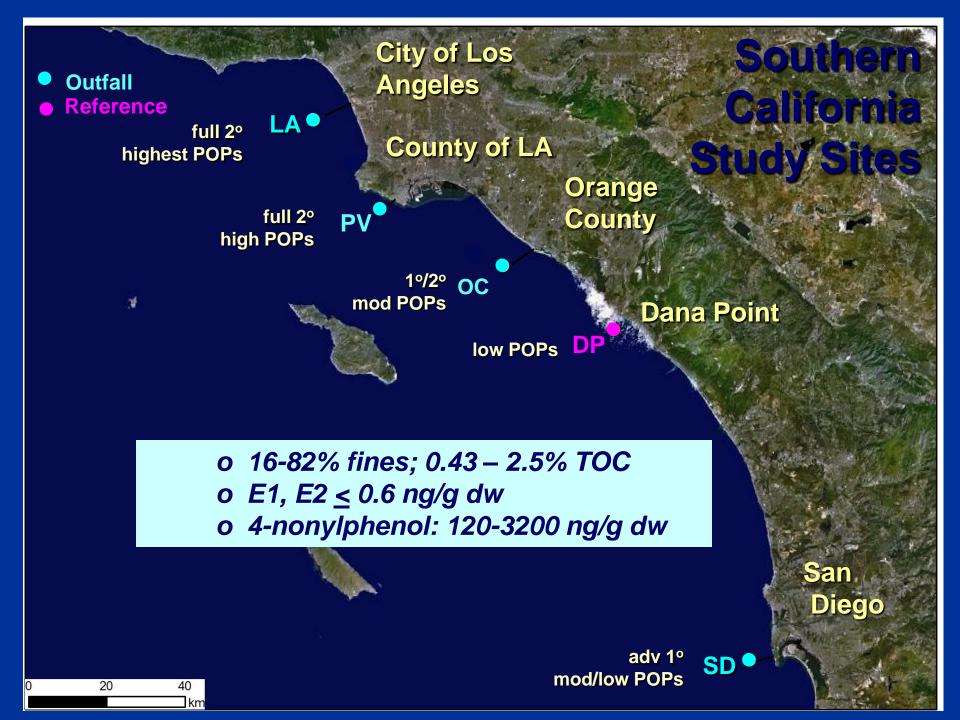
## **CEC Special Studies**

David Tsukada, Wenjian Lao, Nathan Dodder, Keith Maruya

CECs in Coastal & Marine Ecosystems Science Advisory Panel Meeting#2 Sep 30, 2010





## **Previous evidence of endocrine disruption**

In 2003, 11 out of 89 male flatfish (two species) collected throughout SoCalBight identified as having oocytes in testis

			POTW	Original
Species	StationID	ID	Zone	Description
English sole	4038	2	LACSD	Testis-ova
English sole	4038	8	LACSD	Testis-ova
English sole	4086	4	LA/ LACSD	Testis-ova
English sole	4137	1	OC	Testis-ova
English sole	4154	3	OC	Testis-ova
English sole	4154	4	OC	Testis-ova
Hornyhead turbot	4041	3	OC	Testis-ova
Hornyhead turbot	4041	4	OC	Testis-ova
Hornyhead turbot	4042	12	LACSD	Testis-ova
Hornyhead turbot	4045	7	LA	Testis-ova
Hornyhead turbot	4070	10	LACSD	Testis-ova

