Contaminants of Emerging Concern: An Update on RMP Activities

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2009
RMP Annual Meeting
Sediments: Past a Tipping Point

Regional Monitoring Program
for Water Quality in the San Francisco Estuary

RMP Emerging Contaminants Workgroup

Priority Question:

What CECs have the greatest potential to adversely impact beneficial uses in the Bay?

Chemical Screening

↓

Pilot Study

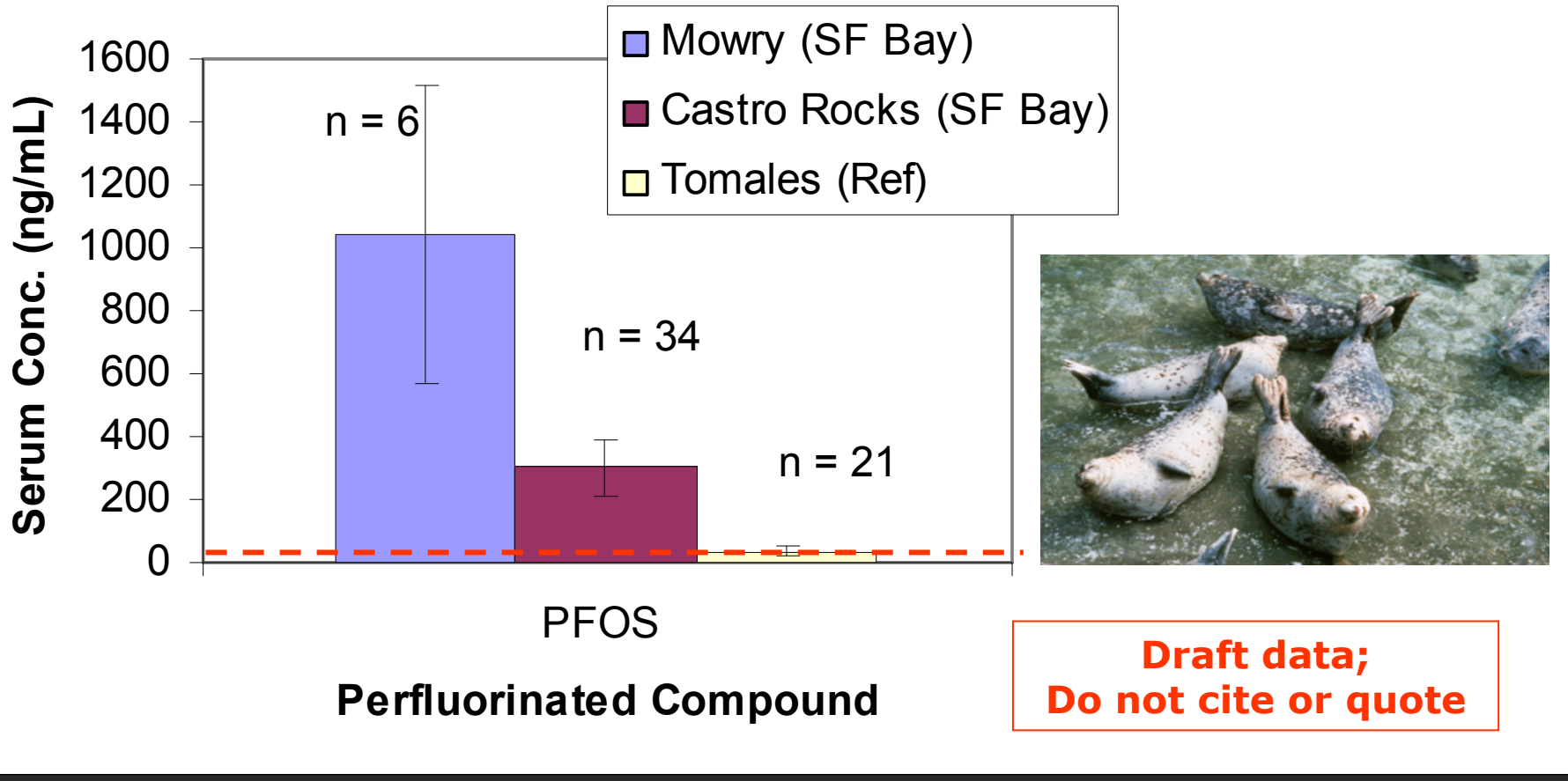
↓

Status and Trends Annual Monitoring

CEC Efforts by the RMP (2003-2009)

