Topic C2: New chemical substances in buildings

ECOS-POUSS: A NATIONWIDE SURVEY OF SEMI-VOLATILE ORGANIC COMPOUNDS IN HOME SETTLED DUST

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SUMMARY

Forty-eight SVOCs, e.g. phthalates, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pyrethroids, organochlorine and organophosphorous pesticides, synthetic musks, and tributylphosphate, were measured in home settled dust collected from household vacuum cleaner bags. Thirty-two compounds were detected in more than half of the dwellings. Permethrin and bisphenol-A concentrations appeared to be higher in France in comparison to other countries.

INTRODUCTION

Semi-volatile organic compounds (SVOCs) are of concern due to their known or suspected health effects and due to the widespread exposure through different environmental media and pathways (Weschler and Nazaroff, 2008). The objective of this study was to assess the SVOC concentrations in household settled dust at a nationwide scale. Vacuum cleaner bags were collected across mainland France in 300 dwellings occupied by at least one child aged 6 months to 6 years. The sampling design made it possible to extrapolate the measured concentrations to the population of French dwellings occupied by these children.

METHODOLOGIES

Target compounds

The target SVOCs were selected using a ranking method based on toxicity and indoor exposure levels. A literature review provided, for each target SVOC, data on its frequency of detection and reported concentrations in home settled dust, primarily in France or by default in other countries. On the other hand, the toxicity reference doses were retrieved from toxicity databases or were calculated from No Observed Effect Levels (or Lowest Observed Effect Levels) and uncertainty factors. Ranking scores were calculated (Bonvallot et al., 2010).

The SVOCs at the top of the prioritization list were: phthalates, pesticides, short-chain chlorinated paraffins, polybrominated diphenyl ethers (PBDEs), perfluorinated chemicals (PFCs), organotins, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). Those which could be analyzed by gas chromatography coupled with mass spectrometry (GC-MS) were selected. Some substances were added, which could be analyzed simultaneously with the same analytical method.

The final 48 SVOCs were: organophosphorous and organochlorine pesticides: dichlorvos, chlorpyrifos, diazinon, dieldrin, aldrin, endrin, γ-hexachlorohexane (lindane), 4,4'-dichloro-diphenyldichloro-ethylene (4,4'-DDE), oxadiazon, endosulfan; pyrethroids: cyfluthrin, cypermethrin, deltamethrin, permethrin; PCBs: 28, 31, 52, 77, 101, 105, 118, 126, 138 and 153 congeners; phthalates: benzylbutyl phthalate (BBP), di-n-butyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), di-iso-butyl phthalate (DiBP), di-iso-nonyl phthalate (DiNP); PBDEs: 28, 47, 153, 154, 85, 99, 100, 119 and 209 congeners; synthetic musks: galaxolide®, tonalide®; PAHs: anthracene, acenaphthene, benzo(a)pyrene, fluorene, phenanthrene; bisphenol-A, and tributylphosphate.

Dust collection

A subsample of children aged 6 months to 6 years enrolled in a nationwide survey on blood lead levels (Etchevers et al., 2014) were selected for this nationwide survey of dwellings. 484 dwellings were investigated in 2008-2009 (Lucas et al., 2012). Trained inspectors collected the vacuum cleaner bags in 300 of these dwellings.

Samples and pre-treatment

The bags containing dust from outside the dwelling, or not containing enough dust (< 200 mg) after sieving to <100 µm were discarded. The conditions of storage (packaging, temperature and duration) were examined during a study on the influence of storage conditions (Blanchard et al., 2014). The bags which did not meet the conservation criteria were discarded.

Chemical analysis

The analytical methods are described in detail in (Mercier et al., 2014). 200 mg of <100 µm sieved dust were mixed with Celite® 545 and extracted by pressurized liquid extraction (PLE) with dichloromethane (ASE 350, Dionex). Organic extracts were cleaned up by solid phase extraction (SPE) on aminopropyl columns and then analyzed by gas chromatography coupled with simple mass spectrometry (GC/MS) or tandem mass spectrometry (GC/MS/MS) depending on the compounds.

For all the compounds except BDE-209 and BPA, analyses were performed using a Trace GC Ultra coupled to a TSQ Quantum GC (Thermo Scientific). The GC system was equipped with a PTV injector (Programmable Temperature Vaporizing). Chromatographic separation was performed on a Rtx-PCB capillary column (60 m length x 0.25 mm I.D., 0.25 µm film thickness) supplied by Restek (Lisses, France). The mass spectrometer (triple quadrupole) was used in Multiple Reaction Monitoring (MRM) mode. The two most sensitive and specific transitions were monitored for each compound.

BDE-209 analyses were performed using a 6890A GC system coupled to a 5975C mass selective detector (MSD) (Agilent Technologies). The GC system was equipped with a PTV

injector. Chromatographic separation was performed on a DB-5ms capillary column (15 m length x 0.25 mm I.D., 0.25 µm film thickness) supplied by Agilent J&W. The mass spectrometer was operated in selective ion monitoring (SIM) mode and the two most sensitive and specific ions were monitored.

