

Organic contaminants of emerging concern in sediments & flatfish near marine outfalls

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Southern California Study Sites

- Outfall
- Reference

full 2^o
highest POPs

LA

City of Los Angeles

County of LA

full 2^o
high POPs

PV

1^o/2^o
mod POPs

OC

Orange County

low POPs

DP

Dana Point

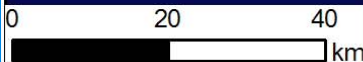
Outfall sediment extracts tested for
estrogenic activity (Schlenk et al. 2005)

- o 16-82% fines; 0.43 – 2.5% TOC
- o $E1, E2 \leq 0.6 \text{ ng/g dw}$
- o 4-nonylphenol: 120-3200 ng/g dw

San Diego

adv 1^o
mod/low POPs

SD



Questions

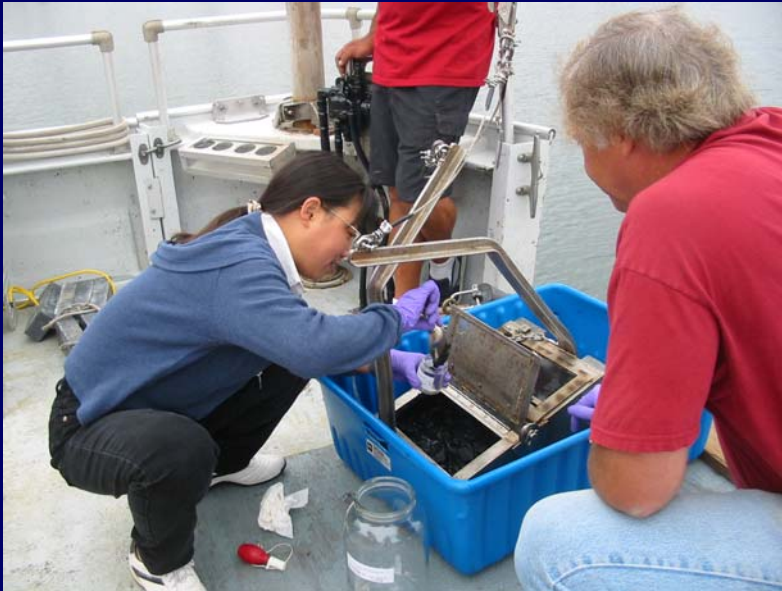
What CECs are detected most frequently?

What are the concentrations of the most frequently detected CECs?

Do levels vary among large POTW outfalls?

Are they lower at the study reference site?

Are fish tissue levels gender specific?



Sampling strategy

- ***Joint collection effort***
- ***Spring-Summer 2006***
- ***5 sediment samples***
 - surface (0-2 cm)
 - 3 grabs per station
- ***10 fish liver samples***
 - hornyhead turbot (*Pleuronichthys verticalis*)
 - adult F & M
 - 15-35 livers per gender per station



Category	Class	No. Target Analytes	
		Sediment	Tissue
CUP	OP pesticides	4	4
CUP	pyrethroids	12	12
CUP	urea herbicides	5	5
HOR	hormones	3	1*
ICC	PBDEs	5	5
ICC	phenolics	5	1**
ICC	phthalates	7	n/a
LP	butyltins	4	n/a
LP	OC pesticides	20	20
LP	PCBs	28	28
PPCP		5	5
	<i>Total</i>	98	79

* 17a-ethinylestradiol (EE2); ** 4-nonylphenol (4-NP)

Target PPCPs

	MW	$\log K_{ow}$	$t_{1/2}$	NOEC (ug/L)
carbamazepine	236	2.8	1-3d	>100
diazepam (Valium)	285	3.0	1-4d	>1000
oxybenzone	228	3.4	?	10-100
simvastatin (Zocor)	419	3.8	3h	>10000
EE2	296	4.15	1-2d	≤ 0.001
triclosan	290	4.5-5.5	?	~1.0

