	74.67	7.48	0.53	70.83	7.69	0.65	64.11	7.80



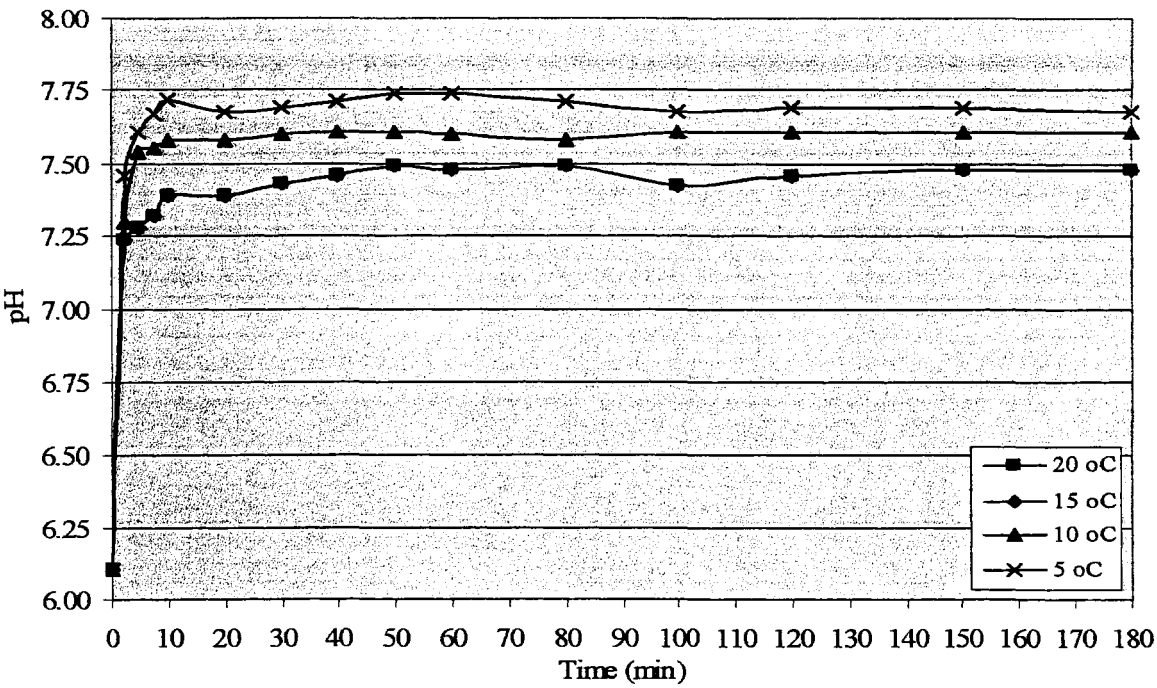
(a) pH



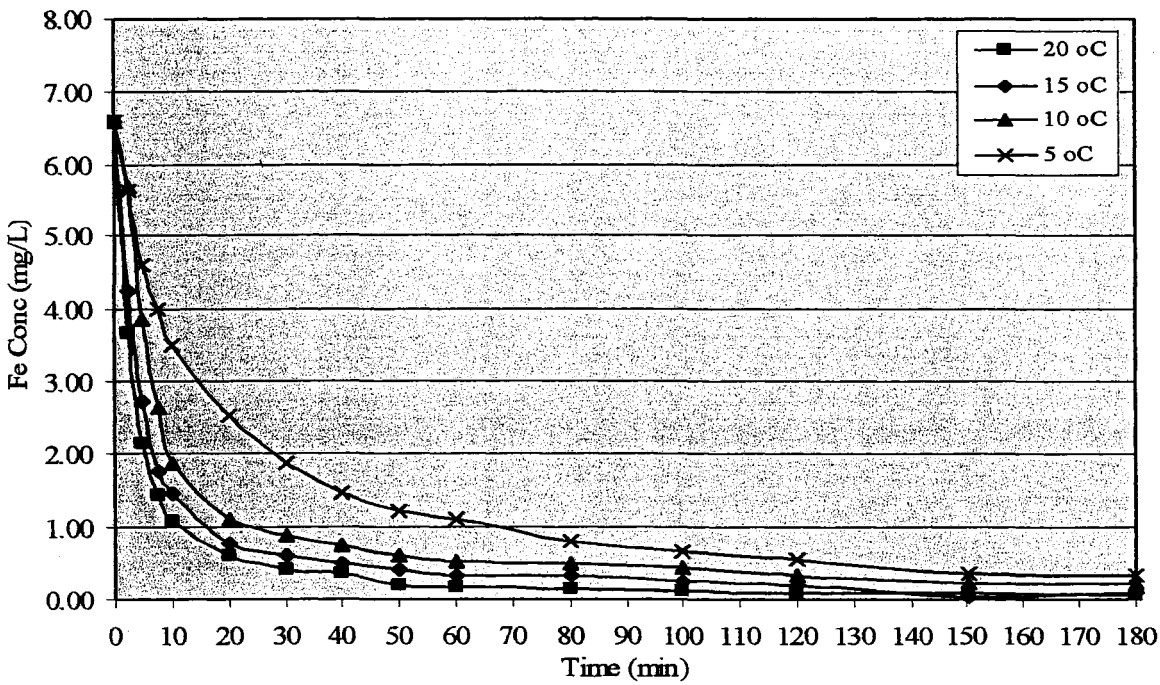
(b) Iron

Figure 7.11. Iron concentrations and pH of water obtained from the beaker-limestone filter treating Fe containing wastewater under batch conditions at different temperatures.

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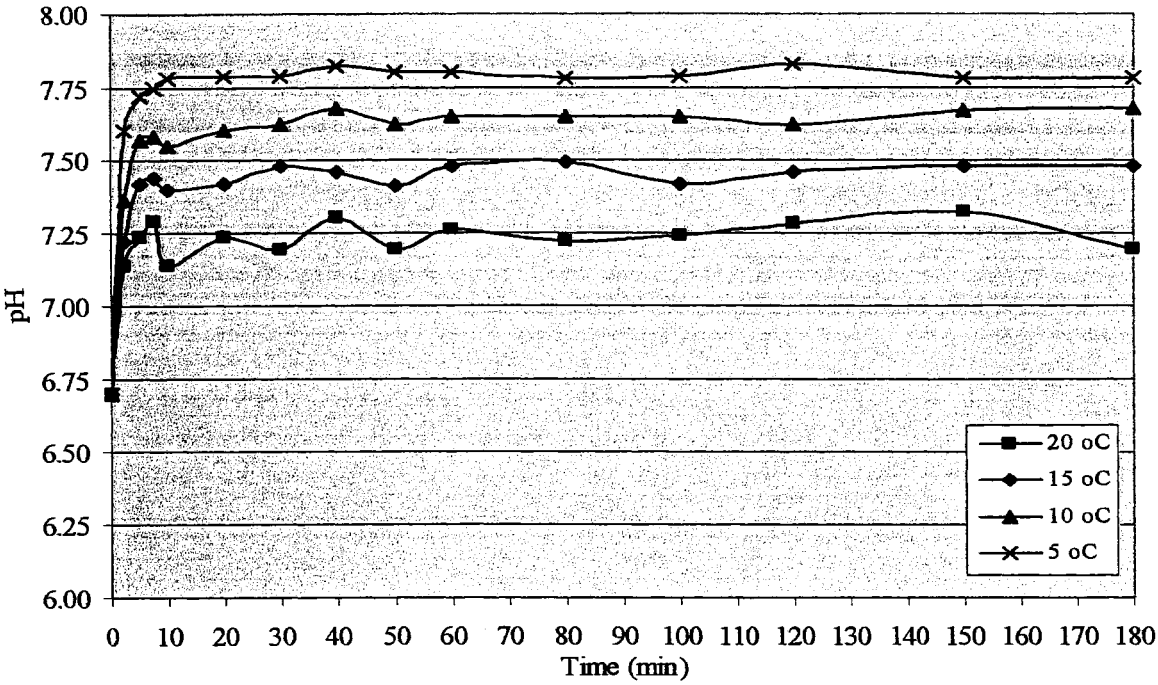
(a) pH



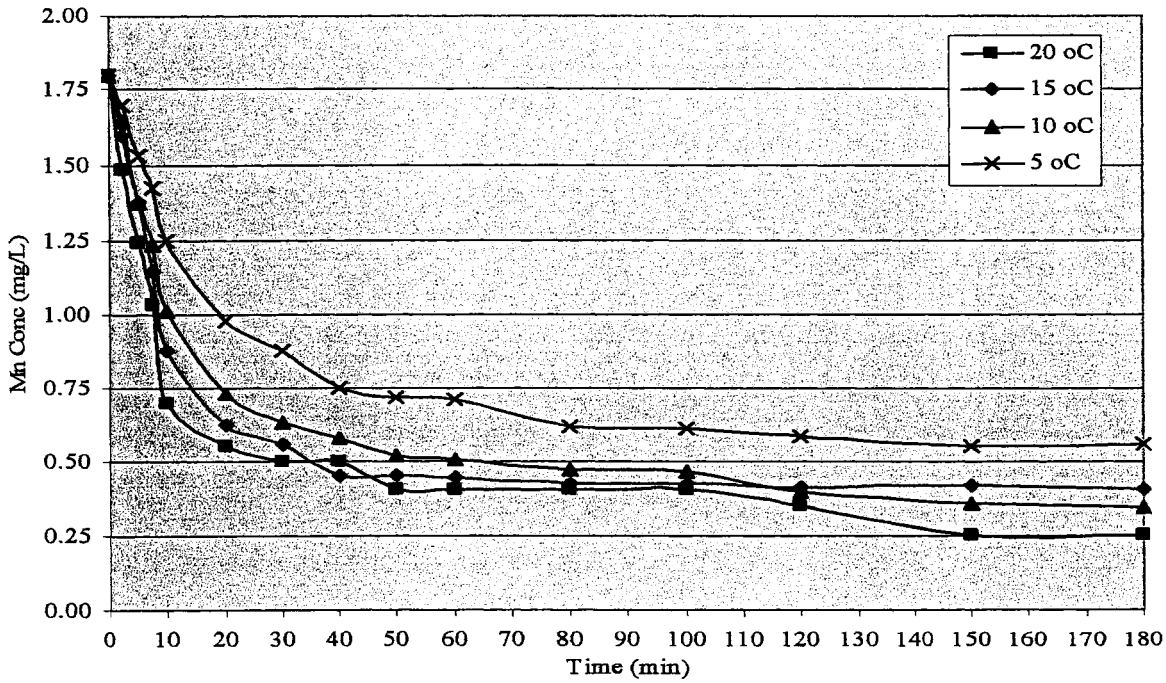
(b) Iron

Figure 7.12. Iron concentrations and pH of water obtained from the-beaker limestone/sandstone filter treating Fe containing wastewater under batch conditions at different temperatures.

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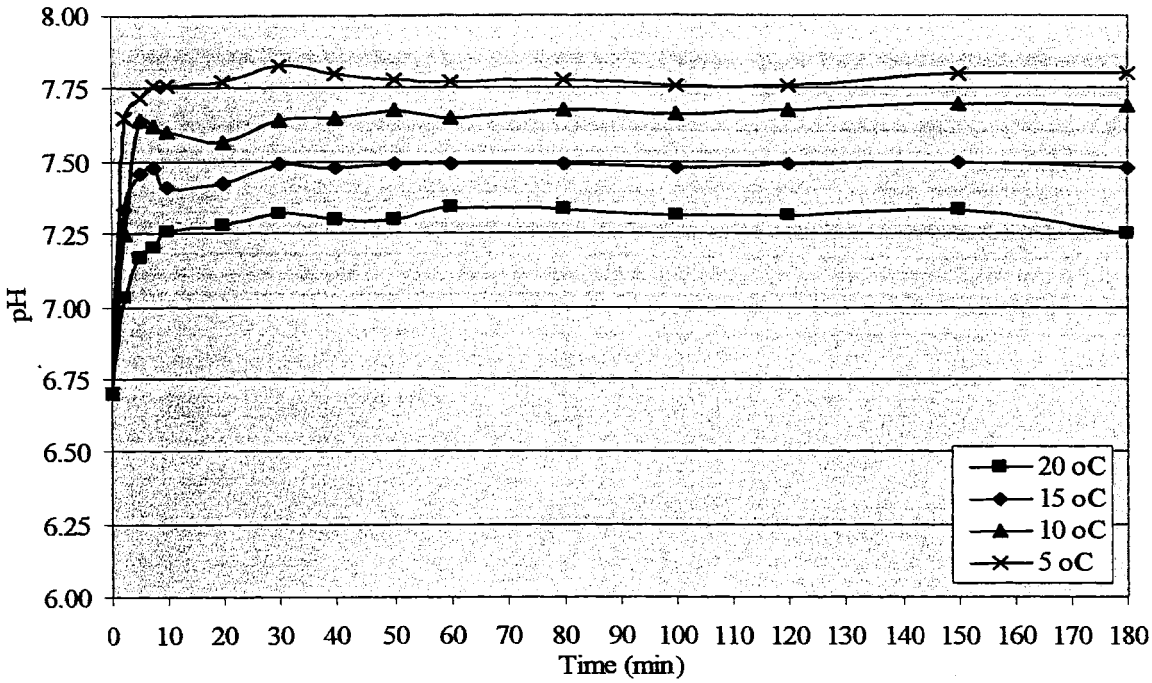
(a) pH



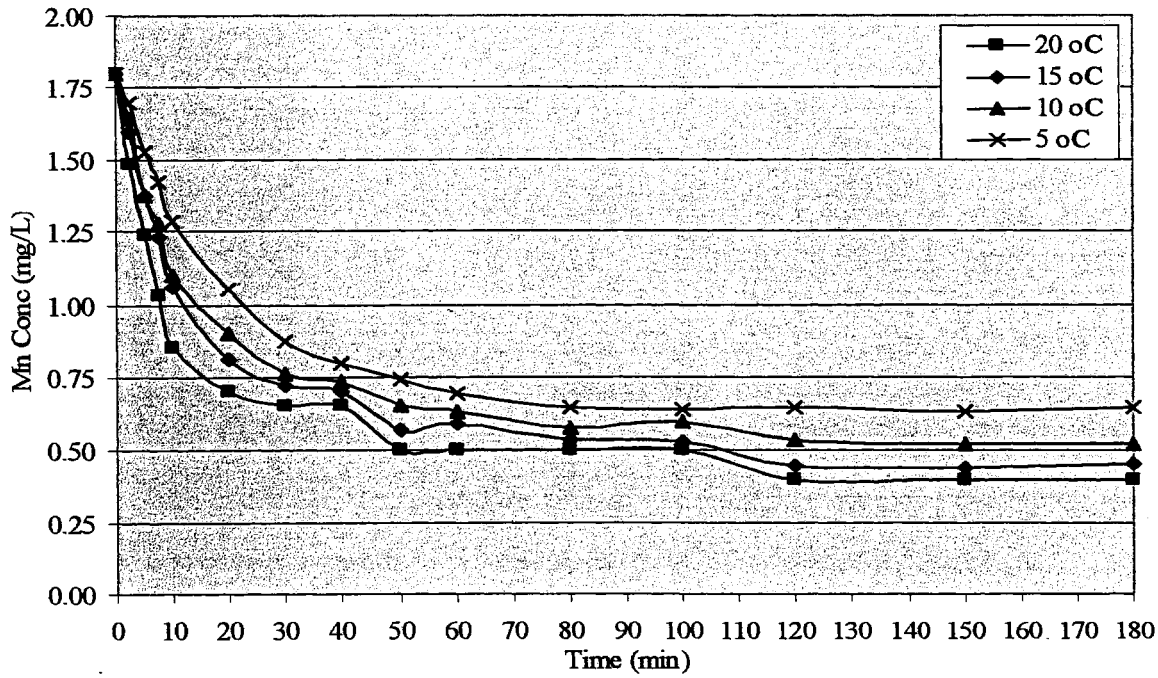
(b) Manganese

Figure 7.13. Manganese concentrations and pH of water obtained from the beaker-limestone filter treating Mn containing wastewater under batch conditions at different temperatures.

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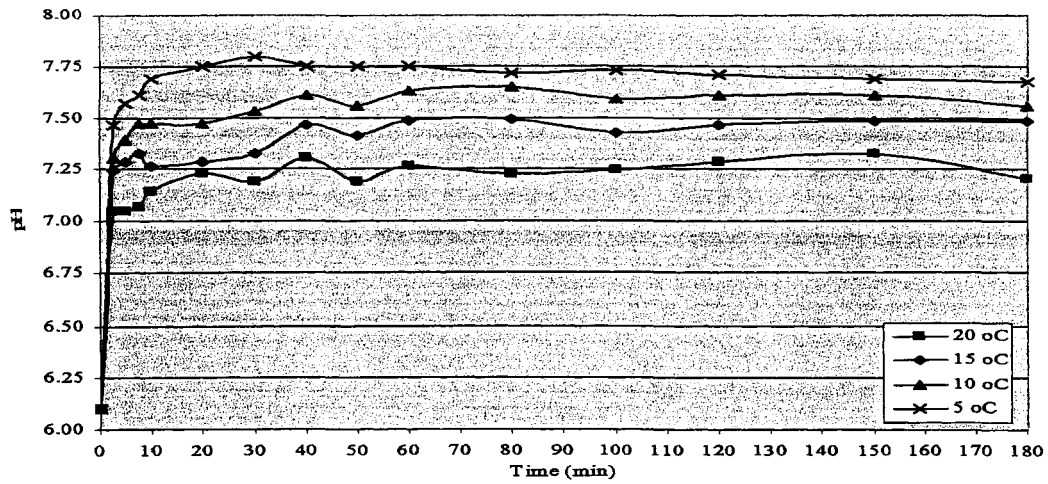
(a) pH



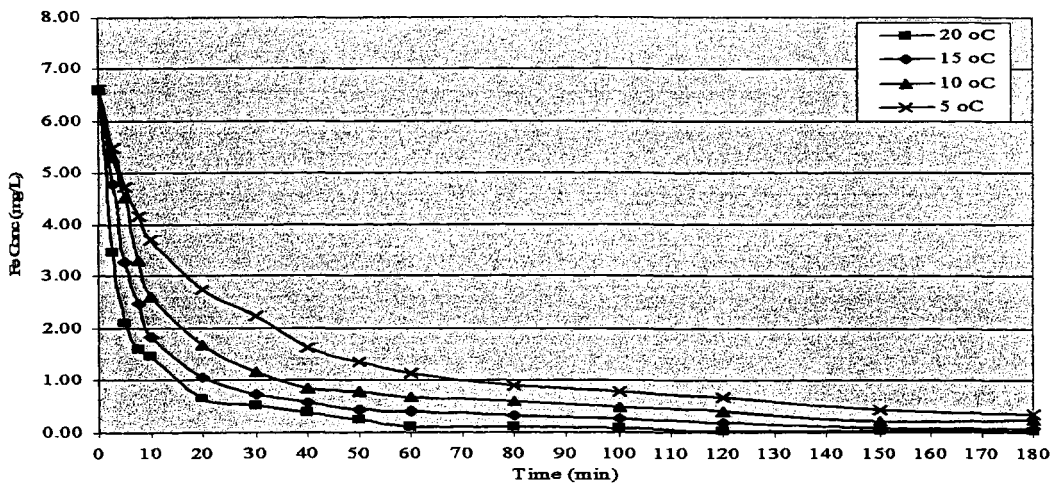
(b) Manganese

Figure 7.14. Manganese concentrations and pH of water obtained from the beaker-limestone/sandstone filter treating Mn containing wastewater under batch conditions at different temperatures.

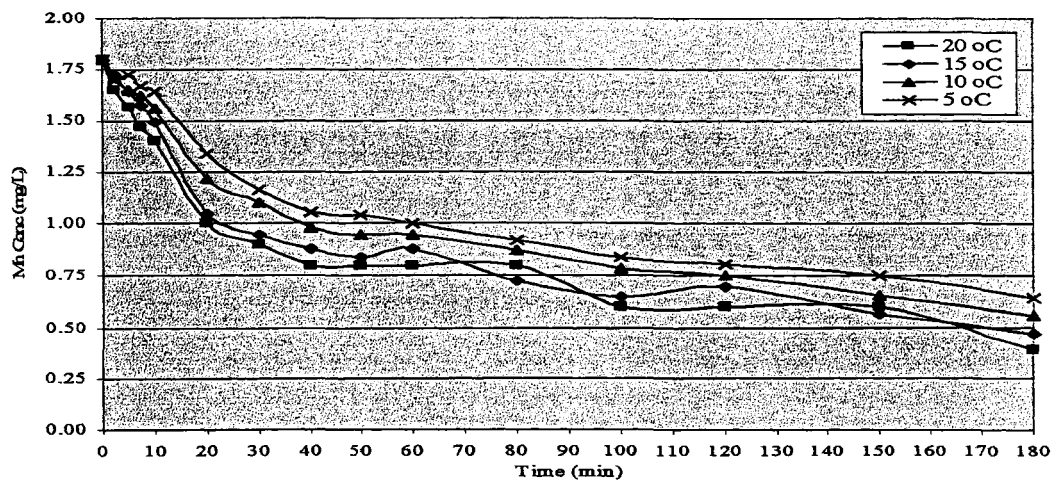
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(a) pH



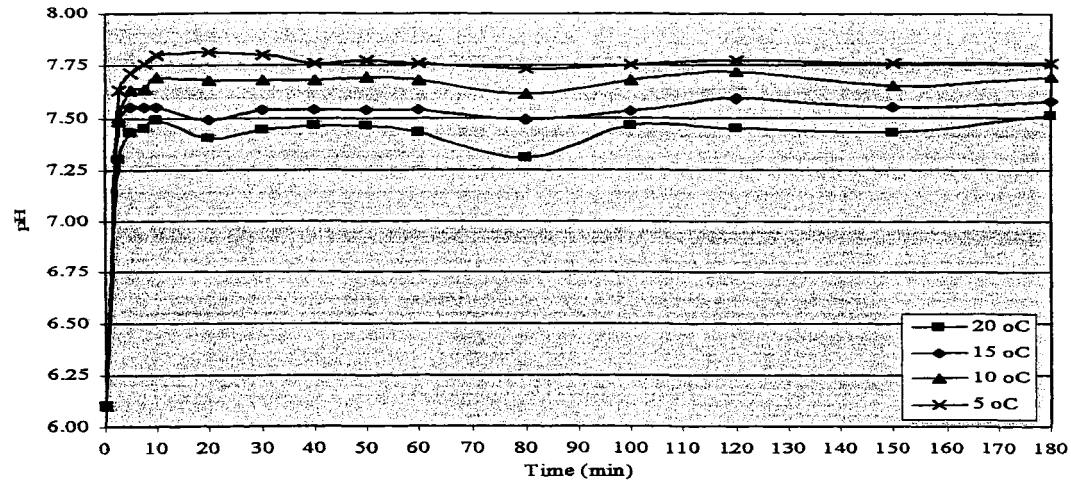
(b) Iron



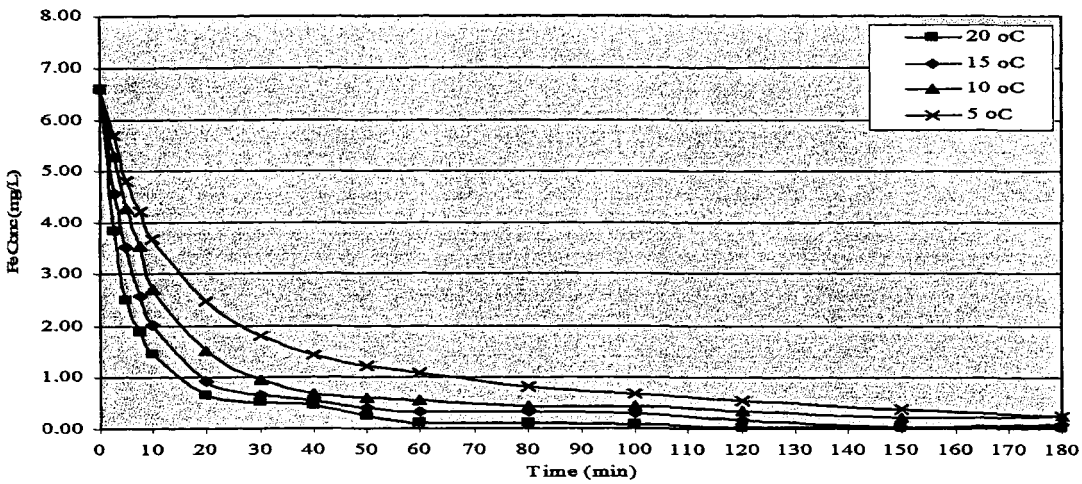
(c) Manganese

Figure 7.15. Iron and manganese concentrations and pH of water obtained from the beaker-limestone/sandstone filter treating Fe and Mn containing wastewater under batch conditions at different temperatures.

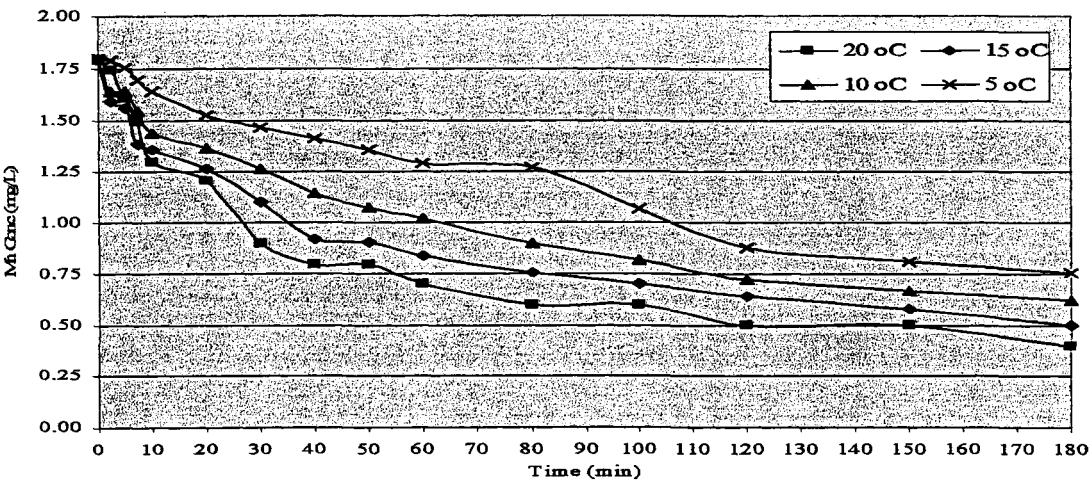
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(a) pH



(b) Iron



(c) Manganese

Figure 7.16. Iron and manganese concentrations and pH of water obtained from the beaker-limestone/sandstone filter treating Fe and Mn containing wastewater under batch conditions at different temperatures.

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7.6.2.2 Manganese

The manganese concentrations in the water samples obtained after 3 hours from the limestone filters were 0.25, 0.40, 0.34 and 0.56 mg/L with average removal efficiencies of 86.11, 77.78, 80.89 and 68.89 % for the temperatures of 20, 15, 10 and 5 °C, respectively. The manganese concentrations in the water samples obtained after 3 hours from the limestone/sandstone filters were 0.40, 0.46, 0.53 and 0.65 mg/L with average total removal efficiencies of 77.78, 74.67, 70.83 and 64.11 % for the temperatures of 20, 15, 10 and 5 °C, respectively. About 69.44, 65.44, 59.39 and 45.61 % of the manganese were removed from solution by the limestone filters and about 61.11, 55.00, 50.06 and 41.61 % of the manganese were removed from the solution by the limestone/sandstone filters after 20 minutes for the temperatures of 20, 15, 10 and 5 °C, respectively.

Removal of manganese from the solutions containing iron and manganese was lower than that from solutions containing manganese alone for both the limestone and the limestone/sandstone filters. The manganese concentrations in the water samples obtained from the limestone filters were 0.40, 0.48, 0.56 and 0.64 mg/L with average total removal efficiencies of 77.78, 73.61, 68.89 and 64.44 % for the temperatures of 20, 15, 10 and 5 °C, respectively. The manganese concentrations in the water samples obtained after 3 hours from limestone/sandstone filters were 0.41, 0.50, 0.62 and 0.76 mg/L with average total removal efficiencies of 77.78, 72.28, 65.61 and 58.00 % for the temperatures of 20, 15, 10 and 5 °C, respectively. About 44.44, 42.00, 32.33 and 25.61 % of the manganese were removed from solution by the limestone filters and about 33.33, 29.67, 24.22 and 15.33 % of the manganese were removed from the solution by the limestone/sandstone filters after 20 minutes for the temperatures of 20, 15, 10 and 5 °C, respectively.

7.6.2.3 pH

The initial pH of the iron solution was 6.1 which increased to 7.3 - 7.8 during the experiment. The initial pH of the manganese solution was 6.7 which increased to 7.2 - 7.8 during the experiment. The initial pH of the iron/manganese solution was 6.1 which

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increased to 7.20 - 7.76 during the experiment. The outlet pH of iron solution was 7.68 - 7.76, 7.61 - 7.69, 7.48 - 7.58 and 7.26 - 7.51 at the temperatures of 5, 10, 15 and 20 °C, respectively. The outlet pH of manganese solution was 7.78 - 7.80, 7.68 - 7.69, 7.48 - 7.50 and 7.19 - 7.29 at the temperatures of 5, 10, 15 and 20 °C, respectively. The outlet pH of iron/manganese solution was 7.68 - 7.76, 7.56 - 7.69, 7.48 - 7.58 and 7.21 - 7.51 at the temperatures of 5, 10, 15 and 20 °C, respectively.

7.6.3 Continuous Flow Experiment

Figures 7.17 – 7.18 show the iron and manganese concentrations and the pH in the effluent of the filters containing sandstone of different particle sizes and limestone/sandstone of different ratios.

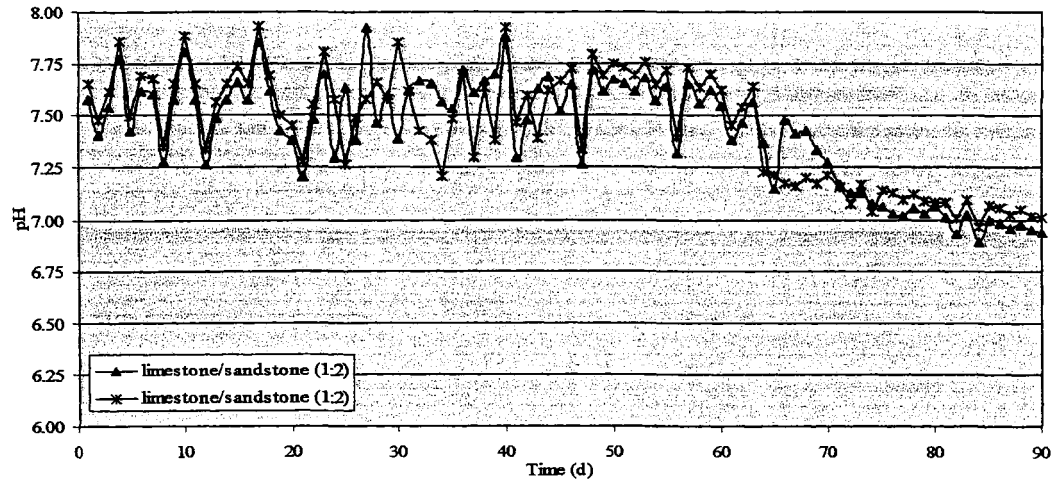
7.5.3.1 Iron

The initial iron concentration in the wastewater was 6.60 mg/L. The iron concentrations in the water samples obtained at the end of the experimental period from the filters that contained limestone and small particles of sandstone of the ratios of 1:1 and 1:2 were 1.02 and 1.12 mg/L, respectively. The iron concentrations in the water samples obtained at the end of the experimental period from the filters that contained limestone and large particles of sandstone of the ratios of 1:1 and 1:2 were 1.08 and 1.20 mg/L, respectively.

