A SPME-based passive sampler for improving sediment quality assessment of hydrophobic organic contaminants (HOCs)

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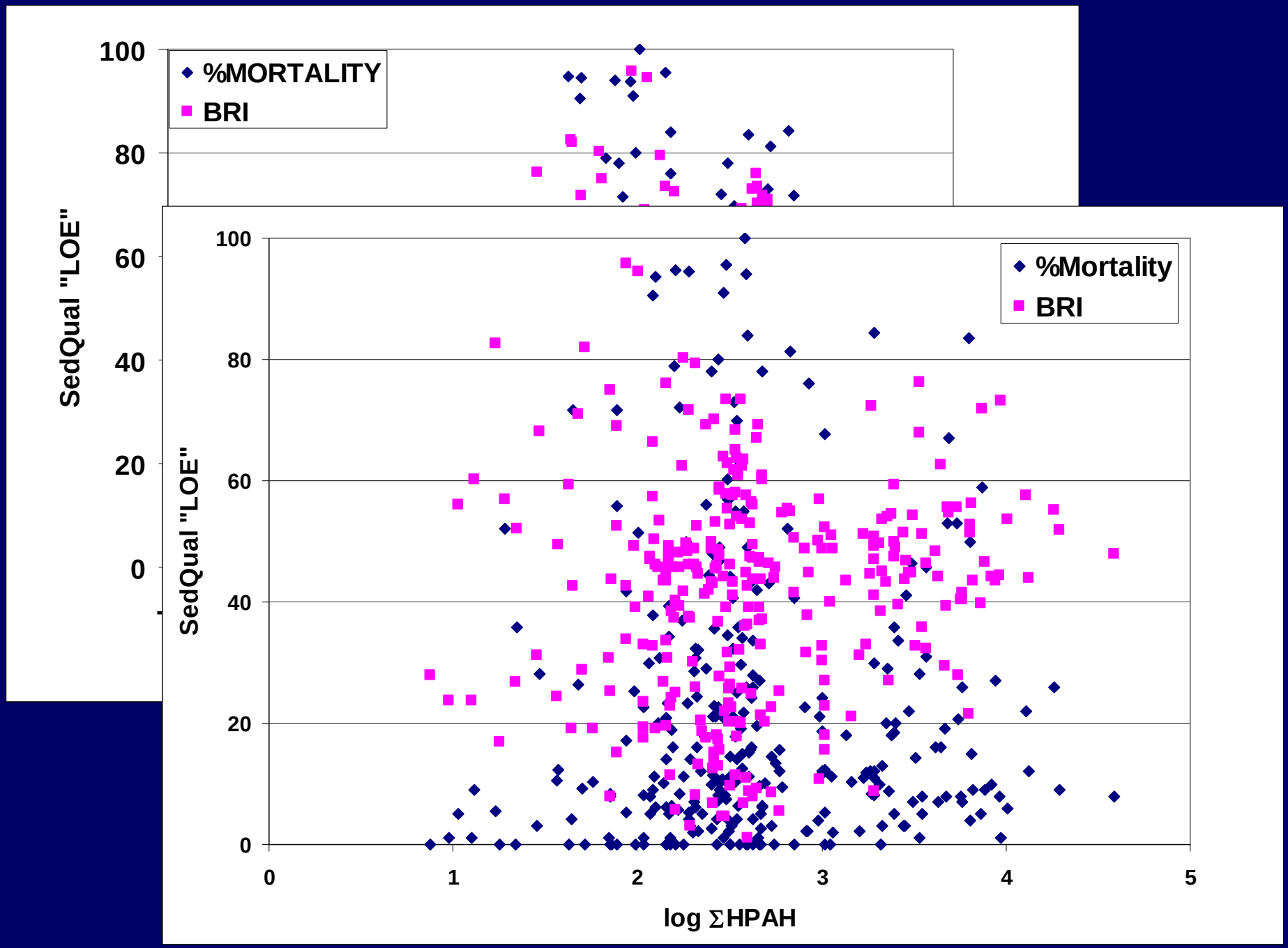
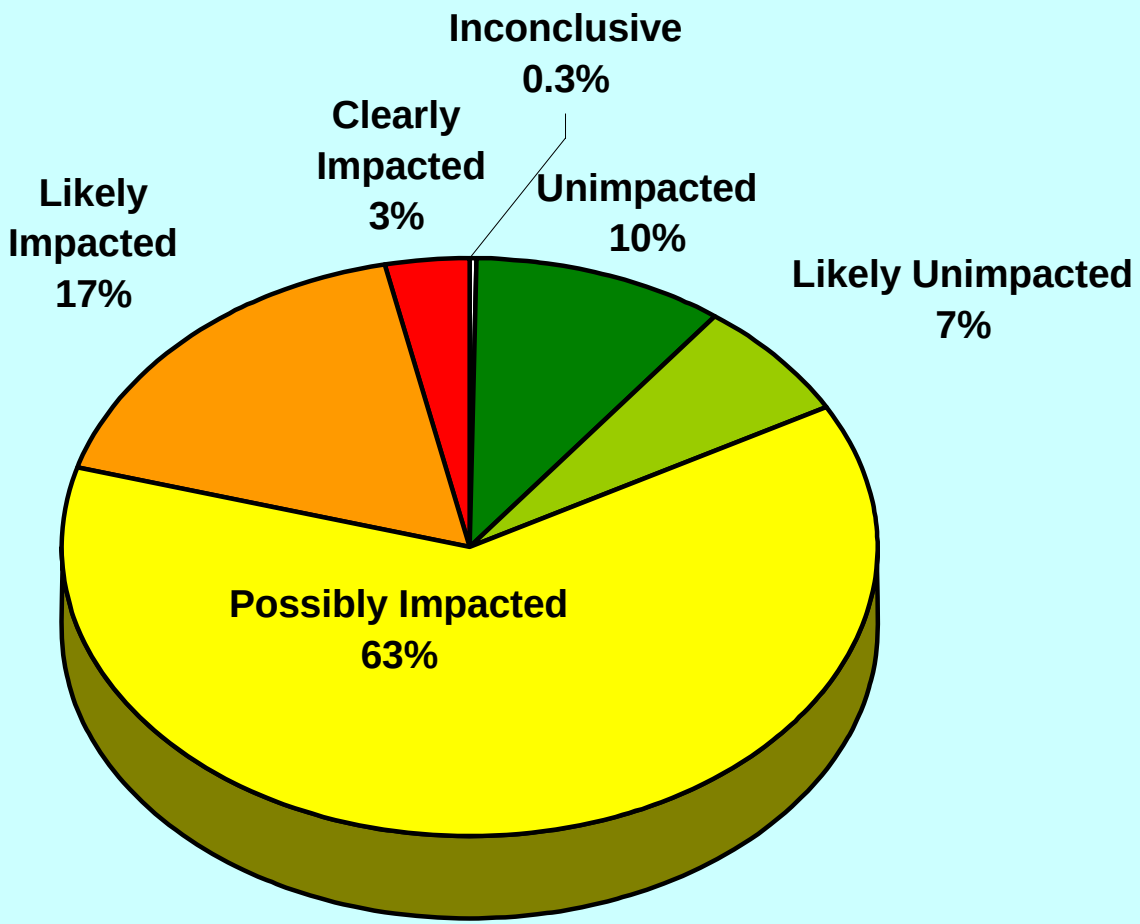
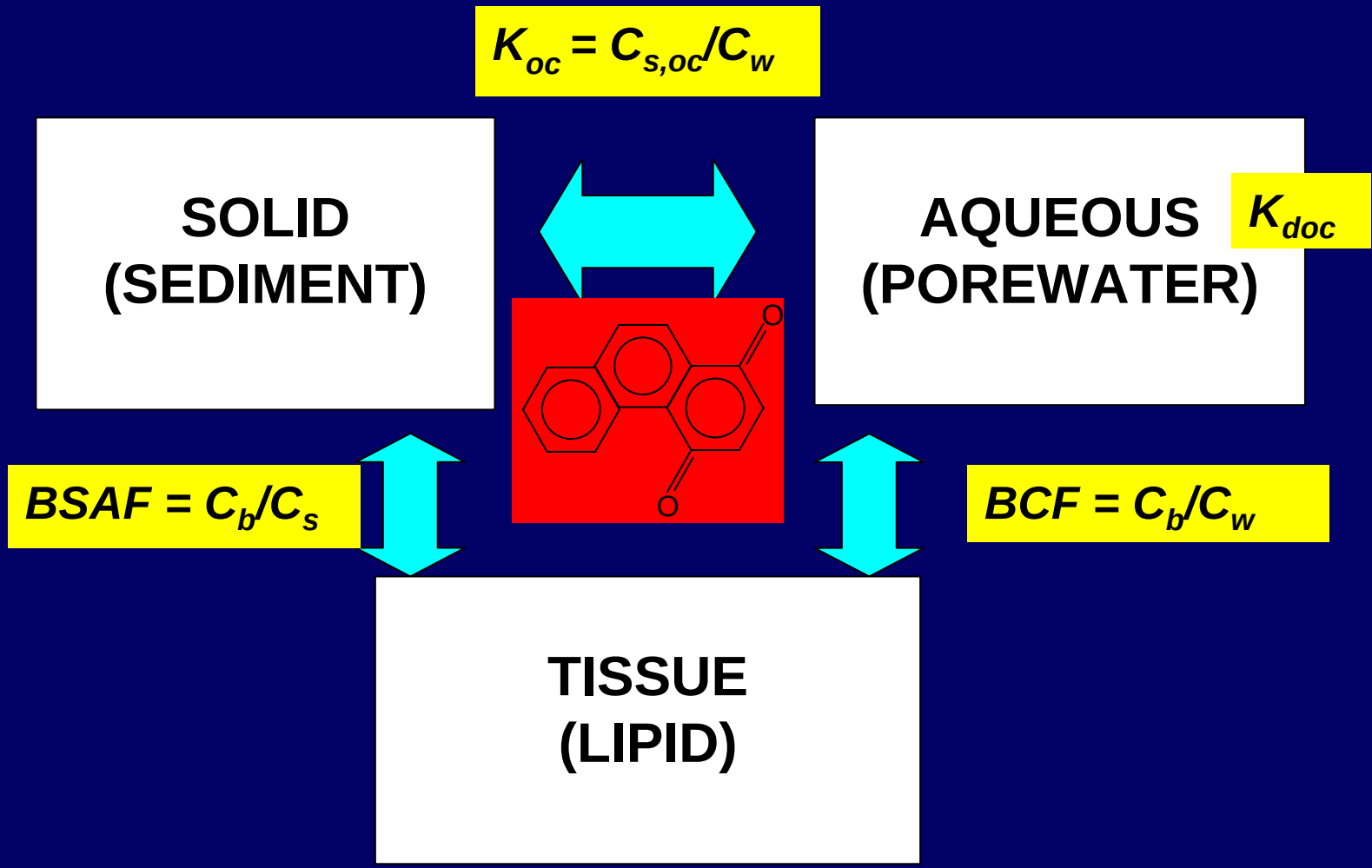

%MORTALITY
BRI
SedQual "LOE"
100
80
60
40
20
0
%Mortality
BRI
SedQual "LOE"
100
80
60
40
20
0
0
1
2
3
4
5
log ΣHPAH

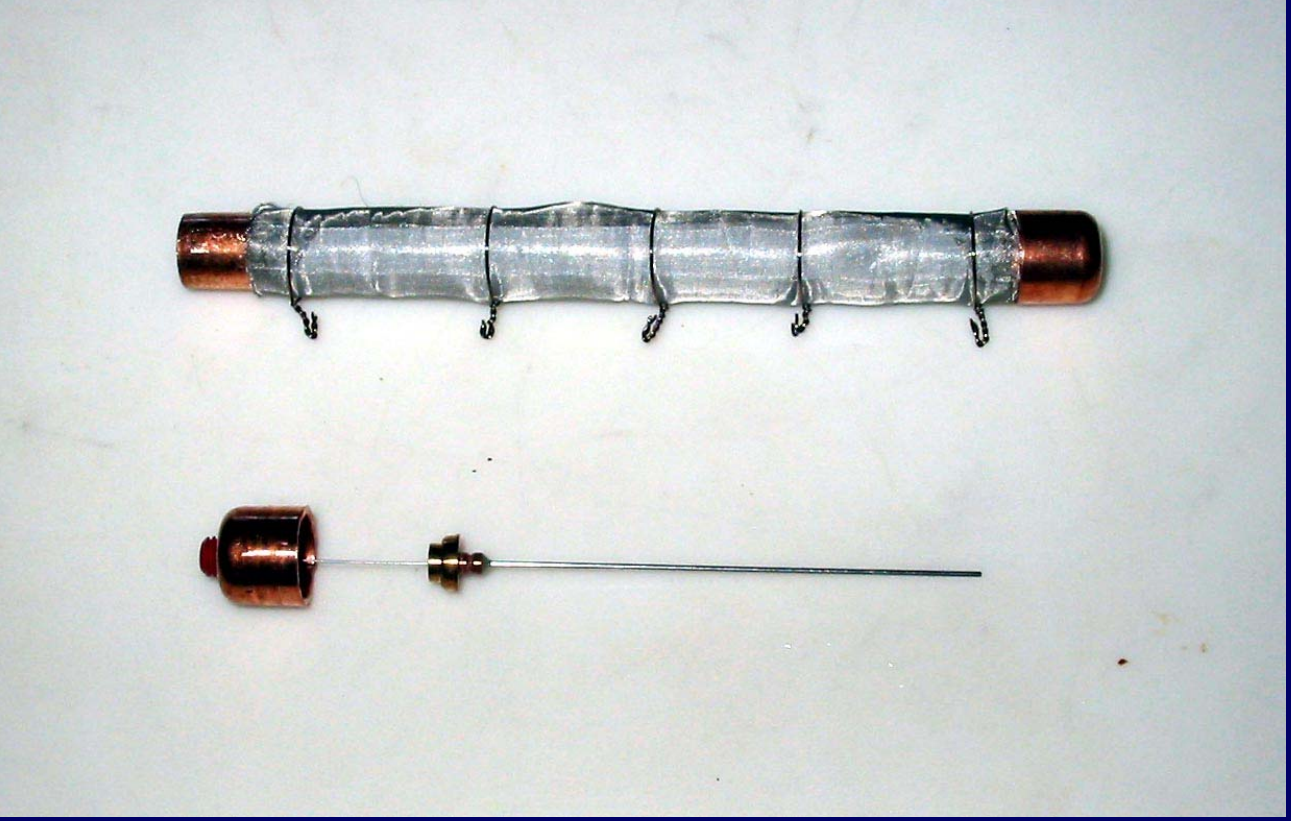
Statewide (CA) Condition





K_{oc} (~ K_{ow}) >> 10^3 —> C_w << 1 mg/L

Can we quantify the bioavailable fraction of HOCs (at ultratrace levels)?



Housing:

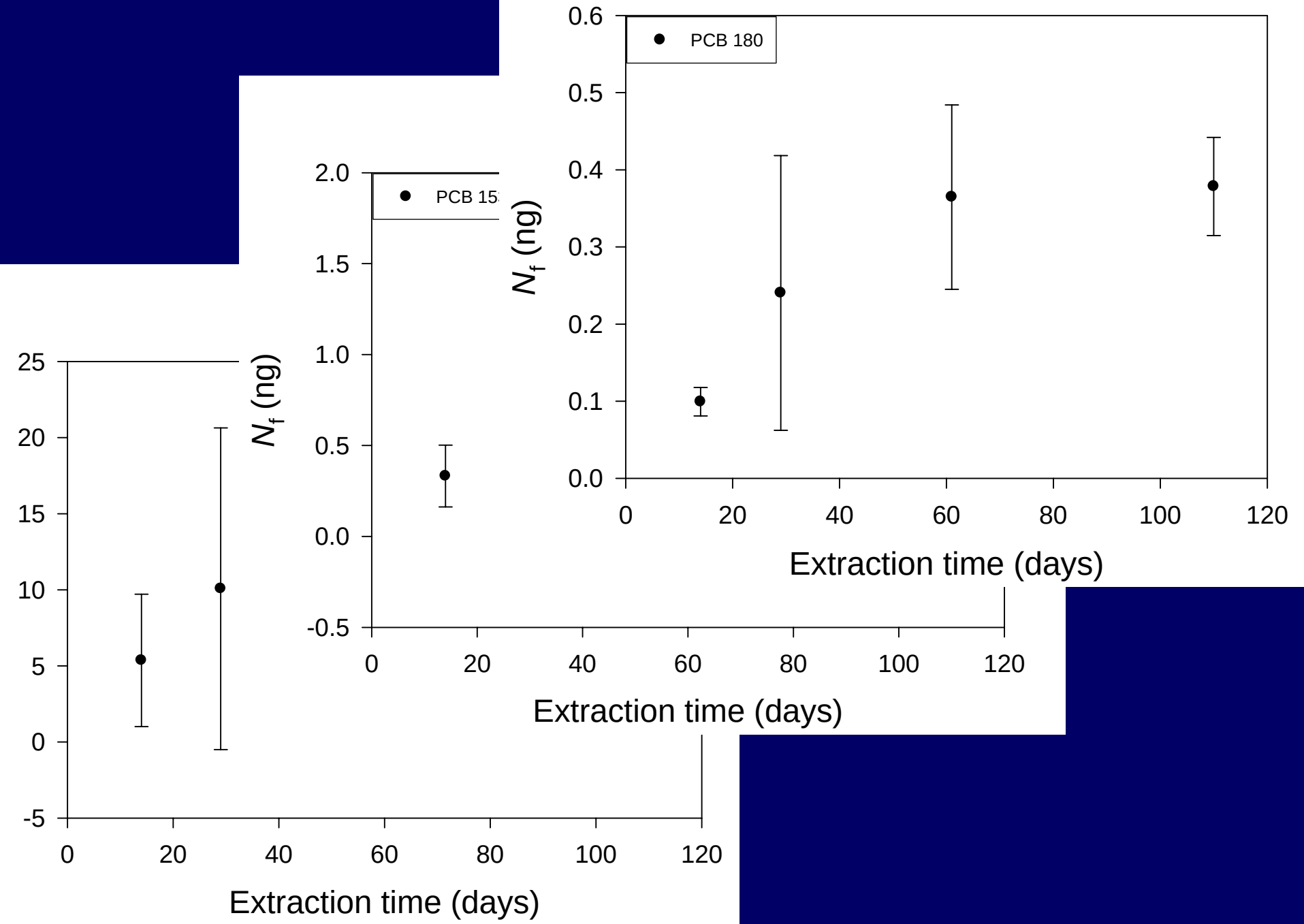
- 11 x 1 cm o.d. (1 mm) Cu tube
- Interior "cavity" volume: 4.9 cm^3
- GF/F (0.7 μm eff pore dia.)
- 270 mesh 316 stainless screen

SPME Fiber:

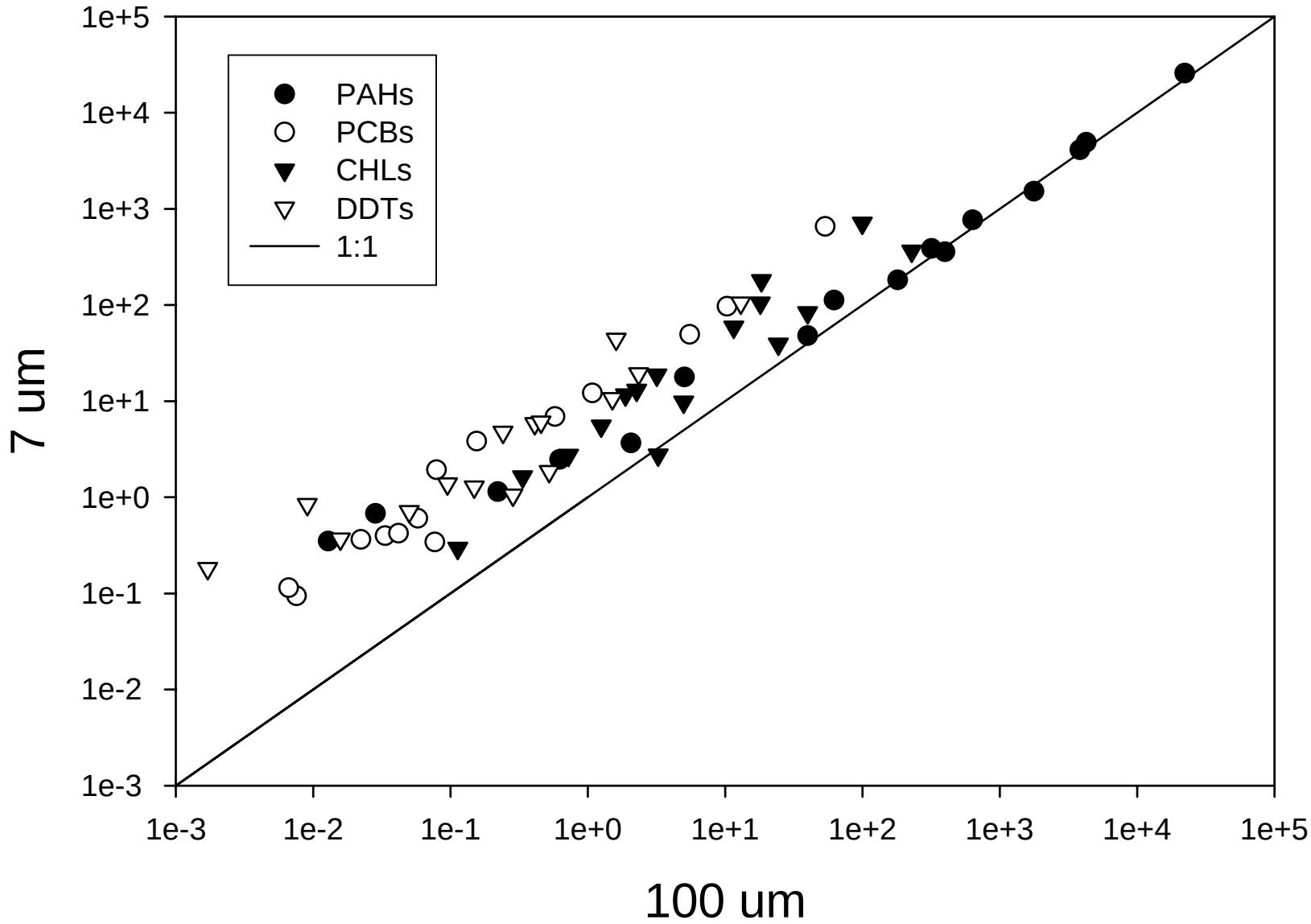
- Length: 1 cm
- PDMS coating:
- 7, 30 or 100 μm
- Reusable
- Reinjectable
- Comm avail.
- (Supelco)

