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Organophosphate flame retardants in household dust before and after introduction of new furniture

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HIGHLIGHTS

- New flame retardant (FR) furniture was introduced in college housing.
- TDCIPP was found at weight percent levels in new couch foam.
- TDCIPP and TCEP levels in dust decreased with new furniture.
- TPHP levels may have decreased slightly with new furniture.
- Mechanical breakdown of older furniture foam dominates release of FR's to dust.

GRAPHICAL ABSTRACT

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ABSTRACT

Flame retardant compounds originating from household items collect in household dust, a reasonable proxy for human exposure. Contributions of specific items or behaviors to dust are difficult to separate. This study examined standardized college housing before and after the introduction of new, flame retardant couches in order to explore any effect that changing upholstered furniture may have on flame retardant concentrations in dust. Two contradictory hypotheses were posited: (1) that new furniture might increase flame retardant releases immediately after introduction due to initial off-gassing of new materials or (2) that older furniture would release more flame retardants due to mechanical breakdown of polyurethane foam. This study was designed to determine which of these processes dominated. Prior to the introduction of new furniture, TDCIPP was detected in 12/20 samples at a median concentration of 22 μg/g and TCEP was detected in 1/20 samples at a concentration of 16 μg/g. TDCIPP and TCEP were not detected in any samples ($N = 29$) after the introduction of new couches. TPHP was detected both before (in 11/20 samples) and after (in 5/29 samples) introduction of new couches; the median concentrations before and after were 63 ± 49 and 16 ± 11 μg/g (standard deviation shown). Introduced couches contained TDCIPP (and not TPHP) at ~1.25% (w/w). These data support the second hypothesis and indicate that removal of older furniture decreases TDCIPP and TCEP concentrations in dust and may potentially reduce total flame retardant concentrations in dust, at least immediately after introduction of the new furniture.

1. Introduction

In 1975, California passed Technical Bulletin 117 (TB 117), requiring furniture and baby products to be fire resistant; this

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became a *de facto* US regulation (Green Science Policy Institute, 2014). Manufacturers began using flame retardant-treated polyurethane in furniture immediately thereafter (Lewin et al., 1975; Molbert, 1975; Kehr et al., 1979) despite known risks of flame retardant chemicals (Blum and Ames, 1977). Polybrominated diphenyl ethers (PDBEs) were the main chemical category used, and by 2002 risks to human health and ecosystems from these additives were well documented (Betts, 2002; Solomon and Weiss, 2002). In 2004, voluntary phase-outs of two common flame retardant chemical mixtures, pentaBDE and octaBDE began, in anticipation of a California ban beginning in 2008 (Renner, 2004; Stapleton et al., 2008). Alternate brominated flame retardants including a decaBDE mixture continued to be used and found in household dust in 2008 (Stapleton et al., 2008); organophosphate flame retardants (PFRs) were detected in furniture and household dust by 2009 (Stapleton et al., 2009). Both the alternate brominated flame retardants and PFRs are believed to be hazardous to human health (Shaw, 2010), suggesting that the phase-out of some PDBEs has not necessarily led to a reduction in human exposure to hazardous flame retardant chemicals (Dodson et al., 2012; Stapleton et al., 2012).

Organophosphate flame retardants used include nonchlorinated compounds, such as triphenyl phosphate (TPHP), and chlorinated compounds such as tris (1-chloropropyl) phosphate (TCIPP), tris (1,3-dichloro-2-propyl) phosphate (TDCIPP), and tris (2-chloroethyl) phosphate (TCEP) as shown in Fig. 1 (Stapleton et al., 2009). Abbreviations used are consistent with those suggested in (Bergman et al., 2012). Several chlorinated PFRs are known and/or presumed carcinogens (van der Veen and de Boer, 2012). In February of 2013, California Technical Bulletin 117 was modified (California Department of Consumer Affairs, (2013)) to promote fire safety without flame retardant chemicals (Green Science Policy Institute, 2014); there has not yet been time to fully observe the effect of this change in regulation on human exposure but total exposure can be expected to be decreased. A similar national change has been proposed by the US Consumer Product Safety Commission (Betts, 2008) but there is no timeline for implementation.

