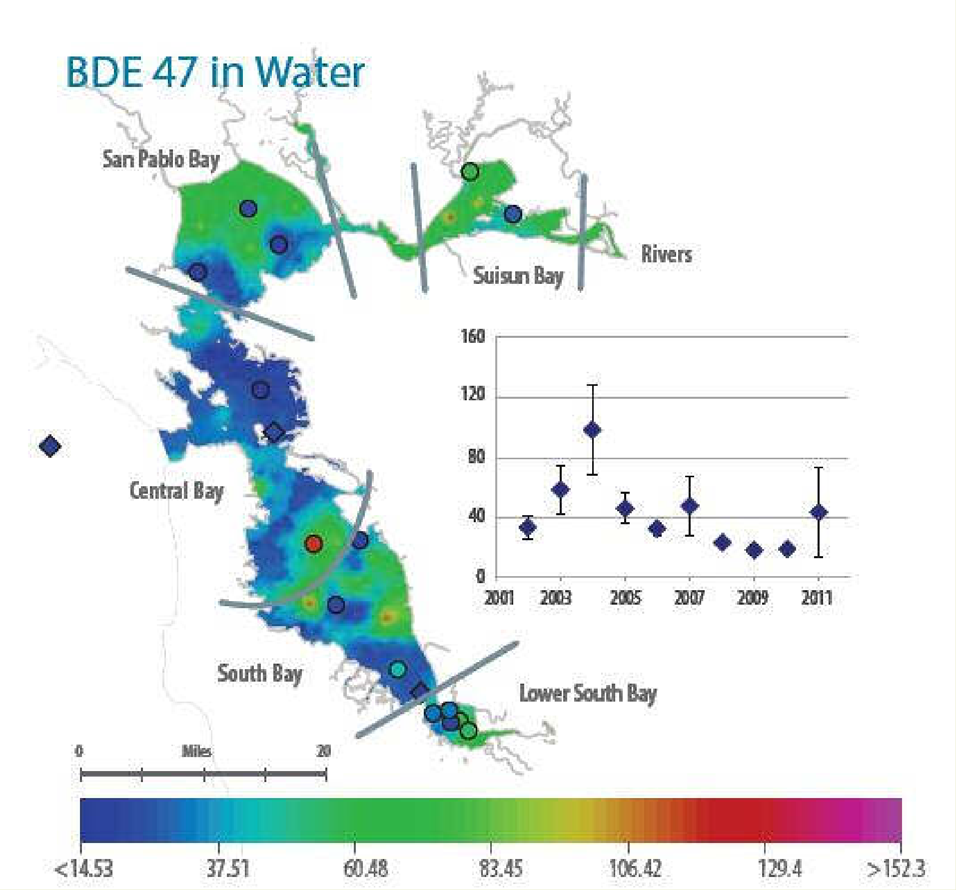
REVIEWING STATUS & TRENDS: WATER

September 17th, 2013

EXISTING: ORGANICS

- Is there value in monitoring organics in water?



EXISTING: ORGANICS

- PCBs, PBDEs, Pesticides, and PAHs
  - Every 4 years, random, Bay

- Limited Information for Management Decisions
  - Hydrophobic compounds
  - Trends and Spatial distribution not that useful
  - Data used?

- Cost
  - $100K

- Menu options
  - Status quo
  - PCBs as reference
  - Some other reference chemical, less expensive
  - Drop organics all together – select special studies when needed

EXISTING: INORGANICS

- Analyzing every other year
  - Random, Bay

- Management Decisions Informed: Data for WQC
  - Site-specific objectives for Cu and Ni
  - Site-specific objectives for CN
  - Se TMDL being developed

- Cost
  - $60K

- Menu Options
  - Stay status quo
    - Bay sampling, dry and random
  - Other?

NEW: CURRENT USE PESTICIDES

- Prioritize based on Tier Classification
- Fipronil – Tier 3
  - Analyzing in Bay water (2013) and stormwater (2012/2013)
  - Random for Bay – characterization of ambient conditions
- Pyrethroids – Tier 4
  - Evaluating effectiveness of Use restrictions
  - Not analyzing in Bay water (sediment only)
  - Analyze Tributaries (2011, 2012, 2013)
- Menu options
  - Status quo
  - Consider other CUPs based on currently work in evaluating DPR data

NEW: CECS

- CEC Tier Classification -Tier 1 - Alternative Flame Retardants
  - Data useful to inform management decisions on CECs
    - High volume, high toxicity => High priority
  - Collecting samples in 2013
    - Stormwater, effluent, and Bay - Targeted
  - Analyzing for water soluble compounds
    - TCPP, TDCPP, TCEP, TBP, and TPhP
    - Others?
- Pharmaceuticals and Personal Care Products
  - Currently evaluating possible chemicals
- Menu TBD

Water

Element	Cost	Management Decisions Informed	Design
Metals	$60K	Compliance with WQOs and permit provisions	Bay, dry season, random and targeted
Legacy organics	$0	PCBs as reference? Drop?	Bay, Random
CUPs	$?	Evaluate use restrictions, ambient data	Tribs, early wet season, targeted
Other CECs	$?	Evaluation of CEC Tier assignment	Effluent, storm water, dry season, targeted

FIPRONIL

- Fipronil
  - Structural pest control, landscaping, and consumer products
  - CA use has tripled since 2003
- RMP monitoring in Bay sediment
  - 1 to 56 ng/g OC
  - Sediment toxicity to midge
    - LC-50 130 ng/g OC (Maul 2008)
- No information on Bay water
  - 9 % of Bay area exceeded USEPA benchmark of 0.011 ug/L
  - Urban runoff in Sacramento/Orange County 0.014 to 0.441 ug/L -exceeds toxicity thresholds (Gan et al. 2012)

REVIEWING STATUS & TRENDS: BIVALVES

September 17th, 2013

EXISTING PROGRAM

- Primarily organics
  - PCBs, PBDEs, PAHs, Pesticides
- Every other year
- Transplanted bivalves at fixed locations/ River stations native
- Management Decisions
  - Informs 303 (d) listings and tracks trends
- Cost
  - $45K

BIVALVES: NO ADDITIONS YET

- Statewide bivalve monitoring detections:
  - Alkylphenols (e.g., 4-nonylphenol, 4-NP1EO)
  - Alternative flame retardants (e.g., HBCD, BTBPE)
  - Pharmaceuticals & personal care products (e.g., lomefloxacin)
  - Current use pesticides (e.g., chlorpyrifos, Dacthal)
- Alkylphenols: Blank contamination, method constraints make monitoring problematic
- Alternative flame retardants, PPCPs, CUPs: Upcoming RMP special studies should provide data on whether these merit Status and Trends monitoring

REVIEWING STATUS & TRENDS: SEDIMENT MONITORING

RMP TRC

September 17, 2013

SEDIMENT MONITORING

- Sediment a major aquatic habitat
- Primary matrix for hydrophobic contaminants, long term storage reservoir (with or without erosion)
- Direct or indirect (via resuspension/water partitioning) pathway for biotic exposure
- Toxicity and benthos provide evidence/ support for pollutant impacts
- Benthos a general characterization of habitat use

RMP MANAGEMENT QUESTIONS

1. Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?

2. What are the concentrations and masses of contaminants in the Estuary and its segments?

3. What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary?

4. Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased?

5. What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?

RMP MQ DECISIONS

1. Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?

   Suitability for habitat/beneficial reuse, effectiveness of actions

2. What are the concentrations and masses of contaminants in the Estuary and its segments?

   Similar to above

3. What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary?

   Identifying and testing local/regional actions

4. Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased?

   Measuring effectiveness of actions

5. What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?

   Predicting & comparing alternatives

CURRENT MONITORING

- Every other year, alternating wet & dry season samplings
  - (4 year cycle for wet season repeat)
- Analyses performed
  - Sediment chemistry: organics, inorganics, & ancillary
  - Sediment toxicity: sed-water interface tests
  - Sediment benthos: ID and abundance
- Distribution
  - Same number of random stations each segment (8 dry, 4 wet), +7 historical

SED CHEM PROS/CONS

- Uses
  - Comparison to tox thresholds
  - Sufficiency for beneficial reuse
  - Bioaccumulation predictions
- Pros
  - Where you find it = where it has been (top 5cm)
    - (on annual+ time scale, >1cm/yr accumulation rare)
  - Measurable everywhere
  - No life cycle complexities
- Cons
  - Not a biological endpoint
  - Exposure relationship variable (conc ≠ exposure)

SED TOX PROS/CONS

- Uses
  - Narrative tox criteria
  - Indicator of pollutant effects
- Pros
  - Direct measurement of impacts on test organism health (no toxins in toxic amounts)
- Cons
  - Proximate causes often not identified
  - Test organisms may not represent dominant or natural (native) species or assemblages
  - Bay endpoint already moderately/highly diluted

BENTHOS PROS/CONS

- Uses
  - Monitor invasives (presence & extent)
  - Comparison of un/impacted areas
- Pros
  - Additional line of evidence for pollutant impacts
  - Direct measure of community (invasive + native)
    - Extent and degree of invasive species
    - May be useful in food web models (conceptual or semi-quantitative)
- Cons
  - Many confounding factors impacting species distribution

FOCUSING QUESTIONS

Do we need sediment monitoring, & what to measure

1. Is bioaccumulation the only concern (drop toxicity, maybe benthos, all but (Me)Hg, Se, orgs)?
2. Is bioaccumulation modeling/prediction empirical/ correlational, not mechanistic? (drop benthos (no food web structure))?
3. What is the smallest needed spatial distinction? (sets distance for compositing, field replicates, & pelagic vs benthic biosentinels)
4. How do we plan to estimate/assign values for unsampled areas? (transect ends around sources may still be biased higher)
5. Do we only need info around known hotspots or sources? (if not deterministic sampling will suffice, “around” can transect away from sources)

CURRENT COSTS SEDIMENT S&T

	2014	2016	2018
Sediment Chemistry (47 dry/27 wet)	$185,000	$110,000	$185,000
Sediment Toxicity (27 dry/27 wet)	$51,500	$51,500	$51,500
Sediment Benthos (27 dry/27 wet)	$61,800	$61,800	$61,800
Fieldwork and Logistics	$230,000	$230,000	$230,000

SITE REALLOCATIONS?

- >90-95% power (detect PCBs -50%/20yrs, Hg -25%/30yrs) for biennial, 4 samples each segment (except Suisun)
  - PCBs 90-95% power from 2 in LSB, SB, 3 in CB, 4 in SPB, 10+ in SUB
  - Hg 90-95% power from 2 in SB, CB, SPB, 4 in LSB, >12 in SUB
  - Power analysis driven by variance in PCBs, Hg, may differ for CECs

Table 9. Power analysis results for detecting long-term trends in PCBs and DDT in sediment. Results are based on estimated inter- and intra-annual variability for each segment, and assumed rates of decline. Red text represents the current monitoring design for each segment, and the blue areas highlight results that are > 95% power.

			Lower South Bay					South Bay					Central Bay					San Pablo Bay					Suisun Bay				
			Sampling Interval (years)					Sampling Interval (years)					Sampling Interval (years)					Sampling Interval (years)					Sampling Interval (years)				
			1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Scenario:	Samples/year	2	100%	97%	92%	78%	67%	100%	99%	97%	85%	74%	100%	94%	87%	73%	60%	96%	75%	64%	43%	36%	76%	51%	37%	26%	23%
PCBs		4	100%	100%	98%	95%	89%	100%	100%	100%	99%	94%	100%	99%	97%	91%	86%	100%	95%	88%	73%	61%	93%	71%	64%	50%	43%
Sediment		6	100%	100%	100%	97%	95%	100%	100%	100%	100%	99%	100%	100%	100%	96%	92%	100%	97%	95%	86%	78%	98%	84%	74%	63%	55%
20 Year		8	100%	100%	100%	98%	96%	100%	100%	100%	100%	99%	100%	100%	100%	97%	95%	100%	99%	97%	90%	84%	99%	88%	82%	68%	62%
3.5% Annual Decline		10	100%	100%	99%	99%	97%	100%	100%	100%	100%	100%	100%	100%	100%	99%	96%	100%	99%	98%	93%	89%	100%	92%	88%	72%	67%
		12	100%	100%	100%	99%	97%	100%	100%	100%	100%	99%	100%	100%	100%	98%	97%	100%	100%	99%	95%	91%	99%	92%	87%	78%	71%
Scenario:	Samples/year	2	99%	87%	74%	72%	56%	100%	97%	88%	81%	62%	100%	99%	95%	93%	79%	100%	100%	95%	93%	81%	51%	29%	20%	17%	16%
Mercury		4	100%	94%	87%	83%	76%	100%	100%	100%	97%	89%	100%	100%	99%	99%	95%	100%	100%	99%	98%	93%	76%	48%	35%	34%	22%
Sediment		6	100%	96%	91%	90%	81%	100%	100%	100%	100%	96%	100%	100%	100%	100%	98%	100%	100%	99%	99%	97%	91%	60%	46%	44%	34%
30 Year		8	100%	98%	92%	92%	84%	100%	100%	100%	100%	99%	100%	100%	100%	100%	99%	100%	100%	100%	99%	97%	96%	74%	60%	55%	43%
1% Annual Decline		10	100%	97%	94%	93%	85%	100%	100%	100%	100%	100%	100%	100%	100%	100%	99%	100%	100%	100%	100%	97%	98%	83%	67%	65%	45%
		12	100%	98%	94%	93%	88%	100%	100%	100%	100%	100%	100%	100%	100%	100%	99%	100%	100%	100%	100%	98%	98%	89%	73%	68%	54%

Melwani et al., 2006

REDUCTIONS/ELIMINATIONS?

- Sediment toxicity
  - Continued effects seen, but causes still largely unresolved (e.g., grainsize impacts?)
  - Is there any substitute for demonstrating (or relative lack of) toxicity?
- Sediment benthos
  - Cause of community variations ambiguous
  - Baseline data for food web modeling, invasives tracking?
- Non-bioaccumulative trace elements
  - Cost/savings relatively low ($5k for 27 sites)
- Lower priority organics
  - OCPs, PBDEs mostly < effects levels and trending down
- 27 sites all seasons
  - Lower power but few decisions only from Bay *trends*
  - SUB inherently too variable, most segments OK power with 2-4

ADDITIONS?

- CECs
  - Tier 3+ additions/eliminations?
  - Add on once concerns from (near)/source monitoring established
- Margins
  - Probably(?) important habitat within ecosystem
  - Largely unsampled
  - If we sample margins, why/ when/ where/ how?

FOCUSING QUESTIONS

Margins similar as for sediment monitoring in general

1. Is bioaccumulation the only concern (no toxicity, maybe benthos, nothing but (Me)Hg, Se, orgs)?
2. Is bioaccumulation modeling/prediction empirical/ correlational, not mechanistic? (no benthos (no food web structure))?
3. What is the smallest needed spatial distinction? (sets distance for compositing, field replicates, & pelagic vs benthic biosentinels)
4. How do we plan to estimate/assign values for unsampled areas? (transect ends around sources may still be biased higher)
5. Do we only need info around known hotspots or sources? (If not deterministic sampling will suffice, “around” can transect away from sources)

5b. Are margins compared to the Bay (if so need ambient data)?

POSSIBLE ANSWERS

1. Is bioaccumulation the only concern (no toxicity, maybe benthos, nothing but (Me)Hg, Se, orgs)?

Probably not. Some concerns are not bioaccumulative (current use pesticides, other known and unknown CECs).

*Tox test results may be indicators of pollutant impacts, but open Bay often likely too dilute to be **early** indicators. Might be more distinct in tributaries (though not evidence of lack of estuarine impact), or margins (estuarine & some but less dilution).*

Benthos needs depend in part on bioacc modeling plans, and also whether/how invasives are tracked.

POSSIBLE ANSWERS

2. Is bioaccumulation modeling/prediction empirical/ correlational, not mechanistic? (no benthos (no food web structure))?

Maybe. Gobas model is semi-mechanistic, but will we develop or use region/site specific data to evaluate/predict bioaccumulation at higher trophic levels?

If only correlational predictions made, one less need for benthos in margins ambient or targeted sites.

POSSIBLE ANSWERS

3. What is the smallest needed spatial distinction? (sets distance for compositing, field replicates, & pelagic vs benthic biosentinels)

If needs are km or less many fish (e.g., topsmelt and silversides) range too far, PCB data suggest 3-4 km radius home range integration for those species.

Sediment or benthic tissue grabs can be composited if interests are > ~10m patches (to overcome micro-scale variance).

POSSIBLE ANSWERS

4. How do we plan to estimate/assign values for unsampled areas? (transect ends around sources may still be biased higher)

With deterministic sampling the best we can do is best/worst case scenario guessing (e.g., continual gradient between hotspots, or drop to open Bay ambient at a midpoint, etc.)

POSSIBLE ANSWERS

5. Do we only need info around known hotspots or sources? (If not deterministic sampling will suffice, "around" can transect away from sources)

Probably need more. "Trends" best measured around sites of known action/change, but "Status" of the ecosystem needs representativeness (in margins too, if part of the Bay ecosystem). Likely need both deterministic SS & ambient S&T sites.

MANAGEMENT LINKAGE

Element	Cost (27 site)	Management Decisions Informed	Design
(Me)Hg, Se	$15k	Ambient for dredging permits, TMDLs	Bay random & historic
Other TEs	$5K	Ambient for dredging permits	Bay random & historic
PAHs PCBs OCPs PBDEs	$10k $20k $16k $18k	Ambient for dredging permits, TMDLs, use restriction effectiveness	Bay random & historic, drop OCPs, ? PBDEs
pyrethroids	$12k	Use restriction effectiveness	Bay random & historic
Other CECs	$?	Use restrictions CEC Tier assignment	Semi/targeted (near/in source areas)

MANAGEMENT LINKAGE

Element	Cost (27 site)	Management Decisions Informed	Design
Benthos	$0k ($60k)	Dredging/action impacts, anti- invasives steps, TMDLs (models)	Drop Bay
Toxicity	$0k ($50k)	Habitat status, linkage to sources	Drop Bay
Margins (ambient)	$11-12k /site	Ambient for dredging permits, anti-invasives, TMDLs	Ambient, chem, tox, & benthos
Margins (targeted)	$7-8k /site	Local action effectiveness	SS targeted, chem only
Margins (targeted)	$1.5-2k /site	Local action effectiveness	SS targeted, +tox or +benth (chem/ action dependent)

STRAW PROPOSAL CHANGES

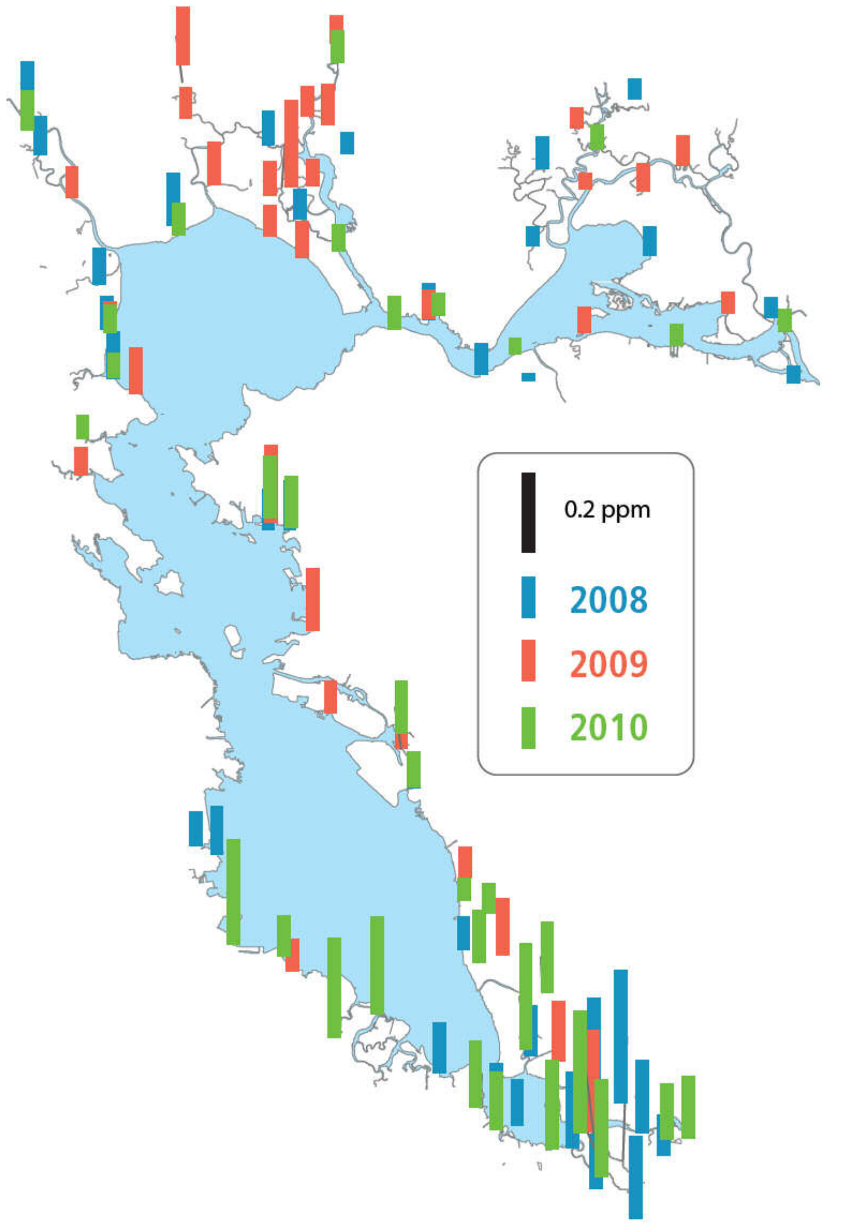
- Stop/reduced frequency of tox and benthos in open Bay (-$110k)
  - Indefinite/permanent pause until more consensus on what results show?
- Reduce number of open Bay ambient (random) sites to 27 in both wet & dry years (-$75k)
  - Lower power from 4/segment but not much trend to find anyway
    - Reallocate somewhat among segments?
    - CECs may differ from Hg/PCBs
  - Keep seasons for representativeness of status
    - If seasons not different, statistically combinable anyway

STRAW PROPOSAL CHANGES

- Reduce organics analyte list/frequency
  - OCPs low and declining (-$16k)
  - PBDEs mostly < effects levels in biota, already declining (-$18k)
    - 1 (of >200 sites) > benthic effect level open Bay, 2 (of <10) in margins
    - Reduce frequency open Bay?
- Continual review/addition/removal of CECs (+$?)
- Add ambient margins sampling (~ +$11-12k/site, scalable)
  - Deterministic sites can be added later via/for SS
    - Includes chem, tox, & benthos
    - Cost /site somewhat lower if only a subset of RMP contaminants

Small Fish Survey: Mercury

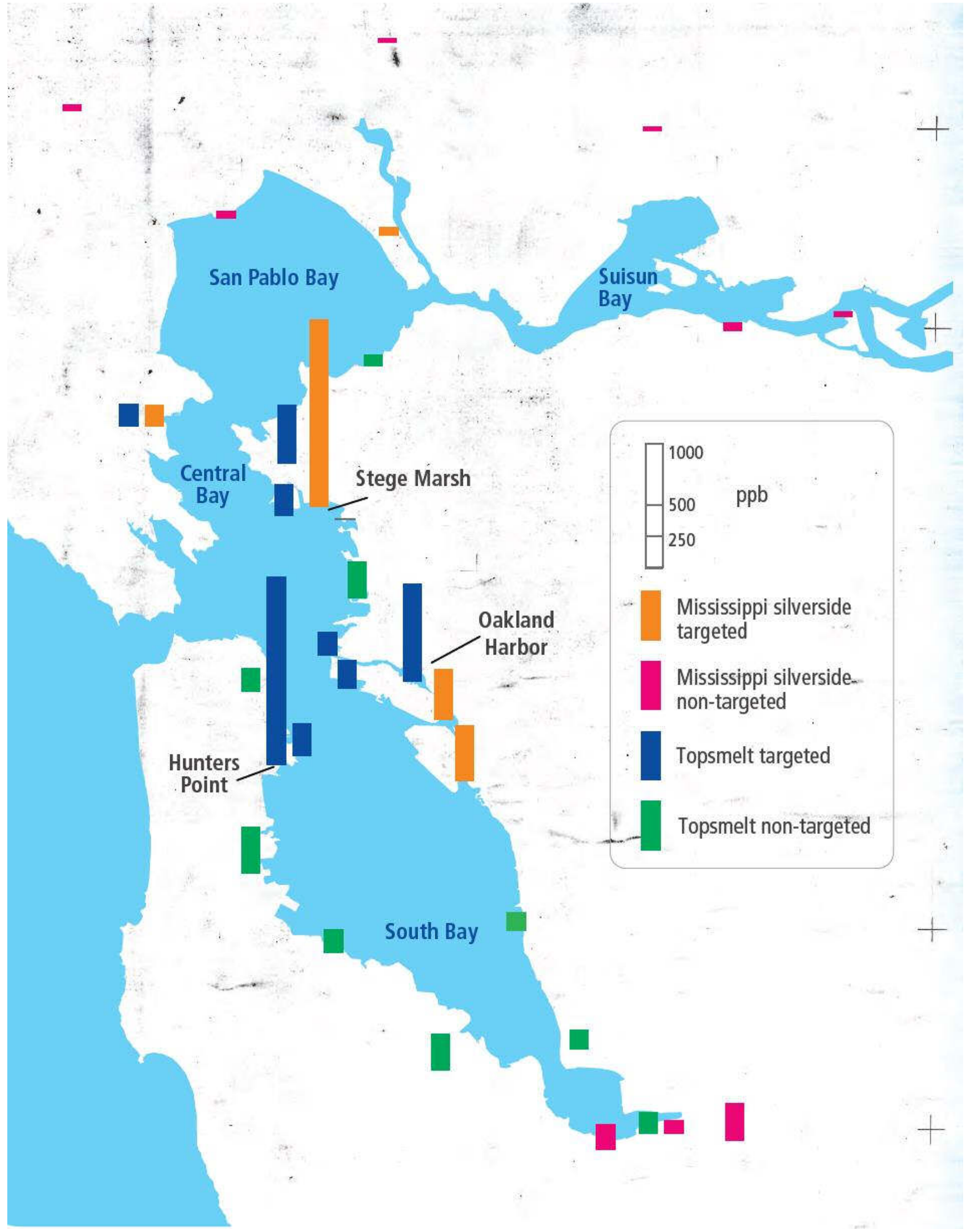
- Regional variation
- Lots of seasonal variation
- No clear high leverage pathways
- POTW effluent appears to be a low leverage pathway



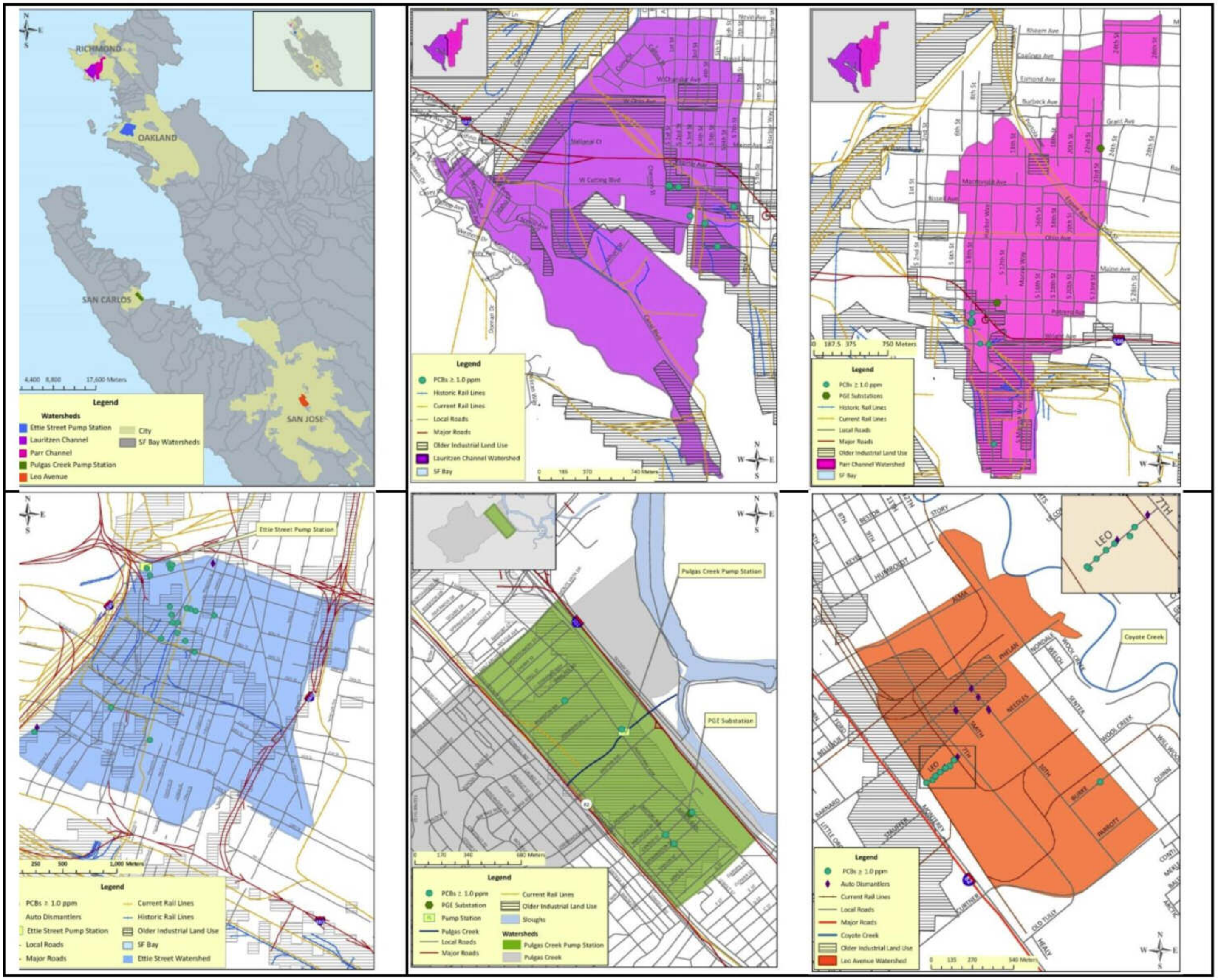
Mercury concentrations (ppm) in silverside from 2008-2010.

