

University of Nevada, Reno

Fate of Trace Organic Contaminants in Semi-Arid Areas

A dissertation submitted in partial fulfillment of the
requirements for the degree of Doctor of Philosophy in
Civil and Environmental Engineering

by

Priyamvada Sharma

Dr. David Hanigan, Dissertation Advisor

May 2021



THE GRADUATE SCHOOL

We recommend that the dissertation
prepared under our supervision by

entitled

be accepted in partial fulfillment of the
requirements for the degree of

Advisor

Committee Member

Committee Member

Committee Member

Graduate School Representative

David W. Zeh, Ph.D., Dean
Graduate School

ABSTRACT

Semi-arid areas including the state of Nevada, has been exploring reclaimed water for direct or indirect potable reuse. Numerous research articles have discussed the occurrence of trace organic contaminants (TrOCs) in reclaimed water, surface water, soil, sediments, studied their photodegradation in water, and their transport and accumulation in plants when reclaimed water is used for irrigation. To safely reuse reclaimed water for irrigation in semi-arid areas, there is a need to determine the fate of TrOCs in various environmental media receiving reclaimed water. Therefore, the overarching goal of this dissertation was to investigate the fate of TrOCs in semi-arid areas to safely reuse the reclaimed water. To accomplish this goal, experiments were conducted to determine the fate of TrOCs in semi-arid areas. The specific objectives of this dissertation were to A) determine the fate of TrOCs in reclaimed water in an agricultural farm irrigated with reclaimed water for over 10 years, B) compare the fate of TrOCs in terminal lakes (TLs) influenced by reclaimed water to terminal lakes which are not influenced by reclaimed water, C) determine the photodegradation kinetics of TrOCs in terminal lakes and freshwater lake.

To accomplish Objective A, the fate of 12 TrOCs in wastewater samples, 11 in plants and in soil pore water, and 10 in soil at an agricultural research farm were studied, which was irrigated with reclaimed wastewater for more than 10 years. Reclaimed wastewater contained 11 of 12 TrOCs, with concentrations ranging from 26 ± 9 ng/L (DEET) to 1539 ± 1899 ng/L (trimethoprim). Soils from 0 to 60 cm contained nine TrOCs from below the reporting limit (fluoxetine) to 329 ng/g (carbamazepine). TrOC concentrations decreased with increasing soil depth, except carbamazepine, which was more recalcitrant. Nine

TrOCs were in the shoots and leaves of alfalfa grown in the reclaimed wastewater irrigated plots, at concentrations ranging from <1 ng/g (diphenhydramine and fluoxetine) to 49 ng/g dry weight (DW) (carbamazepine). Overall, despite some accumulation of TrOCs in the soil, alfalfa uptake was limited, which results in low exposure to foraging animals.

To achieve Objective B, a preliminary assessment of the occurrence of ten TrOCs in three TLs receiving reclaimed wastewater and one TL which does not directly receive reclaimed wastewater were conducted. Concentrations of caffeine, carbamazepine, diphenhydramine, fluoxetine and meprobamate were significantly higher in TLs receiving reclaimed wastewater from a secondary treatment plant compared to those which received tertiary treated wastewater. Carbamazepine, fluoxetine, sulfamethoxazole, and trimethoprim were present at concentrations greater than is typical of other U.S. freshwater lakes, but other TrOC concentrations were at lower concentrations than in other freshwater lakes.

Based on the outcomes of Objective B, carbamazepine and diphenhydramine were selected for further study because they were at higher and lower concentrations in TLs than U.S. freshwater lakes. In published literature, photodegradation of pharmaceuticals is considered as the main route of degradation of TrOCs in natural waters. To study photodegradation (Objective C), laboratory-scale solar simulated experiments were conducted on carbamazepine and diphenhydramine using surface water from terminal lakes and a freshwater lake. Photodegradation kinetics of CBZ and DPH in two terminal lakes (Walker Lake, NV and, Swan Lake, NV) were compared to the rates in one oligotrophic freshwater lake (Lake Tahoe). Dilutions of lake water samples containing 20 mg/L of CBZ and DPH were prepared and, exposed to simulated solar light for a maximum

of 2 days. Photodegradation of CBZ and DPH followed a pseudo-zero order kinetics. Dissolved organic carbon up to 65 mgC/L and alkalinity of 5,198 mg CaCO₃/L in terminal lakes enhanced the rate of photodegradation rate of DPH and CBZ but photodegradation rates of DPH were higher than CBZ. Degradation rate constants ranged from 0.33 to 2.68 mg/L-hr for CBZ and DPH in terminal lakes compared to 0.19 to 0.88 mg/L-hr for CBZ and DPH in a freshwater lake. Overall, TrOCs were persistent at low concentrations in semi-arid areas. Water constituents in the presence of sunlight and soil have the potential to either degrade or sorb TrOCs, reducing the concentrations of aqueous and mobile TrOCs in the environment.

DEDICATION

I dedicate my dissertation in the loving memory to my father Mr. Harshvardhan Sharma who lost his battle to cancer in 2014. It was his dream to see me graduate with a doctorate degree. His dream has been my motivation throughout my PhD journey.

ACKNOWLEDGEMENTS

I would like to express my immense appreciation to my advisor, Dr. David Hanigan for his constant mentorship, guidance, and support throughout my PhD program. I am grateful to my doctoral committee members: Dr. Krishna Pagilla, Dr. Frank (Yu) Yang, Dr. Paul Verburg and Dr. Joanna R. Blaszczak for their assistance in multiple areas like research funding, providing soil and lysimeter samples, assisting in solving research problems, coursework and as co-authors.

I would like to recognize Dr. Sage Hiibel for helping me during terminal lake sampling. I would also like to thank Dr. David Quilici and Dr. Rebekah Woolsey for training me on LC-MS/MS at UNR Proteomics laboratory. I would acknowledge Dr. Teshome Shenkoru for assisting me in fixing the ASE instrument and our lab manager Dr. Veronica Edirveerasingam for her help with procurements and instrumentation.

This dissertation research was supported by AFRI Grant No. 2017-69007-26309 from the USDA National Institute of Food and Agriculture and partially supported by the National Science Foundation under Grant No. 1804255, and the Nevada Proteomics Center, which is supported in part by the Nevada INBRE, a grant from the National Institute of General Medical Sciences within the National Institutes of Health.

I would also like to extend my gratitude to my colleagues; Andrew Poustie, Dr. Utsav Thapa, Elizabeth McKenna, Srinidhi Lokesh, Grant Busse, Tatiana Guarin, and Yingshi Feng for their immense assistance during sampling events, laboratory experiments and analysis. Cheers to my landlady Tina and my friend Michelle for their constant

encouragement during stressful and long working hours in the laboratory. In addition, I would like to thank my mother, brother, in-laws, and my husband Akshay Grover for their endless support throughout my PhD journey.

TABLE OF CONTENTS

Abstract.....	i
List of Tables	ix
List of Figures	x
Abbreviations.....	xii
1 Introduction and Dissertation Structure	1
2 Literature Review.....	5
2.1 TrOCs in treated wastewater and the environment.....	5
2.2 TrOCs in soil.....	7
2.3 TrOC translocation into plants.....	9
2.4 TrOCs in surface water	13
2.5 TrOCs in sediments.....	14
2.6 Potential human health risks of TrOCs.....	15
2.7 Ecotoxicity of TrOCs.....	17
2.8 Terminal Lakes	18
2.9 TrOC photodegradation	19
2.9.1 Direct photolysis	20
2.9.2 Indirect photolysis influenced by DOM	20
2.9.3 Indirect photolysis influenced by anions and pH.....	22
2.10 Knowledge gaps	23
3 Trace Organic Contaminants in Field-scale Cultivated Alfalfa, Soil, and Pore Water after 10 Years of Irrigation with Reclaimed Wastewater*	24
3.1 Introduction.....	25
3.2 Materials and Methods.....	28
3.2.1 Chemicals and Reagents	28
3.2.2 Sample Collection.....	29
3.2.3 Sample Extraction.....	30
3.2.4 Analytical Methods.....	32
3.2.5 Calculations.....	33
3.2.5.1 TrOC accumulation in soil and alfalfa.....	33
3.3 Results and Discussion	34
3.3.1 Reclaimed wastewater	34
3.3.2 Soil	36
3.3.3 Pore Water	38
3.3.4 Alfalfa	41
3.3.5 Mass Balance	44
3.4 Conclusions.....	46
4 Evidence of Low Levels of Trace Organic Contaminants in Terminal Lakes*	48
4.1 Introduction.....	49
4.2 Materials and Methods.....	51

4.2.1	Chemicals.....	51
4.2.2	Sample Collection.....	52
4.2.3	TrOC Concentrations in U.S. Freshwater Lakes from Literature.....	53
4.2.4	Description of Sampled Lakes.....	53
4.2.5	Sample Extraction and Analysis.....	55
4.2.6	Statistical methods.....	56
4.3	Results and Discussion.....	56
4.3.1	TrOC occurrence in TLs.....	56
4.3.2	Variability among TLs.....	59
4.3.3	Losses in the TLs.....	61
4.3.4	Comparisons of TLs with U.S. surface waters.....	62
4.4	Conclusions.....	65
5	Dissolved Constituents in Endorheic Lakes Cause Faster Photodegradation of Pharmaceuticals than those in Freshwater Lakes*.....	66
5.1	Introduction.....	67
5.2	Materials and Methods.....	69
5.2.1	Chemicals and Reagents.....	69
5.2.2	Sampling.....	69
5.2.3	Photodegradation Experimental Apparatus.....	70
5.2.4	Analytical Methods.....	71
5.2.5	Linear Mixed Effect Model.....	72
5.3	Results and Discussion.....	73
5.3.1	Lake Characteristics.....	73
5.3.2	Degradation Rates.....	74
5.3.3	Contribution of DOC.....	76
5.3.4	Contribution of Other Dissolved Constituents.....	78
5.4	Conclusions.....	81
6	Synthesis of Results.....	82
7	Conclusions and Recommendations for Future Research.....	87
7.1	Conclusions.....	87
7.2	Recommendations for Future Research.....	88
8	References.....	90
9	Appendix A.....	105
10	Appendix B.....	115
11	Appendix C.....	129

LIST OF TABLES

Table 2-1 Respective concentrations of TrOCs in soil when irrigated with reclaimed water.....	7
Table 2-2 TrOCs in plants when a known concentration of TrOCs were spiked in water, hydroponic, field-scale, and greenhouse studies.....	10
Table 3-1 Distribution of analytes in soil, alfalfa shoots and leaves.	45
Table 5-1 Water characteristics of lakes in this research.....	73
Table 5-2 Photodegradation kinetics in three lakes and deionized water.	75
Table A- 1 Percent recoveries of compounds in a representative spiked soil sample.	107
Table A- 2 Surface soil (0-20 cm) properties.	108
Table A- 3 Properties of the selected TrOCs selected for this study.	109
Table A- 4 LC-MS/MS parameter values for ESI positive and negative modes.....	112
Table A- 5 Method reporting limits for target compounds in aqueous (ng/L), soil and alfalfa samples (ng/g).....	113
Table A- 6 Target compound's LC-MS/MS conditions.	114
Table B- 1 MS/MS parameter values for ESI+ mode.....	115
Table B- 2 Method reporting limits for target compounds in aqueous (ng/L), soil and sediment samples (ng/g).	115
Table B- 3 LC-MS/MS conditions for target analytes.....	116
Table B- 4 ANOVA of TrOC concentrations in surface water samples.....	116
Table B- 5 ANOVA of TrOC concentrations in sediment samples.....	117
Table B- 6 TrOC concentrations in terminal lakes (TLs, Bold) and in U.S. lakes, rivers, streams, and sediments from literature	118
Table B- 7 TrOC concentrations in terminal lakes' surface water, sediments, and soil.	120
Table C- 1 Photodegradation kinetics in diluted samples of three lakes	137
Table C- 2 Results from the linear mixed-effect model	138

LIST OF FIGURES

- Figure 3-1 TrOC concentrations across the wastewater reclamation facility. Error bars are the standard deviation of four samples collected at 10 am across four days in the spring of 2018. No bar indicates the analyte was below the reporting limit. The treated effluent (reclaimed wastewater) was used for alfalfa irrigation. 36
- Figure 3-2 TrOC concentrations in MSFL soil at three depths. No bar indicates that the TrOC concentration was below the reporting limit. Error bars represent the standard deviation among triplicate samples..... 38
- Figure 3-3 TrOCs in seven lysimeter samples from three lysimeters, sampled between October 2018 and April 2019. Lysimeter 1 is the mean of 3 sampling events, lysimeter 2, mean of 2 sampling events, and lysimeter 3, mean of 2 sampling events. The error bars are standard deviation of triplicate samples. No bar indicates below reporting limit. 41
- Figure 3-4 TrOC concentrations in alfalfa sampled in 2018 and irrigated with reclaimed wastewater from regional wastewater treatment plant..... 44
- Figure 4-1 TrOCs in the mixing zone (A, represented by solid bars) and the average of three nearshore sampling sites (B/C/D, pattern fills). Error bars show the standard deviation of three or more samples collected at location A and B/C/D of TL1, TL2, TL3 and CTL. Asterisks indicate the concentration is significantly different in the lake compared to the mixing zone. No bar indicates the analyte was below detection limit. 58
- Figure 4-2 TrOCs in sediments at the mixing zone (A) and the average of three points near the lakeshore (B/C/D). Error bars represents the standard deviation among three or more samples. Asterisks indicate the concentration is significantly different in the lake compared to the mixing zone. No bar indicates the analyte was below detection limit. 59
- Figure 4-3 TrOCs soils at locations A & B/C/D, where locations B, C & D are the average of three TLs and one control lake. Error bars show the standard deviation of three or more samples. No bar indicates the analyte was below detection limit. 61
- Figure 4-4 Comparison between TrOCs in surface water of TLs (this study, n=4) and literature (ranging from n=1 to 4). Median shown by line, box shows interquartile range, cross is mean and individual points are outliers. Outliers (TLs PMD- 1128 ng/L, 1739 ng/L, 2901 ng/L and 3932 ng/L and Literature CAF- 800 ng/L) are not shown. 64
- Figure 4-5 TrOCs in sediments of TLs (this study, n=4) and other U.S. lakes (literature, ranging from n= 1 to 3). Outliers (TLs PMD- 37 ng/g DW, 143 ng/gDW and

Literature DPH- 36 ng/gDW, 37 ng/gDW, 44 ng/gDW, 48 ng/gDW, 82 ng/gDW) are not shown.....	64
Figure 5-1 Pseudo zero-order degradation rate constants (k_{obs}) of CBZ are extracted from Table 5-1 and Table C-1 for all three lakes and plotted against DOC in terminal lakes and a freshwater lake which are based on dilution calculations.	77
Figure 5-2 Pseudo zero-order k_{obs} of DPH are extracted from Table 5-1 and Table C-1 for all three lakes and plotted against DOC in terminal lakes and a freshwater lake which are based on dilution calculations.	78
Figure 5-3 Pseudo zero-order k_{obs} of CBZ are extracted from Table 5-1 and Table C-1 for all three lakes and plotted against alkalinity in terminal lakes and a freshwater lake which are based on dilution calculations.	79
Figure 5-4 Pseudo zero-order k_{obs} of DPH are extracted from Table 5-1 and Table C-1 for all three lakes and plotted against alkalinity in terminal lakes and a freshwater lake which are based on dilution calculations.	79
Figure 6-1 The impact of reclaimed water on agricultural farm, terminal lakes on accumulation and photodegradation of TrOCs.	86
Figure C- 1 Removal of CBZ in Walker Lake May with six dilutions over time.	130
Figure C- 2 Removal of CBZ in Walker Lake July over time in various dilutions. 0-100 represents the removal of CBZ in 100% deionized water over time.	130
Figure C- 3 Removal of CBZ in diluted and undiluted samples of Swan Lake over time.	131
Figure C- 4 Removal of CBZ in Lake Tahoe's diluted and undiluted water over time.	131
Figure C- 5 Removal of DPH in Walker Lake May's diluted and undiluted water sample over time.	132
Figure C- 6 Removal of DPH in Walker Lake July's diluted and undiluted samples over time. 0-100 represents the removal of DPH in 100% deionized water over time. ..	132
Figure C- 7 Removal of DPH in Swan Lake's diluted and undiluted sample over time.	133
Figure C- 8 Removal of DPH in Lake Tahoe's diluted and undiluted samples over time. The simulated light exposure for these samples was longer than 10 hours because DPH did not get removed in Lake Tahoe samples within 10 hours of exposure.....	133
Figure C- 9 Degradation rate constants (k_{obs}) for CBZ vs SUVA values of each studied lakes.	134
Figure C- 10 k_{obs} for DPH vs SUVA values for each lake.	134
Figure C- 11 k_{obs} for CBZ vs SO_4^{2-} for each lake.	135
Figure C- 12 k_{obs} for DPH vs SO_4^{2-} for each lake.	135
Figure C- 13 k_{obs} for CBZ vs $PO_4\text{-P}$ for each lake.	136
Figure C- 14 k_{obs} for DPH vs $PO_4\text{-P}$ for each lake.	136

ABBREVIATIONS

ATZ- Atrazine

CAF- Caffeine

CBZ- Carbamazepine

CTL- Control Terminal Lake

DBP- Disinfection Byproducts

DEET- N, N-diethyl-meta-toluamide

DPH- Diphenhydramine

DOC- Dissolved Organic Carbon

DOM- Dissolved Organic Matter

FLX- Fluoxetine

MPB- Meprobamate

NDMA- N-nitrosodimethylamine

NOM- Natural Organic Matter

PMD- Primidone

PPCP- Pharmaceuticals and Personal Care Products

PFAS- Per- and polyfluoroalkyl substances

SMX- Sulfamethoxazole

SUVA- Specific Ultraviolet Absorbance

TLs- Terminal Lakes

TMP- Trimethoprim

TOC- Total Organic Carbon

TrOCs- Trace Organic Contaminants

WWTP- Wastewater Treatment Plant

CHAPTER 1

INTRODUCTION AND DISSERTATION STRUCTURE

Water demand is increasing, where 70% of worldwide freshwater withdrawals are currently used in agriculture (WWAP, 2017). Advanced technologies in wastewater treatment plant are used to treat wastewater (WWAP, 2017), and this treated reclaimed water is sometimes used as an irrigation source in water scarce areas (Calderón-Preciado et al., 2011; Feng Chen et al., 2011; Hyland et al., 2015; Nason et al., 2019; Xiaoqin Wu et al., 2012; Xiaoqin Wu et al., 2014). However, reclaimed water has various trace organic contaminants (TrOCs) at ng/L to µg/L (Wancen Liu et al., 2020) because wastewater treatment plants do not completely remove all TrOCs (Blair et al., 2013). Either by direct (wastewater effluent (Sun et al., 2014)) or indirect pathways (run off from industries, agriculture etc. (Gaw et al., 2014)), TrOCs are introduced into surface water (Kasprzyk-Hordern et al., 2009), sediments (Gaw et al., 2014; Richardson et al., 2005), soil (Weiping Chen et al., 2013; Xu et al., 2010) and plants (Boxall et al., 2006; Chenxi Wu et al., 2010; Xiaoqin Wu et al., 2012). The fate of TrOCs in aquatic and agricultural environments depend on the respective contaminant concentrations, physiochemical properties, volatilization, dilution, biodegradation, partitioning to sediments/soil, photodegradation, uptake by aquatic biota, translocation in plants and transformation into other products (Xiaoqin Wu et al., 2013; Yamamoto et al., 2009). Some TrOCs can bioaccumulate in aquatic animals (Miège et al., 2009; Richardson et al., 2005), plants and livestock (Geyer et al., 2000), which may lead to adverse effects such as impaired reproduction and

behavioral modification in fish (Brown et al., 2007; Kidd et al., 2007), or impact plant development (Carter et al., 2015; Hammad et al., 2018; Herklotz et al., 2010).

In this dissertation, a literature review is first presented to familiarize the reader with the available research and data gaps (Chapter 2). The data gaps identified in the literature review motivated me to identify the overarching goal: to investigate the fate of TrOCs in semi-arid areas to safely reuse the reclaimed water.

Most commonly, wastewater treatment plants discharge treated water into a nearby surface water body or distribute it to local agricultural farm or golf courses/turf fields. Many publications focus on translocation of TrOCs in plants from soil when reclaimed water is used as an irrigation source. However, the majority of such studies add a known concentration of TrOCs in soil to understand the extent/degradation of that specific TrOCs in soil (Carter et al., 2014; Revitt et al., 2015) or conduct field-scale studies irrigated with reclaimed water to understand specific compounds' biodegradability/movement in soil over a single growing season (Feng Chen et al., 2011; Grossberger et al., 2014; Chad A. Kinney et al., 2006a). Limited scientific studies have focused on field-scale experiments that have been irrigated with reclaimed wastewater for a significant period of time (Feng Chen et al., 2011; Weiping Chen et al., 2013; Dalkmann et al., 2012). There is a need for more field-scale data to improve risk estimates in humans and animals exposed to applied TrOCs. To fill this research gap, a published manuscript follows in Chapter 3, which describes the field-scale investigation of TrOCs fate in a field irrigated with reclaimed water for over 10 years.

Some portion of treated wastewater is typically released to nearby surface water, and many research articles have published the occurrence of TrOCs in ng/L to $\mu\text{g/L}$ levels in the surface water (Blair et al., 2013; Robert N Brent et al., 2001b; Elliott et al., 2017; Kolpin et al., 2002; Melissa M. Schultz et al., 2010a). Terminal lakes may potentially accumulate TrOCs present in surface flows. However, there is limited research on fate of TrOCs in terminal lakes. Therefore, there is a need to determine the fate of TrOCs in terminal lakes to investigate TrOCs accumulation. TrOCs concentration in terminal lakes were measured and the statistical difference between terminal lakes influenced by reclaimed water, terminal lakes not influenced by reclaimed water, and U.S. freshwater lakes is presented in Chapter 4.

Natural attenuation of TrOC concentrations in surface water can occur via biodegradation, sorption to sediments, volatilization, and photolysis (Dong et al., 2015). Photodegradation is an important pathway in eliminating TrOCs in surface waters (Chiron et al., 2006; Doll and Frimmel, 2003; Lam and Mabury, 2005), especially for contaminants that are recalcitrant to biodegradation (De Laurentiis et al., 2012). Photodegradation of TrOCs has been studied in surface water, wastewater, and synthetic water but none of such studies in terminal lake waters is in the literature. Photodegradation involves two pathways: direct photolysis and indirect photolysis. Indirect photolysis involves irradiation of some compounds such as dissolved organic matter to form reactive species such as $\cdot\text{OH}$, $^1\text{O}_2$, and ^3OM (Chiron et al., 2006; De Laurentiis et al., 2012; Dong et al., 2015). Therefore, the photodegradation kinetics of TrOCs in terminal lakes was studied. The results of photodegradation of carbamazepine and diphenhydramine in terminal and freshwater lake

water are discussed in Chapter 5. Finally, a synthesis of the research results is provided in Chapter 6 and, conclusions and recommendation for future research in Chapter 7.

Chapter 2

LITERATURE REVIEW

Water resources in both developed and developing countries are experiencing stresses due to population growth, food and energy demand, economic development and climatic variability (Bulkley, 2000; WWAP, 2012). Similarly, water availability in the United States has become a major concern in both urban and rural areas (Anderson and Lloyd H. Woosley, 2006; Burtz et al., 2020). Increase in the U.S. population (Burtz et al., 2020), climate variability, scattered precipitation, and frequent droughts in parts of the U.S. has created unprecedented stress on water resources (Anderson and Lloyd H. Woosley, 2006; Dodgen et al., 2015; Hyland et al., 2015). Therefore, effective water management is necessary to decrease the stress on the available water resources for agronomic, public and industrial use (Burtz et al., 2020). The most common exercise is the use of reclaimed wastewater in water scarce areas for irrigation but the overall environmental and human exposure to trace organic contaminants TrOCs is poorly understood (Calderón-Preciado et al., 2011; Feng Chen et al., 2011; Hyland et al., 2015; Nason et al., 2019; Xiaoqin Wu et al., 2012; Xiaoqin Wu et al., 2014).

2.1 TrOCs in treated wastewater and the environment

Reclaimed water is “treated (‘fit-for-purpose’) wastewater that can be used under controlled conditions for beneficial purposes, such as irrigation (WWAP, 2017). However, reclaimed water contains TrOCs such as pharmaceuticals and personal care products (PPCPs), endocrine-disrupting compounds (EDCs), pesticides, disinfection byproducts and other synthetic compounds (Anumol et al., 2013; Feng Chen et al., 2011; Dodgen et al., 2015; Goldstein et al., 2014; Y. Carrie Guo and Krasner, 2009a; Wancen Liu et al.,

2020; Chang-Gui Pan et al., 2016; Xiaoqin Wu et al., 2014; Xu et al., 2008) with concentrations in the ng/L to µg/L range (Jin-Lin Liu and Wong, 2013; Wancen Liu et al., 2020).

Some TrOCs are incompletely removed by the conventional wastewater treatment plants (Melissa M. Schultz and Furlong, 2008) due to their poor biodegradability or sorption to biosolids (Awfa et al., 2018; Chang-Gui Pan et al., 2016) and later released in the environment. Concentrations of various pharmaceuticals in wastewater effluent range from non-detect to 9460 ng/L in China and non-detect to 1070 ng/L in Finland. Antibiotics (90-1140 ng/L) in New Mexico and Colorado, U.S., hormones (0.3-110 ng/L) in Japan (Jin-Lin Liu and Wong, 2013). Duloxetine and venlafaxine (antidepressants) concentrations ranged from 1.9 ng/L to 2190 ng/L in the Metropolitan Wastewater Treatment Plant effluent of City of Boulder, Colorado (Melissa M. Schultz and Furlong, 2008). Other examples of TrOCs released in treated effluent are tris (1-chloro-2-propyl) phosphate (TCPP) at 2595 ng/L, sucralose at 13860 ng/L, and carbamazepine, gemfibrozil, meprobamate, naproxen, primidone and sulfamethoxazole between 85–755 ng/L (Anumol et al., 2013). Atrazine (herbicide) has been detected at ng/L to µg/L in surface water but not in wastewater treated effluent because it was removed by the ozone treatment (Hua et al., 2006). Reclaimed water is released to the environment via irrigation or to surface water and thus, wastewater treatment plants are a source of TrOCs in surface water, groundwater, soil and plants (Jin-Lin Liu and Wong, 2013).

2.2 TrOCs in soil

TrOCs in the reclaimed water have the potential to accumulate in soil when used for irrigation (Biel-Maeso et al., 2018a; Xu et al., 2009b). Many field-scale or greenhouse studies have listed TrOCs accumulation in soil when irrigated with reclaimed water. TrOC accumulation in soil from these studies are listed in Table 2-1.

Table 2-1 Respective concentrations of TrOCs in soil when irrigated with reclaimed water.

TrOC	Concentration Range (ng/gDW)	Reference
Acetaminophen	ND-5.95	(Biel-Maeso et al., 2018b)
Bezafibrate	ND-0.38	(Biel-Maeso et al., 2018a)
Bisphenol A	<LOQ-1.5	(Xu et al., 2009a)
Caffeine	33-317	(Chad A Kinney et al., 2006b)
	0.51-3.21	(Biel-Maeso et al., 2018a)
Carbamazepine	3.33-19.91	(Grossberger et al., 2014)
	114-549	(Chad A Kinney et al., 2006b)
	710, 460	(Carter et al., 2014)
	0.08-1.36	(Biel-Maeso et al., 2018a)
Clofibric Acid	2.2-5.97	(Grossberger et al., 2014)
	4.5-9.5	(Xu et al., 2009a)
Diclofenac	70, 50	(Carter et al., 2014)
	ND-5.06	(Biel-Maeso et al., 2018a)
Diltiazem	ND-41	(Chad A Kinney et al., 2006b)
Diphenhydramine	ND-67	(Chad A Kinney et al., 2006b)
Erythromycin	125-6250	(Chad A Kinney et al., 2006b)
Estrone	1-4.5	(Xu et al., 2009a)
Flumequine	ND-5.31	(Biel-Maeso et al., 2018a)
Fluoxetine	5-376	(Chad A Kinney et al., 2006b)
	470, 550	(Carter et al., 2014)
Gemfibrozil	0.02-0.06	(Biel-Maeso et al., 2018a)
Glyburide	ND-0.02	(Biel-Maeso et al., 2018a)
Hydrochlorothiazide	0.38-1.20	(Biel-Maeso et al., 2018a)
Ibuprofen	<LOQ	(Biel-Maeso et al., 2018a)
	1-6	(Xu et al., 2009a)
Lamotrigine	2.09-5.35	(Grossberger et al., 2014)
Lincomycin	ND-0.03	(Grossberger et al., 2014)
Mefenamic acid	0.09-1.60	(Biel-Maeso et al., 2018a)
Metoprolol	0.26-9.61	(Grossberger et al., 2014)
Naproxen	1-12	(Xu et al., 2009a)

Table 2-1 continued.

TrOC	Concentration Range (ng/gDW)	Reference
Ornidazole	ND-0.47	(Biel-Maeso et al., 2018a)
Oxytetracycline	1.1-212	(Feng Chen et al., 2011)
Phenazone	ND-0.36	(Biel-Maeso et al., 2018a)
Primidone	<LOQ-3.3	(Feng Chen et al., 2011)
Propranolol	160, 210	(Carter et al., 2014)
Salicylic acid	1.4-10.7	(Feng Chen et al., 2011)
Sildenafil	1.24-9.6	(Grossberger et al., 2014)
Sulfamethoxazole	17-502	(Chad A Kinney et al., 2006b)
	<LOQ, 10	(Carter et al., 2014)
	ND-0.25	(Biel-Maeso et al., 2018a)
	0.11-0.37	(Grossberger et al., 2014)
Sulfapyridine	0.23-0.48	(Grossberger et al., 2014)
Tetracycline	<LOQ-20	(Feng Chen et al., 2011)
Triclosan	9310, 50	(Carter et al., 2014)
	6-60	(Chad A Kinney et al., 2006b)
Trimethoprim	ND-0.04	(Biel-Maeso et al., 2018a)
	<LOQ-2.6	(Feng Chen et al., 2011)

Organic compound accumulation in soil and groundwater depends on various factors such as wastewater treatment processes in-place, physio-chemical properties of TrOCs, and other conditions such as precipitation, temperature and sunlight (Biel-Maeso et al., 2018a). Soil properties such as its moisture and pH, influence TrOCs movement and their accumulation in soil, plants roots, stem, shoots, leaves, and fruits (Dodgen et al., 2015; Xiaoqin Wu et al., 2012; Xiaoqin Wu et al., 2013; Xiaoqin Wu et al., 2014). Weiping Chen et al. (2013) observed that some TrOCs with low K_d values accumulated at the soil surface and after irrigation, some TrOCs were degraded, leached to deeper depths, and volatilized. Most studies in literature are conducted either by spiking a known concentration of TrOCs in soil (Carter et al., 2014; González-Naranjo et al., 2013; Revitt et al., 2015) or conducted on fields irrigated with reclaimed water with fortified reclaimed water (Feng Chen et al., 2011; Grossberger et al., 2014; Chad A. Kinney et al., 2006a). However, due to the

complexity of conducting experiments at field-scale, a limited number of studies which focus on occurrence and transport of multiple TrOCs have been published (Biel-Maeso et al., 2018b; Bondarenko et al., 2012; Christou et al., 2017; Gottschall et al., 2012; Jayampathi et al., 2019; Karnjanapiboonwong et al., 2011; Martínez-Piernas et al., 2019; Min Pan and Chu, 2017; Min Pan et al., 2014; Xiaoqin Wu et al., 2014). Fewer publications emphasize fields irrigated with reclaimed wastewater for more than one growing season (Feng Chen et al., 2011; Weiping Chen et al., 2013; Dalkmann et al., 2012; Ternes et al., 2007; Xu et al., 2010). Therefore, there is a need to conduct more field-scale studies and collect data to improve estimation for the human health risk associated with these TrOCs.

2.3 TrOC translocation into plants

When reclaimed water is used for irrigation in an agricultural field, there is potential for TrOCs present in reclaimed water to translocate into the plant. To understand the translocation of these TrOCs, researchers have conducted a) hydroponic studies b) greenhouse studies with plants irrigated with spiked known TrOCs concentration c) greenhouse studies using reclaimed water used as irrigation source d) field-scale studies with either spiked TrOC concentration or reclaimed water as irrigation source. These studies are summarized in Table 2-2.

Table 2-2 TrOCs in plants when a known concentration of TrOCs were spiked in water, hydroponic, field-scale, and greenhouse studies.

TrOC	Type of Study	Plants	Concentration (ng/gDW)	References
Acetaminophen	Hydroponics	Iceberg lettuce, Spinach	ND, ND	(Xiaoqin Wu et al., 2012)
Amitriptyline	Greenhouse	Strawberry, lettuce	<LOQ-4.51, <LOQ-2.94	(Hyland et al., 2015)
	Hydroponics	Spinach	350-35000	(Nason et al., 2019)
Atenolol	Hydroponics	Iceberg lettuce, Spinach	ND, 1.1	(Xiaoqin Wu et al., 2012)
Atorvastatin	Hydroponics	Iceberg lettuce, Spinach	1.6, 2.3	(Xiaoqin Wu et al., 2012)
Bezafibrate	Greenhouse	Cucumber, tomato	19	(Goldstein et al., 2014)
	Hydroponics	Iceberg lettuce, Spinach	3.2, 1.8	(Xiaoqin Wu et al., 2012)
		Celery, carrot	0.80,1.8	(Xiaoqin Wu et al., 2014)
Caffeine	Field-scale	Cucumber, tomato	0.1-7, 0.1-1.5	(Goldstein et al., 2014)
	Greenhouse	Tomato	2	(Martínez-Piernas et al., 2019)
Carbamazepine	Hydroponics	Iceberg lettuce, Spinach	28.7, 2.9	(Xiaoqin Wu et al., 2012)
		Cabbage, Wisconsin Fast plants	23, 107	(Herklotz et al., 2010)
	Field-scale	Spinach	150-20000	(Nason et al., 2019)
		Celery, lettuce, cabbage, spinach, carrot, cucumber, bell pepper, tomato	0.4, 1.4, 0.18, 0.09, 0.21, 0.51, 0.35, 0.19	(Xiaoqin Wu et al., 2014)
Greenhouse	Strawberry, lettuce	<LOQ-15.11, <LOQ-265	(Hyland et al., 2015)	
	Cucumber, tomato	0.1-42, 0.75-1.5	(Goldstein et al., 2014)	
	Ryegrass, radish leaf, radish bulb	30000, 45000, 8000	(Carter et al., 2014)	
Clofibric acid	Greenhouse	Cucumber	3	(Goldstein et al., 2014)
DEET	Hydroponics	Iceberg lettuce, Spinach	2.8, ND	(Xiaoqin Wu et al., 2012)
Diazepam	Hydroponics	Iceberg lettuce, Spinach	17.8, ND	(Xiaoqin Wu et al., 2012)

Table 2-2 continued.

TrOC	Type of Study	Plants	Concentration (ng/gDW)	References
Diclofenac	Hydroponics	Iceberg lettuce, Spinach	ND, ND	(Xiaoqin Wu et al., 2012)
	Greenhouse	Ryegrass, radish leaf, radish bulb	300, 800, 400	(Carter et al., 2014)
Dilantin	Hydroponics	Iceberg lettuce, Spinach	9.2, 2.1	(Xiaoqin Wu et al., 2012)
	Field-scale	Celery, lettuce, cabbage, spinach, carrot, cucumber	0.43, 0.66, ND, 0.27, 0.30, ND	(Xiaoqin Wu et al., 2014)
Diphenhydramine	Greenhouse	Strawberry, lettuce	<LOQ-56, <LOQ-61	(Hyland et al., 2015)
	Hydroponics	Iceberg lettuce, Spinach	21.6, 34.0	(Xiaoqin Wu et al., 2012)
Fluoxetine		Spinach	10000	(Nason et al., 2019)
	Greenhouse	Ryegrass, radish leaf, radish bulb	50, 50, 150	(Carter et al., 2014)
Gemfibrozil	Hydroponics	Iceberg lettuce, Spinach	0.2, 0.2	(Xiaoqin Wu et al., 2012)
	Greenhouse	Cucumber	5	(Goldstein et al., 2014)
Ibuprofen	Hydroponics	Iceberg lettuce, Spinach	ND, ND	(Xiaoqin Wu et al., 2012)
	Greenhouse	Cucumber, tomato	0-3, 0.5-0.75	(Goldstein et al., 2014)
Ketoprofen	Greenhouse	Cucumber	10	(Goldstein et al., 2014)
Lamotrigine	Greenhouse	Cucumber	15	(Goldstein et al., 2014)
	Hydroponics	Spinach	10-10000	(Nason et al., 2019)
Meprobamate	Hydroponics	Iceberg lettuce, Spinach	5.0, 0.9	(Xiaoqin Wu et al., 2012)
	Field-scale	Celery, cabbage, spinach	ND, 0.03, 0.03	(Xiaoqin Wu et al., 2014)
Metoprolol	Greenhouse	Cucumber, tomato	19, 0.6	(Goldstein et al., 2014)
Naproxen	Hydroponics	Iceberg lettuce, Spinach	ND, 0.04	(Xiaoqin Wu et al., 2012)
	Field-scale	cabbage, spinach, carrot, tomato, cucumber, bell pepper	0.26, ND, ND, 0.39	(Xiaoqin Wu et al., 2014)
	Greenhouse	Cucumber	3	(Goldstein et al., 2014)
Primidone	Hydroponics	Iceberg lettuce, Spinach	8.5, ND	(Xiaoqin Wu et al., 2012)
	Field-scale	Celery, lettuce, cabbage, cucumber	1, 1.8, 0.19, ND	(Xiaoqin Wu et al., 2014)

Table 2-2 continued.

