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Contamination des logements français en composés organiques semi-volatils en phase particulaire

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Remerciements

Sommaire

Liste des sigles et acronymes

4,4’-DDE	2,2-bis(p-chlorophényl)-1,1-dichloroéthylène
4,4’-DDT	4,4’-dichlorodiphényltrichloroéthane
Anses	Agence nationale de sécurité sanitaire
ATSDR	*Agency for Toxic Substances and Disease Registry*
B(a)P	Benzo(a)pyrène
BBP	Phtalate de butyle et de benzyle
BDE	Bromodiphényl éther
BPA	Bisphénol A
COSV	Composé organique semi-volatil
DBP	Phtalate de dibutyle
DEHP	Phtalate de bis (2-éthylhexyle)
DEP	Phtalate de diéthyle
DiBP	Phtalate de diisobutyle
DiNP	Phtalate de di-isononyle
DMEP	Phtalate de di-2-méthoxyéthyle
DMP	Phtalate de diméthyle
DOP	Phtalate de dioctyle
EHESP	Ecole des hautes études en santé publique
GC/MS	*Gas Chromatography – Mass Spectrometry*
HAP	Hydrocarbures aromatiques polycycliques
HCH	Hexachlorocyclohexane
InVS	Institut de veille sanitaire
K_{oa}	Coefficient de partage entre l’air et l’octanol
K_{ow}	Coefficient de partage entre l’eau et l’octanol

K_p	Coefficient de partage gaz/particules
LERES	Laboratoire d'étude et de recherche en environnement et santé
NIST	*National Institute of Standards and Technology*
OEHHA	*Office of Environmental Health Hazard Assessment*
OQAI	Observatoire de la qualité de l’air intérieur
PBDE	Polybromodiphényl éthers
PCB	Polychlorobiphényles
$PM_{2,5}$	Particules en suspension dans l'air dont le diamètre médian est inférieur à 2,5 µm
PM_{10}	Particules en suspension dans l'air dont le diamètre médian est inférieur à 10 µm
REACh	Registration, Evaluation, Authorisation and Restriction of Chemicals
RIVM	Agence de santé environnementale des Pays-Bas
SRM	Standard Reference Material
TBBPA	Tétrabromobisphénol A
TBP	Tributylphosphate
US-EPA	*US Environmental Protection Agency*
VGAI	Valeur guide de qualité de l’air intérieur
VTR	Valeur toxicologique de référence

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Introduction

Au cours des dix dernières années, les études d'imprégnation des populations humaines conduites dans différents pays ont mis en évidence la présence d'un grand nombre de substances chimiques et de leurs métabolites dans les matrices comme le sang ou les urines (CDC, 2009). Parallèlement, un faisceau convergent de connaissances tend à mettre en avant des effets avérés ou suspectés de certaines de ces substances sur la santé humaine. Les effets de perturbation endocrinienne ont par exemple été montrés pour certaines molécules, et pourraient être en lien avec des malformations à la naissance, des effets sur le système reproducteur ou l'augmentation de l'obésité (Rudel et Perovich, 2009 ; Inserm, 2011). Une meilleure connaissance des voies et des situations d'exposition de la population s'impose pour être en mesure de mettre en œuvre des moyens de réduction des expositions aux substances présentant des effets connus, probables ou possibles pour la santé.

Parmi ces substances posant question, on compte celles désignées sous le terme de « composés organiques semi-volatils » ou COSV. Les COSV représentent un ensemble de composés définis par leurs propriétés physico-chimiques, et plus particulièrement une température d'ébullition allant de (240 à 260 °C) à (380 à 400 °C) et par une pression de vapeur comprise entre 10^{-9} et 10 Pa (NF ISO 16006-6, 2012 ; Weschler et Nazaroff, 2008). Ainsi, dans les environnements intérieurs, ces substances se retrouvent à la fois dans l'air, en phases gazeuse et particulaire, et dans les poussières déposées au sol, sur le mobilier, les parois et les objets. En outre, certaines persistent dans l'environnement intérieur en l'absence des phénomènes de biodégradation en œuvre dans l'environnement extérieur (photochimie, lixiviation, etc.). Cette persistance peut s'observer durant plusieurs années pour certains COSV, ce qui justifie le fait de s'intéresser également aux composés dont l'utilisation est aujourd'hui interdite en France. Les COSV incluent des substances de différentes familles chimiques parmi lesquelles les phtalates, les polychlorobiphényles, des composés organochlorés, organobromés et organophosphorés, les hydrocarbures aromatiques polycycliques, les pyréthrinoïdes, les phénols et alkylphénols, les muscs synthétiques, les parabènes, par exemple.

Par ailleurs, ces substances ont des propriétés très variées ; elles sont utilisées comme insecticide, ignifugeant, plastifiant, conservateur, antisalissure, etc. Ainsi, elles sont intégrées depuis les années 1970 dans de nombreuses applications industrielles. Dans les environnements intérieurs, elles peuvent ainsi être présentes dans les revêtements, les isolants, les produits de traitement du bois, les textiles, les appareils électriques et électroniques, les insecticides, les antiparasitaires animaux et humains, les produits d'entretien, les produits cosmétiques et de soin, les ustensiles de cuisine, etc. (Weschler et Nazaroff, 2008 ; Mercier et al., 2011). Ces matériaux et produits émettent dans l'environnement intérieur les COSV qu'ils contiennent par dispersion lors de l'usage (insecticide en aérosol par exemple) ou par évaporation ou abrasion.

Dans un contexte où la population passe près de 90 % de son temps dans des environnements clos, ces substances, largement utilisées, présentes dans différents milieux et persistantes, conduisent à des expositions potentiellement non négligeables via l'air intérieur et les poussières déposées. Cette exposition implique différentes voies d'exposition : l'inhalation, l'ingestion non intentionnelle et le contact cutané. Les jeunes enfants, de par leurs comportements (contacts main-sol et main-bouche fréquents, marche à quatre-pattes), sont ainsi particulièrement exposés aux COSV.

La présente thèse visait à développer la connaissance des expositions aux COSV dans les logements. Elle a plus particulièrement porté sur les COSV présents en phase particulaire. Une hiérarchisation des molécules jugées prioritaires au regard de leur impact sanitaire potentiel avait permis au préalable d'établir une liste de COSV d'intérêt. Le travail de thèse s'est fondé sur l'exploitation des mesures de 66 COSV dans les particules en suspension de diamètre aérodynamique médian inférieur à 10 µm (PM_{10}) et 48 COSV dans les poussières au sol de taille inférieure à 100 µm considérées comme étant celles adhérant aux mains. Ces mesures ont été réalisées dans le cadre de deux campagnes nationales : d'une part, la campagne « Logements » de l'Observatoire de la qualité de l'air intérieur (OQAI) conduite en 2003-2005 (Kirchner et al., 2007) et d'autre part, le projet Plomb-Habitat dont les prélèvements ont eu lieu en 2008-2009 (Lucas et al., 2012).

Ce travail s’est inséré dans le cadre plus global du projet ECOS-Habitat « Expositions cumulées aux composés organiques semi-volatils dans l’habitat ». Il a ainsi bénéficié des travaux menés en amont sur les développements analytiques (Mercier et al., 2012, 2014), puis des résultats des analyses conduites par le Laboratoire d’études et de recherche en environnement et santé (LERES) à l’École des hautes études en santé publique (EHESP) et de l’évaluation des concentrations rencontrées dans les logements à l’échelle du parc français.

Un travail bibliographique initial, présenté au Chapitre 1, a permis de mettre en lumière un ensemble de facteurs déterminants de l’exposition aux COSV : influence de la taille des particules, du type de poussières collectées, de leur bioaccessibilité, qui ne sont pas toujours considérés et qui limitent par ailleurs la comparabilité des résultats. Puis, les données de contamination des poussières déposées au sol et des particules en suspension dans l’air ont été exploitées et sont présentées dans les Chapitre 2 et Chapitre 3 respectivement. Ce travail a notamment porté sur l’identification d’éventuelles spécificités françaises au regard des molécules en présence et/ou des concentrations mesurées. La discussion globale développée au Chapitre 4 porte sur l’évaluation rétrospective de la hiérarchisation sanitaire conduite pour le choix des COSV à étudier. De plus, les concentrations des COSV quantifiés à la fois dans l’air et au sol ont été mises en perspective afin d’examiner dans quelle mesure les particules en suspension et les poussières déposées sont similaires en termes de concentrations et de mélanges de COSV en présence. Il s’agissait plus particulièrement d’étudier si les concentrations mesurées dans un milieu peuvent être prédictives de celles observées dans l’autre. Enfin, l’estimation des doses d’exposition aux COSV en phase particulaire à partir d’équations simples, de variables humaines d’exposition et des données de contamination a permis une première évaluation des contributions respectives de l’inhalation et de l’ingestion aux expositions domestiques des enfants et adultes à ces composés en phase particulaire dans le logement.

Chapitre 1 : Contexte scientifique

1.1 Les composés organiques semi-volatils

Les COSV sont des substances appartenant à un grand nombre de familles chimiques différentes et ayant des usages multiples dans les bâtiments. Le Tableau 1 présente quelques exemples d'usage et de sources de COSV dans les environnements intérieurs.

Tableau 1 : Exemples des usages et sources de composés organiques semi-volatils dans les bâtiments

Familles chimiques	**Usages**	**Sources**
Alkylphénols	Surfactants, conservateurs	Détergents et produits d'entretien, lessives, cosmétiques
Bisphénol A (BPA)	Composant de polymère, révélateur chimique	Plastiques de type polycarbonate et résines époxydes, papiers thermiques
Hydrocarbures aromatiques polycycliques (HAP)	Non intentionnels (présents dans les produits pétroliers ; résidus de combustion)	Tabagisme, cuisson, combustion d'encens, chauffage domestique (charbon, bois) Air extérieur (trafic, émissions industrielles, feux de forêt, etc.)
Muscs de synthèse	Parfums	Produits de soin, cosmétiques, produits d'entretien
Pesticides organochlorés et organophosphorés, pyréthrinoïdes	Pesticides, biocides	Produits insecticides, antiparasitaires humain et animal, de traitement des plantes Air extérieur (traitement des cultures)
Phtalates	Plastifiants	Matières plastiques souples (revêtements de sol ou muraux, câbles électriques, rideaux de douche, matériel médical, etc.), lubrifiants, parfums
Polybromodiphényléthers (PBDE)	Retardateurs de flamme	Textiles, mobiliers rembourrés, plastiques durs (ordinateurs, téléviseurs, etc.)
Polychlorobiphényles (PCB)	Stabilisateurs, retardateurs de flamme	Vieux joints d'étanchéité (ouvrants, revêtements de sol)
Tributylphosphate (TBP)	Solvant, plastifiant, retardateur de flamme	Revêtements, peintures
Triclosan	Désinfectant, biocide	Produits d'hygiène corporelle, produits de consommation courante

Adapté de (Mercier et al., 2011)

L'utilisation de ces composés a démarré dans les années 1950 et n'a pas cessé depuis. Les usages ont cependant beaucoup évolué au fil des interdictions et de la mise sur le marché de nouvelles molécules. Dans son historique sur la pollution de l'air intérieur des cinquante dernières années, CJ Weschler (2009) rapporte les tendances des évolutions des concentrations en COSV dans l'air intérieur. Il note :

- l'augmentation puis la diminution des concentrations de pesticides (pentachlorophénol, aldrine, chlordane, chlorpyrifos, dieldrine, 4,4'-DDT, 4,4'-DDE, etc.), des retardateurs de flamme bromés (BDE 47, BDE 99) et des PCB après leurs interdictions successives ;
- la diminution des concentrations en dioxines et furanes du fait d'une baisse des concentrations dans l'air extérieur ;
- l'augmentation des concentrations en triclosan, perméthrine, muscs, 4-nonylphénol, bisphénol A, phtalates, etc., du fait de l'augmentation de leurs usages respectifs.

La persistance de certains d'entre eux explique leur présence dans l'air ou les poussières des bâtiments même des années après leur interdiction ou restriction d'usage. Le mélange des COSV en présence dans les bâtiments est donc potentiellement très important.

Parallèlement, les travaux de recherche se sont développés et l'amélioration des capacités analytiques a permis de quantifier les niveaux de concentrations de ces composés dans l'air intérieur et les poussières. Depuis plus de dix ans, les publications sur les COSV dans les environnements intérieurs sont en croissance, comme le montre la Figure 1. Cette dernière montre également que les poussières déposées au sol ou sur les surfaces sont préférentiellement étudiées en comparaison de l'air. Un graphique identique exprimé par lieu de vie au lieu du milieu fait apparaître une prépondérance des études dans les logements ; viennent ensuite les écoles et les immeubles de bureaux. Les voitures font également l'objet d'un nombre non négligeable d'études. Les hôpitaux, magasins, universités, lieux de culte, gymnases, laboratoires, musées, théâtres et cinémas ont été étudiés plus ponctuellement.

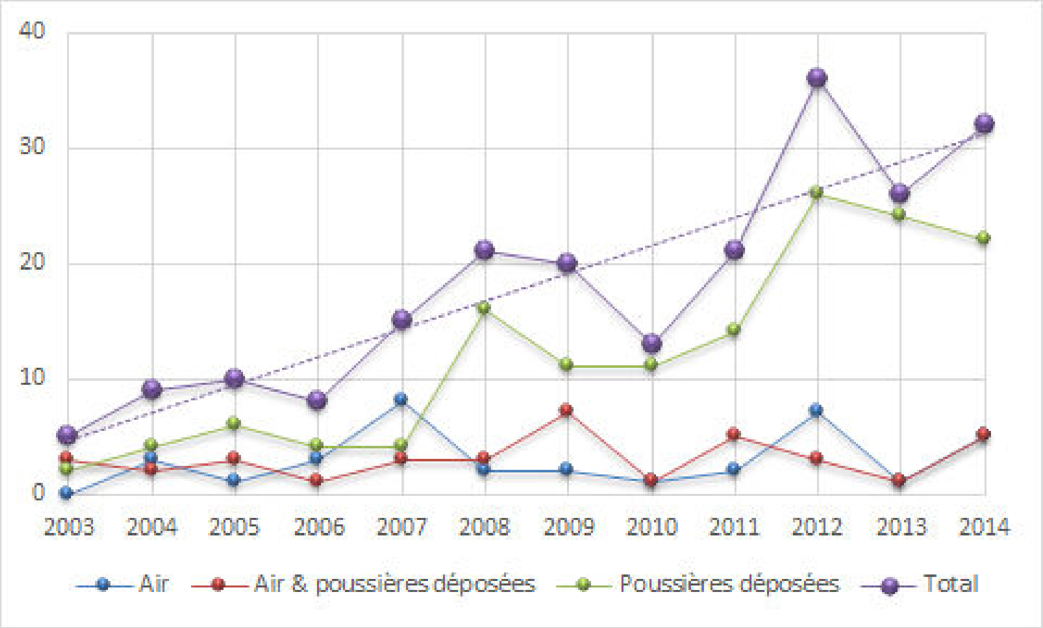


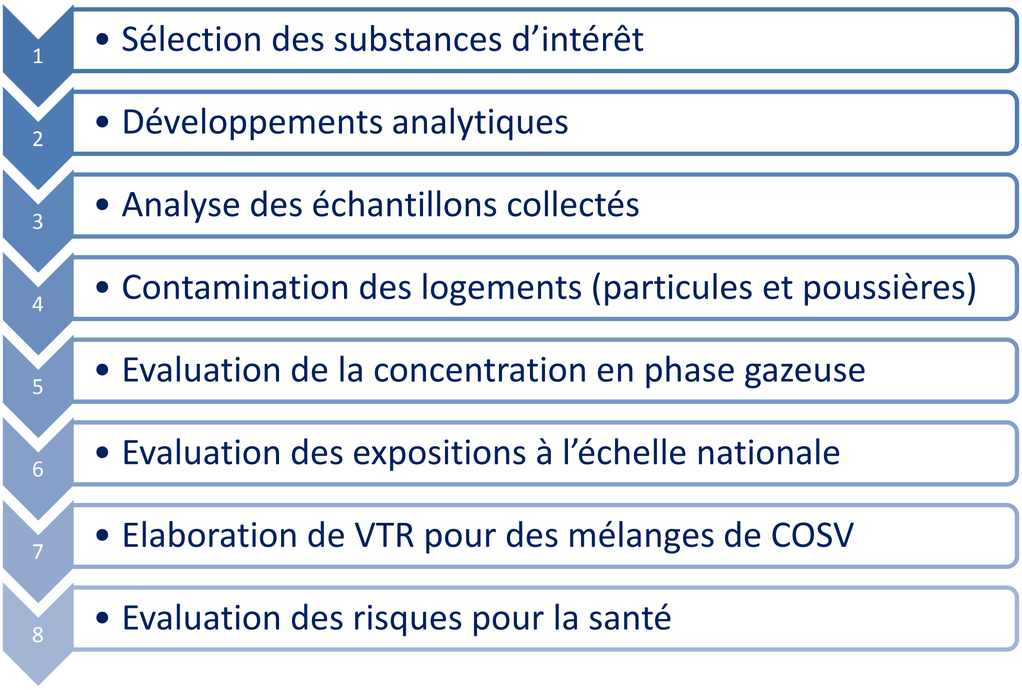
Figure 1 : Évolutions des publications sur les COSV depuis 2003 par milieu considéré (n=216)

En France, les travaux sur les COSV sont récents et aucune étude ne s'était intéressée aux concentrations dans l'environnement intérieur d'un large échantillon de logements sur tout le territoire national. Les études françaises rapportant des mesures de COSV dans les bâtiments portent sur certaines familles chimiques comme les pesticides (Bouvier et al., 2006a,b), certaines régions françaises comme la Bretagne (Blanchard et al., 2014a ; Dallongeville et al., 2015) ou sur des développements de méthode de prélèvement et d'analyse (Marchand et al., 2012 ; Alliot et al., 2014 ; Cettier et al., 2014 ; Laborie et al., 2016). Afin d'être en mesure d'évaluer l'exposition de la population française aux COSV, le projet ECOS-Habitat, auquel cette thèse est associée, a démarré en 2009.

1.2 Le projet ECOS-Habitat

Le projet ECOS-Habitat a pour objectif d'apprécier l'importance du problème de santé publique posé par les COSV dans le logement par une approche d'évaluation des risques, en prenant en compte le cumul des expositions selon les différentes voies d'absorption, puis en tenant compte de l'additivité ou de la potentialisation des effets pour les substances ayant un mécanisme d'action commun (Glorennec et al., 2011).

Les principales étapes du projet sont décrites sur la Figure 2. L'une d'elles passe par la connaissance et la compréhension de la contamination de l'environnement intérieur (étape n°4) à laquelle est plus spécifiquement associée la présente thèse.



1. Sélection des substances d'intérêt
2. Développements analytiques
3. Analyse des échantillons collectés
4. Contamination des logements (particules et poussières)
5. Evaluation de la concentration en phase gazeuse
6. Evaluation des expositions à l'échelle nationale
7. Elaboration de VTR pour des mélanges de COSV
8. Evaluation des risques pour la santé

Figure 2 : Les principales étapes du projet ECOS-Habitat

Les COSV d'intérêt dans le projet ECOS-Habitat ont fait l'objet d'un travail préalable de hiérarchisation sanitaire basée sur le calcul d'un score[1] pour chacun des COSV recensés comme potentiellement présents dans l'environnement intérieur, considérant, d'une part, les concentrations déjà mesurées dans les poussières des logements en France ou dans d'autres pays à défaut, et d'autre part, les repères toxicologiques existants (Bonvallot et al., 2010). La liste des COSV retenus pour des mesures dans l'air intérieur et les poussières déposées au sol est présentée dans le Tableau 2.

