National Water Research Institute

FINAL PROJECT REPORT

Source, Fate, and Transport of Endocrine Disruptors, Pharmaceuticals, and Personal Care Products in Drinking Water Sources in California

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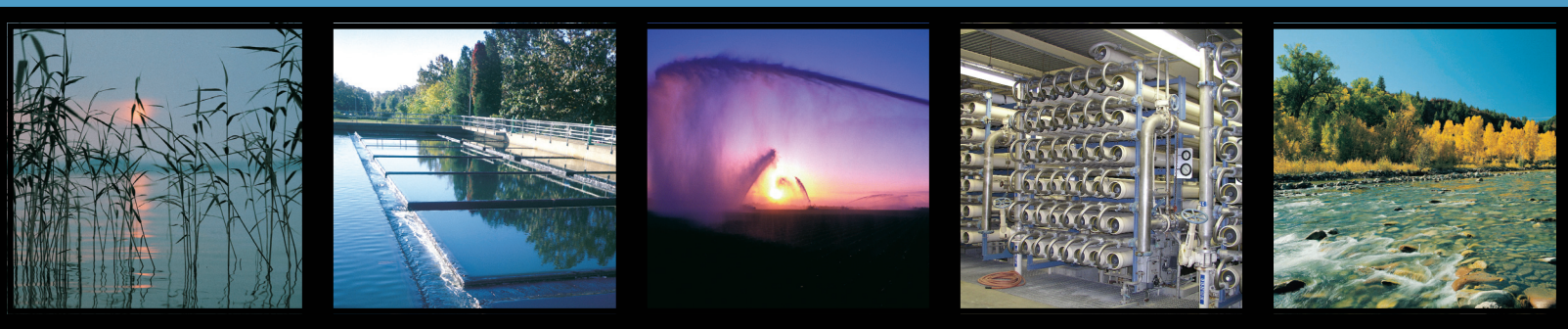

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ABOUT NWRI

A 501c3 nonprofit organization, the National Water Research Institute (NWRI) was founded in 1991 by a group of California water agencies in partnership with the Joan Irvine Smith and Athalie R. Clarke Foundation to promote the protection, maintenance, and restoration of water supplies and to protect public health and improve the environment. NWRI's member agencies include Inland Empire Utilities Agency, Irvine Ranch Water District, Los Angeles Department of Water and Power, Orange County Sanitation District, Orange County Water District, and West Basin Municipal Water District.

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ABBREVIATIONS

ADI	Acceptable daily intake
CEC	Constituent of emerging concern
CRW	Colorado River water
DEET	*N*,*N*-Diethyl-*meta*-toluamide
DWEL	Drinking water equivalent level
DWR	California Department of Water Resources
DWTP	Drinking water treatment plant
EC	Emerging constituent
EDC	Endocrine disrupting compound
EEq	Estradiol equivalent
HLB	Hydrophilic-lipophilic-balanced cartridges
GC/MS	Gas chromatography/mass spectrometry
LC/MS	Liquid chromatography/mass spectrometry
LC/MS/MS	Liquid chromatography/tandem mass spectrometry
LFB	Laboratory-fortified blanks
MDL	Method detection limit
MeOH	Methanol
MGD	Million gallons per day
mg/L	Milligram per liter
MRL	Minimum reporting level
MSD	Matrix-spiked duplicate sample
MSS	Matrix-spiked sample
MW	Molecular weight
MWD	Metropolitan Water District of Southern California

ng/L	Nanogram per liter
OCWD	Orange County Water District
OPW	Organic-free pure water
OWC	Organic wastewater contaminant
PAH	Polyaromatic hydrocarbon
PPCP	Pharmaceutical and personal care product
QA/QC	Quality assurance/quality control
RPD	Relative percent difference
RSD	Relative standard deviation
RO	Reverse osmosis
SAR	Santa Ana River
SNWA	Southern Nevada Water Authority
SPE	Solid-phase extraction
SPW	California State Project water
TCEP	Tris(2-chloroethyl)phosphate
TOC	Total organic carbon
WWTP	Wastewater treatment plant

1. EXECUTIVE SUMMARY

1.1 Background

The increasing production and use of pharmaceuticals and personal care products (PPCPs) – some of which may be endocrine disrupting compounds (EDCs) – have led to a growing concern about the occurrence of these compounds in the environment. Recent studies have reported the occurrence worldwide of EDCs, PPCPs, and other organic wastewater contaminants (OWCs) – collectively referred to as "constituents of emerging concern" (CECs) or "emerging constituents" (ECs) – in wastewater treatment plant (WWTP) effluents, surface waters used as drinking water supplies, and in some cases, finished drinking waters. More information on the occurrence of these chemicals and their fate and transport in the environment is needed by the water industry, as well as regulatory agencies, for risk assessment, future water resource planning, pollution prevention programs, and public communication.

1.2 Research Objectives

Three main drinking water sources for California were evaluated for this project (Figure ES-1): State Project Water (SPW), also known as State Water Project water, starting from the Sacramento-San Joaquin River Delta (Delta) in Northern California and brought into Southern California; Colorado River Water (CRW) starting at Lake Mead (NV) and brought into Southern California; and the Santa Ana River (SAR) in Orange County. The three sources combined, after treatment or groundwater recharge, supply drinking water to more than 25-million people in California. The objectives of this project were to assess the occurrence of a wide range of EDCs, PPCPs, and OWCs in these drinking water sources, to evaluate the impact of treated wastewater discharges, and also to evaluate the fate and transport of these chemicals in each watershed.

1.3 Sampling Design

A total of 32 sampling locations were selected (11 from SPW, 8 from CRW, and 13 from SAR), including those that are upstream and downstream of WWTP discharges, selected WWTP effluents, and various points in each watershed. Sample collections were conducted quarterly in each watershed from April 2008 to April 2009.

1.4 Analytical Methods

All samples were split two ways between Metropolitan Water District of Southern California (MWD) and Orange County Water District (OCWD). In addition, four of the eight CRW samples collected each quarter were also analyzed by the Southern Nevada Water Authority (SNWA).

Thirty-three EDCs, PPCPs, and OWCs were analyzed at MWD by two methods: gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/tandem mass spectrometry (LC/MS/MS). The GC/MS method was applied to 20 volatile or semi-volatile chemicals, with minimum reporting levels (MRLs) ranging from 10 to 50 nanograms per liter (ng/L). The LC/MS/MS method was applied to 14 polar, non-volatile, or thermally labile compounds, most of which were not amenable to GC/MS analysis.

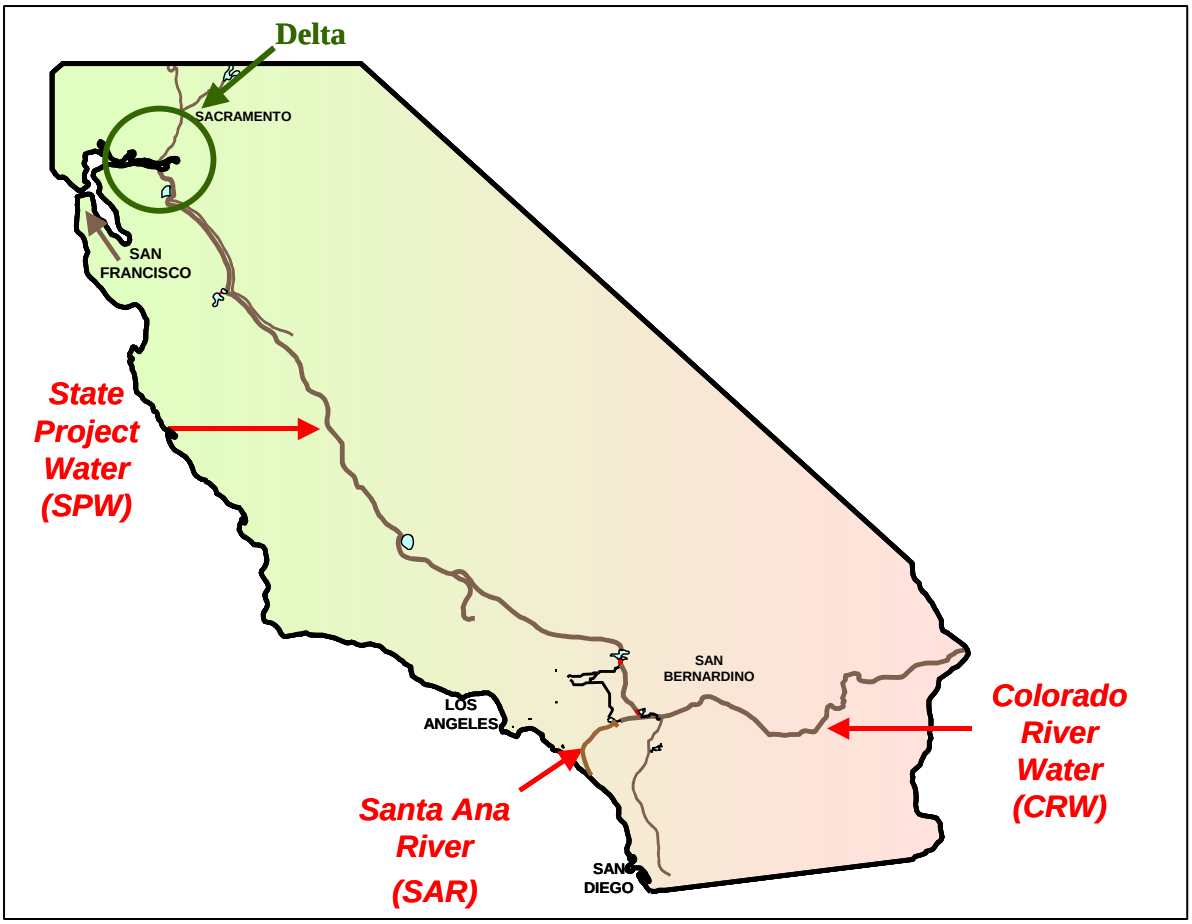

Figure ES-1. Map of central and southern California depicting the three watersheds studied for the project.

The MRLs for the LC/MS/MS method ranged from 1 to 10 ng/L. Atrazine was analyzed by both methods. Furthermore, total phosphorus was analyzed with an MRL of 0.004 milligrams per liter (mg)/L.

Twenty-eight chemicals were analyzed at OCWD by three methods according to the types of analytes (i.e., the PPCPs method, the hormones method, and the phenols method). The PPCPs method analyzed for 11 chemicals by LC/MS/MS, with MRLs ranging from 1 to 10 ng/L. The hormones method analyzed for nine chemicals by LC/MS, with an MRL of 10 ng/L for each chemical. The phenols method analyzed for eight chemicals by LC/MS, with MRLs ranging from 1 to 10 microgram (µg)/L.

Taking into account that MWD and OCWD's methods shared 12 common analytes, a total of 50 analytes, including EDCs, PPCPs, OWCs, and total phosphorus, were analyzed for in this project.

Extensive quality assurance/quality control (QA/QC) protocols were applied to ensure high-quality data, given that there are no standard methods currently available. Within each laboratory, these protocols included field blanks, method blanks, duplicate samples, matrix-spiked samples, and matrix spiked duplicate samples. Inter-laboratory QA/QC practices included split samples between MWD and OCWD for all samples, and split samples among MWD, OCWD, and SNWA for 16 samples (four samples each quarter) throughout the project. Moreover, a round robin test among the three laboratories was conducted before sample collection began in April 2008. Overall, the results from the three laboratories compared very well.

1.5 Project Findings

1.5.1 Occurrence

Of the 126 samples analyzed for the project, one sample (American River at Fairbairn drinking water treatment plant [DWTP] intake collected in April 2008) had no detectable levels of any EDCs, PPCPs, or OWCs. All other samples had one or more analytes detected at or above the corresponding MRLs. The five most frequently detected PPCPs were caffeine, carbamazepine, primidone, sulfamethoxazole, and tris(2-chloroethyl) phosphate (TCEP).

At the sample sites upstream of WWTP discharges in all three watersheds, the concentrations of selected PPCPs, except for caffeine, were low (i.e., ≤ 13 ng/L), pointing to WWTP discharges as the main source of most PPCPs and OWCs in the environment.

Caffeine represented an exception to the overall trend. The median and maximum concentrations of caffeine at the upstream sites were 47 and 2,160 ng/L, respectively, indicating other sources of caffeine in the environment (e.g., urban runoff, plants that produce caffeine).

For the SPW watershed, the median occurrence of targeted analytes in the river samples was <30 ng/L each, except for diuron (81 ng/L). However, maximum concentrations for some analytes exceeded 100 ng/L. The highest levels of gemfibrozil in this watershed were detected in the Sacramento River at Hood (83-162 ng/L), which is downstream of the Sacramento WWTP. Diuron was detected in 88% of the SPW samples, with a maximum concentration of 873 ng/L, which is consistent with the fact that diuron is used extensively in California as a pre-emergent herbicide.

For the CRW watershed, the median occurrence of targeted analytes in the river samples was <20 ng/L each. The median occurrence of a number of the PPCPs in a Nevada blended WWTP effluent, which represented the discharge into Lake Mead, were >100 ng/L, and the maximum occurrence of sulfamethoxazole was >1,000 ng/L. High levels of caffeine (519-1,370 ng/L) and DEET (64-297 ng/L) were sometimes detected at the inlet to Lake Havasu, most likely from human activities in this portion of the watershed.

For the SAR watershed, the median occurrence of a number of the analytes in the WWTP discharges was >100 ng/L, and the maximum occurrence of some PPCPs was >1,000 ng/L. The levels of PPCPs in the river and tributary samples varied widely, as this included sample sites upstream and downstream of WWTPs. The concentrations of most PPCPs were lower in the river and tributary samples than those in the WWTP effluents, but were substantially higher than

those in the SPW and the CRW watersheds, consistent with the fact that the SAR consisted of greater than 50% tertiary treated wastewater under non-storm conditions during this study.

In the WWTP effluents collected from CRW and SAR, the concentrations of carbamazepine and primidone did not vary extensively between different samples, whereas those of caffeine, gemfibrozil, and sulfamethoxazole varied from not detected to >1,000 ng/L. The general trend was that WWTPs with ultraviolet (UV) disinfection had high levels of gemfibrozil and sulfamethoxazole, and WWTPs with chlorination had low levels of these two PPCPs. One WWTP (WWTP #3 in the SAR watershed) that added chlorine but did not achieve breakpoint in one sample event (i.e., formed chloramines) also had high levels of these two PPCPs.

Carbamazepine and primidone had been shown to be conservative wastewater tracers by previous work of members of the project team and other research groups. The occurrence of these two anticonvulsants in the SPW and CRW watersheds relative to that of the Nevada WWTP blended effluent (assuming similar levels in WWTP effluents from the Sacramento-San Joaquin River Delta [Delta]) suggested that SPW and CRW were <10% treated wastewater. On the other hand, the SAR was effluent-dominated (>50% treated wastewater).

The seasonal variations of selected PPCPs in the WWTP effluents were evaluated, and overall the concentrations did not vary significantly during different seasons. The exception was one of the WWTPs in the SAR watershed (WWTP #3), which experienced plant upsets during two of the four sampling events and resulted in much higher levels of caffeine (>400 ng/L), and gemfibrozil and sulfamethoxazole (both at >1,000 ng/L).

Also evaluated were the seasonal variations of selected PPCPs in three river samples: the Hood and Holt Road sites in the Delta representing surface water samples downstream of WWTPs in the Sacramento and San Joaquin Rivers, respectively, and the Imperial Highway site in the SAR, which was downstream of a number of WWTPs and was the location at which SAR was diverted for groundwater recharge. The highest occurrence of caffeine at the two sites in the Delta was in the winter (January 2009), reflecting possibly less biodegradation at the WWTPs and/or less biodegradation in the rivers during this season. In addition, there should be less photolysis in the winter than in the summer. However, biodegradation is believed to be the dominant elimination process for caffeine in surface water supplies. Also in January 2009, the concentrations of all of the representative PPCPs were relatively high in the San Joaquin River at Holt Road, suggesting that the San Joaquin River flow at Holt Road during this sample event may have been lower than normal. In the SAR at Imperial Highway, there was less carbamazepine and primidone in the February 2009 sample event, when there was a major storm event.

1.5.2 Fate and Transport

For the SPW watershed, the amounts of certain PPCPs (i.e., carbamazepine, primidone, gemfibrozil, sulfamethoxazole) were highly attenuated. The attenuation of carbamazepine and primidone can be attributed to dilution with non-wastewater-impacted water. The attenuation of gemfibrozil and sulfamethoxazole were most likely due to a combination of dilution with other sources of water and some natural degradation processes, such as biodegradation, photolysis, and sorption. The occurrence data suggested that water at the Banks pumping plant (the outflow from the Delta and the start of SPW) during this study reflected a greater percentage of water

from the Sacramento River than from the San Joaquin River and/or other sources of water with less PPCP impact.

For the CRW watershed, the averages of carbamazepine, primidone, and sulfamethoxazole detected at Hoover Dam was 1.7%, 1.9%, and 2.1%, respectively, of the levels detected in the Las Vegas Wash, consistent with previous studies that showed the annual inflow via the Las Vegas Wash was ~1.5% of the total inflow to Lake Mead.

For the SAR watershed, the attenuation of primidone was evaluated at four sites downstream of WWTP discharges: SAR at Riverside Avenue; MWD Crossing; River Road; and Mill/Cucamonga Creek at Chino Corona Road. The attenuation at Riverside Avenue, River Road, and Chino Corona Road were all within the coefficient of variation of the method; however, the attenuation at MWD Crossing was consistently high, ranging from 37-55%. One possibility at this site was loss of water to an adjacent aquifer as well as dilution elsewhere from groundwater sources adjacent to the river (both a losing stream and gaining stream scenario may have existed). Evaluation of carbamazepine at these four sites showed similar trends. Evaluation of gemfibrozil and sulfamethoxazole at the same sites showed additional attenuation relative to primidone, indicating other loss mechanisms.

The Prado Wetlands in the SAR watershed proved effective in removing/transforming PPCPs to varying extents. For example, azithromycin was completely attenuated. Many other PPCPs (e.g., caffeine, gemfibrozil, ibuprofen, sulfamethoxazole, acetaminophen) were highly attenuated (42-100%) in two or three of the sample events, whereas there was often little or no attenuation in the May 2008 sample event, which was shortly after the wetlands had been rebuilt and put back in service. There was no substantial attenuation of primidone (-8 to 27%, median of 5%). The attenuation through the wetlands of DEET and TCEP was low (median values of 24 and 33%, respectively).

The amount (on a volume basis) of the SAR water that originated from treated wastewater effluent was evaluated for two SAR sites at below Prado Dam and Imperial Highway, based on the presence of two conservative wastewater tracers, primidone and carbamazepine. The primidone results suggested that the SAR at below Prado Dam was effluent-dominated (78-82% treated wastewater effluent) in three of the four sample events, and was effluent-impacted (37% treated wastewater effluent) in February 2009, when there was a major storm event. The results at the SAR at Imperial Highway suggested that it was effluent-dominated (52-70% treated wastewater effluent) in two of the sample events, and was effluent-impacted (33-48% treated wastewater effluent) in the other two. The calculation based on carbamazepine showed similar trends.

1.5.3 Correlations between Certain PPCPs

The concentrations of several frequently detected PPCPs were plotted against that of primidone, used as a conservative indicator of wastewater impact for the purpose of this report, to identify any possible correlations.

For the SPW and CRW river samples, the best correlations with primidone were found with two other anticonvulsants, carbamazepine and dilantin, with the correlation coefficient (R^2) being

0.76 and 0.73, respectively. The correlation coefficient for sulfamethoxazole with primidone was 0.62, indicating a fair level of correlation, whereas the correlation coefficient for TCEP was 0.41, indicating poor correlation. Caffeine, gemfibrozil, and DEET showed no correlation with primidone. Diuron in the environment came mainly from agricultural runoff, and it showed no correlation with primidone and other PPCPs, which were WWTP-originated. In the SPW watershed, there was a fair linear correlation ($R^2 = 0.61$) between sulfamethoxazole and gemfibrozil, which are known to degrade in the environment.

For the SAR watershed, dilantin showed a fair correlation with primidone in all samples including the WWTP effluents, with a $R^2 = 0.67$; carbamazepine ($R^2 = 0.40$), DEET ($R^2 = 0.39$), and TCEP ($R^2 = 0.35$) showed poor correlations with primidone. Caffeine, gemfibrozil, and sulfamethoxazole showed no correlation with primidone. The correlation of gemfibrozil and sulfamethoxazole in WWTP effluents was excellent (R^2=0.92), as WWTP disinfection processes had a similar impact on these two PPCPs. The correlation of these two PPCPs in the river and tributary samples in the SAR watershed was poor ($R^2 = 0.46$). The correlation of total phosphorus with primidone was also examined in the SAR watershed. The group of samples of WWTP effluents with high phosphorus and their corresponding downstream sites showed a poor correlation ($R^2 = 0.41$) between total phosphorus and primidone, whereas the other group of samples of WWTP effluents with low phosphorus and the corresponding downstream sites showed no correlations between total phosphorus and primidone.

1.6 Future Research Needs

Significant information was obtained from this project on the occurrence, fate, and transport of EDCs, PPCPs, and OWCs in three watersheds that provide water to California. It is recommended that future research be directed toward the following areas:

- Standardized analytical methods are needed to ensure high quality data and to be able to compare results from different studies. Currently, approaches from laboratories performing PPCP analysis vary widely on key analytical issues, such as blank contamination and matrix effects. This is being addressed in part by the current Water Research Foundation Project 4167 entitled "Evaluation of Analytical Methods for EDCs and PPCPs via Inter-laboratory Comparison," which will evaluate current methodology commonly used for the analysis of EDCs and PPCPs, with the goal of providing guidelines to drinking water utilities on optimizing data quality for EDCs and PPCPs. Twenty-five laboratories are participating in Project 4167, including the three laboratories that participated in this project. The results of that study are expected in 2011.

- Collection and analysis of treated effluents from the Delta WWTPs will provide a better understanding of the SPW watershed. The effluents from the Sacramento or Stockton WWTPs were not available for this project. However, the Stockton WWTP has recently agreed to be sampled for another study in the Delta.

- A Lagrangian sampling design, which follows a plug of water, will allow a more in-depth fate and transport analysis. A good understanding will be needed of the hydrology of the watershed of interest, as well as significant effort and resources for sampling. A good

candidate to consider is the SAR (e.g., between Prado Dam and Imperial Highway, where the flow conditions are defined and no inflows enter the river during non-storm conditions). Some work in this vein was conducted in the past, but more is needed.

- Certain locations in the watersheds studied need better characterization of the hydrology. For example, although the discharge rate of the Stockton WWTP was known, the flow in the San Joaquin River was difficult to access because of "reverse" flows due to tidal impact. In addition, the portion of the SAR near the sampling point referred to as "MWD Crossing" needs to be evaluated in terms of losing and/or gaining stream.

- Groundwater monitoring wells can be included in future sampling plans to understand the occurrence of PPCPs in regions that practice groundwater recharge. This sampling has been done in other areas of the U.S. and in Europe.

- Examining the concentrations of these emerging constituents in sediments may help in better understanding the fate and transport of these chemicals in natural waters.

- Expand the list of analytes based on prescription patterns, use levels, and toxicological significance.

- Within a watershed, characterize drinking water samples together with the source water and wastewater samples for a better understanding of the significance of the results.

- Identification of significant conversion products resulting from treatment or environmental degradation of these emerging constituents.

- Information on the toxicological relevance of EDCs and PPCPs in drinking water is available in terms of acceptable daily intakes (ADIs) and drinking water equivalent levels (DWELs). The general consensus is that there is no evidence of human health risk from low levels of the commonly detected EDCs and PPCPs in drinking water or drinking water supplies. Nonetheless, more toxicological studies of PPCPs are needed.

- The occurrence of EDCs and PPCPs in water supplies is a sensitive issue for the public, and the perceived risks by the public should be addressed effectively. A collaborative effort in arriving at public communications tools will be of value to wastewater and drinking water agencies. In addition, this issue provides an opportunity to enhance the public's awareness that they are personally connected to the environment; therefore, information is needed on how individuals can contribute to pollution prevention measures.

2. INTRODUCTION

2.1 EDCs, PPCPs, and Their Occurrence

The increasing production and use of pharmaceuticals and personal care products (PPCPs) – some of which may be endocrine disrupting compounds (EDCs) – have led to a growing concern about the occurrence of these compounds in surface water and groundwater used as drinking water supplies, and in finished drinking waters. EDCs refer to those chemicals that interfere with natural hormonal functions. Together with other PPCPs and organic wastewater contaminants (OWCs), they represent diverse groups of chemicals, consisting of natural and synthetic estrogens, anticonvulsants, antibiotics, X-ray contrast media, sunscreen agents, insect repellents, and many others. They may enter the aquatic environment on a continuous basis via agricultural runoff, municipal landfill leachates, or discharges from wastewater treatment plants (WWTPs), which are not designed to completely remove EDCs and PPCPs. Although these chemicals may have been released into the environment as long as they have been in production, they are often referred to as "emerging" contaminants because better analytical techniques have allowed for nanogram-per-liter (ng/L) level detection of EDCs and PPCPs that were previously not detectable. As a result, they have gathered attention from scientists, as well as the general public (Donn et al., 2008).

2.1.1 Occurrence of EDCs and PPCPs in Treated Wastewater Effluents

Recent studies have reported the occurrence worldwide of a vast array of EDCs, PPCPs, and OWCs in treated wastewater effluents (e.g., Sedlak et al., 2005; Glassmeyer et al., 2005; Snyder et al., 2008a). The number of EDCs and PPCPs and their concentrations in wastewater effluents depend on the type of the treatment processes and vary from region to region. Some of the representative PPCPs and their concentrations in wastewater effluents are shown in Table 1. Differences in the presence or absence of some PPCPs may reflect methodological differences (e.g., presence or absence of dechlorination agent and/or preservative; sensitivity issues), as there were no standard methods available.

2.1.2 Impact of Treatment Processes on EDCs and PPCPs

The occurrence of EDCs and PPCPs in WWTP effluents is determined (in part) by the type of treatment/disinfection processes used at each plant. Snyder et al. (2007) evaluated various physical, chemical, and biological drinking water treatment plant (DWTP) processes on the removal/transformation efficiencies of EDCs and PPCPs in natural waters. Table 2 shows the impact of the disinfection processes. For the same type of oxidation process, the removal/transformation efficiencies of individual contaminants were dependent on their chemical structures. Overall, ozone was highly effective at reacting with the majority of EDCs and PPCPs, with the exception of the flame retardant, tris(2-chloroethyl) phosphate (TCEP). Under the conditions evaluated, it was likely that ozone transformed the PPCPs, but did not mineralize them. Free chlorine was more efficient than chloramines at reacting with EDCs and PPCPs. In other research, the widely used antimicrobial agent triclosan was shown to react with chlorine to form chloroform and other chlorinated organic compounds (Rule et al., 2005). UV at germicidal doses was not effective at reacting with certain PPCPs. Alternatively, UV and hydrogen peroxide (an advanced oxidation process) can be used to destroy/transform more

micropollutants. Although the study was conducted in natural waters at DWTP disinfectant dosages, it is expected that these general trends would extend to WWTP disinfectant dosages. When free chlorine is added to treated wastewater, a chlorine dose of 7.6 mg/L as Cl_2 is *theoretically* required for each 1.0 mg/L of ammonia-nitrogen (NH_3-N) in order to achieve breakpoint chlorination. However, in actual WWTP practice, a higher chlorine dose (e.g., 10 mg/L for each 1.0 mg/L of NH_3-N) is required (White, 1999). Therefore, the presence of a high amount of ammonia in some treated wastewaters may result in the formation of combined chlorine (chloramines) when chlorine is added (Krasner et al., 2009), hence less transformation of PPCPs.

As many PPCPs can undergo biodegradation, the extent and nature of the biological treatment processes (e.g., no nitrification, nitrification, and denitrification) at WWTPs can impact certain PPCPs. At water reclamation plants with reverse osmosis (RO), PPCPs can be highly rejected (Xu, et al. 2005).

Table 1. Occurrence of Representative PPCPs in Treated Wastewater Effluents

Reference:		**Sedlak et al., 2005**		**Glassmeyer et al., 2005**		**Snyder et al., 2008a**	
PPCP	Use	Detection Frequency (n = 6-8)[#]	Median Conc. (ng/L)	Detection Frequency (n = 10)	Median Conc. (ng/L)	Detection Frequency*	Average Conc. (ng/L)
Carbamazepine	Anti-convulsant	-	-	82.5%	74	>80%	>400
Diclofenac	Anti-inflammatory	88%	60	-	-	>70%	<50
Gemfibrozil	Anti-cholesterol	100%	920	0	ND[†]	>70%	<50
Ibuprofen	Analgesic	50%	50	0	ND	>80%	>100
Sulfamethoxazole	Antibiotic	83%	1,400	72.5%	68	-	-
Triclosan	Antibacterial	-	-	62.5%	120	100%	1,000

[#]n = Number of samples analyzed.
*Based on literature review; number of samples not available.
"-" = Not analyzed.
[†]ND = Not detected.

Table 2. PPCP Removal/Transformation Efficiencies
in Selected Drinking Water Treatment Processes[#]

PPCP	UV[1]	Chlorination[2]	Chloramination[3]	Ozonation
Caffeine	<20%	<20%	<20%	>80%[4a]
Carbamazepine	<20%	<20%	<20%	>95%[4b]
Diclofenac	50-80%	>80%	50-80%	>95%[4b]
Gemfibrozil	<20%	50-80%	<20%	>95%[4b]
Ibuprofen	<20%	<20%	<20%	50-80%[4a]
Sulfamethoxazole	50-80%	>80%	<20%	>95%[4b]
TCEP	<20%	<20%	<20%	<20%[4a]
Triclosan	50-80%	>80%	>80%	>95%[4b]

[#]Adapted from Snyder et al., 2007
[1]UV Dose = 40 mJ/cm^2
[2]Chlorine dose = 3 mg/L, contact time = 24 hours
[3]Chloramine dose = 3 mg/L, contact time = 24 hours
[4a]Ozone dose = 2.5 mg/L, contact time = 24 minutes
[4b]Ozone dose = 2.5 mg/L, contact time = 2 minutes

2.1.3 Fate and Transport of EDCs and PPCPs in the Aquatic Environment

Once EDCs and PPCPs enter into the aquatic environment, the fate of individual compounds can fall into three categories: transport, sequestration, and degradation (Glassmeyer et al., 2008). Transport is the least disruptive category (i.e., the chemicals are transferred without any changes in structures and properties) and includes dispersion and dilution by water from other sources. Sequestration refers to processes such as sorption and bioconcentration, in which the contaminants are transferred into other compartments without degradation. Degradation includes processes such as photolysis, hydrolysis, and biodegradation, which transform the contaminants into other chemicals.

The fate and transport of EDCs and PPCPs in the environment is determined by many factors, including the physical properties of individual compounds and the environment in which they are present. For example, the anti-convulsants carbamazepine and primidone have been shown to be highly recalcitrant (Loffler et al., 2005; Krasner et al., 2006) and were considered conservative for the purpose of this report. Sulfonamide antibiotics, including sulfamethoxazole, on the other hand, have been shown to undergo biodegradation and sorption to sediments or soils (Boxall, 2008; Radke et al., 2009). Attenuation of gemfibrozil and ibuprofen by photolysis and

biodegradation has been reported in an effluent-dominated river, and the average concentrations decreased by 75-90% as the water traveled downstream of WWTP discharge (Fono et al., 2006).

An important aspect of research on EDCs and PPCPs has been their use as tracers of wastewater discharges (Glassmeyer et al., 2005; Guo and Krasner, 2009). Previously, some researchers used boron as a wastewater indicator (Schreiber and Mitch, 2006). However, in many waters in the western U.S., ambient levels of boron are elevated, precluding the use of this chemical as a wastewater indicator. Glassmeyer and colleagues (2005) examined multiple chemicals for their potential use as tracers of human wastewater and indicated that several of the 35 most commonly detected chemicals are good indicator candidates, including the anticonvulsant carbamazepine, the antihistamine diphenhydramine, caffeine, the fecal sterol coprostanol, and the fragrances ethyl citrate, galaxolide, and tonalide. Krasner and colleagues (2006) found that the anticonvulsant primidone was a conservative tracer of wastewater impact on downstream drinking water supplies. A more recent study showed that caffeine, carbamazepine, and primidone were present in all effluent-impacted drinking-water samples investigated, and that either carbamazepine or primidone could be used as conservative wastewater tracers (Guo and Krasner, 2009). Although caffeine is a good indicator of anthropogenic effects (Buerge et al., 2003), it is not a conservative tracer because it can undergo biodegradation in the environment.

2.1.4 Occurrence of EDCs and PPCPs in Drinking Water Sources and Finished Drinking Water

The occurrence of EDCs, PPCPs, and OWCs in wastewater-impacted surface waters has been reported by several research groups (Kolpin et al., 2002; Buerge et al.; 2003; Snyder et al., 2003; Glassmeyer et al., 2005). The impact from treated wastewater on the water quality of drinking water supplies will only increase with population growth and increasing agricultural and industrial development. Furthermore, increasing water demand and drought have resulted in an increase in water recycling and reuse (direct and indirect). This is an emerging area of concern for groundwater basins that are recharged with recycled wastewater, which may contain various EDCs and PPCPs.

One of the more comprehensive studies of streams susceptible to contamination, conducted by the U.S. Geological Survey (USGS), found 82 of the 95 targeted pharmaceuticals, hormones, and OWCs at the nanogram to microgram per liter range (Table 3) in 80% of 139 streams sampled across the U.S (Kolpin et al., 2002). In a national reconnaissance for pharmaceuticals and other OWCs in untreated drinking water sources in the U.S. conducted by the USGS (Focazio et al., 2008), 25 groundwater and 49 surface-water sources were sampled and analyzed for 100 analytes. Sixty-three of the 100 targeted chemicals were detected in at least one sample. In a more recent study, Benotti and colleagues (2009) analyzed source waters, finished drinking waters, and distribution system water samples from 19 U.S. water utilities for 51 EDCs and PPCPs. Some of the frequently detected compounds, together with the median and maximum concentrations, are listed in Table 3.

Although some DWTP processes are capable of removing/transforming a variety of PPCPs (Westerhoff et al., 2005; Snyder et al., 2007), trace levels of EDCs and PPCPs may still be present in finished drinking water (Stackelberg et al., 2004; Stackelberg et al., 2007; Benotti et al., 2009). In general, the occurrence of these chemicals is more frequent and at higher median

concentrations in source waters than in finished drinking water, and the persistence of these contaminants into finished drinking waters depends on their occurrence in source waters and the DWTP processes. Of the 18 finished drinking water samples collected from water utilities across the U.S. in the most recent study (Benotti et al., 2009), the five most frequently detected PPCPs were atrazine, meprobamate, phenytoin, atenolol, and carbamazepine, with median concentrations less than 10 ng/L, except for atrazine (49 ng/L).

Table 3. Some of the Frequently Detected EDCs and PPCPs in Surface Waters from Literature

Reference:	**Kolpin et al., 2002**			**Benotti et al., 2009**		
PPCP	**Det. Freq. (n = 70-85)**	**Median conc. (ng/L)**	**Maximum conc. (ng/L)**	**Det. Freq. (n = 19)**	**Median conc. (ng/L)**	**Maximum conc. (ng/L)**
Coprostanol	86%	88	150,000	-[*]	-	-
Cholesterol	84%	830	60,000	-	-	-
DEET[#]	74%	60	1,100	32%	85	110
Caffeine	71%	100	5,700	-	-	-
Triclosan	58%	140	2,300	32%	3.0	6.4
TCEP	58%	100	540	53%	120	530
Nonylphenol	51%	800	40,000	42%	100	130
Sulfamethoxazole	19%	66	520	89%	12	110
Meprobamate	-	-	-	84%	8.2	73
Atrazine	-	-	-	79%	32	870
Carbamazepine	-	-	-	79%	4.1	51
Estrone[†]	21%	27	112	79%	0.3	0.9
Phenytoin	-	-	-	74%	5.1	29
Atenolol	-	-	-	63%	2.3	36
Naproxen	-	-	-	58%	0.9	32
Trimethoprim	-	-	-	58%	0.8	11

[*]"-" = Not reported

[#]DEET = *N*,*N*-Diethyl-*meta*-toluamide

[†]Note that there were some issues with the concentrations of hormones in the Kolpin et al. (2002) study.

2.2 Health Effects

There have been studies conducted on the adverse health effects for aquatic species and wildlife, such as disrupted physiological processes and impaired reproductive functions, from exposure to EDCs and PPCPs in surface waters impacted by treated wastewater (Daughton and Ternes, 1999; Giesy et al., 2000; Snyder et al., 2001). Understandably, scientists, regulators, and the general public are concerned about the human health effects of PPCPs in drinking water supplies.

Different approaches have been used to evaluate the potential risks and toxicological relevance of low concentrations of PPCPs in drinking water. One common approach is to use the PPCP

therapeutic doses, which are in milligrams per dose, as references. The PPCP concentrations detected in the environment are generally at low ng/L levels, which are orders of magnitudes lower than therapeutic doses. Other approaches (Snyder et al., 2008b) included the use of estradiol equivalent (EEq), acceptable daily intakes (ADIs), and drinking water equivalent levels (DWELs). EEqs measure the cumulative estrogenitciy of compounds using an *in vitro* cellular bioassay. ADIs are defined as the amount of a chemical to which a person can be exposed on a daily basis over an extended period of time (usually a lifetime) without suffering a deleterious effect (U.S. Environmental Protection Agency [USEPA], 1993). ADIs can be converted to DWELs by multiplying the ADI by an assumed body weight (70 kilograms, the USEPA default adult body weight) and dividing by an average daily drinking water ingestion rate (two liters per day). Snyder and colleagues (2008b) showed that none of the EDCs and PPCPs detected in their drinking water samples exceeded the calculated health risk threshold (i.e., ADIs and DWELs). Furthermore, EEqs in the drinking water samples were either not detected or extremely low, much lower than some of the common food and beverage items, such as vegetable juice, coffee, and soy milk. Nonetheless, more information on the occurrence and health effects of EDCs and PPCPs are needed by the water and wastewater industry, as well as regulatory agencies, for risk assessment, future water resource planning, pollution prevention programs, and public communications.

2.3 Project Objectives

Three main drinking water sources in California were evaluated for this project: State Project Water (SPW), also known as State Water Project water, from the Sacramento-San Joaquin River Delta (Delta) in Northern California and brought into Southern California; Colorado River Water (CRW) brought into Southern California via the Colorado River Aqueduct from Lake Havasu on the California-Arizona border; and the Santa Ana River (SAR) in Orange County. The three sources combined, after treatment or groundwater recharge, supply drinking water to more than 25-million people in California. All three water sources were exposed to wastewater discharges, agricultural runoff, recreation, and/or other activities that may impact water quality. The wastewater contribution to SPW and CRW has varied from 1-2% in winter or in high-flow periods to considerably higher percentages in summer or during a drought or other low-flow event. Baseflow in the SAR has typically consisted of greater than 50% tertiary treated wastewater from upstream WWTPs. The occurrence data of EDCs and PPCPs in these three watersheds were limited. The USGS study (Kolpin et al., 2002) included 10 streams in California, with results that ranged from not detected to low microgram per liter levels. One study (Loraine and Pettigrove, 2006) reported the occurrence of PPCPs in the San Diego area, where the source of contamination was ascribed to SPW and/or CRW, even though neither source water was sampled, except as part of a blend with local reservoir water. The objectives of this project were to assess the occurrence of a wide range of EDCs and PPCPs in three major drinking water sources to California, to evaluate the impact of treated wastewater discharges on a seasonal basis, and also to evaluate the fate and transport of these contaminants. Future efforts can be directed toward those PCCPs that were found to have the highest concentrations relative to their respective ADIs and/or DWELs.

