



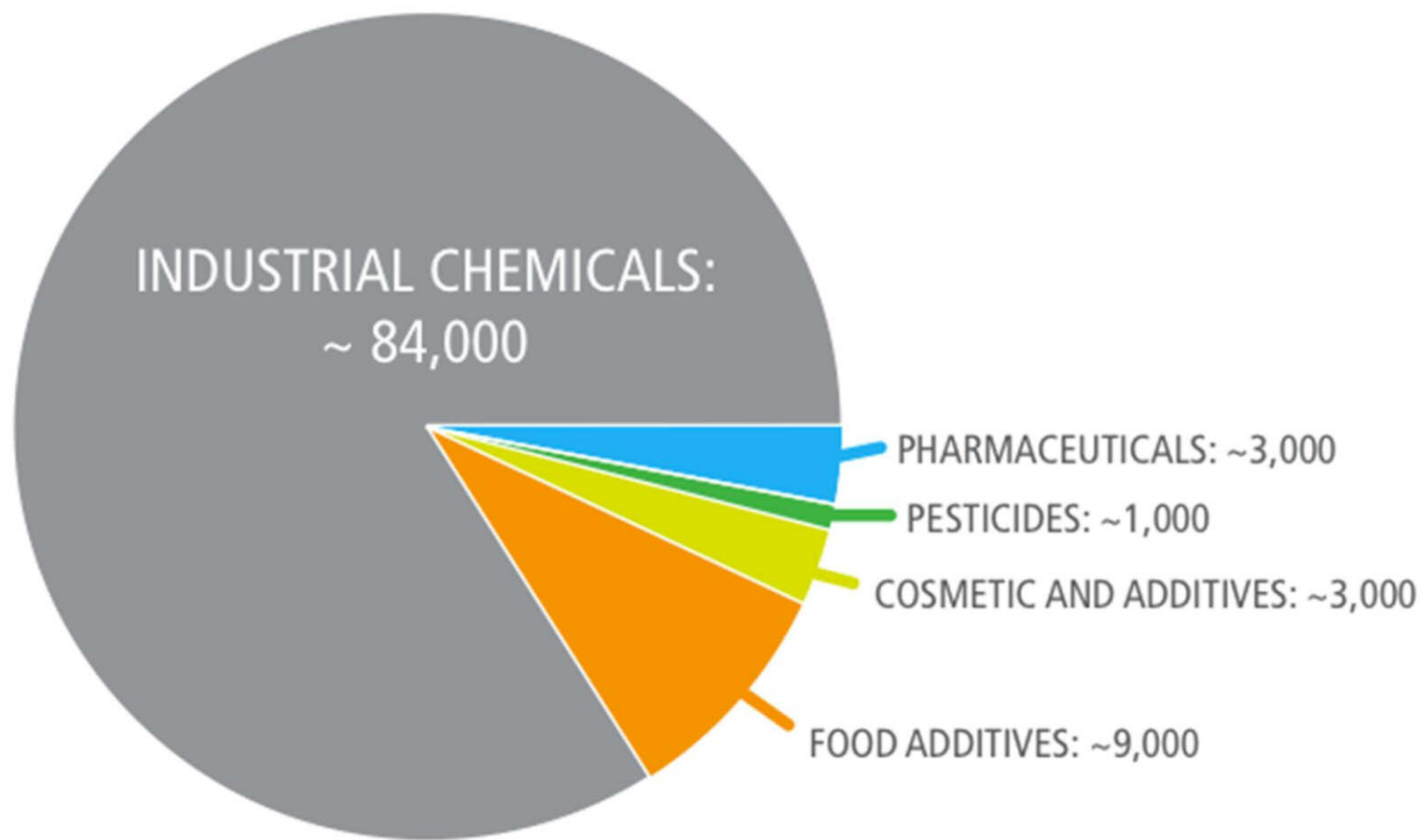
Emerging Contaminant WG Update

Presentation to SC - Aug 6th 2012

Meg Sedlak



The Universe of Chemicals to Monitor



Goal of WG

- What contaminants of emerging concern (CECs) have the potential to adversely impact beneficial uses in San Francisco Bay?

