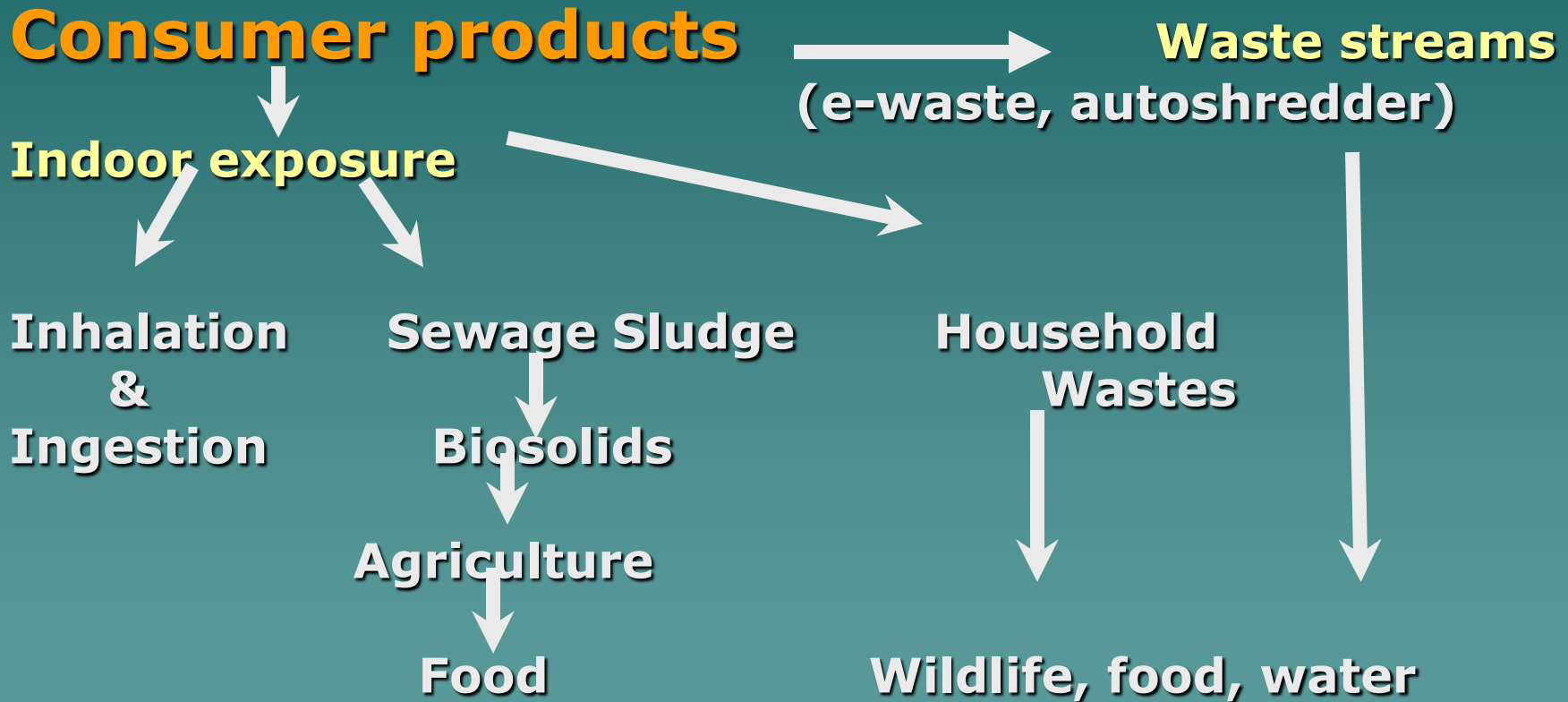


***BFRs, CFRs, PFRs:
Where are we with the Toxic Alphabet Soup?***

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Environmental Chemistry Laboratory
California Department of Toxic Substances Control



Major PBDE Exposure Pathways



PBDEs in CA

- Use of Penta-BDEs (furniture) and Octa-BDEs (electronics) restricted after 2006;
 - Deca-BDE unrestricted
 - No enforcement
-
- What are the levels of PBDEs after the ban?
 - What are the replacement FR to meet CA TB117?