TrOC	Type of Study	Plants	Concentration (ng/gDW)	References
Propranolol	Greenhouse	Ryegrass, radish leaf, radish bulb	2400, 250, 250	(Carter et al., 2014)
Salbutamol	Hydroponics	Cabbage, Wisconsin Fast Plants	13, 82	(Herklotz et al., 2010)
Sildenafil	Greenhouse	Cucumber, tomato	20, 0.1-0.2	(Goldstein et al., 2014)
Sulfamethoxazole	Hydroponics	Iceberg lettuce, Spinach	ND, ND	(Xiaoqin Wu et al., 2012)
		Cabbage, Wisconsin Fast Plants	24, 441	(Herklotz et al., 2010)
	Greenhouse	Strawberry, lettuce	<LOQ-17, <LOQ-33	(Hyland et al., 2015)
Triclocarban	Hydroponics	Iceberg lettuce, Spinach	0.3, 2.5	(Xiaoqin Wu et al., 2012)
	Greenhouse	Strawberry, lettuce	<LOQ-0.8, <LOQ-62	(Hyland et al., 2015)
Triclosan	Hydroponics	Iceberg lettuce, Spinach	ND, ND	(Xiaoqin Wu et al., 2012)
	Field-Scale	Carrot	1.3	(Xiaoqin Wu et al., 2014)
	Greenhouse	Ryegrass, radish leaf, radish bulb	2000, 1000, 1250	(Carter et al., 2014)
Trimethoprim	Hydroponics	Iceberg lettuce, Spinach	1.1, 1.1	(Xiaoqin Wu et al., 2012)
		Cabbage, Wisconsin Fast Plants	13, 180	(Herklotz et al., 2010)
Tris (2-chloroethyl) phosphate	Greenhouse	Strawberry, lettuce	<LOQ-371, 14-4206	(Hyland et al., 2015)
Tris (1-chloro-2-propyl)	Greenhouse	Strawberry, lettuce	<LOQ-1042, <LOQ-27-4657	(Hyland et al., 2015)
Tris (1,3-dichloro-2-propyl)-phosphate	Greenhouse	Strawberry, lettuce	<LOQ-428, 110-426	(Hyland et al., 2015)

For hydroponic studies, an increase in dose of TrOCs, generally results in increased uptake by the studied plants. Concentrations of TrOCs in roots were generally higher than the leaves and fruits. TrOCs in the plants at greenhouse/field scale have typically <1000 µg/gDW. This concentration is approximately three orders of magnitude less than the

therapeutic dose for a compound consumed by the livestock. Thus, the health risk for livestock feeding on these crops is likely to be minimal (Carter et al., 2014; Xiaoqin Wu et al., 2015).

Neutral compounds in soil are accumulated in plants more than ionized compounds (Goldstein et al., 2014; Xiaoqin Wu et al., 2013). However, other ionic compounds can accumulate in leaf tissues (Hyland et al., 2015). Also, soil organic carbon content interacts with TrOCs, thus both cationic and anionic compounds tend to remain in the soil and have less translocation in plants (Blaine et al., 2014). Overall, the soil and roots of the plant act as a barrier, while compound degradability, sorption, organic content reduce translocation of various TrOCs in plants.

2.4 TrOCs in surface water

TrOCs are present in reclaimed water due to incomplete removal by wastewater treatment plants. Wastewater treatment plants release their treated effluent to rivers, streams, or used as reclaimed water for irrigation and sometimes can be used for groundwater aquifer replenishment. When TrOCs are released to rivers/streams, their fate depends on volatilization, biological and photodegradation, partitioning of compounds to sediments, and transformation to other byproducts (Blair et al., 2013; Jin-Lin Liu and Wong, 2013).

One of the most comprehensive TrOC monitoring studies was conducted from 1999-2000 where 139 U.S. streams were analyzed for the presence of 95 organic wastewater contaminants (Kolpin et al., 2002). At least one or more contaminant was detected in 80% of the U.S. streams at concentrations less than 1 $\mu\text{g/L}$ (Kolpin et al., 2002). Only two exceeded maximum contaminant levels, for which maximum contaminant levels have been

regulated (0.2 $\mu\text{g/L}$ and 6.0 $\mu\text{g/L}$ for benzo[*a*]pyrene and bis(2-ethylhexyl)phthalate) (Kolpin et al., 2002).

In another study, the Detroit River was sampled for carbamazepine, cotinine, and atrazine, which were at low ng/L concentrations (Hua et al., 2006). Benzophenone, caffeine, DEET, meprobamate, sucralose, and TCPP were in both Colorado River and Sacramento River; sucralose was at 47 ng/L and 620 ng/L in Sacramento River and Colorado River respectively (Anumol et al., 2013). Four southern sites of Michigan Lake were sampled for TrOCs. Acetaminophen, caffeine, carbamazepine, cotinine, gemfibrozil, ibuprofen, lincomycin, naproxen, paraxanthine, 1,7-dimethylxanthine, sulfadimethoxine, sulfamethazine, sulfamethoxazole, sulfathiazole, triclocarban, trimethoprim, and tylosin were present at low ng/L levels (0.92 ng/L to 46.2 ng/L) (Ferguson et al., 2013). In Australia, 73 river sites were sampled where 42 TrOCs were in 92% of the samples. The most commonly detected compounds were acetaminophen, caffeine, carbamazepine, paracetamol, salicylic acid and TCP with maximum concentrations ranging from 184 to 7150 ng/L (Scott et al., 2014). Overall, TrOCs are present in surface water at varying concentrations worldwide.

2.5 TrOCs in sediments

There have been monitoring studies conducted to determine the fate of various TrOCs in sediments because sediments are a TrOC sink and TrOCs can be released back in surface water after environmental changes such as pH and salinity (Liang et al., 2013). TrOC accumulation in sediments can also affect marine plants and benthic life (John L Wilkinson et al., 2018). Over 200 TrOCs were investigated in Great Basin sediments and 28 of them

(i.e., aromatic hydrocarbons, hormones, and fragrances) were at quantifiable amounts ranging from 1.75 ng/g (diphenhydramine) to 20800 ng/g (fluoranthene) (Elliott et al., 2017). Pharmaceuticals, illicit drugs, perfluorinated compounds and plasticizers were investigated in three London rivers sediments that received effluent from five wastewater treatment plants. Plasticizers, perfluorinated compounds, benzoylecgonine and diclofenac were major compounds detected in the river sediments (John L Wilkinson et al., 2018). There are many other monitoring studies that quantified the TrOCs in sediments of rivers/streams/lakes (Blair et al., 2013; Gaw et al., 2014; Jiehong Guo et al., 2016; Kiesling et al., 2019; Kathy E Lee et al., 2015a; Nilsen et al., 2014; M. M. Schultz et al., 2010b; John Wilkinson et al., 2017), however there are limited or no information on TrOC accumulation in sediments of terminal lakes. Factors that influence the TrOC accumulation in sediments are the vicinity of wastewater treatment outfalls, treatment processes at the wastewater treatment plants, low or high dilution of effluent with river (Gaw et al., 2014). TrOC concentration in sediments decreased with increased distance from effluent outfalls (John L Wilkinson et al., 2018), however the opposite trend was observed by M. M. Schultz et al. (2010b).

2.6 Potential human health risks of TrOCs

It is important to understand the human and animal health risks associated with different TrOCs present in the environment. Many reports have shown some adverse ecotoxicological effects of some TrOCs at relevant concentrations (Vasquez et al., 2014; Xiaoqin Wu et al., 2014). These TrOCs can have possible health risks such as reproductive damage, toxicity, endocrine disruptive effects and antibiotic resistance in humans and other

organisms (Wancen Liu et al., 2020). However, at trace concentrations, some contaminants may not be damaging to the natural environment (Xu et al., 2008).

The potential intake of TrOCs into crops represents a dietary intake exposure pathway for humans and livestock. The human risk from dietary intake has been predicted to be trivial for individual TrOCs, given that the concentrations are too low to be impactful (Carter et al., 2014; Xiaoqin Wu et al., 2013). Various plant uptake models for TrOCs have been explored over the years with the focus on the octanol–water partition coefficient (K_{ow}) to determine the partitioning of compounds between soil-water-plant systems (Blaine et al., 2014; Goldstein et al., 2014; Hyland et al., 2015; Zhaoyang Liu et al., 2017).

The capability of a plant to translocate TrOCs from soil can be estimated using the bioconcentration factor (BCF), the ratio of the concentration of TrOCs in the plant to the concentration of TrOCs in the soil (dry weight). The amount of human exposure can be calculated as:

$$\text{Amount of human exposure} = C \times D \times W \times T \quad \text{Equation 2-1}$$

where C is the concentration of TrOCs in the edible plant (ng/g wet weight), D is the average daily consumption of edible plant (g wet weight/kg body weight day), W is the weight (kg) of the person ingesting the edible plant (ideally consider 70 kg for adults), and T is the contact time (day) (Min Pan et al., 2014). One of the studies used a toxicological concern (TCC) approach to estimate the health risk based on ingestion of root vegetables irrigated with wastewater (Malchi et al., 2014). According to their results, lamotrigine's TCC value can be exceeded for a child by regular consumption of 1/2 a carrot, thus

indicating that some pharmaceuticals can accumulate at concentrations of concern (Malchi et al., 2014). However, another study showed that consumptive levels of antibiotics is less than the therapeutic dose of that antibiotics (Min Pan et al., 2014). However, antibiotics and other TrOCs in plant tissues could pose antibiotic resistance and unknown chronic effects to humans and animals by consumption of such plants (Franklin et al., 2015).

2.7 Ecotoxicity of TrOCs

Studies indicate that some of TrOCs are persistent in surface water (primidone and sucralose) and could pose harmful effects to aquatic life (Ferguson et al., 2013). One of the study found that anticonvulsants, anti-inflammatory and β -blockers were identified below 10 ng/g in fish in Spain (Huerta et al., 2018; Valdés et al., 2016) which can impact their reproduction cycle. Another study was conducted to determine the combined effect of exposure to atenolol, bezafibrate, carbamazepine, cyclophosphamide, ciprofloxacin, furosemide, hydrochlorothiazide, ibuprofen, lincomycin, ofloxacin, ranitidine, salbutamol, and sulfamethoxazole. This mixture hindered human embryonic cell HEK293 growth, with a 30% decline in cell proliferation. Overall this mixture of pharmaceuticals at 100 ng/L could impact the morphology and physiology of the cells and could also be a potential influencer on aquatic life (Pomati et al., 2006). More studies have been conducted with a mixture of various TrOCs to assess their impact on endocrine receptor systems of two Australian fish i.e. rainbowfish (*Melanotaenia fluviatilis*) and mosquitofish (*Gambusia holbrooki*) and results showed that the risk is low for endocrine disruptions for these two species (Scott et al., 2017). Other studies focused on the bioconcentration factors of various TrOCs in rainbow trout (Lahti et al., 2011), freshwater shrimp and, the water boatman (Meredith-Williams et al., 2012) and others fish species (Barreto et al., 2020) and generally

bioconcentration of pharmaceuticals was low for some fish species but it could be more depending on varying factors such as type of species, metabolic activity of the fish, type and concentration of TrOCs. Further work is required to examine the uptake of different types of TrOCs by a wider range of aquatic species and estimating the ecotoxicity levels.

2.8 Terminal Lakes

Terminal lakes (TLs) receive water from surface runoff and lose water only to evaporation and slow groundwater infiltration. In the United States, TLs majorly reside in the western U.S. as compared to the eastern U.S. due to their climatic conditions. Major TLs in the western U.S. are Great Salt Lake, Salton Sea, Lahontan Basin, Mono Lake and many more (Joe et al., 2014). These lakes are an important habitat to water birds and migratory birds to feed on shrimp and other aquatic life (Joe et al., 2014; Wurtsbaugh et al., 2017). Similarly, TLs are also enjoyed by the public for swimming, hunting, boating, fishing and bird watching activities (Wurtsbaugh et al., 2017). Every TL has distinct physiochemical properties. For example Walker Lake surface water temperature varies from 5 to 25°C and has anions concentrations of: chloride (115mM), carbonate (20mM) and sulfate (40mM) (Berelson et al., 2008). Sediments of Walker Lake are fine grained with 50% clays and silts, and also contains 2-3% of organic carbon (Berelson et al., 2008). Mono Lake has salinity of 83 g/L with 60 feet of average depth, and total dissolved solids mainly consisting of a mixture of sulfate, carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and chloride salts at a pH ~10 (Joe et al., 2014). Pyramid lake, located in Paiute reserved area of Nevada, receives its water from the Truckee River; has salinity of 3.5 g/L and pH of 9.4 and is a home for Lahontan cutthroat trout (Joe et al., 2014; Wilkie et al., 1993).

The increasing water demand for municipal, agricultural and industrial practices has stressed the inflow water in TLs, making them susceptible to desiccation (Joe et al., 2014). Increased salinity impacts bird habitats and other aquatic species (Joe et al., 2014). One solution is to supplement inflow with reclaimed water. However, TLs, being a closed system, can bioaccumulate and biomagnify pollutants at higher concentrations than freshwater lakes (Williams, 2002). Reclaimed water (treated wastewater) contains various TrOCs at ng/L to $\mu\text{g/L}$ concentrations based on the scientific literature. Therefore, there is a potential to have TrOCs at higher concentration than freshwater lakes but there is currently little to no literature focused on this topic.

2.9 TrOC photodegradation

There are two types of photodegradation pathways in aqueous systems a) direct photolysis: if the absorption spectrum of the organic compound matches with the spectrum of the solar irradiance b) indirect photolysis involving photosensitizers (Mestre and Carvalho, 2019). Molecules that absorb photons and form reactive species are known as photosensitizers (e.g. natural organic matter (NOM)). Some photosensitizers can then react with another molecule to degrade them (Albaigés et al., 2016). Some reactive species are singlet oxygen ($^1\text{O}_2$), superoxide anion (O_2^-), organic peroxy radical, hydroxyl and carbonate radicals ($\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$), and the excited triplet states of chromophoric dissolved organic matter ($^3\text{CDOM}^*$) (Carena and Vione, 2020; Lam et al., 2003; McNeill and Canonica, 2016). CDOM is the most important photosensitizer (Lam et al., 2003) compared to others such as nitrates and nitrites etc (Bergheim et al., 2014), because on absorption of light by CDOM produces $^3\text{CDOM}^*$, $^1\text{O}_2$, and $\cdot\text{OH}$ (McNeill and Canonica, 2016). CDOM and DOM can also inhibit photodegradation of organic compounds by sunlight screening, shifting the

reactive species and quenching excited states of organic compounds (Carena and Vione, 2020; Niu et al., 2013; Jieqiong Wang et al., 2020a). Along with these reactive species, photodegradation depends on other factors such as functional groups on compound, pK_a , pH, solubility, water constituents (DOM, CO_3^{2-} etc.) and light absorption (visible light, UVA or UVB) etc. (Ahmad et al., 2016; Jieqiong Wang et al., 2020a).

2.9.1 Direct photolysis

Direct photolysis plays an important role in photodegrading TrOCs (Carena and Vione, 2020). Sometimes the maximum absorbance of the individual compound doesn't overlap with the solar spectrum and negligible photodegradation of that compound is observed. There are some organic compounds that degrade by direct photolysis such as triclosan (Lei Chen et al., 2018), sulfamethoxazole (Niu et al., 2013), mefenamic acid (Fatta-Kassinos et al., 2011) and some do not degrade by direct photolysis but need photosensitizers such as cimetidine (Boreen et al., 2003), primidone (Yingjie Liu et al., 2019), iomeprol and clofibric acid (Doll and Frimmel, 2003). A study was conducted where carbamazepine (CBZ) was exposed to 150 W Xe solar simulator and a MP UV lamp for an hour, and CBZ was removed 2% and 95% respectively (Avisar et al., 2013). Higher removal of CBZ was observed under MP UV lamp exposure because CBZ maximum absorbance aligned with the MP UV lamp wavelengths. Direct photolysis of CBZ in deionized water had at least 50% removal but only after long exposure in a solar simulator (15 to 39 hrs) (Doll and Frimmel, 2003; Matamoros et al., 2009).

2.9.2 Indirect photolysis influenced by DOM

Indirect photolysis involves photosensitizers that photodegrade TrOCs. DOM is a photosensitizing species (Challis et al., 2014; Luster et al., 2017). On absorption of

photons, DOM/CDOM produce $^3\text{CDOM}^*/^3\text{DOM}^*$, $\cdot\text{OH}$ and $^1\text{O}_2$ in presence of oxygen (Carena and Vione, 2020; McNeill and Canonica, 2016; Jieqiong Wang et al., 2020a). $^1\text{O}_2$ and $\cdot\text{OH}$ in the presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ produces $\text{CO}_3^{\cdot-}$, and nitrate (NO_3^-), nitrite (NO_2^-), and $\cdot\text{OH}$ (Carena and Vione, 2020). These reactive species further help in photodegradation of TrOCs. To understand the role of different water characteristics impact on the photodegradation of TrOCs in natural waters, varying concentration of different water characteristics (DOM, anions, pH etc.) has been studied.

One study with 10 μM neбиволол in seawater and freshwater under solar simulated conditions (1000 W Xenon with 290nm filters) demonstrated rate constants of $0.68 \pm 0.02 \text{ h}^{-1}$ and $0.44 \pm 0.03 \text{ h}^{-1}$ respectively (Jieqiong Wang et al., 2020a). In another study, carbamazepine (an epileptic drug) with low [C] of NOM had faster degradation compared to high [C] of NOM conditions because high [C] of NOM screened light (Doll and Frimmel, 2003). Low [C] promoting faster photodegradation was also supported by another study where 4 to 8 mgC/L of NOM increased the percent removal of carbamazepine from 11% to 24% (Luster et al., 2017). The faster degradation rates of carbamazepine in presence of low [C] of NOM could be due to the formation of photosensitizing species and a lack of light screening effects (Doll and Frimmel, 2003). Similarly, in presence of simulated sunlight, 10 mgC/L of NOM along with dissolved oxygen contributed in photodegradation of 0.23 μM primidone (Yingjie Liu et al., 2019). However, at 2.5 mgC/L of NOM, trimethoprim degradation was suppressed (Ji et al., 2016) and at 1 mgC/L of NOM, the rate constants for gemfibrozil and bezafibrate declined by 50.3% and 36.2% respectively (Kong et al., 2018). These conflicting results of TrOC photodegradation indicate that the role of

DOM is dependent on the TrOC and DOM concentrations where it can either promote or inhibit the photodegradation of TrOCs.

2.9.3 Indirect photolysis influenced by anions and pH

There are studies that tested the photodegradation rates of some pharmaceuticals in presence of anions such as chloride, bicarbonate and nitrate as they are naturally present in water or wastewater (Lei Chen et al., 2018). Bicarbonate ions at 1mM had a slightly accelerating effect on sulfamethoxazole degradation compared to higher concentrations of bicarbonate ions (Luo et al., 2019). Solar simulated photodegradation of sulfamethoxazole (SMX) in presence of NO_3^- (10 and 20 mg/L) and in solution of DOC (4.75 mg/L and 7.40 mg/L) had similar degradation rates, meaning that nitrate and DOC did not have a significant effect on degradation rate constants (Trovó et al., 2009). Along with anions, pH also plays an important role during photodegradation of organic compounds because protonation/deprotonation creates different molar absorptions spectra and photodegradation pathways (Young et al., 2014). For example, during photolysis of sulfamethoxazole, the pH was increased from 3 to 10 and the rate of degradation declined almost ten times (Niu et al., 2013). Further, the neutral form of sulfamethoxazole absorbs more light than the ionic form and thus is degraded faster (Niu et al., 2013). Similarly, acidic pH facilitated the photodegradation of trimethoprim (Ji et al., 2016) and lamotrigine (Young et al., 2014) but not for sarafloxacin (Fatta-Kassinos et al., 2011).

Other photodegradation studies has been conducted in synthetic water (spiked known concentration DOM, nitrate and bicarbonate to reciprocate natural water constituents concentration) (Hellauer et al., 2019; Lam and Mabury, 2005; Lam et al., 2003),

wastewater (Bahn Müller et al., 2014; Dong et al., 2015), seawater (Matamoros et al., 2009; Mead et al., 2014), and surface water (Batchu et al., 2014; Bonvin et al., 2013). These studies were conducted to understand the role of various water characteristics in photodegradation of TrOCs in natural waters. All these studies concluded that DOM, NO_3^- and HCO_3^- either contributed in increasing the rate of photodegradation of TrOCs or inhibited the photodegradation. Overall, the rate of photodegradation of TrOCs is dependent on concentration and type of DOM, type of TrOCs, pH, anions and the irradiation source (Batchu et al., 2014).

2.10 Knowledge gaps

There is limited or no research on the long-term fate of TrOCs from reclaimed water usage in an agricultural farm for over many years. The fate of TrOCs accumulation in TLs, their degradation, and the impact of long-term reclaimed water use on TLs in semi-arid regions is relatively unknown. This dissertation seeks to fill these knowledge gaps.

Chapter 3

**TRACE ORGANIC CONTAMINANTS IN FIELD-SCALE CULTIVATED
ALFALFA, SOIL, AND PORE WATER AFTER 10 YEARS OF IRRIGATION
WITH RECLAIMED WASTEWATER***

*Published: Priyamvada Sharma, Andrew Poustie, Paul Verburg, Krishna Pagilla, Yu Yang, David Hanigan, Trace organic contaminants in field-scale cultivated alfalfa, soil, and pore water after 10 years of irrigation with reclaimed wastewater, Science of The Total Environment, Volume 744, 2020, 140698, ISSN 0048-9697, <https://doi.org/10.1016/j.scitotenv.2020.140698>

Abstract

Several studies have assessed the presence of trace organic contaminants (TrOCs) in reclaimed wastewater and their uptake into crops but there are limited data from field-scale studies. In this research, the fate of 12 TrOCs in wastewater samples, 11 in plants and in soil pore water, and 10 in soil at an agricultural research farm was studied, which was irrigated with reclaimed wastewater for more than 10 years. First, the presence of the compounds in the primary, secondary, and treated effluent of a regional water reclamation facility which provides the irrigation water was examined. The agricultural field produced alfalfa, and the contaminants in the alfalfa, soil, and porewater was measured. Reclaimed wastewater contained 11 of 12 TrOCs, with concentrations ranging from 26 ± 9 ng/L (DEET) to 1539 ± 1899 ng/L (trimethoprim). Atrazine was not detected. Pore water collected during non-irrigating periods contained all analyzed TrOCs, from 3 ± 0.1 ng/L (diphenhydramine) to 343 ± 360 ng/L (primidone). TrOCs measured in pore water samples indicated that they may leach to shallow groundwater even when fields are not being irrigated. Soils from 0 to 60 cm contained nine TrOCs from below the reporting limit (fluoxetine) to 329 ng/g (carbamazepine). Atrazine was not detected. TrOC concentrations

decreased with increasing soil depth, except carbamazepine, which was more recalcitrant. Nine TrOCs were present in the shoots and leaves of alfalfa grown in the reclaimed wastewater irrigated plots, at concentrations ranging from <1 ng/g (diphenhydramine and fluoxetine) to 49 ng/g dry weight (carbamazepine). Atrazine and caffeine were not detected. A maximum of 14% of DEET was estimated from the reclaimed wastewater was accumulated in alfalfa. Overall, despite some accumulation of TrOCs in the soil, alfalfa uptake was limited, which results in low exposure to foraging animals.

3.1 Introduction

Approximately, 70% of worldwide freshwater withdrawals are currently used for agriculture (Calderón-Preciado et al., 2011) and water demand is expected to increase in the coming decades (WWAP, 2017). To combat water shortages, reclaimed wastewater has been used as an irrigation source for centuries (Calderón-Preciado et al., 2011; Feng Chen et al., 2011; Hyland et al., 2015; Nason et al., 2019; Xiaoqin Wu et al., 2012; Xiaoqin Wu et al., 2014; WWAP, 2017). Reclaimed wastewater contains trace organic contaminants (TrOCs) including pharmaceuticals, personal care products, endocrine disruptors, disinfection by-products, and other anthropogenic chemicals at the ng/L to µg/L levels because they are formed in the wastewater (e.g., disinfection by-products), directly released into the sewer (e.g., personal care products), or incompletely metabolized by humans and poorly removed by conventional wastewater treatment plants (e.g., pharmaceuticals) (Awfa et al., 2018; Feng Chen et al., 2011; Dodgen et al., 2015; Goldstein et al., 2014; Y. Carrie Guo and Krasner, 2009a; Chang-Gui Pan et al., 2016; Xiaoqin Wu et al., 2014; Jinwei Zhang et al., 2016). Some TrOCs are environmentally persistent and may have

profound environmental impacts (Daughton and Ternes, 1999; Ebele et al., 2017; Schaffer and Licha, 2015).

Soil and crops are exposed to TrOCs and other wastewater constituents upon irrigation with reclaimed wastewater (Dodgen et al., 2015; Ebele et al., 2017; Goldstein et al., 2014; Chad A. Kinney et al., 2006a; Xiaoqin Wu et al., 2012; Xiaoqin Wu et al., 2013; Xiaoqin Wu et al., 2014). TrOCs present in reclaimed water used for irrigation may also pollute groundwater (Weiping Chen et al., 2013; Haruta et al., 2008; Wright et al., 2012). Various field-scale studies found that TrOCs accumulate in the soil profile from 30 to 150 cm upon irrigation with reclaimed wastewater (Biel-Maeso et al., 2018a; Chad A. Kinney et al., 2006a; Xu et al., 2009a). Alfalfa has been shown in one study to accumulate 17 α -ethinylestradiol, trimethoprim, and sulfamethoxazole (Christou et al., 2016), and six of nine compounds measured in another (Calderón-Preciado et al., 2011).

The presence of TrOCs in reclaimed wastewater and their translocation and accumulation in(to) irrigated crops may pose a phytotoxicological risk (Herklotz et al., 2010), leading to decreased yields (Poustie et al., 2020), exposure to humans and livestock, or increase the proliferation of antibiotic resistance (Boxall et al., 2006). The human health risk associated with dietary intake of individual TrOCs present in produce has been predicted to be trivial (Carter et al., 2014; Xiaoqin Wu et al., 2013) but the sources of data for such risk assessments are typically garnered from studies utilizing hydroponic exposure (Herklotz et al., 2010; Nason et al., 2019; Tanoue et al., 2012), conducted in pots under well controlled conditions in greenhouses (Carter et al., 2014; Hyland et al., 2015; Revitt et al., 2015), and exposed to an individual, spiked TrOCs (González-Naranjo et al., 2013). Concentrations

of spiked TrOCs are not always representative of environmental conditions, with spiked concentrations ranging from the ng/L to mg/L range in greenhouse and hydroponic studies (Dodgen et al., 2015; Goldstein et al., 2014; Nason et al., 2019; Revitt et al., 2015; Chenxi Wu et al., 2010). These conditions are useful in understanding transport but poorly represent reclaimed wastewater irrigation at the field-scale and uptake of trace constituents by the plants.

Because of the difficulty and complexity of field conditions compared to greenhouse conditions, a limited number of studies which focus on occurrence and transport of multiple TrOCs at field-scale have been published over the last decade (Biel-Maeso et al., 2018b; Bondarenko et al., 2012; Christou et al., 2017; Gottschall et al., 2012; Jayampathi et al., 2019; Karnjanapiboonwong et al., 2011; Martínez-Piernas et al., 2019; Min Pan and Chu, 2017; Min Pan et al., 2014; Xiaoqin Wu et al., 2014). Even fewer publications focus on fields that have been irrigated with reclaimed wastewater for 10 or more years (Feng Chen et al., 2011; Weiping Chen et al., 2013; Dalkmann et al., 2012; Ternes et al., 2007; Xu et al., 2010). There is a need for a greater abundance of field-scale data to improve estimates of human and animal health risk associated with TrOCs.

To fill this gap, 12 TrOCs (i.e., atrazine, caffeine, carbamazepine, DEET, diphenhydramine, fluoxetine, ibuprofen, ketoprofen, meprobamate, primidone, sulfamethoxazole and trimethoprim) were quantified in reclaimed wastewater which has been used to irrigate an agricultural field for over a decade. Alfalfa, soil, and soil pore water was sampled from an experimental research farm irrigated with reclaimed wastewater. The compounds from the treatment facility were tracked through the soil and alfalfa and found

their wide distribution at low concentrations, including in soil pore water outside of the growing and irrigation season.

3.2 Materials and Methods

3.2.1 Chemicals and Reagents

Twelve compounds with a range of pKa values from -3.75 to 15.96, solubility from 18 mg/L to 8877 mg/L and log Kow values from -0.79 to 4.19 were selected to represent compounds having diverse physicochemical, environmental transport and degradation properties. These compounds were also selected because of their well-documented presence in treated wastewater effluent (Dickenson et al., 2011; Roback et al., 2018). Caffeine, carbamazepine, N, N-diethyl-meta-toluamide (DEET), diphenhydramine, fluoxetine, ibuprofen, ketoprofen, meprobamate, primidone, trimethoprim, atrazine-d5, caffeine-d3, carbamazepine-d10, diphenhydramine-d3, ibuprofen-d3, ketoprofen-d3, and meprobamate-d3 were purchased from Sigma-Aldrich (St. Louis, MO). Atrazine and fluoxetine-d5 were purchased from Cayman Chemicals (Ann Arbor, MI). Sulfamethoxazole was purchased from MP Biomedicals (Solon, OH). DEET-d10, primidone-d5, sulfamethoxazole-d4, and trimethoprim-d3 were purchased from Santa Cruz Biotechnology (Dallas, TX). Analytical standards and solvents used were $\geq 98\%$ purity. Methanol, methyl tertiary-butyl ether (MTBE), ultrapure water, 0.1% formic acid (v/v) in water and 0.1% formic acid (v/v) in acetonitrile were obtained from Thermo Fisher Scientific (Pittsburgh, PA). Ammonium acetate ($\geq 97\%$ purity) was obtained from VWR International, LLC (Solon, OH). Diatomaceous earth used as fill for accelerated solvent extraction (ASE) was acquired from Thermo Fisher Scientific (Memphis, TN).

3.2.2 Sample Collection

A regional water reclamation facility was sampled and has traveling screens, vortex grit chambers, primary sedimentation tanks, aeration tanks, secondary sedimentation tanks, nitrification and denitrification towers, post aeration tanks, dual media filters, and a chlorine contactor. The disinfected reclaimed wastewater is pumped directly to the University of Nevada, Reno Main Station Field Lab (MSFL), which is adjacent (<1 mi) to the reclamation facility and has been irrigated with reclaimed water for more than 10 years. MSFL is primarily used for growing alfalfa for onsite livestock production. Grab samples were collected from the effluent of the primary sedimentation tanks, secondary clarifiers, and the chlorine contactor of the reclamation facility from early-March 2018 to mid-April 2018 at approximately 10 AM on each sampling day, four times per month. Sampling was conducted from these unit processes to provide a comprehensive evaluation of TrOCs in the overall wastewater irrigation system. Lagrangian sampling was not conducted and therefore changes across samples from various unit processes may imperfectly represent removal. Grab samples were collected over one month rather than a composite sample over a single day to capture longer term variability at the expense of capturing diurnal variability. The collected wastewater/reclaimed wastewater samples were analyzed at UNR laboratory, and for one set of samples, analyzed by an external laboratory as validation of in-house instrumentation and methods. Both laboratories used solid phase extraction (SPE) and liquid chromatography tandem mass spectroscopy (LC-MS/MS) for aqueous samples. Soil samples at depths of 0-20 cm, 20-40 cm and 40-60 cm were collected in April 2018 from the MSFL agricultural fields. Sampling depths were chosen to facilitate comparison with published literature (Dalkmann et al., 2014; Min Pan et al., 2014; Xiaoqin Wu et al.,

2014). Soil properties were measured by a commercial laboratory and the properties are provided in the Table A- 2. Alfalfa is the primary crop and was sampled in July and September 2018. Soil and alfalfa samples were stored at -20°C until analyzed. Soil and alfalfa samples were oven dried at 60°C for 48 hours to calculate the moisture content for water loss.

Six suction lysimeters were installed during the non-irrigating/non-growing season (October 2018) to measure residual analytes in the pore water at MSFL. Precipitation measurements were obtained from the Western Regional Climate Center WRCC (2020) and MSFL is approximately six miles from the weather station. Lysimeters were installed at the depth of 40 cm, separated by approximately 250 m. Lysimeters were installed during the non-irrigating periods to determine the potential for TrOC desorption and transport to deeper depths. In late March 2019, the lysimeters were removed from the field, prior to the start of irrigation, and therefore intentionally only captured infiltrated precipitation and soil pore water.

All samples were transported on ice to the University of Nevada, Reno. Water samples were stored at 4°C and soil and plant samples at -20°C , respectively, until analysis, which was typically conducted in less than 2 weeks.

3.2.3 Sample Extraction

The aqueous sample extraction and analytical method was adopted from Anumol et al. (2013). One liter of aqueous sample was collected in previously washed and combusted amber glass bottles. Lysimeter sample volumes were dependent on soil-moisture conditions and ranged from 150 to 450 mL. Each bottle contained 50 mg ascorbic acid to

quench residual chlorine and 1 g of sodium azide to arrest microbial activity. Samples were filtered through previously combusted 47 mm glass microfiber filters (GF/F, 0.7 μm pore size), stored in the dark at 4°C, and extracted within 14 days of sampling. 1 mL of a working stock of 12 isotopically labelled standards (100 $\mu\text{g/L}$ each) in water was spiked to the filtered samples to correct for extraction losses for a final concentration of 100 ng/L of each compound. These samples were extracted using an AutoTrace 280 automated SPE (Thermo Fisher, Sunnyvale, CA) with Oasis Hydrophilic Lipophilic Balance (HLB) cartridges (6 cc/200 mg, Waters Corporation, MA, USA). The detailed extraction and clean-up procedures are presented in Appendix A. Briefly, eluate from the SPE was evaporated to less than 500 μL using ultrahigh purity (UHP) nitrogen in a Biotage TurboVap LV and the final volume was adjusted to 1 mL with methanol. Final extracts were stored in darkness at -20°C until analyzed by LC-MS/MS.

The soil extraction method was adopted from Radjenović et al. (2009). Soil samples were stored at -20°C until analysis, typically less than two months. The soil samples were freeze dried and extracted with an ASE 200 (Thermo Fisher Scientific, Sunnyvale, CA) using 1:2 v/v methanol-water solvent solution. The ASE eluate was diluted with water to make a volume of 1000 mL and later cleaned up with SPE using HLB cartridges conditioned with water and methanol. The methanol eluates were evaporated to less than 1 mL. 100 $\mu\text{g/L}$ internal standards and methanol:water (25:75 v/v) solution were added to make the final sample volume of 1 mL. The isotopically labeled standards were spiked to the cleaned-up soil extracts due to the high mass required to be spiked to the soils before extraction. Because the labeled standards were spiked to the soil samples after extraction, no attempt

was made to account for extraction losses and therefore the concentrations in soil are likely to be conservatively low for some compounds. Analyte recoveries and reporting limits are provided in Table A-1 and A-5 respectively. All samples were analyzed by LC-MS/MS. The detailed extraction procedure and method recovery is described in Appendix A.

Alfalfa samples were rinsed with ultrapure water, lyophilized, cut, ground, and the resulting powder was sieved with a US Standard #60 sieve (250 μm). The sieved samples were spiked with isotopically labeled analytes, 20 mL MTBE was added, and the samples were sonicated, centrifuged, and decanted. The sonication, centrifugation, and decanting step was then repeated with acetonitrile. The decantate was cleaned up by SPE with HLB cartridges and eluted with methanol. Samples were first dried under nitrogen gas and then reconstituted with 1 mL methanol, filtered, and analyzed by LC-MS/MS.

3.2.4 Analytical Methods

Methodology from Anumol et al. (2013) was adapted to quantify TrOCs. LC was performed on the sample extracts with a Thermo Scientific Ultimate 3000 UPHLC with an Agilent RRHD ZORBAX Eclipse Plus reverse phase C18 column (2.1 \times 50 mm, and 1.8 μm). The mobile phase flowrate was 400 $\mu\text{L}/\text{min}$ and the column was maintained at 30°C. Ultrapure water with 0.1% formic acid (solvent A) and acetonitrile with 0.1% formic acid (solvent B) was used as a mobile phase solvent in ESI positive mode (ESI+). Solvent B was linearly increased to 20% at 3 min, 45% at 6 min, 65% at 8 min, 100% at 12.20 min and held until 14.9 min. A post-run of 5 min was added to allow the column to re-equilibrate before the next analysis resulting in a total run-time of 20 min.

The mobile phase for ESI negative mode (ESI-) was 5 mM ammonium acetate in ultrapure water (solvent C) at 80%, and 5 mM ammonium acetate in 10:90 (v/v) water: acetonitrile (solvent D) at 20%. Solvent D was linearly increased to 96% at 4.5 min, 100% at 5 min, and held until 7.8 min. A post-run of 2.2 min at 20% solvent D was added to allow the column to re-equilibrate before the next analysis, resulting in a total run-time of 10 min.

Mass spectrometry was performed on Thermo Scientific TSQ Vantage triple quadrupole mass spectrometer in MRM mode. Further information, including ion transitions, is provided in the Appendix A. Analytical check standards were run after every 10 samples and were within $\pm 20\%$ of their known concentration.

3.2.5 Calculations

3.2.5.1 TrOC accumulation in soil and alfalfa

The fraction of TrOCs which accumulated in alfalfa shoots and leaves in comparison to the mass of TrOCs irrigated to the field was determined using Equation 3-1.

$$\text{TrOC fraction in alfalfa leaves/shoots} = \left(\frac{\text{TrOC shoot or leaf concentration} \left(\frac{\text{ng}}{\text{g}} \text{DW} \right) * \text{Harvest} \left(\frac{\text{g}}{\text{m}^2 * \text{yr}} \text{DW} \right)}{\text{Aqueous TrOC concentration} \left(\frac{\text{ng}}{\text{L}} \right) * \text{Irrigation applied} \left(\frac{\text{L}}{\text{m}^2 * \text{yr}} \right)} \right) \text{Eq.3-1}$$

The alfalfa harvest was approximately 3.6 tons/acre-yr (or 807 g/m²-yr) dry weight and irrigation was 1200 L/m²-yr. Harvesting occurs at least twice per year and irrigation for a minimum of six months. Both harvest and irrigation in Eq. 3-1 represent growing season annualized values, and therefore are not divided by the number of harvests or duration between harvests, as those normalizations do not change the calculated fraction. The biomass sampled was collected at near peak biomass, immediately before a harvest, and therefore the accumulation presented likely represents the maximum accumulation. The

average reclaimed wastewater TrOC concentration measured across all sampling times was used.

