



The Flame Retardant Tris (1,3-dichloroisopropyl) phosphate (TDCPP): What are the Health Risks?

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Outline

1. Introduction and Background

- a. What is a flame retardant (FR)?
- b. What regulations govern the use of FRs in products?
- c. What type of products contain FRs?

2. Identification of Flame Retardants in Consumer Products

- a. In Baby Products
- b. In Residential Furniture
- c. In Tents

3. Exposure to TDCPP

- a. In Children
- b. In Adults

4. Known health effects of TDCPP

5. Conclusions



Definition:

“A substance added or a treatment applied to a material in order to suppress, significantly reduce or delay the combustion of the material” *EHC:192, WHO 1997*

Regulations That Govern the Use of FRs

U.S. Residential Furniture:

- California Technical Bulletin 117

Textiles:

- Children’s Sleepwear (CPSC)
- Seats and Drapes in Public Buildings (NFPA 701, CA TB 133)
- Camping Equipment (CPAI-84)





What Type of Products are Treated with Flame Retardants in Your Home?



Sleep Positioners

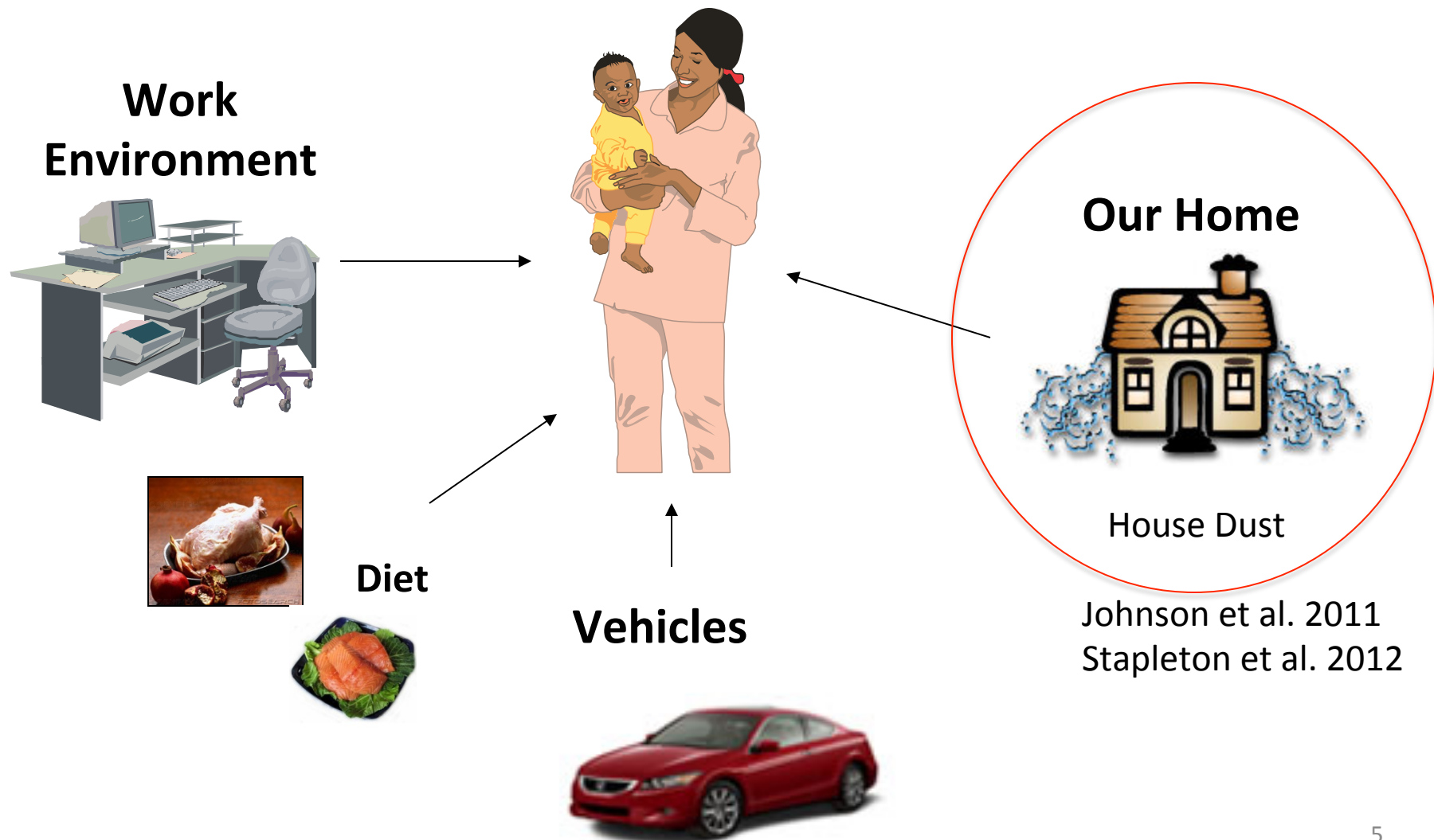


Nursing Pillow



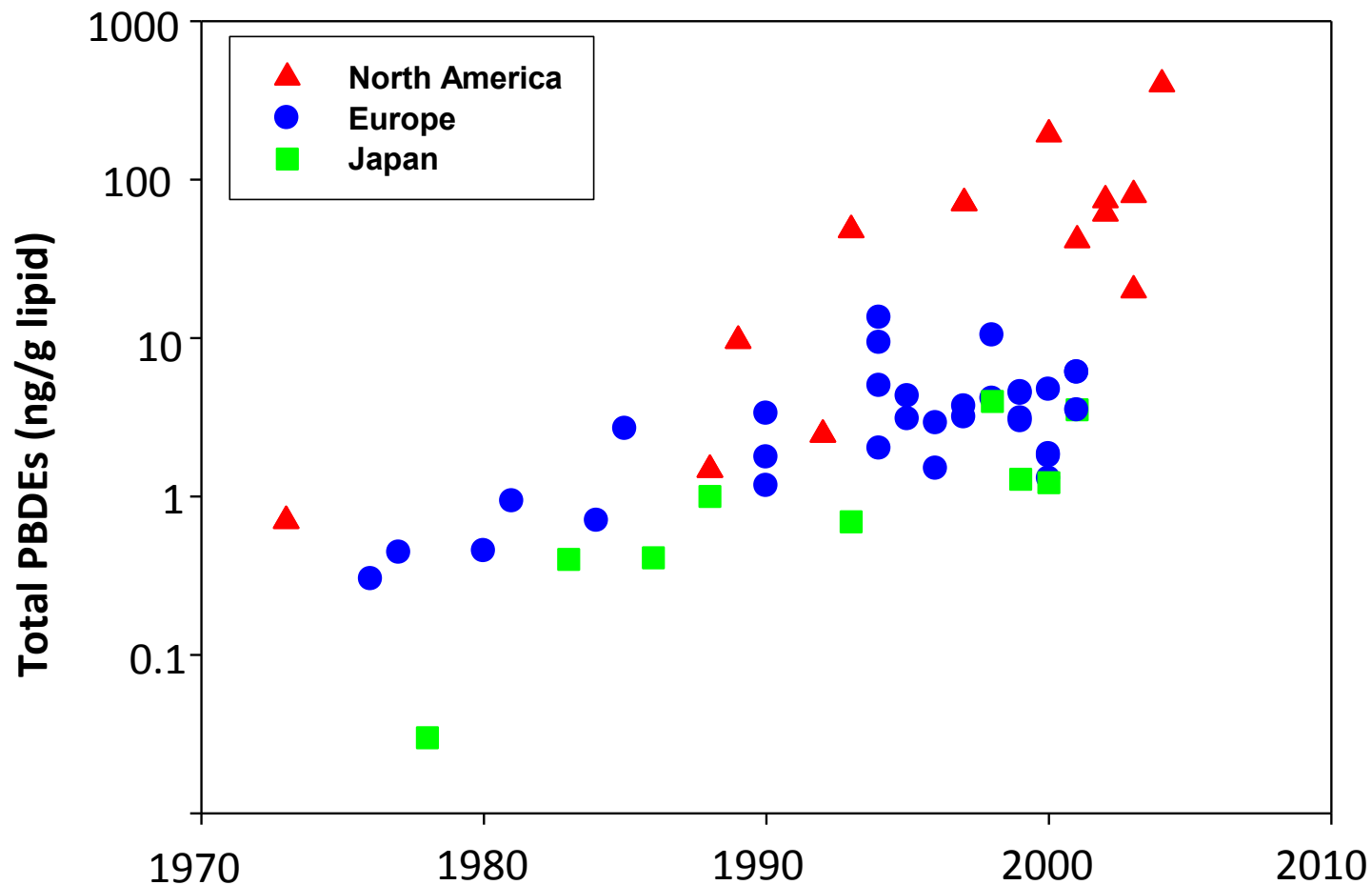


How Are We Exposed to Flame Retardants?