## **Re-analysis of gonad histopathology**

			POTW	Original	Revised	
Species	StationID	ID	Zone	Description	Description	Basis For Revision
English sole	4038	2	LACSD	Testis-ova	Normal	Oocyte contamination in testis
English sole	4038	8	LACSD	Testis-ova	Normal	Oocyte contamination in testis
English sole	4086	4	LA/ LACSD	Testis-ova	Normal	Oocyte contamination in testis
English sole	4137	1	OC	Testis-ova	Normal	Oocyte contamination in testis
English sole	4154	3	OC	Testis-ova	Normal	Oocyte contamination in testis
English sole	4154	4	OC	Testis-ova	Normal	Oocyte contamination in testis
Hornyhead turbot	4041	3	OC	Testis-ova	Normal	Oocyte contamination in testis
Hornyhead turbot	4041	4	OC	Testis-ova	Normal	Oocyte contamination in testis
Hornyhead turbot	4042	12	LACSD	Testis-ova	Probable testis-ova	-
Hornyhead turbot	4045	7	LA	Testis-ova	Equivocal testis-ova	Structural detail is not clear
Hornyhead turbot	4070	10	LACSD	Testis-ova	Probable testis-ova	-

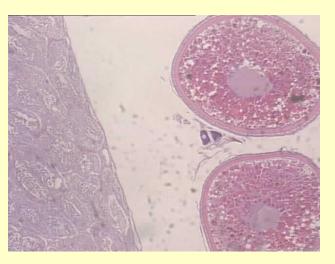
All slides from 2003 study re-examined by NOAA/NFSC (M. Myers)

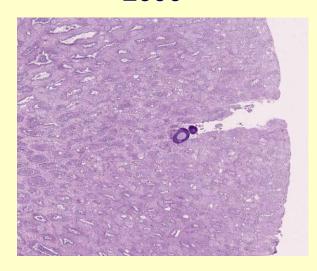
Most observations of oocytes in testis due to <u>contamination</u> <u>during sampling or slide preparation</u>

2 cases of testis-ova in hornyhead turbot confirmed; 1 possible

## **Oocyte Contamination**

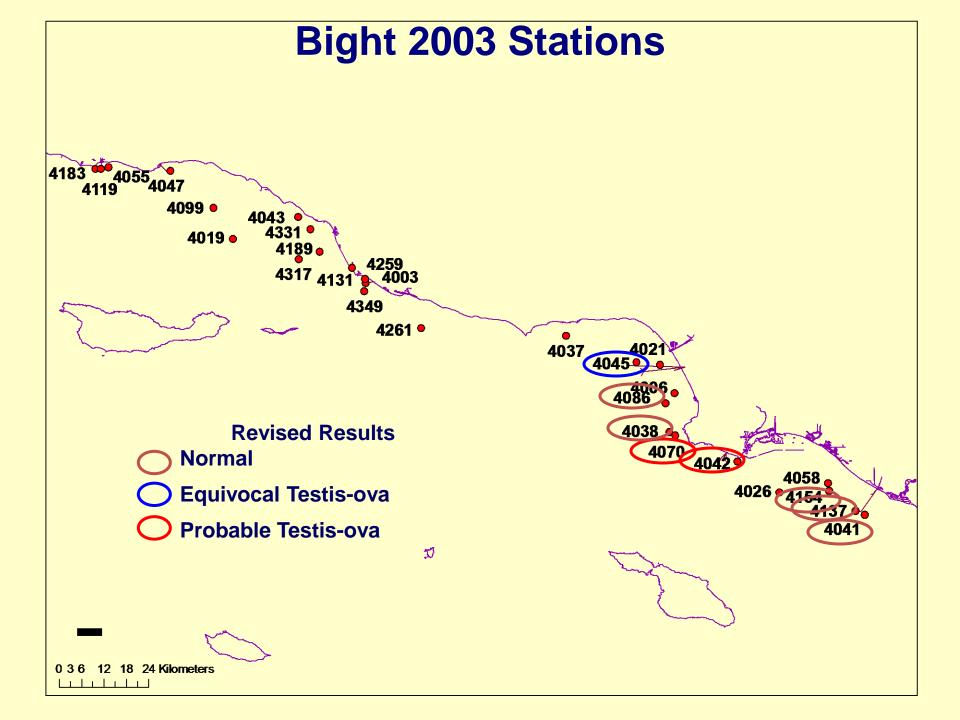
2003





2006

- Oocytes in ducts or tissue tears/voids, not integrated into testis structure
- 2006 example of testis-ova (1 of 373 males) also suspect (under review)



