10 Minute Break

Review of Six Flame Retardants Uses, Toxicity, Exposure

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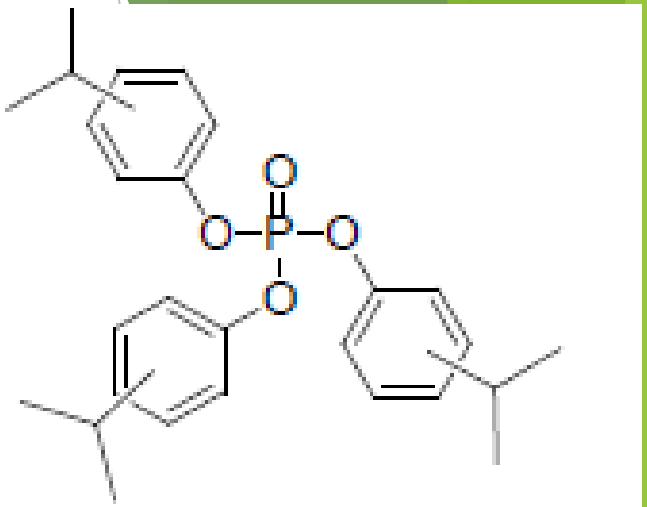
Office of Environmental Public Health Sciences

IPTPP



Representative structure

CAS	68937-41-7
Uses	Additive flame retardant, plasticizer

- foam seating and bedding
- automotive care products
- Photographic supplies
- Unspecified plastic and rubber products

National	14.9 million lbs (2011)
Production	2.9-3.2 million lbs (2012, 2013)
Volume	5.6-6.0 million lbs (2014, 2015)

Source: EPA CDR 2016 initial reporting cycle; www.epa.gov/chemical-data-reporting

Screening Level Toxicology Hazard Summary

This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion by-products are discussed in the report but not addressed directly in the hazard profiles. The caveats listed below must be taken into account when interpreting the information in the table.

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Chemical	CASRN	Human Health Effects											Aquatic Toxicity		Environmental Fate	
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Isopropylated triphenyl phosphate (IPTPP)	68937-41-7	L	*M*	L	H	*H*	*H*	H	L		L	L	VH	VH	M	*H*

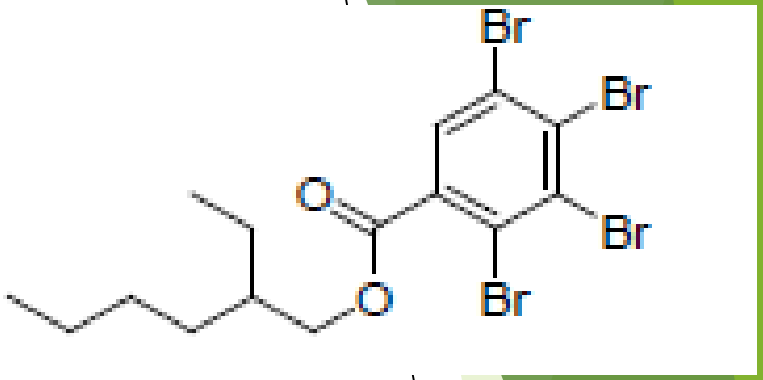
Source: EPA, Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update, Sept 2015

IPTPP – Evidence of Exposure

- IPTPP is an ingredient in Firemaster 550. Product testing identified the Firemaster®550 profile in foam baby products and U.S. upholstered furniture [1,2]
- U.S. biomonitoring studies indicate that exposure to adults and children is occurring[3,4]
  - >90% detection frequency of a urinary metabolite in urine of moms and their children

