Bioavailability of Pyrethroids in Surface Aquatic Systems

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Outline

- Why bioavailability?
- Measurement methods
  - Biomimetic polymer fibers
- Bioavailability in surface water
- Bioavailability in sediment
- Future directions

Why Bioavailability?

- **Many significant pollutants are highly hydrophobic:**
  - DDT, PCBs, PAHs, chlordane, ..
  - Synthetic pyrethroid insecticides
- **Hydrophobic pollutants adsorb strongly to solid particles and DOM**
- **Adsorbed pollutants are not or less bioavailable**

Pyrethroids vs. DDT

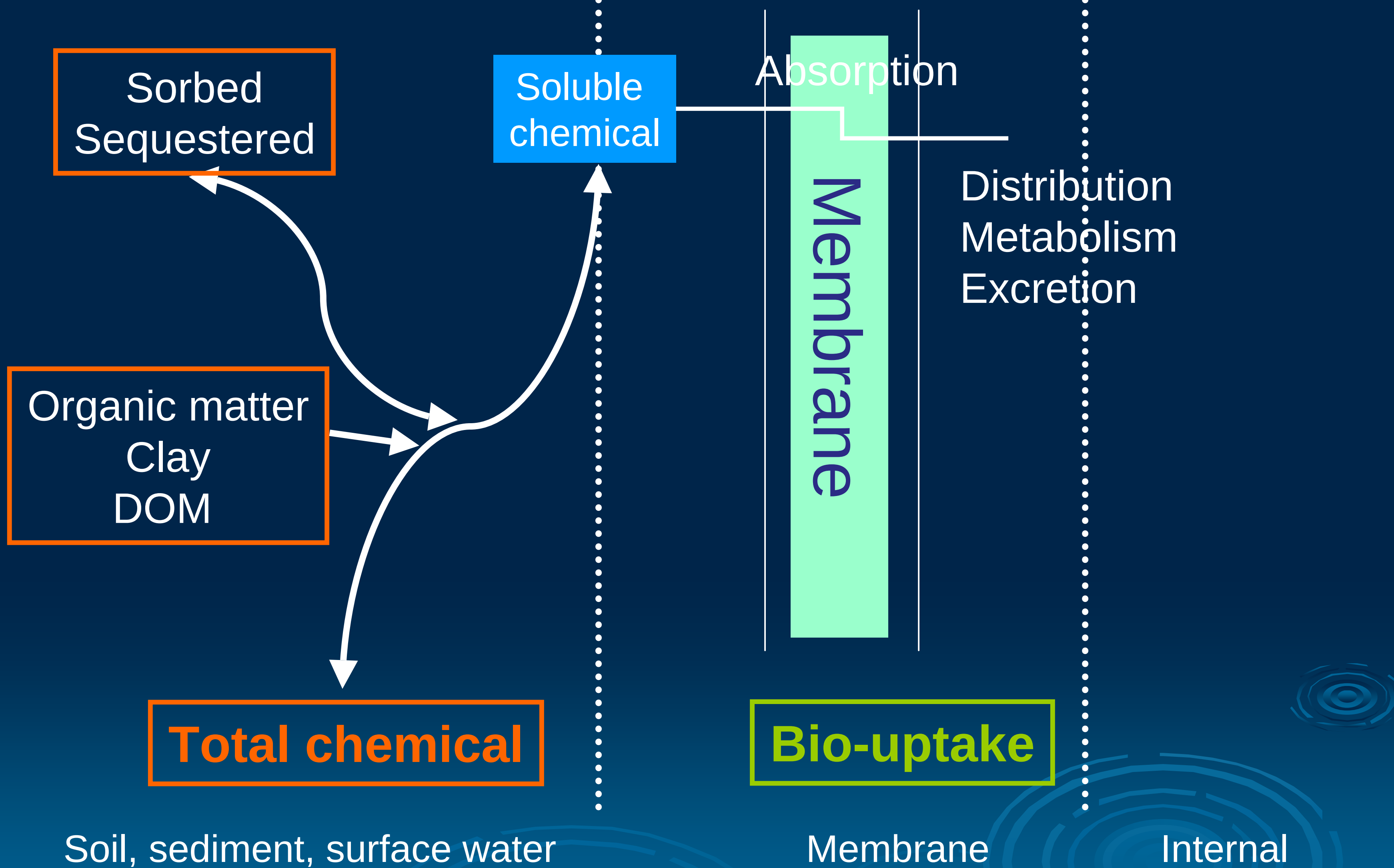
Pyrethroids

- Nearly insoluble
- Strongly adsorbing
- High aquatic toxicity

DDT likes

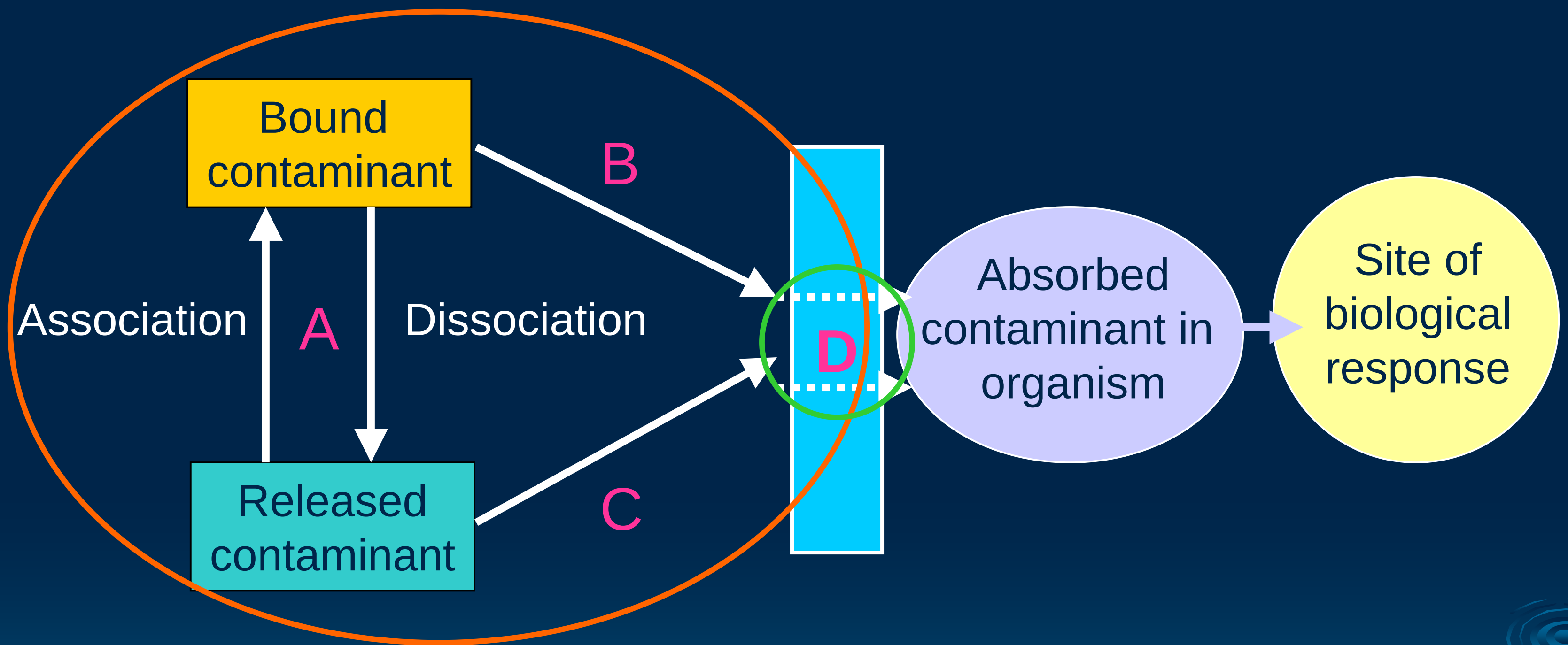
- Nearly insoluble
- Strongly adsorbing
- Low aquatic toxicity
- High bioaccumulation potential

Environmental availability | **Environmental bioavailability**



(Lanno et al., 2004)

Bioavailability vs. Bioaccessibility



Bioavailability: **D**

Bioaccessibility: **A ⇒ D**

Ehlers, L.J., and R.G. Luthy, *ES&T*, 2003, 37: 295A-302A

Detections of Pyrethroids in Sediment
(Central Valley, CA)

Permethrin: 75%

Concentration 0-129 µg/kg

Esfenvalerate: 32%

Concentration 0-30 µg/kg

Bifenthrin: 18%

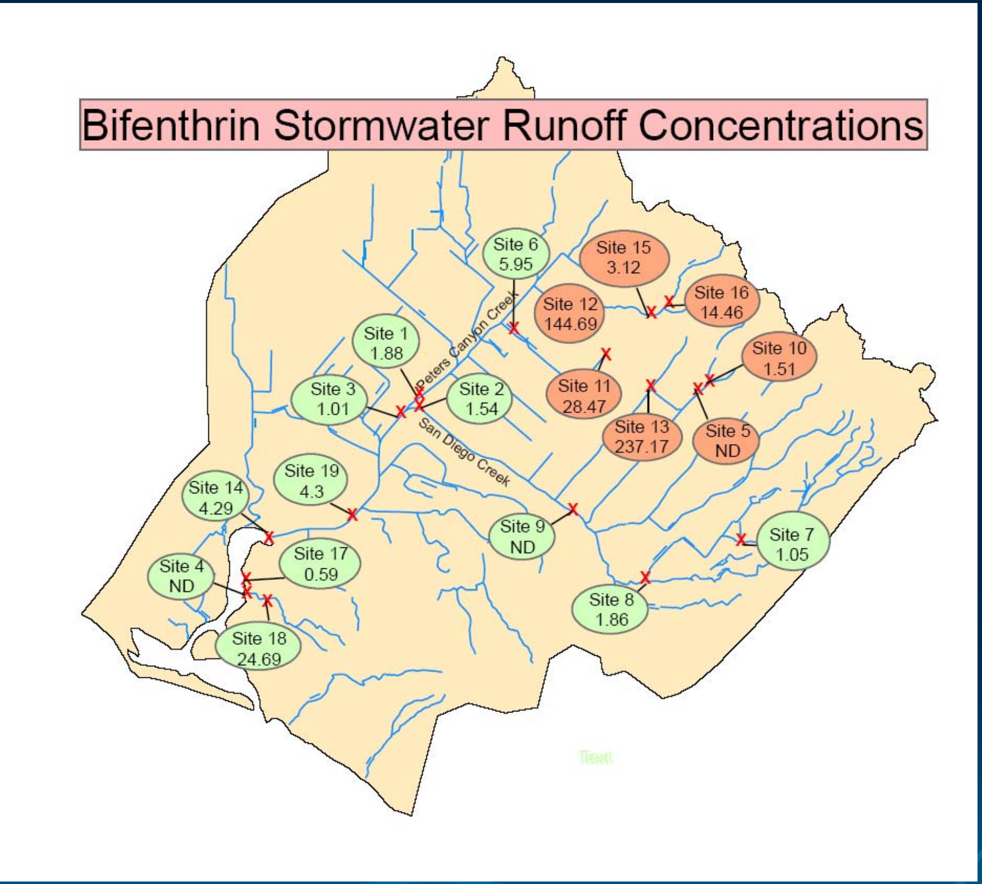
Concentration 0-21 µg/kg

λ-Cyhalothrin: 12%

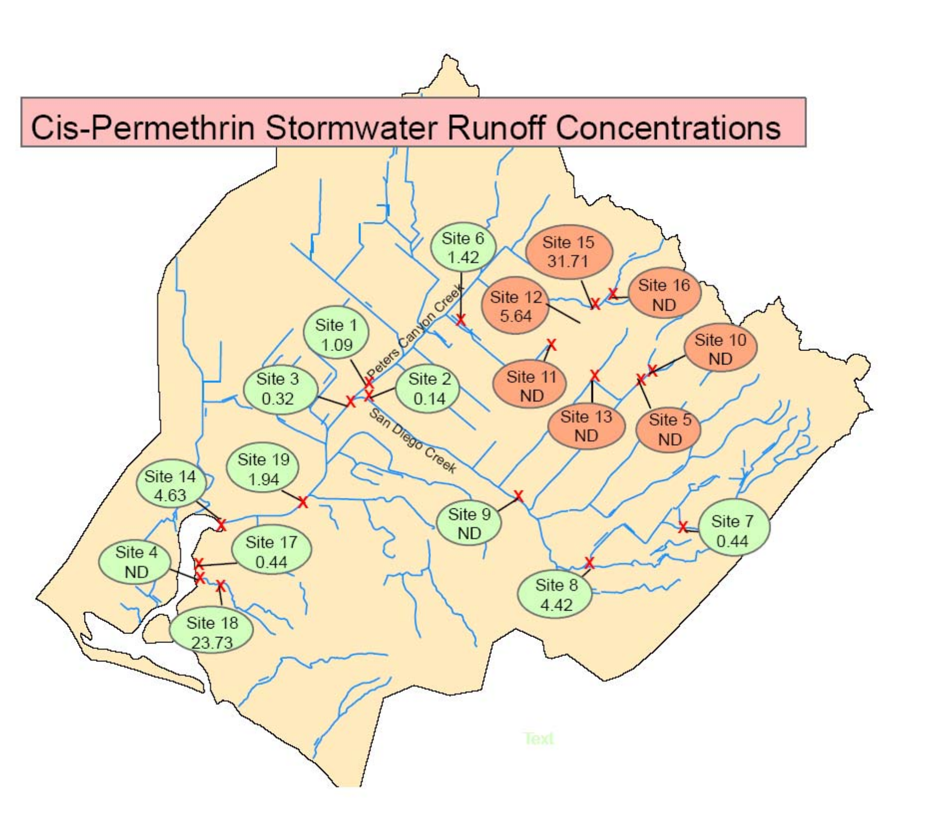
Concentration 1-8 µg/kg

Source: *Weston et al., 2004, EST, 38: 2752-2759*

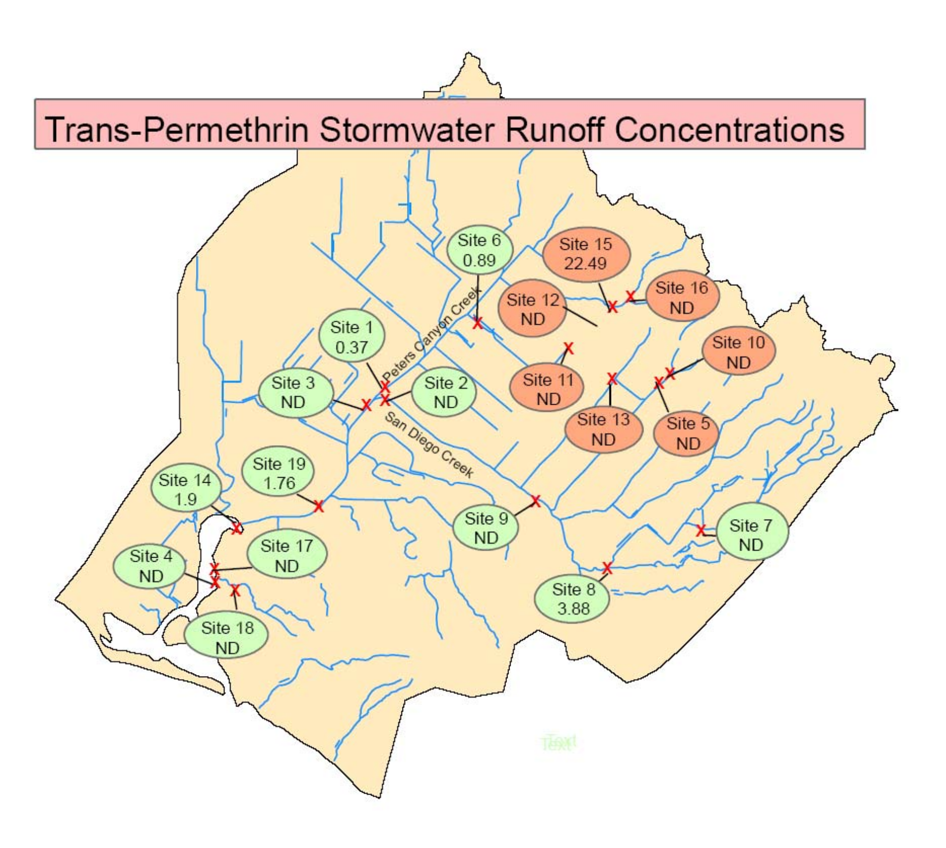
Spring Sediment Samples
(Bifenthrin, µg/kg)



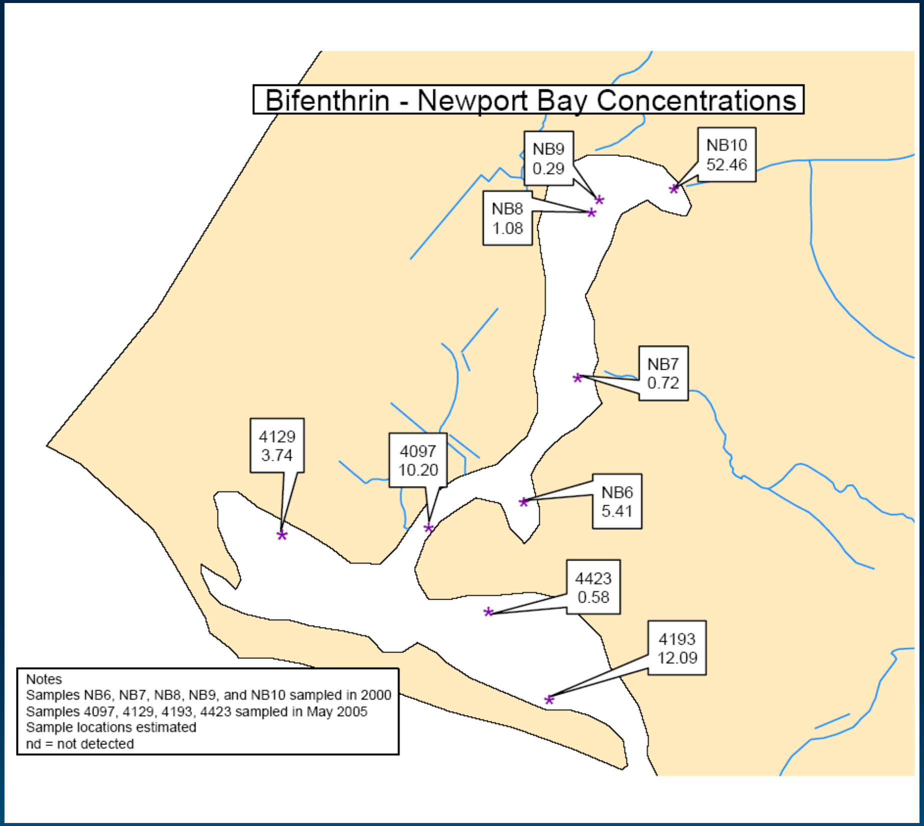
Spring Sediment Samples (*cis*-permethrin, µg/kg)



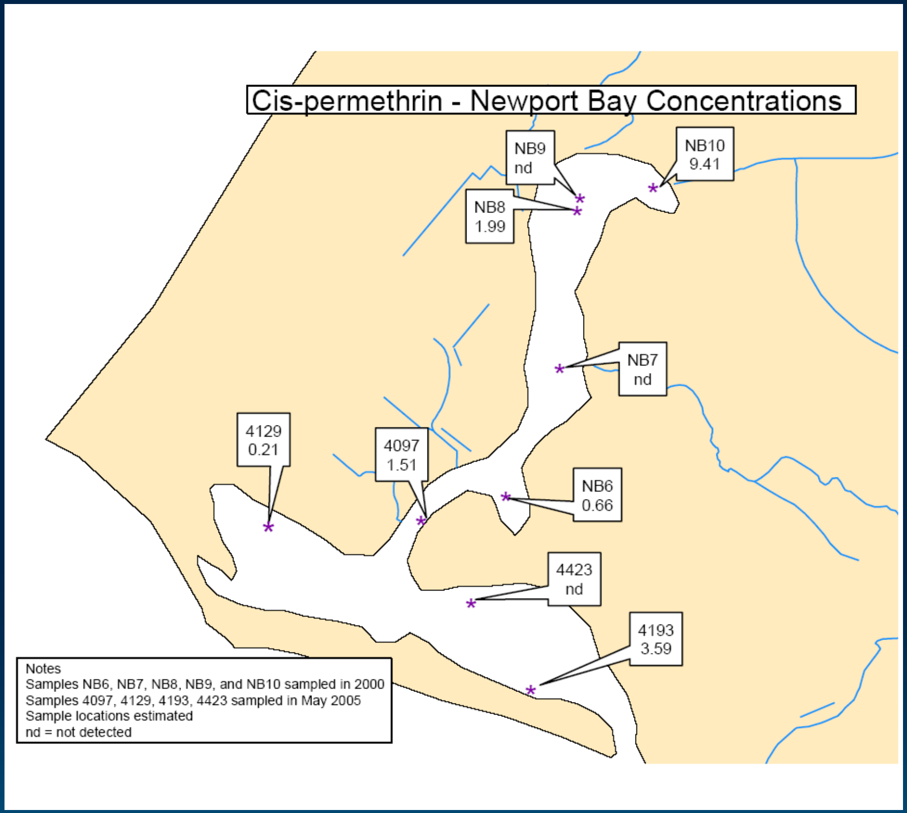
Spring Sediment Samples (*trans*-permethrin, µg/kg)



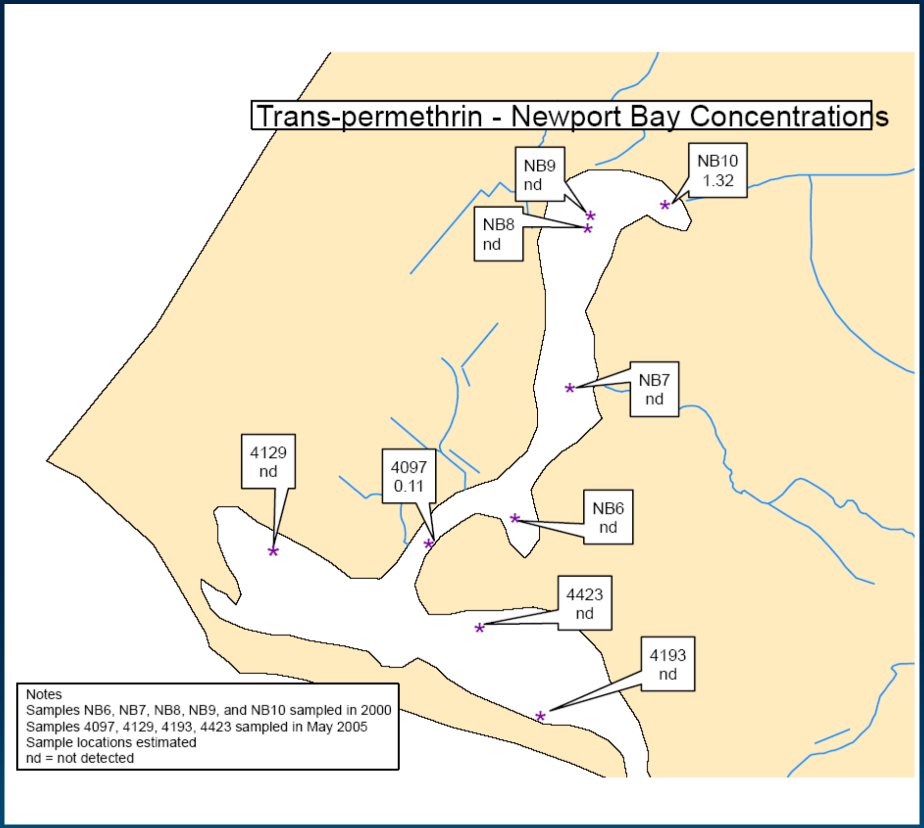
Newport Bay Sediment (Bifenthrin, µg/kg)



Newport Bay Sediment
(*cis*-permethrin, µg/kg)



Newport Bay Sediment
(*trans*-Permethrin, µg/kg)



Phase Partitioning

Water column:

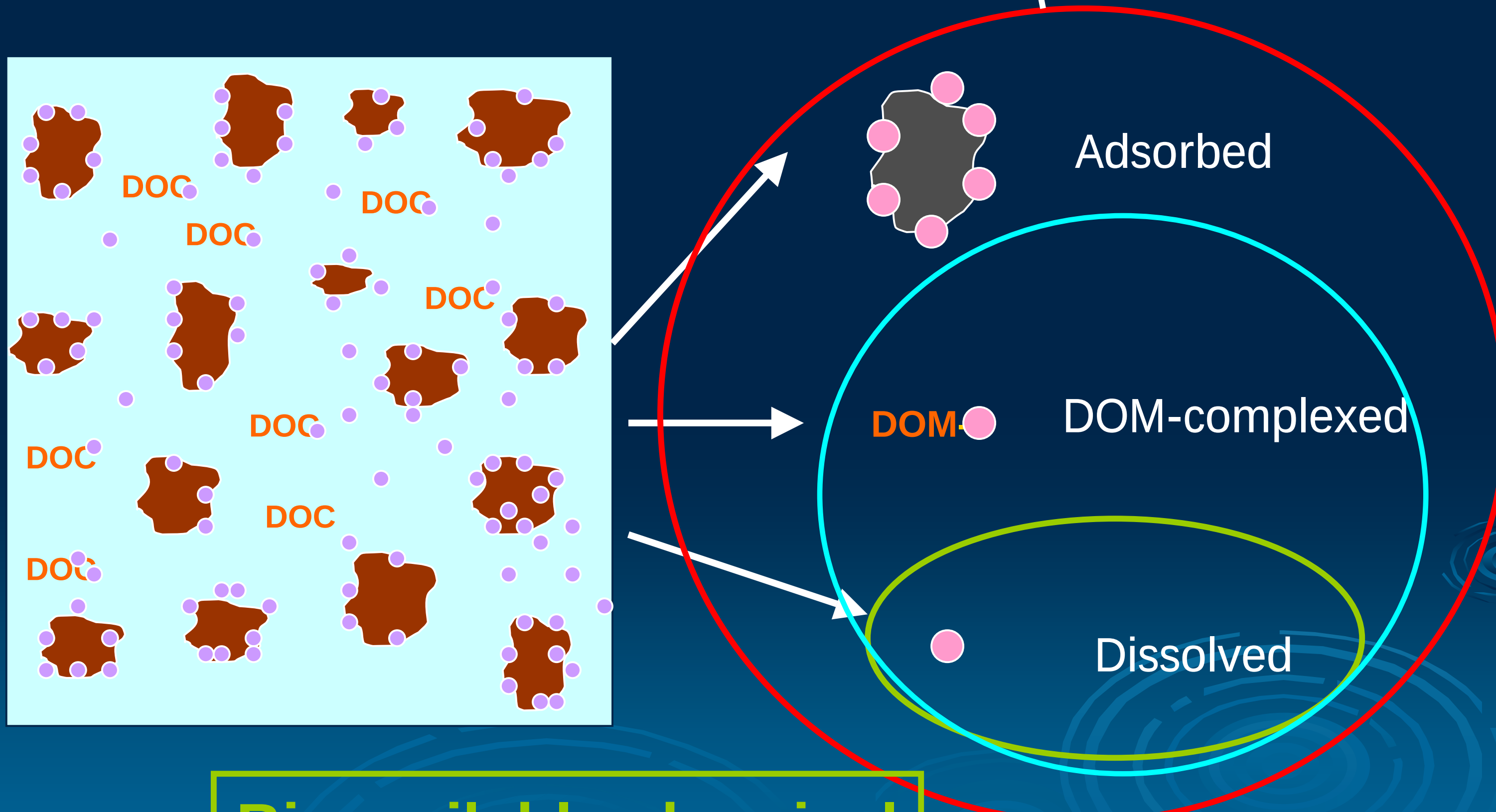
Suspended solids
Dissolved organic matter
Water phase

Sediment:

Solid phase
Dissolved organic matter
Water phase

Surface Water

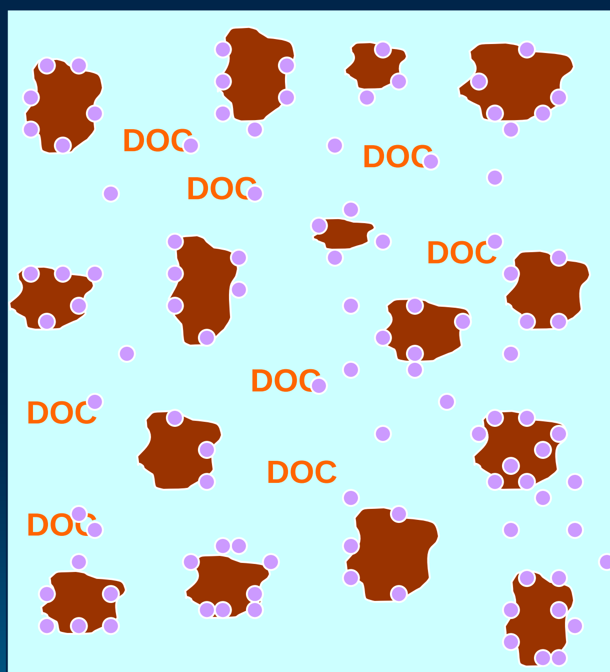
Total chemical



Bioavailable chemical

Dissecting C_w

- **Overestimation of availability:**



$$C_w = \frac{C_t}{1 + k_{DOM}[DOM] + k_d[SS]}$$

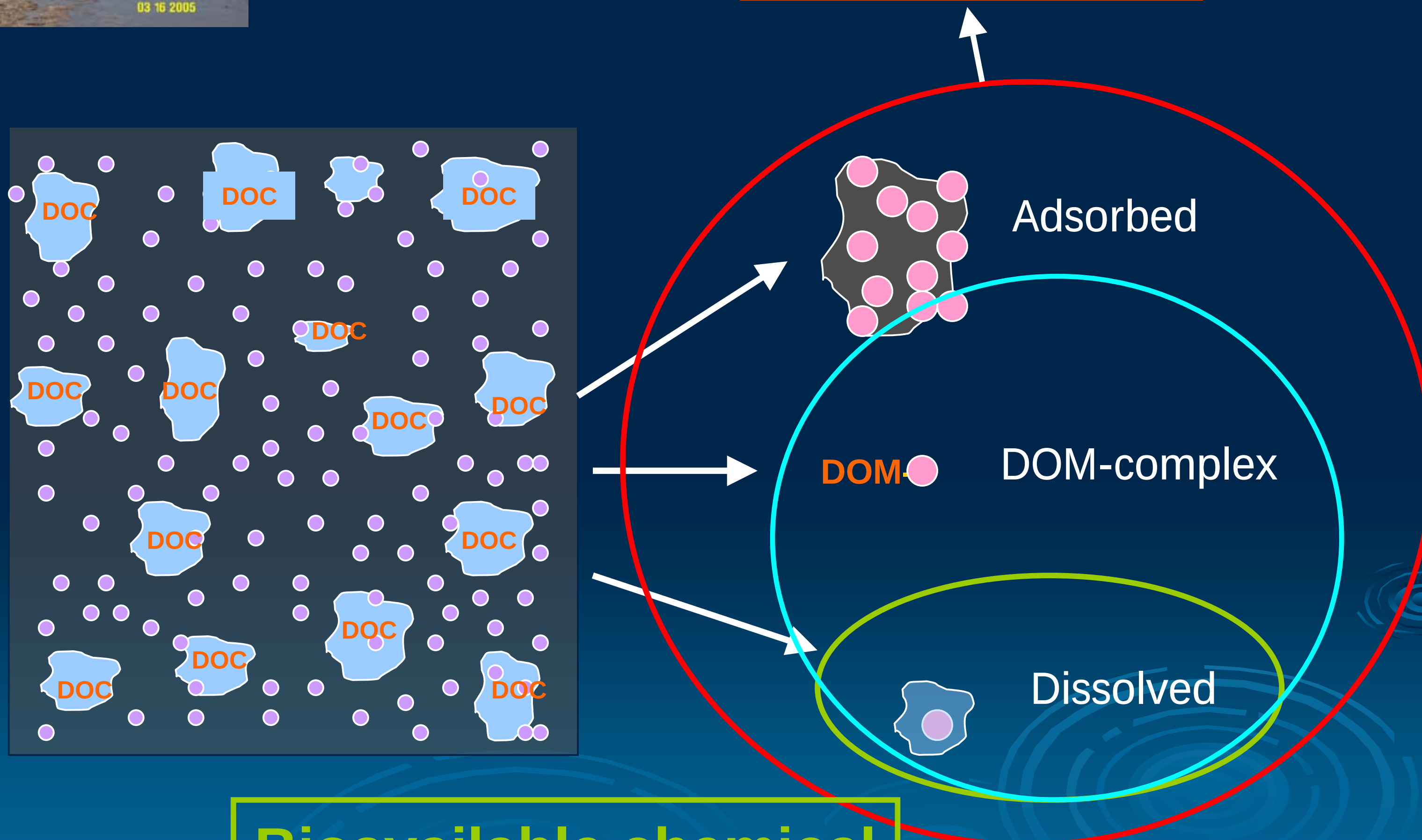
$$C_w = \frac{C_t}{1 + k_{DOM}[DOM]}$$

α

α = 1
α < 1
α > 1

Sediment/Soil

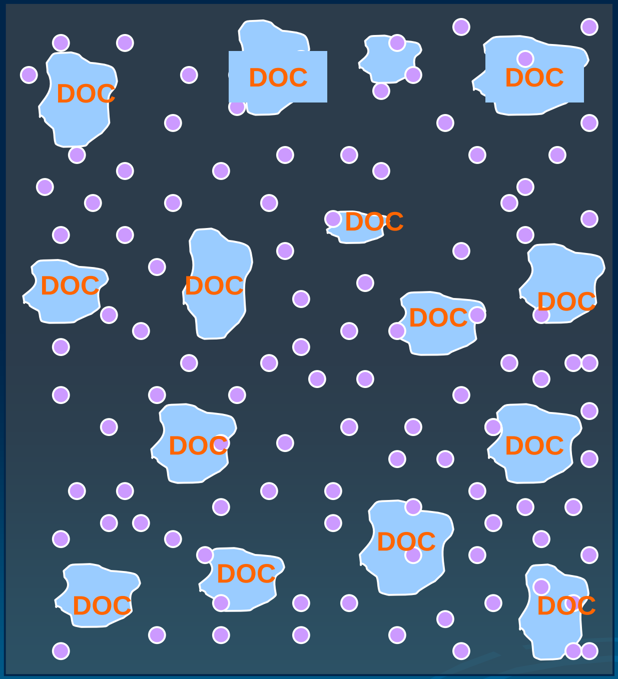
Total chemical



Bioavailable chemical

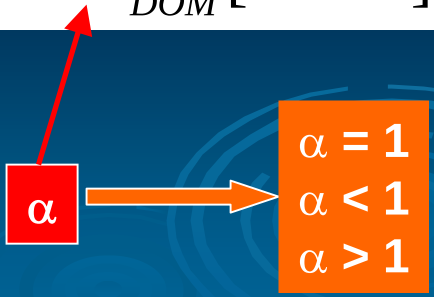
Dissecting Pore-water C_w

- **Overestimation of availability:**



$$C_w = \frac{C_t}{1 + k_{DOM}[DOM] + k_d[S]}$$

$$C_w = \frac{C_t}{1 + k_{DOM}[DOM]}$$



Implications

- Total concentration is used in monitoring, regulation, etc
- Aquatic toxicity may be caused only by the dissolved fraction

