



Presence and select determinants of organophosphate flame retardants in public swimming pools



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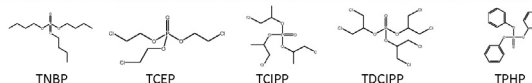
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HIGHLIGHTS

- TNBP, TCEP, TCIPP, TDCIPP and TPHP were detected in chlorinated swimming pools.
- PFRs were below the LOQ in fill water samples collected from 3 locations.
- TCIPP was observed to have the highest concentrations in swimming pools.
- PFRs are leaching from swimsuits and may be a source in swimming pools.
- Health risks through oral and dermal exposure to PFRs in swimming pools were low.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence of five organophosphate flame retardants (PFRs) consisting of tributyl phosphate (TNBP), tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCIPP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) and triphenyl phosphate (TPHP) in swimming pools were investigated. Fifteen chlorinated public swimming pools were sampled, including indoor pools, outdoor pools and spa pools. The analyses were carried out using isotope dilution gas chromatography tandem mass spectrometry. All five PFRs were detected in swimming pool waters with concentrations ranging from 5–27 ng/L (TNBP), 7–293 ng/L (TCEP), 62–1180 ng/L (TCIPP), 10–670 ng/L (TDCIPP) and 8–132 ng/L (TPHP). The concentrations of PFRs were generally higher in indoor swimming pools compared to outdoor swimming pools. In municipal water supplies, used to fill the swimming pools in three of the sampling locations, the five PFRs were all below the limit of quantifications, eliminating this as the source. Potential leaching of PFRs from commonly used swimming equipment, including newly purchased kickboards and swimsuits was investigated. These experiments revealed that PFRs leached from swimsuits, and may be a source of PFRs in swimming pools. A quantitative risk assessment revealed that the health risk to PFRs via swimming pools was generally low and below commonly applied health risk benchmarks.

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1. Introduction

Various chemical contaminants have been reported in swimming pools including disinfection by-products and components of personal care products (Zwiener et al., 2007; Terasaki and Makino, 2008; Chowdhury et al., 2014; Teo et al., 2015a). More recently, tris(2-chloroethyl) phosphate (TCEP), an organophosphate flame retardant (PFR) was detected in swimming pool waters (Weng et al., 2014). Due to their prevalent usage, PFRs have been detected globally in the environment including in indoor and outdoor air (Hartmann et al., 2004; Marklund, 2005), indoor dust (Van den Eede et al., 2011), surface water (Andresen et al., 2004; Martínez-Carballo et al., 2007; Regnery and Püttmann, 2010), ground water (Fries and Püttmann, 2001), rain-water (Regnery and Püttmann, 2009), snow (Marklund et al., 2005c; Regnery and Püttmann, 2009) and drinking water (Bacaloni et al., 2007; Stackelberg et al., 2007).

Some PFRs are potential endocrine disruptors and may pose a risk to human health (Meeker and Stapleton, 2010; Dishaw et al., 2011; Liu et al., 2012; Zhang et al., 2014). It has been suggested that PFRs may be associated with altered thyroid levels and reduced sperm quality in men (Meeker and Stapleton, 2010). Contact dermatitis from TPHPs has also been reported (Camarasa and Serra-Baldrich, 1992). PFRs that were reported to have a significant estrogenic effect include TPHP, tricresyl phosphate (TMPP) and TDCIPP. Furthermore, some chlorinated PFRs are considered to be potential carcinogens (Van der Veen and de Boer, 2012). PFRs have been detected in human milk (Sundkvist et al., 2010; Kim et al., 2014), human plasma (Shah et al., 2006), human hair and nails (Liu et al., 2015) and their metabolites in human urine (Reemtsma et al., 2011; Van den Eede et al., 2015). Although the toxicity of PFRs to humans is as yet unknown, environmental exposure to these chemicals may lead to possible adverse health effects and their occurrence in swimming pools may potentially be the main source of exposure to humans. Swimmers may be exposed to PFRs in swimming pools via a variety of exposure routes including accidental ingestion, inhalation and dermal absorption.

Studies have shown that brominated flame retardants can leach or diffuse from various materials including items made out of plastic (Kim et al., 2006; Choi et al., 2009). PFRs are used and have been detected in various plastic materials including furniture foam and polyurethane foam (Stapleton et al., 2009; Stapleton et al., 2011) and thus may also have the potential to leach. In swimming pools, plastic materials are used in kickboards and swimsuits. Further research is needed to determine if leaching of PFRs from these materials into swimming pools is possible and whether this is a source in swimming pools. PFRs may also already be present in the fill water used for swimming pools, thus contributing to their presence in the pool. As swimming pool water is continuously recirculated, the accumulation of these compounds may occur over time.