BPA analyses were performed following a derivation step using a 7890A GC system coupled to a 5975C MSD (Agilent Technologies). The GC system was equipped with a Multi-Mode Inlet injector (MMI). Chromatographic separation was performed on a DB-5ms capillary column (30 m length x 0.25 mm I.D., 0.25 µm film thickness). The mass spectrometer was operated in SIM mode and the three most sensitive and specific ions were monitored.

Statistical Analysis

Data were analyzed with R software (http://www.R-project.org) with the R "survey package" (Lumley, 2004, 2010a, 2010b).

Each dwelling (n = 484) has a sampling weight, the inverse of the probability of inclusion in the sample, which makes it possible to obtain national estimates. Nevertheless, due to dwellings without SVOC measurements either from non-selection or discarded bags (called the non-respondent), the sampling weights needed to be adjusted for nonresponse to avoid bias in estimates. The weights of the respondents (i.e. dwellings with SVOC analyses in dust) were corrected to compensate for the elimination of the non-respondents. 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 *p* to provide the adjusted weight of each dwelling. To estimate *p*, a logistic regression model was used. The model provided the variables which were able to predict *p* (the dwelling inspector and the season). Nine groups of dwellings were then built by the cross-classification method. The number of groups was defined not to get too low *p* (*p* higher than 0.10), which would have resulted in unstable estimators. It was then possible to express the results obtained from the sample as national estimates of SVOC concentration in home settled dust.

Quantiles were calculated when more than 75% of concentrations were above the limits of quantification (LOQ). Concentrations below the limits of detection (LOD) and the LOQ were set respectively at LOD/2 and LOQ/2.

RESULTS AND DISCUSSION

Concentrations in floor settled dust

From the 300 dust samples, 145 met the election criteria and were analyzed.

The frequency of detection, frequency of quantification and median concentrations of the 48 SVOCs are presented in Figure 1. The results are expressed for the target population, namely the 3,581,991 dwellings with children aged 6 months to 6 years in mainland France, excluding overseas.

Thirty-two compounds are present in more than half of the dwellings.