Similarly, the TrOC's fraction in soil was estimated using Equation 3-2. Unlike the alfalfa mass balance, where alfalfa is regularly cut and removed from the field, soils are likely to accumulate TrOCs. Therefore, Eq. 3-2 provides an estimation of TrOC accumulation including carry over from periods before the sampling was conducted. The bulk soil density was $1400 \times 10^3 \text{ g/m}^3$ and the irrigation volume applied to the soil was $6000 \text{ L/m}^3\text{-yr}$. The soil moisture content was 12.9%.

$$\text{TrOC fraction in soil} = \left(\frac{\text{Sum of TrOC soil concentration at each depth} \left(\frac{\text{ng}}{\text{g}} DW \right) * \text{Wet soil density} \left(\frac{\text{g}}{\text{m}^3} \right) * \text{Percent solids (87.1)}}{\text{Aqueous TrOC concentration} \left(\frac{\text{ng}}{\text{L}} \right) * \text{Irrigation applied} \left(\frac{\text{L}}{\text{m}^3 * \text{yr}} \right)} \right) \text{Eq. 3}$$

– 2

3.3 Results and Discussion

3.3.1 Reclaimed wastewater

Aggregated data from sampling conducted on four days in 2018 is shown in Figure 3-1. 11 of the 12 compounds were detectable in all samples, including the treated effluent. Atrazine was only present above the reporting limit in the primary effluent. The concentrations of the individual compounds tended to decrease across the treatment processes among the four days sampled and ranged from 3 ± 0.04 to $77,838 \pm 11,166 \text{ ng/L}$ in the primary effluent, from 25 ± 10 to $3,557 \pm 3,558 \text{ ng/L}$ in secondary effluent, and from $26 \pm 9 \text{ ng/L}$ to $1,539 \pm 1,899 \text{ ng/L}$ in the treated effluent. The treated effluent concentrations align well with those reported in a meta-analysis of similar treatment processes Miège et al. (2009)

suggesting that this irrigation source water is broadly representative of that which is produced at other facilities.

More than 90% of caffeine, atrazine, DEET, diphenhydramine, and ibuprofen were removed across the treatment plant. The remaining compounds were removed from 13% to 72%, except carbamazepine, where a slight increase was observed across the plant, from 189 to 235 ng/L. This increase is generally small given the overall variability in the data (not statistically significant via t-test, $p > 0.05$) and likely indicates that the compound was not removed at all or reflects variability in the influent concentration with time (i.e., not Lagrangian sampling) rather than production or intermittent desorption in the treatment plant. The coefficients of variation for individual compounds concentration ranged from 15% (caffeine and ibuprofen) to 152% (trimethoprim) in the influent samples, indicating temporal variability in the month of sampling, despite samples being taken at approximately the same time of day. Overall, there was a significant amount of TrOCs present in the treated effluent. While some compounds were well removed by treatment, others persisted in the treated effluent.

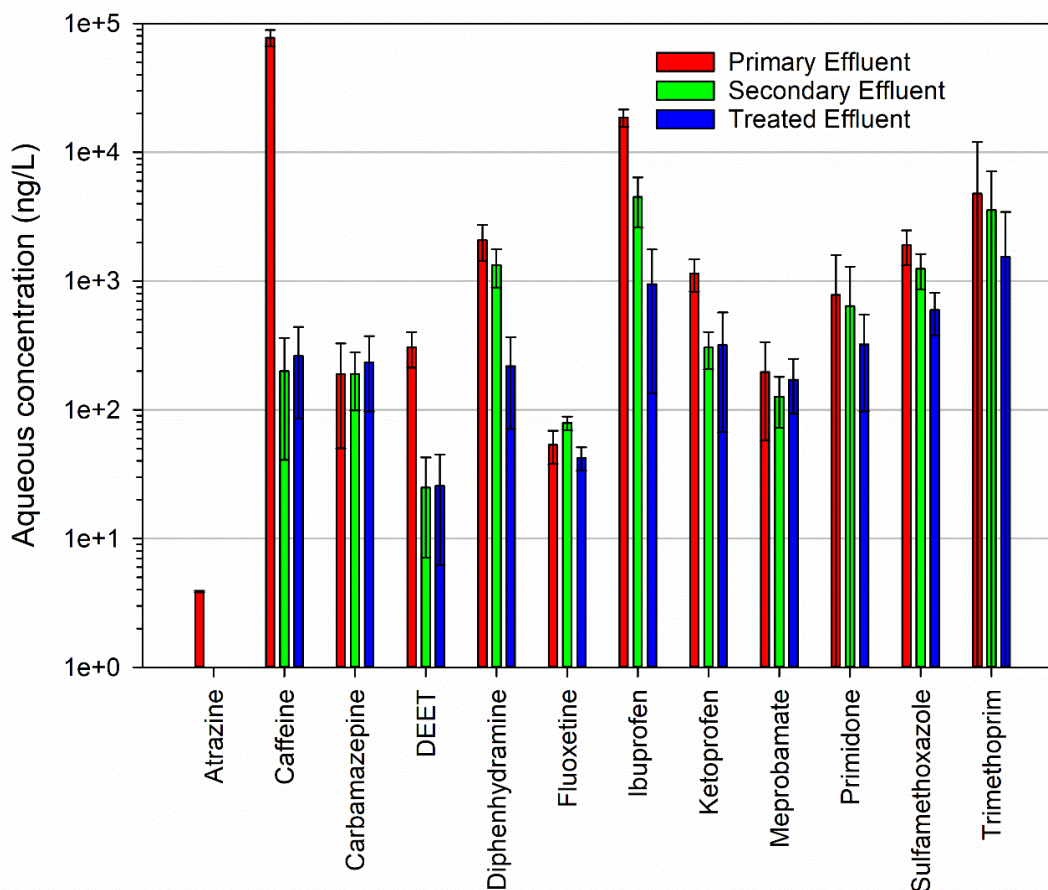


Figure 3-1 TrOC concentrations across the wastewater reclamation facility. Error bars are the standard deviation of four samples collected at 10 am across four days in the spring of 2018. No bar indicates the analyte was below the reporting limit. The treated effluent (reclaimed wastewater) was used for alfalfa irrigation.

3.3.2 Soil

Of 10 compounds quantified (ibuprofen and ketoprofen were not quantified in soil samples), eight were present above the reporting limits in soil samples at 0-20 cm and 40-60 cm, ranging from 0.03 ± 0.04 to 329 ± 560 ng/g dry soil (Figure 3-2). Atrazine has not been used recently at this field recently, which corresponds to the lack of atrazine detection in all soil samples. K_{ow} and solubility were poor descriptors of soil concentrations, likely owing to the complexity of field-scale retention and loss mechanisms.

The concentration of five compounds (carbamazepine, fluoxetine, primidone, sulfamethoxazole, and trimethoprim) declined $\geq 48\%$ from 0-20 cm to 20-40 cm. Diphenhydramine, DEET, and caffeine increased 7%, 155%, and 162%, respectively, from 0-20 cm to 20-40 cm. From 0-20 cm to 40-60 cm, the concentration of TrOCs decreased $\sim 10\%$ for all compounds except carbamazepine, which increased from 12 ± 2 ng/g to 329 ± 560 ng/g, and meprobamate, which was present at 5 ng/g at 40-60 cm but was not detected at shallower depths (Figure 3-2). It is possible that specific soil constituents (sandy, high organic matter) at this depth caused preferential sorption of carbamazepine (Chefetz et al., 2008; Durán-Álvarez et al., 2012; Revitt et al., 2015), and carbamazepine has been shown in at least one study to be present at greater concentrations at 30 to 40 cm than in topsoil (Durán-Álvarez et al., 2012). Notably, the measured concentration was highly variable among the triplicate samples at this depth which strongly implicates variability in the sampled soil or water flow. Other research has shown similar trends in concentration with soil depth, with much research observing decreasing concentrations with depth, and others observing increasing concentration of selected compounds with depth (Biel-Maeso et al., 2018a; Weiping Chen et al., 2013; Xu et al., 2009a). The concentration ranges measured in the studied soil samples align well with another study which used reclaimed wastewater for irrigation (Chad A. Kinney et al., 2006a).

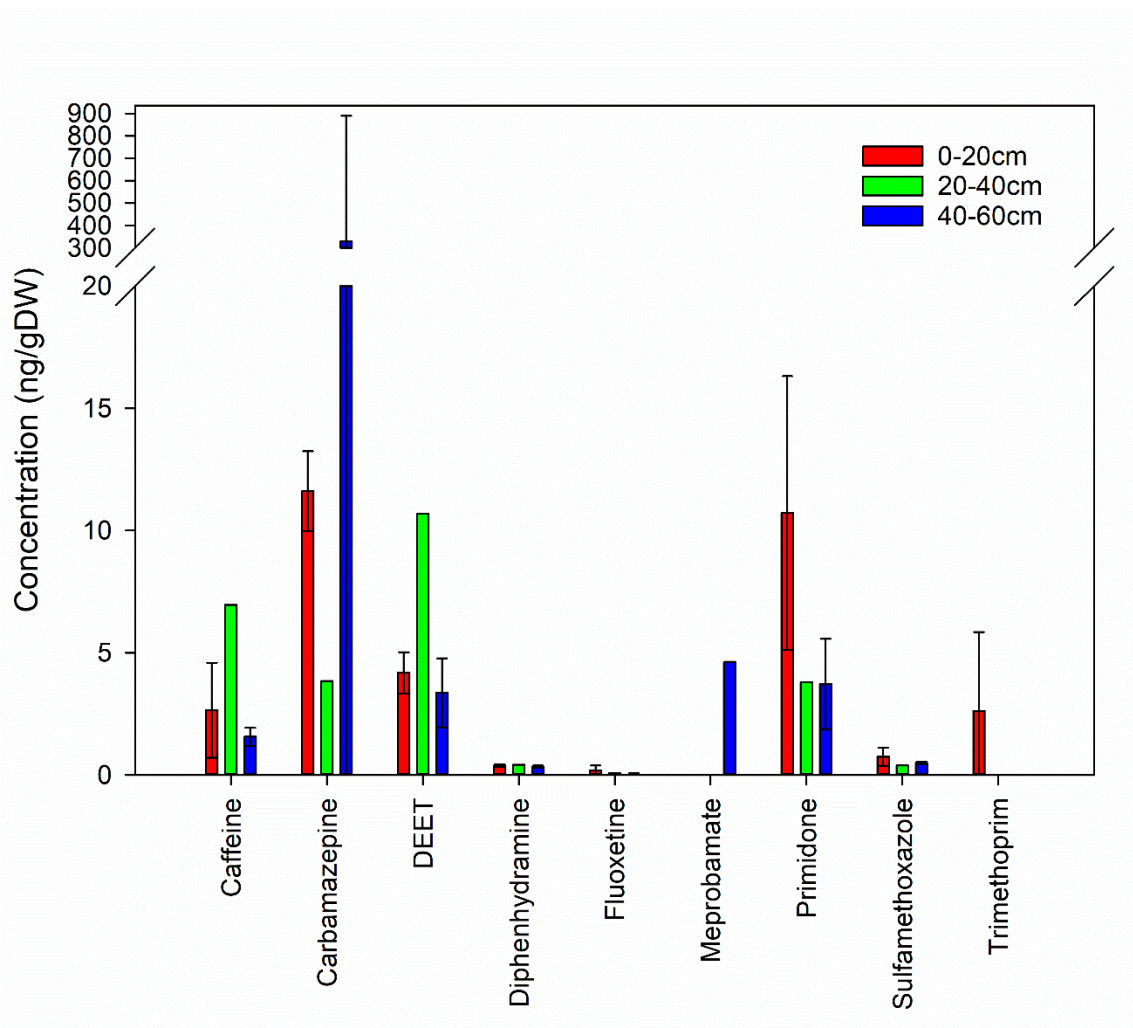


Figure 3-2 TrOC concentrations in MSFL soil at three depths. No bar indicates that the TrOC concentration was below the reporting limit. Error bars represent the standard deviation among triplicate samples.

3.3.3 Pore Water

Pore water in 2018 in six lysimeters were collected to determine the concentration of residual TrOCs in the soil pore water during the non-growing/non-irrigation period. Lysimeters were not installed during the irrigation period because they are difficult to protect from grazing animals, rodents, and farm equipment. Only three lysimeters collected pore water over the six months that the lysimeters were in the ground due to lack of precipitation (< 4.5 mm). Samples were withdrawn after one week of four separate

precipitation events in which ~4.5 mm of rain fell, or, after one event in which a total of 7.8 mm of rain fell. Results are presented in Figure 3-3.

The measured compounds were present at concentrations ranging from 3 ± 0.1 ng/L to $2,414 \pm 950$ ng/L in the soil pore water. Primidone and carbamazepine were present at concentrations ranging from 47 ± 11 ng/L to 343 ± 360 ng/L and 31 ± 9 ng/L to 78 ± 56 ng/L, respectively. These two compounds are highly recalcitrant and are strong indicators of the presence of wastewater and wastewater constituents (Gibson et al., 2010; Y. Carrie Guo and Krasner, 2009a) several months after application of wastewater was ceased. Primidone may have been present in the pore water at slightly greater concentrations than the reclaimed wastewater (treated effluent) because it was accumulated in the soil and pore water, but, more likely, the dates and times in which it was sampled at the treatment plant reflect periods in which primidone was present at somewhat lower concentrations than other times of the day or days of the year (i.e., variability in influent concentration).

Atrazine was present from 18 ± 4 to 276 ng/L despite having not been used for at least six years at the site and not being detectable in the reclaimed wastewater on the four days of sampling. However, the field site is in an urban area, and atrazine is likely a low-level environmental contaminant from use near the site. DEET was present at the greatest concentrations of all measured compounds, ranging from $1,897 \pm 923$ ng/L to $2,414 \pm 950$ ng/L in three lysimeters. Further investigation into the presence of DEET in the pore water samples revealed that field workers regularly apply insect repellent and that the sampling team was unaware that DEET was part of the sampling campaign, and applied insect repellent during sampling. Thus, the discussion of DEET occurrence in the lysimeters will be limited as it could be present in the lysimeters from the sampling team.

Excepting atrazine and DEET, the remaining compounds were present in the pore water from below the method reporting limit (MRL) to 63% of the reclaimed wastewater concentration. Caffeine, carbamazepine, diphenhydramine, fluoxetine, ibuprofen, meprobamate, primidone, sulfamethoxazole and trimethoprim were present from 1.4 ± 1 ng/L to 343 ± 359 ng/L, indicating that several of these anthropogenic chemicals are recalcitrant and remain in the soil pore water for several months and possibly longer, although at relatively low concentrations with respect to their concentration in reclaimed wastewater. Again, physicochemical descriptors were poorly correlated with concentration, similar to the findings of another field-scale study which concluded that models that are based on physicochemical descriptors are useful in ranking leachability, but poorly predict concentration (Xu et al., 2009a).

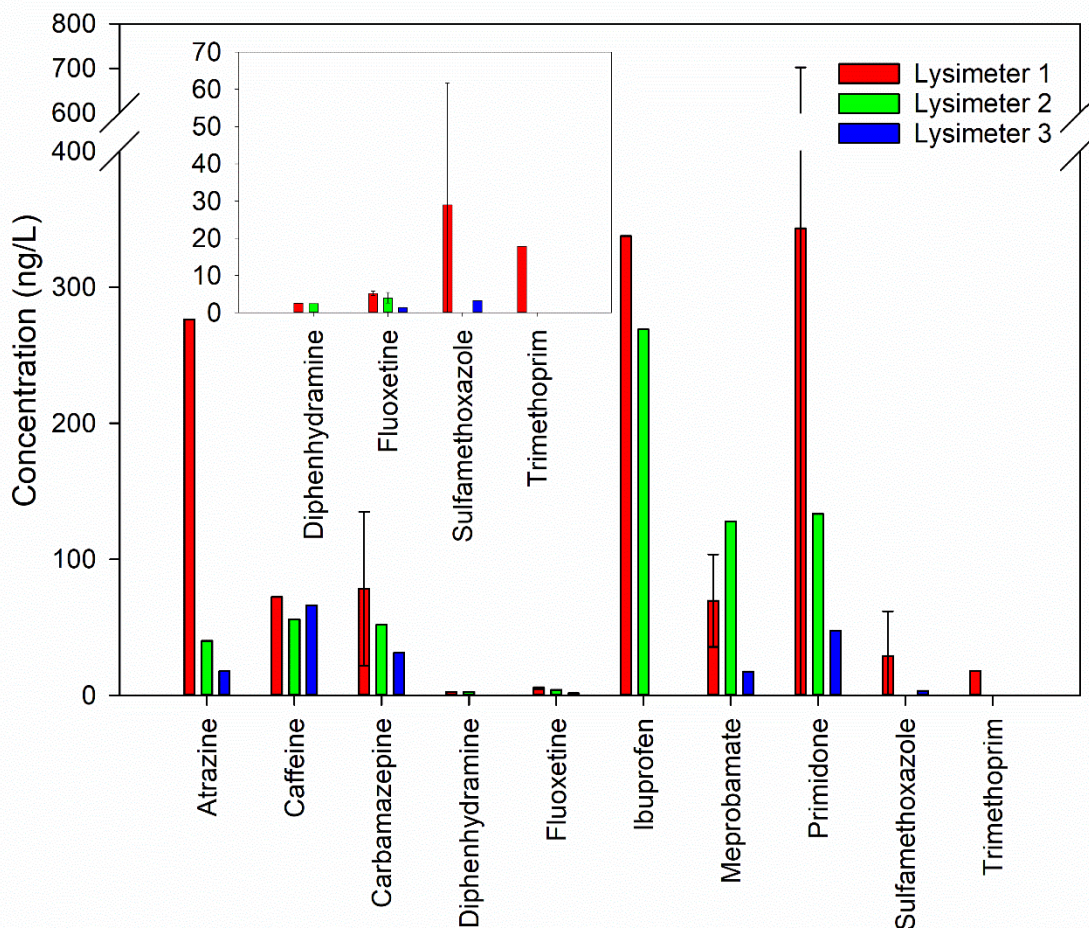


Figure 3-3 TrOCs in seven lysimeter samples from three lysimeters, sampled between October 2018 and April 2019. Lysimeter 1 is the mean of 3 sampling events, lysimeter 2, mean of 2 sampling events, and lysimeter 3, mean of 2 sampling events. The error bars are standard deviation of triplicate samples. No bar indicates below reporting limit.

3.3.4 Alfalfa

Nine TrOCs were present in the shoots and leaves of alfalfa at concentrations greater than the MRLs (Figure 3-4). Caffeine was not present above the MRL and atrazine was not quantified due to poor atrazine isotope recovery.

From the samples harvested in July, shoots tended to contain greater concentrations of neutral compounds than ionic compounds. Ionization of each compound (f_n) was calculated

based on the soil pH (7.5) and pKa of the compounds, listed in Appendix A. Carbamazepine (49 ng/g), DEET (1 ng/g), primidone (37 ng/g) and trimethoprim (21 ng/g) are primarily neutral at this pH and were all present above the reporting limit. Ionized compounds (diphenhydramine (0.4 ng/g), fluoxetine (0.4 ng/g) and ibuprofen (2 ng/g) tended to be present at lower concentrations. Sulfamethoxazole, which is ~90% ionized at this pH, was present at relatively high concentrations in the plant material overall (shoots = 15 ng/g, leaves = 13 ng/g) compared to other ionized compounds (<2 ng/g), which likely corresponds to the soil pH being near the pKa of sulfamethoxazole. Generally, neutral compounds are accumulated to a greater extent due to root membrane rejection of ionized species (Goldstein et al., 2014; Xiaoqin Wu et al., 2013) which agrees well with the general trend in this studied observation.

Leaves sampled in July also contained neutral compounds at greater concentrations (e.g., 49 ng/g carbamazepine, 1 ng/g DEET, 20 ng/g primidone, and 22 ng/g trimethoprim) than ionic compounds; diphenhydramine (1 ng/g), fluoxetine (1 ng/g), except again sulfamethoxazole (13 ng/g). The presence of trimethoprim at slightly higher concentration than sulfamethoxazole in both shoots and leaves is well supported by other studies of alfalfa (Christou et al., 2016), cabbage (Herklotz et al., 2010) and vegetables (Xiaoqin Wu et al., 2013). Overall, the concentration of TrOCs measured in shoots and leaves are similar (Figure 3-4).

In leaves harvested in September, TrOCs were present at lower concentrations than samples from July and ranged from 0.2 to 13 ng/g. Ionic compounds were present at ≤ 1 ng/g except ibuprofen (3 ng/g) and several neutral compounds were present at 2 ng/g (carbamazepine), 4 ng/g (DEET) and 13 ng/g (trimethoprim). Leaves sampled in

September had the same general trend; neutral compounds accumulated in leaves at higher concentration compared to ionic compounds. Ibuprofen was not present in leaves sampled in July but was present at relatively low concentrations (3 ng/g) in the leaves sampled in September. Enough shoots in September were not collected for extraction, and therefore only leaf concentrations were provided.

In all alfalfa samples caffeine was below the reporting limit but was present at low concentrations (2 to 7 ng/g) in the soil. Overall, several TrOCs were present at low concentrations in the alfalfa and accumulation of compounds in shoots and leaves tended to be greater for neutral compounds than ionic compounds.

Published greenhouse studies using reclaimed wastewater for irrigation observed TrOCs in soybean plants from 1 to 7 ng/g (Chenxi Wu et al., 2010), 1 to 18 ng/g in tomato plants (Martínez-Piernas et al., 2019), 0.05 µg/g to 40 µg/g in ryegrass and radish (Carter et al., 2014), 0.02 to 17 ng/g in apple tree leaves and alfalfa (Calderón-Preciado et al., 2011), and 0.01 to 4 ng/g in eight vegetables (Xiaoqin Wu et al., 2014).

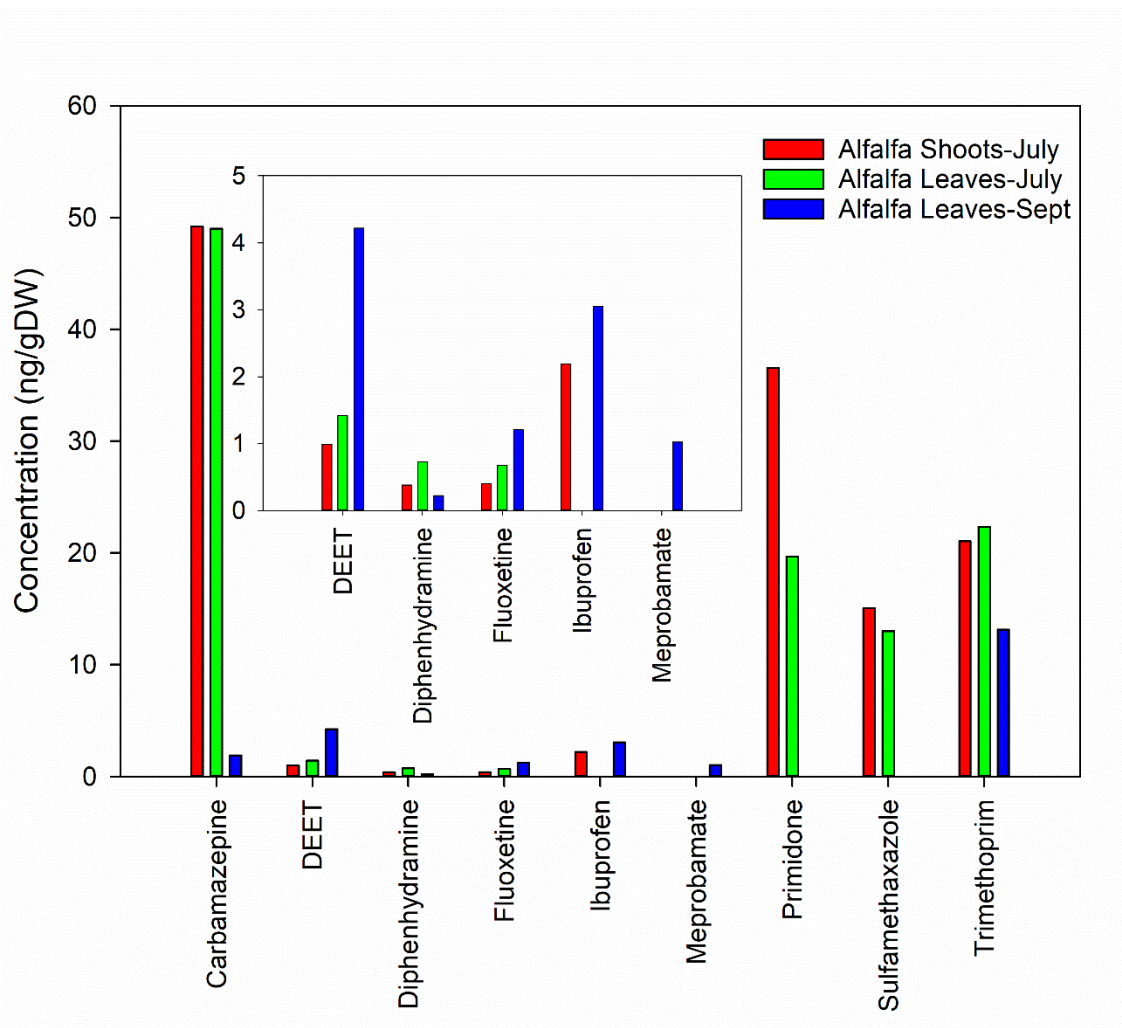


Figure 3-4 TrOC concentrations in alfalfa sampled in 2018 and irrigated with reclaimed wastewater from regional wastewater treatment plant.

3.3.5 Mass Balance

A mass balance was conducted using Eq. 3-1 and Eq. 3-2 to estimate the percent of applied compounds that were present in soil up to 60 cm deep, in the alfalfa shoots and leaves. The fractions of pharmaceuticals in soil, alfalfa shoots/leaves, and losses (applied but not present in samples) are provided in Table 3-1. Assumption was made that after one year, the soil would reach steady state and therefore one year was used as the irrigation period in Eq. 3-2.

Table 3-1 Distribution of analytes in soil, alfalfa shoots and leaves. Atrazine was present only in pore water samples and therefore is not included. Ketoprofen is not included because it was not measured in alfalfa, soil, or pore water.

TrOC	Total mass applied (mg/m ³)	Percent in soil	Percent in alfalfa shoots & leaves	Percent losses ²
Caffeine	1.8	893	<1	-793
Carbamazepine	1.6	68169	13	-68081
DEET	0.2	15989	14	-15903
Diphenhydramine	1.3	116	<1	-16
Fluoxetine	0.3	222	3	-19
Ibuprofen	5.7	NQ ¹	<1	NQ ¹
Meprobamate	0.8	0	2	98
Primidone	2.8	1113	10	-1022
Sulfamethoxazole	4.3	58	5	37
Trimethoprim	1.7	41	2	57

¹ NQ is not quantified

² Negative loss indicates accumulation in the field during periods before the irrigation application period assumed in Eq. 3-1 and 3-2.

DEET accumulation may be partially attributable to sources other than the reclaimed wastewater, such as application by field workers. Much more was present in the soil (41% to 68169%), but the soil has been irrigated with reclaimed wastewater for over a decade. This study's assessment does not capture accumulation from previous years, which results in greater than 100% recovery in the soil (i.e., the denominator is only the mass that was applied in a single growing season while the numerator may capture years of accumulation) and highlights that certain TrOCs may persist in the soil well beyond the irrigating season. Carbamazepine had the greatest accumulation in soil, and it is well known that it is highly persistent in the environment (Carter et al., 2014). $\geq 37\%$ of the three pharmaceuticals were lost (i.e., not present in either the crop or the measured soil), likely either to deeper soil depths, groundwater, or bio/environmentally degraded. Very little of the applied

compounds were accumulated in the alfalfa shoots and leaves (<1% to 14%), and DEET was accumulated to the greatest extent.

Cattle weigh approximately 690 kg (Ringwall, 2018) and consume 2.5% of their body weight of alfalfa (dry weight) per day (Selk, 2018). Thus, based on the presence and consumption of alfalfa, cattle will be exposed to a maximum of ~0.85 mg carbamazepine per day, or 0.05 mg/kg-day, compared to the human therapeutic dose of 11.4 mg/kg-day. This comparison of consumption and therapeutic dose for carbamazepine was presented because it was present at the greatest concentration in the alfalfa, but similar conclusions follow for all pharmaceuticals measured in this study. Therefore, there are likely to be minimal health impacts on livestock.

3.4 Conclusions

TrOCs in alfalfa cultivated at field-scale and irrigated with reclaimed wastewater for over a decade were measured. 12 TrOCs were tracked through the water reclamation facility, the soil, and the alfalfa plant. Atrazine was only detected in primary effluent samples and pore water (soil pore water) even though it has not been used at the field. Carbamazepine was generally present at higher concentrations than other measured compounds in soil and alfalfa. $\geq 41\%$ of the applied mass of caffeine, carbamazepine, DEET, diphenhydramine, fluoxetine, ibuprofen, meprobamate, primidone, sulfamethoxazole, and trimethoprim were estimated to be present in the soil. Accumulation of greater than 100% of the applied annual mass demonstrated accumulation over multiple growing seasons in the soil. <1% to 14% of the applied TrOC mass was present in the shoots and leaves of the alfalfa, which is harvested at least twice a year. The fractional accumulation of DEET was the greatest of the measured compounds. Based on calculations which compared therapeutic doses and

cattle exposure through foraging, minimal to no health impact was expected through ingestion of residual TrOCs derived in reclaimed wastewater irrigation. Future research may assess human health risk by modeling translocation through the food chain, although exposure will be lower than to the animal due to metabolism by the animal.

Chapter 4

**EVIDENCE OF LOW LEVELS OF TRACE ORGANIC CONTAMINANTS IN
TERMINAL LAKES***

Priyamvada Sharma and David Hanigan

*Submitted in April 2021 to Chemosphere Environmental Chemistry, Under Review

Abstract

Endorheic lakes (or terminal lakes, TLs) have no natural outlet other than evaporation and slow infiltration. Some TLs receive reclaimed wastewater which contains poorly removed trace organic contaminants (TrOCs). To determine if TLs accumulate TrOCs a preliminary assessment of the occurrence of ten TrOCs in three TLs receiving reclaimed wastewater and one TL which does not directly receive reclaimed wastewater were conducted. Five of ten TrOCs (carbamazepine, DEET, fluoxetine, primidone, and trimethoprim) were in all four TLs' surface waters (0.3 to 1109 ng/L), six (caffeine, carbamazepine, DEET, diphenhydramine, primidone and trimethoprim) were in sediment samples (0.1 to 77 ng/gDW) and in soil samples (0.1 to 137 ng/gDW). Concentrations of caffeine, carbamazepine, diphenhydramine, fluoxetine and meprobamate were significantly higher in TLs receiving wastewater from a secondary treatment plant compared to those TLs which received tertiary treated wastewater. Carbamazepine, fluoxetine, sulfamethoxazole, and trimethoprim were at concentrations greater than is typical of other U.S. freshwater lakes, but other TrOC concentrations were at lower concentrations than in other freshwater lakes. Conclusion can be made that some TrOCs may accumulate in TLs, but to a lesser extent than would be expected based on hydrology alone.

4.1 Introduction

Endorheic lakes (commonly known as terminal lakes (TLs)), are hydrologically closed basins common in arid and semi-arid environments (Moore, 2017). TLs receive water from surface water flow and precipitation and have only two outlets: evaporation and groundwater infiltration. In the U.S., TLs primarily reside in the western part of the U.S. (Larson, 2014). TLs are an important habitat to bird species such as white pelicans and eared grebe (Schrage, 2016; Sorensen et al., 2020) which feed on shrimp, fish and other aquatic life (Larson, 2014; Moore, 2017; Schrage, 2016). Similarly, TLs are also enjoyed by the public through swimming, hunting, boating, fishing and bird watching activities (Moore, 2017).

One of the major threats that TLs face is increasing salinity and total dissolved solids due to water diversion, reduced precipitation, and increased evaporation. Loss of lower food web species impacts the food chain of that lake (Baxter and Butler, 2020; Dickerson and Vinyard, 1999; Marioni, 2007) and stresses higher food web species such as Lahontan cutthroat trout (Dickerson and Vinyard, 1999; Sedinger et al., 2012). To reduce water stress on TLs, some TLs directly receive treated wastewater and all treated wastewater contains trace organic contaminants (TrOCs) (Sharma et al., 2020); pharmaceuticals and personal care products (PPCPs), per- and polyfluoroalkyl substances, endocrine-disruptors, or other organic synthetic compounds (Dodgen et al., 2015; Goldstein et al., 2014; Chang-Gui Pan et al., 2016; Xiaoqin Wu et al., 2014).

Exposure to TrOCs present in treated wastewater is known to proliferate antibiotic resistance, disrupt the endocrine system (e.g. reduce fertility, feminization of males, and

intersex phenomena) (Richardson et al., 2005) and cause mode of action driven effects in fish (e.g. consuming abnormality, predator abstention and courtship display) (Geyer et al., 2000; Kemper, 2008; Tanoue et al., 2015). TrOCs have varying environmental fate and transport processes such as biodegradation, sorption, photodegradation, volatilization, oxidation and hydrolysis, ultimately leading to their reduced aqueous concentrations (John Wilkinson et al., 2017; Yi et al., 2020). Some TrOCs bioaccumulate in aquatic animals (Richardson et al., 2005), plants and livestock (Geyer et al., 2000), which may lead to adverse effects such as impaired reproduction in fish (Brown et al., 2007; Kidd et al., 2007), or impact plant development (Carter et al., 2015; Hammad et al., 2018). Other TrOCs bio magnify, leading to multi-species effects (Sathishkumar et al., 2020).

Multiple published studies have examined the occurrence of TrOCs in streams, freshwater lakes and oceans/seas (Kolpin et al., 2002; Melissa M. Schultz et al., 2010a; Lu Yang et al., 2020; Shaoyuan Zhang et al., 2007). For example, caffeine, carbamazepine and primidone were present in a river influenced by wastewater at concentrations between 2 and 687 ng/L (Y. Carrie Guo and Krasner, 2009a), and, caffeine, metformin, sulfamethoxazole, and triclosan were frequently detected in surface water and sediments of Lake Michigan (Blair et al., 2013; Ferguson et al., 2013). Several other PPCPs were also present in marine sediments in the ng/gDW range (Elliott et al., 2017; Long et al., 2013).

While there is a significant body of research that has been conducted related to TrOCs in streams, freshwater lakes, and oceans/seas, no such literature related to TLs was available. Because TLs are important for the existence of multiple protected and unprotected species, it is important to understand the fate of TrOCs in TLs. It is believed that this is to be the

first assessment of TrOCs in TLs. Objectives of this study were to a) determine the concentrations of ten TrOCs in TLs influenced by reclaimed wastewater and compare their concentrations to a TL which was not influenced by wastewater, b) compare results with other U.S. lakes and sediments published in the literature and c) determine TrOCs in shore soils vs nearshore sediments at each TLs to investigate the impact of shoreline recreational activity.

4.2 Materials and Methods

4.2.1 Chemicals

Ten compounds were selected based on their frequent detections in wastewater treatment effluents. Caffeine (CAF), carbamazepine (CBZ), *N,N*-diethyl-meta-toluamide (DEET), diphenhydramine (DPH), fluoxetine (FLX), meprobamate (MPB), primidone (PMD), trimethoprim (TMP), atrazine-d₅, caffeine-d₃, carbamazepine-d₁₀, diphenhydramine-d₃, and meprobamate-d₃ were purchased from Sigma-Aldrich (St. Louis, MO). Atrazine (ATZ) and fluoxetine-d₅ were purchased from Cayman Chemicals (Ann Arbor, MI). Sulfamethoxazole (SMX) was obtained from MP Biomedicals (Solon, OH). DEET-d₁₀, primidone-d₅, sulfamethoxazole-d₄, and trimethoprim-d₃ were purchased from Santa Cruz Biotechnology (Dallas, TX). Methyl tertiary-butyl ether (MTBE), methanol, HPLC grade water, diatomaceous earth, 0.1% formic acid (v/v) in water and 0.1% formic acid (v/v) in acetonitrile were acquired from Thermo Fisher Scientific (Waltham, MA). All analytical solvents and standards were of $\geq 98\%$ pure except ammonium acetate, $\geq 97\%$, purchased from VWR International, LLC (Solon, OH).

4.2.2 Sample Collection

Four TLs surface water, their nearshore sediments and shoreline soils in the U.S. state of Nevada were sampled once in the Fall of 2018 and Spring of 2019. Three to four locations at each lake were chosen based on accessibility. TL1 TL2, and TL3 are influenced by reclaimed wastewater. One TL does not receive reclaimed wastewater (CTL). For each lake, sampling location A is at the mixing zone with the inflow, locations B, C, and D were along the length of the shoreline of the lake. ~20% of the collected samples were collected in triplicate.

Surface water samples were collected at least 2 m from the shore with a HDPE container attached to a pole. Samples were immediately transferred into a 1L amber glass bottles which had been washed, baked at 500°C for 3 hours, and preserved with 50 mg of ascorbic acid and 1 g of sodium azide.

Sediments were sampled with a stainless-steel hand auger from the lakebed, approximately 2 m from the shore, generally at a depth of ~10 cm. For sampling sites with more gravel which filled the hand auger, samples were collected at a depth >10 cm but less than 20 cm, where fine sediments were observed.

Surface soil samples (0-5 cm) were collected with a trowel. Soils were sampled from areas with minimal or no interaction with the lake water to determine the direct impact of human activity to the soil. The soil samples from TL1 to CTL were sampled from a location where the lake water does not interact with each TL's soil but is close to surface water/sediment sampling location of A, B, C & D for TL2, TL3 and CTL. Only a single soil sample at location A of TL1 was sampled as other soil areas were inaccessible at TL1.

All sampling containers or tools were rinsed with DI water three times before and between samplings to minimize contamination. The trowel and hand auger were also rinsed and wiped with a paper towel between samples. Samples were transferred on ice to the University of Nevada, Reno laboratories. Soil and sediment samples were stored at -20°C until analysis. Water samples were stored at 4°C and typically analyzed within 2 weeks.

4.2.3 TrOC Concentrations in U.S. Freshwater Lakes from Literature

To compare TrOCs concentrations in TLs with other U.S. lakes, published peer reviewed literature was searched using the keywords pharmaceuticals, TrOCs, lakes, streams, rivers, and lake sediments by Google Scholar. TrOC concentrations extracted from the literature are compiled in Table B-6 (Blair et al., 2013; Robert N Brent et al., 2001b; Elliott et al., 2017; Ferguson et al., 2013; Furlong, 2002; K.E. Lee et al., 2015b; Tierney et al., 1999; Shiru Wang et al., 2020b) and the data from this study is in Table B-7.

