Flame Retardant Applications in Residential Furniture: Results from the Duke Superfund Foam Screening Project

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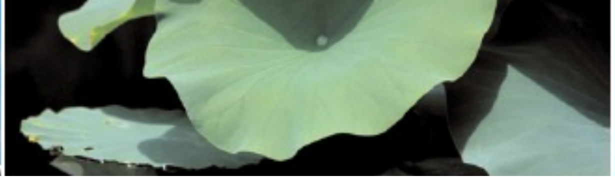
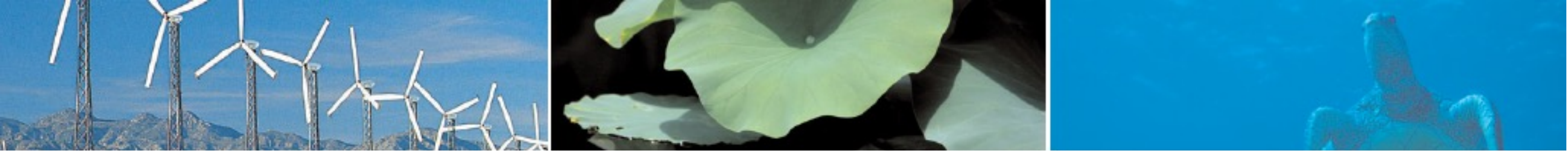


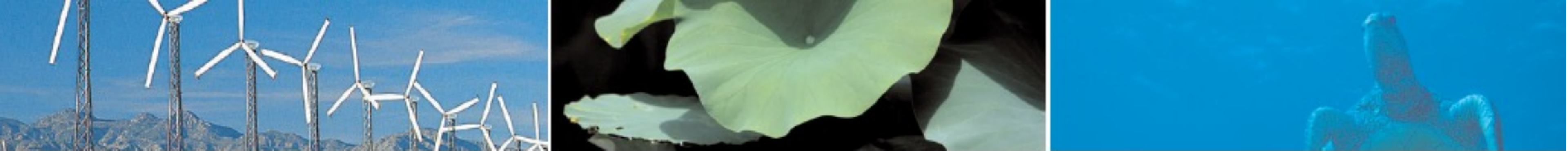

Agenda

1. Background on the use of flame retardants in furniture
2. Describe motivation for this project
3. Overview of sample submission and processing
4. Discussion of data collected to date
5. Discussion on exposure and potential health effects
6. Questions?



Why are there Flame Retardants (FRs) in Furniture?

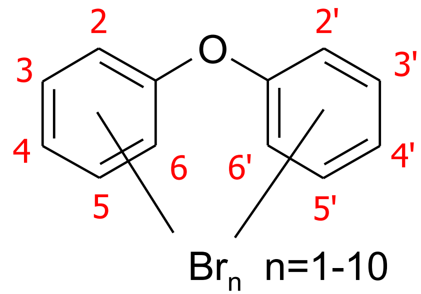
- Due to concerns about fire, and furniture acting as an ignition source, the California Bureau of Home Furnishing and Thermal Insulation implemented Technical Bulletin 117 in 1972.
- Required filling material to withstand a 12-second open flame test
- Led to the use of high volumes of additive flame retardants in residential furniture



PentaBDE Flame Retardant Mixture

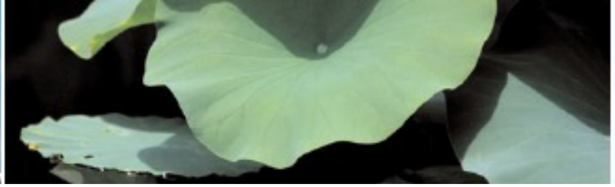
- An additive flame retardant mixture applied to polyurethane foam in furniture

- 98% of world market demand for PentaBDE was in North America, primarily to meet CA TB 117
- Studies demonstrated that PBDEs were ubiquitously detected in human tissues; increasing concentrations detected in biotic and abiotic samples (Hites, 2004)



Polybrominated Diphenyl Ether (PBDE)

- Concern about persistence, bioaccumulation and potential toxicity led to ban on use in Europe Union (2002); voluntary phase-out in US (2005)
- What would be used as a replacement?

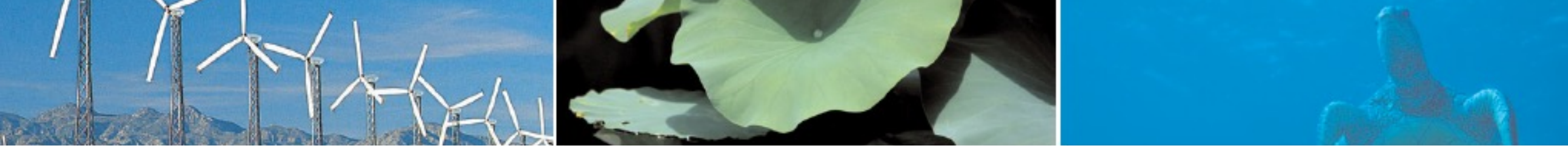




Identifying Flame Retardants (FRs) Used to Meet California's TB 117

- Previous research in our laboratory has focused on identifying FR chemical additives in polyurethane foam:
  - Baby Products (Stapleton et al. 2011)
  - Residential Sofas (Stapleton et al. 2012)

Sleep Positioners

- The most common FRs identified in furniture are:
  - PBDEs associated with PentaBDE
  - Tris (1,3-dichloro-isopropyl) phosphate (TDCPP)
  - Chemicals associated with Firemaster® 550 (FM 550)
  - Triphenyl phosphate (TPP) and isomers of tris(4-isobutyl) phenyl phosphate
  - Tris (1-chloro-isopropyl) phosphate (TCPP)

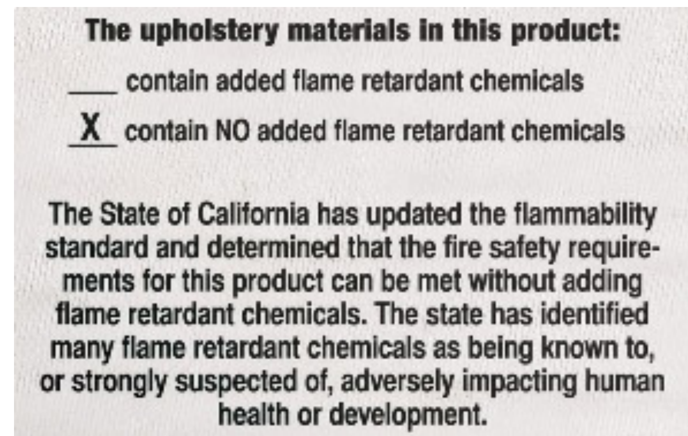


New Questions Have Been Raised

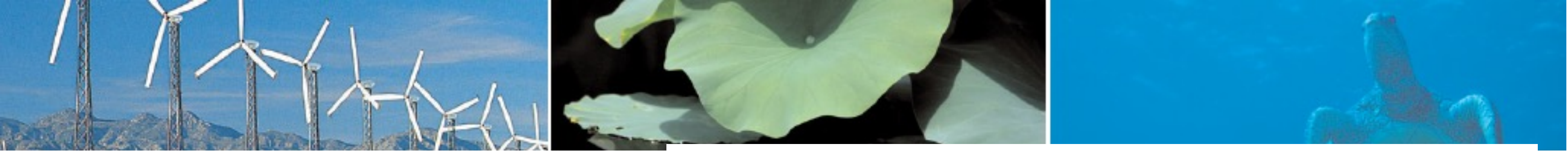
1. How frequently are flame retardants used in other furniture items?

2. With addition of TDCPP to the California Proposition 65 list (“Prop 65”), will its use in furniture decrease?

3. How will use of flame retardants change in response to changes in TB 117? (i.e. TB 117-2013; changed from an open flame to smolder test)



