



## Non-targeted Screening of Marine Sentinel Species and Drinking Water: Newly Identified Persistent Pollutants

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# Beyond the Regulated Persistent Organic Pollutants?

*Environ. Sci. Technol.* 2006, 40, 7157–7166

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## **Are There Other Persistent Organic Pollutants? A Challenge for Environmental Chemists<sup>†</sup>**

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Persistence/Bioaccumulation/Biomagnification

-> Halogenated Organic Compounds (HOCs):  
Chlorinated and/or Brominated Organic Compounds

# Sentinels

- Marine mammals are at the highest biomagnification level and constitute an “early warning system” for contaminants

Bottlenose dolphin

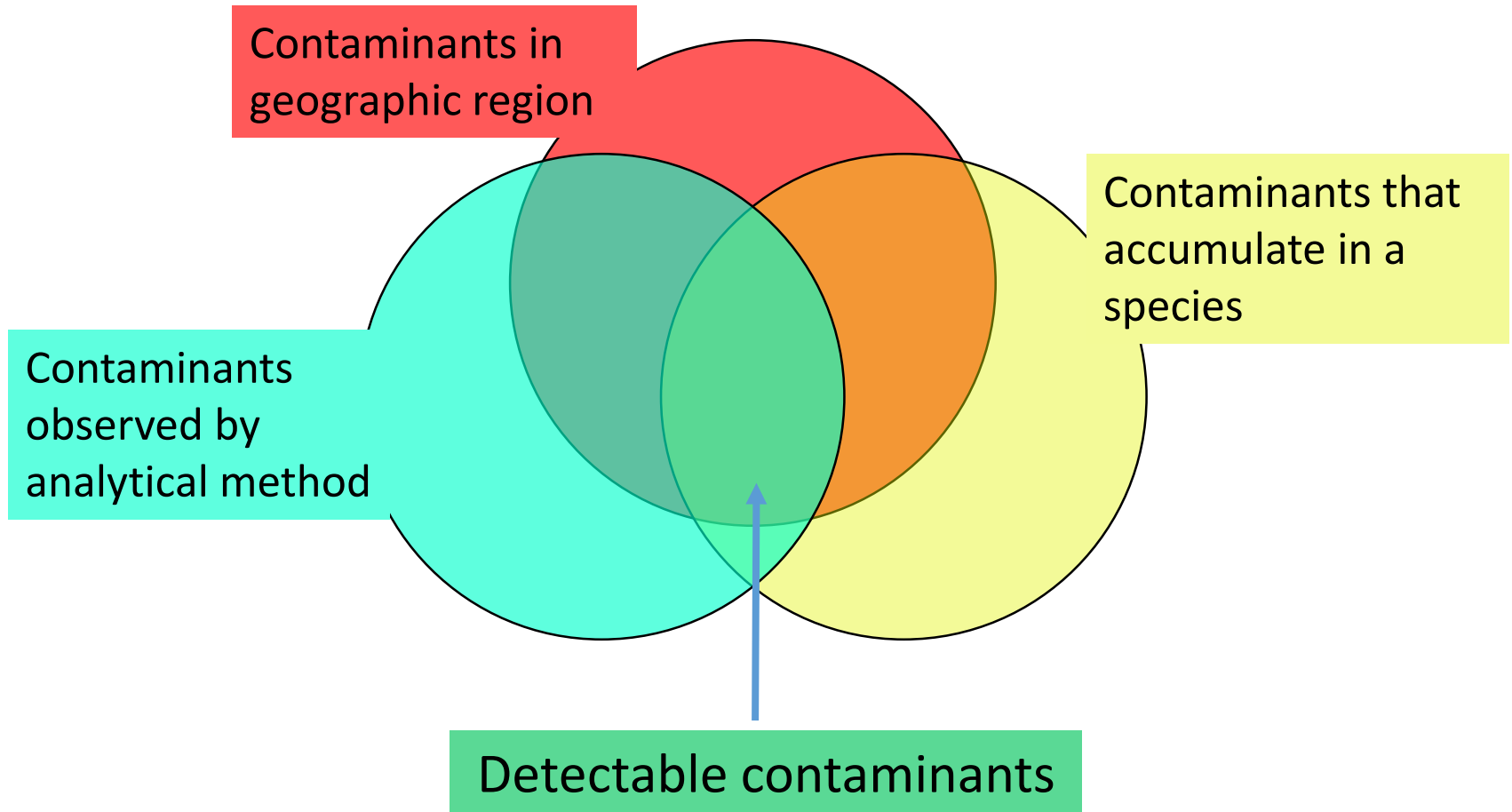


California sea lion



- Selection of appropriate sentinel species ensures effort is not wasted
- What is the best sentinel species?
  - High abundance of a broad set of contaminant classes
  - Understood habitat range and diet
  - Specimen availability

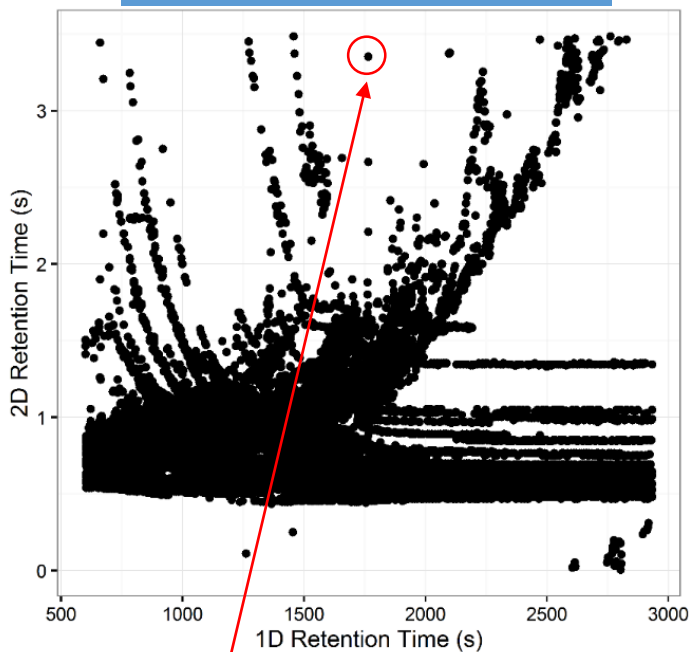
# Detection Factors



Can we widen the scope of detected compounds using a non-targeted mass spectrometry method?

# GC×GC/TOF-MS and Automated Data Reduction

Raw 2D Chromatogram,  
Dolphin Blubber Extract



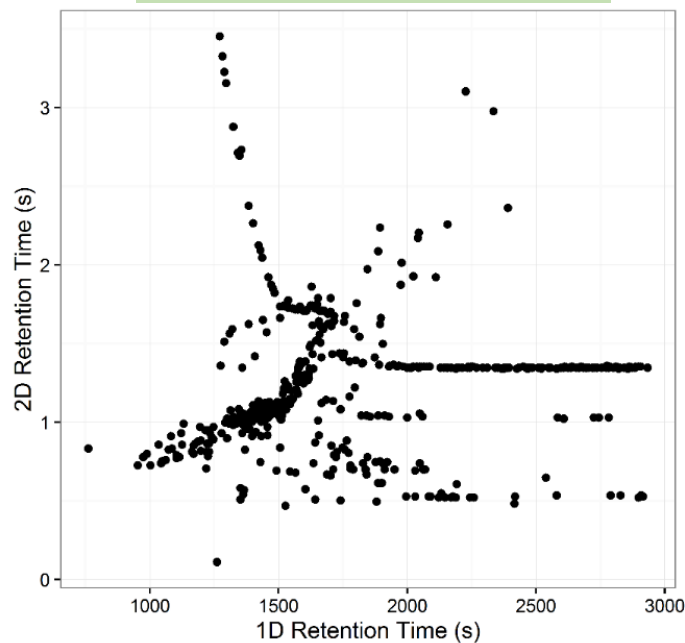
Chromatographic “feature” with associated mass spectrum

