Pyrethroids and fipronil in southern California waterways

Wenjian Lao
Keith Maruya

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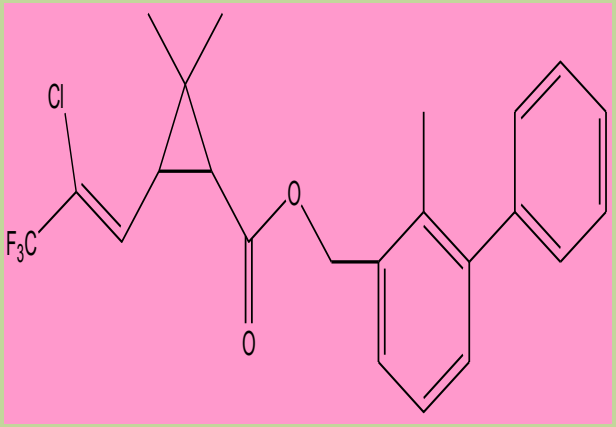
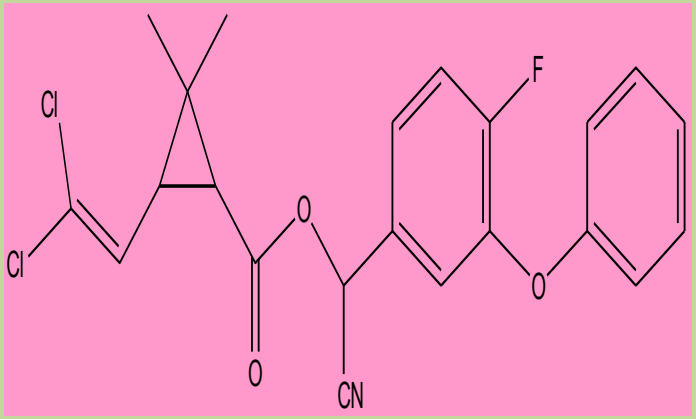
Southern California Coastal Water Research Project

Pyrethroids are persistent & toxic



***Bifenthrin* (Type I)**



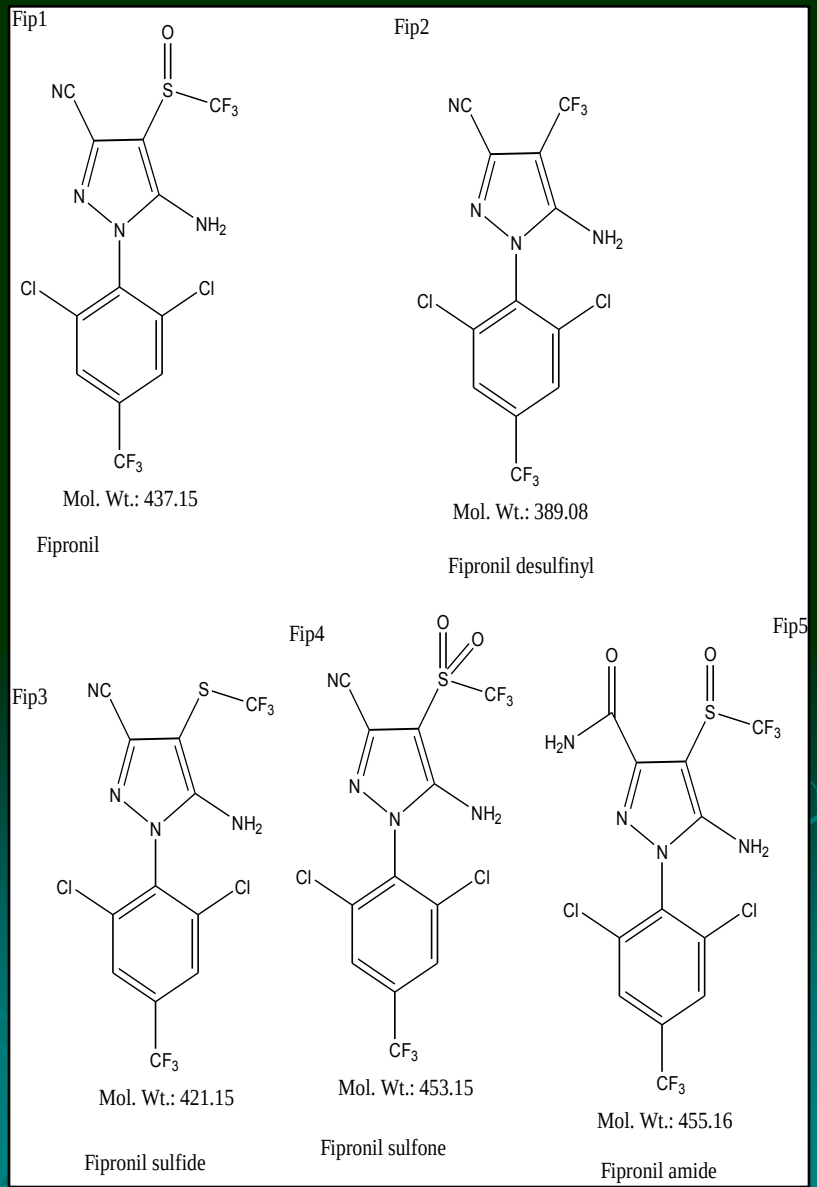
***Cyfluthrin* (Type II)**

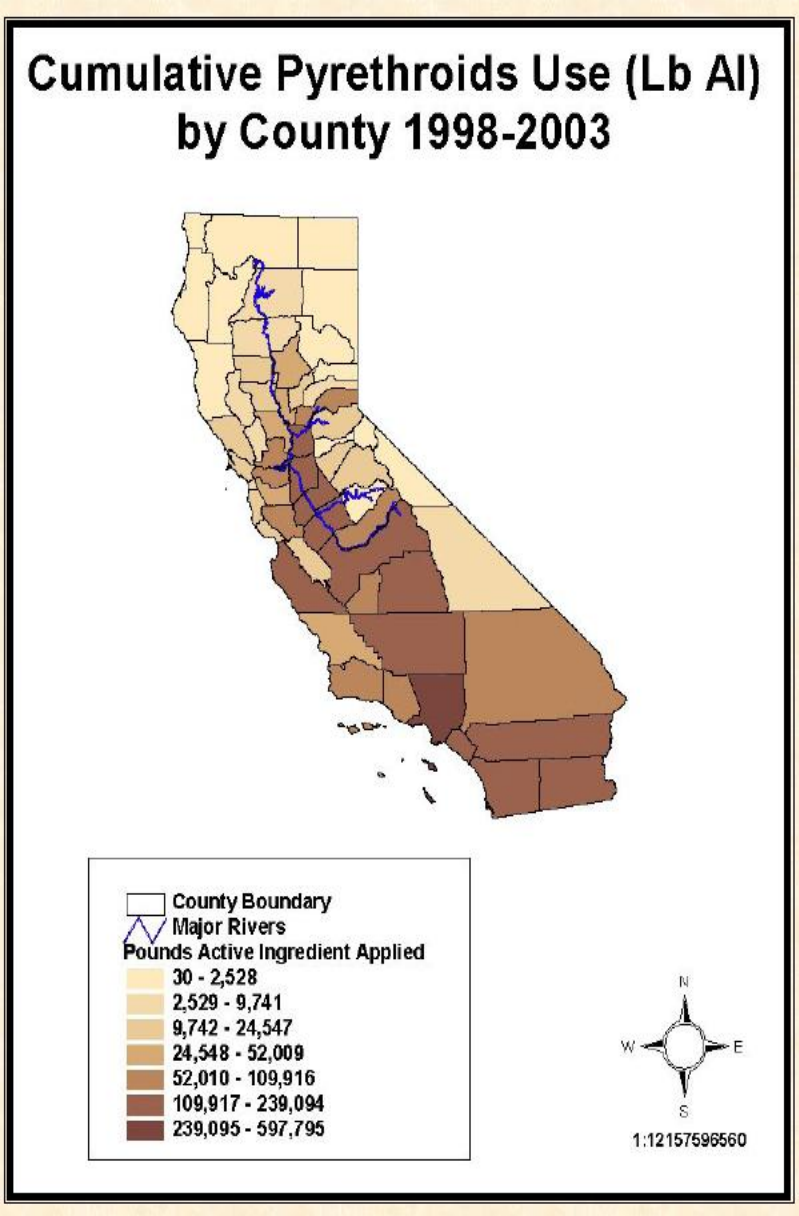
- Hydrophobic (log K_{ow} 5.5 to 6.5)
- Long half lives in sediment (2-65 Months)

	LC50 (ug/g OC)			LC50 (ug/g OC)
	H. azteca	*Eohaustorius*		*H. azteca*
bifenthrin	0.52	**1.0**	esfenvalerate	1.5
cyfluthrin	1.1	**0.33**	λ-cyhalothrin	0.45
cypermethrin	0.38	**1.4**	deltamethrin	0.79
permethrin	10.83	**17.9**		

Fipronil and degradates

- Moderately hydrophobic (K_{ow} ~ 4)
- Aerobic soil half-life ~188 days
- High potential toxicity
  - *Daphnid* LC_{50}=18 ug/L
  - Mysid NOEC < 5 ng/L





- Pyrethroids & fipronil are widely used in CA
- Active ingredient in >1000 mostly non-ag products
- ***2.3 million lbs*** pyrethroids applied (1998-2008)
- ***119,000 lbs*** fipronil applied (in 2006)
- No statewide regulation or monitoring in ambient waters

Previous findings

- ✓ Pyrethroids likely toxicants in CA freshwater sediments (*Weston & Lydy 2010*)
  - ✓ Suspected in estuarine & marine sediments (*Anderson et al. 2010; Lao et al. 2010)*
- ✓ Fipronil and its degradates cause for non-target organism mortality
  - ✓ Procambrus (*Schlenk et al. 2001*) & Palaemonetes spp. (*Wirth et al. 2004*)

- ✓ **No/little occurrence data in southern CA coastal sediments**
- ✓ **Less certainty in toxicity of estuarine & marine sediments**
- ✓ **Little consensus on accuracy of analytical methods**

Research & Monitoring Priorities

- Develop/validate sampling & analytical methods for fipronil and pyrethroids
  - (single quad) GC-NCI-MS
  - passive sampling devices (PSDs)

- Characterize occurrence in southern CA coastal watersheds and ocean
  - Ballona estuary (2007-09)
  - embayment sediments (Bight 2008)
  - effluent-dominated rivers (2010)

Sediment method

- Pyrethroids (8) & Fipronil+degradates (4)
- 46 PAH; 41 PCB congeners; 18 OCPs; 14 PBDES
- Accelerated solvent extraction (ASE)
- Florisil packed column cleanup
- Quantitation by GC-EI & NCI-MS