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[1] ou deux scores en cas d'effets critiques à seuil et sans seuil pour une même substance

Tableau 2 : Composés recherchés dans les poussières au sol (48) et dans l'air (66)

Familles chimiques	**Composés**
Alkylphénols	4-tert-butylphénol (A), 4-tert-octylphénol (A) et 4-n-nonylphénol (A)
Hydrocarbures aromatiques polycycliques (HAP)	acénaphtène (P), anthracène, benzo[a]pyrène, fluorène, phénanthrène, fluoranthène (A), pyrène (A), benzo(a)anthracène (A), chrysène (A), benzo(b)fluoranthène (A), benzo(k)fluoranthène (A), dibenzo(a,h)anthracène (A), indéno(1,2,3-c,d)pyrène (A) et benzo(g,h,i)pérylène (A)
Muscs de synthèse	galaxolide et tonalide
Pesticides organophosphorés	dichlorvos (P), chlorpyrifos, diazinon
Pesticides organochlorés	aldrine, atrazine (A), dieldrine, endrine, α-HCH (A), γ-HCH (lindane), oxadiazon, 4,4'-DDE, 4,4'-DDT (A), α-endosulfan, cis- et trans-chlordane (A), heptachlore (A), métolachlore (A)
Phtalates	benzylbutylphtalate (BBP), di-n-butylphtalate (DBP), diéthylhexylphtalate (DEHP), diéthylphtalate (DEP), di-iso-butylphtalate (DiBP), di-iso-nonylphtalate (DiNP), diméthylphtalate (DMP) (A), di-(2-méthoxyéthyl)phtalate (DMEP) (A) et di-octylphtalate (DOP) (A)
Pyréthrinoïdes	cyfluthrine (P), cyperméthrine (P), deltaméthrine (P), perméthrine
Polybromodiphényléthers (PBDE)	congénères 28, 47, 85, 99, 100, 119, 153, 154 et 209 (P)
Polychlorobiphényles (PCB)	congénères 28, 31, 52, 77, 101, 105, 118, 126, 138, 153 et 180 (A)
Autres composés	bisphénol A, tributylphosphate (TBP), triclosan (A)

(P) = mesuré seulement dans les poussières au sol ; (A) = mesuré seulement dans l'air

1.3 Présentation du sujet de thèse

La thèse visait à caractériser la phase particulaire de COSV d'intérêt sanitaire dans les logements, dans une perspective d'évaluation des expositions de la population en France. Il s'agissait notamment :

- d'identifier les déterminants de la représentativité des mesures de COSV dans les logements ;
- d'analyser les mesures des concentrations en COSV particulaires dans les logements français, de caractériser les mélanges en présence et d'identifier les possibles spécificités en termes de substances et de niveaux de concentrations ;
- d'examiner les relations pouvant exister entre les milieux « air » et « poussières » ;
- de quantifier les parts respectives des expositions par inhalation et par ingestion de poussières à l'exposition totale aux COSV particulaires dans le logement.

La revue bibliographique, qui a constitué la première étape du travail, a permis de recenser et d'analyser précisément les points de vigilance relatifs à la représentativité des mesures et, de façon générale, à l'évaluation des expositions aux COSV dans l'environnement intérieur basée sur une approche environnementale. L'évaluation des expositions par mesure de l'imprégnation humaine, dans les urines, le sang, les cheveux, etc., n'entrait pas dans le périmètre de la recherche.

De nombreuses revues documentaires existent sur les COSV dans l'environnement intérieur, mais elles portent soit sur l'inventaire des concentrations mesurées et l'évaluation des expositions associées comparées à la contribution via l'alimentation par famille de substances comme par exemple les PBDE (Frederiksen et al., 2009 ; Besis et Samara, 2012 ; Coelho et al., 2014) ou les composés perfluorés (Fromme et al., 2009), soit sur des thématiques spécifiques comme les méthodes analytiques (Mercier et al., 2011), l'influence de la fraction granulométrique (Cao et al., 2012), la répartition entre les phases gazeuse, particulaire de l'air et déposée sur les sols et les surfaces (Weschler et Nazaroff, 2010), l'exposition cutanée (Weschler et Nazaroff, 2012) ou les mesures de remédiation pour diminuer les expositions (Roberts et al., 2009). La revue bibliographique réalisée a donc abordé différemment la question des expositions.

Review article

Semi-volatile organic compounds: key issues regarding indoor exposure

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ABSTRACT

The interest for semi-volatile organic compounds (SVOCs) has considerably increased over the past years. They represent a large variety of chemicals emitted by numerous sources. SVOCs are detected at various concentrations both in indoor air and settled dust and contribute to the total exposure through different pathways. This review addresses some key issues regarding SVOC measurements in a perspective of human exposure assessment. The exposure assessment through environmental monitoring is thus difficult on several aspects. One is the representativeness of sampled media relatively to exposure contact media. Neither the dust nor the indoor air sampling and analyzes are standardized, leading to different collection methods and sample treatment like selected size fractions for example. The spatial and temporal variabilities should also be considered to correctly assess the exposure. With respect to the highlighted difficulties, the possibilities to use surrogates, models, questionnaires or indicators are also reviewed. This review concludes with the perspectives to fill in some gaps in knowledge to better characterize exposure to SVOC indoors.

KEY-WORDS: Indoor Environment, Environmental Exposure, Settled Dust, Size Fraction, Representativeness, Partitioning, Bioaccessibility

INTRODUCTION

Semi-volatile organic compounds (SVOCs) correspond to a large class of organic compounds with vapor pressures between 10^{-14} and 10^{-4} atm (10^{-9} to 10 Pa).[1] Synthetic SVOCs have been added since the 1960s to a large variety of consumer products and building materials for diverse properties: they are used as plasticizer, flame-retardant, anti-oxidant, coalescing agent, pesticide and biocide, stain repellant, sealant, or fragrance.[1] Many materials and products include these molecules in their formulation: floor, wall and ceiling materials, insulating products, furniture, textiles and clothes, electric and electronic devices and wires, food packages, papers, toys, house cleaning, human and pet care products, etc.[2] The partial volatility of these compounds, the changes in environmental conditions (e.g., rise of temperature) and to a lesser extent the brittleness of materials lead to the release of SVOCs in indoor air over time. Once emitted in the indoor environment, the SVOCs partition between the gas-phase and available indoor surfaces, including airborne particles, settled dust, human skin and other surfaces.[3] Consequently SVOCs have become ubiquitous in indoor environments and occupant exposure may be non-negligible. In addition to exposure through inhalation and ingestion of floor dust, the dermal pathway should not be ignored.[4] As a consequence of the exposure through these different pathways, the contribution of indoor environments to the total human exposure to SVOCs, particularly young children exposure, seems not negligible in some cases, e.g., for polybromodiphenyl ethers (PBDEs),[5-6] phthalates,[7-8] alkylphenols,[9] or chlorinated paraffins.[10] The studies remain scarce, and the indoor contribution to the total human exposure remains unknown for some SVOCs.

Concurrently, the health effects of these chemicals are more and more extensively described. Young children spend a large amount of time in indoor environments and have high exposure behavior such as frequent crawling on floor and hand-to-mouth contacts. SVOCs are associated with numerous adverse health effects. Endocrine disruption, adverse birth outcome, developmental delay, lower cognitive function, autism, hyperactivity disorder, thyroid disease, asthma and allergies, are some of the very diverse health effects associated to some SVOCs.[11-20]

Despite this increasing knowledge, some questions regarding exposure assessment are still pending. Even if the use of biomarkers (e.g., metabolites in urine, blood, hair, etc.) is increasing due notably to its capacity to be integrative of time and all environmental exposures, the indirect assessment based on environmental contamination knowledge remains valuable. This latter approach allows to better understand the respective contribution of the environmental media to the exposure. This knowledge is fundamental in a goal of reducing human exposure. In that context, the objective of this review is to provide an overview on the current issues with respect to exposure assessment to SVOCs indoors through indoor air and indoor settled dust monitoring or modeling. The existing reviews on exposure to SVOCs report available data on indoor concentrations and related human exposure for the chemical groups respectively, such as PBDEs,[5,21-25] polycyclic aromatic hydrocarbons (PAHs),[22,26] polychlorinated biphenyls (PCBs),[22] perfluorinated compounds (PFCs),[21,27,28] pesticides,[29,30] or phthalates, bisphenol A and parabens,[31] or on a specific issue, such as partitioning between settled dust and indoor air,[32] organic contamination of settled dust and sampling and analytical methods,[2,22] size fraction of settled dust,[33] dermal pathway,[4] intervention studies to reduce children exposure to settled dust contamination.[34] The present review targets the key issues for exposure assessment to environmental monitoring or modeling. In that perspective, the representativeness of measurement results was questioned on different aspects, e.g., selected size fraction, temporal and spatial variabilities and bioavailability, and type of accessible dust (only accessible settled dust was studied, e.g., dust from the attic was not considered). Alternative ways to assess exposure either through modeling or by use of questionnaires were also examined. In the first part of the review, the measuring conditions that have direct implications on the representativeness of exposure are discussed. In the second part, the different possibilities of predicting indoor SVOC concentrations in the different indoor media are reviewed.

MATERIAL AND METHODS

Peer-reviewed publications published over the past ten years approximately on indoor contamination by SVOCs were retrieved from the Pubmed/Medline, Springerlink, Wiley Interscience and Elsevier Science Direct databases. The target compounds were: alkylphenols, flame retardants, including PBDEs, chlorinated paraffins, PFCs, synthetic musks, nicotine, organochlorine (OC) and organophosphorous (OP) pesticides, organophosphate esters, organotins, parabens, phenols, phthalates, PCBs, PAHs, pyrethroids, and triclosan. The key-words used were a combination of ‘indoor’ and the names of the SVOC targeted group of compounds.

For the purpose of this review, only papers dealing with measurements or modeling of the indoor concentrations were considered. Exposure assessment based only on biological sampling (urine, blood, hand wipe, etc.) were not included. Moreover the review focused on dwellings, the main living building in terms of time spent. Results involving other indoor environments were included in case dwellings could not be treated alone. Publications presenting analytical developments with limited *in situ* measurements were excluded. Publications on case studies and specific situations, e.g., PBDE indoor contamination due to the neighborhood of an electronic waste recycling plant, PCB contaminated buildings, or biocide contamination after a home or carpet insecticide treatment were excluded. Finally only papers published in English language were considered.

We compiled 240 original articles relevant to exposure to indoor SVOCs in dwellings. Overall we noticed an increase number of literature on the topic over the past decade: 2003: 5, 2004: 9, 2005: 10, 2006: 8, 2007: 15, 2008: 21, 2009: 20, 2010: 13, 2011: 21, 2012: 36, 2013: 26, 2014: 32 and 24 for the first 2015 semester. The studies mainly focused on settled dust with 159 studying settled dust only (66%) and 41 targeting both dust and indoor air (17%), the last 40 papers dealing with indoor air only (17%). The most studied SVOCs were brominated flame retardants (86 papers; 36%), particularly PBDEs.

Out of these 240 articles, 71 were selected for analysis according to the assigned objectives of the review. As far as correlations were reported, the studies including a low number of buildings (<10) were not considered to avoid any bias from specificities that could have weight in a small sample. Similarly, the review of determinants of SVOCs in indoor environments was based on studies having investigated more than 50 dwellings.

SVOCS ON INDOOR DUST AND AIRBORNE PARTICLES: SAMPLING REPRESENTATIVENESS

Floor dust or multi-surface dust?

Dust in indoor environments deposits on the floor and on all the other indoor surfaces such as tops of doors, shelves, cupboards, frames, etc., called multi-surface dust hereinafter. Due to the frequency of cleaning (i.e. more or less dust accumulation), the influence of outdoor dust (track-in), the proximity to indoor emission sources and to deposition/resuspension phenomena, the dust may be different according to its location, in terms of size fraction, content and respective concentration of its contaminants. Children are exposed to both floor and multi-surface settled dust. But the respective contributions of each type of dust to the exposure are not known. There is to date no international consensus on which dust should be sampled. The question is to know if one type of dust can be used as a surrogate to the other types. In that case, it would not be useful to address all types of dust while measuring concentrations to assess human exposure. Only the most accessible dust, with enough mass to satisfy analytical requirements, should be sampled. For example, floor vacuuming may be time-consuming in the frame of a large survey or may be disturbing for the building occupant. An alternative is to sample dust in places where enough mass can be quickly collected, e.g., on furniture, on mechanical ventilation system filters or on air inlets.

In their review on the assessment of children exposure to pesticides, Fenske *et al.* (2005) mentioned the dust wiping on the top of doorframes.[30] The advantages are the low cost and the low burden for the participants. The disadvantage is that the collected dust mass is low. Nevertheless the authors added that this method deserved further developments to know if this alternative dust is comparable in terms of both particle size distribution and concentrations to the floor settled dust to which the children are exposed.

From studies that investigated the relationships between exposure to phthalates and health effects, we noticed that house dust was vacuumed from various indoor elements above the floor in the children's bedroom.[35-38] Rudel *et al.* (2003) enlarged the floor dust sampling to the surface of rugs, upholstery, windowsills, ceiling fans, and furniture of the main rooms.[39] Three studies have addressed the differences between floor dust and 'above floor' dust. Kanazawa *et al.* (2010) sampled dust in 41 dwellings from all the floor of the main rooms with a vacuum cleaner, and from surfaces such as tops of doors, shelves, cupboards, frames, etc., also called multi-surface dust.[40] The concentrations of DiBP, BBP, DEHP, and DiNP in multi-surface dust were respectively significantly correlated with the concentrations in floor dust; no correlation was observed for DMP, DEP and DBP. The concentrations of DiBP and BBP were significantly higher in floor dust. A significant correlation was also observed for nonylphenol and BHT between concentrations in multi-surface dust and in floor dust, with a higher concentration in multi-surface dust for both compounds. Finally, regarding organophosphate esters, the concentrations of TCPP, TEHP, TBEP, and TPP in multi-surface dust were significantly correlated with those in floor dust. The concentrations of TCPP, TDCPP, TPP, and TCP were significantly higher in multi-surface dust than those in floor dust, whereas those of TBP, TEHP, and TBEP were significantly lower in multi-surface dust compared to floor dust. Kanazawa *et al.* (2010) concluded that the concentration for a given compound is higher in the type of dust that remains in contact with or the closest to the source(s) of the chemical. Araki *et al*. (2014) came to the same conclusion regarding organophosphate esters after their measurements both in multi-surface dust and in floor dust in a larger set of Japanese dwellings (n=112 considered for the comparison).[41] For 8 out of 11 compounds, the concentrations were significantly positively correlated, with higher concentrations either in multi-surface dust (TBP, TCPP, TCEP, TDCPP, TPP) or in floor dust (TEHP, TBEP). Ait Bamai *et al.* (2014) also vacuumed two types of dust in 128 dwellings: from the floor surface and objects within 35 cm above the floor, and from the surfaces of objects that were located more than 35 cm above the floor including furniture, moldings, doorframes, windowsills, electronic devices such as TV sets, computers, toys, and interior materials such as wallpaper and the ceiling.[42] Significant weak positive correlations were found between phthalate concentrations in floor dust and multi-surface dust (DiBP: $\rho s = 0.293$, $p < 0.001$; DBP: $\rho s = 0.206$, $p = 0.02$; BBP: $\rho s = 0.263$, $p = 0.003$; DiNP: $\rho s = 0.258$, $p = 0.003$), except for DEHP. Higher concentrations for all the 7 target phthalates were measured in dust 'above 35 cm' rather than in dust 'below 35 cm'. The variability of concentration in multi-surface dust can be explained by the fact that this dust is collected directly on many objects that contain phthalates, and that these surfaces are less often cleaned in comparison to the floor. Ait Bamai *et al.* (2014) concluded that these two types of dust are not equivalent considering exposure assessment. They suggest that sampling multi-surface dust is relevant to assess exposure to phthalate over long time periods due to accumulation, while sampling floor dust is relevant for exposure over short time periods.

Tan *et al.* (2007) collected with steel tweezers dust from filters of air conditioning units and ceiling fan blades in 31 homes for PBDE concentration analysis (8 congeners).[43] The results were compared with previous studies where dust was collected on floor by vacuum cleaning. The concentrations measured by Tan *et al.* appeared to be lower except for BDE 209. The congener profiles were relatively similar and even more consistent when BDE-209 was excluded.

As a conclusion, many alternative dusts have been used. Information is still missing on concentrations as well as on accessibility for exposure to conclude on the use of alternative dusts to characterize exposure. On the basis of the available data, we would conclude that floor dust and multi-surface dust are not equivalent.

Fresh floor dust versus vacuum cleaner bag dust

Similarly to the issue on the type of dust, there is to date no consensus on the fact to carry out a dedicated sampling of floor dust or to use the vacuumed dust from the household cleaner bag. The purpose is not to describe advantages and drawbacks from the different sampling methods; several authors have already addressed this issue. The aim here is to discuss the impact of dust sampling representativeness on exposure considering some recently published results. The dust from the vacuum cleaner bag is considered integrative of all the floor dust in the dwelling, including all vacuumed rooms. Most of the time, a vacuum cleaner bag is used several times by the occupants and accumulates several dust masses that are collected at different time periods. In this case, the dust retrieved from the bag can be considered as an aged dust as opposed to fresh dust when the vacuum cleaner bag is only used once. But, within that aged dust chemical reactions and partitioning equilibrium may have occurred that would lead to a different mixture of compounds compared to fresh dust. As such, the aged dust may not be representative of the occupant exposure to SVOCs.

Kubwabo *et al.* (2012, 2013) and Fan *et al.* (2014) compared the concentrations measured in floor dust sampled according to two methods: the collection from the household vacuum cleaner bag on the one hand or ‘old dust’, and the dust vacuuming in the main rooms on the other hand of ‘fresh dust’.[44-46] Strong and significant positive correlations were observed between the two methods for the 7 target musks (n = 49 pairs).[44] For the 17 target phthalates (n = 38 pairs), the correlations between the two methods were strong ($\rho s > 0.5$) for twelve compounds, moderate ($\rho s = 0.3\text{-}0.5$) for three compounds and weak ($\rho s < 0.3$) for two.[45] These correlations were significant for all the target phthalates except two (DUP and DiBP). Three compounds displayed higher medians in the old dust samples (DIDP, DMCHP2, and DUP) while three displayed lower medians in the old dust (DIBP, BBP, and DBP). For 8 organophosphate esters, the correlations between the two methods were all significant ($p < 0.001$), and were strong (ρs > 0.5) for seven compounds and moderate for one (ρs = 0.32).[46] The concentrations were significantly either higher in fresh dust for three compounds (TBEP, TCP, and TCPP) or lower in fresh dust for DPEHP ($p < 0.05$). No significant difference in median values was observed for the four other compounds (TBP, TCEP, TPP, and TDCPP). Regarding PBDEs, Allen *et al.* (2008) and Björklund *et al.* (2012) found different results according to the bromination degree while comparing the two types of collected dust.[47,48] Strong and significant positive correlations were observed for octa-BDEs and deca-BDEs between freshly vacuumed dust and aged dust from the vacuum cleaner bag. But no correlation was found for penta-BDEs. The authors hypothesized that the more volatile PBDEs (BDE 17) would blow off from the vacuum cleaner bag, more than the less volatile compounds (BDE 209). Blanchard *et al*. (2014a) performed conservation test of SVOCs in settled dust stored at different temperatures and in different packaging.[49] They showed the stability of the two PBDEs included in the study, namely BDE 99 and BDE 100 concentrations in settled dust at 20 °C and 35 °C during two months.

To summarize, no conclusion can made set in favor of the sampling of fresh dust or old dust. The choice between fresh floor dust and vacuum cleaner bag dust must be done on a case by case approach, depending on the target molecules and their respective volatility. The conservation study of Blanchard *et al*. (2014a) may help to make this choice.[49]

Size fraction of floor settled dust and airborne particles

Settled Dust. Independently from the sampling method, one additional key issue is the sieving fraction of settled dust. It is necessary to sieve settled dust because of the important fraction of dirt, such as hairs or food, which could be present and that is not relevant in terms of exposure assessment. Besides the sieving fraction should represent the dust which adheres to skin and that could then be ingested after hand-to-mouth contact and promote dermal exposure. Cao *et al.* (2012) reviewed data on the influence of dust size on SVOC concentrations.[33] They reported limited data for organic compounds. Actually the evaluation of concentrations on different size fractions of the same sample of home settled dust was only carried out for pesticides, PAHs, and PBDEs.[33,50]

Cao *et al*. (2012) reported a study where a composite sample of home dust was separated into seven fractions: < 4; 4-25; 25-53; 53-106; 106-150; 150-250; 250-500 µm. The concentrations of nearly all the target SVOCs, i.e., 28 pesticides and 10 PAHs, increased with decreasing particle diameter. Wei *et al.* (2009) measured 13 PBDEs in two dust samples taken from two household vacuum cleaner bags and segmented in four fractions with the following particle diameters: < 75 µm; 75-150 µm; 150-250 µm; and 250-420 µm.[50] The PBDE concentrations appeared to be in the same order of magnitude whatever the particle size. But the respective masses of the dust fractions were inversely related to the particle size and over 50% of each total dust sample mass were particles with diameters less than 75 µm. Considering the PBDE mass distribution, over 80% of the total PBDEs were associated with particles <150 µm in diameter.