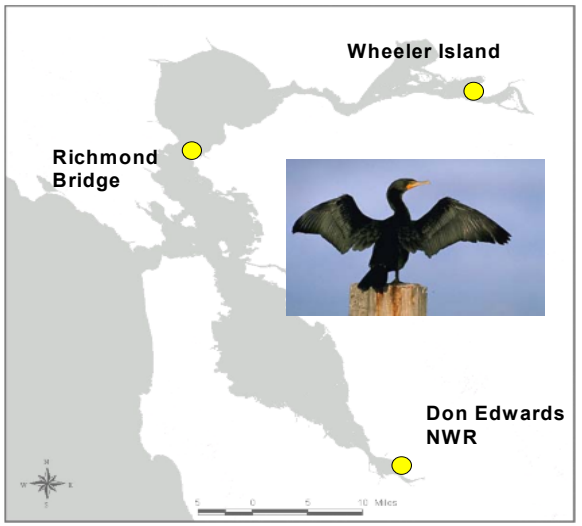
- Screening of Bay samples for previously unknown organic contaminants (2003)
- South Bay Pharmaceutical Study (2006-2007)
- Perfluorinated compounds (2007-2009)
- Chlorinated paraffins (2008)
- Triclosan (2008)
- Pyrethroid pesticides (2008)
- Alternative flame retardants (2008-2009)

High Concentrations of Perfluorooctane Sulfonate (PFOS) in South Bay Harbor Seals



Mean of US population in 2003-2004 (NHANES) : ~20 ng/ml

PFOS in Bird Eggs is a Concern



PFOS (ng/g wet weight)

1800
1600
1400
1200
1000
800
600
400
200
0

Predicted No Effect Concentration (PNEC)

Draft data;
Do not cite or quote

Northern Fulmar	Ring-billed gull	Glaucus gull	Herring Gull	Guillemot	Guillemot	Night heron	Parrot bill	Cormorant	Cormorant	Cormorant	Cormorant	Cormorant
Faroe Island	Lake Huron	Artic Norway	Norway	Baltic sea	Sweden	China	Korea	Manitoba	Lake Winnipeg	SF Bay Wheeler Island	SF Bay Don Edwards	SF Bay Richmond Bridge

Why do we 'need' flame retardants?

CA furniture flammability standard (TB 117, 1975)

CA mattress/futon/boxspring flammability standard (2005)

CA bed clothing flammability standard (pending)

National mattress flammability standard (2007)

National furniture flammability standard (in development)

Other electronics standards (current and proposed)






Regulatory Status of Polybrominated Diphenyl Ethers (PBDEs)

PBDE Mixture	Primary Application	Regulatory Status
Penta-BDE	Polyurethane Foam	Banned in EU (2004) Production ceased (2004) Banned in CA (2006) Stockholm Convention (2009)
Octa-BDE	Thermoplastics	Banned in EU (2004) Production ceased (2004) Banned in CA (2006) Stockholm Convention (2009)
Deca-BDE	Thermoplastics	Banned in Sweden, WA, ME, VT, OR (2006-2009) Banned in EU (2008)