## What CECs occur in stormwater?

Handy Creek

HD

Open

LD

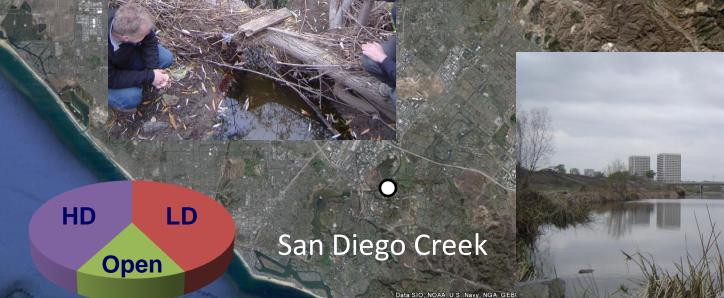


Image © 2010 DigitalGlobe

nage U.S. Geological Survey N 117°47'52 65" W elev

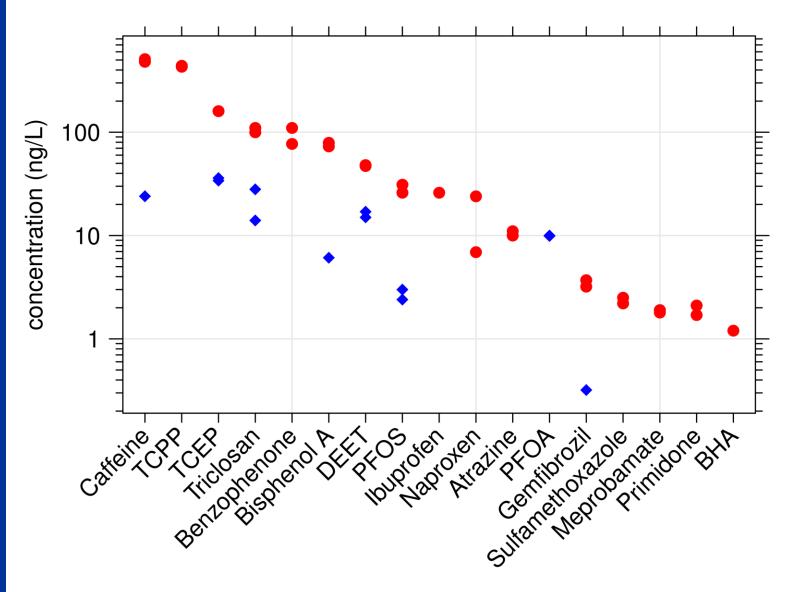
### Stormwater methods

- Grab samples (1 L) collected during March 2010 storm
  - analyzed by Southern Nevada Watershed Authority for PPCPs, PFCs
- Passive sampling devices (PSDs) deployed for 22 d in between storm events (March-April 2010)
  - Solid phase microextraction (SPME) and polyethylene (PE)
  - Polar compound integrated sampler (POCIS)

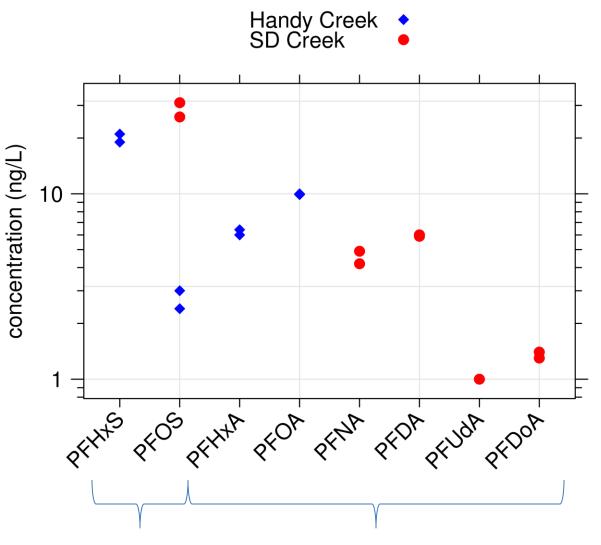




Handy Creek SD Creek



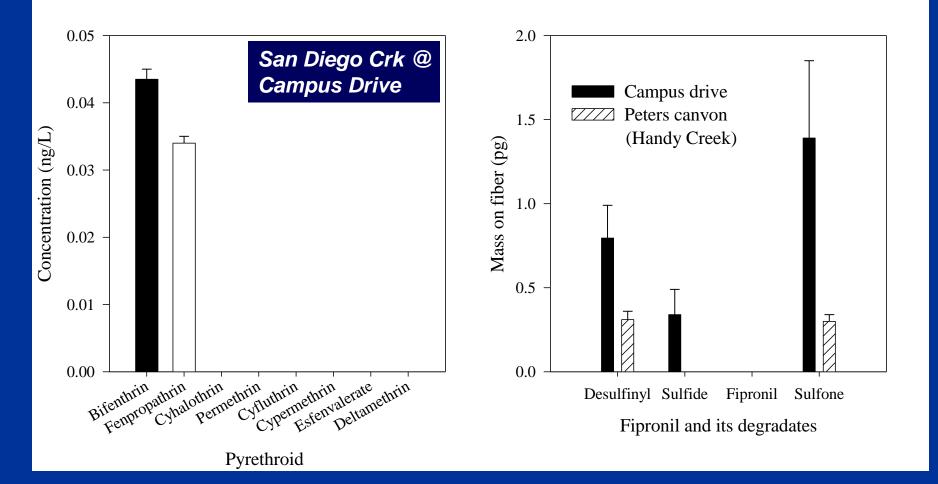




**Sulphonic Acids** 

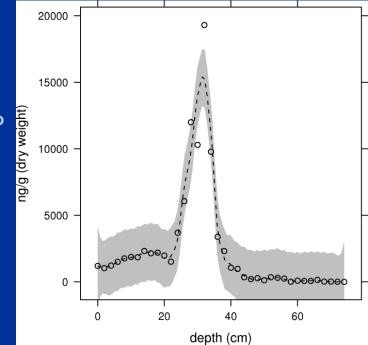
Carboxylic Acids, increasing carbon number

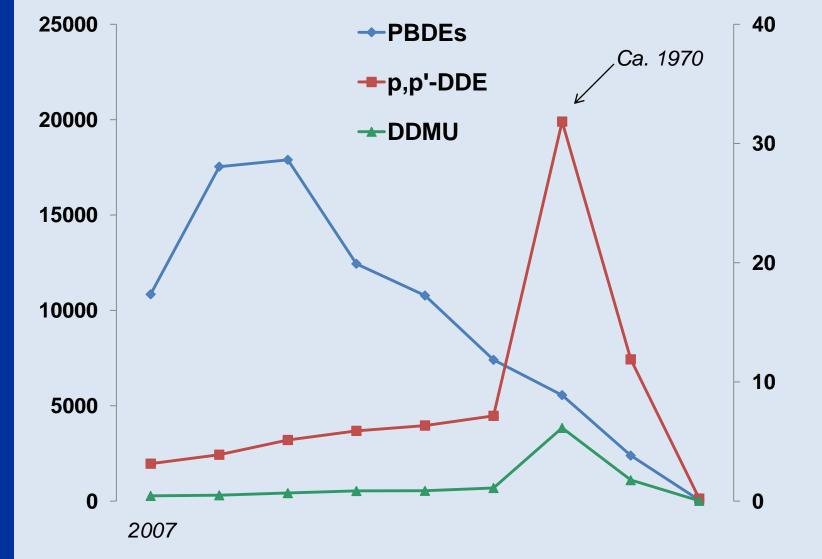
### SPME results for current use pesticides