Approx. 9000 chromatographic features/sample



Data reduction algorithm that identifies halogenation patterns in the mass spectra

Filtered 2D Chromatogram

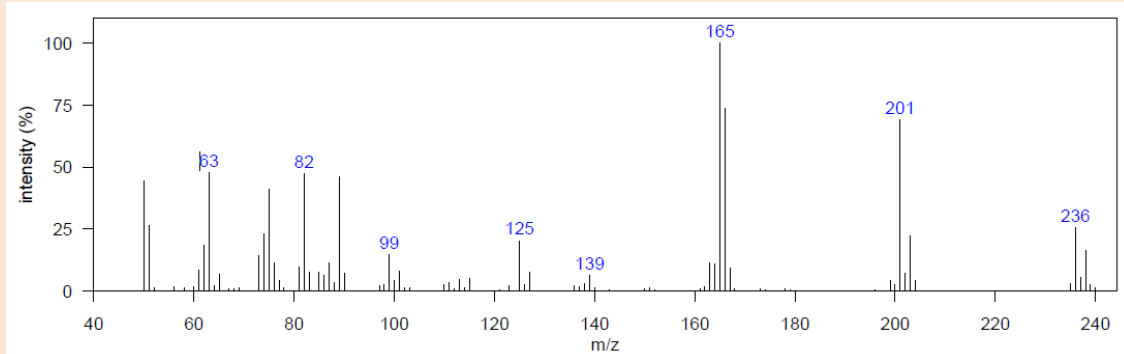


Approx. 400 compounds identified as halogenated

Approx. 8 hours/sample to manually verify

# Objectives of Non-Targeted Analysis

Non-targeted analysis is a systematic method of identifying both expected and unexpected contaminants.

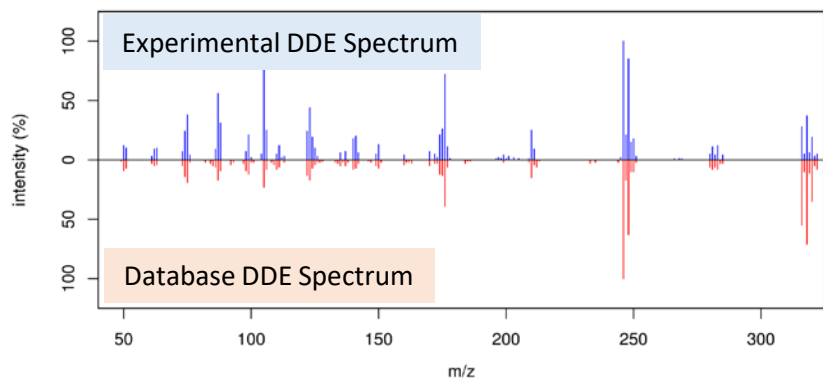


Full scan mass spectrometry

- Examines the “total” contaminant load and allows profile comparisons.
- Identifies contaminants missed by targeted analysis.
- May be used to direct toxicity/risk studies of new contaminants.
- May be used to investigate causes of observed toxicity.

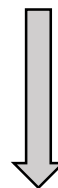
# Compound Identification

## Identification of Halogenated Compounds



### Identifications based on:

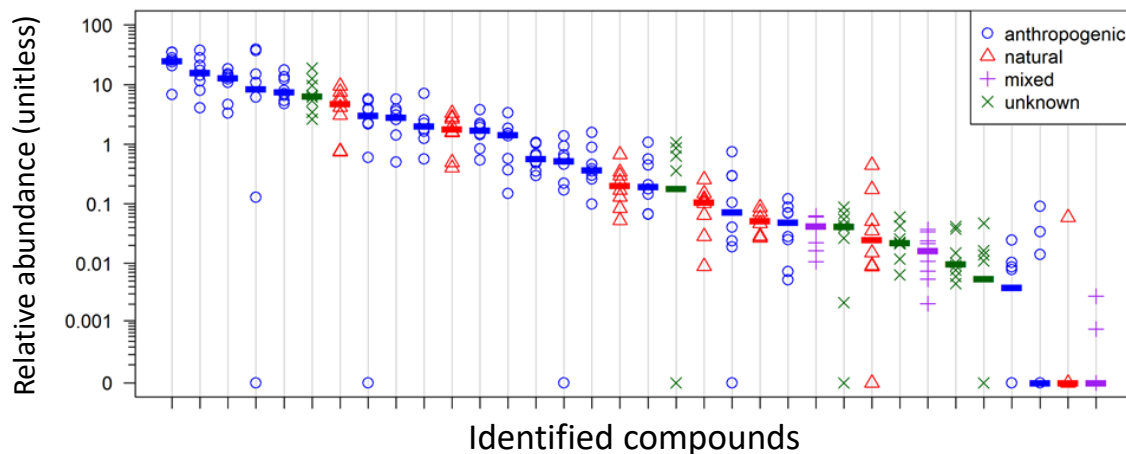
1. Confirmation with authentic standards
2. Database match
3. Manual interpretation
4. Classified as unknown



