

SCCWRP/SFEI Collaborations: Emerging Contaminants

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RMP TRC/SCCWRP CTAG Joint Meeting
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Joint Research Projects (from 2009)

NOAA Mussel Watch Program

- Facilitate incorporation of CECs
- CA-based pilot study
 - Samples from NOAA archives and/or new samples
 - Recommend priority CECs to NOAA
 - e.g. PPCPs, HBCD and other FRs, PFCs
 - Assessment of new techniques
 - passive samplers
 - genomic based technologies

REFOCUSING THE PROGRAM

- **SCCWRP Commission critiqued Mussel Watch**
 - Less interested in legacy contaminants - needs more focus on CECs
- **NOAA held workshop in April 2009**
 - How to re-engineer and foster multiagency participation
 - Use results to trigger toxicological studies
- **Focus 2009-10 effort on CA-based pilot study**
 - Kickoff meeting in Oct 2009
 - Expand analyte list to include high priority CECs
 - Relocate some sites to focus on CEC sources
 - Investigate new/alternative methods (passive samplers)
 - Sampling commenced Dec 2009, to continue through Summer 2010

An early warning system for contaminants of emerging concern (CECs): A multiagency Mussel Watch pilot study in California

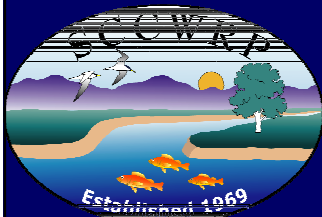
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Southern California Coastal Water Research Project

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"Mussel Watch"

A Sentinel for Safe, Healthy & Productive Coasts

Moving Forward

Prioritizing the CEC List

- ✓ Analytical methods established
- ✓ Represent a diverse group of threats to the environment, fate & transport mechanisms, and modes of action
- ✓ Potential impacts to ecosystem condition and human health
- ✓ Production scale
- ✓ Regional and National significance
- ✓ Logistics (field & contracts)
- ✓ COST
 - NOAA Mussel Watch brought \$360,000 to the project
 - Partners leveraging funds and providing field support





"Mussel Watch"

A Sentinel for Safe, Healthy & Productive Coasts

The New Mussel Watch Contaminant List

✓ Phenolics

Bisphenol A, Alkylphenols, Triclosan

✓ Perfluorinated Compounds

PFOS, PFOA

✓ Current use Pesticides:

Pyrethroids, triazines, diuron, strobilurin fungicides

✓ Hormones

17-alpha-ethinylestradiol, 17-beta-estradiol, musks

✓ Pharmaceuticals

Carbamazepine, Erythromycin, Diazepam, Acetaminophen

✓ Replacement Flame Retardants*

PBDEs, TBBPA, TCPP, TCEP, PBEB, TPP, DBDPE, BTBPE

✓ Nanoparticles*

Nano-silver, carbon-nano tubes



SFEI/AXYS SFB PILOT STUDY

- Sediment, water, mussels from 5 sites
- PPCP, alkylphenol, PFC data pro bono from AXYS Analytical
- Guide target analytes in statewide effort
- Which ones accumulate in mussels?
- Method development
 - e.g. MDLs, PPCPs in tissue

