The occurrence and fate of chemicals of emerging concern (CECs) in coastal urban rivers receiving discharge of treated municipal wastewater effluent

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Abstract

To characterize the occurrence and fate of chemicals of emerging concern (CECs) in two effluent-dominated rivers in Southern California, USA, water samples were collected during low-flow conditions above and below discharges of water reclamation plants (WRPs), and screened for more than 60 pharmaceuticals and personal care products (PPCPs), commercial/household chemicals, current use pesticides and hormones. Approximately 50% of targeted CECs were detectable at stations downstream from WRPs, compared to <31 and <10% for stations above the WRPs for the Los Angeles River (LAR) and the San Gabriel River (SGR), respectively. Chlorinated phosphate flame-retardants were detected at the highest concentrations, with a mean total aggregate concentration of TCEP, TCPP, and TDCPP of 3400 and 2400 ng/L for the two rivers examined. Maximum instream concentrations of bifenthrin, diclofenac, galaxolide, and permethrin exceeded risk-based thresholds established by an expert panel to identify CECs for monitoring in receiving waters. In contrast, concentrations of PPCPs commonly detected in treated wastewater (e.g., acetaminophen, DEET, and gemfibrozil) were less than 10% of established thresholds. Attenuation of CECs was not observed downstream of WRP discharge, due in part to the short hydraulic residence times in these highly channelized systems (<3 days). These results will inform the selection of CECs for future WRP effluent and instream monitoring in semi-arid, effluent-dominated systems, as well as assessment of mass loading for terminal water bodies at the bottom of these watersheds.

Introduction

Chemicals of emerging concern (CECs) are a diverse group of chemicals not widely regulated or routinely monitored. Engineered treatment works do not completely remove pharmaceuticals and personal care products (PPCPs), commercial and industrial chemicals, natural hormones, food additives, and some current use pesticides from industrial and municipal waste streams, resulting in their discharge

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and detection in aquatic systems in the United States (US) and abroad (Kolpin *et al.* 2002, Tixier *et al.* 2003, Snyder *et al.* 2004, Pal *et al.* 2010). Some particularly potent CECs (e.g., steroid hormones and pesticides) can exert toxic effects to aquatic life at parts per billion or lower concentrations (Chandler *et al.* 2004, Ankley *et al.* 2005) while others may accumulate in fish tissues (Ramirez *et al.* 2009) and ultimately biomagnify in higher trophic level species, including birds, marine mammals, and humans (Fisher *et al.* 2006, Meng *et al.* 2009, Sedlak and Greig 2012). Though low-level CEC exposure may not have an immediate impact, growing evidence indicates deleterious effects aggregate over time (Ankley *et al.* 2008).

Previous studies found that treated effluent discharge from municipal wastewater treatment plants (WWTPs) into aquatic systems results in maximum concentrations of various CECs ranging from <1 ng/L to several µg/L, depending on the chemical (Pal *et al.* 2010, Tixier *et al.* 2003, Snyder *et al.* 2004, Pal *et al.* 2010). Once released, some CECs rapidly attenuate through dilution, hydrolysis, photodegradation, biotransformation, and/or sorption to sediments (Jurgens *et al.* 2002, Fono *et al.* 2006, Lin *et al.* 2008, Guo and Krasner 2009, Zeng and Arnold 2013). In contrast, some wastewater-derived chemicals persist in river systems (Dickerson *et al.* 2011). Agricultural and urban runoff also contribute CECs in receiving waters (Pereira and Rostad 1990, Schottler *et al.* 1994). Few studies have investigated the fate of CECs in "effluent-dominated" waterways subject to a high degree of hydromodification, channelization, flow diversion, and removal of soft bottom and riparian habitat (Ackerman *et al.* 2003). However, the potential for CEC exposure to aquatic life is heightened in arid and semi-arid water bodies where limited or negligible dilution takes place during low flow conditions (Maruya *et al.* In press).

To make efficient use of available resources, current analytical protocols specified in monitoring programs focus on a finite list of constituents, such as those identified as priority pollutants. However, dozens to perhaps hundreds of new chemicals are introduced each year (Howard and Muir 2010), some of which are eventually discharged into the environment. Because synthesis and production of new chemicals will continue in the future, characterizing the occurrence, fate, and potential for adverse health effects due to CECs is critical to informing management actions. These might include monitoring the most problematic chemicals to maintain and protect aquatic ecosystem integrity (Diamond *et al.* 2011, Olsen *et al.* 2013).

The present study characterized: 1) occurrence of multiple CEC classes in two effluent-dominated rivers during low-flow conditions (worst case exposure), 2) fate and transport of target CECs to the coastal ocean, and 3) CECs appropriate for targeted future monitoring based on their potential risk to ecological receptors. The study collected and analyzed water samples from two coastal urban river systems in southern California (USA), a densely populated, semi-arid coastal region. Samples collected during two sampling events at multiple locations on each river during two events were analyzed for a broad suite of CECs, and observed concentrations were mapped vs. WWTP discharge location, and compared to published CEC thresholds derived to protect aquatic life.

Methods

Watersheds

The present study focused on the Los Angeles and San Gabriel Rivers, two highly modified, coastal urban watersheds of the metropolitan Los Angeles region of Southern California (USA). Covering a watershed area of 2170 km^2, the Los Angeles River (LAR) extends 89 km from headwaters in the San Fernando Valley to its estuary near Long Beach (Figure 1). Large portions (84 km) of the LAR are channelized, although ~19 km of the riverbed is unlined and contains extensive riparian habitat. Constructed for flood control, the LAR's low-flow channel has a trapezoidal cross-section (3 to 6 m wide; average depth of 0.3 m) that is fully contained within a wider and deeper concrete-lined channel. A number of tributaries, including the Burbank Western Channel, Arroyo Seco, and Pacoima, Tujunga, and Verdugo Washes, contribute flow to the LAR. The San Gabriel River (SGR) encompasses a watershed area of 1800 km^2 and extends 98 km, starting in the San Gabriel Mountains to the northeast of Los Angeles and entering the Pacific Ocean at Seal Beach, <10 km east of the LAR estuary (Figure 2). The SGR has also been subject to extensive hydromodification, with flow diversions for water storage and conservation in the upper and middle reaches and a trapezoidal low-flow notch embedded within a larger concrete lined channel in the lower reaches.