Because of flammability standards, alternatives are inevitable

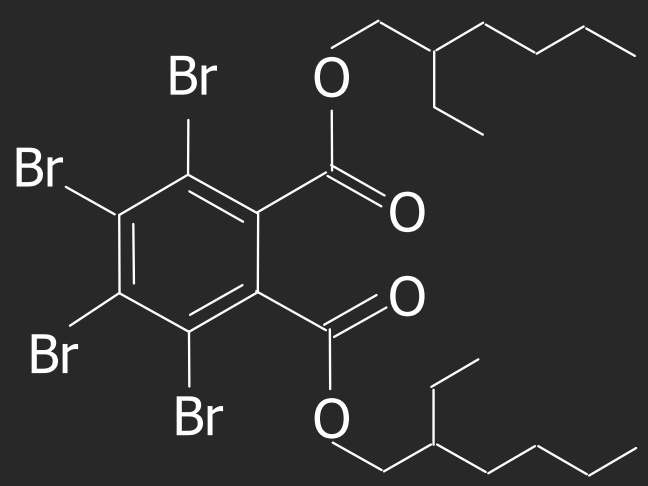
What's in my couch?

My couch
(purchased June 2007)

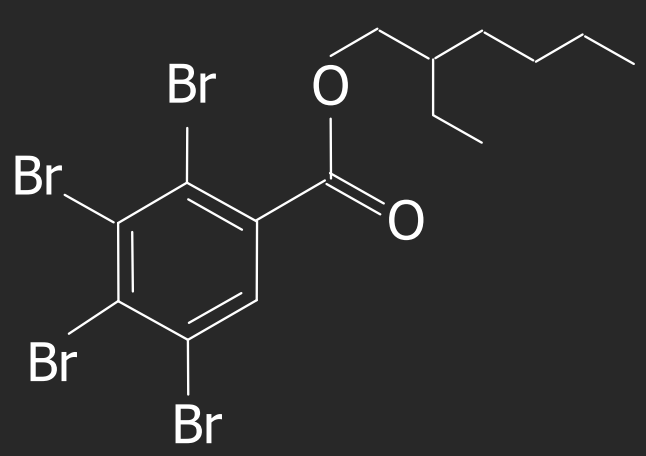
Arlene Blum with XRF

(Photo: Barry Bergman, UC Berkeley News)

Brominated chemicals in Firemaster® 550 (and my couch)



Di(2-ethylhexyl)-
tetrabromophthalate
(TBPH)



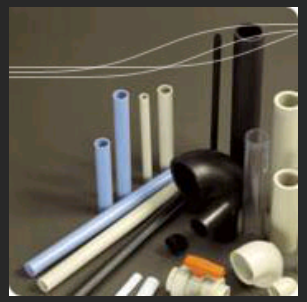
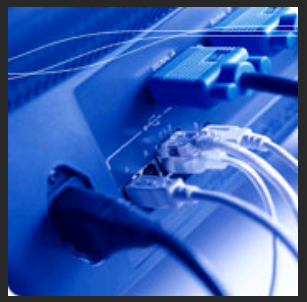
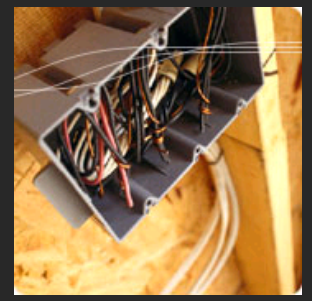
2-ethylhexyl-
2,3,4,5-tetrabromobenzoate
(TBB)

What else do we know about TBPH?

- 1-10 million lbs/yr produced in US since 1990

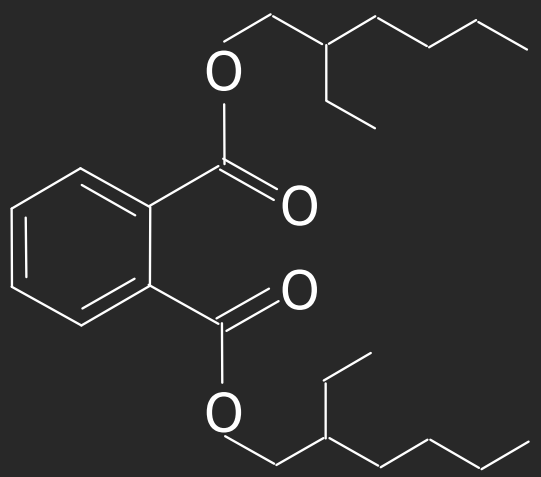
Applications

- polyurethane foam
- PVC adhesives, coatings, elastomers
- conduit, transport, building, power, appliance cables
- textiles