Timeline

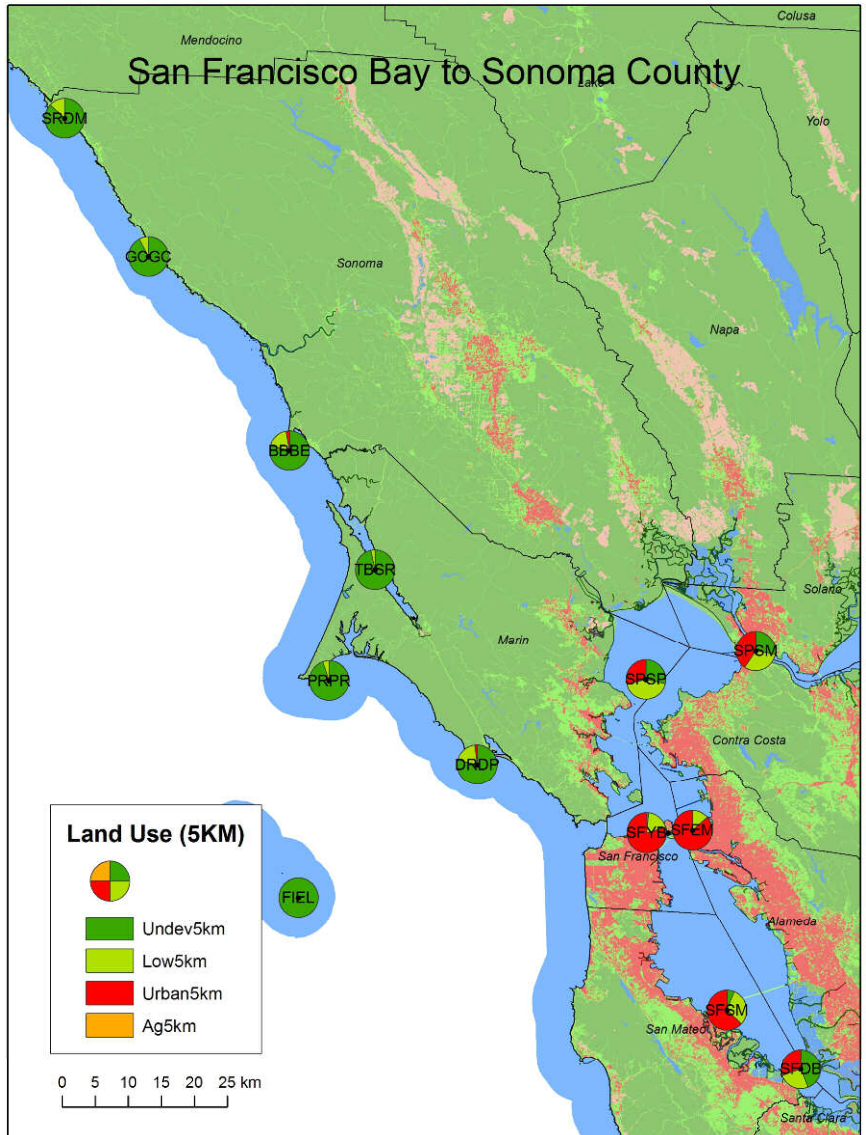
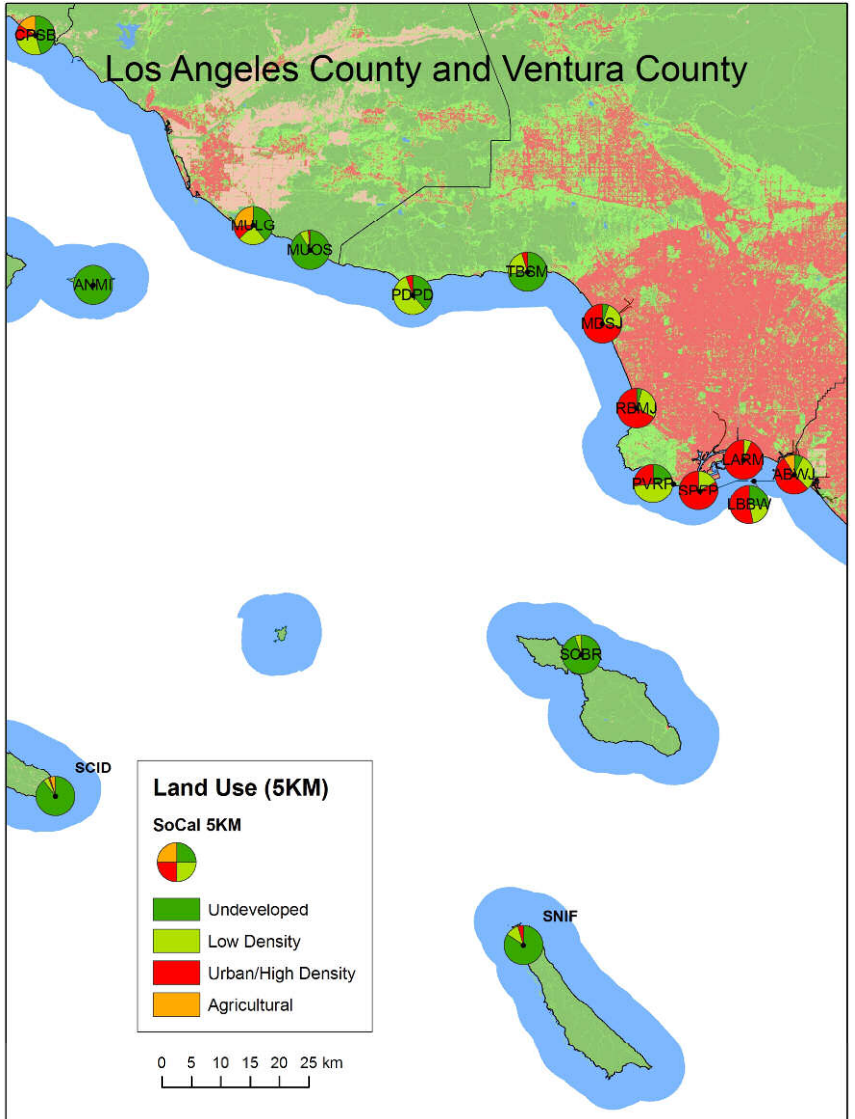
- RMP data review (May-June)
- Data to Mussel Watch group (mid-May)
- Report (late Summer/Fall 2010)



