A SPME-based sampler for in situ assessment of sediment-associated organic contaminants: comparison with invertebrate body burdens

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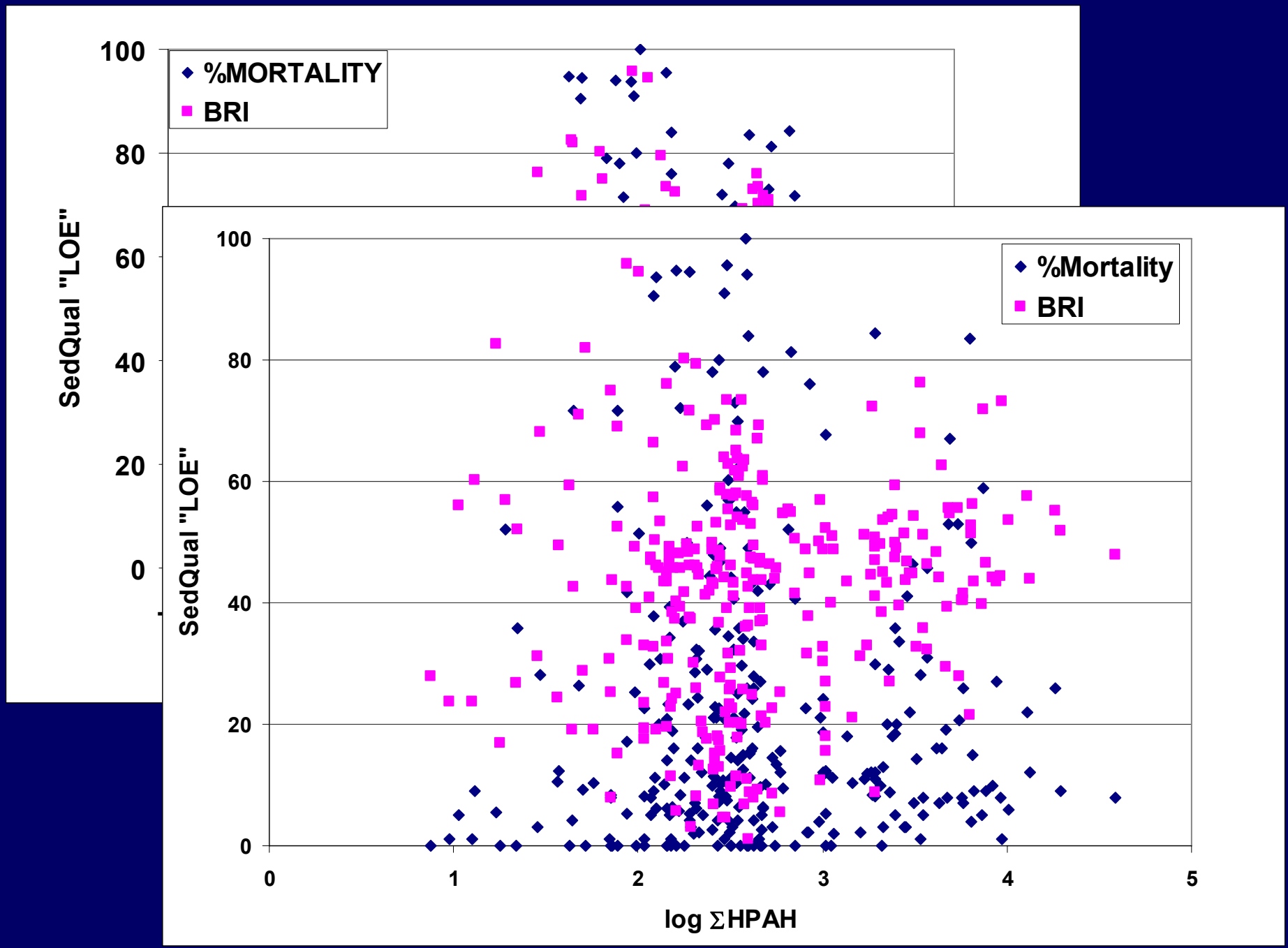
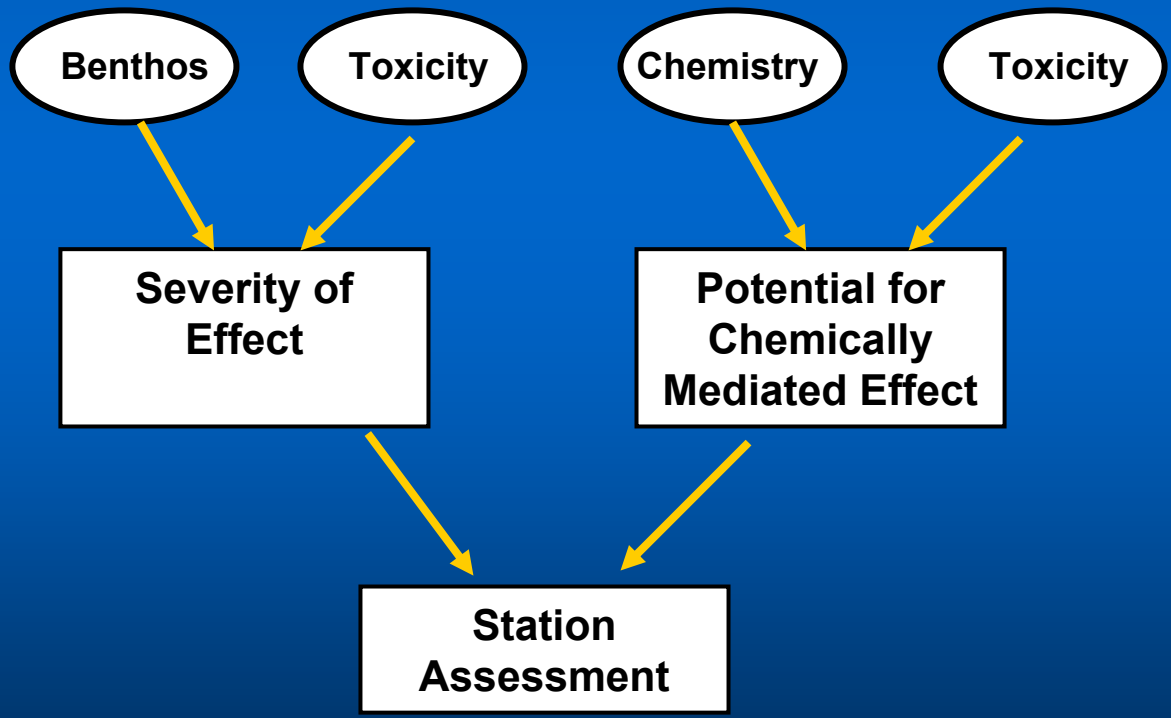
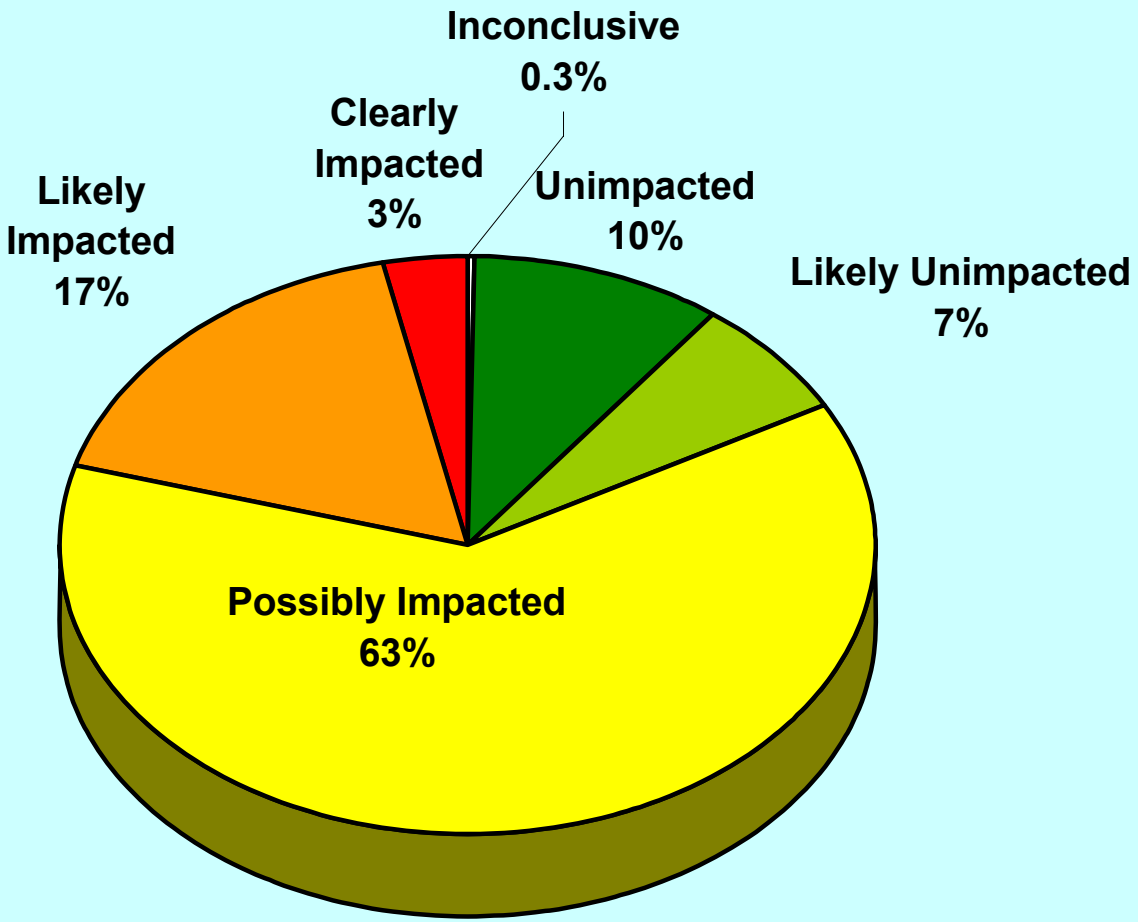

