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Seasonal Variations in Concentrations of Pharmaceuticals and Personal Care Products in Drinking Water and Reclaimed Wastewater in Southern California

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Southern California imports nearly all of its potable water from two sources: the Colorado River and the California State Water Project (Sacramento−San Joaquin River Basin). Sewage treatment plant effluent (STPE) heavily impacts both of these sources. A survey of raw and treated drinking water from four water filtration plants in San Diego County showed the occurrence of several polar organic "pharmaceuticals and personal care products" (PPCP). These included phthalate esters, sunscreens, clofibrate, clofibric acid, ibuprofen, triclosan, and DEET. Several of these were also found in the finished water, such as di(ethylhexyl) phthalate, benzophenone, ibuprofen, and triclosan. Occurrence and concentrations of these compounds were highly seasonally dependent, and reached maximums when the flow of the San Joaquin River was low and the quantity of imported water was high. The maximum concentrations of the PPCPs measured in the raw water were correlated with low flow conditions in the Sacramento−San Joaquin Delta that feeds the State Water Project. The PPCP concentrations in raw imported water in the summer months approached that of reclaimed nonpotable wastewater.

Introduction

The Metropolitan Water District of Southern California (Metro) imports, on average, 1.7 billion gallons a day of freshwater to serve the 18 million inhabitants of Southern California (*1*). In 2001, the San Diego County Water Authority (SDCWA), a Metro member agency and Metro's largest customer, imported 8.3×10^8 m^3, roughly 90% of the water used in the county (*2*).

The water comes from two main sources: the Colorado River and the California State Water Project. The Colorado River Aqueduct carries water from the Colorado River above the Parker Dam over 240 miles to reservoirs operated by Metro. Due to its high salinity it is blended with water from the State Water Project (SWP) before distribution to water filtration plants. The SWP is a system of reservoirs, groundwater banks, and aqueducts that collect and store precipitation from the wetter northern part of the state and transport it to the more populous south (*1*).

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Both the Colorado River and the SWP are heavily impacted by sewage treatment plant effluent (STPE). The Sacramento−San Joaquin Rivers, which feed the SWP, receive an average of 22.3 cubic meters per second (cms) of STPE from the roughly 5.2 million people who live in this watershed (*3*). The estimated population of the lower Colorado River Basin in 1990 was 1.07 million and is expanding rapidly. The STPE entering the river above Parker Dam is estimated to be 9.97 cms with the majority coming from Las Vegas, NV (*4*).

Like most rivers in the southwest United States, the Colorado and Sacramento−San Joaquin are primarily snow fed and have flows that vary seasonally and annually. The average monthly flows in the San Joaquin Delta, the inlet to the SWP, and the Colorado River are shown in Figure 1. During this study (August 2001 to November 2002) the southwest experienced a severe drought, so the monthly average flows for 2001 are also plotted. The estimated STPE contributions are also plotted. In August and September of 2001 greater than 70% of the flow in the San Joaquin Delta was due to STPE. The estimated STPE contribution in the Colorado was less than 5%. On average, roughly a third of the water supplied by Metro originates from the SWP with the proportions varying daily with the cost and availability of water. Thus, under normal flow conditions in the rivers, the percentage of STPE in the imported water varies from roughly 5.5% in February to 17% in November. Under drought conditions such as 2001, the percentage of STPE would increase (23% in August 2001). This situation is not unique to Southern California. More than two dozen major utilities in the United States draw water from rivers where more than 50% of the flow in dry conditions is due to STPE (*6*).

Recently STPE has been identified as a source of pharmaceuticals, hormones, personal care products (fragrances, sunscreens, antimicrobials, etc.), and plasticizers in surface waters and groundwater. In a national survey of surface waters, Kolpin et al. (2002) found organic wastewater contaminants in 80% of 139 streams sampled through out the United States (*7*).

A great deal of work has been done recently to identify trace organic contaminants in STPE (*8−17, 56−57*), and surface water (*7−9, 15, 17−22, 58*). Much of this work has focused on natural and synthetic hormones and antibiotics, but other compounds such as prescription and over-the-counter pharmaceuticals, surfactants, sunscreens, pesticides, and flame retardants have been reported as well. Collectively these compounds have been referred to as "pharmaceuticals and personal care products" (PPCP).

Several studies have identified these compounds in finished drinking water (*12, 23−24, 42, 45−50*). Stackelberg et al. analyzed for 106 organic wastewater related contaminants upstream, throughout a coagulation−flocculation−sedimentation drinking water treatment plant (*42*). Forty compounds were identified in the upstream or raw water samples and 17 were found in the finished water. Boyd et al. examined the fate of 9 PPCP in wastewater effluent, surface water, and water treatment plants in the United States and Canada (*45*). However, none of the analytes were detected in the finished drinking water. Halden and Paull analyzed 36 samples for triclocarban, an antimicrobial, including raw and finished drinking water, but concentrations were below detection limits (*46*). Phthalate esters have been reported in drinking water and bottled water (*23, 24*). Heberer reported the occurrence of clofibric acid, propylphenazone, and diclofenac in drinking water (*12*). Soliman et al. examined reclaimed wastewater from Southern California for 19 compounds including pharmaceuticals, antioxidants, hor-