1. Stapleton, H.M., et al., *Identification of flame retardants in polyurethane foam collected from baby products.* Environ Sci Technol, 2011. **45**(12): p. 5323-31.
2. Stapleton, H.M., et al., *Novel and high volume use flame retardants in US couches reflective of the 2005 PentaBDE phase out.* Environ Sci Technol, 2012. **46**(24): p. 13432-9.
3. Hoffman, K., et al., *High Exposure to Organophosphate Flame Retardants in Infants: Associations with Baby Products.* Environ Sci Technol, 2015.
4. Butt, C.M., et al., *Metabolites of organophosphate flame retardants and 2-ethylhexyl tetrabromobenzoate in urine from paired mothers and toddlers.* Environ Sci Technol, 2014. **48**(17): p. 10432-8.
5. Butt, C.H., K; Chen, A; Lorenzo, A; Congleton, J; Stapleton, HM, *Regional comparison of organophosphate flame retardant (PFR) urinary metabolites and tetrabromobenzoic acid (TBBA) in mother-toddler pairs from California and New Jersey.* Environment International, 2016. **94**: p. 627-34.

TBB (also EH-TBB)



CAS	183658-27-7
Uses	Additive flame retardant
	foam seating and bedding (max 30% by wt.)
National Production Volume	Withheld (CBI)

Source: EPA CDR 2016 initial reporting cycle; www.epa.gov/chemical-data-reporting

Screening Level Toxicology Hazard Summary

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Chemical	CASRN	Human Health Effects											Aquatic Toxicity**		Environmental Fate	
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Benzoic acid, 2,3,4,5-tetrabromo-, 2-ethylhexyl ester (TBB)	183658-27-7	*L*	*M*	*L*	*M*	*M*	*M*	*M*	*M*		*M*	*L*	*L*	*L*	*H*	*H*

**Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

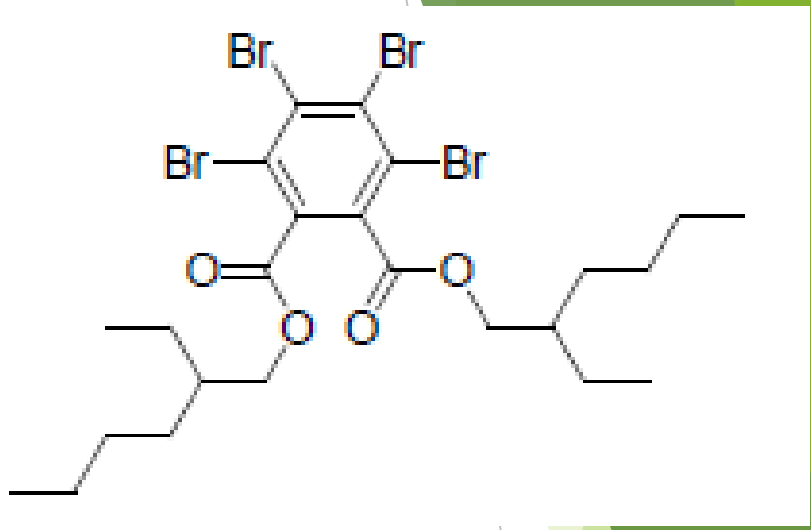
Source: EPA, Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update, Sept 2015

TBB – Exposure

- Detected in foam products.
- High frequency detection in indoor dust (homes, childcares, gymnastic facility).[1-8]
- Metabolites of TBB detected in serum, breast milk, and urine.[9-11]

1. Dodson, R.E., et al. Environ Sci Technol, 2012. **46**(24): p. 13056-66.
2. Johnson, P.I., et al. Sci Total Environ, 2013. **445-446**: p. 177-84.
3. Stapleton, H.M., et al. Environ Sci Technol, 2008. **42**(18): p. 6910-6.
4. Brown, F.R., et al., Environ Res, 2014. **135**: p. 9-14.
5. Shoeib, M., et al.,. Environmental Pollution, 2012. **169**(0): p. 175-182.
6. Bradman, A., et al.,. Chemosphere, 2014. **116**: p. 61-6.
7. Hoffman, K., et al., Environ Health Perspect, 2014. **122**(9): p. 963-9.
8. Carignan, C.C., et al., Environmental Science & Technology, 2013. **47**(23): p. 13848-13856.
9. Butt, C.M., et al., Environ Sci Technol, 2014. **48**(17): p. 10432-8.
10. Butt, C.H., et al. , Environment International, 2016. **94**: p. 627-34.
11. Zhou, S.N., et al., Environ Sci Technol, 2014. **48**(15): p. 8873-80.