Considering that the finest fractions adhere better to children's hands than larger ones and knowing that the highest concentrations are generally measured in those fine fractions, the sieving fraction appears to be a fundamental parameter to correctly assess exposure. Concurrently this fraction is extremely heterogeneous among studies, from 63 µm to 2 mm or no sieving at all, as reviewed by Mercier *et al.* (2011).[2] In addition to a possible underestimation of exposure, this broad range of sieving fractions represents an important limit to a rigorous comparison of results between studies.

Indoor Air. Regarding airborne particles, the size fraction also matters. The sampled fraction should represent the real fraction of airborne particles likely to be inhaled and to penetrate in the airways, i.e., the inhalable fraction of particles. As such, the cut-off diameter of the sampling head selected to collect airborne particles is of major importance. The smaller the particles are, the deeper they penetrate in the lung. But the smaller they are, the more difficult it is to achieve a sufficient collected mass to reach a relevant analytical limit of quantification for a given duration of active sampling. This duration should be kept at a minimum to limit the disturbance of occupants, and the sampling air flow rate must not be too high to prevent artificial dilution with outdoor air. Moreover the emerging concern associated with the recent and extensive use of engineered nanomaterials and their ability to emit nanoparticles in the environment has highlighted the importance of specific surface area.[51] For particles sharing the same chemical nature, the greater surface area per mass of ultrafine or nanoparticles compared with larger particles favors stronger sorption of chemicals and potentially more biologically active particles. Paradoxically, few papers have reported the influence of particle size on SVOC concentration adsorbed on those particles.

Rakkestad *et al.* (2007) measured phthalate concentrations (BBP, DBP, DCHP, DEHP) on PM_{10} and $PM_{2.5}$ in the air of fourteen different indoor environments (dwelling, kindergartens, primary schools, universities).[52] The contribution of total phthalates in $PM_{2.5}$ to total phthalates in PM_{10} ranged from 23% to 81% (w/w %), confirming that according to the collected size fraction, the exposure concentration may be under- or overestimated. Wang *et al.* (2013a, 2014) measured 16 PAHs and 26 PBDEs on airborne $PM_{2.5}$ and total suspended particles (TSP), respectively, in seven houses (sixty samples).[53,54] Overall the sum of PAH concentrations on TSP was nearly twice the sum of PAH concentrations on matched $PM_{2.5}$. Similarly, except for 5 compounds (BDE- 3, 196, 197, 206, and 207), both the median concentration and the range expressed in pg/m^3 were always higher on TSP compared to $PM_{2.5}$ for each BDE respectively. However standardized on the airborne particle mass (i.e., concentrations expressed in in ng/g), the PBDE loading was higher for the $PM_{2.5}$ rather than for TSP confirming that the SVOCs adsorb more on smaller size fractions.

As for settled dust, the size fraction of airborne particles has a direct influence on the measured concentration, and consequently on exposure assessment. The use of different size fractions in the studies reviewed in this paper may lead to the misclassification of the associated exposure and prevent from any rigorous comparison between studies.

Temporal and spatial variabilities of air and settled dust concentrations

Seasonal Variability. To assess the relevance of a given concentration to represent an average exposure concentration, the variation of concentrations according to seasons must be known. Nevertheless in comparison to the high number of papers dealing with SVOC measurements, few of them have repeated measurements in the same buildings at different seasons. Lu *et al.* (2004) measured organophosphorous pesticides in indoor air and settled dust at two seasons, summer and fall, in the home of 13 children.[55] Due to the small number of dwelling per stratum, agricultural and non-agricultural, and due to the non-detection of some compounds, no clear tendency could be observed. Diazinon in house dust was more frequently found and in higher concentrations during summer than during the fall. This was explained by the use of this compound for lawn treatment and the greater track-in in summer. Obendorf *et al.* (2006) also observed high pesticide concentrations in settled dust from 41 homes in summer compared to winter.[56] For SVOCs originating from outdoors, the sampling season is of importance, e.g., for agricultural pesticides due to seasonal culture treatment and PAHs due to emissions from the residential heating in winter. Romagnoli *et al*. (2014) in Italy, Zhu and Jia (2012) in the USA, Ohura *et al.* (2004) in Japan, and Zhu *et al.* (2009) in China observed significantly higher concentrations of particle-bound PAHs in the winter compared to the summer.[57-60] In addition to seasonality of the emission sources, the window opening vary also according to the season, having an expected impact on the air exchange rate and consequently on indoor air concentrations. The window opening in warm season leading to a higher ventilation might be less influent on settled dust concentration than on indoor air ones.

Temporal Variability Independently from Seasons. Whitehead *et al.* (2012) and Deziel *et al.* (2013) carried from one to seven measurements of PCB and pesticide carpet dust concentrations, by vacuuming the same area in the same room from 21 households, over a period of three years.[61,62] The target pesticides were: carbaryl, propoxur, chlordane, methoxychlor, chlorpyrifos, diazinon, cyfluthrin, cypermethrin, permethrin, dacthal, simazine, and trifluralin. Visits were distant from three to fifteen months. They calculated within-household variances and the impact on odds ratio from a hypothetical case-control study. They showed that for PCB- 138, 153, and 180, two dust measurements per dwelling were sufficient to reduce the attenuation bias to less than 20%. In other words, one single measurement is not enough to correctly characterize exposure concentration. Conversely for pesticides, the use of only one dust sample to represent an exposure period of approximately two years would not be expected to substantially attenuate odds ratio. Similarly for indoor air, Whyatt *et al.* (2007) measured insecticides in indoor air (gas + $PM_{2.5}$) over the final two months of pregnancy among a cohort of women from New York City.[63] The target pesticides were: chlorpyrifos, diazinon, malathion, methyl parathion, propoxur, bendiocarb, carbofuran, and cis- and trans-permethrin. No significant difference in air concentrations within homes was observed over time ($p \geq 0.2$), possibly because each sampling was integrated over 2 weeks. This was integrative and limited the influence of punctual events which would have more impacted a shorter sampling.

Muenhor and Harrad (2012) repeated settled dust measurements for eight consecutive months in two houses in Birmingham, UK, for PBDE measurements.[64] They showed that PBDE concentrations over time can differ, especially with the introduction or withdrawal of suspected sources. Batterman *et al.*

(2009) also observed that PBDE concentrations in dust samples collected at two different periods showed little consistency.[65] Vorkamp *et al.* (2011) collected two sets of dust samples in 43 dwellings occupied by pregnant women, immediately prior to delivery and approximately three months later.[66] BDE 183 and BDE 209 were analyzed in the two sets. Their respective concentrations (ln-transformed) were significantly correlated over the time, but varied in absolute values ($r = 0.564$ and $r = 0.700$ respectively, $p < 0.05$). On the contrary, Allen *et al.* (2008) reported no significant differences on concentrations of PBDEs in dust samples taken from the same indoor environments eight months apart.[47]

Spatial Variability within the Dwelling. For practical reasons and to minimize the operational and analytical costs, dust (if vacuumed) or air sampling is often performed in one given room (e.g., child bedroom, living room). The question of the spatial variability between rooms appears to be of interest while aiming at describing indoor exposure. Muenhor and Harrad (2012) sampled settled dust respectively in four and two separate rooms in two houses in Birmingham, UK, for PBDE measurements.[64] They showed that concentrations of PBDEs in separate rooms can differ quite markedly, particularly when suspected PBDE sources are present in one of the rooms, especially according to the type of flooring (carpet *vs.* hard surface). Allen *et al.* (2008) had previously come to the same conclusion.[47] Regarding the air, Pei *et al.* (2012) analyzed phthalates in indoor air samples from 10 newly decorated apartments (gas and particulate phases; 8-10 h sampling).[67] Three rooms were instrumented in each apartment: the bedroom, the living room and the study room. The phthalate concentrations differed in the rooms, with concentration in the living room generally higher than in the bedroom and the study room. The hypothesis provided by the authors is that the living room is the place of most of the household daily activities and is more decorated than the other rooms.

Spatial Variability within a Room. With respect to settled dust, when vacuumed or wiped, the question of variability within the room needs to be addressed first. Muenhor and Harrad (2012) sampled up to four different 1 m² areas per room, in the two homes that they have instrumented in Birmingham, UK, for PBDE measurements.[64] Overall they observed consistent PBDE levels except when one measurement area is close to a suspected source (TV, computer, chair, or sofa). Brommer *et al.* (2012) vacuumed dust from two different areas in a living room on three different dates.[68] They did not observe any within-room variability in organophosphate ester concentrations.

As a conclusion, data on temporal and spatial variabilities of SVOC concentrations in air or settled dust are scarce. One single measurement may not be enough in a given building and over a given period to correctly characterize the exposure of occupants. The results remain however inconsistent regarding the temporal variabilities; this could be, at least partially, due to the different sampling techniques from one study to another that might lead to opposite tendencies.

Bioaccessibility

The bioaccessibility of contaminants has been studied for a long time in environmental sciences, particularly in the field of soil contamination. It corresponds to the fraction of the pollutant that is adsorbed by the human organism and that contributes to the internal exposure dose.[69] It refers to digestive and dermal bioaccessibilities as well as bioaccessibility through respiratory tract. It was rarely taken into account in studies relative to indoor environments. For the first time, some recent publications addressed this issue for settled dust. Physiologically based *in vitro* digestion tests simulating stomach and intestine digestion were carried out to assess the bioaccessibility of pesticides,[69,70] PBDEs,[71] PCBs,[69,72] and phthalates[73] in settled dust. The methods used by Ertl and Butte (2012) included additionally the saliva digestion.[69] Moreover they studied the dermal bioaccessibility by the use of an artificial sweat close in composition to the natural one.

Pesticides. Ertl and Butte (2012) measured the following digestive bioaccessibilities respectively without and with whole milk mixed to the dust (sieved at 63 µm): pentachlorophenol: 12%/24%; lindane: 31%/51%; methoxychlor: 10%/29%; chlorpyrifos: 13%/41%; DDT 8%/30%; and permethrin: 7%/41%.[69] The authors concluded that the diet had a strong influence on the bioaccessibility. The dermal bioaccessibility was higher for all the compounds: pentachlorophenol: 35%; lindane: 94%; methoxychlor: 69%; chlorpyrifos: 56%; DDT 45%; and permethrin: 40%. The authors showed that the dermal bioavailability decreased when the molecular weight increased, as well as when the octanol-water partition coefficient decreased. Finally the authors tested the dermal bioaccessibility after the use of skin-care products separately: shower gel, skin cream, and body lotion. The results were heterogeneous between the compounds; in some case such as for pentachlorophenol, the dermal bioaccessibility increased dramatically. Wang *et al.* (2013b) determined digestive bioaccessibility, excluding saliva digestion, for indoor and outdoor settled dust samples (n=90 and 120 respectively; sieving fraction 63 µm).[70] They presented their results without separating indoor and outdoor dust samples, and reported that no significant difference was observed between indoor and outdoor dust ($p < 0.05$). The average digestive bioaccessibility was respectively: DDTs: 25%; hexachlorohexanes: 10%; heptachlor, trans-chlordane, cis-chlordane, trans-nonachlor, and cis-nonachlor: 13%; aldrin, dieldrin, and endrin: 12%; hexachlorobenzene: 14%; and Mirex 9.4%. Due to the different method and compounds, these results cannot be compared with Ertl and Butte (2012). Nevertheless the orders of magnitude are consistent in both studies.

PBDEs. Yu *et al.* (2012) studied the digestive bioaccessibility, saliva digestion excluded, of PBDEs in settled dust samples collected in homes by vacuuming the floor, sofa and electric appliances, and sieved at 250 µm.[71] The measurements were repeated at the four seasons. No relationship between the bioaccessibility and the bromination degree appeared; for example, the following mean values were observed in the summer samples: tri-BDEs (17, 28): 56%-35%; tetra-BDEs (47, 66): 32%-34%; penta-BDEs (85, 99, 100): 39%-24%-37%; hexa-BDEs (138, 153, 154): 52%-36%-36%; hepta-BDEs (183, 190): 41%-31%; and deca-BDE (209): 19%. For the winter samples, the mean bioaccessibilities were respectively: tri-BDEs (17, 28): 20%-37%; tetra-BDEs (47, 66): 22%-26%; penta-BDEs (85, 99, 100): 19%-16%-20%; hexa-BDEs (138, 153, 154): 35%-26%-26%; hepta-BDEs (183, 190): 28%-35%; and deca-BDE (209): 19%. No statistically significant correlation was found between the bioaccessibility and the octanol-water partition coefficient. Considering all the indoor and outdoor samples, the authors showed a significant negative correlation between the average digestive bioaccessibility of the total 13 target PBDEs and the organic matter content of dust ($p = 0.013$). However some individual PBDEs (5 out of 13, namely, BDE- 66, 99, 100, 153, and 183) showed a significant negative correlation ($p < 0.05$).

PCBs. Ertl and Butte (2012) reported an average digestive bioaccessibility for the six PCB congeners (28, 53, 101, 138, 153, and 180; 63-µm sieved dust) from less than 30% (dust only) to 90% (dust and skimmed milk to study the influence of food in the digestive tract).[69] For dust only, the digestive bioaccessibility ranged from 70% for PCB 28 to around 10% for PCB 180, decreasing with the chlorination degree increase. The same global trend was observed for dust with whole milk, except for PCB 180 which showed a very high digestive bioaccessibility, around 90%. The dermal bioaccessibility was higher for all the PCBs: 100% for PCB 28 and PCB 53; 68% for PCB 138; 32% for PCB 153; and 28% for PCB 180, showing a decrease with the chlorination degree increase. Wang *et al.* (2013c) presented results without separating indoor (n=40; dust vacuumed on floor, sofa, and electric appliances, and sieved at 100 μm) and outdoor (n=120; sieving fraction: 100 μm) dust samples.[72] Their reported that the digestive bioaccessibility of indoor settled dust samples was comparable with the results for outdoor dust samples. The median digestive bioaccessibility values of all the samples were the following: 3 tri-PCBs: 37%; 7 tetra-PCBs: 21%; 10 penta-PCBs: 18%; 9 hexa-PCBs: 21%; 6 hepta-PCBs: 15%; 2 octa-PCBs: 14%; and sum of the 37 PCBs: 20%. It also appears that the digestive bioaccessibility is decreasing with the chlorination degree increase.

Phthalates. Wang *et al.* (2013d) determined the digestive bioaccessibility for the same indoor and outdoor samples as previously described in this section.[73] Results for indoor and outdoor dust were not distinguished. The digestive bioaccessibilities of DiBP, DHP, BBP, DEHP, DCHP, DnOP and DNP + DiDP (2.4 to 13%) were significantly lower ($p < 0.05$) than those of DMP, and DPP (17 to 27%).

These studies emphasize the importance of the bioaccessibility. A default assumption of 100% intake in the human body will lead to possible over-estimation of exposure doses. A better evaluation of respective bioaccessibility according to the different exposure pathways would lead to a more accurate understanding of their contribution to total exposure. Meanwhile many factors influence this parameter such as the physical and chemical properties of the molecules (molecular weight, chlorination or bromination degree, octanol-water partition coefficient, etc.), and, for a given compound, the size of particles to which it is adsorbed, the organic matter content of dust, the type of diet, the other contaminants present in dust or airborne particles, the use of skin-care products, etc. Studies are too scarce to have a clear overview on SVOC bioaccessibility. Now that dermal exposure is considered to be a non-negligible exposure pathway, it is even more important to take into account bioaccessibility.[4]

SVOCS ON INDOOR DUST AND AIRBORNE PARTICLES: PREDICTION OF CONCENTRATIONS

Partitioning of SVOCs between gas and particulate phases

SVOCs in indoor air can partition between the gas and the particulate phases. In some studies only the gas phase or the particulate phase was measured depending on the available instruments and practices. Thus, to predict SVOC concentrations in an unmeasured phase, it is important to know how the SVOCs partition between the two phases under common indoor conditions. In some previous studies, SVOC concentrations in the gas and the particulate phases were measured separately. Such studies are rather scarce since breakthrough of SVOCs from the particle collection filter towards the polyurethane foam (PUF) may be observed[74] and lead to misinterpretation of the partitioning.

Batterman *et al.* (2009) monitored 12 private houses in southeastern Michigan, USA, during one week, at two different seasons from March 2006 to August 2007.[65] TBBPA and 21 PBDEs were analyzed in the gas and particulate phases (total suspended particles (TSP) on PTFE filters). Regarding TBBPA, the gas phase varied from 0 to 100% (w/w %) with a mean value of 43%, and the particulate phase from 0 to 100% with a mean value of 57%. The predominant phase was highly dependent on the season and can be completely reverse from one season to another. As for PBDEs, the percentage of the gas phase decreased when the bromination-degree increased. The following mean values for gas and particulate phases, respectively, were measured: BDE 17 (100%/0%); BDE 28 (88%/2%); BDE 47 (85%/15%); BDE 49 (80%/20%); BDE 66 (76%/24%); BDE 71 (83%/17%); BDE 75 (95%/5%); BDE 85 (45%/55%); BDE 99 (69%/31%); BDE 100 (77%/23%); BDE 153 (64%/36%); and BDE 154 (41%/59%).

For all the five phthalates (DMP, DEP, DBP, BBP, DEHP) measured in both the gas phase and the TSP in 10 newly decorated apartments, the concentration appeared to be non-negligible in any phase.[67] For DMP and DEP, the concentration was higher in the gas phase, approximately 80% considering the mean value in each phase. For DBP and BBP, the concentrations were in the same order of magnitude in both phases. Finally, the concentration of DEHP was generally higher in the particulate phase than in the gas phase. The authors conclude that the gas phase accounts for overall 60% of the sum of the five considered phthalates.

Lv *et al.* (2009) studied the concentrations of 16 PAHs in the gas and particulate phases in 9 dwellings in Yunnan, China, in January 2007.[75] The mass fractions in the gas phase compared to the total sampled mass in the air were higher than 91% for three-ring PAHs, between 50% and 54% for four-ring PAHs, and less than 5% for five-ring PAHs.

Takeuchi *et al.* (2014) measured the concentrations of 34 SVOCs in the gas and particulate phases in 6 houses in Sapporo, Japan, during 12 hours in summer and autumn in 2012.[76] The SVOCs include 12 phthalate plasticizers, 10 non-phthalate plasticizers, 10 phosphorous flame retardants, and 2 brominated flame retardants. The mass proportions of the SVOCs captured in the filters were compared with the molecular weights of the SVOCs. The mass proportions of DEP (molecular weight: 222 g/mol) in the particulate phase in the measured houses were less than 2%, while DiNP (molecular weight: 418 g/mol) existed only in the particulate phase. The authors concluded that SVOCs with higher molecular weight, namely with lower volatility, exist preferentially in the particulate phase. Similarly, Blanchard *et al.* (2014b) targeted a broad spectrum of SVOCs in gas and particulate phases (PM_{10}).[77] A total of 34 out of the 57 target compounds were detected in both media. The authors also concluded that the partitioning was also consistent with the compound volatility.

As a conclusion, partitioning of SVOCs between the gas and the particulate phase depends on the chemical family of SVOCs, and within some chemical families, on the congener itself depending on its physical and chemical parameters. Before planning any SVOC sampling, this issue must be considered in order to implement the adequate sampling methods to cover all the airborne concentration.

Partitioning of SVOCs between air and settled dust

Since SVOCs are present in both indoor air (gas and particulate phases) and settled dust, it would be interesting to predict the concentration in one media (e.g., gas phase) knowing the concentration in another one (e.g., settled dust). Some authors have thus investigated relationships between indoor air and settled dust concentrations. Weschler and Nazaroff (2008) proposed a partitioning model characterized by the particle-gas and dust-gas partition coefficients.[1] It allows calculating SVOC concentration in the air (gas phase and/or particulate phase) once the SVOC concentration in the settled dust is measured. As mentioned by the authors, such a model is relevant to provide a central tendency for a large number of buildings, but not for a given room. One possible reason is that SVOC concentrations measured in settled dust represent average levels of contamination over a longer period of time in comparison to air concentrations.

Regardless the theoretical model, the SVOC partitioning between air and settled dust has been reported from the field measurements.[7,79-82] The correlation coefficients observed are reported in Table 1.

[Table 1. Correlations between SVOC concentrations in indoor air and settled dust]

Despite different time frames associated to the respective sampling of air and dust, positive correlations exist between the two media, as far as both gas and particulate phases are sampled. Correlations are rather strong for some SVOCs, particularly for the more volatile ones: they partition more easily between the different phases. Future studies on the improvements of the estimation of the physical and chemical parameters of SVOCs (e.g., dust-gas partition coefficient) and of the standardization of the SVOC measurement in the air and settled dust may lead to better understandings of their partitioning between air and settled dust.

Relationships between different compounds

Some SVOCs belonging or not to the same chemical family may be used together as a formula in products or materials (e.g., commercial PCB mixtures) for a same purpose or combined effects. In that context, we can imagine that the concentration of a given compound in indoor air or settled dust could be predicted by the concentration of another chemical in the same media. The concentrations of the correlated compounds in indoor environment are associated to the mass fractions of the compounds in the emission source(s). Conversely the strong and positive correlation of two SVOCs could help identifying the emission source(s). In that perspective, we compiled in the Table 2 the correlations that have been reported between SVOC concentrations.

[Table 2. Correlations between SVOC concentrations]

Most of the reported correlations deal with SVOCs from the same group. The correlations observed between the PBDEs are consistent with the different commercial mixtures: the penta-BDE congeners were more used in textiles, particularly in polyurethane foams, while the deca-BDE was more used in electrical and electronic devices.[11] Overall too few data exist to make it possible to identify some compounds that could be considered as indicators of the other SVOCs and that would not require to measure all of them.

Prediction of concentrations: the contribution of modeling

In previous studies, the development of models to predict indoor SVOC concentrations was mainly carried out in two steps based on the mass transfer mechanism of SVOCs and the kinetics of indoor particles, respectively.

The first step based on the mass transfer mechanism of SVOCs describes the dynamic emission process of SVOCs from building materials. The pioneer model was developed by Xu and Little (2006) in environmental chambers.[90] The model considered the diffusion of SVOCs in the building material, the partition of SVOCs between the source material and the gas phase, the convective mass transfer of SVOCs between the source material and the chamber gas, and the partition of SVOCs between the chamber gas, the airborne particles, and the interior chamber surface. The model was validated by the experimental studies of the emission of DEHP from vinyl flooring in environmental chambers (i.e., FLEC and CLIMPAQ) for the duration of about 150 days to reach steady state. Then the model was improved by considering the convective mass transfer of SVOCs between the chamber gas and the interior chamber surface.[91] A new chamber system was developed to shorten the measurement of the emission characteristic parameters (e.g., the emission rate of SVOCs and the initial SVOC concentration in the building material) of DEHP from vinyl flooring to about 40 days to reach steady state. The model can be applied to the prediction of indoor SVOC concentration in the gas and particulate phases in environmental chambers as well as real indoor environment under temperature and ventilation controlled condition.

The second step based on the kinetics of indoor particles describes the behavior of indoor particles and their interactions with settled dust. Zhang *et al.* (2009) adapted an indoor multimedia fugacity model to investigate the emission and fate of PBDE taken into account the dynamic behaviors of the deposition of the airborne particles and the resuspension of the settled dust.[92] Liu *et al.* (2010) developed a model to describe the dynamical concentration of indoor airborne particles taken into account the emission rate of the indoor particle source, the interaction between indoor and outdoor particles, and the deposition and resuspension of particles.[93] Then they combined the model with the Xu and Little's model assuming a linear instantaneous equilibrium relationship between the SVOC concentrations in the gas phase and the particulate phase. However, SVOCs in the gas phase and particulate phase frequently cannot reach equilibrium instantaneously, particularly the SVOCs with high octanol/air partitioning coefficients and the particles with large diameters.[1] Therefore, Shi and Zhao (2012) developed a model taking into account the kinetical partitioning process between the gas and particulate phases of SVOCs.[94-96]

As a conclusion, the proposed models can predict SVOC concentrations in indoor environment provided that some key emission characteristic parameters are known. In addition, all of the models are applicable only in temperature and ventilation controlled environment.

Prediction of SVOC concentrations: the contribution of questionnaires

The prediction of a given SVOC concentration on the basis of a questionnaire describing the outdoor environment, the building characteristics, and the occupant past and current habits was also considered. The possibility to predict concentrations or range of concentrations would be of high interest, because much less expensive, less disturbing for the occupants, and independent from the environmental conditions at the time the sampling is made. However only one study was identified, that compared modeling on the basis of a questionnaire and measurements in indoor air and settled dust. Sexton *et al.* (2003) measured three organophosphate insecticides (chlorpyrifos, diazinon, malathion) and a herbicide (atrazine) in indoor air and settled dust from 102 houses in Minnesota, US.[100] The questionnaire consisted in questions related to the occupants and household characteristics (16 questions), the household pesticide use (23), and the occupant activities (6). Scores were calculated according to the reported pesticides used. But single questions as well as combinations of questions failed to predict higher individual pesticide concentrations in any of the sampling media.

To help in identifying the possibility to build questionnaires to predict concentrations on the basis of the existing knowledge, all the determinants, i.e., sources, building characteristics, occupant behavior and habits, and environmental factors, which were correlated with SVOC concentrations either in settled dust or indoor air were compiled in Table 3.

[Table 3. SVOC determinants in indoor air and settled dust]

This compilation shows the strong heterogeneity in knowledge regarding SVOC determinants. The brominated compounds and phthalates are those for which the most studies were carried out. Dust is the media for which SVOC determinants were mainly looked for. Overall, even if some factors are commonly reported by several studies, e.g., the building construction date, the floor and wall materials, and the frequency of cleaning, it appears not possible to substitute the environmental measurements of SVOCs by questionnaires to characterize population indoor exposure, even in groups defining the exposure strength (low, medium, and high). The age of the building has an important influence on measured concentration, which is quite expected since over the time the materials used do not contain forbidden or restricted compounds anymore (e.g., organochlorine and organophosphorous pesticides, phthalates, PCBs), or conversely they are too old to contain some new chemicals (e.g. PFC).

RESEARCH PERSPECTIVES

This review shows the high complexity of the exposure assessment to SVOCs and the numerous pending issues. One of the major issues is settled dust sampling that has already been emphasized by previous authors.[2,22,23] The sampling of settled dust was largely preferred due to its integrative nature; there is less fluctuation over time compared to air sampling and it reflects the past concentration as well. Nevertheless, many questions relative to settled dust sampling remain. To date, no consensus exists worldwide on which sampling method to use, which type of dust to sample and at which size fraction should it be sieved. The choice of the method depends on the research objective and the technical and financial constraints. To help in choosing the 'best' method in terms of type of dust and sieving fraction, studies combining the measurements of biomarkers and concentrations in different fractions from floor dust (vacuumed and collected from the vacuum cleaner bag) and multi-surface dust should be reviewed. Meanwhile without any certainty that the different types of dust can be considered as similar, it is fundamental that the sampling type and the sieving size are mentioned while comparing results.

The issue of bioaccessibility was also emphasized in this review. First orders of magnitude and influencing factors were listed. This parameter had not been addressed until recently, and it has never been studied for indoor airborne particles. But it appears to be a major element to better assess the human exposure and understand the bridge between environmental concentrations and human body burden.

Moreover an important heterogeneity is observed between the existing knowledge available for the different SVOC groups. Correspondingly, this review tends to show that more than the chemical group itself, it is the volatility of compounds that has a major influence on indoor partitioning. Partitioning between air and dust, correlation between 'fresh' vacuum dust and 'old' dust taken from the vacuum cleaner bag appear to be different between the more volatile compounds and the less ones. It could be interesting to check those observations for SVOC chemical groups that have not been addressed with respect to these questions to date.

Some other research perspectives were identified, especially for some SVOCs that have been less extensively considered. The Table 4 provides a summary of the target exposure key issues for which data exists on specific SVOC families. It emphasizes a continuing body of research on indoor SVOCs. A better understanding of distribution of concentrations according to the size of particles, spatial and temporal variabilities, dust homogeneity and in case of heterogeneity the respective contributions of the different dust to exposure is needed.

[Table 4. Synoptic table on environmental measurements and exposure issues for the different SVOC groups]

This review showed that few studies have considered a large spectrum of SVOCs simultaneously, and that indoor air contamination was less studied than settled dust. Knowing that SVOCs have common health effects and are acting through various exposure pathways, it is important to understand which kinds of SVOC mixtures are present in indoor environments, both in air and settled dust.

Environmental monitoring, as a complementary approach to biomonitoring, makes it possible to better understand the respective contributions of exposure media and pathways, and consequently to provide recommendations to reduce human exposure.

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LIST OF CHEMICAL NAME ABBREVIATIONS

8:2 FTOH: perfluoro octyl-ethanol

BADGE: bisphenol A diglycidyl ether

BBP: benzylbutyl phthalate

BDE: brominated diphenyl ether

BHT: dibutylhydroxytoluene

BPA: bisphenol A

BTBPE: 1,2-bis (2,4,6-tribromophenoxy) ethane

DBP: di-n-butyl phthalate

DCHP: dicyclohexyl phthalate

DEHA: di-(2-ethylhexyl) adipate

DEHP: di-2-ethylhexyl phthalate

DEP: diethyl phthalate

DiBP: di-isobutyl phthalate

DiDP: diisodecyl phthalate

DiNP: di-isononyl phthalate

DMCHP2: bis(methylcyclohexyl) phthalate

DMP: dimethyl phthalate

DMPP: dimethylpropyl phthalate

DNOP: di-n-octyl phthalate

DPEHP: diphenyl (2-ethylhexyl) phosphate

DPP: dipropyl phthalate

DUP: diundecyl phthalate

FOSA: perfluorooctane sulfonamide

FOSE: perfluorooctane sulfonamido ethanol

HBCD: hexabromocyclododecane

HCDBCO: hexachlorocyclopentadienyl-dibromocyclooctane

MeFOSE: N-methyl perfluorooctane sulfonamido ethanol

PBDE: polybrominated diphenyl ether

PFCAs: perfluoroalkyl carboxylates

PFOS: perfluoro-1-octane sulfonate

PFOA: perfluro-n-octanoic acid

PFHS: perfluorohexane sulfonate

TBB: 2-ethylhexyl-2,3,4,5-tetrabromobenzoate

TBBPA: tetrabromobisphenol A

TBEP: tris(2-butoxyethyl)phosphate

TBP: tri-butyl-phosphate

TBPH: bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate

TCEP: tris(2-chloroethyl)phosphate

TCP: tricresyl phosphate

TCPP: tris(2-chloro-iso-propyl)phosphate

TDC(I)PP: tris(1,3-dichloropropyl) phosphate

TEHP: tris(2-ethylhexyl)phosphate

TPP: triphenylphosphate

Table 1. Correlations between SVOC concentrations in indoor air and settled dust.

Reference	Compounds	Sampling strategy (sampled media and dust sieving fraction)	Number and type of buildings, country, sampling year	Relationships (correlation coefficient[1] and p-value in brackets)
(Bennett et al., 2015)[78]	Brominated compounds (BDEs 47, 99, 100, 153, 154, and 209)	Air: gas phase Dust: from vacuum cleaner bag, 150 µm	139 dwellings, USA, 2008-2009	BDE 47: 0.56 (< 0.001) ^{S} BDE 99: 0.55 (< 0.001) ^{S} BDE 100: 0.41 (< 0.001) ^{S} BDE 153: 0.25 (< 0.001) ^{S} BDE 154: 0.33 (< 0.001) ^{S}
(Imm et al., 2008)[79]	Brominated compounds (13 PBDEs)	Air: gas phase Dust: from vacuum cleaner bag, 1 mm	38 dwellings, USA, 2008	No correlation
(Thuresson et al., 2012)[74]	Brominated compounds (PBDEs, HBCD)	Air: gas + particulate phases Dust: vacuumed on the floor, no sieving	10 houses, 34 apartments, 10 day care centers and 10 offices, 2006	BDE 47 in houses, and BDE 28, BDE 99 and ΣPentaBDEs in apartments: 0.48-0.79 (<0.05)
(Wilford et al., 2005; Zhu et al., 2008)[80,81]	Brominated compounds (13 PBDEs, HCDBCO)	Air: gas phase Dust: from vacuum cleaner bag, 150 µm	64 homes in Ottawa, Canada, 2002-2003	PBDEs in dust all correlated with PBDEs in the air, except BDE 183 and BDE 209: 0.30-0.62 (<0.045), log-transformed concentrations HCDBCO: no correlation
(Bergh et al., 2011)[82]	Organophosphates (13 compounds)	Air: gas + particulate phases Dust: vacuumed on surfaces above floor, no sieving	10 homes, 10 day-care centers and 10 workplaces, Sweden, ?	TBP: 0.77 (0.05) TCEP: 0.71 (0.05) TCPP: 0.63 (0.05)
(Shoeib et al., 2011)[83]	Perfluorinated compounds (16 compounds; FTOHs, FOSAs, FOSEs, PFOS, PFCAs)	Air: gas phase Dust: from vacuum cleaner bag or swept on the floor, 150 µm	59 homes in Vancouver, Canada, 2006-2007	MeFOSE: 0.73 (<0.001) 8:2 FTOH: 0.33 (<0.01)
(Fromme et al., 2004)[7]	Phtalates (DMP, DEP, DBP, DiBP, BBzP, and DEHP)	Air: gas phase Dust: from vacuum cleaner bag, no sieving	59 urban apartments in Berlin, Germany (dust in a sub-sample of 30), 2000-2001	No correlation
(Bergh et al., 2011)[82]	Phthalates (DMP, DEP, DBP, DiBP, BBzP, and DEHP)	Air: gas + particulate phases Dust: vacuumed on surfaces above floor, no sieving	10 homes, 10 day-care centers and 10 workplaces, Sweden, ?	DBP: 0.44 (0.05) BBP: 0.44 (0.05)

[1] Pearson correlation coefficient except when marked with ^{S}: Spearman correlation coefficient; (-): p-value not provided. Only significant correlations are reported.

Table 2. Correlations between SVOC concentrations.

Reference	Compounds	Media: sampling; sieving fraction or duration	Number and type of buildings, country, sampling year	Relationships (correlation coefficient[1] and p-value in brackets)
(Ali *et al.,* 2012)[83]	Brominated flame retardants (11 PBDEs + BTBPE, TBB, TBPH)	Dust: vacuumed dust on floor; no sieving	34 homes, New Zealand, ?	BDE 47-TBB: 0.304 (0.040) [S] BDE 183-BTBPE: 0.411 (0.008) [S] BDE 197-BTBPE: 0.405 (0.009) [S]
(Batterman *et al.,* 2009)[65]	Brominated flame retardants (21 PBDEs + TBBPA)	Dust: vacuumed dust on floor; no sieving	12 single-family homes, USA, 2006-2007	BDE 28-BDE 47: > 0.75 (-) [S] BDE 47-BDE 99: > 0.75 (-) [S] BDE 85-BDE 100-BDE 190: > 0.75 (-) [S] BDE 207-BDE 208: > 0.75 (-) [S] BDE 206-BDE 207-BDE 209: > 0.75 (-) [S]
(Kubwabo *et al.,* 2012)[44]	Musks (13 compounds[#])	Dust: vacuum cleaner bag + vacuumed dust on floor; 80 µm	49 randomly selected urban single family dwellings, Canada, 2007-2010	No correlation found
(Araki et al., 2014)[41]	Organophosphates (TBP, TCPP, TCEP, TEHP, TBEP, TDCIPP, TPP)	Dust: vacuumed on floor or on multi-surface above floor; no sieving	156 single-family homes, Japan, 2006	Floor dust: Overall weak but significant positive correlations TDCIPP: the less correlated Higher r: TEHP-TBEP: 0.733 (<0.01) Multi-surface dust: Overall weak but significant positive correlations TBEP: the less correlated Higher r: TCPP-TDCIPP: 0.516 (<0.01)
(Wang *et al.,* 2012)[84]	Parabens (methyl-, ethyl-, propyl-, butyl-, benzyl- and heptyl-parabens) and bisphenols (BPA, BADGE)	Dust: vacuumed dust on floor + swept dust; 2 mm	158 dwellings, offices and laboratories from USA, South Korea, China and Japan, 2006-2012	Methyl paraben-propyl paraben: 0.70 (<0.0001) BPA-BADGE: 0.308 (<0.0001) (expressed in nmol/g of dust)
(Kubwabo *et al.,* 2005)[85]	Perfluorinated compounds (PFOS, PFOA, PFHS)	Dust: vacuum cleaner bag; 150 µm	67 randomly selected urban homes, Canada, 2002-2003	PFOS-PFOA: 0.753 (<0.0001) [S] PFOS-PFHS: 0.868 (<0.0001) [S] PFOA-PFHS: 0.591 (<0.0001) [S]

Reference	Compounds	Media: sampling; sieving fraction or duration	Number and type of buildings, country, sampling year	Relationships (correlation coefficient[1] and p-value in brackets)
(Shoeib *et al.*, 2011)[86]	Perfluorinated compounds (16 compounds; FTOHs, FOSA, FOSE, PFOS, PFCAs)	Air: gas phase; 4 weeks	59 homes in Vancouver, Canada, 2007-2008	6:2 FTOH, 8:2 FTOH, and 10:2 FTOH: 0.88 (<0.001) MeFOSE, MeFOSA, and EtFOSA: 0.86 (<0.001)
		Dust: vacuum cleaner bag + swept dust on floor if no vacuum cleaner; 150 µm	152 homes in Vancouver, Canada, 2007-2008	6:2 FTOH, 8:2 FTOH, and 10:2 FTOH: 0.97 (<0.001) MeFOSE-MeFOSA: 0.78 <0.001) MeFOSE-PFOA: 0.46 (<0.001) MeFOSE-PFOS : 0.51 (<0.001) PFOS-PFOA: 0.79 (<0.001)
(Gevao *et al.*, 2013)[87]	Phthalates (BBP, DBP, DEHP, DEP, DMP, DNOP, DCHP, DNHP)	Dust: vacuum cleaner bag; 250 µm	21 homes, Kuwait, ?	DBP-DEP: 0.6 (0.004) [S] BBP-DBP: 0.46 (0.036) [S] DEHP-BBP: 0.57 (0.006) [S]
(Van den Eede *et al.*, 2011)[88]	Brominated flame retardants (14 compounds) and organophosphates (10 compounds)	Dust: vacuumed dust on floor; 500 µm	33 dwellings, Belgium, 2008	TCPP-Penta-BDEs: 0.418 (0.02) [S] TCPP-Octa-BDEs: 0.565 (0.002) [S] (TPP+TCP)-Penta-BDEs: 0.532 (0.003) [S] TPP-Penta-BDEs: 0.451 (0.014) [S] TCP-Penta-BDEs: 0.466 (0.011) [S] TCP-Deca-BDEs: 0.533 (0.003) [S]
(Hoffman et al., 2015)[89]	Brominated flame retardants (6 PBDEs) and organophosphates (TDCIPP, TPHP)	Dust: vacuumed dust on floor; 500 µm	49 dwellings, USA, 2012	Tetra-, penta-, and hexa-BDEs: all correlated: 0.88-0.97 (<0.001) [S] BDE 209 correlated with the other PBDEs: 0.31-0.44 (<0.05) [S] TDCIPP correlated with all the PBDEs: 0.50-0.57 (<0.001) [S] TPHP-BDE 47: 0.37 (<0.01) [S] TPHP-BDE 100: 0.33 (<0.05) [S] TPHP-BDE 209: 0.29 (<0.05) [S]

[1] Pearson correlation coefficient except when marked with [S]: Spearman correlation coefficient; (-): p-value not provided. Only significant correlations are reported.

[#]: musk ketone, musk xylene, musk ambrette, musk moskene, Galaxolide®, Tonalide®, Celestolide®, Phantolide®, Traseolide®, Cashmeran®, Musk T, HHCB-lactone, and OTNE (Iso E Super®)

Table 3. SVOC determinants in indoor air and settled dust.

Reference	Compounds	Media: sampling; sieving fraction or duration	Number and type of buildings, sampling year	Determinant factors (as labeled by the authors)	Relationships *
(Cequier et al., 2014)[97]	Brominated compounds (BDEs 28, 47, 85, 99, 100, 153, 154, 183, and 209)	Air: gas and particulate phases; 24h Dust: vacuumed on floor; 150 µm	47 dwellings in the greater Oslo area, Norway, 2012	Number of vacuum cleaning in the living room per week	BDE 47 / air: β=0.093 (0.04) BDE 99 / air: β=0.091 (0.044) BDE 100 / air: β=0.093 (0.046)
				Number of DVD and video players	BDE 85 / air: β=0.282 (0.001)
				Distance (m) of the sampling equipment from TV in the living room	BDE 47 / air: β=0.104 (0.01) BDE 99 / air: β=0.122 (0.003) BDE 100 / air: β=0.113 (0.007)
				Renovation of the house in the last 5 years (no/yes)	BDE 85 / air: β=0.236 (0.029)
				Electric panel heaters (no/yes)	BDE 85 / air: β=-0.371 (0.003) BDE 28 / dust: β=-0.456 (0.001) BDE 47 / dust: β=-0.551 (0.013)
				Construction year	BDE 28 / dust: β=-0.008 (0.008)
				Size of the living room in m²	BDE 28 / dust: β=-0.010 (0.032) BDE 47 / dust: β=-0.016 (0.037)
				Size of the apartment in m²; Number of tube TVs in the household; Humidity; Temperature; Location of the house (rural/urban); Type of household (non-detached/detached); Fireplace in the living room (no/yes); Carpets in the living room (no/yes); Chairs made of PUF in the living room (no/yes)	No significant associations
(Wang et al., 2015)[98]	Brominated compounds (BDEs 28, 47, 99, 100, 153, 154, 183, and 209)	Dust: vacuumed on floor; 150 µm	216 urban dwellings, China, 2011	Solid wood floor	BDE 28 (ln): β=0.62 (<0.05)
				Wet mop used	BDE 28 (ln): β=1.24 (<0.05)
				Outdoor concentration (ln)	BDE 47 (ln): β=0.19 (<0.05)
				Frequency of cleaning	BDE 154 (ln): β=-0.351 (<0.001)
				Wall paper	BDE 154 (ln): β=0.86 (<0.05)
				Frequency of window opening	BDE 153 (ln): β=-0.52 (<0.05)

Reference	Compounds	Media: sampling; sieving fraction or duration	Number and type of buildings, sampling year	Determinant factors (as labeled by the authors)	Relationships *
(Whitehead *et al.*, 2013)[99]	Brominated compounds (22 PBDEs)	Dust: vacuum cleaner bag; 150 µm	292 dwellings, USA, 2001-2007; 2010	Outdoor environment	Significantly lower [tri- to hexa-BDEs] in rural residences (37-44% lower; $p<0.05$) Significantly lower [BDE-183] in rural dwellings (42% lower; $p<0.05$)
				Upholstered furniture with exposed foam	Significantly higher [tri- to hexa-BDEs] in dwellings with (52-62% higher; $p<0.05$)
				New carpet installed at any time after move-in, round 2 (2010) *versus* round 1 (2001-2007)	Significantly lower [BDE-28, -47, and -153] if carpet change (respectively 34, 35, and 30% lower; $p<0.05$)
				Carpet coverage (<25%) Residence square footage Residence construction date Household annual income (≥$75,000) Number or use of television or computers Number of upholstered pieces of furniture	No significant association with a change in concentration between dwellings for any BDE
(Araki et al., 2014)[41]	Organophosphates (TBP, TCPP, TCEP, TEHP, TBEP, TDCIPP, TPP)	Dust: vacuumed on floor or on multi-surface above floor; no sieving	156 single-family homes, Japan, 2006	Building structure (wooden *vs*. other) Age of house (3-5 or 6-8) Renovation with the past year (yes *vs*. no) Wall materials (PVC *vs*. other) Floor materials (wooden *vs*. other) Wall-to-wall carpeting (PVC *vs*. other) Frequency of window opening (more or less than 15 times per month) Mechanical ventilation equipment (in use vs. never used/no equipment)	Floor dust: ↑ TBEP with wooden structure (0.002) ↓ TCPP, TCEP, TEHP, and TBEP with frequency of window opening over 15 times/month (<0.034) ↑ TEHP, and TBEP with the use of a mechanical ventilation equipment (<0.013) Multi-surface dust: ↑ TCPP, TCEP, and TPP with wooden structure (<0.04) ↑ TCPP in older homes (0.049) ↑ TBEP with wooden floor (0.016) ↓ TCPP, TEHP, TDCIPP, and TPP with frequency of window opening over 15 times/month (<0.046) ↑ TCPP, TEHP, and TDCIPP with the use of a mechanical ventilation equipment (<0.029)

Reference	Compounds	Media: sampling; sieving fraction or duration	Number and type of buildings, sampling year	Determinant factors (as labeled by the authors)	Relationships *
(Kubwabo *et al.,* 2005)[85]	Perfluorinated compounds (PFOS, PFOA, PFHS)	Dust: vacuum cleaner bag; 150 µm	67 randomly selected urban Canadian homes, 2002-2003	House age	PFOS: ρs=-0.340 (0.0049) PFOA: ρs=-0.335 (0.0055) PFHS: ρs=-0.212 (0.0845)
				Percentage of surface covered by carpet	PFOS: ρs=0.385 (0.0013) PFOA: ρs=0.365 (0.0024) PFHS: ρs=0.356 (0.0031)
				Percentage of surface covered by carpet	Sum of the 5 phthalates: none
(Ait Bamai *et al.,* 2014)[42]	Phthalates (BBP, DBP, DEHP, DEP, DiBP, DiNP, DMP), DEHA, BHT	Dust: vacuumed on floor or on multi-surface above floor; no sieving	128 dwellings in Sapporo, Japan, 2009-2010	Age of building	Floor dust: DBP: ρs=0.241 (<0.01) DEHP: ρs=0.235 (<0.01) Multi-surface dust: BBP: ρs=0.188 (<0.05) DBP: ρs=0.460 (<0.01) DEHP: ρs=0.180 (<0.05) BHT: ρs=0.227 (<0.01)
				Height of ceiling	Multi-surface dust: DBP: ρs=-0.201 (<0.05) DEHP: ρs=-0.253 (<0.01) BHT: ρs=-0.179 (<0.05)
				Frequency of living room cleaning	Floor dust: DiBP: ρs=0.197 (<0.05)
				Floor materials (4 categories) PVC wall paper (yes *vs*. no) PVC ceiling (yes *vs*. no) Number of PVC interior materials (floor, wall and ceiling) (from 0 to 3) Type of dwelling (single- *vs*. multi-family) Building structure (wooden *vs*. reinforced concrete) Dampness index (from 0 to 5) Annual household income (5 categories)	Floor dust: ↑ DBP with no PVC ceiling (<0.01) ↑ DEHP with PVC floor (<0.01) Multi-surface dust: ↑ DBP with no PVC ceiling (<0.05) ↓ DBP with dampness index=0 (<0.01) ↑ DEHP with PVC wall paper (<0.05) ↓ DEHP with 0 PVC material (<0.05) ↑ DEHP in single-family house (<0.05) ↑ DEHP with wooden structure (<0.05) ↓ DEHP with dampness index=0 (<0.05)

Reference	Compounds	Media: sampling; sieving fraction or duration	Number and type of buildings, sampling year	Determinant factors (as labeled by the authors)	Relationships *
					↑ DiNP with PVC wall paper (<0.01) ↑ DiNP with PVC ceiling (<0.01) ↑ BHT in single-family house (<0.05)
(Bornehag *et al.,* 2005)[35]	Phthalates (BBP, DEHP)	Dust: vacuumed on multi-surface above floor; no sieving	390 dwellings, Sweden, 2001-2002	PVC as flooring (yes *vs.* no)	Dust concentration above the median: BBP: OR=3.85 (95%CI 2.37-6.24) DEHP: OR=1.85 (95%CI 1.15-2.98)
				Construction period (before 1960 *vs.* after 1983)	DEHP: OR=2.30 (95%CI 1.17-4.52)
				Water leakage during previous 3 years (yes *vs.* no)	BBP: OR=1.84 (95%CI 1.05-3.22)
				Vinyl as wall material Type of building (single- *vs.* multi-family) Ventilation rate in the room	No significant association
(Fromme *et al.,* 2004)[7]	Phthalates (BBP, DBP, DEHP, DEP, DMP, DMPP, DNOP, DPP, DCHP)	Air: gas phase, 7h Dust: vacuum cleaner bag; no sieving	59 urban apartments in Berlin, Germany (dust in a sub-sample of 30), 2000-2001	Smoking; Home age; Furnishings; Floor coverings; Type of heating; Heating material; Renovation within the previous few months; Temperature; Humidity	No significant association
(Becker *et al.*, 2006)[101]	Pesticides (permethrin)	Dust: vacuum cleaner bag; 2 mm	503 dwellings, Germany, 2001-2002	Carpet in natural fibres (surface in m²) Use of biocide for pets (*vs.* no use) Use of biocides against insects indoors (*vs.* no use)	β=0.35 (<0.001) β=0.15 (<0.001) β=0.11 (0.011)

* The relationship is described by i) the Pearson correlation coefficient r or the Spearman correlation coefficient ρ_s, with the p-value in brackets (or - if not reported) in case of continuous variables, ii) the p-value in case of a significant difference obtained from a test performed on categorical variables (e.g., Mann-Whitney, Kruskal-Wallis tests), iii) the standardized regression coefficient β for multiple linear regression, or iv) the odds ratio OR with the 95% confidence interval (95%CI) for multiple logistic regression. (ln) means that concentrations were log-transformed.

Table 4. Synoptic table on environmental measurements and exposure issues for the different SVOC groups.

Chemical groups	**Type of settled dust**	**Vacuum cleaner bag dust *vs.* vacuumed dust**	**Concentration *vs.* size (A=air; D=dust)**	**Temporal variability (A=air; D=dust)**	**Spatial variability (A=air; D=dust)**	**Bio-accessibility (DI=digestive ; DE=dermal)**	**Partitioning gas/particles in indoor air**	**Partitioning air/settled dust**	**Correlations between congeners (A=air; D=dust)**	**Determinants (A=air; D=dust)**
Alkylphenols										
Chlorinated paraffins										
Brominated compounds	✓	✓	✓ (A+D)	✓ (D)	✓ (D)	✓ (DI)	✓	✓	✓ (D)	✓ (D)
Fluorinated compounds								✓	✓ (A+D)	✓ (D)
Musks		✓							✓ (D)	
OC and OP pesticides			✓ (D)	✓ (A+D)		✓ (DI+DE)				
Organophosphate esters	✓	✓			✓ (D)			✓	✓ (D)	✓ (D)
Organotins										
PAHs			✓ (A+D)	✓ (A)			✓			
Parabens									✓ (D)	
PCBs				✓ (D)		✓ (DI+DE)				
Phenols										
Phthalates	✓	✓	✓ (A)		✓ (A)	✓ (DI)	✓	✓	✓ (D)	✓ (D)
Pyrethroids						✓ (DI+DE)				✓ (D)
Triclosan										

Chapitre 2 : Contamination en COSV des poussières des logements français

2.1 Matériel et méthodes

L'étude de la contamination des logements en COSV a été permise grâce à la collecte de sacs d'aspirateur réalisés dans les logements inclus dans l'enquête nationale Plomb-Habitat (Lucas et al., 2012 ; Glorennec et al., 2015). Cette dernière avait pour objectif la connaissance de la contamination en plomb dans les poussières au sol, les peintures, l'eau du robinet, le sol extérieur, etc., des logements français accueillant des enfants âgés de 6 mois à 6 ans. L'enquête Plomb-Habitat était elle-même nichée au sein de l'enquête nationale Saturn'Inf, qui visait à la détermination de la prévalence du saturnisme infantile en France (Etchevers et al., 2014). Le recrutement des enfants de Saturn'Inf s'est fait via le tirage au sort d'hôpitaux, puis l'inclusion « en tout venant » parmi les enfants hospitalisés dans 125 services de pédiatrie et 18 services de chirurgie pédiatrique. Un sous-échantillon d'enfants de Saturn'Inf a été tiré au sort et les parents se sont vu proposer une visite à domicile pour des mesures. 484 familles ont accepté ; les 484 logements inclus sont visualisés la Figure 3. Lors des investigations de terrain, le sac de l'aspirateur domestique a été demandé à la famille par le technicien.

Figure 3 : Localisation géographique des 484 logements enquêtés dans le cadre de « Plomb-Habitat »

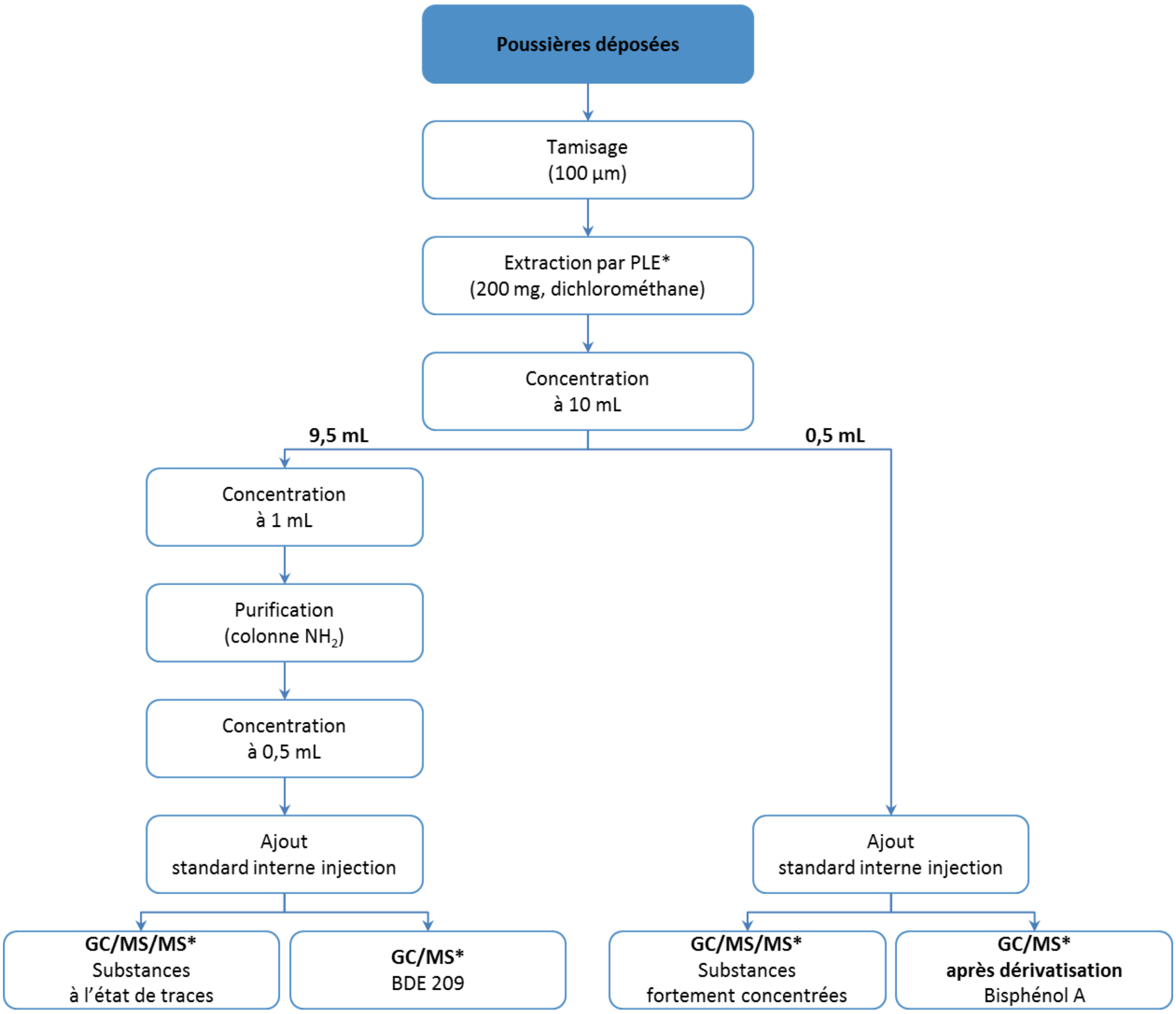
Les logements considérés dans le contexte de l'analyse des COSV sont ceux pour lesquels un sac d'aspirateur a bien été récupéré lors de la visite du logement par le technicien enquêteur et dont l'aspirateur n'avait pas servi à aspirer la cheminée, le barbecue ou l'extérieur. Les sacs ayant servi en partie au nettoyage de l'intérieur d'une voiture ont été analysés et inclus *a posteriori* constatant que les distributions de leurs concentrations en COSV ne différaient pas de celles de ceux n'ayant pas été utilisés à cette fin. Il a aussi été vérifié que les logements avec des sacs exclus ne différaient pas de l'ensemble des autres logements pour l'année de construction, le type de logement et le revenu du ménage. Le deuxième critère requis pour l'analyse du sac d'aspirateur a été la conservation des échantillons de poussières dans des conditions acceptables au vu des molécules visées. Les travaux de Blanchard et al. (2014b) ont été utilisés pour cette sélection et les sacs n'ayant pas rempli les conditions de stockage garantissant la conservation des molécules ont été exclus. Plus précisément, les sacs conservés pour l'analyse sont ceux avec :

- conditionnement en sac poubelle moins de 60 jours chez l'enquêteur, incluant le transport, à température ambiante et moins de 180 jours à 5°C au laboratoire ;
- conditionnement en sachet zippé moins de 60 jours chez l'enquêteur, incluant le transport, à température ambiante et moins de 90 jours à 5°C au laboratoire.

Le dernier critère de sélection des sacs d'aspirateur portait sur une quantité minimum de 200 mg après tamisage, masse nécessaire pour réaliser la quantification des molécules recherchées. Un tamisage à 100 µm a été retenu pour deux raisons : d'une part, d'après la littérature scientifique analysée par Mercier et al. (2011) et Cao et al. (2012), les particules de diamètre inférieur à 100-200 µm adhèrent plus à la peau, donc contribuent à l'exposition aux composés étudiés. D'autre part, le matériau de référence certifié SRM 2585 fourni par le *National Institute of Standards and Technology* (NIST), utilisé pour la mise au point et l'évaluation des performances des méthodes d'analyse des poussières sédimentées, est un mélange de poussières tamisées à 90 et 100 µm.

Au final, 145 échantillons de poussières tamisées à 100 µm, représentant 145 logements, répondent à tous les critères de sélection.

La Figure 4 résume les différentes étapes de traitement analytique des échantillons de poussières sédimentées, dont le détail est publié par Mercier et al. (2014).



*GC/MS : Gas Chromatography/Mass Spectrometry ; GC/MS/MS : Gas Chromatography/tandem Mass Spectrometry ; PLE : Pressurized Liquid Extraction

Figure 4 : Filières analytiques selon le type de composés analysés dans les poussières au sol

L'application des poids de sondage (i.e. l'inverse de la probabilité d'être tiré au sort lors de l'échantillonnage) à chacun des 145 logements a permis d'exprimer les concentrations mesurées à l'échelle du parc des logements accueillant des enfants de 6 mois à 6 ans. Compte tenu de l'analyse des poussières de 145 logements sur les 484 instrumentés, les poids de sondage ont dû être corrigés.

2.2 Résultats et conclusion

Les résultats obtenus montrent que 32 des 48 COSV recherchés sont présents dans les poussières au sol d'au moins un logement sur deux. Les 6 phtalates recherchés, 3 HAP, la galaxolide et la tonalide, le BDE 209, la perméthrine, le bisphénol A et le tributylphosphate sont détectés dans plus de 98 % des logements. Le dichlorvos n'a jamais été détecté. Les concentrations sont très hétérogènes, puisqu'elles vont de valeurs maximales supérieures à 1 mg/g pour quatre phtalates : DEHP, DiNP, DiBP, BBP et la perméthrine, tandis qu'elles sont de l'ordre de quelques dizaines de ng/g pour plusieurs BDE et quelques PCB.

De la mise en perspective avec les concentrations déjà mesurées en France et dans d'autres pays, il ressort que les concentrations médianes sont du même ordre de grandeur pour l'ensemble des COSV, à l'exception du DiBP et du bisphénol A pour lesquels les concentrations apparaissent supérieures en France.

La mise en perspective des concentrations observées avec celles déjà mesurées dans d'autres pays a rappelé l'hétérogénéité des méthodes de mesure des COSV dans les poussières, qu'il s'agisse d'échantillonnage des poussières (méthode et type de poussières collectées), de préparation des échantillons (tamisage notamment) et d'analyse. Une attention particulière doit être portée à chacun de ces aspects lors de l'utilisation de données de mesure, afin de garantir une meilleure comparaison des concentrations. L'établissement de normes internationales ou *a minima* de lignes directrices faisant consensus est vivement souhaité, afin de permettre, outre une meilleure comparabilité des résultats, une analyse globale de ceux-ci afin d'identifier d'éventuelles spécificités géographiques et d'étudier les évolutions temporelles des concentrations en COSV. A ce jour, malgré les nombreuses données disponibles, on ne peut pas les considérer dans leur ensemble ; trop de facteurs varient d'une étude à l'autre en plus des lieux et dates de prélèvement.

Les exploitations détaillées sont présentées dans la publication soumise à *Indoor Air*.

Semi-volatile organic compounds in home settled dust: A nationwide survey in France

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Abstract

Forty-eight semi-volatile organic compounds (SVOCs)—phthalates, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pyrethroids, organochlorine and organophosphorous pesticides, synthetic musks, bisphenol-A, and tributylphosphate—were measured in home settled dust collected from 145 household vacuum cleaner bags. Using sampling weights, the concentration estimates were provided for the entire stock of French dwellings with at least one child aged 6 months to 6 years, namely, 3,581,991 housing units. Thirty-two compounds were detected in more than half of the dwellings. Among them, six phthalates, three PAHs, galaxolide and tonalide, BDE 209, permethrin, bisphenol-A, and tributylphosphate were detected in more than 98% of the dwellings. The median di-iso-butyl phthalate (DiBP) and bisphenol-A concentrations in France (17 and 4.2 µg/g, respectively) were higher than those in other countries. Approximately 40% of the dwellings showed high levels for several SVOCs in settled dust, in particular, PCBs, whereas 15% shared the lowest levels of SVOCs. The year of building construction and the frequency of floor dry cleaning appeared to correlate with SVOC concentrations.

Keywords: Indoor environment; Dwelling; Hierarchical cluster analysis; Phthalate; PBDE; PCB

Practical implications

Semi-volatile organic compounds (SVOCs) are estimated in home settled dust at a national level. Thirty-two out of forty-eight target SVOCs are found in at least 50% of dwellings. Phthalates, bisphenol-A, permethrin, and galaxolide are the most concentrated compounds (medians > 1 µg/g). The dwellings can be classified in four groups according to their pattern of SVOC mixtures. The age of the building and the frequency of floor dry cleaning are associated with the concentrations of some SVOCs in home settled dust.

Introduction

Home settled dust contains numerous environmental contaminants, including semi-volatile organic compounds (SVOCs). SVOCs correspond to a class of organic compounds with vapor pressures between 10^{-14} and 10^{-4} atm (10^{-9} to 10 Pa) (Weschler and Nazaroff, 2008). These molecules have a large spectrum of properties and, accordingly, are integrated (or were integrated regarding those that are now phased-out) in a broad variety of applications and consumer products (Weschler and Nazaroff, 2008; Mercier et al., 2011). For example, polybrominated diphenyl ethers (PBDEs) are used as flame retardants in furniture, textiles, wire insulation, and electronic appliances (Birnbaum and Staskal, 2004). Phthalates are used as plasticizers to improve polymer flexibility and thus added to numerous polyvinyl chloride materials (Kamrin, 2009). Some are also used in adhesives, detergents, cosmetics and personal care products. Bisphenol-A is used to produce polycarbonate and epoxy resins, which are integrated into a variety of consumer products, including baby bottles or food cans (Vandenberg et al., 2007). Evaporation or abrasion from these manufactured products leads to the emission of SVOCs in the indoor environment and to the contamination of settled dust.

Numerous studies worldwide have investigated concentrations of various SVOCs in home settled dust, mainly halogenated compounds including PBDEs, phthalates, perfluorinated compounds (PFCs), pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and organophosphate flame retardants, and, to a lesser extent, bisphenol-A, alkylphenols, synthetic musks, parabens, chlorinated paraffins, and organotins (Roberts et al., 2009; Mercier et al., 2011; Whitehead et al., 2011; Besis et al., 2012; Coelho et al., 2014; Nadal and Domingo, 2014; Ma and Harrad, 2015).

For some SVOCs, home settled dust has been shown to be a non-negligible contributor to children's exposure. Fromme et al. (2004a) evaluated that home settled dust contributed to 25% of the daily dose of di(2-ethylhexyl) phthalate (DEHP) for a child weighing 13 kg. Wormuth et al. (2006) also showed that the ingestion of settled dust was a non-negligible route of exposure to phthalates for infants and toddlers in Europe, reaching 70% of the mean daily dose for butylbenzyl phthalate (BBP), 40% for di-iso-decyl phthalate (DiDP), 35% for DEHP, 30% for di-iso-butyl phthalate (DiBP), and 10% for di-n-butyl phthalate (DBP). Regarding PBDEs, Jones-Otazo et al. (2010) found that the ingestion of settled dust was the largest contributor to the PBDE exposure of toddlers among the population of urban Canadians. Trudel et al. (2011) also showed that for infants in North America, the ingestion of indoor settled dust comprised 30-70% of the total daily dose.

Concurrently, the overall exposure of the population to SVOCs raises concerns because the health effects for some of them are now well established or suspected (Birnbaum and Staskal, 2004; Jaakkola and Knight, 2008; Kamrin, 2009; Van der Veen and De Boer, 2012; Lyche et al., 2015; Saillenfait et al., 2015). Some have the potential to disrupt endocrine functions while interfering with hormones (Hwang et al., 2008; Rudel and Perovich, 2009).

The main objective of this study was to assess the SVOC concentrations in home settled dust at a nationwide level in France, with the final goal of assessing the domestic cumulative exposure to these substances and associated health risks (Glorennec et al., 2015). Additional objectives were: i) to study the relationships between SVOC concentrations in settled dust and some variables describing the environment, building and floor cleaning habits and ii) to determine the percentage of dwellings that were polluted by multiple SVOCs in settled dust.

Materials and methods

Sample of dwellings

As part of a national survey regarding the blood lead levels of children aged 6 months to 6 years (Etchevers et al., 2014), 484 dwellings were randomly selected for residential environmental sampling. These dwellings were distributed across France, excluding oversea territories. The sampling design has been extensively described by Lucas et al. (2012). It was designed such that these 484 dwellings represented the entire housing stock where at least one child aged 6 months to 6 years lived. The size of the target population was 3,581,991 dwellings.

The environmental sampling was performed between October 2008 and August 2009. It included the collection of household vacuum cleaner bags; 300 households provided their consent. Additional information, such as urban or rural setting, the type of building (single house or multi-family building), the building construction year, and the type and weekly frequency of floor cleaning, was also collected.

Target compounds

The SVOCs to be analyzed in the dust samples were selected using a ranking method based on their toxicity and indoor concentrations. For each SVOC in a starting list of 156 compounds, a literature review provided data on its frequency of detection and reported concentrations in home settled dust, primarily in France or, most of the time, in other countries by default. The toxicity reference doses were retrieved from toxicity databases or were calculated based on the No Observed Adverse Effect Levels (or Lowest Observed Adverse Effect Levels) and uncertainty factors. Ranking scores were calculated by comparing the contamination levels and reference doses (Bonvallot et al., 2010).

The SVOCs at the top of the prioritization list were phthalates, pesticides, short-chain chlorinated paraffins, PBDEs, PFCs, organotins, PCBs, and PAHs. Those that could be analyzed simultaneously through a multi-residue analytical method by gas chromatography coupled with mass spectrometry (GC-MS) were selected. Despite a lower ranking, some substances were added because they could be analyzed with the same analytical method.

The final list included 48 SVOCs—7 organochlorine pesticides: dieldrin, aldrin, endrin, γ-hexachlorohexane (γ-HCH or lindane), 4,4'-dichloro-diphenyldichloro-ethylene (4,4'-DDE), oxadiazon, and α-endosulfan; 3 organophosphorous pesticides: dichlorvos, chlorpyrifos, and diazinon; 4 pyrethroids: cyfluthrin, cypermethrin, deltamethrin, and permethrin; 10 PCBs: congeners 28, 31, 52, 77, 101, 105, 118, 126, 138 and 153; 6 phthalates: benzylbutyl phthalate (BBP), di-n-butyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), di-iso-butyl phthalate (DiBP), and di-iso-nonyl phthalate (DiNP); 9 PBDEs: congeners 28, 47, 153, 154, 85, 99, 100, 119 and 209; 2 synthetic musks: galaxolide and tonalide; 5 PAHs: anthracene, acenaphthene, benzo(a)pyrene, fluorene, phenanthrene; bisphenol-A; tributylphosphate.

Sample selection and preparation

The vacuum cleaner bags were sorted before the treatment of dust. Those containing dust from outside the dwelling or from the fireplace, as reported by the household, were discarded. The bags that did not meet the conservation packaging, temperature and duration criteria established by Blanchard et al. (2014a) were discarded. Before the analysis, the dust was sieved at 100 µm. Consequently, the samples with an insufficient amount of dust remaining after sieving, i.e., < 200 mg, were discarded. Among the 300 dust samples, the 145 that met the selection criteria were analyzed.

Sample analysis

SVOCs were simultaneously analyzed via pressurized liquid extraction and gas chromatography/mass spectrometry or tandem mass spectrometry depending on the compounds. Details of the chemical analysis, including quality assurance and quality control, are provided in the Supporting Information. Moreover, a detailed description of the analytical methods is available in (Blanchard et al., 2014b; Mercier et al., 2014).

Data analysis

Management of missing and censored values

Among the 145 samples, three had a missing value for DEP, one had a missing value for permethrin and one had a missing value for BDE 209. These missing values were imputed by the median estimated based on the respondents (i.e., dwellings where the respective concentrations were available). The concentrations below the limits of detection (LODs) were set at LOD/2, and the concentrations between the LODs and the limits of quantification (LOQs) were substituted by the raw values provided by the laboratory to avoid losing variability despite higher uncertainties in this range.

Extrapolation to the French housing stock with children

Each dwelling (n = 484) has a sampling weight, i.e., the inverse of the probability of inclusion in the sample, which makes it possible to compute national estimates. Nevertheless, due to dwellings without SVOC measurements (the non-respondents), either due to no agreement to collect the vacuum cleaner bag or discarded bag, the sampling weights needed to be adjusted for non-response to avoid bias in the estimates. The weights of the 145 respondents 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 calculating the rate of the number of respondents divided by the number of dwellings belonging to the group. Each sampling weight of a 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. The model provided the variables that were able to predict p (the dwelling inspector and the season). Nine groups of dwellings were built through this cross-classification method. The number of groups was defined so as not to lead to an overly low value of 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. The 'survey' package from the R software (http://www.R-project.org) was used (Lumley, 2004, 2010a, 2010b).

Quantile calculation

Quantiles were estimated with the function 'svyquantile' from the R software 'survey' package based on the cumulative distribution function (CDF). Estimating the CDF and thus the quantiles is challenging. Under a simple random sampling, the median is not unique if the sample has an even size: any value between two successive observations is a valid candidate. In the case of complex survey samples, the problem is the same if the sum of sampling weights of the first half of units is not precisely equal to the sum of the sampling weights from the other half. 'svyquantile' uses a linear extrapolation between two adjacent observations when the quantile is not uniquely defined. Moreover, tied values represent a problem in quantile estimation, as the latter is a function of the ranking order of weighted observations and thus depends on which observation comes first. The option 'rounded' in the function 'svyquantile' was used to alleviate this effect. The 'Wald' type of interval was used to estimate confidence intervals. All of the details about these options and computations of quantiles and their standards errors are available in (Lumley, 2010a). The geometric mean was estimated when more than 75% of the concentrations were higher than the LOQ.

Statistical tests

Statistical tests were applied to the weighted sample according to Lumley and Scott (2013) to identify possible associations between SVOC concentrations and the different variables describing the environment, building and floor cleaning. For dry and wet floor cleaning, the frequency was the average of the weekly cleaning frequencies in each room. Then, each dwelling was categorized as either ‘low frequency’, i.e., a cleaning frequency lower than the median value of the frequencies for all the dwellings, or ‘high frequency’, i.e., higher than this median value. Statistical analysis was applied to the 24 SVOCs for which the concentrations were quantified in more than half of the dwellings. The Wilcoxon rank test was used to compare two groups of dwellings. In the case of three groups or more, the Kruskal-Wallis test was used and, if significant, was followed by a median test to study the pairs. The statistical level for significance was set at $P < 0.05$. The Bonferroni correction was applied for the median test to account for the multiple comparisons.

Classification

Two hierarchical cluster analyses (HCAs) were performed, one to identify groups of SVOCs sharing similar concentrations profiles and another to identify groups of dwellings sharing similarities in terms of SVOC concentrations. For both classifications, the HCA was based on $[R_{ij}]$, the matrix of the ranks of the dwelling i for the SVOC j. The rank matrix $[R_{\mathrm{ij}}]$ was constructed according to Lumley and Scott (2013). The ‘hclust(D)’ command from the R ‘stats’ package was then used to perform the two HCAs. For the classification of SVOCs, the HCA was performed with the distance matrix D, defined by $D = (1\text{-Cor}([R_{ij}]))/2$. For the classification of dwellings, the HCA was performed with the Euclidian distance matrix D calculated from $[R_{ij}]$. The package ‘NbClust’ from the R software was used to identify the optimum number of groups (Charrad et al., 2014). The agglomeration method in both HCAs was Ward’s criterion (Murtagh and Legendre, 2014).

Results

Concentrations in floor settled dust

The frequency of quantification and the concentration distributions 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. The results, expressed with the 95% confidence intervals of the estimates, are provided in the Supporting Information (Table S3).

Thirty-two SVOCs (67%) were detected in more than half of the dwellings. The six phthalates, three PAHs: anthracene, benzo(a)pyrene and phenanthrene, galaxolide and tonalide, BDE 209, permethrin, bisphenol-A, and tributylphosphate were detected in more than 98% of the dwellings. Most of the BDEs (congeners 28, 85, 100, 119, 153, and 154) and 4 out of 10 PCBs (congeners 28, 31, 77, and 126) were detected in less than half of the dwellings. The frequency of detection was also below 50% for aldrin, α-endosulfan, diazinon, endrin, and cypermethrin. Dichlorvos was never detected.

Twenty-four SVOCs (50%) were quantified in more than half of the dwellings. Several orders of magnitude were observed between the concentration ranges. The highest concentrations were measured for the phthalates, bisphenol-A, permethrin and galaxolide, from several µg/g to maximum values of over 1 mg/g for DEHP (6.2 mg/g), DiBP and DiNP (1.4 mg/g), BBP (1.3 mg/g), and permethrin (1.6 mg/g). BDE 209, tonalide, phenanthrene, and tributylphosphate followed, with median values of approximately several hundred ng/g. Then, the other BDEs (99 > 47), the remaining PAHs (benzo(a)pyrene > anthracene > fluorene), and lindane had median values of approximately several dozen ng/g. The lowest concentrations were observed for the PCBs and 4,4'-DDE. Even if some SVOCs were not detected in a large number of dwellings, such as α-endosulfan (detected in 34% of the sample), cypermethrin (47%), deltamethrin (55%), and chlorpyrifos (67%), rather high concentrations (approximately 20 µg/g) were found in some dwellings.

Proximities between SVOCs

Various significant correlations were observed between all of the ranked SVOC concentrations, excluding dichlorvos. The 47 SVOCs were grouped into five clusters (Figure 2). The most homogeneous cluster contained all of the PCBs except PCB 126, which was rarely detected. This indicates that PCBs correlate more with each other than with other SVOC chemical groups. The five PAHs also formed a single homogeneous group. The third homogeneous cluster included 6 pesticides: cyfluthrin, cypermethrin, aldrin, dieldrin, lindane and 4,4'-DDE. The fourth cluster, albeit more heterogeneous, regrouped all of the PBDEs except BDE 209 and included diazinon, deltamethrin and permethrin. The last cluster held all the remaining SVOCs and, in particular, all of the phthalates.

Relationships with the environment, building characteristics and floor cleaning habits

The SVOC median concentrations, according to the descriptive variables, are presented in Tables 1-5, where significant differences were observed.

Table 1 shows the SVOC concentrations according to the geographical areas representing the French administrative climatic zones. H1 represents Northeast France, with a continental cold climate; H2 corresponds to western part of the country, by the Atlantic Ocean, with an oceanic climate. Finally, H3 represents the Southeast coast by the Mediterranean Sea, with a warm Mediterranean climate. The paired comparison shows differences for DEHP, galaxolide and tributylphosphate, with higher concentrations in H1 compared to H2 and H3 and in H2 compared to H3.

Table 2 shows the significant associations observed between the SVOC concentrations and the rural or urban setting. Dwellings were categorized as urban in cities with more than 2,000 inhabitants and as rural otherwise. Significant differences were observed for DBP, galaxolide and tonalide, and tributylphosphate, with a common trend toward higher concentrations observed in urban dwellings.

Table 3 presents the two significant associations found between SVOC concentrations and the type of building. Both DiBP and 4,4'-DDE displayed higher concentrations in multi-family dwellings than in single houses.

Table 4 reports significant associations between the year of building construction and 12 SVOCs. For PAHs, the concentrations appeared to be significantly higher in dwellings built before 1949 compared to those built after 1974. For lindane and 4,4'-DDE, the concentrations decreased over time, which is consistent with the ban of their use for roof timber treatment. Finally, the PCB concentrations were significantly higher in the 1949-1974 construction period than in the dwellings built either before 1949 or after 1974. This trend is also consistent with their complete ban from products since 1987 in France.

The significant associations between SVOC and the weekly dry or wet cleaning frequency of the floor are presented in Table 5. The median frequency was 2.8 times per week and 1.4 times per week for dry and wet floor cleaning, respectively. Significant associations were mainly observed for the dry cleaning (only two for the wet cleaning). For 11 out of 24 SVOCs, the concentrations in settled dust were significantly lower for a high frequency of floor dry cleaning.

The comparison of SVOC concentrations and the sampling season (spring/summer *versus* autumn/winter) did not show any significant difference except for BDE 99, with a higher concentration in a warmer season compared to a colder season ($P = 0.034$). Thus, the year of construction appeared to be the major factor related to SVOC presence and concentration, followed by the weekly frequency of floor dry cleaning.

Distribution patterns of SVOCs in home settled dust

Another objective was to identify the percentage of buildings that were simultaneously polluted by several SVOCs in settled dust and, conversely, those that showed the lowest concentrations. The classification provided an optimum partition in four groups of dwellings that shared similar SVOC patterns.

The first group represents 15% of the dwellings where SVOCs are either not detected or detected at low concentrations. The second group corresponds to 20% of the dwellings with high concentrations for only a few SVOCs. The third group (41%) represents the dwellings with rather high SVOC concentrations, particularly PCBs. Finally, the fourth group (24%) is also characterized by high SVOC concentrations for some SVOCs and, in particular, BDE 209. The median concentrations within each of the four groups were standardized to account for the large differences in concentration range between SVOCs and are plotted in Figure S1.

Table 6 reports the median concentrations for the 21 SVOCs that showed significant differences between the groups. When looking at what differentiates the groups of buildings in terms of the environment, building and cleaning variables (Figure S2), only the year of building construction was significantly different between the groups of dwellings according to Chi-tests. The third group has a significantly higher percentage of dwellings built between 1949 and 1974 (65%) ($P < 0.0001$). This is consistent with the fact that PCB concentrations are higher in this group. Furthermore, 98% of the dwellings from the fourth group were built after 1975 ($P < 0.0001$). This is also consistent with the absence of PCBs in these dwellings and the high prevalence of BDE 209, used largely since the 1980s. Additional information regarding building materials, furniture, equipment (in particular, electronic appliances in the dwelling), occupant habits regarding the use of cleaning products, window opening, cooking, and smoking would need to be studied in detail to determine the SVOC concentration patterns.

Discussion

Comparison with data from other countries

The comparison of our results with data from other studies requires that both the sampling and analysis use similar techniques. However, this is not often the case, as there is no standardized method for either the sampling or analysis of SVOCs in settled dust. Therefore, various methods are used worldwide according to the respective context of the research (Mercier et al., 2011). Dust may be sampled from different locations: the floor, surfaces above the floor, on electronic equipment, furniture or toys, on ceiling fans, or on the filters of heating, ventilating and air-conditioning systems. Different sampling techniques are used to collect the dust, e.g., taking it from household vacuum cleaner bags, vacuuming the floor/surfaces for a dedicated dust collection, or using a wipe, brush, or broom. The sample preparation, particularly the sieving, may also vary; the sieving fraction may range from 63 µm to 2 mm, or no sieving may be used at all. The extraction can be performed in different ways, including, e.g., the accelerated solvent extraction, Soxhlet extraction, or sonication. Finally, purification and analysis may also differ. Furthermore, the quantile estimation method, which is rarely described, may produce differences in result comparisons.

In the context of this comparison, we intended to compare the results with studies carried out after 2000 (approx.) with the closest methods to identify any specificity of the French dwellings in terms of indoor SVOC concentrations. Due to the large heterogeneity in the sieving fraction used in the different studies and despite its acknowledged influence on SVOC concentrations (Cao et al., 2012), this criterion was not used to reject a study from the comparison. The following selection criteria were used:

- results should target dwellings exclusively;
- because the present study provides estimates at the national scale, only studies including at least 30 units have been selected to avoid any bias from specificities that could have weight in a small sample of dwellings;
- dust should be collected from the floor, and all other types of dust should be excluded; the study was included when the collected dust came from both the floor and other indoor surfaces, either by direct vacuuming or by taking out the occupant's vacuum cleaner bag;
- measurements should be expressed in similar units; the studies based on the use of wipes (concentration expressed in µg or ng per square meter) were excluded;
- studies targeting dwellings in specific environments, such as an agricultural zone or in the neighborhood of specific industries (e.g., electronic waste recycling industry), were not selected; similarly, case studies investigating dwellings already 'polluted', e.g., containing PCB materials, were not considered;
- in the case of repeated measurements, the results for the series corresponding to the period closest to the one from the present study (2008-2009) were considered.

The only other French study related to SVOCs in home settled dust was also used for the comparison (Blanchard et al., 2014b).

The comparison for the 24 SVOCs quantified in more than half of the dwellings is presented in Figure 3. Numerous studies meeting our criteria exist for phthalates and BDEs. The comparison remains limited for some SVOCs, such as synthetic musks, PCBs, lindane and 4,4'-DDE. PCB 101 is not shown because only one study with at least 30 dwellings was found (Whitehead et al., 2014). The median PCB 101 concentration was equal to 3.4 ng/g, which is on the same order of magnitude as in the present study: 7.7 ng/g. Considering all of the studies, regardless of sampling size, the concentrations measured by Harrad et al. (2009) remain on the same order of magnitude: 8.7 ng/g in the US (n=20), 1.2 ng/g in the UK (n=20), 8.8 ng/g in Canada (n=10), and 1.6 ng/g in New Zealand (n=20).

For phthalates, the concentrations measured in the present study appear to be in the range of those from other countries, except for DiBP. The DiBP medians from other studies range between 1.9 and 5.2 µg/g *versus* 17 µg/g in our study. The same trend toward higher DiBP concentrations was also observed by Blanchard et al. (2014b) (median: 19 µg/g). This could be explained by its use as a substitute for DBP in Europe according to the European Council for Plasticisers and Intermediates (ECPI). Coherently, the DBP concentrations measured in France appear to be lower than those measured in other countries, including Germany, where the sampling was performed in 2000-2001 (Fromme et al., 2004a).

Regarding bisphenol-A, a trend toward higher concentrations in France is observed both in this study and by Blanchard et al. (2014b). The medians from the other studies range between 0.12 and 0.82 µg/g *versus* 4.2 and 4.7 µg/g in our study and Blanchard et al. (2014b), respectively. Considering all of the studies without any threshold in the number of investigated dwellings, the same observation is made: the 19 medians range between 0.07 µg/g in Pakistan (n=22 dwellings; Wang et al., 2015a) and 2.3 µg/g in Japan (n=20; Liao et al., 2012). No assumption can be suggested to explain this difference. The differences in the analytical methods should be considered in detail.

For all of the other SVOCs, i.e., PBDEs, permethrin, lindane, 4,4'-DDE, tributylphosphate, synthetic musks, PAHs, and PCBs, the median concentrations in home floor settled dust are similar in France as in other countries. The median PBDE values are highly scattered between studies. For example, the median BDE 209 concentrations range from 20 ng/g in Pakistan (Ali et al., 2012a; 31 homes investigated in April 2011) to 8 µg/g in the UK (Harrad et al., 2008; 30 homes investigated between July 2006 and June 2007). The high PBDE concentrations encountered in indoor environments in the UK and North America (Harrad et al., 2008; Imm et al., 2009; Johnson et al., 2010; Shoeib et al., 2012; Whitehead et al., 2013a; Hoffman et al., 2015) are due to stricter fire safety standards (Whitehead et al., 2011; Besis et al., 2012).

As a conclusion, DiBP and bisphenol-A median concentrations appear to be higher in France than those measured in other countries. This should be considered with caution because the comparison with other studies remains difficult for the aforementioned reasons, and considering the temporal evolution of concentrations. Using a narrower period for the comparison, i.e., closer to our sampling period, would have decreased the number of studies meeting our criteria even more and would not have allowed for comparison.

Relationships with the environment, building characteristics and floor cleaning habits

In the present study, associations between SVOC concentration and environmental or building variables were found, as previously noted in other studies.

Whitehead et al. (2013a) observed significantly lower concentrations of tri- to hexa-BDEs in settled dust from rural residences compared to those in urban areas. Referring to other authors who measured higher PBDE concentrations in soil closer to urbanized areas, Whitehead et al. (2013a) suggested that the contribution from outdoor soil could explain the difference between PBDE concentration in rural and urban settings. However, such a relationship with PBDEs was not observed in our study; the same trend toward higher concentrations in an urban setting was noted for DBP, galaxolide, tonalide, and tributylphosphate.

We observed significant differences between single- and multi-family dwellings only for DiBP and 4,4’-DDE. Whitehead et al. (2013b) observed significantly higher PAH concentrations in multiple-family dwellings compared to single-family homes. Two explanations are proposed. First, there is a constant number of PAH indoor sources (i.e., heaters, stoves, smokers) regardless of the size of the dwelling, and a smaller residence would have a higher PAH concentration than a larger one. Second, the resident turnover is higher in apartments, which can increase the PAH contamination from previous smoking occupants. In contrast, Ait Bamai et al. (2014a) observed no relationship between the type of dwelling and any of the phthalate concentrations.

Similar to the present study, Whitehead et al. (2013b) reported that the age of the residence had the most significant effect on PAH indoor dust concentrations, with older houses having higher PAH concentrations. They suggested that older homes had a higher probability of using older carpets, from which adsorbed PAHs are not easily removed via ‘typical’ cleaning. Wang et al. (2014) also observed that the residence age was associated with most of the PAH concentrations, with higher ones in older dwellings. The increase with building age was also observed for lindane and 4,4'-DDE by Anthopolos et al. (2003), as well as for 4,4’-DDE by Colt et al. (2004) in several American regions, as observed here for both compounds. Knobeloch et al. (2012) reported that higher PCB concentrations corresponded with homes built between 1942 and 1977 and that lower concentrations were associated with homes built between 1972 and 1997. Whitehead et al. (2014) also observed that residences built prior to 1980 had higher PCB loadings. Hinwood et al. (2014) identified the age of the dwelling as the only significant factor influencing the PCB concentrations in settled dust. Regarding phthalates, Ait Bamai (2014a) observed a positive and significant correlation between the age of a building and the DBP and DEHP concentrations, which was observed here for BBP. With regard to PBDEs, De Wit et al. (2012) reported that BDE 47 and BDE 99 concentrations in settled dust from homes were negatively correlated ($P < 0.05$) to the building construction year. In our study, the category ‘After 1974’ is too broad: PBDEs largely began to be used in Europe at the beginning of the 1980s after the phase-out of polybrominated biphenyls, but penta-BDE and octa-BDE have been banned since 2004 in articles introduced on the market (EU, 2003).

The frequency of floor cleaning, especially dry cleaning, was associated with most of the SVOC concentrations in the present study. Maertens et al. (2008) also observed a significant negative relationship between PAH concentrations and the frequency of vacuuming. Cequier et al. (2014) observed that PBDE concentrations in settled dust were likely to be lower when a room is vacuumed frequently. Ait Bamai (2014a) did not observe any significant relation between phthalate concentration in floor dust and frequency of cleaning the living room, except for DiBP. The cleaning defined by the authors may not correspond only to floor cleaning.

Similar to our results, Whitehead et al. (2013b) did not observe any relationship between PAH concentrations in settled dust and the season of dust collection. As hypothesized by Whitehead et al. (2013), the dust from a vacuum cleaner bag may have been collected over a long period, hiding any seasonal effect.

Strengths and limitations

This study targeted a large number of substances from different chemical groups, which makes it possible to obtain an overview of the respective ranges of concentrations of many SVOCs of concern. Furthermore, this will enable to perform a risk assessment considering the cumulative exposure to SVOCs that have similar health effects and mechanisms of action (Fournier et al., 2014). The counterpart of such a large approach is the use of the multi-residue analytical method, with limits of detection and quantification slightly higher than they would be for specific targeted analyses.

This national survey only targeted French dwellings with at least one child younger than 6 years. SVOC concentrations in dwellings without any child, e.g., homes with young adults of childbearing age or primiparous pregnant women who may also represent sensitive populations, are not available. Our concentration estimates may not be extended to these dwellings. Indeed, Bennett et al. (2015) compared PBDE concentrations in settled dust from vacuum cleaner bags from dwellings with young children (n = 66) and from dwellings with older adults (n = 39). A significant difference ($P < 0.01$) was observed for BDE 209, with a higher concentration in dwellings with children, but not for BDEs 47, 99, 100, 153, and 154.

Conclusion

To our knowledge, this is the first study that provides SVOC concentration estimates at a national level. It is now possible to perform health risk assessment related to SVOC ingestion from settled dust for the entire population of children in France. Moreover, this study shows that SVOC contamination is not homogeneous among dwellings and that some patterns can be drawn, particularly in relation with the chemical families. The presence and concentrations of the target SVOCs are shaped by both the evolution of their regulations over the past decades and floor cleaning frequency.

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Table 1. SVOC median concentrations in settled dust according to geographical area

Compound	**Unit**	**H1**	**H2**	**H3**	***P-value*** [§]	**Paired comparison** [#]
%	-	53%	34%	13%	-	-
BaP	ng/g	121	98	52	0.0472	No paired difference
DEHP	µg/g	335	385	198	0.0048	H2 > H3 **
Galaxolide	ng/g	1,444	468	675	0.0158	H1 > H2 * H1 > H3 **
TBP	ng/g	305	176	171	0.0065	H1 > H2 * H1 > H3 *

%: percentage of dwellings in each geographical area; BaP: benzo(a)pyrene; TBP: tributylphosphate; [§]: *P*-value of the Kruskal-Wallis test; [#]: median test with adjusted *P*-values; *: $P < 0.05$, **: $P < 0.01$ and *** $P < 0.001$ adjusted with the Bonferroni correction to account for the multiple comparisons

Table 2. SVOC median concentrations in settled dust according to rural or urban setting

Compound	**Unit**	**Rural**	**Urban**	***P-value*** §
%	-	24%	76%	-
DBP	µg/g	9.1	13	0.0088
Galaxolide	ng/g	389	1,384	0.0116
Tonalide	ng/g	207	367	0.0268
TBP	ng/g	< LOQ	281	0.0348

%: percentage of dwellings in each environment category; TBP: tributylphosphate; LOQ: limit of quantification; §: *P*-value of the Wilcoxon test

Table 3. SVOC median concentrations in settled dust according to single- or multi-family dwellings

Compound	**Unit**	**Multi-family dwellings**	**Single houses**	***P-value*** §
%	-	18%	82%	-
DiBP	µg/g	29	16	0.0311
4,4'-DDE	ng/g	7.2	< LOQ	0.0157

%: percentage of dwellings in each building category; LOQ: limit of quantification; §: *P*-value of the Wilcoxon test

Table 4. SVOC median concentrations in settled dust according to the year of building construction

Compound	**Unit**	**Before 1949 (1)**	**1949-1974 (2)**	**After 1974 (3)**	***P-value*** [§]	**Paired comparison** [#]
%	-	19	32	49	-	-
Anthracene	ng/g	75	113	29	0.0178	(1) > (3) ** (2) > (3) **
BaP	ng/g	181	418	33	< 0.0001	(1) > (3) ***
Phenanthrene	ng/g	433	665	200	0.0088	(1) > (3) **
γ-HCH/lindane	ng/g	33	27	< LOQ	0.005	(1) > (3) * (2) > (3) ***
4,4'-DDE	ng/g	18	6.0	< LOD	< 0.0001	(1) > (2) ** (1) > (3) *** (2) > (3) ***
Permethrin	µg/g	2.6	4.8	1.1	0.0362	No paired difference
BBP	µg/g	16	11	7.4	< 0.0001	(2) > (3) ***
DEP	µg/g	3.6	3.0	5.2	0.0062	(1) > (2) *
PCB 101	ng/g	10	120	< LOQ	0.0009	(1) > (3) *** (2) > (3) ***
PCB 118	ng/g	10	125	< LOD	0.0004	(1) > (3) *** (2) > (3) ***
PCB 138	ng/g	11	131	< LOQ	0.0007	(1) > (3) *** (2) > (3) ***
PCB 153	ng/g	11	224	< LOQ	0.0012	(1) > (3) *** (2) > (3) ***

%: percentage of dwellings in each age category; BaP: benzo(a)pyrene; LOD: limit of detection; LOQ: limit of quantification; [§]: *P*-value of the Kruskal-Wallis test; [#]: median test with adjusted *P*-values; *: $P < 0.05$, **: $P < 0.01$ and *** $P < 0.001$ adjusted with the Bonferroni correction to account for the multiple comparisons

Table 5. SVOC median concentrations in settled dust according to floor cleaning frequencies

Compound	**Unit**	**Dry cleaning**			**Wet cleaning**		
		Low F	**High F**	***P-value*** §	**Low F**	**High F**	***P-value*** §
Fluorene	ng/g	-	-	-	32	52	0,0173
4,4’-DDE	ng/g	5.5	< LOQ	0.0063	-	-	-
PCB 101	ng/g	28.	< LOQ	0.0184	-	-	-
PCB 118	ng/g	23	< LOQ	0.0058	-	-	-
PCB 138	ng/g	26	< LOQ	0.0109	-	-	-
PCB 153	µg/g	23	< LOQ	0.0328	-	-	-
BBP	µg/g	-	-	-	7.3	11	0.0195
Galaxolide	ng/g	1,463	632	0.0082	-	-	-
Tonalide	ng/g	453	214	0.0258	-	-	-
BPA	µg/g	5.4	3.3	0.0148	-	-	-
TBP	ng/g	220	< LOQ	0.0156	-	-	-

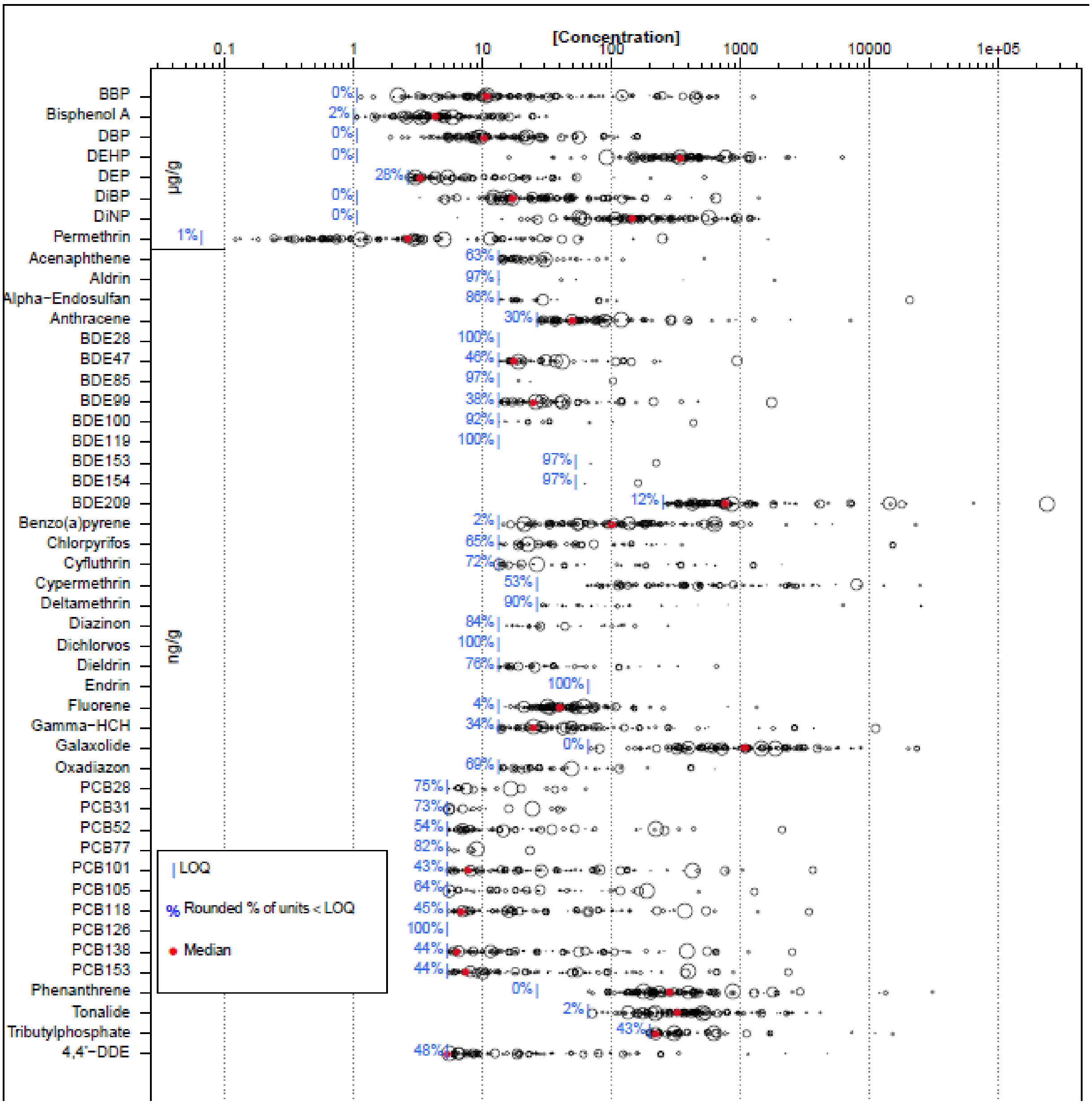
F: frequency; %: percentage of dwellings in each frequency category; BPA: bisphenol-A; TBP: tributylphosphate; LOQ: limit of quantification; §: *P*-value of the Wilcoxon test

Table 6. SVOC median concentrations in settled dust according to the four dwelling groups

Compound	Unit	Group 1 (G1)	Group 2 (G2)	Group 3 (G3)	Group 4 (G4)	*P-value* [§]	Paired comparison [#]
%	-	15%	20%	41%	24%	-	-
Anthracene	ng/g	31	84	89	< LD	0.0004	(G1) < (G2) *** (G1) < (G3) ** (G2) > (G4) *
BaP	ng/g	37	130	187	21	<0.0001	(G1) < (G2) * (G2) > (G4) *** (G3) > (G4) ***
Fluorene	ng/g	28	51	61	32	0.0005	(G3) > (G4) *
Phenanthrene	ng/g	207	353	625	177	0.0001	(G1) > (G4) * (G2) > (G4) ** (G3) > (G4) ***
γ-HCH/lindane	ng/g	14	45	26	< LOQ	<0.0001	(G1) < (G2) *** (G2) > (G4) ***
4,4’-DDE	ng/g	< LOQ	< LOQ	6.2	< LOD	<0.0001	(G2) > (G4) *** (G3) > (G4) *
BDE 47	ng/g	< LOQ	29	19	23	0.0007	(G1) < (G3) * (G1) < (G4) *
BDE 99	ng/g	< LOQ	23	24	35	0.0085	(G1) < (G2) **
BDE 209	ng/g	< LOQ	748	754	108,500	0.001	(G1) < (G2) ***
BBP	µg/g	4.4	19	13	2.2	<0.0001	(G1) < (G2) ** (G3) > (G4) *
DBP	µg/g	6.6	8.5	19	21	<0.0001	No paired difference
DEHP	µg/g	204	487	337	92	0.0001	(G1) < (G3) **
DEP	µg/g	< LOQ	< LOQ	3.0	4.8	<0.0001	(G1) < (G4) *** (G2) < (G4) *** (G3) < (G4) *
DiNP	µg/g	89	101	380	57	<0.0001	(G1) < (G3) *** (G2) < (G3) *
Galaxolide	ng/g	329	499	1,870	1,236	<0.0001	(G1) < (G3) * (G1) < (G4) *** (G2) < (G3) * (G2) < (G4) **
Tonalide	ng/g	154	173	481	218	<0.0001	(G1) < (G3) ** (G2) < (G3) **
PCB 101	ng/g	< LOQ	5.7	81	< LOD	<0.0001	(G1) < (G3) ** (G2) < (G3) *** (G2) > (G4) *** (G3) > (G4) ***
PCB 118	ng/g	< LOQ	< LOQ	69	< LOD	<0.0001	
PCB 138	ng/g	< LOQ	5.5	86	< LOD	<0.0001	
PCB 153	ng/g	< LOQ	6.1	79	< LOD	<0.0001	
BPA	µg/g	3.0	3.6	5.7	3.3	0.0199	(G1) < (G3) **

%: percentage of dwellings in each group; BaP: benzo(a)pyrene; BPA: bisphenol-A; LOD: limit of detection; LOQ: limit of quantification; [§]: *P*-value of the Kruskal-Wallis test; [#]: median test with adjusted *P*-values; *: $P < 0.05$, **: $P < 0.01$ and *** $P < 0.001$ adjusted with the Bonferroni correction to account for the multiple comparisons

Figure 1. Concentration distributions of the 48 SVOCs in home settled dust (N = 3,581,991)



The sizes of the bubbles are directly proportional to the respective numbers of dwellings in the weighted sample.