New TB 117 Label

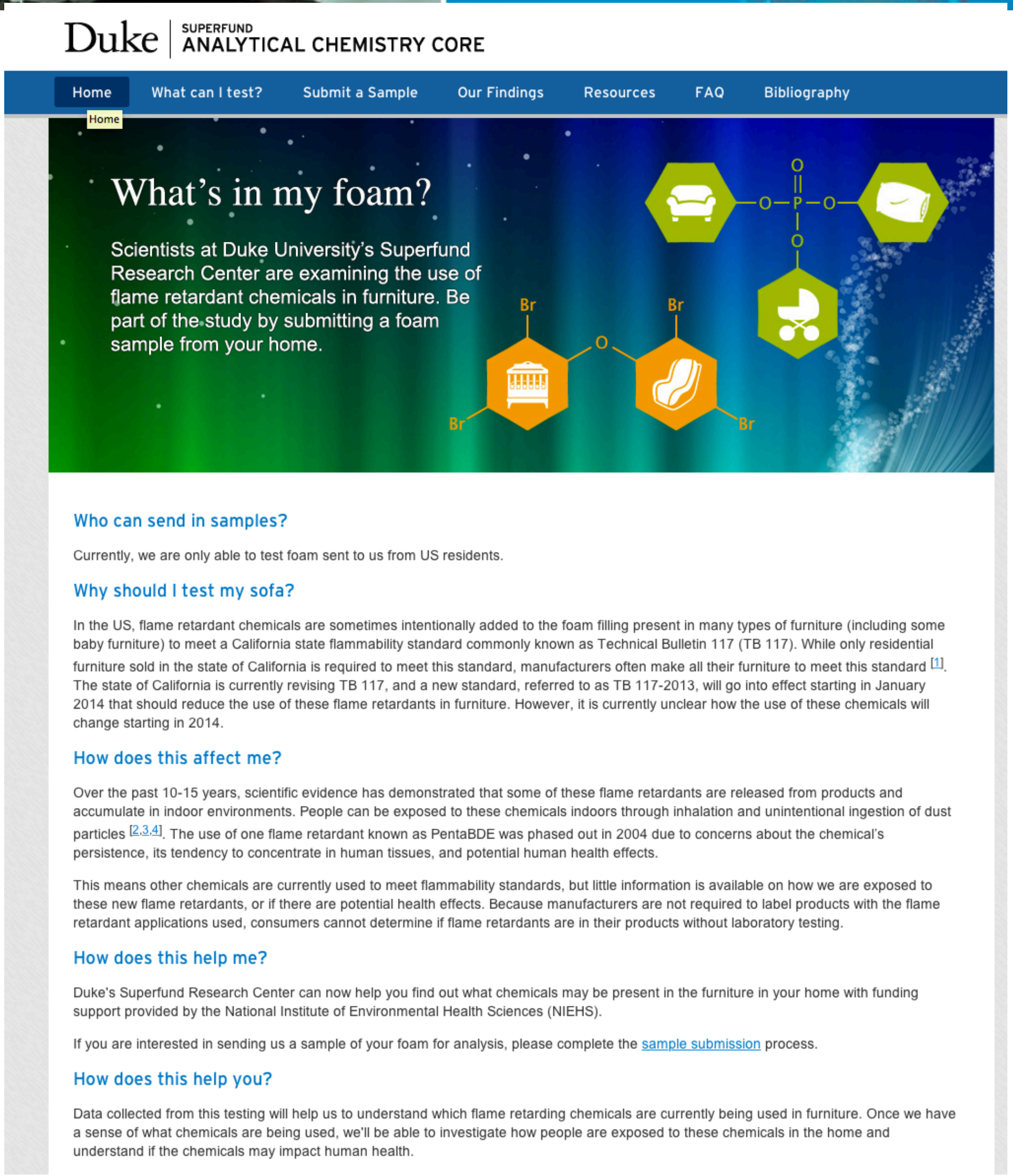


- Unique FR testing service launched in February 2014

- Intended to screen PUF samples and provide information to the general public

- Supported by Superfund Research Program

http://foam.pratt.duke.edu



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Home | What can I test? | Submit a Sample | Our Findings | Resources | FAQ | Bibliography

Who can send in samples?

Currently, we are only able to test foam sent to us from US residents.

Why should I test my sofa?

In the US, flame retardant chemicals are sometimes intentionally added to the foam filling present in many types of furniture (including some baby furniture) to meet a California state flammability standard commonly known as Technical Bulletin 117 (TB 117). While only residential furniture sold in the state of California is required to meet this standard, manufacturers often make all their furniture to meet this standard [1]. The state of California is currently revising TB 117, and a new standard, referred to as TB 117-2013, will go into effect starting in January 2014 that should reduce the use of these flame retardants in furniture. However, it is currently unclear how the use of these chemicals will change starting in 2014.

How does this affect me?

Over the past 10-15 years, scientific evidence has demonstrated that some of these flame retardants are released from products and accumulate in indoor environments. People can be exposed to these chemicals indoors through inhalation and unintentional ingestion of dust particles [2,3,4]. The use of one flame retardant known as PentaBDE was phased out in 2004 due to concerns about the chemical's persistence, its tendency to concentrate in human tissues, and potential human health effects.

This means other chemicals are currently used to meet flammability standards, but little information is available on how we are exposed to these new flame retardants, or if there are potential health effects. Because manufacturers are not required to label products with the flame retardant applications used, consumers cannot determine if flame retardants are in their products without laboratory testing.

How does this help me?

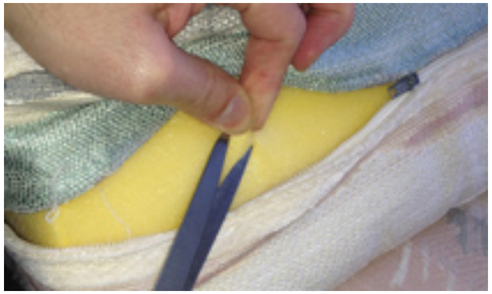
Duke's Superfund Research Center can now help you find out what chemicals may be present in the furniture in your home with funding support provided by the National Institute of Environmental Health Sciences (NIEHS).

If you are interested in sending us a sample of your foam for analysis, please complete the sample submission process.

How does this help you?

Data collected from this testing will help us to understand which flame retarding chemicals are currently being used in furniture. Once we have a sense of what chemicals are being used, we'll be able to investigate how people are exposed to these chemicals in the home and understand if the chemicals may impact human health.

Submitting a Sample



- What type of product is the PUF from?
- In what year was it purchased?
- In what state was it purchased?
- Does it have a TB-117 label affixed to the product, and if so, what version?
- In what country was it manufactured?

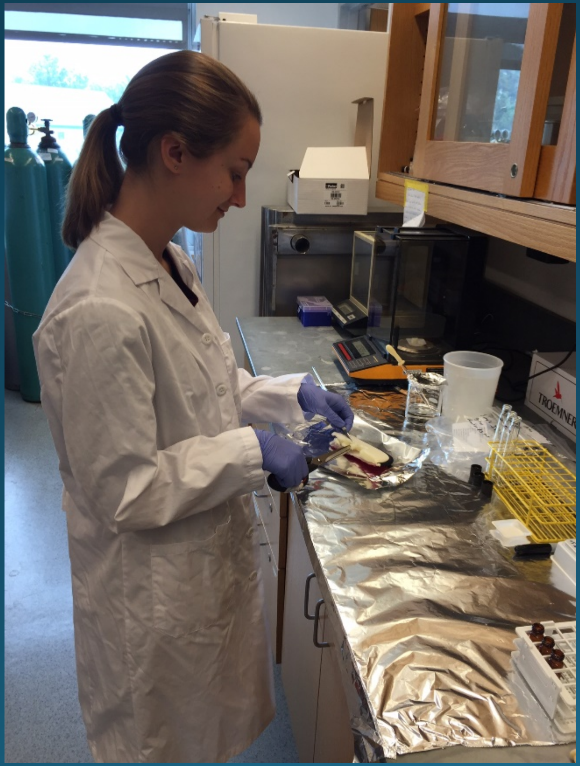
- Since opening the program in February 2014 we have now received more than 1500 samples for screening.

How we prepare a foam sample

Cut a piece of foam

Remember:

Our service only analyzes polyurethane foam. Other materials sent in (e.g., styrofoam) are not analyzed.

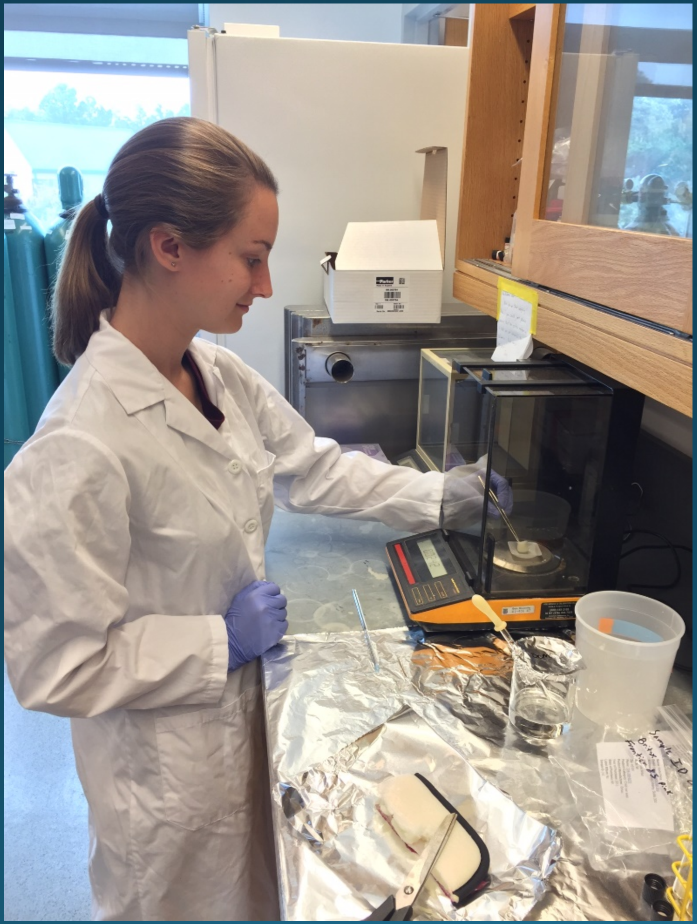


Throughout the entire process, care is taken to minimize contamination, and carryover between samples.

