REMOVAL OF EMERGING CONTAMINANTS AND CONVENTIONAL POLLUTANTS BY A CONSTRUCTED WETLAND DURING THE FIRST YEAR OF ESTABLISHMENT

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ABSTRACT

Constructed wetlands can remove many pollutants from wastewaters, offering a cost-effective and energy-efficient treatment alternative for small communities, however, the size and time period over which wetland processes remain effective is unknown. Commissioned in June 2016, the pilot-scale Sewanee wetland receives lagoon-treated wastewaters from a rural community and employs native plants, sediments, microbes and photolysis zones for tertiary treatment. We compared concentrations of nitrogen (N), phosphorus (P), coliform bacteria and 14 pharmaceuticals and personal care products (PPCPs) in lagoon-treated wastewater before and after it flowed through the 0.25-ha wetland. Seasonal sampling revealed the wetland to be very effective at reducing N and *E. coli* bacteria for the first 12 months, but P reductions were not significant. By the second summer, removal of nutrients and bacteria started to decline. Pharmaceuticals and personal care products were also removed from lagoon treated water. Removal efficiencies for PPCPs were similar for all three seasons, but greater numbers of compounds were removed in the warmer months (autumn and summer). The greatest removal for individual compounds occurred in autumn, four months after commissioning. This study demonstrates that constructed wetlands can effectively reduce compounds not removed during conventional wastewater treatment, but vegetation must be managed to maintain and improve removal rates. Further research is needed to elucidate the roles of season, plant uptake and wetland size in pharmaceutical removal.

Keywords: *constructed wetland; nutrients; emerging contaminants; wastewater management*

1. INTRODUCTION

Wastewater treatment facilities may lack the infrastructure to effectively remove many wastewater contaminants, including conventional pollutants and emerging contaminants, such as pharmaceutical compounds and personal care products (PPCPs) [1]. Most PPCPs do not have established concentrations at which they are regulated nor are long-term environmental and human health risks well documented [1,2]. Some research indicates that constructed wetlands can efficiently remove many of these pollutants from wastewaters and offer a cost-effective and energy-efficient treatment alternative for small communities in rural areas and developing countries [3]. However, removal efficiencies can be very dependent on season, hydraulic retention time [4] and wetland size. Total nitrogen, ammonia, and nitrite have been shown to have removal efficiencies of 41%, 55%, and 61% respectively while total phosphorus removal is less efficient in CW with most long-term removal occurring in soil and peat accretion [5]. The objective of this study was to quantify seasonal removal rates of conventional pollutants and emerging contaminants during the establishment year of a small constructed wetland.

2. METHODS

The Sewanee Wetland is a pilot-scale constructed wetland that receives conventional lagoon-treated wastewaters from a small rural community in Tennessee. Commissioned in June 2016, the wetland consists of three cells, employing native wetland plants, sediments, microbes and photolysis zones for tertiary wastewater treatment (Figure 1).