4.2.4 Description of Sampled Lakes

TL1: Relatively shallow with a ~ 2 m maximum depth, 4 km^2 of surface area, and dominated by peri-urban surface runoff. The lake also receives reclaimed wastewater from two wastewater treatment plants via outfalls, one has biological treatment with disinfection and the other has tertiary treatment processes (sand filtration). The biological and tertiary treatment plants have flow rates of $< 0.04 \text{ m}^3/\text{s}$ and discharges treated wastewater from 0.02 to $0.11 \text{ m}^3/\text{s}$ respectively. Samples were collected on March 29th, 2019. One surface water, sediment and soil sample were collected from the mixing zone where the wastewater treatment plant's effluent canal mixes with the lake (location A). Only one soil sample was collected because other soil sample locations were strongly influenced seasonally by lake

water and the lake is not regularly used for shore recreation. Overall, three surface water and sediment samples were collected at TL1.

TL2: Maximum depth of ~4 m with surface area of ~1 km² and receives water from a river which receives tertiary treated wastewater from a wastewater treatment plant. The river has an average annual flow rate of 11 m³/s. The wastewater treatment plant flow averages 0.22 m³/s. The plant consists of primary treatment, aerated biological treatment, filtration, and disinfection. Four surface water, sediment, and soil samples were collected on March 23rd, 2019. This TL has a moderate level of shore recreation (e.g., hunting).

TL3: ~91 m deep with surface area of 490 km² and receives water from a river which is influenced by reclaimed wastewater (tertiary treatment with sand filters). This treatment plant treats an average flow of 1.36 m³/s and discharges approximately 1.2 m³/s to the river. The river has an annual average flow rate of 23 m³/s. Four surface water, sediment and soil samples were collected on November 29th, 2018. This TL has a high level of shore recreation (e.g., bathing, fishing).

CTL: ~152 m deep with 130 km² of surface area. Receives water from a river which is not impacted by reclaimed wastewater. Three surface water, sediment and soil samples were collected on May 8th, 2019. Annual average flow of the river is 4.6 m³/s, some of which is diverted for irrigation prior to the lake.

WW effluent samples were inaccessible during sampling the sampling campaign. The names and locations of the lakes are intentionally concealed.

4.2.5 Sample Extraction and Analysis

The aqueous, soil and sediment samples were extracted and analyzed using methods described previously (Sharma et al., 2020). Briefly, aqueous samples were filtered with a 0.7 μm microfiber glass filters and 10 isotopically labeled standards were spiked to make the sample concentration equal to 100 ng/L of each labeled standard. Oasis Hydrophilic Lipophilic Balance (HLB) 6cc/200 mg cartridges were preconditioned sequentially with 5 mL of MTBE, methanol, and ultrapure water, samples were then loaded to cartridges by an automated solid phase extraction system, the cartridges were dried under N_2 gas, and eluted with 5 mL of methanol followed by 5 mL of 10/90 (v/v) methanol/MTBE solution. The eluate was evaporated to near dryness under nitrogen gas flow, reconstituted to 1 mL with methanol, and stored at -20°C until analyzed by liquid chromatography-tandem mass spectrometry (LC/MS-MS) in positive electrospray ionization (ESI+) mode.

Soil and sediment samples were freeze-dried and extracted by pressurized liquid extraction (ASE 200). Briefly, the freeze-dried sample was packed into extraction cells with diatomaceous earth used as filler. The extraction solvent was 2:1 v/v water-methanol solution at 100°C and 1500 psi, and extraction was conducted three times. The extract was diluted to 1 L with ultrapure water. Solid phase extraction with HLB cartridges and elution with methanol was conducted as a clean-up method. Eluates were dried, reconstituted to 1 mL with (2:1, v/v) water-methanol solution, spiked with isotopes and stored at -20°C until measurement by LC/MS-MS.

Quantification was achieved following the analytical method described by Sharma et al. (2020). Briefly, a Thermo Scientific Ultimate 3000 UPHLC with an Agilent RRHD

ZORBAX Eclipse Plus reverse phase C18 column (2.1×50 mm, and 1.8 μm) was used for LC. Mobile phase of ultrapure water with 0.1% formic acid (solvent A) and acetonitrile with 0.1% formic acid (solvent B) with flowrate of 400 μL/min at 30°C in ESI+ mode. The Thermo Scientific XX triple quad MS was tuned daily with caffeine and one ion transition was used for quantitation of each compound. Another transition was used for qualification. MS/MS parameters, analyte reporting limits and LC-MS/MS ion transitions are provided in Table B-1, B-2, and B-3 respectively. Analytical check standards were within ±20% of their known concentration.

4.2.6 Statistical methods

ANOVA with post-hoc Tukey's HSD was conducted in R. The threshold for statistical significance was set at $p=0.05$.

4.3 Results and Discussion

4.3.1 TrOC occurrence in TLs

Ten TrOCs were quantified in the surface water of four TLs and the results are presented in the Figure 4-1. Surface water enters from location A into each TL, and locations B, C & D are along the lake shore between 1.1 km and 6.4 km from A. Nine TrOCs were detectable in TL1, and more than any other lake. TL1 receives wastewater from two WW facilities, one is highly treated reclaimed wastewater, and the other treatment facility discharges to evaporation ponds which are directly adjacent to the lake. During the sampling event, the lake level was extremely high, causing localized flooding, and the evaporation ponds likely comingled with the lake water to some extent. CBZ, DEET, PMD and TMP were present in all four lakes from 1 ± 0.6 (CBZ) to 1109 ± 1887 ng/L (PMD).

Sediment TrOC concentrations are presented in Figure 4-2. Six TrOCs (CAF, CBZ, DEET, DPH, PMD and TMP) were present in all four lakes from 0.15 ± 0.10 (DEET in TL1) to 12.40 ± 5.2 ng/gDW (TMP in TL1). Primidone at location B/C/D in TL1 was at 77 ng/gDW, the highest TrOC concentration observed in all sediment samples. ATZ and MPB were not detected in any sediments collected. FLX and SMX ranged from below the detection limit (BDL) to 2 ng/gDW.

Soil samples were collected to understand the effects of shoreline recreational activities (Figure 4-3). Six TrOCs (CAF, CBZ, DEET, DPH, PMD and TMP) were present at quantifiable levels in all TLs from 0.1 ± 0.15 to 137 ± 195 ng/gDW (CAF). CAF was at the greatest concentration of 361 ng/gDW in TL3 soil at location C. This specific soil sampling location is a relatively high traffic recreational beach. Similarly, at high public traffic location A, CBZ at CTL was at 133 ng/gDW. Other compounds were observed at low concentration such as FLX and MPB were at 0.1 ng/g DW and 1 ng/gDW at TL3 respectively, whereas SMX was at ~1 ng/gDW at TL2 and TL3 soil samples. ATZ was below the detection limit in soil samples at all four lakes.

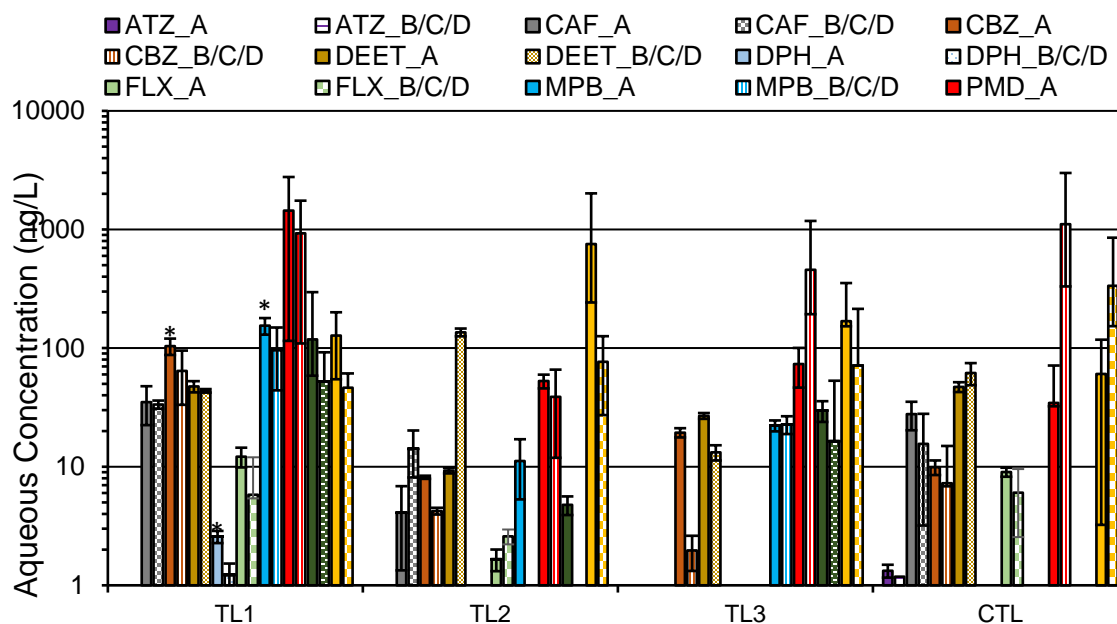


Figure 4-1 TrOCs in the mixing zone (A, represented by solid bars) and the average of three nearshore sampling sites (B/C/D, pattern fills). Error bars show the standard deviation of three or more samples collected at location A and B/C/D of TL1, TL2, TL3 and CTL. Asterisks indicate the concentration is significantly different in the lake compared to the mixing zone. No bar indicates the analyte was below detection limit.

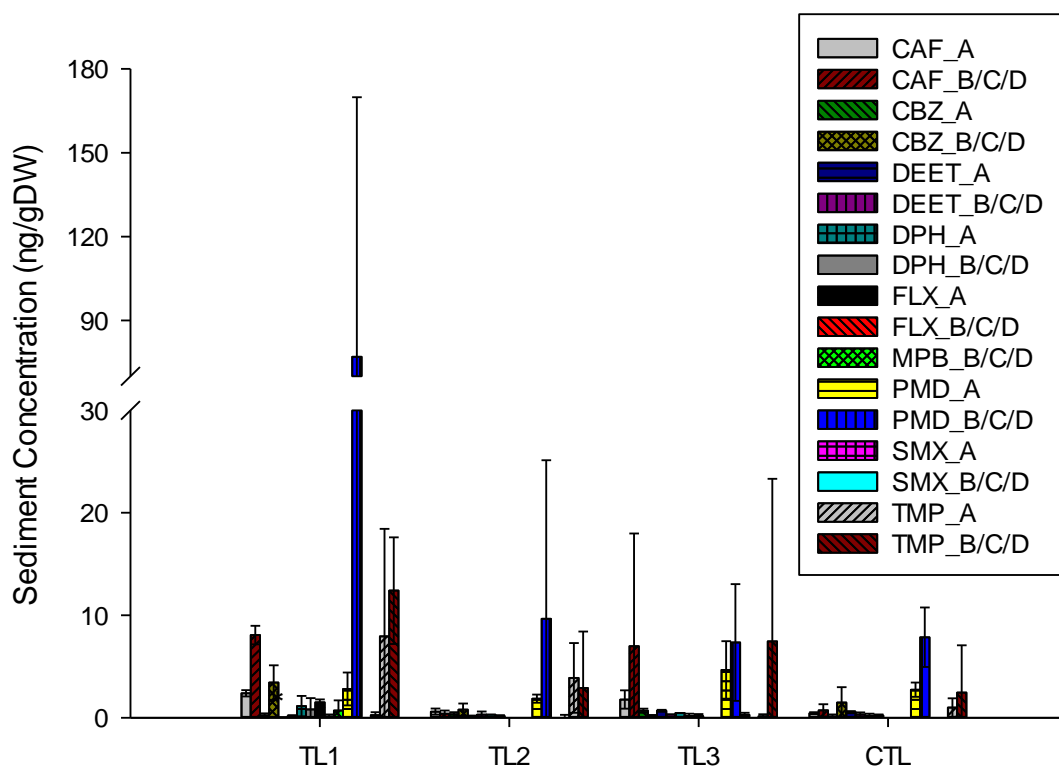


Figure 4-2 TrOCs in sediments at the mixing zone (A) and the average of three points near the lakeshore (B/C/D). Error bars represents the standard deviation among three or more samples. Asterisks indicate the concentration is significantly different in the lake compared to the mixing zone. No bar indicates the analyte was below detection limit.

4.3.2 Variability among TLs

ANOVA was used to determine differences between samples (Table B-4 and B-5). CAF, CBZ, DPH, and MPB were present in TL1 at greater concentrations than TL2, TL3 and CTL. TL1 receives wastewater with the lowest level of treatment and therefore the greater concentration of TrOCs was somewhat expected. CAF was non-detect in TL1 but was present in all other three lakes. There was no significant difference in concentrations of CBZ, DPH, MPB, PMD, SMX and TMP between TL2, TL3 and CTL. DEET and FLX were present at lower concentrations in both TL2 and TL3 compared to CTL, even though TL2 & TL3 receives tertiary treated wastewater and CTL does not receive reclaimed

wastewater. However, TL2 has more DEET than TL3 which could be due to TL2 being a shallower lake than TL3, TL2 (i.e., less dilution) or that it attracts a greater population (i.e., sportsmen/sportswomen) compared to TL3. Overall, concentrations of TrOCs were similar in lakes with direct reclaimed wastewater input to those in a lake without wastewater input. For the lake with both reclaimed wastewater input and only biologically treated wastewater input, concentrations were significantly elevated.

Similarly, for sediments, DPH and FLX concentrations were greater in TL1 than TL2, TL3 and CTL but DEET was lower in TL1 than TL2, TL3 and CTL. The concentration of CAF, CBZ, PMD, SMX & TMP were not significantly different between the lakes but CAF, PMD and TMP were present at modestly greater concentrations in TL1 sediments compared to the other three lakes. MPB was below the method reporting limit for all samples.

On comparing the TrOCs concentrations in sediments to soil, concentrations in TL1's soil were either similar to or less than respective lake sediments. However, at every sampling location (A/B/C/D) of TL2 soil CAF concentrations were greater than sediments concentrations. Also in TL2, the concentrations of CBZ at location B, DEET at location D, and TMP at location A were greater than their respective sediment concentrations. Further, in TL3, CAF, DEET and PMD and in CTL, CBZ, PMD and TMP, were present at higher concentration in soil at some sampling locations compared to respective sediment samples. There was no significant difference in TrOCs concentrations in soil samples of TLs impacted by reclaimed wastewater compared to the CTL lake. The lakes in this research all have some level of public shoreline activity; this is well demonstrated by the

intermittently greater concentrations in respective soils compared to sediments, and indicates that at least some of the TrOCs present in the lakes originated in shoreline activity rather than wastewater flows.

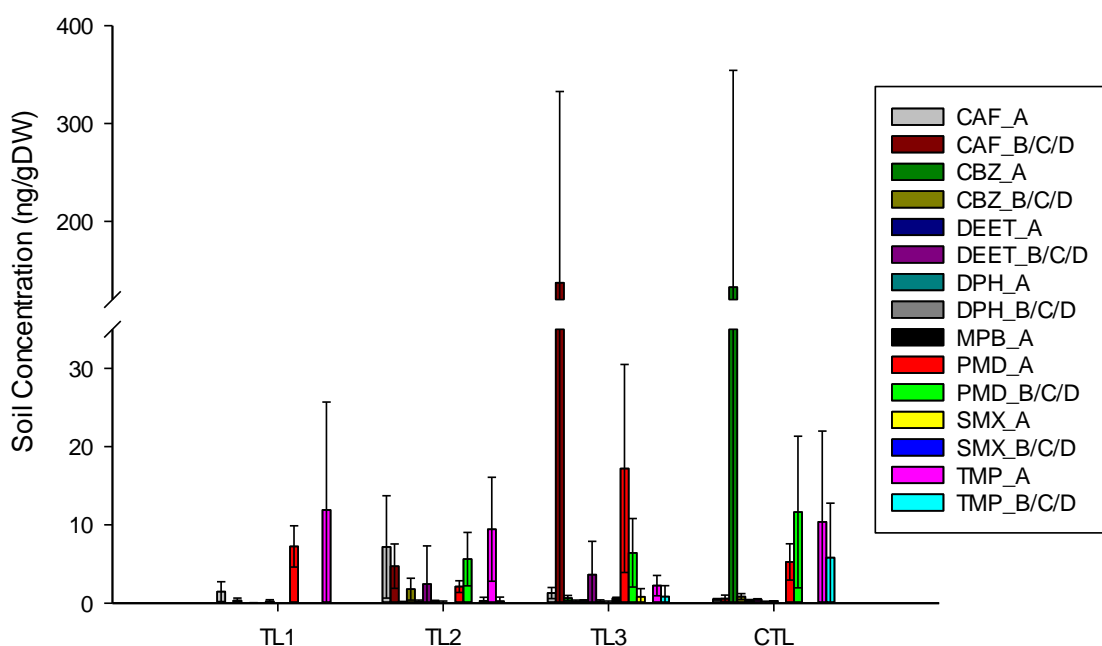


Figure 4-3 TrOCs soils at locations A & B/C/D, where locations B, C & D are the average of three TLs and one control lake. Error bars show the standard deviation of three or more samples. No bar indicates the analyte was below detection limit.

4.3.3 Losses in the TLs

The concentrations of TrOCs would be greater in the lake compared to the mixing zone was expected due to accumulation in the lake. For CAF and DEET in TL2, PMD in TL3, and PMD and TMP in CTL, this was true; concentrations were greater at location B/C/D than location A in surface water samples. However, for TL1, the mixing zone (Location A) had significantly greater concentrations of CBZ, DPH, FLX & MPB than location B/C/D (Figure 4-1). In TL2, TL3 and CTL the concentrations at locations B/C/D of surface

water samples were not significantly different from their respective mixing zones. Thus, sediment sorption and biodegradation and/or photolysis likely mediate TrOCs in the lakes, resulting in concentrations that are not significantly amplified by evaporative lake water losses.

This is further supported by sediment concentrations where TrOCs tended to be present at higher concentrations in lake sediments than in the mixing zone sediments. This is most apparent for CAF and PMD, which were significantly greater in lake sediment than mixing zone sediment. Other TrOCs had an overall similar trend but were differences were not statistically significant.

4.3.4 Comparisons of TLs with U.S. surface waters

TrOC concentrations in the U.S. lakes/rivers/streams and sediments published in the scientific literature were compiled and are presented in Figures 4-4 and 4-5. The aggregated data is presented in Table B-6. Comparisons here are made between TLs in this study and lakes with natural discharges to surface water (literature) because no data exists for TLs but also because TLs may accumulate TrOCs was expected. Comparisons between TLs and U.S. surface waters were variable, with some TrOCs present at greater concentrations in TLs and some at lower concentrations. Average concentrations of ATZ, CAF, and DPH were at least four times greater in the U.S. lakes reported in the literature compared to the four TLs. DEET concentrations in the literature were greater by an average of 18 ng/L compared to TLs measured in this study. However, CBZ, FLX, and SMX were present in TLs at concentrations approximately double that of the literature and TMP approximately

50 times higher than literature. MPB and PMD were also present at high concentrations in TLs but no similar literature was found with which to compare.

Concentrations of TrOCs that were present above the reporting limits in sediment samples in this study and in literature, were 5, 55 and 71 times greater in freshwater lakes than in the TLs (CAF, DPH and FLX, respectively) (Blair et al., 2013; K.E. Lee et al., 2015b). CBZ, DEET, SMX and TMP were either below the detection limits or no comparable data was available (MPB & PMD) in published literature. In this study, DEET, ATZ, MPB and SMX were below the detection/reporting limits and therefore are also not compared with literature.

Overall, CBZ, FLX, SMX and TMP were present at higher concentrations and ATZ, CAF, DEET and DPH at lower concentrations in the aqueous phase of TLs compared to freshwater. ATZ, CAF, DPH and FLX were present at lower concentrations in TLs sediments than freshwater lake sediments. TMP was present at higher concentration in TLs sediments. These differences highlight the variable mechanisms of degradation and transport of TrOCs from surface water to sediment. The samples investigated in this study represent only two seasons in a single 12-month period but it is believed that the data is sufficient to demonstrate that TLs do not significantly accumulate TrOCs.

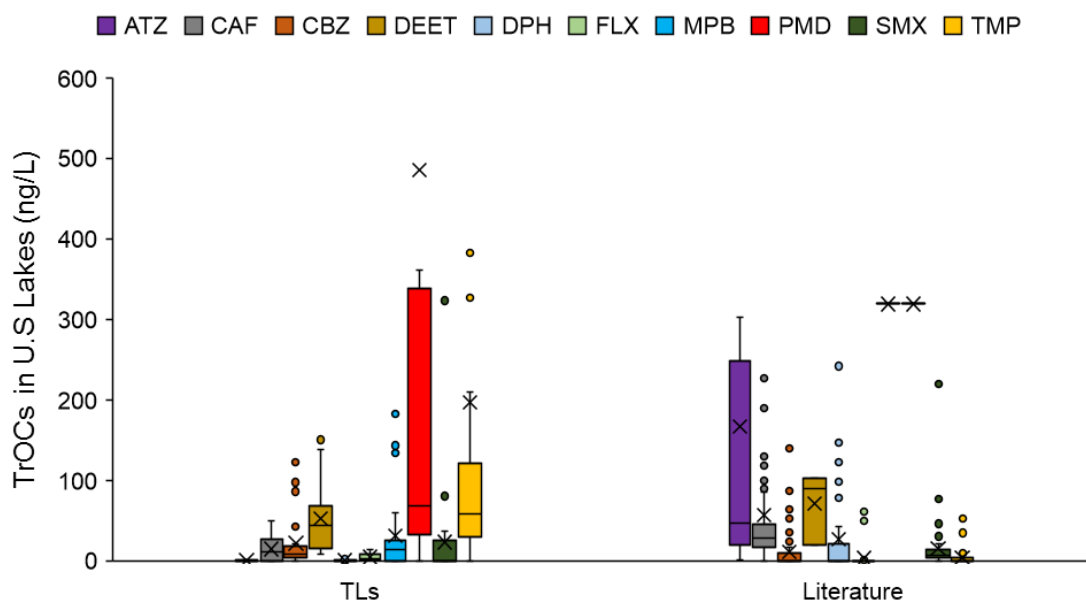


Figure 4-4 Comparison between TrOCs in surface water of TLs (this study, n=4) and literature (ranging from n=1 to 4). Median shown by line, box shows interquartile range, cross is mean and individual points are outliers. Outliers (TLs PMD- 1128 ng/L, 1739 ng/L, 2901 ng/L and 3932 ng/L and Literature CAF- 800 ng/L) are not shown.

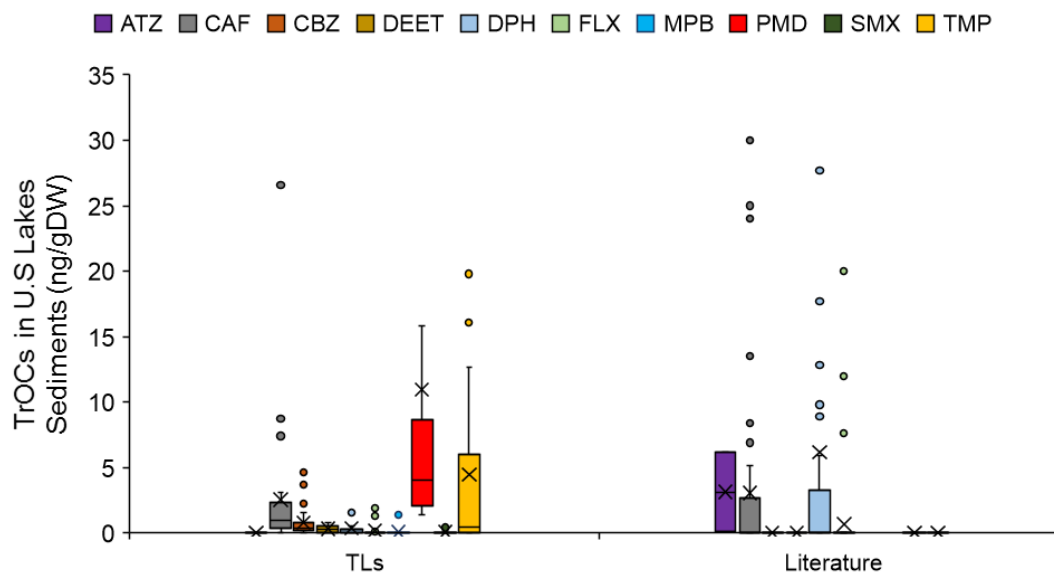


Figure 4-5 TrOCs in sediments of TLs (this study, n=4) and other U.S. lakes (literature, ranging from n= 1 to 3). Outliers (TLs PMD- 37 ng/g DW, 143 ng/gDW and Literature DPH- 36 ng/gDW, 37 ng/gDW, 44 ng/gDW, 48 ng/gDW, 82 ng/gDW) are not shown.

4.4 Conclusions

Some TrOCs (CBZ, FLX, SMX and TMP) were present at higher concentration in multiple TL surface waters compared to their concentrations in other U.S. lakes, but generally concentrations were less than would be expected based on hydrology alone, indicating biological activity or photolysis in TLs play key roles in TrOCs degradation. There was no significant difference in TrOC concentrations in TL soils near lakes impacted by reclaimed wastewater compared to those which were not wastewater impacted. In select cases, TrOC concentrations were greater in soils compared to their respective sediment samples, likely due to shoreline human activity. PMD concentrations was ubiquitous in aqueous and sediment samples, respective of its relatively high use and its long environmental lifespan.

Chapter 5

**Dissolved Constituents in Endorheic Lakes Cause Faster Photodegradation of
Pharmaceuticals than those in Freshwater Lakes***

Priyamvada Sharma, Joanna Blaszczak, and David Hanigan

* In preparation to submit to Chemosphere Environmental Chemistry

Abstract

A plethora of research has been conducted on photodegradation of pharmaceuticals in wastewater effluents, streams, rivers, and lakes at either laboratory or field-scale. Our previous research indicated that carbamazepine (CBZ) was at higher concentrations and diphenhydramine (DPH) at lower concentrations in terminal lakes than in non-terminal freshwater lakes across the U.S. Terminal lakes contain higher amounts of organic matter and are more saline than freshwater lakes. To understand if the photodegradation of pharmaceuticals in terminal lakes was impacted by organic matter and salt content. The rate of photodegradation of CBZ and DPH in two terminal lakes (Walker Lake, NV and Swan Lake, NV) was measured and compared the rates to one oligotrophic freshwater lake (Lake Tahoe). To determine the role of dissolved constituents, dilutions of lake water was prepared containing 20 mg/L of CBZ and DPH and, exposed the samples to the full-spectrum artificial light for a maximum of 2 days. Photodegradation of CBZ and DPH followed pseudo-zero order kinetics. A linear mixed-effect model was used to determine the contribution of individual dissolved characteristics of lake water to the photodegradation of CBZ and DPH. Dissolved organic carbon up to 65 mgC/L and alkalinity of 5198 mg CaCO₃/L in terminal lakes enhanced the rate of photodegradation rate of DPH and CBZ but photodegradation rates of DPH were higher than CBZ.

Degradation rate constants ranged from 0.33 to 2.68 mg/L-hr for CBZ and DPH in terminal lakes compared to 0.19 to 0.88 mg/L-hr for CBZ and DPH in freshwater lake. More than 84% of CBZ and 78% of DPH were degraded in terminal and freshwater lake samples, respectively.

5.1 Introduction

Trace organic contaminants have been widely detected in surface water, groundwater, and freshwater and terminal lakes due to inputs from agricultural run-off and reclaimed wastewater, nearby human activity, and industrial waste (Avisar et al., 2013; Boreen et al., 2003; Kolpin et al., 2002; Sharma and Hanigan, 2021). Environmental trace organic contaminants in surface waters can have negative impacts on aquatic and human health, such as bioaccumulation in aquatic animals (Boreen et al., 2003; Kolpin et al., 2002; Liu et al., 2019; Real et al., 2009; Richardson et al., 2005). An important degradation pathway for trace organic contaminants in surface waters is sunlight-activated photochemical breakdown (Boreen et al., 2003; Carena and Vione, 2020; Chen et al., 2009; Maddigapu et al., 2010; Jieqiong Wang et al., 2020a).

Contaminants in the environment can be degraded either by direct photolysis or indirect photolysis (Calisto et al., 2011). Direct photolysis occurs when contaminants are degraded if their absorption spectrum coincides with the irradiation spectrum (Liu et al., 2019; Pereira et al., 2007). Indirect photolysis occurs when contaminants are degraded by intermediate reactive species that are formed by irradiation of other compounds present in water (Carena and Vione, 2020), such as dissolved organic matter (DOM) and carbonates. Important reactive species are excited triplet state of dissolved organic matter ($^3\text{DOM}^*$),

singlet oxygen ($^1\text{O}_2$), hydroxyl radicals ($\cdot\text{OH}$) and carbonate radicals ($\text{CO}_3^{\cdot-}$) (Chiron et al., 2006; De Laurentiis et al., 2012; Dong et al., 2015; Lam and Mabury, 2005; Lam et al., 2003). While these reactive species degrade many contaminants in the environment (Dong et al., 2015), they can also inhibit photodegradation reactions. For example, DOM can scavenge some photoreactive species such as $^3\text{DOM}^*$, $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$ (Carena and Vione, 2020), thereby preventing degradation of organic contaminants.

In the U.S., terminal lakes are mostly present in semi-arid region of the west. Evaporation is the primary water loss pathway, which causes increased accumulation of soluble salts such as Ca, Mg, Na, and CO_3 , Cl, etc. (Berelson et al., 2008; Yapiyev et al., 2017). Dissolved organic carbon (DOC) concentrations vary in freshwater lakes (6.7 mgC/L mean of five lakes) and terminal lakes (27.4 mgC/L mean of five lakes) (Song et al., 2019). Our prior research showed that carbamazepine (CBZ) was at higher concentrations, and diphenhydramine (DPH) at lower concentrations in terminal lakes than freshwater lakes in the U.S., but the mechanisms explaining this difference are unknown (Sharma and Hanigan, 2021). One possible mechanism explaining differences in levels of pharmaceuticals may be photodegradation of these compounds due to higher DOC concentrations and high solar radiation inputs given that most terminal lakes are in dry parts of the U.S. However, there is little published literature addressing the fate of pharmaceuticals in terminal lakes. Thus, to understand the impact of dissolved constituents on pharmaceutical degradation kinetics, the objectives of this study were to a) determine the impact of water constituents on the photodegradation kinetics of CBZ and DPH in

terminal and freshwater lakes, and b) compare photodegradation kinetics between freshwater and terminal lakes.

5.2 Materials and Methods

5.2.1 Chemicals and Reagents

CBZ and DPH as trace organic contaminants of interest were selected for this study because they are at higher (CBZ) and lower (DPH) concentrations in terminal lakes compared to other U.S. freshwater lakes (Blair et al., 2013; Boyd and Furlong, 2002; Lee et al., 2015; Sharma and Hanigan, 2021; Shiru Wang et al., 2020b). Both CBZ and DPH were purchased from Sigma-Aldrich (St. Louis, MO). Methanol and acetonitrile were obtained from Thermo Fisher Scientific (Pittsburgh, PA). All standards and solvents had a purity level of $\geq 98\%$. Standard solutions were prepared with ≥ 18.2 M Ω -cm water (Milli-Q) obtained from Thermo Scientific Barnstead GenPure and stored in amber vials at 4°C.

5.2.2 Sampling

To compare photodegradation rates between terminal and freshwater lakes, Swan Lake (Reno, NV) and Walker Lake (near Hawthorne, NV) as representative terminal lakes and Lake Tahoe as an oligotrophic freshwater lake were selected. Swan Lake has shown to receive inputs from wastewater whereas Walker Lake does not. Samples were collected from Swan Lake, Walker Lake, and Lake Tahoe in May 2020 and Walker Lake was sampled second time in July 2020. Other lakes were not sampled twice as the water quality did not change over summer months. Samples from the surface of each lake were collected at least 2 m from the shore with a HDPE container (pre-washed with alconox, rinsed with deionized water and conditioned with the lake water) fastened to a pole. Samples were immediately transferred to a 20 L HDPE container which had been pre-washed with

alconox and rinsed with deionized water three times. Samples were transported to the University of Nevada, Reno laboratory on ice, and filtered the same day and later stored at 4°C.

5.2.3 Photodegradation Experimental Apparatus

All water samples were filtered in the lab using pre-combusted 47 mm glass microfiber filters (GF/F, 0.45 µm pore size). After filtration, each of the collected terminal lake water samples were diluted with deionized water using lake:DI ratios of 10:90, 25:75, 35:65, 50:50, 60:40, 75:25 and 100:0. Lake Tahoe water samples were diluted with deionized water 50:50, 60:40, 70:30, 80:20, 90:10, 100:0. These dilutions were different than terminal lakes because of Lake Tahoe water characteristics results. It was predicted that any further dilutions of <50% with deionized water would result in either very less or no photodegradation of the pharmaceuticals.

CBZ and DPH were each spiked at 20 mg/L to diluted and undiluted lake water samples. 5 mL of each spiked solution was added to ACE Glass Inc. (Vineland, NJ) quartz test tubes with 11 mm internal diameter. Test tubes containing spiked solution were either covered with foil (dark controls) or not covered with foil (light exposed samples). Control samples were also prepared by adding 20 mg/L of CBZ or DPH to deionized water. Samples in test tubes were capped with LDPE caps to avoid sample losses due to evaporation during the experiments.

Samples were exposed to artificial sunlight using a Suntest CPS containing a 1500 W Xenon lamp and filters that replicate the solar emission spectrum. Tubes were aligned at an angle of 45° above horizontal on a metal rack to approximate the mid-latitudes of

Nevada. The intensity of the incident light was equivalent to sunlight. The solar simulator had a constant inner temperature of 45°C, which was measured by a Fluke 54 II B thermometer.

Exposure duration and sampling intervals were based on preliminary photodegradation experiments. The CBZ-spiked samples were exposed to light for a total of 44 hours, and 1 mL aliquot after every 4 hours was collected. For terminal lake samples, DPH-spiked samples were exposed to light for 10 hours and sampled every hour. Lake Tahoe samples spiked with DPH water were exposed for 24 hours and sampled after every 4 hours. Aliquots were placed in 2 mL amber screw-top vials and refrigerated at 4°C until analysis (analyzed within a week).

5.2.4 Analytical Methods

Lake water sampled were characterized prior to the photodegradation studies. The pH was measured using a calibrated Thermo Fisher pH meter (Waltham, MA). The UV-Vis measurements were conducted with a Hach DR6000 spectrophotometer. The DOC concentrations were measured using a Shimadzu TOC-L analyzer with MRL of 1 mg/L. Terminal lake samples were diluted 10 times with deionized water prior to DOC measurements due to their high salt content interfering with the DOC measurement. Specific ultraviolet absorbance (SUVA) was calculated as the UV absorbance divided by the DOC concentration. Turbidity and alkalinity were measured with a Hach turbidimeter and an automatic titrator, respectively. Both May and July samples from Walker Lake and Swan Lake samples were diluted with deionized water 10 times to measure alkalinity.

Fluoride, chloride, nitrate, nitrite, bromide, and sulfate were measured using a Dionex ICS-3000 equipped with an anion exchange column (Dionex IonPac AG19 4 × 50 mm guard column and AS19 4 × 250 mm analytical column). The mobile phase was 12 mM potassium hydroxide at a flow rate of 500 µL/min with 800 µl as the injection volume. Terminal lake samples were diluted 500 times to increase accuracy of the anion measurements. Fluoride could not be measured because it was at below the detection limit in more diluted samples. Orthophosphate was measured using a Hach reactive phosphate kit with a Hach spectrophotometer DR3900. The DPH and CBZ concentrations were measured using an Agilent 1260 Infinity HPLC-UV instrument, within a week of exposure (ZORBAX Eclipse plus C-18 column, Agilent Technologies (4.6 mm x 150 mm x 5 µm). Instrumental conditions were similar to Thapa and Hanigan (2020) for CBZ but DPH was determined using 65:35 v/v 0.01 N potassium dihydrogen orthophosphate (pH 3) adjusted with diluted phosphoric acid: acetonitrile and the total run time was 6 mins. The column was operated at 30°C with the injection volume of 10 µL where DPH measurements were conducted at 205 nm wavelength (Ge et al., 2011).

5.2.5 Linear Mixed Effect Model

To determine which dissolved constituents may play a role in each lake in either promoting or inhibiting photodegradation, the data was analyzed using a linear mixed-effects model. In this study, lake and exposure duration were used as fixed-effects, dilutions while other lake water characteristics were random effects using Eq. 5-1.

$$\text{Concentration of CBZ or DPH} = \beta_0 \text{ Hour} + \beta_1 \text{ Dilution} + \beta_2 \text{ DOC} + \text{Intercept} \quad \text{Equation 5-1}$$

With β_0 , β_1 , and β_2 being the slope of the hour, dilution, and DOC. The random slope and fixed intercept method were applied. All the data values were z-scored due to differences in scales between variables. Our analysis was conducted using (R version 3.6.1, model lme4) and the model output are presented in Table C- 2.

5.3 Results and Discussion

5.3.1 Lake Characteristics

Surface water characteristics of each lake are presented in Table 5-1. In general, the concentrations of various water constituents in the terminal lakes were greater than the freshwater lake concentrations. Lake characteristics for Walker Lake in May were like July, indicating stability in surface water chemistry is impacted more by longer-term accumulation of organic and inorganic matter than the spring snowmelt of 2020. Walker Lake had higher concentrations of DOC, alkalinity, Cl^- and SO_4^{2-} than Swan Lake and Lake Tahoe. The $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations were higher in Swan Lake than both samplings of Walker Lake and Lake Tahoe, potentially because the lake receives surface runoff from the surrounding community. Swan Lake also had higher SUVA, indicative of greater humic acid content, and green algae were visible in the sample, reflecting anthropogenic inputs.

Table 5-1 Water characteristics of lakes in this research.