STUDY DESIGN

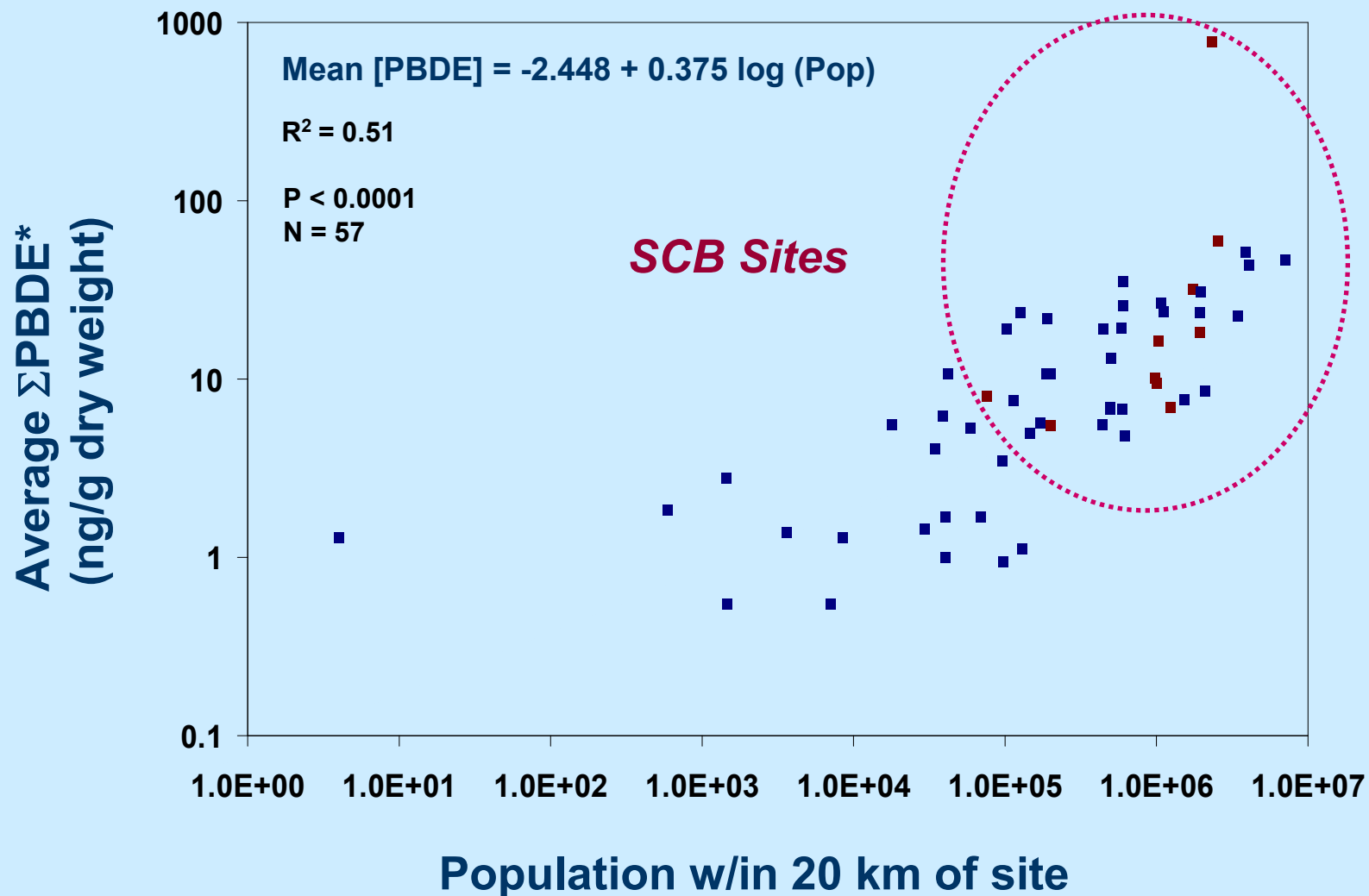
- **Winter sampling at existing sites ($n=69$)**
 - historic analyses on subset ($n=25$)
 - stratify by land use (urban; low development; agricultural)
- **Summer sampling at targeted sites ($n\sim 10$)**
 - large POTWs
 - stormwater discharge
 - warm season ag runoff
 - employ caged bivalves & PSDs (where necessary)

Existing Urban Sites



NOAA | National Ocean Service | National Centers for Coastal Ocean Science
National Status & Trends Program – Mussel Watch

► Polybrominated Diphenyl Ethers in *Mytilus spp.*



MW CA Pilot Ag Sites

- Ag dominated watersheds in Southern, Central and San Francisco Bay
- Large suite of unmonitored pesticides applied
 - New fungicides (USGS study)
- Winter collection of native mussels at selected sites
- Summer deployment of caged bivalves & passive samplers
 - Mallard Island (Delta runoff)
 - Napa and Petaluma Rivers

POTWs

- **City of Los Angeles Terminal Island WRP**
 - 4.5 mgd serving 130K residents
 - tertiary treatment + microfiltration/RO
 - discharges into outer LA Harbor (15 m)
- **City of Palo Alto RWQCP**
 - 40 mgd (capacity) serving ~220K residents
 - 100% secondary treatment
 - discharges into south SF Bay
- **San Jose/Santa Clara WPCP**
 - 167 mgd serving 1.5M residents
 - Advanced (tertiary) treatment
 - discharges into extreme south SF Bay
 - passive samplers only

EXPANDING BEYOND MUSSELS

- **Passive samplers (POCIS, SPME, PEDs)**
 - flexibility in timing/location
 - easy sample processing
- **Caged bivalves**
 - flexibility in timing/location
 - historical data & “know how” for SF Bay
- **New bioscreening technology**
 - *Mytilus* microarrays for exposure fingerprinting/toxicity pathway discovery

