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Removal of nutrients, trace organic contaminants, and bacterial indicator organisms in a demonstration-scale unit process open-water treatment wetland

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ABSTRACT

A demonstration-scale unit process open-water wetland system was built to treat water from an effluent-dominated river (i.e., a river in which the flow consisted almost entirely of municipal wastewater effluent from May to October). Monitoring of the system over a two-year period indicated effective removal of nitrate, with concentrations decreasing by over 90% during summer. The temperature-independent areal first-order nitrate removal rate constant, k_{20}, ranged from 61.7 to 68.1 m yr^{-1} after the microbial community was established, which is significantly higher than values typically observed in full-scale surface flow wetlands. The beta-adrenergic blockers, atenolol and propranolol, as well as the antiviral drug, acyclovir, were removed by photolysis and biotransformation in the wetland biomat, whereas the antiepileptic drug, carbamazepine, exhibited little removal. The bacterial indicators *E. coli* and enterococci decreased substantially during summer, mainly through sunlight exposure. Models of contaminant removal based upon measured flow rates and performance data collected at a similar pilot-scale system agreed well with measured data for nitrate and the trace organic contaminants. The model accurately predicted removal of enterococci but systematically over-predicted the removal of *E. coli*. During the two-year study period, routine maintenance was necessary to prevent colonization of the water surface with duckweed (*Lemna* spp.). Unit process open-water (UPOW) wetlands may offer a low-cost means of improving water quality in natural treatment systems that can be integrated with conventional surface-flow wetlands and other managed natural systems. The quantitative models of contaminant removal described in this study can be used to design natural treatment systems that balance the needs for local water quality requirements, available land and site-specific requirements.

1. Introduction

Surface flow constructed wetlands have been used for over five decades to remove suspended solids, nutrients and metals from municipal wastewater effluent and wastewater effluent-receiving surface waters (Kadlec, 2012; Kadlec and Wallace, 2009; Vymazal, 2011). Although surface-flow treatment wetlands are capable of removing certain trace organic compounds and pathogens from wastewater under laboratory or pilot-scale conditions (Hijosa-Valsero et al., 2010; Jasper et al., 2013; Kadlec et al., 2010; Matamoros et al., 2008), their ability to remove contaminants in full-scale systems is often lower than expected due to hydraulic inefficiencies (Gray and Sedlak, 2005; Lightbody et al., 2009). Furthermore, rates of biotransformation of many compounds are slow relative to hydraulic residence times (HRTs) employed in full-scale systems (Jasper et al., 2013). In addition, utilities are often hesitant to build surface flow wetlands because the vegetation requires a considerable amount of maintenance, particularly with respect to removal of accumulated plant material (Thullen et al., 2005).

Unit process open-water (UPOW) wetlands were developed to complement conventional surface-flow treatment wetlands, by providing low-maintenance, modular cells that could be built at the same time as surface-flow wetlands or retrofit into existing basins (Jasper et al., 2014a; Jasper and Sedlak, 2013). UPOW wetlands consist of shallow (i.e., depths < 30 cm) rectangular basins with geotextile liners at the water-sediment interface to prevent the growth of emergent macrophytes. The absence of macrophytes results in improved

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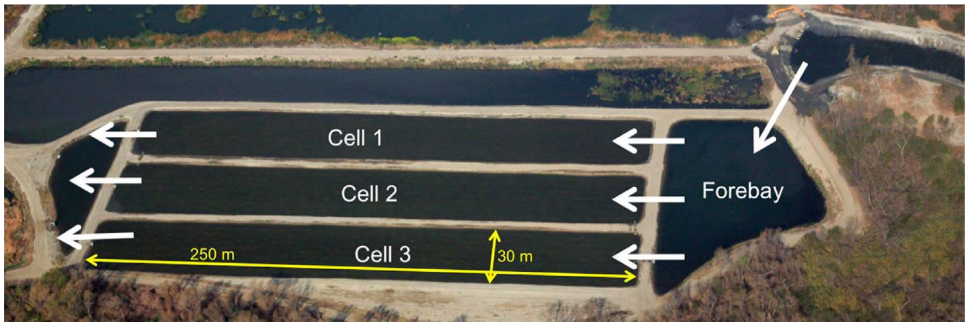

Fig. 1. UPOW cells prior to reconfiguration of the forebay. White arrows indicate direction of water flow.

hydraulic performance and the formation of a 2–10 cm biomat layer on top of the liner (Jasper et al., 2014a). Sunlight passing through the water column transforms organic contaminants and inactivates viruses and bacteria over hydraulic residence times ranging from one to four days. Previous research conducted at a pilot-scale (0.04 ha) UPOW treatment wetland receiving nitrified, municipal wastewater effluent demonstrated removal of a suite of photolabile trace organic compounds (Jasper and Sedlak, 2013) as well as trace organic compounds amenable to biotransformation (Jasper et al., 2014b). The removal of nitrate (Jasper et al., 2014a), *E. coli*, enterococci (Nguyen et al., 2015), and F+ coliphage (Silverman et al., 2015) observed in the pilot-scale open-water system was as good as or better than that observed in vegetated surface flow wetlands. During the four years in which the pilot-scale wetland system operated, the biomat reached a relatively constant thickness and the system retained its ability to remove contaminants.

To further assess the performance of UPOW wetlands, a demonstration-scale system was built in 2013. The system received water from an effluent-dominated section of the Santa Ana River in Riverside County, California. The system consisted of three parallel cells that covered an area of approximately 2.25 ha (Fig. 1). During a two-year period, the demonstration system was monitored to gain insight into system performance and maintenance needs, and to assess effects of season and hydraulic residence time on the removal of trace organic contaminants, nitrate, and pathogen indicator organisms. Results from this demonstration-scale study can inform design decisions related to the construction, operation, and maintenance of UPOW wetland systems.

