Distribution of legacy and emerging semivolatile organic compounds in five indoor matrices in a residential environment

Lisa Melymuk [a, *], Pernilla Bohlin-Nizzetto [a, b], Šimon Vojta [a], Martina Krátká [a],
Petr Kukučka [a], Ondřej Audy [a], Petra Přibylová [a], Jana Klánová [a]

[a] Research Centre for Toxic Compounds in the Environment (RECETOX), Faculty of Science, Masaryk University, Kamenice 753/5, Pavilion A29, 625 00 Brno, Czech Republic
[b] Norwegian Institute for Air Research (NILU), Instituttveien 18, PO Box 100, NO-2027, Kjeller, Norway

HIGHLIGHTS

- SVOCs indoors can be characterized using a combination of air and dust samples.
- Legacy SVOCs are in equilibrium between indoor air, floor and surface dust.
- Dust has high within-room spatial heterogeneity.
- Multimedia levels of current SVOCs cannot be estimated from single measurements.

ARTICLE INFO

ABSTRACT

Seven types of indoor samples, covering five indoor matrices, were collected in a residential room, and analyzed for five classes of semivolatile organic compounds (SVOCs). The goal was to improve the understanding of the relationship between indoor air, surface films and dust, based on differences in sources, physicochemical properties, and indoor environmental characteristics. Comparisons of the five matrices (gas- and particle-phase air, floor dust, surface dust/films and window films) demonstrated that within our test room a semi-quantitative measurement of the SVOC distributions and concentrations could be obtained by air, and composite dust or furniture surface wipes. Dust concentrations varied within the room, and spot samples were not necessarily representative of the average room conditions.

Polyurethane foam passive air samplers (PUF-PAS) successfully quantified the total air concentrations of the studied SVOC compound groups, as indoor air concentrations were dominated by gas-phase compounds, however air concentrations of individual particle-bound compounds had higher uncertainty. Measured concentrations of dust/surfaces could be used to estimate air concentrations of legacy SVOCs, demonstrating equilibrium in the room. However, air concentrations of current-use compounds (flame retardants, polycyclic aromatic hydrocarbons (PAHs)) could not be estimated from dust/surface concentrations, demonstrating the influence of ongoing primary emissions and non-equilibrium status in the room.

1. Introduction

Indoor environments are receiving greater recognition as key contributors to human exposure to semivolatile organic contaminants (SVOCs), particularly as in developed countries more than 90% of peoples' time is spent indoors (Schweizer et al., 2007), indoor materials are major sources of SVOCs, and indoor concentrations of many SVOCs are often higher than outdoors (Rudel et al., 2010). Moreover, many SVOCs are linked to negative human health effects (Bonvallot et al., 2010) and subject to national and international control strategies (e.g., Stockholm Convention, www.pops.int; Convention of Long-Range Transboundary Air Pollution, http://www.unece.org/env/lrtap/lrtap_h1.html; REACH, http://echa.europa.eu/regulations/reach).

A multitude of compounds exist in indoor environments as a consequence of their presence in consumer products, building

materials and intrusion of outdoor air. It is crucial to understand the distributions and pathways of these compounds indoors to link emissions to human exposure. Herein we examine polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), novel halogenated flame retardants (NFRs) and polycyclic aromatic hydrocarbons (PAHs). These compounds have a range of sources (e.g., building materials/consumer products/outdoor sources), physicochemical properties, and also represent different regulatory statuses: PCBs and OCPs are legacy compounds with no current/recent indoor use, while NFRs have current indoor sources, and PAHs have on-going emissions. PBDEs can be considered as both legacy and current-use compounds, as there should be no significant new use in Europe (Betts, 2008) but there is a high probability that indoor materials from recent decades contain additive PBDEs. Thus examination of the distributions of these compounds in indoor matrices gives a broad description of indoor SVOCs.

Knowledge of multimedia indoor concentrations is crucial considering the relevant human exposure routes (inhalation, dermal uptake, dust ingestion). Multimedia concentrations have often been estimated through indoor models (Liagkouridis et al., 2014), but simultaneous measurements of multiple indoor matrices are more limited. This is partially due to the resource burden of collecting many matrices (air, aerosols, dust, surfaces, windows, etc.) to characterize a single room. Thus, studies have often focused on one or two matrices (e.g., dust or air) and used these as surrogates for whole room conditions. However, use of surrogate matrices is challenging, as they may represent localized non-equilibrium room conditions, and the relationship between dust/films and air is not fully characterized. Some comparisons of surrogate matrices (mainly dust) and indoor air have concluded that dust cannot be used as a surrogate for air (Allen et al., 2008; Salthammer and Schripp, 2015), while others have concluded that it is possible (Dodson et al., 2015; Watkins et al., 2013).

