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Treatment of Stormwater Runoff and Landfill Leachates Using a Surface Flow Constructed Wetland

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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. The ability of the constructed wetland to retain iron and manganese from the influent water was investigated and the change in pH of the water as it flowed through the cells was assessed. In 2004, the total iron removal efficiency of the constructed wetland ranged from a low of 47.13 % to a high of 84.74 % and in 2006 ranged from a low of 35.56 % to a high of 78.49 % depending on rain events. The outlet total iron concentrations in 2006 were not significantly different from those reported for 2004. In 2004, the total manganese removal efficiency of the constructed wetland ranged from a low of 25.75 % to a high of 51.61 % and in 2006 ranged from a low of 0.0 % to a high of 33.33 % depending on rain events. The inlet and the outlet total manganese concentrations in the constructed wetland from August to October 2006 were significantly higher than the inlet and the outlet total manganese concentrations reported for August to October 2004 because water levels in the constructed wetland were very low and the average pH of the outlet water was lower in 2006. In 2004 and 2006, the pH of the water in the constructed wetland had average inlet values of 6.70 and 6.26 and average outlet values of 7.28 and 6.70, respectively.

Key words: Surface flow wetland, landfill leachates, stormwater, iron, manganese, pH

INTRODUCTION

Landfills are physical facilities constructed in the surface soils of the earth for the purpose of solid waste disposal. Historically, landfills have been the most economical and environmentally acceptable method for the disposal of solid wastes throughout the world^[11]. However, landfills generate leachates, which are produced when waters from rain and snow percolate through the waste materials and contaminants are leached into solution. Leachates are one of the main environmental concerns associated with landfills because of their extreme variability in quality and quantity and potential to damage the quality of groundwater, surface water and soil^[2,3]. Leachate quality and quantity are affected by a number of factors including the age of the landfill, the waste composition, the landfilling technology and climate conditions^[3,4].

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^[5,6]. Constructed and natural wetlands have been used to treat many types of wastewaters including landfill leachates^[7-9]. According to Ye *et* $al.^{[10]}$, constructed wetlands are better able to handle fluctuations in the quality and quantity of wastewater than conventional treatment systems. Wetlands improve water quality through a variety of physical (sedimentation, flocculation, filtration, adsorption), chemical (chelation, precipitation, chemical adsorption) and biological (bacterial mediated reactions, vegetation uptake) mechanisms that operate independently or collectively^[11,12].

A surface flow constructed wetland was established in the Burnside Industrial Park, Dartmouth, Nova Scotia, to treat stormwater runoff from the surrounding watersheds (107 ha) which are comprised primarily of commercial and light industrial properties (77 ha) and two former landfills (a 5.34 ha site that operated from 1968 to 1974 and a 5.42 ha site that

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Table 1: Heavy	y metal loads entering Wright'	's Brook
Element	Average Concentration	Guidelines ^[14]
	$(mg L^{-1})$	$(mg L^{-1})$
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 ^[15]
Zinc	0.158	0.030

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operated from 1976 to 1977). The average precipitation for the area from 1971 to 2000 was 116.6 mm month^{-1[13]}. 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 and manganese concentrations of 15.508 mg L^{-1} and 3.029 mg L^{-1} , respectively, which exceeds the allowable limits established by the Canadian Water Quality Guidelines for the Protection of Aquatic Life^[14,15]. 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 total surface area of 6300 m^2 and 2 naturally vegetated islands that are surrounded by a system of external berms with a total surface area of approximately 6100 m^2 . 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 (tweedy's rush), Juncus effusus (soft rush), Scripus validus (soft stem bulrush), Calamagrostis canadensis (bluejoint grass), Alisma plantagoaquatica (water plantain), Pontederia cordata (pickerelweed), Nymphaea alba (white waterlily) and Potamageton natans (pondweed). The two naturally vegetated islands consist of untamed early successional brush dominated by low shrubs such as Comptonia (sweet fern), Viburnum cassinoides peregrina (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).

