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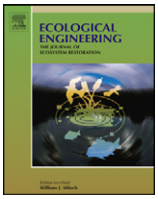

Floating treatment wetland retrofit to improve stormwater pond performance for suspended solids, copper and zinc

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ABSTRACT

A field trial study with side-by-side monitoring of two parallel stormwater treatment ponds, one of which contained a floating treatment wetland (FTW), has been carried out to assess the benefit of retrofitting a conventional retention pond with a FTW. Inflow and outflow event mean concentrations (EMCs) were quantified and used to assess the overall pollutant removal efficiency of each system. Findings show that a FTW can significantly improve the runoff water quality and thus reduce the impact on the receiving environment. The present study reveals that a pond retrofit with a FTW would be more efficient than a conventional retention pond, exhibiting a 41% (for total suspended solids – TSS), 40% (for particulate zinc – PZn), 39% (for particulate copper – PCu) and 16% (for dissolved copper – DCu) lower effluent EMC. Physical entrapment of the particulate pollutants into the roots' biofilm seems be a significant removal pathway, which could be impacted by the inflow volume. Due to higher humic content, lower dissolved oxygen and more neutral water column pH induced by the FTW, there was increased potential for adsorption processes and/or precipitation as insoluble copper sulphides, in addition to the direct Cu uptake by the plants. The dissolved zinc (DZn) inlet EMCs, which already met the Australian and New Zealand Environment Conservation Council (ANZECC) water quality guidelines and could correspond to an irreducible concentration of the system, were too low to differentiate the performance of either pond.

1. Introduction

Constructed wetlands and retention ponds are practices widely used to reduce the impact of nonpoint source pollution from stormwater runoff on the environment. Nevertheless retention basins generally provide limited efficiency regarding dissolved contaminants, being more efficient at removing coarse, particulate-attached forms (Van Buren et al., 1996). On the other hand, wetland vegetation provides removal mechanisms for soluble pollutants or finer particles (Bavor et al., 2001) but usually require larger areas and show limited tolerance for extended periods of high water levels. A novel approach, the floating treatment wetland (FTW), offers a solution able to overcome these disadvantages. A FTW is a vegetated device typically installed on the surface of a pond (Fig. 1). The matrix composing the mat of the FTW is made of recycled polyethylene terephthalate (PET) and expended foam which provides buoyancy. Plant roots grow through the fibrous matrix to reach the underneath of the mat and hang into the water column (Fig. 2). A FTW is suitable for new construction or retrofit installation.

There are limited published data on FTW applications in stormwater systems and monitored at full scale (Headley and Tanner, 2012). Previous studies have identified the nutrient removal capability of FTWs (Stewart et al., 2008; Hubbard, 2010; Van De Moortel et al., 2010; De Stefani et al., 2011). These studies mainly reported the nitrogen and phosphorus removal efficiency for influent concentrations ranging from 6 to 230 mg/L total nitrogen (TN) and 0.5 to 30 mg/L total phosphorus (TP). These values are significantly higher than the typical urban stormwater runoff concentrations (median of inlet event mean concentrations (EMCs) ranging from 0.75 to 2.37 mg/L TN and 0.11 to 0.36 mg/L TP

Abbreviations: FEP, fluorinated ethylene propylene; std. dev., standard deviation; ADP, antecedent dry period; AMA/NZTA, Auckland Motorway Alliance/New Zealand Transport Agency; BMPs, best management practices; DCu, dissolved copper; DI, de-ionized; DZn, dissolved zinc; EMC, event mean concentration; FSO, full scale output; FTW, floating treatment wetland; IANZ, International Accreditation New Zealand; ICP-MS, Inductively Coupled Plasma Mass Spectrometry; MDL, method detection limits; MRE, mass removal efficiency; PCu, particulate copper; PM, particulate matter; PP, polypropylene; PT, pressure transducer; PZn, particulate zinc; SH, State Highway; TCu, total copper; TSS, total suspended solids; TZn, total zinc.

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Fig. 1. FTW on the surface of a retention pond which is the experimental site of the present study – left: conventional (Control in this study) pond, right: FTW pond, foreground: inlet forebay.

(Geosyntec Consultants Inc and Wright Water Engineers Inc 2012)). Two mesocosm studies addressed metals' treatment for concentrations similar to stormwater runoff. Tanner and Headley (2011) reported efficiencies up to 65–75% for Cu and 40% for Zn after 7 days, while Van De Moortel et al. (2010) did not observe any significant improvement in the presence of FTWs. There is thus a need to assess FTWs performance for metals treatment in stormwater runoff at a full scale.

This paper summarizes the findings of a field study with side-by-side monitoring of two geometrically similar retention ponds, one of which contained a FTW with fully developed vegetation (Fig. 1). During storm events, inflow and outflow event mean concentrations (EMCs) were quantified and used to assess the overall pollutant removal efficiency of each system. EMCs and factors such as flow ratio (runoff inflow volume/permanent pool volume of the pond), water column temperature and antecedent dry days were investigated to try to identify common influences on pollutant removal. This paper focuses on total suspended solids (TSS), dissolved and particulate copper (Cu) and zinc (Zn) pollutant removal performance.

Fig. 2. Cut section of a FTW planted with *Schoenoplectus tabernaemontani*.

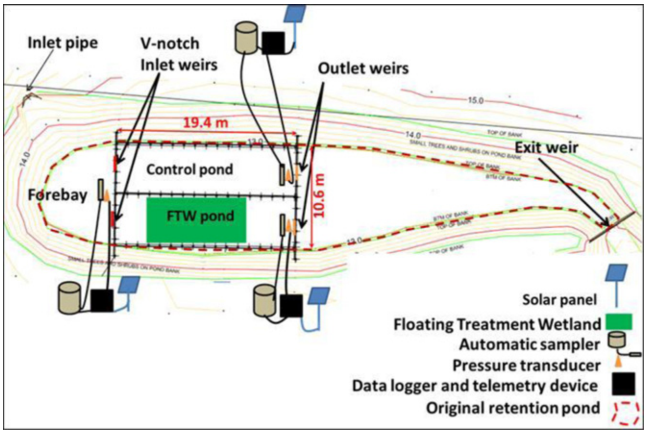

Fig. 3. Pond partitioning and instrumentation location.

