FIELD STUDY ON HEAVY METAL REMOVAL IN A NATURAL WETLAND RECEIVING MUNICIPAL SEWAGE DISCHARGE

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ABSTRACT

Constructed and natural wetlands have been used successfully in the treatment and polishing of municipal wastewater all over the world, including in South Africa. Here we report on the heavy metal removal in a natural wetland that is receiving municipal sewage discharge, Limpopo province, South Africa. The natural wetland is located downstream of Makhado oxidation ponds and is dominated by the reed plant *Phragmites australis*. The changes in the metal variation from discharge of oxidation ponds to middle section and downstream of the natural wetland was analysed for heavy metals by ICP-MS over a 12 month period. The annual rainfall data were obtained from Agricultural Research Council. The following heavy metals: total chromium, zinc, cadmium and lead were effectively reduced during the passage through the wetland, to levels below the Department of Water & Sanitation (DWS) guidelines for waste water discharge. In contrast, the manganese and iron was reduced slightly above the DWS guideline value during the drier season and was higher during the wet season indicating a contribution of soil and water erosion. With copper it was effectively reduced during the wet and dry seasons with the exception in April, June and September when the downstream section was three times higher than the DWS guideline value. Thus the natural wetland was able to reduce considerable the heavy metals in the municipal discharge during its passage in the wetland. This is able to render the water in downstream of the wetland safe for rural communities to use the water for irrigation purposes.

Keywords: drinking water, heavy metal reduction, natural wetland, phragmites australis rural communities.

1 INTRODUCTION

Constructed and natural wetlands have been used successfully in the treatment and polishing of municipal wastewater all over the world, including in South Africa. In South Africa, freshwater resources are deteriorating due to the impacts of anthropogenic activities [1] and some of the country's water bodies are already hypertrophic [2]. From a South African perspective, nutrient rich materials in wastewater treatment works (WWTW) alone are in higher concentration than in nonpoint sources [3]. Oberholster *et al*. [3] indicate that in South Africa, only 7.4% of WWTW were awarded the green drop certification. About 92.6% of the South African WWTW may be said to be noncompliant and their continued operation raises the risks of eutrophication in South African freshwater resources. Oxidation ponds or stabilization ponds are an alternative wastewater treatment option that is practiced in South Africa to serve smaller towns and urban centres [4]. The oxidation ponds are cheaper to operate with low level skills but require more land, which is available in rural areas [5]. The use of oxidation ponds purifying domestic wastewater has achieved mixed success [5–8]. The oxidation

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ponds have been effective in reducing heavy metals in domestic wastewater before discharge to a water course [5]. The heavy metal removal efficiencies have been variable. For example the study of Butler *et al*. [5] showed the removal efficiency as follows: Iron (75% to 98%); cobalt (58% to 60%); lead (85% to 95%); Zinc (74% to 82%); copper (39%); nickel (16%); chromium (41%). Thus the release of these heavy metals to the water body may be detrimental to human health [9–11].

Thus to improve the quality of discharge effluent there is a need for wetlands (natural or constructed). The wetlands are located downstream of the oxidation ponds and habited by a variety of plants such as reeds and emergent hydrophytes [12]. The reed plant *Phragmites australis* has known to effectively remove and reduce heavy metals in wetlands according to Vymazal *et al*. [13]. There are several processes that are known to be taking place in wetlands environments and their role in reducing metal concentration and neutralizing the acidity of influent water have been examined. These processes include physical, chemical and biological processes [14]. This process involves the settling and sedimentation of particles and has been efficient in the removal of metals in water [15]. When heavy metals are in wetland environments, whether water is a flowing body or stagnant water body, they undergo a particular transformation [15]. There are a wide range of chemical processes that are involved in wetlands with regard to the removal of heavy metals and they are: adsorption, sorption and oxidation and hydrolysis of metals [15]. Biological removal is the most important process in wetlands and its most important pathway is by plants uptake [15]. There are a number of categories of plants found in wetland environments, which include emergent, surface floating, or free floating rooted leaves, sub-merged macrophytes and trees [15]. These plants use both leaves and roots to extract pollutants (as nutrients). Those with their roots systems submerged under water have the ability to extract their nutrients from sediments where metal atoms are captured.

