HHS Public Access

Author manuscript

Environ Pollut. Author manuscript; available in PMC 2022 January 01.

Published in final edited form as:

Environ Pollut. 2021 January 01; 268(Pt A): 115586. doi:10.1016/j.envpol.2020.115586.

Removal of Urban-Use Insecticides in a Large-Scale Constructed Wetland

Zachary Cryder[1,*], **Douglas Wolf**[1], **Craig Carlan**[2], **Jay Gan**[1]

[1]Department of Environmental Sciences, University of California Riverside, CA, 92521, USA

[2]Department of Neuroscience, University of California Riverside, CA, 92521, USA

Abstract

Water treatment and reuse initiatives are essential to combat declining water supplies in a changing climate, especially in arid and semi-arid regions. Pollution of water resources intensifies the search for strategies to provide water for potable and non-potable reuse that mitigates detrimental ecological and human health effects. Fipronil and synthetic pyrethroids are common urban-use insecticides that exert aquatic toxicity at trace levels and have been often found in urban surface streams. In this study, samples were collected from the 182 ha Prado Wetlands in Southern California for seven months to assess the occurrence of fipronil and its degradation products as well as pyrethroids (bifenthrin and cyfluthrin) in water, sediment, and plants in a 4.45 ha vegetated surface flow constructed wetland (CW). Concentration-based removal values and changes in mass flux were calculated to determine the efficacy of CW treatment. Observed water concentrations were further used to calculate toxic units for the invertebrates *Hyalella azteca* and *Chironomus dilutus*. Pesticide concentrations in water, sediment, and plant samples consistently decreased during passage through the CW at all time points. Removal values for fipronil desulfinyl, fipronil sulfide, fipronil, fipronil sulfone, bifenthrin, and cyfluthrin were 100%, 99.7-100%, 57.8-88.1%, 75.6-100%, 74.7-100%, and 36.6-82.2%, respectively, and there was a general net deposition of pesticides into CW compartments. Toxic unit values decreased in every instance for both aquatic invertebrates. Settling of contaminated particles, adsorption to sediment, plant uptake or adsorption, and subsequent degradation contributed to the effective removal of these urban-use insecticides, which highlights the potential of CWs for protecting urban water quality.

[*]**Corresponding author:** zcryd001@ucr.edu.

Zachary Cryder: conceptualization, methodology, formal analysis, investigation, writing – original draft, writing – review and editing, visualization, project administration

Douglas Wolf: methodology, investigation, writing – review and editing

Craig Carlan: investigation, writing – review and editing

Jay Gan: resources, writing – review and editing, supervision, project administration, funding acquisition

CONFLICT OF INTEREST

The authors declare no conflict of interest.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CAPSULE

A full-scale surface flow constructed wetland reduced concentrations of common urban-use insecticides in surface water and alleviated their associated toxicities.

Keywords

fipronil; pyrethroids; constructed wetland; water treatment; invertebrate toxicity

INTRODUCTION

The combination of rampant urbanization, rapid population growth, and global climate change has resulted in an extraordinary reduction in the potable and non-potable water supply worldwide (Arnold and Gibbons, 1996; Kummu et al., 2010; McDonald et al., 2011; Seto et al., 2012). The deficiency of clean water supplies has led several nations, including the United States, to encourage a reduction in water use (Farré and Faci, 2009; Fielding et al., 2013; Tabbal et al., 2002) and pursue a myriad of water treatment and recycling initiatives (Adhikari et al., 2011; Anderson et al., 2016; Friedler, 2001; Greenway, 2005; Haile et al., 2016; Kadlec and Wallace, 2008; Yang et al., 2006). Water scarcity is exacerbated by pollution of surface water and ground water resources by anthropogenic contaminants such as pesticides. Indoor and outdoor use of insecticides in urban areas has been shown to cause contamination of urban surface water sources. Urban-use insecticides are incompletely removed at wastewater treatment plants (WWTPs) before the release of effluent into surface streams, and runoff after rain and irrigation events further exacerbates surface water contamination.

Fipronil and the synthetic pyrethroids are insecticides utilized at high rates in urban environments for professional and homeowner control of structural pest species such as ants, termites, spiders, and roaches, as well as for elimination of fleas and ticks in veterinary medications (Ensminger, 2014; Sadaria et al., 2017; Teerlink et al., 2017; USEPA, 2011; Weston et al., 2005, 2009). Fipronil and its primary degradation products, fipronil desulfinyl, fipronil sulfide, and fipronil sulfone (abbreviated as fiproles hereafter) are moderately hydrophobic compounds (log K_{ow} = 3.9-4.1; Demcheck and Skrobialowski, 2003) while the pyrethroids are highly hydrophobic with log K_{ow} =5.7-7.6 (Laskowski, 2002). Numerous studies have shown occurrence of both insecticide classes in urban surface water (CDPR, 2016; Gan et al., 2012; Weston et al., 2009; Weston and Lydy, 2012) at concentrations that are toxicologically relevant to aquatic invertebrates (Anderson et al., 2006; Maund et al., 1998; Weston and Jackson, 2009; Weston and Lydy, 2014) as well as in the sediment where residues may persist long after deposition (Lao et al., 2010; Lin et al., 2008). Furthermore, fipronil's major degradation products exhibit toxicity equal to or greater than that of the parent compound (Schlenk et al., 2001; Weston et al., 2014). There is also evidence of additive and synergistic pyrethroid toxicity in sensitive organisms (Trimble et al., 2009). Fiproles and pyrethroids are easily transported in surface runoff (Jiang et al., 2010, 2012; Jorgenson and Young, 2010; Laskowski, 2002; Richards et al., 2016; Thuyet et al., 2012) and are present in WWTP effluents (Sadaria et al., 2017; Supowit et al., 2016; Weston et al., 2013), aggravating the risk of toxicity to non-target aquatic species.

In arid or semi-arid regions such as California, some urban streams are predominantly fed with urban runoff drainage and WWTP effluents. Constructed wetlands (CWs) are one potential solution to the shortcomings of WWTPs and the general lack of stormwater treatment. They have been shown to remove nitrogen and phosphorous species, metals, antibiotic resistance genes, and various organic compounds (Chen et al., 2019; Dong et al., 2020; Kodituwakku and Yatawara, 2020). Existing data suggest that CWs are effective in reducing concentrations of fiproles and pyrethroids (Budd et al., 2009; Supowit et al., 2016). However, field data on the performance of urban wetlands are limited, and in-depth information on the role of various wetland compartments is scarce.

In this study, samples were collected from the Prado Wetlands, a 182 ha constructed treatment wetland system located in Southern California containing open water and vegetated cells, from June 2018-January 2019 and analyzed for fiproles and pyrethroids. The primary objectives were to determine the removal of these trace contaminants by the surface flow wetland, to understand the underlying processes most responsible for contaminant removal, and to estimate potential alleviations in invertebrate toxicity. It was hypothesized that sediment sorption and biodegradation would play a major role in the removal of fiproles and pyrethroids, resulting in reduced aquatic toxicity to organisms exposed to the treated water. Results from this study may be used to optimize the design of CWs and related water treatment systems to improve the quality of recycled water and to attenuate ecotoxicological and human health risks from potable and non-potable applications.

MATERIALS AND METHODS

Chemicals and materials

Fipronil (98.9%), fipronil desulfinyl (97.8%), fipronil sulfide (98.8%), and fipronil sulfone (99.7%) were obtained from the United States Environmental Protection Agency's National Pesticide Standard Repository (Fort Meade, MD). Bifenthrin (98%) and deuterated (d5) bifenthrin (99%) were purchased from Toronto Research Chemicals (Toronto, Ontario, Canada). Cyfluthrin (98%) was purchased from Santa Cruz Biotechnology (Dallas, TX). Ethiprole (97.4%) was obtained from the Shanghai Pesticide Research Institute (Shanghai, China). Decachlorobiphenyl (99.1%) was purchased from AccuStandard (New Haven, CT). Isotopically labeled fipronil ($^{13}C_4$-$^{15}N_2$-fipronil, 99.1%) was obtained from Cambridge Isotope Laboratories (Andover, MA). Solvents and other chemicals used were of pesticide or gas chromatography-mass spectrometry (GC-MS) grade.

Site description

This study was undertaken at the Prado Wetlands in Corona, CA (Figure S1). This 182 ha complex of 45 surface flow wetland ponds was constructed in the 1990s and was initially established to remove NO_3^- from the Santa Ana River (OCWD, 2018). Up to 50% of the Santa Ana River flow, which consists primarily of treated wastewater during non-storm seasons, is diverted into the wetland system for treatment (OCWD, 2018). Due to the dry climate of Southern California, the majority of samples were collected during non-storm seasons. Additional details regarding the Prado Wetlands are provided in the Supporting Information (SI).

The ponds selected for use in this study were cells S5 and S6 (Figure S1; connected by an underground pipe), which together constitute a 4.45 ha vegetated CW complete with inlet and outlet weir boxes. In the context of this study, this vegetated CW will be referred to as the Prado Constructed Wetland (PCW). The hydraulic retention time of the PCW was estimated to be 1.29 d based on the results of a pilot-scale rhodamine WT tracer experiment conducted at the Prado Wetlands (Lin et al., 2003). Samples and measurements were taken at the inlet weir box (inlet), the interface between ponds S5 and S6 following the connection pipe (midpoint), and the outlet weir box (outlet).