2. Methods and materials

2.1. Chemicals

Analytical reference standards of the trace organic compounds and the isotopically-labeled internal standards (purity > 99%) were purchased from Toronto Research Chemicals (Ontario, Canada) or Sigma-Aldrich (St. Louis, MO) except carboxyacyclovir, which was synthesized as described previously (Prasse et al., 2011; see Table S1). All other chemicals and solvents were purchased from Fisher Scientific (Fairlawn, NJ) at the highest purity available. All solutions were prepared using Milli-Q water (resistivity > 18 MΩ) from a Millipore system (Billerica, MA).

2.2. Unit process open-water wetland cells

The demonstration-scale system was located at the Prado Wetlands, a complex consisting of approximately 180 ha of surface flow constructed wetlands in Riverside County, California (Belitz et al., 2004). The wetlands were improved in 1992 to enhance the nitrate removal from the wastewater-impacted Santa Ana River (Orange County Water District, 2016). During the dry season (i.e., May through October), the flow of the Santa Ana River consists almost entirely of discharge from twelve upstream municipal wastewater treatment plants. During the remainder of the year, stormwater runoff and snowmelt accounted for the majority of the flow of the river. Along the 12 km-stretch of the river upstream of the wetlands, biotransformation and photolysis in the flowing water resulted in the partial removal of some trace organic contaminants (Fono et al., 2006; Gross et al., 2004; Lin et al., 2006).

In 2013, three open-water unit process wetland cells were constructed adjacent to the existing off-river vegetated wetlands (Fig. 1). The UPOW system received water directly from the river through a diversion channel and forebay that distributed the water to three parallel cells. The cells were each approximately 30 m wide and 250 m long (combined area of approximately 2.25 ha). The cells were lined with a geotextile fabric to prevent growth of emergent macrophytes. Within two months of the introduction of river water, a diffuse biomat layer developed on top of the liner. In most places, the biomat layer reached a thickness of approximately 3 cm within the first year. In the 30 m region adjacent to the inlets to the cells, the biomat was up to 10 cm thick. Flows through the cells were controlled by weir boxes at the inlets and nominal residence times were set at two days for all three cells from December 2013 until September 2014. Subsequently, the residence times were set at one, two and four days for cells 3, 1 and 2, respectively.

Shortly after the construction of the demonstration-scale wetland system, the surface of the geotextile liner was colonized by a biomat composed of photosynthetic diatoms and an associated microbial community. Activity in the biomat resulted in diurnal pH fluctuations and oxygen supersaturation. As the water temperature increased from 15 °C in January to 21 °C in April, increased biological activity and biomat accumulation was observed. During 2014, the hydraulic residence time was maintained at a nominal value of two days in all three cells. Rhodamine-WT tracer tests indicated that all three cells exhibited similar hydraulic performance, with tracer reaching the outlets after only a few hours, and mean HRTs of 1.4, 2, and 1.7 days (Fig. S3). Starting in January 2015, the nominal hydraulic residence time of cell 2 was increased to four days, the residence times of cell 3 was decreased to one day, and that of cell 1 was maintained at two days (Fig. S4). The biomat community stabilized over the course of the first two years as reported elsewhere (Jones et al., in preparation).

In November 2014, the forebay was reconfigured to reduce the growth of suspended algae by filling in all but a narrow channel (i.e., approximately three meters wide) immediately adjacent to the inlets to the cells. This change resulted in greater water clarity and less growth of floating algae (Fig. S1). The effect of suspended algae on contaminant removal was modest (compare results from 2014 with cells operated at 4-day hydraulic residence times in 2015 in the results and discussion section).

2.3. Monitoring

Samples were collected periodically between January 2014 and November 2015 (see Table S2A for specific sampling dates) at the weir box adjacent to the location where water entered the forebay (representative of the inlet concentrations of all three cells) and at the

Table 1
Comparison of conditions in Prado Open-Water Wetland Cells with those employed in the photolysis model from Discovery Bay Wetlands.

Condition	Employed in Photolysis Model (Discovery Bay Wetlands)[a]	Prado Wetlands[b]
Depth (cm)	0–50	25–30
pH	7–10	7.7–9.0
$[NO_3^-]$ (mg L^{-1} N)	0–20	3.5–7.5
[DOC] (mg L^{-1}C)	1–15	3.7–5.6
[DIC] (mg L^{-1}C)	60	45–54

[a] Jasper and Sedlak (2013).
[b] measured in this study, used as inputs to photolysis model (see Table S4 for additional details).

outlet weirs of each of the cells. After the forebay reconstruction (November 2014), inlet samples were collected adjacent to the location where water entered the open channel. For trace organic compounds and water quality parameters, grab and composite samples (*vide infra*) were collected in amber glass bottles which were kept at 4 °C and shipped overnight to UC Berkeley for processing. Samples were filtered through 1-μm glass fiber filters immediately upon receipt and analyzed within 48 h. For pathogen indicator organisms, samples were collected in sterilized polypropylene bottles, kept at 4 °C and shipped overnight to UC Berkeley for processing immediately upon arrival.

Between January 2014 and September 2014, when all three cells were running with nominal hydraulic residence times of two days, two grab samples were collected monthly at a two day interval. This form of synoptic sampling was chosen because the first inlet sample could be paired with the second outlet sample if a pulse of contaminants was observed. In all cases, concentrations of the contaminants were similar in the two inlet or two outlet samples and the results were averaged for each sampling period. Starting in January 2015, 24-h composite samples were collected simultaneously at the inlet and outlets with Teledyne ISCO GLS Composite Samplers (Lincoln, NE) for trace organic compounds and water quality parameters. Due to concerns about sample holding times, samples for pathogen indicator organisms were still collected as grab samples immediately before samples were to be shipped out for analysis. The composite samplers employed 9.5 L amber glass bottles which were kept on ice during sample collection—a process that kept the samples at approximately 4 °C. Upon conclusion of the 24-h sampling period, 1-L sub-samples were decanted into clean, baked amber glass bottles, placed on ice, and shipped overnight to UC Berkeley for processing.

