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► To cite this version:

Corinne Mandin, Fabien Mercier, Olivier Ramalho, Jean-Paul Lucas, Erwann Gilles, et al.. Semi-volatile organic compounds in the particulate phase in dwellings: A nationwide survey in France. Atmospheric Environment, 2016, 136, pp.82-94. 10.1016/j.atmosenv.2016.04.016 . hal-01304354

HAL Id: hal-01304354

<https://hal-univ-rennes1.archives-ouvertes.fr/hal-01304354>

Submitted on 20 Apr 2016

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

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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 PM₁₀ 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)anthracene (44.4 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 PM₁₀ concentration, suggesting that any factor that raises the mass of indoor airborne particles also increases the exposure to SVOCs through inhalation.

Keywords: Indoor air quality, indoor environment, airborne particles, PM₁₀, particulate matter, endocrine disruptors

Highlights

- ▶ 66 SVOCs were measured in airborne particles (PM₁₀) 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 PM₁₀ concentrations promote SVOCs in the particulate phase.

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 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 polybrominated 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 PM₁₀ 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 overseas 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 pm to 8 am 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 PM₁₀ 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 PM₁₀ PEMS impactors operating at $1.8 \pm 0.2 \text{ L min}^{-1}$. The flow rate was checked onsite with a flow rate calibrator DryCal DC-Lite (Bios International, Butler, NJ). The total sampled volume was $12.6 \pm 0.6 \text{ m}^3$. 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., 2011), 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 PM₁₀ 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.

Reagents and chemicals

Acetone Pestipur[®] was purchased from Carlo Erba Reagents (Val de Reuil, France). Certified standards of aldrin, cis- and trans-chlordane, 4,4'-DDE, 4,4'-DDT, dieldrin, α -endosulfan, endrin, heptachlor, α -HCH, γ -HCH, metolachlor, chlorpyrifos, diazinon, fenchlorphos, atrazine, methoprotetryne, oxadiazon, fenprothrin, permethrin, tri-n-butylphosphate, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene,

benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, phenanthrene, pyrene, PCB 77, PCB 105, PCB 126, butylbenzyl phthalate (BBP), di-n-butyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), DiBP D₄, di-isononyl phthalate (DiNP), di-(2-methoxyethyl) phthalate (DMEP), dimethyl phthalate (DMP), di-n-octyl phthalate (DOP), 4-n-amyphenol, 4-tert-butylphenol, 4-n-nonylphenol, 4-tert-octylphenol, bisphenol-A and triclosan were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The standard of parathion D₁₀ was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The purity of the certified standards was above 95%. Individual standard stock solutions (1 g L⁻¹) were prepared in acetone by accurately weighing 25 mg ($\pm$ 0.1 mg) of standards into 25 mL volumetric flasks and stored at -18 °C.

Acetone solutions (100 mg L⁻¹) of 4,4'-DDT ¹³C₁₂, metolachlor D₆, chlorpyrifos D₁₀ and trans-cypermethrin D₆, acetonitrile solution (100 mg L⁻¹) of trans-cyfluthrin D₆, cyclohexane solutions (10 mg L⁻¹) of chrysene D₁₂, pyrene D₁₀, galaxolide and tonalide, cyclohexane solution (100 mg L⁻¹) of BBP D₄ and cyclohexane mixture (10 mg L⁻¹) of 8 PCBs (PCB 28, 31, 52, 101, 118, 138, 153 and 180) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Nonane solutions (50 mg L⁻¹) of BDE 28, 47, 85, 99, 100, 119, 153 and 154, nonane/toluene (3%) mixture (5 mg L⁻¹) of ¹³C₁₂-PBDE 47, 99 and 153, nonane/toluene (10%) solution (50 mg L⁻¹) of ¹³C₁₂-triclosan and toluene solution (50 mg L⁻¹) of tri-n-butylphosphate-d₂₇ were purchased from Wellington Laboratories (Guelph, ON, Canada). Acetonitrile solution (100 mg L⁻¹) of bisphenol-A ¹³C₁₂ and isooctane solution (100 mg L⁻¹) of pentachlorobenzene ¹³C₆ were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA).

Calibration solutions were prepared in acetone by the appropriate dilution of individual standard stock solutions and commercial solutions.

Pesticide-grade glass wool was purchased from Supelco (Bellefonte, PA, USA). Glass desorption tubes (17.8 cm length $\times$ 6 mm O.D. $\times$ 4 mm I.D.) were purchased from Gerstel GmbH & Co. KG (Mülheim an der Ruhr, Germany). Prior to use, glass wool plugs and glass desorption tubes were heated at 350 °C for 5 min to remove trace organic compounds and minimize background peaks.

Sample and calibration preparation

Each PTFE membrane was cut into four quarters using a scalpel on a glass support. The first quarter of the membrane was used for the analysis of trace compounds, and the remaining three quarters were dedicated to the analysis of highly concentrated compounds, such as PAHs or phthalates. Each quarter was then inserted into a glass desorption tube fitted with a glass wool plug to prevent system contamination due to particles pulled by the helium flow.

Each calibration solution in acetone was spiked (1 μ L) on a glass wool plug inside a glass desorption tube also fitted with one-quarter of an unused PTFE membrane.

After the addition of internal standards (ISTDs) by spiking 1 μ L of the ISTD solution on the glass wool plug, each glass desorption tube was then immediately transferred to the autosampler for analysis.

Thermal extraction

Thermal extraction of the analytes was performed using a Gerstel TDS3/TDSA2 automatic thermal desorption device (Gerstel GmbH & Co. KG, Mülheim an der Ruhr, Germany) coupled by a transfer line to a Cooled Injection System (CIS, Gerstel GmbH & Co. KG). The thermal extraction process can be divided into two main steps. In the first step, target compounds are thermally extracted (30 to 325 °C (hold 8 min) at 60 °C min⁻¹ in the TDS splitless mode) and carried by the helium flow (100 mL min⁻¹) through the heated transfer line (325 °C) to the cold CIS equipped with a baffled glass liner and cooled with liquid carbon dioxide (-40 °C) during the thermal extraction process to cryo-focus and concentrate the

analytes prior to transfer to the capillary column. Following the thermal extraction step, the trapped compounds are rapidly transferred to the capillary column for analysis by heating the CIS (-40 °C to 325 °C (hold 15 min) at 12 °C s⁻¹ in the solvent vent mode). Several methods, differing only in the amount of sample introduced into the capillary column (from 2 to 12.5% of the sample), were used to cover a wide dynamic range from ultra-trace to highly concentrated compounds.

GC/MS analysis

The thermal desorption device was interfaced to a 7890 GC system coupled to a 7000B GC/MS Triple Quad (Agilent Technologies) operated in electron impact ionization (EI) mode (70 eV). Chromatographic separation was performed on a Rtx[®]-PCB capillary column (30 m length × 0.25 mm I.D., 0.25 µm film thickness) supplied by Restek. Helium was used as the column carrier gas at a constant flow rate of 2.0 mL min⁻¹. Chromatographic separation was carried out with the following oven temperature program: 50 °C (hold 2 min), first ramp at 30 °C min⁻¹ to 140 °C, and second ramp at 10 °C min⁻¹ to 320 °C (hold 7 min to reach an analysis time of 30 min). The transfer line, ion source and quadrupole temperatures were fixed at 325, 300 and 180 °C, respectively. The mass spectrometer was operated in multiple reaction monitoring (MRM) mode. The two most intense and specific MRM transitions for each compound (quantifier and qualifier transitions) were monitored for identification, confirmation and quantification.

Quality Assurance and Quality Control (QA/QC)

This TE-GC/MS/MS method was previously validated in terms of accuracy and precision (Mercier et al., 2012; 2014) via a replicated analysis of the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) standard reference materials SRM 1649b (urban dust) and 2585 (house dust). The limits of detection (LODs) and limits of quantification (LOQs) are reported in Table 1.