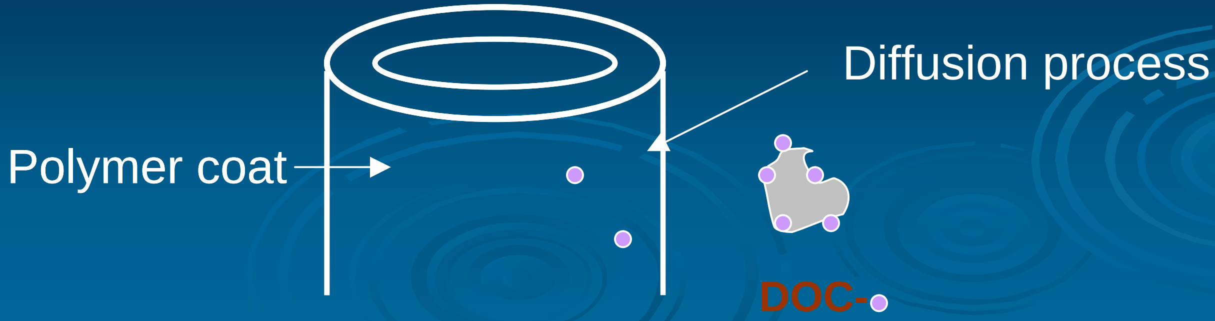
- Need "biomimetic" sampling
- What is not bioavailable? (α = 1?)
- How to predict?

Measuring Bioavailability

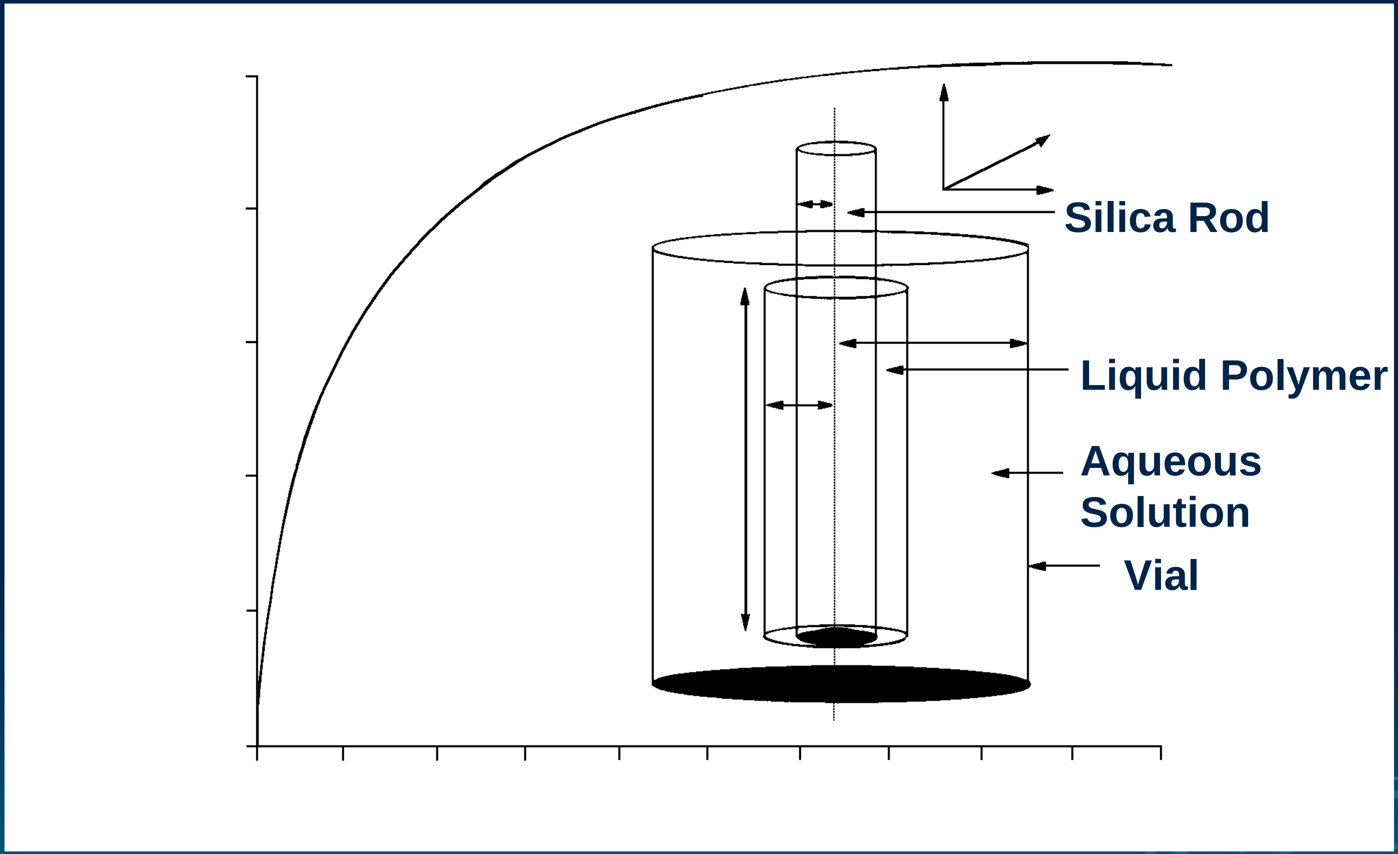
- **Conventional:**
  - Dialysis membranes
  - Fluorescence quenching
  - Ultrafiltration
  - Ultracentrifugation
  - Size exclusion chromatography
  - Reverse phase
  - Affinity chromatography
- **Negligible extraction:**
  - Single drop extraction
  - SPMD
  - Empore disk
  - **SPME**

Solid phase microextraction (SPME)

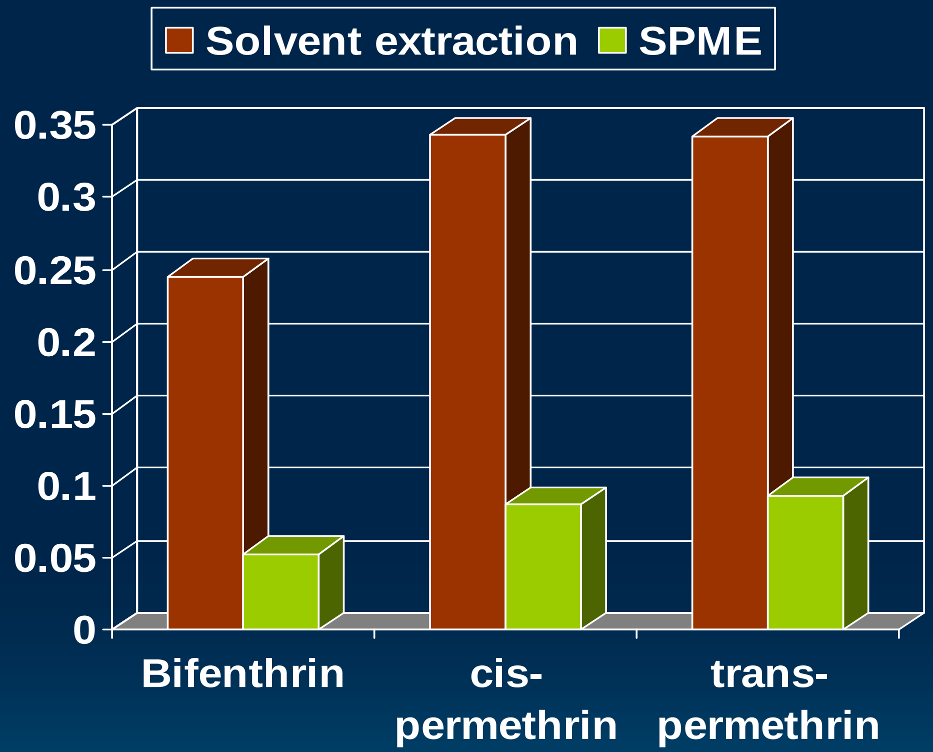
Solid phase microextraction (SPME) detects dissolved concentration C_w



Adsorption Mechanism for SPME

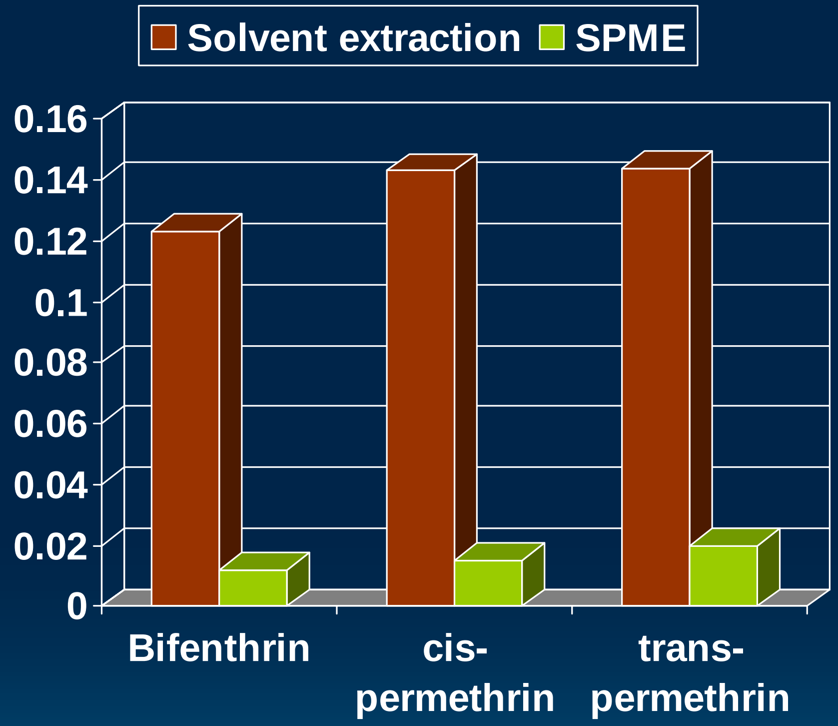


Solvent Extraction vs. SPME (µg/L, ppb)



Runoff inlet

Solvent Extraction vs. SPME (µg/L, ppb)

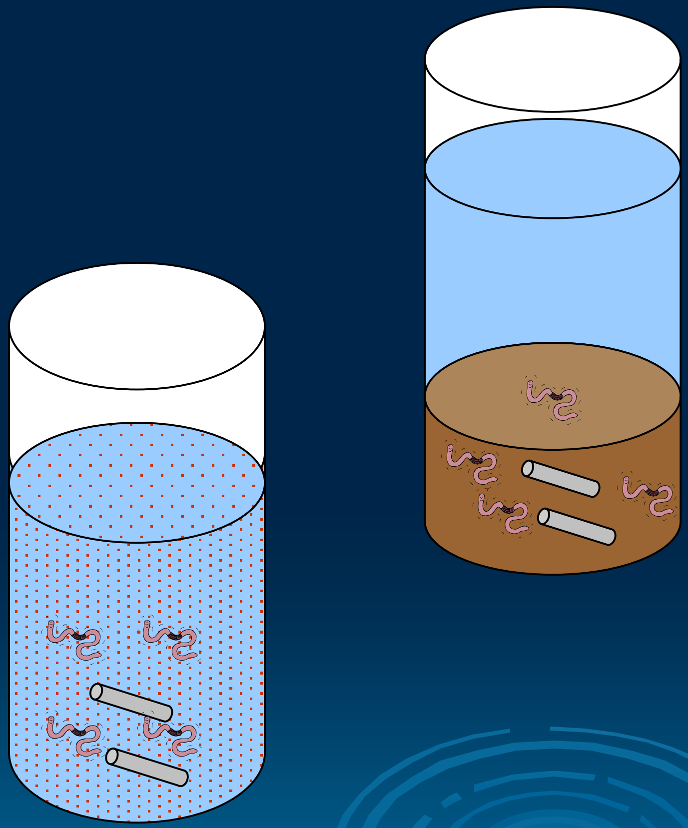


Runoff outlet

"Biomimetic" Fibers

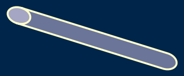
- Polymer-coated fibers
  - Optical fiber companies
- Simultaneous exposure of fiber and organisms in sediment or water
- Measurement of C_f and C_b
- Measurement of LC_{50}
- Correlation

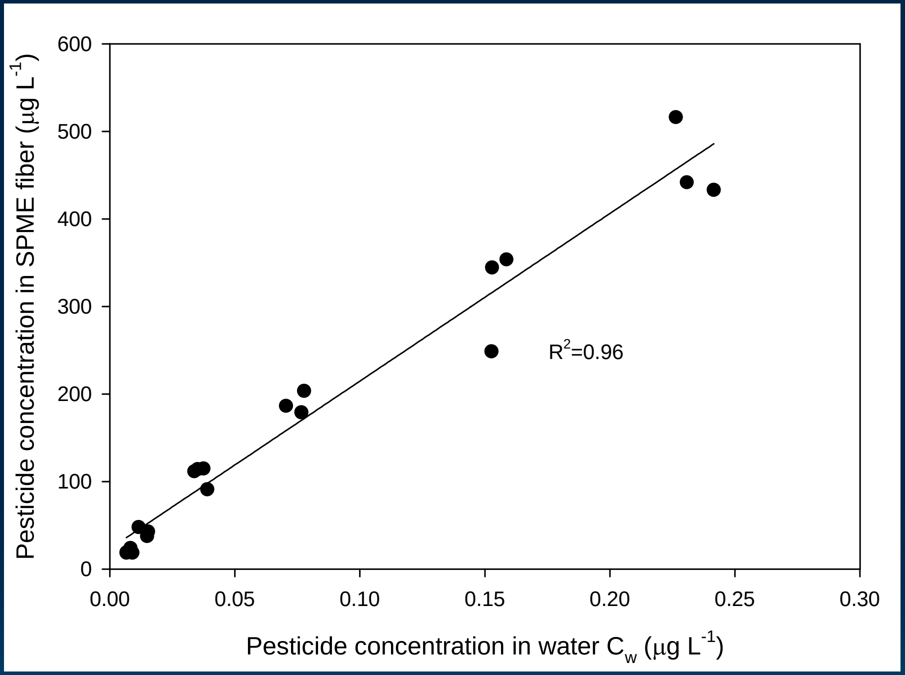
- Advantages:
  - "Negligible" depletion
  - Inexpensive
  - "Real time"
  - Large deployment



Mayer, P. et al., *EST*, 2000
Leslie, H. et al., *ETC*, 2002

K_{fiber}

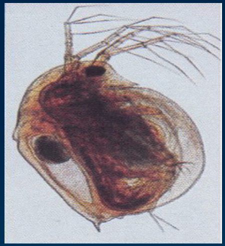


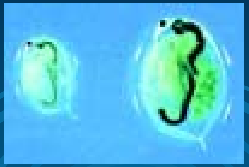

Pesticide concentration in SPME fiber (µg L-1)
Pesticide concentration in water Cw (µg L-1)
R2=0.96
0
100
200
300
400
500
600
0.00
0.05
0.10
0.15
0.20
0.25
0.30