In August 2014, multi-parameter sensors from INW (Seattle, WA) were installed at the inlet to the forebay and the outlets of each cell adjacent to the sampling locations. The sensors continuously recorded flow, temperature, pH, dissolved oxygen, and conductivity.

2.4. Analytical methods

Established methods were employed for analysis of water quality parameters, trace organic contaminants, and pathogen indicator organisms. Nitrate was measured using ion chromatography (Dionex ICS 1100) and dissolved organic carbon was measured using a TOC-V analyzer (Shimadzu). Trace organic compounds were quantified using direct injection or solid-phase extraction (SPE), isotope dilution liquid chromatography/tandem mass spectrometry (Agilent LC/MS-MS) (details in the Supporting Information section). *E. coli* and enterococci were measured using Colilert and Enterolert defined substrate assays, respectively, implemented in 97 well Quanti-Trays following vendor instructions (IDEXX).

2.5. Tracer tests and models

Tracer tests were conducted using Rhodamine-WT for all three cells in both 2014 and 2015 (see Supporting Information section for details). A tanks-in-series model (Kadlec and Wallace, 2009) best represented the hydraulic conditions in the wetland cells compared with an ideal plug-flow model. The numbers of tanks in series (N) for each cell varied from 2.3 to 3 (Figs. S3 and S4).

Nitrate removal predictions were made using pseudo-first order areal nitrate removal rates from a pilot-scale open-water unit process wetland (Jasper et al., 2014a). To predict nitrate removal at the demonstration-scale UPOW system, water temperature data from sensors or water temperature measured when subsamples were collected (prior to sensor installation) were used (Jasper et al., 2014a; Kadlec, 2012). For trace organic contaminants, a previously published photolysis model (Jasper and Sedlak, 2013) was used to predict photolysis rates for compounds throughout the year. Biotransformation rates were predicted by using data from microcosm experiments with biomat materials from a pilot-scale system (Jasper et al., 2014b) which were adjusted to account for seasonal changes in wetland water temperature. Inactivation of *E. coli* and enterococci was predicted using data from a pilot-scale system (Nguyen et al., 2015). The pseudo-first order transformation rates of all contaminants were then used to calculate C/C_o values using the tanks-in-series model (details of calculations in SI). Water depths measured in the UPOW cells and solar irradiance predicted using the Simple Model of the Atmospheric Radiative Transfer of Sunshine (SMARTS) at the site of the Prado wetlands (33°53′23“N, 117°38′28“W) were used in the model (Gueymard, 2008). A comparison of the conditions in the UPOW cells with those at the pilot-scale system in Discovery Bay, from which model predictions were made, is shown in Table 1.

2.6. Statistical tests

GraphPad Prism 7.0a (La Jolla, CA) was used for statistical analyses. To compare observed values with model values for each contaminant, paired *t*-tests were conducted for each cell and each year separately using P values of 0.05.

3. Results and discussion

To assess contaminant fate in the cells, results from the model predictions were compared to measured results. Particular attention was paid to situations in which observations deviated from predictions.

3.1. Nitrate

Nitrate concentrations at the inlets of the UPOW system ranged from 0.25 to 0.54 mM with an average concentration of 0.44 ± 0.01 mM (6.21 ± 0.15 mg N-NO3/L) (see Table S4). As expected from previous research, the main mechanism of nitrate removal in the open water wetland is denitrification by microbes living below the surface of the biomat (Jasper et al., 2014a). Annamox linked to sulfide-induced reduction of nitrate to ammonium also occurred (Jones et al., 2017), but results of microcosm studies showed that it typically accounted for less than 10% of the observed removal. Nitrate removal varied seasonally (Fig. 2) with the greatest removal observed between May and September of both years, when average water temperatures ranged from 20 °C to 30 °C. The importance of the biomat layer to nitrate removal was evident in the period between January and April. In 2014, prior to accumulation of the biomat layer, less than 20% nitrate removal was observed. In contrast, during the same period in 2015, over 40% of the influent nitrate was removed. Nitrate removal increased as the HRT increased in the second year, when the cells were operated at different HRTs. In cell two, which had a nominal HRT of 4 d during 2015, 60–100% of the influent nitrate was removed over the entire year. The observed data for nitrate agreed well with model predictions in 2014 and 2015 (Fig. 2); observed removal was not statistically different from predicted removal (paired *t*-tests;

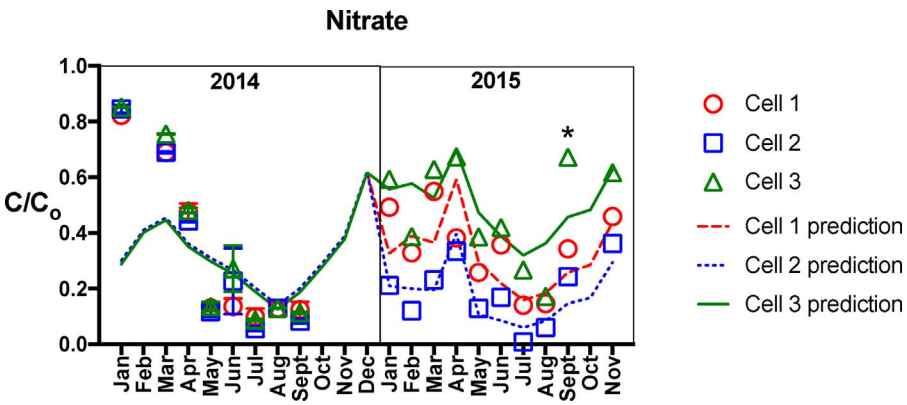

Fig. 2. Nitrate removal in the unit process open-water wetlands. Measured data (points) are compared with predicted values (lines); * denotes period of duckweed coverage. 2014 data include average and SEM of duplicate samples; 2015 data show results from 24-h composite samples. Nominal HRTs of cells as follows: 2014: all cells = 2 d; 2015: cell 1 = 2d; cell 2 = 4 d; cell 3 = 1 d.