Because of the diversity of the compounds with different chemical and physical properties, labeled and unlabeled ISTDs were selected to match the physical and chemical properties of the analytes as closely as possible, covering volatility differences in particular. 4,4'-DDT $^{13}\text{C}_{12}$, metolachlor D_6 , pentachlorobenzene $^{13}\text{C}_6$, chlorpyrifos D_{10} , fenchlorphos, parathion D_{10} , trans-cyfluthrin D_6 , trans-cypermethrin D_6 , methoprotetryne, fenpropathrin, tri-n-butylphosphate- d_{27} , chrysene D_{12} , pyrene D_{10} , $^{13}\text{C}_{12}$ -PBDE 47, 99 and 153, BBP D_4 , DiBP D_4 , 4-n-amyphenol, bisphenol-A $^{13}\text{C}_{12}$ and $^{13}\text{C}_{12}$ -triclosan were added prior to the thermal extraction step and used as ISTDs. All compounds were quantified with the appropriate ISTD to compensate for the variability associated with the TE-GC/MS/MS analysis from quadratic calibration curves generated for each compound by analyzing at least five different calibration solutions.

Each batch of 20 samples included: i) several instrumental (a glass wool plug) and procedural (one-quarter of a PTFE membrane and a glass wool plug) blank samples analyzed as regular samples to assess whether the samples may have been contaminated during analysis, ii) several calibration samples analyzed at least at the beginning and end of the batch to check for the stability of the detector response, and iii) one calibration sample prepared from commercial solutions provided by other suppliers to validate the preparation of the calibration solutions.

Positive values for each substance were confirmed by comparing retention times and MRM transition ratios between the calibration solutions and the samples.

Eleven field blank samples from different dwellings were treated identically to the samples except that no air was drawn through the sampler. For 59 of the 66 SVOCs, the quantities on the field blank filters were not detectable. For DEHP, DEP, DiBP, DiNP, benzo(k)fluoranthene, permethrin and triclosan, the amounts on the field blank filter were

below the LOQ. On one filter, the mass of both benzo(k)fluoranthene and permethrin reached the LOQ.

2.5. Statistical analysis

For the statistical analyses, all concentrations below the LOD were set at LOD/2. Concentrations below the LOQ were substituted with the raw output values provided by the laboratory to maintain variability despite higher uncertainties in this range. The geometric mean was estimated only when more than 75% of the concentrations were above the LOQ.

Each dwelling ($n = 567$) is associated with a sampling weight, which is the inverse of the probability of inclusion in the sample, which enables the calculation of national estimates for all SVOCs. Because only 285 filters were available for SVOC analysis, the sampling weights needed to be adjusted for nonresponse (i.e., dwellings without SVOC measurements) to avoid bias in the estimates. The weights of the 285 respondents were corrected to compensate for the elimination of the non-respondents. The weights were increased based on the response probability, p , within a group of dwellings. p was estimated by the rate of the number of respondents divided by the number of dwellings belonging to the group. Each sampling weight of the group was then multiplied by the estimated $1/p$ to provide the adjusted weight of each dwelling. A logistic regression model was used to estimate p , and nine groups of dwellings were built by the cross-classification method. The number of groups was defined to avoid being too low p ($p > 0.10$), which would have resulted in unstable estimators. It was then possible to express the results obtained from the sample in terms of national estimates of SVOC concentration on airborne particles. The ‘survey’ package from the R software application (<http://www.R-project.org>) was used (Lumley, 2004, 2010a, 2010b). Quantiles were estimated with the function ‘svyquantile’ of the ‘survey’ package based on the

cumulative distribution function (CDF). Details about these calculations and computations of quantiles and their standard error are available in (Lumley, 2010a; Mandin et al., 2014). A non-parametric Kruskal-Wallis test was used to compare ranked SVOC concentrations between dwellings with or without smokers and between dwellings investigated during the heating or the non-heating season. A Dunn test was performed in the case of a significant Kruskal-Wallis test to identify the pairs of categories that differ. Because the study was not originally designed to be representative of smoking habits inside dwellings or the heating season at a nationwide level, sampling weights were not used in these analyses. The statistical level for significance was assigned as $P < 0.05$, and the Bonferroni correction was applied to account for multiple comparisons. The Spearman correlations between the ranked SVOC concentrations were calculated with XLSTAT 2015.4.01 (Addinsoft, Paris, France). This statistical analysis was applied to the 35 SVOCs detected in more than half of the dwellings. Five SVOCs detected in nearly 50% of the dwellings or of particular concern were also considered: bisphenol-A, oxadiazon, BDE 100, 4-tert-octylphenol and galaxolide.

3. Results and discussion

3.1. SVOC concentrations in airborne PM_{10}

The concentrations of the 66 particle-bound SVOCs at the nationwide level ($N = 24,672,136$) are reported in Table 1.

[Table 1]

Thirty-five compounds (53%) were detected in more than half of the dwellings. The compounds detected in more than 98% of the dwellings were the thirteen PAHs, DEHP, DiNP and triclosan. The other phthalates were also frequently detected, except for the more volatile ones, DMP and DMEP, which were only detected in 39% and 8% of the dwellings, respectively. BDE 47 and BDE 99 were the more concentrated PBDEs on PM_{10} . Among

PCBs, the tri- and tetra-congeners were less frequently detected on PM_{10} because they are more volatile; PCBs 101, 118, 138, and 153 (penta- and hexa-) were the major ones (detected in > 80% of the dwellings). 4-n-nonylphenol was scarcely detected, whereas 4-tert-butylphenol and 4-tert-octylphenol were detected in approximately one of every two dwellings. Except lindane, oxadiazon, 4,4'-DDT and 4,4'-DDE, the organochlorine and organophosphorous pesticides were detected on PM_{10} in less than 20% of the dwellings. Four compounds were never detected on PM_{10} , namely BDE 119, PCB 126, heptachlore, and cis-chlordane.

Twenty-seven SVOCs (41%) were quantified in more than half of the dwellings. Several orders of magnitude were observed between the concentration ranges. The highest median concentrations were measured for the phthalates with values around 1 ng m^{-3} up to 46 ng m^{-3} for DEHP. Some PAHs followed with median values around several hundred pg m^{-3} , with benzo(b)fluoranthene having the highest median concentration (306 pg m^{-3}) on PM_{10} . Triclosan, permethrin, and the remaining PAHs stayed within an order of magnitude lower—i.e., medians of approximately $10\text{--}100\text{ pg m}^{-3}$. The lowest particle-bound PAH concentrations were observed for 3-ring congeners (anthracene and fluorene), and the highest were measured for 5- or 6-ring PAHs—namely, benzo(b)fluoranthene and benzo(g,h,i)perylene. Since the 3-ring PAHs are mainly found in the gas phase, low concentrations in the particulate phase were expected. Overall, the lowest particle-bound concentrations were observed for BDE 47 > BDE 99 > 4,4'-DDT > PCBs.

The results from studies targeting SVOCs exclusively in the particulate phase or separately from the gas phase concentration were considered for an adequate comparison. Only studies targeting dwellings were considered. The median values are reported in Table 2a.