2. Materials and methods

2.1. Experimental site

The experimental site is a stormwater retention pond located about 35 km north of Auckland, New Zealand, along a highway interchange (crossing of State Highway [SH] 1 and SH17), in Silverdale. This pond primarily serves a water quality function (rather than peak flow control). The pond is expected to receive 330 m^3 of stormwater runoff during the design storm event for water quality treatment (28.3 mm rainfall over 24 h (Auckland Regional Council, 1999, 2003)). The catchment is approximately 1.7 ha (75% impervious) comprising the south bound on-ramp and a section of the full carriageway width of SH1, including shoulder and grass berms.

The retention pond has been bifurcated into straight-walled parallel sections (~100 m^2 each) with a permanent water depth of 0.75 m, in order to allow a side by side study. The forebay (~100 m^2) is common to both sections and has a permanent pool of 1.09 m (Fig. 3). Each partition section functions as a plug flow system, no inflow is expected during dry weather, and no infiltration is expected due to thick clay on the bottom. Inlets and outlets, and overall partition geometry have the same dimensions, inflows and outflows present similar hydrographs with same water volumes.

An approximately 50 m^2 (5.2 m × 9.75 m) FTW planted with 863 *Carex virgata* (~17 plants/m^2) was installed on the 8 December 2010 (summer in the Southern Hemisphere) in one partition (FTW pond) while the other partition (Control pond) serves as a control. The FTW extends fully across its section's width. The plants were 1 l specimens.

2.2. Hydrologic monitoring

Three pressure transducers (PT) (INW AquiStar® PT12, 3 m range, accuracy: ±0.1% full scale output (FSO)), were installed to measure the water level. One PT was located in the forebay, just upstream of the inlet weirs, and one upstream of each outlet weir (Fig. 3). PT measurements coupled with the standard equation for a fully contracted sharp-crested 90° V-notch weir (Bos, 1989) were used to calculate inflows at 2 min intervals.

Due to a leak in the outlet walls of both ponds, implying that part of the outflows were released through the leakage rather than the

V-notch weir, hydrologic routing was used to calculate outflows with Eq. (1) (Chanson, 2004):

$$\frac{dS(t)}{dt} = Q_{in}(t) - Q_{out}(t) \tag{1}$$

where

S: storage in the partition section = partition area × water level in the partition section,
$Q_{in}(t)$: inflow of the partition section,
$Q_{out}(t)$: outflow of the partition section.
t: time

Since each partition section is rectangular with vertical walls, outflow for each section/pond was determined using the inflows, the partition section's area and the variation in water depth over 2 min intervals as per Eq. (2):

$$Q_{out}(t) = Q_{in}(t) - A \times dh(t)/dt \tag{2}$$

where

A: partition section surface area
$h(t)$: water level in the partition section at time t

The "flow ratio" was calculated as the ratio of the runoff inflow volume to the permanent pool volume of the pond.

2.3. Storm events sampling and analysis

The sampling program started after six months of plant growth and lasted over a period of 1 year (May 2011–June 2012), during which 17 storm events were sampled. Three ISCO 3700 automatic samplers connected to fluorinated ethylene propylene (FEP) lined polyethylene tubing (3/8 inch internal diameter, Jensen Inert product) were installed in the forebay and upstream of each outlet weir to collect storm event samples (Fig. 3). The samplers were driven by three Iquest DS4483 data loggers. Three solar panels (SX 310, 10 W, BP Solar) provided energy to each data logger and sampler. Individual (discrete) samples were collected over the duration of the storm hydrograph. A maximum of 24 one litre bottles per storm were collected at each sampling location. Within 24 h of each storm event, the collected samples were transported to the University of Auckland laboratory to make flow-weighted composite samples which were sent immediately for analysis to an external laboratory. Composite samples were made from 8 to 96 aliquots (average of 33 for the inlet and 15 for the outlets) representing at least 63% of the runoff hydrograph with an overall average for all storm events of 88%.

The polypropylene (PP) sampling bottles used in the automatic samplers were soaked in diluted Decon 90 detergent overnight, rinsed with tap water, then rinsed with 1:1 hydrochloric acid (37%, Instra-analysed J.T. Baker) followed by 1:1 nitric acid (70%, Instra-analysed J.T. Baker), and finally rinsed three times with de-ionized (DI) water.

Flow-weighted composite samples were analysed by Watercare Ltd. (Auckland, New Zealand), an International Accreditation New Zealand (IANZ) accredited laboratory. The analysis of each composite sample gave the event mean concentrations (EMCs) for each sampling station. Analytical methods are presented in Table 1.

Particulate copper (PCu) and particulate Zinc (PZn) concentrations were calculated by subtracting the dissolved form to the total element concentration. Zinc and copper are primary contaminants of concern from urban runoff for Auckland's receiving environments (Timperley et al., 2005). Dissolved copper and zinc were found to be the primary cause of toxicity in highway runoff tested for five fresh water and marine species (Kayhanian et al., 2008). Hardness was measured at the outlet of both ponds for 5 storm events collected across the entire monitoring period. Results were reported within 20% accuracy. For the purposes of determining Australian and New Zealand Environment Conservation Council (ANZECC) Cu and Zn freshwater trigger values for species' protection (ANZECC and ARMCA, 2000), the limited accuracy does not influence the interpretation of results.