Decreasing confidence

## Contaminant Profiles

Internal standards are used to determine relative abundances of all compounds

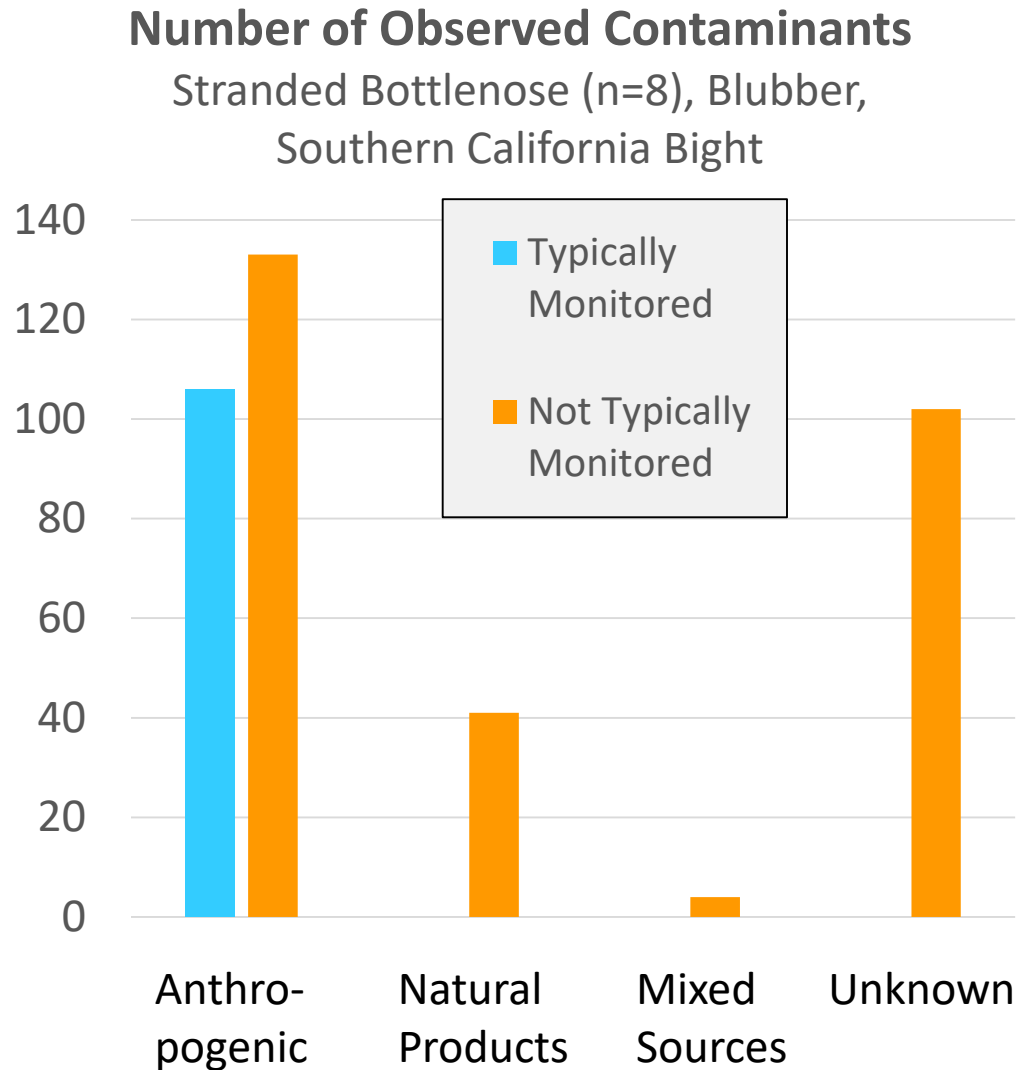






# A Majority of Identified Compounds are Not Typically Monitored

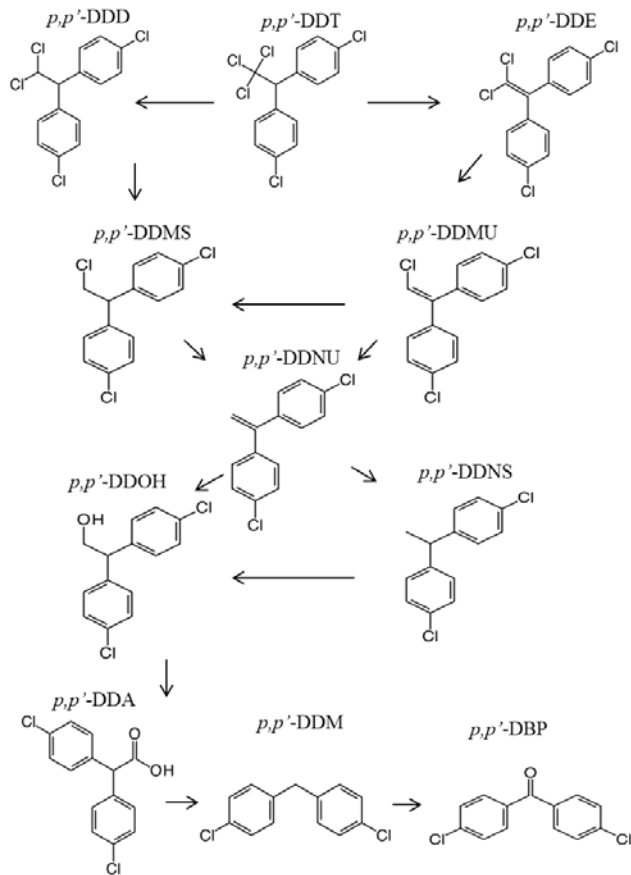
- 86% not typically monitored
- 61% not in standard mass spectral database



# Neglecting Important DDT-related Compounds?

*Mackintosh et al. Environ. Sci. Technol. 2016, 50, 12129-12137.*

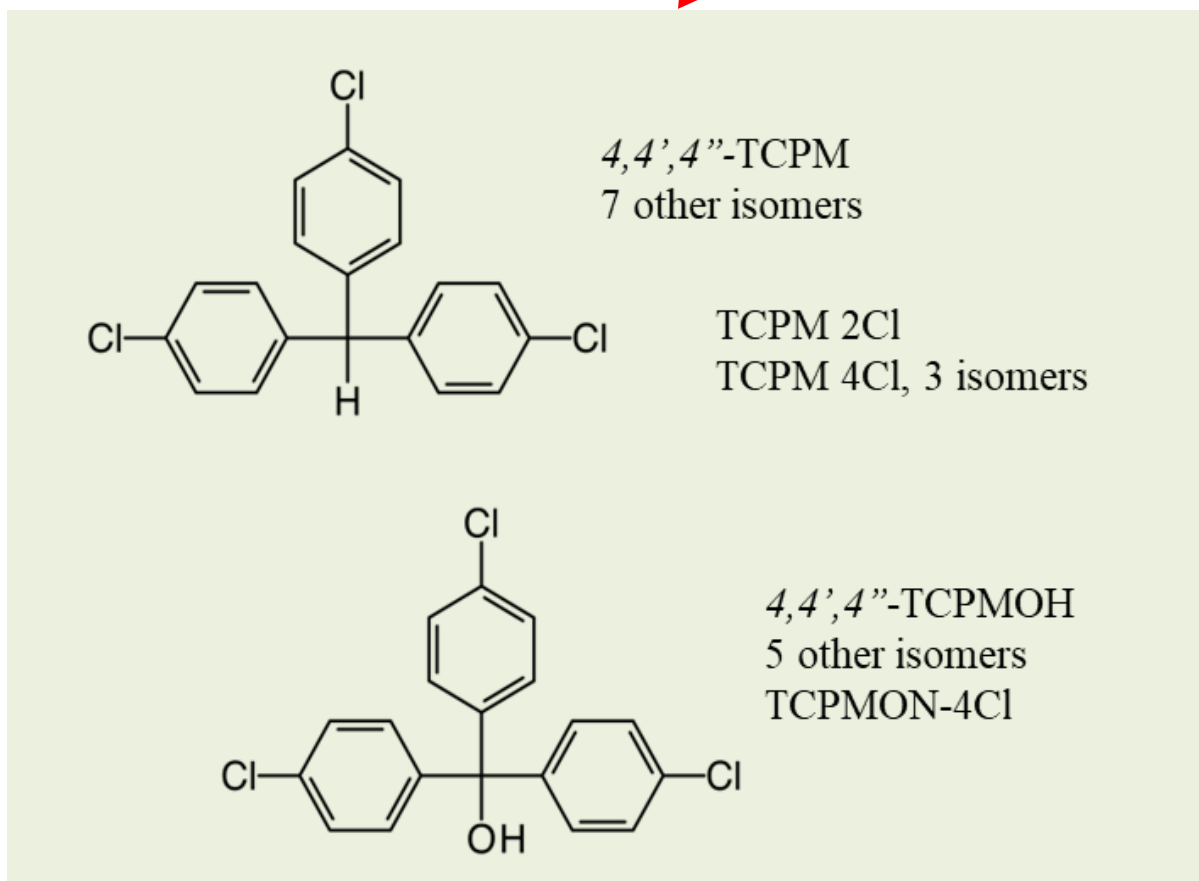
Class	No. Cmpds.	Source	No. Not Monitored
DDT-related	23	Anthropogenic	15-17
Tris(chlorophenyl)methane (TCPM)	12	Anthropogenic	12
TCPMOH	7	Anthropogenic	7
Hexa to octa-chlorinated diphenylethylene	8	Unknown	8