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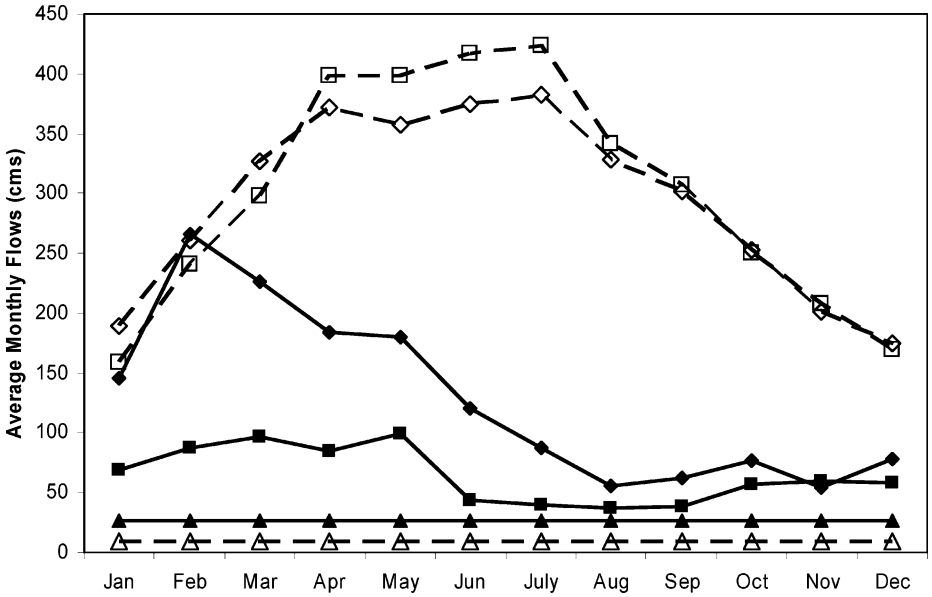

FIGURE 1. Flow in the Colorado River below Parker Dam (dashed lines, open points) and the San Joaquin Delta near the intake of the SWP (solid lines, solid points). The 10 year average of monthly flows (◆), the 2001 monthly averages (■), and the estimated STPE input (▲) from POTWs are shown (*3*–*5*).

TABLE 1. Water Filtration Plants and Wastewater Reclamation Plants Sampled

plant	capacity (m^3d^{-1})	technology	sample dates
WFP1	1.3×10^5	coagulation, sedimentation, filtration	08/01, 10/01, 11/01, 05/02
WFP2	4.6×10^5	coagulation, sedimentation, filtration	09/01, 10/01, 11/01, 03/02, 05/02
WFP3	4.6×10^5	coagulation, sedimentation, filtration	08/01, 10/01, 11/01, 03/01, 08/02, 11/02
WFP4	4.0×10^5	coagulation, sedimentation, ozonation, filtration	05/02, 06/02
WWRP	9.8×10^4	sedimentation, activated sludge, filtration, electrodialysis reversal	09/01, 10/01, 11/01, 01/02, 04/02, 06/02

TABLE 2. Occurrence and Concentrations of PPCPs in Raw Drinking Water

analyte	MDL μg/L	occurrences	mean detected μg/L	range μg/L	total mean μg/L	literature values μg/L	ref
dimethyl phthalate	0.039	5/13	0.386	0.098–0.784	0.148		
diethyl phthalate	0.49	2/13	1.20	0.899–1.49	0.184	0.16–0.3	23, 24
dibutyl phthalate	1.35	4/13	5.00	1.44–8.34	1.54	0.12–8.8	15
butyl benzyl phthalate	0.033	2/13	0.622	0.053–1.19	0.096	2.95	15
DEHP	1.76	2/13	4.31	2.67–5.94	0.66	7	7
hydrocinnamic acid	4.95	3/13	10.12	4.99–20.3	2.33		
benzophenone	0.26	3/13	0.511	0.36–0.79	0.12	0.13	42
octyl methoxy cinnamate	0.28	2/13	3.09	0.56–5.61	0.47		
clofibrate	0.055	2/13	0.58	0.26–0.90	0.09		35
clofibric acid	0.13	1/13	0.63		0.05	.005–0.17	35
ibuprofen	0.28	1/13	5.85		0.45	0.07–0.2	7, 8
Ibuprofen methyl ester	0.11	1/13	9.22		0.71		
triclosan	0.125	1/13	0.734		0.056	0.14	7
surfynol	0.096	4/13	0.515	0.326–0.818	0.158		
BHA	0.07	2/13	3.50	3.49–3.52	0.54	0.1	7
DEET	0.082	1/13	0.131		0.010	0.003–0.268	7, 18, 42

mones, and metabolites (*41*). Using on-line continuous liquid–liquid extraction of large sample volumes (10–40 L) GC/MS detection limits in μg/L were obtained. Three reclaimed wastewater samples were analyzed and 14 of the compounds were detected.