2.4. Data analysis

The overall system efficiency is assessed for each individual storm event by calculating the pollutant mass removal efficiency (MRE) as per Eq. (3):

$$\text{MRE}\,(\%) = \frac{(V_{in} \times EMC_{in}) - (V_{out} \times EMC_{out})}{V_{in} \times EMC_{in}} \times 100\% \tag{3}$$

where V_{in} and V_{out} are volume of runoff in and out, respectively, and EMC_{in} and EMC_{out} are event mean concentrations of inlet and outlet samples, respectively. When EMCs were below the MDL, the MRE was calculated using the MDL value.

Table 1
Analytical methods.

Parameters	Analytical methods	Method detection limits (MDL)
Total copper (TCu) and total zinc (TZn)	Digestion: Method 3030 E (APHA, 2005) – modified to allow automated digestion process using a Hotblock® rather than hotplate and with a nitric/hydrochloric acid digest (4:1 ratio).	TCu: 0.0002 mg/L
	Analysis: Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in accordance with EPA method 200.8 (USEPA, 1994) modified to use reaction cell to minimize interferences. No laboratory fortified blank analysed but laboratory fortified samples. Analysis of second source calibration standards each 12 samples instead of 10.	TZn: 0.001 mg/L
Dissolved copper (DCu) and dissolved zinc (DZn)	Filtered according to Method 3030 B (APHA, 2005) – modified to acidify to 10 mL HNO_3/L of sample to match standard/control acid concentration used during subsequent analysis.	DCu: 0.0002 mg/L
	Analysis: Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in accordance with EPA method 200.8 (USEPA, 1994) modified to use reaction cell to minimize interferences. No laboratory fortified blank analysed but laboratory fortified samples. Analysis of second source calibration standards each 12 samples instead of 10.	DZn: 0.001 mg/L
Total suspended solids (TSS)	Method 2540 D	1 mg/L
Hardness ($CaCO_3$)	Ca and Mg determined by ICP-MS in accordance with EPA method 200.8 (USEPA, 1994) modified as above. Hardness calculation as per method 2340 B (APHA, 2005)	0.03 mg/L

The water quality data of each pond were compared to quantify performance enhancement induced by the FTW. The data were statistically analysed to compare paired influent and effluent concentrations, paired FTW pond effluent and Control pond effluent concentrations and paired FTW and Control ponds MREs. The difference between each set of paired data was tested for normality using the Shapiro–Wilk test. If data were normally distributed, a paired Student's *t*-test was performed. Otherwise, a Wilcoxon signed rank test was used.

Correlation analysis between each element EMCs, antecedent dry days, water column temperature and flow ratio was performed with a Pearson test, if data distributions were normal or lognormal, otherwise a Spearman test was used. Each significant correlation was graphically verified with scattered plots. Only useful significant correlations are discussed in the text. All tests were achieved using the software SPSS statistics 19 (IBM).

2.5. Plant biomass measurement

Plant biomass measurement was performed each three months to assess the vegetation establishment. Eleven removable 30 cm × 30 cm squares of the planted mat inserted into an enamel coated aluminium frame were incorporated into the FTW (Fig. 4) to allow easy access to measure roots. These removable inserts utilized the same matrix materials as the remainder of the FTW and were planted with a single *Carex virgata* plant.

Shoots and roots measurements were performed 8 times: the day the FTW was installed and then approximately each 3 months. The maximum shoot and root length were measured for each plant pot from the upper (for shoots) and lower (for roots) surface of the mat. As per Tanner and Headley (2011), the length below which about 90% of roots and shoots occurred was reported as the majority length. Shoots and roots density was estimated by counting the number of shoots and roots per plant (one plant per insert).

2.6. Water column pH and temperature measurement

pH was periodically measured concurrently with the plant sampling in both ponds to assess the impact of the FTW on this parameter and possible impact on pollutants' availability. Water column pH measurement was performed on 8 occasions: one week after the FTW was installed and then approximately each 3 months, always at similar time in the morning. Ten tubes (FEP lined polyethylene tubing, 1/8 inch internal diameter, Jensen Inert product) were inserted permanently into the FTW mat in five different locations to reach the underneath water column at two different depths (just below the FTW ~ 10 cm depth and at 40 cm depth). Connected to a peristaltic pump (Model 410, Solinst, 40 mL/min and up to 900 mL/min), these tubes allowed water sampling from the embankment of the pond. pH was measured using a multiparameter probe (YSI 556 MPS) while pumping the water at low flow rate. Water in the tube was purged before each measurement to discard the water which could have been present in the tubing prior pumping. Measurements in uncovered areas (close to the inlet and outlet weirs of both ponds and in the middle of the Control pond) were performed directly in the ponds by sinking the multiparameter probe in the water at 10 and 40 cm depth. Continuous temperature monitoring was carried out below the FTW and in the Control pond at same depth at 15 min intervals using a D-Opto logger (Zebra-Tech Ltd, Nelson, NZ).

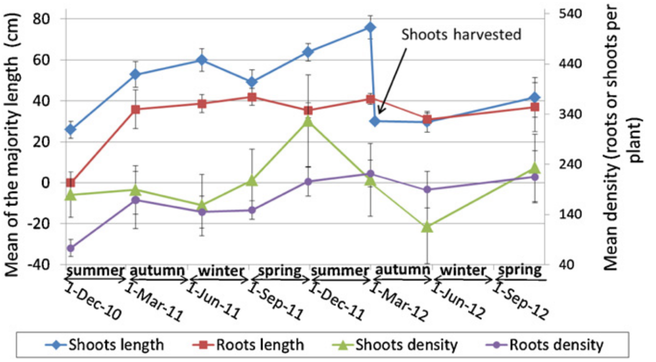

Fig. 5. Mean and standard deviation of roots and shoots length and density over time (first measurement $n = 6$, other measurements $n = 11$).