%MORTALITY
BRI
SedQual "LOE"
100
80
60
40
20
0
%Mortality
BRI
SedQual "LOE"
100
80
60
40
20
0
0
1
2
3
4
5
log ΣHPAH

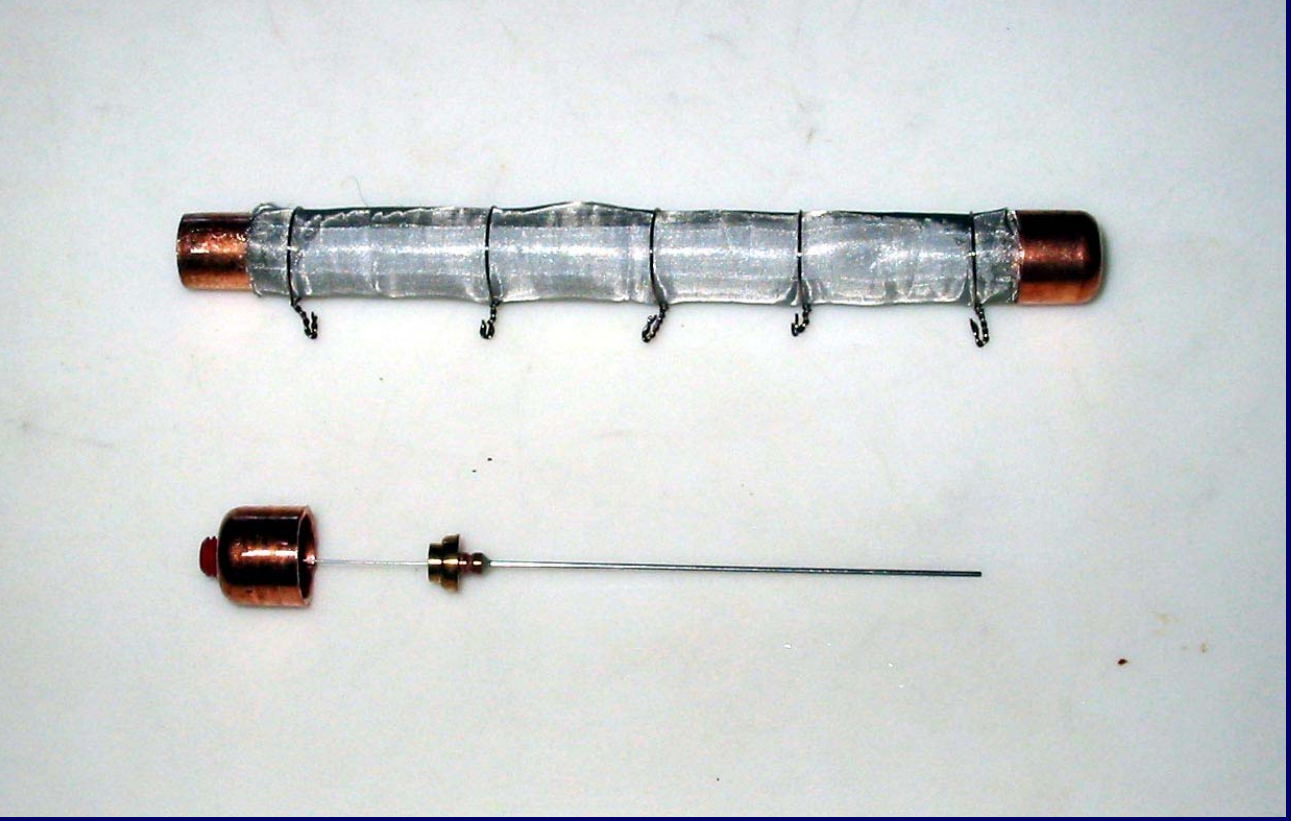
MLOE Conceptual Framework for CA SQO Development

Three lines of evidence (LOE) needed to assess direct effects – ***is bulk sediment chemistry good enough?***



Statewide (CA) Condition





SPME Fiber:

Length: 1 cm

PDMS coating:

7, 30 or 100 μm

Reusable, comm avail. (Supelco)