Small Fish Survey: PCBs

- Distinct spatial variation at a local scale
- Suggesting high leverage pathways and priority areas for cleanup
- Key performance measure for cleanup



Watershed Cleanup Efforts



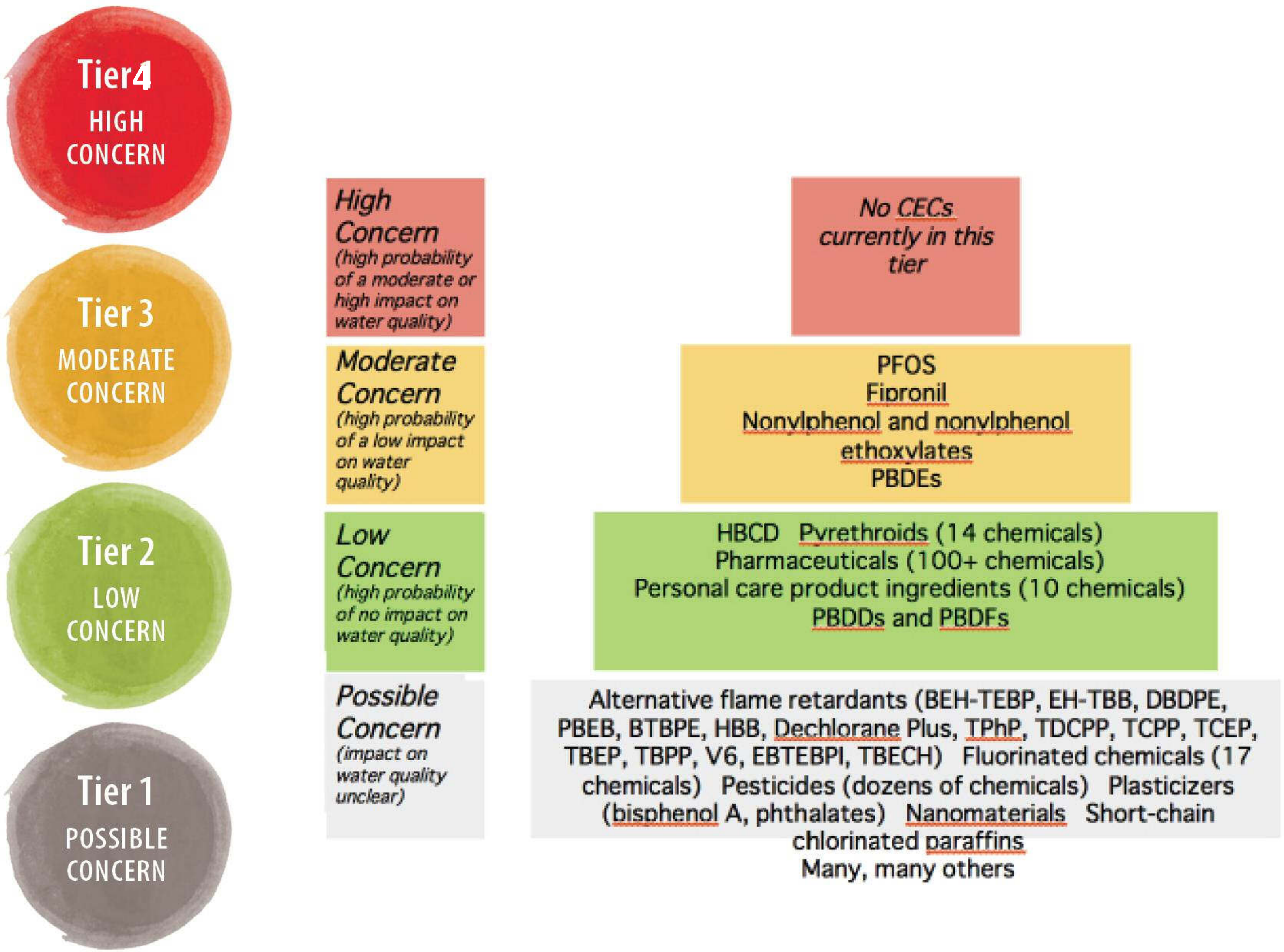
Connecting the Dots

Small Fish Menu

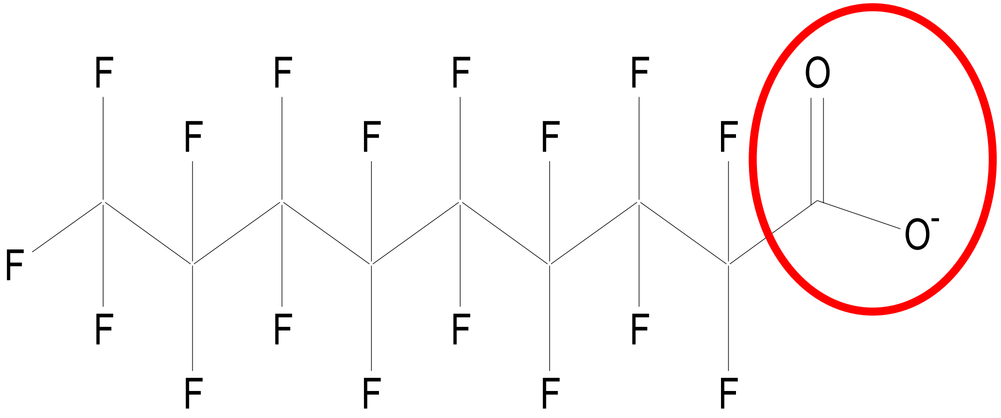
Element	Design	Cost	Management Decisions Informed
PCBs	Targeted, selected high priority locations, repeated visits (3 reps per site)	$7.5K per site 5 areas - $40K	• Local-scale performance measure for actions in watersheds and in-Bay and shoreline hotspots
PCBs	Targeted, systematic survey	40 sites $300K	• Prioritization of local margin areas for cleanup action
PCBs	Random	30 sites	• Segment-scale impairment and performance measure
Mercury	Targeted, selected high priority locations, repeated visits	$xxK	• Local-scale performance measure for actions in watersheds, in-Bay and shoreline hotspots, **wetlands**
Mercury	Targeted, systematic survey (repeat)		• Segment-scale 303(d) and TMDL (impairment and performance measure) - better for trends? • Marsh restoration
Mercury	Random		• Segment-scale 303(d) and TMDL (impairment and performance measure) – better for segment average condition • Marsh restoration
CECs	Piggyback on PCB/Hg sampling		• Tier prioritization

Perfluorinated Compounds in the Bay

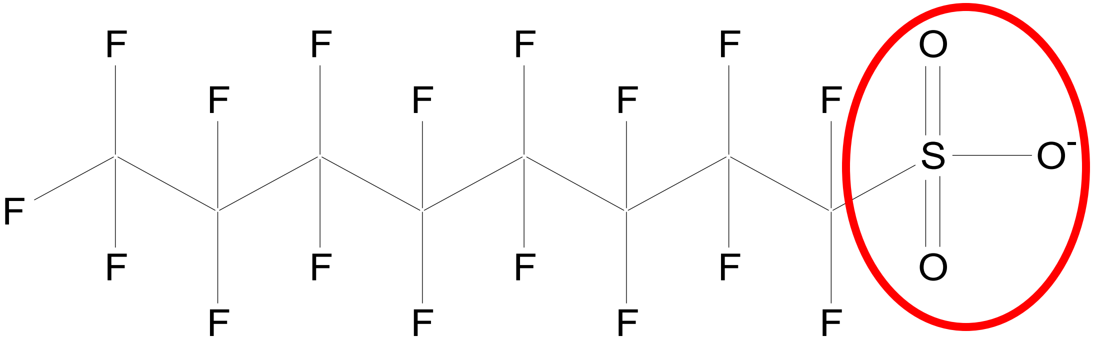
Meg Sedlak (SFEI)
October 29th, 2013


Tier4
HIGH CONCERN
Tier 3
MODERATE CONCERN
Tier 2
LOW CONCERN
Tier 1
POSSIBLE CONCERN
High Concern (high probability of a moderate or high impact on water quality)
No CECs currently in this tier
Moderate Concern (high probability of a low impact on water quality)
PFOS
Fipronil
Nonylphenol and nonylphenol ethoxylates
PBDEs
Low Concern (high probability of no impact on water quality)
HBCD Pyrethroids (14 chemicals)
Pharmaceuticals (100+ chemicals)
Personal care product ingredients (10 chemicals)
PBDDs and PBDFs
Possible Concern (impact on water quality unclear)
Alternative flame retardants (BEH-TEBP, EH-TBB, DBDPE, PBEB, BTBPE, HBB, Dechlorane Plus, TPhP, TDCPP, TCPP, TCEP, TBEP, TBPP, V6, EBTEBPI, TBECH) Fluorinated chemicals (17 chemicals) Pesticides (dozens of chemicals) Plasticizers (bisphenol A, phthalates) Nanomaterials Short-chain chlorinated paraffins
Many, many others

What are PFCs?

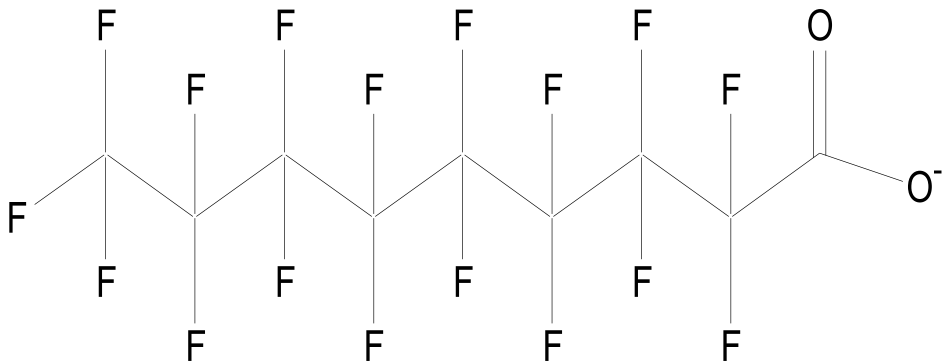


Perfluorinated carboxylic acids



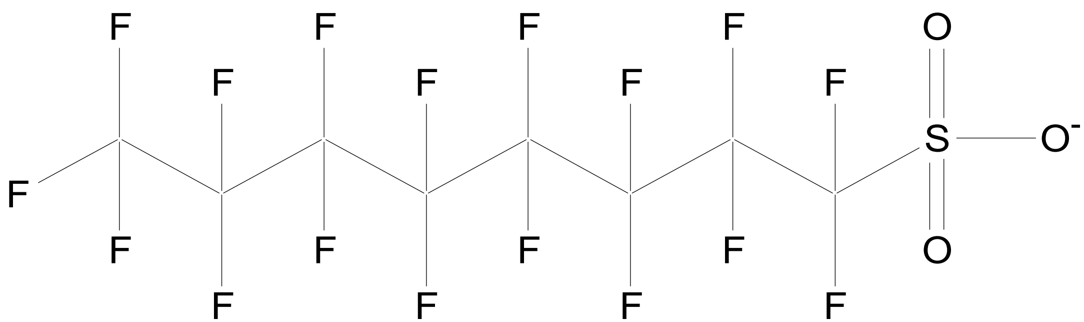
Perfluorinated alkyl sulfonates

What are PFCs?



PFOA

Perfluorinated carboxylic acids



PFOS

Perfluorinated alkyl sulfonates

What is PFOS?

- Oil and water repelling
- Excellent surfactant/ wetting agent
- Binds to proteins
- Very stable

What is it used for?

- High usage:
  - 96,000 tonnes worldwide (Paul et al 2009)

Chromium VI plating bath

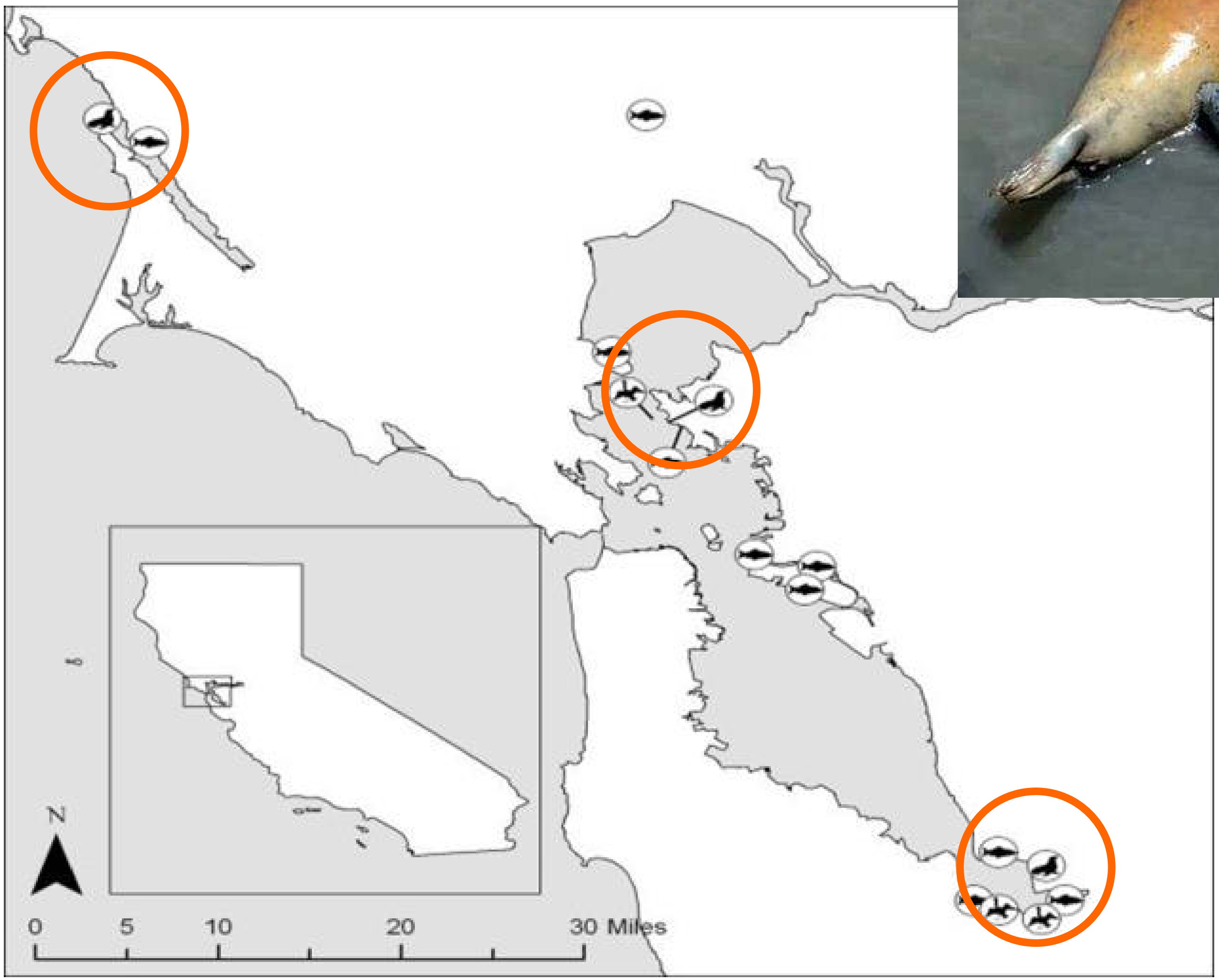
What is it used for?

- High usage:
  - 96,000 tonnes worldwide (Paul et al 2009)

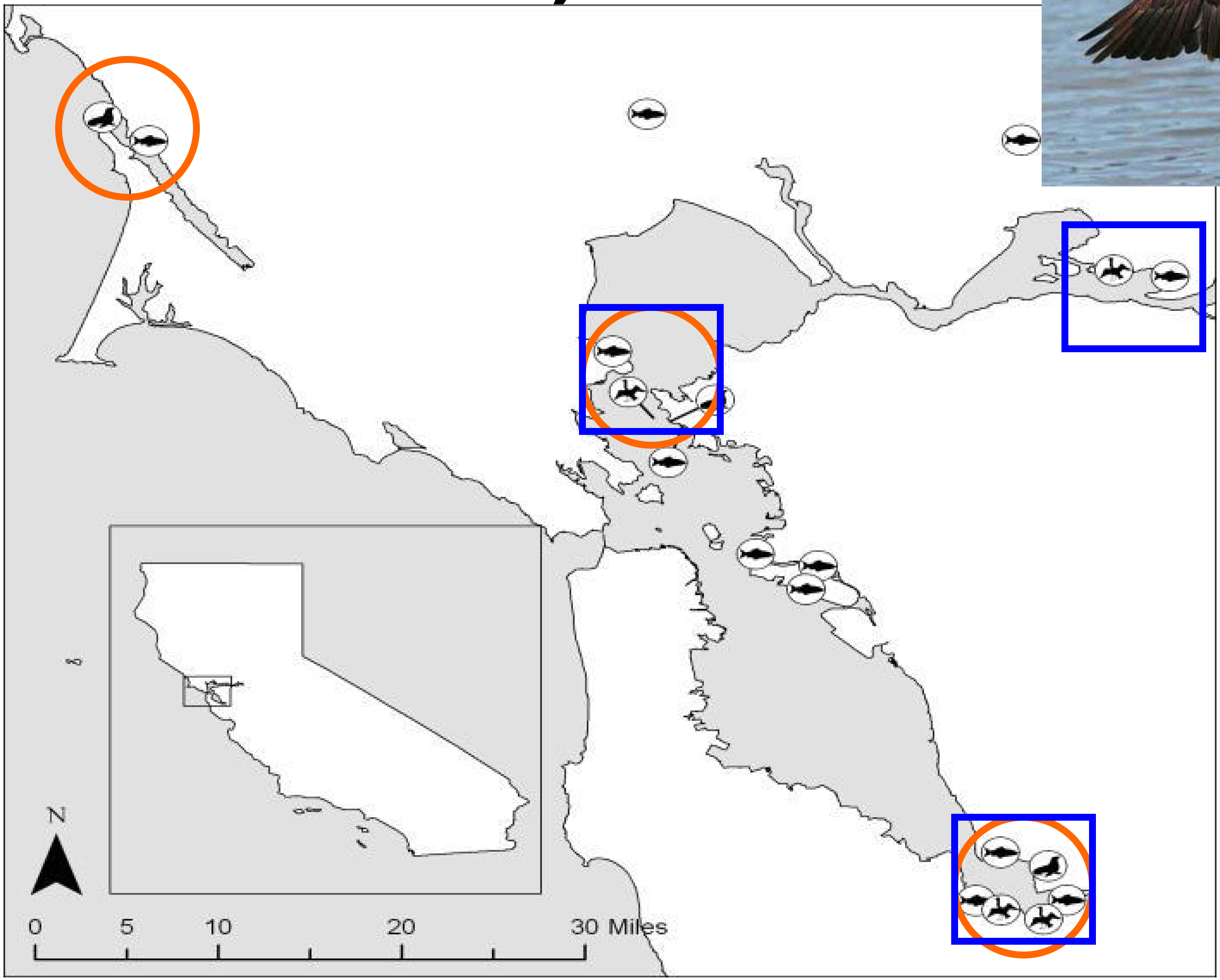
PFOS Effects

- Adversely affects neonatal outcomes
- Compromised immune system
- Affects thyroid functioning
- Induces liver tumors