P > > 0.05).

To compare the nitrate removal capacity of the open-water wetland cells with other wetland systems, a pseudo-first order areal removal rate at 20 °C (k_{20}) was calculated for each cell (see SI for details). This parameter was independent of temperature and HRT. It also accounted for the hydraulics of the cells, as determined from tracer tests, by incorporating the tanks-in-series model (Kadlec, 2012). During the first year of operation, when the biomat was just beginning to get established and the nominal residence times of the cells were identical (2 d), the k_{20} values for the three cells ranged from 32.1 to 39.0 m yr^{-1}. The k_{20} values increased dramatically in 2015, likely due to the increased thickness of the biomat, ranging from 61.7 to 68.1 m yr^{-1}. These areal removal rates compare favorably with other wetland systems. For example, Jasper et al. (2014b) reported a k_{20} value of 59.4 ± 6.2 m yr^{-1} for a pilot-scale open-water wetland system over six years of operation. A review of 44 surface flow wetlands indicated k_{20} values ranging from 5 to 168 m yr^{-1} with a median of 25 ± 8 m yr^{-1} for surface flow wetlands (Kadlec, 2012). The UPOW cells exhibited more efficient removal of nitrate than over 75% of the wetlands considered in the review.

3.2. Trace organic contaminants

3.2.1. Atenolol and propranolol

Removal of trace organic contaminants was consistent with predictions based on previous studies. Atenolol is a beta adrenergic blocker (i.e., β-blocker) amenable to biotransformation but not phototransformation (Jasper et al., 2014b; Jasper and Sedlak, 2013; Ramil et al., 2010; Yamamoto et al., 2009). Its concentration followed similar trends to those observed for nitrate, with removals of over 70% from May through August when the hydraulic residence time was two days (average initial concentration 60.1 ± 4.4 ng/L; Fig. 3). Between 70 and 90% of the observed removal of atenolol was due to biotransformation, according to model predictions (Tables S10 and S11). The primary biotransformation product of atenolol, metoprolol acid (Svan et al., 2016), was also monitored in the UPOW cells (Fig. S5). Propranolol, another β-blocker, was more efficiently removed than atenolol because its conjugated rings made it susceptible to photolysis (i.e., direct photolysis and reactions with ^{3}DOM*) (Fig. 3). Photolysis was predicted to be the primary transformation mechanism for propranolol, accounting for approximately 60–85% of the observed transformation. Due to its lower concentrations in wastewater effluent and its photolysis in the river and diversion channel upstream of the wetland, propranolol concentrations in the water entering the open-water cells were lower than those of atenolol (11.3 ± 1.0 ng/L). Propranolol concentrations decreased by approximately 90% between May and July. The seasonal removal trend was similar to that of atenolol and nitrate because sunlight intensity increased in summer along with water temperature, which increased biotransformation rates.

Observed data for both atenolol and propranolol showed good agreement with model predictions (paired *t*-tests; P > > 0.05). However, the removal of both compounds was much lower than predicted in September 2015, with a greater discrepancy for propranolol. These anomalous data was attributed to coverage of all three wetland cells by the floating macrophyte duckweed (*Lemna* spp.), which prevented penetration of sunlight through the water column, thereby inhibiting phototransformation on the days that samples were collected. The effect of surface coverage was more pronounced for propranolol because a substantial portion of the atenolol removal was due to biotransformation in the biomat. Interestingly, nitrate removal was also lower than predicted in the September 2015 sample (Fig. 2). These findings suggest that the microbial community was less active during the period when duckweed blocked the sunlight, though further research is required to assess the importance of this phenomenon.

3.2.2. Acyclovir and carbamazepine

Acyclovir, an antiviral compound, and carbamazepine, an antiepileptic compound, exhibited only modest removals in the open-water cells (Fig. 4). The concentration of acyclovir (average influent concentration = 302 ± 58 ng/L)—a compound that undergoes slow biotransformation (Prasse et al., 2015)—decreased by about 50% in all three cells from May to July of 2014 (concentrations of the primary biotransformation product, carboxyacyclovir, shown in Fig. S5). Approximately 70% of the acyclovir was removed when the hydraulic residence time for cell 2 was increased to four days. Carbamazepine (average influent concentration 156 ± 7.1 ng/L) does not undergo biotransformation at appreciable rates under the conditions encountered in the open-water wetland cells. Its primary removal mechanism is through reactions with hydroxyl radical (·OH), which is mainly produced via nitrate photolysis in open-water cells (Jasper and Sedlak, 2013). The model over-predicted carbamazepine removal in both years for all three cells (P < 0.05) possibly because the model used nitrate concentrations in the influent water to predict ·OH production rates, despite the fact that over 80% of the nitrate was removed as the water flowed through the cells during summer.