TBPH (also BEH-TEBP)



CAS 26040-51-7

Uses Additive flame retardant, plasticizer

- Fabric, textile and leather products
- Electrical coatings (max 30% by wt)
- Foam bedding and seating (max 30% by wt)
- Consumer plastics and rubber products (max <1% by wt)

National Production Volume 1-10 million pounds/yr (2012-2015)

Source: EPA CDR 2016 initial reporting cycle; www.epa.gov/chemical-data-reporting

Screening Level Toxicology Hazard Summary

This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion by-products are discussed in the report but not addressed directly in the hazard profiles. The caveats listed below must be taken into account when interpreting the information in the table.

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		Human Health Effects											Aquatic Toxicity**		Environmental Fate	
Chemical	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Di(2-ethylhexyl) tetrabromophthalate	26040-51-7	*L*	*M*	M	*M*	*M*	*M*	M	L		L	L	*L*	*L*	*H*	*H*

**Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

Source: EPA, Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update, Sept 2015

TBPH – Endocrine Disruptor?

- TBPH appears to be an endocrine disruptor in rodents [1,2]
- House dust concentrations of TBPH in one study were positively associated with higher levels of circulating thyroid hormone (T3) in men[3]

1. Patisaul, H.B., et al., *Accumulation and endocrine disrupting effects of the flame retardant mixture Firemaster(R) 550 in rats: an exploratory assessment.* J Biochem Mol Toxicol, 2013. **27**(2): p. 124-36.
2. Springer, C., et al., *Rodent thyroid, liver, and fetal testis toxicity of the monoester metabolite of bis-(2-ethylhexyl) tetrabromophthalate (TBPH), a novel brominated flame retardant present in indoor dust.* Environ Health Perspect, 2012. **120**(12): p. 1711-9.
3. Johnson, P.I., et al., *Associations between brominated flame retardants in house dust and hormone levels in men.* Sci Total Environ, 2013. **445-446**: p. 177-84.

TBPH – Exposure

- Detected in product testing.[1,2]
  - foam baby products, residential furniture
- Detected in indoor dust with high frequency.[3-8]
  - homes, cars, childcare
- Detected in serum and breast milk.[9-11]
- Global contaminant.[12]

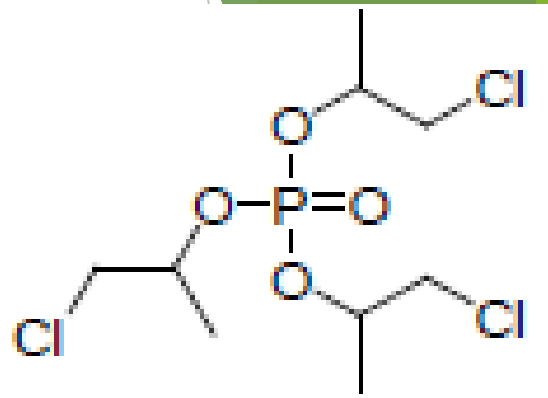
1. Stapleton, H.M., et al Environ Sci Technol, 2011. **45**(12): p. 5323-31.
2. Stapleton, H.M., et al. Environ Sci Technol, 2012. **46**(24): p. 13432-9.
3. Dodson, R.E., et al., Environ Sci Technol, 2012. **46**(24): p. 13056-66.
4. Stapleton, H.M., et al.,, 2008. **42**(18): p. 6910-6.
5. Brown, F.R., et al.,. Environ Res, 2014. **135**: p. 9-14.
6. Shoeib, M., et al.,. Environmental Pollution, 2012. **169**(0): p. 175-182.
7. Peng, H et al. Environ Sci & Technol, 2015. **49**(5): p. 2999-2006.
8. Bradman, A., et al.,. Chemosphere, 2014. **116**: p. 61-6.
9. Hoffman, K., et al,. Environ Int, 2014. **63**: p. 169-72.
10. Liang-Ying Liu, et al. Environ. Sci. Technol. 2016, 2016. **50:** p. 3065−3073.
11. Zhou, S.N., et al.,. Environ Sci Technol, 2014. **48**(15): p. 8873-80.
12. Ma Y et al; (2011) Environ Sci Technol 46: 204-8.