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

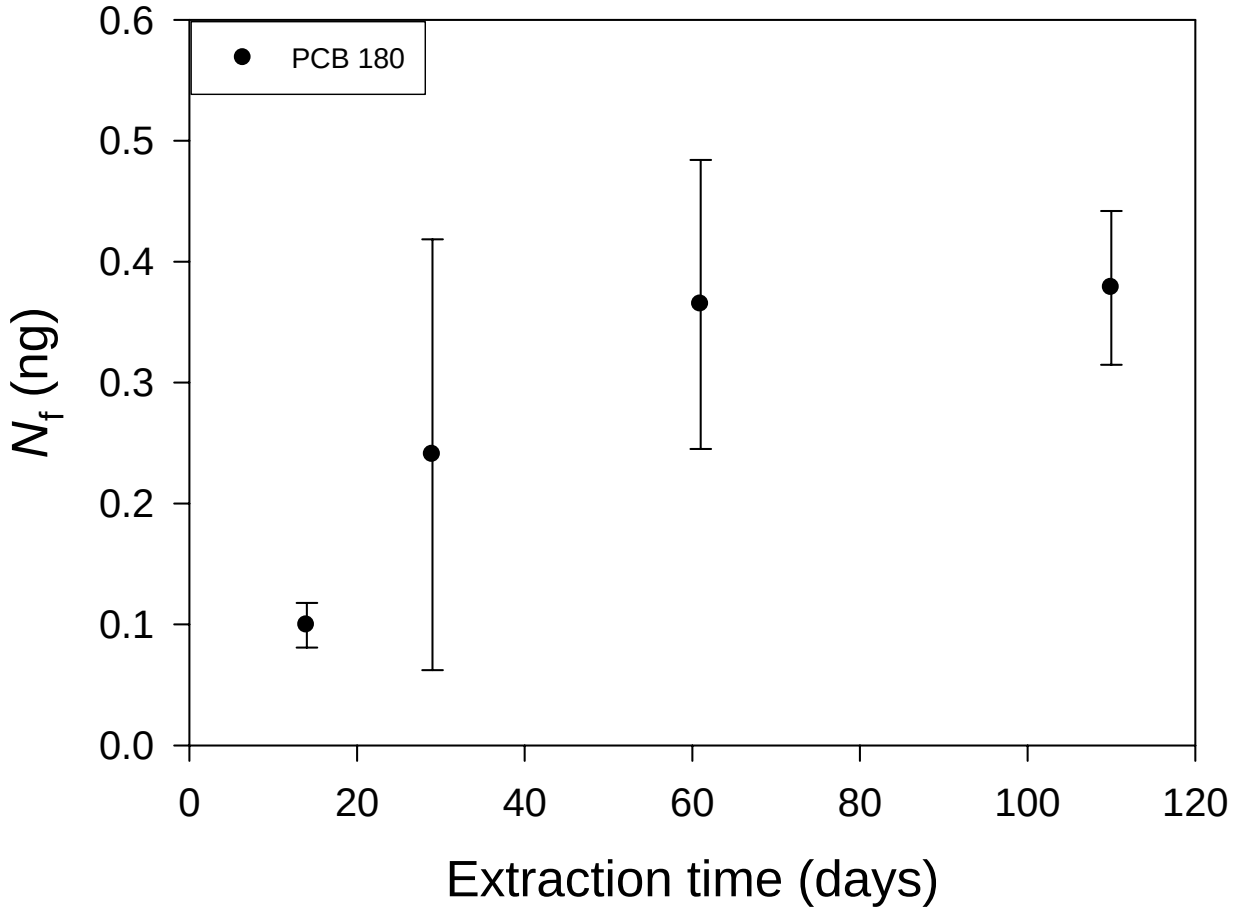
Maruya et al. *ET&C*

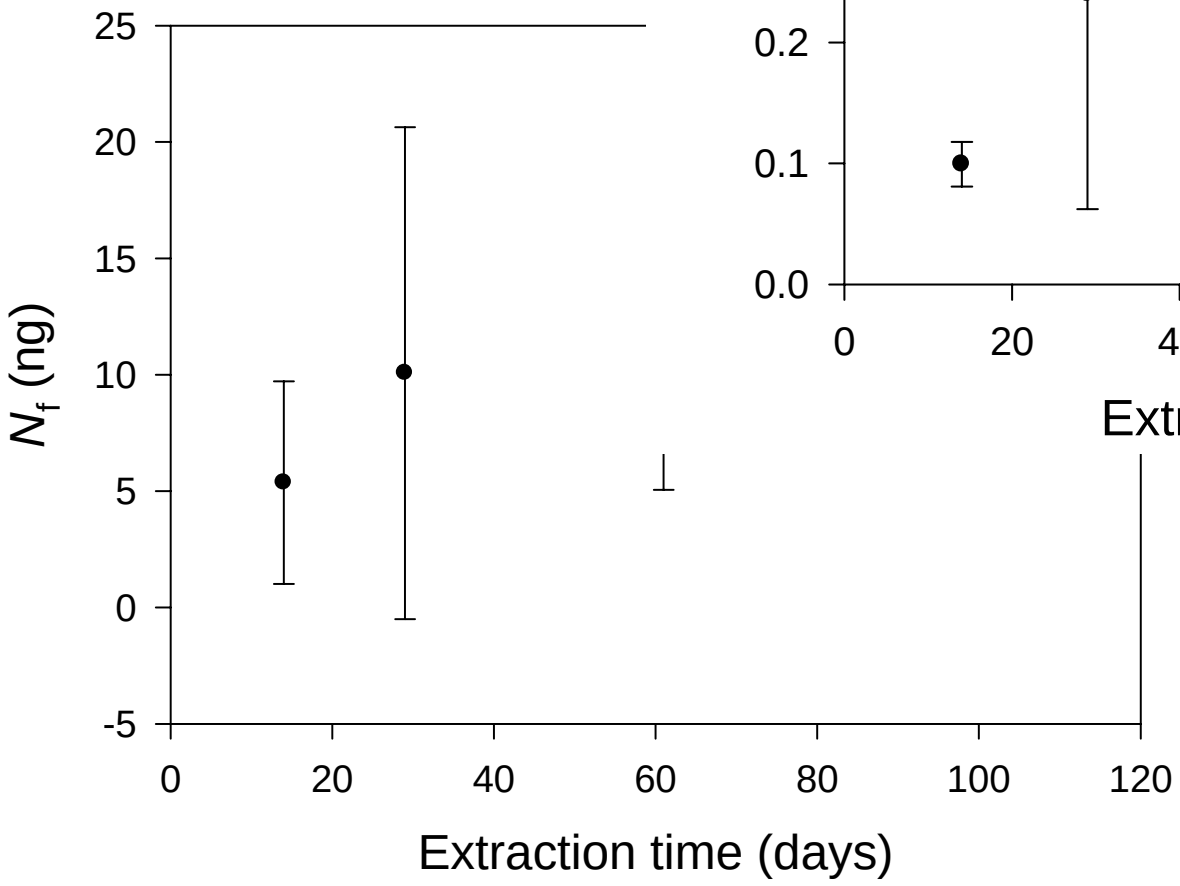
in press (avail online)

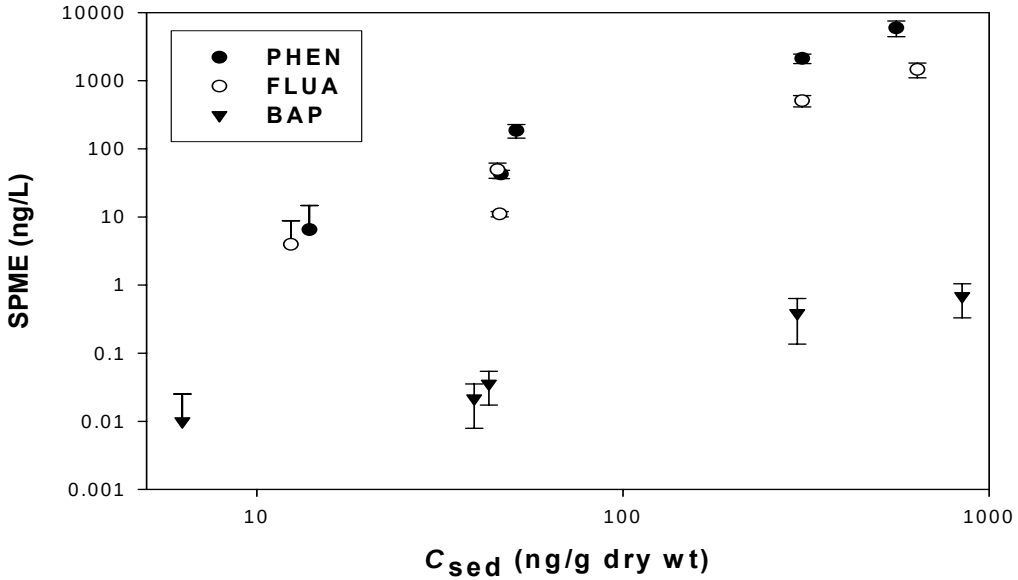
Model HOCs

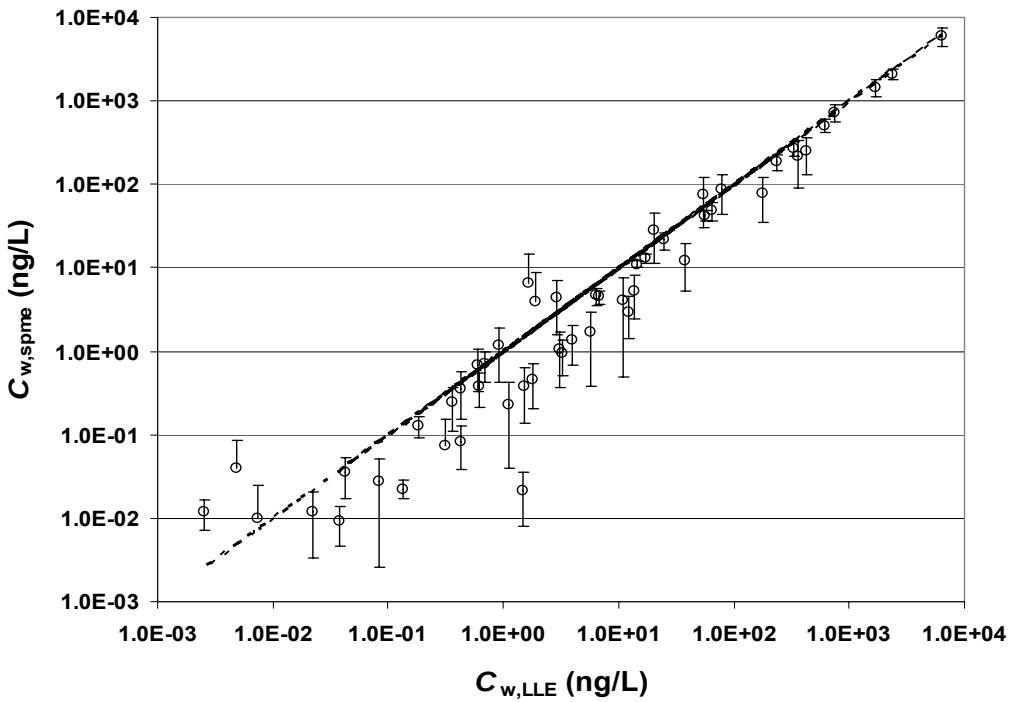
	C_{sat} (μg/L)	log K_{ow}	log $K_{f,7}$	log $K_{f,100}$	$K_{f,7}$ / $K_{f,100}$	MDL_{100} (ng/L)
PHEN	1200	4.46	4.32	3.90	2.6	2.1
FLUA	260	5.16	4.69	4.26	2.7	1.5
BAP	1.5	6.13	6.06	5.82	1.7	0.16
PCB-52	15	5.84	5.66	5.52	1.4	0.04
PCB-153	0.95	6.92	6.68	6.45	1.7	0.02
PCB-180	0.37	7.36	6.76	6.54	1.7	0.02
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


0.6
0.5
0.4
0.3
0.2
0.1
0.0
N_f (ng)
0
20
40
60
80
100
120
Extraction time (days)


25
20
15
10
5
0
-5
N_f (ng)
0
20
40
60
80
100
120
Extraction time (days)