Sediment and water properties

Sediment from the inlet, midpoint, and outlet of the PCW was collected from the 0-15 cm depth in 1 L amber glass jars using a small hand shovel and composited for determination of sediment physicochemical properties (Table S1). Sediment was air dried and sieved through a 2 mm mesh before analysis. Sediment particle size composition was determined to be 43% sand, 29% silt, and 28% clay using the 12-h hydrometer method (Klute, 1986). Sediment pH was measured to be 7.34 using a 1:2 (v/v) soil slurry (Donohue, 1992). The organic matter content was 2.35% (w/w), measured via loss-on-ignition (Gavlak et al., 2003). A total organic carbon content of 1.42% was determined using high temperature combustion on an Elementar Vario MAX C/N Analyzer (Elementar Americas, Mt. Laurel, NJ) after the addition of HCl for removal of carbonates (Schumacher, 2002).

The flow rate of the water entering and exiting the PCW at each time point was calculated based on an equation provided by Prado Wetlands staff:

$$CFS = 3.33\ L\ H^{3/2} \quad (1)$$

where CFS is the flow ($ft^3\ s^{-1}$), L is the length of the weir box (ft), and H is the height of the water flowing through the weir box (ft). The calculated flow rates were then converted into metric units (Table S2). Sedimentation rates were subsequently derived using these flow rates and the concentration of total suspended solids (TSS) in water samples collected from the PCW inlet and outlet (Table S2; Budd et al., 2009). Water temperatures were measured *in situ* at the PCW inlet, midpoint, and outlet (Table S3). After water sample collection, water pH measurements were performed *ex situ* in the laboratory prior to extraction (Table S3).

Collection and extraction of wetland samples

Water, sediment, and plant samples were collected from the PCW monthly during the period of June 2018-January 2019, with the exception of September 2018 when there were ongoing maintenance activities. Triplicate 1 L water samples were collected in amber glass bottles at the inlet, midpoint, and outlet of the PCW. Inlet and outlet samples were collected from the water flowing into the corresponding weir boxes, while midpoint samples were collected by placing bottles below the surface of the water against the direction of flow. Sample bottles were transported to the laboratory on ice and stored at 4 °C until extraction. Before extraction, water samples were passed through 0.7 μm filters to separate the TSS from the water. Filtered TSS samples were then dried in preparation for extraction.

Wetland water samples were extracted using a method in Gan et al. (2012), with modifications. Briefly, 30 mL of NaCl was combined with each water sample and liquid-liquid extraction was performed with 60 mL aliquots of dichloromethane (x 3). Each extract was drained through a funnel containing anhydrous Na_2SO_4 to remove residual water, evaporated with a Büchi RE121 Rotovapor (Flawil, Switzerland), and solvent exchanged into 9:1 hexane:acetone (v/v). Samples were then evaporated to approximately 0.5 mL under a gentle nitrogen stream and reconstituted in 1.0 mL hexane for analysis.

Sediment and plant samples were also collected at the PCW inlet, midpoint, and outlet. Sediment samples were collected as described above. Whole samples of California bulrush (*Schoenoplectus californicus*) were collected by pulling the roots out of the sediment. All samples were transported on ice prior to laboratory storage at 4 °C. Sediment samples were dried and ground with a mortar and pestle before extraction. Plant samples were thoroughly washed with DI water to remove any attached sediment particles and biofilms. The cleaned plant samples were dried before pulverizing the tissue in the presence of liquid nitrogen using a mortar and pestle.

The TSS, sediment, and plant samples were extracted by pressurized fluid extraction on a Dionex ASE 350 (Thermo Fisher Scientific, Waltham, MA) using a method similar to Brennan et al. (2009) and Maul et al. (2008). Briefly, sample cells were filled with 1: 1 dichloromethane:acetone (v/v), heated to 100 °C, and extracted at 1500 psi for two 5 min cycles before being flushed with 60% solvent for 1 min. For the TSS samples, the entirety of the solids from each water sample was extracted. Aliquots of the prepared sediment (25 g) and whole plant (5 g) samples were extracted and subjected to in-cell cleanup with Cu powder (Lin et al., 2008) packed between cellulose filters. All extracts were evaporated to approximately 2 mL under a gentle nitrogen stream. Each sample then underwent clean-up on a Florisil cartridge preconditioned with hexane and was eluted with 9:1 hexane:acetone (v/v). Cleaned extracts were again evaporated under a gentle stream of nitrogen to approximately 0.5 mL and reconstituted in 1.0 mL hexane for final analysis.

Chemical analysis and quality control

Samples were analyzed using an Agilent 6890N/5973N GC/MSD (Santa Clara, CA) operated in EI mode and equipped with a 30 m x 0.25 mm x 0.25 μm DB-5MS column. Additional analytical information is provided in the SI. Following sample quantification, student's t-tests and linear regressions were performed using SAS® 9.4 (SAS Institute, Cary, NC). Numerous steps were taken to ensure the accuracy and quality of analysis. Instrumental controls during analysis included running a calibration standard every 10 samples, adding $^{13}C_4$-$^{15}N_2$-fipronil and d5-bifenthrin as internal standards to each extract, and determining method detection limits (MDLs) using EPA Method 40 CFR Part 136, Appendix B (USEPA, 2012). Calculated MDLs were 2 μg L^{-1} for all analytes except for fipronil desulfinyl, which had an MDL of 1 μg L^{-1}. In addition, several procedural controls were utilized. Reagent blanks were analyzed with every set of 7 liquid-liquid extraction samples and 10 pressurized fluid extraction samples. Reagent blanks revealed no presence of the target analytes. Matrix spike samples were analyzed to measure extraction efficiencies, which are listed in the SI. In addition, ethiprole and decachlorobiphenyl were added to all

samples prior to extraction to assess surrogate recoveries, which were 105 ± 23% and 121 ± 18% for liquid-liquid extraction, respectively, and 108 ± 21% and 116 ± 18% for pressurized fluid extraction, respectively. Additional quality control measures are described in the SI.

RESULTS AND DISCUSSION

Spatiotemporal trends of fiproles and pyrethroids

The concentrations of fiproles and pyrethroids in water samples collected from the PCW are depicted in Figure 1. In general, mean whole water concentrations progressively decreased on a spatial level when moving from the inlet to midpoint to outlet for all compounds of interest. In addition, mean outlet concentrations were always lower than mean inlet concentrations. Furthermore, statistically significant ($p < 0.05$) differences existed for the majority of inlet and outlet concentration comparisons. When the differences between inlet and outlet concentrations were not statistically significant, inlet concentrations were found at low levels and with relatively high variability. Since water and the associated TSS is all that enters and leaves the PCW, these findings provide evidence indicating that statistically significant removal of fiproles and pyrethroids occurred as a result of treatment in the PCW. Previous research by agricultural and WWTP effluent-polishing CWs has similarly shown removal of fiproles and pyrethroids (Budd et al., 2009; Supowit et al., 2016).

The mean whole water concentrations of fiproles and pyrethroids also exhibited distinct temporal trends during the sampling period (Figure 1). Mean fipronil concentrations peaked in June 2018, gradually decreased until October 2018, and then increased until January 2019. Mean whole water concentrations of fipronil desulfinyl, fipronil sulfide, and fipronil sulfone incrementally increased from June-August 2018, decreased, and then increased until January 2019. The peak mean whole water concentrations for fipronil desulfinyl and fipronil sulfone occurred in January 2019 while the peak for fipronil sulfide occurred in August 2018. Taken together, these trends correspond to high fipronil application rates in the summer months, gradual decrease via degradation of the parent compound and delayed formation of degradates, and increased transport of applied and degraded residues due to rainfall events in the winter months of 2018-2019. The mean whole water concentrations of bifenthrin and cyfluthrin, on the other hand, steadily increased from June-August 2018, gradually decreased until November 2018, and then increased in December 2018 and January 2019. The mean bifenthrin concentrations peaked in August 2018 while mean cyfluthrin concentrations peaked in January 2019. These trends indicate high use of pyrethroids in the summer months, followed by a period of reduced use and transport, and finally an increase due to runoff from the rain events in the winter that could have transported additional residues through the CW and/or caused resuspension of residues from the sediment bed.

Fipronil and cyfluthrin were detected at the highest levels in whole water PCW samples, with mean concentrations ranging from 13.5-369 and 13.8-455 ng L^{-1}, respectively (Figure 1). Fipronil sulfone and bifenthrin were detected at moderate mean concentrations of ND-32.5 and ND-63.9 ng L^{-1}, respectively. The compounds detected at the lowest levels, fipronil desulfinyl and fipronil sulfide, had mean whole water concentrations of ND-2.48 and ND-4.09 ng L^{-1}, respectively. The water concentrations of fiproles and pyrethroids

measured in this study were similar to previous measurements in California in urban runoff (Gan et al., 2012; Weston et al., 2009).

Figure 2 shows the sediment concentrations (dry weight basis) of fiproles and pyrethroids in the PCW. As was the case with mean levels in whole water samples, mean sediment concentrations for all compounds followed a decreasing spatial trend from the inlet to midpoint to outlet. Since the same spatial pattern was observed for mean water concentrations, this suggests that sediment binding was partially responsible for the dissipation of fiproles and pyrethroids from the water. This finding was to be expected due to the hydrophobicity and strong affinity of these two insecticide classes, particularly for pyrethroids. This was in agreement with previous studies where sediment binding was shown to be an important removal mechanism for pyrethroids in flow-through wetlands receiving agricultural drainage (Budd et al., 2009, 2011). However, based on this spatial trend alone, it was unclear whether the contaminants were temporarily retained by the sediment and available for partition back into the passing water or if they were subsequently degraded in the sediment.