### Sediment record of CECs

- LACSD collected cores on Palos Verdes Shelf in 2007
  - station 3C exhibited well preserved deposition record & relatively low interfering contaminant levels
- Frozen core slices (2 cm) composited into 9 time horizons dating back to pre-1950
- Samples analyzed for
  - PPCPs and alkyl-phenols by Axys
  - current use pesticides & PBDEs by SCCWRP



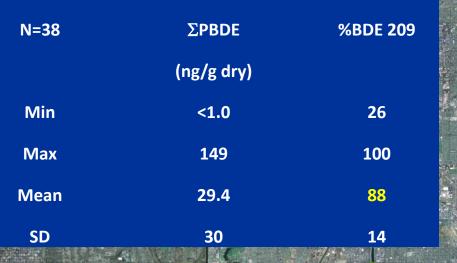


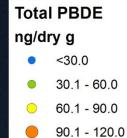
**ZPBDE Concentration (ng/g)** 

**Core Horizon** 

San Diego

San Diego

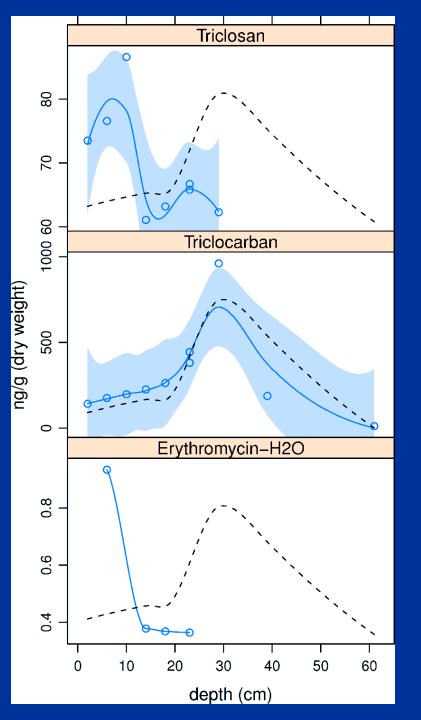


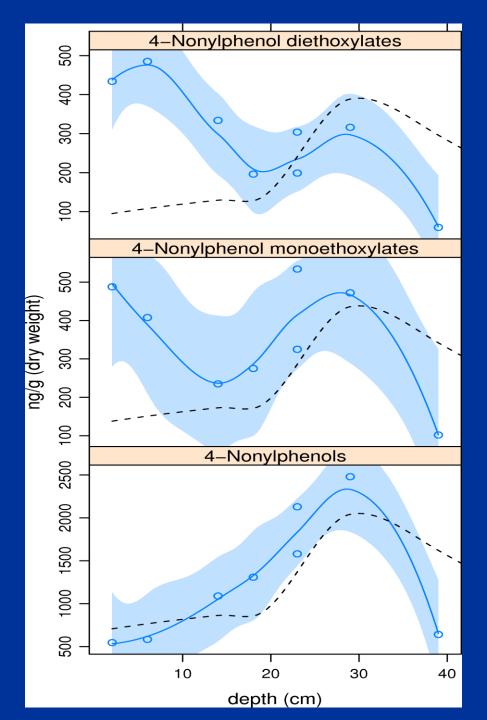


120.1 - 150.0

Bight 08 special study data courtesy of NOAA & TDI Brooks

LA Harbor-Long Beach





### San Francisco Estuary Pilot Study

- SFEI Axys partnership
- Water, sediment, mussels from 5 sites in 2009
- PPCPs, AP/APEOs, PFCs
- Guide target analyte selection statewide
- Which CECs accumulate in sediments? mussels?