Goal of WG

- What contaminants of emerging concern (CECs) have the potential to adversely impact beneficial uses in San Francisco Bay?
- Challenge:
 - Proprietary information
 - Lack of analytical methods
 - Dearth of relevant toxicity information

ECWG's 3-Pronged Approach

➤ Existing information:

- Known toxicity
- High volume/production
- Detected at other sites
- BPJ

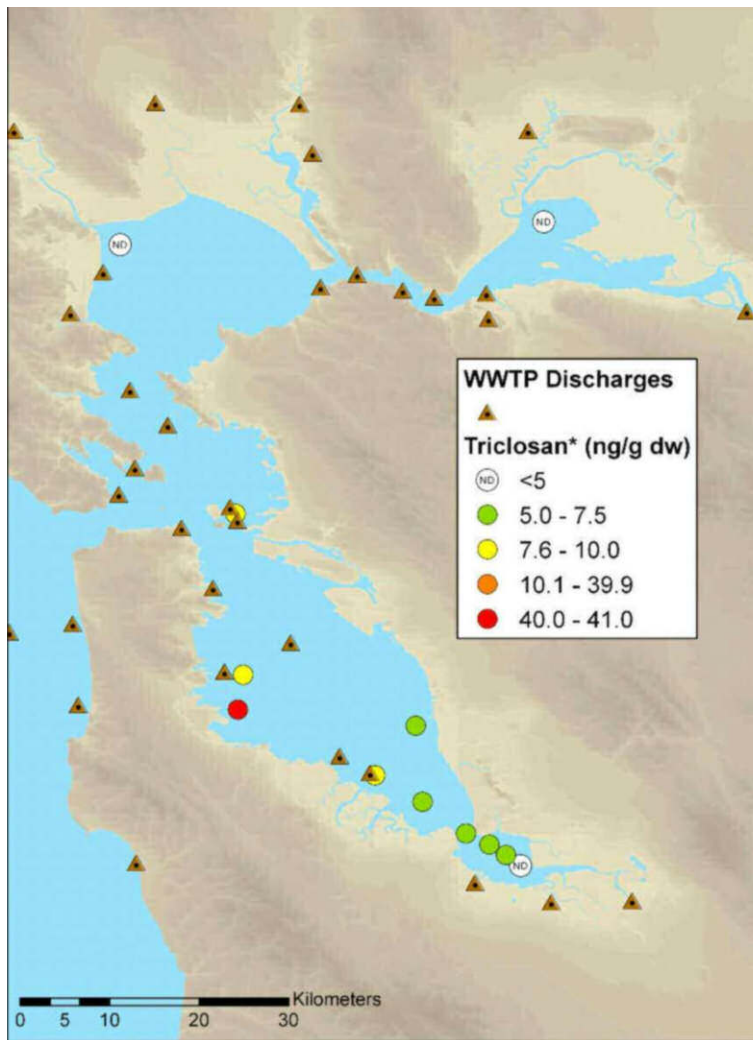
➤ Occurrence:

- Nontargeted
- Environmental fate modeling

➤ Effect-based:

- Using similar modes of action to identify contaminants
- Bioassays

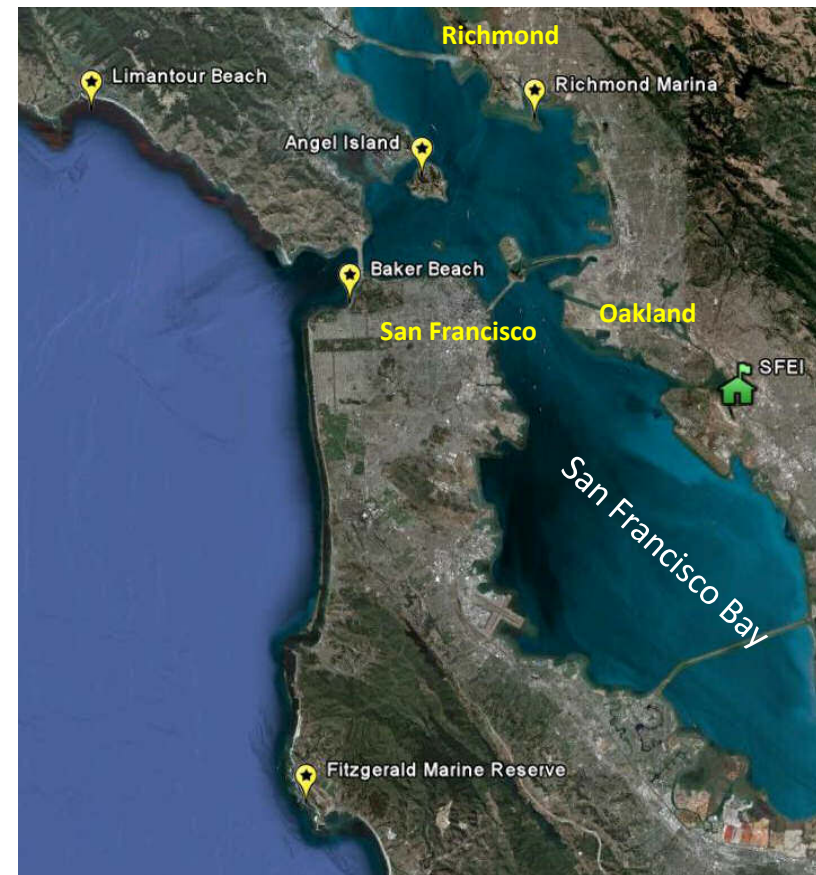
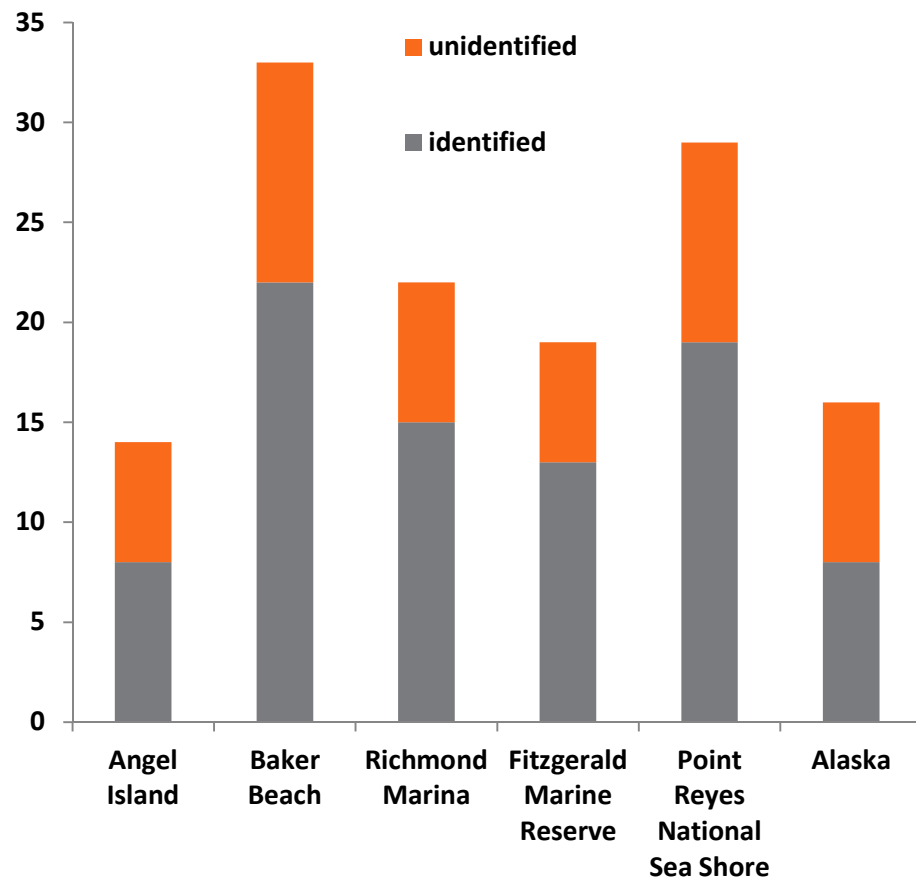
Existing Information: Triclosan example



* Limit of quantification 5 ng/g

- High usage – 10 mil. lbs
- Toxic – EDC (fish/mammals), acute toxicity to algae (200 ng/L)
- Several studies
 - Low concentrations observed in sediment (2008)
 - Not detected in mussel, sediment and water (2010)
- Conc < available thresholds