The natural wetland is located downstream of Makhado oxidation ponds, Limpopo province of South Africa. In our study, the urban centre of Makhado township (Dzanani) has a population of 5673 in 2011 and the domestic sewage is discharged into Makhado oxidation ponds (http://census2011.adrianfrith.com/places/968027001). The wetland is dominated by the reed plant *Phragmites australis.* The main objective was to determine the levels of heavy metals in water as it flows downstream of the wetland.

2 MATERIALS AND METHODS

2.1 The study area

The three sampling points were selected (Fig. 1), effluent discharge (upstream) point (S22.89764; E30.04792), midstream point (S22.88833; E30.05620) and the downstream point (S22.88319; E30.06167). The water samples were monthly collected for a period of twelve months starting from November 2013 until October 2014. The downstream part of wetland is part of Mawoni River, a tributary of the Nzhelele River which is also a tributary of Limpopo River.

2.2 Samples preparation and analysis

The water samples were collected in to the 250 mL plastic bottles and stored in the cooler bag and be transported to the University of Venda laboratory. Once in the laboratory, the samples were filtered through Sartorius membrane filter nylon, 0.45 μm (Germany) in a 20 mL centrifuge tube and acidified with a drop of dilute nitric acid. The samples were analysed for metals

Figure 1: The location of Makhado oxidation ponds and the three sampling points and the tarred road (R523) (Google earth).

at Stellenbosch University in duplicate by ICP-MS (Agilent 7,700 instrument). The Agilent 7,700 instrument reported the trace element concentrations in parts per billion (ppb).

2.3 Climate data

The data (rainfall, air temperature and evapotranspiration) were obtained from the ARC-Institute of Soil, Climate and Water in Pretoria, South Africa. The data would assist in the interpretation of observed variables.

2.4 Data analysis

The graphs were drawn using Microsoft *Excel* 2010 and was used for correlation analysis of rainfall data and individual heavy metal content in different sections of the wetland was carried out and in calculating the percentage removal efficiency.

$$\% \text{ Removal efficiency was calculated} = \left(1-\left(\frac{\text{downstream}}{\text{discharge}}\right)\right)*100$$

3 RESULTS AND DISCUSSION

There was variation in the levels of heavy metals, total chromium, zinc, cadmium, lead, manganese, iron and copper in different sections of the wetland (Figs. 2–8).

3.1 Removal of total chromium

The levels of total Cr were lower than the Department of Water Affairs guideline value of 50 ppb for discharge of effluent to a water body (Fig. 2) and with the exception of May which was higher than the regulatory limit [18]. There was weak association (–0.30) of rainfall events and