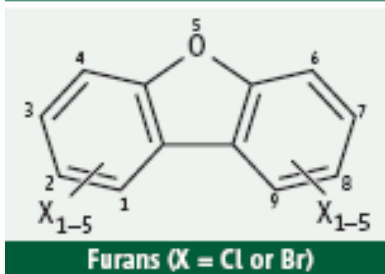
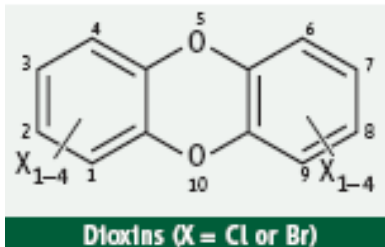
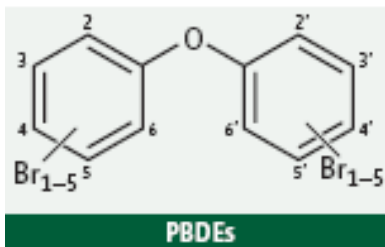
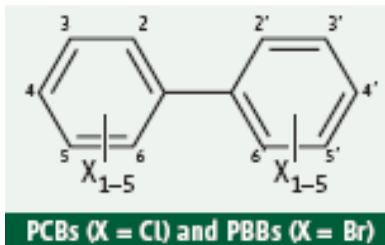
PBDEs in Human Samples From Around the World



From Hites et al., 2005



History of PBDEs and their Phase Out



- Polybrominated diphenyl ethers (PBDEs) have chemical structures which are very similar to known cancer causing and toxic compounds: **PCBs, dioxins, furans, etc.**
- Animal and Human studies have demonstrates that PBDEs are significantly associated with changes in thyroid hormone levels (Birnbaum and Staskal, 2003; Chevrier et al. 2010; Stapleton et al. 2011)
- Human health studies have found significant associations between PBDEs in blood at birth and deficits in cognitive function and behavior (Herbstman et al 2010; Eskenazi et al 2012)
- Phased out in European Union (2002); voluntary phase out in the US (Penta- and OctaBDE- 2005; Deca-2013) ⁷



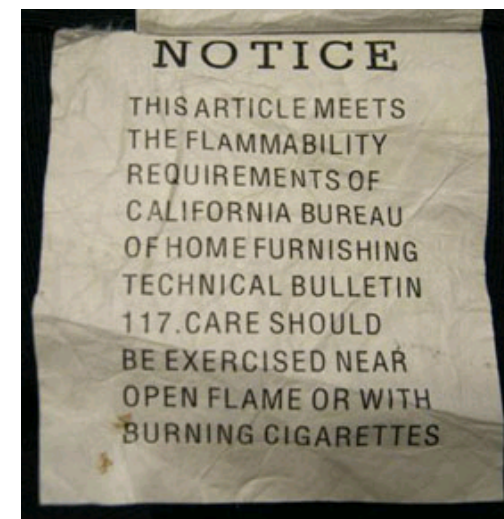
What Types of FRs are Being Used to Meet TB 117 Today?

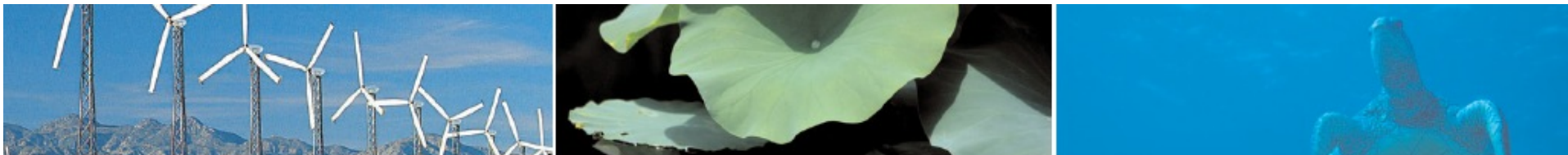
- With the phase-out of PentaBDE, what type of chemical flame retardants would be most common in residential furniture?
- Will these new/alternate FRs accumulate in indoor dust and air- leading to human exposure?
- What is known about health effects for these new flame retardants?



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

- Promulgated by California Bureau of Home Furnishing and Thermal Insulation, within the Department of Consumer Affairs
- Requires 12-second open flame testing for polyurethane inside furniture





PentaBDE Alternatives Assessment

Table 4-1 Screening Level Toxicology and Exposure Summary

L = Low hazard concern
M¹ = Moderate hazard concern
H = High hazard concern
L, M¹, or H = Endpoint assigned using estimated values and professional judgment (Structure Activity Relationships)

N = No
 Y = Yes
 P = Yes for pure chemical

*Ongoing studies may result in a change in this endpoint
 ^Persistent degradation products expected²