[Table 2a]

The PAH concentrations in the French dwellings are largely consistent with the other studies worldwide. The concentrations observed in China (Wang et al., 2013, 2014a) appear to be higher but remain on the same order of those measured during winter in Rome, Italy (Romagnoli et al., 2014). The median PBDE concentrations are considerably lower in France than in North America (Batterman et al., 2009), which has already been reported when comparing PBDE use and population exposure over the world: the higher PBDE concentrations encountered in the United Kingdom and North America indoor environments are due to stricter fire safety standards (Birnbaum and Staskal, 2004; Fromme et al., 2009). BDE 47 and BDE 99 reported in Hong Kong on PM_{2.5} (Wang et al., 2013, 2014a) are lower than the medians measured in the present study. Regarding phthalates, the median concentrations are of the same order of magnitude as the ones measured elsewhere except for DiBP. Compared to Blanchard et al. (2014b) and other countries, DiBP median concentrations are lower because the sampling was performed earlier (2003–2005) and because DiBP has been used as a substitute for DBP in Europe according to the European Council for Plasticisers and Intermediates (ECPI) over the past decade. The phthalate median concentrations reported in one Chinese study are rather high (Wang et al., 2014b). Another study carried out in China also reported high BBP and DEHP concentrations in ten newly decorated apartments, with median concentrations of 1.9 and 1.3 $\mu\text{g m}^{-3}$, respectively (Pei et al., 2013).

For the SVOCs that were not quantified in more than half of the dwellings (no median reported), the ranges of concentrations were compared, considering studies reporting particle-bound SVOCs in indoor air of dwellings. They are presented in Table 2b.

[Table 2b]

Regarding particle-bound PBDEs (28, 85, 100, 153, and 154), the concentration ranges measured in France were lower than those measured in the US by Batterman et al. (2009);

they were of the same order of magnitude as those observed in Hong-Kong (Wang et al., 2014a). With regard to phthalates, the DBP and DEP concentration ranges were lower than in Norway (Rakkestad et al., 2007) and the US (Tran and Kannan, 2015) and much lower than in China (Wang et al., 2014a; Zhang et al., 2014). Finally, in the frame of the RIOPA Study (Relationship of Indoor, Outdoor and Personal Air), chlordane was measured in PM_{2.5} in 104 non-smoker dwellings from three large cities in the US (Zhu and Jia, 2012). The maximum and median concentrations for trans- and cis-chlordane were high (medians: 17 and 7 pg m⁻³, respectively). In the French housing stock, trans-chlordane was detected in only 1% of the dwellings (vs. 29% in RIOPA) and never quantified, and cis-chlordane was never detected (vs. 22% in RIOPA). Chlordane was banned in Europe and the US in 1981 and 1983, respectively, but its use as termicide in building construction remained until it was later banned in 1988 (Offenberg et al., 2004). The longer use in the US and a sampling period nearer to the banning date in RIOPA (1999–2000) could explain the higher chlordane concentrations observed in the US compared to France.

No large studies were found in the literature to compare the concentrations of 4,4'-DDE, permethrin, PCBs or triclosan to our results.

3.2. Particle-bound SVOC concentrations according to season and smoking in the dwelling

The particle-bound SVOC concentrations were compared between dwellings with no smokers vs. dwellings with at least one indoor smoker. In addition, the sampling season may have an influence considering that the dwellings were not investigated during the same period. The season was defined by the heating system turned on or off during the week of measurement. The season appeared to have a strong influence on the indoor concentrations for the other parameters measured during the housing survey, i.e., volatile organic compounds and aldehydes (Langer et al., 2016). To determine whether this relation with the heating period is also observed for SVOCs, their concentrations were stratified over the heating and non-heating seasons. The median concentrations in the heating season with or without smoking, along with the concentration in the non-heating season with or without smoking, are presented in Table 3.

[Table 3]

The resulting *P*-values of the Kruskal-Wallis test for these four categories were <0.0001 for all SVOCs except permethrin ($P=0.032$), indicating that the concentration in at least one category is globally higher or lower than that of one or the other groups. This result confirmed the major influence of smoking and the season on the particle-bound concentration of all SVOCs.

According to the results from the multiple comparisons, SVOCs on PM_{10} can be categorized into four groups. Half of the SVOCs—i.e., 20 of the 40 for which the statistical test was performed—were associated with both the season and tobacco smoking. Their concentrations were significantly higher during the heating season and in smokers' dwellings. Most of the PAHs can be found in this group. Synthetic musks, most of the organochlorine pesticides and PCBs, and two phthalates also belong to this group. The second group included 15 SVOCs that are more influenced by smoking than by the season: PBDEs, oxadiazon, permethrin,

triclosan, two PAHs, four phthalates and PCBs. In contrast, benzo(g,h,i)perylene and bisphenol-A are more influenced by the season than by smoking. In these two groups, the trend remains similar, with higher concentrations during the heating season or in smokers' dwellings. Finally, anthracene and 4-tert-octylphenol cannot be classified in any of the three previous groups.

Indoor sources of PAHs are related to combustion processes, such as tobacco smoking, cooking, and wood burning (Fromme et al., 2004; Ma and Harrad, 2015). Additionally, outdoor PAHs from traffic exhausts, industries, and residential heating penetrate into the buildings. In the winter, outdoor PAH concentrations are higher due to residential heating combined with less favorable atmospheric dispersion conditions, which could explain the higher indoor concentrations observed during the heating season. Romagnoli et al. (2014) in Italy, Zhu and Jia (2012) in the American RIOPA study, Ohura et al. (2004) in Japan, and Zhu et al. (2009) in China also observed significantly higher concentrations of particle-bound PAHs in the winter compared to the summer. Zhu and Jia (2012) determined that $55 \pm 9\%$ of the variance of particulate PAH concentrations were attributable to the season. To study the influence of season and smoking on the PAH profile, the average relative contribution of every PAH to the total PAH concentrations on PM_{10} was calculated in the dwellings according to the season and smoking status. The profiles are presented in Figure 1.

[Figure 1]

Overall, the PAHs show similar trends, with a higher relative contribution of high-molecular-weight congeners. Nevertheless, the contribution of 3- and 4-ring PAHs (here, fluorene, benzo(a)anthracene, and chrysene) was higher in smokers' dwellings, whereas the contribution of 5- and 6-ring PAHs (e.g., benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(g,h,i)perylene) was lower, as observed by previous authors (Slezakova et al., 2009).

The opposite trend was observed when comparing the heating season to the non-heating season.

In contrast to our observations, Zhang et al. (2014) found significantly higher concentrations of phthalates (BBP, DBP, DEP, DEHP, DMP, and DOP) on PM_{10} and $PM_{2.5}$ in summer compared to winter in 13 dwellings in Tianjin, China. This result may be explained by different climatic conditions—e.g., a hotter and more humid summer in China than in France. In summer, with higher temperatures, the equilibrium between the gas phase and particulate phase is expected to favor the gas phase, leading to lower SVOC concentrations in the particulate phase. Additionally, in our study different dwellings were investigated at the two seasons. Therefore the seasonal effect was only assessed as an overall factor and not for a particular dwelling.

Finally, one of the more important differences between dwellings was associated with triclosan concentrations, which were 4 to 5 times higher in smokers' dwellings than in those of non-smokers. The use of triclosan is not associated with tobacco products. Nevertheless, Kim et al. (2011) found a significant association between cigarette smoking and the urine concentration of triclosan in the Korean adult population aged 18–69.

3.3. Correlations between SVOC and PM_{10} concentrations

The correlations between ranked concentrations of SVOCs are presented in Figure 2. With the exception of five pairs, all the SVOCs were significantly and positively correlated.