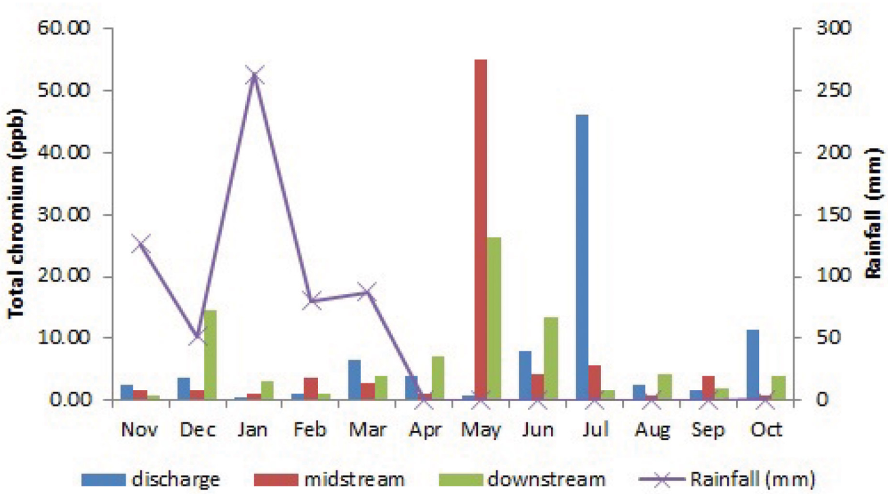

Figure 2: Variation in total chromium (ppb) concentration through the wetland.

levels of total Cr in the wetland. The removal efficiency was variable (–3,095% to 96.2%) with the downstream sections having more total Cr than the upstream sections. Dense vegetation between the discharge and midstream point may have resulted to high plant uptake the metals may have been the cause for the reduction in total Cr. The downstream section of the wetland has less vegetation and is transected by tarred road. Thus the factors may have contributed to higher levels of total Cr in downstream section. The study of Omprakash in Ethiopia showed that 54% of Cr was reduced in a constructed wetland [16]. Thus the wetland is able reduce the levels of Cr in different sections [17].

3.2 Removal of zinc

The levels of Zn were lower than the Department of Water Affairs guideline value of 300 ppb for discharge of effluent to water body (Fig. 3; [18]). There was weak association (–0.43) of rainfall events and levels of Zn in the wetland. The removal efficiency was variable (–688.5% to 99.2%) with the downstream sections. However, in February during the rainy season the wetland midsection had increasing Zn concentration than at the discharge point.

During April after the March rainfall the downstream point measured the highest concentration above both discharge and midstream point and at this point Zn concentrations were increased by more than 100% due to runoff transporting matter from the upstream to the downstream. Due to slow water flow in the wetland, Zn concentration remained increased by more than 100% in the following May and June months. However, these increased concentrations were followed by the highest reduction in July by 99.24%. July was one of the dry months in the area and by this time runoff matter could have completely settled and allow for plant uptake. Zn removal by wetland can be removed by between 54%–99% [19].

3.3 Removal of cadmium

Cadmium measurements were in very low concentration in the wetland throughout the sampling period and always measured less than 0.30 ppb (Fig. 4) and the levels conformed to the

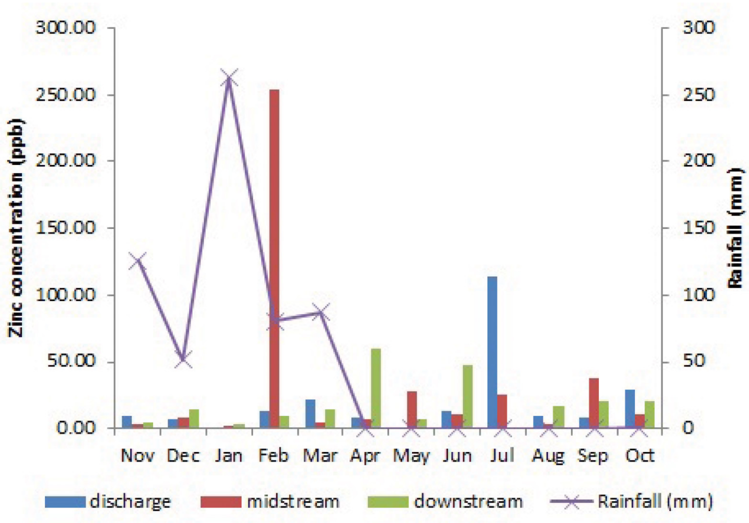

Figure 3: Variations in zinc (ppb) concentrations through the wetland.