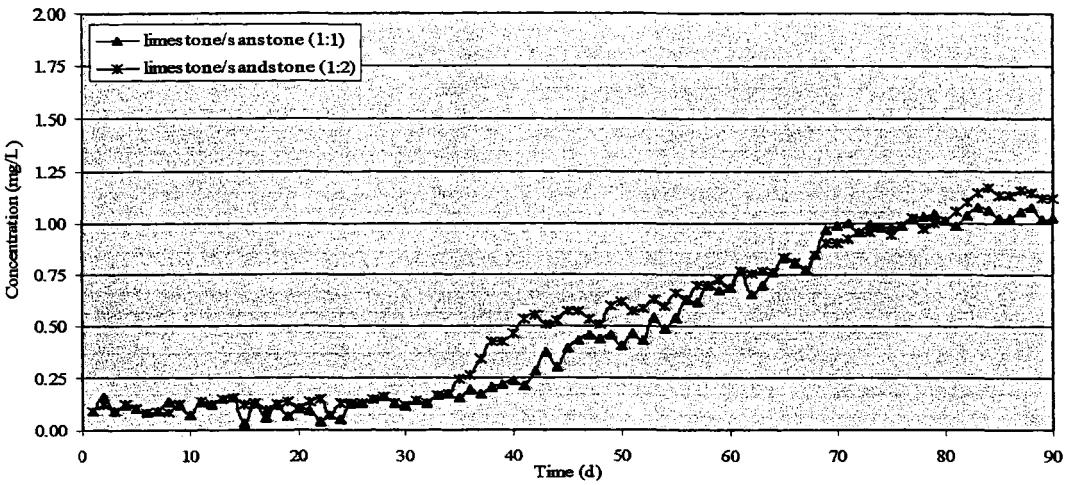
7.6.3.2 Manganese

The initial concentration of manganese in the wastewater was 1.8 mg/L. The manganese concentrations in the samples obtained at the end of the experimental period from the filters that contained limestone and small particles of sandstone of the ratios of 1:1 and 1:2 were 0.47 and 0.48 mg/L, respectively. The manganese concentrations in the water samples obtained at the end of the experimental period from the filters that contained limestone and large particles of sandstone of the ratios of 1:1 and 1:2 were 0.52 and 0.47 mg/L, respectively.

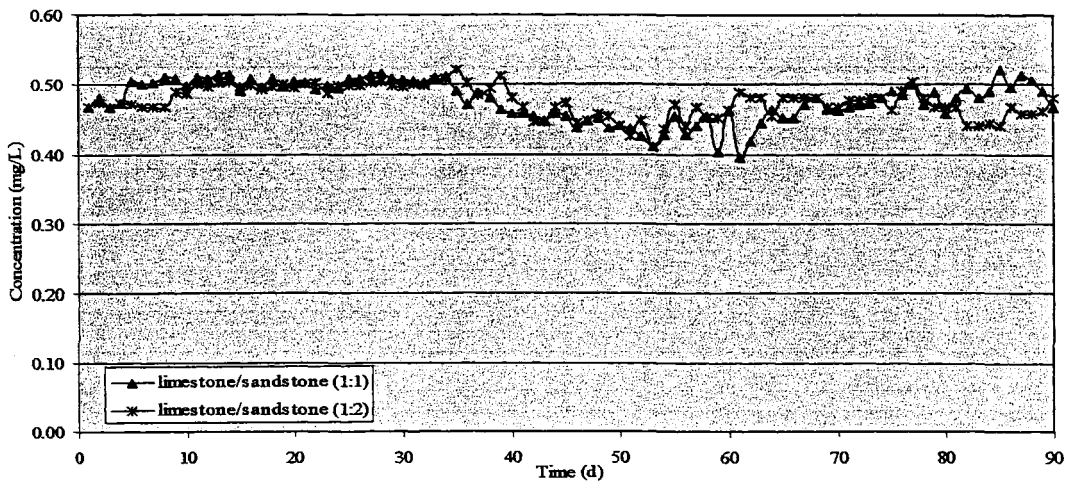
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(a) pH



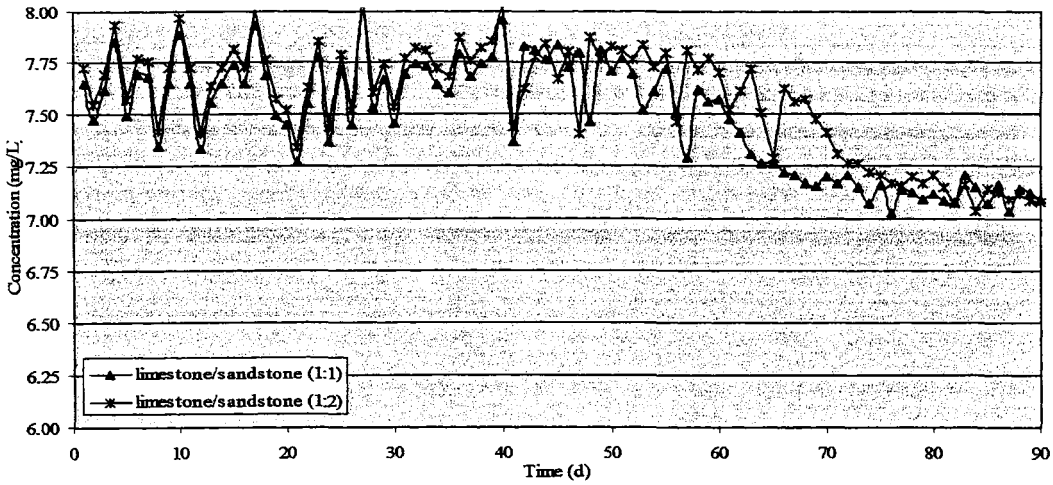
(b) Iron



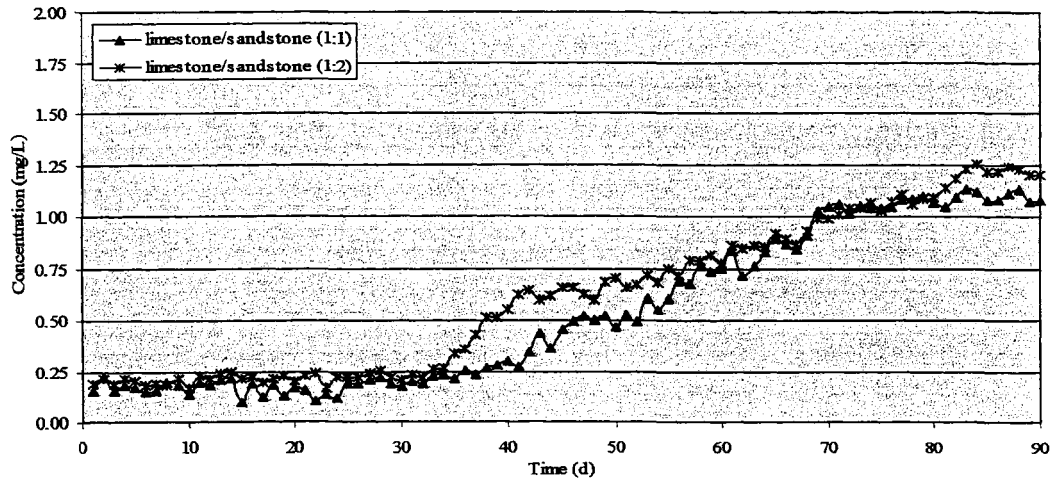
(c) Manganese

Figure 7.17. The iron and manganese concentrations and pH of the effluent from the filter containing limestone and small particles of sandstone of the ratios of 1:1 and 1:2 and treating Fe and Mn containing wastewater.

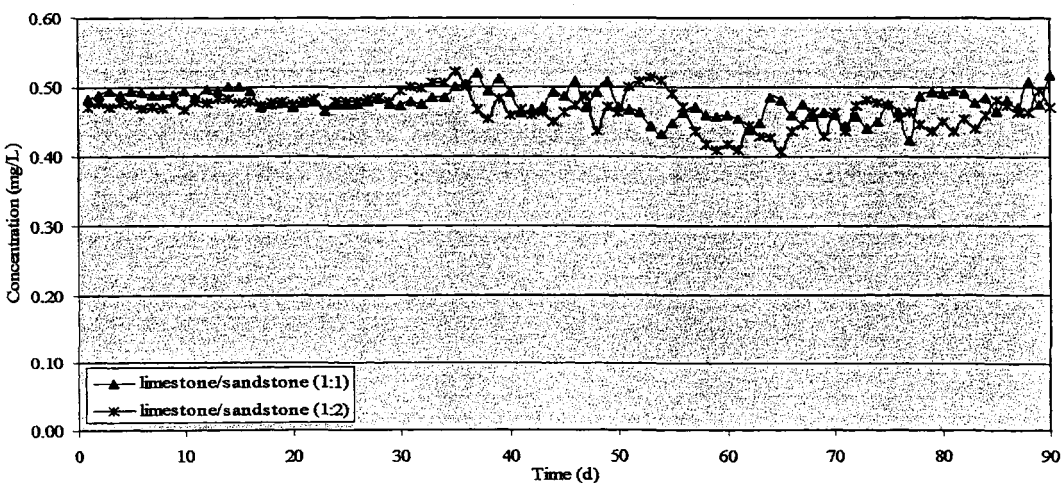
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(a) pH



(b) Iron



(c) Manganese

Figure 7.18. The iron and manganese concentrations and pH of the effluent from the filter containing limestone and large particles of sandstone of the ratios 1:1 and 1:2 and treating Fe and Mn containing wastewater.

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7.6.3.3 pH

The initial pH in the water samples was 6.1. The pH of the water samples obtained from the filter that contained limestone and small particles of sandstone of the ratios of 1:1 and 1:2 at the end of the experimental period were 6.94 and 7.01, respectively. The pH levels in the water samples obtained from the filters that contained limestone and large particles of sandstone of the ratios of 1:1 and 1:2 at the end of the experimental period were 7.09 and 7.08, respectively.

7.7 Discussion

7.7.1 Tank Batch Experiment

7.7.1.1 Iron

Limestone is a sedimentary rock, which is primarily composed of the mineral calcium carbonate ($CaCO_3$). The successful iron removal can be attributed to the dissolution of calcium carbonate and the resulting increase in the pH of the solution. The dissolution of calcium carbonate can increase the concentration of alkalinity ($HCO_3^- + OH^-$) in water as follows (Sun, 2000; and Cravotta III and Trahan, 1999):

$$2\ CaCO_{3s} + 2\ H_2O \rightarrow 2\ Ca^{2+} + 2OH^- + 2\ HCO_3^- \qquad (7.1)$$

According to Gazea et al (1996), iron usually drains from landfills in the reduced ferrous form (Fe^{2+}). In an aerobic environment, ferrous iron oxidation occurs quickly at a pH $\geq$ 5 with a rate constant of 0.064-0.086 min^{-1} (Wolthoorn et al., 2004). As ferrous iron is oxidized to ferric iron, it is subjected to hydrolysis that results in the precipitation of iron hydroxides. Ferric iron hydrolysis and precipitation occurs quickly at a pH $\geq$ 3.5. Equations (5.8) and (5.9) demonstrate iron oxidation, hydrolysis and precipitation (PDEP, 2003 and Berghorn and Hunzeker, 2001). Since the pH of all water samples analyzed was about 7.05 and oxygen was supplied to the water by an aeration unit, ferrous iron oxidation and ferric iron hydrolysis and precipitation occurred rapidly.

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Most of iron (96%) was removed in the first two hours of the experiment. Tables 7.11 and 7.12 show the average iron removal rates during this period from wastewaters containing an initial iron concentration of 6.6 mg/L and initial concentrations of 6.6 mg/L for iron and 1.8 mg/L for manganese, respectively. A two-sample t-test was performed at 95 % confidence intervals to determine if the means of iron removal rates of the four populations (iron in limestone filter, iron in limestone/sandstone, iron and manganese in limestone filter and iron and manganese in limestone/sandstone filter) were different from one another. The results are presented in the Minitab printout shown in Figure 7.19. The 95 % confidence intervals for each comparison included zero and the p-values calculated for all six tests were greater than the chosen α level of 0.05 which indicated that there was no evidence for differences between the mean removal rates of the populations.

Analysis of variance (ANOVA) was performed on the removal efficiency data using MINITAB Release 14 (MINITAB Inc., State College, PA). The ANOVA results (Tables 7.13 and 7.14) showed that the pH and time have significant effects on the removal efficiency ($P < 0.0001$). The results also showed significant interactions ($P < 0.0001$) between the parameters.

The limestone and limestone/sandstone filters removed between 99.24 and 100 % of the iron from solution in 24 h. The results obtained in this experiment are in agreement with other results reported in the literature. Aziz et al (2003) conducted a study using limestone as a filter media to treat landfill leachate and reported an iron removal of 83 - 95 % over a 30 day period. Sun (2000) conducted batch experiments in which limestone was used as a filter media to treat an iron acid solution that initially contained 27.93 mg iron/L and reported an iron removal of 100 % after 150 minutes. Xu et al (1997) conducted batch experiments using calcite and quartz grains as filter media and reported a drop in iron concentrations from 560 mg/L to 1.12 mg/L. Aziz et al. (2004) reported 90 % removal of iron by limestone filter from landfill leachate treated containing 19.5 mg/L iron. Smith et al. (1993) used limestone filters to treat contaminated groundwater containing iron concentration of 5.0 mg/L and reported final concentration of iron of 0.2 mg/L.

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Table 7.11. Fe average removal rate (during the first 2 hours) from wastewater containing an initial Fe concentration of 6.6 mg/L.

Time (day)	Limestone		Limestone/Sandstone	
	Concentration (mg/L)	Removal Rate[a] (mg/L/h)	Concentration (mg/L)	Removal Rate[b] (mg/L/h)
1	0.35	3.13	0.40	3.10
2	0.35	3.13	0.45	3.08
3	0.25	3.18	0.20	3.20
4	0.35	3.13	0.25	3.18
5	0.25	3.18	0.15	3.23
6	0.25	3.18	0.25	3.18
7	0.20	3.20	0.20	3.20
Average	0.29	3.16	0.29	3.16

[a] population 1
[b] population 2

Table 7.12. Fe average removal rate (during the first 2 hours) from wastewater containing initial Fe and Mn concentrations of 6.6 mg/L and 1.8 mg/L, respectively.

Time (day)	Limestone		Limestone/Sandstone	
	Concentration (mg/L)	Removal Rate[c] (mg/L/h)	Concentration (mg/L)	Removal Rate[d] (mg/L/h)
1	0.35	3.13	0.40	3.10
2	0.35	3.13	0.40	3.10
3	0.30	3.15	0.05	3.28
4	0.30	3.15	0.25	3.18
5	0.25	3.18	0.40	3.10
6	0.25	3.18	0.30	3.15
7	0.20	3.20	0.20	3.20
Average	0.29	3.16	0.29	3.16

[c] population 3
[d] population 4

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Two-Sample T-Test and CI: Population 1, Population 2

```
Two-sample T for Population 1 vs Population 2

             N   Mean  StDev  SE Mean
Population 1  7  0.307  0.102    0.038
Population 2  7  0.271  0.111    0.042


Difference = mu (Population 1) - mu (Population 2)
Estimate for difference:  0.035714
95% CI for difference:  (-0.089728, 0.161157)
T-Test of difference = 0 (vs not =): T-Value = 0.63  P-Value = 0.544  DF = 11
```

Two-Sample T-Test and CI: Population 1, Population 3

```
Two-sample T for Population 1 vs Population 3

             N   Mean  StDev  SE Mean
Population 1  7  0.307  0.102    0.038
Population 3  7  0.421  0.413     0.16


Difference = mu (Population 1) - mu (Population 3)
Estimate for difference:  -0.114286
95% CI for difference:  (-0.507831, 0.279259)
T-Test of difference = 0 (vs not =): T-Value = -0.71  P-Value = 0.504  DF = 6
```

Two-Sample T-Test and CI: Population 1, Population 4

```
Two-sample T for Population 1 vs Population 4

             N   Mean  StDev  SE Mean
Population 1  7  0.307  0.102    0.038
Population 4  7  0.286  0.131    0.050


Difference = mu (Population 1) - mu (Population 4)
Estimate for difference:  0.021429
95% CI for difference:  (-0.116824, 0.159681)
T-Test of difference = 0 (vs not =): T-Value = 0.34  P-Value = 0.739  DF = 11
```

Two-Sample T-Test and CI: Population 2, Population 3

```
Two-sample T for Population 2 vs Population 3

             N   Mean  StDev  SE Mean
Population 2  7  0.271  0.111    0.042
Population 3  7  0.421  0.413     0.16


Difference = mu (Population 2) - mu (Population 3)
Estimate for difference:  -0.150000
95% CI for difference:  (-0.545738, 0.245738)
T-Test of difference = 0 (vs not =): T-Value = -0.93  P-Value = 0.389  DF = 6
```

Two-Sample T-Test and CI: Population 2, Population 4

```
Two-sample T for Population 2 vs Population 4

             N   Mean  StDev  SE Mean
Population 2  7  0.271  0.111    0.042
Population 4  7  0.286  0.131    0.050


Difference = mu (Population 2) - mu (Population 4)
Estimate for difference:  -0.014286
95% CI for difference:  (-0.157514, 0.128942)
T-Test of difference = 0 (vs not =): T-Value = -0.22  P-Value = 0.830  DF = 11
```

Two-Sample T-Test and CI: Population 3, Population 4

```
Two-sample T for Population 3 vs Population 4

             N   Mean  StDev  SE Mean
Population 3  7  0.421  0.413     0.16
Population 4  7  0.286  0.131    0.050


Difference = mu (Population 3) - mu (Population 4)
Estimate for difference:  0.135714
95% CI for difference:  (-0.251779, 0.523208)
T-Test of difference = 0 (vs not =): T-Value = 0.83  P-Value = 0.435  DF = 7
```

Figure 7.19. Minitab printout for t-test for iron removal data.

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Table 7.13. Analysis of variance of iron removal efficiency.

Source	DF	SS	T	F	P
Model	3	56466	18822	576.29	0.0001
Residual Error	45	1470	33		
Total	48	57935			

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 97.5%

Table 7.14. P-values of factors affecting iron removal efficiency.

Predictor	Coeffient	SE Coeffient	T	P
Time (T)	35.641	6.637	5.37	0.0001
pH	68.897	1.940	35.52	0.0001
T x pH	-4.729	0.867	-5.45	0.0001

The highest average concentration of iron remaining in solution in this study was 0.1 mg/L which is lower than the CCME (2002) guidelines for the protection of aquatic life of 0.3 mg/L.

The significance of including sandstone in the filter is to minimize the metal hydroxide armoring of the limestone and thus increase the useful lifetime of the filter. Xu et al. (1997) and Sasowsky et al (2000) determined that iron preferentially precipitates on the sandstone surface. Xu et al. (1997) concluded that the surface charge of calcite and ferrihydrite are positive and the surface charge of quartz is negative over the pH range 2.0-8.0. Sasowsky et al. (2000) also determined that sandstone had a more negative charge than limestone over the pH range 4.0-7.0. The effect of sandstone on the removal efficiency was not clear due to the short duration of the experiment.

7.7.1.2 Manganese

Dissolved manganese (Mn^{2+}) is another common metal contaminant in landfill leachates. However, the mechanisms of abiotic Mn^{2+} oxidation and precipitation have not been fully

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explained in the limestone. According to Gazea et al (1996), one possible mechanism for abiotic manganese precipitation involves the oxidation of Mn^{2+} to either Mn^{3+} or Mn^{4+}, which is similar to ferrous iron oxidation. Then, the trivalent (Mn^{3+}) or tetravalent (Mn^{4+}) form precipitates as MnOOH. The overall reaction for manganese oxidation and precipitation was presented in Equation (5.12). In alkaline environments, Mn^{2+} can also precipitate in the carbonate form, which in the presence of oxygen may also further oxidize to MnO_2 (Gazea et al, 1996).

$$Mn^{2+} + HCO_3^- \rightarrow MnCO_{3\,(s)} + H^+ \quad (7.2)$$

$$MnCO_3 + O_2 \rightarrow MnO_2 + CO_2 \quad (7.3)$$

The overall reaction can be described by the following equation:

$$Mn^{2+} + HCO_3^- + O_2 \rightarrow MnO_2 + CO_2 + H^+ \quad (7.4)$$

A large percentage of the manganese (70 %) was removed from the solution during the first 4 hours. Tables 7.15 and 7.16 show the average manganese removal rates during this period from wastewaters containing an initial manganese concentration of 1.8 mg/L and initial concentrations of 6.6 mg/L for iron and 1.8 mg/L for manganese, respectively. The average manganese removal rate was 0.29 and 0.26 mg/L/h for samples obtained from limestone and limestone/sandstone filter containing manganese solution, respectively. The average manganese removal rate was 0.26 and 0.24 mg/L/h for samples that obtained from limestone and limestone/sandstone filter containing manganese/iron solution, respectively.

A two-sample t-test (Figure 7.20) was performed at 95 % confidence intervals on the mean of manganese removal rates of the four populations (Mn in limestone filter, Mn in limestone/sandstone filter, Mn/Fe in limestone filter and Mn/Fe in limestone/sandstone filter). The results showed that the 95 % confidence intervals for each comparison included zero and the p-values calculated for all six tests were greater than the chosen α level of 0.05 which indicated that there was no evidence for differences between the mean removal rates of the populations.

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Table 7.15. Mn average removal rates (during the first 4 hours) from wastewater containing an initial Mn concentration of 1.8 mg/L.

Time (day)	Limestone		Limestone/Sandstone	
	Concentration (mg/L)	Removal Rate[a] (mg/L/h)	Concentration (mg/L)	Removal Rate[b] (mg/L/h)
1	0.10	0.43	0.60	0.30
2	0.60	0.30	0.90	0.23
3	0.80	0.25	1.20	0.15
4	0.60	0.30	0.60	0.30
5	0.80	0.25	0.90	0.23
6	0.60	0.30	0.80	0.25
7	0.80	0.25	0.50	0.33
Average		0.29		0.26

a population 1
b population 2

Table 7.16. Mn average removal rates (during the first 4 hours) from wastewater containing initial Fe and Mn concentrations of 6.6 mg/L and 1.8 mg/L, respectively.

Time (day)	Limestone		Limestone/Sandstone	
	Concentration (mg/L)	Removal Rate[c] (mg/L/h)	Concentration (mg/L)	Removal Rate[d] (mg/L/h)
1	0.50	0.33	0.40	0.35
2	0.60	0.30	0.90	0.23
3	1.00	0.20	0.80	0.25
4	0.50	0.33	0.80	0.25
5	1.40	0.10	1.00	0.20
6	0.60	0.30	1.00	0.20
7	0.80	0.25	1.00	0.20
Average		0.26		0.24

c population 3
d population 4

The ANOVA results (Tables 7.17 and 7.18) showed that the pH and time have significant effects on the removal efficiency of manganese confidence levels of 99.99 % (P = 0.0001) and 92.50 % (P=0.0750), respectively. The results also showed significant interactions between the parameters at 93 % confidence level (P = 0.0740).

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Two-sample T for population 1 vs population 2

```
    N    Mean   StDev  SE Mean
C1  7  0.2971  0.0637    0.024
C2  7  0.2557  0.0605    0.023

Difference = mu (C1) - mu (C2)
Estimate for difference:  0.041429
95% CI for difference:  (-0.031660, 0.114517)
T-Test of difference = 0 (vs not =): T-Value = 1.25  P-Value = 0.238  DF = 11
```

Two-sample T for population 1 vs population 3

```
    N    Mean   StDev  SE Mean
C1  7  0.2971  0.0637    0.024
C3  7  0.2586  0.0840    0.032

Difference = mu (C1) - mu (C3)
Estimate for difference:  0.038571
95% CI for difference:  (-0.049093, 0.126236)
T-Test of difference = 0 (vs not =): T-Value = 0.97  P-Value = 0.354  DF = 11
```

Two-sample T for population 1 vs population 4

```
    N    Mean   StDev  SE Mean
C1  7  0.2971  0.0637    0.024
C4  7  0.2400  0.0535    0.020

Difference = mu (C1) - mu (C4)
Estimate for difference:  0.057143
95% CI for difference:  (-0.012079, 0.126364)
T-Test of difference = 0 (vs not =): T-Value = 1.82  P-Value = 0.097  DF = 11
```

Two-sample T for population 2 vs population 3

```
    N    Mean   StDev  SE Mean
C2  7  0.2557  0.0605    0.023
C3  7  0.2586  0.0840    0.032


Difference = mu (C2) - mu (C3)
Estimate for difference:  -0.002857
95% CI for difference:  (-0.090009, 0.084295)
T-Test of difference = 0 (vs not =): T-Value = -0.07  P-Value = 0.943  DF = 10
```

Two-sample T for population 2 vs population 4

```
    N    Mean   StDev  SE Mean
C2  7  0.2557  0.0605    0.023
C4  7  0.2400  0.0535    0.020


Difference = mu (C2) - mu (C4)
Estimate for difference:  0.015714
95% CI for difference:  (-0.051502, 0.082931)
T-Test of difference = 0 (vs not =): T-Value = 0.51  P-Value = 0.617  DF = 11
```

Two-sample T for population 3 vs population 4

```
    N    Mean   StDev  SE Mean
C3  7  0.2586  0.0840    0.032
C4  7  0.2400  0.0535    0.020

Difference = mu (C3) - mu (C4)
Estimate for difference:  0.018571
95% CI for difference:  (-0.065283, 0.102425)
T-Test of difference = 0 (vs not =): T-Value = 0.49  P-Value = 0.632  DF = 10
```

Figure 7.20. Minitab printout for t-test for manganese removal data.

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Table 7.17. Analysis of variance of manganese removal efficiency.

Source	DF	SS	T	F	P
Model	3	19978.6	6659.5	31.98	0.0001
Residual Error	45	9369.9	208.2		
Total	48	29348.5			

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 68.1 %

Table 7.18. P-values of factors affecting manganese removal efficiency.

Predictor	Coefficient	SE Coefficient	T	P
Time (T)	37.90	20.82	1.82	0.0750
pH	74.09	9.43	7.86	0.0001
T x pH	-5.04	2.76	-1.83	0.0740

Manganese removal by both the limestone and the limestone/sandstone filter was not as effective as iron. With the limestone filter, at least 66.67 % of the manganese was removed from solution on days 1, 4 and 6 (Table 7.3). However, this performance was not maintained throughout the seven days of the experiment. For example, there were instances where the measured manganese concentration reached values of up to 77.88 % of influent concentration (Tables 7.3 and 7.4).

Komnitsas et al (2004) and Gazea et al (1996) stated that manganese is very difficult to remove from solution. Manganese is an extremely mobile ion and elevated levels of manganese may be caused by re-dissolution of unstable precipitates or desorption of manganese from surfaces (Komnitsas et al, 2004). Gazea et al (1996) suggest that when both iron and manganese are present in solution, manganese removal will be less efficient than iron because iron and manganese precipitations do not occur at the same time, they occur sequentially. The following two reactions can explain why manganese removal was not as efficient as iron removal (Gazea et al, 1996).

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$$MnO_2 + 2\,Fe^{2+} + 2\,H_2O \rightarrow 2FeOOH_{(S)} + Mn^{2+} + 2H^{+} \quad (7.5)$$

$$MnOOH + Fe^{2+} \rightarrow FeOOH_{(S)} + Mn^{2+} \quad (7.6)$$

A second mechanism for manganese removal is the abiotic manganese precipitation which occurs slowly at pH values ≤ 8 according to Gazea et al (1996). The highest pH of the water samples was 7.69.

7.7.1.3 pH

As pH increased the dissolved iron concentration in the wastewater decreased. Strong correlations (Figure 7.21) were observed between the iron removal efficiencies and the pH of the water obtained from the limestone (R^2 = 0.94 and 0.84 for the iron and iron/manganese solutions, respectively) and the limestone/sandstone (R^2 = 0.86 and 0.84 for the iron and iron/manganese solutions, respectively) filters. The results presented in this study were similar to the results found in the literature. Cravotta and Trahan (1999) reported that concentrations of iron in acid mine drainage decreased down flow through an open limestone drains due to the increased pH and the consequent precipitation of hydrous Fe oxides. Wajon et al. (1985) reported increases in the removal of iron from contaminated wastewater due to increases in the pH.

In the case of manganese, there were no correlations between the manganese removal efficiencies and pH of the wastewater obtained from any of the filter as shown in Figure 7.22. The results presented in this study were similar to those found in the literature. Cravotta and Trahan (1999) reported that for the entire monitoring period, ratios of Mn to Fe in the wastewater did not show a consistent trend with respect to pH. Aziz and Smith (1992) found no correlation between manganese removal and pH when the pH was less than 8.5.