60 d static test

Estuarine sediments

spiked 50-1000 ng/g

Aging: 60 d

V_{sed} = 400 mL

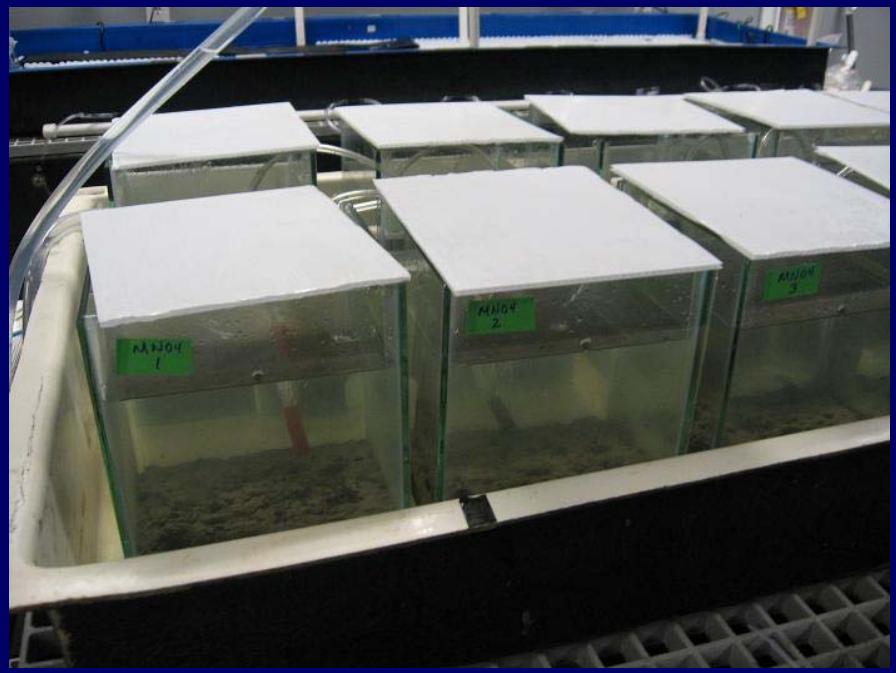
3 small, 1 lg samplers

Fibers, sediment, pw

by GC-MS

sed TOC, pw DOC

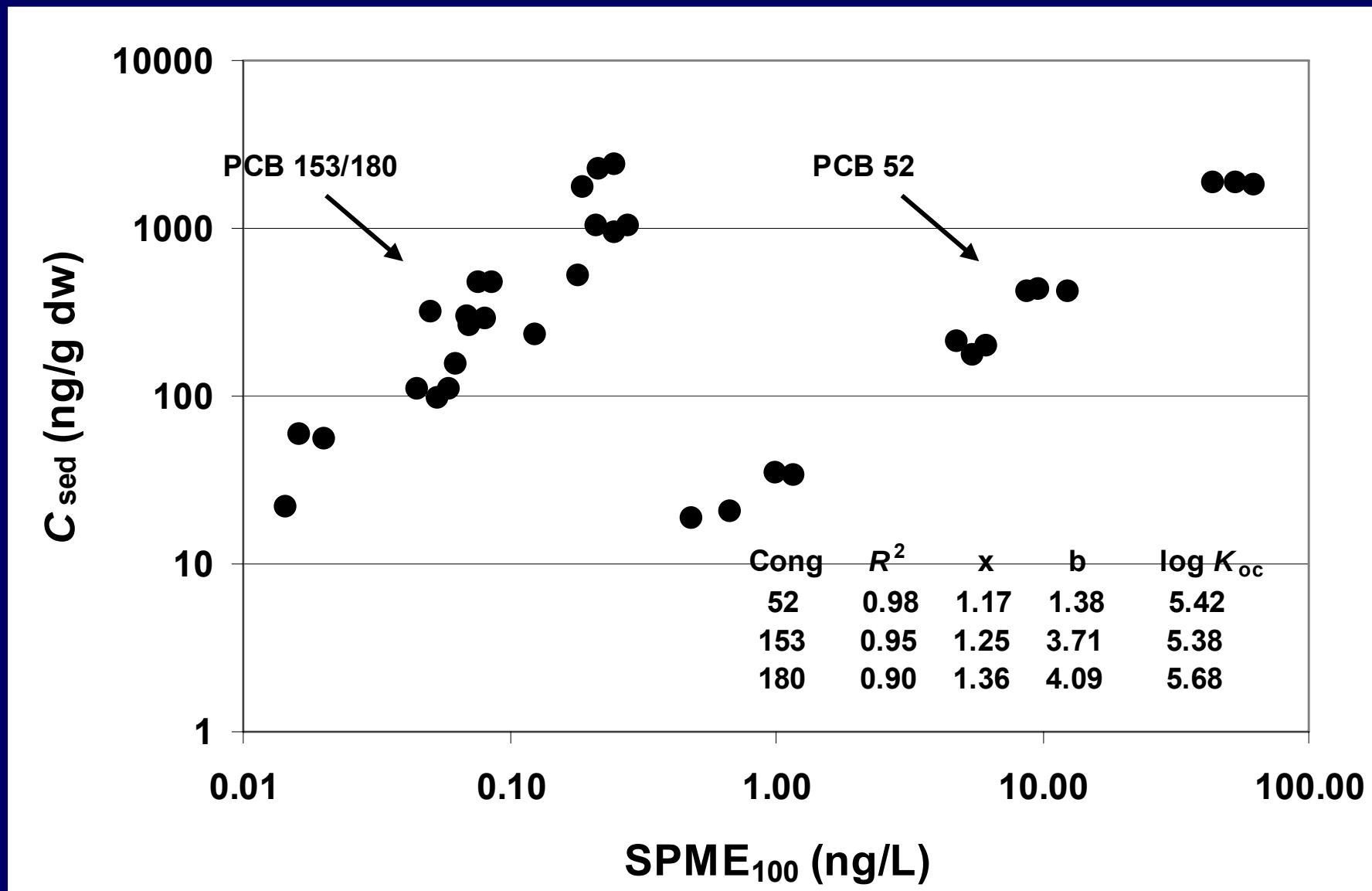
Centrifuged, filt. pw by liq-liq extraction (“LLE”)

