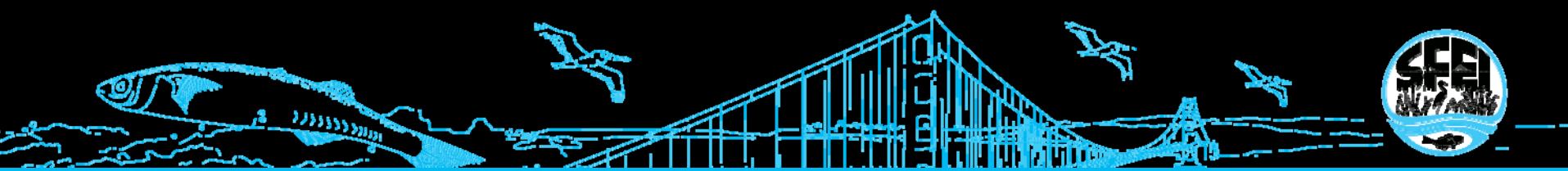
The New Generation of Contaminants That Could Affect the Bay: Flame Retardants, Pharmaceuticals, Perfluorinated Compounds

Mike Connor

San Francisco Estuary Institute

GETA Fall Meeting
October 2, 2007



Acknowledgements

Susan Klosterhaus, SFEI

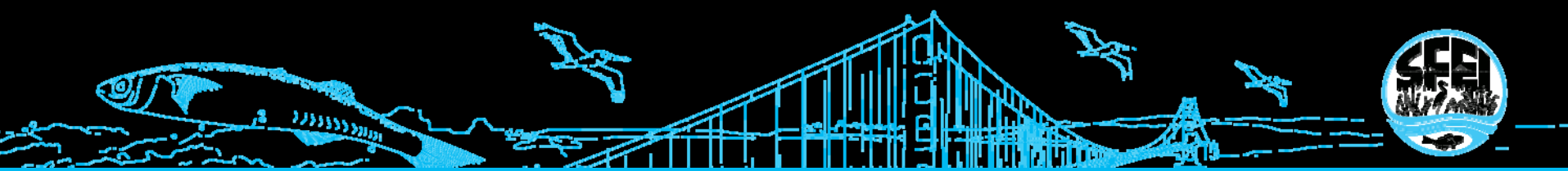
Meg Sedlak, SFEI

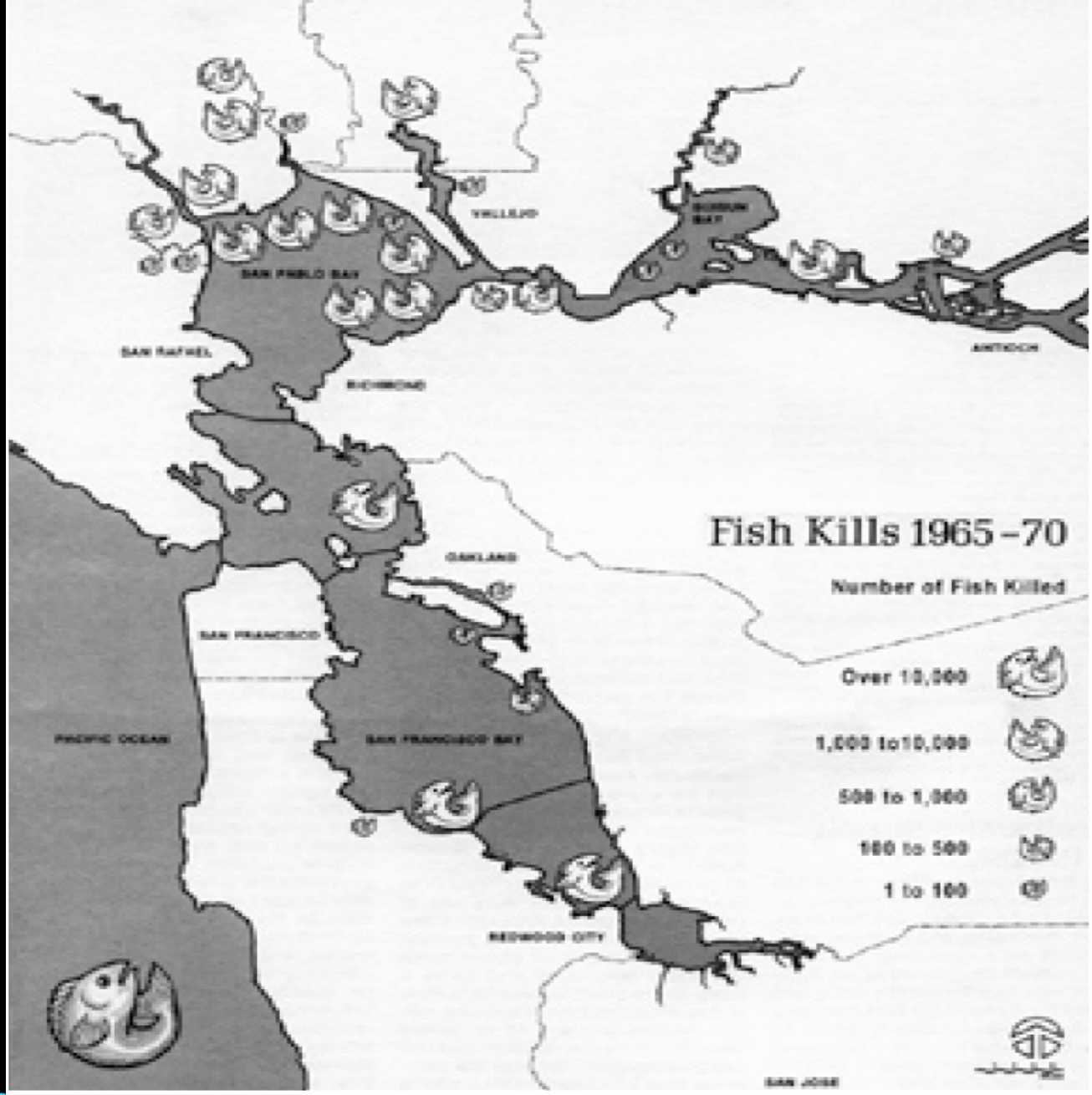
Don Weston, UCB

Kelly Moran,

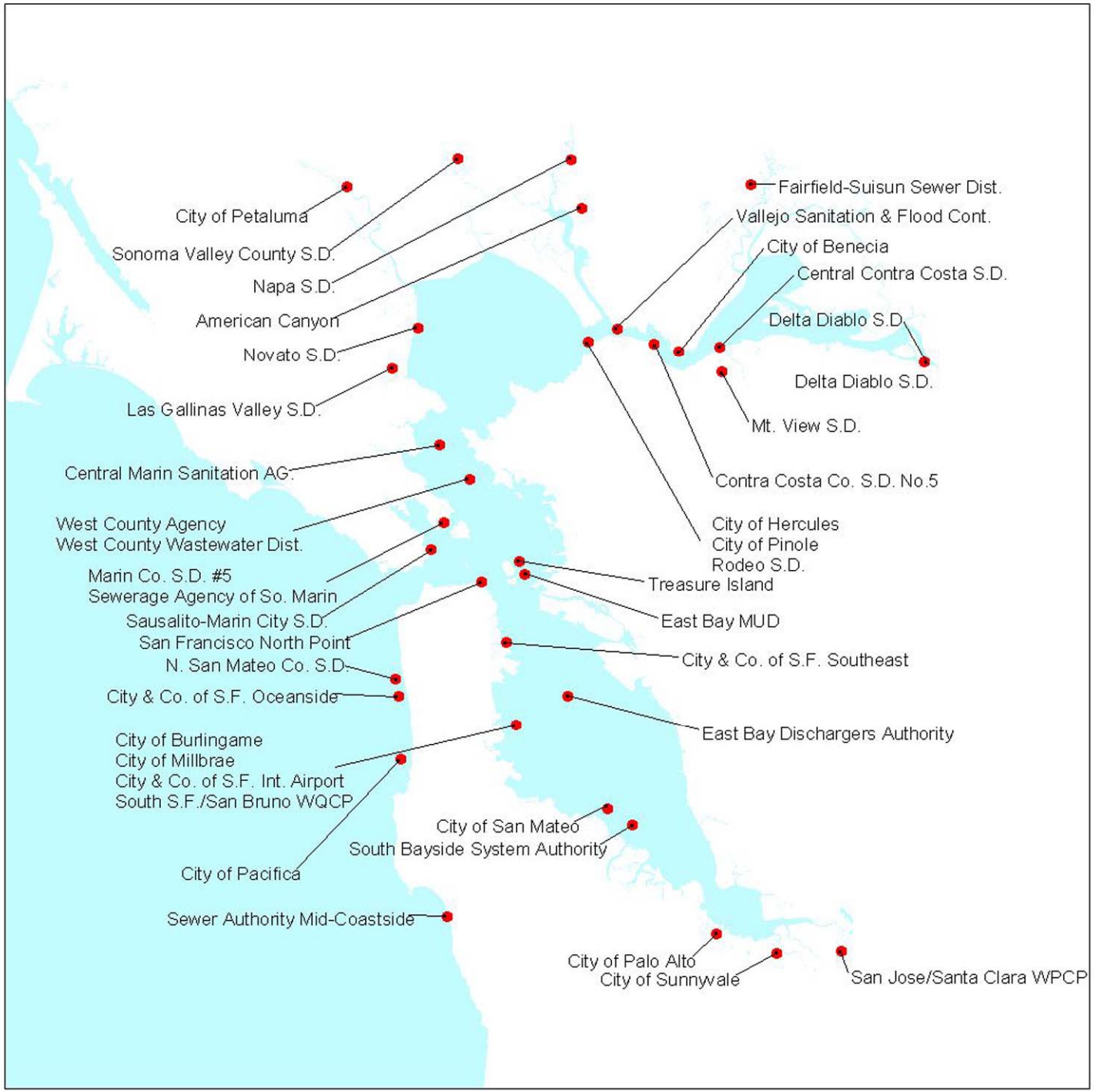
Karin North, Palo Alto WWTP

Kevin Kelley, CSU Long Beach

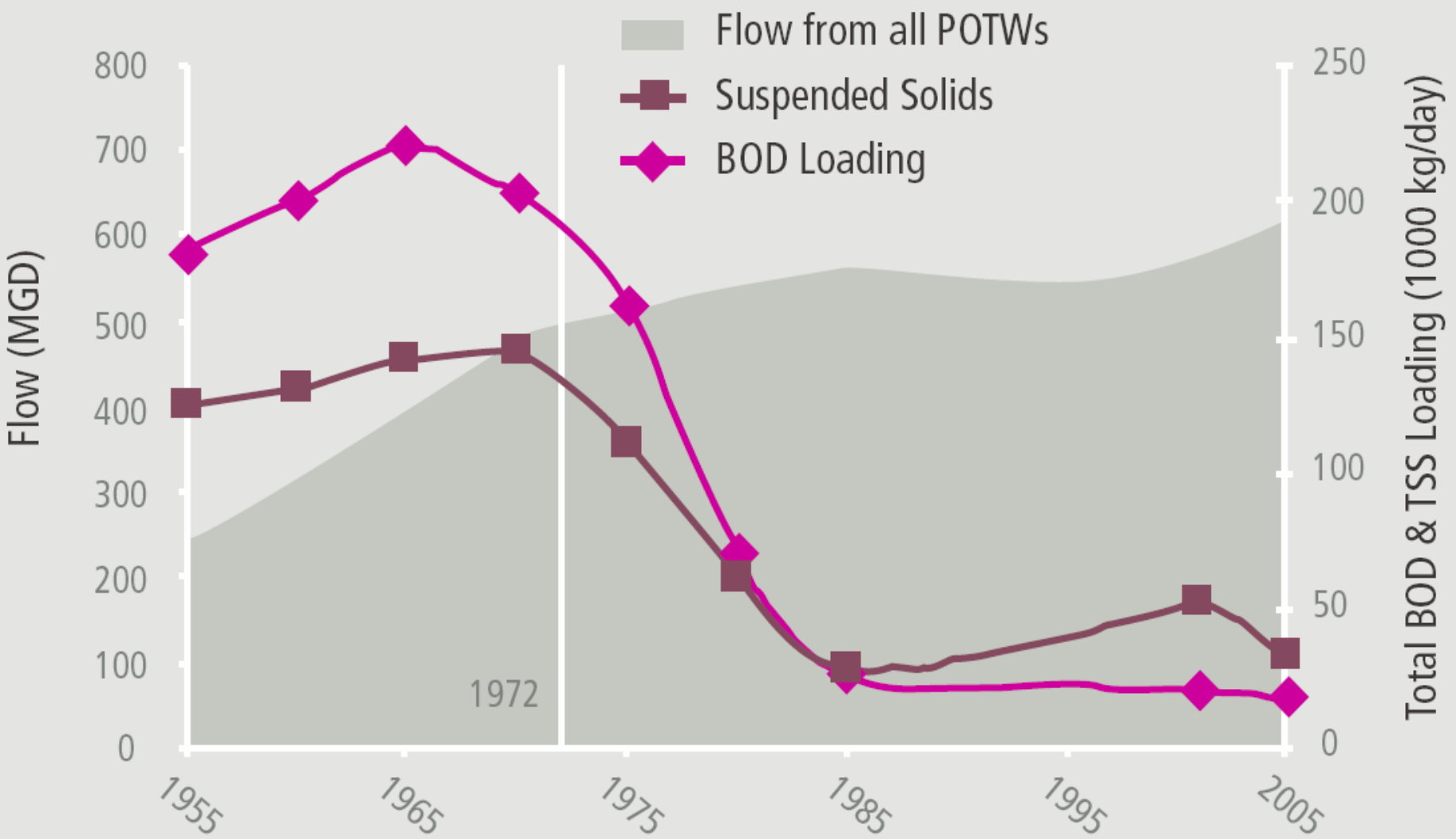



Fish Kills 1965–70
Number of Fish Killed
Over 10,000
1,000 to10,000
500 to 1,000
100 to 500
1 to 100
VALLEJO
SAN PABLO BAY
SAN RAFAEL
RICHMOND
ANTIOCH
OAKLAND
SAN FRANCISCO
PACIFIC OCEAN
SAN FRANCISCO BAY
REDWOOD CITY
SAN JOSE

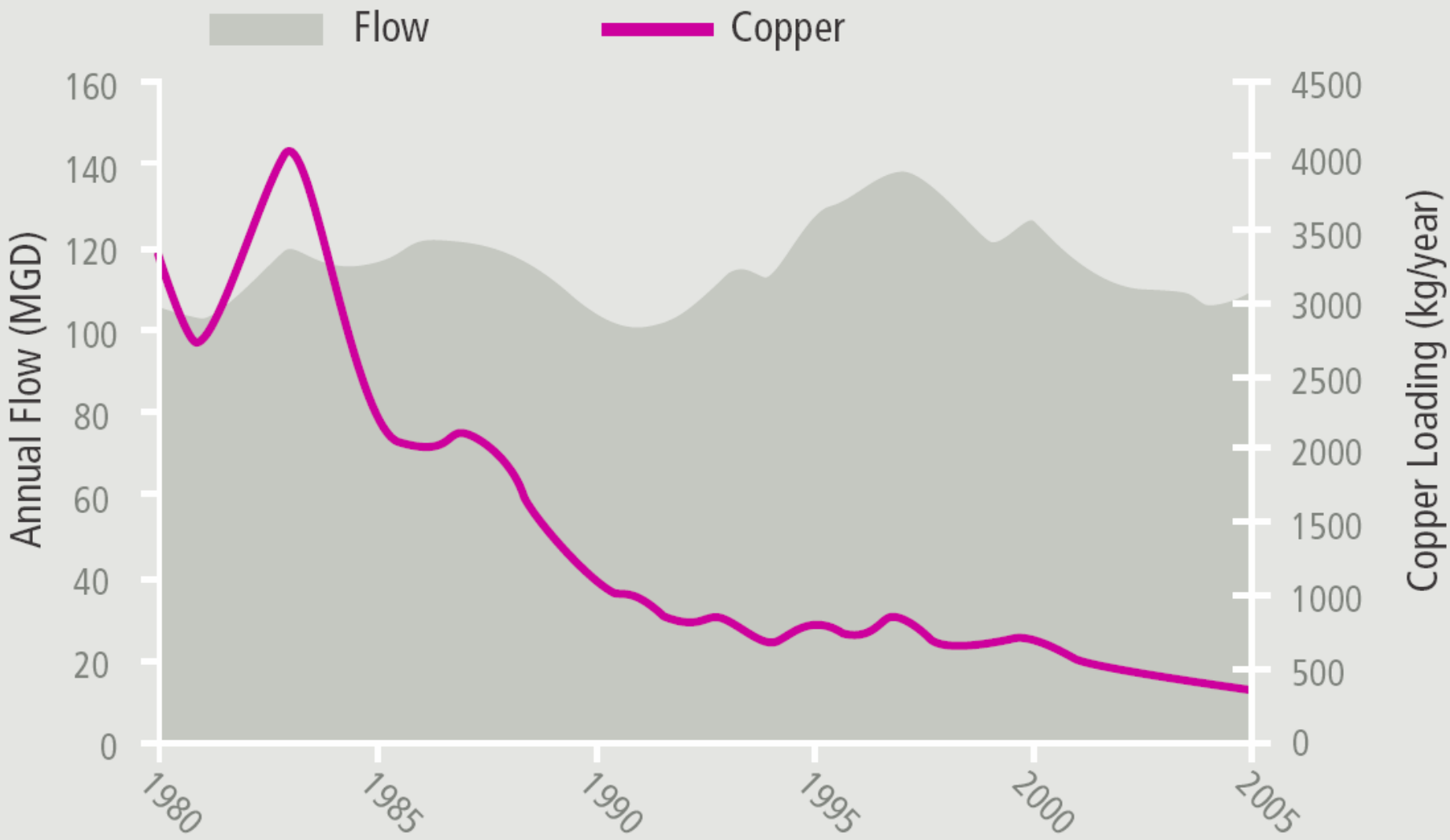
The Old Days


City of Petaluma
Sonoma Valley County S.D.
Napa S.D.
American Canyon
Novato S.D.
Las Gallinas Valley S.D.
Central Marin Sanitation AG.
West County Agency
West County Wastewater Dist.
Marin Co. S.D. #5
Sewerage Agency of So. Marin
Sausalito-Marin City S.D.
San Francisco North Point
N. San Mateo Co. S.D.
City & Co. of S.F. Oceanside
City of Burlingame
City of Millbrae
City & Co. of S.F. Int. Airport
South S.F./San Bruno WQCP
City of Pacifica
Sewer Authority Mid-Coastside
City of San Mateo
South Bayside System Authority
City of Palo Alto
City of Sunnyvale
San Jose/Santa Clara WPCP
Fairfield-Suisun Sewer Dist.
Vallejo Sanitation & Flood Cont.
City of Benecia
Central Contra Costa S.D.
Delta Diablo S.D.
Delta Diablo S.D.
Mt. View S.D.
Contra Costa Co. S.D. No.5
City of Hercules
City of Pinole
Rodeo S.D.
Treasure Island
East Bay MUD
City & Co. of S.F. Southeast
East Bay Dischargers Authority

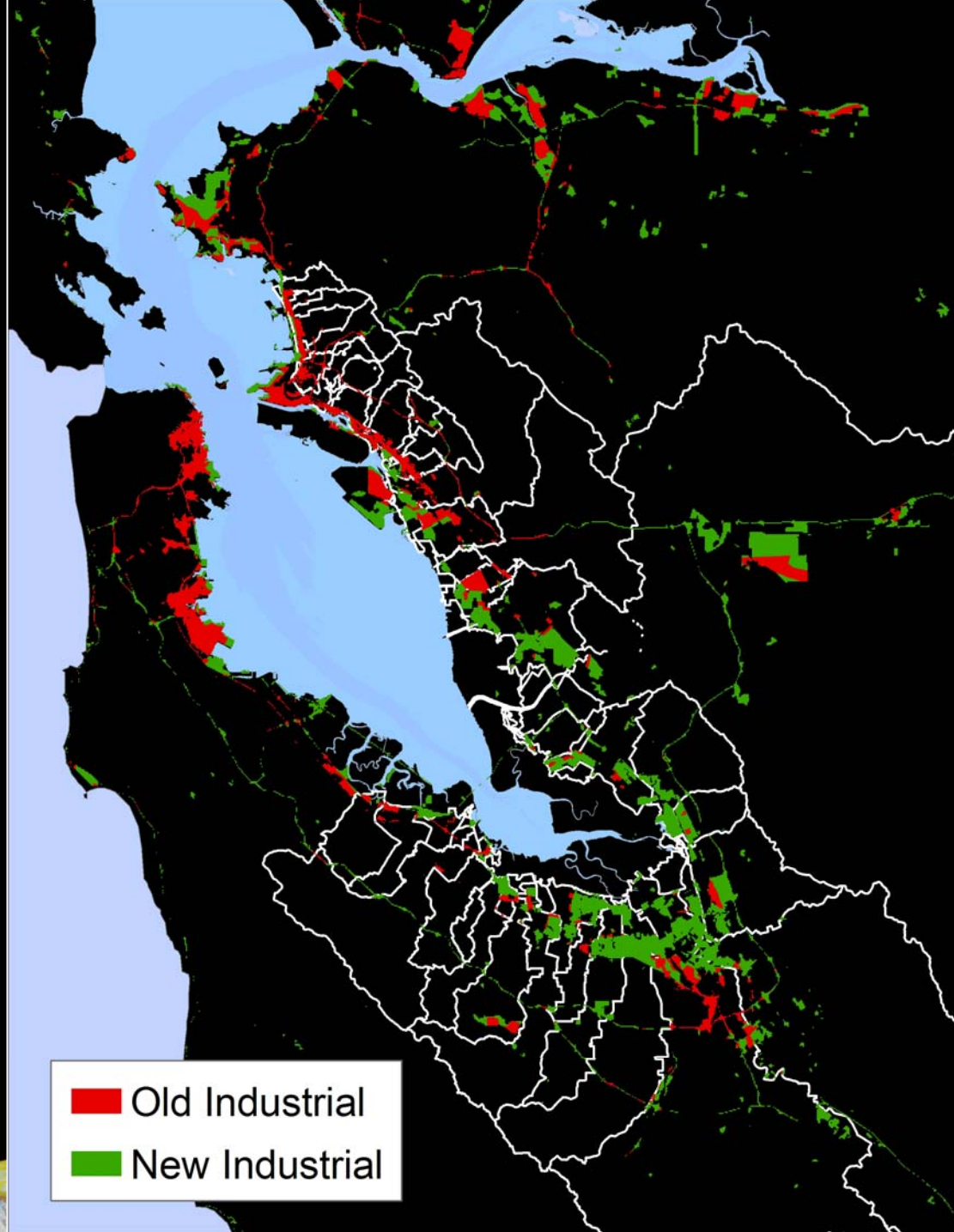
Total BOD and TSS Loading to the Bay



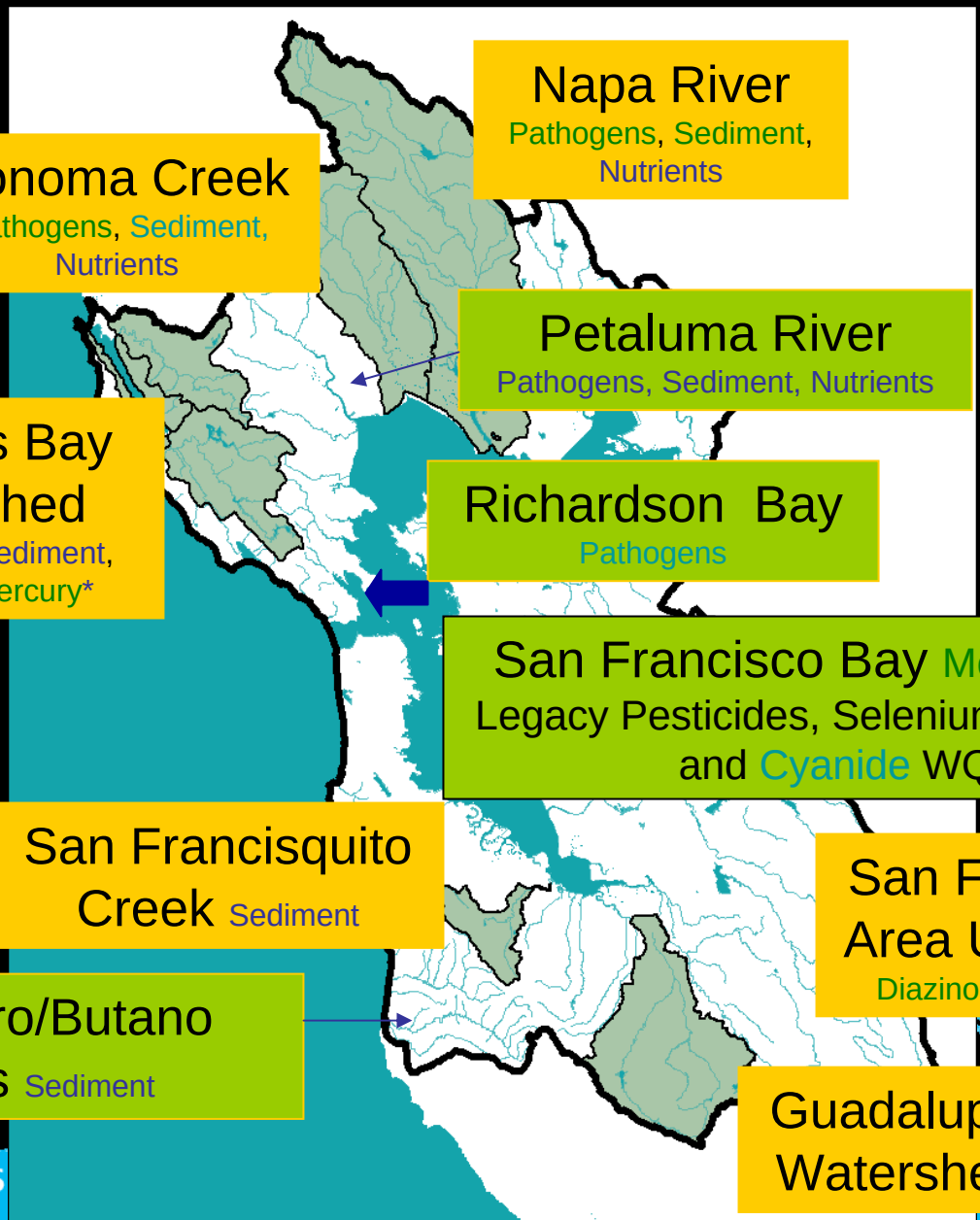
Copper Loadings from San Jose/Santa Clara



Urban Runoff now dominates Bay loading issues



SF Bay Region TMDL Projects



Napa River
Pathogens, Sediment, Nutrients

Sonoma Creek
Pathogens, Sediment, Nutrients

Petaluma River
Pathogens, Sediment, Nutrients

Tomales Bay Watershed
Pathogens, Sediment, Nutrients, Mercury*

Richardson Bay
Pathogens

San Francisco Bay Mercury, PCBs, Legacy Pesticides, Selenium, plus Copper and Cyanide WQOs

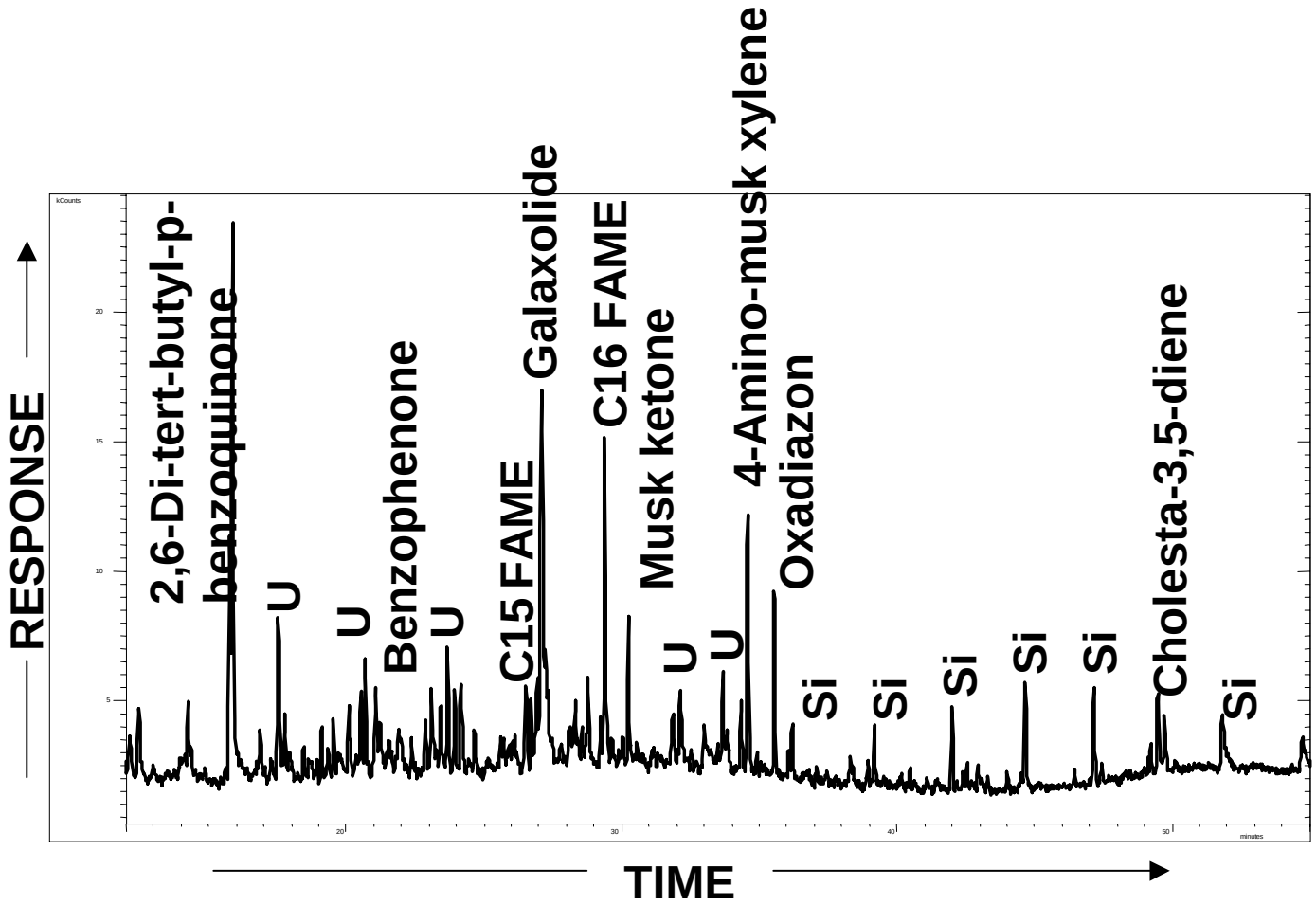
San Francisquito Creek Sediment

San Francisco Bay Area Urban Creeks
Diazinon, Pesticide Toxicity

Pescadero/Butano Creeks Sediment

Guadalupe River Watershed Mercury

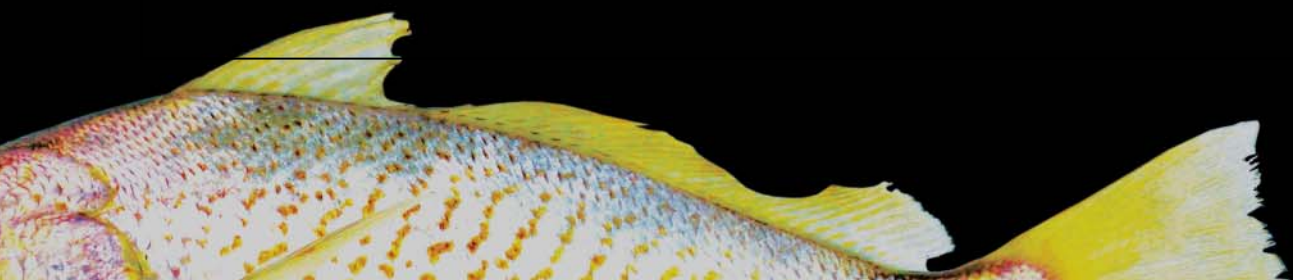
Green = done
Blue = this year
Maroon = next



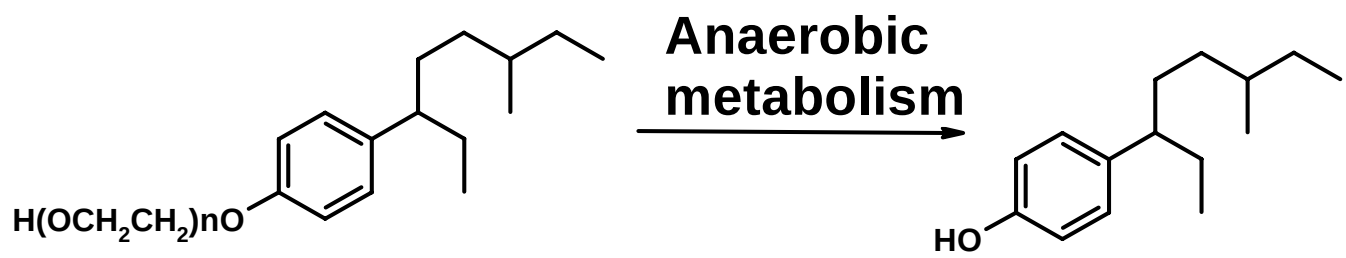
GC-MS total ion current trace of a 1993 water sample from Dumbarton Bridge showing dissolved organic components (F3). Abbreviations: FAME = fatty acid methyl ester, Si = silicone, U = unknown.

Major anthropogenic compound groups found in 1999-2000

- Surfactants
- Plasticizers
- Musks
- Flame retardants
- Personal care product ingredients



Surfactants

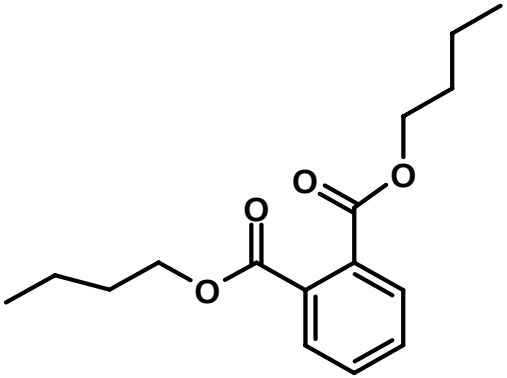


4-Nonylphenol ethoxylates (n= 1-15)

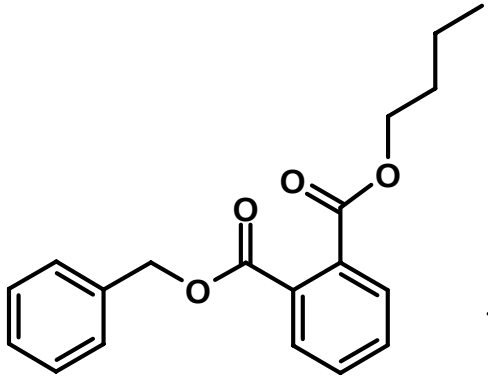
4-Nonylphenol

Sources: household and industrial products
Max level: ppt (ng/L) in water. Far below level of impact
Concern: endocrine system disruption, bioaccumulation

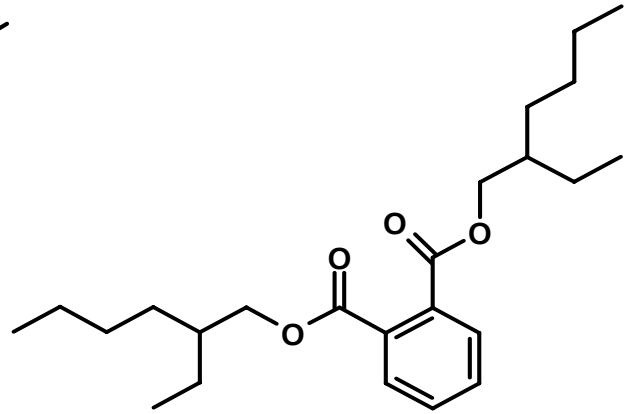
Plasticizers



Di-n-butylphthalate



Butylbenzyl phthalate

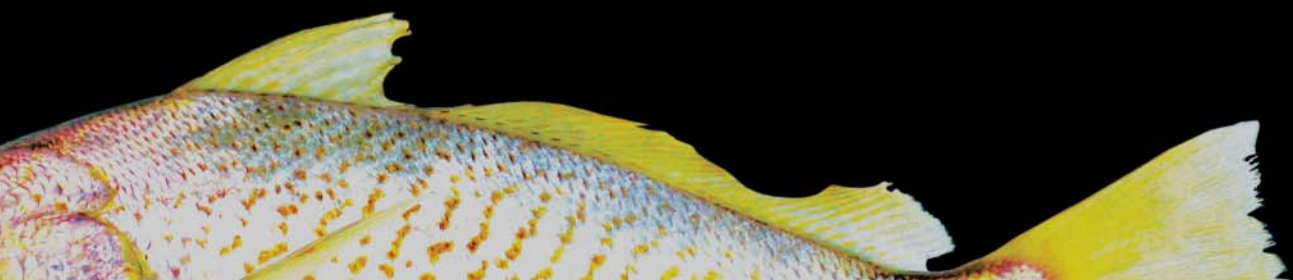


Bis(2-ethylhexyl)-phthalate

Sources: household and industrial products
Max level: ppb (μg/L) in water, ubiquitous contaminants
Concern: endocrine system disruption, bioaccumulation

Flame Retardant Found in Lake Michigan

And Lots of It! *New Yorker comment*



RMP ANNUAL MEETING 2006

Alternative Flame Retardants: Flammability Standards

1. Consumer product-specific standards



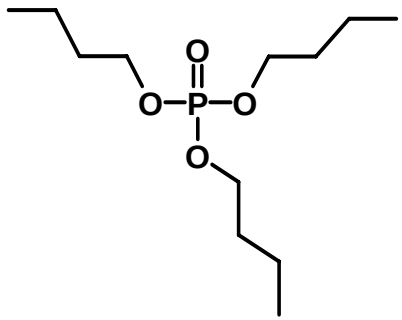


2. CA Furniture Flammability Standard (TB 117, 1975)
   - Polyurethane foam
   - CA first, only state to have standard
   - Penta-BDE

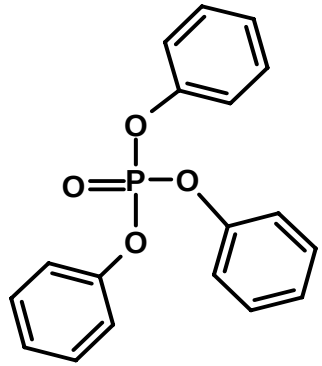
3. National Mattress Flammability Standard (July 1, 2007)

4. National Furniture Flammability Standard (in development)

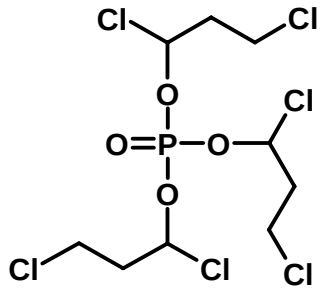
Flame Retardants



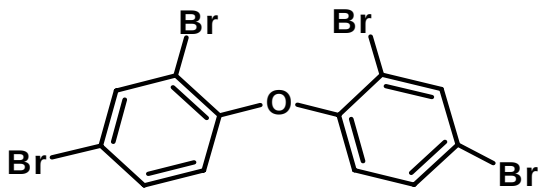
Tributylphosphate



Triphenylphosphate



Tris(1,3-dichloro-2-propyl)phosphate



PBDEs (mainly congeners 47, 99, 100, 153, 154)

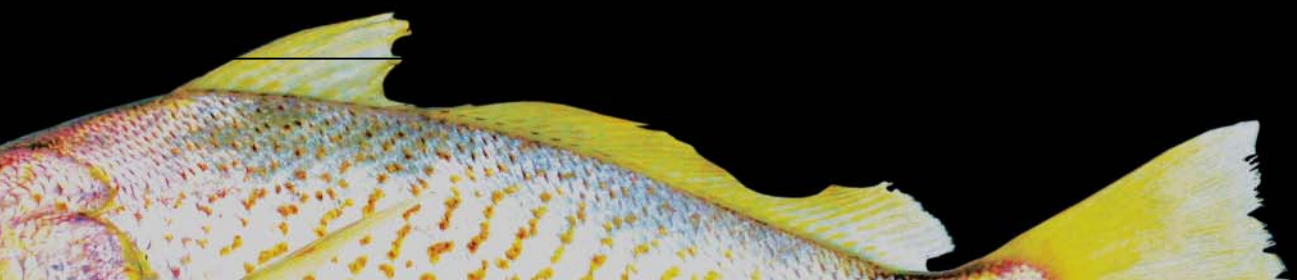
Sources: textiles, household and industrial products
Max level: ppb (μg/kg) in sediments and bivalve tissues
Concern: endocrine system disruption, bioaccumulation

PBDE Timetable

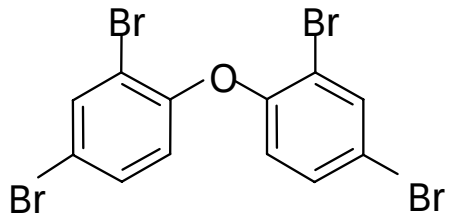
2002: RMP begins monitoring PBDEs

2003: AB 302 - Wilma Chan (Oakland-D) bans Penta- and Octa- PBDEs in CA

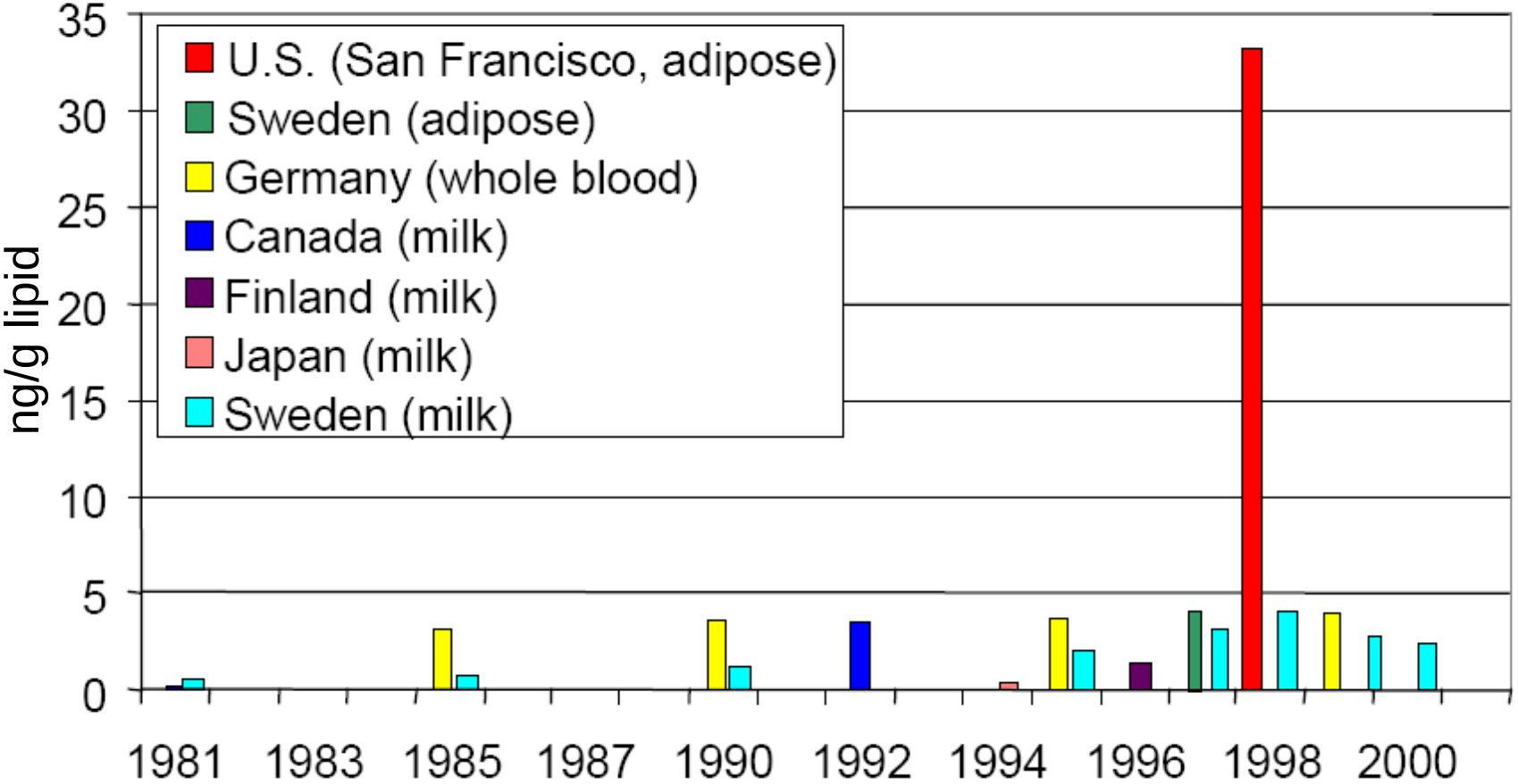
2006: CA begins phase-out of Penta- and Octa- (but not Deca-BDEs)



Polybrominated Diphenyl Ethers (PBDEs)



BDE 47 in Human Tissues



Petreas et al. 2001

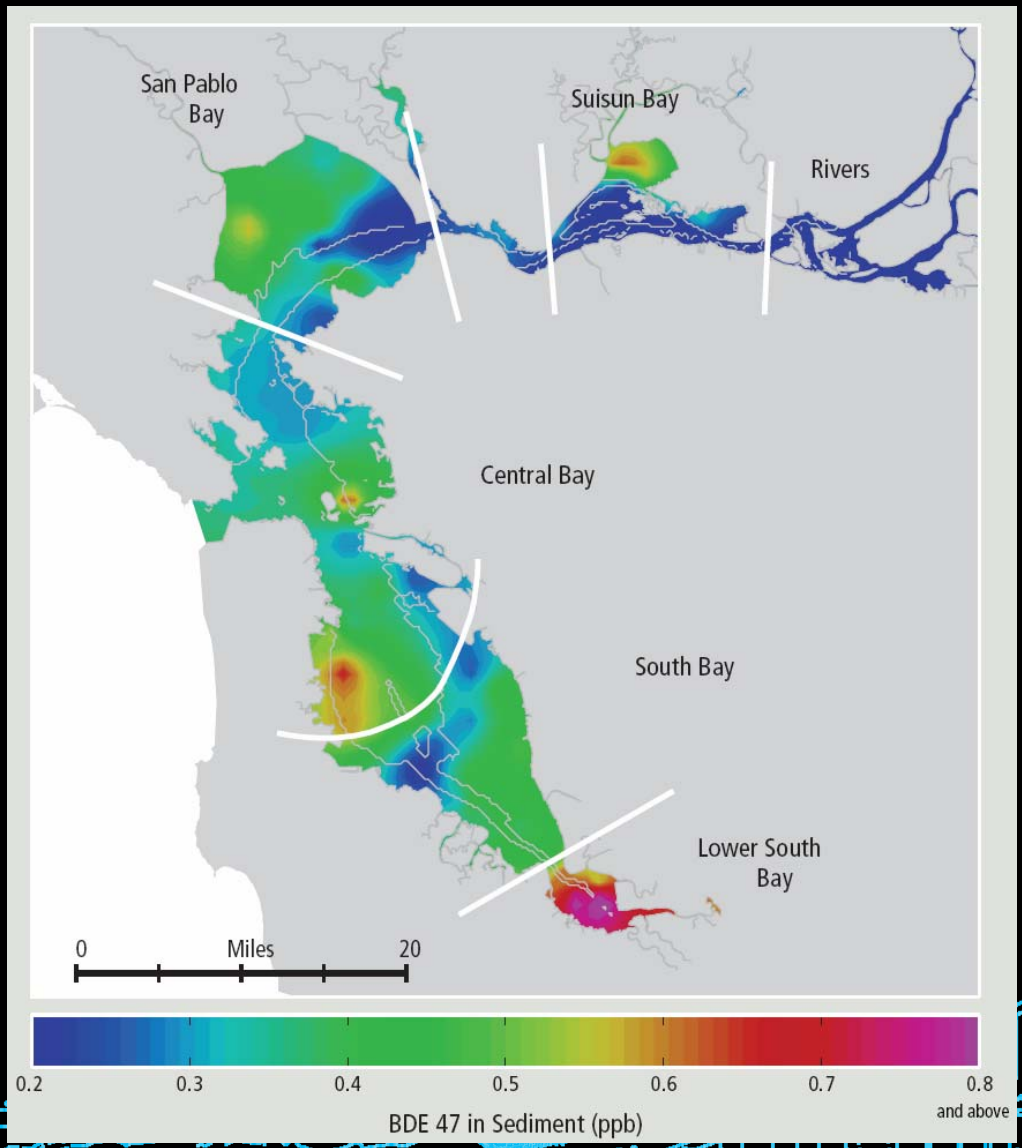
PBDEs in the Bay Area

Detected in:

- Water, WW effluent, sediment
- Bivalves
- Sport fish
- Harbor seals
- Bird eggs
- People

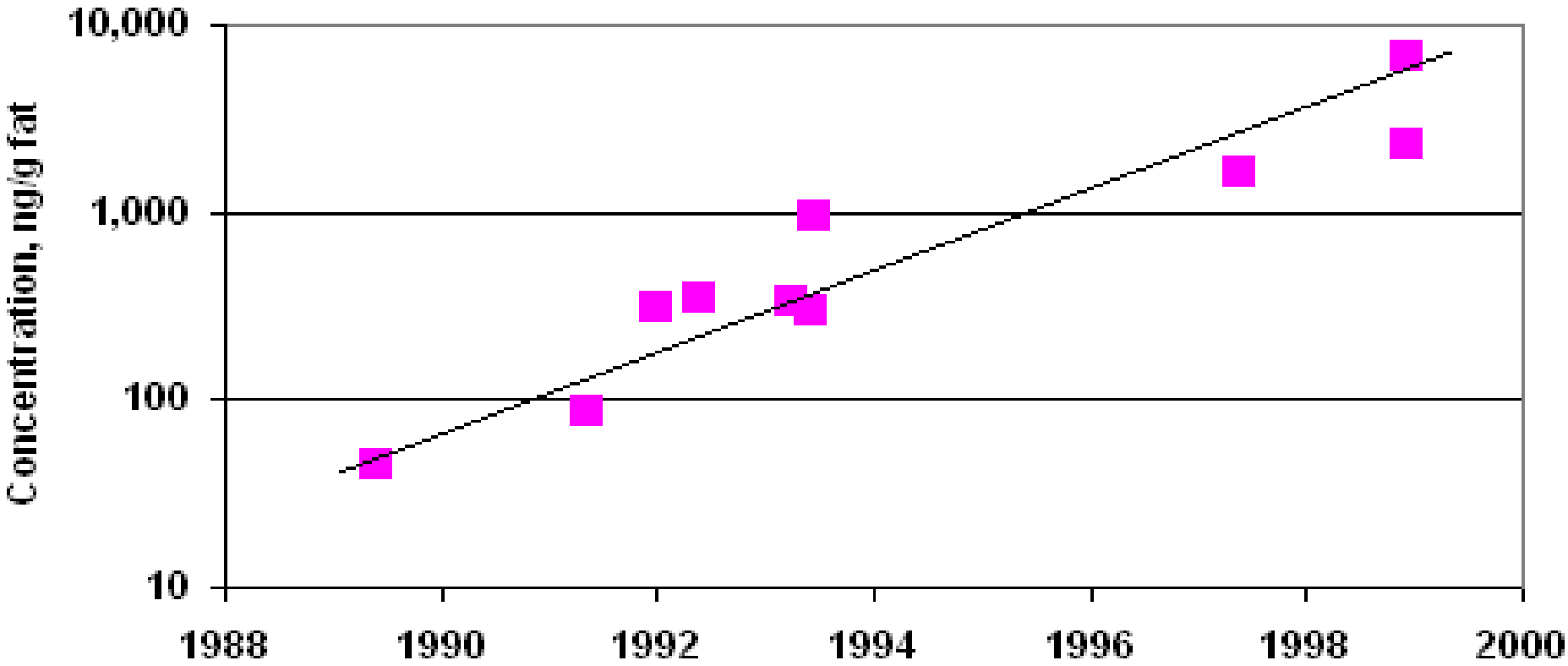
Penta- and Octa-BDE mixtures banned in 2006

BDE 47 in Sediment (2004 - 2006)



- Sources in most segments
- No trend
- Similar or higher than other locations worldwide

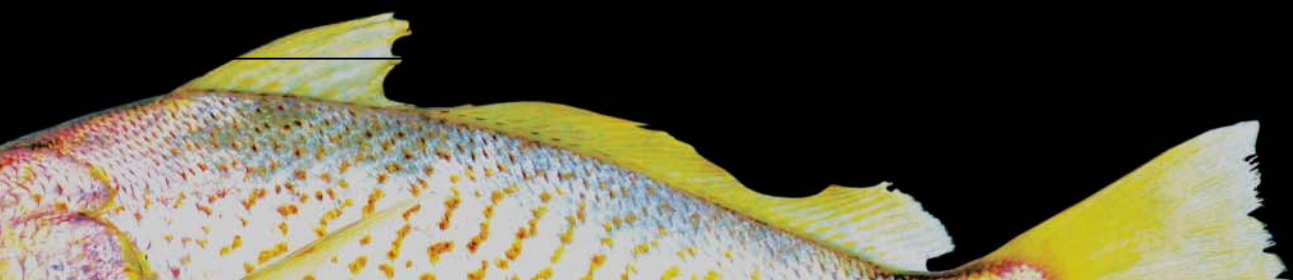
PBDEs in SF Bay Harbor Seal Blubber ***doubled every 1.8***



Source: She et al. (2002)

Our first conceptual model

- Concentrations of PBDEs are increasing rapidly.
- Levels are at or near levels of concern for human health.
- Are PBDEs the next PCB-like problem?

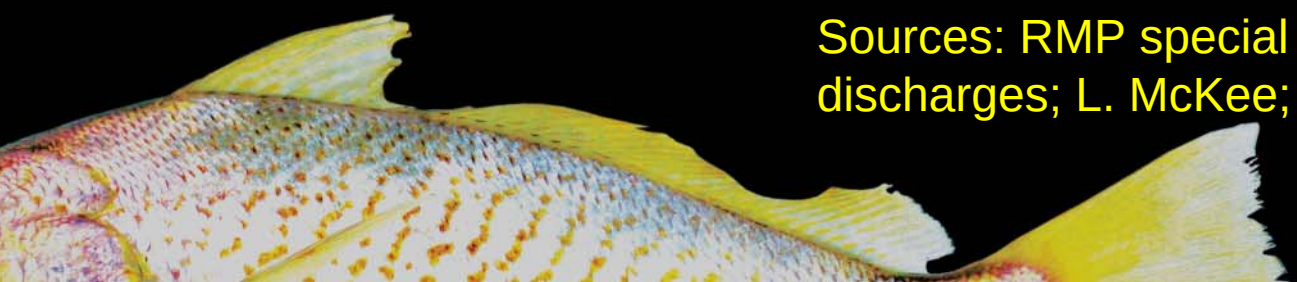


Annual Loading Estimates

PBDE loads are 3-11x PCB loads.

Source	PBDE (kg/yr)	PCB (kg/yr)
Wastewater	37	2.5
Small tributaries	~64	9-15
Delta	~11	6-23
Atmosphere	1-2	-7
Total	**~114**	**10-34**

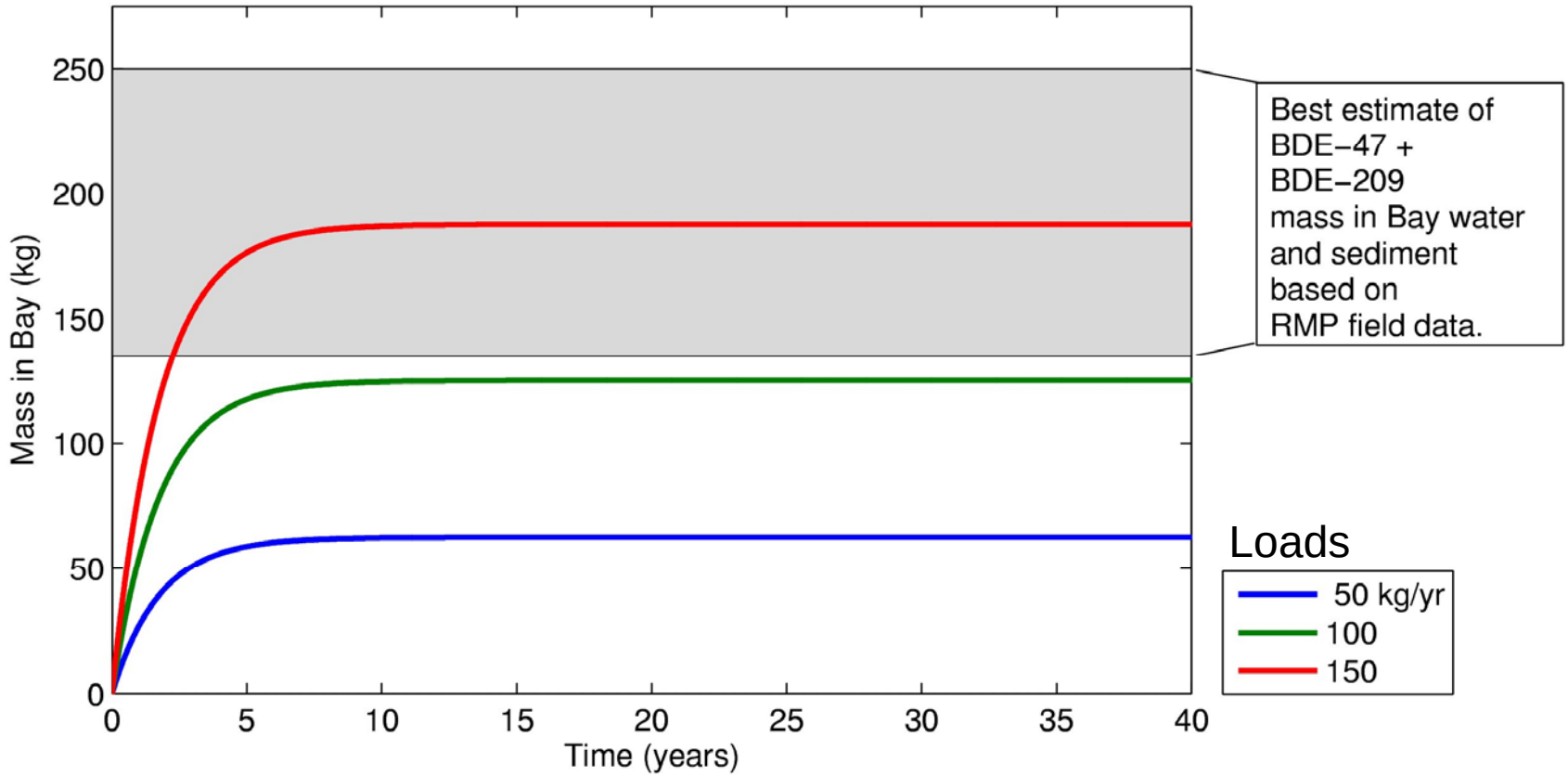
Sources: RMP special study on wastewater discharges; L. McKee; CARB (2005); D. Yee



Modeling PBDEs

**Predicted inventories are consistent with those estimated from monitoring.*

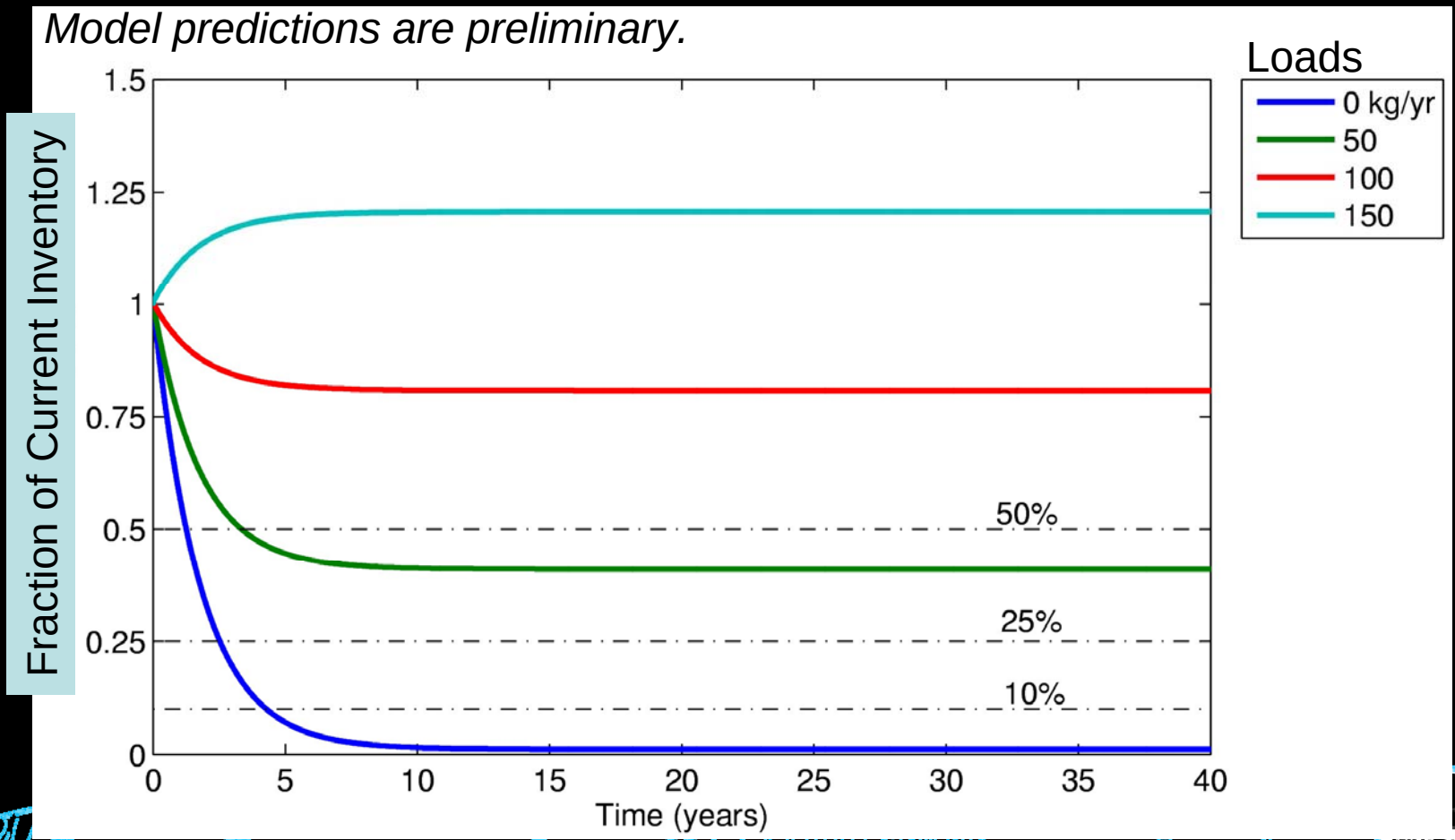
Model predictions are preliminary.