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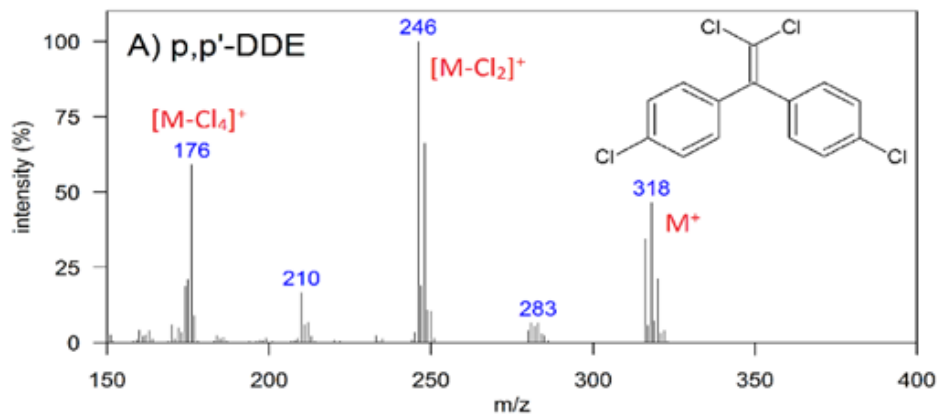
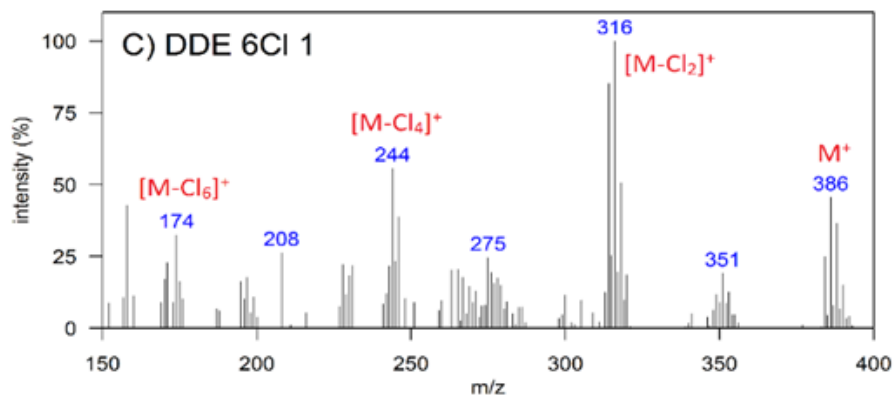
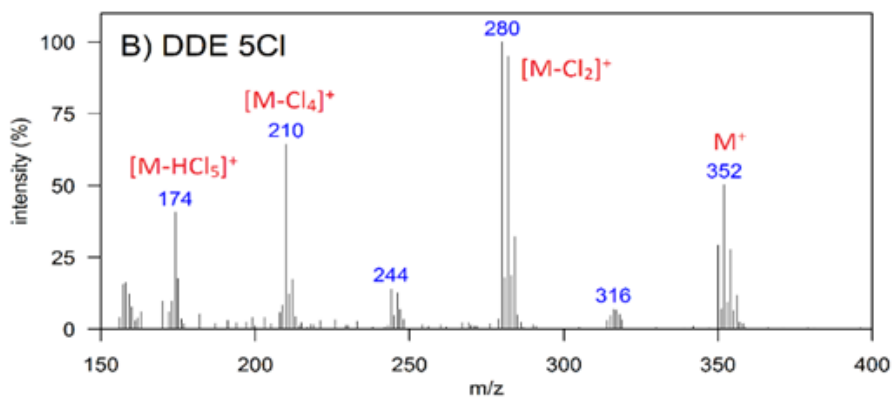
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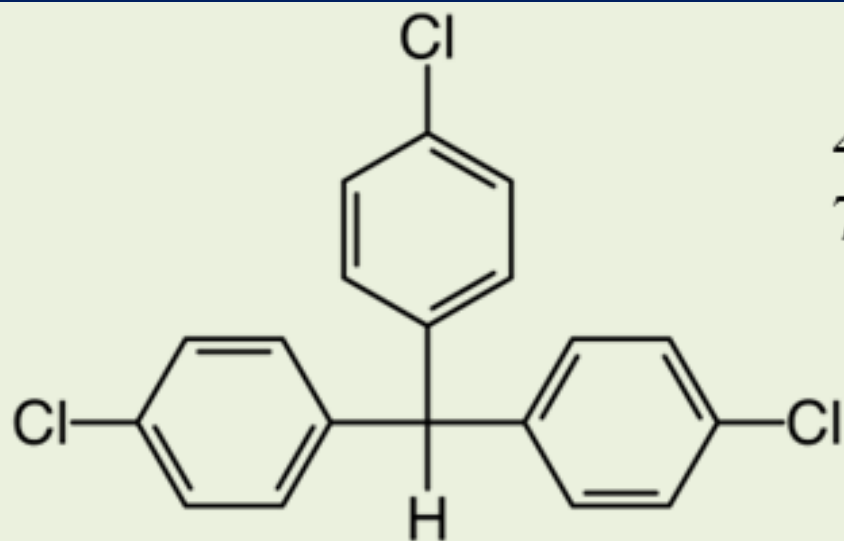
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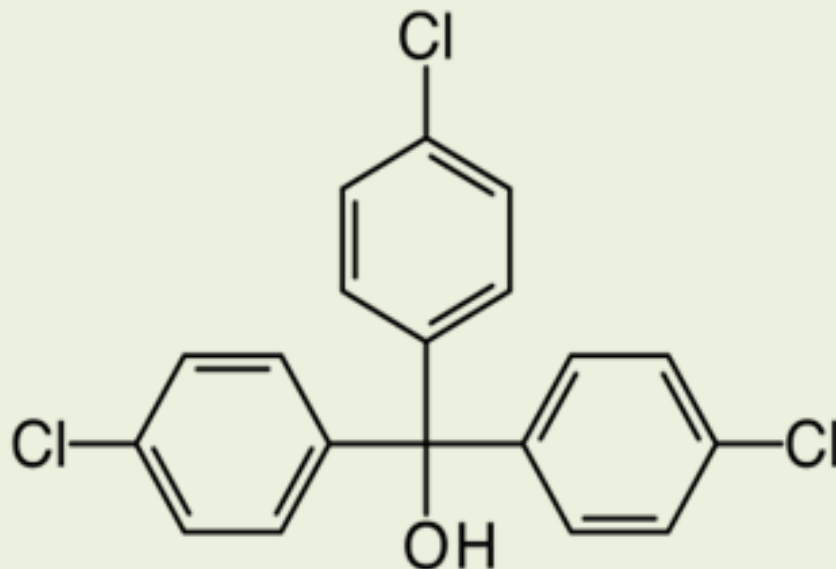