3. SAMPLE COLLECTION

3.1 Overview of Sampling Plan

A map of central and southern California depicting the three watersheds studied for the project is shown in Figure 1. A total of 32 sampling locations were selected (11 from SPW, 8 from CRW, and 13 from SAR), including those that are upstream and downstream of wastewater discharges, selected WWTP effluents, and various points in each watershed. Sample collections were conducted quarterly at each watershed from April 2008 to April 2009. The sampling schedule is shown in Table 4.

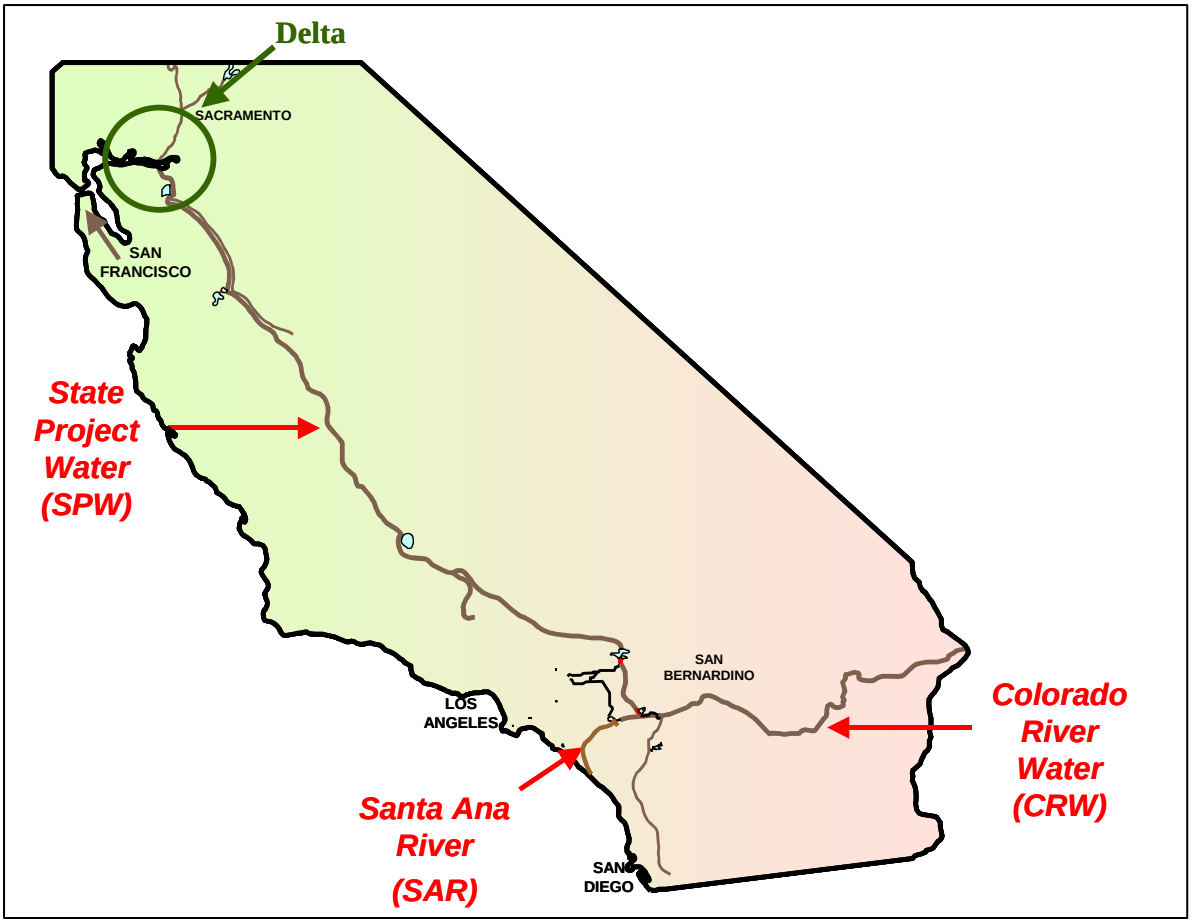

Figure 1. Map of central and southern California depicting the three watersheds studied for the project.

Table 4. Sampling Schedule of the Three Watersheds

Quarter	Sampling Date	Watershed
First	April 2008	SPW
	May 2008	SAR
	June 2008	CRW
Second	July 2008	SPW
	August 2008	SAR
	September 2008	CRW
Third	October 2008	SPW
	November 2008	SAR
	December 2008	CRW
Fourth	January 2009	SPW
	February 2009	SAR
	April 2009	CRW

3.2 SPW

The SPW (Figure 2) is a major drinking water source for California. The Sacramento River is California's longest river, running from north to south through the City of Sacramento out through the Sacramento-San Joaquin River Delta (Delta) towards the Pacific Ocean. In addition to the Sacramento River, the American River and the Natomas East Main Drainage Canal (NEMDC) also flow through the City of Sacramento. The San Joaquin River is the second largest river in California. The river flows from south to north into the Delta, joining the Sacramento River near Sherman Island. The Delta, formed at the confluence of the two rivers and composed of 57 leveed island tracts and 700 miles of sloughs and winding channels, serves not only as a drinking water source, but also provides irrigation water for millions of acres of farmland and serves as the receiving body to several WWTPs. There are nine WWTPs discharging from 0.3-181 million gallons per day (MGD) into the Delta (DWR, 2007). The two largest WWTPs are in the cities of Sacramento and Stockton.

SPW travels 444 miles from the H.O. Banks Delta pumping plant to Southern California, where it splits into two branches at Check 41. SPW (as well as Delta water from the Central Valley Project) is initially stored in Northern California in the San Luis Reservoir and O'Neill Forebay (Check 13), which is 75 miles south of the Delta. In Southern California, water from the East Branch is stored in Silverwood Lake (a few weeks or less detention time) and flows through the Devil Canyon Afterbay. Water from the West Branch is stored in Pyramid and Castaic Lakes (~8-month detention time) and flows through the Foothill Pressure Control Structure (PCS).

Currently, the Municipal Water Quality Investigations Program of the Division of Environmental Services in the California Department of Water Resources (DWR) is charged with monitoring and research of water quality in the Delta. Water quality parameters that are monitored (DWR, 2005) include total organic carbon (TOC), salinity (e.g., bromide), nutrients (i.e., nitrate, total Kjeldahl nitrogen, and phosphorus), pH, alkalinity, hardness, turbidity, and metals. The Program has researched on the impact of agricultural tracts of land situated on peat soil, which can be a

substantial source of TOC in the Delta, and the impact of seawater intrusion, which is one of the primary sources of bromide in SPW (Krasner et al., 1994). To the best of our knowledge, there have not been any previous systematic studies on the occurrence of EDCs and PPCPs in the Delta region.

Eleven locations in the SPW watershed (Table 5) were sampled by the Metropolitan Water District of Southern California (MWD) and DWR staff, utilizing existing MWD and DWR sampling stations. The treated effluents from the Sacramento and Stockton WWTPs were not available for this project. Nonetheless, samples collected upstream and downstream of both WWTPs provided important information on the contribution of EDCs and PPCPs from their discharges. In addition, some of the sampling sites in the Delta were seasonally impacted by agricultural runoff or discharges in the Delta area and the Central Valley.

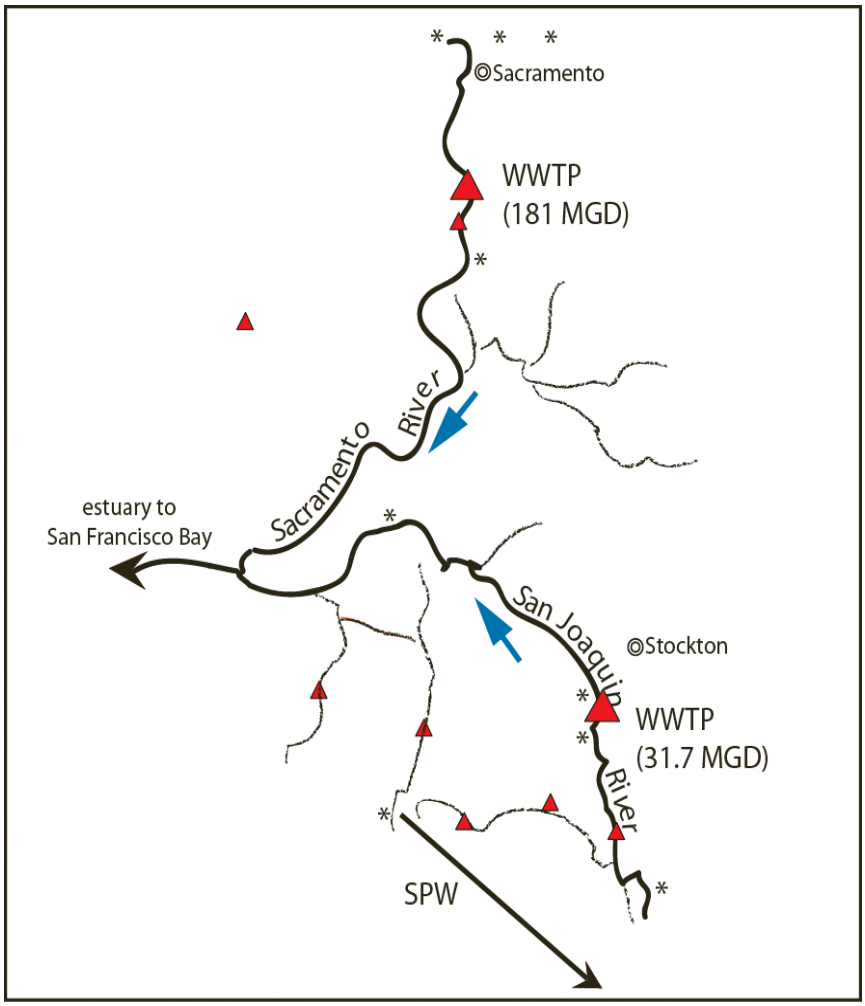

Figure 2. Map of the Delta with the two largest WWTPs, seven smaller WWTPs, and sampling locations. Triangle = WWTP; * = Sampling location. Not all sampling locations are shown because some are off of the map.

Table 5. Sampling Locations in the SPW System

Sampling Location	Significance of the Location
Natomas East Main drainage canal (NEMDC)	Urban drainage
American River at E.A. Fairbairn DWTP	River that enters into the Sacramento River; upstream of the Sacramento WWTP
Sacramento River at W. Sacramento DWTP intake	Upstream of Sacramento WWTP
Sacramento River at Hood	Downstream of Sacramento WWTP
San Joaquin River at Mossdale Landing	Upstream of Stockton WWTP
San Joaquin River at Holt Road	Downstream of Stockton WWTP
H.O. Banks Delta pumping plant	SPW from the Delta
O'Neill Forebay (Check 13)	Integration point of the Delta output
Check 41	Entry point into Southern California; also impacted by agricultural runoff from the Central Valley
East Branch SPW at Devil Canyon	Representing a terminal reservoir
West Branch SPW at Foothill PCS	Representing a terminal reservoir

3.3 CRW

The Colorado River provides a major source of drinking water to California, Nevada, and Arizona. The river flows from Colorado through Utah, into Nevada at Lake Mead, and continues south into Arizona. Water is brought into Southern California via the Colorado River Aqueduct (CRA), which originates from the Whittsett Intake at Lake Havasu (Figure 3). Three major WWTPs discharges a combined 244 MGD (design flow) of treated wastewater into the Las Vegas Wash, a waterway used to carry treated wastewater from the Las Vegas metropolitan area into the Lake Mead watershed. In the Lake Havasu watershed, there is one municipal discharger with a design flow over 5 MGD. There are no municipal or industrial dischargers along the CRA or in the Lake Mathews watershed, which is a terminal reservoir of the aqueduct.

Previous studies in Lake Mead and the Las Vegas Wash reported the occurrence of numerous EDCs and PPCPs in the ng/L range (Snyder et al., 2000; Boyd and Furlong, 2002; Vanderford et al., 2003). A report by the USGS (Boyd and Furlong, 2002) on PPCPs in Lake Mead and the Las Vegas Wash found 13 of 33 targeted compounds in at least one water sample at less than or equal to 200 ng/L. Caffeine, acetaminophen, carbamazepine, cotinine, 1,7-dimethylxanthine (caffeine metabolite), and sulfamethoxazole were detected in Lake Mead (Boyd and Furlong, 2002). No comprehensive studies are known to have been conducted in CRW at locations below Lake Mead.

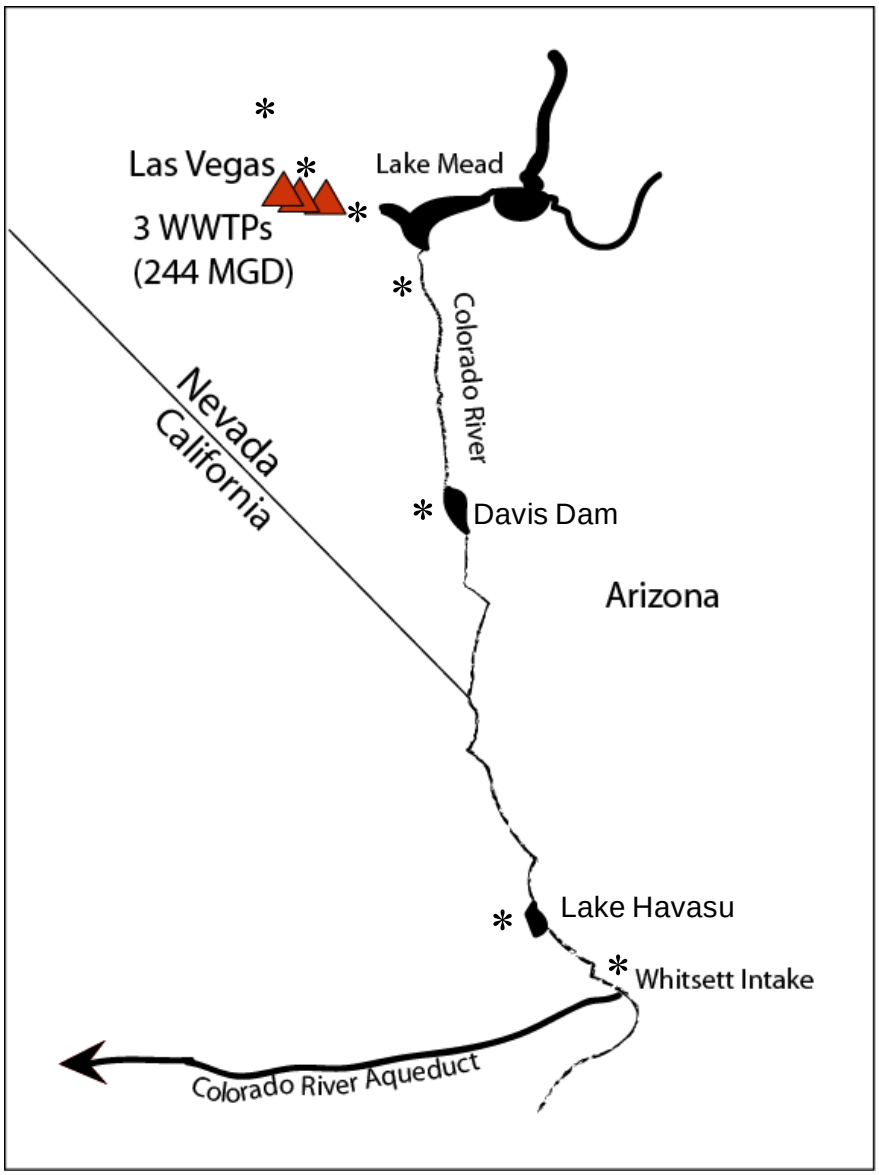

Figure 3. Map of CRW. Triangle = WWTP; * = Sampling location.
Not all sampling locations are shown because some are off of the map.

This project studied the river system from Las Vegas Wash before it entered Lake Mead to MWD's terminal reservoir in Southern California. The eight sampling locations are shown in Table 6. Staff at Southern Nevada Water Authority (SNWA) and the Clean Water Coalition collected samples in the Las Vegas Wash and Lake Mead areas. The treated effluents of the three WWTPs were blended on the day of sampling based on the flows of the individual WWTPs and was used as a single sample representing the overall WWTP discharge. MWD staff collected samples at locations from Davis Dam to Lake Mathews.

Table 6. Sampling Locations in the CRW System

Sampling Location	Significance of the Location
Upstream of the Las Vegas Wash	Upstream of WWTP discharges
Blended effluent from three WWTPs	WWTP discharge
Downstream of the Las Vegas Wash	Downstream of WWTP discharges
Hoover Dam	Effluent of Lake Mead
Davis Dam	Upstream of municipal discharger
Lake Havasu inlet	Downstream of municipal discharger
Whittsett Intake	Intake for CRA
Effluent of Lake Mathews	Terminal reservoir in Southern California

3.4 SAR

The SAR is the main source of water for groundwater recharge for the Orange County Groundwater Basin. With supplements from CRW and SPW, the basin supplies water to more than 20 cities and water agencies and 2-million residents. Baseflow in the SAR has typically consisted of greater than 50% tertiary treated wastewater from a number of WWTPs (Figure 4). The river also receives storm flows, natural runoff, and rising groundwater, especially during winter months. The wastewater discharges in the SAR watershed are a significant component of total stream flow during non-storm conditions. During storm conditions, total stream flow is impacted by stormwater runoff and stormwater stored in reservoirs such as Seven Oaks Dam and Prado Dam. Storage and release of stormwater from reservoirs can also impact total stream flow for a period of time after precipitation has ended. From 2001 to 2005, the percentage of baseflow in the river varied from approximately 24-93%, depending on the rainfall during the year (Woodside, 2006). Behind the Prado Dam in Riverside County, the Prado Wetlands – 465 acres of constructed wetlands – removes nitrate from the SAR (approximately 50% of the SAR is diverted through the wetlands) before it is recharged into the groundwater.

Orange County Water District (OCWD) recharges the Orange County Groundwater Basin using SAR water at the Anaheim forebay recharge facility, and has routine sampling locations along the SAR. Of the nine WWTPs in this watershed (two smaller ones not shown in Figure 4), effluents from the three largest WWTPs (WWTPs #2 - #4) were collected (Table 7). An additional 10 sampling locations included river and tributary sites upstream and downstream of each of these three WWTPs, Prado Wetlands inlet and outlet, and at Imperial Highway, where SAR was diverted to the recharge facility (Table 7).

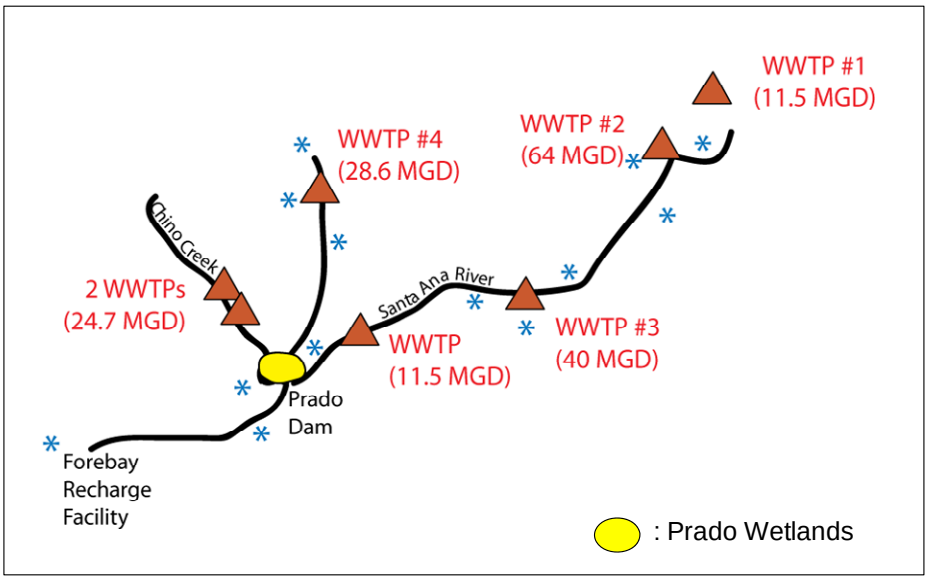

Figure 4. Map of SAR. Triangle = WWTP; * = Sampling location. The flows in brackets are design flows.

Table 7. Sampling Locations in the SAR System

Description	Sampling Location/Significance	Disinfection at the WWTP
WWTPs	Effluent of WWTP #2	UV
	Effluent of WWTP #3	Chlorination
	Effluent of WWTP #4	Chlorination
SAR and tributary sites	North of WWTP #2; 100-feet upstream of WWTP #2 (primarily effluent from WWTP #1)	Not applicable (except for WWTP #1, which used chlorination and UV)
	SAR at Riverside Avenue; 1-mile downstream of WWTP #2	
	SAR at MWD Crossing; 7-miles downstream of Riverside Avenue; ~1/2 mile upstream of WWTP #3	
	SAR at River Road; ~10-miles downstream of WWTP #3	
	Deer/Cucamonga Creek channel; upstream of WWTP #4 (urban runoff during non-storm flow period)	
	Mill/Cucamonga Creek at Chino Corona Road; ~5-miles downstream of WWTP #4	
	Prado Wetlands inlet	
	Prado Wetlands outlet (after flow through two thirds of the Wetlands)	
	SAR below Prado Dam	
	SAR at Imperial Highway, before recharge facility	

3.5 Sample Handling Prior to Analysis

Samples were collected in 1-liter amber glass bottles and shipped to the laboratories overnight in ice chests with frozen Blue Ice. For the SAR sites, samples were delivered to the OCWD laboratory on the day of sample collection and MWD staff picked up cooled samples the following day. For the CRW samples upstream of Davis Dam, samples were delivered to the SNWA laboratory on the day of sample collection in addition to those samples that were shipped to MWD and OCWD. The samples were preserved with 1 gram per liter of sodium azide (a biocide) and dechlorinated with 50 mg/L of ascorbic acid (Vanderford and Snyder, 2006), where the reagents were in the sample bottles before they were sent to field staff for collection. All samples were grab samples. A Lagrangian sampling plan to follow the same parcel of water as it moved through each watershed was not used for this study; therefore, the samples collected along a stretch of river were not collected at times that matched the actual flow times. However, in a previous study, primidone samples were collected from an effluent-dominated river in two sample events, either once each day on consecutive days or twice on the same day, and the values were not found to be significantly different over these time frames (Krasner et al., 2006). Upon arrival at the laboratory, at either MWD or OCWD, samples were filtered with Nylon membrane filters (0.45-micron) with a glass microfiber pre-filter and kept at 4°C until extraction. To evaluate sample collection protocols and potential contamination issues, field blanks were collected along with the samples, where organic-free pure water (OPW) was poured into empty sample bottles during the same time period when samples were collected. The field blanks were processed in the same way as the samples.

4. ANALYTICAL METHODS

4.1 Selection of Analytes

Multiple analytical methods from different research groups have been developed and reported for the detection of hundreds of EDCs and PPCPs in water in recent years. However, unlike standard methods commonly used by water utilities to monitor for regulated contaminants in water, currently there are no standard methods available for the analysis of EDCs and PPCPs. Moreover, there is not a common list of analytes for EDCs and PPCPs.

The project team chose the analytes for this project based on the following criteria:

- Commonly occurring EDCs and PPCPs based on the literature (Vanderford et al., 2003; Westerhoff et al., 2005; Trenholm et al., 2006).
- EDCs and PPCPs representing a variety of categories (e.g., uses, chemical structure, and functional groups).
- Suggested monitoring list from the Groundwater Recharge Reuse Regulations Draft (Endnote 5) by the California Department of Health Services (CDHS, 2007).
- In addition to EDCs and PPCPs, OWCs such as polyaromatic hydrocarbons (PAHs) and pesticides were included.
- Consistent quality assurance/quality control (QA/QC) data. Some pharmaceuticals (e.g., erythromycin) were initially considered; however, the QA/QC data for these analytes were inconsistent due to a variety of factors, such as matrix interferences. Therefore, they were not included in the final analyte list.
- EDCs and PPCPs that were impacted to varying degrees by different loss mechanisms in the watershed (e.g., photolysis, biodegradation, and sorption), as well as those believed to be stable.
- To follow the fate and transport of atrazine in the aquatic environment, two main triazine degradates (i.e., desethyl-atrazine, desisopropyl-atrazine) were included in the list of analytes.
- Total phosphorus was analyzed as another indicator of wastewater impact.
- Complementary analyte lists between the different laboratories were used to (1) maximize the number of target compounds being measured and (2) allow for an inter-laboratory calibration for common analytes.

4.2 Analytical Methods at MWD

Compounds that are volatile or semi-volatile (e.g., certain industrial byproducts and pesticides) were analyzed by gas chromatography (GC)/mass spectrometry (MS), whereas those that are not amenable to GC/MS (e.g., polar, non-volatile, high molecular weight [MW], thermally labile) were analyzed by liquid chromatography (LC)/MS/MS. The list of analytes at MWD is shown in Table 8, along with their minimum reporting levels (MRLs).

Table 8. List of Analytes at MWD

Class	Analyte	Use or Structure	MW (g/mole)	MRL (ng/L)
I. GC/MS Method				
Industrial	Anthracene	PAH	178	10
	Benzo[a]pyrene	PAH	252	25
Pesticides	Atrazine	Herbicide	215	20
	γ-BHC (lindane)	Pesticide	291	10
	Cyanazine	Herbicide	240	20
	Cyprazine	Herbicide	227	20
	Desethyl-atrazine	Atrazine degradate	187	20
	Desisopropyl-atrazine	Atrazine degradate	173	20
	o,p-DDD	DDT breakdown product	320	20
	Methoxychlor	Pesticide	346	20
	Propazine	Herbicide	229	20
	Simazine	Herbicide	201	20
Personal Care Products	Bisphenol A	Used to make plastics	228	30
	Butylparaben	Antibaterial	194	20
	Diethyltoluamide (DEET)	Insect repellant	191	20
	Ethylparaben	Antibaterial	166	20
	Methylparaben	Antibaterial	152	20
	Nonylphenol	Detergent metabolite	220	50
	Octylphenol	Detergent metabolite	206	20
	Propylparaben	Antibaterial	180	20
II. LC/MS/MS method				
Pharmaceuticals	Carbamazepine	Anti-convulsant	236	1
	Diclofenac, sodium salt	Anti-inflammatory	318	5
	Dilantin	Anti-convulsant	252	5
	Gemfibrozil	Anti-cholesterol	250	5
	Ibuprofen	Pain reliever	206	10
	Primidone	Anti-convulsant	218	2
	Sulfamethoxazole	Antibiotic	253	1
Personal Care Products	Caffeine	Stimulant	194	5
	Tris(2-chloroethyl) phosphate (TCEP)	Flame Retardant	285	5
	Triclosan	Antibacterial	288	5
Hormone	Ethynylestradiol	Synthetic birth control	296	10
Pesticide	Atrazine	Herbicide	215	1
	Diuron	Herbicide	232	5
	Linuron	Herbicide	248	5
III. Phosphorus (total)		Phosphate detergents	31	4,000

4.2.1 Materials

Atrazine-d_5 (with five deuterium atoms), bisphenol A, butyl-4-hydroxybenzoate (butylparaben), caffeine, carbamazepine, diclofenac sodium salt, dilantin, ethyl-4-hydroxybenzoate (ethylparaben), ethynylestradiol, gemfibrozil, ibuprofen, methyl-4-hydroxybenzoate (methylparaben), nonylphenol, octylphenol, primidone, propyl-4-hydroxybenzoate (propylparaben), sulfamethoxazole, triclosan, and TCEP were purchased from Sigma-Aldrich.

Atrazine, diuron, and linuron were purchased from Ultra Scientific. Anthracene, benzo[a]pyrene, lindane, *o,p*-DDD, DEET, cyanazine, cyprazine, desethyl-atrazine, desisopropyl-atrazine, methoxychlor, propazine, simazine, acenaphtene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12} were purchased from AccuStandard.

Caffeine-$^{13}C_3$ (with three carbon-13 atoms), carbamazepine-d_{10}, dilantin-d_{10}, ethynylestradiol-$^{13}C_2$, ibuprofen-$^{13}C_3$, sulfamethoxazole-$^{13}C_6$, and triclosan-$^{13}C_{12}$ were purchased from Cambridge Isotope Laboratories.

Diclofenac-d_4, diuron-d_6, gemfibrozil-d_6, linuron-d_6, and primidone-d_5 were purchased from C/D/N Isotopes.

OmniSolv-grade methanol (MeOH) was purchased from VWR.

OPW was obtained from a Millipore UV Plus system.

4.2.2 GC/MS Method

Solid-phase extraction (SPE) was performed on an AutoTrace automated SPE work station from Caliper Life Sciences, using 200-mg hydrophilic-lipophilic-balanced (HLB) cartridges from Waters Corporation. The cartridges were conditioned sequentially with 5 mL of dichloromethane, 5 mL of methyl *t*-butylether (MtBE), 5 mL of MeOH, and 10 mL of OPW. Samples (500-mL) were loaded onto the cartridges, after which the cartridges were dried with nitrogen for 30 min. The cartridges were eluted with 8 mL of 10% MeOH/90% MtBE, followed by 5 mL of dichloromethane. The eluant was concentrated down to 0.5 mL on a TurboVap evaporation system from Caliper Life Sciences.

The sample extracts were analyzed on a Varian Saturn 2200 ion trap MS coupled to a Varian CP-3800 GC with a 1079 programmable temperature vaporizing (PTV) injector. The GC column used was a 30 m × 0.25 mm inner diameter × 0.25 μm thickness Restek Rtx-5 Sil column. MeOH was used as the chemical ionization (CI) reagent, where applicable. An injection volume of 2 μL was used in all analyses. The instrument operating conditions are listed in Table 9. The compound-dependant parameters of the analytes are shown in Table 10. Compounds were identified by matching both the retention time and the quantitation ion peak (or MS/MS transition) of each analyte in the samples with those of the same analyte in authentic standards.

Table 9. GC/MS Instrumental Operating Conditions

GC Conditions	
Injector temperature program	48°C for 0.05 min, 48-280°C at 200°C/min, 280°C for 20 min
Injector split program	Off at 0 min; on at 2 min, split ratio = 50; on at 3 min, split ratio = 20
Column oven temperature program	45°C for 2 min, 45-150°C at 20°C/min, 150-280°C at 3°C/min, 280°C for 5 min, 280-315°C at 30°C/min, 315°C for 2.5 min
MS Conditions	
Ion trap temperature	150°C
Manifold temperature	80°C
Transfer line temperature	200°C
Operation modes*	EI/SIS; CI; CI/MS/MS
CI reagent	MeOH

*EI/SIS = electron ionization/selected ion storage; CI = chemical ionization; CI/MS/MS = CI with tandem MS.

4.2.3 LC/MS/MS Method

SPE was performed on the AutoTrace SPE workstation using the same HLB cartridges as those used in the GC/MS analysis. The cartridges were conditioned with 5 mL of MeOH, followed by 5 mL of OPW. Samples (500-mL) were loaded onto the cartridges, after which the cartridges were rinsed with 5 mL of OPW and dried with nitrogen for 60 min. The cartridges were eluted with 8 mL of MeOH, which was concentrated down to 0.5 mL on the TurboVap evaporation system. Immediately before analysis, 0.5 mL of OPW was added to the sample extract.

The sample extracts were analyzed under either electrospray positive or negative ionization (ESI positive or negative) mode (Vanderford et al., 2003), on an Applied Biosystems API 4000 triple quadrupole MS coupled with an Agilent 1100 LC and an HTC PAL autosampler from Leap Technologies. The LC column used was a 150 × 2 mm Phenomenex Luna C18 (2) column with 5-µm particle size. The instrument operating conditions are listed in Table 11. The elution gradients are shown in Table 12. The initial equilibration time was 4 min. The precursor/product ion pairs used for the MS/MS transitions and the retention times for the analytes are listed in Table 13. Compounds were identified by matching both the retention time and MS/MS transition of each analyte in the samples with those of the same analyte in authentic standards.

Table 10. Compound-Dependant Parameters for GC/MS Analytes

Compound	Retention Time (min)	Precursor Ion (m/z†)	Product Ion/ Quantitation Ion (m/z)	Internal Standard
CI/MS/MS Mode				
Acenaphtene-d_{10}*	10.21	165	161	-
Atrazine-d_5*	14.78	221	179	-
Atrazine	14.87	216	174	Atrazine-d_5
Butylparaben	14.36	195	139	Acenaphtene-d_{10}
DEET	11.43	192	119	Acenaphtene-d_{10}
Desisopropyl-atrazine	12.72	173	132	Atrazine-d_5
Desethyl-atrazine	12.91	188	146	Atrazine-d_5
Ethylparaben	10.56	167	139	Acenaphtene-d_{10}
Methylparaben	9.68	152	109	Acenaphtene-d_{10}
Propazine	15.05	230	172	Atrazine-d_5
Propylparaben	12.24	181	139	Acenaphtene-d_{10}
Simazine	14.66	202	124	Atrazine-d_5
EI/SIS mode				
Anthracene	16.01	N/A‡	178	Phenanthrene-d_{10}
Bisphenol A	25.71		228	Phenanthrene-d_{10}
Chrysene-d_{12}*	32.76		240	-
Cyanazine	20.71		240	Phenanthrene-d_{10}
Cyprazine	17.85		227	Phenanthrene-d_{10}
o,p-DDD	26.09		318	Phenanthrene-d_{10}
Lindane	15.13		109	Phenanthrene-d_{10}
Methoxychlor	33.65		344	Chrysene-d_{12}
Nonylphenol	17.84		220	Phenanthrene-d_{10}
Octylphenol	15.29		206	Phenanthrene-d_{10}
Phenanthrene-d_{10}*	15.65		188	-
CI Mode				
Benzo(a)pyrene	42.10	N/A	252	Chrysene-d_{12}

*Internal standards.
†m/z = Mass-to-charge ratio.
‡N/A = Not applicable.

Table 11. LC/MS/MS Instrument Operating Conditions at MWD

LC Operating Conditions	
Flow rate	0.4 mL/min
Autosampler temperature	10°C
Injection volume	20 µL
Column temperature	Ambient
MS/MS Operating Conditions	
Collision gas	6 psi
Curtain gas	10 psi
Ion spray voltage	5000 V
Temperature	500°C
Entrance potential	10 V

Table 12. LC Gradients Used in the Analysis at MWD

Time (min)	Solvent A*	Solvent B*
ESI Positive		
0.00	100	0
1.00	100	0
1.50	40	60
1.51	40	60
11.00	0	100
13.00	0	100
13.50	100	0
14.00	100	0
ESI Negative		
0.00	100	0
1.00	100	0
1.50	30	70
1.51	30	70
11.00	0	100
13.00	0	100
13.50	100	0
14.00	100	0

* Solvent A = 0.05% formic acid (v/v) in 90% water/10% MeOH;
Solvent B = 0.05% formic acid (v/v) in MeOH.

One of the drawbacks of LC/MS analysis in the electrospray mode is that matrix suppression and enhancement often occurs, which adversely affects the accuracy of the results. The most effective way to compensate for matrix effects has proven to be isotope dilution, where an isotopically labeled standard is used as the internal standard for the unlabeled counterpart and, as a result, the accuracy of the results can be significantly improved (Vanderford and Snyder, 2006). This isotope dilution approach was used for 13 of the 14 LC/MS/MS analytes. The only analyte that was not analyzed by isotope dilution was the flame retardant TCEP. As a result, the spike recoveries for TCEP could be biased low in some matrices. It was decided not to purchase a labeled TCEP standard because (1) the matrix suppression for TCEP was found only in a limited number of samples, (2) matrix suppression of TCEP, when it occurred, was rather mild, with low spike recoveries generally in the 50-70% range (refer to section 4.2.4, Table 16), and (3) the isotopically labeled TCEP was cost prohibitive at >$6,000 for the initial synthesis and purchase.

4.2.4 Total Phosphorus

Total phosphorus was analyzed by modified 4500-P B (digestion) and E (analysis) sections of *Standard Methods for the Examination of Water and Wastewater* (20th edition). Samples were digested with potassium persulfate at 103ºC. After digestion, the ortho-phosphate reacted with ammonium molybdate and potassium antimonyl tartrate in acid media to form phosphomolybdic acid, which was reduced by ascorbic acid to molybdenum blue, and was measured photometrically at 880 nm on a Shimadzu UV-VIS spectrophotometer. The results of phosphate were then converted to total phosphorus. The MRL was 0.004 mg/L.

Table 13. Compound-Dependant Parameters for LC/MS/MS Analytes at MWD

Compound	Retention Time (min)	Precursor Ion (m/z)	Product Ion (m/z)	Declustering Potential (V)	Collision Energy (eV)	Collision Cell Exit Potential (V)
ESI Positive Mode						
Atrazine	6.74	216	174	71	25	12
Atrazine-d_5	6.71	221	179	81	27	12
Caffeine	4.85	195	138	71	29	8
Caffeine-$^{13}C_3$	4.85	198	140	76	29	8
Carbamazepine	6.14	237	194	76	27	12
Carbamazepine-d_{10}	6.09	247	204	71	29	12
Dilantin	5.98	253	182	86	25	12
Dilantin-d_{10}	5.93	263	192	86	27	12
Ethynylestradiol	7.49	279	133	56	21	8
Ethylnylestradiol-$^{13}C_2$	7.49	281	133	71	25	8
Linuron	7.55	249	160	71	25	10
Linuron-d_6	7.51	255	160	86	27	10
Primidone	5.25	219	162	61	19	10
Primidone-d_5	5.23	224	167	71	25	10
Sulfamethoxazole	4.91	254	156	76	23	10
Sulfamethoxazole-$^{13}C_6$	4.90	260	162	66	23	10
TCEP	5.98	285	223	71	19	6
ESI Negative Mode						
Diclofenac	7.57	294	250	-60	-14	-15
Diclofenac-d_4	7.52	298	254	-20	-30	-5
Diuron	6.13	231	186	-71	-24	-15
Diuron-d_6	6.09	237	186	-71	-22	-11
Gemfibrozil	8.74	249	121	-55	-26	-15
Gemfibrozil-d_6	8.71	255	121	-65	-16	-5
Ibuprofen	7.75	205	161	-55	-10	-9
Ibuprofen-$^{13}C_3$	7.75	208	163	-60	-10	-9
Triclosan	8.81	287	35	-55	-26	-5
Triclosan-$^{13}C_{12}$	8.81	299	35	-55	-26	-5

4.2.5 MDLs, MRLs, and Calibration

The method detection limit (MDL) for each analyte was determined in accordance with USEPA guidelines (USEPA, 1990). A set of seven replicate OPW samples fortified at or near the expected MDLs were extracted on the same day and analyzed according to the standard operating procedures. The MDL of each analyte was calculated using the following formula:

$$MDL = 3.14 \times Standard\ Deviation$$

where:

The coefficient 3.14 represents the student's T value for n-1 degrees of freedom.

