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## A Comparative Assessment of the Characteristics of Saturated Wetland Soil and a Well Drained Forest Soil

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**Abstract:** A surface flow wetland was constructed in the Burnside Industrial Park, Dartmouth, Nova Scotia, to treat stormwater runoff from the surrounding watersheds which are comprised primarily of commercial properties and two former landfills. The aim was to protect a freshwater ecosystem that consists of a 4.6 km long brook and two lakes. A comparative analysis of the pH, total and plant available iron, total and plant available manganese and organic carbon content of a saturated soil collected from a naturally vegetated island in the constructed wetland and a drained soil collected from a nearby forest was performed. The pH of the soil of the constructed wetland was significantly greater than the pH of the forest soil. The total iron concentrations in the soil of the constructed wetland were significantly greater than those in the forest soil. There was no significant difference between the plant available iron concentrations in the soil of the constructed wetland and those in the forest soil. The total manganese and the plant available manganese concentrations in the soil of the constructed wetland were significantly greater than those in the forest soil. There was no significant difference between the organic carbon concentrations in the soil of the constructed wetland and those in the forest soil.

**Key words:** Iron, manganese, pH, organic carbon, surface flow wetland, forest soil

### INTRODUCTION

Soil is a general term used to describe the thin, unconsolidated layer of mineral and organic material at the Earth's surface that is capable of supporting plant growth. Soils are formed from their base by the physical and chemical weathering of rocks and minerals and from their surface by the biological decomposition of organic materials<sup>[1]</sup>.

Wetlands are ecosystems that are covered by water or have water present near the soil surface for all or part of the year, which results in saturated soils that support aquatic vegetation<sup>[2,3]</sup>. Wetland soil characteristics are largely influenced by water. Water affects wetland soil properties by reducing the exposure of the soil to the atmosphere. When well-aerated soils are flooded, they rapidly experience a decline in soil oxygen and redox potential resulting in anaerobic soil conditions. According to Kadlec and Knight<sup>[3]</sup>, oxygen diffusion in flooded soils is nearly 10,000 times slower than in aerobic soils. As a result, flooded soils can have greater concentrations of plant available nutrients such as iron and manganese than well drained soils<sup>[4]</sup>. Flooded acidic and alkaline soils tend to move toward a neutral pH<sup>[5]</sup>. Accumulation of organic

matter in flooded soils occurs because anaerobic conditions are less favorable for decomposition<sup>[6]</sup>.

The objective of this study was to compare the characteristics of soil collected from a flooded naturally vegetated island in a constructed wetland and soil collected from a nearby forest. The soil characteristics that were studied included pH, total and plant available iron, total and plant available manganese and organic carbon content.

### MATERIALS AND METHODS

**Constructed wetland:** A surface flow constructed wetland was established in the Burnside Industrial Park, Dartmouth, Nova Scotia, to treat stormwater runoff from the surrounding watersheds which are comprised primarily of commercial properties and two former landfills (a 5.34 ha site that operated from 1968 to 1974 and a 5.42 ha site that operated from 1976 to 1977). The aim was to protect a freshwater ecosystem that consists of a 4.6 km long brook (Wright's Brook) and two lakes (Enchanted Lake and Flat Lake). A previously conducted environmental site assessment (Table 1) had determined that the water entering the brook contained average iron

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Table 1: Heavy metal loads entering Wright's Brook

Element	Average concentration (mg L <sup>-1</sup> )	Guidelines[7] (mg L <sup>-1</sup> )
Aluminium	7.720	0.005-0.100
Arsenic	0.009	0.005
Chromium	0.013	0.001-0.009
Copper	0.039	0.002-0.004
Iron	15.508	0.300
Lead	0.075	0.001-0.007
Manganese	3.029	1.000-1.500[8]
Zinc	0.158	0.030

and manganese concentrations of 15.508 and 3.029 mg L<sup>-1</sup>, respectively, which exceeds the allowable limits established by the Canadian Water Quality Guidelines for the Protection of Aquatic Life<sup>[7,8]</sup>. The wetland consists of 9 deep open water cells that are separated by shallow internal vegetated berms and surrounded by a system of external berms with a surface area of 6300 m<sup>2</sup> and 2 naturally vegetated islands that are surrounded by a system of external berms with a surface area of approximately 6100 m<sup>2</sup>.