Predicting Recovery from PBDEs

**At 0 PBDE load, 10% of the current inventory will be reached in 5 yrs.*

Model predictions are preliminary.

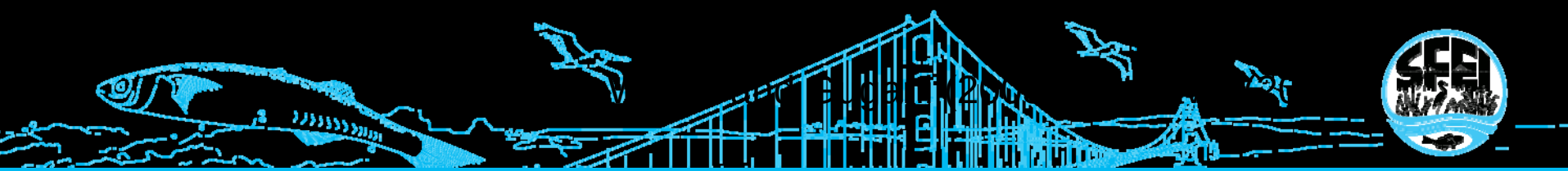


Source: Gran

Why are predicted recoveries so fast?

*PBDEs degrade much faster than PCBs

Parameter	BDE-47[a]	PCB-118[b]
Degradation half-life in water (years)	0.5	56
Degradation half-life in sediment (years)	1.5	56



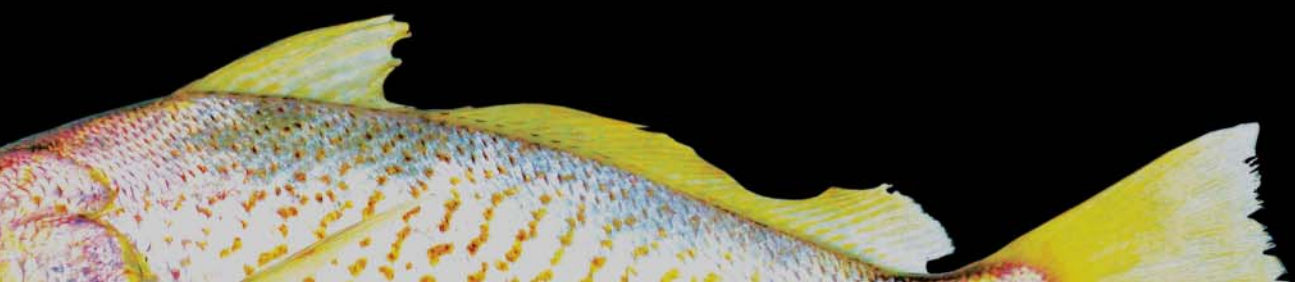
PBDE Future Scenarios

IF

- PBDE inputs are ~5 times PCB inputs, but PBDE inventories are >10 times lower.
- PBDEs degrade more quickly than PCBs.

THEN

- With the bans on Penta- and Octa-formulations, improvements in a few years.
- Risks to the biota remain unknown.
- What about replacements?



Chemical	2002 Prod. Vol. (lbs)	Accumulates	Persists	Eco Tox	Mam Tox
Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)	10-50M	?	M?	M	H
Triphenylphosphate (TPP)	10-50M	H?	L?	H	?
Octyl tetrabromobenzoate (OTB)	?	?	?	H?	?
Tetrabromobisphenol A (TBBPA)	100-500M	L	M	H	H
Hexabromocyclododecane (HBCD)	10-500K	H	H	H	H
Decabromodiphenylethane (DBDPE)	?	L	H?	?	?
1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE)	1-10M	H?	M?	?	?
Pentabromoethylbenzene (PBEB)	0	M?	M?	?	?
Dechlorane Plus (DP)	1-10M	L	H	?	?

2008 Pilot Study: Alternative Flame Retardants in San Francisco Bay

with the Marine Mammal Center
EBMUD, Duke University, Skidaway Institute of Oceanography

Analyze bioaccumulative compounds in:

- harbor seal blubber
- sport fish
- cormorant eggs

Analyze non-bioaccumulative compounds in:

- Bay surface water
- WWTP influent, effluent (if feasible)

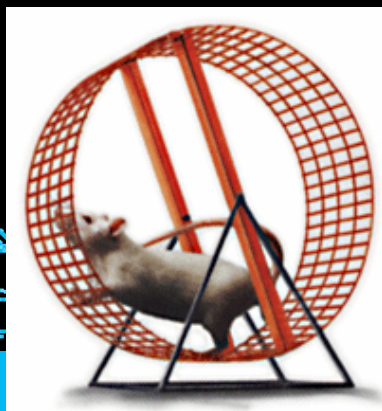
Common Outdoor Urban Insecticides Are Also Common in Surface Water

1950s — Organochlorines
- – DDT, Chlordane, Dieldrin, etc.

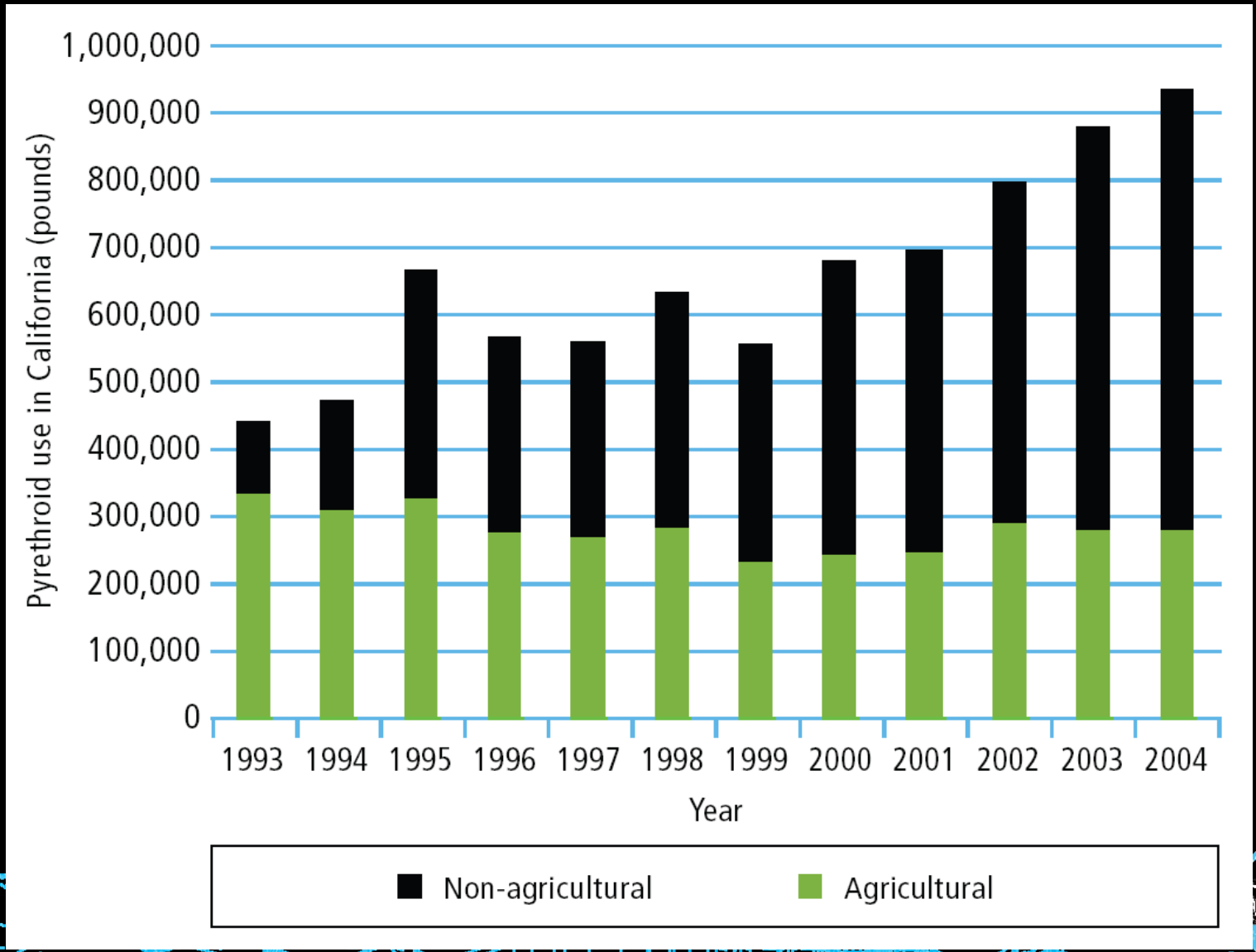
1970s — Organophosphates
- – Diazinon, Chlorpyrifos, etc.

1990s — Pyrethroids

2010s — ????



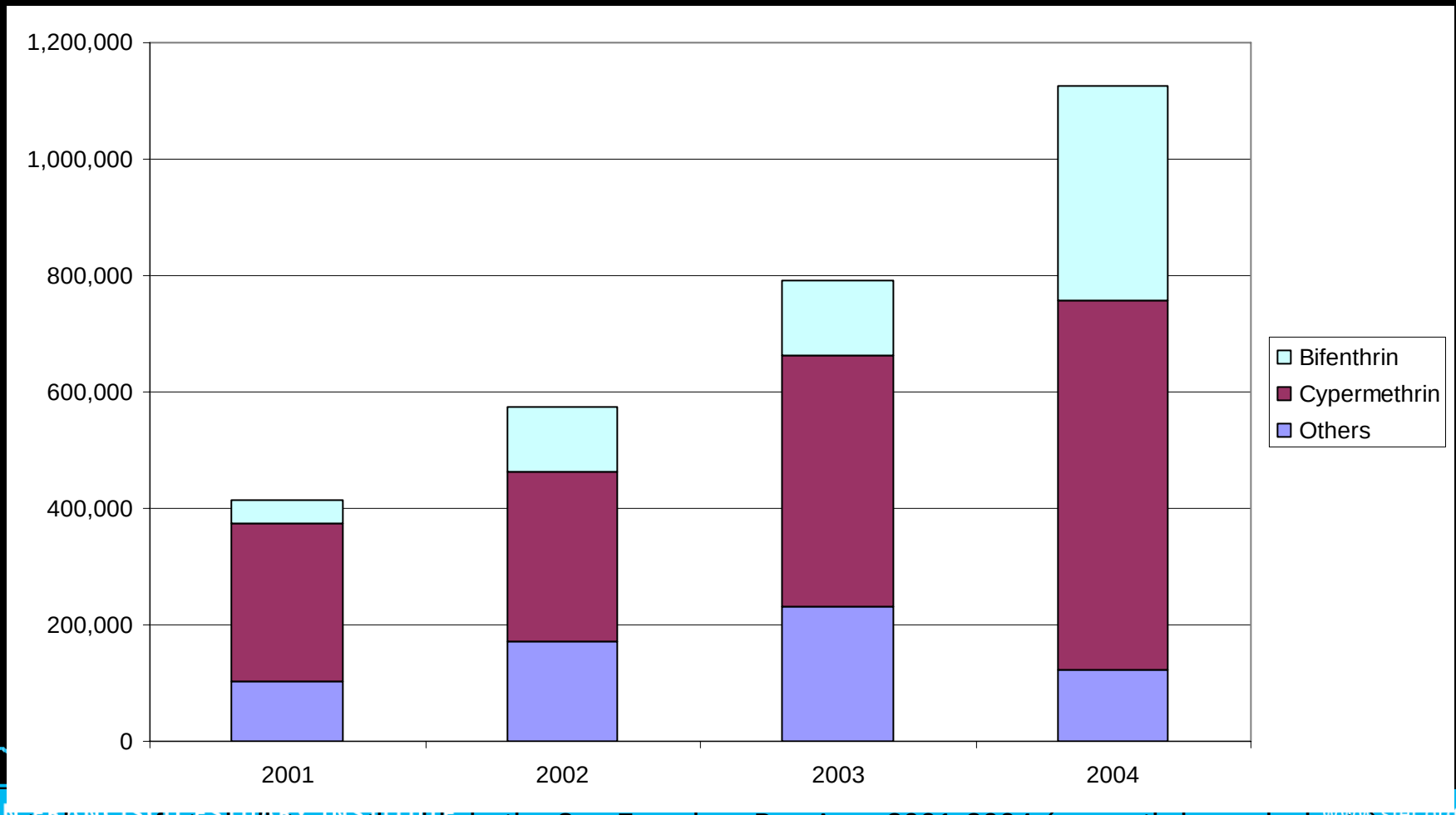
Pyrethroid Pesticides



Data from the Pesticide Use Reporting database of the CA Dept. of Pesticide Regulation

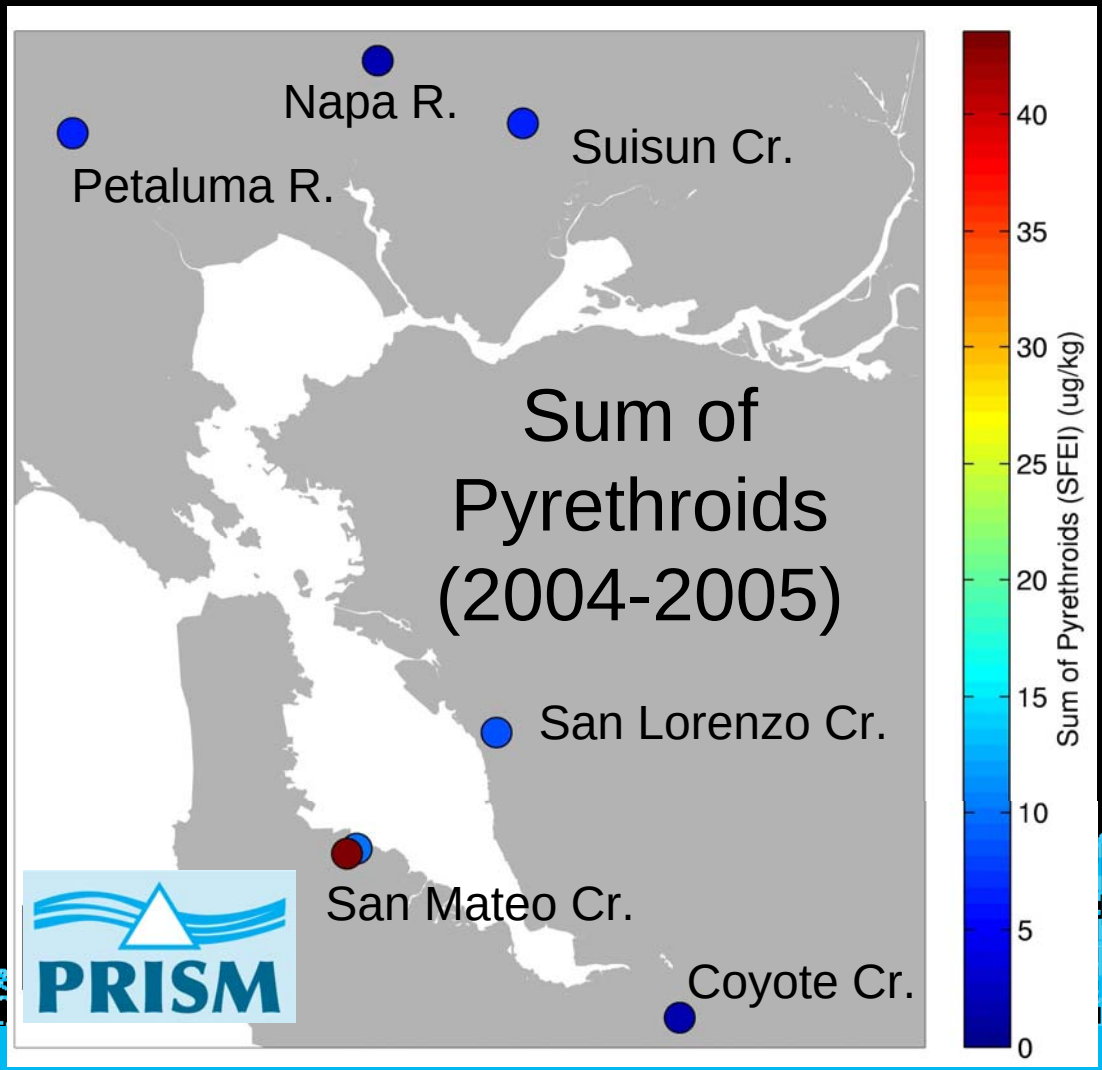
Toxicity of Bay Area Pyrethroids Use Almost Tripled Between 2001 & 2004

