California Science Advisory Panel recommendations for CEC monitoring in receiving waters.

Daniel Schlenk

Department of Environmental Sciences University of California, Riverside



PANEL MEMBERS

- Dr. Paul Anderson
 - Human Health Toxicologist
 - Arcadis US
- Dr. Nancy Denslow
 - Biochemist
 - University of Florida
- Dr. Jörg Drewes
 - Civil Engineer
 - Colorado School of Mines
 - Dr. Geoff Scott
 - Marine Resources
 - NOAA

- Dr. Adam Olivieri
 - Risk Assessor
 - EOA Incorporated
- Dr. Daniel Schlenk (Chair)
 - Environmental Toxicologist
 - UC Riverside
- Dr. Shane Snyder
 - Analytical Chemist
 - University of Arizona

HOW DO WE MONITOR FOR CECs?

- What are the relative contributions from stormwater & WWTP effluent?
- What are the appropriate CECs to be monitored, including analytical methods and detection limits?
- What is the fate of CECs in WWTPs, storm & receiving waters?
- What approaches should be used to assess biological effects?
- What is the appropriate monitoring design?
- What levels of CECs should trigger additional action? What range of actions should be considered?

PANEL DELIVERED FOUR PRODUCTS

- Decision making "risk-based" framework
 - A tool to prioritize CECs now and into the future
- Application of framework to discharge scenarios of interest
 - Initial list of CECs to monitor in water, sediment, biota
- Monitoring recommendations and interpretation
 - How, where and when to monitor; how to respond to results
 - A process that can *adapt* to changing science & chemical use
- Future recommended activities
 - Develop better monitoring tools to improve & refine the process



Anderson et al. 2012

RISK-BASED SCREENING FRAMEWORK

- Step 1: measure or predict occurrence (MEC or PEC)
 - Provided through investigative monitoring (e.g. regional, special studies)

• Step 2: determine concentration that is protective of resource (aka "monitoring trigger level" or MTL)

- Published information on no/low observable effects concentrations

- Step 3: calculate "Monitoring Trigger Quotient" (MTQ)
 = MEC (or PEC) / MTL
 - If MTQ < 1, no concern
 - If $MTQ \ge 1$, add to candidate list

DISCHARGE SCENARIOS

Effluent dominated inland waterway

- Low flow (dry weather) conditions
- No dilution of WWTP effluent

Coastal embayment

- WWTP effluent and stormwater discharge
- 10 fold dilution of source input

Offshore ocean discharge

- Large WWTP outfalls in deeper water
- 100 fold dilution of WWTP effluent

MEC/PEC--EXPOSURE

WWTP effluent

CEC Recycled Water Panel for WWTP effluents

Surface water/Sediments/Tissues

- Within the State of California
- Within the United States
- (Lowest relevance) from countries outside US
- No occurrence

1-Box Model for Fate (eg PBDE 47, 99)

DATA SOURCES FOR EXPOSURE

- Ca. Recyled Water report
- WERF report
- HPV-PBT
- Literature

(Anderson et al. 2010)

(Diamond et al. 2011)

(Howard & Muir 2010; 2011)

(Kumar & Xagoraraki 2010)

MTL--EFFECTS

Receptors of Interest

Microbial, Non-microbial Invertebrate, Fish, Bird, Mammals

• "When available"--NOEC/PNEC

(Reproduction, Growth, Survival)

- EPA EcoTox website (WERF report; Diamond et al. 2011)
- MistraWikiPharma database
- Literature
 - Pubmed
 - Scifinder Scholar
 - Web of Science

Uncertainty Factors (10 X)

- Acute to chronic (if NOEC was not available)
- Freshwater to Saltwater
- EDC mode of action
- Antibiotics (MICs) x UFs

CECs IN WATER*

Pesticides

- bifenthrin, permethrin, chlorpyrifos

Consumer products

- bisphenol A, diclofenac, galaxolide, ibuprofen

Natural hormones

– 17 β -estradiol, estrone

Antibiotics

- triclosan (River scenario only)
- * River & Bay scenarios only

CECs IN SEDIMENT AND TISSUE

- Sediments (Bay & Ocean scenarios)
 - Plasticizers (bis-2-ethylhexyl, butylbenzyl phthalates)
 - Flame retardants (PBDE-47, -99)
 - Detergents (4-nonylphenol)
 - Pyrethroids (bifenthrin, permethrin) Bays only
- Biological tissue (All Scenarios)
 - Polybrominated diphenyl ethers (PBDEs)
 - Perfluorinated chemicals (e.g. PFOS)

Table 8.2. Guidance for developing targeted/pilot CEC monitoring workplans. FW = fresh water; M = include in monitoring programs; NA = not applicable; RW = receiving water

General Monitoring Design Parameters	Large POTW Discharging to Ocean ^a	Small POTW Discharging to Embayment ^b	Stormwater (MS4) Discharge Receiving Water Stations ^c	POTW Dischaging to Effluent Dominated Waterway ^d
Parameter List	Table 8.1	Table 8.1	Table 8.1	Table 8.1
Spatial coverage – Receiving Water (RW)	2-D grid (up to 6 sites each location)	2-D gradient (up to 6 sites in estuary)	1-D gradient (up to 6 sites for each location)	1-D (up to 6 sites for each location)
Number of POTW and/or FW Locations	Two POTWs and corresponding RWs	Five POTWs in one estuary/embayment	Two large FW streams and the Delta	One POTW and RW
Frequency	Semi-annual over three years	Semi-annual over three years	Wet and Dry Season over three years	Wet and Dry Season over three years
Background	М	м	М	М
Aqueous (non- filtered)	NA	Μ	Μ	М
Sediment (top 5 cm)	Μ	м	м	М
Tissue ^e	Μ	М	М	М
Bioanalytical Screening Assays ^f	Pilot evaluation and validation studies	Pilot evaluation and validation studies	Pilot evaluation and validation studies	Pilot evaluation and validation studies
Toxicity ^g	Pilot screening study at one POTW	Pilot screening study at one POTW	NA	Pilot screening study at POTW
Antibiotic Resistance ^h	NA	Pilot investigation at one POTW	NA	Pilot investigation at one POTW
Passive Sampling Devices (PSDs)	Pilot investigation at one POTW	NA	NA	Pilot investigation at one POTW



ADAPTIVE MONITORING STRATEGY INCLUDES "OFF-RAMPS"...