Gloves are worn for personal protection, but also to prevent contamination.

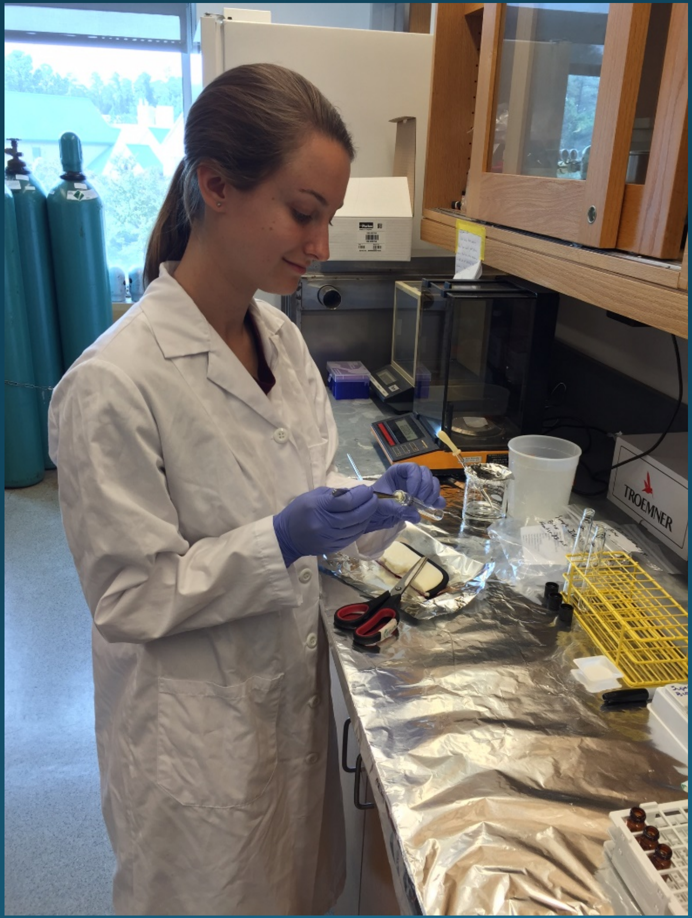
Tools are rinsed with solvent between each sample, and the workspace is kept clean.

Weigh the sample: 0.05 g



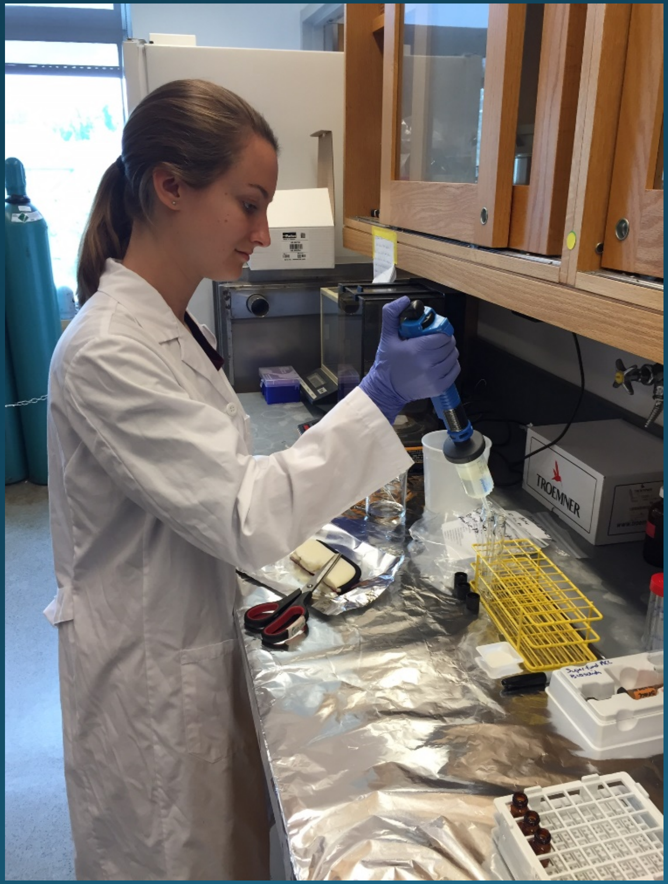
Sample weights are kept consistent to ensure consistency in analysis.

Put sample in a clean glass test tube

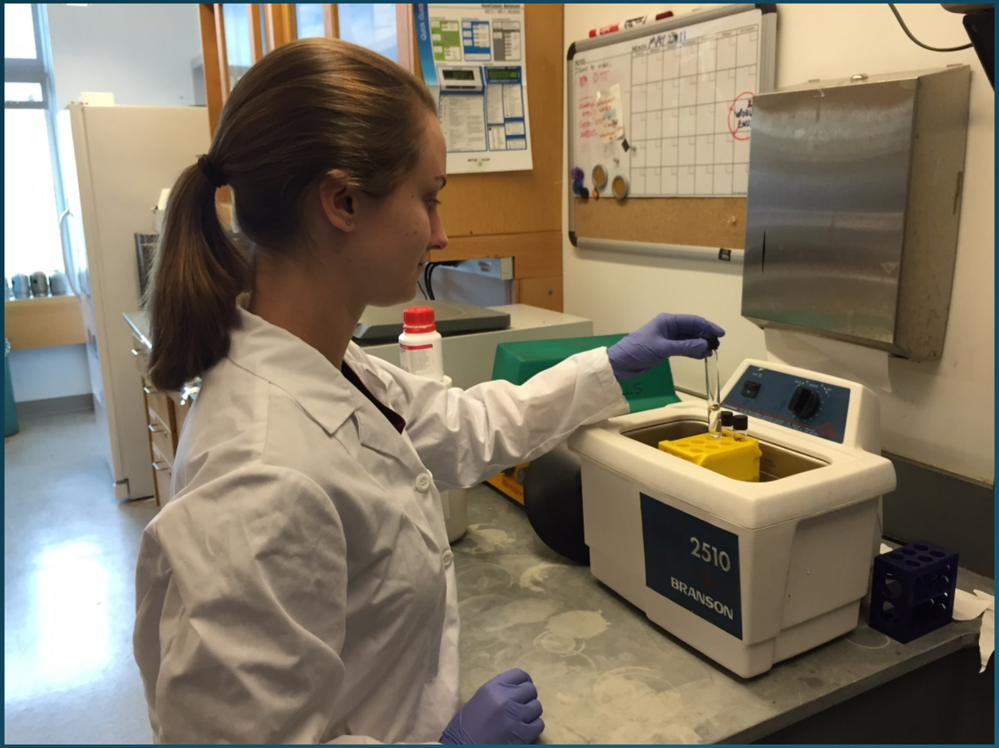


Glass is used because most flame retardants we analyze “stick” to plastic.

Add solvent (5 mL dichloromethane)



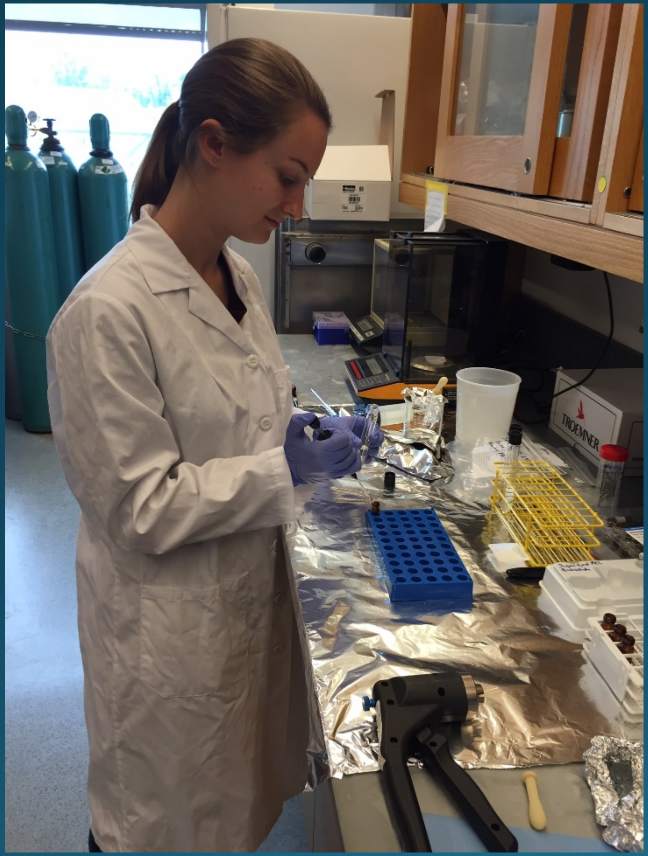
Sonicate the sample for 15 min



Ultrasonic waves facilitate the extraction of the flame retardant chemicals from the foam.

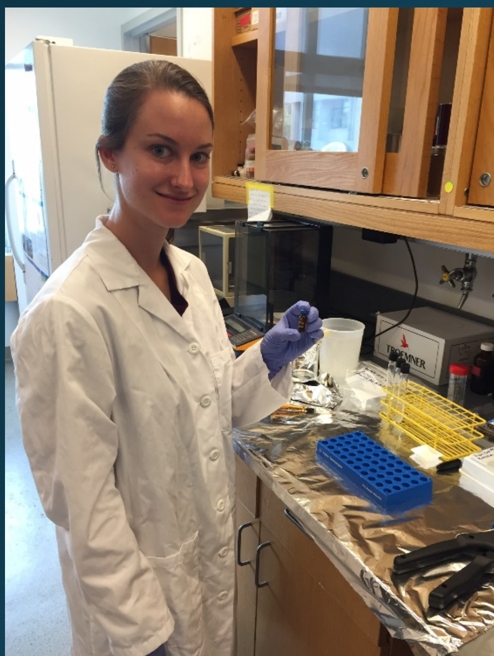
Remember, these flame retardants are just added to the foam, not incorporated into the foam's structure, so they come out easily.

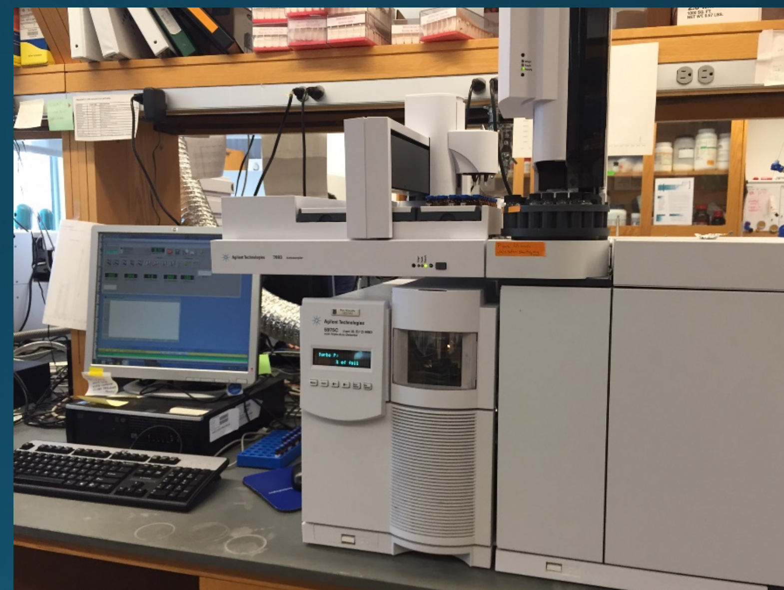
Transfer 100 μL aliquot to a vial and dilute to 1 mL



We dilute the extract because flame retardants are added at very high levels in foam that can overwhelm our instrument.

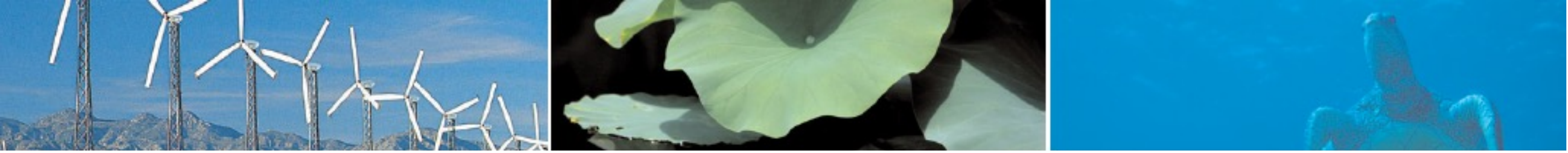
Cap, label and run on GC/MS (Thanks, Katie!)



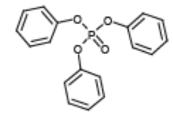
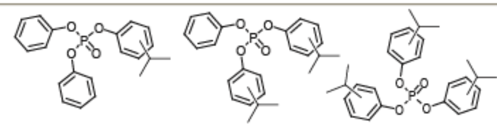
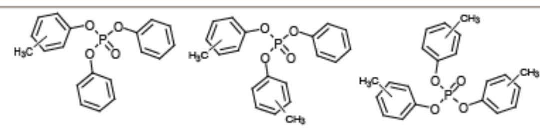
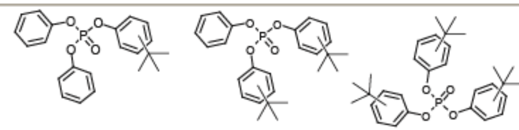
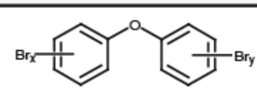


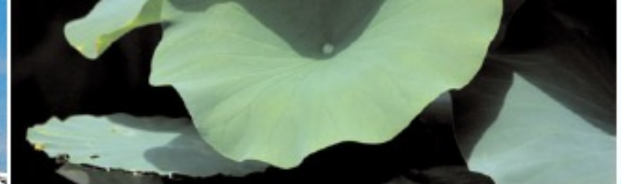
Then we:

- Identify flame retardants (using authentic standards)
- Enter information into database
- Turn things over to Bryan for reporting…

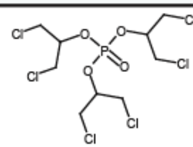
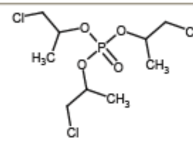
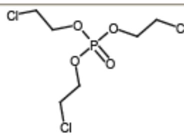
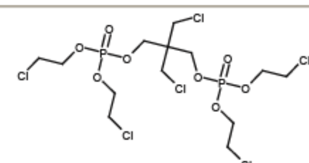
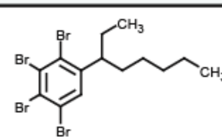
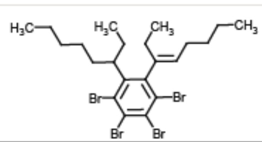


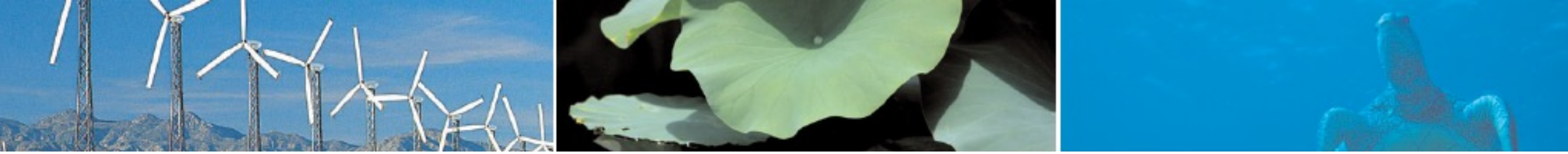
Flame retardants included in screening

Compound	Structure	Flame Retardant Mixes/Products
Non-halogenated organophosphates		
Triphenyl phosphate (TPP)		FireMaster® 550, FireMaster® 600, PentaBDE, TBPP, MPP
Isopropylated TPP		FireMaster® 550,
Methylated phenyl phosphates		MPP
t-butylated phenyl phosphates		TBPP, FireMaster® 600
Bromodiphenyl ethers		
e.g., BDE-99, BDE-47, BDE-100		PentaBDE (x + y = 4 to 6)


Flame retardants included in screening

Compound	Structure	Flame Retardant Mixes/Products
Chlorinated Organophosphates		
tris(1,3-dichloro-2-propyl) phosphate (TDCIPP)		TDCIPP
tris(1-chloro-2-propyl) phosphate (TCIPP)		TCIPP
tris(1-chloro-2-ethyl) phosphate (TCEP)		V6 (present as impurity) Thermolin® 101 (impurity?)
2,2-bis(chloromethyl)propane-1,3-diyl-tetrakis(2-chloroethyl)bis(phosphate (V6)		Antiblaze V6
Other Br FRs		
2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB)		FireMaster® 550, FireMaster® 600
Bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH)		FireMaster® 550, FireMaster® 600



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Results from Screening Polyurethane Foam Based Consumer Products for Flame Retardant Chemicals: Assessing Impacts on the Change in the Furniture Flammability Standards

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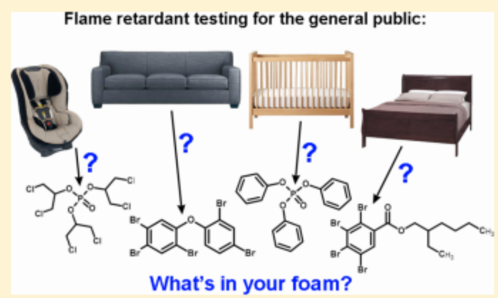
Supporting Information

ABSTRACT: Flame retardant (FR) chemicals have often been added to polyurethane foam to meet required state and federal flammability standards. However, some FRs (e.g., PBDEs and TDCIPP) are associated with health hazards and are now restricted from use in some regions. In addition, California's residential furniture flammability standard (TB-117) has undergone significant amendments over the past few years, and TDCIPP has been added to California's Proposition 65 list. These events have likely led to shifts in the types of FRs used, and the products to which they are applied. To provide more information on the use of FRs in products containing polyurethane foam (PUF), we established a screening service for the general public. Participants residing in the US were allowed to submit up to 5 samples from their household for analysis, free of charge, and supplied information on the product category, labeling, and year and state of purchase. Between February 2014 and June 2016, we received 1141 PUF samples for analysis from various products including sofas, chairs, mattresses, car seats and pillows. Of these samples tested, 52% contained a FR at levels greater than 1% by weight. Tris(1,3-dichloroisopropyl)phosphate (TDCIPP) was the most common FR detected in PUF samples, and was the most common FR detected in all product categories. Analysis of the data by purchasing date suggests that the use of TDCIPP decreased in recent years, paralleled with an increase in the use of TCIPP and a nonhalogenated aryl phosphate mixture we call "TBPP." In addition, we observed significant decreases in FR applications in furniture products and child car seats, suggesting the use of additive FRs in PUF may be declining, perhaps as a reflection of recent changes to TB-117 and Proposition 65. More studies are needed to determine how these changes in FR use relate to changes in exposure among the general population.



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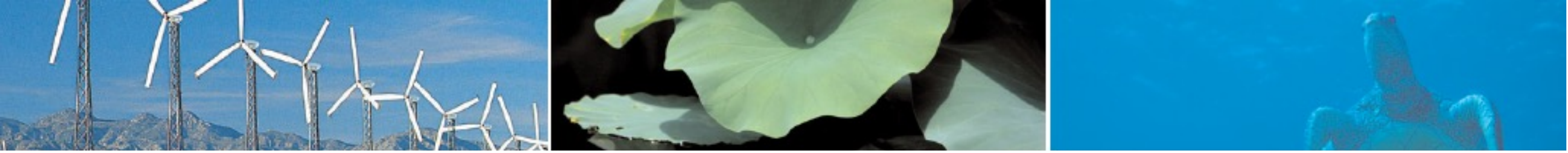


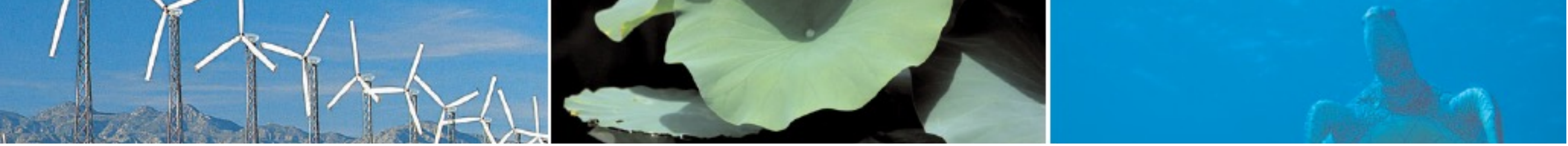
Sample Descriptions

Table 1. Description of foam samples received from project inception through June 2016.

Category	Total products	Products with FR[a]	Products with no FR Detected
Sofas and loveseats	451	250 (28.4%)	201 (14.9%)
Chairs	130	82 (15.9%)	48 (16.7%)
Mattress pad	106	31 (19.4%)	75 (18.7%)
Child car seat	98	72 (31.9%)	26 (54.0%)
Mattress	71	22 (18.2%)	49 (16.3%)
Other	59	25 (20.0%)	34 (17.6%)
Other child products	49	21 (28.6%)	28 (28.6%)
Rocking chairs and recliners	44	27 (22.2%)	17 (0%)
Child mattress	36	13 (15.0%)	23 (22.0%)
Pit cubes	39	33 (15.2%)	6 (50.0%)
Pillows	32	9 (11.1%)	23 (21.7%)
Other furniture	26	13 (23.0%)	13 (23.1%)
Total	1141	598 (24.2%)	543 (19.2%)

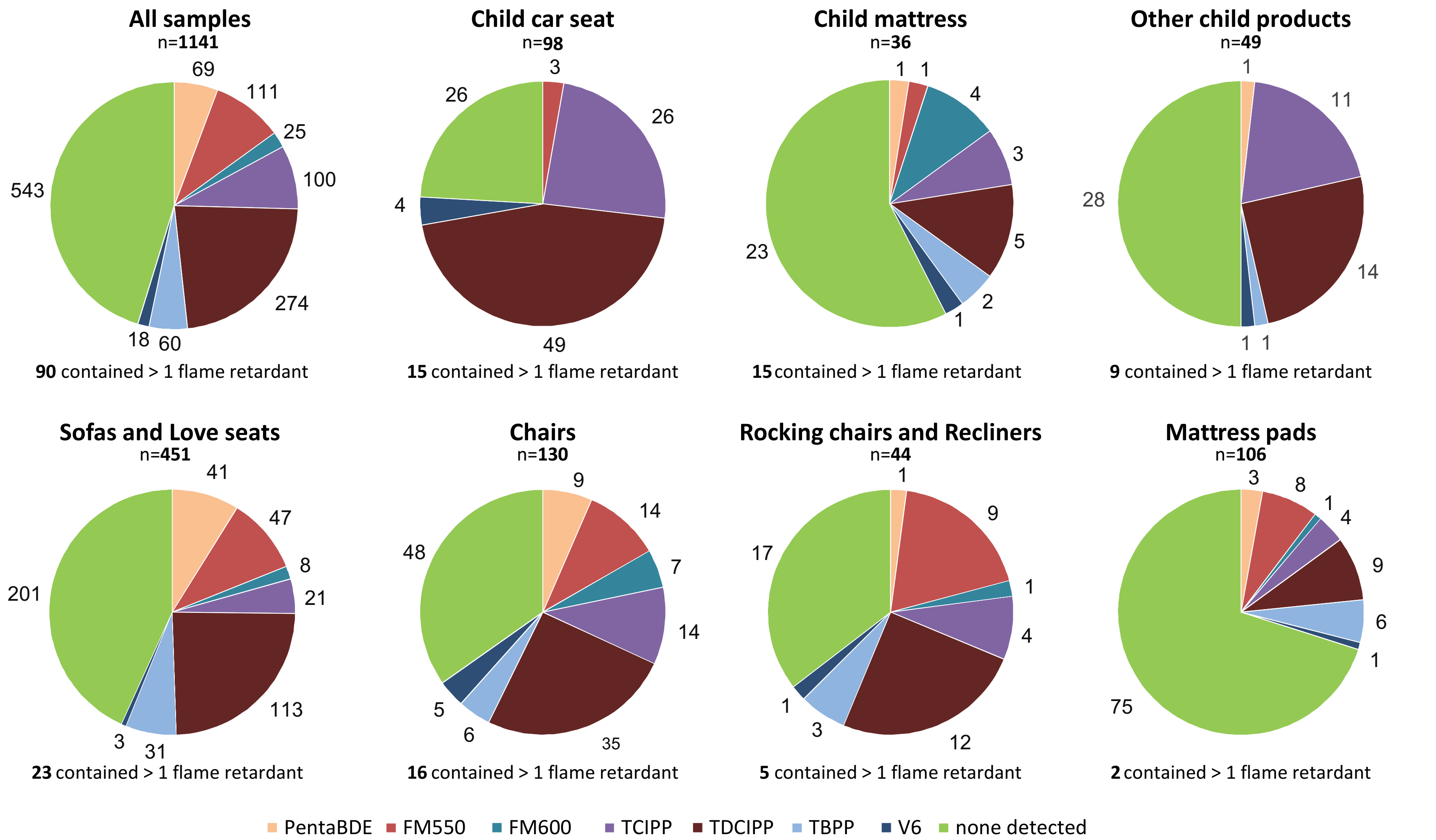
[a] Values in parenthesis are percentages of products purchased in California under each column header.

