Emerging Contaminants
Workgroup Meeting

Amy Kleckner, RMP Manager
April 16-17, 2024 – Hybrid
SFEI Housekeeping Reminders

Gender diversity is welcomed here. All are encouraged to use the restroom that best fits their identity.

Out the doors and to the right

Password: sfsfsfsfsf

Please silence cell phones & laptops

FREE LUNCH
Zoom tips

1. Update your name and add your affiliation
2. Raise your hand if you have a comment or question
3. Unmute yourself and turn on video when you are speaking
4. Use the chat function if you have a comment, question, or technical issue

In person attendees

1. Mute your microphone and the volume on your laptop.
2. Turn off your camera.
Guidelines for Inclusive Conversations

1. Try it on
2. Practice self focus
3. Understand the difference between intent and impact
4. Practice both / and
5. Refrain from blaming or shaming self and others
6. Move up / move back
7. Practice mindful listening
8. Right to pass
9. Avoid jargon
10. It’s okay to disagree
We acknowledge the San Francisco Bay is the ancestral homeland of many indigenous people, including the Ohlone, Patwin, Coast Miwok, and Bay Miwok.
ECWG Expert Advisors

- Miriam Diamond
  University of Toronto

- Lee Ferguson
  Duke University

- Derek Muir
  Environment & Climate Change Canada

- Heather Stapleton
  Duke University

- Bill Arnold
  University of Minnesota

- Dan Villeneuve
  US EPA
INTRODUCTIONS
**Meeting Agenda: DAY ONE**

<table>
<thead>
<tr>
<th>1. Introduction and Goals for Meeting</th>
<th>9:00</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. Information: RMP CECs Science Update</td>
<td>9:15</td>
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<tr>
<td>3. Discussion: CEC Strategy Revision</td>
<td>9:45</td>
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<tr>
<td>Break</td>
<td>10:30</td>
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<tr>
<td>3. Discussion: CEC Strategy Revision cont.</td>
<td>10:45</td>
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<tr>
<td>LUNCH</td>
<td>11:30</td>
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<tr>
<td>4. Information: Update on Nontarget Analysis of Bay Harbor Seals</td>
<td>12:10</td>
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<tr>
<td>Meeting Agenda: DAY ONE cont.</td>
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<tr>
<td><strong>5. Discussion: Proposed Study Design for S&amp;T NTA of Bay Water</strong></td>
<td>12:30</td>
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<tr>
<td><strong>6. Information: Update from the DTSC Safer Consumer Products Program</strong></td>
<td>1:00</td>
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<tr>
<td><strong>Break</strong></td>
<td>1:30</td>
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<tr>
<td><strong>7. Information: Update on the State Water Board CEC Strategy</strong></td>
<td>1:40</td>
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<tr>
<td><strong>8. Information: Update on PFAS in San Francisco Bay</strong></td>
<td>2:10</td>
</tr>
<tr>
<td><strong>9. Information: Chlorinated Paraffins in Bay Sediment</strong></td>
<td>2:40</td>
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<tr>
<td><strong>10. Information: Setting the Stage for Day 2</strong></td>
<td>2:55</td>
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<tr>
<td><strong>ADJOURN</strong></td>
<td>3:00</td>
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<td></td>
<td>Meeting Agenda: DAY TWO</td>
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<tr>
<td>11.</td>
<td>Summary of Yesterday, Goals for Today</td>
</tr>
<tr>
<td>12.</td>
<td>Information: PFAS Sources to Solutions Project</td>
</tr>
<tr>
<td>Break</td>
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<tr>
<td>13.</td>
<td>Introductions and Goals for the Meeting</td>
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<tr>
<td>15.</td>
<td>Discussion: Stormwater CECs Integrated Modeling &amp; Monitoring Approach: Straw proposal for monitoring design</td>
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<td>16.</td>
<td>Information: Next Steps</td>
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# Meeting Agenda: DAY TWO cont.

<table>
<thead>
<tr>
<th>Time</th>
<th>Item</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:00</td>
<td>LUNCH</td>
</tr>
<tr>
<td>12:30</td>
<td>17. Summary of Proposed ECWG Special Studies for 2025</td>
</tr>
<tr>
<td>1:15</td>
<td>18. Discussion of Recommended Special Studies for 2025 - General Q&amp;A, Prioritization</td>
</tr>
<tr>
<td>2:10</td>
<td>19. Closed Session – Decision: Recommendations for 2024 Special Studies Funding</td>
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<tr>
<td>2:50</td>
<td>20. Report out on Recommendations</td>
</tr>
<tr>
<td>3:00</td>
<td>ADJOURN</td>
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Goals for Meeting

• Provide updates on recent and ongoing ECWG activities (today & tomorrow)
• Discuss CEC Strategy Revision and future direction of the program (today)
• Review Status and Trends monitoring data (today)
• Overview of PFAS Sources to Solutions project and implications for RMP PFAS science (tomorrow)
• Discuss ongoing stormwater CECs projects; joint meeting with Sources, Pathways, and Loadings Workgroup (tomorrow)
• Recommend special study proposals for funding in 2025 (tomorrow)
Regional Monitoring Program

Collect data and communicate information about water quality in San Francisco Bay in support of management decisions

~ 68 entities in the Program
  • Municipal wastewater
  • Industrial wastewater
  • Municipal stormwater
  • Dredgers
RMP Program Structure

You are here!

Steering Committee

Technical Review Committee

Sediment Workgroup

Emerging Contaminants Workgroup

Sources, Pathways, and Loadings Workgroup

PCB and Dioxin Workgroup

Microplastics Workgroup

Sport Fish Strategy Team

Small Tributary Strategy Team

PCB Strategy Team
Regional Monitoring Program

RMP Budgeted Expenses: 2024

- Special Studies: $1,768,074
- Status & Trends: $1,947,500
- Program Mgmt: $369,500
- Governance: $415,000
- QA and Data Services: $280,000
- Reporting: $222,000
- Communications: $214,000
Special Studies Budget for 2025

Predicted RMP Special Studies Budget for 2025 = $1.54M
★ Includes: AMR Funds + Stormwater CECs funds

But wait there’s more!

USEPA San Francisco Bay Program Office

● Expected $54M per year (!) for San Francisco Bay
EPA Region 9
San Francisco Bay Program Office
FY24 Draft Annual Priority List

- Subtidal eelgrass and oyster reef restoration
- Wetlands Regional Monitoring Program
- Beneficial Reuse of Dredged Material Support
- In-Bay Monitoring of Pollutants, including trash, and algal species under the Regional Monitoring Program
- Nutrient Management Strategy
- Large scale tidal wetlands restoration
- Special studies/projects for addressing PCBs under TMDL implementation plan
- Large scale implementation of urban green stormwater infrastructure
- Special studies/projects for addressing PFAS in SF Bay
- Large scale shoreline resilience, multi-benefit projects including horizontal levees and wastewater treatment/reuse
- BRRIT (Bay Restoration Regulatory Integration Team)
Getting the RMP Bucket Ready

- SC guidance to workgroups and staff: aim for 50% funding increase in 2025, 100% increase starting in 2026
- Important to include EJ and climate adaptation
- Great time for bigger ideas
CECs Science Update

Rebecca Sutton, PhD
ECWG Meeting
April 16-17, 2024 – Hybrid
CECs Team at SFEI

Rebecca Sutton (she/her)  
Diana Lin (she/her)  
Kelly Moran (she/her)  
Ezra Miller (ze/zir)

Jennifer Dougherty (she/her)  
Miguel Mendez (he/him)  
Pedro Avellaneda (he/him)  
Martin Trinh (he/him)  
Alicia Gilbreath (she/her)  
Kayli Paterson (she/they)
Update on Current Activities

Learning from Others, Sharing Expertise

Pathways Monitoring & Modeling

CEC Monitoring, Risk Evaluation

Novel Approaches (Nontarget, NAMs)
<table>
<thead>
<tr>
<th><strong>Very High Concern</strong></th>
</tr>
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<tbody>
<tr>
<td>NONE</td>
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<td>Alkylphenols/ethoxylates, bisphenols, fipronil &amp; degradates, imidacloprid, microplastics</td>
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<tr>
<td>Chlorpyrifos &amp; diazinon, HBCD, PBDEs, personal care &amp; cleaning, pharmaceuticals, pyrethroids</td>
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<td>Alternative flame retardants, BZT-Uvs, indole, 4-methylphenol, plastic additives, PCB-11, PHCZs, QACs</td>
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1. Bay Monitoring: **High** Concern CECs

**PFAS**
- Synthesis and Strategy – Launching
- Water – Ongoing Status & Trends monitoring and special study (TOP)
- Sediment – Ongoing S&T and SEP-funded monitoring
- Biota – Ongoing S&T monitoring, expanded fish investigation, pilot marine mammals & prey fish studies