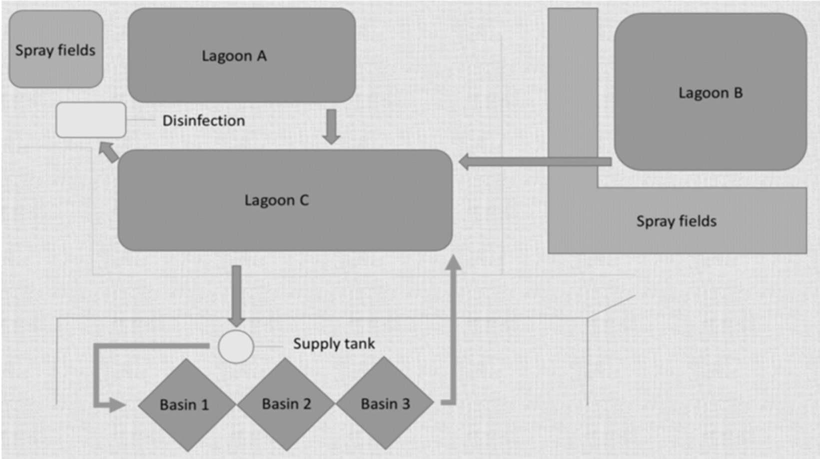

Figure 1. The conventional Sewanee Utility District (SUD) wastewater treatment system consists of three facultative lagoons (6 ha), a chlorination tank and 25-ha of hardwood spray fields. The CW basins (≅0.2 ha total, 30 cm deep) have 30-cm of compacted local topsoil overlying a geotech clay liner. Basin 1 (840 m^2) is planted in softstem bulrush (*Schoenoplectus tabernaemontani*), Basin 2 (photolysis zone) contains raised native plant "islands" but has no submerged vegetation and Basin 3 (380 m^2) has the first half planted in pickerelweed (*Pontederia cordata*), with the second half leading to the outflow left unvegetated for photolysis.

We compared concentrations of nitrogen (N), phosphorus (P), coliform bacteria and 14 pharmaceuticals and personal care products (PPCPs) in lagoon-treated wastewater before and after it flowed through the wetland. Approximately every other month (nutrients and *E. coli*) and following 4, 8 and 12 months of operation (PPCPs), three 1-liter grab samples were collected from each of the following locations: (i) treatment lagoon outflow (ii) inflow of constructed wetland and (iii) outflow of each the three constructed wetland basins.

Nitrite (NO_2^-), nitrate (NO_3^-), ammonia plus ammonium (NH_3+NH_4^+), total nitrogen (TN), reactive phosphate (orthophosphate PO_4), total phosphorus (TP), and fecal indicator bacteria were determined following the Standard Methods for the Examination of Water and Wastewater [6]. Nitrate+nitrite was determined colorimetrically after a modified cadmium reduction to NO_2^- and NH_3+NH_4^+ was measured using an ion selective electrode (Thermo Scientific). Total nitrogen, the sum of organic N, NO_2^-, NO_3^-, NH_3+NH_4^+) was determined after persulfate digestion and analyzed as NO_2^-. Reactive phosphate was measured colorimetrically using the ascorbic acid method (APHA, 1998). Following persulfate digestion, total P was measured as reactive phosphate. Fecal indicator bacteria (*E. coli*) were

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quantified with an enzyme substrate coliform test using the IDEXX Colilert test kit and Quanti-Tray/2000 system. Conductivity and pH were measured simultaneously using electrometric methods.

Pharmaceuticals were extracted following a modification of EPA Method 1694 [7]. Water samples were filtered to remove particulates and pharmaceuticals were extracted by SPE (Oasis HLB cartridges, Waters Scientific) and eluted with methanol. Samples were evaporated, reconstituted in 10% acetonitrile and analyzed by LC-MS/MS (Accela HPLC, TSQ Quantum Ultra mass spectrometer, Thermo Scientific) with separation achieved on a Kinetex 3 μm C18 column with 1.8 μm particle size. The LC mobile phase consisted of a gradient of 0.1% formic acid and acetonitrile and the mass spectrometer was operated in positive ion electrospray mode. Among the 14 potential analytes, nine PPCPs were above detection limits: atenolol, acetaminophen, caffeine, diphenhydramine, carbamazepine, N,N-diethyl-meta-toluamide (DEET), norethindrone, norgestrel and valsartan.

The effect of treatment location (lagoon vs. wetland basin 3) and season (summer 1-summer 2) and their interaction on analyte concentrations were compared in a mixed effects general linear model using SPSS Statistics V 5 (IBM 2017). After inspection of season x treatment location interaction, treatment means across seasons were compared using t-tests.

3. RESULTS AND DISCUSSION

3.1. Conventional pollutants

As wastewater moved from the outflow of the treatment lagoon through the CW basins, there was a significant reduction in total N across all seasons (ANOVA p=0.001, Figure 2). Mean total N concentrations of effluent sampled at the outflow of Basin 3 dropped below the U.S. Environmental Protection Agency's recommended 6 mg N/L by Basin 3 [8] for all seasons except spring.