Cooper et al. 2016



Results Through June 2016

(Detection indicates FR is >1.0% by weight)



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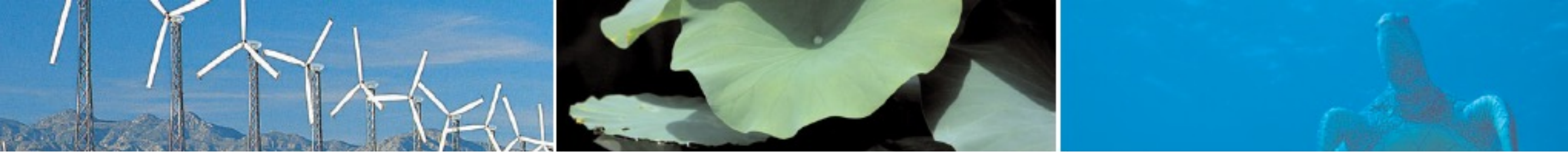
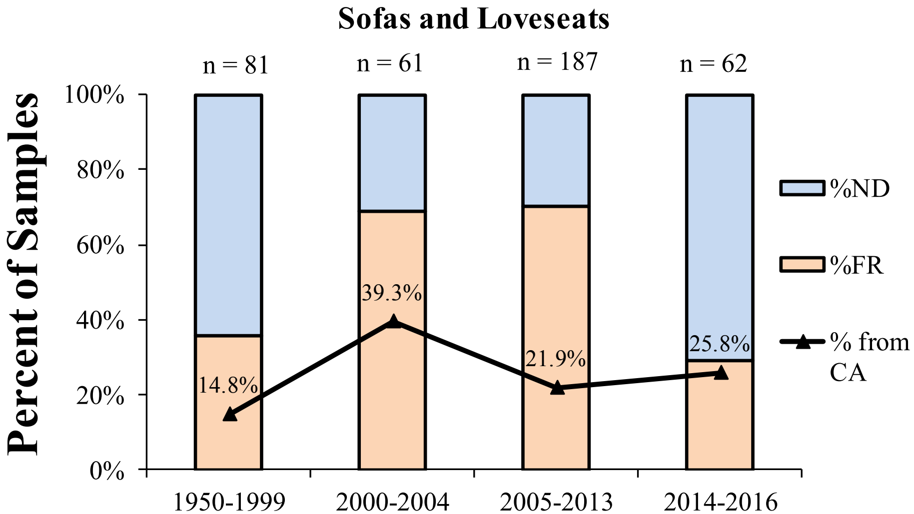
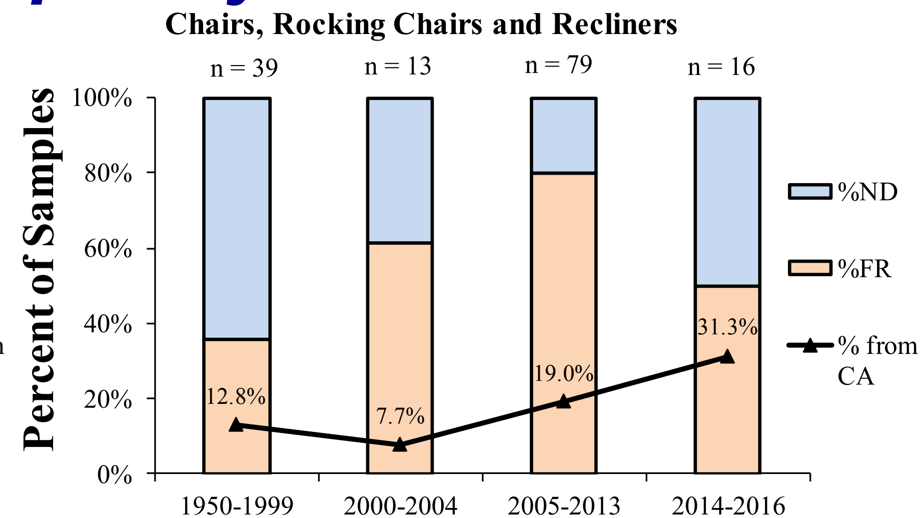
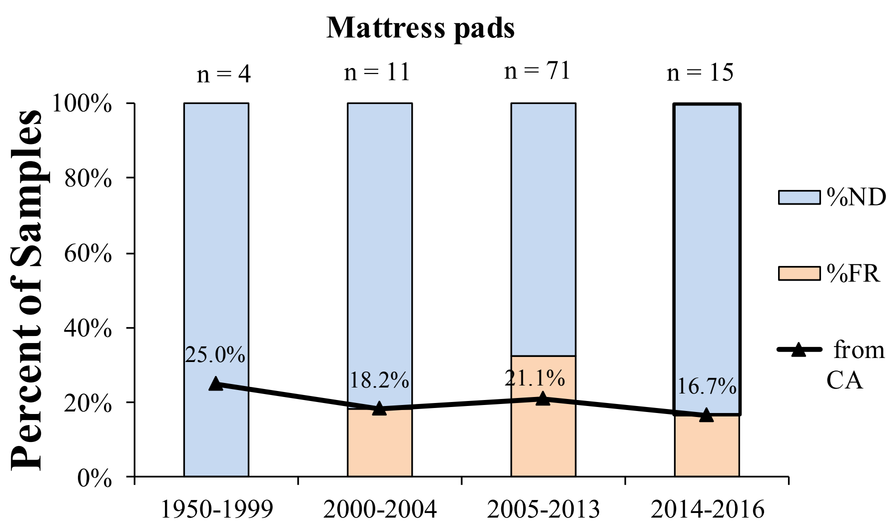
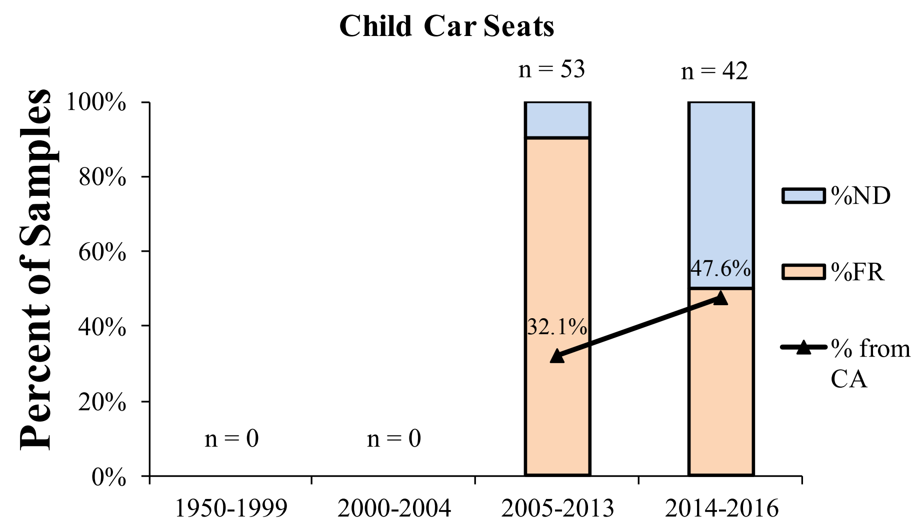


FR detection frequency trends









ND: none detected; FR: FR detected

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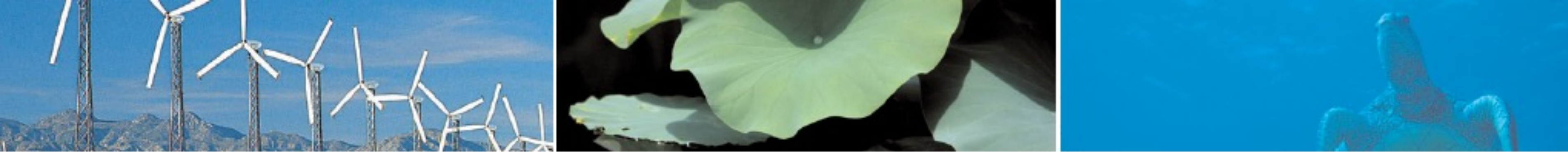
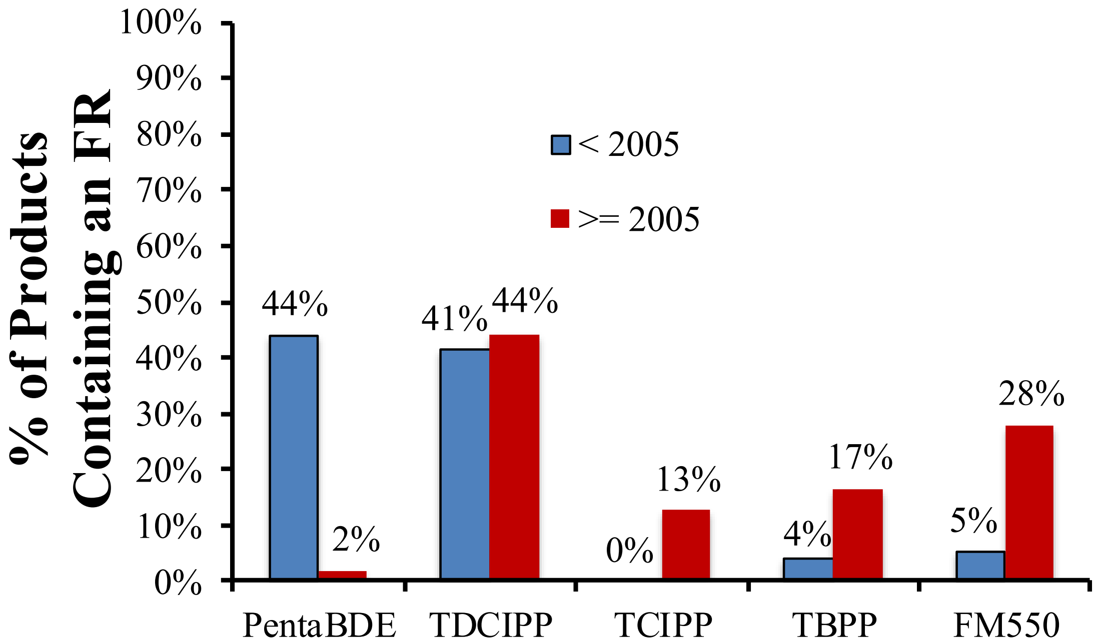
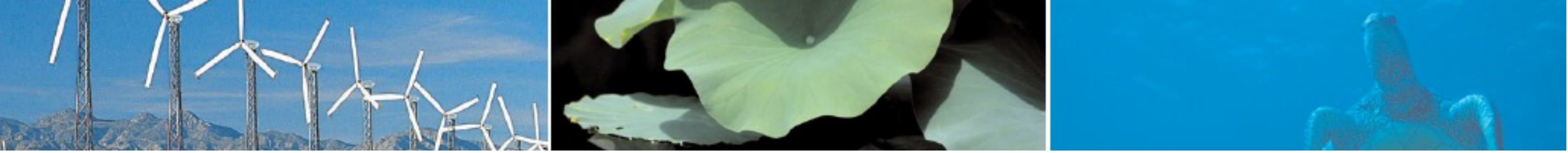