[Figure 2]

The strongest correlations were observed within chemical families. All PAHs were highly correlated ($\rho > 0.8$) except the 3-ring PAHs, i.e., anthracene, fluorene and phenanthrene. This result suggests that lower- and higher-molecular-weight PAHs share different sources, which was already observed in previous studies (Delgado-Saborit et al., 2011). The organochlorine

pesticides were moderately correlated with each other ($\rho > 0.4$). The strong correlation between 4,4'-DDT and 4,4'-DDE ($\rho=0.8$) is expected because 4,4'-DDE is a metabolite of 4,4'-DDT. The correlations with and between the other organochlorine, lindane and oxadiazon, suggest common sources or uses of these pesticides, which are now all banned in France. They were substituted in North America and Europe by pyrethroids, such as permethrin (Williams et al., 2008), which displayed a low correlation with lindane and oxadiazon ($\rho < 0.2$) in our study. PBDEs were highly correlated with each other ($\rho > 0.8$) as well as with PCBs ($\rho > 0.8$). Among phthalates, two groups could be distinguished: BBP, DBP and DEHP on one side (cross-correlated with $\rho > 0.6$), with DEP, DiBP and DiNP slightly less correlated with each other. The strong correlation between DBP and DiBP ($\rho=0.86$) suggests common sources for these two compounds and could be explained by the use of DiBP as a substitute for DBP. Overall, the weaker correlations observed between phthalates could indicate that they share different sources. Phthalates are used in a large number of domestic and consumer products, as diverse as building products (vinyl floorings, cables), domestic items (shower curtains, tablecloths, toys, food packages), care products (nail polishes) and perfumes (Hauser and Calafat, 2010). Galaxolide and tonalide were strongly correlated ($\rho=0.81$), which is consistent with the fact that they are used commonly in personal care products and perfumes in Europe (Roosens et al., 2007). Finally, the two alkylphenols are poorly correlated ($\rho < 0.2$), illustrating that they do not share similar sources.

When comparing correlations between chemical families, positive correlations ($\rho > 0.6$) between PCBs and organochlorine pesticides were found, particularly between 4,4'-DDE and PCB 101 ($\rho=0.81$). PCBs were largely used in buildings in the 1970s—e.g., as sealants—and are still measured in dust and indoor air in dwellings constructed during this period (Lehmann et al., 2015). Organochlorine pesticides were used contemporarily before being phased out. The correlations between these two groups suggest that they were both used during the same

period in the dwellings. Whitehead et al. (2014) observed this trend in the US for settled dust concentrations. Moderate correlations ($\rho > 0.6$) were also observed between PCBs and some phthalates, particularly DBP and DEHP. Strong correlations ($\rho > 0.8$) between tonalide and PCB 52, and tonalide and DEHP were also found, but no appropriate assumption could explain these associations. Three compounds displayed low correlations or none at all with the other SVOCs, namely, permethrin, 4-tert-butylphenol and bisphenol-A. This result confirms that they have their own specific uses and sources indoors.

The median PM_{10} concentration measured in the French housing stock was $31 \mu\text{g m}^{-3}$, and the 95th percentile was $182 \mu\text{g m}^{-3}$. The concentrations of the 40 most detected particle-bound SVOCs were significantly correlated with PM_{10} concentration, with a correlation coefficient ranging from 0.29 (permethrin) to 0.77 (DBP; Figure 2). A higher available surface in a given room, including suspended particulate matter, is able to adsorb more SVOCs. Thus, increasing PM_{10} indoor concentrations should lead to higher particle-bound SVOC concentrations: in addition to their adsorption on surface coatings, such as walls and furniture, SVOCs will also adsorb on newly available airborne particles. This finding is consistent with the influence of tobacco smoking, a major source of particles indoors, on the concentrations of nearly all SVOCs. If this increase is particularly noticeable for smoking, the emissions of particles from other indoor sources—including cooking, incense or candle burning, and resuspension—should similarly lead to higher particle-bound SVOC concentrations as well as an increase in the exposure to SVOCs through inhalation. Because ultrafine particles are associated with a larger specific surface, adsorbed SVOCs are likely to be found in the most inhalable fraction of the PM_{10} mass fraction. The influence of the particle dynamics as well as the size fraction collecting the most SVOCs was shown by Liu et al. (2010), based on a modeling approach.

4. Conclusion

To our knowledge, this is the first time that indoor concentrations of such a wide range of SVOCs have been assessed simultaneously at a national level. The survey was initially designed for the sampling of particles and thus the analysis of particle-bound SVOCs. To obtain a full understanding of indoor air concentrations in homes for the studied 66 SVOCs, their respective gas phase concentration is currently being modeled from their measured concentration on PM₁₀. The nationwide total concentrations of SVOCs will enable an exposure assessment for the general population in France. The significant correlations observed among all major SVOCs and PM₁₀ imply that all sources of indoor particles may increase exposure to SVOCs through inhalation.

Acknowledgements

This study was supported by the French Agency for Food, Environmental and Occupational Health and Safety (ANSES; Grant n°2011-1-128), the French Indoor Air Quality Observatory (OQAI), and by both EHESP and CSTB research funding. The authors thank Delphine Pellé and Gaëlle Raffy at LERES for their contributions to this work.

References

- Batterman SA, Chernyak S, Jia C, Godwin C, Charles S. 2009. Concentrations and emissions of polybrominated diphenyl ethers from U.S. houses and garages. *Environ. Sci. Technol.*, **43**, 2693–2700.
- Bedoux G, Roig B, Thomas O, Dupont V, Le Bot B. 2012. Occurrence and toxicity of antimicrobial triclosan and by-products in the environment. *Environ. Sci. Pollut. Res. Int.*, **19**, 1044–1065.
- Birnbaum L, Staskal DF. 2004. Brominated flame retardants: Cause for concern? *Environ. Health Perspect.*, **112**, 9–17.

- Blanchard O, Mercier F, Ramalho O, Mandin C, Le Bot B, Glorennec P. 2014a. Measurements of semi-volatile organic compounds in settled dust: Influence of storage temperature and duration. *Indoor Air*, **24**, 125–135.
- Blanchard O, Glorennec P, Mercier F, Bonvallot N, Chevrier C, Ramalho O, Mandin C, Le Bot B. 2014b. Semivolatile organic compounds in indoor air and settled dust in 30 French dwellings. *Environ. Sci. Technol.*, **48**, 3959–3969.
- Bonvallot N, Mandin C, Mercier F, Le Bot B, Glorennec P. 2010. Health ranking of ingested semi-volatile organic compounds in house dust: An application to France. *Indoor Air*, **20**, 458–472.
- Delgado-Saborit JM, Stark C, Harrison RM. 2011. Carcinogenic potential, levels and sources of polycyclic aromatic hydrocarbon mixtures in indoor and outdoor environments and their implications for air quality standards. *Environ. Int.*, **37**, 383–392.
- European Commission. (2015) Endocrine disruptors, database and categorization, Available at: http://ec.europa.eu/environment/chemicals/endocrine/strategy/substances_en.htm (Accessed on September 28, 2015)
- Fromme H, Lahrz T, Piloty M, Gebhardt H, Oddoy A, Rüdén H. 2004. Polycyclic aromatic hydrocarbons inside and outside of apartments in an urban area. *Sci. Total Environ.*, **326**, 143–149.
- Fromme H, Korner W, Shahin N, Wanner A, Albrecht M, Boehmer S, Parlar H, Mayer R, Liebl B, Bolte, G. 2009. Human exposure to polybrominated diphenyl ethers (PBDE), as evidenced by data from a duplicate diet study, indoor air, house dust, and biomonitoring in Germany. *Environ. Int.*, **35**, 1125–1135.
- Golliot F, Annesi-Maesano I, Delmas MC, Dor F, Le Moullec Y, Nedellec V, Ribéron J, Salines G, Kirchner S. 2003. The French national survey on indoor air quality: sample survey design. *Proceedings Healthy Buildings 2003*, Singapore, 712–717.
- Hauser R, Calafat AM. 2005. Phthalates and human health. *Occup. Environ. Med.*, **62**, 806–818.
- Hwang, H.M., Park, E.K., Young, T.M., Hammock, B.D. 2008. Occurrence of endocrine-disrupting chemicals in indoor dust. *Sci. Total Environ.*, **404**, 26–35.
- IARC. 2010. IARC monographs on the evaluation of carcinogenic risks to humans. Volume 92. Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. Lyon: International Agency for Research on Cancer.

- Kim K, Park H, Yang W, Lee JH. 2011. Urinary concentrations of bisphenol A and triclosan and associations with demographic factors in the Korean population. *Environ. Res.*, **111**, 1280–1285.
- Kirchner S, Arenes JF, Cochet C, Derbez M, Duboudin C, Elias P, Gregoire A, Jedor B, Lucas JP, Pasquier N, Pigneret M, Ramalho O. 2007. État de la qualité de l'air dans les logements français. *Environ. Risque Santé*, **6**, 259–269.
- Langer S, Ramalho O, Derbez M, Ribéron J, Kirchner S, Mandin C. 2016. Indoor environmental quality in French dwellings and building characteristics. *Atmos. Environ.*, **128**, 82–91.
- Lehmann GM, Christensen K, Maddaloni M, Phillips LJ. 2015. Evaluating health risks from inhaled polychlorinated biphenyls: Research needs for addressing uncertainty. *Environ. Health Perspect.*, **123**, 109–113.
- Liu C, Zhao B, Zhang Y. 2010. The influence of aerosol dynamics on indoor exposure to airborne DEHP. *Atmos. Environ.*, **44**, 1952–1959.
- Lumley T. 2004. Analysis of complex survey samples. *JSSOBK*, **9**, 1–19.
- Lumley T. 2010a. Complex Surveys. John Wiley & Sons, Inc., Hoboken, NJ, USA.
- Lumley T. 2010b. Survey: analysis of complex survey samples. R package version 3.22-4.
- Lyche JL, Rosseland C, Berge G, Polder A. 2015 Human health risk associated with brominated flame-retardants (BFRs). *Environ. Int.*, **74**, 170–180.
- Ma Y, Harrad S. 2015. Spatiotemporal analysis and human exposure assessment on polycyclic aromatic hydrocarbons in indoor air, settled house dust, and diet: A review. *Environ. Int.*, **84**, 7–16.
- Mandin C, Mercier F, Lucas JP, Ramalho O, Blanchard O, Bonvallot N, Raffy G, Gilles E, Glorennec P, Le Bot B. ECOS-POUSS: a nationwide survey of semi-volatile organic compounds in home settled dust. *Proceeding Indoor Air 2014*, 13th International conference on indoor air quality and climate, July 7-12, 2014, Hong Kong, CHN.
- Mercier F, Glorennec P, Blanchard O, Le Bot B. 2012. Analysis of semi-volatile organic compounds in indoor suspended particulate matter by thermal desorption coupled with gas chromatography/mass spectrometry. *J. Chromatogr. A*, **1254**, 107–114.
- Mercier F, Gilles E, Raffy G, Glorennec P, Mandin C, Le Bot B. 2014. A multi-residue method for the simultaneous analysis of several classes of semi-volatile organic compounds in airborne particles. *Proceedings Indoor Air 2014*, 13th International conference on indoor air quality and climate, July 7-12, 2014, Hong Kong, CHN.

- Messer A. 2010. Mini-review: polybrominated diphenyl ether (PBDE) flame retardants as potential autism risk factors. *Physiol. Behav.*, **100**, 245–249.
- Offenberg JH, Naumova YY, Turpin BJ, Eisenreich SJ, Morandi MT, Stock T, Colome SD, Winer AM, Spektor DM, Zhang J, Weisel CP. 2004. Chlordanes in the indoor and outdoor air of three U.S. cities. *Environ. Sci. Technol.*, **38**, 2760–2768.
- Ohura T, Amagai T, Fusaya M, Matsushita H. 2004. Polycyclic aromatic hydrocarbons in indoor and outdoor environments and factors affecting their concentrations. *Environ. Sci. Technol.*, **38**, 77–83.
- Pei XQ, Song M, Guo M, Moa FF, Shen XY. 2013. Concentration and risk assessment of phthalates present in indoor air from newly decorated apartments. *Atmos. Environ.*, **68**, 17–23.
- Rakkestad KE, Dye CJ, Yttri KE, Holme JA, Hongslo JK, Schwarze PE, Becher R. 2007. Phthalate levels in Norwegian indoor air related to particle size fraction. *J. Environ. Monit.*, **9**, 1419–1425.
- Ramalho O, Derbez M, Gregoire A, Garrigue J, Kirchner S. 2006. French permanent survey on indoor air quality – Part 1: Measurement protocols and quality control. *Proceedings Healthy Building 2006*, Lisbon (Portugal), vol. 3, 321–326.
- Romagnoli P, Balducci C, Perilli M, Gherardi M, Gordiani A, Gariazzo C, Gatto MP, Cecinato A. 2014. Indoor PAHs at schools, homes and offices in Rome, Italy. *Atmos. Environ.*, **92**, 51–59.
- Roosens L, Covaci A, Neels H. 2007. Concentrations of synthetic musk compounds in personal care and sanitation products and human exposure profiles through dermal application. *Chemosphere*, **69**, 1540–1547.
- Rudel RA, Perovich LJ. 2009. Endocrine disrupting chemicals in indoor and outdoor air. *Atmos. Environ.*, **43**, 170–181.
- Rudel RA, Dodson RE, Perovich LJ, Morello-Frosch R, Camann DE, Zuniga MM, Yau AY, Just AC, Brody JG. 2010. Semivolatile endocrine-disrupting compounds in paired indoor and outdoor air in two Northern California communities. *Environ. Sci. Technol.*, **44**, 6583–6590.
- Saillenfait AM, Ndiaye D, Sabaté JP. 2015. Pyrethroids: exposure and health effects – an update. *Int. J. Hyg. Environ. Health*, **218**, 281–292.
- Saito I, Onuki A, Seto H. 2004. Indoor air pollution by alkylphenols in Tokyo. *Indoor Air*, **14**, 325–332.

- Slezakova K, Castro D, Pereira MC, Morais S, Delerue-Matos C, Alvim-Ferraz MC. 2009. Influence of tobacco smoke on the elemental composition of indoor particles of different sizes. *Atmos. Environ.*, **43**, 486–493.
- Tran TM, Kannan K. 2015. Occurrence of phthalate diesters in particulate and vapor phases in indoor air and implications for human exposure in Albany, New York, USA. *Arch. Environ. Contam. Toxicol.*, **68**, 489–499.
- Wang W, Huang MJ, Chan C-Y, Cheung KC, Wong MH. 2013. Risk assessment of non-dietary exposure to polycyclic aromatic hydrocarbons (PAHs) via house PM_{2.5}, TSP and dust and the implications from human air. *Atmos. Environ.*, **73**, 204–213.
- Wang W, Zheng J, Chan C-Y, Huang MJ, Cheung KC, Wong MH. 2014a. Health risk assessment of exposure to polybrominated diphenyl ethers (PBDEs) contained in residential air particulate and dust in Guangzhou and Hong Kong. *Atmos. Environ.*, **89**, 786–796.
- Wang X, Tao W, Xu Y, Feng J, Wang F. 2014b. Indoor phthalate concentration and exposure in residential and office buildings in Xi'an, China. *Atmos. Environ.*, **87**, 146–152.
- Ward MH, Colt JS, Metayer C, Gunier RB, Lubin J, Crouse V, Nishioka MG, Reynolds P, Buffler PA. 2009. Residential exposure to polychlorinated biphenyls and organochlorine pesticides and risk of childhood leukemia. *Environ. Health Perspect.*, **117**, 1007–1013.
- Weschler CJ, Nazaroff W. 2008. Semivolatile organic compounds in indoor environments. *Atmos. Environ.*, **42**, 9018–9040.
- Whitehead TP, Metayer C, Ward MH, Colt JS, Gunier RB, Deziel NC, Rappaport SM, Buffler PA. 2014. Persistent organic pollutants in dust from older homes: learning from lead. *Am. J. Public Health*, **104**, 1320–1326.
- Williams MK, Rundle A, Holmes D, Reyes M, Hoepner LA, Barr DB, Camann DE, Perera FP, Whyatt RM. 2008. Changes in pest infestation levels, self-reported pesticide use, and permethrin exposure during pregnancy after the 2000-2001 U.S. Environmental Protection Agency restriction of organophosphates. *Environ. Health Perspect.*, **116**, 1681–1688.
- Zhang L, Wang F, Jia Y, Jiao J, Zou D, Liu L, Shan C, Bai Z, Sun Z. 2014. Phthalate esters (PAEs) in indoor PM₁₀/PM_{2.5} and human exposure to PAEs via inhalation of indoor air in Tianjin, China. *Atmos. Environ.*, **85**, 139–146.
- Zhu L, Lu H, Chen S, Amagai T. 2009. Pollution level, phase distribution and source analysis of polycyclic aromatic hydrocarbons in residential air in Hangzhou, China. *J. Hazard Mater.*, **162**, 1165–1170.