3.3. Bacterial indicator organisms

Bacterial indicator organisms (*E. coli* and enterococci) were also removed to a moderate degree in the open-water wetland cells (Fig. 5). The maximum removal achieved was around 99% (i.e., 2 log removal) for *E. coli* and 99.9% (i.e., 3 log removal) for enterococci in summer 2014. The indicators are susceptible to sunlight inactivation (Nguyen et al., 2015), which was predicted to contribute up to 87% and 74% of the observed removal of *E. coli* and enterococci, respectively (Table S9). Similar to propranolol, which is susceptible to photolysis, the removal of the bacterial indicators showed a seasonal trend with the highest removals observed during summer. For enterococci, the contribution of dark inactivation mechanisms was predicted to be significant throughout the monitoring period and greatest in winter, explaining the

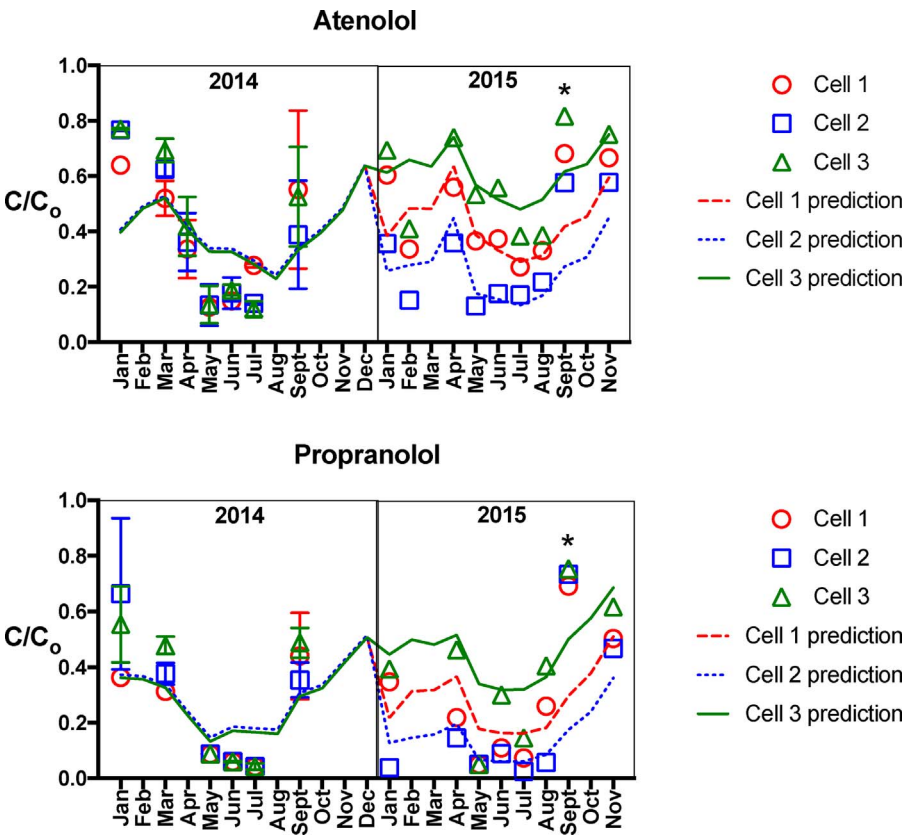

Fig. 3. Atenolol and propranolol removal in the unit process open-water wetlands. Measured data (points) are compared with predicted values (lines); * denotes period of duckweed coverage. 2014 data include average and SEM of duplicate samples; 2015 data show results from 24-h composite samples. Nominal HRTs of cells as follows: 2014: all cells = 2 d; 2015: cell 1 = 2d; cell 2 = 4 d; cell 3 = 1 d.

weaker seasonal effect compared to that of *E. coli*. It should be noted that dark inactivation rates for the indicators were assumed to be the same every month because the effect of temperature on dark inactivation is not well understood.

Despite uncertainty in quantification of bacterial indicators at the low concentrations observed in the Santa Ana River, the model showed reasonable agreement with measured data for enterococci. The model over-predicted the removal of *E. coli* in both 2014 and 2015 (paired *t*-tests; $P < 0.05$). The disagreement between measured and predicted data could be explained by several factors. First, the inlet

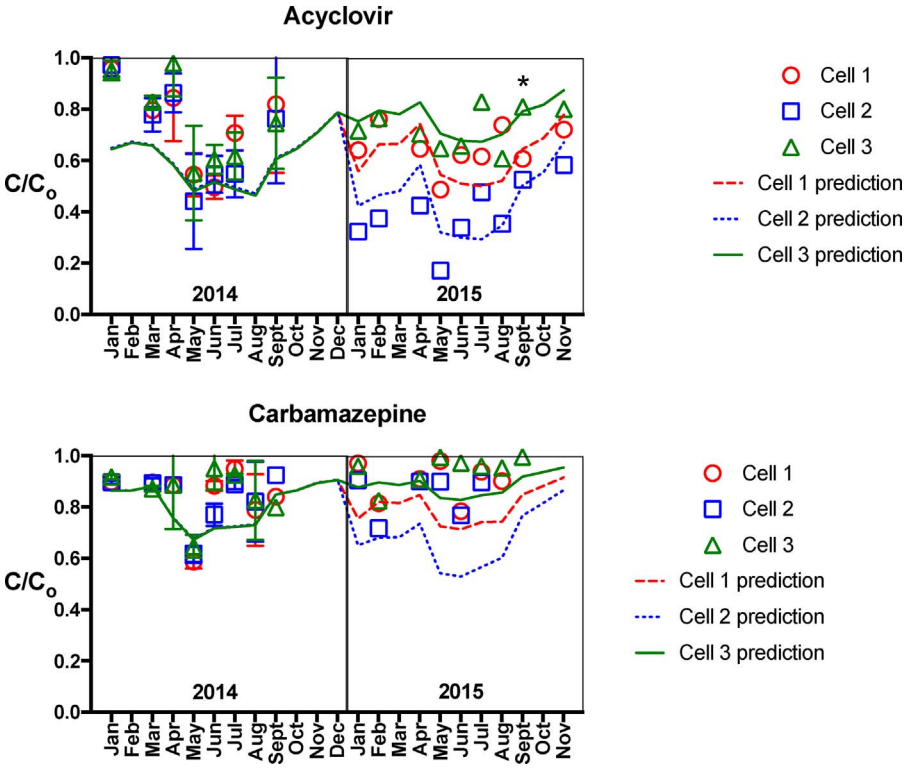

Fig. 4. Acyclovir and carbamazepine removal in the unit process open-water wetlands. Measured data (points) are compared with predicted values (lines); * denotes period of duckweed coverage. 2014 data include average and SEM of duplicate samples; 2015 data show results from 24-h composite samples. Nominal HRTs of cells as follows: 2014: all cells = 2 d; 2015: cell 1 = 2d; cell 2 = 4 d; cell 3 = 1 d. For carbamazepine, one of the September 2014 duplicates was excluded as an outlier.

