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

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.

Ashmita Sengupta¹, J. Michael Lyons², Deborah J. Smith², Jörg E. Drewes³, Shane A. Snyder⁴, Ann Heil⁵ and Keith A. Maruya¹

¹Southern California Coastal Water Research Project, Costa Mesa, CA
²CA Regional Water Quality Control Board, Los Angeles Region, Los Angeles, CA
³Colorado School of Mines, Department of Civil and Environmental Engineering, Advanced Water Technology Center (AQWATEC), Golden, CO
⁴University of Arizona, Chemical and Environmental Engineering Department, Tucson, AZ
⁵Los Angeles County Sanitation Districts, Whittier, CA
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 km², 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 km² 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.
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 m³/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...
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, NaN₃, or CH₂Cl₂). 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,

---

**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.**

<table>
<thead>
<tr>
<th>Treatment Plant</th>
<th>Effluent Treatment</th>
<th>Discharge Point (km)</th>
<th>Estimated Discharge (m³/day)</th>
<th>C_{effluent} (ng/L)</th>
<th>C_{est} (ng/L)</th>
<th>C_{meas} (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Los Angeles River</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D.C. Tilman WRP</td>
<td>Tertiary</td>
<td>74</td>
<td>200,000</td>
<td>NA</td>
<td>NA</td>
<td>185 - 191</td>
</tr>
<tr>
<td>Burbank WRP</td>
<td>Tertiary</td>
<td>66</td>
<td>19,800</td>
<td>NA</td>
<td>NA</td>
<td>179 - 216</td>
</tr>
<tr>
<td>LA-Glendale</td>
<td>Tertiary</td>
<td>50</td>
<td>52,700</td>
<td>NA</td>
<td>NA</td>
<td>192 - 220</td>
</tr>
<tr>
<td>San Gabriel River</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>San Jose Creek WRP</td>
<td>Chlorinated-Tertiary</td>
<td>36</td>
<td>136,000</td>
<td>188 - 289</td>
<td>250</td>
<td>35 - 294</td>
</tr>
<tr>
<td>Los Coyotes WRP</td>
<td>Chlorinated-Tertiary</td>
<td>16</td>
<td>72,000</td>
<td>265 - 308</td>
<td>255</td>
<td>318 - 330</td>
</tr>
<tr>
<td>Long Beach WRP</td>
<td>Chlorinated-Tertiary</td>
<td>8</td>
<td>37,000</td>
<td>197 - 204</td>
<td>221</td>
<td>194 - 241</td>
</tr>
</tbody>
</table>
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-NCl-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:

\[ V_u C_u + V_{wrp} C_{wrp} + V_n C_n - \Delta_{loss} = V_d C_d \quad \text{Eq. 1} \]

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 (\( \Delta_{loss} \)) 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.

\[ \frac{V_{sj} C_{sj} + V_{lc} C_{lc} + V_{lb} C_{lb} + V_{cc} C_{cc} - \Delta_{loss}}{V_{sj} + V_{lc} + V_{lb} + V_{cc}} = C_d \quad \text{Eq. 2} \]

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 \( C_{\text{max}} \)) 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.

\[ MTQ = \frac{C_{\text{max}}}{(\text{NOEC or PNEC})(\text{uncertainty factor})} \quad \text{Eq. 3} \]

where \( C_{\text{max}} \) 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...
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, deltamethrin, fenpropathrin, and permethrin) were non-detects for Event #1, though bifenthrin, permethrin, and cyflurathrin 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 during Event #2, respectively.

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.

<table>
<thead>
<tr>
<th></th>
<th>PPCPs</th>
<th>Commercial</th>
<th>Pesticides</th>
<th>Hormones</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ev#1</td>
<td>Ev#2</td>
<td>Ev#1</td>
<td>Ev#2</td>
<td>Ev#1</td>
</tr>
<tr>
<td>No. Target CECs</td>
<td>22</td>
<td>24</td>
<td>21</td>
<td>25</td>
<td>14</td>
</tr>
<tr>
<td>No. CECs Detected</td>
<td>20</td>
<td>19</td>
<td>7</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>% CECs Detected</td>
<td>91</td>
<td>79</td>
<td>33</td>
<td>32</td>
<td>39</td>
</tr>
<tr>
<td>No. CECs Detected -- SGR REF</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>No. CECs Detected -- LAR REF</td>
<td>10</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>
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 #1 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 represented the effluent quality and mass loading into the LAR and SGR during low flow conditions.