TCPP

CAS 13674-84-5

Uses Additive flame retardant

- Insulating foam (max 1-30% by wt)
- Wood and engineered wood products (max <1% by wt.,
- unspecified building construction material (≥ 90% by wt)
- Fabrics, textiles, leather products (max 30-60% by wt.)



Representative structure

National Production 10-50 million lbs/yr (2012,13)

Volume 50-100 million lbs/yr (2014,15)

Source: EPA CDR 2016 initial reporting cycle; www.epa.gov/chemical-data-reporting

Screening Level Toxicology Hazard Summary

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Chemical	CASRN	Human Health Effects											Aquatic Toxicity		Environmental Fate	
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Tris (2-chloro-1-methylethyl) phosphate (TCPP)	13674-84-5	L	*M*	L	H	H	*M*	M	L		L	L	M	*M*	H	L

Source: EPA, Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update, Sept 2015

TCPP – Exposure

Detected in residential furniture, children's products[1-3]

- car seats, changing table pads, sleep positioners, portable mattresses, nursing pillows

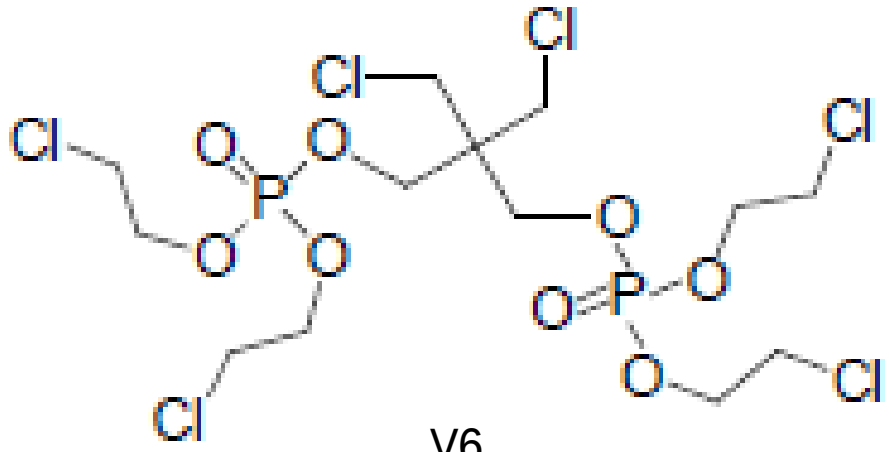
Detected in indoor dust and air[3-8]

Two TCPP metabolities detected in urine, including in infants, TCPP detected in breast milk[9-13]

1. Stapleton, H.M., et al.,. Environ Sci Technol, 2011. **45**(12): p. 5323-31.
2. Ecology, *Flame Retardants in General Consumer and Children's Products*. 2014.
3. Stapleton, H.M., et al.,. Environmental Science & Technology, 2009. **43**(19): p. 7490-7495.
4. La Guardia, M.J. and R.C. Hale. Environ Int, 2015. **79**: p. 106-14.
5. Dodson, R.E., et al.,. Environ Sci Technol, 2012. **46**(24): p. 13056-66.
6. Stapleton, H.M., et al., Chemosphere, 2014. **116**: p. 54-60.
7. Fan, X., et al.,. Sci Total Environ, 2014. **491-492**: p. 80-6.
8. Schreder, E et al. *Inhalation Exposure to Chlorinated Organophosphate Flame Retardants: Respirable vs. Inhalable intake*. 2014, Washington Toxics Coalition: Seattle, Washington.
9. Butt, C.M., et al.,. Environ Sci Technol, 2014. **48**(17): p. 10432-8.
10. Hoffman, K., et al., Environ Sci Technol, 2015.
11. Butt, C.H., et al. , Environment International, 2016. **94**: p. 627-34.
12. Dodson, R.E., et al.,. Environ Sci Technol, 2014. **48**(23): p. 13625-33.
13. Sundkvist, A.M., et al. . J Environ Monit, 2010. **12**(4): p. 943-51.

V6

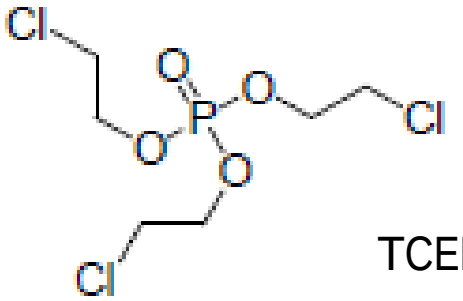
CAS	38051-10-4
Uses	Withheld (CBI)



V6

Commercial V6 contains TCEP as an impurity[1]

National Production Volume	Withheld (CBI



TCEP

Source: EPA CDR 2016 initial reporting cycle; www.epa.gov/chemical-data-reporting

V6 - Other information on Uses

- Additive flame retardant
- Polyurethane foam
  - baby products (Ave 4.6% by wt),
  - carpet pads
  - auto upholstery (typical 6% by wt)
- Tent fabric

1. Fang, M., et al., *Investigating a novel flame retardant known as V6: measurements in baby products, house dust, and car dust.* Environ Sci Technol, 2013. **47**(9): p. 4449-54.
2. Stapleton, H.M., et al., *Identification of flame retardants in polyurethane foam collected from baby products.* Environ Sci Technol, 2011. **45**(12): p. 5323-31.
3. Ecology, *Flame Retardants in General Consumer and Children's Products*. 2014.
4. ECHA, *2,2-bis(chloromethyl) trimethylene bis[bis(2-chloroethyl) phosphate] (V6) - Summary Risk Assessment Report*. 2008, European Union: Ireland and United Kingdom.
5. EPA, Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update. 2015, Environmental Protection Agency.

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Chemical	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Phosphoric acid, P,P'-[2,2-bis(chloromethyl)-1,3-propanediyl] P,P,P',P'-tetrakis(2-chloroethyl) ester	38051-10-4	L	*M*	L	M	H	L	M	L		L	L	M	*M*	H	*L*

Source: EPA, Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update, Sept 2015

V6 – Exposure

Detected in product testing

- tent fabric, foam carpet pads, baby products

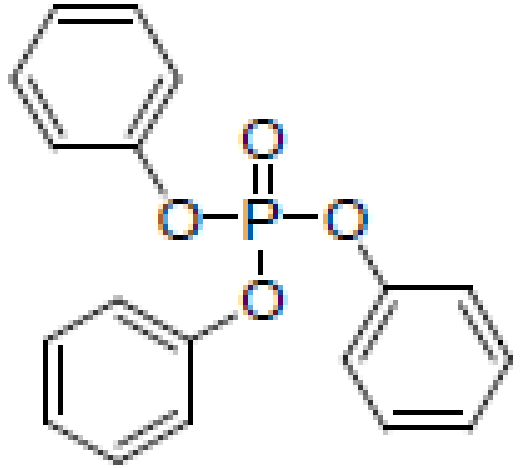
  (Fang et al. 2013; Stapleton et al. 2011; Ecology 2014).

