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Pharmaceuticals and Personal Care Products in an Effluent-Dominated Stream: Seasonal Variability and Downstream Fate

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PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN AN EFFLUENT-DOMINATED STREAM: SEASONAL VARIABILITY AND DOWNSTREAM FATE

by

Bradley R. Buswell

A thesis submitted in partial fulfillment
of the requirements for the degree

of

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in

Environmental Engineering

Approved:

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UTAH STATE UNIVERSITY
Logan, Utah

2017

ABSTRACT

Pharmaceuticals and Personal Care Products in an Effluent-Dominated Stream: Seasonal Variability and Downstream Fate

by

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Utah State University, 2017

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Wastewater treatment plant (WWTP) effluents are major sources of pharmaceuticals and personal care products (PPCPs) in the environment and effluent-dominated streams (EDSs) represent worst-case scenarios for PPCP exposures to aquatic organisms. The concentrations of PPCPs downstream from a WWTP can be altered by dilution and fate processes such as biodegradation, photodegradation and sorption. The relative importance of these processes depends on the individual PPCPs and environmental variables that vary seasonally. The primary objective of this study was to determine the concentrations of selected PPCPs in an EDS as a function of season and distance from a WWTP with the hypothesis being that the downstream attenuation of the PPCPs would vary based on their corresponding physicochemical properties. A secondary objective was to evaluate the ability of the constructed wetlands located between the plant and creek to reduce PPCP concentrations. Samples were collected seasonally from above and below the East Canyon Water Reclamation Facility (ECWRF) and within the constructed wetlands for selected PPCPs. Except for caffeine, downstream PPCP concentrations were higher than upstream, indicating that the ECWRF effluent is the major source of PPCPs in East Canyon Creek. Generally, the highest PPCP concentrations in the stream were observed in July and the lowest in May corresponding to the times of lowest and highest ratio of stream to effluent flows, respectively. Dilution was the major factor associated with the declining PPCP concentrations downstream of the ECWRF but the extent of decline varied between compounds suggesting other fate mechanisms also play a role. Sorption of PPCPs to wetland sediments was greater than stream sediments but overall the retention time within the wetlands was too short to significantly reduce the amount of PPCPs moving into the stream. The observed concentrations of individual PPCPs in East Canyon Creek were lower than those expected to negatively impact the health of aquatic organisms but mixture effects are still a potential concern.

(84 pages)

PUBLIC ABSTRACT

Pharmaceuticals and Personal Care Products in an Effluent-Dominated Stream: Seasonal Variability and Downstream Fate

by

Bradley R. Buswell

Pharmaceuticals and personal care products (PPCPs) consist of a large group of compounds including medicines, lotions, soaps, shampoos, and even flame retardants and insect repellants. After use, PPCPs often enter waste streams that are directed to municipal wastewater treatment plants (WWTPs). Due to inefficient removals in conventional wastewater treatment processes, WWTP discharges into streams and rivers are a major source of PPCPs to the environment.

The East Canyon Water Reclamation Facility (ECWRF) is a WWTP in Park City, Utah. After treatment, the ECWRF effluent is discharged into a small constructed wetland area before it enters East Canyon Creek. Due to low base flows in the late summer months, East Canyon Creek is a stream that is effluent-dominated seasonally. There is concern that PPCP levels in the creek might negatively impact aquatic organisms.

The focus of this study was to determine the concentrations of selected PPCPs in East Canyon Creek over different seasons and at varying distances from the ECWRF. A secondary objective of this study was whether the small constructed wetlands that receives ECWRF effluent decreases PPCP concentrations before entering the creek. Additionally, it was investigated whether sorption to wetland and stream sediments played a role in the fate of PPCPs in the wetlands and creek.

Except for caffeine, the ECWRF was found to be the major source of PPCPs in East Canyon Creek. In general, the highest concentrations of PPCPs in the creek were observed during late July, when approximately 76% of downstream water originated from ECWRF. Also, the lowest PPCP concentrations were observed during May, coinciding with a period of high spring snowmelt runoff. Downstream concentrations tended to decrease with increasing distance downstream (up to 10 km) for five out of the eleven selected PPCPs. For all selected PPCPs, concentrations did not tend to decrease within the small constructed wetlands, indicating that the wetlands are too small to have an impact. Analysis of sediment samples indicated that PPCPs tended to sorb more to wetland sediments than stream sediments, likely because of higher levels of organic carbon content.

Comparison of instream PPCP concentrations to risk value concentrations indicates that individual levels of PPCPs in East Canyon Creek are too low to have an impact on fish and other aquatic organisms, although little is known about the potential impact of PPCP mixtures.

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I would like to express my sincere thanks to my major professor Dr. William Doucette. His patience, support, and expertise were fundamental in completing this degree. I would also like to thank the members of my thesis committee, Dr. Laurie McNeill and Dr. David Stevens, for their feedback and assistance.

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INTRODUCTION

Literature Review

Due to their widespread use and near-ubiquitous presence in the environment, pharmaceuticals and personal care products (PPCPs) have been labeled as contaminants of emerging concern (US EPA 2015; Sima et al. 2014). A large and diverse group of compounds, PPCPs include pharmaceuticals used in human and animal treatment, personal care products such as soaps, lotions, and shampoos, and compounds such as flame retardants, plasticizers, and insect repellants. After use, PPCPs are often washed down the drain or enter water systems that eventually make it to wastewater treatment plants (WWTPs). Unfortunately, WWTPs do not often completely remove PPCPs during treatment and WWTP effluents are a major source of PPCPs in the environment. Currently there are no federal regulations regarding the discharge of PPCPs by WWTPs, although the United States Environmental Protection Agency does monitor selected PPCPs (e.g., steroidal hormones) in drinking water under the Unregulated Contaminant Monitoring Rule (US EPA 2012a).

In streams that receive WWTP effluents, particularly in arid/semi-arid regions of the world, a large portion of the flow may be comprised of the effluent during some of the year (Brooks et al. 2006). Effluent-dominated streams (EDSs) represent worst-case scenarios for concentrations of PPCPs in the environment (Brooks et al. 2006; Du et al. 2015) and may pose a risk to aquatic organisms and ecosystems. For example, in a study of U.S. surface waters, Anderson et al. (2012) found that only aquatic organisms in effluent-impacted surface waters, and not all surface waters at large, are at risk from steroid estrogenic compounds and associated impacts.

Studies performed throughout the United States and Canada have found ng/L PPCP concentrations in many surface waters and EDSs (Schultz and Furlong 2008; Waiser et al. 2011). In a review of research done in the Great Lakes region during the period 2007-2012, Uslu et al. (2013) found that high ng/L concentrations of PPCPs were reported in WWTP influents and effluents. Additionally, PPCPs were found in streams and lakes in the ng/L concentration range. In an earlier study in the same region, Metcalfe et al. (2003) found pharmaceuticals, including carbamazepine, at ng/L concentrations 500 m downstream from a WWTP.

Schultz et al. (2010) conducted a study along two EDSs in Colorado and Iowa. Antidepressant levels were below the limit of quantitation at sampling sites upstream from the respective WWTPs, whereas antidepressants were found at ng/L concentrations as far as 8.4 km downstream from the discharge points. Additionally, concentrations of antidepressants were found to be at ng/g levels in streambed sediment and ng/g levels in the brain tissue of fish collected in the EDSs.

In the spring, the flow in Wascana Creek in Saskatchewan, Canada is dominated by snow melt. However, in the winter months, the effluent provides almost 100% of the flow. Waiser et al. (2011) found a mixture of antibiotics, analgesics, anti-inflammatories, a lipid regulator, caffeine, cocaine, nicotine, and DEET in the creek at ng/L levels, with the highest concentrations during winter months.

In EDSs, dilution often tends to decrease PPCP concentrations downstream from WWTP effluents (Barber et al. 2013). However, some PPCPs in EDSs have been found to show little attenuation for large distances downstream from WWTPs, with reported values of maximum distances ranging from 8 km up to 60 km (Barber et al. 2013;

Massey et al. 2010; Waiser et al. 2011). A study of three EDSs in Arkansas determined that antibiotics in the water column traveled km-scale distances before significant dilution occurred (Massey et al. 2010).

In addition to dilution, decreasing concentrations could also be caused by biodegradation, sorption, hydrolysis, and photodegradation (Brown et al. 2015). For example, acetaminophen has been shown to be biodegradable in water-sediment systems (Loffler et al. 2005) and fluoxetine is readily photodegraded in natural waters (Lam et al. 2005). Many PPCPs, depending on their physicochemical properties, can be found in streambed sediment (Sima et al. 2014). In a 2010 study, PPCPs levels were reported in streambed sediment at ng/g concentrations, with antidepressants venlafaxine and fluoxetine having the highest detection frequencies and concentrations (Schultz et al. 2010). Massey et al. (2010) found several antibiotics in streambed sediment at concentrations up to 1000 ng/g, with corresponding pseudo-partitioning coefficients ranging from 4-8000 L/kg. Adsorption of sulfamethoxazole to solid surfaces has been demonstrated to be dependent on pH (Zhang et al. 2010). Sorption of PPCPs to plant foliar material was shown to be related to octanol-water partitioning coefficients, log K_{ow}, and Henry's law constants, K_H (Calderon-Preciado et al. 2013).

PPCPs in EDSs can bioaccumulate in aquatic organisms (Sima et al. 2014). Various pharmaceuticals have been measured in fish tissues, including fillet, brain, liver tissues and blood samples, at ng/g levels (Barber et al. 2015; Brooks et al. 2005; Grabicova et al. 2014, Ramirez et al. 2009).

Exposure through gills and skin, instead of dietary exposure, has been shown to be the primary route of uptake by fish and other aquatic organisms (Du et al. 2014; Du et al. 2015; Melvin et al. 2014). Uptake of diphenhydramine in fish was shown to be dependent on pH due to speciation of ionic and neutral forms, suggesting that bioavailability of ionizable PPCPs is pH dependent (Nichols et al. 2015). Exposure to PPCPs has been linked to deleterious effects in aquatic organisms such as sex changes and intersex organisms due to estrogenic compounds (Barber et al. 2015; Woodling et al. 2006), and cell biology alterations and behavioral/reproductive changes in mussels (Franzellitti et al. 2014; Hazelton et al. 2014). Lab studies have shown that exposure to mixtures of PPCPs pose a greater impact and risk to aquatic organisms than exposure to individual compounds (Franzellitti et al. 2015; Melvin et al. 2014).

Another potential concern is human exposure through the use of reclaimed water for crop irrigation. Paltiel et al. (2016) found higher levels of the antiseizure drug carbamazepine in the urine of healthy individuals who had consumed reclaimed wastewater-irrigated produce relative to similar individuals who had consumed fresh water-irrigated produce.

Du et al. (2012) conducted a study of pharmaceuticals in fish tissues in East Canyon Creek. Fish were sampled from an upstream location relative to the ECWRF and from a location downstream. Pharmaceuticals were not detected in any fish from the upstream location. In fish tissues from the downstream location, 3 and 10 compounds (out of 17 target analytes) were detected in fillet (0.14-12 ng/g range) and liver tissues (0.27-600 ng/g), respectively.

Site Background and Description

East Canyon Water Reclamation Facility (ECWRF) is a WWTP in Summit County, Utah, USA. ECWRF is one of two WWTPs that treat wastewater from Park City, Utah and surrounding areas. The total population of Park City is 7,558 (US Census Bureau 2010). With a capacity of 4.0 MGD, ECWRF treated an average of 2.89 MGD (4.87 cfs) in 2016 (Michael Boyle, personal communication, February 27, 2017). The plant consists of aerobic and anaerobic bioreactors that, in addition to removing incoming solids, provide biological phosphorus removal, aided by chemical phosphorous removal.

The ECWRF effluent is discharged into a constructed wetland area before entering East Canyon Creek. Constructing new wetlands was required during the ECWRF upgrade project of 1994-1997 when the construction of new clarifiers encroached upon the existing wetlands (Michael Boyle, personal communication, November 2, 2016). The area of the constructed wetlands is approximately 6000 m^2. The effluent discharge flows through several constructed channels. The approximate flow length through the wetlands is 215 m, depending on the channel and specific flow path.

East Canyon Creek is a relatively shallow stream whose flow is dominated by snow melt during the spring and summer months and ECWRF effluent the rest of the year.

Objectives

The primary objective of this study was to determine the concentrations of selected PPCPs in East Canyon Creek as a function of season and distance from ECWRF with the hypothesis that downstream attenuation of these PPCPs would vary based on their physicochemical properties (e.g., charge, hydrophobicity). In addition to ECWRF effluent, water and sediment samples were collected from locations upstream and downstream from ECWRF six times during 2016 to test this hypothesis.

Table 1: Target analyte abbreviations, structures (at pH = 8), and corresponding uses.

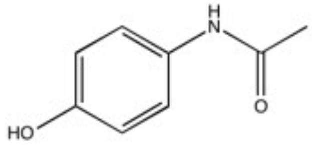
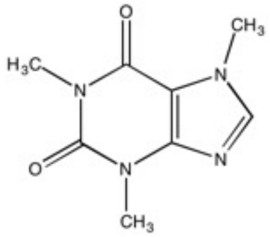
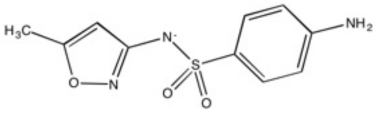
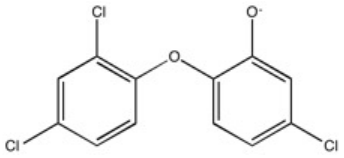
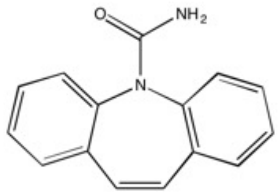
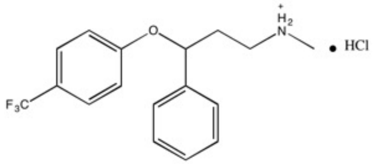
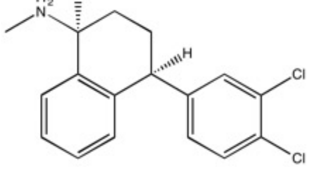
Compound	Abbreviation	Structure	Class/Use
Acetaminophen	ACM		Analgesic and antipyretic
Caffeine	CAF		Stimulant
Sulfamethoxazole	SMZ		Antibiotic
Triclosan	TRI		Antimicrobial
Carbamazepine	CBZ		Antiseizure
Fluoxetine	FLX		Antidepressant
Sertraline	SER		Antidepressant

Table 1: (Continued)

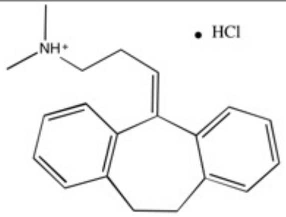
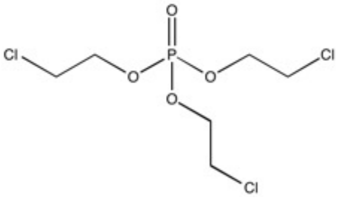
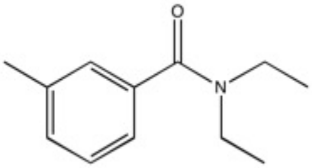
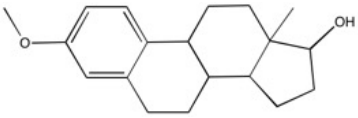
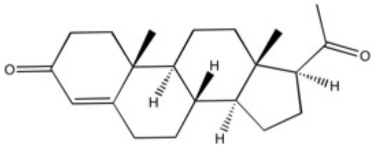
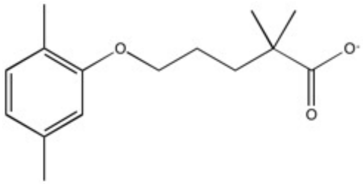
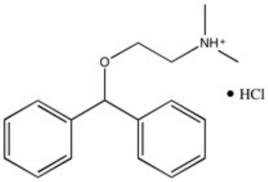
Compound	Abbreviation	Structure	Class/Use
Amitriptyline	AMT		Antidepressant
Tris (2-chloroehtyl) Phosphate	TCEP		Flame Retardant
DEET	DEET		Insect repellent
β-Estradiol	β-ESD		Reproductive hormone
Progesterone	PRG		Reproductive hormone
Gemfibrozil	GEM		Antihyperlipidemic
Diphenhydramine	DPH		Antihistamine

Table 2: Physicochemical properties of target analytes, including molecular weight, pK_a, K_H, log K_{ow}, water solubility, and charge of major species at pH = 8.