The wetland berms and cells were planted with a variety of native plant species such as *Carex crinita* (fringed sedge), *Carex lurida* (yellow green sedge), *Juncus brevicaudatus* (tweedys rush), *Juncus effusus* (soft rush), *Scirpus validus* (soft stem bulrush), *Calamagrostis canadensis* (bluejoint grass), *Alisma plantagoaquatica* (water plantain), *Pontederia cordata* (pickerelweed), *Nymphaea alba* (white waterlily) and *Potamogeton natans* (pondweed). The two naturally vegetated islands consist of untamed early successional brush dominated by low shrubs such as *Comptonia peregrina* (sweet fern), *Viburnum cassinoides* (witherod) and *Spiraea alba* (meadowsweet), deciduous and evergreen trees such as *Acer rubrum* (red maple), *Betula papyrifera* (white birch) and *Picea rubens* (red spruce) and emergent macrophytes such as *Typha latifolia* (cattails).

**Forested area:** The forest was not influenced by stormwater runoff or leachate from the former landfills and it was never flooded during the study period. According to MacDougall *et al.*<sup>[9]</sup>, the soil in the forest was porous and well drained. The forest was dominated by several species including *Acer rubrum*, *Betula papyrifera*, *Betula populifolia* (grey birch), *Picea rubens*, *Abies balsamea* (Balsam fir) and *Populus grandidentata* (large toothed aspen).

**Soil collection and preparation:** Soil samples were collected from the two naturally vegetated islands in the constructed wetland and from a nearby forested area

(Fig. 1). Soil samples from a depth of 0~30 cm were collected using a stainless steel spade from the root zone around trees in an area between the outer branch tips and the trunk. Two sub-samples were collected around each tree and mixed to make one sample. Soil samples were placed in clean, plastic containers and transported to the laboratory for analyses. Approximately one liter of soil was collected per sample. Soil samples were placed on aluminum plates and oven dried at a temperature of 80°C for approximately 48 h in a laboratory oven (Isotemp Oven, Model No. 655F, Fisher Scientific Co., Ontario, Canada). Soil samples were reduced in size by grinding in a coffee grinder (Toastermaster, Model No. 1119CAN, China). Prepared samples were stored in air tight plastic containers under refrigerated conditions (4°C). Samples were delivered to the Minerals Engineering Center at Dalhousie University, Halifax, Nova Scotia and were analyzed for pH, total and plant available concentrations of iron and manganese and organic carbon content.

**pH determination:** The Paste pH procedure was used to measure the pH of soil samples. Initially, 20.0 g of dried soil was added to 20 mL of distilled water and mixed on a mechanical stirrer (Fisher Thermix Stirrer, Model No. 120MR, Fisher Scientific Co., Ontario, Canada) for 5 sec. Then the soil water solution was allowed to stand for 10 min. An electrode (Fisher Accumet pH meter, Model No. 805MP, Fisher Scientific Co., Ottawa, Ontario, Canada) was inserted into the solution. When the reading remained constant, the pH was recorded and the electrode was removed from the beaker. After every 10 samples, the calibration of the pH meter was checked with standard buffers.

**Determination of total iron and total manganese:** A wet acid digestion procedure was performed for destruction of organic matter present in soil samples. Initially, 1.0 g of dried, ground sample was placed in a Teflon beaker and 30 mL (38% HCl) hydrochloric acid (Cat. No. A144-S212, Fisher Scientific Co., Ontario, Canada), 10 mL (70% HNO<sub>3</sub>) nitric acid (Cat. No. A200-212, Fisher Scientific Co., Ontario, Canada), 10 mL (49% HF) hydrofluoric acid (Cat. No. A147-1LB, Fisher Scientific Co., Ontario, Canada) and 5 mL (70% HClO<sub>4</sub>) perchloric acid (Cat. No. A2296-1LB, Fisher Scientific Co., Ontario, Canada) were added. Under a fume hood, the samples were heated to dryness (overnight) on a hot plate (Model No. SP46925, Barnstead/Thermolyne, Dubuque, Iowa) at a temperature of 125°C. Then, 10 mL of HCl and 30 mL of H<sub>2</sub>O were added to dissolve the

residue. Under a fume hood, the samples were heated on a hot plate at a temperature of 125°C for 30 min. The samples were filtered through Fisher No. 4 filter paper (Cat. No. 09-803-6A, Fisher Scientific Co., Ontario, Canada) and the filtrate was collected in a 100 mL volumetric glass flask and made up to a final volume of 100 mL with distilled-deionized water. Total iron and total manganese concentrations were determined by inductively coupled plasma-optical emission spectroscopy (Vista Pro, Varian Inc., Victoria, Australia) with a detection limit of 0.25 ppm for Mn and 1.00 ppm for Fe.

