COMPLYING WITH NEW CALIFORNIA LAW (SB 1019): METHODOLOGY TO SCREEN UPHOLSTERED FURNITURE FOR FLAME RETARDANTS

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ECL Team Acknowledgment

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- Sayaka Takaku-Pugh (ICP)
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- Miaomiao Wang (LC-TOF)
- Emily Parry (LC-TOF)

- John Quinn, June-Soo Park

Outline

- Flame retardants
- Flammability Standards
- Measuring FRs in furnishings
  - Conventional methods
  - Screening methods
  - QA/QC
- Applicability of screening methods

Flame retardants added to consumer products to meet flammability standards

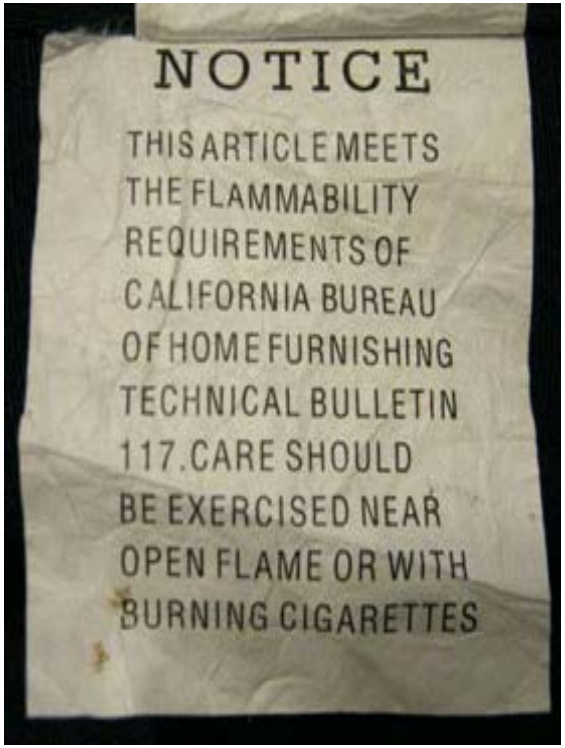
Brominated FRs (BFRs)

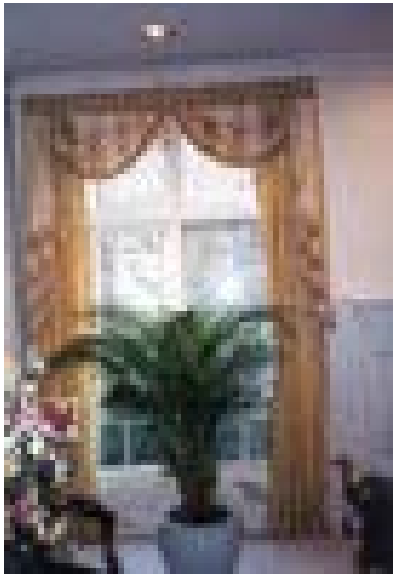
Polybrominated diphenyl ethers (PBDEs)

Organophosphate FRs (OPFRs)

PBDEs

- Consumer products
- Not bound
- Indoor contaminant
- **Dubious efficacy**





Toxicity Concerns

PBDEs

- Endocrine disruption
- Developmental effects

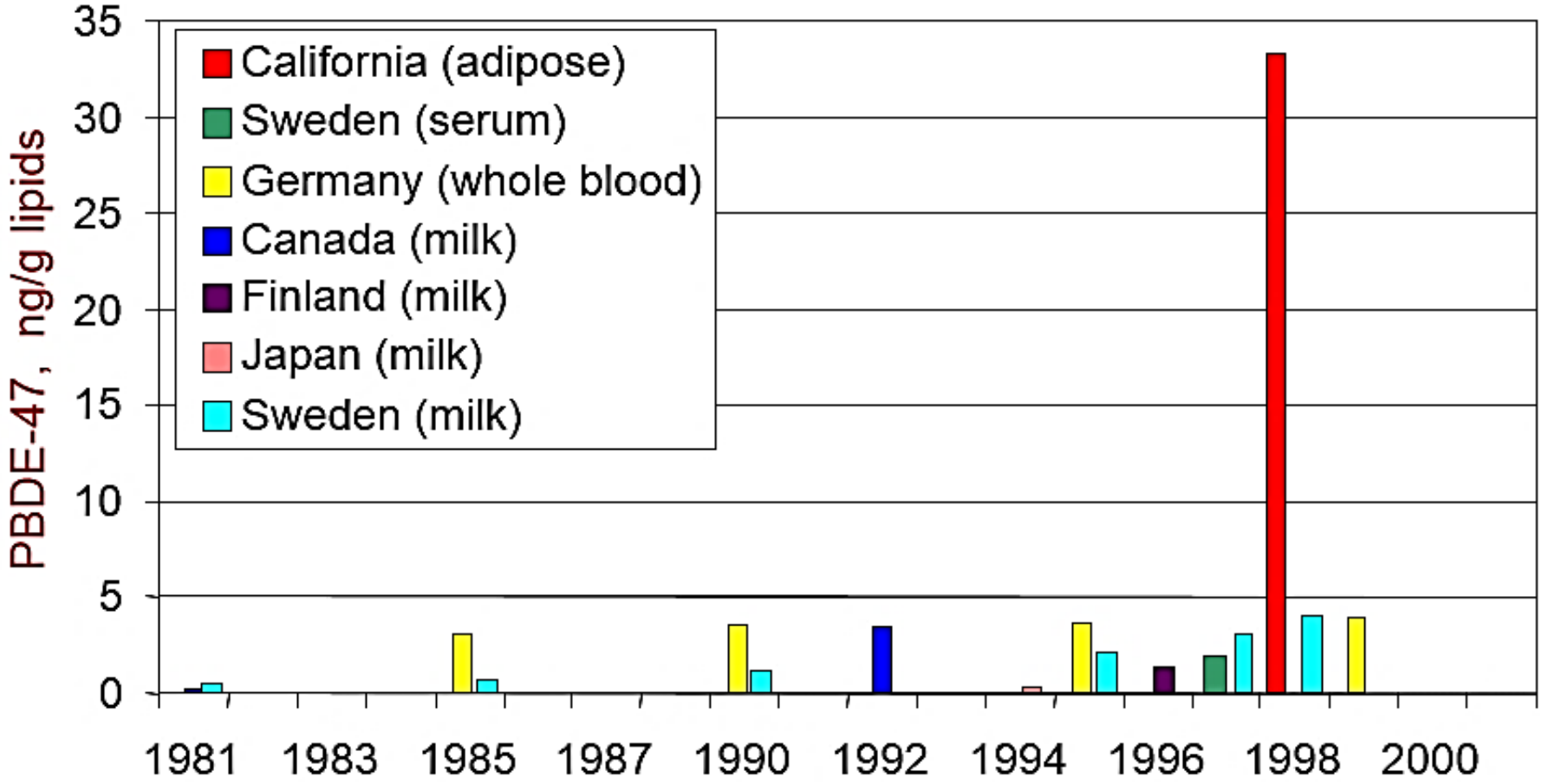
- Environmental conversion to brominated dioxins/furans