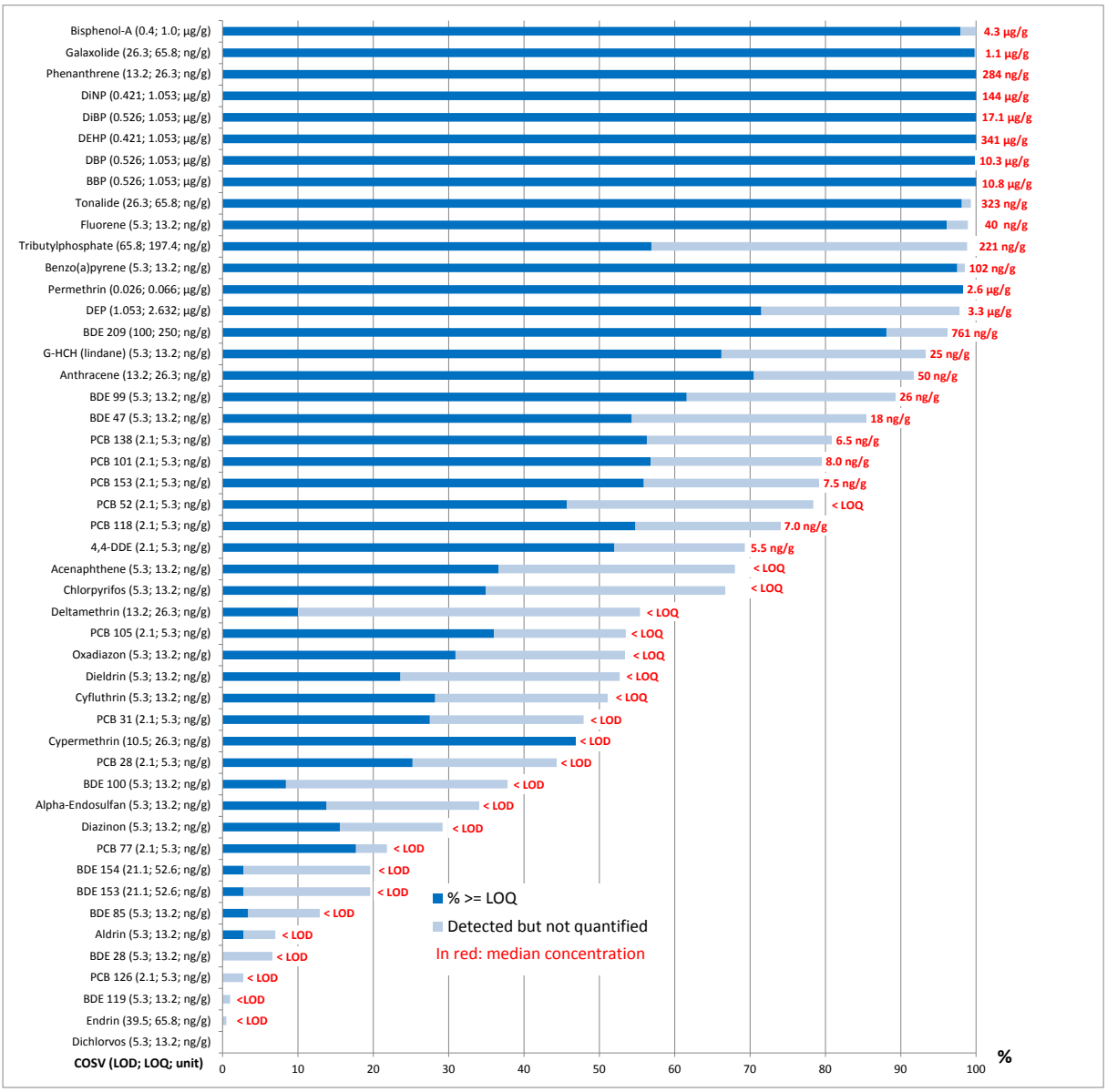

Figure 1. Frequency of detection (%; light blue), frequency of quantification (%; dark blue) and median concentrations (µg/g or ng/g; red labels) of the 48 SVOCs. France, 2008-2009, N = 3,581,991.

Comparison with other countries

The twelve most concentrated compounds are listed in Table 1. For comparison, concentrations measured in settled dust on floor in dwellings were retrieved from recent peer-reviewed papers (>2003). Studies focusing on surface dust were not taken into account.

Due to the large number of publications on SVOCs in household settled dust, the comparison was limited, for each compound, to the study that was the closest in terms of geography and sampling design. When several studies were available, the choice was done on the basis of the following criteria: 1/ study carried out in Europe; 2/ dust from a vacuum cleaner bag instead of specifically vacuumed dust; 3/ sieving fraction equal to 100 µm or closer to. The concentrations are presented in Table 1.

Table 1. SVOC concentrations in floor settled dust (µg/g), France, 2008-2009, and comparison with other countries.

SVOC	Median – this study (µg/g)	Concentrations measured in dwellings in other countries					
		n	Sampling method	Sieving fraction (µm)	Median (µg/g)	Country, year	Reference
DEHP	341	30	Vacuum cleaner bag	63 µm	604	Germany, n/a	(Abb et al., 2009)
DiNP	144				129		
DiBP	17.1	38	Vacuum cleaner bag	80 µm	5.2	Canada, n/a	(Kubwabo et al., 2013)
BBP	10.8	30	Vacuum cleaner bag	63 µm	15.2	Germany, n/a	(Abb et al., 2009)
DBP	10.3				87.4		
Bisphenol-A	4.3	12	Vacuum cleaner bag	63 µm	0.55	Germany, 2005	(Völkel et al., 2008)
DEP	3.3	38	Vacuum cleaner bag	80 µm	2.0	Canada, n/a	(Kubwabo et al., 2013)
Permethrin	2.6	503	Vacuum cleaner bag	2 mm	0.09	Germany, 2001-2002	(Becker et al., 2006)
Galaxolide	1.1	35	Vacuum cleaner bag	63 µm	0.59	Germany, 1998-1999	(Butte, 2004)
BDE-209	0.76	42 47	Vacuum cleaner bag	75 µm	0.33 0.43	Denmark, 2007	(Vorkamp et al., 2011)
Tonalide	0.32	35	Vacuum cleaner bag	63 µm	0.69	Germany, 1998-1999	(Butte, 2004)
Phenanthrene	0.28	123	Vacuum cleaner bag	No sieving	0.96	Germany, 1997-2000	(Fromme et al., 2004)

n: number of dwellings; n/a: not available

The comparison presented in Table 1 shows that the concentrations of all phthalates but DBP, galaxolide and tonalide, BDE-209, and phenanthrene in household settled dust are roughly similar in France as in other countries. Permethrin and bisphenol-A concentrations appear to be higher in France. No assumptions are made at this stage.

CONCLUSIONS

This is the first time that indoor concentrations of a wide range of SVOCs were measured simultaneously in a large number of settled dust samples in France. Thirty-two compounds were present in more than half of the dwellings. Phthalates (BBP, DBP, DEHP, DiBP, DiNP), bisphenol-A, galaxolide and phenanthrene were detected in 100% of dwellings. The maximum concentrations were measured for four phthalates (DEHP, DiNP, DiBP, BBP) and permethrin.

The estimated nationwide concentrations for home settled dust in addition to those for indoor air phase will enable an exposure assessment for the general population in France. In parallel, pollutants were grouped by common modes of action (Fournier et al., 2014) and were considered to derive toxicological indexes. This will enable a cumulative health risk assessment of indoor SVOC mixtures within the ECOS-project (Glorennec et al., 2011 and Glorennec et al. IA2014 presentation).

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