Company	Chemical	% in Formulation ³	Human Health Effects						Ecotoxicity		Environmental		Potential Routes of Exposure						Reactive or Additive?			
			Cancer Hazard	Skin Sensitizer	Reproductive	Developmental	Neurological	Systemic	Genotoxicity	Acute	Chronic	Persistence	Bioaccumulation	Worker			General Population			Aquatic		
														Inhalation	Dermal	Ingestion	Inhalation	Dermal			Ingestion	
Supresta	AB053																					
	Tris(1,3-dichloro-2-propyl)Phosphate CAS # 13674-87-8		M	L	M	M	L	M	M	M	M	M	L	N	Y	Y	N	Y	Y	Y	Y	Additive
Supresta	AC003																					
	Proprietary I Organic phosphate ester	92-99%	L	L	L	L	L	M	L	H	H	H	L	P	Y	Y	N	Y	Y	Y	Y	Additive
	Triphenyl Phosphate CAS # 115-86-6	1-8%	L	L	L	L	L	M	L	H	H	L	L	Y	Y	Y	Y	Y	Y	Y	Y	Additive
Supresta	AC073																					
	Triphenyl Phosphate CAS # 115-86-6	38-48%	L	L	L	L	L	M	L	H	H	L	L	Y	Y	Y	Y	Y	Y	Y	Y	Additive
	Proprietary J Aryl phosphate	40-46%	L	L	L	L	L	M	M*	L	H	L	L	Y	Y	Y	Y	Y	Y	Y	Y	Additive
	Proprietary K Aryl phosphate	12-18%	L	L	L	L	L	M	L	L	L	L	L	P	Y	Y	N	Y	N	N	N	Additive
	Proprietary L Aryl phosphate	1-3%	L	L	L	L	L	M	L	L	L	L	L	P	Y	Y	N	Y	N	N	N	Additive
Supresta	Fyrol FR-2																					
	Tris(1,3-dichloro-2-propyl)phosphate CAS # 13674-87-8	99%	M	L	M	M	L	M	M	M	M	M	L	N	Y	Y	N	Y	Y	Y	Y	Additive

(Furniture Flame Retardancy Partnership V 1, EPA 2005)



Screening Consumer Products for FR Chemicals:

Project 1- Baby Products

Project 2- Residential Couches



Screening Consumer Products Meeting CA TB 117 :

Project 1- Baby Products (Stapleton et al. 2011)

- car seats, nursing pillows, changing table pads, portable mattresses, sleep positioners, strollers, high chairs, etc

Project 2- Residential Couches (Stapleton et al. 2012)

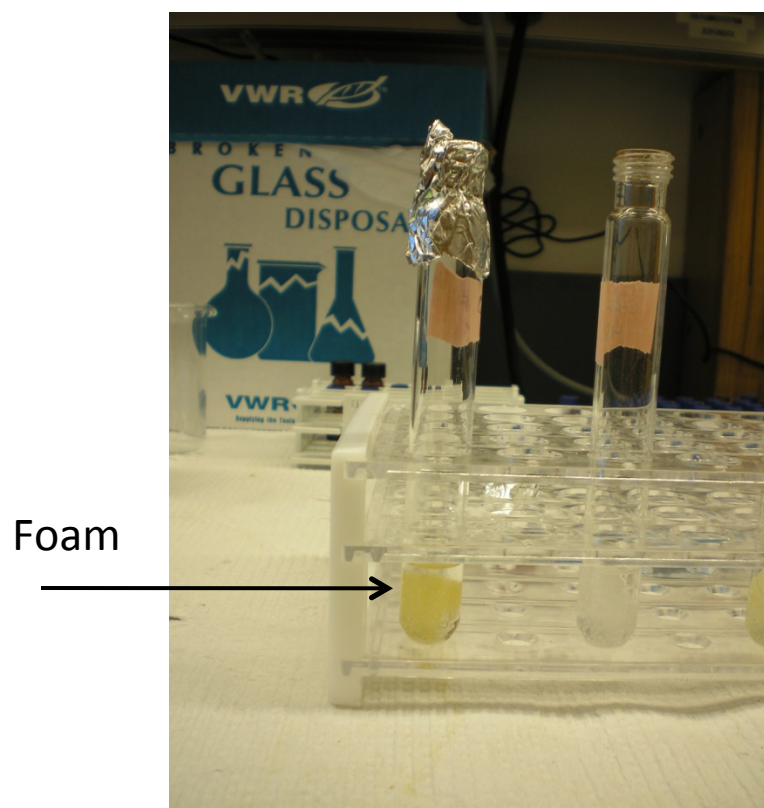
- only residential couches
- information on date and state of purchase

Project 3- Camping and Children's Tents (ongoing)

