

# Pilot Study of Contaminants of Emerging Concern (CECs) in the Russian River Watershed

### Lessons Learned

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### Background

Contaminants of emerging concern (CECs) can be defined as any chemicals that are not regulated or commonly monitored but have the potential to enter the environment and cause adverse ecological or human health impacts. Determining which of the thousands of chemicals in commerce are CECs and whether or not they may be a problem is a formidable challenge. For most chemicals in use, a number of limitations prevent researchers from measuring their presence and assessing their potential risks. It is therefore difficult to monitor and manage CECs.

In response, scientists and managers recently completed a Pilot Study Design<sup>1</sup> for monitoring CECs in aquatic ecosystems throughout California. The Russian River watershed (RRW) study was the first regional



implementation of this Pilot Study Design. The collected data provide useful information for both the Russian River region and the implementation of the monitoring framework in other areas.

The primary objective of this study was to investigate the occurrence of high priority CECs in receiving water, sediment, and fish tissue within the RRW to address the management question:

#### Are CECs in wastewater effluent and stormwater runoff impacting beneficial uses in the Russian River watershed?

The project involved three tasks:

- 1. Monitor priority CECs in river water, sediment, and wastewater effluent using targeted chemical analysis and bioanalytical tools
- 2. Monitor priority CECs in fish tissue
- 3. Prioritize and monitor agricultural pesticides relevant to the region

Full Report:

<sup>&</sup>lt;sup>1</sup> Dodder, N.G., Mehinto, A.C., Maruya, K.A. 2015. Monitoring of Constituents of Emerging Concern (CECs) in California's Aquatic Ecosystems – Pilot Study Design and QA/QC Guidance. SCCWRP Technical Report 854. Southern California Coastal Water Research Project, Cosa Mesa, CA.

### What Did We Learn?

#### Task 1

## Monitor priority CECs in Russian River water, sediment, and wastewater effluent with targeted chemical analysis and bioanalytical tools

Targeted chemical analysis of 12 CECs in water and wastewater effluent samples and 20 CECs in sediment samples indicated that while some of these compounds were frequently detected, concentrations of most CECs were below recommended monitoring trigger levels (MTLs). The exceptions were the current use pesticides bifenthrin, permethrin, and fipronil, which were detected in sediment at concentrations that exceeded MTLs. These pesticides are primarily associated with suburban and urban applications (for example, ant, termite, and pet flea control) and were found at sites near Santa Rosa, the largest city in the RRW.

Responses in the aqueous and sediment samples in standardized in-vitro bioassays



Santa Rosa Wastewater Treatment Plant. Image courtesy Google Earth.

(IVBs) that screen for estrogenic and glucocorticoid activity were uniformly low, indicating little cause for concern for endocrine related toxicity across the RRW. Relative estrogen IVB responses across samples were consistent with concentrations of known estrogenic compounds detected in the targeted chemical analysis, suggesting that the assay shows promise as an effective screening tool for receiving water environments.

#### Task 2

#### Monitor priority CECs in fish tissues



Sacramento Pikeminnow (*Ptychocheilus grandis*). CC image courtesy Jake on Flickr. CC BY-NC-SA 2.0

Fish tissue samples were analyzed for 13 polybrominated diphenyl ethers (PBDEs) and 13 perfluorinated alkyl substances (PFASs), including perfluorooctanesulfonic acid (PFOS). Seven of 13 PBDE congeners analyzed were detected in fish tissue. PBDE 47, a ubiquitous tetrabrominated congener, was detected in all 13 samples. PFOS was also detected in all 13 samples. Three additional PFASs were detected: perfluorodecanoate (in 7 samples), and perfluoroundecanoate and perfluorododecanoate (both in 4 samples).

#### PBDE concentrations measured in RRW fish

tissue samples were well below thresholds of concern for human consumption established by the

California Office of Environmental Health Hazard Assessment (OEHHA). Whereas OEHHA has not established fish consumption thresholds for PFASs, the levels of PFOS were well below an advisory level issued by the State of Minnesota (40 ng/g for a consumption rate of one meal per week). The upper range of PFOS measured (11 ng/g), however, exceeded an advisory level issued by the State of Michigan (9 ng/g for 16 or more meals per month), suggesting potential concern for humans if they consume relatively large amounts of fish caught in the watershed. While fish tissue levels of PBDEs and PFOS/PFASs are currently of limited concern to human consumers, they may be of higher concern to the health of piscivorous predators (mammals and birds).