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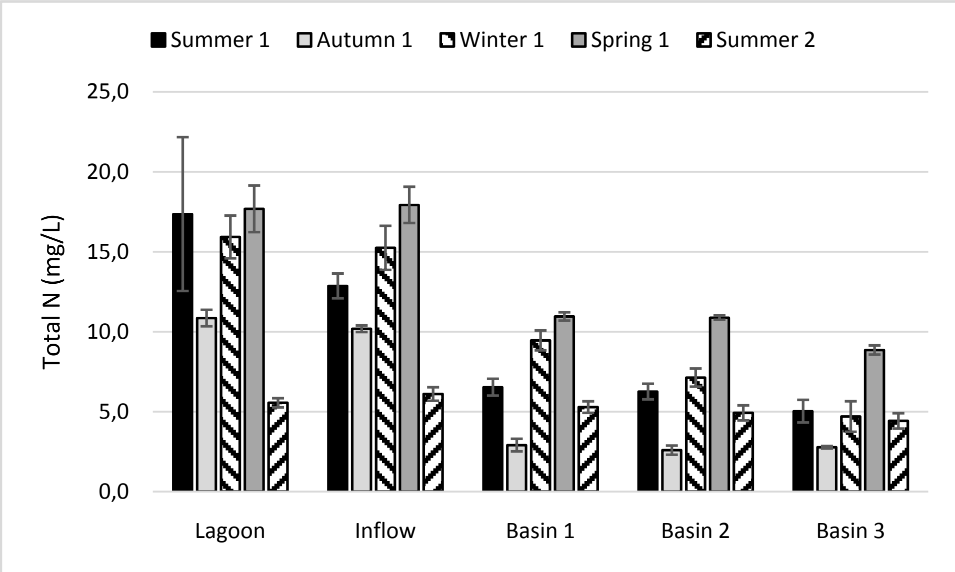

Figure 2. A comparison by season of mean (± one std err) TN concentrations in wastewater effluent from the lagoon outflow to wetland inflow and through CW basins to B3 outflow.

Table 1. A comparison across seasons of mean (± one std err) effluent properties from the outflow of a wastewater treatment lagoon and the outflow of last constructed wetland basin (n= 3 samples per location x 7 sampling periods during the first year of establishment).

	NO_3^- mg/L	NO_2^- mg/L	NH_3+NH_4^+ mg/L	Organic N mg/L	PO_4 mg/L	*E. coli* CFU/100mL
Lagoon	0.08 ± 0.03	0.04 ± 0.01	7.5 ± 3.0	8.2 ± 1.6	0.79 ± 0.22	1182 ± 438
Wetland	0.42 ± 36	0.03 ± 0.02	2.6 ± 1.0	4.0 ± 0.5	0.80 ± 0.12	298 ± 102
P-value	0.18	0.30	0.001	0.04	0.98	0.04

Across all five seasons, mean total N for the lagoon (16 ± 3 mg N/L) was twice that found in the wetland basins (7 ± 2 mg/L, t-test p=0.01). Removal of NH_3+NH_4^+, the second largest N fraction measured, peaked at 92% (autumn) and drove significant reductions in TN during the first nine months of wetland establishment, despite declining to 18% by the end of the

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first year (summer 2, Figure 2, Table 1). Organic N removal peaked after 10 months in spring (64%) and summer (55%). Across seasons, both organic N and NH_3+NH_4^+ were significantly lower in the wetland (Table 1). Overall, NH_3+NH4 and organic N removal by the newly established CW was very high compared to values reported in other studies of constructed wetlands [5,9]. Following lagoon treatment, NO_3^- entered the wetland at very low concentrations (Table 1) and increased during the winter months, presumably due to dormant and decomposing wetland vegetation (Figure 3).