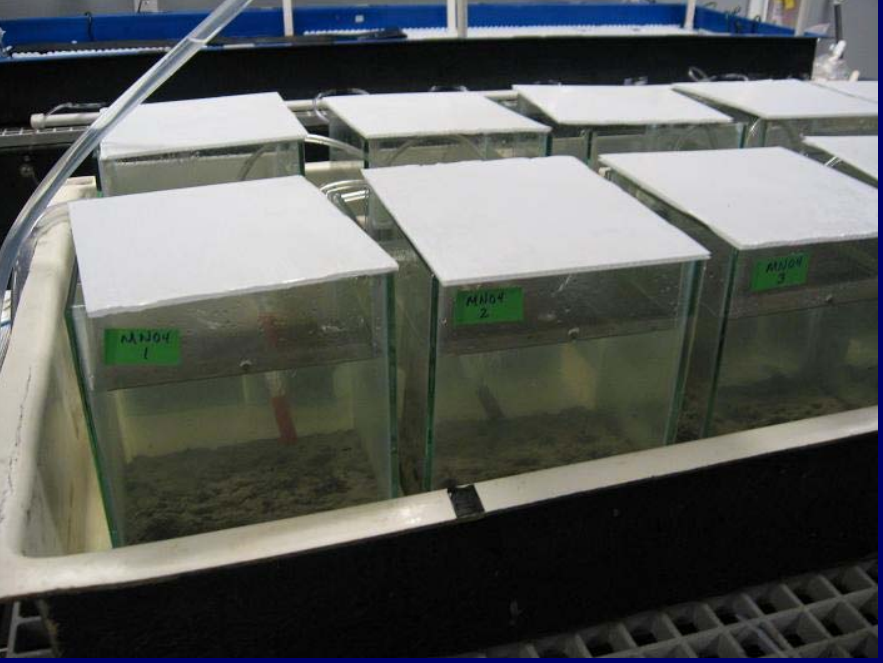
Model HOCs

	C_{sat} (μg/L)	log K_{ow}	log $K_{f,7}$	log $K_{f,100}$	$K_{f,7}$ / $K_{f,100}$	MDL_{100} (ng/L)
PHEN	1200	4.46	4.32	3.90	2.6	2.1
FLUA	260	5.16	4.69	4.26	2.7	1.5
BAP	1.5	6.13	6.06	5.82	1.7	0.16
PCB-52	15	5.84	5.66	5.52	1.4	0.04
PCB-153	0.95	6.92	6.68	6.45	1.7	0.02
PCB-180	0.37	7.36	6.76	6.54	1.7	0.02
HEPT EPOX	280	4.98	4.64	4.48	1.4	1.3
α-CHL	56	6.22	5.59	5.37	1.7	0.18
t-NON	32	6.35	5.94	5.68	1.8	0.09
p,p'-DDE	1.3	6.96	6.27	6.17	1.3	0.02
p,p'-DDD	160	6.22	6.04	6.11	0.9	0.02
p,p'-DDT	3.1	6.91	5.83	5.76	1.2	0.13


PCB 180
PCB 15
N_f (ng)
Extraction time (days)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
2.0
1.5
1.0
0.5
0.0
-0.5
25
20
15
10
5
0
-5
0
20
40
60
80
100
120

SPME CONCENTRATION (ng/L)





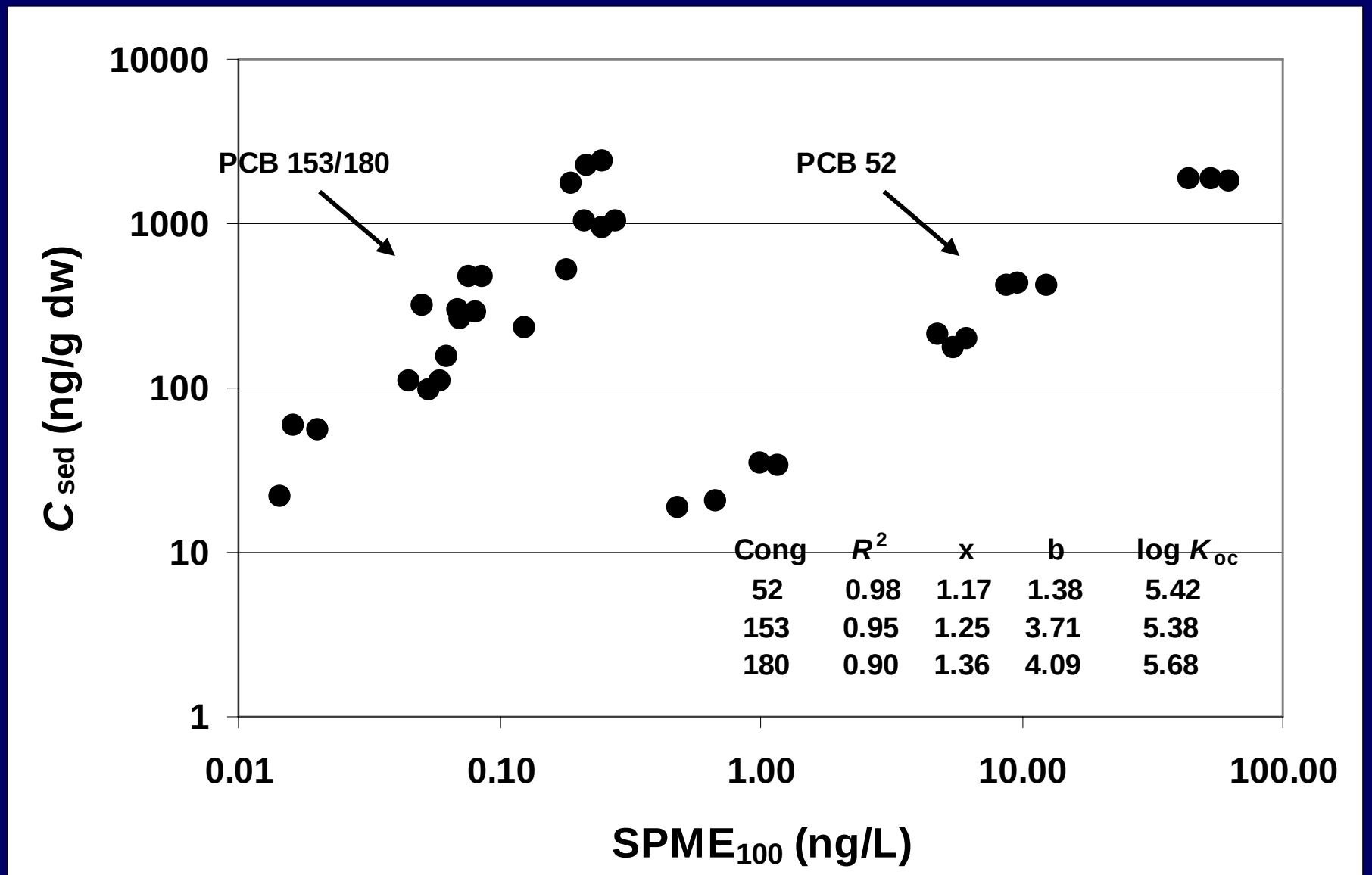
28-d "bioaccumulation test"

