Chemosphere 206 (2018) 132–141

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Small-scale spatial variability of flame retardants in indoor dust and implications for dust sampling

Simona Jílková [a], Lisa Melymuk [a, *], Šimon Vojta [a, 1], Martina Vykoukalová [a], Pernilla Bohlin-Nizzetto [b], Jana Klánová [a]

[a] Research Centre for Toxic Compounds in the Environment (RECETOX), Masaryk University, Brno, Czech Republic
[b] Norwegian Institute for Air Research (NILU), Kjeller, Norway

## HIGHLIGHTS

- Flame retardant levels in indoor dust varied significantly between and within rooms.
- Up to 1000-fold differences exist in flame retardant levels within the same room.
- Levels of hexabromobenzene were elevated in computer room dust.
- Composite dust samples are recommended due to within-room spatial variability.

## ARTICLE INFO

*Article history:*
Received 24 January 2018
Received in revised form
18 April 2018
Accepted 22 April 2018
Available online 23 April 2018

Handling Editor: Myrto Petreas

*Keywords:*
Indoor dust
Flame retardants
Spatial variability
Sampling methods

## ABSTRACT

Indoor dust is often used to evaluate levels of organic compounds indoors, particularly for compounds with indoor sources, such as flame retardants (FRs). Yet there are uncertainties about the type of information that can be obtained from indoor dust. This study reports detailed dust sampling to assess spatial variability in indoor dust concentrations, the relationship between FR sources and dust, and the implications when interpreting dust concentrations. Multiple dust samples were collected from a range of surface types in three large rooms: a residential flat, a university seminar room, and a university computer room. Samples were analysed for polybrominated diphenyl ethers (PBDEs), novel halogenated flame retardants (NFRs) and organophosphate esters (OPEs).

FR levels in dust varied significantly between and within rooms. Levels typically ranged over one order of magnitude within a room, and up to four orders of magnitude for a few OPEs. The spatial distribution of FRs related (in some cases) to proximity to sources, surface properties, and dust surface loadings. Differences also existed between surface and floor dusts, e.g., the contribution of TBOEP to ∑OPEs was higher in floor than surface dust, which has implications for human exposure assessment; adults typically have more contact with elevated surfaces, while young children have greater contact with floor surfaces. Overall, significant spatial heterogeneity exists in indoor dust, even in seemingly homogeneous indoor spaces, thus hampering comparability between studies and locations when single samples are collected. Composite samples are strongly recommended to limit the influence of spatial heterogeneity.


## 1. Introduction

Flame retardants (FRs) are chemicals used in electronics, furniture, and building materials to reduce flammability in order to meet fire safety regulations (de Wit, 2002). Two types of organic FRs are commonly used: (1) halogenated flame retardants (HFRs) and (2) organophosphate esters (OPEs). HFRs consist of brominated and chlorinated flame retardants (Bergman et al., 2012), including polybrominated diphenyl ethers (PBDEs) and so-called "novel" halogenated flame retardants (NFRs) used as replacements for banned PBDEs (Betts, 2008). OPEs are used as both FRs and plasticizers and, as with the NFRs, OPE production also increased after restrictions on PBDEs (van der Veen and de Boer, 2012).

Due to the nature of FR use, high concentrations are found in

* Corresponding author. RECETOX, Masaryk University, Kamenice 753/5, pavilion A29, 62500 Brno, Czech Republic.
*E-mail address:* melymuk@recetox.muni.cz (L. Melymuk).
[1] Present address: Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island 02882-1197, USA.

https://doi.org/10.1016/j.chemosphere.2018.04.146
0045-6535/

indoor environments, and differences in indoor levels have been noted between countries (Harrad et al., 2008b; Sjödin et al., 2008; Venier et al., 2016; Vykoukalová et al., 2017) or within countries (Karlsson et al., 2007; Stapleton et al., 2008); between types of buildings (Ali et al., 2011; Cequier et al., 2014; Harrad et al., 2008a); as well as between rooms within a building (Al-Omran and Harrad, 2018; Kuang et al., 2016; Muenhor and Harrad, 2012; Stapleton et al., 2008). Comparisons of different rooms in the same buildings have identified that measured concentrations are influenced by the presence of furniture and electronics. For example, Muenhor and Harrad (2012) suggested that where and when an indoor dust sample is taken exerts a substantial influence on the level of contamination detected, and relates to the proximity to potential sources such as electronics and carpet. Harrad et al. (2009) found decreasing concentrations of hexabromocyclododecane with increasing distance from a TV. Al-Omran and Harrad (2018) identified consistently higher FR concentrations in dust from elevated surfaces than from floors, and differences in dusts from two areas of the same rooms. Kuang et al. (2016) identified higher levels of PBDEs and NFRs in living rooms and bedrooms than in kitchens, however, this could not be directly linked to any source. Rather, it was suggested that environmental factors (e.g., higher moisture in kitchen) lead to lower dust concentrations in kitchens. Thus, a key question that arises considering all of the indoor spatial differences between and within buildings is how much of the variation is due to real differences in the indoor environments, and how much is an artifact of the choice of sampling location within a given room. Moreover, in broad indoor studies covering many locations, single dust samples are often considered representative of whole-room or even whole-building conditions, however, it is not clear whether this assumption is valid.

