



# Leaching of TCIPP from furniture foam is rapid and substantial

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## HIGHLIGHTS

- We study TCIPP leaching from furniture polyurethane foam (PUF).
- Leaching of TCIPP from PUF appears to be a first order process.
- In serial batch leaching tests, >95% of TCIPP was depleted from PUF after 168 h.
- TCIPP concentrations between  $13 \text{ mg L}^{-1}$  –  $130 \text{ mg L}^{-1}$  were detected in the leachate.
- Leaching is potentially a significant pathway of environmental TCIPP emissions.

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## ABSTRACT

A series of laboratory experiments were conducted, in which waste furniture polyurethane foam samples containing tris (1-chloro-2-propyl) phosphate (TCIPP) were contacted with a range of leaching fluids, formulated to simulate the composition of landfill leachate. Leaching was examined under a number of different scenarios, such as: dissolved humic matter concentration, pH, and temperature, as well as the effect of agitation, and waste:leaching fluid contact duration. In addition to single batch (no replenishment of leaching fluid), serial batch (draining of leachate and replenishment with fresh leaching fluid at various time intervals) experiments were conducted. Leaching of TCIPP from PUF appears to be a first order process. Concentrations of TCIPP in leachate generated by the experiments in this study ranged from  $13 \text{ mg L}^{-1}$  to  $130 \text{ mg L}^{-1}$ . In serial batch leaching experiments, >95% of TCIPP was depleted from PUF after 168 h total contact with leaching fluid. Our experiments indicate leaching is potentially a very significant pathway of TCIPP emissions to the environment.

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## 1. Introduction

A widely used group of flame retardants are the chlorinated phosphorous flame retardants (PFRs) also known as phosphinates, such as tris(1-chloro-2-propyl)phosphate (TCIPP), tris(2-chloroethyl)phosphate (TCEP) and tris(1,3-dichloroisopropyl) phosphate (TDCIPP). These and other PFRs have been applied to a wide range of commercial products such as: textiles, rubber, polyurethane foam (PUF), cellulose, cotton, electronic equipment cables, casting resins, glues, engineering thermoplastics, epoxy resins, and phenolic resins to meet and comply with fire safety codes, standards and regulations (van der Veen and de Boer, 2012). TCIPP has been found to be resistant to degradation (Leisewitz et al.,

2000; Kawagoshi et al., 2002). PFR contamination of indoor air and dust, lakes, river sediment and marine biota across Europe, USA and Japan is well documented (Carlsson et al., 1997; Marklund et al., 2005; Andresen et al., 2004; Björklund et al., 2004; Stapleton et al., 2009; Leonards et al., 2011). Moreover, detection of TCIPP and TCEP in groundwater older than 20 years indicates considerable persistence in aquifers (Regnery et al., 2011). In laboratory experiments, Regnery and Püttmann (2010) demonstrated that TCEP and TCIPP appeared resistant to photodegradation by sunlight. Furthermore, particulate-bound TDCIPP has been shown capable of mid to long-range transport due to its highly persistent nature in the atmosphere with regard to OH radical oxidation (Liu et al., 2014). TCIPP accumulates in the liver and kidneys (Leisewitz et al., 2000), with work by Dishaw et al. (2011) showing it decreases cell number and alters neuro differentiation. “Skin and eye irritations in animals are unquestioned” (Leisewitz et al., 2000) and is considered potentially carcinogenic (Ni et al., 2007). Concerns over such health impacts are exacerbated by the detection of a metabolite of TCIPP, bis(1-

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chloro-2-propyl)phosphate (BCIPP) in human urine (Dodson et al., 2014).

Notwithstanding this combination of suspected health effects and demonstrable human exposure, in 2000 the total TCIPP production in Europe was 36,000 tonnes. It is used in applications such as rigid foams in the production of construction blocks and panels used for insulation purposes, and in flexible PUF for soft furnishings and mattresses (EU RAR, 2008). Currently, used furniture polyurethane foams treated with TCIPP are treated as municipal rather than hazardous waste, and are thus landfilled or incinerated. In the UK alone, it is estimated that around 670,000 tonnes of furniture of which a proportion will be PUF was disposed of by householders annually (WRAP, 2012). This reservoir of TCIPP within furniture polyurethane foams has and will continue to gradually enter the waste stream. An EU risk assessment report (EU RAR, 2008) predicts that a typical UK landfill with a leachate flow of  $100 \text{ m}^3 \text{ day}^{-1}$  would emit a maximum TCIPP mass via leachate of  $6.7 \text{ g day}^{-1}$ . There is hence a pressing need to understand the fate of chemicals like TCIPP associated with furniture PUF following disposal. Potential emission pathways for chemicals associated with landfill include contamination of leachate and volatilisation (Stubbings and Harrad, 2014). The physicochemical properties of TCIPP (water solubility =  $1600 \text{ mg L}^{-1}$  at  $20^\circ \text{C}$ , vapour pressure =  $1.4 \times 10^{-8} \text{ Pa}$  at  $21^\circ \text{C}$  and  $\text{Log } K_{\text{OW}} = 2.59$  (van der Veen and de Boer, 2012; Tremain, 2002)), suggest that following disposal to landfill such leaching and volatilisation of TCIPP associated with treated PUF may be extensive. TCIPP is an additive chemical not covalently bound to the PUF material and therefore TCIPP escape is relatively facile. Considering that these products are often treated with TCIPP at percent levels by weight (EU RAR, 2008), it is apparent that furniture PUF constitutes a significant potential source of TCIPP to the environment. Despite this, very little research has been undertaken that examines end-of-life management of TCIPP associated with waste soft furnishings (items made of cloth, such as curtains, chair coverings, etc., used to decorate a room) and furniture. In the absence to our knowledge of empirical data related to the fate of TCIPP treated furniture foam in landfill, this study conducts a series of controlled laboratory experiments to test the hypothesis that TCIPP is capable of leaching from waste furniture PUF.