The objectives of this study were: (a) to evaluate the overall iron and manganese removal efficiencies of the constructed wetland in 2004 and 2006 and (b) to assess the change in water pH as the water flowed through the wetland cells.

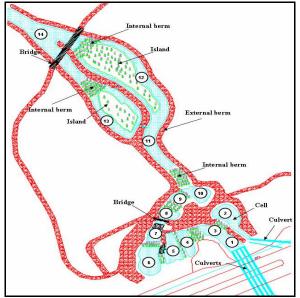


Fig. 1: Location of water samples in the constructed surface flow wetland

MATERIALS AND METHODS

Biweekly water samples were collected from the constructed wetland during the months of May -October. In 2004, water samples were collected from eleven locations in the constructed wetland and in 2006 from fourteen locations (Fig. 1). Grab samples mL were collected in 500 high density bottles using the bottle polyethylene (HDPE) submersion method^[16]. The samples were transported to the Environmental Engineering Laboratory at Dalhousie University in Halifax, Nova Scotia and at 4 °C until needed for chemical refrigerated analyses.

Water samples were analyzed for total iron and total 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 total manganese ^[17]. The pH of the water samples was measured using a pH meter (Fisher Accumet® pH meter, Model # 805MP, Fisher Scientific Co., Ottawa, Ontario, Canada).

The data from 2004 and 2006 were analyzed statistically using a two sample-t-test. The statistical analyses were performed using Minitab (Minitab Release 14.20, Minitab Inc., State College, PA) and differences were considered significant at a p-value \leq 0.05 (95 % confidence interval).

RESULTS AND DISCUSSION

Total iron: Figure 2 displays the total iron concentrations in the inlet and the outlet in 2004 and 2006. The total iron concentration in the constructed wetland fluctuated during the spring – fall period but generally decreased as the water flowed through the cells. The inlet iron concentrations ranged from 6.25 to 7.21 mg L⁻¹ with an average concentration of 6.78 mg L⁻¹ for 2004 and ranged from 2.52 to 17.90 mg L⁻¹ with an average concentration of 8.29 mg L⁻¹ for 2006. The outlet iron concentration of 2.27 mg L⁻¹ for 2004 and ranged from 1.74 to 3.85 mg L⁻¹ with an average concentration of 2.74 mg L⁻¹ with an average concentration of 2.74 mg L⁻¹ for 2006.

The iron removal efficiencies for 2004 and 2006 are shown in Table 2. The total iron removal efficiency of the constructed wetland ranged from a low of 47.13 % to a high of 84.74 % in 2004 and ranged from a low of 35.56 % to a high of 78.49 % in 2006. The inlet and the outlet total iron concentrations in the constructed wetland in 2006 were compared with those determined in 2004 as shown in Table 3 and 4. The inlet total iron concentrations in September and October of 2006 were significantly higher than the inlet total iron concentrations earlier in the season and in September and October of 2004 (p-value = 0.025). The outlet total iron concentrations in the constructed wetland in 2006 were not significantly different from the outlet total iron concentrations in 2004 (p-value = 0.243). One possible reason for the higher inlet total iron concentrations in September and October 2006 than those observed earlier in the season was that water levels in the constructed wetland in September and October were very low. From August 15th to August 31st, 2006, the wetland and surrounding area received a total of 7.6 mm of rainfall and the total rainfall for the month of September 2006 was only 37 mm. The area also received either small amounts of rainfall or no rainfall in the five days prior to sample collection^[18]. The lower total iron concentrations in the inlet of the constructed wetland that were observed earlier in the season may have been the result of higher water levels and larger diluted water inflows which the total iron concentrations. Also, the water levels in the constructed wetland in September and October 2006 were lower than in September and October 2004. From August 15th to August 31st, 2004, the wetland and surrounding area received a total rainfall of 67 mm and the total rainfall for the month of September 2004 was 69.2 mm^[18]. One would expect an increase in iron removal efficiency overtime. A possible explanation for not observing

