Monitoring of Trace-Level Pharmaceuticals and Personal Care Products in Salt River Project Waters

Final Report

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ABSTRACT

To investigate the occurrence of pharmaceutical, personal care products (PPCPs), and endocrine disrupt compounds (EDCs) in surface and ground waters throughout Arizona, 26 compounds were analyzed in samples from surface waters, water treatment plants (WTP), wastewater treatment plants (WWTP), ground water recharge facilities, and water recreation areas during September 2007 to July 2009. 116 samples in total were collected and analyzed using liquid chromatograph/tandem mass spectrometry (LC/MS/MS) analytical methods during spring, 2008 to summer, 2009. These compounds (PPCP/EDC) were prevalent during this study, being found in 95% of the samples collected. The most frequently detected compounds in surface waters were oxybenzone (up to 0.60 µg/L), caffeine (up to 0.05 µg/L), and sucralose (up to 0.33 µg/L). Three surface waters show different patterns of PPCP/EDC content: oxybenzone was most prevalent in Salt River and Verde River while sucralose occurred at an elevated level in one CAP canal location. The total concentration of PPCP/EDC varied seasonally with highest concentration detected during summer time. For WTP, the prevalent PPCP/EDC detected in surface water were also detected with high concentration in WTP raw waters and samples from sedimentation basin, However, chlorination could exert further oxidation on some compounds (especially oxybenzone) after disinfection. The raw wastewater was detected with high PPCP/EDC concentration and certain compounds (e.g. oxybenzone, ibuprofen, DEET, etc.) shows increasing trend during summer. WWTP processes can remove 11 out of 16 compounds up to 98% efficiency but shows poor removal for erythromycin, carbamazepine, and sulfamethoxazole (< 10%). Sucralose and sulfamethoxazole were dominated compounds (> 60%) in WWTP effluent. The data from water recreation area shows strong effect of human activity on PPCP/EDC in downstream waters, mostly from skin-applied products. These compounds were also present in ground water system of Phoenix water supply area (< 5 ng/L). Only sucralose and sulfamethoxazole were detected to be higher than 0.1 µg/L from one monitoring well. Overall, the top 6 detected a) most frequently: oxybenzone, caffeine, sucralose, DEET, sulfamethoxazole, and acetaminophen; b) with highest concentration: oxybenzone, caffeine, sucralose, DEET, sulfamethoxazole, and dilantin.

Results of this study demonstrate that PPCP/EDC levels are very low in central

Arizona drinking water supplies. Other sources of PPCP/EDC which might impact drinking water, like recreational activities, WWTP recharging sites, landfill sites, need to be investigated for overall water resource management in Arizona. To control the occurrence of PPCP/EDC in drinking water system, advanced techniques (e.g. AOPs, GAC adsorber, etc.) could be applied in water facilities, especially WWTPs. Long term monitoring of PPCP/EDCs in drinking water system is recommended.

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INTRODUCTION

Endocrine disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs) have been detected in water supplies and wastewater effluents around the world [1-4]. Some EDC/PPCPs exhibit adverse ecological impacts that have raised concern among public and regulatory groups about the fate of such compounds during potable water treatment and human exposure in drinking water [3,5-13]. Some EDC/PPCPs are more polar than currently USEPA regulated polyaromatic contaminants. This, coupled with occurrence at trace levels (parts per trillion), creates unique challenges for analytical detection and assessment of removal performance by potable water treatment plant (WTP) processes[3,12]. Drinking water treatment primarily relies upon adsorptive and oxidative processes to remove or transform organic materials. Recent studies for selected groups of EDC/PPCPs, pesticides and herbicides indicate that coagulation, sedimentation, and filtration achieve minimal levels of removal[13-16]. However, addition of common disinfectants (e.g., chlorine or ozone) can result in reaction and transformation of these compounds[17-26]. Below is short description of the potential removal of EDC/PPCPs by drinking water treatment plants.

Chemical coagulation and softening aid in removing suspended solids (i.e., turbidity) from the water and aid in removing dissolved organic carbon (DOC). Chemical coagulation in water treatment usually employs aluminum or iron based salts, which precipitate as metal hydroxides. Chemical lime softening removes dissolved calcium and magnesium using lime and soda-ash to precipitate calcium carbonate at lower pH and magnesium hydroxide at pH>11. Coagulation alone is generally not effective at removing trace-level organic pollutants [31,32].

Activated carbon adsorbs many organic pollutants [33]. The USEPA identifies packed-bed granular activated carbon (GAC) as a "Best Available Technology" for treating numerous regulated organic pollutants. Powder activated carbon (PAC) effectively removes many problematic organic pollutants (e.g., taste and odor compounds, some pesticides and herbicides). In GAC systems adsorbed contaminant concentrations equilibrate with influent liquid-phase concentrations, whereas in traditional PAC applications the solid phase contaminant concentrations approach equilibrium with reactor effluent liquid-phase concentrations. Traditional PAC applications add a PAC slurry at dosages of 1 to 25 mg/L to a solids-contact, or flocculation, chamber that have contact times of 0.5 to 5 hours; removal of PAC (with adsorbed compounds) occurs during sedimentation and filtration processes [34]. Sophisticated stand-alone systems using fluidized PAC reactors and recirculating PAC reactors coupled with ultrafiltration membrane systems both lead to long contact times between PAC and organics in the water, allowing full utilization of the PAC adsorption capacity [35-37].

For some organic compounds adsorptive removal by PAC may not be effective, but the compounds may be reactive with oxidants [38]. During water treatment, chlorine or ozone addition disinfectants inactivate microbes, oxidize reduced metals, and oxidize organic material. Electron density effects of functional groups, and degree of protonation affect the potential reactivity of organic compounds with oxidants [25,39,40]. Electron-donating (e.g., hydroxyl, amine) or electron-withdrawing (e.g., carboxyl) functional groups lead to increasing and decreasing reactivity, respectively, for substituted aromatic rings [40]. For example, free chlorine reacts rapidly with phenolic

compounds, mainly through the reaction between HOCl and the deprotonated phenolate anion [41]. This results in sequential chlorine addition to the aromatic ring followed by ring cleavage. The reactivity of the phenolic functional group likely explains the rapid transformation during chlorination of some estrogenic hormones (estradiol, ethynylestradiol, estriol, estrone) which contain phenolic moieties [17,21,27]. The formation, fate, detection, and toxicity of oxidative by-products from pesticides and EDC/PPCPs is of potential concern [17,27,42].

Several studies have investigated EDC or PPCP removal by ozone or chlorine, but direct comparisons are lacking between these two oxidants and a broad range of EDC/PPCPs under conditions typical of drinking water treatment facilities. The transformation of several amine-containing antibiotics, diclofenac, and caffeine were observed in laboratory experiments with chlorine [14,24,43]. Ozonation of estrogenic chemicals is effective [21,44], but there is limited data on the reactivity of non-estrogen based hormones (e.g., testosterone, progesterone, androstenedione), and hence these were included in our study. Ozonation significantly reduced concentrations of several estrogens, musk fragrances and some pharmaceuticals (diclofenac, carbamazepine, and bezafibrate), but not clofibric acid [45,46]. Removal of clofibric acid, ibuprofen, and diclofenac improved when ozonation was conducted in the presence of hydrogen peroxide (0.4 to 0.7 mgH_2O_2 / mgO_3 dosed) [26,47]. As ozone decays in water, the reactions produce hydroxyl ($HO^{\bullet}$) radicals. H_2O_2 addition increases the rate of molecular ozone decay (i.e., lower molecular ozone concentrations) but also increases $HO^{\bullet}$ concentrations. Molecular ozone is a selective electrophile that reacts with amines, phenols, and double bonds, whereas $HO^{\bullet}$ reacts less selectively with organic compounds

[25,48,49]. Due to the selective nature of ozone, micropollutant transformation may require the use of advanced oxidation processes (AOPs), such as O_3/H_2O_2 [42,50].

Recently, Westerhoff's research group published a series of papers investigating the removal EDC/PPCPs and their biological attenuation in the subsurface (e.g., [52-59]). With seed funding the Arizona Water Institute, Westerhoff (ASU) worked with Arizona Department of Health Services (ADHS) to develop analytical methods for the detection of this same suite of EDC/PPCPs in the environment. The project is taking advantage of a state-of-the-art liquid chromatographic mass spectrometry (LC/MS/MS) instrument purchased by ADHS/CDC for use during terrorist emergencies. This equipment sees routine CDC testing usage only a few weeks of the year and ADHS has made it available to trained staff for ASU as part of collaborative projects. We would like to leverage this opportunity with ADHS to understand the distribution of EDC/PPCPs in the Salt River Project watershed. Recently the Associate Press (AP) has published stories about EDC/PPCPs in drinking water. Many municipalities are concerned about the potential for EDC/PPCPs to be present in their water supplies, and their presence may affect future treatment decisions.

The goals of this project were to provide SRP with baseline data for EDC/PPCPs in the SRP watershed, including canals and recharge systems. This data provides information on the occurrence of these compounds, but also their natural attenuation in the environment. The sampling were integrated into the Regional Water Quality Monitoring project lead by Prof. Westerhoff and supported by the Cities of Phoenix, Tempe, Peoria, and Chandler plus Central Arizona Project. The work involves the

following tasks:

- **Task 1 – Watershed Sampling**
- **Task 2 – Canal Sampling**
- **Task 3 – Recharge and Groundwater Sampling**
- **Task 4 – Recommendations for Monitoring for Organics of Wastewater Origin**

MATERIALS AND METHODS

Site Selection and Sampling

To provide a state-wide view of PPCP/EDC present in Salt River Project waters in Arizona, all samples were collected according to the tasks descript earlier. Surface waters were collected from three different water sources for Phoenix area water supply: Verde River (Verde River at Beeline Highway), the Waddell Canal (near Lake Pleasant Road), and the Salt River (Blue Point Bridge) and these samples were collected bi-monthly (see Appendix A). Samples were also collected bi-monthly from one water treatment plant (WTP A, see Appendix A) to represent the drinking water samples including raw water, sedimentation effluent and finished waters (after chlorination). Wastewater samples were collected once during this project from 8 wastewater treatment plants (see Appendix A&B) effluents and full-investigation (samples from raw wastewater, tertiary effluent, and effluent) only conducted for WWTP A. Three measuring wells of GRUSP recharging project (see Appendix C) were selected as samples represented for groundwater in Phoenix area water supply. These groundwater samples were collected three times during this project. In addition, two water recreation sites (see Appendix D) were selected to testify the occurrence of PPCP/EDC in surface waters resulted from human activities. All

these samples were collected during September 2007 to July 2009.

All samples were collected by ASU using 1-Liter ashed amber bottles and stored on ice. 100 mg/L of sodium azide and 50 mg/L of ascorbic acid were added right after bringing back to laboratory to prevent biodegradation and samples were filtered using 0.7 μm filter paper (GF/F, Whatman) before analysis. For the purpose of recovery correction (based upon EPA Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS), all the standard and field samples were spiked with the same amount (50 ng/L) of IS (Acetaminophen-D4, Caffeine-13C3, 13C-Naproxen-D3, Carboamazepine-D10, Estradiol-13C2) before filtration.

Analytical Methods

Solid phase extraction was performed for each of filtered water samples taken from the WWTPs and surface water samples using a Caliper Life Sciences Auto Trace extraction manifold. Methanol (HPLC grade, Fisher Chemical), MTBE (HPLC grade, Fisher Chemical), toluene (HPLC grade, Fisher Chemical) and water (HPLC grade, Honeywell, B&J) were used as solvents conducted with Waters Oasis HLB extraction cartridges. PPCP analysis was performed with cooperation from Arizona Department of Health Services using Applied Biosystems API4000 triple quadrupole mass spectrometer and Agilent 1100 Series HPLC system. A Phenomenex Synergi 4 micron Max RP 80A column was used for analyte separation. An LC gradient of water with 0.01% formic acid (A) and methanol with 0.01% formic acid (B) at a flow rate of 700uL/min was used. The gradient was as follows: 5% (B) held for 3.5 min, increased linearly to 80% (B) at 10 min. and held for 3 min., at 13.5 min ramped to 100 % (B) and held until 21 min., at

21.5 min ramped back down to 5% (B) and held until 30.0 min.