The MRL for caffeine was defined as five times the MDL, taking into account that caffeine was sometimes detected in field blanks at low levels (1-2 ng/L), less than two times the levels found in corresponding samples. For all other analytes, the MRLs were defined as three times the

corresponding MDLs. Overall, the MRLs ranged from 1-50 ng/L (see Table 8). For a particular analyte, a standard curve was constructed by plotting peak area ratios (peak area of analyte/peak area of internal standard) versus concentrations of standards. Standard curves generally contained a minimum of five points, ranging from the analyte's respective MRL to 500 ng/L. Depending on the analytes, either linear or quadratic regression was used, with a correlation coefficient (R^2) of >0.985. For GC/MS analysis, internal standards were added to both calibration standards and samples at 100 ng/L each. The concentration of an analyte in a sample was calculated by using the peak area ratio (peak area of analyte/peak area of internal standard) in that sample compared to the same ratio in the calibration curve. For LC/MS/MS analysis, isotopically labeled standards were used as internal standards, with the exception of TCEP, and were added to both calibration standards and samples at 50 ng/L each. Caffeine-$^{13}C_3$ was used as the internal standard for TCEP. Quantitation was based on peak area ratios in the same way as the GC/MS analysis, with the exception that isotopically labels standards were used as internal standards. On occasions, when the concentration of an analyte in a particular sample exceeded the highest point of calibration, the sample was diluted and re-analyzed.

4.2.6 QA/QC at MWD

QC protocols included analysis of method blanks, field blanks, matrix-spiked (MS) samples, matrix-spiked duplicates (MSDs), and in some cases duplicate samples. Because many of the analytes were often not detected, duplicate samples would have not yielded much information on the precision of the method. Alternatively, the analysis of MSD samples resulted in two sets of recovery (accuracy) data, as well as one set of precision data for all analytes. For every batch of 12 samples, at a minimum, one method blank, one MS sample, and one MSD or duplicate sample were analyzed.

A method blank is an aliquot of OPW treated exactly as a sample, including exposure to all glassware, reagents, and other materials used in the analysis. An internal standard was added and it was processed through the entire extraction procedure. It was analyzed with each extraction batch to demonstrate freedom from possible contamination from the laboratory environment, the reagents or the apparatus. The method blanks had no detectable amount of any analytes throughout the project.

Field blanks were collected at selected sample sites, where OPW was poured into empty sample bottles during the same time period in which samples were collected to evaluate possible contamination from the sample collection procedures or from aerial contamination at the sample site. Due to the large amount of samples collected for the project, the field blanks were collected and analyzed by the LC/MS/MS method, but not by the GC/MS method, as there was more detection of LC/MS/MS analytes in the samples. Of the 126 samples collected for the project, 118 field blanks were collected and analyzed (Table 14). Triclosan was found in one field blank at 6 ng/L, whereas sulfamethoxazole was found in 12 field blanks at levels up to 18 ng/L. Although the source of the contamination is unknown, these levels were normally five or more times lower than the amounts in the samples from the corresponding sites, therefore the results in the samples were reported without any adjustments for field blanks.

Table 14. Field Blanks Analyzed by the LC/MS/MS Method at MWD

Sampling Date	Number of Sampling Sites	Number of Sites with Field Blanks	Analyte in Field Blanks and Levels (ng/L)	Same Analyte in Corresponding Samples and Levels (ng/L)
April 2008	11	11	None	---
May 2008	13	6	Sample 1: SMX*, 17 Sample 2: SMX, 18 Sample 3: SMX, 6	Sample 1: SMX, 332 Sample 2: SMX, 148 Sample 3: SMX, 87
June 2008	7	6	SMX, 2	SMX, ND† (<1)
July 2008	11	11	None	---
August 2008	13	13	Sample 1: SMX, 10 Sample 2: SMX, 13 Sample 3: SMX, 14 Sample 4: SMX, 3	Sample 1: SMX, 431 Sample 2: SMX, 410 Sample 3: SMX, 128 Sample 4: SMX, 1295
September 2008	8	8	SMX, 1.5	SMX, 4
October 2008	10	10	None	---
November 2008	13	13	SMX, 1.3	SMX, 10
December 2008	8	8	None	---
January 2009	11	11	None	---
February 2009	13	13	Sample 1: SMX, 2 Sample 2: SMX, 6; Triclosan, 6	Sample 1: SMX, 172 Sample 2: SMX, 41; Triclosan, ND
April 2009	8	8	None	---

*SMX=sulfamethoxazole.
†ND = Not detected.

To assess the precision of the methods, MSDs and, in some cases, duplicate samples (when the sample volume was not enough for MSDs) were prepared and analyzed. The relative percent difference (RPD) was calculated using the following equation:

$$RPD = \frac{(MSD - MS)}{(MSD + MS)/2} \times 100$$

where:

MS = measured concentration in the matrix-spiked sample, and
MSD = measured concentration in the matrix-spike duplicate sample (if a MSD was not prepared, then the RPD of the two duplicate samples was determined).

Spike recoveries were used to determine the accuracies of the methods. A matrix-spiked sample was prepared by spiking a sample with a set level of analytes, usually 100 or 200 ng/L each. The percent recovery (R) was calculated for each analyte using the following equation:

$$R = \frac{(A - B)}{C} \times 100$$

where:

A = measured concentration in the spiked sample,
B = measured concentration in the unspiked sample, and
C = spike concentration.

The minimum, maximum, and average of the RPDs and spike recoveries for each analyte throughout the project are shown in Table 15 (GC/MS method) and Table 16 (LC/MS/MS method). Overall, 98% of the RPDs were within 20% (for individual analytes, the average RPD was 1-12%), which indicated that the precision of both analytical methods was acceptable. Of the spike recoveries, 96% were from 70-130% (for individual analytes, the average recovery was 87-123%), which indicated that the accuracy of both analytical methods was acceptable.

Table 15. QC Data for the GC/MS Method at MWD

	% RPD			% Recovery		
	Minimum	**Maximum**	**Average**	**Minimum**	**Maximum**	**Average**
Anthracene	0	19	4	82	124	93
Atrazine	0	17	3	58	109	90
Benzo[a]pyrene	0	14	7	45	133	103
Bisphenol A	4	18	12	92	222	123
Butylparaben	0	14	3	74	129	111
Cyanazine	0	16	4	84	138	112
Cyprazine	0	7	2	84	119	103
o,p-DDD	0	3	1	69	121	97
DEET	0	14	8	75	125	102
Desethyl-atrazine	0	18	8	67	138	102
Desisopropyl-atrazine	0	11	8	85	140	109
Ethylparaben	0	9	3	84	131	110
Lindane	0	7	2	84	123	101
Methoxychlor	0	5	1	91	131	116
Methylparaben	2	14	7	72	124	105
Nonylphenol	0	6	3	81	134	111
Octylphenol	0	20	7	84	147	113
Propazine	0	18	7	76	135	99
Propylparaben	0	17	2	62	142	110
Simazine	0	14	6	74	125	102

Representative accuracy and precision control charts are shown in Figures 5-6, together with an upper limit of 130% and a lower limit of 70% for spike recoveries, and an upper limit of 20% for RPDs. As expected, temporal variability oscillated up and down about the average line, with no bias observed over time.

Table 16. QC Data for the LC/MS/MS Method at MWD

	% RPD			% Recovery		
	Minimum	**Maximum**	**Average**	**Minimum**	**Maximum**	**Average**
Atrazine	0	26	3	72	121	107
Caffeine	0	12	2	78	124	104
Carbamazepine	0	8	2	85	142	114
Diclofenac	0	23	5	68	137	87
Dilantin	0	15	4	75	117	101
Diuron	0	7	3	84	169	109
Ethynylestradiol	0	26	4	73	115	99
Gemfibrozil	0	30	4	70	145	112
Ibuprofen	0	19	5	68	168	110
Linuron	0	23	4	85	120	105
Primidone	0	24	6	82	132	99
Sulfamethoxazole	0	7	3	83	116	102
TCEP	0	38	7	53	171	87
Triclosan	0	14	4	86	115	101

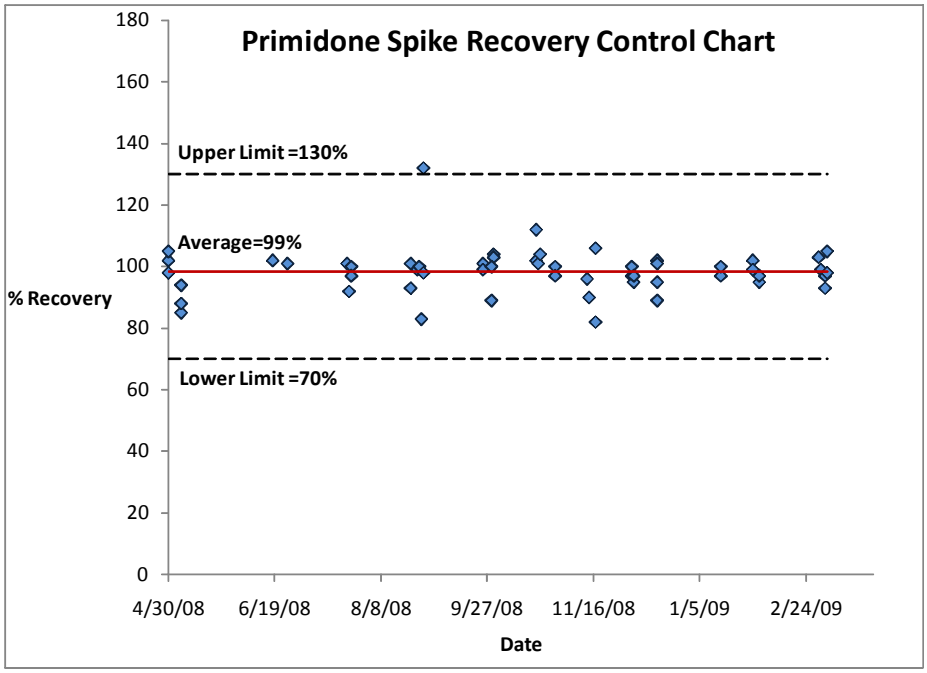

Figure 5. Spike recovery control chart for primidone.

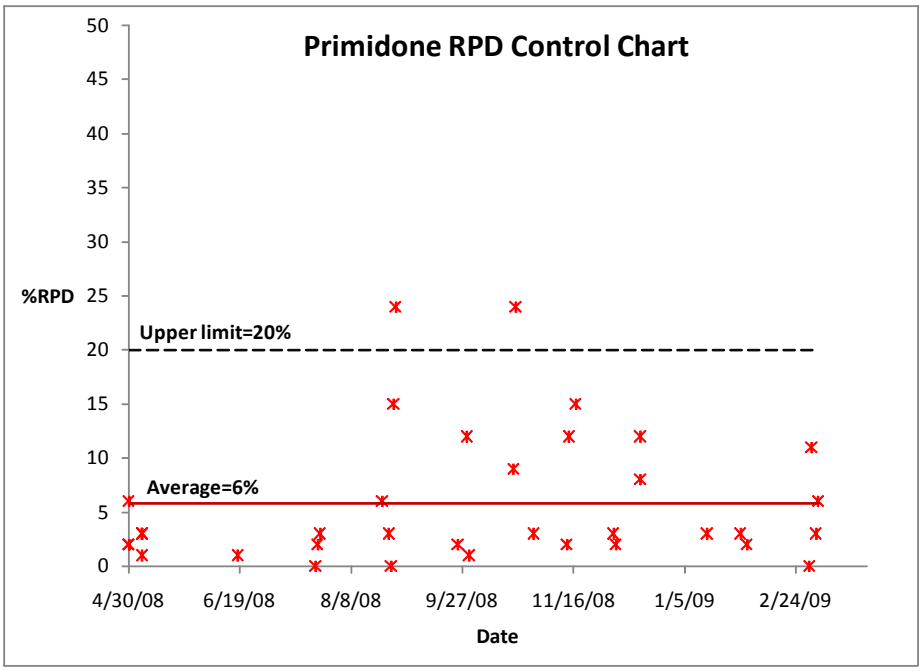

Figure 6. RPD control chart for primidone.

4.2.7 Holding Studies

Preservation and holding studies were carried out at MWD to evaluate the following parameters:

- The use of ascorbic acid as the quenching agent for residual chlorine and chloramines that might be present in treated wastewater and drinking water.
- The use of sodium azide as a biocide.
- The use of silanized glass bottles (in contrast to routinely used I-CHEM glass bottles) for sample collection and storage to evaluate if there is any adsorption of analytes to the glass surface of regular containers.

All sample bottles were amber because some of the analytes (e.g., gemfibrozil, ibuprofen) are known to undergo sunlight photolytic degradation. The stabilities of the 14 LC/MS/MS analytes were evaluated in four matrices (Table 17):

- DWTP plant influent.
- DWTP filter effluent with a free chlorine residual.
- DWTP plant effluent with a chloramine residual.
- SAR collected at Below Prado Dam, which represented a complex matrix dominated by treated wastewater discharges.

Table 17. Preservation and Holding Study Matrices and Parameters Investigated

Matrix	Disinfectant Residual	Samples with Different Parameters	Spiked Concentration (ng/L)* of Each Analyte
DWTP Plant Influent (PLTINF)	None	1. No preservatives, I-CHEM bottle	50
		2. No preservatives, silanized bottle	
		3. Ascorbic acid, sodium azide, I-CHEM bottle	
		4. Ascorbic acid, sodium azide, silanized bottle	
DWTP Filter Effluent (FILEFF)	Chlorine	5. No preservatives, silanized bottle	50
		6. Ascorbic acid, silanized bottle	
DWTP Plant Effluent (PLTEFF)	Chloramines	7. No preservatives, silanized bottle	50
		8. Ascorbic acid, silanized bottle	
		9. Ascorbic acid, sodium azide, silanized bottle	
SAR at Below Prado Dam	None	10. No preservatives, I-CHEM bottle	0
		11. No preservatives, I-CHEM bottle	100
		12. Ascorbic acid, I-CHEM bottle	100
		13. Ascorbic acid, sodium azide, I-CHEM bottle	100

*Concentration spiked into sample on top of ambient levels.

The following conclusions can be drawn based on these holding study experiments:

1. In the presence of both ascorbic acid and sodium azide, the concentrations of all 14 LC/MS/MS analytes remained constant for a period up to 30 days, with no degradation observed. An example, caffeine, is shown in Figure 7. Although caffeine is known to undergo biodegradation in the environment, this did not occur in the DWTP influent matrix, which was filtered. Thus, this test was repeated with the SAR matrix (see discussion under #3).

2. The degradation of some analytes (e.g., sulfamethoxazole [Figure 8] and ethynylestradiol) was observed in the samples with residuals that were not quenched, whereas other analytes showed no difference in the samples with disinfectant residuals quenched or not. The degradation was faster in the presence of chlorine (i.e., FILEFF sample), which was more reactive than chloramines (i.e., PLTEFF sample). This pointed to the need for ascorbic acid in any treated wastewater and drinking water samples with possible disinfectant residuals.

3. SAR at Below Prado Dam was collected in May 2008 for the holding study experiments. Analysis from the same site collected in May 2007 showed that, per 100 mL of sample, it

contained ≥2800 colony forming units (CFUs) of total coliforms, 240 CFUs of fecal coliforms, and 95 CFUs of *E. coli*. This sample was not filtered in order to evaluate biodegradation. Biodegradation was indeed observed in this matrix for some analytes (e.g., sulfamethoxazole and triclosan) when sodium azide was not used. When sodium azide was used as the biocide, biodegradation was non-existent, and the concentrations of all 14 LC/MS/MS analytes remained constant for a period up to 30 days. This pointed to the need for sodium azide (or other biocides) to minimize biodegradation, especially in surface water samples with relative high counts of microorganisms.

4. The concentrations of the LC/MS/MS analytes investigated showed no differences in regular amber glass bottles compared with silanized amber glass bottles. Therefore, all sample collections and analyses for the project were carried out in regular I-CHEM amber glass bottles.

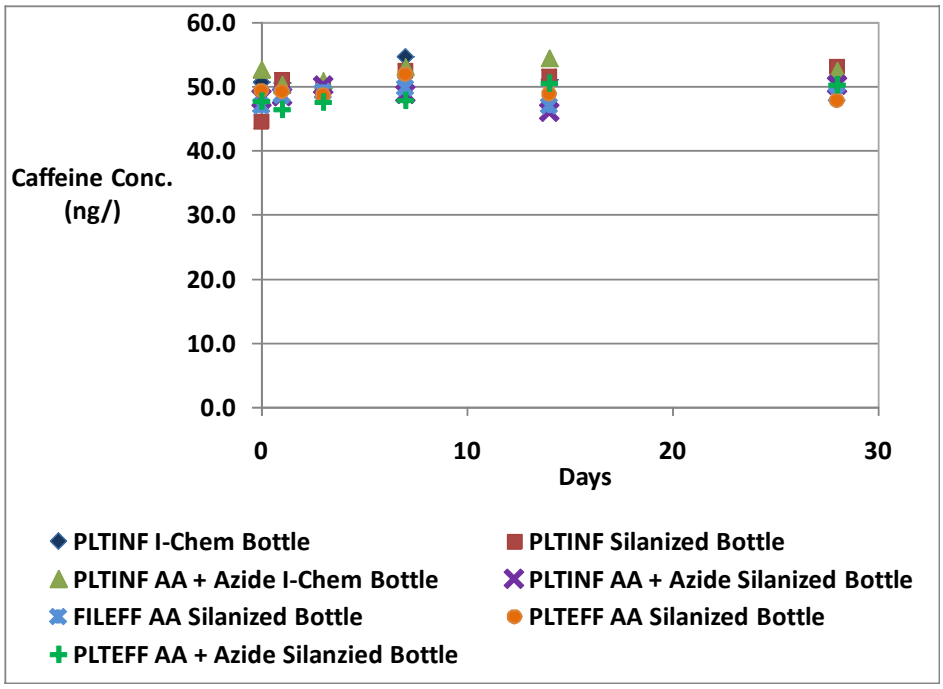

Figure 7. Holding study results for caffeine in selected matrices (AA = ascorbic acid).

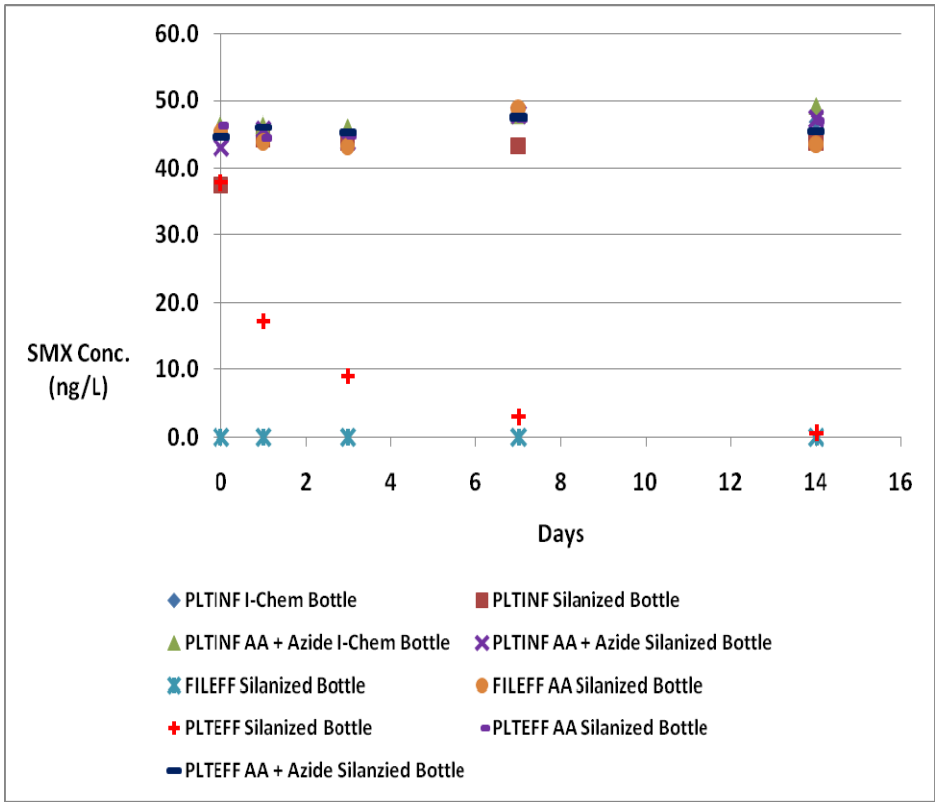

Figure 8. Holding study results for sulfamethoxazole in selected matrices.

4.3 Analytical Methods at OCWD

The analysis at OCWD's laboratory was divided into three methods within this study: PPCPs method; hormones method; and phenols method.

4.3.1 PPCPs Method by LC/MS/MS.

The PPCPs method was similar to MWD's LC/MS/MS method, with the isotopic dilution technique used for all 11 targets (Table 18).

Pre-filtered samples (500-mL) were loaded onto the conditioned SPE cartridges (HLB 200 mg, Waters Oasis cartridges) at a load rate of 10 mL/min on an automated AutoTrace SPE workstation. The cartridges were rinsed with 15 mL of Milli-Q water and then dried with nitrogen for 30 min. The analytes were eluted from the cartridges with two aliquots of 6 mL of methanol. The extracts were concentrated on a Zymark Turbo-Vap workstation to 1 mL, under nitrogen (9 psi) at 40ºC. Each final 1-mL extract was divided into two amber autosampler vials with 400 µL inserts and stored at 4ºC until analysis.

A six-point extracted calibration curve was used, representing 1, 10, 20, 50, 100, and 200 ng/L levels. The R^2 for the linear regression of each curve was verified to be ≥ 0.980.

Table 18. List of Analytes for the OCWD PPCPs Method

Analyte	Use	MW (g/mole)	ESI Mode	MRL (ng/L)
Acetaminophen	Pain reliever	151	Positive	10
Azithromycin	Antibiotic	749	Positive	1
Caffeine	Stimulant	194	Positive	3
Carbamazepine	Anti-convulsant	236	Positive	1
Ciprofloxacin	Antibiotic	331	Positive	10
DEET	Insect repellant	191	Positive	1
Gemfibrozil	Anti-chloesterol	250	Negative	1
Ibuprofen	Pain reliever	206	Negative	1
Primidone	Anti-convulsant	218	Positive	1
Sulfamethoxazole	Antibiotic	253	Positive	1
Triclosan	Antibacterial	288	Negative	1

The concentration of an analyte was determined using the isotopic dilution technique (refer to Section 4.2.3). Target standards, as well as isotopic standards, were eventually supplied by MWD to OCWD's laboratory, as OCWD experienced quality control issues with standards from some of their vendors. The LC/MS/MS system used for the analysis was the Applied Biosystems 4000-Q TRAP, using the Analyst Data workstation. The LC unit was an Agilent 1200 binary pump system with column oven. A Phenomenex Gemini C6 phenyl column was used (2.0 × 150 mm, 5 µm) within the LC system. A 5-µL sample injection was made with a CTC PAL autosampler. The LC gradients are shown in Table 19. The column oven was set at 50°C. The equilibration duration was 2 min. The flow rate was 500 µL/min. The MS/MS operating conditions are shown in Table 20.

Table 19. LC Gradients Used in the OCWD PPCPs Method

Time (min)	Solvent A*	Solvent B#
ESI Positive		
0.0	50	50
1.0	50	50
4.5	0	100
5.0	0	100
6.5	50	50
12	50	50
ESI Negative		
0.0	60	40
0.5	60	40
5.0	0	100
5.5	0	100
6.5	60	40
8.0	60	40

*A = 0.03% v/v NH_4OH in water for ESI positive, and 5 mM ammonium acetate in water for ESI negative;
#B = 0.03% v/v NH_4OH in methanol for ESI positive, and methanol for ESI negative.

Table 20. MS/MS Operating Conditions for the OCWD PPCPs Method

Compound	Retention Time (min)	Precursor Ion (m/z)	Product Ion (m/z)	Declustering Potential (V)	Collision Energy (eV)	Collision Cell Exit Potential (V)
ESI Positive						
Sulfamethoxazole	0.57	254	156	71	25	28
Ciprofloxacin	0.64	332	314	91	31	20
Acetaminophen	0.94	152	110	76	23	20
Caffeine	1.47	195	138	66	29	24
Primidone	1.93	219	162	71	19	8
Carbamazepine	4.72	237	194	81	29	10
DEET	5.09	192	119	76	27	20
Azithromycin	6.67	749.6	591.5	176	43	16
ESI Negative						
Ibuprofen	5.43	205	161	-45	-10	-9
Gemfibrozil	6.12	249	121	-50	-20	-5
Triclosan	6.61	287	35	-45	-30	-3

4.3.2 Hormones Method by LC/MS

OCWD's hormones method analyzed for nine target compounds on a Waters/Micromass ZQ LC/MS system, with an MRL of 10 ng/L for each analyte (Table 21).

Table 21. List of Analytes for the OCWD Hormones Method

Analyte	MW	MRL (ng/L)
Estrone	270	10
Epitestosterone (cis-Testosterone)	288	10
Testosterone (trans-)	288	10
Estriol	288	10
17α-Estradiol	272	10
17β-Estradiol	272	10
17-alpha-Ethynylestradiol	296	10
Progesterone	314.5	10
Diethylstilbestrol	268	10

The pre-filtered sample (1-liter) was spiked with a surrogate standard (2,3,5,6-tetrafluoro-4-[pentafluorophenyl] phenol) at 20 ng/L and loaded onto a conditioned SPE disk (Empore C18 0.5 g, 8 µm octadecyl bonded silica) at a load rate of 25 mL/min, using a manual SPE manifold. After the sample was completely loaded, the disk was air dried for 10 min. The hormones were eluted off the disk with three aliquots of 5 mL of acetonitrile and one 5-mL aliquot of methylene chloride. The extract was concentrated to 0.1 mL on a Zymark concentrator workstation, brought up to a 1-mL volume with 60:40 methanol/water, and a bisphenol A-d_{16} internal standard was added to achieve a final concentration of 50 ng/L. The extracts were stored at 4ºC until time of analysis.

Concentrations of the target analytes were calculated based on a five-point extracted calibration curve representing 5, 10, 20, 50, and 100 ng/L levels. A Waters/Micromass ZQ LC/MS system was used. A Phenomenex Gemini C18 column (2.0 × 150mm, 5 µm) was used within the LC system, along with a guard column (Varian MetaGuard, 2.0 mm Pursuit, 3 µm C18). A 15-µl aliquot of each extract was injected into the system by an Alliance 2695 Waters autosampler system. Column temperature was held at 35°C. The auto equilibration duration was 2 min. The flow rate was set at 0.3 mL/min. The LC gradients are shown in Table 22. The MS/MS operating conditions are shown in Table 23.

Table 22. LC Gradients Used in the OCWD Hormones Method

Time	Acetonitrile	5 mM Ammonium Acetate
0	25	75
0.5	25	75
15	95	5
16	25	75
30	25	75

Table 23. MS/MS Operating Conditions for the OCWD Hormones Method

Analyte	SIM Mass (m/z)*	Dwell (secs)	Cone Volts
ESI positive			
Testosterone (trans-)	289	0.30	25
Epitestosterone (cis-Testosterone)	289	0.30	25
Progesterone	315	0.30	30
ESI Negative			
Diethylstilbestrol	267	0.30	35
Estrone	269	0.30	30
17α-Estradiol	271	0.40	25
17β-Estradiol	271	0.40	25
Estriol	287	0.40	25
17 α-Ethynylestradiol	295	0.30	30
Surrogate#	331	0.40	25
Bisphenol A d_{16}	241	0.30	35

*SIM = Selected ion monitoring; acquisition time = 0-16 min.
#Surrogate=2,3,5,6-tetrafluoro-4-(pentafluorophenyl) phenol.

4.3.3 Phenols Method by LC/MS

This method analyzed for eight target phenolic compounds, with MRLs in the µg/L range (Table 24). Because bisphenol A has normally been detected in water at ng/L levels, results for this analyte relied more on the more sensitive GC/MS method used at MWD.

Table 24. List of Analytes for the OCWD Phenols Method

Target	MW (g/mole)	MRL (µg/L)
4-Nonylphenol	220	1
4-*n*-Octylphenol	206	1
4-*t*-Octylphenol	206	1
Bisphenol A	228	1
Pentachlorophenol	264	1
2,4,6-Trichlorophenol	196	1
4-Phenylphenol (4-Hydroxybiphenyl)	170	1
Tetrabromobisphenol A	544	1
Nonylphenol diethoxylate	308	10
Nonylphenol monoethoxylate	264	10

The pre-filtered sample (500-mL) was spiked with surrogate standards (4-[4-bromo-phenyl] phenol) and loaded onto a conditioned SPE cartridge (Varian Bond Elute PPL 1 gram) at a load rate of 20 mL/min on a manual SPE manifold. After the sample was loaded, the cartridge was air dried for 15 min using high vacuum. The analytes of interest were eluted from the cartridge with methylene chloride, with three 6-mL aliquots first, followed by two 2-mL aliquots. The extract was dried with sodium sulfate and then concentrated on a Zymark concentrator workstation at 45ºC under nitrogen (10 psi) to almost dryness. Internal standard (bisphenol A-d_{16}) was added to each extract and brought to a 1-mL final volume with 60:40 methanol/water. Both the internal and surrogate levels were spiked at a 10-µg/L concentration level. The extracts were stored at -10ºC until time of analysis.

Concentration of a target analyte was determined using a five-point extracted calibration curve representing 1, 2, 5, 10, and 20 µg/L levels. The LC unit was a Waters Alliance system with a column oven. A Phenomenex Gemini C6 phenyl column (2.0 × 150 mm, 5 µm) was used. A 15-µl sample injection was made on a Waters Alliance 2695 autosampler. Column temperature was held at 50°C. The auto equilibration duration was 2 min. The flow rate was set at 0.3 mL/min. The LC gradients are shown in Table 25. The MS/MS operating conditions are shown in Table 26.

Table 25. LC Gradients Used in the OCWD Phenols Method

Time	Acetonitrile	5 mM Ammonium Acetate
0	50	50
0.5	50	50
13	100	0
14	50	50
40	50	50

Table 26. MS/MS Operating Conditions for the OCWD Phenols Method

Analyte	SIM Mass* (m/z)	Dwell (secs)	Cone Volts
ESI Positive			
Nonylphenol monoethoxylate	265	0.30	50
Nonylphenol diethoxylate	309	0.30	50
ESI negative			
4-Phenylphenol (4-Hydroxybiphenyl)	169	0.30	45
2,4,6-Trichlorophenol	195	0.30	50
4-n-Octylphenol	205	0.30	50
4-t-Octylphenol	205	0.30	50
4-Nonylphenol	219	0.30	45
Bisphenol A	227	0.30	45
Bisphenol A d_{16}	241	0.30	50
Surrogate#	247	0.30	45
Pentachlorophenol	263	0.30	45
Tetrabromobisphenol A	543	0.30	55

*Acquisition time = 0-15 min; #Surrogate = 4-(4-bromo-phenyl) phenol.

4.3.4 QA/QC at OCWD

Samples were delivered to OCWD by MWD staff, and were extracted at OCWD in complete sets, as much as possible, keeping them grouped within their delivery sets. Method blanks were analyzed within each extraction set to check for potential interferences from the extraction process. Laboratory fortified blanks (LFBs) were extracted and analyzed at several concentration levels within each analytical run, depending on the extraction set and the methods used. A low-level LFB was used to confirm the MRLs of the analytes, whereas the other LFBs were used to verify mid- and high-level points within the calibration curve. Calibration check standards were also analyzed at the beginning and end of each analytical run and verified to be within +/-30% of the expected value at the mid-level concentrations and +/-50% at the MRL concentration levels. Whenever possible, second source standards were used to verify the calibration standard. During extended runs, additional check standards were interspersed within the sample sequence, so that QA/QC verification would be analyzed for every 10 samples. Duplicate samples were analyzed within each extraction batch at 10% of the total sample load, and the RPDs were verified to be within +/-20%. Spike samples were extracted and analyzed when there were enough sample volumes to do so, at levels relevant to the individual method.

The overall percent recoveries for the three methods are summarized in Tables 27-29. Most analytes showed good spike recoveries within the 70-130% range of true values. There were some targets that did show poor method performance. For example, ciprofloxacin and azithromycin were found to be the most problematic analytes, with recoveries as low as 16 and 12%, respectively, in some matrices, even with isotope dilution. However, for these two analytes, the average recoveries (62 and 92%, respectively) were fair to good. The average recoveries for all of the analytes ranged from 62-132%.

Table 27. Percent Recoveries of Matrix-Spiked Samples for the OCWD PPCPs Method

Analyte	Minimum	Maximum	Average
Sulfamethoxazole	88%	140%	101%
Ciprofloxacin	16%	117%	62%
Acetaminophen	70%	142%	97%
Caffeine	55%	106%	97%
Primidone	88%	109%	100%
Carbamazepine	77%	124%	99%
DEET	98%	117%	109%
Azithromycin	12%	119%	92%
Ibuprofen	65%	109%	95%
Gemfibrozil	85%	130%	108%
Triclosan	80%	118%	98%

Table 28. Percent Recoveries of Matrix-Spiked Samples for the OCWD Hormones Method

Analyte	Minimum	Maximum	Average
Estrone	79%	135%	103%
Epitestosterone	58%	163%	126%
Testosterone	66%	253%	117%
Estriol	108%	167%	132%
17α-Estradiol	63%	145%	103%
17β-Estradiol	70%	139%	101%
17α-Ethynylestradiol	72%	143%	100%
Progesterone	25%	88%	62%
Diethylstilbestrol	57%	153%	102%

Table 29. Percent Recoveries of Matrix-Spiked Samples for the OCWD Phenols Method

Analyte	Minimum	Maximum	Average
4-Nonylphenol	88%	140%	101%
4-n-Octylphenol	42%	132%	87%
4-tert-Octylphenol	56%	127%	88%
Bisphenol A	58%	144%	93%
Pentachlorophenol	54%	148%	87%
2,4,6-Trichlorophenol	55%	97%	78%
4-Phenylphenol (4-Hydroxybiphenyl)	67%	127%	88%
Tetrabromobisphenol A	55%	146%	85%
Nonylphenol diethoxylate	33%	85%	63%
Nonylphenol monoethoxylate	33%	203%	88%

4.4 Inter-Laboratory QA/QC

4.4.1 Round-Robin Test

Although there is a moderate amount of information in the literature on the occurrence of PPCPs in the environment, comparison of results from different studies can be difficult, as no standardized analytical methods exist and laboratory practices vary widely. To ensure high quality data for this project, an inter-laboratory comparison of the analytical methods (round robin) among the three analytical laboratories participating in the project (MWD, OCWD, and SNWA) was conducted in March 2008, prior to the first sampling event.

All three laboratories used the analytical methods that were previously published (Vanderford et al., 2003; Trenholm et al., 2006; Vanderford and Snyder, 2006) or slightly modified versions. In general, samples were extracted by SPE, followed by analysis with LC/MS, LC/MS/MS, and/or GC/MS (Table 30).

Table 30. Summary of Analytical Methods and MRLs Used for the Round-Robin Test

	MWD		OCWD		SNWA	
	Method	**MRL (ng/L)**	**Method**	**MRL (ng/L)**	**Method**	**MRL (ng/L)**
Bisphenol A	GC/MS	30	LC/MS	1,000	LC/MS/MS	5.0
Caffeine	LC/MS/MS	5	LC/MS/MS	3	LC/MS/MS	5.0
Carbamazepine	LC/MS/MS	1	LC/MS/MS	1	LC/MS/MS	0.5
DEET	GC/MS	20	LC/MS/MS	1	LC/MS/MS	1.0
Diclofenac	LC/MS/MS	5	-	-	LC/MS/MS	0.5
Dilantin	LC/MS/MS	5	-	-	LC/MS/MS	1.0
Ethynylestradiol	LC/MS/MS	10	LC/MS	10	-	-
Gemfibrozil	LC/MS/MS	5	LC/MS/MS	1	LC/MS/MS	0.25
Ibuprofen	LC/MS/MS	10	LC/MS/MS	1	LC/MS/MS	1.0
Nonylphenol	GC/MS	50	LC/MS	1,000	-	-
Octylphenol	GC/MS	20	LC/MS	1,000	LC/MS/MS	25
Primidone	LC/MS/MS	2	LC/MS/MS	1	LC/MS/MS	0.5
Sulfamethoxazole	LC/MS/MS	1	LC/MS/MS	1	LC/MS/MS	0.25
TCEP	LC/MS/MS	5	-	-	LC/MS/MS	10
Triclosan	LC/MS/MS	5	LC/MS/MS	1	LC/MS/MS	1.0

"-" = Not analyzed.

There were 15 analytes that were measured by two or more of the laboratories. SNWA used LC/MS/MS for all analytes with the isotope dilution technique. MWD used LC/MS/MS for 11 of the 15 round-robin analytes at the time of the round robin test, and GC/MS for the remaining four analytes. OCWD used three separate methods for PPCPs, hormones, and phenols, with the majority of the analytes in the PPCPs method done with isotope dilution at the time of the round robin test.

Three different matrices were collected: a DWTP influent, the corresponding chloraminated plant effluent, and SAR below Prado Dam, which represented a river sample dominated by wastewater discharges. All samples were filtered (0.45 µm) and dechlorinated with 50 mg/L of

ascorbic acid and preserved with 1 gram per liter of sodium azide. The samples were spiked at MWD with analytes at different levels (Table 31), and analyses were carried out at the three laboratories in parallel. A primary standard solution containing a mixture of the analytes was supplied to the laboratories and was used at MWD and OCWD, but not at SNWA. Each laboratory used its own mixtures of internal standard solutions.

Table 31. Description of Round-Robin Samples

Sample Number	Description	Spiked Levels for Selected Analytes (ng/L)
1	DWTP Influent	100
2	DWTP Influent	100, 200, or 500
3	DWTP Effluent	100 or 200
4	SAR at Below Prado Dam	0
5	SAR at Below Prado Dam	100 or 200

The results are shown in Tables 32-35. For those analytes analyzed by two of the three laboratories only, RPDs were calculated. For those analytes analyzed by all three laboratories, relative standard deviations (RSDs) were determined.

Table 32. Round-Robin Results of Sample 1 (DWTP Influent Spiked with Selected Analytes)

	Spiked Amount (ng/L)	Lab A (ng/L)	Lab B (ng/L)	Lab C (ng/L)	RPD/RSD (%)
Bisphenol A	0	ND	ND	< 5.0	N/A[*]
Caffeine	100	112	104	150	20%
Carbamazepine	100	100	109	100	5%
DEET	0	ND	4.4	5.6	25%
Diclofenac	100	86	-	100	15%
Dilantin	100	NR[#]	-	120	N/A
Ethynylestradiol	100	94	100	-	6%
Gemfibrozil	100	122	85.6	110	18%
Ibuprofen	100	123	101	100	12%
Nonylphenol	0	ND	ND	-	N/A
Octylphenol	0	ND	ND	< 25	N/A
Primidone	100	102	90.6	96	6%
Sulfamethoxazole	100	108	90	84	13%
TCEP	100	69	-	110	46%
Triclosan	100	106	80	100	14%

[#]N/A = Not applicable; [*]NR = Not reported.

Table 33. Round-Robin Results of Sample 2 (DWTP Influent Spiked with Analytes)

	Spiked Amount (ng/L)	Lab A (ng/L)	Lab B (ng/L)	Lab C (ng/L)	RPD/RSD (%)
Bisphenol A	500	475	509	410	11%
Caffeine	100	131	113	150	14%
Carbamazepine	100	107	110	110	1%
DEET	500	517	429	600	17%
Diclofenac	200	177	-	190	7%
Dilantin	100	116	-	98	17%
Ethynylestradiol	100	98	-	-	N/A
Gemfibrozil	200	282	123	210	39%
Ibuprofen	200	258	201	200	15%
Nonylphenol	500	421	469	-	11%
Octylphenol	500	497*	299*	ND#	90%
Primidone	100	105	104	98	4%
Sulfamethoxazole	100	113	104	92	10%
TCEP	100	91	-	120	28%
Triclosan	200	242	156	210	21%

*One of these two laboratories had an MRL of 1,000 ng/L for octylphenol, so the value provided is a semi-quantitative estimate.