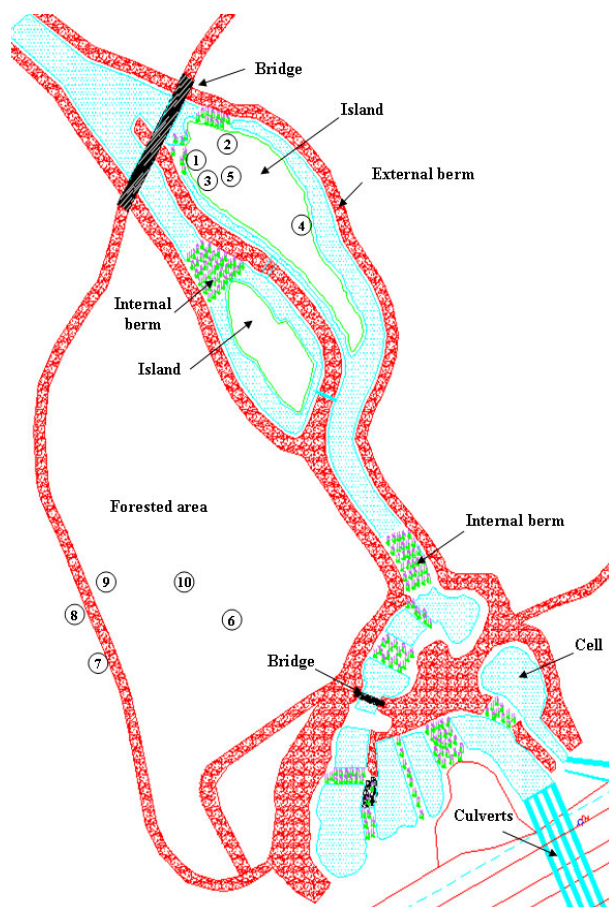


Fig. 1: Location of soil samples in the constructed wetland and forested area

**Determination of plant available iron and manganese:**

An organic solvent extraction with ammonium acetate (NH<sub>4</sub>-acetate) was used to determine the amount of iron and manganese available to plant roots<sup>[10,11]</sup>. To determine plant available iron concentrations, a 1 M solution of NH<sub>4</sub>-acetate was prepared by dissolving 77.08 g of NH<sub>4</sub>-acetate (Cat. No. A637B-500, Fisher Scientific Co.,

Ontario, Canada) in 1 L of distilled-deionized water. The pH of the NH<sub>4</sub>-acetate solution was adjusted to 4.8±0.5 using 17.4 N glacial acetic acid (Cat. No. A38<sup>SL</sup>-212, Fisher Scientific Co., Ontario, Canada). Initially, 5.0 g of dried, ground soil was placed in a 250 mL wide-mouth Erlenmeyer flask (Cat. No. Z140783, Pyrex, Sigma-Aldrich Canada Ltd., Ontario, Canada). A volume of 100 mL of NH<sub>4</sub>-acetate was added to the flask. The flask was placed on a specially designed platform shaker (capacity of 18 flasks, agitation of 250 rpm) for 1 h. The resulting soil NH<sub>4</sub>-acetate solution was vacuum filtered through a Buchner funnel (Cat. No. Z178144-1EA, Sigma-Aldrich Canada Ltd., Ontario, Canada) using 7.0 cm diameter ashless Whatman filter paper No. 42 (Whatman International Ltd., Cat. No. 1442150, Maidstone, England). The filtrate was analyzed for plant available iron concentrations using inductively coupled plasma-optical emission spectroscopy (Vista Pro, Varian Inc., Victoria, Australia). To determine plant available manganese concentrations, the same procedure was used except the 1 M NH<sub>4</sub>-acetate solution was adjusted to a pH of 7.0±0.5 and a volume of 125 mL of NH<sub>4</sub>-acetate was added to the Erlenmeyer flask.

**Determination of organic carbon:**

A 10.0 g sample of soil was treated with HCl (Cat. No. A144-S212, Fisher Scientific Co., Ontario, Canada) and then analyzed for organic carbon using the LECO gasometric system (Model No. 516-000, Leco Corporation, St. Joseph, MI, USA) which was composed of a tube furnace and a gasometric analyzer. The HCl treatment removes carbonates (CaCO<sub>3</sub> and MgCO<sub>3</sub>) from the sample. Then a 30-200 mg sample of treated soil was weighted into a crucible and mixed with iron and tin accelerators. The sample was heated in a tube furnace in a 100% oxygen atmosphere to 1500°C, which converts the carbon in the sample to CO<sub>2</sub> gas. The CO<sub>2</sub> was transferred to the gasometric analyzer where it was absorbed into a solution of potassium hydroxide (KOH) and the organic carbon was read from the graduated burette. Reference standards from CANMET-MMSL and the Canadian Certified Reference Materials Project (CCRMP) were used to check the accuracy and repeatability of the analysis.