Compound	Molecular Weight	pK_a	K_H (atm-m^3/mole)	log K_{ow}	Solubility (mg/L), 25°C	Charge of Dominant Species at pH = 8
ACM	151	9.38	6.42E-13	0.46	14000	Neutral
CAF	194	0.61, 3.6[1]	3.58E-11	-0.07	21600	Neutral
SMZ	253	1.6, 5.7[2]	9.56E-13	0.89	610	Negative
TRI	290	7.9[3]	4.99E-09	4.76	10	Negative[a]
CBZ	236	13.9[4]	1.08E-10	2.25[4]	112[10]	Neutral
FLX	346	9.8[5]	8.90E-08	2.45	14000[3]	Positive
SER	343	9.85[6]	3.90E-15	2.18	94	Positive
AMT	314	9.4[7]	4.33E-15	2.18	10.8	Positive
TCEP	285	NA	2.55E-08	1.44	7000	Neutral
DEET	191	NA	2.08E-08	2.02	666	Neutral
β-ESD	272	NA	3.64E-11	4.01	3.9	Neutral
PRG	314	NA	6.49E-08	3.87	8.81	Neutral
GEM	250	4.5[8]	1.19E-08	4.77	5.0	Negative
DPH	292	8.9[9]	2.33E-16	3.27	602	Positive[b]

[1] Bundy et al. (2007); [2] Boreen et al. (2004); [3] O'Neil (2006); [4] Jones et al. (2002); [5] ChemAxon (2005); [6] ChemAxon (2016); [7] Haynes (2014); [8] ChemAxon (2009); [9] Sangster (1997); [10] Ferrari et al. (2003). All other values were obtained using EPI Suite (US EPA 2012b).

[a] At pH = 8, the speciation of TRI is approximately 55% negatively charged and 45% neutral. [b] At pH= 8, approximately 88% of DPH is positively charged and 12% is neutral. All other major species listed are greater than 98% of the indicated speciation.

NA = Not applicable (i.e., lacks functional group that participates in acid/base chemistry).

A secondary objective was to investigate if any significant removal of PPCPs could be attributed to the small constructed wetlands located between the ECWRF and East Canyon Creek. To address this objective, wetland water and sediment samples were collected during five sampling events in 2016 and analyzed for PPCP concentrations.

Physicochemical Properties of Target Analytes

Target PPCPs listed in Table 1 were selected for this study based on chemical properties (Table 2), widespread use, frequent detection in surface waters, and potential risk to the environment and aquatic organisms. The target PPCPs represent a range of therapeutic uses and several of the compounds have been detected previously in fish in the East Canyon Creek. The selected PPCPs include both prescription and over-the-counter medications, food additives (caffeine), antibiotics linked to antibiotic resistance in bacteria (sulfamethoxazole and triclosan), hormonal steroids (β-estradiol and progesterone), an insect repellant (DEET), and a flame retardant (TCEP).

MATERIALS AND METHODS

Sampling Overview

Sampling Locations

Samples were collected from East Canyon Creek at 2 locations upstream and 3 locations downstream from the ECWRF as shown in Figure 1. Samples were also collected from 4 locations within the constructed wetlands that are adjacent to the ECWRF (Figure 2). Stream sampling locations are designated by number with negative numbers representing upstream locations and positive numbers denoting downstream locations. The larger the number, the greater the distance from the ECWRF. Similarly, the four wetland sample locations are also numbered in order of increasing distance from the ECWRF effluent discharge point. GPS coordinates of the stream and wetland sampling locations are included in Table 3 and Table 4, respectively. Grab samples of the ECWRF effluent were also collected. The last downstream sampling location, S+3, was chosen as a site because it was the last point downstream before another surface water input enters East Canyon Creek. The other specific sampling locations were selected mainly based on accessibility during winter and high stream flow sampling periods.

Sampling Method

At each sampling site pH, temperature, and conductivity were collected using a HI 98194 Multiparameter meter (Hannah Instruments, Woonsocket, RI). Approximate stream depth was also recorded. Surface water grab samples were collected in triplicate using 4 L amber bottles. Following the USGS general protocol for collecting stream bed sediment (Shelton 1994), stream bed sediment was collected in glass jars by removing the

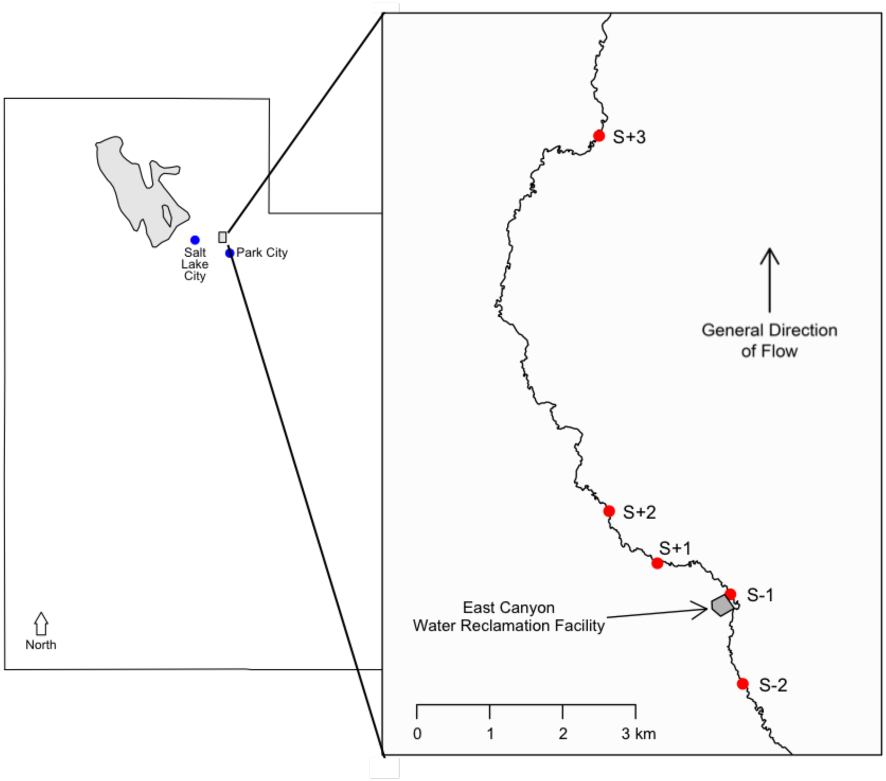


Figure 1: Map of sampling locations along the East Canyon Creek.

Table 3: GPS coordinates and elevation for the East Canyon Creek sampling locations.

Location	Latitude	Longitude	Elevation	Distance from Effluent-Stream Confluence
S-2	40.747886°	-111.561975°	6290 ft	-1.88 km
S-1	40.758969°	-111.563989°	6250 ft	-0.03 km
S+1	40.762811°	-111.575858°	6220 ft	1.72 km
S+2	40.769258°	-111.583706°	6210 ft	3.14 km
S+3	40.815713°	-111.585343°	6050 ft	9.99 km

top layer (approximately 1 cm deep and over an area of about 10 cm^2) of fine-grained particulate matter from depositional zones within approximately 50 m of water sampling locations. After collection, samples were stored on ice until delivery to the Utah Water Research Laboratory (UWRL). Upon delivery, samples were stored in the dark at <4ºC until analysis.

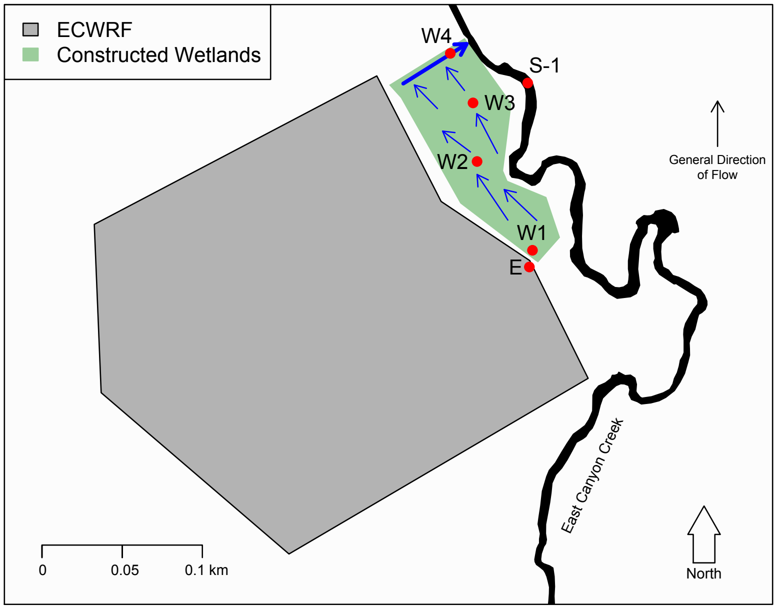


Figure 2: Aerial view of the ECWRF and adjacent wetland sampling locations. Blue arrows indicate the general direction of flow through the wetland channels.

Table 4: GPS coordinates of the sampling locations within the constructed wetlands.

Location	Latitude	Longitude
W1	40.757960°	-111.563770°
W2	40.758460°	-111.564180°
W3	40.758790°	-111.564210°
W4	40.759069°	-111.564378°

Sampling Occurrence

Samples were collected in February (2/25/16), May (5/17/16), June (6/8/16), July (7/28/16), August (8/25/16), and October (10/13/16). Water samples were collected at each stream location and from the ECWRF effluent during each sampling event, with the exception that effluent and S+3 samples were not collected during the February sampling event due to lack of accessibility during the winter. Water samples were collected from W1 and W3 during the August sampling event and from W1 and W2 during the October sampling event. Sediment sampling varied from month to month. Tables A1-A2 summarize the sample types, locations and time.

Chemicals

Individual standards were prepared by dissolving known masses of pure compounds in LC-MS grade methanol. The individual standard solutions were then used to prepare calibration curve standards and a mixed standard of all 14 compounds that was used as a spike solution to evaluate compounds recoveries. The spike solution was prepared to have a concentration of 2.0 ng/µL for each compound in LC-MS grade methanol. Calibration curve standards (8 standards ranging from 0.1 µg/L to 100 µg/L) were also made in LC-MS grade methanol. All standard solutions were stored in the dark at 4ºC.

Deuterated standards of acetaminophen-*d*4, sulfamethoxazole-*d*4, carbamazepine-*d*10, fluoxetine-*d*5, gemfibrozil-*d*6, triclosan-*d*3, and sertraline-*d*3 were purchased from CDN Isotopes (Pointe-Claire, Quebec, Canada). The deuterated standards, prepared by dissolving known masses of labeled compounds in LC-MS grade methanol, were only used during the October sampling event. From these individual standards, a labeled spike solution was prepared to have of 2.0 ng/µL for each of the 7 individual compounds in LC-MS grade methanol.

Sample Preparation – Solid Phase Extraction

Compounds of interest were extracted from unfiltered water samples using solid phase extraction (SPE). SPE was performed using Oasis^{TM} HLB (divinylbenzene and N-vinylpyrrolidone monomers) cartridges (500 mg, 6 cc; Waters corporation, Milford, MA).

Triplicate 2 L aqueous samples were extracted for each sampling location per sampling event. The 4 L amber bottles were weighed before and after extraction, with the corresponding weight used to determine the volume of water that passed through the SPE cartridge. Deionized (DI) water was used as a laboratory blank sample (LBS) and spiked DI water (20 µL of 2.0 ng/µL of spike stock solution) was used as a laboratory control spike (LCS) during each SPE event. Two sub-samples (one upstream and one downstream) were spiked with 20 µL of spike stock solution to serve as matrix spikes (MSs). Matrix spikes were also prepared from effluent and wetland sub-samples for each event in which those samples were collected. Laboratory blank samples, LCSs, and MSs were weighed and otherwise treated the same as other samples. Before extraction, samples, blanks, and quality control spikes were allowed to equilibrate at room temperature for 2 hours. The SPE cartridges were attached to a Waters (Milford, MA) 12-port vacuum manifold and conditioned with 15 mL of LC-MS grade methanol and 15 mL of DI water before sample extraction. All samples and spike solutions were passed through cartridges at a flow rate of approximately 10 mL/min. After the samples were extracted, the SPE cartridges were air dried using the vacuum manifold for one hour. Analytes were eluted from the cartridges using 10 mL LC-MS grade methanol. The eluents were then refrigerated at 4°C until LC-MS analysis.

Sample Preparation – Accelerated Solvent Extraction

Accelerated solvent extraction (ASE) is commonly used to extract PPCPs from sediment samples (Chitescu et al. 2012; Kinney et al. 2006; Massey et al. 2010; Schultz et al. 2010). In this study, an automated Dionex ASE 150 system (Dionex Co., Sunnyvale, CA) was used to perform the extraction of sediment samples. Prior to extraction, sediment samples were disaggregated with a mortar and pestle. An ASE circular glass fiber filter (Thermo Scientific, Waltham, MA) was placed at the bottom of a 34-mL stainless steel ASE vessel before the addition of sample. Four grams of sample were mixed with an amount of diatomaceous earth so that the combination would fill the ASE vessel. Samples were extracted with LC-MS grade methanol at 120ºC. Other ASE parameter settings included two 1-minute static cycles, a solvent rinse volume of 60% and a purge time of 100 s. The final volume of extracts was approximately 55 mL. Extracts were then centrifuged as a clean-up step. Lastly, extracts were brought to a final volume of approximately 10 mL using TurboVap® II (nitrogen gas at 15-20 psi and water temperature of 59ºC, Biotage, Charlotte, NC).

Sediment Characterization

Sediment samples were sent to the Utah State University Analytical Laboratories (USUAL, Logan, UT) for organic carbon matter characterization. For each sample an organic matter loss on ignition test was performed and results were reported in percent organic matter.

Quality Assurance/Quality Control

Calibration curve standards with concentrations of 0.1, 0.5, 1, 5, 10, 20, 50, and 100 µg/L were prepared in LC-MS grade methanol. Extraction efficiencies were evaluated using laboratory control spikes (LCSs) and matrix spikes (MSs). Laboratory blank samples (LBSs) were used to check for contamination issues and to help determine detection limits. Continuous calibration verification (CCV) samples were used every 7-10 samples during LC-MS analysis. For the October sampling event, isotope dilution was used to quantify the target analytes for which deuterated standards were purchased.

Laboratory Blank Samples

Aqueous laboratory blank samples (LBSs) comprised of 2 L of DI water were analyzed after going through each step of the extraction procedure. Sediment LBSs were prepared and analyzed by extracting diatomaceous earth in the ASE procedure.

Laboratory Control Spikes

Laboratory control spikes for aqueous samples were prepared by spiking 2 L of DI water with 20 µL of 2.0 ng/µL of spike stock solution (i.e., 40 ng of each target analyte). The aqueous LCSs were extracted in the same manner as other aqueous samples (i.e., SPE). LCSs for sediment samples were prepared by spiking diatomaceous earth with 20 µL of 2.0 ng/µL of spike stock solution and extracted using ASE.

Matrix Control Spikes

Matrix control spikes were prepared and analyzed for each sampling event. Aqueous MSs were prepared during each sampling event for each water media, i.e., a MS for an upstream sample, a downstream sample, a wetland sample, and an effluent sample. These aqueous MSs were prepared by spiking 20 µL of spike stock solution (2.0 ng/µL) into the corresponding sample. Aqueous MSs were extracted following the SPE process as described in the Sample Preparation section. Sediment MSs were prepared by spiking 20 µL of spike stock solution (2.0 ng/µL) between mixing and extraction.

Continuous Calibration Verification

According to the U.S. EPA Method 1694, the acceptable range for continuous calibration verification samples (CCVs) is between 70-130% of the expected value (US EPA 2007). CCVs were analyzed after every 7-10 samples during LC-MS analysis to ensure that the instrument wasn’t drifting. Samples were rerun between or around CCVs that were not within the 70-130% range.

Isotope Dilution

Isotope dilution involves adding an isotopically labeled analog for each target analyte to the sample before extraction, and improves accuracy and precision by correcting for extraction losses, matrix effects within the LCMS system, and instrument variability. In complex matrices, such as WWTP influent and effluent, isotope dilution has repeatedly been shown to be the superior method for adjusting and accounting for matrix interferences (either suppression or enhancement) in which electrospray ionization (ESI) is used in the LCMS system (Du et al. 2012, Delatour 2004, Stoob et al. 2005, Stuber and Reemtsma 2004). If possible, using a labeled analog for each target PPCP is recommended (US EPA 2007) but can be cost-prohibitive with long analyte lists.

Isotope dilution was used for seven of the selected PPCPs during October in order to evaluate if deuterated analogs would significantly improve the accuracy and precision of MS recoveries and to correct for matrix effects. Each October water and sediment sample was spiked with 20 μL of the labeled spike stock solution (2.0 ng/μL) before extraction (SPE or ASE). In addition, each LCS, MS, and LBS was also spiked with the same amount of labeled spike stock solution.