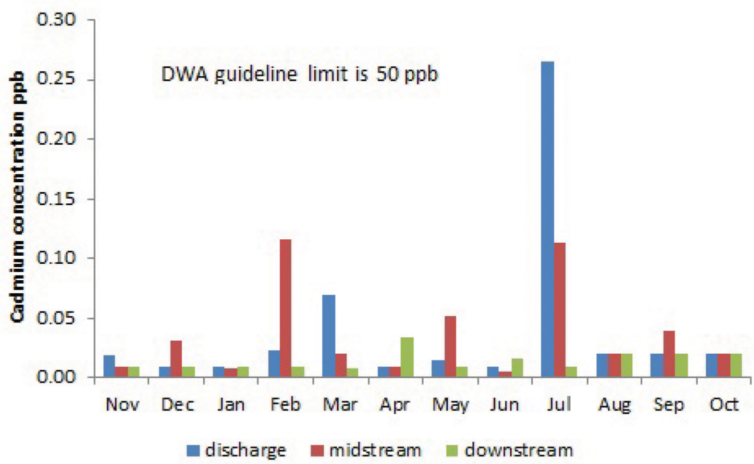

Figure 4: Variations in cadmium (ppb) concentrations through the wetland.

target water quality range for 50 ppb in irrigation [18]. Although at low concentrations, it was neither reduced nor increased for a period of months of the sampling period. During March 2014, Cd was reduced by 88.1% in the wetland. There was weak association (–0.46) of rainfall events and levels of Cd in the wetland. However, this was followed by more than 100% increased concentrations during April 2014. March 2014 was a rainy season in the area and it is expected that the assimilative capacity of the wetland could have diluted the concentrations of Cd since it was always in very small concentrations. In April 2014 when runoff stopped it is expected that Cd may have settled down and dissolved in the wetland.

3.4 Removal of lead

Lead concentrations were generally low in the wetland with the highest measured at 5.77 ppb in the midsections of the wetland during May 2014 with the lowest measured at 0.05 ppb during February 2014 (Fig. 5) and did conform to the target water quality range set at ≤ 100 ppb [18]. There was weak association (–0.38) of rainfall events and levels of Pb in the wetland. During the rainfall season Pb was increased in the wetland by more than 100% and again in April 2014 immediately after rainfall season.

During rainy seasons it is expected that runoff could have eroded matter of different chemical composition and may have contributed to the increasing levels of Pb. During dry seasons when runoff was off, the wetland, through its slow water movement, may have allowed for the dissolving of matter and hence the increase in Pb concentrations. In the same time plant uptake may have started to play in the wetland when sediments have settled down and allow reach by plants roots and there was a significant reduction in Pb concentration in the wetland at the end of the sampling period in October 2014. The efficiency of Pb removal from wetland can be between 95% and 99% and totally depend on its concentration and with little relation to its residence time [19].

3.5 Removal of manganese

Manganese levels in the wetland varied considerably with the discharge point recording the highest value at 2271.48 ppb during December 2013, while the midstream recorded the lowest value at 0.39 ppb during August 2014 (Fig. 6) and did not conform to the target water quality range for irrigation set at 100 ppb [18]. There was strong association (0.85) of rainfall events and levels of Pb in the downstream section of the wetland. There were increases in the Mn concentration throughout the wetland and may be attributed rainfall events. The rainfall may have eroded soil material outside the wetland and then deposited this in the wetland thus contributing to high concentrations of Mn in the wetland.

However, during July, August and September of 2014 there were highest reductions of Mn through the wetland. During this period there was no rainfall recorded in the area so plant metal uptake may have been the source of metal reduction in the wetland.