Monitoring Trigger Quotient (MTQ) High concern – control (all controllable) sources

Elevated concern – confirm levels; expand monitoring; refine risk assessment; control (easy) sources

Moderate concern – continue monitoring to ensure concentrations not increasing

Little/No concern – discontinue monitoring

- Assess the risks associated with CECs relative to currently monitored constituents
 - Make efficient use of finite monitoring resources

...AND "ON-RAMPS"

- Panel recommended investigative monitoring and special studies for "data poor" CECs
 - Newly developed and/or registered drugs, pesticides and flame retardants
- Panel recommended development of modeling tools to prescreen for problematic CECs
 - Consider production, usage, fate and potential for toxicity
- Use Panel's assessment framework to determine if CECs warrant inclusion in future monitoring ("On-Ramp")
- Incorporate new information and revisit recommendations every 3-5 years
 - Infuse the latest science and update CEC lists and tools

DEVELOP BIOLOGICAL SCREENING TOOLS

Targets impact to resources

- more relevant than simple exposure
- different types of damage are targeted

Better performance, efficiency

- less time & money than status quo
- works for priority pollutants & CECs

In vitro bioassays to screen for CECs by mode of action

- cell lines are commercially available
- used for screening & selected monitoring elsewhere





Recommendation Updates

• Fill data gaps on sources, fate, occurrence and effects

- CUPs (fipronil, pyrethroids)
- HHCB-Galaxolide EcoRisk Assessment--EPA
- GR data indicating persistent activity (Immune apical effects?; TIE?)
- PR agonists (Progestins) show potent masculinization (AR vs. PR)

• Link Screening Bioassays with Toxicity (adverse effects)

- EPA Toxcast (Toxicology in 21st Century NRC) linkage with in vivo studies
 EPA/OECD AOP/MOA strategies for risk assessment
- Estuarine fish model (Menidia spp) to link apical population endpoints to cellular/histological endpoints (FHM-FSTRA EDSP Tier 1)

Statewide Chemicals of Emerging Concern (CECs) Pilot Monitoring Study

Keith Maruya Southern California Coastal Water Research Project

Kickoff Meeting September 12, 2013



MANAGEMENT NEEDS

- What is the impact of discharged CECs on the beneficial uses of receiving waters?
- What CECs are appropriate for current/future monitoring in waters receiving WWTP effluent and stormwater discharge?
- What approaches and methods are most effective for monitoring of CECs?

DISCHARGE SCENARIOS

Effluent dominated inland waterway

- Low flow (dry weather) conditions
- No dilution of WWTP effluent

Coastal embayment

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Offshore ocean discharge

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PROJECT GOALS

- Provide design and technical requirements for implementation of expert panel recommendations
- Targeted (chemical specific) monitoring
 - What, in what, where, how and how low/precise?
- Special studies to improve CEC monitoring
 - Comprehensiveness, efficiency
 - Which endpoints, methods, matrices, and test species?
 - What additional supporting information is needed?
- Identify and take advantage of leveraging opportunities
 - Existing regional monitoring programs
 - Partnerships with academia, government on special studies

CECs FOR TARGETED MONITORING

Compound	Freshwater System Aqueous	Coastal Embayment Aqueous	WWTP Effluent	Freshwater stormwater Aqueous, Sediment	Coastal Embayment Sediment	Marine Sediment	All Scenarios Tissue
Bis(2-ethylhexyl) phthalate	NO	NO	YES-O	NO	NO	YES	NO
Bisphenol A	YES	YES	Y–E/F	YES	NO	NO	NO
Bifenthrin	YES	YES	Y-E/F	YES	YES	NO	NO
Butylbenzyl phthalate	NO	NO	Y-0	NO	NO	YES	NO
Permethrin	YES	YES	Y-E/F	YES	YES	NO	NO
Chlorpyrifos	YES	YES	Y-E/F	YES	NO	NO	NO
Estrone	YES	YES	Y-E/F	YES	NO	NO	NO
Ibuprofen	YES	NO	Y-F	YES	NO	NO	NO
17-b estradiol	YES	YES	Y-E/F	YES	NO	NO	NO
Galaxolide	YES	YES	Y-E/F	YES	NO	NO	NO
Diclofenac	YES	NO	Y-F	YES	NO	NO	NO
p-Nonylphenol	NO	NO	Y-0	NO	NO	YES	NO
PBDE-47 & -99	NO	NO	Y-E/F/O	YES	YES	YES	YES
PFOS	NO	NO	Y-E/F/O	YES	YES⁵	YES⁵	YES
Triclosan	YES	NO	Y-F	YES	NO	NO	NO

MONITORING QUESTIONS

(What CECs are appropriate for continued/future monitoring?)

- 1. What is the occurrence (frequency of detection, concentrations) of CECs identified by the expert panel in
 - -- freshwaters receiving POTW effluent during low flow/dry season conditions?
 - -- coastal embayments that receive POTW effluent and stormwater discharge?
 - -- marine waters adjacent to large (> 100 mgd) POTW outfalls?
- 2. What is the direction and magnitude of change in CEC concentrations (in water, sediment and tissue) over a 5 year time period?
- 3. Does the first cycle of statewide CEC monitoring data suggest continued monitoring? (i.e., are MTQs > 1?)

MONITORING QUESTIONS (cont.)

(What are the major CEC sources to receiving waters?)

- 1. Which CECs are detected in receiving waters influenced by POTW outfalls, and which CECs are detectable in receiving waters that are influenced largely by stormwater discharge?
- 2. What happens to CECs in receiving waters? Do they degrade? Attach to particles/sediment? Accumulate in biota?
- 3. How quickly and/over what distance or dilution scenarios are discharged CECs attenuated?

