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Monitoring Strategies for Chemicals of Emerging Concern (CECs) in California's Aquatic Ecosystems: Recommendations of a Science Advisory Panel

Paul D. Anderson[1], Nancy D. Denslow[2], Jörg E. Drewes[3], Adam W. Olivieri[4], Daniel Schlenk[5], Geoffrey I. Scott[6] and Shane A. Snyder[7]

[1] *ARCADIS and Boston University, Boston, MA*

[2] *University of Florida, Gainseville, FL*

[3] *Colorado School of Mines, Golden, CO*

[4] *EOA, Inc., Oakland, CA*

[5] *University of California, Riverside, CA*

[6] *National Oceanic and Atmospheric Administration, Washington, DC*

[7] *University of Arizona, Tucson, AZ*

EXECUTIVE SUMMARY

Although thousands of substances can now be detected in the environment, a small percentage of known chemicals – approximately 200 -- are currently regulated and/or routinely monitored in California receiving waters. The much larger group of chemicals that remain largely unregulated and/or unmonitored in the aquatic environment, known as chemicals of emerging concern (CECs), may originate from a wide range of point and non-point sources. Upon discharge to receiving waters, CECs that are readily soluble in water will remain in the dissolved (aqueous) phase and provide a route of exposure to aquatic life. A smaller subset of CECs that are hydrophobic will associate with particles, where they may remain suspended in the water column or accumulate in sediments and ultimately in tissues of aquatic and terrestrial biota. The larger concern is that exposure to aqueous, sediment and tissue CECs may affect wildlife and humans.

In response, the California Water Resources Control Board (State Water Board) in conjunction with the David and Lucile Packard Foundation and a group of stakeholder advisors tasked a group of leading scientists to address the issues associated with CECs in the State's aquatic systems that receive discharge of treated municipal wastewater effluent and stormwater. The group was charged to identify potential sources and evaluate the fate and effects of CECs, and ultimately to provide guidance for developing monitoring programs that assess those chemicals with the highest potential to cause effects in the State's receiving waters. Seven experts in chemistry, biochemistry, toxicology, chemical and risk assessment, engineering and coastal and marine environmental health science were convened as the CEC Ecosystems Panel ("Panel") in October 2009. The Panel held six in-person meetings to formulate their approach and recommendations, while soliciting input from stakeholders and the public. This report provides the results from the Panel's deliberations, including four products intended to assist the State in developing a monitoring process for CECs based on sound, up-to-date scientific principles.

Product #1: A conceptual, risk-based approach to assess and identify CECs for monitoring in California receiving waters

Given the thousands of chemicals that are potentially present in the aquatic environment and that information about CECs is rapidly evolving, the Panel created a transparent approach to focus the universe of CECs based on their potential for health effects and their occurrence in waters receiving discharge of municipal wastewater treatment plant effluent ("WWTP effluent") and stormwater. The health and environmental risk for individual CECs within this select group was then assessed to guide prioritization of chemicals which should be included in monitoring programs both now and in the future. The Panel adopted a risk-based screening framework, which includes four primary steps:

1. Develop monitoring trigger levels (MTLs) for CECs that pose the greatest potential risk to aquatic systems based on published effects concentrations.
2. Compile measured or predicted environmental concentrations (MECs or PECs) for CECs for which MTLs could be estimated.
3. Identify those CECs that have the greatest potential to pose a risk by comparing MECs (or PECs) to MTLs. CECs with a monitoring trigger quotient (MTQ = MEC(or PEC)/MTL) greater than "1" were identified for monitoring. (Note than an MTQ of greater than 1.0 does not indicate a risk is present, only that sufficient potential for a risk exists that the chemical should be considered for inclusion in a monitoring program.)
4. Apply the risk-based screening framework (steps 1-3) to each of three representative scenarios that capture the key types of exposure (sources and fate) to CECs in the State's inland, coastal and marine receiving water systems.

The risk based screening framework focused on CECs for which occurrence and toxicity information could be obtained, giving priority to those data representing California sources and receiving waters. Priority was also given to CECs for which adequate quality assurance/quality control (QA/QC) information was available. Occurrence data were obtained for WWTP effluent and stormwater (where available), and in relevant receiving water matrices (i.e., water, sediment and biological tissue). Toxicological information was obtained for the most sensitive aquatic species based on expected mode of action, which included organisms across a wide spectrum of trophic levels (i.e., microbes, invertebrates, fish, birds and marine mammals).

Product #2: Application of the risk-based screening framework to identify a list of CECs for initial monitoring

Several conservative assumptions were used in the risk-based screening framework (Product #1) to identify appropriate CECs for monitoring. The framework was applied to three representative receiving water scenarios:

Scenario 1: a WWTP effluent-dominated inland (freshwater) waterway;

Scenario 2: a coastal embayment that receives both WWTP effluent and stormwater discharge; and

Scenario 3: offshore ocean discharge of WWTP effluent.