**Organophosphate Esters**
- Water – Ongoing S&T monitoring
1. Bay Monitoring: Moderate Concern CECs

Bisphenols
- Water – Ongoing Status & Trends monitoring
- Sediment – Ongoing S&T monitoring

Alkylphenol Ethoxylates & other surfactants
- Water – Ongoing special study
- Sediment – Ongoing special study
1. Bay Monitoring: Possible Concern CECs

**Quaternary Ammonium Compounds**
- Water – Ongoing special study
- Sediment – Ongoing special study

**Tire Chemicals** (not classified in tiered risk-based framework)
- Water – Ongoing special study

**Chlorinated Paraffins**
- Sediment – Ongoing SEP-funded study
2. Pathways Monitoring

**Stormwater**

- Multi-year screening of PFAS, OPEs, bisphenols, tire chemicals, ethoxylated surfactants – Nearing completion
- SFEI Mayfly remote sampler – Piloting for PFAS
- Monitoring approach – In development
- USEPA-funded tire chemicals and microplastics – Ongoing project
2. Pathways Monitoring

Wastewater

- BACWA PFAS Phase 2 – Now complete
- Quaternary ammonium compounds – Ongoing special study
- Ethoxylated surfactants – Ongoing special study
- Plastic additives, including OPEs and bisphenols – Launching
Additional Elements

Pathways Monitoring & Modeling

CEC Monitoring, Risk Evaluation

Learning from Others, Sharing Expertise

Novel Approaches (Nontarget, NAMs)
3. Novel Approaches

Nontarget Analysis
• Sediment NTA
  • GC-based, nonpolar compounds – Masters theses complete
  • LC-based, polar compounds – Manuscript in preparation
  • Fact sheet summarizing results is in development
• Marine mammals – Study ongoing (GC & LC methods)
• Sport fish – Launching (GC & LC methods)
• Data mining of past results – Later this year

Ecotoxicology (New Approach Methodologies)
• Pro bono application to stormwater – Method in development
4. Learning from Others, Sharing Expertise

SCIENTIFIC PUBLICATIONS

- Quaternary Ammonium Compounds: A Chemical Class of Emerging Concern
- Pharmaceuticals, Pesticides, and Ultraviolet Filters in Wastewater Discharges to San Francisco Bay as Drivers of Ecotoxicity
- Where the Rubber Meets the Road: Emerging Environmental Impacts of Tire Wear Particles and their Chemical Cocktails
- Storms Mobilize Organophosphate Esters, Bisphenols, PFASs, and Vehicle-derived Contaminants to San Francisco Bay Watersheds (submitted)
- Interstate Technology and Regulatory Council: Tire Anti-Degradants (6PPD) Guidance Documents (in review)
- Evaluation of Per- and Polyfluoroalkyl Substances in San Francisco Bay Fish from 2009 to 2019 (in prep)
4. Learning from Others, Sharing Expertise
4. Learning from Others, Sharing Expertise
Questions?

CEC Monitoring, Risk Evaluation

Pathways Monitoring & Modeling

- Learning from Others, Sharing Expertise
- Novel Approaches (Nontarget, NAMs)
Draft CEC Strategy Revision V1.0

1. Introduction

2. Risk-based Approach to Identify and Prioritize CECs

3. CEC Risk Evaluation and Monitoring Recommendations
   Profiles of 21 contaminants or classes

4. Scanning the Horizon: Identifying New CECs

5. Conclusion: Multi-year Plan
What’s Missing?
V1.1, Summer

• Additional chemical profiles?
  • Alkylphenol ethoxylates // Ethoxylated surfactants
  • Carbendazim
  • Chlorinated paraffins
  • Tire/roadway CECs, including 6PPDQ

• Additional insights from nontarget analysis data mining

• Final Report: October 2024
Topics for Today

• Review final management questions
• Placement of key CECs in the tiered risk-based framework
  • PFAS
  • OPEs
  • Fipronil and Degradates
  • Imidacloprid
  • NEW: Carbendazim (not yet included in strategy document)
  • NEW: Chlorpyrifos and Diazinon
  • Smaller refinements
• BREAK ~ 10:30
• Ecotoxicology approach
• Multi-year plan, future directions
Final ECWG Management Questions

1. Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?

2. What are the sources, pathways, loadings, and processes?

3. What are the physical, chemical, and biological processes that may affect transport and fate?

4. Have levels of individual CECs or groups of CECs changed over time in the Bay or pathways? What are potential drivers contributing to change?

5. Are CECs predicted to increase or decrease in the future?

6. What are the effects of management actions?
Key CECs in the Tiered Risk-based Framework
Possible Concern: $RQ = ?$
Significant uncertainty in occurrence data and/or the level of effect on Bay wildlife or people

High Concern: $10 < RQ_{eco} < 100, 1 < RQ_{human} < 10$
Occurrence data suggest a high probability of an adverse impact on Bay wildlife or people

Moderate Concern: $1 < RQ_{eco} < 10, RQ_{human} < 1$
Occurrence data suggest a moderate probability of an adverse impact on Bay wildlife or people

Low Concern: $RQ << 1$
Occurrence data suggest minimal impact on Bay wildlife or people

Very High Concern: $RQ_{eco} >> 100, RQ_{human} >> 10$
Occurrence data suggest a very high probability of an adverse impact on Bay wildlife or people
<table>
<thead>
<tr>
<th>Category</th>
<th>Concerns</th>
</tr>
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<tbody>
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<tr>
<td>Monitoring Recommendations</td>
<td>Management Recommendations</td>
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<tr>
<td><strong>Very High Concern</strong></td>
<td>• 303(d) listing</td>
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<tr>
<td>• Studies to support TMDL</td>
<td>• TMDL or alternate management plan</td>
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<tr>
<td>• S&amp;T monitoring</td>
<td>• Aggressive control / treatment</td>
</tr>
<tr>
<td><strong>High Concern</strong></td>
<td>• Prioritize action plan / strategy</td>
</tr>
<tr>
<td>• S&amp;T monitoring</td>
<td>• Aggressive pollution prevention</td>
</tr>
<tr>
<td>• Studies on sources, pathways</td>
<td>• Cost-effective control / treatment</td>
</tr>
<tr>
<td>• Consider studies on fate, effects</td>
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</tr>
<tr>
<td><strong>Moderate Concern</strong></td>
<td>• Action plan / strategy</td>
</tr>
<tr>
<td>• Consider S&amp;T monitoring</td>
<td>• Moderate pollution prevention</td>
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<tr>
<td><strong>Low Concern</strong></td>
<td>• Low-cost source identification / control</td>
</tr>
<tr>
<td>• Periodic screening – Bay, pathways</td>
<td>• Low-level pollution prevention</td>
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<tr>
<td>• Transitional – Sunset S&amp;T monitoring</td>
<td>• Track product use / market trends</td>
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<tr>
<td>• Deprioritized</td>
<td>• Continue to identify / prioritize CECs</td>
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<tr>
<td><strong>Possible Concern</strong></td>
<td>• Track external efforts</td>
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<tr>
<td>• Periodic screening – Bay, pathways</td>
<td>• Develop screening methods</td>
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<tr>
<td>• Deprioritized</td>
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Organophosphate Esters: **High Concern**

**Sources:** Widely used flame retardants and plastic ingredients

**Risk driver:** Water concentrations exceed aquatic toxicity thresholds

- Maximum risk quotient (TDCPP, n=34): **120**
- Secondary factor: Cumulative impacts

**Management:** Bans on flame retardants in some products

**Monitoring strategy**

- Status & Trends water
- Special studies in wastewater & stormwater
- Synthesis & strategy, conceptual model
PFAS: **High Concern**

**Sources**: Numerous consumer and industrial products

**Risk driver**: Fish tissue concentrations exceed human health thresholds
- Maximum fish tissue risk quotient (PFOS, n=134): **39**
- Secondary factors: Persistence, bioaccumulation, cumulative impacts

**Management**: Recent product bans; prior long-chain PFAS phase-out

**Monitoring strategy**
- S&T water, sediment, biota
- Special studies in wastewater, stormwater, precipitation
- Complementary use of novel analytical methods
- Synthesis & strategy, conceptual model
Fipronil & Degradates: Moderate Concern… or High?