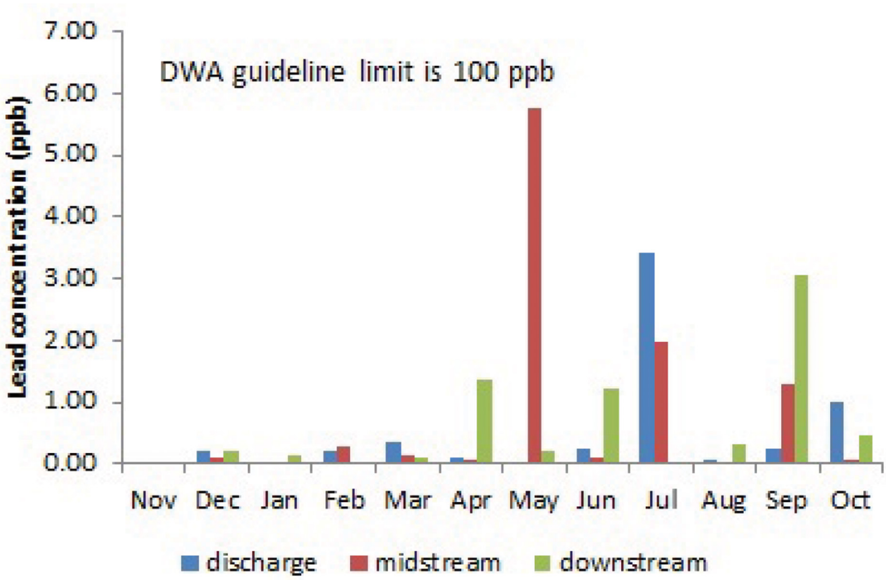

Figure 5: Variations in lead (ppb) concentrations through the wetland.

3.6 Removal of iron

There were mostly high concentrations of Fe in the wetland (Fig. 7) and did not conform to the target water quality range for irrigation water set at 300 ppb [18]. There was strong association (0.77) of rainfall events and levels of Fe in the downstream section of the wetland. During rainfall seasons Fe may have been introduced in the midsections of the wetland and given the fact that wetland are characterized by very slow movement of water Fe may have been given longer residence time in the wetland.

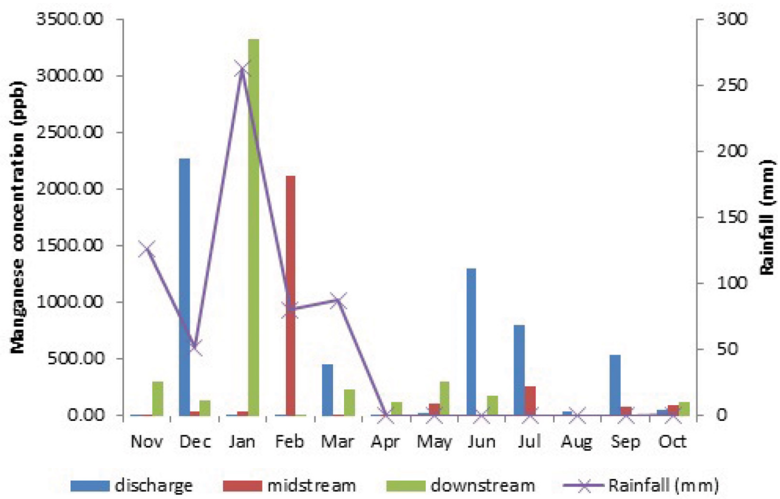

Figure 6: Variation in manganese (ppb) concentration through the wetland.

