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A Preliminary Analysis of the Correlation of Heavy Metals with TN, TP and TSS in Constructed Wetland

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Abstract **–** Constructed wetland (CW) has been receiving increased popularity in urban cities to treat stormwater runoffs following the best practice management guidelines which only focuses on TN, TP and TSS. However, the presence of heavy metals is also detected in CWs. This paper presents the water quality monitoring results of a CW in Melbourne, Australia. A statistical analysis has been undertaken to determine the correlation of heavy metals with TN, TP and TSS. The analysis revealed that the treatment performance did not comply with the best practice management guidelines and the wetland is experiencing significant metal pollution. The results showed that TN and TP concentrations are negatively correlated and TSS are strongly correlated with the concentration of metal pollutants including Al, Cu and Fe. Meanwhile, significant correlations are discovered between metals such as Zn and Cu, Al and Cr than between the common pollutants. As this is a preliminary analysis, further investigations are needed to validate the relationships. It is envisioned that the outcome of this research will assist CWs owners and managers to assess the effectiveness of CWs in reducing the levels of not only the common three pollutants but also heavy metals.

Keywords**:** Constructed wetland, heavy metal pollution, best practice management guideline, correlation

1. Introduction

Constructed wetland (CW) is an effective measure to attenuate stormwater runoffs and improve the water quality through a series of physical and chemical processes [1]. The Best Practice Management (BPM) guidelines for CWs stipulated the treatment objectives to reduce 45% TN, TP and 80% TSS [2]. CWs are well recognised in reducing nutrients and sediments as per the treatment objectives of BPM However, BPMs objectives only emphasize the percentage reduction of the three pollutants (TN, TP and TSS) without giving guidance on water quality evaluation for CWs and other pollutants. Despite various pollutants appearing in stormwater wetlands, the existing management of stormwater runoffs is heavily relying on the interpretation of previous observations [3]. As a result, mainstream studies are more interested in the percentage reduction of TN, TP and TSS, other pollutants such as heavy metals are less discussed in the literature.

Therefore, the effectiveness of CWs in treating heavy metal pollutants are impeded as these are not included in the BPM Guidelines and by data scarcity because water quality monitoring covering the full spectrum of pollutants is often financially demanding [4]. However, the enhancement of metal pollutants in the freshwater environment will largely depress the development of aquatic species. Hence, it is essential to develop a cost-effective method to infer the metal concentration and predict its removal rate by establishing correlations between heavy metals and TN, TP and TSS.

Existing literature has suggested that heavy metal concentrations are related to the TN content [5]. Furthermore, the mechanisms of heavy metal removal in CWs are largely related to chemical precipitation and sedimentation, hence, removal of TSS will improve the reduction of heavy metals. However, the relationships are yet to be confirmed. Hence, this study aims to holistically assess the treatment effectiveness of CW and investigate the correlation between the common pollutants and heavy metals using water quality data from an established CW in Melbourne, Australia.

2. Study Area

Marie Wallace CW was constructed in 2015 and in a catchment classified as mixed industrial, residential and commercial land uses. The wetland is in the North-Western side of Marie Wallace Reserve in Bayswater, Victoria. The south side of the wetland is connected to a playground and the Dandenong Creek walking trail seals the east side (Figure 1). In addition to treating stormwater runoffs before entering Dandenong Creek, Marie Wallace CW also provides recreational values to the public.

The design of Marie Wallace CW follows a simple free water surface flow design, where the pond is shallow and vegetated with emergent plants. The inflow firstly meets a 154 m^3 sediment pond, followed by 2400 m^2 dry creek bed embedded with quarry rock to slow down flow rate and extend the detention period. The area backing up the sediment pond is densely vegetated and constantly filled with water. The average precipitation of this region ranged from 850 to 1100 mm [6] and the wetland is designed to endure a 5-year ARI (1665.5 L/s flow rate) with a retention of 39 hours. It is designed to receive and treat stormwater runoffs from an 11ha catchment with approximately 90% impervious surfaces.

Fig1. Marie Wallace Constructed Wetland

During the operation of Marie Wallace CW, inspections are performed monthly by the owner Knox City Council to ensure no blockages are observed at the inlet and outlet. Vegetation enhancement is also highly valued by the owner as weed control and infill planting are also part of the routine inspection. As a result, the water is covered up by dense vegetation from an aerial point of view.

3. Methods

3.1 Field Sampling

Water sampling was carried out at Marie Wallace between 2017 and 2019. Seven water samples were collected in August and September 2017 and another three water samples were collected in April and May 2019. Water samples were collected in both dry and wet weather and when the precipitation ranged from 0 to 6.8mm.