- 646 Zhu X, Jia C. 2012. Apportioning variability of polycyclic aromatic hydrocarbons (PAHs)
647 and chlordanes in indoor and outdoor environments. *J. Environ. Monit.*, **14**, 1926–1934.

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Table 1. Frequency of detection, frequency of quantification and national concentration estimates of 66 particle-bound SVOCs (N = 24,672,136)

SVOC	Unit	LOD	% > LOD	LOQ	% > LOQ	P5	P25	P50	P75	P95	GM	GSD
Polycyclic aromatic hydrocarbons												
Anthracene	pg m ⁻³	0.8	98	2.1	97	4.1	7.8	12.6	19.5	51.2	12.9	2.5
Benzo(a)anthracene	pg m ⁻³	2.1	100	4.2	99	6.5	18.0	44.4	143	655	53.4	4.4
Benzo(a)pyrene	pg m ⁻³	2.1	100	4.2	99	7.5	31.2	138	327	1,097	109	4.9
Benzo(b)fluoranthene	pg m ⁻³	4.2	100	8.4	100	42.7	117	306	636	1,806	299	3.3
Benzo(g,h,i)perylene	pg m ⁻³	4.2	100	8.4	100	27.3	92.2	229	432	1,153	210	3.1
Benzo(k)fluoranthene	pg m ⁻³	2.1	100	4.2	100	9.2	24.7	64	142	337	60.9	3.2
Chrysene	pg m ⁻³	2.1	100	4.2	100	13.6	34.0	75.9	187	1,403	91.5	3.8
Dibenzo(a,h)anthracene	pg m ⁻³	2.1	95	4.2	87	<2.1	7.8	21.6	45.4	126	19.2	3.6
Fluoranthene	pg m ⁻³	4.2	100	8.4	100	19.1	38.6	68.2	128	570	75.9	2.8
Fluorene	pg m ⁻³	2.1	99	4.2	99	6.0	13.4	19.5	44.1	213	25.7	3.0
Indeno(1,2,3-c,d)pyrene	pg m ⁻³	8.4	99	20.9	94	<8.4	70.6	178	312	959	155	3.2
Phenanthrene	pg m ⁻³	4.2	100	8.4	98	16.8	33.9	54.1	104	300	60.7	2.5
Pyrene	pg m ⁻³	4.2	100	8.4	99	14.6	30.7	53.9	103	463	61.4	2.9
Organochlorine pesticides												
Aldrin	pg m ⁻³	2.1	0.5	4.2	0.5	<2.1	<2.1	<2.1	<2.1	<2.1	NA	NA
α -endosulfan	pg m ⁻³	10.4	19	20.9	8	<10.4	<10.4	<10.4	<10.4	28.2	NA	NA
α -HCH	pg m ⁻³	2.1	9	4.2	2	<2.1	<2.1	<2.1	<2.1	<2.1	NA	NA
Atrazine	pg m ⁻³	4.2	0.3	10.4	0.3	<4.2	<4.2	<4.2	<4.2	<4.2	NA	NA
Cis-chlordane	pg m ⁻³	2.1	0	4.2	0	NA	NA	NA	NA	NA	NA	NA
Dieldrin	pg m ⁻³	4.2	23	8.4	13	<4.2	<4.2	<4.2	<4.2	32.0	NA	NA
Endrin	pg m ⁻³	10.4	1	20.9	1	<10.4	<10.4	<10.4	<10.4	<10.4	NA	NA
Heptachlor	pg m ⁻³	10.4	0	20.9	0	<10.4	<10.4	<10.4	<10.4	<10.4	NA	NA
γ -HCH / Lindane	pg m ⁻³	2.1	56	4.2	33	<2.1	<2.1	<4.2	6.4	39.7	NA	NA
Metolachlor	pg m ⁻³	1.0	1	2.1	1	<1.0	<1.0	<1.0	<1.0	<1.0	NA	NA
Oxadiazon	pg m ⁻³	0.4	47	1.0	25	<0.4	<0.4	<0.4	<1.0	4.3	NA	NA
Trans-chlordane	pg m ⁻³	2.1	1	4.2	0	<2.1	<2.1	<2.1	<2.1	<2.1	NA	NA
4,4'-DDE	pg m ⁻³	0.4	53	1.0	33	<0.4	<0.4	<1.0	1.9	27.8	NA	NA
4,4'-DDT	pg m ⁻³	1.0	84	2.1	75	<1.0	<2.1	5.1	24.6	142	NA	NA

SVOC	Unit	LOD	% > LOD	LOQ	P5	P25	P50	P75	P95	GM	GSD
Organophosphorous pesticides											
Chlorpyrifos	pg m ⁻³	41.8	10	83.5	< 41.8	< 41.8	< 41.8	< 41.8	< 83.5	NA	NA
Diazinon	pg m ⁻³	41.8	2	83.5	< 41.8	< 41.8	< 41.8	< 41.8	< 41.8	NA	NA
Pyrethroids											
Permethrin	pg m ⁻³	20.9	76	41.8	< 20.9	< 41.8	55.9	162	1,836	NA	NA
PBDEs											
BDE 28	pg m ⁻³	0.4	22	1.0	< 0.4	< 0.4	< 0.4	< 0.4	1.9	NA	NA
BDE 47	pg m ⁻³	2.1	88	4.2	< 2.1	< 4.2	11.0	33.2	126	NA	NA
BDE 85	pg m ⁻³	4.2	1	8.4	< 4.2	< 4.2	< 4.2	< 4.2	< 4.2	NA	NA
BDE 99	pg m ⁻³	2.1	87	4.2	< 2.1	< 4.2	8.9	19.5	60.3	NA	NA
BDE 100	pg m ⁻³	2.1	47	4.2	< 2.1	< 2.1	< 2.1	4.3	13.6	NA	NA
BDE 119	pg m ⁻³	4.2	0	8.4	NA	NA	NA	NA	NA	NA	NA
BDE 153	pg m ⁻³	4.2	7	8.4	< 4.2	< 4.2	< 4.2	< 4.2	< 4.2	NA	NA
BDE 154	pg m ⁻³	4.2	3	8.4	< 4.2	< 4.2	< 4.2	< 4.2	< 4.2	NA	NA
PCBs											
PCB 28	pg m ⁻³	0.4	18	1.0	< 0.4	< 0.4	< 0.4	< 0.4	2.2	NA	NA
PCB 31	pg m ⁻³	0.4	23	1.0	< 0.4	< 0.4	< 0.4	< 0.4	2.2	NA	NA
PCB 52	pg m ⁻³	0.4	58	1.0	< 0.4	< 0.4	< 1.0	1.9	11.5	NA	NA
PCB 77	pg m ⁻³	0.4	11	1.0	< 0.4	< 0.4	< 0.4	< 0.4	1.5	NA	NA
PCB 101	pg m ⁻³	0.4	89	1.0	< 0.4	< 1.0	1.5	5.2	29.9	NA	NA
PCB 105	pg m ⁻³	0.4	61	1.0	< 0.4	< 0.4	< 1.0	2.6	18.5	NA	NA
PCB 118	pg m ⁻³	0.4	86	1.0	< 0.4	< 1.0	1.5	5.7	47.9	NA	NA
PCB 126	pg m ⁻³	1.0	0	2.1	NA	NA	NA	NA	NA	NA	NA
PCB 138	pg m ⁻³	0.4	89	1.0	< 0.4	< 1.0	2.3	8.4	53.6	NA	NA
PCB 153	pg m ⁻³	0.4	89	1.0	< 0.4	< 1.0	2.4	7.5	40.2	NA	NA
PCB 180	pg m ⁻³	0.4	77	1.0	< 0.4	< 1.0	1.3	4.4	25.1	NA	NA
Phthalates											
BBP	ng m ⁻³	0.17	98	0.42	< 0.42	0.6	1.6	5.3	31.9	2.0	5.0
DEHP	ng m ⁻³	1.7	100	4.2	9.1	22.3	46.2	110	389	52.6	3.3
DBP	ng m ⁻³	0.42	72	0.84	< 0.42	< 0.42	< 0.84	3.2	25.2	NA	NA