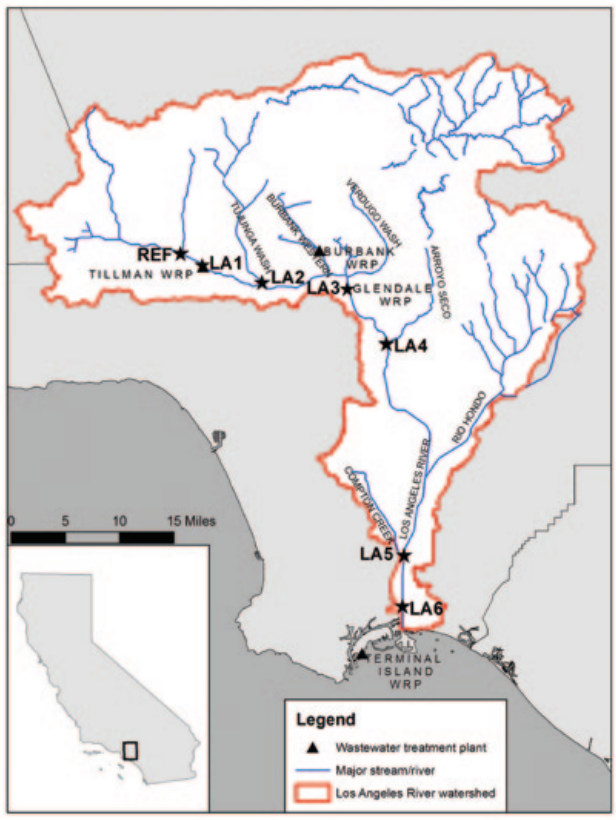

Figure 1. Sampling stations for the Los Angeles River (LAR) watershed; river water samples were collected during two events (July and October 2011) during low-flow conditions.

Major tributaries of the SGR include San Jose and Coyote Creeks (Stein and Ackerman 2007).

The D.C. Tillman and Los Angeles Glendale Water Reclamation Plants (WRPs) at river kilometers (RKs) 74 and 50, respectively, discharge directly into the LAR (Figure 1). A third facility (Burbank WRP) discharges into the Burbank Western Channel tributary. Five WRPs discharge into the SGR, with three larger capacity plants (San Jose Creek, Los Coyotes, and Long Beach) discharging into the segment below RK 40 (Figure 2). Although numerous storm-drain outfalls discharge either directly into the main stem or tributaries in both systems, up to 98 and 90% of the flow in the SGR and the LAR, respectively, can be attributed to WRP effluent during dry weather, low-flow conditions (Ackerman *et al.* 2003, Stein and Ackerman 2007). For the period investigated, discharge rates associated with the WRPs described above totaled 272,000 and 348,000 m^3/day for the LAR and SGR, respectively (Table 1).

An important distinction between these two systems is the extent of water management practiced by the County of Los Angeles. For the SGR, controlled discharge and stream diversions result in drastically different daily flows, particularly in the reach below the San Jose Creek WRP (RK 40) and above the Los

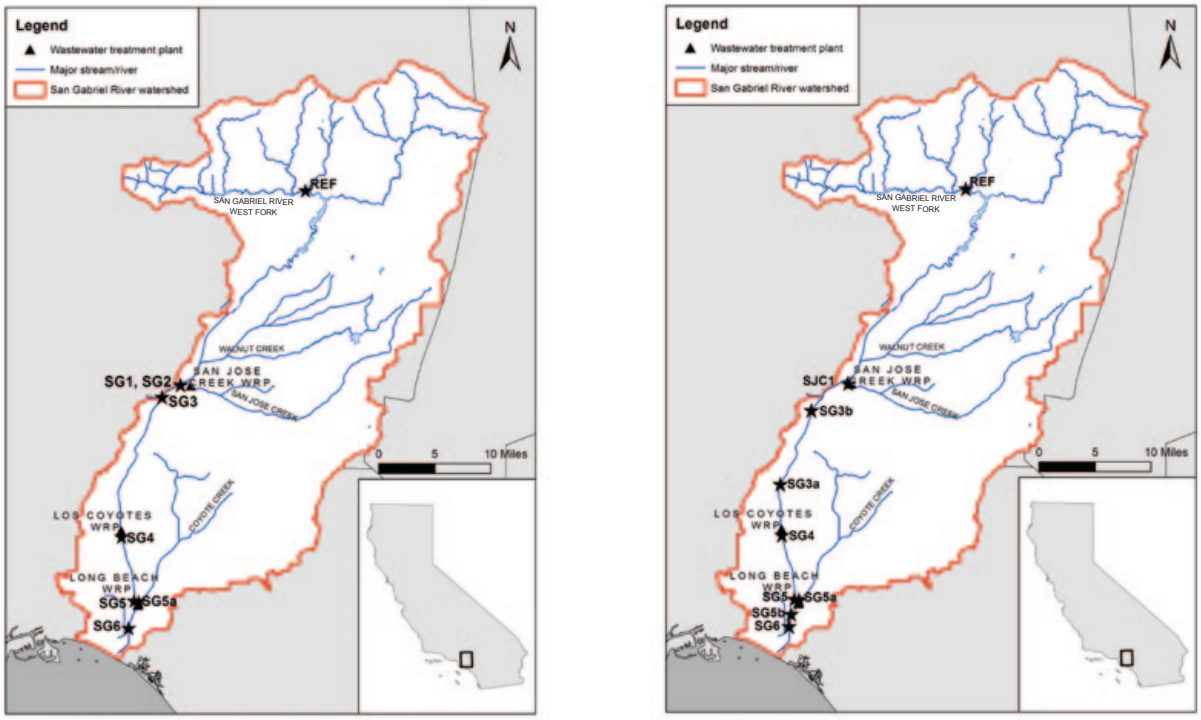

Figure 2. Sampling stations for the San Gabriel River (SGR) watershed; river water samples were collected during two events during low-flow conditions. The left map is for Event #1 (July 2011), and right map is for Event #2 (October 2011). The location of station SG3 differed between events due to managed flow diversions.