Occurrence: Nontargeted Analysis

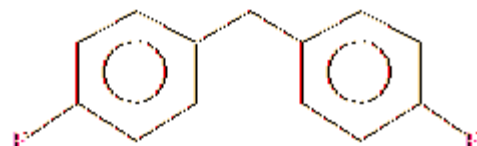


Example: Fluorinated Compounds

| Compound | CAS# | Comments |
|----------------------------------------|----------|----------------------|
| octafluorodecane | -- | degradation product? |
| 1,1,2,2-Tetrafluoro-1,2-diphenylethane | 425-32-1 | |
| 4,4'-Difluorodiphenylmethane | 457-68-1 | polymer subunit |
| Difluorobenzophenone | 345-92-6 | polymer use? |
| Monofluorobenzophenone | 345-83-5 | polymer use? |



1,1,2,2-Tetrafluoro-1,2-diphenylethane



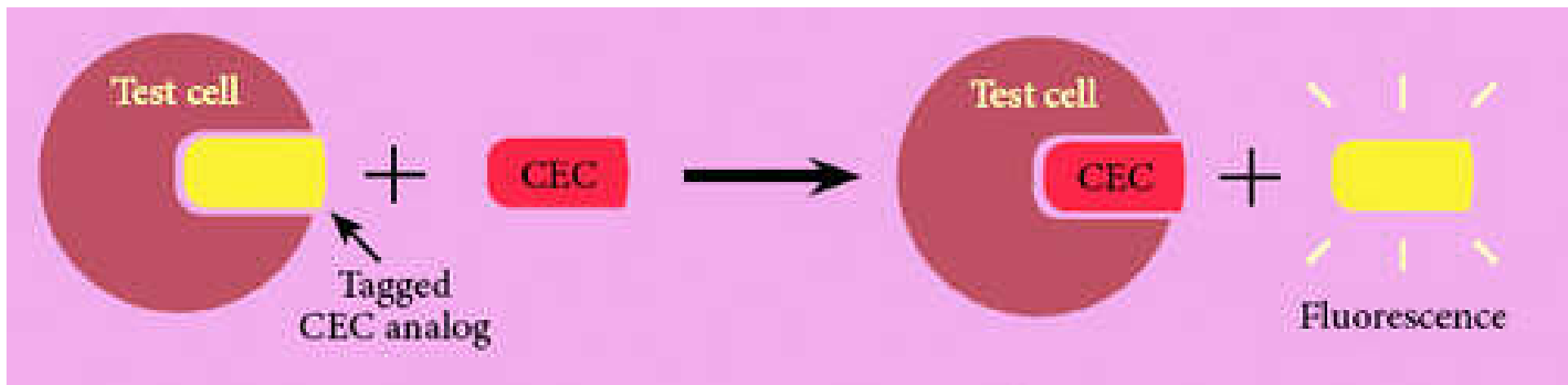
4,4'-Difluorodiphenylmethane



fluorobenzophenones

Bioanalytical tools

- Linking exposure to common mode of action
- Bioassays developed for EDCs
- Great for mixtures and evaluating synergistic effects