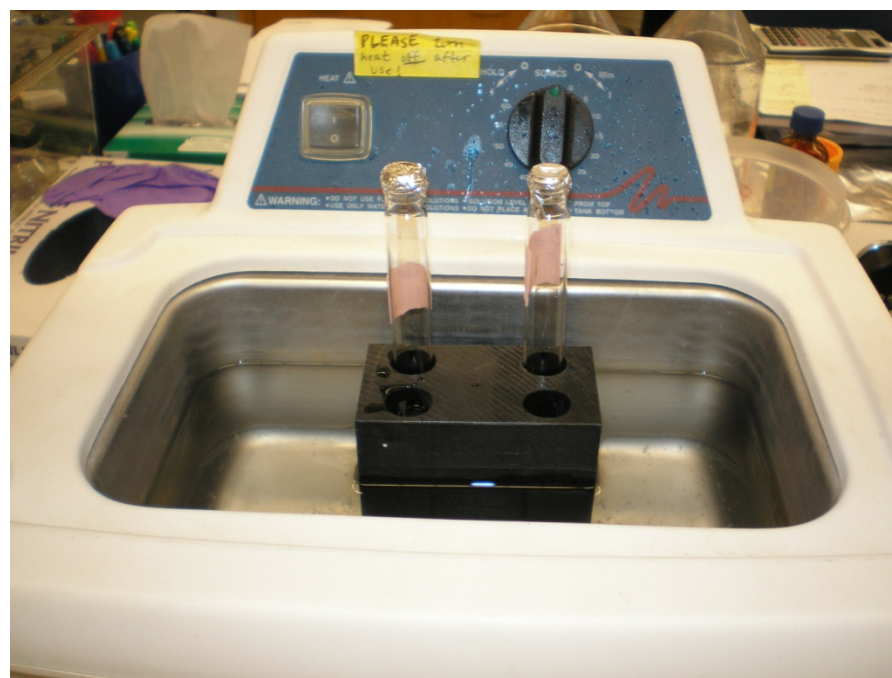
- Children's toy tents and tunnels
- Camping tents and alcoves



Analysis of the Foam Samples



Step 1. Place a small piece of foam into a test tube with dichloromethane



Step 2. Sonicate the test tube for 15 min.

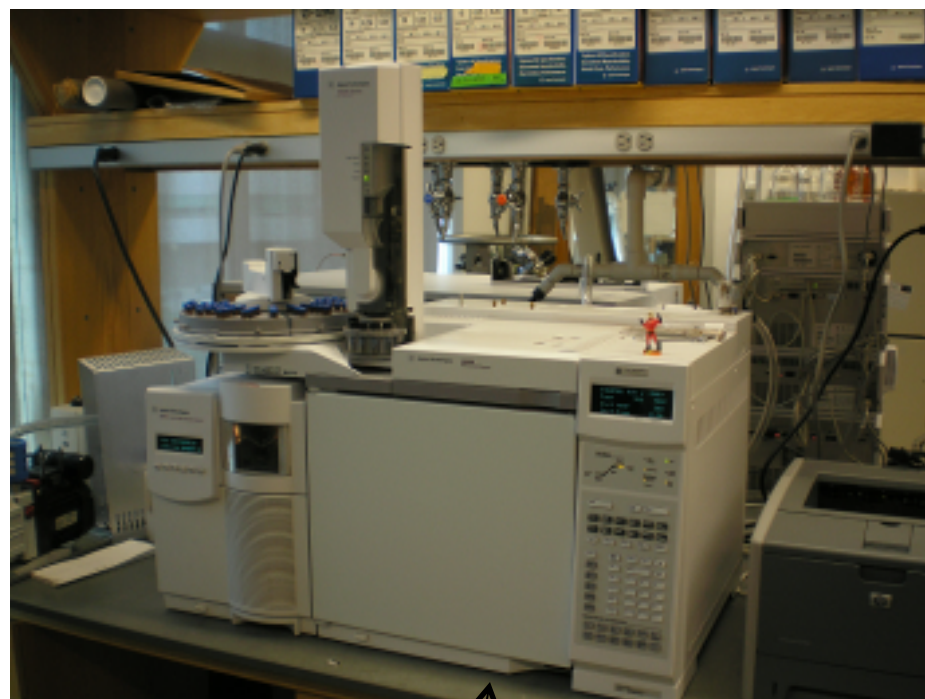


Analysis of the Foam Samples

Step 3. Remove the dichloromethane, filter out the particles, and then inject the extract into a GC/MS*.

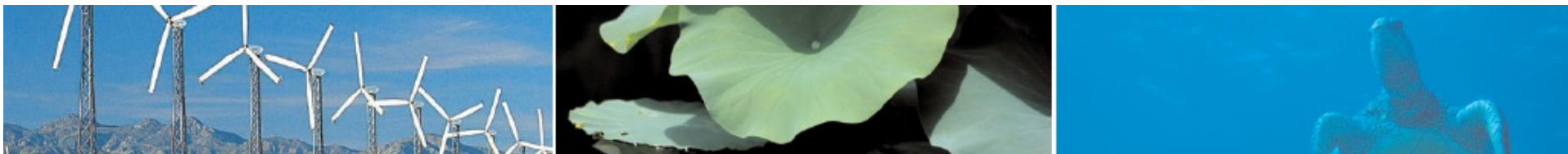
- Samples are run in full scan mode
- Signals detected are compared against a NIST mass spectral database
- For commonly known FRs we also now compare to authentic standards.