Few studies have looked at PPCPs in the same water source over an extended period of time (*13*, *25*). The most comprehensive study was done by Kolpin et al., who sampled upstream and downstream of 10 cities in Iowa during high, normal, and low flow conditions (*44*). The occurrence and concentrations of some 62 PPCPs were found to increase during periods of low flow and decrease during high flow.

Experimental Section

Sample Collection. Samples were collected from 4 water filtration plants (WFP1–4) and a wastewater reclamation plant (WWRP) in San Diego County, California (Table 1 and map in Supporting Information). Three plants were conventional coagulation–flocculation–sedimentation (C–F–S) plants. WFP4 was a coagulation–sedimentation–ozonation–filtration plant. Raw water for all four plants was a mix of imported water from Metro (Colorado River and SWP) and reservoir water. During the sampling period (August 2001 to June 2002) the reservoirs were supplemented with

TABLE 3. Occurrence and Concentrations of PPCPs in Finished Drinking Water

analyte	occ.	mean μg/L	range μg/L	total mean μg/L
dimethyl phthalate	1/15	0.54		0.04
diethyl phthalate	1/15	2.47		0.16
dibutyl phthalate	1/15	2.73		0.18
butyl benzyl phthalate	5/15	0.552	0.056−0.911	0.184
DEHP	2/15	2.56	2.43−2.68	0.34
hydrocinnamic acid	3/15	10.0	4.97−20.1	2.0
benzophenone	1/15	0.26		0.02
octyl methoxy cinnamate	1/15	0.45		0.03
clofibrate		ND[a]		
clofibric acid		ND		
ibuprofen	2/15	0.93	0.51−1.35	0.12
ibuprofen methyl ester	1/15	4.95		0.33
triclosan	1/15	0.734		0.049
surfynol	4/15	0.161	0.12−0.24	0.043
BHA	1/15	3.45		0.23
DEET		ND		

[a] ND = not detected.

imported water due to drought conditions. Samples were collected from raw water, post coagulation−sedimentation, post filtration, and prior to final chlorination. At WFP4 samples were also collected after ozonation.

The WWRP produced 26 MGD (9.8×10^4 m^3 d^{-1}) of reclaimed wastewater for nonpotable use. The treatment process consisted of primary sedimentation, followed by aerobic biological treatment with activated sludge, secondary clarification, and filtration through anthracite (9 ft). Depending on effluent total dissolved solids (TDS) a portion of the effluent was passed through electrodialysis reversal (EDR) units to remove TDS. The EDR effluent and the remaining filtrate were mixed and chlorinated prior to release. Samples were collected at the plant headworks, after primary settling, after secondary clarification, post-filtration and after EDR, but before chlorination.

Samples were collected in 2-L glass jars with Teflon-lined lids. Sample volumes for the WFP samples were 4 L, and for wastewater samples were 2 L. Exact sample volumes were used to calculate the concentrations. Samples were taken from existing sampling locations in the plants. All samples were grab samples and were collected simultaneously, thus removal efficiencies were not calculated.

Extraction and Analysis. The samples were refrigerated and extracted within 24 h. Influent and primary effluent samples from the WWRP were prefiltered through two glass fiber filters (Fisherbrand G8, 2.5-mm particle retention, and TCLP filter, 0.7-mm pore size, Fisher Scientific, Tustin, CA). 2,4-Dichlorophenylacetic acid (Supelco) was used as a recovery standard.

The aqueous samples were acidified and extracted using sulfonated polystyrene divinylbenzene solid-phase extraction disks (3M Empore SDB-RPS). The disks were conditioned per manufacturers recommendation. The flow rate through the disk was maintained at less than 50 mL/min. The SPE disks were rinsed with 25% methanol and eluted with acetone (3 mL) and a triple aliquot of ethyl acetate (5 mL). The eluate was dried over Na_2SO_4 and the volume was reduced to 0.5 mL. This method was similar to those of Ollers et al. (2001) and Jonsson et al.) (*37*, *38*). The concentrate was transferred to a 2-mL crimp-top amber GC vials sealed with aluminum caps with PTFE-coated rubber septa. 4,4-Dibromooctafluorobiphenyl (Supelco) was added as an internal standard.

Analysis was performed on an HP 6890 GC with HP 5973 MS detector. The GC method was as follows: 2.0-μL injection, splitless, injector temperature 175 °C, 40 °C for 2 min, then 10 °C/min ramp to 250 ° C, hold for 14 min, ramp to 290 °C at 25 °C/min, hold for 2 min. The column was an RTX-MS5 30 m × 0.25 mm i.d., 0.25-um film thickness (Restek). The detector was run in total ion count (TIC) mode. The masses from 25 to 550 m/z were scanned. All compounds reported were confirmed against standards using both retention time and mass spectra. Calibration curves were constructed for each compound using at least 4 concentrations of the pure compound in ethyl acetate. All correlation coefficients were at least $R^2 = 0.95$.