Sources: Urban insecticide against ants, termites, pet fleas

Risk driver: Water concentrations exceed aquatic toxicity thresholds
  • Maximum risk quotient (fipronil sulfone, n=22, 3 detections): 27
  • Secondary factors: Persistence, potential cumulative impacts

Management: Recent label changes for professional application outdoors

Monitoring strategy
  • Deprioritized, DPR does not need estuarine data
Imidacloprid: Moderate Concern

**Sources:** Agricultural and urban insecticide (ants, fleas, termites)

**Risk driver:** Water concentrations similar to aquatic toxicity thresholds
  - Risk quotients, depending on toxicity threshold (n=50): 0.29 – 0.96
  - Secondary factor: N/A

**Management:** Regulation and legislation is restricting some uses

**Monitoring strategy**
  - Deprioritized, DPR does not need estuarine data
Carbendazim: Moderate Concern?

**Potential sources:** Preservative ingredient in paints
- Also the degradate of a pesticide with little use

**Risk driver:** Water concentrations exceed aquatic toxicity thresholds
- ECHA threshold (PNEC): 150 ng/L
- Risk quotient (n=10): ~4
- Secondary factor: N/A

**Monitoring strategy**
- Continued screening in Bay water, stormwater via stormwater CECs suite
Chlorpyrifos & Diazinon: **Low Concern?**

**Sources:** Agricultural and urban insecticides

**Risk driver:** Not detected in Bay water
  - Sufficiently sensitive method, n=24
  - Secondary factor: Anticipated declines due to effective management

**Monitoring strategy**
  - Deprioritized
Smaller Refinements

- **PBDD/Fs** category collapsed into **PBDEs**
  - Polybrominated dioxins & furans are impurities in PBDEs and can be derived from natural sources
  - Older data indicate low risk, declines anticipated due to PBDE bans
- **Phthalates** category expanded into **Other Plastic Additives**
  - Recent pilot data include phthalates and alternatives in Bay water
- **Siloxanes** moved to a future priority
  - Recent data include qualitative tentative identifications in sediment via nontarget analysis
  - Older pro bono observations in bivalves
Specific Discussion Topics

• Is there consensus on **OPEs** and **PFAS** as High Concern contaminants?
• Do **fipronil and degradates** belong in the Moderate or High Concern tier?
  • Are there implications for future RMP monitoring?
• Is there consensus on **imidacloprid** as a Moderate Concern contaminant?
• Are there any considerations we should factor into our review and risk screening of **carbendazim**?
• Is it useful to document our data and Low Concern classification for **chlorpyrifos and diazinon**?
Ecotoxicology
Approach
Thresholds Spreadsheet

• Compilation of ecosystem effects level thresholds
• Living document updated periodically
• Available by request (EzraM@sfei.org)
Ecotox Thresholds

Single species toxicity test
(one endpoint e.g., mortality OR change in reproduction)
Ecotox Thresholds

Single species toxicity test
(one endpoint e.g., mortality OR change in reproduction)

Increasing effect on measured endpoint

---

Not listed as rows in the spreadsheet
Ecotox Thresholds

Single species toxicity test
(one endpoint e.g., mortality OR change in reproduction)

Test many species & endpoints

Ecosystem-level threshold
e.g., Predicted No Effect Concentration (PNEC)

Increasing effect on measured endpoint

50%

NOEC

EC<sub>50</sub>

Increasing Dose

Concentration

EC<sub>50</sub> Deterministic Methods

× uncertainty factors

Ecosystem-level threshold
e.g., Predicted No Effect Concentration (PNEC)
Ecotox Thresholds

Single species toxicity test (one endpoint e.g., mortality OR change in reproduction)

Test many species & endpoints

Species Sensitivity Distribution (compares one endpoint across species)

% Species Affected

Concentration

HC5

EC50

× uncertainty factors

Ecosystem-level threshold e.g., Predicted No Effect Concentration (PNEC)

NOEC

EC50

50%

5%

Increasing effect on measured endpoint

Increasing Dose

Probabilistic Methods

Deterministic Methods

Rows in the spreadsheet
When Multiple Thresholds are Available

• Preference to
  • data for the appropriate matrix (e.g., freshwater vs. marine)
  • more species (and more trophic levels)
  • chronic exposures (rather than acute)
  • more experimental data (rather than predicted)
  • lower (more protective) thresholds
  • California-specific values when available

• No calculations of new thresholds when established literature threshold is available

Filter Column O to “Y”
When No Established Threshold Is Available

• Calculations of new thresholds
  • When single species ecotox data is available
  • Deterministic methods

• Read Across
  • When a threshold for a structurally similar compound is available

  E.g., 6PPD-quinone
  E.g., bisphenols
  E.g., biota thresholds

• In some cases, simply no threshold for comparison
Human Health

• For fish consumption only
  • Thresholds exist for some CECs for tissue and/or water matrix
  • No comparison with drinking water thresholds

• Preference to
  • California-specific values when available
  • Lowest (most protective) available threshold when there are no California-specific values

• No calculations of new thresholds
Cumulative Impacts

- Co-exposure to members of the same class of CECs or to commonly co-occurring contaminants from different chemical classes with the same mode of action
Cumulative Impacts

• Co-exposure to members of the same class of CECs or to commonly co-occurring contaminants from different chemical classes with the same mode of action

• Approach: Compare sums of relevant contaminants with the toxicity threshold of the most potent (known) compound
  • Assumes additive impacts and equivalent potency
  • More likely to over-estimate rather than under-estimate mixture effects (protective)

E.g., bisphenols
Bioassay Screening

• High-throughput *in vitro* assays
• Focus on biological modes of action instead of specific chemical classes

**Known Chemicals Detected in SF Bay**
• Individual chemical assay data
Bioassay Screening

- High-throughput *in vitro* assays
- Focus on biological modes of action instead of specific chemical classes

**Known Chemicals Detected in SF Bay**
- Individual chemical assay data
- Identify potential toxicity of specific individual chemicals (including those without available ecotox thresholds)
- Estimate potential mixture toxicity based on shared mode of action

Example: Corsi et al., *Sci Total Environ*, 2019
Bioassay Screening

• High-throughput *in vitro* assays
• Focus on biological modes of action instead of specific chemical classes

Whole Environmental Samples
Bioassay Screening

• High-throughput *in vitro* assays
• Focus on biological modes of action instead of specific chemical classes

**Whole Environmental Samples**
• Screen for biological activity / toxicity
• Identify mixture effects not predicted from known chemicals
• Compare whole sample results with those of specific chemicals to identify drivers of toxicity

**Proposals:**
• Stormwater tox screen
• S&T Bay Water NTA
Multi-year Plan & Future Directions
Multi-year Plan Organization

- Strategy
- Stormwater monitoring & modeling
- High Concern CECs
- Moderate Concern CECs
- Low or Possible Concern CECs
- Nontarget analysis, toxicology (novel methods)
Stormwater Monitoring and Modeling

• Significant ongoing focus of resources anticipated
  • Stakeholder-Science Advisor Team (SST) previously advised RMP contribution of $300k annually
  • Two EPA Water Quality Improvement Fund projects provides additional resources 2024-2027
  • Additional funds could be allocated to important priorities during this critical startup period

More discussion tomorrow during joint ECWG-SPLWG meeting
High Concern: PFAS

Current / ongoing
• Status & Trends water, sediment, sport fish, bird eggs
  • Pilots: Marine mammals, prey fish
• Synthesis and strategy
• TOP assay in Bay water and sediment
• Integrated monitoring and modeling in stormwater
• Soon: PFAS Sources to Solutions (EPA WQIF) – discussed tomorrow

Tier Two Concepts
• PFAS NMR in wastewater and stormwater, other matrices
• PFAS in precipitation
• PFAS stormwater depth profile pilot
High Concern: Organophosphate Esters

Current / ongoing
• Status & Trends water
• RMP stormwater, wastewater

Ideas for future years
• Synthesis and strategy
• Conceptual model
• Follow-up study
Moderate Concerns

Current / ongoing: Bisphenols
• RMP stormwater, wastewater
• Status & Trends water, sediment

Current / ongoing: Ethoxylated surfactants
• RMP wastewater, stormwater, sediment
Future Work on Other Classes

**Current / ongoing**
- Other plastic additives
- Quaternary ammonium compounds (SEP)
- Chlorinated paraffins in sediment (SEP)
- Tire-derived compounds

**Ideas for future years**
- Alternative brominated flame retardants
- Other plastic additives
Nontarget Analysis

Current / ongoing
• Sediment
• Status & Trends marine mammals pilot
• Data mining for new CECs priorities
• Sport fish

Ideas for future years
• Data mining follow-up studies
• Microplastic fibers and stormwater
• Status & Trends water
Toxicology

Current / ongoing

• Toxicology strategy development (CEC Strategy Revision)
  • Spreadsheet of thresholds (living document)

Ideas for future years

• Stormwater monitoring using new in vitro assay in development
  • Based on rainbow trout gill cells
  • Modest add-on to larger external study
Multi-year Plan
Discussion Questions

• Are we missing anything?
  • What should we add as additional resources become available?
• Are there upcoming management actions we can inform?
CEC Strategy Revision Timeline

Preferred deadline for comments (V1.0): May 3, 2024

• Draft Report (V1.1) to ECWG: Summer 2024
• Final Report: October 2024
Time for lunch!
Preliminary Results of The Halogenated Contaminants found in Bay Harbor Seals

