EXPOSURE OF CALIFORNIA PEREGRINE FALCON (*FALCO PEREGRINUS*) TO BROMINATED FLAME RETARDANTS (PBDES AND ALTERNATIVES)

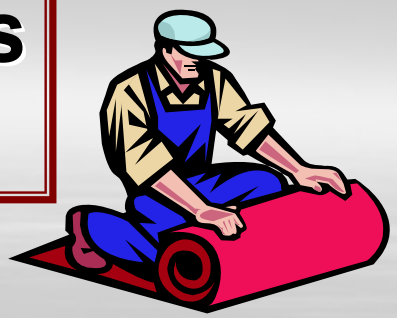
June-Soo Park[1], Arthur Holden[1], Vivian Chu[1], Seth D. Newsome[2], R. William Henry[3], Alexandra Rhee[1], Puja Patel[1], Michele Kim[1], Allison Fong[1], Janet Linthicum[3], Karen McKeown[4], Miaomiao Wang[1], Kim Hooper[1]

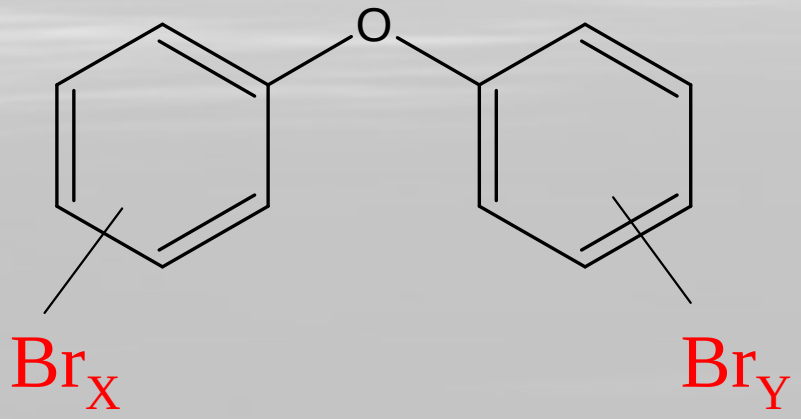
[1]California Environmental Protection Agency, Berkeley, CA 94710, USA
[2]Carnegie Institution for Science, Washington, DC 20015, USA
[3]Long Marine Laboratory, University of California-Santa Cruz, CA 95060 USA
[4]Division of Biostatistics, School of Public Health, University of California-Berkeley, Berkeley, CA, 94707, USA

OUTLINE

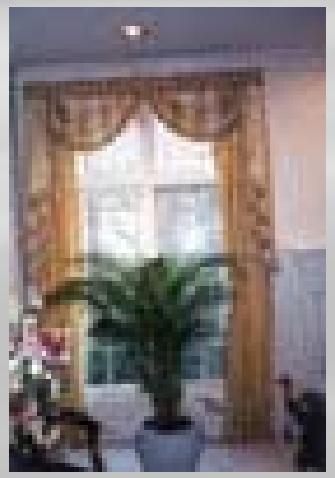
- PBDEs and Deca (BDE-209)
- Study of Peregrine Falcon Eggs:
  - Design
  - Methods
  - Results (Level, Time Trend, Profile)
- “Peregrine Hypothesis”: Prey & Isotope
- Evidence for BDE-209 Debromination
- Alternative BFRs

Polybrominated Diphenylethers (PBDEs): Flame Retardant





- Consumer products
- Not bound
- Indoor contaminant



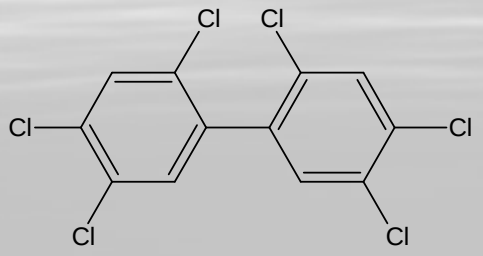
Properties

Tetra-BDE ➔➔➔ Deca-BDE

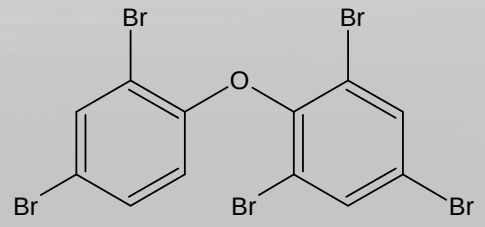
↓ Lipophilicity ➔➔➔ ↓ Uptake

↓ Stability ➔➔➔ ↓ $t_{1/2}$

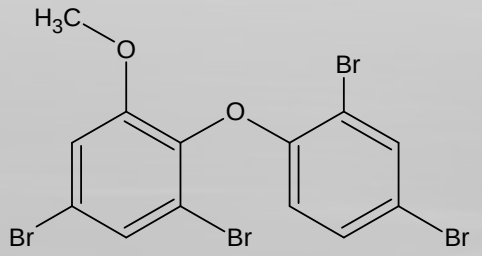
Structural Similarity of PBDEs, Their Metabolites and Environmental Derivatives to Thyroid Hormone