7.7.2 Beaker Batch Experiment

Since most of the iron was removed from the wastewater during the first two hours, small reactors (2.1 L volume) were used and the experiment was designed for a shorter

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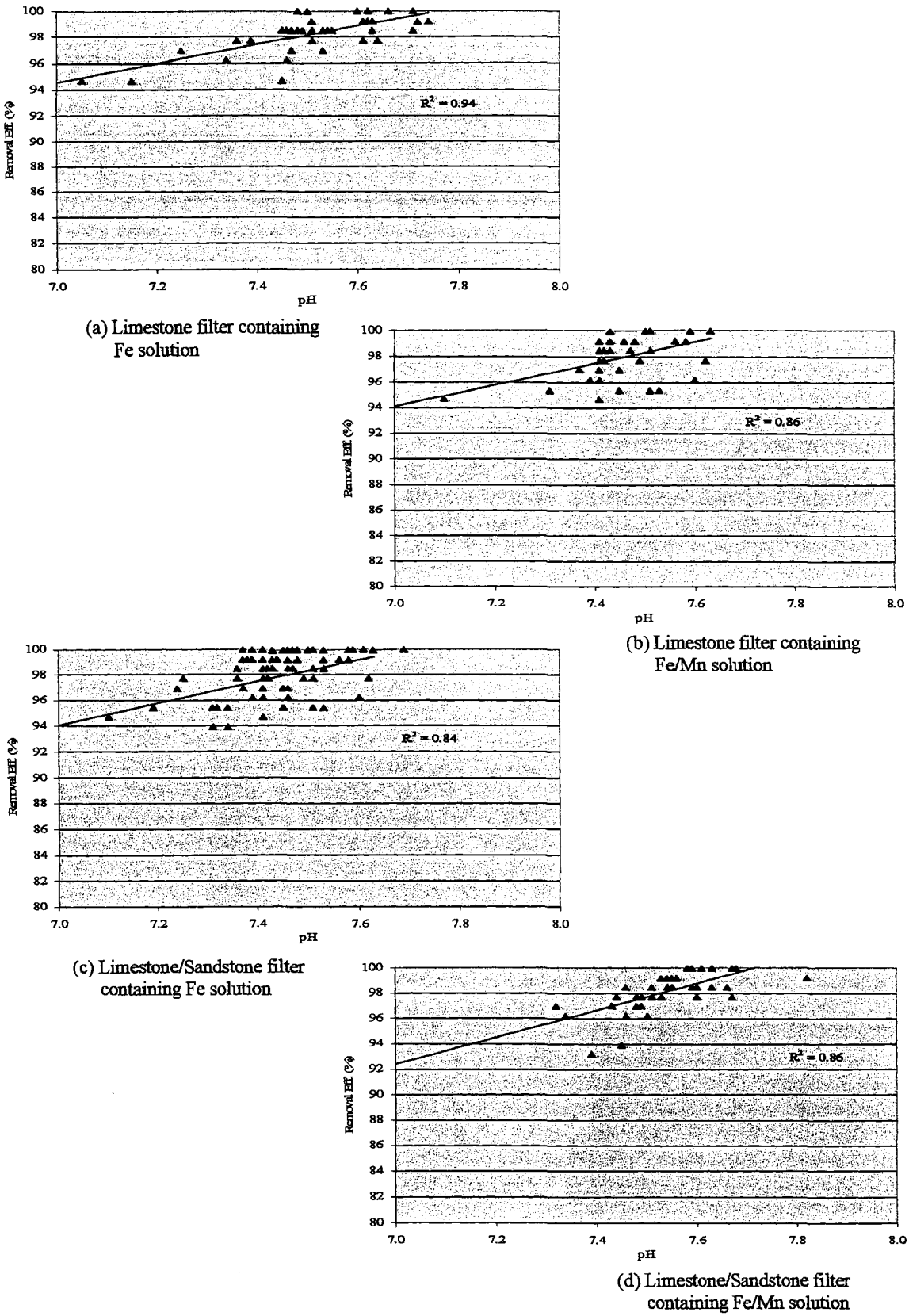


Figure 7.21. Correlations between the iron removal efficiencies and the pH.

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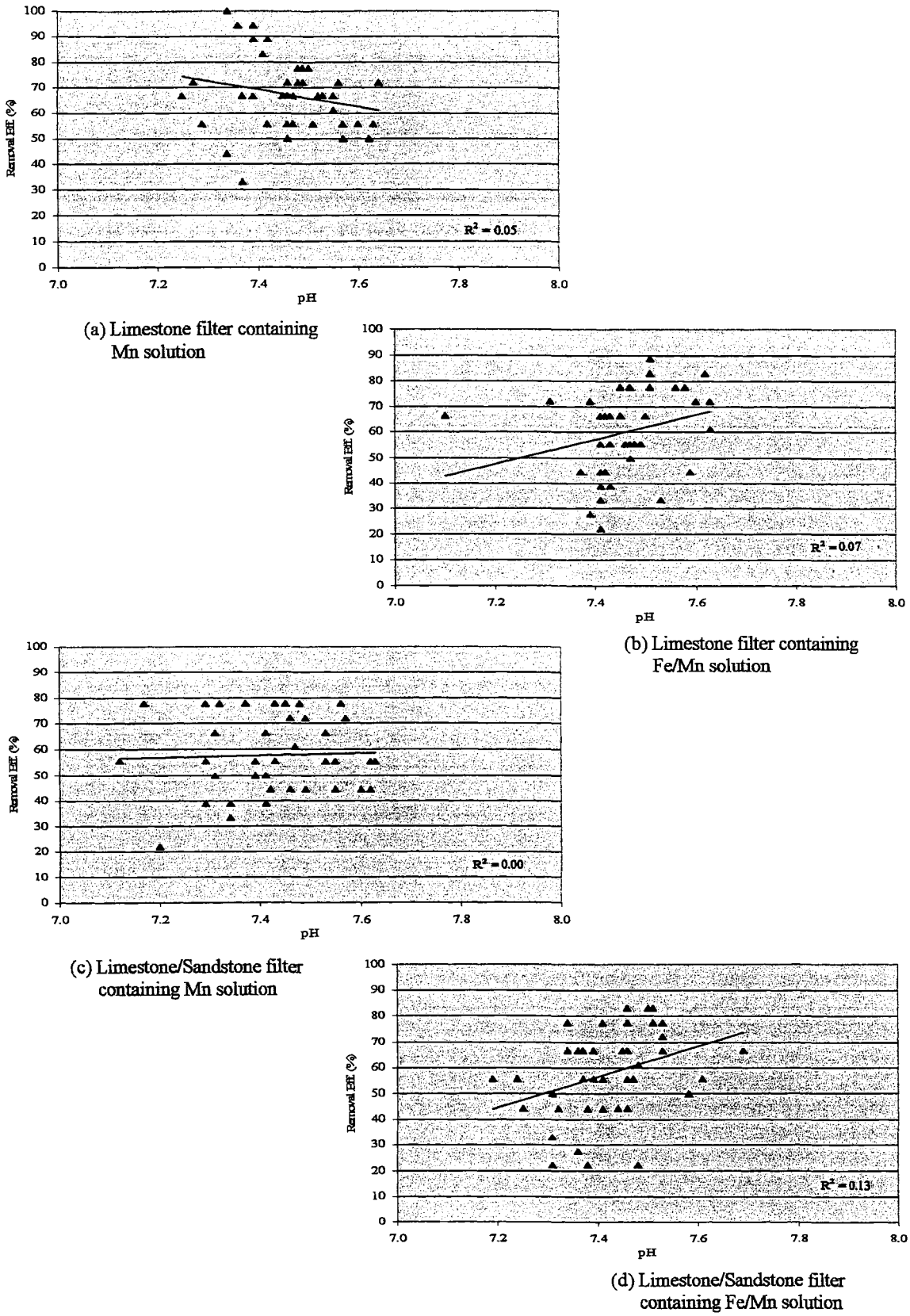


Figure 7.22. Lack of correlation between the manganese removal efficiencies and the pH.

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period (3 hours) and more frequent sampling. Also, the effect of temperature changes on the removal efficiency and removal rates of iron and manganese were investigated in this experiment.

7.7.2.1 Iron

The iron removal efficiencies in the limestone and limestone/sandstone filters containing iron and iron/manganese solutions decreased as the temperature decreased as shown in Tables (7.5-7.8). Most of iron was removed from solution within the first 10 minutes at 20 °C while the removal of iron from solution at 5 °C took much longer time. The average iron removal efficiency for limestone and limestone/sandstone filters containing iron solution calculated after 10 min was 95.45 and 83.71 % at 20°C and 47.73 and 46.97 % at 5°C, respectively. However, the average iron removal efficiency for limestone and limestone/sandstone filters containing iron/manganese solution calculated after 10 min at 20 °C was 77.88 and 77.83 % and at 5 °C 43.79 and 44.39 %, respectively.

It was, however, noted that by the end of the experiment (180 min) the difference in iron removal due to the effect of temperature (20°C vs. 5°C) was approximately 4.92 %. The average iron removal efficiency for limestone and limestone/sandstone filters containing iron solution calculated at the end of the experimental period (180 min) was 99.77 and 99.32 % at 20°C and 96.42 and 94.48 % at 5°C, respectively. The average iron removal efficiency for limestone and limestone/sandstone filters containing iron/manganese solution calculated after 180 min was 99.70 and 99.67 % at 20 °C and 94.85 and 96.32 % at 5 °C, respectively. These results are very useful when designing the field filters because the runoff during the winter is slower and the temperature of the water is lower, compared to those during the summer, thus requiring a longer retention time in order to maintain constant removal of iron during the year.

Cravotta et al. (1999) indicated that the oxidation of iron in surface waters can be described by the following differential rate expression:

$$dC_{Fe}/dt = K_I C_{Fe} \qquad (7.7)$$

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Where:

C_{Fe} = Iron concentration in the solution (mg/L)

K_I = Iron oxidation rate constant (min^{-1})

Equation (7.7) on integration yields the following exponential equation:

$$C_{Fet} = C_{Fei}\, e^{-K_I t} \qquad (7.8)$$

Where:

C_{Fet} = Iron concentration at time t (mg/L)

C_{Fei} = Initial iron concentration (mg/L)

The experimental data was fitted to the above equation and the iron removal rate constants for limestone and limestone/sandstone filters containing iron and iron/manganese solutions were calculated (Table 7.19). The iron removal rate constants were affected by the temperature and the presence of manganese (Figure 7.23). Increasing the temperature increased the iron removal rate constant. The relationship between the temperature and the iron removal rate constant was linear. The presence of manganese in the solution decreased the iron removal rate constant due to the competition between iron and manganese ions. The results also showed higher iron removal rate constants in the limestone filter compared to those of limestone/sandstone.

Although several researchers (Xu et al., 1997; and Sasowsky et al., 2000) suggested that the use of a mixture of limestone and sandstone to treat iron contaminated wastewater in order to avoid armoring of limestone and to increase the lifetime of the filter, the result obtained from this study (Table 7.19) showed that at a given temperature, the iron removal rate constant was affected by the amount of limestone placed in the filter. To confirm these results an experiment was conducted in which several ratios of limestone:sandstone (1:4, 1:2, 1:1 and 1:0) were used. The results obtained from this experiment (Figure 7.24) showed that increasing the percent of limestone in the filter increase the iron removal rate constant. According to Equations (5.8 and 5.9), the precipitation reaction of ferric hydroxide ($Fe(OH)_3$) produced protons that would

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Table 7.19. Iron removal rate constants (min^{-1}) for limestone and limestone/sandstone filters containing iron and iron/manganese solutions.

	Iron Solution		Iron/Manganese Solution	
Temperature	**Limestone**	**Limestone/sandstone**	**Limestone**	**Limestone/sandstone**
5	0.07	0.07	0.06	0.05
10	0.19	0.12	0.09	0.09
15	0.23	0.16	0.13	0.12
20	0.33	0.20	0.18	0.16

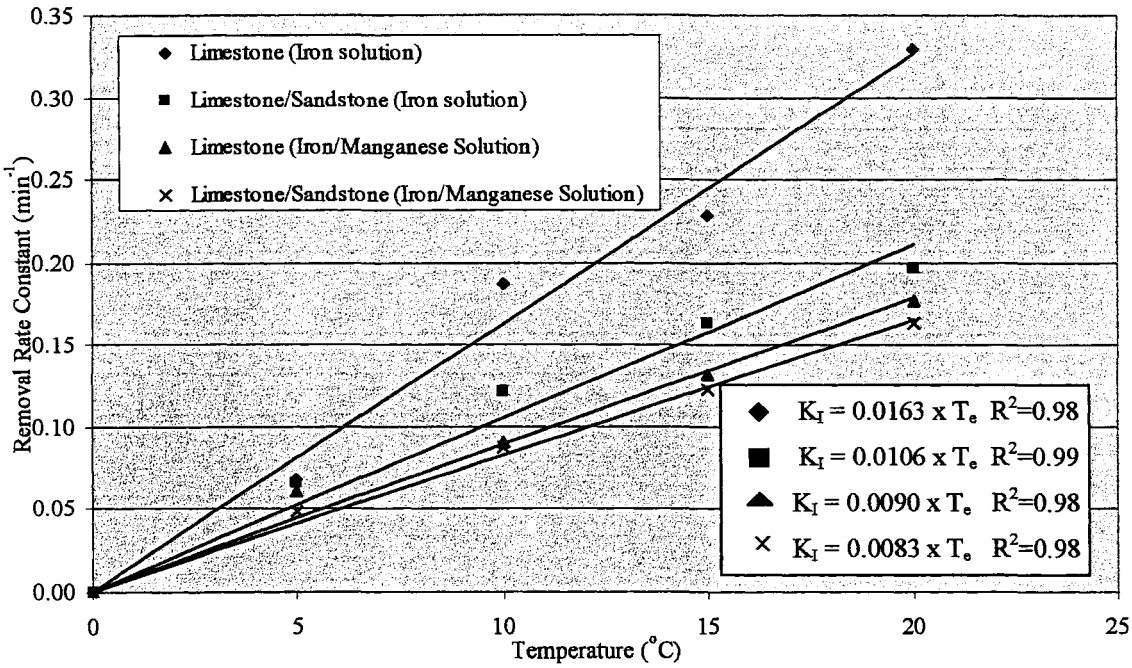


Figure 7.23. Effect of temperature on iron removal rate constants.

consequently decreased the pH of the solution and increase the solubility of $Fe(OH)_3$.

However, in the presence of limestone stone, the protons produced from precipitation reaction were consumed by the calcium carbonate dissolution reaction as shown in the following equation:

$$CaCO_3 + 2\,H^+ \longrightarrow Ca^{2+} + H_2CO_3 \qquad (7.9)$$

As the limestone increased, the neutralization capacity of the solution increased (the pH of the solution increased) as shown in Table 7.20. The results showed that the higher the pH of the solution the lower the solubility of $Fe(OH)_3$ and, therefore, the smaller the rate constant.

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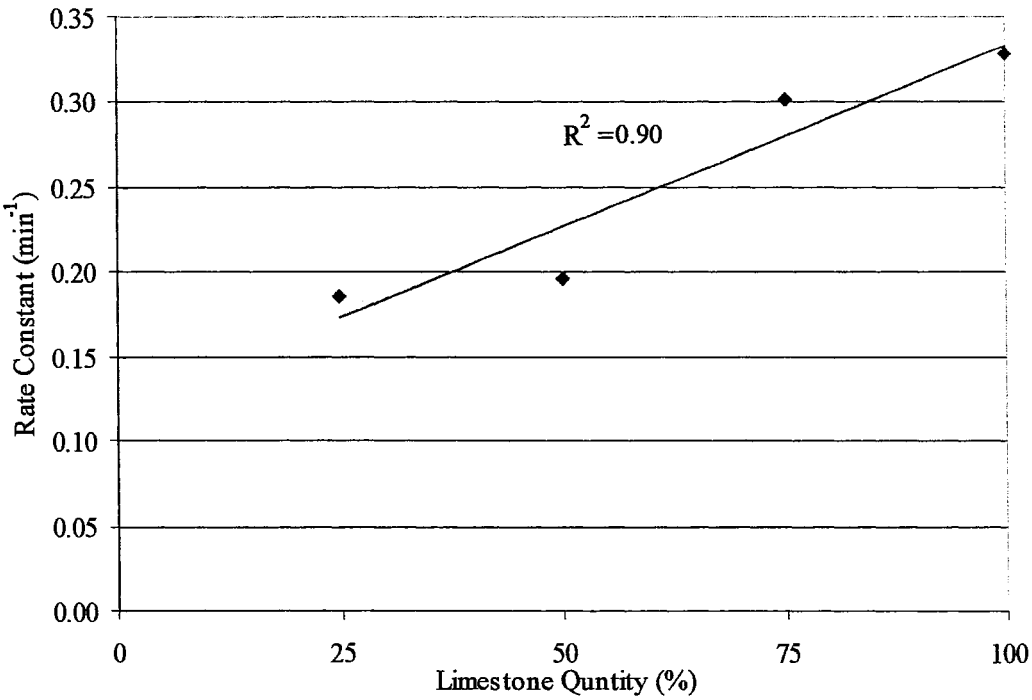


Figure 7.24. Correlation between iron removal rate constants and limestone quantity in the filter.

Table 7.20. Effect of percent of limestone in the filter on the pH of the solution.

Time	Limestone[a]	Limestone/Sandstone[b]
0.0	6.10	6.10
2.5	7.30	7.12
5.0	7.43	7.14
7.5	7.45	7.11
10.0	7.49	7.14
20.0	7.40	7.23
30.0	7.44	7.29
40.0	7.46	7.30
50.0	7.46	7.35
60.0	7.43	7.32
80.0	7.31	7.29
100.0	7.46	7.25
120.0	7.45	7.28
150.0	7.43	7.32
180.0	7.51	7.26

The table was constructed from Tables 7.5 and 7.6

a 100% Limestone

b 50% limestone

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Analysis of variance (ANOVA) was performed on the iron removal rate constant data using MINITAB Release 14 (MINITAB Inc., State College, PA). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA results (Table 7.21) showed that the filter type, solution type and temperature have significant effects on the removal rate constants at confidence levels of 96% (P = 0.04) , 99.5 % (P=0.005) and 99.99 % (0.0001), respectively. The results showed no significant interactions between the factors at a 95% confidence level (P > 0.05). The results of Duncan's Multiple Range test (Table 7.22) showed that the means of the filter types, solution types and temperatures were significantly different from one another at a 95% confidence level.

Analysis of variance (ANOVA) was performed on the removal efficiency data using MINITAB Release 14 (MINITAB Inc., State College, PA). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA results (Table 7.23) showed that the time and temperature have significant effects on the removal efficiency (P = 0.0001). However, the filter type and solution type had no significant effects on the removal efficiency. The results also showed significant interactions (P = 0.0001) between the time and temperatures but no interactions between other factors. The results of Duncan's Multiple Range test (Table 7.24) showed that the means of the filter types and of solution types were not significantly different from one another but the four levels of temperatures and all the periods (except for the periods 150 and 180) were significantly different from one another at a 95% confidence level.

The results obtained from this experiment showed that the overall iron removal efficiency was affected by the type of filter (limestone vs. limestone/sandstone). Sasowsky et al. (2000) reported that sandstone has more negative surface charge than limestone. This would indicate that in addition to more rapid aqueous Fe^{2+} oxidation at pH > 6.5 due to increased hydroxide ion, the decrease in zeta potential (i.e. surface charge) with increasing pH would promote Fe^{2+} surface reaction. A synergistic effect clearly occurs when limestone and sandstone are mixed, promoting the precipitation of metal oxide on

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Table 7.21. Analysis of variance of the iron removal rate constant data.

Source	DF	SS	MS	F-Value	P
Total	15	0.08267	0.00551		
Filter Type (F)	1	0.00580	0.00580	5.32	0.0440
Solution Type (S)	1	0.01429	0.01429	13.11	0.0050
Temperature (Te)	3	0.05165	0.01721	15.78	0.0001
F x S	1	0.00323	0.00323	0.65	0.4350
F x Te	3	0.00216	0.00072	0.25	0.8590
S x Te	3	0.00339	0.00113	0.68	0.5880
Error	10	0.01091	0.00109		

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 0.87
CV = 2.55 %

Table 7.22. Differences among the means of the filter types, solution types and temperatures.

Parameter	Number of Observations	Iron Removal Rate Constant	Duncan Grouping
Filter Type			
Limestone	8	-0.159225	A
Limestone/Sandstone	8	-0.121132	B
Solution Type			
Iron	8	-0.170075	A
Iron/Manganese	8	-0.110288	B
Temperature (°C)			
5	4	-0.060875	A
10	4	-0.121800	B
15	4	-0.161500	C
20	4	-0.216550	D

Means with the same letter are not significantly different from each other at 95% confidence level.

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Table 7.23. Analysis of variance of the iron removal efficiency data.

Source	DF	SS	MS	F-Value	P
Total	223	112373.1	503.92		
Filter Type (F)	1	160.00	159.77	0.32	0.5750
Time (T)	13	89852.19	6911.71	192.94	0.0001
Solution Type (S)	1	814.00	813.59	1.61	0.2060
Temperature (Te)	3	13033.00	4344.28	199.82	0.0001
F x T	13	342.00	26.29	0.23	0.9980
S x T	13	1107.00	85.13	0.81	0.6490
F x S	1	220.00	219.74	0.43	0.5100
F x Te	3	82.00	27.20	0.06	0.9810
S x Te	3	148	49.22	0.11	0.9550
T x Te	39	5836	149.63	6.88	0.0001
Error	168	19762.94	117.64		

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 0.88
CV = 1.75 %

Table 7.24. Differences among the means of the filter types, periods, solution types and temperatures.

Parameter	Number of Observations	Iron Removal Efficiency	Duncan Grouping
Filter Type			
Limestone	112	81.22	A
Limestone/Sandstone	112	79.52	A
Periods (min)			
2.5	16	29.13	A
5.0	16	49.32	B
7.5	16	61.24	C
10.0	16	69.05	D
20.0	16	80.67	E
30.0	16	85.65	F
40.0	16	88.79	G
50.0	16	90.72	H
60.0	16	92.13	I
80.0	16	93.35	J
100.0	16	94.37	K
120.0	16	95.59	L
150.0	16	97.47	M
180.0	16	97.69	M
Solution Type			
Iron	112	82.28	A
Iron/Manganese	112	78.46	A
Temperature (°C)			
5	52	68.77	A
10	52	78.98	B
15	52	84.45	C
20	52	89.29	D

Means with the same letter are not significantly different from each other at 95% confidence level.

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the sandstone, while allowing the limestone to remain uncoated and continue neutralizing the solution.

7.7.2.2 Manganese

The manganese removal efficiencies in the limestone and limestone/sandstone filters containing iron and iron/manganese solutions decreased as the temperature decreased as shown in Tables (7.7-7.10). Larger percentage of manganese was removed from solution within the first 20 minutes at 20 °C compared to that removed at 5 °C. The average manganese removal efficiencies for limestone and limestone/sandstone filters containing manganese solutions calculated after 20 min were 69.44 and 61.11 % at 20 °C and 45.61 and 41.61 % at 5 °C, respectively. Lower manganese removal occurred in the presence of iron. The average manganese removal efficiencies for limestone and limestone/sandstone filters containing manganese/iron solutions calculated after 20 min were 44.44 and 33.33 % at 20 °C and 25.61 and 15.33 % at 5 °C, respectively.

However, by the end of the experiment (180 min), the differences in the removal efficiencies caused by the temperature were much smaller. The average manganese removal efficiencies for limestone and limestone/sandstone filters containing manganese solutions calculated at 180 min were 86.11 and 77.78 % at 20°C and 68.89 and 64.11 % at 5°C, respectively. The average manganese removal efficiency for limestone and limestone/sandstone filters containing iron/manganese solutions calculated after 180 min were 77.80 and 76.70 % at 20 °C and 64.44 and 58.00 % at 5 °C, respectively.

The oxidation of manganese in surface waters can also be described by the following differential rate expression (Stumm and Morgan, 1981):

$$dC_{Mn}/dt = k_M C_{Mn} \qquad (7.10)$$

Where:

C_{Mn} = Manganese concentration in the solution (mg/L)

k_M = Manganese oxidation rate constant (min^{-1})

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By the integration of Equation (7.10) the following equation was obtained:

$$C_{Mnt} = C_{Mni}\, e^{-k_M t} \qquad (7.11)$$

Where:

C_{Mnt} = Manganese concentration at time t (mg/L)

C_{Mni} = Initial manganese concentration (mg/L)

The manganese data were fitted into the above equation and the manganese removal rate constants for limestone and limestone/sandstone filters containing manganese and manganese/iron solutions were calculated (Table 7.25). The manganese removal rate constant was affected by the temperature and presence of iron (Figure 7.25). Increasing the temperature increased the manganese removal rate constant. The relationship was polynomial. Presence of iron in the solution decreased the manganese removal rate constant. As in the case of iron, the limestone filters had higher removal rate constants than those of limestone/sandstone filters. Increasing the percent of limestone increased the pH and, thus, reduced the solubility of MnOOH which resulted in a smaller rate constant as shown in Figure 7.26.

Analysis of variance (ANOVA) was performed on the manganese removal rate constant data using MINITAB Release 14 (MINITAB Inc., State College, PA). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA results (Table 7.26) showed that the filter type, solution type and temperature had significant effects on the removal efficiency (P = 0.05, 0.0001 and 0.0001, respectively). The results showed no significant interactions between the factors. The results of Duncan's Multiple Range test (Table 7.27) showed that the means of the filter types, solution types and temperatures were significantly different from one another at a 95% confidence level.

Analysis of variance (ANOVA) was also performed on the removal efficiency data using MINITAB Release 14 (MINITAB Inc., State College, PA). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor.

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Table 7.25. Manganese removal rate constants (min^{-1}) for limestone and limestone/sandstone filters which containing iron and iron/manganese solutions.

	Manganese Solution		Manganese/Iron Solution	
Temperature	**Limestone**	**Limestone/sandstone**	**Limestone**	**Limestone/sandstone**
5	0.032	0.029	0.013	0.008
10	0.048	0.039	0.018	0.017
15	0.057	0.044	0.025	0.022
20	0.068	0.057	0.027	0.023

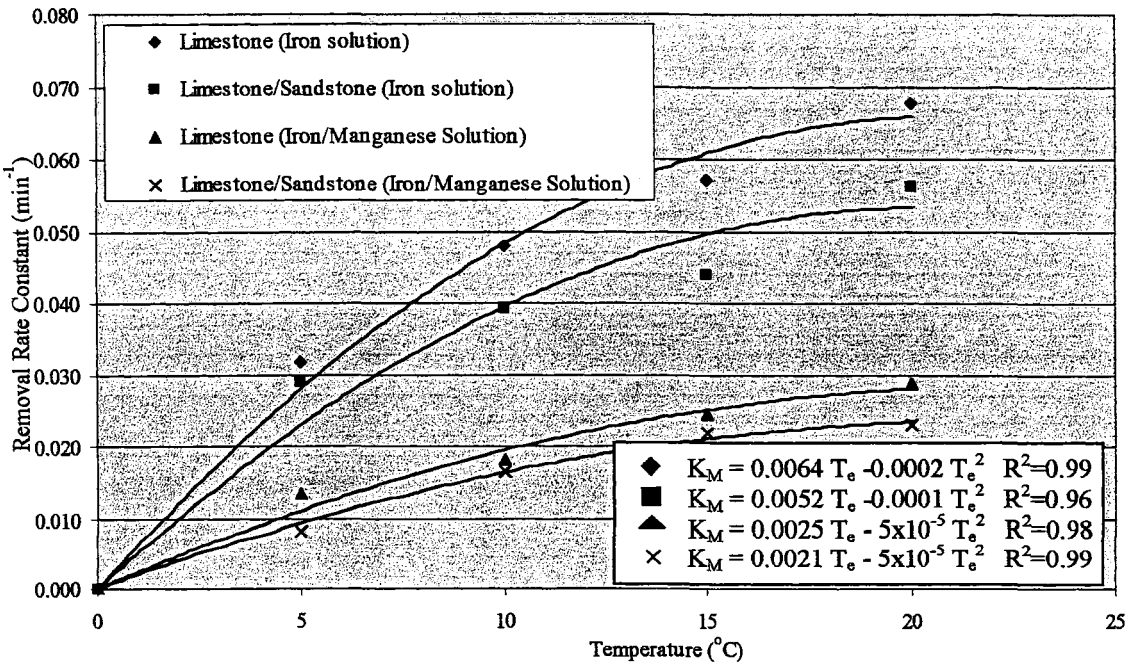


Figure 7.25. Temperature effect on manganese removal rate constants.

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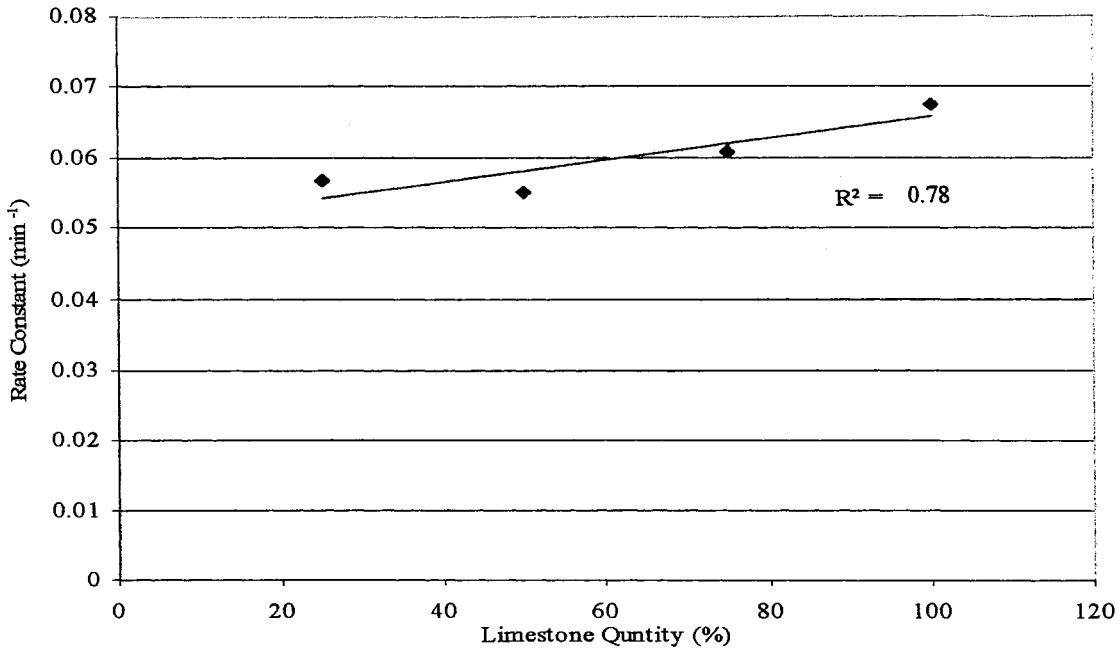


Figure 7.26. Correlation between manganese removal rate constants and limestone quantity in the filter.

Table 7.26. Analysis of variance of the manganese removal rate constants.

Source	DF	SS	MS	F-Value	P
Total	15	0.004572	0.000305		
Filter Type (F)	1	0.000158	0.000158	7.61	0.0200
Solution Type (S)	1	0.003011	0.003011	144.86	0.0001
Temperature (Te)	3	0.001194	0.000398	19.15	0.0001
F x S	1	0.000026	0.000026	0.23	0.6410
F x Te	3	0.000012	0.000003	0.01	0.9990
S x Te	3	0.000148	0.000049	1.82	0.2220
Error	10	0.000207	0.000021		

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 0.95
CV = 1.39 %

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Table 7.27. Differences among the filter types, solution types and temperatures.