3. Results and discussion

3.1. Plant biomass

Fig. 5 presents the evolution of the plant biomass over the monitoring period. The FTW was planted in early summer, December 2010, which allowed a fast growth of the above and below mat vegetation (Fig. 5). The biomass stopped increasing after the end of the first summer and some die back occurred during autumn. While root density seems to follow a seasonal pattern with an increase in spring and summer and a decrease in autumn and winter, the root length remained relatively consistent after the first summer, fluctuating around an average of 37 cm. Rapid shoot biomass growth over spring resulted in dense vegetation beginning December 2011. At the end of summer (February 2012) some plants started to die,

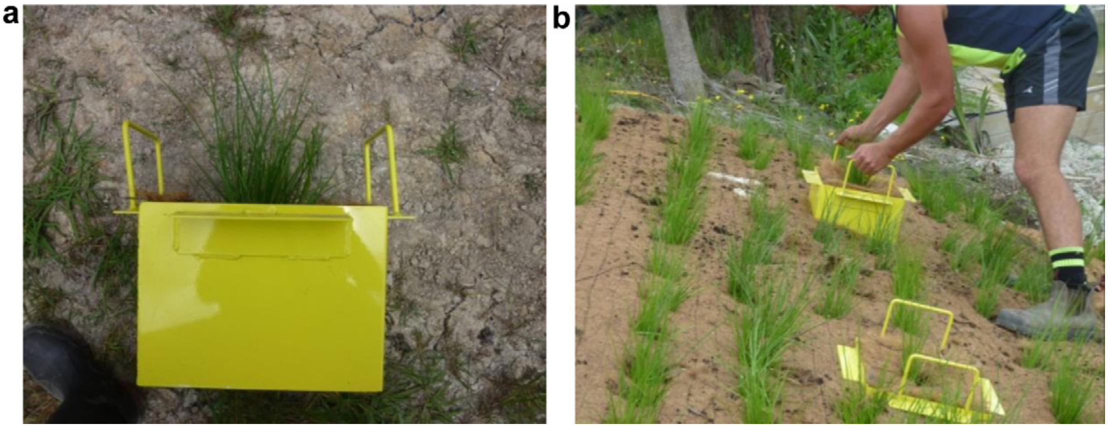

Fig. 4. Removable plant inserts: (a) side view, (b) setting up of the insert.

resulting in a drop of the shoot density. Severe deoxygenation beneath the mat over summer (Borne et al., submitted) producing toxic conditions due to anaerobic processes (Lamers et al., 1998; Reddy and Delaune, 2008) appears to be the most plausible cause of the die back. Shoots were harvested in the beginning of March 2012 and dead shoots were taken off the FTW. Plants slowly re-established in scattered areas. In order to speed up the re-establishment, the areas which were free of shoots were re-planted mid July 2012.

3.2. Suspended solids

Seventeen storm events were sampled successfully for all sampling stations and one additional event was collected only for the outlets. Outlet TSS EMCs were less than the inlet EMCs during most events (Fig. 6); however 6 storms in the Control pond showed net export of TSS. This suggests that resuspension is more likely to occur in a conventional stormwater pond than in a pond retrofit with a FTW. The reduction of resuspension has already been highlighted by Huang et al. (2007) in a lake covered by floating macrophytes.

The inlet EMCs (Fig. 6) are consistent with data recorded in the Auckland region which ranged from 8.8 to 100.8 mg/L (median values of samples collected at four different sites on main roads in the Auckland region (Moores et al., 2009)). In the absence of locally relevant guidelines, TSS EMCs are compared to the European Union (EU) Directive 2006/44/EC providing guidelines to support fish life in fresh water (European Parliament, 2006). Both ponds median outlet EMC met the recommended 25 mg/L. TSS outlet EMCs of the FTW system were significantly lower than the Control pond outlet EMCs with $p < 0.0001$. The FTW system showed significantly higher TSS MRE than the Control pond ($p = 0.0001$), clearly due to the cleaner effluent from the FTW pond.

TSS outlet EMCs were positively correlated with the flow ratio with a stronger correlation for the FTW pond ($r = 0.858$, $p < 0.0001$) compared to the Control pond ($r = 0.761$, $p < 0.001$ – Fig. 7). Two storm events were excluded from this correlation analysis as their associated flow ratios were outliers. Outlet EMCs of the FTW system is thus more strongly linked to the runoff volume than a conventional retention pond.

Visual inspection of the roots revealed that a substantial amount of TSS was trapped into the roots' biofilm (Fig. 8), which suggests it might be a significant removal pathway. A large inflow volume would either reduce the capability of roots to efficiently trap incoming particles or wash off part of the sediments already trapped. Greater inflow volume would thus reduce TSS treatment performance, as observed with generally increasing outlet EMC with increasing flow ratio. Nonetheless the FTW pond always showed lower outlet EMCs than the Control pond. No correlation was established between inlet and outlet TSS EMCs of either system which means that for an influent ranging from 19 to 89 mg/L TSS, the performance of either pond is mostly driven by the flow volume and probably the hydraulic efficiency of the ponds. Hydraulic efficiency is a measure of how well the available detention storage is used and increases by limiting short-circuiting and promoting good distribution of the inflow. High hydraulic efficiency provides appropriate conditions promoting the necessary biological and chemical processes for stormwater treatment (Persson et al., 1999). The study site ponds likely have different hydraulic efficiencies as the physical presence of the FTW close to the inlet might increase the distribution of the inflow and thus improve pollutant removal.