The mean sediment concentrations of fipronil desulfinyl, fipronil sulfide, and bifenthrin followed a similar trend over time (Figure 2). These contaminants generally increased in concentration from June-August 2018, when they reached a peak for the entire study, followed by a decreasing trend until November 2018 before gradually increasing until January 2019. Fipronil in the sediment increased from June-July 2018 when it reached its peak level, decreased until November 2018, and then increased until January 2019. Fipronil sulfone and cyfluthrin peaked in January 2019 and June 2018, respectively, but they followed the same trend as the other compounds. An inspection of Figure 1 and Figure 2 reveals similar seasonal temporal trends for fiproles and pyrethroids in both whole water and sediment samples. In other words, when analytes were present at high levels in whole water samples, they tended to also be present at high levels in the sediment. This finding, combined with the fact that sediment concentrations (Figure 2) did not continuously increase over the duration of the study, indicates that fiproles and pyrethroids were likely actively degraded once partitioned into the sediment phase. Another possibility is that the contaminated sediment particles underwent resuspension and were carried out of the PCW; however, the generally lower whole water concentrations (Figure 1) at the outlet relative to the inlet suggested that the contribution of this process was likely negligible.

Among the six compounds, fipronil (1.93-82.7 ng g^{-1}) and cyfluthrin (0.263-52.4 ng g^{-1}) were detected at the highest mean sediment concentrations during the study period (Figure 2). Fipronil sulfone and bifenthrin were present at moderate levels ranging from 0.166-4.42 and ND-5.40 ng g^{-1}, respectively. The lowest mean levels were found for fipronil desulfinyl and fipronil sulfide, at ND-0.740 and ND-0.718 ng g^{-1}, respectively. This pattern was also reflected in the whole water concentrations (Figure 1). These results again suggest that fiprole and pyrethroid residues in PCW water partitioned into the sediment and underwent degradation on site, rather than accumulated over time.

Fiprole and pyrethroid concentrations in whole plant samples are shown in Figure 3. Mean plant concentrations follow the same spatial trend as whole water or sediment

concentrations, with levels generally decreasing from inlet to midpoint to outlet for all compounds. Since the spatial trends of fiproles and pyrethroids are the same in whole water and plant samples, it appears that plant uptake played a role in the removal of these insecticides in the PCW. Fipronil is a systemic insecticide, so some degree of plant uptake of fiproles was to be expected (Simon-Delso et al., 2015). Detection of pyrethroid residues in whole plant samples was an unexpected finding due to the hydrophobicity of these insecticides and their consequent affinity for sediment. However, there are studies that have documented detection of pyrethroids in plant samples, either by uptake (Bouldin et al., 2006; Mikami et al., 1985) or by apparent irreversible sorption to plant tissues (Hand et al., 2001).

Different temporal trends were observed for fipronil, fipronil degradation products, and the pyrethroids in plant tissues (Figure 3). Fipronil mean plant concentrations initially decreased from June-July 2018, increased to peak levels in August 2018, gradually decreased until November 2018, and progressively increased until January 2019. This trend of fipronil concentrations over time coincided with the temporal trends of fipronil in whole water and sediment samples, providing more evidence that plant uptake contributed to the removal of fipronil in the PCW. Moreover, it is likely that fipronil initially adsorbed to wetland sediment and was then absorbed into macrophyte roots. The mean plant concentrations of fipronil desulfinyl, fipronil sulfide, and fipronil sulfone all gradually increased from June 2018-January 2019, indicating some degree of accumulation in plant tissues over time. However, since fipronil did not follow this temporal trend of accumulation in wetland macrophytes, it is likely that some of the parent compound was metabolized into these derivatives upon uptake. Fipronil sulfone was present at higher concentrations in plant samples than the other degradation products, which was in agreement with previous studies showing that *in vivo* plant oxidation is a major metabolic pathway for absorbed fipronil (Simon-Delso et al., 2015). Bifenthrin and cyfluthrin displayed no temporal trend in plant tissues since they were both only detected in inlet samples at one time point. This suggests that plant adsorption or absorption did not play a major role in the removal of pyrethroids by the PCW.

Fipronil was detected at the highest levels in PCW plants, with mean concentrations of 4.70-194 ng g^{-1} (Figure 3). Moderate mean concentrations of ND-17.7 ng g^{-1} were observed for fipronil sulfone. The lowest mean plant concentrations were measured for fipronil desulfinyl (ND-1.35 ng g^{-1}), fipronil sulfide (ND-0.300 ng g^{-1}), bifenthrin (ND-0.341 ng g^{-1}), and cyfluthrin (ND-3.18 ng g^{-1}). The results of plant tissue analysis reveal that plant uptake played an important role for the removal, degradation, and storage of fipronil, but did not contribute substantially to the removal of fipronil degradation products or pyrethroids. However, it must be noted that the dense vegetation was essentially slowing down the flow and filtering off suspended solids, contributing greatly to the removal through sedimentation. In addition, microbial activity in the rhizosphere of plant roots likely facilitated the degradation of these chemicals in the sediment, further contributing to the overall pesticide removal.

Removal and mass flux of fiproles and pyrethroids

The concentration-based removal values of fiproles and pyrethroids from water flowing through the PCW are given in Table 1; they were calculated using the following equation:

$$Percent\ Removal = \frac{(Mean\ Inlet\ Analyte\ Concentrations) - (Mean\ Outlet\ Analyte\ Concentrations)}{(Mean\ Inlet\ Analyte\ Concentrations)} * 100 \quad (2)$$

Where all concentrations are reported in units of ng L^{-1}. It is essential to mention that estimates of 100% removal included outlet concentrations that were below the detection limit. Therefore, it is possible that removal is slightly less than 100% if compounds are present at very low levels. Over the entire course of the study, removal values for fipronil desulfinyl, fipronil sulfide, fipronil, fipronil sulfone, bifenthrin, and cyfluthrin were 100%, 99.7-100%, 57.8-88.1%, 75.6-100%, 74.7-100%, and 36.6-82.2%, respectively. The compounds with the highest removal values were fipronil desulfinyl, fipronil sulfide, fipronil sulfone, and bifenthrin, while fipronil and cyfluthrin showed the lowest removal. It is important to note that only fipronil, bifenthrin, and cyfluthrin were detected every month, and fipronil and cyfluthrin were detected at higher levels than all the other compounds. Previous studies have similarly shown that the average CW removal rates of fipronil and pyrethroids were 44% and 52-94%, respectively, for other CW systems (Budd et al., 2009; Supowit et al., 2016).

Removal of fiproles and pyrethroids followed no apparent monthly or seasonal trends (Table 1). Based on this finding, and on the conclusions drawn from the data presented in Figures 1–3, it is likely that removal of these compounds was not markedly influenced by seasonal fluctuations in temperature or weather patterns and was more dependent on availability of sediment bindings sites, degradation in the sediment compartment, and, in the case of fipronil, rate of plant uptake. Sediment microorganisms responsible for biotic degradation likely appeared to be unaffected by seasonal temperature variations because temperatures are relatively high year-round in Southern California. In addition, the emergent macrophytes present in the PCW experience rampant growth due to the constant availability of nutrients in the Santa Ana River water. Therefore, aquatic macrophytes were always available for plant uptake and subsequent transformation of fipronil.

In addition to concentration removal, another important metric for ascertaining the efficacy of the PCW is the mass flux of fiproles and pyrethroids (Table 1), which were calculated using the following equation:

$$Mass\ Flux = (Whole\ Water\ Analyte\ Concentration) * (Water\ Flow\ Rate) \quad (3)$$

Whole water concentrations were in units of ng L^{-1} and water flow rate was in units of L d^{-1}. Mass flux values were converted to the units found in Table 1 as appropriate. It is important to note that these flux values are discrete estimates from the time of sampling, but they do provide useful information. In particular, mass influx, mass efflux, and change in mass flux were calculated for the inlet, the outlet, and the difference between the inlet and outlet, respectively. Fipronil, bifenthrin, and cyfluthrin were imported into the PCW at the highest rates, with mean mass influxes of 115 to 12700 mg d^{-1}, 2.37 to 701 mg d^{-1}, and 100 to 6090 mg d^{-1}, respectively. Fipronil desulfinyl (0 to 22.2 mg d^{-1}), fipronil sulfide (0 to 44.9 mg d^{-1}), and fipronil sulfone (0 to 292 mg d^{-1}) exhibited much lower import rates into

the wetland. Changes in mass flux, which represents the net import (positive value) or export (negative value) of chemicals to or from the PCW, were also the highest for fipronil (−426 to 12100 mg d^{-1}), bifenthrin (2.37 to 626 mg d^{-1}), and cyfluthrin (−193 to 5380 mg d^{-1}). The majority of changes in mass flux for these three compounds were statistically significant ($p < 0.05$). In contrast, only one of the changes in mass flux values was statistically significant for fipronil desulfinyl (0 to 6.53 mg d^{-1}), fipronil sulfide (0 to 44.8 mg d^{-1}), and fipronil sulfone (0 to 76.5 mg d^{-1}) since the difference between the mass influxes and effluxes for these compounds was much smaller.

Negative changes in mass flux values were found for fipronil and cyfluthrin in the months of November and December 2018, though only two of these four measurements were statistically significant (Table 1). However, the export of these compounds during this time corresponded to higher outflow than inflow for the PCW (Table S2), which likely resulted in resuspension of sediment particles as evidenced by the negative sedimentation rates observed during these two months. The flow of water through the entire Prado wetlands is regulated to optimize water quality and quantity, which leads to occasional net outflow from certain wetland cells, as was the case for the PCW in November and December 2018. Therefore, although net mass export of fipronil and cyfluthrin occurred during this time, it was compensated for by the high volume of water exiting the PCW, as indicated by the positive concentration removal values (Table 1). Although no outflow, mass efflux, or change in mass flux values could be calculated for January 2019, it is important to mention that the rainfall that occurred during this month resulted in spikes of chemical mass influx and possibly additional resuspension of contaminated sediment particles. However, positive removal values again showed that dilution prevented an increase in outlet concentrations.