Table 1. Stream concentrations of carbamazepine, estimated and measured at discharge points for water reclamation plants (WRPs) on the Los Angeles and lower San Gabriel river systems. The confluence point of the river and the ocean is considered as river kilometer = 0. $C_{effluent}$ = concentration of carbamazepine (ng/L) measured in treated wastewater effluent; $C_{r,est}$ = in stream concentration of carbamazepine (ng/L) estimated using Equation 2; $C_{r,meas}$ = in stream concentration of carbamazepine (ng/L) measured in the present study; and NA = data not available

Treatment Plant	Effluent Treatment	Discharge Point (km)	Estimated Discharge (m^3/day)	$C_{effluent}$ (ng/L)	$C_{r,est}$ (ng/L)	$C_{r,meas}$ (ng/L)
Los Angeles River						
D.C. Tillman WRP	Tertiary	74	200,000	NA	NA	185 - 191
Burbank WRP	Tertiary	66	19,800	NA	NA	179 - 216
LA-Glendale	Tertiary	50	52,700	NA	NA	192 - 220
San Gabriel River						
San Jose Creek WRP	Tertiary	36	136,000	188 - 289	250	35 - 294
Los Coyotes WRP	Chlorinated-Tertiary	16	72,000	265 - 308	255	318 - 330
Long Beach WRP	Chlorinated-Tertiary	8	37,000	197 - 204	221	194 - 241

Coyotes WRP (RK 16; Figure 2). Stream flow varies widely in this stretch depending on which of the three San Jose Creek WRP outfalls (one discharging into San Jose Creek near the confluence with the SGR, the second discharging into the SGR just below the confluence with San Jose Creek, and the third into the SGR at Firestone Boulevard ~12 km downstream from the plant) operate on a given day. In contrast, diversions and managed flows are uncommon for the LAR, resulting in less day-to-day variation in volumes discharged to the main channel.

Sampling Design and Procedures

Water samples were collected from the LAR and SGR during two dry weather low-flow events (July and October 2011). Seven stations were targeted on the LAR for both events (Figure 1). Eight (Event #1/July) and nine stations were targeted (Event #2/October) on the SGR (Figure 2) and two of its tributaries (San Jose and Coyote Creeks). For Event #2, very low or non-existent surface water at stations SG1, SG2, and SG3 necessitated sampling of the alternate outfall location at Firestone Blvd. (SG3a). A station in the lower SGR where the riverbed converts to soft bottom (SG5b) was also sampled. Reference stations located above WRP discharges were identified and sampled during both events.

Three surface grabs collected from the stream bank or highway bridges at each station with an 8-L stainless steel bucket were composited and sub-divided into three pre-cleaned 1-L amber glass bottles with preservative (ascorbic acid, NaN_3, or CH_2Cl_2). Three 1-L field blanks were also collected for each event. The bucket was rinsed with high purity methanol prior to sampling of the next station. Sampling was conducted during daylight hours to minimize the effect of diurnal variability in effluent quality (Nelson *et al.* 2011) and to coincide with an ebbing tide for the tidally influenced stations. Samples were kept in the dark on ice and transported to participating labs for analysis within 48 hours of collection, accompanied by chain of custody forms. All bottles were received intact after shipping and with enough ice to maintain sample integrity.

Analytical Methods

A total of 62 and 74 analytes were analyzed in samples for Events #1 and #2, respectively. Target analytes included PPCPs (e.g., carbamazepine, DEET, fluoxetine, galaxolide, ibuprofen, sulfamethoxazole, triclosan), natural and synthetic hormones (e.g., 17β-estradiol, estrone, norgestrel) and commercial and industrial chemicals such as octyl- and *p*-nonylphenol, chlorinated flame retardants including tris (1-chloro-2-propyl) phosphate (TCPP), tris (1,3-dichloro-2-propyl) phosphate (TDCPP) and tris (2-chloroethyl) phosphate (TCEP), perfluorochemicals (e.g., PFOA, PFOS), polybrominated diphenyl ethers (PBDEs), pyrethroids, fipronil and degradates. These constituents represent a broad cross-section of CECs for which robust analytical methods exist. Erythromycin and tonalide were analyzed in Event #1 samples only. Several hormones (e.g., dexamethasone, norgestrel, prednisone, and triamcinolone), atorvastatin, galaxolide, iopromide,

NDMA p-nonyphenol, and octylphenol were added to the analyte list for Event #2 samples.

PPCPs were concentrated from 1-L water samples using solid phase extraction (SPE) and subsequent elution into methanol. For PBDEs, fipronil, and pyrethroids, 1-L water samples were extracted by shaking with dichloromethane in a 2-L separatory funnel. Target analytes were identified and quantified using isotope dilution LC-MS/MS with APCI (hormones), ESI negative and positive multiple reaction monitoring (MRM) modes (PPCPs), GC-MS/MS (for galaxolide and NDMA), and GC-NCI-MS (PBDEs, pyrethroids and fipronil) following previously published methods (Vanderford *et al.* 2003, Vanderford and Snyder 2006, Lao *et al.* 2010, Teerlink *et al.* 2012). Procedural (laboratory) and preserved field blanks were processed and analyzed in parallel with the water samples. Detection limits ranged from 0.03 (PBDEs) to 1350 (octylphenol) ng/L. Analysis of split samples from Event #2 by the Colorado School of Mines and University of Arizona labs showed excellent agreement (relative percent difference ≤23%) for eight PPCP analytes in common.