PBDEs in CA

- Still highest levels of PBDEs in humans, cats, wildlife, dust
- PBDE metabolites cross the placenta (cord blood, fetal liver)

Park et al. 2010; 2011; Zota et al. 2011; Petreas et al. 2011; Tarrant et al. 2011; Guo et al. 2012



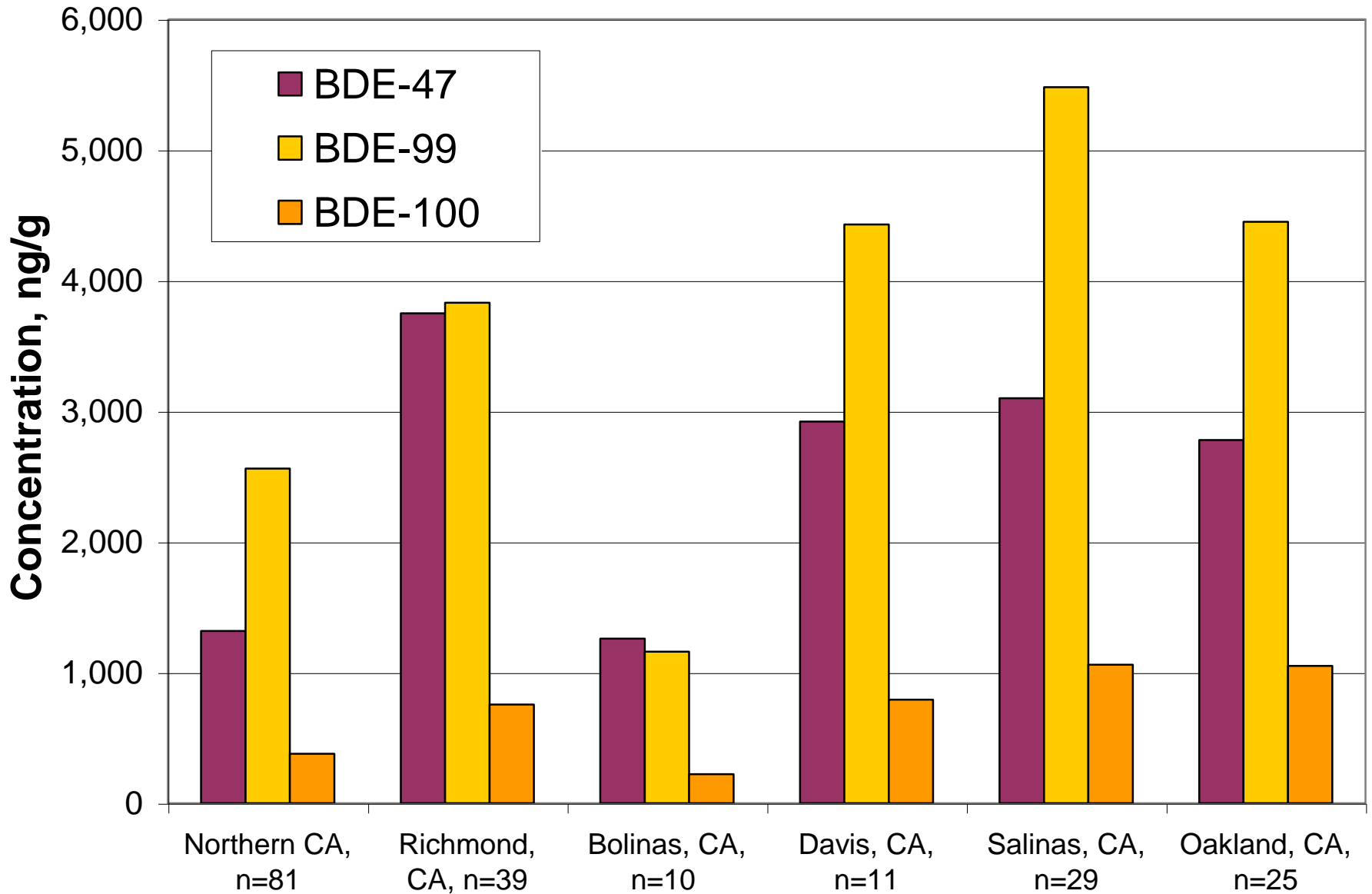
PBDEs in Dust

Whitehead et al. 2011

Household Dust (UCB Childhood Leukemia Study)

- Vacuum cleaner dust from 204 houses sampled twice (2001-07 and 2010)
 - No statistically significant decrease in Penta- or Deca-BDEs; some decrease in Octa-BDEs (preliminary data, n=52)
 - Reflecting different use patterns?
 - Evidence of Deca-BDE debromination
 - Expanded analysis to measure new BFRs
- **PBDEs may persist in residential dust for many years after their production has ceased**

PBDEs in Dust from CA



Are PBDEs an EJ problem?