#This laboratory had an MRL << 500 ng/L for octylphenol.

Table 34. Round-Robin Results of Sample 3 (DWTP Effluent Spiked with Analytes)

	Spiked Amount (ng/L)	Lab A (ng/L)	Lab B (ng/L)	Lab C (ng/L)	RPD/RSD (%)
Bisphenol A	0	ND	ND	< 5.0	-
Caffeine	100	109	106	170	28%
Carbamazepine	100	102	103	100	2%
DEET	0	ND	4	5	29%
Diclofenac	200	166	-	200	18%
Dilantin	100	108	-	110	2%
Ethynylestradiol	100	95	100	-	5%
Gemfibrozil	200	236	186	200	12%
Ibuprofen	200	226	209	190	9%
Nonylphenol	0	ND	ND	-	N/A
Octylphenol	0	ND	ND	ND	N/A
Primidone	100	107	97.1	94	7%
Sulfamethoxazole	100	101	103	86	10%
TCEP	100	95	-	130	31%
Triclosan	200	218	175	200	11%

Table 35. Round-Robin Results of Samples 4 (SAR at Below Prado Dam Unspiked) and 5 (SAR at Below Prado Dam Spiked with Analytes)

Sample Number		Spiked Amount (ng/L)	Lab A (ng/L)	Lab B (ng/L)	Lab C (ng/L)	RPD/RSD (%)	Average Recovery (%)
4 (Unspiked)	Bisphenol A	0	ND	ND	10	N/A	N/A
	Caffeine	0	124	111	180	26%	
	Carbamazepine	0	97.6	101	100	2%	
	DEET	0	33	63	83	42%	
	Diclofenac	0	ND	-	6	N/A	
	Dilantin	0	99	-	110	11%	
	Ethynylestradiol	0	ND	ND	-	N/A	
	Gemfibrozil	0	56.0	20.5	49	45%	
	Ibuprofen	0	12	8	15	30%	
	Nonylphenol	0	ND	ND	-	N/A	
	Octylphenol	0	ND	ND	ND	N/A	
	Primidone	0	68.4	62.0	72	8%	
	Sulfamethoxazole	0	96	104	68	21%	
	TCEP	0	257	-	250	3%	
	Triclosan	0	ND	1	1	0%	
5 (Spiked)	Bisphenol A	0	ND	ND	6.3	N/A	N/A
	Caffeine	100	232	213	220	4%	83%
	Carbamazepine	100	208	190	200	5%	100%
	DEET	0	34	62	83	41%	N/A
	Diclofenac	200	210	-	210	0%	104%
	Dilantin	100	250	-	280	11%	160%
	Ethynylestradiol	100	108	87	-	21%	98%
	Gemfibrozil	200	344	151	240	39%	102%
	Ibuprofen	200	190	195	200	2%	92%
	Nonylphenol	0	ND	ND	-	N/A	N/A
	Octylphenol	0	ND	ND	ND	N/A	N/A
	Primidone	100	180	161	170	6%	103%
	Sulfamethoxazole	100	200	151	120	26%	68%
	TCEP	100	386	-	370	4%	125%
	Triclosan	200	216	187	210	7%	102%

Overall, the results from the three laboratories were quite comparable, with 89% of all the RPDs and the RSDs at less than 30%, indicating good precision of the methods. Of the 15 analytes that were analyzed by two or three laboratories, 11 analytes had an RPD or RSD less than 30%. The other four (DEET, gemfibrozil, octylphenol, TCEP) on at least one occasion exceeded an RPD/RSD of 30%. At the time of the analyses, gemfibrozil and TCEP were not analyzed at all participating laboratories by isotope dilution, which explained the higher than 30% RPDs/RSDs in some samples. Also, octylphenol was not detected by one laboratory in Sample 2, even

though their MRL was well below the concentration level of the spike. Note that RPDs and RSDs cannot be directly compared *per se*. For example, the RSD for gembrizol for Sample 2 was 39%, whereas the RPD between Laboratory A and B or between Laboratory B and C for this analyte in this sample was higher (79 and 52%, respectively) and between Laboratory A and C was lower (29%).

Spike recoveries were calculated by comparing the results from Sample 4 *versus* those from Sample 5, which was Sample 4 spiked with different levels of selected analytes, and the averages of the spike recoveries from the three laboratories were calculated (see Table 35). The overall accuracies were typically within 70 and 130%, with the exception of dilantin at a higher spike recovery (160%) and sulfamethoxazole at a slightly lower spike recovery (68%). This indicated that good accuracy was typically achieved.

4.4.2. Split Samples Among the Three Laboratories Throughout the Project

All samples collected from April 2008 to April 2009 were split between MWD and OCWD. There were 12 overlapping analytes between the two laboratories. Both the standard solutions and internal standard solutions were prepared at MWD and shared between the two laboratories. Overall, 89% of the results between the two laboratories had RPDs less than 30%, indicating the results were quite comparable.

Furthermore, four samples collected from the CRW system during each of the sampling events in June, September, and December of 2008, and April of 2009, were split three ways among MWD, OCWD, and SNWA. Although MWD and OCWD used the same standard and internal standard solutions, SNWA prepared and used its own standard and internal standard solutions throughout the project.

When comparing the 15 overlapping analytes between the analytical methods used at MWD and SNWA, 88% of the results had an RPD less than 30%, indicating good comparability between these two laboratories. When comparing the 11 overlapping analytes among the methods used at all three labs, 91% of the results had a RSD less than 30%, indicating good comparability among the three laboratories.

The following criteria were applied when calculating the RPDs and RSDs:

- The MRLs of bisphenol A, nonylphenol, and octylphenol were significantly different at MWD (20-50 ng/L each) and OCWD (1,000 ng/L each). Comparisons would not be meaningful and were excluded from the comparison of results.

- From April to June 2008, OCWD encountered problems with a mixture of standards purchased from a vendor. From January to February 2009, OCWD encountered problems with the DEET standard. As a result, the corresponding results from OCWD were excluded from the comparison of results.

- When an analyte was detected at or below 10 ng/L, most of the time the concentration was at or near the MRL at one or more laboratories, which potentially resulted in more variability in determining the concentration as compared with higher levels. Therefore,

the results were deemed comparable when the concentrations from all laboratories were below 10 ng/L. If one or more of the laboratories had concentrations higher than 10 ng/L, a RPD or RSD was calculated and used in summarizing the results. If an analyte was a non-detect, half of the MRL was used in the calculation of an RPD or RSD.

5. OCCURRENCE

5.1 Overview

Of the 126 samples analyzed for the project, one sample (American River at Fairbairn DWTP intake collected in April 2008) had no detectable levels of any PPCPs or OWCs. All other samples had one or more PPCPs and OWCs detected at or above the corresponding MRLs. The samples from the three watersheds can be further grouped into three categories: (1) river samples with low impact from WWTP discharges (<10% treated wastewater), which included samples collected from SPW and CRW; (2) river samples dominated by WWTP discharges (>50% treated wastewater), which included the SAR samples; and (3) WWTP effluents, collected from the CRW and SAR watersheds. The ten (nine for CRW river samples) most frequently detected PPCPs and OWCs in each category are shown in Table 36, listed from the most to the least frequently detected. When two or more analytes had the same detection frequency, they were listed in alphabetical order. In each of the Nevada WWTP blended effluent samples, the same 12 analytes were always detected (100% detection frequency) with various concentrations, and were listed in alphabetical order. The five commonly detected PPCPs in all categories were caffeine, carbamazepine, primidone, sulfamethoxazole, and TCEP. Most of the latter PPCPs were also frequently detected in other studies (Table 3).

Table 36. Most Frequently Detected PPCPs and OWCs in the Three Watersheds

SPW	**CRW**		**SAR**	
River Samples	**WWTP Effluent***	**River Samples**	**WWTP Effluents**	**River Samples**
Carbamazepine	Azithromycin	Carbamazepine	Carbamazepine	Caffeine
Diuron	Caffeine	Sulfamethoxazole	Dilantin	TCEP
Sulfamethoxazole	Carbamazepine	Primidone	Diuron	DEET
Caffeine	Ciprofloxacin	Caffeine	Primidone	Diuron
Primidone	DEET	Acetaminophen	Sulfamethoxazole	Carbamazepine
TCEP	Diclofenac	TCEP	TCEP	Primidone
Gemfibrozil	Dilantin	DEET	DEET	Sulfamethoxazole
Dilantin	Diuron	o,p-DDD	Gemfibrozil	Dilantin
Simazine	Gemfibrozil	Azithromycin	Caffeine	Gemfibrozil
Atrazine	Primidone		Atrazine	Atrazine
	Sulfamethoxazole			
	TCEP			

*Blended from the effluents of the three WWTPs in the Las Vegas area based on flows.

Of the 49 targeted analytes, 27 were detected at least once. Twenty-two analytes were not detected in any samples (Table 37) at or above the corresponding MRLs, which ranged from 10-10,000 ng/L. In some cases, the latter PPCPs were not detected, mostly likely, due to MRLs that were not sufficiently sensitive. For example, the median occurrence of estrone in one study (Benotti et al., 2009) was 0.3 ng/L, where there was an 83% frequency of detection. In the current study, the MRL of 10 ng/L for estrone most likely precluded its detection. In contrast, the occurrence of the most frequently detected PPCPs were substantially higher than their MRLs (Figure 9). Currently, there are no standardized methods for the PPCPs, so MRLs and, thus, frequency of detection may vary from laboratory to laboratory.

Table 37. Analytes Not Detected in Any of the Samples

Targeted Analyte	MRL (ng/L)
Anthracene	10
Atrazine-desethyl	20
Butylparaben	20
Cyanazine	20
Cyprazine	20
Diethylstilbestrol	10
Epiestrosterone	10
17 α-Estradiol	10
17 β-Estradiol	10
Estriol	10
Estrone	10
Ethylparben	20
Ethynylestradiol	10
Lindane	10
Nonylphenol ethoxylates	10,000
Pentachlorophenol	1,000
4-Phenylphenol	1,000
Progesterone	10
Propazine	20
Testosterone	10
Tetrabromobisphenol A	1,000
2,4,6-Trichlorophenol	1,000

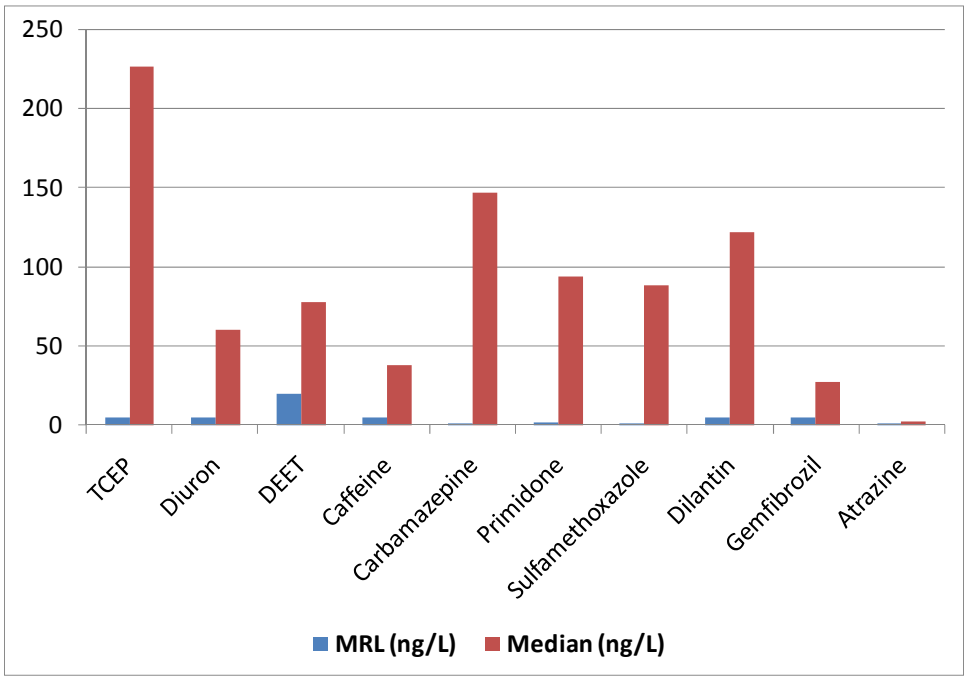

Figure 9. Comparison of median values and MRLs for the most frequently detected PPCPs in the SAR watershed.

The concentrations of the six most frequently detected PPCPs (>70% detection frequency) in the SPW watershed are shown in a box-and-whisker plot in Figure 10, along with their occurrence in the CRW watershed and in the Nevada WWTP blended effluent for comparison. The following conclusions can be drawn based on these results:

- The median concentrations of caffeine, carbamazepine, sulfamethoxazole, primidone, and TCEP in both SPW and CRW river samples were similar, all below 12 ng/L.

- Diuron was not detected in any of the CRW river samples, but was detected in 88% of the SPW samples, with a median concentration of 81 ng/L and a maximum concentration of 873 ng/L. This is consistent with the fact that diuron is used extensively in California as a pre-emergent herbicide.

- The levels of most of the PPCPs in the WWTP blended effluent had a tight concentration range (e.g., carbamazepine was 187-204 ng/L).

- The occurrence of some PPCPs in the Nevada WWTP blended effluent (e.g., carbamazepine, primidone, sulfamethoxazole) was similar to that reported in other WWTP effluents (Table 1). For example, Krasner and colleagues (2006) found that primidone was typically present at ~100-200 ng/L levels in U.S. WWTP effluents. The relatively high occurrence of sulfamethoxazole in the Nevada WWTP blended effluent is consistent with that of other WWTPs that disinfect with UV, where germicidal doses of UV do not substantially impact this PPCP (Snyder et al., 2007).

- The amounts of certain PPCPs (i.e., carbamazepine, sulfamethoxazole, primidone, and TCEP) were highly attenuated in both watersheds. Carbamazepine and primidone are conservative wastewater tracers (Guo and Krasner, 2009). The occurrence of these anticonvulsants in the SPW and CRW watersheds relative to that of the Nevada WWTP blended effluent (assuming similar levels in the Delta WWTP effluents) suggest that SPW and CRW are <10% treated wastewater. This is consistent with the modeled volumetric fingerprint of the Sacramento WWTP at the Sacramento River at Hood for the last three sample events (1.5-2.6%). The attenuation of PPCPs will be discussed in more detail in the fate-and-transport chapter.

- The amount of caffeine in the CRW watershed was sometimes higher than what was in the WWTP blended effluent, implying other sources (e.g., urban runoff, plants that produce caffeine).

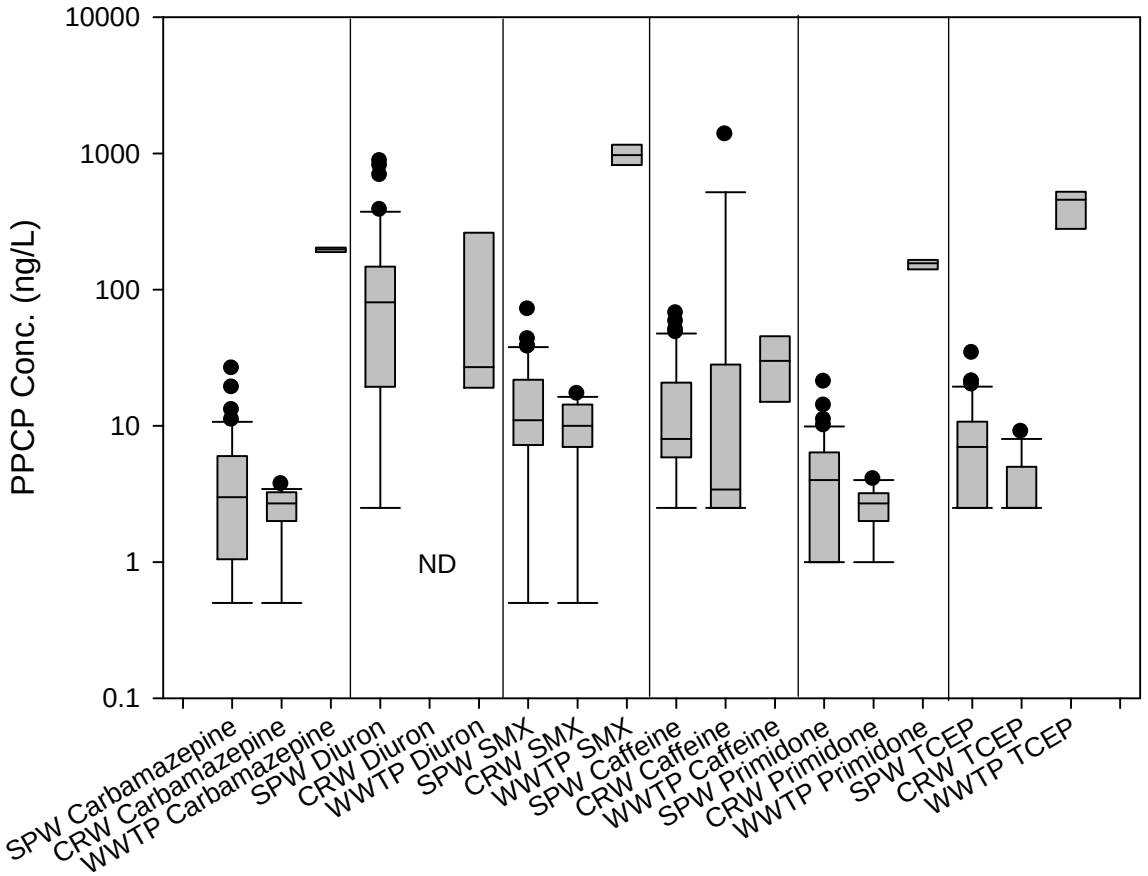

Figure 10. Occurrence of the six most frequently detected PPCPs and OWCs in the SPW watershed and their occurrence in the CRW watershed and in the Nevada WWTP blended effluent (April 2008 – April 2009). Top and bottom of box = 75th and 25th percentiles, respectively; top and bottom of whiskers = 90th and 10th percentiles, respectively; line across inside of box = median (50th percentile); and points beyond whiskers = outliers. ND = Not detected.

The concentrations of the ten most frequently detected PPCPs (>70% detection frequency) in the SAR watershed and their occurrence in the WWTPs that discharged into this watershed are shown in Figure 11. The concentrations of most PPCPs were lower in the river and tributary samples than those in the WWTP effluents, but were substantially higher than those in the SPW and the CRW watersheds, which was expected as SAR is effluent-dominated. Caffeine and diuron levels in this watershed were typically higher than the amounts in the WWTP effluents, suggesting other sources (e.g., urban runoff, plants that produce it). The amounts of some PPCPs (TCEP, carbamazepine, primidone) were relatively tight in range, and similar to that detected in the Nevada WWTP blended effluent. The amounts of other PPCPs in the effluents of the WWTPs in the SAR watershed (e.g., sulfamethoxazole, gemfibrozil) spanned a very large range, reflecting the impact of different disinfection practices on these PPCPs (see discussion below).

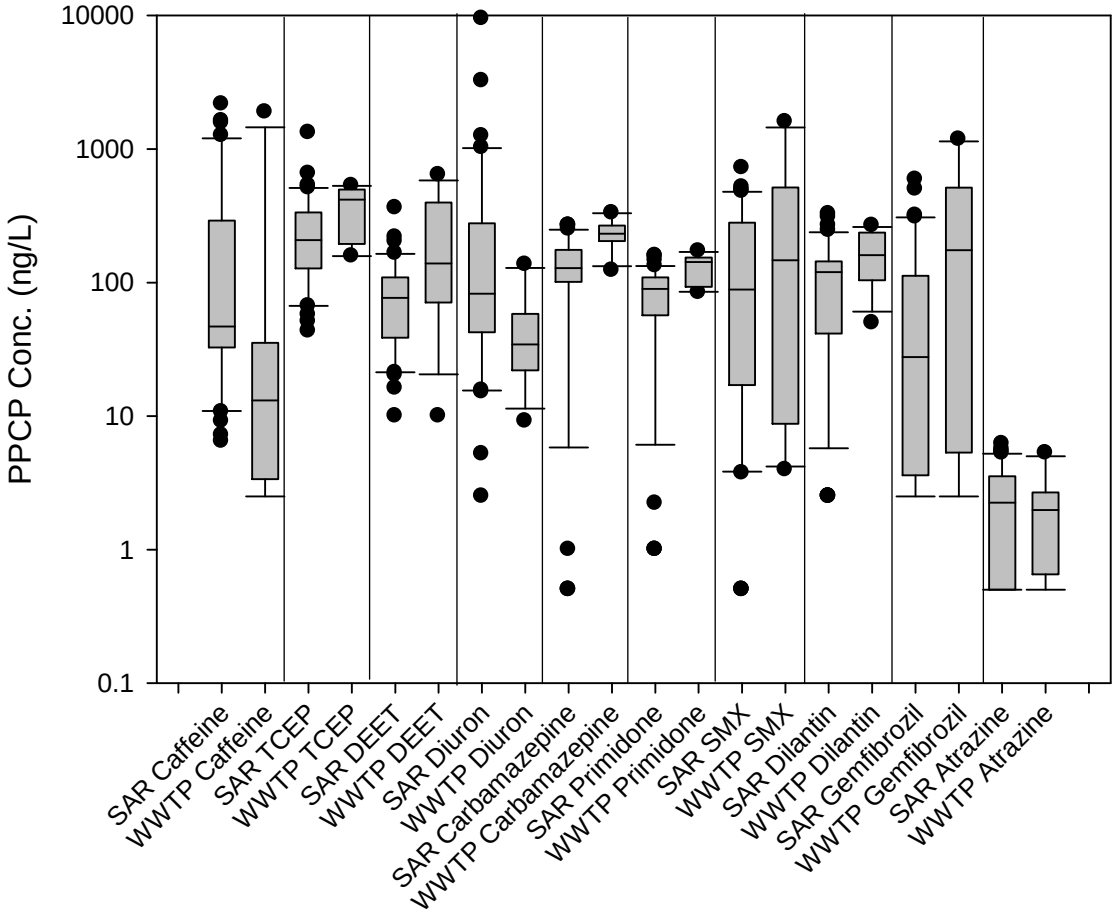

Figure 11. Occurrence of the 10 most frequently detected PPCPs in the SAR watershed and their occurrence in the WWTPs that discharged into this watershed (May 2008 – February 2009).

The occurrence of five selected PPCPs (caffeine, carbamazepine, gemfibrozil, primidone, sulfamethoxazole) was further summarized based on the types of samples (i.e., WWTP effluents, upstream sites, downstream sites in each watershed) in Tables 38-42. These five PPCPs were chosen based on their common occurrence in treated wastewater and in effluent-impacted waters (Table 1; Buerge et al., 2003; Guo and Krasner, 2009), different fate-and-transport loss mechanisms in the environment (section 2.1.3), and different removal/transformation efficiencies from treatment processes (Table 2).

The concentrations of carbamazepine and primidone in WWTP effluents did not vary significantly between different samples, whereas those of caffeine, gemfibrozil, and sulfamethoxazole varied from not detected to >1,000 ng/L. Although WWTP influents were not sampled and evaluation of WWTP treatment efficiencies was outside the scope of work for this project, the general trend was that WWTPs with UV disinfection had high levels of gemfibrozil and sulfamethoxazole, and WWTPs with chlorination had low levels of these two PPCPs. Also, one of the WWTPs with chlorination experienced unusual circumstances during two of the four sampling events (e.g., somewhat higher ammonia level during one event), which resulted in >1,000 ng/L levels of the two PPCPs. In the case of a higher ammonia level, the chlorine dose used was not able to achieve breakpoint, which would have resulted in chloramine formation, where chloramines are not as efficient at reacting with some PPCPs (Table 2). In addition, caffeine tended to be higher in some of these instances. This may reflect (in part) poorer biological treatment, as caffeine can be biodegraded to varying extents.

At the sample sites upstream of WWTP discharges, the concentrations of these selected PPCPs, except for caffeine, were low (≤ 13 ng/L), pointing to WWTP discharges as the main source of most PPCPs and OWCs in the aquatic environment. In terms of caffeine, the median and maximum concentrations of 47 and 2,160 ng/L, respectively, at the upstream sites indicate that caffeine in the environment can come from sources that are not WWTP originated (e.g., urban runoff, plants that produce it). Sample sites downstream of WWTP discharges in the SAR watershed were dominated by treated wastewater, whereas the SPW and CRW watersheds were impacted by treated wastewater to a much lower extent. With the exception of caffeine, the median and maximum concentrations of the PPCPs in the SAR downstream sites were substantially higher than those from the SPW and CRW downstream sites.

Table 38. Occurrence and Concentrations of Caffeine in All Three Watersheds (ng/L)

	Minimum	**Median**	**Maximum**
WWTPs (n=16):	<5	14	1883
Upstream sites (n=16):	<5	47	2160
Downstream sites (n=79):			
SPW (n=28)	<5	8	67
CRW (n=19)	<5	<5	1370
SAR (n=32)	9	47	1620

Table 39. Occurrence and Concentrations of Carbamazepine in All Three Watersheds (ng/L)

	Minimum	**Median**	**Maximum**
WWTPs (n=16):	123	208	331
Upstream sites (n=16);	<1	<1	6
Downstream sites (n=79):			
SPW (n=28)	<1	4	26
CRW (n=19)	<1	3	4
SAR (n=32)	49	135	267

Table 40. Occurrence and Concentrations of Gemfibrozil in All Three Watersheds (ng/L)

	Minimum	**Median**	**Maximum**
WWTPs (n=16):	<5	22	1178
Upstream sites (n=16):	<5	<5	12
Downstream sites (n=79):			
SPW (n=28)	<5	8	162
CRW (n=19)	<5	<5	<5
SAR (n=32)	<5	48	590

Table 41. Occurrence and Concentrations of Primidone in All Three Watersheds (ng/L)

	Minimum	**Median**	**Maximum**
WWTPs (n=16):	84	146	171
Upstream sites (n=16):	<2	<2	9
Downstream sites (n=79):			
SPW (n=28)	<2	5	21
CRW (n=19)	<2	3	4
SAR (n=32)	41	90	146

Table 42. Occurrence and Concentrations of Sulfamethoxazole in All Three Watersheds (ng/L)

	Minimum	Median	Maximum
WWTPs (n=16):	4	417	1593
Upstream sites (n=16):	<1	3	13
Downstream sites (n=79):			
SPW (n=28)	5	17	71
CRW (n=19)	<1	10	17
SAR (n=32)	4	160	721

The occurrence of total phosphorus in all three watersheds is summarized in Table 43. The concentration range in the WWTP effluents was rather wide, as some WWTPs are designed for phosphorus removal and others are not. Of the three watersheds, CRW had the lowest levels, whereas SAR had the highest. More discussion on total phosphorus will be given in Chapter 7.

Table 43. Occurrence and Concentrations of Total Phosphorus in All Three Watersheds (mg/L)

	Minimum	Median	Maximum
WWTPs (n=16):	0.007	0.577	3.100
Upstream sites (n=14):	<0.004	0.078	0.258
Downstream sites (n=79):			
SPW (n=24)	0.054	0.102	0.164
CRW (n=12)	<0.004	0.006	0.012
SAR (n=32)	<0.004	1.080	1.870

5.2 Occurrence in SPW Watershed

A total of 43 samples were collected from the SPW watershed during 4 sampling events. Detectable amounts of PPCPs and OWCs were found at all locations, except for the American River at the Fairbairn DWTP intake in April 2008, which had no detectable levels of any PPCPs or OWCs. Of the 49 PPCPs and OWCs analyzed, 21 analytes were detected at or above the MRLs, whereas the other 28 were not detected at all locations in this watershed with the existing MRLs. The occurrence of PPCPs in the SPW watershed is shown in Table 44, from the most to the least frequently detected.

Table 44. PPCPs and OWCs Detected in the SPW Watershed

Analyte	Detection Frequency (n=40)	Minimum (ng/L)	Median (ng/L)	Maximum (ng/L)
Carbamazepine	88%	<1	3	26
Diuron	88%	<5	81	873
Sulfamethoxazole	88%	<1	11	71
Caffeine	83%	<5	8	67
Primidone	70%	<2	4	21
TCEP	70%	<5	7	34
Gemfibrozil	53%	<5	5	162
Dilantin	50%	<5	4	33
Simazine	38%	<20	<20	408
Atrazine	25%	<1	<1	2
o,p-DDD	20%	<20	<20	82
Methoxychlor	18%	<20	<20	66
DEET	13%	<20	<20	35
Methylparaben	10%	<20	<20	744
Acetaminophen	5%	<1	<1	28
Linuron	5%	<5	<5	5
Bisphenol A	3%	<30	<30	140
Desisopropyl-atrazine	3%	<20	<20	25
Ibuprofen	3%	<10	<10	47
Octylphenol	3%	<20	<20	68
Propylparaben	3%	<20	<20	83

Although the NEMDC site (Table 5) was collected during three of the four sampling events, it was not part of the river system of SPW, and was not included in the statistical analysis for minimum, median, and maximum concentrations. The occurrence of certain PPCPs was relatively high at NEMDC (20-90 ng/L caffeine, 25-79 ng/L carbamazepine, 23-132 ng/L DEET, 27-71 ng/L primidone, 17-95 ng/L sulfamethoxazole, 21-79 ng/L dilantin, 25-273 ng/L diuron, and 24-147 ng/L TCEP), which was impacted by urban drainage. Alternatively, the levels of most PPCPs were quite low (ND to 2 ng/L carbamazepine, ND for DEET, ND to 2 ng/L primidone, ND to 8 ng/L sulfamethoxazole, ND for dilantin, and ND to 6 ng/L TCEP) at certain

upstream sites (i.e., American River at the Fairbairn DWTP intake, Sacramento River at W. Sacramento WTP intake). However, caffeine (6-22 ng/L) and diuron (7-83 ng/L) were sometimes detected at these two upstream sites (and were ND at other times).

For the SPW watershed overall, the median occurrence of targeted PPCPs was <30 ng/L, except for diuron (81 ng/L). However, maximum concentrations for some PPCPs exceeded 100 ng/L. For example, the highest levels of gemfibrozil in this watershed were detected at the Sacramento River at Hood (83-162 ng/L), which is downstream of the Sacramento WWTP. The highest occurrence of diuron (39-686 ng/L, except for ND in the American River) and simazine (23-408 ng/L, except for ND in the American and Sacramento [including at Hood] Rivers) was in the springtime (April 2008). As diuron is a pre-emergence herbicide, higher occurrence in the springtime is expected. Simazine is also an herbicide. In some cases, a high occurrence of certain PPCPs (e.g., 140 ng/L of bisphenol A) was an isolated occurrence and was not detected in any other samples.

In this watershed, the highest occurrence of carbamazepine (8-26 ng/L) and primidone (9-21 ng/L) was in the San Joaquin River at Holt Road, which is downstream of the Stockton WWTP. The next highest occurrence of these two anticonvulsants (3-11 ng/L carbamazepine, 5-7 ng/L primidone) was in the Sacramento River at Hood, which is downstream of the Sacramento WWTP. Although the discharge rate at the Sacramento WWTP was higher than that of the Stockton WWTP, the flow of the Sacramento River was much higher than that of the San Joaquin River, where the attenuation of these two conservative wastewater tracers is due to dilution with non-impacted water. Alternatively, as noted above, the highest occurrence of gemfibrozil was in the Sacramento River at Hood; the concentration (11-95 ng/L) was lower in the San Joaquin River at Holt Road. This suggests that the levels of this PPCP in the Sacramento WWTP discharge were probably higher than in the discharge of the Stockton WWTP. The Stockton WWTP operated with chloramines.

5.3 Occurrence in SAR Watershed

A total of 52 samples were collected from the SAR watershed during four sampling events. Detectable amounts of PPCPs and OWCs were found at all locations. Of the 49 PPCPs and OWCs analyzed, 20 analytes were detected in the WWTP effluents at or above the MRLs, whereas 22 analytes were detected in the river and tributary samples at or above the existing MRLs. The occurrence of PPCPs and OWCs in the WWTP effluents are shown in Table 45, and the occurrence in the river and tributary samples are shown in Table 46, both listing the analytes from the most to the least frequently detected.

As discussed above, the levels of certain PPCPs (e.g., carbamazepine, primidone, and TCEP) in the WWTP discharges were relatively consistent over time and space and similar to that in other studies, whereas the amounts of other PPCPs (e.g., caffeine, gemfibrozil, and sulfamethoxazole) varied widely. The median occurrence of a number of the PPCPs studied in the WWTP discharges were >100 ng/L, and the maximum occurrence of some PPCPs was >1,000 ng/L. This is consistent with other studies (Table 1). The impact of disinfection practices at the WWTPs on PPCP occurrence is discussed below.

The levels of PPCPs in the river and tributary samples varied widely, as this included sample sites upstream and downstream of WWTPs. What also impacted the occurrence of some PPCPs

(e.g., gemfibrozil, sulfamethoxazole) was whether the location was downstream of a WWTP that used UV or chlorine (see Chapter 6 for more discussion on this issue). The median occurrence of a number of PPCPs was substantially higher in the SAR watershed than in the SPW watershed, as the SAR was effluent-dominated. The median and maximum concentration of diuron in the SAR watershed (83 and 9,440 ng/L, respectively) was substantially higher than the levels in the WWTP discharges (34 and 136 ng/L, respectively), indicating other sources of this herbicide in the watershed. Unlike the SPW watershed, there was no seasonal trend for the occurrence of diuron in the SAR watershed, except perhaps lower occurrence in the summer (August 2008).

Table 45. PPCPs and OWCs Detected in the WWTP Effluents in the SAR Watershed

Analyte	Detection Frequency (n=12)	Minimum (ng/L)	Median (ng/L)	Maximum (ng/L)
Carbamazepine	100%	123	232	331
Dilantin	100%	50	161	266
Diuron	100%	9	34	136
Primidone	100%	84	142	171
Sulfamethoxazole	100%	4	147	1593
TCEP	100%	157	418	530
DEET	92%	<20	139	638
Gemfibrozil	83%	<5	175	1178
Atrazine	75%	<1	2	5
Caffeine	75%	<5	13	1883
Ibuprofen	67%	<10	16	1460
Azithromycin	58%	<1	15	660
Triclosan	58%	<5	7	35
Acetaminophen	50%	4	9	420
Ciprofloxacin	33%	<40	<40	58
Linuron	33%	<5	<5	6
Simazine	33%	<20	<20	61
Diclofenac	25%	<5	<5	67
Desisopropyl-atrazine	8%	<20	<20	22
Benzo[a]pyrene	8%	<25	<25	254

Table 46. PPCPs and OWCs Detected in River and Tributary Samples in the SAR Watershed

Analyte	Detection Frequency (n=40)	Minimum (ng/L)	Median (ng/L)	Maximum (ng/L)
Caffeine	100%	6	47	2160
TCEP	100%	43	208	1320
DEET	98%	<20	77	361
Diuron	98%	<5	83	9440
Carbamazepine	93%	<1	128	267
Primidone	93%	<2	89	158
Sulfamethoxazole	93%	<1	89	721
Dilantin	90%	<5	120	325
Gemfibrozil	75%	<5	28	590
Atrazine	70%	<1	2	6
Acetaminophen	68%	3	10	460
Ibuprofen	65%	<10	17	530
Simazine	50%	<20	<20	115
Ciprofloxacin	28%	10	25	69
Azithromycin	25%	<1	3	600
Desisopropyl-atrazine	25%	<20	<20	450
Triclosan	25%	<5	<5	13
Linuron	18%	<5	<5	8
o,p-DDD	15%	<20	<20	51
Benzo[a]pyrene	8%	<25	<25	422
Diclofenac	8%	<5	<5	15
Methoxychlor	8%	<20	<20	31

5.4 Occurrence in CRW Watershed

A total of 31 samples were collected from the CRW watershed during four sampling events. Detectable amounts of PPCPs and OWCs were found at all locations. Of the 49 PPCPs and OWCs analyzed, 16 analytes were detected in the WWTP blended effluent at or above the MRLs, and 12 analytes were detected in the surface water samples at or above the existing MRLs. The results of the WWTP blended effluent are shown in Table 47, and the results of the CRW samples are shown in Table 48, both listing the analytes from the most to the least frequently detected. When two or more analytes had the same detection frequency, they were listed in alphabetical order. Although two sampling sites in the Las Vegas Wash (upstream and downstream of the WWTP discharge) were collected for the project, they were not part of the river system of CRW; thus, they were not included in the statistical analysis for minimum, median, and maximum concentrations.

As discussed above, the levels of certain PPCPs (e.g., carbamazepine, primidone, TCEP) in the Nevada WWTP blended effluent were relatively consistent over time and similar to that in other studies, as well as to that detected at the WWTPs in the SAR watershed. Also, the amounts of other PPCPs (e.g., caffeine, gemfibrozil, sulfamethoxazole) were relatively consistent over time in the Nevada WWTP blended effluent, suggesting that the Nevada WWTPs in this study did not substantially vary their treatment/disinfection practices over the course of the study. The median occurrence of a number of the PPCPs studied in the WWTP discharges were >100 ng/L, and the maximum occurrence of sulfamethoxazole was >1,000 ng/L. This is consistent with other studies (Table 1), as well as with that detected at the WWTPs in the SAR watershed.

In general, the levels of most PPCPs in the Las Vegas Wash upstream of the WWTP discharges were low (ND for carbamazepine, ND for DEET, ND to 2 ng/L for primidone, ND to 3 ng/L for sulfamethoxazole, ND for dilantin). Alternatively, there were more appreciable levels of other PPCPs in the wash upstream of the WWTPs (46-185 ng/L of caffeine, 14-99 ng/L diuron, 10-20 ng/L TCEP, ND and 36-61 ng/L acetaminophen). Consistent with other watersheds in this study, caffeine and diuron occurrence was common, even in upstream locations. In contrast, the levels of the PPCPs in the Las Vegas Wash downstream of the WWTP discharges were high and (in general) similar in concentration to that in the WWTP blended effluent. However, the levels of three antibiotics, sulfamethoxazole (565-817 ng/L), azithromycin (9-90 ng/L) and ciprofloxacin (21-69 ng/L), and one anti-inflammatory drug (2-14 ng/L diclofenac) in the wash downstream of the WWTPs were substantially lower than their concentrations in the WWTP blended effluent (762-1,240, 62-280, 36-140, and 14-31 ng/L, respectively). Various studies have shown that certain antibiotics (e.g., ciprofloxacin) can degrade in the environment (Zhang and Huang, 2005). The fate-and-transport chapter discusses the loss of other PPCPs in this watershed further.

For the CRW watershed, the median occurrence of targeted PPCPs was <20 ng/L (unless the MRL was higher for a particular PPCP). However, maximum concentrations for a few PPCPs exceeded 100 ng/L. For example, high levels of caffeine (519-1370 ng/L) and DEET (64-297 ng/L) were sometimes detected at the inlet to Lake Havasu, most likely from human activities in this portion of the watershed (see additional discussion in the fate-and-transport chapter). In some cases, a high occurrence of certain PPCPs (e.g., 143 ng/L of nonylphenol) was an isolated occurrence and was not detected in any other samples. The median occurrence of carbamazepine

(3 ng/L) and primidone (3 ng/L) in the CRW watershed suggest that it is 1.5-1.9% treated wastewater, when compared to the median occurrence of these PPCPs in the WWTP blended effluent (197 and 156 ng/L, respectively).