Surface Water

- Types of surface water:
  - Runoff effluents
  - Water column

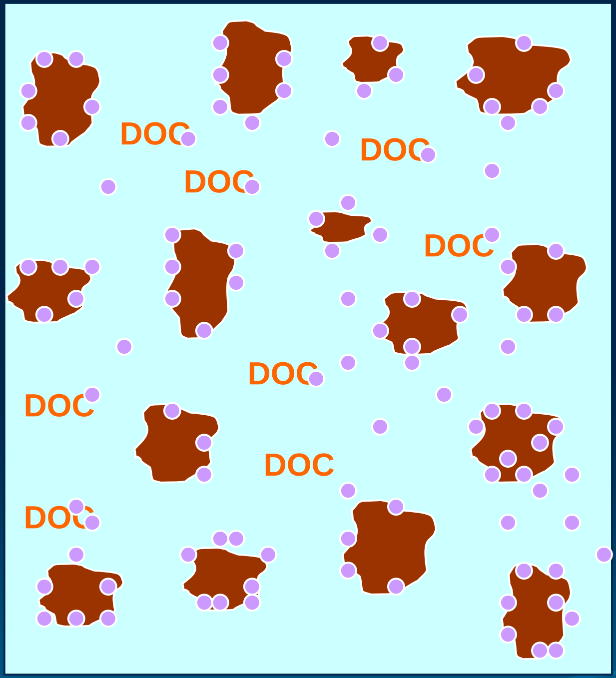
- Study design
  - Bioaccumulation (uptake) (*D. magna*)
  - Acute toxicity (*C. dubia*)





Bioaccumulation

- Overestimation of availability:



$$C_{PDMS} = \frac{C_0}{1 + k_{DOC}[DOC]}$$

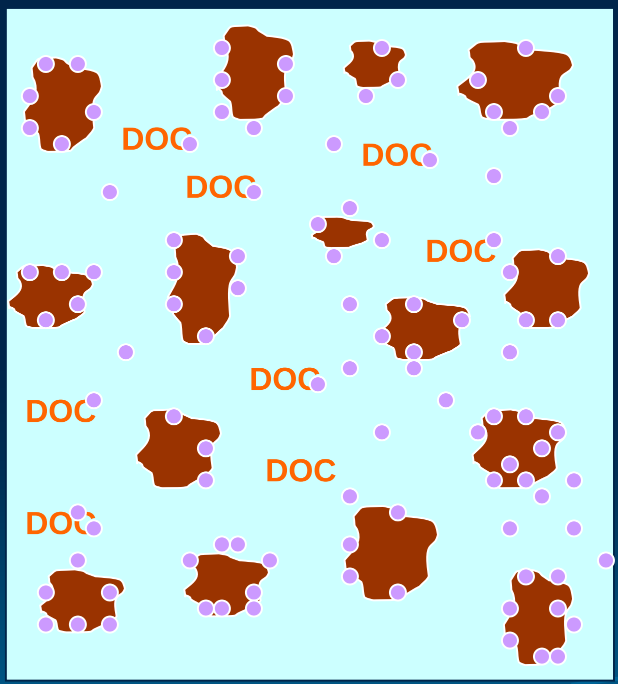
$$BAF = \frac{BAF_{[0]}}{1 + \alpha k_{DOC}[DOC]}$$

α

$\alpha = 1$
$\alpha < 1$
$\alpha > 1$

Acute Toxicity

- **Overestimation of toxicity:**



$$C_{PDMS} = \frac{C_0}{1 + k_{DOC}[DOC]}$$

$$\frac{1}{LC50} = \frac{1}{LC50_{[0]} \times (1 + \alpha k_{DOC}[DOC])}$$

$$LC50 = LC50_{[0]} \times (1 + \alpha k_{DOC}[DOC])$$

α

α = 1
α < 1
α > 1

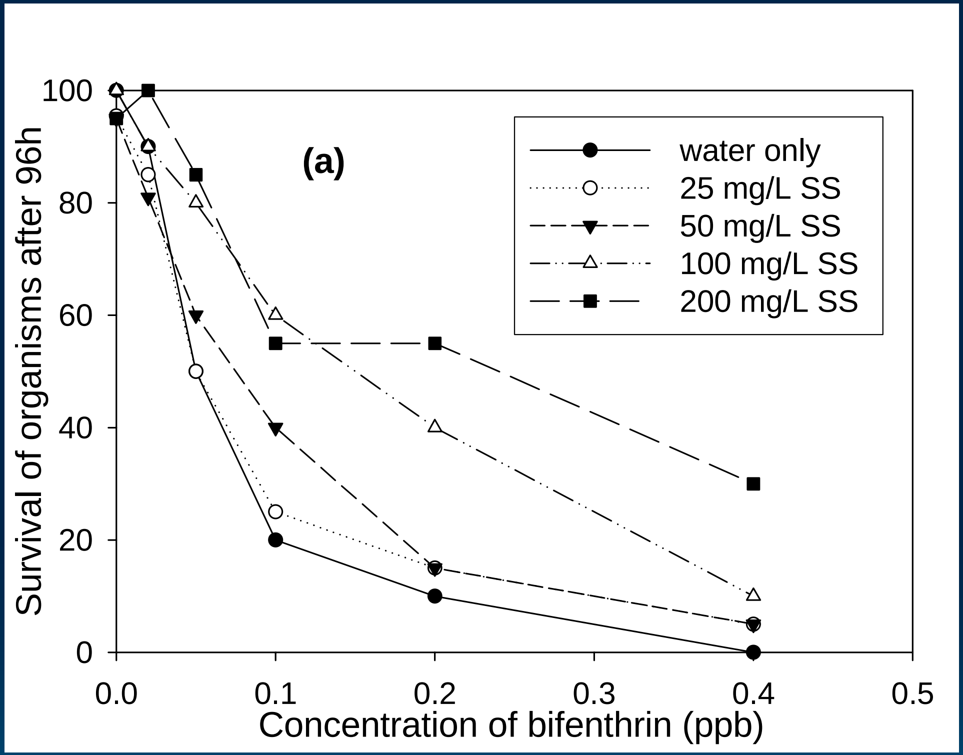
Study I

- LC50 in surface water with suspended solids
  - 4 sediments
  - Washed and unwashed
  - Bifenthrin, permethrin, cypermethrin, esfenvalerate
  - *C. dubia* 96-h static tests
  - Supelco SPME at specific time points
  - LC50, C_w

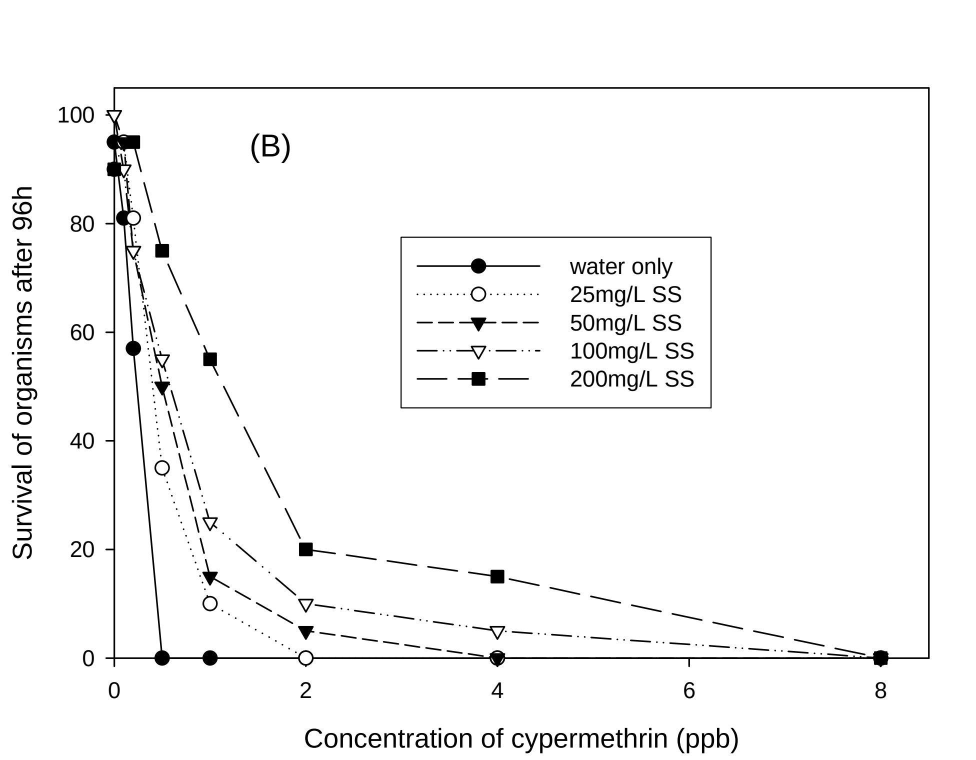
Sediment Properties

Sediment	pH	OM(%)	C-Org(%)
San Diego Creek	7.9	0.87	0.50
Field Furrow	7.7	4.22	2.45
Salinas River	7.9	0.13	0.07
Miles Creek	5.6	2.35	1.36

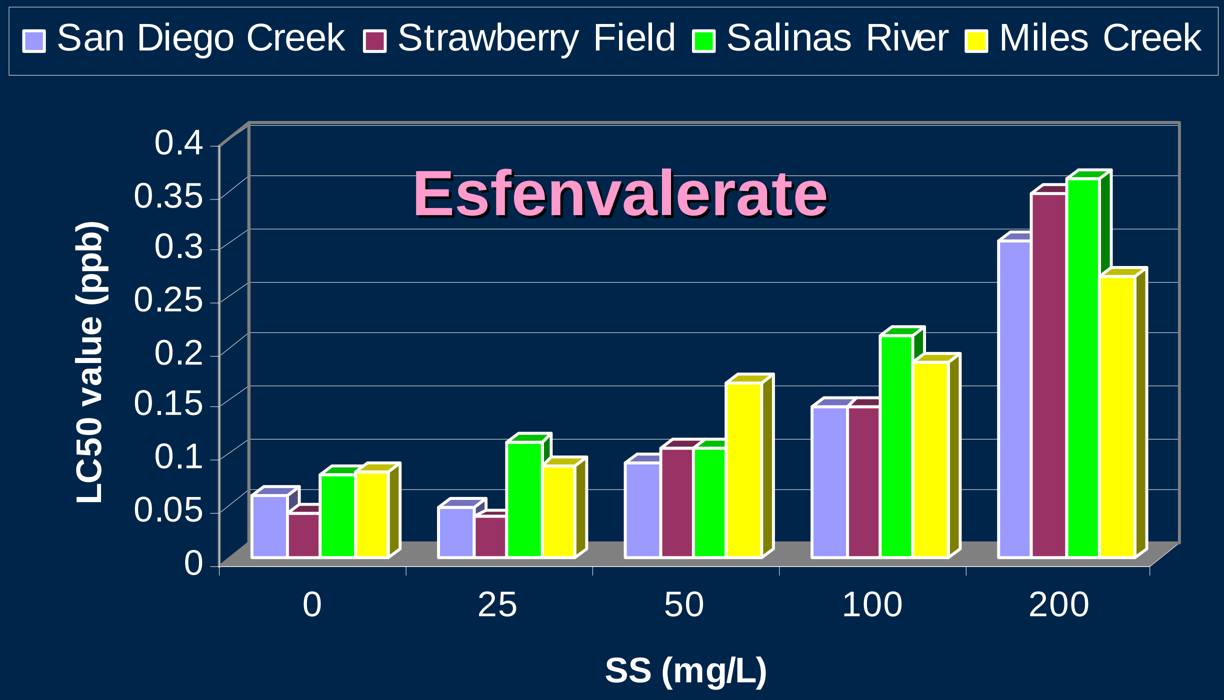
Toxicity Curve
(Bifenthrin-SD Creek Sediment)



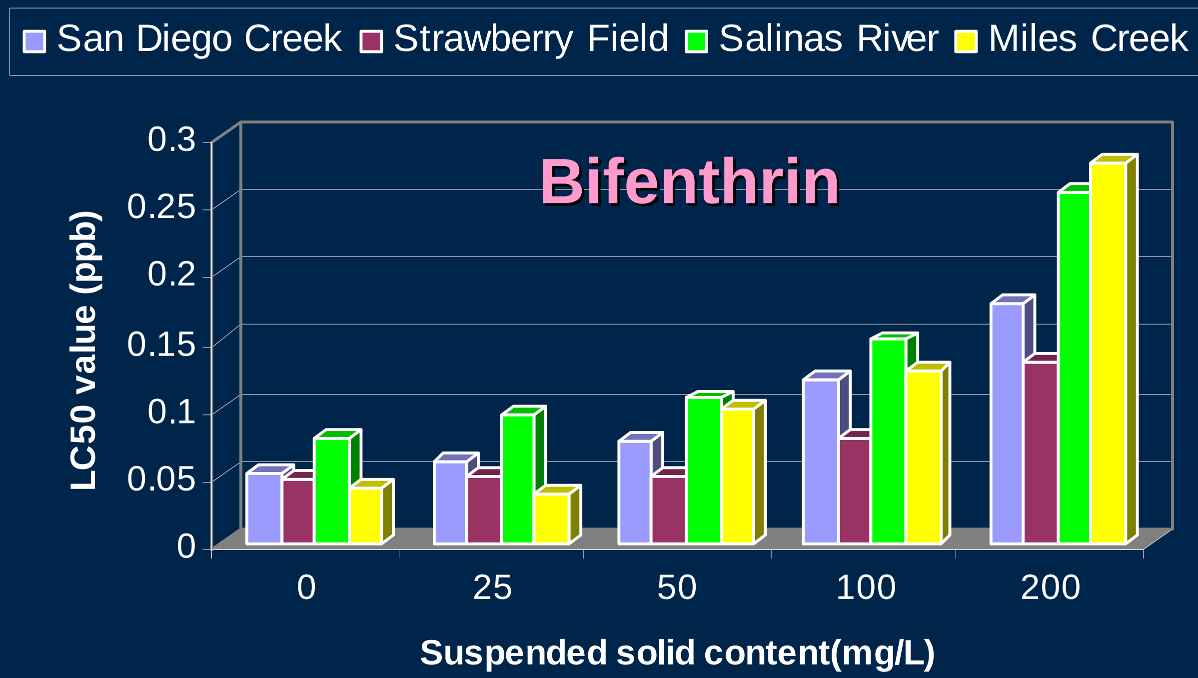
Toxicity Curve
(Cypermethrin-SD Creek Sediment)



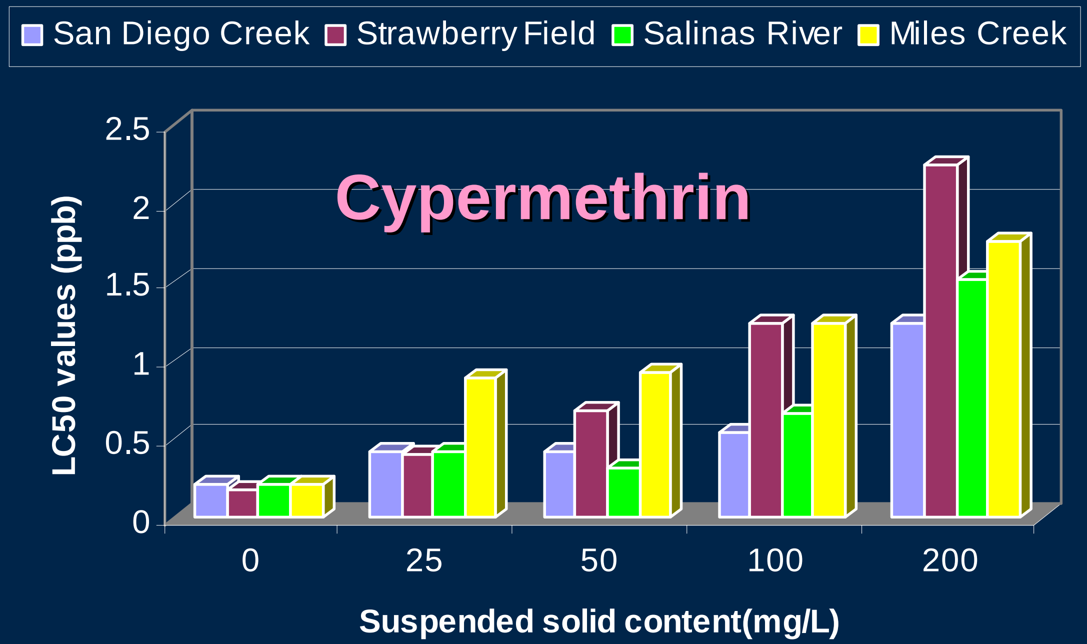
SS Effect on *C.dubia* toxicity



Effect of SS on *C.dubia* Toxicity



SS Effect on *C.dubia* toxicity



Bifenthrin LC50 (ppb)
(San Diego Creek)