- Evidence from dust:
 - Richmond > Bolinas 2006 (*Zota et al, 2008*)
 - Low SES (Salinas, Oakland) highest levels in CA (*Quirós-Alcalá, 2011*)
- Evidence from Biomonitoring:
 - NHANES: Blacks, Mex Am > Whites (*Sjodin et al. 2008*)
 - NHANES: Income inversely related to levels (*Zota et al. 2008; 2010*)
 - PBDEs in blood of 6-8 yr old girls from CA > OH; and Blacks > Whites (*Windham et al. 2010*)

If PBDEs are now phased out, what are their replacements?

Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products

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[‡]San Francisco Estuary Institute, Oakland, California, United States

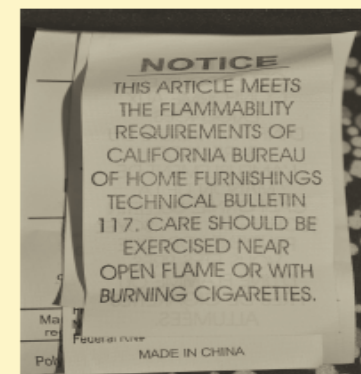
[§]East Bay Municipal Utility District, Oakland, California, United States

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[⊥]Department of Chemistry, University of California, and Green Science Policy Institute, Berkeley, California, United States

S Supporting Information

ABSTRACT: With the phase-out of PentaBDE in 2004, alternative flame retardants are being used in polyurethane foam to meet flammability standards. However, insufficient information is available on the identity of the flame retardants currently in use. Baby products containing polyurethane foam must meet California state furniture flammability standards, which likely affects the use of flame retardants in baby products throughout the U.S. However, it is unclear which products contain flame retardants and at what concentrations. In this study we surveyed baby products containing polyurethane foam to investigate how often flame retardants were used in these products. Information on when the products were purchased and whether they contained a label indicating that the product meets requirements for a California flammability standard were recorded. When possible, we identified the flame retardants being used and their concentrations in the foam. Foam samples collected from 101 commonly used baby products were analyzed. Eighty samples contained an identifiable flame retardant additive, and all but one of these was either chlorinated or brominated. The most common flame retardant detected was tris(1,3-dichloroisopropyl) phosphate (TDCPP; detection frequency 36%), followed by components typically found in the Firemaster550 commercial mixture (detection frequency



What are the PBDE replacements?

Baby products contained: *(Stapleton et al. 2011)*

- PBDEs
 - Firemaster 550 (TBPH, TBB, TPP)
 - tris(1,3-dichloroisopropyl) phosphate (TDCPP)
 - FR with Cl, P
 - Many products contain more than one FR
- Lab challenges (diverse chemical classes, no standards available)