Table 47. PPCPs and OWCs Detected in the Nevada WWTP Blended Effluent*

Analyte	Detection Frequency (n=4)	Minimum (ng/L)	Median (ng/L)	Maximum (ng/L)
Azithromycin	100%	62	250	280
Caffeine	100%	11	30	50
Carbamazepine	100%	187	197	204
Ciprofloxacin	100%	36	130	140
DEET	100%	61	117	408
Diclofenac	100%	14	20	31
Dilantin	100%	129	145	159
Diuron	100%	15	27	402
Gemfibrozil	100%	9	17	40
Primidone	100%	134	156	167
Sulfamethoxazole	100%	762	969	1240
TCEP	100%	211	456	523
Acetaminophen	75%	3	10	29
Triclosan	50%	<5	6	12
Ibuprofen	25%	<10	<10	13
Methylparaben	25%	<20	<20	29

*A blend of effluents from three WWTPs based on the flows.

Table 48. PPCPs and OWCs Detected in the CRW Watershed

Analyte	Detection Frequency (n=19)	Minimum (ng/L)	Median (ng/L)	Maximum (ng/L)
Carbamazepine	89%	<1	3	4
Sulfamethoxazole	84%	<1	10	17
Primidone	79%	<2	3	4
Caffeine	47%	<5	<5	1370
Acetaminophen	42%	<1	2	14
TCEP	26%	<5	<5	9
o,p-DDD	21%	<20	<20	46
DEET	21%	<20	<20	103
Azithromycin	16%	<1	3	13
Ibuprofen	5%	<10	<10	36
Methylparaben	5%	<20	<20	35
Nonylphenol	5%	<50	<50	143

5.5 Seasonal Variations

5.5.1 WWTP Effluents

The concentrations of five representative PPCPs (caffeine, carbamazepine, gemfibrozil, primidone, and sulfamethoxazole) in the WWTP effluents collected throughout the project are shown in Figures 12-15. Overall, the concentrations did not vary significantly during different seasons. For example, the maximum concentration of sulfamethoxazole in the Nevada blended effluent came from December 2008, which was 1.6 times the minimum concentration from June 2008. The exception was WWTP #3 in the SAR watershed (Figure 14), which experienced unusual circumstances (plant upsets) during two of the four sampling events and resulted in much higher levels of caffeine (>400 ng/L) and gemfibrozil and sulfamethoxazole (both at >1,000 ng/L), ranging from 55 to 235 times the concentrations of the corresponding lowest levels. At WWTP #3, during one of the unusual events (February 2009), the effluent had a somewhat higher ammonia level than normal. In the latter instance, the chlorine dose used was not able to achieve breakpoint (it takes ~7.6 to 10 mg/L as Cl_2 of chlorine to breakout 1.0 mg/L of ammonia-nitrogen), which would have resulted in chloramine formation, where chloramines are not as efficient at reacting with gemfibrozil or sulfamethoxazole (Table 2). In addition, caffeine was higher, which may reflect (in part) poorer biological treatment, as caffeine can be biodegraded to varying extents. Although the exact reasons of the high levels of PPCPs during

the other unusual event (August 2009) are unknown at WWTP #3, the variations were attributed to the plant upset and not to seasonal effects *per se*.

Table 49. Water Quality and Operations at WWTP #3 in the SAR Watershed

Date	Ammonia (mg/L as N)	Chlorine Dose (mg/L as Cl_2)	Cl_2/N Ratio (mg/mg)	Disinfectant Present
May 22, 2008	<0.2	9.59	>48:1	Free chlorine
August 19, 2008	0.4	13.92	35:1	Free chlorine
November 5, 2008	<0.2	9.15	>46:1	Free chlorine
Feburary 25, 2009	1.6	10.56	6.6	Chloramines

In fact, a comparison of PPCP occurrence between the WWTPs shows that the levels of gemfibrozil and/or sulfamethoxazole were typically high when UV was used (i.e., Nevada WWTP blended effluent, WWTP #2 in SAR watershed), and were normally low when chlorine was used (i.e., WWTP #3 and #4 in the SAR watershed), unless the chlorine dose was insufficient to achieve breakpoint or there was a plant upset (i.e., two samples from WWTP #3 in the SAR watershed).

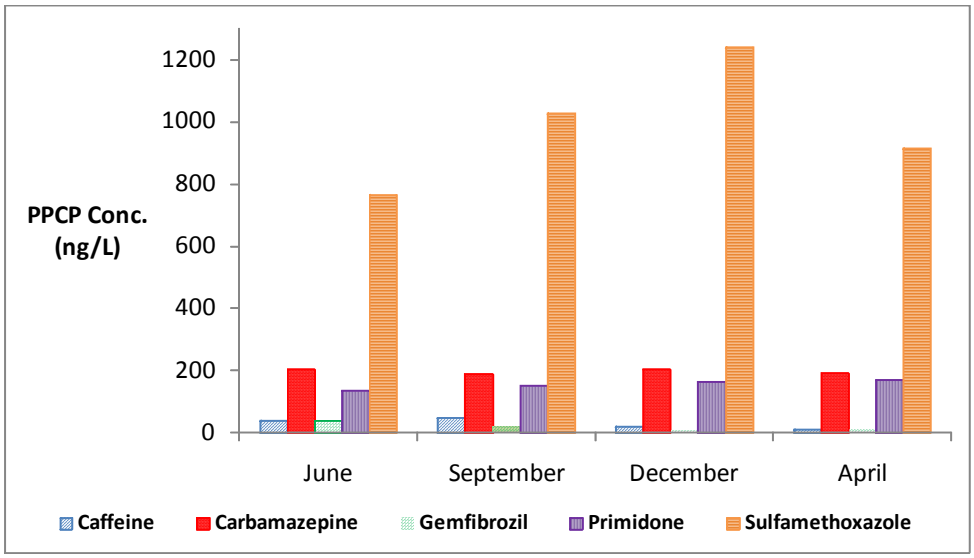

Figure 12. Concentrations of five representative PPCPs in the Nevada WWTP blended effluent.

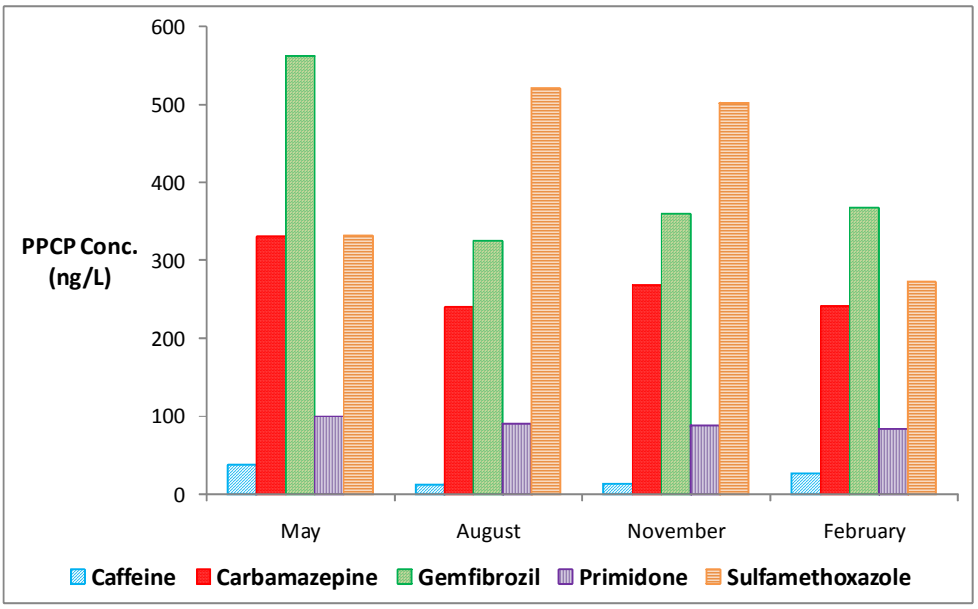

Figure 13. Concentrations of five representative PPCPs in the effluent of WWTP #2 in the SAR watershed.

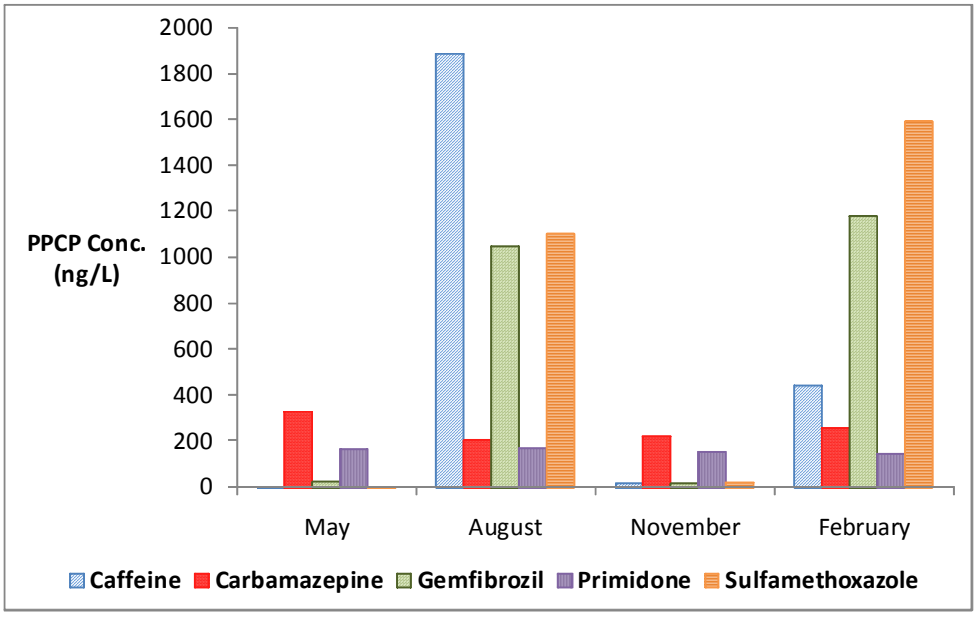

Figure 14. Concentrations of five representative PPCPs in the effluent of WWTP #3 in the SAR watershed.

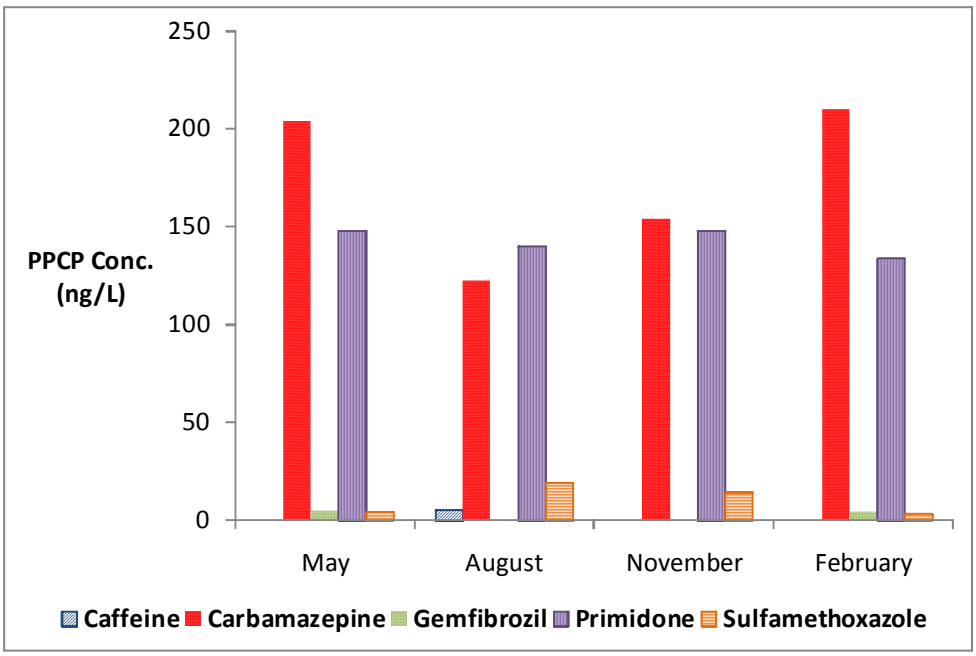

Figure 15. Concentration of five representative PPCPs in the effluent of WWTP #4 in the SAR watershed.

5.5.2 Surface Water Samples

The concentrations of five representative PPCPs (caffeine, carbamazepine, gemfibrozil, primidone, sulfamethoxazole) in three surface water samples collected throughout the project are shown in Figures 16-18. The Hood and Holt Road sites in the SPW watershed represented surface water samples downstream of WWTPs and under low WWTP influence, whereas the Imperial Highway site in the SAR was effluent-dominated. The factors affecting the variations in PPCP concentrations may include: (1) the concentrations of PPCPs in the WWTP discharges upstream and the WWTP discharge rates; (2) flows in the river, which are generally higher in winter and spring months than in summer and fall months; and (3) attenuation of PPCPs in the watershed due to dilution, biodegradation, photolysis, or other processes, where there may be more biodegradation and/or sunlight photolysis in warmer and sunnier seasons.

For example, the highest occurrence of caffeine in the SPW watershed at the two downstream sites was in the winter (January 2009). This could reflect (in part) less biodegradation at the WWTPs and/or less biodegradation in the rivers during this season. However, in January 2009, the concentrations all of the representative PPCPs were relatively high in the San Joaquin River at Holt Road, including carbamazepine and primidone. This suggests that this site was more effluent impacted during this sample event. Typically, WWTP discharge rates do not vary that much from season to season, whereas river flows can vary widely. These data suggest that the San Joaquin River flow at Holt Road during this sample event may have been lower than normal. Note, because of reverse flows in the river because of tidal impact, it is difficult to fully evaluate flows in this river at this site. Alternatively, during the last three sample events, a hydrologic model used by the California Department of Water Resources suggested that the contribution of the Sacramento WWTP to flow in the Sacramento River at Hood did not vary that much (5-2.6%).

In the SAR at Imperial Highway, there was less carbamazepine and primidone in the February 2009 sample event, when there was a major storm event. The other seasonal variation was in the amount of caffeine present. However, the caffeine occurrence pattern for this downstream site does not match that of the WWTP discharges, suggesting other sources in the watershed. More in-depth discussion is included in the fate-and-transport chapter.

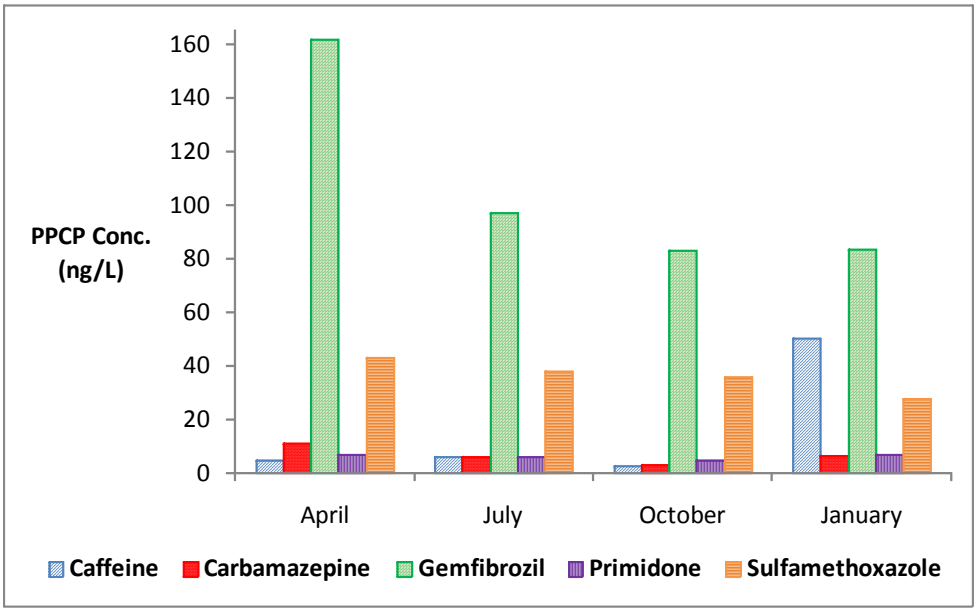

Figure 16. Concentrations of five representative PPCPs in the Sacramento River at Hood in the SPW watershed.

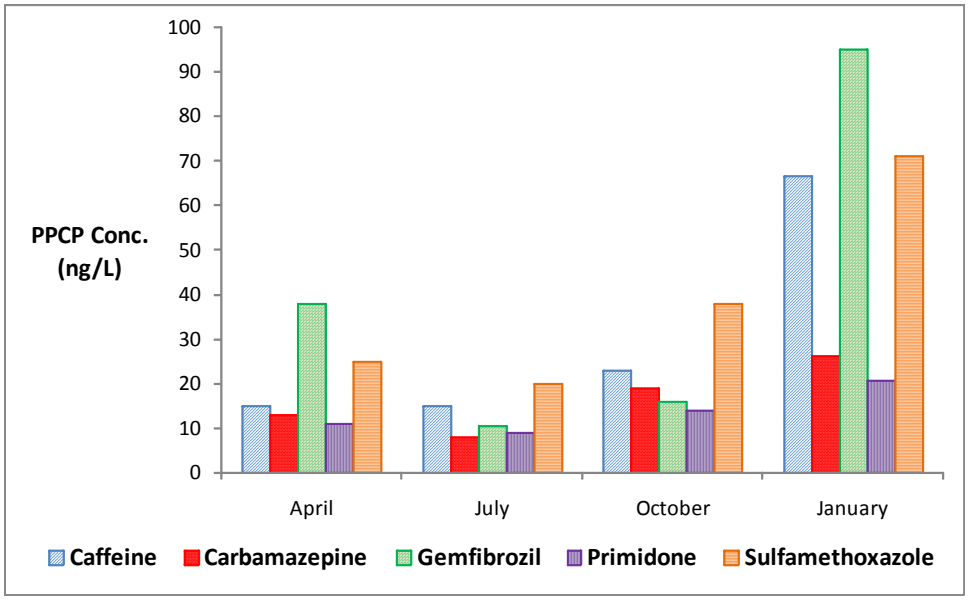

Figure 17. Concentrations of five representative PPCPs in the San Joaquin River at Holt Road in the SPW watershed.

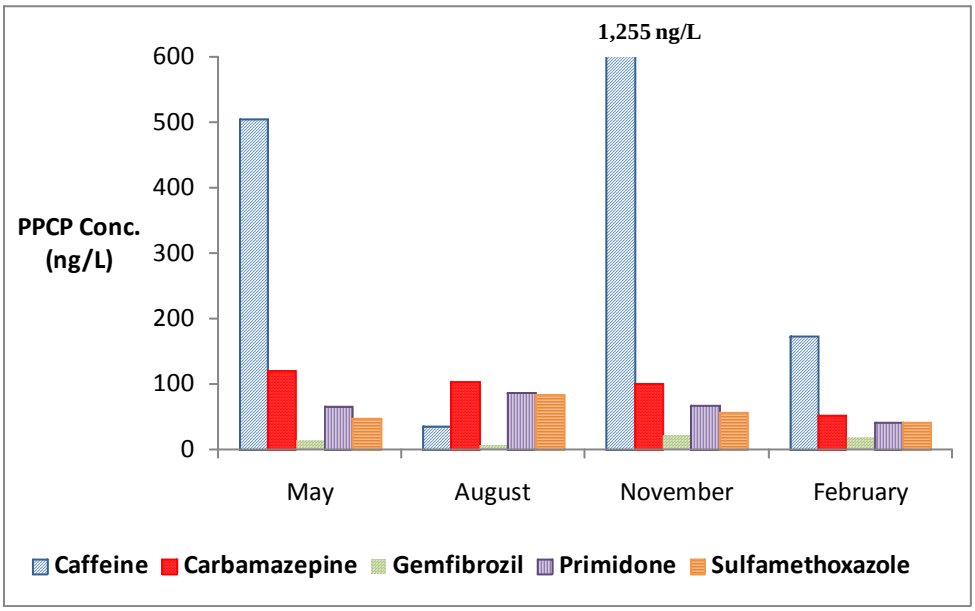

Figure 18. Concentrations of five representative PPCPs in the SAR at Imperial Highway. The y-axis was cut off at 600 ng/L; therefore, the caffeine result is noted above for the November 2008 sample.

6. FATE AND TRANSPORT

6.1 SPW

Figure 19 summarizes the occurrence of carbamazepine in the SPW system, beginning with the sites downstream of the two major WWTPs in the Delta region. As this PPCP is known to be stable, these results suggest that water at the Banks pumping plant during this study reflected a greater percentage of water from the Sacramento River (e.g., Hood) than from the San Joaquin River (e.g., Holt Road) and/or other sources of water (e.g., other tributaries into the Delta, saltwater intrusion) with less PPCP impact. Although the water at Check 13 represented a combination of water from Banks pumping plant and the Central Valley Project, there was no substantial change in the concentration of carbamazepine by Check 13, even when paired data (from the same sample event) were examined. However, there was a substantial drop in the interquartile range (25th to 75th percentile) of concentrations for this PPCP by Check 41. During this time period, deliveries of SPW were highly curtailed and a substantial amount of groundwater in the Central Valley was pumped into the California Aqueduct, which most likely diluted the concentration of carbamazepine. At Devil Canyon, there was no substantial change in the level of carbamazepine compared to Check 41. Although there was a considerable detention time in the Pyramid/Castaic Lake system, there was no substantial change in the interquartile range of concentrations of carbamazepine at Foothill PCS. Similar trends were observed for primidone, another conservative wastewater tracer (median concentrations at Hood, Holt, Banks, Check 13, Check 41, Devil Canyon, and Foothill PCS were 6, 12, 5, 4, 3, 3, and <2 ng/L, respectively).

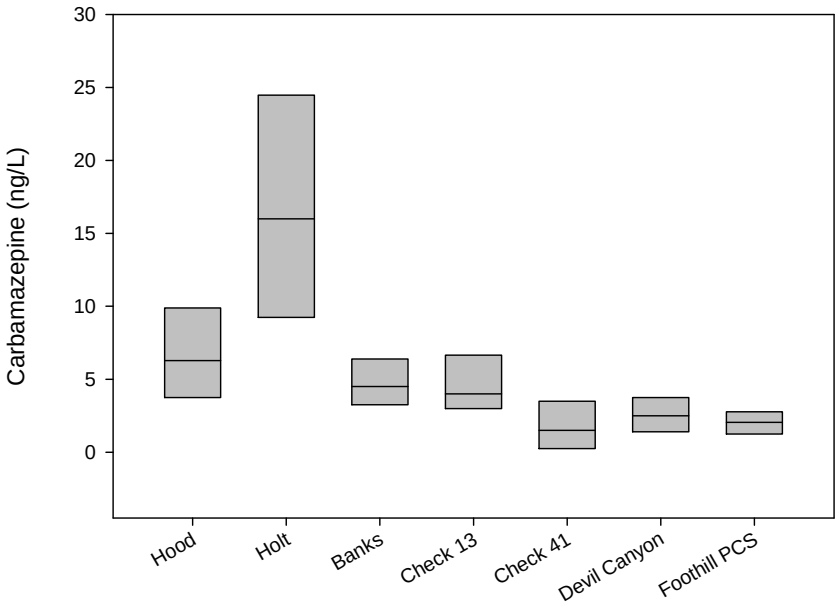

Figure 19. Occurrence of carbamazepine in the SPW system.

Figure 20 summarizes the occurrence of gemfibrozil in the SPW system. Presuming that the Sacramento River provided a substantial portion of the water pumped out of the Delta at Banks, these results suggest an appreciable attenuation of gemfibrozil in the Delta. Although this PPCP was always detected at Check 13 above its MRL of 5 ng/L (7–24 ng/L), it was not detected three out of four times at Check 41 and at Foothill PCS or at all at Devil Canyon. The absence of gemfibrozil at downstream sites probably reflects a combination of dilution by pump in groundwater to below its MRL and degradation in the SPW system.

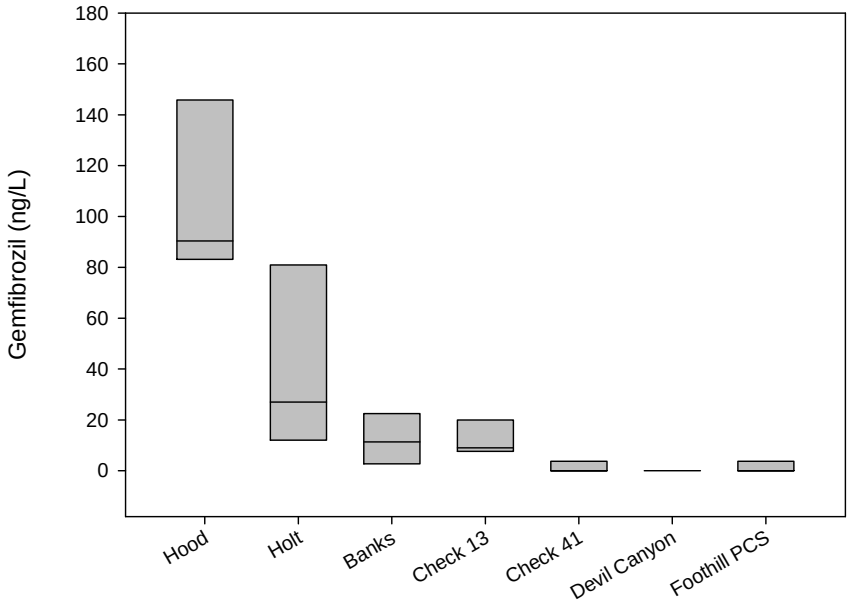

Figure 20. Occurrence of gemfibrozil in the SPW system.

Figure 21 summarizes the occurrence of sulfamethoxazole in the SPW system. Because this PPCP was detected throughout the SPW system, it was easier to follow its fate and transport. In some sample events (e.g., April 2008), its concentration was relatively unchanged from Check 13 to Southern California (11–15 ng/L). Alternatively, in other sample events (e.g., January 2009), its concentration was substantially lower at Check 41 and at the Southern California reservoirs (5-9 ng/L) than at Check 13 (29 ng/L). Likewise, carbamazepine and primidone were highly attenuated during the latter sample event. Because of the pump-in programs, interpretation of these data is not straight forward. Nonetheless, the levels of certain PPCPs detected downstream of the two major WWTPs in the Delta were attenuated in the SPW system, most likely due to a combination of dilution with other sources of waters and some natural degradation processes. However, detectable levels of some PPCPs were found at terminal reservoirs in Southern California.

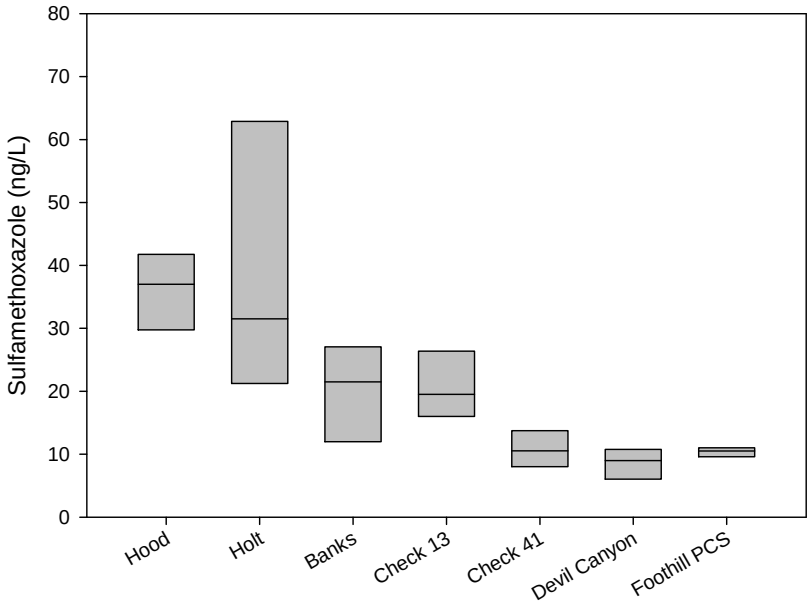

Figure 21. Occurrence of sulfamethoxazole in the SPW system.

6.2 CRW

Treated wastewater from the Las Vegas area WWTPs flowed into Lake Mead via the Las Vegas Wash. Typically, most of the water in the wash was from the WWTP discharges. Annual inflow via the wash was ~1.5% of the total inflow to Lake Mead (LaBounty and Burns, 2007). For the four sample events, the amount of carbamazepine or primidone detected at Hoover Dam was 1.0-2.1 (average = 1.7) and 0.7-2.5 (average = 1.9) %, respectively, of the levels detected in the Las Vegas Wash. These results confirm that these two anti-convulsants were conservative tracers of wastewater impact in Lake Mead. Moreover, the levels of carbamazepine (25th percentile, median, and 75th percentile = 2, 3, and 3 ng/L, respectively) and primidone (25th percentile, median, and 75th percentile = 2, 3, and 3 ng/L, respective) were unchanged throughout the CRW system (Figure 22). Furthermore, the amounts detected at Lake Mathews in Southern California (<1 to 2 ng/L of carbamazepine and <2 to 3 ng/L of primidone) were consistent with historical levels in this reservoir (e.g., in 2007, 1-2 ng/L of carbamazepine and <1-2 ng/L of primidone) (Dale, 2008).

For the four sample events, the amount of sulfamethoxazole detected at Hoover Dam was 1.5-2.9 (average = 2.1) % of the levels detected in the Las Vegas Wash. This percentage was consistent with those of carbamazepine and primidone. Alternatively, sulfamethoxazole appeared to degrade somewhat through the Nevada/Arizona portion of the CRW system (from 11-17 [median of 14] to 7-13 [median of 8] ng/L), and was substantially degraded through the California portion of the system (Figure 23). The amounts detected at Lake Havasu (7-13 ng/L) and Lake Mathews (<1-1 ng/L) were consistent with historical levels in this reservoir (e.g., in 2007, 4-12 and 1-4 ng/L, respectively) (Dale, 2008).

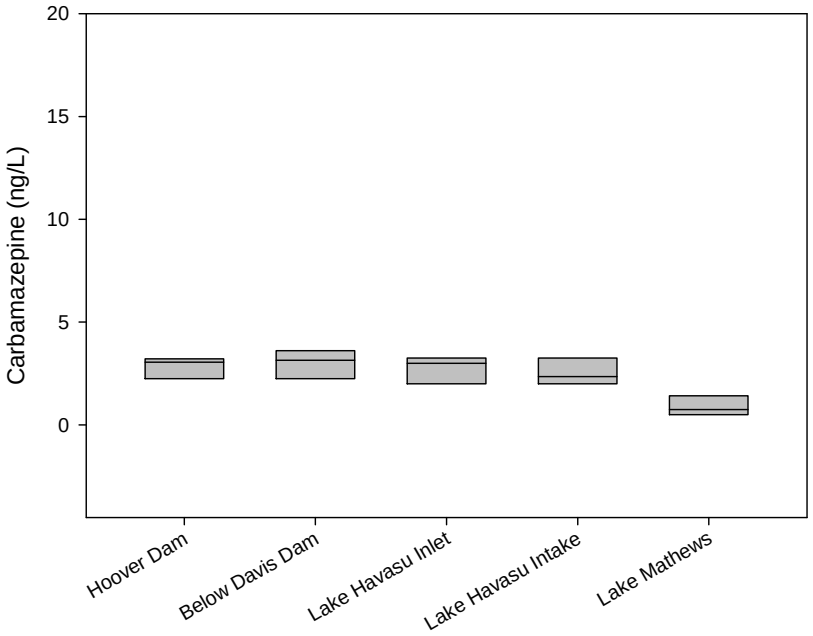

Figure 22. Occurrence of carbamazepine in the CRW system.

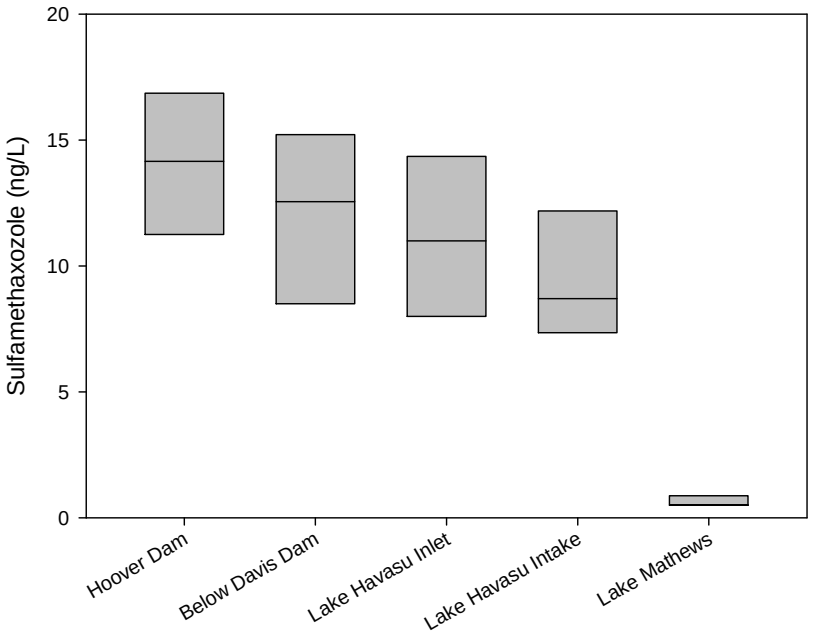

Figure 23. Occurrence of sulfamethoxazole in the CRW system.

The fate and transport of other PPCPs could not be tracked because of sensitivity issues. For example, the concentration of dilantin in the Las Vegas Wash was 102-137 ng/L, which after attenuation (due to dilution) in Lake Mead (assuming a 1.5% dilution factor, which was the historical percentage of inflow to Lake Mead attributed to the Las Vegas Wash) would have resulted in an amount (2 ng/L) that was less than its MRL (5 ng/L). Many other PPCPs were detected at much lower levels in the wash.

An unusual occurrence pattern was observed for DEET in the CRW system (Figure 24). The concentration of DEET in the Las Vegas Wash was 82-113 ng/L, which after attenuation (due to dilution) in Lake Mead would have resulted in an amount (1-2 ng/L) that was less than its MRL (20 ng/L), which is consistent with it not being detected at Hoover Dam. However, relatively high amounts (10-297 ng/L) were detected at Lake Havasu inlet. As DEET is a commonly used insect repellant, and there are body contact activities in this portion of the CRW system, there are other sources for this PPCP besides WWTP discharges. Nonetheless, DEET was highly attenuated in Lake Havasu.

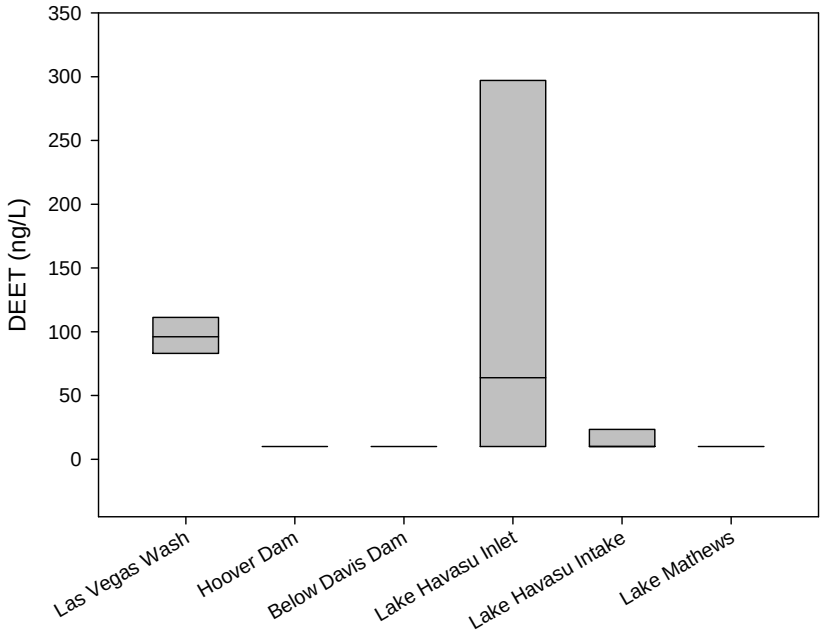

Figure 24. Occurrence of DEET in the CRW system.

Likewise, an unusual occurrence pattern was observed for caffeine (16-39 ng/L in the Las Vegas Wash, <5-28 ng/L at Hoover Dam, <5-5 ng/L below Davis Dam, <5-1,370 ng/L at Lake Havasu inlet, <5-338 ng/L at Lake Havasu intake, and <5 ng/L at Lake Matthews). This has been noted for caffeine in other watersheds (Guo and Krasner, 2009). Clearly, there are ubiquitous sources for this PPCP, which can undergo biodegradation in the environment. Thus, it is difficult to follow its fate and transport. Nonetheless, its occurrence in this study is somewhat similar to historical data (e.g., in 2007, 5-18 ng/L at Lake Havusu intake and 3-7 ng/L at Lake Matthews) (Dale, 2008), in that the amounts transported to Southern California tended to substantially diminish.

6.3 SAR

Because primidone was used successfully as a conservative tracer of wastewater impact in the effluent-dominated South Platte River (Krasner et al., 2008), it was evaluated in the SAR watershed. Figure 25 shows locations in the SAR watershed that were used to study the attenuation of PPCPs. Table 50 shows flows and primidone concentrations in the SAR watershed for November 5, 2008. The flows listed were daily mean flows or, in some cases, the flows close in time to the sampling, whereas some of the data were from November 12, 2008. Nonetheless, this information can be used to understand the fate and transport of primidone in this watershed.

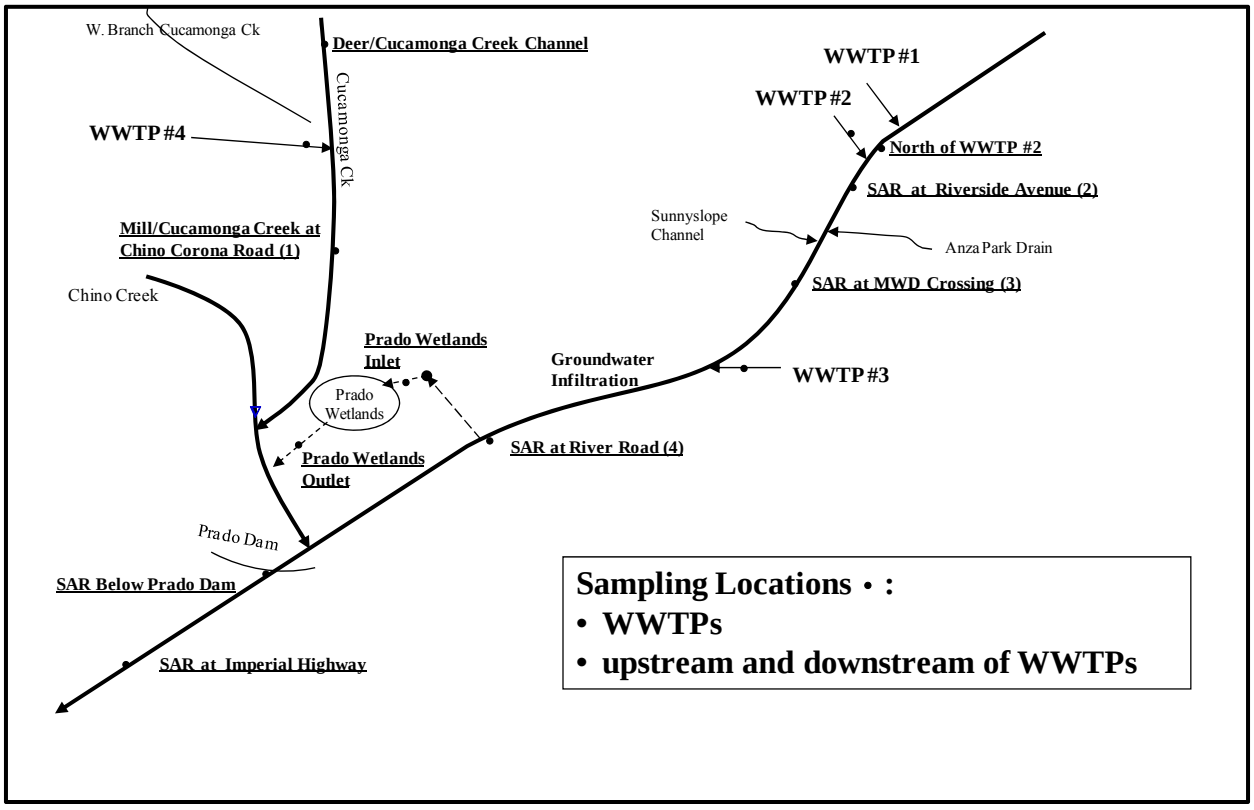

Figure 25. Locations in the SAR watershed that were used to study the attenuation of PPCPs.