Analytical Methods

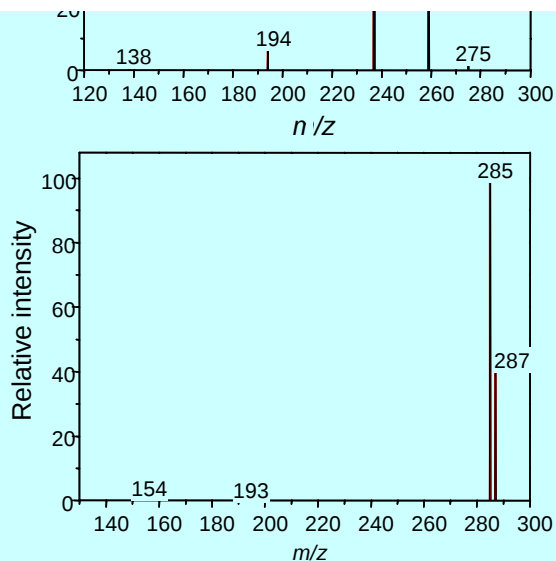
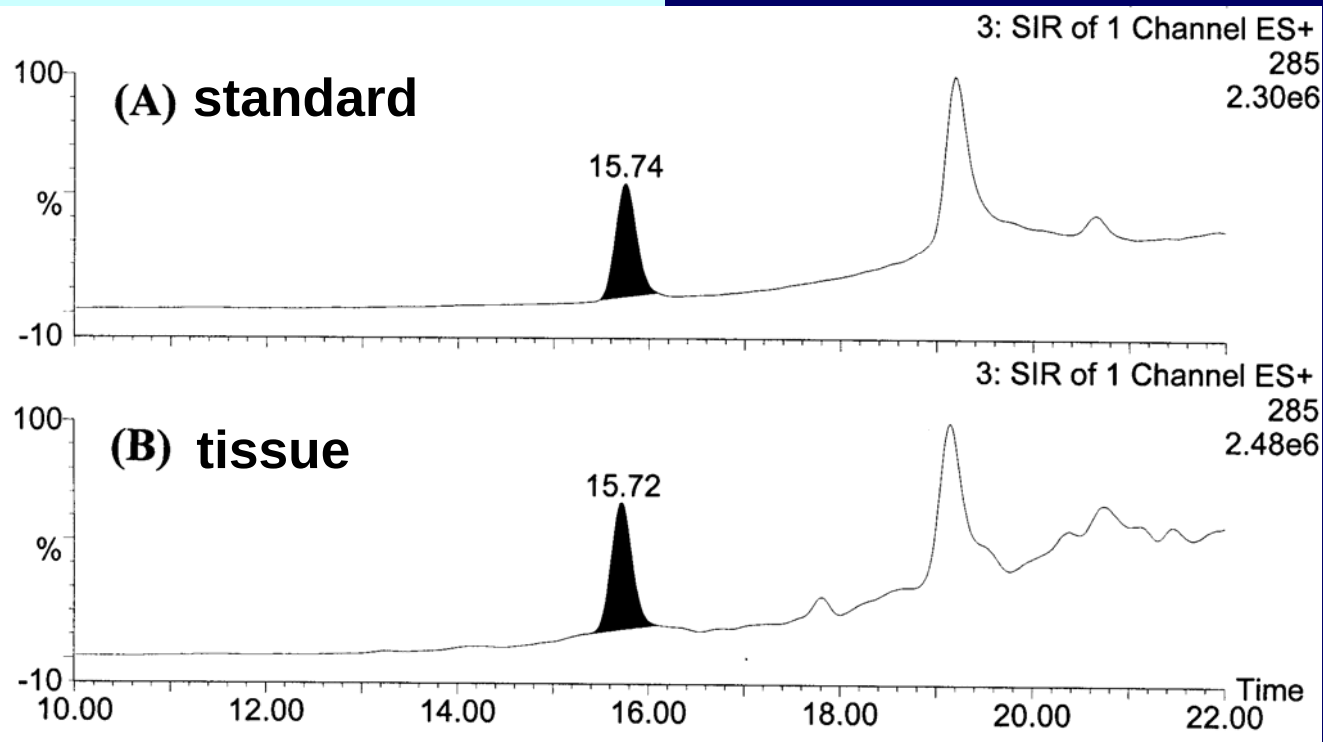
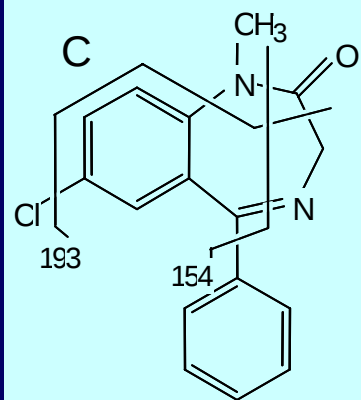
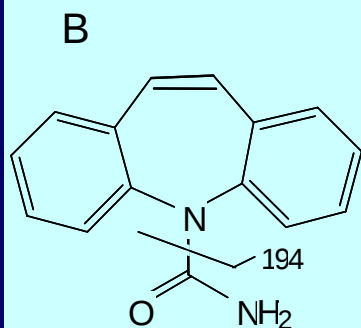
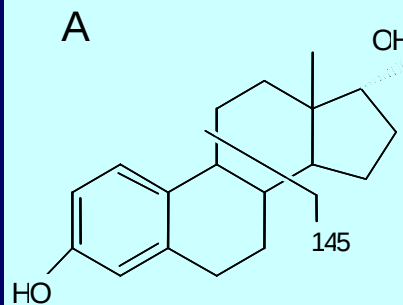
- SOPs (15) developed/in use @ MSCL
- LPs, ICCs by ASE/GC-MS
- CUPs by GC-ECD, TSD, HPLC
- *Hormones/PPCPs by LC/MS(/MS)*
 - Hormones: ESI- (MRM)
 - PPCPs: ESI- (SIR), ESI+/MRM
- Performance-based QA/QC