Sally Abskhroun\textsuperscript{1}, Sujan Fernando\textsuperscript{2}, Bernard Crimmins \textsuperscript{3,4}

\textsuperscript{1}Department of Chemistry and Biomolecular Science
\textsuperscript{2}Center for Air and Aquatic Resources Engineering and Science
\textsuperscript{3}AEACS, LLC, New Kensington, Pennsylvania 15068, United States
\textsuperscript{4}Clarkson University, Department of Civil and Environmental Engineering, 8 Clarkson Avenue, Potsdam, New York 13699, United States
Introduction
Analytical Protocol

1. Grinding
2. Accelerated solid extraction
3. Gel permeation Chromatography
4. Solid Phase extraction
Instrumentation

2-dimensional gas chromatograph equipped with a high-resolution time-of-flight mass spectrometer

Multi mode ion source

Exact mass measurements

Electron Impact Ionization (EI)

Negative Chemical Ionization (NCI)

Molecular mass

Structural information

Mass to charge ratio ($m/z$)

Intensity
Comparison of EI and NCI Chromatograms

117 halogenated features

419 halogenated features
Results—Estimated Total Concentration of Halogenated Features

### Blubber Sample 1
- **Concentration (ng/g)**
  - EI: 111
  - NCI: 443

### Blubber Sample 2
- **Concentration (ng/g)**
  - EI: 71
  - NCI: 255

### Blubber Sample 3
- **Concentration (ng/g)**
  - EI: 117
  - NCI: 419
Knowns-Polychlorobiphenyl (PCBs)
Knowns-Polychloroterphenyl

Terphenyls

H/Cl Mass Defect

Terphenyls

Concentration (ng/g)

Mass-to-Charge (m/z)
Knowns - Polychloro/bromo diphenyl ether

**Diphenylethers**

- $\text{C}_{12}\text{H}_4\text{Cl}_5\text{OS}$
- Cl$_4$, Cl$_5$, Cl$_6$, Cl$_7$, Cl$_8$
- Br$_3$, Br$_4$, Br$_5$, Br$_6$

**PCDEs**

- Blubber 1: 7 ng/g (EI), 10 ng/g (NCI)
- Blubber 2: 4 ng/g (EI), 1 ng/g (NCI)
- Blubber 3: 4 ng/g (EI), 1 ng/g (NCI)

**PBDEs**

- Blubber 1: 5 ng/g (EI), 10 ng/g (NCI)
- Blubber 2: 8 ng/g (EI), 8 ng/g (NCI)
- Blubber 3: 8 ng/g (EI), 9 ng/g (NCI)
Knowns—Polychloronaphthalenes (PCNs)

PCNs

<table>
<thead>
<tr>
<th>Mass-to-Charge (m/z)</th>
<th>Cl₄</th>
<th>Cl₅</th>
<th>Cl₆</th>
<th>Cl₇</th>
<th>Cl₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/Cl Mass Defect</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PCNs

- **Blubber 1**: 18 ng/g
- **Blubber 2**: 4 ng/g
- **Blubber 3**: 12 ng/g
Knowns - Organochlorine pesticides (OCPs)

https://pubs.acs.org/doi/10.1021/acs.est.6b03150
Knowns - Organochlorine pesticides (OCPs)

Chlordane Related

H/Cl Mass Defect

Mass-to-Charge (m/z)

Concentration (ng/g)

Blubber 1
Blubber 3

https://pubs.acs.org/doi/10.1021/acs.est.6b03150
Knowns—Polychloro/bromo dibenzofurans

Dibenzofurans

PCDFs

PBDFs
Unknwons - *Halomethoxyphenols*

Halomethoxyphenols

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Concentration (ng/g)</th>
<th>Blubber 1</th>
<th>Blubber 2</th>
<th>Blubber 3</th>
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</thead>
<tbody>
<tr>
<td>1500.0</td>
<td></td>
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</tr>
<tr>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Bromomethoxyphenol**
- **Chloromethoxyphenol, acetate**
- **Chloromethoxyphenol isomer 2**
- **Chloromethoxyphenol isomer 1**

Only detected in EI
Unknowns—Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons

PAHs-3 fused rings

PAHs-5 fused rings

PAHs-4 fused rings
Unknowns—Diphenyl Sulfides

Diphenyl Sulfides

[H/Cl Mass Defect vs. Mass-to-Charge (m/z)]

Concentration (ng/g)

1 4
Blubber 1

1
Blubber 2

6
Blubber 3

Unkowns—MethylSulfonyl PCBs

MethylSulfonyl-PCBs

H/Cl Mass Defect

Mass-to-Charge (m/z)

Concentration (ng/g)

https://ehp.niehs.nih.gov/doi/abs/10.1289/ehp.59-1568084
https://ehp.niehs.nih.gov/doi/abs/10.1289/ehp.97105644
Unknowns-Dienochlor

Bicyclopentadienyl

H/Cl Mass Defect

Concentration (ng/g)

Mass-to-Charge (m/z)
Unknowns–Dechlorane 602

Unknowns \( \triangle \text{C}_{14} \text{H}_{(16-x)} \text{Cl}_{x} \text{O} \)

H/Cl Mass Defect

Mass-to-Charge (m/z)

<table>
<thead>
<tr>
<th>Concentration (ng/g)</th>
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</thead>
<tbody>
<tr>
<td>15.0</td>
</tr>
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</table>

\( \text{C}_{14} \text{H}_{6} \text{Cl}_{10} \text{O} \)
\( \text{C}_{14} \text{H}_{5} \text{Cl}_{11} \text{O} \)
\( \text{C}_{14} \text{H}_{4} \text{Cl}_{12} \text{O} \)

Blubber 1
Blubber 3
Unknowns-Dechlorane 603

Unknowns $\text{C}_{17}\text{H}_{(20-x)}\text{Cl}_x$

![Graph showing mass-to-charge (m/z) and concentration (ng/g) for unknowns Cl_{10}, Cl_{11}, Cl_{12} in Blubber 1 and Blubber 3.](image)

<table>
<thead>
<tr>
<th>Concentration (ng/g)</th>
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</thead>
<tbody>
<tr>
<td>Blubber 1</td>
</tr>
<tr>
<td>30.0</td>
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<td>Blubber 3</td>
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<tr>
<td>20.0</td>
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<tr>
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</tbody>
</table>

[Image showing molecular structure of Dechlorane 603 with chlorine atoms.]
Unknowns-Chlordene Plus

$$\text{Unknowns} \quad \text{brown: } \text{C}_{15}\text{H}_{(18-x)}\text{Cl}_x$$

![Chemical Structure](image)

- **H/Cl Mass Defect**
- **Mass-to-Charge (m/z)**

![Graph](image)

- **Concentration (ng/g)**
  - Blubber 1
  - Blubber 2
  - Blubber 3
Conclusion

• The total number of halogenated features was over 400 for adult seals. *Blubber sample 1 > Blubber sample 3 > Blubber sample 2*

• The estimated concentration of halogenated contaminants reached 20,000 ppb in adult seals. *Blubber sample 1 > Blubber sample 3 > Blubber sample 2*

• Major contributors: PCBs, OCPs, and Methoxyphenols.

• 13 Unknowns were found in the Great Lakes fish, indicating the widespread of these contaminants beyond regional barriers.
Acknowledgment

Prof. Sujan Fernando
Prof. Bernard Crimmins
Prof. Thomas Holsen
Prof. Philip Hopke
Aikebaier Renaguli, Juby Varghese, Sivachandiran Loganathan, Alesia Carroll, Elizabeth Brown, Shasha Yang, Ogechukwu Ofodum, Nicholas Multari, Krish Weraduwage, Mia D'Angelico, Junda Ren.
Comparison with other seals

Coastal Chukotka ringed, spotted and bearded seals (2019)

- Total POPs around 200 ppb.
- PCBs around 120 ppb

Canadian Arctic (Ulukhaktok, NT) ringed seals (2010)

- Total POPs around 1500 ppb.
- PCBs around 600 ppb.

