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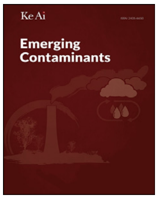

Mass transfer of an organophosphate flame retardant between product source and dust in direct contact

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ABSTRACT

Organophosphate flame retardants (OPFRs) are a group of semi-volatile organic compounds (SVOCs) and among the most abundant contaminants indoors. Their indoor presence has been associated with potential health risks however there is limited understanding as to how they are released from indoor sources. This study uses an emission micro-chamber to explore one of the currently understudied chemical migration pathways; direct transfer between a source material and settled dust in contact with the source. A tris(2-chloroisopropyl) phosphate (TCIPP)-treated insulation board is used as the source material. Rapid and substantial transfer was observed after only 8 h of source-dust contact, resulting in 80 times higher concentrations in dust compared to pre-experiment levels. Further time points at 24 h and 7 d showed similarly high average dust levels and the TCIPP in the dust and air in the chamber was calculated to be close to thermodynamic equilibrium. It was concluded that TCIPP was effectively transferred from the insulation board to the dust on its surface and the surrounding air via gas-phase diffusion. In a real room, a gradient of TCIPP concentrations in air above the surface of a product could result in higher concentrations in dust sitting on the product than dust in the rest of the room.

1. Introduction

Several groups of semi-volatile organic compounds (SVOCs) are identified as indoor environmental pollutants worldwide [1]. The organophosphate flame retardants (OPFRs) are a group of SVOCs which are ubiquitous and among the most abundant contaminants indoors [2]. OPFRs are widely used in a variety of commercial applications such as building materials and consumer products [3]. Most OPFRs are present in materials and products as additives where they can reach tens of % in content [4]. Due to the fact that OPFRs are not chemically bound to the product material they can be released to the indoor environment where they may pose a risk to human health. Certain human health risks have been documented to be associated with exposure to OPFRs, including endocrine disrupting effects [5–7].

The mode of entry of organic pollutants into the environment is known to be an influential factor for their environmental fate [8]. So far both experimental emission chamber and indoor fate modelling studies have largely focused on diffusive gas-phase emissions (volatilization) to air as the major emission mechanism from indoor sources [9–11]. However, the occurrence of alternative pathways that can lead to direct chemical migration to dust have been hypothesized [12–14]; these include, i) abrasion/physical weathering of the chemically treated product and ii) chemical transfer from the chemically treated product to the dust in direct contact with the material surface. These migration pathways can provide a plausible explanation for the high dust concentrations of SVOCs observed indoors (often in dust collected in close proximity to or on the surface of likely sources) [15–17] that cannot be convincingly explained by volatilization and subsequent deposition to dust, especially for low volatility SVOCs (i.e. decabromodiphenyl ether, (BDE-209)). However the influence of potential emission-to-dust mechanisms on indoor dust levels has also been demonstrated for relatively volatile OPFRs (with log K_{OA} of <9) [18].

Chemical migration from product to dust (pathway ii above) could theoretically take place either (a) via the gas phase or (b) in the liquid or solid phase; directly from the FR-containing polymer

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in the product to the organic matter in the dust [19]. The dust in direct contact with the product could reach a fugacity that is higher than the air and dust in the rest of the room if the air in the room is not well mixed with air close to the surface of a product. This phenomenon has been demonstrated experimentally [20,21]. Although the enhanced migration to dust is likely a combined effect of both migration pathways i) and ii), uncertainties still remain regarding how exactly these occur in the indoor environment. This study aims to shed further light on one of the suggested migration-to-dust pathways, namely; chemical transfer between the source and settled dust in contact with the source. The magnitude and timescale of this source-to-dust chemical transfer is experimentally determined in a commercially available emission micro-chamber using a building material treated with an OPFR, tris(2-chloroisopropyl) phosphate (TCIPP), and well-characterised dust. Compared to 1,2,5,6,9,10-hexabromocyclododecane (HBCDD), di(2-ethylhexyl) phthalate (DEHP) and BDE-209 studied before (log K_{OA} = 11, 12.6, 16.5 respectively) [20–22], TCIPP (with log K_{OA} = 9 [23]) is a relatively volatile SVOC. This allows us to examine whether direct source-dust contact results in a significant chemical transfer for the more volatile SVOCs but also to investigate the underlying mechanism of such transfer.

2. Materials and methods

2.1. Micro-chamber

A Micro-Chamber/Thermal Extractor™ - 120 (μ-CTE™, Markes International) (Fig. 1) located at the Flemish Institute for Technological Research (VITO), Belgium [24] was used to investigate chemical transfer between the source (i.e. the test material containing the chemical) and dust in direct contact. The μChamber consists of six separate emission test cells (ETCs) each having a diameter of 4.5 cm and a height of 2.8 cm, resulting ín a total internal surface area of 71 cm^2 and a total volume of 44 cm^3. The internal surfaces of each cell are made of inert-coated stainless steel. To maintain a constant temperature during the test, the μ-CTE unit was placed in a laboratory where the temperature was controlled at 23 ± 1 °C.