Not widely studied in indoor dust:

- Boston area study (Fang et al. 2013)
  - found V6 in 95% vehicle dust, 75% of house dust samples.
  - Car dust concentrations were higher than house dust.
  - Median levels in dust were 103 ng/g.

No biomonitoring studies identified

TPP (also TPhP)



CAS	115-86-6
Uses	Additive flame retardant, plasticizer

- Polyurethane foam (<1% in foam seating and bedding)
- Computer and electronics
- Photographic films and photo chemicals (<1% by wt)
- Unspecified consumer plastics and rubber (1-90% by wt)
- Commercial lubricants and greases (60-90% by wt)
- Manufacturing (computer products, apparel, leather, textiles)

National	1-10 million lbs (2012,13)
Production	10-50 million lbs (2014)
Volume	1-10 million lbs (2015)

Source: EPA CDR 2016 initial reporting cycle; www.epa.gov/chemical-data-reporting

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Chemical	CASRN	Human Health Effects											Aquatic Toxicity		Environmental Fate	
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Triphenyl phosphate (TPP)	115-86-6	L	*M*	L	L	L	L	H	L		L	VL	VH	VH	L	M

Source: EPA, Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update, Sept 20

TPP – Endocrine Disruptor?

- Decreased testosterone and gene expression in testes in mice fed TPP.[1]
- Estrogen receptor agonist, androgen receptor inhibitor in *in vitro* studies.[2-4]
- Long-lasting metabolic disruption in rats exposed to TPP during fetal and nursing periods. [5,6]
- Decreased sperm count in men associated with TPP in residential house dust.[7]

1. Chen, G., et al., *Exposure of male mice to two kinds of organophosphate flame retardants (OPFRs) induced oxidative stress and endocrine disruption.* Environ Toxicol Pharmacol, 2015. **40**(1): p. 310-8.
2. Hiroyuki Kojima, S.T., Nele Van den Eede, Adrian Covaci, *Effects of primary metabolites of organophosphate flame retardants on transcriptional activity via human nuclear receptors.* Toxicology Letters, 2016. **245**: p. 31-39.
3. Boris V. Krivoshiev, F.D., Adrian Covaci, Ronny Blust, Steven J. Husson, *Assessing in-vitro estrogenic effects of currently-used flame retardants.* Toxicology in Vitro, 2016. **33**: p. 153-162.
4. EPA, Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update. 2015, Environmental Protection Agency.
5. Patisaul, H.B., et al., *Accumulation and endocrine disrupting effects of the flame retardant mixture Firemaster(R) 550 in rats: an exploratory assessment.* J Biochem Mol Toxicol, 2013. **27**(2): p. 124-36.
6. Green, A.J., et al., *Perinatal triphenyl phosphate exposure accelerates type 2 diabetes onset and increases adipose accumulation in UCD-type 2 diabetes mellitus rats.* Reprod Toxicol, 2016.
7. Meeker, J.D. and H.M. Stapleton, *House dust concentrations of organophosphate flame retardants in relation to hormone levels and semen quality parameters.* Environ Health Perspect, 2010. **118**(3): p. 318-23.

TPP - Exposure

- On surfaces of computer monitors, TV sets, cell phones
- Nail polish
- High levels in indoor dust.[1-4]
- Metabolite found frequently in urine.[5-9]

1. Hoffman, K., et al., Environ Health Perspect, 2015. **123**(2): p. 160-5.
2. Stapleton, H.M., et al., Environmental Science & Technology, 2009. **43**(19): p. 7490-7495.
3. Dodson, R.E., et al., Environ Sci Technol, 2012. **46**(24): p. 13056-66.
4. Fan, X., et al., Sci Total Environ, 2014. **491-492**: p. 80-6.
5. Meeker, J.D., et al., Environ Health Perspect, 2013. 121(5): p. 580-5.
6. Butt, C.M., et al., Environ Sci Technol, 2014. 48(17): p. 10432-8.
7. Butt, C.H., et al., Environment International, 2016. 94: p. 627-34.
8. Hoffman, K., et al., Environ Sci Technol, 2015.
9. Cequier, E., et al., Environ Int, 2015. 75: p. 159-65.