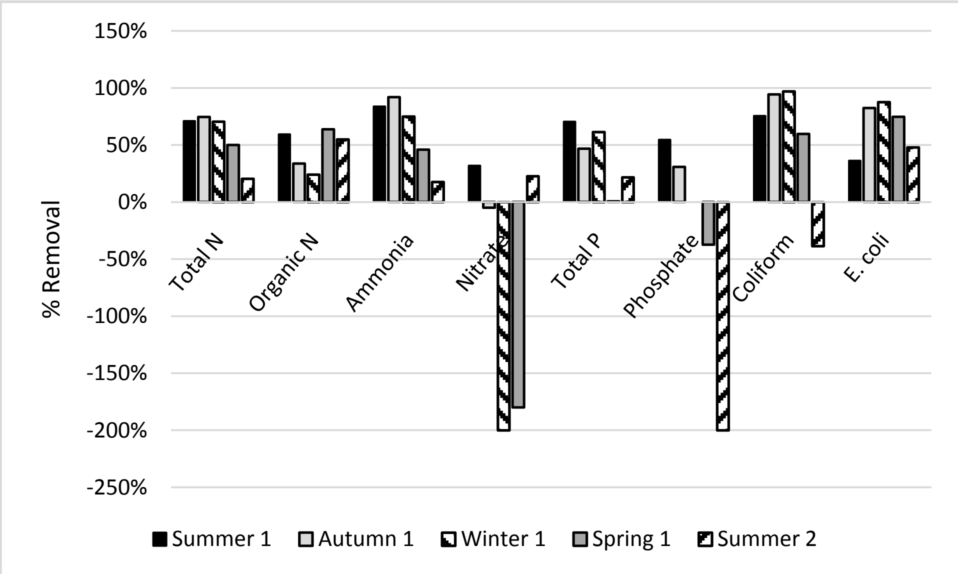

Figure 3. Seasonal removal rates of conventional pollutants by tertiary treatment in a constructed wetland during the first year following wetland commissioning.

Mean total P concentration across seasons was lower in the wetland (1.09 ± 0.11 mg P/L) than the lagoon (1.6 ± 0.3 mg P/L, p=0.04) but in both locations total P was higher than the EPA's recommended level of 40 µg P/L [9]. The wetland was not consistent at reducing PO_4, with the highest removal during the first summer (55%) but also large increases during the spring (-37%). Across seasons, PO_4 did not differ significantly between the two locations. Wetland removal rates for fecal indicator (total coliforms and *e-coli)* bacteria were well over 50% during most seasons (Figure 3) and wetland *e-coli* counts were at the very low range of values reported in other studies of constructed wetland with emergent macrophytes [9,11]. Mean *e-coli* counts in the lagoon were nearly four times higher than in the wetland (Table 1). Mean pH was significantly higher in the lagoon (7.54 ± 0.09) than in the wetland (6.95 ± 0.02; t-test p-value=0.001) but mean conductivity (236-245 mS/cm) did not differ between the two locations.

3.2. Emerging Contaminants

After 4, 8 and 12 months of operation representing three seasons (autumn 1, winter 1, and summer 2), up to 88% of the 14 targeted PPCPs measured in lagoon C were removed by the wetland, with removal efficiencies dependent upon the analyte and season (Figure 4). The greatest overall PPCP removal (mean of 47% removal for 9 of 14 PPCP analytes) was

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measured in autumn 1, followed by 43% removal in summer 2 (9 of 14 PPCP analytes detected) and 39% removal in winter 1 (6 of 14 analytes detected). Removal trends for individual compounds in the Sewanee Wetland are consistent with published accounts for larger, established surface flow wetlands [reviewed in 2, 12]. With increasing wetland age, less removal was observed for some PPCPs (atenolol, carbamazepine, norethindrone), although the trend was not significant. Reduced removal with increased wetland age is likely due to saturation of plant removal processes, as was observed with ammonia and ammonium ion. Other PPCPs (caffeine, diphenhydramine, DEET, valsartan, norgesterel) were removed less in the first winter than in the warmer months of year one (October and June), perhaps as a result of reduced microbial activity and/or plant dormancy at colder winter temperatures. Plant decomposition that occurred in all wetland cells during colder weather may have driven release of norgestrel and valsartan from plants to the wetland, resulting in their net export from the wetland.