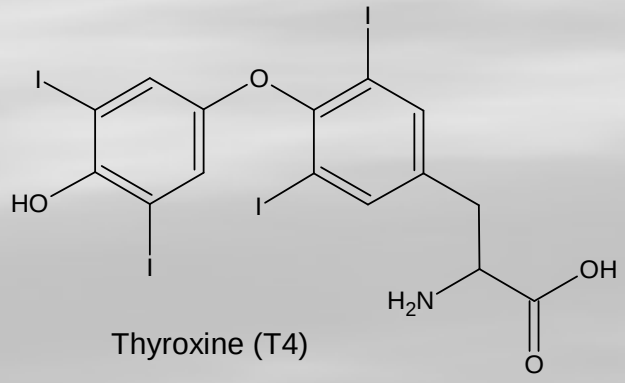
2,2',4,4',5,5'-hexachlorobiphenyl
(PCB-153)



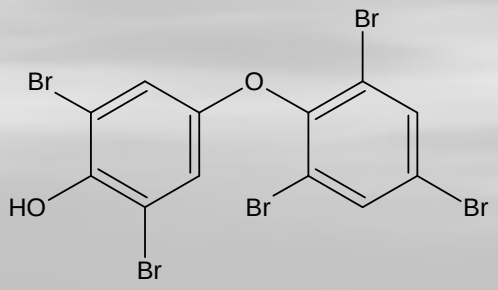
2,2',4,4',6-pentabromodiphenylether
(PBDE-100)



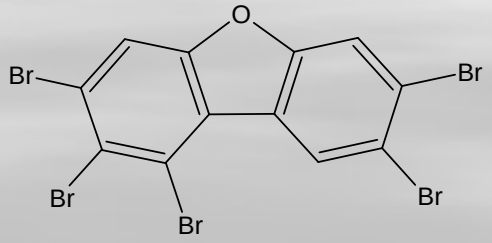
2-(2',4'-dibromophenoxy)-4,6-dibromoanisol
(methoxy-PBDE)



Thyroxine (T4)



4-(2',4',6'-tribromophenoxy)-2,6-dibromophenol
(hydroxy-PBDE)



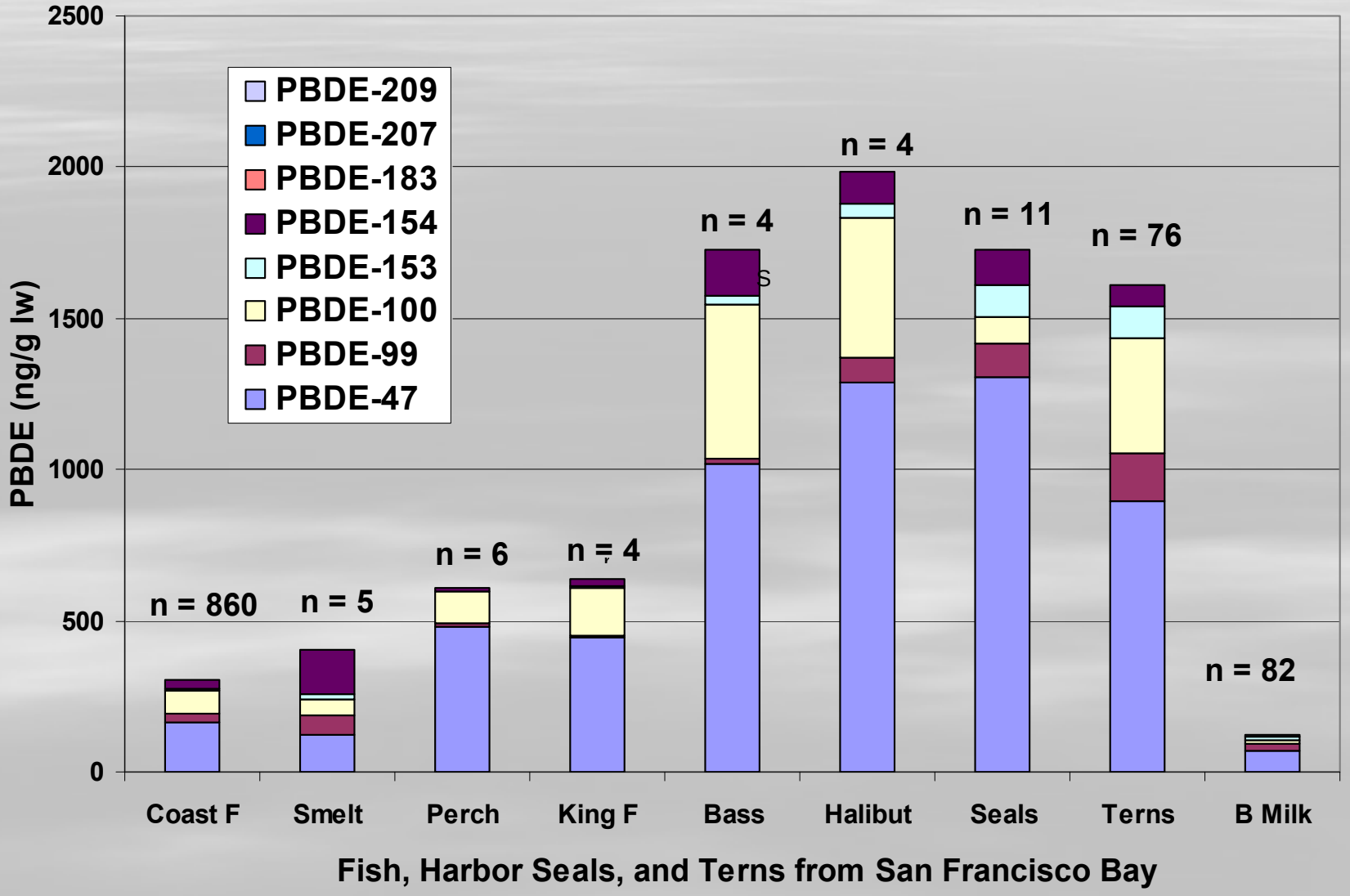
2,3,4,7,8-pentabromodibenzofuran
(PBDF)

PBDEs in the AMERICAS

PBDE Technical Mixture	M lbs/yr 2001	Product Uses
Penta† *	15.6 (25%)	Furniture (foam cushions)
Octa*	3.3 (5%)	Electronics (ABS plastics, cable)
Deca††	65 (70%)	Electronics (HIPS plastics, textiles)

† High bioaccumul †† Major PBDE * Banned BSEF, 2003

Aquatic Food Web PBDE Patterns: California Coastal and San Francisco Bay Fishes (2001-2003), Harbor Seals (1989-98), and Forster's Terns (00-03)



Top predator
Long life
Stable nest
Strong pair-bond
Clutch size
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Study Design

- Peregrine Recovery Program (UCSC)
- CA: 90 eggs (57 birds) + 7 chicks
- Cross-section: 42 locales
- Collection period: 21-year (1986-2007)
- Time-series nests: 20 nests, 56 eggs
- Prey data: 27 nest-year overlaps (feather & bone remains)

Sample Preparation

4 Steps:

- **Lyophilization**
- **Accelerated solvent extraction (ASE200)**
- **Fat determination (gravimetric)**
- **Clean-up (acid-, base-, and neutral-silica gel, and gel permeation chromatography)**

Batch size = 12 slots

(9 samples + Duplicate + Blank + Pos Cntl)

Sample Analysis

- Isotope dilution / HRGC-HRMS (MAT95)

  81 PCBs: report 12 (70% total mass)

  18 PBDEs:

  3 nonas (206-, 207-, 208-BDE)

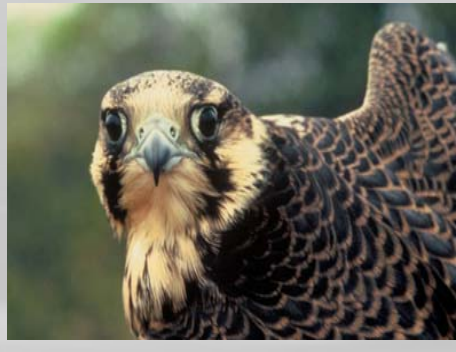
  5 octas (196-,197-,201-,202-,203-BDE)

- Prey Analysis: feathers & bones → 185 species → 15 categories based on diet
- Stable Isotope Analysis: $\delta^{13}C$, $\delta^{15}N$, and δD

High PBDE Levels

- **Among highest in world for biota: ppm**

	Max	Mean
$\sum_{18}$PBDEs	94 ppm	9 ppm
BDE-153	29 ppm	3 ppm
BDE-183	8 ppm	1 ppm
BDE-209	4 ppm	0.5 ppm



$\sum$PBDEs = ~5-20 ppm:

Neurodevelopmental toxicity in rats

Impaired reproduction, brood, growth size in raptors (e.g., kestrel & peregrine falcon)

(Meerts et al 2000, Fernie et al, 2007, Johansson et al 2008)

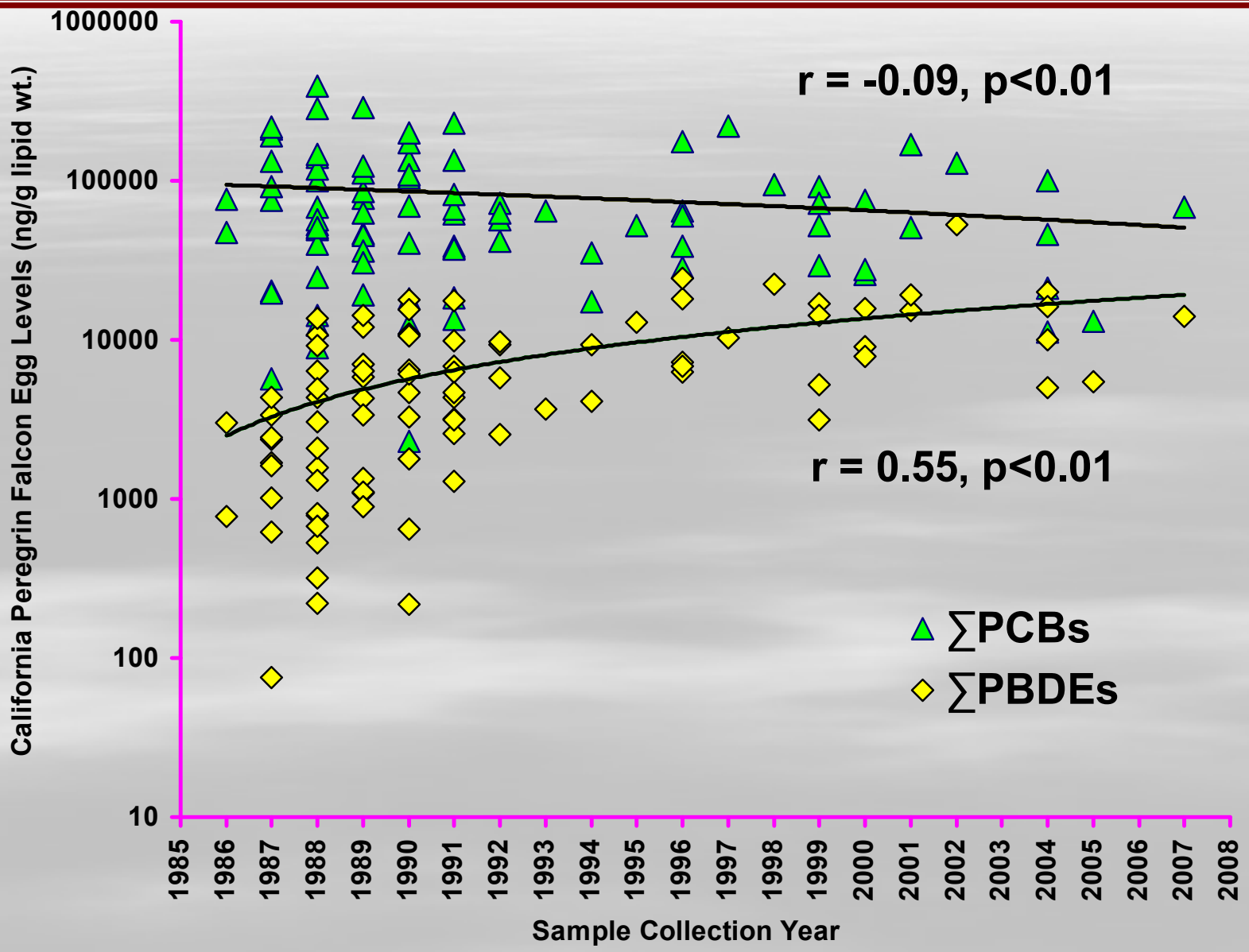
PCB Levels: Higher

- Among highest in world for biota
- 5-10 X higher than PBDEs

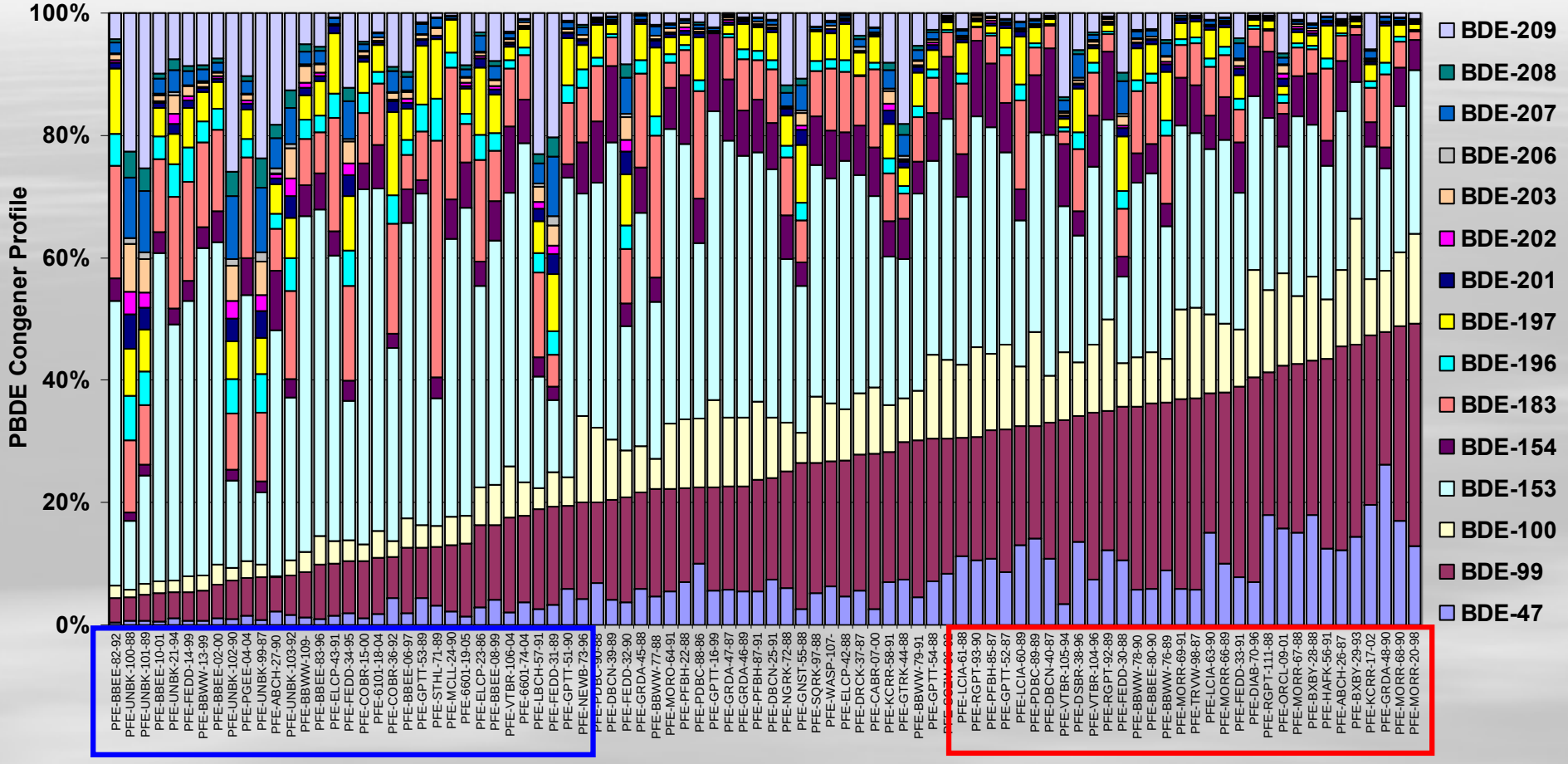
	Max	Mean
$\sum_{12}$PCBs	761 ppm	84 ppm
PCB-153	58 ppm	28 ppm