OPFRs

- Cancer
- Neurodevelopment

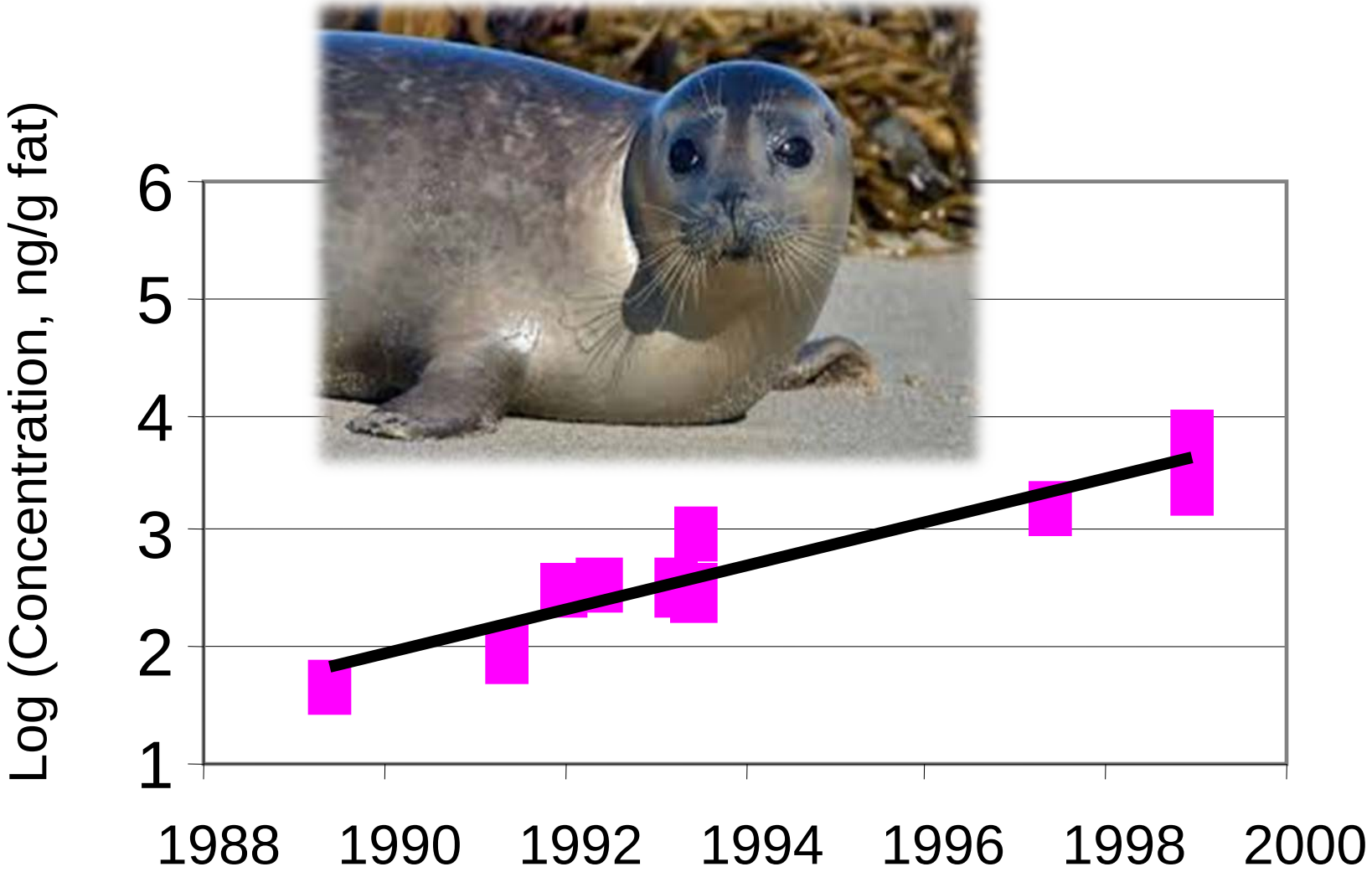
PBDEs became ubiquitous in California

PBDEs in Human Tissues



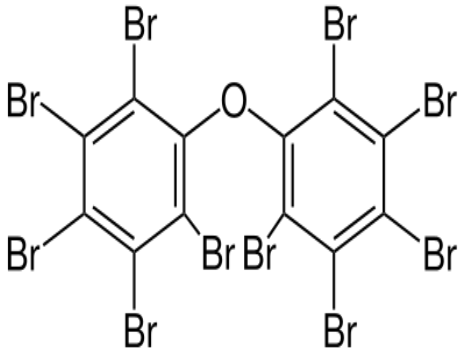
CA data from Petreas *et al.* (2001)

PBDEs IN SF BAY HARBOR SEALS

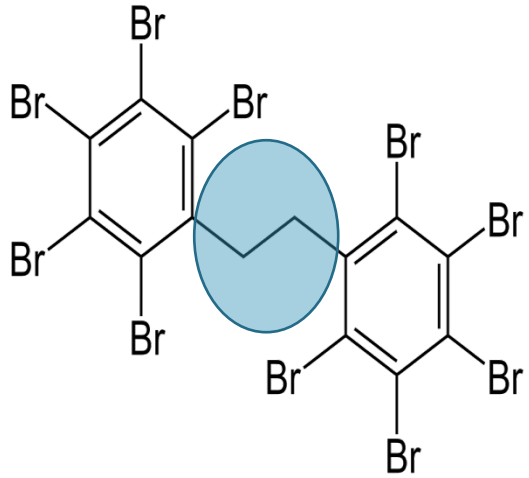


She et al., Chemosphere, 46:697-707, 2002

How to meet TB117? Regrettable Substitutions

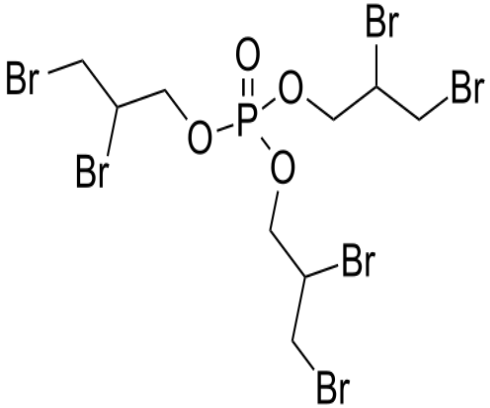


Decabromodiphenyl ether (BDE-209)

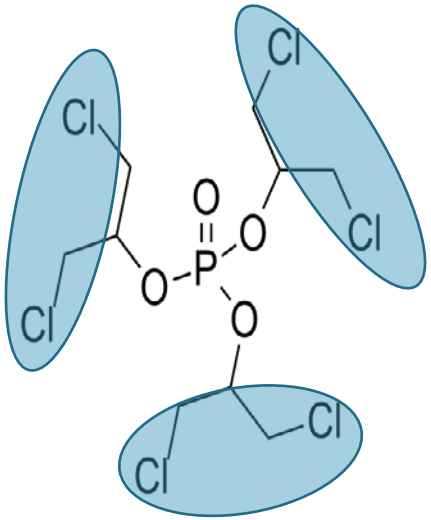


Decabromodiphenyl ethane (DBDPE)

CA Dust
Firehouse vs Residential:
FM550 (TBPH, TBB)
BTBPE
DBDPE
(Brown et al 2015)



Tris(2,3-dibromopropyl) phosphate (TDBPP)



Tris(1,3-dichloroisopropyl) phosphate (TDCIPP)

Dust OPFRs
(Gill et al)

Urinary OPFR
metabolites
(Petropoulou et al)

Changes in CA Flammability Standards

- TB117 required that foam withstand both open-flame and smolder tests
- TB117-2013 focuses on the ability of upholstery fabric to pass an updated smolder test
- SB1019: Manufacturers can meet TB117-2013 without the use of chemical FRs, but if FRs are used, they must be declared on the product label

NOTICE

THIS ARTICLE MEETS THE FLAMMABILITY REQUIREMENTS OF CALIFORNIA BUREAU OF ELECTRONIC AND APPLIANCE REPAIR, HOME FURNISHINGS AND THERMAL INSULATION TECHNICAL BULLETIN 117-2013. CARE SHOULD BE EXERCISED NEAR OPEN FLAME OR WITH BURNING CIGARETTES.

The upholstery materials in this product:

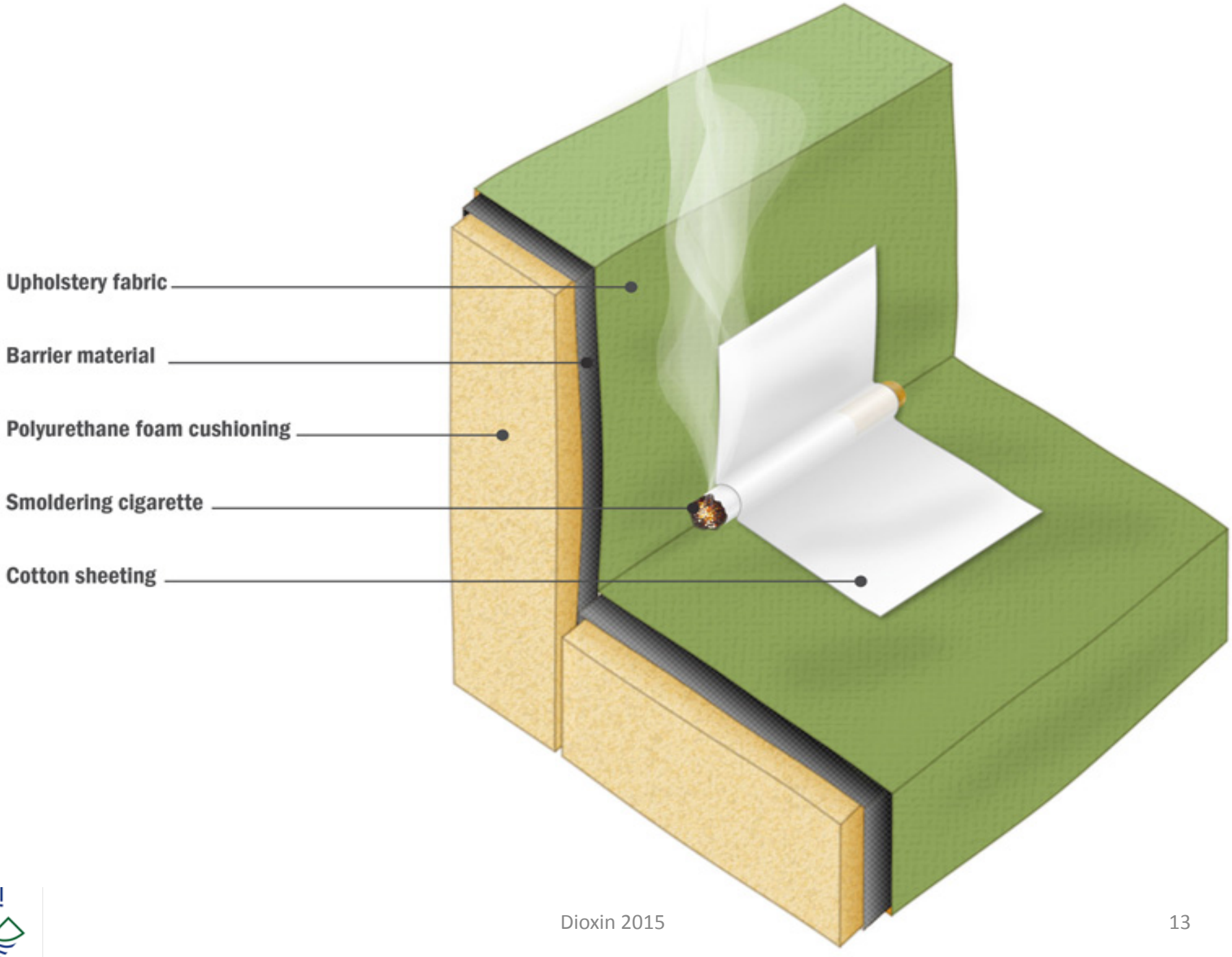
____ contain added flame retardant chemicals

_X_ contain NO added flame retardant chemicals

The State of California has updated the flammability standard and determined that the fire safety requirements for this product can be met without adding flame retardant chemicals. The state has identified many flame retardant chemicals as being known to, or strongly suspected of, adversely impacting human health or development.

< 1,000 ppm for sum of FRs

Penalty for false labeling, issued by Dept. of Consumer Affairs (DCA)


Upholstery fabric
Barrier material
Polyurethane foam cushioning
Smoldering cigarette
Cotton sheeting

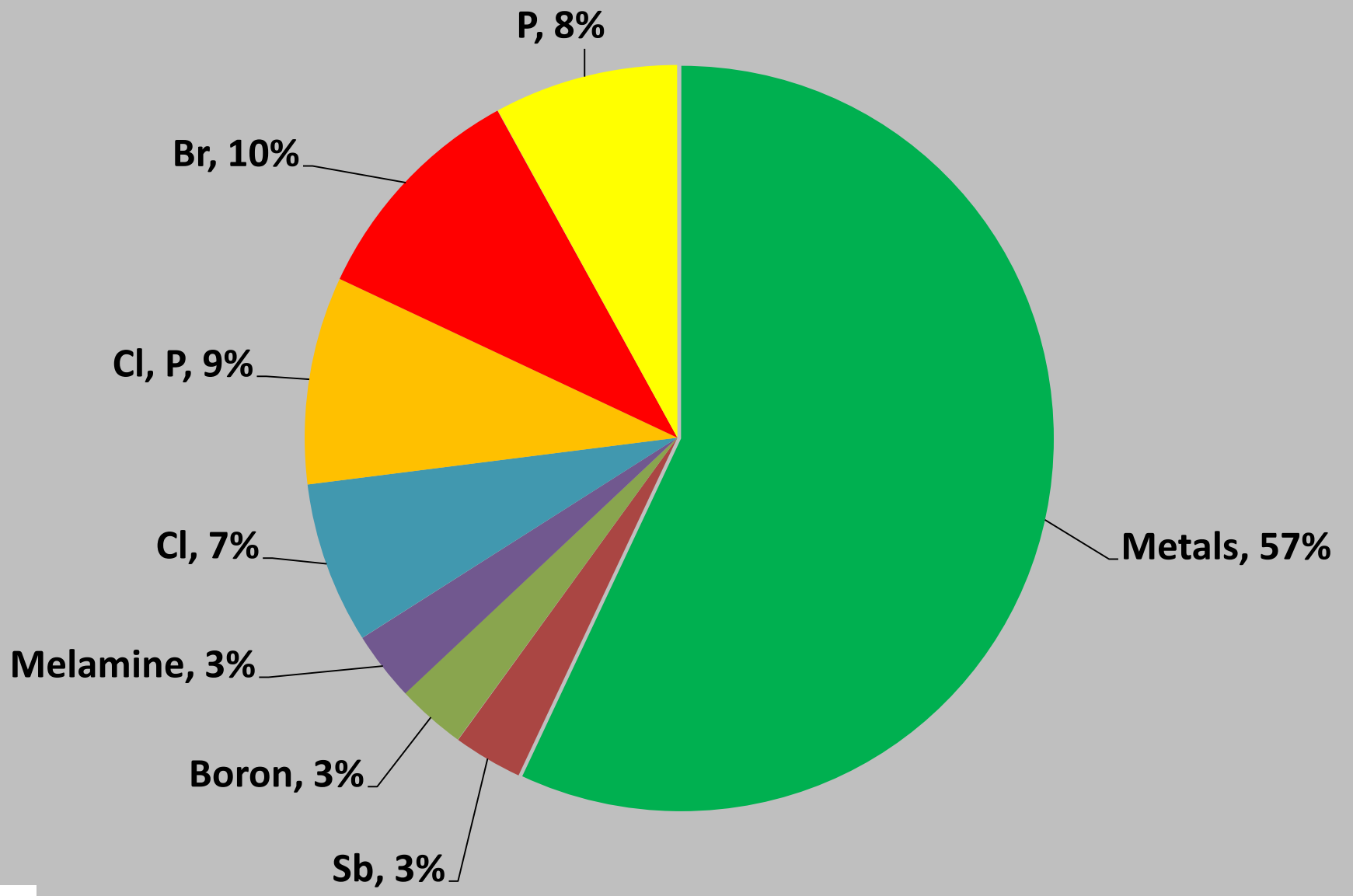
Our Lab's Abilities

- Long history of measuring FRs in products, dust, tissues, blood, etc.
- Advanced equipment, skilled staff
- Gas and Liquid Chromatography; Mass Spectrometry; Time-of-Flight
- Analytical methods for many FRs available

What to measure?

- Many classes of chemical FRs
- Few are compatible with fabric and PUF
- FRs containing Br, Cl, P are of highest concern
  - Toxic
  - Can escape from products
  - Well studied
- As newer FR are introduced and studied, the FR list expands

FR Consumption in Europe (2007)



Karlsruhe Research Center, 2007

Examples from Major Classes of Flame Retardants

- Metals: $Al(OH)_3$, $Mg(OH)_2$
- Br: PBDEs, TBBPA, HBCDD
- Cl, P: TDCIPP, TCEP
- P: Triphenyl phosphate (TPHP)
- Cl: Chlorinated paraffins