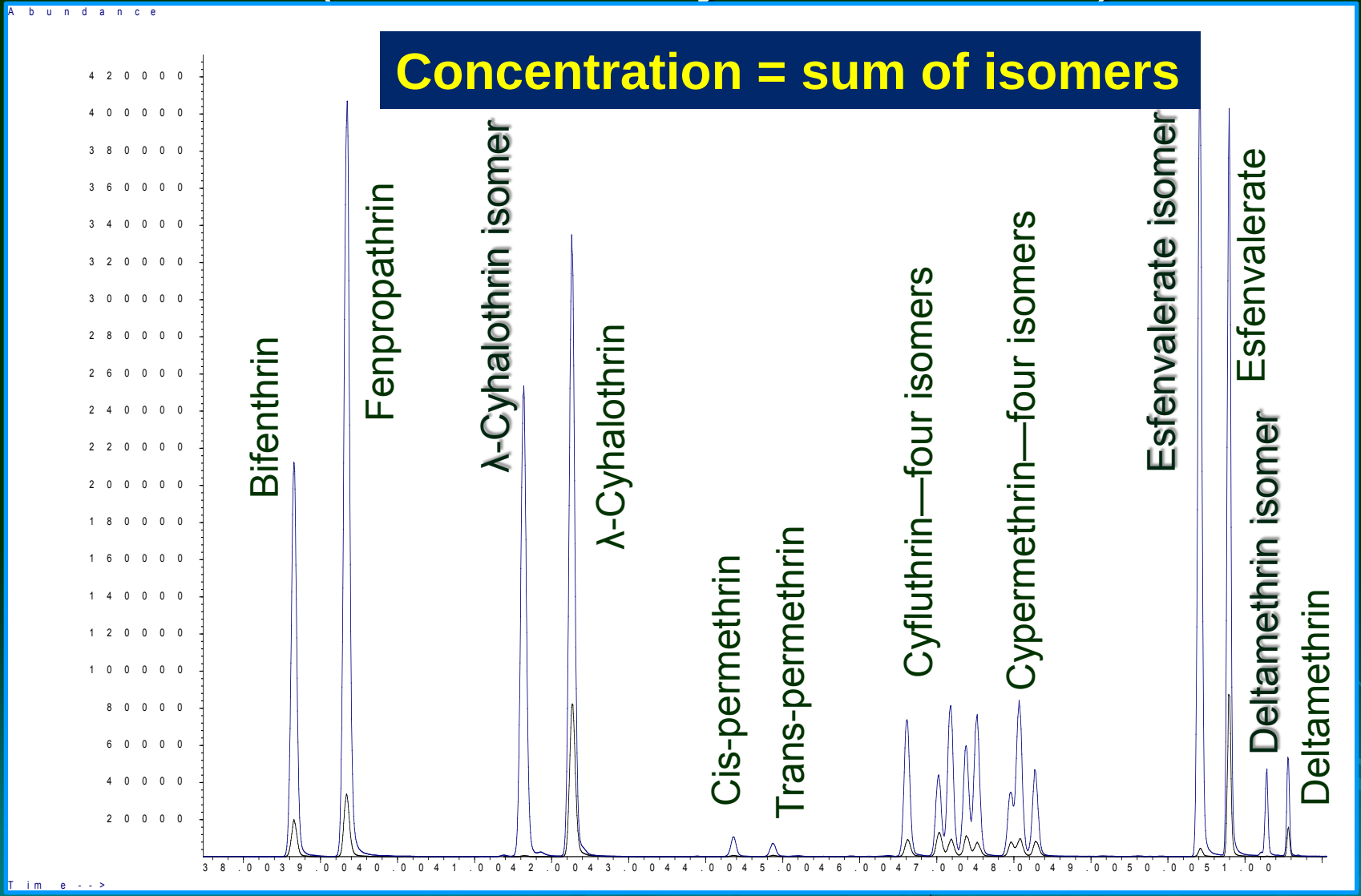
GC-NCI/MS Method Development

- Agilent 7890 + 5975C Inert MSD
- Negative chemical ionization (NCI), CH4
- Post-column splitter to μ-ECD, MSD
  - simultaneous ECD, NCI-MS chromatograms
- Performance-based QA/QC
  - Matrix spikes 8 target pyrethroids (n=14), fipronil/degradates (n=6)
  - Mean recovery:

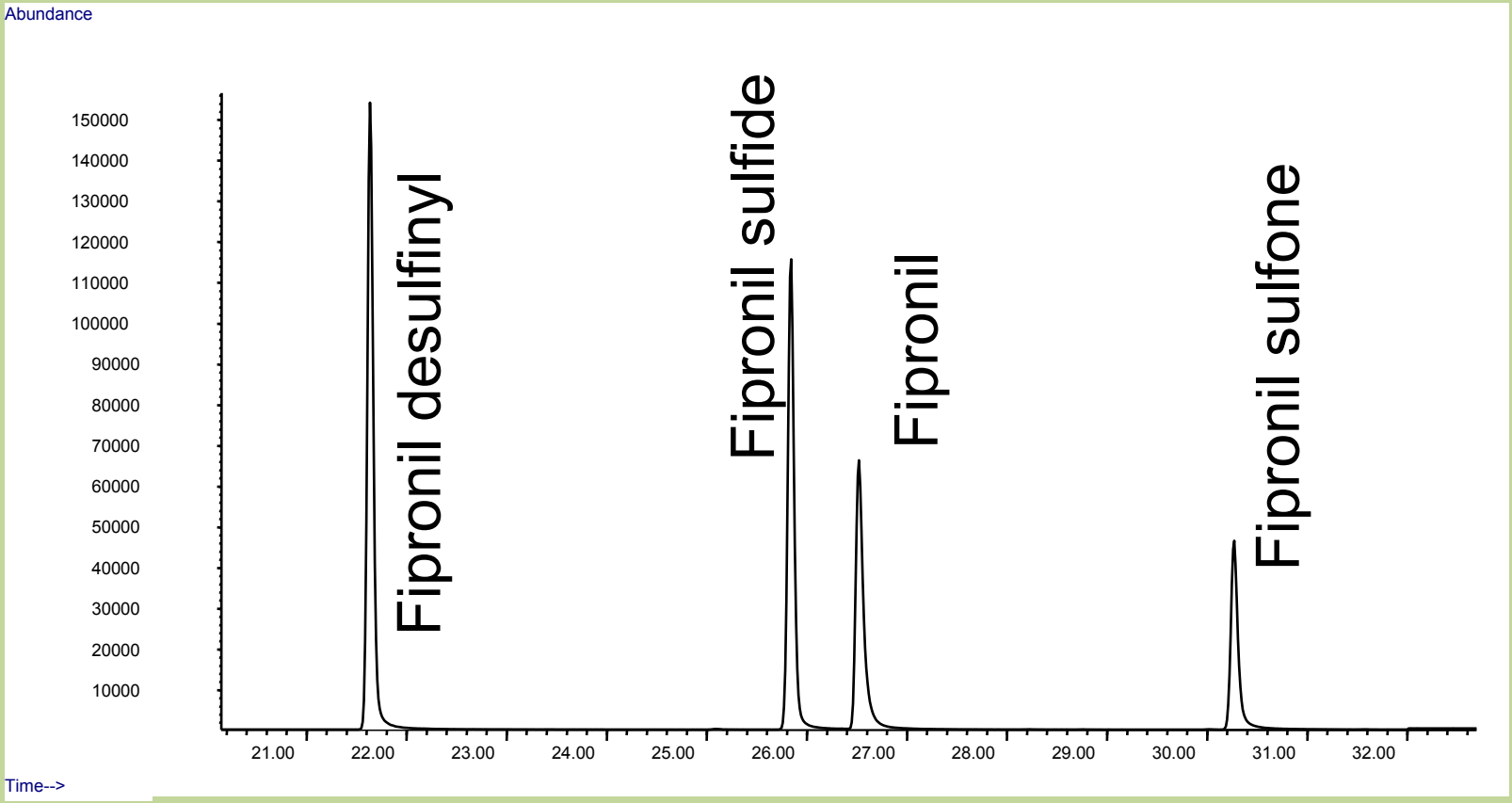
    Pyrethroid: 99 ± 4.9% (95% conf. interval)

    Fipronil/degradates: 93 ± 9.6%
  - Mean RSD for sediment duplicates: 8.7 ± 3.0%
- No SRM currently available
- Reporting limits 2 ng/g (25 ng/g for permethrin)
- Lao et al. (2010) *Environ Toxicol Chem* **29**, *834*

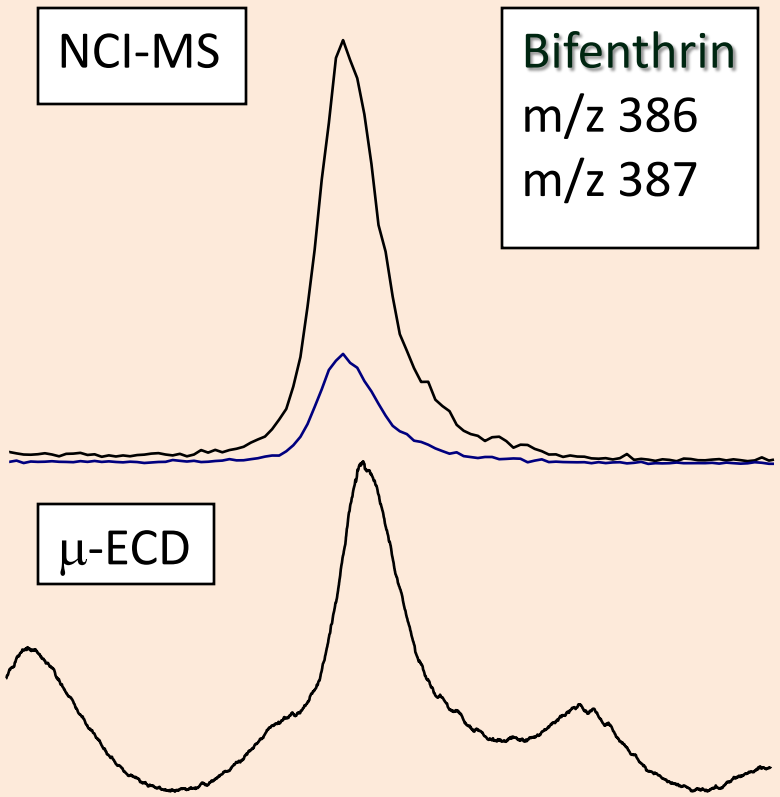
Isomerization in seawater (measured by SPME fiber)

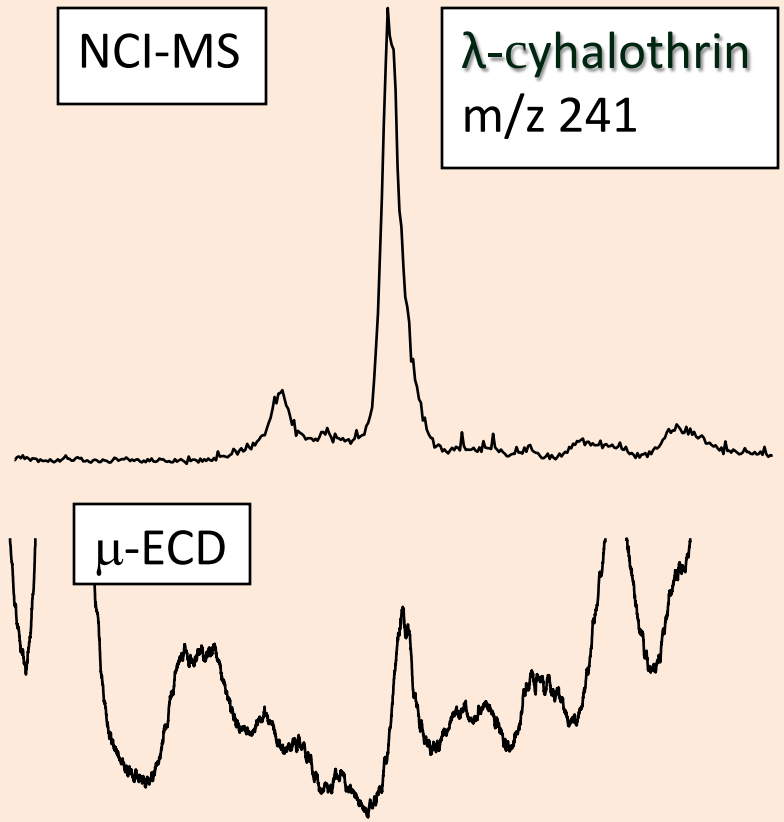


- Fipronil breaks down into 3 primary products
- Well resolved peaks by GC-NCI/MS
- no isomerization



Is NCI-MS-SIM *more selective* than ECD?



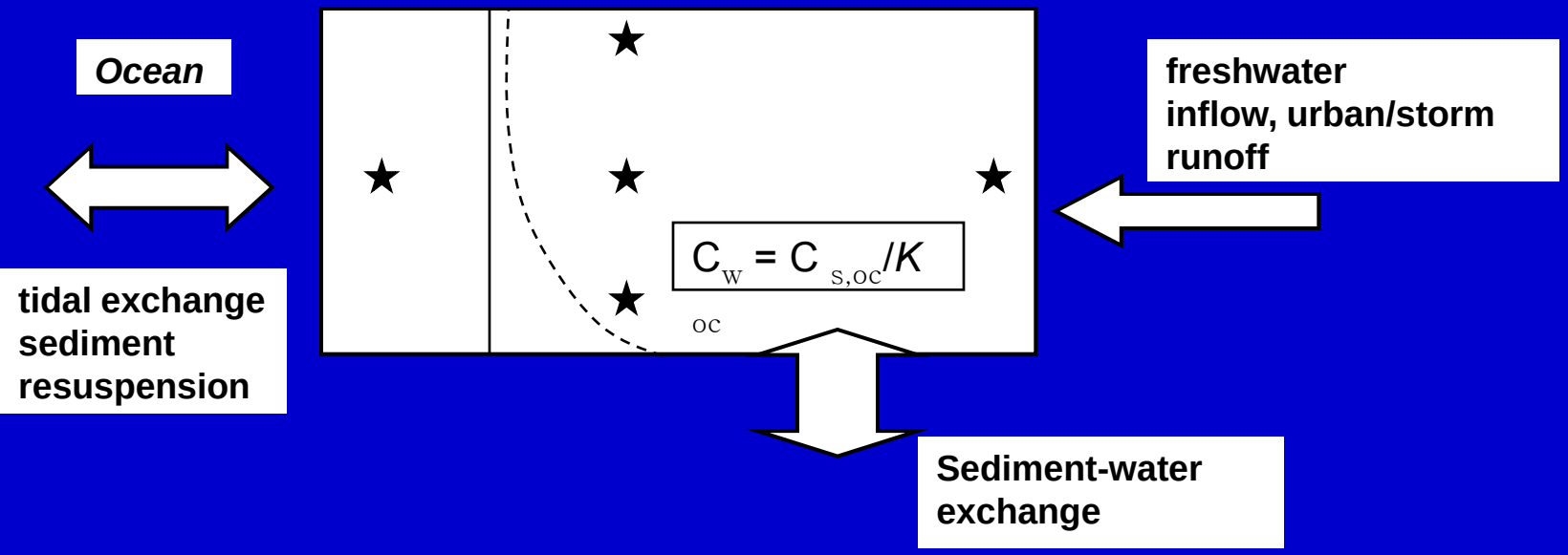


Ballona Creek sediment extract analyzed simultaneously by GC-NCI/MS-SIM and μ-ECD via post-column splitter

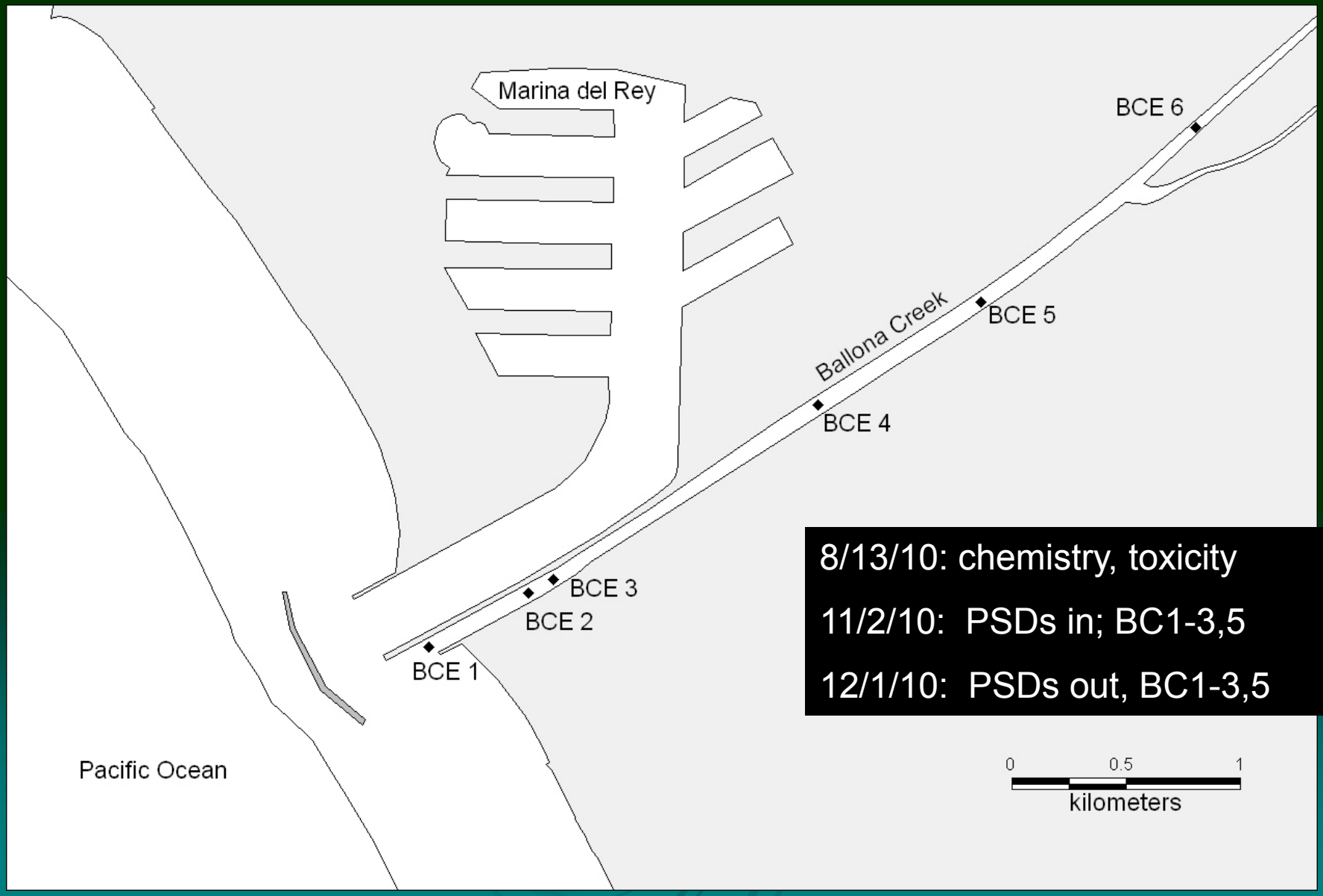
Ballona Creek

(LA County)

303d listed for sediment chemistry, toxicity



Sampling sites

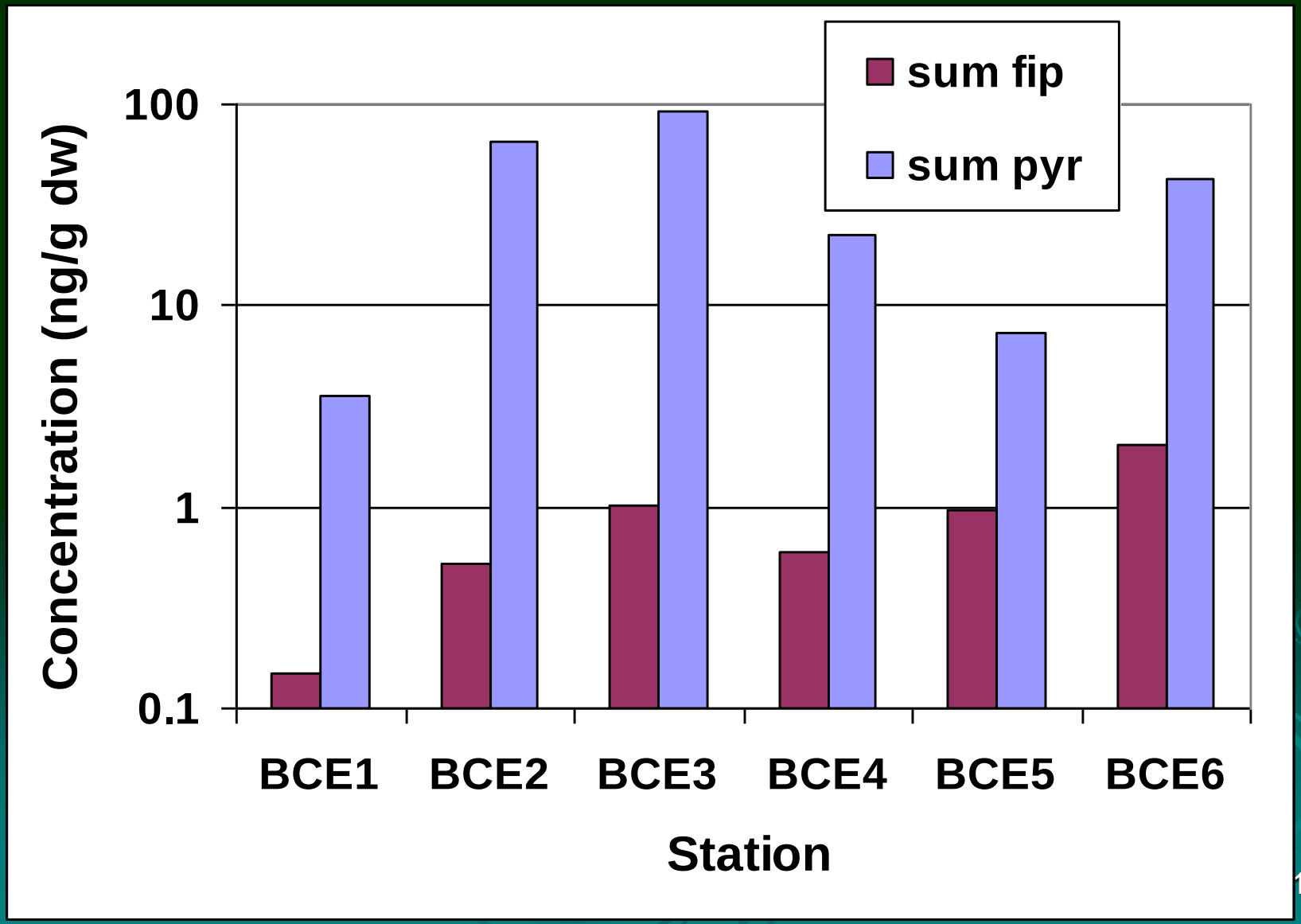


8/13/10: chemistry, toxicity

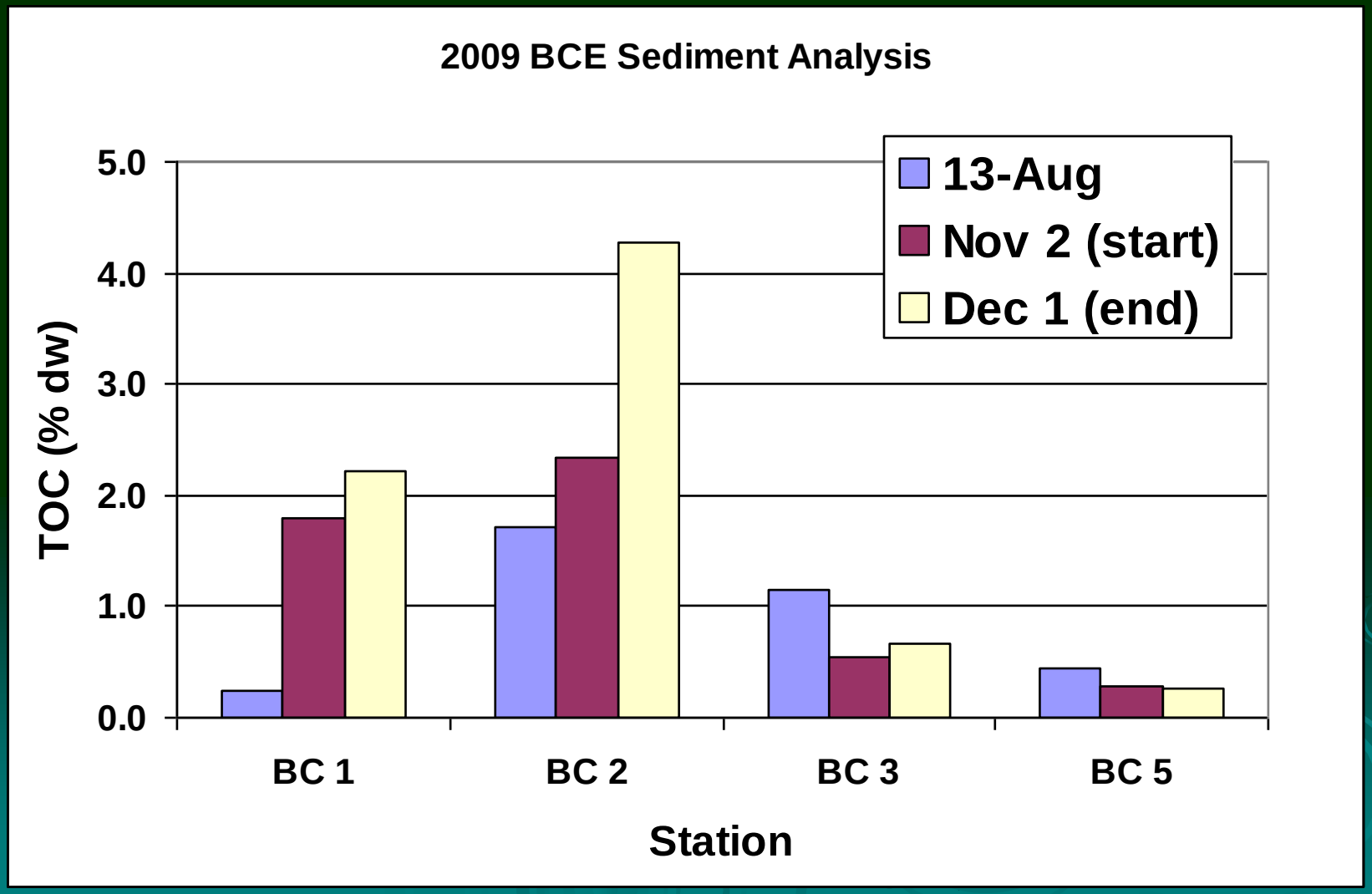
11/2/10: PSDs in; BC1-3,5

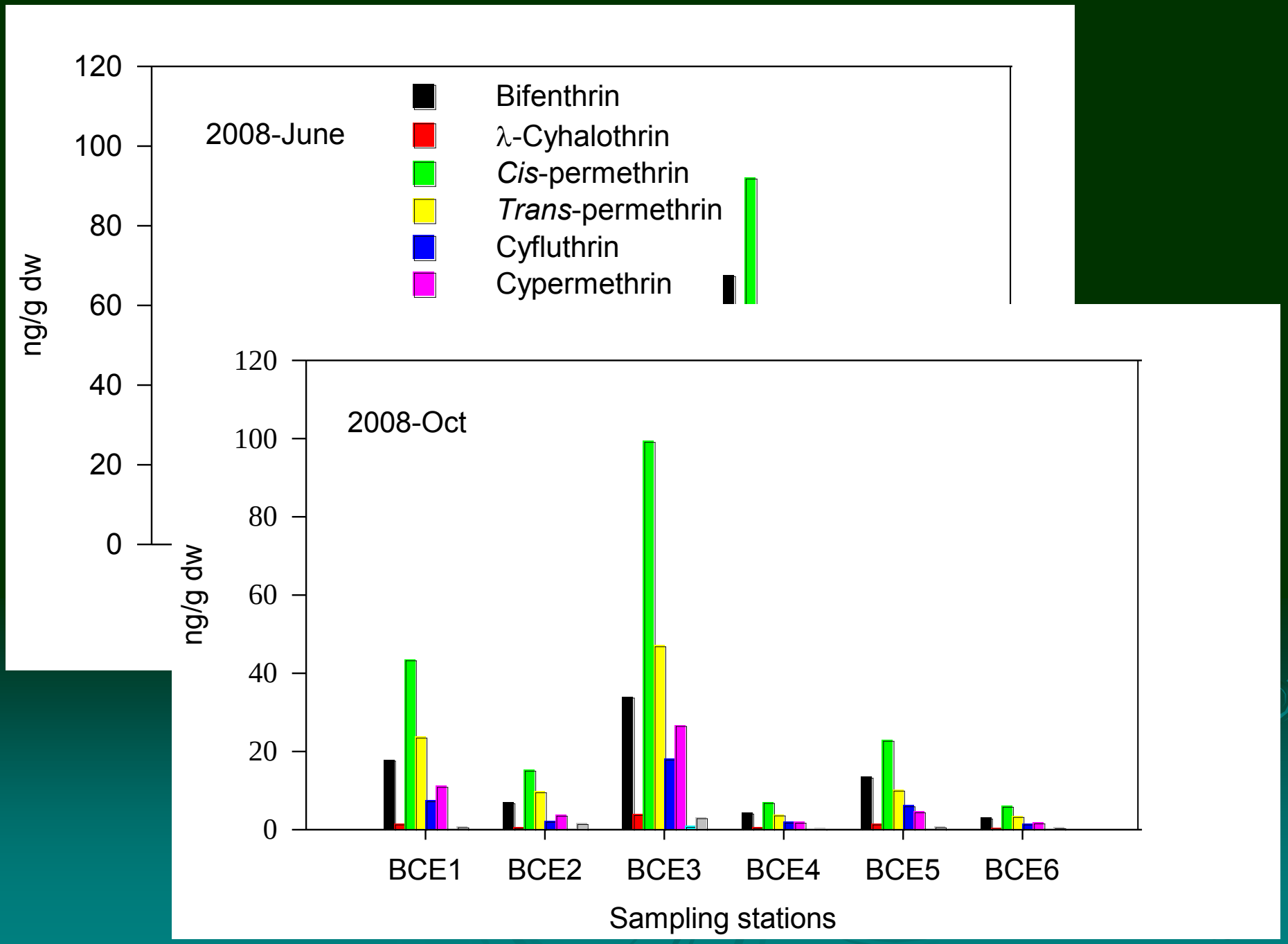
12/1/10: PSDs out, BC1-3,5

Pyrethroids >> Fipronil

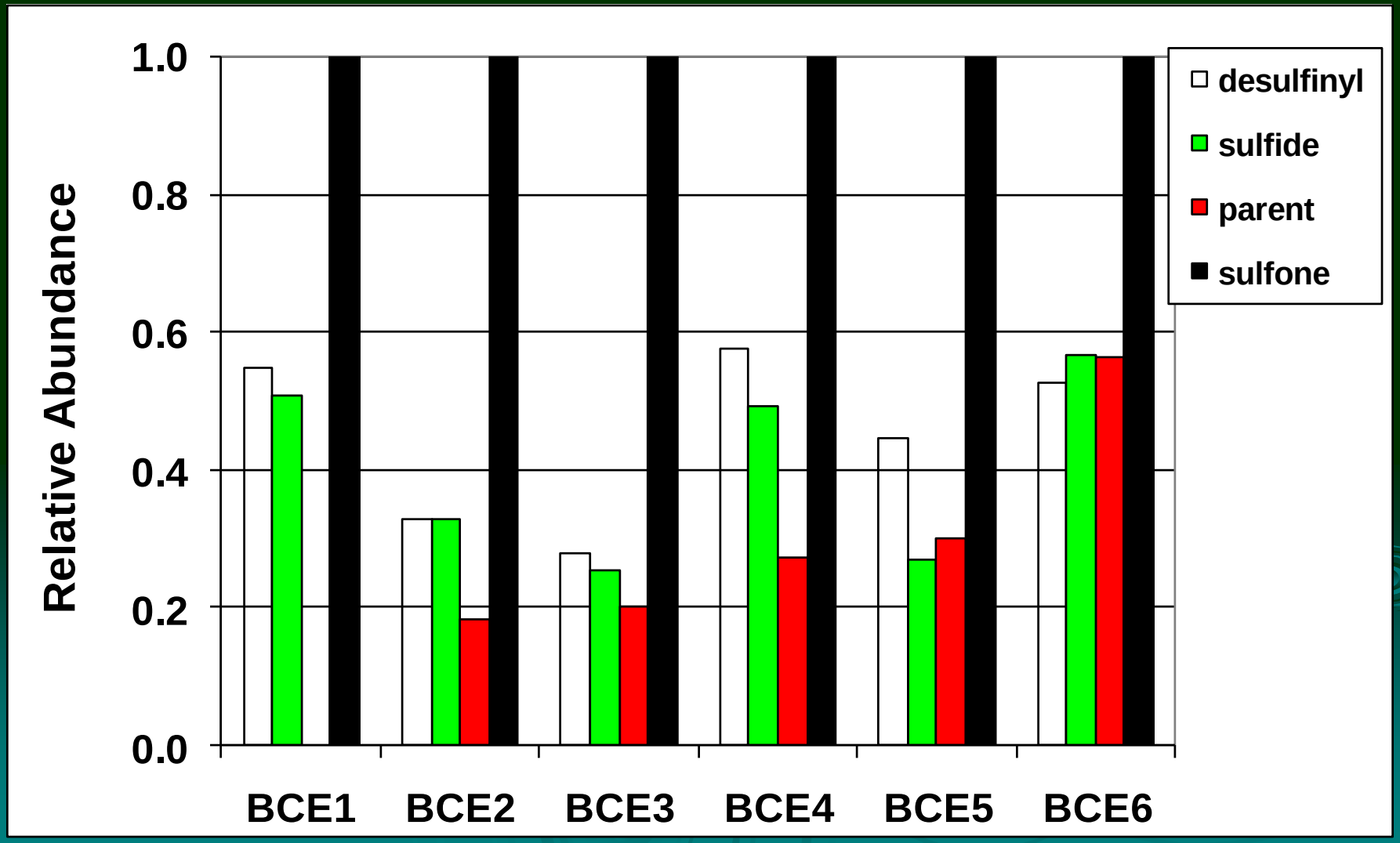


Total Org. C

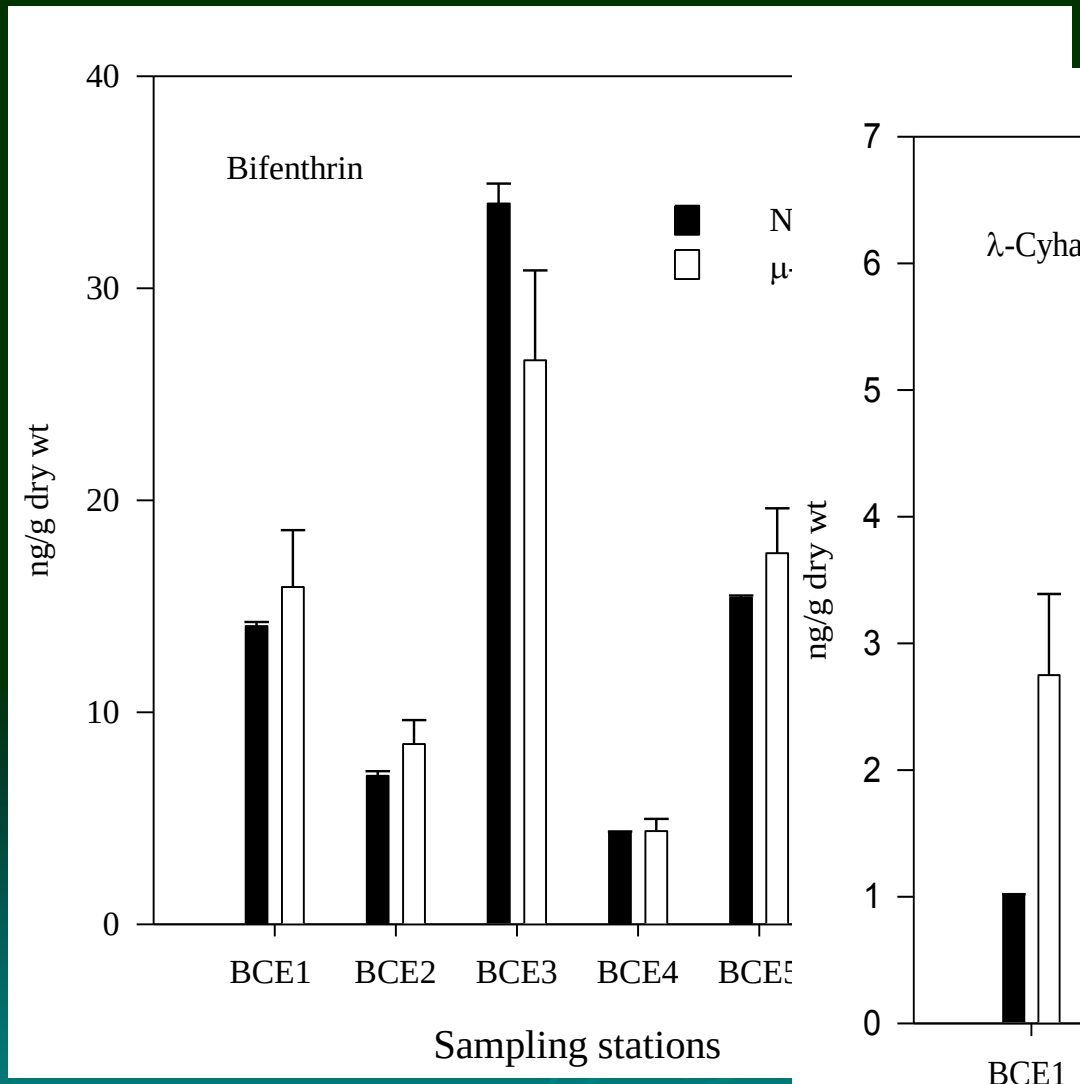

2009 BCE Sediment Analysis
13-Aug
Nov 2 (start)
Dec 1 (end)
TOC (% dw)
5.0
4.0
3.0
2.0
1.0
0.0
BC 1
BC 2
BC 3
BC 5
Station