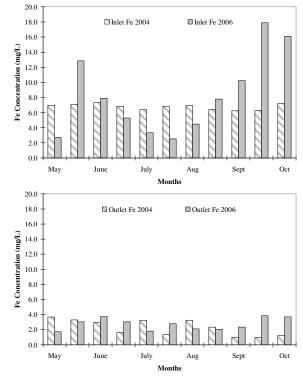


Fig. 2: The inlet and outlet total Fe concentrations in the constructed wetland for the 2004 and 2006 seasons

greater iron removal efficiencies in 2006 was that the inflow of water to the constructed wetland had also increased significantly because of development (servicing and grading) of lots within the industrial park.

Generally, wetlands are capable of removing large quantities of trace elements from wastewaters. However, there is significant variability among trace elements and also between wetlands in the degree to which each element is removed from the wastewater^[19]. Ye et al.^[10] reported that the average removal efficiencies of iron from a surface flow wetland that was constructed to treat coal combustion leachate from an electrical power station in Pennsylvania in the first and second years of the study were 90.8 and 94 %, respectively. Eckhardt et al.^[20] observed that the average removal efficiency of iron from a surface flow wetland that was constructed to remediate leachate from a landfill in New York was 70.6 %. DeBusk^[21] reported that the average reduction in iron concentration achieved by a constructed wetland treating landfill leachate in Northwest Florida over a six year period was 98 %.

		Removal E	Removal Efficiency (%)					
Month		Fe	Mn					
	2004	2006	2004	2006				
May	47.13	35.56	45.50	0.00				
May	53.79	76.26	49.75	20.00				
June	59.56	52.53	33.51	28.57				
	76.20	42.45	25.75	20.00				
July	49.06	46.27	34.48	33.33				
	80.29	-10.32	33.33	9.09				
August	53.24	53.13	34.43	-33.33				
August	63.57	73.72	28.26	-50.00				
Santambar	83.68	77.07	45.79	-25.00				
September	84.74	78.49	50.77	-12.50				
October	82.94	77.02	51.61	-28.57				
Average	66.75	54.74	39.38	-3.49				

Table 2: Fe and Mn removal efficiencies

Table 3: Two-sample	t-test for the in	nlet total Fe conc	centrations in the co	onstructed wetland	from September t	o October 2004 and	2006
Source	n	DF	М	σ	SE	T-value	P-value
Inlet Fe 2004	3	4	6.583	0.543	0.31	-3.50	0.025
Inlet Fe 2006	3	4	14.75	4.00	2.30		

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

Table 4: Two-sample t-test for the outlet total Fe concentrations in the constructed wetland from May	to October 2004 and 2006

Source	n	DF	М	σ	SE	T-value	P-value
Outlet Fe 2004	11	20	2.27	1.05	0.32	-1.20	0.243
Outlet Fe 2006	11	20	2.747	0.793	0.24		

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

According to Hall *et al.*^[22], one of the fundamental processes responsible for successful iron removal in surface flow (aerobic) wetlands is the oxidation of ferrous iron (Fe²⁺) to ferric iron (Fe³⁺) and the hydrolysis of Fe³⁺ to ferric iron hydroxide Fe(OH)₃ as shown in the following equations. Precipitates such as Fe(OH)₃, cause an orange staining and sludge build up on substrate surfaces^[23].

 $\begin{array}{l} \operatorname{Fe}^{2+} + \frac{1}{4}\operatorname{O}_2 + \operatorname{H}^+ \to \operatorname{Fe}^{3+} + \frac{1}{2}\operatorname{H}_2\operatorname{O} & (1) \\ \operatorname{Fe}^{3+} + 3\operatorname{H}_2\operatorname{O} \to \operatorname{Fe}(\operatorname{OH})_3 + 3\operatorname{H}^+ & (2) \\ \operatorname{Hedin} \text{ and Nairn}^{[24]} \text{ state that the removal of iron} \end{array}$

Hedin and Nairn^[24] state that the removal of iron from aerobic waters with a pH > 4 is limited by the oxidation process (Equation 1). At a pH > 6, abiotic oxidation processes dominate over bacterial oxidation processes. In natural systems with circumneutral pH values, the kinetics of abiotic oxidation processes are typically 5 - 10 times faster than biological mechanisms of oxidation at lower pH values. Ferric iron hydrolysis occurs quickly at a pH $\ge 3.5^{[23]}$.