Decomposition products -may be released in a fire

- IPTPP - emit toxic vapors of phosphorous oxides.
- TPP - Toxic gases and vapors of phosphoric acid and carbon monoxide
- TBPH - Carbon oxides, hydrogen bromide
- TCPP - Carbon oxides, phosphorous oxides, hydrogen chloride gas

Summary

Flame Retardants	EPA rating for reproductive (R) and developmental (D) Toxicity
IPTPP	**High**
TBPH	**Moderate**
TBB	**Moderate**
TPP	**High** hazard for repeat doses; (positive findings for R and D)
TCPP	**High**
V6	**High** (D) **Moderate** (R); also contains TCEP, a carcinogen

Source: EPA, Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update, Sept 2015

Summary

Flame Retardant	Children's Products	House Dust/Air	Biomonitoring
IPTPP	✓	✗	✓
TBPH	✓	✓	✓
TBB	✓	✓	✓
TPP	✓	✓	✓
TCPP	✓	✓	✓
V6	✓	✓	✗

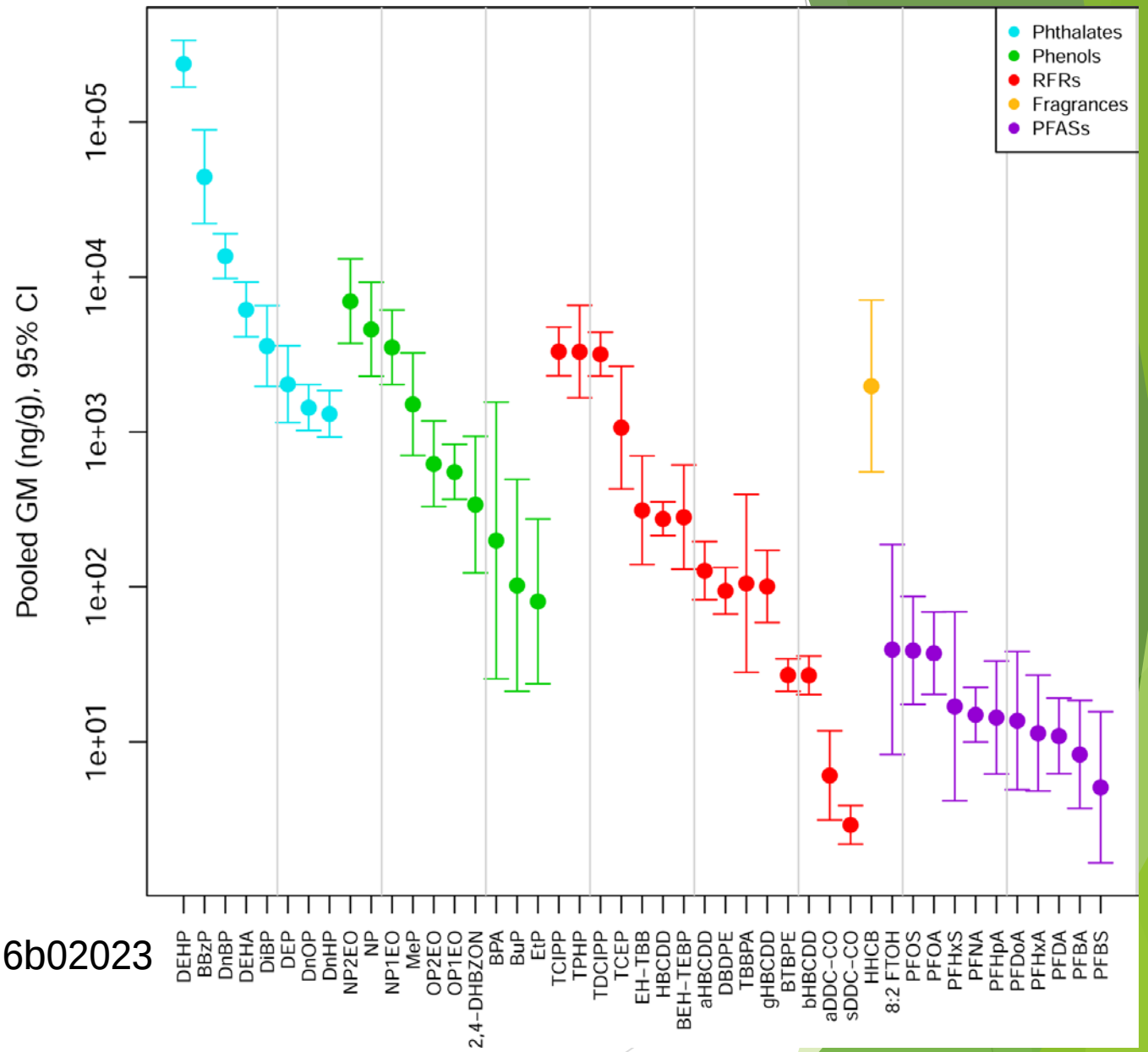
Types of treated consumer products – combined