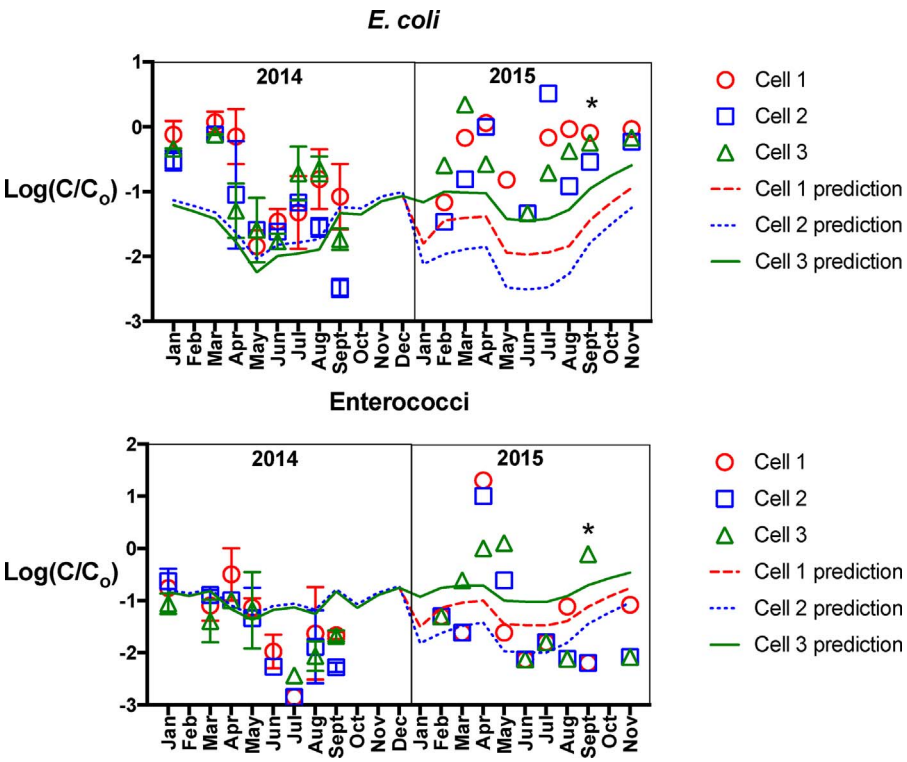

Fig. 5. *E. coli* and enterococci removal in the unit process open-water wetlands. Measured data (points) are compared with predicted values (lines); * denotes period of duckweed coverage. 2014 data include average and SEM of duplicate samples; 2015 data show results from one grab sample collected at 9 am. Nominal HRTs of cells as follows: 2014: all cells = 2 d; 2015: cell 1 = 2d; cell 2 = 4 d; cell 3 = 1 d.

concentrations of the indicators varied considerably during the course of the monitoring period, ranging from 0.063 to 2.0 × 10^3 MPN/100 mL for *E. coli*, and from 1.0 to 3.0 × 10^3 MPN/100 mL for enterococci (Fig. S6). The variable and relatively low influent concentrations of the indicator organisms complicated efforts to quantify their removal. Furthermore, variations in the hydraulics of the system could have affected the results in ways that are difficult to predict. For example, tracer tests indicated that cell 1 was prone to hydraulic short-circuiting, possibly due to its greater exposure to the prevailing winds (Figs. S3 and S4). A modest amount of short-circuiting would be expected to have a larger impact on observed concentrations of pathogen indicator organisms than chemical contaminants because preferential flow paths and shorter-than-expected residence times have a greater negative impact on performance when higher removal efficiencies occur (note log scale of y axis in Fig. 5).

Although we were unable to measure removal of virus indicators (the concentrations of somatic and F+ coliphage in the wetland influent were too low to document removal, based on several months of monitoring data), open water wetlands have been shown to achieve inactivation of viruses through sunlight inactivation (Silverman et al., 2015). This ability is an important advantage compared to vegetated wetlands, and further highlights the benefits of combining different types of unit process wetlands within a constructed wetland system.

3.4. Maintenance

Unit process open-water wetlands require maintenance to assure optimal performance (Silverman et al., in preparation). During the two-year operation period, maintenance costs remained stable at approximately $35,000 to $40,000 per year for all three cells combined based on staff time required for maintenance activities. The most significant maintenance activities included periodic removal of emergent vegetation and control of duckweed (*Lemna* spp.).

Although there was a geotextile liner along the bottom of the open-water cells to prevent establishment of emergent vegetation, plants could still get established around the edges of the wetland cells. If they were to be left unattended, the emergent vegetation could colonize the edges of the cell and dislodge the geotextile liner. Emergent vegetation was removed about once a month for six months of each year, both manually and using heavy equipment, adding up to around 120 h of labor (approximately $4800) per month. Commonly encountered emergent vegetation included California Bulrush (*Schoenoplectus californicus*), Common Cattail (*Typha latifolia*), and various species of pondweed (see Table S12 for full list of emergent vegetation species removed).