West Antarctica Weddell, Ross and crabeater seals (2021)

- Total POPs around 750 ppb.
- PCBs around 65 ppb.
<table>
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<th>Sample</th>
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<th>Observed Monoisotopic mass on NCI</th>
<th>Predicted Formula (EI)</th>
<th>Predicted Formula (NCI)</th>
<th>1DRT EI</th>
<th>2DRT EI</th>
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<td>174.9491</td>
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<td>865</td>
<td>1.81</td>
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<tr>
<td></td>
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<td>1100</td>
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<td>256.0874</td>
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<td>C13H17ClO3 C13H17ClO3</td>
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<td>1.705</td>
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<td>1.695</td>
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<tr>
<td>Blubber 3</td>
<td>4</td>
<td>256.0857</td>
<td>256.0874</td>
<td>C13H17ClO3 C13H17ClO3</td>
<td>C13H17ClO3 C13H17ClO3</td>
<td>2280</td>
<td>1.705</td>
<td>2280</td>
<td>1.695</td>
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<tr>
<td>Blubber 1</td>
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<tr>
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<td>336.8665</td>
<td>371.8371</td>
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<td>234.9964</td>
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<td>C12H7Cl2N</td>
<td>3480</td>
<td>1.777</td>
<td>3485</td>
<td>1.773</td>
</tr>
</tbody>
</table>

**Note:** The difference in 1DRT and 2DRT is calculated based on the comparison of observed and predicted values for each compound.
## Results - Other knowns

<table>
<thead>
<tr>
<th>Name</th>
<th>1st Dimension Time (s)</th>
<th>2nd Dimension Time (s)</th>
<th>Observed Ion m/z</th>
<th>Formula</th>
<th>Concentration (ng/g)</th>
<th>Mode</th>
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</thead>
<tbody>
<tr>
<td>Hexachlorobenzene</td>
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<td>2.28</td>
<td>281.8138</td>
<td>C6Cl6</td>
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<tr>
<td>Heptachlorostyrene</td>
<td>1735</td>
<td>2.37</td>
<td>341.7902</td>
<td>C8HCl7</td>
<td>5.3</td>
<td>0.7</td>
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<td>Pentachloroanisole</td>
<td>1755</td>
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<td>Heptachlorostyrene</td>
<td>1815</td>
<td>2.43</td>
<td>341.7902</td>
<td>C8HCl7</td>
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<tr>
<td>Octachlorostyrene</td>
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<td>375.7517</td>
<td>C8Cl8</td>
<td>4.0</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Total Unknowns concentration

**Cl containing Unknowns**

- Blubber 1: 197 ng/g (EI), 30 ng/g (NCI)
- Blubber 2: 116 ng/g (EI), 15 ng/g (NCI)
- Blubber 3: 181 ng/g (EI), 18 ng/g (NCI)

**Cl/Br containing Unknowns**

- Blubber 1: 1 ng/g (EI), 4 ng/g (NCI)
- Blubber 2: 6 ng/g (EI)
- Blubber 3: 57 ng/g (EI)

**Br containing Unknowns**

- Blubber 1: 2 ng/g (EI), 30 ng/g (NCI)
- Blubber 2: 2 ng/g (EI), 26 ng/g (NCI)
- Blubber 3: 2 ng/g (EI), 2 ng/g (NCI)
Response factor calculations

\[ RF = \frac{\text{Average area of authentic standard} \times \text{Concentration of injection standard}}{\text{Area of Injection standard} \times \text{concentration of authentic standard}} \]
Response factor of PCBs

![Graph showing response factors of PCBs for EI and ECNI.

The graph compares the response factors (RF) of different PCBs for two categories: EI (blue bars) and ECNI (red bars). The PCBs are labeled from PCB 3 to PCB 10 on the x-axis. The y-axis represents the RF values from 0.00 to 1.25. The bars show varying levels of response factors for each PCB, indicating differences in performance or efficiency between the two categories.]
Response factor of OCPs
Response factor of PBDEs
Concentration calculations

- Concentration of $x = \frac{\text{area} \times \text{Conc.IS} \left( \frac{ng}{\mu L} \right) \times 100 \mu L}{RF \times \text{sample weight} (g)}$

- IS: internal standard
- Conc.: Concentration
- RF: Global response factor
Nontargeted vs targeted concentrations

The total PCB and PBDE concentrations for SRMs 1946 and 1947 were within 11% of the certified values.

Total PCB and PBDE concentrations measured using the GC×GC-HRT and global response factors were also within 17% of the values obtained from targeted methods.
Identifying unknowns

- H9Br2Cl3N4O4
- C3H9BrCl6N3O
- CH2Cl6N4O7
- C12H3Cl7
- C8H10Br3ClN
## Confidence levels

<table>
<thead>
<tr>
<th>Confidence Level</th>
<th>Identification</th>
<th>Confirmed with</th>
<th>Criteria</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Confirmed Structure</td>
<td>Authentic standard, Accurate mass measurement</td>
<td>The retention time and mass spectra of the acquired spectrum and standard are a match. Mass accuracy within 5ppm.</td>
</tr>
<tr>
<td>2</td>
<td>Probable Structure</td>
<td>Library spectrum match, Accurate mass measurement, Isotopic profile</td>
<td>Library match score 600 or higher, molecular formula is within 5ppm mass error and isotopic profile is in agreement.</td>
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<tr>
<td>3</td>
<td>Tentative Structure(s)</td>
<td>Accurate mass measurement, Isotopic profile</td>
<td>Molecular formula is within 5ppm mass error and isotopic profile is in agreement. Corresponding structures available in ChemSpider database.</td>
</tr>
<tr>
<td>4</td>
<td>Molecular formula</td>
<td>Accurate mass measurement, Isotopic profile</td>
<td>In this case the selected molecular formula is within 5ppm mass error and isotopic profile is in agreement.</td>
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<tr>
<td>5</td>
<td>Exact mass of interest</td>
<td>Isotopic profile</td>
<td>In this case no meaningful molecular formula(s) are obtained for the observed m/z.</td>
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</tbody>
</table>
Detecting The Molecular Ion

«β»-Dihydroheptachlor

EI

NCI
Unknwons found in the Great Lakes top predator fish

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<thead>
<tr>
<th>Unknown ID</th>
<th>1D RT</th>
<th>2D RT</th>
<th>Observed Ion m/z</th>
<th>Proposed Formula</th>
<th>Concentration (ng/g)</th>
<th>Blubber 1</th>
<th>Blubber 2</th>
<th>Blubber 3</th>
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<tbody>
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Proposed Study Design: S&T Water Nontarget Analysis

Rebecca Sutton & Tom Young
ECWG Meeting
April 16-17, 2024 – Hybrid
Identifying new CECs with nontarget analysis
RMP DETECTIVE WORK: IDENTIFYING NEW ORGANIC CONTAMINANTS IN THE ESTUARY

The recent addition of a surveillance component to the Regional Monitoring Program for Trace Substances (RMP) was prompted by a need to make the regulatory system more proactive in anticipating potential problem contaminants in the San Francisco Estuary. Our efforts have focused mainly on identifying as many as possible of the "unknown" organic compounds that were resolved by gas chromatography/mass spectrometry (GC/MS).

All samples were collected by the RMP and during the earlier SEQUAL program from 1996 to the present year. Water samples were extracted in situ with polyurethane foam or XAD resins. Rain water, filtrates, and sediments were each applied with surrogate standards then extracted with organic solvents (MeOH and CHCl).

Recent evidence suggests that some of these compounds and their metabolites may induce toxicity, disrupt endocrine systems, and accumulate in marine biota (fish, crabs, and biwackers) and in higher food chains consumers (birds, marine mammals, and humans).

Map showing distribution of contaminants across the San Francisco Estuary.
NTA led to RMP focus on stormwater CECs

Overdahl et al. 2021
Status & Trends Redesign

- **Sport Fish**: Every 5 Years
- **Bird Eggs**: Every 3 Years
- **Bivalves**: Archive only
- **Bioaccumulation matrices**
- **Nontarget Analysis**: Every ~10 Years
- **Water**: Every 2 Years
- **Sediment**: Every 5 Years
- **Core matrices**
Objectives of Status & Trends
Nontarget Analysis

- Apply nontarget analysis to Bay water to assess the status (initially) and trends (eventually) of unanticipated CECs
- Relatively consistent study design and methods in future years; maintain complete data and archives for benchmarking
- First implementation (2025) can be considered a pilot effort
Broad screening: Dry & wet season

Seasonal influence relates to pathways
Broad screening: LC and GC methods

**Unified Data Analysis Scheme**
- Analysis Base
- File Converter
- MS-DIAL
- MS-FINDER

**Confirmation Scheme**
- Sirius:CSI-FingerID and Unknowns Analysis

**Aqueous: Solid Phase Extraction**
- HLB or layered
- Solvent exchange
- ISTD addition

**Solids: Sonication**
- hexane: acetone
- acetone
- ISTD addition

**Evaporation and Filtration**

**LC-QTOF-MS**
- Zorbax Eclipse Plus C 18
- ESI+: \( H_2O + FA / ACN + FA \)
- ESI-: \( H_2O + NH_4F / ACN \)
- Data Acquisition:
  - All-Ion CE 0, 10, 20, 40 (target + nontarget)
  - tMS/MS follow-up on priority features

**GC-QTOF-MS**
- HP-5MS (30m x 0.25mm, 025µm)
- Temp gradient: linear increase
  - 35-325°C in 80 min
- Data Acquisition:
  - EI (target + nontarget)