## **17 PPCPs Detected in Mussels**

Compound (# sites detected)	Use	ng/g wet wt		
	030	Max	Mean	
Diethyl-3-methyl-benzamide, N,N- (DEET) (5)	insect repellent	14	7	
Digoxigenin (3)	cardiac drug metabolite	10	5	
Carbamazepine (5)	anticonvulsant	5	3	
Amphetamine (3)	stimulant	4	1	
Triclocarban (2)	antimicrobial	2	0.5	
Sertraline (5)	antidepressant	1	0.5	
Dehydronifedipine (5)	antianginal	0.7	0.4	
Triamterine (3)	antihypertensive	0.6	0.2	
Ranitidine (3)	antacid	0.4	0.2	
Diphenhydramine (3)	antihistamine	0.3	0.2	
Atenolol (1)	beta blocker	0.3	0.1	
Cocaine (2)	stimulant	0.3	0.1	
Amitryptiline (2)	antidepressant	0.2	0.1	
Sulphamethizole (1)	antibiotic	0.2	0.04	
Erythromycin-H20 (4)	erythromycin metabolite	0.2	0.1	
Enalapril (2)	antihypertensive	0.1	0.04	
Diltiazem (2)	antianginal	0.1	0.04	

## PFC Tissue Results (ng/g wet wt.)

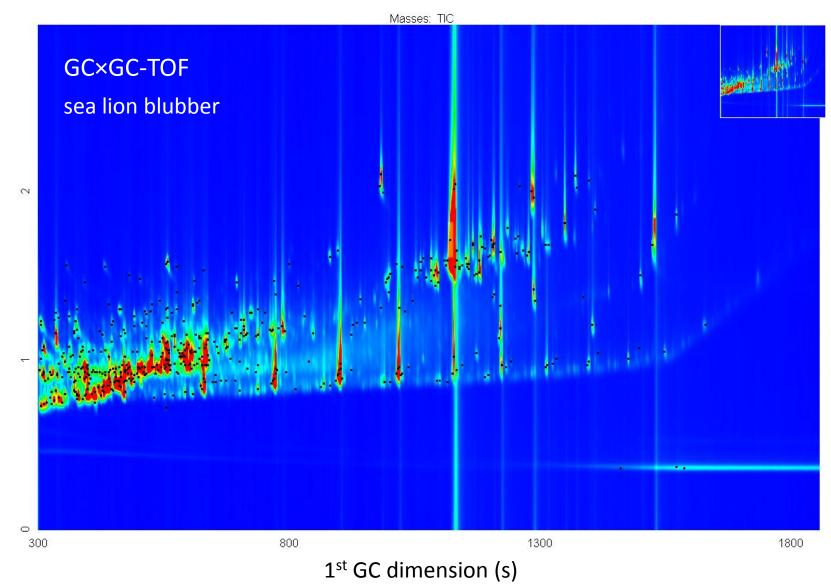
ANALYTE	# Detect Minimum		Maximum	
	n = 5	ng/g	ng/g	
PFBA	1	ND (2.3 – 2.5) n	2.965	
PFPeA	0	ND (2.3)	ND (2.5)	
PFHxA	0	ND (2.3)	ND (2.5)	
PFHpA	0	ND (2.3)	ND (2.5)	
PFOA	0	ND (2.3)	ND (2.5)	
PFNA	0	ND (2.3)	ND (2.5)	
PFDA	0	ND (2.3)	ND (2.5)	
PFUnA	1	ND (2.3)	ND (2.5)	
PFDoA	0	ND (2.3)	ND (2.5)	
PFBS	0	ND (4.5)	ND (4.9)	
PFHxS	1	ND (4.5)	5.1	
PFOS	1	ND (4.5)	76.2	
PFOSA	0	ND (2.3)	ND (2.5)	

# Alkyl-phenols

Analyte	Foster City	Cooley Landing	San Leandro Bay	Eden Landing	Richmond
NP	81	75	90	95	56
NPEO1	<=18	<=31	41	<=17	<=19
NPEO2	<=23	69	192	<=5	81
OP	ND	ND	ND	ND	ND