Hydrology and Flow Balance

Daily discharge data from flow gauges maintained by the US Geological Survey and County of Los Angeles were used to determine characteristic residence times for different reaches of the LAR and SGR. The mass balance accounting for loss from the water column due to instream attenuation is shown in Equation 1:

$$V_u C_u + V_{wrp} C_{wrp} + V_n C_n - \Delta_{loss} = V_d C_d \qquad \textbf{Eq. 1}$$

where V is the flow rate, C is the CEC concentration, the subscripts u and d, denote locations upstream and downstream of a WRP discharge point, n accounts for all non-point input, and wrp indicates the WRP discharge. The generic loss term (Δ_{loss}) represents mass lost from the water column due to processes such as hydrolysis, photodegradation, sorption, and volatilization.

Equation 1, tailored to the SGR for the CEC concentration (~RK 8), below all the WRP discharges, and above the tidal intrusion is shown in Equation 2.

$$\frac{V_{sj} C_{SJ} + V_{LC} C_{LC} + V_{LB} C_{LB} + V_{CC} C_{CC} - \Delta_{loss}}{V_{sj} + V_{LC} + V_{LB} + V_{CC}} = C_d \qquad \textbf{Eq. 2}$$

where C_{SJ}, C_{LC}, and C_{LB} were the CEC concentrations in discharged effluent from the San Jose Creek, Los Coyotes and Long Beach WRPs, respectively; V_{SJ}, V_{LC}, and V_{LB}, were the discharge flow rates from the WRPs; C_{CC} and V_{CC} were the concentrations and discharge flow rates for Coyote Creek, respectively; and C_d was the CEC concentration downstream of the last WRP discharging into the SGR, in this case, the Long Beach plant (Figure 2).

Selection of Monitoring Thresholds

A risk-based method that compares occurrence (as maximum concentrations or C_{max}) to toxicity thresholds for ecological receptors (e.g., no observable effects concentrations or NOECs) was used to identify CECs for monitoring in waters that receive treated WWTP effluent and stormwater discharge in the state of California (Maruya *et al.* In press). This approach defined chemical-specific monitoring trigger quotients (MTQs) in Equation 3.

$$MTQ = Cmax \,/\, [(NOEC \text{ or } PNEC)(uncertainty\ factor)] \qquad \textbf{Eq. 3}$$

where C_{max} is the maximum measured environmental concentration, PNEC is the predicted no effects concentration, and uncertainty factors range from 10 to 1000. Values of MTQs that exceeded a set threshold (unity) were used to identify CECs to include in investigative monitoring for different classes of receiving waters, including effluent dominated waterways similar to those studied herein (Maruya *et al.* In press).

Results and Discussion

Occurrence of Target CECs

More than half of the CECs targeted were detected in at least one sample for Events #1 (52%) and #2 (51%; Table 2). Broken down by general class, nearly all of the targeted PPCPs (91 and 83% for Events #1 and #2, respectively) were detected in at least one sample. Hydrocortisone, naproxen, atorvastatin, and diltiazem were the only target PPCPs not detected, although it should be noted that atorvastatin and diltiazem were analyzed only for Event #2. Natural hormones such as 17β-estradiol, estrone, progesterone, testosterone, and their synthetic analogs 17α-ethinylestradiol, dexamethasone, norethistrone, prednisone, and triamcinolone were

Table 2. The number and percentage of target analytes (aggregated for LAR and SGR) detected in sampling Event #1 (Ev#1; July 2011) and Event #2 (EV#2; October 2011). PPCPs = pharmaceuticals and personal care products; REF = reference station.

	PPCPs		Commercial		Pesticides		Hormones		TOTAL	
	Ev#1	Ev#2	Ev#1	Ev#2	Ev#1	Ev#2	Ev#1	Ev#2	Ev#1	Ev#2
No. Target CECs	22	24	21	25	14	15	5	10	62	74
No. CECs Detected	20	19	7	8	5	10	0	1	32	38
% CECs Detected	91	79	33	32	36	67	0	10	52	51
No. CECs Detected -- SGR REF	3	1	3	0	0	0	0	0	6	1
No. CECs Detected -- LAR REF	10	4	5	6	4	7	0	0	19	17

not detected in any of the samples at reporting limits ranging from 0.5 to 50 ng/L. Norgestrel was the only synthetic hormone detected in samples from Event #2, with concentrations ranging from 12 to 40 ng/L. Approximately one third of commercial chemicals tested were detectable in at least one sample. The chlorinated phosphates TCPP, TDCPP and TCEP, triclocarban, triclosan, and PFOA were more frequently detected compared to others (e.g., PFOS). Of the 14 PBDEs analyzed, BDE-47 and -99 were the only congeners detected, at a maximum concentration of 2.2 ng/L. Octylphenol was detected in Event #2 samples, but nonylphenol (<5 ng/L) and bisphenol A (<25 ng/L) were not detected.

Fipronil, a phenylpyrazole insecticide, and its three major environmental degradates (fipronil desulfinyl, sulfide, and sulfone) were the only pesticides detected. The eight synthetic pyrethroids analyzed (bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, λ-cyhalothrin, detamethrin, fenpropathrin, and permethrin) were non-detects for Event #1, though bifenthrin, permethrin, and cyflurathin were detected in Event #2. Triazine herbicides, such as atrazine and simazine were analyzed only for Event #2, with atrazine detected in a number of SGR samples.