A second mechanism for iron removal from wastewater in constructed wetlands is the formation of insoluble metal sulphides by sulphate reducing bacteria in anoxic zones. Sulphate reducing bacteria are obligate anaerobes that require a pH in the range of 5 - 8 in order to survive. Sulphate reducing bacteria oxidize simple organic compounds (CH₂O) and use sulphate (SO₄²⁻) as the terminal electron acceptor. The result is the production of hydrogen sulphide (H₂S) which reacts

with iron and forms insoluble iron sulphide (FeS) as shown in the following equations^[25].

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^{-}$$
(3)
$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+$$
(4)

The iron precipitates formed in the above two mechanisms are subject to adsorption by wetland substrates and filtration and sedimentation in wetland cells. Vegetation is also of primary importance for iron retention in wetlands. Plants play a critical role in iron removal via filtration of water and adsorption of iron and iron particulates on submerged stems and leaves. Plants can excrete oxygen via their root mass into the surrounding sediment which makes their rhizosphere more aerobic and more favourable for Fe³⁺ precipitation. Plants provide habitat and energy sources to maintain and stimulate a diverse microbial population in the wetland. Plants also participate in iron retention in wetlands via phytoremediation^[6, 10, 25].

In the present study, the primary sink for metal retention in the constructed wetland is the bottom sediments because the pH of the water is greater than 6 and substantial orange staining and sludge have been observed in the wetland cells. A second important mechanism is adsorption of iron precipitates on the submerged stems of *Potamageton natans* (pondweed). According to Ye *et al.*^[26], approximately 40 to 70 % of the total iron retained by wetlands was found as ferric hydroxides. Plant uptake and retention of metals was

generally small compared to sediment accumulation and typically accounted for < 5 % of the metals retained in a wetland^[12, 19].

Total manganese: Figure 3 displays the total manganese concentrations in the inlet and the outlet in 2004 and 2006. In 2004, the manganese concentration generally decreased as the water flowed through the cells, but did not appear to significantly increase or decrease as the water flowed through the cells in 2006. The inlet manganese concentration ranged from 1.67 to 2.32 mg L^{-1} with an average concentration of 1.91 mg L^{-1} for 2004 and ranged from 4.0 to 0.1 mg L^{-1} with an average concentration of 1.7 mg L^{-1} for 2006. For 2004, the maximum manganese concentration in the outlet was $1.52 \text{ mg } \text{L}^{-1}$ while the minimum manganese concentration was 0.9 mg L^{-1} with an average of 1.16 mg L^{-1} while for 2006, the highest manganese concentration observed in the effluent was 5.0 mg L⁻¹ and the lowest concentration was 0.1 mg L^{-1} with an average concentration of 1.9 mg L^{-1} .

The manganese removal efficiencies of the constructed wetland for 2004 and 2006 are shown in Table 2. In 2004, the total manganese removal efficiency of the constructed wetland ranged from a low of 25.75 % to a high of 51.61 % with an average removal efficiency of 39.38 %. In 2006, the total manganese removal efficiency of the constructed wetland ranged from a low of 0.0 % to a high of 33.33 %. However, there were higher manganese concentrations in the outlet than in the inlet in the months of August – October of 2006.