In units of ng/g wet tissue; <= blank impacted estimate

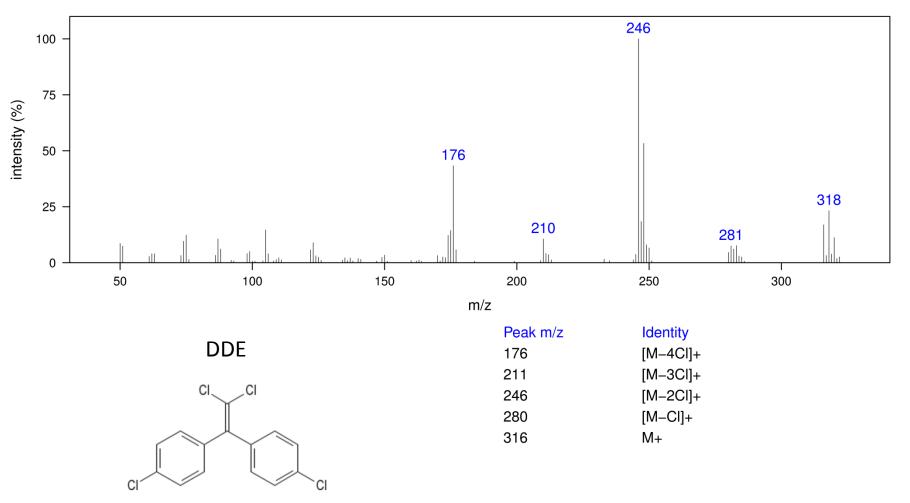
### **Untargeted Analysis by GC×GC-TOF**



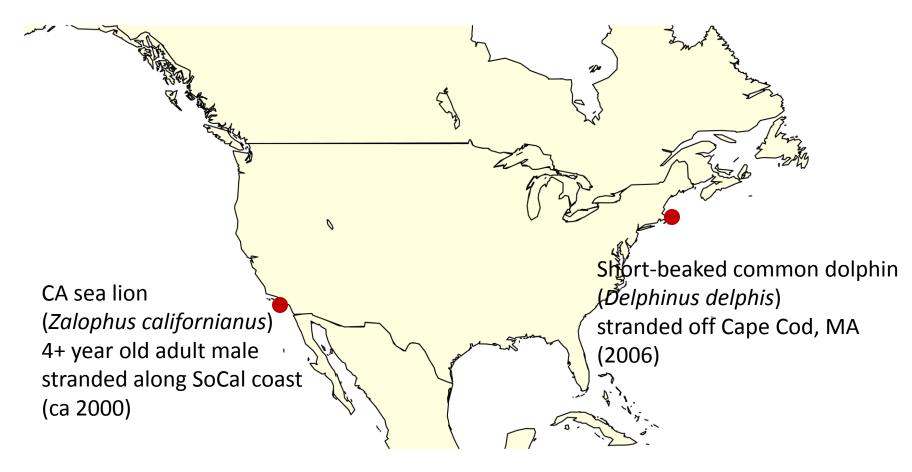
2<sup>nd</sup> GC dimension (s)