- Ammonium polyphosphate
  - Forest fires

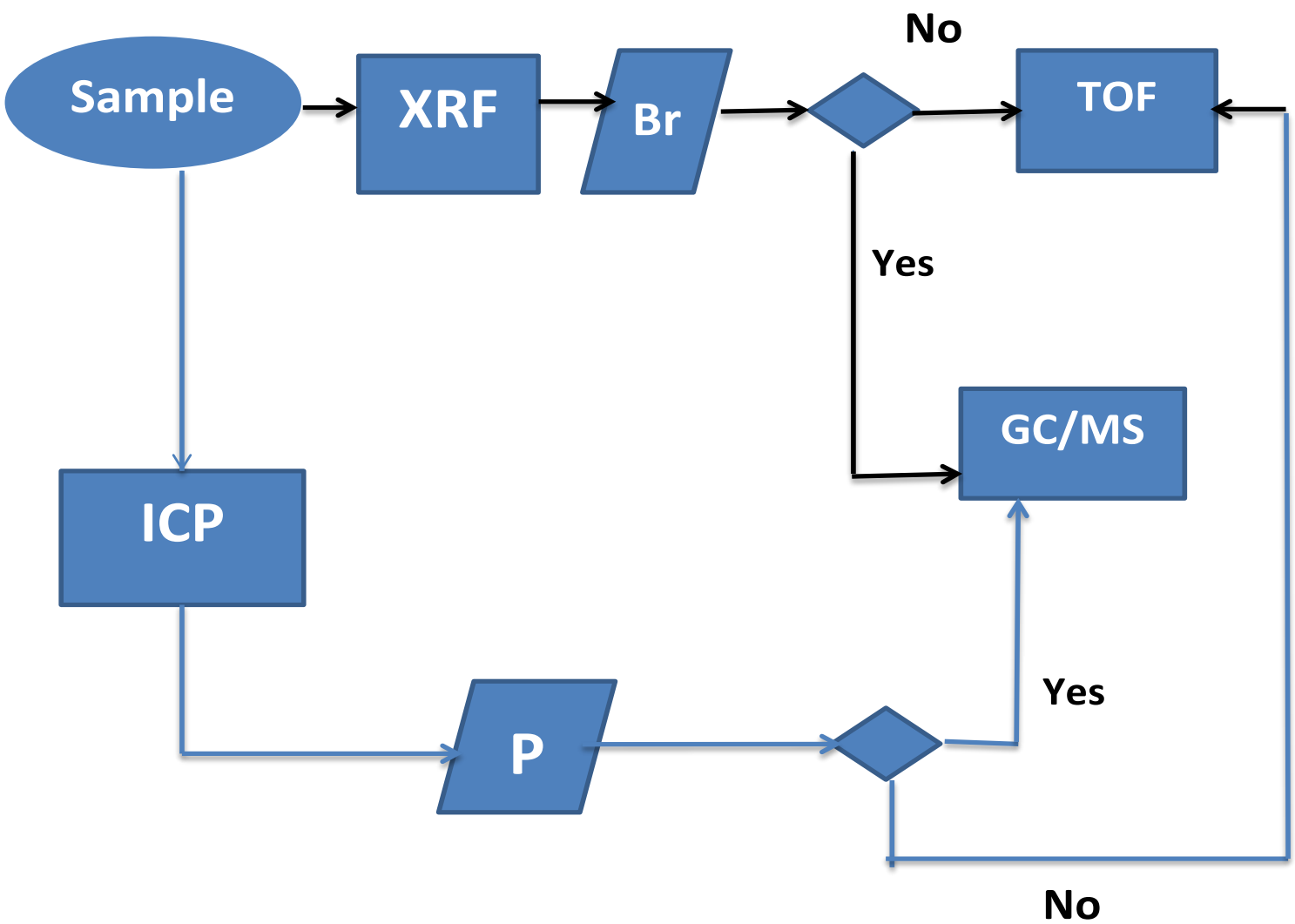
Shifts in use of FRs in Furniture

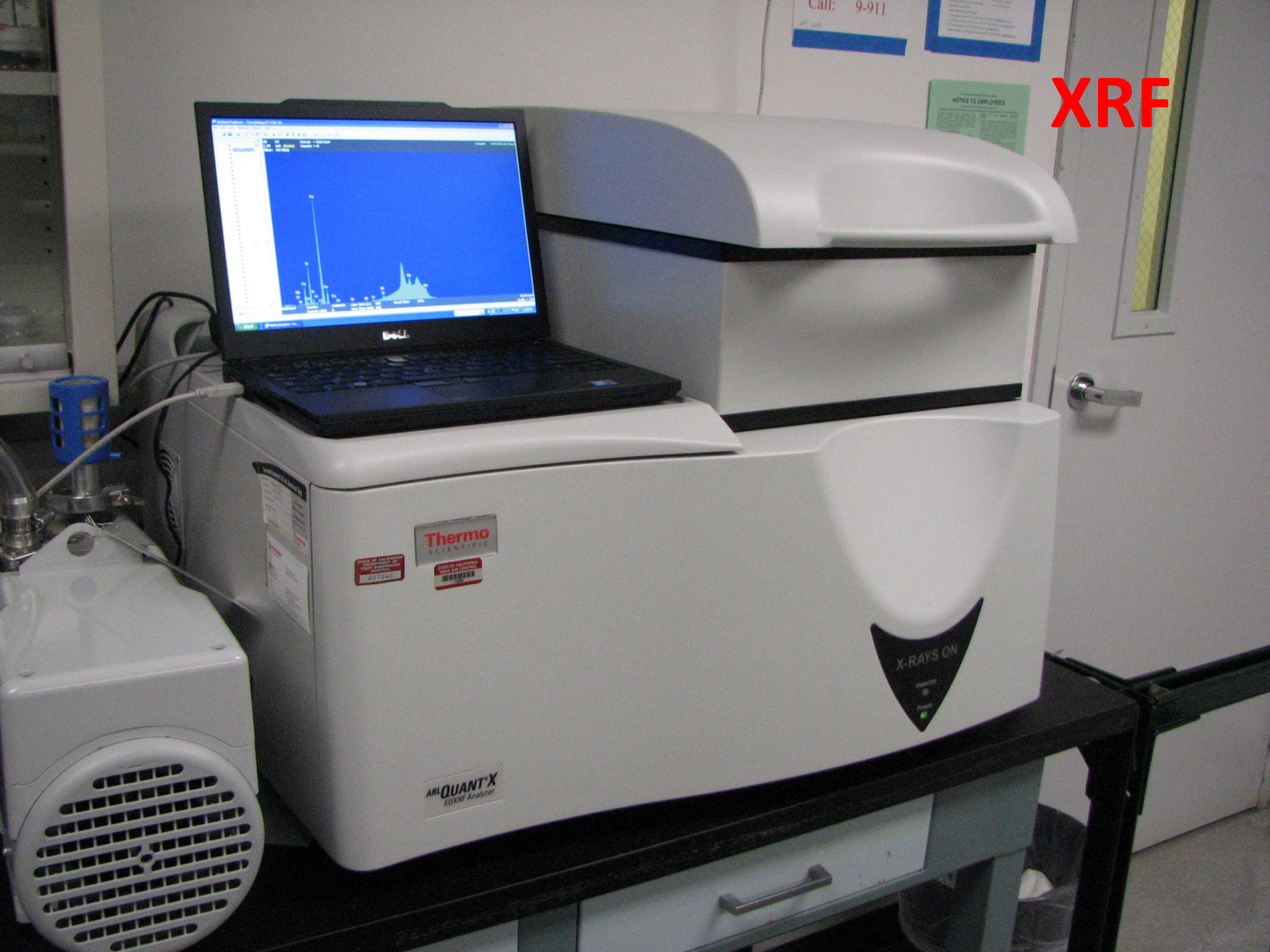
- Decreasing use of PBDEs, Firemaster
- Decreasing use of halogenated FRs
- Increasing use of non-halogenated OP
- Increasing use of TBBPA (as additive)
- Polymers?
- Nanoclays?
- ?

Need for a Screening Method

- Improve throughput by limiting number of samples for analysis
- Make method available to commercial labs with standard equipment
  - Manufacturers, suppliers
  - Consumers