TARGETED STUDY DESIGN PARAMETERS

- a. list of CEC analytes, preferred methods & desired reporting limits
- b. list of candidate waterbodies that represent exposure scenarios identified by the expert panel
- c. list of target media (e.g. water, sediment, biological tissue), and candidate species
- d. frequency, number, and location of sampling stations for each candidate waterbody
- e. QA/QC goals for measurement of CECs to be incorporated into the Project Quality Assurance Project Plan (QAPP)
- f. list of appropriate monitoring questions for each exposure scenario
- g. data analysis and assessment methods for each exposure scenario
- n. data management plan
- strategy to coordinate with existing monitoring programs

SPECIAL STUDIES

General Monitoring Design Parameters	WWTP Discharging to <i>Ocean</i>	WWTP Discharging to Coastal <i>Embayment</i>	<i>Stormwater</i> (MS4) Receiving Water Stations	WWTP Discharging to <i>Inland</i> <i>Freshwater</i> Waterway
Bioanalytical Screening Assays ^a	YES	YES	YES	YES
Toxicity ^b	YES	YES	NO	YES
Antibiotic Resistance ^c	NO	YES	NO	YES
Passive Sampling Devices (PSDs) ^d	YES	NO	NO	YES

MONITORING QUESTIONS (cont.)

What is the impact of CECs on receiving water ecosystems? What methods are most effective for monitoring of CECs?

- 1. Can we utilize newly developed *bioanalytical tools* to screen for a wide variety of CECs by mode of biological action?
- 2. Do toxicity estimates from current NPDES testing methods provide adequate safety for CECs that have sublethal impacts on *endocrine, immune or reproductive endpoints*?
- 3. How do we effectively monitor for *antibiotic resistance (ABR)* and how do we link microbial assessment endpoints with antibiotic-specific occurrence?

SPECIAL STUDY DESIGN PARAMETERS

- 1. list of target parameters, preferred methods and desired measurement goals
- 2. list of candidate waterbody(ies) for each special study
- 3. list of target media (e.g. water, sediment, biological tissue), and candidate target species
- 4. the frequency, number and location of sampling stations to be evaluated within each candidate waterbody
- 5. QA/QC goals for measurement of specified parameters to be incorporated into the QAPP
- 6. the rationale for exclusion/inclusion of studies that differ from the Science Advisory Panel's final recommendations.

PARTICIPANTS

- Contractor (SCCWRP)
 - Facilitator for CEC expert panels (recycled water; aquatic ecosystems)
- Technical Advisory Committee
 - Original members of expert panel for Aquatic Ecosystems
- Stakeholder Advisory Committee
 - Regulators, dischargers, public interest and regional monitoring experts
- Interested public

SCCWRP TEAM

- Dr. Keith Maruya Proj. Mgr.
 - Dept Head, Chemistry
 - Lead facilitator, CEC panel
- Dr. Nathan Dodder Targeted Monitoring Lead
 - Environmental Chemist
 - Bight'13 Chemistry Coordinator
- Dr. Alvina Mehinto Special Studies Lead
 - Ecotoxicologist
 - Linkage of molecular responses & higher order effects

TECHNICAL ADVISORS

- Dr. Paul Anderson
 - Human Health Toxicologist
 - Arcadis US
- Dr. Nancy Denslow
 - Biochemist
 - University of Florida
- Dr. Jörg Drewes
 - Civil Engineer
 - TU Munich

- Dr. Adam Olivieri
 - Risk Assessor
 - EOA Incorporated
- Dr. Daniel Schlenk (Chair)
 - Environmental Toxicologist
 - UC Riverside
- Dr. Shane Snyder
 - Analytical Chemist
 - University of Arizona
- Dr. Geoff Scott
 - Marine Resources
 - NOAA

STAKEHOLDER ADVISORS

- Philip Friess (CASA, Tri-TAC)
- Geoff Brosseau (CA Stormwater Quality Association)
- Sara Aminzadeh (CA Coastkeeper Alliance)
- Rich Breuer (SWRCB, SWAMP)
- Thomas Mumley (San Francisco Bay RWQCB)
- Deborah Smith (Los Angeles RWQCB)
- Jay Davis (SF Bay Regional Monitoring Program)
- Kenneth Landau (Delta Regional Monitoring Program)
- Richard Gossett (Commercial Services)

DELIVERABLES & SCHEDULE

- Targeted Monitoring Design Requirements Apr 2014
- Special Study Design requirements July 2014
- Quality Assurance Project Plan July 2014
- Statewide CEC Monitoring Workshop Fall 2014
- Project End (Final Report) Jan 2015

* Mid-term & final SAC/TAC meetings

Spr, Fall 2014

Surface Water Ambient Monitoring Program (SWAMP)







Mission

To provide resource managers, decision makers, and the public with timely, high quality information to evaluate the condition of surface waters throughout California.


Background

 The State Legislature created SWAMP in 2000 to develop a comprehensive monitoring program to assess beneficial use attainment in all of the State's waterbodies.







Monitoring, Assessment & Reporting

Statewide Programs

- <u>Bioaccumulation Monitoring Program (BOG)</u>
- Bioassessment Monitoring Programs
- Stream Pollution Trends Monitoring Program (SPoT)

Regional Programs

Question-driven monitoring at the Regional scale



Fishable – Large Rivers, Lakes, Coastal Waters

Bioaccumulation Monitoring Program

 What is the status of contamination in sportfish from lakes, coastal waters, and large rivers?





September 12, 2013

SPoT Monitoring Questions

- What are concentrations of pollutants in streams sediments?
- Are sediments in streambeds toxic and what is the magnitude of toxicity?



- What is the contribution of land uses to pollutant concentrations and toxicity in the watershed?
- What is the magnitude of change in pollutant concentrations and toxicity?



