

ISOPROPYLATED TRIARYLPHOSPHATE ESTERS (ITPS) IN COMMERCIAL FLAME RETARDANT MIXTURES AND INDOOR HOUSE DUST

Phillips, A. L.¹, Hammel, S. C.¹, Hoffman, K.¹, Lorenzo, A. M.¹, Konstantinov, A.², Stapleton, H. M.¹

¹Nicholas School of the Environment, Duke University, Durham, NC, USA

²Wellington Laboratories, Inc., Guelph, Ontario, Canada

Introduction

Organophosphate flame retardant mixtures are frequently applied to polyurethane foam to meet residential flammability requirements.^{1,2} One commercial mixture currently on the market is Firemaster® 550 (FM550), which contains two brominated compounds and a suite of isopropylated triarylphosphate esters (ITPs), compounds which have been shown to have widespread human exposure and be potentially neuro- and developmentally toxic.^{3,4} There is growing evidence that the organophosphate components of FM 550 may drive the mixture's observed toxicity.⁵⁻⁷ The current study determined the relative contribution of individual ITPs to the composition of FM550 and to the composition of a second commercial mixture containing only ITPs purchased from a Chinese manufacturer. Levels of these compounds were also measured in recently collected indoor house dust samples.

Materials and Methods

Commercial Flame Retardant Mixtures

FM 550 was provided by Chemtura and the commercial mixture containing only ITPs was purchased from Jinan Great Chemical Industry Co. Flame retardant mixtures were weighed and dissolved in isooctane to make a low (~1 µg/ml) and high (~5 µg/ml) concentration stock solution. Each stock solution was run in triplicate and individual ITP isomers were quantified.

Indoor House Dust

Study participants were part of a North Carolina thyroid cancer cohort. House dust samples ($n=84$) were collected from the main living room using a Eureka Might-Mite vacuum cleaner and crevice tool attachment. Dust samples were sieved to <500 µm, spiked with internal standards, and then sonication extracted in dichloromethane. Dust extracts were cleaned using solid phase extraction (SPE) with Supelclean ENVI-Florisil cartridges (6 mL, 1.0 g; Supelco, Bellefonte, PA). ITPs were eluted using 10 mL of ethyl acetate, and individual isomers were quantified. Values <MDL were assigned a value equal to half of the detection limit for statistical analyses.

ITP Quantification

Individual, authentic ITP standards were supplied by Wellington Laboratories. Individual ITP isomers were quantified with previously described GC/MS using ¹³C-TPHP as an internal standard.^{8,9} **Table 1** outlines the m/z ions and retention times used for quantification of ITP isomers.

Table 1. *m/z* Ions and Retention Times Used for Quantification of ITP Isomers

ITP isomer	<i>m/z</i> Quantifier	<i>m/z</i> Qualifier	Retention Time** (min)
2IPPDPP	251	368	15.82
4IPPDPP	353	368	17.71
24DIPPDPP	145	160	18.21
B2IPPPP	251	410	17.46
B4IPPPP	395	410	20.18
B24DIPPPP	145	160	21.78
T3IPPP	452	438	21.10
T4IPPP	452	438	23.56
4tBPDPP*	367	382	18.32

*not an ITP isomer

**as observed on a 15 m DB5-MS Agilent J & W column

Results and Discussion

Commercial Flame Retardant Mixtures

FM 550 was found to contain 19.8% triphenyl phosphate (TPHP), 11.8% 2-isopropylphenyl diphenyl phosphate (2IPPDPP), 11.0% 2,4-diisopropylphenyl diphenyl phosphate (24DIPPDPP), 5.1% bis(2-isopropylphenyl) phenyl phosphate (B2IPPPP), 2.3% 4-isopropylphenyl diphenyl phosphate (4IPPDPP), and 0.3% bis(4-isopropylphenyl) phenyl phosphate (B4IPPPP), with the remainder being comprised of the two brominated components, tetrabromobenzoate (TBB; 29.7%) and bis (2,ethylhexyl) 2,3,4,5-tetrabromophthalate (TBPH; 13.9%). While there is currently no commercially available standard for 3-isopropylphenyl diphenyl phosphate (3IPPDPP), a peak eluting between 2IPPDPP and 4IPPDPP with *m/z* of 368 suggests its presence in FM 550. The ITP commercial mixture was found to contain 44.6% TPHP, 26.9% 2IPPDPP, 11.1% B2IPPP, 7.2% 24DIPPDPP, 4.9% 4IPPDPP, and 1.1% B4IPPPP (**Figure 1**). Notably, the contribution of the individual organophosphate components in the ITP mixture is roughly twice that of their contribution in FM 550, suggesting a common ITP mixture formulation.