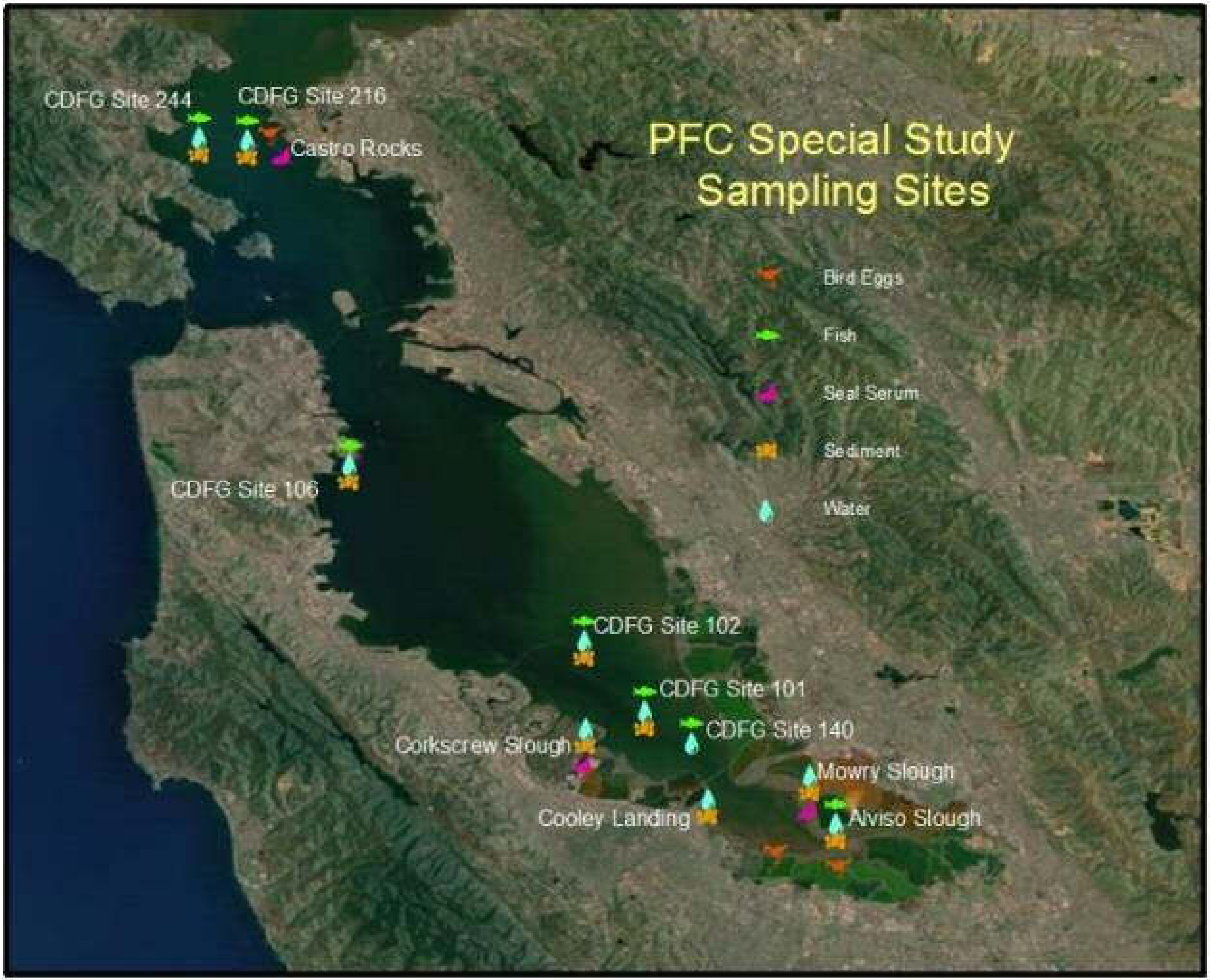
Seal Sampling 2006-2008



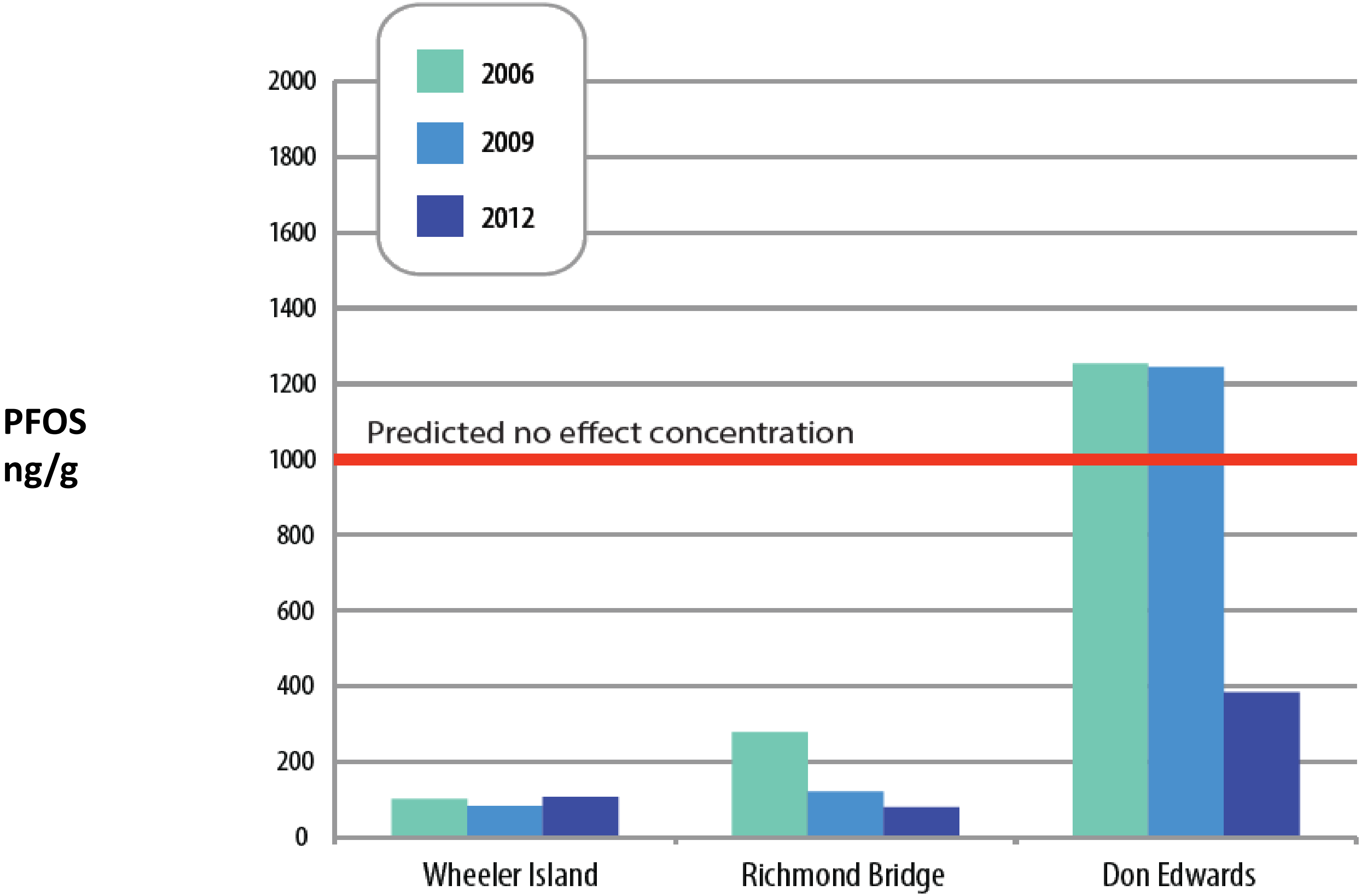
Bird Sampling
2006, 2009



Bay Sampling -2012

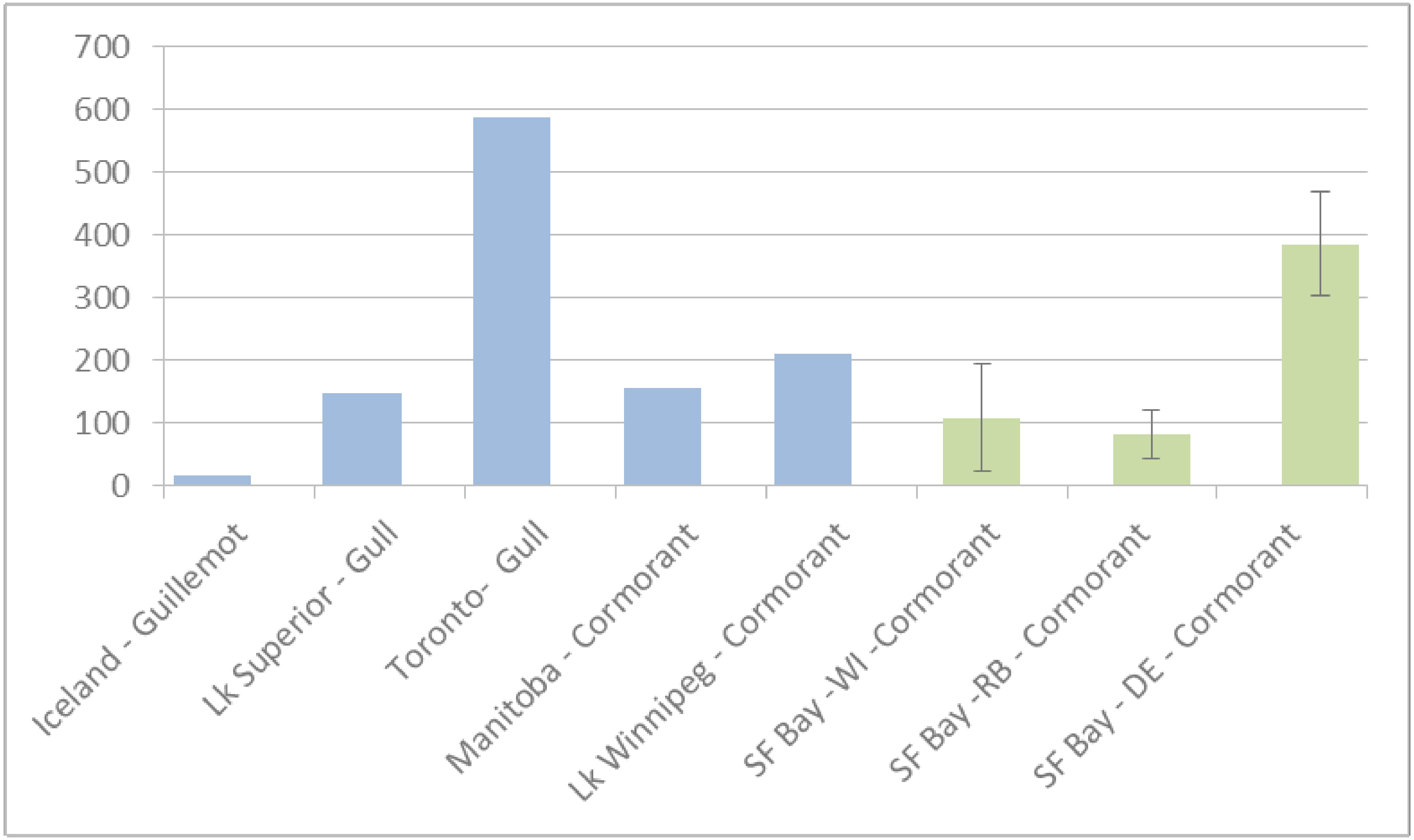


PFOS in Cormorant Eggs



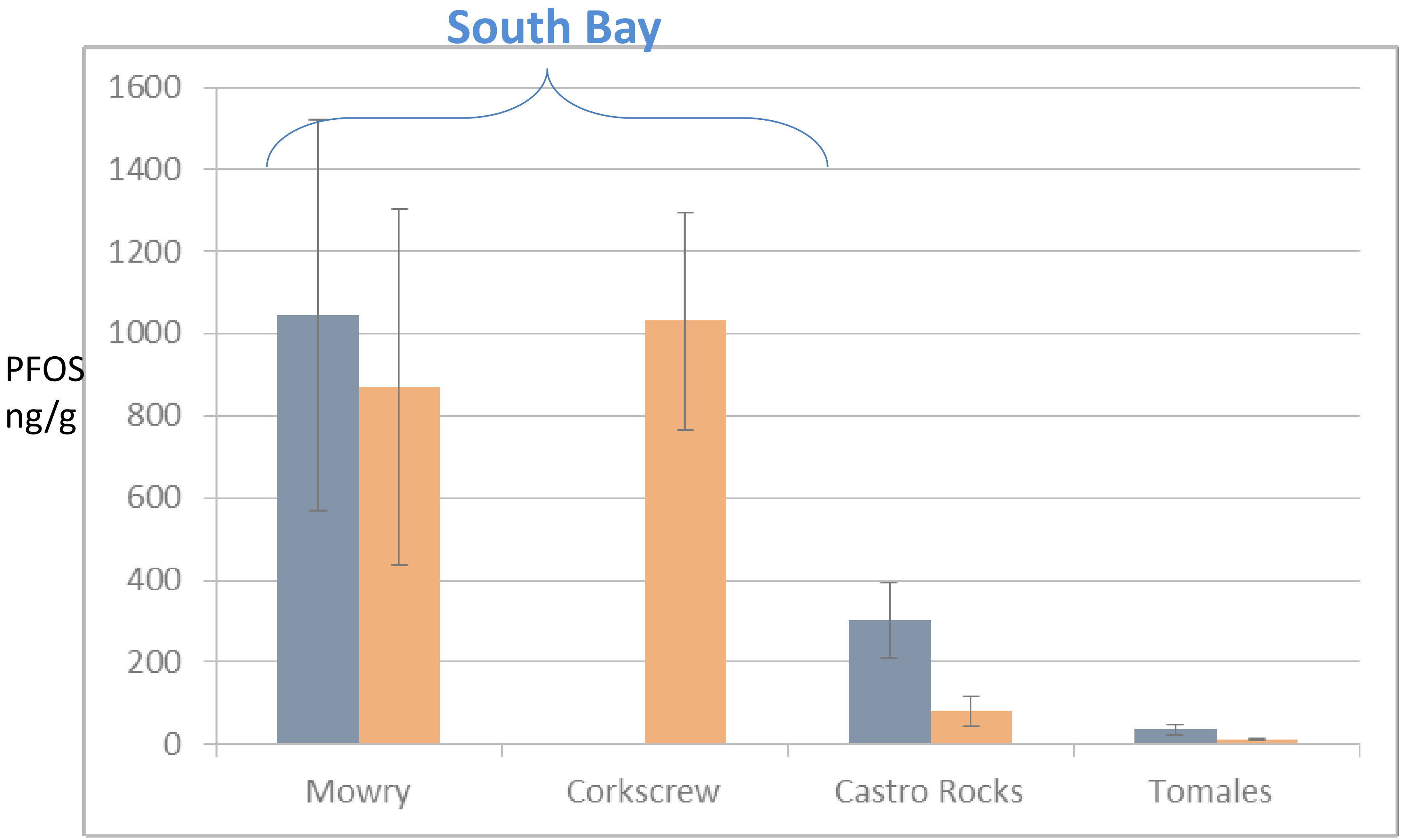
PFOS Concentrations Elsewhere

ng/g



Source: Gebbink and Letcher 2010, Lofstrand et al. 2008, Kannan et al 2001, Giesey and Kannan 2001

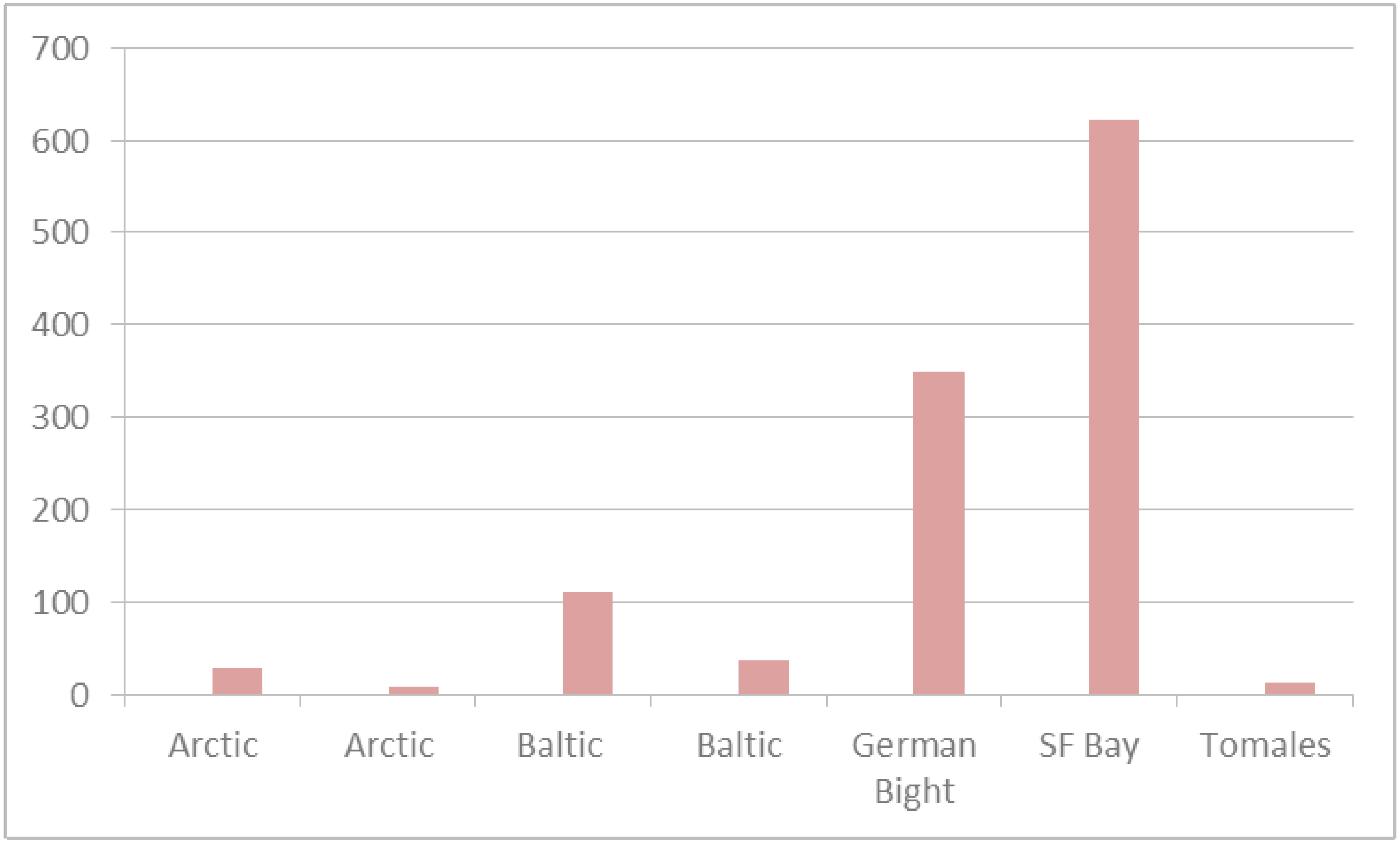
PFOS in Seals



Blue – prior RMP study (2004-2008)   Orange – this study (2010-2011)

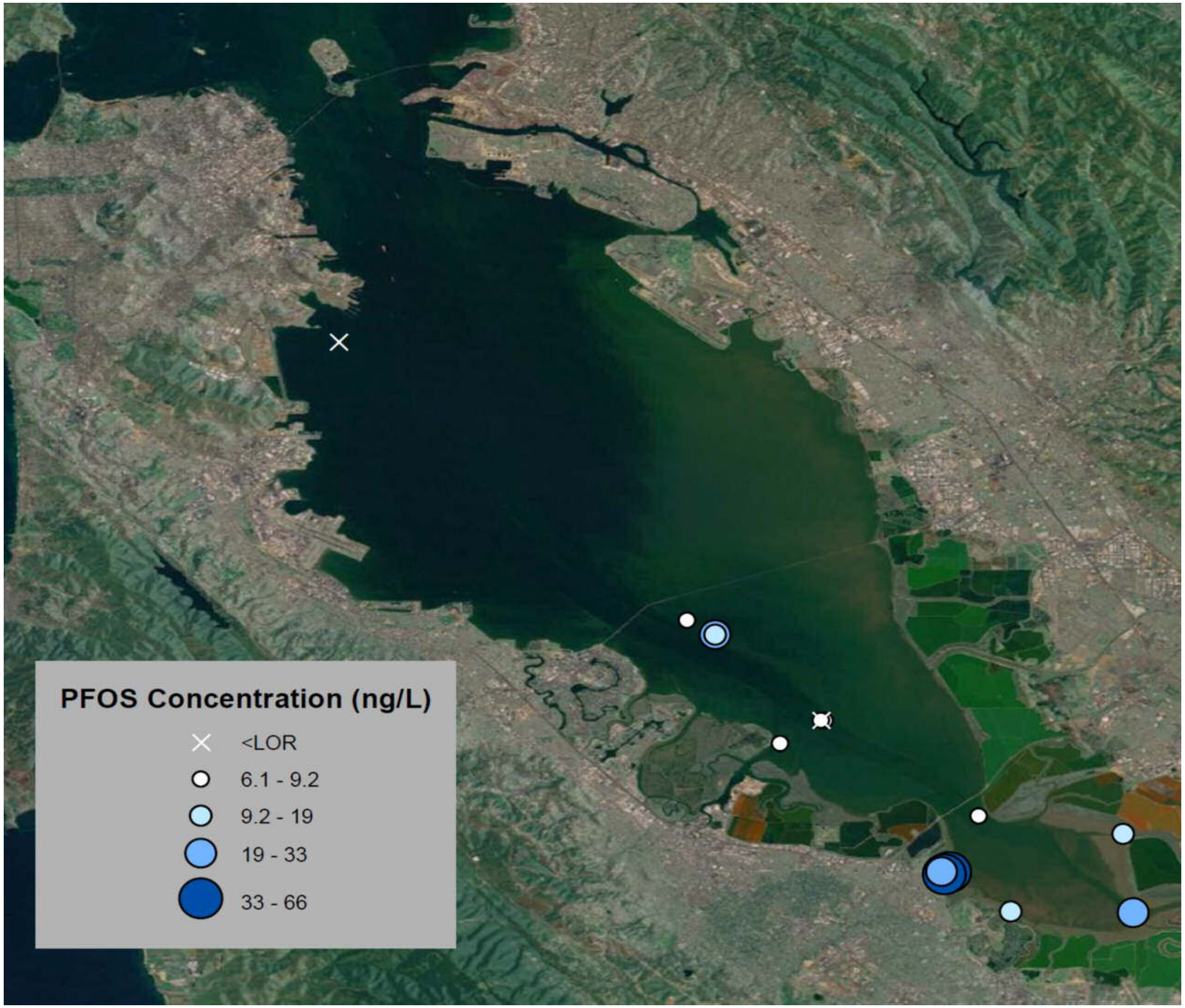
PFOS in Seals Elsewhere

PFOS ng/g



Source: Ahrens et al 2009; Giesy and Kannan 2001

PFOS in Water

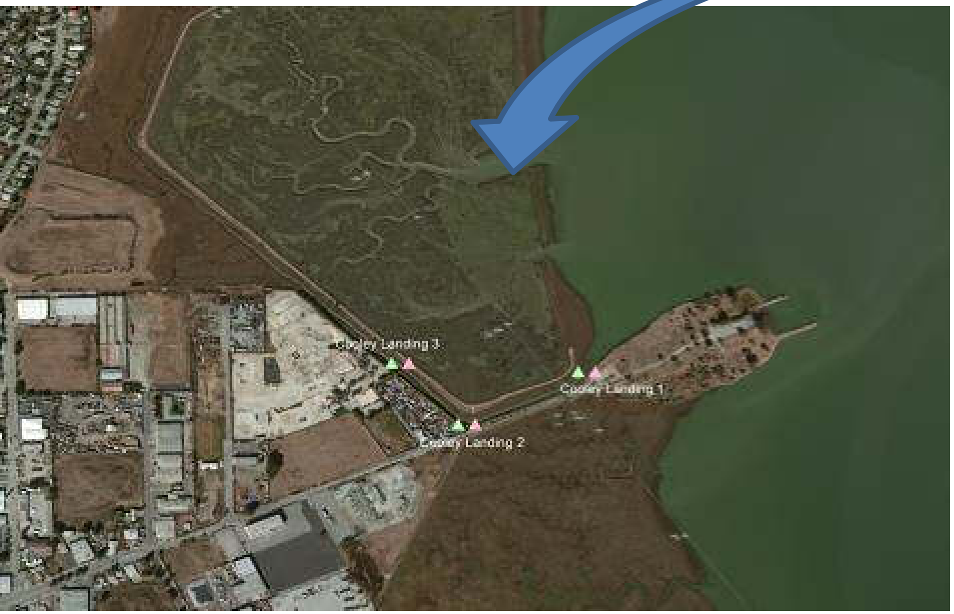


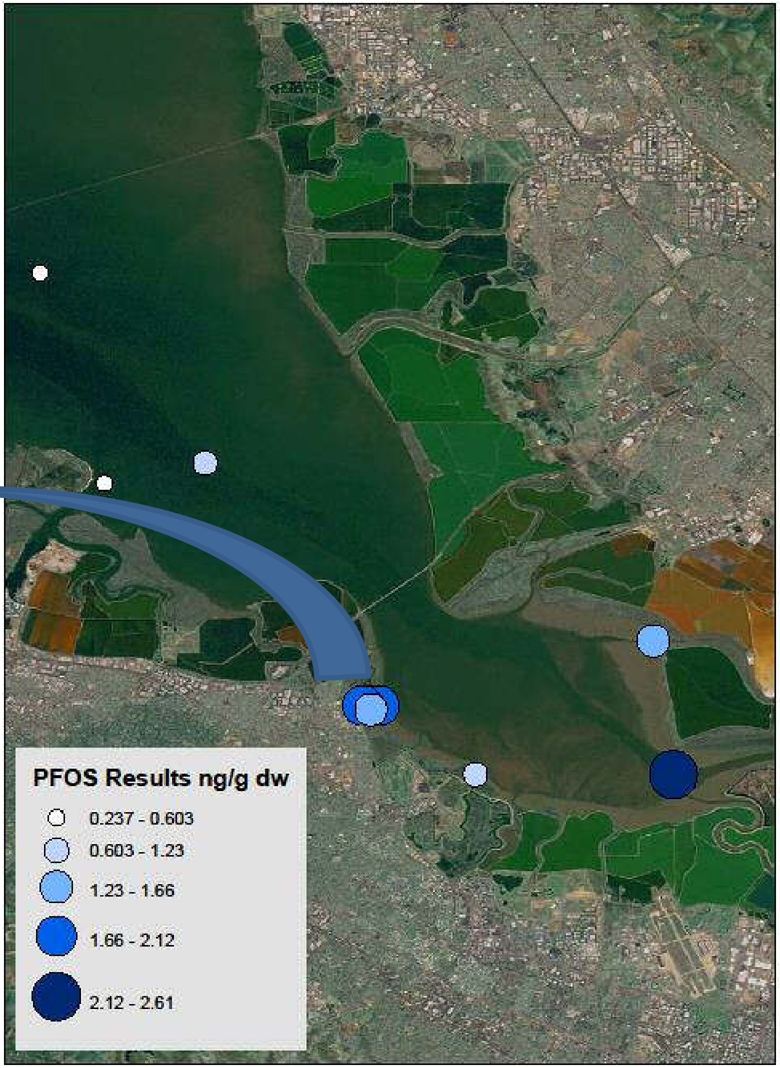
PFOS in Sediment

- Almost all ND in 3 Central Bay sites (1 detect of PFOS - 0.24 ng/g)
- Highest and most frequent detect in Bay - PFOS
  - Detected at 9/13 sites (0.24-2.6 ng/g)

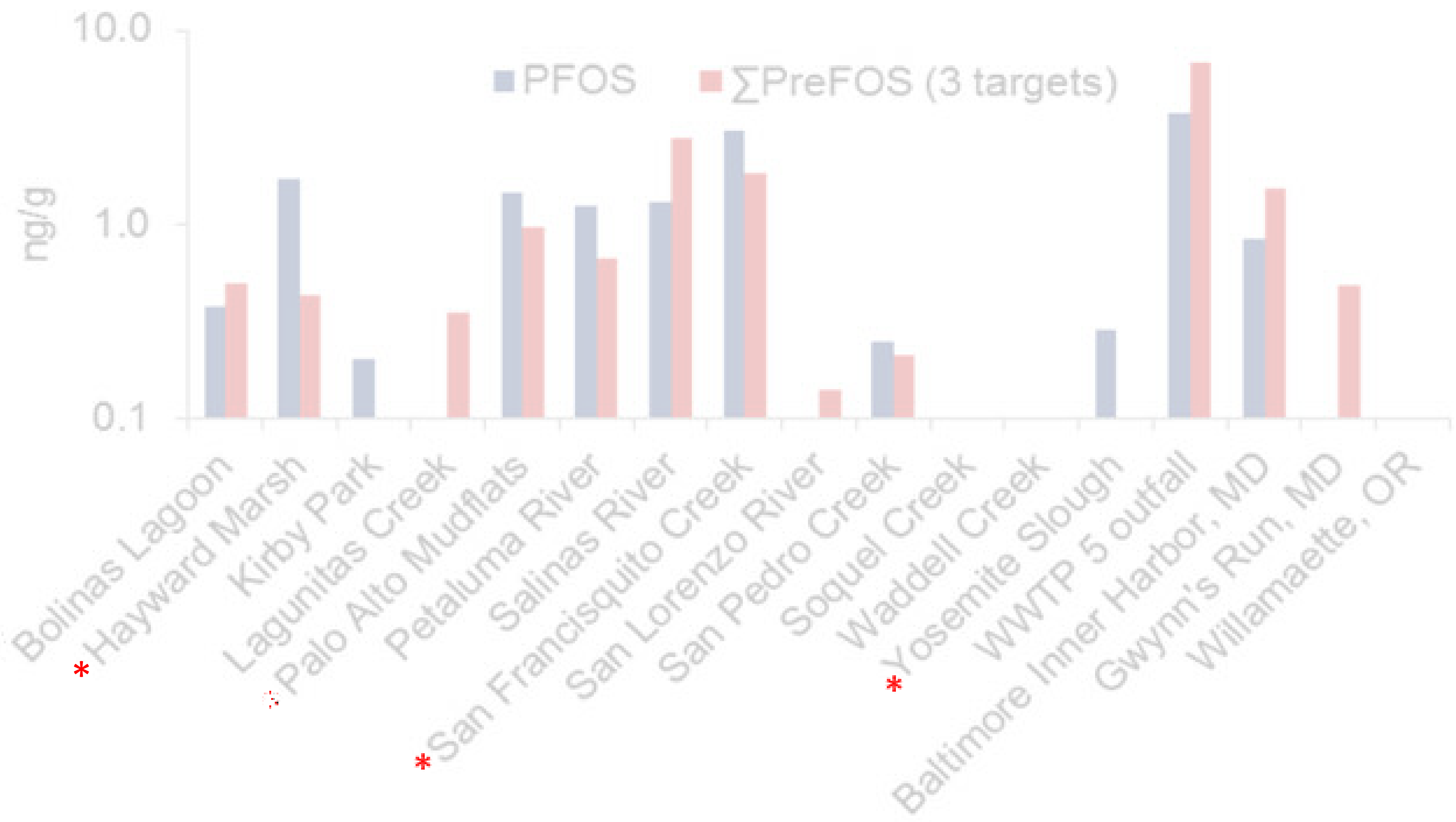
Cooley Landing

- Cooley Landing:
  - 3 sites along a gradient





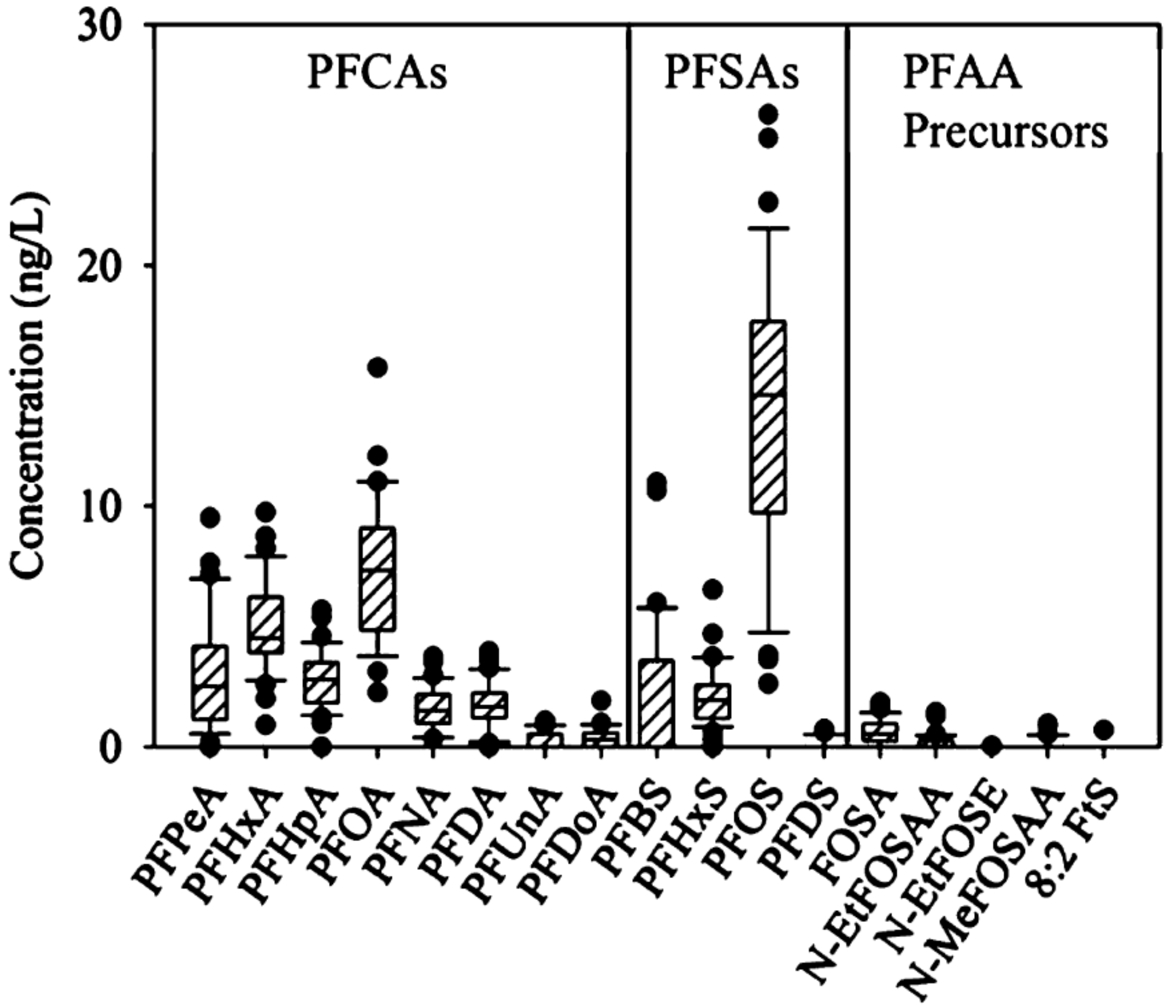
PFOS in Sediment Elsewhere



Source: Higgins, Field, et al 2005

PFCs in Stormwater

- 70% conversion
- AXYS 2013 pro bono study



Houtz and Sedlak 2012 Environmental Science & Technology

Conclusions

- 2012 Cormorant PFOS concentrations ~ 60% of 2006/2009 and are below PNEC
- Seal PFOS concentrations remain elevated
- PFOS concentrations show spatial trend; decreasing to the North
- Source of PFOS remains elusive

RMP San Francisco Bay 2013

Thanks!

- Ellen Willis-Norton and Emily Novik, SFEI
- Paul Salop, AMS
- Max Fish and Kathy Hieb, CA FWS
- Denise Grieg, The Marine Mammal Center
- Josh Ackerman and Colin Eagles-Smith USGS

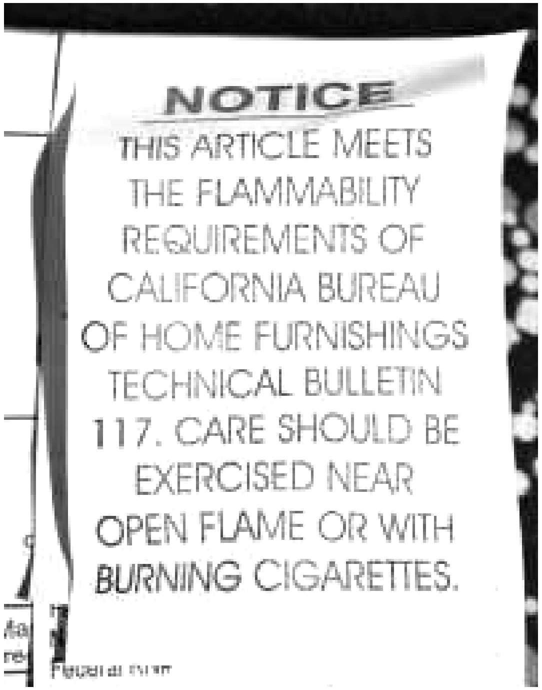
RMP ANNUAL MEETING 2013

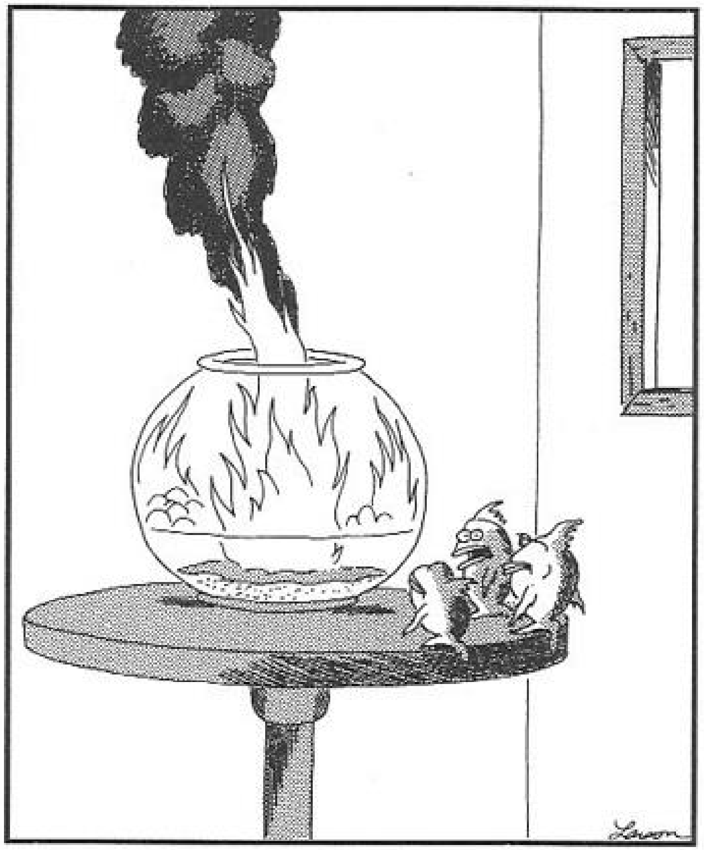
Flame Retardants – Effects of Flammability Standards and Bans

REBECCA SUTTON Ph.D
SAN FRANCISCO ESTUARY INSTITUTE

Why add flame retardants?