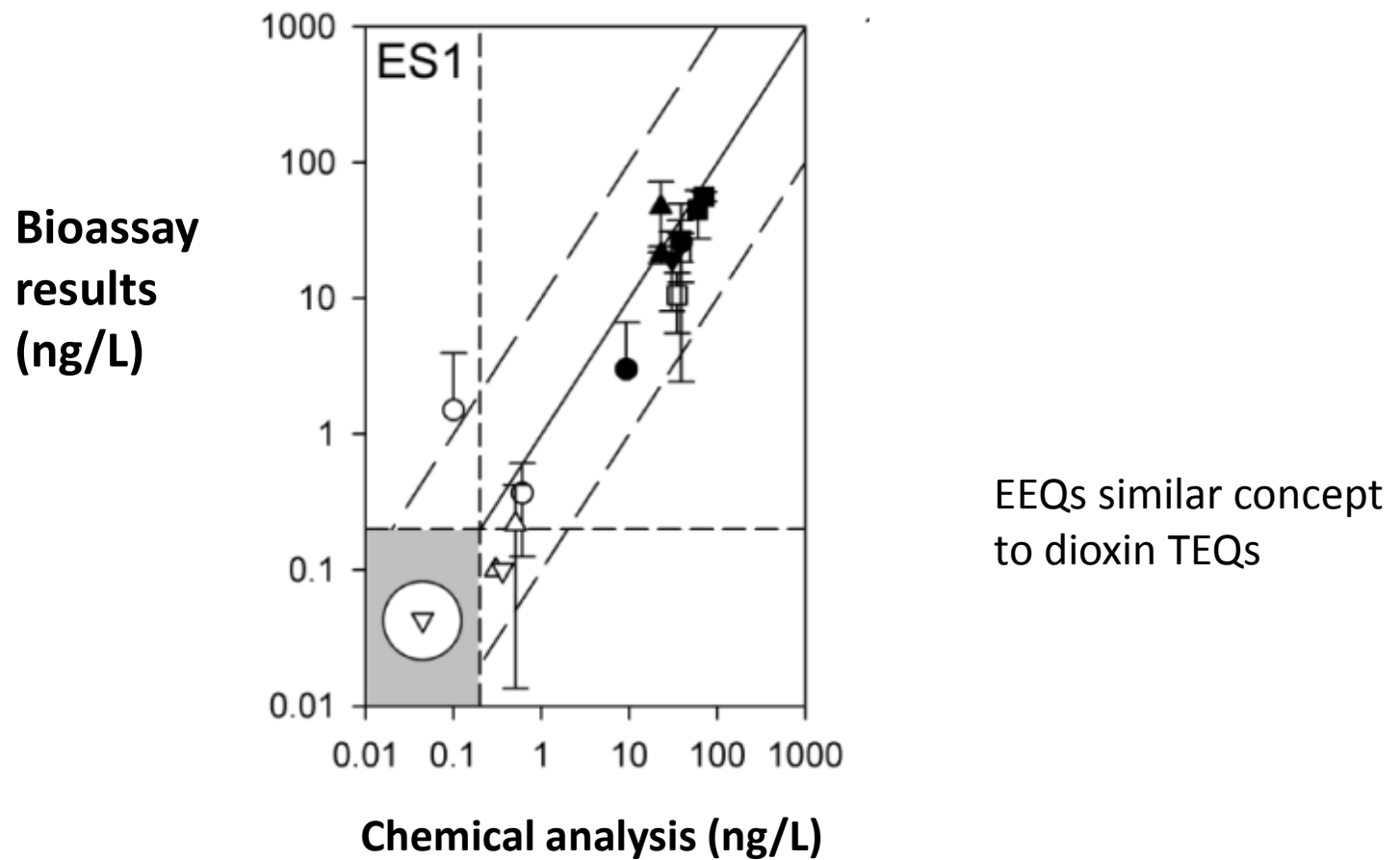
2013 Bioanalytical Special Study

- Recommendation of State CEC Panel Report –“Monitoring Strategies for CECs in CA’s Aquatic Ecosystems”
- Evaluating estrogenic pathway
 - Reproductive systems
 - Growth and development
 - Cardiac function
- Dr. Nancy Denslow (University of Florida) & Keith Mayura / Steve Bay (SCCWRP)
- 2-year study - \$126,000 (42K match SCCWRP)
 - \$70K –first year

Laboratory exposures (Yr 1)

- Chemicals: Estrone, 4-NP, BPA, galaxolide
- Early Life Stage (embryo): End points – survival & growth
 - 5 molecular biomarkers
- Juvenile: Endpoints - growth, Vtg, & hormones
 - 5 molecular biomarkers
- High throughput assays – Estrogen Receptor (human)
 - Commercially available in vitro assays
 - Leveraging off of existing SCCWRP work

Linking Biology to Chemistry



Source: Leusch et al 2010

Field Exposures (Yr 2)

- Validate lab work using effluent & receiving water from WWTPs in So Cal and SFB
- Assays:
 - Embryo and juvenile assays
 - Molecular biomarkers
 - Estrogen receptor high throughput assays

Why now? Why not the RMP?

- Important to link molecular response to organism effects (e.g., survival, growth, reproduction, or susceptibility to disease)
- At our request, using estuarine fish, silversides (*Menidia beryllina*)
 - Most of work to date is freshwater
- Leveraging off of \$800K work (SCCWRP)
 - Will use SF Bay site and Bay relevant fish
- Many chemicals in universe – one more tool to determine whether effluents/waters have the potential to impact biota

Why not now? Why the RMP?