SS Mg/L	unwashed			washed		
	LC50	*NOEC*	*LOEC*	*LC50*	*NOEC*	*LOEC*
0	0.052±0.017	0.02	0.05	0.052±0.017	0.02	0.05
25	0.060±0.025	0.02	0.05	0.052±0.016	0.02	0.05
50	0.075±0.031	0.02	0.05	0.061±0.021	0.02	0.05
100	0.121±0.060	0.05	0.1	0.110±0.047	0.02	0.05
200	0.176±0.059	0.1	0.2	0.156±0.045	0.05	0.1

Bifenthrin LC50 (ppb)
(Field Furrow)

SS Mg/L	Unwashed			washed		
	LC50	*NOEC*	*LOEC*	*LC50*	*NOEC*	*LOEC*
0	0.048±0.020	0.05	0.1	0.048±0.020	0.05	0.1
25	0.051±0.018	0.05	0.1	0.040±0.011	0.01	0.02
50	0.049±0.015	0.02	0.05	0.048±0.016	0.02	0.05
100	0.077±0.025	0.05	0.1	0.061±0.025	0.05	0.1
200	0.133±0.042	0.1	0	0.113±0.036	0.05	0.1

Bifenthrin LC50 (ppb)
(Salinas River)

SS Mg/L	unwashed			washed		
	LC50	*NOEC*	*LOEC*	*LC50*	*NOEC*	*LOEC*
0	0.079±0.021	0.02	0.05	0.079±0.021	0.02	0.05
25	0.096±0.022	0.02	0.05	0.069±0.020	0.02	0.05
50	0.107±0.030	0.05	0.1	0.081±0.020	0.05	0.1
100	0.150±0.038	0.1	0.2	0.135±0.037	0.05	0.1
200	0.258±0.070	0.1	0.2	0.208±0.064	0.1	0.2

Bifenthrin LC50 (ppb)
(Miles Creek)

SS mg/L	unwashed			washed		
	LC50	*NOEC*	*LOEC*	*LC50*	*NOEC*	*LOEC*
0	0.041±0.014	0.02	0.05	0.041±0.014	0.02	0.05
25	0.037±0.021	0.02	0.05	0.055±0.022	0.05	0.1
50	0.100±0.032	0.02	0.05	0.097±0.031	0.02	0.5
100	0.127±0.038	0.1	0.2	0.133±0.046	0.05	0.1
200	0.281±0.068	0.1	0.2	0.231±0.059	0.1	0.2

cis-Permethrin LC50 (ppb)
(San Diego Creek)

SS (mg/L)	unwashed			washed		
	LC50	*NOEC*	*LOEC*	*LC50*	*NOEC*	*LOEC*
0	0.516±0.101	0.4	0.8	0.516±0.101	0.4	0.8
25	0.610±0.139	0.4	0.8	0.628±0.135	0.4	0.8
50	0.802±0.155	0.4	0.8	0.742±0.155	0.4	0.8
100	1.051±0.225	0.8	1.2	0.921±0.179	0.4	0.8

cis-Permethrin LC50 (ppb)
(Field Furrow)

SS Mg/L	unwashed			washed		
	LC50	NOEC	LOEC	LC50	NOEC	LOEC
0	0.525±0.102	0.4	0.8	0.525±0.102	0.4	0.8
25	0.651±0.104	0.4	0.8	0.592±0.120	0.4	0.8
50	0.775±0.152	0.4	0.8	0.747±0.161	0.4	0.8
100	0.942±0.183	0.4	0.8	0.883±0.124	0.4	0.8

cis-Permethrin LC50 (ppb)
(Salinas River)

SS Mg/L	unwashed			washed		
	LC50	*NOEC*	*LOEC*	*LC50*	*NOEC*	*LOEC*
0	0.507±0.085	0.2	0.4	0.507±0.085	0.2	0.4
25	0.596±0.101	0.4	0.8	0.576±0.101	0.2	0.4
50	0.711±0.147	0.4	0.8	0.663±0.135	0.4	0.8
100	0.883±0.188	0.4	0.8	0.830±0.182	0.4	0.8

cis-Permethrin LC50 (ppb)
(Miles Creek)

SS Mg/L	unwashed			washed		
	LC50	*NOEC*	*LOEC*	*LC50*	*NOEC*	*LOEC*
0	0.494±0.100	0.2	0.4	0.494±0.100	0.2	0.4
25	0.694±0.146	0.4	0.8	0.663±0.130	0.4	0.8
50	0.817±0.168	0.4	0.8	0.782±0.156	0.4	0.8
100	1.041±0.237	0.4	0.8	0.930±0.176	0.4	0.8

Esfenvalerate LC50 (ppb)
(San Diego Creek)

SS (mg/L)	unwashed			washed		
	LC50	*NOEC*	*LOEC*	*LC50*	*NOEC*	*LOEC*
0	0.059±0.027	0.05	0.1	0.059±0.027	0.05	0.1
25	0.049(a)	0.4	>0.4	0.079±0.037	0.05	0.1
50	0.092±0.028	0.02	0.05	0.066±0.028	0.02	0.05
100	0.144±0.075	0.05	0.1	0.104±0.051	0.05	0.1
200	0.302±0.137	0.2	0.4	0.295±0.100	0.2	0.4

Esfenvalerate LC50 (ppb)
(Field Furrow)

SS (mg/L)	unwashed			washed		
	LC50	NOEC	LOEC	LC50	NOEC	LOEC
0	0.043±0.015	0.02	0.05	0.043±0.015	0.02	0.05
25	0.039±0.036	0.02	0.05	0.057±0.020	0.02	0.05
50	0.106±0.049	0.05	0.1	0.075±0.036	0.02	0.05
100	0.145±0.094	0.05	0.1	0.138±0.084	0.05	0.1
200	0.349±0.154	0.2	0.4	0.266±0.128	0.1	0.2

Esfenvalerate LC50 (ppb)
(Salinas River)

SS (mg/L)	unwashed			washed		
	LC50	*NOEC*	*LOEC*	*LC50*	*NOEC*	*LOEC*
0	0.079±0.028	0.05	0.1	0.079±0.028	0.05	0.1
25	0.112±0.049	0.05	0.1	0.102±0.041	0.05	0.1
50	0.105±0.51	0.1	0.2	0.101±0.074	0.05	0.1
100	0.212±0.134	0.1	0.2	0.127±0.059	0.1	0.2
200	0.363±0.160	0.2	0.4	0.266±0.095	0.1	0.2

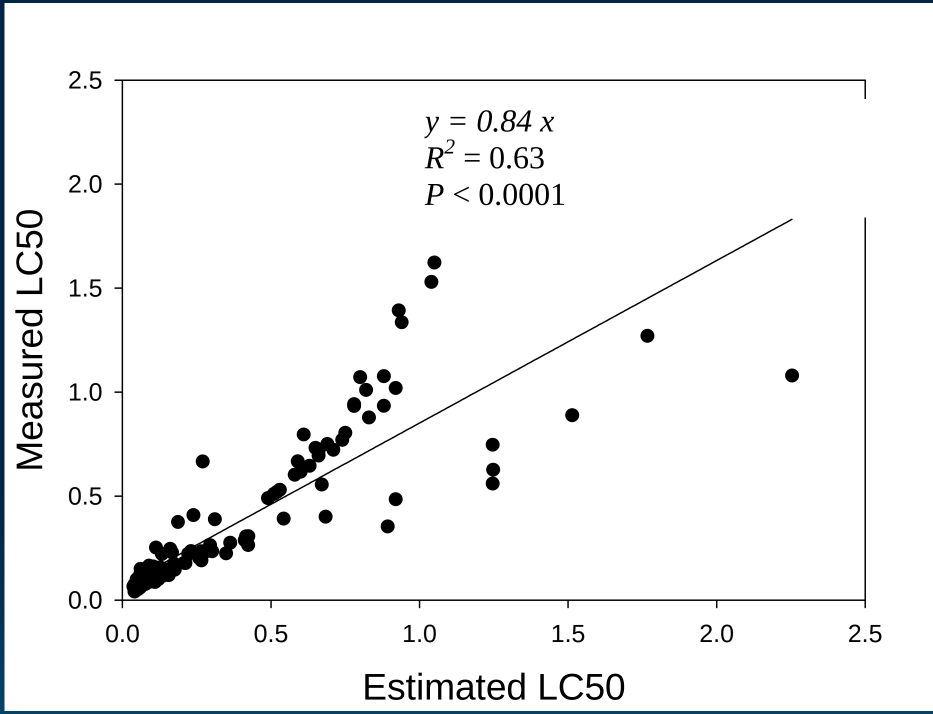
Esfenvalerate LC50 (ppb)
(Miles Creek)

SS (mg/L)	unwashed			washed		
	LC50	*NOEC*	*LOEC*	*LC50*	*NOEC*	*LOEC*
0	0.083±0.031	0.02	0.05	0.083±0.031	0.02	0.05
25	0.088±0.036	0.05	0.1	0.060±0.028	0.02	0.05
50	0.167±0.091	0.1	0.2	0.090±0.035	0.1	0.2
100	0.187±0.109	0.1	0.2	0.161±0.092	0.1	0.2
200	0.270±0.080	0.1	0.2	0.239±0.132	0.1	0.2

Bifenthrin Kd
(Unwashed Sediments)

Compound	San Diego Creek (×10^4)	Field furrow (×10^4)	Salinas River (×10^4)	Miles Creek (×10^4)
Bifenthrin	0.86±0.07	1.54±0.17	0.81±0.38	2.44±0.51
Esfenvalerate	1.62±0.38	2.23±0.84	1.03±0.15	2.53±0.56
cis-Permethrin	2.27±0.73	1.71±0.37	0.61±0.26	1.77±0.49
Cypermethrin	0.96±0.11	2.75±0.73	1.53±0.30	2.90±0.88

LC50 Prediction
(All combined)



$\alpha \approx 1$?

- Mean 1.07 (±0.35) (95% CI)
- 0.28 to 2.39

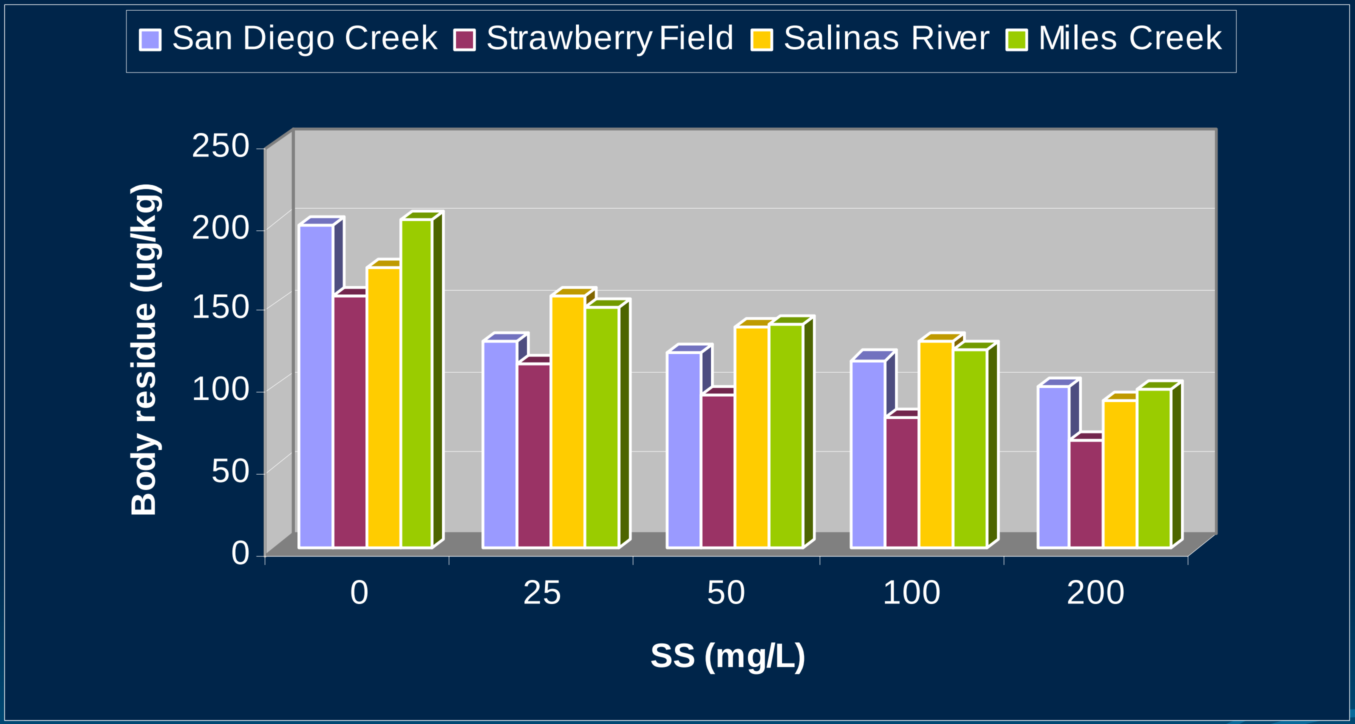
- Variation likely inherent of biological tests
- $\alpha \approx 1$ ⇨ Adsorbed fraction not available
- $\alpha > 1$:
  - Antagonism?
  - Matrix effect

- Prediction:
  - With a factor of 2 (95% CI)

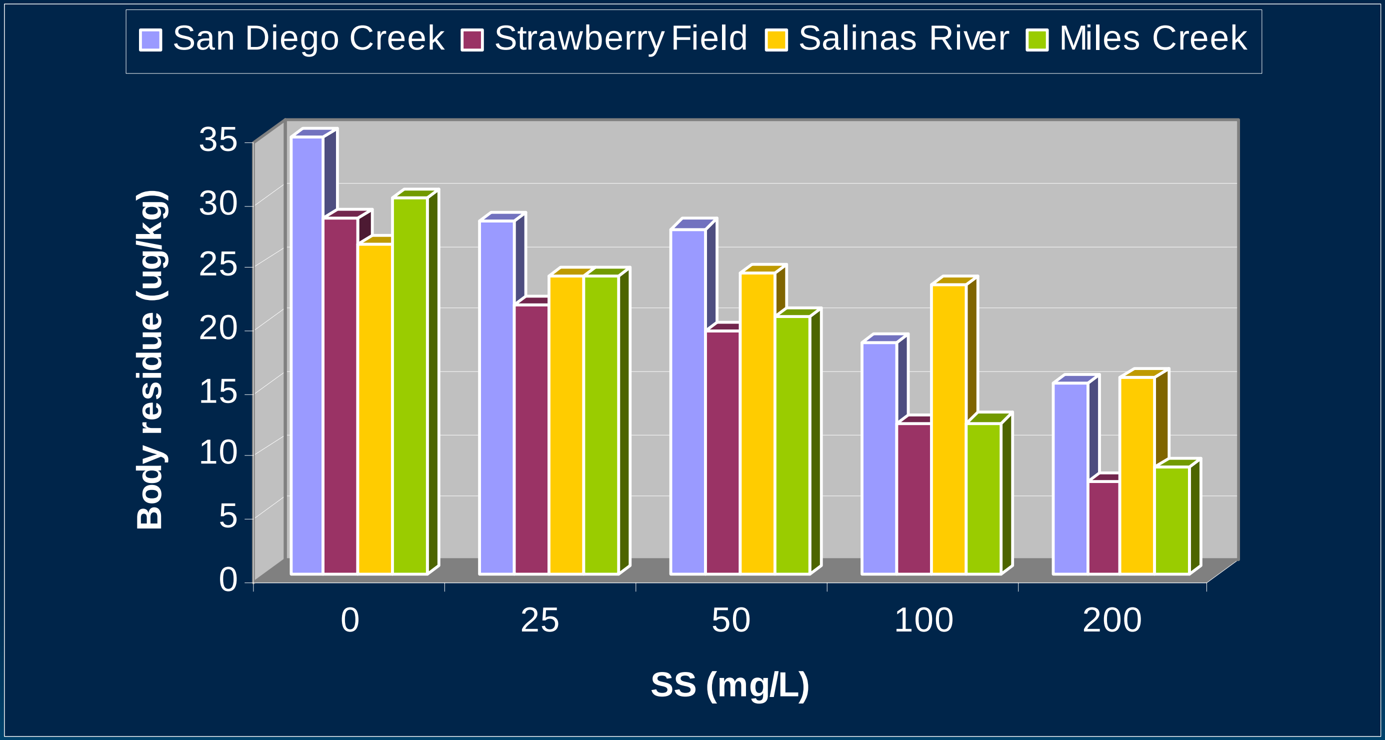
Study II

- Bioaccumulation in surface water with suspended solids
  - 4 sediments
  - Washed and unwashed
  - *D. magna* 24-h static tests
  - ^{14}C-permethrin and ^{14}C-bifenthrin
  - Simultaneous PDMS fibers
  - Body residue, C_{PDMS}, BAF