### **Untargeted Analysis by GC×GC-TOF**

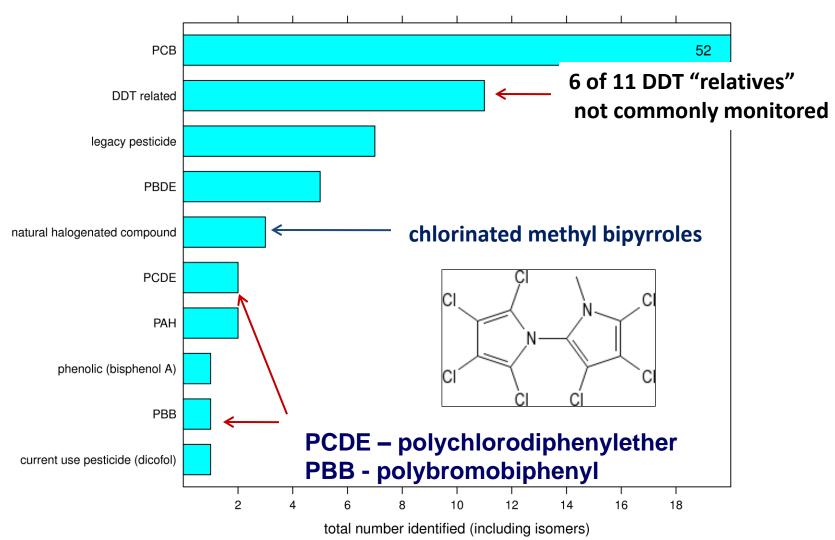
DDE electron impact mass spectrum



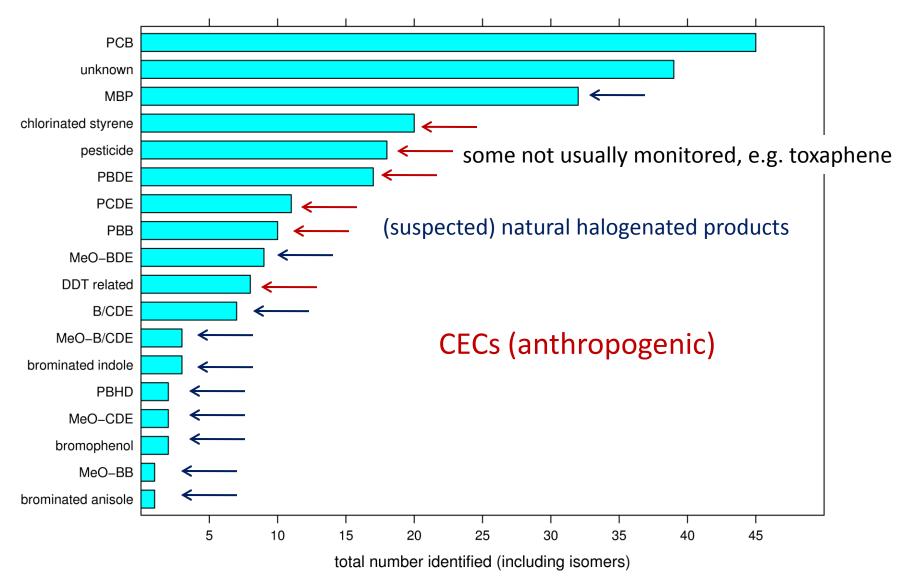
**Study design** – compare west coast pinniped vs. east coast cetacean to develop the instrumental and computational methods, and initial "broad-scan" spectral database



### CA sea lion blubber 85 compounds identified to date



# MA Dolphin Blubber – number of compounds identified (230 total)



### **Summary & Conclusions**

Low incidence of intersex in So Cal Bight flatfish

- Snapshot of stormwater: CECs present at <1 to 510 ng/L</li>
  Land use impacts "downstream" site
- Sediment record shows recent input of PBDEs & some but not all PPCPs, AP/APEOs
- Mussel tissue from SF Bay show elevated AP/APEOs
- Untargeted analysis can identify persistent, bioaccumulative chemicals not routinely measured

### **Next steps**

Compile & analyze results for

- POCIS at San Diego Creek stormwater sites (Jan 2011)
- archived mussel tissue (November 2010)
- targeted CECs in marine mammal tissue (April 2011)

Monitor progress/results from related CEC studies

- Relationship between chemistry & biomolecular assay results
- Mussel Watch CA Pilot Study (early 2011)
- Broadscan analysis of marine mammal tissue

Collate and analyze results for Panel (future meetings)

#### Publish findings

### Acknowledgments

David & Lucile Packard Foundation

#### Collaborators

- SCCWRP Member Agencies (LACSD)
- SFEI
- NOAA (NCCOS, NMFS)
- USGS
- UC Riverside, CSULB, SDSU
- Axys Analytical, TDI-Brooks, SNWA, MacTec
- SCCWRP Staff