Sample Analysis

An Agilent 1290 Infinity LC system with an Agilent 6490 Triple Quadrupole MS system was used to analyze sample extracts for the target compounds. Separation of the analytes was achieved with an Agilent Eclipse Plus C18 column (2.1 x 50 mm, 1.8 µm I.D, 0.45 mL/min flow rate, 10 min. run time, 3 µL injections). The LC-MS system utilized a binary pump with mobile phase A prepared with 0.1 % formic acid (by volume) in DI water and mobile phase B prepared with 0.1 % formic acid (by volume) in LC-MS grade acetonitrile. The gradient chromatographic settings are given in Table 5. The MS system utilizes the technique of electrospray ionization (ESI) to create ions that can be analyzed and quantified by the detector.

Up to and including the August sampling event, target analyte concentrations were determined in each sample, blank, and spike using external calibration. For the October sampling event, concentrations were determined by the isotope dilution method for the compounds with corresponding deuterated standards and by external calibration for all other compounds. The isotope dilution method comprises determining concentrations based on the ratio of the response for the target analyte to the response for the labeled analog.

Table 5: Chromatography gradient settings. Mobile phase A comprises 0.1 % formic acid in water. Mobile phase B comprises 0.1 % formic acid (by volume) in LC-MS grade acetonitrile.

Time (min)	Mobile Phase A (%)	Mobile Phase B (%)
0.0	95.0	5.0
10.0	5.0	95.0
13.0	5.0	95.0

RESULTS AND DISCUSSION

Quality Assurance/Quality Control

Method Detection Limit

The method detection limit (MDL) was determined following standard EPA guidelines (US EPA 2016). The MDL was determined separately for both the external calibration and isotope dilution methods (Table B1).

Blanks – Laboratory and Instrument Blanks

At least one LCB was analyzed with each batch of SPE and ASE extractions. In addition, instrument blanks (comprised of LC-MS grade methanol) were analyzed periodically during each LCMS run. All LCBs and instrument blanks were below the MDL for all PPCP analytes.

Laboratory Control Spikes – Water

Table 6 shows average LCS recoveries for both the external calibration and isotope dilution methods. As described above, the isotope dilution method only applies to those compounds with deuterated analogs for the October sampling event, whereas the external calibration method applies to all sampling events (minus October for those compounds just described).

Acetaminophen, diphenhydramine, and amitriptyline consistently had very low recoveries (<45%). Other than fluoxetine and sertraline (67% and 65% recoveries, respectively), all other compounds had recoveries greater than 80%.

The recoveries for the isotope dilution method were statistically different ($p < 0.05$) than the external calibration recoveries for acetaminophen, sulfamethoxazole, and sertraline. Although the recoveries are statistically different for sulfamethoxazole, both the external calibration and the isotope dilution recoveries are very good (between 80-120%). Although the recoveries for the two methods for fluoxetine were not statistically different (due to the relatively high variability of the external calibration LCSs), the isotope dilution method recoveries seem to be higher than for the external calibration method (89% vs. 67%). Thus, it appears that for acetaminophen, fluoxetine, and sertraline the use of deuterated analogs in the isotope dilution method corrects for the low extraction recoveries. Despite very poor recoveries for acetaminophen, diphenhydramine, and amitriptyline, and poor recoveries for fluoxetine and sertraline, data for these compounds will still be reported.

Table 6: Average aqueous LCS percent recoveries (± standard deviation) for external calibration and isotope dilution. *Indicates that the external calibration and isotope dilution recoveries are statistically different.

Compound	External Calibration	Isotope Dilution
ACM*	44 ± 5	97 ± 7
CAF	99 ± 5	
SMZ*	107 ± 8	87 ± 15
TRI	87 ± 15	84 ± 8
CBZ	105 ± 13	105 ± 12
FLX	67 ± 27	89 ± 5
SER*	65 ± 9	88 ± 12
AMT	42 ± 8	
TCEP	109 ± 11	
DEET	105 ± 16	
β-ESD	86 ± 12	
PRG	83 ± 7	
GEM	90 ± 23	98 ± 8
DPH	39 ± 8	

Matrix Spikes – Water

Table 7 shows the average matrix spike percent recoveries for the different water matrices (upstream, downstream, effluent, and wetlands) for the external calibration method as well as for the isotope dilution method. External calibration recoveries represent the average MS recoveries for the February through August sampling events for those compounds with labeled analogs and the average MS recoveries for all sampling events for the remaining compounds. No trend was observed between MS recoveries and sampling event. Recoveries that are much greater than 100% are likely a result of ionization enhancement within the LCMS system due to the matrix.

In general, the MS recoveries trend from good recoveries/low variability in the simplest matrix (upstream) to poor recoveries/high variability in the most complex matrix (effluent/wetlands). The upstream MS recoveries are similar to those of the LCS external calibration recoveries (Table 6). I chose not to report results for compounds whose MS recoveries were greater than 200% in a specific matrix. Specifically, sulfamethoxazole will not be reported for stream samples (average MS recovery of 532% in the downstream matrix) or for effluent/wetlands samples (average MS recoveries of 1933% and 1848% in the effluent and wetlands matrices, respectively). In addition, carbamazepine, TCEP, and DEET will not be reported in effluent and wetland samples due to average MS recoveries ranging from 325% to 426%.

The method of isotope dilution generally seemed to improve MS recoveries and lowers variability but without sufficient replication (N=1) this is still uncertain (Table 7). The exception to this is sulfamethoxazole, which had a recovery of 212% in the downstream matrix and a recovery of -447% in the effluent matrix. All other compounds

Table 7: Average matrix spike percent recoveries (± standard deviation) for each water matrix using the external calibration method and isotope dilution (N=1). *Indicates recoveries calculated using isotope dilution. For compounds that had a deuterated analog, the number of replicates for the external calibration method is one less than indicated in the table.

Compound	Upstream (N=6)	Downstream (N=6)	Effluent (N=5)	Wetlands (N=5)
ACM	47 ± 11	47 ± 24	64 ± 45	71 ± 49
ACM*	91	81	96	115
CAF	81 ± 28	81 ± 20	64 ± 15	66 ± 10
SMZ	90 ± 30	532 ± 290	1933 ± 2065	1848 ± 1466
SMZ*	83	212	-447	128
TRI	106 ± 37	123 ± 54	162 ± 67	165 ± 61
TRI*	81	84	78	63
CBZ	109 ± 34	197 ± 170	357 ± 310	362 ± 220
CBZ*	96	105	60	60
FLX	44 ± 17	51 ± 18	98 ± 80	106 ± 78
FLX*	87	91	73	89
SER	39 ± 12	39 ± 5	72 ± 43	74 ± 35
SER*	82	85	79	71
AMT	47 ± 9	51 ± 4	68 ± 34	71 ± 30
TCEP	103 ± 34	180 ± 159	339 ± 383	325 ± 287
DEET	114 ± 43	183 ± 149	434 ± 472	426 ± 429
β-ESD	102 ± 32	97 ± 30	98 ± 43	99 ± 38
PRG	75 ± 19	66 ± 16	89 ± 26	86 ± 26
GEM	125 ± 30	123 ± 42	144 ± 57	163 ± 57
GEM*	92	129	106	147
DPH	46 ± 11	60 ± 11	145 ± 177	135 ± 140

with labeled analogs had recoveries between 60% and 147%. Isotope dilution should improve recoveries by accounting for poor recoveries and matrix interferences and it would likely be advantageous in future studies to use a labeled analog for each target analyte. However, because most of the analysis in this study involves comparing samples within a given matrix (e.g., downstream), isotope dilution does not change the conclusions of this study.

The reported results in this study have not been corrected for extraction efficiencies or matrix effects, except in October for the compounds with labeled analogs.

Laboratory Control Spikes – Sediment

Table 8 shows average percent recoveries for sediment LCSs. All compounds had an average recovery of 70% or higher for all sampling events. Low variability (standard deviation < 30%) was observed for all compounds except for DEET and gemfibrozil.

Matrix Spikes – Sediment

The average MS percent recoveries were calculated for sediment samples for both the external calibration and the isotope dilution methods (Table 9). The external calibration MS recoveries represent the average of the MSs for the February through August sampling events for those compounds with labeled analogs and the average of MSs over all sampling events for all other compounds. The only exception to this is triclosan. For triclosan, a labeled analog was used for the October water samples but not for the October sediment samples because of the non-linear nature of the calibration curve (linear calibration curves were used for quantification for all the sampling events).

Isotope dilution did not significantly improve recoveries for sulfamethoxazole, carbamazepine or gemfibrozil in the sediment matrix. Although recoveries improved for fluoxetine and sertraline, recoveries were still highly variable with standard deviations of 105% and 56%, respectively. The average recovery and associated variability did not improve for acetaminophen. Acetaminophen has poor recoveries due to co-elution of interferences under the chromatography settings of the LCMS method.

Table 8: Average LCS percent recoveries (± standard deviation) for sediment samples.

Compound	Percent Recovery
ACM	70 ± 11
CAF	75 ± 12
SMZ	84 ± 16
TRI	85 ± 23
CBZ	83 ± 8
FLX	70 ± 14
SER	70 ± 13
AMT	75 ± 16
TCEP	88 ± 20
DEET	96 ± 35
β-ESD	79 ± 16
PRG	78 ± 12
GEM	84 ± 37
DPH	74 ± 16

Table 9: Average matrix spike percent recoveries (± standard deviation) for sediment samples for both the external calibration and isotope dilution methods.

Compound	External Calibration	Isotope Dilution
ACM	41 ± 42	24 ± 34
CAF	46 ± 21	
SMZ	72 ± 15	65 ± 17
TRI	68 ± 30	
CBZ	74 ± 13	82 ± 16
FLX	23 ± 94	132 ± 105
SER	59 ± 17	88 ± 56
AMT	67 ± 12	
TCEP	31 ± 69	
DEET	4 ± 166	
β-ESD	67 ± 21	
PRG	43 ± 82	
GEM	88 ± 37	73 ± 33
DPH	68 ± 124	

Based on acceptable recoveries and variability (i.e., recoveries greater than 40% and standard deviations below 40%), sediment results will be reported for the following compounds: caffeine, sulfamethoxazole, triclosan, carbamazepine, sertraline, amitriptyline, and gemfibrozil. Despite having acceptable recoveries and variability, β-estradiol will not be reported in sediment samples due to non-detect results in all sediment samples. All other compounds will not be reported for sediment samples due to poor recoveries and/or high variability.

A summary of which selected PPCPs are reportable within a given matrix (i.e., stream, effluent/wetlands, and sediment matrices) is given in Table 10.

East Canyon Creek Flows: Overview

In an effort to determine the seasonal variability of PPCP concentrations within East Canyon Creek, sampling events were spread throughout different seasons: winter (February), spring (May/June), summer (July/August), and fall (October). Figure 3 shows

Table 10: Summary of which selected PPCPs are reportable within a given matrix. ✓ = acceptable QAQC; * = acceptable QAQC but results below the MDL in the given matrix.

Compound	Stream	Effluent/ Wetlands	Sediment
ACM	✓	✓	
CAF	✓	✓	✓
SMZ			✓
TRI	✓	✓	✓
CBZ	✓		✓
FLX	✓	✓	
SER	✓	✓	✓
AMT	*	✓	✓
TCEP	✓		
DEET	✓		
β-ESD	*	*	*
PRG	*	*	
GEM	*	✓	
DPH	✓	✓	

the flow in East Canyon Creek at the USGS Jeremy Ranch gage station (USGS 2017), which is approximately 200 m downstream from ECWRF, from January through the end of October in 2016. Also shown is the effluent flow from ECWRF over the same period, as well as the percent of the downstream flow that derives from ECWRF effluent.

Flow downstream ranged from a minimum 5.6 cfs in late July to a maximum of 96 cfs in late April. The effluent flows from ECWRF were relatively stable, ranging from 3.19 cfs to 6.65 cfs, with an average 4.57 cfs. Thus, the percentage of downstream flow that derives from ECWRF is dependent on the upstream base flow in East Canyon Creek. The May sampling event took place during a period of snowmelt and high base flow, with 5.8% of the downstream flow deriving from ECWRF (Figure 4). At the other extreme, upstream base flow was very low during the July sampling event with ECWRF effluent making up 76% of the downstream flow (Figure 5).

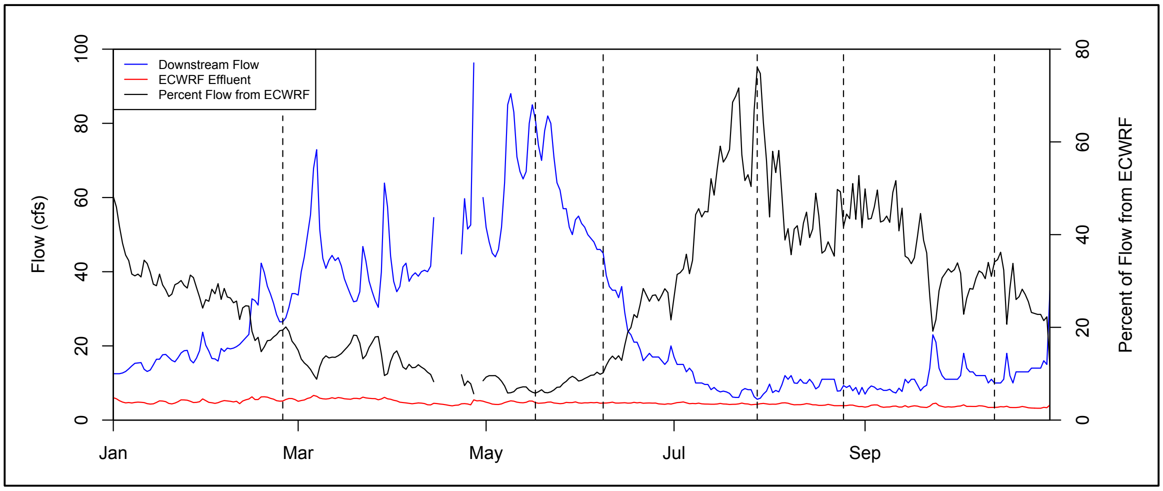


Figure 3: Downstream flow as measured at the USGS Jeremy Ranch gage station (USGS 2017) of East Canyon Creek, effluent flow out of ECWRF, and percent of creek flow from ECWRF. Vertical dotted lines indicate when the sampling events occurred.

Figure 4: Flow in East Canyon Creek at sampling location S+1 during the May 2016 sampling event.

Figure 5: Flow in East Canyon Creek at sampling location S+1 during the July 2016 sampling event.

Estimations of the time for a parcel of water to travel from the ECWRF discharge point into East Canyon Creek (i.e., the point where the water from the wetlands enters the creek) to the last downstream sampling point (S+3) were calculated (Table 11). Calculations were made by assuming average depths ranging from 0.2 m (July) to 1 m (May) and average widths ranging from 4 m (July) to 5 m (May). ECWRF effluent took approximately 6 hours to reach the farthest downstream sampling site (S+3) in May and more than twice as long in July. Sampling was not done in a Lagrangian manner (i.e., sampling the same parcel of water as it moves downstream) due to a lack of resources.

Water Quality Parameters

Water quality parameters such as pH and conductivity were recorded at each sampling site throughout the study period (Table B2). The pH of the effluent and wetland samples (7.3 to 7.9) were consistently lower than in stream samples (8.0 to 9.0). In addition, the conductivity and total dissolved solids (TDS) measurements were consistently higher in effluent and wetland samples than in stream samples. The background conductivity (i.e., conductivity upstream of ECWRF) varied over the

Table 11: Estimates of travel time for water to go from W4 (where effluent enters the stream) to the last downstream sampling location S+3. The reported flows come from the USGS Jeremy Ranch gage station.

Sampling Event	Flow (cfs)	W4 to S+3 (hr)
May	81	6.1
June	45	7.0
July	5.6	14.0
August	9.3	12.6
October	10	11.8

sampling events. Downstream samples tended to have higher conductivity/TDS measurements than upstream samples due to mixing with ECWRF effluent.

The reported DO measurements for all sampling events were collected at the USGS Jeremy Ranch gage station (USGS 2017).

Effluent PPCP concentrations

All stream, effluent, and wetland PPCP concentrations are reported Table B3. Effluent results are only reported for the following compounds: acetaminophen, caffeine, triclosan, fluoxetine, sertraline, amitriptyline, gemfibrozil, and diphenhydramine. Concentrations for these compounds in the ECWRF effluent ranged from 3.02 to 57.3 ng/L. There was no apparent trend for effluent concentrations with sampling event or season. Progesterone and β-estradiol were below the MDL even in effluent samples. Therefore, no results are reported for these two compounds hereafter. In general, effluent concentrations were higher than stream concentrations. The only exceptions to this were acetaminophen in July and caffeine in May and July.