12, 2013

SPoT Goals

 Determine long-term trends in stream pollutants concentration and effects at the bottom of large watersheds statewide



- 2. Relate water quality indicators to land-use characteristics and management efforts
- Establish a network of sites throughout the state to serve as a backbone for collaboration with local, regional, and federal monitoring





SPoT Indicators & Measurements

- Toxicity 10-day growth & survival test, the standard amhipod *H. azteca*
- Pyrethroid pesticides at all sites
- Microcystin at all sites
- DDTs, PAHs, PCBs at all sites
- PBDEs at 42 urban sites
- Fipronil at 42 urban sites
- Metals (Ag, Al, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn at all sites
- Additional CEC's under consideration
 Neonicitinoid pesticides (e.g. imidacloprid)

SPoT samples from 92– 100 fixed monitoring stations, annually



September 12, 2013

Regional Monitoring



Regional Monitoring

- Emerging contaminants
 - Region 3 Region 9
 - Microcystin and Cyano bacteria
 - Region 4 –Pilot CEC program
 - *Region 5 fipronil TIE study*
 - Region 7 Chlopyrifos
 - Region 9 PBDEs and pyrethroids in fish tissue





September 12th, 2013

THE REGIONAL MONITORING PROGRAM AND CECS

State of California Pilot Study: Monitoring Constituents of Emerging Concern (CECs) in Aquatic Ecosystems

Rebecca Sutton and Jay Davis San Francisco Estuary Institute, Richmond CA

The RMP



- Goal: Collect data and communicate information about water quality in the San Francisco Estuary to support management decisions
- Multi-Year Plan updated annually
- \$3.5 million per year
- Monitoring focus:
 - Status and Trends
 - Special Studies

RMP Annual Budget



RMP CEC STRATEGY



Articulated in RMP CEC Strategy Document

1. MEASURING & PRIORITIZING

Hundreds of chemicals monitored in the Bay

 Summarized in RMP CEC Synthesis
 Document and the
 latest Pulse of the Bay Acetaminophen Albuterol **Bifenthrin** Chlorothalonil Chlorpyrifos **Chlorpyrifos methyl** Chlorpyrifos, oxon Chlorpyrifos, oxy Cinerin-1 Cyanazine Cyfluthrin, total Cyhalothrin, lambda, total Cypermethrin, total Dacthal DCBP(p,p')Deltamethrin Desethylatrazine Diazinon Diazoxon Dimethoate Diuron Esfenvalerate/Fenvalerate, total Esfenvalerate/Fenvalerate-1 Ethion

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1. MEASURING & PRIORITIZING

Risk Level Description	CECs in San Francisco Bay
Tier IV: High Concern	Bay occurrence data suggest a high probability of a moderate or high level effect on Bay wildlife
Tier III: Moderate Concern	Bay occurrence data suggest a high probability of a low level effect on Bay wildlife
Tier II: Low Concern	Bay occurrence data or predicted environmental concentrations suggest a high probability of no effect on Bay wildlife
Tier I: Possible Concern	Potential for concerns or uncertainty in measured or predicted Bay concentrations or toxicity thresholds suggest uncertainty in the level of effect on Bay wildlife

1. MEASURING & PRIORITIZING

Risk Level Description	CECs in San Francisco Bay
Tier IV: High Concern	None
Tier III: Moderate Concern	PFOS Fipronil Nonylphenol & nonylphenol ethoxylates PBDEs
Tier II: Low Concern	Pyrethroids Pharmaceuticals & personal care products HBCD
Tier I: Possible Concern	Alternative flame retardants Bisphenol A Plasticizers Pesticides Many, many others

2. LEARN FROM OTHERS

Review the literature

- Occurrence
- Toxic
- Persistent
- Bioaccumulative
- Consulting with experts: Emerging Contaminants Workgroup
 - Lee Ferguson (Duke)
 - Jennifer Field (OSU)
 - Phil Gschwend (MIT)
 - Derek Muir (Environment Canada)
 - David Sedlak (UCB)

Identifying New Persistent and Bioaccumulative Organics Among Chemicals in Commerce

PHILIP H. HOWARD^{*,†} AND DEREK C. G. MUIR[‡]

SRC, Environmental Science Center, 6502 Round Pond Road, North Syracuse, New York, and Aquatic Ecosystem Protection Research Division, Environment Canada, 867 Lakeshore Road, Burlington, Ontario

Received November 6, 2009. Revised manuscript received January 19, 2010. Accepted January 22, 2010.

The goal of this study was to identify commercial chemicals that might be persistent and bioaccumulative (P&B) and that were not being considered in current Great Lakes, North American, and Arctic contaminant measurement programs. We combined the Canadian Domestic Substance List (DSL), a list of 3059 substances of "unknown or variable composition complex reaction products and biological materials" (UVCBs), and the U.S. Environmental Protection Agency (U.S. EPA) Toxic Substances

Environ. Sci. Techno

3. USING NON-TARGETED APPROACHES: BROADSCAN ANALYSES

- Challenge to evaluate individual CECs
- New GC x GC TOF/MS instrument
 - Two-year RMP study with NIST to evaluate Bay seal and bivalve tissue
- Large libraries to identify compounds
 - NIST library plus Howard and Muir list



3. USING NON-TARGETED APPROACHES: BIOANALYTICAL TOOLS

- Broad, non-targeted approach to identifying estrogenic compounds
 - Linking cellular level effects to effects in fish

2013 RMP Study with Nancy Denslow (Univ. Florida)/SCCWRP

- Estuarine fish (Menidia beryllina)
- Endocrine disrupting compounds: Estrone, Bisphenol A, 4-nonylphenol, Galaxolide



PBDEs

- Polybrominated diphenyl ethers
- Synthetic flame retardants added to all kinds of products





TRIBUNE WATCHDOG

Playing with fire

A deceptive campaign by industry brought toxic flame retardants into our homes and into our bodies. And the chemicals don't even work as promised.



BY PATRICIA CALLAHAN AND SAM ROE

r. David Heimbach knows how to tell a story. Before California lawmakers last year, the noted burn surgeon drew gasps from the crowd as he described a 7-week-old baby girl who was burned in a fire started by a candle while she lay on a pillow that lacked flame retardant chemicals.

"Now this is a tiny little person, no bigger than my Italian greyhound at home," said Heimbach, gesturing to approximate the baby's size. "Half of her body was severely burned. She ultimately died after about three weeks of pain and misery in the hospital."

Heimbach's passionate testimony about the baby's death made the long-term health concerns about flame retardants voiced by doctors, environmentalists and even firefighters sound abstract and petty.

But there was a problem with his testimony: It wasn't true. Records show there was no dangerous pillow or candle fire. The baby he described didn't exist.