Twenty two prescription drugs, artificial sweetener, and personal care products and four steroids were selected as target compounds because of high frequency of household application and previous research (Kolpin et al., 2002) identified them as prevalent in the environment. None of the 26 PPCP/EDC compounds have the regulated criteria or guidelines of Maximum contaminant level (MCL). The effects of short term-high dose exposure conducted in aquatic-life were summarized in Table 1 and the detected concentrations of these compounds in the surface waters were much lower than the aquatic-life criteria. However, chronic effects from long term-low level environmental exposure to select PPCP/EDC appear to be of much greater concern and sufficient data collection will be required for further study. Samples were analyzed in each of three modes: APCI positive, ESI positive, and ESI negative. Compounds detected by APCI positive mode included the steroids- estradiol, ethynyl estradiol, progesterone, and testosterone. Compounds analyzed in ESI positive mode were: acetaminophen, caffeine, carbamazepine, cotinine, deet, diazepam, fluoxetine, hydrocodone, meprobamate, pentoxifylline, primidone, oxybenzone, sulfamethoxazole, erythromycin, and trimethoprim. Compounds detected by ESI negative were: ibuprofen, naproxen, dilantin, triclosan, diclofenac, tetrabromobishpenol a, and suclralose. Standards for these compounds were supplied by ADHS and the LC/MS/MS operating conditions were shown in Appendix E. Internal standards including acetaminophen- D4 (Cerilliant), 13C-naproxen- D3 (Cambridge Isotope), estradiol- 13C2 (Cambridge Isotope), caffeine-D3 and carbamazepine- D10 (Cambridge Isotope) were spiked before filtration for recovery correction.

Quality Assurance Protocol

Laboratory blanks were used to assess potential sample contamination. These blanks were prepared using nanopure waters in laboratory. Field blanks were also used to determine the effect, if any, of filed equipment and procedures on the concentrations of PPCP/EDC during water sampling. These field blanks were also prepared using nanopure water and transferred into another clean, ashed bottle during water sampling. All these blanks were subject to the same sample processing, handling, and equipment as the real samples. Concentrations obtain from blanks were not subtracted from environmental results. Environmental concentrations within the values observed in the set of blanks plus two times of standard deviation were reported as insignificant concentration or zero. The results of measured concentration in all blank samples and the statistical report were shown in Appendix F. Furthermore, 50 μg/L of 5 internal standards were spiked into calibration standards and all field samples and blanks for recovery calculation (summarized in Appendix G). All the data shown in this research are compared with blank results to be significantly detected and corrected with recovery efficiency. However, no recovery test was performed for sucralose and steroids and the results of these compounds shown in this research represent the minimum contamination level.

RESULTS AND DISCUSSION

Occurrences of PPCP/EDC in Surface Waters

Three surface waters in Phoenix metropolitan area drinking water supply were investigated in this study: Waddell Canal, Salt River, and Verde River. From September 2007 to July 2009, 24 samples in total were collected from these three surface waters. One or more PPCPs/EDCs were found in more than 95% of the 24 surface water samples for this study. The PPCPs/EDCs results were compared with lab-blank samples and field-blank samples to make sure the measurements were significant and were not due to artificial error.

Table 2 shows the detected results of PPCPs/EDCs in three surface waters during this study. Progesterone was the only endocrine disrupting compound detected in the surface water samples analyzed. Measured concentrations were generally low (less than 50 ng/L) with two compounds (oxybenzone and sucralose) exceeding 300 ng/L in some samples during this study. 15 out of 26 target compounds were identified to be prevalent anthropogenic contaminants in the surface waters (> 50% occurrences) while caffeine, DEET, sucralose, and oxybenzone were detected in most of the samples (> 90% occurrences).

To obtain a broader view of the long-term variation for individual surface water, the monthly results were divided into two groups, summer and other seasons. Figure 1 shows the monthly total PPCP/EDC concentration for different surface waters and different PPCP/EDC content between summer and other seasons. Overall, the occurrence and measured concentration for three surface waters were all higher during summer than other seasons. Salt River water was detected with highest PPCP/EDC concentration during summer (> 350 ng/L, averagely) but reduced mostly during other seasons (to 120

ng/L). CAP canal and Verde River samples shows less variance (30% difference) between summer and other seasons and CAP canal was detected with highest total concentration during other seasons. From the point of view of content percentage, sucralose was detected with highest concentration in CAP canal at any season (60% to 75%). For Salt River, oxybenzone was detected as more than 80% in total PPCP/EDC measured but decreased to 16% during other seasons. Verde River was measured with lowest concentration of total PPCP/EDC and oxybenzone was detected as the highest concentration among total PPCP/EDC during summer. The different patterns of PPCP/EDC content between different water sources during different seasons could be important information for water treatment plants planning switch source waters throughout a year.

Occurrences and Fate of PPCP/EDC in Water Treatment Plant

Samples collected from water treatment plant A (WTP A) were used for PPCP/EDC analysis and examination of the fate during water treatment processes. WTP A is a utility on a SRP canal. Raw water, settled water, and finished water from this water treatment plant were collected for analysis in this study. 31 samples in total were collected from September 2007 to July 2009. 4 out of 11 raw water samples were detected with > 0.1 μg/L of total PPCP/EDC content. 8 out of 9 finished water samples were detected with PPCP/EDC residual (27 ng/L, averagely).

Table 3 shows the detected results of PPCPs/EDCs in WTP A during this study. The measured concentrations for each compound were generally lower than 5 ng/L and hydrocodone was not detected significantly in all WTP A samples. For raw waters, 5 compounds (caffeine, cotinine, DEET, oxybenzone, and sucralose) were defined as

prevalent emerging contaminants (> 50% occurrences) while 90% of raw waters were detected with DEET present. Caffeine, DEET, oxybenzone, and sucralose were also detected with higher than 10 ng/L in some samples and oxybenzone was detected to be higher than 100 ng/L in one sample. The water treatment processes shows > 50% removal when these compounds were detected as higher than 5 ng/L in raw waters. Chlorination shows further oxidation on oxybenzone which can remove 60% more in the finished water. The PPCP/EDC residual remained in finished could be potential drinking water issue that further investigation on source waters and fate of PPCP/EDC in drinking water system are important.

Seasonal effects were observed for PPCP/EDC detected in WTP waters. Figure 2 summarized the summer and other seasons total PPCP/EDC content. During summer, oxybenzone was detected with the highest concentration (59%) in raw waters. However, oxybenzone would be removed totally after chlorination. During the other three seasons, the concentration of oxybenzone decreased and sucralose increased and the total concentration of PPCP/EDC detected declined to only half of summers level. Before chlorination, WTP processes (coagulation, sedimentation, and filtration) shows similar capacity to remove oxybenzone during different (16 ng/L for summer and 12 ng/L for the other seasons). However, > 99% of oxybenzone will be oxidized further by chlorination in all seasons. The similar total PPCP/EDC concentration in finished water in all seasons indicated that these residue of PPCP/EDC remained in water phase were relatively stable which can resist most of chemical, biological, and physical degradation throughout environmental system and water treatment processes.

Occurrence and Fate of PPCP/EDC in Wastewater Treatment Plant

Wastewater samples were collected from wastewater treatment plant A. Raw wastewaters, tertiary effluent, and effluent after UV treatment were collected in this study. 30 samples in total were collected from September 2007 to July, 2009. All 26 compounds were detected in more than one raw wastewater samples and the highest measured concentration was acetaminophen (250 μg/L) and lowest was diazepam (2 ng/L).

Table 4 shows the detected PPCP/EDC from wastewater treatment plant A samples. In raw wastewaters, most of the compounds were detected from 0.1 to 10 μg/L (16/26) and acetaminophen, caffeine, ibuprofen, and naproxen were detected to be higher than 10 μg/L, averagely. Hormone concentrations were generally from 20 to 80 ng/L as detected in raw wastewaters. In tertiary effluent and effluent after UV treatment wastewaters, the total concentration of PPCP/EDC was declined significantly from 250 μg/L (in raw wastewaters) to 9 μg/L. The highest detected amount were sucralose and sulfamethoxzole (about 2.4 μg/L). Hormones and diazepam were detected to be lowe than 5 ng/L. However, the removal efficiency of each compounds by wastewater treatment processes are varied (shown in Figure 3). Several compounds (acetaminophen, caffeine, naproxen, ibuprofen, oxybenzone, cotinine, triclosan, TBBA, testosterone, pentoxifylline, estradiol, ethinyl estradiol, and progesterone) were removed > 90% during wastewater treatment units. For some compounds (sulfamethoxazole, carbamazepine, dilantin, and erythromycin) the removal efficiency was much lower (< 20%). K_{ow} and solubility (in Table 1) were not the main factors that dominated the PPCP/EDC removal during wastewater treatment processes because the poor correlations were found.

There also appears to be a seasonal effect in the raw wastewaters. Of the 26 compounds detected in raw wastewaters, 73% were found at higher concentrations during the summer (May to August), and 46% were detected to be more than 50% difference

between summer and other seasons. The average summer concentrations of hormones and fluoxetine were higher than those in the other seasons. These data of PPCP/EDC in raw wastewaters can reflect the Arizona household pharmaceutical using trends.

To provide state-wide view of PPCP/EDC in wastewater effluent which might be potential emerging contaminants in drinking water, wastewater effluent samples were collected once during May, 2009 from eight wastewater treatment plants (Table 5) (see Appendix A&B for WWTPs location). Overall, three hormones (ethinyl estradiol, progesterone, and testosterone), diazepam, and TBBA were reported to be not detectable or less than 5 ng/L. Sucralose consistently remained in all 8 wastewater effluents (3±1.74 μg/L). Sulfamethoxazole was also present in all effluents with high concentration (2.3±0.95 μg/L) expect one sample with 12 ng/L of sulfamethoxazole detected. This might result from different wastewater processes in different wastewater treatment plants. Generally, total PPCP/EDC concentration remaining in wastewater effluents varied from 3.5 μg/L to 1.2 μg/L depending on different treatment techniques. Except sucralose and sulfamethoxazole, caffeine (0.02 to 4 μg/L), carbamazepine (0.15 to 0.3 μg/L), DEET (0.03 to 0.5 μg/L), oxybenzone (0.04 to 0.3 μg/L), and primidone (0.03 to 0.2 μg/L) were also constantly detected in wastewater effluents.

Occurrence of PPCP/EDC in Groundwater at a Recharge Site

Groundwater samples were collected from three monitoring wells at GRUSP during August, 2008, January and July, 2009 in this study. 9 samples in total were collected and three well volumes of groundwater were pumped out until pH and conductance were constant before sampling.

Table 6 shows the PPCP/EDC results detected from the groundwater samples. Most

of the compounds were detected with concentration lower than 5 ng/L from these three sampling. 7 out of 26 compounds were not detected significantly from any of these samples. Erthromycin, meprobamate, and pentoxifylline were most prevalent compounds which were detected from all 9 samples but with low concentrations (< 10 ng/L). Dilantin, oxybenzone, sucralose, and sulfamethoxzole were detected to be higher than 10 ng/L in some samples while sucralose and sulfamethoxzole have been detected to be higher than 100 ng/L in samples from measuring well No. 3. As discussed in section "Wastewaters" sucralose and sulfamethoxzole were mentioned to be highest amount of PPCP/EDC residuals remaining in wastewater effluent, the high concentration of them found in groundwater might be correlated with Arizona household drug usage habit. However, these high concentration compounds detected in groundwater need further investigation to clarify the possible sources, like surface water discharge, wastewater discharge, or intrusion from landfill sewage. Groundwater hydrology is worth investigation for understanding the occurrence of PPCP/EDC in groundwater system as part of drinking water sources.