Indoor House Dust

ITPs were also detected in indoor house dust (n=84) at geometric mean levels similar to those found for PBDEs: 181.68 ng/g 2IPPDPP, 163.74 ng/g B2IPPPP, 125.50 ng/g 24DIPPDPP, 62.44 ng/g 4IPPDPP, and 42.65 ng/g B4IPPPP. Detection frequencies for these compounds ranged from 13 to 53%. Also present in the dust, 4-*tert*-butylphenyl diphenyl phosphate (4tBPDPP) was detected at a geometric mean concentration of 168.47 ng/g in 54% of the samples. Notably, the geometric mean dust concentrations of many of these phosphate triester isomers were strikingly similar to those found for BDE-47 (geometric mean = 222 ng/g) in the same sample group. In contrast, the observed lower detection frequencies of ITPs and 4tBPDPP compared to PBDEs may be attributable to their relatively recent introduction to the market. For instance, detection frequencies for a *tert*-butylphenyl diphenyl phosphate mixture containing 4tBPDPP increased by 4-fold in household products containing polyurethane foam purchased after 2005 compared to those purchased prior to 2005.² As older products are discarded and replaced with new ones in homes over the next decade, it is likely that ITPs and 4tBPDPP may become even more prevalent in indoor house dust. Importantly, the dust levels measured in this study suggest the potential for chronic human exposure of a magnitude similar to that for PBDEs; as preliminary studies indicate these compounds may also be neurodevelopmentally toxic, additional studies focusing on these compounds are warranted.

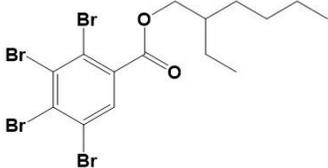
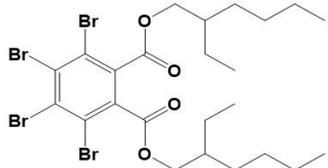
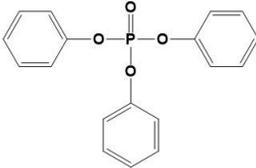
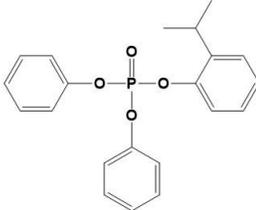
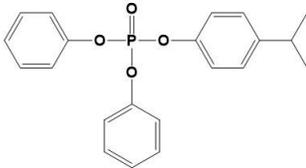
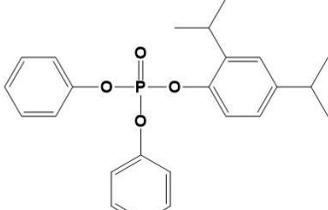
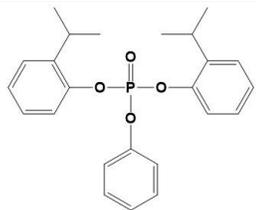
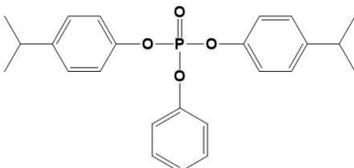
Component Name	Structure	Mass Concentration (w/v) in FM 550	Mass Concentration (w/v) in ITP Mix
TBB		$29.7 \pm 0.3\%$	none
TBPH		$13.9 \pm 0.1\%$	none
TPHP		$19.8 \pm 0.1\%$	$44.6 \pm 0.9\%$
2IPDPP		$11.8 \pm 0.2\%$	$26.9 \pm 1.1\%$
4IPDPP		$2.3 \pm 0.2\%$	$4.9 \pm 0.8\%$
24DIPDPP		$11.0 \pm 0.1\%$	$7.2 \pm 0.9\%$
B2IPPPP		$5.1 \pm 0.2\%$	$11.1 \pm 0.9\%$
B4IPPPP		$0.3 \pm 0.1\%$	$1.1 \pm 0.3\%$

Figure 1. Percent Composition (w/v) of Individual ITP Isomers in Commercial Flame Retardant Mixtures.

Acknowledgements

The authors are grateful to the participants in Cancer in the Environment (CIE) study cohort for providing dust samples and to Wellington Laboratories for graciously providing individual ITP standards.

References

1. Dodson, R. E. *et al. Environ. Sci. Technol.* **46**, 13056–66 (2012).
2. Cooper, E. M. *et al. Environ. Sci. Technol.* **50**, 10653–60 (2016).
3. Hammel, S. *et al. Environ. Sci. Technol.* **50**, 4483–91 (2016).
4. Behl, M. *et al. Neurotoxicol. Teratol.* **52**, 181–93 (2015).
5. Belcher, S. M. *et al. Toxicol. Lett.* **228**, 93–102 (2014).
6. Morris, P. J. *et al. ACS Chem. Biol.* **9**, 1097–1103 (2014)
7. Pillai, H. K. *et al. Environ. Health Perspect.* **11**, 1225–32 (2014).
8. Stapleton, H. M. *et al. Environ. Sci. Technol.* **42**, 6910–16 (2008).
9. Stapleton, H. M. *et al. Environ. Sci. Technol.* **43**, 7490–7495 (2009).