**Validated methods:**
- Ambient water
- Household dust
- Skin wipe samples
- SVOCs in air
- Wildfire ash
- Biosolids
- Aldehydes/carbonyls in air
- Wastewater (influent/effluent)
- Drinking water

8. *ES&T*, 2023, 57: 5404
9. In preparation
Prioritizing NTA interpretation via targeted chemistry

Statistical relationships between nontarget signals and targeted data can reveal additional insights

Available RMP targeted chemical data

- CECs in all samples: PFAS, organophosphate esters, bisphenols
- 2025 dry season cruise:
  - Copper, cyanide
  - Other California Toxics Rule parameters (PCBs, PAHs, legacy pesticides, etc.)
  - Ancillary data
Prioritizing NTA interpretation via bioassays

Prior experience connecting chemicals detected using NTA and biological activity (e.g., drinking water)

**Recommended bioassays**

- *Xenopus laevis* tadpole induced metamorphosis assay, tests for thyroid hormone and retinoid-X receptor (RXR) signaling in vivo
- TH responsive mammalian (rat) pituitary cell line with an integrated TH responsive reporter gene
- A mammalian RXR only reporter transfection assay, to rule in or out compounds affecting TR activity through its RXR partner
- Cell based bioassay for glucocorticoid receptor activity
- Cell based bioassay for progesterone receptor activity
Deliverables to support trends analysis

- List of tentatively identified compounds
- Publicly accessible baseline spectra for future NTA comparisons (including retrospective analysis)
- Archived extracts of water samples
- Draft manuscript to be submitted to a peer-reviewed journal
## Budget

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<th>Expense</th>
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<th>Estimated Cost</th>
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<td><strong>Grand Total</strong></td>
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</table>
Discussion

Is this study design heading in the right direction?
• Are there elements we’re missing?

If resources are limited, which aspects are essential vs. optional?
• Dry and wet season sample collection
• Geographic scope
• LC and GC methods
• Bioassays (add or subtract tests)
Bioassays Useful in NTA Prioritization

• Concentrated extracts used for chemical analysis are solvent exchanged into bioassay compatible solvent
• Results in excellent connection between chemicals detected using NTA and bioassay activity
• This approach has provided sufficient sensitivity for detecting estrogenic activity in a CALUX estrogen receptor assay using drinking water samples

BW-Bottled Water  LA-Los Angeles  SM-San Mateo
EB-EBMUD  MC-Merced  WV-Weaverville
IR-Irvine Ranch  MD-Madera  YT-Yurok Tribe
Assays to detect T3 induced changes in one week old *X. laevis* tadpoles (12-15 mm)

Expose tadpoles to natural hormones, synthetic agonists, suspected THD compounds, environmental samples
Morphological assay example with indicated measurements (DMSO and TH treated one week old tadpoles)

- Head area
- Meckel's Cartilage (MC)
- Brain width (tectum)

+/- T3
+/- test samples
TRE-LUC transgenic *Xenopus laevis* tadpoles (Lens promoter:GFP construct co-integrated with TH responsive luciferase reporter gene)
California’s Safer Consumer Products Program: Advancing chemically safer products for people and the environment

Anne-Cooper Doherty, Ph.D.
Lead, Chemical Evaluation Unit

April 16, 2024
Safer Consumer Products (SCP) Process

1. Candidate Chemical List
   - Create and maintain a menu of chemicals that we can choose from

2. Priority Products
   - Prioritize Product-Chemical combinations that may cause harm + Rulemaking

3. Alternatives Analysis
   - Manufacturer evaluation of alternatives

4. Regulatory Response
   - Wide range of possible actions

Compliance and Enforcement
Menu of chemicals that we can choose from

N(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

Related Priority Product
(No related priority products.)

Basis for Listing

Bioaccumulation - OSPAR Priority Action Part A - Date Listed 01/01/2002
Chemicals that are identified on Part A of the list of Chemicals for Priority Action, Oslo and Paris Conventions for the Protection of the Marine Environment of the North-East Atlantic.

Environmental Persistence - OSPAR Priority Action Part A - Date Listed 01/01/2002
Chemicals that are identified on Part A of the list of Chemicals for Priority Action, Oslo and Paris Conventions for the Protection of the Marine Environment of the North-East Atlantic.

Toxicity Undefined - OSPAR Priority Action Part A - Date Listed 01/01/2002
Chemicals that are identified on Part A of the list of Chemicals for Priority Action, Oslo and Paris Conventions for the Protection of the Marine Environment of the North-East Atlantic.
Prioritize Product-Chemical combinations that may cause harm + Rulemaking

SCP Process

1. Candidate Chemical List
2. Priority Products
3. Alternatives Analysis
4. Regulatory Response
Scope of Products

- Exclusions:
  - FIFRA pesticides
  - Prescription drugs
  - Radioactive chemicals
  - Natural toxins

- Priority Product Work Plan = menu of products
  - Released every 3 years

New Work Plan coming soon – input welcomed!

2024-2026 Priority Product Work Plan – Under Consideration

Product Categories Currently Under Evaluation

- Beauty, Personal Care, and Hygiene Products
- Building Products & Materials Used in Construction and Renovation
- Cleaning Products
- Children’s Products
- Products that Contain or Generate Microplastics
- Paints

SAFER CONSUMER PRODUCTS PROGRAM • DEPARTMENT OF TOXIC SUBSTANCES CONTROL
2024-2026 Priority Product Work Plan – Under Consideration
**Product Categories Intended For Evaluation**

- **Food Contact Articles**
- **Motor Vehicle Parts, Accessories, Maintenance, and Repair Materials**
- **Electronics**
- **Sporting and Athletic Equipment**
- **Products Used or Produced by Metal Plating and Finishing Facilities**
- **Pet Care Products**
Priority Product Prioritization Process

- Evaluate chemicals in the context of products.

- Consider the potential for:
  - Exposure to the chemical from the product
  - Significant or widespread harm from that exposure

- Narrative standard

Safer Consumer Products Framework

Manufacturers search for and evaluate alternatives
The AA process seeks to avoid regrettable substitutions

Answers key questions:

- Is it necessary?
- Is there a safer alternative?
- What are the tradeoffs?

Requires:

- Ecological impacts
- Life cycle impacts
- Economic analysis
- Performance evaluation
- Public comment
The Regulatory Response is customized to each entity

Options include:

- No response
- Additional info to DTSC
- Additional info to consumers
- Additional safety measures
- Sales restrictions/prohibitions
- End-of-life product stewardship
- Research funding
Priority Product Designation
Case Study: 6PPD in Motor Vehicle Tires
6PPD

- Antidegradant (ozone, oxygen)
- Prevents cracking of rubber
- Reacts with ozone to form 6PPD-quinone
  - recently discovered to be acutely toxic to coho salmon, rainbow trout, and brook trout
Potential for Exposure to 6PPD, 6PPD-Quinone from Tires

- Used in presumably all tires
- High rates of release of tire wear particles containing 6PPD, 6PPD-quinone to the aquatic environment
- End-of-life applications may further contribute
- Detections of 6PPD-quinone in California runoff and waterways
Potential for Significant Adverse Impacts

- 6PPD toxic at multiple trophic levels
- 6PPD-quinone acutely toxic to coho, an endangered species, at a variety of life stages
- Environmental detections of 6PPD-quinone in California above the concentration that kills half of the exposed coho
- Impacts to California’s Native American tribes

Tian et al. (2022)
Leading the way on 6PPD

- Regulations effective October 2023
- First agency in the world to regulate 6PPD in tires
- Preliminary Alternatives Analyses were due March 29, 2024
  - 33 PAAs submitted by the USTMA consortium, 20 from non-USTMA manuf
  - Total of about 10 unique PAAs of varying quality
  - Alternatives under evaluation include PPD derivatives, graphene, lignin, TMPPD (Durazone 37), Irganoz 1076 (hindered phenol), SP-120 DLD (styrenated phenol), and SA 6000
Ongoing Work Related to CECs
Additional Work on Tires

- Proposed Priority Product: Motor Vehicle Tires Containing Zinc
  - Working on finalizing rulemaking proposal documents

- Other Chemicals in Tires and Motor Vehicles:
  - Proposed expansion of product category
  - Continue to monitor and evaluate
Candidate Chemical Additions

- Potential CC List Addition: PPD Derivatives
  - Require additional scrutiny during the AA process for 6PPD
  - Rulemaking later this year

- Potential CC List Addition: Microplastics
  - Finishing the External Scientific Peer Review process
  - Rulemaking coming soon
PFAS

- Two Adopted Priority Products:
  - Carpets and Rugs Containing PFAS
  - Treatments Containing PFAS for use on Converted Textiles or Leathers

- Our Technical document on Food Packaging Containing PFAS heavily informed subsequent legislation