Dilution Ratios

Based on dilution from the upstream flow (i.e., based on a mass balance between upstream, effluent, and downstream), it is expected that the concentration of any compound *i* at the first downstream sampling site will be:

$$C_{i,S+1} = C_{i,Effluent}\left(\frac{Q_{Effluent}}{Q_{Downstream}}\right) \tag{1}$$

where $C_{i,S+1}$ is the concentration of compound *i* at location S+1, $C_{i,Effluent}$ is its concentration in the ECWRF effluent, $Q_{Effluent}$ is the volumetric flow of the effluent, and $Q_{Downstream}$ is the volumetric flow in East Canyon Creek downstream from ECWRF. The following relationship is then derived from Equation 1:

$$\frac{C_{i,S+1}}{C_{i,Effluent}} = \frac{Q_{Effluent}}{Q_{Downstream}} \tag{2}$$

The left-hand side of the Equation 2 shall hereafter be referred to as the concentration ratio and the right-hand side as the flow ratio.

The flow ratios for each sampling event were calculated using the flows from the ECWRF and the average downstream flows (as reported by USGS at the Jeremy Ranch gage station) from the day of each sampling event. Next, the concentration ratios were calculated for each compound by comparing the concentrations at S+1 to the concentrations in the effluent. The concentration ratios were only calculated for those compounds whose effluent concentrations were reported. The average concentration ratios were then calculated for each selected PPCP and each sampling event. Concentration values below the MDL were not used in computing the average concentration ratios (i.e., May & June results were <MDL and were therefore not used in calculating the acetaminophen, triclosan, fluoxetine, and sertraline average concentration ratios).

The flow ratio for each sampling event was plotted next to the corresponding average concentration ratio (Figure 6). As seen from the error bars in Figure 6, there is a lot of variability in the concentration ratios, especially for the sampling events in July, August, and October. There were no statistical differences between the flow ratios and the average concentration ratios for all sampling events. On average, the concentration of each compound at the first downstream sampling site (S+1) is based on the dilution of the effluent by the upstream base flow.

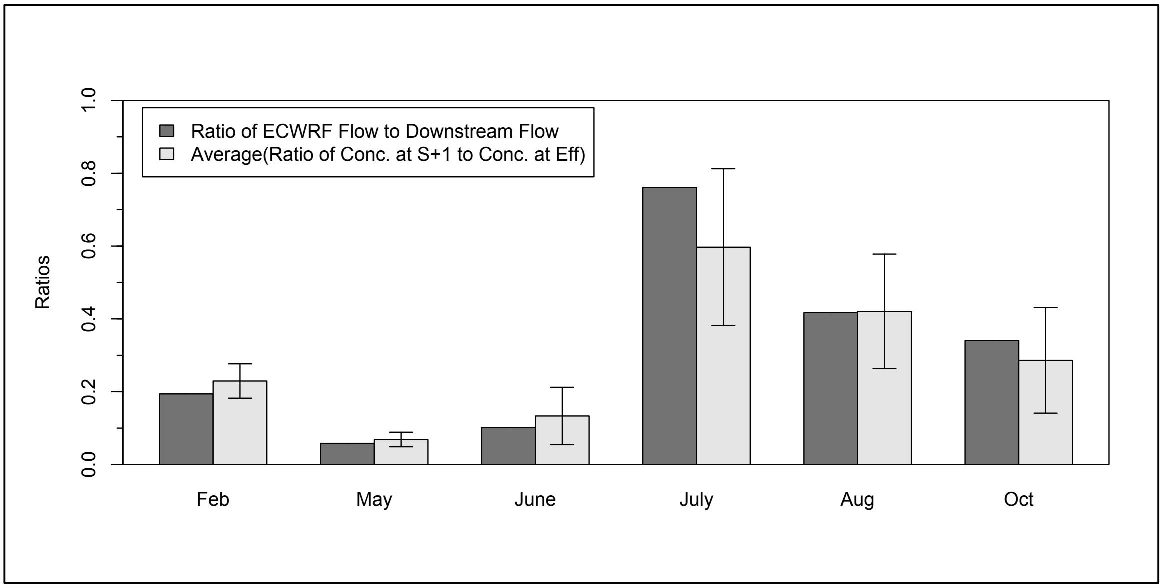


Figure 6: Comparison of flow ratio (ratio of ECWRF effluent flow to downstream flow) to the average concentration ratio (ratio of concentration at S+1 to concentration in effluent).

Stream—Concentrations and Percent Change

Concentrations

All upstream and downstream PPCP concentrations are reported in Appendix B (Table B3). Because samples were not filtered, reported concentrations represent total concentrations, which are expected to be >99% dissolved in most cases. Samples were not collected from location S+3 during the February sampling event. For all compounds, ANOVA and Tukey tests ($\alpha = 0.05$) were performed to determine whether statistical differences existed among stream sampling sites (Table B4). Except for caffeine and occasions when downstream concentrations were below the MDL, upstream concentrations were consistently statistically lower than downstream concentrations.

In general, individual PPCPs demonstrated the same trends as carbamazepine (Figure 7) and diphenhydramine (Figure 8). Carbamazepine was detected in some upstream samples but at levels much lower than downstream concentrations (Figure 7). Diphenhydramine was not detected at upstream sampling sites (Figure 8). Low or non-detect upstream results indicate that the ECWRF is the major source of PPCPs in East Canyon Creek. Consistent with expectations, observed concentrations of carbamazepine and diphenhydramine were highest during the July sampling event and lowest during the May sampling event. Carbamazepine concentrations did not seem to change much with increasing distance downstream, whereas statistical decreases were observed for diphenhydramine during four out of the six sampling events (p-values < 0.05). Other individual PPCPs showed similar trends with low/non-detect upstream concentrations, with the highest downstream concentrations occurring in July and the lowest in May. Individual PPCPs exhibited different behavior as to downstream behavior (i.e., downstream decreases). Stream concentrations for selected PPCPs other than carbamazepine, diphenhydramine, and caffeine are shown in Appendix B (Figures B1-B8).

Caffeine was a major exception to all the trends observed for PPCPs in East Canyon Creek. Caffeine was found upstream of ECWRF during all sampling events (Figure 9). Concentrations were higher upstream than downstream during the February and May sampling events. There was no observable trend based on season for this compound. Based on these data, there is an upstream source of caffeine to East Canyon Creek, which is suspected to come from a truck stop and an adjacent neighborhood septic system (Michael Luers, personal communication, February 15, 2017).

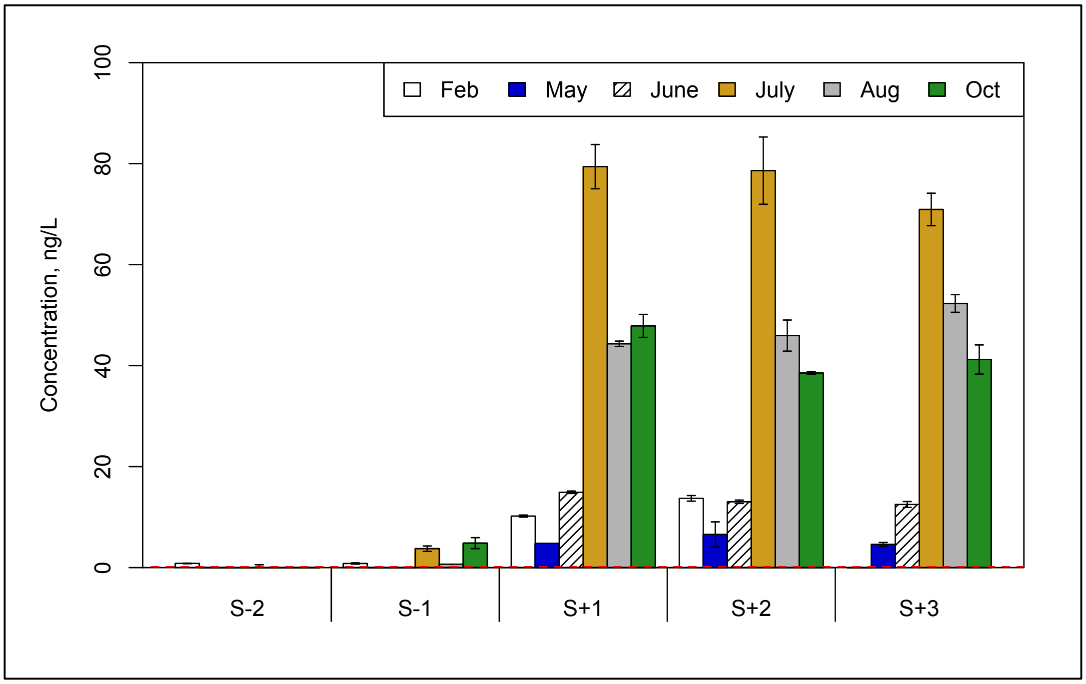


Figure 7: Average stream concentrations (N = 3) of carbamazepine (red dashed line represents the MDL). Error bars represent 95% confidence intervals.

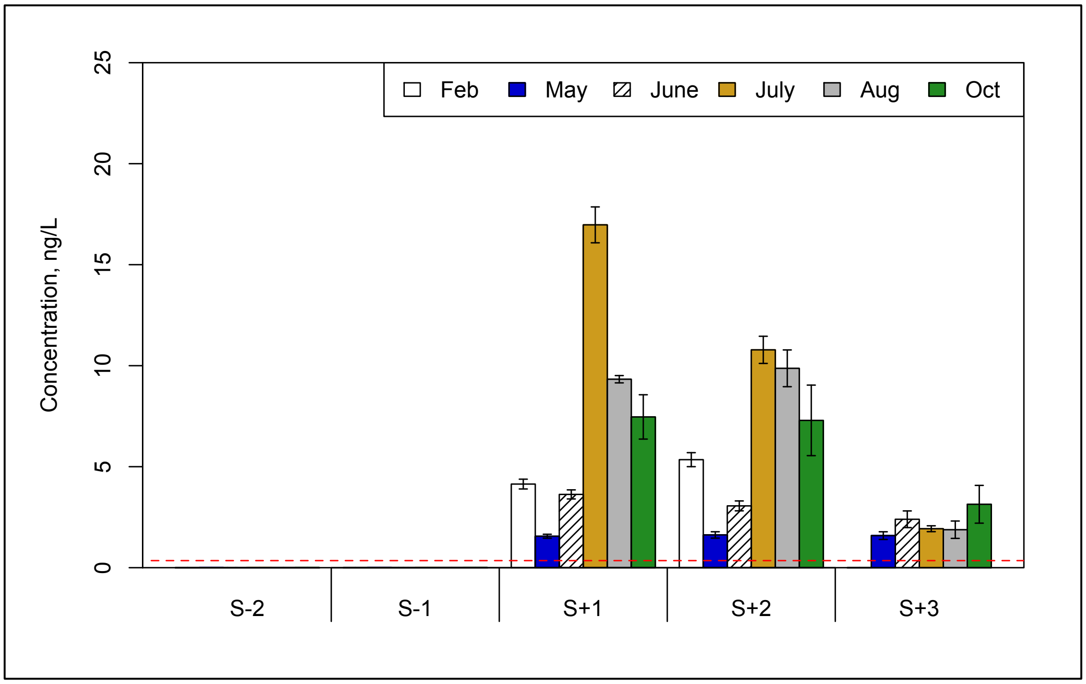


Figure 8: Average stream concentrations (N = 3) of diphenhydramine (red dashed line represents the MDL). Error bars represent 95% confidence intervals.

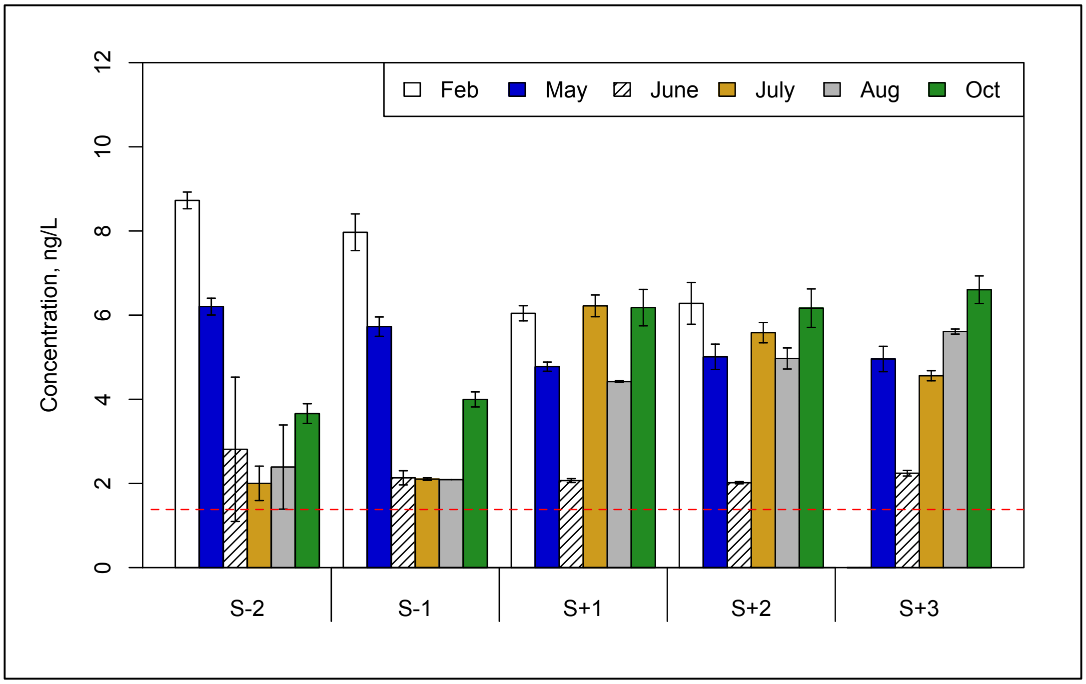


Figure 9: Average stream concentrations (N = 3) of caffeine (red dashed line represents the MDL). Error bars represent 95% confidence intervals.

In summary, upstream concentrations for most selected PPCPs were <MDL or very small. Except for caffeine, ECWRF is the major source of PPCPs in East Canyon Creek. In general, the highest observed concentrations of PPCPs occurred in July, while the lowest concentrations were observed in May. This corresponds to the sampling events with the lowest and highest levels of upstream dilution, respectively. Some compounds tended to decrease with increasing distance downstream (e.g., acetaminophen, triclosan, fluoxetine, sertraline, and diphenhydramine), with other compounds either showing little-to-no change or even increasing slightly (e.g., DEET).

Downstream Percent Change

The percent change in concentration between the first downstream sampling site (S+1) and the last downstream sampling site (S+3) was calculated for each compound during each sampling event except February since there was no S+3 during that sampling event. The average percent change over the relevant sampling events was then calculated for each compound. The individual percent change values for each compound and relevant sampling event and the average percent change values for each compound were plotted (Figure 10).