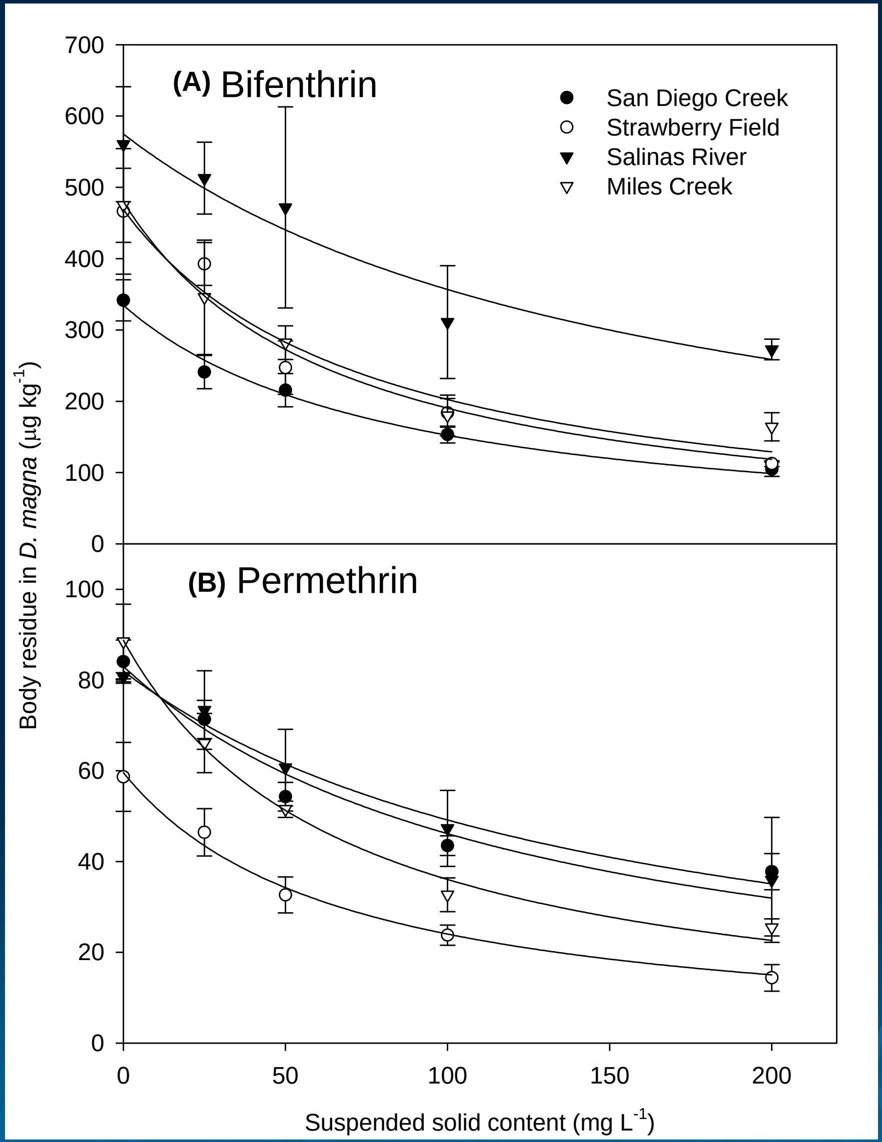
Bioaccumulation of ^{14}C-Bifenthrin (unwashed sediments)



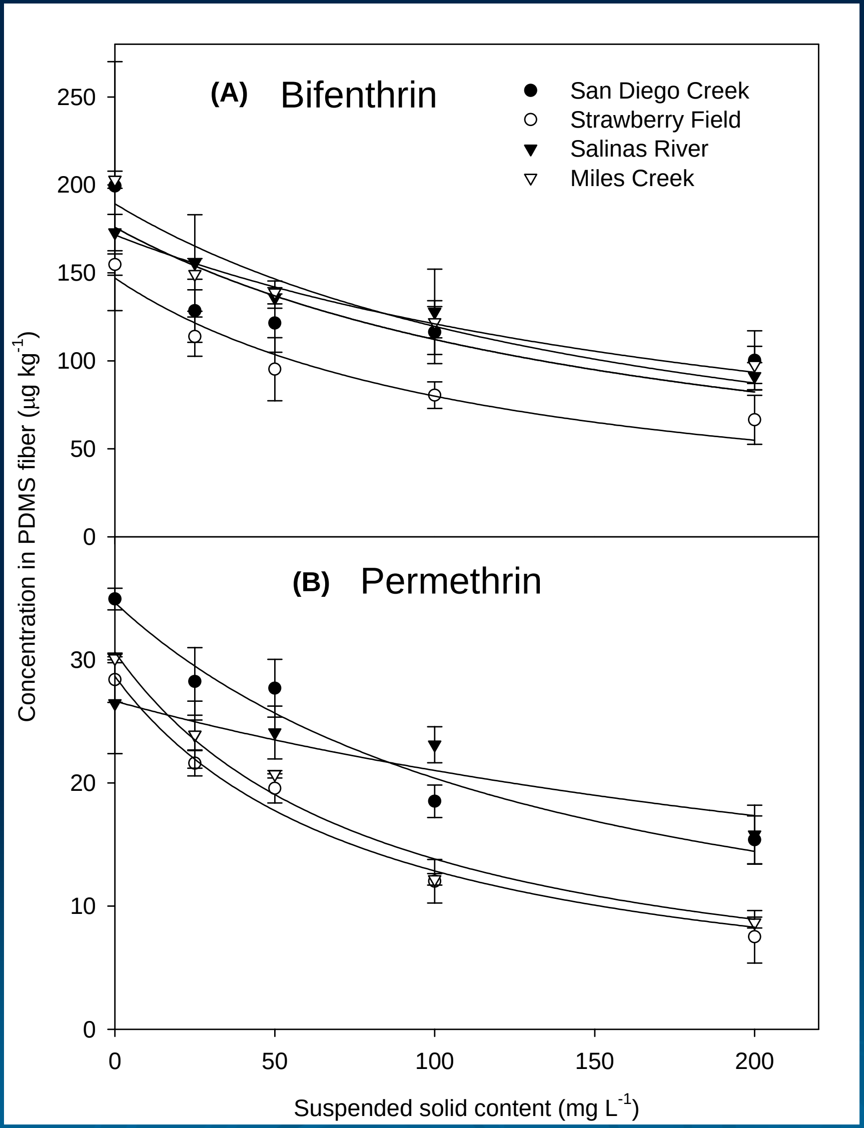
Bioaccumulation of ^{14}C-Permethrin (unwashed sediments)



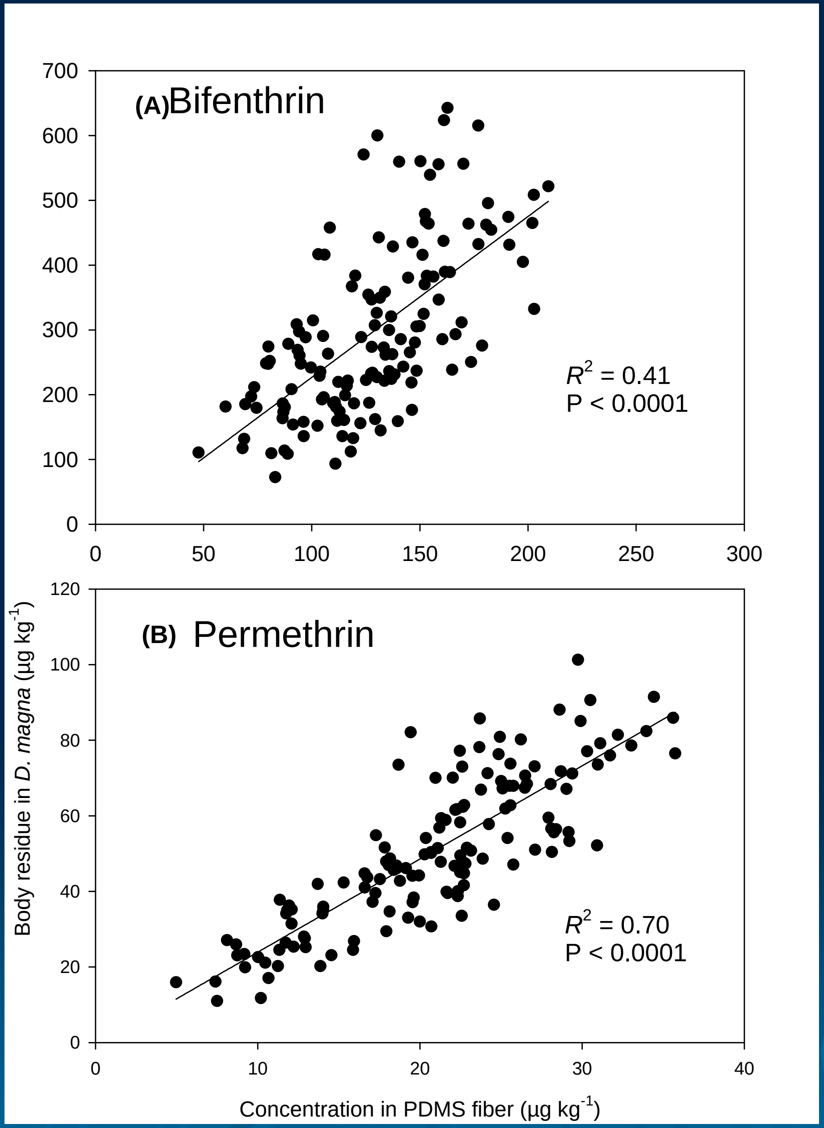
Bioaccumulation in *D. magna*



Accumulation in PDMS fibers



Correlation between *BR* and C_{PDMS}



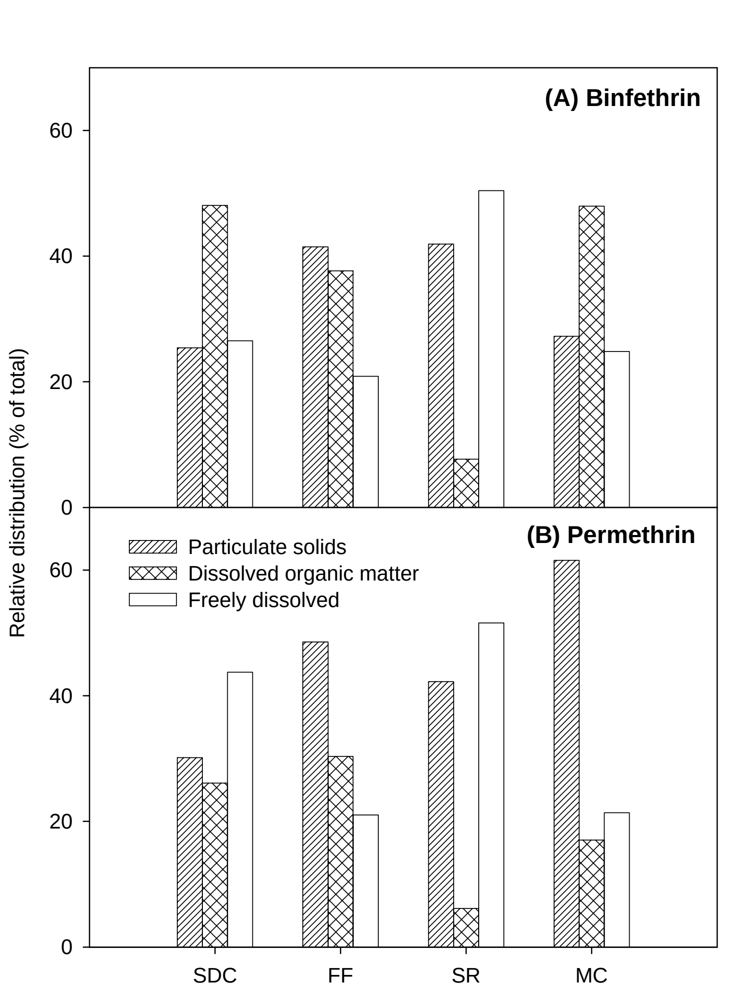
K_d Estimated from BAF and PDMS

Bifenthrin				
Source sediment	Unwashed (×10^3)		Washed (×10^3)	
	PDMS	BAF	PDMS	BAF
San Diego Creek	5.7±2.2	12.4±1.2	4.2±1.5	6.5±1.0
Field furrow	7.1±1.5	15.1±2.2	4.0±1.2	9.0±1.8
Salinas River	4.5±1.0	6.1±1.5	1.4±0.5	5.6±1.4
Miles Creek	5.8±0.8	13.1±2.1	7.9±1.1	7.1±1.9
Permethrin				
Source sediment	Unwashed (×10^3)		Washed (×10^3)	
	PDMS	BAF	PDMS	BAF
San Diego Creek	7.0±0.8	7.4±1.0	4.9±0.2	4.9±0.8
Field furrow	12.3±1.2	15.0±1.7	9.7±0.8	10.1±1.6
Salinas River	2.7±0.6	5.9±1.2	1.8±0.6	5.5±1.3
Miles Creek	12.2±1.0	14.8±1.4	7.8±0.3	12.5±1.9

Partition Coefficients

Source sediment	Bifenthrin			Permethrin		
	K_P ($\times 10^3$)	K_{DOC} ($\times 10^5$)	K_{POC} ($\times 10^5$)	K_P ($\times 10^3$)	K_{DOC} ($\times 10^5$)	K_{POC} ($\times 10^5$)
SDC	4.28±1.08	1.63±0.22	2.95±0.74	3.96±0.88	0.69±0.18	2.73±0.61
FF	7.92±1.67	1.57±0.36	3.34±0.70	9.23±1.37	1.26±0.30	3.89±0.58
SR	5.16±1.93	0.68±1.38	3.02±1.13	5.15±1.66	0.54±1.20	3.01±0.97
MC	4.75±1.97	2.16±0.51	2.35±0.98	11.60±1.64	0.83±0.42	5.74±0.81

Relative Phase Distribution



$\alpha \approx 1$?

- $\alpha \approx 1$ (8 of 16)
- $\alpha > 1$ (8 of 16)

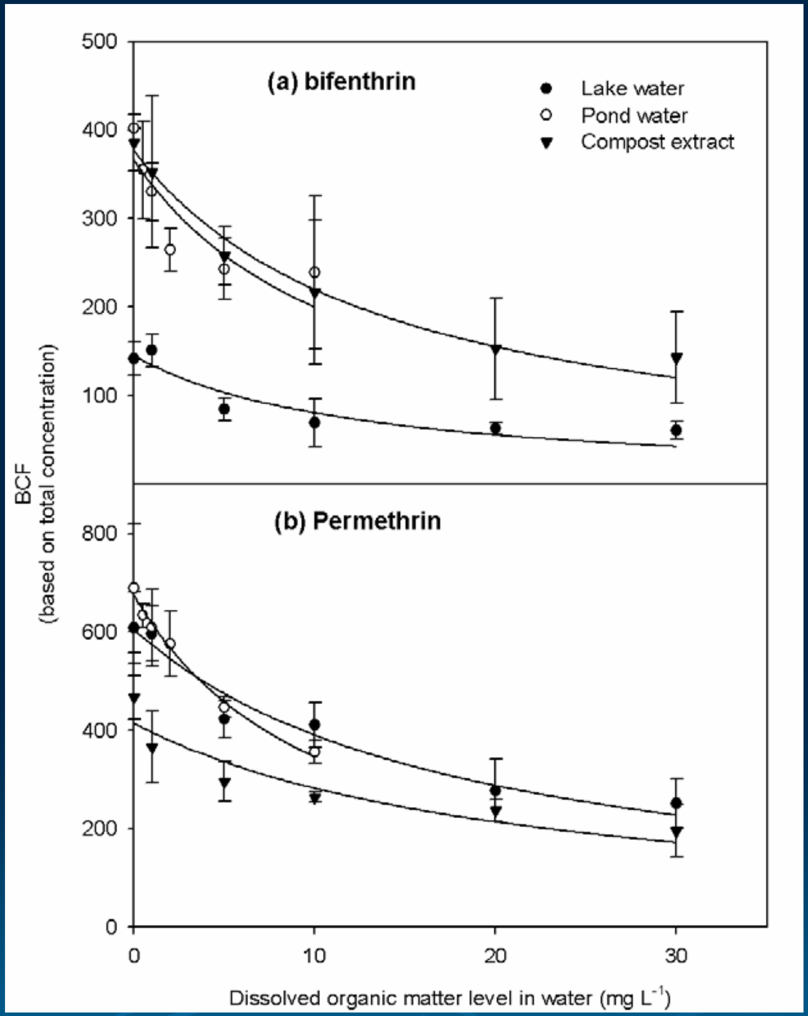
- Variation likely inherent of biological tests
- $\alpha \approx 1$ ⇨ Adsorbed fraction not available
- $\alpha > 1$:
  - Antagonistic effect
  - Matrix effect

- Prediction:
  - Excellent predictions
  - Bifenthrin: $BR = 2.40\ (\pm 0.24)^{*}C_{PDMS}$
  - Permethrin: $BR = 2.47\ (\pm 0.14)^{*}C_{PDMS}$