Table 50. Flows and Primidone Concentrations in the SAR Watershed for the November 5, 2008, Sample Event

Sampling Location	Flow (cfs)[#]	Primidone (ng/L)
Upstream of WWTP #1	1.6	---
Effluent of WWTP #1	7.9	---
North of WWTP #2	---	158
Effluent of WWTP #2	58.9	88
SAR at Riverside Avenue	---	95
SAR at MWD Crossing	66	55
Effluent of WWTP #3	53.6	156
SAR at Etiwanda (downstream of WWTP #3)	108.1	---
SAR at River Road	76.9	89
Deer/Cucamonga Creek channel	---	2
W. Branch Cucamonga Ck	4.6	--
Effluent of WWTP #4	30.8	148
Mill/Cucamonga Creek at Chino Corona Road	34	146
Prado Wetlands inlet	---	114
Prado Wetlands outlet	---	103
SAR below Prado Dam	175	103
SAR at Imperial Highway	177	68

[#]Daily mean flows or, in some cases, the flows closest in time to the sampling; some of the data from November 12, 2008

Table 51 shows the attenuation of primidone in the SAR watershed (upstream of the wetlands) during the November 5, 2008, sample event. Because primidone is known to be stable in the environment, its attenuation should be from dilution with non-wastewater-impacted water. In this analysis, flow-weighted primidone concentrations (C) were determined as follows:

$$C = (C_1F_1 + C_2F_2) / (F_1 + F_2)$$

where C_i = primidone concentration at location i

and F_i = flow at location i

Although primidone was measured in the SAR at the location north of WWTP #2, the flow at this site was not. Thus, it was assumed to be equal to the flow in the SAR upstream of WWTP #1 (1.6 cfs) plus the discharge rate from WWTP #1 (7.9 cfs). This calculated flow (9.5 cfs) was added to the discharge rate from WWTP #2 (58.9 cfs) to estimate the flow in the SAR downstream of WWTP #2 (68.4 cfs). Then the equation above was used to determine a flow-weighted primidone concentration downstream of WWTP #2 (97.9 ng/L). This primidone value was then compared to the concentration detected at the next downstream site (i.e., SAR at Riverside Avenue: 95 ng/L), which suggests a 4% attenuation. In reality, there was no attenuation in the level of primidone up to this point within the coefficient of variation (CV) of the results.

Table 51. Attenuation of Primidone in the SAR Watershed (Upstream of the Wetlands) During the November 5, 2008, Sample Event

Sampling Location	Primidone (ng/L)	Flow (cfs)*	Flow-Weighted Primidone (ng/L)	Attenuation
Upstream of WWTP #1	---	1.6		
Effluent of WWTP #1	---	7.9		
North of WWTP #2	158	*9.5*		
Effluent of WWTP #2	88	58.9		
Downstream of WWTP #2	---	*68.4*	97.9	
SAR at Riverside Avenue	95	---		4%
SAR at MWD Crossing	55	66		43%
Effluent of WWTP #3	156	53.6		
Downstream of WWTP #3	---	*119.6*	100.2	
SAR at Etiwanda	---	108.1		
SAR at River Road	89	76.9		11%
Deer/Cucamonga Creek channel	2	*0*		
W. Branch Cucamonga Ck	---	4.6		
Effluent of WWTP #4	148	30.8		
Downstream of WWTP #4	---	*35.4*	128.8	
Mill/Cucamonga Creek at Chino Corona Road	146	34		-13%

*Flow in italics is calculated value.

However, at the SAR at MWD Crossing, there was no change in river flow (66 cfs), yet there was a substantial reduction in the concentration of primidone (55 ng/L), which suggests a 43% attenuation. As there is no known mechanism for the attenuation of primidone in a water body other than dilution, this would suggest something else was occurring at this site. One possibility is that the river was "losing" water (and primidone) to an aquifer adjacent to the river and was "gaining" water (without primidone) from groundwater along another stretch of the river, with no net change in river flow, yet a change in the concentration of primidone. After SAR at MWD Crossing, there was another input of primidone from WWTP #3, which appeared to only be attenuated by 11% by SAR at River Road, which is again within the CV of the method. A similar examination of the Cucamonga Creek suggested a -13% attenuation of primidone, which is within the analytical variability.

Table 52 summarizes the attenuation of primidone in the SAR watershed (upstream of the wetlands) during the four sample events. Most of the values (-13 to 13%) were within the CV of the method, whereas all of the values (37-55%) at SAR at MWD Crossing were consistently high. This suggests that something was happening in this region of the watershed, so the hypothesis of a losing and gaining stream should be more fully explored. Also, there was one anomalously high value (55%) in the Cucamonga Creek.

Figure 26 compares the attenuation of primidone and carbamazepine in the SAR watershed (upstream of the wetlands) during the study. Similar to primidone, carbamazepine is also stable in the environment and its attenuation is attributed to dilution with non-wastewater-impacted

water (Guo and Krasner, 2009). There was a good correlation ($R^2 = 0.74$) with a slope close to 1 (0.87). Moreover, most of the attenuations of these two anticonvulsants were within ±20%, whereas both were highly and similarly attenuated at SAR at MWD Crossing.

Table 52. Attenuation of Primidone in the SAR Watershed (Upstream of the Wetlands) During the Four Sample Events

Sampling Location	Attenuation
SAR at Riverside Avenue	1 to 13%
SAR at MWD Crossing	37 to 55%
SAR at River Road	1 to 12%
Mill/Cucamonga Creek at Chino Corona Road	-13 to -2% and 55% (1 quarter was atypical)

Thus, the attenuation of each PPCP was evaluated relative to that of primidone:

$$= 1 - ([PPCP_2 / PPCP_1] \times [primidone_1 / primidone_2])$$

where $PPCP_i$ = PPCP concentration at location i
and $primidone_i$ = primidone concentration at location i

Figure 27 shows relative attenuations for carbamazepine (CBZ), gemfibrozil, sulfamethoxazole (SMX), and TCEP at one site in the Cucamonga Creek and three locations in the SAR during the August 19, 2008, sample event. For example, the attenuation of primidone at SAR at Riverside Avenue and at MWD Crossing was 1 and 53%, respectively. Likewise, the absolute attenuation of carbamazepine at these two locations was similar (-2 and 60%, respectively). Thus, relative to primidone, the attenuation of carbamazepine at these two sites was -3 and 16%, respectively. The absolute attenuation of gemfibrozil at SAR at Riverside Avenue was similar (-13%), whereas there was substantially more attenuation of this PPCP at SAR at MWD Crossing (79%). Thus, relative to primidone, the attenuation of gemfibrozil at these two sites was -14 and 55%, respectively. In this sample event, gemfibrozil and sulfamethoxazole were attenuated at some of the downstream SAR sites relative to that of primidone, which suggests that they degraded to some extent in this reach of the river.

Figures 28-31 summarize the attenuation of these selected PPCPs relative to primidone during the four sampling events. The attenuation of gemfibrozil and sulfamethoxazole is consistent with the literature (Fono et al., 2006; Boxal, 2008; Radke et al., 2009), in which photolysis and biodegradation or biodegradation and sorption were the loss mechanisms, respectively. The attenuation of TCEP at SAR at MWD Crossing is somewhat anomalous, as TCEP is expected to be persistent in the environment.

For gemfibrozil and sulfamethoxazole, there is an added layer of complexity in studying their fate and transport. In addition to undergoing loss mechanisms in the receiving waters, they can react with free chlorine at the WWTPs. Figure 32 shows that a high level (502 ng/L) of sulfamethoxazole was present at WWTP #2, which used UV disinfection, whereas low levels (15-21 ng/L) were present at WWTPs #3 and 4, which used chlorine. Thus, SAR at River Road received water from two WWTPs with very different levels of sulfamethoxazole, which also underwent degradation in the water body. However, during two sample events, WWTP #3 had high levels of sulfamethoxazole (and gemfibrozil) due to plant upsets.

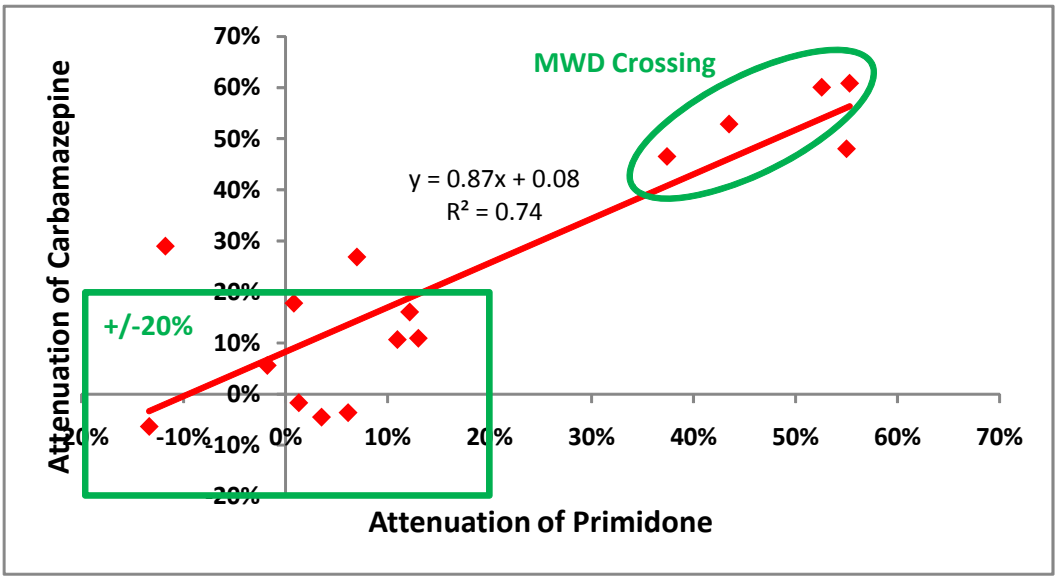

Figure 26. Attenuation of primidone and carbamazepine in the SAR watershed (upstream of the wetlands) during the four sample events.

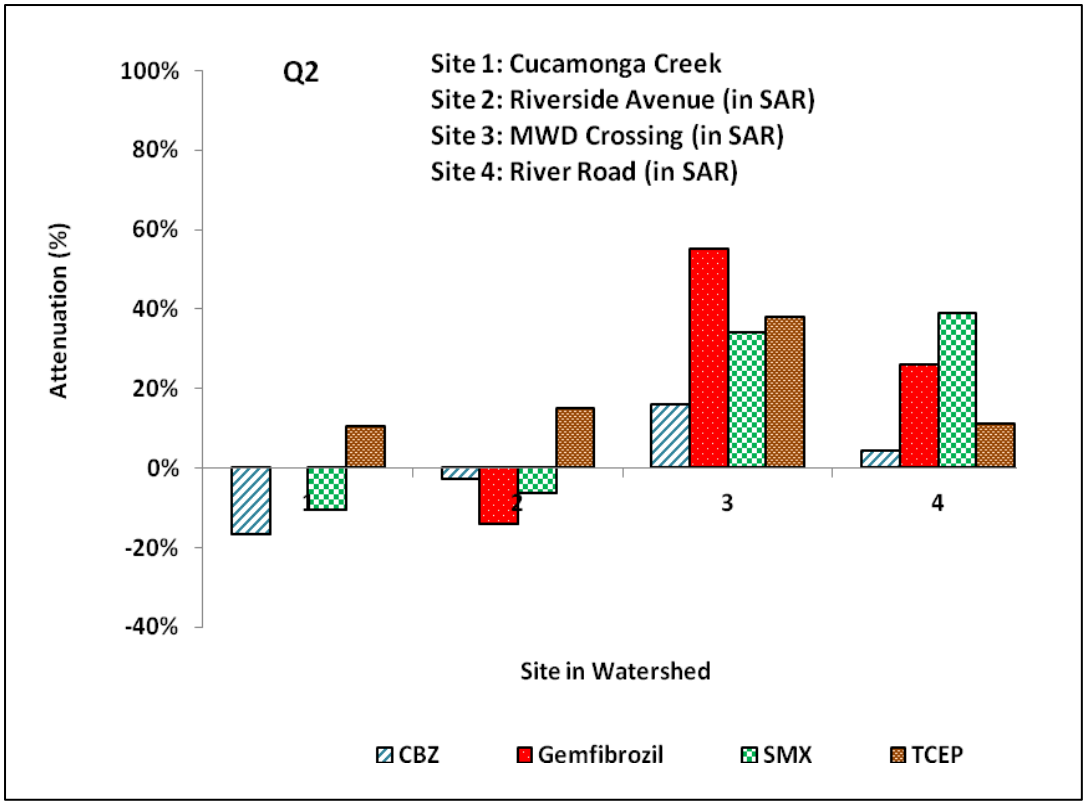

Figure 27. Attenuation of selected PPCPs relative to primidone during August 19, 2008, sample event (1 = Mill/Cucamonga Creek at Chino Corona Road, 2 = SAR at Riverside Avenue, 3 = SAR at MWD Crossing, 4 = SAR at River Road).

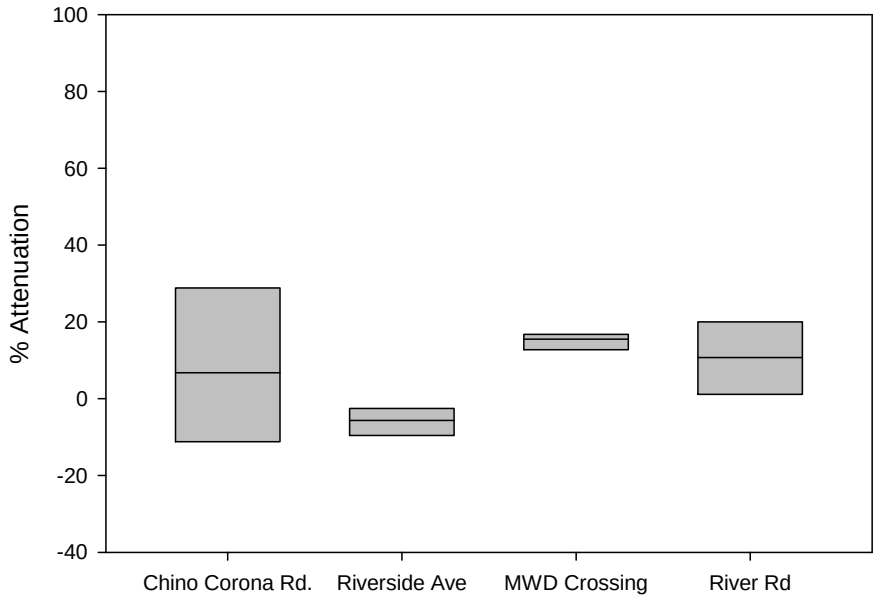

Figure 28. Attenuation of carbamazepine relative to primidone during the four sampling events.

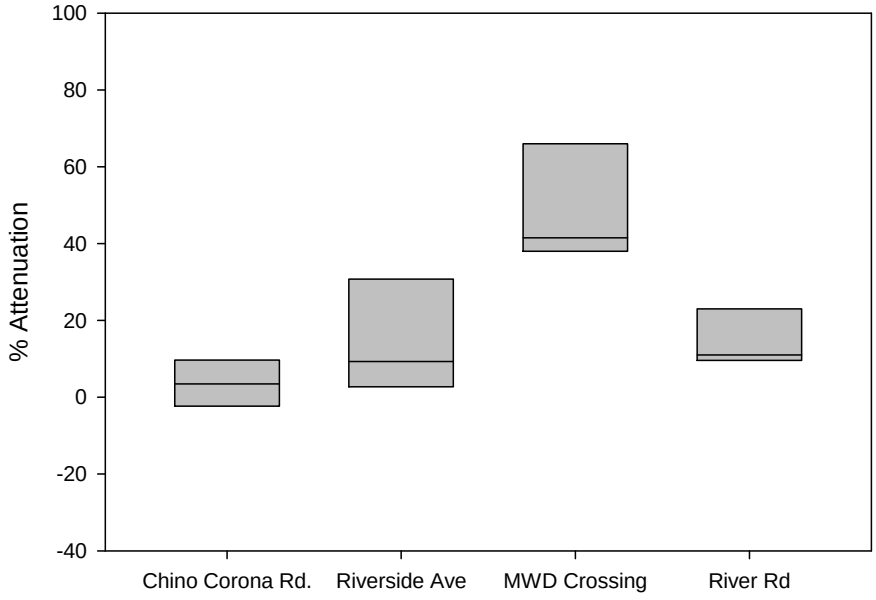

Figure 29. Attenuation of TCEP relative to primidone during the four sampling events.

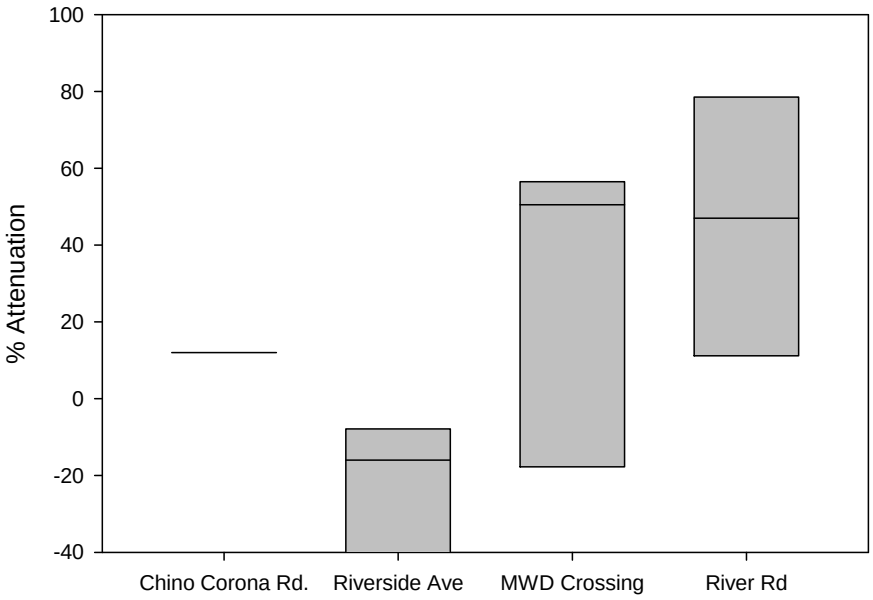

Figure 30. Attenuation of gemfibrozil relative to primidone during the four sampling events.

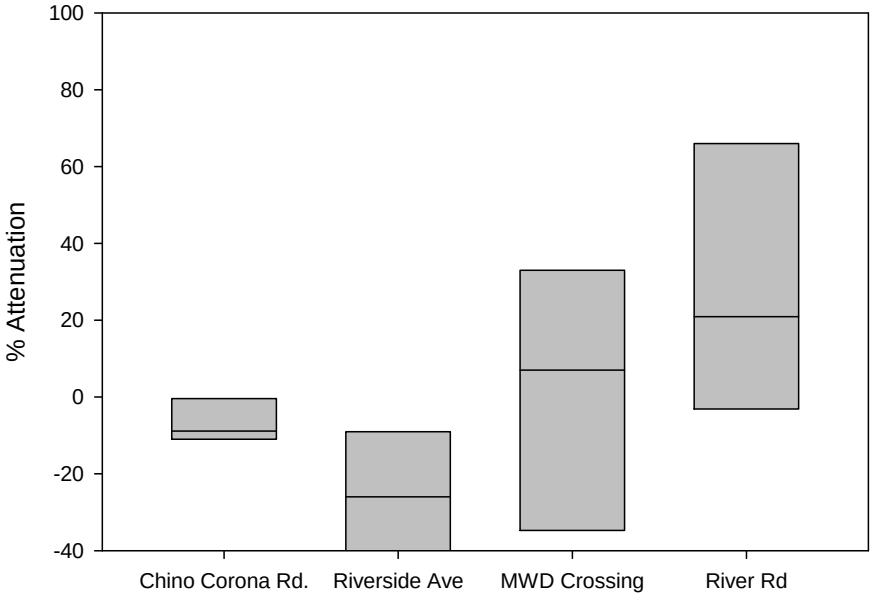

Figure 31. Attenuation of sulfamethoxazole relative to primidone during the four sampling events.

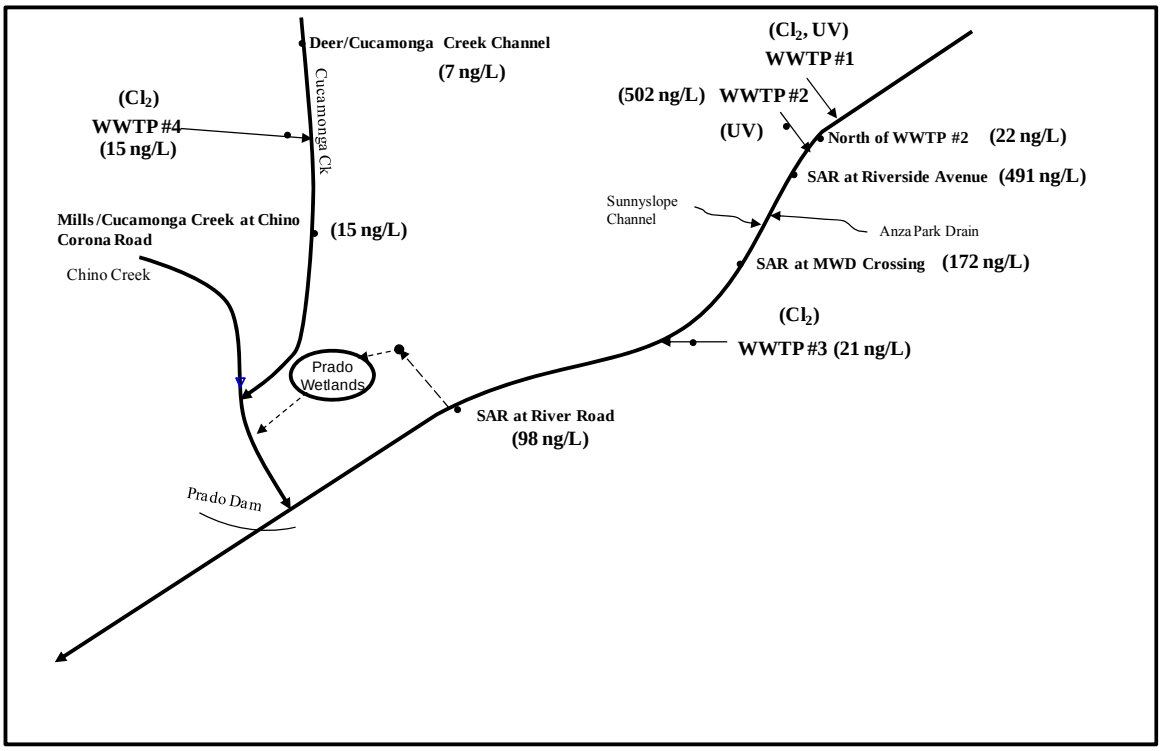

Figure 32. Fate and transport of sulfamethoxazole in SAR watershed (upstream of wetlands) during the November 5, 2008, sample event.

6.3.1 Impact of the Prado Wetlands

A portion of the SAR flow was diverted through the Prado Wetlands, which was constructed to remove nitrate from the water. The detention time through the wetlands at the current outlet sampling location was approximately two days. The outlet sampling location is approximately two-thirds through the wetlands. The final outlet location was inaccessible due to flooding. Table 53 shows the temperature and nitrate levels at the wetlands on the days of sampling or on dates close in time. For the dates shown, the highest removal of nitrate occurred in June 2008 and the lowest was in January 2009. Some of the differences in nitrate removal were due to variations in temperature.

Figure 33 shows the attenuation of selected PPCPs through the Prado Wetlands. There was no substantial attenuation of primidone (-8 to 27%, median of 5%). Figure 34 shows the attenuation of other possible conservative PPCPs compared to that of primidone. In addition to carbamazepine, dilantin, atrazine, and an atrazine degradation product did not (in general) undergo substantial attenuation through the wetlands (median values of 8, 21, 16, and 12%, respectively). Alternatively, other PPCPs underwent varying levels of attenuation through the wetlands (Figure 33). For example, azithromycin was completely attenuated (levels in the wetlands influent were 23-600 ng/L). Many other PPCPs (e.g., caffeine, gemfibrozil, ibuprofen, SMX, acetaminophen) were highly attenuated (42-100%) in two or three of the sample events, whereas there was often little or no attenuation in the May 2008 sample event. In May 2008, the conditions in the wetlands were not representative of normal operating conditions, as the

wetlands had just been returned to service after reconstruction from a flooding event. In comparison, the attenuation through the wetlands of DEET and TCEP was low (median values of 24 and 33%, respectively). Attenuation mechanisms of potential importance in wetlands include biotransformation, photolysis, and hydrolysis (Sedlak and Pinkston, 2001).

Table 53. Temperature and Nitrate Levels at the Prado Wetlands During (or Near) the Four Sample Events

	Temperature (ºC)		Nitrate (mg/L as N)	
Date	**Wetlands In**	**Wetlands Out**	**Wetlands In**	**Wetlands Out**
5/22/08*	22.5	21.7	---	---
6/10/08	23.8	23.6	1.66	<0.1
8/12/08	23	25	5.48	2.97
8/19/08*	21.8	24.3	4.69	2.95
11/5/08*	19.6	16.8	---	---
11/12/08	17	14.5	5.93	1.38
1/6/09	12	10.7	7.19	5.42
2/25/09*	19.3	14	---	---

*Days of sampling are asterisked.

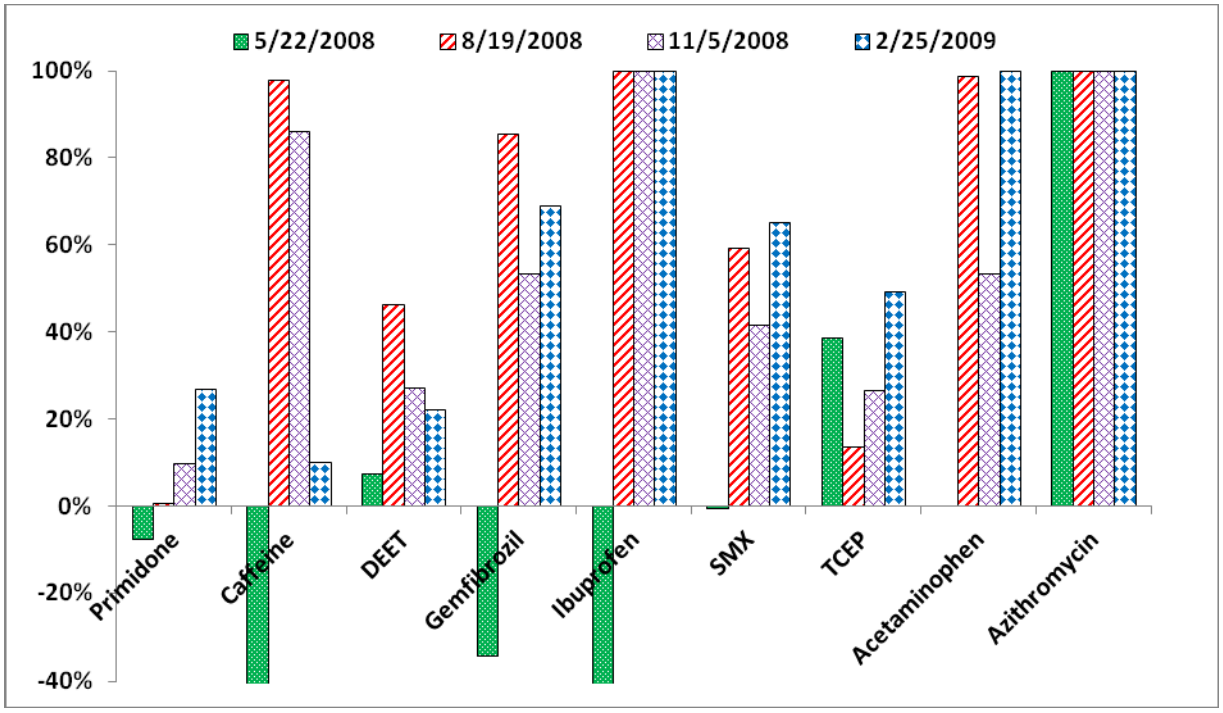

Figure 33. Attenuation of selected PPCPs through the Prado Wetlands.

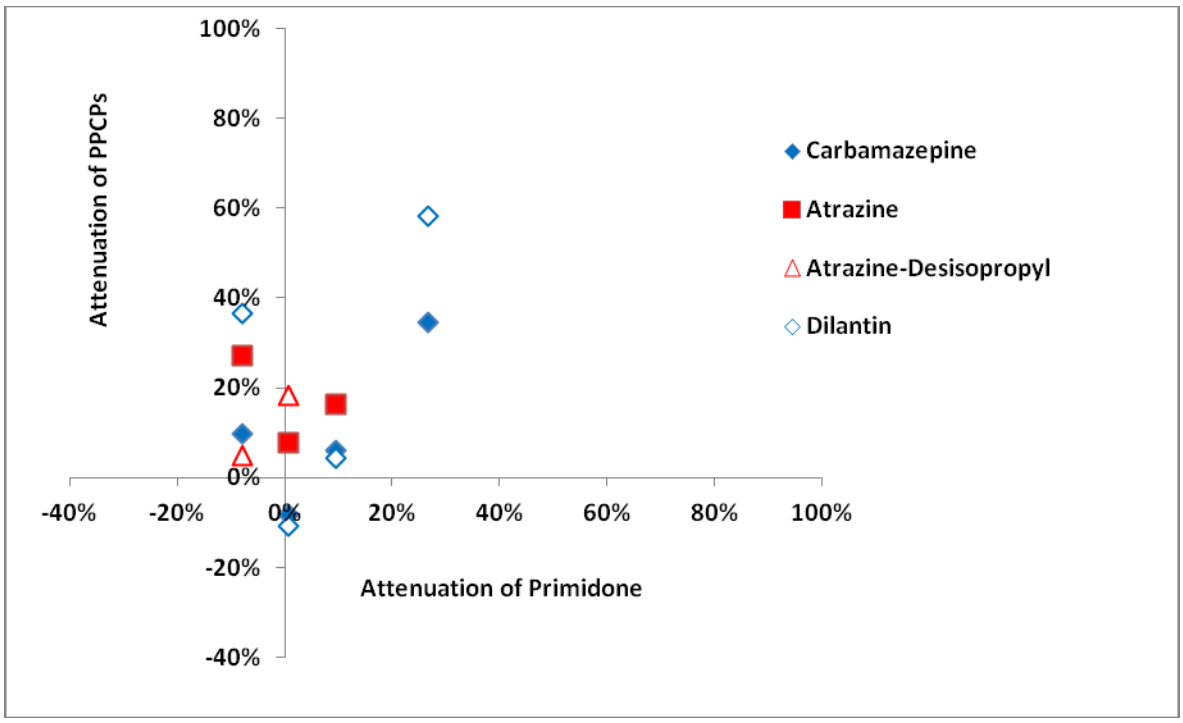

Figure 34. Conservative PPCPs through the Prado Wetlands.

6.3.2 Impact of Treated Wastewater Effluent

Depending on the flow of a river and the discharge rates of WWTPs in that watershed, the amount of river water that originated from treated wastewater effluent can be calculated. The presence of a conservative wastewater tracer, such as primidone, can also be used to characterize a water body as effluent-dominated (>50% treated wastewater effluent), effluent-impacted (10-50% treated wastewater effluent), and low impact (<10% treated wastewater effluent) (Krasner et al., 2006). Note, in this context, % treated wastewater effluent refers to the volume of river water that originated from WWTP discharges and not the mass of dissolved organic carbon (DOC) from the treated wastewater effluent (likewise, in other research, Nam and colleagues [2007] evaluated different mixtures of treated wastewater effluent and river water and referred to each blend on a volume-per-volume (v/v) basis).

Table 54 shows the % treated wastewater effluent at the SAR below Prado Dam and at Imperial Highway based on primidone concentrations. First, a flow-weighted primidone value was determined for the four WWTPs that were sampled in this study. For example, on May 22, 2008, the flows of WWTPs #1, 2, 3, and 4 were 9.8, 59.5, 48.3, and 21.8 cfs, respectively, and the primidone levels in their discharges were 157, 100, 167, and 148 ng/L, respectively, where the flow-weighted primidone level was 135 ng/L. Note that the effluent of WWTP #1 was not directly measured, rather the SAR was sampled upstream of WWTP #2, which represented the effluent of WWTP #1 plus water from upstream of WWTP #1. When there was flow in the SAR upstream of WWTP #1, the amount of primidone in the effluent of WWTP #1 had to be calculated based on any dilution from upstream water. Also note that the amount of primidone was based on only four of the WWTPs in this watershed. However, three of the WWTPs studied

represented the largest dischargers in the watershed, and primidone values were found to be relatively comparable between the different WWTPs in the study. Then the amount of primidone detected at the SAR below Prado Dam or at Imperial Highway was compared to the flow-weighted amount from the WWTPs. These results suggest that the SAR at below Prado Dam was effluent-dominated (78-82% treated wastewater effluent) in three of the four sample events and was effluent-impacted (37% treated wastewater effluent) in February 2009, when there was a major storm event. The results at the SAR at Imperial Highway suggest that it was effluent-dominated (52-70% treated wastewater effluent) in two of the sample events and was effluent-impacted (33-48% treated wastewater effluent) in the other two.

Table 54. Percent Treated Wastewater Effluent (v/v basis) in the SAR below Prado Dam and at Imperial Highway Based on Primidone Data

Parameter	Sampling Event			
	5/22/2008	8/19/2008	11/5/2008	2/25/2009
WWTP flow-weighted primidone (ng/L)	135	123	130	124
Primidone at Below Prado Dam (ng/L)	111	97	103	46
Primidone at Imperial Highway (ng/L)	65	87	68	41
% Treated wastewater effluent at Below Prado Dam	82%	78%	79%	37%
% Treated wastewater effluent at Imperial Highway	48%	70%	52%	33%

Likewise, the percent of treated wastewater effluent in the SAR was determined based on carbamazepine data (Table 55). These results suggest that the SAR at below Prado Dam was effluent-dominated (50-55% treated wastewater effluent) in two sample events and was effluent-impacted (20-47% treated wastewater effluent) in the other two. The results at the SAR at Imperial Highway suggest that it was effluent-dominated (51% treated wastewater effluent) in one sample event and was effluent-impacted (21-45% treated wastewater effluent) in the other two. Figure 35 shows a comparison of the percent treated wastewater effluent based on these two wastewater tracers. Although the primidone data suggested that the SAR was somewhat more effluent-dominated, the trend was consistent.

Table 55. Percent Treated Wastewater Effluent (v/v basis) in the SAR below Prado Dam and at Imperial Highway Based on Carbamazepine Data

Parameter	Sampling Event			
	5/22/2008	8/19/2008	11/5/2008	2/25/2009
WWTP flow-weighted carbamazepine (ng/L)	294	200	226	251
Carbamazepine at Below Prado Dam (ng/L)	146	110	107	49
Carbamazepine at Imperial Highway (ng/L)	120	103	101	52
% Treated wastewater effluent at Below Prado Dam	50%	55%	47%	20%
% Treated wastewater effluent at Imperial Highway	41%	51%	45%	21%

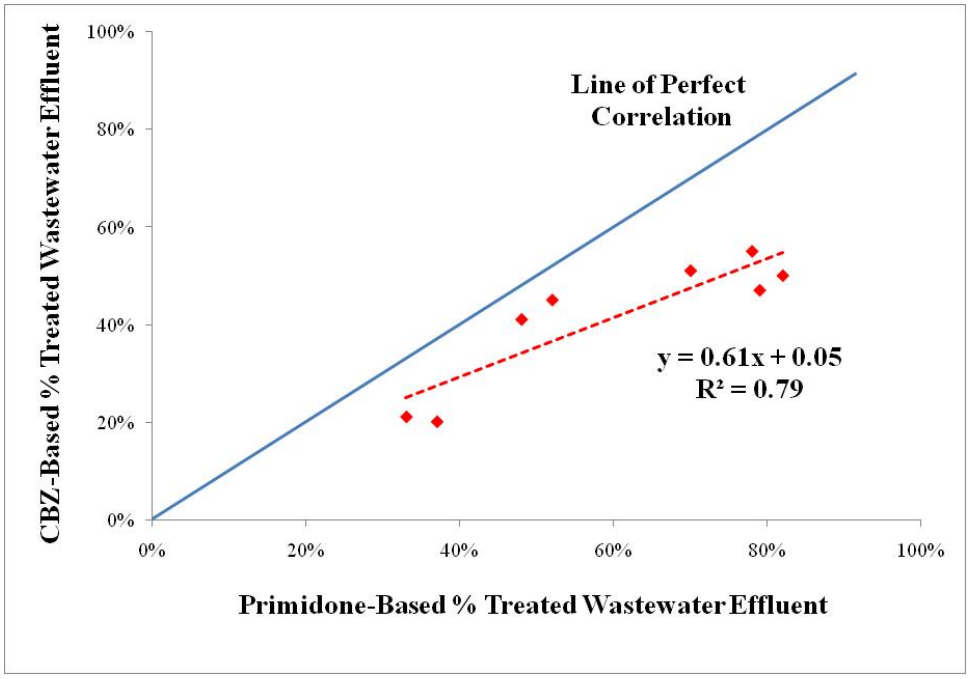

Figure 35. Percent treated wastewater effluent (v/v basis) in the SAR below Prado Dam and at Imperial Highway based on two wastewater tracers. CBZ=carbamazepine.

Figure 36 shows the fate and transport of gemfibrozil in the SAR watershed during the February 2009 sample event. High levels of this PPCP (368-1,178 ng/L) were in the effluents of WWTPs #2 and 3, whereas a low level (5 ng/L) was present at WWTP #4 due to the use of chlorine under normal operationing conditions, which can react with this PPCP. Gemfibrozil was attenuated downstream of WWTP #3 by the SAR at River Road (Figures 30 and 36). In addition, it was attenuated through the wetlands (Figures 33 and 36). Moreover, it was further attenuated by the SAR below Prado Dam (Figure 36). Table 56 summarizes the percent attenuation of gemfibrozil in the SAR below Prado Dam and at Imperial Highway. In this instance, the flow-weighted amount of gemfibrozil considered that some WWTPs had high levels in their discharges and others had low levels (which varied seasonally). In each of the four sample events, the attenuation (relative to the WWTP loading into the river) was high (84-99%). Thus, this PPCP was attenuated at some WWTPs due to the use of chlorine and was attenuated in the river system.