Parameter	Number of Observations	Mn Removal Rate Constant	Duncan Grouping
Filter Type			
Limestone	8	0.0362	A
Limestone/Sandstone	8	0.0299	B
Solution Type			
Iron	8	0.0467	A
Iron/Manganese	8	0.0193	B
Temperature (°C)			
5	4	0.0206	A
10	4	0.0305	B
15	4	0.0369	C
20	4	0.0441	D

Means with the same letter are not significantly different from each other at 95% confidence level.

The ANOVA results (Table 7.28) showed that the time, solution type, filter type and temperature had significant effects on the removal efficiency (P = 0.0001). The results also showed a significant interaction (P = 0.0001) between the time and solution type but no interaction between the other factors. The results of Duncan's Multiple Range test (Table 7.29) showed that the means of filter types, temperatures and solution types and the periods (except for the periods 50 and 60) were significantly different from one another at a 95% confidence level.

Table 7.28. Analysis of variance of the manganese removal efficiency.

Source	DF	SS	MS	F-Value	P
Total	223	121356.8	544.20		
Filter Type (F)	1	782.2	782.2	30.03	0.0001
Time (T)	13	91385.1	7029.6	269.84	0.0001
Solution Type (S)	1	15740.8	15740.8	604.24	0.0001
Temperature (Te)	3	8108.2	2702.7	103.75	0.0001
F x T	13	535.0	41.2	0.28	0.9940
S x T	13	2355.0	181.2	2.99	0.0010
F x S	1	65.0	64.8	0.14	0.7130
F x Te	3	104.0	34.5	0.07	0.9780
S x Te	3	76.0	25.4	0.06	0.9820
T x Te	39	470.0	12.0	0.09	1.0000
Error	205	5340.4	26.10		

DF = Degrees of Freedom
SS = Sum of Squares
MS = Mean of Squares
R^2 = 0.96
CV = 1.75 %

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Table 7.29. Differences among the means of the filter types, periods, solution types and temperatures.

Parameter	Number of Observations	Mn Removal Efficiency	Duncan Grouping
Filter Type			
Limestone	112	50.23	A
Limestone/Sandstone	112	46.49	B
Periods (min)			
2.5	16	8.36	A
5.0	16	15.96	B
7.5	16	22.74	C
10.0	16	30.62	D
20.0	16	43.41	E
30.0	16	49.94	F
40.0	16	54.32	G
50.0	16	57.32	H
60.0	16	58.53	H
80.0	16	61.74	I
100.0	16	64.49	J
120.0	16	67.51	K
150.0	16	69.79	L
180.0	16	72.47	M
Solution Type			
Iron	112	56.75	A
Iron/Manganese	112	39.98	B
Temperature (°C)			
5	52	39.32	A
10	52	47.10	B
15	52	51.47	C
20	52	55.57	D

Means with the same letter are not significantly different from each other at 95% confidence level.

It was observed that the manganese removal efficiencies relatively decreased during the presence of Fe^{2+} ions. This is because Fe^{2+} controlled Mn oxidation rates by contributing electrons to previously precipitated Mn oxides to produce Mn^{2+} as reported by Burdige et al. (1992). Barton and Karathanasis (1999) also reported Mn oxidation inhibition during the presence of Fe^{2+} within the system. The relatively lower removal efficiencies of manganese observed in this experiment compared to iron show the slow kinetics of Mn^{2+} oxidation as reported by Stumm and Morgan (1981).

7.7.2.3 pH

The temperature affected the dissolution rate of limestone and in turn the pH. As pH of the solution increased, the dissolved iron concentration decreased. The results showed

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good correlations ($R^2 = 0.86 - 0.93$) between the removal efficiencies of iron and the pH of the solutions in all filters as shown in Figure 7.27. The results obtained from this study were in agreement with those reported in the literature (Wajon et al., 1985; and Cravotta and Trahan, 1999) and those obtained from the previous tank experiments.

Also, as pH of the solution increased the dissolved manganese concentrations decreased, but no consistent correlations ($R^2 = 0.29 - 0.91$) were observed between the removal efficiencies of manganese and the pH of the solution among the filters as shown in Figure 7.28. The results obtained from this study were in agreement with the previous tank experiments. Aziz and Smith (1992) and Cravotta and Trahan (1999) found no correlation between the manganese removal efficiency and the pH of the solution.

7.7.2.4 Calcium Carbonate Dissolution

In order to calculate the filter life time expectancy on the basis of calcium carbonate dissolution, the calcium ion concentration in the solution was calculated using the measured pH data following the procedure given by Myrna and White (1999). The overall equilibrium reaction of the dissolution of limestone is as follows:

$$CaCO_3 + CO_2 + H_2O \longleftrightarrow Ca^{2+} + 2HCO_3^- \qquad (7.12)$$

According to Myrna and White (1999) and Drever (1988), the charge in neutrality for the above equation requires that:

$$[H^+] + 2\,[Ca^+] = [HCO_3^-] \qquad (7.13)$$

Where:

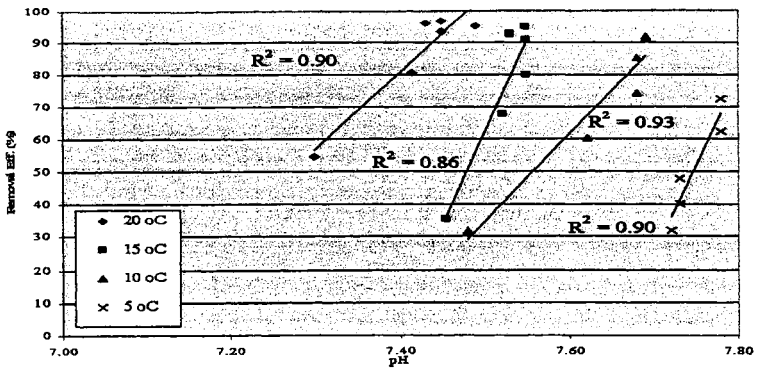
$[H^+]$ = Concentration of hydrogen ion (mol/L)

$[Ca^+]$ = Concentration of calcium ion (mol/L)

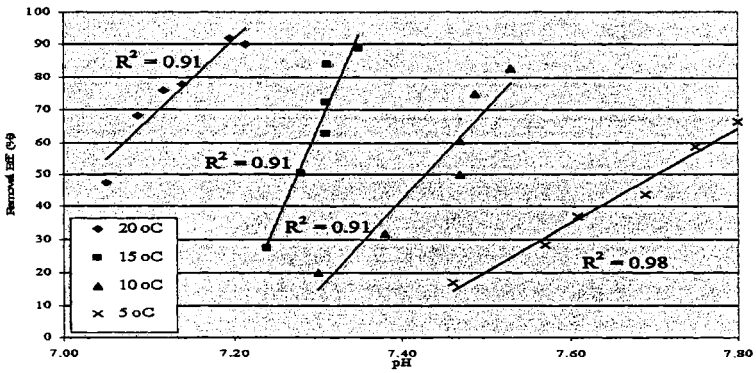
$[HCO_3^-]$ = Concentration of bicarbonate (mol/L)

Equation (7.16) can be written in terms of ion activities as follows:

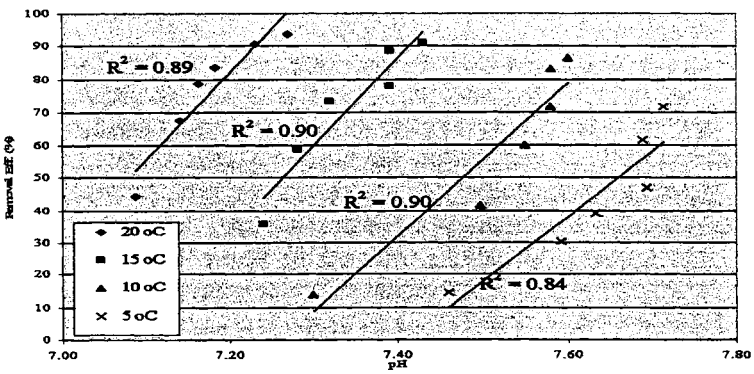
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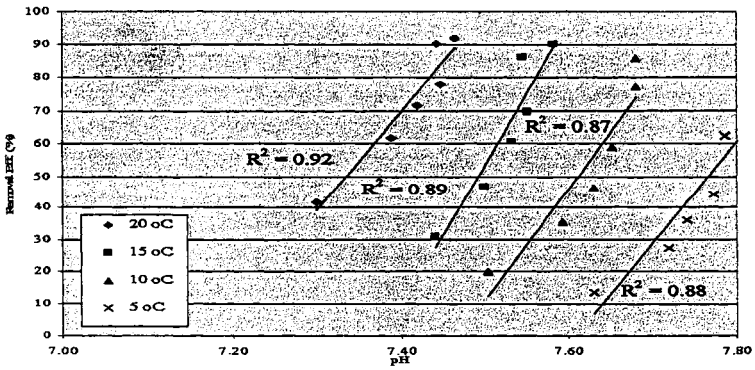
(a) Limestone filter containing Fe solution



(b) Limestone filter containing Fe/Mn solution



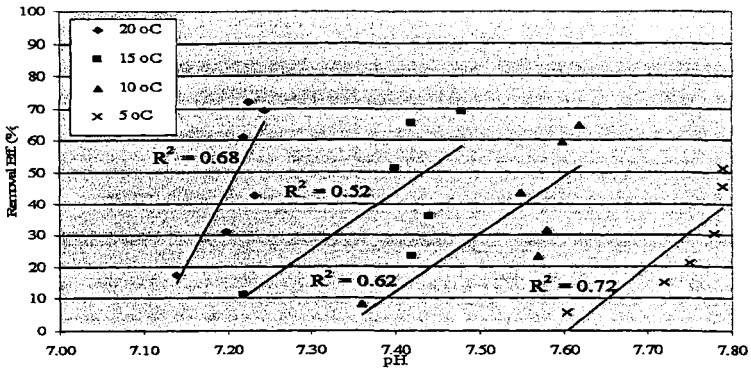
(c) Limestone/Sandstone filter containing Fe solution



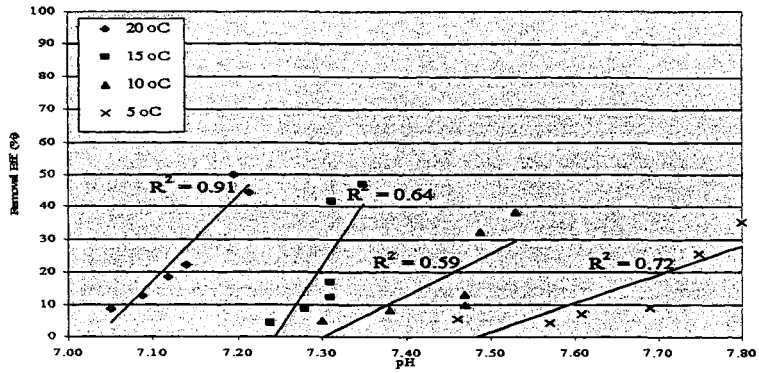
(d) Limestone/sandstone filter containing Fe/Mn solution

Figure 7.27. Correlation between iron removal efficiencies and pH.

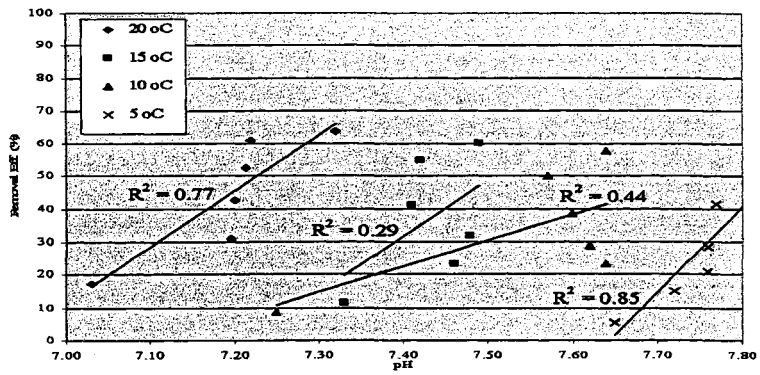
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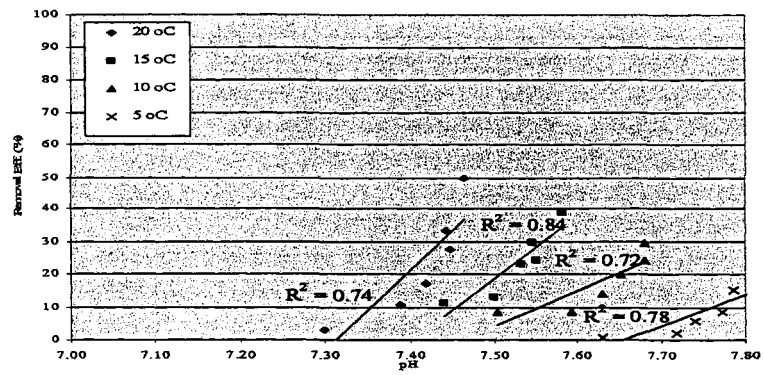
(a) Limestone filter containing Mn solution



(b) Limestone filter containing Mn/Fe solution



(c) Limestone/Sandstone filter containing Mn solution



(d) Limestone/sandstone filter containing Mn/Fe solution

Figure 7.28. Lack of correlation between manganese removal efficiencies and pH.

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$$\frac{a_{H^+}}{\gamma_{H^+}} + 2\frac{a_{Ca^{2+}}}{\gamma_{Ca^{2+}}} = \frac{a_{HCO_3^-}}{\gamma_{HCO_3^-}} \quad (7.14)$$

Where:

a = Activity of the given ion (mol/L)

γ = Activity coefficient of the same ion (-)

When CO_2 gas is brought into contact with water, it will dissolve forming carbonic acid (H_2CO_3) until equilibrium is reached. At equilibrium, the concentration of dissolved carbon dioxide will be proportional to the partial pressure of CO_2 in the gas phase. The normal convention is to refer to all dissolved carbon dioxide as H_2CO_3 and, thus, the dissolution of carbon dioxide in water can be represented by the following equilibrium equation (Myrna and White, 1999):

$$CO_2 + H_2O \quad \leftrightarrow \quad H_2CO_3^0 \quad (7.15)$$

The equilibrium constant for CO_2 in the above equation is given as follows (Drever, 1988):

$$\frac{a_{H_2CO_3}}{P_{CO_2} \times a_{H_2O}} = K_{CO_2} \quad (7.16)$$

Where:

P_{CO_2} = Carbon dioxide partial pressure (atm)

K_{CO_2} = Equilibrium constant of carbon dioxide dissolving reaction (-)

For dilute solutions, the activity of water (a_{H2O}) is very close to 1 (Chapra, 1997). Therefore, Equation (7.16) can be rewritten as follows:

$$\frac{a_{H_2CO_3}}{P_{CO_2}} = K_{CO_2} \quad (7.17)$$

H_2CO_3 tends to dissociate into hydrogen and bicarbonate ions according to the following equilibrium equation:

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$$H_2CO_3 \quad \leftrightarrow \quad H^+ + HCO_3^- \tag{7.18}$$

Since the hydrogen in the above equation is in the form of ion (produced from the carbonic acid), an equilibrium constant for H_2CO_3 in the above reaction can be written as follows (Letterman, 1999):

$$\frac{a_{H^+} \times a_{HCO_3}}{a_{H_2CO_3}} = K_1 \tag{7.19}$$

Where:

K_1 = Equilibrium constant of carbonic acid dissolution reaction (-)

The reactions in Equations (7.15) and (7.18) are assumed to be in equilibrium. Therefore, by combining the two equations, the bicarbonate activity for a system open to CO_2 can be given by the following equation:

$$a_{HCO_3^-} = \frac{K_1 K_{CO_2} P_{CO_2}}{a_{H^+}} \tag{7.20}$$

Substituting Equation (7.20) into Equation (7.18) and rearranging terms yields the following equation:

$$\frac{a_{Ca^{2+}}}{\gamma_{Ca^{2+}}} = \frac{1}{2}\left[\frac{K_1 K_{CO_2} P_{CO_2}}{a_{H^+}\gamma_{HCO_3^-}} - \frac{a_{H^+}}{\gamma_{H^+}}\right] \tag{7.21}$$

From equations (7.13) and (7.14), $[Ca^{2+}] = \frac{a_{Ca^{2+}}}{\gamma_{Ca^{2+}}}$. Therefore, $[Ca^{2+}]$ can be calculated as follows:

$$[Ca^{2+}] = \frac{1}{2}\left[\frac{K_1 K_{CO_2} P_{CO_2}}{a_{H^+}\gamma_{HCO_3^-}} - \frac{a_{H^+}}{\gamma_{H^+}}\right] \tag{7.22}$$

Chapra (1997) and Letterman (1999) found that P_{CO_2} is equal to $10^{-3.5}$ atm. The value of K_1 can be calculated as function of absolute temperature using the following equation (Harned and Davis, 1943):

$$pK_1 = \frac{3404.71}{T_a} + 0.032786T_a - 14.8435 \tag{7.23}$$

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Where:

T_a = Temperature in Kelvin (T °C + 273.15)

Also, the value of K_{CO_2} can be computed as a function of temperature as follows (Edmond and Gieskes, 1970):

$$pK_{CO_2} = -\frac{2385.73}{T_a} - 0.0152642\,T_a + 14.0184 \quad (7.24)$$

Chapra (1997) stated that the activity of an ion (a) can be determined by multiplying its molar concentration by an activity coefficient (γ)

$$a_{H^+} = \gamma_{H^+} \times [H^+] \quad (7.25)$$

The activity coefficient can be determined by the following Debey-Huckel limiting law (Chapra, 1997):

$$\log \gamma_i = -0.5\, Z_i^2\, \sqrt{u} \quad (7.26)$$

Where:

Z_i = the charge of species *i* (-)

u = Ionic strength (mg/L)

The ionic strength can be calculated by the following equation (Langelier, 1936):

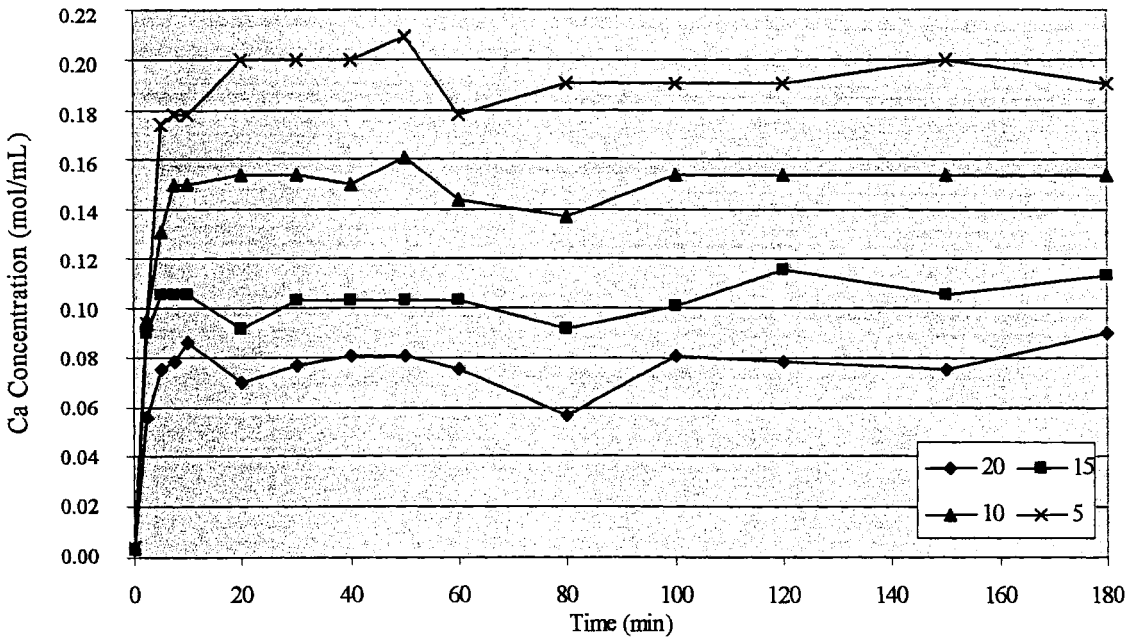
$$u = 2.5 \times 10^{-5}\ (TDS) \quad (7.27)$$

Where:

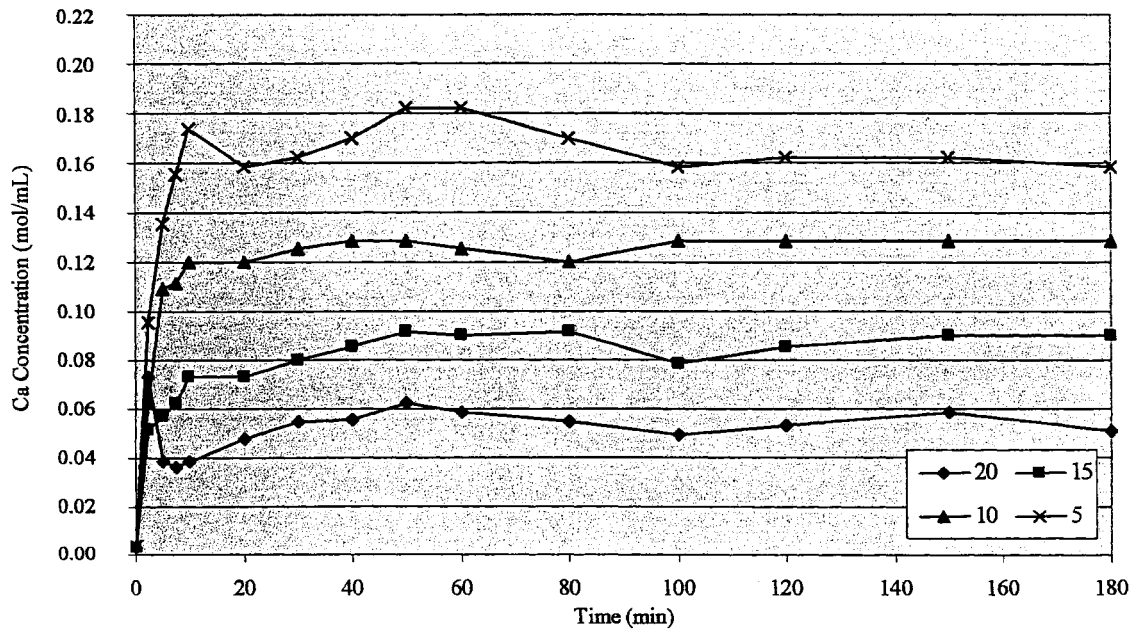
TDS = Total dissolved solids (mg/L)

The calcium ion concentrations in the limestone and limestone/sandstone filters containing iron and iron/manganese solutions were calculated at different temperatures during the course of the experiment. The results are shown in Figures 7.29-7.31. The results showed that higher temperature resulted in lower calcium ion concentration. Since the only source of the calcium in the filters is the dissolution of calcium carbonate found in the limestone, the calcium carbonate dissolution rates were estimated based on the calculated calcium ion concentrations.

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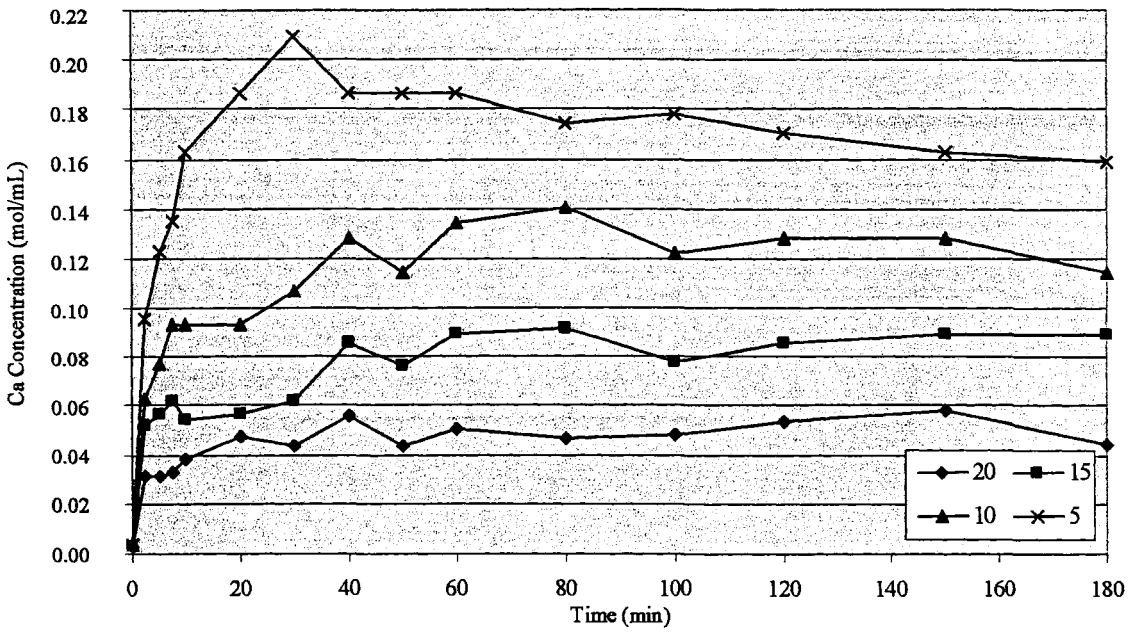
(a) Limestone



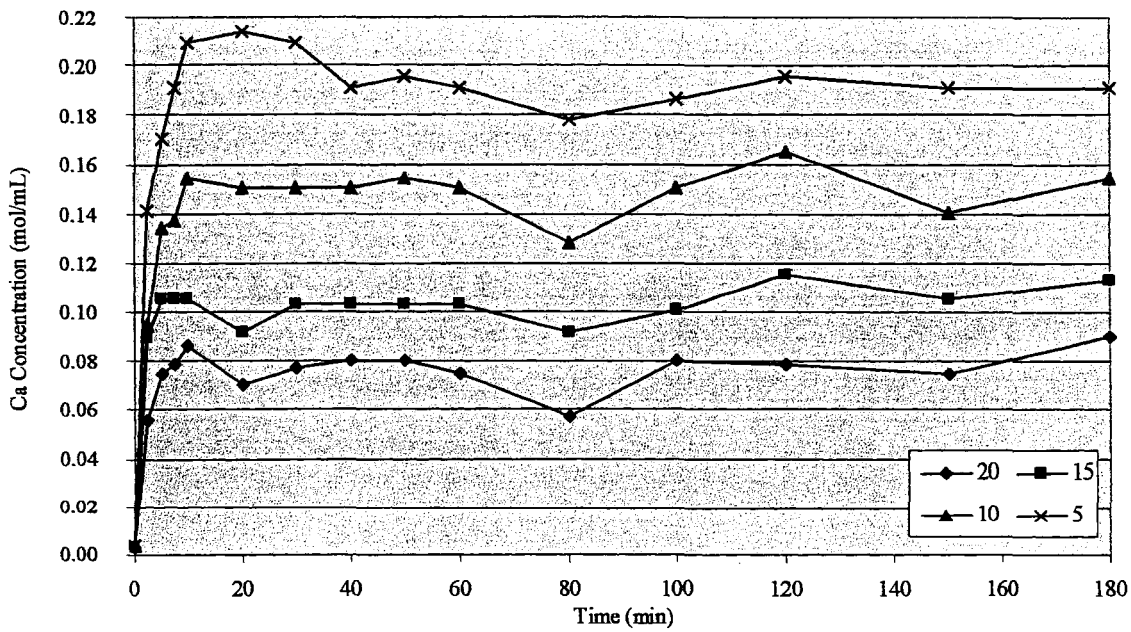
(b) Limestone/sandstone

Figure 7.29. Calculated calcium concentrations in the limestone and limestone/sandstone filters that contained iron solutions.

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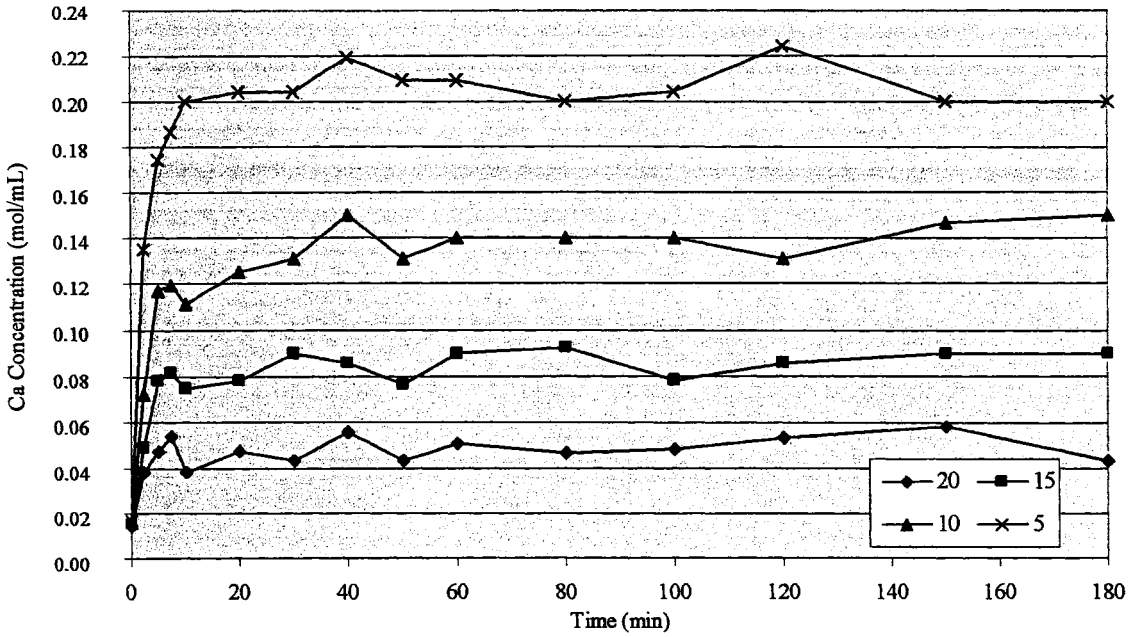
(a) Limestone



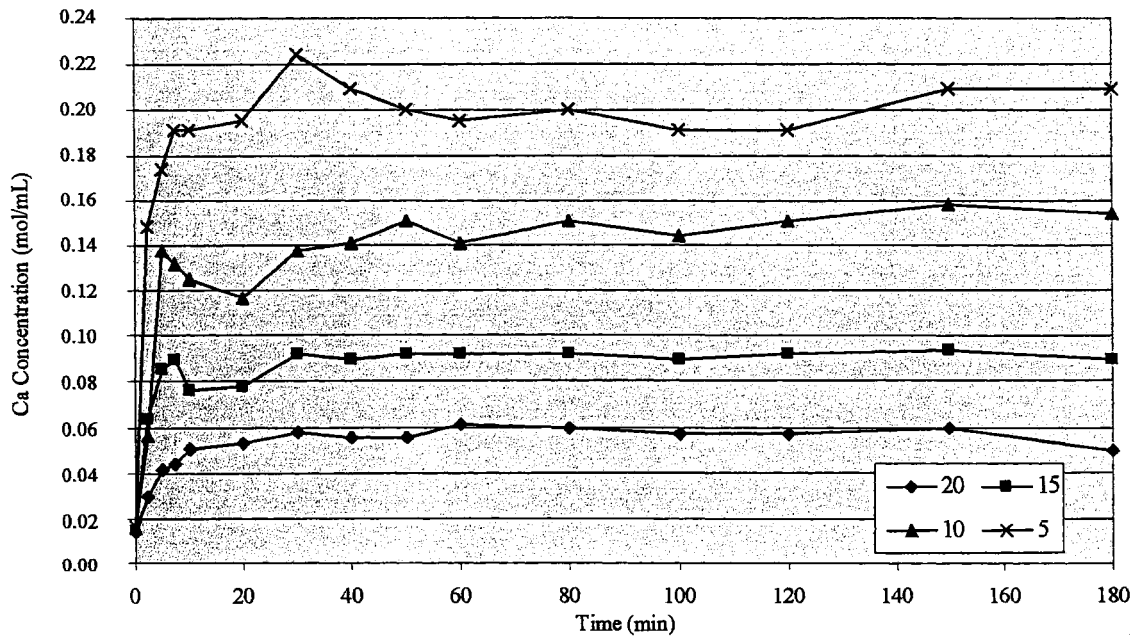
(b) Limestone/sandstone

Figure 7.31. Calculated calcium concentrations in the limestone and limestone/sandstone filters that contained iron/manganese solutions.