Analyses Flow Chart

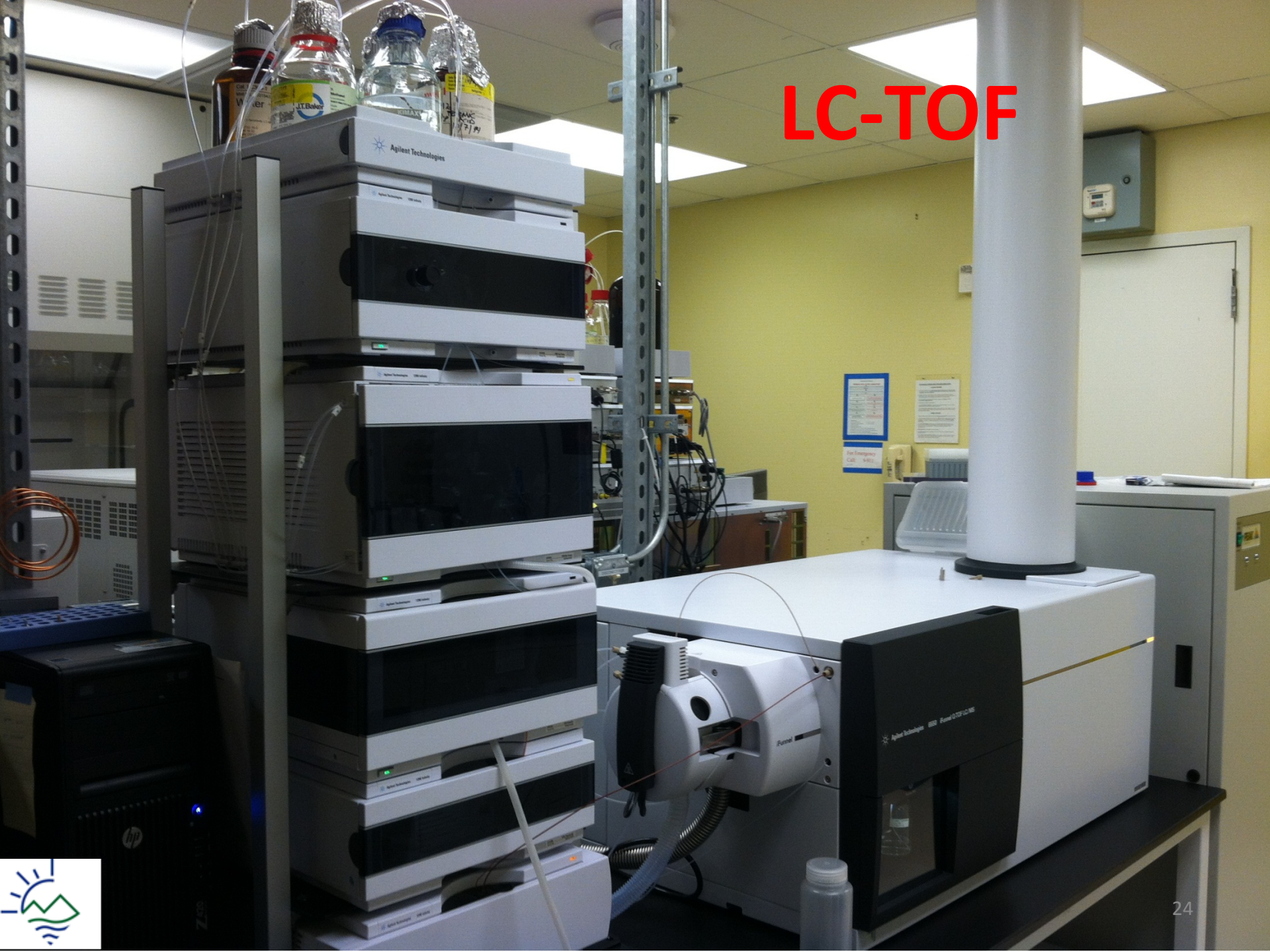



XRF
Call: 9-911
NOTICE TO EMPLOYEES
Thermo
SCIENTIFIC
X-RAYS ON
ARL QUANT'X
EDXRF Analyzer

ICP

GC-MS/MS

LC-TOF



Methodologies

Elements	Specific Chemicals
• ICP (quantitative): – P, Sb, Al, ….	• GC-MS/MS (quantitative): – BFRs, OPFRs, Total P
• XRF (semi-quantitative): – Br, Cl, P, Sb	• LC-TOF (semi-quantitative): – Identifying unknowns

We only report specific FRs

Experimental approach

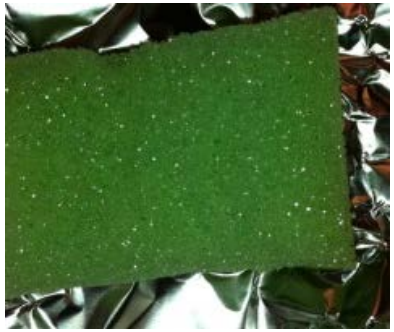
- Received 45 samples of foam, fabric, fill
  - 40 from DCA, 5 from Duke University
  - 35 samples labelled as Non-containing FRs
  - 10 samples prior to SB1019 (2000-2012)
- Analyzed by screening methods (XRF, ICP) and by advanced methods (GC-MS/MS, LC-TOF)
- Compared screening and MS results

Foam Samples

Sample A

Sample B

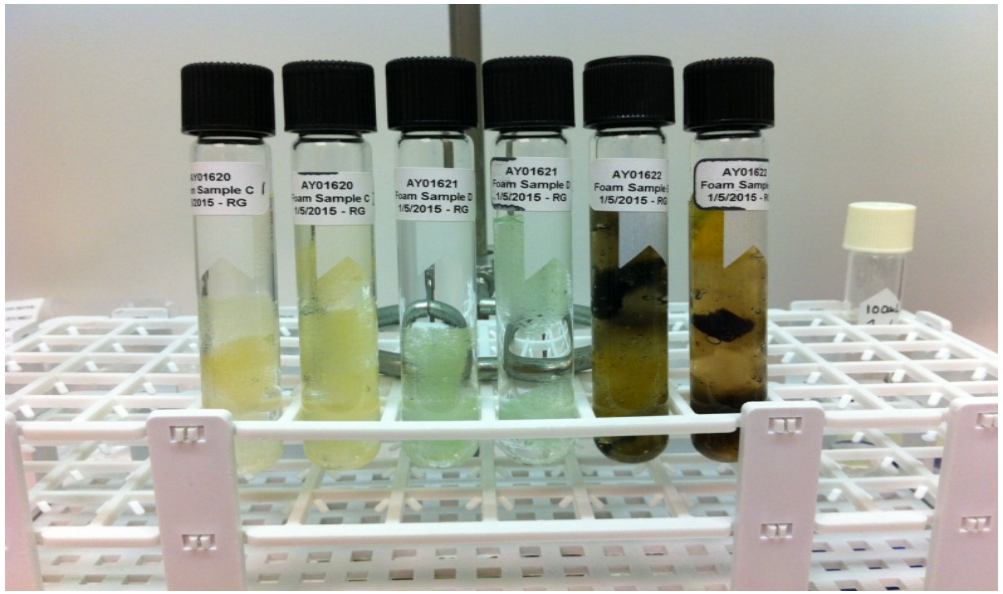
Sample C



Sample D

Sample E

Foam Samples C, D, & E



Sample E

- Multi component foam/compressed together or adhesive?
  - Cloth, Fibers, plastic mesh, different color foam
- Challenges sampling heterogeneous foam sample
  - Extract for Sample and Duplicate have different color