**RESULTS AND DISCUSSION**

Table 2 displays the pH, total and plant available iron and manganese concentrations and organic carbon content of soil samples collected from the constructed wetland and the nearby forest. The data was analyzed statistically

Table 2: Characteristics of soil collected around the various trees

Location	Sample No.	pH	Fe (mg kg <sup>-1</sup> )		Mn (mg kg <sup>-1</sup> )		Organic Carbon (%)
			Total	Available	Total	Available	
Wetland	1	4.80	80000	208	2850	190.0	4.51
	2	4.65	51000	328	1419	265.0	4.43
	3	5.05	63000	176	1820	215.0	5.24
	4	5.50	57100	526	1701	300.0	5.36
	5	4.35	94600	798	2609	302.5	3.83
Forest	6	2.80	23200	268	115	2.5	7.57
	7	3.35	46975	220	245	2.5	3.84
	8	3.60	46264	182	413	2.5	4.28
	9	3.45	24700	104	58	2.5	4.25
	10	3.35	30916	326	285	2.5	3.15

Table 3: One-way analysis of variance for soil characteristics of the constructed wetland and forest

Source	DF	SS	MS	F	P
<b>pH</b>					
Total	9	7.204			
Location	1	6.084	6.084	43.46	0.000
Error	8	1.12	0.14		
<b>Total Fe</b>					
Total	9	4823683375			
Location	1	3015258603	3015258603	13.34	0.006
Error	8	1808424772	226053097		
<b>Available Fe</b>					
Total	9	382294			
Location	1	87610	87610	2.38	0.162
Error	8	294685	36836		
<b>Total Mn</b>					
Total	9	10217629			
Location	1	8617409	8617409	43.08	0.000
Error	8	1600220	200027		
<b>Available Mn</b>					
Total	9	168965			
Location	1	158760	158760	124.46	0.000
Error	8	10205	1276		
<b>Organic carbon</b>					
Total	9	13.32			
Location	1	0.01	0.01	0.00	0.947
Error	8	13.31	1.66		

Differences are considered significant at a p-value = 0.05 (95% confidence interval)

using a one-way analysis of variance. The statistical analyses were performed using SPSS (SPSS Inc., SPSS 14.0.1, Chicago, IL) and differences were considered significant at a p-value = 0.05 (95% confidence interval). The results of the statistical analysis are shown in Table 3.

**pH:** The pH of the soil in the constructed wetland ranged from a low of 4.35 to a high of 5.50 with an average of 4.87. The pH of the forest soil ranged from a low of 2.80 to a high of 3.60 with an average of 3.21. According to MacDougall *et al.* [9], the soil in the forest was classified as Halifax series. It was developed from moderately coarse textured glacial till derived primarily from

quartzite rock. The pH of the soil was 3.6, 4.9, 5.1 and 5.0 for the 0-7.6, 7.6-12.7, 12.7-43.2 and 43.2+ cm depths, respectively. The pH of the soil of the constructed wetland was significantly greater than the pH of the soil of the forest (p-value = 0.000) as shown in Table 3.

A possible explanation for the higher pH of the soil of the constructed wetland than that of the forest soil was that the soil in the constructed wetland was flooded. Wetland soil characteristics are largely influenced by water. Upon flooding of an aerobic soil, its pH decreases because of aerobic decomposition and accumulation of CO<sub>2</sub>. After this initial change in pH, both acidic and alkaline soils tend to move toward a neutral pH (6.7 to 7.2). Acid soils tend to move toward neutral values of pH due to soil reduction. All of the important reduction reactions that occur in nature involve the consumption of H<sup>+</sup>. Most soils contain more ferric oxide hydrates than any other oxidant. Therefore, the increase in pH of acid soils is due to the reduction of ferric iron<sup>[5]</sup>. Acid soils that are low in organic matter or active iron slowly attain pH values that are less than 6.5. Alkaline soils tend to move toward neutral values of pH because of the accumulation of CO<sub>2</sub>. Draining and exposure to air reverses the pH changes in submerged soils<sup>[2,5]</sup>.

Elhottova *et al.*<sup>[12]</sup> conducted a study to determine the effect of flooding on soil pH. The initial pH of the soil before flooding was 5.07 and after exposure to flooded conditions the pH of the soil increased to 7.04. The authors concluded that flooding caused the pH of the soil to shift from acidic values to neutral values. Gelsomino *et al.*<sup>[13]</sup> conducted a study to determine the effect of recurrent flooding by wastewater on the chemical and biological soil properties of an agricultural soil. The initial pH of the soil was 6.1±0.4, 6.0±0.3 and 5.5±0.2 which increased to 6.9±0.3, 6.9±0.2 and 6.7±0.4 for the first, second and third flooding, respectively. Masscheleyn *et al.*<sup>[14]</sup> conducted a study to determine the



effect of redox potential and pH on metal speciation in a contaminated soil. The initial soil pH of 5.6 increased to  $5.7 \pm 0.1$ ,  $6.4 \pm 0.2$ ,  $7.0 \pm 0.2$  and  $7.0 \pm 0.3$  after 1, 3, 15 and 35 days of flooding, respectively.