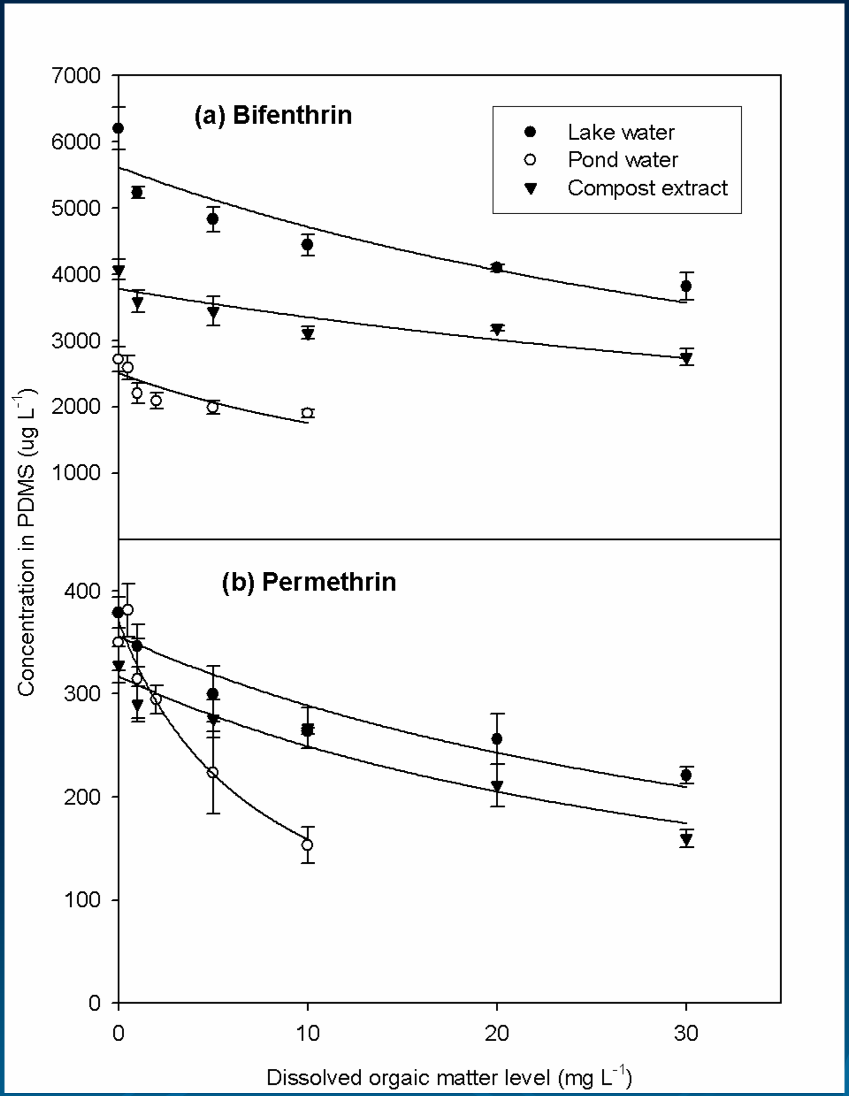
Study III

- Bioaccumulation and LC50 in surface water with DOM
  - 3 source waters with DOM
  - Filter through 0.45 µm
  - *D. magna* 24-h tests for bioaccumulation
  - ^{14}C-permethrin and ^{14}C-bifenthrin
  - Simultaneous PDMS fibers
  - Body residue, C_{PDMS}, BAF
  - LC50 for *C. dubia*

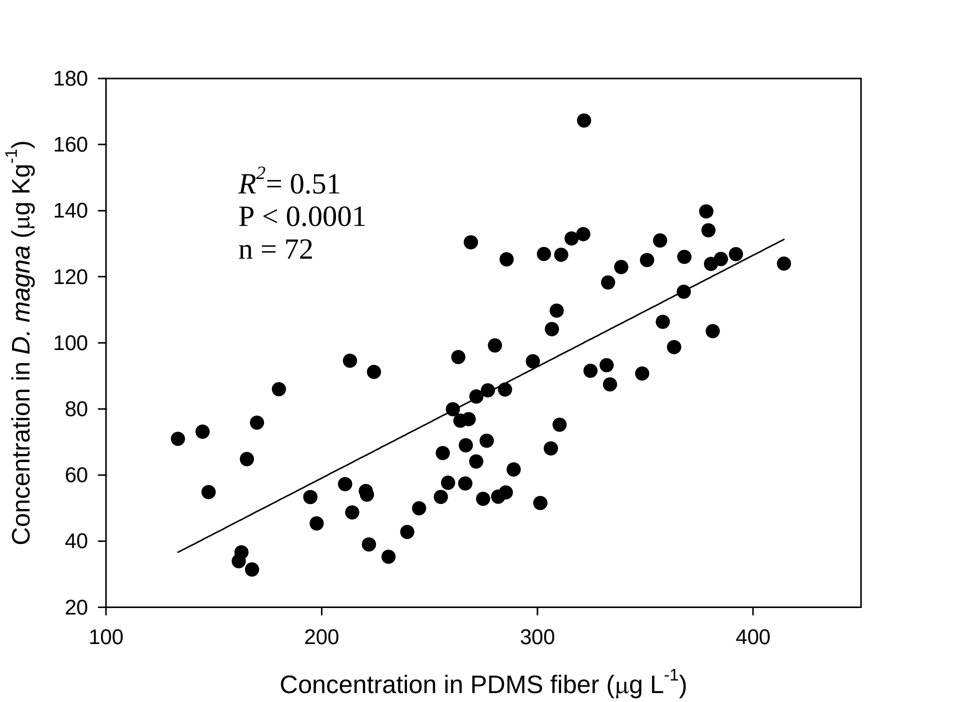
Effect of DOM on Bioaccumulation in *D. Magna*



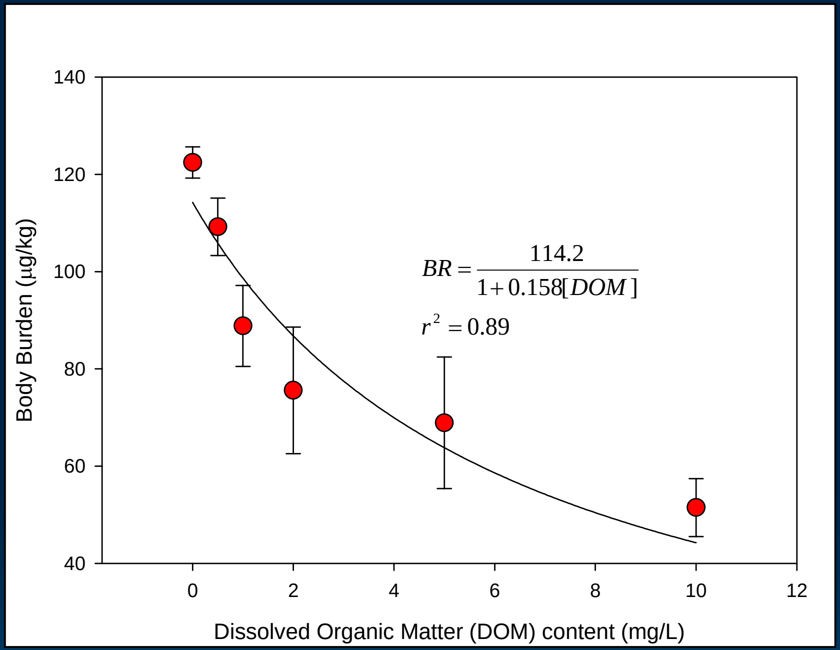
Effect of DOM on Accumulation in PDMS Fibers



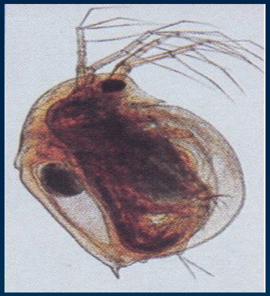
Correlation between *BR* and C_{PDMS} (Permethrin)



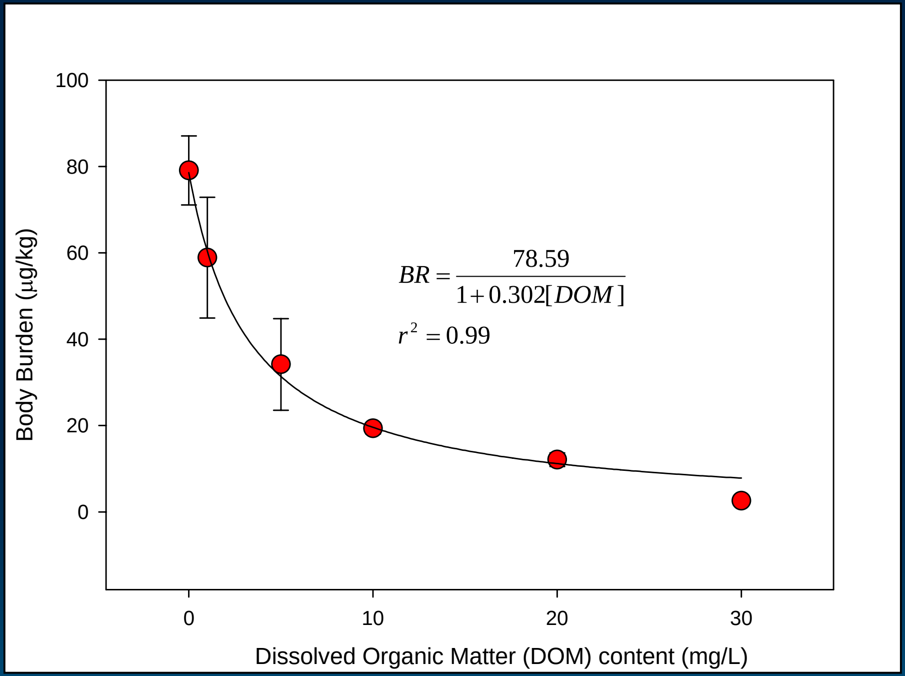
Bioavailability vs. DOM level (Permethrin)



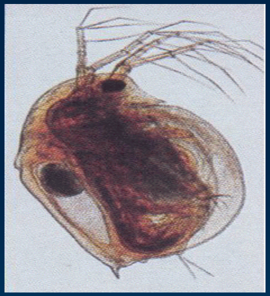
Garden Pond



Bioavailability vs. DOM level (Permethrin)



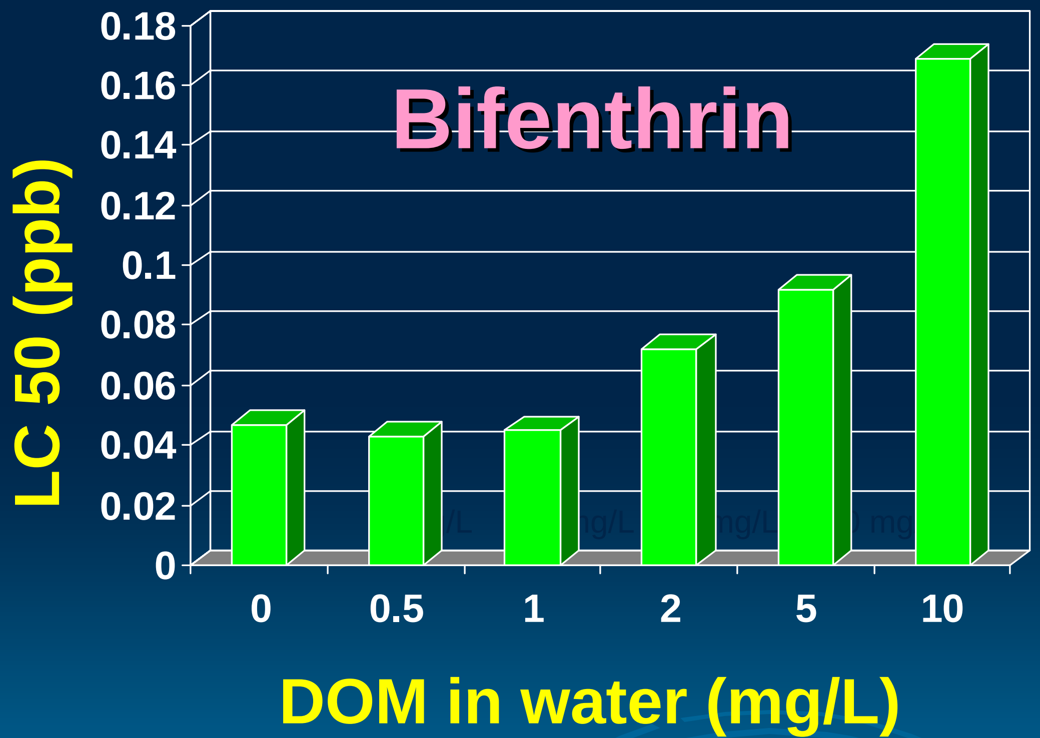
Lake Elsinore



Estimated K_{DOC} Values

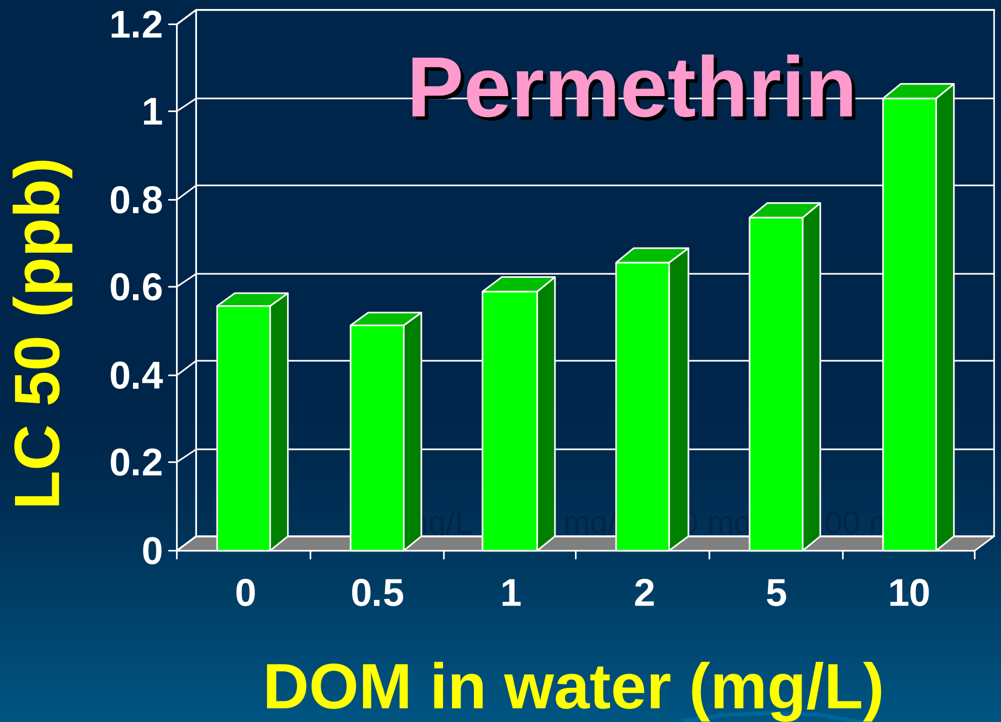
DOM source	PDMS (×10^4)	BCF (×10^4)	LC50 (×10^4)
		Bifenthrin	
Lake water	6.54 ± 1.86	8.05 ± 2.72	14.9 ± 1.51
Pond water	9.04 ± 1.96	8.32 ± 3.17	18.2 ± 2.14
Compost extract	4.61 ± 1.86	6.13 ± 0.88	4.1 ± 0.6
		Permethrin	
Lake water	4.74 ± 2.84	5.52 ± 0.89	3.4 ± 0.5
Pond water	11.21 ± 1.38	9.51 ± 0.66	9.2 ± 0.7
Compost extract	3.10 ± 0.69	4.69 ± 1.39	3.1 ± 0.3

DOM Effect on Toxicity
(*C. dubia* LC50 (ppb))



Garden Pond

DOM Effect on Toxicity
(*C. dubia* LC50 (ppb))