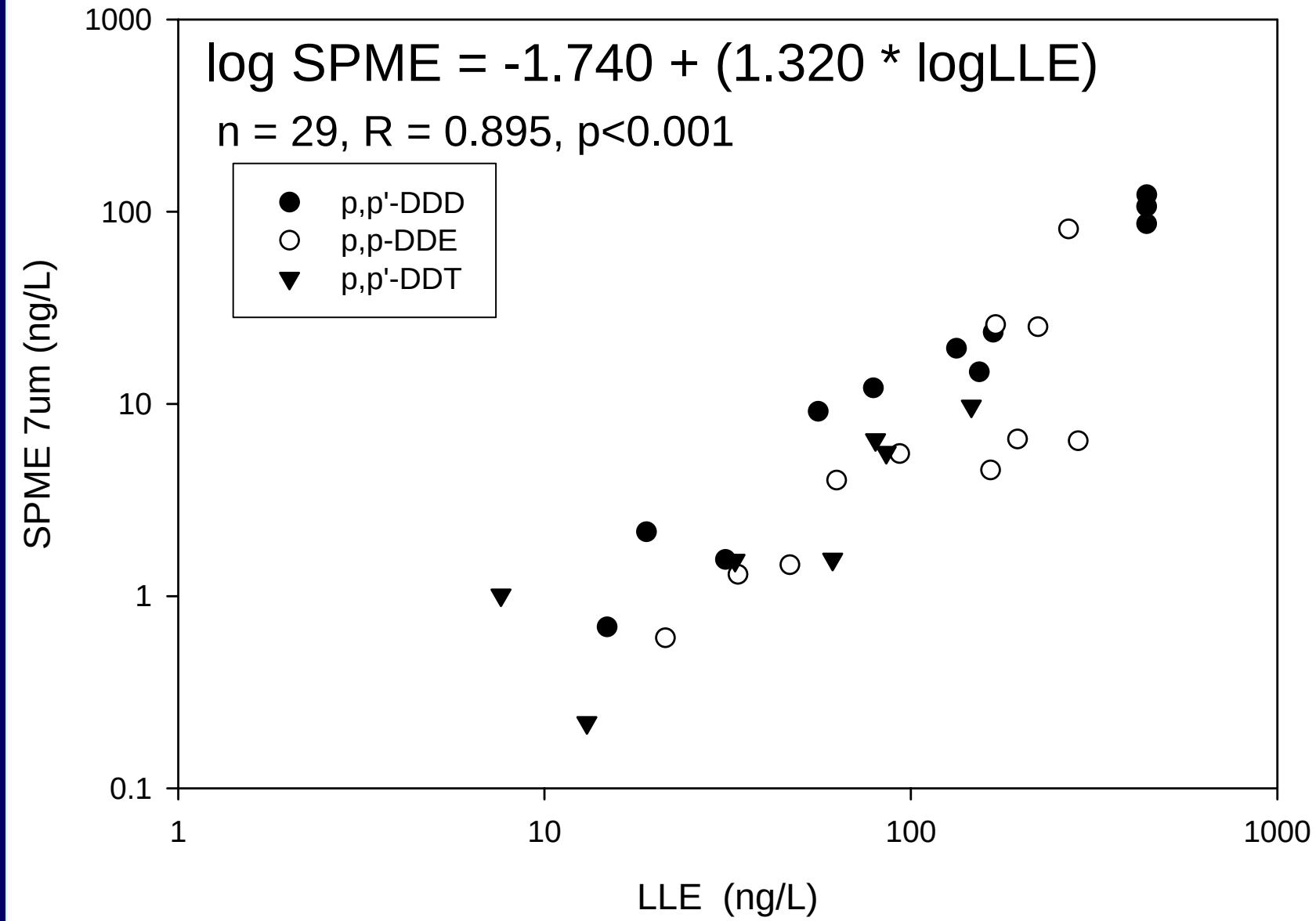
- **field-collected, spiked & aged estuarine sediments**
  - **70% fines; ~1% TOC**
  - **5 treatments + unspiked control (18 tanks)**
- ***Macoma nasuta & Nereis virens***
  - **5 ea per tank**
- **SPME samplers**
  - **7 and 100 um PDMS fibers**
  - **1 ea per tank**
- **Static renewal (50% every 3d)**
- **Compare C_b, $C_{pw,tot}$ and $C_{pw,\ spme}$ determined by GC-MS**

Survival of *Macoma nasuta & Nereis virens*
Spiked sediment experiment (2A)

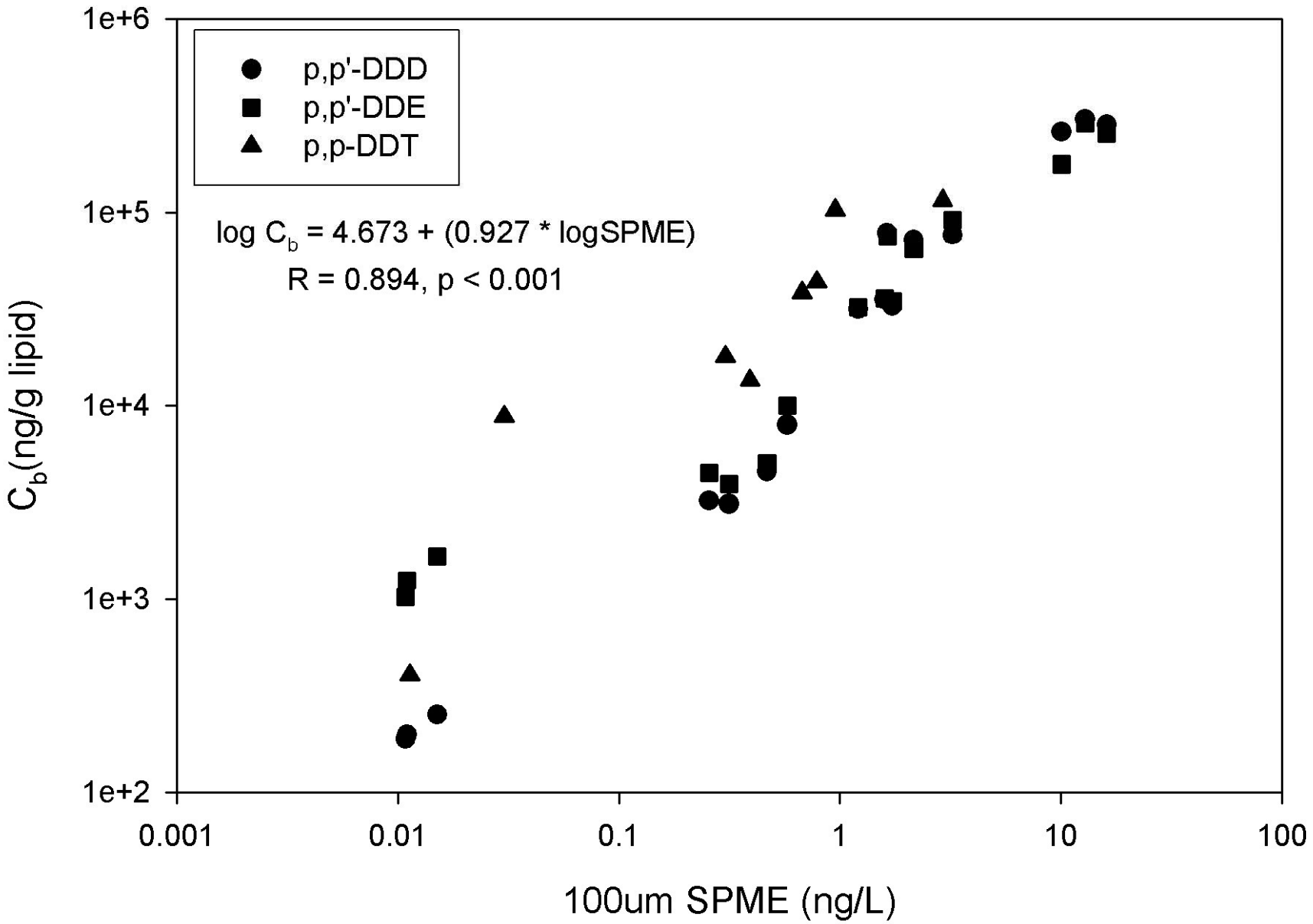
Treatment	% Survival	
	Worms	Clams
Control sediment	100	93
50 ppb mixed organic sediment	100	100
100 ppb mixed organic sediment	100	100
500 ppb mixed organic sediment	93	100
1000 ppb mixed organic sediment	100	100
5000 ppb mixed organic sediment	100	93

MATRIX	MDL (ppb)	BLANK	SUR REC (%)	RANGE (ppb)
sediment	~1	< 0.55	77 ± 13	<1 – 3820
SPME-7	0.028-0.004	<0.0004	n/a	<0.004 – 32.5
SPME-100	0.0021-0.00002	<0.00002	n/a	<0.00002-26.3
LLE	~0.01	<0.01	73 ± 8.6	<0.01-4.6
Macoma sp.	~5	≤ 6.7	90 ± 21	<5 – 26500
Nereis sp.	~5	≤ 6.7	81 ± 14	<5 – 34100


10000
1000
100
10
1
0.01
0.10
1.00
10.00
100.00
PCB 153/180
PCB 52
C_{sed} (ng/g dw)
$SPME_{100}$ (ng/L)
Cong R^2 x b log K_{oc}
52 0.98 1.17 1.38 5.42
153 0.95 1.25 3.71 5.38
180 0.90 1.36 4.09 5.68


log SPME = -1.740 + (1.320 * logLLE)
n = 29, R = 0.895, p<0.001
p,p'-DDD
p,p-DDE
p,p'-DDT
SPME 7um (ng/L)
LLE (ng/L)
1000
100
10
1
0.1
1
10
100
1000

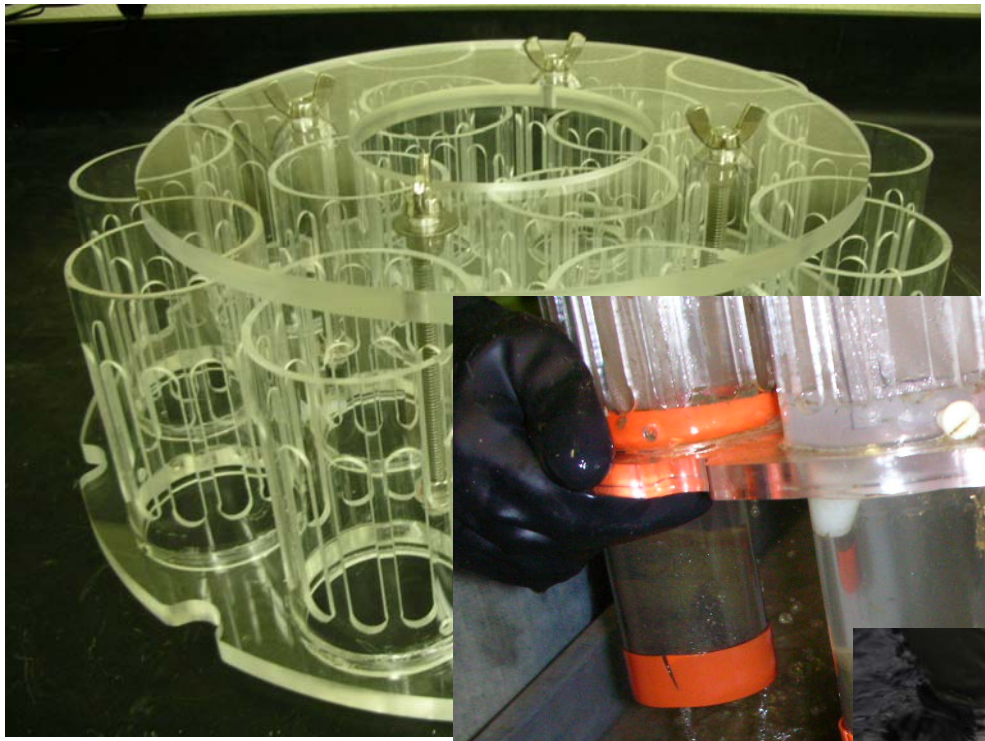
Macoma nasuta



Next steps……

Field-collected sediments for 28 day SPME-bioaccumulation experiment

Location	TOC (%)	BC (%)	DOC (mg/L)	%MORT	ΣPAH ng/g dw	ΣPCB ng/g dw	ΣDDT ng/g dw	ΣCHL ng/g dw
Dominguez Channel	4.9	0.48	5.5	92	6860	nd	126	31
Dominguez Channel	3.1	0.74	5.5	54	3800	nd	73	8
San Diego Bay	1.6	0.37	3.3	40	17800	1071	nd	nd
San Diego Bay	1.8	0.36	2.2	21	24500	363	nd	nd
LA/LB Harbor	1.0	0.19	3.0	15	1230	4	54	nd
San Pedro Shelf	0.2	0.03	5.9	na	na	na	na	na



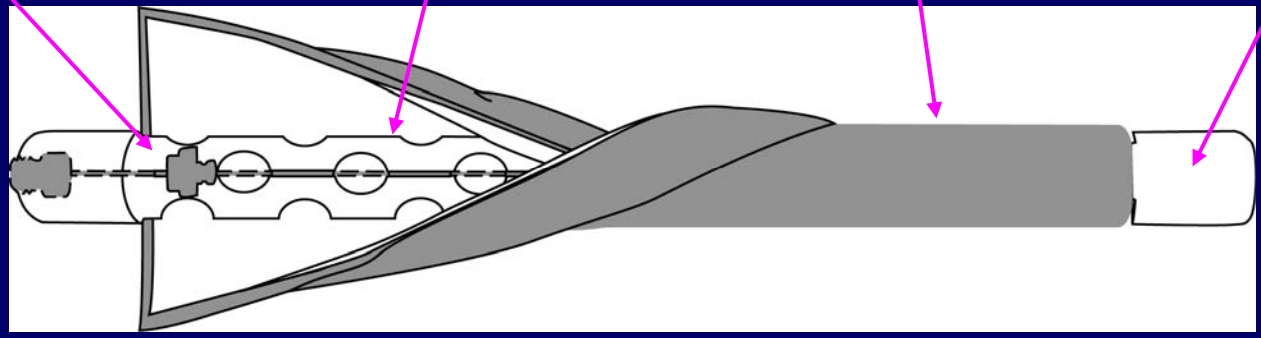
SPME fiber assy

(100 μm PDMS)

Housing (Cu)

GFF "wrap"

end cap



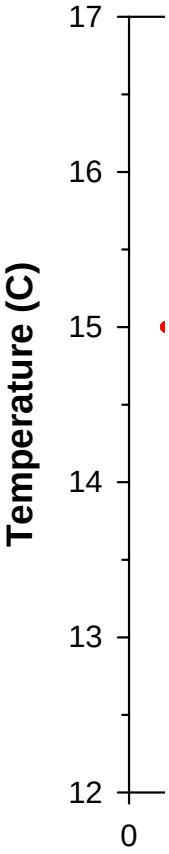
=??

LOE Responses (% Area)

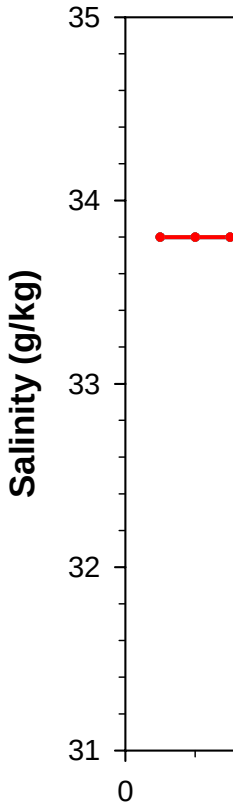
Region	Response	Benthos	Toxicity	Chemistry
North	Affected	51	20	7
SFB	Affected	62	86	46
South	Affected	24	29	44

Affected: Moderate or High response

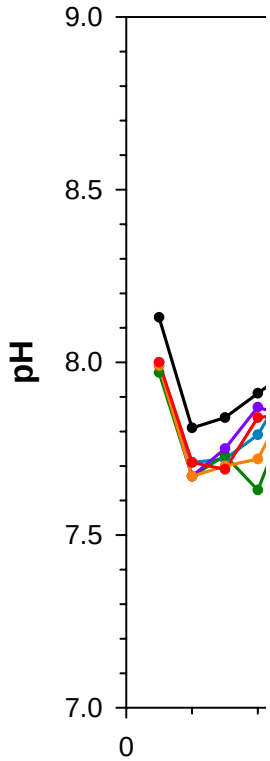
Temperature for Experiment MNO4
Macoma nasuta and *Nereis virens*



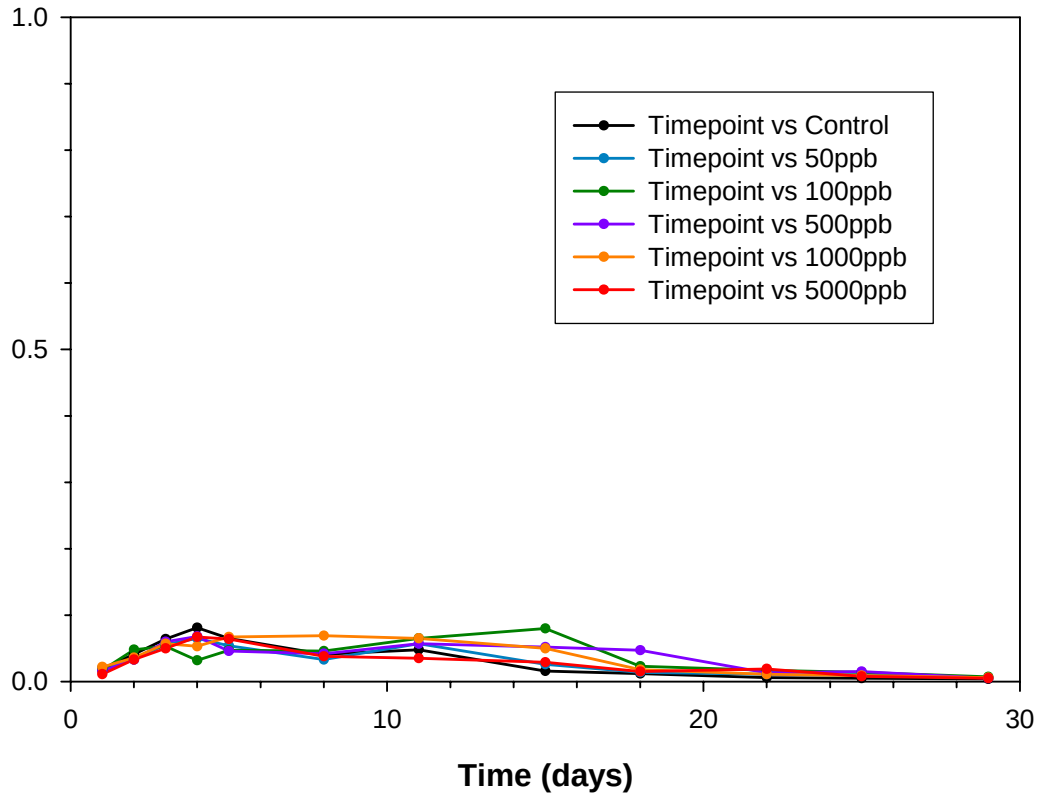
Salinity for Experiment MNO4
Macoma nausta and *Nereis virens*