QA/QC

CLASS (#)	SEDIMENT			TISSUE		
	MDL	Spike	%REC	MDL	Spike	%REC
	(ppb)	(ppb)		(ppb)	(ppb)	
PBDEs (5)	1.0	25	85 $\pm$ 9.1	1.0	25	99 $\pm$ 4.4
PPCPs (5)	0.10-0.50	10	86 $\pm$ 12	4.0-10	50	80 $\pm$ 6.4
OPs (4)	10-50	500-1000	62 $\pm$ 0.54	10-50	500-1000	67 $\pm$ 15*
Hormones (3)	0.6-4.0	10-50	91 $\pm$ 8.0	10**	50**	100**
4-NP	20	80	87.5	50	2000	100***

* no recovery of metalochlor; ** EE2 only; *** corrected for base level

Chemical Group	Chemical Name	Median (µg/kg)	Average (µg/kg)	Standard Deviation (µg/kg)	Minimum (µg/kg)	Maximum (µg/kg)	Occurrence %
Sediment							
ICC	bis(2-ethylhexyl)phthalate	121	171	190	4.00	471	100
ICC	4-nonylphenol	30	104	161	0.00	380	100
PPCP	Triclosan	5.1	4.96	3.06	1.70	8.6	100
LP	p,p'-DDE	5.0	189	398	1.00	900	80
ICC	PBDE47	2.2	1.7	1.12	0.50	2.8	60
ICC	PBDE99	1.4	1.08	0.54	0.50	1.6	60
PPCP	Diazepam	0.04	0.04	0.02	0.04	0.07	20
Tissue							
LP	p,p'-DDE	313	12200	24700	12.0	64700	100
ICC	PBDE47	155	156	112	11.0	330	100
ICC	4-nonylphenol	85	102	82.7	25.0	290	90
ICC	PBDE99	55	69	53	8.0	150	100
PPCP	Diazepam	52	56	27	23.0	110	100
ICC	PBDE100	46	47	31.6	4.0	97	100
LP	PCB138	25	111	143	3.5	360	100
LP	PCB153	23	132	177	2.3	470	100
ICC	PBDE154	10	11	7.48	1.0	25	100