Garden Pond

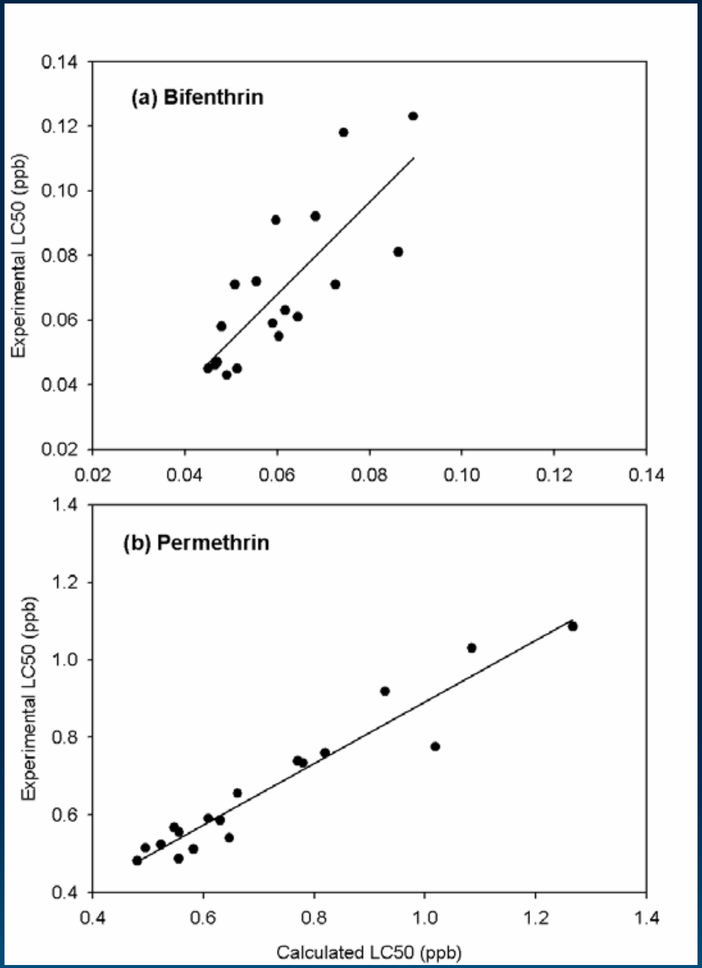
Effect of DOM on LC50 to *C. dubia*

DOC (mg L^{-1})	Bifenthrin	DOC (mg L^{-1})	Permethrin
Lake water			
0	0.045 (0.032-0.059)	0	0.523 (0.384-0.645)
0.5	0.046 (0.030-0.063)	1	0.567 (0.423-0.687)
1	0.058 (0.039-0.077)	5	0.540 (0.434-0.657)
2	0.071 (0.051-0.092)*	10	0.739 (0.568-0.947)
5	0.091 (0.055-0.127)*	20	0.776 (0.626-0.952)*
10	0.118 (0.086-0.153)*	30	1.085 (0.805-1.391)*
Pond water			
0	0.047 (0.033-0.061)	0	0.556 (0.409-0.677)
0.5	0.043 (0.028-0.059)	0.5	0.512 (0.382-0.622)
1	0.045 (0.028-0.064)	1	0.591 (0.478-0.719)
2	0.072 (0.052-0.095)	2	0.656 (0.490-0.813)
5	0.092 (0.066-0.126)*	5	0.760 (0.565-0.954)*
10	0.123 (0.081-0.169)*	10	1.030 (0.808-1.318)*
Compost extract			
0	0.059 (0.045-0.076)	0	0.481 (0.389-0.583)
0.5	0.055 (0.034-0.075)	1	0.515 (0.391-0.629)
1	0.063 (0.044-0.084)	5	0.487 (0.388-0.597)
2	0.061 (0.046-0.079)	10	0.586 (0.423-0.738)
5	0.071 (0.052-0.092)	20	0.734 (0.520-0.903)*
10	0.081(0.059-0.107)	30	0.919 (0.706-1.190)*

Estimated K_{DOC} Values

DOM source	PDMS ($\times 10^4$)	BCF ($\times 10^4$)	LC50 ($\times 10^4$)
		Bifenthrin	
Lake water	6.54 ± 1.86	8.05 ± 2.72	14.9 ± 1.51
Pond water	9.04 ± 1.96	8.32 ± 3.17	18.2 ± 2.14
Compost extract	4.61 ± 1.86	6.13 ± 0.88	4.1 ± 0.6
		Permethrin	
Lake water	4.74 ± 2.84	5.52 ± 0.89	3.4 ± 0.5
Pond water	11.21 ± 1.38	9.51 ± 0.66	9.2 ± 0.7
Compost extract	3.10 ± 0.69	4.69 ± 1.39	3.1 ± 0.3

Predicted and Measured LC50 for *C. dubia*



$\alpha \approx 1$?

- BAF: $\alpha \approx 1$ (6 of 6)
- LC50: $\alpha \approx 1$ (4 of 6); $\alpha > 1$ (2 of 6)

- Variation likely inherent of biological tests
- $\alpha \approx 1 \Rightarrow$ Adsorbed fraction not available

- Prediction:
  - BAF:
    - *Bifenthrin:* $R^2 = 0.47\text{-}0.62$; $P < 0.001$
    - Permethrin: $R^2 = 0.50\text{-}0.75$; $P < 0.0001$
  - LC50:
    - Bifenthrin: $R^2 = 0.93 – 0.96$; $P < 0.005$
    - Permethrin: $R^2 = 0.92 – 0.98$; $P < 0.005$
    - Both: $R^2 = 0.62$; $P < 0.001$

Study IV

- Bioaccumulation in surface water with DOM
  - ~17 surface waters with DOM
  - *D. magna* 24-h static tests
  - *C. dubia* LC50 tests
  - ^{14}C-permethrin and ^{14}C-cyfluthrin
  - Simultaneous PDMS fibers
  - Characterization of aquatic DOM:
    - UV absorbance to determine E4/E6
    - UV absorbance at 254 and 280 nm to determine aromaticity
    - Fluorescence to determine aromaticity
    - Titration to determine total and aromatic acids

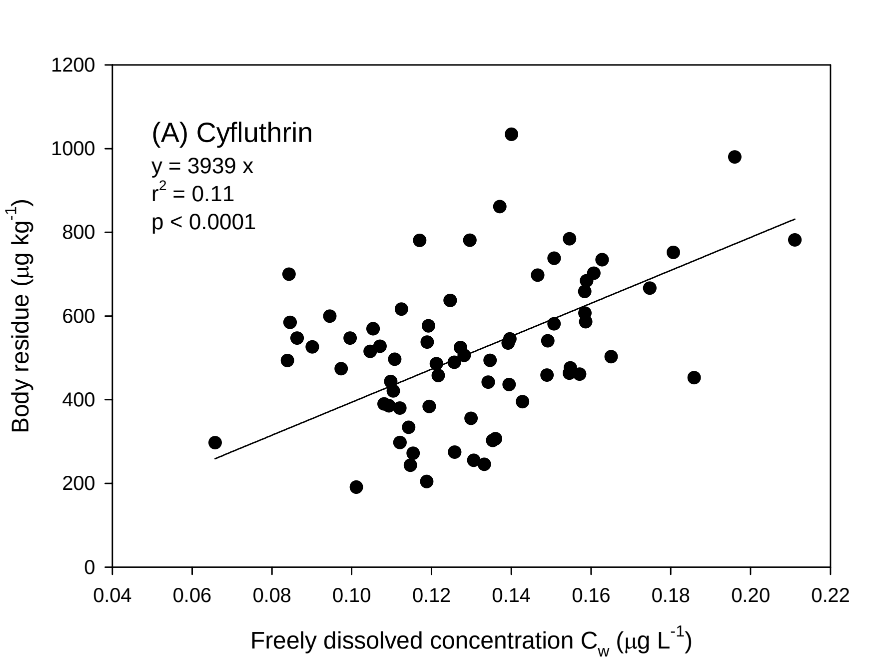
17 "Natural" Surface Water Samples

Water samples	pH	Alkalinity (mg L^{-1})	Hardness (mg L^{-1})	Ammonia (mg L^{-1})	Cl^{-} (mg L^{-1})	DOC (mg L^{-1})
SJI	7.30	323	303	0.07	<0.2	20.2±2.6
SDC	6.87	318	>1000	<0.02	<0.2	7.8±0.3
EL	6.85	180	200	<0.02	<0.2	3.6±0.2
BL	7.36	118	162	<0.02	<0.2	4.5±0.1
FL	7.76	204	223	<0.02	<0.2	3.3±0.9
PC	7.02	361	>1000	<0.02	<0.2	7.0±0.3
SDI	7.14	317	>1000	0.02	<0.2	5.5 ±0.8
SJ	7.75	470	>1000	<0.02	<0.2	18.1±0.4
GC	7.48	215	242	<0.02	<0.2	1.2±0.1
SAR	7.70	230	270	<0.02	<0.2	3.4±0.4
SY	7.24	269	365	<0.02	<0.2	4.4±0.1
BG	6.95	235	308	<0.02	<0.2	5.8±0.9
SC	7.05	470	>1000	<0.02	<0.2	5.9±0.1
SA	7.73	130	440	<0.02	<0.2	5.3±0.9
LE	7.29	223	200	<0.02	<0.2	18.9±0.1
RJ	6.67	304	302	<0.02	<0.2	5.5±1.1
TC	6.85	198	220	<0.02	<0.2	4.6±1.5

Measured Free Concentration (ng/L)

Water samples	Permethrin	Cyfluthrin
Control	97±9	182±26
SJI	73±4	80±10
SDC	75±5	139±22
EL	76±6	166±15
BL	82±4	138±23
FL	88±8	158±20
PC	84±10	97±6
SDI	87±9	125±15
SJ	64±8	122±10
GC	79±12	121±18
SAR	78±20	126±10
SY	101±11	131±15
BG	99±6	116±11
SC	101±14	116±23
SA	97±5	154±10
LE	91±5	118±13
RJ	96±5	128±16
TC	96±3	126±24

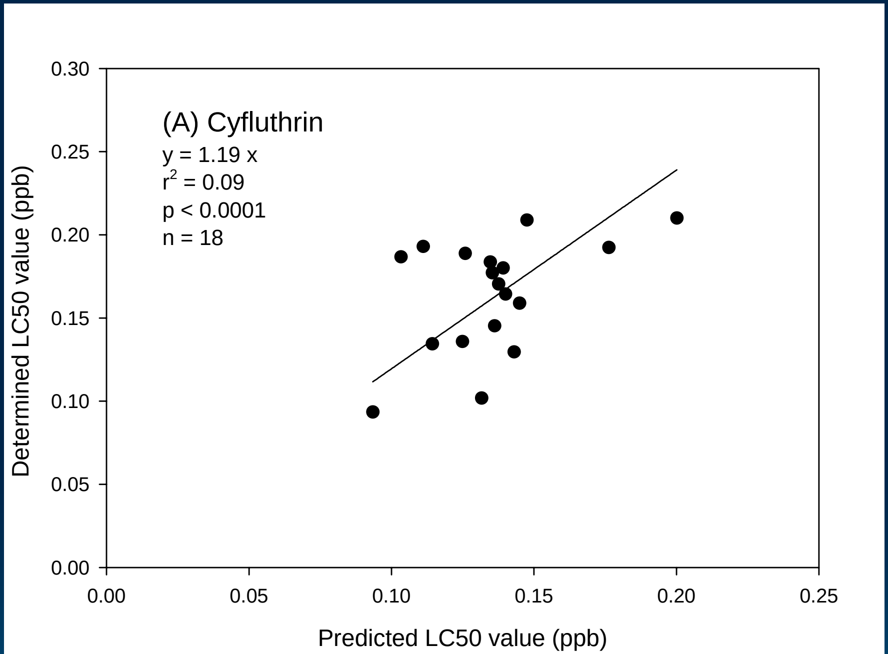
Correlation between *BR* and C_w (Cyfluthrin)



Measured LC50 Values (μg/L)

Water samples	*cis*-Permethrin	Cyfluthrin
Control	0.652 (0.484-0.856)	0.093(0.050-0.146)
SJI	0.788(0.545-1.040)	0.210(0.154-0.288)*
SDC	0.622(0.427-0.824)	0.136(0.103-0.185)
EL	0.772(0.574-1.013)	0.187(0.138-0.271)*
BL	0.745(0.568-0.957)	0.189(0.112-0.292)*
FL	0.858(0.591-1.138)	0.134(0.097-0.194)*
PC	0.571(0.427-0.740)	0.192(0.126-0.279)*
SDI	0.580(0.407-0.718)	0.170(0.121-0.229)
SJ	0.299(0.212-0.385)*	0.164(0.113-0.231)*
GC	0.343(0.308-0.383)*	0.130(0.097-0.179)*
SAR	0.609(0.486-0.747)	0.145(0.105-0.185)*
SY	0.570(0.459-0.689)	0.102(0.027-0.395)*
BG	0.827(0.669-1.012)	0.209(0.144-0.298)
SC	0.585(0.677-0.793)	0.177(0.131-0.253)
SA	0.849(0.655-1.085)	0.193(0.142-0.283)*
LE	0.889(0.666-1.120)	0.159(0.105-0.234)
RJ	0.865(0.672-1.098)	0.184(0.121-0.275)*
TC	0.996(0.764-1.286)*	0.180(0.127-0.280)

Predicted and Measured LC50 for *C. dubia* (Cyfluthrin)

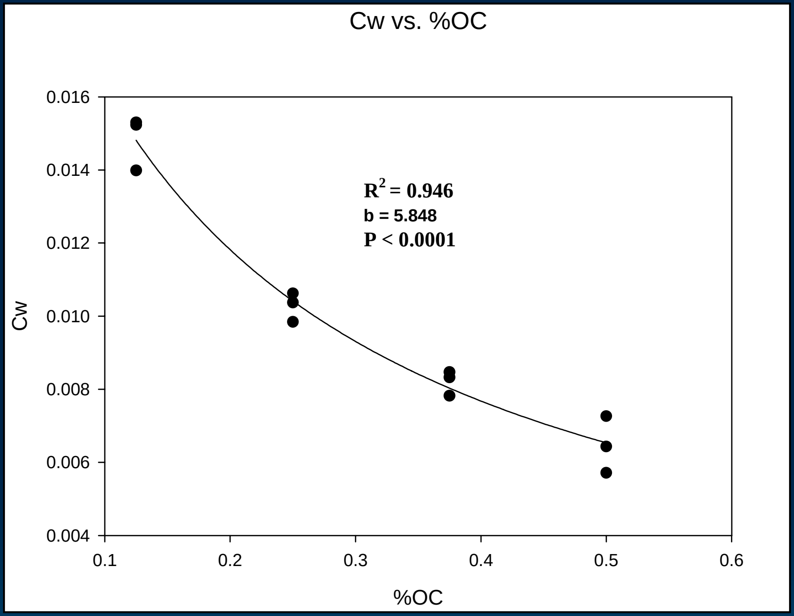


Sediment

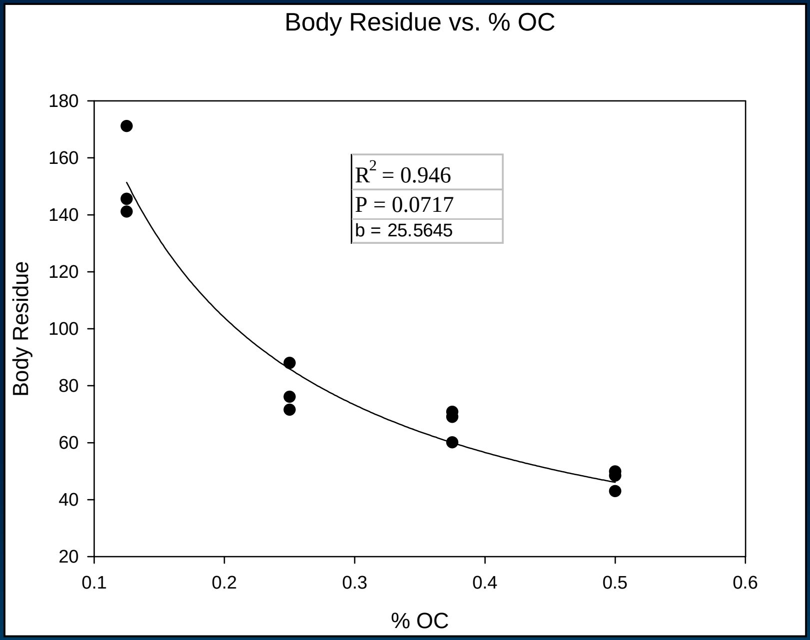
- **Just started**…
- **Pore-water:**
  - Method development
  - Phase distribution
  - Role of DOM
  - …

- **Study design**
  - Bioaccumulation (*C. tentans*)
  - Acute toxicity (*C. tentans, H. azteca)*
  - Aging effect

Pore-water "Free" Concentrations vs. Sediment OC%



C. Tentan Body Residue (μg/kg) vs. Sediment OC%



α ≈ 4 (matrix effect? Not at equilibrium? …)

Future Directions

- Water column data
  - Possible to introduce a correction factor?
  - Possible to predict toxicity from C_{PDMS}?
  - Feasibility of using PDMS fibers for routine monitoring?
  - Feasibility for field deployment?
  - Other biomimetic samplers?
  - …

$$LC_{50}^{*} = (1 + a[DOC])LC_{50}$$

$$LC_{50}^{*} = (1 + b[SS])LC_{50}$$

Future Directions

- Bioavailability in sediments
  - Matrix effect, method development
  - ^{14}C Bioaccumulation by *C. tentans* and other benthic organisms
  - Correlation of *BR* and C_{PDMS}
  - LC50 of *C. tentans* and H. azteca
  - Correlation of LC50 with C_{PDMS}
  - Effect of sediment OC%
  - Effect of properties of sediment OM
  - Effect of aging
  - Prediction models

  - Fibers to measure non-labeled porewater Cw
  - Evaluation of field sediment samples
  - …