2.2. Test material

A Polyisocyanurate (PIR) insulation board (1.2 × 0.6 × 0.09 m) acquired from a Belgian do-it-yourself shop was used as the test material in the source-to-dust direct migration experiment. The PIR insulation board was treated with TCIPP in order to meet fire safety regulations. A 2.2% w/w TCIPP content was analytically determined in this study using the same method applied for dust analysis described in a Section 2.5.2.

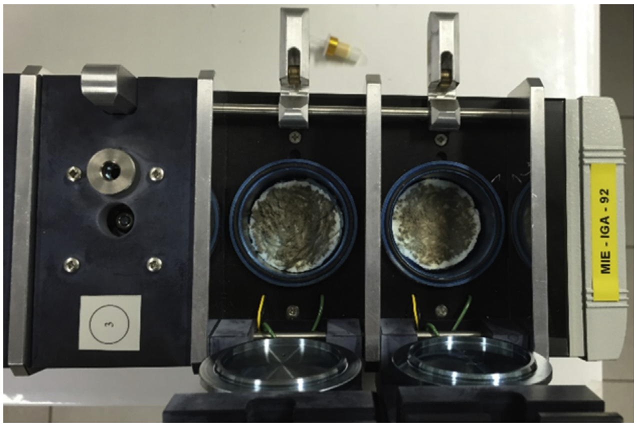

Fig. 1. Emission test cells prior to the start of the experiment. A layer of dust (brown colouration) is covering the surface of the test material (white).

2.3. Chemicals

TCIPP of 99.5% purity was purchased from LGC Promochem AB (Borås, Sweden). Biphenyl of ≥99% purity was purchased from Sigma Aldrich (Steinheim, Germany) and d-12 tri(2-chloroethyl) phosphate (TCEP) of >98% purity from Wellington Laboratories (Ontario, Canada). Acetone, n-hexane and methyl tert-butyl ether (MTBE) were obtained from Rathburn Chemicals (Wakerburn, Scotland). Standard Reference Material 'organic contaminants in house dust' (SRM 2585) was obtained from the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

2.4. Experimental design for investigating chemical transfer between source and dust in direct contact

Prior to the start of the test, the inner surface of each of the ETCs was cleaned with acetone, methanol and then finally dried under clean air flow at 90 °C for 72 h. After the cleaning procedure, the ETCs were purged at test conditions (Table 1) for an additional 24 h. Six round pieces (d = 4.5 cm, h = 1 cm) were cut randomly from the central part (at least 10 cm from the edges) of the PIR board using a pre-cleaned utility knife. The test pieces were placed inside the ETCs and 40–100 mg of SRM dust was evenly distributed on the surface of each piece, resulting in a dust loading factor of 2.5–6.3 mg/cm^2 (Fig. 1). The time was recorded immediately after closing the ETCs. The experiment was run for three durations with duplicates for each duration: 8 h (cells 1 & 2), 24 h (cells 3 & 4) and 7 days (cells 5 & 6). After each experimental run was terminated, the dust was collected on 0.45 μm membrane filters (Gelman-Sciences) using a vacuum pump.

Air was continually flushed through the ETCs (Table 1), and samples of air were collected from ETCs 5 and 6 at 24 h and 7 d by active air sampling as described in Ref. [25]. The sampling details are given in Table S1. An 8 h air sample was not collected due to complications with the vacuum pump. The cartridges for sampling and thermal desorption were stainless steel tubes (Markes International Ltd.) with the following dimensions: 9 cm length, 6.53°.d., and 5 mm i.d. and packed with polydimethylsiloxane (PDMS)/Tenax TA sorbent material. Prior to each use, the sampling tubes were conditioned by thermal cleaning under a nitrogen flow rate of 75 mL min^{-1} at 300 °C for 60 min, then sealed with end caps, and stored under nitrogen atmosphere to prevent any contamination of the sorbent.

2.5. Sample extraction and chemical analysis

2.5.1. Air samples

Analyses were performed on a TD-GC-MS system, which includes a TD100 thermal desorber (TD) equipped with a multi-tube autosampler (Markes International Ltd.) and coupled to a gas chromatograph Thermo Trace GC Ultra and a mass selective detector Thermo DSQII (Thermo Fisher Scientific Inc.). The analytical procedure described in Lazarov et al. [25] was followed. Thermal desorption of the sampling tubes was carried out at 300 °C with a flow rate of 20 mL min^{-1} for 10 min, followed by cold trap (10 °C) focusing. The chromatographic separation of TCIPP was conducted on ZB-SemiVolatiles capillary column (Phenomenex) 30 m × 0.25 mm (i.d.) x 0.25 μm film thickness. The oven programs were the following: initial temperature of 100 °C maintained for 7 min followed by ramps of 10 °C/min to 300 °C maintained for

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