# Abundance of TCPM and TCPMOH in marine mammals from Sothern California Bight and birds from California Coast



4,4',4''-TCPM  
7 other isomers

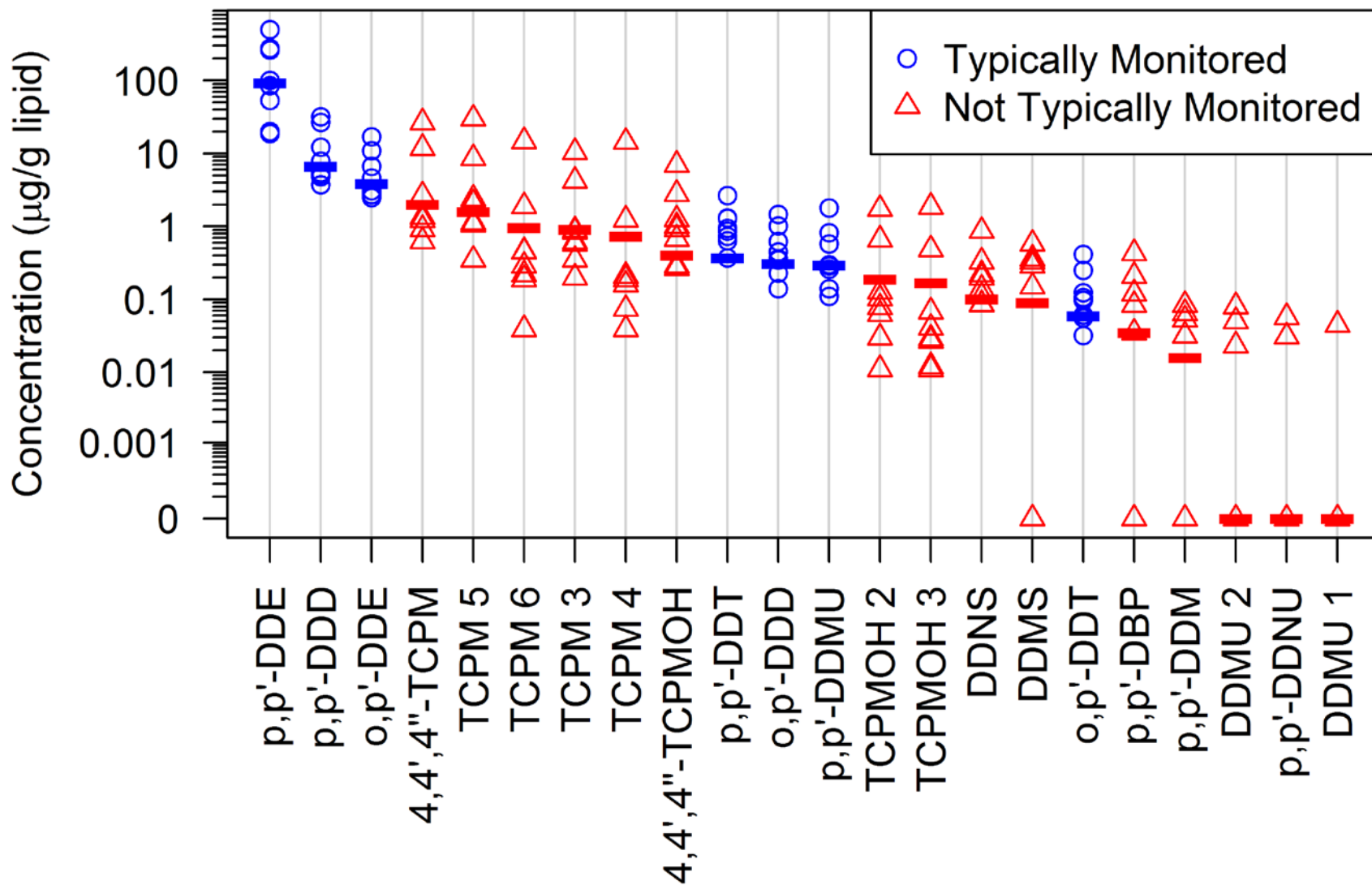
TCPM 2Cl  
TCPM 4Cl, 3 isomers



4,4',4''-TCPMOH  
5 other isomers  
TCPMON-4Cl

# TCPM and TCPMOH (bottlenose dolphins)

Mackintosh et al. Environ. Sci. Technol. 2016, 50, 12129-12137.



# TCPM and TCPMOH (short-beaked common dolphins)

Trego et al. Environ. Sci. Technol. 2018, 52, 3101-3109.

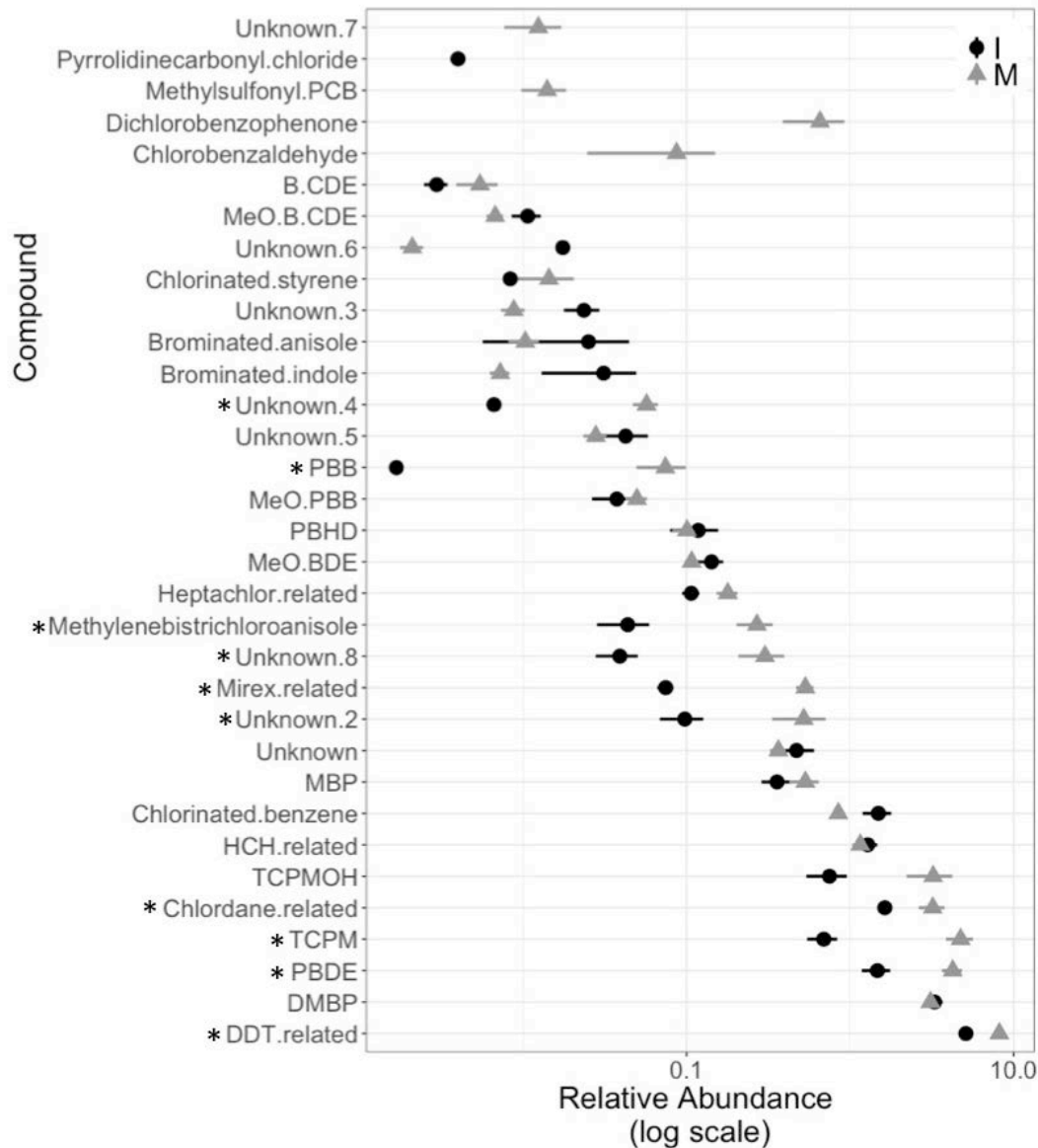
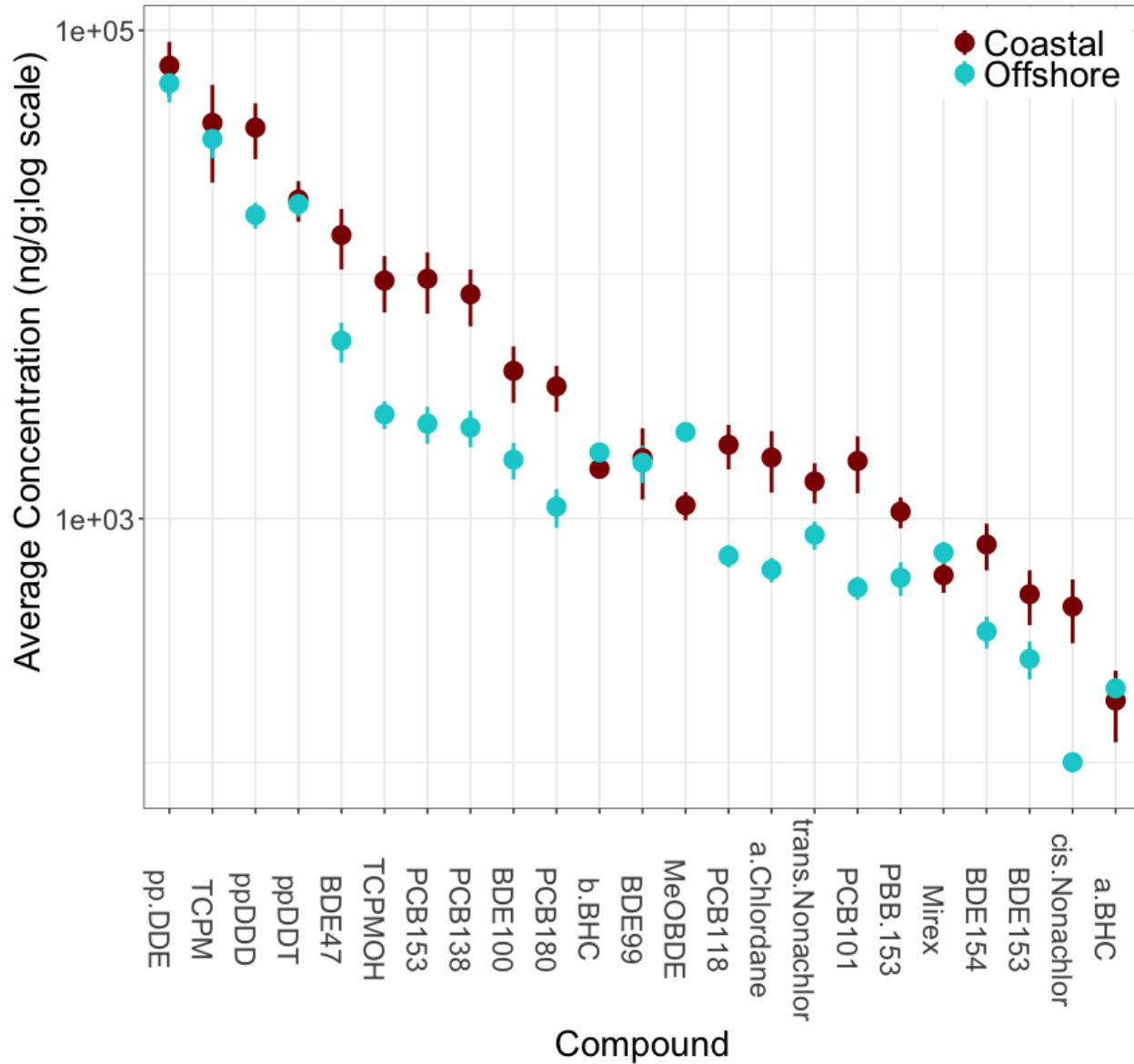


