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Inhalation a significant exposure route for chlorinated organophosphate flame retardants

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HIGHLIGHTS

- Inhalation exposure to chlorinated organophosphate flame retardants was assessed.
- Respirable and inhalable particulate fractions were collected.
- Concentrations of ∑ClOPFRs (respirable and inhalable) ranged from 97.1 to 1190 ng m^{-3} (mean 426 ng m^{-3}).
- Total intake of ClOPFRs via inhalation was estimated to exceed that via dust.

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ABSTRACT

Chlorinated organophosphate flame retardants (ClOPFRs) are widely used as additive flame retardants in consumer products including furniture, children's products, building materials, and textiles. Tests of indoor media in homes, offices, and other environments have shown these compounds are released from products and have become ubiquitous indoor pollutants. In house dust samples from Washington State, U.S.A., ClOPFRs were the flame retardants detected in the highest concentrations. Two ClOPFRs, tris(1,3-dichloro-2-propyl)phosphate (TDCPP or TDCIPP) and tris(2-chloroethyl)phosphate (TCEP), have been designated as carcinogens, and there is growing concern about the toxicity of the homologue tris(1-chloro-2-propyl)phosphate (TCPP or TCIPP). In response to concerns about exposure to these compounds, the European Union and a number of U.S. states have taken regulatory action to restrict their use in certain product categories. To better characterize exposure to ClOPFRs, inhalation exposure was assessed using active personal air samplers in Washington State with both respirable and inhalable particulate fractions collected to assess the likelihood particles penetrate deep into the lungs. Concentrations of ∑ClOPFRs (respirable and inhalable) ranged from 97.1 to 1190 ng m^{-3} (mean 426 ng m^{-3}), with TCPP detected at the highest concentrations. In general, higher levels were detected in the inhalable particulate fraction. Total intake of ClOPFRs via the inhalation exposure route was estimated to exceed intake via dust ingestion, indicating that inhalation is an important route that should be taken into consideration in assessments of these compounds.

1. Introduction

Chlorinated organophosphate flame retardants (ClOPFRs) are additive chemical flame retardants used in polyurethane foam, PVC plastic, and textiles (van der Veen and de Boer, 2012). Global production of these compounds—tris(1,3-dichloro-2-propyl)phosphate (TDCPP or TDCIPP), tris(2-chloroethyl)phosphate (TCEP), and tris(1-chloro-2-propyl)phosphate (TCPP or TCIPP)—has been high since the 1990s, when it exceeded 50,000 tonnes (van der Veen and de Boer, 2012). In the U.S., their production increased from less than 14,000 tonnes $year^{-1}$ in the mid-1980s to approximately 38,000 tonnes $year^{-1}$ in 2012 (Fig. 1). The higher production level is presumably due to an increase in use in polyurethane foam, with TCPP and TDCPP becoming more dominant in this use with the phaseout of polybrominated diphenyl ethers (PBDEs) (Stapleton et al., 2012; U.S. Environmental Protection Agency, 2012). In addition, increased use of TCPP in the European Union has been related to greater installation of building insulation in compliance with the Kyoto

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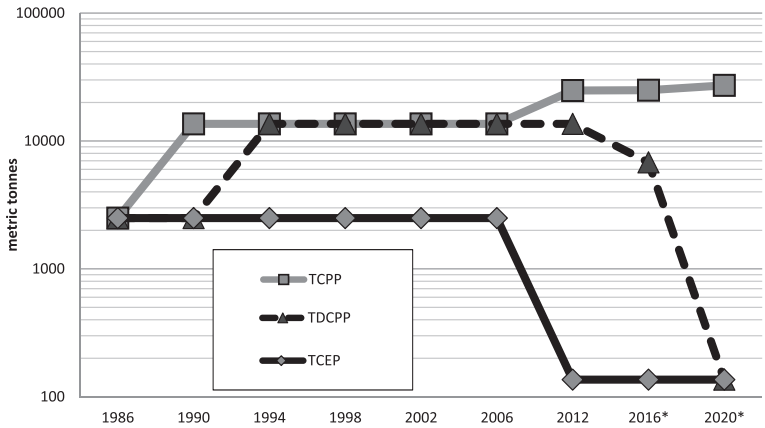

Fig. 1. 1986–2012 USEPA Chemical Data Reporting for TCPP, TDCPP and TCEP, with 2016–2020 projections. Values presented are median values of reported ranges; projections based on current production and announced phaseout plans.

protocol (Ireland/UK, 2008). Two ClOPFRs, TDCPP and TCEP, have been designated as carcinogens by the State of California, U.S.A., under Proposition 65, and the European Chemicals Agency has designated TCEP as a substance of very high concern due to reproductive toxicity (European Chemicals Agency, 2015; Office of Environmental and Health Hazard Assessment, (2015)). Carcinogenicity testing has not been completed on TCPP, but its molecular similarity to the other two compounds raises concerns of similar toxicity and there is evidence of reproductive and developmental toxicity (Ireland/UK, 2008). A growing body of research on the neurotoxic impacts of ClOPFRs using the zebrafish model has also linked developmental exposure to TCEP, TDCPP, and TCPP to altered behavior similar to that seen with known neurotoxic organophosphate pesticides such as chlorpyrifos (Dishaw et al., 2014; Oliveri et al., 2015).