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(a) Limestone



(b) Limestone/sandstone

Figure 7.31. Calculated calcium concentrations in the limestone and limestone/sandstone filters that contained manganese solutions.

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The rate of calcium carbonate dissolution can be described by the following differential rate expression (Stumm and Morgan, 1981):

$$dC_C/dt = + k_C C_C \quad (7.28)$$

Where:

C_C = Calcium carbonate concentration in the solution (mol/L)

k_C = Calcium carbonate dissolution rate constant (min^{-1})

By the integration of Equation (7.28) the following equation was obtained:

$$C_{Ct} = C_{Ci}\, e^{k_C t} \quad (7.29)$$

Where:

C_{Ct} = Calcium carbonate concentration at time t (mol/L)

C_{Ci} = Initial calcium carbonate concentration (mol/L)

The calculated calcium concentration data were fitted into the above equation and the calcium carbonate dissolution rate constants for limestone and limestone/sandstone filters containing iron, manganese and manganese/iron solutions were calculated. The calcium carbonate dissolution rate constant increased as the temperature decreased as shown in Table 7.29. It was noted that the calculated calcium carbonate dissolution rate was affected by the presence of iron ions; the dissolution rate constants were higher in the filters containing iron and iron/manganese than those containing manganese alone.

The precipitation reaction of ferric hydroxide ($Fe(OH)_{3(s)}$) (Equation 7.3) and manganite hydroxide ($MnOOH_{(s)}$) (Equation 7.4) produced protons that decreased the pH of the solution and consequently increased the dissolution of calcium carbonate. Rickard and Sjoberg (1983) stated that the rate of calcium carbonate dissolution in the H^+-dependent regime is controlled by mass transfer, which assumed to be the diffusion of H^+ from the bulk solution through the mass transfer boundary layer to the stone surface. In the H^+-independent regime the surface chemical reaction controls the mass transfer and in the transition region between these limits the kinetics is a function of both the surface reaction and mass transfer. Lower temperatures cause the surface chemical reaction rate constant

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Table 7.30. Calcium carbonate dissolution rate constant (min^{-1}) for limestone and limestone/sandstone filters that contained iron, manganese and iron/manganese solutions.

Temperature (°C)	Iron		Manganese		Iron/Manganese	
	Limestone	Limestone/ Sandstone	Limestone	Limestone/ Sandstone	Limestone	Limestone/ Sandstone
5	0.1345	0.1239	0.0851	0.0805	0.1331	0.1315
10	0.1241	0.1192	0.0730	0.0741	0.1075	0.1229
15	0.0998	0.1019	0.0587	0.0539	0.0762	0.0998
20	0.0995	0.0886	0.0389	0.0529	0.092	0.0994

to be become smaller and the extent of the transition region expands into the H^+-dependent region that cause the calcium carbonate rate constant increase as temperature decrease.

The data obtained from limestone/sandstone filters will be used for the design of the continuous flow experiment and the field filter. The ambient temperature in the field varies during the year and affects the kinetic constants. The dissolution rate constant of calcium carbonate increases while the precipitation of iron and manganese rate constants decrease with decreases in the temperature (Table 7.30). The amounts of calcium carbonate dissolved and those required for the precipitation of iron and manganese were calculated at different temperatures. The amount of dissolved calcium carbonate required to precipitate iron removal was calculated using Equation (7.33) given by Cravotta and Trahan (1999) whereas that required to precipitate manganese was calculated using Equation (7.34) given by Gazea et al. (1996) as follows

$$Fe^{2+} + 0.25O_2 + 2CaCO_{3\,(s)} + 2.5H_2O \rightarrow Fe(OH)_{3\,(s)} + 2Ca^{2+} + 2HCO_3^- \qquad (7.30)$$

$$Mn^{2+} + 0.25O_2 + 0.5CaCO_{3\,(s)} + 1.5H_2O \rightarrow MnOOH_{(s)} + 0.5Ca^{2+} + 0.5HCO_3^- + H^+ \qquad (7.31)$$

According to the above equations, 2 moles of calcium carbonate must be available in solution for each mole of Fe^{2+} removed from the solution and 0.5 mole of calcium carbonate must be available in solution for each mole of Mn^{2+} removed from the solution.

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Table 7.31. Iron, manganese removal rate constant and calcium carbonate dissolution rate constant for limestone/sandstone filters that contained iron/manganese solutions.

Temperature (°C)	Fe Removal Constant (min^{-1})	Mn Removal Constant (min^{-1})	$CaCO_3$ Dissolution Constant (min^{-1})
5	0.050	0.008	0.1315
10	0.090	0.018	0.1229
15	0.120	0.025	0.0998
20	0.160	0.027	0.0994

Since, the removal of iron and manganese from the solution by the limestone/sandstone filter followed exponential expressions as shown in Equations (7.12) and (7.15). Therefore, iron removal rate from the solution depends on the initial concentration of iron in the solution at the start of the experiment. As the time passed, the iron concentration in the solution decreased and the effect of the initial concentration on the iron removal rate decreased until the iron was removed completely. Because the system operated under batch condition for 180 min, the amount of iron and manganese removed from the solution and the amount of calcium carbonate dissolved were calculated at the end of the experiment. The calculations are presented in Appendix B and the results are shown in Table 7.31. The total amount of calcium carbonate dissolved in the solution was greater than that required for iron and manganese precipitation by 58.74, 48.75, 18.13 and 17.37 at 5, 10, 15 and 20 °C. This would not be a problem in a batch reactor because the calcium carbonate remained in the reactor. However, in the case of a continuous flow system, the calcium carbonate would be removed as the water flows through the filter and, thus, have a significant effect on the life time of the filter.

7.7.3 Continuous Flow Experiment

This experiment was conducted to assess the effects of sandstone particle size and iron armoring on the performance of the limestone/sandstone filters. Approximately 96 % of iron was removed within the first 20 min during the beaker experiment leaving only 0.2 mg/L which is below the CCME (2003) recommended levels. Thus, a retention time of 20 min was selected for the continuous flow experiment.

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Table 7.32. Iron and manganese removed and calcium carbonate dissolved and required after 180 min for limestone/sandstone filters that contained iron/manganese solutions.

Temperature (°C)	Fe Removed		Mn Removed		Calcium Carbonate					
					Dissolved (mg)	Required (mg)			Balance	
	(mg)	(%)	(mg)	(%)		Fe[a]	Mn[b]	Total	(mg)	(%)
5	6.59	99.99	1.37	76.31	69.36	23.64	4.98	28.62	40.74	58.74
10	6.60	100.00	1.73	96.08	58.41	23.64	6.29	29.93	28.48	48.75
15	6.60	100.00	1.78	98.89	36.79	23.64	6.48	30.12	6.67	18.13
20	6.60	100.00	1.79	99.22	36.50	23.64	6.52	30.16	6.37	17.37

a Calculated from Equation 7.33 (Appendix B)

b Calculated from Equation 7.34 (Appendix B)

7.7.3.1 Iron

During the 3-month experimental period, the treated effluent appeared clear and contained on average less than 0.66 mg/L (10 %) of the influent dissolved iron concentration. According to Sun et al. (2000), anoxic landfill leachate can hold more dissolved Fe^{2+} than Fe^{3+}. When this anoxic water is exposed to the atmosphere, the Fe^{2+} is oxidized to Fe^{3+}, and the insoluble Fe^{3+} precipitates from solution:

$$Fe^{3+} + 3\,H_2O \leftrightarrow Fe(OH)_{3(s)} + 3\,H^+ \quad (7.32)$$

$$Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+}_{(s)} + H^+ \quad (7.33)$$

$$Fe^{3+} + 2\,H_2O \leftrightarrow Fe(OH)_2^{+}{}_{(s)} + 2\,H^+ \quad (7.34)$$

$$Fe^{3+} + 4\,H_2O \leftrightarrow Fe(OH)_4^{-}{}_{(s)} + 4\,H^+ \quad (7.35)$$

This armoring "yellowboy" coats limestone particles and fills in the pore spaces in filters. These iron hydrolysis and precipitation reactions have two implications. First, by coating the limestone, there is less surface area available for limestone dissolution. Second, the iron precipitation reaction is affected because there is no immediate increase in pH. The mechanisms by which iron armors limestone is poorly understood, although Loeppert and Hossner (1984) reported that Fe^{3+} does not physically bind to the limestone surface.

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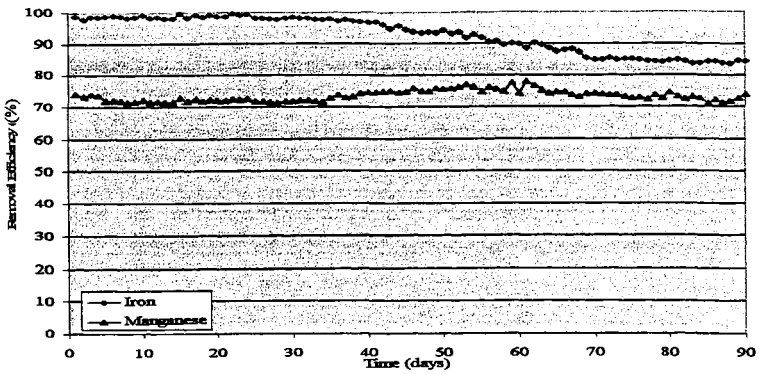
The iron removal efficiencies for all the filters tested in this experiment were higher at the beginning of the experiment and then declined with time (Figure 7.32). The iron removal efficiencies for the filters containing limestone and the small particles of sandstone at ratio of 1:1 and 1:2 were approximately 98.2 and 98.0 % at the beginning of the experiment which then decreased by the end of the experiment to 83.4 and 84.0 %, respectively. The iron removal efficiencies for the filters containing limestone and large particles of sandstone at ratio of 1:1 and 1:2 were approximately 98.3 and 98.1 % at the beginning of the experiment which then decreased by the end of the experiment to 83.2 and 84.1 %, respectively. The reductions in iron removal efficiency with time were due to the armoring build up on the limestone particles. Pearson and McDonnell (1975) and Ziemkiewicz et al. (1997) found that armored limestone has been estimated to be from 4 to 62% as effective as fresh limestone, depending on the level of armoring.

There were no noticeable effects of the ratio of limestone and sandstone or the size of the sandstone particles on the iron removal efficiency. The averages of iron removal efficiencies over the entire experimental period were 92.77, 92.01, 91.84 and 90.63 % for the filters containing limestone and small particles of sandstone at ratios of 1:1 and 1:2 and those containing limestone and larges particles of sandstone at ratios 1:1 and 1:2, respectively.

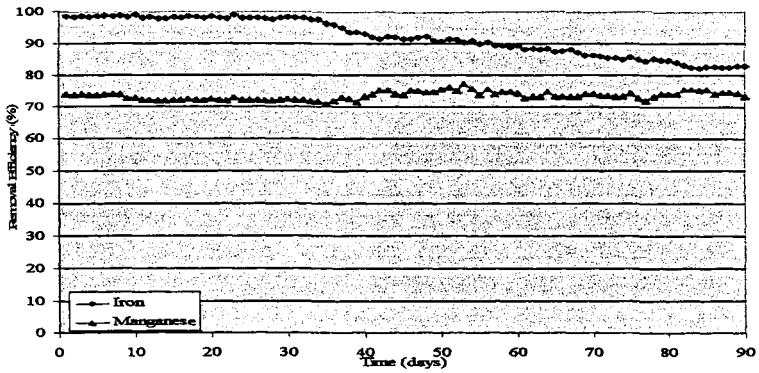
7.7.3.2 Manganese

The manganese removal efficiencies fluctuated during the 3 month experimental period. The manganese removal efficiencies for the filters containing limestone and the small particles of sandstone at ratio of 1:1 and 1:2 were 73.95 and 73.92 % at the beginning of the experiment and 74.00 and 73.20 % at the end of the experiment, respectively. The manganese removal efficiencies for the filters containing limestone and large particles of sandstone at ratio of 1:1 and 1:2 were 73.21 and 73.81 % at the beginning of the experiment and 71.30 and 73.80 % at the end of the experiment, respectively.

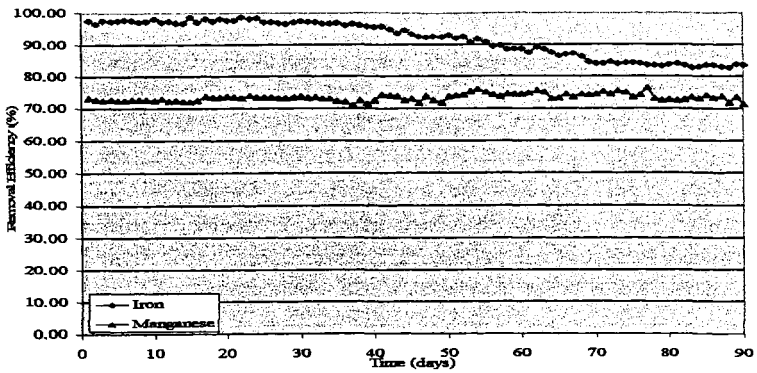
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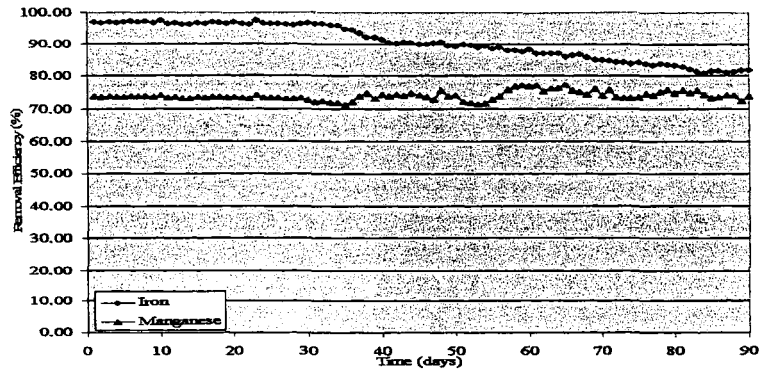
(a) 1:1 Limestone:Small particles Sandstone



(b) 1:2 Limestone:Small particles Sandstone



(c) 1:1 Limestone:Large particles Sandstone



(d) 1:2 Limestone:Large particles Sandstone

Figure 7.32. The removal efficiencies of iron and manganese in the limestone/sandstone filters at different limestone to sandstone ratios and different sandstone particle sizes.

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The removal of dissolved Mn from solution resulted from sorption and coprecipitation reactions with the hydrous oxides of Fe(III) as described by several investigators (Hem, 1963, 1964, 1977, 1978; Loganathan and Burau, 1973; McKenzie, 1980; Benjamin and Leckie, 1981; Kooner, 1993; Coston et al., 1995; Smith et al., 1998). Adsorption of Mn^{2+} on hydrous Fe and Mn oxides is very fast, on the order of minutes, and tends to be much faster than the Fe^{2+} and Mn^{2+} oxidation rates (Benjamin and Leckie, 1981; Davies and Morgan, 1989). Hem (1963) described the autocatalytic sorption and coprecipitation reaction as follows:

$$2\ Fe(OH)_{3(s)} + Mn^{2+} + 2\ H^{+} \longrightarrow MnO_{2(s)} + 4\ H_2O + 2\ Fe^{3+} \qquad (7.36)$$

There were no apparent effects of the ratio of limestone to sandstone or the size of the sandstone particles on the manganese removal efficiency. The average manganese removal efficiencies were 73.53, 73.45, 73.48 and 74.01 % for the filters containing limestone and small particles of sandstone at ratios of 1:1 and 1:2 and those containing limestone and larges particles of sandstone at ratios 1:1 and 1:2, respectively.

7.7.3.3 Calcium Carbonate Dissolution

The calcium ion concentration in the solution was calculated using the measured pH data following the procedure adapted from Myrna and White (1999). The results are shown in Figures 7.33-7.34. The concentrations of calcium carbonate for the filters containing limestone and the small particles of sandstone at ratio of 1:1 and 1:2 were approximately 0.13 and 0.15 mmol/L at the beginning of the experiment which then decreased by the end of the experiment to 0.03 and 0.03 mmol/L, respectively. The calcium carbonate concentrations for the filters containing limestone and large particles of sandstone at ratio of 1:1 and 1:2 were approximately 0.15 and 0.18 mmol/L at the beginning of the experiment which then decreased by the end of the experiment to 0.04 and 0.04 mmol/L, respectively. The reductions of calcium concentrations with time were due to the armoring build up on the limestone particles (Pearson and McDonnell, 1975 and Ziemkiewicz et al., 1997).

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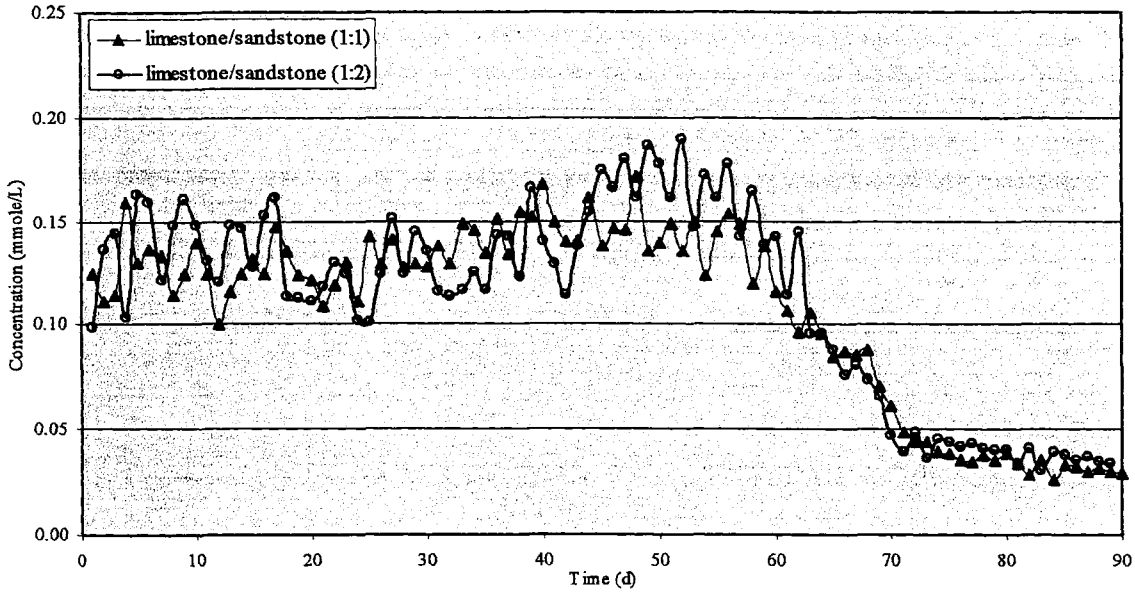


Figure 7.33. Calculated calcium carbonate concentrations in the filters that contained limestone and small particles of sandstone.

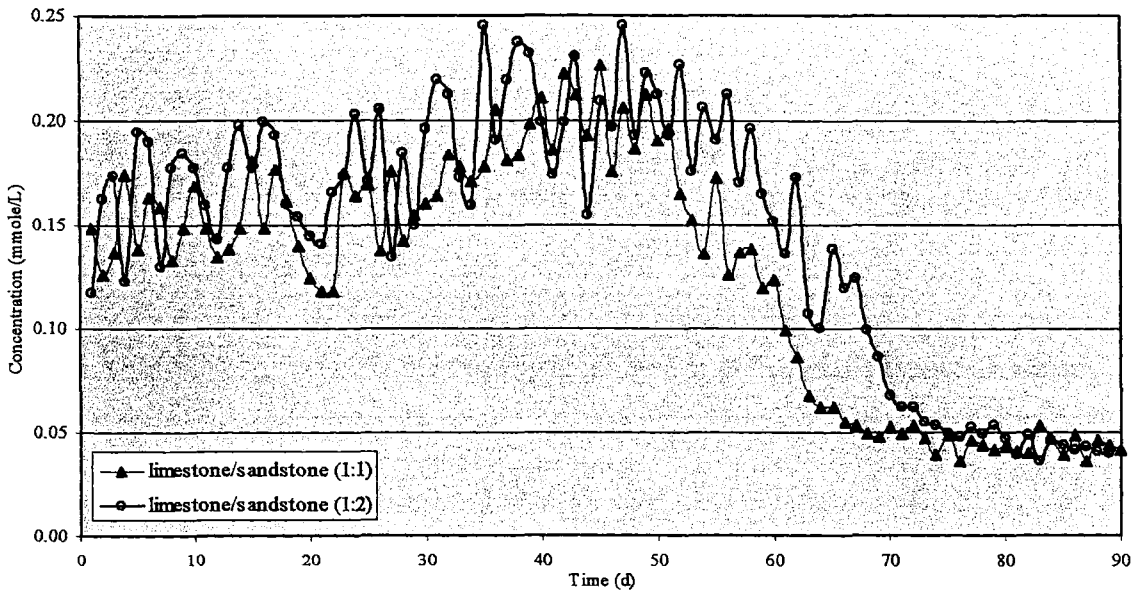


Figure 7.34. Calculated calcium carbonate concentrations in the filters that contained limestone and large particles of sandstone.

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7.7.3.4 Limestone/Sandstone Continuous Flow Filter Model

In order to predict the iron and manganese concentrations in the outlet of a continuous flow limestone/sandstone filter (LSF) and filter lifetime, a mathematical model was developed. The model consists of four components: (a) the governing equation for the filter, (b) the limestone dissolution rate, (c) the iron oxidation rate and (d) the manganese oxidation rate.

7.7.3.4.1 Governing Equation: In batch limestone/sandstone filters only chemical reactions such as oxidation, precipitation and dissolution are affecting the concentrations of iron, manganese and calcium carbonate in the system. However, in continuous, mixed flow filters, advection, dispersion/diffusion and chemical reaction also affect the concentration of elements in the solution. Mixed-flow reactors are assumed to be well-mixed in the radial plane (Figure 7.35). Thus, variations occur in the vertical dimension (z). In order to predict the concentration of elements along the vertical dimension and at the outlet of the filter, a mass balance is taken for a differential element of length Δz:

$$\Delta V \frac{dC}{dt} = J_{in} A_c - J_{out} A_c \pm \text{reaction} \qquad (7.37)$$

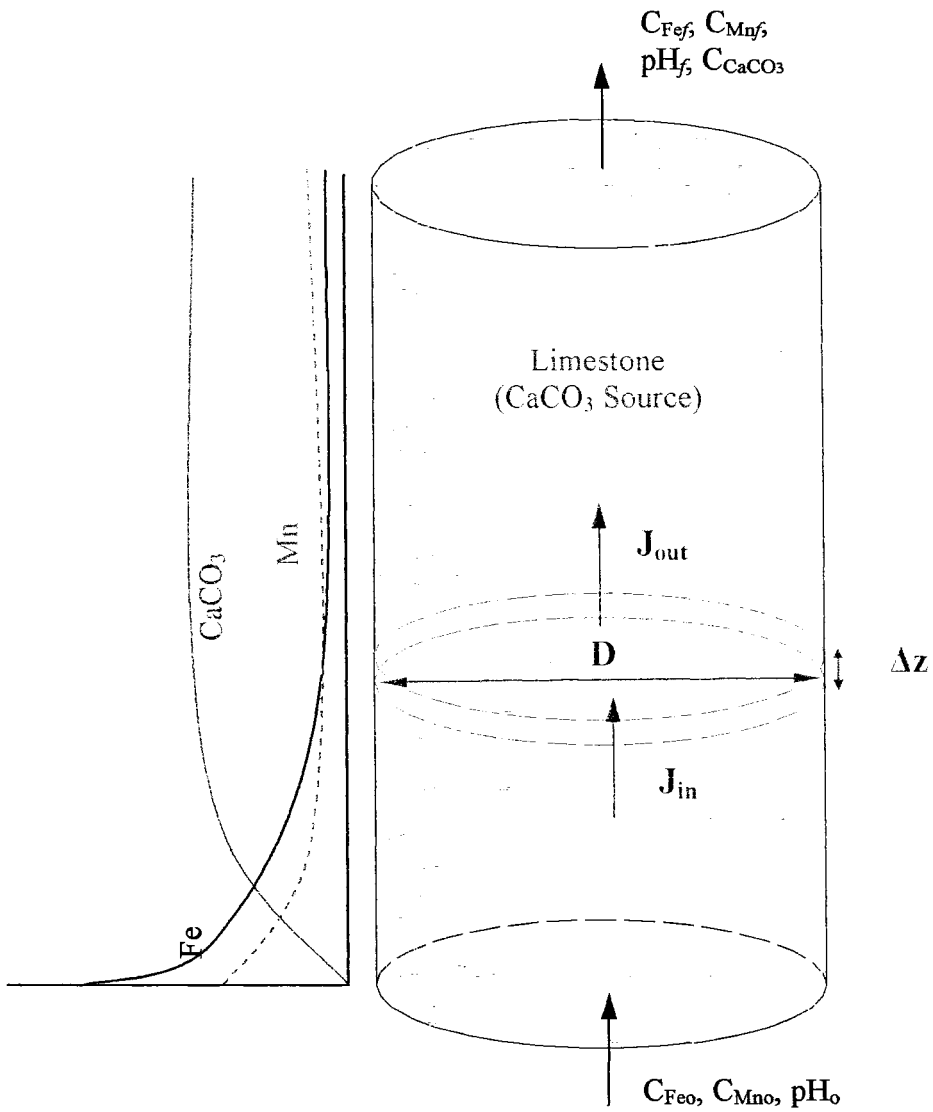
Where:

ΔV	= Differential volume ($A_c\ \Delta z$) of a length Δz (cm^3)
C	= Concentration of element (mg/cm^3)
t	= Time (s)
A_c	= Cross-sectional area of the reactor (cm^2)
J_{in}	= Flux-in of mass of the element due to transport ($mg/cm^2/s$)
J_{out}	= Flux-out of mass of the element due to transport ($mg/cm^2/s$)
reaction	= Gain or loss of mass within the element due to reaction (mg/s)

For the mixed-flow reactor, the flux-in is defined by Chapra (1997) as follows:

$$J_{in} = \underbrace{U \cdot C}_{\text{Advection}} - \underbrace{E\frac{dC}{dz}}_{\text{Diffusion/Dispersion}} \qquad (7.38)$$

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C_{Feo} = Initial iron concentration (mg/cm^3)
C_{Fef} = Final iron concentration (mg/cm^3)
C_{Mno} = Initial manganese concentration (mg/cm^3)
C_{Mnf} = Final manganese concentration (mg/cm^3)
pH_o = Initial pH
pH_f = Final pH
C_{CaCO3} = Calcium carbonate concentration (mg/cm^3)

Figure 7.35. Schematic diagram of the limestone/sandstone filter (LSF) showing the trends of iron, manganese and calcium carbonate concentrations along the vertical direction of the filter.