- 30 years after ban on PCBs
- 300 ppm DDT = eggshell thinning

∑PBDEs = X2/decade , ∑PCBs = ↓(?)



“Big City” Peregrines: Higher Brominateds



"Big City" ← → **"Coastal"**

Median ∑PBDEs = 10.5 ppm
Median BDE-209 = 1.04 ppm

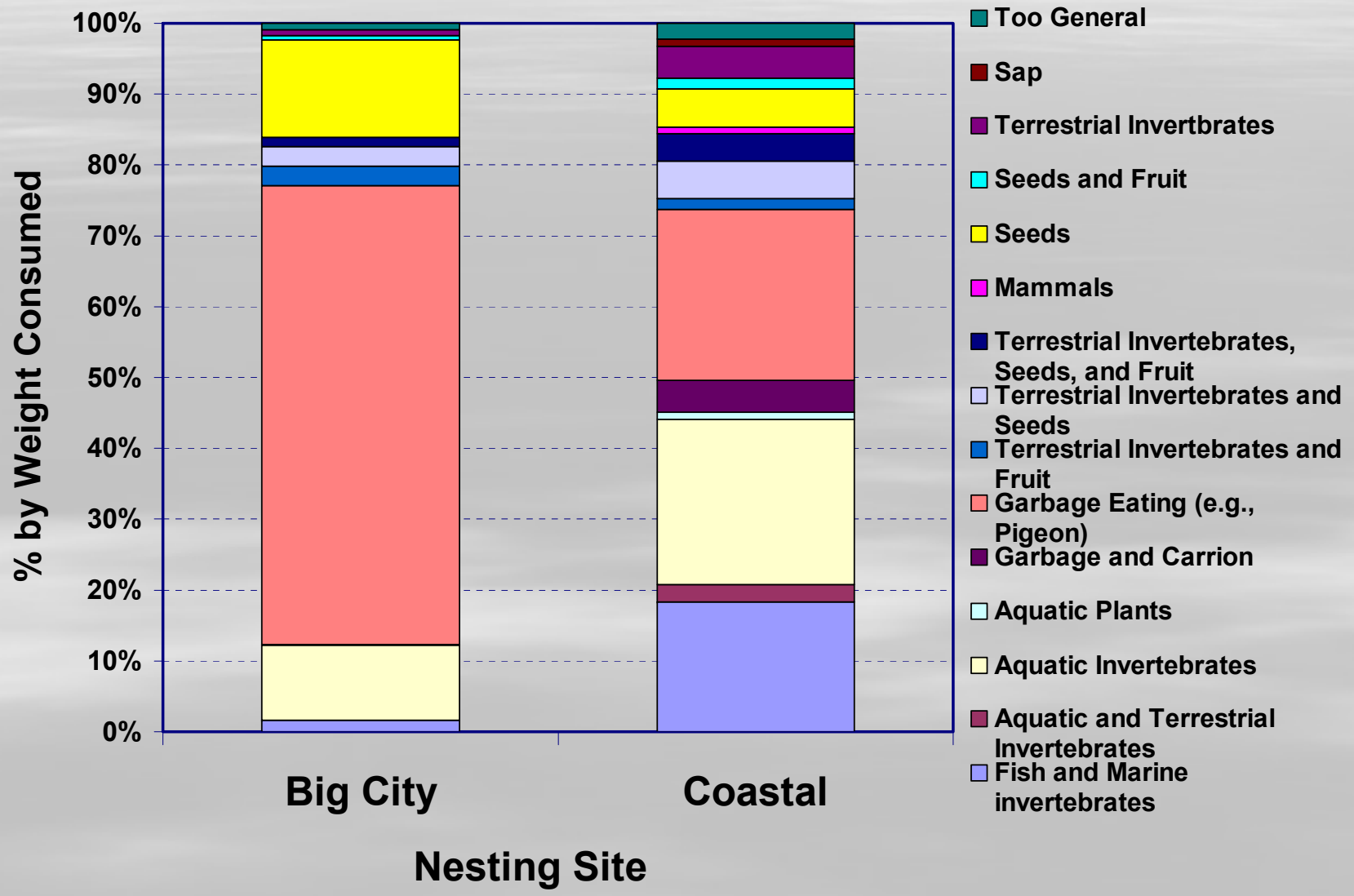
Median ∑PBDEs = 2.45 ppm
Median BDE-209 = 0.03 ppm

Why “Coastal” vs “Big City” Peregrines show “Aquatic” vs “Terrestrial” Patterns?