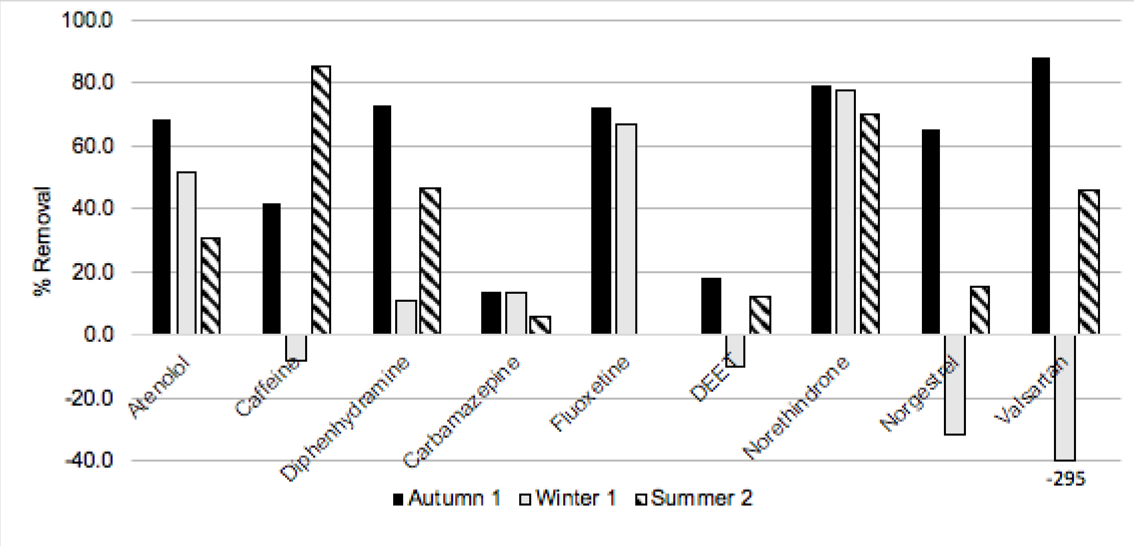

Figure 4. Seasonal removal of pharmaceuticals and personal care products by tertiary treatment in a constructed wetland during the first year following wetland commissioning.

During the first autumn of operation a linear relationship was observed between removal efficiencies and hydrophobicity (log Kow) for the more hydrophobic PPCPs (log Kow >2), suggesting that removal was more influenced by sorption to sediments, than plant uptake. In the two subsequent months (winter 1 and summer 2) no relationship was observed between compound hydrophobicity and removal, suggesting increased importance of other routes (plant uptake, microbial degradation) as the wetland matured. In preliminary data from wetland plants collected in February of year 2 (data not shown), DEET and caffeine (both hydrophilic PPCPs) were detected at the highest concentrations in bulrush and pickerelweed compared to the more hydrophobic analytes. These results are consistent with preferential accumulation of hydrophilic PPCPs by terrestrial plants from PPCP-spiked soils [13]. Further characterization of plant uptake of PPCPs in subsequent years will allow a more robust analysis of the roles of the dominant wetland plants (bulrush, pickerelweed) in PPCP removal from wetland effluents.

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In summary, removal efficiencies of nutrients, fecal indicator bacteria and PPCPs by the pilot scale constructed wetland were at the high end of values reported in other studies, presumably driven by rapid uptake and growth of newly emergent macrophytes during the early establishment phase. However, within a year, wetland removal of nutrients began to decline, signaling the importance of vegetation management to maintain maximum treatment potential. Ongoing research will analyze PPCP and nutrient concentrations in water and wetland plants at frequent intervals to identify pathways and conditions most crucial to wetland removal of wastewater contaminants and to inform better wetland management.

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