On average, acetaminophen, triclosan, fluoxetine, sertraline, and diphenhydramine decreased in concentration as they moved downstream from ECWRF. For acetaminophen, triclosan, fluoxetine, and sertraline, the only sampling events in which negative percent changes (i.e., decreasing concentrations) were not observed was during the May and June sampling events due to <MDL results. Despite this, it is

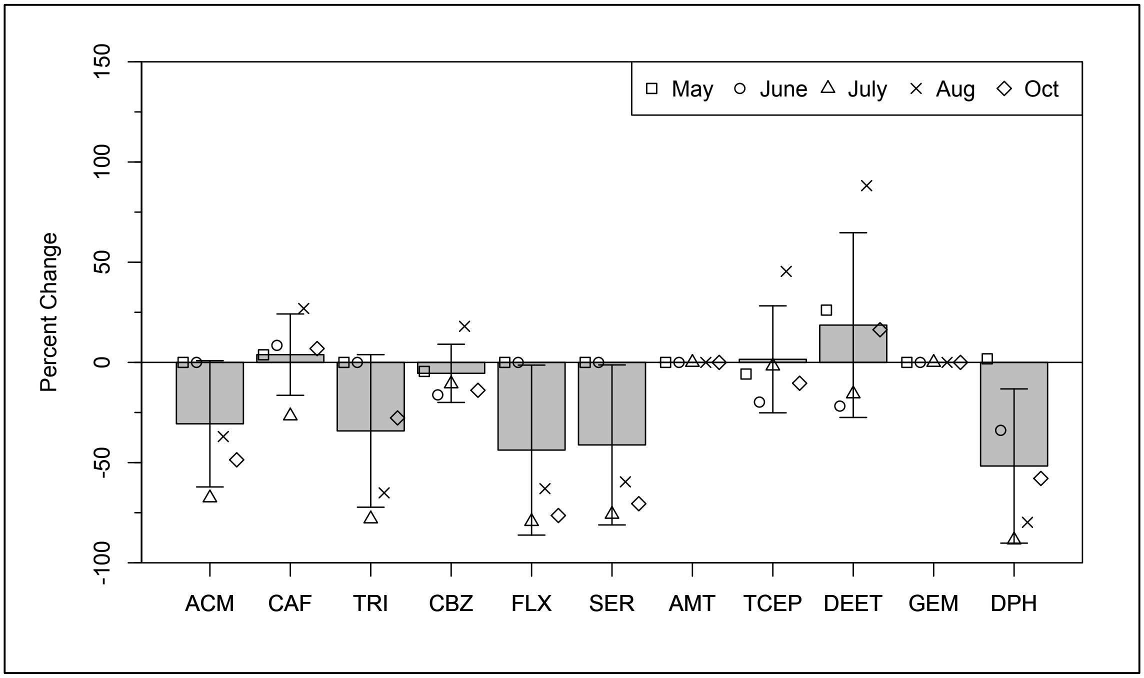


Figure 10: Percent change between the concentrations at the first and the last downstream sampling sites (S+1 and S+3). Individual points indicate the value for each sampling event, while the grey bars show the average percent change over the study period. Positive values indicate an increase in concentration, while negative indicates a decrease.

possible that decreases did occur for these compounds but was not observed based downstream concentrations being below the MDL.

An increase in DEET concentrations was observed in three out of the five relevant sampling events (May, August, and October). Although a decrease was observed for this compound between S+1 and S+3 in July, the highest observed concentration during that sampling event was at S+2. In general, DEET increased in concentration farther downstream. This could be explained by the fact that East Canyon Creek flows through the Jeremy Ranch golf course, where many people likely apply DEET-containing insect repellents while golfing.

On average, the remaining PPCPs did not seem to exhibit a consistent decrease between the downstream locations.

Percent Change vs. Physical and Chemical Properties

The average percent change values for selected PPCPs were plotted against the corresponding physical and chemical properties: octanol-water partitioning coefficient (Figure B9), water solubility (Figure B10), charge of the dominant species at the environmentally relevant pH of 8 (Figure B11), and molecular weight (Figure B12). No correlation was observed between the average percent change values and the physical/chemical properties. Coefficient of determination values (R^2) ranged from 0.005 to 0.228 and p-values ranged from 0.137 to 0.830.

Effluent to Wetlands—Concentrations and Percent Change

Concentrations of target analytes in effluent and wetland samples are shown in Table B3. Effluent samples were not collected during the February sampling event. The percent change in concentration from effluent to the last wetland sampling point (W4) was calculated for each compound and relevant sampling event. Additionally, the average of all individual percent change values was calculated for each compound. The percent change and average percent change values were plotted for each compound (Figure 11). There is a lot of variability, but on average, the average percent change for most compounds is not significantly different from zero. The exceptions to this are acetaminophen and caffeine, for which average increases were observed. The reason for the increases is unclear but it could be the result of de-conjugation of metabolites back into the parent compounds upon entering the wetlands (Brown and Wong 2016).

It can be concluded that the constructed wetlands did not aid in attenuation of PPCP levels before the effluent discharge enters East Canyon Creek. Matamoros et al. (2008) and Hijosa-Valsero et al. (2010) have reported decreasing concentrations for some

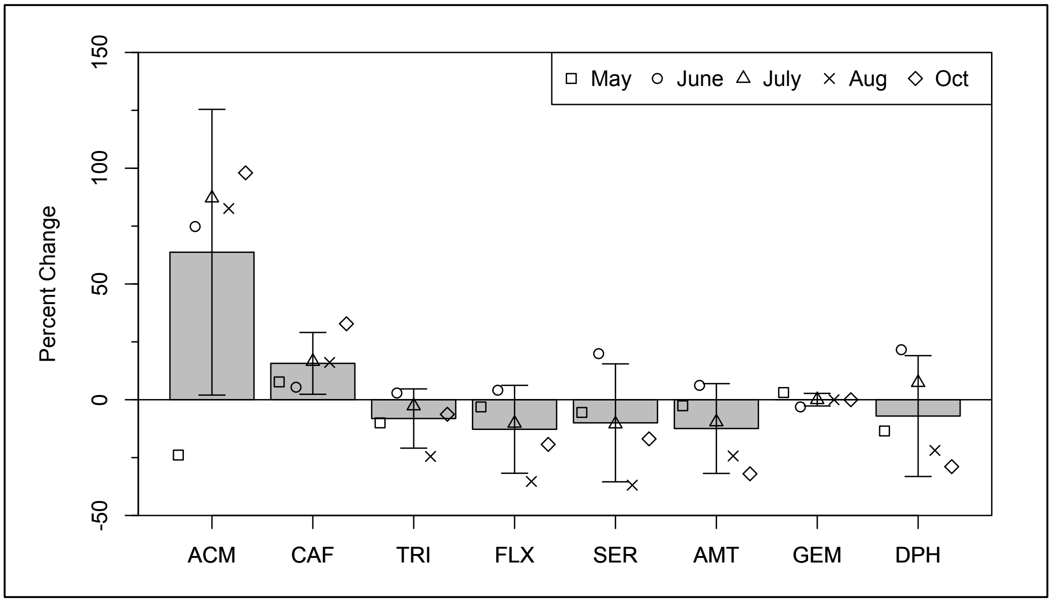


Figure 11: Percent change between the concentrations in the effluent and at the last wetland location W4. Individual points indicate the value for each sampling event, while the grey bars show the average percent change over the study period.

PPCPs within constructed wetlands due to several fate mechanisms. However, the reported flow rates and hydraulic retention times ranged from 0.005 MGD to 0.026 MGD and from 1.2 d to 30 d, respectively. In comparison, the average ECWRF wetland flow rate is 2.89 MGD, while the estimated hydraulic retention time is less than one hour. Thus, the characteristics of the ECWRF wetlands (i.e., size, flow rate, hydraulic retention time) are not favorable for PPCP removal.

Sediment Results

Table C1 shows organic matter content results from the USUAL lab loss on ignition tests for each sediment sample collected. Wetland sediment samples had an average organic matter content (by mass) of 6.3% (standard deviation = 5.1%), whereas stream sediment samples had an average of 2.1% (standard deviation = 1.6%). In general, the wetland sediments had higher organic matter content than stream sediments (p-value < 0.05). There was no statistical difference observed in organic matter content between the different sampling events (p-values > 0.05). If sorption of PPCPs to sediment is a function of organic matter content, it would be expected that higher PPCP sediment concentrations would be observed in wetland sediments than in stream sediments.

The average sediment concentrations for those compounds that had acceptable matrix spike recoveries are shown in Table C2. The only exception is for gemfibrozil which is not shown due to non-detect results in all sediment samples. There is high sample to sample and month to month variability but, in general, wetland sediments tended to have higher PPCP concentrations than stream sediments.

Sediment to water concentration ratios (L/kg) were calculated for those samples containing levels of PPCPs above MDL in both phases (Table C3). Because water samples were not collected from W2 and W3 during May, June, and July, the water concentrations at W4 were used to calculate the corresponding sediment to water concentration ratios. The sediment to water concentrations ratios were compared to experimentally-derived equilibrium K_d values reported in the literature.

Sediment to water concentration ratios were further normalized by organic carbon (OC) content (Table C1) and are reported in Table C4. The OC normalized ratios were then transformed further by taking the log of these ratios (Table C5).

The average of all observed sediment to water concentration ratios (Table C3) and log OC normalized ratios (Table C5) for each compound were calculated and are reported in Table 12. In addition to the average ratios, the range from minimum to maximum observed ratios is depicted. As observed with laboratory determined sorption coefficients (Tolls 2001), there was no apparent trend in sorption and ratios based on PPCP properties such as pK_a or log K_{ow}. For example, although caffeine has a log K_{ow} of -0.07, observed log OC normalized ratios for caffeine were similar to those of triclosan (log $K_{ow} = 4.76$), sertraline (log $K_{ow} = 2.18$), and amitriptyline (log $K_{ow} = 2.18$), and higher than those for carbamazepine (log $K_{ow} = 2.25$). This suggests that sorption to sediment is more complex than just being a function of log K_{ow} for a specific compound and the OC content in sediments.

Average sediment to water concentration ratios tended to be within the range of literature reported K_d values. Although the maximum observed sediment to water concentration ratios for caffeine and triclosan fall outside the range of reported K_d values, the average ratios for these compounds fall within the reported range for different sediments. The sediment to water concentration ratios for carbamazepine all fall within

Table 12: Summary of sediment data including compound pK_a and log K_{ow} values, average sediment to water concentration ratios (L/kg), the log of the normalized (by organic carbon) sediment to water concentration ratio, and comparison of the ratios to literature values. Values in parentheses represent the range of ratios observed.

Compound	pK_a	log K_{ow}	Average (Range) Sediment to Water Ratio (L/kg)	Literature K_d (L/kg)	Average (Range) log of OC Normalized Ratio	Literature log K_{oc}
CAF	0.61, 3.6	-0.07	188 (31.5-720)	25-250[a, b, c]	3.7 (2.8-5.1)	1.89-3.89[a, b, c]
TRI	7.9	4.76	778 (205-1880)	220-1573[d, e]	4.7 (3.7-5.5)	3.54-4.30[a, c]
CBZ	13.9	2.25	9.61 (0.488-44.0)	1.4-174[f, g, h]	2.0 (0.5-3.3)	1.92-2.74[k, g]
SER	9.85	2.18	817 (50.5-1880)	139-787[a, i]	4.4 (3.6-5.4)	3.58-4.85[a, i]
AMT	9.4	2.18	467 (152-867)	8.79-248[a, j]	4.4 (3.5-5.2)	3.0-4.1[a, j]

[a] Barron et al. (2009); [b] Lin et al. (2010); [c] Karnjanapiboonwong et al. (2010); [d] Huang et al. (2015); [e] Lin et al. (2011); [f] Stein et al. (2008); [g] Yamamoto et al. (2009); [h] Radjenovic et al. (2009); [i] Kwon and Armbrust (2008); [j] Al-Khazrajy and Boxall (2016); [k] Loffler et al. (2005).

reported ranges of experimentally derived K_d values. The observed sediment to water concentration ratios for sertraline and amitriptyline tended to be higher than but are within an order of magnitude of the literature-reported K_d values.

The averages of observed log OC normalized ratios for caffeine, carbamazepine, and sertraline all fell within the range of reported log K_{oc} values, while the averages for triclosan and sertraline were higher than reported values. The maximum observed log OC normalized ratios were higher than reported log K_{oc} ranges for all the compounds.

The fact that the calculated sediment-to-water and log OC normalized ratios are similar to laboratory-derived equilibrium K_d and log K_{oc} values, respectively, suggests that PPCP sorption tends to be rapid, reversible, and at or near equilibrium. Without new sorptive material being introduced into the system faster than the PPCPs, this also suggests that sorption is unlikely to be a significant removal mechanism in this system.

Potential PPCP Attenuation Mechanisms in East Canyon Creek

The decreasing instream concentrations of acetaminophen, triclosan, fluoxetine, sertraline, or diphenhydramine indicate that some removal of these compounds is occurring. However, based on the sediment-water concentration ratios discussed previously, sorption to sediments is unlikely to be a significant removal mechanism.

The literature suggests that biodegradation and photodegradation could have contributed to the declining concentrations observed for some of the PPCPs within East Canyon Creek. For example, carbamazepine did not decline downstream of ECWRF, consistent with literature reports of its recalcitrance in environmental systems (Duran-Alvarez et al. 2015), while concentrations of acetaminophen, triclosan and fluoxetine did decline (Figure 10). Acetaminophen has been shown to be biodegradable in water-sediment systems (Loffler et al. 2005), but stable in sunlight-affected surface waters (Yamamoto et al. 2009). Photodegradation and biodegradation occur more readily for triclosan than for carbamazepine (Duran-Alvarez et al. 2015). Triclosan has been shown to be readily photodegraded in surface waters (Dhillon et al. 2015) and the rate of photodegradation of fluoxetine is faster in surface water than is deionized water, likely due to indirect photolysis (Lam et al. 2005).

Although they were not studied directly, it can be inferred from the literature that degradation processes were likely major factors in the decreasing concentrations of acetaminophen, triclosan, fluoxetine, sertraline, and diphenhydramine.

Comparison to Risk Values

A comparison of stream PPCP concentrations found in this study and lowest observed effect concentrations (LOECs) is provided in Table 13. LOECs represent aquatic concentrations at which deleterious effects have been observed in fish and other aquatic species. Observed concentrations were orders of magnitude lower than LOEC risk values. Negative impacts to aquatic organisms would not be expected due to the individual PPCPs, but it cannot be definitively stated what the combined effects of the PPCP mixture in East Canyon Creek would be. Further work would be required to see if there are observable effects to aquatic organisms with the mixture and levels of PPCPs in this study.

Table 13: Comparison of PPCP concentrations in East Canyon Creek and LOEC risk values to aquatic organisms.

Compound	This Study (ng/L)	LOEC (ng/L)	Species	Trophic Group
ACM	1.5-39	100,000[1]	*B. Americanus*	Amphibian
CAF	2.0-6.6	50,000,000[1]	*P. Promelas*	Fish
TRI	3.6-7.0	220,000[2]	*D. rerio*	Fish
CBZ	4.6-79	1000[1]	*O. mykiss*	Fish
FLX	3.0-6.5	100-500[1]	*O. latipes*	Fish
SER	1.1-1.9	45,000[1]	*C. dubia*	Invertebrate
AMT	<4.36	780,000[1]	*S. proboscideus*	Invertebrate
TCEP	5.1-72	90,000,000[3]	Unspecified	Unspecified
DEET	1.6-73	521,000[4]	*P. subcapitata*	Green Algae
GEM	ND-10.6	30,000,000[5]	*D. magna*	Invertebrate
DPH	1.6-17	374,000[1]	*D. magna*	Invertebrate

[1] Brauch et al. (2012), [2] Tatarazako et al. (2004), [3] WHO (1998); [4] Weeks et al. (2012); [5] Zurita et al. 2007.

SUMMARY AND CONCLUSIONS

Water and sediment samples were collected from East Canyon Creek during six sampling events during 2016: February, May, June, July, August, and October. Flows in East Canyon Creek were highest in May due to spring runoff and lowest during the July sampling event, during which 76% of the downstream flow originated from ECWRF effluent.

Isotope dilution was only used during one sampling event due to the high cost of purchasing deuterated standards but was shown to improve the accuracy of QAQC spike recoveries by correcting for extraction efficiencies and matrix effects. Therefore, it is recommended that, if available, a labeled analog should be used for each selected PPCP. However, because results were mostly compared within the same matrix, the use of isotope dilution did not change the conclusions of this work.

On average, dilution of the ECWRF effluent by upstream flow was the major factor impacting PPCP concentrations at the first downstream sampling site (S+1). Except for caffeine, PPCPs were not detected or were detected at levels much lower than downstream concentrations, indicating that the ECWRF is the major source of PPCPs in East Canyon Creek. In general, PPCP concentrations in the creek were highest in July and lowest in May, corresponding to times of the lowest and highest levels of dilution. During most sampling events, acetaminophen, triclosan, fluoxetine, sertraline, and diphenhydramine decreased with increasing distance downstream from ECWRF, while other PPCPs showed little attenuation, indicating that fate mechanisms other than dilution are important for some PPCPs. There was no correlation between the average percent decrease values for the selected PPCPs and their corresponding physical and chemical properties (such as charge, log K_{ow}, etc.).

Significant decreases in PPCP concentrations were not observed within the ECWRF constructed wetlands, suggesting that the area of the wetlands is too small to have an impact on PPCP attenuation. On average, PPCP concentrations were about six times higher in wetland sediments than in stream sediments, likely due to the higher levels of organic carbon content. There was no apparent trend or correlation between calculated sediment to water concentration ratios and the PPCP physicochemical properties. Sediment to water concentration ratios were generally similar to experimentally derived sorption ratios (e.g., K_d, log K_{oc}) reported in the literature, suggesting steady-state conditions associated with rapid sorption and desorption kinetics.

Due to finding near steady-state conditions, sorption can likely be ruled out as a potential attenuation mechanism for the declining concentrations of acetaminophen, triclosan, fluoxetine, and diphenhydramine. Although not studied directly, the literature suggests that degradation processes such as photodegradation and biodegradation were possibly major factors in the observed attenuation.