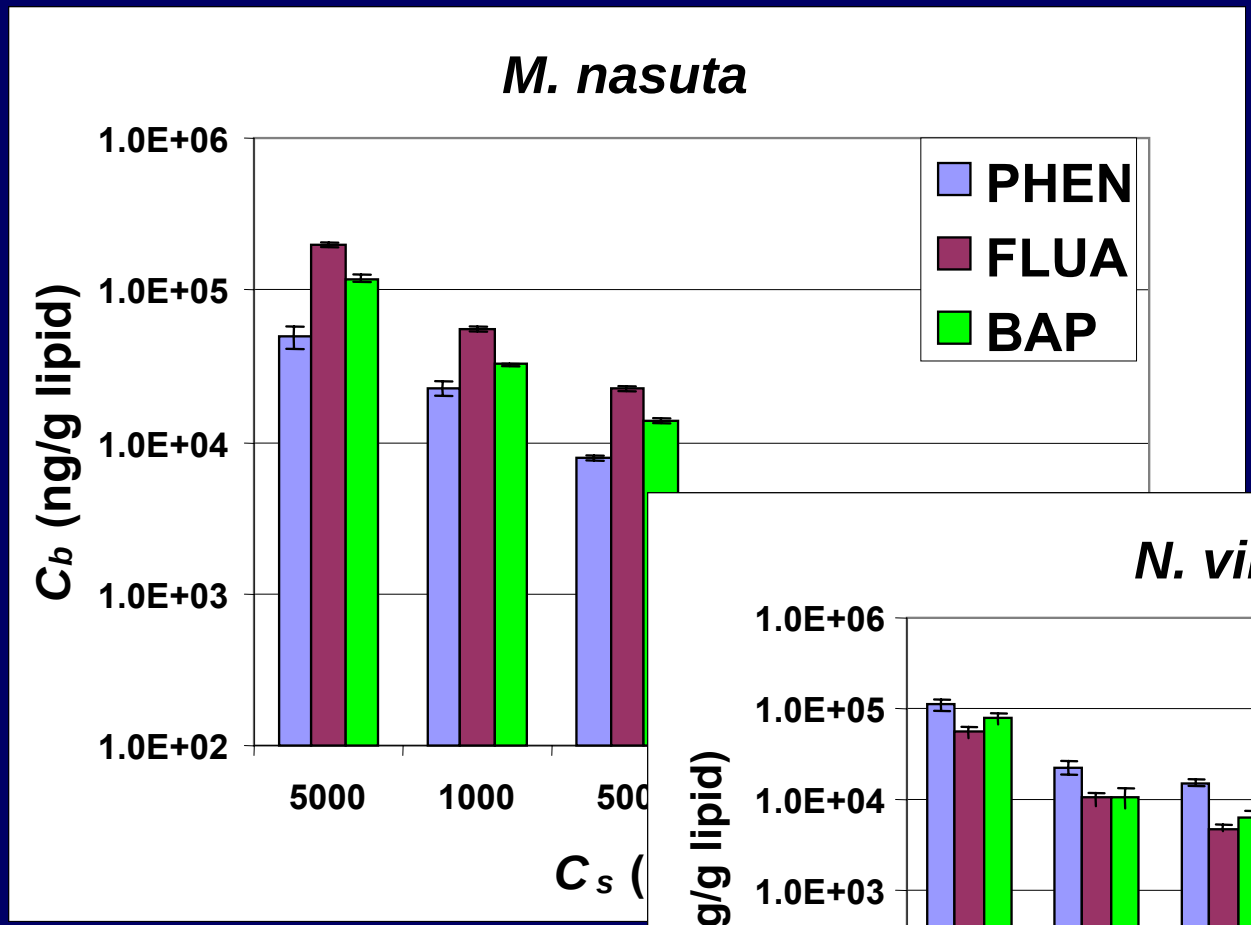


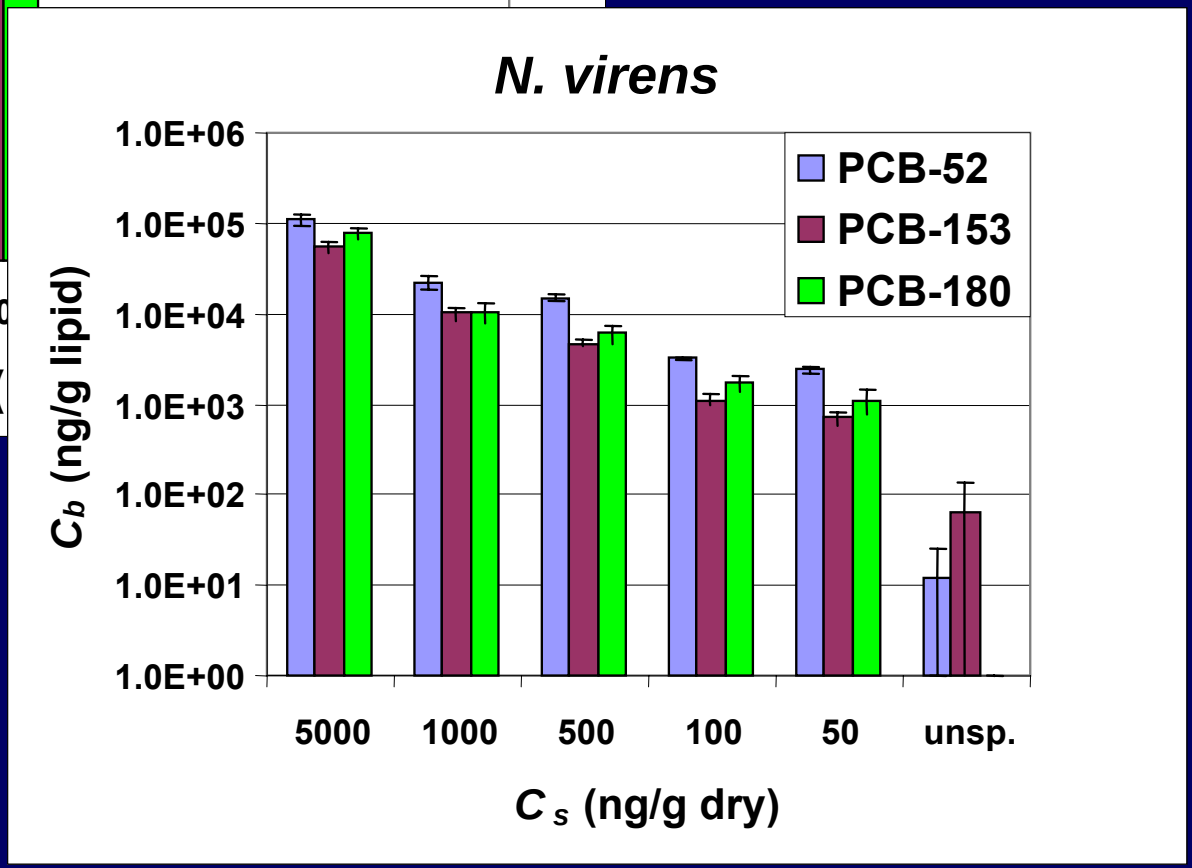
28-d Bioaccumulation Test

- Spiked/aged estuarine sediments
  - 70% fines; ~1% TOC
  - 5 treatments + unspiked control (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

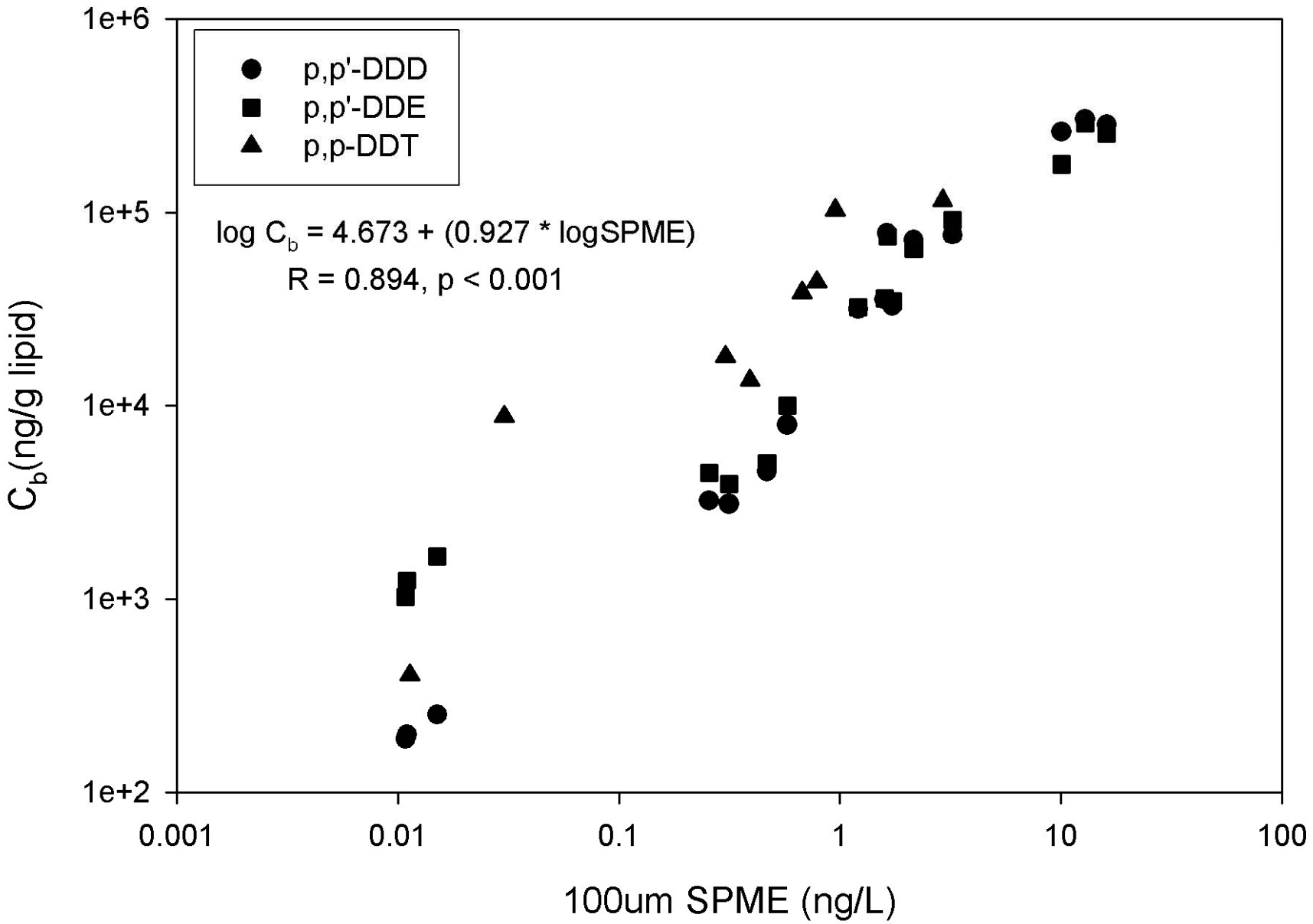
MATRIX	MDL (ppb)	BLANK	SUR REC (%)	RANGE (ppb)
sediment	~1	< 0.55	77 ± 13	<1 – 3820
SPME-7	0.028-0.004	<0.0004	n/a	<0.004 – 32.5
SPME-100	0.0021-0.00002	<0.00002	n/a	<0.00002-26.3
LLE	~0.01	<0.01	73 ± 8.6	<0.01-4.6
Macoma sp.	~5	≤ 6.7	90 ± 21	<5 – 26500
Nereis sp.	~5	≤ 6.7	81 ± 14	<5 – 34100