To further highlight the importance of adsorption in the removal of fiproles and pyrethroids by the PCW, the relative presence of each compound on TSS obtained from water samples was calculated (Table 2). With two exceptions, the % of each chemical on TSS at the wetland inlet was statistically similar to the outlet value. In August 2018, an average of 87.7% of the bifenthrin in the whole water sample was associated with TSS at the inlet, as compared to 100% at the outlet. In contrast, values decreased from 92.1% at the inlet to 71.9% at the outlet for cyfluthrin in December 2018. In addition, inlet, midpoint, and outlet values were anomalously low for fipronil and cyfluthrin in July 2018. It is likely that some cyfluthrin was associated with dissolved organic matter and included in the aqueous phase concentration (Gustafsson et al., 2001). The lower values for fiproles may be attributed to their moderate hydrophobicity as compared to the pyrethroids. The overall results suggested that the fractions of these compounds on TSS were similar throughout the PCW and were also similar over time, with inlet and outlet values ranging from 60-100%. Combined with the evidence for the importance of sediment binding in the removal of pyrethroids and fiproles, it may be concluded that adsorption to suspended particles and subsequent sedimentation was likely a dominant process governing the fate and transport of these contaminants in CW systems.

Linear regression was carried out to identify additional factors contributing to the removal of fiproles and pyrethroids in the PCW (Table 3). Two dependent variables, concentration-based removal and change in mass flux, and three independent variables, sedimentation rate,

water pH, and water temperature, were considered. Statistically significant ($p < 0.05$) linear relationships were observed between fipronil removal and water pH ($p = 0.0248$, $R^2 = 0.67$), between change in fipronil mass flux and sedimentation rate ($p = 0.0001$, $R^2 = 1$), and between change in cyfluthrin mass flux and sedimentation rate ($p = 0.0175$, $R^2 = 0.88$). These results demonstrate that water pH and water temperature had minimal impact on the removal of fiproles and pyrethroids in the PCW, with the exception of the influence of water pH on the concentration-based removal of fipronil. This finding may emphasize the importance of pH in determining the ionization state of fipronil and hence its adsorption onto sediment particles under field conditions. In addition, the effect of sedimentation rate on the changes in mass flux for fipronil and cyfluthrin—the analytes detected at the highest concentrations and mass influxes—further supports the notion that settling of insecticide-laden particles played a major role in the removal of fiproles and pyrethroids. The evidence provided by this study therefore highlights that settling of contaminated particles and partition into the wetland sediment are crucial in achieving the removal of these urban-use insecticides, which is in agreement with findings from an agricultural drainage wetland (Budd et al., 2009, 2011).

Invertebrate toxicity estimation

To understand the effect of PCW treatment in mitigating the potential toxicity of fiproles and pyrethroids to sensitive aquatic invertebrates, toxic units (TUs) were calculated using the following equation (Weston and Lydy, 2014):

$$TU = \frac{Observed\ Analyte\ Concentration}{Species{-}specific\ Analyte\ Toxicity\ Value} \quad (4)$$

A TU value of 1 or greater indicates that toxicity would occur if the organism in question were exposed to an analyte at the observed concentration. The toxicity threshold values used in the calculations may be found in Table S4 (Weston and Jackson, 2009; Weston and Lydy, 2014).

Calculated TUs based on the concentrations measured at the PCW inlet and outlet are given in Table 4. Sublethal (EC_{50}) and lethal (LC_{50}) toxicity values for the amphipod *Hyalella azteca* were used to determine the change in potential pyrethroid toxicity between inlet and outlet measurements since previous research has demonstrated this organism's sensitivity to pyrethroids (Anderson et al., 2006; Maund et al., 1998; Weston and Jackson, 2009). Mean sublethal bifenthrin TUs decreased from 0.704-19.4 at the inlet to 0-4.91 at the outlet, while mean lethal TUs decreased from 0.302-8.30 to 0-2.10 at the inlet and outlet, respectively. All decreases were statistically significant ($p < 0.05$) except for the month of November 2018 when inlet TUs were relatively low with high variability and outlet TUs were 0 since no bifenthrin was detected. Cyfluthrin mean sublethal TUs were 26.0-240 at the inlet, and decreased to 7.27-68.0 at the outlet. The corresponding mean lethal TUs were 21.5-198 and 6.01-56.1 at the inlet and outlet, respectively. All decreases in cyfluthrin TUs were statistically significant.

The midge *Chironomus dilutus* was selected for the calculation of fiprole TUs (Table 4) since it has been shown to be extremely sensitive to these chemicals (Weston and Lydy,

2014). Mean sublethal TUs for fipronil sulfide decreased from 0-0.414 at the inlet to 0-0.00131 at the outlet in a statistically significant manner. Similarly, mean lethal fipronil sulfide TUs underwent statistically significant decreases from 0-0.0592 at the inlet to 0-1.88 x 10^{-4} at the outlet. Fipronil mean sublethal TUs decreased from 0.984-11.4 at the inlet to 0.416-2.72 at the outlet, while mean lethal TUs decreased from 0.392-4.53 at the inlet to 0.166-1.08 at the outlet. All inlet-outlet comparisons for fipronil were statistically significant except for TUs corresponding to the month of January 2019 when variability in concentrations at the inlet was high. Mean sublethal fipronil sulfone TUs were 0-4.22 at the inlet, decreasing to 0-1.03 at the outlet. Mean lethal TUs for fipronil sulfone were 0-0.312 and 0-0.0761 at the inlet and outlet, respectively. Statistically significant differences for fipronil sulfone were only observed in the months of October 2018, December 2018, and January 2019, but TU values for the other months were all <1 at the inlet and 0 at the outlet.

These results showed that removal of fiproles and pyrethroids by the PCW resulted in toxicity reductions for all urban-use insecticides, and the reductions were statistically significant in most instances (Table 4). The TU values reported in this study represent hypothetical worst-case single chemical exposure scenarios for the most sensitive aquatic invertebrates. Furthermore, the TU values were derived from whole water concentrations and did not take into account bioavailable concentrations. For pyrethroids, studies have shown that bioavailability in whole water and sediment is inhibited by DOM or organic matter (Cui et al., 2013; Xue et al., 2017). Therefore, it is likely that the TU values in this study overestimated the actual toxicity and would serve as a conservative assessment. The influence of bioavailability on fiproles should be less significant given their moderate hydrophobicity. Moreover, the TUs calculated from PCW data do not represent the Prado Wetlands as a whole, since it is composed of many interconnected ponds operating in series. The effluent from the PCW undergoes dilution as it recombines with additional treated water emanating from adjacent wetland cells, is subjected to further treatment, and is ultimately deposited into Chino Creek. As a result, the TU values for the entire treatment chain would very likely be further reduced.

CONCLUSIONS

The results of this study have revealed that a CW receiving water from an urban river was effective in removing the common urban-use insecticides considered in this study. It is clear that sedimentation of contaminated particles, adsorption of dissolved analytes to wetland sediment, uptake into or adsorption to macrophyte tissues, and subsequent degradation were the major mechanisms responsible for removal of these compounds. In addition, this removal coincided with reductions in potential toxicity to sensitive aquatic invertebrates. These findings indicate that CWs would be effective in removing these and similar contaminants from stormwater runoff or treated wastewater as a component of decentralized stormwater treatment or as a polishing step in WWTPs, respectively. CWs require a great deal of land to install and develop, but do not necessitate high operating costs relative to traditional wastewater treatment. Therefore, they could be utilized in conjunction with pollution mitigation efforts to reduce the overall contamination of surface water, reducing potential ecotoxicity and providing higher quality water for reuse initiatives. Future research should focus on further examining the kinetics of, mechanisms responsible, and ideal

conditions required for removal of hydrophobic organic contaminants in CWs to optimize the design and size of such systems, including an investigation of fiprole and pyrethroid mass balance in vegetated constructed wetlands. In addition, continued investigation of the Prado Wetlands, including the removal of contaminants throughout the entire wetland complex and determination of freely dissolved contaminant concentrations using passive samplers, would provide more insight into the overall efficacy of constructed wetland treatment systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

The authors would like to acknowledge the California Department of Pesticide Regulation and the NIEHS T32 Training Grant (T32 ES018827) for funding support. In addition, the authors wish to express their gratitude to the Prado Wetlands staff for site access, to Dr. Megan Plumlee and Christine Pham for their help with planning and logistics, and to Mark Petty for on-site transport and sampling support at the Prado Wetlands.

REFERENCES

Arnold CL Jr., and Gibbons CJ. 1996 Impervious surface coverage: The emergence of a key environmental indicator. Journal of the American Planning Association 62: 243–258.

Kummu M, Ward PJ, de Moel H, and Varis O. 2010 Is physical water scarcity a new phenomenon? Global assessment of water shortage over the last two millennia. Environmental Research Letters 5: 1–10.

McDonald RI, Green P, Balk D, Fekete BM, Revenga C, Todd M, and Montgomery M. 2011 Urban growth, climate change, and freshwater availability. PNAS 108: 6312–6317. [PubMed: 21444797]

Seto KC, Güneralp B, and Hutyra LR. 2012 Global forecasts of urban expansion to 2030 and direct impacts on biodiversity and carbon pools. PNAS 109: 16083–16088. [PubMed: 22988086]

Farré I and Faci J-M. 2009 Deficit irrigation in maize for reducing agricultural water use in a Mediterranean environment. Agricultural Water Management 96: 383–394.