- Unlikely to have an off-the-shelf ready to use assay in the near future
- Likely that additional studies funding will be needed
 - WERF, SCCWRP, State, etc.
- Estrogen receptor and estrogen impacts widely studied
 - Less likely to produce new information regarding new contaminants
 - No studies to date in SF Bay
- Likely to result in a TIE being conducted

How does RMP Approach compare to State CEC Panel recommendations?

- Phase 1 - Identify priority CECs
- Phase 2 - Conduct studies to determine whether further monitoring of these CECs is needed
- ➔ **Phase 3 - Reassessment of monitoring efforts and updating the list of target CECs**
 - RMP CEC Synthesis Report and Strategy
- Phase 4 – Develop action plans to minimize impacts

State Panel Recommendations

Table 1. CECs identified by the Advisory Panel for monitoring in coastal embayments

| Surface waters | Sediments | Tissue |
|-----------------------------|-----------------------------------|-----------------------------------|
| 17-beta estradiol (hormone) | ✓ Bifenthrin (pesticide) | ✓ PBDEs 47, 99 (flame retardants) |
| Estrone (hormone) | ✓ Permethrin (pesticide) | ✓ PFOS (PFC) |
| Bisphenol A (PPCP) | ✓ PBDEs 47, 99 (flame retardants) | |
| HHCB - Galaxolide (PPCP) | ✓ PFOS (PFC) | |
| Bifenthrin (pesticide) | | |
| ✓ Permethrin (pesticide) | | |
| ✓ Chlorpyrifos (pesticide) | | |

CEC Synthesis

- Summarized existing Bay occurrence studies
 - Analytes by year and matrix
 - Max concentration reported
- Compared to other locations
- Compared to toxicity thresholds where available
- Placed in risk-management framework

CECs in the Monitoring Tiers

| Compound(s) | Management Tier | Rationale |
|---------------------------------------|----------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Pyrethroids | Tier V: Very High Concern | Detected in Bay sediments, tributary sediment concentrations comparable or higher than toxicity thresholds, toxic at low concentrations, high volume use, present in urban runoff |
| PFOS | Tier IV: High Concern | Bird egg concentrations greater than PNEC, high concentrations in seal blood, high volume use of precursors |
| Fipronil | Tier IV: High concern | May be above toxicity thresholds at some sites for calculated porewater concentrations, need better ambient data and/or toxicity thresholds for sediment matrices to better assess risk |
| PBDEs | Tier III: Moderate Concern | Detected in Bay wildlife, toxicity in mammalian models, bird egg concentrations below toxicity threshold, sport fish concentrations below CA fish contaminant goal, possible immune system and behavioral impacts on fish, use declining |
| Nonylphenol, Nonylphenoethoxylates | Tier III: Moderate Concern | Bay concentrations below most toxicity thresholds, possible impacts on larval barnacle settlement, high volume use, estrogenic compounds |

CEC Strategy: Next Steps

- Address CECs currently in upper tiers
- Evaluate Advisory Panel recommendations for estuaries
- Identify “New” CECs (watch list)
- Fall/Winter 2012

CEC Watch List

Compound Rationale

| | |
|---------------------------------|-------------------------------------------------------------------------------|
| Siloxanes | HPV; Detected in Canada, Europe PEC > toxicity thresholds? |
| Quaternary ammonium compounds | High concentrations in NY estuaries Limited toxicity data |
| Nanomaterials | Limited analytical methods for environmental samples Limited toxicity data |
| Estrone 17 beta estradiol | Toxic at low concentrations No Bay occurrence data |
| Bisphenol A | Toxic at low concentrations No (good) Bay occurrence data |