Water samples were collected at the inlet and the outlet of the wetland. The collected water samples were sent to an independent laboratory within 24 hours of collection for testing for levels of TN, TP, TSS and 24 trace metals. Test results were then evaluated against Australian & New Zealand Guidelines for Fresh & Marine Water Quality [7] as well as the Australian Drinking Water Guideline [8]. In detail, the concentrations of the pollutants are compared against the 95% trigger value for the protection of the ecosystem

3.2 Statistical Analysis

Statistical analysis was performed using RStudio. Spearman's rank correlation was used to examine the relationships between different pollutants. Spearman's rank correlation is a non-parametric test, which does not assume linear relationships. The correlation coefficient ρ varies from -1 to 1, with -1 indicating an absolute negative correlation between different parameters, whereas 1 shows a 100% positive correlation. 0 on the other hand returns no association. The closer the data is to 1, the stronger the correlation is. For the interpretation of the results, a strong correlation is to be observed when ρ is greater than -0.6 or 0.6. When the coefficient reached -0.8 or 0.8 and above, a more vigorous association will be reported [9].

It should be noted that the three common pollutants and 24 trace metals are only tested in three samples collected in 2019, thus, correlation analysis was only performed on the samples collected at that period.

4. Results and Discussion

4.1 Pollutant Concentrations

Table 1 recorded the average pollutant concentrations from the inlet and the outlet at all sampling periods and percentage reductions of TN, TP, TSS and common metal pollutants found in stormwater. It is evident that the wetland failed to meet the treatment objectives for TN and TP as the reduction rate fell well below 45%. In the meantime, the wetland removed a significant amount of TSS (>75%), nevertheless, the performance is considered unsatisfactory when compared to the 80% reduction target. Unfortunately, the trigger values of the above pollutant are not discussed in the Australian freshwater quality guidelines[7]. It is a concern that the actual performance of the wetland is not matching the design, more importantly, the impact of the three common pollutants should not be only assessed as a form of percentage reduction, even if the treatment objectives are met, it is highly likely that the outflowing water still contains excessive pollutants.

Meanwhile, the removal of metal pollutants in Marie Wallace CW ranged from -85.7% to 77%, where the reduction of Fe is the most significant whilst Cu and Mn concentrations remained almost unchanged. In addition to complex mechanisms, it would be difficult to infer if there are no treatment objectives for heavy metals. Moreover, the treatment outcomes vary significantly among existing literature. For instance, the efficiency of CWs in removing Zn ranges from 18% [10] to 65% [11], Nonetheless, the percentage reduction of Zn in Marie Wallace CW is comparable to the average Zn removal rate discussed by Ghermandi, et al. [12].

However, it is worth noting that stormwater wetlands are generally effective in treating Cu, many studies have reported over 50% of Cu removal [10, 13-15]. In the meantime, the efficiency of Marie Wallace CW is largely questioned when the mean percentage reduction for Cu and Mn became negative in 2019 compared to 2017, where the pollutant concentrations at the outlet exceeded the inlet. Considering the wetland had been operating since 2015 and the sediments were not removed, it is likely that the background concentration accumulates over time, hence higher pollutant concentrations were observed at the outlet.

Table 1: Pollutant Concentration in Marie Wallace CW

Pollutants	Mean Concentration (m/L)	% Reduction	Treatment Objectives	Trigger Value
TN	0.756	0~43.33	45%	ID
TP	0.061	-20~32.84	45%	ID
TSS	4	-66~77	80%	ID
Zn	0.042	-85.7~42.9	N/A	0.008
Al	0.338	20~60.87	N/A	0.055
Cu	0.002	0~25	N/A	0.0014
Fe	0.985	-78~73	N/A	0.3*
Mn	0.345	-53~44	N/A	1.9

* Australian Drinking Water Guideline [8].

Although Marie Wallace CW as well as other established CWs are capable of reducing TN, TP and TSS, existing literature often fails to address the importance of maintaining the water quality under an acceptable threshold. It is evident that the mean concentrations of the metal pollutants in the studied wetland almost all exceeded the trigger value of the Australian Freshwater Quality Guideline, indicating that a potential impact on the aquatic environment. Similarly, many CWs serving industrial catchments are experiencing metal pollutions [16, 17]. If a great number of the established CWs suffer from excessive metal concentrations, the BPMs and the design guidelines should also include treatment objectives for heavy metals considering their environmental impacts on water quality and marine environment.