Fielding KS, Spinks A, Russell S, McCrea R, Stewart R, and Gardner J. 2013 An experimental test of voluntary strategies to promote urban water demand management. Journal of Environmental Management 114: 343–351. [PubMed: 23168251]

Tabbal DF, Bouman BAM, Bhuiyan SI, Sibayan EB, and Sattar MA. 2002 On-farm strategies for reducing water input in irrigated rice; case studies in the Philippines. Agricultural Water Management 56: 93–112.

Adhikari AR, Acharya K, Shanahan SA, and Zhou X. 2011 Removal of nutrients and metals by constructed and naturally created wetlands in the Las Vegas Valley, Nevada. Environmental Monitoring Assessment 180: 97–113. [PubMed: 21125423]

Anderson BS, Phillips BM, Voorhees JP, Siegler K, and Tjeerdema R. 2016 Bioswales reduce contaminants associated with toxicity in urban storm water. Environmental Toxicology and Chemistry 35: 3124–3134. [PubMed: 27145488]

Friedler E 2001 Water reuse—an integral part of water resources management: Israel as a case study. Water Policy 3: 29–39.

Greenway M 2005 The role of constructed wetlands in secondary effluent treatment and water reuse in subtropical and arid Australia. Ecological Engineering 25: 501–509.

Haile TM, Hobiger G, Kammerer G, Allabashi R, Schaerfinger B, and Fuerhacker M. 2016 Hydraulic performance and pollutant concentration profile in a stormwater runoff filtration system. Water, Air, and Soil Pollution 227: 34.

Kadlec RH, and Wallace SD. 2008 Treatment Wetlands, 2nd ed. CRC Press, Boca Raton, FL.

Yang B, Lan CY, Yang CS, Liao WB, Chang H, and Shu WS. 2006 Long-term efficiency and stability of wetlands for treating wastewater of a lead/zinc mine and the concurrent ecosystem development. Environmental Pollution 143: 499–512. [PubMed: 16469422]

Ensminger M 2014 Review of representative currently registered fipronil product labels in California. Department of Pesticide Regulation, Sacramento, CA.

Sadaria AM, Sutton R, Moran KD, Teerlink J, Brown JV, and Halden RU. 2017 Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. Environmental Toxicology and Chemistry 36: 1473–1482. [PubMed: 27808432]

Teerlink J, Hernandez J, and Budd R. 2017 Fipronil washoff to municipal wastewater from dogs treated with spot-on products. Science of the Total Environment 599-600: 960–966.

USEPA. 2011 Problem formulation for the environmental fate and ecological risk, endangered species, and drinking water assessments in support of the registration review of fipronil. Office of Pesticide Programs, Washington, D.C.

Weston DP, Holmes RW, You J, and Lydy MJ. 2005 Aquatic toxicity due to residential use of pyrethroid insecticides. Environmental Science & Technology 39: 9778–9784. [PubMed: 16475366]

Weston DP, Holmes RW, and Lydy MJ. 2009 Residential runoff as a source of pyrethroid pesticides to urban creeks. Environmental Pollution 157: 287–294. [PubMed: 18676072]

Demcheck DK and Skrobialowski SC. 2003 Fipronil and degradation products in the rice-producing areas of the Mermentau River Basin, Louisiana, February-September 2002. FS-010-03 U.S.G.S., Baton Rouge, LA.

Laskowski DA 2002 Physical and chemical properties of pyrethroids. Review of Environmental Contamination and Toxicology 174: 49–170.

CDPR. 2016 Urban monitoring in southern California watersheds FY 2014-2015. Environmental Monitoring Branch, California Environmental Protection Agency: Sacramento, CA.

Gan J, Bondarenko S, Oki L, Haver D, and Li JX. 2012 Occurrence of fipronil and its biologically active derivatives in urban residential runoff. Environmental Science & Technology 46: 1489–1495. [PubMed: 22242791]

Weston DP and Lydy MJ. 2012 Stormwater input of pyrethroid insecticides to an urban river. Environmental Toxicology and Chemistry 31*:* 1579–1586. [PubMed: 22504879]

Anderson BS, Phillips BM, Hunt JW, Connor V, Richard N, and Tjeerdema RS. 2006 Identifying primary stressors impacting macroinvertebrates in the Salinas River (California, USA): Relative effects of pesticides and suspended particles. Environmental Pollution 54: 408–417.

Maund SJ, Hamer MJ, Warinton JS, and Kedwards TJ. 1998 Aquatic ecotoxicology of the pyrethroid insecticide lambda-cyhalothrin: Considerations for higher-tier aquatic risk assessment. Pesticide Science 54: 408–417

Weston DP and Jackson CJ. 2009 Use of engineered enzymes to identify organophosphate and pyrethroid-related toxicity in toxicity identification evaluations. Environmental Science & Technology 43: 5514–5520. [PubMed: 19708390]

Weston DP and Lydy MJ. 2014 Toxicity of the insecticide fipronil and its degradates to benthic macroinvertebrates of urban streams. Environmental Science & Technology 48: 1290–1297. [PubMed: 24368023]

Lao W, Tsukada D, Greenstein DJ, Bay SM, and Maruya KA. 2010 Analysis, occurrence, and toxic potential of pyrethroids and fipronil in sediments from an urban estuary. Environmental Toxicology and Chemistry 29: 843–851. [PubMed: 20821513]

Lin K, Haver D, Oki L, and Gan J. 2008 Transformation and sorption of fipronil in urban stream sediments. Journal of Agricultural and Food Chemistry 56: 8594–8600. [PubMed: 18729374]

Schlenk D, Huggett DB, Allgood J, Bennett E, Rimoldi J, Beeler AB, Block D, Holder AW, Hovinga R, and Bedient P. 2001 Toxicity of fipronil and its degradation products to Procambrus sp.: Field and laboratory studies. Archives of Environmental Contamination and Toxicology 41: 325–332. [PubMed: 11503069]

Trimble AJ, Weston DP, Belden JB, and Lydy MJ. 2009 Identification and evaluation of pyrethroid insecticide mixtures in urban sediments. Environmental Toxicology and Chemistry 28: 1687–1695. [PubMed: 19245272]

Jiang W, Lin K, Haver D, Qin S, Ayre G, Spurlock F, and Gan J. 2010 Wash-off potential of urban use insecticides on concrete surfaces. Environmental Toxicology and Chemistry 29: 1203–1208. [PubMed: 20821561]

Jiang W, Haver D, Rust M, and Gan J. 2012 Runoff of pyrethroid insecticides from concrete surfaces following simulated and natural rainfalls. Water Research 46: 645–652. [PubMed: 22153959]

Jorgenson BC and Young TM. 2010 Formulation effects and the off-target transport of pyrethroid insecticides from urban hard surfaces. Environmental Science & Technology 44: 4951–4957. [PubMed: 20524665]

Richards J, Reif R, Luo Y, and Gan J. 2016 Distribution of pesticides in dust particles in urban environments. Environmental Pollution 214: 290–298. [PubMed: 27105165]

Thuyet DQ, Jorgenson BC, Wissel-Tyson C, Watanabe H, and Young TM. Wash off of imidacloprid and fipronil from turf and concrete surfaces using simulated rainfall. Science of the Total Environment 414: 515–524.

Supowit SD, Sadaria AM, Reyes EJ, and Halden RU. 2016 Mass balance of fipronil and total toxicity of fipronil-related compounds in process streams during conventional wastewater and wetland treatment. Environmental Science & Technology 50: 1519–1526. [PubMed: 26710933]

Weston DP, Ramil HL, and Lydy MJ. 2013 Pyrethroid insecticides in municipal wastewater. Environmental Toxicology and Chemistry 32: 2460–2468. [PubMed: 23893650]

Chen J, Deng W, Liu Y, Hu L, He L, Zhao J, Wang T, and Ying G. 2019 Fate and removal of antibiotics and antibiotic resistance genes in hybrid constructed wetlands. Environmental Pollution 249: 894–903. [PubMed: 30965541]

Dong C, Li M, Zhuang L, Zhang J, Shen Y, and Li X. 2020 The improvement of pollutant removal in the ferric-carbon micro-electrolysis constructed wetland by partial aeration. Water 12: 389.

Kodituwakku KARK and Yatawara M. 2020 Phytoremediation of industrial sewage sludge with Eichhornia crassipes, Salvinia molesta and Pistia stratiotes in batch fed free water flow constructed wetlands. Bulletin of Environmental Contamination and Toxicology 10.1007/s00128-020-02805-0

Budd R, O'geen A, Goh KS, Bondarenko S, and Gan J. 2009 Efficacy of constructed wetlands in pesticide removal from tailwaters in the Central Valley, California. Environmental Science & Technology 43: 2925–2930. [PubMed: 19475972]

OCWD 2018 Prado Wetlands fact sheet. Fountain Valley, CA.

Lin AY, Debroux J, Cunningham JA, and Reinhard M. 2003 Comparison of rhodamine WT and bromide in the determination of hydraulic characteristics of constructed wetlands. Ecological Engineering 20: 75–88.

Klute A 1986 Water retention: laboratory methods In: Klute A (Ed.), Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods, second ed. Soil Science Society of America, Madison, WI, pp. 635–660.