For each scenario, MECs were compiled from the literature and from the most recent studies in California. The maximum MEC was selected for use in the risk-based screening framework. In cases

where MECs were not available, PECs were employed. To derive MTLs the toxicological literature was reviewed to identify lowest observed effect concentrations (LOECs) and no observed effect concentrations (NOECs) from studies of reproduction, growth of survival of fish and invertebrates. LOECs and NOECs were also identified for antibiotic resistance (ABR). MTLs were derived by adjusting LOECs and NOECs by safety factors ranging from 1-1,000 to account for several sources of uncertainty including extrapolation of toxicity data across species and differences in receiving water environments. Monitoring trigger quotients (MTQs), equal to the MEC or PEC divided by the MTL, were estimated for aqueous, sediment and tissue matrices for each scenario when data were available.

For effluent dominated freshwater systems (Scenario 1), 10 compounds [*17-beta estradiol, and estrone (hormones); bifenthrin, permethrin, and chlorpyrifos (insecticides); ibuprofen, bisphenol A, galaxolide, diclofenac, and triclosan (pharmaceuticals and personal care products*)] were identified for aqueous phase monitoring based on MTQs exceeding unity. For coastal embayments (Scenario 2), 8 of the 10 compounds identified in Scenario 1 were identified for monitoring (diclofenac and ibuprofen were the exceptions). No aqueous phase CECs were identified for monitoring near WWTP ocean outfalls (Scenario 3).

For sediments in coastal embayments, *bifenthrin, permethrin and* two flame retardants (*PBDEs 47 and 99)* were identified for monitoring. For ocean sediments, the high production volume chemicals, *bis (2-ethylhexyl) phthalate, butylbenzyl phthalate, p-nonylphenol* and polybrominated diphenyl ether (PBDE) flame-retardants (*PBDEs 47 and 99)* were identified for monitoring. For tissue monitoring, *PBDEs 47 and 99* and perfluorooctane sulfonate (*PFOS*), a perfluorinated chemical used in consumer product manufacture, were prioritized for monitoring. The Panel emphasizes that these CECs represent an initial prioritization list based on available data and a number of qualifying assumptions. While their identification at this time represents a conservative screening of "CECs at large", the information available for performing such screening continues to grow rapidly. The Panel thus urges the State to consider this an initial list that will evolve over time, to which more CECs may be added and others removed (see also Product #3).

Product #3: An adaptive, phased monitoring approach with interpretive guidelines that direct and update actions commensurate with potential risk.

The Panel recommends an adaptive, four-phase approach for implementing CEC monitoring programs for WWTP effluent and stormwater discharges to receiving waters of the State.

- In Phase 1, the Panel reduced the universe of chemicals to an initial list of CECs based on available toxicity and occurrence information. This list was evaluated following the risk-based screening framework resulting in 16 CECs recommended for initial monitoring (Table ES-1). The Panel recommends adopting this list for any initial CEC screening efforts. Any additional chemicals should only be added to this list upon screening through the risk-based framework.
- In Phase 2, guidance is provided for development and implementation of pilot monitoring studies with the objective to generate data needed to assess the occurrence and potential effects of the 16 CECs identified in Phase 1. This initial list of CECs is not intended to represent a target list for statewide compliance monitoring, but to execute focused regional monitoring efforts that will result in the development of a final list of CECs (see Phase 3). Further, to assist with assessment and update of the monitoring information collection during Phase 2, the Panel strongly recommends development or adaptation of environmental fate models (e.g., such as the 1-Box source and fate model utilized by the Panel for PBDEs in Section 3) as tools for

summarizing and synthesizing existing knowledge including CEC production and usage, loading and loss rates in receiving water scenarios and environmental compartment transfer rates. In addition, the Panel recommends development and testing of a pilot screening-level mass-based model that would be used to assist in estimating the predicted environmental concentrations (PECs) in effluents coupled with structure-based toxicity assessments.

- In Phase 3, monitoring data from Phase 2 are evaluated to refine their potential to pose adverse human health and ecological effects. Based on the initial screening efforts, the ultimate goal is to derive a final list of CECs that are recommended for routine monitoring as part of discharge permits. During this process, CECs may be added to or removed from the list based on the trends in production/use, occurrence, or findings of directed effects studies.
- In Phase 4, action plans are developed, if warranted, to respond to conditions identified in Phase 3.

Table ES-1. CECs recommended for initial monitoring (Phase 2) by scenario and environmental matrix (i.e., aqueous, sediment, tissue). M = include in monitoring program (discharges to: E = embayments, F = freshwater, O = ocean waters); NA = not applicable.