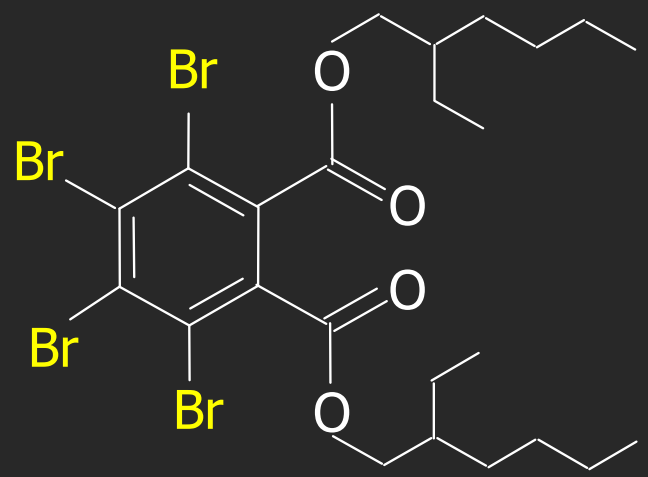
- In US house dust: 10X < PBDEs (Stapleton et al 2008)

TBPH is the brominated cousin of DEHP



Di(2-ethylhexyl) phthalate
(DEHP)

- Moderately persistent
- Bioaccumulative
- Reproductive, developmental toxin; carcinogen



Di(2-ethylhexyl)
tetrabromophthalate
(TBPH)

- Persistent?
- Bioaccumulative?
- Toxic?

Alternative Flame Retardants in San Francisco Bay

Objective:
Measure alternative flame retardants in sediments and wildlife

Samples analyzed:
Sediments (n=11, 2007)
Mussels (n=10, deployed 2008)
Sport fish (shiner surfperch and white croaker, n=14, 2006)
Harbor seal blubber (pups n=15, adults n=5, 2007-2008)
Cormorant eggs (one site, n=3 composites of 21 eggs, 2008)

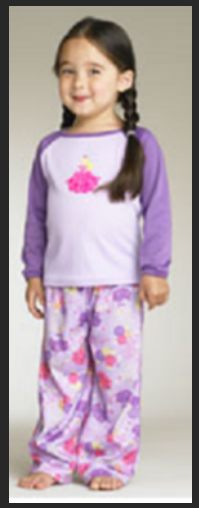
Concentrations of alternatives were lower than PBDEs

PBDEs	Detected
Hexabromocyclododecane (HBCD)	Detected
Pentabromoethylbenzene (PBEB)	Detected
Dechlorane Plus®	Detected
Di(2-ethylhexyl) tetrabromophthalate (TBPH)	Not detected
Tetrabromobenzoate (TBB)	Not detected
Decabromodiphenylethane (DBDPE)	Not detected
1,2-Bis(2,4,6 tribromophenoxy)ethane (BTBPE)	Not detected
Hexabromobenzene (HBB)	Not detected
Tetrabromobisphenol-A (TBBPA)	Not yet analyzed