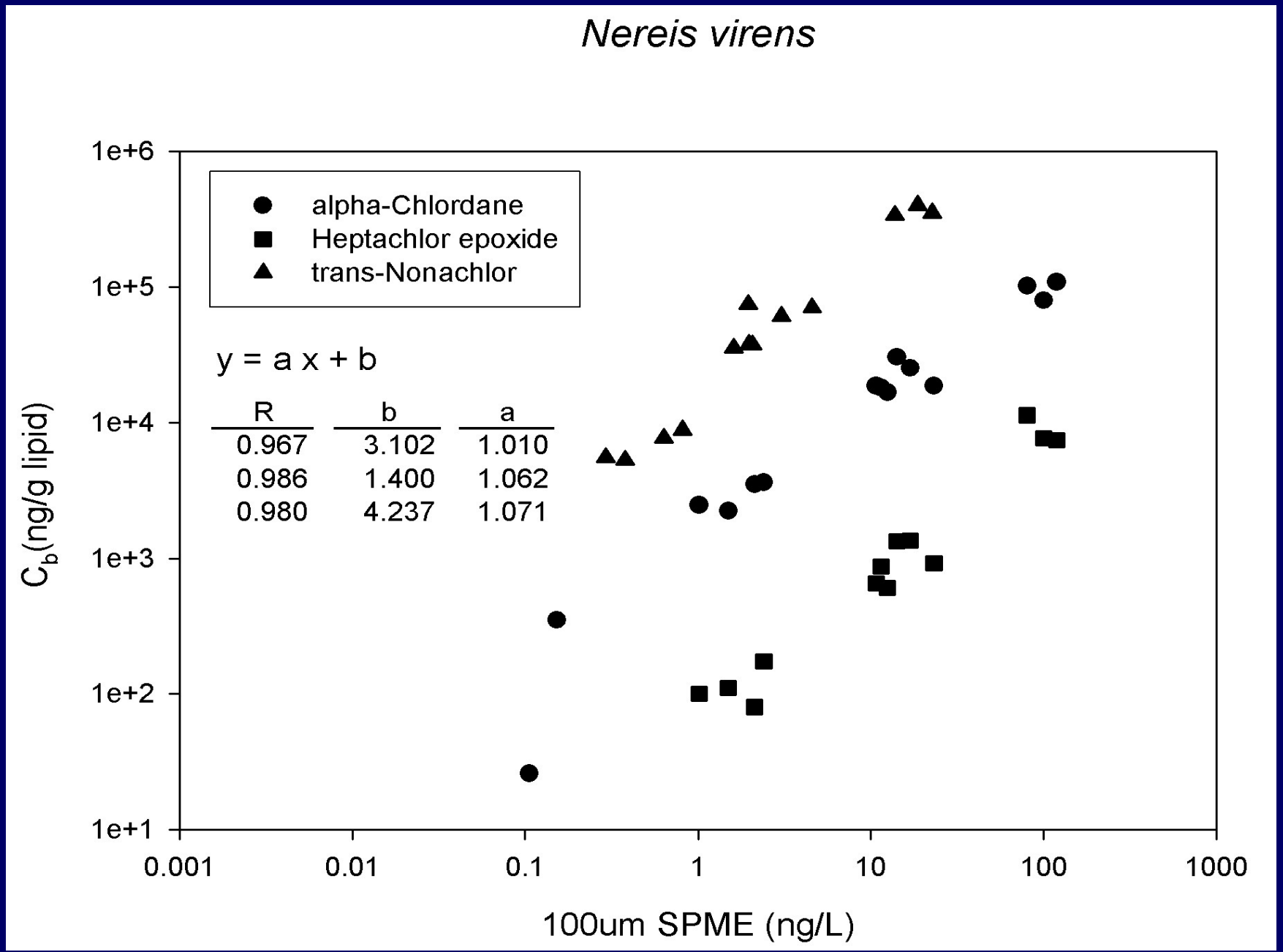

10000
1000
100
10
1
0.01
0.10
1.00
10.00
100.00
PCB 153/180
PCB 52
C_{sed} (ng/g dw)
$SPME_{100}$ (ng/L)
Cong R^2 x b log K_{oc}
52 0.98 1.17 1.38 5.42
153 0.95 1.25 3.71 5.38
180 0.90 1.36 4.09 5.68


M. nasuta
1.0E+06
1.0E+05
1.0E+04
1.0E+03
1.0E+02
C_b (ng/g lipid)
PHEN
FLUA
BAP
5000
1000
500
C_s (


N. virens
1.0E+06
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
1.0E+00
C_b (ng/g lipid)
PCB-52
PCB-153
PCB-180
5000
1000
500
100
50
unsp.
C_s (ng/g dry)

Macoma nasuta



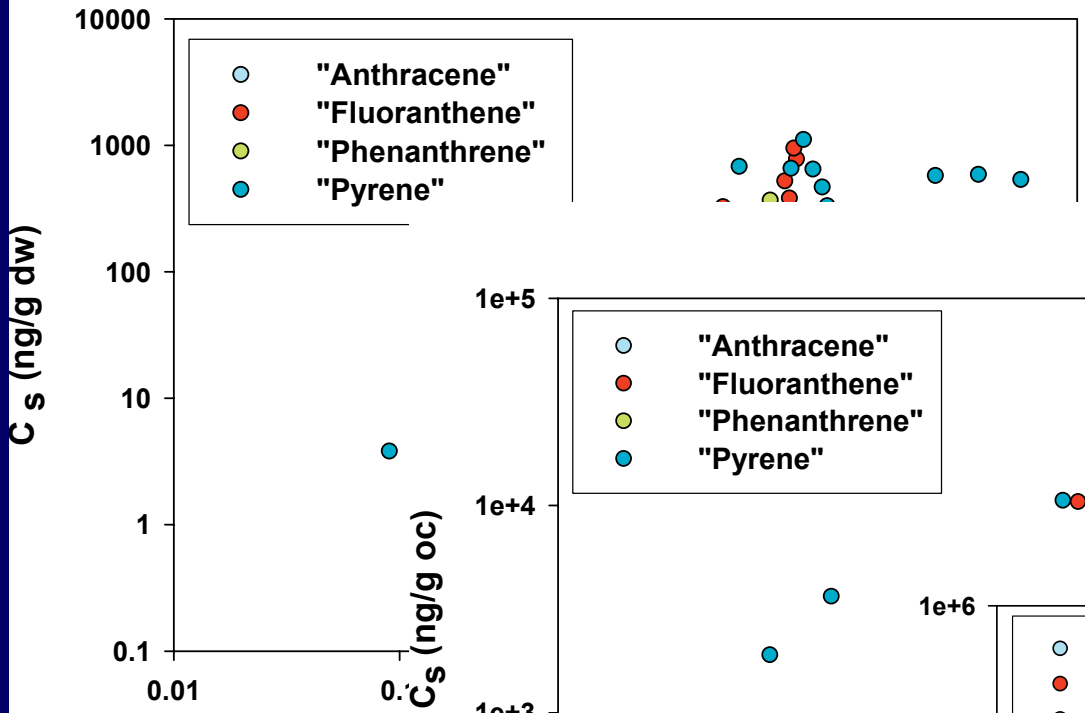

Nereis virens
alpha-Chlordane
Heptachlor epoxide
trans-Nonachlor
y = a x + b
R b a
0.967 3.102 1.010
0.986 1.400 1.062
0.980 4.237 1.071
1e+6
1e+5
1e+4
1e+3
1e+2
1e+1
C_b(ng/g lipid)
0.001
0.01
0.1
1
10
100
1000
100um SPME (ng/L)

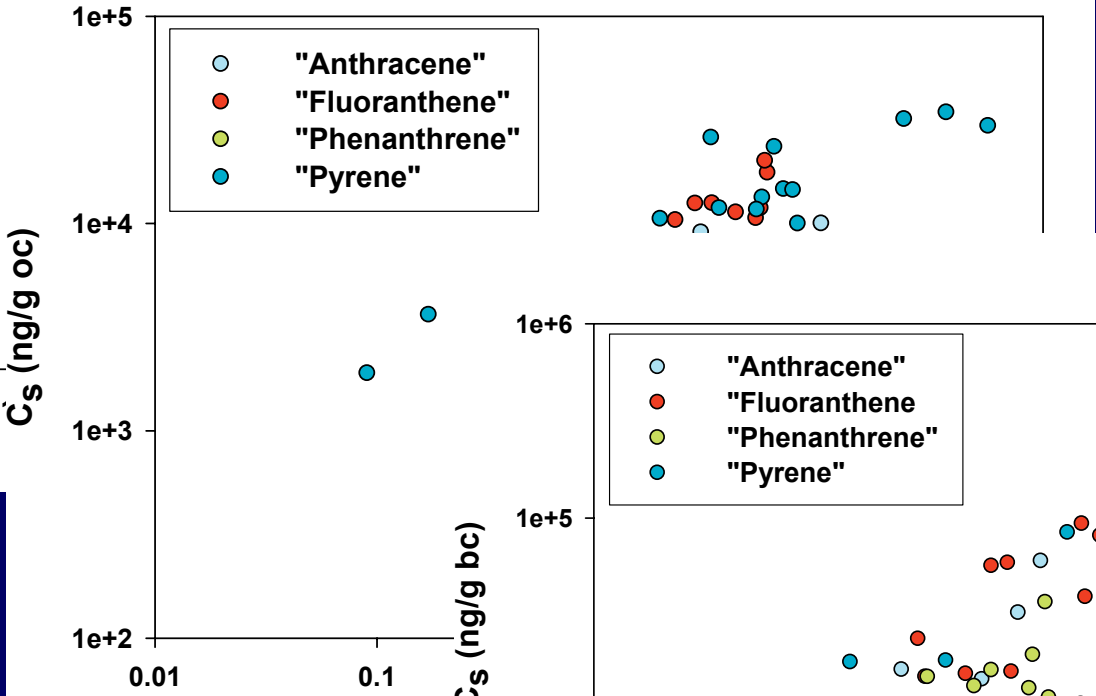
Pre-characterized, field sediments for 28 day co-exposure