PBDE Replacements

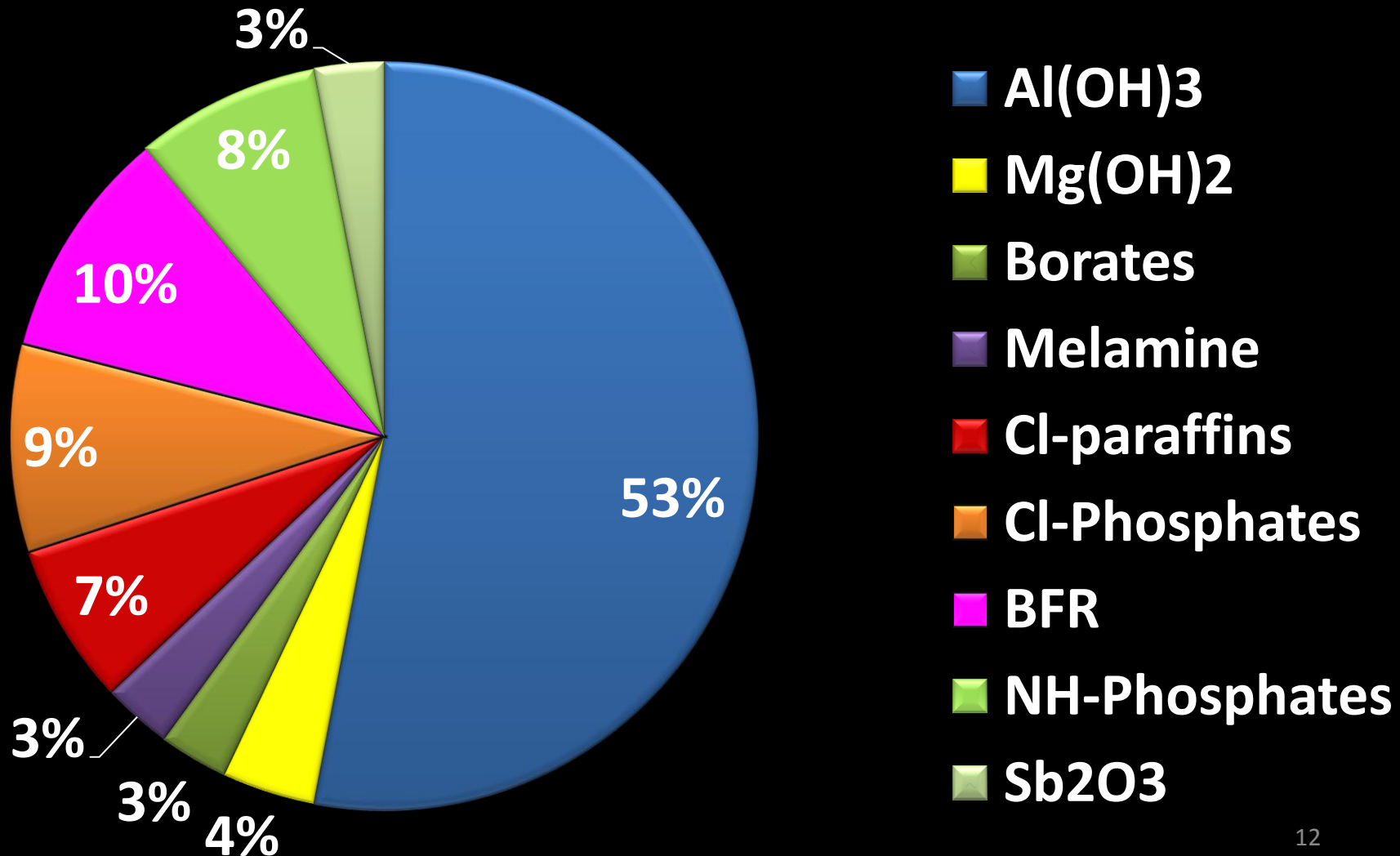
- Tris(1,3-dichloro-2-propyl) phosphate (TDCPP)
 - Furnishings, dust
 - Metabolite in urine
- Triphenyl phosphate (TPP)
 - Furnishings, dust
- Dust levels of TDCPP, TCPP, TPP higher than PBDEs (Boston area)

PBDE Replacements

- FR in consumer products in Japan (electronics, curtains, wallpaper)
- Triphenylphosphate (TPP) present in all
- BFRs (PBDEs, TBBPA, TBP) present in all products
 - Levels too low for flame retardancy => recycling streams

