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Semi-volatile organic compounds in the particulate phase in dwellings: A nationwide survey in France

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HIGHLIGHTS

- 66 SVOCs were measured in airborne particles (PM_{10}) in dwellings.
- PAHs, phthalates and triclosan have the highest concentrations.
- Concentrations are higher in smokers' dwellings and during the heating season.
- Correlations between SVOCs provide trends regarding common determinants.
- High indoor PM_{10} concentrations promote SVOCs in the particulate phase.

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ABSTRACT

Sixty-six semi-volatile organic compounds (SVOCs)—phthalates, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), one pyrethroid, organochlorine and organophosphorous pesticides, alkylphenols, synthetic musks, tri-*n*-butylphosphate and triclosan—were measured on PM_{10} filters collected over 7 days during a nationwide survey of 285 French dwellings, representative of nearly 25 million housing units. Thirty-five compounds were detected in more than half of the dwellings. PAHs, phthalates and triclosan were the major particle-bound SVOCs, with a median concentration greater than 1 ng m^{-3} for butylbenzyl phthalate (BBP) (median: 1.6 ng m^{-3}), di(2-ethylhexyl) phthalate (DEHP) (46 ng m^{-3}) and di-iso-nonyl phthalate (DiNP) (7.9 ng m^{-3}), and greater than 0.1 ng m^{-3} for triclosan (114 pg m^{-3}), benzo(*a*)pyrene (138 pg m^{-3}), benzo(*b*)fluoranthene (306 pg m^{-3}), benzo(*g,h,i*)perylene (229 pg m^{-3}), and indeno(1,2,3-*c,d*)pyrene (178 pg m^{-3}). For most of the SVOCs, higher concentrations were found in the dwellings of smokers and during the heating season. The concentrations of banned SVOCs—namely, PCBs and organochlorine pesticides—were correlated. Permethrin, 4-*tert*-butylphenol and bisphenol-A showed no correlation with the other SVOCs and seemed to have their own specific sources. Most SVOCs were positively associated with PM_{10} concentration, suggesting that any factor that raises the mass of indoor airborne particles also increases the exposure to SVOCs through inhalation.

1. Introduction

Semi-volatile organic compounds (SVOCs) are a broad spectrum of molecules from different chemical families that have numerous properties (Weschler and Nazaroff, 2008). They can be used as pesticides, biocides, plasticizers, flame retardants, surfactants, and

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lubricants. Consequently, they are introduced in numerous applications in buildings or used daily by the entire population. Some SVOCs are also emitted by combustion processes, such as polycyclic aromatic hydrocarbons (PAHs) or polychlorinated dibenzo-*p*-dioxins/furans. Once emitted through evaporation or abrasion in the indoor environment or introduced from the outdoors, their chemical or biological degradation is limited, and they persist indoors (Weschler and Nazaroff, 2008). This persistence also explains why some SVOCs that were banned a few years ago, such as polychlorinated biphenyls (PCBs), are still detected in the air and dust inside buildings (Lehmann et al., 2015).

SVOCs are of concern due to their widespread exposure through different environmental media and pathways and their established or suspected health effects, e.g., effects on the reproductive system (Hauser and Calafat, 2005; Saillenfait et al., 2015), lung cancer (IARC, 2010), leukemia (Ward et al., 2009), effects on the cognitive and behavioral development (Lyche et al., 2015), and autism (Messer, 2010). Moreover some SVOCs have the potential to disrupt endocrine functions while interfering with hormones (Hwang et al., 2008; Rudel and Perovich, 2009).

In indoor environments, SVOCs are divided between the gas phase, airborne particles, and dust settled on floors and surfaces. Of the extensive literature published on SVOCs in buildings, few studies have focused on indoor air compared to settled dust. Moreover, most studies on indoor air have considered PAHs (Ma and Harrad, 2015).

The objective of this study was to assess the concentrations of SVOCs bound to indoor PM_{10} at a nationwide level. Sixty-six SVOCs—including phthalates, polybrominated diphenyl ethers (PBDEs), PCBs, PAHs, one pyrethroid, organochlorine and organophosphorous pesticides, alkylphenols, synthetic musks, tri-*n*-butylphosphate and triclosan—were studied. Correlations between SVOCs were analyzed, and the influence of the season, smoking in the dwelling, and indoor PM_{10} concentration on particle-bound SVOCs was assessed.

2. Materials and methods

2.1. Sample design

The samples were collected via a nationwide survey carried out by the French Observatory of indoor air quality (2003–2005) in a representative sample of the housing stock (Kirchner et al., 2007). Occupied main residences were randomly selected from the 24,672,136 permanently occupied housing units in mainland France, excluding oversea territories. The dwelling selection method for the survey was a three-stage process using a probability proportional to size sampling design to ensure that each housing unit had an equal probability of being selected (Golliot et al., 2003). The first stage of the design consisted of randomly selecting primary sampling units (PSUs) among the smallest territorial divisions of France. The second stage corresponded to the sampling of segments within each PSU. In the third stage, housing units were randomly selected within each segment. At the end, 6,268 addresses were drawn at random, and 4,165 households were contacted. The final sample comprises 567 dwellings representing the French housing stock.

2.2. Sampling of PM_{10}

The measurements were conducted from October 2003 to December 2005. Approximately 70% of the measurements were performed during the heating season (October–April), and the remaining dwellings were visited during the non-heating season (May–September). The sampling period was one week (7 days) in each dwelling. The sampling was activated during predefined occupation hours—i.e., in the evening from 5 p.m. to 8 a.m. the next day (Monday to Friday) and in continuous mode throughout the weekend—, to characterize the indoor concentrations to which the occupants are exposed over one week.

The PM_{10} were collected in the living room through a 2100 Mini-Partisol air sampler (Rüpprecht & Patashnick, Albany, NY, USA), coupled to a ChemPass model 3400 sampling system integrating both $PM_{2.5}$ and PM_{10} PEMS impactors operating at 1.8 ± 0.2 L min^{-1}. The flow rate was checked onsite with a flow rate calibrator DryCal DC-Lite (Bios International, Butler, NJ, USA). The total sampled volume was 12.6 ± 0.6 m^3. Particles were collected on pre-weighed 37 mm diameter PTFE membranes (polytetrafluoroethylene, 2 μm porosity, Gelman Sciences, Ann Arbor, MI, USA). The filters were weighted using a microbalance with a precision of 1 μg (Mettler MT5, Sartorius AG, Goettingen, Germany) in a temperature- and humidity-controlled room. After the gravimetric analysis, the filters were stored at −18 °C until SVOC analysis in 2014. Conservation tests showed that storage at −18 °C does not lead to any loss of the target molecules (Blanchard et al., 2014a). Damaged filters, equipment failure and invalid sampling flow rate reduced the number of valid filters for analysis to 285 (Ramalho et al., 2006).

2.3. Selection of compounds

A health-based ranking was the starting point for the selection of the compounds (Bonvallot et al., 2010). Briefly, compounds were ranked based on published concentrations in home settled dust and toxicity indicators. In addition, the technical feasibility was considered: some compounds were dropped because they could not be analyzed simultaneously with the others through a multi-residue analytical method (e.g., perfluorinated compounds), whereas other compounds were added, such as triclosan and alkylphenols. Triclosan is an antibacterial agent used in a broad range of household and personal care products (Bedoux et al., 2012), but no data exist on indoor air concentrations. Alkylphenols are used in numerous and various products. 4-*tert*-butylphenol has been classified as an endocrine disruptor by the European Commission (EC, 2015). However, few studies have reported indoor air concentrations. In the US, 4-*tert*-butylphenol was recently detected in all 50 homes investigated in California (Rudel et al., 2010) (median: 12 ng m^{-3}). In Japan, 4-*tert*-butylphenol was detected in 99% of the 45 homes studied by Saito et al. (2004), and 4-*tert*-octylphenol was detected in 52%. The median concentrations of 4-*tert*-butylphenol and 4-*tert*-octylphenol were 36 and 3.2 ng m^{-3}, respectively. Sixty-six SVOCs were ultimately considered for analysis. Table S1 in the supporting information provides the target SVOC names, abbreviations, CAS numbers, molecular weights, and boiling points.

2.4. Sample preparation and SVOC analysis

The SVOCs were simultaneously analyzed in PM_{10} samples using a simple and efficient multi-residue method based on thermal extraction (TE) and gas chromatography/tandem mass spectrometry (GC/MS/MS). A detailed description of the analytical method is already available elsewhere (Mercier et al., 2012; Blanchard et al., 2014b). This method has been slightly modified for the purposes of this study, as described below (and see Mercier et al., 2014); namely, internal standards and tandem mass spectrometry instead of mass spectrometry were used to minimize matrix interference and background noise.

2.4.1. Reagents and chemicals

Acetone Pestipur® was purchased from Carlo Erba Reagents (Val