- Evaluating as part of work on Artificial Turf

- Class based approach
Nonylphenol Ethoxylates

- Proposed Priority Product: Laundry Detergents Containing Nonylphenol Ethoxylates

- Rulemaking proposed, finalizing now
Additional Screening/Early Research

- Quaternary Ammonium Compounds in Personal Care and Cleaning Products
  - Background document to be released and workshop held later this year

- Artificial Turf
  - Background document to be released and workshop held later this year
Questions?

annecooper.doherty@dtsc.ca.gov
Water Quality, Water Resiliency, and Protecting California’s Aquatic Ecosystems

Maintain and Diversify Water Supplies

Be prepared for climate change

Flexible and integrated water management

Build connections: share science, data and technology

Protect and enhance natural ecosystems

The urban cycle moves water through a system of pipes. Photo courtesy: WET Science Center
Impetus for CEC Programmatic Approach

Monitoring and management based on local requirements

Stakeholders requested holistic approach

Development of the Recycled Water Policy

Program development for data driven process guided by risk-based framework

(2006)

(2009; and 2013, 2018)

(late 90s to early 2000s)

(2015 to current)
The CEC Program is a technical resource for the Water Boards to guide decision-making processes and address issues with CECs.
CEC Program Extended Team

Maggie Monahan, P.E.
Senior Water Resource Control Engineer
San Francisco Bay Region

Wendy Linck, P.G.
Senior Engineering Geologist
State Board PFAS Lead

Claire Waggoner
Environmental Program Manager
Sustainable Water Plans and Policies

Sarabeth George, M.Sc.
Engineering Geologist
Pretreatment and CEC Unit

Manoela Romano de Orte, Ph.D.
Research Scientist III
Pretreatment and CEC Unit

Erica Kalve, P.G.
Senior Engineering Geologist
Pretreatment and CEC Unit
CEC Program Support

**Steering Committee**

- Comprised of 12 members
- Representatives from OIMA, DWQ, DDW, Region 2, Region 4, Region 5, and Region 8
- Role:
  - Make recommendations for CEC Program priorities
  - Offer guidance and expertise to inform CEC Program decisions
  - Facilitate communication within the Water Boards (e.g., DMC) and externally

**Technical Team**

- Comprised of ~20 Water Boards staff
- Representatives from OIMA, DWQ, DDW, and many regional water boards
- Role:
  - Provide technical input and expertise
  - Communicate regional priorities and interests
  - Develop recommendations for CEC program activities, and priorities
  - Facilitate communication within the Water Boards and externally
Freshwater Preliminary Screening Results

~100 High Priority
~25 Moderate Priority
~65 Low Priority
~115 No Concern

- ✔ Pesticides
- ✔ Pharmaceuticals
- ✔ AP/APEs
- ✔ Phthalates
- ✔ PBDEs
- ✔ BFRs
- ✔ PFAS
- ✔ PCPs
- ✔ Bisphenols
- ✔ OPEs
- ✔ Natural toxins
## CEC Definition

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<th>Any Media</th>
<th>Without Environmental / Health Standard</th>
<th>Incomplete Physiochemical Characterization</th>
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<td>• Soil</td>
<td>• Notification Level</td>
<td>• Occurrence</td>
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<td>• Water</td>
<td>• MCL</td>
<td>• Fate</td>
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<td>• Radiological</td>
<td>• Air (via aerial deposition)</td>
<td>• Water Quality Objective</td>
<td>• Transport</td>
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<td>• Biota</td>
<td>• TMDL</td>
<td>• Toxicology</td>
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<td>• Analytical Method</td>
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April 2024
CEC Lifecycle

Periodic Review and On-Ramping

Off-Ramping

Awareness → Sources/Occurrence → Receptors and Exposure Pathways → Toxicity → Management
CEC Management Approach

Most Preferred

True Source Control

Water Quality Control

Mitigation

Remediation

Least Preferred
Risk-Based Prioritization Processes

Current – Targeted Data and Toxicity Thresholds

- Summarize Data
- Identify
- Prioritize

Future – Non-Targeted Analyses

- Traditional monitoring
  - Targeted Chemistry
  - Whole organism toxicity test
- Next generation monitoring
  - Non-targeted chemistry
  - Bioanalytical cell assays
  - Other effects-based tools
### Upcoming Program Actions & Documents

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<th>Program Action/Document</th>
<th>Description</th>
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<td>CEC Program Strategic Plan</td>
<td>Describes how the Program will guide decision-making processes to address issues with CECs</td>
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<tr>
<td>Quality Assurance Program Plan</td>
<td>Roadmap for implementing quality control measures for CEC monitoring in the State</td>
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<tr>
<td>Data Management Plan</td>
<td>Describes CEC data management procedures as well as the process to compile CEC data from statewide databases</td>
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<tr>
<td>Gain Experience Using Advanced Monitoring Tools</td>
<td>Support current efforts to further develop the necessary skills to appropriately apply advanced monitoring tools for CECs monitoring and management</td>
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<tr>
<td>Program Mapping</td>
<td>Leverage experience working on current CEC issues and projects (e.g., PFAS, microplastics, 6PPD-quinone, etc.) and create a map for optimal coordination on future issues and topics</td>
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Collaboration with Existing Statewide Monitoring Programs

Stream Pollution Trends Monitoring Program (SPoT)

Goal: Leverage SPoT’s annual sediment chemistry and toxicity monitoring by adding surface water analyses and advance monitoring tools

- Cell Bioassays
- Non-Target Analysis
CEC Program – Internal Program Coordination

Constituents of Emerging Concern

- Oil Field Produced Water
- Underground Storage Tanks
- Non-point Source
- Recycled Water
- Stormwater
- Irrigated Lands
- Land Disposal
- Drinking Water
- Oceans Beaches
- Pre-treatment
Achieve Program Goals and Objectives by Working with Many Partners

Government Agency

Tribes and Interested Parties

California Native American Tribes (Tribes), non-governmental organizations, academic, research, association, public entities/utilities, community organizations, other members of the public

And more!
Key Take Home Messages

1. Ensure high-quality, open, and transparent data management
2. Apply risk-based prioritization and use advanced monitoring tools
3. Leverage experience (e.g., trash, microplastics, PFAS, 6ppd-quinone) to identify effective and efficient CEC monitoring and management strategies
4. Coordinate strategic approach to implement CEC management actions
5. Collaborate with partners to maximize efficiency and minimize response action timeframes
Thank You!

Follow up with us at EmergingContaminants@waterboards.ca.gov

Check out the Program website at www.waterboards.ca.gov/water_issues/cec/index.html
Update on PFAS in SF Bay

Preliminary Findings

Miguel Mendez
ECWG Meeting
4/17/2024
Per- and Polyfluoroalkyl Substances (PFAS)

3M Reaches $10.3 Billion Settlement in ‘Forever Chemicals’ Suits

The deal followed an agreement by Chemours, DuPont and Corteva to pay $1.19 billion to help resolve claims that the chemical manufacturers contaminated drinking water across the country.

Biden Administration to Restrict Cancer-Causing ‘Forever Chemicals’

The government will strictly limit in drinking water two chemicals that are ubiquitous in modern society but are linked to a range of health effects.

Lots of Tap Water Contains ‘Forever Chemicals.’ Take These Steps to Reduce Your Risk.

You can’t escape PFAS chemicals completely but you can reduce your exposure at home.

Island residents seek $40M from Wisconsin city over PFAS contamination

In a Wisconsin town over 500 wells were found to be contaminated with PFAS as of June 2021.

Forever Chemicals Are in Nearly Half of America’s Tap Water. Here’s How to Reduce Your Exposure.