Individually, PPCP concentrations in the creek were lower than levels at which negative impacts would be expected in fish and other aquatic organisms. The additive impact of the PPCP mixture on aquatic organisms is unknown but could still be a potential concern.

RECOMMENDATIONS FOR FUTURE WORK

If any future work is to be conducted which will add upon this thesis, the following are a few recommendations that could be found useful.

First, the use of deuterated standards for each target PPCP would be advantageous in order to improve the accuracy and precision of matrix spikes. In particular, it would help improve the quality of spikes in effluent and wetland matrices and, consequently, increase the confidence in any reported data.

Secondly, it would be advantageous to sample at sites that have already been established by state and federal agencies. For example, it would be beneficial to sample adjacent to the USGS Jeremy Ranch gage station, for which there is an abundance of ongoing water quality data collection (e.g., pH, DO, conductivity, flow, etc.). Other sites exist for which other water quality data has been collected.

Sampling in a Lagrangian manner (i.e., using tracers to ensure the sampling of the same parcel of water as it travels down the stream) would increase the confidence of the conclusions related downstream attenuation of PPCPs. Related to this, it would be helpful to make flow measurements at each sampling site so as to know the exact flow when each sample was collected. Additionally, recording DO measurements at each individual site would be helpful.

ENGINEERING SIGNIFICANCE

This study confirmed that ECWRF is the major source of most PPCPs in East Canyon Creek (caffeine being the exception). Consistent with our hypothesis, levels of PPCPs within the stream were generally highest during periods of low dilution (i.e., during times in which the stream was effluent-dominated).

The clear majority of conventional WWTPs do not treat to remove PPCPs due to several reasons including cost restraints. The data collected in this work could help decision makers in determining whether PPCPs should be removed in the ECWRF and other WWTPs that discharge into similar EDSs. The main reason to remove these compounds would be to protect the health of aquatic organisms and possibly human health in the case of water reuse. Analysis of PPCP concentrations in East Canyon Creek revealed that, individually, PPCP concentrations in the stream are lower than levels believed to exert negative impacts on fish and other aquatic organisms, although the additive effect of PPCP mixtures could still be a potential concern.

If wastewater treatment decision makers were to decide to remove PPCPs, activated carbon adsorption, advanced oxidation processes, nanofiltration, reverse osmosis, and membrane bioreactors have been shown to be effective treatment technologies (Luo et al. 2014). A pilot study conducted at ECWRF found that selected PPCPs were effectively removed from effluent using granular activated carbon filtration and advanced oxidation processes, but full implementation was deemed to be cost prohibitive (Mike Luers, personal communication, February 15, 2017).

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APPENDICES

APPENDIX A – Summary of occurrence of sampling type, location, and time.

Table A1: Occurrence of water sampling at each location during each sampling event.

	Water									
	S-2	S-1	S+1	S+2	S+3	E	W1	W2	W3	W4
Feb	X	X	X	X						X
May	X	X	X	X	X	X				X
June	X	X	X	X	X	X				X
July	X	X	X	X	X	X				X
Aug	X	X	X	X	X	X	X		X	X
Oct	X	X	X	X	X	X	X	X		X

Table A2: Occurrence of sediment sampling at each location during each sampling event.

	Sediment								
	S-2	S-1	S+1	S+2	S+3	W1	W2	W3	W4
Feb									
May	X		X	X	X		X	X	X
June	X		X		X		X	X	X
July	X	X	X	X			X	X	
Aug	X	X	X	X	X			X	X
Oct	X		X		X		X		X

APPENDIX B – Supporting Tables and Figures for Water Samples

Table B1: Method detection limit (MDL) values.

Compound	External Calibration (ng/L)	Isotope Dilution (ng/L)
ACM	1.41	1.50
CAF	1.38	
SMZ	0.62	0.91
TRI	3.05	2.90
CBZ	0.17	0.28
FLX	2.67	1.53
SER	0.93	0.80
AMT	4.36	
TCEP	3.36	
DEET	1.45	
β-ESD	4.82	
PRG	3.81	
GEM	12.12	6.34
DPH	0.35	

Table B2: Water quality parameter measurements throughout the 2016 sampling events. *Indicates DO measurements at the USGS Jeremy Ranch gage station (USGS 2017).

Sampling Event	Location	Time	Temp (°C)	pH	Conductivity (µS/cm)	TDS (ppm)	DO (mg/L)
February	S-2	10:45 am	3.1	8.0	1407	703	
	S-1	11:50 am	3.6	8.1	1577	788	
	S+1	1:20 pm	7.7	8.1	1618	806	11.1*
	S+2	1:50 pm	8.0	8.1	1590	792	
	W4	12:35 pm	12.3	7.4	2126	1062	
May	S-2	2:20 pm	10.6	8.4	530	265	
	S-1	1:12 pm	10.7	8.3	540	274	
	S+1	2:50 pm	11.0	8.4	625	315	10.2*
	S+2	3:20 pm	11.3	8.4	665	330	
	S+3	3:45 pm	13.5	8.5	640	320	
	E	10:35 am	13.4	7.3	1540	775	
	W4	12:35 pm	12.8	7.4	1550	770	
June	S-2	1:35 pm	18.0	9.1	585	294	
	S-1	12:35 pm	18.1	9.1	623	311	
	S+1	2:00 pm	19.4	9.0	721	360	10.6*
	S+2	2:25 pm	19.3	9.1	727	364	
	S+3	2:45 pm	21.5	9.0	716	358	
	E	10:55 am	16.5	7.3	1610	804	
	W4	12:10 pm	19.0	7.6	1640	820	
July	S-2	12:55 pm	25.2	8.9	1020	510	
	S-1	11:55 am	22.4	8.9	1363	681	
	S+1	1:40 pm	25.9	8.8	1560	800	9.5*
	S+2	2:00 pm	25.7	9.0	1613	807	
	S+3	2:25 pm	26.3	9.5	1305	652	
	E	10:25 am	20.2	7.3	1836	918	
	W4	11:40 am	24.2	7.8	1800	802	
August	S-2	10:30 am	14.2	8.5	810	405	
	S-1	11:15 am	17.1	8.7	1098	548	
	S+1	2:10 pm	19.9	8.6	1466	733	9.3*
	S+2	2:30 pm	18.6	8.8	1215	608	
	S+3	3:15 pm	18.8	9.0	1465	731	
	E	12:55 pm	20.1	7.3	1837	919	
	W1	1:10 pm	20.5	7.4	2186	1091	
	W3	12:05 pm	22.2	7.9	1885	943	
	W4	11:25 am	20.1	7.7	1781	891	
October	S-2	11:05 am	9.1	8.1	885	445	
	S-1	11:30 am	10.4	8.5	995	500	
	S+1	2:50 pm	15.6	8.7	1130	566	10.5*
	S+2	3:05 pm	13.7	8.8	1122	561	
	S+3	3:30 pm	12.4	8.9	1125	562	
	E	12:30 pm	16.5	7.3	1710	855	
	W1	1:25 pm	16.2	7.4	1696	848	
	W2	1:15 pm	18.7	7.5	1706	854	
	W4	11:45 am	17.1	7.6	1706	855	

Table B3: Average concentrations (ng analyte / L) in stream, effluent, and wetland samples (N=3) at each sampling location and each sampling event. Effluent and wetland concentrations are not included for CBZ, TCEP, and DEET due to unreliable matrix spike recoveries. ND = non-detect; <MDL = below method detection limit. *October results for these compounds were corrected using isotope dilution.

Sampling Event	Location	ACM*	CAF	TRI*	CBZ*	FLX*	SER*
February	S-2	ND	8.73	ND	0.831	<MDL	ND
	S-1	ND	7.97	ND	0.816	<MDL	ND
	S+1	2.24	6.04	5.73	10.2	3.72	1.10
	S+2	2.73	5.73	7.00	13.7	5.22	1.32
	W4	15.7	3.49	48.8		12.2	4.96
May	S-2	ND	6.20	ND	ND	ND	ND
	S-1	ND	5.73	ND	ND	ND	ND
	S+1	<MDL	4.78	<MDL	4.82	<MDL	<MDL
	S+2	<MDL	5.01	<MDL	6.57	<MDL	<MDL
	S+3	<MDL	4.96	<MDL	4.60	<MDL	<MDL
	E	15.7	3.02	26.8		12.4	4.32
	W4	11.9	3.25	24.2		12.1	4.08
June	S-2	<MDL	2.81	ND	ND	ND	ND
	S-1	ND	2.13	ND	ND	ND	ND
	S+1	<MDL	2.07	<MDL	14.9	<MDL	<MDL
	S+2	<MDL	2.02	<MDL	13.0	<MDL	<MDL
	S+3	<MDL	2.24	<MDL	12.5	<MDL	<MDL
	E	4.42	3.37	30.6		16.1	9.05
	W4	3.61	2.90	31.5		16.8	10.8
July	S-2	<MDL	2.00	ND	ND	ND	ND
	S-1	ND	2.10	ND	3.75	ND	ND
	S+1	4.70	6.22	6.63	79.4	6.47	1.92
	S+2	4.11	5.58	6.27	78.6	2.98	<MDL
	S+3	1.52	4.56	<MDL	70.9	ND	ND
	E	4.06	5.95	17.9		24.2	11.2
	W4	7.59	6.93	17.4		21.7	10.0
August	S-2	ND	2.39	ND	<MDL	ND	ND
	S-1	ND	2.09	ND	0.67	ND	ND
	S+1	3.57	4.42	4.15	44.3	3.61	1.15
	S+2	3.41	4.97	4.64	46.0	3.04	<MDL
	S+3	2.25	5.61	<MDL	52.3	<MDL	ND
	E	4.02	5.97	15.5		21.4	8.38
	W1	3.83	5.68	14.1		20.1	7.32
	W3	6.68	6.62	12.6		14.7	5.88
	W4	7.34	6.93	11.7		13.9	5.29
October	S-2	ND	3.66	ND	ND	ND	ND
	S-1	ND	4.00	ND	4.85	ND	ND
	S+1	38.9	6.18	4.98	47.9	3.24	1.58
	S+2	27.1	6.17	3.83	38.5	3.02	1.37
	S+3	20.0	6.60	3.60	41.2	<MDL	ND
	E	57.3	8.55	20.9		25.1	21.4
	W1	58.4	7.66	24.8		30.3	23.5
	W2	105	8.92	20.7		27.4	22.5
	W4	113	11.4	19.6		20.2	17.8

Table B3: Continued

Sampling Event	Location	AMT	TCEP	DEET	GEM*	DPH
February	S-2	<MDL	<MDL	<MDL	ND	<MDL
	S-1	<MDL	<MDL	1.72	ND	<MDL
	S+1	<MDL	11.6	3.92	<MDL	4.14
	S+2	<MDL	15.3	11.9	<MDL	5.35
	W4	5.38			63.6	19.2
May	S-2	ND	ND	<MDL	ND	ND
	S-1	ND	ND	<MDL	ND	ND
	S+1	<MDL	5.40	9.19	ND	1.56
	S+2	<MDL	5.70	9.04	ND	1.62
	S+3	<MDL	5.09	11.6	ND	1.59
	E	6.89			15.9	29.9
	W4	6.71			16.4	28.5
June	S-2	ND	<MDL	1.59	ND	ND
	S-1	ND	<MDL	1.77	ND	ND
	S+1	<MDL	17.6	18.3	ND	3.63
	S+2	<MDL	15.3	15.4	ND	3.06
	S+3	<MDL	14.1	14.3	ND	2.40
	E	11.2			26.3	46.0
	W4	11.9			25.5	55.9
July	S-2	ND	<MDL	2.66	ND	ND
	S-1	ND	4.70	7.34	ND	ND
	S+1	<MDL	70.1	52.3	<MDL	17.0
	S+2	<MDL	72.3	72.7	<MDL	10.8
	S+3	ND	68.8	44.1	<MDL	1.93
	E	10.6			<MDL	27.7
	W4	9.58			<MDL	29.8
August	S-2	ND	ND	7.86	ND	ND
	S-1	ND	ND	2.93	ND	ND
	S+1	<MDL	45.8	15.1	<MDL	9.33
	S+2	<MDL	47.2	18.7	<MDL	9.87
	S+3	<MDL	66.6	28.4	<MDL	1.88
	E	7.81			<MDL	20.9
	W1	6.82			<MDL	20.6
	W3	6.01			<MDL	17.0
	W4	4.61			<MDL	16.3
October	S-2	ND	ND	<MDL	ND	ND
	S-1	ND	ND	1.55	ND	1.91
	S+1	<MDL	33.5	7.89	ND	7.46
	S+2	<MDL	30.0	6.84	ND	7.29
	S+3	ND	30.0	9.18	ND	3.14
	E	6.78			<MDL	26.5
	W1	6.01			<MDL	26.4
	W2	5.89			<MDL	23.4
	W4	4.61			<MDL	18.8

Table B4: Results from Tukey tests expressed in letters indicating statistical differences between sampling sites for a given sampling event and the corresponding compound. If concentrations were <MDL, values were considered to be non-detect results.

Month	Site	ACM	CAF	TRI	CBZ	FLX	SER	AMT	TCEP	DEET	GEM	DPH
Feb	S-2	a	a	a	a	a	a	a	a	a	a	a
	S-1	a	a	a	a	a	a	a	a	a	a	a
	S+1	b	b	b	b	b	b	a	b	a	b	b
	S+2	c	b	c	c	b	c	a	c	a	c	c
May	S-2	a	a	a	a	a	a	a	a	a	a	a
	S-1	a	a	a	a	a	a	a	a	a	a	a
	S+1	a	b	a	b	a	b	a	b	b	a	b
	S+2	a	b	a	b	a	bc	a	b	b	a	b
	S+3	a	b	a	b	a	c	a	b	c	a	b
June	S-2	ab	a	a	a	a	a	a	a	a	a	a
	S-1	a	a	a	a	a	a	a	a	a	a	a
	S+1	b	a	a	b	a	b	a	b	b	a	b
	S+2	b	a	a	c	a	c	a	c	b	a	bc
	S+3	b	a	a	c	a	c	a	c	b	a	c
July	S-2	ac	a	a	a	a	a	a	a	a	a	a
	S-1	a	a	a	a	a	a	a	a	a	a	a
	S+1	b	b	b	b	b	b	a	b	b	a	b
	S+2	b	b	b	b	c	c	a	b	c	a	c
	S+3	c	c	c	b	a	a	a	b	d	a	d
Aug	S-2	a	a	a	a	a	a	a	a	a	a	a
	S-1	a	a	a	a	a	a	a	a	a	a	a
	S+1	b	b	b	b	b	b	a	b	b	a	b
	S+2	b	b	b	b	b	c	a	b	b	a	b
	S+3	c	b	c	c	a	a	a	c	c	a	c
Oct	S-2	a	a	a	a	a	a	a	a	a	a	a
	S-1	a	a	a	b	a	a	a	a	a	a	a
	S+1	b	b	b	c	b	b	a	b	bc	a	b
	S+2	c	b	b	d	b	b	a	c	b	a	b
	S+3	d	b	b	d	a	a	a	c	c	a	a

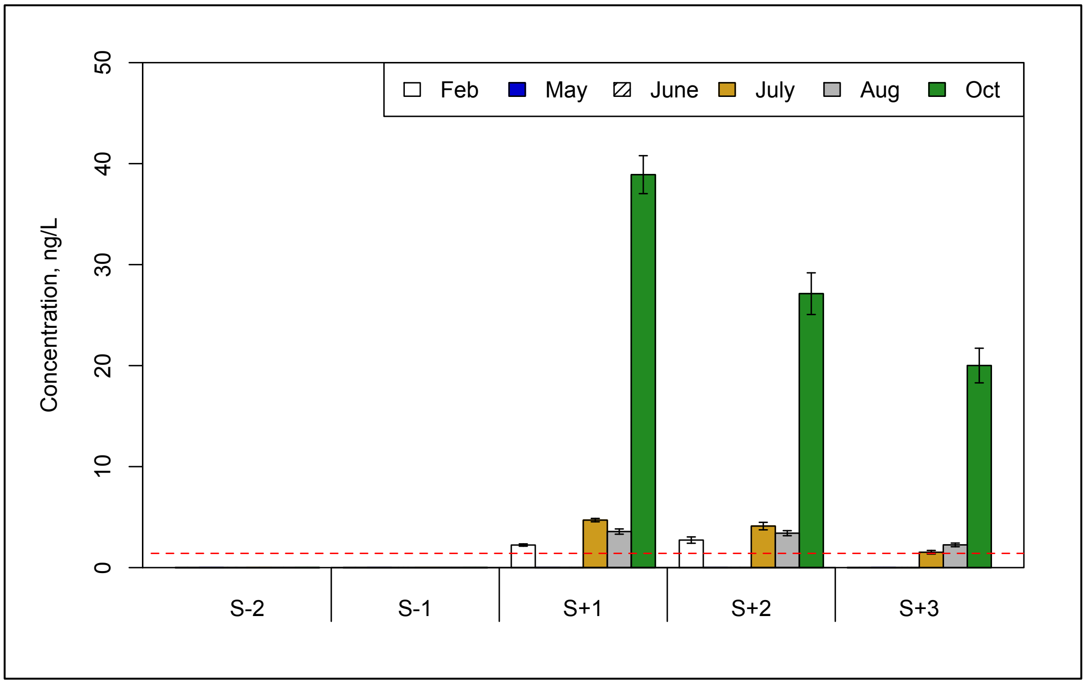

Figure B1: Average stream concentrations (N = 3) of acetaminophen (red dashed line represents the MDL). Error bars represent 95% confidence intervals.