Non-foam Samples

Fiber batting

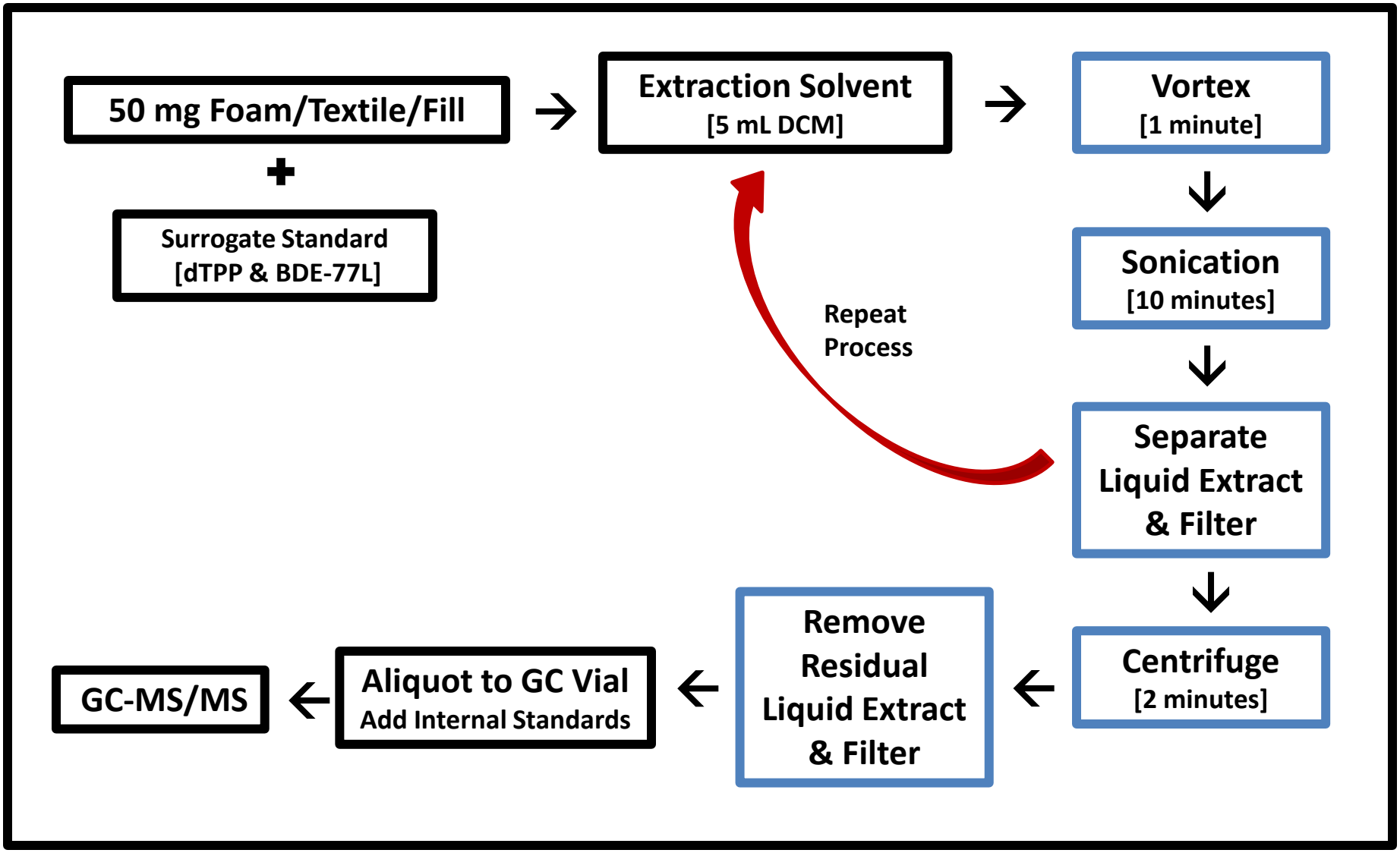
Fiber padding

Cover fabric

Precision & sample homogeneity (%RSD)

	Homogeneous sample	Heterogeneous sample
P by XRF	4%	32%
Cl by XRF	4%	35%
P by ICP	3.3%	29%

Sample Extraction



GC-MS/MS Analysis

- Agilent 7000 Series Triple Quadrupole System
- Agilent DB-5ms Ultra Inert Column
- 32 minute Acquisition Method

Simultaneous analysis of OPFRs/PBDEs/BFRs

Abbreviation	Compound Name	RL (ppm)*
TNBP	Tri-n-butyl phosphate	0.31
TCEP	Tris(2-chloroethyl) phosphate	2.5
TCIPP	Tris(1-chloro-2-propyl) phosphate	2.5
TDCIPP	Tris(1,3-dichloro-2-propyl) phosphate	4
TPHP	Triphenyl phosphate	4
TBOEP	Tris(2-butoxyethyl) phosphate	25
TEHP	Tris(2-ethylhexyl) phosphate	8
o-TMPP	ortho-Tris(methylphenyl) phosphate	2.5
m-TMPP	meta-Tris(methylphenyl) phosphate	2.5
p-TMPP	para-Tris(methylphenyl) phosphate	2.5
TDBPP	Tris(2,3-dibromopropyl) phosphate	25
BDE-17	2,2',4-Tribromodiphenyl ether	0.15
BDE-28	2,4,4'-Tribromodiphenyl ether	0.16
BDE-47	2,2',4,4'-tetrabromodiphenyl ether	0.16
BDE-85	2,2',3,4,4'-pentabromodiphenyl ether	0.16
BDE-99	2,2',4,4',5-pentabromodiphenyl ether	0.16
BDE-100	2,2',4,4',6-pentabromodiphenyl ether	0.16
BDE-153	2,2',4,4',5,5'-hexabromodiphenyl ether	0.32
BDE-154	2,2',4,4',5,6'-hexabromodiphenyl ether	0.32
BDE-183	2,2',3,4,4',5',6-heptabromodiphenyl ether	0.32
EH-TBB	2-Ethylhexyl 2,3,4,5-tetrabromobenzoate	2.5
BEH-TEBP	Bis(2-ethylhexyl) tetrabromophthalate	2.5

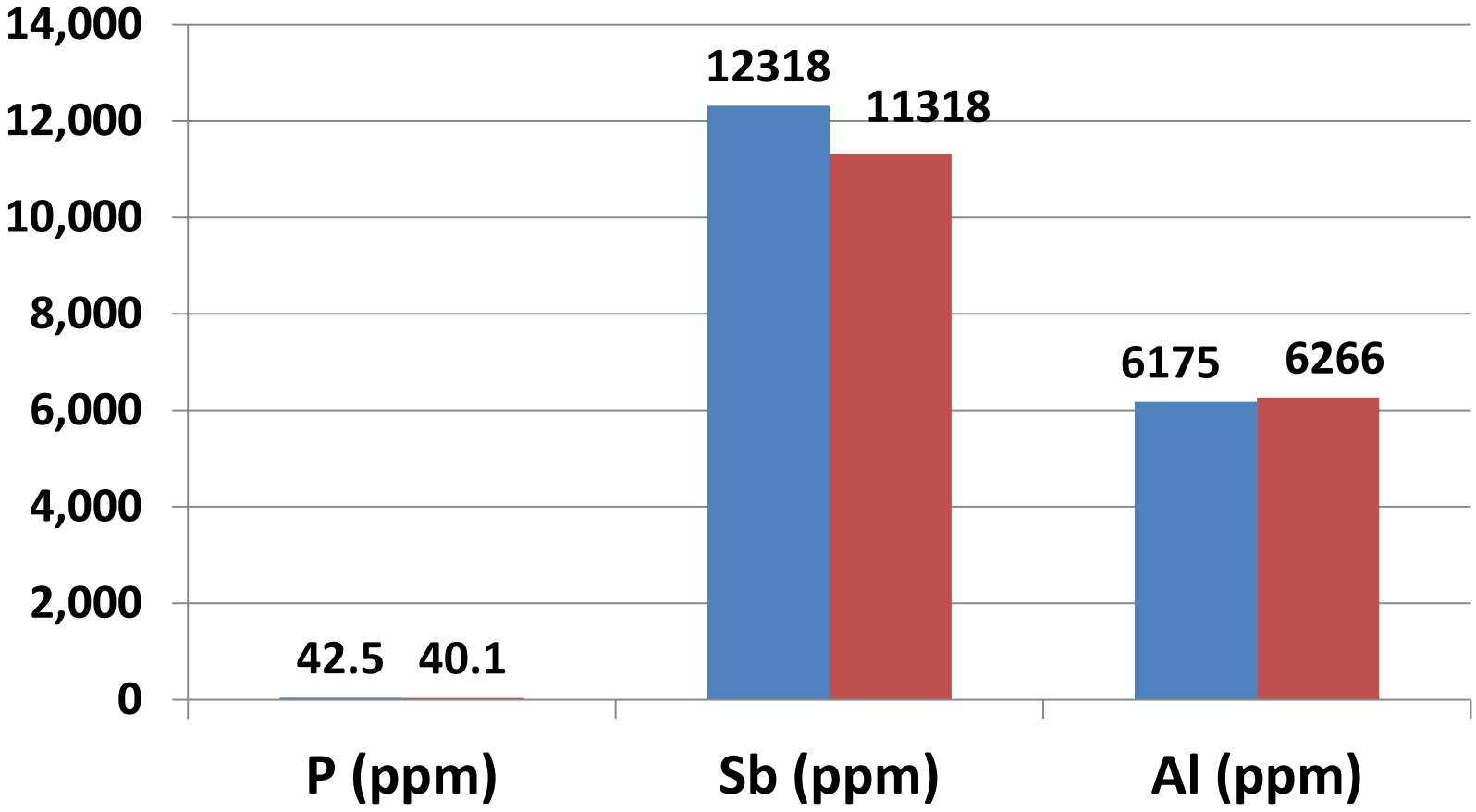
* Assuming 100% Extraction Efficiency and 50 mg Foam Sample Size