The aim of this study was to investigate the occurrence of five PFRs consisting of TNBP, TCEP, TCIPP, TDCIPP and TPHP in swimming pools. Various types of chlorinated public swimming pools were sampled including indoor pools, outdoor pools and spa pools. Laboratory simulation studies were conducted to investigate the potential leaching of PFRs into swimming pools from commonly used swimming equipment. A quantitative risk assessment on the potential health risks associated with the exposure to PFRs in swimming pools based on the Australian EnHealth Environmental Health Risk Assessment Guidelines was also carried out.

2. Sample preparation and analysis

2.1. Materials

TNBP, TCEP, TCIPP, TDCIPP and TPHP were purchased from Sigma-Aldrich (Castle Hill, NSW, Australia). Tris(1-chloro-2-propyl) phosphate-D18, tris(1,3-dichloro-2-propyl) phosphate-D15 and triphenyl

phosphate-D15 were purchased from TRC Inc. (Ontario, Canada). Tributyl phosphate-D27 was purchased from Novachem (Collingwood, Vic, Australia). Tris(2-chloroethyl) phosphate-D12 was purchased from Sapphire Bioscience (Waterloo, NSW, Australia). Stock standard solutions and isotope labeled organophosphate flame retardants were prepared in methanol (1 g/L, 10 mL) in amber vials and then further serially diluted with methanol to obtain working standard solutions of lower concentrations. All standard solutions were stored at 4 °C. Calibration standards were prepared by serial dilution in methanol from working stocks.

2.2. Sample collection

Swimming pool water samples were collected from five locations in Sydney, NSW, Australia. The swimming pools selected to undergo sampling were based on the swimming pool operators' agreement to participate in the study. A total of 15 chlorinated public swimming pools were sampled which consisted of indoor pools, outdoor pools and spa pools. Swimming pool fill waters were also collected where possible. In total, fill water samples were collected from three of the locations – Location A, C and D, all of which were sourced from reticulated municipal drinking water. Fill water samples from Location A and D were collected from the pump room while fill water samples from Location C were collected from a tap on location. Characteristics and the number of swimmers at the time of sampling for each swimming pool are presented in Table 1. For each swimming pool, three grab samples were collected in 1 L amber glass bottles without headspace from three various locations around the pool as a representation of the whole pool and to account for some variability within the pool. In total, 45 swimming pool water samples and 15 fill water samples were collected for this study. All samples were then quenched with approximately 1 g/L sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) to eliminate residual chlorine before the bottles were tightly sealed with a screw cap and transported directly to the laboratory.

Samples were spiked with a solution containing 50 ng of an isotopically labeled version of each analyte for accurate isotope dilution quantification. Spiked samples were extracted using solid phase extraction without any further treatment or processing within 24 h of collection and spiking.

As PFRs are often used in commercially available items, contamination is often unavoidable. Steps to minimise their levels have been taken in this study, such as wearing gloves at all times, avoiding the use of plastic materials where possible, all glassware and SPE tubes were pre-cleaned with solvents before use and analysing procedural blanks for every sample batch.

2.3. Leaching experiments

Laboratory experiments were undertaken to investigate potential leaching of PFRs from two brands of kickboards and one brand of swimsuit over a period of time. The kickboards and swimsuit tested were chosen based on their commercial availability in shops in Sydney. The kickboards were made from rigid high density foam and the swimsuit was made from nylon, polyamide, elastane and polyester. Aqueous samples for analysis were prepared by soaking the kickboards and swimsuit in chlorinated water for 15, 30, 180 and 1440 min (24 h) in 1 L amber glass bottles. Each material was cut into small pieces (roughly about 1 cm²) and weighed to a total of 1 g for swimsuits and 2 g for kickboards. These were then placed into glass bottles which were then filled with chlorinated water (sodium hypochlorite added to ultrapure water) which had a free available chlorine concentration of approximately 4 ppm. Triplicate samples were prepared for each time set. A separate set of triplicate samples were prepared by soaking the materials in just ultrapure water for 180 and 1440 min to investigate the effect of free chlorine on the leaching of PFRs. Blank control samples were also prepared in triplicates for 180 and 1440 min, each with ultrapure

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