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Where:

U = Velocity (cm/s)

E = Diffusion/Despersion coefficient (cm^2/s)

z = Distance from inlet (cm)

Chapra (1997) also defined the flux-out as follows:

$$J_{out} = \underbrace{U\left(C + \frac{dC}{dz}\Delta z\right)}_{\text{Advection}} \underbrace{- E\left(\frac{dC}{dz} + \frac{d}{dz}\left(\frac{dC}{dz}\right)\Delta z\right)}_{\text{Diffusion/Dispersion}} \quad (7.39)$$

Schnoor (2003) defined the reaction as follows:

$$\text{Reaction} = k\,\Delta V\,C \quad (7.40)$$

Where:

k = First order oxidation/dissolution rate constant (s^{-1})

Substituting Equations (7.38), (7.39) and (7.40) into Equation (7.37) yields the following equation:

$$\Delta V\frac{dC}{dt} = A_c\left(UC - E\frac{dC}{dz}\right) + A_c\left[U\left(C + \frac{dC}{dz}\Delta z\right) - E\left(\frac{dC}{dz} + \frac{d}{dz}\left(\frac{dC}{dz}\right)\Delta z\right)\right] - k\Delta\, V\,C \quad (7.41)$$

Arranging the above equation yields the following equation:

$$\Delta V\frac{dC}{dt} = UA_cC - UA_c\left(C + \frac{dC}{dz}\Delta z\right) - EA_c\frac{dC}{dz} + EA_c\left(\frac{dC}{dz} + \frac{d}{dz}\left(\frac{dC}{dz}\right)\Delta z\right) - k\,\Delta\,V\,C \quad (7.42)$$

Simplifying Equation (7.43) yields the following equation:

$$\Delta V\frac{dC}{dt} = -UA_c\frac{dC}{dz}\Delta z + EA_c\frac{d^2C}{dz^2}\Delta z - k\,\Delta\,V\,C \quad (7.43)$$

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Since $\Delta V = A_c \Delta z$, dividing Equation (7.43) by ΔV yields the following equation:

$$\frac{dC}{dt} = -U\frac{dC}{dz} + E\frac{d^2C}{dz^2} - kC \tag{7.44}$$

At the steady-state, $\frac{dC}{dt} = 0$ and Equation (7.48) can be rewritten as follows:

$$0 = -U\frac{dC}{dz} + E\frac{d^2C}{dz^2} - kC \tag{7.45}$$

Assuming $\lambda = \frac{dC}{dz}$, the above equation can be rewritten as follows:

$$E\lambda^2 - U\lambda - k = 0 \tag{7.46}$$

The solution for Equation (7.46) is as follows:

$$\lambda = \frac{U}{2E}\left(1 \pm \sqrt{1 + \frac{4kE}{U^2}}\right) \tag{7.47}$$

Or
$$\lambda_1 = \frac{U}{2E}\left(1 + \sqrt{1 + \frac{4kE}{U^2}}\right) \tag{7.48}$$

And
$$\lambda_1 = \frac{U}{2E}\left(1 + \sqrt{1 + \frac{4kE}{U^2}}\right) \tag{7.49}$$

The general solution for Equation (7.45) can be obtained in a variety of ways. The following simple approach was given by Chapra (1997):

$$C = e^{\lambda z} \tag{7.50}$$

Therefore, the general solution for Equation (7.45) is as follows:

$$C = Fe^{\lambda_1 z} + Ge^{\lambda_2 z} \tag{7.51}$$

Where:

F & G = The general solution constants

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The constants of the above equation can be evaluated by boundary conditions. For the limestone/sandstone filter, the first boundary condition can be developed by taking a mass balance at the inlet (Danckwerts, 1953):

$$\text{Accumulation} = \text{Advection} - \text{Dispersion} \tag{7.52}$$

Mathematically, Equation (7.52) can be rewritten as follows:

$$Q\,C_{in} = Q\,C_o - E\,A_c\,\frac{dC_o}{dz} \tag{7.53}$$

Where:

Q = Water flow rate (cm^3/s^1)

Since $A_c = \frac{Q}{U}$, dividing Equation (7.53) by A_c yields the following equation:

$$U\,C_{in} = U\,C_o - E\,\frac{dC_o}{dz} \tag{7.54}$$

Substituting Equation (7.54) in Equation (7.51) gives the following equation:

$$U\,C_{in} = (F+G)\,U - E\,(F\frac{d}{dz}e^{\lambda_1 z} + G\frac{d}{dz}e^{\lambda_2 z}) \tag{7.55}$$

Differentiation of the above equation and substituting $z = 0$ yields the following equation:

$$U\,C_{in} = (F+G)\,U - E\,(F\,\lambda_1 + G\,\lambda_2) \tag{7.56}$$

The second boundary condition relates to the fact that no diffusion of mass is assumed to occur through the outlet (Danckwerts, 1953). Therefore, no gradient should exist at the end of the filter:

$$\frac{dC}{dz}(L) = 0 \tag{7.57}$$

Therefore, differentiating Equation (7.51) yields the following equation:

$$F\left(\lambda_1 e^{\lambda_1 L}\right) + G\left(\lambda_2 e^{\lambda_2 L}\right) = 0 \tag{7.58}$$

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The above equation can be rearranged as follows:

$$F = -\frac{G\left(\lambda_2 e^{\lambda_2 L}\right)}{\left(\lambda_1 e^{\lambda_1 L}\right)} \tag{7.59}$$

Or

$$G = -\frac{F\left(\lambda_2 e^{\lambda_2 L}\right)}{\left(\lambda_1 e^{\lambda_1 L}\right)} \tag{7.60}$$

Substituting Equation (7.60) into Equation (7.56) and rearranging gives the following equation:

$$F = \frac{UC_{in}\lambda_2 e^{\lambda_2 L}}{(U - E\lambda_1)\lambda_2 e^{\lambda_2 L} - (U - E\lambda_2)\lambda_1 e^{\lambda_1 L}} \tag{7.61}$$

Substituting Equation (7.59) into Equation (7.56) yields the following equation:

$$G = \frac{UC_{in}\lambda_1 e^{\lambda_1 L}}{(U - E\lambda_2)\lambda_1 e^{\lambda_1 L} - (U - E\lambda_1)\lambda_2 e^{\lambda_2 L}} \tag{7.62}$$

7.7.3.4.2 <u>Limestone Dissolution Rate</u>: Haddad (1986) described the dissolution of calcite in limestone filters by adapting the rate model derived by Rickard and Sjoberg (1983) which assumes that the dissolution of calcium carbonate in solutions is controlled by heterogeneous reaction, the rate of which is determined by a mass transfer resistance and a surface reaction acting in series. According to this assumption, the rate of calcium carbonate dissolution is given as follows:

$$k_{Ca} = k_o\, a \tag{7.63}$$

Where:

k_{Ca} = Calcium carbonate dissolution rate (sec^{-1})

k_o = Overall dissolution rate constant (cm/sec)

a = Interfacial area of calcium carbonate per unit volume (cm^2/cm^3)

The interfacial area of calcium carbonate per unit volume can be calculated by Letterman (1995) as follows:

$$a = 6(1 - p) / (d \,.\, p \,.\, s) \tag{7.64}$$

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Where:

d	= Volume mean diameter of limestone particles (cm)
p	= Bed porosity (cm^3/cm^3)
s	= Sphericity of limestone particles (-)

The volume mean diameter of limestone particles can be computed by the following equation (Haddad, 1986):

$$d = (6W/\pi N\rho)^{0.33} \tag{7.65}$$

Where:

ρ	= Mass density of high calcium limestone (~2.7g/cm^3)
W	= Mass of specific number limestone particles (g)
N	= Number of limestone particles (at least 50)

The sphericity of limestone particles can be calculated by as follows (Letterman, 1999):

$$s = 6/(A \cdot \rho \cdot d) \tag{7.66}$$

Where:

A	= Spherical limestone mass-specific surface area (cm^2/g)

The spherical limestone mass-specific surface area can be computed by the following equation (Sun, 2000):

$$A = \frac{N \pi d^2}{W} \tag{7.67}$$

The overall dissolution rate constant (k_o) is given by Haddad (1986) as follows:

$$k_o = [\ (1/k_L) + (1/k_c) - (1/k_f)\ ]^{-1} \tag{7.68}$$

Where:

k_L	= Mass transfer rate constant for calcium ion (cm/s)
k_c	= First order surface reaction rate constant (cm/s)
k_f	= Armoring layer mass transfer coefficient (cm/s)

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The k_f term was added to the above equation to take into account the effect of armoring on the lifetime of the filter and effectiveness of the filter in precipitating iron and manganese. The iron and manganese oxidation rates are depend on the concentration of hydrogen ions in the solution. The iron and manganese oxidation rates increase as the pH increases and the hydrogen ion decreases. As the armoring coated the limestone particles in the system, the amount of calcium carbonate dissolution decreased and the neutralization capacity of the system decreased which led to decreases in pH and increases hydrogen ions concentration.

According to Letterman et al. (1991), for crushed limestone bed, the magnitude of k_L can be determined using equations derived by Chu et al. (1953). The following equation was used for values of the modified Reynold's number (MRe) in the range of $1 \leq MRe \leq 30$:

$$k_L = 5.7\ U\ (MRe)^{-0.87}\ (Sc)^{-2/3} \qquad (7.69)$$

Where:

MRe	= Modified Reynold's number (-)
Sc	= Schmidt number (-)
U	= Velocity (cm/s)

While the following equation was used for values in the range of $30 < MRe \leq 10000$:

$$k_L = 1.8\ U\ (MRe)^{-0.44}\ (Sc)^{-2/3} \qquad (7.70)$$

The modified Reynold's number (MRe) the Schmidt number are given by the following equations (Letterman, 1999):

$$MRe = d\ U / (\upsilon\ (1 - p)) \qquad (7.71)$$

$$Sc = \upsilon / D \qquad (7.72)$$

Where:

υ	= Kinematic viscosity (m^2/s)
D	= Calcium ion diffusivity (m^2/s)

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Hadded (1986) assumed that the magnitude of k_c is determined by the chemistry of the solution at the $CaCO_3$ surface and used the data from Sjoberg and Rickard (1984) to drive the following empirical relationship:

$$k_c = 1.6 \times 10^{14} [H_{eq}]^{1.7} \quad (7.73)$$

Where:

$[H_{eq}]$ = Interfacial (equilibrium) hydrogen ion concentration (mol/L)

The following equations are used to calculate the equilibrium pH and equilibrium calcium concentration when calcium carbonate dissolves in a solution that is in equilibrium with atmospheric carbon dioxide. Equation 7.78 and Equation 7.79 were solved numerically for the equilibrium calcium ion concentration and the pH using known values of K_{sp}.

$$2[Ca] + C_C + [H^+] = K_H P_{CO_2} (\alpha_1 + 2\alpha_2) / \alpha_o + K_w / [H^+] + C_a \quad (7.74)$$

$$[Ca] = K_{sp} \alpha_o / \alpha_2 K_H P_{CO_2} \quad (7.75)$$

Where:

C_C = Influent concentrations of cations excluding hydrogen (equl/L)

C_a = Influent concentrations of anions excluding inorganic carbon species and hydroxide (equl/L)

K_H = The Henry's Law constant (mol/L atm.)

K_w = Water ion product (-)

K_{sp} = Calcium carbonate solubility product (-)

The value of K_H can be computed as function of temperature as follows (Plummer and Bussenburg, 1982):

$$\log K_H = 108.3865 + 0.0198507\,T + \frac{66936.5}{T^2} - \frac{6919.53}{T} - 40.45154 \log T \quad (7.76)$$

The value of K_w can be computed at different temperatures as follows (Harned and Hamer, 1933):

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$$pK_w = \frac{4787.3}{T} + 7.1321 \log T + 0.010365T - 22.80 \quad (7.77)$$

The values of the constants α_o, α_1 and α_2 can be determined as function of hydrogen ion concentration, first and second dissociation constants of carbonic acid as following (Letterman, 1995):

$$\alpha_o = \frac{1}{\{1 + (K_1/[H^+]) + (K_1K_2/[H^+]^2)\}} \quad (7.78)$$

$$\alpha_1 = \frac{1}{\{1 + ([H^+]/K_1) + (K_2/[H^+])\}} \quad (7.79)$$

$$\alpha_2 = \frac{1}{\{1 + ([H^+]/K_2) + ([H^+]^2/K_1K_2)\}} \quad (7.80)$$

Where:

K_2 = The second dissociation constant of carbonic acid (-)

The second dissociation constant of carbonic acid, K_2, can be computed as function of temperature as following (Harned and Scholes, 1941):

$$pK_2 = \frac{2902.39}{T} + 0.02379T - 6.498 \quad (7.81)$$

Due to the complex nature of modeling the transport of calcium ions across the residue layer, the data obtained from Letterman (1999) on the effect of armoring on the transport of calcium ion across the armoring layer was used to derive the following empirical relationship:

$$K_f = 31.95 \times 10^3 (Ca_{dis})^{-1.0012} \quad (7.82)$$

Where:

Ca_{dis} = Dissolved calcium ion per area of limestone (mg/cm^2)

7.7.3.4.3 <u>Iron and Manganese Oxidation</u>: Successful treatment requires nearly complete oxidation of Fe(II) to Fe(III) which must be followed by the precipitation of an Fe hydroxide. Singer and Stumm (1970) suggest that Fe(III) hydrolysis and precipitation

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proceed more rapidly than Fe(II) oxidation, thus oxidation is apparently the rate-limiting step. Kirby and Elder-Brady (1998) found that the field rate of precipitation of Fe hydroxide is faster than the field rate of Fe oxidation. Stumm and Lee (1961) proposed a rate law for Fe(II) oxidation under abiotic conditions, and Stumm and Morgan (1981) present this rate law, recast with H^+ instead of OH^- and O_2 concentration instead of partial pressure of oxygen as follows:

$$dC_{Fe^{2+}}/dt = -k\, C_{O_2} / (C_{H^+})^2 \qquad (7.83)$$

Where:

$C_{Fe^{2+}}$ = Aqueous ferrous iron concentration (mol/L)

C_{H^+} = Aqueous hydrogen ion concentration (mol/L)

The rate of Fe(II) oxidation has also been proposed to be affected by numerous other inorganic and biological parameters (Kirby and Elder Brady, 1998). There is a broad range of Fe-oxidizing bacteria which may contribute to the biogeochemical oxidation of Fe in natural systems. They include *Thiobacillus* spp. which are acidophiles preferring an optimum growth pH<3 (Traord et al., 1973; Amaro et al., 1991) typically associated with sulfuric mine tailings and neutrophilic filamentous organisms such as *Gallionella* spp. (Ivarson and Sojak, 1978), *Leptothrix* spp. (Crerar et al., 1979), Metallogenium (Walsh and Mitchell, 1972) and *Sphaerotilus* spp. (Stokes, 1954), which typically occur at groundwater seeps containing Fe(II) (Emerson and Revsbech, 1994). The rate law given by Stumm and Morgan (1981) can be employed to model abiotic Fe(II) oxidation

$$k_{Fea} = \frac{-k_{abiotic} C_{O_2}}{(C_{H^+})^2} = \frac{-\left\{A_{abiotic} \exp\left(\frac{-E_{a,abiotic}}{RT}\right)\right\} C_{O_2}}{(C_{H^+})^2} \qquad (7.84)$$

Where:

k_{Fea} = Abiotic iron oxidation first order rate (s^{-1})

$k_{abiotic}$ = Abiotic rate constant (mol/L/s)

$A_{abiotic}$ = Pre-exponential factor (4.00×10^5 mol/L/s)

$E_{a,abiotic}$ = Activation energy (kJ/mol)

R = Gas constant (kJ/mol/K)

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T = Temperature (K)

To model the contribution of iron oxidizing bacteria to Fe(II) oxidation, the rate law of Pesic et al. (1989) can be employed:

$$k_{Febio} = -k_{bio} C_{bact} C_{O_2} C_{H^+} = -\left\{ A_{bio} \exp\left(\frac{-E_{a,bio}}{RT} \right) \right\} C_{bact} C_{O_2} C_{H^+} \qquad (7.85)$$

Where:

k_{Febio} = Biotic first order iron oxidation rate constant (s^{-1})

k_{bio} = Biotic rate constant ($L^3/mg/mol^2/s$)

C_{bact} = Concentration of *T. ferrooxidans* (dw mg/L)

A_{bio} = Pre-exponential factor (1.09×10^9)

$E_{a,bio}$ = Activation energy (kJ/mol)

However, the rate of iron oxidation by bacteria was neglected because the landfill leachate has a pH in the range of 6 – 7, and the iron oxidizing bacteria needs very low pH for growth. According to Ehrlich (1996), there is as yet no unequivocal evidence that *Gallionella* significantly promotes Fe oxidation at pH around 7. Schrenk et al. (1998) demonstrated high concentrations of *Leptospirillum* ferrooxidans under extremely low pH conditions, but very low concentration in pH range of 6-7. It is well documented that *Thiobacillus ferrooxidans* catalyzes Fe(II) oxidation (e.g., Lacey and Lawson, 1970; Nordstrom, 1985) such that at low pH, field rates can be 105 to 106 times faster than abiotic laboratory rates. Optimal conditions for *T. ferrooxidans* growth occur at pH values near 3 (Schnaitman et al., 1969).

The formulation used in this study to calculate the kinetic rate of manganese oxidation and precipitation was obtained from Stumm and Morgan (1981):

$$k_{Mn} = \frac{-A_{Mn} \exp\left(\frac{-E_{Mn}}{RT} \right) C_{Fe^{3+}} C_{O_2}}{\left(C_{H^+} \right)^2} \qquad (7.86)$$

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Where:

K_{Mn}	= Manganese oxidation first order rate (s^{-1})
A_{Mn}	= Pre-exponential factor (s^{-1})
E_{Mn}	= Activation energy of manganese oxidation (kJ/mol)
R	= Gas constant (kJ/mol/K)
T	= Temperature (K)
C_{Fe+3}	= Fe(III) concentration in the system (mol/L)

7.7.3.4.4 Model Results: The effect of the presence of sandstone was not included in the model due to the lack of information in the literature about the specific mechanism by which sandstone contribute to the precipitation of iron and manganese or affect the dissolution of the limestone. The effect of the size of sandstone was indirectly included in the model because of the change in the velocity of the water inside the reactor caused by the change in the porosity of the limestone/sandstone filter.

7.7.3.4.4.1 Calcium Concentration: The predicted and experimental (as calculated from pH results) calcium concentrations in the limestone/sandstone filters are shown in Figure 7.36. The calcium concentration in the effluent of the filters with small sandstone particles at limestone to sandstone ratios of 1:1 and 1:2 was 0.14 mmol/L at the beginning of the experimental period and decreased with time reaching 0.03 mmol/L by the end of the experiment. The calcium concentration in the effluent of the filters containing large sandstone particles at limestone to sandstone ratios of 1:1 and 1:2 was 0.15 mmol/L at beginning of experimental period and decreased to 0.03 mmol/L by the end of the experimental period. The predicted calcium concentrations at the beginning and the end of the experiment were in a good agreement with the results obtained from the experiments. However, the experimental results showed fluctuation in the calcium concentrations over time.

A comparison of the predicted and experimental calcium concentrations in the effluent of limestone/sandstone filters are presented in Figure 7.37. The correlation coefficient (R^2) ranged from 0.67 to 0.74. The lower R^2 values can be attributed to the fact that the

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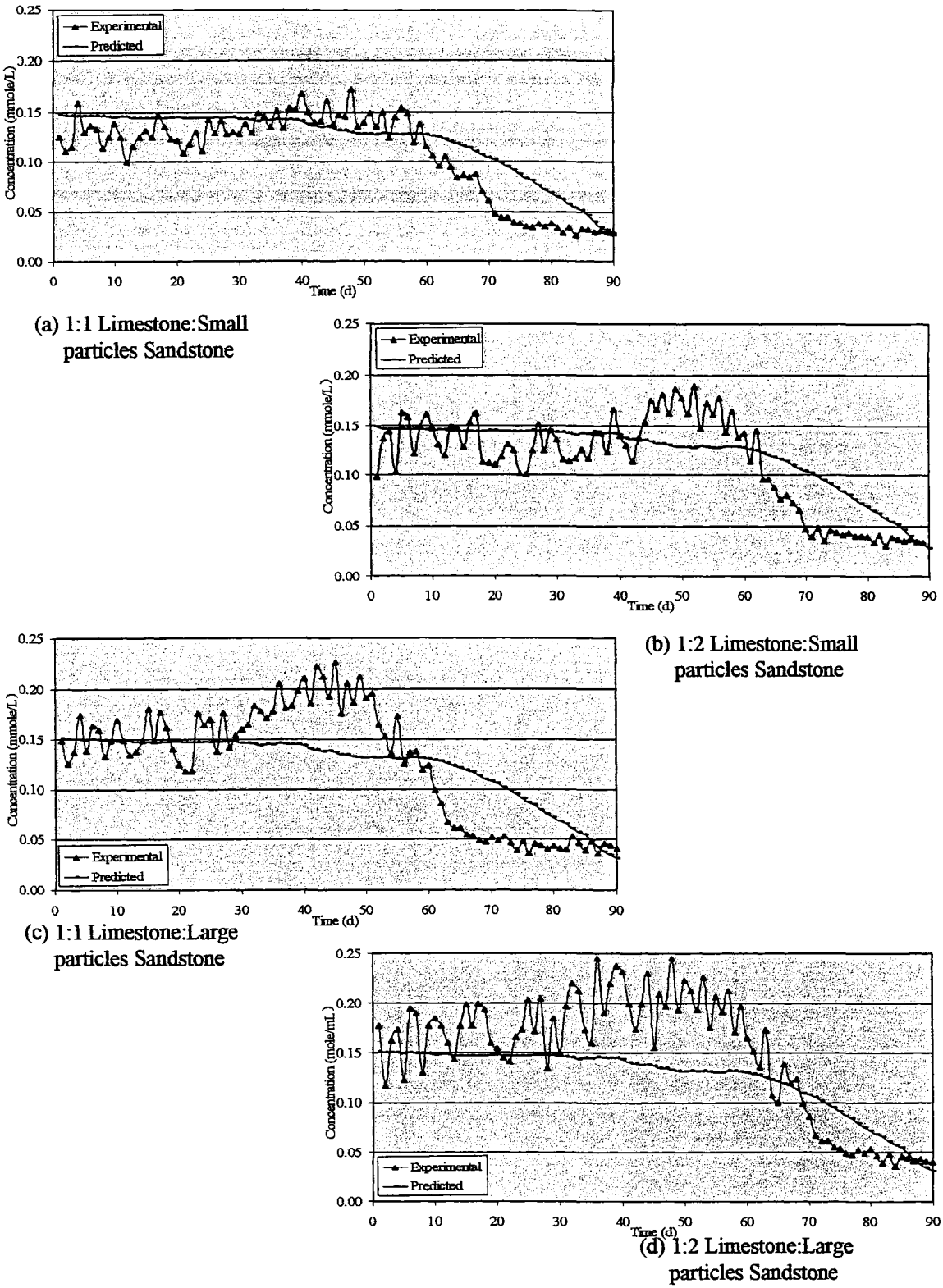
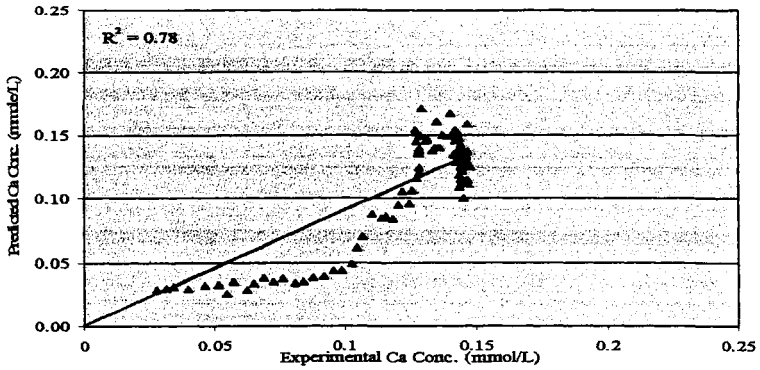
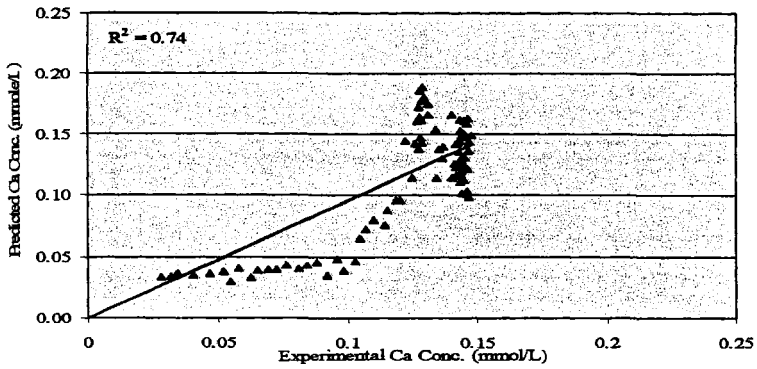


Figure7.36. The experimental and predicted calcium concentrations at outlet of the limestone/sandstone filters.

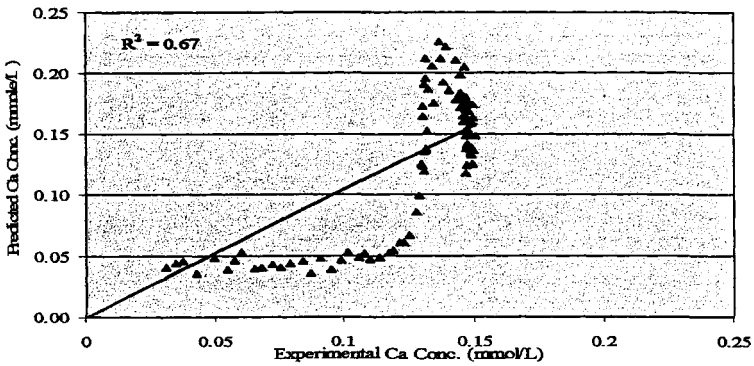
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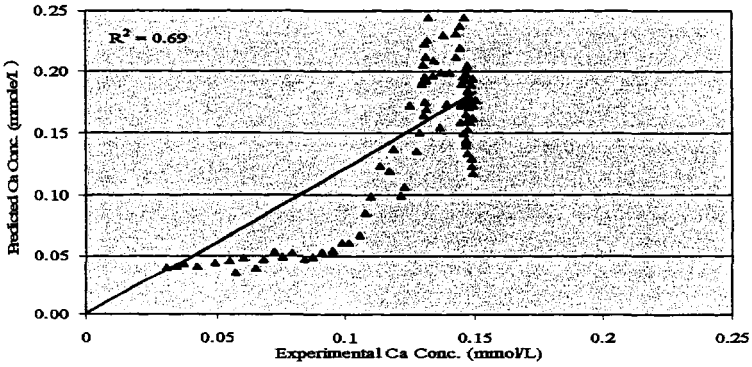
(a) 1:1 Limestone:Small particles Sandstone



(b) 1:2 Limestone:Small particles Sandstone



(c) 1:1 Limestone:Large particles Sandstone



(d) 1:2 Limestone:Large particles Sandstone

Figure7.37. Comparison between the experimental and predicted calcium concentrations at the outlet for the limestone/sandstone filters.

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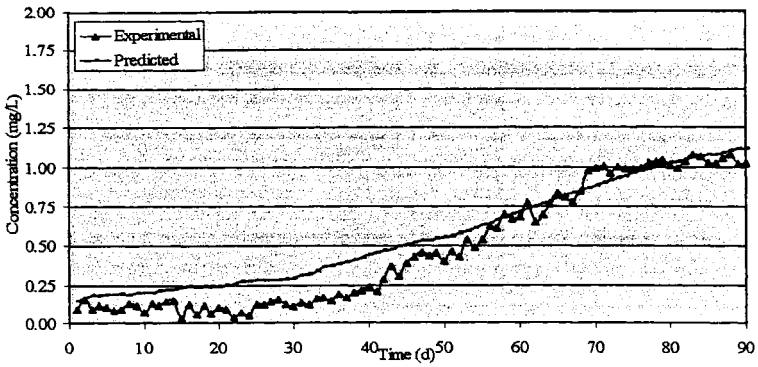
calcium concentrations in the experiment were not measured but were calculated based on the model adapted Myrna and White (1999).The results obtained from this study shows that the procedure proposed by Myran and White (1999) may not be very accurate as the pH may have been affected by factors, other than dissolution of calcium carbonate, that were not considered in the model.

7.7.3.4.4.2 ***Iron Concentration:*** The predicted and experimental iron concentrations in the limestone/sandstone filters are shown in Figure 7.38. The iron concentration in the effluent of the filters containing small sandstone particles at limestone to sandstone ratios of 1:1 and 1:2 was 0.14 mg/L at the beginning of the experimental period and increased to 1.1 mg/L by the end of the experiment. The iron concentration in the effluent of the filters with large sandstone particles at limestone to sandstone ratios of 1:1 and 1:2 was 0.15 mg/L at the beginning of the experimental period and increased to 1.1 mg/L by the end of the experiment. The experimental results obtained from the filters at the beginning of the experiment were slightly lower than those predicted by the model. However, the model predictions at the latter part of the experiment were in agreement with the experimental results. This may be because the rate of calcium ion transfer through the armoring included in the model was higher than the actual value at the beginning of the experiment when armoring was still not significant.

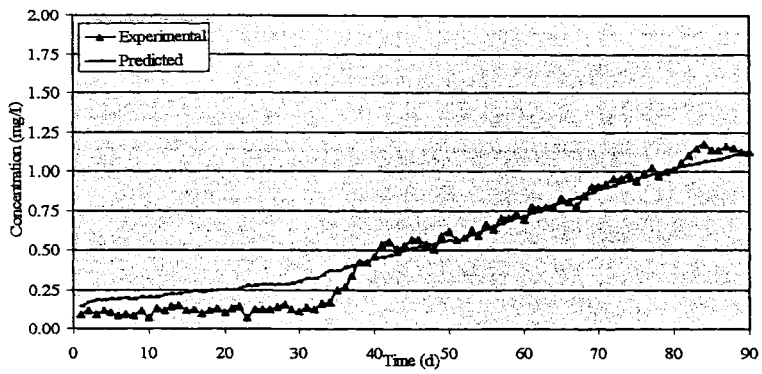
A comparison of the predicted and observed iron concentration in the effluent of the filters are shown in Figure 7.39. The correlation coefficient (R^2) ranged from 0.91 to 0.95. These correlation factors showed that the model is capable of predicting the experimental data with a relatively high confidence.

7.7.3.4.4.3 ***Manganese Concentration:*** The predicted and experimental manganese concentrations in the limestone/sandstone filters are shown in Figure 7.40. The manganese concentrations in the effluent of the filters containing small sandstone particles at limestone to sandstone ratios of 1:1 and 1:2 was 0.48 mg/L at the beginning of the experimental period and slightly increased to 0.51 mg/L by the end of the experiment. The manganese concentration in the effluent of the filters containing large

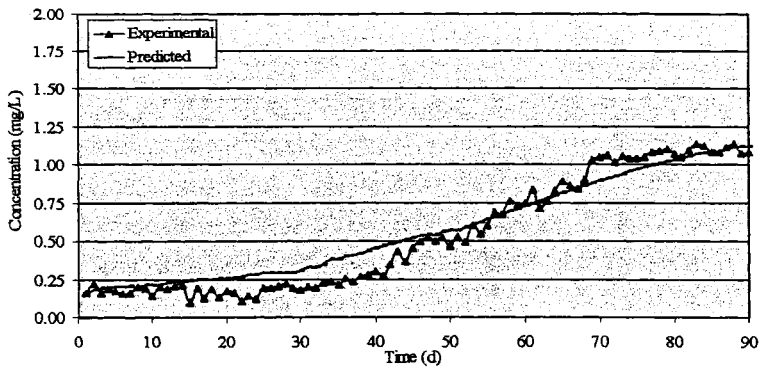
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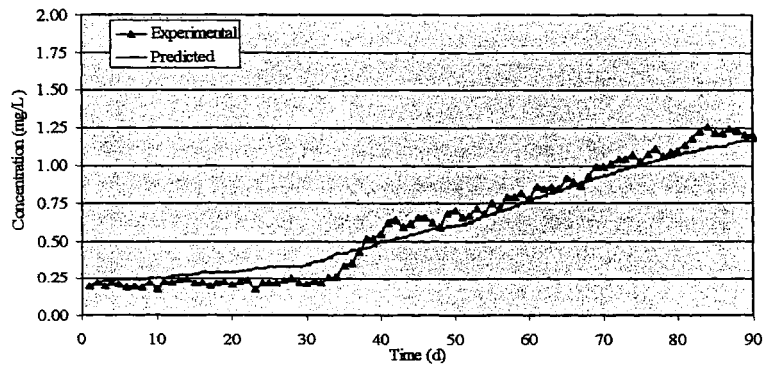
(a) 1:1 Limestone:Small particles Sandstone



(b) 1:2 Limestone:Small particles Sandstone



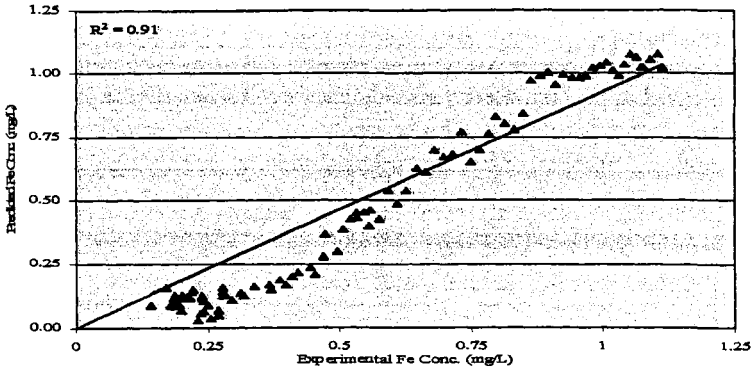
(c) 1:1 Limestone:Large particles Sandstone



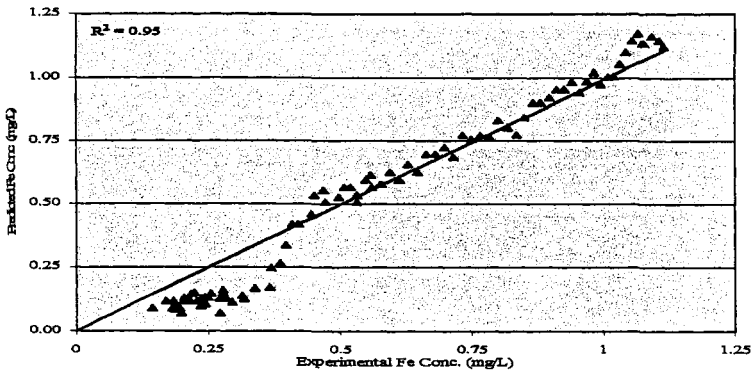
(d) 1:2 Limestone:Large particles Sandstone

Figure7.38. The experimental and predicted iron concentrations at outlet of the limestone/sandstone filters.