Chemicals. Selection of the analytes in this study and their common usage is given in the Supporting Information. Hydrocinnamic acid (HCA, >99% pure), methyl 3-phenylpropionate (99%), ethyl 3-phenylpropionate (99%), 4-chloroxylenol (99%), 2,2-dimethoxy-2-phenylacetophenone (99%), butylated hydroxyanisole (BHA, 98%) oxybenzone (98%), and ibuprofen (Ibu, 98%), were purchased from Sigma-Aldrich. Octyl 4-methoxycinnamate (98%), *o*-hydroxybiphenyl (99%), naproxen (99%), ethyl acetate,

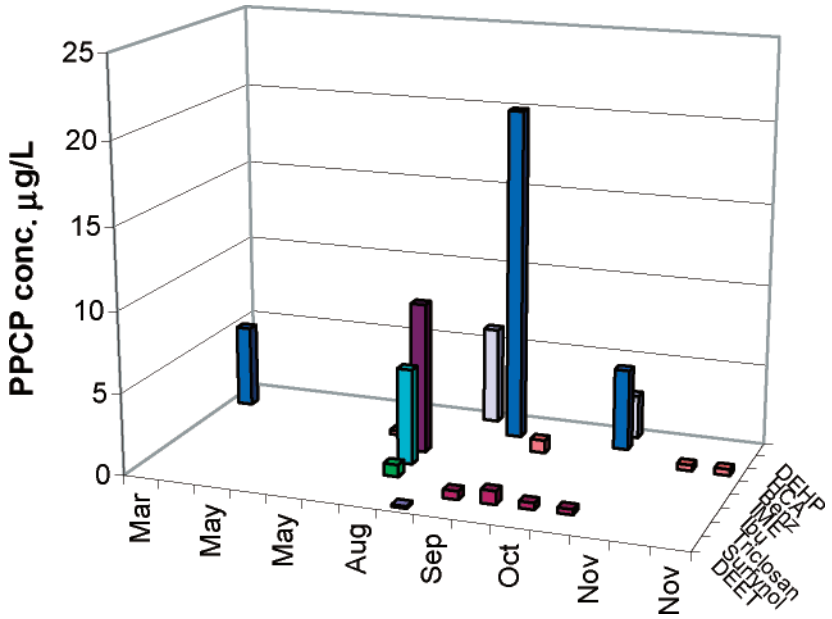

FIGURE 2. Concentrations of 8 PPCPs detected in raw water plotted against sample date.

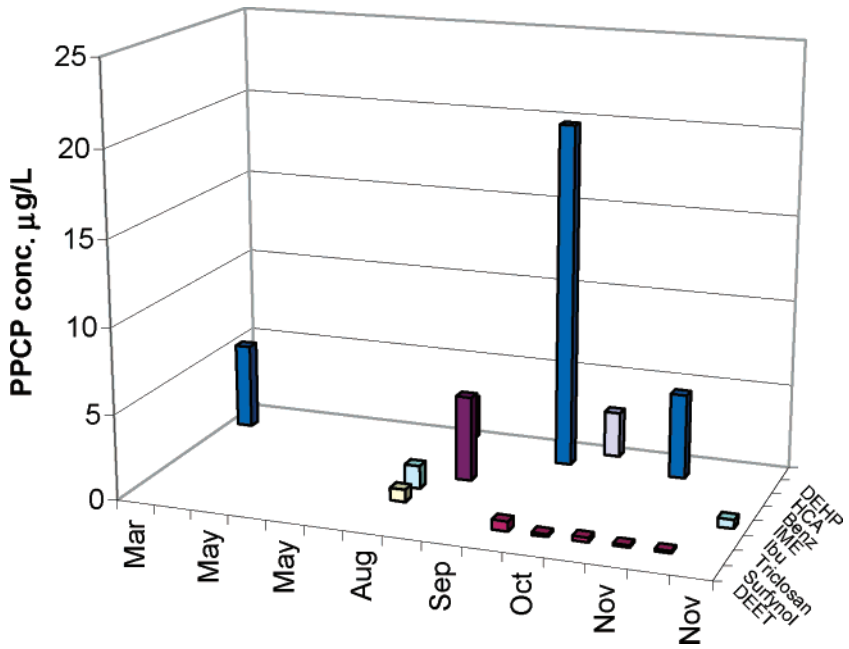

FIGURE 3. Concentrations of PPCPs detected in finished drinking water plotted against sampling date.

TABLE 4. PPCPs in Reclaimed Wastewater: Occurrence, Concentrations, and Comparison to Literature Values

