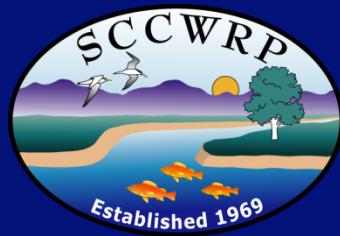
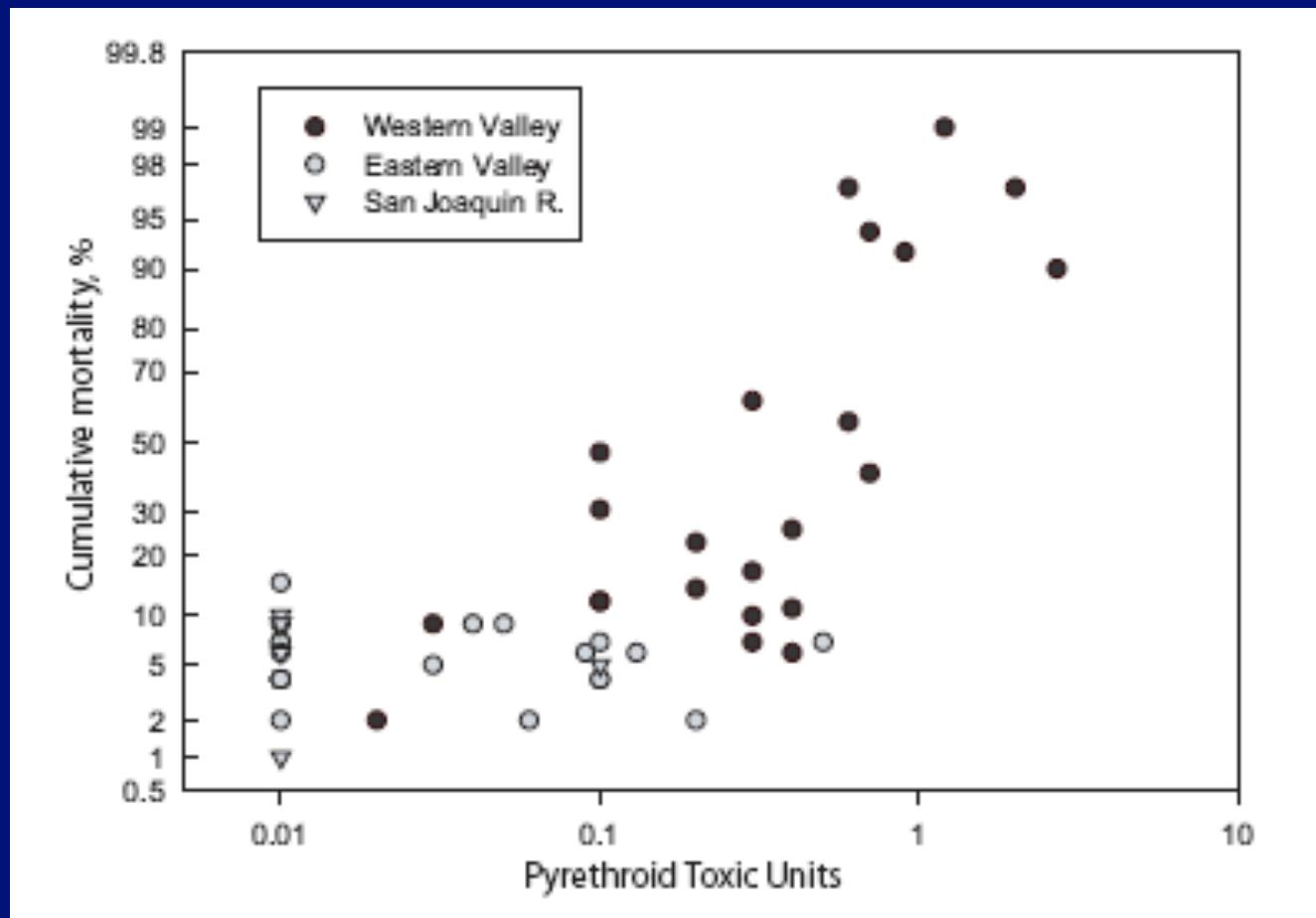


# Identifying chemicals responsible for sediment toxicity: Analytical challenges

Keith Maruya and Kelly Smalling

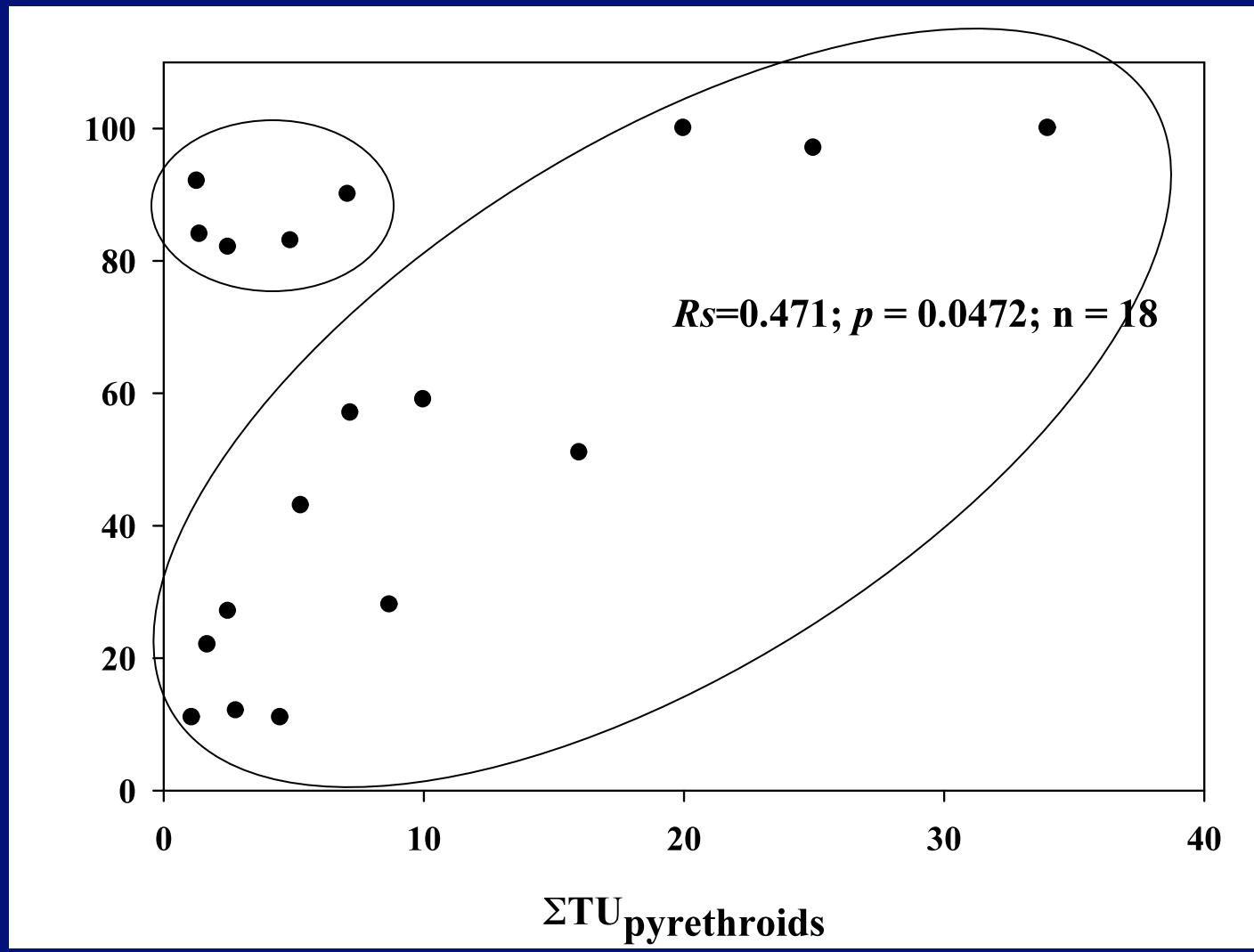


# San Joaquin pyrethroid study

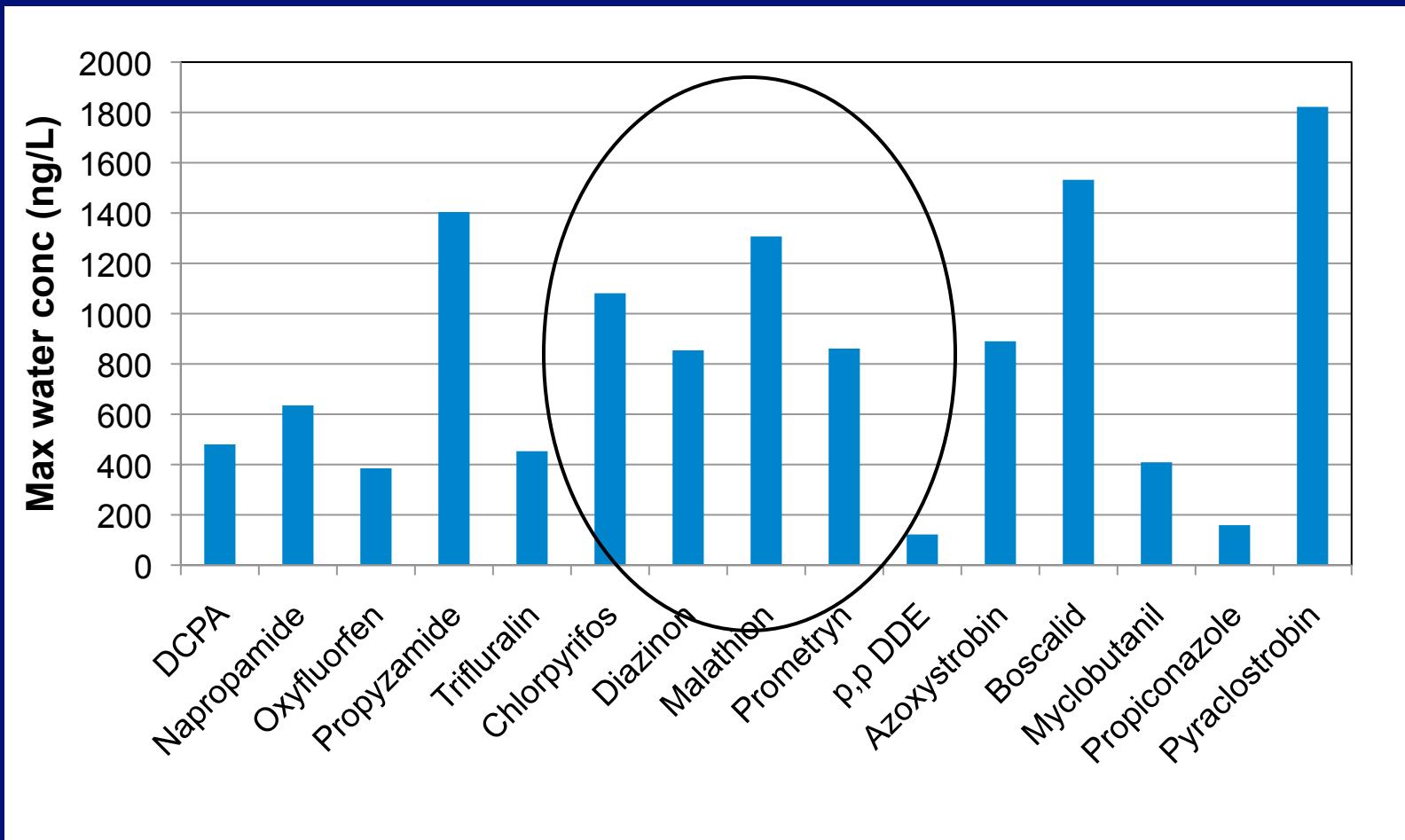


Domagalski et al. 2010. *Environ. Toxicol. Chem.* 26:813-823

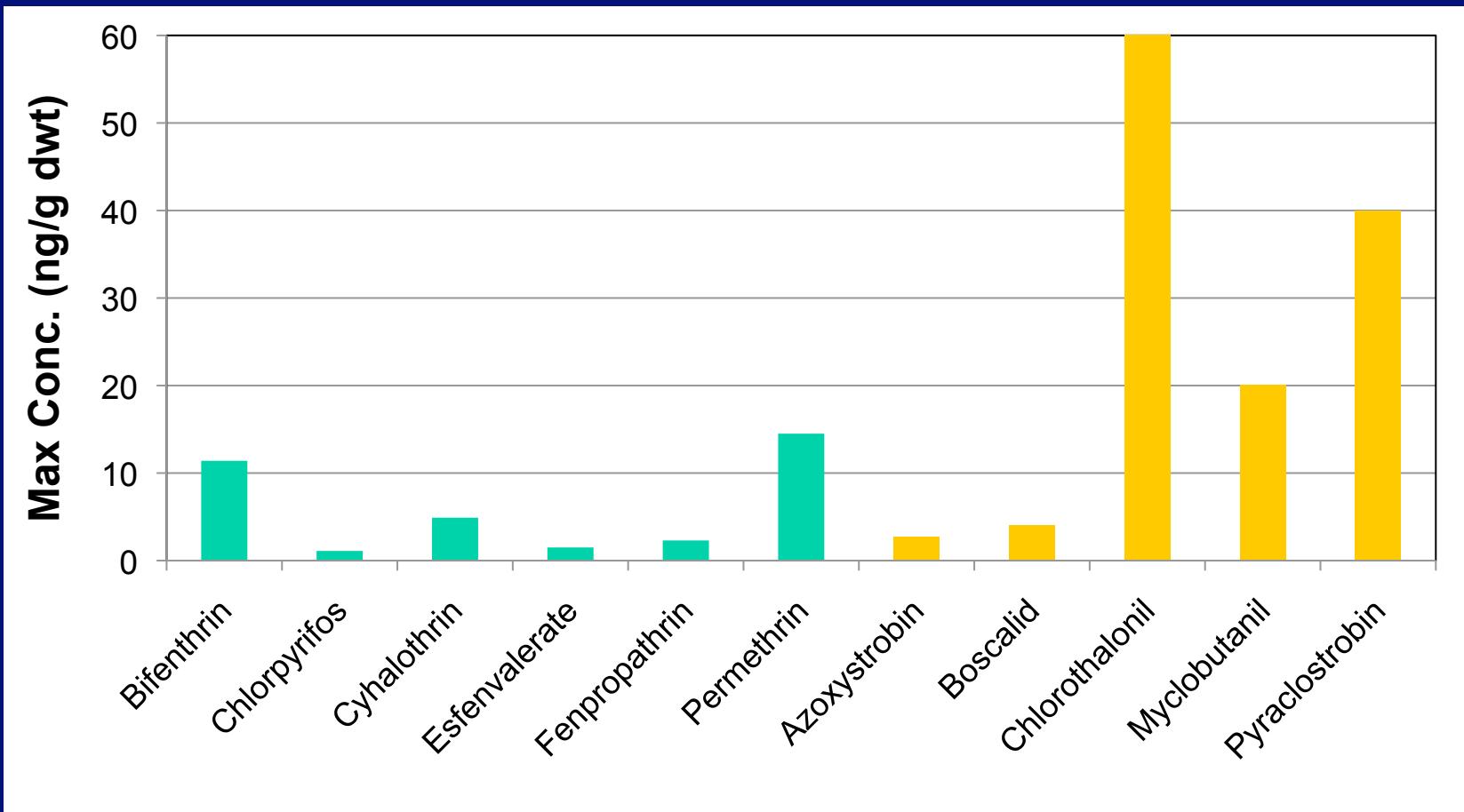
# Pyrethroids as a likely cause of toxicity, or not?



# High levels of nonstandards pesticides in selected tox studies



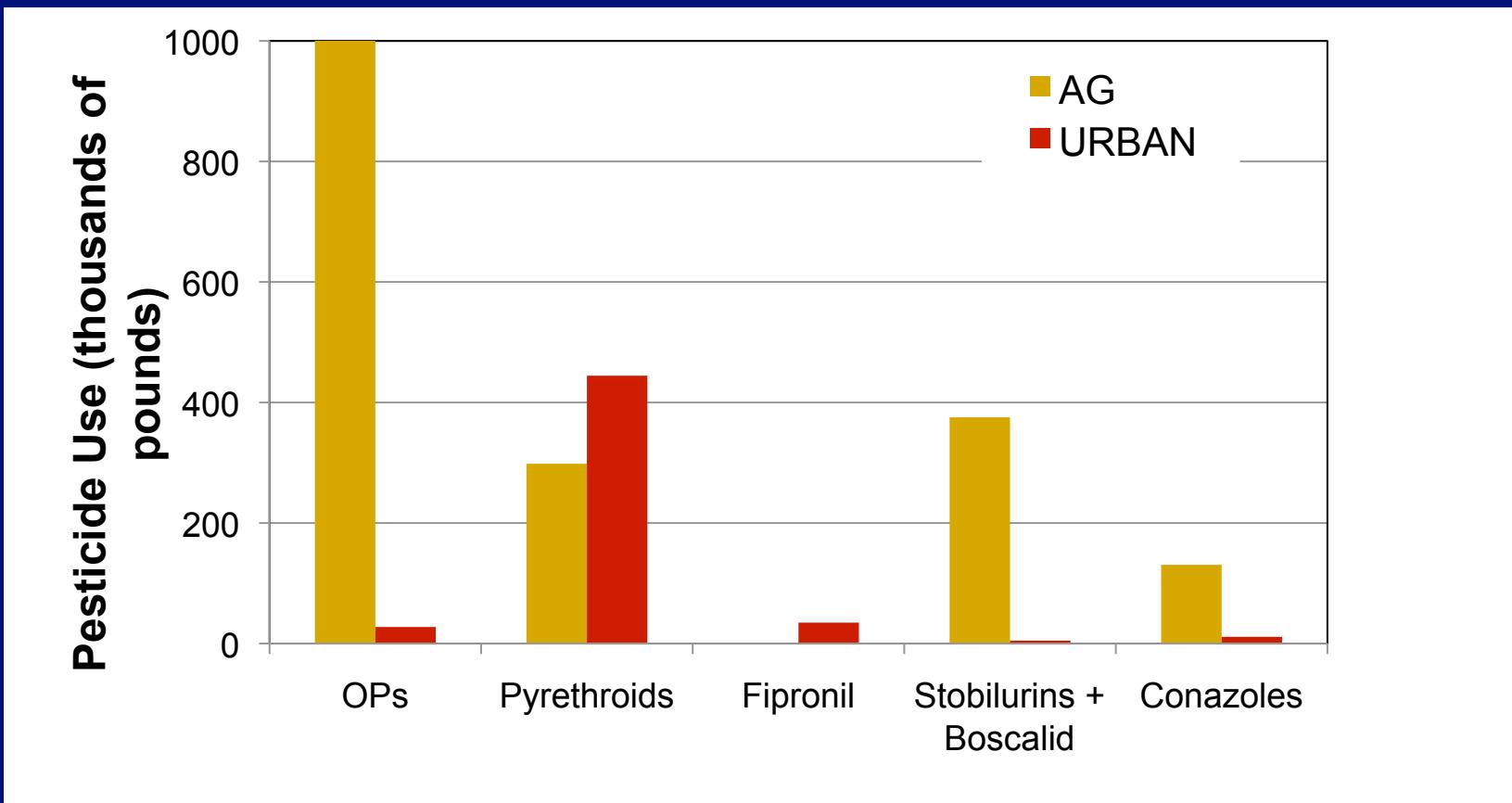
# Complex mixture of target and non target chemicals in ag sediments



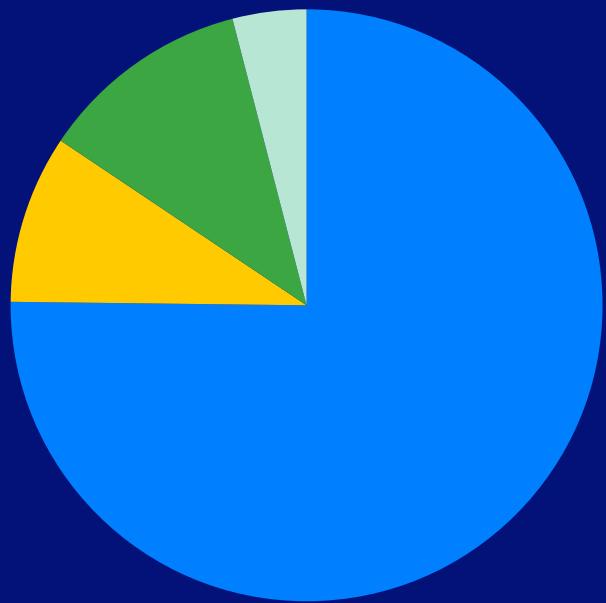
# How to prioritize analyte lists?

- Use DPR pesticide use database to rank chemicals by land-use
- Look at occurrence in sediment/water
  - Understand partitioning
- Rank by toxicity
  - Need information on LC, EC50s for new analytes of interest

# Urban vs. ag pesticide use for the state

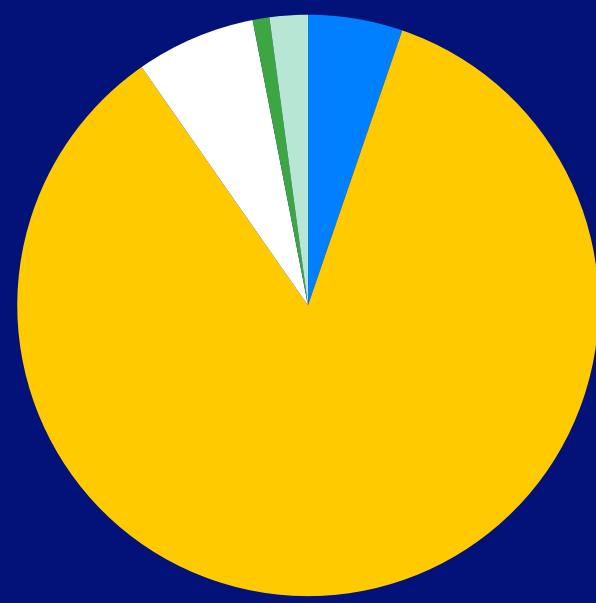


# Understanding use helps prioritize target analytes



Agricultural use

- OPs
- Pyrethroids
- Fipronil
- Stobilurins + Boscalid
- Conazoles

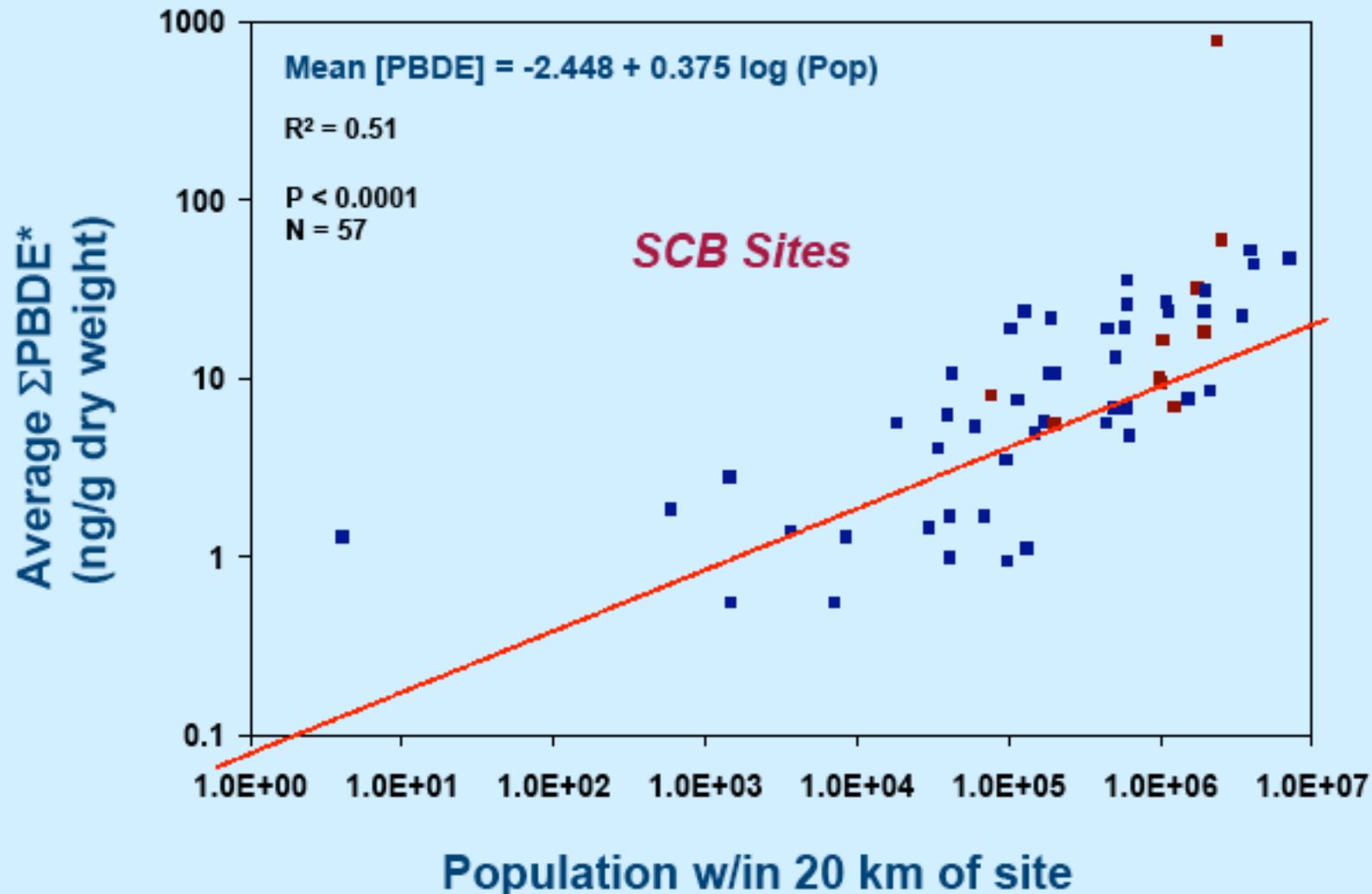


Urban/suburban use

NOAA | National Ocean Service | National Centers for Coastal Ocean Science

## National Status & Trends Program – Mussel Watch

### ► Polybrominated Diphenyl Ethers in *Mytilus spp.*



# Variability in pyrethroid analyses

	SCCWRP	SIU	USGS	%RSD	Ratio
Bifenthrin	34	16	11	48	3
Cyhalothrin	4.0	<2	<2.4		
Cyfluthrin	18	7.4	<2	42	2
Cypermethrin	27	2.6	16.9	64	10
Deltamethrin	3.2	<2	<2.5		
Esfenvalerate	0.9	<2	<2.1		
Cis-permethrin	99	20	--	66	5
Trans-permethrin	47	14	--	55	3
$\Sigma$ permethrin	147	34	31		
$\Sigma$ pyrethroids	233	60	59	76	5

## We need robust low level methods

- Growing interest to measure priority chemicals at low levels (sub ppb)
- Accuracy/precision is key to properly identifying toxicants
- Various protocols and analytical techniques available
- Need to validate currently used research methods

# How do we get there?

- Identify/create control or standard reference sediment
  - contains pyrethroids, fungicides, etc.
- Organize lab intercalibration to compare performance of different methods
- Investigate non-traditional screening (bioanalytical) methods

# **Short term suggestions**

- Generate targeted lists based on
  - Land use
  - Occurrence
  - Toxic potential (need LC, EC50s)
- Identify a sediment control material for analytical labs
- Organize a lab intercalibration exercise for high priority (low level) toxicants
- Possible partners
  - DPR & other pesticide agencies (PAN)
  - DTSC/OPC
  - Existing Workgroups, expert panels

# *A SPME-based sampler to measure the bioavailability of sediment- associated organic contaminants*

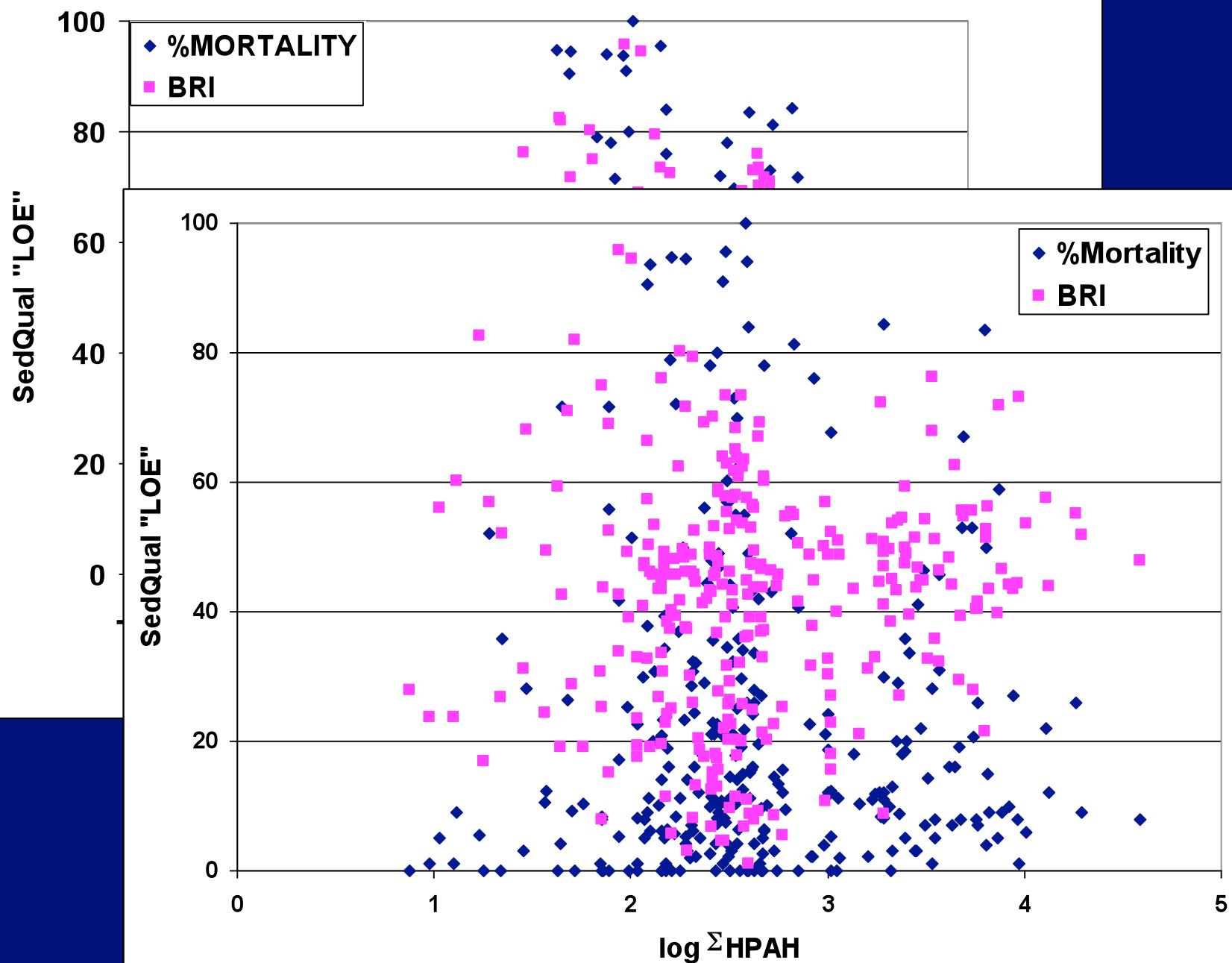
Keith Maruya

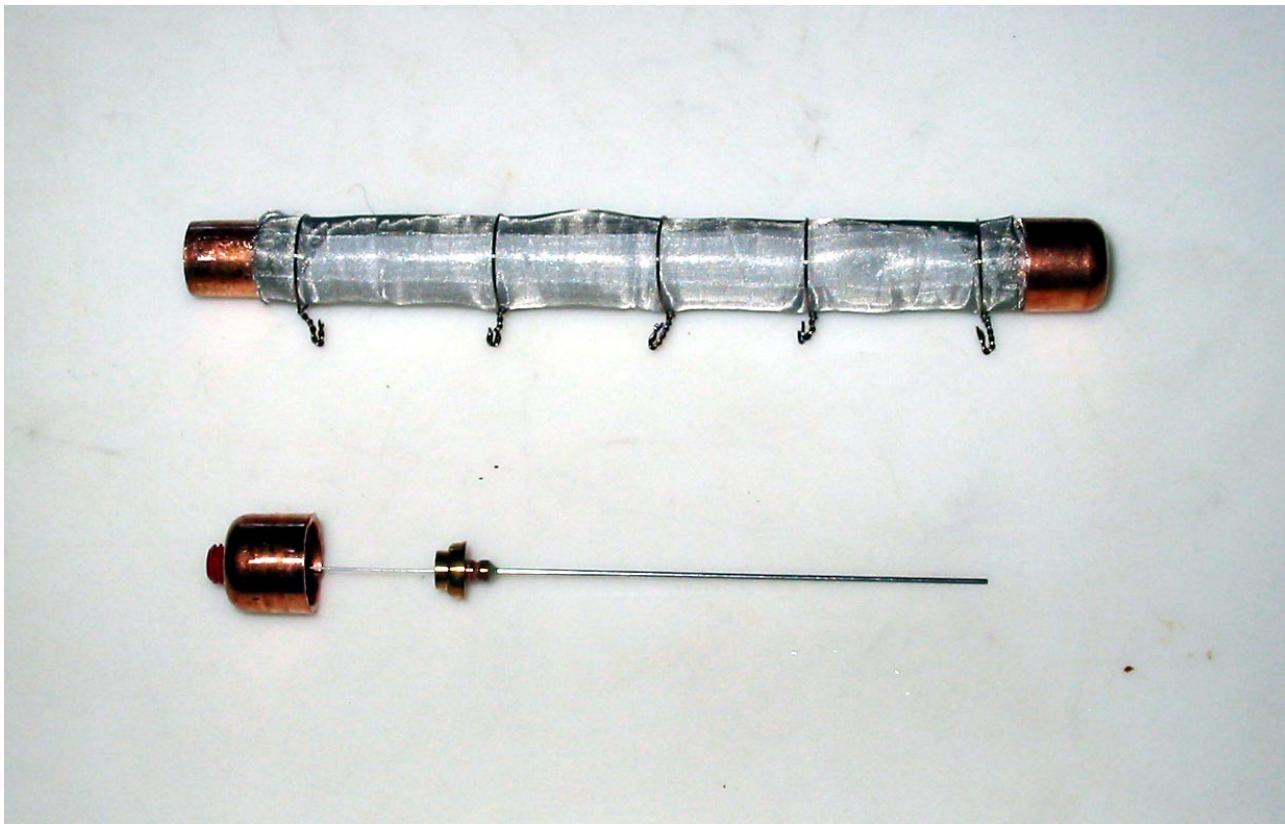
Southern California Coastal Water Research Project  
Costa Mesa, CA



中国科学院广州地球化学研究所  
Guangzhou Institute of Geochemistry Chinese Academy of Sciences







**Housing:**

***11 x 1 cm o.d. (1 mm) Cu tube***

***Interior “cavity” volume: 4.9 cm<sup>3</sup>***

***GF/F (0.7 µm eff pore dia.)***

***270 mesh 316 stainless screen***

***SPME Fiber:***

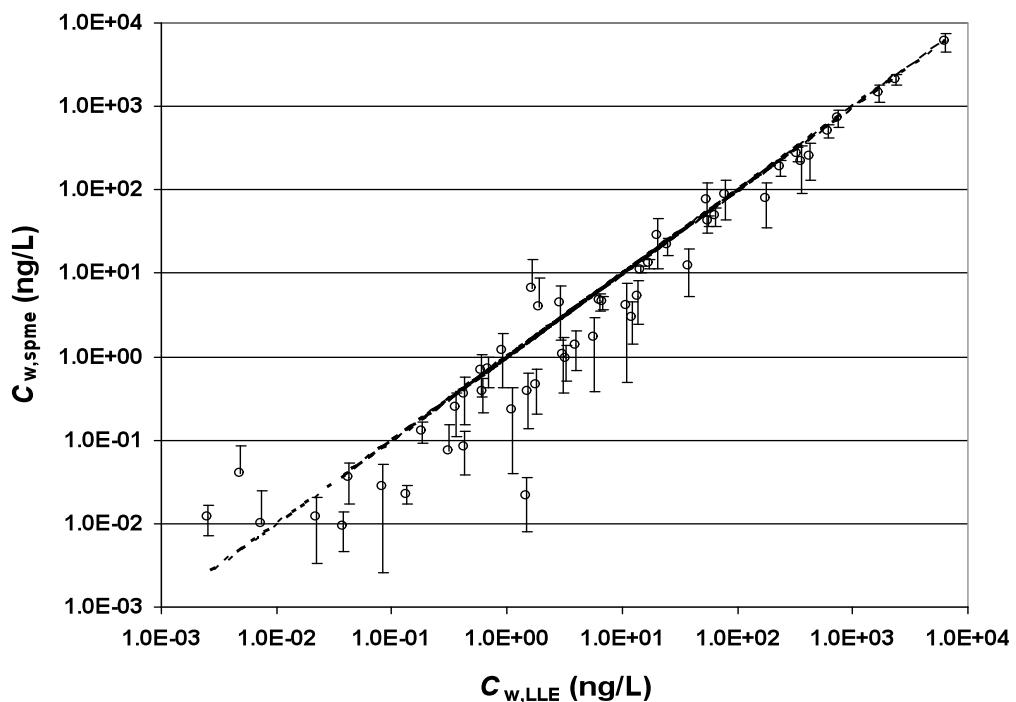
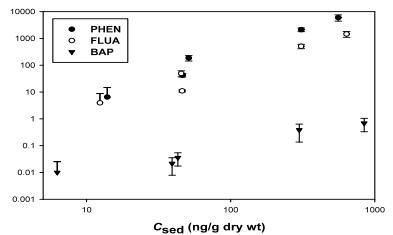
***Length: 1 cm***

***PDMS coating:***

***7, 30 or 100 µm***

***Reusable, comm  
avail. (Supelco)***

***ET&C (2009) 28, 733***



**60 d static test**

**Estuarine sediments**

**spiked 50-1000 ng/g**

**Aging: 60 d**

**V<sub>sed</sub> = 400 mL**

**3 small, 1 lg samplers**

**Fibers, sediment, pw**

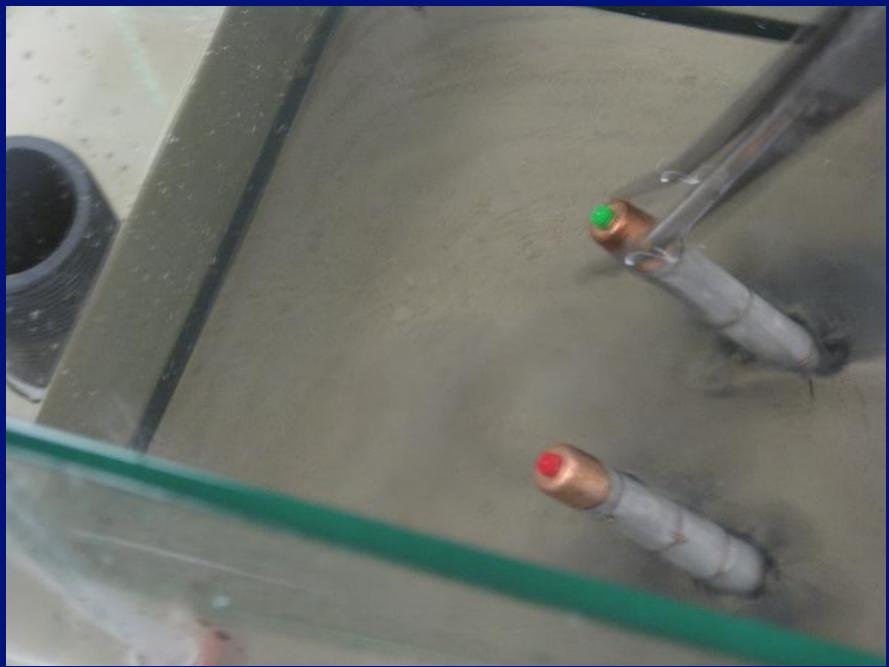
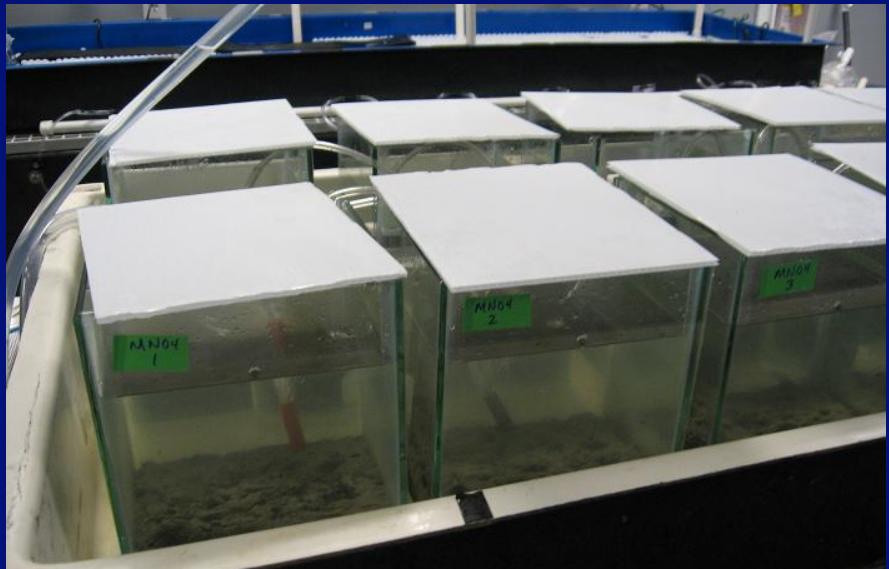
**by GC-MS**

**sed TOC, pw DOC**

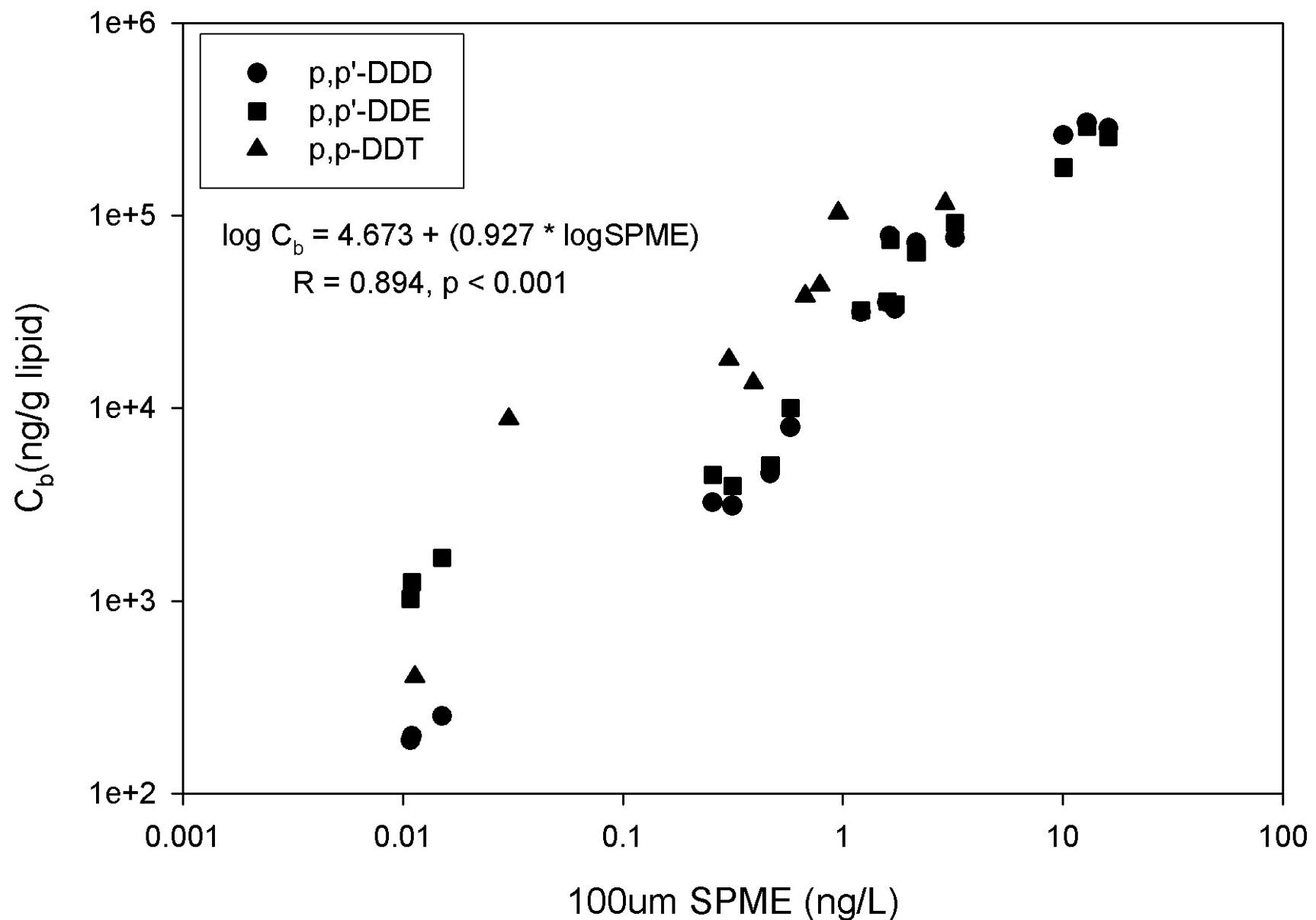
**Centrifuged, filt. pw by  
liq-liq extraction (“LLE”)**

## 28-d Bioaccumulation Tests

- Spiked & field-collected estuarine sediments
  - fine-grained; <0.5 to 5% TOC
  - 5 treatments + unspiked control or ref site (18 tanks)
  - static renewal (50% every 3d)
- *Macoma nasuta* & *Nereis virens*
  - 5 ea per tank
- SPME samplers
  - 7 and 100 um PDMS fibers
  - 1 ea per tank
- Isolated porewater by LLE
- Compare  $C_b$ ,  $C_{pw,tot}$  and  $C_{pw, diss}$  determined by GC-MS



## *Macoma nasuta*



## ***Pre-characterized, field sediments for 28 day co-exposure***

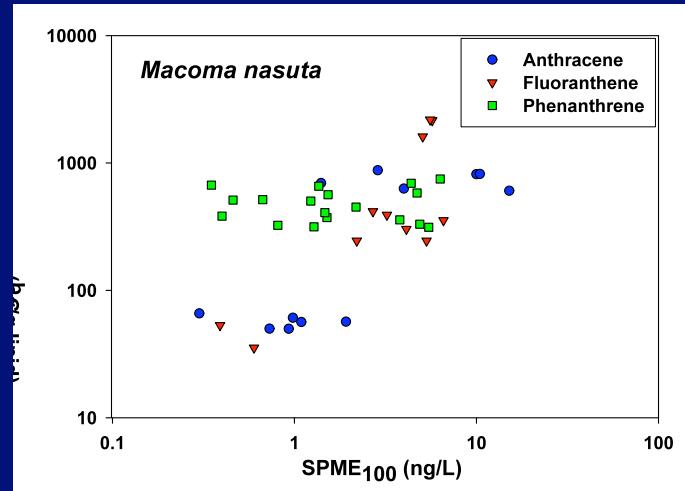
Location	TOC (%)	BC (%)	%MORT	$\Sigma$ PAH	$\Sigma$ PCB	$\Sigma$ DDT	$\Sigma$ CHL
Dominguez Ch.	4.9	0.48	92	6300	12	120	<10
Dominguez Ch.	3.1	0.74	54	4400	23	84	24
San Diego Bay	1.6	0.37	40	5800	54	4.8	<10
San Diego Bay	1.8	0.36	21	7200	130	4.1	<10
LA/LB Harbor	1.0	0.19	15	390	0.92	51	<10
San Pedro Shelf	0.2	0.03	na	26	<4.7	2.5	<10

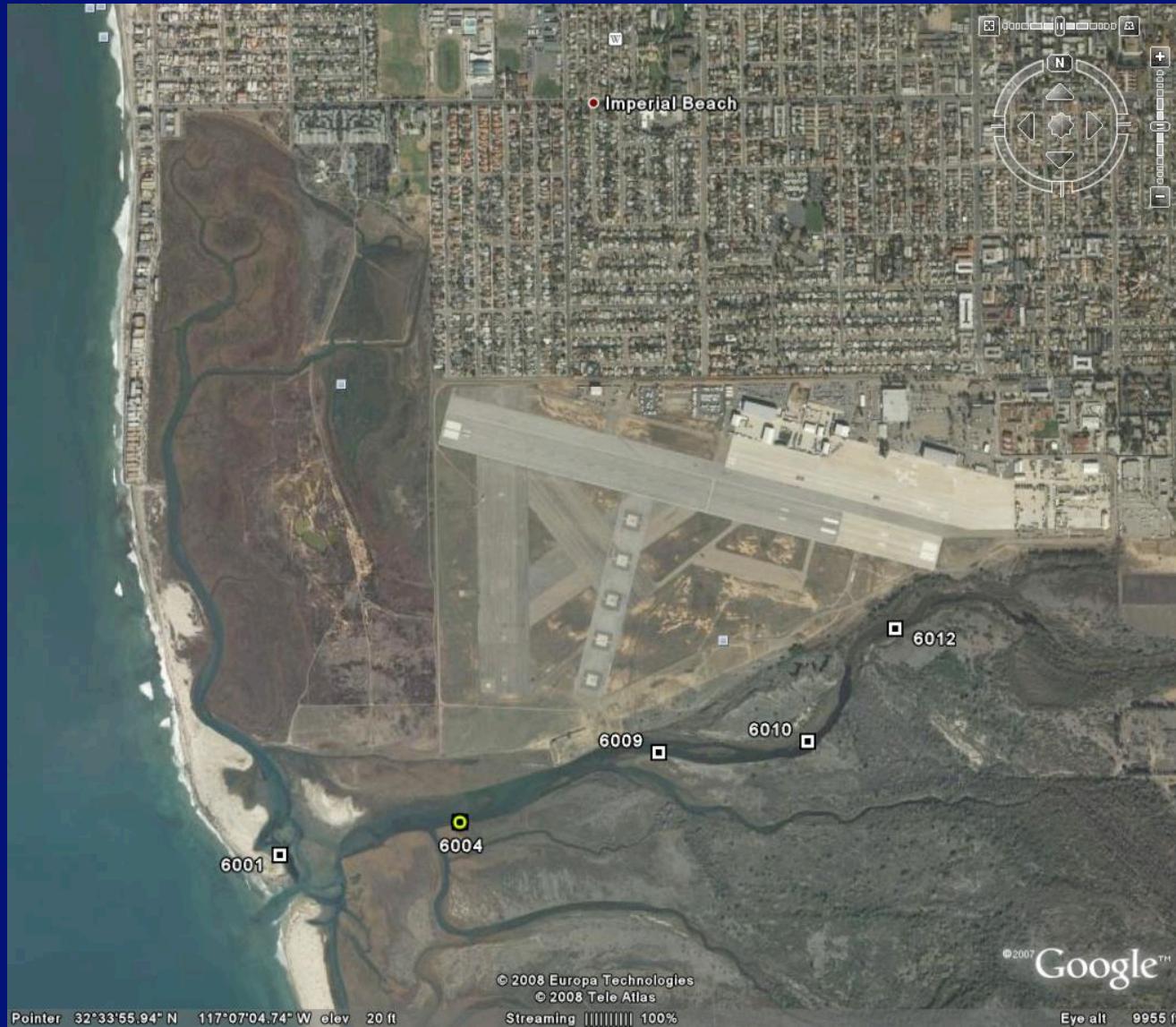
Units are ng/g

BC = black carbon

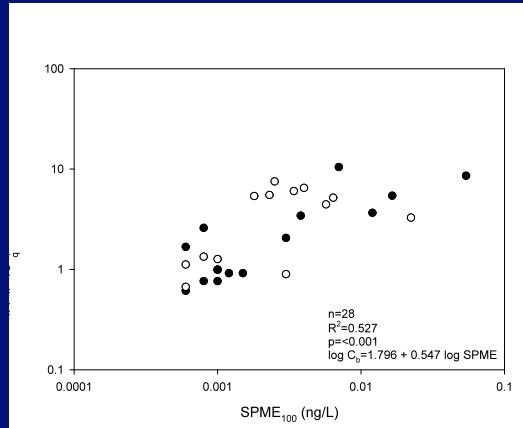
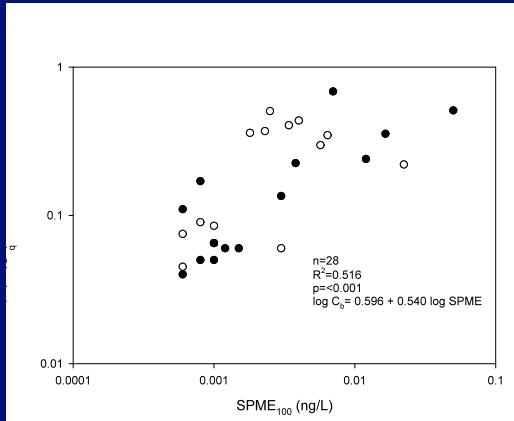
$\Sigma$ CHL = total chlordane

%MORT = 96 h amphipod (*Eohaustorius* spp.) mortality





*Protothaca*: filled circles  
*Tagelus*: open circles



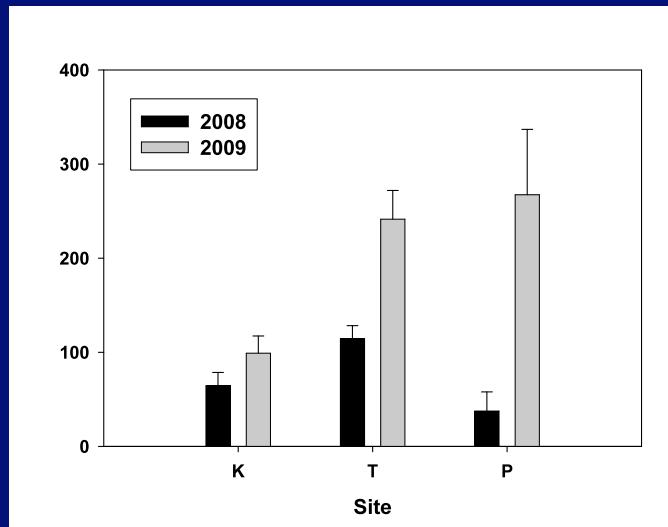
Total PCBs in bivalves  
(*Protothaca*, *Tagelus*  
spp.) from the Tijuana  
River NERR (2008, 09).

## *Other trials*

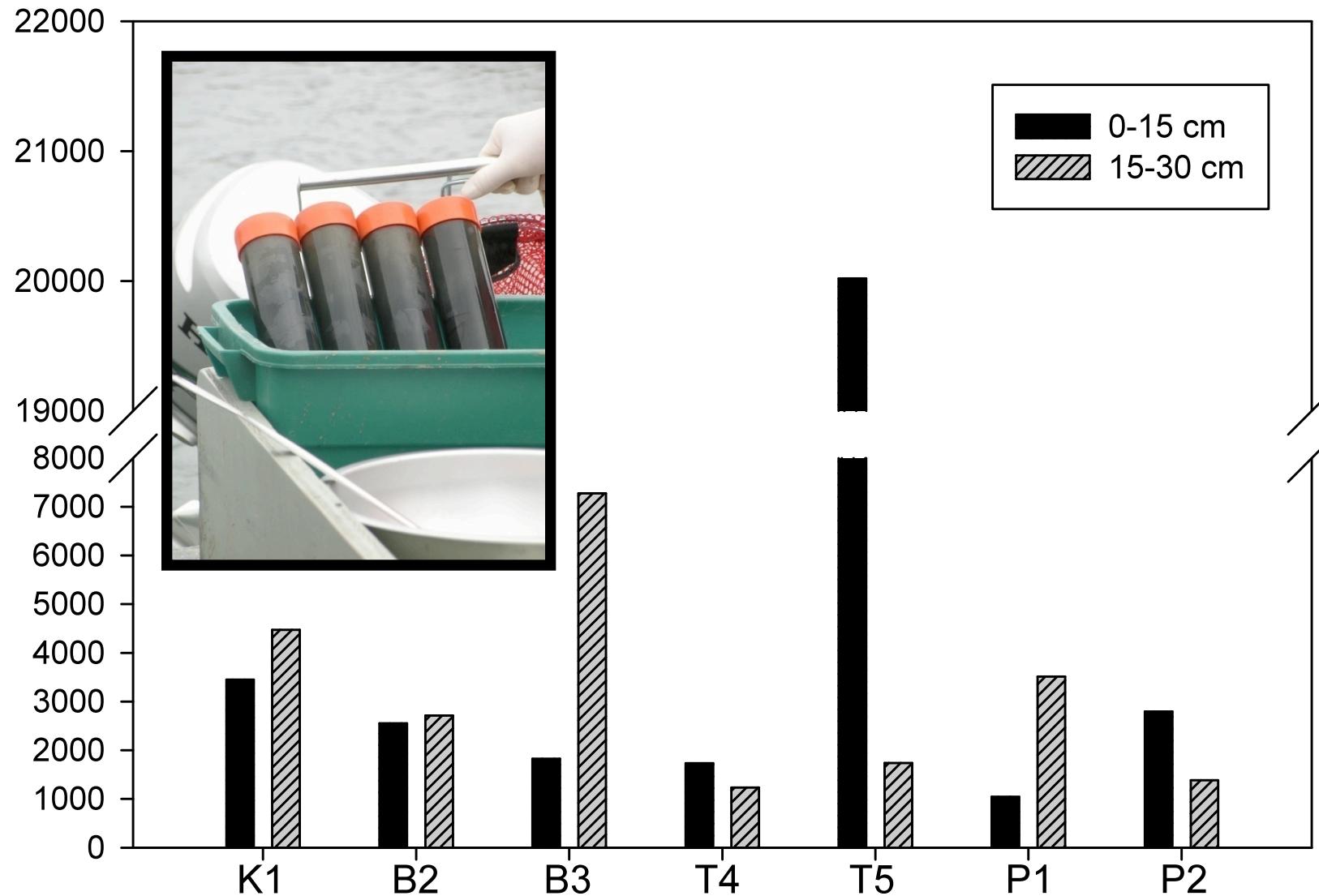
- San Diego Bay (SPAWAR) - 2008
- Lower Duwamish (EPA Reg 10)- 2008-09
- Pyrethroid bioavailability (lab)- 2009
- Sediment LC50 with *E. estuarius* (2010)
  - Disposable PDMS, 10 d fixed exposure time
  - Cyfluthrin, DDT, chlordane

## ***Next steps***

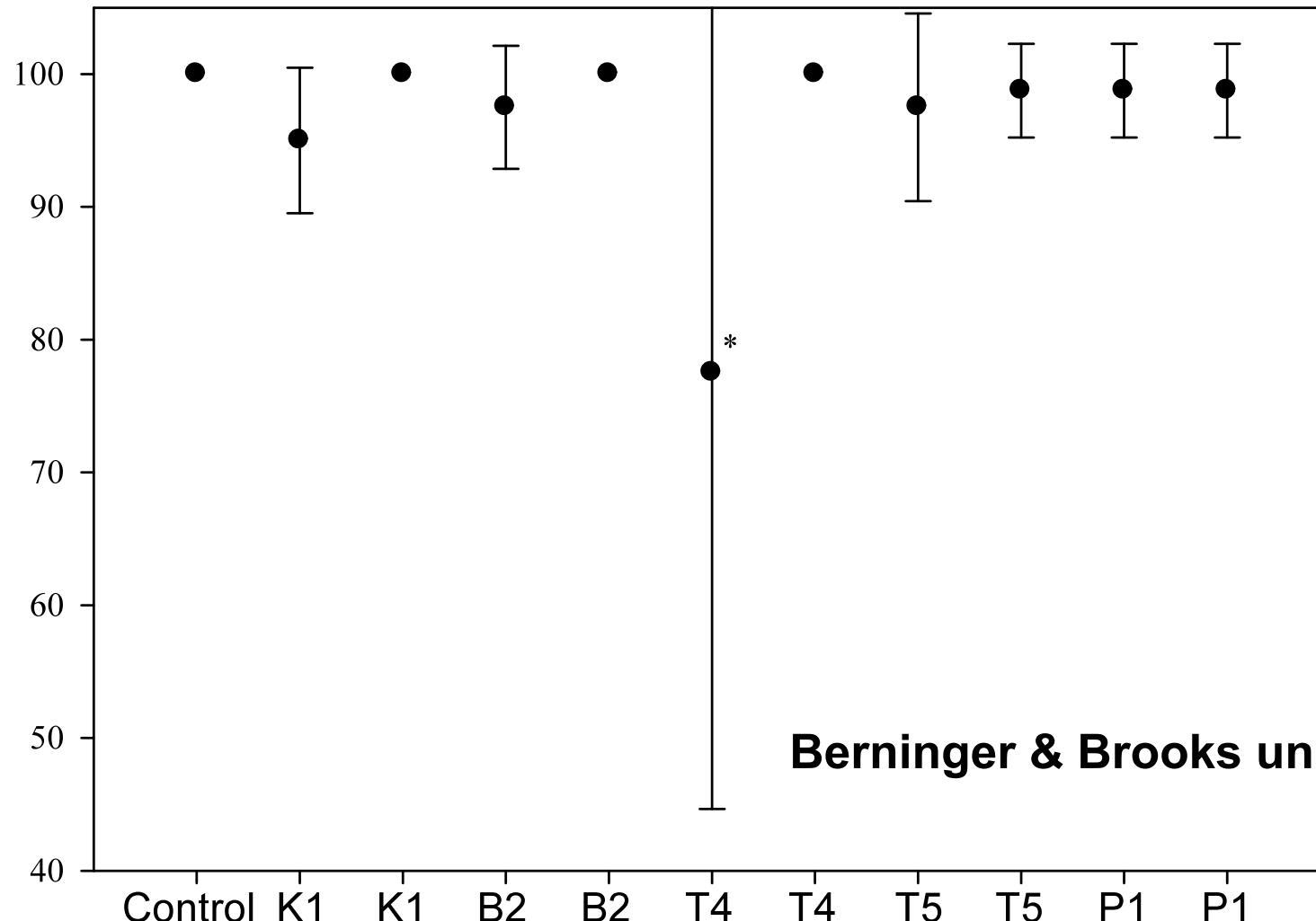
- Assess SPME vs. sediment toxicity (LC, EC50s)
- Compare water column SPME with caged mussel burdens
- Comprehensive in situ comparison of SPME porewater and invertebrate burdens, community structure
- Calibration of additional analyte classes
  - current use pesticides
  - Industrial/commercial chemicals (alkylphenols)
  - PPCPs



## LDW 2008 tPAHs in Sediment



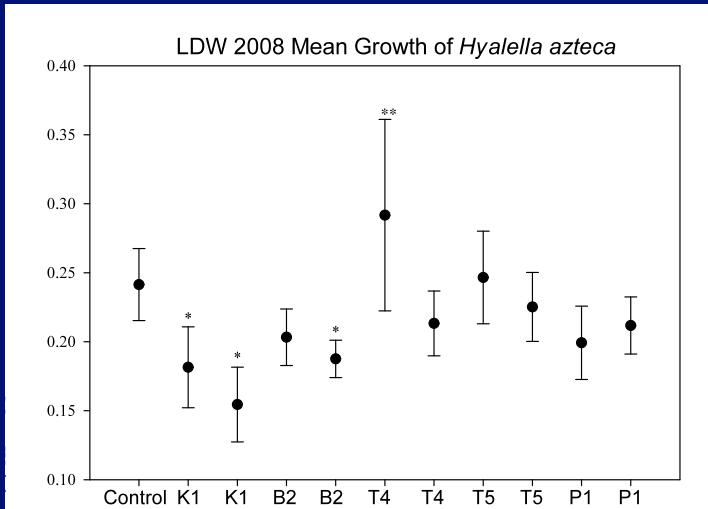
### LDW 2008 Mean Survival of *Hyalella azteca*



# LDW 2008

## Sediment TOC and Distribution

Site	% TOC (Average)	% TOC StDev	% Sand >63 µm	% Silt 2 - 63 µm	% Clay <2 µm
K1	2.76	0.11	10.06	84.07	5.87
K1	2.45	0.10	12.91	80.81	6.28
B2	1.21	0.20	23.17	72.97	3.86
B2	1.55	0.11	37.79	59.05	3.16
T4	1.09	0.39	21.57	74.51	3.92
T4	1.68	0.53	12.51	82.59	4.9
T5	1.55	0.12	32.86	63.76	3.38
T5	0.94	0.31	39.32	57.84	2.84
P1	1.58	0.38	20.97	75.3	3.73
P1	1.99	0.10	26.01	70.44	3.55



# Bioassays

Berninger & Brooks unpubl.