Effects of long-term exposure to low concentrations unknown

‘Chlorinated Tris’
aka tris(1,3-dichloro-2-propyl) phosphate or TDCPP

- Phased out of use in children’s sleepwear in late 1970s



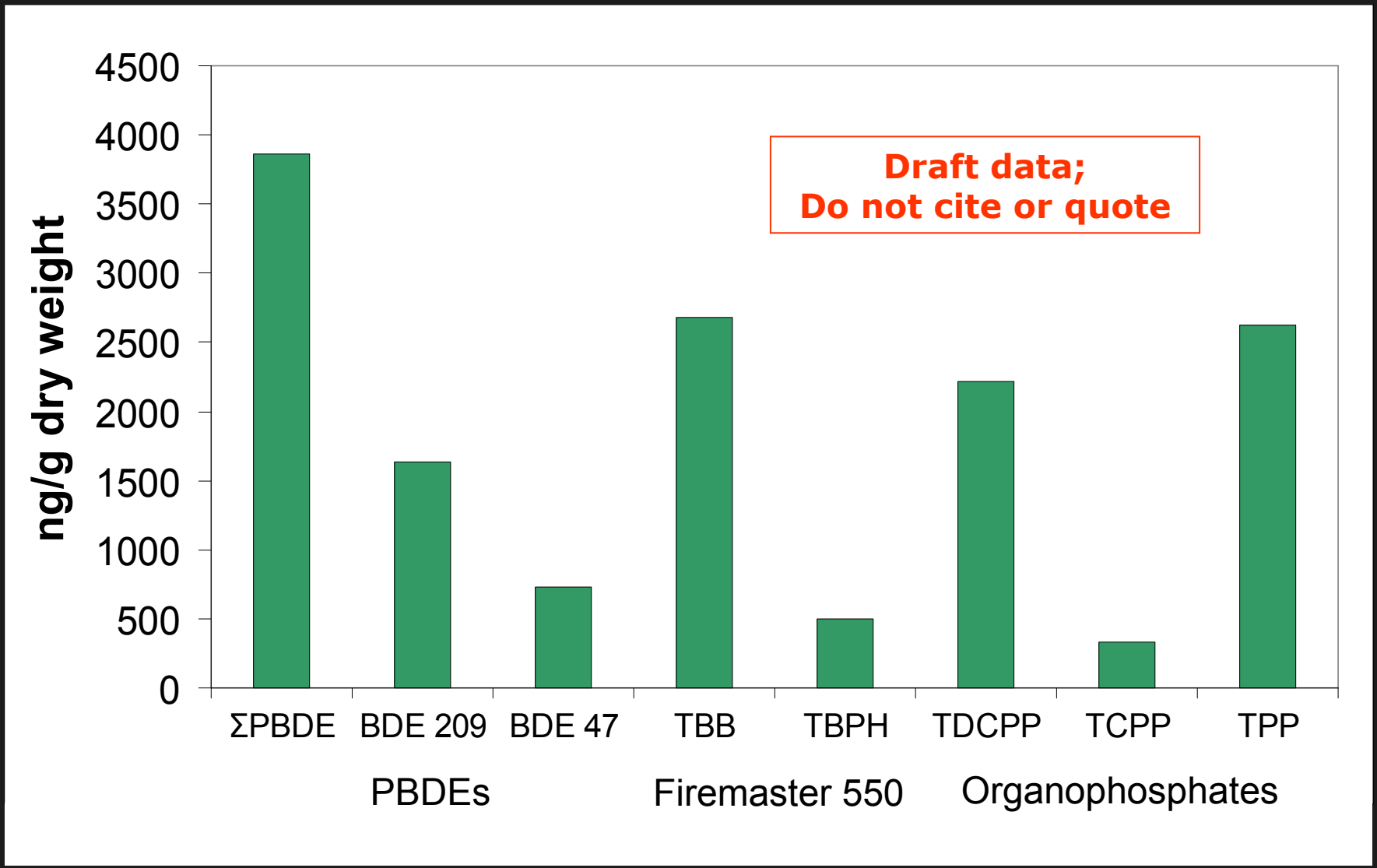
Another Flame Retardant, Tris-(1,3-Dichloro-2-Propyl)-Phosphate, and Its Expected Metabolites Are Mutagens