The other significant maintenance activity was control of duckweed during the summer months. Near the end of June in 2014 and 2015, duckweed began to grow on the surface of the open-water cells. Duckweed removal was necessary because it shades the water column and slows photolysis of organic contaminants (Jasper and Sedlak, 2013) and prevents sunlight inactivation of microbial indicator organisms (Nguyen et al., 2015). It could also affect the diatoms and bacteria in the biomat. Duckweed growth was observed previously in the pilot-scale system, where it was removed manually about once a month between June and September. Manual removal of duckweed at the Prado UPOW demonstration-scale system was deemed impractical due to the large surface area of the wetland cells. Hence, the duckweed was controlled by flushing the cells at a high flow rate as soon as duckweed was observed (generally in June). Treatment continued on a biweekly basis through the duckweed bloom season (generally ending in September). To flush duckweed out of the system, 100% of the full flow to all three cells was diverted through a single wetland cell for 24 h with the stop-block in the outflow weir removed. This reduced the hydraulic residence time of the cell to several hours and facilitating flushing of the duckweed from the cell. Once maximum daily water temperatures were below 20 °C, duckweed growth slowed and flushing was no longer necessary.

The flushing protocol controlled duckweed effectively. If this approach were to be adopted for an entire treatment system, the water that rapidly flushed through the cells might require additional treatment if the overall system were to achieve the desired water quality at its outlet. If the flushed water were directed back to the influent of the system, the duckweed would need to be physically removed prior to introduction of the water back into the wetland cells, perhaps by coarse

filtration or surface skimming.

4. Conclusions

A unit process open-water wetland was operated at a demonstration scale for two years. During the study period, nitrate and trace organic contaminants amenable to bio- or photo-transformation were removed along with microbial indicator organisms. The open water system was effective at removing a diverse set of contaminants because it provided an environment where sunlight and biotransformation reactions were favorable, and the hydraulics of the system minimized the extent of hydraulic short-circuiting. As expected for a managed natural system, the treatment performance exhibited seasonal variations due to changes in incident sunlight intensity and water temperature. The seasonal variations in treatment efficacy and the effects of changing hydraulic residence times could be predicted with a model that employed data collected in the laboratory and in previous pilot-scale studies.

Unit process open-water wetlands represent a practical approach for improving the ability of constructed wetlands to improve water quality. In locations where wetlands have not yet been built, UPOW cells could be incorporated into a larger set of wetlands, with vegetated surface-flow wetlands filtering out any duckweed that is flushed from the system or providing additional habitat. In locations where vegetated surface-flow wetlands have already been built, sections of the wetland could be retrofit by converting a small number of existing cells to the open water configuration. For example, the Tarrant Regional Water District maintains the George W. Shannon Wetlands, a 1730-acre vegetated wetland that polishes water from the effluent-impacted Trinity River (TX) for recharge in the Richland-Chambers Reservoir (Tarrant Regional Water District, 2017). Converting about half of the surface area of the vegetated wetland to a unit process open-water wetland would result in removal of approximately 95% of the inlet nitrate on average and would provide for improved removal of trace organic contaminants and inactivation of pathogens by sunlight.

The water quality models that were developed and tested in this study provide wetland designers with a means of optimizing UPOW systems to meet site-specific requirements. By using information about influent water quality conditions, seasonal targets for wetland effluent and local climate conditions, wetland designers can optimize parameters such as the wetland area, depth and flow rate. This will also allow them to make better estimates of construction, operation and maintenance costs. Although the model yielded good predictions for the removal of nitrate and several trace organic contaminants, additional research is needed to improve the ability of the models to predict removal of other contaminants (e.g., pathogens, pesticides, metals). Further research is also needed to extend the open water unit process wetland to the treatment of other water sources (e.g., non-point source pollution, reverse osmosis concentrate from potable water reuse projects). Finally, research is needed to better understand the potential benefits of placing open water wetlands in series with vegetated surface flow wetlands.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ecoleng.2017.09.017.

References

Belitz, K., Hamlin, S.N., Burton, C.A., Kent, R., Fay, R.G., Johnson, T., 2004. Water Quality in the Santa Ana Basin, California, 1999–2001 (No. Circular 1238). US Department of the Interior, US Geological Survey, Reston, VA.

Fono, L.J., Kolodziej, E.P., Sedlak, D.L., 2006. Attenuation of wastewater-derived contaminants in an effluent-dominated river. Environ. Sci. Technol. 40, 7257–7262. http://dx.doi.org/10.1021/es061308e.

Gray, J.L., Sedlak, D.L., 2005. The fate of estrogenic hormones in an engineered treatment wetland with dense macrophytes. Water Environ. Res. 77, 24–31. http://dx.doi.org/10.2175/106143005x41582.

Gross, B., Montgomery-Brown, J., Naumann, A., Reinhard, M., 2004. Occurrence and fate of pharmaceuticals and alkylphenol ethoxylate metabolites in an effluent-dominated river and wetland. Environ. Toxicol. Chem. 23, 2074–2083. http://dx.doi.org/10.1897/03-606.

Gueymard, C.A., 2008. Prediction and validation of cloudless shortwave solar spectra incident on horizontal, tilted, or tracking surfaces. Sol. Energy 82, 260–271. http://dx.doi.org/10.1016/j.solener.2007.04.007.

Hijosa-Valsero, M., Matamoros, V., Sidrach-Cardona, R., Martin-Villacorta, J., Becares, E., Bayona, J.M., 2010. Comprehensive assessment of the design configuration of constructed wetlands for the removal of pharmaceuticals and personal care products from urban wastewaters. Water Res. 44, 3669–3678. http://dx.doi.org/10.1016/j.watres.2010.04.022.

Jasper, J.T., Sedlak, D.L., 2013. Phototransformation of wastewater-Derived trace organic contaminants in open-Water unit process treatment wetlands. Environ. Sci. Technol. 47, 10781–10790. http://dx.doi.org/10.1021/es304334w.

Jasper, J.T., Nguyen, M.T., Jones, Z.L., Ismail, N.S., Sedlak, D.L., Sharp, J.O., Luthy, R.G., Horne, A.J., Nelson, K.L., 2013. Unit process wetlands for removal of trace organic contaminants and pathogens from municipal wastewater effluents. Environ. Eng. Sci. 30, 421–436. http://dx.doi.org/10.1089/ees.2012.0239.