PROGRESS & SCHEDULE

- **Winter collection: 90% success**
 - target completion date: May 30
- **Summer work to begin June, finish by Sept 2010**
- **Homogenize & ship tissue to participating labs**
 - target completion date: June 30
- **Passive samplers deployed @ 7 existing sites**
 - co-deployment of caged bivalves; target completion is Aug 30
- **Analytical work**
 - preliminary results by Oct 2010
 - final results by June 2011

Risk-based prioritization for future monitoring (from 2009 meeting)

- ***Increase communication on potential target chemicals, collaborative projects***
- Fill data gaps (occurrence, fate, effects)
 - e.g. current use pesticides, pharmaceuticals, wildfire-associated flame retardants
- Fish bioaccumulation (SWAMP, BOG)
- ***POTW effluent/receiving water studies***
 - ***Common or indicator PPCPs***
- ***Refine/implement CEC Workshop recommendations***
 - ***Framework needed for State policies & regional***

PRIORITIZING CECs FOR STATE & REGIONAL MONITORING

- **Increase communication & integration of target constituent “lists”**
 - Emerging Contaminants Work Group – ongoing (SFEI)
 - CA CEC Science Advisory Panels (SCCWRP)
 - *Ecosystem Panel to meet through 2011*
 - 2009 CEC Workshop Report
- **POTW effluent/receiving water studies**
 - Mussel Watch CA Pilot
- **Prioritization Process**
 - Wastewater CEC “White Paper” (SFEI)
 - CA CEC Science Advisory Panel Reports (SCCWRP)

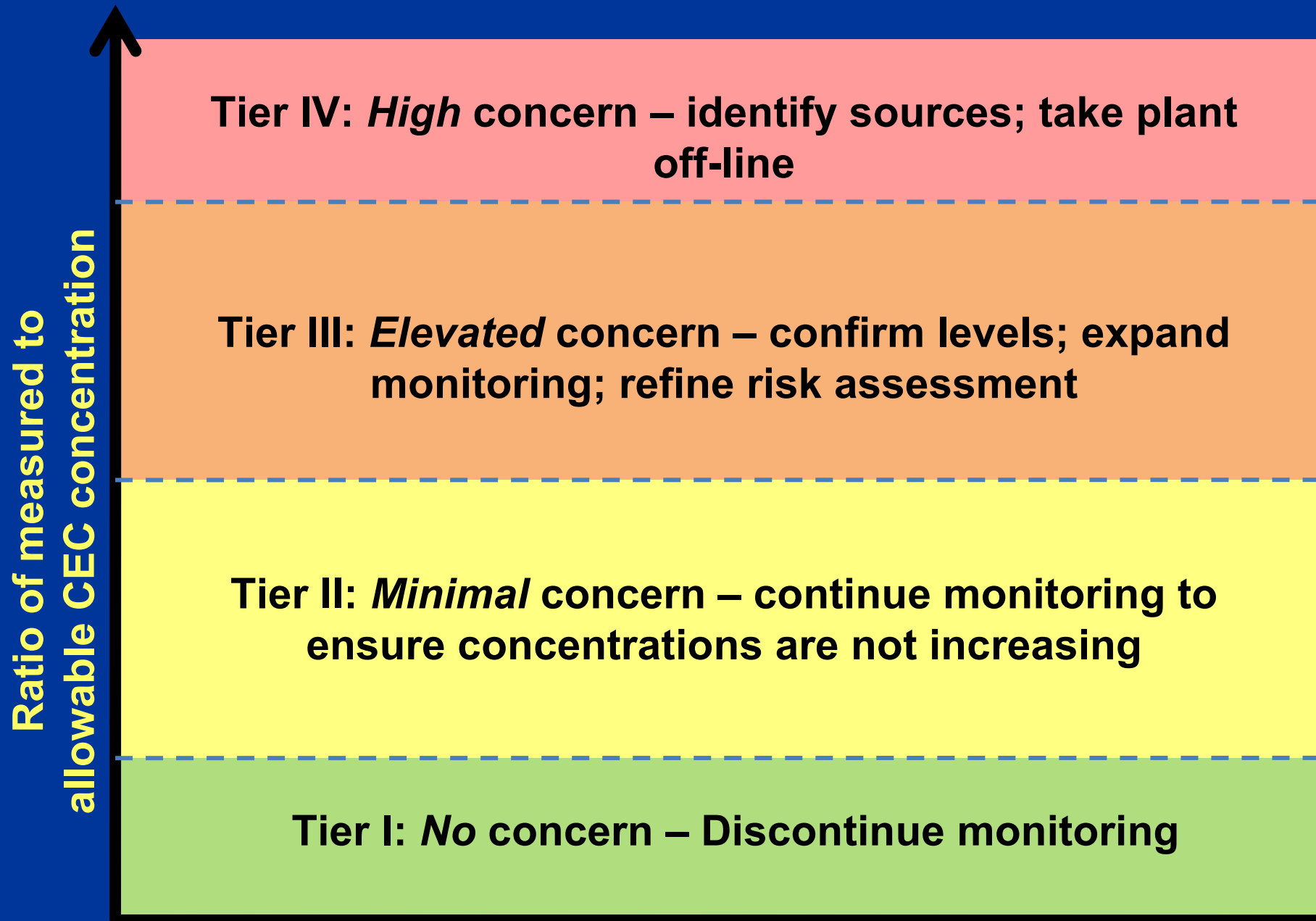
CEC SCIENCE ADVISORY PANEL FOR CECs IN RECYCLED WATER