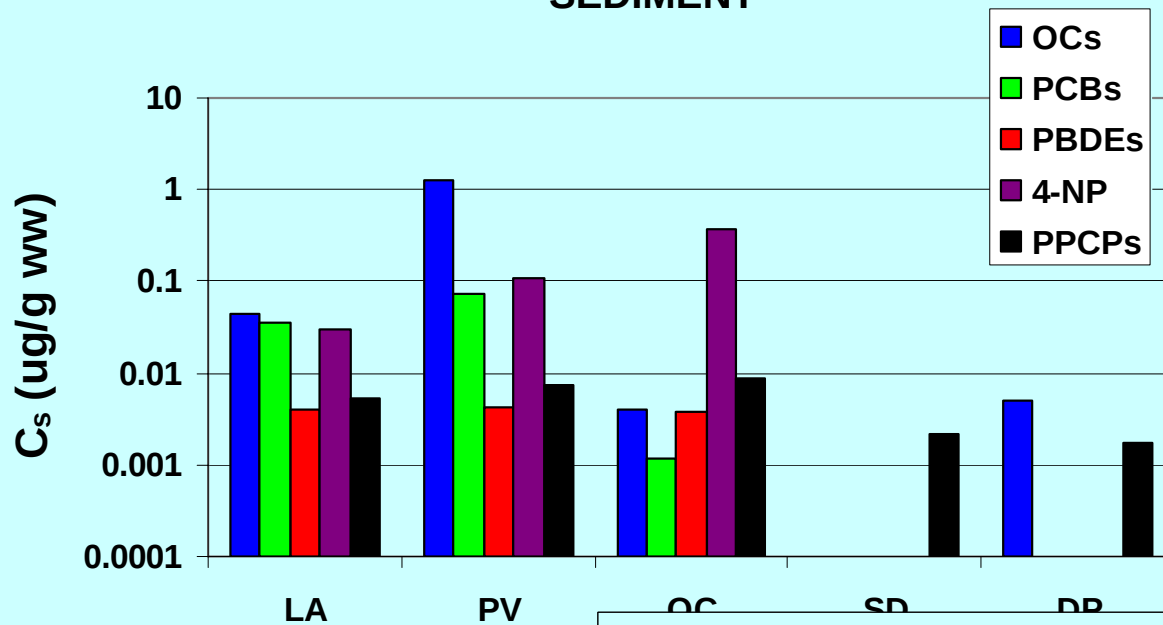
LC/MS

ESI+/SIR

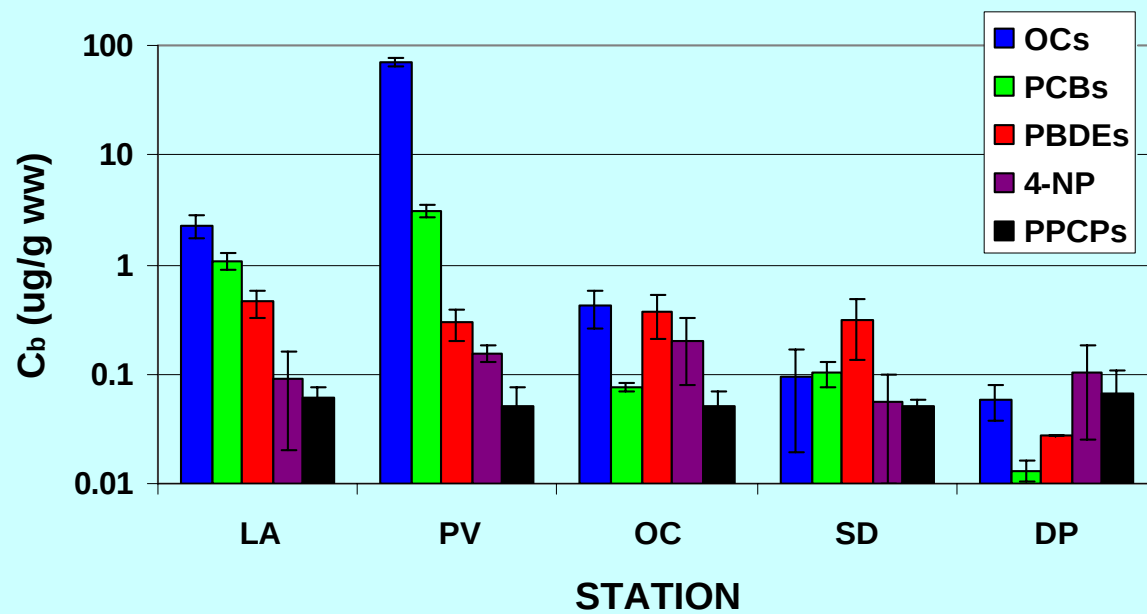
m/z : 285 (193)