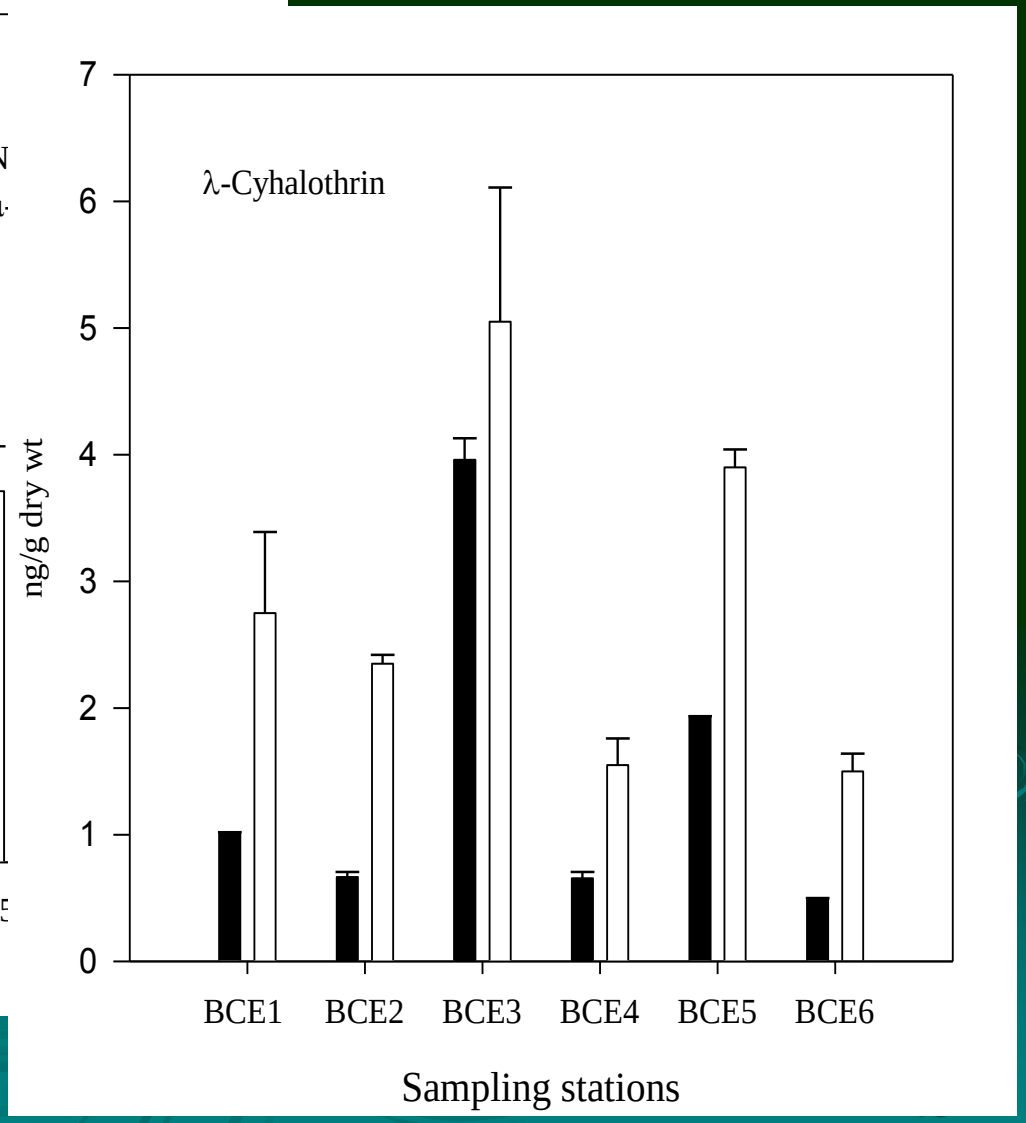

2008-June
Bifenthrin
λ-Cyhalothrin
Cis-permethrin
Trans-permethrin
Cyfluthrin
Cypermethrin
ng/g dw
120
100
80
60
40
20
0
2008-Oct
ng/g dw
120
100
80
60
40
20
0
BCE1
BCE2
BCE3
BCE4
BCE5
BCE6
Sampling stations

Fipronil signature (Aug 2009)

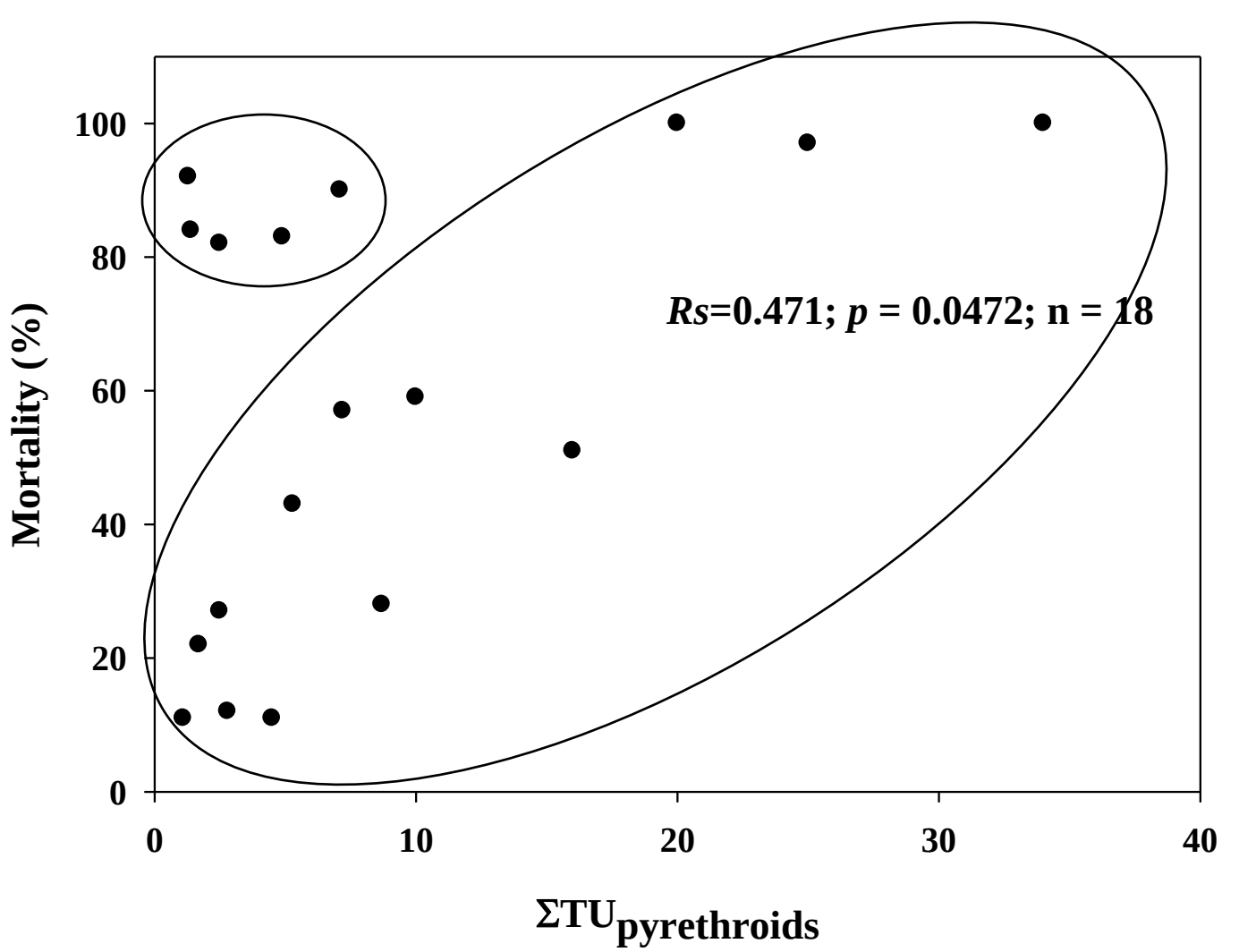


NCI-MS vs u-ECD





Pyrethroids as a likely cause of toxicity, or not?



Bight 2008

- Stratified probabilistic design for surface sediments from SoCal embayments (n=**155**)
- Four substrata -- estuary, marina, bay and ports
- Analyze by GC-NCI/MS (CRG Marine Labs)
- Estimate toxic units (TUs)

$$TU = \frac{\text{Sediment concentration (ug/g oc)}}{LC_{50}\text{ (ug/g oc)}}$$

- Correlate TUs with observed toxicity

- ✓Four
- ✓High

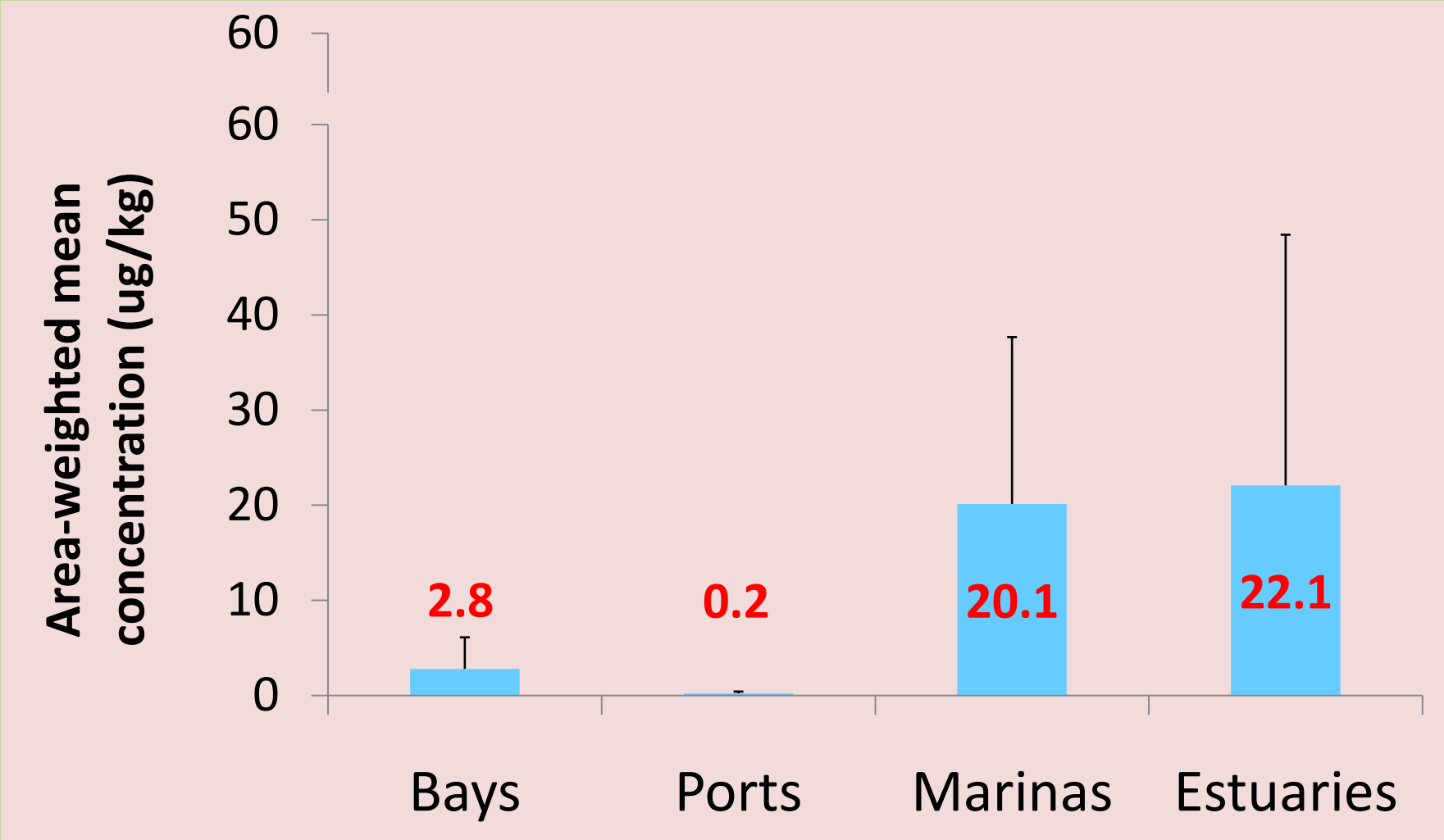
33°0'0"N

Pyrethroids concentration correlate with Total Organic Carbon (TOC)

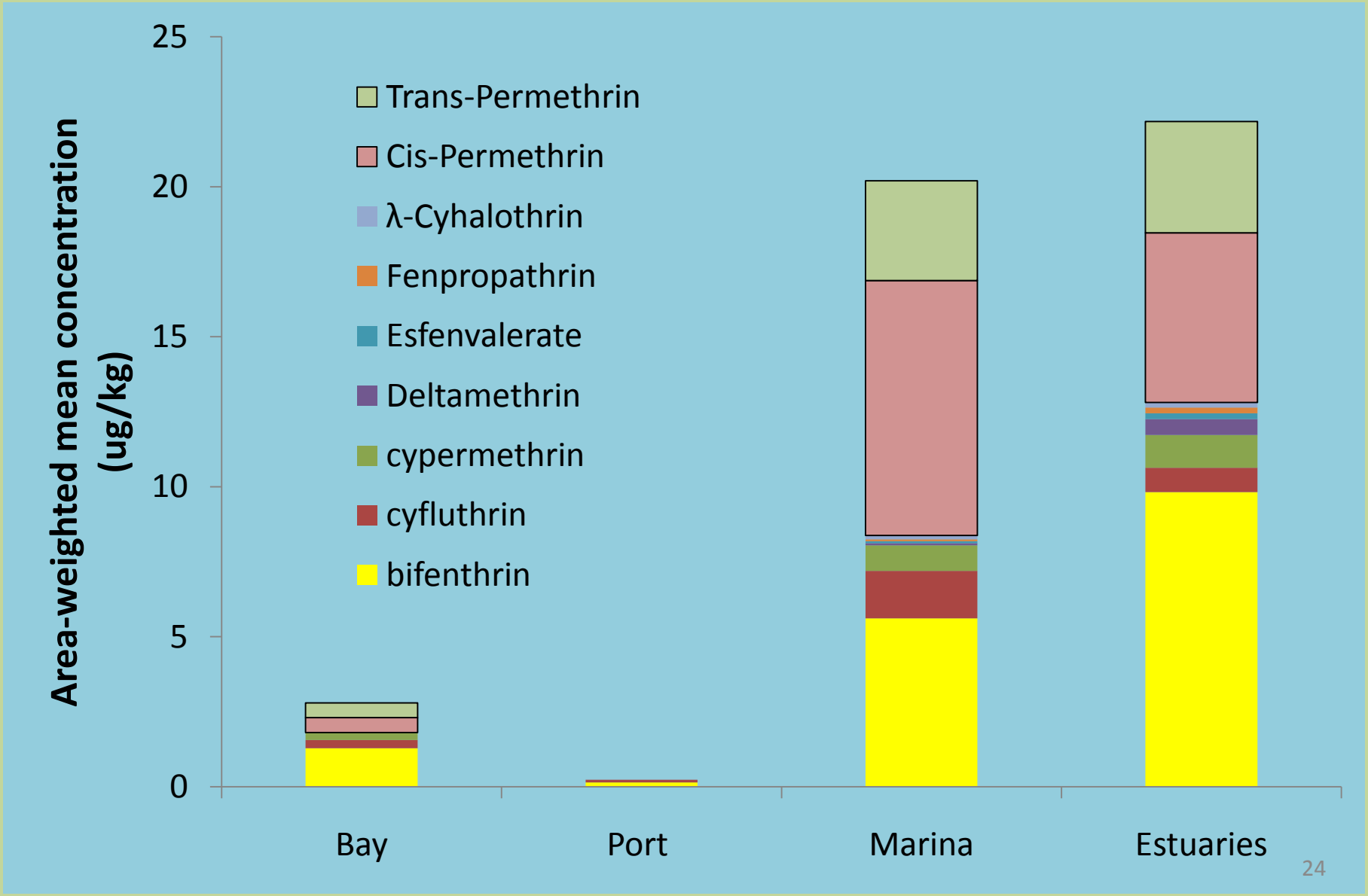
	TOC	TN	Cu	%Fines
Pyrethroids	**0.585** **(p<0.01)**	**0.295** **(p=0.034)**	0.029 (p=0.839)	0.202 (p=0.151)

(Spearman Rank Order correlation coefficient and *p* value)

Total pyrethroids by strata

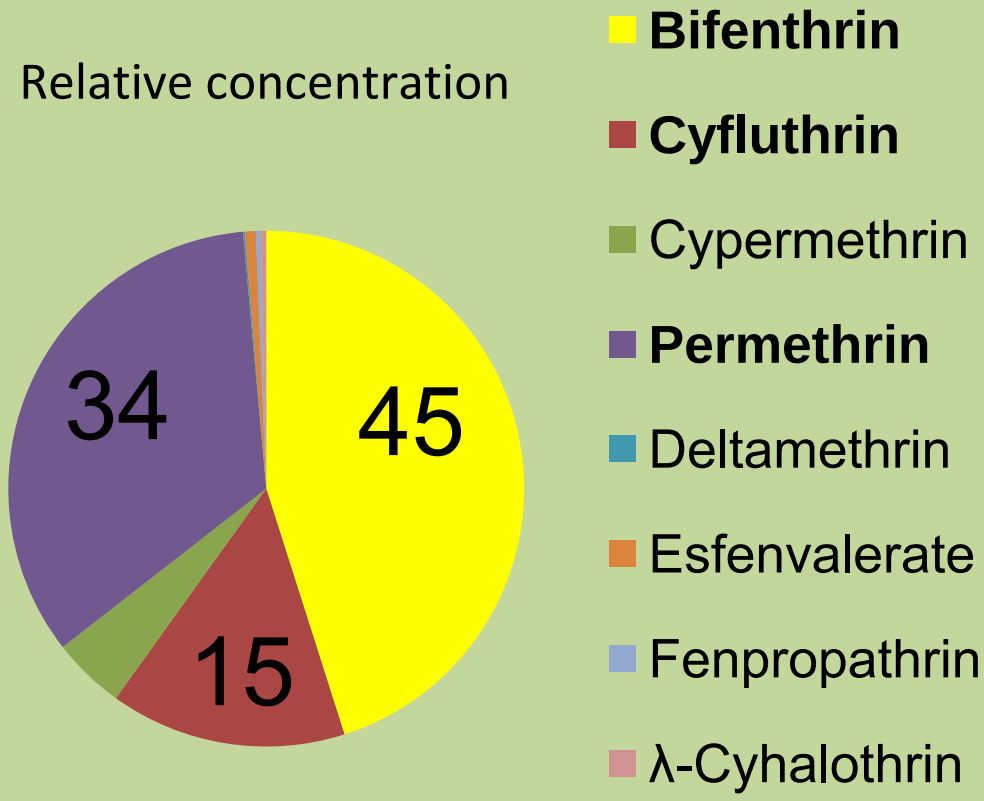


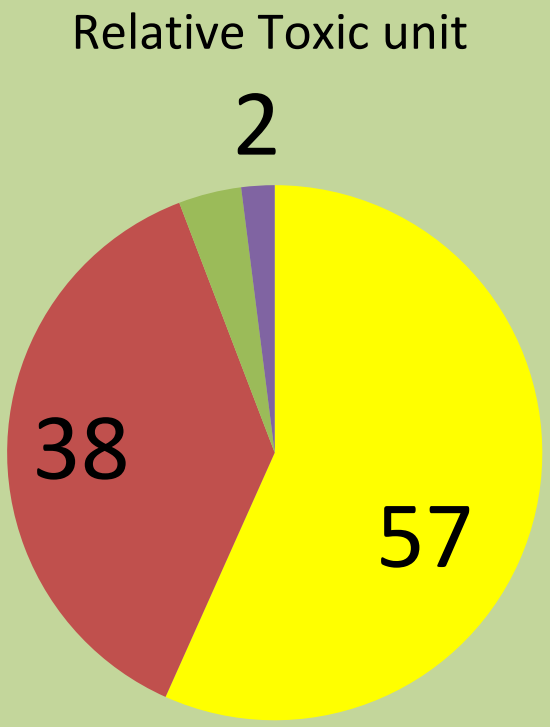
Pyrethroids distribution



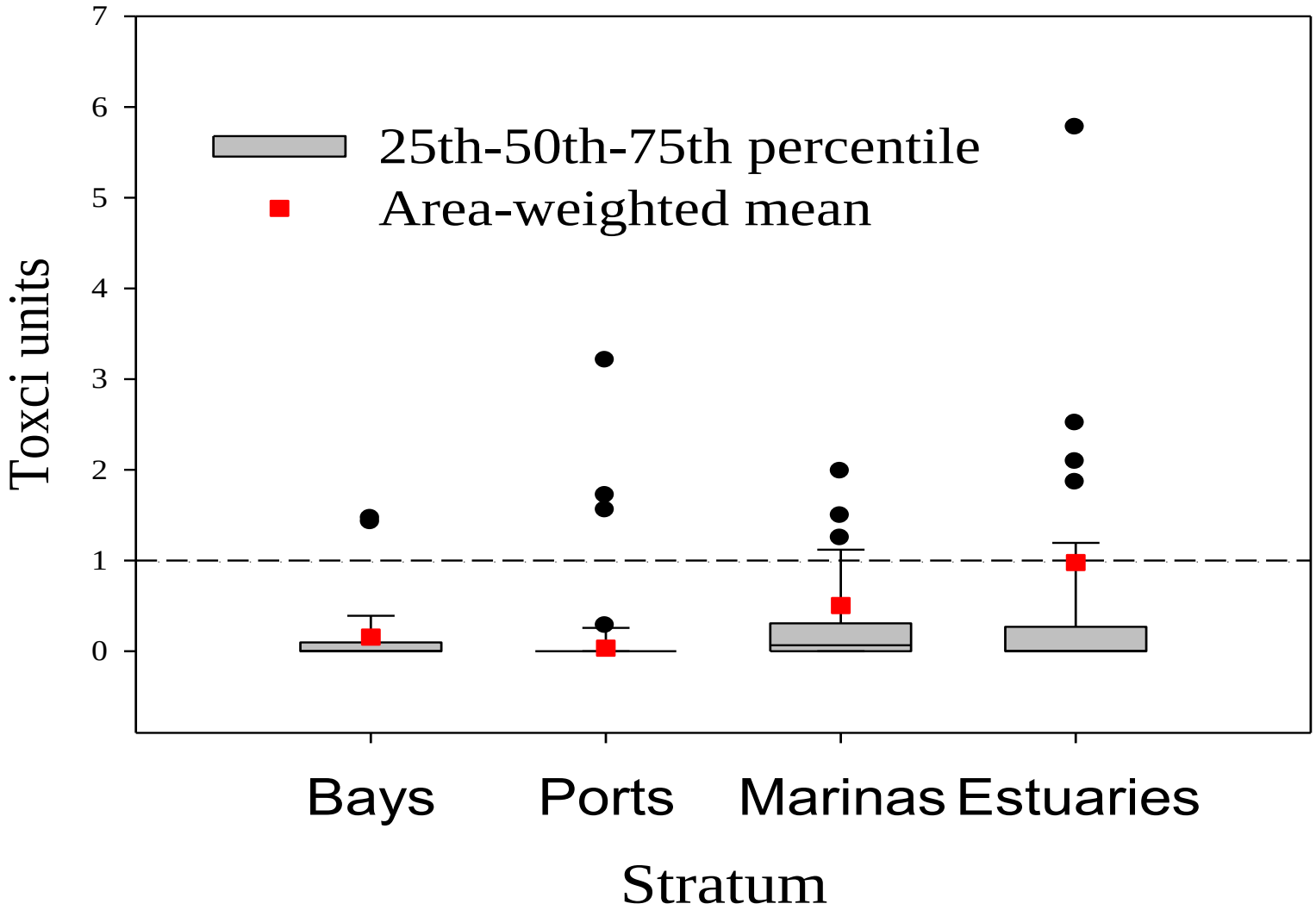
Bifenthrin and **permethrin** were the major contributors to total concentrations

Bifenthrin and **cyfluthrin** were the major contributors to total TUs

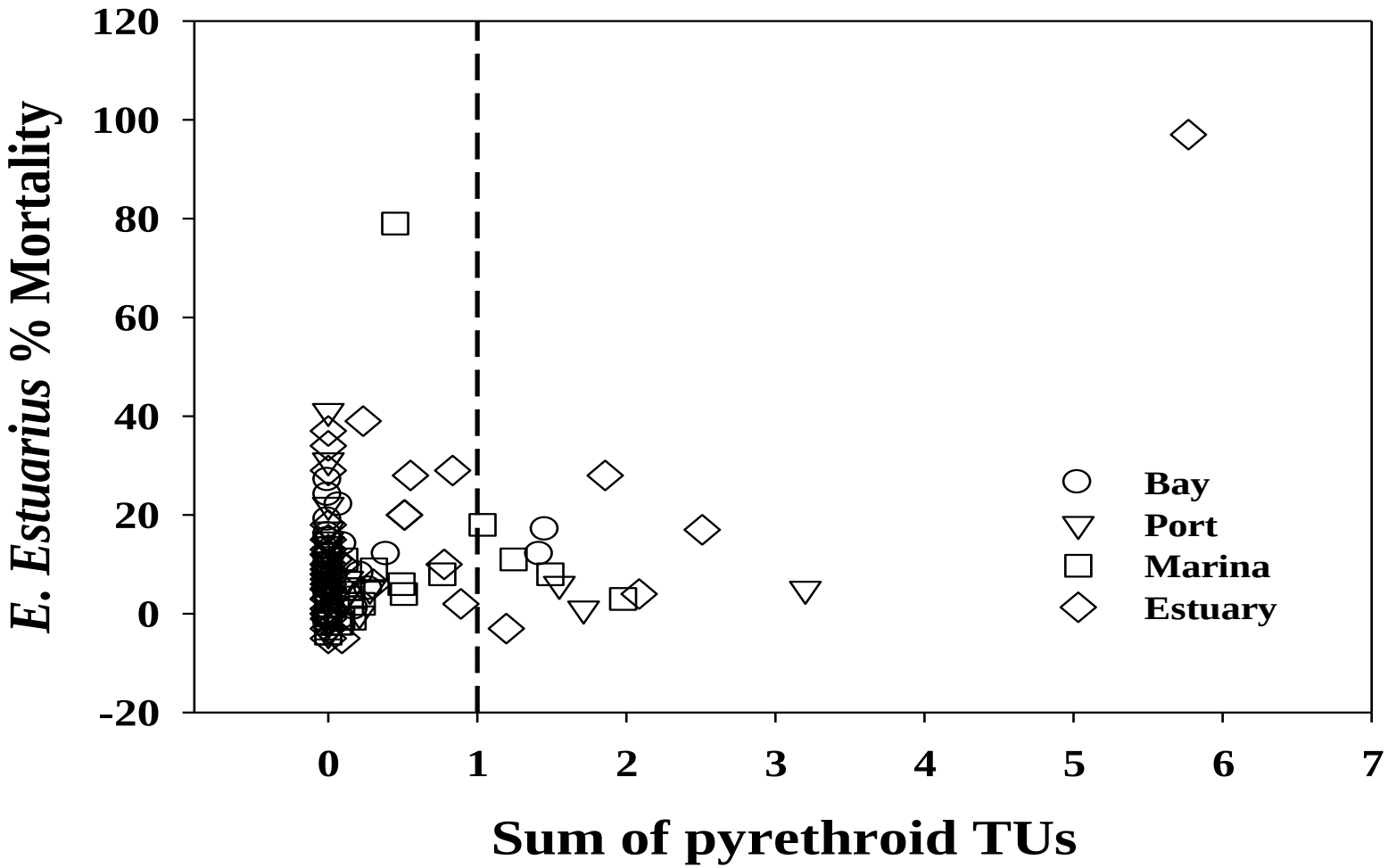




Pyrethroid TUs by stratum



NO correlation between pyrethroid TUs and amphipod mortality



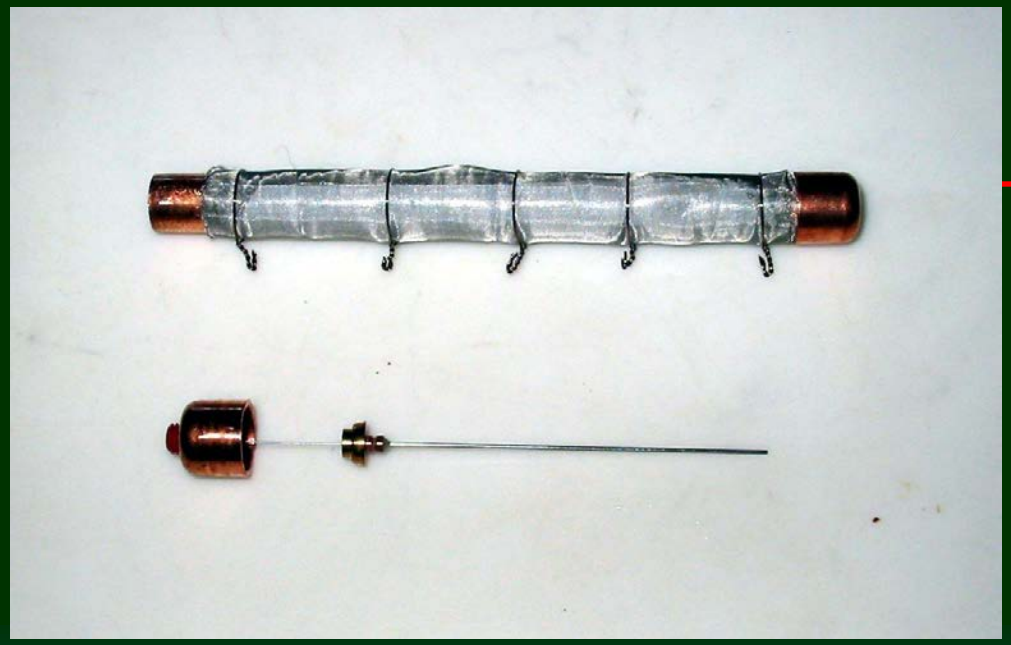
Why no correlation?

1) Other toxicants— e.g. Fipronil and its degradates?
2) Synergism and antagonism
3) Variability in analytical & toxicity data
   - no validated, standard analytical method
   -- explore toxic potential to other marine organisms
4) Uncertainty in LC50s– Need estimate from natural and/or local sediment
5) **Bioavailability?- need to measure dissolved concentrations**

Next step?

Passive Sampling Devices (PSDs)

Quantifying bioavailable pesticides by SPME



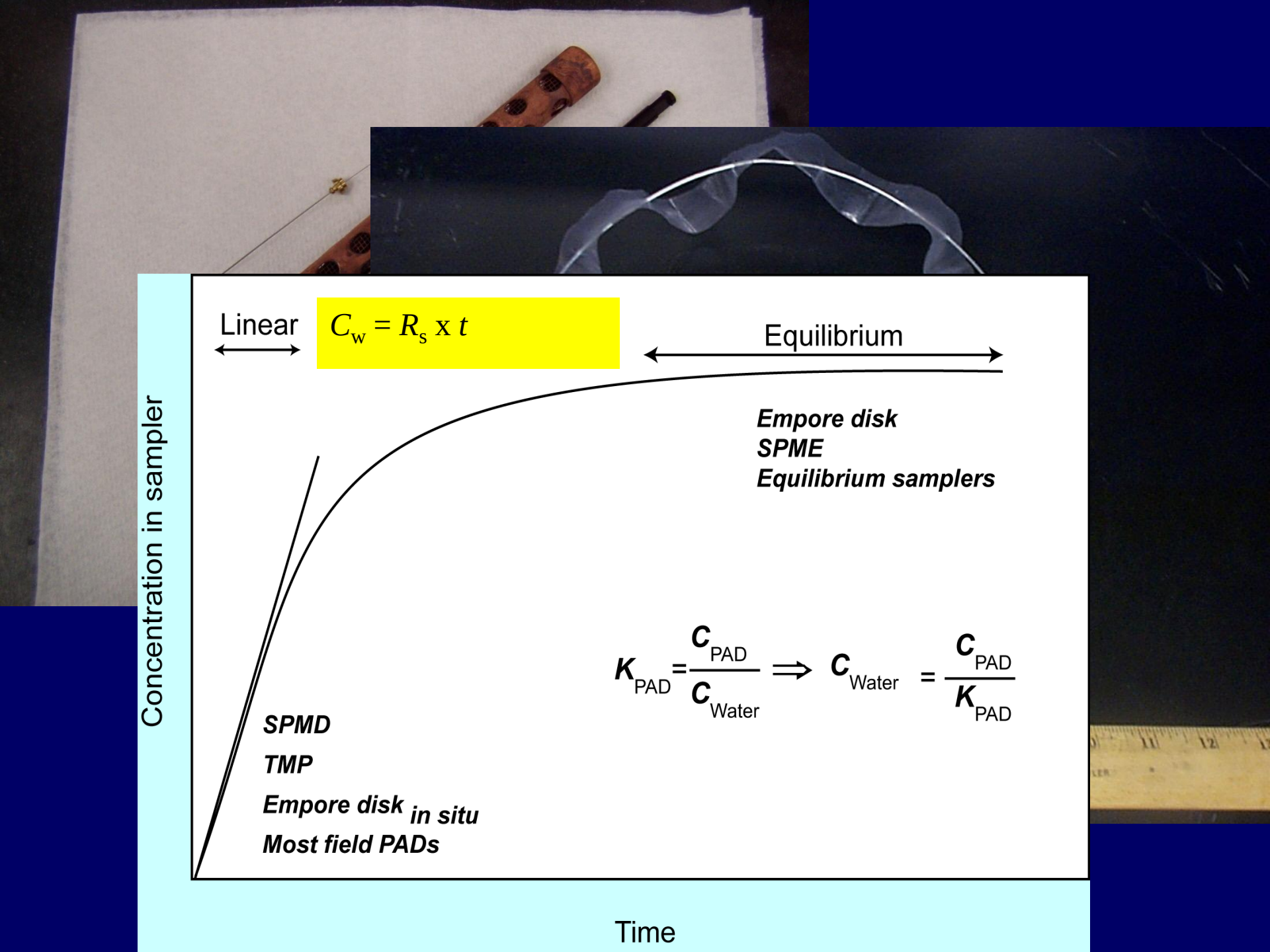
$$C_w = \frac{n_f}{K_f V_f}$$

Pre-calibrate fibers (K_f) for ***pyrethroids/fipronil*** in lab

Expose SPME fibers to contaminated sediment

Measure fibers directly by ECD or MS (ECNI-MS)

Compute —bioavailable" porewater concentration (C_w)


Linear
$C_w = R_s \times t$
Equilibrium
Empore disk
SPME
Equilibrium samplers
$K_{PAD} = \frac{C_{PAD}}{C_{Water}} \Rightarrow C_{Water} = \frac{C_{PAD}}{K_{PAD}}$
SPMD
TMP
Empore disk in situ
Most field PADs
Concentration in sampler
Time

CHALLENGES AND SOLUTIONS

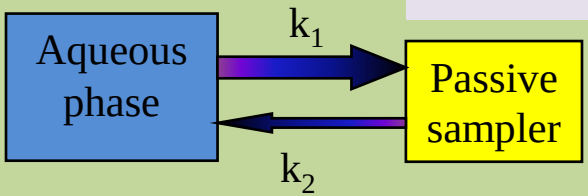
- **Lack of PSD calibration parameters for CECs**
  - Determine/model steady-state partition coefficient (K values) for pesticides

- **Are PSD data accurate and uniform across sorbents?**
  - compare with conventional measurements
  - perform side-by-side comparisons of PE and SPME-PDMS

- **Develop bioavailability LOE based on PSD measurements**
  - Demonstrate concordance of PSDs and bioaccumulation
  - Incorporate PSD measurements in sediment porewater using TU approach

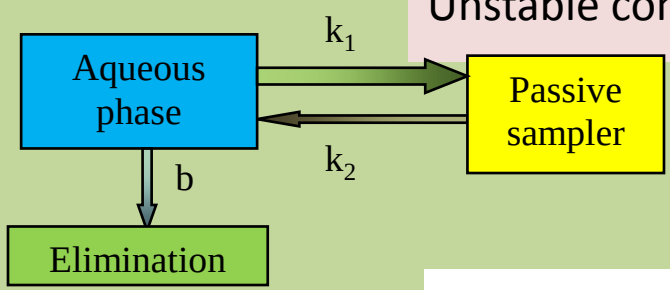
Modeling calibration procedure

Stable compound (e.g. bifenthrin)

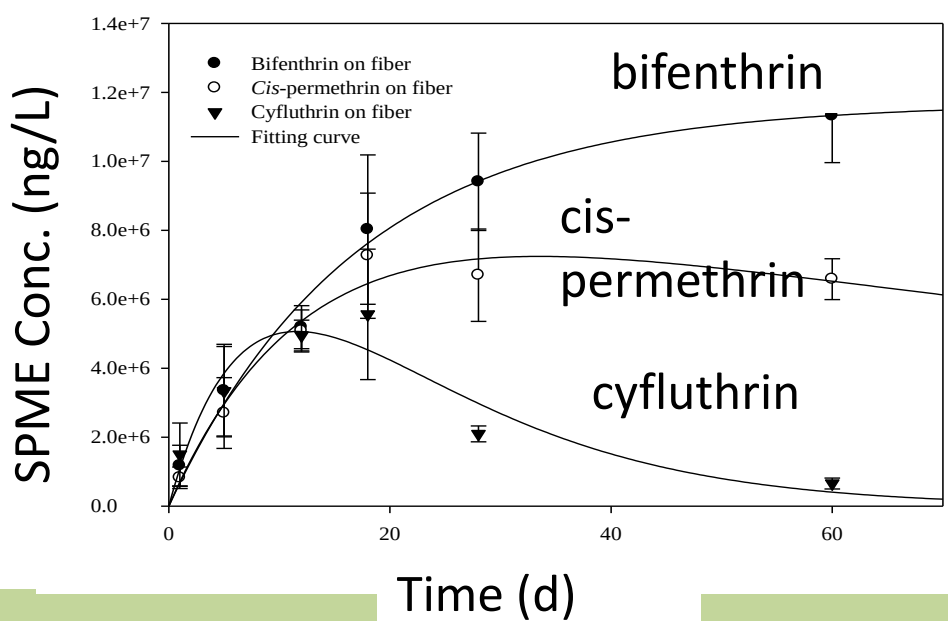


$$C_f = \frac{k_1 \times C_w^0}{B} \times (1 - e^{-B \times t})$$

Unstable compounds (e.g. cyfluthrin)



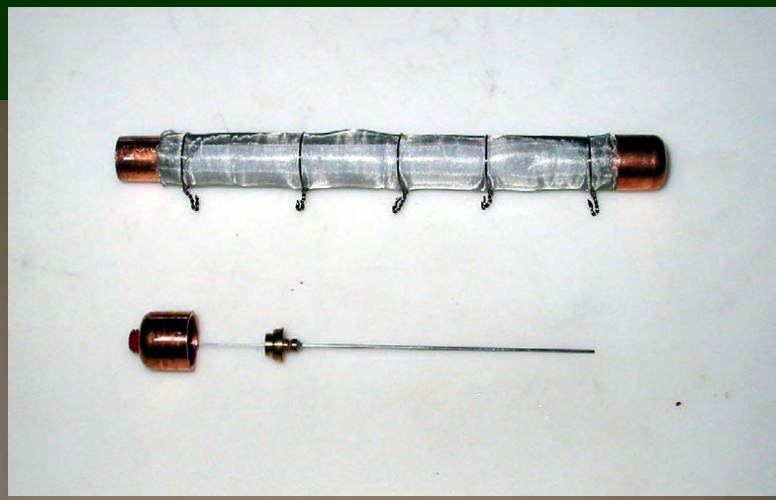
$$C_p = \frac{k_1\, C_w^0}{\alpha - \beta}\left[e^{-\beta t} - e^{-\alpha t}\right]$$



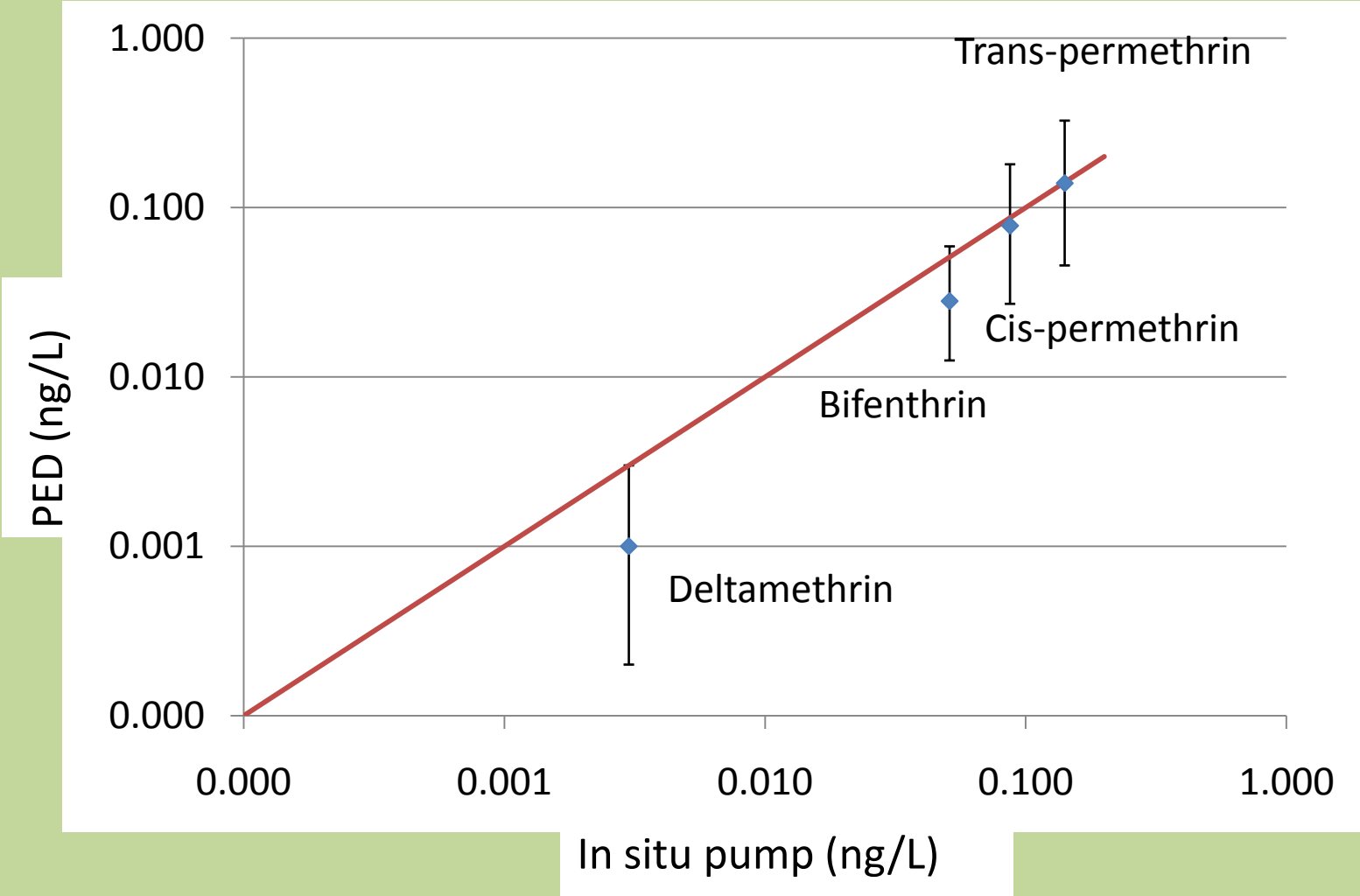
Lab pre-calibration of PSDs (log $K_{psd\text{-}water}$)

	log K_{ow}	SPME	PED
Bifenthrin	6.40	5.87 ±0.10	6.26 ±0.03
Permethrin	6.50	6.38 ±0.10	6.03 ±0.12
Cyfluthrin	5.97	5.93 ±0.12	5.78 ±0.06
Cypermethrin	6.54	5.99 ±0.12	5.97 ±0.07
Deltamethrin	6.10	5.89 ±0.13	5.92 ±0.07
Esfenvalerate	6.24	6.33 ±0.13	5.96 ±0.06
Fenpropathrin	6.00	5.73 ±0.10	6.00 ±0.04
λ-Cyhalothrin	7.00	6.12 ±0.11	5.89 ±0.05

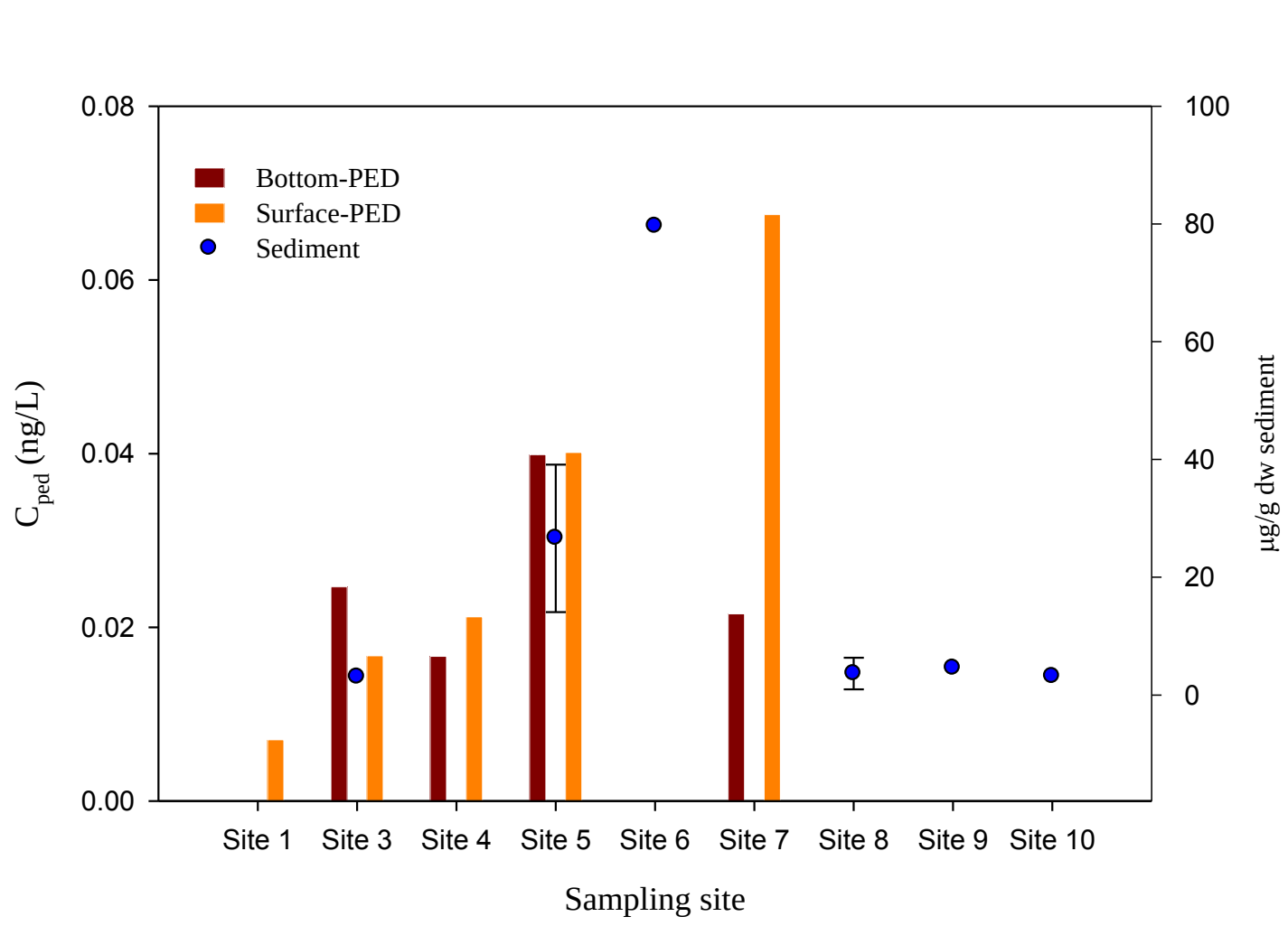
PSD Deployment Fixtures



PED vs. *in situ* pump (Ballona Creek water column)



Bifenthrin in water column and sediment of Ballona creek



Incorporating bioavailability

- *As an independent LOE ("Tier I"),*
  - *SQO = Toxic Units = $C_{w,PSD}$ / TEV*

  where $C_{w,PSD}$ = porewater concentration by PSD

  TEV = aqueous phase threshold value

- *To break "ties" ("Tier II")*

- *To identify/confirm toxicants ("Tier III" TIE)*

Maruya K, Landrum P, Burgess R, Shine J, *IEAM* DOI: 10.1002

FUTURE PLANS

- **Pursue TU approach for sediment toxicants**
  - Refine K values and calibration models for PSDs
  - Work with toxicologists to refine LC50s for estuarine sediments/sentinel species (e.g. Eohaustorius spp.)
  - Incorporate emerging pesticides and other CECs

- **Develop practical guidelines for PSD applications**
  - Sorbents, exposure/analytical protocols, parameter interpretation
  - SETAC Technical Workshop (Nov 2012)
  - Pubs in ET&C, IEAM

ACKNOWLEDGMENTS

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- **K. Schiff (SCCWRP), R. Gossett (CSULB)**
  - SCCWRP member agencies
  - other Bight 08 contributors