Table 57 shows the attenuation of sulfamethoxazole. Likewise, it was highly attenuated (64-94%) by the SAR below Prado Dam and at Imperial Highway. Although the SAR below Prado Dam and at Imperial Highway was effluent-dominated or highly effluent-impacted, the levels of some PPCPs were highest attenuated by those sample locations.

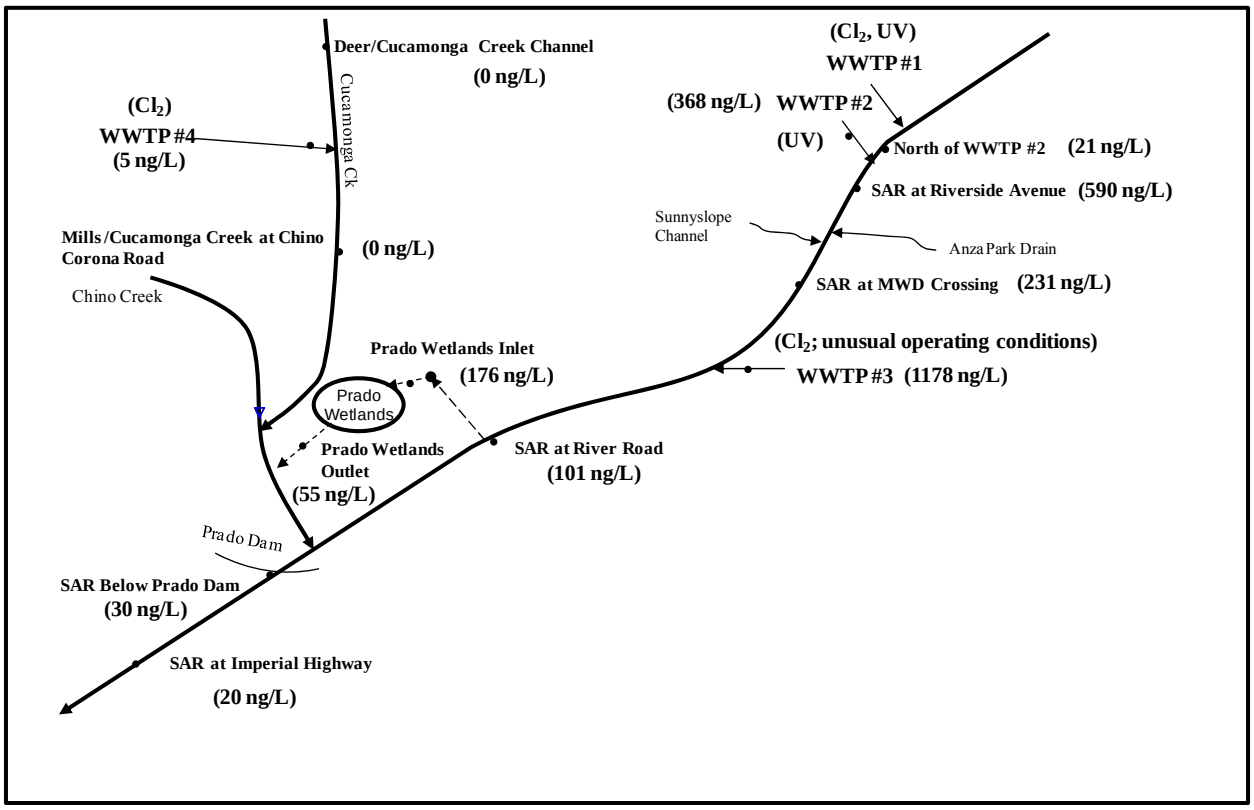

Figure 36. Fate and transport of gemfibrozil in the SAR watershed during the February 25, 2009, sample event.

Figure 11 showed the occurrence of the 10 most frequently detected PPCPs in the SAR watershed and their occurrence in the WWTPs that discharged into this watershed. Figure 37 shows the occurrence of these PPCPs in the SAR at Imperial Highway and compares their levels to that of the WWTP discharges. As discussed above, primidone and carbamazepine are conservative tracers and are attenuated by dilution with freshwater. In addition, dilantin and atrazine appeared to be relatively recalcitrant in this system. Alternatively, sulfamethoxazole and gemfibrozil were highly attenuated. In contrast, caffeine and diuron were present at higher concentrations in the SAR River at Imperial Highway than in the WWTP discharges. Caffeine is a ubiquitous contaminant in the environment (Buerge et al., 2003) and diuron is a commonly used herbicide in California, so their sources are not limited to WWTP discharges. This figure demonstrates that there are a range of attenuation factors for PPCPs in the environment.

Table 56. Percent Attenuation of Gemfibrozil in the SAR below Prado Dam and at Imperial Highway

Parameter	Sampling Event			
	5/22/2008	8/19/2008	11/5/2008	2/25/2009
WWTP flow-weighted gemfibrozil (ng/L)	250	474	146	543
Gemfibrozil at Below Prado Dam (ng/L)	11	11	24	30
Gemfibrozil at Imperial Highway (ng/L)	14	7	23	20
% Attenuation at Below Prado Dam	95%	98%	84%	94%
% Attenuation at Imperial Highway	94%	99%	84%	96%

Table 57. Percent Attenuation of Sulfamethoxazole in the SAR below Prado Dam and at Imperial Highway

Parameter	Sampling Event			
	5/22/2008	8/19/2008	11/5/2008	2/25/2009
WWTP flow-weighted sulfamethoxazole (ng/L)	145	585	207	648
Sulfamethoxazole at Below Prado Dam (ng/L)	53	91	53	51
Sulfamethoxazole at Imperial Highway (ng/L)	48	84	56	41
% Attenuation at Below Prado Dam	64%	85%	74%	92%
% Attenuation at Imperial Highway	67%	86%	73%	94%

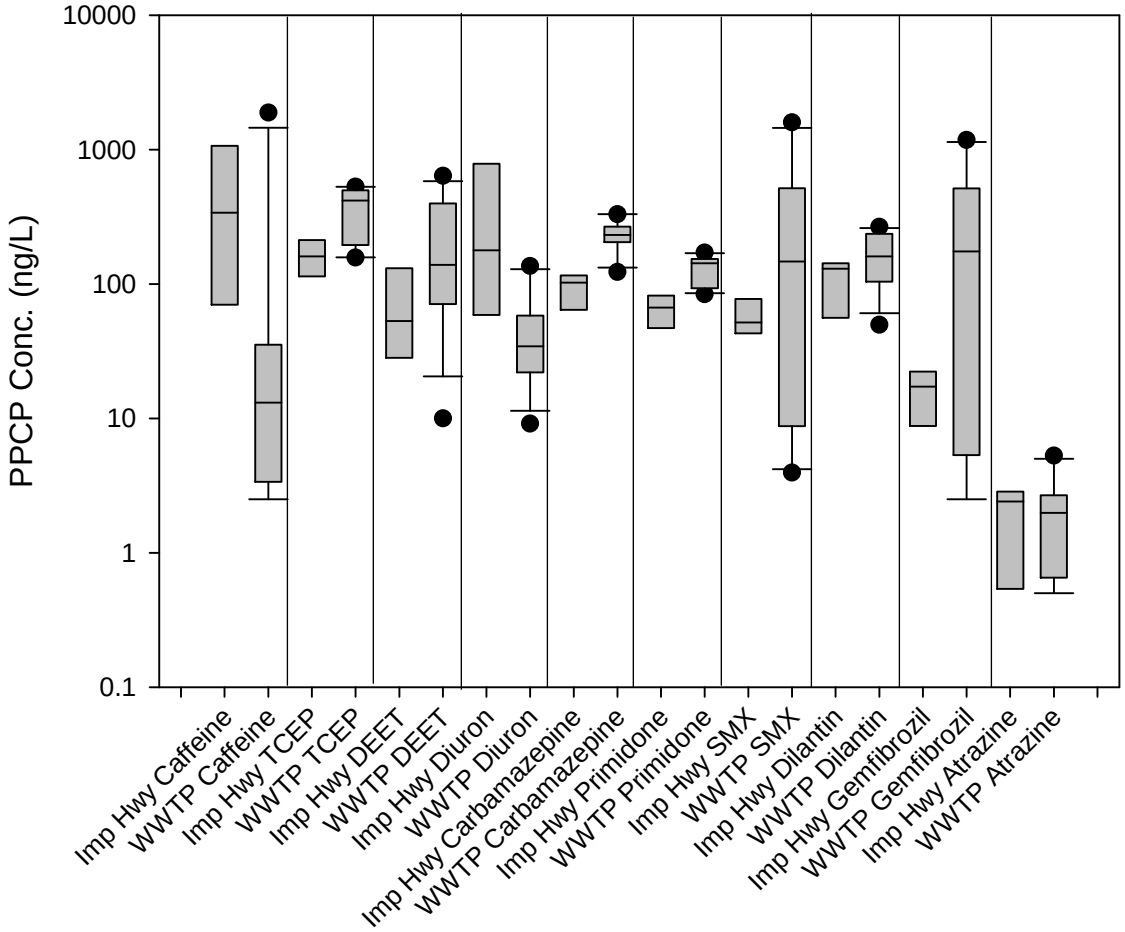

Figure 37. Occurrence at the SAR at Imperial Highway of the 10 most frequently detected PPCPs in the SAR watershed and their occurrence in the WWTPs that discharge in this watershed.

7. CORRELATIONS BETWEEN SELECTED PPCPS

Carbamazepine and primidone have been shown to be conservative indicators of wastewater impact (Krasner et al., 2006; Guo and Krasner, 2009). The concentrations of several frequently detected PPCPs were plotted against that of primidone to identify any possible correlations in the samples collected, which were sorted into three groups according to different characteristics:

- SPW and CRW watershed samples, which were surface water samples with low wastewater impact.
- SAR WWTP effluents, together with SAR river and tributary samples, which were surface water samples dominated by WWTP discharges.
- Nevada WWTP blended effluent.

Note that correlations between PPCPs depend on several issues: (1) the concentration of the PPCPs at the WWTPs; (2) the impact of WWTP disinfection processes on the PPCPs; and (3) the fate and transport of the PPCPs in the watershed. In general, primidone concentrations (~100-200 ng/L) at various WWTPs throughout the U.S. were found to be quite similar (Krasner et al., 2006). Because neither WWTP disinfection processes nor various fate-and-transport mechanisms impact primidone, it has been found to be a conservative tracer of wastewater impact in a watershed. In this study, primidone concentrations in the Nevada WWTP blended effluent (134-167 ng/L) and at the WWTPs in the SAR watershed (84-171 ng/L) were at similar levels as that found in other parts of the U.S.

7.1 SPW and CRW Watershed Samples

For the SPW and CRW watershed samples, the best correlations with primidone were found with the other two anticonvulsants, carbamazepine and dilantin, with the correlation coefficient (R^2) being 0.76 and 0.73, respectively (Figure 38). In the Nevada WWTP blended effluent, there was a consistent level of carbamazepine (187-204 ng/L) and dilantin (129-159 ng/L). The levels of these PPCPs at the WWTPs that discharged in the SPW watershed were not known, but would be expected to be similar if the *per capita* use of anticonvulsants were similar (as has been observed for primidone in many portions of the U.S.). The correlation coefficient of sulfamethoxazole with primidone was 0.62, indicating some fair level of correlation (Figure 38), whereas that of TCEP was 0.41, indicating a poor correlation. Although the level of sulfamethoxazole was relatively consistent in the Nevada WWTP blended effluent (762-1,240 ng/L), where UV disinfection was practiced, different levels may have been present at the WWTPs that discharged in the SPW watershed. The use of chlorine at the Sacramento and Stockton WWTPs probably formed chloramines in the presence of ammonia at those facilities. As shown in the fate-and-transport chapter (Figures 21 and 23), sulfamethoxazole can degrade in the watershed, which would result in a lack of correlation with a conservative tracer such as primidone. Caffeine, gemfibrozil, and DEET showed no correlation with primidone. Again, both caffeine and gemfibrozil can degrade in the environment. The lack of correlation between caffeine and other pharmaceuticals was previously noted in the literature (Glassmeyer et al., 2005; Guo and Krasner, 2009). As shown in the fate-and-transport chapter (Figure 24), there can be other sources for DEET in the CRW watershed besides the Nevada WWTP blended effluent.

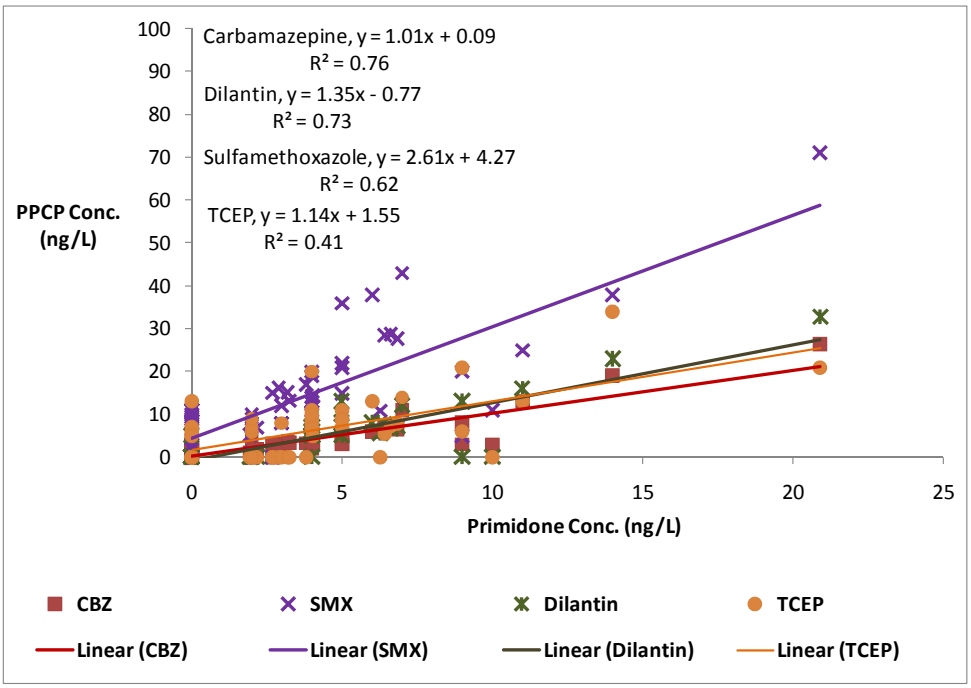

Figure 38. Correlations of PPCP concentrations with primidone in the SPW and CRW watershed samples.

Although diuron was one of the most frequently detected analytes in the SPW samples, it was not included in the correlation analysis, because its source was mainly agricultural runoff and it showed no correlation with primidone and other PPCPs, which were WWTP originated.

Figure 39 shows the correlation of sulfamethoxazole and gemfibrozil concentrations in the SPW watershed samples. The CRW watershed samples were not included in this analysis, as gemfibrozil was not detected in that watershed. Gemfibrozil was detected in the Nevada WWTP blended effluent, but it was at such a low level (9-40 ng/L) that its concentration would have been diluted to below its MRL (5 ng/L) in Lake Mead. In the SPW watershed, there was a fair linear correlation ($R^2 = 0.61$) between these two PPCPs that are known to degrade in the environment. Alternatively, there was a good correlation ($R^2 = 0.77$) when examined with a logarithmic curve. There are two contributing factors to this observation: (1) the levels of these PPCPs may have been different in the effluents of the Sacramento and Stockton WWTPs; and (2) their degradation rates may have been different. Although the concentration of sulfamethoxazole downstream of the two WWTPs was similar (28-43 ng/L [median of 37 ng/L] in the Sacramento River at Hood, 20-71 ng/L [median of 32 ng/L] in the San Joaquin River at Holt Road), the levels of gemfibrozil were quite different (83-162 ng/L [median of 90 ng/L] in the Sacramento River at Hood, 11-95 ng/L [median of 27 ng/L] in the San Joaquin River at Holt Road). In the effluents of the Southern California reservoirs, sulfamethoxazole was detected at levels of 5-11 ng/L, whereas gemfibrozil was typically not detected or was sometimes detected at its MRL (note, non-detects were plotted at one half their MRLs [2.5 ng/L for gemfibrozil]).

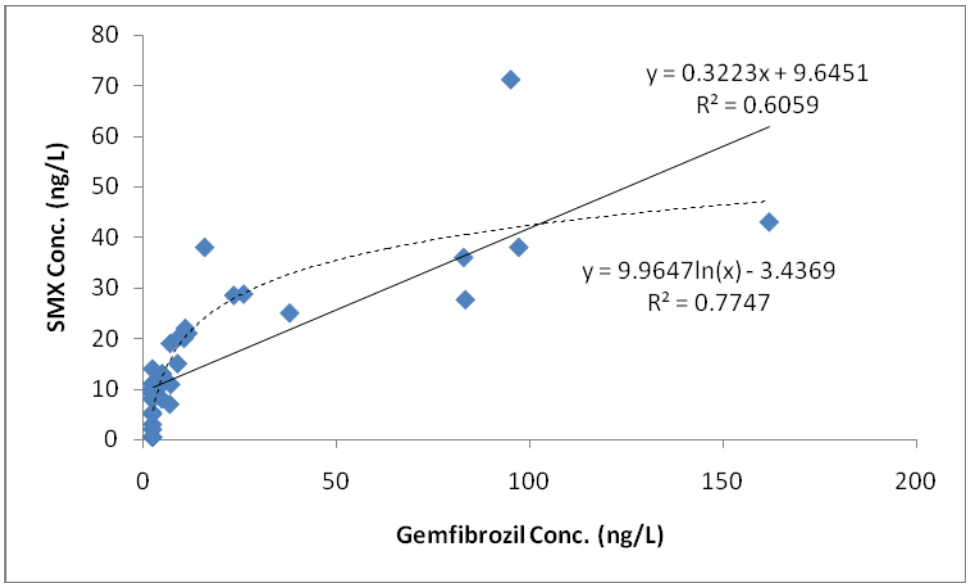

Figure 39. Correlation of sulfamethoxazole and gemfibrozil concentrations in the SPW watershed samples.

7.2 WWTP Effluents and River and Tributary Samples in SAR Watershed

The SAR river and tributary samples were effluent-dominated. Therefore, all the SAR samples, including the WWTP effluents, were grouped together and the concentrations of the seven most frequently detected PPCPs (excluding diuron) were plotted against that of primidone. Dilantin showed a fair correlation with primidone (Figure 40), with a R^2 of 0.67. Carbamazepine (R^2 = 0.40), DEET (R^2 = 0.39), and TCEP (R^2 = 0.35) showed poor correlations with primidone. Caffeine, gemfibrozil, and sulfamethoxazole showed no correlation with primidone. A separate plot for the WWTP effluents in this watershed is shown in Figure 41. The data points for the WWTP effluents were divided into three distinct groups: (1) WWTP #2, which used UV treatment; (2) WWTP #4 and #3 under normal chlorination operations; and (3) WWTP #3 during plant upsets. This contributed to the lower level of correlation in the SAR samples compared with those from the SPW and CRW watersheds. For example, there was a wider range of concentrations for primidone and carbamazepine at the WWTPs in the SAR watershed than in the Nevada WWTP blended effluent (Figure 42). Moreover, WWTP #2 in the SAR watershed had lower levels of primidone than that of the other WWTPs in this study.

Figure 43 shows the correlation of gemfibrozil and sulfamethoxazole at the WWTPs in the SAR watershed. There was an excellent correlation (R^2 = 0.92), as WWTP disinfection processes had a similar impact on these two PPCPs. Figure 44 shows the correlation of these two PPCPs in the river and tributary samples in the SAR watershed, with a R^2 of 0.46. In addition to the impact of the WWTP disinfection process, both gemfibrozil and sulfamethoxazole were found to degrade in the environment (Figures 27, 30, 31, and 33).

Figure 45 shows the correlation of total phosphorus (P) with primidone in the SAR watershed. The data were segmented by WWTPs with high phosphorus and downstream sites and by WWTPs with low phosphorus and downstream sites. For the WWTPs with high phosphorus and

downstream sites, the R^2 was only 0.41. The SAR at MWD Crossing had an unexplained attenuation in primidone. Likewise, this site was similarly attenuated in terms of total phosphorus.

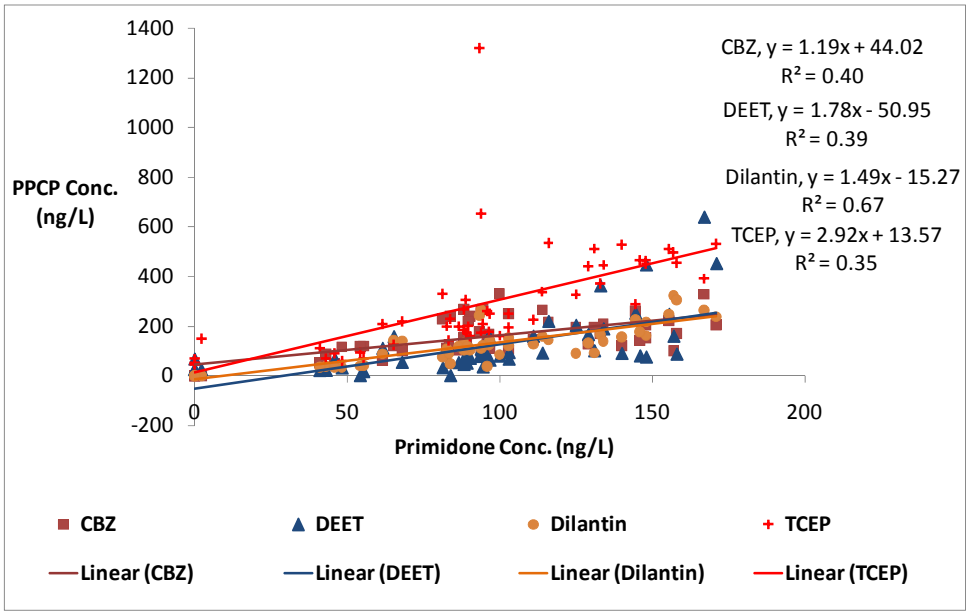

Figure 40. Correlations of PPCP concentrations with primidone in the SAR watershed samples, including the WWTP effluents.

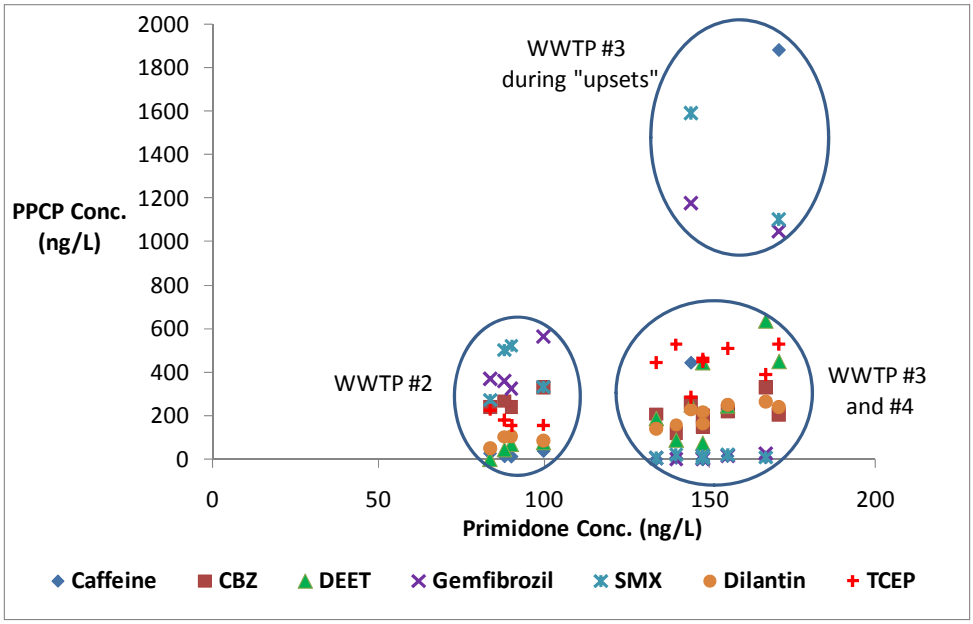

Figure 41. PPCP concentrations in the WWTP effluents in the SAR watershed.

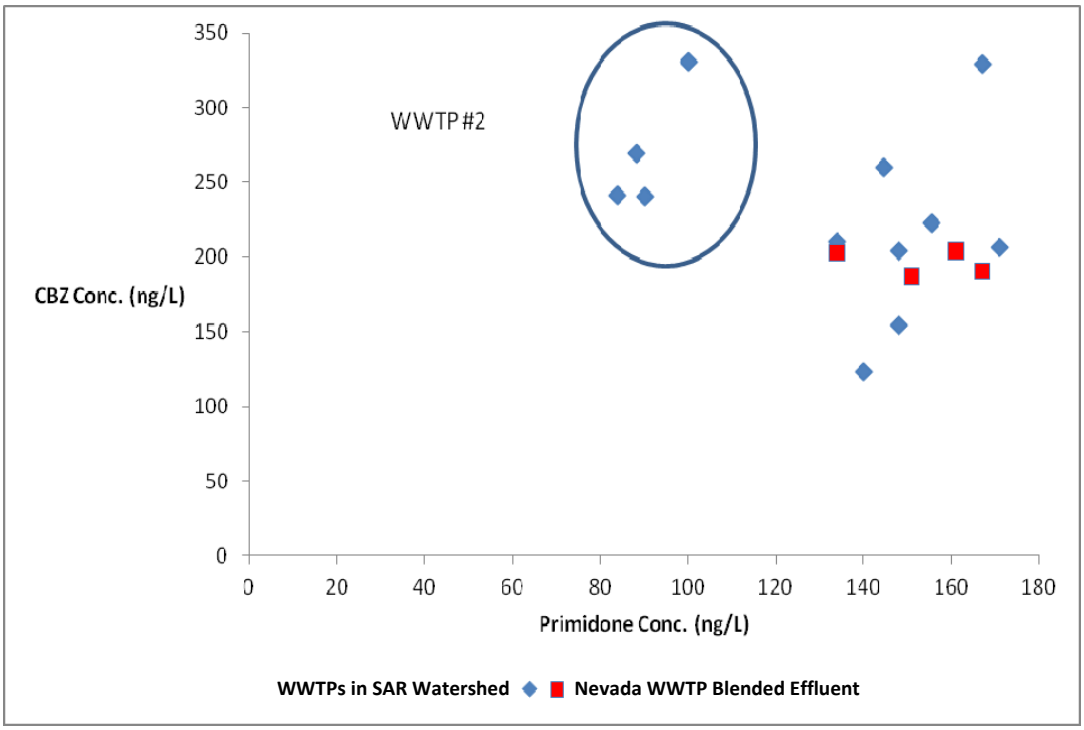

Figure 42. Primidone and carbamazepine concentrations in the WWTP effluents in the SAR and CRW watersheds.

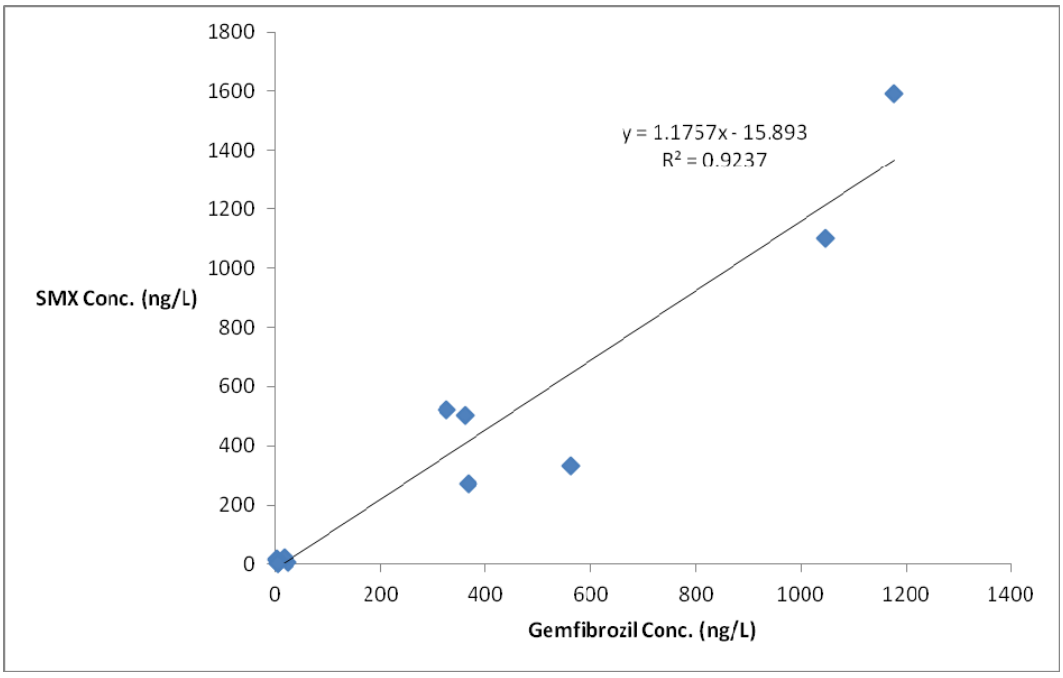

Figure 43. Gemfibrozil and sulfamethoxazole concentrations in the WWTP effluents in the SAR watershed.

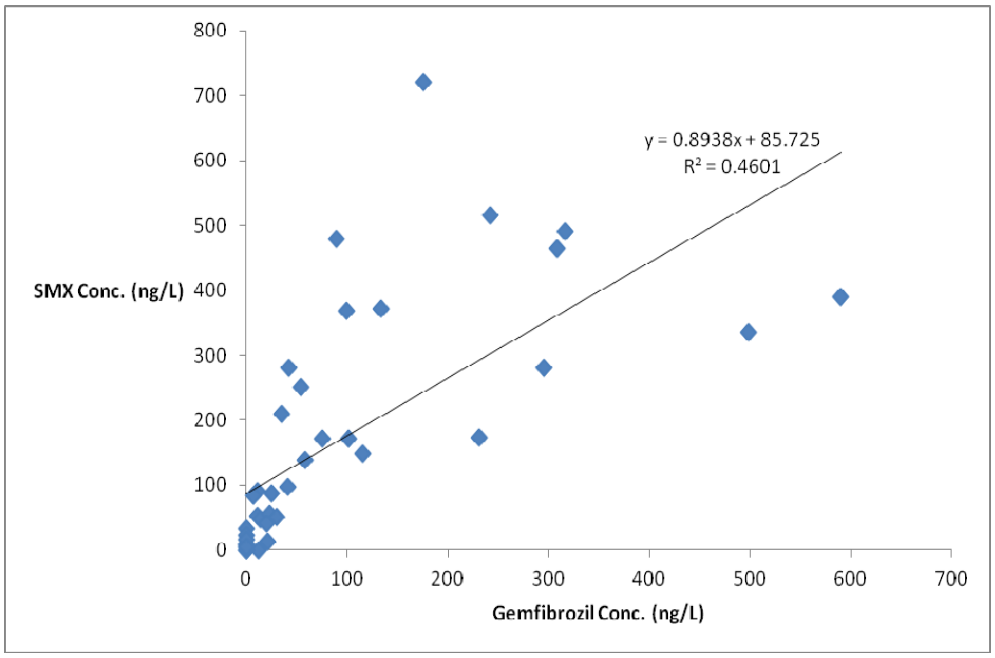

Figure 44. Gemfibrozil and sulfamethoxazole concentrations in the river and tributary samples in the SAR watershed.

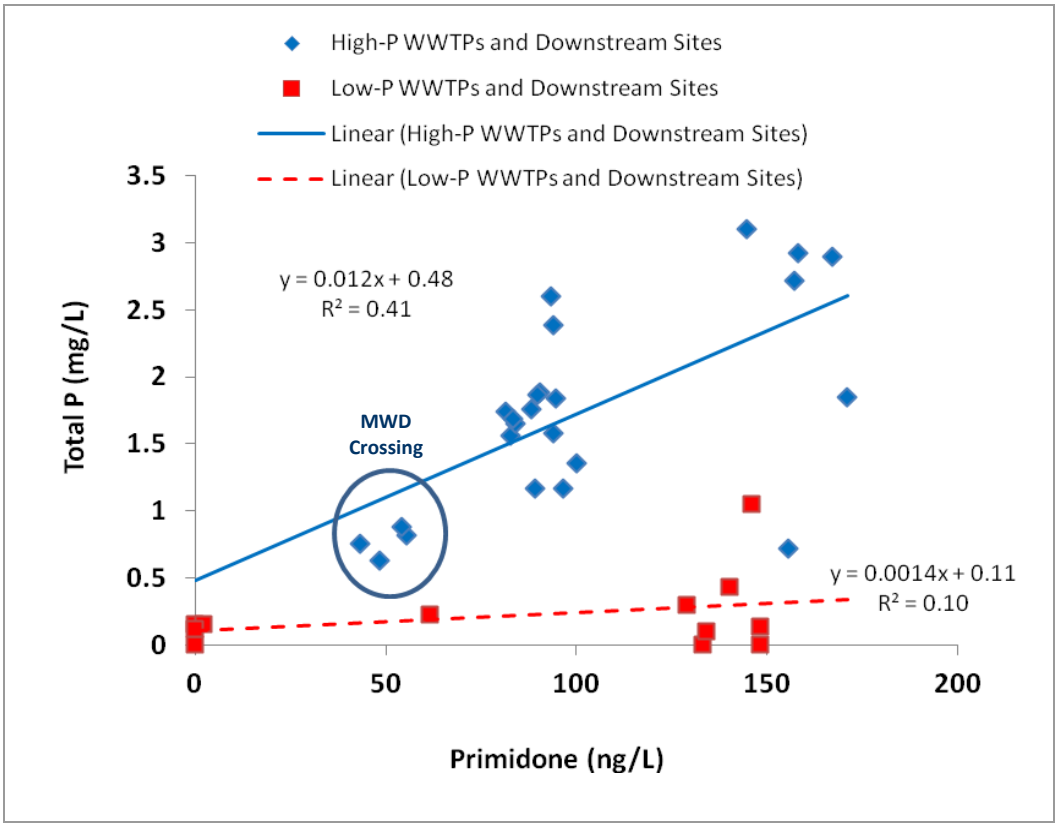

Figure 45. Correlation of total phosphorus with primidone in the SAR watershed.

7.3 Nevada WWTP Blended Effluent

Of the 12 most frequently detected PPCPs and OWCs in the Nevada WWTP blended effluent (Tables 36 and 47), the concentrations of 10 were plotted against that of primidone (Figure 46), with diuron excluded for the same reason as mentioned in section 7.1. The concentration range of primidone was very tight, ranging from 134-167 ng/L. Figure 47 shows the normalized PPCP concentrations relative to that of primidone, where normalized PPCP concentration = (PPCP/primidone)×(average primidone/average PPCP). Carbamazepine, sulfamethoxazole, and dilantin had the tightest groupings centered about the 1.0 line, which meant that their concentrations relative to that of primidone did not vary that much seasonally. Alternatively, caffeine, DEET, and gemfibrozil varied the most.

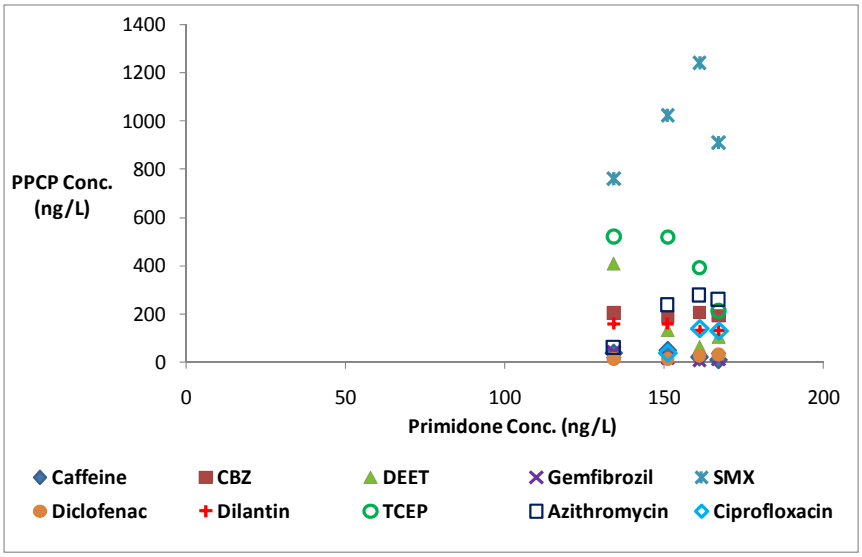

Figure 46. PPCP concentrations in the Nevada WWTP blended effluent.

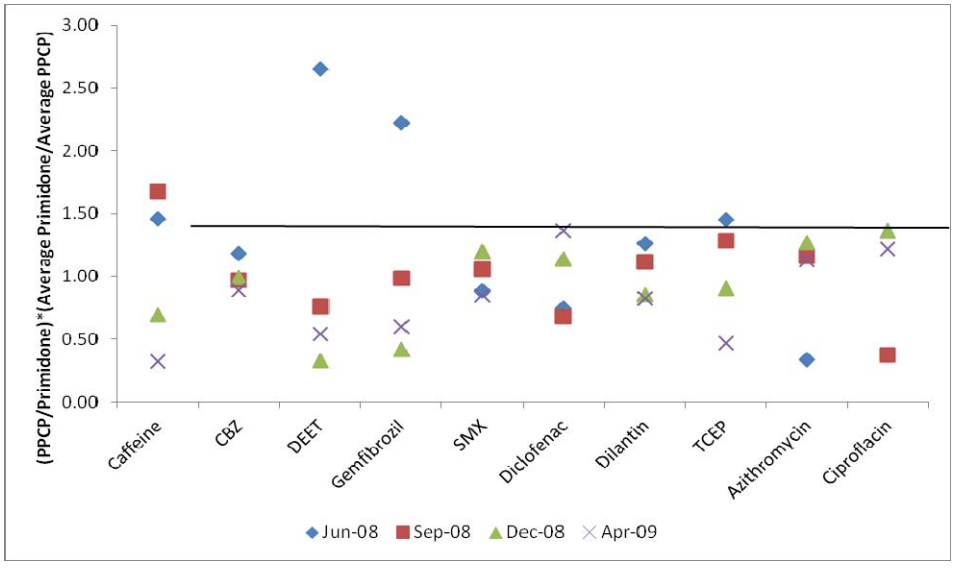

Figure 47. Normalized PPCP concentrations relative to that of primidone in the Nevada WWTP blended effluent.

CONCLUSIONS

The occurrence, fate, and transport of EDCs, PPCPs, and other OWCs were evaluated in three main drinking water sources for California (i.e., SPW, CRW, and SAR). The three sources combined supply drinking water to more than 25-million people in California. The project assessed the occurrence of a wide range of EDCs, PPCPs, and OWCs in these drinking water sources, evaluated the impact of treated wastewater discharges, and also evaluated the fate and transport of these chemicals in each watershed.

8.1 Project Findings

8.1.1 Occurrence

Of the 126 samples analyzed for the project, one sample (American River at Fairbairn DWTP intake collected in April 2008) had no detectable levels of any PPCPs or OWCs. All other samples had one or more PPCPs and OWCs detected at or above the corresponding MRLs. The five most frequently detected PPCPs were caffeine, carbamazepine, primidone, sulfamethoxazole, and TCEP.

At the sample sites upstream of WWTP discharges, the concentrations of selected PPCPs, except for caffeine, were low (i.e., ≤ 13 ng/L), pointing to WWTP discharges as the main source of most PPCPs and OWCs in the environment.

Caffeine represented an exception to the overall trend. The median and maximum concentrations of caffeine at the upstream sites were 47 and 2,160 ng/L, respectively, indicating other sources of caffeine in the environment (e.g., urban runoff, plants that produce caffeine).