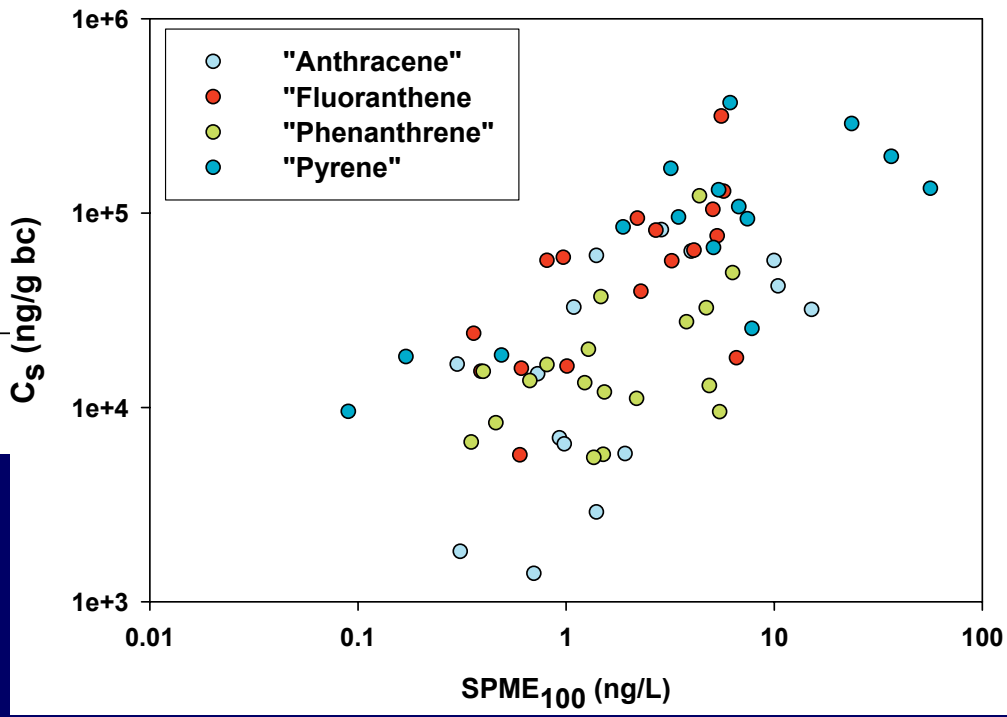
Location	TOC (%)	BC (%)	%MORT	ΣPAH	ΣPCB	ΣDDT	ΣCHL
Dominguez Ch.	4.9	0.48	92	6300	12	120	<10
Dominguez Ch.	3.1	0.74	54	4400	23	84	24
San Diego Bay	1.6	0.37	40	5800	54	4.8	<10
San Diego Bay	1.8	0.36	21	7200	130	4.1	<10
LA/LB Harbor	1.0	0.19	15	390	0.92	51	<10
San Pedro Shelf	0.2	0.03	na	26	<4.7	2.5	<10

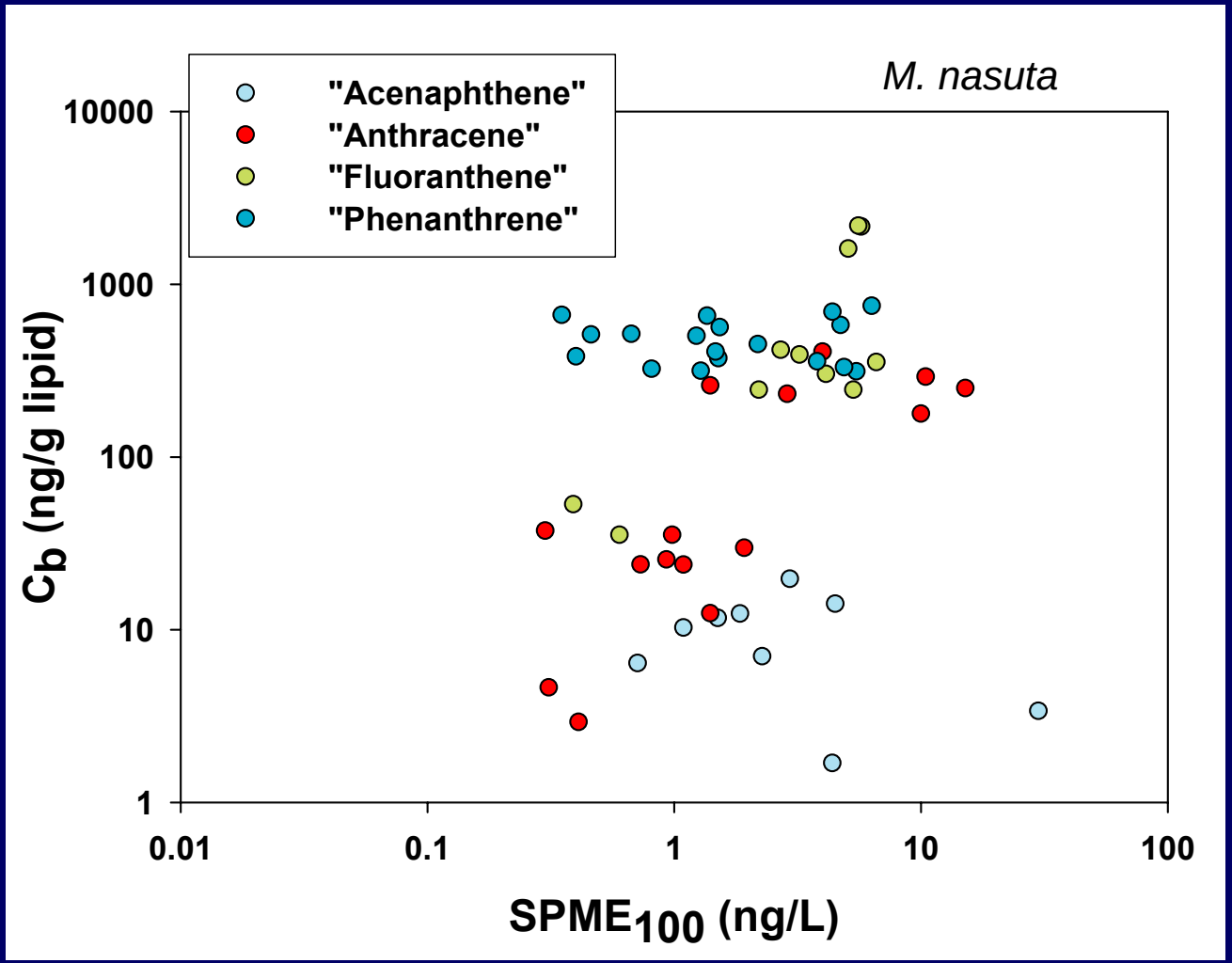
Units are ng/g
BC = black carbon
ΣCHL = total chlordane

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

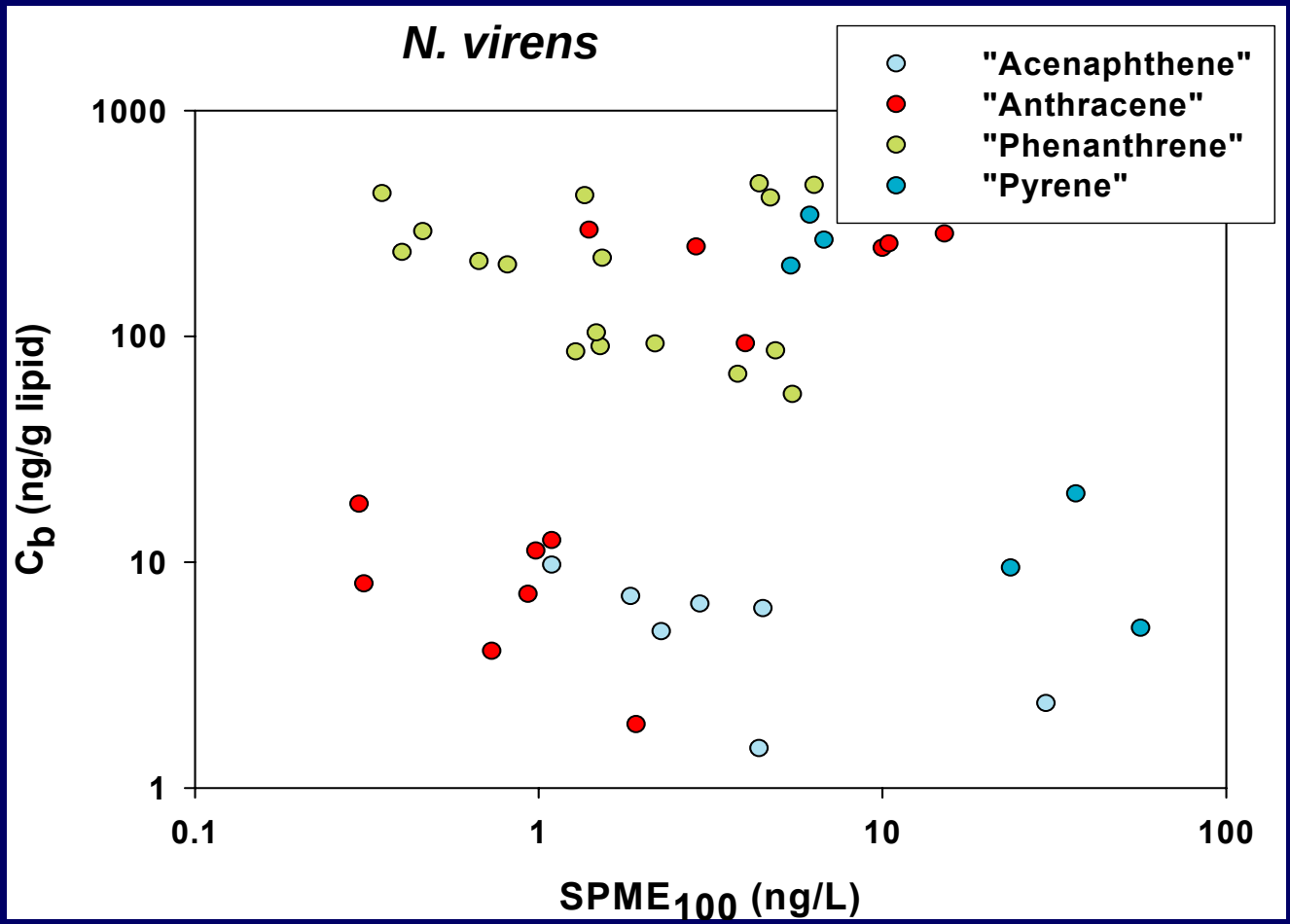

"Anthracene"
"Fluoranthene"
"Phenanthrene"
"Pyrene"
10000
1000
100
10
1
0.1
0.01
C s (ng/g dw)