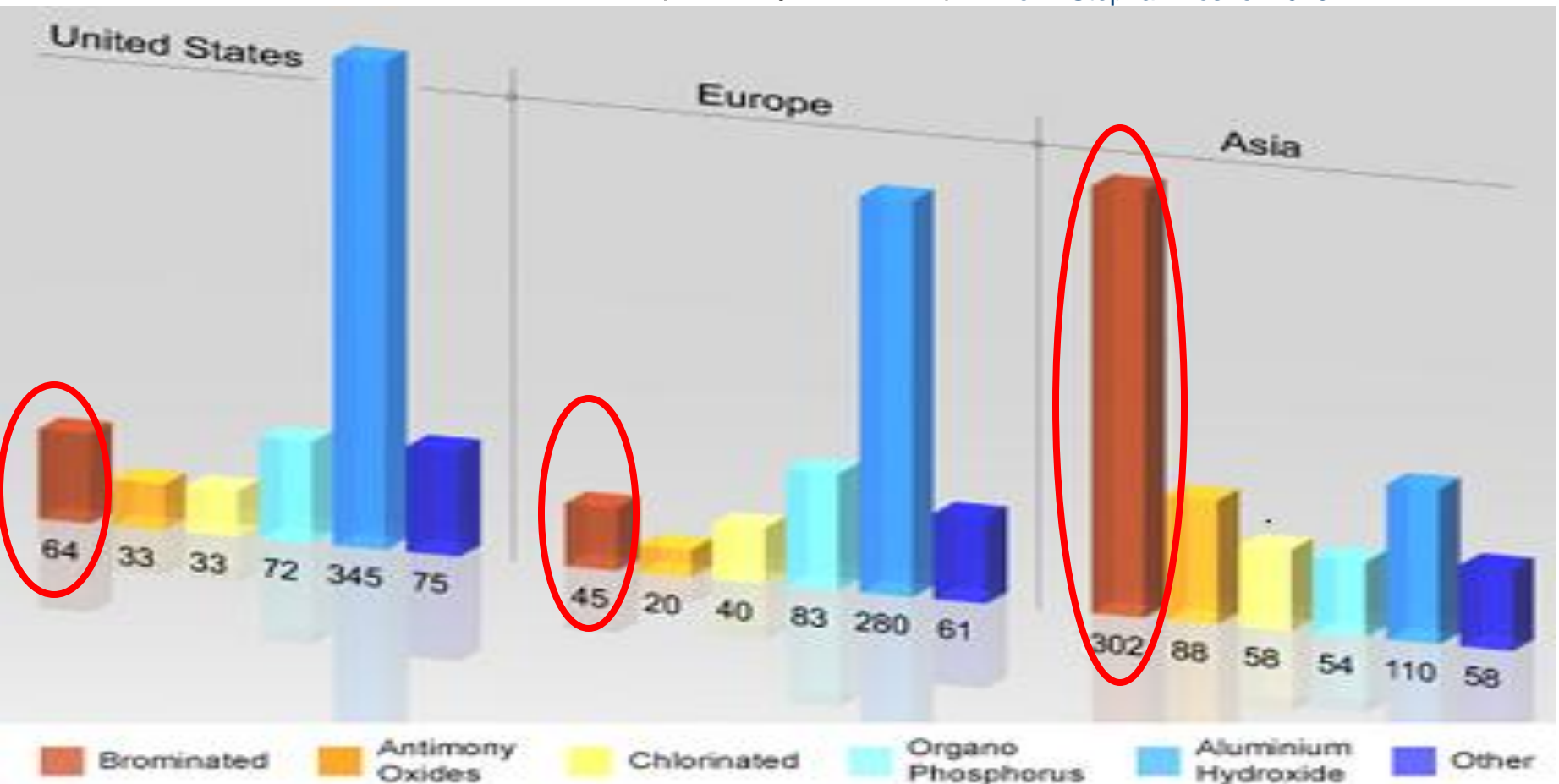
FR Consumption in Europe (2007)

Karlsruhe Research Center, 2007



Asian Market = BFR Global Concern

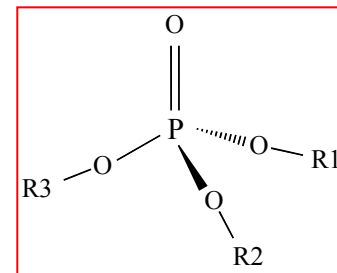
Between 2005-2008 use of BFRs increased from 139,000 to 246,000 TN
(mostly in Asia). From: Stephan Posner 2010



Main uses of aryl phosphates in the EU

- Textile coating
- Adhesives
- Paints, Pigments
- Rubber
- Photographic film
- Printed circuit boards
- PVC
- Polyurethane
- Thermoplastic resins
- Lubricant additive

Main (Additive) PFRs Studied



<u>Compound Name</u>	<u>R1 = R2 = R3</u>	<u>Abbreviation</u>	<u>Toxicity</u>
Triphenyl phosphate		TPP	Neurotoxic
Tricresyl phosphate		TCrP	Neurotoxic
Tris(2-butoxyethyl) phosphate		TBEP	Suspected carcinogenic
Tris(1-chloro-2-propyl) phosphate		TCPP	Suspected carcinogenic
Tris(1,3-dichloro-2-propyl) phosphate		TDCPP	Suspected carcinogenic
Tris(2-chloroethyl) phosphate		TCEP	Carcinogenic