For the SPW watershed, the median occurrence of targeted PPCPs in the river samples was <30 ng/L each, except for diuron. Diuron was detected in 88% of the SPW samples, with a median concentration of 81 ng/L and a maximum concentration of 873 ng/L. Maximum concentrations for some PPCPs exceeded 100 ng/L. The highest levels of gemfibrozil in this watershed were detected in the Sacramento River at Hood (83-162 ng/L), which is downstream of the Sacramento WWTP.

For the CRW watershed, the median occurrence of targeted PPCPs in the river samples was <20 ng/L. The median occurrence of a number of the PPCPs in the Nevada blended WWTP effluent were >100 ng/L, and the maximum occurrence of sulfamethoxazole was >1,000 ng/L. High levels of caffeine (519-1,370 ng/L) and DEET (64-297 ng/L) were sometimes detected at the inlet to Lake Havasu, most likely from human activities in this portion of the watershed.

For the SAR watershed, the median occurrence of a number of the PPCPs in the WWTP discharges was >100 ng/L, and the maximum occurrence of some PPCPs was >1,000 ng/L. The levels of PPCPs in the river and tributary samples varied widely, as this included sample sites upstream and downstream of WWTPs. The concentrations of most PPCPs were lower in the river and tributary samples than those in the WWTP effluents, but were substantially higher than those in the SPW and the CRW watersheds, consistent with the fact that SAR consisted of greater than 50% tertiary treated effluents under non-storm conditions during this study.

In the WWTP effluents, the concentrations of carbamazepine and primidone did not vary extensively between different samples, whereas those of caffeine, gemfibrozil, and sulfamethoxazole varied from not detected to >1,000 ng/L. The general trend was that WWTPs with UV disinfection had high levels of gemfibrozil and sulfamethoxazole, and WWTPs with chlorination had low levels of these two PPCPs. A WWTP (i.e., WWTP #3 in the SAR watershed) that added chlorine but did not achieve breakpoint in one sample event (i.e., formed chloramines) also had high levels of these two PPCPs.

Carbamazepine and primidone had been shown to be conservative wastewater tracers by previous work of members of the project team and other research groups. The occurrence of these two anticonvulsants in the SPW and CRW watersheds relative to that of the Nevada WWTP blended effluent (assuming similar levels in the Sacramento-San Joaquin River Delta WWTP effluents) suggested that SPW and CRW were <10% treated wastewater. On the other hand, the SAR was effluent-dominated (>50% treated wastewater).

The seasonal variations of selected PPCPs in the WWTP effluents were evaluated, and overall the concentrations did not vary significantly during different seasons. The exception was one of the WWTPs in the SAR watershed (WWTP #3), which experienced plant upsets during two of the four sampling events and resulted in much higher levels of caffeine (>400 ng/L), and gemfibrozil and sulfamethoxazole (both at >1,000 ng/L). Also evaluated were the seasonal variations of several PPCPs in selected river samples. The variations in concentrations suggested a possible impact from flow changes in the watersheds.

8.1.2 Fate and Transport

For the SPW watershed, the amounts of certain PPCPs (i.e., carbamazepine, primidone, gemfibrozil, and sulfamethoxazole) were highly attenuated. The attenuation of carbamazepine and primidone can be attributed to dilution with non-wastewater-impacted water. The attenuation of gemfibrozil and sulfamethoxazole were most likely due to a combination of dilution with other sources of waters and some natural degradation processes, such as biodegradation, photolysis, and sorption. The occurrence data suggested that water at the Banks pumping plant during this study reflected a greater percentage of water from the Sacramento River than from the San Joaquin River and/or other sources of water with less PPCP impact.

For the CRW watershed, the averages of carbamazepine, primidone, and sulfamethoxazole detected at Hoover Dam was 1.7%, 1.9%, and 2.1%, respectively, of the levels detected in the Las Vegas Wash, consistent with previous studies that showed the annual inflow via the Las Vegas Wash was ~1.5% of the total inflow to Lake Mead.

For the SAR watershed, the attenuation of primidone was evaluated at four sites downstream of WWTP discharges: SAR at Riverside Avenue; MWD Crossing, River Road; and Mill/Cucamonga Creek at Chino Corona Road. The attenuation at Riverside Avenue, River Road, and Chino Corona Road were all within the coefficient of variation of the method; however, the attenuation at MWD Crossing was consistently high, ranging from 37-55%. One possibility at this site was that both a losing stream and gaining stream scenario may have existed. Evaluation of carbamazepine at these four sites showed similar trends. Evaluation of

gemfibrozil and sulfamethoxazole at the same sites showed additional attenuation relative to primidone, indicating other loss mechanisms.

The Prado Wetlands in the SAR watershed proved effective way in removing/transforming PPCPs to varying extents. For example, azithromycin was completely attenuated. Many other PPCPs (e.g., caffeine, gemfibrozil, ibuprofen, sulfamethoxazole, acetaminophen) were highly attenuated (42-100%) in two or three of the sample events, whereas there was often little or no attenuation in the May 2008 sample event, which was shortly after the wetlands had been rebuilt and put back in service. There was no substantial attenuation of primidone (-8 to 27%, median of 5%). The attenuation through the wetlands of DEET and TCEP was low (median values of 24 and 33%, respectively).

The amount (on a volume basis) of the SAR water that originated from treated wastewater effluent was evaluated for the two SAR sites at below Prado Dam and Imperial Highway, based on the presence of two conservative wastewater tracers, primidone and carbamazepine. The results showed that these two sites were under substantial WWTP influence and could be characterized as either effluent-impacted or effluent dominated during this study.

8.1.3 Correlations between Certain PPCPs

The concentrations of several frequently detected PPCPs were plotted against that of primidone, used as a conservative indicator of wastewater impact, to identify any possible correlations.

For the SPW and CRW river samples, the best correlations with primidone were found with two other anticonvulsants, carbamazepine and dilantin, with the correlation coefficient (R^2) being 0.76 and 0.73, respectively. The correlation coefficient for sulfamethoxazole with primidone was 0.62, indicating a fair level of correlation, whereas the correlation coefficient for TCEP was 0.41, indicating a poor correlation. Caffeine, gemfibrozil, and DEET showed no correlation with primidone. Diuron in the environment came mainly from agricultural runoff, and it showed no correlation with primidone and other PPCPs, which were WWTP-originated. In the SPW watershed, there was a fair linear correlation ($R^2 = 0.61$) between sulfamethoxazole and gemfibrozil, which are known to degrade in the environment.

For the SAR watershed, dilantin showed a fair correlation with primidone in all samples, including the WWTP effluents, with a $R^2 = 0.67$. Carbamazepine ($R^2 = 0.40$), DEET ($R^2 = 0.39$), and TCEP ($R^2 = 0.35$) showed poor correlations with primidone. Caffeine, gemfibrozil, and sulfamethoxazole showed no correlation with primidone. The correlation of gemfibrozil and sulfamethoxazole in WWTP effluents was excellent ($R^2=0.92$), as WWTP disinfection processes had a similar impact on these two PPCPs. The correlation of these two PPCPs in the river and tributary samples in the SAR watershed was poor ($R^2 = 0.46$). As for the correlation between total phosphorus and primidone, the group of samples of WWTP effluents with high phosphorus and their corresponding downstream sites showed a poor correlation ($R^2 = 0.41$), whereas the other group of samples of WWTP effluents with low phosphorus and the corresponding downstream sites showed no correlation.

8.2 Future Research Needs

Significant information was obtained from this project on the occurrence, fate, and transport of EDCs, PPCPs, and OWCs in the three watersheds that provide water to California. It is recommended that future research be directed toward the following areas:

- Standardized analytical methods are needed to ensure high quality data and to be able to compare results from different studies. Currently, approaches from laboratories performing PPCP analysis vary widely on key analytical issues, such as blank contamination and matrix effects. This is being addressed in part by the current Water Research Foundation Project 4167 entitled "Evaluation of Analytical Methods for EDCs and PPCPs via Inter-laboratory Comparison," which will evaluate current methodology commonly used for the analysis of EDCs and PPCPs, with the goal of providing guidelines to drinking water utilities on optimizing data quality for EDCs and PPCPs. Twenty-five laboratories are participating in Project 4167, including the three laboratories participated in this project. The results of that study are expected in 2011.

- Collection and analysis of treated effluents from the Delta WWTPs will provide a better understanding of the SPW watershed. The effluents from the Sacramento or Stockton WWTPs were not available for this project. However, the Stockton WWTP has recently agreed to be sampled for another study in the Delta.

- A Lagrangian sampling design, which follows a plug of water, will allow a more in-depth fate and transport analysis. A good understanding will be needed of the hydrology of the watershed of interest, as well as significant effort and resources for sampling. A good candidate to consider is the SAR (e.g., between Prado Dam and Imperial Highway, where the flow conditions are defined and no inflows enter the river during non-storm conditions). Some work in this vein was conducted in the past, but more is needed.

- Certain locations in the watersheds studied need better characterization of the hydrology. For example, although the discharge rate of the Stockton WWTP was known, the flow in the San Joaquin River was difficult to access because of "reverse" flows due to tidal impact. However, using a computer simulation model, the Department of Water Resources was able to estimate the volumetric contribution of the Stockton WWTP to the flow of the river. It was found to range from ~4 to ~10% on the days of sample collection. In addition, the portion of the SAR near the sampling point "MWD Crossing" needs to be evaluated in terms of losing and/or gaining stream.

- Groundwater monitoring wells can be included in future sampling events to understand the occurrence of PPCPs in regions that practice groundwater recharge. This sampling has been done in other areas of the U.S. and in Europe.

- Examining the concentrations of these emerging constituents in sediments may help in better understanding of the fate and transport of these chemicals in natural waters.

- Expand the list of analytes based on prescription patterns, use levels, and toxicological significance.

- Within a watershed, characterize drinking water samples together with the source water and wastewater samples for a better understanding of the significance of the results.

- Identification of significant conversion products resulting from treatment or environmental degradation of these emerging constituents.

- Information on toxicological relevance of EDCs and PPCPs in drinking water is available in terms of ADIs and DWELs. The general consensus is that there is no evidence of human health risk from low levels of the commonly detected EDCs and PPCPs in drinking water or drinking water supplies. Nonetheless, more toxicological studies of PPCPs are needed.

- The occurrence of EDCs and PPCPs in water supplies is a sensitive issue for the public, and the perceived risks by the public should be addressed effectively. A collaborative effort in arriving at public communications tools will be of value to wastewater and drinking water agencies. In addition, this issue provides an opportunity to enhance the public's awareness that they are personally connected to the environment; therefore, information is needed on how individuals can contribute to pollution prevention measures.

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APPENDIX A:

State Project Water (SPW) Results

Appendix A: State Project Water (SPW) Results

ND=Not detected; Results reported as ng/L

Lab	Analyte	MRL (ng/L)	Sampling Date	ELCAMINO AVE (NEMDC)	FAIRBARN WTP	W SAC WTP	HOOD	MOSS DALE LANDING	HOLT ROAD	BANKS HDWKS	O'NEILL FOREBAY (Check 13)	CHECK 41	SPW at Devil Canyon	SPW at Foothill PCS
MWD and OCWD	Bisphenol A	30 (MWD)	Apr-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Jul-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Oct-08	-	ND	ND	ND	ND	ND	ND	ND	140	ND	ND
			Jan-09	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Caffeine	5	Apr-08	33	ND	ND	5	7	15	6	9	8	6	7
			Jul-08	20	6	ND	6	9	15	8	8	16	8	12
			Oct-08	-	ND	ND	ND	25	23	58	7	23	6	ND
			Jan-09	90	22	18	51	48	67	40	14	6	37	5
	Carbamazepine	1	Apr-08	56	ND	1	11	3	13	4	5	4	3	3
			Jul-08	79	ND	ND	6	1	8	3	3	2	2	1
			Oct-08	-	ND	2	3	6	19	5	3	1	4	2
			Jan-09	25	ND	2	7	6	26	7	7	ND	1	2
	DEET	20	Apr-08	23	ND	ND	22	ND	ND	ND	ND	ND	ND	ND
			Jul-08	132	ND	ND	22	23	ND	ND	23	ND	ND	ND
			Oct-08	-	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Jan-09	32	ND	ND	ND	ND	35	ND	ND	ND	ND	ND
	Ethynylestradiol (EE2)	10	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	Gemfibrozil	5	Apr-08	ND	ND	ND	162	ND	38	ND	9	5	ND	5
			Jul-08	ND	ND	ND	97	ND	11	12	7	ND	ND	ND
			Oct-08	-	ND	5	83	5	16	11	9	ND	ND	ND
			Jan-09	103	ND	7	83	7	95	26	24	ND	ND	ND
	Ibuprofen	10	Apr-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Jul-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Oct-08	-	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Jan-09	ND	ND	ND	ND	ND	47	ND	ND	ND	ND	ND
	4-n-Nonylphenol	50	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	4-*n*- and 4-*t*-Octylphenol	20	Apr-08	ND	ND	ND	ND	ND	ND	68	ND	ND	ND	ND
			Jul-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Oct-08	-	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Jan-09	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Primidone	2	Apr-08	51	ND	ND	7	9	11	ND	5	4	10	ND
			Jul-08	71	ND	ND	6	2	9	5	4	4	4	ND
			Oct-08	-	ND	ND	5	4	14	5	4	2	2	2
			Jan-09	27	ND	2	7	6	21	7	6	ND	2	ND
	Sulfamethoxazole	1	Apr-08	17	ND	2	43	5	25	9	15	13	11	11
			Jul-08	27	ND	3	38	ND	20	21	19	14	10	11
			Oct-08	-	ND	8	36	13	38	22	20	8	8	10
			Jan-09	95	ND	7	28	11	71	29	29	8	5	9
	Triclosan	5	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											

Lab	Analyte	MRL (ng/L)	Sampling Date	ELCAMINO AVE (NEMDC)	FAIRBARN WTP	W SAC WTP	HOOD	MOSS DALE LANDING	HOLT ROAD	BANKS HDWKS	O'NEILL FOREBAY (Check 13)	CHECK 41	SPW at Devil Canyon	SPW at Foothill PCS
MWD	Anthracene	10	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	Atrazine	1	Apr-08	ND	ND	ND	ND	ND	ND	ND	1	1	2	1
			Jul-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Oct-08	-	ND	ND	ND	ND	ND	ND	ND	ND	1	1
			Jan-09	1	ND	ND	ND	ND	ND	1	1	ND	1	1
	Atrazine-Desethyl	20	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	Atrazine-Desisopropyl	20	Apr-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	25	ND
			Jul-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Oct-08	-	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Jan-09	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Benzo(a)pyrene	25	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	Butylparaben	20	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	Cyanazine	20	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	Cyprazine	20	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	o,p-DDD	20	Apr-08	ND	ND	ND	ND	ND	57	82	ND	ND	ND	ND
			Jul-08	ND	ND	ND	ND	ND	21	47	59	ND	ND	ND
			Oct-08	-	ND	ND	ND	ND	43	ND	55	ND	ND	ND
			Jan-09	ND	ND	47	ND	ND	ND	ND	ND	ND	ND	ND
	Diclofenac	5	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	Dilantin	5	Apr-08	45	ND	ND	12	ND	16	5	13	5	ND	ND
			Jul-08	79	ND	ND	8	ND	13	5	5	5	ND	ND
			Oct-08	-	ND	ND	7	7	23	8	6	ND	ND	ND
			Jan-09	21	ND	ND	7	5	33	6	8	ND	ND	ND
	Diuron	5	Apr-08	43	ND	83	39	242	382	280	188	148	686	120
			Jul-08	25	ND	7	6	37	78	29	110	84	127	177
			Oct-08	-	ND	ND	ND	11	51	17	33	38	77	163
			Jan-09	273	8	26	42	805	145	116	873	122	94	128
	Ethylparaben	20	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											

Lab	Analyte	MRL (ng/L)	Sampling Date	ELCAMINO AVE (NEMDC)	FAIRBARN WTP	W SAC WTP	HOOD	MOSS DALE LANDING	HOLT ROAD	BANKS HDWKS	O'NEILL FOREBAY (Check 13)	CHECK 41	SPW at Devil Canyon	SPW at Foothill PCS
	Lindane	10	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	Linuron	5	Apr-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Jul-08	5	ND	ND	ND	ND	ND	5	ND	ND	ND	ND
			Oct-08	-	ND	ND	ND	ND	ND	5	ND	ND	ND	ND
			Jan-09	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Methoxychlor	20	Apr-08	ND	ND	ND	ND	ND	25	43	ND	ND	ND	ND
			Jul-08	ND	ND	ND	ND	ND	ND	37	40	ND	ND	ND
			Oct-08	-	ND	ND	ND	44	ND	63	66	ND	ND	ND
			Jan-09	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Methylparaben	20	Apr-08	ND	ND	ND	ND	ND	27	ND	ND	ND	ND	ND
			Jul-08	ND	ND	ND	ND	ND	ND	23	ND	744	ND	48
			Oct-08	-	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Jan-09	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Propazine	20	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	Propylparaben	20	Apr-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Jul-08	ND	ND	ND	ND	ND	ND	ND	ND	83	ND	ND
			Oct-08	-	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Jan-09	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Simazine	20	Apr-08	ND	ND	ND	ND	23	54	65	24	32	408	25
			Jul-08	ND	ND	ND	ND	ND	ND	ND	28	20	47	53
			Oct-08	-	ND	ND	ND	ND	ND	ND	ND	ND	27	88
			Jan-09	25	ND	ND	ND	78	ND	ND	ND	ND	25	39
	TCEP	5	Apr-08	58	ND	ND	14	6	13	13	7	8	ND	ND
			Jul-08	147	6	6	13	6	21	9	11	9	7	7
			Oct-08	-	ND	ND	11	20	34	9	10	6	ND	7
			Jan-09	24	ND	ND	8	ND	21	7	5	ND	ND	5
OCWD	Acetaminophen	10	Apr-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			NA	-	-	-	-	-	-	-	-	-	-	-
		1	Oct-08	-	ND	ND	ND	ND	ND	ND	6	ND	ND	ND
		10	Jan-09	ND	ND	ND	ND	ND	ND	28	ND	ND	ND	ND
	Azithromycin	1	Apr-08	ND										
			NA											
		5	Oct-08											
		5	Jan-09											
	Ciprofloxacin	40	Apr-08	ND										
			NA											
		10	Oct-08											
		50	Jan-09											
	Diethylstilbestrol	10	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											
	Epitestosterone	10	Apr-08	ND										
			Jul-08											
			Oct-08											
			Jan-09											

Lab	Analyte	MRL (ng/L)	Sampling Date	ELCAMINO AVE (NEMDC)	FAIRBARN WTP	W SAC WTP	HOOD	MOSS DALE LANDING	HOLT ROAD	BANKS HDWKS	O'NEILL FOREBAY (Check 13)	CHECK 41	SPW at Devil Canyon	SPW at Foothill PCS
	17a-Estradiol	10	Apr-08						ND					
			Jul-08											
			Oct-08											
			Jan-09											
	17b-Estradiol	10	Apr-08						ND					
			Jul-08											
			Oct-08											
			Jan-09											
	Estriol	10	Apr-08						ND					
			Jul-08											
			Oct-08											
			Jan-09											
	Estrone	10	Apr-08						ND					
			Jul-08											
			Oct-08											
			Jan-09											
	Nonylphenol ethoxylates (	10000	Apr-08						ND					
			Jul-08											
			Oct-08											
	Pentachlorophenol	1000	Apr-08						ND					
			Jul-08											
			Oct-08											
			Jan-09											
	4-Phenylphenol	1000	Apr-08						ND					
			Jul-08											
			Oct-08											
			Jan-09											
	Progesterone	10	Apr-08						ND					
			Jul-08											
			Oct-08											
			Jan-09											
	Testosterone	10	Apr-08						ND					
			Jul-08											
			Oct-08											
			Jan-09											
	Tetrabromobisphenol A	1000	Apr-08						ND					
			Jul-08											
			Oct-08											
			Jan-09											
	2,4,6-Trichlorophenol	1000	Apr-08						ND					
			Jul-08											
			Oct-08											
			Jan-09											

APPENDIX B:

Santa Ana River (SAR) Results

Appendix B: Santa Ana River (SAR) Results

ND=Not detected; Results reported as ng/L

Lab	Analyte	MRL (ng/L)	Sampling Date	NORTH OF WWTP #2	WWTP #2	RIVERSIDE AVE	MWD XING	WWTP #3	RIVER RD	DEER CREEK CHANNEL	WWTP #4	CHINO CORONA RD	PRADO WETLANDS INLET	PRADO WETLANDS OUTLET	BELOW PRADO DAM	IMPERIAL HWY
MWD and OCWD	Bisphenol A	30 (MWD)	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Caffeine	5	5/22/2008	7	38	37	22	8	32	524	ND	238	38	72	49	505
			8/19/2008	11	12	13	9	1883	1560	522	6	224	1620	37	42	35
			11/5/2008	6	14	13	112	15	295	2160	ND	100	299	42	725	1255
			2/25/2009	29	27	45	35	444	56	279	ND	20	38	34	198	174
	Carbamazepine	1	5/22/2008	102	331	266	117	329	168	ND	204	170	217	196	146	120
			8/19/2008	98	241	222	87	207	113	ND	123	63	142	154	110	103
			11/5/2008	172	269	267	121	223	149	1	154	143	267	250	107	101
			2/25/2009	178	241	231	119	260	128	ND	210	129	197	129	49	52
	DEET	20	5/22/2008	158	78	85	31	638	159	26	446	361	218	202	158	156
			8/19/2008	106	70	76	21	451	106	67	89	110	127	69	62	52
			11/5/2008	86	45	35	16	247	50	24	75	79	90	66	92	53
			2/25/2009	77	ND	32	ND	251	54	25	188	165	100	78	66	20
	Ethynylestradiol (EE2)	10	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Gemfibrozil	5	5/22/2008	ND	563	498	116	25	25	12	6	ND	100	134	11	14
			8/19/2008	ND	325	309	58	1048	295	ND	ND	ND	243	35	11	7
			11/5/2008	ND	361	317	76	17	41	ND	ND	ND	89	42	24	23
			2/25/2009	21	368	590	231	1178	101	ND	5	ND	176	55	30	20
	Ibuprofen	10	5/22/2008	ND	33	47	31	ND	36	148	20	74	24	38	25	309
			8/19/2008	37	17	21	ND	1460	387	ND	ND	ND	530	ND	ND	ND
			11/5/2008	ND	15	12	ND	11	13	21	ND	ND	14	ND	42	72
			2/25/2009	ND	31	44	14	551	29	9	ND	ND	12	ND	62	42
	4-n-Nonylphenol	1000	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	4-*n*- and 4-*t*-Octylphenol	1000	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Primidone	2	5/22/2008	157	100	94	48	167	96	ND	148	133	116	125	111	65
			8/19/2008	94	90	90	43	171	83	ND	140	62	89	88	97	87
			11/5/2008	158	88	95	55	156	89	2	148	146	114	103	103	68
			2/25/2009	93	84	81	54	145	83	ND	134	129	131	96	46	41
	Sulfamethoxazole	1	5/22/2008	7	332	335	148	7	87	ND	5	5	369	371	53	48
			8/19/2008	33	521	465	139	1103	281	ND	20	10	515	211	91	84
			11/5/2008	22	502	491	172	21	98	7	15	15	479	280	53	56
			2/25/2009	13	273	391	174	1593	172	ND	4	4	721	252	51	41
	Triclosan	5	5/22/2008	ND	8	7	ND	ND	ND	ND	ND	ND	ND	5	ND	ND
			8/19/2008	ND	ND	ND	ND	23	ND	ND	ND	ND	ND	ND	ND	ND
			11/5/2008	10	6	5	ND	20	6	ND	18	12	7	ND	6	9
			2/25/2009	ND	ND	ND	ND	35	ND	ND	7	13	ND	ND	ND	ND
MWD	Anthracene	10	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Atrazine	1	5/22/2008	ND	3	3	6	5	5	1	1	2	4	3	3	3
			8/19/2008	ND	3	2	6	4	5	1	1	2	5	4	3	3
			11/5/2008	ND	2	1	5	3	4	4	ND	ND	3	3	2	2
			2/25/2009	ND	ND	ND	3	2	2	ND	ND	ND	ND	ND	ND	ND
	Atrazine-Desethyl	20	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Atrazine-Desisopropyl	20	5/22/2008	ND	ND	ND	450	22	103	ND	ND	ND	85	81	47	ND
			8/19/2008	ND	ND	ND	228	ND	ND	ND	ND	48	48	40	24	ND
			11/5/2008	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			2/25/2009	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Lab	Analyte	MRL (ng/L)	Sampling Date	NORTH OF WWTP #2	WWTP #2	RIVERSIDE AVE	MWD XING	WWTP #3	RIVER RD	DEER CREEK CHANNEL	WWTP #4	CHINO CORONA RD	PRADO WETLANDS INLET	PRADO WETLANDS OUTLET	BELOW PRADO DAM	IMPERIAL HWY
	Benzo(a)pyrene	25	5/22/2008	ND	ND	ND	ND	ND	27	ND	ND	ND	ND	ND	309	ND
			8/19/2008	ND	ND	ND	ND	ND	ND	ND	254	422	ND	ND	ND	ND
			11/5/2008	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			2/25/2009	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Butylparaben	20	5/22/2008													
			8/19/2008													
			11/5/2008								ND					
			2/25/2009													
	Cyanazine	20	5/22/2008													
			8/19/2008													
			11/5/2008								ND					
			2/25/2009													
	Cyprazine	20	5/22/2008													
			8/19/2008													
			11/5/2008								ND					
			2/25/2009													
	o,p-DDD	20	5/22/2008	ND	ND	ND	26	ND	ND	ND	ND	ND	ND	ND	ND	ND
			8/19/2008	ND	ND	ND	ND	ND	ND	ND	ND	41	ND	ND	ND	ND
			11/5/2008	ND	ND	ND	ND	ND	29	51	ND	ND	ND	ND	ND	ND
			2/25/2009	ND	ND	ND	ND	ND	29	51	ND	ND	ND	ND	ND	ND
	Diclofenac	5	5/22/2008	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			8/19/2008	7	8	7	ND	36	ND	ND	ND	ND	ND	ND	ND	ND
			11/5/2008	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	15
			2/25/2009	ND	ND	ND	ND	67	ND	ND	ND	ND	ND	ND	ND	ND
	Dilantin	5	5/22/2008	325	86	110	36	266	126	ND	163	167	145	92	128	143
			8/19/2008	267	106	117	38	239	109	ND	158	90	122	135	144	119
			11/5/2008	308	103	122	43	250	120	ND	218	178	160	153	123	141
			2/25/2009	245	50	77	41	227	90	ND	140	133	92	39	36	35
	Diuron	5	5/22/2008	ND	36	31	699	33	333	241	136	138	56	48	60	77
			8/19/2008	5	17	16	88	40	65	46	9	36	61	94	46	53
			11/5/2008	16	22	30	1020	39	3230	201	22	41	774	55	273	279
			2/25/2009	15	112	107	155	64	147	9440	24	513	29	110	1248	954
	Ethylparaben	20	5/22/2008													
			8/19/2008													
			11/5/2008								ND					
			2/25/2009													
	Lindane	10	5/22/2008													
			8/19/2008													
			11/5/2008								ND					
			2/25/2009													
	Linuron	5	5/22/2008	8	ND	ND	ND	6	ND	ND	5	ND	6	5	ND	ND
			8/19/2008	5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			11/5/2008	8	ND	ND	ND	6	ND	ND	5	ND	5	ND	ND	ND
			2/25/2009	5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Methoxychlor	20	5/22/2008	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			8/19/2008	ND	ND	ND	ND	ND	ND	ND	ND	23	ND	ND	ND	ND
			11/5/2008	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			2/25/2009	ND	ND	ND	ND	ND	23	31	ND	ND	ND	ND	ND	ND
	Methylparaben	20	5/22/2008													
			8/19/2008													
			11/5/2008								ND					
			2/25/2009													
	Propazine	20	5/22/2008													
			8/19/2008													
			11/5/2008								ND					
			2/25/2009													
	Propylparaben	20	5/22/2008													
			8/19/2008													
			11/5/2008								ND					
			2/25/2009													
	Simazine	20	5/22/2008	ND	29	24	36	33	43	115	31	60	23	ND	35	33
			8/19/2008	ND	ND	ND	23	ND	ND	ND	ND	ND	ND	ND	ND	ND
			11/5/2008	ND	ND	ND	38	ND	31	ND	ND	ND	26	27	26	24
			2/25/2009	ND	ND	ND	ND	61	55	81	ND	ND	ND	28	70	60
	TCEP	5	5/22/2008	496	160	174	57	390	175	43	451	370	533	327	225	123
			8/19/2008	653	157	199	69	530	198	51	527	208	306	265	249	198
			11/5/2008	455	183	208	69	509	173	148	463	465	337	248	194	217
			2/25/2009	1320	229	328	93	288	141	67	445	439	511	260	88	111

Lab	Analyte	MRL (ng/L)	Sampling Date	NORTH OF WWTP #2	WWTP #2	RIVERSIDE AVE	MWD XING	WWTP #3	RIVER RD	DEER CREEK CHANNEL	WWTP #4	CHINO CORONA RD	PRADO WETLANDS INLET	PRADO WETLANDS OUTLET	BELOW PRADO DAM	IMPERIAL HWY
OCWD	Acetaminophen	20	5/22/2008	ND	ND	ND	ND	ND	ND	210	ND	ND	ND	ND	ND	ND
		1	8/19/2008	9	4	5	3	420	270	130	7	82	460	6	8	4
		1	11/5/2008	9	6	13	9	26	23	200	14	51	30	14	180	430
		10	2/25/2009	ND	ND	ND	ND	ND	11	67	ND	33	11	ND	23	16
	Azithromycin	1	5/22/2008	ND	21	10	ND	ND	ND	ND	ND	ND	130	ND	ND	ND
		5	8/19/2008	ND	30	26	ND	69	ND	ND	ND	ND	23	ND	ND	ND
		5	11/5/2008	ND	67	54	ND	ND	ND	ND	ND	ND	180	ND	ND	ND
		5	2/25/2009	ND	78	68	ND	660	7	ND	9	38	600	ND	ND	ND
	Ciprofloxacin	40	5/22/2008	ND	57	69	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
		10	8/19/2008	20	58	27	10	21	28	20	28	28	44	41	24	22
		100	11/5/2008	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
		50	2/25/2009	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Diethylstilbestrol	10	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Epitestosterone	10	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	17a-Estradiol	10	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	17b-Estradiol	10	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Estriol	10	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Estrone	10	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Nonylphenol ethoxylate	10000	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Pentachlorophenol	1000	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	4-Phenylphenol	1000	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Progesterone	10	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Testosterone	10	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	Tetrabromobisphenol A	1000	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													
	2,4,6-Trichlorophenol	1000	5/22/2008	ND												
			8/19/2008													
			11/5/2008													
			2/25/2009													

APPENDIX C:

Colorado River Water (CRW) Results

Appendix C: Colorado River Water (CRW) Results

ND=Not detected; NS=Not sampled; NA=Not analyzed; Results reported as ng/L

Lab	Analyte	MRL (ng/L)	Sampling Date	LV WASH UPSTREAM	NEVADA WWTP BLEND	LV WASH DOWN STREAM	HOOVER DAM	BELOW DAVIS DAM	LAKE HAVASU INLET	LAKE HAVASU INTAKE	LAKE MATHEWS OUTLET
MWD and OCWD	Bisphenol A	30 (MWD)	Jun-08	ND	ND	ND	ND	ND	NS	ND	ND
			Sep-08	74	ND	ND	ND	ND	ND	ND	ND
			Dec-08	ND	ND	ND	ND	ND	ND	ND	ND
			Apr-09	ND	ND	ND	ND	ND	ND	ND	ND
	Caffeine	5	Jun-08	88	39	21	28	ND	NS	9	ND
			Sep-08	46	50	33	13	ND	ND	338	ND
			Dec-08	48	22	39	9	5	1370	174	ND
			Apr-09	185	11	16	ND	ND	519	ND	ND
	Carbamazepine	1	Jun-08	ND	203	161	3	3	NS	3	ND
			Sep-08	ND	187	182	3	3	3	2	1
			Dec-08	ND	204	197	2	2	2	2	ND
			Apr-09	ND	191	153	3	4	3	3	2
	DEET	20	Jun-08	ND	408	106	ND	ND	NS	ND	ND
			Sep-08	ND	131	82	ND	ND	10	28	ND
			Dec-08	ND	61	86	ND	ND	64	ND	ND
			Apr-09	ND	103	113	ND	ND	297	ND	ND
	Ethynylestradiol (EE2)	10	Jun-08	ND							
			Sep-08								
			Dec-08								
			Apr-09								
	Gemfibrozil	5	Jun-08	ND	40	4	ND	ND	NS	ND	ND
			Sep-08	ND	20	10	ND	ND	ND	ND	ND
			Dec-08	ND	9	13	ND	ND	ND	ND	ND
			Apr-09	ND	13	14	ND	ND	ND	ND	ND
	Ibuprofen	10	Jun-08	ND	ND	ND	ND	ND	NS	ND	ND
			Sep-08	ND	ND	ND	ND	ND	ND	ND	ND
			Dec-08	ND	ND	ND	ND	ND	ND	ND	ND
			Apr-09	19	13	14	ND	ND	36	ND	ND
	4-n-Nonylphenol	50	Jun-08	ND	ND	ND	ND	ND	NS	ND	ND
			Sep-08	ND	ND	ND	ND	ND	ND	ND	ND
			Dec-08	ND	ND	ND	143	ND	ND	ND	ND
			Apr-09	ND	ND	ND	ND	ND	ND	ND	ND
	4-*n*- and 4-*t*-Octylphenol	20	Jun-08	ND							
			Sep-08								
			Dec-08								
			Apr-09								
	Primidone	2	Jun-08	ND	134	125	3	3	NS	4	3
			Sep-08	ND	151	144	ND	ND	ND	2	2
			Dec-08	ND	161	145	3	3	3	2	2
			Apr-09	2	167	150	4	3	4	3	ND
	Sulfamethoxazole	1	Jun-08	2	762	565	16	15	NS	8	ND
			Sep-08	ND	1025	659	11	10	11	9	ND
			Dec-08	3	1240	817	12	8	8	7	1
			Apr-09	3	913	769	17	15	14	13	ND
	Triclosan	5	Jun-08	ND	ND	ND	ND	ND	NS	ND	ND
			Sep-08	ND	9	8	ND	ND	ND	ND	ND
			Dec-08	ND	12	7	ND	ND	ND	ND	ND
			Apr-09	ND	ND	ND	ND	ND	ND	ND	ND

Lab	Analyte	MRL (ng/L)	Sampling Date	LV WASH UPSTREAM	NEVADA WWTP BLEND	LV WASH DOWN STREAM	HOOVER DAM	BELOW DAVIS DAM	LAKE HAVASU INLET	LAKE HAVASU INTAKE	LAKE MATHEWS OUTLET
MWD	Anthracene	10	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Atrazine	1	Jun-08	ND	ND	ND	ND	ND	NS	ND	ND
			Sep-08	ND	ND	ND	ND	ND	ND	ND	ND
			Dec-08	ND	ND	ND	ND	ND	ND	ND	ND
			Apr-09	1	ND	ND	ND	ND	ND	ND	ND
	Atrazine-Desethyl	20	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Atrazine-Desisopropyl	20	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Benzo(a)pyrene	25	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Butylparaben	20	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Cyanazine	20	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Cyprazine	20	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	o,p-DDD	20	Jun-08	ND	ND	ND	ND	ND	NS	ND	ND
			Sep-08	ND	ND	ND	ND	ND	23	44	46
			Dec-08	ND	ND	ND	31	ND	ND	ND	ND
			Apr-09	ND	ND	ND	ND	ND	ND	ND	ND
	Diclofenac	5	Jun-08	ND	14	ND	ND	ND	NS	ND	ND
			Sep-08	ND	14	6	ND	ND	ND	ND	ND
			Dec-08	ND	25	11	ND	ND	ND	ND	ND
			Apr-09	ND	31	14	ND	ND	ND	ND	ND
	Dilantin	5	Jun-08	ND	159	131	ND	ND	NS	ND	ND
			Sep-08	ND	159	137	ND	ND	ND	ND	ND
			Dec-08	ND	129	119	ND	ND	ND	ND	ND
			Apr-09	ND	130	102	ND	ND	ND	ND	ND
	Diuron	5	Jun-08	16	15	23	ND	ND	NS	ND	ND
			Sep-08	14	26	25	ND	ND	ND	ND	ND
			Dec-08	99	402	318	ND	ND	ND	ND	ND
			Apr-09	42	28	28	ND	ND	ND	ND	ND
	Ethylparaben	20	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								

Lab	Analyte	MRL (ng/L)	Sampling Date	LV WASH UPSTREAM	NEVADA WWTP BLEND	LV WASH DOWN STREAM	HOOVER DAM	BELOW DAVIS DAM	LAKE HAVASU INLET	LAKE HAVASU INTAKE	LAKE MATHEWS OUTLET
	Lindane	10	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Linuron	5	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Methoxychlor	20	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Methylparaben	20	Jun-08	ND	29	ND	ND	ND	NS	35	ND
			Sep-08	ND	ND	ND	ND	ND	ND	ND	ND
			Dec-08	ND	ND	ND	ND	ND	ND	ND	ND
			Apr-09	ND	ND	ND	ND	ND	ND	ND	ND
	Propazine	20	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Propylparaben	20	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Simazine	20	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	TCEP	5	Jun-08	20	523	242	ND	ND	NS	7	ND
			Sep-08	15	519	389	5	ND	ND	9	ND
			Dec-08	10	392	300	8	ND	ND	ND	ND
			Apr-09	11	211	197	ND	ND	5	ND	ND
OCWD	**Acetaminophen**	10	Jun-08	ND	ND	ND	ND	NA	NS	ND	ND
		1	Sep-08	36	29	32	3	ND	4	14	ND
		1	Dec-08	61	14	20	ND	ND	5	3	ND
		1	Apr-09	44	2.7	28	1.2	ND	2.0	1.0	ND
	Azithromycin	1	Jun-08	ND	62	9	ND	ND	NS	ND	ND
		5	Sep-08	ND	240	13	13	ND	ND	ND	ND
		5	Dec-08	ND	280	90	ND	ND	ND	ND	ND
		5	Apr-09	ND	260	34	ND	ND	ND	5.5	ND
	Ciprofloxacin		Jun-08	NA	NA	NA	NA	NA	NA	NA	NA
		10	Sep-08	ND	36	21	ND	ND	ND	ND	ND
		10	Dec-08	ND	140	69	ND	ND	ND	ND	ND
		50	Apr-09	62	130	53	ND	ND	ND	ND	ND
	Diethylstilbestrol	10	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Epitestosterone	10	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								

Lab	Analyte	MRL (ng/L)	Sampling Date	LV WASH UPSTREAM	NEVADA WWTP BLEND	LV WASH DOWN STREAM	HOOVER DAM	BELOW DAVIS DAM	LAKE HAVASU INLET	LAKE HAVASU INTAKE	LAKE MATHEWS OUTLET
	17a-Estradiol	10	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	17b-Estradiol	10	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Estriol	10	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Estrone	10	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Nonylphenol ethoxylat	10000	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Pentachlorophenol	1000	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	4-Phenylphenol	1000	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Progesterone	10	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Testosterone	10	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	Tetrabromobisphenol A	1000	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								
	2,4,6-Trichlorophenol	1000	Jun-08					ND			
			Sep-08								
			Dec-08								
			Apr-09								