Hypothesis:

“Coastal” nesting peregrines eat marine/coastal prey and “Big City” nesting peregrines eat “Big City” prey

“Big City” Peregrines Eat “Big City” Diet

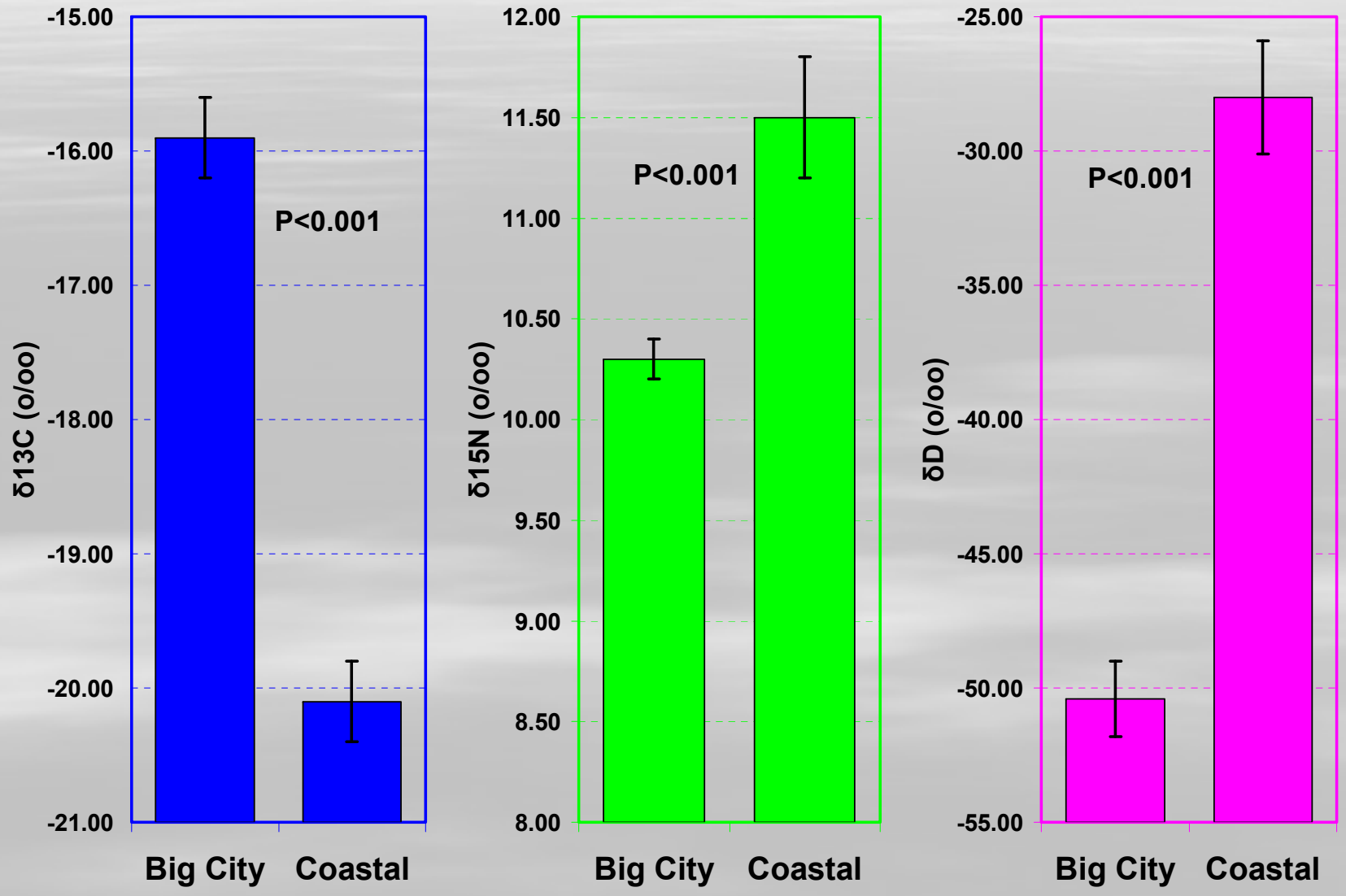


Rare Heavy Isotope ($\delta^{13}C$, $\delta^{15}N$, δD): Marine vs Terrestrial Ecosystem