analyte	MDL µg/L	occurrences	mean detected µg/L	range µg/L	total mean µg/L	literature values µg/L	ref
dimethyl phthalate	0.045	1/6	2.36		0.394		
diethyl phthalate	0.97	1/6	2.10		0.352		
dibutyl phthalate	2.70	1/6	3.71		0.62	0.2−10.4	15
butyl benzyl phthalate	0.26	1/6	0.651		0.108	0.7	15
DEHP	3.53	4/6	10.8	4.49−20.7	7.18	1.74−182	15
ethyl phenylpropionate	0.05	1/6	0.66		0.11		
hydrocinnamic acid	9.9	1/6	22.3		3.7		
benzophenone	0.044	4/6	0.993	0.561−1.35	0.662		
oxybenzone	0.12	1/6	0.84		0.14	0.03−0.36	18
ibuprofen	0.56	3/6	0.79	0.53−1.25	0.40	0.07−1.3	9, 8, 13
naproxen	19.6	1/6	24.6		4.1	0.1−2.6	13, 14, 47
triclosan	0.25	3/6	1.43	0.28−2.11	0.71	0.04−0.21	20
triclosan methyl ester	0.22	4/6	0.73	0.23−1.33	0.49		
chloroxylenol	0.032	1/6	1.71		0.285		
surfynol	0.192	2/6	1.08	0.805−1.34	0.358		
methylparaben	0.12	4/6	1.80	0.52−3.83	1.20		
DEET	0.16	2/6	1.31	0.50−2.11	0.44		
o-hydroxybiphenyl	0.43	1/6	0.44		0.07	0.13−3.6	35
tris (chloroethyl) phosphate	0.76	3/6	1.16	0.80−1.73	0.58	0.1	7
triphenyl phosphate	0.23	5/6	0.670	0.24−1.05	0.56	0.04	7

acetone, methanol, triphenyl phosphate (98%), tris-2-chloroethyl phosphate (99%), clofibrate (99%), clofibric acid (98%), benzophenone (99%), and caffeine (98.5%) were purchased from Fisher Scientific. Dibromooctofluorobiphenyl (98.8%), 2,4-dichlorophenylacetic acid (98%), and EPA phthalate esters mix (98%) containing dimethyl phthalate, diethyl phthalate, dibutyl phthalate, butyl benzyl phthalate, and di(ethylhexyl) phtahalate (DEHP) were purchased from Supelco. Air Products provided a sample of surfynol #104 (99%). Triclosan (Irgasan Op 300, 98%) was provided as a courtesy by Ciba Specialty Chemicals Corp. Diethyltoluamide (DEET, 100.5 µg/mL) was purchased from Ultra Scientific. All standards were used as received.

Method Detection Limits. Method detection limits (MDL) were determined in accordance with USEPA guidelines (*43*). Wastewater treatment plant effluent was collected, and it was filtered using the dual glass fiber filters. Two liters of the sample were extracted and analyzed as a baseline. Seven 2-L aliquots were spiked with a stock solution containing the analytes. The resulting MDLs (µg/L) are listed in Tables 2 and 4. The concentrations used for the MDL studies were no more than 5 times the MDL determined for all of the compounds.

Analytical blanks were run using reagent-grade water (Milli-Q Gradient A10). Three compounds of interest were found in the blanks: diethyl phthalate, dibutyl phthalate, and di(ethylhexyl) phthalate. Extraction of clean SPE disks showed that this was the source of the contamination. Detection of these compounds in the samples was only reported if the concentration was 10 times greater than the mean concentration in the blanks (*36*). These concentrations are given in Table 2 and Table 4 as the MDLs for those compounds, all other MDL values were determined as above.

Results and Discussion

PPCPs and Plasticizers in Drinking Water. Samples were collected from the four WFPs throughout the year, except at

TABLE 5. Average PPCP Concentrations (μg/L) in Raw Drinking Water (RDW), Reclaimed Water, and Wastewater Influent (WWI) in the Dry Season (August to November) and Wet Season (January to June)

compound	RDW dry	RDW wet	reclaimed dry	reclaimed wet	WWI dry	WWI wet
dimethyl phthalate	0.38 (0.098−0.78)	ND[a]	ND	2.36	ND	3.32
diethyl phthalate	1.49	0.90	2.10	ND	14.8 (6.31−23.7)	7.5 (5.3−9.7)
dibutyl phthalate	5.00 (1.44−8.3)	ND	3.71	ND	7.54	14.6
butyl benzyl phthalate	0.62 (0.05−1.19)	ND	0.65	ND	3.50 (2.93−4.07)	ND
DEHP	4.31 (2.67−5.94)	ND	4.58	3.59	ND	11.6 (5.33−20.8)
methyl phenylpropionate	ND	ND	ND	ND	4.33	ND
ethyl phenylpropionate	ND	ND	ND	0.66	2.09 1.18−3.02)	1.05 (0.66−1.42)
hydrocinnamic acid	12.65 (4.99−20.3)	5.04	22.3	ND	25.7 (24.3−27.3)	14.7
benzophenone	0.51 (0.36−0.79)	ND	1.03 (0.87−1.19)	0.96 (0.56-1.35)	2.43 (0.84−4.4)	1.39 (0.71−2.08)
octyl methoxy cinnamate	3.09 (0.565−5.61)	ND	ND	ND	ND	0.40
oxybenzone	ND	ND	ND	0.84	6.87 (5.3-8.3)	6.24 (0.11-10.4)
clofibrate	0.58 (0.26−0.89)	ND	ND	ND	ND	ND
clofibric acid	0.63	ND	ND	ND	ND	ND
ibuprofen	5.85	ND	ND	ND	22.7 (19.5-25.8)	7.50 (3.23-11.7)
ibuprofen methyl ester	9.22	ND	ND	ND	2.62	ND
naproxen	ND	ND	ND	24.6	ND	23.21
triclosan	0.73	ND	2.00 (1.89−2.11)	0.28	0.45 (0.35−0.55)	0.30 (0.29−0.31)
triclosan methyl ester	ND	ND	1.08 (0.84−1.32)	0.38 (0.24−0.52)	ND	ND
chloroxylenol	ND	ND	1.70	ND	3.55 (1.46−5.59)	1.61 (1.28−2.20)
surfynol	0.51 (0.32−0.82)	ND	1.07 (0.81−1.34)	ND	0.73	ND
methylparaben	ND	ND	2.21 (0.52−3.83)	ND	46.0 (12.5−79.6)	18.6 (16.4−21.7)
butylated hydroxyanisole	3.50 (3.49−3.52)	ND	ND	ND	ND	ND
DEET	0.13	ND	1.31 (0.50−2.11)	ND	0.36	ND
o-hydroxy biphenyl	ND	ND	ND	0.436	5.07 (3.76−6.38)	2.44
tris (2-chloroethyl) phosphate	ND	ND	1.73	0.88 (0.80-0.95)	1.01	ND
triphenyl phosphate	ND	ND	0.94 (0.81−1.05)	0.49 (0.24−0.96)	0.30	0.27 (0.26−0.27)