Compound	Scenario 1 Inland Waters Aqueous	Scenario 2 Embayment Aqueous	WWTP Effluent	FW Stream - Storm-water (Aqueous and Sediment)	Scenario 2 Embayment Sediment	Scenario 3 Marine Sediment	All Scenarios Tissue
Bis(2-ethylhexyl) phthalate	NA	NA	M-O	NA	NA	M	NA
Bisphenol A	M	M	M–E/F	M	NA	NA	NA
Bifenthrin	M	M	M-E/F	M	M	NA	NA
Butylbenzyl phthalate	NA	NA	M-O	NA	NA	M	NA
Permethrin	M	M	M-E/F	M	M	NA	NA
Chlorpyrifos	M	M	M-E/F	M	NA	NA	NA
Estrone	M	M	M-E/F	M	NA	NA	NA
Ibuprofen	M	NA	M-F	M	NA	NA	NA
17-beta estradiol	M	M	M-E/F	M	NA	NA	NA
Galaxolide (HHCB)	M	M	M-E/F	M	NA	NA	NA
Diclofenac	M	NA	M-F	M	NA	NA	NA
p-Nonylphenol	NA	NA	M-O	NA	NA	M	NA
PBDE -47 and 99	NA	NA	M-E/F/O	M	M	M	M
PFOS	NA	NA	M-E/F/O	M	M	M	M
Triclosan	M	NA	M-F	M	NA	NA	NA

Incorporation of this phased approach allows for a logical, sequential course of action to develop new information utilizing state-of-the-art monitoring and modeling tools. These include:

- *non-targeted analyses* using advanced bioanalytical and chemical methods;
- *confirmatory biological investigations* linking chemical and bioassay screening data with higher order effects (i.e., at the organism and population level);
- *environmental fate models* and screening-level mass-based model can assist in estimating the *predicted environmental concentrations (PECs)* in effluents coupled with structure-based toxicity assessments to determine the source, occurrence, fate and effects of CECs; and
- baseline *monitoring for antibiotic resistance* in WWTP effluent

The Panel urges the State to incorporate CEC monitoring into the various existing statewide, regional and local monitoring programs (e.g., California Surface Water Ambient Monitoring Program or SWAMP, San Francisco Bay regional monitoring and the southern California Bight regional monitoring programs), taking maximum advantage of regional differences and uniform statewide guidelines for data collection and monitoring designs. The Panel also developed guidelines for designing monitoring plans and for sampling and laboratory measurements to ensure collection of data that address the questions of water safety. The Panel strongly recommends that it be consulted on the design of the proposed work plans. Lastly, the Panel recommends a three-year re-evaluation of this conceptual approach, which would include updating the risk-based screening process and the CEC monitoring lists. After this interval there will undoubtedly be new tools to assess toxicity and occurrence which should be thoroughly evaluated (see Product #4); it will also be important to fully assess the effectiveness of control actions (if any) that have been undertaken by the State at periodic intervals. The Panel recommends that after two to three years of implementation, the Panel, or a similar entity, be reconvened to evaluate the results of the initial monitoring.

Product #4: Research needs to develop bioanalytical screening methods, link molecular responses with higher order effects, and fill key data gaps

The science of CEC investigation is still in its early stages. The Panel recommends that the State promote and support research initiatives in three broad categories to improve the scope and performance of monitoring and data interpretation for waters receiving WWTP effluent and stormwater discharge.

1. *Development of bioanalytical screening tools*. High-throughput *in vitro* bioassays with endpoints that respond to CEC exposure in ecological receptors (e.g., endocrine disrupting activity) can screen for multiple CECs, reducing the need for chemical-specific monitoring and shifting us away from the expensive and time-consuming chemical-by-chemical risk-screening paradigm. Research is also needed to identify adverse outcome pathways at the molecular level that are linked to higher order effects (e.g., fish reproduction). Further development and application of the latest genetic microarrays and targeted toxicity testing for species of highest relevance in California receiving waters is recommended to establish this linkage.
2. *Filling data gaps on CEC sources, fate, occurrence and toxicity*. Information on occurrence and toxicity (e.g., MECs and NOECs) are needed for CECs for which there is currently little or no data for California's aquatic systems. Candidate classes of CECs in this category are newly developed pharmaceuticals, replacement flame retardants and recently registered pesticides. In addition, the Panel recommends development and/or refinement of environmental fate models to predict environmental concentrations of CECs based on their production volume, use and environmental fate, as a means for prioritizing chemicals on which to focus method

development and toxicological investigation.

3. *Assessing the relative risk of CECs and other monitored chemicals*. The Panel urges the State to compare the potential risks associated with CECs with the potential risks posed by other, currently monitored environmental stressors. This assessment is essential for directing future monitoring investments toward those stressors that present the highest potential risk to the beneficial uses of the State's receiving waters.

Full Text

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/692_CECEcosystemsPanelReport_Final.pdf