**Total iron:** Iron is the 4th most abundant element on Earth<sup>[15]</sup>. The average concentration of iron in the Earth's crust is about 50 000 mg kg<sup>-1</sup>. Hardly any rock from which soils are formed is free of iron. In natural compounds, iron displays two oxidation states (II and III)<sup>[4]</sup>. In aerobic environments, Fe<sup>3+</sup> oxides are the most stable form of iron in soils<sup>[16]</sup>. The total iron concentration in the soil of the constructed wetland ranged from a low of 51000 mg kg<sup>-1</sup> to a high of 94600 mg kg<sup>-1</sup> with an average concentration of 69000 mg kg<sup>-1</sup>. The total iron concentration in the forest soil ranged from a low of 23200 mg kg<sup>-1</sup> to a high of 46 975 mg kg<sup>-1</sup> with an average concentration of 34411 mg kg<sup>-1</sup>. The total iron concentrations in the soil of the constructed wetland were significantly greater than those in the forest soil (p-value = 0.006) as shown in Table 3.

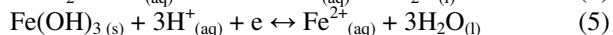
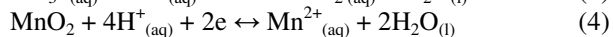
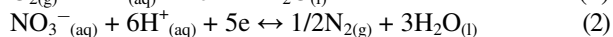
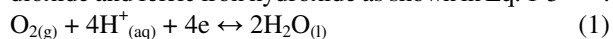
A possible reason for the higher total iron concentrations in the soil of the constructed wetland than those of the forest could be sedimentation of iron hydroxides and sulphides in the constructed wetland. Ye *et al.*<sup>[17]</sup> reported that approximately 40 to 70% of the total iron retained by wetlands was found as ferric hydroxides. Mitsch and Wise<sup>[18]</sup> while conducting a study to determine the ability of a surface flow wetland to treat acid mine drainage from a stream in southeastern Ohio observed iron concentrations in the sediments averaging 143000 mg kg<sup>-1</sup> in the surface 10 cm and 72000 mg kg<sup>-1</sup> in the upper 30 cm. Ye *et al.*<sup>[19]</sup> conducted a study to determine the ability of a 4 cell, vegetated surface flow wetland constructed of sediment having an iron concentration of 9000 mg kg<sup>-1</sup> to treat leachate from an electrical power station in Pennsylvania and found that the average iron concentrations in the sediments of cells 1-4 were 32600, 31630, 32300 and 32600 mg kg<sup>-1</sup>, respectively. Mitchell *et al.*<sup>[20]</sup> conducted a study to determine the ability of a surface flow wetland to treat stormwater runoff from a four lane highway in Ohio and found that the average concentration of iron in the wetland sediments was in the range of 11543 to 16338 mg kg<sup>-1</sup>.

A second possible explanation for the higher total iron concentrations in the soil of the constructed wetland could be diffusion and precipitation of iron from the deeper reduced sediments in the constructed wetland to the aerobic surface layer<sup>[5]</sup>. Howeler and Bouldin<sup>[21]</sup>

studied the distribution of iron in soil cores from a lake and observed that considerable amounts of ferrous iron diffused upward from the reduced zone to the oxidized zone and accumulated as a ferric iron precipitate. Ratering and Schnell<sup>[22]</sup> studied iron profiles in fresh paddy soil cores and observed an accumulation of ferric iron at a depth of 2-4 mm, which they attributed to diffusion of porewater ferrous iron upwards via concentration gradients towards sites of oxidation and precipitation.

**Plant available iron:** The plant available iron concentration in the soil of the constructed wetland ranged from a low of 176 mg kg<sup>-1</sup> to a high of 798 mg kg<sup>-1</sup> with an average concentration of 407.2 mg kg<sup>-1</sup>. The plant available iron concentration in forest soil ranged from a low of 104 mg kg<sup>-1</sup> to a high of 326 mg kg<sup>-1</sup> with an average concentration of 223.6 mg kg<sup>-1</sup>. There was no significant difference between the plant available iron concentrations in the soil of the constructed wetland and those of the forest soil as shown in Table 3.