Neither did the 9-week-old stoked the public's fear of fire patient who Heimbach told and helped organize and steer an association of top fire offi-California legislators died in a candle fire in 2009. Nor did the cials that spent more than a 6-week-old patient who he told decade campaigning for their Alaska lawmakers was fatally cause burned in her crib in 2010. some flame retardants escape

Heimbach is not just a prominent burn doctor. He is a star from household products and witness for the manufacturers settle in dust. That's why todof flame retardants. dlers, who play on the floor and His testimony, the Tribune found, is part of a decades-long campaign of deception that has loaded the furniture and elec-

tronics in American homes

with pounds of toxic chemicals

put things in their mouths, generally have far higher levels these chemicals in their bodies than their parents. Blood levels of certain widel

Today, scientists know that

used flame retardants doubled

PBDEs: SF BAY HOT SPOT



She et al. 2002

PBDEs: BANS & PHASE-OUTS



PBDE DECLINES IN BAY BIOTA

- Bivalves
- Sport Fish
- Cormorant Eggs



PBDEs: MODERATE CONCERN

Risk Level Description	CECs in San Francisco Bay
Tier III: Moderate Concern	Bay occurrence data suggest a high probability of a low level effect on Bay wildlife
PBDEs	Good News: Levels declining Bay sport fish safe to eat (3 servings/week) Tern egg study finds no effects to reproduction or development
	Potential Concern: Sediment levels → polychaete larval settlement and growth Fish levels → pathogenic susceptibility Seal levels → correlation with increased white blood cell count, decreased red blood cell count

ALTERNATIVE FLAME RETARDANTS

CA flammability standards lead to use of flame retardants

- Efforts to change standards:
 - Improve fire safety AND reduce use of flame retardants
- Meanwhile, manufacturers use alternative flame retardants instead of PBDEs
 - SFEI collaboration identified compounds in foam furniture and baby products
- Many flame retardants have little to no toxicity data
 - Chlorinated tris is a carcinogen



BAY MONITORING DATA: ALTERNATIVE FLAME RETARDANTS

Alternative Flame Retardants	Water*	Sediment	Mussels	Fish	Bird Eggs	Seals
HBCD		+	+	+	+	+
Dechlorane Plus (DP)		+	+	+	+	+
PBEB		+	+	-	-	+
DBDPE		-				
BTBPE		+	-	-	-	-
НВВ		-	-	-	-	-
BEH-TBP**		-	-		-	
EH-TBB**		-	-	-	-	-
TDCPP or Chlorinated Tris	+	+	-		-	
ТСРР	+	+	-		+	
TPhP	+	+	+		-	
TCEP	+				+	
ТВР	+				-	
ТВЕР	-				+	
TEHP	-				-	
TPrP					-	
Tris(2,3-dibromopropyl) phosphate, Tricresyl phosphate, 2-Ethylhexyl-						

diphenyl phosphate, Tris(2-bromo-4-

methylphenyl) phosphate

WHAT'S NEXT?

Pulse of the Bay

State of the Estuary Conference
 Combined with RMP Annual meeting
 Downtown Oakland, October 29th and 30th
 Focus on Contaminants of Emerging Concern

RMP CEC Web Page

WHAT'S NEXT?

2014

- Bioanalytical tools
- Monitoring alternative flame retardants
- Reviewing work by others
- PPCP special study proposal
- Ongoing work to prioritize current use pesticides

Beyond

- CECs are a continuing priority
- Reviewing work by others

RESOURCES

- Email: RebeccaS@sfei.org & Jay@sfei.org
- Website: www.sfei.org
- Coming soon: RMP CEC Synthesis & Strategy documents

Thank you! Any questions? Southern California: CEC Monitoring and Technology Development

SCCWRP

Nathan Dodder, Alvina Mehinto, Keith Maruya

Bight Program

- Designed to measure the extent and magnitude of sediment contamination throughout the Bight
- Sampling every 5 years, from 1998 2013, > 300 stations from embayments to the lower slope
- Purpose
 - Measures conditions throughout the Bight
 - Puts smaller scale surveys in a larger context
 - Allows habitat conditions to be compared
- Starting in B '03 efforts were made to incorporate CECs
 - Investigate reproductive anomalies in flatfish

Bight '03 - WWTP Discharge Effects on Flatfish



Measured CECs in:

- 1. effluent
- 2. site water
- 3. sediment
- flatfish liver (hornyhead turbot)

Measures of biological effect:

- 1. Hormones
- 2. Feminization
- 3. Reproduction
- 4. Population size



Bight '03 - Flatfish Results



- Hydrophilic CECs were detected in effluent and seawater at high frequency (50-100%)
- Hydrophobic CECs and legacy contaminants were detected at high frequency in sediments and tissues (e.g., PBDE, nonylphenols)
- But results were inconclusive
- Although alterations in hormone systems were observed,
 - Little relation to POTW discharges
 - Uncertain hormone baseline conditions
 - Low frequency of intersex occurrence
 - Population impacts not evident

Bight '08 and '13 CEC Efforts

• B '08 CEC sediments measurements:

- Observed the highest PBDE (flame retardants) and pyrethroid (pesticides) concentrations in embayments
- B'13 CEC measurements in coastal sediments:
 - 1. PBDE
 - 2. Pyrethroids / Fipronils
 - 3. Alkylphenols (surfactants and byproducts)
 - 4. Perfluorinated compounds (polymers)
- B '13 CEC targeted survey at municipal outfalls:
 - 1. Alkylphenols
 - 2. Perfluorinated compounds

Bight '13 - Bird Survey

Pelagic forager: Caspian tern

(Hydroprogne caspia, formerly Sterna caspia)

Mixed forager: Western Gull



Benthic forager: Cormorant

(Phalacrocorax auritus)



Species of concern: CA Least Tern (Sterna antillarum browni)



- What is the extent and magnitude of PBDE and PFC contamination across 14 sampling locations covering the Bight?
- 2. What is the variation between species and habitats?
Bight Program – Chemistry QA/QC

- Most analytes are measured by multiple laboratories
- There must be assurance that results are comparable
- Every Bight includes intercalibration exercises and follows common QA/QC
- Has resulted in improved laboratory performance and confidence in the combined results

Permethrin in Ballona Creek sediment reference material (B'13)



CECs in Effluent Dominated Rivers

- Sponsored by LARB/SWAMP
- Phase 1 (completed 2011)
 - Document occurrence & fate of >60 CECs in LA and SG rivers
 - Samples downstream of water reclamation plants had higher numbers of detected CECs
 - Chlorinated phosphate flame-retardants detected at the highest concentrations
 - Little attenuation down to the estuary was observed
 - Bifenthrin, diclofenac, galaxolide and permethrin exceeded thresholds to trigger monitoring
- Phase 2 (ongoing)
 - Study occurrence of CECs in the Santa Clara River system
 - Measure CECs in sediment and fish tissues in these systems