The inlet and the outlet total manganese concentrations in the constructed wetland in 2006 were compared to the inlet and the outlet total manganese in 2004 as shown in Table 5 and 6. The inlet and the outlet total manganese concentrations in the constructed wetland from August to October 2006 were significantly higher than the inlet and the outlet total manganese concentrations earlier in the season and from August to October 2004 (p-value = 0.051 and 0.019). A possible reason for the higher total manganese concentrations in the inlet and the outlet of the constructed wetland from August to October 2006 than those observed earlier in the season and from August to October 2004 was that water levels in the constructed wetland from the middle of August to October were very low. The lower total manganese concentrations in the inlet and the outlet earlier in the season may have been the result of higher water levels and larger water inflows which diluted the total manganese concentrations. Also, the average pH of the

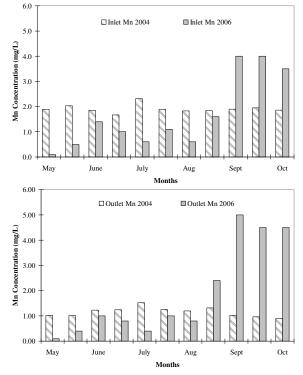


Fig. 3: The inlet and outlet total Mn concentrations in the constructed wetland for the 2004 and 2006 seasons

outlet water was 6.70 in 2006 and 7.27 in 2004. A higher pH is more favourable for manganese oxidation. According to Komnitsas *et al.*^[27] and Gazea *et*

According to Komnitsas *et al.*^[27] and Gazea *et al.*^[23], manganese is very difficult to remove from solution because it is an extremely mobile ion. Elevated levels of manganese may be caused by re-dissolution of unstable precipitates or desorption of manganese from surfaces. Gazea *et al.*^[23] state that when both iron and manganese are present in solution, manganese removal will be less efficient than iron removal because iron and manganese to Mn^{2+} as shown in the following equations^[19, 23].

 $\begin{array}{l} MnO_{2(S)} + 2Fe^{2+} + 2H_2O \rightarrow 2FeOOH_{(S)} + Mn^{2+} + 2H^{+} \\ MnOOH_{(S)} + Fe^{2+} \rightarrow FeOOH_{(S)} + Mn^{2+} \end{array} \tag{5}$

Hallberg and Johnson^[28] note that biological oxidation of manganese does not proceed rapidly in the presence of iron and thus it is not removed significantly in aerobic wetlands where the concentration of ferrous iron exceeds 1 mg L⁻¹. According to Sobolewski^[19], Gazea *et al.*^[23] and Hallberg and Johnson^[28] a second reason manganese removal may not be as successful as

iron removal is that abiotic Mn^{2+} oxidation occurs slowly at pH values < 8. The average pH of the outlet water in the constructed wetland in 2006 was 6.70.

Ye et al.^[10] reported that the average manganese removal efficiencies of a surface flow wetland that was constructed to remediate coal combustion leachate were 91 and 98 % in the first and second years of the study, respectively. The authors contributed the significant manganese retention in the constructed wetland to the high pH of the water (pH > 7.2). Ye *et al.*^[26] conducted a study to determine the ability of a 10 year old surface flow constructed wetland to treat coal ash leachate from an electrical utility in Alabama. The study focused on metal removal from the first two vegetated wetland cells. The degree to which the concentration of manganese was reduced in the outlet water from cell 2 varied considerably between sampling times and ranged from a low of -7 % in May 1996 to a high of 26 % in August 1996. During this time, the average pH of the water within the wetland was 3.9. In order to increase the manganese removal efficiency of the wetland, the authors added sodium hydroxide to cell 1. As a result, the pH in the outlet water from cell 2 rose to greater than 6 and the manganese removal efficiency reached 58 %. DeBusk^[21] reported that the average manganese removal efficiency achieved by a surface flow wetland treating municipal landfill leachate was 95 % over a six year period.