Abstract. *A flame retardant used in children's sleepwear, tris-(1,3-dichloro-2-propyl)phosphate (Fyrol FR2) is a mutagen in the* Salmonella*-mammalian tissue homogenate test after it has been activated by mouse or rat liver homogenate. The expected enzymatic hydrolysis product, 1,3-dichloro-2-propanol, is similarly a mutagen after activation by liver homogenate. A proposed metabolite of the flame retardant, 1,3-dichloro-2-propanone, is a potent mutagen in the absence of such activation. A flame retardant with similar structure, tris-(2,3-dibromopropyl)phosphate (tris-BP), was shown previously to be a mutagen, to cause sterility in animals, to be a carcinogen, and to be absorbed through human skin. These and other flame retardants have characteristic nuclear magnetic resonance spectra that can be used to determine which flame retardant is present in commercially purchased sleepwear. Sleepwear treated with tris-BP, Fyrol FR2, and other chemical additives was being sold in late 1977.*

Gold et al 1978 Science

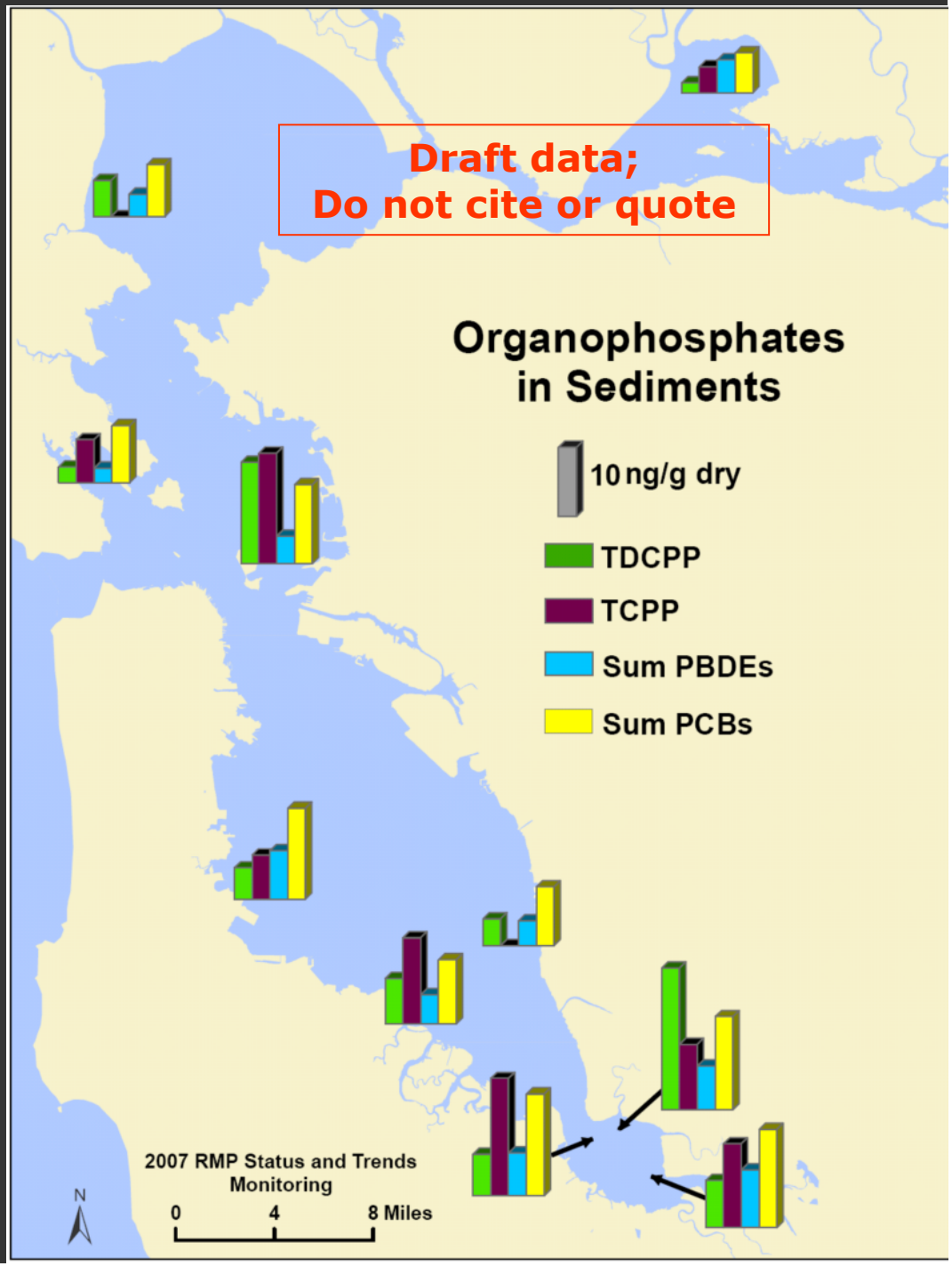
- Uses: polyurethane foam, plastics, resins, textiles
- In US furniture foam (1-5% by weight) (Stapleton et al 2009)
- US house dust concentrations similar to PBDEs (Stapleton et al 2009)
- Probable carcinogen; absorbed by humans; reproductive & developmental hazard
- 10-50 million lbs produced/imported in US in 2006