Donohue SJ 1992 Reference soil and media diagnostic procedures for the southern region on the United States In: Southern Cooperative Services Bulletin 374 Virginia Agric. Exp. Stn., Blacksburg, VA.

Gavlak R, Horneck D, Miller RO, and Kotuby-Amacher J. 2003 Soil, Plant and Water Reference Methods for the Western Region (WCC-103 Publication), second ed. Collins: Colorado State University, Ft.

Schumacher BA 2002 Methods for the determination of total organic carbon (TOC) in soils and sediments. Ecological Risk Assessment Support Cent 1–23.

Brennan AA, You J, and Lydy MJ. 2009 Comparison of cleanup methods for fipronil and its degradation products in sediment extracts. Talanta 78: 1408–1413. [PubMed: 19362209]

Maul JD, Brennan AA, Harwood AD, and Lydy MJ. 2008 Effect of sediment-associated pyrethroids, fipronil, and metabolites on *Chironomus tentans* growth rate, body mass, condition index, immobilization, and survival. Environmental Toxicology and Chemistry 27: 2582–2590. [PubMed: 18699702]

USEPA. 2012 EPA Method 40 CFR Appendix B Part 136. Retrieved from https://www.govinfo.gov/content/pkg/CFR-2012-title40-vol24/pdf/CFR-2012-title40-vol24-part136-appB.pdf.

Budd R, O'geen A, Goh KS, Bondarenko S, and Gan J. 2011 Removal mechanisms and fate of insecticides in constructed wetlands. Chemosphere 83: 1581–1587. [PubMed: 21296378]

Simon-Delso N, Amaral-Rogers V, Belzunces LP, Bonmatin JM, Chagnon M, Downs C, Furlan L, Gibbons DW, Giorio C, Girolami V, Goulson D, Kreutzweiser DP, Krupke CH, Liess M, Long E, McField M, Mineau P, Mitchell EAD, Morrissey CA, Noome DA, Pisa L, Settele J, Stark JD, Tapparo A, Van Dyck H, Van Praagh J, Van der Sluijs JP, Whitehorn PR, and Wiemers M. 2015 Systemic insecticides (neonicotinoids and fipronil): Trends, uses, mode of action and metabolites. Environmental Science and Pollution Research 22: 5–34. [PubMed: 25233913]

Bouldin JL, Farris JL, Moore MT, Smith S Jr., and Cooper CM. 2006 Hydroponic uptake of atrazine and lambda-cyhalothrin in *Juncus effuses* and *Ludwigia peploides*. Chemosphere 65: 1049–1057. [PubMed: 16709423]

Mikami N, Baba Y, Katagi T, and Miyamoto J. 1985 Metabolism of the synthetic pyrethroid fenpropathrin in plants. Journal of Agricultural and Food Chemistry 33: 980–987.

Hand LH, Kuet SF, Lane MCG, Maund SJ, Warinton JS, and Hill IR. 2001 Influences of aquatic plants on the fate of the pyrethroid insecticide lambda-cyhalothrin in aquatic environments. Environmental Toxicology and Chemistry 20: 1740–1745. [PubMed: 11491557]

Gustafsson O, Nilsson N, and Bucheli TD. 2001 Dynamic colloid-water partitioning of pyrene through a coastal Baltic spring bloom. Environmental Science & Technology 35: 4001–4006. [PubMed: 11686359]

Cui X, Mayer P, and Gan J. 2013 Methods to assess bioavailability of hydrophobic organic contaminants: Principles, operations, and limitations. Environmental Pollution 172: 223–234. [PubMed: 23064200]

Xue J, Liao C, Wang J, Cryder Z, Xu T, Liu F, and Gan J. 2017 Development of passive samplers for in situ measurement of pyrethroid insecticides in surface water. Environmental Pollution 224: 516–523. [PubMed: 28259582]

Highlights

- A full-scale constructed wetland (CW) effectively treated fiproles and pyrethroids.
- Wetland sediment was an important sink for fiproles and pyrethroids.
- Plant uptake played a role in wetland removal of fipronil.
- Sediment sorption and subsequent degradation is the primary removal pathway.
- CW treatment reduced fiprole and pyrethroid toxic units for aquatic invertebrates.

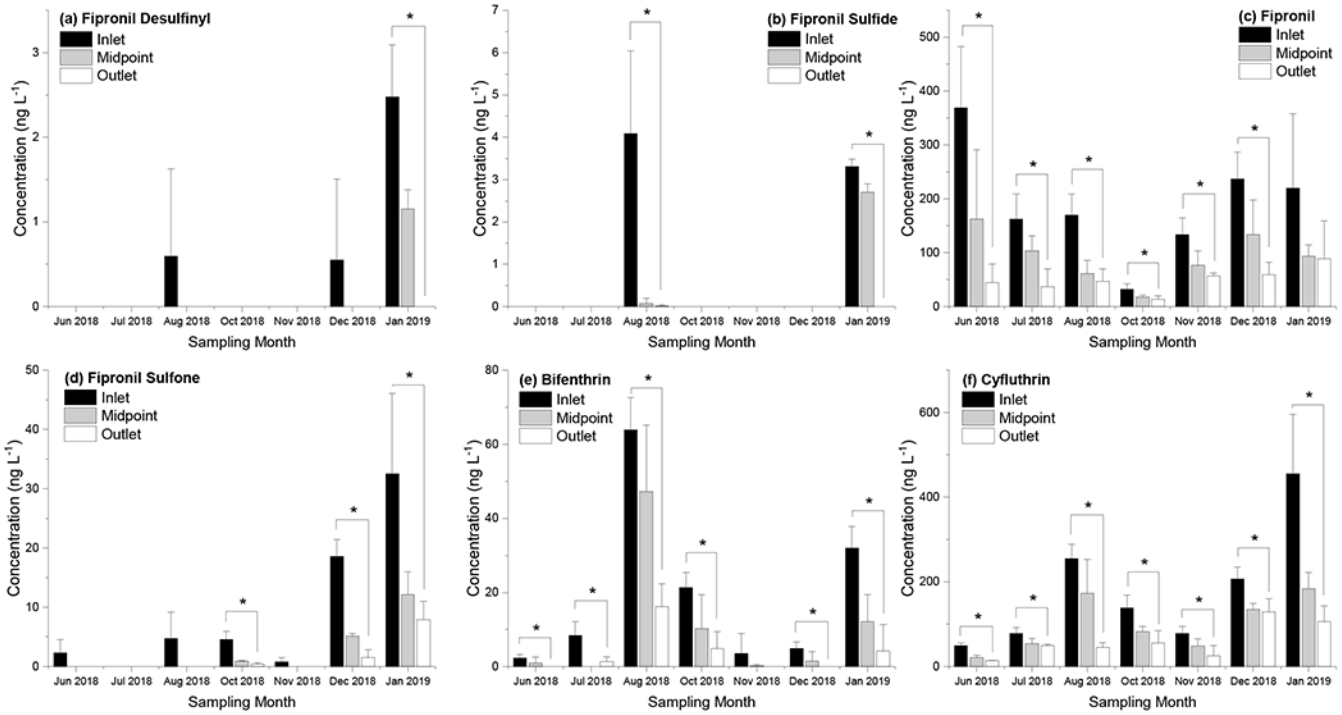

Figure 1:

Whole water concentrations of fipronil desulfinyl (a), fipronil sulfide (b), fipronil (c), fipronil sulfone (d), bifenthrin (e), and cyfluthrin (f) in samples collected from the Prado Constructed Wetland. Data are reported as mean ± 1 SD. Asterisks indicate a statistically significant ($p < 0.05$) difference between inlet and outlet concentrations.

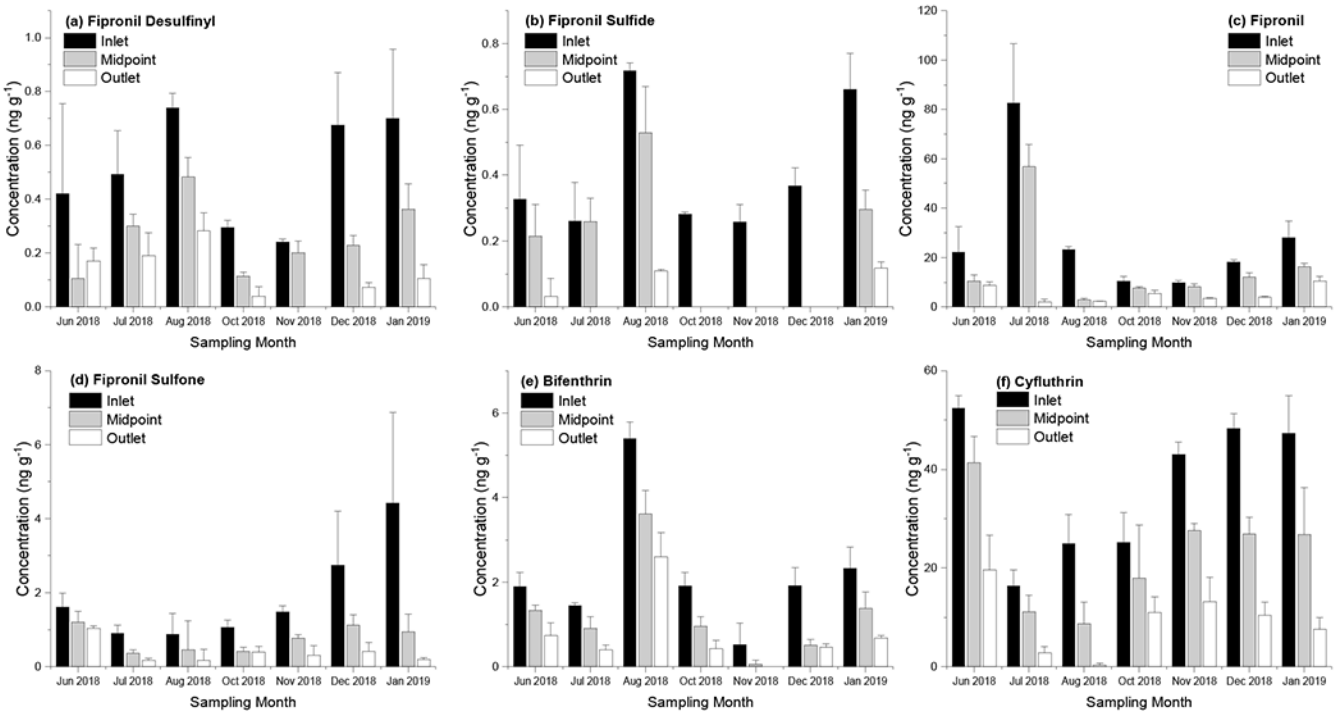

Figure 2:

Sediment (dry weight) concentrations of fipronil desulfinyl (a), fipronil sulfide (b), fipronil (c), fipronil sulfone (d), bifenthrin (e), and cyfluthrin (f) in samples collected from the Prado Constructed Wetland. Data are reported as mean ± 1 SD.