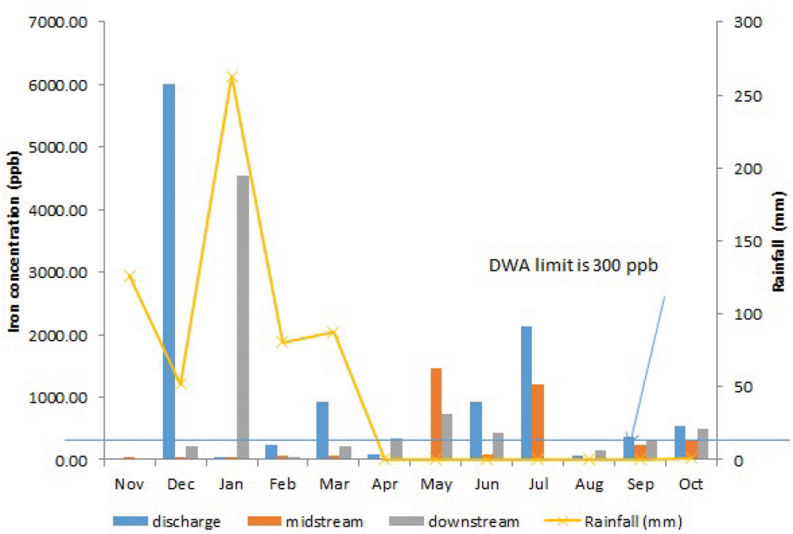

Figure 7: Variation in iron (ppb) concentration through the wetland.

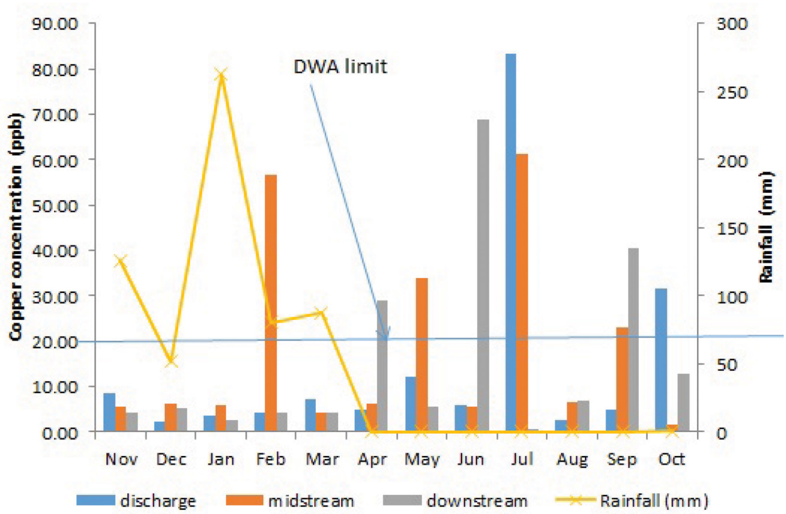

Figure 8: Variations in copper (ppb) concentrations through the wetland.

There was 96.48% reduction in Fe during December 2013. This significant reduction, however, was followed by increases of more than 100% during January, April, May and August of 2014. Another significant reduction occurred at 99.58% in July 2014 though it was followed by more than 100% increase during August 2014.

3.7 Removal of copper

Copper measurements reached the highest in July at the discharge point measuring 83.51 ppb while the lowest measurements were at midstream point in October at 1.8 ppb (Fig. 8). Cu concentrations did conform to the target water quality range in irrigation set at 20 ppb [18]. There was weak association (–0.39) of rainfall events and levels of Cu in the wetland. During the twelve month sampling period Cu reduction in the wetland occurred in seven months and the highest reduction was in July by 99.39%.

There were, however, increase in Cu concentrations in the wetland for five months of the sampling period. In December 2013 there was an increase in Cu concentration by more than 100%. During this month the discharge point measured the lowest concentration of Cu but increased in the midsection and the downstream points. Runoff may have been the cause for the increase through erosional activities by introducing more matters in to wetland. During dry season in July in the area there was high reduction in Cu concentration and this could have been due to high plant uptake of metals. Cu can be removed by between 69% and 99% in wetlands [19]. The presence of excess levels of Fe, Zn and Cu in the wetland may be attributed to use of iron, copper and brass scrubbers that are used during the cleaning of cooking utensils [11].

4 CONCLUSIONS

The slow flow of water through the wetland can be said to have a greater role in ensuring that the heavy metals have longer residence time in the wetland and provide time for the roots plants to absorb the metals. The heavy metals in the wetland did conform to the Department of Water and Sanitation guidelines with the exception of iron and manganese which increased during the rainy season.

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