Additional Regional Studies (2010-2011)

Agency	Watershed	Sampling	Results
Santa Ana Watershed Project Authority (SAWPA)	Santa Ana River	23 WWTP effluents 2 river stations 2 aqueducts 13 CECs	Concentrations did not exceed known effects thresholds
San Diego Regional Board	San Diego, Santa Margarita, and Tijuana Rivers	Targeted septic tanks and WWTP discharge 24 CECs	Study ongoing

Statewide Mussel Watch CEC Pilot

NOAA, SWRCB, SFEI, SCCWRP



- Address data gaps in the occurrence of coastal CECs in California
- Sampling of 68 stations in 2009-2010 for 167 CECs
- Proximity to urbanization and discharges were investigated
- Provides a CEC dataset for the design of future surveys

MW CEC Pilot – Results

stations

1.

2.

Discharge Land Use Alkyphenol, PBDE, and PFC concentrations were higher on average at tissue conc. at station (ng/g dw) in urban areas 10 impacted by stormwater 0 0 0 0 Storm+ Storm None POTW Mixed Ag Low Urban POTW Only Only Dev Dev

Example: Perfluorinated Compounds

Stormwater

- Very few focused studies on CECs in stormwater discharge
- Legacy contaminant data indicates stormwater loading is
 >= WWTP discharge
- In addition to Mussel Watch, Bight '08 indicated stormwater is a source of CECs
- Stormwater contributions to coastal watersheds remains a significant data gap (relative to WWTPs)

Bight '08



CEC Monitoring Summary

Occurrence

- Effluent Dominated Rivers
 - Occurrence of CECs confirmed
 - Some exceeded monitoring trigger quotients; many did not
 - SoCal channelized systems act as rapid conduit to coast

• Embayments and Oceans

- The regionally broad Bight Program and Mussel Watch provide the main datasets
- Occurrence data from focused surveys and an understanding of CEC fate in specific systems is lacking
- Data on stormwater contributions is lacking

Biological Effects

- Endocrine effects on wildlife remain unclear
- Interpretability of methods/tools should be improved

Technology Development

Passive Sampling Devices



 Panel recommendation to investigate the use of passive samplers





SPME

- Diffusion transports contaminants to a sorbent material
- Different sorbent materials target various chemical classes
- Can mimic the exposure of aquatic organisms



Why use passive sampling devices?

- Concentrate trace levels of chemicals resulting in increased sensitivity and lower detection limits than may be possible with a grab sample of 1 to 2 L of water
- PSDs can be tailored to sample a wide range of contaminants, many of which are water soluble and may not bioaccumulate
- Issues of metabolism, excretion and survival/condition (e.g. using live organisms) can be avoided with PSDs



Non-Targeted Mass Spectrometry

Sample Type	Total # of Non-Monitored Anthropogenic Compounds and Unknowns	
SoCal bottlenose dolphin blubber (8)	260	
San Diego Bay black skimmer eggs (4)	30	

- Unexpected compounds are usually lower in abundance than typically monitored contaminants
- But the total number of unexpected contaminants is high enough to warrant further investigation
- Non-targeted methods are not intended to replace targeted quantification
 - Suggest contaminants for larger targeted surveys
 - Identify compounds causing toxicity (TIE)

Monitoring Biological Responses

- In vitro cell assays screen CECs based on toxicological modes of action
 - 1. Identifies potential toxicity related to sexual development and reproduction
 - 2. Detects all contaminants that have the mode of action, including unknowns
 - 3. Higher-throughput and more sensitive relative to other tests
- Currently, the assays are being developed to screen for contaminants in recycled waters (SCCWRP, UF, UCR, USF, UAZ).
 - Promising inter-laboratory comparison results
- SCCWRP initiative to develop assays for environmental matrices (receiving waters, sediment, tissue)

Linkage Study with Fish



- Collaboration with University of Florida, funded by SFEI
- Menidia beryllina (estuarine silverside) model
- Gain a mechanistic understanding of how cell assay response to CECs predicts whole organism response



Thank You

Technology Development for CECs

Three goals:

- 1. Improve water-phase contaminant sampling
- 2. Improve detection of unexpected contaminants
- Sensitive and highthroughput detection of biological responses



Central Valley Regional Monitoring Programs

Ken Landau

Steering Committee Member Delta Regional Monitoring Program Assistant Executive Officer Central Valley Water Board

12 September 2013

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Sacramento River Basin

- Large, reservoir controlled rivers
- Small, ag dominated surface waters
- Larger WWTPs discharge to rivers
- Smaller WWTPs seasonal discharge

San Joaquin River Basin

- Natural flows largely diverted
 - Some water left in rivers
 - Fish, Delta salinity control
- Ag dominated surface waters
- Larger WWTPs discharge to rivers

Tulare Lake Basin

- Internal drainage
- Natural flows diverted
- Limited surface waters
 - Ag dominated
- Wastewater contained on land

Delta Flows



NPDES POTWs

Current treatment levels

- Tertiary filtration with nitrification and denitrification
- Tertiary filtration with nitrification

Secondary

12 September 2013



· SACRAMENTO

NPDES Permit Monitoring Sites

- Routine upstream /downstream for indicators
- Effluent / receiving water characterization
 - 1 to 6 times per permit cycle



POTW Characterization Priority Pollutants plus

- 4,4'-DDD
- 4,4'-DDE
- 4,4'-DDT
- alpha-Endosulfan
- alpha-Hexachlorocyclohexane (BHC)
- Alachlor
- Aldrin
- beta-Endosulfan
- beta-Hexachlorocyclohexane
- Chlordane
- delta-Hexachlorocyclohexane
- Dieldrin
- Endosulfan sulfate
- Endrin
- Endrin Aldehyde
- Heptachlor
- Heptachlor Epoxide
 - Lindane)