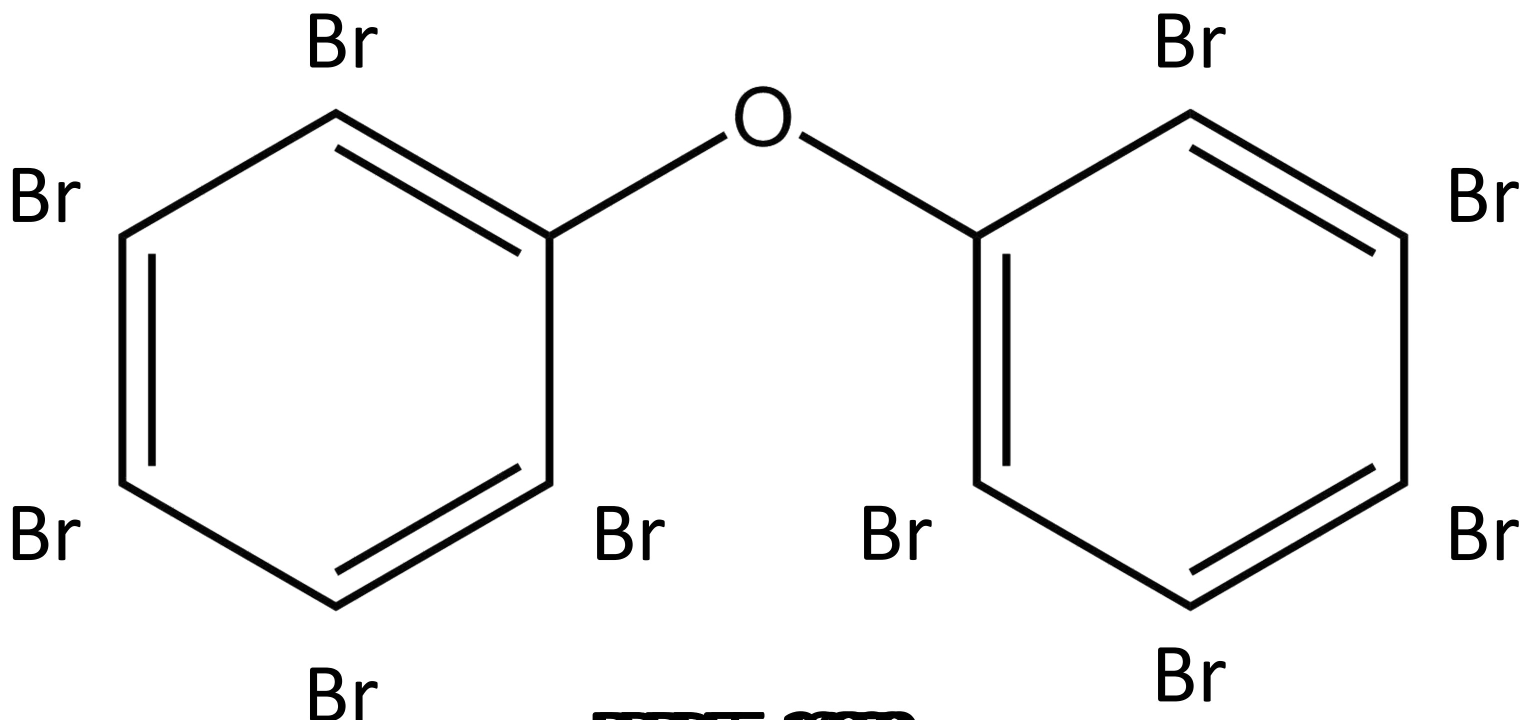
To meet the **California Bureau of** Electronic and Appliance Repair, **Home Furnishings** and Thermal Insulation flammability standards





“Well, thank God we all made it out in time. … ‘Course, now we’re equally screwed.”

Polybrominated Diphenyl Ethers



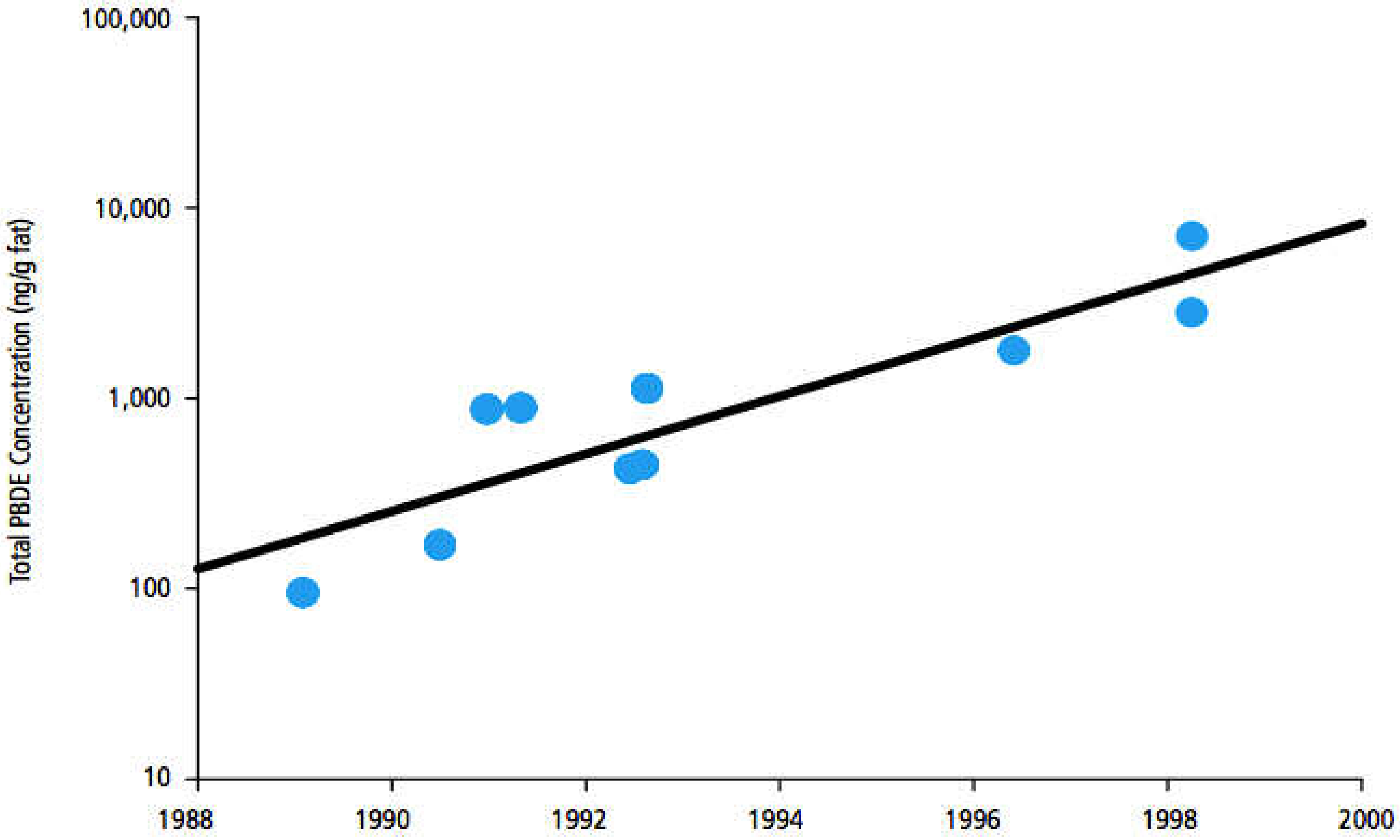
BDE-209

DecaBDE

PBDEs: SF Bay Hot Spot

RMP 2013

Bay harbor seal PBDE levels doubled every 1.8 years



She et al. 2002

PBDEs: Toxicity Concerns

RMP 2013

Research

Hormone Disruption by PBDEs in Adult Male Sport Fish Consumers

Mary E. Turyk,[1] Victoria W. Persky,[1] Pamela Imm,[2] Lynda Knobeloch,[2] Robert Chatterton Jr.,[3] and Henry A. Anderson[2]

[1]Division of Epidemiology and Biostatistics, School of Public Health, University of Illinois at Chicago, Chicago, Illinois, USA; [2]Wisconsin Division of Public Health, Bureau of Environmental Health, Madison, Wisconsin, USA; [3]Departments of Obstetrics and Gynecology and Physiology, Feinberg School of Medicine, Northwestern University, Chicago, Illinois, USA

BACKGROUND: Persistent pollutants, such as polychlorinated biphenyls (PCBs), affect endocrine function. Human exposure to polybrominated diphenyl ethers (PBDEs), which are similar in structure to PCBs, has increased recently, but health effects have not been well studied.

OBJECTIVES: Our goal in this study was to determine whether PBDE body burdens are related to thyroid and steroid hormone levels, thyroid antibodies, and thyroid disease in a cohort of frequent and infrequent adult male sport fish consumers.

METHODS: We tested serum from 405 adult males for PBDE congeners, PCB congeners, testosterone, sex-hormone–binding globulin (SHBG), SHBG-bound testosterone, thyroglobulin antibodies, and the thyroid hormones thyroxine (T_4), triiodothyronine (T_3), thyroid-stimulating hormone (TSH), and T_4-binding globulin (TBG). We collected data on demographics, fish consumption, medical diseases, and medication use.

2001). In 2003, we invited participants from the original cohort to participate in a follow-up study to explore potential mechanisms by which PBDEs, PCBs, and *p,p′*-diphenyldichloroethene (DDE) might be affecting thyroid hormone balance. In addition to the standard hormones (free and total T_4 and T_3, as well as TSH), we explored via additional laboratory parameters specific mechanisms of action suggested by laboratory studies, such as changes in transport by serum-binding proteins (Hallgren et al. 2001; Hamers et al.

PBDEs: Bans & Phase-Outs

US phase-out 2004, California ban 2006

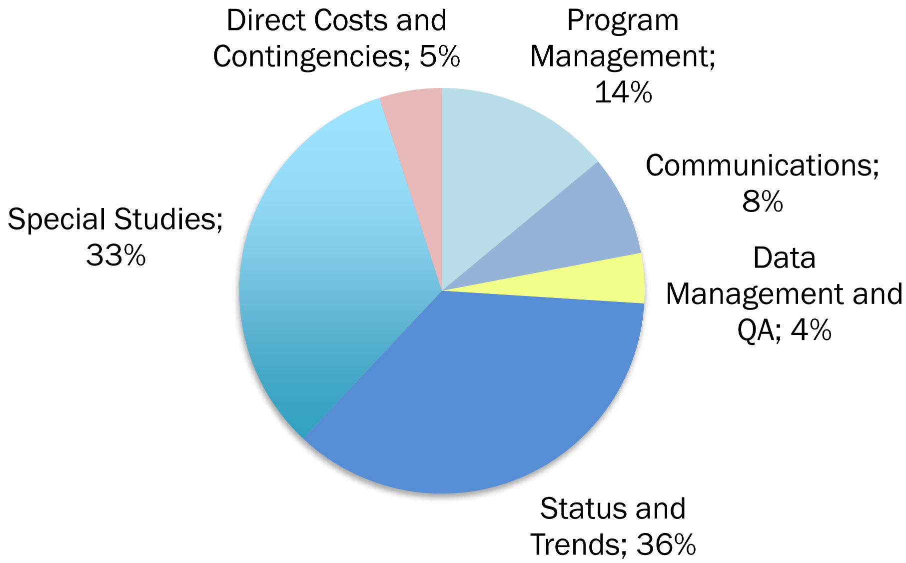
US phase-out 2013

Regional Monitoring Program

Goal: Collect data and communicate information about water quality in the San Francisco Estuary to support management decisions

- Multi-Year Plan updated annually
- $3.5 million per year
- Monitoring focus:
  - Status and Trends
  - Special Studies

RMP Annual Budget

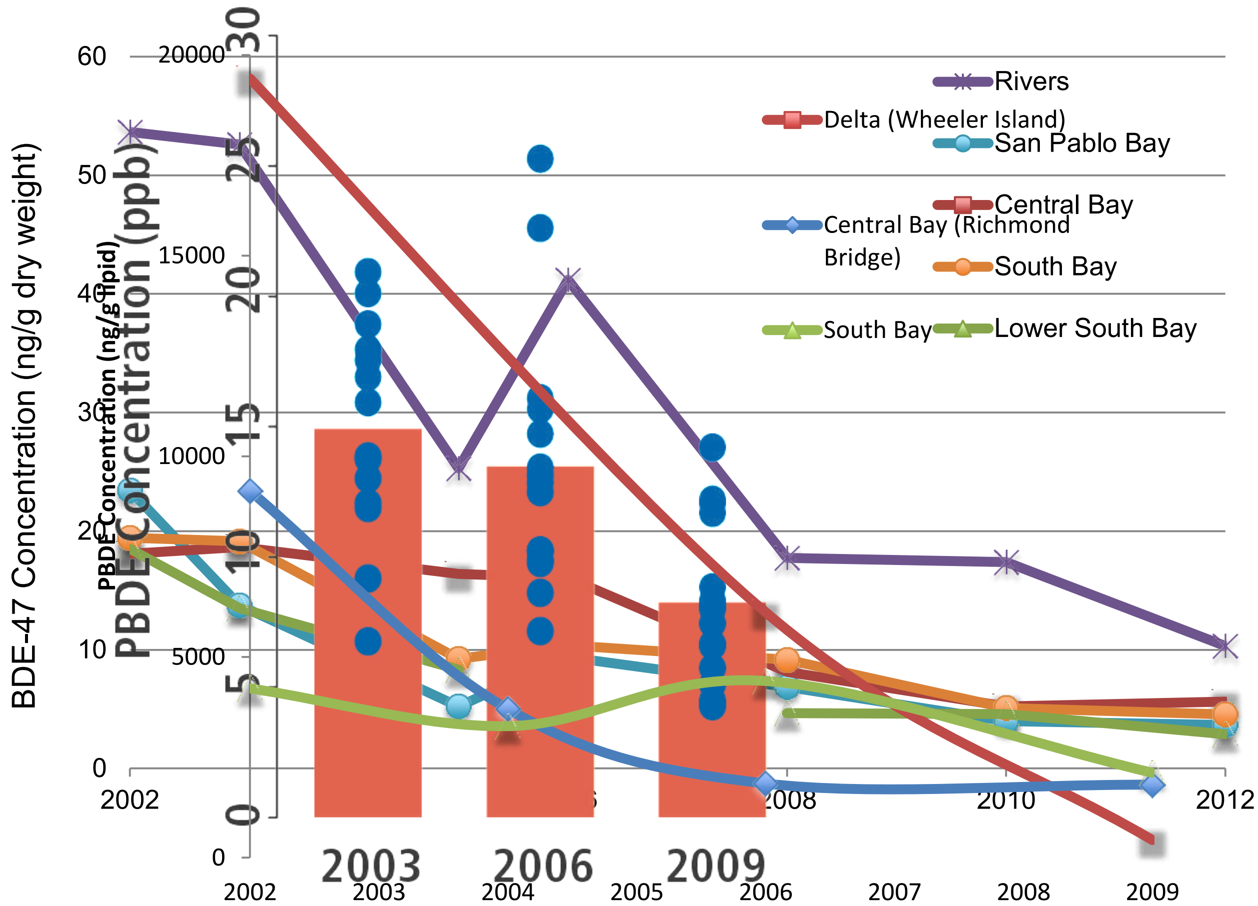


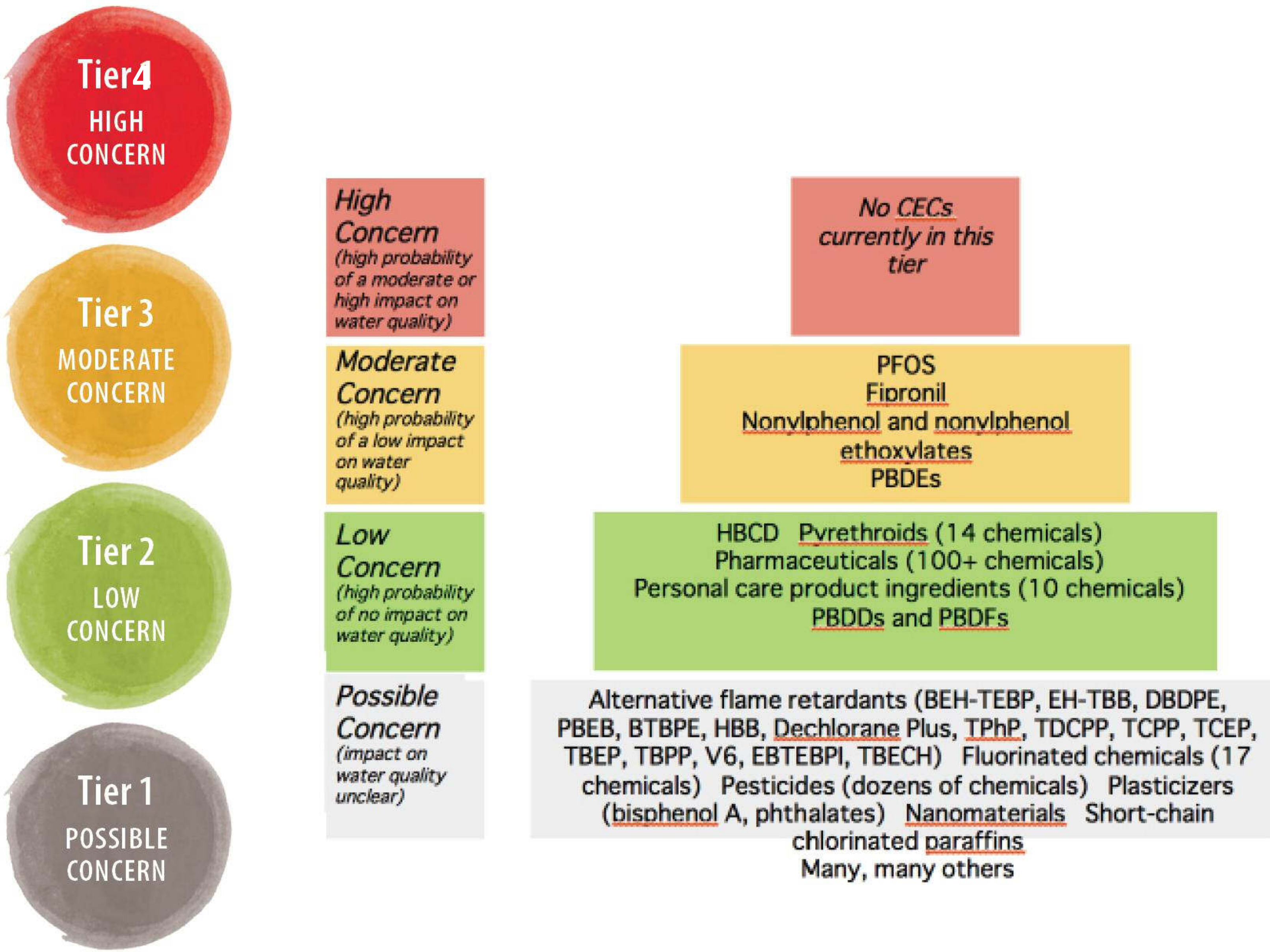
PBDE declines in Bay wildlife

Bivalves

Sport Fish

Cormorant Eggs




Tier4
HIGH CONCERN
Tier 3
MODERATE CONCERN
Tier 2
LOW CONCERN
Tier 1
POSSIBLE CONCERN
High Concern (high probability of a moderate or high impact on water quality)
No CECs currently in this tier
Moderate Concern (high probability of a low impact on water quality)
PFOS
Fipronil
Nonylphenol and nonylphenol ethoxylates
PBDEs
Low Concern (high probability of no impact on water quality)
HBCD Pyrethroids (14 chemicals)
Pharmaceuticals (100+ chemicals)
Personal care product ingredients (10 chemicals)
PBDDs and PBDFs
Possible Concern (impact on water quality unclear)
Alternative flame retardants (BEH-TEBP, EH-TBB, DBDPE, PBEB, BTBPE, HBB, Dechlorane Plus, TPhP, TDCPP, TCPP, TCEP, TBEP, TBPP, V6, EBTEBPI, TBECH) Fluorinated chemicals (17 chemicals) Pesticides (dozens of chemicals) Plasticizers (bisphenol A, phthalates) Nanomaterials Short-chain chlorinated paraffins
Many, many others

PBDEs: Moderate Concern

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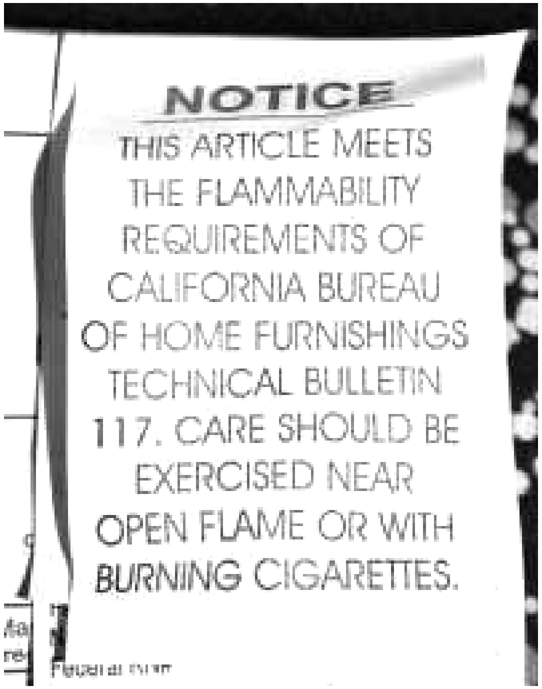
Risk Level Description	CECs in San Francisco Bay
Tier III: Moderate Concern PBDEs	Bay occurrence data suggest a **high probability** of a **low level effect** on Bay wildlife **Good News:** Levels declining Bay sport fish safe to eat (3 servings/week) Tern egg study finds no effects to reproduction or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

Alternative flame retardants

- CA flammability standards lead to use of flame retardants
- Manufacturers use alternative flame retardants instead of PBDEs
  - SFEI collaboration identified compounds in baby products
- Many flame retardants have little to no toxicity data
  - Chlorinated tris is a carcinogen



What are alternative flame retardants?

Dozens of chemicals in use…

Bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH or BEH-TBP)
2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB or EH-TBB)
Tris(1,3-dichloro-2-propyl) phosphate (TDCPP or chlorinated tris)
Tris(1-chloro-2-propyl) phosphate (TCPP)
Triphenyl phosphate (TPhP)
Ethylene bis-tetrabromophthalidimide (EBTEBPI)
1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (DBE-DBCH or TBECH)
Dechlorane 602
Tributyl phosphate (TBP)
Pentabromoethylbenzene (PBEB)
Decabromodiphenyl ethane (DBDPE)
Bis(2,4,6-tribromophenoxy)ethane (BTBPE)
Hexabromobenzene (HBB)
Tetradecabromodiphenoxybenzene (TDBDPB)
Tetrabromobisphenol A (TBBPA)
Isopropylated triaryl phosphate

Bay monitoring data: Alternative flame retardants

Alternative Flame Retardants	Water*	Sediment	Mussels	Fish	Bird Eggs	Seals
HBCD		+	+	+	+	+
Dechlorane Plus (DP)		+	+	+	+	+
PBEB		+	+	-	-	+
DBDPE		-				
BTBPE		+	-	-	-	-
HBB		-	-	-	-	-
BEH-TBP**		-	-		-	
EH-TBB**		-	-	-	-	-
TDCPP or Chlorinated Tris	+	+	-		-	
TCPP	+	+	-		+	
TPhP	+	+	+		-	
TCEP	+				+	
TBP	+				-	
TBEP	-				+	
TEHP	-				-	
TPrP					-	
Tris(2,3-dibromopropyl) phosphate, Tricresyl phosphate, 2-Ethylhexyl-diphenyl phosphate, Tris(2-bromo-4-methylphenyl) phosphate					-	

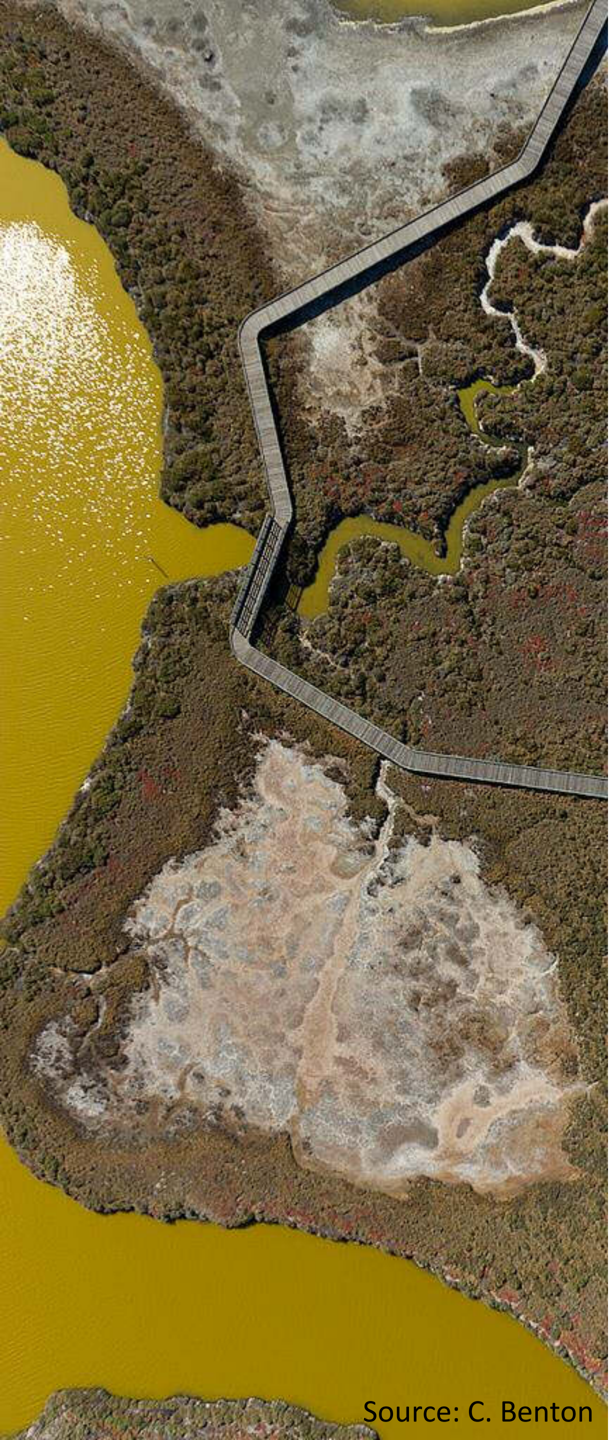
Regulatory changes

- California Bureau of Home Furnishings:
  – New standards for foam furniture, baby products
  – Finalized soon
- California AB 127 (Skinner) – Safer Building Insulation
  – Would require State Fire Marshall to review insulation standards with Bureau, potentially update
- Worldwide ban on HBCD (hexabromocyclododecane):
  – Can be used in polystyrene building insulation until 2019, with labeling

RMP Resources

- Email: RebeccaS@sfei.org
- Website: www.sfei.org
- Coming soon: PBDE synthesis document

Thank you!
Any questions?