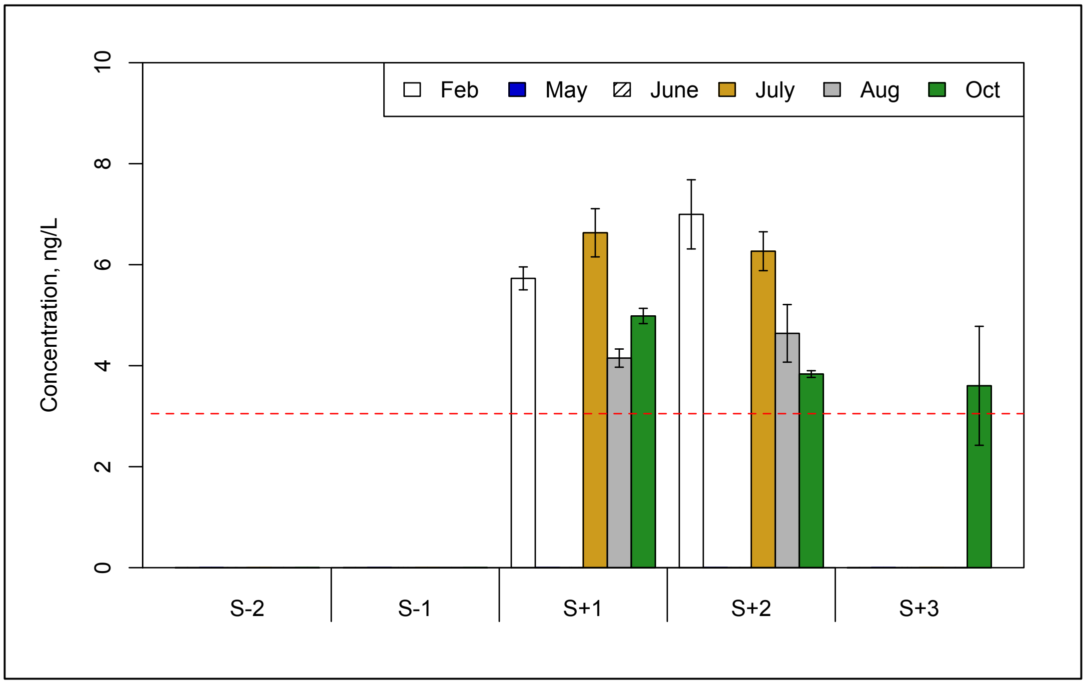

Figure B2: Average stream concentrations (N = 3) of triclosan (red dashed line represents the MDL). Error bars represent 95% confidence intervals.

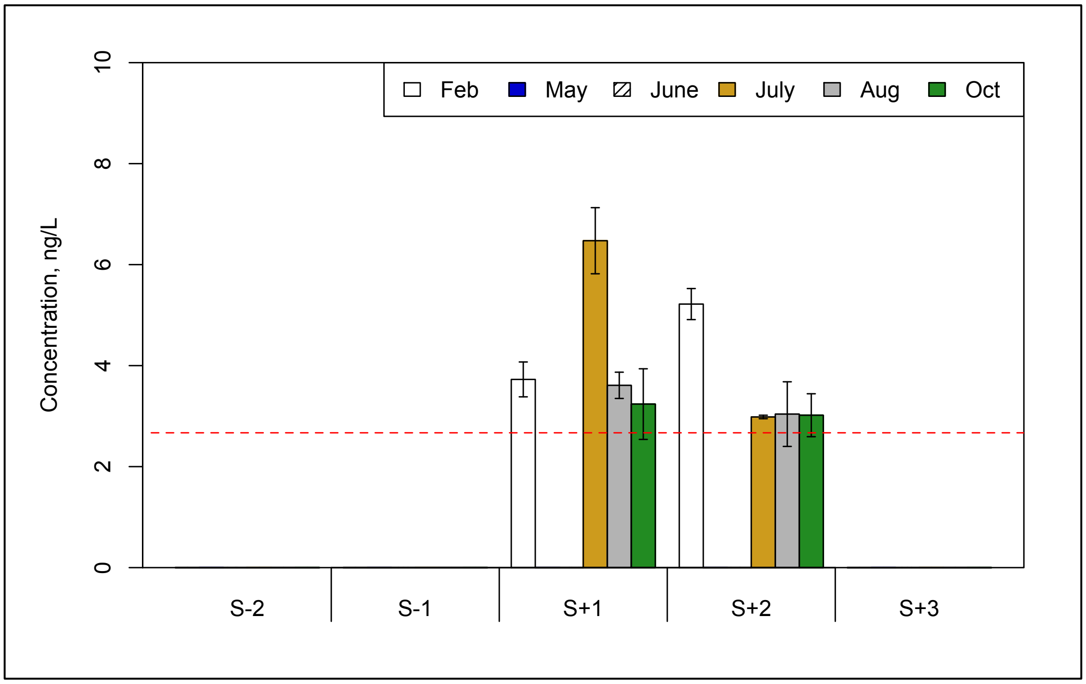

Figure B3: Average stream concentrations (N = 3) of fluoxetine (red dashed line represents the MDL). Error bars represent 95% confidence intervals.

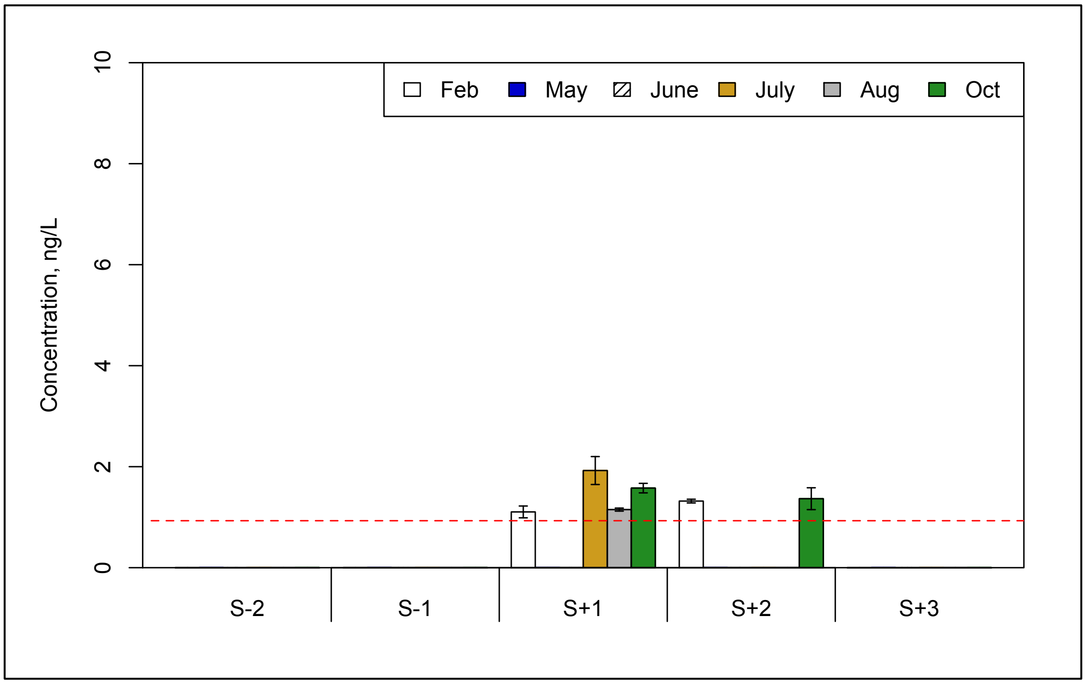

Figure B4: Average stream concentrations (N = 3) of sertraline (red dashed line represents the MDL). Error bars represent 95% confidence intervals.

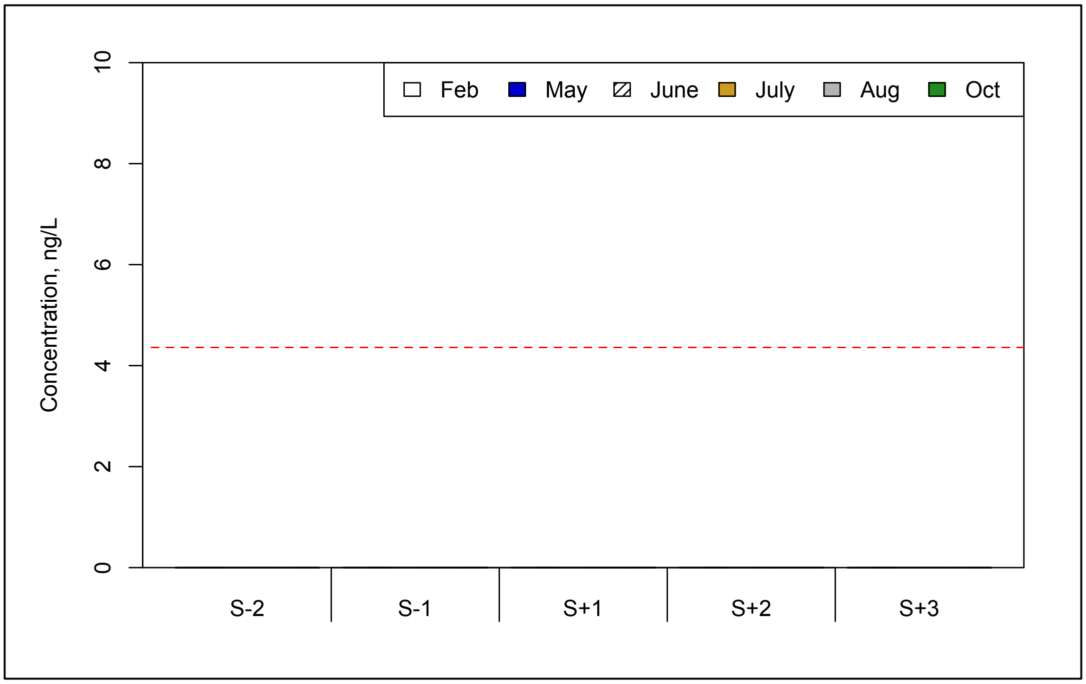

Figure B5: Average stream concentrations (N = 3) of amitriptyline (red dashed line represents the MDL). Amitriptyline was below the MDL for all stream samples.

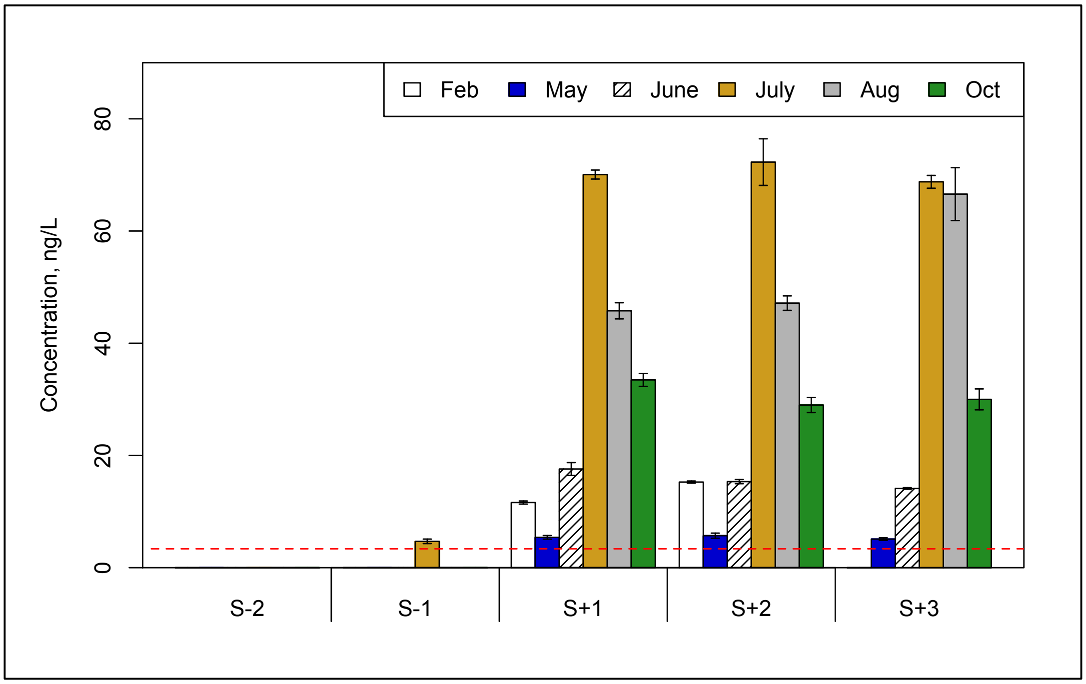

Figure B6: Average stream concentrations (N = 3) of TCEP (red dashed line represents the MDL). Error bars represent 95% confidence intervals.

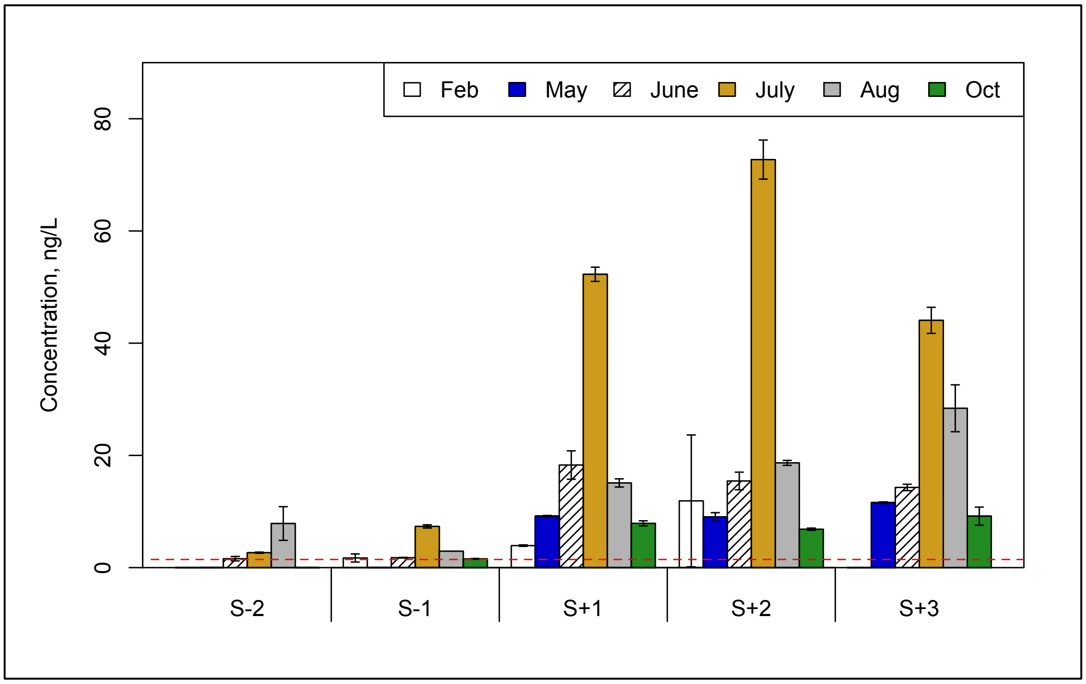

Figure B7: Average stream concentrations (N = 3) of DEET (red dashed line represents the MDL). Error bars represent 95% confidence intervals.