Increase coincident with diazinon phase out



Estimated use of study list pyrethroids in the San Francisco Bay Area 2001-2004 (permethrin equivalents)

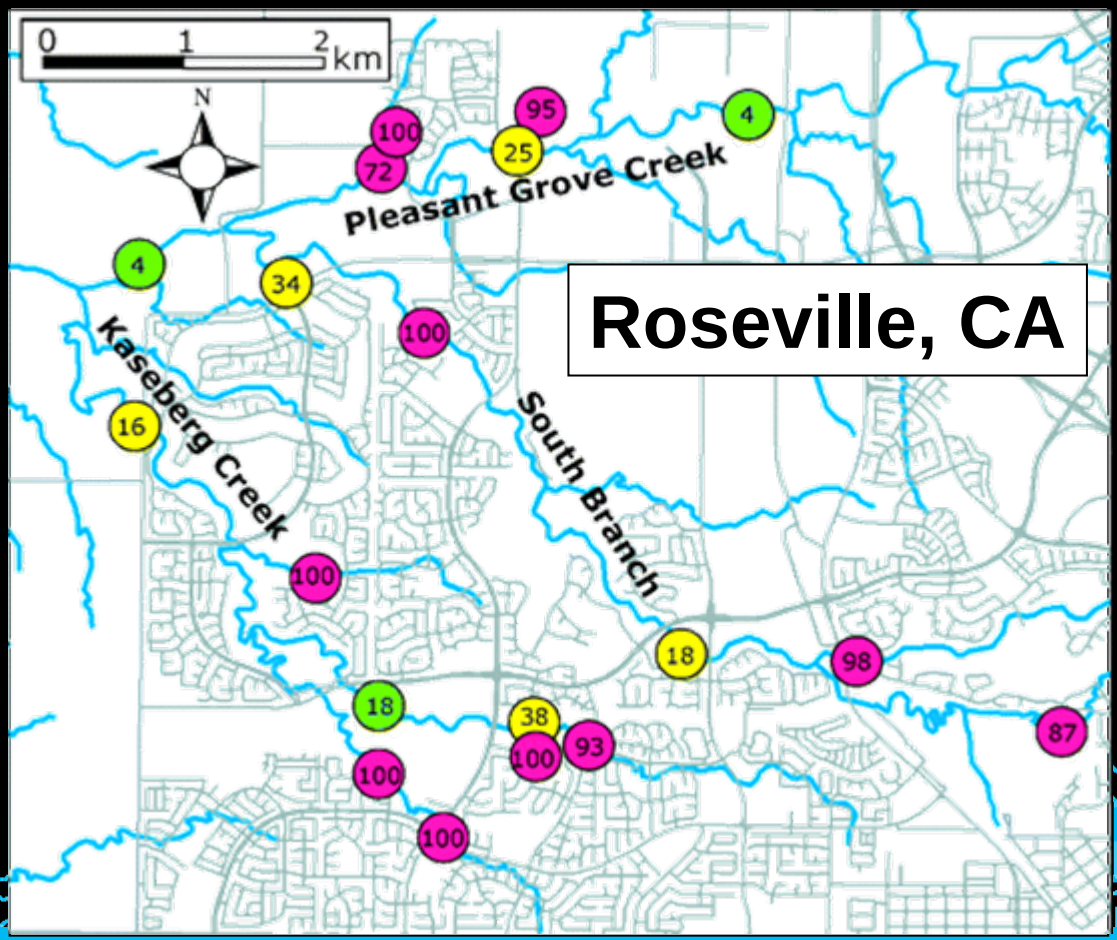
Investigations of Sources and Effects of Pyrethroid Pesticides in Watersheds of the San Francisco Bay Estuary



- Detected in urban tributaries
- Source of toxicity ?

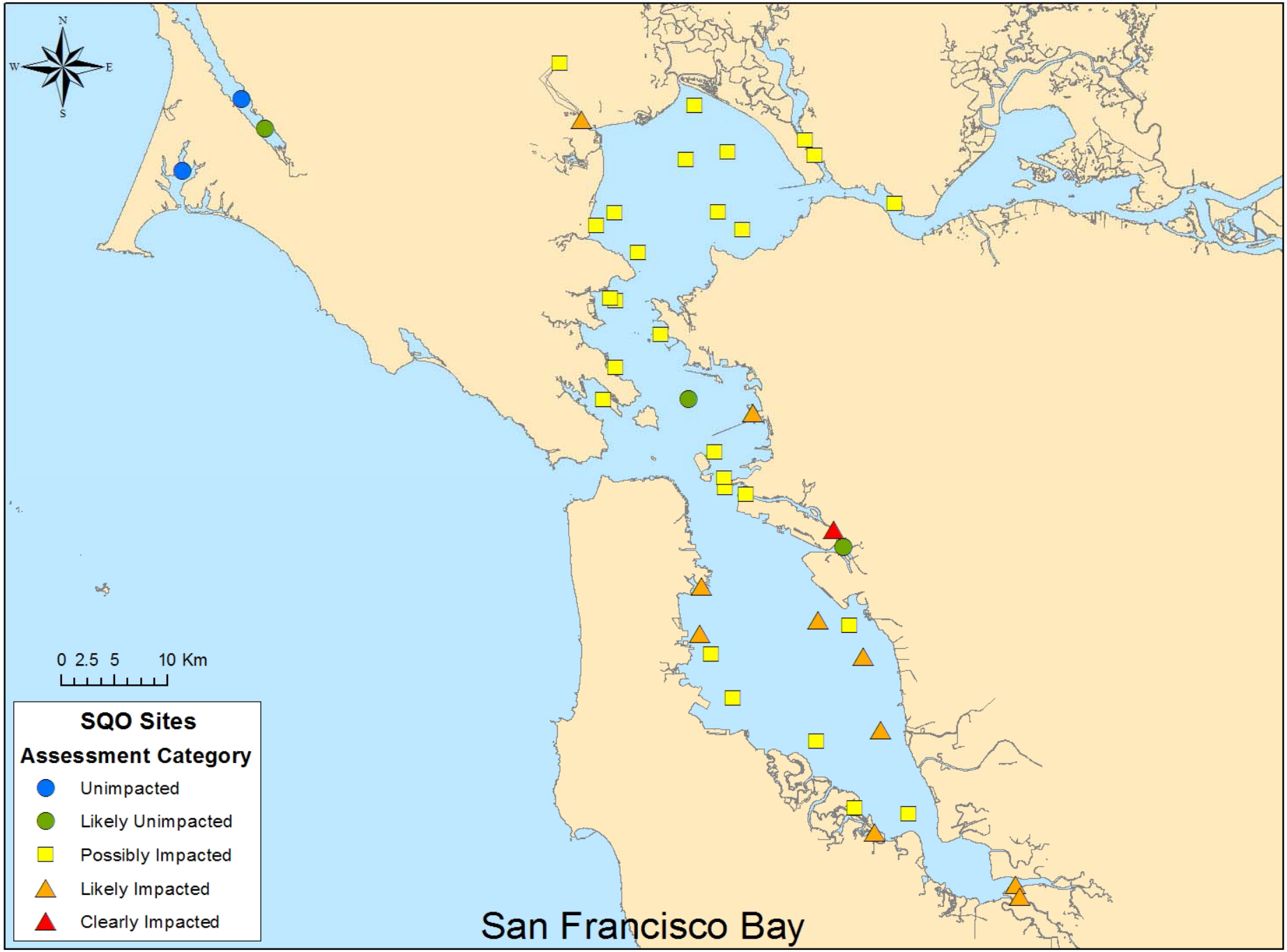
Aquatic Toxicity Due to Residential Use of Pyrethroid Insecticides

(Weston et al. 2005)



- High toxicity
- Moderate toxicity
- Non-toxic

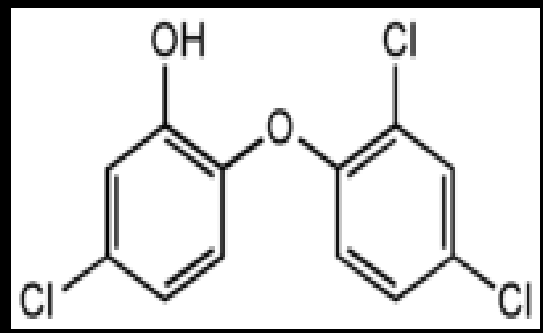
Hyalella azteca
Freshwater amphipod


N
W
E
S
0 2.5 5 10 Km
SQO Sites
Assessment Category
Unimpacted
Likely Unimpacted
Possibly Impacted
Likely Impacted
Clearly Impacted
San Francisco Bay

Emerging Contaminants in Effluent and the Bay

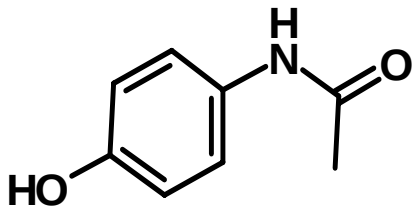
- Determine concentrations of pharmaceuticals and personal care products in:
  - Influent/effluent from two WWTP
  - Ten stations in South Bay

- In-kind contributions
  - City of Palo Alto (Karin North)
  - City of San Jose (Dave Tucker)
  - AXYS analytical (Million Woudneh)

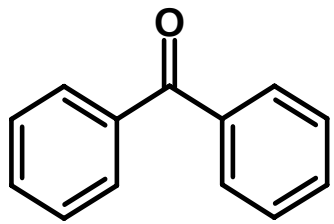


Triclosan

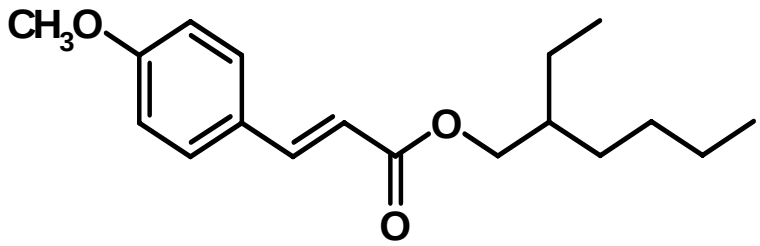
Personal Care Products



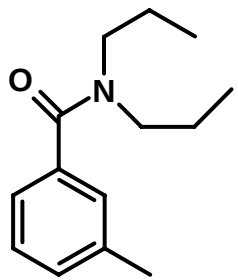
Acetaminophen (analgesic/decongestant)



Benzophenone (fixative)



Octylmethoxycinnamate (sunscreen)



N,N-Diethyltoluamide (DEET)

Sources: consumer and personal care products
Max level: ppt (ng/L) in water
Concern: toxicity

Pharmaceuticals and Personal Care Products in the South Bay

Average concentration (ng/L)

compound	influent	effluent	Bay
Acetaminophen	60,000	<500	<300
Albuterol	20	2	<20
Caffeine	60,000	40	70
Ciprofloxacin	500	<300	<100
Codiene	200	<200	<200
Cotinine	1,000	30	<20
Diltiazem	200	30	2
Erythromycin Hydrate	200	200	10
Fluoxetine	20	30	<20
Gemfibrozil	1,000	30	10
Ibuprofen	10,000	<100	<100
Lincomycin	20	2	<5
Roxithromycin	3	<4	<1
Sulfadimethoxine	2	1	<200
Sulfamethoxazole	1,000	70	200
Sulfathiziazole	4	<4	<100
Trimethoprim	300	26	1
Warfarin	5	<1	<1

- Influent > Effluent > Bay Water
- Concentrations in Bay << toxicity thresholds
- Potential Studies for 2009
  - Triclosan
  - Degradation products

Perfluorinated Chemicals (PFCs)

Applications:
Stain repellants, packaging materials, industrial surfactants, fire-fighting foams

Persistent, bioaccumulative, toxic

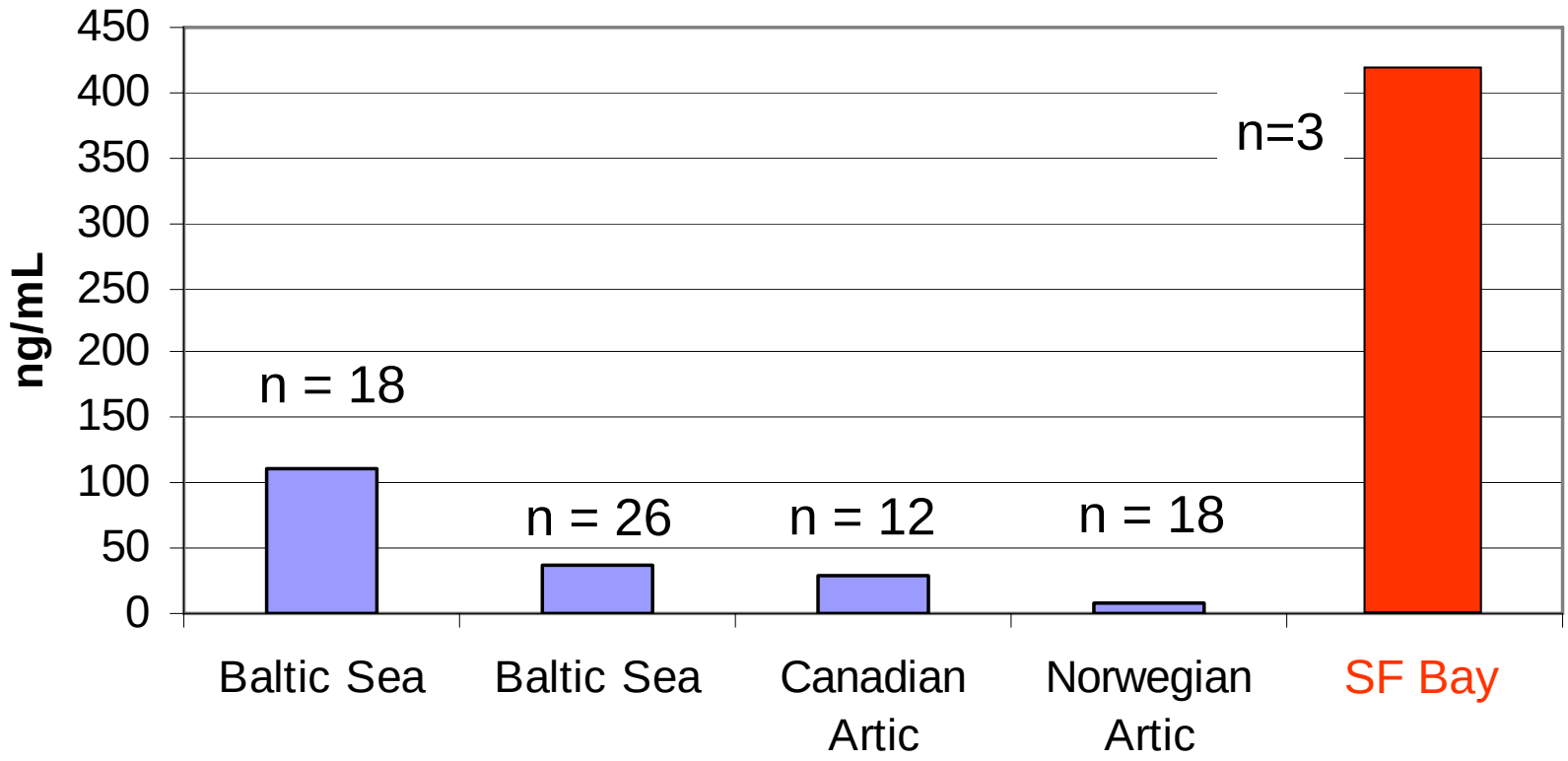
Perfluorinated Chemicals (PFCs)

RMP Pilot Study:

- Collaboration with Marine Mammal Center
- Health of seal population
- PFCs, PBDEs in harbor seal blood
- Exposure to apex predators

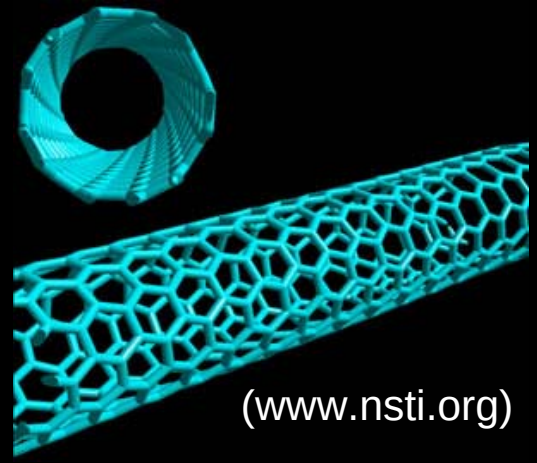
Perfluorinated Chemicals (PFCs)

Perfluorooctanesulfonate (PFOS) in Seal Blood: SF Bay vs. Other Locations



Source: Giesy and Kannan 2001

Nanoparticles



(www.nsti.org)

Applications:

electronics, biomedical, pharmaceutical, cosmetic, environmental

Production: 2000 tons in 2004, 30-fold increase by 2011-2020

A Concern in the Bay?