[a] ND = not detected.

WFP4, which was only sampled in early summer. The sporadic occurrence of PPCP and the relatively small number of samples (4−5 samples per plant) made meaningful statistical analysis of the data from the individual WFPs difficult. However, since the source of the raw water was the same for all four WFPs, the data were combined and analyzed using the whole cohort. The WFP4 data were included in the raw water data but not in the finished water data because of the ozone treatment.

Sixteen PPCPs and plasticizers were quantified in raw water (Table 2) and 13 were quantified in finished water (Table 3). Table 2 lists the MDL, the number of positive detections per total sample number, the mean concentration of positive detections, their range, the mean for all samples including those below the MDL, and the concentrations reported in similar studies. All results below the MDL were treated as zeros. Table 3 lists the occurrence of these compounds in the finished water, the means, ranges, and total means.

Most of the PPCPs found in the raw water were also found in the finished water, with the exception of DEET, clofibrate, and clofibric acid. The conventional C−S−F treatment plants were not able to completely remove all of the PPCPs, which may not be surprising considering the polar nature of the PPCPs. However, none of these compounds is currently regulated with the exception of DEHP, which was below the MCL of 6 ppb in the finished water.

Seasonal Variation in Drinking Water. Eight compounds (DEHP, HCA, benzophenone, ibuprofen, ibuprofen methyl ester (IME), triclosan, Surfynol 104, and DEET) were found in raw water, finished water, and reclaimed water. They are plotted in Figures 2, 3, and 6, so that direct comparisons can be made.

More PPCPs were detected and at higher concentrations in raw water collected from August to November, than in water collected from March to May. A similar pattern was seen for PPCPs in the finished water (Figure 3). For comparison, the mean concentrations were calculated for

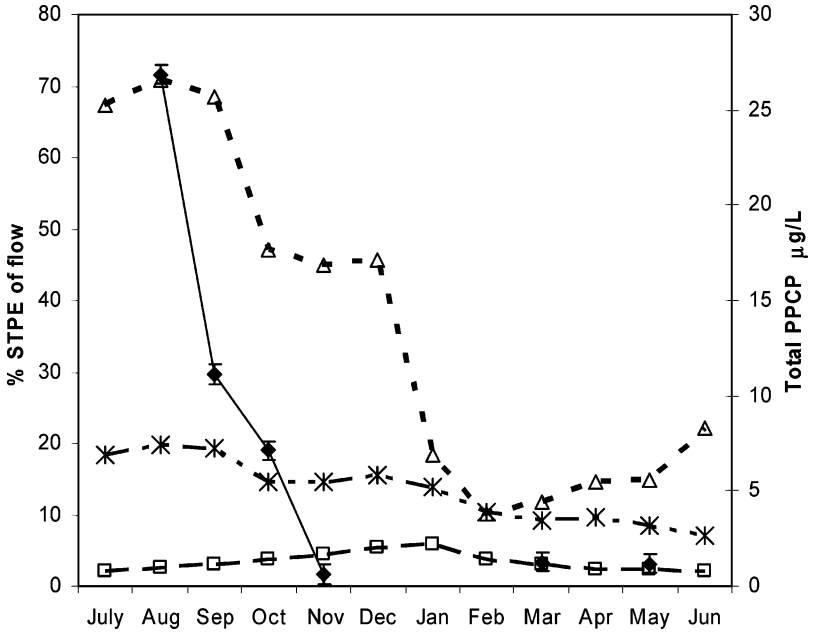

FIGURE 4. Total measured concentrations of PPCP (µg/L) in the raw drinking water (◆) spiked in late summer, correlating with the increase in the estimated percentage of STPE in the SWP (△), Colorado River (□), and water imported by SDCWA (∗) from July 2001 to June 2002 (*3*−*5*).

samples collected from August to November (dry season) and January to June (wet season). These divisions correspond roughly to regional periods of hot dry weather and cooler wet weather. Table 5 lists the mean and range of detected concentrations in raw water, reclaimed wastewater, and untreated wastewater, in the dry season and wet season.