Parameter	Unit	5/13/2020	7/13/2020	8/25/2020	8/25/2020
Lakes		Walker Lake	Walker Lake	Swan Lake	Lake Tahoe
DOC	(mgC/L)	65.5	65.6	33.3	1.2
UV254	(cm^{-1})	0.355	0.37	0.053	0.008
SUVA	(L/mg-m)	0.54	0.56	3.63	0.66
F^-	($\mu\text{g/L}$)	NF	NF	NF	62
Cl^-	(mg/L)	4,392	3,946	2.9	2.5
$\text{NO}_3\text{-N}$	(mg/L)	NF	NF	0.77	NF

SO ₄ ²⁻	(mg/L)	4,451	4,700	183.6	0.4
PO ₄ -P	(mg/L)	0.7	0.3	1.6	0.04
pH		9.1	9.9	10.3	8.8
Alkalinity	(mgCaCO ₃ /L)	5,198	5,112	518.5	45.2
Turbidity	(NTU)	5.1	4.3	93.1	0.66

5.3.2 Degradation Rates

Photodegradation kinetics for CBZ and DPH in lake water are provided in Table 5-2. Dark controls are not presented because no degradation of CBZ and DPH was observed. Pseudo zero-order degradation of CBZ and DPH in terminal lakes at all dilutions were linear ($R^2 \geq 0.90$) with time. However, the linear decrease in Lake Tahoe was weaker ($R^2 \geq 0.83$) than terminal lakes (Table 5-2). Pseudo-zero order fits were more strongly based on the R^2 values for concentration vs time plots, raw files are in the Appendix C. All experimental matrices followed pseudo-zero order kinetics, likely because the formation of reactive radical species from the excitation of dissolved constituents such as DOC was relatively slow compared to the high concentrations (20 mg/L) of spiked DPH and CBZ. Work by Zhang et al. (2012) found similar pseudo zero order kinetics for the degradation of norfloxacin.

The change in CBZ concentration in Walker Lake May over time was plotted in Figure C-1 and each line equation along with its R^2 generated from Figure C-1 is listed in Table C-1. The slope of the line equation is the degradation rate constants for the respective dilution of Walker Lake May water for CBZ. The same steps were repeated to generate the Table 5-2 and Table C-1 (for all dilutions).

Degradation rate constants (k_{obs}) for CBZ in undiluted Walker Lake May and July samples, and Swan Lake and Lake Tahoe were 0.6319 mg/L-hr, 0.4566 mg/L-hr, 0.4392 mg/L-hr

and 0.3487 mg/L-hr, respectively (Table 5-2). The k_{obs} for CBZ was lowest in undiluted Lake Tahoe water. For DPH, k_{obs} were 2.4239 mg/L-hr, 2.2635 mg/L-hr, 1.9085mg/L-hr, and 0.8794 mg/L-hr for Walker Lake May, Walker Lake July, Swan Lake, Lake Tahoe, respectively. In general, k_{obs} values for both CBZ and DPH were greater in terminal lake waters than freshwater, likely due to the greater concentrations of dissolved constituents which are photoexcited to produce radicals.

Table 5-2 Photodegradation kinetics in three lakes and deionized water.
Pseudo-Zero Order Reaction

Pharmaceutical	Percent Lake Water	Kinetic Equation	R ²
Walker Lake May			
CBZ	100	$y = -0.6319x + 24.215$	R ² = 0.98
DPH	100	$y = -2.4239x + 24.012$	R ² = 0.98
Walker Lake July			
CBZ	100	$y = -0.4566x + 19.781$	R ² = 0.96
DPH	100	$y = -2.2635x + 21.61$	R ² = 0.98
Swan Lake			
CBZ	100	$y = -0.4392x + 16.94$	R ² = 0.90
DPH	100	$y = -1.9085x + 18.14$	R ² = 0.96
Lake Tahoe			
CBZ	100	$y = -0.3487x + 22.509$	R ² = 0.83
DPH	100	$y = -0.8794x + 24.449$	R ² = 0.88
Deionized Water			
CBZ	100	$y = -0.1137x + 20.552$	R ² = 0.54
DPH	100	$y = -0.0468x + 20.901$	R ² = 0.14

The CBZ and DPH concentrations in deionized water had k_{obs} of 0.1137 mg/L-hr and 0.0468 mg/L-hr respectively (Table 5-2) indicating that some photodegradation occurred even in the absence of DOC and other dissolved constituents. This is also supported by

other researchers, who observed some photodegradation of DPH by direct photolysis (Chen et al., 2009; Yuan et al., 2009).

5.3.3 Contribution of DOC

Diluted samples had somewhat weaker fits but the R^2 generally still exceeded 0.9, except in Lake Tahoe samples (R^2 generally >0.6) (Table C-1). Overall, reducing dissolved water constituent concentrations caused slower photodegradation of CBZ and DPH in lake water samples. Dilution caused k_{obs} for both CBZ and DPH to decline (Table C-1), likely due to a reduction in photoexcited compounds. The slopes from all the equations in Table 5-1 and Table C-1 were used as degradation rate constants (k_{obs}) and plotted them against the calculated DOC and alkalinity based on dilutions (Figure 5-1 to Figure 5-4).

CBZ and DPH k_{obs} values was plotted against the DOC concentrations for each dilution to determine if k_{obs} values of CBZ and DPH were directly proportional to DOC concentrations (Figures 5-1 and 5-2). The k_{obs} for CBZ and DPH increased linearly with DOC concentration for all lakes. For Lake Tahoe, DOC appeared to be the primary constituent causing photodegradation as the y-intercept is near zero suggesting that DOC being the sole factor in CBZ degradation. However, the intercepts for terminal lakes were higher than 0, indicating that other constituents contribute to photodegradation. For DPH photodegradation reactions in Lake Tahoe, a lag phase of ~12 hours was observed until photodegradation started. The lag phase was shorter for samples having smaller dilutions which indicates that the dissolved constituents such as DOC is contributing in photodegradation of DPH. In diluted samples there is not enough DOC to participate in photodegradation but with longer light exposure, enough radicals produce to participate in

photodegradation of DPH. Based on the variance values of the fixed and random effects in the model, DOC contribution to photodegradation of CBZ and DPH was 20% and 63%, respectively (Table C-2).

The positive coefficients of the random slope for all terminal lakes and negative coefficients for freshwater lakes (Table C-2) indicate that the contribution of DOC to photodegradation of CBZ was largest in the freshwater lake compared to both terminal lakes. However, for DPH photodegradation, negative coefficients were observed for Lake Tahoe and Swan Lake. The negative coefficients listed in Table C-2 suggest that the decline in CBZ and DPH concentration over time is because of DOC. Overall, DOC affected the photodegradation of CBZ and DPH but was more important in Lake Tahoe water.

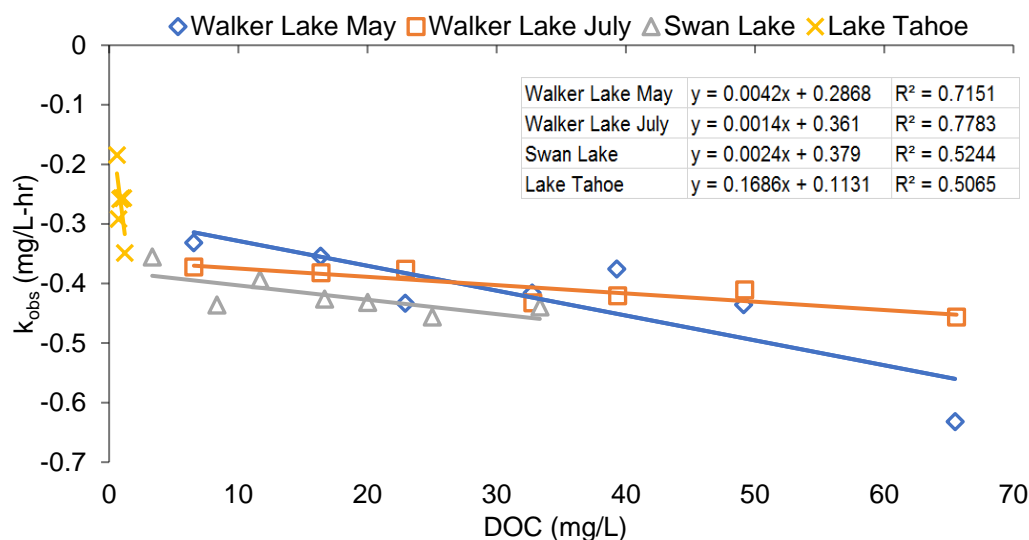


Figure 5-1 Pseudo zero-order degradation rate constants (k_{obs}) of CBZ are extracted from Table 5-1 and Table C-1 for all three lakes and plotted against DOC in terminal lakes and a freshwater lake which are based on dilution calculations.

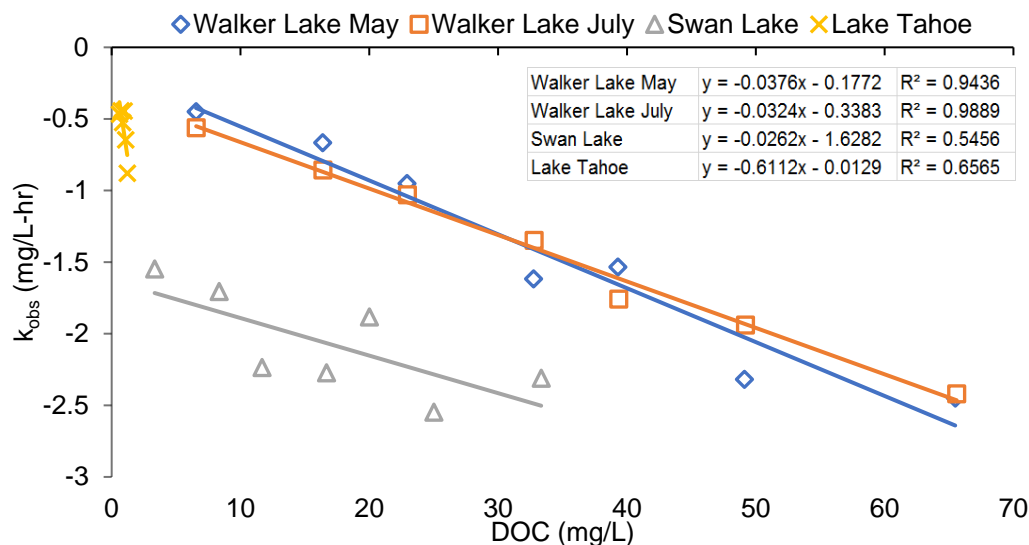


Figure 5-2 Pseudo zero-order k_{obs} of DPH are extracted from Table 5-1 and Table C-1 for all three lakes and plotted against DOC in terminal lakes and a freshwater lake which are based on dilution calculations.

5.3.4 Contribution of Other Dissolved Constituents

The potential contribution of other dissolved compounds to photodegradation of CBZ and DPH is presented in Table 5-1. HCO_3^- is an important species as CO_3^{2-} is generated from the reaction of $\cdot\text{OH}$ with $\text{HCO}_3^-/\text{CO}_3^{2-}$ (Lam and Mabury, 2005), therefore it is important to study the role of alkalinity in photodegradation of CBZ and DPH in various lake samples. The pH of all lake samples is ≥ 8.8 therefore both carbonate species i.e., $\text{HCO}_3^-/\text{CO}_3^{2-}$ will be present in the sample to contribute in photodegradation of CBZ and DPH. The k_{obs} of DPH vs. alkalinity is shown in Figure 5-4. DPH k_{obs} increased with increasing alkalinity for Walker Lake samples. In Swan Lake samples, alkalinity appeared to play a greater role as the slope of the k_{obs} vs alkalinity line was much greater. A similar trend was also observed in CBZ k_{obs} vs alkalinity (Figure 5-3).

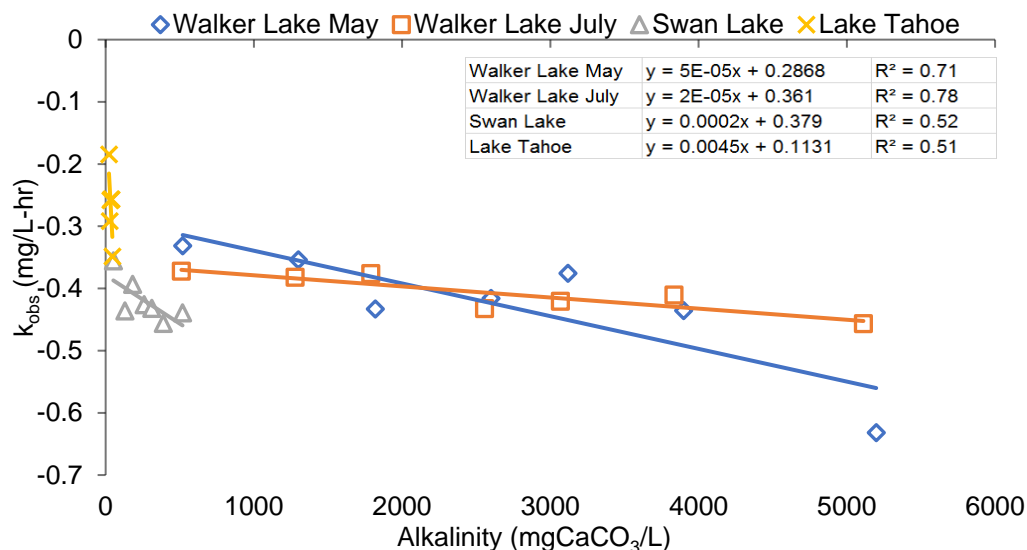


Figure 5-3 Pseudo zero-order k_{obs} of CBZ are extracted from Table 5-1 and Table C-1 for all three lakes and plotted against alkalinity in terminal lakes and a freshwater lake which are based on dilution calculations.

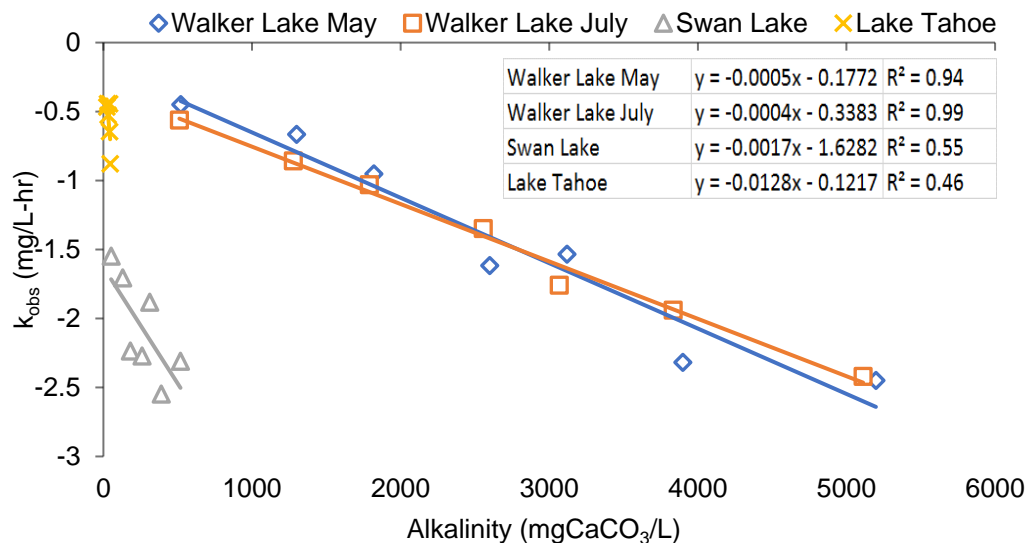


Figure 5-4 Pseudo zero-order k_{obs} of DPH are extracted from Table 5-1 and Table C-1 for all three lakes and plotted against alkalinity in terminal lakes and a freshwater lake which are based on dilution calculations.

$\text{NO}_3\text{-N}$ was only detected in Swan Lake (0.77 mg/L) but its concentrations were below detection limit in the other lakes. Photolysis of NO_3^- produces $\cdot\text{OH}$ (Zepp et al., 1987),

which can contribute to photodegradation of organic compounds. A high concentration of $\text{NO}_3\text{-N}$ in Swan Lake compared to the other two lakes (Walker Lake and Lake Tahoe) could potentially explain a faster photodegradation of CBZ and DPH by generating more $\cdot\text{OH}$. k_{obs} of CBZ and DPH was plotted against SUVA values (Figure C-9 and C-10). High SUVA values for Swan Lake indicates high concentration of organic compounds, that can absorb light and participate in photodegradation of CBZ and DPH. k_{obs} for CBZ and DPH did not increase in Swan Lake samples when SUVA values exceeded 1 L/mg-m. However, when samples had SUVA values < 0.7 L/mg-m (Walker Lake May, Walker Lake July, and Lake Tahoe), a linear trend between k_{obs} and SUVA values was observed. This suggests that SUVA values below 0.7 L/mg-m promote photodegradation of CBZ and DPH. Our results are supported by Somathilake et al. (2018) showing that high concentrations of organic compounds can interfere with photodegradation of CBZ and can promote removal efficiency of CBZ from the sample. Fits for sulfates and phosphates are in the Appendix C.

Based on the linear mixed-effects model, the overall contributions of alkalinity, SUVA, and $\text{NO}_3\text{-N}$ in all lakes in photodegradation of CBZ are 13%, 8% and 11% respectively (Table C-2). Based on the positive coefficients listed in Table C-2 generated after the model of Walker Lake and Swan Lake samples in CBZ photodegradation, alkalinity did not appear to play a major role in photodegradation. However, alkalinity appeared to influence the photodegradation of DPH in Walker Lake and Swan Lake samples based on negative coefficients and may have contributed to 67% of the overall photodegradation. Individualized effect of DOC, alkalinity, and $\text{NO}_3\text{-N}$ on photodegradation of CBZ and

DPH was not tested, therefore these linear mixed model results are indicative of what constituents played a major role in photodegrading CBZ and DPH in varying diluted lake water samples. Other contributing factors such as SUVA may be responsible for 60% in photodegrading DPH in lakes (Table C-2). All other constituents such as DOC contributed >60% to photodegradation of DPH, making it difficult to conclude if some of the constituents inhibited the rate of photodegradation thus making the contribution to >60%. Overall, photodegradation rates were dependent on DOC, alkalinity, NO₃-N, but their contribution was different for CBZ compared to DPH.

5.4 Conclusions

Photodegradation of CBZ and DPH was observed in both terminal lakes and freshwater lakes. The photodegradation rate constants k_{obs} for CBZ and DPH were higher for terminal lakes compared to a freshwater lake, which had lower concentrations of all dissolved organic and inorganic compounds. Terminal lake constituents, particularly DOC and alkalinity appeared to enhance the rates of photodegradation of CBZ and DPH. Sunlight combined with dissolved lake organic and inorganic matter contributes to the photodegradation of pharmaceuticals entering terminal lakes, thus reducing pharmaceutical concentrations in the surface water.

Chapter 6

SYNTHESIS OF RESULTS

This chapter synthesizes the results of the dissertation and supports the overarching goal: to investigate the fate of TrOCs in semi-arid areas to safely reuse reclaimed water. This research will assist future researchers and consultants in estimating the health risk associated with the accumulation of TrOCs in semi-arid areas.

There have been many investigations to determine the occurrence of TrOCs in U.S. lakes, agricultural farms (movement to soil/plant system) and their photodegradation in the environment. What makes this dissertation different is the motivation and purpose of this study; the climate of Nevada is semi-arid; receives less precipitation i.e. ranging from 25 to 35 cm per year (Runkle, 2017) with over 300 clear days per year (Nations and Erwin, 2009) and limited water resources. Stress on water resources has resulted in water reuse.

To accomplish the goal of determining the fate of TrOCs in semi-arid areas, several locations were selected that are impacted by TrOCs; terminal lakes receiving treated wastewater effluent and an agricultural farm, Main Station Field Laboratory (MSFL), that has been receiving reclaimed water for over 10 years. Sampling of the reclaimed water, soil, alfalfa, and soil pore water of MSFL were conducted. Surface water, sediments, and soil of three TLs that receive reclaimed water and one control TL that does not receive reclaimed water but has some human influence (recreational activities) were also sampled. MSFL and TLs were investigated for 12 and 10 TrOC accumulation, respectively. Results of 10 TrOCs from TLs to other U.S. lakes scientific literature were compared. A microcosm photolysis study was performed to determine photodegradation kinetics of some TrOCs in

terminal lakes and an oligotrophic lake water. These investigative studies helped in understanding the overall fate of TrOCs from the source (reclaimed water/humans) to farms/lakes and photodegradation in varying natural environment (terminal lakes/freshwater lakes).

12 TrOCs were present in the wastewater influent and the local wastewater treatment plant (WWTP) with biological, and tertiary treatment did not remove all TrOCs from the wastewater. Some hundreds ng/L to tens $\mu\text{g/L}$ was in reclaimed water for 11 TrOCs. This reclaimed water was used to irrigate MSFL, where the highest soil concentration of eight TrOCs was observed at the soil surface soil, compared to soil's deeper depths, except CBZ which increased with increasing depth. At the farm which uses the reclaimed water for irrigation, 10 TrOCs in pore water and nine TrOCs translocated into alfalfa shoots and leaves. CBZ, PMD, SMX and TMP were the compounds that were at highest concentrations in reclaimed water and at MSFL.

In other regional TLs, some of the TrOCs were at higher concentration in a TL receiving half biological and half tertiary treated wastewater compared to TLs receiving only tertiary treated wastewater. However, TrOCs in TLs receiving tertiary treated wastewater compared to a TL which was not influenced by reclaimed water were not statistically different in TrOC concentrations. On comparing TrOCs in TLs with the U.S. literature; CBZ, FLX, SMX and TMP were at higher concentration in TLs compared to U.S. literature and ATZ, CAF and DPH were at lower concentration in TLs compared to U.S. literature.

To meet the initial goal of fate of TrOCs in semi-arid areas, it is important to know why some TrOCs were higher and lower in TLs vs U.S. lakes. CBZ (higher in TLs than U.S.

literature) and DPH (higher in U.S. lakes than TLs) were selected to study photodegradation kinetics in TLs and freshwater lake. CBZ is an anticonvulsant drug; highly persistent in nature as it was at high concentration in both MSFL and TLs. DPH is an anti-allergy drug which is commonly consumed by people but was at low concentration in both MSFL and TLs. A solar simulator laboratory-scale experiment was conducted to study the kinetics of photodegradation of CBZ and DPH in two TLs (Walker and Swan Lake) and one freshwater lake (Lake Tahoe). Rates of photodegradation were faster for both CBZ and DPH in both Walker Lake and Swan Lake water samples compared to Lake Tahoe samples. High concentration of some water constituents such as dissolved organic carbon (proxy for dissolved organic matter), alkalinity and nitrates in TLs facilitated in faster photodegradation of CBZ and DPH compared to low water constituents in Lake Tahoe. However, the difference in percent removal for CBZ and DPH in both TLs and freshwater lake was less than 10% after 44 and 24 hours of light exposure respectively. Both types of lake water likely generated reactive species in presence of light that photodegraded both CBZ and DPH, but the reactions were slower in a freshwater lake compared to TLs.

TrOCs are present in semi-arid areas, even if the areas are exposed to reclaimed water or not exposed to reclaimed water. TrOC concentrations in the environment are not as alarming as low ng/gDW of some TrOCs translocated in alfalfa after being irrigated by reclaimed water for over 10 years. On comparing low ng/gDW of some TrOCs with their therapeutic doses, exposure of TrOCs to the cattle through ingestion will be minimal to no health impact. The soil matrix sorb compounds when irrigated with reclaimed water and

act as a barrier for less translocation of TrOCs in the plant. From the microcosm photolysis experiment, semi-arid climate causes relatively rapid photodegradation of some TrOCs in both freshwater and TLs. However, percent removal of some TrOCs through photodegradation was faster in terminal lakes compared to freshwater lake.

The combined key conclusions from this dissertation is shown in Figure 6-1, where it presents that the study is conducted in semi-arid areas. The figure displays alfalfa irrigated with reclaimed water for over 10 years. Cattle grazed on the alfalfa grown on this field has minimal health impact (Chapter 3). TrOCs concentration in both types of terminal lakes were similar, hence shown with an equal sign in Figure 6-1. CBZ, FLX, SMX, and TMP were higher in concentration than publications and ATZ, CAF, and DPH were lower in concentration than publications (Chapter 4). Conclusions from Chapter 5; the degradation rate constants for CBZ and DPH in terminal lakes was higher than in freshwater lake. Overall, this figure represents that reclaimed water reuse in semi-arid areas should be encouraged as these areas' climate has the potential to reduce TrOCs from WWTPs or from direct human influence.

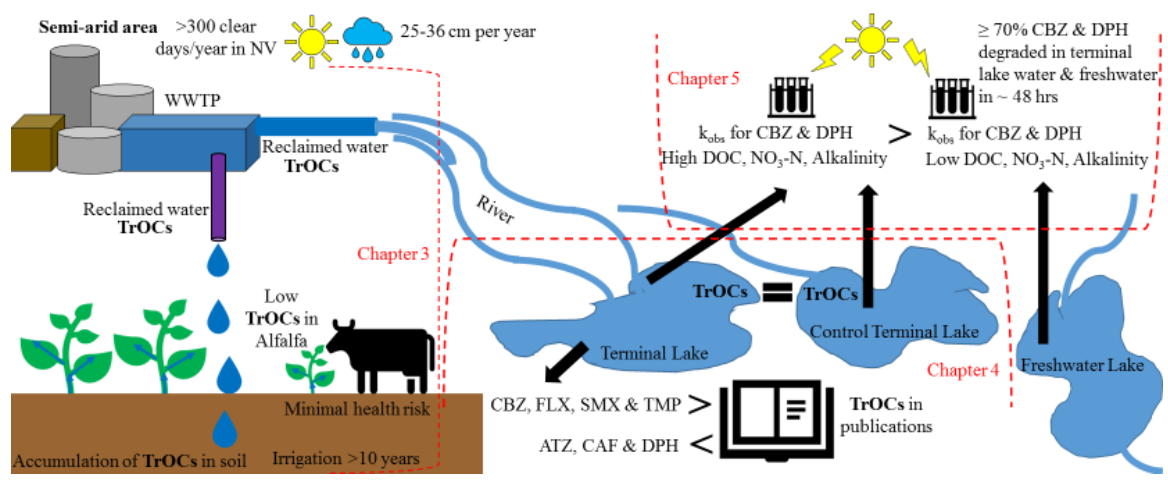


Figure 6-1 The impact of reclaimed water on agricultural farm, terminal lakes on accumulation and photodegradation of TrOCs.

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

The overarching goal of this dissertation was to investigate the fate of TrOCs in semi-arid areas to safely reuse the reclaimed water. The following summarizes the broad conclusions of this dissertation.

7.1 Conclusions

The accumulation of TrOCs in various environmental media in semi-arid areas was studied. All 12 studied TrOCs declined after each treatment processes of the water reclaimed facility, however 11 TrOCs were remained in the reclaimed water. TrOC concentrations declined in soil with increase in soil depth after the soil was irrigated with reclaimed water for over 10 years. During non-irrigation periods, some TrOCs remained in the soil pore water. Neutral compounds accumulated in alfalfa leaves at higher concentrations compared to the ionic compounds. However, limited accumulation of TrOCs in alfalfa was observed, which likely has minimal health impact on foraging animals. A greater risk may be the long-term accumulation of TrOCs in soils, but a formal risk assessment is outside the scope of this dissertation.

TrOCs in terminal lakes was also examined where there is no significant difference between concentrations in terminal lakes receiving tertiary treated water and terminal lakes not receiving reclaimed water. Poorly treated wastewater released higher concentrations of TrOCs to terminal lakes compared to tertiary treated wastewater. 4 of 10 TrOCs were present at higher concentrations in terminal lake surface water compared to freshwater U.S. lakes published in literature. 3 of 10 TrOCs were at greater concentrations in freshwater U.S. lakes compared to the surface water of terminal lakes.

To determine why some TrOCs were present at greater or lesser concentrations in terminal lakes that freshwater lakes, the photodegradation of TrOCs was studied. Both CBZ and DPH photodegraded $\geq 70\%$ in terminal and freshwater lakes in 10 to 44 hours of simulated sunlight exposure. Percent removal of CBZ and DPH by direct photolysis was 18% and 5%, respectively. High concentrations of DOC, $\text{NO}_3\text{-N}$ and alkalinity in terminal lakes tended to promote faster photodegradation kinetics for both CBZ and DPH.

7.2 Recommendations for Future Research

During this research, several questions were raised that are opportunities for further research.

1. Pharmaceuticals, personal care products and herbicide in a farm irrigated with reclaimed water for over 10 years were quantified. Over the past few years, the interest in per- and polyfluoroalkyl substances (PFASs) has increased tremendously due to an establishment of health advisory limit of 70 ng/L for the total of the sum of PFOA and PFOS by the EPA. Efforts to measure PFASs in reclaimed water and their uptake by alfalfa grown at the farm for over 10 years using reclaimed water would be a direct follow-up to this work and provide valuable information for regulators and the public.
2. Only one sample set from each terminal lake was collected to investigate TrOC concentrations. In further studies, multiple samples spaced temporally should be considered to further identify the role of lake turnover or other seasonality of TrOC concentrations.
3. Field samples were collected from terminal lake surface waters and sediments to a quantify TrOCs but solar simulated photodegradation experiments were conducted

only with surface water. There was no degradation of CBZ and DPH without light exposure was observed. Therefore, further laboratory-scale photodegradation/sorption studies of CBZ and DPH should be considered in presence of sediments and surface water of terminal lakes to understand partitioning of selected TrOCs between surface water, sediments, and their photodegradation kinetics.

4. During the solar simulated photodegradation experiments, there were both photoreactive and photo-inhibiting species in the samples. It is difficult to identify the contribution of one reactive specie. Additional study is required to examine the individualized contribution of terminal lake DOM (varying concentration) in photoreactive/inhibiting reactions compared to carbonate and nitrate. Isolations of the DOM which remove inorganic ions may allow for this distinction.
5. DOC, fluorescence, and UV–vis spectroscopy were not measured in photodegradation studies. Further study should be considered to understand the fate of background DOM during the photodegradation of CBZ and DPH. Therefore DOC, fluorescence, and UV–vis spectroscopy should be measured during the experiment and attempts to correlate photodegradation and bulk organic matter measurements should be made.
6. There are limited ecotoxicity studies that have been conducted on endangered or threatened species found in terminal lakes such as Lahontan Cutthroat Trout. Further research should be conducted to determine the adverse effects of various TrOCs and their transformation products on these endangered/threatened species at environmentally relevant concentrations.

Chapter 8

REFERENCES

- . R Core Team *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria, [Http://Www.R-Project.Org](http://www.R-project.org), 2019.
- Ahmad I., Ahmed S., Anwar Z., Sheraz M.A., Sikorski M., 2016. Photostability and Photostabilization of Drugs and Drug Products. *International Journal of Photoenergy*. 2016, 8135608. 10.1155/2016/8135608.
- Albaigés J., Bayona J.M., Radović J.R., 2016. 20 - Photochemical Effects on Oil Spill Fingerprinting, In: Stout S.A., Wang Z., editors. *Standard Handbook Oil Spill Environmental Forensics (Second Edition)*, Academic Press, Boston, pp. 917-959.
- Anderson M.T., Lloyd H. Woosley J., 2006. Water Availability for the Western United States: Key Scientific Challenges. *US Geological Survey Circular*. 1261, 85.
- Anumol T., Merel S., Clarke B.O., Snyder S.A., 2013. Ultra High Performance Liquid Chromatography Tandem Mass Spectrometry for Rapid Analysis of Trace Organic Contaminants in Water. *Chemistry Central Journal*. 7, 104. 10.1186/1752-153x-7-104.
- Avisar D., Horovitz I., Lozzi L., Ruggieri F., Baker M., Abel M.-L., Mamane H., 2013. Impact of Water Quality on Removal of Carbamazepine in Natural Waters by N-Doped TiO₂ Photo-Catalytic Thin Film Surfaces. *Journal of Hazardous Materials*. 244-245, 463-471. <https://doi.org/10.1016/j.jhazmat.2012.09.058>.
- Awfa D., Ateia M., Fujii M., Johnson M.S., Yoshimura C., 2018. Photodegradation of Pharmaceuticals and Personal Care Products in Water Treatment Using Carbonaceous-TiO₂ Composites: A Critical Review of Recent Literature. *Water Research*. 142, 26-45. <https://doi.org/10.1016/j.watres.2018.05.036>.
- Bahn Müller S., von Gunten U., Canonica S., 2014. Sunlight-Induced Transformation of Sulfadiazine and Sulfamethoxazole in Surface Waters and Wastewater Effluents. *Water research*. 57, 183-192.
- Barreto L.S., da Costa Souza A.T., Martins C.C., Araujo S.B.L., de Oliveira Ribeiro C.A., 2020. Urban Effluents Affect the Early Development Stages of Brazilian Fish Species with Implications for Their Population Dynamics. *Ecotoxicology and environmental safety*. 188, 109907.
- Batchu S.R., Panditi V.R., O'Shea K.E., Gardinali P.R., 2014. Photodegradation of Antibiotics under Simulated Solar Radiation: Implications for Their Environmental Fate. *Science of the total environment*. 470, 299-310.
- Baxter B.K., Butler J.K., 2020. Climate Change and Great Salt Lake, In: Baxter B.K., Butler J.K., editors. *Great Salt Lake Biology: A Terminal Lake in a Time of Change*, Springer International Publishing, Cham, pp. 23-52.
- Berelson W., Corsetti F., Johnson B., Vo T., Der C., 2008. Carbonate-Associated Sulfate as a Proxy for Lake Level Fluctuations: A Proof of Concept for Walker Lake, Nevada. *Journal of Paleolimnology*. 42, 25. 10.1007/s10933-008-9245-z.
- Bergheim M., Gminski R., Spangenberg B., Dębiak M., Bürkle A., Mersch-Sundermann V., Kümmerer K., Gieré R., 2014. Recalcitrant Pharmaceuticals in the Aquatic Environment: A Comparative Screening Study of Their Occurrence, Formation of

- Phototransformation Products and Their in Vitro Toxicity. *Environmental Chemistry*. 11, 431-444. <https://doi.org/10.1071/EN13218>.
- Biel-Maeso M., Corada-Fernández C., Lara-Martín P.A., 2018a. Monitoring the Occurrence of Pharmaceuticals in Soils Irrigated with Reclaimed Wastewater. *Environmental Pollution*. 235, 312-321.
- Biel-Maeso M., Corada-Fernández C., Lara-Martín P.A., 2018b. Monitoring the Occurrence of Pharmaceuticals in Soils Irrigated with Reclaimed Wastewater. *Environmental Pollution*. 235, 312-321. <https://doi.org/10.1016/j.envpol.2017.12.085>.
- Blaine A.C., Rich C.D., Sedlacko E.M., Hundal L.S., Kumar K., Lau C., Mills M.A., Harris K.M., Higgins C.P., 2014. Perfluoroalkyl Acid Distribution in Various Plant Compartments of Edible Crops Grown in Biosolids-Amended Soils. *Environmental Science & Technology*. 48, 7858-7865. 10.1021/es500016s.
- Blair B.D., Crago J.P., Hedman C.J., Klaper R.D., 2013. Pharmaceuticals and Personal Care Products Found in the Great Lakes above Concentrations of Environmental Concern. *Chemosphere*. 93, 2116-2123. <https://doi.org/10.1016/j.chemosphere.2013.07.057>.
- Bondarenko S., Gan J., Ernst F., Green R., Baird J., McCullough M., 2012. Leaching of Pharmaceuticals and Personal Care Products in Turfgrass Soils During Recycled Water Irrigation. *Journal of Environmental Quality*. 41, 1268-1274. 10.2134/jeq2011.0355.
- Bonvin F., Omlin J., Rutler R., Schweizer W.B., Alaimo P.J., Strathmann T.J., McNeill K., Kohn T., 2013. Direct Photolysis of Human Metabolites of the Antibiotic Sulfamethoxazole: Evidence for Abiotic Back-Transformation. *Environmental science & technology*. 47, 6746-6755.
- Boreen A.L., Arnold W.A., McNeill K., 2003. Photodegradation of Pharmaceuticals in the Aquatic Environment: A Review. *Aquatic Sciences*. 65, 320-341. 10.1007/s00027-003-0672-7.
- Boxall A.B.A., Johnson P., Smith E.J., Sinclair C.J., Stutt E., Levy L.S., 2006. Uptake of Veterinary Medicines from Soils into Plants. *Journal of Agricultural and Food Chemistry*. 54, 2288-2297. 10.1021/jf053041t.
- Boyd R.A., Furlong E.T., 2002: Human-Health Pharmaceutical Compounds in Lake Mead, Nevada and Arizona, and Las Vegas Wash, Nevada, October 2000-August 2001. *Journal*.
- Brent N.R., Schofield J., Miller K., 2001a: Results of the Lake Michigan Mass Balance Study: Atrazine Data Report *Journal*.
- Brent R.N., Schofield J., Miller K., 2001b. Results of the Lake Michigan Mass Balance Study: Atrazine Data Report. Vol: US Environmental Protection Agency, Great Lakes National Program Office.
- Brown J.N., Paxéus N., Förlin L., Larsson D.J., 2007. Variations in Bioconcentration of Human Pharmaceuticals from Sewage Effluents into Fish Blood Plasma. *Environmental Toxicology and Pharmacology*. 24, 267-274.
- Bulkley J.W., 2000. Global Overview: Water Resources and Distribution Issues. *Arab Studies Quarterly*, 1-12.