The Impact of PPCP/EDC Occurrence in Surface Waters by Water Recreational Activities

To understand the human activities effect on PPCP/EDC occurrence in surface water, two famous water recreation areas were selected for investigation in this study: Slide Rock Park and Salt River Tubing site. The Slide Rock Park is in Coconino National Forest and the water recreation park is on Oak Creek River (branch of Verde River) open from late May to early September every year. The Salt River Tubing is a water recreation site in Tonto National Park near Blue Point Bridge on Salt River which is open from late

May to early September. The sampling location of Slide Rock Park was at Manzanita Camp Ground (1.5 miles downstream Slide Rock Park) and the sampling location for Salt River was at 3 miles downstream Blue Point Bridge. Samples were collected from morning before site open until site closed in one day.

Table 7 shows the total PPCP/EDC detected from the three water recreation events. In the beginning of the event, water samples were collected 1 mile upstream the recreation site as background of the PPCP/EDC present in water. The total PPCP/EDC concentration as background was about 0.1 to 0.3 μg/L for Salt River and was about 0.15 μg/L for Oak Creek River. Along the time, total PPCP/EDC detected in downstream Salt River increased to 0.8 μg/L at noon and increased up to 5 to 6 μg/L at 4:00 pm. The flow rate of Salt River during summer is about 1.2 miles per hour and the tubing area covered about 5 miles of Salt River. The increasing trend of PPCP/EDC in river water indicates that these compounds might be released from tourists and flowed along river. Similar PPCP/EDC trend was also found in Slide Rock water recreation event but the highest total PPCP/EDC concentration detected was 2.4 μg/L at 5:00 pm. Of 26 compounds, only 6 compounds (acetaminophen, caffeine, cotinine, DEET, naproxen, oxybenzone, and sucralose) were detected in at least one sample from 2008 Salt River hourly sampling. Among 6 detected compounds (shown in Figure 4.a), continine and sucralose were detected constantly with low concentration (< 10 ng/L) while other compounds were detected to be increasing over time, especially oxybenzone (up to 6 μg/L). For 2009 Slide Rock hourly sampling (Figure 4.b) 6 compounds (acetaminophen, caffeine, cotinine, DEET, maprobamate, oxybenzone, and sucralose) were detected in at least one sample: continine, maprobamate, and sucralose tended to be constant (< 10 ng/L) and others tended to be increasing over time. The hourly sampling for water recreation areas shows

that human activity exerted significant effect on PPCP/EDC present in surface water even though wastewater was not discharged into river upstream directly. Most of the sources for these detected PPCPs were from skin-applied products, like sunscreen and insect-repellent.

To verify the trend of PPCP/EDC in river after water recreation site closed, few more samples were collected for 2009 Salt River sampling (shown in Figure 4.c). Similar trend was shown for the same compounds as in Figure 4.a before 4:00 pm and a decreasing of these compounds was observed after 4:00 pm. This observation conformed to the closing time of this site at 3:00 pm and testified the increasing of PPCP/EDC concentration in river was due to human activity.

SUMMARY

- The PPCP/EDC detected levels are varied in different waters from less than 10 ng/L (several compounds in groundwater) to 100 μg/L (in raw wastewaters) which is summarized in Table 8.
- Low levels of PPCP/EDC were routinely detected in surface water systems.
- Recreational activities and wastewater inputs are important sources of PPCP/EDC present in canal system of Phoenix area especially during summers.
- Seasonal effects on different surface waters might influence raw water quality of WTP during source water switch by SRP.
- Tracking the occurrences and fate of these PPCP/EDCs in drinking water system and establishing the database is important for water management of metropolitan Phoenix region to control these unregulated organic compounds in case of abrupt issue.

- For future monitoring, other possible sources of PPCP/EDC which might impact drinking water, like lakes, WWTP recharging sites, landfill sites, need to be investigated for overall water resource management in Arizona.
- The monitoring should focus on at least top 10 compounds detected most frequently and with highest concentration, including oxybenzone, caffeine, sucralose, DEET, sulfamethoxazole, acetaminophen, and dilantin.

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REFERENCES

1) Kolpin, D. W.; Furlong, E. T.; Meyer, M. T.; Thurman, E. M.; Zaugg, S. D.; Barber, L. B.; Buxton, H. T., Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999-2000: A national reconnaissance, *Environ. Sci. Technol.,* **2002**, *36*, 1202-1211.

2) Ternes, T. A., Occurrence of drugs in German sewage treatment plants and rivers, *Water Res.,* **1998**, *32*, 3245-3260.

3) Snyder, S. A.; Westerhoff, P.; Yoon, Y.; Sedlak, D. L., Pharmaceuticals, personal care products, and endocrine disruptors in water: implications for water treatment, *Environ. Engin. Sci.,* **2003**, *20*, 449-469.

4) Daughton, C. H.; Ternes, T. A., Special Report: Pharmaceuticals and personal care products in the environment: agents of subtle change? (vol 107, pg 907, 1999), *Environ. Health Perspect.,* **2000**, *108*, 598-598.

5) Ongerth, J. E.; Khan, S., Drug Residuals: How xenobiotics can affect water supply sources, *J. Amer. Water Works Assoc.,* **2004**, *96*, 94-101.

6) Weyer, P.; Riley, D., Endocrine disruptors and pharmaceuticals in drinking water, Awwa Research Foundation, Denver, CO, 2001.
7) Warren, R.; Walker, B.; Nathan, V. R., Environmental factors influencing public health and medicine: Policy implications, *J. Nation. Med. Assoc.,* **2002**, *94*, 185-193.
8) Foster, P. M. D.; McIntyre, B. S., Endocrine active agents: Implications of adverse and non-adverse changes, *Toxicol. Pathology,* **2002**, *30*, 59-65.
9) Mantovani, A.; Macri, A., Endocrine effects in the hazard assessment of drugs used in animal production, *J. Experiment. & Clinic. Cancer Res.,* **2002**, *21*, 445-456.
10) Ankley, G.; Mihaich, E.; Stahl, R.; Tillitt, D.; Colborn, T.; McMaster, S.; Miller, R.; Bantle, J.; Campbell, P.; Denslow, N.; Dickerson, R.; Folmar, L.; Fry, M.; Giesy, J.; Gray, L. E.; Guiney, P.; Hutchinson, T.; Kennedy, S.; Kramer, V.; LeBlanc, G.; Mayes, M.; Nimrod, A.; Patino, R.; Peterson, R.; Purdy, R.; Ringer, R.; Thomas, P.; Touart, L.; Van der Kraak, G.; Zacharewski, T., Overview of a workshop on screening methods for detecting potential (anti-) estrogenic/androgenic chemicals in wildlife, *Environ. Toxicol. Chem.,* **1998**, *17*, 68-87.
11) Daston, G. P.; Cook, J. C.; Kavlock, R. J., Uncertainties for endocrine disrupters: Our view on progress, *Toxicological Sciences,* **2003**, *74*, 245-252.
12) Snyder, S. A.; Vanderford, B. J.; Pearson, R. A.; Quinones, O.; Yoon, Y., Analytical methods used to measure endocrine disrupting compounds in water, *Pract. Periodical of Haz., Toxic, and Radioactive Waste Mgmt,* **2003**, *7*, 224-234.
13) Zhang, T. C.; Emary, S. C., Jar tests for evaluation of atrazine removal at drinking water treatment plants, *Environ. Eng. Sci.,* **1999**, *16*, 417-432.
14) Adams, C.; Wang, Y.; Loftin, K.; Meyer, M., Removal of antibiotics from surface and distilled water in conventional water treatment processes, *J. Environ. Eng.-ASCE,* **2002**, *128*, 253-260.
15) Petrovic, M.; Eljarrat, E.; de Alda, M. J. L.; Barcelo, D., Analysis and environmental levels of endocrine-disrupting compounds in freshwater sediments, *Trac-Trends Anal. Chem.,* **2001**, *20*, 637-648.
16) Ternes, T. A.; Meisenheimer, M.; McDowell, D.; Sacher, F.; Brauch, H. J.; Gulde, B. H.; Preuss, G.; Wilme, U.; Seibert, N. Z., Removal of pharmaceuticals during drinking water treatment, *Environ. Sci. Technol.,* **2002**, *36*, 3855-3863.
17) Alum, A.; Yoon, Y.; Westerhoff, P.; Abbaszadegan, M., Oxidation of bisphenol a, 17b-estradiol, and 17a-ethynyl estradiol and byproduct estrogenicity, *Environmental Toxicology,* **2004**, *19*, 257-264.
18) Hu, J. Y.; Aizawa, T.; Ookubo, S., Products of aqueous chlorination of bisphenol A and their estrogenic activity, *Environ. Sci. Technol.,* **2002**, *36*, 1980-1987.

19) Hu, J. Y.; Cheng, S. J.; Aizawa, T.; Terao, Y.; Kunikane, S., Products of aqueous chlorination of 17 beta-estradiol and their estrogenic activities, *Environ. Sci. Technol.,* **2003**, *37*, 5665-5670.

20) Huber, M.; Canonica, S.; von Gunten, U., Oxidative treatment of pharmaceuticals in drinking waters, AWWA EDC Workshop, Cincinnati, OH2002.

21) Huber, M. M.; Canonica, S.; Park, G. Y.; Von Gunten, U., Oxidation of pharmaceuticals during ozonation and advanced oxidation processes, *Environ. Sci. Technol.,* **2003**, *37*, 1016-1024.

22) Lee, B. C.; Kamata, M.; Akatsuka, Y.; Takeda, M.; Ohno, K.; Kamei, T.; Magara, Y., Effects of chlorine on the decrease of estrogenic chemicals, *Water Res.,* **2004**, *38*, 733-739.

23) Lopez, A.; Mascolo, G.; Tiravanti, G.; Passino, R., Degradation of herbicides (ametryn and isoproturon) during water disinfection by means of two oxidants (hypochlorite and chlorine dioxide), *Water Sci. Technol.,* **1997**, *35*, 129-136.

24) Pinkston, K. E.; Sedlak, D. L., Transformation of aromatic ether and amine containing pharmaceuticals during chlorine disinfection, *Environ. Sci. & Tech.,* **2004**, *38*, 4019-4025.

25) Von Gunten, U., Ozonation of drinking water: Part I. Oxidation kinetics and product formation, *Water Res.,* **2003**, *37*, 1443-1467.

26) Zwiener, C.; Frimmel, F. H., Oxidative treatment of pharmaceuticals in water, *Water Res.,* **2000**, *34*, 1881-1885.

27) Huber, M. M.; Ternes, T. A.; von Gunten, U., Removal of estrogenic activity and formation of oxidation products during ozonation of 17 alpha-ethinylestradiol, *Environ. Sci. & Tech.,* **2004**, *38*, 5177-5186.

28) Beltran, F. J.; Garciaaraya, J. F.; Acedo, B., Advanced oxidation of atrazine in water .1. ozonation, *Water Res.,* **1994**, *28*, 2153-2164.

29) Beltran, F. J.; Garcia-Araya, J. F.; Rivas, J.; Alvarez, P. M.; Rodriguez, E., Kinetics of simazine advanced oxidation in water, *J. Environ. Sci. Health Part B-Pestic. Contam. Agric. Wastes,* **2000**, *35*, 439-454.

30) Gould, J. P.; Richards, J. T., The kinetics and products of the chlorination of caffeine in aqueous-solution, *Water Res.,* **1984**, *18*, 1001-1009.

31) Eldib, M. A.; Aly, O. A., Removal of phenylamide pesticides from drinking waters .1. Effect of chemical coagulation and oxidants, *Water Res.,* **1977**, *11*, 611-616.

32) Montiel, A.; Welte, B., Alternative options for atrazine - incidence on water-treatment device, *Water Sci. Technol.,* **1992**, *25*, 103-110.