QA/QC

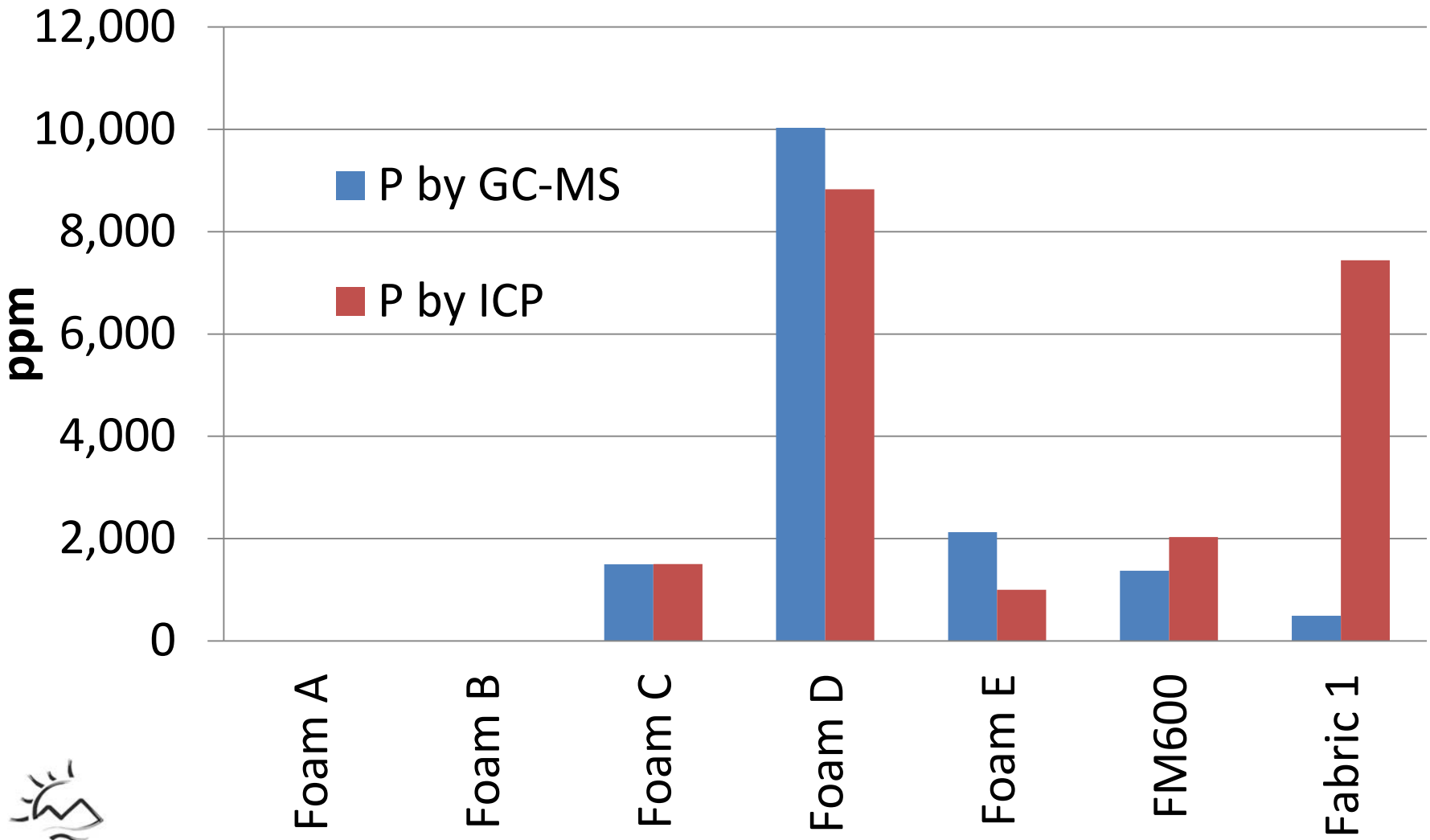
- FR-free foam used as method blank
- Duplicate analyses
- Cross-checked total P:
  - by ICP and
  - in the sum of OPFRs by GC-MS/MS

- Exchanged samples with Duke University
  - Good agreement

Duplicate analysis by ICP
(synthetic fiber batting)



Total P: ICP vs. GC-MS/MS



Results (by GC-MS/MS)

- Of the 35 samples labelled as “Non-FR”:
  - 1 approached 1,000 ppm (990 ppm TCIPP + 6 ppm TPHP)
  - 6 had measurable FRs (2.5-200 ppm)

- Of the 10 older samples:
  - 1 had PBDEs (~67,000 ppm) and OPFRs (TPHP)
  - 5 had OPFRs (~96,000 ppm TCIPP, TPHP, TCEP, etc.)

Reliability of Screening Methods

- Predictive value of a positive:
  - If a screening test detects Br (or P), what is the probability that a BFR (or PFR) is **really present?**

- Predictive value of a negative:
  - If a screening test does not detect Br (or P), what is the probability that a BFR (or PFR) is **really not present?**

Results from 40 samples	Predictive Value (+)	Predictive Value (-)
P by ICP for OPFRs	0.38	1
P by XRF for OPFRs	0.53	0.96
Br by XRF for BFRs	0.2	1

Tentative identification by LC-TOF

- Confirmed FRs measured by GC-MS/MS

- Melamine
- Tetrakis(2-chloroethyl) ethylene diphosphate (Thermolin 101)

- No hexabromo cyclododecane (HBCDD)

Conclusions

- GC-MS/MS method can measure BFRs, OPFRs in PUF, fabric, fibers, batting
- Reliable screening of Br by XRF and P by ICP
  - Predictive Value of a Negative=1

- Most newer samples appear to be correctly labelled as “non-FR”

Transparency

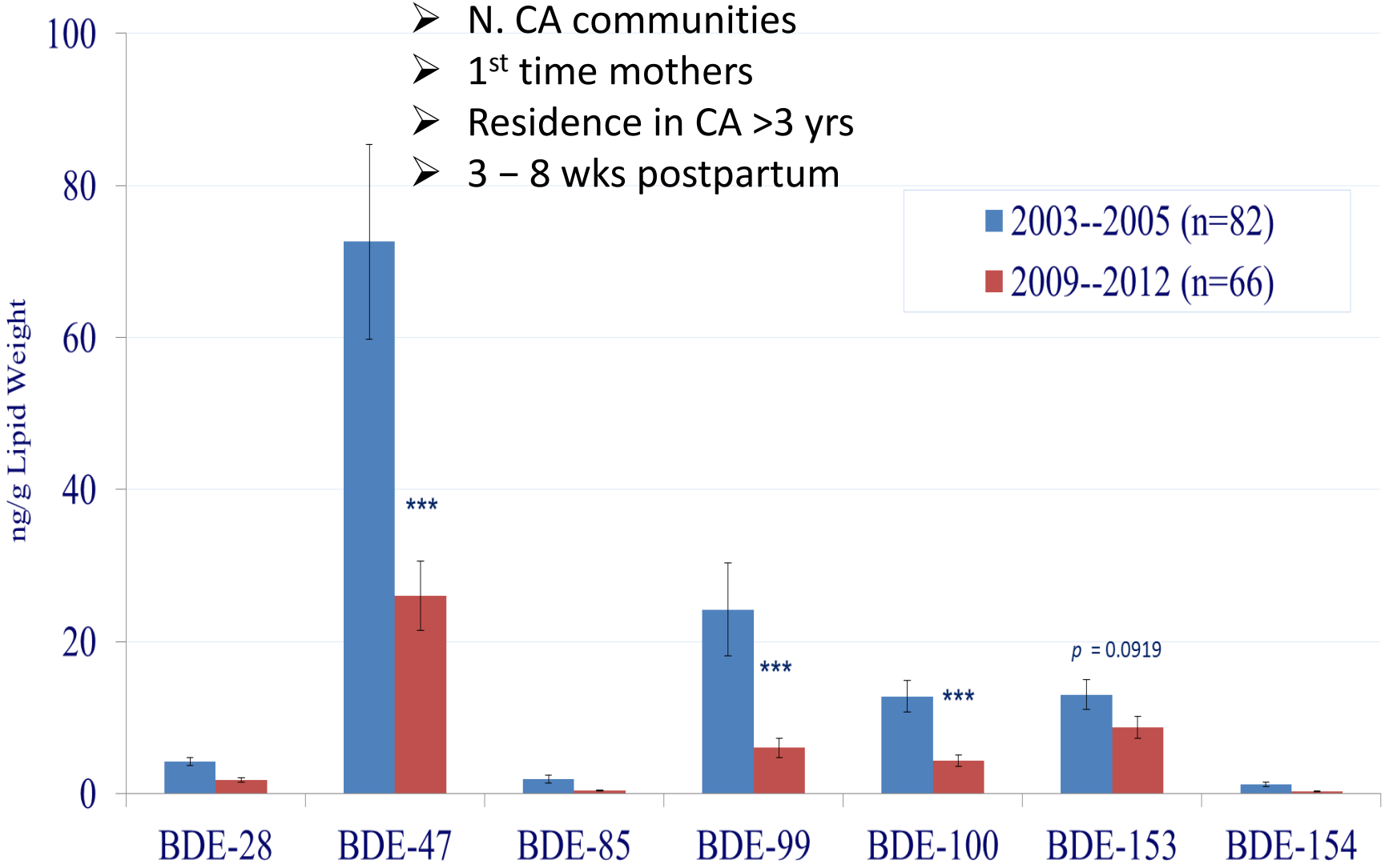
- We updated our website
- We established flameretardants@dtsc.ca.gov
- We respond to requests from manufacturers and commercial labs
- Methodologies will be available on website
- We will share materials for round-robin testing