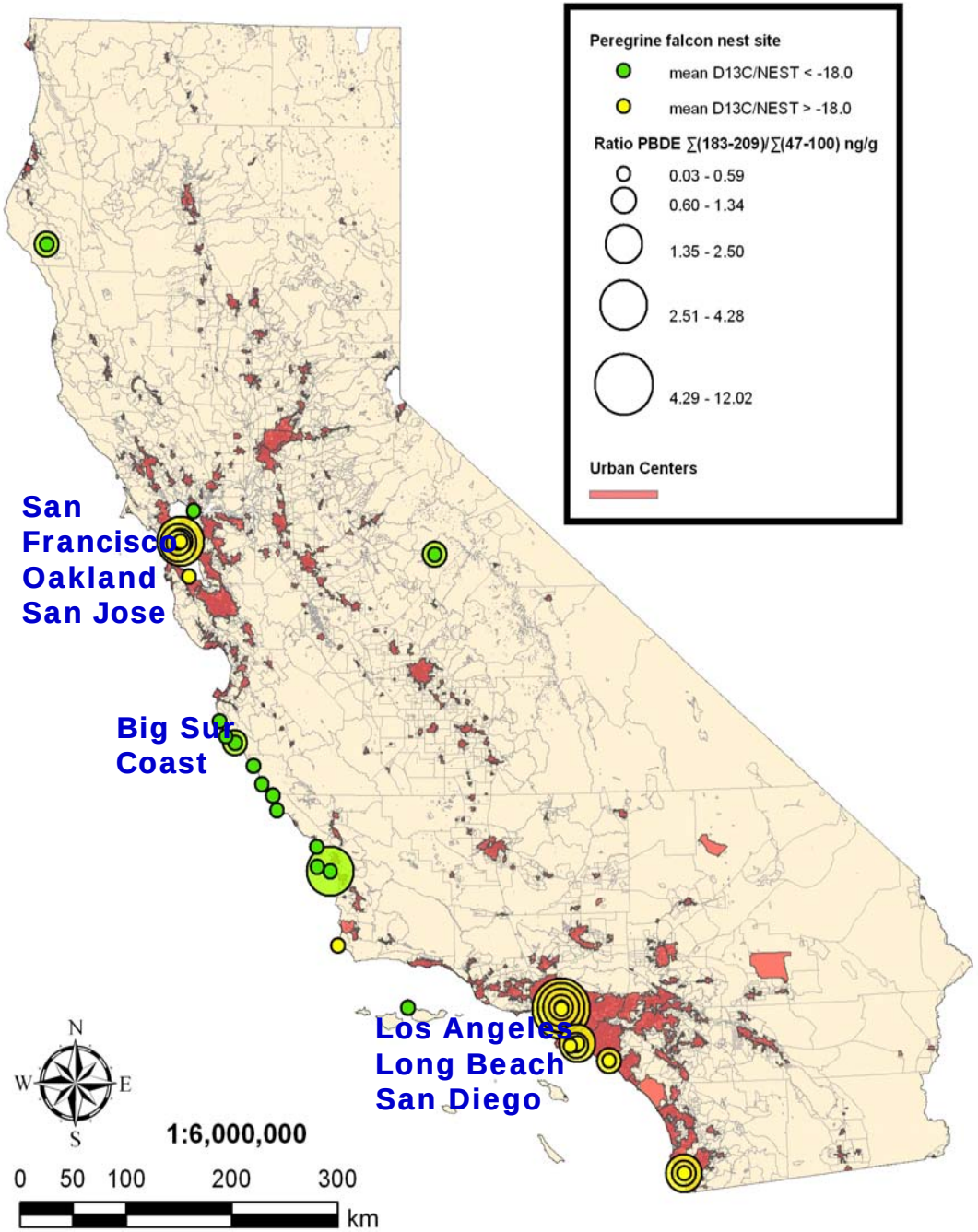
Isotope	Typical Pattern in California	Predictors
$\delta^{13}C$	Terrest < Marine	Diet (C3 vs. C4 Plants)
$\delta^{15}N$	Terrest < Marine	Trophic levels
δD	Terrest < Marine	Water (Rain vs. Ocean)

Personal comunication with Dr. Seth Newsome

“Big City” Peregrine → “Human Diet”?



High Bromnated PBDEs in Relation to $\delta^{13}C$ and Urban Area



“Deca-BDE: A Major FR in CA”

↓

High levels of BDE-209 Accumulated in Urban Ecosystem

↓

High Brominated (Hexa---Nona)

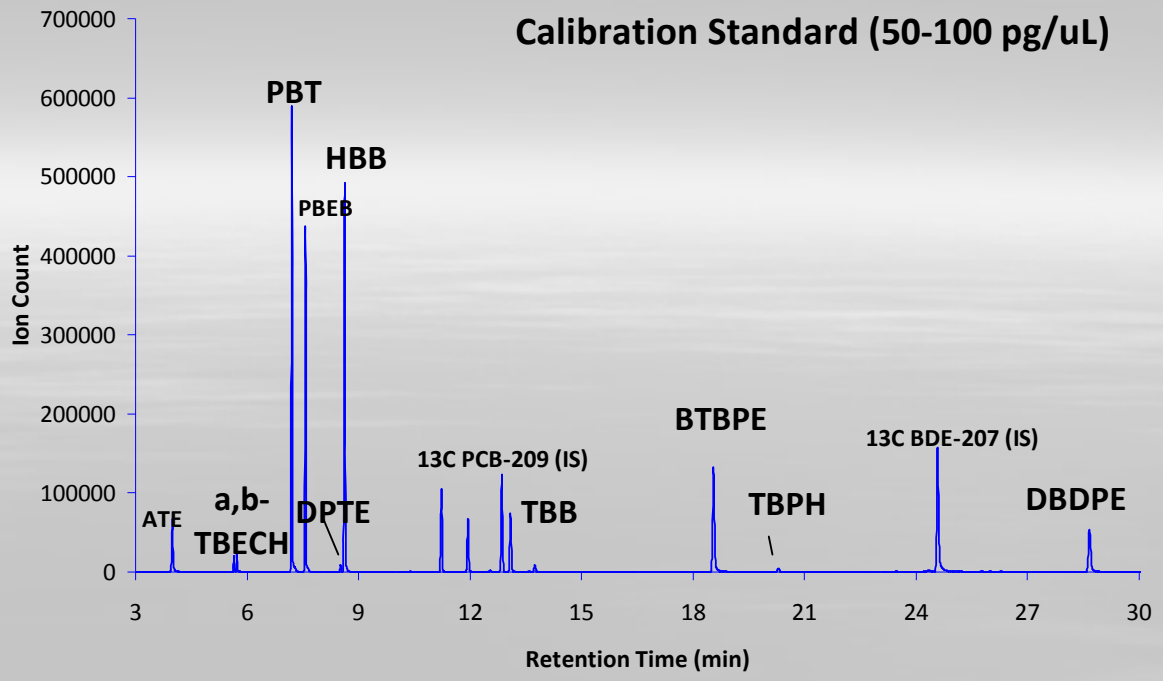
↓

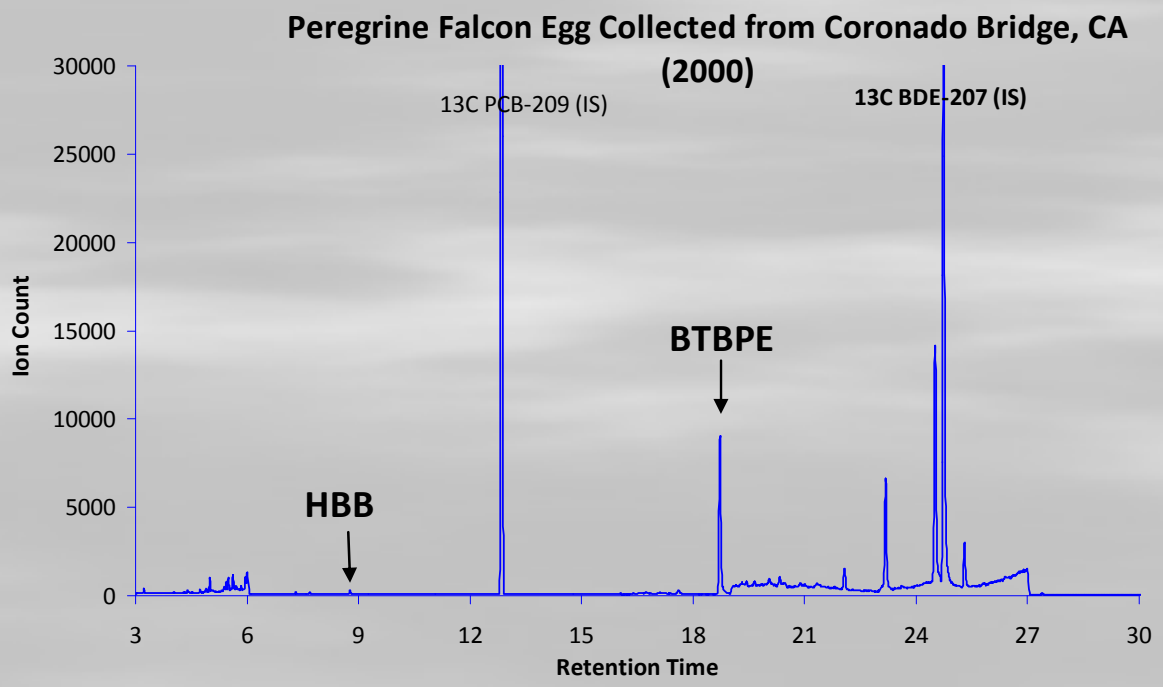
Low Brominated (Tetra---Penta) “More Toxic”

Evidence for Biological Debromination of Deca (BDE-209): Unusual PBDE Patterns

- High BDE-209 in "Big City" eggs → High Nona, Octa, Hepta PBDEs → High BDE-153
- Changing PBDE patterns over time in Time Series Birds
- Profiles of Nona, Octa, Hepta in Egg PBDEs ≠ "Deca", "Octa" commercial mixtures
- Egg PBDEs ≠ "weathered" mixtures (e.g., sediment, sludge, dust)

New Alternative BFRs





Conclusion & Future Work

- The old / new BFRs come out of products
- "Big City" = Greater exposure to BDE-209
- "Big City" peregrines eat "Big City" diet
- BDE-209 = Bioavailable & Breakdown
- Alternative BFRs = Bioavailable
  Breakdown (?)
- Continue to develop data sets on the sources and pathways of exposure to these classic / new BFRs

Acknowledgements

The many ornithologists and bird enthusiasts who have enabled the US peregrine populations to survive DDT-induced egg-shell thinning and reproductive failure in the mid-1950s-60s, and to restore the California breeding pair population from a low of 2 known to >200 over the past thirty years.

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