- Burtz R.T., Bright A.D., Shortsleeve A., 2020. Attitudes toward Water Allocation: Segmenting the Public on Beliefs toward Water Conservation. *Environmental Management*. 65, 306-320. 10.1007/s00267-019-01250-y.
- Calderón-Preciado D., Jiménez-Cartagena C., Matamoros V., Bayona J.M., 2011. Screening of 47 Organic Microcontaminants in Agricultural Irrigation Waters and Their Soil Loading. *Water Research*. 45, 221-231. <https://doi.org/10.1016/j.watres.2010.07.050>.
- Carena L., Vione D., 2020. Mapping the Photochemistry of European Mid-Latitudes Rivers: An Assessment of Their Ability to Photodegrade Contaminants. *Molecules*. 25, 424.
- Carter L.J., Williams M., Böttcher C., Kookana R.S., 2015. Uptake of Pharmaceuticals Influences Plant Development and Affects Nutrient and Hormone Homeostases. *Environmental Science & Technology*. 49, 12509-12518. 10.1021/acs.est.5b03468.
- Carter L.J., Harris E., Williams M., Ryan J.J., Kookana R.S., Boxall A.B.A., 2014. Fate and Uptake of Pharmaceuticals in Soil-Plant Systems. *Journal of Agricultural and Food Chemistry*. 62, 816-825. 10.1021/jf404282y.
- Challis J.K., Hanson M.L., Friesen K.J., Wong C.S., 2014. A Critical Assessment of the Photodegradation of Pharmaceuticals in Aquatic Environments: Defining Our Current Understanding and Identifying Knowledge Gaps. *Environmental Science: Processes & Impacts*. 16, 672-696.
- Chefetz B., Mualem T., Ben-Ari J., 2008. Sorption and Mobility of Pharmaceutical Compounds in Soil Irrigated with Reclaimed Wastewater. *Chemosphere*. 73, 1335-1343. <https://doi.org/10.1016/j.chemosphere.2008.06.070>.
- Chen F., Ying G.-G., Kong L.-X., Wang L., Zhao J.-L., Zhou L.-J., Zhang L.-J., 2011. Distribution and Accumulation of Endocrine-Disrupting Chemicals and Pharmaceuticals in Wastewater Irrigated Soils in Hebei, China. *Environmental Pollution*. 159, 1490-1498.
- Chen L., Wang Z., Qian C., He Y., 2018. Effects of Inorganic Anions on the Photolysis of Triclosan under Uv Irradiation. *Water Science and Technology*. 78, 1476-1480.
- Chen W., Xu J., Lu S., Jiao W., Wu L., Chang A.C., 2013. Fates and Transport of Ppcps in Soil Receiving Reclaimed Water Irrigation. *Chemosphere*. 93, 2621-2630. <https://doi.org/10.1016/j.chemosphere.2013.09.088>.
- Chen Y., Hu C., Hu X., Qu J., 2009. Indirect Photodegradation of Amine Drugs in Aqueous Solution under Simulated Sunlight. *Environmental Science & Technology*. 43, 2760-2765. 10.1021/es803325j.
- Chiron S., Minero C., Vione D., 2006. Photodegradation Processes of the Antiepileptic Drug Carbamazepine, Relevant to Estuarine Waters. *Environmental Science & Technology*. 40, 5977-5983. 10.1021/es060502y.
- Christou A., Karaolia P., Hapeshi E., Michael C., Fatta-Kassinou D., 2017. Long-Term Wastewater Irrigation of Vegetables in Real Agricultural Systems: Concentration of Pharmaceuticals in Soil, Uptake and Bioaccumulation in Tomato Fruits and Human Health Risk Assessment. *Water Research*. 109, 24-34. <https://doi.org/10.1016/j.watres.2016.11.033>.

- Christou A., Antoniou C., Christodoulou C., Hapeshi E., Stavrou I., Michael C., Fattakassinis D., Fotopoulos V., 2016. Stress-Related Phenomena and Detoxification Mechanisms Induced by Common Pharmaceuticals in Alfalfa (*Medicago Sativa* L.) Plants. *Science of The Total Environment*. 557-558, 652-664. <https://doi.org/10.1016/j.scitotenv.2016.03.054>.
- Dalkmann P., Siebe C., Amelung W., Schloter M., Siemens J., 2014. Does Long-Term Irrigation with Untreated Wastewater Accelerate the Dissipation of Pharmaceuticals in Soil? *Environmental Science & Technology*. 48, 4963-4970. 10.1021/es501180x.
- Dalkmann P., Broszat M., Siebe C., Willaschek E., Sakinc T., Huebner J., Amelung W., Grohmann E., Siemens J., 2012. Correction: Accumulation of Pharmaceuticals, Enterococcus, and Resistance Genes in Soils Irrigated with Wastewater for Zero to 100 Years in Central Mexico. *PLOS ONE*. 7, 10.1371/annotation/956a2a7c-714c-4233-ad3e-c7c0cefb1513. 10.1371/annotation/956a2a7c-714c-4233-ad3e-c7c0cefb1513.
- Daughton C.G., Ternes T.A., 1999. Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change? *Environmental health perspectives*. 107, 907-938.
- De Laurentiis E., Chiron S., Kouras-Hadef S., Richard C., Minella M., Maurino V., Minero C., Vione D., 2012. Photochemical Fate of Carbamazepine in Surface Freshwaters: Laboratory Measures and Modeling. *Environmental Science & Technology*. 46, 8164-8173. 10.1021/es3015887.
- Dickerson B.R., Vinyard G.L., 1999. Effects of High Levels of Total Dissolved Solids in Walker Lake, Nevada, on Survival and Growth of Lahontan Cutthroat Trout. *Transactions of the American Fisheries Society*. 128, 507-515.
- Dodgen L.K., Ueda A., Wu X., Parker D.R., Gan J., 2015. Effect of Transpiration on Plant Accumulation and Translocation of Ppcp/Edcs. *Environmental Pollution*. 198, 144-153. <https://doi.org/10.1016/j.envpol.2015.01.002>.
- Doll T.E., Frimmel F.H., 2003. Fate of Pharmaceuticals—Photodegradation by Simulated Solar Uv-Light. *Chemosphere*. 52, 1757-1769.
- Dong M.M., Trenholm R., Rosario-Ortiz F.L., 2015. Photochemical Degradation of Atenolol, Carbamazepine, Meprobamate, Phenytoin and Primidone in Wastewater Effluents. *J Hazard Mater*. 282, 216-23. 10.1016/j.jhazmat.2014.04.028.
- Durán-Álvarez J.C., Prado-Pano B., Jiménez-Cisneros B., 2012. Sorption and Desorption of Carbamazepine, Naproxen and Triclosan in a Soil Irrigated with Raw Wastewater: Estimation of the Sorption Parameters by Considering the Initial Mass of the Compounds in the Soil. *Chemosphere*. 88, 84-90. <https://doi.org/10.1016/j.chemosphere.2012.02.067>.
- Ebele A.J., Abou-Elwafa Abdallah M., Harrad S., 2017. Pharmaceuticals and Personal Care Products (Ppcps) in the Freshwater Aquatic Environment. *Emerging Contaminants*. 3, 1-16. <https://doi.org/10.1016/j.emcon.2016.12.004>.
- Elliott S.M., Brigham M.E., Lee K.E., Banda J.A., Choy S.J., Gefell D.J., Minarik T.A., Moore J.N., Jorgenson Z.G., 2017. Contaminants of Emerging Concern in Tributaries to the Laurentian Great Lakes: I. Patterns of Occurrence. *PloS one*. 12, e0182868.

- Fatta-Kassinos D., Vasquez M.I., Kümmerer K., 2011. Transformation Products of Pharmaceuticals in Surface Waters and Wastewater Formed During Photolysis and Advanced Oxidation Processes–Degradation, Elucidation of Byproducts and Assessment of Their Biological Potency. *Chemosphere*. 85, 693-709.
- Ferguson P.J., Bernot M.J., Doll J.C., Lauer T.E., 2013. Detection of Pharmaceuticals and Personal Care Products (Ppcps) in near-Shore Habitats of Southern Lake Michigan. *Science of The Total Environment*. 458-460, 187-196.
<https://doi.org/10.1016/j.scitotenv.2013.04.024>.
- Ferry M., Martinovic D., Backe W., Andrews A., 2017: Pharmaceuticals and Chemicals of Concern in Rivers: Occurrence and Biological Effects. *Journal*.
- Franklin A., Williams C., Andrews D., Woodward E., Watson J., 2015. Uptake of Three Antibiotics and an Antiepileptic Drug by Wheat Crops Spray Irrigated with Wastewater Treatment Plant Effluent. *Journal of Environment Quality*. 45. 10.2134/jeq2015.05.0257.
- Furlong R.A.B.a.E.T., 2002: Human-Health Pharmaceutical Compounds in Lake Mead, Nevada and Arizona, and Las Vegas Wash, Nevada, October 2000-August 2001 *Journal*.
- Gaw S., Thomas K.V., Hutchinson T.H., 2014. Sources, Impacts and Trends of Pharmaceuticals in the Marine and Coastal Environment. *Philos Trans R Soc Lond B Biol Sci*. 369. 10.1098/rstb.2013.0572.
- Geyer H.J., Rimkus G.G., Scheunert I., Kaune A., Schramm K.-W., Kettrup A., Zeeman M., Muir D.C., Hansen L.G., Mackay D., 2000. Bioaccumulation and Occurrence of Endocrine-Disrupting Chemicals (Edcs), Persistent Organic Pollutants (Pops), and Other Organic Compounds in Fish and Other Organisms Including Humans. *Bioaccumulation–New Aspects and Developments*, Springer, pp. 1-166.
- Gibson R., Durán-Álvarez J.C., Estrada K.L., Chávez A., Jiménez Cisneros B., 2010. Accumulation and Leaching Potential of Some Pharmaceuticals and Potential Endocrine Disruptors in Soils Irrigated with Wastewater in the Tula Valley, Mexico. *Chemosphere*. 81, 1437-1445.
<https://doi.org/10.1016/j.chemosphere.2010.09.006>.
- Goldstein M., Shenker M., Chefetz B., 2014. Insights into the Uptake Processes of Wastewater-Borne Pharmaceuticals by Vegetables. *Environmental Science & Technology*. 48, 5593-5600. 10.1021/es5008615.
- González-Naranjo V., Boltes K., Biel-Maeso M., 2013. Mobility of Ibuprofen, a Persistent Active Drug, in Soils Irrigated with Reclaimed Water. *Plant Soil and Environment*. 59, 68-73. 10.17221/590/2012-PSE.
- Gottschall N., Topp E., Metcalfe C., Edwards M., Payne M., Kleywegt S., Russell P., Lapen D.R., 2012. Pharmaceutical and Personal Care Products in Groundwater, Subsurface Drainage, Soil, and Wheat Grain, Following a High Single Application of Municipal Biosolids to a Field. *Chemosphere*. 87, 194-203.
<https://doi.org/10.1016/j.chemosphere.2011.12.018>.
- Grossberger A., Hadar Y., Borch T., Chefetz B., 2014. Biodegradability of Pharmaceutical Compounds in Agricultural Soils Irrigated with Treated Wastewater. *Environmental Pollution*. 185, 168-177.
<https://doi.org/10.1016/j.envpol.2013.10.038>.

- Guo J., Li Z., Ranasinghe P., Bonina S., Hosseini S., Corcoran M.B., Smalley C., Kaliappan R., Wu Y., Chen D., Sandy A.L., Wang Y., Rockne K.J., Sturchio N.C., Giesy J.P., Li A., 2016. Occurrence of Atrazine and Related Compounds in Sediments of Upper Great Lakes. *Environmental Science & Technology*. 50, 7335-7343. 10.1021/acs.est.6b00706.
- Guo Y.C., Krasner S.W., 2009a. Occurrence of Primidone, Carbamazepine, Caffeine, and Precursors for N-Nitrosodimethylamine in Drinking Water Sources Impacted by Wastewater. *JAWRA Journal of the American Water Resources Association*. 45, 58-67. 10.1111/j.1752-1688.2008.00289.x.
- Guo Y.C., Krasner S.W., 2009b. Occurrence of Primidone, Carbamazepine, Caffeine, and Precursors for N-Nitrosodimethylamine in Drinking Water Sources Impacted by Wastewater 1. *JAWRA Journal of the American Water Resources Association*. 45, 58-67.
- Hammad H.M., Zia F., Bakhat H.F., Fahad S., Ashraf M.R., Wilkerson C.J., Shah G.M., Nasim W., Khosa I., Shahid M., 2018. Uptake and Toxicological Effects of Pharmaceutical Active Compounds on Maize. *Agriculture, Ecosystems & Environment*. 258, 143-148. <https://doi.org/10.1016/j.agee.2018.02.022>.
- Haruta S., Chen W., Gan J., Šimůnek J., Chang A.C., Wu L., 2008. Leaching Risk of N-Nitrosodimethylamine (Ndma) in Soil Receiving Reclaimed Wastewater. *Ecotoxicology and Environmental Safety*. 69, 374-380.
- Hellauer K., Martínez Mayerlen S., Drewes J.E., Hübner U., 2019. Biotransformation of Trace Organic Chemicals in the Presence of Highly Refractory Dissolved Organic Carbon. *Chemosphere*. 215, 33-39. 10.1016/j.chemosphere.2018.09.166.
- Herklotz P.A., Gurung P., Vanden Heuvel B., Kinney C.A., 2010. Uptake of Human Pharmaceuticals by Plants Grown under Hydroponic Conditions. *Chemosphere*. 78, 1416-1421. <https://doi.org/10.1016/j.chemosphere.2009.12.048>.
- Hua W.Y., Bennett E.R., Maio X.-S., Metcalfe C.D., Letcher R.J., 2006. Seasonality Effects on Pharmaceuticals and S-Triazine Herbicides in Wastewater Effluent and Surface Water from the Canadian Side of the Upper Detroit River. *Environmental Toxicology and Chemistry*. 25, 2356-2365. 10.1897/05-571R.1.
- Huerta B., Rodriguez-Mozaz S., Lazorchak J., Barcelo D., Batt A., Wathen J., Stahl L., 2018. Presence of Pharmaceuticals in Fish Collected from Urban Rivers in the U.S. Epa 2008–2009 National Rivers and Streams Assessment. *Science of The Total Environment*. 634, 542-549. <https://doi.org/10.1016/j.scitotenv.2018.03.387>.
- Hyland K.C., Blaine A.C., Dickenson E.R.V., Higgins C.P., 2015. Accumulation of Contaminants of Emerging Concern in Food Crops—Part 1: Edible Strawberries and Lettuce Grown in Reclaimed Water. *Environmental Toxicology and Chemistry*. 34, 2213-2221. 10.1002/etc.3066.
- Jayampathi T., Atugoda T., Jayasinghe C., 2019. 4 - Uptake and Accumulation of Pharmaceuticals and Personal Care Products in Leafy Vegetables, In: Prasad M.N.V., Vithanage M., Kapley A., editors. *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*, Butterworth-Heinemann, pp. 87-113.
- Ji Y., Xie W., Fan Y., Shi Y., Kong D., Lu J., 2016. Degradation of Trimethoprim by Thermo-Activated Persulfate Oxidation: Reaction Kinetics and Transformation

- Mechanisms. *Chemical Engineering Journal*. 286, 16-24.
<https://doi.org/10.1016/j.cej.2015.10.050>.
- Joe E., Ron L., David H.B., R. M.B., Ian B.D., Graham C., Chris H.G., James W.S., Sarah N.E., David T., Michael P., Sandra W., Joseph E., Zak S., 2014: Terminal Lakes. *Journal*. 34.
- Karnjanapiboonwong A., Suski J.G., Shah A.A., Cai Q., Morse A.N., Anderson T.A., 2011. Occurrence of Ppcps at a Wastewater Treatment Plant and in Soil and Groundwater at a Land Application Site. *Water, Air, & Soil Pollution*. 216, 257-273. 10.1007/s11270-010-0532-8.
- Kasprzyk-Hordern B., Dinsdale R.M., Guwy A.J., 2009. The Removal of Pharmaceuticals, Personal Care Products, Endocrine Disruptors and Illicit Drugs During Wastewater Treatment and Its Impact on the Quality of Receiving Waters. *Water Research*. 43, 363-380. <https://doi.org/10.1016/j.watres.2008.10.047>.
- Kemper N., 2008. Veterinary Antibiotics in the Aquatic and Terrestrial Environment. *Ecological indicators*. 8, 1-13.
- Kidd K.A., Blanchfield P.J., Mills K.H., Palace V.P., Evans R.E., Lazorchak J.M., Flick R.W., 2007. Collapse of a Fish Population after Exposure to a Synthetic Estrogen. *Proceedings of the National Academy of Sciences*. 104, 8897-8901.
- Kiesling R.L., Elliott S.M., Kammel L.E., Choy S.J., Hummel S.L., 2019. Predicting the Occurrence of Chemicals of Emerging Concern in Surface Water and Sediment across the U.S. Portion of the Great Lakes Basin. *Science of The Total Environment*. 651, 838-850. <https://doi.org/10.1016/j.scitotenv.2018.09.201>.
- Kinney C.A., Furlong E.T., Werner S.L., Cahill J.D., 2006a. Presence and Distribution of Wastewater-Derived Pharmaceuticals in Soil Irrigated with Reclaimed Water. *Environmental Toxicology and Chemistry*. 25, 317-326. doi:10.1897/05-187R.1.
- Kinney C.A., Furlong E.T., Werner S.L., Cahill J.D., 2006b. Presence and Distribution of Wastewater-Derived Pharmaceuticals in Soil Irrigated with Reclaimed Water. *Environmental Toxicology and Chemistry: An International Journal*. 25, 317-326.
- Kolpin D.W., Furlong E.T., Meyer M.T., Thurman E.M., Zaugg S.D., Barber L.B., Buxton H.T., 2002. Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999–2000: A National Reconnaissance. *Environmental Science & Technology*. 36, 1202-1211. 10.1021/es011055j.
- Kong X., Wu Z., Ren Z., Guo K., Hou S., Hua Z., Li X., Fang J., 2018. Degradation of Lipid Regulators by the Uv/Chlorine Process: Radical Mechanisms, Chlorine Oxide Radical (ClO•)-Mediated Transformation Pathways and Toxicity Changes. *Water research*. 137, 242-250.
- Kumar A., Xagorarakis I., 2010. Human Health Risk Assessment of Pharmaceuticals in Water: An Uncertainty Analysis for Meprobamate, Carbamazepine, and Phenytoin. *Regulatory Toxicology and Pharmacology*. 57, 146-156.
<https://doi.org/10.1016/j.yrtph.2010.02.002>.
- Lahti M., Brozinski J.M., Jylhä A., Kronberg L., Oikari A., 2011. Uptake from Water, Biotransformation, and Biliary Excretion of Pharmaceuticals by Rainbow Trout. *Environmental Toxicology and Chemistry*. 30, 1403-1411.

- Lam M.W., Mabury S.A., 2005. Photodegradation of the Pharmaceuticals Atorvastatin, Carbamazepine, Levofloxacin, and Sulfamethoxazole in Natural Waters. *Aquatic Sciences*. 67, 177-188. [10.1007/s00027-004-0768-8](https://doi.org/10.1007/s00027-004-0768-8).
- Lam M.W., Tantuco K., Mabury S.A., 2003. Photofate: A New Approach in Accounting for the Contribution of Indirect Photolysis of Pesticides and Pharmaceuticals in Surface Waters. *Environmental Science & Technology*. 37, 899-907. [10.1021/es025902+](https://doi.org/10.1021/es025902+).
- Larson J.E.R., 2014. *Lake Line*. North American Lake Management Society. 34.
- Lee K.E., Langer S.K., Menheer M.A., Hansen D.S., Foreman W.T., Furlong E.T., Jorgenson Z.G., Choy S.J., Moore J.N., Banda J., 2015a: Chemicals of Emerging Concern in Water and Bottom Sediment in the Great Lakes Basin, 2012: Collection Methods, Analytical Methods, Quality Assurance, and Study Data. *Journal*.
- Lee K.E., Langer S.K., Menheer M.A., Hansen D.S., Foreman W.T., Furlong E.T., Jorgenson Z.G., Choy S.J., Moore J.N., Banda J., Gefell D.J., 2015b. Chemicals of Emerging Concern in Water and Bottom Sediment in the Great Lakes Basin, 2012—Collection Methods, Analytical Methods, Quality Assurance, and Study Data. U.S. Geological Survey Data Series, 14. <https://dx.doi.org/10.3133/ds910>.
- Liang X., Chen B., Nie X., Shi Z., Huang X., Li X., 2013. The Distribution and Partitioning of Common Antibiotics in Water and Sediment of the Pearl River Estuary, South China. *Chemosphere*. 92, 1410-1416.
- Liu J.-L., Wong M.-H., 2013. Pharmaceuticals and Personal Care Products (Ppcps): A Review on Environmental Contamination in China. *Environment International*. 59, 208-224. <https://doi.org/10.1016/j.envint.2013.06.012>.
- Liu W., Song X., Huda N., Xie M., Li G., Luo W., 2020. Comparison between Aerobic and Anaerobic Membrane Bioreactors for Trace Organic Contaminant Removal in Wastewater Treatment. *Environmental Technology & Innovation*. 17, 100564. <https://doi.org/10.1016/j.eti.2019.100564>.
- Liu Y., Yan S., Lian L., Ma J., Zhou H., Song W., 2019. Assessing the Contribution of Hydroxylation Species in the Photochemical Transformation of Primidone (Pharmaceutical). *Science of The Total Environment*. 696, 133826. <https://doi.org/10.1016/j.scitotenv.2019.133826>.
- Liu Z., Lu Y., Shi Y., Wang P., Jones K., Sweetman A.J., Johnson A.C., Zhang M., Zhou Y., Lu X., Su C., Sarvajayakesavaluc S., Khan K., 2017. Crop Bioaccumulation and Human Exposure of Perfluoroalkyl Acids through Multi-Media Transport from a Mega Fluorochemical Industrial Park, China. *Environment International*. 106, 37-47. <https://doi.org/10.1016/j.envint.2017.05.014>.
- Long E.R., Dutch M., Weakland S., Chandramouli B., Benskin J.P., 2013. Quantification of Pharmaceuticals, Personal Care Products, and Perfluoroalkyl Substances in the Marine Sediments of Puget Sound, Washington, USA. *Environmental Toxicology and Chemistry*. 32, 1701-1710. [10.1002/etc.2281](https://doi.org/10.1002/etc.2281).
- Luo T., Wan J., Ma Y., Wang Y., Wan Y., 2019. Sulfamethoxazole Degradation by an Fe(II)-Activated Persulfate Process: Insight into the Reactive Sites, Product Identification and Degradation Pathways. *Environmental Science: Processes & Impacts*. 21, 1560-1569. [10.1039/C9EM00254E](https://doi.org/10.1039/C9EM00254E).

- Luster E., Avisar D., Horovitz I., Lozzi L., Baker M.A., Grilli R., Mamane H., 2017. N-Doped Tio₂-Coated Ceramic Membrane for Carbamazepine Degradation in Different Water Qualities. *Nanomaterials*. 7, 206.
- Malchi T., Maor Y., Tadmor G., Shenker M., Chefetz B., 2014. Irrigation of Root Vegetables with Treated Wastewater: Evaluating Uptake of Pharmaceuticals and the Associated Human Health Risks. *Environmental Science & Technology*. 48, 9325-9333. 10.1021/es5017894.
- Marioni N.K., 2007. Effects of Declining Lake Levels on Fish Populations in Walker Lake, Nevada. Vol: University of Nevada, Reno.
- Martínez-Piernas A.B., Plaza-Bolaños P., Fernández-Ibáñez P., Agüera A., 2019. Organic Microcontaminants in Tomato Crops Irrigated with Reclaimed Water Grown under Field Conditions: Occurrence, Uptake, and Health Risk Assessment. *Journal of Agricultural and Food Chemistry*. 67, 6930-6939. 10.1021/acs.jafc.9b01656.
- Matamoros V., Duhec A., Albaigés J., Bayona J.M., 2009. Photodegradation of Carbamazepine, Ibuprofen, Ketoprofen and 17 α -Ethinylestradiol in Fresh and Seawater. *Water, Air, and Soil Pollution*. 196, 161.
- McEachran A.D., Shea D., Bodnar W., Nichols E.G., 2016. Pharmaceutical Occurrence in Groundwater and Surface Waters in Forests Land-Applied with Municipal Wastewater. *Environmental toxicology and chemistry*. 35, 898-905. 10.1002/etc.3216.
- McNeill K., Canonica S., 2016. Triplet State Dissolved Organic Matter in Aquatic Photochemistry: Reaction Mechanisms, Substrate Scope, and Photophysical Properties. *Environmental Science: Processes & Impacts*. 18, 1381-1399. 10.1039/C6EM00408C.
- Mead R.N., Barefoot S., Helms J.R., Morgan J.B., Kieber R.J., 2014. Photodegradation of the Antihistamine Cetirizine in Natural Waters. *Environmental Toxicology and Chemistry*. 33, 2240-2245. <https://doi.org/10.1002/etc.2691>.
- Meredith-Williams M., Carter L.J., Fussell R., Raffaelli D., Ashauer R., Boxall A.B., 2012. Uptake and Depuration of Pharmaceuticals in Aquatic Invertebrates. *Environmental pollution*. 165, 250-258.
- Mestre A.S., Carvalho A.P., 2019. Photocatalytic Degradation of Pharmaceuticals Carbamazepine, Diclofenac, and Sulfamethoxazole by Semiconductor and Carbon Materials: A Review. *Molecules (Basel, Switzerland)*. 24, 3702. 10.3390/molecules24203702.
- Miège C., Choubert J.M., Ribeiro L., Eusèbe M., Coquery M., 2009. Fate of Pharmaceuticals and Personal Care Products in Wastewater Treatment Plants – Conception of a Database and First Results. *Environmental Pollution*. 157, 1721-1726. <https://doi.org/10.1016/j.envpol.2008.11.045>.
- Moore W.A.W.C.M.S.E.N.R.J.D.P.W.M.H.F.H.J., 2017. Decline of the World's Saline Lakes. *Nature Geoscience*. 10.1038/ngeo3052.
- Nason S.L., Miller E.L., Karthikeyan K.G., Pedersen J.A., 2019. Effects of Binary Mixtures and Transpiration on Accumulation of Pharmaceuticals by Spinach. *Environmental Science & Technology*. 53, 4850-4859. 10.1021/acs.est.8b05515.

- Nations H., Erwin T., 2009. Tricerascope: An Update on the Triple Threat Robotic Telescope of the College of Southern Nevada. American Astronomical Society Meeting Abstracts# 213. 213, pp. 474.11.
- Nilsen E., Furlong E.T., Rosenbauer R., 2014. Reconnaissance of Pharmaceuticals and Wastewater Indicators in Streambed Sediments of the Lower Columbia River Basin, Oregon and Washington. JAWRA Journal of the American Water Resources Association. 50, 291-301. <https://doi.org/10.1111/jawr.12161>.
- Niu J., Zhang L., Li Y., Zhao J., Lv S., Xiao K., 2013. Effects of Environmental Factors on Sulfamethoxazole Photodegradation under Simulated Sunlight Irradiation: Kinetics and Mechanism. Journal of Environmental Sciences. 25, 1098-1106. [https://doi.org/10.1016/S1001-0742\(12\)60167-3](https://doi.org/10.1016/S1001-0742(12)60167-3).
- Pan C.-G., Liu Y.-S., Ying G.-G., 2016. Perfluoroalkyl Substances (Pfas) in Wastewater Treatment Plants and Drinking Water Treatment Plants: Removal Efficiency and Exposure Risk. Water Research. 106, 562-570. <https://doi.org/10.1016/j.watres.2016.10.045>.
- Pan M., Chu L.M., 2017. Fate of Antibiotics in Soil and Their Uptake by Edible Crops. Science of The Total Environment. 599-600, 500-512. <https://doi.org/10.1016/j.scitotenv.2017.04.214>.
- Pan M., Wong C.K.C., Chu L.M., 2014. Distribution of Antibiotics in Wastewater-Irrigated Soils and Their Accumulation in Vegetable Crops in the Pearl River Delta, Southern China. Journal of Agricultural and Food Chemistry. 62, 11062-11069. 10.1021/jf503850v.
- Pomati F., Castiglioni S., Zuccato E., Fanelli R., Vigetti D., Rossetti C., Calamari D., 2006. Effects of a Complex Mixture of Therapeutic Drugs at Environmental Levels on Human Embryonic Cells. Environmental Science & Technology. 40, 2442-2447. 10.1021/es051715a.
- Poustie A., Yang Y., Verburg P., Pagilla K., Hanigan D., 2020. Reclaimed Wastewater as a Viable Water Source for Agricultural Irrigation: A Review of Food Crop Growth Inhibition and Promotion in the Context of Environmental Change. Science of The Total Environment. 739, 139756. <https://doi.org/10.1016/j.scitotenv.2020.139756>.
- Radjenović J., Jelić A., Petrović M., Barceló D., 2009. Determination of Pharmaceuticals in Sewage Sludge by Pressurized Liquid Extraction (Ple) Coupled to Liquid Chromatography-Tandem Mass Spectrometry (Lc-Ms/Ms). Analytical and Bioanalytical Chemistry. 393, 1685-1695. 10.1007/s00216-009-2604-4.
- Revitt D.M., Balogh T., Jones H., 2015. Sorption Behaviours and Transport Potentials for Selected Pharmaceuticals and Triclosan in Two Sterilised Soils. Journal of Soils and Sediments. 15, 594-606. 10.1007/s11368-014-1025-y.
- Richardson B.J., Lam P.K., Martin M., 2005. Emerging Chemicals of Concern: Pharmaceuticals and Personal Care Products (Ppcps) in Asia, with Particular Reference to Southern China. Marine Pollution Bulletin. 50, 913-920.
- Ringwall K., 2018. Beeftalk: Expect to Hang Two-Thirds of the Cow's Weight on the Rail. [https://www.drovers.com/article/beeftalk-expect-hang-two-thirds-cows-weight-rail.\[4/29/2020\]](https://www.drovers.com/article/beeftalk-expect-hang-two-thirds-cows-weight-rail.[4/29/2020]).

- Runkle J., K. Kunkel, S. Champion, and D. Easterling, 2017: Nevada State Climate Summary. *Journal. NOAA Technical Report NESDIS 149-NV*, 4 pp.
- Sathishkumar P., Meena R.A.A., Palanisami T., Ashokkumar V., Palvannan T., Gu F.L., 2020. Occurrence, Interactive Effects and Ecological Risk of Diclofenac in Environmental Compartments and Biota - a Review. *Science of The Total Environment*. 698, 134057. <https://doi.org/10.1016/j.scitotenv.2019.134057>.
- Schaffer M., Licha T., 2015. A Framework for Assessing the Retardation of Organic Molecules in Groundwater: Implications of the Species Distribution for the Sorption-Influenced Transport. *Science of the Total Environment*. 524, 187-194.
- Schrage J.K., 2016. The Salton Sea's Migratory Birds Mass-Mortality and Those Impacts Along the Pacific Flyway. *SUSTAINABILITY OF THE SALTON SEA: A REVIEW OF THE ENVIRONMENTAL, ECONOMIC, AND SOCIAL CLIMATE AROUND CALIFORNIA'S LARGEST SALINE LAKE*, 7.
- Schultz M.M., Furlong E.T., 2008. Trace Analysis of Antidepressant Pharmaceuticals and Their Select Degradates in Aquatic Matrixes by Lc/Esi/Ms/Ms. *Analytical Chemistry*. 80, 1756-1762. 10.1021/ac702154e.
- Schultz M.M., Furlong E.T., Kolpin D.W., Werner S.L., Schoenfuss H.L., Barber L.B., Blazer V.S., Norris D.O., Vajda A.M., 2010a. Antidepressant Pharmaceuticals in Two U.S. Effluent-Impacted Streams: Occurrence and Fate in Water and Sediment, and Selective Uptake in Fish Neural Tissue. *Environmental Science & Technology*. 44, 1918-1925. 10.1021/es9022706.
- Schultz M.M., Furlong E.T., Kolpin D.W., Werner S.L., Schoenfuss H.L., Barber L.B., Blazer V.S., Norris D.O., Vajda A.M., 2010b. Antidepressant Pharmaceuticals in Two U.S. Effluent-Impacted Streams: Occurrence and Fate in Water and Sediment, and Selective Uptake in Fish Neural Tissue. *Environ Sci Technol*. 44, 1918-25. 10.1021/es9022706.
- Scott P.D., Coleman H.M., Colville A., Lim R., Matthews B., McDonald J.A., Miranda A., Neale P.A., Nugegoda D., Tremblay L.A., Leusch F.D.L., 2017. Assessing the Potential for Trace Organic Contaminants Commonly Found in Australian Rivers to Induce Vitellogenin in the Native Rainbowfish (*Melanotaenia Fluvialtilis*) and the Introduced Mosquitofish (*Gambusia Holbrooki*). *Aquatic Toxicology*. 185, 105-120. <https://doi.org/10.1016/j.aquatox.2017.02.008>.
- Scott P.D., Bartkow M., Blockwell S.J., Coleman H.M., Khan S.J., Lim R., McDonald J.A., Nice H., Nugegoda D., Pettigrove V., Tremblay L.A., Warne M.S.J., Leusch F.D.L., 2014. A National Survey of Trace Organic Contaminants in Australian Rivers. *Journal of Environmental Quality*. 43, 1702-1712. 10.2134/jeq2014.01.0012.
- Sedinger J.S., Blomberg E.J., VanDellen A.W., Byers S., 2012. Environmental and Population Strain Effects on Survival of Lahontan Cutthroat Trout in Walker Lake, Nevada: A Bayesian Approach. *North American Journal of Fisheries Management*. 32, 515-522.
- Selk G., 2018. How Much Hay Will a Cow Consume? [https://www.drovers.com/article/how-much-hay-will-cow-consume-0.\[4/29/2020\]](https://www.drovers.com/article/how-much-hay-will-cow-consume-0.[4/29/2020]).

- Sharma P., Poustie A., Verburg P., Pagilla K., Yang Y., Hanigan D., 2020. Trace Organic Contaminants in Field-Scale Cultivated Alfalfa, Soil, and Pore Water after 10 years of Irrigation with Reclaimed Wastewater. *Science of The Total Environment*. 744, 140698. <https://doi.org/10.1016/j.scitotenv.2020.140698>.
- Snyder S.A., 2007. Removal of Edcs and Pharmaceuticals in Drinking and Reuse Treatment Processes.
- Somathilake P., Dominic J.A., Achari G., Langford C.H., Tay J.-H., 2018. Degradation of Carbamazepine by Photo-Assisted Ozonation: Influence of Wavelength and Intensity of Radiation. *Ozone: Science & Engineering*. 40, 113-121. 10.1080/01919512.2017.1398635.
- Sorensen E.D., Hoven H.M., Neill J., 2020. Great Salt Lake Shorebirds, Their Habitats, and Food Base, In: Baxter B.K., Butler J.K., editors. *Great Salt Lake Biology: A Terminal Lake in a Time of Change*, Springer International Publishing, Cham, pp. 263-309.
- Sun Q., Lv M., Hu A., Yang X., Yu C.-P., 2014. Seasonal Variation in the Occurrence and Removal of Pharmaceuticals and Personal Care Products in a Wastewater Treatment Plant in Xiamen, China. *Journal of hazardous materials*. 277, 69-75.
- Tanoue R., Sato Y., Motoyama M., Nakagawa S., Shinohara R., Nomiyama K., 2012. Plant Uptake of Pharmaceutical Chemicals Detected in Recycled Organic Manure and Reclaimed Wastewater. *Journal of Agricultural and Food Chemistry*. 60, 10203-10211. 10.1021/jf303142t.
- Tanoue R., Nomiyama K., Nakamura H., Kim J.-W., Isobe T., Shinohara R., Kunisue T., Tanabe S., 2015. Uptake and Tissue Distribution of Pharmaceuticals and Personal Care Products in Wild Fish from Treated-Wastewater-Impacted Streams. *Environmental science & technology*. 49, 11649-11658.
- Ternes T.A., Bonerz M., Herrmann N., Teiser B., Andersen H.R., 2007. Irrigation of Treated Wastewater in Braunschweig, Germany: An Option to Remove Pharmaceuticals and Musk Fragrances. *Chemosphere*. 66, 894-904. <https://doi.org/10.1016/j.chemosphere.2006.06.035>.
- Tierney D.P., Nelson P.A., Christensen B.R., Kloiber S.M., 1999. Predicted Atrazine Concentrations in the Great Lakes: Implications for Biological Effects. *Journal of Great Lakes Research*. 25, 455-467. [https://doi.org/10.1016/S0380-1330\(99\)70754-9](https://doi.org/10.1016/S0380-1330(99)70754-9).
- Trovó A.G., Nogueira R.F., Agüera A., Sirtori C., Fernández-Alba A.R., 2009. Photodegradation of Sulfamethoxazole in Various Aqueous Media: Persistence, Toxicity and Photoproducts Assessment. *Chemosphere*. 77, 1292-1298.
- USDA-NRCS, 2020. Soil Water Characteristics. [https://www.nrcs.usda.gov/wps/portal/nrcs/detailfull/national/water/manage/drainage/?cid=stelprdb1045310.\[06/26/2020\]](https://www.nrcs.usda.gov/wps/portal/nrcs/detailfull/national/water/manage/drainage/?cid=stelprdb1045310.[06/26/2020]).
- Valdés M.E., Huerta B., Wunderlin D.A., Bistoni M.A., Barceló D., Rodríguez-Mozaz S., 2016. Bioaccumulation and Bioconcentration of Carbamazepine and Other Pharmaceuticals in Fish under Field and Controlled Laboratory Experiments. Evidences of Carbamazepine Metabolization by Fish. *Science of The Total Environment*. 557-558, 58-67. <https://doi.org/10.1016/j.scitotenv.2016.03.045>.

- Vasquez M.I., Lambrianides A., Schneider M., Kümmerer K., Fatta-Kassinos D., 2014. Environmental Side Effects of Pharmaceutical Cocktails: What We Know and What We Should Know. *Journal of Hazardous Materials*. 279, 169-189. <https://doi.org/10.1016/j.jhazmat.2014.06.069>.
- Wang J., Wang K., Guo Y., Niu J., 2020a. Photochemical Degradation of Nebivolol in Different Natural Organic Matter Solutions under Simulated Sunlight Irradiation: Kinetics, Mechanism and Degradation Pathway. *Water Research*. 173, 115524.
- Wang S., Matt M., Murphy B.L., Perkins M., Matthews D.A., Moran S.D., Zeng T., 2020b. Organic Micropollutants in New York Lakes: A Statewide Citizen Science Occurrence Study. *Environmental Science & Technology*. 54, 13759-13770. 10.1021/acs.est.0c04775.
- Wilkie M.P., Wright P.A., Iwama G.K., Wood C.M., 1993. The Physiological Responses of the Lahontan Cutthroat Trout (*Oncorhynchus Clarki Henshawi*), a Resident of Highly Alkaline Pyramid Lake (Ph 9.4), to Challenge at Ph 10. *Journal of Experimental Biology*. 175, 173-194.
- Wilkinson J., Hooda P.S., Barker J., Barton S., Swinden J., 2017. Occurrence, Fate and Transformation of Emerging Contaminants in Water: An Overarching Review of the Field. *Environmental Pollution*. 231, 954-970. <https://doi.org/10.1016/j.envpol.2017.08.032>.
- Wilkinson J.L., Hooda P.S., Swinden J., Barker J., Barton S., 2018. Spatial (Bio) Accumulation of Pharmaceuticals, Illicit Drugs, Plasticisers, Perfluorinated Compounds and Metabolites in River Sediment, Aquatic Plants and Benthic Organisms. *Environmental pollution*. 234, 864-875.
- Williams W.D., 2002. Environmental Threats to Salt Lakes and the Likely Status of Inland Saline Ecosystems in 2025. *Environmental conservation*. 29, 154-167.
- WRCC, 2020. [http://wrcc.dri.edu/scacis.rcc-acis.org.\[4/15/2020\]](http://wrcc.dri.edu/scacis.rcc-acis.org.[4/15/2020]).
- Wright L., Devitt D.A., Young M.H., Gan J., Vanderford B.J., Snyder S.A., McCullough M., Dodgen L., 2012. Fate and Transport of Thirteen Pharmaceutical and Personal Care Products in a Controlled Irrigated Turfgrass System. *Agronomy journal*. 104, 1244-1254.
- Wu C., Spongberg A.L., Witter J.D., Fang M., Czajkowski K.P., 2010. Uptake of Pharmaceutical and Personal Care Products by Soybean Plants from Soils Applied with Biosolids and Irrigated with Contaminated Water. *Environmental Science & Technology*. 44, 6157-6161. 10.1021/es1011115.
- Wu X., Conkle J.L., Gan J., 2012. Multi-Residue Determination of Pharmaceutical and Personal Care Products in Vegetables. *Journal of Chromatography A*. 1254, 78-86. <https://doi.org/10.1016/j.chroma.2012.07.041>.
- Wu X., Ernst F., Conkle J.L., Gan J., 2013. Comparative Uptake and Translocation of Pharmaceutical and Personal Care Products (Ppcps) by Common Vegetables. *Environment International*. 60, 15-22. <https://doi.org/10.1016/j.envint.2013.07.015>.
- Wu X., Conkle J.L., Ernst F., Gan J., 2014. Treated Wastewater Irrigation: Uptake of Pharmaceutical and Personal Care Products by Common Vegetables under Field Conditions. *Environmental Science & Technology*. 48, 11286-11293. 10.1021/es502868k.