For information on California Flammability Standards

- http://www.bhfti.ca.gov/about/laws/attach_11.pdf
- http://leginfo.legislature.ca.gov/faces/billNavClient.xhtml?bill_id=201320140SB1019

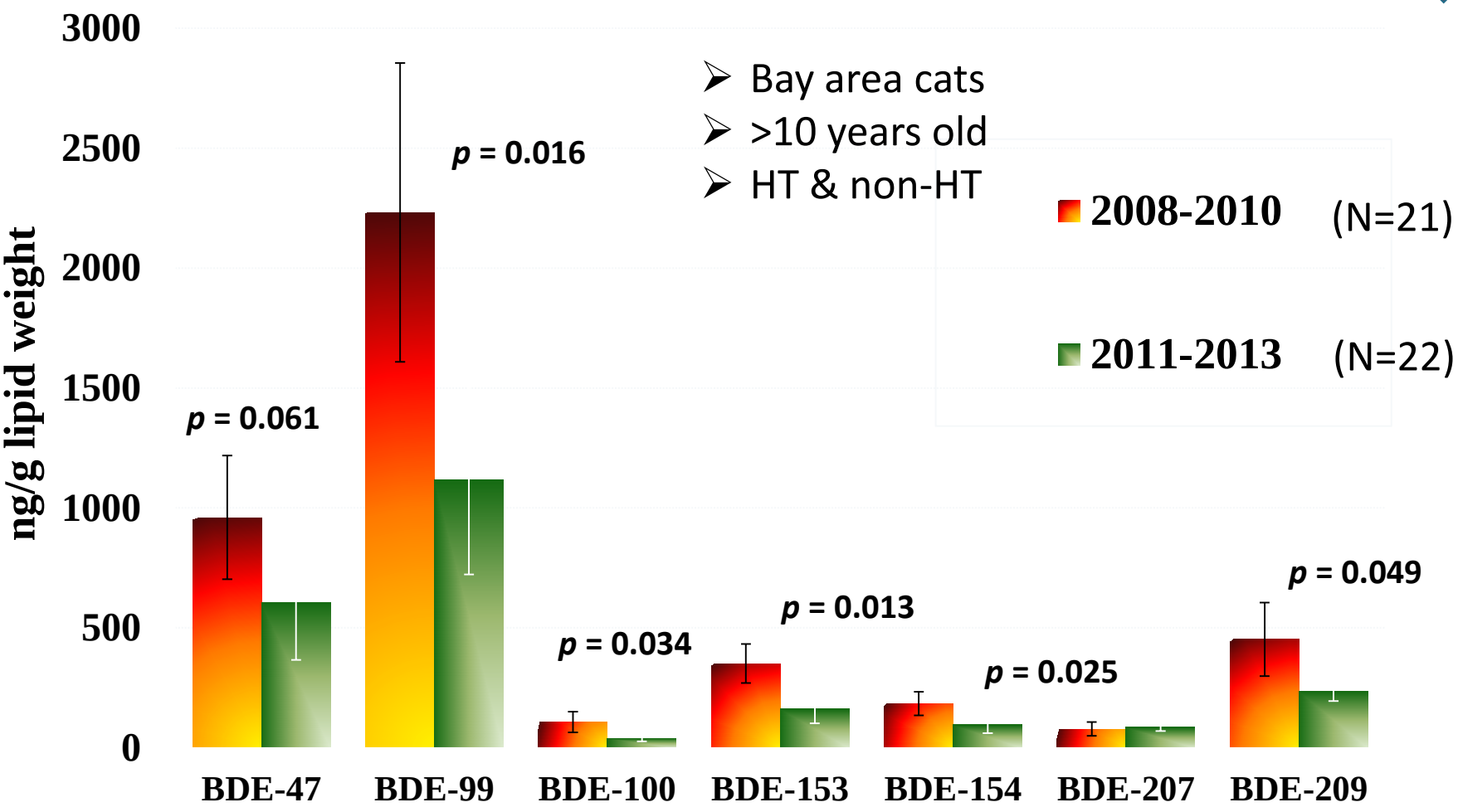
CA Breast Milk PBDEs (ng/g lipid)

- N. CA communities
- 1st time mothers
- Residence in CA >3 yrs
- 3 – 8 wks postpartum



Guo et al., submitted

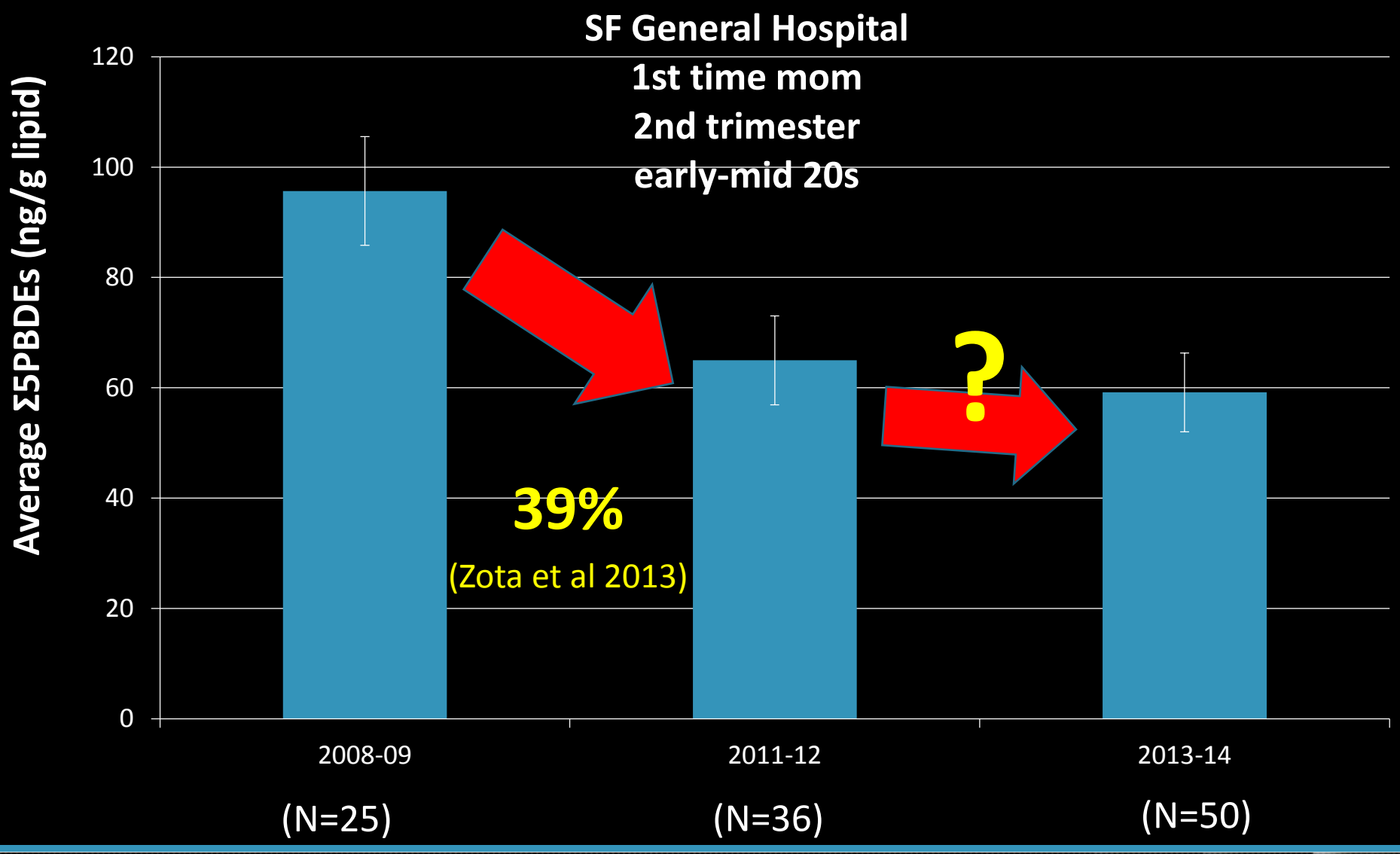
Cat Serum PBDEs



- Bay area cats
- >10 years old
- HT & non-HT

Guo et al. submitted

Serum PBDEs



Σ5PBDEs = BDE -28, 47, 99, 100, 153 (Parry et al. in prep)

Acknowledgment

- DCA staff for providing samples and consultation
- Drs. Cooper and Stapleton (Duke University) for sample exchange, consultation
- Dr. Covaci (Antwerp University) for consultation

- All FR experts who contributed to changing TB117