- Bioavailable, toxic to aquatic organisms
- Urban sources
- Colloidal fraction or form aggregates
- Adsorbent for metals and organic contaminants

EEPS 2006
Endocrine disruption in fish

- Impairment of endocrine system in fish in So CA Bight
  - Kevin Kelley, CSU-Long Beach
  - Suppression of growth, defense capabilities & reproduction
- RMP study
  - Measure cortisol, estradiol, testosterone, and insulin-like growth factors in SF fish

Pacific staghorn sculpin

Shiner surfperch

Shiner Surfperch

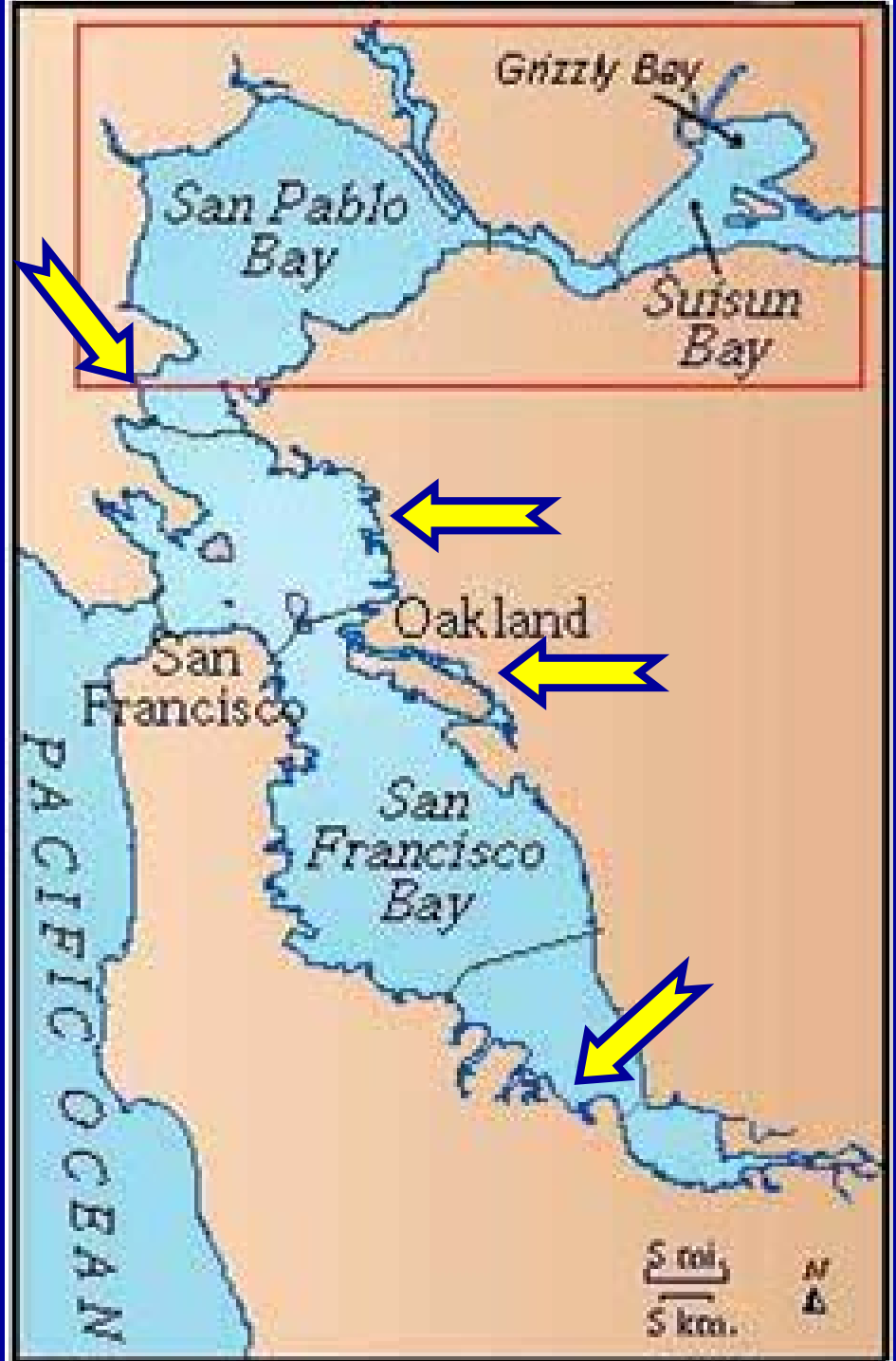
Cymatogaster aggregata

pelagic

benthic

Pacific Staghorn Sculpin

Leptocottus armatus



2006 Field Sites

[pilot year]

San Pablo Bay

Berkeley Waterfront

Oakland Inner Harbor

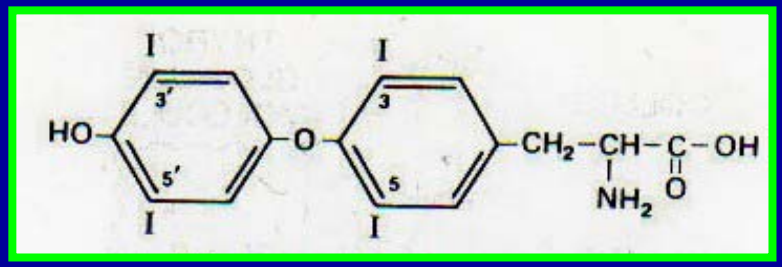
Redwood City

far-field reference:
Tomales Bay

THYROID ENDOCRINE SYSTEM

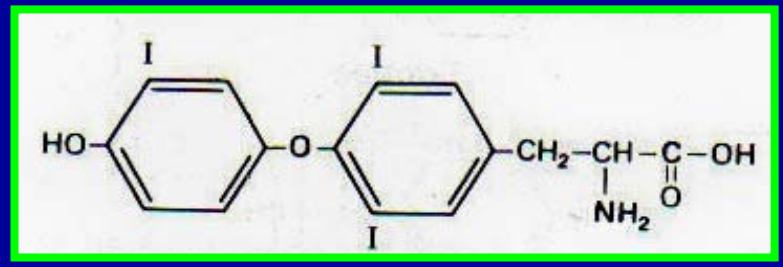
Thyroid Hormones

T4



3,5,3',5'-tetraiodothyronine (thyroxine)

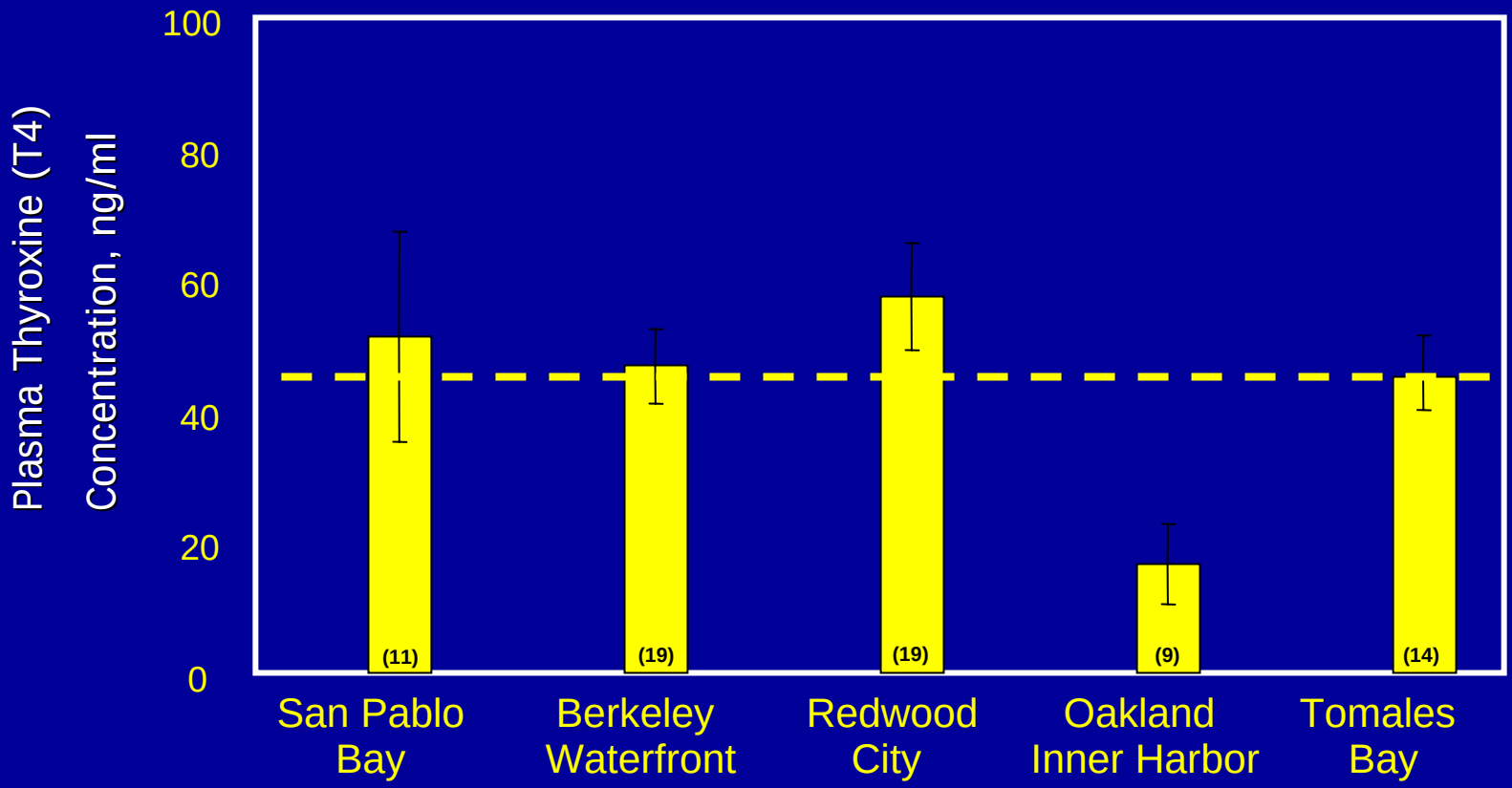
T3



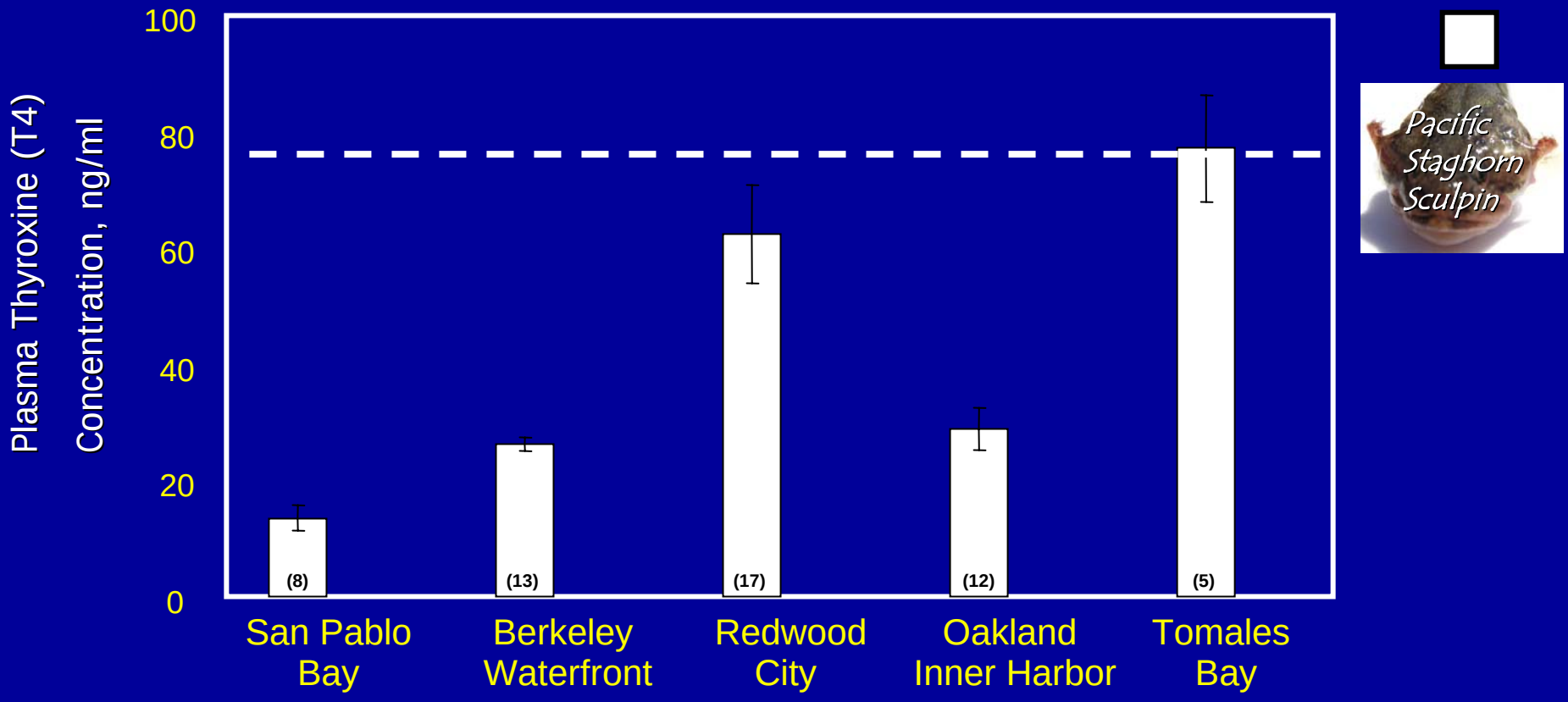
3,5,3'-triiodothyronine

- *broad physiological actions*
- essential for brain/neural development
- permissive to somatic growth
- important regulators of metabolism