In contrast to the stations located downstream of WRPs, <10% of CECs targeted were detectable in samples from the reference station in the upper SGR watershed (Figure 2). Caffeine (34 ng/L), DEET (8.5 ng/L), gemfibrozil (2.0 ng/L), iopromide (2.9 ng/L), and the three chlorinated phosphates (5.1 to 49 ng/L) were detected at this location, which lies in a sparsely populated area, but popular for recreation during the summer months. No pesticides or other targeted commercial chemicals were detected at this station. A larger number of CECs, including caffeine (413 ng/L), DEET (36 ng/L), gemfibrozil (1.3 ng/L), diclofenac (28 ng/L), sulfamethoxazole (95 ng/L), fipronil and degradates (25 ng/L), and the three chlorinated phosphates (64 - 230 ng/L) were detected in samples from the LAR reference station, located <5 km upstream of the Tillman WRP in a suburban recreational area that includes a golf course, a park with a lake and outdoor cooking facilities, and concrete walking paths. Clearly, the LAR reference station was subject to a higher degree of human activity and impact compared to the SGR reference station.

The chlorinated phosphate flame retardants (sum of TCPP, TDCPP, and TCEP) had the highest aggregated concentrations (mean ±standard deviation) of 3080 ±121 ng/L and 3530 ±151 ng/L for the LAR (excluding the reference station) during Events #1 and #2, respectively. For the SGR (excluding the reference and Station SG5a on Coyote Creek), the aggregated concentrations for TCPP, TDCPP, and TCEP were 2100 ±516 ng/L and 3250 ±266 ng/L for Events #1 and #2, respectively. TCPP contributed 50% or more of the sum for the three chlorinated phosphates in the present study. Sucralose, an artificial food and drink sweetener, averaged 1380 ±129 ng/L and 826 ±566 ng/L for the LAR and SGR during Event #1, respectively; and 293 ±37 and 307 ±30 for the LAR and SGR during Event #2, respectively. Mean concentrations of the fragrance galaxolide, analyzed only for Event #2 samples, were 2260 ±319 ng/L and 2410 ±315 ng/L for the LAR and SGR, respectively. Iopromide, an x-ray contrast media used in the medical industry that was analyzed only in Event #2 samples, averaged 1700 ±1660 ng/L for the SGR, but only 35 ±9.3 ng/L in the LAR. The peak concentration of iopromide (5070 ng/L) at Station SJC1 coincided with the San Jose Creek WRP discharge, and decreased steadily to 664 ng/L by Station SG6 in

the tidal estuary, suggesting the majority of loading for this CEC occurred at or above the San Jose Creek WRP. Mean concentrations for all other target CECs, including carbamazepine, DEET, ibuprofen, meprobamate, PFOA and sulfamethoxazole, were <1000 ng/L.

The maximum concentrations of selected CECs reported herein (Table 3) are comparable to or higher than concentrations reported in previous studies. For example, the maximum concentrations of diclofenac observed in the present study (77 and 124 ng/L for Events #l and #2, respectively) were comparable to the concentration in treated wastewater effluent (115 ng/L; Vanderford and Snyder 2006) and similar to or higher than concentrations reported in effluent and freshwater systems (rivers and canals) worldwide, including North America (11 - 82 ng/L), Europe (21 - 41 ng/L), and Asia/Australia (1.1 - 6.8 ng/L; Pal *et al.* 2010). Water samples collected at the point of discharge from the San Jose Creek WRP (Station SJC1) every 6 hours over a 24-hour period and analyzed by LC-MS/MS showed that concentrations for some target CECs (e.g., azithromycin, DEET, diclofenac, estrone, p-nonylphenol, sulfamethoxazole, and triclosan) peaked during periods when influent and effluent discharge flows were highest; in contrast, little-to-no diurnal variation was observed for other CECs (e.g., carbamazepine, meprobamate, TCEP, and triclocarban). The range of CEC concentrations observed for Events #1 and #2 were comparable (Supplemental Information (SI) Table SI-3; ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_013_026SI.pdf), indicating the daytime grab sampling approach adequately representated the effluent quality and mass loading into the LAR and SGR during low flow conditions.

Table 3. Monitoring trigger quotients (MTQs) for individual CECs detected in the Los Angeles and San Gabriel rivers during low flow conditions for Event #1 (Ev#1; July 2011) and Event #2 (EV#2; October 2011). C_{max} = maximum observed aqueous concentration in ng/L; MTL = monitoring trigger level, based on observed or predicted no effect concentrations and uncertainty factors of 1 to 100 (Anderson *et al.* 2012); MTQ = C_{max} / MTL; and NA = data not available. Permethrin values are the sum of *cis*- and *trans*-isomers.

Analyte	MTL (ng/L)	C_{max} (ng/L)		MTQ	
		Ev#1	Ev#2	Ev#1	Ev#2
17β-estradiol	2	<1.25	<1.25	<0.62	<0.62
Acetaminophen	920000	25.8	16.0	<0.01	<0.01
Atrazine	200	13.7	17.1	0.07	0.09
BDE 47	100	1.0	2.2	0.01	0.02
BDE 99	100	0.4	0.9	<0.01	0.01
Bifenthrin	0.4	<1.5	3.6	<3.80	9.00
Bisphenol A	60	<12.5	<25.0	<0.21	<0.42
Carbamazepine	2500	330.0	318.0	0.13	0.13
Chlorpyrifos	5	0.9	4.9	0.18	0.99
DEET	58400	860.0	380.0	0.01	0.01
Diazepam	12700	4.3	6.1	<0.01	<0.01
Diclofenac	100	77.0	124.0	0.77	1.24
Dilantin	33500	291.0	239.0	0.01	0.01
Estrone	6	<2.5	<2.5	<0.42	<0.42
Fipronil	51	13.6	7.4	0.27	0.14
Fipronil desulfinyl	59	13.8	13.3	0.23	0.23
Fipronil sulfide	59	2.0	1.7	0.03	0.03
Fipronil sulfone	59	5.7	10.6	0.10	0.18
Galaxolide	700	n/a	2750.0	NA	3.90
Gemfibrozil	7800	193.0	324.0	0.02	0.04
Ibuprofen	100	40.5	<25.0	0.41	<0.25
Permethrin	1	<18.0	1.7	<18.00	1.70
Sulfamethoxazole	5900	790.0	932.0	0.14	0.16
TCEP	51000	785.0	581.0	0.02	0.01
TCPP	74900	2150.0	2900.0	0.03	0.04
TDCPP	51000	1345 .0	923.0	0.03	0.02
Tonalide	1000	188.0	NA	0.19	NA
Triclocarban	360	102.0	92.0	0.28	0.26
Triclosan	250	18.2	26.3	0.07	0.11
Trimethoprim	4000	78.5	180.0	0.02	0.04