*Some sample extracts also run by LC/HRMS



Gas Chromatograph Mass Spectrometer
(GC/MS)

Agilent Technologies Model 5975



Project 1: Flame Retardants in Children's Products

ENVIRONMENTAL
Science & Technology

(2011)

ARTICLE

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Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products

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[§] Supporting Information

Sleep Positioners



Car Seats



Nursing Pillow



- 101 Baby products screened for flame retardant (FR) chemicals
- 80% contained a FR
- TDCPP, Firemaster 550 (FM 550), and “V6” most common FRs identified
- PentaBDE found in 5 samples
- Identified two new chlorinated organophosphate flame retardant mixtures
- Risk/exposure assessments do not consider exposure from use of these products
- Now 3 infant/juvenile products exempted from TB 117



Project 2: Flame Retardants in Couches

ENVIRONMENTAL
Science & Technology

(2012)

Article
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Novel and High Volume Use Flame Retardants in US Couches Reflective of the 2005 PentaBDE Phase Out

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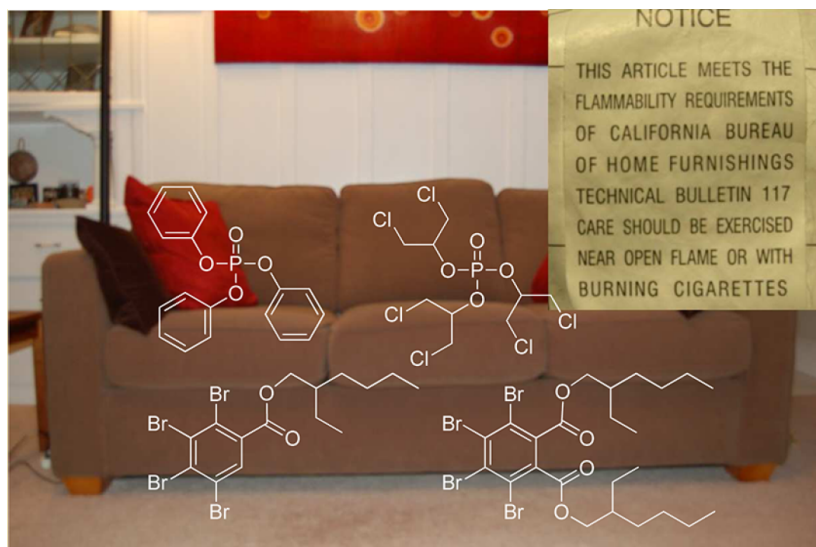
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[‡]Department of Chemistry, University of California, and Green Science Policy Institute, Berkeley, California, United States

Supporting Information

- 102 foam samples collected from residential couches in the US
- Information on year of purchase, state where couch purchased, and presence of TB 117 label recorded
- Samples purchased between 1985-2010
- 87 of 102 samples contained a FR
- TDCPP, PentaBDE, and Firemaster 550 (FM 550) most common FRs identified
- Identified two new organophosphate flame retardant mixtures





Flame Retardant Detection and Measurement:

Table 1. Flame Retardant (FR) Measurements and Descriptive Statistics of Polyurethane Foam Samples ($n = 102$). (Values in parenthesis represent percentage of the total number of samples for that specific column)

flame retardant	number of detects	average FR level (mg/g)	purchased prior to 2005 ^a	purchased 2005 or later ^a	purchased in California ^b	purchased outside California ^b	yes TB 117 ^c	no TB 117 ^c
PentaBDE	17	20.23 ^d	16 (39%)	1 (2%) ^e	7 (29%)	9 (12%)	9 (14%)	8 (24%)
TDCPP	42	44.87	10 (24%)	32 (52%)	10 (42%)	30 (41%)	33 (50%)	9 (26%)
FM 550	13	19.76 ^f	2 (5%)	11 (18%)	3 (13%)	8 (11%)	12 (18%)	1 (3%)
V6/TCEP	1	41.77 ^g	0	1 (2%)	1 (4%)	0	1 (2%)	0
TBPP mix	8	7.90 ^h	0	8 (13%)	1 (4%)	7 (10%)	6 (9%)	1 (3%)
MPP mix	2	3.23 ⁱ	0	2 (3%)	0	2 (3%)	1 (2%)	1 (3%)
TDCPP and PentaBDE	2	22.64	2 (5%)	0	1 (4%)	1 (1%)	1 (2%)	1 (3%)
TDCPP and FM 550	2	19.06	0	2 (3%)	0	2 (3%)	2 (3%)	0
FR < 0.2 mg/g	3 ^j	0.11	1 (2%)	2 (3%)	0	3 (4%)	0	2 (6%)
none detected	12	-	10 (24%)	2 (3%)	1 (4%)	11 (15%)	1 (2%)	11 (32%)
totals	102		41	61	24	73	66	34

- Average Concentration in foam approximately 4-5% by weight of foam (40-50 mg/g)
- Significant increase in FR applications since 2005
- Significant increase in diversity of FR chemicals in furniture since 2005
- 62% of samples without a TB 117 label still contained FRs
- California TB 117 has become a *de facto* standard for the US



TDCPP Use in Camping Tents



- Fabric in tents/tunnels meets a flammability standard referred to as CPAI-84
- We tested 10 children's tunnels and tents purchased in 2011-2012; 4 had TDCPP and were all from same manufacturer. (May have been removed following CA Prop 65)
- We tested 11 camping tents purchased within last decade; 11 out of 12 had detectable flame retardant present;
 - 3 had TDCPP (remaining had BDE 209 and Tripheny phosphate)
 - Concentration of TDCPP ~ 10 mg/g (1% by weight)



Potential Exposure to TDCPP

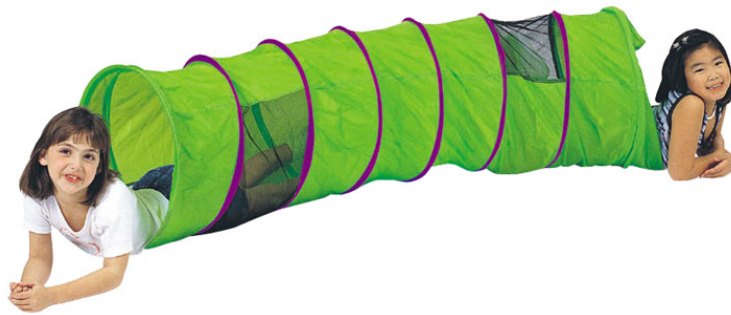


Exposure Threshold for TDCPP

- Consumer Product Safety Commission (CPSC) evaluated risk to TDCPP in a 2006 report. They estimated children's exposure from use in residential furniture was ***higher*** than Acceptable Daily Dose (ADD – 5.0 micrograms/kg/day).
- Levels in Indoor Dust in North Carolina Homes with Children (n=83; collected 2010-2012):
 - Range: 0.4 to 96.8 micrograms/gram of dust (or ppm)



Exposure to TDCPP in Tents (Preliminary Data)



- Levels of TDCPP and TCPP in the air inside the tunnels were >10X higher than outside the tent (ten feet away).
 - TDCPP levels on hands after setting up tunnels averaged 21.8 ± 10.5 micrograms.
-
- After setting up camping tents, we found significant associations between levels of TDCPP on people's hands, and the detection of TDCPP in the tent (n=20).
 - Amount of TDCPP on hands were as high as 8.53 micrograms.



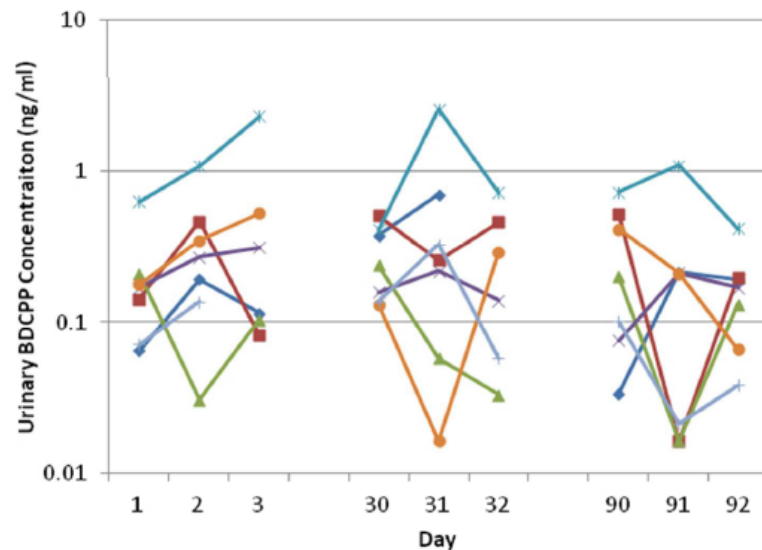
TDCPP Urinary Metabolite Levels

- TDCPP is metabolized in humans to bis (1,3-dichloroisopropyl) phosphate (BDCPP) by cytochrome P450s (Cooper et al., submitted)
- Our laboratory developed a method to measure urinary levels of BDCPP (Cooper et al. 2011)
- Urinary BDCPP levels measured in two cohort studies:
 - 45 Men in fertility study (2002-2007); repeated measures and associations with dust TDCPP levels (Meeker et al., 2013)
 - Male and Female office workers (2009); associations with dust TDCPP levels (Carignan et al., 2013)