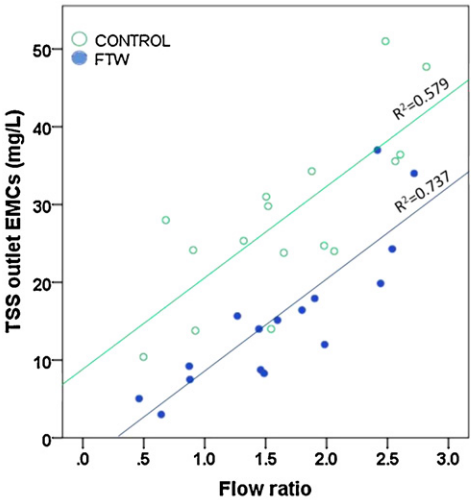

Fig. 7. TSS ($n = 16$) outlet EMCs depend on the flow ratio.

In the present study the FTW pond exhibited a 41% (median of the % difference between paired outlet EMCs) lower TSS outlet EMC, regardless of the inlet concentration. While TSS treatment performance of the FTW pond reduced with increasing runoff volume, it still remained more efficient than a conventional retention pond. This suggests that retrofitting a conventional retention pond with FTWs can markedly improve its TSS removal performance.

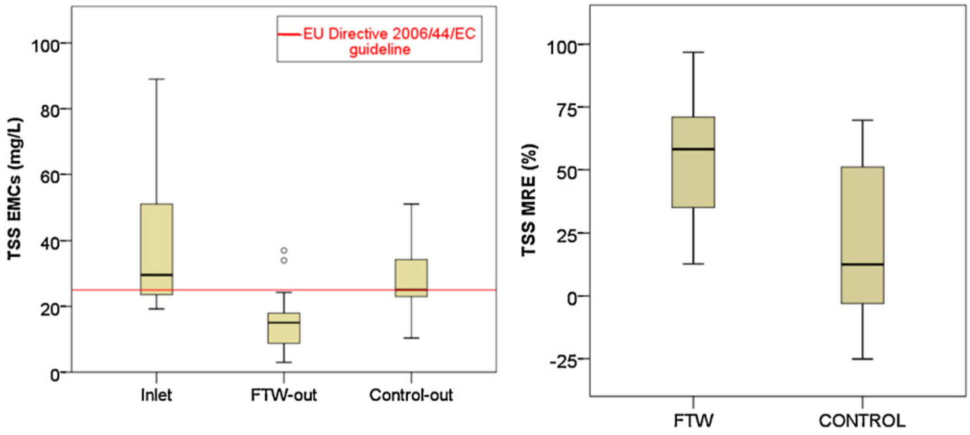

Fig. 6. Total suspended solids event mean concentrations ($n = 17$ for inlet and $n = 18$ for outlets) and mass removal efficiency ($n = 17$).

Fig. 8. Solids trapped into roots' biofilm.

3.3. Heavy metals

3.3.1. Zinc

Over 17 storm events, total zinc (TZn) outlet EMCs of both ponds were below the inlet EMCs except for two storms for the Control pond. TZn inlet median EMC (0.035 mg/L) was in the lower range of the median concentrations (0.034–0.125 mg/L) monitored at four different road sites in the Auckland region (Moores et al., 2009). Similarly to most of the sites monitored by Moores et al. (2009), zinc was mainly in particulate form, which represented 74, 71 and 62% (median values) of total zinc, for the influent, the Control and FTW ponds effluents respectively (Fig. 9). PZn outlet EMCs were significantly lower than influent EMCs ($p < 0.0001$) for both ponds. PZn MREs were significantly ($p < 0.0001$) higher for the FTW pond (median of 65%) than the Control pond (median of 40%).

DZn inlet EMCs were very low, with the median inlet EMC actually meeting the ANZECC trigger value of 8 μg/L (ANZECC and ARMCA, 2000) for the protection of 95% of the species for soft water (the most restrictive hardness for freshwater) and could correspond to an irreducible concentration of the system. Based on several monitoring studies showing consistent outflow concentrations with relatively low variability within BMPs categories, the notion of irreducible concentrations reflects the limitations of a particular removal pathway utilized in a stormwater practice (Schueler, 1996) and has been supported by several researchers (Barrett, 2008; Kadlec and Wallace, 2009; Moore et al., 2011).

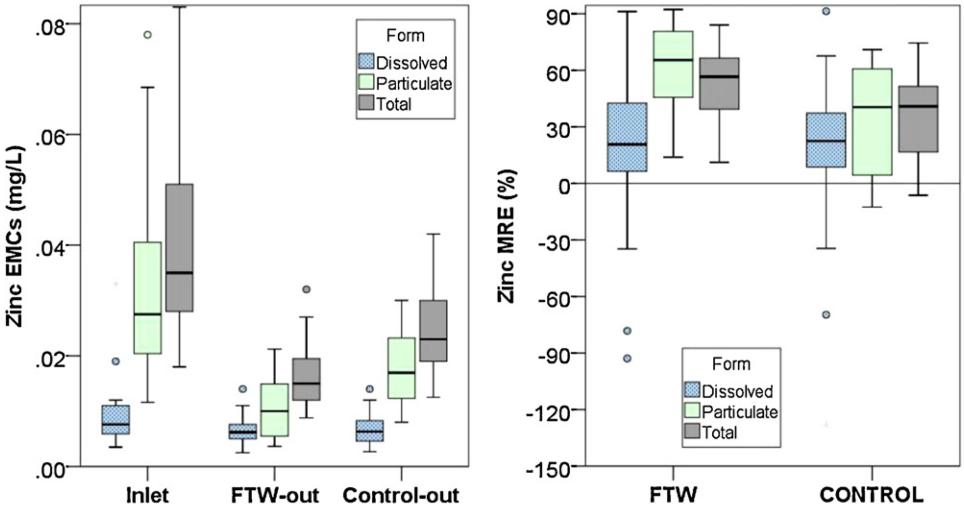

Fig. 9. Zinc EMCs and MREs for FTW and Control ponds ($n = 17$).