Source: C. Benton

Science to inform nutrient management decisions in San Francisco Bay

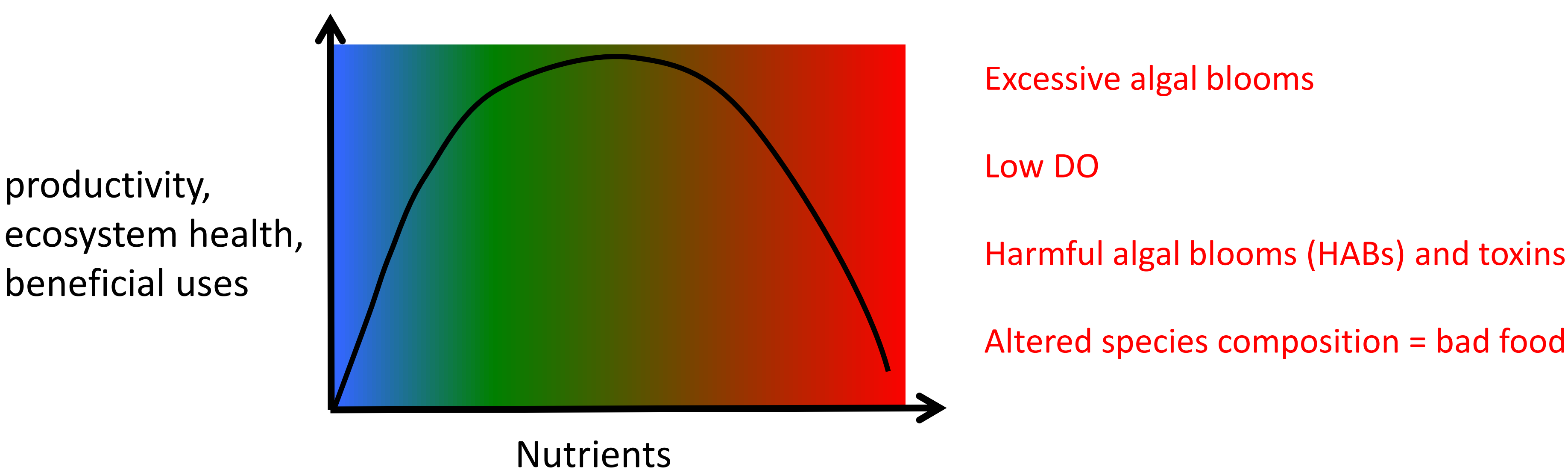
David Senn
October 30 , 2013

How much is too much?

- Nutrients are required to support aquatic life and fisheries…
  - *Base of food web: phytoplankton, benthic algae, aquatic plants*

- But at some point they lead to problems

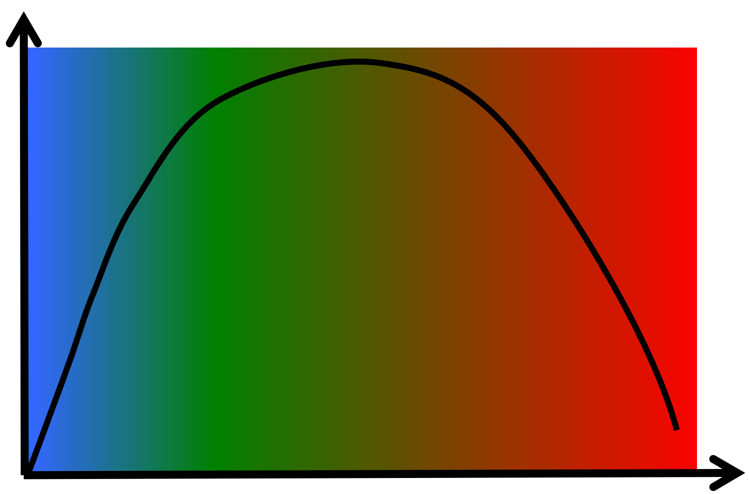
- Individual estuaries respond very differently to nutrient loads



Is San Francisco Bay nutrient-impaired?

How can impairment be mitigated or prevented?

productivity, ecosystem health, beneficial uses



Nutrients

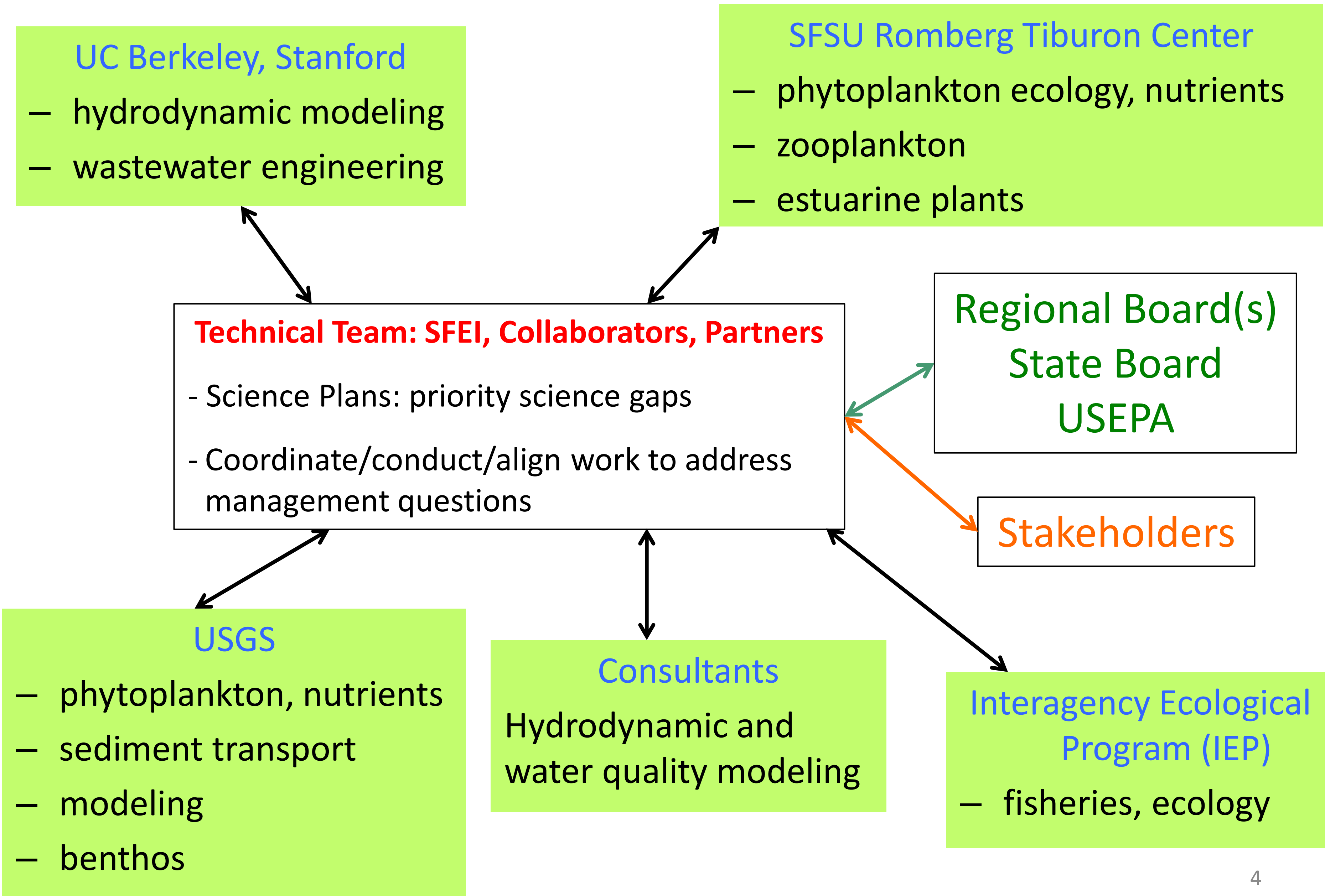
Excessive algal blooms

Low DO

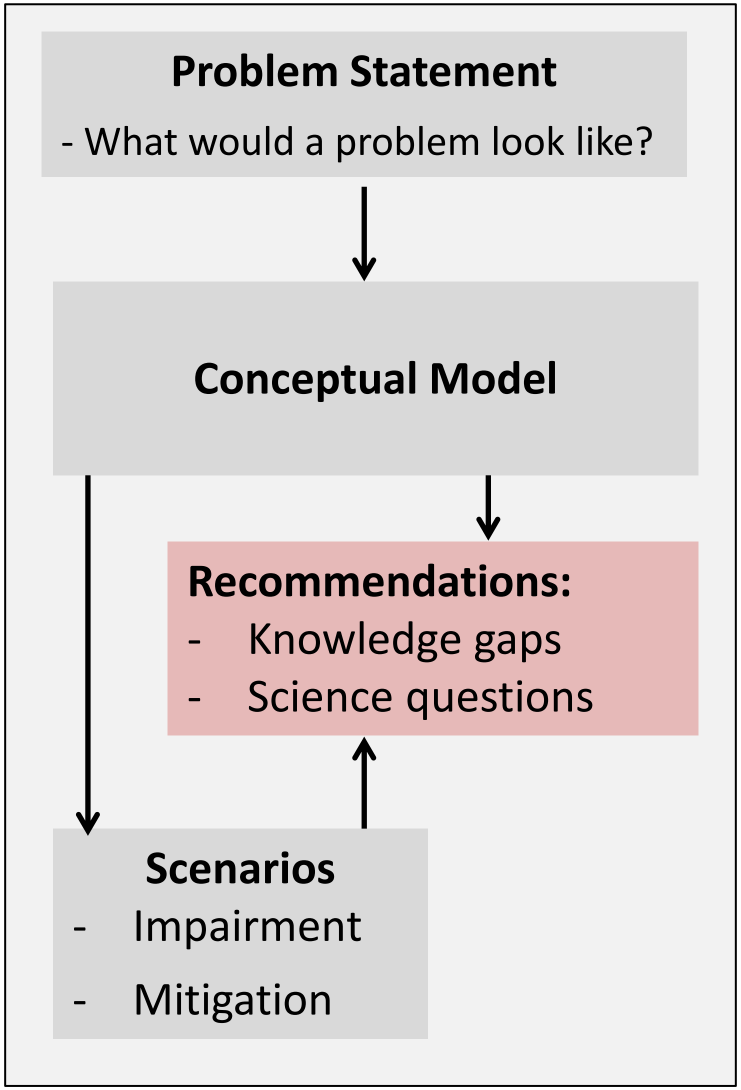
Harmful algal blooms (HABs) and toxins

Altered species composition = bad food

Nutrient Strategy Implementation



'Scientific Foundation for a San Francisco Bay Nutrient Strategy'



Funding: Regional Monitoring Program

Technical Team

J Cloern	USGS
M Connor	EBDA
R Dugdale	SFSU-RTC
JT Hollibaugh	U-Georgia
L Lucas	USGS
W Kimmerer	RTC
R Kudela	UCSC
A Mueller-Solger	IEP
M Stacey	UCB
M Sutula	SCCWRP

Problem Statement

- What would a problem look like?

Conceptual Model

Recommendations:

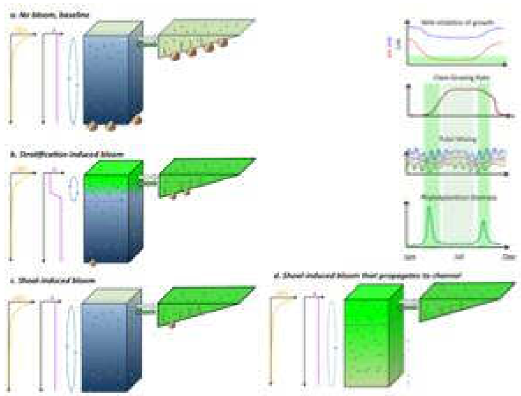
- Knowledge gaps
- Science questions

Scenarios

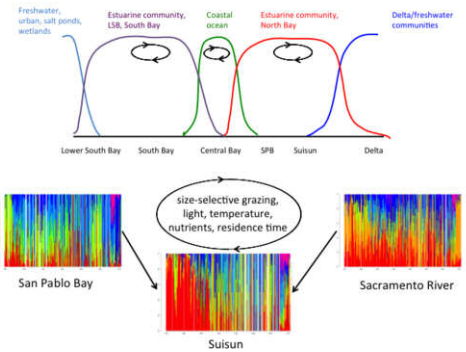
- Impairment
- Mitigation

Funding: Regional Monitoring Program

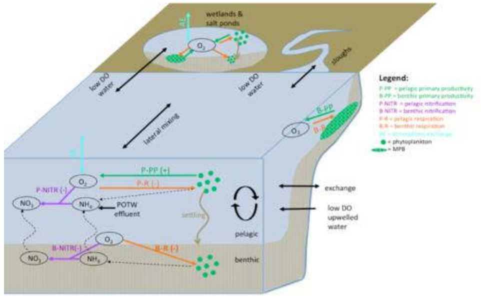
What controls phytoplankton biomass?



What shapes the type of phytoplankton?

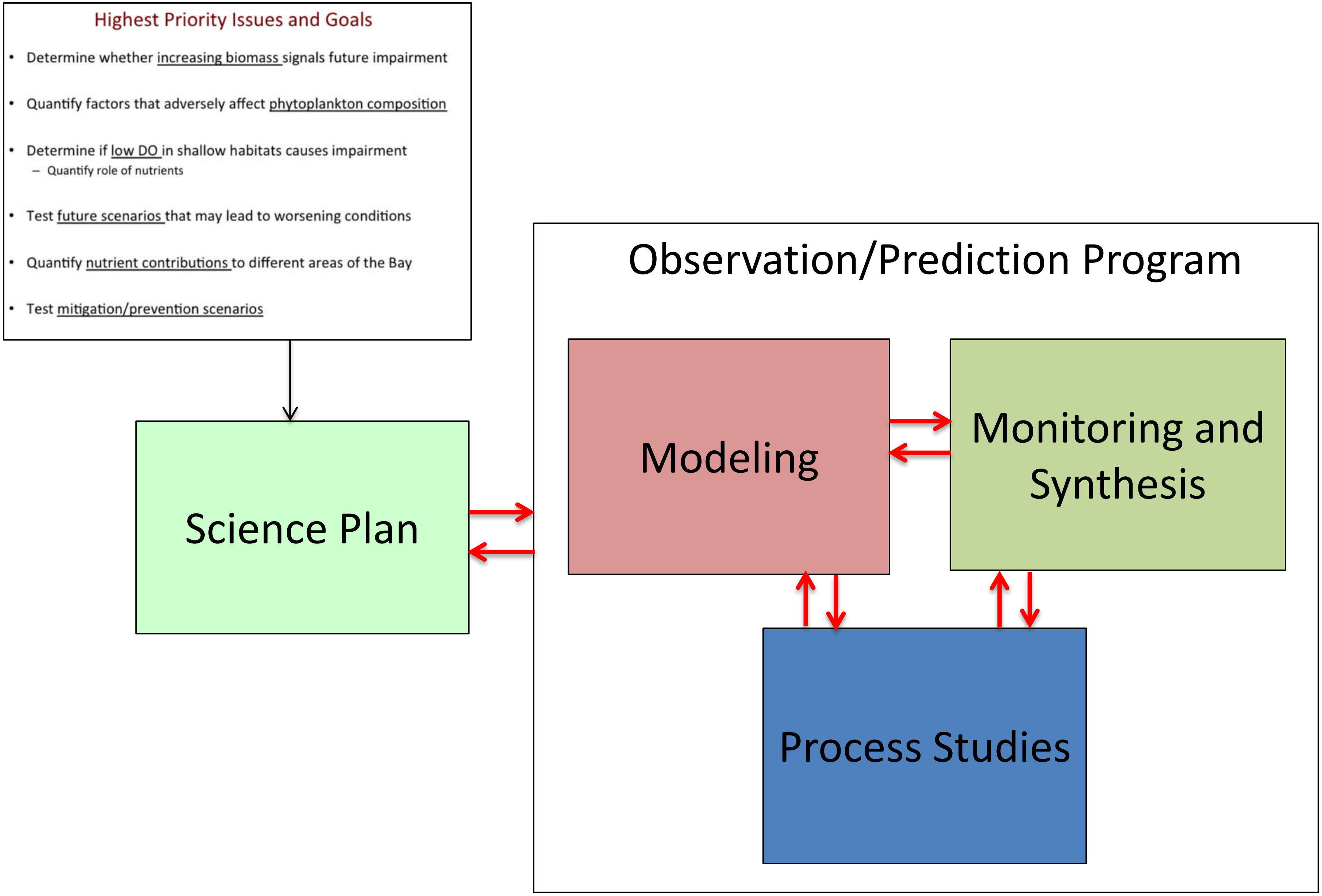


What regulates dissolved oxygen levels?



Highest Priority Issues and Goals

- Determine whether increasing biomass signals future impairment
- Quantify factors that adversely affect phytoplankton composition
- Determine if low DO in shallow habitats causes impairment
  - Quantify role of nutrients
- Test future scenarios that may lead to worsening conditions
- Quantify nutrient contributions to different areas of the Bay
- Test mitigation/prevention scenarios


Highest Priority Issues and Goals
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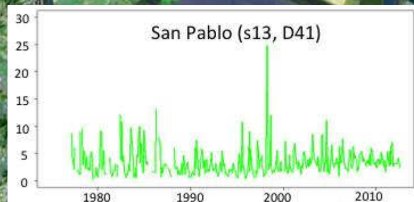
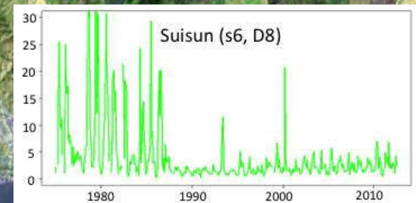
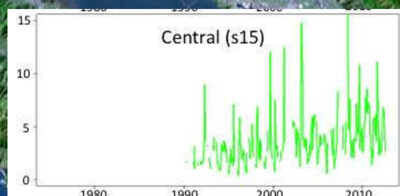
– Quantify role of nutrients
• Test future scenarios that may lead to worsening conditions
• Quantify nutrient contributions to different areas of the Bay
• Test mitigation/prevention scenarios
Science Plan
Observation/Prediction Program
Modeling
Monitoring and Synthesis
Process Studies

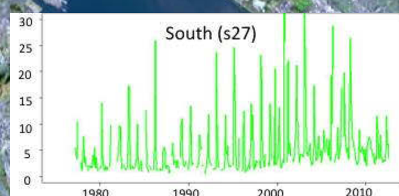
Synthesis of existing data: Chl-a 1970s-present

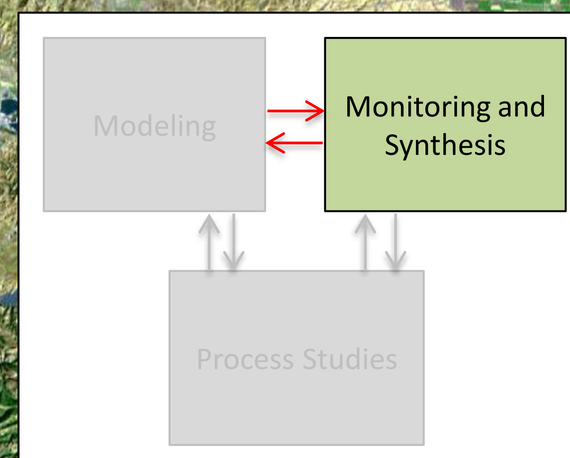


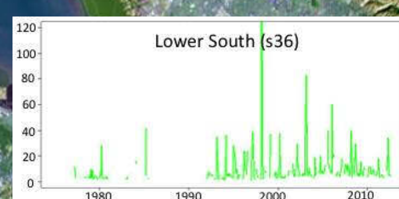




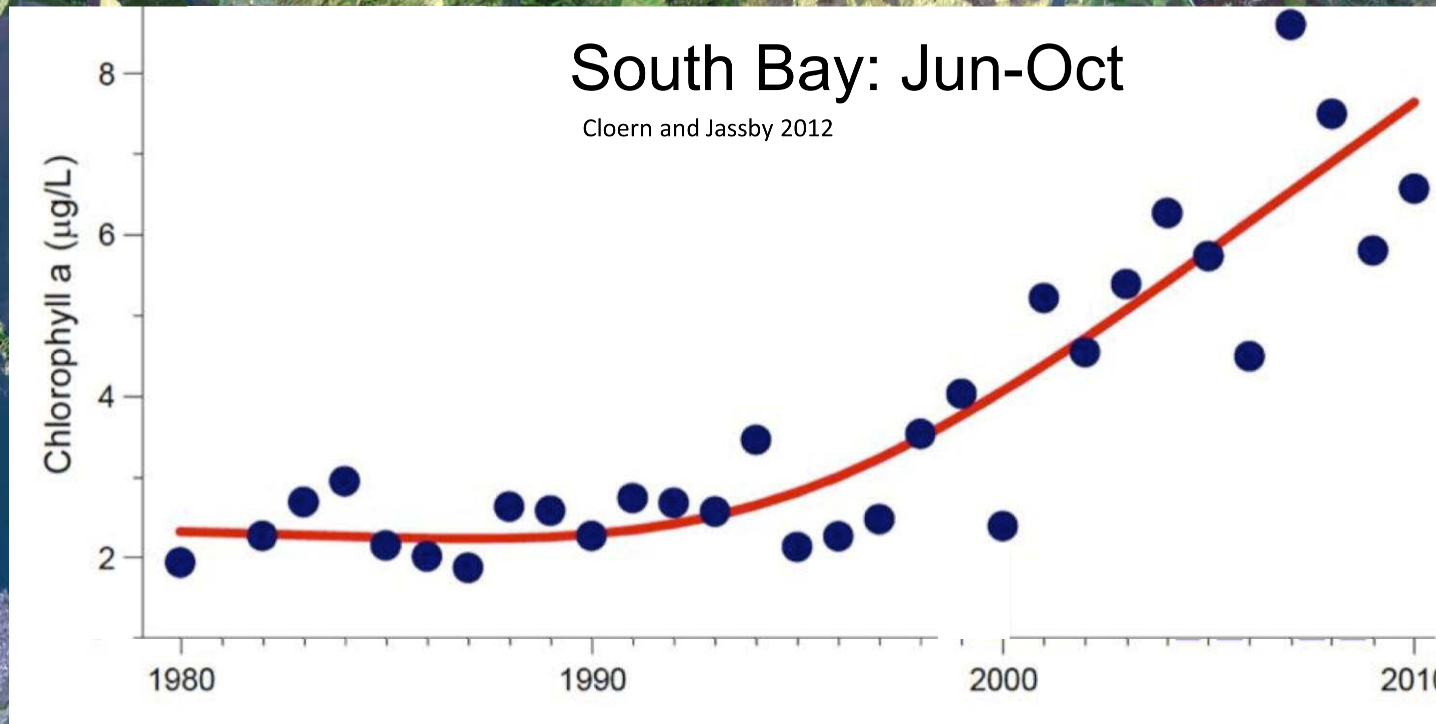
- Assess historic and on-going condition and changing response
- Design optimal monitoring program
- Locate continuous sensors







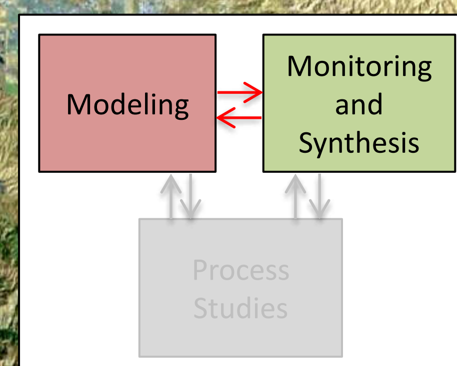
Modeling



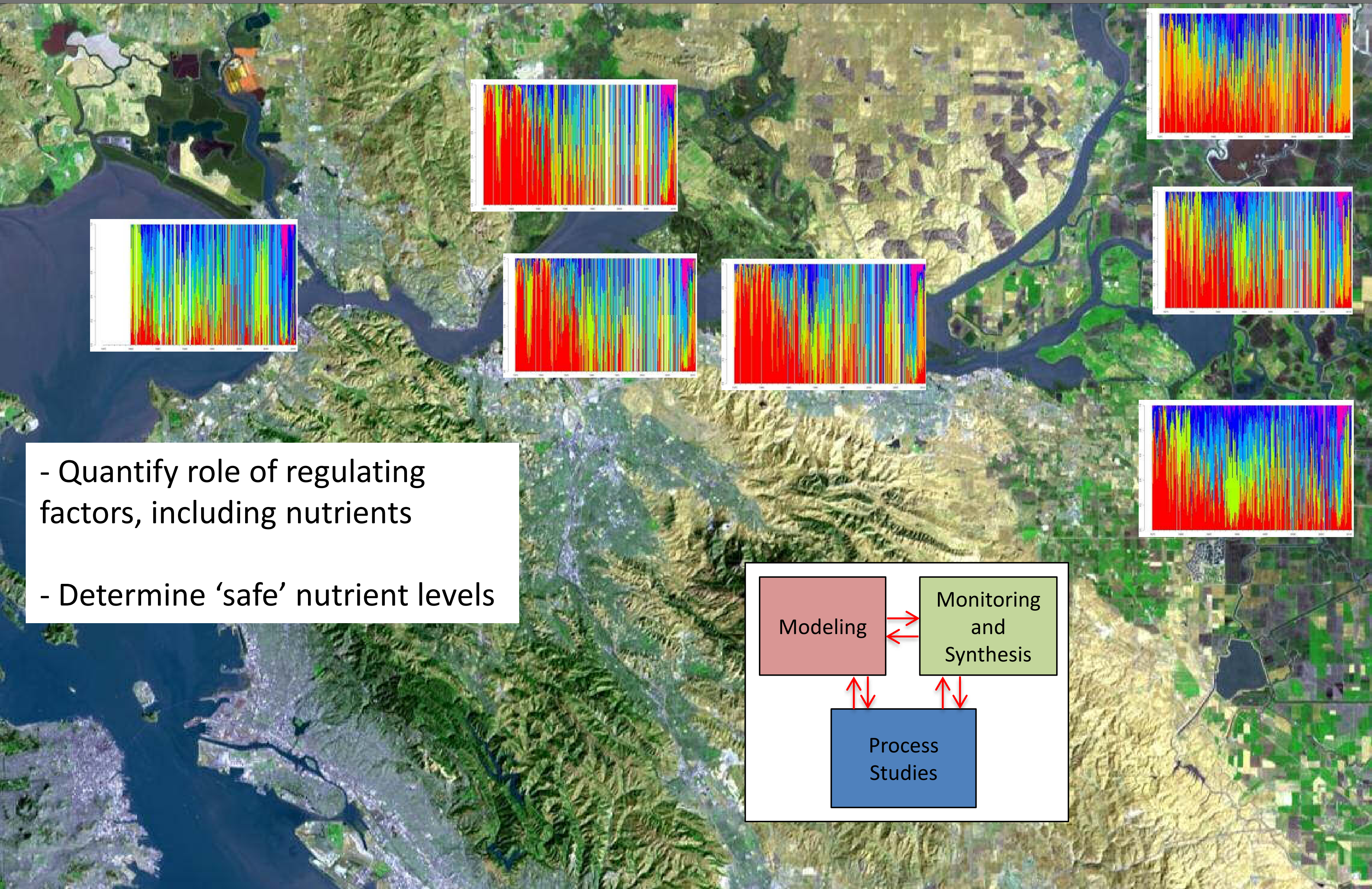
- What factors are contributing to increasing biomass?

- What will future conditions look like?

- What load reductions would mitigate impairment?