Figure 1: The average relative abundance (in log scale) and standard error of all compound classes by maturity type (black circles and gray triangles represent data from immature and mature animal samples, respectively). The \* denotes compound classes with significantly different abundance between mature and immature animals, as determined by Random Forest permutation tests.

# TCPM and TCPMOH (live bottlenose dolphins)

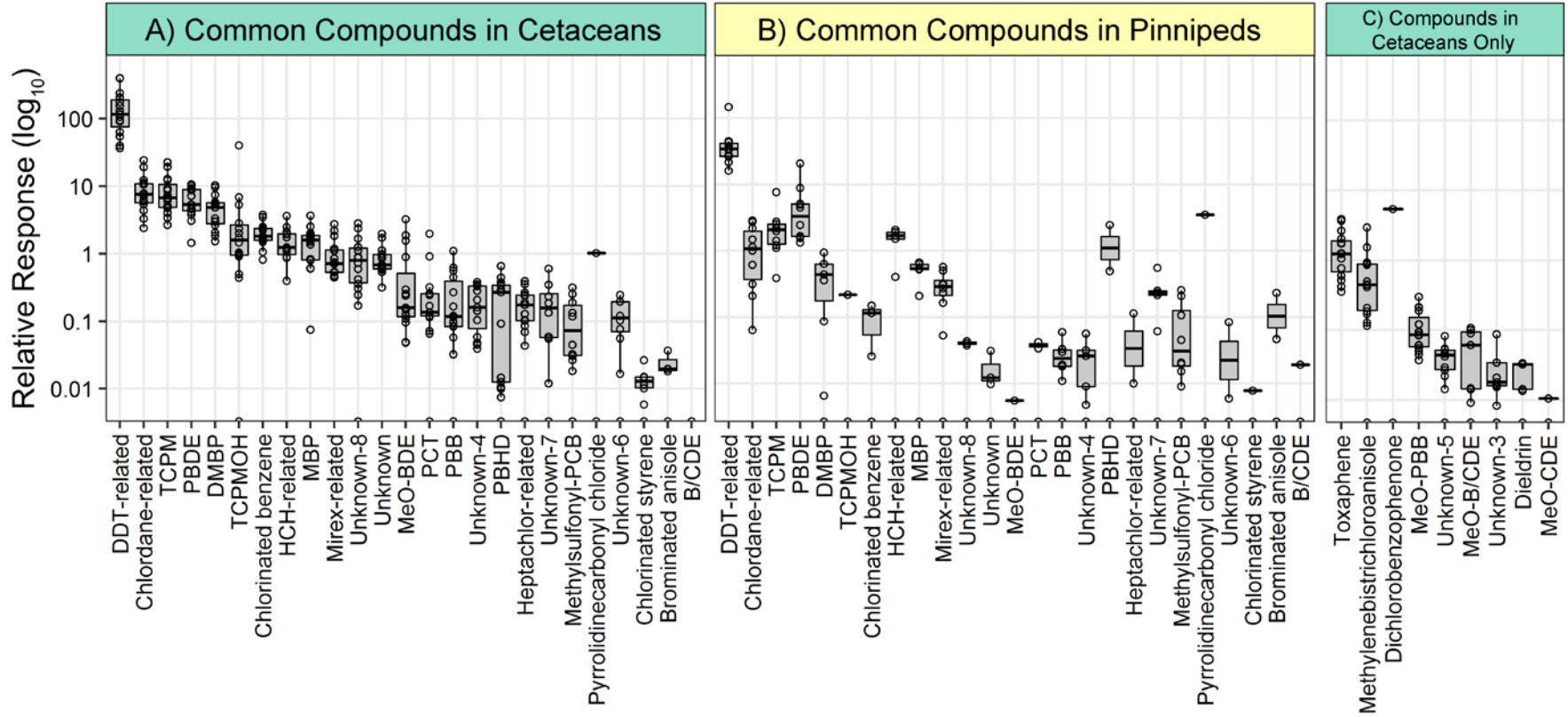
Trego et al. Environ. Sci. Technol. In press.