As can be seen in Table 5, 14 of the 16 PPCPs detected in the raw drinking water were found only in the dry season. It is possible that some of the seasonal variation was due to increased use of pesticides and sunscreens in the summer. However, dry season concentrations are also higher for phthalate esters and pharmaceuticals as well. All four plants are reliant on imported water for roughly 90% of their source water, and several factors affect the raw water quality. The flow rates in both the Colorado River and the San Joaquin Delta (Figure 1) change dramatically during the year. The percentage due to STPE increases as flow declines (Figure 4). The percent contribution of STPE in the imported raw water was estimated from the river flow data for 2001−2002 and the discharge data for publicly owned treatment works in the water sheds and assuming 30% of the water originated from SWP and 70% from the Colorado River (*1*−*5*). In the summer of 2001, due to drought conditions, STPE made up $^2/_3$ of the flow entering the SWP. In the Colorado River however, STPE constituted only a small fraction of total flow. Plotting the sum total of the concentrations of all of the PPCPs measured in the raw water against the percentage of STPE in SWP, Colorado River and imported water shows that the spike in PPCPs observed correlates with the high STPE influence in the San Joaquin Delta. A much weaker effect of STPE in the Colorado is seen (Figure 4).

The percentage of STPE in the imported water was then plotted against the average of the sums of the detected PPCPs and plasticizers in that month (Figure 5). There is a good deal of scatter in the PPCP data (the lowest and highest values are also plotted), but a $R^2 = 0.85$ was found for an exponential curve fit. However, as discussed above, the raw water was a mixture of directly imported water and reservoir water that had been stored from earlier in the year so the real impact of STPE inputs is difficult to calculate. While this is not definitive evidence of a cause of the observed seasonal variation, it does suggest that under low flow conditions a heavily impacted water source can have an exponential impact on PPCP concentrations.

PPCPs and Plasticizers in Reclaimed Water. Table 4 lists the PPCPs and plasticizers detected and confirmed in the reclaimed wastewater. Phthalic esters were found, along with sunscreens, over-the-counter pharmaceuticals such as ibuprofen, naproxen, triclosan, and other biocides, antioxidants, flame retardants, and pesticides. There was a good deal of overlap between Table 2 and Table 4. Several compounds were found in the reclaimed water but not in the drinking water: ethyl-3-phenylpropionate, oxybenzene, naproxen, the methyl ester of triclosan, chloroxylenol, methylparaben, *o*-hydroxy biphenyl, the flame retardant, tris (chloroethyl) phosphate and plasticizer, triphenyl phosphate (*53, 54*). And some found in drinking water were not found in the reclaimed water (octyl methoxycinnamate, clofibrate, clofibric acid, ibuprofen, ibuprofen methyl ester, and BHA). With the exception of dimethyl phthalate and DEET, which were significantly higher in the reclaimed water, and ibuprofen, which was higher in the raw water, most of the PPCPs present in both cohorts were found at nearly the same concentrations (within a factor of 3). The literature values for concentrations of PPCPs in surface water (Table 2) and STPE (Table 4) also show overlap for many compounds.

Seasonal Variations in STPE. There also appears to be a seasonal component in the reclaimed water data (Figure 6). Of the 18 PPCPs detected in reclaimed wastewater, 77% were found at higher concentrations in the dry season, and 44% were only detected during the dry season (Table 5). Also, 77% of the average dry season concentrations in the wastewater treatment plant influent (WWI) were higher than those in the wet season.

The wastewater data were slightly out of phase with the drinking water data. Concentrations were higher from June through October and were lower from November to April, whereas in the drinking water the high concentrations started in August and declined after November, and were low in June. For ease of comparison, wet and dry means were calculated the same way for raw water and reclaimed water in Table 5 (i.e., dry season August − November, and wet season January to June). If the observed seasonal variation in the WWRP data is also occurring in other STPs in the