Synthesis, experimentation, modeling: Phytoplankton composition 1975-present



- Quantify role of regulating factors, including nutrients

- Determine 'safe' nutrient levels

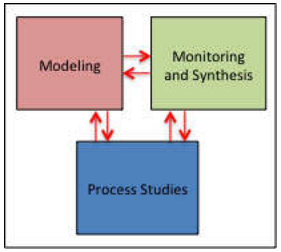
From here…

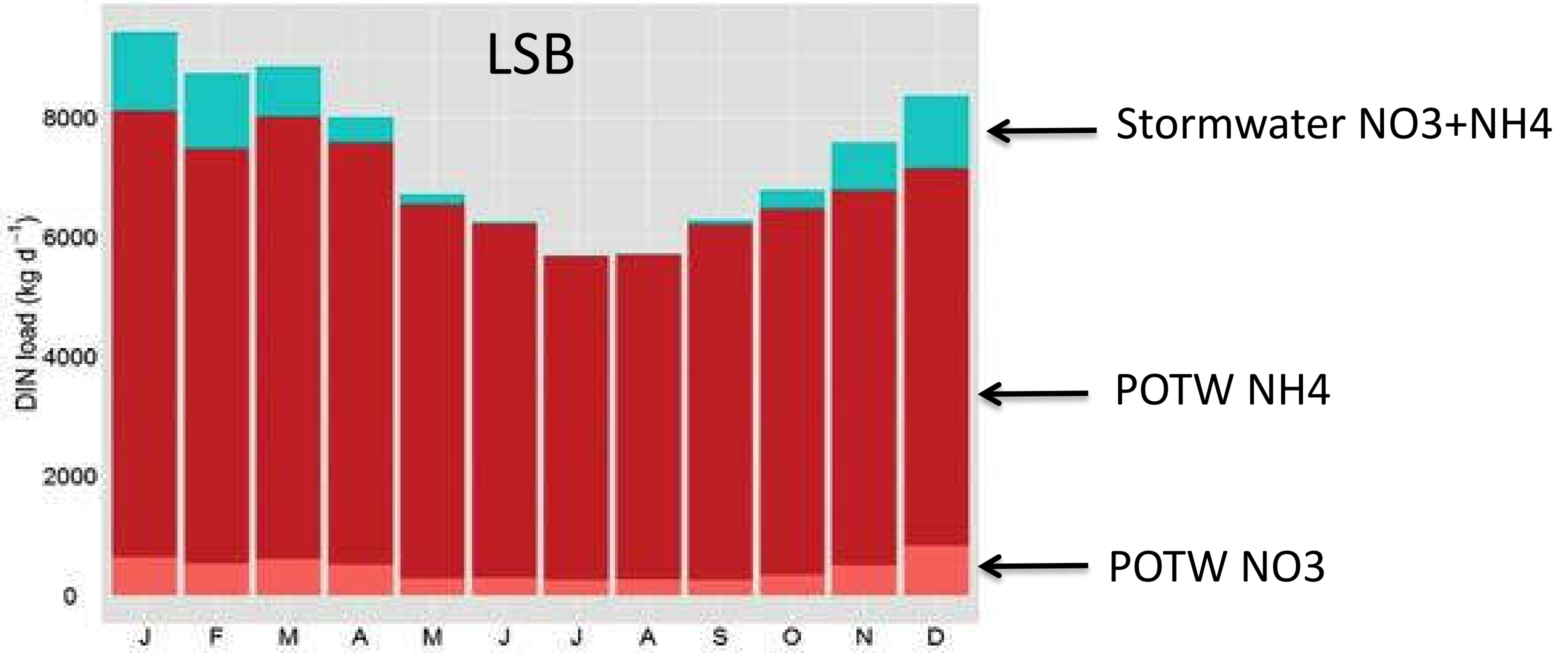
1. Pick 2 or 3 examples to explore in more detail (2-3 slides each). Options
   a. Loads study…loads to Suisun from Delta
   b. Historic water quality data in Lower South Bay
   c. Dissolved oxygen in shallow habitats
   d. New moored sensor stations
   e. Suisun/Delta phytoplankton composition

2. Option 2…stay more general

Nitrogen Loads

- Spatial/temporal contributions
- Best reduction scenarios

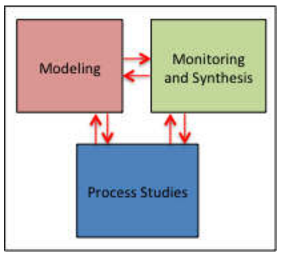


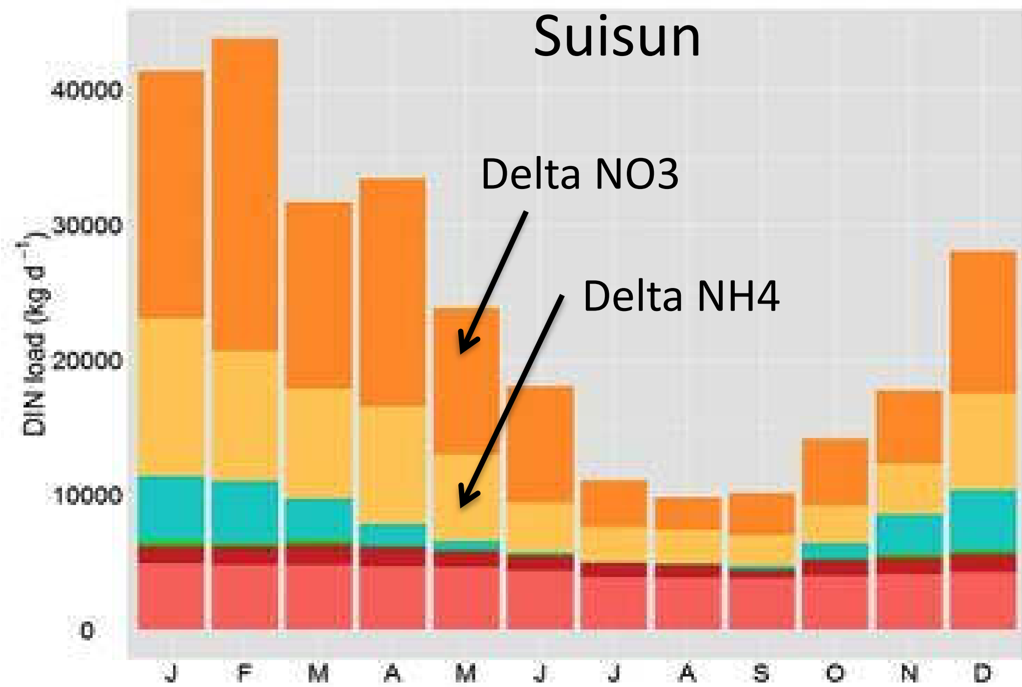


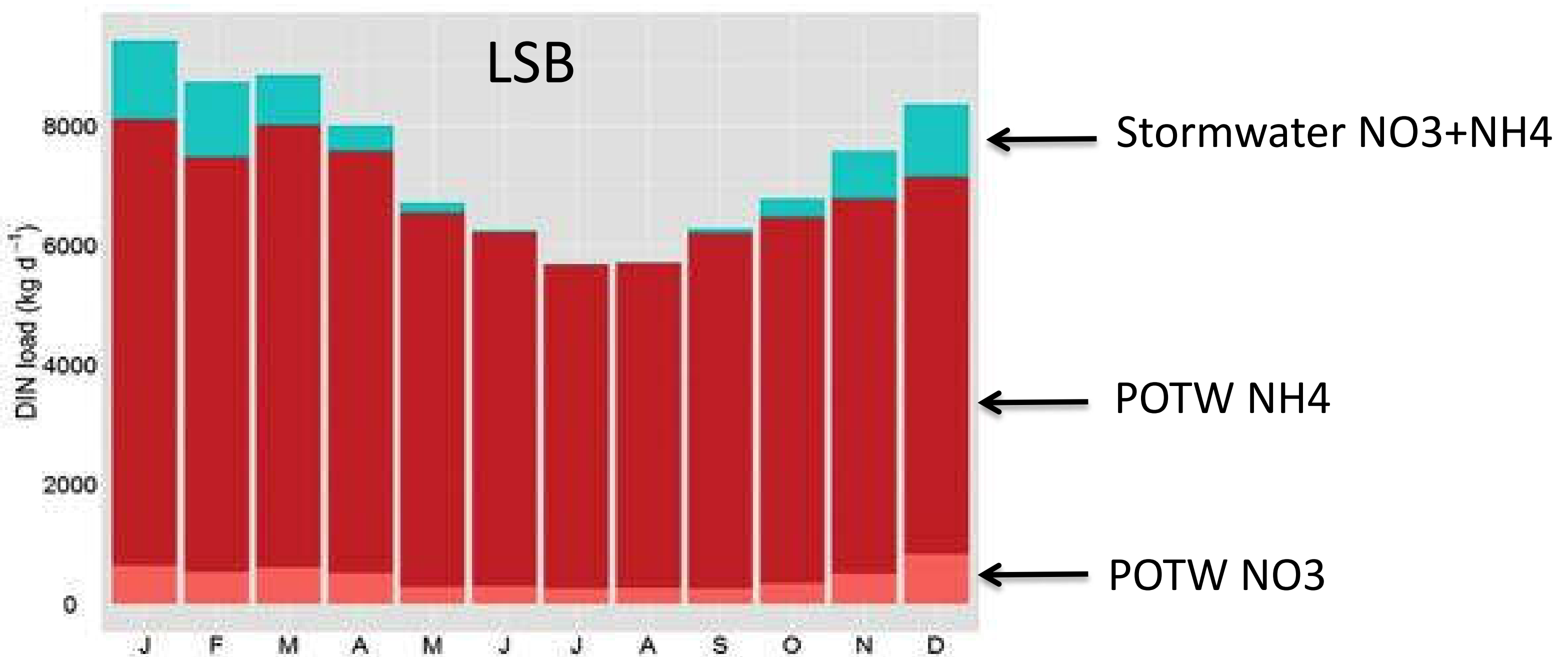
Novick and Senn 2013

Nitrogen Loads

- Spatial/temporal contributions
- Best reduction scenarios

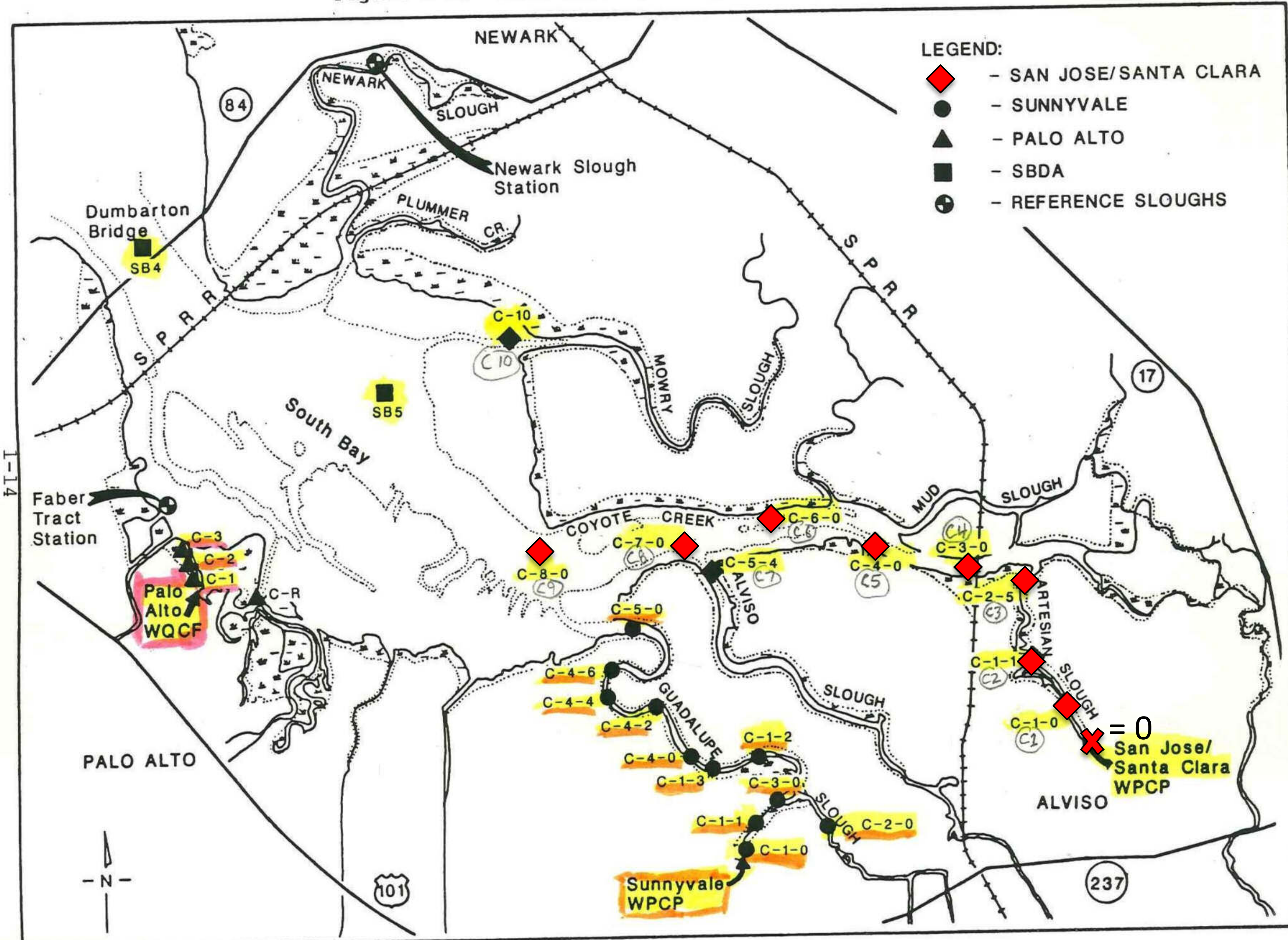






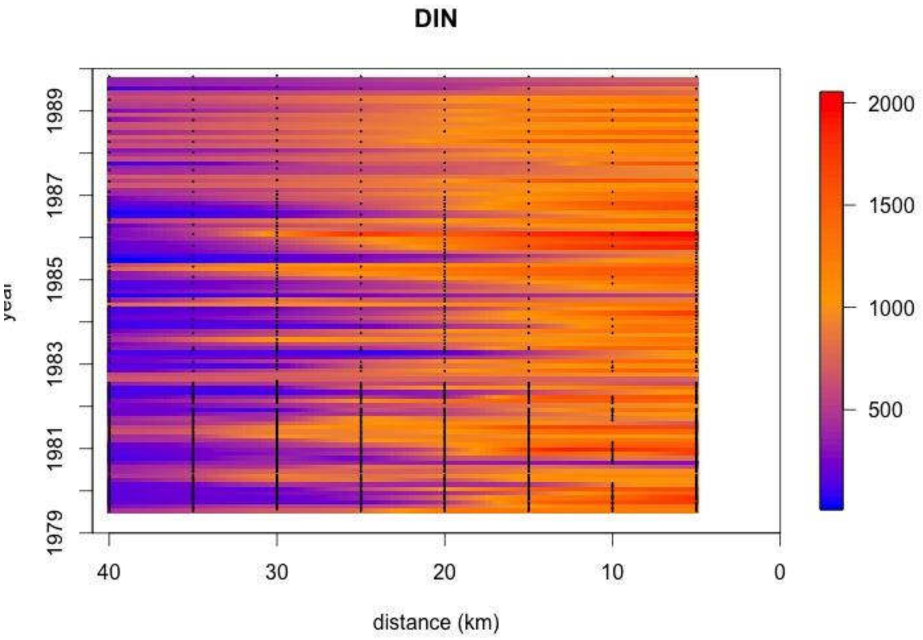
Novick and Senn 2013

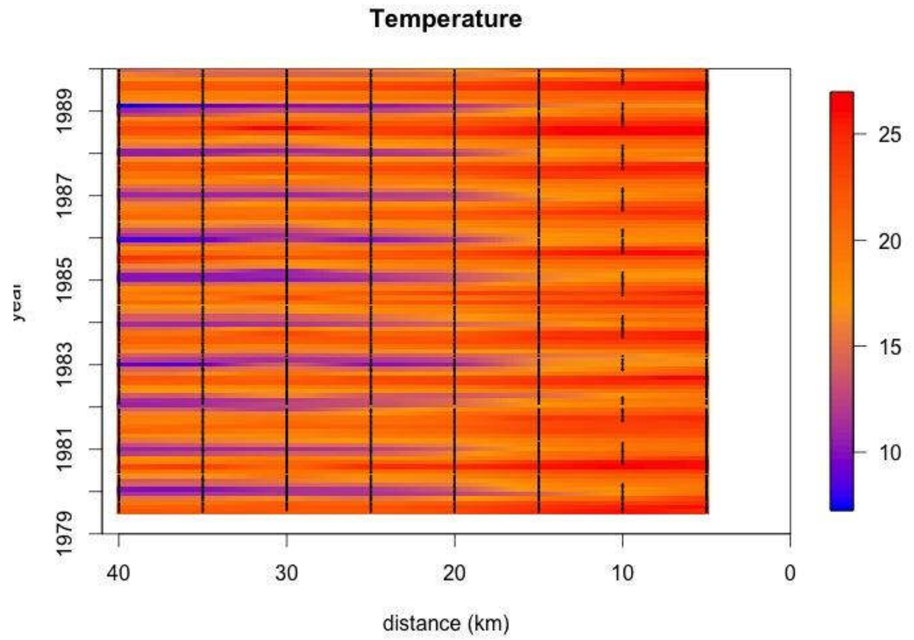
Figure 1-1. SBDA Water Quality Monitoring Stations

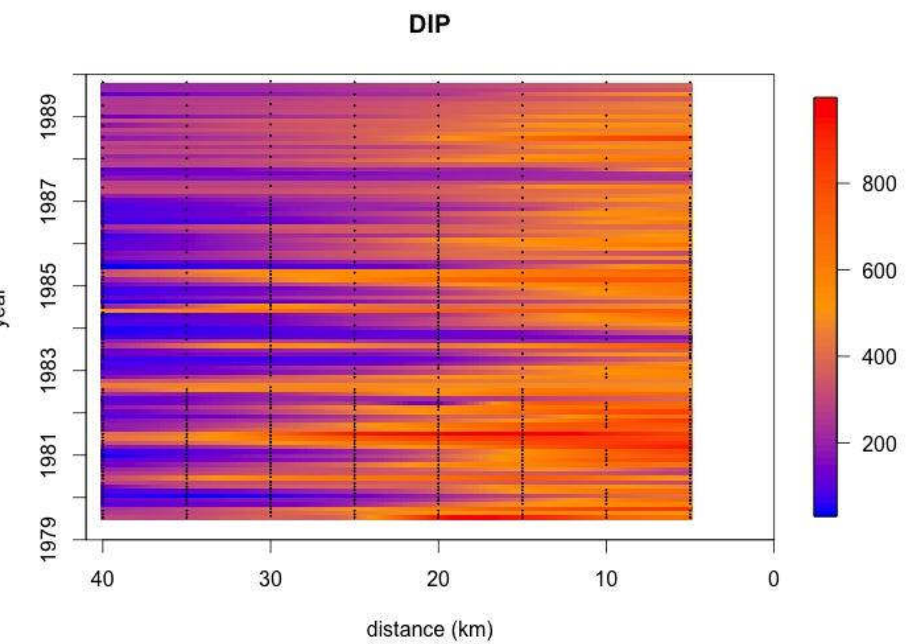


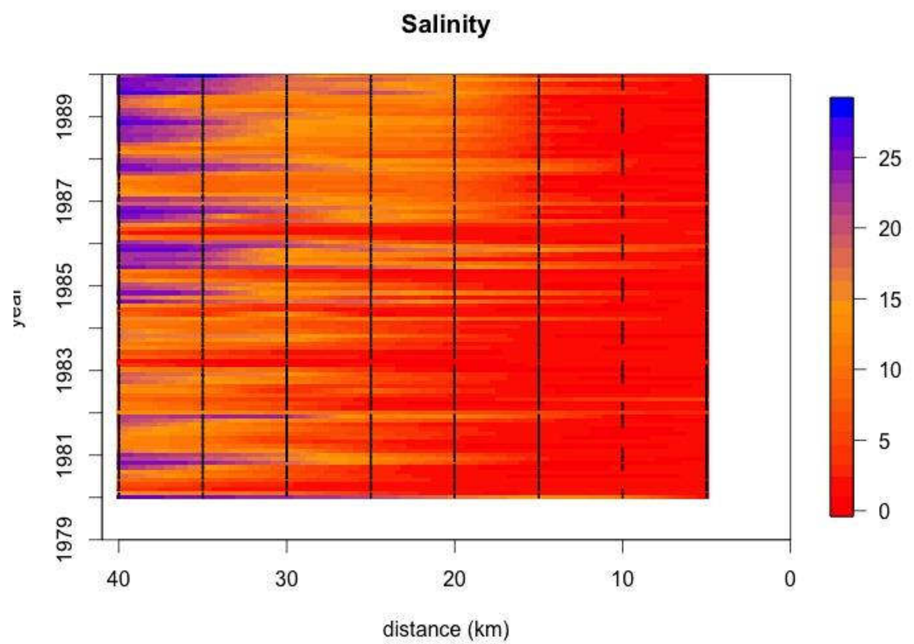
1-14

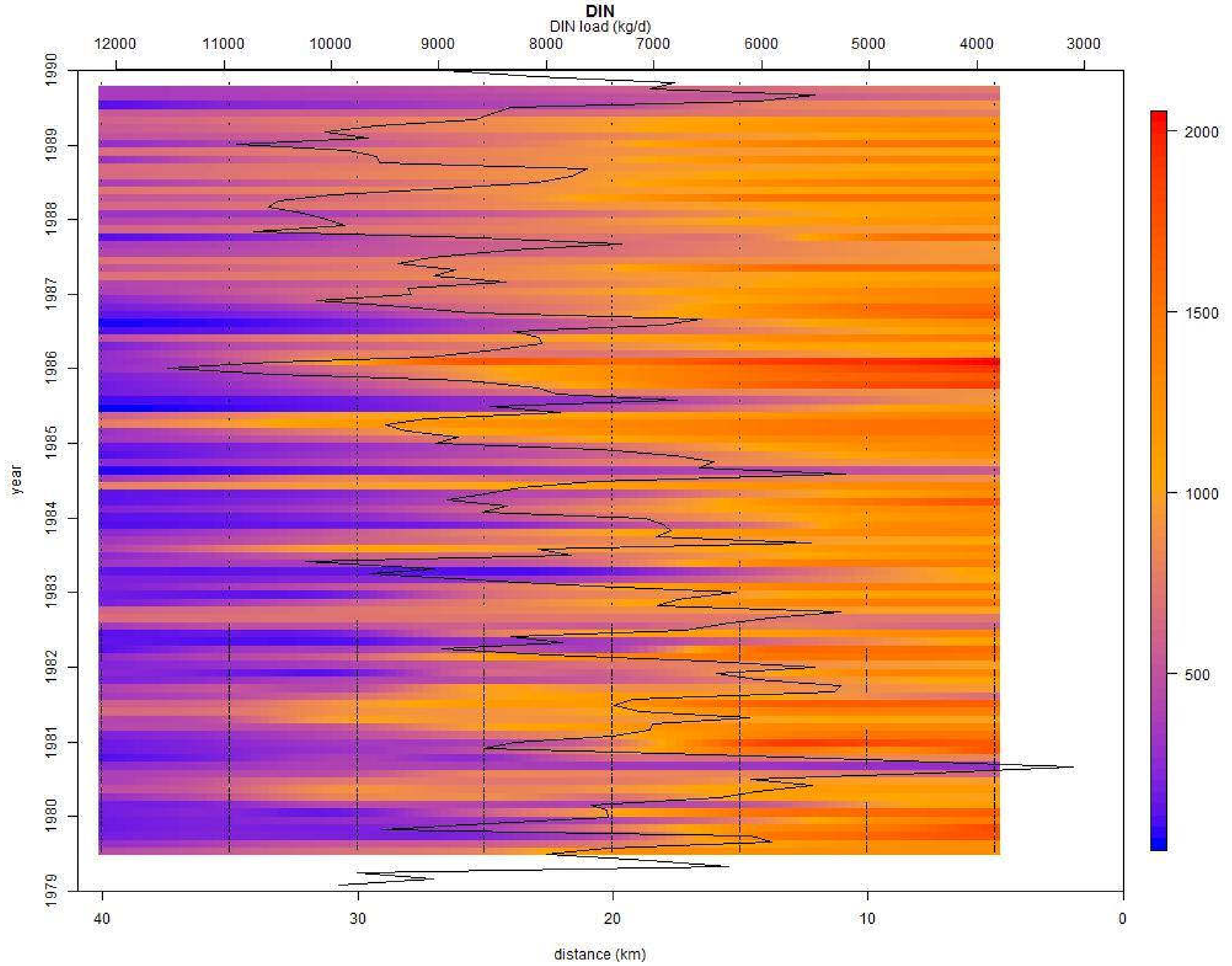
SBDA monitoring data: 1979-1989

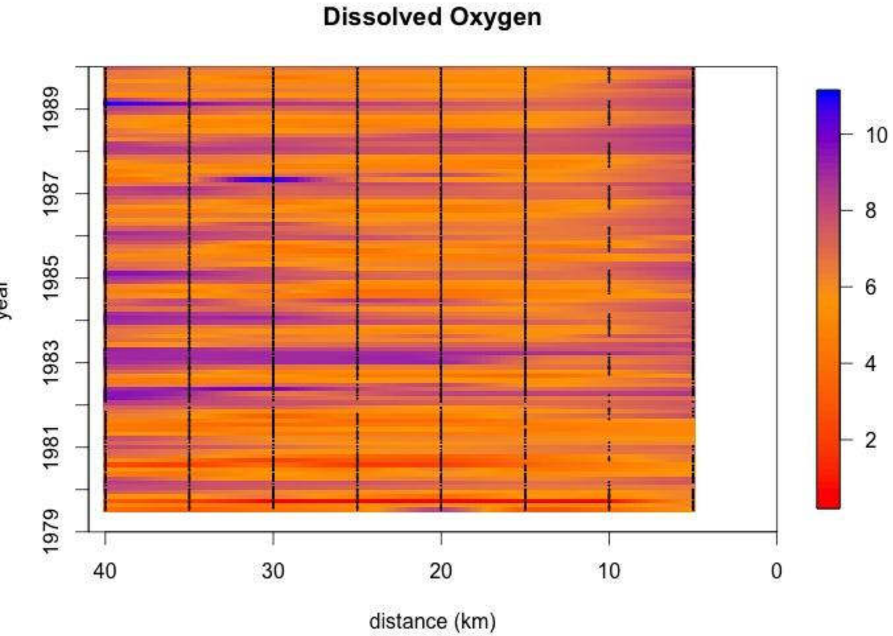


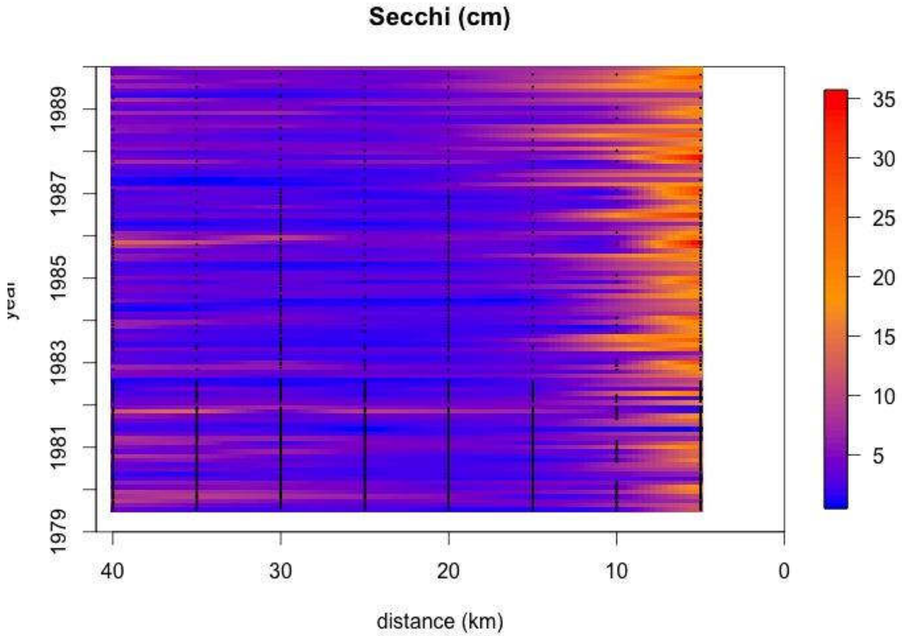






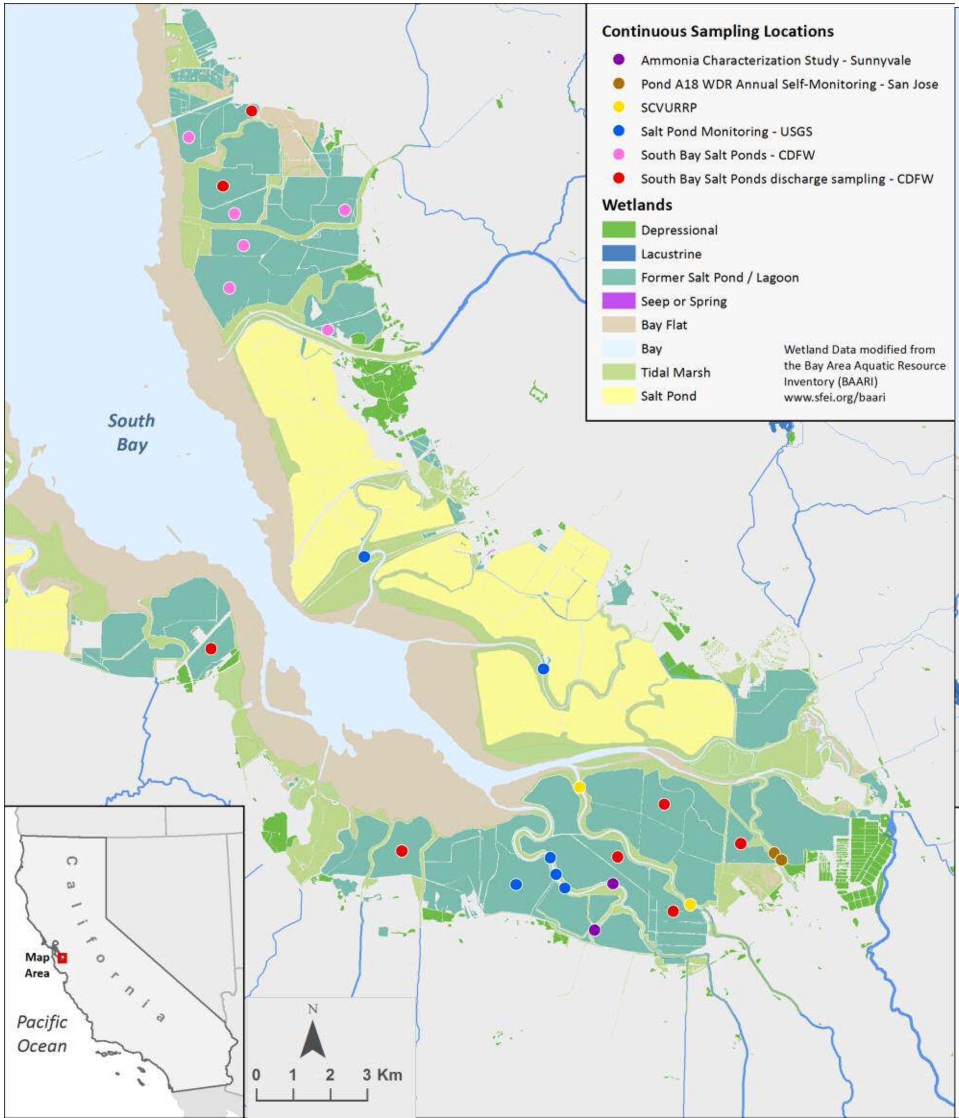

DIN
DIN load (kg/d)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
year
1990
1989
1988
1987
1986
1985
1984
1983
1982
1981
1980
1979
40
30
20
10
0
distance (km)
2000
1500
1000
500