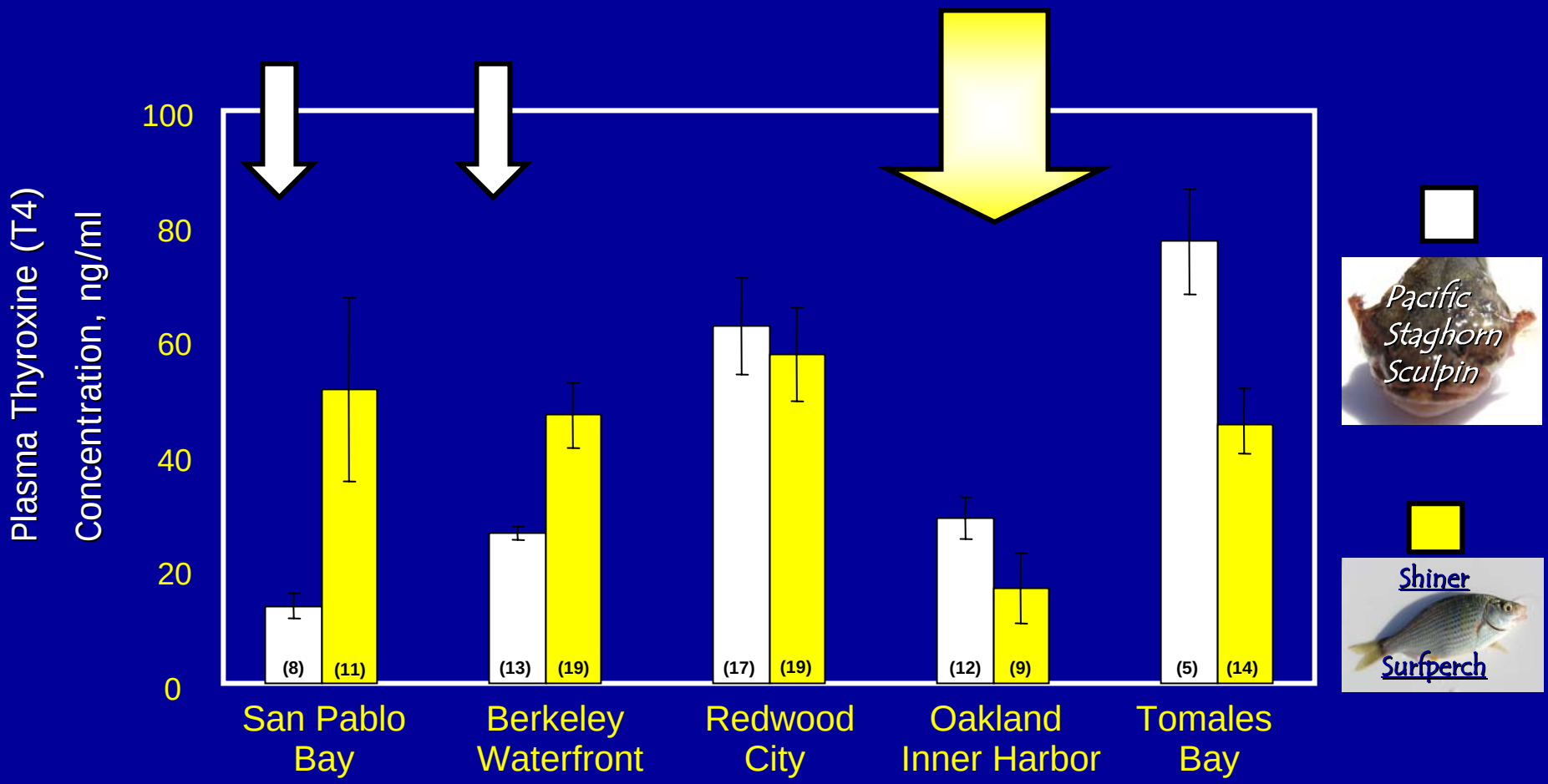
Thryoxine (T4) Levels in Shiner Surfperch



Thryoxine (T4) Levels in Pacific Staghorn Sculpin



Thryoxine (T4) Levels in SF Bay Fish



Environmental Contaminants are Implicated in Thyroid Endocrine Disruption:

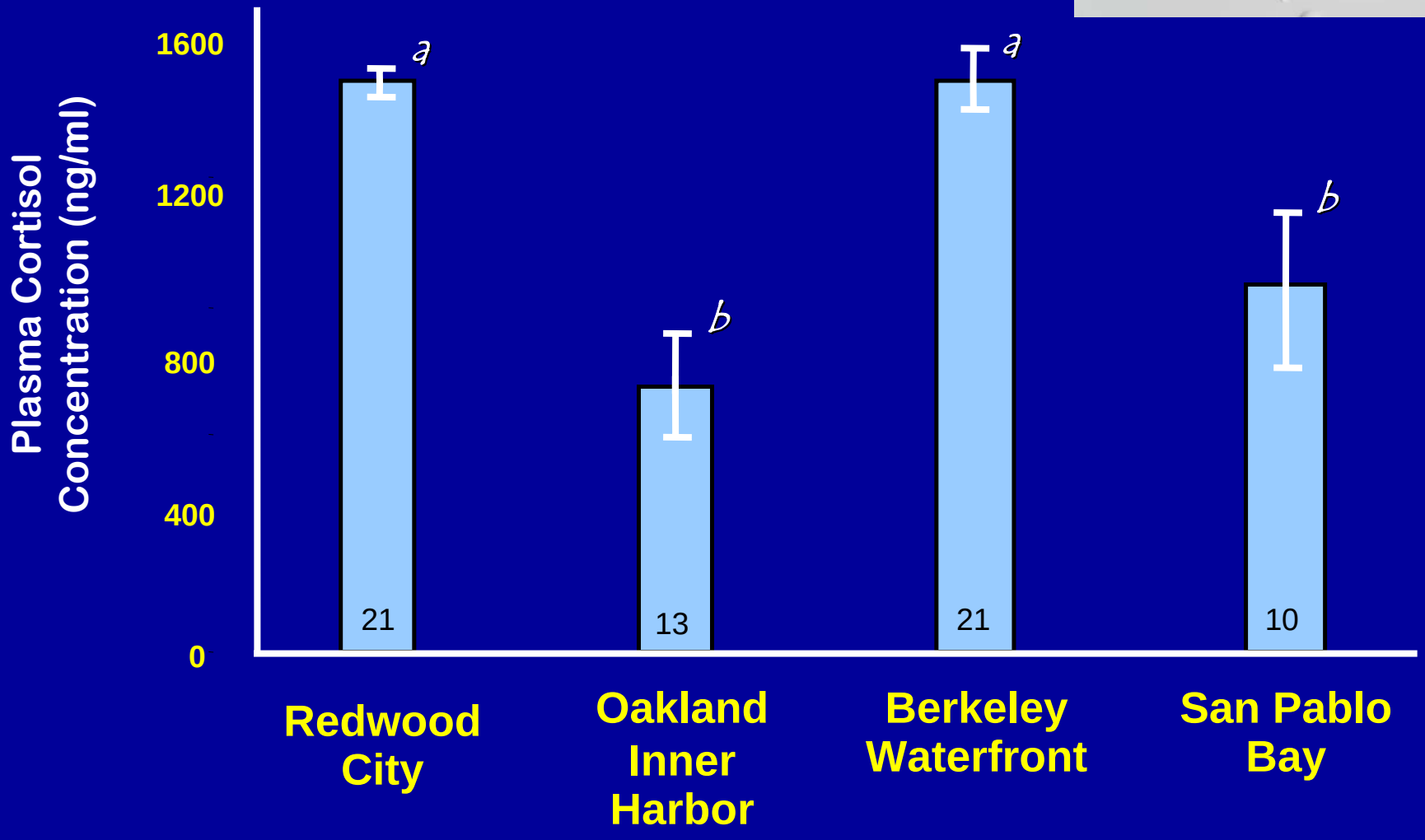
…e.g., Phenols, Hg, Cd impair thyroxogenesis in thyroid follicle cells in fish (Bhattacharya et al., '89)

…e.g., endosulfan, Aroclor 1254 and selected PCBs decrease T4 levels in fish, via effects on **iodotyrosine diodinases** (Coimbra et al., '05; LeRoy et al., '06)

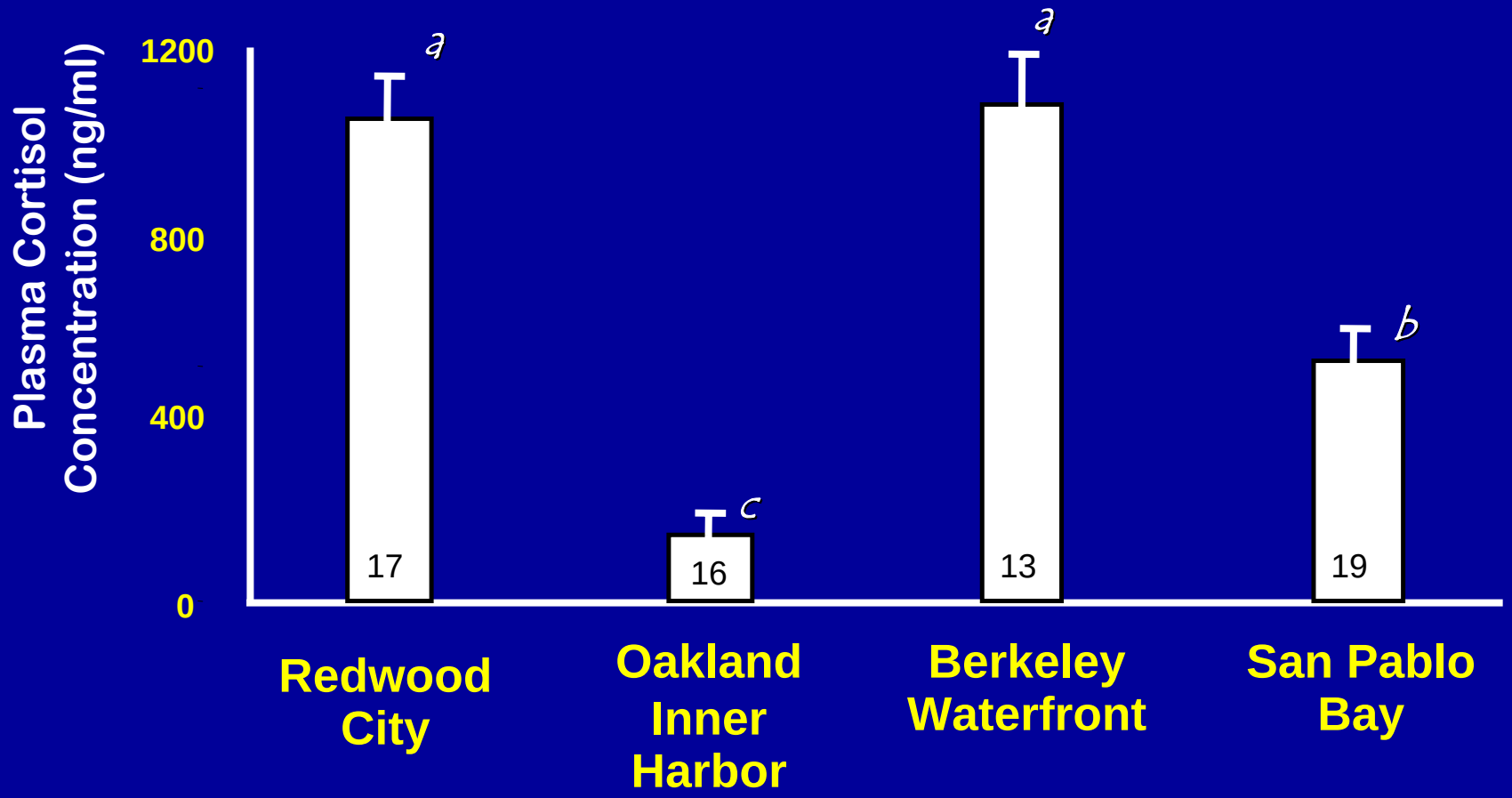
…e.g., ioxynil, certain PCBs and PBDEs bind **transthyretin** and TRs with high affinities, altering T4 and T3 levels/ actions in fish (Tomy et al., '04; Lema et al., '06; Morgado et al., '07)

STRESS RESPONSE ENDOCRINE SYSTEM

Stress Response



Stress Response




Pesticide
PE
Good candidates for Pollution Prevention
• Const
• Human
• Deliberately
– Not waste, not prod ts
• Tiny environmentally relevant concentrations
• Treatment challenging
Courtesy Wikipedia
www.sfei.org

FIFRA (EPA)

Phar & Pe Prod s)

FD&C Act (FDA)

- Almost all are regulated by laws intended to prevent environmental problems

PBDE

TSCA (EPA)

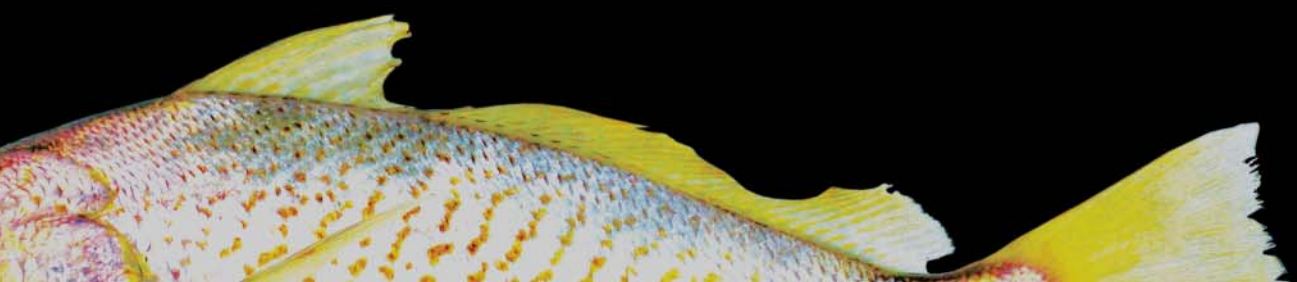
PFCs

Courtesy Wikipedia

www.sfei.org

Lesson #1: The “Urban Gap”

- Pesticides are registered for uses that will cause Clean Water Act violations & municipal compliance problems
  - Urban runoff not considered
  - Sewer discharge evaluation is new
  - Water quality risks usually not mitigated



Lesson #2: Little Municipal Control Over Pesticides

- Can regulate discharge
- Cannot regulate sales or use
- Can use voluntary programs
  - Even expensive programs usually can't obtain reductions needed for compliance

Ability to comply controlled by pesticide regulators & market—not by municipalities

RMP ANNUAL MEETING 2006

Lesson #3: Reactive Laws

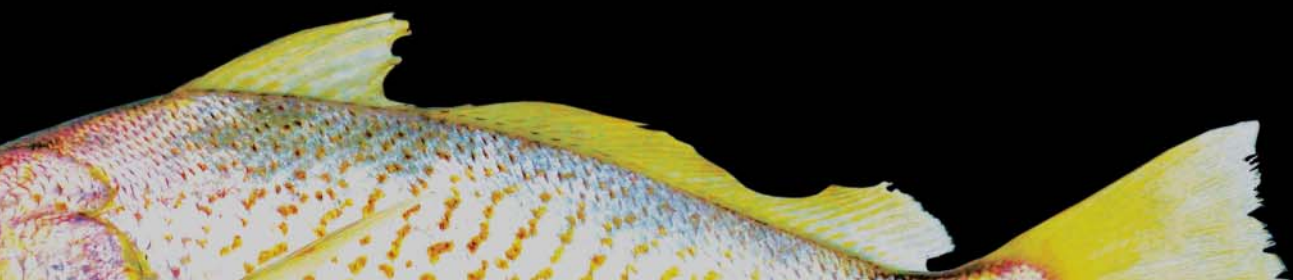
Pesticide laws are not structured to prevent problems

- Proof of harm usually required before pesticide regulatory actions taken
- No penalties for harm due to legal pesticide use

Clean Water Act is proactive—
Penalties start as soon as problems occur

Emerging Pollutant Regulatory Gaps

- No process to prevent replacing one problem with another
- No timely mechanism to address newly identified water quality impacts
- Urban use implications often forgotten



Potential Emerging Contaminants

Pyrethroid pesticides

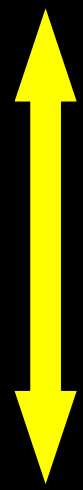
Pharmaceuticals and Personal Care Products

Perfluorinated chemicals

Non-PBDE, alternative flame retardants

Nanoparticles

Most information



Least information