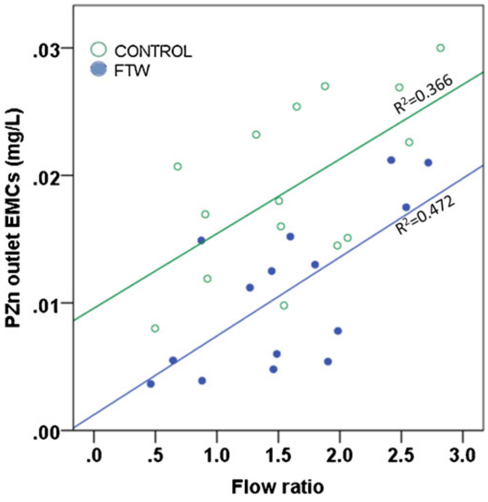

Fig. 10. PZn outlet EMCs depend on the flow ratio.

DZn inlet median EMC also met the 15 μg/L ANZECC trigger value for marine water for the protection of 95% of the species. As the incoming water was already relatively “clean”, little difference was discernible between the performances of either system. However a statistical difference was measured only between the inlet and outlet of the FTW pond ($p = 0.049$), suggesting perceptibly greater DZn removal in the FTW pond. Mesocosm experiments by Tanner and Headley (2011) showed that a FTW planted with *Cyperus ustulatus* was more efficient at removing DZn than a FTW planted with *Carex virgata*. Improved performance might thus be achieved with other species than *Carex virgata*.

The ratio of PZn to TZn EMCs at the outlet of both ponds increased with increasing water column temperature during a storm event ($r = 0.686$, $p = 0.002$ and $r = 0.589$, $p = 0.013$ for the FTW and Control pond, respectively). Warren and Zimmerman (1994) reported that water temperature was among the key variables influencing trace metal partitioning in an urban river with particulate form increasing with increasing temperature. DZn outlet EMCs of both ponds were also negatively correlated with the water column temperature ($r = -0.616$, $p = 0.008$ and $r = -0.709$, $p = 0.001$ for the Control and FTW ponds respectively) suggesting higher removal possibly through sorption on particles during warmest months (Stumm and Morgan, 1981). PZn EMCs were strongly positively correlated with TSS EMCs, for the inlet ($r = 0.844$, $p < 0.0001$) and outlets of the FTW pond ($r = 0.781$, $p < 0.001$) and the Control pond ($r = 0.833$, $p < 0.0001$). Therefore it is not surprising to see that PZn outlet EMCs of the FTW pond were positively correlated with the flow ratio, as for TSS, with a correlation coefficient of 0.687 ($p = 0.005$) (for the same reasons as TSS the same 2 storm events have been excluded from the correlation analysis – Fig. 10). PZn might follow the same removal pathway as TSS and might be trapped in the roots network. For the Control pond, TSS outlet EMCs had a weaker correlation with the flow ratio which results in a weaker correlation ($r = 0.605$, $p = 0.017$) of PZn outlet EMCs with the flow ratio. The Control pond which provided less PZn treatment, released higher outlet EMCs with increasing inlet EMCs ($r = 0.627$, $p = 0.007$) while no correlation was found for the FTW pond.

In the present study the FTW showed a 40% (median of the % difference between paired outlet EMCs) lower PZn outlet EMC than the control pond. While performance of the FTW pond reduced with increasing depth of storm, it still exceeded that of the pond without a FTW. This suggests that retrofitting a conventional retention pond with a FTW has the potential to significantly reduce PZn outlet EMCs.

3.3.2. *Copper*

Over 17 storm events, total copper (TCu) outlet EMCs of either pond were below the inlet EMCs except for 4 storms for the Control pond. TCu inlet median EMC (0.0092 mg/L) was lower than median concentrations monitored at four different road sites (range of 0.0153–0.025 mg/L) in the Auckland region (Moores et al., 2009). Unlike three of the four sites monitored by Moores et al. (2009), copper was mainly in dissolved form in the current study, which represented 59, 70 and 58% of TCu, for the influent, FTW and Control ponds effluents respectively (Fig. 11). Outlet PCu EMCs were statistically lower than inlet EMCs for the FTW pond only ($p < 0.0001$). PCu EMCs of the FTW system were markedly lower than the Control pond ($p < 0.0001$). PCu MREs were even significantly ($p < 0.0001$) higher for the FTW pond (median of 50%) than the Control pond (median of 19%) (Fig. 11). Outlet DCu EMCs were statistically lower than inlet EMCs ($p = 0.0001$ and $p = 0.027$ for the

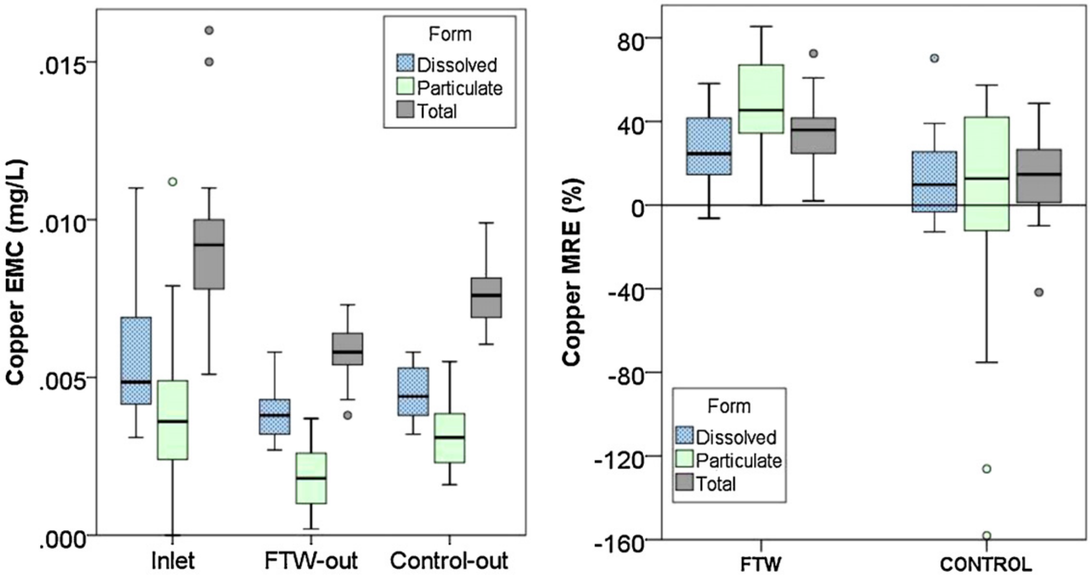

Fig. 11. Copper EMCs and MREs for FTW and Control ponds ($n = 17$).