"Anthracene"
"Fluoranthene"
"Phenanthrene"
"Pyrene"
1e+5
1e+4
1e+3
1e+2
0.01
0.1
Cs (ng/g oc)

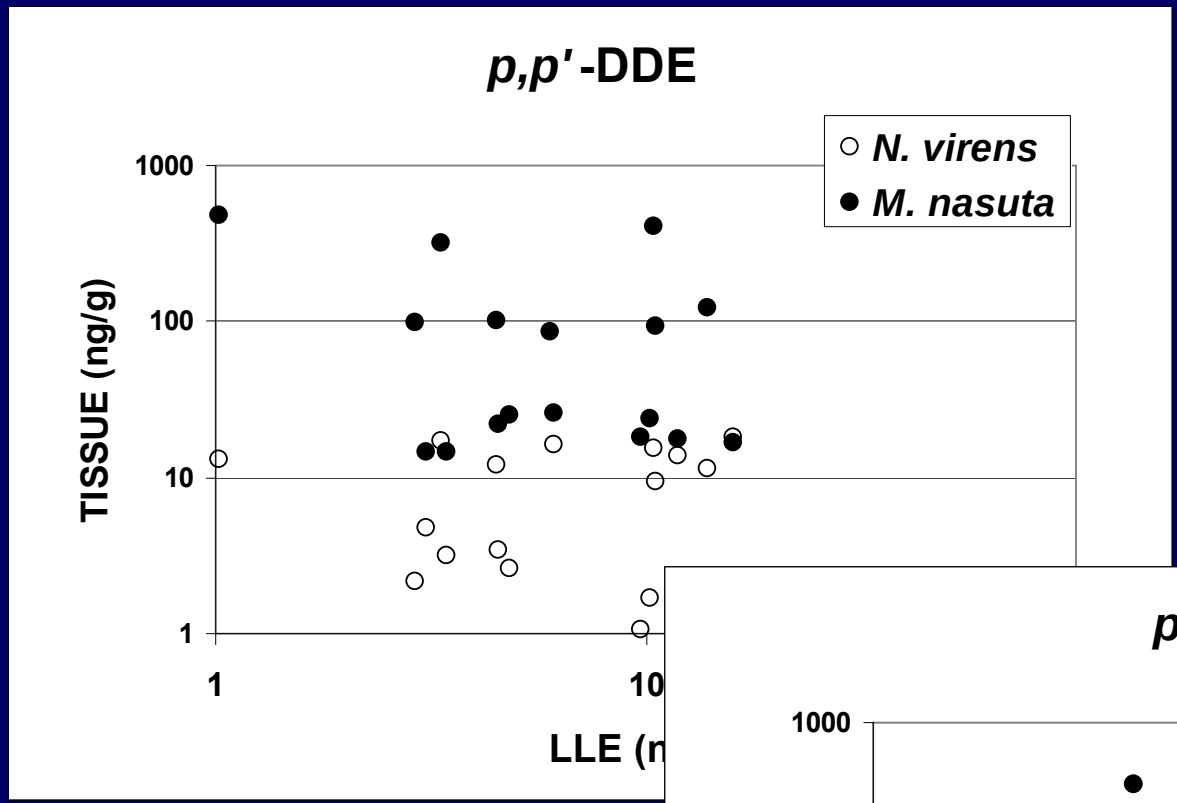

"Anthracene"
"Fluoranthene"
"Phenanthrene"
"Pyrene"
1e+6
1e+5
1e+4
1e+3
0.01
0.1
1
10
100
Cs (ng/g bc)
SPME100 (ng/L)

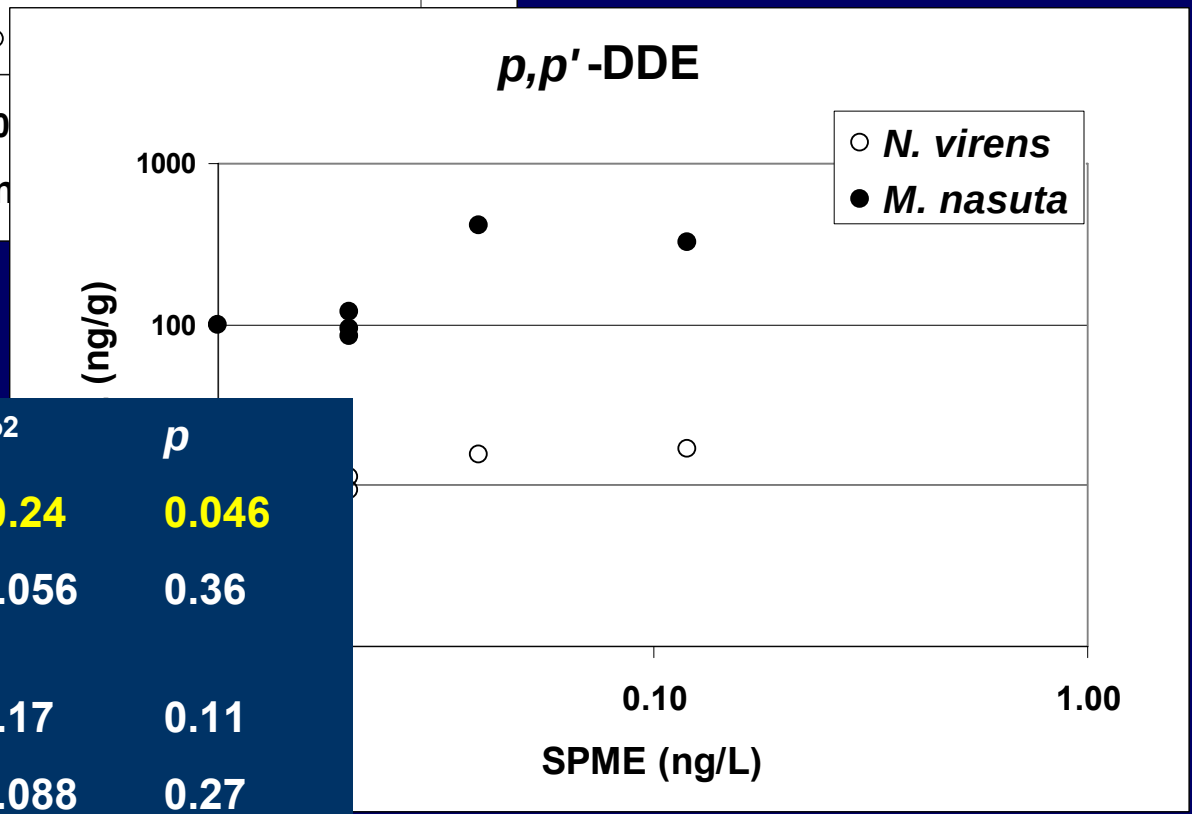


	n	R^2	b	a	P
Acenaphthene	9	0.169	1.02	-0.292	0.272
Anthracene	12	0.605	2.00	0.883	0.003*
Fluoranthene	11	0.682	2.03	1.174	0.002*
Phenanthrene	18	1.05E-05	2.67	-0.001	0.990
all PAH	50	0.0206	2.15	0.248	0.320



	n	R2	b	a	P
Acenaphthene	7	0.45	0.91	-0.42	0.098
Anthracene	13	0.50	1.27	1.03	0.007*
Phenanthrene	17	0.050	2.30	-0.18	0.39
Pyrene	7	0.23	2.06	-0.38	0.27
ΣPAH	44	0.0068	1.76	-0.11	0.59





Species (PV)	*n*	R^2	*p*
M. nasuta (SPME)	17	0.24	0.046
” (LLE)	17	0.056	0.36
N. virens (SPME)	16	0.17	0.11
“ (LLE)	16	0.088	0.27

Related Work

- Ex situ
  - ASTM, EPA methods (Hawthorne et al.)
- Direct exposure (“matrix”)
    - sediments (Mayer/Hermens et al.)
    - soils (Lydy/Landrum et al.)
- Protected
  - sediments in situ (UT/Reible et al.)
- Other technologies
  - Silicone
  - PEDs

Next steps……

- Increase sensitivity
  - disposables/bundles
  - ECNI-MS
- Strengthen linkage to effects
  - multi-endpoint field studies
- In situ deployment schemes
- Parameterize for decision making
  - Site-specific bioavailability assessment
  - SQO frameworks