Flow Velocity and CEC Concentration Profiles

A modeled idealized scenario illustrating the river velocity profiles in the LAR (Figure 3) shows three distinct regimes: 1) high velocity (≥1 m/s), 2) intermediate velocity (0.3 to 0.5 m/s), and 3) low velocity (<0.25 m/s). These segments correspond to 1) flow contained within the trapezoidal cross-sectional low flow channel, 2) water that overflows the low flow channel and spreads over the wider flood control channel, and 3) the tidal estuary where river water mixes with seawater from the Pacific Ocean. For the LAR, flow corresponding to velocity Regime 1 begins with discharge from the D.C. Tillman WRP into the concrete lined flood control channel (RK 74) and ends after discharge from the Glendale WRP (RK 50). At the confluence of the Arroyo Seco (RK 45), the flow spreads out and velocity decreases (Regime 2). In the tidal segment starting at ~RK 15, the riverbank and bottom transitions to natural substrate, resulting in increased friction and reduced water

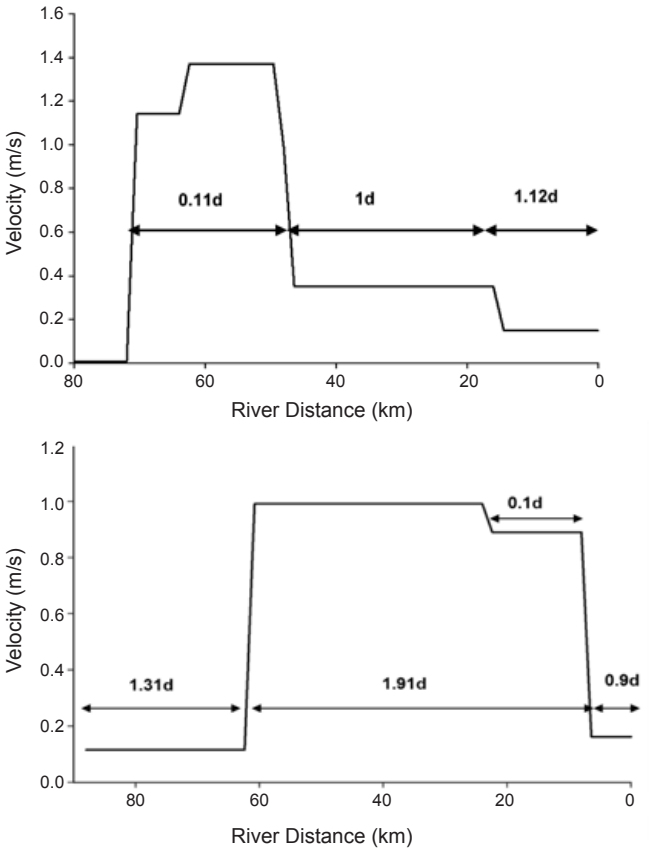

Figure 3. Modeled water velocity profiles and estimated hydraulic residence times in days (d) for the Los Angeles River (top) and San Gabriel River (bottom) during low flow conditions. The confluence point of the river and the ocean is considered as river kilometer = 0.

velocity (Regime 3). The estimated residence time of water discharged at the D.C. Tillman WRP during these low-flow conditions was 2.2 days.

Similar to LAR, the travel time of water discharged from the San Jose Creek WRP at RK 40 to the mouth of the SGR was relatively short, estimated at 1.5 days (Figure 3). Because the Los Coyotes and Long Beach WRPs are situated in or just upstream of the SGR tidal segment, residence times of effluents discharged from these facilities was <1 day. In contrast to the LAR, water in the SGR is routinely diverted by dams to collect runoff and recycled water for groundwater recharge. Active management of SGR flows, sometimes on a daily basis, thus results in spatially and temporally variable flow conditions across the segment below the San Jose Creek WRP. Water velocity data measured in July 2011 shows segments with no flow (RK 30 - 20).

The concentration profiles of TCEP, TCPP, and TDCPP for the LAR show a sharp increase at the Tillman WRP, followed by incremental increases where the Burbank and Glendale WRPs discharge into the river (Figure 4). Downstream of the Glendale WRP (~RK 45), the concentrations decrease gradually upon entering the tidal segment, where attenuation is likely due to dilution. Carbamazepine, DEET, and dilantin show similar concentration-distance profiles in the LAR (Figure 4). A sharp increase in CEC concentration profiles occurred just downstream of the San Jose Creek WRP on the SGR (RK 40), and elevated CEC concentrations were maintained downstream of the discharges from the Los Coyotes and Long Beach WRPs in the lower watershed (Figure 5). Concentrations were uniformly lower in the tidally-influenced SGR segment (Station SGR6), indicating attenuation likely due to seawater dilution. Furthermore, the CEC concentration profiles synchronized with river discharge (Figure