Kwon et al. (in press)

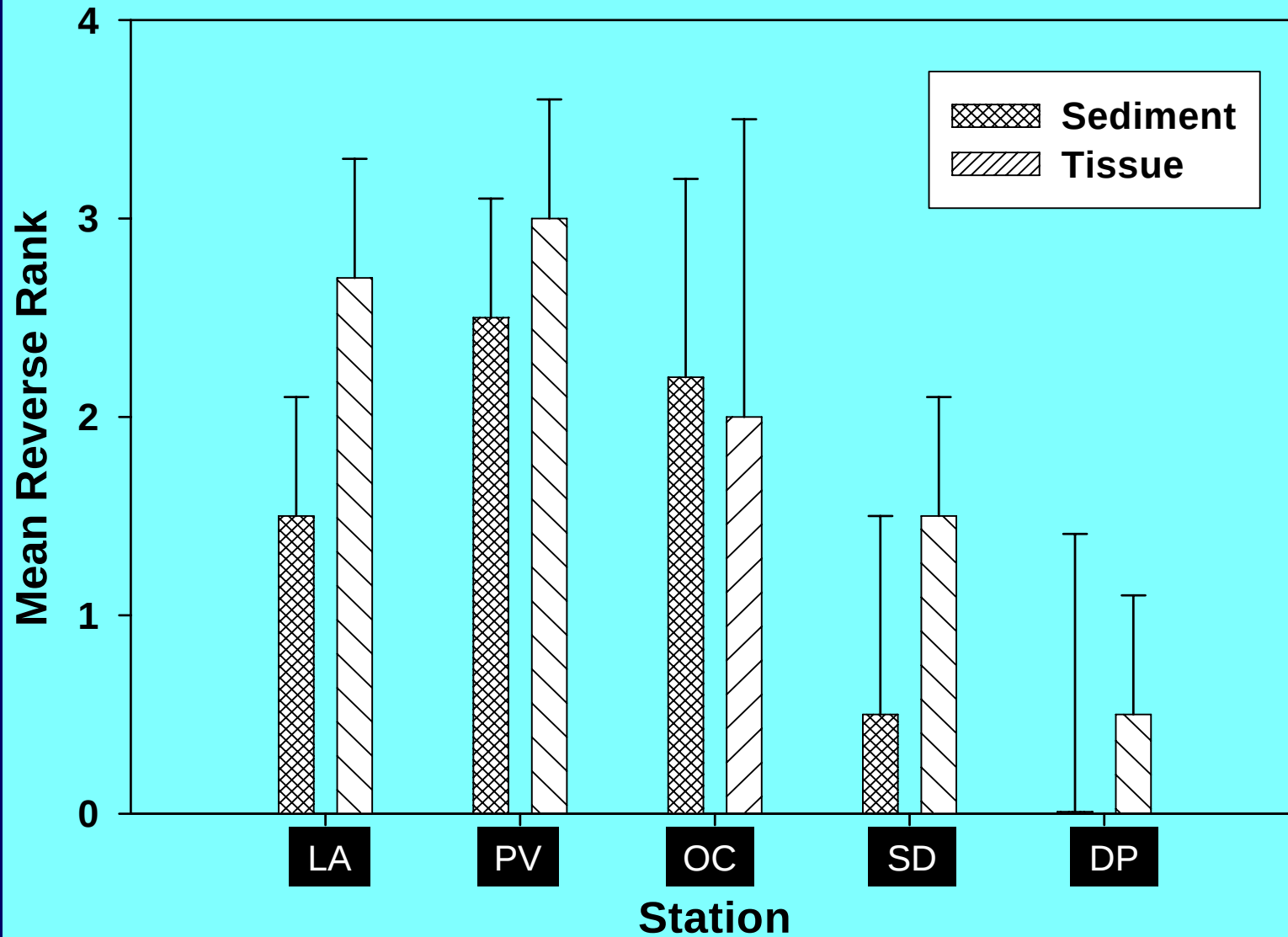
SEDIMENT



TISSUE

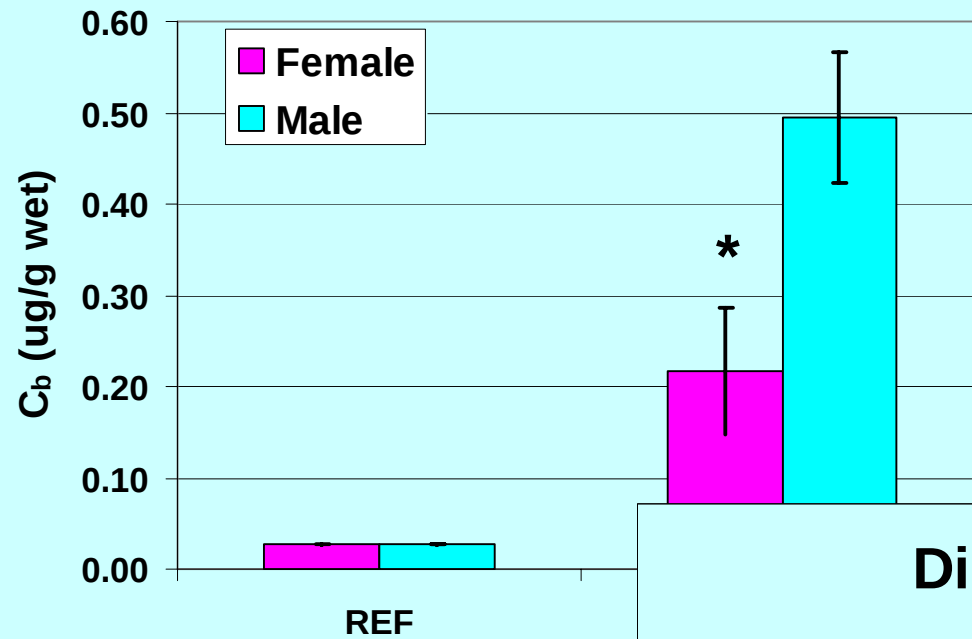


Ranking of CEC Concentrations by Station

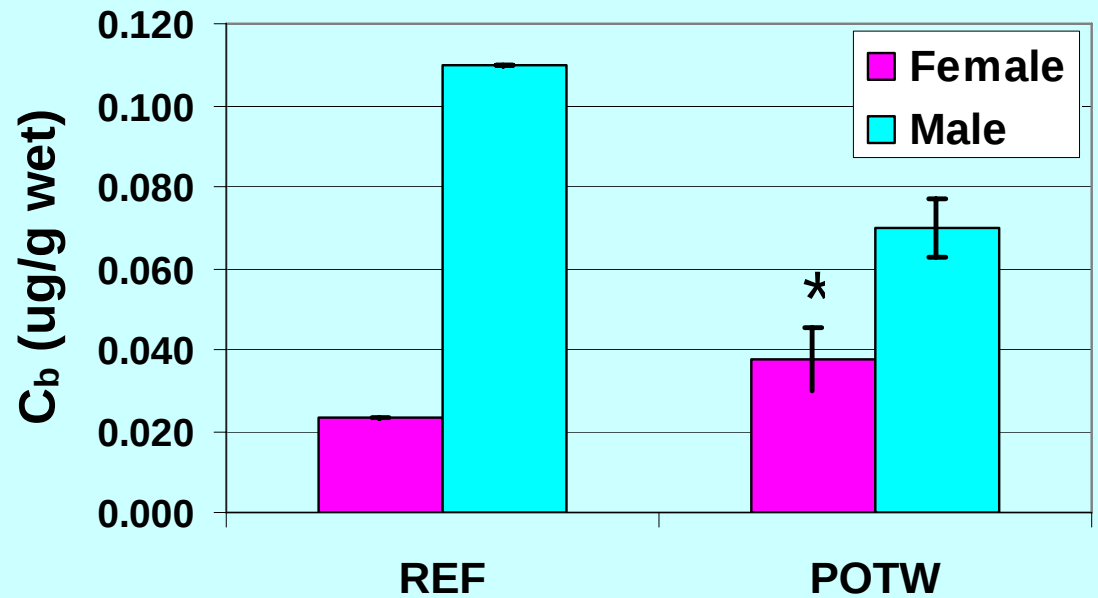


Chemical Group	Target Analyte	Tissue			Sediment			BAF
		Average	Standard	Occur	Average	Standard	Occur	
		(µg/kg)	Deviation (µg/kg)	%	(µg/kg)	Deviation (µg/kg)	%	
PPCP	diazepam	56	27	100	0.04	0.02	20	1405
ICC	PBDE47	156	112	100	1.70	1.12	60	91
LP	PCB153	132	177	100	2.04	2.12	40	65
LP	p,p'-DDE	12212	24696	100	189	398	80	65
ICC	PBDE99	69	53	100	1.08	0.54	60	64
LP	PCB180	61	81	100	1.12	0.86	40	54
LP	PCB99	50	72	100	1.24	1.09	40	40
LP	PCB118	98	155	70	2.82	3.78	40	35
LP	PCB66	51	95	60	1.82	2.17	40	28
LP	o,p'-DDE	752	1561	70	38.2	79.3	40	20
LP	PCB101	65	105	80	3.88	5.85	40	17
LP	p,p'-DDD	168	332	80	19.2	40.7	20	9
LP	oxychlordane	8	11	50	1.40	0.89	20	5
LP	o,p'-DDD	29	46	70	6.00	11.18	20	5
LP	p,p'-DDT	19	23	80	10.8	21.9	20	2
ICC	4-nonylphenol	102	83	90	104	161	100	1