When a soil is flooded, the oxygen supply to the soil is interrupted and there is a switch from aerobic respiration to anaerobic respiration. Facultative and obligate anaerobic microorganisms use carbon compounds as substrates and oxidized soil components as electron acceptors in respiration. Oxygen is the first soil component to be reduced followed by nitrate, manganese dioxide and ferric iron hydroxide as shown in Eq. 1-5<sup>[5,23]</sup>.



In a reduced state, flooded soils can have greater concentrations of plant available Fe<sup>2+</sup> than well drained soils<sup>[4]</sup>. Shahandeh *et al.*<sup>[24]</sup> incubated soil under reducing conditions for a period of 30 days to determine the effect of redox potential on solution concentrations of iron and found that the redox potential of the soil and the concentration of iron in solution were 357 mV and 0.45 mg L<sup>-1</sup>, 125 mV and 12.30 mg L<sup>-1</sup> and -189 mV and 22.00 mg L<sup>-1</sup> at 0, 5 and 20 days, respectively. Moore *et al.*<sup>[25]</sup> conducted a study to determine the effect of redox potential on Fe<sup>2+</sup> concentrations in the sediment of a contaminated river at different depths and found that the redox potential and the Fe<sup>2+</sup> concentration were 369 mV and < 0.1 mg L<sup>-1</sup>, 159 mV and 29 mg L<sup>-1</sup> and 139 mV and 44 mg L<sup>-1</sup> at sediment depths of 45, 65 and 115 cm, respectively. Gotoh and Patrick<sup>[26]</sup> conducted a study

to determine the soluble and exchangeable iron in a waterlogged soil having a pH of 5 as influenced by redox potential and found that the concentrations of water soluble iron and exchangeable iron were 63 and 253 mg kg<sup>-1</sup>, 1201 and 1065 mg kg<sup>-1</sup> and 2185 and 1177 mg kg<sup>-1</sup> at a redox potential of 300, 100 and -100 mV, respectively.

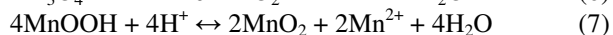
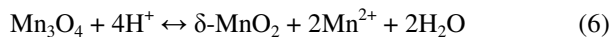
The results obtained from this study showed that despite the saturated soil conditions of the constructed wetland, at a 95% confidence interval, there was no significant difference between the plant available iron concentrations in the soil of the constructed wetland and those of the forest soil. A possible reason for not observing a difference between the plant available iron concentrations in the soil of the constructed wetland and the forest was that the average pH of the forest soil was 3.22. According to MacDougall *et al.*<sup>[9]</sup>, the soil in the forest was porous and well drained. In a well drained soil, the bioavailability of metals is strongly influenced by soil pH. Cheng *et al.*<sup>[27]</sup> and Sharma *et al.*<sup>[28]</sup> demonstrated that the availability of iron in soil for plant uptake increased with a decrease in pH. Hartikainen<sup>[29]</sup> conducted a study to determine the effect of acid percolation on cation leaching from soil and found that upon sulphuric acid percolation, the pH of the soil decreased from an initial value of 4.9 to 3.7 and the cumulative leaching of iron from the soil increased from 1.0 to 15.6 mmol kg<sup>-1</sup> whereas upon water percolation through the control soil, the pH of the soil decreased slightly to 4.8 and the cumulative leaching of iron was 8.5 mmol kg<sup>-1</sup>. Khorsandi<sup>[30]</sup> while conducting a study to determine the effect of soil acidification on the availability of iron for plant uptake observed that as the pH of the soil decreased from an initial value of 8.0 to 7.4, 5.0, 2.9 and 2.6, the plant available iron concentration in the soil increased from 1.19 mg kg<sup>-1</sup> to 3.3, 97.1, 114.1 and 117.1 mg kg<sup>-1</sup>, respectively.

**Total manganese:** Manganese is the 12th most abundant element on Earth. The average concentration of manganese in the lithosphere ranges from 20 to 10000 mg kg<sup>-1</sup> with an average concentration of about 1000 mg kg<sup>-1</sup>. Manganese is widely distributed in metamorphic, sedimentary and igneous rocks because it has a similar ionic size to calcium and magnesium enabling it to replace the two elements in silicate structures. In natural compounds, manganese displays three oxidation states (II, III and IV). In reducing environments, the Mn<sup>2+</sup> species are most stable, while in oxidizing environments the most stable compound is MnO<sub>2</sub><sup>[4]</sup>.