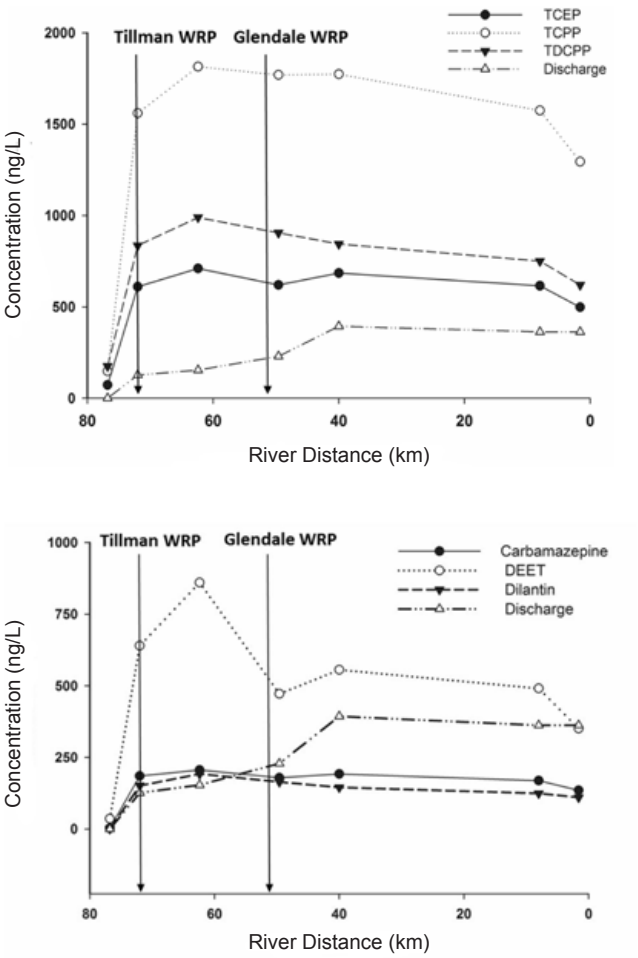

Figure 4. In-stream concentration profiles of chlorinated phosphate flame retardants (TCPP, TDCPP, and TCEP; top) and selected pharmaceuticals and personal care products (PPCPs; bottom) for the Los Angeles River (July 2011). The confluence point of the river and the ocean is considered as river kilometer = 0. The units plotted for discharge are (100 m^3/s). WRP = water reclamation plant

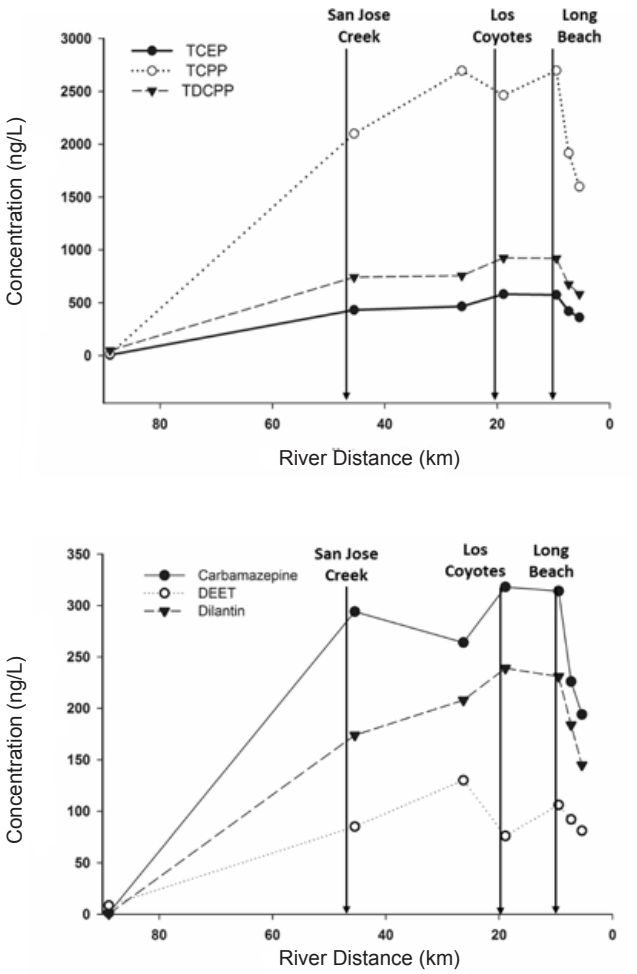

Figure 5. In-stream concentration profiles of chlorinated phosphate flame retarding CECs (TCPP, TDCPP, and TCEP; top) and selected pharmaceuticals and personal care products (PPCPs; bottom) for the San Gabriel River (October 2011). The confluence point of the river and the ocean is considered as river kilometer = 0. WRP = water reclamation plant.

4), clearly indicating the importance of WRPs as a source of the targeted CECs during low flow conditions.

The most notable exceptions to this pattern occurred for the insecticide fipronil and it's degradates, along with the pyrethroid pesticides. Fipronil and its degradates were found at relatively high concentrations in both the LAR reference site and the site on Coyote Creek (a tributary of the SGR) upstream of any WWTPs, where river flow was composed solely of dry weather urban runoff. Permethrin, along with highest observed concentrations of bifenthrin and cyfluthrin, was detected only at the Coyote Creek site. For these pesticides, dry weather runoff appears to be an important contributor in these watersheds.

Flow and CEC Mass Balance

Discharge from the WRPs was the predominant source of flow in the upper reaches of the LAR (Figure 1); however, downstream of Station LA3 the river flow was augmented by diffuse non-point sources (e.g., influx of ground or surface water flow). In the lower reaches (below RK 15), tidal flushing heavily influenced the river flow, with an estimated dilution volume of 75,700 m^3/day added to the freshwater discharge. Carbamazepine, a PPCP that serves as a conservative wastewater input tracer (Guo and Krasner 2009), was detected in all river samples for both events. The mass loading from the WRPs discharging to the LAR was estimated at 53 g/day (or 19 kg/year).

Similarly, the San Jose Creek facility (RK 40) was the predominant source of measured flow in the SGR. The carbamazepine mass balance based on effluent concentrations from the three WRPs discharging to the lower SGR indicated that these point sources were the primary source of instream CECs, and that Δ_{loss} in Equation 2 was negligible (Table 1). Concentrations of nearly all detected pharmaceuticals (such as carbamazepine, diclofenac, fluoxetine, gemfibrozil, meprobamate and sulfamethoxazole) at the Coyote Creek site (Station SG5a) were at least one-tenth those found at stations on the SGR that were both directly downstream and in close proximity to the Los Coyotes and Long Beach WRPs (Figure 2). The most notable exception was caffeine, with the highest concentrations observed at the Coyote Creek site. Commercial chemicals such as TCPP, TCEP, TCPP, PBDEs, and octylphenol were found at concentrations 2 to 5 times lower. PFOA was found at concentrations similar to the rest of the stations investigated in the SGR watershed. Based on spikes observed just downstream of the WRP discharges and the mass balance, the WRPs were the main contributors of pharmaceuticals to the system.