Jasper, J.T., Jones, Z.L., Sharp, J.O., Sedlak, D.L., 2014a. Nitrate removal in shallow, open-water treatment wetlands. Environ. Sci. Technol. 48, 11512–11520. http://dx.doi.org/10.1021/es502785t.

Jasper, J.T., Jones, Z.L., Sharp, J.O., Sedlak, D.L., 2014b. Biotransformation of trace organic contaminants in open-water unit process treatment wetlands. Environ. Sci. Technol. 48, 5136–5144. http://dx.doi.org/10.1021/es500351e.

Jones, Z.L., Mikkelson, K.M., Nygren, S., Sedlak, D.L. and Sharp, J.O. Microbial Evolution and Comparison in Open Water Treatment Wetlands with Distinct Locations and Scale. in preparation.

Jones, Z.L., Jasper, J.T., Sedlak, D.L., Sharp, J.O., 2017. Sulfide-induced dissimilatory nitrate reduction to ammonium supports anaerobic ammonium oxidation (Anammox) in an open-water unit process wetland. Appl. Environ. Microbiol. http://dx.doi.org/10.1128/AEM.00782-17.

Kadlec, R.H., Wallace, S.D., 2009. Treatment Wetlands, second edition. CRC Press Boca Raton, FL.

Kadlec, R.H., Cuvellier, C., Stober, T., 2010. Performance of the Columbia, Missouri, treatment wetland. Ecol. Eng. 36, 672–684. http://dx.doi.org/10.1016/j.ecoleng.2009.12.009.

Kadlec, R.H., 2012. Constructed marshes for nitrate removal. Crit. Rev. Environ. Sci. Technol. 42, 934–1005. http://dx.doi.org/10.1080/10643389.2010.534711.

Lightbody, A.F., Nepf, H.M., Bays, J.S., 2009. Modeling the hydraulic effect of transverse deep zones on the performance of short-circuiting constructed treatment wetlands. Ecol. Eng 35, 754–768. http://dx.doi.org/10.1016/j.ecoleng.2008.12.010.

Lin, A.Y.-C., Plumlee, M.H., Reinhard, M., 2006. Natural attenuation of pharmaceuticals and alkylphenol polyethoxylate metabolites during river transport: photochemical and biological transformation. Environ. Toxicol. Chem. 25, 1458–1464. http://dx.doi.org/10.1897/05-412r.1.

Matamoros, V., Garcia, J., Bayona, J.M., 2008. Organic micropollutant removal in a full-scale surface flow constructed wetland fed with secondary effluent. Water Res. 42, 653–660. http://dx.doi.org/10.1016/j.watres.2007.08.016.

Nguyen, M.T., Jasper, J.T., Boehm, A.B., Nelson, K.L., 2015. Sunlight inactivation of fecal indicator bacteria in open-water unit process treatment wetlands: modeling endogenous and exogenous inactivation rates. Water Res. 83, 282–292. http://dx.doi.org/10.1016/j.watres.2015.06.043.

Orange County Water District. (Available at http://ocwd.us/Environment/PradoWetlands.aspx. Accessed May 10, 2016).

Prasse, C., Wagner, M., Schulz, R., Ternes, T.A., 2011. Biotransformation of the antiviral drugs acyclovir and penciclovir in activated sludge treatment. Environ. Sci. Technol. 45, 2761–2769. http://dx.doi.org/10.1021/es103732y.

Prasse, C., Wenk, J., Jasper, J.T., Ternes, T.A., Sedlak, D.L., 2015. Co-occurrence of photochemical and microbiological transformation processes in open-water unit process wetlands. Environ. Sci. Technol. 49, 14136–14145. http://dx.doi.org/10.1021/acs.est.5b03783.

Ramil, M., El Aref, T., Fink, G., Scheurer, M., Ternes, T.A., 2010. Fate of beta blockers in aquatic-sediment systems: sorption and biotransformation. Environ. Sci. Technol. 44, 962–970. http://dx.doi.org/10.1021/es9027452.

Silverman, A.I., Nguyen, M.T., Schilling, I.E., Wenk, J., Nelson, K.L., 2015. Sunlight inactivation of viruses in open-water unit process treatment wetlands: modeling endogenous and exogenous inactivation rates. Environ. Sci. Technol. 49, 2757–2766. http://dx.doi.org/10.1021/es5049754.

Silverman, A.I., Nelson, K.L., Sedlak, D.L., 2016. Design Guidance for Shallow, Open-water Wetlands. in preparation.

Svan, A., Hedeland, M., Arvidsson, T., Jasper, J.T., Sedlak, D.L., Pettersson, C.E., 2016. Identification of transformation products from beta-blocking agents formed in wetland microcosms using LC-Q-ToF. J. Mass Spectrom. JMS 51, 207–218. http://dx.doi.

org/10.1002/jms.3737.
Tarrant Regional Water District, 2017. George W. Shannon Wetlands Project. (Available at http://www.trwd.com/water-supply/wetlands/. Accessed April 2, 2017).
Thullen, J.S., Sartoris, J.J., Nelson, S.M., 2005. Managing vegetation in surface-flow wastewater-treatment wetlands for optimal treatment performance. Ecol. Eng. 25, 583–593. http://dx.doi.org/10.1016/j.ecoleng.2005.07.013.
Vymazal, J., 2011. Constructed wetlands for wastewater treatment: five decades of experience. Environ. Sci. Technol. 45, 61–69. http://dx.doi.org/10.1021/es101403q.
Yamamoto, H., Nakamura, Y., Moriguchi, S., Honda, Y., Tamura, I., Hirata, Y., Hayashi, A., Sekizawa, J., 2009. Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: laboratory photolysis, biodegradation, and sorption experiments. Water Res. 43, 351–362. http://dx.doi.org/10.1016/j.watres.2008.10.039.