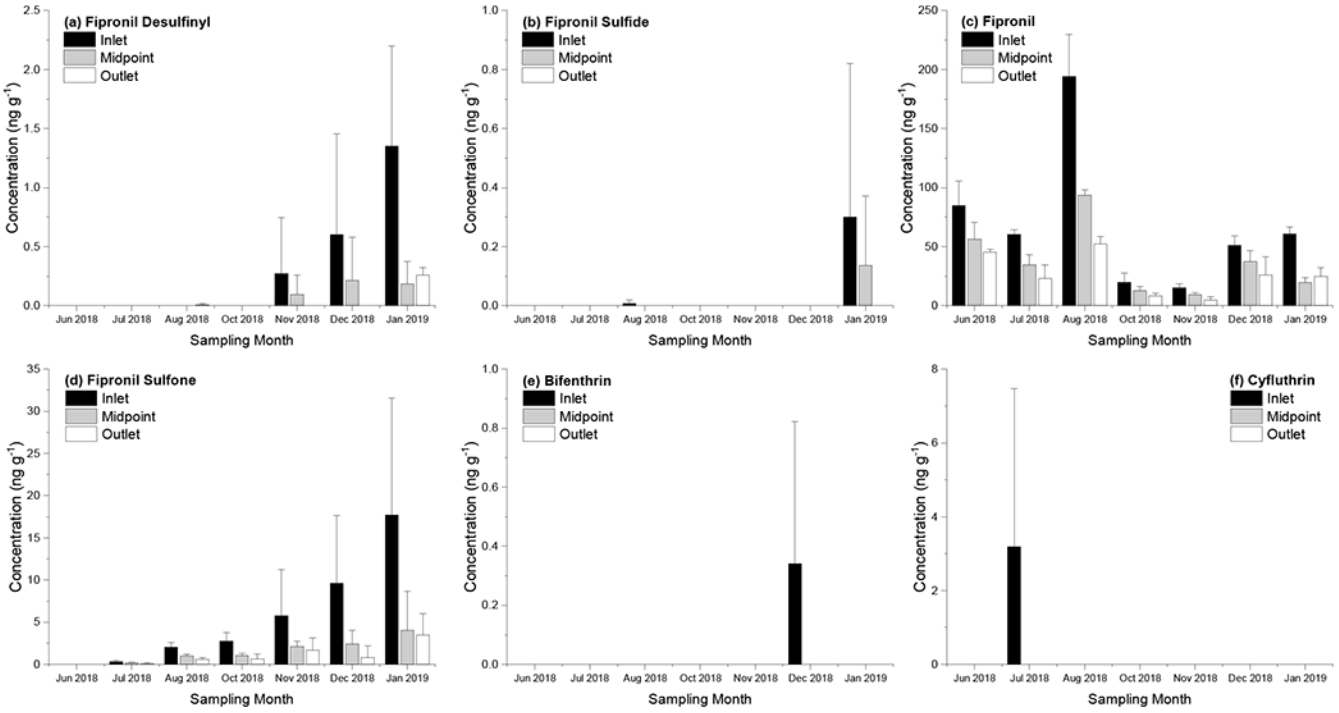

Figure 3:

Plant tissue concentrations of fipronil desulfinyl (a), fipronil sulfide (b), fipronil (c), fipronil sulfone (d), bifenthrin (e), and cyfluthrin (f) in samples collected from the Prado Constructed Wetland. Data are reported as mean ± 1 SD.

Table 1.

Mass flux and concentration-based removal of fiproles and pyrethroids from the Prado Constructed Wetland (2018-2019). Data are reported as mean ± 1 SD where applicable.

		June	July	August	October	November	December	January
Fipronil Desulfinyl	**Mass Influx[a] (mg d^{-1})**	0	0	6.53 ± 11.3	0	0	0.268 ± 0.465	22.2 ± 5.46
	Mass Efflux[b] (mg d^{-1})	0	0	0	0	0	0	-[d]
	Δ Mass Flux (mg d^{-1})	0	0	6.53[c]	0	0	0.268	-[e]
	Removal (%)	-	-	100	-	-	100	100
Fipronil Sulfide	**Mass Influx (mg d^{-1})**	0	0	44.9 ± 21.5	0	0	0	29.7 ± 1.61
	Mass Efflux (mg d^{-1})	0	0	0.143 ± 0.247	0	0	0	-
	Δ Mass Flux (mg d^{-1})	0	0	44.8	0	0	0	-
	Removal (%)	-	-	99.7	-	-	-	100
Fipronil	**Mass Influx (mg d^{-1})**	4050 ± 1250	12700 ± 3560	1870 ± 427	566 ± 183	338 ± 77.0	115 ± 24.0	1980 ± 1240
	Mass Efflux (mg d^{-1})	413 ± 329	532 ± 478	518 ± 212	137 ± 61.9	765 ± 85.1	135 ± 51.9	-
	Δ Mass Flux (mg d^{-1})	3640*[f]	12100*	1350*	429	−426*[g]	−20.0	-
	Removal (%)	88.1	77.3	72.2	57.8	57.8	74.8	59.8
Fipronil Sulfone	**Mass Influx (mg d^{-1})**	25.1 ± 24.6	0	52.0 ± 48.9	81.0 ± 24.1	1.97 ± 1.72	9.02 ± 1.37	292 ± 122
	Mass Efflux (mg d^{-1})	0	0	0	4.53 ± 2.36	0	3.38 ± 2.93	-
	Δ Mass Flux (mg d^{-1})	25.1	0	52.0	76.5*	1.97	5.64	-
	Removal (%)	100	-	100	90.3	100	92.0	75.6
Bifenthrin	**Mass Influx (mg d^{-1})**	25.5 ± 10.8	646 ± 292	701 ± 96.0	376 ± 71.5	8.93 ± 13.6	2.37 ± 0.822	288 ± 52.4
	Mass Efflux (mg d^{-1})	0	19.8 ± 17.6	177 ± 67.2	48.7 ± 46.5	0	0	-
	Δ Mass Flux (mg d^{-1})	25.5	626	524*	328*	8.93	2.37*	-
	Removal (%)	100	83.5	74.7	77.4	100	100	87.0
Cyfluthrin	**Mass Influx (mg d^{-1})**	542 ± 65.3	6090 ± 1100	2790 ± 374	2440 ± 543	198 ± 40.1	100 ± 13.7	4090 ± 1270
	Mass Efflux (mg d^{-1})	129 ± 6.45	716 ± 40.9	497 ± 115	564 ± 291	338 ± 323	293 ± 69.8	-

	June	July	August	October	November	December	January
Δ Mass Flux (mg d^{-1})	413*	5380*	2300*	1880*	−140	−193*	-
Removal (%)	72.0	36.6	82.2	59.7	68.1	37.6	76.7

[a] Influx is the flow of a given analyte into the wetland at the inlet weir box.

[b] Efflux is the flow of a given analyte out of the wetland at the outlet weir box.

[c] Positive values of Δ Mass Flux indicate import of a given analyte to the wetland cell.

[d] Due to rain-induced flooding of the outlet weir box in January, no flow calculation could be performed. As a result, no mass flux at the outlet weir box could be calculated.

[e] Since mass efflux could not be calculated for January, it was not possible to calculate Δ Mass Flux for this time point.

[f] Asterisks indicate a statistically significant ($p < 0.05$) difference in mass flux between inlet and outlet measurements.

[g] Negative values of Δ Mass Flux indicate export of a given analyte from the wetland cell.

Table 2.

Relative presence of fiproles and pyrethroids on total suspended solids (TSS) present in water samples collected from the Prado Constructed Wetland. Data are reported as mean ± 1 SD.