TDCPP Urinary Metabolite Levels

Population	Sample Number	% Detect	Range (pg/mL)	Geomean (pg/mL)	Reference
Men (2002-2007)	45	91	<MDL- 25,000	130	Meeker et al., 2013
Men and Women (2009)	29	100	62-1760	408	Carignan et al., 2013

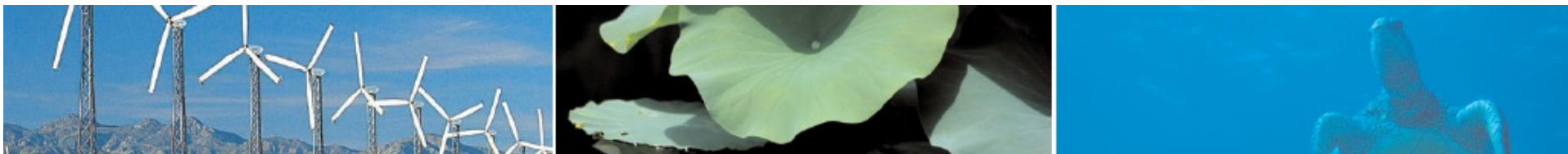


Repeated measurements of BDCPP
In 7 men over 3 month period

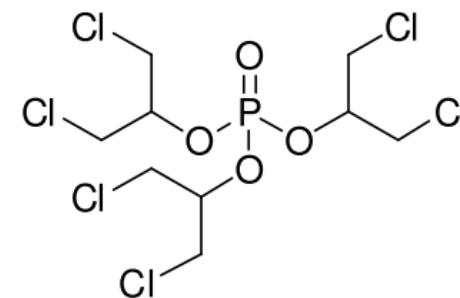
Intraclass correlation coefficient: 0.62



What are the Health Risks for TDCPP?



TDCPP



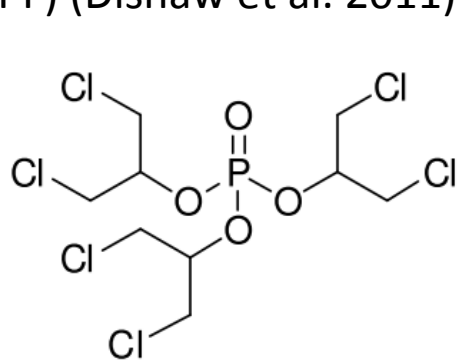
1. Reemtsma et al. 2008
2. Stapleton et al. 2009
3. Takigami et al. 2009
4. Lebel et al. 1989
5. Hudec et al. 1981
6. Gold et al. 1978
7. Meeker and Stapleton 2010

- Trade name: Fyrol FR2
- OPFR used since 1970s¹
- Used in Children's PJs in 1970s⁶
- Primary replacement for PentaBDE
 - Detected in US furniture foam²
 - High concentrations in US and Japanese dust^{2,3}
- Little human toxicity data
 - Persistent¹/suggestion of bioaccumulation^{4,5}
 - Mutagenic⁶
 - Altered hormone levels/reduced semen quality⁷
- Studies conducted by the National Toxicology Program also found Increased Incidence of tumors in rats exposed to TDCPP over 2 years (NTP, 2000);

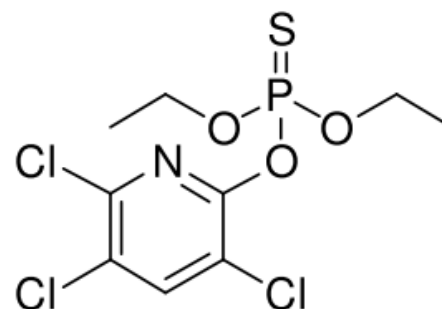


TDCPP

- TDCPP was added to California's Prop 65 List in 2011.
- Studies in fish demonstrate exposure to TDCPP during early development leads to abnormal development/malformations (McGee et al. 2012).
- Studies are now investigating potential neurotoxicity of TDCPP.
- Studies using rodent brain cells in the laboratory found that TDCPP adversely affect DNA synthesis, cell growth, cell numbers, and cellular differentiation similar to chlorpyrifos (CPF) (Dishaw et al. 2011)



TDCPP



CPF



Discussion Points

- TDCPP is currently the most common flame retardant in residential furniture and baby products (in use);
- Chronic exposure to TDCPP is occurring today;
- Exposure to TDCPP may be higher than acceptable daily doses, leading to increased risks of cancer;
- However, TDCPP may be voluntarily phased out.....ICL announced it would stop production by 2015.
- Alternatives to TDCPP are currently available on the market.
- Many of these newer flame retardant chemicals have properties suggestive of toxic effects, yet no studies have been conducted to evaluate potential health impacts on humans;



Acknowledgments



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- **All study participants**