We have conducted detailed multimedia measurements in a single room to improve the understanding of the relationship between gas- and particle-phase air, surface films and dust, based on differences in compound sources (e.g., in-use vs. legacy vs. outdoor) and physicochemical properties. This is a needed step towards a representative and efficient indoor sampling strategy, and provides guidance on how sampling can be simplified for the purpose of large-scale indoor monitoring aiming to assess overall indoor concentrations and distributions.

2. Methods

2.1. Sampling

Twelve samples (details in Table 1) were collected in a residential bedroom in Brno, Czech Republic during 28 days in March/April 2013. The room had a volume of 39.4 m^3 and contained a single bed, desk, shelves and storage unit, and had one window facing north-west onto a garden. The window was closed, the bedroom was unoccupied during the sampling period, and the house was occupied by three people with the door to the rest of the house left open. Air was circulated by natural ventilation. The temperature was ~20 °C. Further description of the site is given in the Supplementary Material (SM).

All floors and surfaces in the room were initially cleaned so that samples would reflect only the sampling period. Air samples were collected during a 28-day sampling period using low-volume active air sampler (LVAAS), polyurethane foam passive air samplers (PUF-PAS) and cascade impactor (Table 1). On day 28, dust and wipe samples were collected. The sampled areas are shown in Fig. S1. Wipe samples were collected using a pre-cleaned kimwipe

moistened with reagent-grade 2-propanol. Floor and bed dust were collected using a pre-cleaned polyester sampling sock inserted into the tube of a conventional household vacuum cleaner, as described by Goosey (2010). After collection, all samples were wrapped in pre-cleaned aluminum foil and sealed in plastic bags for transport to the laboratory. Samples were stored at −18 °C until analysis.

The LVAAS was considered a reference air sampler providing "correct" air concentrations. A general sampling rate of 1.4 m^3/day (Bohlin et al., 2014) was used to convert accumulated amounts in PUF-PAS to air concentrations. A comparison with this rate and the ratio of PAS masses to LVAAS concentrations suggested this was appropriate for this study (see SM).

2.2. Analysis

Samples were analyzed for seven PCBs, 12 OCPs, 15 PAHs, and 25 flame retardants (FRs): 10 PBDEs and 15 NFRs (Table S1). The instrumental methods followed previously published procedures (Lohmann et al., 2013a, 2013b, 2012). Briefly, PUFs, GFFs, and kimwipes were Soxhlet extracted in dichloromethane in an automated extractor, while dust samples were sieved (500 μm) and extracted by sonication in acetone:n-hexane. Samples were analyzed by gas chromatograph-mass spectrometry. For the purposes of statistical analysis, values below the limit of quantification (LOQ) were assigned a value equal to LOQ/2 (Table S2), except for BDE-209 in air samples, as the LOQ was at the same level as the concentrations of Σ_9PBDEs. Further details on the analytical methods and data treatment are given in the SM.

2.3. Distribution estimates

While fugacity-based models have quantified relationships between indoor matrices on a detailed level (e.g., Bennett and Furtaw, 2004; Zhang et al., 2009) we investigated if simple two-compartment relationships (e.g., using K_{OA} and the physical parameters of the matrices) could provide semi-quantitative air concentrations, akin to what is obtained from PAS. Gas-particle partitioning coefficients were estimated assuming absorptive control on partitioning (Salthammer and Schripp, 2015). Gas-phase air concentrations were estimated from surface wipe and dust concentrations based on Weschler and Nazaroff (2010), and particle-phase air concentrations were extrapolated from the estimated gas-phase air concentrations using the particle-gas partitioning coefficient described above. Details on input parameters and equations are described in the SM.

3. Results and discussion

3.1. SVOC concentrations

Table 2 gives the concentrations of the sum of each SVOC class in all matrices. Concentrations of individual SVOCs are given in Table S3. Comparisons to other reported indoor concentrations are given in Table S4.

The measured and estimated particle fractions for PCBs, OCPs, PAHs and PBDEs agreed within a 90% prediction interval, when considering the range of typical particles indoors (Fig. S3). However, NFR estimates were less successful: measured particle fractions were 50% lower than estimates for TBCO, and 40−80% higher for PBT, PBEB, TBP-BAE, TBP-DBPE (Table S5). This may be related to uncertainties in the partitioning coefficients for the NFRs, or evidence of non-equilibrium gas-particle distributions, particularly for compounds with nearby sources.

Particle size distributions varied by compound. The highest concentrations of all PAHs were on particles 0.25−0.5 μm, while FRs