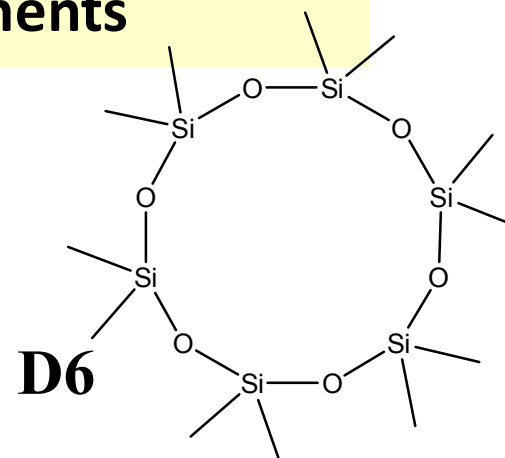
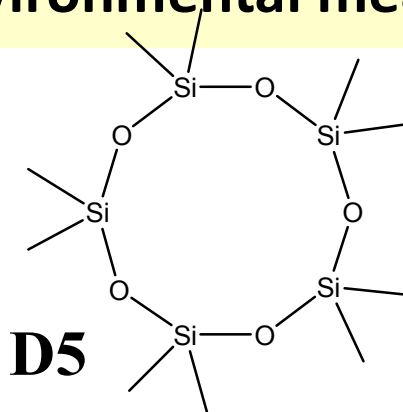
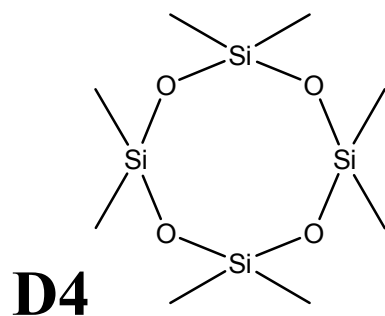
Other 2012 EC Activities

- PFCs in seals, small fish, cormorant and sediment
 - Seals collected
 - Sediment, water and small fish underway
- Session chair for SETAC Long Beach CECs
 - Prioritizing Contaminant of Emerging Concern for Monitoring in California

END

Volatile methyl siloxanes

- Carrier in antiperspirants/deodorants
- Shampoo, conditioners, cosmetics
- VOC exempt cleaning solvents
- Estimated global emissions to the atmosphere of >30000 tonnes/yr not including industrial use for silicone polymer (PDMS) production
- Mammalian toxicology relatively well studied
 - D4 is a possible EDC
- Relatively limited environmental measurements



CECs Recommended for Initial Monitoring (Phase 2)





| 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 |

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PPCP=pharmaceutical and personal care product; PFC=perfluorinated chemical

2.3.1 Phase 1 – Develop Initial CEC List(s) Based on Panel Screening Framework

The Panel identified an initial list of CECs by comparing MECs/PECs to biological effects thresholds (MTLs) that incorporated appropriate safety factors (Section 2.2). If analytical methods are not available, these would need to be developed, or PECs would need to be estimated (e.g., using a conceptual source and fate model), before the CEC could be considered for Phase 2 monitoring.

2.3.2 Phase 2 – Implement Monitoring of Phase 1 List of Initial CECs

Phase 2 involves implementation of monitoring for CECs that have MTQs >1. The overall objectives of Phase 2 are to:

- 1) verify the occurrence of targeted CECs in aqueous, sediment and tissue samples;
- 2) initiate compiling a data set as part of special studies that characterize their occurrence in sources and receiving waters (e.g., WWTP effluents and effluent-dominated receiving waters, stormwater-impacted freshwaters, marine waters, coastal embayment and estuarine waters, and background receiving water, and in the appropriate environmental matrices (water, sediment and tissue));

RMP 2013 Special Studies



2013 Special Study Budget



| | |
|----------------------------------------------------------------------------------------------------------------------------|--------------------|
| TOTAL AVAILABLE FOR SPECIAL STUDIES 2013 | \$1,093,540 |
| Total Proposed Studies | \$1,189,000 |
| Remaining Balance | -\$95,460 |
| PROPOSED PILOT AND SPECIAL STUDIES - 2013 | |
| 1. EC: PBDE Summary Report | \$35,000 |
| 2. EC: Updating RMP Emerging Contaminants Strategy | \$20,000 |
| 3. EC: Current Use Pesticide Focus Meeting | \$15,000 |
| 4. EC/EE: Linkage of In Vitro Assay Results With In Vivo End Points | \$70,000 |
| 5. EE: Developing Benthic Community Condition Indices for Mesohaline Environments | \$76,000 |
| 6. EE: Follow up to Moderate Toxicity Workshop (proposal TBD Fall 2012 after workshop - no study included in this package) | \$50,000 |
| 7. CF: Shared Modeling Proposal | \$100,000 |
| 8. STLS: Stormwater Loads Monitoring in Representative Watersheds | \$343,000 |
| 9. STLS: Develop and Update Spreadsheet Model - Year 4 | \$25,000 |
| 10. STLS: Landuse/ Source Area Specific EMC Development | \$80,000 |
| 11. STLS: Management Support for Spreadsheet Model Outreach and "Land Use" Based Monitoring | \$20,000 |
| 12.1 Nutrients: Project Management | \$20,000 |
| 12.2 Nutrients: Moored Sensor Monitoring Program Development | \$200,000 |
| 12.3 Nutrients: Algal Biotoxin Monitoring | \$65,000 |
| 12.4 Nutrients: Stormwater Nutrient Measurements | \$40,000 |
| 12.5 Nutrients: Nutrient Loads and Data Gaps | \$30,000 |