PBDEs in *P. verticalis*



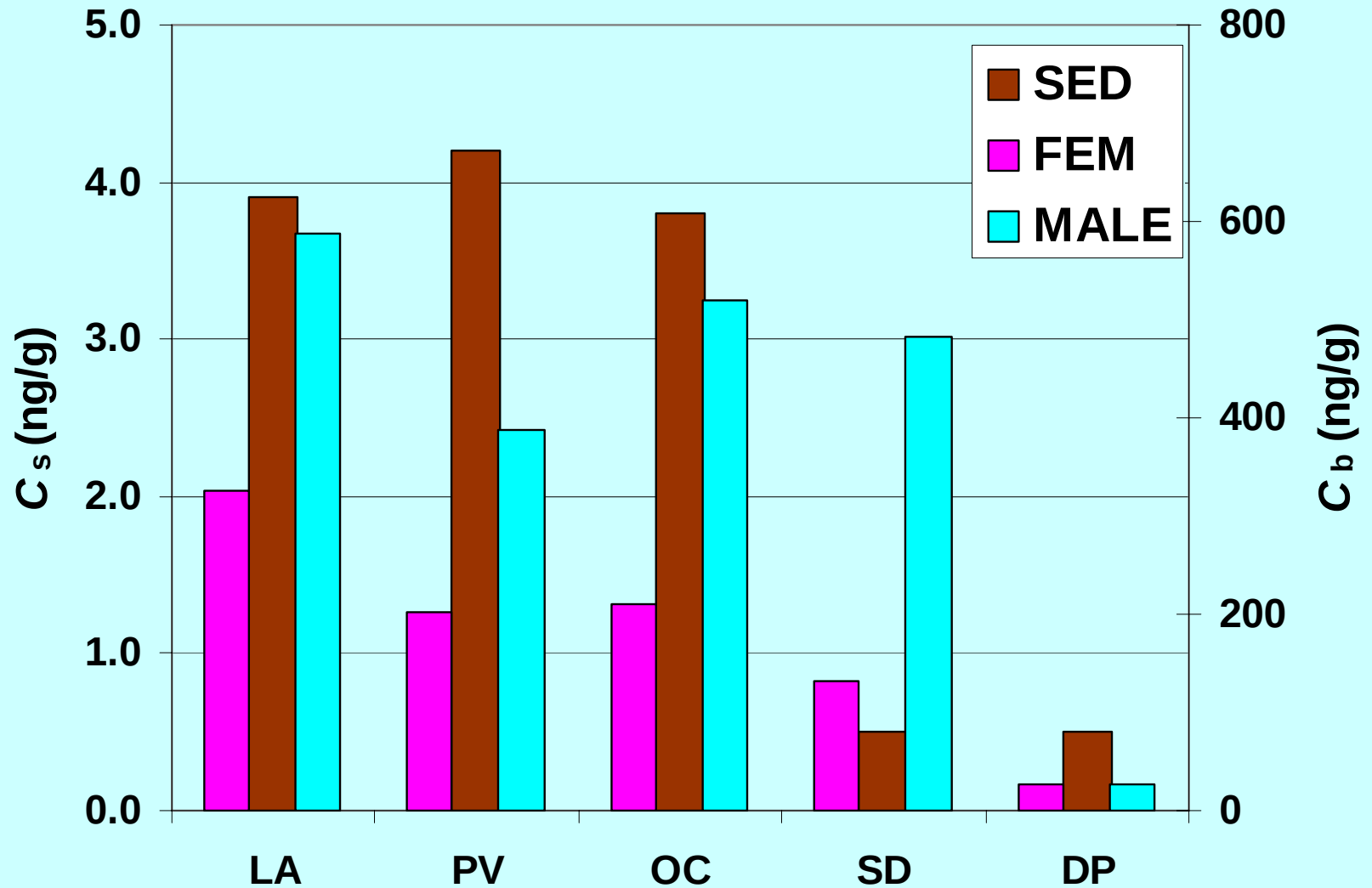
Diazepam in *P. verticalis*



Summary/Conclusions

- Several CECs detected w/hi frequency
 - *4-NP, PBDEs, legacy POPs*
 - *triclosan (sediments); diazepam (tissues)*
 - *hormones not detected (< 1 ppb)*
- Levels ranged from
 - *≤ 1 to 900 ppb (seds), 64700 ppb (tissue)*
 - *p,p'-DDE was highest single constituent*
- Higher overall levels @ PV/LA outfalls
 - *lowest levels at the Reference (DP) station*
- Tissue levels for males > females

PBDEs by Station



Diazepam (Valium)

- Log $K_{ow} \sim 3$
- Fate in sediment-water microcosms (Löffler et al. 2005)
 - Resistant to transformation $\gg 1$ y
 - Preferential partitioning onto sediment ($K_{oc} \sim 200$)
- 50% removal by WWTP (2°) (Carballa et al. 2005)
- Low soil leaching potential (Oppel et al. 2004)
- Sediment interferences?
- Other evidence of bioaccumulation?

Oxybenzone

- Active sunscreen ingredient
- $\log K_{ow} > 3$ (3.8)
- Detected in active fractions of SoCal outfall sediment extracts (Schlenk et al. 2005)
- Not detected in sediment (< 0.16 ppb) (this study)
- Not analyzed in tissue (this study)

Liver composites – male & female contributions

Station	Total	Fem	Male
DP	50	17	33
T4	50	19	31
O1	50	26	24
Z2	50	27	23
SD	50	15	35