33) Crittenden, J. C.; Sanongraj, S.; Bulloch, J. L.; Hand, D. W.; Rogers, T. N.; Speth, T.

F.; Ulmer, M., Correlation of aqueous-phase adsorption isotherms, *Environ. Sci. Technol.,* **1999**, *33*, 2926-2933.

34) Bruce, D.; Westerhoff, P.; Brawley-Chesworth, A., Removal of 2-methylisoborneol and geosmin in surface water treatment plants in Arizona, *J. Water Supply Res Technol.-AQUA,* **2002**, *51*, 183-197.

35) Dosoretz, C. G.; Boddeker, K. W., Removal of trace organics from water using a pumped bed-membrane bioreactor with powdered activated carbon, *J. Membrane Sci.,* **2004**, *239*, 81-90.

36) Herzberg, M.; Dosoretz, C. G.; Tarre, S.; Michael, B.; Dror, M.; Green, M., Simultaneous removal of atrazine and nitrate using a biological granulated activated carbon (BGAC) reactor, *J. Chem. Technol. Biotechol.,* **2004**, *79*, 626-631.

37) Qi, S. Y.; Adham, S. S.; Snoeyink, V. L.; Lykins, B. W., Prediction and verification of atrazine adsorption by PAC, *J. Environ. Eng. -ASCE,* **1994**, *120*, 202-218.

38) Boyd, G. R.; Reemtsma, H.; Grimm, D. A.; Mitra, S., Pharmaceuticals and personal care products (PPCPs) in surface and treated waters of Louisiana, USA and Ontario, Canada, *Sci. Tot. Environ.,* **2003**, *311*, 135-149.

39) Von Gunten, U., Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine, *Water Res.,* **2003**, *37*, 1469-1487.

40) Gallard, H.; Von Gunten, U., Chlorination of phenols: Kinetics and formation of chloroform, *Environ. Sci. Technol.,* **2002**, *36*, 884-890.

41) Faust, B. C.; Hoigne, J., Sensitized Photooxidation of phenols by fulvic-acid and in natural-waters, *Environ. Sci. Technol.,* **1987**, *21*, 957-964.

42) Acero, J. L.; Von Gunten, U., Characterization of oxidation processes: ozonation and the AOP O-3/H2O2, *J. Am. Water Work Assoc.,* **2001**, *93*, 90-100.

43) Huang, C. H.; Sedlak, D., Analysis of estrogenic hormones in wastewater and surface water using ELISA and GC/MS/MS, *Abstr. Pap. Am. Chem. Soc.,* **2000**, *219*, 5-ENVR.

44) Carlile, P.; Fielding, M.; Harding, L.; Hart, J.; Hutchison, J.; Kanda, R., Effect of water treatment processes on oestrogenic chemicals, UK WIR Report 96/DW/05/01, 1996.

45) Ternes, T. A.; Stuber, J.; Herrmann, N.; McDowell, D.; Ried, A.; Kampmann, M.; Teiser, B., Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater?, *Water Res.,* **2003**, *37*, 1976-1982.

46) Sacher, F.; Haist-Gulde, B.; Brauch, H.; Preub, G.; Wilme, U.; Zullei-Seibert, N.; Meisenheimer, M.; Welsch, h.; Ternes, T., Behavior of selected pharmaceuticals

during drinking water treatment, *.American Chemical Society Meeting, San Francisco, March,* **2000**.

47) Carlson, K. *Current and emerging drinking water treatment technologies.*: Place, Published, 2000.

48) Haag, W. R.; Yao, C. C. D., Rate constants for reaction of hydroxyl radicals with several drinking-water contaminants, *Environ. Sci. Technol.,* **1992**, *26*, 1005-1013.

49) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B., Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/•O-) in aqueous solution., J. Physical Ref. Data, **1988**, *17*, 513-851.

50) Acero, J. L.; Stemmler, K.; Von Gunten, U., Degradation kinetics of atrazine and its degradation products with ozone and OH radicals: A predictive tool for drinking water treatment, *Environ. Sci. Technol.,* **2000**, *34*, 591-597.

51) Vanderford, B. J.; Pearson, R. A.; Rexing, D. J.; Snyder, S. A., Analysis of endocrine disruptors, pharmaceuticals, and personal care products in water using liquid chromatography/tandem mass spectrometry, *Anal. Chem.,* **2003**, *75*, 6265-6274.

52) Yoon, Y.; Westerhoff, P.; Snyder, S. A.; Esparza, M., HPLC-fluorescence detection and adsorption of bisphenol A, 17β-estrodiol, and 17α-ethynyl estradiol on powered activated carbon, *Water Research*, **2003**, 37:14, 3530-3537.

53) Synder S.; Westerhoff P.; Yoon Y.; Sedlak D., Pharmaceuticals, personal care products, and endocrine disruptors in water: implications for the water industry, *Environmental Engineering Science*, **2003**, 20:5, 449-469.

54) Alum, A.; Yoon, Y.; Westerhoff, P.; Abbaszadegan, M., Oxidation of bisphenol A, 17β-estradiol, 17α-ethynyl estradiol and by-product estrogenicity, *Environmental Toxicology*, **2004**, 19:3, 257-264.

55) Snyder S.; LeisingJ.; Westerhoff P.; Yoon Y.; Mash H.; Vanderford B.; Biological attenuation of edcs and ppcps: implications for water reuse, *Ground Water Monitoring and Remediation,* **2004**, 24:2, 108-118.

56) Yoon Y.; Westerhoff P.; Yoon J.; Snyder S., Removal of 17-β estradiol and fluoranthene by nanofiltration and ultrafiltration membranes, *ASCE J. Environmental Engineering*, **2004**, 130:12, 1460-1467.

57) Westerhoff, P.; Snyder, S.; Yoon, Y.; Wert, E., Endocrine disruptor, pharmaceutical, and personal care product fate during simulated drinking water treatment processes, *Environmental Science and Technology*, **2005**, 39:17, 6649-6663.

58) Yoon Y.; Westerhoff P.; Snyder S.A., Adsorption of ^{3}H-labeled 17-β estradiol on powdered activated carbon", *Water, Air, & Soil Pollution*, **2005**, 116:1-4, 343-351.

59) Yoon Y.; Westerhoff P.; Snyder S.; Wert E., Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products, *Journal of Membrane Science*, **2006**, 270, 88-100.

Table 1. Summary of PPCP/EDC studied and their properties

Compound name	CAS #	Use	MW	Log Kow (ECOSAR)	lowest predicted LC50 or EC50 for the most sensitive indicator species (ppm)	Water Solubility (mg/L)
Acetaminophen	103-90-2	NSAID	151.17	0.27	41.498	39100
Caffeine	58-08-2	stimulant	194.19	0.16	46.859	65000
Carbamazepine	298-46-4	anticonvulsant	236.27	2.25	6.359	584
Cotinine	486-56-6	metabolite of nicotine	176.22	0.34	112.526	38700
DEET	134-62-3	insect repellent	191.27	2.26	5.064	462
Diazepam	439-14-5	anxiolytic	284.70	2.7	2.258	245
Diclofenac	15307-86-5	NSAID	296.15	4.02	4.238	11
Dilantin	57-41-0	antiepileptic	252.27	2.16	103.818	770
Erythromycin	114-07-8	antibiotic	733.93	2.48	7.822	1057
Fluoxetine	54910-89-3	antidepressant	309.30	4.65	0.178	3
Hydrocodone	125-29-1	narcotic analgesic	299.37	2.16	4.907	914
Ibuprofen	15687-27-1	NSAID	206.28	3.79	4.322	14
Meprobamate	57-53-4	anxiolytic	218.25	0.98	8.899	10650
Naproxen	22204-53-1	NSAID	230.26	3.1	15.144	77
Oxybenzone	131-57-7	sunscreens	228.24	3.52	2.936	29
Pentoxifylline	6493-05-6	antiplatelet drug	278.31	0.56	39.219	36400
Primidone	125-33-7	anticonvulsant	218.25	0.73	73.008	19160
Sucralose	56038-13-2	artificial sweetener	397.64	-1	2341.475	2030000
Sulfamethoxazole	723-46-6	antibiotic	253.28	0.48	4.472	39990
TBBA	79-94-7	flame retardant	543.90	7.2	0.007	0
Triclosan	3380-34-5	antibiotic	289.54	4.66	0.636	2

Compound name	CAS #	Use	MW	Log Kow (ECOSAR)	lowest predicted LC50 or EC50 for the most sensitive indicator species (ppm)	Water Solubility (mg/L)
Trimethoprim	738-70-5	antibiotic	290.32	0.73	2.629	25480
Estradiol	50-28-2	sex hormone	272.38	3.94	2.359	13
Ethinyl Estradiol	57-63-6	estrogen	296.40	4.12	1.957	9
Progesterone	57-83-0	steroid hormone	314.46	3.67	3.278	28
Testosterone	58-22-0	steroid hormone	288.42	3.27	6.145	65

Table 2. Summary of PPCP/EDC detected in surface water

	CAP canal				Salt River				Verde River			
concentration: (ng/L)	mean detected	mean total	Max	Min	mean detected	mean total	Max	Min	mean detected	mean total	Max	Min
Acetaminophen	4	2	8	2	10	2	10	9	5	2	9	2
Caffeine	17	10	50	4	19	11	49	6	14	7	40	6
Carbamazepine	3	2	5	2	2	ND	2	DET	2	ND	2	DET
Cotinine	5	3	8	2	4	2	8	DET	2	DET	3	DET
DEET	6	4	9	4	17	8	39	8	10	5	24	5
Diazepam	DET	ND	DET	DET	2	ND	2	2	DET	ND	DET	DET
Diclofenac	2	ND	2	2	3	ND	3	3	3	ND	3	3
Dilantin	7	3	12	4	10	2	15	4	6	2	8	4
Erythromycin	2	DET	5	DET	3	DET	4	3	2	DET	3	DET
Fluoxetine	3	DET	5	3	6	DET	6	6	3	DET	5	2
Hydrocodone	2	DET	2	2	3	DET	4	3	2	DET	3	2
Ibuprofen	5	DET	5	5	3	DET	3	3	ND	ND	ND	ND
Meprobamate	11	6	15	9	5	DET	8	DET	3	DET	6	DET
Naproxen	3	DET	5	2	5	2	7	4	2	DET	3	2
Oxybenzone	10	6	15	7	231	134	676	7	36	21	188	5
Pentoxifylline	3	DET	8	2	3	DET	5	2	2	DET	4	DET
Primidone	7	3	16	DET	3	ND	3	3	2	DET	3	DET
Sucralose	180	105	328	10	5	2	7	4	13	9	25	3
Sulfamethoxazole	17	8	36	11	6	2	7	5	5	2	6	3
TBBA	4	ND	4	4	6	DET	6	6	4	ND	4	4
Triclosan	13	DET	13	13	8	DET	8	8	7	DET	7	7
Trimethoprim	3	DET	4	DET	6	DET	7	5	3	DET	5	DET
Estradiol	7	3	14	2	13	2	13	13	4	ND	4	4
Ethinyl Estradiol	DET	ND	DET	DET	2	ND	2	2	DET	ND	DET	DET
Progesterone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Testosterone	DET	ND	DET	DET	ND	ND	ND	ND	ND	ND	ND	ND

DET: detected but lower than 2 ng/L
ND: not detected or lower than detected in blank sample

Table 3. Summary of PPCP/EDC detected in WTP on SRP canal

	WTP influent				WTP sedimentation effluent				WTP finished waterSPTCl2			
Concentration: (ng/L)	mean detected	mean total	Max	Min	mean detected	mean total	Max	Min	mean detected	mean total	Max	Min
Acetaminophen	6	2	9	4	6	2	9	5	8	2	10	5
Caffeine	14	10	34	8	13	7	21	6	11	5	18	7
Carbamazepine	DET	ND	2	DET	DET	ND	DET	DET	2	ND	2	2
Cotinine	2	DET	4	DET	2	DET	3	DET	2	DET	3	DET
DEET	6	6	13	4	5	3	8	4	6	3	8	4
Diazepam	DET	ND	DET	DET	DET	ND	DET	DET	DET	ND	DET	DET
Diclofenac	2	ND	2	2	2	ND	2	2	2	ND	2	2
Dilantin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Erythromycin	2	DET	3	DET	2	DET	3	DET	2	DET	3	DET
Fluoxetine	5	ND	5	5	6	DET	6	6	6	DET	6	6
Hydrocodone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ibuprofen	ND	ND	ND	ND	ND	ND	ND	ND	5	DET	7	4
Meprobamate	3	DET	5	DET	3	DET	5	DET	4	DET	5	DET
Naproxen	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Oxybenzone	78	43	223	23	93	25	183	28	ND	ND	ND	ND
Pentoxifylline	3	DET	4	2	3	DET	4	2	3	DET	4	2
Primidone	2	ND	2	DET	2	ND	2	DET	2	DET	2	DET
Sucralose	15	10	31	4	8	4	12	3	11	4	22	3
Sulfamethoxazole	4	DET	5	3	4	DET	5	3	3	ND	3	3
TBBA	4	DET	4	4	4	DET	4	4	4	ND	4	4
Triclosan	ND	ND	ND	ND	ND	ND	ND	ND	9	DET	9	9
Trimethoprim	3	DET	4	2	4	ND	4	4	4	ND	4	4
Estradiol	ND	ND	ND	ND	3	ND	3	3	ND	ND	ND	ND
Ethinyl Estradiol	2	ND	2	DET	DET	ND	2	DET	4	DET	6	DET
Progesterone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Testosterone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

DET: detected but lower than 2 ng/L

ND: not detected or lower than detected in blank sample

Table 4. Summary of PPCP/EDC detected in WWTP A

	Raw wastewater				WWTP tertiary effluent				WWTP effluent after UV			
Concentration: (ng/L)	mean detected	mean total	Max	Min	mean detected	mean total	Max	Min	mean detected	mean total	Max	Min
Acetaminophen	144257	144257	250737	7286	13	4	17	7	20	8	35	11
Caffeine	50948	50948	88384	5219	32	26	42	19	47	37	62	26
Carbamazepine	477	477	859	94	441	441	716	157	452	452	900	151
Cotinine	2249	2249	4316	162	11	11	31	2	14	14	29	4
DEET	1157	1157	3706	147	213	213	408	54	201	201	412	53
Diazepam	11	6	19	2	5	3	14	DET	4	3	14	2
Diclofenac	204	163	326	39	99	89	149	9	48	43	105	7
Dilantin	524	471	1358	150	642	578	1156	242	434	391	722	166
Erythromycin	159	159	360	19	180	162	461	5	185	166	387	5
Fluoxetine	119	72	189	39	63	63	165	17	48	48	143	15
Hydrocodone	99	89	212	22	61	61	103	20	53	53	85	13
Ibuprofen	10214	9193	16741	4717	17	8	22	6	14	8	21	6
Meprobamate	1152	1152	1859	356	675	675	1454	205	692	692	1448	246
Naproxen	21536	19382	38673	4457	130	117	594	18	88	80	383	9
Oxybenzone	8103	8103	23357	1300	93	65	188	35	99	49	164	33
Pentoxifylline	46	32	185	4	7	3	12	4	8	3	15	4
Primidone	655	655	1745	34	245	245	361	92	229	229	373	78
Sucralose	5384	4846	12231	22	2847	2563	7962	560	2748	2473	7105	574
Sulfamethoxazole	2541	2541	6919	90	2988	2988	6982	303	2337	2337	4597	343
TBBA	1058	635	2607	4	138	69	229	4	88	44	144	6
Triclosan	1503	1353	2357	406	146	116	338	25	90	81	229	15
Trimethoprim	838	838	2824	19	266	239	548	6	283	255	601	10
Estradiol	68	30	164	11	6	2	6	6	5	DET	5	5
Ethinyl Estradiol	25	17	90	5	2	DET	2	2	DET	ND	DET	DET
Progesterone	22	15	38	12	2	DET	2	2	ND	ND	ND	ND
Testosterone	75	67	136	24	3	DET	4	DET	ND	ND	ND	ND

DET: detected but lower than 2 ng/L
ND: not detected or lower than detected in blank sample

Table 5. Summary of PPCP/EDC in effluent of 8 WWTPs (one time sampling on May, 2009)

	WWTP A	WWTP B	WWTP C	WWTP D	WWTP E	WWTP F	WWTP G	WWTP H
Concentration: (ng/L)	before UV	before chlorination	before chlorination	before chlorination	after chlorination	after chlorination	after chlorination	before chlorination
Acetaminophen	ND	ND	ND	165	53	52	276	27
Caffeine	44	37	1020	49	14	253	4025	55
Carbamazepine	292	249	149	290	161	245	214	232
Cotinine	4	11	27	22	13	407	183	20
DEET	194	31	486	225	139	95	82	184
Diazepam	ND	ND	ND	2	2	3	DET	3
Diclofenac	41	17	ND	20	322	11	24	18
Dilantin	473	152	ND	216	117	241	178	819
Erythromycin	ND	ND	ND	70	64	60	ND	4
Estradiol	14	ND	10	ND	61	10	16	9
Ethinyl Estradiol	ND	ND	ND	ND	ND	ND	ND	2
Fluoxetine	25	ND	ND	51	ND	126	36	49
Hydrocodone	51	37	ND	38	10	70	47	45
Ibuprofen	ND	6	ND	39	23	37	97	ND
Meprobamate	433	280	11	671	63	494	434	606
Naproxen	ND	ND	ND	268	47	439	1044	30
Oxybenzone	35	64	59	130	45	60	338	55
Pentoxifylline	5	ND	ND	ND	27	21	33	4
Primidone	180	122	78	89	30	112	54	234
Progesterone	ND	ND	ND	ND	ND	ND	ND	ND
Sucralose	3213	1740	2535	4043	1366	2885	2000	7022

	WWTP A	WWTP B	WWTP C	WWTP D	WWTP E	WWTP F	WWTP G	WWTP H
Sulfamethoxazole	3213	1740	2535	4043	1366	2885	2000	7022
TBBA	3207	783	12	2138	3081	1554	1529	2848
Testosterone	ND	ND	ND	ND	ND	ND	ND	ND
Triclosan	ND	ND	ND	ND	ND	ND	ND	ND
Trimethoprim	ND	ND	ND	41	13	32	42	13

DET: detected but lower than 2 ng/L
ND: not detected or lower than detected in blank sample

Table 6. Summary of PPCP/EDC detected in groundwater

	GW MW1				GW MW2				GW MW3			
Concentration: (ng/L)	mean detected	mean total	Max	Min	mean detected	mean total	Max	Min	mean detected	mean total	Max	Min
Acetaminophen	4	2	4	4	4	2	4	4	4	2	4	4
Caffeine	8	3	8	8	5	2	5	5	6	2	6	6
Carbamazepine	DET	DET	DET	DET	DET	DET	DET	DET	DET	DET	DET	DET
Cotinine	2	DET	2	2	2	DET	2	2	2	DET	2	2
DEET	4	DET	4	4	ND	ND	ND	ND	5	2	5	5
Diazepam	DET	DET	DET	DET	DET	DET	DET	DET	DET	DET	DET	DET
Diclofenac	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dilantin	ND	ND	ND	ND	ND	2	7	7	ND	8	13	10
Erythromycin	2	2	2	DET	2	2	2	DET	2	2	2	DET
Fluoxetine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hydrocodone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ibuprofen	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Meprobamate	3	3	5	DET	3	3	5	DET	3	3	5	DET
Naproxen	7	2	7	7	ND	ND	ND	ND	ND	ND	ND	ND
Oxybenzone	17	6	17	17	24	8	24	24	ND	ND	ND	ND
Pentoxifylline	2	2	2	2	2	2	2	2	2	2	2	2
Primidone	DET	ND	DET	DET	DET	ND	DET	DET	2	2	3	DET
Sucralose	3	2	3	3	3	2	3	3	92	92	133	51
Sulfamethoxazole	5	3	6	5	17	11	26	8	246	246	345	116
TBBA	ND	ND	ND	ND	ND	DET	2	ND	3	DET	3	3
Triclosan	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trimethoprim	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Estradiol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethinyl Estradiol	ND	ND	ND	ND	ND	ND	ND	ND	DET	ND	DET	DET
Progesterone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Testosterone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

DET: detected but lower than 2 ng/L
ND: not detected or lower than detected in blank sample

Table 7. Total PPCP/EDC detected in river downstream of water recreation site

Sampling date	Sampling location and time	Total PPCP/EDC (ng/L)
September, 2008	Salt River (1 mile upstream Blue Point Bridge), 09:00	100
September, 2008	Salt River (3 miles downstream), 09:00	86
September, 2008	Salt River (3 miles downstream), 10:00	852
September, 2008	Salt River (3 miles downstream), 13:00	807
September, 2008	Salt River (3 miles downstream), 14:00	1415
September, 2008	Salt River (3 miles downstream), 15:00	1721
September, 2008	Salt River (3 miles downstream), 16:00	5443
September, 2008	Salt River (3 miles downstream), 17:00	6006
July, 2009	Benjo Bill Camp Ground (1 mile upstream Slide Rock Park)	146
July, 2009	Manzanita Camp Ground 11:00	2058
July, 2009	Manzanita Camp Ground 12:00	250
July, 2009	Manzanita Camp Ground 13:00	314
July, 2009	Manzanita Camp Ground 14:00	1720
July, 2009	Manzanita Camp Ground 15:00	2114
July, 2009	Manzanita Camp Ground 16:00	2152
July, 2009	Manzanita Camp Ground 17:00	2406
July, 2009	Salt River (1 mile upstream Blue Point Bridge), 9:00	294
July, 2009	Salt River (3 miles downstream), 9:00	107
July, 2009	Salt River (3 miles downstream), 10:00	139
July, 2009	Salt River (3 miles downstream), 11:00	128
July, 2009	Salt River (3 miles downstream), 12:00	140
July, 2009	Salt River (3 miles downstream), 13:00	473
July, 2009	Salt River (3 miles downstream), 14:00	1164
July, 2009	Salt River (3 miles downstream), 15:00	1825
July, 2009	Salt River (3 miles downstream), 16:00	2332
July, 2009	Salt River (3 miles downstream), 17:00	1842
July, 2009	Salt River (3 miles downstream), 18:00	1587

Table 8. Summary of PPCP/EDCs levels in different waters

Source	< 2 ng/L & ≤ Blank	2 to 10 ng/L	10 to 20 ng/L	20 ng/L to 1 ug/L	> 1 ug/L
Ground water at recharge site	Steroids and others	Acetaminophen, caffeine, DEET, erythromycin, meprobamate oxybenzone, pentoxifylline	None	Sulfamethoxazole, sucralose (in one site)	None
SRP waters (Verde River & Salt River)	Steroids and others	Sucralose, sulfamethoxazole, acetaminophen, cotinine, dilantin,	Caffeine, DEET	Oxybenzone	None
CAP Canal from Colorado River	Ethinyl estradiol, progesterone, testosterone, and others	Sulfamethoxazole, oxybenzone, meprobamate, DEET, cotinine, dilantin, carbamazepine, acetaminophen, primidone, estradiol	Caffeine, triclosan	Sucralose	None
Activated sludge WWTP with nitrification	Estradiol, ethinyl estradiol, progesterone, testosterone	Acetaminophen, ibuprofen, diazepam, pentoxifylline	Cotinine	Caffeine, naproxen, oxybenzone, TBBA, carbamazepine, hydrocodone, meprobamate, sulfamethoxazole, DEET, erythromycin, trimethoprim, primidone, dilantin, triclosan, diclofenac, sucralose, fluoxetine	None
Raw wastewater	None	None	Diazepam, ethinyl estradiol, progesterone	Testosterone, hydrocodone, pentoxifylline, erythromycin, trimethoprim, primidone, fluoxetine carbamazepine, dilantin, diclofenac	Ibuprofen, naproxen, triclosan, sucralose, acetominophen, caffeine, cotinine, oxybenzone, DEET, meprobamate, TBBA, sulfamethoxazole