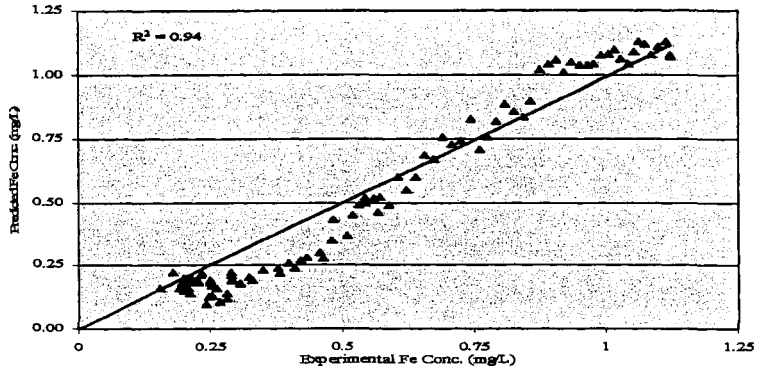
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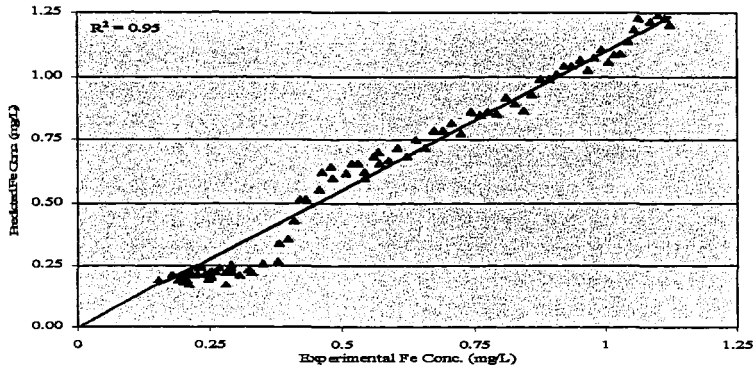
(a) 1:1 Limestone:Small particles Sandstone



(b) 1:2 Limestone:Small particles Sandstone



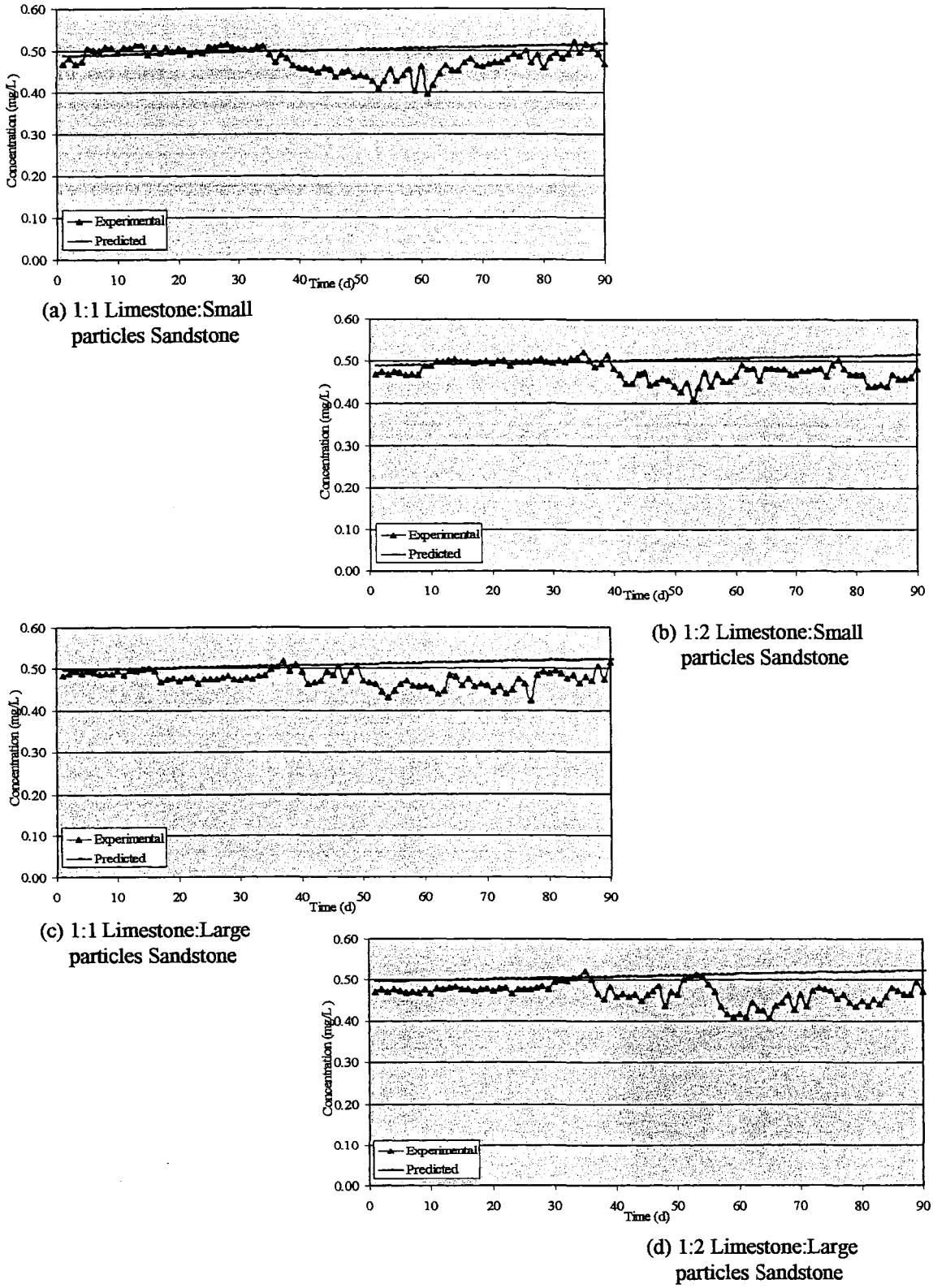
(c) 1:1 Limestone:Large particles Sandstone



(d) 1:2 Limestone:Large particles Sandstone

Figure7.39. Comparison between the experimental and predicted iron concentrations at the outlet for the limestone/sandstone filters.

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(a) 1:1 Limestone:Small particles Sandstone

(b) 1:2 Limestone:Small particles Sandstone

(c) 1:1 Limestone:Large particles Sandstone

(d) 1:2 Limestone:Large particles Sandstone

Figure7.40. The experimental and predicted manganese concentrations at outlet of the limestone/sandstone filters.

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sandstone particles at limestone to sandstone ratios of 1:1 and 1:2 was 0.49 mg/L at the beginning of the experimental period and increased slightly to 0.52 mg/L by the end of the experiment. The experimental results showed some fluctuation in the manganese concentrations over time relative to the model results.

A comparison between the predicted and experimental manganese concentrations in the solution at the outlet of the limestone/sandstone filters are shown in Figure 7.41. The low values of the correlation coefficient (R^2 = 0.42-0.45) was due to the very narrow ranges of manganese concentrations observed in the experiment (between 0.4 and 0.5 mg/L).

7.8 Filter Design

The proposed filter will be implemented on the north and east ditches adjacent to the Don Bayer's Sports Field (former Burnside landfill) as shown in Figure 7.42. The storm water from the four watersheds and the landfill leachates from the Black Lake landfill and Burnside landfill are collected in these ditches. The north ditch is located to the north of the Don Bayer's Sports Field (former Burnside Landfill) parallel to Akerley Boulevard. It receives stormwater from a 16.02 ha watershed area and the leachate of the former black lake landfill. The ditch has a trapezoidal shape (Figure 7.43a) with a bottom base width of 2.74 m, a top base width of 7.62 m, a side slope of 3.47 m and a height of 2.4 m. The length of the ditch is 126.5 m. The east ditch is located to the east of the Don Bayer's Sports Field (former Burnside Landfill). It receives stormwater from a 38.04 ha watershed area and the leachate of the former burnside landfill. The north ditch (Figure 7.43b) has a bottom base width of 1.45 m, a top base width of 7.62 m, a side slope of 3.95 m and a height of 2.29 m. The length of ditch is 126.5 m.

The treatment wetland water analysis results (Table 7.32) showed a minimum iron removal efficiency of 47.13 %. In order to completely remove iron from the water, the filter should remove at least 60 % of the inlet iron concentration before entering the wetland. Based on the site watershed characteristics, the average runoff and peak runoff rate were calculated using the Rational Formula Equation (5.1).

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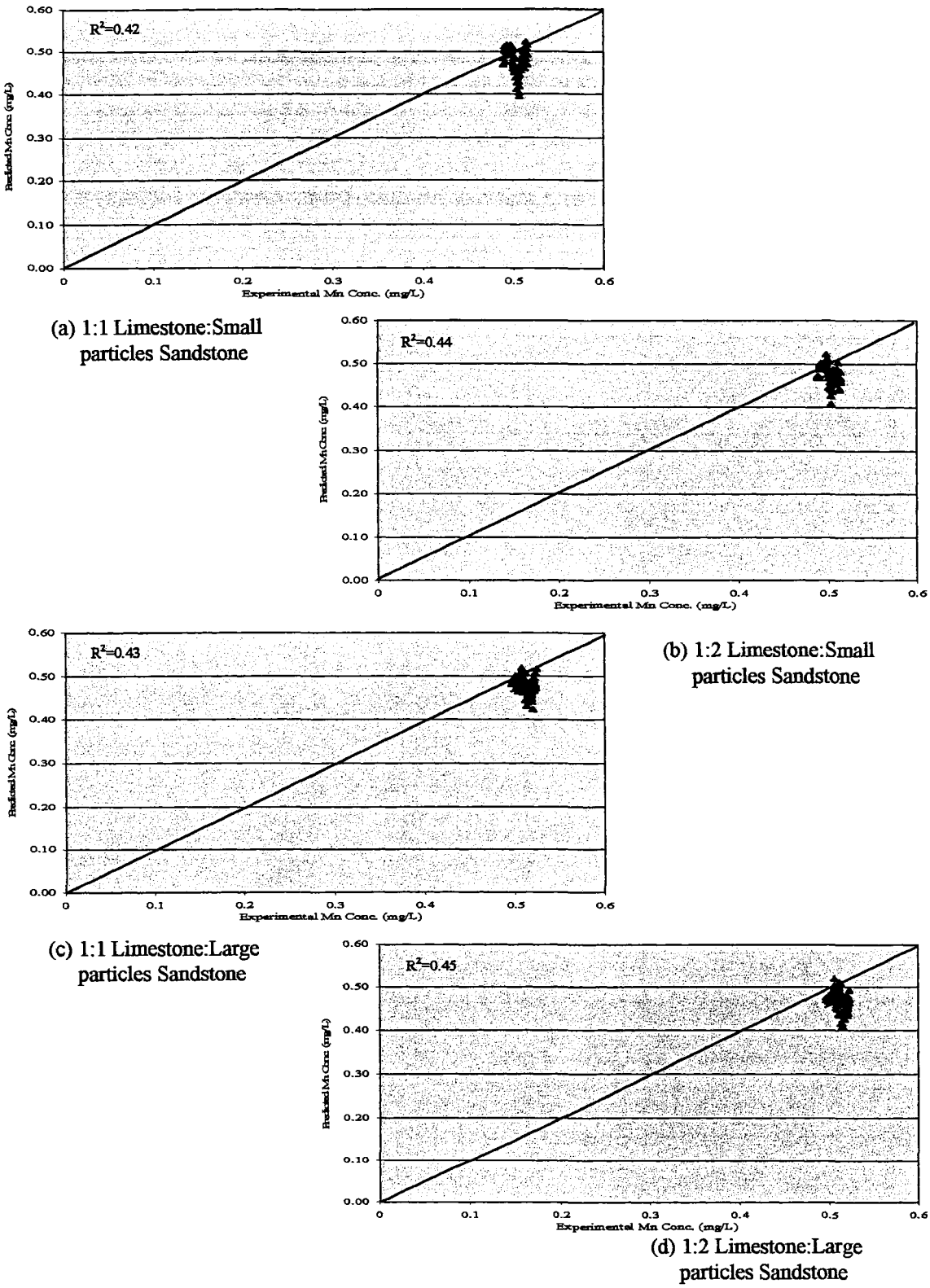


Figure7.41. Comparison between the experimental and predicted manganese concentrations at the outlet for the limestone/sandstone filters.

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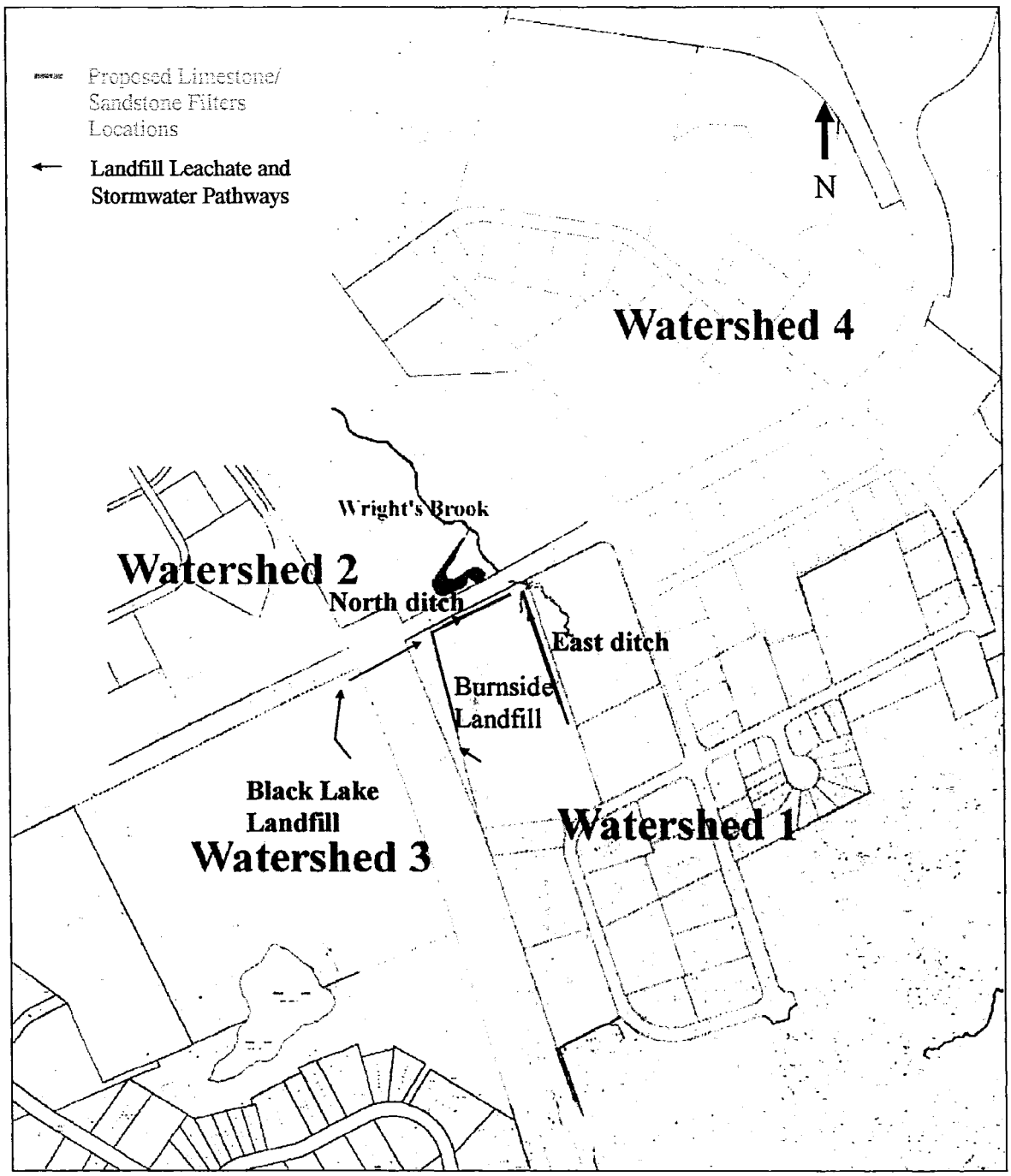
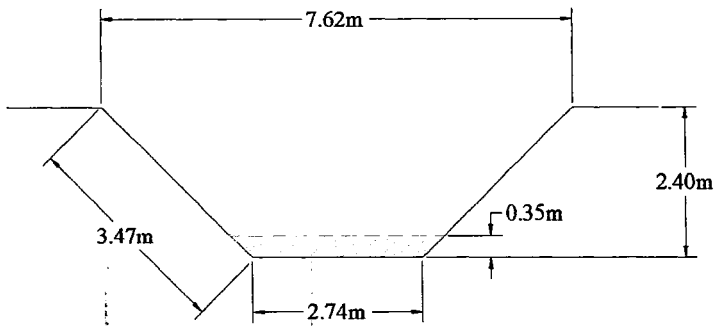
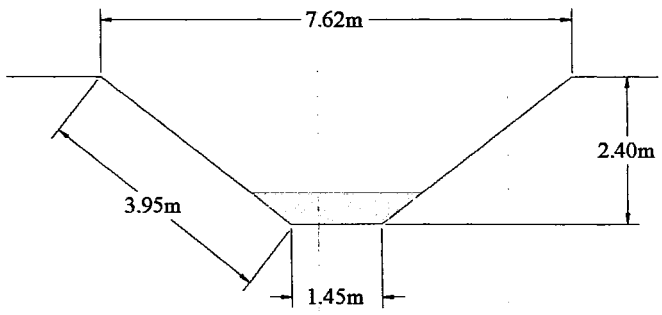


Figure 7.42. Location of the proposed limestone/sandstone filters and the pathways of landfill leachate from both landfills and stormwater.

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(a) Cross Section of the North Ditch



(b) Cross Section of the East Ditch

Figure 7.43. Cross section of the ditches.

A runoff coefficient of 0.47 was used based on the land area designated for each purpose and the effects of that land use on the runoff amounts. A rainfall intensity of 39 mm/h was determined based on a one-hour, fifty-year return storm period which gave a peak runoff rate of 0.84 and 1.97 m^3/s for the north ditch and the east ditch, respectively. This storm event period was chosen in order to avoid wash out of the limestone filter during high intensity storms. The velocity and the depth of water inside the limestone channel were determined during the peak storm event by solving the continuity equation (Equation 7.87) and manning equation (Equation 7.88) simultaneously.

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Table 7.33. Iron concentrations in the inlet and the outlet of the wetland during year 2004.

SAMPLING DATE	Location	Fe (mg/L)	Removal Eff. (%)
May 15, 2004	Inlet	6.96	47.13
	Outlet	3.68	
June 1, 2004	Inlet	7.12	53.79
	Outlet	3.29	
June 15, 2004	Inlet	7.32	59.56
	Outlet	2.96	
July 1, 2004	Inlet	6.85	76.20
	Outlet	1.63	
July 16, 2004	Inlet	6.38	49.06
	Outlet	3.25	
Aug. 2, 2004	Inlet	6.85	80.29
	Outlet	1.35	
Aug. 16, 2004	Inlet	6.95	53.24
	Outlet	3.25	
Sept. 1, 2004	Inlet	6.45	63.57
	Outlet	2.35	
Sept. 17, 2004	Inlet	6.25	83.68
	Outlet	1.02	
Oct. 4, 2004	Inlet	6.29	84.74
	Outlet	0.96	
Oct. 20, 2004	Inlet	7.21	82.94
	Outlet	1.23	

Minimum Removal Efficiency = 47.13 %
Maximum Removal Efficiency = 84.74 %
Average Removal Efficiency = 66.75 %

$$V = \frac{Q}{A} \tag{7.87}$$

$$V = \frac{1}{n} R^{2/3} S^{1/2} \tag{7.88}$$

Where:

V = Velocity (m/s)

Q = Total Runoff (m^3/s)

A = Area of Channel Cross Section

n = Manning's roughness coefficient

R = Hydraulic radius (m)

S = Channel bed slope (m/m)

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The Manning's roughness coefficient and hydraulic radius can be calculated as follow:

$$n = 0.04\ d_{50}^{(1/6)} \quad (7.89)$$

$$R = A/P \quad (7.90)$$

Where:

d_{50}	:	Filter material size (m)
P	:	Wetted perimeter (m)

The cross sectional area of the channel was assumed to take a rectangular shape of 4.00 m width (based on the bottom base width of the north and east ditches). The selected bed slope was 10 % and the average size of the available filter material in Nova Scotia is 0.15 m. The calculated depth of the filter was found to be 0.25 and 0.45 m, the filter cross sectional area was found to be 1.00 and 1.80 m^2 and the velocity of the water was found to be 0.84 and 1.10 m/s for the north and the east ditches, respectively.

The filter materials will be 1.0 m high to insure full contact of the water with the filter. This will result in a filter cross sectional area of 4 m^2. The slope of the filter should be 10 % to insure splashing which enhances limestone dissolution and prevents iron and manganese precipitates from settling in voids in the limestone channel as recommended by Ziemkiewicz et al. (1997). The ditch has to be leveled by gravels and fill to maintain the 10% slope.

The laboratory experiments indicated that the filter is capable of removing an average of 95 % of the iron in the leachate in less than twenty minutes. This removal efficiency will reduce the iron concentration in the water to a level below the guideline value of 0.3 mg/L recommended by the CCME (2003).

The amount of dissolved calcium carbonate required to precipitate iron removal was calculated using Equation (7.30) given by Cravotta and Trahan (1999) whereas that required to precipitate manganese was calculated using Equation (7.31) given by Gazea et al. (1996). According to these equations, 2 moles of calcium carbonate must be

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available in solution for each mole of Fe^{2+} removed from the solution and 0.5 mole of calcium carbonate must be available in solution for each mole of Mn^{2+} removed from the solution. Iron and manganese removed and calcium carbonate dissolved and required after 20 min in the field limestone/sandstone filter at different temperatures are shown in Table 7.33.

To calculate the calcium carbonate dissolved in the solution based on the calcium carbonate dissolution rate constant determined using the data from the batch beaker experiment, the local area climate normals were investigated (Table 5.1). The average monthly temperatures used to determine the calcium carbonate dissolution rate constant were the above zero temperatures because during the sub zero months the soil freezes and the chemical reactions are at minimum. Based on these assumptions, the average temperature used to determine the calcium carbonate dissolution rate was 11.5 °C. From Table 7.9, the calcium carbonate dissolution rate ranged from 0.0998 to 0.1229 min^{-1}. Therefore, the amount of calcium carbonate dissolved ranged rate from 108.80-172.68 and 254.15-403.40 g/20 min for the north and east ditches, respectively.

Sasowsky et al. (2000) recommended limestone/sandstone ratio 1:1 to reduce armoring of limestone. Although, the results revealed that sandstone was not as effective as it was reported in literature, the sandstone will be included in the design of the filter to act as extra surface area that can help decrease the iron and manganese precipitation on the limestone filter over time which will in turn increase the lifetime of the filter by avoiding filter clogging. The limestone has a density of 2.70 t/m^3 and is composed of 98 % calcium carbonate. The active life of the landfill was assumed to be 50 years. Since the landfill is now 28 years old (was closed in 1977), it is estimated that it will remain active for another 22 years. Assuming a filter lifetime of 22 years, the mass of limestone calculated from the dissolution rate, was estimated to be 50 and 130 t for the north and east ditches, respectively. The filter volumes will be 74.1 and 173.3 m^3 and the filter lengths will be 18.5 and 43.5 m for the north and east ditches, respectively. The amount of limestone and dimensions of the limestone/sandstone filter were in agreement with literature (Ziemkiewicz et al., 1997 and Skousen et al., 1999). The dimensions of the

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Table 7.34. Iron and manganese removed and calcium carbonate dissolved and required after 20 min for the field limestone/sandstone.

Temperature (°C)	Fe Removed		Mn Removed		Calcium Carbonate											
					Dissolved (g)		Required (g)						Balance			
							Fe[a]		Mn[b]		Total		(g)		(%)	
	(mg)	(%)	(mg)	(%)	E	N	E	N	E	N	E	N	E	N	E	N
5	4.17	63.21	0.27	14.79	479.10	205.11	103.15	44.16	1.70	0.73	104.85	44.89	374.25	160.22	78.11	78.12
10	5.51	83.47	0.54	30.23	403.40	172.68	136.30	58.35	3.39	1.46	139.70	59.81	263.70	112.87	65.37	65.37
15	6.01	90.93	0.71	39.34	254.15	108.80	148.67	63.65	4.46	1.91	153.14	65.56	101.01	43.24	39.75	39.75
20	6.33	95.92	0.75	41.73	252.12	107.93	156.59	67.04	4.72	2.02	161.30	69.05	90.82	38.88	36.02	36.02

E East Ditch
N North Ditch
a Calculated from Equation 7.33 (Appendix B)
b Calculated from Equation 7.34 (Appendix B)

filters are presented in Table 7.34 whereas the cross sectional areas are shown in Figures 7.42 and 7.43.

The results revealed that 65.37 % of the calcium carbonate dissolved in the system will be washed out with the water, and not being actively used to precipitate iron and manganese. This will make the effectiveness of the filter for both ditches about 35 %. These results were in agreement with the literature, Skousen et al. (1999) stated that the efficiency of limestone filter in treating acid mine drainage was 30 %. However, limestone filters have several advantages: (a) free maintenance, (b) no power required to operate the filter, (c) high removal efficiency of iron and manganese, (d) availability of the filter materials in Nova Scotia and (e) cost effective compared to other chemical treatment methods. Skousen et al. (1999) compared the prices of five different chemicals used to elevate the pH of acid mine drainage and precipitate metals and found that the prices were US$10, 60, 80, 200 and 680 (prices at year 1996) for limestone, hydrated lime, Pebble Quick lime, soda ash and caustic soda, respectively. These advantages favored the use of limestone/sandstone filters, over other treatment systems, to treat landfill leachate despite the low efficiency.

7.9 Conclusions

1. The results obtained from the tank experiment showed that the limestone and the limestone/sandstone filters successfully removed iron and manganese from the leachate solutions.
   (a) The iron removal efficiency was 97.60 % and most of the iron (96%) was removed in the first two hours of the experiment.
   (b) The manganese removal efficiency fluctuated between 22.22 % and 100 % and a large percentage of the manganese (70 %) was removed during the first four hours.
2. The results obtained from the beaker experiments showed that the dissolution of $CaCO_3$ and the precipitation of iron and manganese were affected by temperature.
   (a) The temperature affected the dissolution rate of limestone and in turn affected the pH in the filters.

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Table 7.35. Design Parameters for the Limestone/Sandstone Filters.

PARAMETER	NORTH DITCH	EAST DITCH
Watershed Information		
Watershed Area (ha)	16.02	38.04
One hour-50 year precipitation (mm/h)	39.00	39.00
Runoff Coefficient	0.47	0.47
Runoff (m^3/s)	0.85	1.97
Ditch Top Base (m)	7.62	7.62
Ditch Bottom Base (m)	2.74	1.45
Ditch Depth (m)	2.40	2.29
Ditch Length (m)	126.50	126.50
Water Depth (m)	0.35	0.50
Bed Slope (%)	1.00	1.00
Estimated Filter Dimensions		
Filter Materials Diameter (cm)	15.24	15.24
Filter Slope (%)	10.00	10.00
Manning's Coefficient	0.029	0.029
Water Depth (m)	0.25	0.45
Assumed Filter Width (m)	4.00	4.00
Cross Sectional Area (m^2)	1.00	1.80
Water Velocity (m/s)	0.84	1.10
Final Filter Design		
Average Runoff (m^3/h)	9.02	27.78
Slope (%)	10.00	10.00
Filter Depth (m)	1.00	1.00
Filter Width (m)	4.00	4.00
Filter Length (m)	18.50	43.50
Filter Cross Sectional Area (m^2)	4.00	4.00
Filter Volume (m^3)	74.10	173.30
$CaCO_3$ Dissolution Rate (g/min)	172.68	403.40
Limestone (tons)	50.00	130.00
Sandstone (tons)	50.00	130.00
Life Time (years)	22.00	22.00

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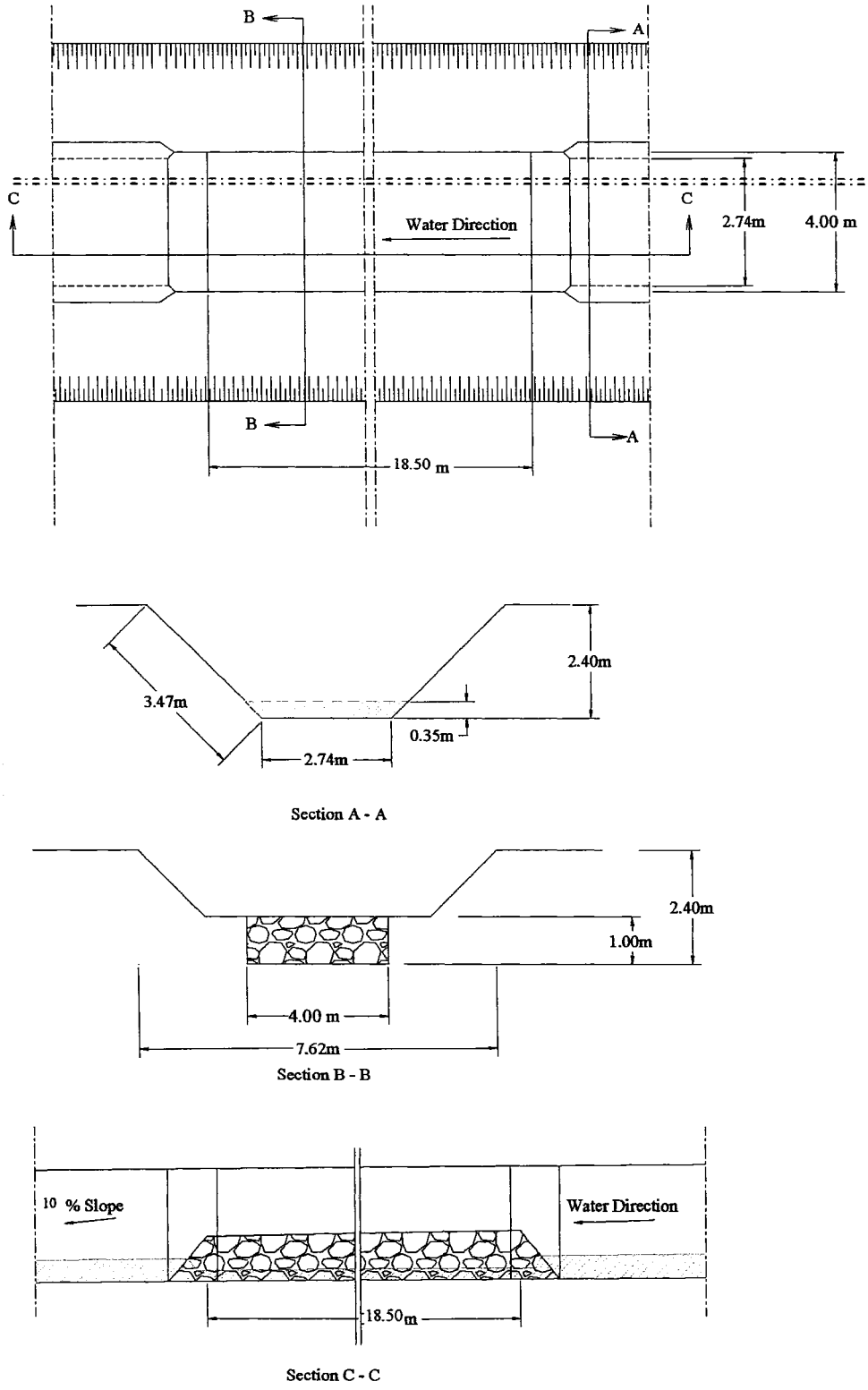


Figure 7.44. Cross sectional area of filter in the north ditch.