SVOC	Unit	LOD	% > LOD	LOQ	% > LOQ	P5	P25	P50	P75	P95	GM	GSD
DEP	ng m ⁻³	0.42	62	0.84	45	< 0.42	< 0.42	< 0.84	2.6	9.8	NA	NA
DiBP	ng m ⁻³	0.17	96	0.42	70	< 0.42	< 0.42	0.861	2.8	22.9	NA	NA
DiNP	ng m ⁻³	0.84	99	1.7	97	2.0	4.0	7.9	17.6	50.1	8.7	3.0
DMEP	ng m ⁻³	0.04	8	0.08	5	< 0.04	< 0.04	< 0.04	< 0.04	< 0.08	NA	NA
DMP	ng m ⁻³	0.02	39	0.04	13	< 0.02	< 0.02	< 0.02	< 0.04	0.070	NA	NA
DOP	ng m ⁻³	0.42	4	0.84	2	< 0.42	< 0.42	< 0.42	< 0.42	< 0.42	NA	NA
Synthetic musks												
Galaxolide	pg m ⁻³	41.8	47	83.5	31	< 41.8	< 41.8	< 41.8	122	759	NA	NA
Tonalide	pg m ⁻³	10.4	58	20.9	41	< 10.4	< 10.4	< 20.9	40.8	377	NA	NA
Alkylphenols												
4-n-nonylphenol	pg m ⁻³	10.4	2	20.9	1	< 10.4	< 10.4	< 10.4	< 10.4	< 10.4	NA	NA
4-tert-butylphenol	pg m ⁻³	10.4	56	20.9	28	< 10.4	< 10.4	< 20.9	23.7	52.8	NA	NA
4-tert-octylphenol	pg m ⁻³	10.4	46	20.9	26	< 10.4	< 10.4	< 10.4	22.5	108	NA	NA
Other SVOCs												
Bisphenol-A	ng m ⁻³	1.0	38	2.6	13	< 1.0	< 1.0	< 1.0	< 2.6	6.0	NA	NA
Triclosan	pg m ⁻³	10.4	98	20.9	95	< 20.9	42.9	114	359	1,855	138	4.4
Tri-n-butylphosphate	pg m ⁻³	41.8	12	83.5	7	< 41.8	< 41.8	< 41.8	< 41.8	107	NA	NA

LOD: limit of detection; LOQ: limit of quantification; Px: centile x; GM: geometric mean; GSD: standard deviation of the geometric mean (dimensionless); NA: non-applicable

LOD and LOQ represent the limits of detection and quantification for the lowest sampled volume (9.6 m³).

Table 2a. Particle-bound SVOC median concentrations in residential indoor air measured worldwide

Country	France	UK	Italy	US	Hong-K.	China	USA	Norway	USA	China
Size fraction	PM ₁₀	TSP	PM _{2.5}	PM _{2.5}	PM _{2.5}	PM _{2.5} /TSP	TSP	PM ₁₀	TSP	PM ₁₀
Period of measurements	Dec. 2010 - April 2011	May 2005 - May 2007	Winter 11-12+ Spring 12+ Summer 12	June 1999- May 2000	April - Dec. 2010	April - Dec. 2010	March 2006 - Aug. 2007	NA	Jan. - May 2014	Sept. 2012 - Jan. 2013
Estimate	Median	GM	AM	Median	Median	Median	Median	AM	Median	Median
n Dwellings	n=30	n=162	n=10	n=115	n=6	n=7	n=12	n=2	n=20	n=28*
This study	Blanchard et al., 2014b	Delgado-S. et al., 2011	Romagnoli et al., 2014 [#]	Zhu and Jia, 2012	Wang et al., 13,14a	Wang et al., 13,14a	Batterman et al., 2009	Rakkestad et al., 2007	Tran and K., 2015	Wang et al., 2014b
Anthracene	12.6	50		5.7	10	80/190				
Benzo(a)anthracene	44.4	60	208/50/36 [#]	22	60	270/730				
Benzo(a)pyrene	138	90	980/124/64 [#]	52	100	600/970				
Benzo(b)fluoranthene	306	180		3.6						
Benzo(g,h,i)perylene	229	150	1,780/224/142 [#]	170	170	1,200/1,560				
Benzo(k)fluoranthene	64	110								
Chrysene	75.9	140			100	520/1,050				
Dibenzo(a,h)anthracene	21.6	30	170/28/18 [#]	7.4	20	190/340				
Fluoranthene	68.2	360		57	340	2,200/5,260				
Fluorene	19.5	130			90	870/2,950				
Indeno(1,2,3-c,d)pyrene	178	110	1,390/180/94 [#]	150	180	1,150/1,500				
Phenanthrene	54.1	340		58	470	2,880/10,200				
Pyrene	53.9	290		69	290	980/3,400				
4,4'-DDT	5.1									
Permethrin	55.9									
BDE 47	11				1.0	34.9/102	110			
BDE 99	8.9				0.03	13.8/34.3	110			
PCB 101	1.5									
PCB 118	1.5									
PCB 138	2.3									
PCB 153	2.4									
PCB 180	1.3									
BBP	1.6							5.5	1.2	0.138
DEHP	46.2							13.5	22.9	560*
DiBP	0.861								33.9	720*
DiNP	7.9									
Triclosan	114									

TSP: total suspended particles; NA: not available; AM: arithmetic mean; GM: geometric mean; *: 14 dwellings and 14 offices; [#]: the reported means correspond to the average of the means measured in Winter (4 homes), Spring (5 homes) and Summer (9 homes) respectively.

Bold highlights studies with the same size fraction sampled (PM₁₀). Case studies conducted in one or two locations were excluded for this comparison. Studies targeting only new or newly decorated dwellings were not used for the comparison. For PAHs, studies performed in the context of solid biomass combustion were not considered.