•

- Toxaphene
- Atrazine
- Bentazon
- Carbofuran
- 2,4-D
- Dalapon
- 1,2-Dibromo-3-chloropropane (DBCP)
- Di(2-ethylhexyl)adipate
- Dinoseb
- Diquat
- Endothal
- Ethylene Dibromide
- Glyphosate
- Methoxychlor
- Molinate (Ordram)
- Oxamyl
- Picloram
- Simazine (Princep)
- Thiobencarb
- 2,3,7,8-TCDD (Dioxin)
- 2,4,5-TP (Silvex)
- Diazinon
- Chlorpyrifos

Phase I MS4s



Stockton MS4 Monitoring Stations



Stockton MS4 Monitoring

PESTICIDES IN WATER COLUMN

- Chlorpyrifos
- Diazinon
- Pyrethroids

PYRETHROID PESTICIDES IN SEDIMENT

- Bifenthrin
- Cyfluthrin-1
- Cyfluthrin-2
- Cyfluthrin-3
- Cyfluthrin-4
- Cypermethrin-1
- Cypermethrin-2
- Cypermethrin-3
- Cypermethrin-4
- Deltamethrin
- Esfenvalerate/Fenvalerate-1
- Esfenvalerate/Fenvalerate-2
- Lambda-cyhalothrin-1
- Lambda-cyhalothrin-2
- Permethrin-1
- Permethrin-2

Regional Monitoring

Central Valley Monitoring Directory

 http://www.centralvalley monitoring.org/



Irrigated Lands Regulatory Program

- Hundreds of sites with regular or event monitoring
- Includes pesticides
 - Chlorpyrifos
 - Water col & sediment
 - Pyrethroids
 - Sediment
- Selected to NOT include urban impacts



Sac. River Coordinated Monitoring Program

- Sac Wastewater and Stormwater Programs
- Initiated 1991
- 5 sampling sites
- 6x/year monitoring
 - 70 parameters
- 3x/year monitoring
 - +250 parameters

http://www.srcsd.com/cmp.php





Sacramento Coordinated Monitoring Program

Parameters	Sample Type	Frequency
General Water Quality: DO, EC, pH, TDS, Temperature, TSS, Turbidity, UV (abs 254 nm)	Water Quality	6-8 times/year
Major Ions & Minerals: Chloride, Cyanide, Hardness	Water Quality	6-8 times/year
Mercury: Mercury (Dissolved), Methylmercury (Dissolved),	Water Quality	6-8 times/year
Metals & Trace Elements: Arsenic (Dissolved), Cadmium (Dissolved), Chromium (Dissolved), Copper (Dissolved), Lead (Dissolved), Nickel (Dissolved), , Silver (Dissolved), Zinc (Dissolved)	Water Quality	6-8 times/year
Nutrients: Ammonia as N, Dissolved Ortho-PO ₄ , Nitrate, Total N, Total P	Water Quality	6-8 times/year
Organic Carbon: DOC, TOC	Water Quality	6-8 times/year
Organic Contaminants: Acid extractable, Base- neutral extractable, Bis(2-ethylhexyl)phthalate, Hexachlorobenzene, N-Nitroso-din-propylamine, Pentachlorophenol, PAHs, VOCs	Water Quality	6-8 times/year
Pathogens & Bacteria: E. coli, Fecal Coliforms, Total Coliforms	Water Quality	6-8 times/year
Pesticides: Carbamates, Herbicides, Organophosphates	Water Quality	6-8 times/year

Data Availability	URL	Available by request
Annual Report	http://srcsd.com/cmp.php	Yes
In an electronic form (Excel)		Yes

4

Delta RMP



Kicked off in Sept. 2008

Broad range of participants

Consensus on diagnosis of problem / opportunity
Building interest, involvement and momentum

12 September 2013

Photo courtesy of Steven Moore

Steering Committee

POTWs (3)

Stormwater (Phase I & Phase II)

Water Supply (SFCWA)

Regulatory (EPA and CVRWQCB)

Coordinated Monitoring (IEP)

Agriculture

Resource Agencies



Steering Committee Activities

- Mission Statement
- Committee roles and responsibilities
- Management Questions
 - Status and Trends
 - Sources and Loadings
 - Forecasting
 - Effectiveness Tracking

- Technical Advisory Committee
 Design monitoring framework
- Steering Committee
 - Determine funding sources
 - Selecting initial study project(s)
 - Toxicity, pesticides, pathogens, nutrients
- Regional Board
 - Permit revisions to facilitate RMP
- Plan to implement monitoring in 2014

Questions ?



POTW Perspective on Statewide CEC Monitoring Pilot Study

Phil Friess, Technical Services Department Head Sanitation Districts of Los Angeles County 1955 Workman Mill Road, Whittier, CA 90601 562/908-4288, x2501 pfriess@lacsd.org

September 12, 2013





Overview

- POTW efforts to date
- General position on CECs
- Specific recommendations on upcoming studies


POTW Efforts to Date

- Wastewater community has already invested significant resources to address CECs
- Actions include:
 - Laboratory method development
 - Effluent sampling
 - Receiving water sampling
 - Numerous special studies
 - Pollution prevention efforts
 - Public outreach/education





POTW Efforts – Laboratory Method Development

- Southern Nevada Water Authority led efforts
- LACSD started development in 2006
- Robust, accurate analytical methods









POTW Efforts – Voluntary Effluent Sampling

- Example: LACSD
- JWPCP and eight tertiary water reclamation plants
- Over 5,500 analytical results spanning five years
- 64 compounds
- Analyzed data using expert panel human health and aquatic life monitoring trigger levels
- Conclusion: only 2 compounds above MTLs: NDMA, estrone





POTW Efforts – Required Effluent Sampling

- NPDES permits in Los Angeles Region
- Required CEC special studies
- Two years of annual samples, 41 parameters
- Hormones, surfactants, PBDEs, pharmaceuticals, personal care products, pyrethroids, other current use pesticides, PFOS





POTW Efforts – Receiving Water/ Ecosystem Sampling

- Example: Regional Monitoring Program for Water Quality in San Francisco Bay (RMP)
- 10-year ongoing effort overseen by SFEI
- 3-pronged approach:
 - Targeted monitoring of prioritized CECs in water, sediment, fish tissue and bird eggs
 - Tracking literature, other monitoring efforts
 - Non-targeted screening monitoring
- CECs assigned to monitoring/management tiers based on degree of risk
- 19 discrete studies to date