The total manganese concentration in the soil of the constructed wetland ranged from a low of 1419 mg kg<sup>-1</sup> to a high of 2850 mg kg<sup>-1</sup> with an average concentration of 2079.8 mg kg<sup>-1</sup>. The total manganese concentration in the forest soil ranged from a low of 58 mg kg<sup>-1</sup> to a high of 413 mg kg<sup>-1</sup> with an average concentration of 223.2 mg kg<sup>-1</sup>. The total manganese concentrations in the soil of the constructed wetland were significantly greater than those of the forest soil (p-value = 0.000) as shown in Table 3.

A possible reason for the higher total manganese concentrations in the soil of the constructed wetland than those of the forest soil could be sedimentation of manganese precipitates in the constructed wetland. Eckhardt *et al.*<sup>[31]</sup> conducted a study to determine the ability of a 2 cell, vegetated surface flow wetland to treat leachate from a landfill in New York and found that the concentrations of manganese in the sediment of the first and second cells after two years were 307 and 298 mg kg<sup>-1</sup>, respectively. Ye *et al.*<sup>[19]</sup> conducted a study to determine the ability of a 4 cell, vegetated surface flow wetland to treat leachate from an electrical power station in Pennsylvania and found that the average manganese concentrations in the uppermost sediments of cells 1-4 were 3310, 1350, 830 and 872 mg kg<sup>-1</sup>, respectively. They also noticed that the concentration of manganese in the sediment increased with time over the 2 year study period. Ye *et al.*<sup>[17]</sup> conducted a study to determine the ability of a 10 year old, 2 cell, vegetated surface flow wetland to treat leachate from an electrical utility in Alabama and found that average concentrations of manganese in the sediment from the two cells were in the range of 200 to 400 mg kg<sup>-1</sup>.

A possible explanation for the lower total manganese concentrations in the forest soil was the acidic pH of the soil. The chemical forms of manganese in the soil are known to depend on pH. Under acidic soil conditions, manganese bearing minerals dissolve and the water soluble manganese content of the soil (Mn<sup>2+</sup>) increases as shown in the following equations<sup>[32]</sup>.



The water soluble manganese content of the soil may then be washed out of the soil during a rainfall event. The result is a decrease in the concentration of total manganese in the soil<sup>[32]</sup>.

Bergkvist<sup>[33]</sup> conducted a three year study to determine the influence of soil acidity on leaching of

metals from a spruce forest soil. The input of manganese to the soil was  $1.6 \text{ g m}^{-2}$ . The outputs of manganese from the soil at soil pH's of 3.40 and 3.16 were  $0.93$  and  $1.3 \text{ g m}^{-2}$ ,  $0.21$  and  $0.40 \text{ g m}^{-2}$  and  $0.43$  and  $0.92 \text{ g m}^{-2}$  for soil depths of 0-5, 0-15 and 0-35 cm, respectively. The author concluded that increased soil acidification by acid rain may increase the concentrations of several metals including manganese in the soil solution.

Bergkvist<sup>[34]</sup> conducted a study to determine the effects of soil acidification by nitrogen deposition on manganese in a beech forest soil. The outputs of manganese in the soil solution for the control soil plots (no nitrogen addition), low nitrogen soil plots and high nitrogen soil plots were  $6.0$ ,  $35.6$  and  $66.5 \text{ meq m}^{-2}$  per year, respectively. The authors concluded that manganese was an element with a great increase in mobilization and was very susceptible to changes in soil acidity.

Tani *et al.*<sup>[35]</sup> found the concentration of manganese in waters draining from a tea plantation, from an exposed aquifer beneath the plantation and from an agricultural irrigation pond were in the range of  $245$ - $733 \text{ } \mu\text{g L}^{-1}$ . These waters had a very low pH (4.28-5.05) and the authors attributed the high manganese concentrations to soil acidification, which led to manganese leaching from soils in the watershed.

**Plant available manganese:** The plant available manganese concentration in the soil of the constructed wetland ranged from a low of  $190 \text{ mg kg}^{-1}$  to a high of  $302.5 \text{ mg kg}^{-1}$  with an average concentration of  $254.5 \text{ mg kg}^{-1}$ . The plant available manganese concentration in the forest soil was  $2.5 \text{ mg kg}^{-1}$  at all locations. The plant available manganese concentrations in the soil of the constructed wetland were significantly greater than those of the forest soil (p-value = 0.000) as shown in Table 3. This could be due to the fact that the concentration of total manganese in the soil of the constructed wetland was significantly greater than in the forest soil and the plant available manganese in the forest soil was more easily washed out of the well drained, acidic soil.