Dissolved Oxygen
year
1979
1981
1983
1985
1987
1989
40
30
20
10
0
distance (km)
2
4
6
8
10

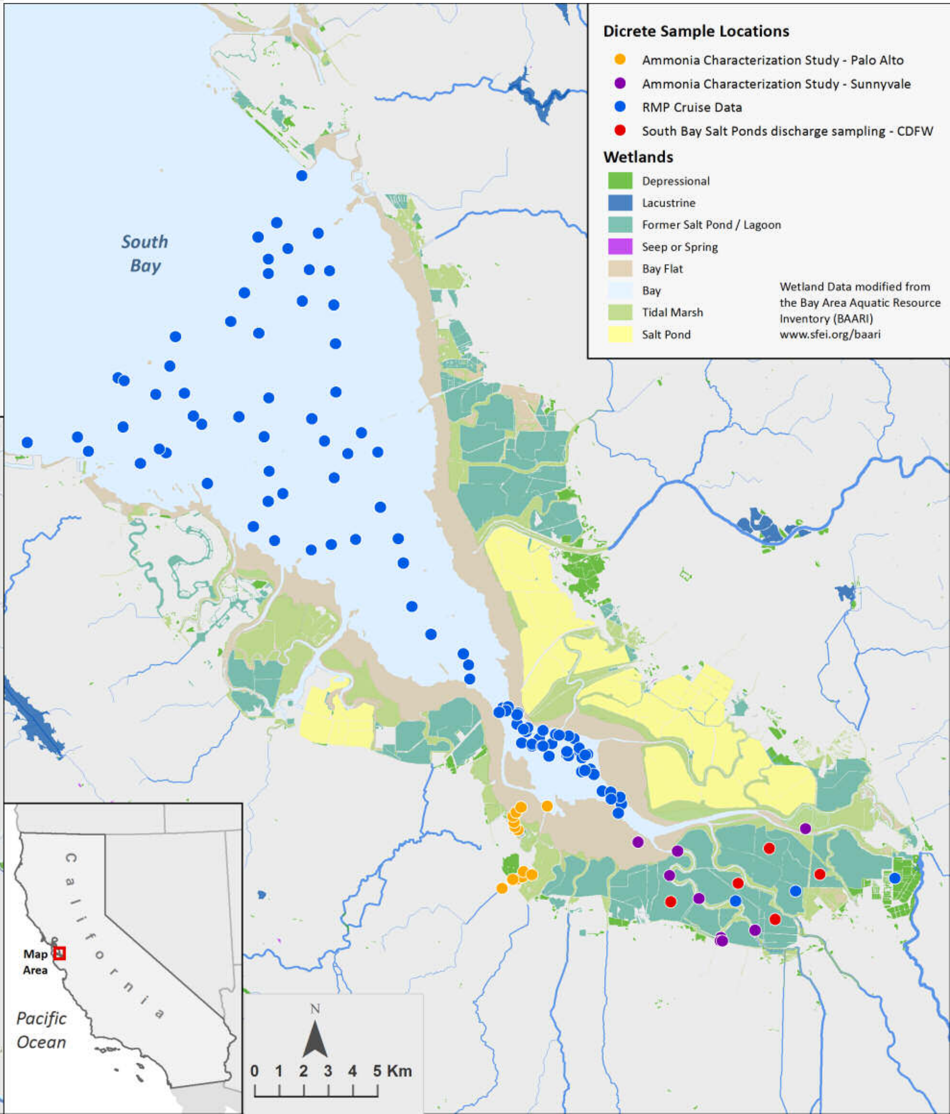

Secchi (cm)
year
1979
1981
1983
1985
1987
1989
40
30
20
10
0
distance (km)
5
10
15
20
25
30
35

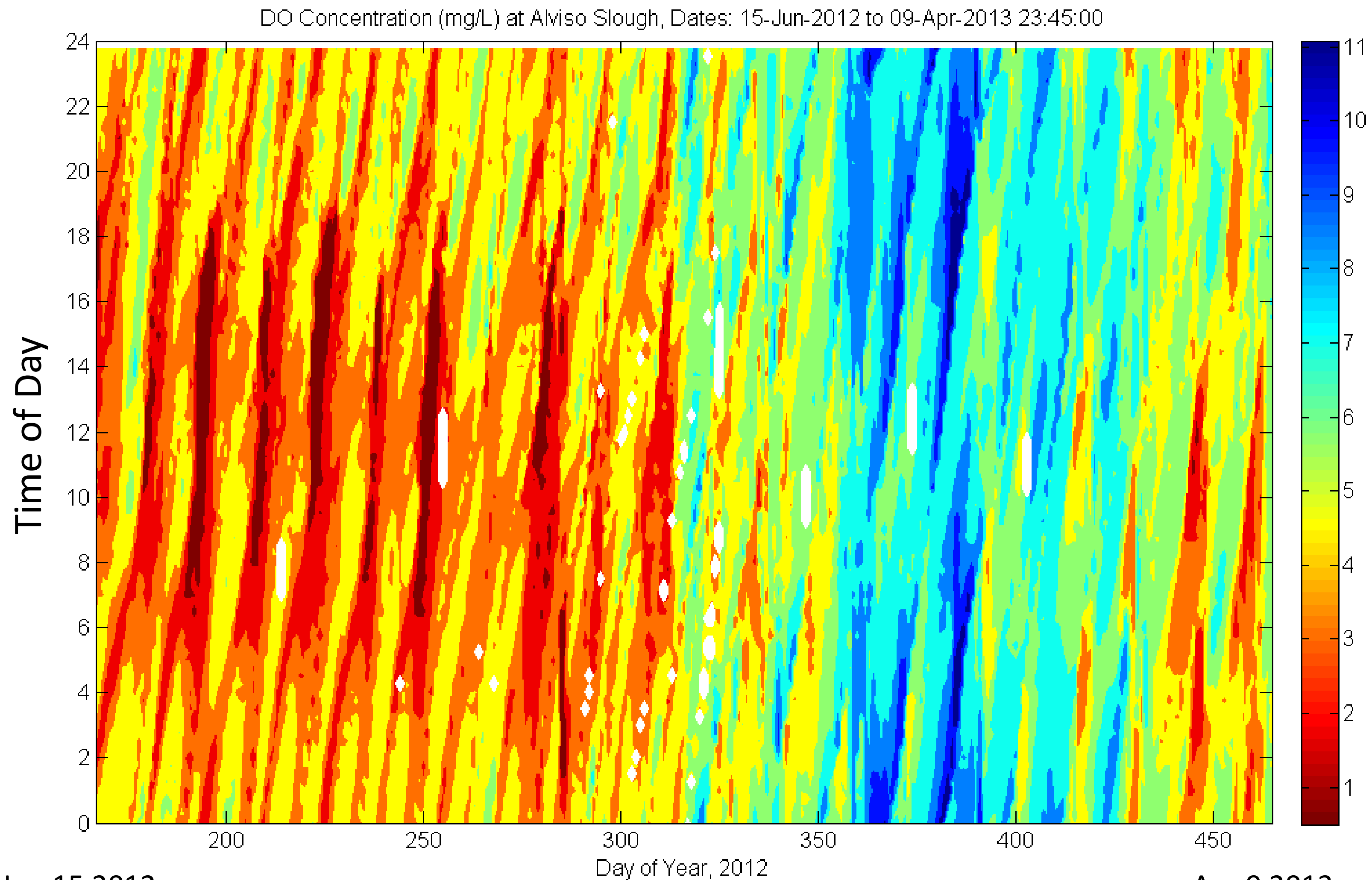
Analysis of dissolved oxygen data in Lower South Bay

Continuous



Discrete



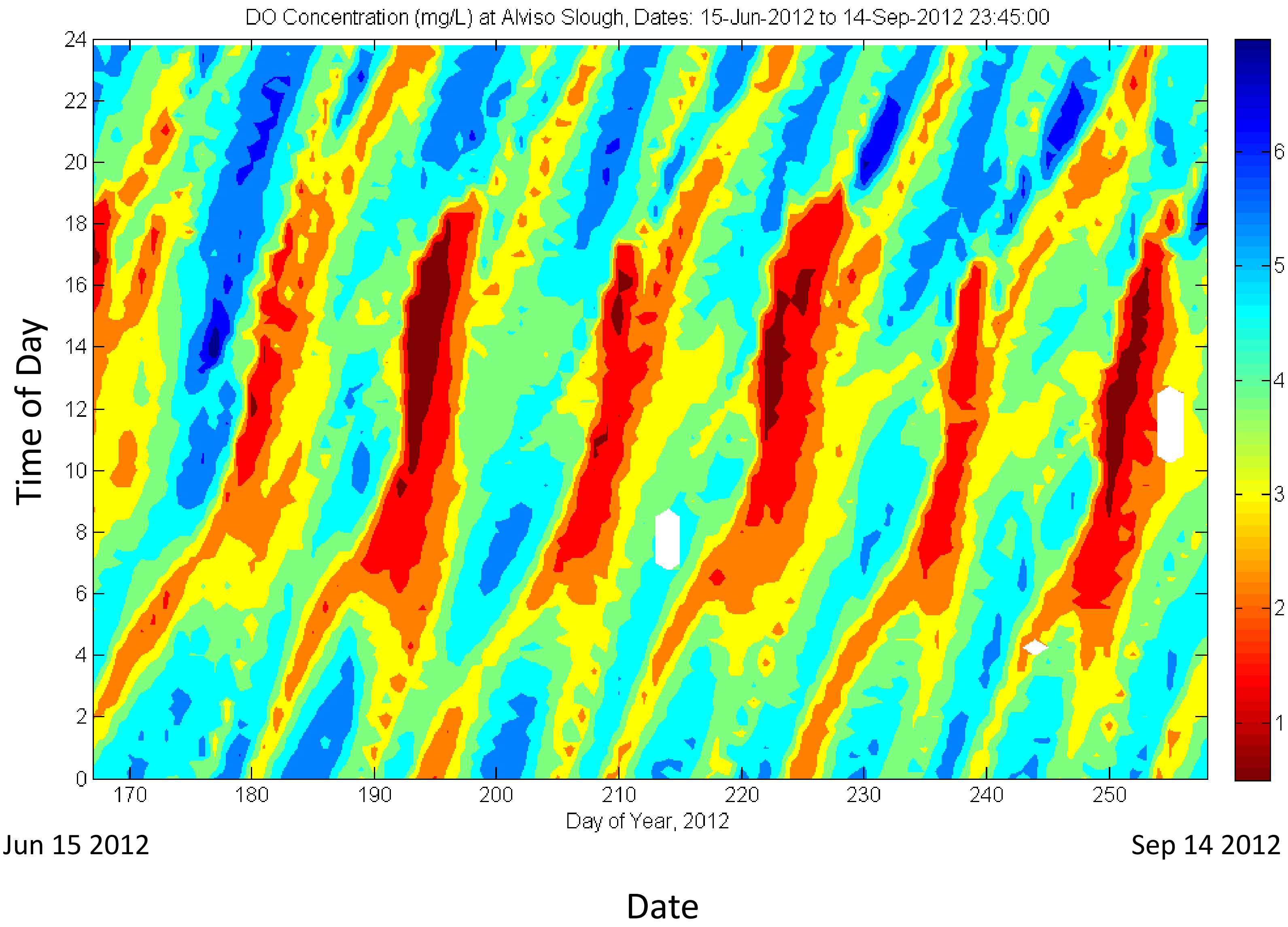


Jun 15 2012

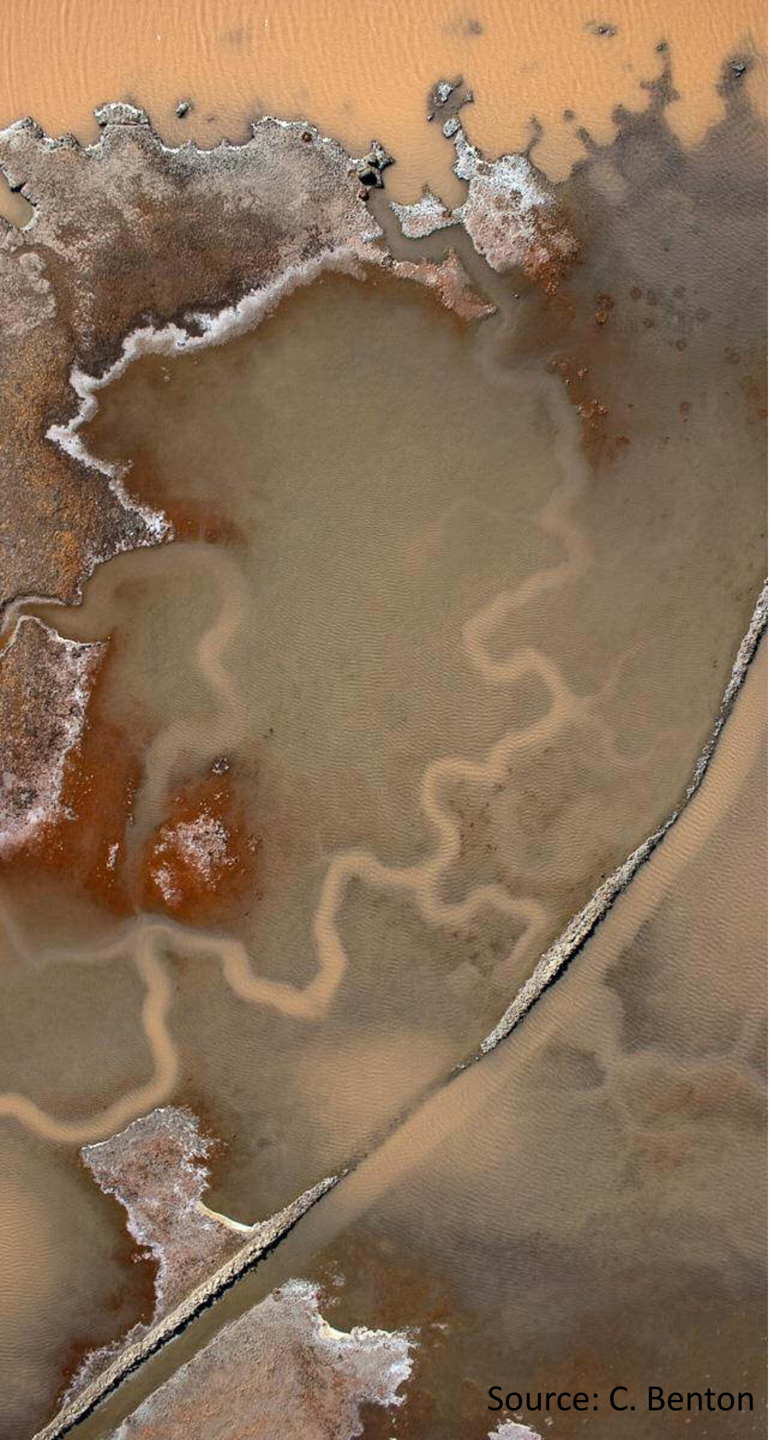
Apr 9 2013

Date

Data: M Downing-Kunz, USGS



Data: M Downing-Kunz, USGS


Source: C. Benton

Acknowledgements:

Funding: Regional Monitoring Program; State Water Resources Control Board; Bay Area Clean Water Agencies (BACWA)

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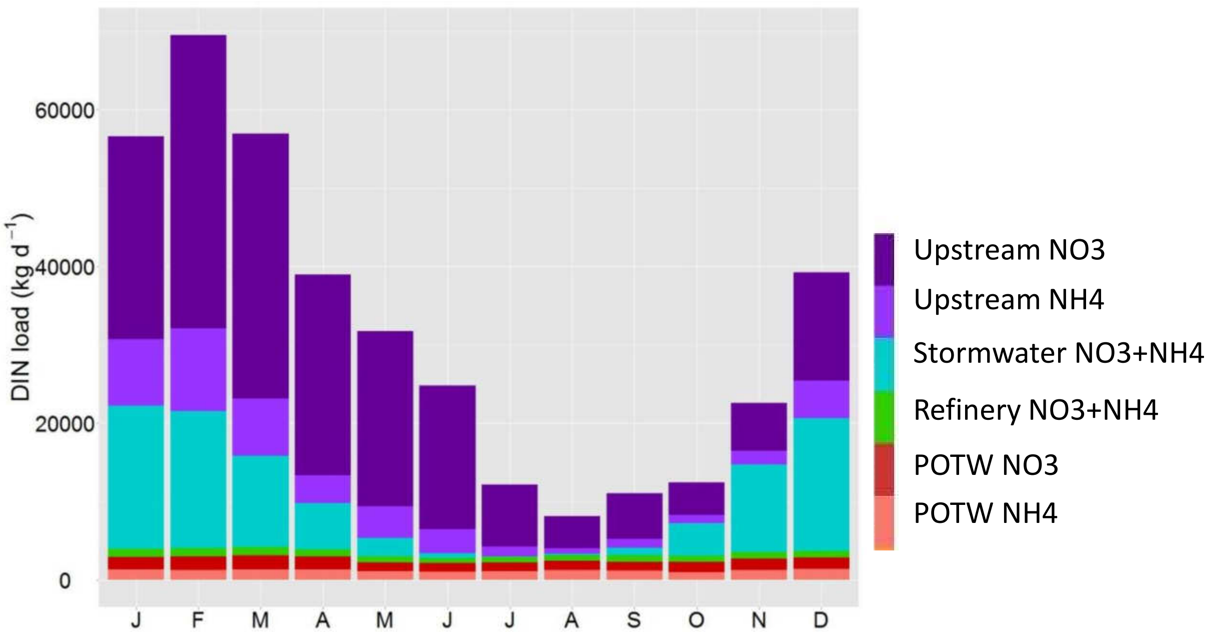
Update: Stormwater Nutrient Load Estimates

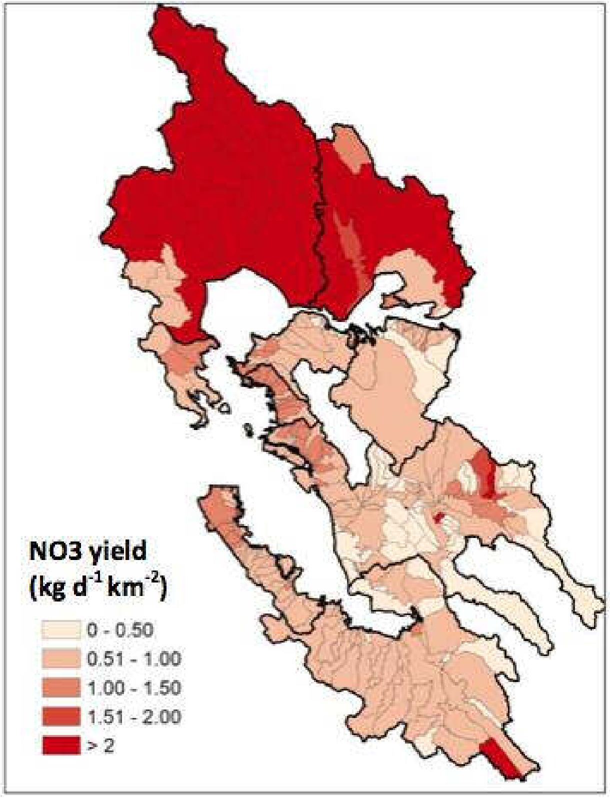
TRC Meeting

September 17, 2013

Background

- RMP-funded loading study suggested that stormwater loads potentially be substantial nutrient sources in certain Bay segments





Proposed Stormwater Nutrient Study

- Compare RWSM estimates to other model-derived load estimates, and identify potential next steps

- Develop a hydrological simulation model

  to improve load estimates and quantitatively explore uncertainty

  $30,000 from 2013 and $50,000 from 2014

Effort to Date on Stormwater

- Initial effort focused on Napa River watershed

  - Existing hydrological and nutrient load modeling work

  - Nutrient concentrations in runoff from vineyard

  - Monitoring data for model development

Analysis of RWSM Load Estimates

- RWSM load estimates higher than estimates from SWAT and WARMF models

Model	Stormwater TDN load (kg N/day)	Total load (kg N/day)	Stormwater % of total
SWAT	562	830	68
WARMF	567	873	65
RWSM	3060	3680	83

- Nutrient concentrations (1.3 mg/L NH_4^+ and 8.9 mg/L NO_3) used in RWSM compatible with literature values
  2.6-25.5 mg/L TN in Spain, 4.7-6.0 mg/L TN in Australia

- Nutrient loss in river system could be substantial
  57% in-stream loss according to SWAT. Could bring RWSM estimates down to 1300 kg N/day

[1] Soil and Water Assessment Tool
[2] Watershed Analysis Risk Management Framework

Review of Monitoring Data for Model Development

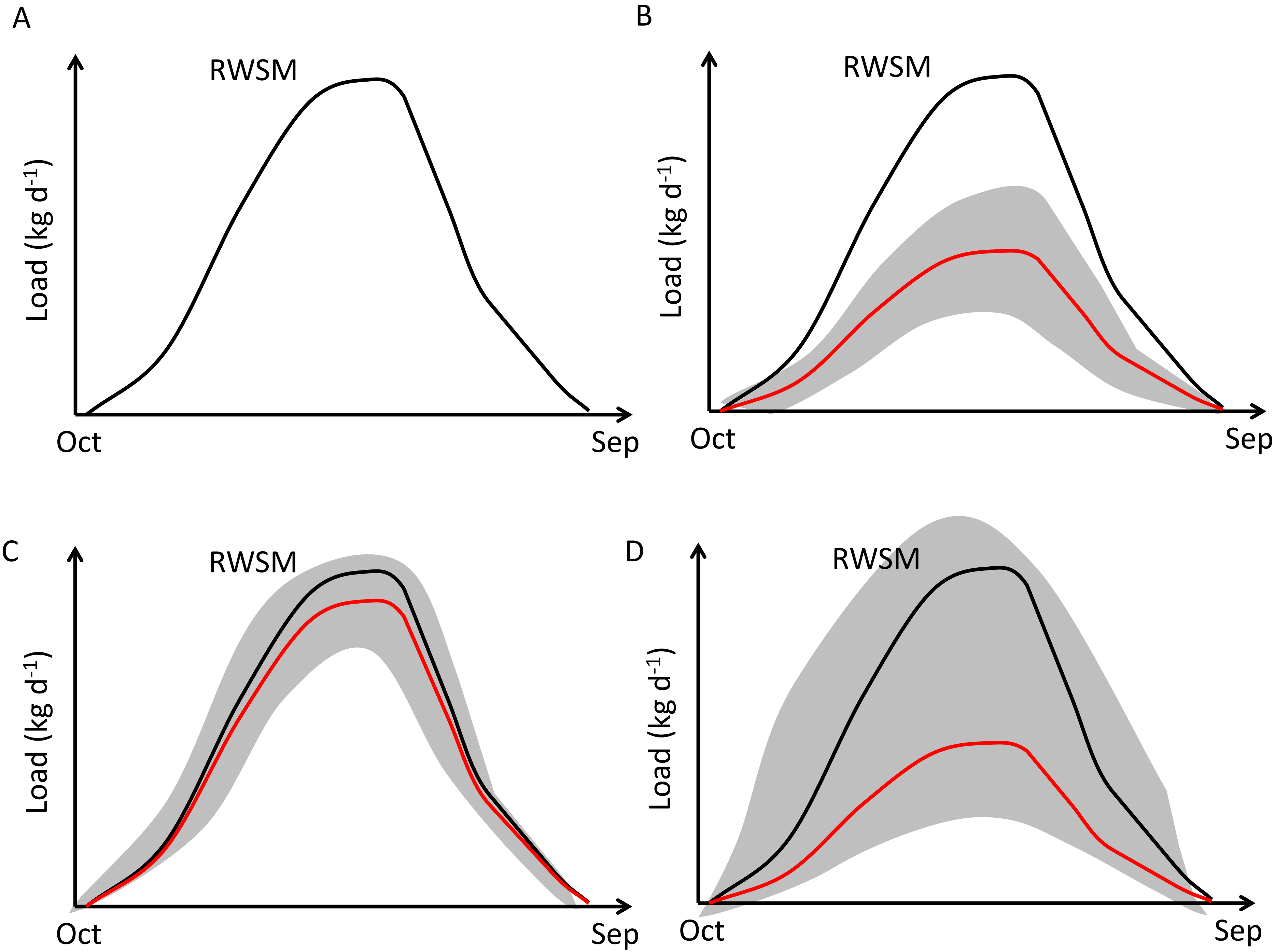
- Two USGS stations with multi-decadal flow data
- Sparse nutrient data, mostly collected in dry weather

Station	Description	No of sampling
N-06	Napa R. @ Zinfandel Lane	8
N-03	Ritchey Ck. nr. Ranger Station	7
N-09	Napa R. @ Yountville Ecopreserve	7
N-02	Mill Ck. @ the old Bale Mill	6
N-11	Tulukay Ck. @ Terrace Court (close to N 44)	6
N-04	Napa Ck. @ Jefferson	5
N-05	Napa R. @ Calistoga Community Center	5
N-13	Murphy Ck. @ "Stone Bridge" on Coombsville Road	5
N-18	Brown Valley Ck. @ "Little Stone Bridge"	5
N-26	Bell Canyon Ck. @ Silverado	5
N-52	Salvadore Channel @ 121 near school	5

Next Steps – Four Options

- Develop and apply a mechanistically-based hydrological and nutrient load model
- Apply existing Brake Pad Partnership Cu model or Bay Area Hydrological Model
- Refine the existing WARMF model to focus primarily on the nutrient-related uncertainty
- Stop, or pause for the time being. Reallocate $50,000 to within-Bay modeling

Option	Description	Pros	Cons
A	Develop and apply a mechanistically-based hydrological and nutrient load model	• Allows for quantitatively exploring uncertainty • Use beyond this specific project, in other contaminant studies or other watersheds • SFEI likely to invest heavily in similar platforms for stormwater/LID projects	• Requires effort for model setup and hydrological calibration, which will carve into time (funding) available for exploring the nutrient goal • Limited data for nutrient calibration
B	Apply existing Brake Pad Partnership Cu model or Bay Area Hydrological Model	• Already calibrated for hydrology, faster start-up than Option A • Napa and Sonoma both calibrated, so can study two watersheds • Could be used to develop flow and load estimates for within-Bay modeling effort	• Unknown if possible to get the calibrated model (proprietary) • Extremely low spatial resolution • May eventually need to move to Option A. • Limited data for nutrient calibration
C	Refine the existing WARMF model to focus primarily on the nutrient-related uncertainty	• Already calibrated for hydrology and limited calibration for nutrient • Much higher spatial resolution than Option B (but similar resolution as A)	• User interface may substantially limit the types of uncertainty analysis that can be conducted • Not the ideal model for future stormwater/sediment/nutrient work
D	Stop, or pause for the time being. Reallocate $50,000 to within-Bay modeling	• Helpful reallocation of resources if stormwater loads unlikely a high priority • The within-Bay modeling work would benefit from the additional funds	• Lingering uncertainty about stormwater loads • Missed opportunity to develop a model platform in-house for RMP for future applications



A
RWSM
Load (kg d-1)
Oct
Sep
B
RWSM
Load (kg d-1)
Oct
Sep
C
RWSM
Load (kg d-1)
Oct
Sep
D
RWSM
Load (kg d-1)
Oct
Sep

Regional Watershed Spreadsheet Model (RWSM) UPDATE

Lester McKee

Clean Water Program
San Francisco Estuary Institute
Richmond California

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2013 STLS budget and activities at a glance

- Total 2013 Budget - $468k
  - Pollutants of Concern (POC) Monitoring - $343k
  - Regional watershed spreadsheet model (RWSM) - $25k
  - Event Mean Concentration (EMC) Development - $80k
  - Management support to help ensure full coordination - $20k