### 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

### 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).

<table>
<thead>
<tr>
<th>CEC Name</th>
<th>MTL (ng/L)</th>
<th>Cmax (ng/L)</th>
<th>MTQ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ev#1</td>
<td>Ev#2</td>
<td>Ev#1</td>
</tr>
<tr>
<td>17β-estradiol</td>
<td>2</td>
<td>&lt;1.25</td>
<td>&lt;0.62</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>920000</td>
<td>25.8</td>
<td>0.01</td>
</tr>
<tr>
<td>Atrazine</td>
<td>200</td>
<td>13.7</td>
<td>0.07</td>
</tr>
<tr>
<td>BDE 47</td>
<td>100</td>
<td>1.0</td>
<td>0.01</td>
</tr>
<tr>
<td>BDE 99</td>
<td>100</td>
<td>0.4</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Bifenphrin A</td>
<td>0.4</td>
<td>&lt;1.5</td>
<td>3.80</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>60</td>
<td>&lt;12.5</td>
<td>&lt;0.21</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>2500</td>
<td>330.0</td>
<td>0.13</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>5</td>
<td>9.0</td>
<td>0.18</td>
</tr>
<tr>
<td>DEET</td>
<td>58400</td>
<td>860.0</td>
<td>0.01</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>12700</td>
<td>4.3</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>100</td>
<td>77.0</td>
<td>0.77</td>
</tr>
<tr>
<td>Dilantin</td>
<td>33500</td>
<td>291.0</td>
<td>0.01</td>
</tr>
<tr>
<td>Estrone</td>
<td>6</td>
<td>&lt;2.5</td>
<td>&lt;0.42</td>
</tr>
<tr>
<td>Fipronil</td>
<td>51</td>
<td>13.6</td>
<td>0.27</td>
</tr>
<tr>
<td>Fipronil desulfanyl</td>
<td>59</td>
<td>13.8</td>
<td>0.23</td>
</tr>
<tr>
<td>Fipronil sulfide</td>
<td>59</td>
<td>2.0</td>
<td>0.03</td>
</tr>
<tr>
<td>Fipronil sulfone</td>
<td>59</td>
<td>5.7</td>
<td>0.10</td>
</tr>
<tr>
<td>Galaxolide</td>
<td>700</td>
<td>n/a</td>
<td>NA</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>7800</td>
<td>193.0</td>
<td>0.02</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>100</td>
<td>40.5</td>
<td>0.41</td>
</tr>
<tr>
<td>Permethrin</td>
<td>1</td>
<td>&lt;18.0</td>
<td>&lt;18.0</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>5900</td>
<td>790.0</td>
<td>0.14</td>
</tr>
<tr>
<td>TCEP</td>
<td>51000</td>
<td>785.0</td>
<td>0.02</td>
</tr>
<tr>
<td>TCPP</td>
<td>74900</td>
<td>2150.0</td>
<td>0.03</td>
</tr>
<tr>
<td>TDCPP</td>
<td>51000</td>
<td>1345.0</td>
<td>0.03</td>
</tr>
<tr>
<td>Toluene</td>
<td>1000</td>
<td>188.0</td>
<td>0.19</td>
</tr>
<tr>
<td>Triclocarban</td>
<td>380</td>
<td>102.0</td>
<td>0.26</td>
</tr>
<tr>
<td>Triclosan</td>
<td>250</td>
<td>18.2</td>
<td>0.07</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>4000</td>
<td>78.5</td>
<td>0.02</td>
</tr>
</tbody>
</table>

CECs in coastal urban rivers receiving treated municipal wastewater effluent - 19
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 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.

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
CECs in coastal urban rivers receiving treated municipal wastewater effluent - 21

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 $\Delta_{\text{loss}}$ 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 3 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 ($k = 0.09 \text{ day}^{-1}$) 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

![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.](image)
shallow, clear water conditions were not conducive for photodegradation (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., pyrethroids, 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 $C_{\text{max}}$ 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 ($\mu$g/L) water concentrations (Mehinto et al. 2010).

A larger number of CECs could be considered for second tier investigative monitoring based on the criteria $0.1 < \text{MTQ} < 1.0$. 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 $C_{\text{max}}$ 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 $C_{\text{max}}$ 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.

**Literature Cited**


**ACKNOWLEDGEMENTS**

The present study was supported by the California Water Resources Control Board (Agreement No. 10-085-140). The authors thank W. Lao, D. Tsukada, D. Heil, T. Anumol, S. Hernandez-Ruiz, D. Jones, K. Franklin, G. McGowan, E. Nelson, M. Brown, M. Gasca, P. Markle, and P. Friess for their contributions.

**SUPPLEMENTAL INFORMATION**