Another possible explanation for the higher plant available manganese concentrations in the soil of the constructed wetland than those of the forest soil could be due to the fact that the submerged soil in the constructed wetland was in a reduced state. As shown in Eq. 4, the main transformation of manganese in flooded soils involves the reduction of manganese dioxide to manganous manganese ( $\text{Mn}^{2+}$ ) resulting in an increase in the concentration of  $\text{Mn}^{2+}$  in the soil.<sup>[4]</sup> Manganese is reduced at a higher reduction potential than iron and will increase in solution first followed by a rapid increase in

the concentration of available iron.

Shahandeh *et al.*<sup>[24]</sup> incubated two soils for 35 days under reducing conditions and found that initially under oxidizing conditions, the exchangeable and water soluble manganese concentrations were  $43 \pm 3$  and  $0.25 \pm \text{mg kg}^{-1}$  and  $33 \pm 3$  and  $0.29 \pm 0.03 \text{ mg kg}^{-1}$  for the first and second soil which then increased to  $289 \pm 15$  and  $6.43 \pm 0.90 \text{ mg kg}^{-1}$  and  $154 \pm 14$  and  $6.91 \pm 0.90 \text{ mg kg}^{-1}$  after 35 days of incubation under reducing conditions, respectively.

Markel *et al.*<sup>[36]</sup> conducted a study to determine the biogeochemical characteristics of an aquatic system in a re-flooded wetland. The  $\text{Mn}^{2+}$  concentrations in the lake water and sediment porewater at a depth of 20 cm were  $177 \pm 140$  and  $6450 \pm 3240 \text{ } \mu\text{g L}^{-1}$ , respectively. The authors concluded that the  $\text{Mn}^{2+}$  concentration in the porewater was significantly higher than that of the lake water because the redox potential decreased from  $-100 \text{ mV}$  at the sediment-water interface to  $-220 \text{ mV}$  at a depth of 30 cm.

Hossner and Phillips<sup>[37]</sup> conducted a study to determine the effect of flooding on the concentration of available manganese in the soil. After 1, 8, 15, 22, 29 and 36 days of flooding, the concentration of available manganese in the soil increased from  $0.2 \text{ mg kg}^{-1}$  to 1.8, 5.0, 10.6, 12.0 and  $15.0 \text{ mg kg}^{-1}$ , respectively.

**Organic carbon:** The organic carbon concentrations in the soil of the constructed wetland ranged from a low of 3.83% to a high of 5.36% with an average concentration of 4.67%. The organic carbon concentrations in the forest soil ranged from a low of 3.15% to a high of 7.57% with an average concentration of 4.62%. There was no significant difference between the organic carbon concentrations in the soil of the constructed wetland and those in the forest soil as shown in Table 3.

The wetland soil had similar organic carbon content to those of the forest soil. This could be due to the immaturity of the location where soil samples were collected in the constructed wetland. According to Mitsch and Gosselink<sup>[2]</sup>, most constructed wetlands are initially dominated by mineral soils which typically have less than 12-20% organic carbon. As a constructed wetland matures, the percent of organic matter in the soil generally increases.

Anderson and Mitsch<sup>[38]</sup> conducted a study to determine the sediment organic carbon and accumulation rates in two 10 year old constructed wetlands in Ohio and found that the organic carbon in the soil accumulated at a rate of  $152.5$ - $166.0 \text{ g m}^{-2} \text{ year}^{-1}$  during the ten year period. Euliss Jr. *et al.*<sup>[39]</sup> conducted a study to determine the ability of prairie wetlands to store carbon in the soil and determined that wetland restoration in the prairie

pothole region of Canada and the United States would have the potential to sequester 264 Tg of organic carbon in the soil over a 10 year period. Craft *et al.*<sup>[40]</sup> conducted a study to determine the soil organic carbon accumulation rates in transplanted marshes along the coast of North Carolina and determined that over a period of 10-15 years, organic carbon in the soil of the transplanted marshes accumulated at a rate of 84-218 kmol ha<sup>-1</sup> year<sup>-1</sup>.

### CONCLUSIONS

The pH of the soil of the constructed wetland was significantly greater than the pH of the forest soil because of the flooded soil conditions in the constructed wetland. The total iron concentrations in the soil of the constructed wetland were significantly greater than those in the forest soil. There was no significant difference between the plant available iron concentrations in the soil of the constructed wetland and those of the forest soil because of the flooded soil conditions of the constructed wetland and the acidic soil conditions of the forest. The total manganese concentrations in the soil of the constructed wetland were significantly greater than those in the forest. The plant available manganese concentrations in the soil of the constructed wetland were also significantly greater than those in the forest soil because of the flooded soil conditions in the constructed wetland and the acidic soil conditions in the forest. There was no significant difference between the organic carbon concentrations in the soil of the constructed wetland and those in the forest soil because of the immaturity of the location where soil samples were collected in the constructed wetland.

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