Clean, safe drinking water is a luxury that many people in the United States take for granted. But your tap water may not be as safe as you think.
Per- and Polyfluoroalkyl Substances (PFAS)

**PFOA**
Perfluorooctanoic acid

**PFOS**
Perfluorooctane sulfonic acid
Per- and Polyfluoroalkyl Substances (PFAS)

PFOA
Perfluorooctanoic acid

PFOS
Perfluorooctane sulfonic acid

PFCAs
Perfluorocarboxylic Acids

PFSAs
Perfluorosulfonic Acids

Long-Chain:  ≥ 8 Carbons  

≥ 6 Carbons
Monitoring PFAS in San Francisco Bay
Monitoring **PFAS** in San Francisco Bay
Bird Eggs: Sampling and Analysis

- Began in 2006
  - Near double-crested cormorant nesting sites
  - 3 sites each monitoring year

- Most recently in 2022
  - 10 composite samples
  - Expansion from 13 to 40 analytes (EPA Method 1633)
Bird Eggs: 2022 Results

- 18 Analytes detected
  - 14 detected in 100% of samples
  - 10 for the first time

- PFOS predominantly detected
  Range: 37-251 ng/g  Median: 97 ng/g

- 7:3 FTCA and PFDA next highest
  Medians: 29 & 10 ng/g

- Long-chain PFCAs widely found
  \( \text{C}_8 - \text{C}_{14} \)
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  - \((C_8 \text{ - } C_{14})\)

- Highest levels in South Bay and Lower South Bay
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  Medians: 29 & 10 ng/g
- Long-chain PFCAs widely found (C\textsubscript{8} - C\textsubscript{14})
- Highest levels in South Bay and Lower South Bay
Bird Eggs: PFOS Declines in South Bay 2006-2022
Bird Eggs: PFOS Declines in South Bay
2006-2022

PFOS Concentration (ng/g)

1,900 ng/g
Canada
Guideline

150 ng/g
Tree
Swallows
Study

South Bay
Richmond Bridge
Wheeler/Rich Island
Main Takeaways

● PFAS detected across the Bay
  ○ Many new PFAS detected especially 7:3 FTCA and long-chain PFCAs

● Higher concentrations in the South Bay and Lower South Bay
  ○ Decline of PFOS

● Still overall concern for potential risks
Bay Water: Sampling and Analysis

- **Broad study in 2021**
  - 22 sites (dry season)
  - Targeted: 40 analytes (EPA Method 1633)

- **Continued monitoring in 2023 (S&T)**
  - Similar 22 sites (dry season)
  - 40 Analytes
  - Special Study: Total Oxidizable Precursors (TOP) Analysis
  - Wet Season Monitoring (2023-2024)
Bay Water: Targeted Analysis (2023)

- 11 analytes detected
  - Only three were detected at greater than 50% of sites: PFHxA, PFOS, and PFOA
- Samples in South Bay and Lower South Bay typically highest
  - Site in San Pablo Bay particularly high and all made up of 6:2 FTS (178 ng/L!)
- Median Sum of PFAS: 2.3 ng/L
## Bay Water: Targeted Analysis Comparison 2021 & 2023 Data

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<th>Medians (ng/L)</th>
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<th>2023</th>
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<td># of Analytes Detected (≥ 50%)</td>
<td>11 (7)</td>
<td>11 (3)</td>
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<td>PFHxA</td>
<td>1.5</td>
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<tr>
<td>PFOS</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>PFOA</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Sum of PFAS</td>
<td>5.9</td>
<td>2.3</td>
</tr>
</tbody>
</table>
Bay Water: Targeted Analysis Comparison
2021 & 2023 Data

North to South

PFAS Concentration (ng/L)

Sum of PFAS (2021)
Sum of PFAS (2023)
Bay Water: Targeted Analysis Comparison
2021 & 2023 Data

North to South

Sum of PFAS (2021)
Sum of PFAS (2023)
Bay Water: Targeted Analysis Comparison
2021 & 2023 Data

North to South

PFAS Concentration (ng/L)

Sum of PFAS (2021)

Sum of PFAS (2023)
Bay Water: Targeted Analysis Comparison
2021 & 2023 Data

PFAS Concentration (ng/L)

North to South

Sum of PFAS (2021)
Sum of PFAS (2023)
Bay Water: TOP Analysis

- **PFAS**
- **TOP** (Total Oxidizable Precursors)
- **Targeted PFAS**
- PFCAs + PFSAs (e.g. PFOA)
Bay Water: TOP Analysis

TOP (Total Oxidizable Precursors)

Oxidize Precursors to Terminal PFAS

PFAS

Targeted PFAS

PFCAs + PFSAs (e.g. PFOA)
Bay Water: Targeted and TOP Analysis

- Method detection limits (MDLs) are different across analyses

<table>
<thead>
<tr>
<th></th>
<th>MDLs in ng/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Target</td>
</tr>
<tr>
<td>PFBA</td>
<td>2</td>
</tr>
<tr>
<td>PFOA</td>
<td>0.5</td>
</tr>
<tr>
<td>PFOS</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Bay Water: TOP Analysis Results

- 5 analytes detected
  - PFBA predominant
  - PFHxA, PFOA, PFOS, and 6:2 FTS also found
  - Half of samples were ND
- Range of Sum of PFAS: 7 - 156 ng/L
  - Median: 3.5 ng/L (ND = 0)
- Samples in South and Lower South Bays are highest but not as consistently as in target
- Otherwise, limited consistency across target and top samples
Bay Water: Target and TOP Analysis (2023)

Graph showing PFAS Concentration (ng/L) for various locations.

- Orange dots: Sum of PFAS (2023)
- Purple triangles: Sum of PFAS (TOP, 2023)
Bay Water: Main Takeaways

- PFAS detected across Bay (all segments)
- Target levels appear lower than previous sampling but TOP concentrations particularly high across Bay sites
- Samples in South Bay and Lower South Bay typically highest
Bay Water: Main Takeaways

● PFAS detected across Bay (all segments)
● Target levels appear lower than previous sampling but TOP concentrations particularly high across Bay sites
● Samples in South Bay and Lower South Bay typically highest
● CA Environmental Screening Levels for Water
  **Target:** PFOS Median: 0.6 ng/L          PFOA Median: 0.3 ng/L
     ○ For Aquatic Ecotoxicity:
         ■ PFOS: 75 ng/L
         ■ PFOA: 4,400 ng/L
     ○ For Human Health (seafood ingestion)
         ■ PFOS: 0.0047 ng/L
         ■ PFOA: 0.022 ng/L
Next Steps

● Bay Water Wet Season sample analysis completion
● Full Report on PFAS in Bay Water and Sediment (Fall 2024)
● Ongoing monitoring of PFAS
  ○ Bird Eggs (2024)
  ○ Bay Water (2025)
  ○ Sport Fish (2025)

Questions?
About Me

❖ Joined SFEI in April 2023

❖ PhD in Environmental Engineering
Outline

- Chlorinated paraffins?
- Motivation
- Study design and method
- Results
- Risk assessment
- Next steps
Overview of Chlorinated Paraffins

\[ \text{vLCCP} \quad (\geq \text{C21}) \]

\[ \text{SCCP} \quad \text{(C10-C13)} \]

\[ \text{MCCP} \quad \text{(C14-C17)} \]

\[ \text{LCCP} \quad \text{(C18-C20)} \]

\[ \text{vLCCP} \quad (\geq \text{C21}) \]
Widely applied in various products as coolants, flame retardants, and plasticizers

Enter the environment during production, transportation, and recycling processes and through leaching and volatilization from landfills

Current global production volume estimate of 1.3 million metric tons per year (C. Chen et al., 2022), production began in 1930’s

Management action for SCCP in US, Canada, EU & Stockholm Convention, MCCP proposed to Stockholm & elsewhere
Study Design and Method

- Archived sediment (2014-2020) from 10 sites

- SGS AXYS MLA-117 (2020)
  - Dr. Ehrenstorfer standards
  - C_{10}—C_{20} and Cl_{5}—Cl_{11}
  - UPLC-MSMS
Results

- Reporting Limits for 63 isomer groups
  - 0.6 - 11.5 ng/g
  - Median 3.5 ng/g
  - ND for all
Risk assessment

Limited effects & exposure data

Thresholds use equilibrium partitioning method

Figure from Environment and Climate Change Canada - Federal Environmental Quality Guidelines Chlorinated Alkanes. Government of Canada, 2016
Is the method sufficiently sensitive? Does lack of detection mean low risk?

- Thought experiment: What if all isomer groups are present at levels just below the isomer specific reporting limits?
  - $\sum$SCCP(20) = ~75.6 ng/g $\ll$ 1800 ng/g
  - $\sum$MCCP(28) = ~91.2 ng/g $\ll$ 5400 ng/g
  - $\sum$LCCP(15) = ~144.4 ng/g $\ll$ 100,000 ng/g

- Risk Screening: Method is sufficiently sensitive and indicates Low Concern
Next Steps

❖ Report coming Summer 2024

❖ Recommend screening in biota
  ➢ Blubber
  ➢ Fish tissue
  ➢ Bird eggs

❖ Re-evaluate sediment
  ➢ with more certain ecotox thresholds
  ➢ with lowering current thresholds
  ➢ methods for vSCCPs
Setting the Stage for Day Two

Rebecca Sutton, PhD
ECWG Meeting
April 16-17, 2024 - Hybrid
<table>
<thead>
<tr>
<th>Time</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:15</td>
<td>PFAS Sources to Solutions project</td>
</tr>
<tr>
<td>10 to noon</td>
<td>ECWG &amp; SPLWG Joint Meeting</td>
</tr>
<tr>
<td></td>
<td>● Review progress on stormwater CECs projects</td>
</tr>
<tr>
<td></td>
<td>● Discuss stormwater CECs monitoring approach</td>
</tr>
<tr>
<td>12:30 to 3</td>
<td>2025 ECWG Special Studies</td>
</tr>
<tr>
<td></td>
<td>● Closed door session</td>
</tr>
</tbody>
</table>
Adjourn

Thank you!