Flame Retardants in Biosolids from a Bay Area WWTP



Phosphates are comparable to PBDEs, PCBs in sediment

- TDCPP, TCPP not detected in seals or cormorant eggs
- 1-2 orders of magnitude below draft PNEC (Europe)
- Effects of chronic low level exposure largely unknown

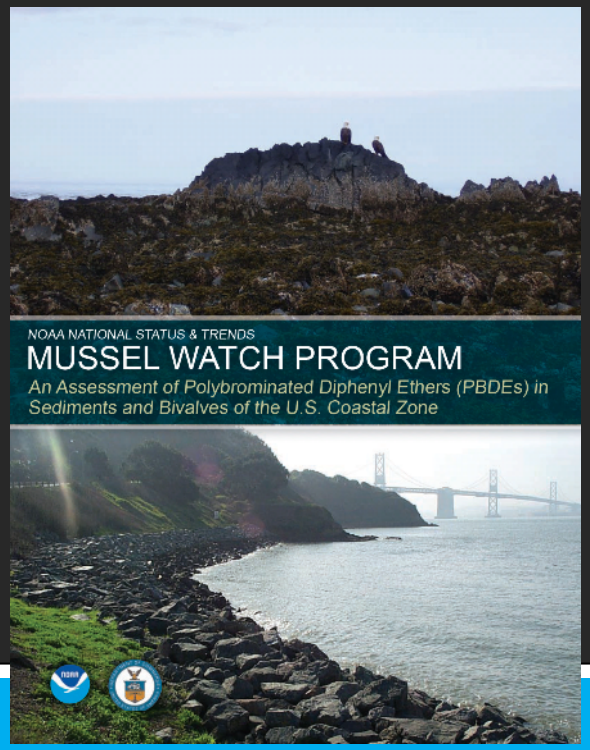


Do we need flame retardant chemicals added to our furniture foam?

- No evidence that TB 117 is effective in preventing fire deaths
- CA Senate Bill 772- would exempt strollers, high chairs, nursing pillows, bassinets from CA foam flammability standard (pending 2010 Senate vote)
- Alternatives?
  - control ignition sources (fire-safe cigarettes, candles)
  - non-halogenated, non-toxic chemicals
  - barrier technology; inherently flame retardant materials
- CA Green Chemistry Initiative

Current Activities with CECs

- White paper on potential impacts of wastewater chemical contaminants
- Sources of perfluorinated compounds to the Bay
- Workshop on management of CECs in California
- NOAA Mussel Watch Program CEC list; CA pilot study
- Brominated dioxins study
  - collaboration with AXYS Analytical



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