- Flexible polyurethane foam in furniture and consumer products: in residential, transportation, preschools, offices, gym settings.
- Fabrics, textiles, leather products
- Building construction materials (insulation, sealants, adhesives, wood)
- Electrical and electronic products (computers, cellphones, cables)
- Consumer plastics and rubber materials
- Paints and coatings
- Photographic supplies, film, and photo chemicals
- lubricants, greases

Questions

15 min break

Flame retardants in US House Dust



Mitro, SD et al. 2016
Consumer Product Chemicals in Indoor Dust:
A Quantitative Meta-analysis
of U.S. Studies.
Environ. Sci. Technol. DOI: 10.1021/acs.est.6b02023

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (*VL, L, M, H,* and *VH*) were assigned using values from predictive models and/or professional judgment.
* Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. For Firemaster® mixtures there is no corresponding profile in Section 7.
^ This component of Firemaster® 550 may be used alone or in other mixtures as an alternative.
ǂ Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

Chemical (for full chemical name and relevant trade names see the individual profiles in Section 7)	CASRN	Human Health Effects											Aquatic Toxicity		Environmental Fate	
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Halogenated Flame Retardant Alternatives																
Firemaster® 550 Components																
Firemaster® 550*	Mixture	L	*M*	M	H	*H*	*H*	H	*M*		L	L	VH	VH	*H*	*H*
Benzoic acid, 2,3,4,5-tetrabromo-, 2-ethylhexyl ester (TBB)ǂ	183658-27-7	*L*	*M*	*L*	*M*	*M*	*M*	*M*	*M*		*M*	*L*	*L*	*L*	*H*	*H*
Di(2-ethylhexyl) tetrabromophthalate (TBPH)^ǂ	26040-51-7	*L*	*M*	M	*M*	*M*	*M*	M	L		L	L	*L*	*L*	*H*	*H*
Isopropylated triphenyl phosphate (IPTPP)^	68937-41-7	L	*M*	L	H	*H*	*H*	H	L		L	L	VH	VH	M	*H*
Triphenyl phosphate (TPP)^	115-86-6	L	*M*	L	L	L	L	H	L		L	VL	VH	VH	L	M
Firemaster® 600																
Firemaster® 600*	Mixture; Proprietary	L	*M*	M	M	*M*	M	H	*M*		L	M	VH	VH	*H*	H

Source: EPA, Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update, Sept 201

- CPSC
- Hays and Kirman 2017 – TBB
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- https://www.ncbi.nlm.nih.gov/pubmed/28735244
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- Hayes and Kirman 2017 – TBB
- Danish EPA - TCPP