		July[a]	August	October	November	December	January
Fipronil Desulfinyl on TSS (%)	**Inlet**	-[b]	100[c]	-	-	100	100 ± 0
	Midpoint	-	-	-	-	-	100 ± 0
	Outlet	-	-	-	-	-	-
Fipronil Sulfide on TSS (%)	**Inlet**	-	79.3 ± 2.19	-	-	-	100 ± 0
	Midpoint	-	98.1	-	-	-	100 ± 0
	Outlet	-	100	-	-	-	-
Fipronil on TSS (%)	**Inlet**	3.30 ± 5.72	84.7 ± 13.9	100 ± 0	71.9 ± 9.12	82.3 ± 1.51	95.2 ± 4.19
	Midpoint	0	100 ± 0	100 ± 0	76.8 ± 8.06	98.6 ± 2.50	98.4 ± 2.76
	Outlet	1.13 ± 1.60	93.6 ± 11.1	100 ± 0	61.6 ± 7.71	75.8 ± 8.16	100 ± 0
Fipronil Sulfone on TSS (%)	**Inlet**	-	94.9 ± 7.20	100 ± 0	100 ± 0	100 ± 0	100 ± 0
	Midpoint	-	-	100 ± 0	-	100 ± 0	100 ± 0
	Outlet	-	-	100 ± 0	-	100 ± 0	100 ± 0
Bifenthrin on TSS (%)	**Inlet**	100 ± 0	87.7 ± 3.08	95.2 ± 8.34	100 ± 0	92.5 ± 13.1	100 ± 0
	Midpoint	-	84.1 ± 3.07	100 ± 0	100	100	100 ± 0
	Outlet	66.7 ± 57.7	100 ± 0*[d,e]	100 ± 0	-	-	100 ± 0
Cyfluthrin on TSS (%)	**Inlet**	32.5 ± 9.64	93.5 ± 5.88	100 ± 0	84.6 ± 11.6	92.1 ± 5.44	100 ± 0
	Midpoint	25.7 ± 12.7	96.3 ± 6.45	100 ± 0	86.9 ± 12.1	100 ± 0	100 ± 0
	Outlet	21.7 ± 7.44	100 ± 0	100 ± 0	100 ± 0	71.9 ± 4.05*	100 ± 0

[a] Values for June 2018 are not included since the method used to separate the water and TSS phases for this initial time point resulted in incomplete filtration based on visual inspection of filtered samples. A more robust method was adopted for the remaining samples. Whole water concentrations were still obtained for these incompletely filtered samples.

[b] Hyphens indicate that the analyte was not detected in the aqueous or TSS phase.

[c] Data reported without a standard deviation indicate that only one sample contained analyte at a detectable level.

[d] Statistical tests were performed when there was mean inlet and outlet data available.

[e] Asterisks indicate a statistically significant ($p < 0.05$) difference in the percentage of analyte adsorbed to TSS between inlet and outlet measurements.

Table 3.

Linear regression analyses of fiprole and pyrethroid concentration-based removal and change in mass flux versus sedimentation rate, water pH, and water temperature.

	Fipronil	Fipronil Sulfone	Bifenthrin	Cyfluthrin
Removal (%) vs. Sedimentation Rate (kg d^{-1})	Removal = (Sedimentation Rate)*(0.00326) + 65.1	-[a]	Removal = (Sedimentation Rate)*(−0.00239) + 89.2	Removal = (Sedimentation Rate)*(−0.00555) + 61.8
R^2	0.35	-	0.11	0.23
p-value	0.294	-	0.580	0.410
Removal (%) vs. Water pH	Removal = (Water pH)*(67.3) − 436	Removal = (Water pH)*(49.5) − 278	Removal = (Water pH)*(21.4) − 71.8	Removal = (Water pH)*(−11.2) + 146
R^2	0.67	0.53	0.074	0.008
p-value	0.0248*[b]	0.101	0.555	0.854
Removal (%) vs. Water Temperature (°C)	Removal = (Water Temperature)*(1.22) + 52.2	Removal = (Water Temperature)*(1.08) + 77.6	Removal = (Water Temperature)*(−0.467) + 95.6	Removal = (Water Temperature)*(1.01) + 47.5
R^2	0.36	0.50	0.058	0.10
p-value	0.152	0.116	0.602	0.491
Δ Mass Flux (mg d^{-1}) vs. Sedimentation Rate (kg d^{-1})	Δ Mass Flux = (Sedimentation Rate)*(3.09) − 59.9	-	Δ Mass Flux = (Sedimentation Rate)*(0.128) + 183	Δ Mass Flux = (Sedimentation Rate)*(1.25) + 732
R^2	1	-	0.59	0.88
p-value	0.0001*	-	0.130	0.0175*
Δ Mass Flux (mg d^{-1}) vs. Water pH	Δ Mass Flux = (Water pH)*(22300) − 166000	Δ Mass Flux = (Water pH)*(−61.7) + 496	Δ Mass Flux = (Water pH)*(112) − 592	Δ Mass Flux = (Water pH)*(3970) − 28300
R^2	0.38	0.070	0.0028	0.061
p-value	0.192	0.668	0.921	0.637
Δ Mass Flux (mg d^{-1}) vs. Water Temperature (°C)	Δ Mass Flux = (Water Temperature)*(148) + 558	Δ Mass Flux = (Water Temperature)*(2.57) − 8.36	Δ Mass Flux = (Water Temperature)*(16.0) + 4.24	Δ Mass Flux = (Water Temperature)*(76.3) + 419
R^2	0.025	0.21	0.086	0.034
p-value	0.764	0.432	0.573	0.726

[a] Hyphens indicate that there was insufficient data to perform linear regression analysis.

[b] Asterisks indicate a statistically significant ($p < 0.05$) linear correlation.

Table 4.

Toxic units (TU) of fiproles and pyrethroids in whole water samples collected from the Prado Constructed Wetland. Data are reported as mean ± 1 SD.

				June	July	August	October	November	December	January
Hyalella azteca[a,b]	Bifenthrin	TU EC_{50}	Inlet	0.704 ± 0.297	2.52 ± 1.14	19.4 ± 2.65	6.44 ± 1.22	1.07 ± 1.63	1.48 ± 0.513	9.70 ± 1.77
			Outlet	0*[e]	0.417 ± 0.371*	4.91 ± 1.86*	1.46 ± 1.39*	0	0*	1.26 ± 2.19*
		TU LC_{50}	Inlet	0.302 ± 0.127	1.08 ± 0.488	8.30 ± 1.14	2.76 ± 0.525	0.460 ± 0.700	0.635 ± 0.220	4.16 ± 0.758
			Outlet	0*	0.179 ± 0.159*	2.10 ± 0.796*	0.624 ± 0.595*	0	0*	0.542 ± 0.938*
	Cyfluthrin	TU EC_{50}	Inlet	26.0 ± 3.13	41.3 ± 7.44	134 ± 17.9	72.6 ± 16.1	41.3 ± 8.37	109 ± 14.9	240 ± 74.3
			Outlet	7.27 ± 0.363*	26.2 ± 1.49*	23.9 ± 5.54*	29.3 ± 15.1*	13.2 ± 12.6*	68.0 ± 16.2*	55.8 ± 19.7*
		TU LC_{50}	Inlet	21.5 ± 2.59	34.1 ± 6.14	111 ± 14.8	60.0 ± 13.3	34.1 ± 6.91	89.9 ± 12.3	198 ± 61.4
			Outlet	6.01 ± 0.300*	21.6 ± 1.23*	19.7 ± 4.58*	24.2 ± 12.5*	10.9 ± 10.4*	56.1 ± 13.4*	46.1 ± 16.3*
Chironomus dilutus[c,d]	Fipronil Sulfide	TU EC_{50}	Inlet	0	0	0.414 ± 0.198	0	0	0	0.334 ± 0.0181
			Outlet	0	0	0.00131 ± 0.00228*	0	0	0	0*
		TU LC_{50}	Inlet	0	0	0.0592 ± 0.0284	0	0	0	0.0479 ± 0.00260
			Outlet	0	0	1.88E-4 ± 3.26E-4*	0	0	0	0*
	Fipronil	TU EC_{50}	Inlet	11.4 ± 3.50	5.02 ± 1.41	5.24 ± 1.20	0.984 ± 0.318	4.13 ± 0.939	7.28 ± 1.52	6.77 ± 4.25
			Outlet	1.36 ± 1.08*	1.14 ± 1.02*	1.45 ± 0.700*	0.416 ± 0.188*	1.74 ± 0.194*	1.83 ± 0.703*	2.72 ± 2.19
		TU LC_{50}	Inlet	4.53 ± 1.40	2.00 ± 0.563	2.09 ± 0.477	0.392 ± 0.127	1.65 ± 0.375	2.90 ± 0.607	2.70 ± 1.69
			Outlet	0.540 ± 0.432*	0.454 ± 0.407*	0.580 ± 0.279*	0.166 ± 0.0749*	0.694 ± 0.0773*	0.730 ± 0.281*	1.08 ± 0.875
	Fipronil Sulfone	TU EC_{50}	Inlet	0.296 ± 0.292	0	0.615 ± 0.579	0.595 ± 0.177	0.102 ± 0.0886	2.41 ± 0.366	4.22 ± 1.76
			Outlet	0	0	0	0.0580 ± 0.0303*	0	0.193 ± 0.168*	1.03 ± 0.399*
		TU LC_{50}	Inlet	0.0219 ± 0.0216	0	0.0455 ± 0.0429	0.0440 ± 0.0131	0.00752 ± 0.00656	0.179 ± 0.0271	0.312 ± 0.131
			Outlet	0	0	0	0.00429 ± 0.00224*	0	0.0143 ± 0.0124*	0.0761 ± 0.0295*

[a]Toxicity values for *Hyalella azteca* sourced from Weston and Jackson, 2009.

[b] Sublethal end point for EC_{50}: ability to swim.

[c] Toxicity values for *Chironomus dilutus* sourced from Weston and Lydy, 2014.

[d] Sublethal end point for EC_{50}: ability to thrash when prodded.

[e] Asterisks indicate a statistically significant ($p < 0.05$) difference between the inlet and outlet TU values.