#### Task 3

#### Prioritize and monitor agricultural pesticides relevant to the region

River water and sediment samples, collected at 5 sites representing agricultural and mixed use subwatersheds during wet weather conditions (for water) and during dry weather (for sediment), were analyzed for more than 100 pesticides by the USGS California Water Science Center laboratory. Water samples fractionated into particulate and dissolved phases prior to analysis revealed a low proportion of detectable analytes: 22 of 162 in water (dissolved); 0 of 131 analytes in water (particulate); and 6 of 118 analytes in sediment. Most (16 of 22) pesticides detected in water were found only at an agricultural-urban, mixed use site near Santa Rosa, including several pesticides that are commonly used in urban settings.

Pesticide concentrations in water were low relative to published aquatic toxicity thresholds. Imidacloprid, a neonicotinoid insecticide, was the lone exception, exceeding a newly established EPA Office of Pesticide Prevention (OPP) chronic invertebrate benchmark (10 ng/L). Pesticide

concentrations in sediment were below published USGS benchmarks. However, recent toxicity data suggest that fipronil and its degradates could be approaching levels of concern in water and sediment collected from the mixed use site near Santa Rosa, and Windsor, the largest urban areas in the RRW. Bifenthrin, an urban use pyrethroid pesticide, was detected in sediment below a USGScalculated sediment toxicity benchmark, but above a recommended MTL for estuarine sediments.



Vineyard. CC image courtesy pixabay.com, CC0

### Summary of Findings with Statewide Significance

- 1. Urban areas are major contaminant sources to the aquatic environment. The targeted chemistry monitoring for priority CECs in the RRW demonstrated the strong influence of urban centers like Santa Rosa on the surrounding environment. Additional monitoring designed to supplement this targeted chemistry effort, including an effects-based screening using IVBs, as well as a screening primarily designed to detect agricultural pesticides, also indicated a higher potential for exposure and effects in urban-influenced portions of the watershed.
- 2. Study design, implementation, and interpretation must take region-specific contaminant sources and other factors into account. The Pilot Study Design for CECs provides a statewide template for initial CECs monitoring, but is most effective when supplemented with information specific to the region. For the RRW, unique considerations include extensive agricultural activity and associated pesticides; land application of biosolids; and flow-dependent wastewater effluent discharge limits.
- 3. Future regional pilot study designs should capture the full range of potentially important time **periods.** For example, pesticide use patterns change over the seasons, and the fall runoff sampling performed for the pesticide-focused task of the study may not be representative of other potentially critical periods, such as spring runoff.
- 4. **Employ storm sampling strategies that can provide a robust characterization of runoff.** This study highlighted the challenge of collecting representative storm samples with limited resources. Alternative sampling strategies that can provide a more robust characterization of runoff while keeping costs down include composite sampling or passive sampling over the duration of a storm period. These strategies may be of particular value in more rural or agricultural regions, where the timing and volume of stormwater runoff can vary significantly among different areas within a watershed.
- 5. Coordinate with other statewide CEC efforts and use existing tools for standardized and integrated data sharing. Some data gaps may be filled, and more comprehensive management questions might be addressed, through pooling resources, coordinating sampling designs, and integrating collected data with those of other statewide programs such as the SWAMP Stream Pollution Trends (SPoT) program and the Department of Pesticide Regulation (DPR) Surface Water Monitoring Program (SWMP). The California Environmental Data Exchange Network (CEDEN) provides tools to ensure data quality and comparability and facilitates access to and integration of diverse data sources.
- 6. Continue periodic monitoring to identify any potential new concerns over time, even if there are no immediate and urgent concerns. The number of CECs is continually increasing and pesticide use patterns are continually changing. At the same time, analytical methods continue to improve and new toxicity information continues to be generated. Periodic monitoring (for example, every five years) can help to ensure that levels of already monitored analytes do not rise unexpectedly in the future, and that any potentially emerging problems don't go unnoticed.
- 7. **Expand the monitoring toolbox.** We recommend the inclusion of new, innovative approaches on a less frequent but recurring basis in order to identify any potential concerns that may not be recognized using traditional targeted chemical analyses. Non-targeted analysis can identify high priority compounds that may not be captured using traditional targeted chemistry analyses, including pesticide degradates. Moreover, non-targeted analysis can help inform the selection of target analytes for future studies. This study also serves as a successful case study for the employment of 'bioanalytical tools' or in-vitro bioassays (IVBs), which measure the mixture toxicity in water or sediment samples and can yield information on the presence of specific modes of toxic action (for example, estrogenic activity), even when the contaminant or contaminants causing toxicity are unknown.

Full Report: