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# Passive air sampling of flame retardants and plasticizers in Canadian homes using PDMS, XAD-coated PDMS and PUF samplers☆

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## ABSTRACT

Passive air samplers (PAS) were evaluated for measuring indoor concentrations of phthalates, novel brominated flame retardants (N-BFRs), polybrominated diphenyl ethers (PBDEs), and organophosphate esters (OPEs). Sampling rates were obtained from a 50-day calibration study for two newly introduced PAS, polydimethylsiloxane (PDMS) or silicone rubber PAS (one with and one without a coating of styrene divinyl benzene co-polymer, XAD) and the commonly used polyurethane foam (PUF) PAS. Average sampling rates normalized to PAS surface area were 1.5 ± 1.1 $m^3$ $day^{-1}$ $dm^{-2}$ for both unsheltered PDMS and XAD-PDMS, and 0.90 $m^3$ ± 0.6 $day^{-1}dm^{-2}$ for partially sheltered PUF. These values were derived based on the compound-specific sampling rates measured here and in the literature for the PAS tested, to reasonably account for site-specific variability of sampling rates.

PDMS and PUF were co-deployed for three weeks in 51 homes located in Ottawa and Toronto, Canada. Duplicate PUF and PDMS samplers gave concentrations within 10% of each other. PDMS and PUF-derived air concentrations were not statistically different for gas-phase compounds. PUF had a higher detection of particle-phase compounds such as some OPEs. Phthalate and OPE air concentrations were ~100 times higher than those of N-BFRs and PBDEs. Concentrations were not systematically related to $PM_{10}$, temperature or relative humidity.

We conclude that both PAS provide replicable estimates of indoor concentrations of these targeted semi-volatile organic compounds (SVOCs) over a three-week deployment period. However, PUF is advantageous for collecting a wider range of compounds including those in the particle phase.

## 1. Introduction

Phthalates, novel brominated flame-retardants (N-BFRs), polybrominated diphenyl ethers (PBDEs) and organophosphate esters (OPEs) are examples of semi-volatile organic compounds (SVOCs) used in many household products. Numerous studies have documented indoor levels of these compounds which, after release, partition amongst different indoor media, including dust, indoor surfaces, air and skin (e.g., Xu et al., 2009; Zhang et al., 2011; Venier et al., 2016; Vykoukalová et al., 2017). Whereas dust ingestion can be the dominant exposure route of less volatile SVOCs (Jones-Otazo et al., 2005; Stapleton et al., 2012), inhalation may be a significant route of exposure of more volatile SVOCs such as some polychlorinated biphenyls (PCBs) and OPEs (Harrad et al., 2008; Schreder et al., 2016). Exposure to some SVOCs is of human and ecological health concern (e.g., Król et al., 2011; Scheringer et al., 2012; North et al., 2014). As such, knowledge of air concentrations of SVOCs is a necessary first step towards assessment of

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exposure, followed by the development of strategies to reduce exposure.

Active air samplers (AAS) have been primarily used to measure the abundance of SVOCs both outdoors and indoors (e.g., Salamova et al., 2014, 2016; Rudel et al., 2003, 2010). An advantage of using AAS is that they collect known volumes of air that can be varied to allow air concentrations to be accurately measured, particularly for short deployment times. AAS sampling trains, commonly consisting of a filter followed by a sorbent, enable AAS to distinguish particle- from gas-phase compounds. However, AAS have clear disadvantages indoors as they are noisy, obtrusive and expensive to deploy, especially when studying many locations (Shoeib and Harner, 2002). These disadvantages have encouraged a shift towards using passive air samplers (PAS).

Non-equilibrium PAS measure time-averaged concentrations that are not influenced by short temporal variations. However, PAS require longer deployment times to achieve analytical detection. Furthermore, PAS cannot distinguish between gas- and particle-phase compounds and they require calibration, for example against AAS, to derive uptake rates of gas- and particle-phase compounds. PAS can also be calibrated using depuration compounds, but this approach is restricted to gas-phase uptake (Moeckel et al., 2009) and has yet to be used indoors in homes.

For measuring SVOC concentrations outdoors, several types of PAS have been widely used including polyurethane foam (PUF), styrene divinylbenzene copolymer (XAD), and sorbent impregnated PUF (SIP) (e.g., Wania et al., 2003; Chaemfa et al., 2008; Persoon and Hornbuckle, 2009; Melymuk et al., 2011; Abdollahi et al., 2017). Indoors, a growing number of studies have both calibrated and used PUF PAS to measure concentrations of SVOCs including PCBs, N-BFRs, PBDEs, and OPEs (Wilford et al., 2004; Bohlin et al., 2014; Venier et al., 2016; Vykoukalová et al., 2017) and to estimate cumulative exposures to PCBs (Ampleman et al., 2015; Marek et al., 2017).

Due to the impracticality of calibrating PAS at each study site, generic uptake rates measured at one study location are commonly used to interpret PAS results obtained at different locations (e.g., Zhang et al., 2011; Gevao et al., 2006). However, uptake rates vary amongst studies (e.g., Melymuk et al., 2014), questioning the extent to which generic uptake rates are applicable across several indoor locations. Moreover, this variability has implications for the inter-study comparability of data.

Uptake rates vary outdoors due to changes in conditions such as wind speed, for which a PAS housing is used to minimize these influences (Zhang et al., 2013). Other factors such as relative humidity (RH) and temperature also affect uptake rates (Herkert et al., 2016) but their influence cannot be easily minimized. Indoors, variations in factors such as wind speed and temperature are expected to be minimal, suggesting less variability of inter-location uptake rates. However, this expectation of uniform uptake rates in indoor locations has not been well tested. In addition to the limited understanding of inter-location uptake variability, few studies have compared air measurements obtained from different types of PAS deployed side-by-side. Further, PUF needs to be tested indoors to better characterize its uptake for a wider range of phthalates, BFRs (N-BFRs + PBDEs) and OPEs.

Silicone rubber or polydimethylsiloxane (PDMS) and the XAD-Pocket have been recently introduced for measuring phthalates and BFRs indoors (Okeme et al., 2016b). PDMS is versatile and easy to use for collecting and retaining a wide range of compounds (Seethapathy and Górecki, 2012; Okeme et al., 2016a). Its sorption properties have been characterized for many compounds using a PDMS-coated gas chromatographic column (Okeme et al., 2016a). PDMS has been tested for the stationary indoor sampling of phthalates and BFRs (Okeme et al., 2016b), for measuring air concentrations of BFRs to which herring gulls are exposed (Sorais et al., 2017), and as a bracelet for assessing personal exposure of humans to PAHs, OPEs and other SVOCs (O'Connell et al., 2014; Hammel et al., 2016). Its use has not been well tested against the more popular PUF PAS nor has it been well characterized for uptake of particle-phase compounds.

This study aimed to further characterize PAS for use indoors. PDMS was calibrated and compared to XAD-PDMS that is introduced here, and the popular PUF (single-bowl housing) for measuring indoor air concentrations of phthalates, BFRs and OPEs. XAD-coated PDMS is introduced as a PAS to increase the efficiency of PDMS to sample particle-phase compounds. This PAS consists of PDMS with a surface layer of XAD to create a rough surface morphology for trapping particles. We compared uptake rates measured using these PAS with those reported in the literature to assess inter-location variability and to derive generic uptake rates. Finally, we compared air concentrations obtained from PDMS and PUF and the replicability of the measurements made using each PAS that was co-deployed in 51 homes in the cities of Toronto and Ottawa, Canada.

## 2. Methods

### 2.1. Description of the study sites

The calibration study to measure uptake rates of PDMS, XAD-PDMS and PUF was conducted for 50 days from May to July 2016 in a computer laboratory of volume 280 $m^3$ located in a 120-year old building on the University of Toronto, downtown campus. The windows and the doors of the room were kept closed throughout the sampling period with no heating or air-conditioning in use or human traffic. The daytime room temperatures ranged from 27 to 29 °C. Potential sources of SVOCs in the room included desktop computers, PUF-containing chairs, tables with vinyl covering, and vinyl flooring. Active and passive air samplers were co-deployed for the entire 50-day period of the study.

Home sampling was conducted between February and August 2015 in 32 and 19 homes in the Greater Toronto area (GTA) and Ottawa, Canada, respectively. The sampled homes included 5 apartments, 34 detached houses, 7 semi-detached houses, 3 townhouses and 2 condominium units, with the number of residents ranging from one to seven. Of those homes, PDMS and PUF with a single-bowl housing were co-deployed in the bedroom of 25 homes and in the bedroom and Most Used Room (MUR) of 26 homes.

### 2.2. Sampling

#### 2.2.1. Calibration study

Duplicate active air samples were collected every 10 days during the 50-day calibration study using low volume active air samplers (LV-AAS) (BGI 400S, Packwill Environmental, Beamsville, ON, Canada) that ran throughout the study period. The device pumped air at 9–10 L $min^{-1}$, sampling 13–14 $m^3$ $day^{-1}$ through a sampling train consisting of a glass fibre filter (GFF) (diameter 42.5 mm, thickness 435 μm, pore size 1.5 μm; Sigma-Aldrich, Oakville, ON, Canada) to collect particle-phase compounds, and gas-phase compounds were collected in a PUF/XAD-2/PUF sandwich (each PUF: length, 30 mm; Amberlite XAD-2: mass 1.5 g, diameter 2.2 cm × length 10 cm; Sigma-Aldrich, Oakville, ON, Canada). The second PUF of the sandwich, positioned at the outlet of the sampling train, was used to assess compound breakthrough. The LV-AAS was deployed in a horizontal orientation with the inlet pointing sideways.

Triplicate passive air samples were collected every 10 days for