One possible mechanism for manganese removal in aerobic wetlands involves the oxidation of dissolved Mn^{2+} to the tetravalent form Mn^{4+} , which is similar to ferrous iron oxidation. Then, the hydrolysis of Mn^{4+} produces MnO_2 as shown in the following equations^[24]. $Mn^{2+} + \frac{1}{2}O_2 + 2H^+ \rightarrow Mn^{4+} + H_2O$ (7) $Mn^{4+} + 2H_2O \rightarrow MnO_2 + 4H^+$ (8)

 Mn^{2+} can also precipitate in the form of carbonate in alkaline environments, which in the presence of oxygen may further oxidize to MnO_2 as shown in the following equations^[23].

$$Mn^{2+} + HCO_3 \rightarrow MnCO_{3(s)} + H^+$$
(9)
$$MnCO_{3(s)} + CO_{3(s)} + (10)$$

 $MnCO_3 + O_2 \rightarrow MnO_2 + CO_2$ (10)

pH: Figure 4 displays the pH in the inlet and the outlet in 2004 and 2006. In 2004, the pH of the water in the constructed wetland fluctuated as the water flowed through the cells whereas in 2006, the pH of the water increased as the water flowed through the cells. The inlet pH values ranged from 6.70 to 7.60 with an average value of 6.70 for 2004 and ranged from 6.13 to 6.55 with an average value of 6.26 for 2006. The maximum pH in the outlet was 7.60 while the minimum pH was 6.70 with an average of 7.28 for 2004 and ranged from 6.70

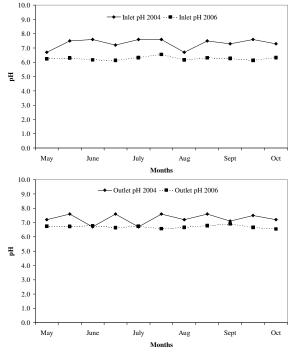


Fig. 4: The inlet and outlet pH values in the constructed wetland for the 2004 and 2006 seasons

for 2006. The inlet and the outlet water pH in the constructed wetland in 2006 were compared to the inlet and the outlet water pH in the constructed wetland in 2004 as shown in Table 7 and 8. The inlet and the outlet water pH values in the constructed wetland in 2006 were significantly lower than the inlet and the outlet water pH values in the constructed wetland in 2004 (p-value = 0.000).

One possible explanation for the increase in pH in 2006 was the presence of rapidly growing algae and submerged aquatic vegetation in the constructed wetland which remove carbon dioxide (CO₂) from the water during photosynthesis as shown in Equation 11. A decrease in the dissolved CO₂ concentration in the water results in a lower concentration of carbonic acid (H₂CO₃) as shown in Equation 12. As the H₂CO₃ concentration in the water decreases, the concentration of H⁺ decreases as shown in Equation 13. As a result, the pH of the water within the wetland increases^[29].

$6H_2O + 6CO_2 + light energy \rightarrow C_6H_{12}O_6 + 6O_2$	(11)
$CO_2 + H_2O \leftrightarrow H_2CO_3$	(12)
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	(13)

The increase in pH could also be due to bacterial sulphate reduction in anaerobic zones within the wetland. Bacterial sulphate reduction (Equation 3) within the anaerobic zones of wetlands produces bicarbonate ions (HCO₃), which results in a decrease in

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Source	n	DF	μ	σ	SE	T-value	P-value
Inlet Mn 2004	4	6	1.8875	0.0486	0.024	-2.43	0.051
Inlet Mn 2006	4	6	3.28	1.14	0.57		
Differences are consid	dered significa	nt at a p-value ≤	0.05 (95 % confide	nce interval)			

Table 5: Two-sample t-test for the inlet total Mn concentrations in the constructed wetland from August to October 2004 and 2006

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Source	n	DF	μ	Σ	SE	T-value	P-value
Outlet Mn 2004	5	8	1.082	0.174	0.078	-2.94	0.019
Outlet Mn 2006	5	8	3.49	1.78	0.80		
Differences are consider	red significant	at a p-value ≤ 0	.05 (95 % confiden	ce interval)			

Table 7: Two-sample t-test for the inlet water pH in the constructed wetland in 2004 and 2006

Source	n	DF	μ	σ	SE	T-value	P-value
Inlet pH 2004	11	20	7.327	0.341	0.10	9.73	0.000
Inlet pH 2006	11	20	6.265	0.123	0.037		
Differences are consi	dered signific:	ant at a p-value	$\le 0.05 (95 \% \text{ confide})$	ence interval)			

Table 8: Two-sample t-test for the outlet water pH in the constructed wetland in 2004 and 2006

Source	п	DF	μ	σ	SE	T-value	P-value
Outlet pH 2004	11	11	7.273	0.344	0.10	5.25	0.000
Outlet pH 2006	11	11	6.705	0.103	0.031		

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

H⁺ concentration and an increase in pH as shown in Equation 13^[25].