Aromatic Phosphate FRs/Plasticizers

CPSC requested NTP review for:

Triphenyl phosphate (TPP)

tert-Butylphenyl diphenyl phosphate (BPDP)

Resorcinol bis(diphenyl phosphate) (RDP)

Bisphenol A bis(diphenyl phosphate)

Tricresyl phosphate (TCrP) o-, m-, p-

2-Ethylhexyl diphenyl phosphate (EHDP)

Isodecyl diphenyl phosphate (IDDP)

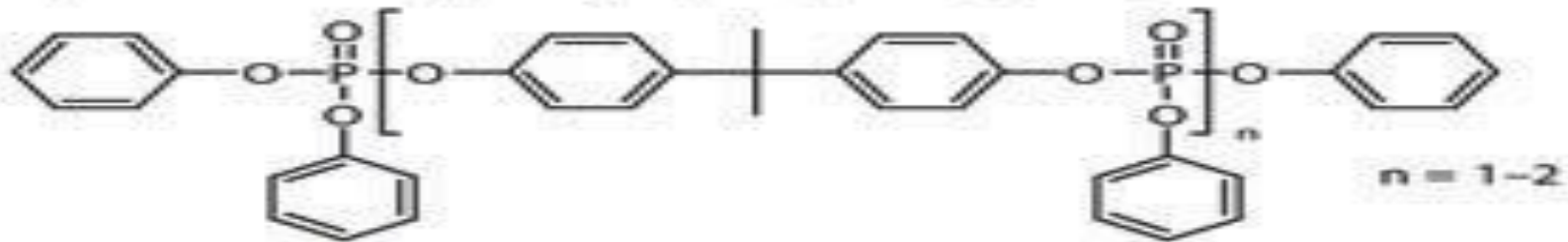
Isopropylated triphenyl phosphate (IPP)

PFR alternatives to Deca-BDE (for consumer electronics)

Reofos[®] BADP by Chemtura;
Fyroflex BDP by Supersta (bought by Israeli Chemicals)

BPA release??

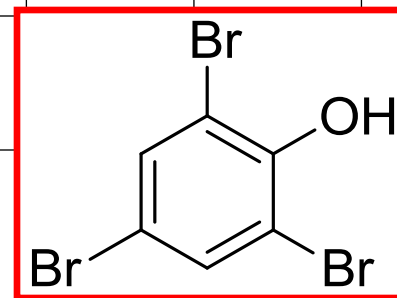
Bis-phenol A bis (diphenyl phosphate) (BDP)



BFR, CFR, PFR Abbreviations

(Manuscript from BFR International Committee, *Environ Intern*)

CAS#	118-79-6						
CA name	Phenol, 2,4,6-tribromo-						
Suggested Abbreviation(s)	2,4,6-TBrP						
Previously Used Abbreviation(s)	2,4,6-TBP						
Common names	1,3,5-Tribromo-2-hydroxybenzene	2,4,6-Tribromo phenol	Bromkal Pur 3	Bromol	Flamme x 3BP	NSC 2136	PH 73
Comments							
MW	330.80						
Log Kow	4.40						
Koc	pH-dep.						
pKa	6.34±0.23						
Vapour pressure (Torr)	1.50E-3						



ENFIRO Programme

<http://www.enfiro.eu>

- EU-funded
- Assessment approach for alternative FRs :
 1. Flame retardant: hazard characterization and exposure assessment
 2. Material: fire performance
 3. Product: impact assessment (life cycle assessment, life cycle costing, social life cycle assessment)

Non-Halogen Fire Safety Solutions?

www.pinfra.org

pinfa

Newsletter for non-halogen fire safety solutions



Phosphorus, Inorganic and Nitrogen Flame Retardants Association

Recommendations

- **If** FRs are needed, use halogen-free (HFFR)
- Alternative assessments
 - Persistence, Bioaccumulation, Toxicity
 - Recycling impediments
 - Exposures (production, use and waste disposal)
 - By-products of fire (smoke toxicity)
- Data gaps
- Regulatory response



Disclaimer

Authors' views do not necessarily express the views of
the California Department of Toxic Substances
Control





Sixth International Symposium on Flame Retardants BFR2013

April 7 - 10, 2013

Sir Francis Drake Hotel, Union Square
San Francisco, California, USA

www.bfr2013.com