Changes in FR Use: Sofas and Loveseats pre/post 2005



- **PentaBDE in very few samples purchased >2005**
- **Use of alternate flame retardants increase >2005**
- **TCIPP <u>not</u> observed <2005**

Cooper et al. 2016

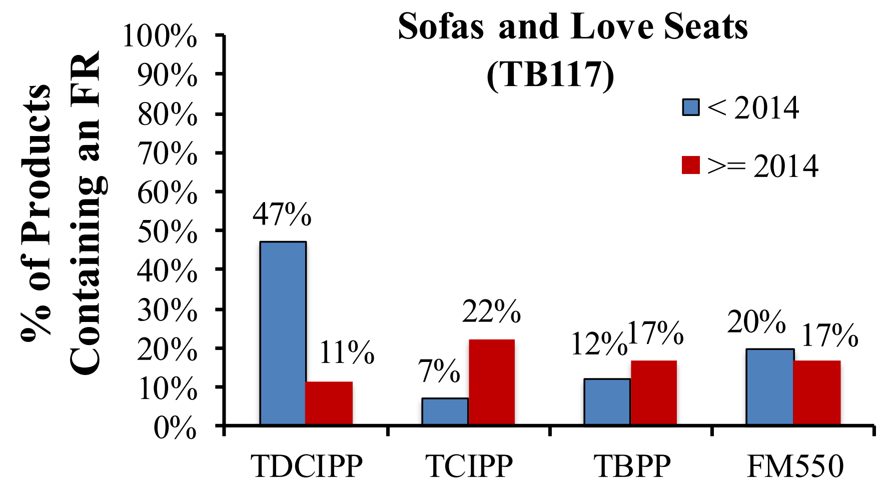


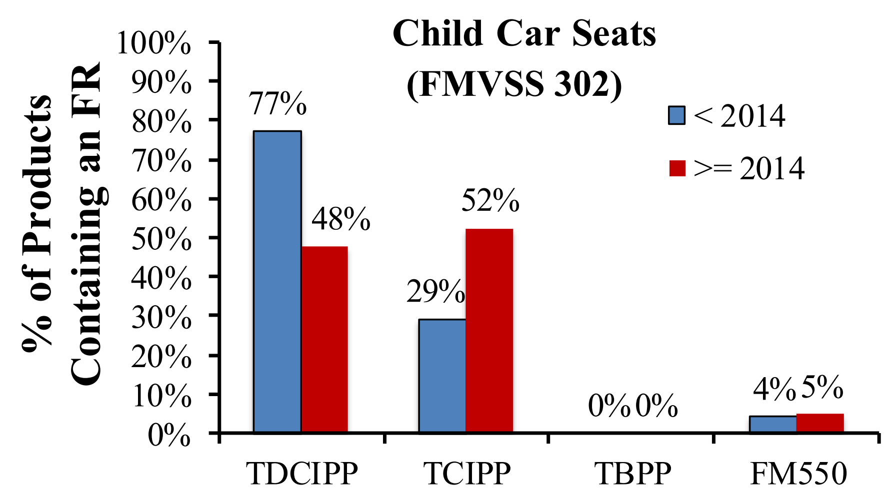
Changes in FR Use: pre/post 2014

- Between 2000-2014, >70% of sofas and loveseats were treated with FRs. Since 2014, less than 40% of sofas and loveseats are treated with FRs.

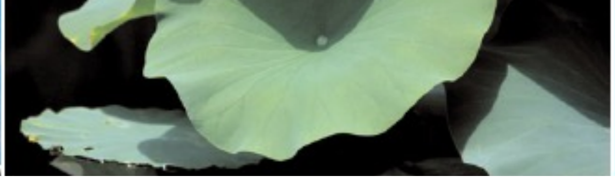
- Use varies with product type: noticeable shifts in products that fall under TB117
  - TDCIPP clearly **decreases** >2014
  - TBPP and TCIPP use **increases** >2014 in TB117 products
  - No TBPP in Car Seats

- Decrease in TDCIPP in products >2014 may also reflect TDCIPP addition to Prop 65



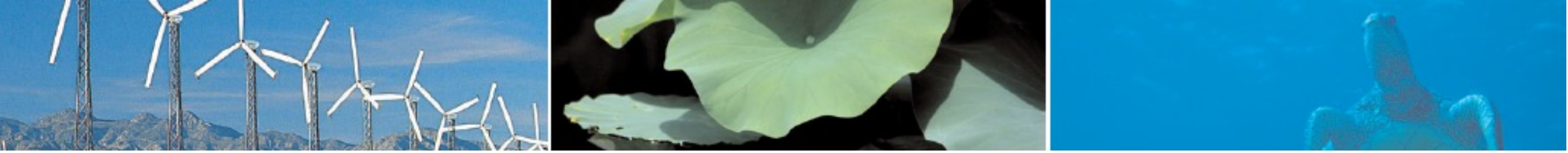


Cooper et al. 2016

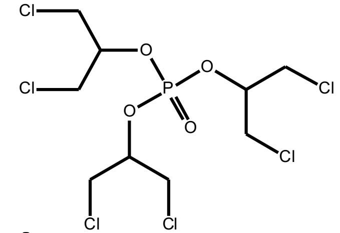


Results from Foam Screening Suggest:

- PentaBDE use (and thus exposure) has significantly decreased since 2005
- Use of alternate flame retardants has increased
- The use of TDCIPP appears to be decreasing since 2014; coinciding with addition of TDCIPP to CA Prop 65 list
- Over last two years, increasing detection of TCIPP and organophosphate mixtures observed
- Studies on health effects of new organophosphate flame retardants are limited or lacking



TDCPP



- **TDCPP (e.g. Fryrol FR-2) was used as a FR in children's pajamas in the 1970s**

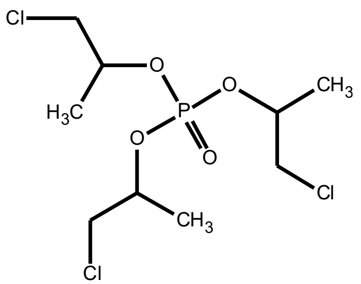
- **Research published in Science suggests that TDCPP and its brominated analogue were mutagenic (likely to cause cancer). (Gold et al 1978; Blum et al 1977)**

- **Studies conducted by the National Toxicology Program also found Increased Incidence of tumors in rats exposed to TDCPP over 2 years (NTP, 2000)**

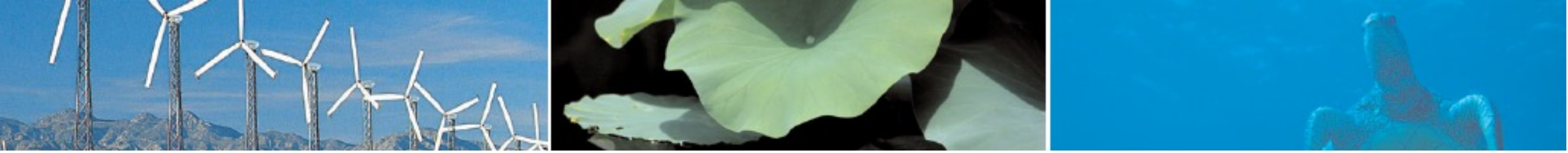
- **Several recent toxicology studies have found that exposure to TDCPP in rats and fish has led to significant changes in thyroid regulation (Xu et al. 2015; Wang et al. 2015; Zhao et al. 2016)**

- **Urinary metabolites detected in more than 90% of US population; levels significantly higher in children relative to adults (Hoffman et al. 2015 Butt et al. 2016)**