4.2 Correlation between TN, TP and TSS

The correlation between the measured pollutants at the inlet and the outlet are performed separately and illustrated in Figure 2 and Figure 3**.**

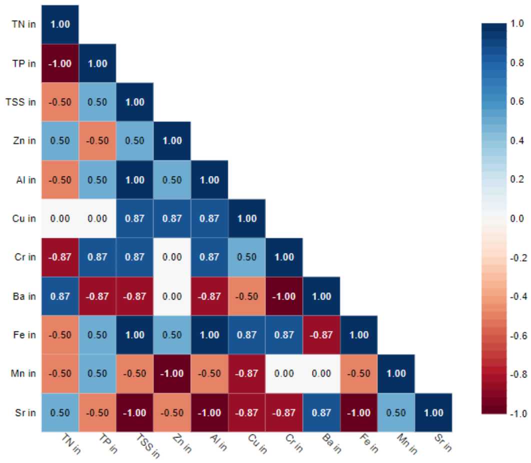

Fig2. Correlations Between Pollutant at the Inlet

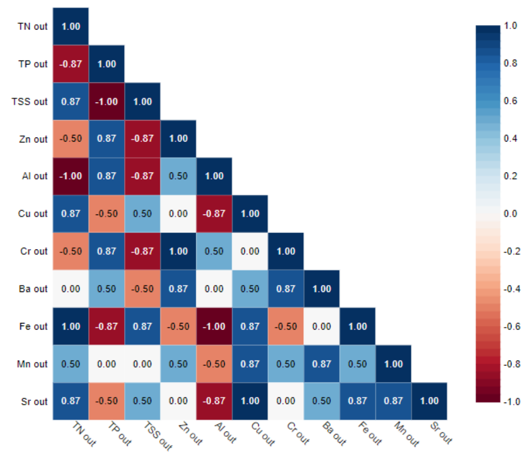

Fig3. Correlations Between Pollutant at the Outlet

It is worth noticing that the incoming TN and TP concentrations are 100% negatively correlated, hence a high concentration of TN measured at the inlet of Marie Wallace CW, resulted in a low concentration of TP.

At the outlet, TN has a less strong negative correlation with TP (ρ=-0.87) compared to the correlation at the inlet. TSS at the outflowing water is now highly correlated with the concentration of TN (ρ=0.87), consequently, the reduction of TSS at the outlet will result in the reduction of TN concentration.

4.3 Correlation between TN, TP, TSS and Metal Pollutants

At the inlet of Marie Wallace CW, TN displayed a negative strong correlation with Cr (ρ=-0.87) and a positive correlation with Ba (ρ=0.87). On the contrary, the relationships between TP, Cr and Ba are positive. Meanwhile, TSS demonstrated very strong positive correlations between Al (ρ=1), Cu (ρ=0.87), Cr (ρ=0.87) and Fe (ρ=1), whereas strong negative associations are found between TSS and Ba (ρ=-0.87) and Sr (ρ=-1). Considering sedimentation is a major pathway for metal removal in CWs, strong correlations are expected between TSS and metal pollutants. The results are supported by Li, et al. [18] and Environment Protection Authority Victoria [19].

Regarding the correlation among metal pollutants at the inlet, significant positive associations are discovered between Zn and Cu, Cu and Al, Al and Cr (ρ=0.87), whilst negative correlations are found between Mn and Zn, Mn and Cu, Ba and Fe (ρ=-0.87).

At the outlet, TN has a less strong negative correlation with TP (ρ = -0.87) and Al (ρ = -1), and a stronger positive correlation with TSS (ρ = 0.87), Fe (ρ = 1) and Sr (ρ=0.87). TP at the outlet again showed more associations with the metals, positive and strong correlations are found between TP, Zn, Al and Cr (ρ=0.87). Similarly, TSS at the outlet displayed more negative correlations with Zn, Al and Cr (ρ=-0.87).

Concerning the metals, Zn at the outlet of Marie Wallace CW illustrated a strong bond between Cr and Ba(ρ>=0.87)., whereas Al is heavily and negatively correlated with Cu, Fe and Sr (ρ>=-0.87). Cu at the outlet does not correlate with Cr and more positive correlations with Fe, Mn and Sr Ba(ρ>=0.87).

5. Conclusion

Based on the analysis of the available water quality samples from Marie Wallace at Melbourne, Australia, it can be concluded that the CW performs poorly in terms of reducing TN, TP and TSS levels as per the BPM Guidelines treatment objectives. The mean concentrations of the metal pollutants well exceeded the Australian water quality guideline.. To advocate a more holistic performance assessment and alleviate the financial burden of field monitoring, this study also attempted to investigate the relationships between different pollutants. It is found that different correlation trends were shown shown at the inlet and the outlet of the Marie Wallace CW. It is therefore recommended that further investigations be undertaken to confirm the relationships between the common pollutants and the metals, as well as among the metal pollutants. pollutants.

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