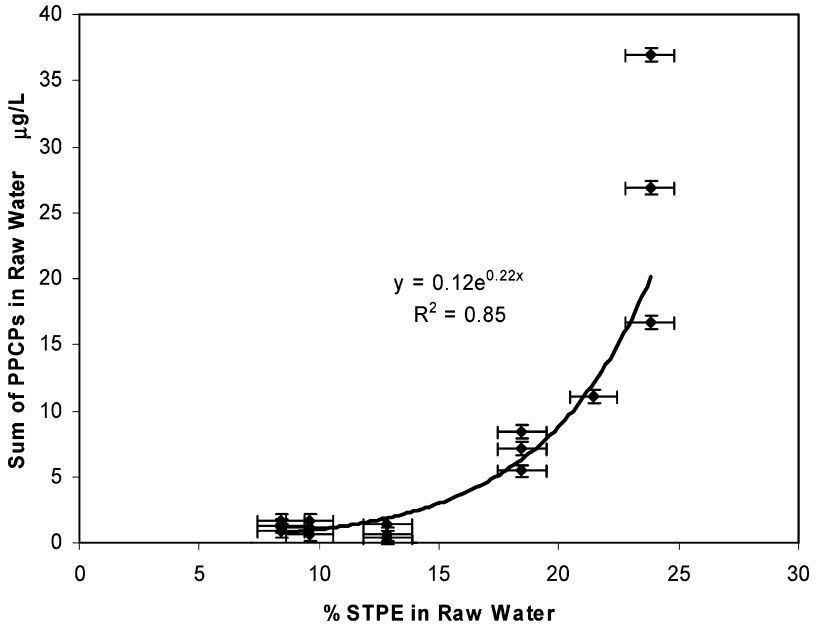

FIGURE 5. Correlation of the average sum of concentrations PPCPs and plasticizers found in raw water and the estimated percent contribution of STPE in the imported water in 2001−2002 (*3*−*5*). The highest and lowest sums of PPCP concentrations are also plotted.

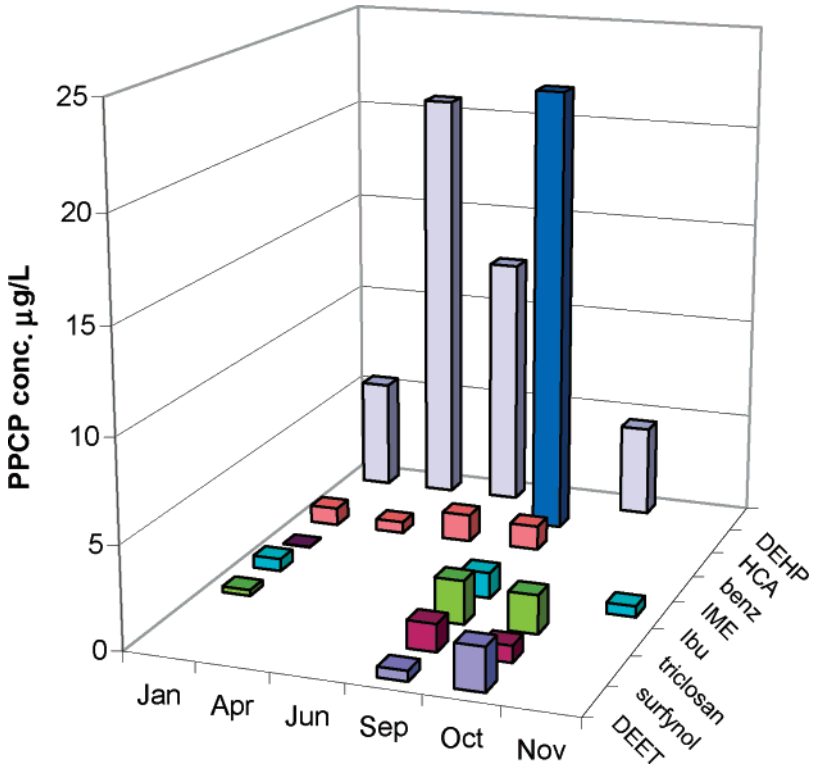

FIGURE 6. Occurrence and concentrations of PPCPs measured in the reclaimed wastewater were higher in summer and early autumn than in the winter and spring.

region, then there would be a higher PPCP load in surface waters impacted by STPE in the summer. Unfortunately, there is a lack of data on the seasonal variability of PPCP in STPEs in the United States, so it is not possible to determine if this is an isolated incident or if it is typical in the region.

This leads to the question of why the PPCP concentrations are higher in the summer than in winter. At the WWRP sampled there was no major variation in influent wastewater temperature throughout the year: the mean temperature in January was 23.8 °C and in August it was 29.2 °C. Influent characteristics such as BOD, pH, etc., were consistent through out the year as well. BOD removal efficiencies for January and August were both 98%.

One factor may be that several compounds such as DEET and the sunscreens are used more in the summer months. In addition, PPCP concentrations were higher in the imported water. There was an elevated background of PPCPs in the potable water even before it entered the waste stream. Higher dry season concentrations were found in drinking water for diethyl phthalate, butyl benzyl phthalate, hydrocinnamic acid, benzophenone, ibuprofen, ibuprofen methyl ester, triclosan, and surfynol. All of these compounds were also

found in wastewater influent and effluent at higher dry season concentrations. Table 5 shows that most (77%) of the PPCPs in the influent wastewater were found at higher concentrations in the dry months.

Currently reclaimed water is used for nonpotable uses, and none is being used for direct reuse as a drinking water supply (*40*). However, population growth and drought cycle are limiting the availability of freshwater throughout the Southwestern United States. It is estimated that by 2020 water demand for San Diego County will increase by 2.73×10^8 m^3 (*2*). To attempt to meet increasing demand, local and regional water authorities have begun a campaign of water reuse. California now leads the world in the use of reclaimed wastewater (4.95×10^8 m^3 in 2000) (*40*). And the fate of PPCPs in water supplies may become an issue of concern as water reuse becomes more intensive in arid regions around the world.

Acknowledgments

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Supporting Information Available

Brief description of compounds analyzed for and rational for their selection, and a map of the sampling locations. This material is available free of charge via the Internet at http://pubs.acs.org.

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