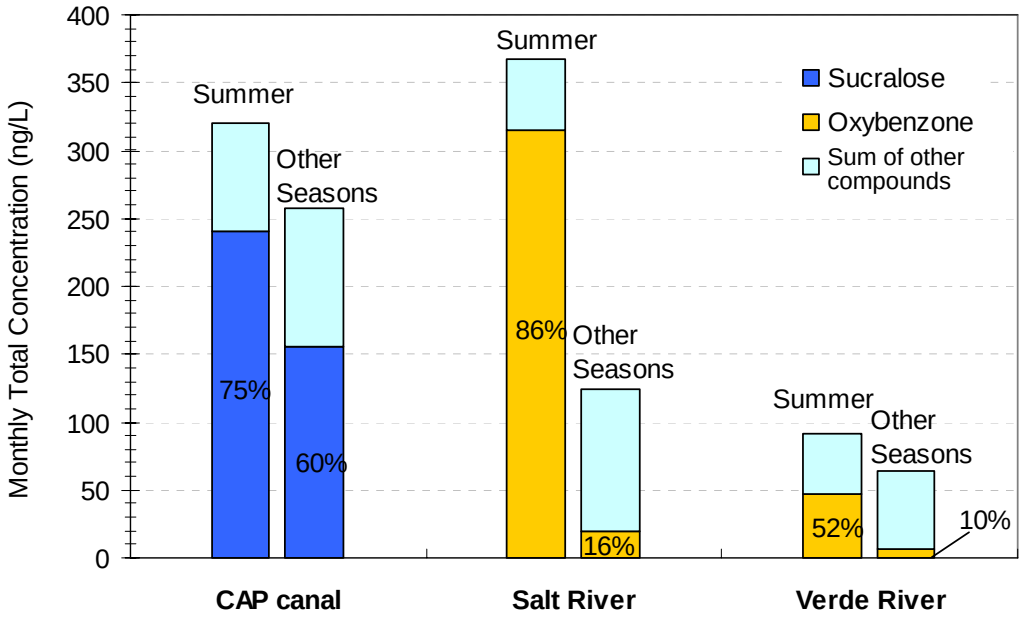


Figure 1. Seasonal variation of PPCP/EDC detected in surface waters

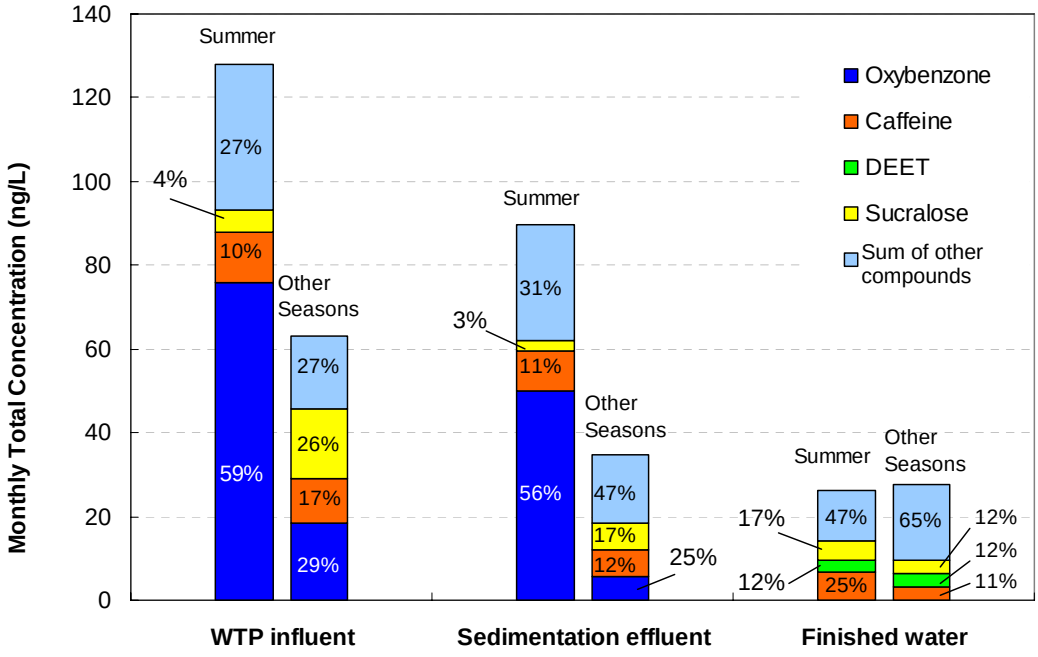


Figure 2. Seasonal variation of PPCP/EDC detected during WTP treatment processes

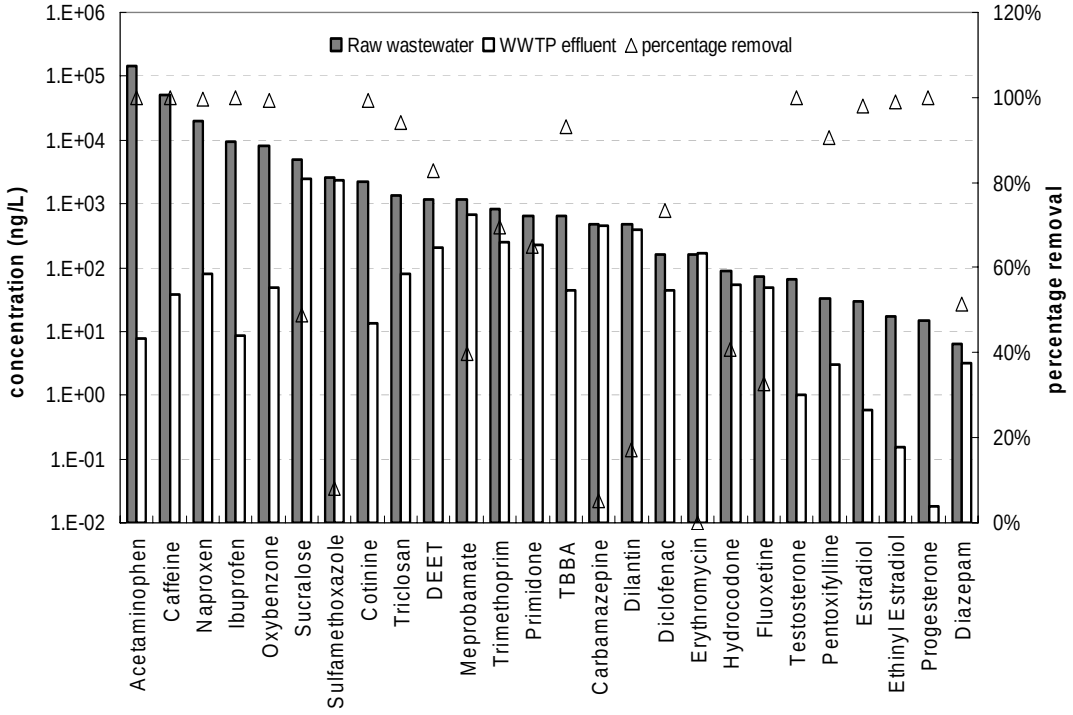


Figure 3. PPCP/EDC in raw wastewater and WWTP effluent and the percentage removal of each compound.

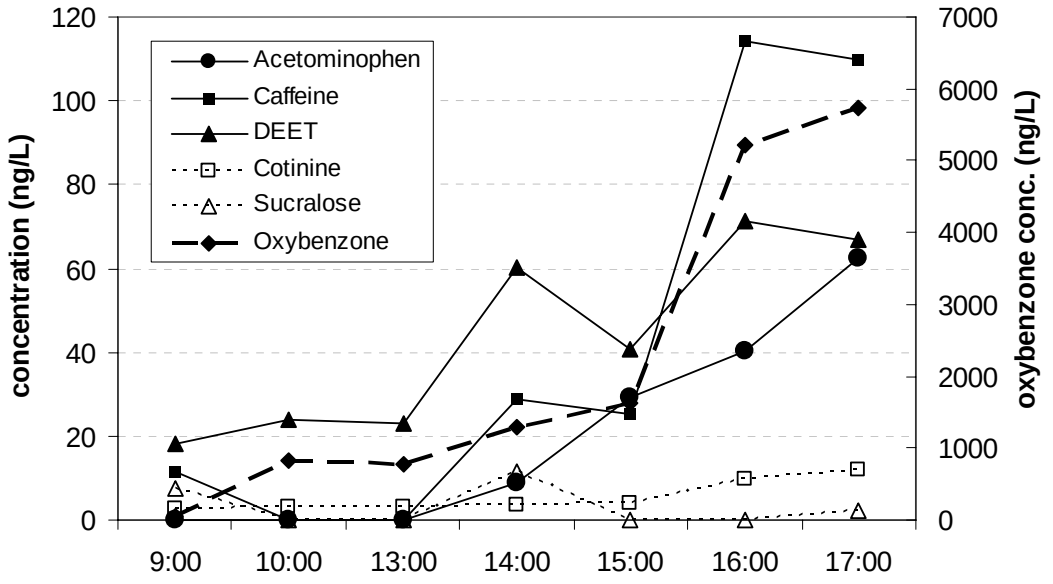


Figure 4.a. PPCP/EDC detected over time in Salt River downstream of recreational site (September, 2008)

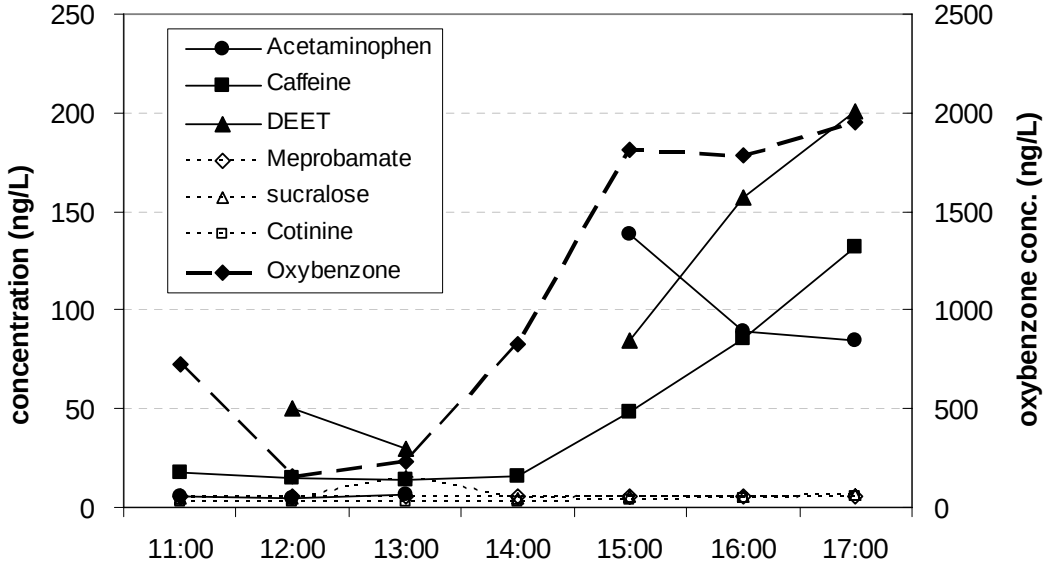


Figure 4.b. PPCP/EDC detected over time in downstream of Slide Rock Park (July, 2009)