- **Draft report released for public comment**
 - final due 6/25/10
- **Decision making framework**
 - A tool to prioritize CECs now and into the future
- **Application to recycled water projects state-wide**
 - Preliminary CEC monitoring list (“what” to monitor)
- **Monitoring recommendations and interpretation**
 - How, where and when to monitor; and how to respond to results
- **Future recommended activities**
 - Research, support tools and audits to improve & refine the process

APPLICATION OF FRAMEWORK – CEC LIST FOR GROUNDWATER RECHARGE

Constituent	Chemical Class	Analytical Method	Method Detection Limit (ng/L)
17- β estradiol	Natural hormone	•LC-MS/MS	•<1.0
Caffeine	Food product	•GC-MS	•<350
Triclosan	Personal care product	•LC-MS/MS	•<350

#3: INTERPRETATION OF MONITORING RESULTS



RECOMMENDED FUTURE ACTIVITIES

- **Technical studies to bolster the science**
 - *Improve our methods for targeted chemicals and screening purposes*
 - Develop a process to predict CEC levels
 - Refine our drinking water benchmarks, prioritizing those CECs with increasing occurrence
- **Programmatic support to manage the process**
 - *Develop a process to manage data & apply framework*
 - Implement periodic health surveillance activities in areas impacted by water reuse
 - Perform independent audit of Panel's initial recommendations
 - *Revisit monitoring recommendations every 3-5 years*

Wastewater Contaminants 'White Paper'

Objectives:

- identify CECs that have the greatest potential to impact human health and aquatic life in the Bay and should be considered for future monitoring
- communication/outreach, factsheets to WW community and general public

Selection criteria:

- high frequency of detection in municipal wastewater effluent
- high volume use in California
- potentially toxic to wildlife or humans
- low to moderate wastewater treatment removal efficiency
- relatively water soluble ($\log K_{ow} < 5$)
- not already part of routine monitoring in San Francisco Bay
- potential for management action

Estimate potential for impacts:

- Compare occurrence data to toxicity data

Chemicals to be evaluated

High priority:

Triclosan, triclocarban (antimicrobials) – draft complete

Alkylphenols (surfactants) – Fall 2010

Chlorinated OP flame retardants (TDCPP, TCPP, TCEP) – Fall 2010

Carbamazepine (neuroactive compound) – Fall 2010

Others considered:

Sulfamethoxazole (antibiotic)

17-estradiol and 17-ethinyl estradiol (hormones)

Atenolol (beta blocker)

Gemfibrozil (blood lipid lowering agent)

Nanoparticles

Quaternary ammonium compounds (surfactants)

Outcomes:

- decision on future monitoring of selected chemicals
- communicate info to WW community, general public (short tech report, factsheets)

Analytical Method Development (from 09)

- ***Low level method for BFRs/CUPs (SCCWRP)***
 - ***0.5 ng/g PBDEs, pyrethroids, fipronil + degradates***
- Developing GC-MS derivatization methods (SCCWRP)
 - bisphenol A, alkylphenols (e.g. nonylphenol)
 - triclosan
- Can adapt current methods for alternate BFRs (SCCWRP)
 - Tetrabromophthalate, benzoate (Firemaster)
 - Tetrabromobisphenol A
- Chemicals on Muir and Howard list (SCCWRP or other lab)
- ***Lab inter-calibration exercises with NIST, USGS, academics, contract labs***
- ***Passive sampling methods***
 - ***bioavailable organics, MeHg using SPME, PEDs***

ANALYTICAL METHODS DEVELOPMENT

- **Low level methods published for**
 - brominated flame retardants (Meng et al. 2009)
 - current use pesticides (Lao et al. 2010)
- **Passive sampling methods for bioavailable organics**
 - Mussel Watch CA Pilot for CECs
- **Lab intercalibration**
 - Multilab comparison for pyrethroids in sediment
 - Sediment Toxicity Stressor ID Workshop recommendations

ENHANCE USE OF BIOLOGICAL SCREENING

- **Ultimate endpoint of interest**
 - Chemical exposure is of lesser concern if the animals are reproducing normally
- **A less expensive alternative than measuring several hundred chemicals**
 - Easily incorporated into regional monitoring programs
 - More efficiently gauges effectiveness of management action
- **Need better tools**
 - Receptor binding assays
 - Gene expression microarrays

GENETIC MICROARRAY DEVELOPMENT

- Small and large arrays for fish & inverts are available
 - however most are untested
- Preliminary results suggest field collected fish exhibit different gene expression signatures
- Near term plans
 - Incorporate supporting chemistry data
 - targeted lab studies to distinguish between physical and chemical stress responses
 - New habitats & species (e.g. *Mytilus*)

MORE IDEAS FOR FUTURE COLLABORATION

- Monitoring threshold development for high priority CECs
 - e.g. PBDEs in bird eggs; marine mammals
- Data management strategies
 - catalog “new” types of data
 - compatibility with RMP, Bight and SWAMP formats
 - Mussel Watch CA Pilot (case study)

Joint Research Projects

Effects threshold development*

- PBDE/nonylphenol fish exposure study
 - Sensitive SF Bay/Bight species
 - Spiked water, sediment, food exposure
 - Endocrine, reproductive endpoints (hormones, gonad anomalies, enzyme activity)
- PBDE threshold development for marine mammals
 - Extrapolation from mammalian/eco risk assessments?
- Sediment TIE studies
 - LC, EC50 for pyrethroids, fipronil, methoprene

* Possibly in collaboration with SFEI Exposure & Effects Workgroup

Data Management Strategies

- Help create ambient CEC database & analysis tools
 - Hundreds, potentially thousands of target chemicals
 - Focus on surrogates, indicators
- New & different types of data
 - Sublethal effects, thresholds
 - Use, restrictions, products (Green Chemistry Initiative)
- Collaborative opportunities with
 - CEDEN/SWAMP (SWRCB, SFEI, SCCWRP)
 - Green Chemistry Initiative (DTSC)
 - Drinking/Groundwater Monitoring (DPH)
 - Expert Panels (CA, WERF/Tetra Tech)
 - EPA CCL3