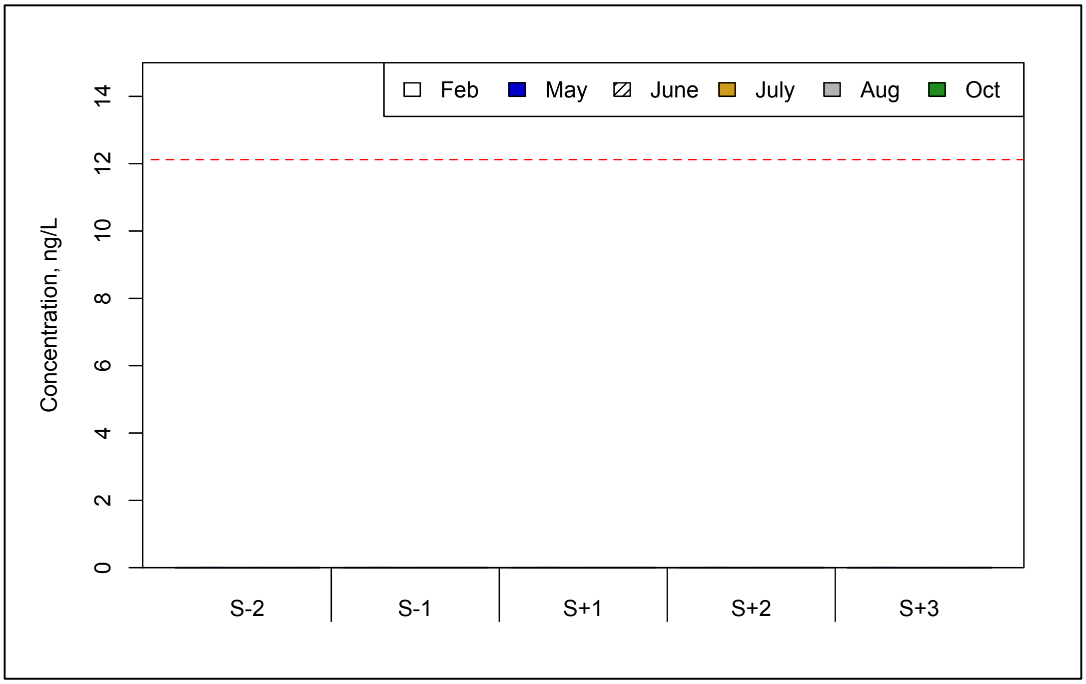

Figure B8: Average stream concentrations (N = 3) of gemfibrozil (red dashed line represents the MDL). Gemfibrozil was below the MDL for all stream samples.

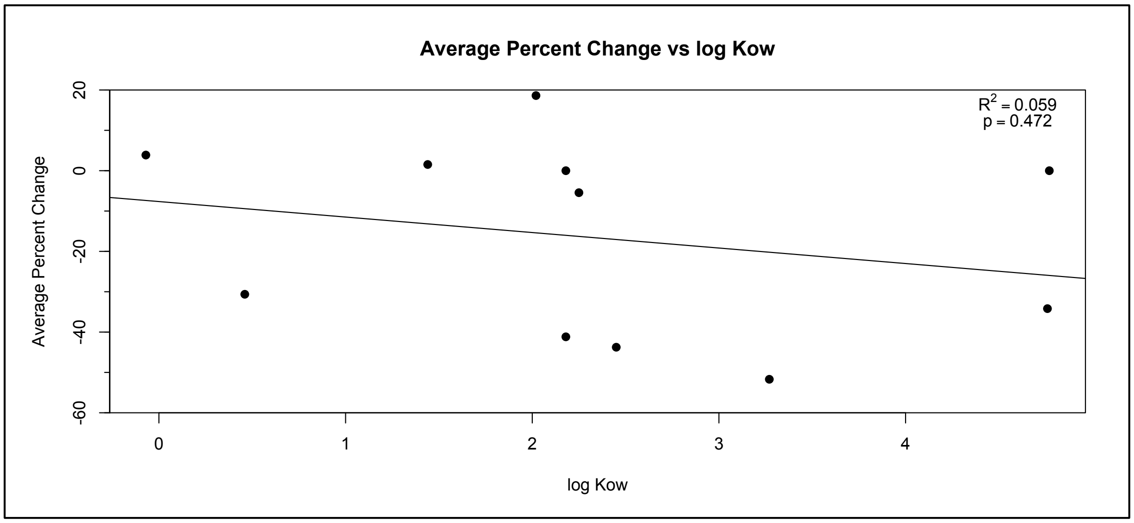

Figure B9: Plot of the average percent change between S+1 and S+3 concentrations for each compound vs. the log of the corresponding octanol-water partition coefficient.

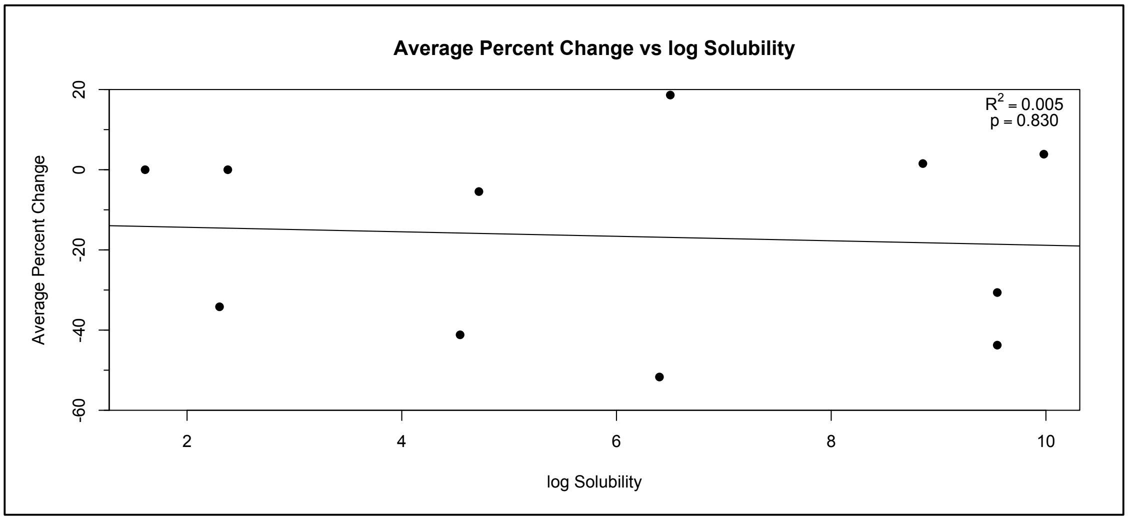

Figure B10: Plot of the average percent change between S+1 and S+3 concentrations for each compound vs. the log of corresponding water solubility.

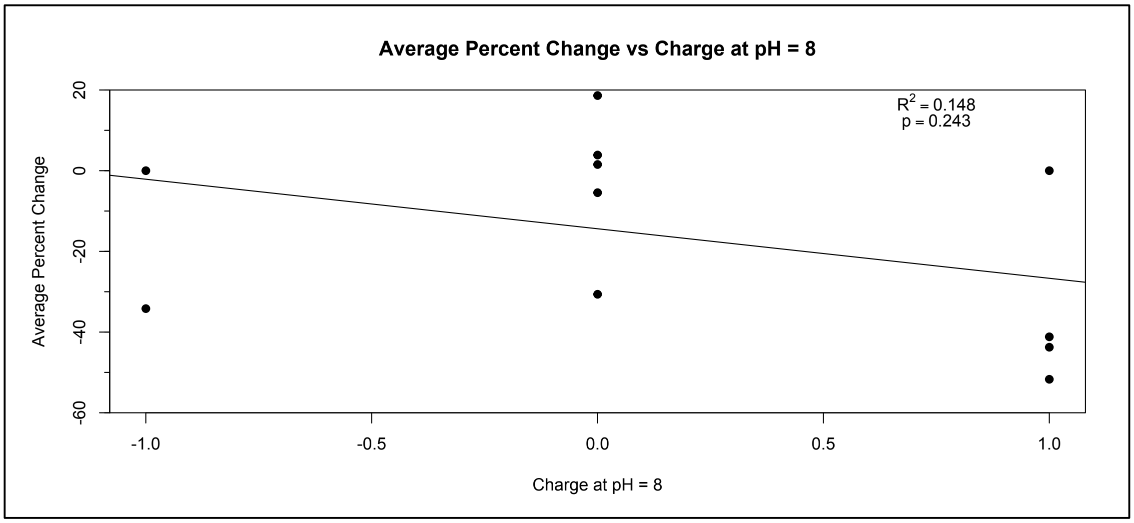

Figure B11: Plot of the average percent change between S+1 and S+3 concentrations for each compound vs. the corresponding charge of the dominant species at environmentally relevant pH (pH = 8; charge labeled -1.0 for negative, 0.0 for neutral, 1.0 for positive).

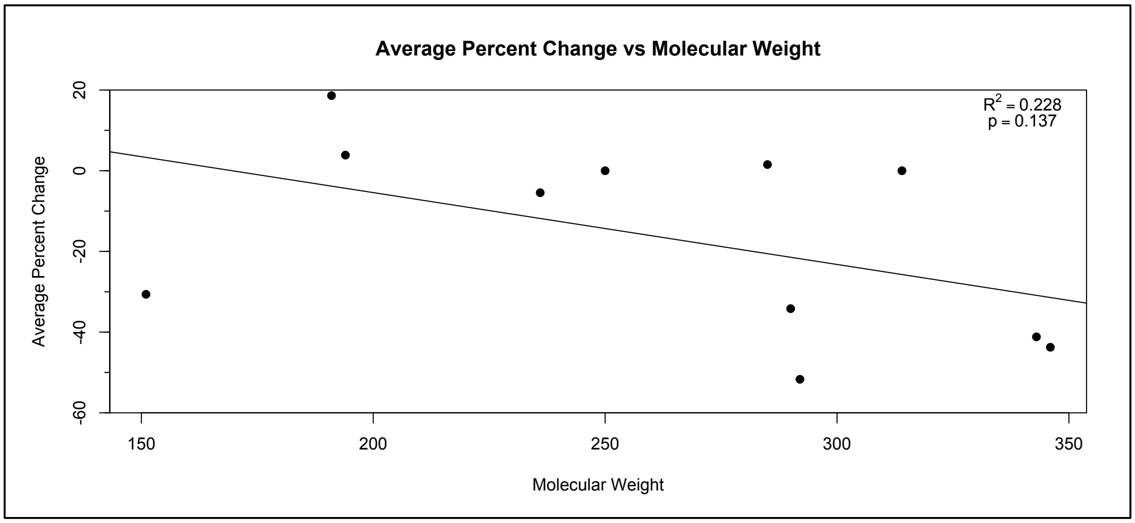

Figure B12: Plot of the average percent change between S+1 and S+3 concentrations for each compound vs. the corresponding molecular weight.

APPENDIX C – Supporting Tables for Sediment Samples.

Table C1: Organic content results for sediment samples.

Sampling Event	Location	Organic Matter (%)
June	S-2	5.0
	W2	10.8
	W3	3.7
	W4	2.1
	S+1	0.6
	S+3	4.6
July	S-2	1.4
	S-1	1.5
	W2	5.1
	W3	0.8
	S+1	1.3
	S+2	0.8
August	S-2	3.3
	W3	16.3
	W4	2.4
	S+1	0.8
	S+2	0.8
	S+3	1.2
October	S-2	4.5
	W2	5.0
	W4	10.1
	S+1	1.9
	S+3	2.2

Table C2: Average concentrations (ng analyte / kg sediment) in sediment samples (N=3) at each relevant sampling location and each sampling event. Gemfibrozil results are not shown due to non-detect results in all sediment samples. ND = non-detect.

Sampling Event	Location	CAF	SMZ	CBZ	AMT	SER	TRI
May	S-2	494	ND	53.0	ND	64.4	5120
	W2	637	338	685	3320	7670	24200
	W3	654	152	888	3620	6040	21800
	W4	653	215	607	3080	5080	21300
	S+1	1830	ND	95.2	1460	2600	7970
	S+2	805	ND	122	661	1340	4950
June	S-2	572	ND	ND	ND	ND	ND
	W2	2090	88.8	5220	10300	17900	58500
	W3	818	129	1320	4010	5300	21100
	W4	676	83.7	1310	4310	6260	18400
	S+1	256	ND	137	255	323	1710
	S+3	740	ND	550	1430	1490	9680
July	S-2	144	ND	ND	ND	ND	293
	S-1	201	ND	ND	ND	ND	206
	W2	1250	275	3020	2520	5640	16600
	W3	219	90.4	284	1450	1730	3480
	S+1	254	ND	293	1820	2860	4100
	S+2	365	ND	129	524	503	1280
August	S-2	382	ND	22.2	167	323	ND
	W3	4520	ND	1790	4880	7470	23700
	W4	1740	ND	510	3140	1890	15400
	S+1	215	ND	27.5	83.5	58.1	6510
	S+2	488	182	22.4	389	890	ND
	S+3	1120	ND	109	119	289	7940
October	S-2	352	ND	ND	ND	ND	ND
	W2	1040	290	573	1450	2630	13300
	W4	946	2210	2480	2520	8440	14100
	S+1	319	ND	119	767	1740	ND
	S+3	508	ND	533	308	405	ND

Table C3: Sediment to water concentration ratios (L/kg). NA = Not available (due to water concentration below the method detection limit). CBZ wetland ratios are blank because of unreliable QAQC in the wetland water matrix (Table 10).

Sampling Event	Location	CAF	CBZ	AMT	SER	TRI
May	S-2	79.7	NA	NA	NA	NA
	W2	196		495	1880	1000
	W3	201		539	1480	901
	W4	201		459	1250	883
	S+1	384	19.8	NA	NA	NA
	S+2	161	18.5	NA	NA	NA
June	S-2	203	NA	NA	NA	NA
	W2	720		867	1650	1860
	W3	282		336	189	671
	W4	233		362	577	585
	S+1	124	9.21	NA	NA	NA
	S+3	330	44.0	NA	NA	NA
July	S-2	71.8	NA	NA	NA	NA
	S-1	95.8	0	NA	NA	NA
	W2	180		263	562	958
	W3	31.5		152	172	201
	S+1	40.9	3.69	NA	NA	619
	S+2	65.4	1.64	NA	NA	205
August	S-2	160	NA	NA	NA	NA
	W3	683		812	1270	1880
	W4	251		532	358	1310
	S+1	48.7	0.621	NA	50.5	1570
	S+2	98.1	0.488	NA	NA	0
	S+3	200	2.08	NA	NA	NA
October	S-2	96.0	NA	NA	NA	NA
	W2	116		246	117	642
	W4	83.3		548	474	720
	S+1	51.6	2.48	NA	1100	0
	S+3	77.0	12.9	NA	NA	0

Table C4: Sediment to water concentration ratios normalized by organic content (L/kgC). NA = Not available (due to water concentration below the method detection limit). May values not included because the May sediment samples were not characterized for organic carbon content.

Sampling Event	Location	CAF	CBZ	AMT	SER	TRI
June	S-2	4070	NA	NA	NA	NA
	W2	120000		144000	275000	310000
	W3	6140		7310	10600	14600
	W4	2160		3350	5340	5420
	S+1	3340	249	NA	NA	NA
	S+3	15700	2090	NA	NA	NA
July	S-2	5130	NA	NA	NA	NA
	S-1	6380	0	NA	NA	NA
	W2	13900		20200	43300	73700
	W3	3940		18900	21500	25100
	S+1	802	72.3	NA	NA	12100
	S+2	8170	204	NA	NA	25600
August	S-2	4840	NA	NA	NA	NA
	W3	85400		102000	159000	235000
	W4	31400		66400	44800	164000
	S+1	4060	51.8	NA	4210	131000
	S+2	602	2.99	NA	NA	0
	S+3	8320	86.5	NA	NA	NA
October	S-2	2130	NA	NA	NA	NA
	W2	6110		12900	6160	33800
	W4	3790		24900	21500	32700
	S+1	1030	49.6	NA	22100	0
	S+3	762	128	NA	NA	0

Table C5: Log values of the sediment to water concentration ratios normalized by organic carbon content.

Sampling Event	Location	CAF	CBZ	AMT	SER	TRI
June	S-2	3.6				
	W2	5.1		5.2	5.4	5.5
	W3	3.8		3.9	4.0	4.2
	W4	3.3		3.5	3.7	3.7
	S+1	3.5	2.4			
	S+3	4.2	3.3			
July	S-2	3.7				
	S-1	3.8				
	W2	4.1		4.3	4.6	4.9
	W3	3.6		4.3	4.3	4.4
	S+1	2.9	1.9			4.1
	S+2	3.9	2.3			4.4
August	S-2	3.7				
	W3	4.9		5.0	5.2	5.4
	W4	4.5		4.8	4.7	5.2
	S+1	3.6	1.7		3.6	5.1
	S+2	2.8	0.5			
	S+3	3.9	1.9			
October	S-2	3.3				
	W2	3.8		4.1	3.8	4.5
	W4	3.6		4.4	4.3	4.5
	S+1	3.0	1.7		4.3	
	S+3	2.9	2.1			