To address this question, the main objectives of this study were (1) to identify the differences in FR profiles and levels obtained by two sampling methods (wet wipes and vacuuming), (2) to identify the range of concentrations within individual rooms and thus identify what effect the choice of sampling location may have on reported concentrations, and (3) to determine the extent to which concentration levels are influenced by room type and proximity to room elements (electronics, furnishings, different usage of the space, etc.), and identify whether greater heterogeneity in room furnishings and use leads to greater heterogeneity in indoor dust. These objectives were addressed by detailed dust sampling (>9 samples per room) in three indoor environments.

## 2. Methods

### 2.1. Sampling strategy

Three indoor environments were chosen for sampling. The first was a residential flat, where the entrance, living room and kitchen were sampled in March 2014. The second and third were university classrooms—one classroom without computers (seminar room - SR) and one with computers (computer room - CR), sampled in July 2014. The seminar and computer rooms were the same size and shape and located in the same university building, differing only by building storey and room equipment. The classrooms are normally vacuumed 3 times/week and desks are wiped 4–5 times/week, but sampling took place after the conclusion of the academic year and there was no regular activity in the lecture room in the two weeks prior to sampling. Both locations were not vacuumed/dusted for two weeks prior to sampling.

In the flat, eight vacuum samples were collected from floors, which included the entrance area, living, dining room, kitchen, and from the sofa. The flat was not cleaned in the week prior to sample collection. Ten wipe samples were collected from horizontal surfaces, including electronics, a chair, and kitchen furnishings, and one vertical surface (i.e. windows). Samples were also collected from areas with high dust accumulation (F4, F6, and F14 in Fig. 1), i.e., places with infrequent cleaning, such as under a sofa and on an inaccessible window sill. In the classrooms, four vacuum samples were collected from the carpet and five wipe samples were collected from desks in both SR and CR. Additionally, six wipe samples were collected from monitors (all-in-one PCs) and keyboards in CR. The sampling locations are shown in Fig. 1 and more details are given in Table S1 in the Supplementary Data.

#### 2.1.1. Sampling

Two dust sampling methods were used – wet wipe sampling for settled dust on smooth elevated surfaces and a vacuum cleaner with sock insert for floor dust and dust from the sofa.

The wet wipe samples were collected using laboratory kimwipes. The kimwipes were pre-cleaned via soxhlet extraction in dichloromethane (DCM) for 8 h. At the site, the kimwipes were moistened by approximately 2–3 ml of propan-2-ol and were used to wipe each target surface. Depending on surface area and amount of dust, 1–5 wipes were used for each surface, and combined into one sample per surface. The area of the sampled surface was measured. Wipes were packed in aluminium foil and sealed in a plastic bag. Wipe samples were transported to the laboratory in a cooler box and stored at −18 °C until processing.

Dust samples from floors and fabric surfaces (e.g., sofa) were collected using a household vacuum cleaner with polyester sock inserts. Socks were precleaned via soxhlet extraction in DCM for 8 h, and before sampling and between samples, the vacuum nozzle and tube were cleaned with propan-2-ol. To collect each sample, a polyester sock was inserted into the front of the vacuum tube and held in place by the vacuum nozzle. Each target surface was vacuumed and its area measured. The sock was removed from the vacuum cleaner, sealed by a plastic cable tie, packed in aluminium foil and sealed in a plastic bag. Socks were transported to the laboratory in a cooler box and stored at −18 °C until processing.

### 2.2. Sample extraction and clean-up

The wipes were extracted using automated warm Soxhlet extraction in a Büchi B-811 automatic extractor, with DCM as the extraction solvent. Before extraction, samples were spiked with isotopically labelled ($^{13}$C) internal standards, including triphenyl phosphate, BDE 28, 47, 99, 100, 153, 154, 183 and 209, HBB, PBBZ, syn- and anti-DDC-CO, BTBPE, and DBDPE (all from Wellington Laboratories, Inc., Guelph, Ontario, Canada, except DDC-CO from Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA). The soxhlet extraction was cycled for 40 min, followed by 20 min where solvent was diverted to concentrate the extract. The extract was then concentrated to less than 10 ml and quantitatively transferred to a vial. Then the extract was split 3:7 by weight (30% and 70% aliquots) and each fraction was concentrated to a volume of 1–2 ml by nitrogen flow.

Vacuum-collected dust samples were extracted via sonication. Before extraction, samples were weighed and sieved with a 500 μm sieve (Newark Wire Cloth Company, USA) to remove coarse particles (e.g., hair, large fibres). Approximately 100 mg of the sieved dust was used for extraction. The sock was rinsed with 20 ml of 1:1 hexane:acetone (v/v) and this volume was added to the accurately weighed dust sample and the mass difference between unrinsed sock and rinsed sock was included to the mass of extracted dust. Before sonication, the sample was spiked with the same set of internal standards as the wipe samples. The sample and 20 ml of hexane:acetone were sonicated for 10 min, then the sample was allowed to settle for 20 min and the solvent supernatant was