FTW and Control ponds respectively). A statistical difference was not measured between outlet EMCs of both ponds at the beginning of the study (winter to spring 2011), while a statistical difference existed in the latter period (summer to autumn 2012) ($p = 0.014$). This suggests that DCu removal improved over time in the FTW pond, or during summer when temperatures were warmer. As for Zn, the ratio of PCu to TCu EMCs at the outlet of the FTW pond increased with increasing water column temperature during a storm event, nevertheless this correlation was weaker ($r = 0.544$, $p = 0.024$) (no correlation was found in the Control pond). The reason for this mediocre correlation is still unclear but could possibly result from the competitive sorption which can occur when several components are present in the solution (Polcaro et al., 2003). Other processes might be responsible for the noticeable improvement in the FTW pond and are discussed later. This increased DCu removal resulted in statistically overall better performance over the 1 year period with statistically lower outlet EMCs ($p = 0.008$) and higher MREs ($p = 0.006$) than the Control pond. The median hardnesses were 130 mg/L $CaCO_3$ (25–75th percentile: 76–165 mg/L $CaCO_3$) and 110 mg/L (25–75th percentile: 81–145 mg/L $CaCO_3$) for the FTW and Control pond respectively. DCu outlet median EMCs of the FTW and Control ponds met the ANZECC trigger values for the protection of 95–99% (i.e. 4.9–4.1 μg/L) and 90–95% (i.e. 4.9–4.5 μg/L) of the species in fresh water respectively (ANZECC and ARMCA, 2000). Both ponds' outlet median EMCs also met the trigger value for the protection of 80% of the species in marine water,8 μg/L.

Inlet PCu EMCs were less strongly correlated ($r = 0.606$, $p = 0.01$) with inlet TSS EMCs than was PZn ($r = 0.844$, $p < 0.0001$). PCu were correlated with TSS at the outlet of the Control pond only ($r = 0.628$, $p = 0.007$). This suggests that PCu and TSS followed somewhat different removal processes in the FTW pond. This might have occurred because copper might be bound to small particles with a diameter less than 1.2 μm, which were not recovered in the TSS analysis using a filter pore size of 1.2 μm. Several studies reported the association of copper with finer particles like colloidal organic matter and/or clay (Harrison and Wilson, 1985; McBride, 1994; Nelson et al., 2009; Bechet et al., 2010). Unlike TSS, PCu outlet EMCs were not correlated to the flow ratio, for either pond, but with PCu inlet EMCs, ($r = 0.686$, $p = 0.002$ and $r = 0.611$, $p = 0.009$ for the FTW and the Control ponds respectively). If trapped in the roots network and its associated biofilm, smaller particles might be less easily torn off by the flow than bigger particles like TSS. Indeed the latter might be less strongly attached and more easily settleable. This could explain the non-correlation of outlet PCu EMCs with the flow ratio. Settlement, usually responsible for particulate pollutant removal in conventional retention ponds, has somehow been limited for PCu, as evidenced by the mediocre treatment provided by the Control pond (no statistical differences between inlet and outlet EMCs). It is not surprising to see that inflow volume, impacting TSS settlement, did not have any effect on PCu removal in the Control pond. PCu and PZn EMCs were strongly positively correlated ($r = 0.766$, $p = 0.0003$) at the inlet of both systems and stayed strongly positively correlated for the Control pond outlet ($r = 0.795$, $p = 0.0001$) while a mediocre correlation appeared for the FTW outlet ($r = 0.545$, 0.024). This suggests that both metals probably followed similar removal mechanisms in the Control pond but different processes in the FTW pond. This could be explained by the different particle size distribution of both metals and the physical presence of the roots which might impact PCu and PZn differently.

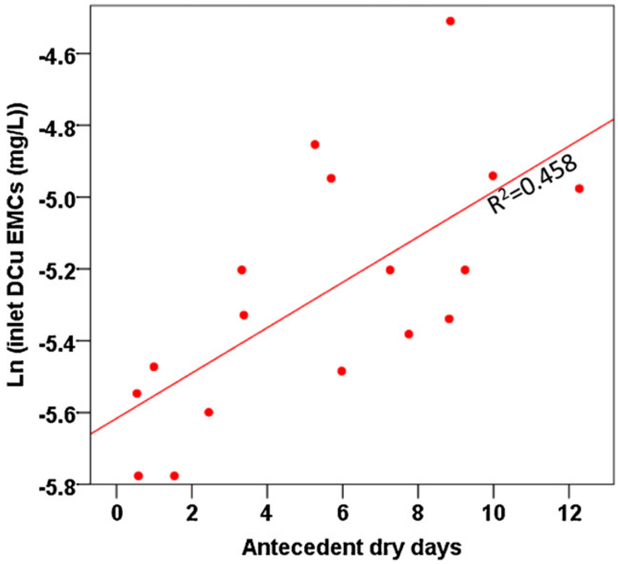

Fig. 12. Inlet DCu EMCs versus antecedent dry days.