Table 2b. Ranges of particle-bound SVOC concentrations in residential indoor air measured worldwide

Country	France	USA	China	Hong-Kong	Norway	USA	China	China
Size fraction	PM ₁₀	TSP	PM _{2.5} /TSP	PM _{2.5}	PM ₁₀	TSP	TSP	PM ₁₀
Period of measurements	Dec. 2010 - April 2011	March 2006 - Aug. 2007	April - Dec. 2010	April - Dec. 2010	NA	Jan. - May 2014	Sept. 2012 - Jan. 2013	Dec. 2010 + June 2011
n Dwellings	n=30	n=12	n=7	n=6	n=2	n=20	n=28*	n=13
Unit	This study (min-P95)	Batterman et al., 2009	Wang et al., 2014a	Wang et al., 2014a	Rakkestad et al., 2007	Tran and Kaman, 2015	Wang et al., 2014b	Zhang et al., 2014
BDE 28	pg m ⁻³ nd - 1.9	nd - 25	nd - 45 / nd - 52	nd - 1.8				
BDE 85	pg m ⁻³ nd - <4.2	nd - 44	nd - 7.7 / nd - 10.2	nd - 2.1				
BDE 100	pg m ⁻³ nd - 13.6	nd - 370	0.5 - 57.9 / 1.8 - 141	nd - 22.1				
BDE 153	pg m ⁻³ nd - <4.2	nd - 110	nd - 20.6 / nd - 58.6	nd - 1.0				
BDE 154	pg m ⁻³ nd - <4.2	nd - 230	nd - 14.5 / nd - 192	nd - 0.6				
DBP	ng m ⁻³ nd - 25.2				74 - 85	0.9 - 451	nd - 4,920*	7.3 - 1,466
DEP	ng m ⁻³ nd - 9.8					3.4 - 361		0.08 - 7.4
DMP	ng m ⁻³ nd - 0.07					nq - 2.4	nd - 1,750*	0.3 - 47.6
t-chlordane	pg m ⁻³ nd - <2.1							nd - 1,700
c-chlordane	pg m ⁻³ <2.1							nd - 670

TSP: total suspended particles; NA: not available; *: 14 dwellings and 14 offices; P95: 95th percentile; nd: not detected; nq: not quantified; t- and c-chlordane: trans- and cis-chlordane

Bold highlights studies with the same size fraction sampled (PM₁₀). Case studies conducted in one or two locations were excluded for this comparison. Studies targeting only new or newly decorated dwellings were not used for the comparison.

Table 3. SVOC median concentrations (pg m⁻³) according to the heating season and smoking in the dwelling

SVOC	Heating season		Non heating season		Paired comparison
	Smoker H+S	Non-smoker H+NS	Smoker NH+S	Non-smoker NH+NS	
%	43	25	11	21	-
SVOCs showing influence of both the season and the smoking					
Benzo(a)anthracene	170	53	42	13	} H+S > H+NS > NH+NS*** H+S > NH+S > NH+NS***
Chrysene	259	85	80	30	
Benzo(a)pyrene	380	170	93	17	} H+S > H+NS > NH+NS*** H+S > NH+S > NH+NS**
Benzo(b)fluoranthene	724	374	243	94	
Pyrene	123	59	52	23	} H+S > H+NS** > NH+S* NH+S > NH+NS*
Benzo(k)fluoranthene	145	88	46	18	
Dibenzo(a,h)anthracene	58	29	13	< LOQ	H+S > H+NS** > NH+S** NH+S > NH+NS**
Fluoranthene	171	75	74	34	H+S > H/NH+NS*** H+S > NH+S** > NH+NS***
Indeno(1,2,3-cd)pyrene	324	234	120	48	H+S/NS > NH+NS/S*** NH+S > NH+NS*
Lindane	7.6	< LOD	< LOQ	< LOD	H+S > NH+S* > H/NH+NS**
4,4'-DDE	2.0	< LOD	< LOQ	< LOD	H+S > NH+S* > NH+NS* H+S > H+NS***
4,4'-DDT	16	3.7	9.2	2.4	H+S > H/NH+NS***
PCB 138	9.9	1.6	3.6	< LOQ	H/NH+S > NH+NS** H+S > H+NS***
PCB 118	7.0	1.1	2.1	< LOQ	} H+S > NH+S* > NH+NS** H+S > H+NS***
PCB 153	9.3	1.5	3.1	< LOQ	
PCB 180	4.5	< LOQ	1.6	< LOQ	
BBP	6,222	1,290	1,708	736	H+S > H+NS*** H+S > NH+S* > NH+NS**
DEHP #	143	43	83	22	H+S > H+NS > NH+NS*** H+S > NH+S** > NH+NS***
Galaxolide	158	< LOD	50	< LOD	H+S > H/NH+NS*** H+S > NH+S** > NH+NS*
Tonalide	65	< LOQ	24	< LOD	H+S > NH+S* > H/NH+NS*

SVOCs influenced predominantly by smoking

Fluorene	56	17	38	14	H/NH+S > H/NH+NS**
Phenanthrene	95	51	63	43	H/NH+S > NH+NS** H+S > H+NS***
Oxadiazon	< LOQ	< LOD	1.0	< LOD	H/NH+S > H/NH+NS***
Permethrin	90	78	124	53	NH+S > NH+NS*
BDE 47	45	12	23	4.8	H/NH+S > NH+NS*** H+S > H+NS*** > NH+NS*
BDE 99	19	8.8	15	5.5	H/NH+S > NH+NS** H+S > H+NS***
BDE 100	5.0	< LOD	< LOQ	< LOD	H/NH+S > H/NH+NS*
PCB 52	2.6	< LOQ	1.0	< LOD	H/NH+S > H/NH+NS**
PCB 101	6.8	1.2	2.6	< LOQ	H/NH+S > H/NH+NS*
PCB 105	2.7	< LOQ	1.0	< LOD	H/NH+S > H/NH+NS*
DBP	5,298	< LOQ	1,161	< LOD	H+S > NH+S*** > H+NS* H+NS > NH+NS*
DEP	1,795	< LOQ	< LOQ	< LOD	H+S > H/NH+NS*** NH+S > NH+NS*
DiBP	3,370	613	1,329	454	H/NH+S > H/NH+NS**
DiNP	16,570	7,940	8,803	5,606	H+S > H/NH+NS*** NH+S > NH+NS*
4-tert-butylphenol	< LOQ	< LOD	< LOQ	< LOD	H/NH+S > H/NH+NS*
Triclosan	305	81	313	67	H/NH+S > H/NH+NS***

SVOCs influenced predominantly by the season

Benzo(g,h,i)perylene	487	333	159	69	H+S/NS > NH+S/NS***
Bisphenol-A	1,091	< LOD	< LOD	< LOD	H+S > NH+NS*** H+NS > NH+NS**

SVOCs with no trend regarding influence of season and smoking

Anthracene	16	14	15	9.1	NH+NS < other **
4-tert-octylphenol	28	< LOD	< LOQ	< LOD	H+S > other ***

#: percentage of dwellings in each group of season and smoking status; LOD: limit of detection;

LOQ: limit of quantification; *: $P < 0.05$, **: $P < 0.01$ and *** $P < 0.001$ adjusted with the Bonferroni correction to account for the multiple comparisons; # concentrations expressed in ng m^{-3} .

The SVOCs with concentrations < LOQ in each of the four categories are not reported.

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Figure 1. Average relative contribution (%) of each PAH to the total concentrations of PAHs in PM₁₀ according to season and smoking in the dwelling

Figure 2. Spearman rank correlation coefficients between concentrations of 40 particle-bound SVOCs and PM₁₀ concentration

Figure 1. Average relative contribution (%) of each PAH to the total concentrations of PAHs in PM₁₀ according to season and smoking in the dwelling

The figure next to each PAH name indicates the number of rings.

Figure 2. Spearman rank correlation coefficients between concentrations of 40 particle-bound SVOCs and PM₁₀ concentration

1: ANT=Anthracene; 2: BaA=Benzo(a)anthracene; 3: BaP=Benzo(a)pyrene; 4: BbF=Benzo(b)fluoranthene; 5: BgP=Benzo(ghi)perylene; 6: BkF=Benzo(k)fluoranthene; 7: CHR=Chrysene; 8: DBA=Dibenzo(a,h)anthracene; 9: FAN=Fluoranthene; 10: FLU=Fluorene; 11: IND=Indeno(1,2,3-c,d)pyrene; 12: PHE=Phenanthrene; 13: PYR=Pyrene; NS: non-significant ($P > 0.05$)

Highlights

- ▶ 66 SVOCs were measured in airborne particles (PM₁₀) 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 PM₁₀ concentrations promote SVOCs in the particulate phase.