RWSM objectives and reporting

- Improve regional average annual estimates of suspended sediment and pollutant loads
  - Support prioritization and management of “high leverage” watersheds in relation to sensitive areas of the Bay margin
  - Provide input data for food web models of the Bay
  - Help prioritize watershed “patches” for management
- Reporting template has been developed and approved through STLS

RWSM basic model structure

For each watershed, generate average annual:

- Discharge volume
- Sediment load
- POC loads

Runoff volume* x Concentration = Load

*or sediment load

RWSM plan

Hydrology
Suspended Sediment
Cu (Test Case)
Hg
PCBs
Selenium
OC Pest
PBDEs

1) Develop fact sheet/methodology

2) Develop GIS layers

3) Collate input data and calibration data

4) Run Version 1 of the model

5) Improve model structure or input data

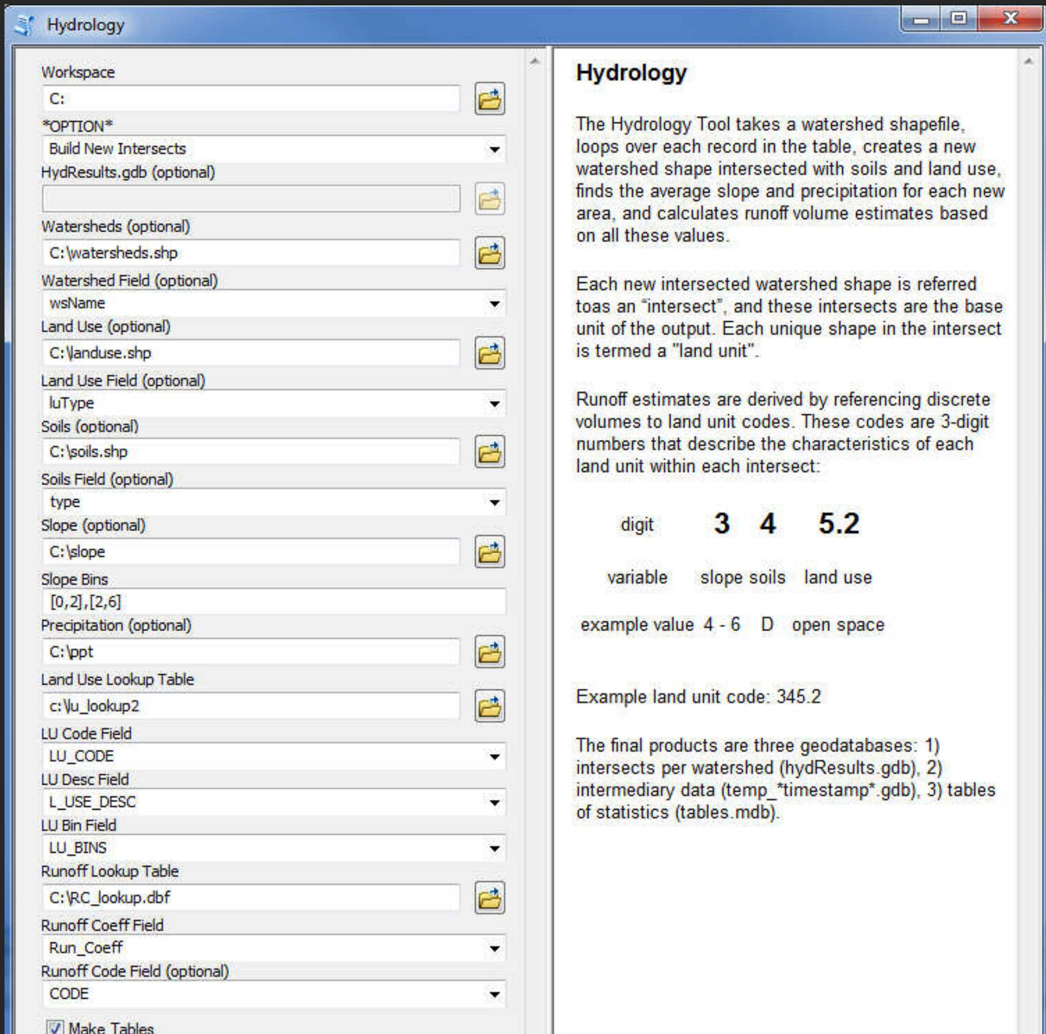
6) Run Version 2 of the model

7) Complete FINAL input dataset

8) Run Version 3 (FINAL) of the model

9) Complete model packaging and user manual

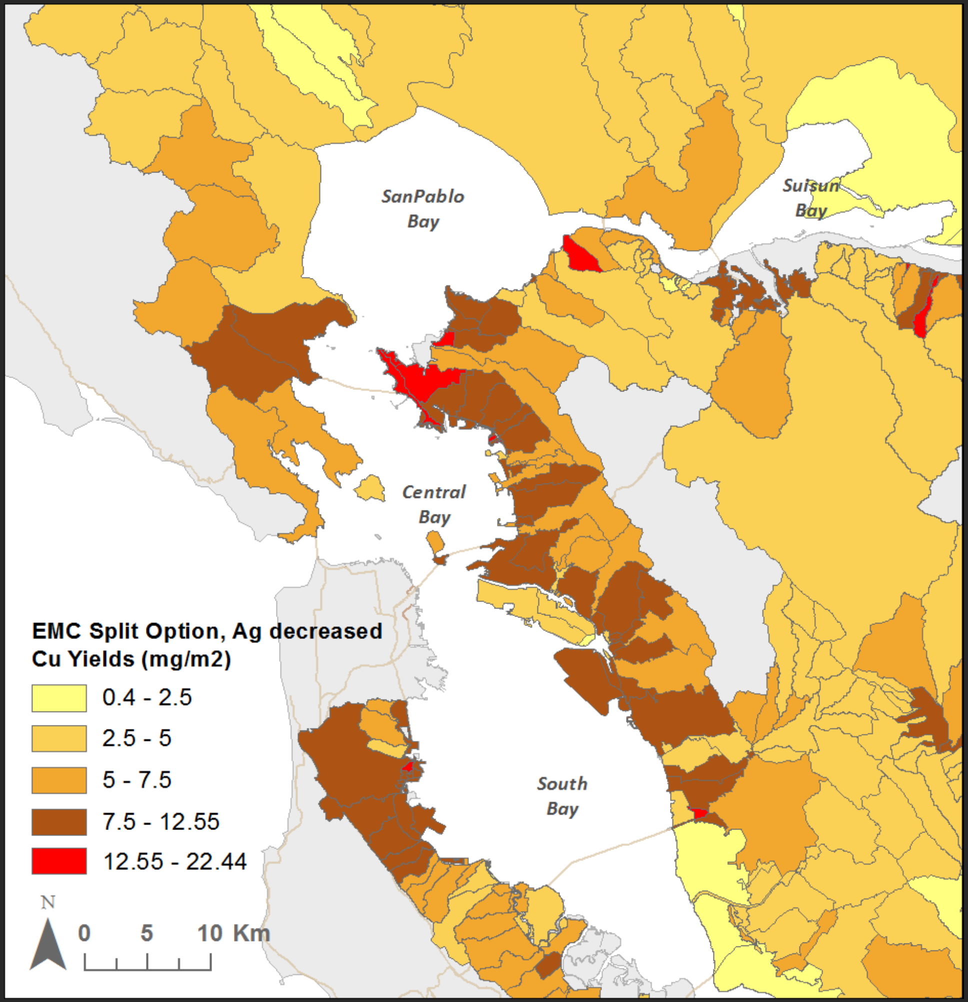
Tool input interface



- Started with ArcGIS standard tool interface
- Advance user-interface GUI was developed for easier manipulation by a moderately-able GIS user
- All parameters have help text

Copper test case model

- Example of output
  - 10 “Highest” yielding watersheds
- Can start to imagine what the PCB and Hg model outcomes will look like

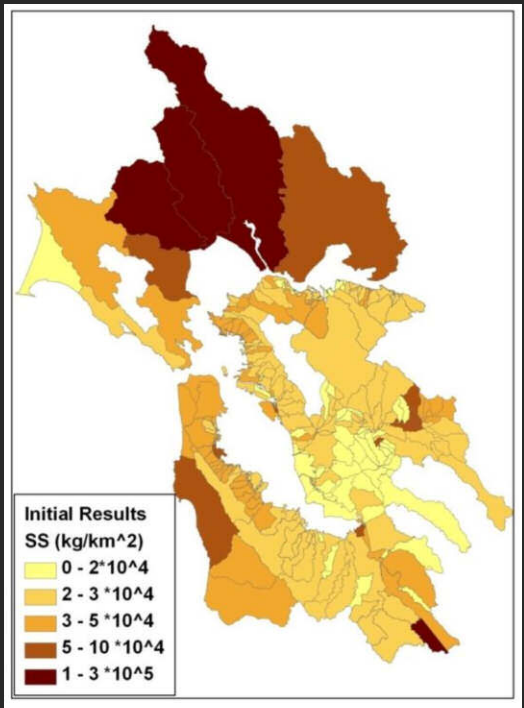


Improved basis for local sediment coefficients

- Old model
  - Land use and a land use based yield (Lewicki and McKee, 2010)
  - Flow x land use based concentrations (Lent, RWSM V1)

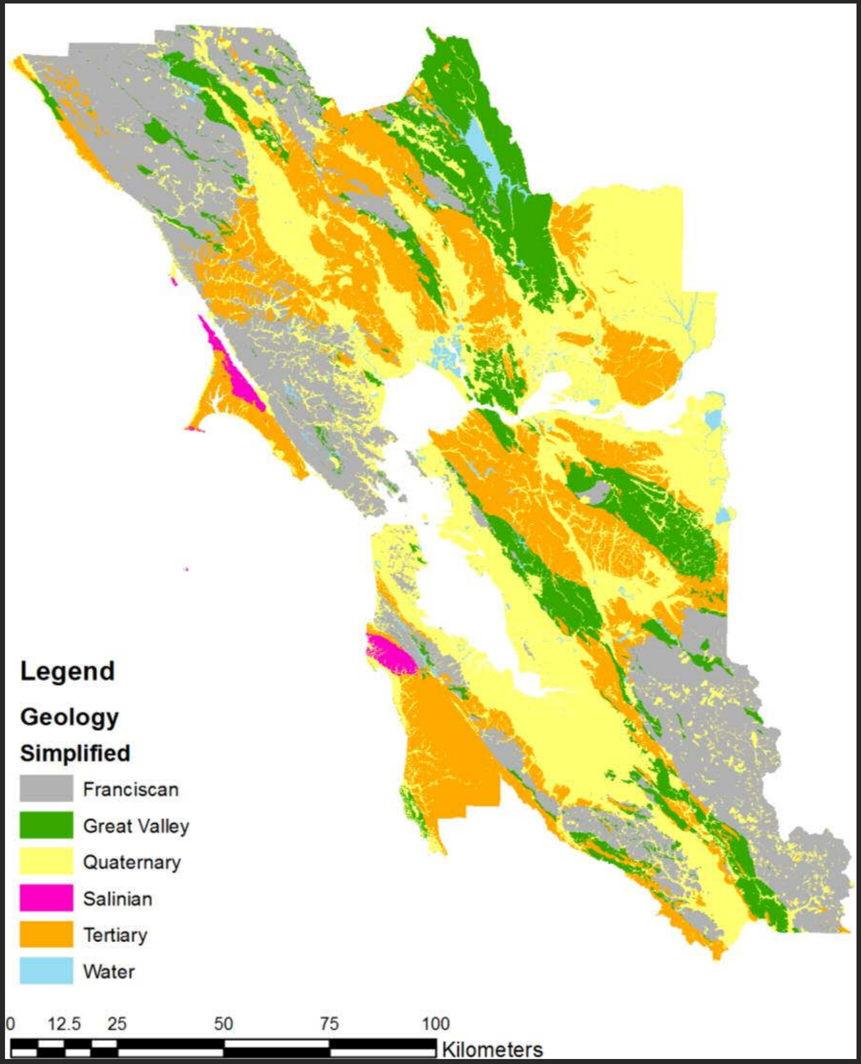
- MRP Provision C.8.e(vi) requires permittees to design a robust sediment delivery estimate/sediment budget for local tributaries and urban drainages

- New model (RWSM V2)
  - Geology
  - Slope
  - Land use

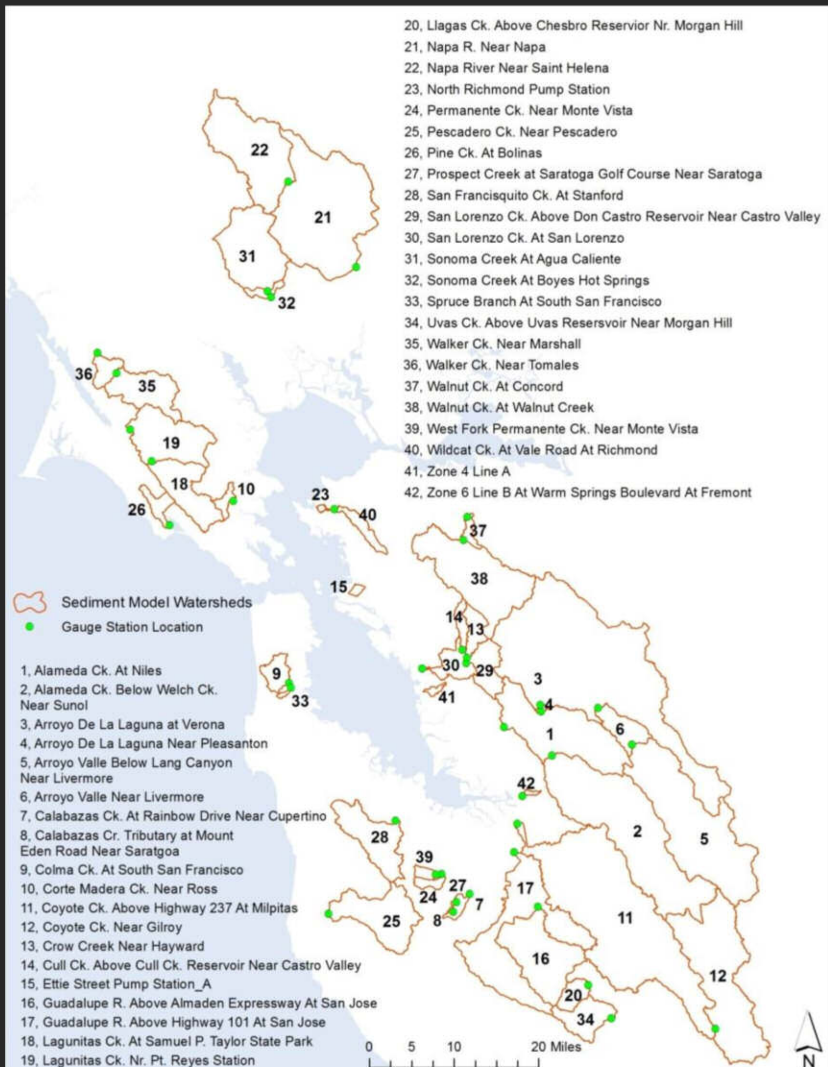


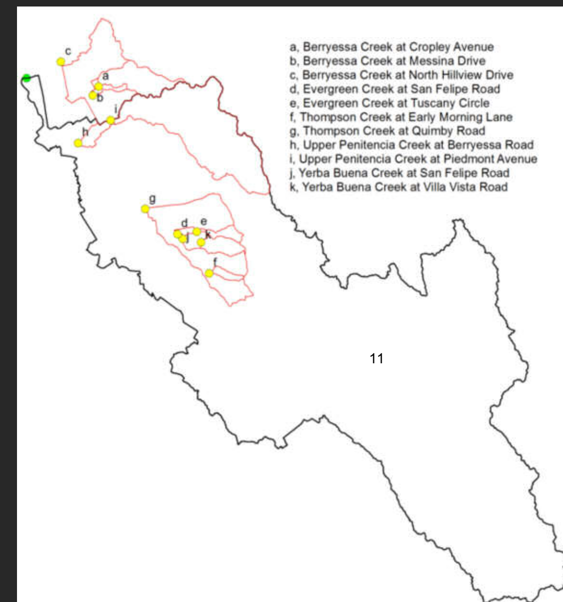
Bay Area simplified geology

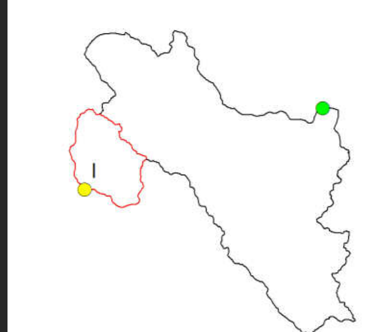
- USGS Geologic Map of the San Francisco Bay Region (Graymer et al, 2006)
- Five classes:
  - Franciscan
  - Great Valley
  - Quaternary
  - Salinian
  - Tertiary
- Three slope classes
  - <10; 10-30; >30 degrees



Updated suspended sediment data set

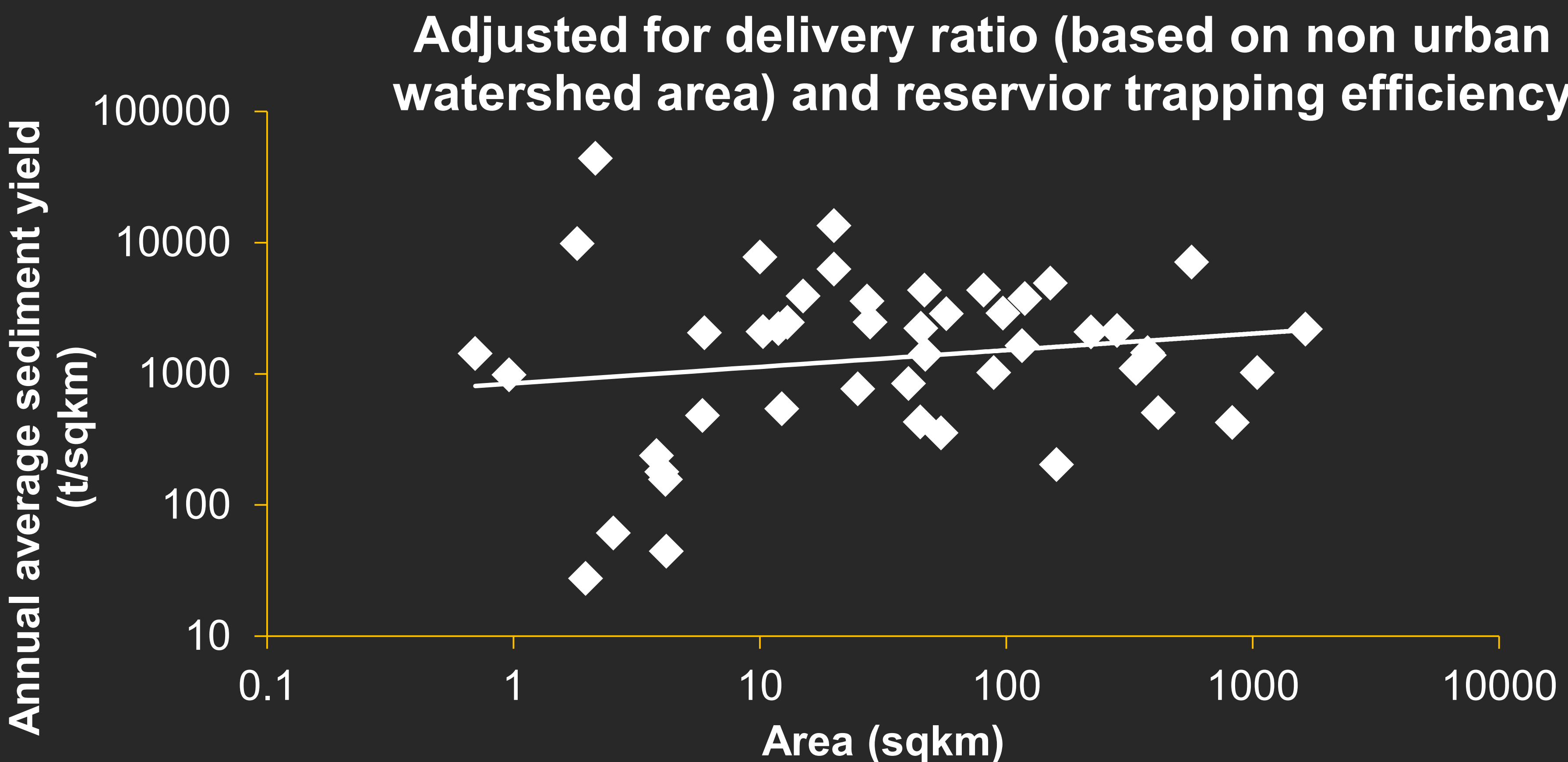






l, El Corte de Madera At Virginia Mill Trail

Area yield relation



- The affect of area largely removed

Results (Suspended sediment RWSM V2)

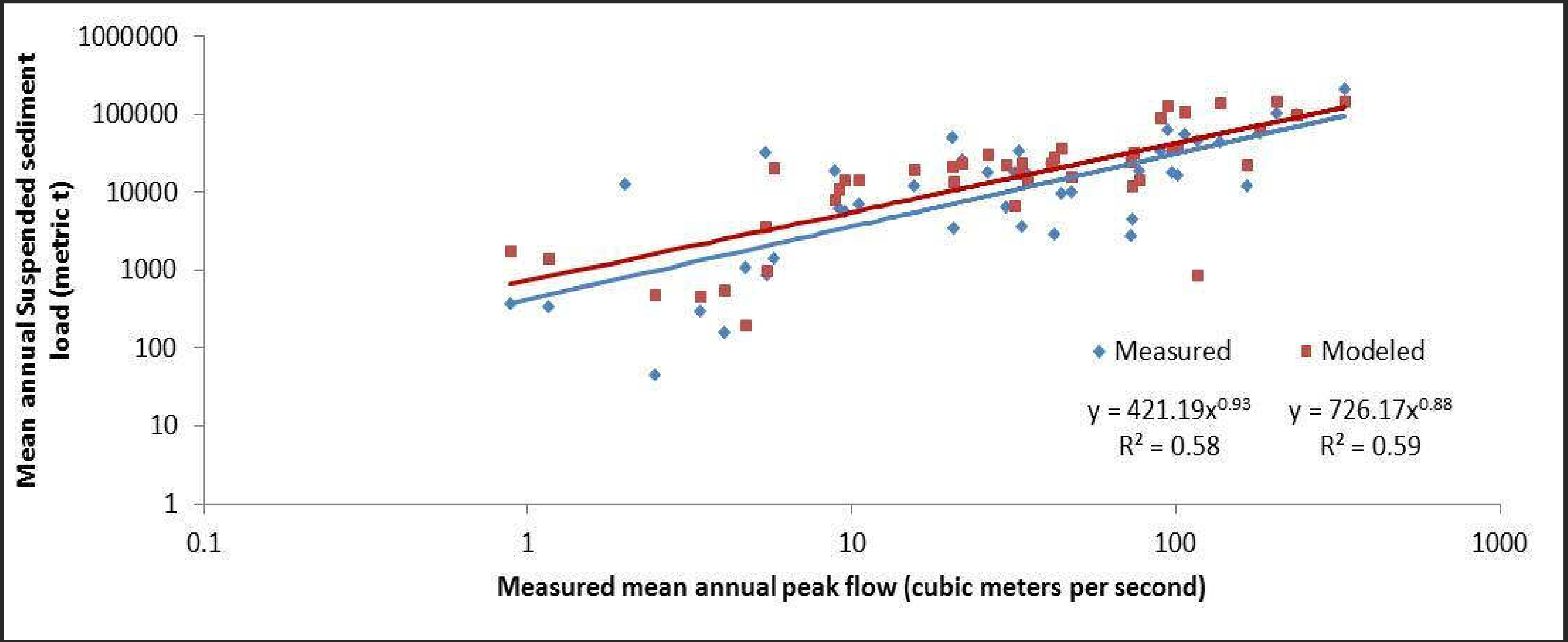
- Convened a local sediment experts workshop
  - Hecht, Haltiner, Sklar, McKee, Pearce

- Completed the auto-calibration scripting recommended by Stenstrom ("the Box method")

Adjusted data watershed loads calibrations (% difference)	Baseline 5000	Baseline 10000	Baseline 20000	No Nesting	Close-Match Locations	Under-simulated Locations	Over-simulated Locations	Reduced Parameter Set (8)	Reduced Parameter Set (6)
High quality data watersheds	-17	-8	-11	-70	17	13	-90	-86	-4
Medium quality data watersheds	48	76	72	-18	-17	101	-80	-71	82
Individual High/Medium watersheds calibrations (Min)	-48	-90	-96	-97	-53	-70	-100	-98	-29
Individual High/Medium watersheds calibrations (Max)	299	272	262	-1	236	349	23	-7	3697
All 46 watersheds	0	8	5						
All 32 non-nested watersheds	-	-	-	-55	-10	71	-88	-83	-2

  - Calibration unstable

How much is good enough?



- Next step - add a climatic factor (in progress)

PCBs and Hg GIS basis improved

Land use or source area	Data points assigned to each land use or source area	Median Hg (mg/kg)	Median Rank	Mean Hg (kg/kg)	Mean Rank
oilRefineries	1	0.98	1	0.98	2
recycDrums	3	0.67	2	0.68	3
Military	4	0.42	3	0.50	8
transpShip	14	0.35	4	0.51	7
recycMetals	4	0.32	5	0.53	5
electricPower	3	0.31	6	1.22	1
recycWaste	44	0.31	7	0.66	4
manufMetals	25	0.31	8	0.52	6
crematoria	47	0.14	9	0.18	10
oldIndustrial	197	0.13	10	0.20	9
transpAir	11	0.11	11	0.14	11

- **Completed a new GIS compilation of “source areas” using RMP and BASMAA funding**
- **Example of Hg sediment/soil concentration assignment**

PCB EMC input data improved

	GIS layers available in	PCBs conceptual concentration	Water (ng/L)				Sediment (mg/kg)											
			Method				Method										Variation (Max/Min)	Mean
			1	6	7	7	5	2	3	4	8	9	10	11	14	15		
All industrial	**Yes**		96				0.13										1	0.13
Older industrial	**20**	M									2.80	1.80		0.60	0.48	0.07	40	1.15
Newer industrial	**Yes**	M/L												0.093	0.23	0.03	8	0.12
Military	**1**	H						1.92	0.49	0.80				4.2	0.67	0.72	9	1.47
Electrical transformer and capacitor (manufacture/repair/testing/storage/use)	**12**	VH						10.71	0.46	1.33				36	0.01		3,600	9.70
Electric power generation								10.71	0.46	1.33				36	0.01		3,600	9.70
Cement production																		
Cremation	**4**																	
Oil refineries / petrochemicals		M						0.04	0.03	0.03				0.60	0.03	0.03	21	0.13
Manufacture (steel or metals)	**13**	M						3.16	0.11	0.73				0.60	0.15	0.06	53	0.80
Recycling (drum)	**1**	H						1.09	1.09	1.09				4.2	0.14	0.01	420	1.27
Metals recycling	**4**	M/L						1.78	0.76	0.80				0.093	0.15	0.04	44	0.60
Marine repair and marine scrap yards														0.093			1	0.09
Auto recycling/ refurbishing	**8**							0.60	0.11	0.17				0.093	0.37	0.02	30	0.23
General waste recycling / disposal	**7**													0.093	7.14	2.22	77	3.15
All transportation	**Yes**																	
Marina's																		
Transport (ship)		M						2.97	1.13	1.29				0.60	0.45	0.26	11	1.12
Transport (rail)	**Yes**							1.27	0.17	0.41		1.50	0.00061	0.60			2,459	0.66
Transport (air)	**4**														0.06		1	0.06
Freeways	**Yes**																	
Streets	**Yes**																	
Urban (except industrial)	**Yes**	L	32				0.088				0.083			0.011			8	0.06
Commercial	**Yes**														0.95	0.16	6	0.56
Older urban	**Yes**											0.15	0.15				1	0.15
High density residential	**Yes**														0.22	0.03	7	0.13
Low density residential	**Yes**																	
All nonurban	**Yes**	VL	19	1.15	0.35	4.32	0.0015				0.017	0.0140	0.00031	0.0009			55	0.01
Agriculture	**Yes**														0.03		1	0.03
Open space	**Yes**														0.23	0.01	23	0.12
Marine sedimentary geology / soils																		
																	Variation (Max/Min)	1,437

PCB and Hg models next steps

- **In summary**
  - ✓ GIS basis completed
  - ✓ Auto-calibration programming completed and tested
  - ✓ EMC data generation completed
  - ✓ Calibration data compiled
  - ✓ Unstable sediment V2 RWSM completed
- **Working on sediment RWSM V3**
- **Run PCB and Hg RWSM V2s as soon as we get a calibrated sediment model**

2014 STLS budget approved

- Total 2014 Budget - $487k
  - Pollutants of Concern (POC) Monitoring - $352k
  - Regional watershed spreadsheet model (RWSM) - $30k
  - Event Mean Concentration (EMC) Development - $80k
  - Management support to help ensure full coordination - $25k

QUESTIONS?