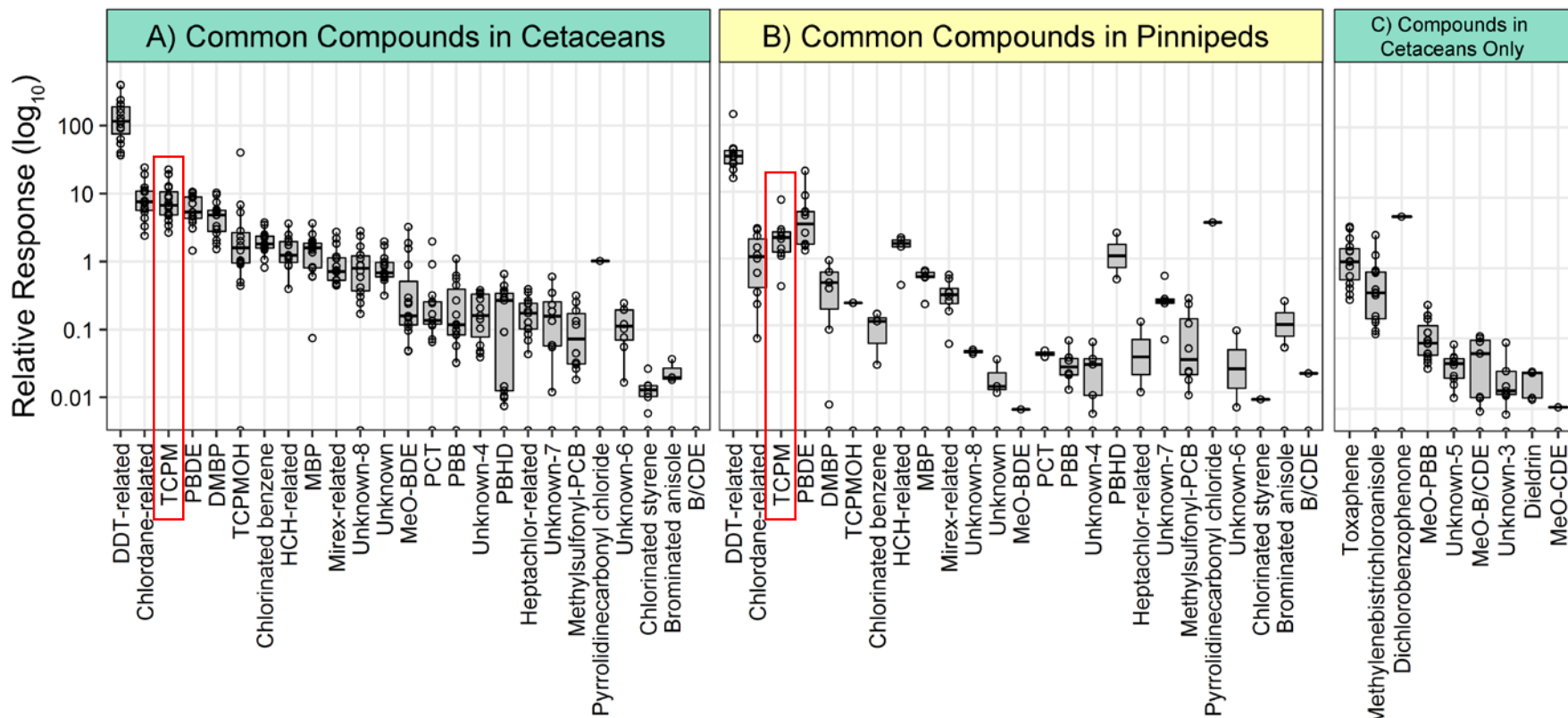
# TCPM and TCPMOH in Cetaceans and Pinnipeds

Cossaboon et al. Chemosphere. 2019, 221, 656-664.



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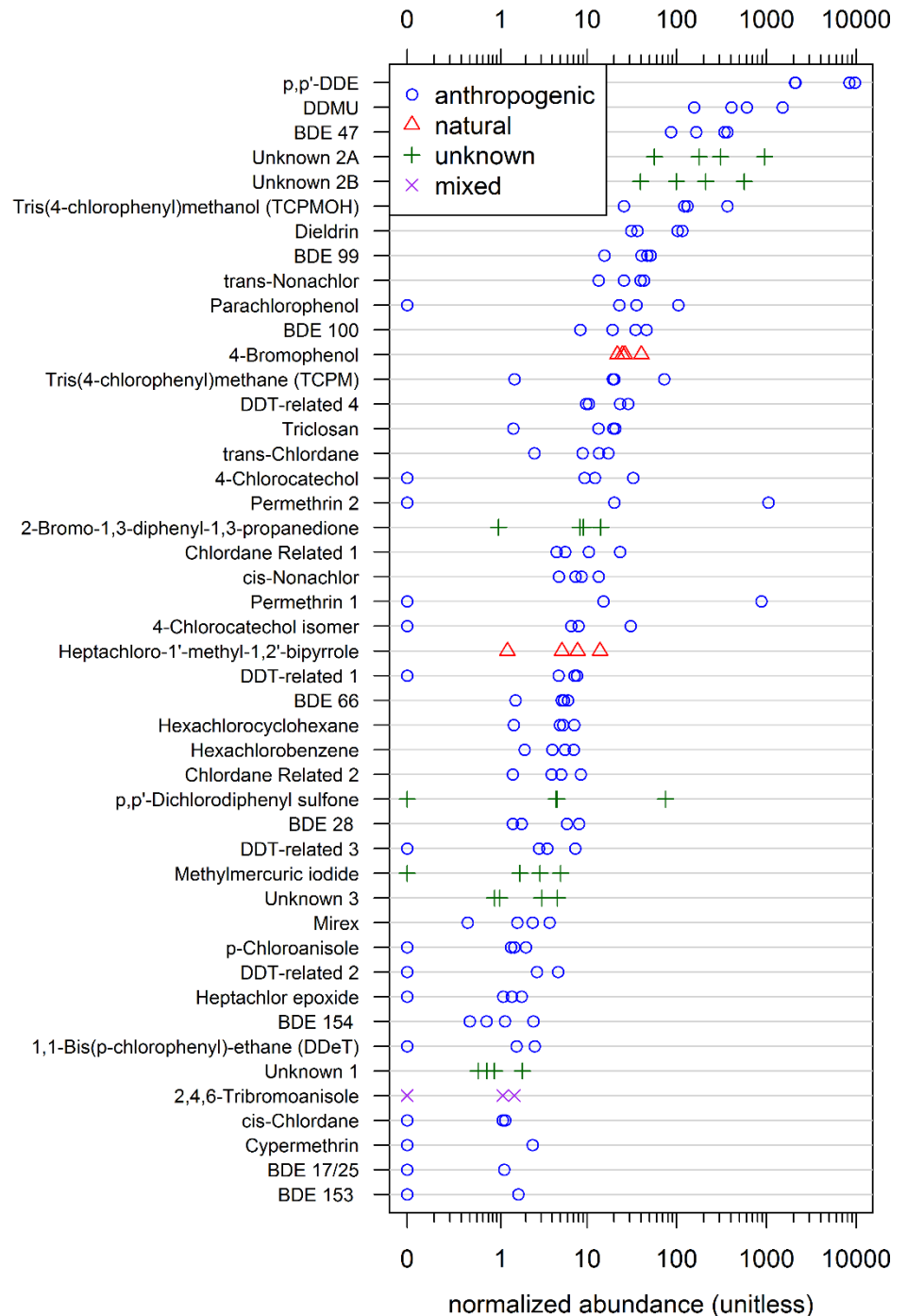


HOC profiles are different between cetaceans and pinnipeds due to different metabolism. But TCPM and TCPMOH were abundant in both, which suggests biomagnification in both cetaceans and pinnipeds.