Apparent Fate of CECs

No appreciable attenuation due to instream photolysis, hydrolysis, or dilution was expected given the short residence time, as evidenced by the agreement between discharged effluent and instream concentrations (Table 1) and confirmed in the concentration profiles (Figures 4 and 5). Though in some studies rapid photodegradation (k = 0.09 day^{-1}) was observed for diclofenac (Poiger *et al.* 2001), it behaved conservatively in these systems, implying that either the transport occurred more rapidly than estimated or the

shallow, clear water conditions were not conducive for photodegration (Zeng and Arnold 2013). For more recalcitrant CECs, e.g., carbamazepine with an aqueous half-life of 63 days, even less instream degradation can be expected (Tixier *et al.* 2003). However, coagulation followed by sedimentation may remove hydrophobic CECs (e.g., pyrethoids, fipronil, carbamazepine) from the water column, particularly in the tidal estuaries. Since pyrethroids were not detectable in most water column samples, collection and analysis of bed sediment for the more hydrophobic CECs would be useful in assessing the importance of sedimentation as a removal process in the tidal portion of these systems.

Implications for Environmental Quality and Future Monitoring

Because of minimal attenuation below the WRPs in these systems, we compared instream concentrations to published thresholds of biological concern. Using NOECs and uncertainty factors ranging from 1 to 100 to account for suspected endocrine disrupting and/or unknown modes of action for a given chemical (Zeng and Arnold 2013), and C_{max} as measured in the present study, the maximum MTQs for bifenthrin (9), galaxolide (3.9), permethrin (1.7), and diclofenac (1.2) exceeded "unity," indicating that ambient concentrations were high enough to warrant additional attention in local and/or regional monitoring efforts (Table 3). Bifenthrin and permethrin are among the most widespread and persistent of the commonly used synthetic pyrethroid insecticides, having been implicated in impaired water and sediment quality in California (Amweg *et al.* 2006, Holmes *et al.* 2008, Lao *et al.* 2010), but whose occurrence appears to be limited to freshwater and estuarine systems (Lao *et al.* 2012). Galaxolide and tonalide (MTQ = 0.19; Table 3), synthetic musk compounds that are hydrophobic and bioaccumulative, are suspected of eliciting endocrine effects in wildlife due to their polycyclic aromatic structure (Breitholtz *et al.* 2003, Schreurs and Sonneveld 2005). This provides additional justification for their inclusion in future monitoring efforts in these systems. Diclofenac, an anti-inflammatory pharmaceutical linked to catastrophic mortality of raptors (Schultz *et al.* 2004), has been shown in lab studies to induce biochemical alterations and cause tissue damage in rainbow trout at trace (µg/L) water concentrations (Mehinto *et al.* 2010).

A larger number of CECs could be considered for second tier investigative monitoring based on the criteria 0.1 <MTQ <1.0. These include chlorpyrifos (0.99), ibuprofen (0.41), triclocarban (0.28), fipronil (0.27) and its desulfinyl (0.23) and sulfone (0.18) metabolites, sulfamethoxazole (0.16), carbamazepine (0.13), and triclosan (0.11). Of particular interest are the antibiotics within this grouping (e.g., sulfamethoxazole, triclocarban, and triclosan), which as a class have been hypothesized to induce antibiotic resistance in microbial communities associated with aquatic invertebrates (Uyaguari *et al.* 2009).

In contrast, compounds with MTQs <<1 (e.g., acetaminophen, atrazine, DEET, dilantin, gemfibrozil) were detectable at concentrations well below published NOECs, even after application of the aforementioned uncertainty factors. Published effects thresholds are in the ug/L to mg/L range for these CECs (Diamond *et al.* 2011, Maruya *et al.* In press) , which is not surprising as therapeutic doses for humans are orders of magnitude higher than observed environmental concentrations, including C_{max} from the present study. Accordingly, these CECs do not warrant inclusion in future monitoring efforts based on current knowledge of risk to aquatic system health.

Although C_{max} for the chlorinated phosphate flame retardants were the highest in the study, their relative potency to aquatic life is thought to be low, compared to other CECs, such as natural and synthetic hormones. As replacements for banned or phased out chemicals such as PBDEs, however, it can be argued that monitoring for compounds such as TCEP, TCPP, and TDCPP is warranted to assess changes in future concentrations over time, based on demand, production, and usage of flame retarding chemicals in consumer and commercial products.

The loading and fate of CECs that survive transport in channelized, effluent-dominated systems such as the LAR and SGR is a final consideration worth discussion. These CECs will be discharged, largely without attenuation, to coastal estuaries and embayments at the bottom of these watersheds. Some CECs (e.g., pyrethroids) subject to rapid hydrolysis under alkaline pH may not occur at and/or accumulate to levels of concern once exposed to seawater (Lao *et al.* 2012). Other more hydrophobic and/or persistent compounds like carbamazepine and PBDEs may associate with bottom sediments and be available to higher biota via food web transfer. Additional studies are needed to address the loading,

fate, and effects of CECs discharged into coastal estuaries and embayments. As with other risk-based studies, chemical mixture effects remain largely unknown but progress is being made toward grouping and estimating potency of environmental toxicants by mode of biological activity. In conjunction with relevant toxicological information, the results from the present and future follow-up studies can be used to prioritize and select CECs for monitoring and assessment in semi-arid, coastal, and effluent-dominated receiving waters.

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Supplemental Information

Supplemental Information is available at ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_013_025SI.pdf.