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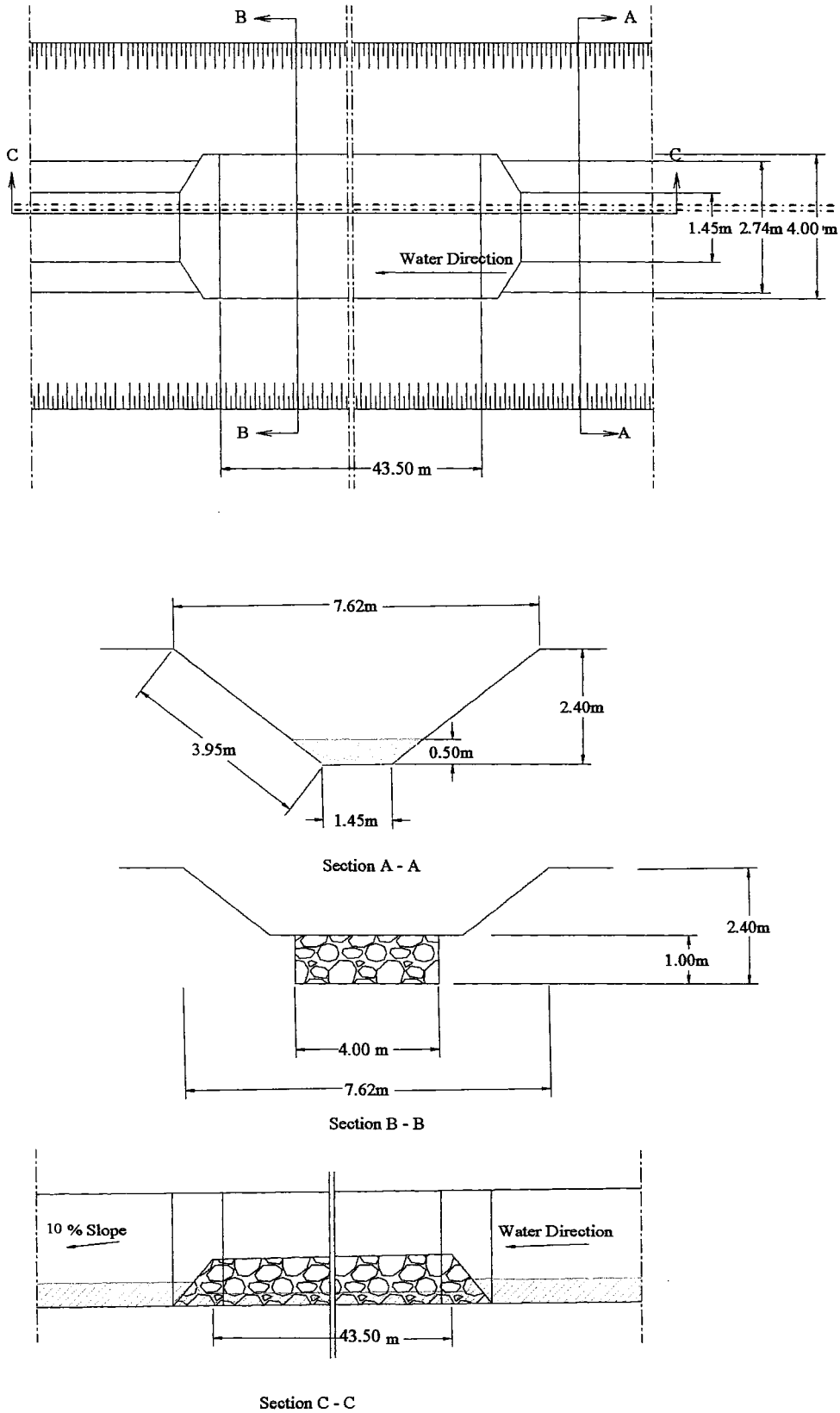


Figure 7.45. Cross sectional area of filter in the east ditch.

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(b) The dissolution rate constants were higher in the filters containing iron and iron/manganese than these containing manganese alone.

(c) Most of iron was removed from solution within the first 10 minutes at 20 °C while the removal of iron from solution took much longer time (50 min) at 5 °C.

(d) Larger percentage (69 %) of manganese was removed from solution within the first 20 minutes at 20 °C compared to that removed (42 %) at 5 °C.

(e) The time and temperature have significant effects on the iron and manganese removal efficiencies.

(f) The iron and manganese removal rate constants of the limestone filters were higher than those of the limestone/sandstone and increased with increases the temperature.

3. The pH of the water samples did not exceed 7.7, which is below the Canadian guidelines for the protection of aquatic life. Therefore, the wetland ecosystem should be able to adjust to water having a slight alkalinity without suffering adverse effects.

4. The treated effluent of the continuous flow filters contained on average less than 0.66 mg/L iron (10 % of the influent dissolved iron concentration) and 0.47 mg/L manganese (26 % of the influent manganese concentration).

   (a) There were no noticeable effects of the ratio of limestone and sandstone or the size of the sandstone particles on the iron and manganese removal efficiency.

   (b) The iron removal efficiency was higher at the beginning of the experiment and then declined over time due to the armoring build up on the limestone particles, but the manganese removal efficiency fluctuated during the experimental period.

5. A mathematical model capable of predicting the calcium, iron and manganese concentrations in the outlet of a continuous flow limestone/sandstone filter was developed.

   (a) The predicted calcium concentrations at the beginning and the end of the experiment were in a good agreement with the results obtained from the experiments. However, the experimental results showed fluctuations in the calcium concentrations over time. This could be due to the inaccuracy of the procedure used for calculating the experimental data.

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(b) The model is capable of predicting the iron experimental data with a relatively high confidence (R^2 = 0.91 - 0.95).

(c) The model prediction of manganese concentrations was low (R^2 = 0.42 - 0.45) due to the fluctuation in experimental results and the narrow range of the experimental measurements.

6. Two limestone filters were designed and the various dimensions of the filters were calculated.

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8. OVERALL SUMMARY AND CONCLUSIONS

Landfill leachates are highly toxic to aquatic life and degrade water quality. The main objective of this study was to investigate the effectiveness of combining a constructed wetland with a passive treatment technology for the treatment of landfill leachate and to shed some light on the mechanisms of heavy metals removal in constructed wetlands. The study was carried out in five parts.

The first part was devoted to the evaluating of the performance of the Burnside treatment wetland, which was constructed in the fall of 2000 at the head of Wright's Brook. The quantity and quality of the leachate and runoff that enters the constructed wetland were assessed. Site investigations along with discussions, maps and schematics lead to the discovery of four watersheds which directly drain into the constructed wetland system. The average and peak runoff rates for each watershed area were calculated. The overall removal efficiencies for heavy metals (Fe and Mn), COD, TSS, TDS, Ortho-phosphate, Ammonium-Nitrogen, TKN, NO_3-N, NO_2-N, DO and pH, the rates of heavy metals uptake by the plants precipitates were determined. The water quality at the outlet of the constructed wetland improved significantly over time. Increasing the number of cells from 4 cells in season I to 9 cells in season II improved the removal efficiencies for ortho-PO_4, TKN, NH_4-N, NO_3-N, COD, TSS, TDS, Fe and Mn by 33.3, 33.3, 30.6, 8.00, 26.7, 52.2, 43.5, 54.1, 44.44 and 18.52 %, respectively. The water pH fluctuated around 7 due to precipitation and generation of organic substances which acted as buffer. The pH values observed during seasons I and II were within the limits (5.0 to 9.0) of the CCME (2003) guidelines for the protection of freshwater aquatic life. The DO concentration was affected by the organic and inorganic pollutants discharged into the wetland, water temperature and plant growth and maturity. The DO concentrations observed during seasons I and II were within the range (4.5 and 9) established by the CCME (2003). However, it dropped below the lower limit of 4.5 mg/L in the outlet during the months of June-August of season I due to high water temperature. The iron removal efficiency was affected by the amount of flocs present in the wastewater, the site vegetation, the plant maturity and rain events. The manganese removal efficiency was affected by rain event,

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plant density and maturity, and manganese and iron concentrations in the wastewater. Plant species (woolgrass, soft rush, tweedy's rush, pickerelweed, yellow-green sedge, fowl mannagrass, soft stem bulrush, fringed sedge, reed canary grass and broad-leaved cattail) differed widely in their ability to accumulate and translocate iron and manganese. The root tissues of the plants accumulated significantly greater concentrations of iron than the shoots and flowers. While the leaf and flower tissues accumulated significantly greater concentrations of manganese than the roots, indicating high manganese mobility inside the plant. A first-order kinetic model was used to determine iron and manganese specific uptake rates by wetland plants and the maximum concentration that can be accumulated by each plant at the end of the growing season. The plants used in the constructed wetland did not accumulate high concentrations of manganese due to Mn-Fe antagonism.

The objectives of the second part were to investigate the effect of initial concentrations of heavy metals (Fe, Mn and Zn) on the overall removal efficiency of these metals by obligate and facultative wetland plants (wool grass, soft rush, broad-leaved cattails and soft stem bulrush), to determine the translocation of heavy metals in the different parts of each plant species (root, stem, leaves and flower), to determine the plant heavy metals selectivity and the fraction of heavy metals removed by precipitation in relation to initial metal concentrations. The results showed that the plant type, time and initial concentrations of heavy metals have significant effects on the plant uptake and the removal efficiency of these metals. The iron, manganese and zinc concentrations in the plant tissues were directly proportional to their initial concentrations in the wastewater. Due to the high affinity of the four plants for iron and manganese, the plants in the compartments receiving the control and wetland influent utilized some of the phytoavailable portions found in the soil. No zinc was removed from the soil by the plants.

The purpose of the third part was to develop a passive technology consisting of filters composed of a mixture of limestone and sandstone rocks for the pretreatment of landfill leachates before they enter the wetland system. Laboratory experimental work was

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performed to determine the effectiveness of limestone and limestone/sandstone filters in removing dissolved iron and manganese from landfill leachate and to determine the suitability of the treated wastewater for aquatic life in the wetland as measured by its final pH. The work was carried out under batch condition at different temperatures and under continuous flow condition at ambient temperature with different ratios of limestone:sandstone and various particle sizes of sandstone. The results showed that the limestone/sandstone filters successfully removed iron and manganese from the leachate solutions. The first set of experiments showed that the iron removal efficiency was 97.60 % and most of the iron (96%) was removed in the first two hours of the experiment. The manganese removal efficiency fluctuated between 22.22 % and 100 % and a large percentage of the manganese (70 %) was removed during the first four hours. The second set of experiments showed that dissolution of $CaCO_3$ and the precipitation of iron and manganese were affected by temperature. The temperature affected the dissolution rate of limestone and in turn affected the pH in the filters. The dissolution rate constants were higher in the filters containing iron and iron/manganese than those containing manganese alone. Most of the iron was removed from solution within the first 10 minutes at 20 °C while the removal of iron from solution took much longer time (50 min) at 5 °C. Larger percentage (69 %) of manganese was removed from solution within the first 20 minutes at 20 °C compared to that removed (42 %) at 5 °C. The pH of the water samples did not exceed 7.7, which is within the Canadian guidelines for the protection of aquatic life. The effluent of the continuous flow filters contained on average less than 0.66 mg/L iron (10 % of the influent dissolved iron concentration) and 0.47 mg/L manganese (26 % of the influent manganese concentration). There were no noticeable effects of the ratio of limestone and sandstone or the size of the sandstone particles on the iron and manganese removal efficiency. However, the iron removal efficiency was higher at the beginning of the experiment and then declined over time due to armoring build up on the limestone particles.

The purpose of the forth part was to develop a model capable of predicting the amounts of heavy metals removed from the water using limestone/sandstone filter. The predicted calcium concentrations at the beginning and the end of the experiment were in a good

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agreement with the results obtained from the experiments. However, the experimental results showed fluctuations in the calcium concentrations over time. This could be due to the inaccuracy of the procedure used for calculating the experimental data. The model is capable of predicting the iron experimental data with a relatively high confidence (R^2 = 0.91 - 0.95) but prediction of manganese concentrations was low (R^2 = 0.42 - 0.45) due to the narrow range of the experimental measurements.

The purpose of the fifth part was to design a limestone/sandstone field filter. The life of the two filters was estimated based on the amount and quality of landfill leachate. Then, the dimensions of two filters were calculated and the materials were estimated. Drawing plans for construction were also produced.

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10. APPENDICES

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APPENDIX A

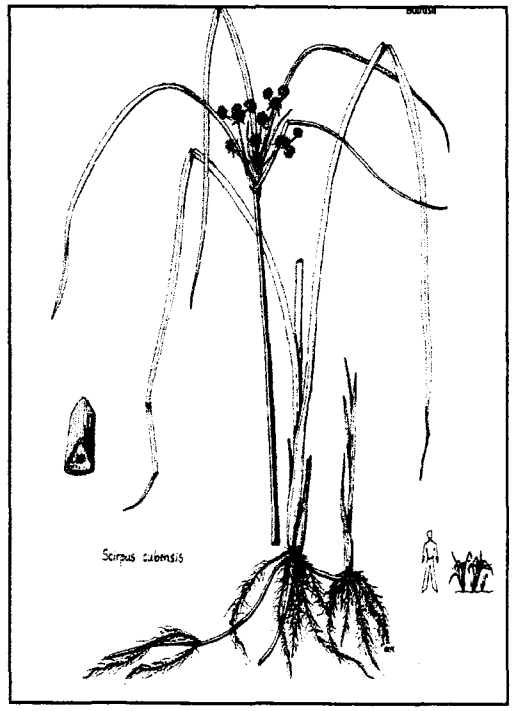
Facultative and Obligate Wetland Plants used in the Laboratory Experiments

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1. Facultative Wetland Plants

1.1 Wool grass

Wool grass (*Scipus cypernus*) is an emergent, unbranched, perennial, grass-like herb growing 1 to over 2 meters tall in dense clusters. It is a facultative wetland plant, occurring in wetland environments 67-99% of the time. This coarse, tufted wetland plant of the Cyperaceae (sedge) family can be found in wet meadows, swamps, marshes and ditches across Canada and the United States (Wetlands Program, 2003; and Crow and Hellquist, 2000). It is capable of tolerating seasonal inundation (total saturation of 13 to 25 % of growing season) but grows best in moist, well-drained soil. Wool grass also prefers full sunlight for growth but will tolerate partial shade and has a moderate annual spread of about 15 cm (Thunhorst, 1993). It is a freshwater species which generally prefers organic, nutrient-rich soils but can tolerate nearly all soil conditions with a pH ranging from 4.8 to 7.2 (ASTA, 2003). Wool grass reproduces sexually by seed (up to 63,500 seeds per gram) and vegetativly by rhizome growth (USDA Forest Service, 2003).



Wool grass

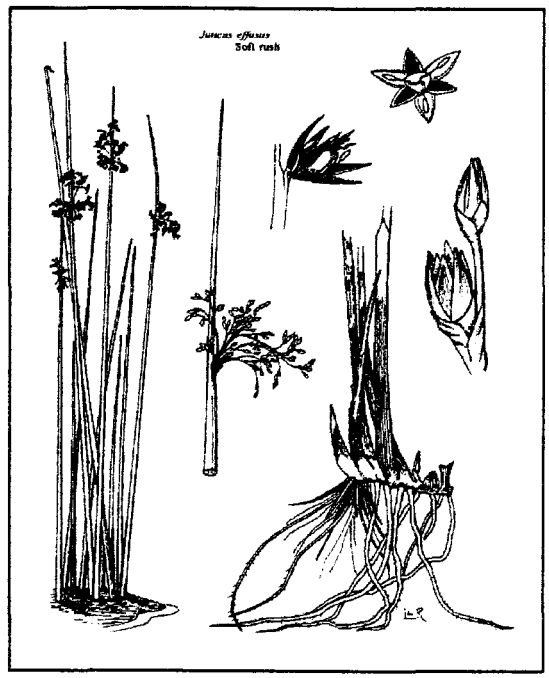
Wool grass has deeply penetrating (up to 1 m) branching rhizomes, forming tussocks. The upper part of its stems are obtusely 3-angled with enclosed leaf sheaths and flat, elongated, smooth leaves which are rough-margined and droop near the tips. The leaves are less than 1 cm wide and are mostly crowded near the base of plant. The dense inflorescence which flowers in June through to September is terminal with spikelets that are subtended by 3 to 6 involucral bracts which are leaf like and not appearing as a continuation of the stem. The numerous spikelets, which are ovate and short at approximately 0.6 cm long and 0.1 to 0.4 cm wide, are green in their flowering stage but

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become dark brown in late August to October. The spikelets, which become somewhat lax when mature, are in glomerules with poorly developed pedicels. The scales range from pale brown to blackish, are narrowly lanceolate, pointed and approximately 1.1 to 2.1 mm long with an obscure midrib. The achene which is whitish, are elongated and 0.6 to 1 mm long has 6 long, curly bristles when mature, which cumulatively add to give the spikelets their characteristically "woolly" look (Wetlands Program, 2003; Larson, 1993; and Crow and Hellquist, 2000).

1.2 Soft rush

Soft rush (*Juncus effuses*) is an erect, unbranched, perennial, facultative wetland plant of 0.6 to 2.5 m in height. It is common to marshes, swamps, thickets, pond shores and ditches across Canada and the U.S., especially in the northeastern regions. It occurs in wetland environments 67 to 99% of the time. It is capable of tolerating regular to permanent inundation (total saturation of 26 to 100% of growing season) in up to 100 cm of water. However, this species tends to prefer much shallower waters (<30 cm), with periods of dry down (Thunhorst, 1993). Soft rush requires full sunlight for growth, has a slow annual spread of about 6 cm, prefers neutral soils and can tolerate fresh to brackish waters with a pH ranging from 4 to 6 (Thunhorst, 1993; and North Carolina State University, 2002). It can occur in large clumps of several hundred fanning green stems, which are pithy and round in cross section (as all true rushes). The stems emerge from thick, lengthy (up to 1 m), rhizomes forming tussocks. This leafless plant bears reddish, short, bladeless, basal sheaths (Crow and Hellquist, 2000).



Soft rush

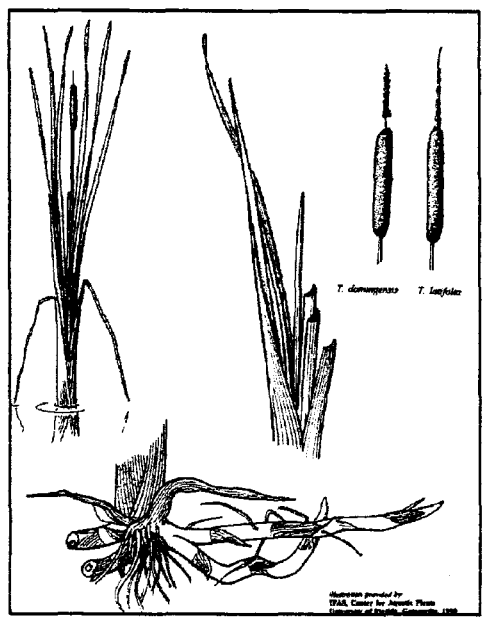
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Soft rush reproduces sexually by seed (up to 53,000 seeds per gram) and vegetatively by underground rhizome growth but seed dispersal is the primary means of reproduction. The seeds can remain viable for 60 years in sediments. Nursery and greenhouse production are equally effectively accomplished with seed or vegetative divisions. A transplanted unit must contain at least 3 to 5 culms (stems) to grow successfully (North Carolina State University. 2002). The open, branched, inflorescences which are approximately 5 cm in length and appear to be borne laterally sustain compact spikelets bearing 30 to 100 small flowers per branch that are greenish brown in color, each on its own stalk. The individual flowers have 6 tepals and are subtended by 3 bracteoles at the base of the pedicel. The fruit is a 3-valved capsule bearing numerous seeds, which is again characteristic of the Juncaceous family. An erect, rolled, pointed involucral bract, 5 to 10 cm in length and brown to grayish when mature, appears as a continuation of the stem above the inflorescence (University of Florida, 2003; and Crow and Hellquist, 2000).

2. Obligate Wetland Plants

2.1 Broadleaf cattail

Broadleaf cattail (*Typha latifolia*) is an obligate wetland plant, occurring almost always in wetland environments (> 99% of the time). It is capable of tolerating permanent inundation (total saturation of 76 to 100% of growing season) in up to 30 cm of water, but it prefers to grow along wetland margins in waters no deeper than 15 cm. Broadleaf cattails are perennial, emergent plants with stems ranging in height from 1 to 3 m tall. It is common to nearly all wet places across North America including shorelines,



Broadleaf cattail

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marshes, swamps and river margins and is often one of the first colonizers of excavated ponds and ditches (Crow and Hellquist, 2000; and Purdue University, 1998). It requires full sunlight for growth, but can tolerate partial shade, and has a rapid annual spread of about 45 cm (Thunhorst, 1993; and Rook, 2002). This cattail species grows well in both acid and calcareous soils and it tends to prefer soils with organic matter in the surface layers hence fertilization of this species in cultivated areas is often unnecessary. It is also known to grow on fine texture mineral soils, and grows mostly in fresh water but also occurs in slightly brackish marshes (Rook, 2002).

As with all other cattail species, broad-leaved cattail reproduces sexually by seed (up to 268,000 seeds per spike) and vegetatively by rhizome growth. Vegetative reproduction is responsible is for the maintenance and expansion of existing stands, while sexual reproduction responsible for the colonization of new areas. Within established stands, seedlings are practically nonexistent because existing vegetative cover greatly reduces light and temperature required for seed germination. Leaves and stems may also produce allelopathic inhibitors (Rook, 2002). Broadleaf cattails have round erect and tapering stems that are up to 2.5 cm in diameter at the base, emerging from a thick, white, creeping rhizome up to 70 cm in length. It has 12 to 16 long (typically not extending the height of the stem), narrow, alternate, grayish green basal leaves that are 6 to 23 mm wide, erect and twisting, D-shaped and pithy in cross section, which sheath at the base of the stem (Crow and Hellquist, 2000; Larson, 1993; and Purdue University, 1998).

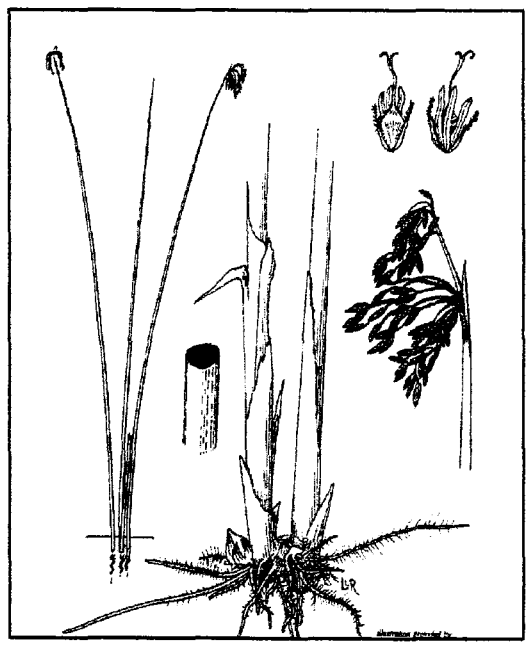
The flower structure which blossoms May through June is a terminal, cylindrical spike-like inflorescence, with the pistillate (female, seed producing) and delicate staminate (male, pollen producing) portions usually contiguous. The pistillate which is 2.5 to 20 cm long and at least 2.5 cm in diameter when mature is located below the narrower staminate, which is about 7 to 13 cm long (Crow and Hellquist, 2000; Purdue University, 1998). The staminate flowers are minute, light brown and thickly clustered on a club-like spadix. They typically bear 3 to 5 stamens, linear anthers, and connate filaments, which are subtended by numerous slender hairs (Larson, 1993). The pistillate flowers are each comprised of a simple pistil intermixed with some sterile flowers, surrounded by

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numerous long, slender hairs (gynophores hair) near the base. The pistillates are pale green when flowering, drying to brownish, blackish brown or reddish brown when fruiting. In fruiting, the pistillate bears innumerable, tiny, downy hair-tufted and persistent stigma-bearing achene, which are fusiform, light brown, ellipsoidal, about 1 mm long and designed to float in wind or water. These seeds are released as the pistillate gradually breaks apart in the fall, taking on the appearance of a wooly mass due to its crowded stigmas and gynophore hairs (Crow and Hellquist, 2000; Larson, 1993; and Purdue University, 1998).

2.2 Soft stem bulrush

Soft stem bulrush (*Scirpus validus*) is an erect, unbranched, 2.45 m tall emergent and obligate, perennial wetland plant that can be found in fresh to brackish shores of ponds, lakes streams and marshes across North America (Crow and Hellquist, 2000). It occurring almost always in wetland environments (> 99% of the time). It is capable of tolerating permanent inundation (total saturation of 76 to 100% of growing season) in up to 30 cm of water, requires full sunlight for growth and has a rapid annual spread of about 45 cm (Thunhorst, 1993). It grows well in either poorly-drained or continually saturated organic and sandy soils with a pH ranging from 4 to 7.5. It tends to prefer more silty peaty soils. It is quite tolerant of a wide range of saline conditions (USDA Forest Service, 2003; ASTA 2003; and USDA Forest Service, 2003). Soft-stem bulrush reproduces both vegetatively through rhizomes and sexually through seeds. Soil-stored seed can remain viable for as long as 20 years (USDA Forest Service, 2003).



Soft stem bulrush

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The stems of this bulrush are smooth and spongy, round in cross section, up to 2.5 cm in diameter, with its upper parts becoming obtusely 3-angled. Basal sheaths clasp the bases of the stems, with upper parts of the stems supporting sheaths with long, tapering blades. Its rhizomes are thick, scaly, stout and horizontal (Crow and Hellquist, 2000). The inflorescence of this plant is terminal, open and lax, and much branched with numerous, hanging clusters of brown spikelets that are solitary or in 1 to 5 compact clusters of 2, 3 or more spikelets. The spikelets are tightly ovoid, 3 to 7 mm long, sessile or peduncled, with rounded or pointed tips. Each spikelet contains up to 50 bristly flowers. The inflorescence is subtended by a small, solitary, leaf-like, rolled, involucral bract appearing as a continuation of the stem. The involucral bract is 1 to 7 cm long, and is shorter than the inflorescence. The nutlet bristles are barbed, and narrow (University of Florida, 2003; Crow and Hellquist, 2000). The scales are ovate/round and are bright orange brown, with obscure darker spots, and a short (0.2-1.0 mm) awn that is nearly straight. The scales also bear a pronounced greenish mid-vein. The achenes are usually partly exposed beyond scales, and bear distinctly plumose bristles (Crow and Hellquist, 2000).

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APPENDIX B

Calculation of Limestone Dissolution

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The amount of dissolved calcium carbonate required to precipitate iron removal was calculated using Equation (7.33) given by Cravotta and Trahan (1999) whereas that required to precipitate manganese was calculated using Equation (7.34) given by Gazea et al. (1996) as follows

$$Fe^{2+} + 0.25O_2 + 2CaCO_{3\,(s)} + 2.5H_2O \rightarrow Fe(OH)_{3\,(s)} + 2Ca^{2+} + 2HCO_3^-$$

$$Mn^{2+} + 0.25O_2 + 0.5CaCO_{3\,(s)} + 1.5H_2O \rightarrow MnOOH_{(s)} + 0.5Ca^{2+} + 0.5HCO_3^- + H^+$$

According to the above equations, 2 moles of calcium carbonate must be available in solution for each mole of Fe^{2+} removed from the solution and 0.5 mole of calcium carbonate must be available in solution for each mole of Mn^{2+} removed from the solution.

Therefore, the number of moles of metal (Fe and Mn) removed per liter per hour (N_m)

$$= \frac{\text{Total metal removed (g/L) per hour}}{\text{Atomic Weight of the metal (g/mole)}}$$

The number of moles of metal removed by the filter per hour (N_{Fe} or N_{Mn}) was
= N_m x Flow rate (L/h for continuous flow filter) (or volume of the batch system (L))

The number of moles of $CaCO_3$ required to precipitate Fe (N_{CFe}) or Mn (N_{CMn}) was
$N_{CFe} = 2 \times N_{Fe}$
Or
$N_{CMn} = 0.5 \times N_{Mn}$

Since the molecular weight of $CaCO_3$ equal 100 g/mole, the rate of $CaCO_3$ dissolution (R_{Fe} or R_{Mn})
$R_{Fe} = N_{CFe} \times 100$ g/mole
$R_{Mn} = N_{CMn} \times 100$ g/mole

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