PBDE Summary Report



- \$35,000
- ECWG reviewed and approved
- Objective: Summarize PBDE data (2002 – 2012, sediment, water, bivalve, eggs) and provide context (comparison to OEHHA and tern thresholds)
 - Work needs to be completed by March 2013

Update EC Strategy



- \$20,000
- ECWG reviewed and approved
- Objective: track new EC information and revise/update EC strategy
 - Strategy based on existing information, effects (bioassays) and occurrence (NIST work, fate modeling)
 - Gray literature (Env. Canada, Great Lakes, Baltic, etc.)
 - Journals (ES&T, SETAC, etc.)
 - Update tiered risk-management table
 - Add/remove chemicals from “unmonitored CEC list”

Current Use Pesticides



- \$15,000
- ECWG reviewed and approved
- Objective: Evaluate existing information on CUPs and organize a focus meeting with key individuals (Kuivila, Moran, Kegley, Weston, labs)
 - Number of CUPs are not being monitored
 - Recommendation from State CEC panel to monitor (bifenthrin and permethrin in surface water)

Bioassays



- Year 1 (2013) \$70,000. Year 2 (2014) pending acceptable progress in Year 1 - \$56,000
- ECWG/EEWG reviewed – concerns about timeline/ research orientation
- Objective: to develop a tool to identify CECs through common modes of action
 - Recommendation of State CEC Panel report
 - Linking in vitro (cellular) to in vivo response (organism)
 - No research to date on estuarine organisms
 - ✦ Will evaluate Silversides
 - ✦ Evaluate endocrine disruptors (estrone, BPA, 4NP, and galaxolide)

Development of a Mesohaline Index



- \$75,800 (2013); \$50,000 already allocated in 2012
- EEWG reviewed and approved
- Objective: Develop and calibrate a mesohaline index for San Francisco Bay
 - Polyhaline (Central Bay) has been developed
 - No index for low salinity (mesohaline) and freshwater

Stormwater Monitoring



- 343,000
- SPLWG/ STLS: reviewed and approved
- Monitoring in 2 watersheds
 - Will monitor 6 watersheds in 2013 – Sunnyvale, Guadalupe, Lower Marsh Creek, San Leandro, Pulgas, and Richmond)

Update SS Model – Year 4



- \$25,000
- SPLWG/STLS reviewed and approved
- Objective: to develop and refine mass emissions of Hg and PCBs using single watersheds for calibration and verification
 - Inexpensive tool for estimating regional loads
 - Building upon prior tool development
 - ✦ Yr 1 – Hydrology
 - ✦ Yr 2 – Additional watersheds and preliminary Hg/PCB developed
 - ✦ Yr 3 – Cu test case for model

Land Use/ Source Specific EMC



- \$80,000
- SPLWG/STLS approved
- Objective: to generate even mean concentration data for the regional watershed spreadsheet model

Management Support for STLS



- \$20,000
- SPLWG/STLS
- Objective: Coordination and meetings regarding monitoring, EMC development and input on RWSM

Nutrients



- \$355,000
- Approved by Nutrient SAG
- Objective:
 - Install moored sensors
 - Develop Solid Phase Adsorption Tracking as a tool for monitoring HABs
 - Stormwater monitoring in 6 catchments
 - Continuing to develop storm water loads for Central and North Bay (South Bay completed in 2011)

Modeling



- \$100,000 (2013) / \$100,000 (2012)
- Endorsed by Nutrient SAG; in accordance with CFWG direction
- Objective:
 - Develop tactical plan
 - Establish model team
 - Check in with TRC/SC
 - Develop hydrodynamic/sediment transport model
 - Develop basic phytoplankton water quality model for Suisun and South Bay