# TCPM and TCPMOH in Black Skimmers eggs (San Diego Bay)

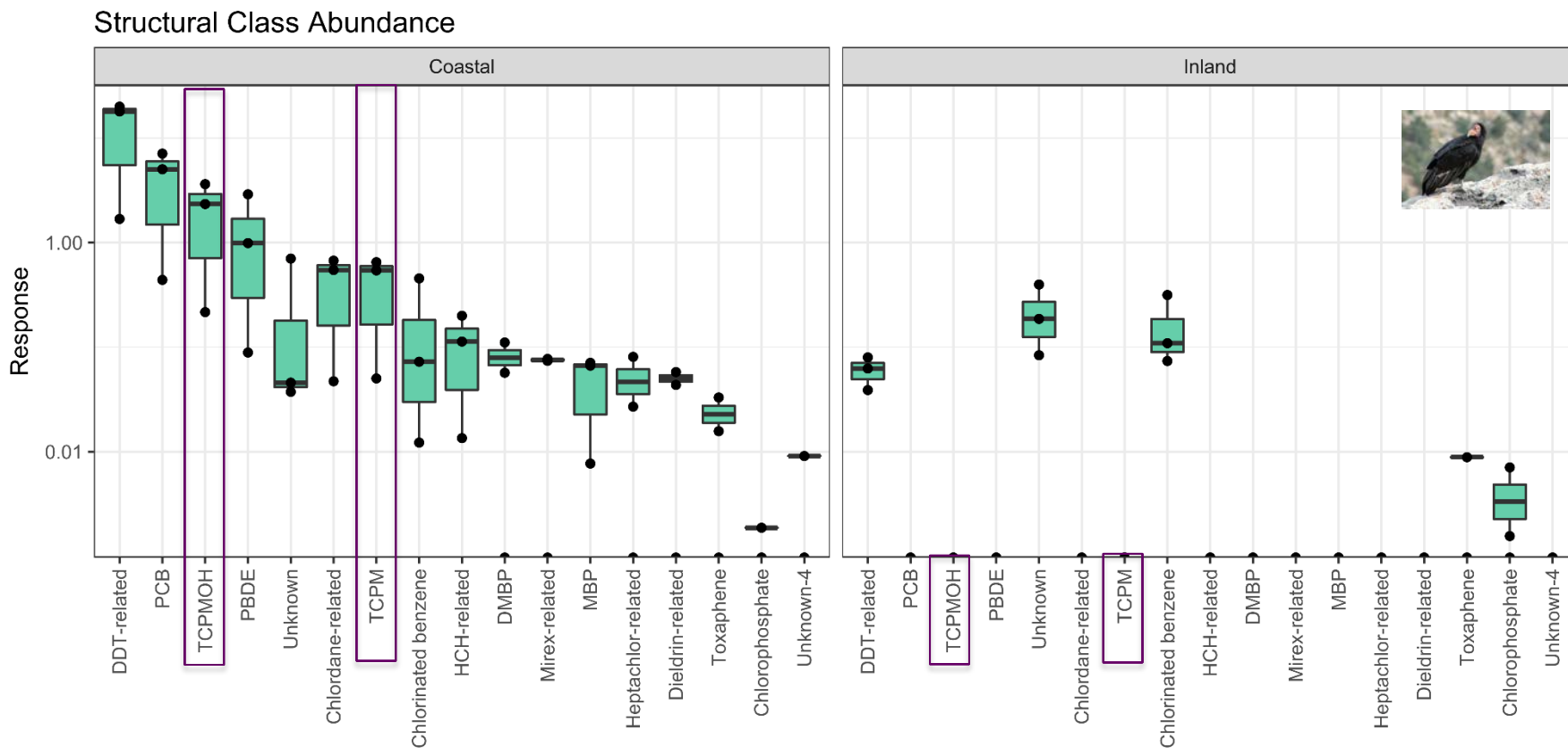
Millow et al. PLOS ONE. 2015

Black Skimmers are not top predators, but TCPM and TCPMOH were still abundant in their eggs.



# California condors (coastal vs. inland)

preliminary data: CA Sea Grant



# Non-Targeted Analysis to Characterize Trace Organics in Advanced Water Purification Facility in California

Objective: To assess the utility of non-targeted analysis (NTA) and the effectiveness of the ultraviolet (UV) advanced oxidation process (AOP)

Specific Aims

- Identify trace organic compounds in reverse osmosis permeate (ROP) and UV/AOP product water (UVP) waters collected at Advanced Water Purification Facility
- Identify organic breakdown products in UVP and compounds resistant to UV/AOP

Exploratory aim:

Compare chemical profiles in ROP and UVP source waters with tap waters collected at the facility

## Sample Collection

Sampling Dates and Triplicate Collection Times				
	Collection Time (A.M.)			
Set/Sampling date	ROP	UVP	Field Blank	Tap
<b>1, 11/03/2015</b>	10:47	10:46	10:52	--
	10:49	10:48	10:52	--
	10:50	10:50	10:53	--
<b>2, 11/17/2015</b>	9:17	9:15	9:17	10:12
	9:18	9:15	9:17	10:12
	9:19	9:16	9:21	10:13
<b>3, 1/05/2016</b>	11:29	11:28	11:34	--
	11:30	11:29	11:34	--
	11:31	11:30	11:35	--
<b>4, 1/12/2016</b>	9:26	9:24	9:29	--
	9:27	9:25	9:29	--
	9:28	9:26	9:30	--
<b>5, 1/19/2016</b>	10:56	10:52	11:00	11:16
	10:57	10:53	11:03	11:16
	10:58	10:53	11:00	11:17

## Number of Organic Compounds Found in Tap Water

<b>Sampling Event No./Date</b>	<b>Tap</b>
<b>11/17/2015</b>	<b>28</b>
<b>1/19/2016</b>	<b>29</b>

## Number of Organic Compounds Uniquely Found in Individual Sample Types

<b>Sampling Event No./Date</b>	<b>Tap</b>
<b>11/17/2015</b>	28
<b>1/19/2016</b>	29

Five compounds were detected in both sampling events and were tentatively identified

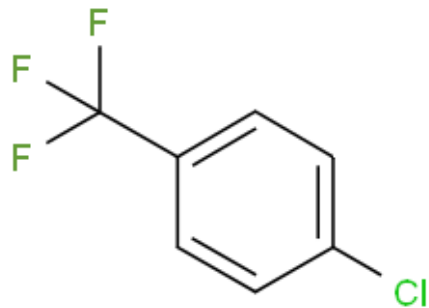


## Tap Water Detected Compound Features

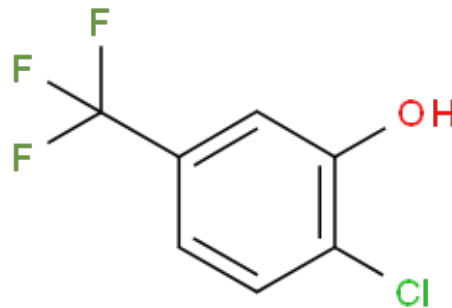
- Five compounds were detected in both sampling events and were tentatively identified. Among them, four compounds were confirmed with the authentic standards. One compound was not matched with the authentic standard.
- None of the five compounds was present either UVP or ROP Water.
- Two confirmed compounds contain halogens (chlorine and fluorine).

## Two confirmed compounds contain halogens

Parachlorobenzotrifluoride  
CAS No. 98-56-6



2-Chloro-5-(trifluoromethyl)phenol  
CAS No. 40889-91-6



# Take home messages

- Non-targeted screening for halogenated organic compounds (HOCs) in sentinel species can provide a list of bioaccumulative/biomagnifying HOCs to be examined in human biomonitoring.
  - DDT degradation products
- Unexpected/neglected but abundant HOCs found in CA coast marine species: TCPM and TCPMOH should be examined in CA population
- Monitoring implication: Non-targeted screening of HOCs in tap water (drinking water)
  - Tap water in different regions/seasons and bottled water

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- California State University Program for Education and Research in Biotechnology
- EPA STAR fellowship

# Acronyms

- HOCs: halogenated organic compounds
- PCB: polychlorinated biphenyl
- DDT: dichlorodiphenyltrichloroethane
- DDE: dichlorodiphenyldichloroethene
- DMBP: 1,1'-dimethyl-2,2'-bipyrrrole
- MeO-BDE: methoxy brominated diphenyl ether
- MBP: 1'-methyl-1,2'-bipyrrrole
- PBHD: polybrominated hexahydroxanthene derivative
- TCPM: tris(chlorophenyl)methane
- TCPMOH: tris(chlorophenyl)methanol