POTW Efforts – Special Studies

- Dozens of studies with California POTW participation
- Studies by individual agencies and joint studies with research organizations, universities, regulatory agencies, and national organizations
- Occurrence in treated water/receiving waters/sewage sludge/land
- Assessment of treatment performance
- Risk assessment
- Assessment of EDC effects on organisms all levels, from gene regulation activity up to population level effects







POTW Efforts – Pollution Prevention

- Efforts on-going for over a decade
- Key contributors include Tri-TAC, Bay Area Pollution Prevention Group, Palo Alto, EBMUD, City of San Jose, LACSD, City of LA, OCSD, and many more
- Conducted hospital outreach on pharmaceutical disposal
- Worked with CDPH on medical waste regulations and their interpretation
- Led national efforts to develop message points for residential pharmaceutical outreach
- Set up residential outreach/collection programs for pharmaceuticals



POTW Efforts – Pollution Prevention

- Residential outreach on pesticides e.g., Our Water, Our World Program
- Pesticide regulatory efforts work with EPA and California Department of Pesticide Regulation
- Other regulatory efforts DTSC Safer Consumer Products Regulations
- Legislative e.g., support product stewardship efforts, including SB 727 (pharmaceuticals)





General Position on CECs

- POTW community supports focused, riskbased CEC monitoring
- Overall, efforts should be targeted at identifying problematic compounds, to inform and facilitate source control efforts

Support Expert Panel Process

- Have supported expert panel process since its inception
- Balanced panel with key specialties represented
- Systematic, scientific approach to setting monitoring priorities
- Informed, rational approach to gathering information needed to make appropriate management decisions



Support Risk-Based Prioritization

- Allows focus to be on pollutants of highest concern
- Most useful information obtained
 - Avoids use of limited resources on low risk compounds
 - Quantification of some compounds may compromise accuracy of quantification of other compounds.
 - Example: salicylic acid
 - No aquatic life threshold of concern known
 - Requires method alterations that reduce reliability and sensitivity of results for other compounds
- Most cost effective approach

Pilot Study Recommendations

- Initial studies should be designed as much as possible to identify relative POTW and stormwater contributions to focus source control efforts
- Initial studies should be designed to be compatible with future agricultural sector monitoring studies
- Special bioanalytical screening, toxicity, and antibiotic resistance studies should:
 - ✓ Utilize realistic exposures in terms of matrix and toxicant delivery
 - Examine endpoints of biological concern such as reproduction, development, and growth

Pilot Study Recommendations

- Follow framework established by the expert panel
- Maximize use of current POTW and stormwater CEC monitoring
- Leverage work with regional monitoring programs (e.g., Bight, SMC, RMP)
- Leverage work with POTWs willing to provide additional voluntary in-kind services

Pilot Study Recommendations

- Endeavor to collect accurate, representative data with adequate QA/QC that can be used on a statewide basis
- Accurate data is critical bad data could lead to bad management decisions
- Test for appropriate compounds in appropriate matrices, as recommended by the expert panel
- Don't waste resources running all compounds in all matrices (e.g., water, sediment, tissue)
- Overall, collect information to inform meaningful management actions in a cost effective manner



Summary

- Extensive, early voluntary efforts by POTWs to address CECs
- Strongly support risk-based monitoring approach



- Strongly support expert panel process
 - Both past efforts and continuing expert panel involvement
- Some POTWs willing to provide voluntary in-kind services in current study, to promote costeffectiveness
- Future NPDES CEC monitoring requirements should be based on Statewide Pilot Study results

Monitoring CECs in Aquatic Ecosystems

Regulatory Agency Perspective September 12, 2013

> Thomas Mumley Assistant Executive Officer SF Bay Water Board

Regulatory Actions



Product or chemical bans Product or chemical use restrictions Source discharge or disposal controls

EPA wants more control of chemicals

EPA from page A1 very leg clothing and pillows. Of particular concern are rising levels of toxise found in chilldren and developing fetuses. EPA chief's call "Chemicals are ubiquitous we

would work with Congress on legislation that would, among other things, call for chemleals to be evaluated based on health and safety risks and for manufacturers to submit toxicity data for existing and new chemicals. Legislation would also give the EPA au-



Regulatory Actions



Human health protection standards Ecological protection standards Monitoring / information requirements





Department of Toxic Substances Control Green Chemistry Initiative

- Safer Alternative Regulations
- Toxics Information Clearinghouse

Department of Pesticide Regulation

Office of Environmental Health Hazard Assessment

State and Regional Water Boards

- Evaluation & registration of pesticide products
- Use restrictions

 \rightarrow

- Risk Assessment
- Environmental and toxicological end-points
- Water Quality Standards
- Discharge Requirements
- Monitoring Requirements

Water Board Regulatory Actions

Water quality standards

- Numerical or narrative (no toxics in toxic amounts)
- Water, sediment, or biota
- Discharge requirements
 Monitoring / Information requirements
- Impaired waters 303(d) list
 - → Total Maximum Daily Loads

Challenges





Limited data and tools

- Lack of analytical methods
- Lack of thresholds / standards
- Difficult to link



- Occurrence of a chemical to an effect
- An effect to a chemical or group of chemicals
- Difficult to control sources or pathways

Tiered Risk Monitoring and Management

Tier IV: High Concern – 303(d) list →TMDL or alternative(s)

Tier III: Moderate Concern

- Action plan or strategy
 - Aggressive pollution prevention
 - Seek product or chemical alternatives
 - Low-cost control actions

Tier II: Low Concern

- Track product use and market trends
- Easy, low-cost source identification and pollution prevention actions

Tier I: Possible Concern

- Identify and prioritize potential CECs
- Develop bio and chemistry methods

Tiered Risk Monitoring and Management

Tier IV: High Concern

Studies to support TMDL or alternatives

Tier III: Moderate Concern

- Trend monitoring and/or
- Fate, effects, and

sources and loadings studies

Tier II: Low Concern

- Periodic ambient trend screening
- Periodic source trend screening

Tier I: Possible Concern

Screening monitoring

Regulatory Perspective

- @Goal = prevent CECs problems
- Monitoring
 - Inform management decisions
 - Based on informed hypotheses