- Wu X., Dodgen L.K., Conkle J.L., Gan J., 2015. Plant Uptake of Pharmaceutical and Personal Care Products from Recycled Water and Biosolids: A Review. *Science of The Total Environment*. 536, 655-666. <https://doi.org/10.1016/j.scitotenv.2015.07.129>.
- Wurtsbaugh W.A., Miller C., Null S.E., DeRose R.J., Wilcock P., Hahnenberger M., Howe F., Moore J., 2017. Decline of the World's Saline Lakes. *Nature Geoscience*. 10, 816-821.
- WWAP, 2012: The United Nations World Water Development Report 4: Managing Water under Uncertainty and Risk. *Journal*.
- WWAP, 2017. Wastewater: The Untapped Resource, the United Nations World Water Development Report, UNESCO, Paris.
- Xu J., Wu L., Chen W., Chang A.C., 2008. Simultaneous Determination of Pharmaceuticals, Endocrine Disrupting Compounds and Hormone in Soils by Gas Chromatography–Mass Spectrometry. *Journal of Chromatography A*. 1202, 189-195.
- Xu J., Wu L., Chang A.C., Zhang Y., 2010. Impact of Long-Term Reclaimed Wastewater Irrigation on Agricultural Soils: A Preliminary Assessment. *Journal of Hazardous Materials*. 183, 780-786. <https://doi.org/10.1016/j.jhazmat.2010.07.094>.
- Xu J., Chen W., Wu L., Green R., Chang A.C., 2009a. Leachability of Some Emerging Contaminants in Reclaimed Municipal Wastewater-Irrigated Turf Grass Fields. *Environmental Toxicology and Chemistry: An International Journal*. 28, 1842-1850.
- Xu J., Chen W., Wu L., Green R., Chang A.C., 2009b. Leachability of Some Emerging Contaminants in Reclaimed Municipal Wastewater-Irrigated Turf Grass Fields. *Environmental Toxicology and Chemistry*. 28, 1842-1850. 10.1897/08-471.1.
- Yamamoto H., Nakamura Y., Moriguchi S., Nakamura Y., Honda Y., Tamura I., Hirata Y., Hayashi A., Sekizawa J., 2009. Persistence and Partitioning of Eight Selected Pharmaceuticals in the Aquatic Environment: Laboratory Photolysis, Biodegradation, and Sorption Experiments. *Water research*. 43, 351-362.
- Yang L., Zhou Y., Shi B., Meng J., He B., Yang H., Yoon S.J., Kim T., Kwon B.-O., Khim J.S., Wang T., 2020. Anthropogenic Impacts on the Contamination of Pharmaceuticals and Personal Care Products (Ppcps) in the Coastal Environments of the Yellow and Bohai Seas. *Environment International*. 135, 105306. <https://doi.org/10.1016/j.envint.2019.105306>.
- Yang Y.-y., Toor G.S., Williams C.F., 2015. Pharmaceuticals and Organochlorine Pesticides in Sediments of an Urban River in Florida, USA. *Journal of Soils and Sediments*. 15, 993-1004. <http://dx.doi.org/10.1007/s11368-015-1077-7>.
- Yi C., Song L., Wu Q., Li Z., Zhang W., Yin K., 2020. Enhanced Photodegradation of Diphenhydramine in Aqueous Solution Containing Natural Sand Particles. *RSC Advances*. 10, 17228-17234. 10.1039/D0RA02019B.
- Young R.B., Chefetz B., Liu A., Desyaterik Y., Borch T., 2014. Direct Photodegradation of Lamotrigine (an Antiepileptic) in Simulated Sunlight–Ph Influenced Rates and Products. *Environmental Science: Processes & Impacts*. 16, 848-857.

- Zepp R.G., Hoigne J., Bader H., 1987. Nitrate-Induced Photooxidation of Trace Organic Chemicals in Water. *Environmental Science & Technology*. 21, 443-450. 10.1021/es00159a004.
- Zhang J., Hanigan D., Westerhoff P., Herckes P., 2016. N-Nitrosamine Formation Kinetics in Wastewater Effluents and Surface Waters. *Environmental Science: Water Research & Technology*. 2, 312-319. 10.1039/C5EW00234F.
- Zhang S., Zhang Q., Darisaw S., Ehie O., Wang G., 2007. Simultaneous Quantification of Polycyclic Aromatic Hydrocarbons (Pahs), Polychlorinated Biphenyls (Pcbs), and Pharmaceuticals and Personal Care Products (Ppcps) in Mississippi River Water, in New Orleans, Louisiana, USA. *Chemosphere*. 66, 1057-1069. <https://doi.org/10.1016/j.chemosphere.2006.06.067>.

Chapter 9

APPENDIX A

The following contains the supplementary information for: Trace Organic Contaminants in Field-scale Cultivated Alfalfa, Soil, and Pore Water after 10 Years of Irrigation with Reclaimed Wastewater*

*Published: Priyamvada Sharma, Andrew Poustie, Paul Verburg, Krishna Pagilla, Yu Yang, David Hanigan, Trace organic contaminants in field-scale cultivated alfalfa, soil, and pore water after 10 years of irrigation with reclaimed wastewater, Science of The Total Environment, Volume 744, 2020, 140698, ISSN 0048-9697, <https://doi.org/10.1016/j.scitotenv.2020.140698>

Method for water, soil, and alfalfa extraction

Aqueous samples were filtered, and 100 μ g/L of isotopes added. Samples were then extracted using an AutoTrace 280 automated SPE (Thermo Fisher, Sunnyvale, CA) with Oasis Hydrophilic Lipophilic Balance (HLB) cartridges (6 cc/200 mg, Waters Corporation, MA, USA) to clean up the filtered aqueous samples. Samples were then reconstituted with 1 mL methanol, filtered, and analyzed by LC-MS/MS. HLB cartridges were preconditioned sequentially with 5 mL of MTBE, methanol, and ultrapure water. Samples were then loaded at 10 mL/min onto the cartridges. The cartridges were rinsed with ultrapure water and dried under gentle nitrogen flow for 30 mins. Finally, analytes were eluted with 5 mL of methanol followed by 5 mL of 90/10 (v/v) MTBE/methanol. The approximately 10 mL of eluent was then evaporated to less than 500 μ L using a gentle stream of ultrahigh purity (UHP) nitrogen flow in a Biotage TurboVap LV and the final volume was adjusted to 1 mL with methanol. Final extracts were transferred into 2-mL amber vials and stored in darkness at -20°C until analyzed by LC-MS/MS.

Soil samples were first frozen at -20°C overnight, transferred into freeze-dryer vials the next day, and placed in a FreeZone 4.5 L freeze-dryer (Labconco Corporation, MO, USA) set to -40°C and 0.1 mBar for >24 hrs, and stored at -20°C until analysis. The samples were extracted with an ASE 200 (Dionex, Sunnyvale, CA) fit with 11 mL stainless extraction cells. Freeze-dried soil (2 g) was mixed with diatomaceous earth to act as a sample dispersant, extraction cell filler and drying agent.

The soil extraction method was optimized by testing various extraction solvents, temperature, and time with freeze dried soil spiked with 250 ng/g DW of 12 TrOCs. The extraction solvents were 7:3 acetonitrile-water, 1:1 and 1:2 methanol-water, on a volume basis, and pure methanol. Three extraction temperatures (75°C , 100°C , and 120°C) and two extraction time periods (5 min and 15 min) were tested. The selected ASE 200 operating conditions included preheat- 5 min, static- 5 min, pressure- 1500 psi, temperature- 100°C , three extraction cycles with 100% solvent flush and 60 s nitrogen purge with extraction solvent (1:2 v/v) methanol-water. The optimized method resulted in recovery from a spiked soil sample of $\geq 56\%$ for seven TrOCs and ranged from 15% to 36% for the remaining three pharmaceuticals and one herbicide.

The ASE extract (~ 43 mL) was diluted with ultrapure water to a final volume of 1000 mL and cleaned-up by SPE with HLB cartridges. The cartridges were conditioned with 5 mL methanol followed by 5 mL of ultrapure water. 1,000 mL of sample was loaded on the cartridge at a rate of 10 mL/min and dried with UHP nitrogen for 30 min. Analytes were eluted with 8 mL methanol at 1 mL/min and evaporated to < 1 mL in a Biotage Turbovap LV under UHP nitrogen flow. The final volume was adjusted to 1 mL with methanol-water

solution (25:75, v/v). 100 µg/L of internal standards (isotopes) were added and transferred into 2 mL amber vials and stored in darkness at -20°C until analyzed by LC-MS/MS in ESI+ mode. Isotopically labeled standards are typically spiked to the soil extract rather than the soil itself because of the relatively large mass needed to be spiked to the soil and associated costs. The recoveries of TrOCs with various solvents is in Table A-1.

Table A- 1 Percent recoveries of compounds in a representative spiked soil sample.

Compounds	7:3 Acetonitrile: water (no SPE)	1:1 Methanol: Water	1:2 Methanol: Water
Atrazine	20	14±0.8	15±1
Caffeine	45	53±11	74±17
Carbamazepine	80	165±14	265±160
DEET	52	172±79	124±6
Diphenhydramine	12	9±12	15±3
Fluoxetine	28	14±7	17±2
Meprobamate	55	144±35	118±13
Primidone	94	94±19	86±29
Sulfamethoxazole	29	31±15	36±5
Trimethoprim	20	100±59	56±6

Alfalfa samples were separated into their respective components (shoots and leaves). Samples were thoroughly rinsed with ultrapure water to remove soil or other organic matter. Shoots and leaves were cut into 5 mm pieces and frozen overnight. Frozen plant material was transferred into freeze-dryer vials and placed in a FreeZone 4.5 L freeze-dryer, set to -50°C and 0.1 mBar for >24 hr. Freeze dried shoots and leaves were ground to powder using a mortar and pestle or a conical burr coffee grinder (Capresso, NJ, USA) at the finest setting. Ground material was sieved with a US Standard #60 (250 micron) sieve and kept in vials. 0.2 g of ground material was placed into a 50 mL centrifuge tube, spiked with isotopes (25 ng g⁻¹ DW), 20 mL MTBE was added, and samples were sonicated for 20 min and then centrifuged at 1,000 RCF for 20 min. The supernatant was decanted

into a separate 50 mL centrifuge tube. The sonication, centrifugation, and decanting step was then repeated on the original tube with 20 mL acetonitrile. The combined decantate was then evaporated to near dryness under a gentle nitrogen gas stream. The residue was reconstituted with 20 mL ultrapure water and 1 mL methanol. SPE was performed using HLB cartridges. HLB cartridges were conditioned with 5 mL methanol and 5 mL ultrapure water before the samples were loaded at 3 mL/min. Cartridges were then dried with UHP nitrogen gas for 60 min before being eluted with 5 mL methanol. The eluates were evaporated in a TurboVap LV under a gentle nitrogen stream to near dryness. Samples were then reconstituted with 1 mL methanol and filtered with 0.2 µm PTFE filters (Cole-Parmer, Illinois, USA) to remove remaining solids. 2-mL amber vials containing the final sample were stored at -20°C, before being analyzed by LC-MS/MS.

TrOCs speciation

Soil pH was measured from 7.24 to 7.91 for 0-20 cm, 20-40 cm, and 40-60 cm depth, respectively. Surface soil (0-20 cm) was characterized by A&L Western Laboratories, Modesto, CA, and soil properties are listed in Table A-2. The USDA-NRCS (2020) soil classification is sandy loam.

Table A- 2 Surface soil (0-20 cm) properties.

Parameter	Unit	Value
pH		7.9
Organic matter	(%)	5.8
Salinity	(dS/cm)	< 1
Base saturation	(%)	100
CEC	(meq/100g)	34
Clay	(%)	18
Silt	(%)	21
Sand	(%)	61

Table A- 3 Properties of the selected TrOCs selected for this study.

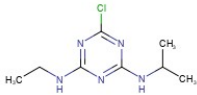
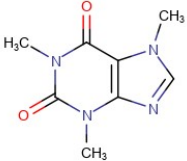
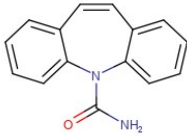
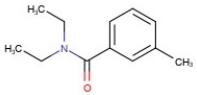
Compound & CAS Number	Atrazine 1912-24-9	Caffeine 58-08-2	Carbamazepine 298-46-4	DEET 134-62-3
Classification	Herbicide	Stimulant	Anticonvulsant	Topical Agent
Elemental Composition	C ₈ H ₁₄ ClN ₅	C ₈ H ₁₀ N ₄ O ₂	C ₁₅ H ₁₂ N ₂ O	C ₁₂ H ₁₇ NO
Molecular Weight (g mol ⁻¹)	215	194	236	191
Structure ¹				
Solubility (mg/L ³)	214	2,632	18	666
pK _a ¹	4.20, 14.48, 15.84	-1.16	-3.75, 15.96	-0.95
log K _{ow} ¹	2.06	-0.79	3.22	2.34
f _n ² (pH=7.5)	0.9995	1	1	1

Table A- 3. continued.

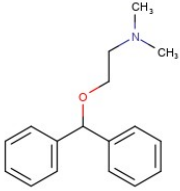
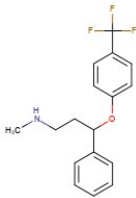
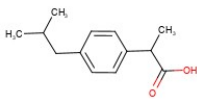
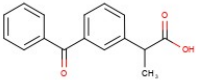
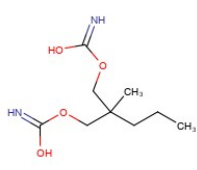
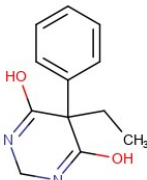
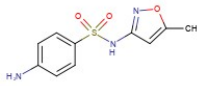
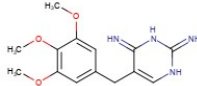
Compound & CAS Number	Diphenhydramine 58-73-1	Fluoxetine 2-84-9	Ibuprofen 15687-27-1	Ketoprofen 22071-15-4
Classification	Antihistamine	Antidepressant	Anti-Inflammatory	Anti-Inflammatory
Elemental Composition	C ₁₇ H ₂₁ NO	C ₁₇ H ₁₈ F ₃ NO	C ₁₃ H ₁₈ O ₂	C ₁₆ H ₁₄ O ₃
Molecular Weight (g mol⁻¹)	255	309	206	254
Structure¹				
Solubility (mg/L³)	363	60	41	120
pK_a¹	8.87	9.8	4.85	3.88
log K_{ow}¹	3.62	4.19	3.83	3.46
f_n² (pH=7.5)	0.0409	0.005	0.0022	0.0002

Table A- 3. continued.

Compound & CAS Number	Meprobamate 57-53-4	Primidone 125-33-7	Sulfamethoxazole 723-46-6	Trimethoprim 738-70-5
Classification	Tranquilizer	Anticonvulsant	Antibacterial	Antibacterial
Elemental Composition	C ₉ H ₁₈ N ₂ O ₄	C ₁₂ H ₁₄ N ₂ O ₂	C ₁₀ H ₁₁ N ₃ O ₃ S	C ₁₄ H ₁₈ N ₄ O ₃
Molecular Weight (g mol⁻¹)	218	218	253	290
Structure¹				
Solubility (mg/L³)	8,877	5,874	3,942	2,334
pK_a¹	15.17, 15.63	11.50, 11.62	0.25, 1.97, 6.16	0.10, 7.16
log K_{ow}¹	0.96	1.49	1.04	1.05
f_n² (pH=7.5)	1	0.9999	0.0438	0.6881

Analytical Method

Mass spectrometry was performed on Thermo Scientific TSQ Vantage triple quadrupole mass spectrometer. Fragment ions of each pharmaceutical compound were optimized by direct infusion of each compound (1 mg/L) into the mass spectrometer at a flowrate of 5 $\mu\text{L}/\text{min}$. The two most abundant product ions were selected except for ibuprofen and ketoprofen, where only one product ion was observed. Caffeine and ibuprofen were used to tune the mass spectrometer for ESI+ and ESI- modes respectively before each run for gas temperature, nozzle voltage, flow rate, nebulizer, and capillary voltage. Data analysis was carried out with the Thermo Xcalibur QuanBrowser.

Calibration standards in the range of 1 $\mu\text{g}/\text{L}$ to 9 mg/L were analyzed in ESI+ and ESI- modes. The mass spectrometer parameters and reporting limit values for all compounds measured in aqueous, soil and alfalfa samples are shown in Table A-4, A-5, and A-6.

Table A- 4 LC-MS/MS parameter values for ESI positive and negative modes.

Parameters	Unit	ESI Positive	ESI Negative
Capillary Temperature	($^{\circ}\text{C}$)	345	345
Vaporizer Temperature	($^{\circ}\text{C}$)	280	280
Sheath Gas Pressure	(Arb)	40	40
Aux Gas Pressure	(Arb)	5	15
Spray Voltage	(V)	4000	4000
Discharge Current	(μA)	4.0	4.0

Table A- 5 Method reporting limits for target compounds in aqueous (ng/L), soil and alfalfa samples (ng/g).

Compounds	Mode	Reporting Limit (ng/L)	Reporting Limit (ng/g)
Atrazine	ESI+	0.002	10
Caffeine	ESI+	0.03	0.12
Carbamazepine	ESI+	0.06	0.8
DEET	ESI+	0.002	0.6
Diphenhydramine	ESI+	0.01	0.1
Fluoxetine	ESI+	0.07	0.1
Ibuprofen	ESI-	0.03	0.2
Ketoprofen	ESI-	0.01	0.2
Meprobamate	ESI+	0.02	4
Primidone	ESI+	0.60	1.5
Sulfamethoxazole	ESI+	0.03	2
Trimethoprim	ESI+	0.02	2.0

Table A- 6 Target compound's LC-MS/MS conditions.

Compounds	Retention time	Precursor Ion	Fragment Ion 1	Fragment Ion 2	S-lens	CE-1	CE-2
	(mins)	(m/z)	(m/z)	(m/z)		(eV)	(eV)
ATZ	7.94	216.03	174.1	68.1	69	13	34
ATZ d5	7.89	221	179.1	69.1	52	14	34
CAF	3.81	195	138.1	110.1	93	14	19
CAF ¹³ C ₃	3.81	198	140.1	112.1	93	16	19
CBZ	7.52	236.9	194.1	192.1	112	17	21
CBZ d10	7.46	246.9	204.2	201.1	95	18	22
DEET	8.14	191.98	119.1	65.1	85	14	42
DEET d10	8.08	202	46.1	119.1	93	29	15
DPH	6.84	256	165.1	167.1	90	44	13
DPH d3	6.84	259	152.1	166.1	50	46	42
FLX	7.95	310	44.1	183.1	64	12	43
FLX d5	7.9	315	44.1	42.1	61	13	20
Ibuprofen	5.09	205.1	161.2		58	11	
Ibuprofen d3	5.1	208.2	164.2		59	11	
Ketoprofen	3.73	252.9	209.1		56	11	
Ketoprofen d3	3.75	255.9	212.1		57	11	
MPB	6.24	219.1	69.2	158.1	59	16	4
MPB d3	6.22	222.1	72.1	161.2	60	17	4
PMD	5.01	218.9	91.1	162.1	62	27	8
PMD d5	4.98	224	93.1	94.1	59	21	37
SMX	5.9	253.8	92.1	156	73	26	14
SMX d4	5.85	258.9	96.1	160	96	25	13
TMP	4.26	291	123	230.1	116	25	19
TMP d3	4.23	294	81	123.1	117	41	23

APPENDIX B

The following contains the supplementary information for: Evidence of Low Levels of Trace Organic Contaminants in Terminal Lakes*

*Submitted in April 2021 to Chemosphere Environmental Chemistry, Under Review

Table B- 1 MS/MS parameter values for ESI+ mode.

Parameters	Unit	ESI Positive
Capillary Temperature	(°C)	345
Vaporizer Temperature	(°C)	280
Sheath Gas Pressure	(Arb)	40
Aux Gas Pressure	(Arb)	5
Spray Voltage	(V)	4000
Discharge Current	(µA)	4.0

Table B- 2 Method reporting limits for target compounds in aqueous (ng/L), soil and sediment samples (ng/g).

Compounds	Aqueous Reporting Limit (ng/L)	Soil and Sediment Reporting Limit (ng/g)
Atrazine	0.002	10
Caffeine	0.03	0.12
Carbamazepine	0.06	0.8
DEET	0.002	0.6
Diphenhydramine	0.01	0.1
Fluoxetine	0.07	0.1
Meprobamate	0.02	4
Primidone	0.60	1.5
Sulfamethoxazole	0.03	2
Trimethoprim	0.02	2.0

Table B- 3 LC-MS/MS conditions for target analytes

Compounds	Retention time	Precursor Ion	Product ion (quant)	Product ion 2 (qual)	S-lens	CE-1	CE-2
	(min)	(m/z)	(m/z)	(m/z)		(eV)	(eV)
ATZ	7.94	216.03	174.1	68.1	69	13	34
ATZ d ₅	7.89	221	179.1	69.1	52	14	34
CAF	3.81	195	138.1	110.1	93	14	19
CAF ¹³ C ₃	3.81	198	140.1	112.1	93	16	19
CBZ	7.52	236.9	194.1	192.1	112	17	21
CBZ d ₁₀	7.46	246.9	204.2	201.1	95	18	22
DEET	8.14	191.98	119.1	65.1	85	14	42
DEET d ₁₀	8.08	202	46.1	119.1	93	29	15
DPH	6.84	256	165.1	167.1	90	44	13
DPH d ₃	6.84	259	152.1	166.1	50	46	42
FLX	7.95	310	44.1	183.1	64	12	43
FLX d ₅	7.9	315	44.1	42.1	61	13	20
MPB	6.24	219.1	69.2	158.1	59	16	4
MPB d ₃	6.22	222.1	72.1	161.2	60	17	4
PMD	5.01	218.9	91.1	162.1	62	27	8
PMD d ₅	4.98	224	93.1	94.1	59	21	37
SMX	5.9	253.8	92.1	156	73	26	14
SMX d ₄	5.85	258.9	96.1	160	96	25	13
TMP	4.26	291	123	230.1	116	25	19
TMP d ₃	4.23	294	81	123.1	117	41	23

Table B- 4 ANOVA of TrOC concentrations in surface water samples.

TrOC	p value from ANOVA	Difference among TL (p<0.05, Tukey HSD)
ATZ	6.0E-14	TL1-CTL, TL2-CTL & TL3-CTL
CAF	5.29E-07	TL1-TL2, TL1-TL3, TL1-CTL & TL3-CTL
CBZ	1.46E-10	TL1-TL2, TL1-TL3 & TL1-CTL
DEET	8.1E-03	TL2-TL3
DPH	1.6E-07	TL1-TL2, TL1-TL3 & TL1-CTL
FLX	3.8E-06	TL1-TL2, TL1-TL3, TL2-TL3 & TL3-CTL
MPB	2.5E-11	TL1-TL2, TL1-TL3 & TL1-CTL

Table B- 5 ANOVA of TrOC concentrations in sediment samples.

TrOC	p value from ANOVA	Difference among TL (p<0.05, Tukey HSD)
DEET	8.6E-03	TL1-TL3, TL1-CTL
DPH	6.8E-03	TL1-TL2, TL1-TL3 & TL1-CTL
FLX	1.2E-04	TL1-TL2, TL1-TL3, TL1-CTL

Table B- 6 TrOC concentrations in terminal lakes (TLs, **Bold**) and in U.S. lakes, rivers, streams, and sediments from literature

TrOC	Locations	Surface water (ng/L)	References
Atrazine (ATZ)	Lakes & TLs (ng/L)	22 - 58; 18.4 - 814; 35 - 85; 1 - 302; ND - 1.3	(N. Robert Brent et al., 2001a; Elliott et al., 2017; Tierney et al., 1999; Shiru Wang et al., 2020b)
	Rivers/streams (ng/L)	2 - 2700	(N. Robert Brent et al., 2001a)
	Lake & TLs sediments (ng/g)	0.06 - 6.18; ND	(Jiehong Guo et al., 2016)
	Rivers and streams sediments (ng/g)	NA	NA
Caffeine (CAF)	Lakes & TLs (ng/L)	5 - 227; 18 - 100; 2 - 138; 3 - 800; ND - 35	(Blair et al., 2013; Ferguson et al., 2013; Furlong, 2002; Shiru Wang et al., 2020b)
	Rivers/streams (ng/L)	81 - 6000; 26 - 687	(Y Carrie Guo and Krasner, 2009b; Kolpin et al., 2002)
	Lake & TLs sediments (ng/g)	14 - 30; <3.1 - 30; 0.4 - 9	(Blair et al., 2013; K.E. Lee et al., 2015b)
	Rivers and streams sediments (ng/g)	0.2 - 24.38; 2.6 - 5	(Elliott et al., 2017; Yun-ya Yang et al., 2015)
Carbamazepine (CBZ)	Lakes & TLs (ng/L)	4.2 - 38; 0.5 - 10; ND - 140; 6 - 35; 2 - 104	(Blair et al., 2013; Ferguson et al., 2013; Furlong, 2002; Shiru Wang et al., 2020b)
	Rivers/streams (ng/L)	14 - 116; 10.9; 1.2 - 6.2	(Ferry et al., 2017; Y. Carrie Guo and Krasner, 2009a; Kumar and Xagorarakis, 2010; Snyder, 2007)
	Lake & TLs sediments (ng/g)	ND; <3.3; 0.2 - 5	(Blair et al., 2013; K.E. Lee et al., 2015b)
	Rivers and streams sediments (ng/g)	0.1 - 32.89; 3.3 - 12	(Elliott et al., 2017; Yun-ya Yang et al., 2015)
N,N-diethyl-meta-toluamide (DEET)	Lakes & TLs (ng/L)	20 - 90; 103; 9 - 150	(Ebele et al., 2017; K.E. Lee et al., 2015b)
	Rivers/streams (ng/L)	30 - 130; 29	(K.E. Lee et al., 2015b; McEachran et al., 2016)
	Lake & TLs sediments (ng/g)	<70 - <240; 0.1 - 0.8	(K.E. Lee et al., 2015b)
	Rivers and streams sediments (ng/g)	<70 - <240	(K.E. Lee et al., 2015b)

Diphenhydramine (DPH)	Lakes & TLs (ng/L)	4.1 - 43; <80; ND - 2.6	(Blair et al., 2013; K.E. Lee et al., 2015b)
	Rivers/streams (ng/L)	1.83	(Ferry et al., 2017)
	Lake & TLs sediments (ng/g)	13 - 82; <2.7 - 47.6; 0.1 - 2	(Blair et al., 2013; K.E. Lee et al., 2015b)
	Rivers and streams sediments (ng/g)	NA	NA
Fluoxetine (FLX)	Lakes & TLs (ng/L)	1.2 - 62; 4 - 7; 1 - 12	(Blair et al., 2013; Shiru Wang et al., 2020b)
	Rivers/streams (ng/L)	BDL - 12; 2.79	(Ferry et al., 2017; Kolpin et al., 2002)
	Lake & TLs sediments (ng/g)	<3.5 - 20; <4.4; ND - 2	(Blair et al., 2013; K.E. Lee et al., 2015b)
	Rivers and streams sediments (ng/g)	NA	NA
Meprobamate (MPB)	Lakes & TLs (ng/L)	<320; 1 - 155	(K.E. Lee et al., 2015b)
	Rivers/streams (ng/L)	5.49; 1.4 - 16	(Ferry et al., 2017; Kumar and Xagorarakis, 2010)
	Lake & TLs sediments (ng/g)	ND	NA
	Rivers and streams sediments (ng/g)	NA	NA
Primidone (PMD)	Lakes & TLs (ng/L)	<320; 18 - 1510	(K.E. Lee et al., 2015b)
	Rivers/streams (ng/L)	5 - 37; 43 - 130	(Y. Carrie Guo and Krasner, 2009a; K.E. Lee et al., 2015b)
	Lake & TLs sediments (ng/g)	2 - 143	NA
	Rivers and streams sediments (ng/g)	NA	NA
Sulfamethoxazole (SMX)	Lakes & TLs (ng/L)	4.5 - 77; 1.5 - 220; ND - 200; 39 - 46; ND - 118	(Blair et al., 2013; Ferguson et al., 2013; Furlong, 2002; Shiru Wang et al., 2020b)
	Rivers/streams (ng/L)	66 - 1900; 51	(Ferry et al., 2017; Kolpin et al., 2002)
	Lake & TLs sediments (ng/g)	ND; <3.2; ND - 0.3	(Blair et al., 2013; K.E. Lee et al., 2015b)
	Rivers and streams sediments (ng/g)	3.2 - 467	(Elliott et al., 2017)
Trimethoprim (TMP)	Lakes & TLs (ng/L)	3.4 - 52; 2.5 - 18; ND - 98; 1 - 753	(Blair et al., 2013; Ferguson et al., 2013; Furlong, 2002)
	Rivers/streams (ng/L)	13 - 710; 51.4	(Ferry et al., 2017; Kolpin et al., 2002)
	Lake & TLs sediments (ng/g)	ND; <2.9; 0.2 - 36	(Blair et al., 2013; K.E. Lee et al., 2015b)

Rivers and streams sediments (ng/g)	0.01 - 0.83; 2.9 - 217	(Elliott et al., 2017; Yun-ya Yang et al., 2015)
--	------------------------	---

Table B- 7 TrOC concentrations in terminal lakes' surface water, sediments, and soil.

TrOC	Terminal Lake	Location	Surface Water (ng/L)		
ATZ	TL1	A	ND	ND	ND
		B	ND		
		C	ND		
	TL2	A	ND	ND	ND
		B	ND	ND	ND
		C	ND		
		D	ND		
	TL3	A	ND	ND	ND
		B	ND	ND	ND
		C	ND		
		D	ND		
	CTL	A	1.52	1.24	1.23
B		1.18	1.12	1.15	
C		1.18			
CAF	TL1	A	28.79	26.79	49.63
		B	35.34		
		C	31.6		
	TL2	A	4.42	6.68	1.19
		B	13.68	6.47	17.8
		C	22.05		
		D	10.8		
	TL3	A	ND	ND	ND
		B	ND	ND	ND
		C	ND		
		D	ND		
	CTL	A	32.9	19.18	31.27
B		25.45	11.22	25.57	
C		ND			
CBZ	TL1	A	91.56	97.67	122.52
		B	86.18		
		C	42.35		
	TL2	A	8.41	8.12	7.91
		B	4.12	4.27	4.3
		C	3.75		
		D	4.49		
	TL3	A	18.5	18.28	21.39
		B	2.18	1.02	1.69
		C	2.21		
		D	2.74		
	CTL	A	10.52	8.31	10.88

		B	17.66	3.26	8.15
		C	ND		
DEET	TL1	A	45.62	43.54	53.32
		B	42.57		
		C	44.71		
	TL2	A	9.79	8.81	9.22
		B	135.15	137.76	135.9
		C	150.28		
		D	121.35		
	TL3	A	26.3	25.67	28.56
		B	17.01	12.9	14.23
		C	12.84		
		D	12.11		
	CTL	A	52.12	45.59	43.54
B		45.75	72.18	72.56	
C		56.31			
DPH	TL1	A	2.23	2.8	2.69
		B	1.81		
		C	0.64		
	TL2	A	ND	ND	ND
		B	ND	ND	ND
		C	ND		
		D	ND		
	TL3	A	1.1	ND	1
		B	ND	ND	ND
		C	ND		
		D	ND		
	CTL	A	ND	ND	ND
		B	ND	0.25	0.27
		C	ND		
	FLX	TL1	A	12.65	14.18
B			10.19		
C			1.42		
TL2		A	2.06	1.46	1.46
		B	2.91	2.7	2.11
		C	2.28		
		D	2.91		
TL3		A	1.8	0.83	0.8
		B	1.54	0.68	0.6
		C	0.52		
		D	0.66		
CTL		A	8.23	9.03	9.8
		B	6.88	7.8	8.62
		C	0.9		
MPB		TL1	A	143.24	137.46
	B		133.77		

		C	59.42		
	TL2	A	17.16	5.43	10.93
		B	1.6	2.65	ND
		C	ND		
		D	ND		
	TL3	A	20.01	24.68	21.94
		B	19.17	27.23	24.9
		C	24.25		
		D	18.18		
	CTL	A	ND	ND	ND
		B	ND		
		C	ND		
PMD	TL1	A	301.25	2901.44	1128.01
		B	349.73		
		C	1509.88		
	TL2	A	59.6	53	45.6
		B	22.4	85.6	36.2
		C	30.8		
		D	19.4		
	TL3	A	52.6	63.8	103.9
		B	213.2	60.5	259.8
		C	1738.5		
		D	18.2		
	CTL	A	73.21	ND	30.42
B		122	22.05	3932.26	
C		360.78			
SMX	TL1	A	29.04	323.39	2.51
		B	24.02		
		C	80.49		
	TL2	A	4.34	5.75	4.22
		B	ND	ND	ND
		C	ND		
		D	ND		
	TL3	A	27.61	25.24	36.46
		B	ND	ND	82.01
		C	ND		
		D	ND		
	CTL	A	ND	ND	ND
B		ND			
C		ND			
TMP	TL1	A	71.11	101.69	209.98
		B	35.78		
		C	56.83		
	TL2	A	2212.47	30.94	15.97
		B	159.37	57.07	32.18
		C	81.16		
		D			

		D	53.41			
	TL3	A	60.5	63.6	382.1	
		B	8.9	0.1	20.7	
		C	0.6			
		D	326.5			
	CTL	A	126.6	29.1	25.8	
		B	97.3	1110.9	97.6	
		C	36			
TrOC	Terminal Lake	Location	Sediment (ng/gDW)			
ATZ	TL1	A	ND	ND	ND	
		B	ND			
		C	ND			
	TL2	A	ND	ND	ND	
		B	ND	ND	ND	
		C	ND			
		D	ND			
	TL3	A	ND	ND	ND	
		B	ND	ND	ND	
		C	ND			
		D	ND			
	CTL	A	ND	ND	ND	
		B	ND			
		C	ND			
	CAF	TL1	A	2.15	2.65	2.33
			B	8.72		
C			7.39			
TL2		A	0.86	0.69	0.21	
		B	0.32	0.33	ND	
		C	0.96			
		D	0.35			
TL3		A	2.51	2.09	0.7	
		B	1.34	3.11	2.19	
		C	1.71			
		D	26.56			
CTL		A	0.48	0.48	0.35	
		B	0.25	0.89	0.2	
		C	1.52			
CBZ		TL1	A	0.33*	0.36*	ND
			B	4.6		
	C		2.24			
	TL2	A	0.19*	0.53*	0.29*	
		B	1.57	1.16	0.72*	
		C	0.24*			
		D	0.22*			
	TL3	A	0.56*	0.85	0.63*	
		B	0.17*	0.31*	0.16*	

		C	ND		
		D	0.22*		
	CTL	A	ND	ND	ND
		B	1.19	0.68*	0.34*
		C	3.69		
DEET	TL1	A	ND	ND	0.06*
		B	0.20*		
		C	0.10*		
	TL2	A	0.04*	0.25*	0.01*
		B	0.32*	0.07*	0.07*
		C	0.78		
		D	0.25*		
	TL3	A	0.77	0.73	0.52*
		B	0.38*	0.28*	0.29*
		C	0.32*		
		D	0.31*		
	CTL	A	0.46*	0.64	0.52*
		B	0.26*	0.56	0.20*
		C	0.25*		
DPH	TL1	A	ND	1.84	1.56
		B	1.62		
		C	ND		
	TL2	A	0.29	0.29	0.29
		B	0.27	0.29	0.18
		C	ND		
		D	ND		
	TL3	A	0.5	0.42	0.5
		B	ND	0.32	ND
		C	0.28		
		D	0.29		
	CTL	A	0.28	ND	0.27
		B	0.29	0.27	0.28
		C	ND		
FLX	TL1	A	1.35	1.86	1.27
		B	0.23		
		C	ND		
	TL2	A	ND	ND	ND
		B	ND	ND	ND
		C	ND		
		D	ND		
	TL3	A	0.38	0.03*	0.07*
		B	ND	ND	ND
		C	ND		
		D	ND		
	CTL	A	ND	ND	ND
		B	ND		

		C	ND		
MPB	TL1	A	ND	ND	ND
		B	ND		
		C	1.39*		
	TL2	A	ND	ND	ND
		B	ND	ND	ND
		C	ND		
		D	ND		
	TL3	A	ND	ND	ND
		B	ND	ND	ND
		C	ND		
		D	ND		
	CTL	A	ND	ND	ND
B		ND			
C		ND			
PMD	TL1	A	1.56	4.66	2.16
		B	11.28		
		C	142.72		
	TL2	A	2.2	2	1.4*
		B	2.32	37.37	2.01
		C	4.87		
		D	1.66		
	TL3	A	6.5	1.5	6
		B	10.05	2.6	15.86
		C	5.8		
		D	2.4		
	CTL	A	3.41	2.79	1.99
		B	11.21	4.9	5.98
		C	9.3		
	SMX	TL1	A	ND	ND
B			ND		
C			0.5*		
TL2		A	ND	ND	ND
		B	ND	0.4*	ND
		C	ND		
		D	ND		
TL3		A	ND	0.43*	0.4*
		B	ND	ND	ND
		C	ND		
		D	ND		
CTL		A	ND	ND	ND
	B	ND			
	C	ND			
TMP	TL1	A	ND	3.99	19.8
		B	16.05		
		C	8.76		

	TL2	A	5.44	6.19	ND
		B	ND	1.88	ND
		C	12.66		
		D	ND		
	TL3	A	ND	ND	0.4*
		B	ND	ND	1.3*
		C	35.9		
		D	ND		
	CTL	A	1.55*	1.44*	ND
		B	ND	0.50*	ND
		C	9.4		
TrOC	Terminal Lake	Location	Soil (ng/gDW)		
ATZ	TL1	A	ND	ND	ND
		B	ND	ND	ND
	TL2	A	ND	ND	ND
		B	ND	ND	ND
		C	ND		
		D	ND		
	TL3	A	ND	ND	ND
		B	ND		
		C	ND		
		D	ND		
	CTL	A	ND	ND	ND
		B	ND		
C		ND			
CAF	TL1	A	0.6	2.92	0.9
	TL2	A	3.59	14.72	3.23
		B	4.82	4.99	4.83
		C	0.47		
		D	8.47		
	TL3	A	0.98	2.09	0.8
		B	1.46		
		C	361.27		
		D	49.15		
	CTL	A	0.44	0.42	0.6
		B	0.19	0.33	0.56
		C	1.2		
CBZ	TL1	A	0.32*	0.65*	ND
	TL2	A	0.19*	0.15*	0.18*
		B	2.44	3.2	2.71
		C	0.29*		
		D	0.26*		
	TL3	A	1.02	0.39*	0.50*
		B	ND		
		C	0.23*		
		D	0.35*		
	CTL	A	0.48*	388.59	9.06

		B	0.97	1.3	0.52*
		C	0.52*		
DEET	TL1	A	ND	0.06*	ND
	TL2	A	ND	0.41*	0.10*
		B	0.42*	0.34*	0.11*
		C	0.14*		
		D	11.14		
	TL3	A	0.37*	0.42*	0.29*
		B	8.47		
		C	1.97		
		D	0.50*		
CTL	A	0.46*	0.25*	0.27*	
	B	0.45*	0.58	0.46*	
	C	0.43*			
DPH	TL1	A	0.34	ND	0.34
	TL2	A	0.27	0.27	ND
		B	0.28	ND	ND
		C	0.27		
		D	ND		
	TL3	A	0.33	ND	0.3
		B	ND		
		C	0.3		
		D	ND		
	CTL	A	0.27	ND	ND
		B	0.28	0.28	0.27
		C	0.28		
FLX	TL1	A	ND	ND	ND
	TL2	A	ND	ND	ND
		B	ND	ND	ND
		C	ND		
		D	ND		
	TL3	A	ND	0.2	ND
		B	ND		
		C	ND		
		D	ND		
	CTL	A	ND	ND	ND
		B	ND		
		C	ND		
MPB	TL1	A	ND	ND	ND
	TL2	A	ND	ND	ND
		B	ND	ND	ND
		C	ND		
		D	ND		
	TL3	A	0.50*	0.63*	0.73*
		B	ND		
		C	ND		

		D	ND		
	CTL	A	ND	ND	ND
		B	ND		
		C	ND		
PMD	TL1	A	4.41	9.62	7.68
		B			
	TL2	A	1.3*	2.7	2.3
		B	10.45	6.99	5.14
		C	4.34		
		D	1.18*		
	TL3	A	16.2	31	4.5
		B	11.02		
		C	5.95		
		D	2.31		
	CTL	A	7.86	4.44	3.46
		B	5.14	22.05	17.5
C		1.8			
SMX	TL1	A	ND	ND	ND
		B			
	TL2	A	ND	ND	ND
		B	1.04*	0.38*	ND
		C	ND		
		D	ND		
	TL3	A	0.49*	ND	1.96
		B	ND		
		C	ND		
		D	ND		
	CTL	A	ND	ND	ND
		B	ND		
C		ND			
TMP	TL1	A	ND	8.7	27
		B			
	TL2	A	6.66	4.63	17
		B	ND	1.18*	ND
		C	ND		
		D	ND		
	TL3	A	3	0.75*	3
		B	2.4		
		C	ND		
		D	ND		
	CTL	A	1.13*	6.6	23.4
		B	ND	15.9	4.5
C		2.87			

ND= Not Detected, *= <Method Reporting Limit

Note: Table modified from journal submitted to adhere to formatting policy.