The ClOPFRs have been widely detected in household dust, furniture, children's products, surface water, drinking water, and biota (Kolpin et al., 2002; Andresen et al., 2004; Regnery and Püttman, 2010; Stapleton et al., 2011; van der Veen and de Boer, 2012; Schreder and La Guardia, 2014). Recently, Butt et al. detected ClOPFR metabolites in paired urine samples from US. mothers and toddlers, finding an average of nearly five times higher levels of TDCPP metabolites in toddlers as compared to their mothers (Butt et al., 2014). TDCPP, also known as Chlorinated Tris, was removed from children's sleepwear in the 1970s after researchers identified it as a mutagen (Gold et al., 1978), but its use in other products, including children's products, continued (Stapleton et al., 2011).

As a result of the reports of the widespread presence of ClOPFRs in products and indoor and outdoor environments, concern has increased about their adverse health impact on people and the environment. Beginning in 2011 with New York State, five U.S. states (New York, Maryland, Vermont, Oregon, and Minnesota) have now passed laws restricting the use of TDCPP and TCEP, primarily in children's products with the Minnesota law also including residential upholstered furniture (Safer States, 2015). Three of these states (Vermont, Minnesota, and Oregon) also included provisions designed to prevent manufacturers from substituting other toxic compounds once these flame retardants are removed from products. The European Union has also taken policy action, banning all three ClOPFRs from toys beginning December 31, 2014 (European Union, 2014). Finally, in October 2014, Canada prohibited the use of polyurethane foam containing TCEP in products intended for children under three (Government of Canada, (2015)).

Assessment of human exposure to flame retardants has focused on diet and ingestion of contaminated household dust as exposure routes, particularly in the case of PBDEs (Wu et al., 2007; Stapleton et al., 2009; Bradman et al., 2014; Sahlström et al., 2015). Allen et al. examined inhalation exposure using personal samplers worn by study participants in Boston, northeast USA (Allen et al., 2007). For PBDEs, it was estimated that inhalation accounts for 11% (non-209 BDEs) to 22% (BDE-209) of the total exposure, and the authors concluded inhalation may be more important than previously hypothesized due to the presence of a cloud of suspended particles generated by participant activities. In the case of the ClOPFRs, however, there has been some indication that inhalation is a more important exposure route than it is for PBDEs (Carlsson et al., 1997; Hartmann et al., 2004; Marklund et al., 2005; Mäkinen et al., 2009). Recent research in the U.S. compared dust and air levels of flame retardants in gymnastics facilities with those in homes using personal air samplers, and found significantly elevated TDCPP levels in air in gymnastics facilities (La Guardia and Hale, 2015).

Using personal air samplers, La Guardia and Hale identified the inhalable fraction of airborne particulates (>4 μm) as a more important source of halogenated flame retardant exposure than the respirable fraction (<4 μm) (La Guardia and Hale, 2015). Inhalable particulates are deposited primarily in the upper parts of the respiratory tract, whereas respirable dust penetrates deep into the lungs where gas exchange takes place. The larger particles are more likely to deposit in the nasal-pharyngeal or the tracheobronchial region; in these regions, pollutants deposit in the mucus lining the cells and may diffuse into tissue or be cleared by cilia into the digestive tract (Ferro and Hildemann, 2007). Smaller particles (<4 μm) are able to penetrate into the pulmonary region where the particle itself can migrate into tissue.

The hydrophilicity and high water solubility of the ClOPFRs likely increase the importance of the inhalation route for these compounds. The hydrophobicity (log K_{ow}) of TCEP, TDCPP, and TCPP ranges from 1.44 to 3.8, orders of magnitude lower than that of PBDEs, with log K_{ow} values greater than 5 (La Guardia et al., 2012; van der Veen and de Boer, 2012). More soluble compounds, such as the ClOPFRs, have a greater ability to desorb from particles and diffuse directly into tissue. More hydrophilic compounds may also be more bioavailable if they are transported to the digestive tract from the upper part of the respiratory tract: Fang et al. observed flame retardants with log K_{ow} values less than 5 were about 80% bioaccessible compared to approximately 25–60% for PBDEs (Fang and Stapleton, 2014).

The present study tested the personal air of ten adults in Washington State using active personal air samplers. To assess the likelihood of these compounds penetrating deep into the lungs,

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