TCPP



- **Structurally similar to TDCPP**
- **In zebrafish studies, it was not as acutely toxic as TDCPP. No impacts on neurobehavioral assessments (Dishaw et al. 2014)**
- **In a study with chicken embryos, exposure to TCPP resulted in delayed development and disruption of thyroid endpoints (Farhart et al. 2013)**
- **A rodent carcinogenicity study is currently being conducted by the National Toxicology Program.**
- **Urinary metabolites detected in 100% of samples recently tested (Butt et al. 2016)**



Firemaster 550

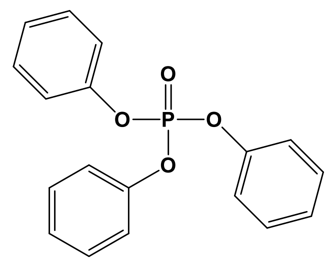
- FM 550 has gained market share since the phase-out of pentaBDE
- (Stapleton *et al.*, 2012)

- Human exposure to FM 550 is widespread (Hoffman *et al.*, 2014; Butt *et al.*, 2014; Liu *et al.*, 2015)

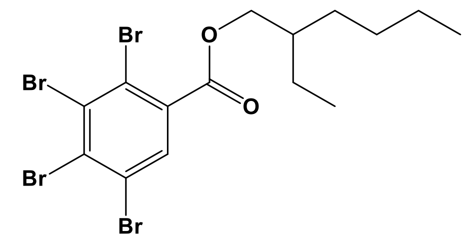
- Components of FM 550 have been demonstrated to be potentially
  - Adipogenic
  - Endocrine disrupting
  - Neuro- and developmentally toxic

  (Patisaul *et al.*, 2013; Pillai *et al.*, 2014; Belcher *et al.*, 2014; Behl *et al.*, 2015)

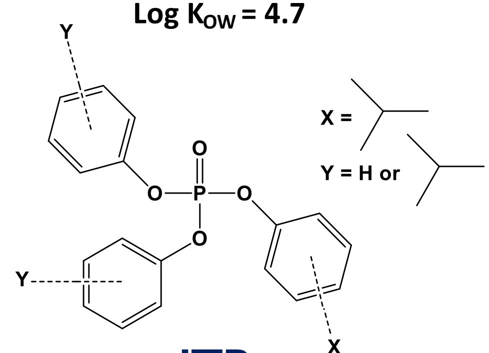
- FM 550 components are prioritized for risk assessment by the U.S. EPA



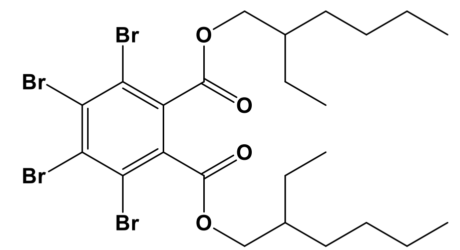
TPP
Log K_{OW} = 4.7



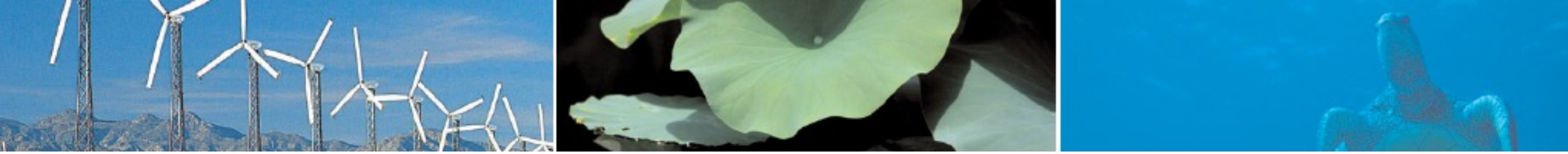
TBB
Log K_{OW} = 7.7



ITPs
Log K_{OW} = 5.3 – 9.1



TBPH
Log K_{OW} = 12.0



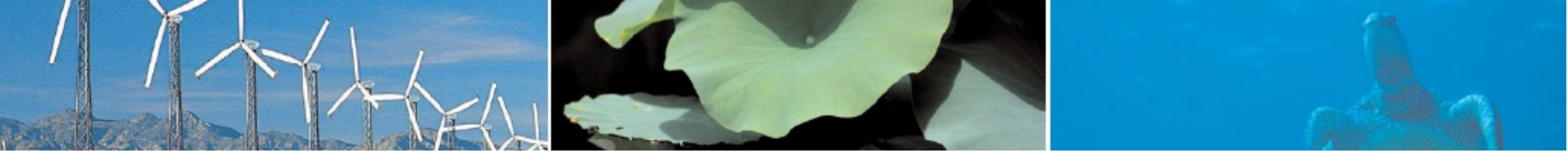
Toxicity Assessments by NTP (Behl et al. 2015)

- A series of studies conducted by researchers at the National Toxicology Program and the US EPA evaluated the relative toxicities of new flame retardants (FRs) compared to BDE-47 (PentaBDE)

- Several of the organophosphate flame retardants found in Firemaster 550 (TPP, ITP), and the mixture we identify as “TBPP” (BPDP) were equally or more toxic than BDE-47

- Relative “potency” of several FRs based on developmental toxicity, developmental neurotoxicity, and acute toxicity:

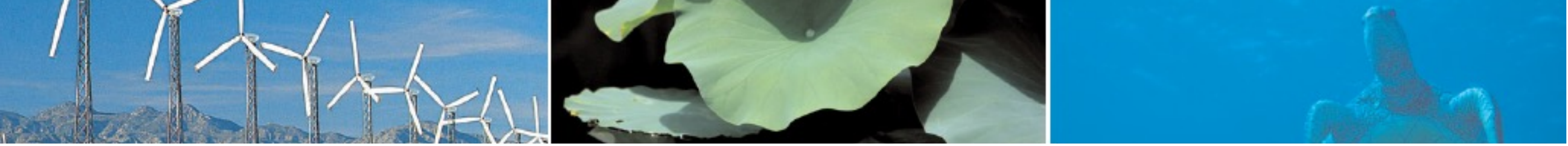
  - TPP, ITP and BPDP displayed greater overt toxicity in zebrafish compared to BDE-47
  - ITP and BPDP displayed greater impacts on neuronal firing rates in rat neurons compared to BDE-47



How Can one Reduce Exposure?

- **More than 90% of the population has detectable levels of these FRs in their bodies; levels are generally higher in children. To reduce exposure, one can take these steps:**
  - **Exchange furniture if economically feasible**
  - **Wash hands frequently, particularly before eating (Hoffman et al. 2014, 2015, Butt et al. 2016)**
  - **Vacuum and clean home more frequently**
  - **Air purifiers help remove particles from the indoor air, which will reduce some exposures, but not all.**

- **See our website for more information**
  - **http://foam.pratt.duke.edu/resources**

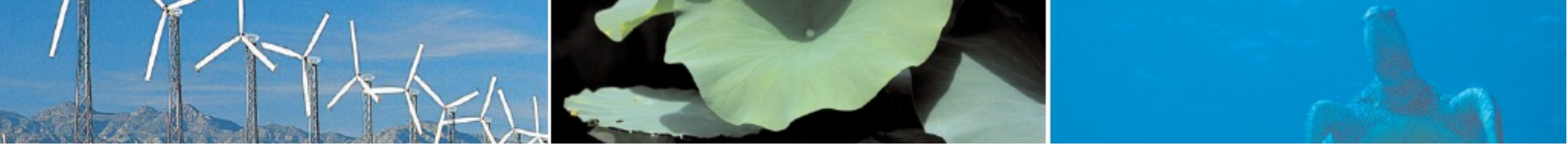


Our Next Steps…

1. We will continue to analyze PUF for FRs for at least another year with our current funding.

2. We are considering analyzing textiles in future studies.

3. We are currently trying to understand links between use of specific chemicals in consumer products and exposure (which products contribute most to our exposure?)



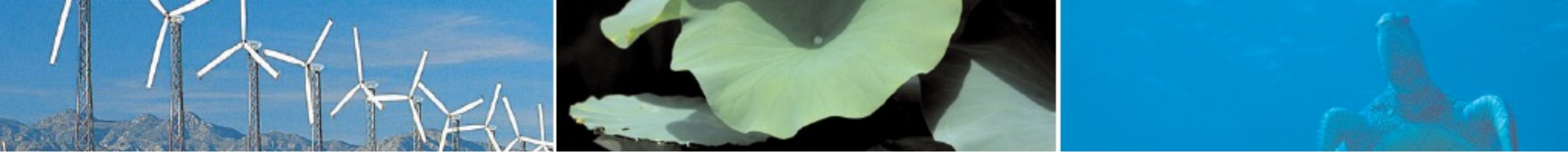
Questions Received:

1. Where can I have my blood tested for flame retardants?

2. Can you tell me which manufacturers are still using FRs in furniture?

3. Which flame retardant is most toxic?

4. Where can I purchase furniture without FRs?



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