APPENDIX C

The following contains the supplementary information for: Dissolved Constituents in Endorheic Lakes Cause Faster Photodegradation of Pharmaceuticals than those in Freshwater Lakes*

*In preparation to submit to Chemosphere-Environmental Chemistry

Degradation Rate Constants

Declining CBZ and DPH concentration in diluted and undiluted samples of lake water was plotted against its respective sampling time from Figure C-1 to Figure C-8. Concentration vs time plot followed a linear trend with $R^2 \geq 0.82$ for terminal lake samples (Walker Lake and Swan Lake) and $R^2 \geq 0.45$ for a freshwater lake (Lake Tahoe) thus following a pseudo zero order kinetics. The linear equation generated for CBZ and DPH from each diluted and undiluted sample for all lakes are listed in Table 5-2 of the main text. The slope of these linear equation is degradation rate constant (k_{obs}) for that sample which was used to generate Figure C-9 to Figure C-14, and Figure 5-1 to Figure 5-4 against various lake water characteristics. Lake water characteristics such as DOC, alkalinity, SUVA, SO_4^{2-} , PO_4-P in Figure 5-1 to Figure 5-4 and, Figure C-9 to Figure C-14 are based on dilution calculations and are plotted against the k_{obs} for each type of lake. The dilutions 10-90, 25-75 etc. means that 10% and 25% are terminal lake water and rest 90% and 75% is deionized water to make the dilutions, respectively.

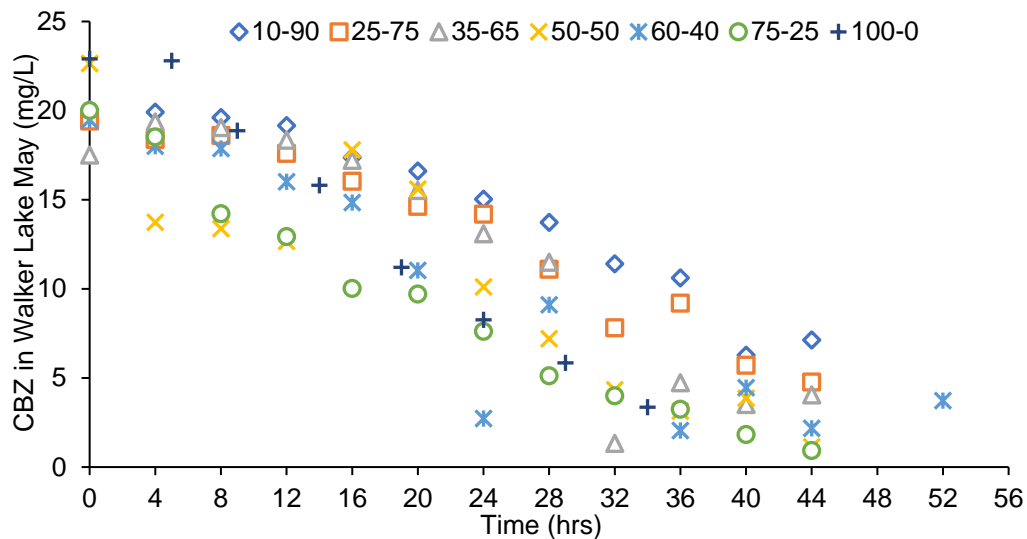


Figure C- 1 Removal of CBZ in Walker Lake May with six dilutions over time.

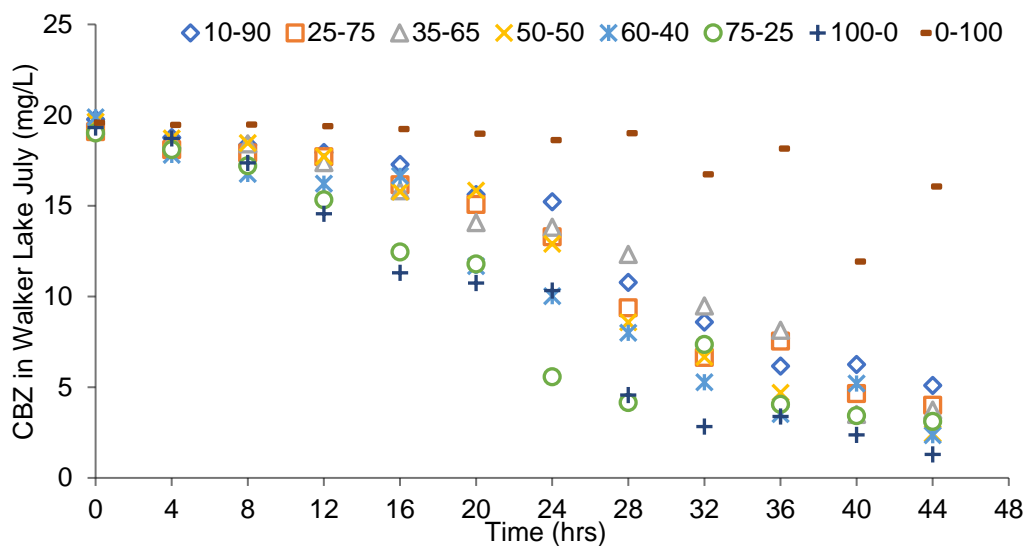


Figure C- 2 Removal of CBZ in Walker Lake July over time in various dilutions. 0-100 represents the removal of CBZ in 100% deionized water over time.

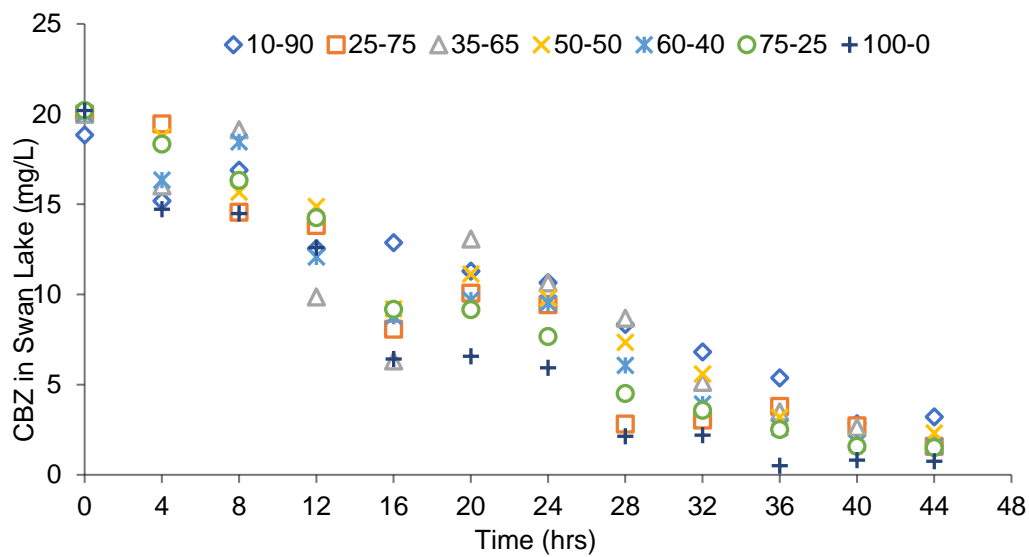


Figure C- 3 Removal of CBZ in diluted and undiluted samples of Swan Lake over time.

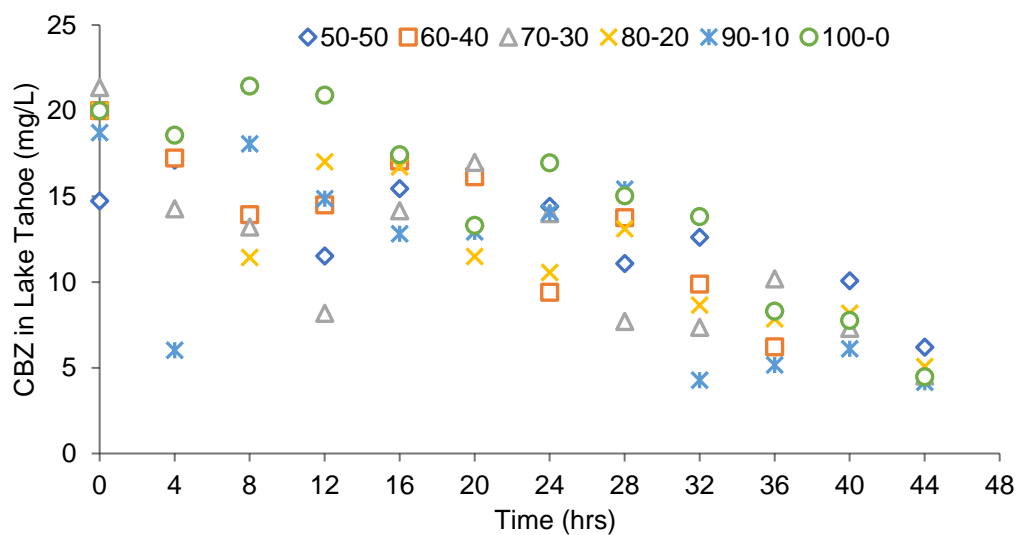


Figure C- 4 Removal of CBZ in Lake Tahoe's diluted and undiluted water over time.

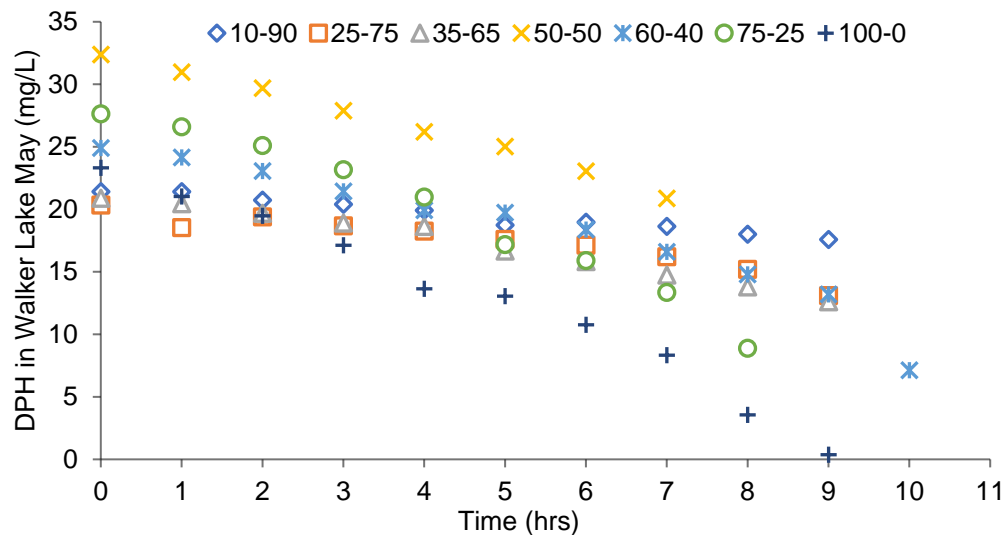


Figure C- 5 Removal of DPH in Walker Lake May's diluted and undiluted water sample over time.

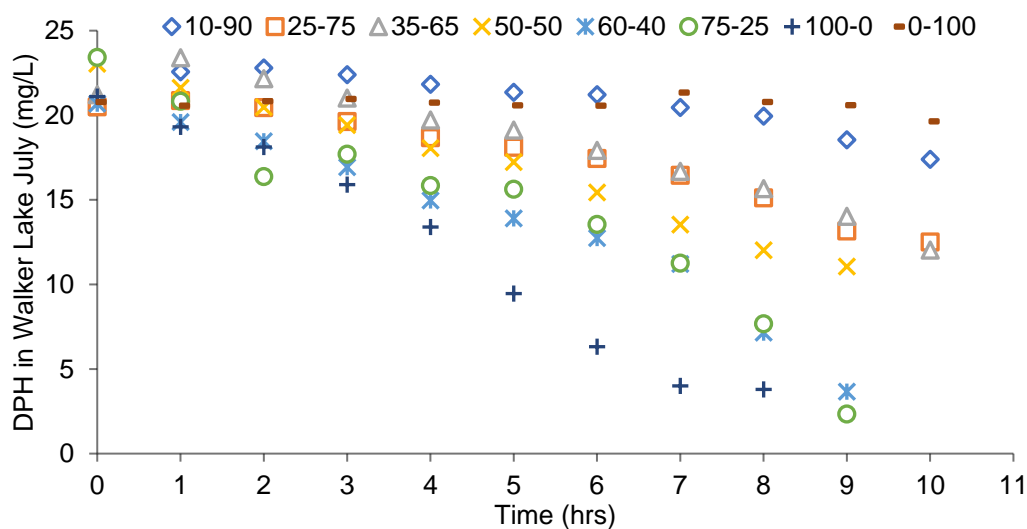


Figure C- 6 Removal of DPH in Walker Lake July's diluted and undiluted samples over time. 0-100 represents the removal of DPH in 100% deionized water over time.

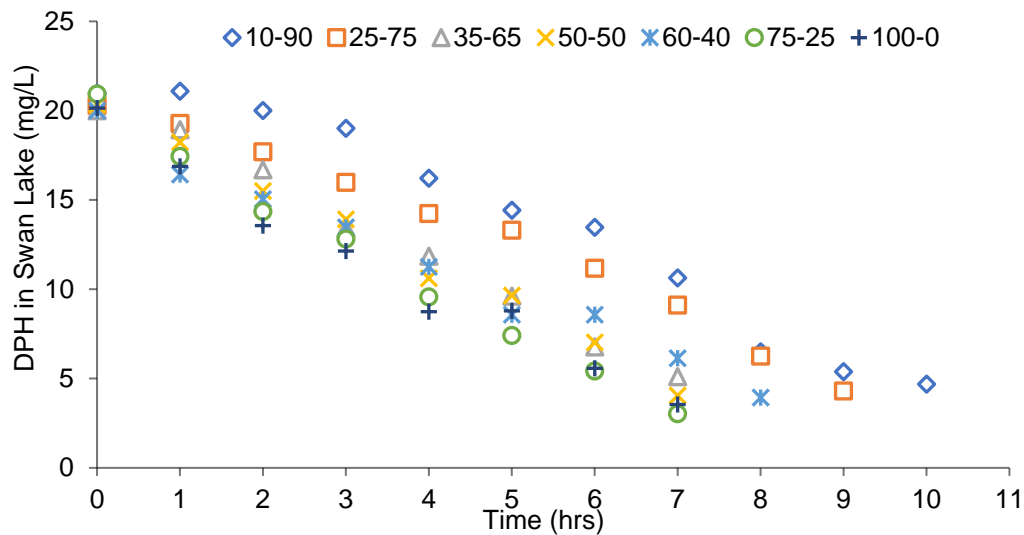


Figure C- 7 Removal of DPH in Swan Lake's diluted and undiluted sample over time.

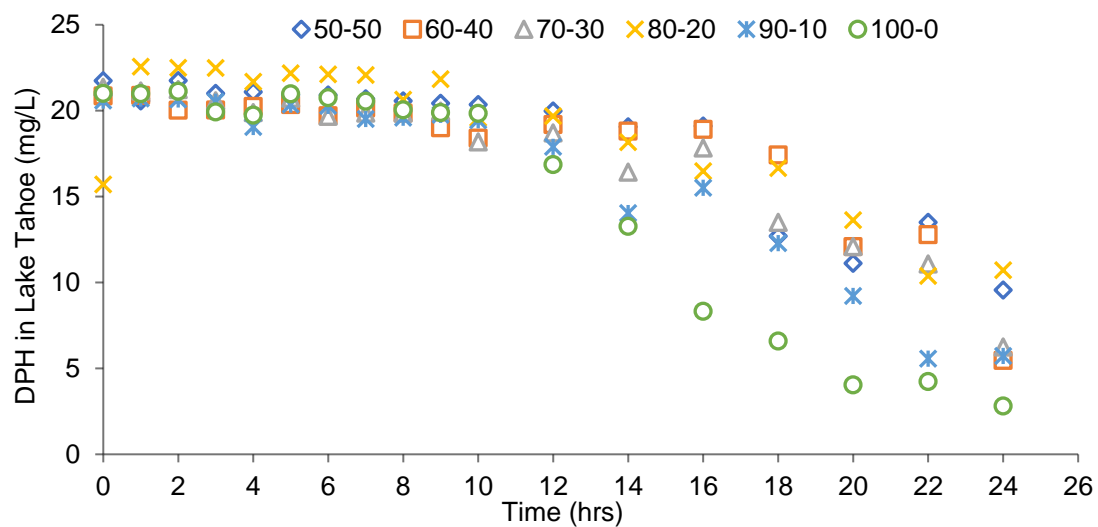


Figure C- 8 Removal of DPH in Lake Tahoe's diluted and undiluted samples over time. The simulated light exposure for these samples was longer than 10 hours because DPH did not get removed in Lake Tahoe samples within 10 hours of exposure.

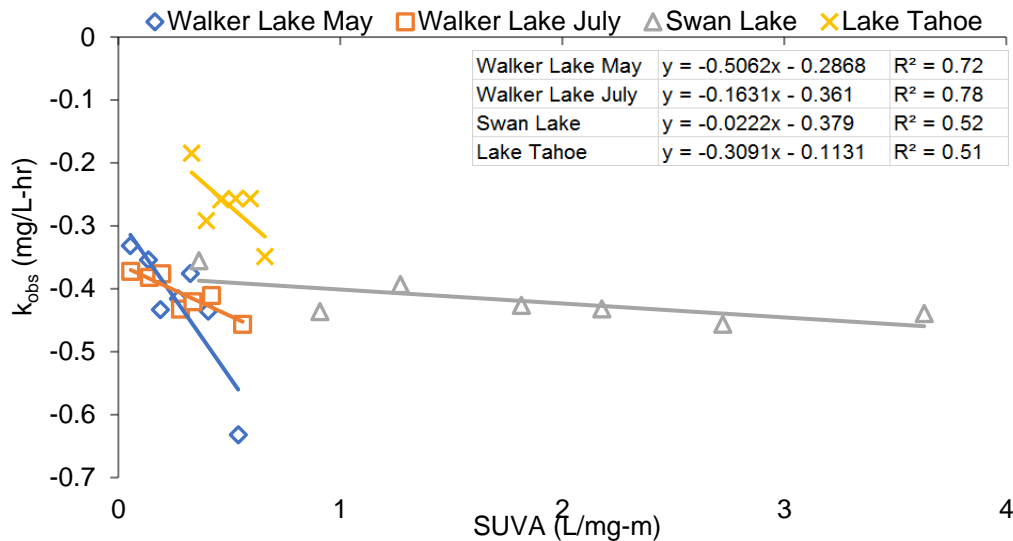


Figure C- 9 Degradation rate constants (k_{obs}) for CBZ vs SUVA values of each studied lakes.

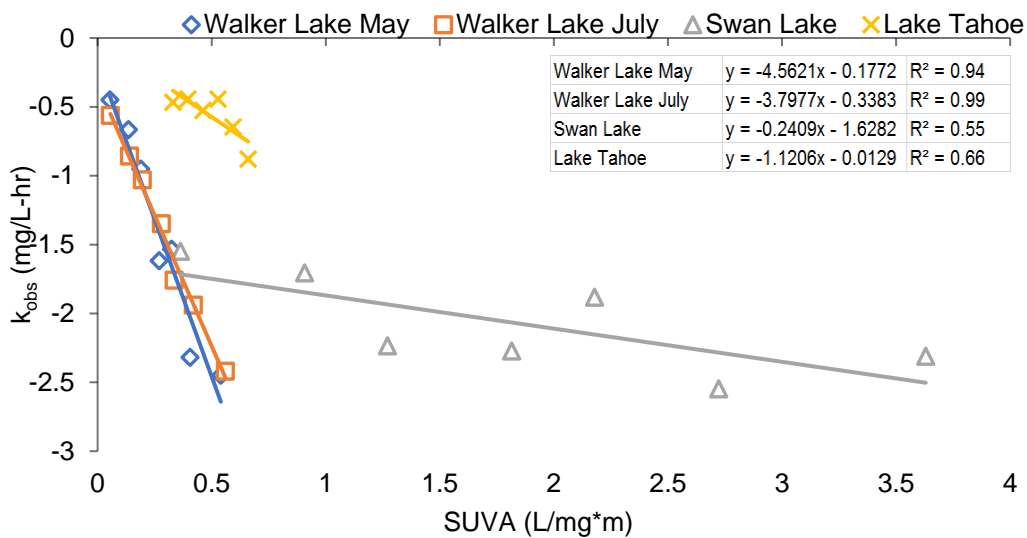
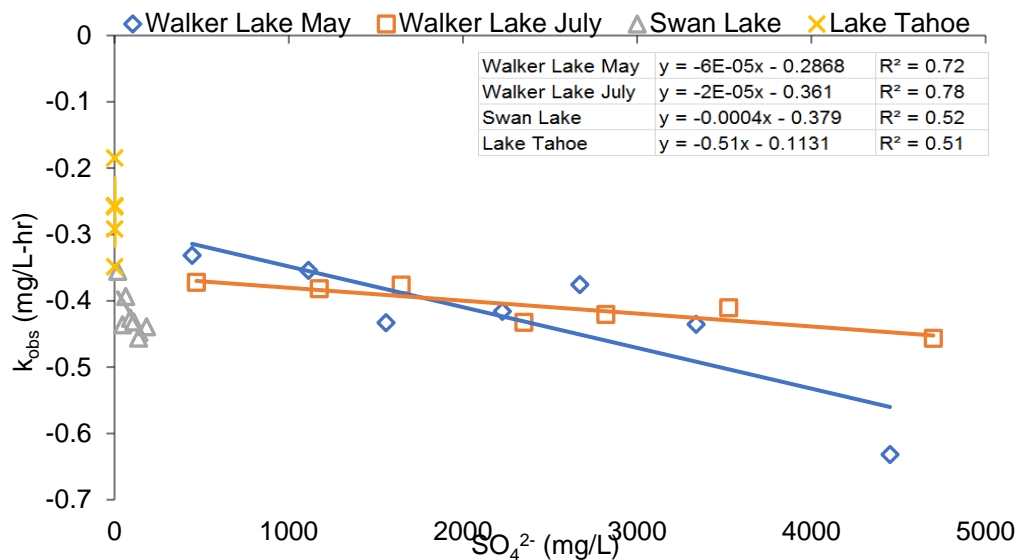
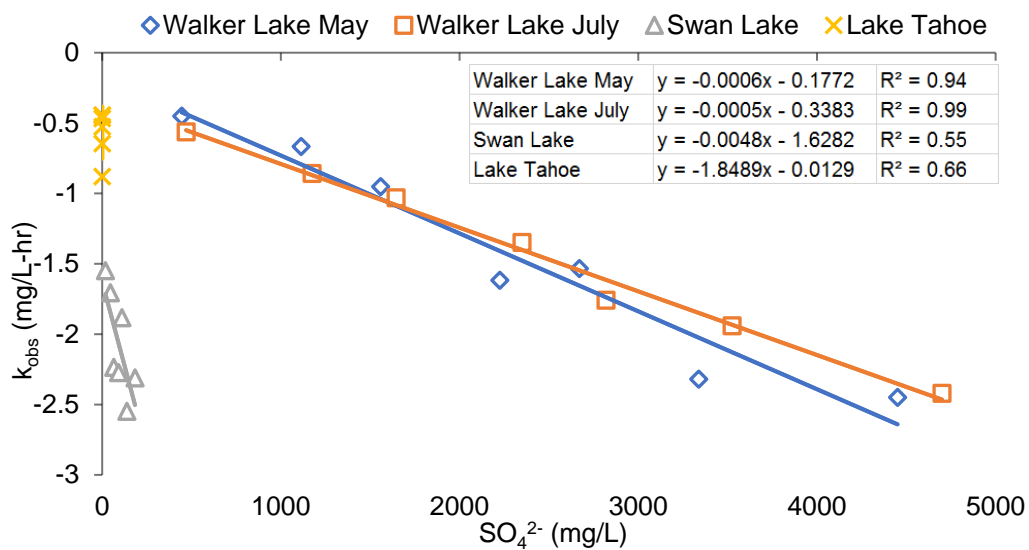


Figure C- 10 k_{obs} for DPH vs SUVA values for each lake.

Figure C- 11 k_{obs} for CBZ vs SO_4^{2-} for each lake.Figure C- 12 k_{obs} for DPH vs SO_4^{2-} for each lake.

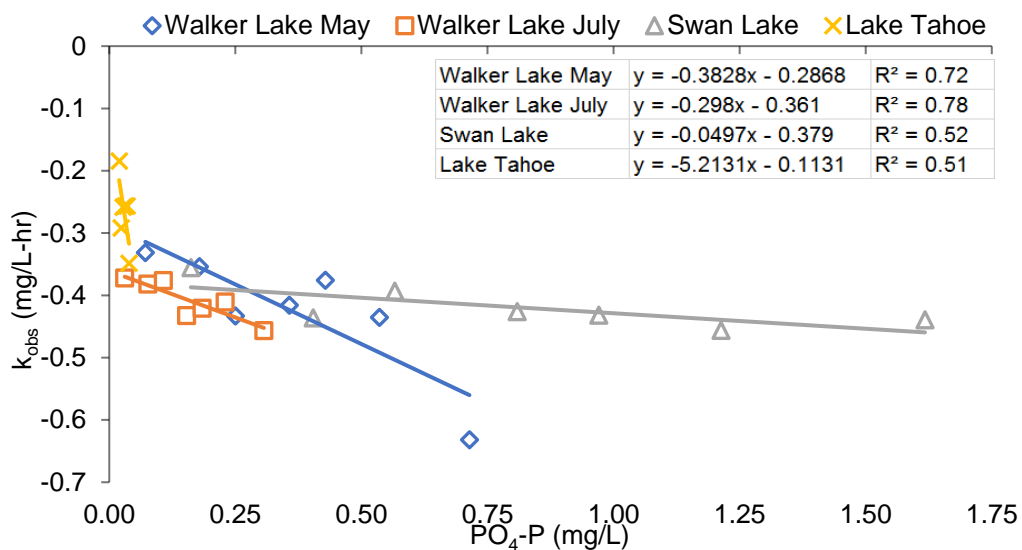
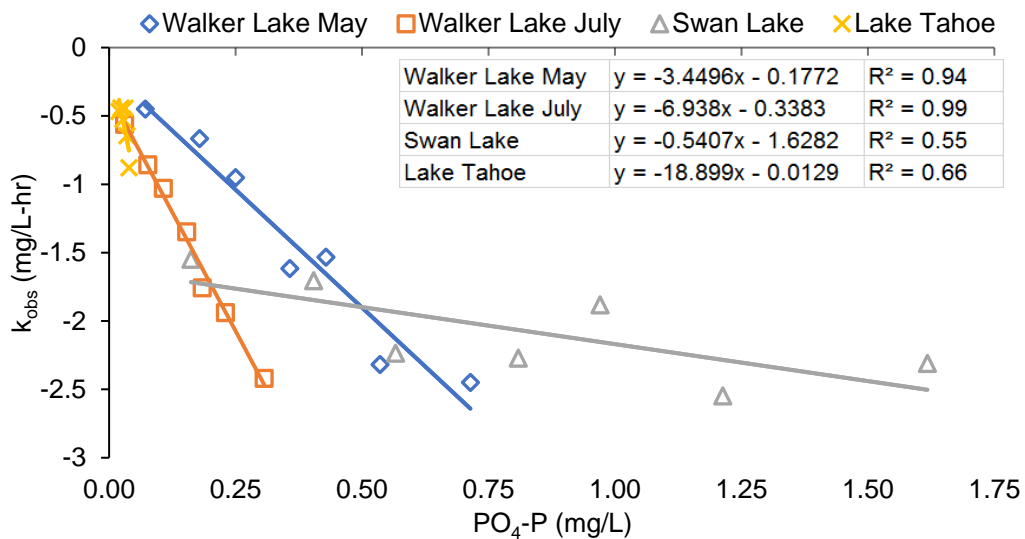
Figure C- 13 k_{obs} for CBZ vs PO_4 -P for each lake.Figure C- 14 k_{obs} for DPH vs PO_4 -P for each lake.

Table C- 1 Photodegradation kinetics in diluted samples of three lakes
Pseudo-Zero Order Reaction

Pharmaceutical	Percent Lake Water	Kinetic Equation	R ²
Walker Lake May			
CBZ	10	$y = -0.3315x + 22.033$	R ² = 0.94
	25	$y = -0.3541x + 20.908$	R ² = 0.95
	35	$y = -0.4331x + 21.63$	R ² = 0.83
	50	$y = -0.416x + 19.618$	R ² = 0.82
	60	$y = -0.3757x + 19.014$	R ² = 0.82
	75	$y = -0.4355x + 18.592$	R ² = 0.97
DPH	10	$y = -0.4472x + 21.595$	R ² = 0.98
	25	$y = -0.7617x + 20.722$	R ² = 0.89
	35	$y = -0.9953x + 21.632$	R ² = 0.98
	50	$y = -2.5853x + 35.203$	R ² = 0.91
	60	$y = -1.5339x + 26.149$	R ² = 0.92
	75	$y = -2.6754x + 30.136$	R ² = 0.97
Walker Lake July			
CBZ	10	$y = -0.3723x + 21.515$	R ² = 0.93
	25	$y = -0.382x + 20.868$	R ² = 0.94
	35	$y = -0.3763x + 21.175$	R ² = 0.94
	50	$y = -0.4325x + 21.668$	R ² = 0.94
	60	$y = -0.4207x + 20.371$	R ² = 0.95
	75	$y = -0.4107x + 19.172$	R ² = 0.91
DPH	10	$y = -0.5621x + 23.94$	R ² = 0.91
	25	$y = -0.8577x + 21.819$	R ² = 0.94
	35	$y = -1.0307x + 23.602$	R ² = 0.92
	50	$y = -1.3432x + 23.237$	R ² = 0.99
	60	$y = -1.8374x + 22.077$	R ² = 0.96
	75	$y = -2.0455x + 23.503$	R ² = 0.93
Swan Lake			
CBZ	10	$y = -0.3555x + 18.224$	R ² = 0.97
	25	$y = -0.4362x + 18.704$	R ² = 0.90
	35	$y = -0.3934x + 18.381$	R ² = 0.82
	50	$y = -0.4262x + 19.349$	R ² = 0.96
	60	$y = -0.4319x + 18.735$	R ² = 0.93
	75	$y = -0.4563x + 19.102$	R ² = 0.96
Swan Lake			
DPH	10	$y = -1.8569x + 23.138$	R ² = 0.96
	25	$y = -1.8066x + 21.248$	R ² = 0.99
	35	$y = -2.111x + 20.228$	R ² = 0.98

	50	$y = -2.1017x + 19.862$	$R^2 = 0.98$
	60	$y = -1.8158x + 18.824$	$R^2 = 0.99$
	75	$y = -2.1159x + 19.059$	$R^2 = 0.97$
Lake Tahoe			
CBZ	50	$y = -0.1845x + 16.553$	$R^2 = 0.67$
	60	$y = -0.3309x + 19.516$	$R^2 = 0.80$
	70	$y = -0.2584x + 17.292$	$R^2 = 0.58$
	80	$y = -0.2849x + 18.567$	$R^2 = 0.76$
	90	$y = -0.2567x + 16.703$	$R^2 = 0.45$
DPH	50	$y = -0.4668x + 23.306$	$R^2 = 0.79$
	60	$y = -0.4433x + 22.466$	$R^2 = 0.69$
	70	$y = -0.5259x + 22.971$	$R^2 = 0.86$
	80	$y = -0.4445x + 23.305$	$R^2 = 0.67$
	90	$y = -0.6456x + 23.195$	$R^2 = 0.86$

Table C- 2 Results from the linear mixed-effect model

		CBZ		DPH	
		Variance	Percent contribution	Variance	Percent contribution
CaCO₃	Hour	0.024		1.519	
	Dilution	0.048		0.051	
	CaCO ₃	0.027		4.339	
	Hour:Dilution	0.007		0.491	
	Residual	0.106		0.103	
	Sum of Variance	0.211	12.74%	6.503	66.72%
		Coefficients (Random Slope)		Coefficients (Random Slope)	
CaCO₃	Deionized Water	-0.091		-1.164	
	Lake Tahoe	-0.074		-1.849	
	Swan Lake	0.252		3.362	
	Walker Lake July	0.175		-0.816	
	Walker Lake May	0.167		-0.690	
	AIC	282.49		286	
		Variance		Variance	
DOC	Hour	0.024		1.623	
	Dilution	0.095		8.673	
	DOC	0.059		18.205	
	Hour:Dilution	0.007		0.454	
	Residual	0.106		0.103	
	Sum of Variance	0.290	20.31%	29.058	62.65%

		Coefficients (Random Slope)		Coefficients (Random Slope)	
DOC	Deionized Water	0.149		-0.357	
	Lake Tahoe	-0.190		-4.146	
	Swan Lake	0.312		-6.645	
	Walker Lake July	0.360		2.287	
	Walker Lake May	0.357		2.280	
	AIC	282.55		286.54	
		Variance		Variance	
SUVA	Hour	0.022		1.663	
	Dilution	0.025		3.866	
	SUVA	0.014		9.252	
	Hour:Dilution	0.007		0.440	
	Residual	0.106		0.103	
	Sum of Variance	0.175	8.12%	15.323	60.38%
		Coefficients (Random Slope)		Coefficients (Random Slope)	
SUVA	Deionized Water	-0.349		1.935	
	Lake Tahoe	-0.065		-0.725	
	Swan Lake	-0.134		-2.149	
	Walker Lake July	-0.267		4.057	
	Walker Lake May	-0.259		4.068	
	AIC	281.38		283.99	
		Variance		Variance	
NO₃-N	Hour	0.023		1.642	
	Dilution	0.030		1.475	
	NO ₃ -N	0.020		6.241	
	Hour:Dilution	0.007		0.447	
	Residual	0.106		0.103	
	Sum of Variance	0.186	10.75%	9.91	62.99%
		Coefficients (Random Slope)		Coefficients (Random Slope)	
NO₃-N	Deionized Water	-0.413		0.619	
	Lake Tahoe	-0.076		-2.036	
	Swan Lake	-0.121		-1.599	
	Walker Lake July	-0.280		2.563	
	Walker Lake May	-0.279		2.697	
	AIC	281.49		283.15	