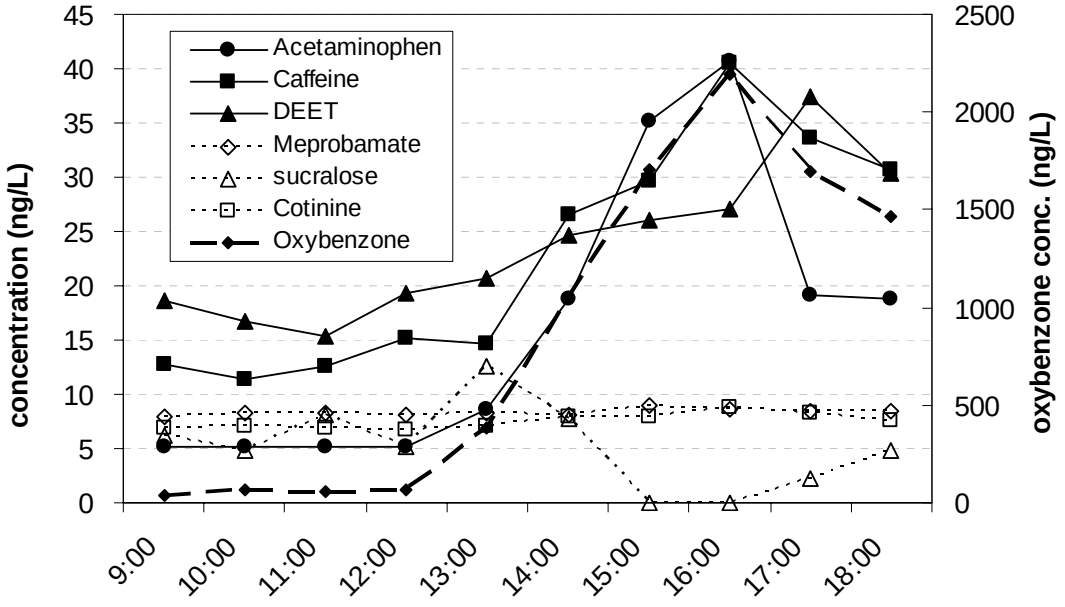
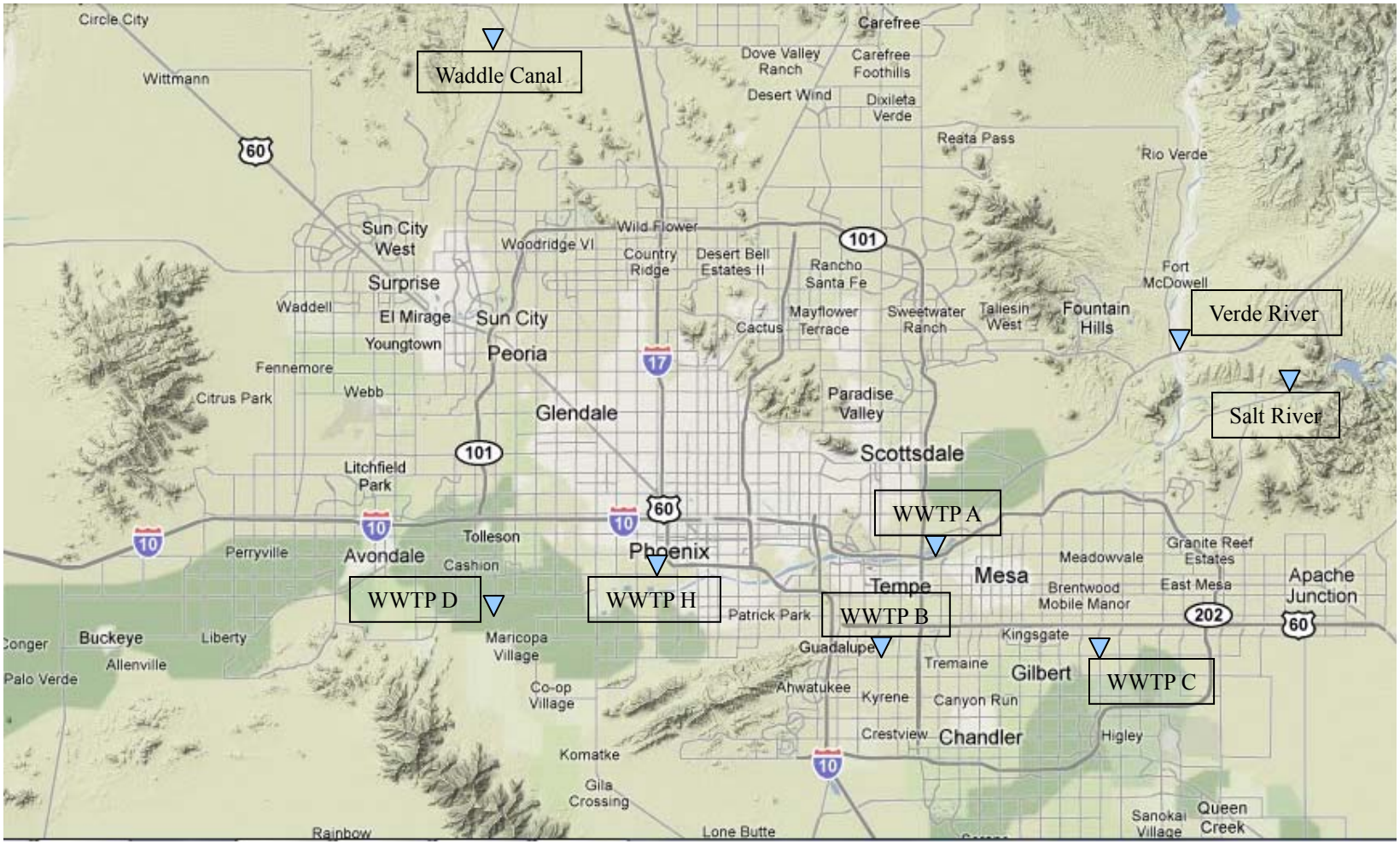
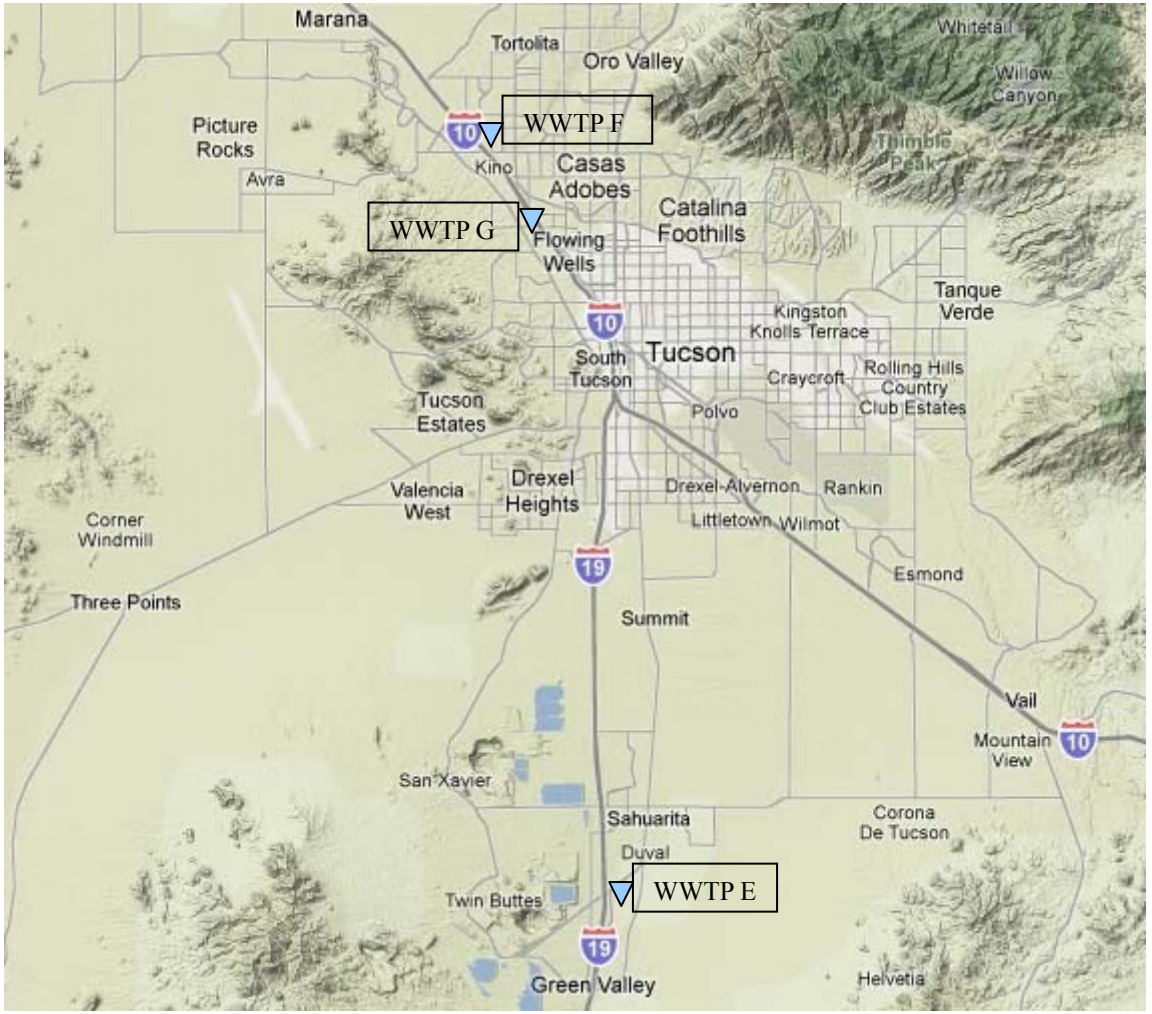


Figure 4.c. PPCP/EDC detected over time in Salt River downstream of recreational site (July, 2009)

Appendix A


Waddle Canal
Verde River
Salt River
WWTP A
WWTP B
WWTP C
WWTP D
WWTP H
Circle City
Wittmann
Carefree
Dove Valley Ranch
Carefree Foothills
Desert Wind
Dixileta
Verde
Reata Pass
Rio Verde
Sun City West
Wild Flower
Woodridge VI
Country Ridge
Desert Bell Estates II
Rancho Santa Fe
Fort McDowell
Surprise
Waddell
El Mirage
Sun City
Youngtown
Peoria
Cactus
Mayflower Terrace
Sweetwater Ranch
Taliesin West
Fountain Hills
Fennemore
Webb
Citrus Park
Glendale
Paradise Valley
Scottsdale
Litchfield Park
Tolleson
Perryville
Avondale
Cashion
Phoenix
Meadowvale
Granite Reef Estates
Mesa
Tempe
Brentwood Mobile Manor
East Mesa
Apache Junction
Patrick Park
Kingsgate
Buckeye
Liberty
Maricopa Village
Guadalupe
Tremaine
Gilbert
Allenville
Palo Verde
Co-op Village
Ahwatukee
Kyrene
Canyon Run
Crestview
Chandler
Higley
Komatke
Gila Crossing
Rainbow
Lone Butte
Sanokai Village
Queen Creek
101
60
10
17
202

Appendix B


Marana
Tortolita
Oro Valley
Whitetail
Willow Canyon
Picture Rocks
Avra
WWTP F
Kino
Casas Adobes
Thimble Peak
WWTP G
Flowing Wells
Catalina Foothills
Tanque Verde
Kingston Knolls Terrace
South Tucson
Tucson
Craycroft
Rolling Hills Country Club Estates
Tucson Estates
Polvo
Valencia West
Drexel Heights
Drexel-Alvernon
Rankin
Littletown
Wilmot
Corner Windmill
Esmond
Three Points
Summit
Vail
Mountain View
San Xavier
Sahuarita
Corona De Tucson
Duval
WWTP E
Twin Buttes
Green Valley
Helvetia