Inlet DCu EMCs were positively correlated with outlet DCu EMCs especially for the Control pond as it provided less treatment ($r = 0.662$, $p = 0.004$ and $r = 0.831$ $p < 0.0001$ for FTW and Control ponds respectively). Inlet DCu EMCs were also correlated with the antecedent dry period (ADP) before a storm event ($r = 0.677$, $p = 0.003$, Fig. 12). Positive correlation between DCu runoff concentration from a highway and the length of the ADP was also observed by Hewitt and Rashed (1992). A longer dry period allows greater copper accumulation in the catchment which is washed off during a storm. The impact of antecedent dry period on pollutants built up on roads was reported in several studies, as summarized by Opher and Friedler (2010). Ying and Sansalone (2010a) reported that dry deposition particulate matter (PM) are transported and solubilised in runoff generating dissolved solids (TDS). Several leaching studies of dry deposition PM have demonstrated the potential of metals to be leached from the road sediments (Joshi and Balasubramanian, 2010; Munksgaard and Lottermoser, 2010; Ying and Sansalone, 2010b). The leaching of metals, from particulate-bound fraction in dry deposition on the roads into dissolved fraction in rainfall-runoff, is also influenced by factors such as pH value, ion exchange, aeration and agitation, and metal binding (Sansalone and Ying, 2008). These parameters might thus also have influenced Cu leaching, in addition to ADP. Part of the copper bound to dry deposition PM on SH1 may have become labile when transported in runoff resulting in a higher inlet fraction of dissolved copper than particulate copper.

While no correlation was found for the Control pond, a negative correlation appeared to exist between DCu outlet EMCs and PCu inlet EMCs for the FTW system ($r = -0.555$, $p = 0.021$). The outlet dissolved copper EMC of the FTW system decreased when a higher particulate copper EMC entered the pond. PCu entering the pond might have provided particles with adequate adsorption sites for dissolved copper. A high degree of copper adsorption occurs when the pH is nearly neutral, the particulate organic matter is high, and the concentration of solids is elevated (Grassi et al., 2000). Both ponds received the same amount of PCu but the more neutral water column pH induced by the FTW (mean of 7.34 (std. dev. 0.25) for the FTW pond and 8.25 (std. dev. 0.51) for the Control pond) might have provided better conditions for the adsorption of DCu in the FTW pond. The effect of FTW on water column pH was also reported by Van De Moortel et al. (2010) with a significant decrease between the control and FTW system. Although pH was measured only during dry weather, it was always lower in the FTW pond than the Control pond over the 8 missions which covered the entire monitoring period. Part of copper sorption occurs during dry weather period, in between storm events when no water enters the ponds, explaining the lower DCu outlet EMC leaving the FTW pond. The release of rhizodeposits (dead tissues, exudates, excretions and lysates) from roots hanging in the water can increase humic content of suspended particles and promote complexation and flocculation of dissolved metals (Neori et al., 2000; Mucha et al., 2008). The die back of the part of the plants in summer/autumn 2012 and associated release of organic compounds in the water column might have contributed to higher sorption of DCu in the FTW pond, which could explain the increased removal of DCu over this period. The noticeable lower dissolved oxygen in the water column below the FTW, from late winter to end of autumn (median of 1.1 mg/L) (Borne et al., submitted), could have provided adequate conditions for the formation of particulate metal sulphides (Reddy and Delaune, 2008; Kadlec and Wallace, 2009). Direct uptake of dissolved copper by the roots might have also contributed to copper removal in spring, during the growing season.

In the present study DCu and PCu outlet EMCs of the FTW pond were 16 and 39% (median of the % difference between paired outlet EMCs) lower respectively than the control pond outlet EMCs. PCu treatment performance of the FTW pond decreased with increasing inlet concentration while still being more efficient than a conventional retention pond. This suggests that retrofitting a conventional retention pond with a FTW has the potential to significantly lower DCu and PCu outlet EMCs.

4. Conclusion

A FTW improves runoff water quality and thus reduces the impact on the receiving environment. The present study showed that a pond retrofit with a FTW would be more efficient, with cleaner effluent than a conventional retention pond, exhibiting a 41% (for TSS), 40% (for PZn) and 39% (for PCu) and 16% (for DCu) lower outlet EMCs. The low DZn inlet EMC which already met ANZECC water quality guidelines and could correspond to an irreducible concentration of the system did not allow the performance of either pond to be differentiated. Nevertheless a statistical difference was measured only between the inlet and outlet of the FTW pond, suggesting perceptibly greater DZn removal in the FTW pond.

PCu and PZn seemed to respond differently to the hydrological condition of the pond probably due to their different particle size distribution. Unlike PZn, PCu was not easily settleable and was probably associated with finer particles like colloidal organic matter and/or clay (McBride, 1994; Nelson et al., 2009; Bechet et al., 2010). While both might be trapped into the sticky biofilm of the roots, outlet PZn, most likely associated with bigger particles than PCu, was positively correlated with the flow ratio, as for TSS. A large inflow volume would either reduce the capability of roots to efficiently trap incoming "big particles" or wash off some of the large particles already trapped into the roots biofilm. A greater inflow volume would reduce TSS treatment performance of a FTW while still being more efficient than the conventional retention pond. On the contrary, smaller particle size PCu was not correlated with the flow volume but with PCu inlet EMCs. Presumably less easily settleable, the flow had a lesser impact on PCu removal which might have been driven by the efficiency of the physical filter provided by the roots.

The better performance of the FTW pond for DCu might be attributed to the humic compounds released by the plants, and a more neutral pH and reduced oxygen concentrations induced by the FTW. These conditions can contribute to processes like adsorption and/or metal sulphides formation in addition to the direct uptake by the plants. The Zn and Cu removal processes thus seem to differ substantially. Physical entrapment into the roots' biofilm is thought to be a significant removal pathway for particulate contaminants which appeared to be reduced with large storms.

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