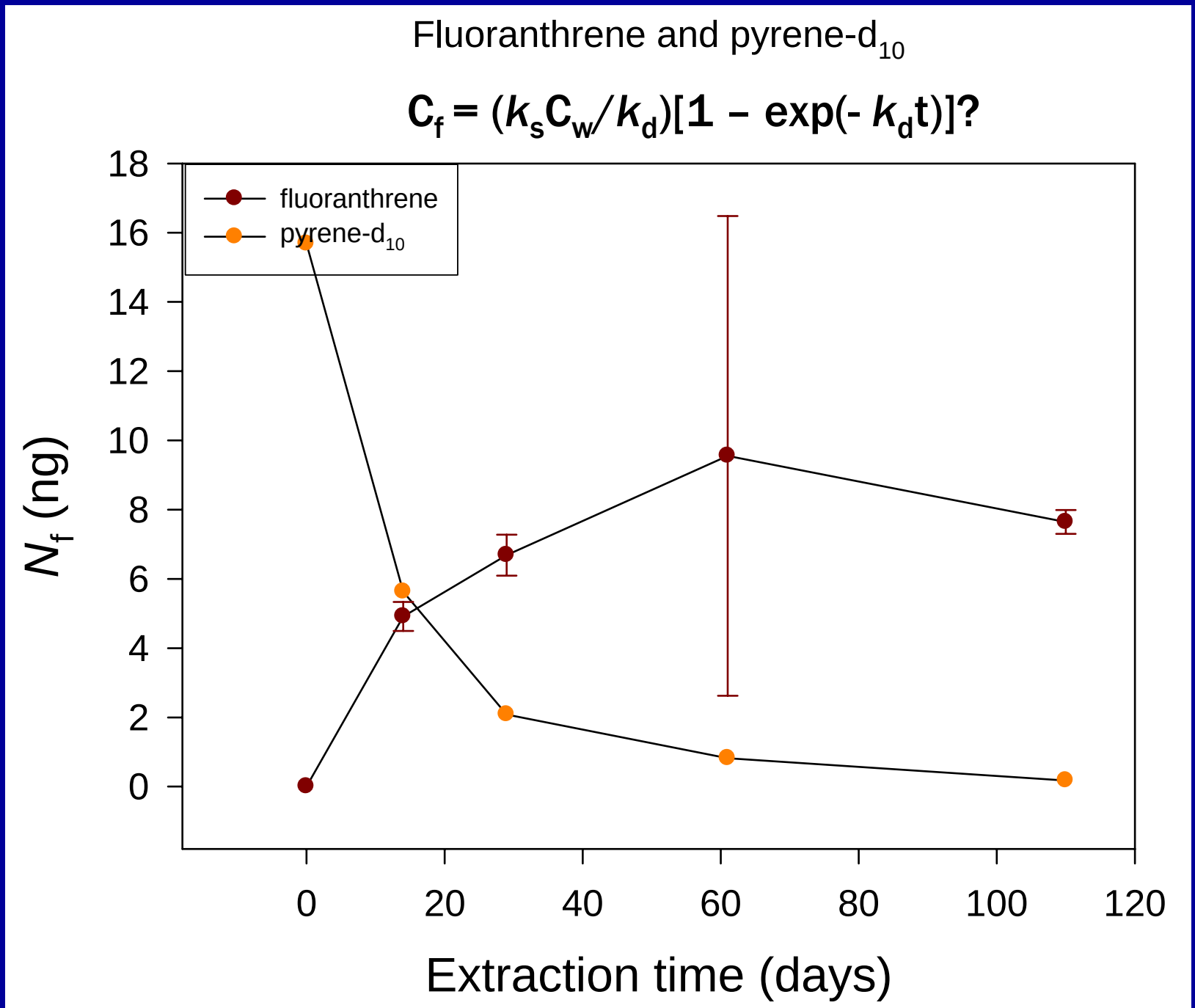


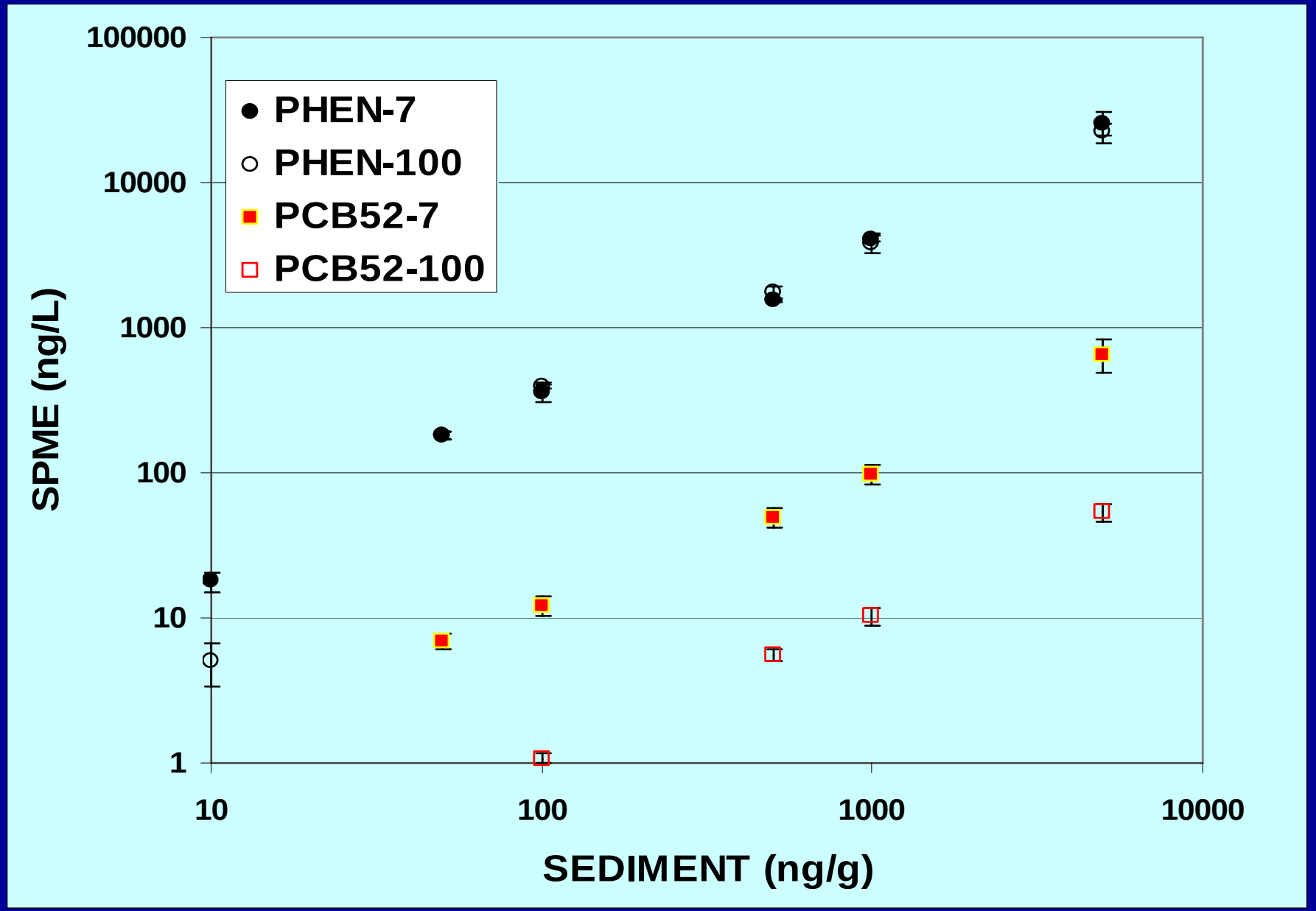
pH for Experiment MNO4
Macoma nasuta and *Nereis virens*



Un-ionized Ammonia for Experiment MNO4
Macoma nausta and *Neries virens*




Fluoranthrene and pyrene-d10
Cf = (ksCw/kd)[1 – exp(- kdt)]?
fluoranthrene
pyrene-d10
Nf (ng)
0
2
4
6
8
10
12
14
16
18
0
20
40
60
80
100
120
Extraction time (days)


PHEN-7
PHEN-100
PCB52-7
PCB52-100
SPME (ng/L)
100000
10000
1000
100
10
1
10
100
1000
10000
SEDIMENT (ng/g)