Appendix C


recharging
GRUSP 3
GRUSP 2
GRUSP 1
Salt River
N Beeline Hwy
N Gilbert Rd
N Power Rd
N Bush Hwy
87
202
Red Mountain Fwy
Red Mountain Ranch Country Club
Las Sendas Golf Club
Spook Hill
Schlechts Butte
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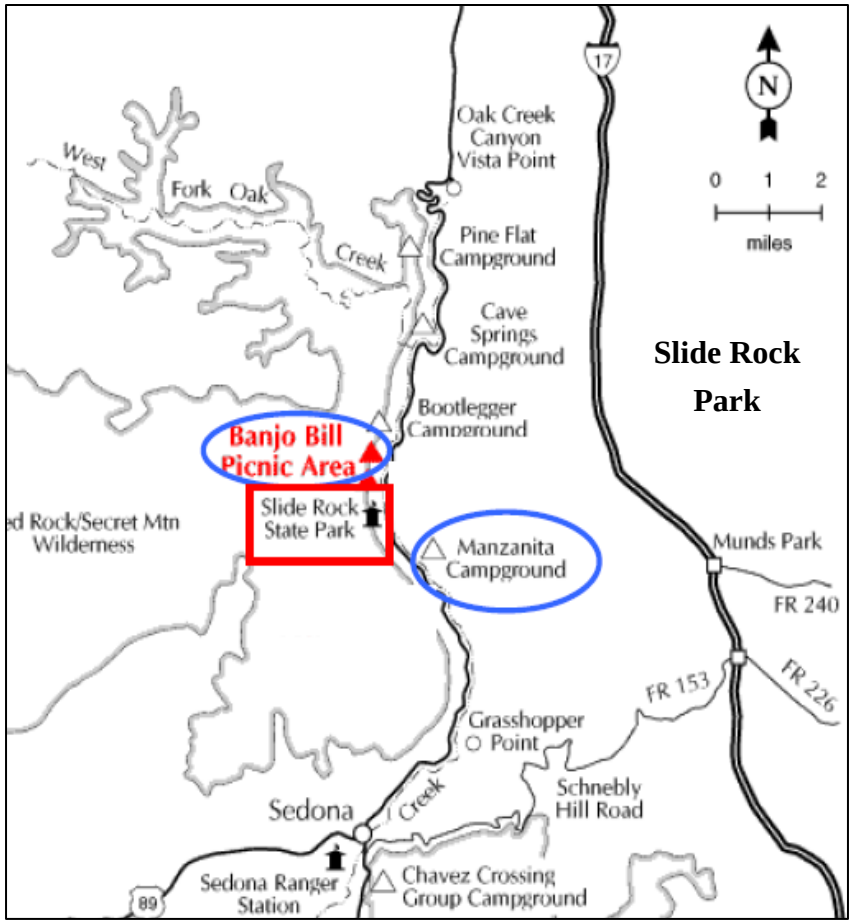
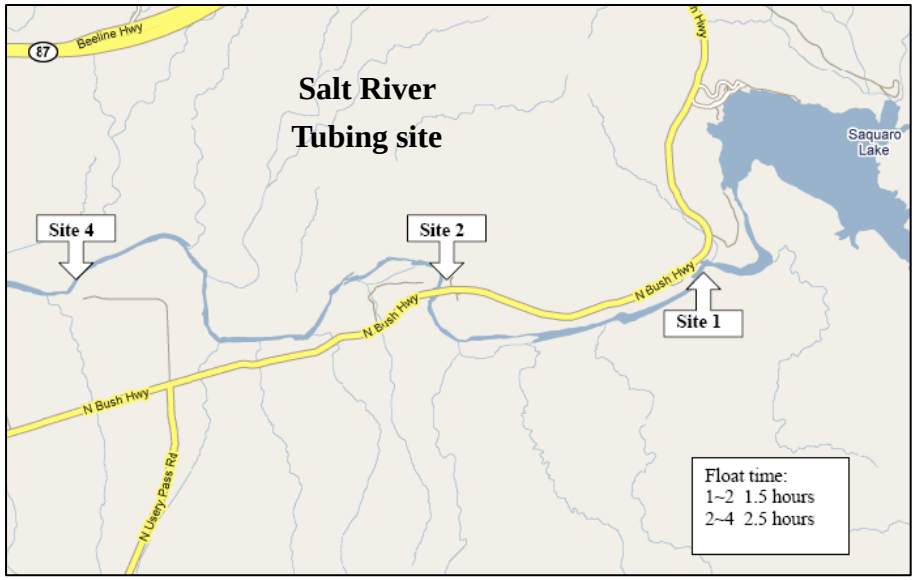
Appendix D


Slide Rock
Park
17
N
0 1 2
miles
West Fork Oak Creek
Oak Creek Canyon Vista Point
Pine Flat Campground
Cave Springs Campground
Bootlegger Campground
Banjo Bill Picnic Area
Slide Rock State Park
Manzanita Campground
d Rock/Secret Mtn Wilderness
Munds Park
FR 240
FR 153
FR 226
Grasshopper Point
Schnebly Hill Road
Sedona
Oak Creek
Sedona Ranger Station
89
Chavez Crossing Group Campground


Salt River
Tubing site
87
Beeline Hwy
Saquaro Lake
Site 4
Site 2
Site 1
N Bush Hwy
N Usery Pass Rd
Float time:
1~2 1.5 hours
2~4 2.5 hours

Appendix E

Ionization Source	Compound	Class/Use	Quantifier Ion	Qualifier Ion(s)
			Q1/Q3	Q1/Q3
APCI Positive	Estradiol	Steroid/Estrogen	255.3/159.2	255.30/133.1
	Ethynyl Estradiol	Steroid/Synthetic Estrogen	279.2/133.0	279.2/159.1
	Progesterone	Steroid/Estrogen	315.3/97.3	315.3/109.0, 315.3/109.2
	Testosterone	Steroid/Androgen	289.3/97.3	289.3/109.2, 289.3/123.3
ESI Negative	Cotinine	Personal Care Product/Nicotine metabolite	177.2/80.2	177.2/98.3
	Diclofenac	Pharmaceutical/Anti-arthritic	294.3/250.0	294.3/214.0
	Dilantin (Phenytoin sodium)	Pharmaceutical/Anti-convulsant	251.4/102.0	251.4/180.0
	Ibuprofen	Pharmaceutical/Analgesic	205.1/159.0	205.1/161.0
	Naproxen	Pharmaceutical/Analgesic	229.0/169.0	229.0/185.1, 229.0/140.9
	Sucralose	Personal Care Product/Sweetener	395.3/359.0	397.2/361.1
	Tetrabromobisphenol A	Personal Care Product/Flame retardant	442.9/239.0	442.9/102.9
	Triclosan (Ingasan)	Personal Care Product/Antibiotic	287.2/34.9	287.2/241.1
	Warfarin	Pharmaceutical/Anti-coagulant	307.3/161.0	307.3/250.0, 307.3/117.0
ESI Positive	Acetaminophen	Pharmaceutical/Analgesic	152.1/110.2	152.1/65.3
	Atrazine	Pesticide	216.1/174.2	216.1/104.2
	Caffeine	Personal Care Product/Stimulant	195.2/138.3	195.2/110.0
	Carbamazepine	Pharmaceutical/Anti-seizure	237.3/194.0	237.3/179.3
	DEET	Personal Care Product/Insect Repellant	192.1/119.3	192.1/91.3
	Diazepam	Pharmaceutical/Muscle relaxant	285.2/193.3	285.2/154.0, 285.2/222.0
	Diuron	Pesticide	233.3/72.3	233.3/159.9
	Erythromycin-H2O	Pharmaceutical/Antibiotic	716.5/158.3	716.5/558.6
	Fluoxetine	Pharmaceutical/Anti-depressant	310.3/44.2	310.3/148.3
	Hydrocodone	Pharmaceutical/Analgesic	300.3/199.2	300.3/171.3, 300.3/128.3
	Imazamox	Pesticide	306.4/261.2	306.4/245.2
	Imazthapyr	Pesticide	290.3/245.2	290.3/177.2
	Meprobamate	Pharmaceutical/Anti-anxiety	219.2/158.3	219.2/97.3
	Oxybenzone	Personal Care Product/Sunscreen	229.3/151.2	229.3/105.1
	Pentoxifylline	Pharmaceutical/Blood thinner	279.4/138.2	279.4/99.2
	Primidone	Pharmaceutical/Anti-convulsant	219.2/162.1	219.2/91.3
	Prometryne	Pesticide	242.2/157.9	242.2/200.3
	Sulfamethoxazole	Pharmaceutical/Antibiotic	254.3/156.2	254.3/108.1
	Trimethoprim	Pharmaceutical/Antibiotic	291.3/123.3	291.3/230.4, 291.3/261.2
INST/Surrogate	Acetaminophen-D4		156.2/114.1	156.2/69.1
	Cotinine-D3		180.3/80.10	180.3/101.2
	Diazepam-D5		290.3/198.4	290.3/154.0, 290.3/227.4
	Estradiol-D5		260.3/161.10	260.3/135.10
	Fluoxetine-D6		316.2/44.2	316.2/154.2
	Hydrocodone-D6		306.3/202.3	306.3/174.3, 306.3/128.3

Appendix F

	Blank samples		
	Average (ave)	Standard Deviation (SD)	ave+2SD
Acetaminophen	0.2	0.3	0.9
Caffeine	1.0	1.0	3.0
Carbamazepine	0.1	0.3	0.7
Cotinine	0.1	0.1	0.3
DEET	1.1	1.0	3.0
Diazepam	0.1	0.2	0.5
Diclofenac	0.4	0.5	1.3
Dilantin	0.7	1.1	2.8
Erythromycin	0.1	0.3	0.7
Fluoxetine	0.3	0.4	1.1
Hydrocodone	0.5	0.8	2.0
Ibuprofen	0.6	1.0	2.6
Meprobamate	0.2	0.3	0.8
Naproxen	0.2	0.5	1.3
Oxybenzone	2.0	1.3	4.6
Pentoxifylline	0.2	0.5	1.1
Primidone	0.1	0.2	0.6
Sucralose	0.4	0.7	1.7
Sulfamethoxazole	0.3	0.7	1.7
TBBA	0.5	0.9	2.4
Triclosan	1.0	1.0	3.0
Trimethoprim	0.1	0.4	0.8

Appendix G

	CAP canal	Salt River	Verde River	WTP influent	WTP sedimentation effluent	WTP finished water	WWTP raw water	WWTP tertiary effluent	WWTP effluent
Acetaminophen	34%	27%	34%	33%	31%	27%	14%	16%	18%
Caffeine	72%	48%	63%	66%	62%	61%	59%	33%	32%
Carbamazepine	77%	49%	70%	80%	79%	75%	54%	49%	51%
Cotinine	77%	49%	70%	80%	79%	75%	54%	49%	51%
DEET	77%	49%	70%	80%	79%	75%	54%	49%	51%
Diazepam	77%	49%	70%	80%	79%	75%	54%	49%	51%
Diclofenac	77%	49%	70%	80%	79%	75%	54%	49%	51%
Dilantin	36%	17%	32%	26%	27%	29%	23%	14%	18%
Erythromycin	72%	48%	63%	66%	62%	61%	59%	33%	32%
Fluoxetine	34%	27%	34%	33%	31%	27%	14%	16%	18%
Hydrocodone	77%	49%	70%	80%	79%	75%	54%	49%	51%
Ibuprofen	77%	49%	70%	80%	79%	75%	54%	49%	51%
Meprobamate	77%	49%	70%	80%	79%	75%	54%	49%	51%
Naproxen	36%	17%	32%	26%	27%	29%	23%	14%	18%
Oxybenzone	34%	27%	34%	33%	31%	27%	14%	16%	18%
Pentoxifylline	72%	48%	63%	66%	62%	61%	59%	33%	32%
Primidone	77%	49%	70%	80%	79%	75%	54%	49%	51%

Note: No recovery data available for sucralose and steroids. The results of these compounds represent the minimum contamination level.