## 2. Materials and methods

### 2.1. Samples

We investigated a flame retardant-treated polyurethane foam sample taken from a sofa cushion. The sample was collected from a sofa prior to entry into the UK waste stream in Birmingham, UK, 2012. As the presence of flame retardants present in the foam was unknown, its chemical content was determined prior to deployment in our leaching experiments. To do so, small pieces of foam (approx.  $5 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm}$ ) were taken from random points from the sample totalling approximately 50 mg. An accurately weighed aliquot of foam (50 mg) and 5 mL of ethyl acetate were added to a pre-washed test tube, vortexed for 1 min and sonicated for 5 min before being centrifuged for 2 min at 2000 rpm. The supernatant was transferred to a clean tube, the extraction was repeated and both supernatants were combined (10 mL total) and vortexed for 1 min 1 mL of sample was then transferred to a clean tube and diluted using 9 mL ethyl-acetate. Finally  $10 \mu\text{L}$  of the first dilution was transferred to and diluted further using  $90 \mu\text{L}$  methanol containing 90 ng  $d_{15}$ -labelled TPhP as internal standard ( $\times 10,000$  dilution in total). The test PUF was analysed via LC-MS/MS (see section 2.4) in quintuplicate.

### 2.2. Leaching test methods

Four distinct experimental scenarios were undertaken to examine the effects of: (a) contact time (single batch experiments); (b) duration of serial or periodic wetting and draining of waste (serial batch experiments); (c) temperature (20, 50, and  $80^\circ \text{C}$ ); and (d) pH level (acidic 5.8, slightly acidic 6.5, and alkaline 8.5) of the leaching fluid on the leachability of the target analyte from the sample material (SI; Table S1). In scenario (a) contact time, the treated sample is contacted once with the leaching fluid for a set predetermined time of either, 6 h, 24 h or 48 h. In scenario (b) serial batch, the sample is contacted with the leaching fluid for 168 h in total, with the resulting leachate being removed from the contact vessel and replenished with fresh leaching fluid 6 times, at intervals of 6 h (batch 1), 24 h (batch 2), 48 h (batch 3), 72 h (batch 4), 96 h (batch 5) and 168 h (batch 6). The leachate was extracted from the contact vessel via pouring or draining through a  $0.45 \mu\text{m}$  pore size glass fibre filter (Advantec, Japan), in which the contact vessel was inverted for approximately 5 min to ensure as much leachate was removed as possible. Each batch of leachate were analysed for analyte concentrations at the given intervals. Leaching fluids were prepared as previously described in Stubbings and Harrad (2016). PTFE bottles (500 mL) were used as contact vessels during controlled leaching experiments. The contact vessel was not completely filled with leaching fluid and as a result headspace was present inside the contact vessel. In all experiments, 1 g of PUF sample was contacted with 100 mL of Milli-Q water giving a liquid-solid ratio of 100:1 (v/w). Following addition of the sample and leaching fluid, contact vessels were horizontally agitated on a mechanical shaker at 200 rpm for the desired contact time. In scenario (c) samples examining the influence of temperature, the contact vessels were not agitated and instead were submerged in a water bath for 24 h at the desired temperature. In scenario (d) experiments were agitated at 200 rpm for 6 h and the initial pH of the leaching fluid before contact with flame retarded PUF samples was recorded. Each of the above leaching experiments were conducted in duplicate.

### 2.3. Sample preparation and chemical analysis

Each leachate sample was filtered through a  $0.50 \mu\text{m}$  size particle retention glass fibre filter (Advantec, Japan) to remove any textile fibres from the leachate and then spiked with  $10 \mu\text{g}$  of  $d_{15}$ -labelled Tri-phenyl-phosphate (TPhP) as internal (or surrogate) standard. The filtrate was then extracted in series using  $2 \times 50 \text{ mL}$  dichloromethane (DCM) by liquid-liquid extraction with mechanical shaking for 30 min each time. Approximately 5–10 mL 2% NaCl solution was used to enhance separation after extraction. The combined DCM extracts were dried via filtration through  $\text{Na}_2\text{SO}_4$ . The dried extract was concentrated to 0.5 mL using a Zymark Turbovap II with solvent exchange to *n*-hexane before being loaded on to a 2 g pre-cleaned, activated florisil column and washed with 20 mL *n*-hexane. The TCIPP was then eluted using 20 mL ethyl acetate. The eluate was evaporated to incipient dryness and then reconstituted to  $100 \mu\text{L}$  with addition of 25 ng  $d_{27}$ -labelled TnBP as a recovery standard in methanol. Prior to analysis via LC-ESI-MS/MS the samples underwent further dilution in which a  $10 \mu\text{L}$  aliquot was taken and diluted with  $990 \mu\text{L}$  of methanol, and then an additional  $10 \mu\text{L}$  aliquot of that first 1 mL dilution was taken and diluted with  $990 \mu\text{L}$  of methanol to yield a 10,000 times dilution. This was necessary due to the very high concentrations of TCIPP in samples.

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