A possible explanation for the lower pH of the water in the constructed wetland in 2006 compared to 2004 was the build up of organic matter within the wetland cells during the period of 2004 - 2006. The decomposition of organic substances is a natural source of acidity in a wetland^[30]. In shallow wetlands, aerobic decomposition occurs in the entire water body including the upper sediment layers. During the process of aerobic decomposition, microorganisms use dissolved oxygen to oxidise organic compounds into CO_2 , H_2O , inorganic compounds(NH_4^+ , SO_4^{-2} and PO_4^{-3}) and energy. Anaerobic decomposition occurs in anoxic zones and anaerobic sediments in wetlands. In order for anaerobic decomposition to occur, nitrate, nitrite or sulphate must be available. Organic carbon can be completely mineralized to CO₂ or CO₂ and methane (CH_4) . In most freshwater wetland sediments, methanogenesis is the common pathway for organic matter decomposition and the most frequent mechanism of CH₄ formation in freshwater environments involves the substrate acetate (CH₃COOH) as shown in Equation 14^[31, 32]

 $CH_3COOH \rightarrow CO_2 + CH_4$ (14)

An increase in the dissolved CO₂ concentration in the water results in a higher concentration of carbonic acid (H_2CO_3) as shown in Equation 12. As the H_2CO_3 concentration in the water increases so does the concentration of H⁺ as shown in Equation 13 and as a result, the pH of the water within the wetland decreases.

A second possible explanation for the lower pH of the water in the constructed wetland in 2006 compared to 2004 was the build up of iron and manganese precipitates in the wetland as the wetland gets older. The hydrolysis and precipitation of dissolved iron (Equation 1) and manganese (Equation 6) and the formation of insoluble metal sulphides (Equation 4) increases the H⁺ concentration in the water and decreases the pH.

Eckhardt *et al.*^[20] reported that the pH of the water in a surface flow wetland that was constructed to remediate leachate from a landfill in New York increased from 6.9 in the inlet to 7.4 in the outlet. Sartaj^[8] recorded that the pH of the water in a surface flow wetland that was constructed to treat leachate from a landfill in Ontario increased from values of 6.5 - 7.6 in the inlet water to values as high as 9 in the outlet water. Johnson *et al.*^[3] reported that the pH of the water in a surface flow wetland constructed to treat groundwater contaminated with leachate from a landfill in Alabama ranged from 5.33 to 7.05 in the inlet water and 6.06 to 7.95 in the outlet water.

CONCLUSION

In 2004, the total iron removal efficiency of the constructed wetland ranged from a low of 47.13 % to a high of 84.74 % and in 2006 ranged from a low of 35.56 % to a high of 78.49 % depending on rain events. The outlet total iron concentrations in 2006 were not significantly different from those reported for 2004.

In 2004, the total manganese removal efficiency of the constructed wetland ranged from a low of 25.75 % to a high of 51.61 % and in 2006 ranged from a low of 0.0 % to a high of 33.33 % depending on rain events. There were higher manganese concentrations in the outlet than in the inlet in the months of August - October 2006 because water levels in the constructed wetland from the middle of August to October were very low. The inlet and the outlet total manganese concentrations from August to October 2006 were significantly higher than the inlet and the outlet total manganese concentrations reported for August to October 2004 because water levels in the constructed wetland were very low and the average pH of the outlet water was lower in 2006. In 2004 and 2006, the pH of the water in the constructed wetland had average inlet values of 6.70 and 6.26 and average outlet values of 7.28 and 6.70, respectively. The inlet and the outlet water pH in 2006 were significantly lower than those reported for 2004.

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