Human exposure to flame retardants, both PBDEs and PFRs, occurs through diet and indoor exposure (Frederiksen et al., 2009). Diet is considered to be of minor importance (Sundkvist et al., 2010; Kim et al., 2011). Dust and air are more significant predictors of the presence of PFRs and their metabolites in urine (Fromme et al., 2014) and this exposure has been shown to be reasonably constant over a period of months (Hoffman et al., 2014) to years (Stapleton et al., 2014). A positive correlation has been found between concentrations of brominated flame retardants in dust and blood plasma (Karlsson et al., 2007). Positive correlations have also been observed between PFRs in dust and PFRs on children's handwipes (Stapleton et al., 2014). Positive correlations between PFRs in dust and PFRs and their metabolites in urine (Meeker et al., 2013; Fromme et al., 2014; Hoffman et al., 2014) are also seen, although relationships are only weakly positive for TDCIPP and TCEP and their respective metabolites in at least one study (Dodson et al., 2014). Dust is commonly sampled as a proxy for human exposure, e.g. (Stapleton et al., 2008; Stapleton et al., 2009; Van den Eede et al., 2011; Brommer et al., 2012; Dodson et al., 2012; Stapleton et al., 2012).

Multiple factors can impact flame retardant concentrations in household dust, and therefore human exposure (Stuart et al., 2008). Factors which may influence flame retardant concentrations in dust include amount and type of furniture, age of furniture, presence and quantity of electronics, size of dwelling, number of residents, and dust loading/cleaning habits among others (Whitehead et al., 2011). It can be difficult to separate these factors. In this study it was possible to examine the effect of furniture age on flame retardant levels in dust because many other factors were held relatively constant and numerous identical dwellings were investigated. In particular the question explored was: will introduction of new flame retardant treated furniture increase concentrations of flame retardants due to off-gassing of new materials, or will it decrease concentrations of flame retardants due to decreased mechanical breakdown of treated polyurethane foam?

Mechanisms for transferring flame retardants from treated furniture to dust have been studied in test chambers (Rauert et al., 2014a, 2014b) as well as by examining distribution of flame

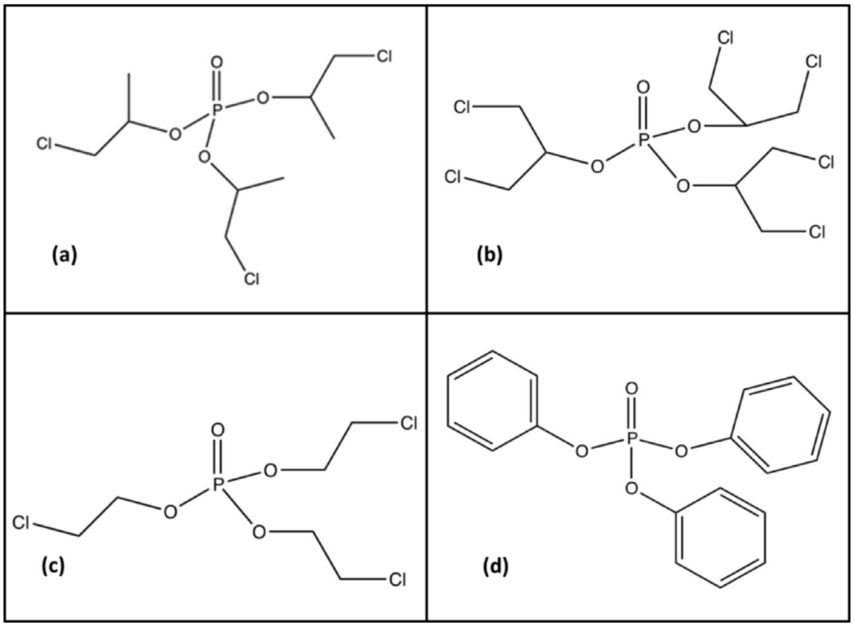

Fig. 1. Structures of common organophosphate flame retardants (PFRs). (a) tris (1-chloropropyl) phosphate (TCIPP); (b) tris (1,3-dichloro-2-propyl) phosphate (TDCIPP); (c) tris (2-chloroethyl) phosphate (TCEP); (d) triphenyl phosphate (TPHP).