Figure 2. Hierarchical cluster analysis of ranked SVOC concentrations with a partition in five clusters

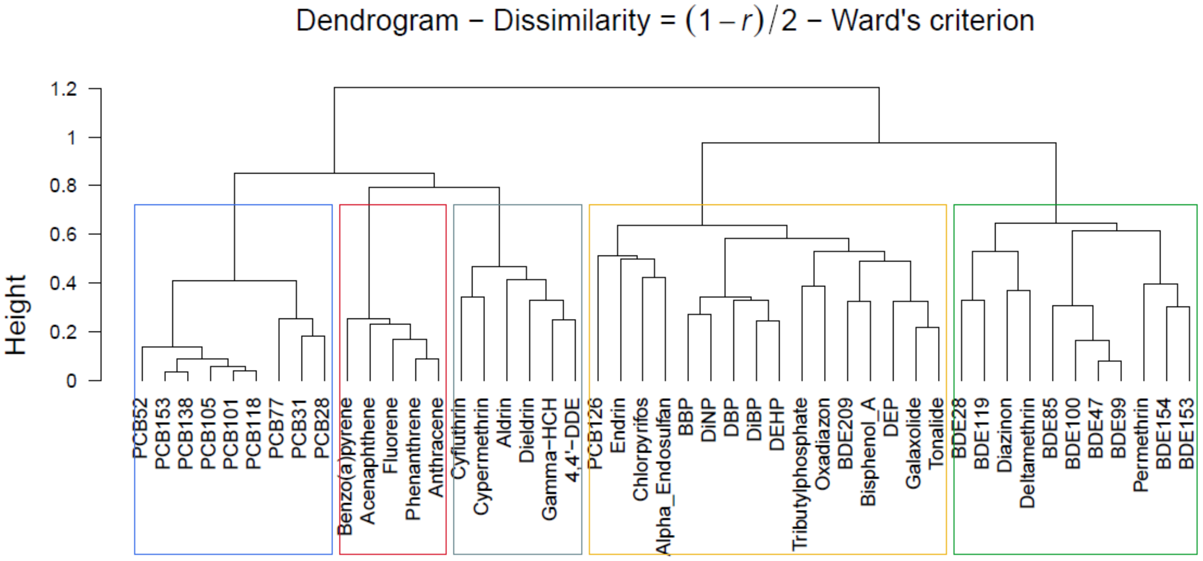
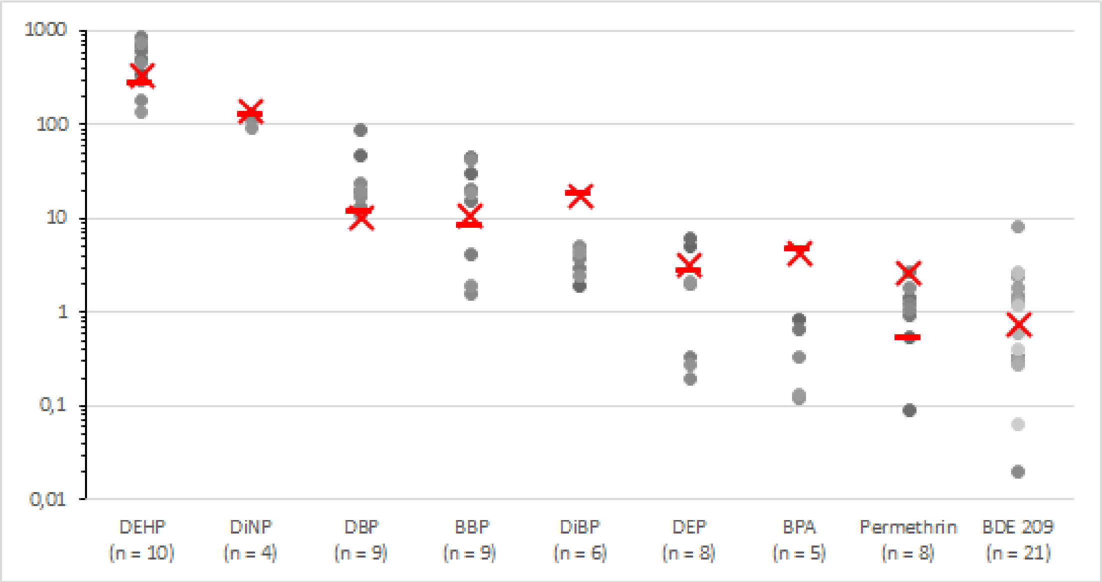
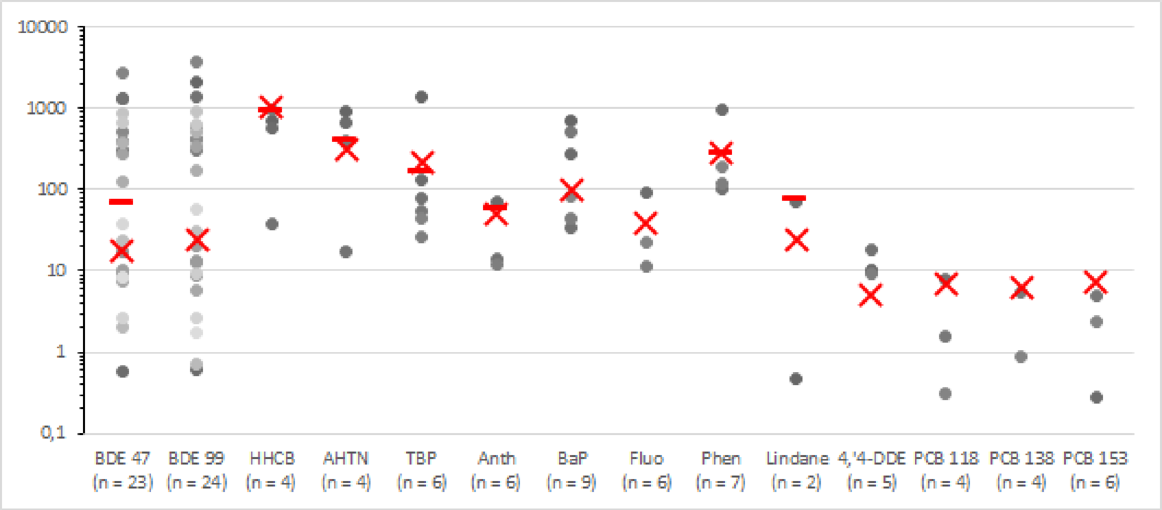


Figure 3. Comparison of the SVOC median concentrations in home floor settled dust measured worldwide

a) Median concentrations in µg/g, log-scale



b) Median concentrations in ng/g, log-scale



Cross: this study; Horizontal line: French study from Blanchard et al. (2014b); n: number of international studies considered, except for bisphenol-A for which Wang et al. (2015a) reported medians for three different countries

HHCB: galaxolide; AHTN: tonalide; Anth: anthracene; BaP: benzo(a)pyrene; Fluo: fluorene; Phen: phenantrene

References for phthalates: (Rudel et al., 2003; Fromme et al., 2004a; Becker et al., 2004; Abb et al., 2009; Kanazawa et al., 2010; Guo and Kannan, 2011; Zhang et al., 2013; Kubwabo et al., 2013; Ait Bamai et al., 2014b; Dodson et al., 2015); **bisphenol-A**: (Rudel et al., 2003; Loganathan and Kannan, 2011; Wang et al., 2015a); **permethrin**: (Rudel et al., 2003; Colt et al., 2004; Becker et al., 2006; Julien et al., 2008; Starr et al., 2008; Anthopolos et al., 2012; Deziel et al., 2015; Dodson et al., 2015); **tributylphosphate**: (Kanazawa et al., 2010; Van den Eede et al., 2011; Ali et al., 2012b; Dirtu et al., 2012; Cequier et al., 2014; Fan et al., 2014); **galaxolide and tonalide**: (Fromme et al., 2004a; Butte, 2004; Lu et al., 2011; Kubwabo et al., 2012); **PAHs**: (Rudel et al., 2003; Fromme et al., 2004b; Maertens et al., 2008; Anthopolos et al., 2012; Hoh et al., 2012; Wang et al., 2013; Whitehead et al., 2013b; Wang et al., 2014; Dodson et al., 2015); **lindane**: (Ali et al., 2012a; Dirtu et al., 2012); **PBDEs**: (Rudel et al., 2003; Wilford et al., 2005; Harrad et al., 2008; Fromme et al., 2009; Imm et al., 2009; D'Hollander et al., 2010; Huang et al., 2010; Johnson et al., 2010; Chen et al., 2011; Vorkamp et al., 2011; Ali et al., 2012a; Dirtu et al., 2012; Shoeib et al., 2012; Stapleton et al., 2012; Watkins et al., 2012; Coakley et al., 2013; Lee et al., 2013; Stasinska et al., 2013; Whitehead et al., 2013a; Cequier et al., 2014; Kefeni et al., 2014; Bennett et al., 2015; Dodson et al., 2015; Hoffman et al., 2015; Wang et al., 2015b); **PCBs** (Hedgeman et al., 2009; Ali et al., 2012a; Dirtu et al., 2012; DellaValle et al., 2013; Hinwood et al., 2014; Whitehead et al., 2014; Dodson et al., 2015; Wang et al., 2015c); and **4,4'-DDE**: (Colt et al., 2004; Ward et al., 2009; Ali et al., 2012a; Anthopolos et al., 2012; Dodson et al., 2015)

Semi-volatile organic compounds in home settled dust: A nationwide survey in France

Corinne Mandin, Fabien Mercier, Jean-Paul Lucas, Olivier Ramalho, Olivier Blanchard, Nathalie Bonvallot, Gaëlle Raffy, Erwann Gilles, Philippe Glorennec and Barbara Le Bot

SUPPORTING INFORMATION

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2. Additional figures and tables

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1. Chemical analysis

Reagents and chemicals

Certified standards of aldrin, 4,4'-DDE, dieldrin, α-endosulfan, endrin, γ-HCH (lindane), chlorpyrifos, diazinon, dichlorvos, cyfluthrin, cypermethrin, deltamethrin, permethrin, tributylphosphate, acenaphthene, anthracene, benzo(a)pyrene, fluoranthene, fluorene, phenanthrene, PCB 77, 105 and 126, butylbenzyl phthalate (BBP), di-n-butyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), diisononyl phthalate (DiNP), bisphenol-A, fenpropathrin (surrogate standard), methoprotryne (surrogate standard), 4-n-amylphenol (ISTD) and 2,3,4-trichloronitrobenzene (TCNB, ISTD) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Purity of certified standards was above 97%, except for permethrin (94%). Acetone and dichloromethane (DCM) (PLUS-for residual pesticide analysis) were purchased from Carlo Erba Reagents (Val-de-Reuil, France). Individual standard stock solutions (1 g/L) were prepared in acetone by accurately weighing 25 mg (± 0.1 mg) of certified standards into 25 mL volumetric flasks and stored at -18° C. Nonane solutions (50 mg/L) of BDE 28, 47, 85, 99, 100, 119, 153 and 154, and toluene solutions of BDE 209 (50 mg/L) and 13C-BDE 209 (25 mg/L) were purchased from Wellington Laboratories (Guelph, ON, Canada). Cyclohexane solutions (10 mg/L) of galaxolide (HHCB) and tonalide (AHTN) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). A mixture (PCB Mix 21) containing 10 mg/L of 8 PCBs (PCB 28, 31, 52, 101, 118, 138, 153 and 180) in cyclohexane was supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany). Calibration solutions were prepared by appropriate dilution of individual standard stock solutions and commercial solutions in DCM.

N-methyl-n-(trimethylsilyl) trifluoroacetamide (MSTFA, derivatization reagent) was supplied by ULTRA Scientific (North Kingstown, RI, USA). The Standard Reference Material SRM 2585 (Organic Contaminants in House Dust) was purchased from the National Institute of

Standards and Technology (NIST, Gaithersburg, MD, USA). Celite® 545 was purchased from Merck KGaA (Darmstadt, Germany). Chromabond® NH_2 (aminopropyl modified silica) glass columns (3 mL / 500 mg) were purchased from Macherey-Nagel GmbH & Co. KG (Düren, Germany).

Sample extraction

After the addition of internal standards (ISTDs) (13C-BDE 209 and 4-n-amylphenol) and surrogate standards (fenpropathrin and methoprotryne) to each dust sample (200 mg of sieved dust (100 µm) mixed with 2,600 mg of Celite® 545), SVOC extractions were performed with DCM using an Accelerated Solvent Extractor ASE 350 (Dionex Corporation, Sunnyvale, USA). Organic extracts were concentrated to 10 mL at 30 °C under a nitrogen stream. A volume of 500 µL was transferred into a 1.5 mL amber glass vial, spiked with an ISTD solution (TCNB) and stored at -18 °C prior to analysis. This aliquot was dedicated to the quantification of bisphenol-A and the most concentrated compounds such as phthalates. The remaining 9.5 mL were concentrated to 1 mL and quantitatively transferred onto Chromabond® NH_2 glass columns prewashed with 6 mL of DCM. Elution was performed with 5 mL of DCM. Organic extracts were then concentrated to 0.5 mL, spiked with the TCNB solution, transferred into a 1.5 mL amber glass vial and stored at -18 °C prior to analysis. These extracts were dedicated to the quantification of the less concentrated compounds.

Determination

Analyses of organic extracts for SVOCs other than bisphenol-A and BDE 209 were performed using a gas chromatograph (GC) Trace GC Ultra coupled to a mass spectrometer (MS) TSQ Quantum GC operated in electron impact ionization (EI) mode (70 eV) (Thermo Scientific). The GC system was equipped with a TriPlus Autosampler and a PTV (Programmable Temperature Vaporizing) injector. Calibration solutions and organic extracts were injected (1 µL) in splitless mode. Helium was used as column carrier gas at a constant flow rate of

2 mL/min. 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 operated in the Multiple Reaction Monitoring (MRM) mode and the two most sensitive and specific transitions were monitored for each compound.

Organic extracts were analysed for BDE 209 using a 6890A GC system coupled to a 5975C MSD operated in EI mode (Agilent Technologies). The GC system was equipped with a 7683 Autosampler and a PTV injector. A volume of 10 µL was injected in solvent vent mode. Helium was used as column carrier gas at a constant flow rate of 1.5 mL/min. 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 the Single Ion Monitoring (SIM) mode and the two most sensitive and specific ions of BDE 209 were monitored.

Organic extracts were analysed for bisphenol-A following a derivation step (addition of MSTFA at room temperature with a minimum reaction time of 30 min) using a 7890A GC system coupled to a 5975C MSD operated in EI mode (Agilent Technologies). The GC system was equipped with a 7683 Autosampler and a Multi-Mode Inlet (MMI) injector. 2 µL were injected in splitless mode. Helium was used as column carrier gas at a constant flow rate of 1 mL/min. Chromatographic separation was performed on a DB-5ms capillary column (30 m length x 0.25 mm I.D., 0.25 µm film thickness) supplied by Agilent J&W. The mass spectrometer was operated in SIM mode and the three most sensitive and specific ions of bisphenol-A were monitored.

Quality Assurance (QA) and Quality Control (QC)

Analytical methods were previously validated in terms of accuracy and precision (Mercier et al., 2014). The limits of detection (LOD) and quantification (LOQ) are reported in Table S1.

Quadratic calibration curves were established for each compound by analysing at least five calibration solutions.

Because of the diversity of the target compounds with very different chemical and physical properties, internal and surrogate standards were selected to match the physical and chemical properties of the analytes as closely as possible, covering volatility differences in particular. Fenpropathrin, methoprotryne, 13C-BDE 209 and 4-n-amylphenol were added prior to the extraction step and TCNB at the end of the extraction procedure. Fenpropathrin and methoprotryne were used as surrogate standards to monitor recoveries. 13C-BDE 209 was used as internal standard (ISTD) for BDE 209 and 4-n-amylphenol for bisphenol-A to monitor recoveries and guarantee that the derivatization reaction was complete. TCNB was used as ISTD for all the other target substances.

One procedural blank sample (2,800 mg of Celite® 545) and one sample of the NIST standard reference material SRM 2585 (200 mg of SRM 2585 mixed with 2,600 mg of Celite® 545) were extracted and analysed as regular samples for every ten samples to assess whether the samples may have been contaminated during analysis, and to check for method accuracy, respectively. To minimize procedural blank contamination, glass materials and stainless-steel cells were solvent-rinsed prior to use and plastic materials were avoided. Despite these precautions, some compounds such as phthalates and tributylphosphate were detected in the procedural blank samples. As concentrations in a procedural blank sample never exceeded 25% of concentrations in a sample from the same batch, concentrations reported here were not corrected for procedural blank concentrations. Measured concentrations (arithmetic mean) in SRM 2585 were compared to indicative, reference or certified concentrations available for some PAHs, PCBs, chlorinated pesticides, PBDEs, synthetic musks, phthalates, pyrethroids and organophosphorous pesticides. Results are summarized in Table S2.

Overall, measured concentrations in SRM 2585 were in very good agreement with indicative, reference or certified concentrations. Measured concentrations ranged from 68% (PCB 153) to 120% (PCB 128) of the indicative, reference or certified concentrations, except for anthracene (193%). A possible explanation for anthracene is the likely presence of an interfering compound in the standard reference material. Concentrations of anthracene in dust samples were nevertheless reported here. Depending on the compounds, the method precision (RSD %) ranged from 7% (fluorene) to 28% (BDE 154) and was most often below 20%, indicating good precision.

Positive values for each substance are confirmed by comparing retention times and ions (GC/MS) or MRM transitions (GC/MS/MS) ratios between calibration solutions and samples.

Table S1. Limits of detection (LOD) and limits of quantification (LOQ) of the 48 SVOCs

Compound	Unit	LOD	LOQ	Compound	Unit	LOD	LOQ
Polycyclic aromatic hydrocarbons				**PCBs**			
Acenaphthene	ng/g	5.3	13.2	PCB 28	ng/g	2.1	5.3
Anthracene	ng/g	13.2	26.3	PCB 31	ng/g	2.1	5.3
Benzo(a)pyrene	ng/g	5.3	13.2	PCB 52	ng/g	2.1	5.3
Fluorene	ng/g	5.3	13.2	PCB 77	ng/g	2.1	5.3
Phenanthrene	ng/g	13.2	26.3	PCB 101	ng/g	2.1	5.3
				PCB 105	ng/g	2.1	5.3
Organochlorine pesticides				PCB 118	ng/g	2.1	5.3
Aldrin	ng/g	5.3	13.2	PCB 126	ng/g	2.1	5.3
α-Endosulfan	ng/g	5.3	13.2	PCB 138	ng/g	2.1	5.3
4,4’-DDE	ng/g	2.1	5.3	PCB 153	ng/g	2.1	5.3
Dieldrin	ng/g	5.3	13.2				
Endrin	ng/g	39.5	65.8	**Phthalates**			
γ-HCH/lindane	ng/g	5.3	13.2	BBP	µg/g	0.526	1.053
Oxadiazon	ng/g	5.3	13.2	DBP	µg/g	0.526	1.053
				DEHP	µg/g	0.421	1.053
Organophosphorous pesticides				DEP	µg/g	1.053	2.632
Chlorpyrifos	ng/g	5.3	13.2	DiBP	µg/g	0.526	1.053
Diazinon	ng/g	5.3	13.2	DiNP	µg/g	0.421	1.053
Dichlorvos	ng/g	5.3	13.2				
				Synthetic musks			
Pyrethroids				Galaxolide	ng/g	26.3	65.8
Cyfluthrin	ng/g	5.3	13.2	Tonalide	ng/g	26.3	65.8
Cypermethrin	ng/g	10.5	26.3				
Deltamethrin	ng/g	13.2	26.3	**Other SVOCs**			
Permethrin	µg/g	0.026	0.066	Bisphenol-A	µg/g	0.4	1
				Tributylphosphate	ng/g	65.8	197.4
PBDEs							
BDE 28	ng/g	5.3	13.2				
BDE 47	ng/g	5.3	13.2				
BDE 85	ng/g	5.3	13.2				
BDE 99	ng/g	5.3	13.2				
BDE 100	ng/g	5.3	13.2				
BDE 119	ng/g	5.3	13.2				
BDE 153	ng/g	21.1	52.6				
BDE 154	ng/g	21.1	52.6				
BDE 209	ng/g	100	250				

Table S2. SVOC concentrations (ng/g) in SRM 2585 (n = 18)

Compound	Measured concentration (RSD %)	Indicative, reference or certified concentration	Measured / indicative, reference or certified concentration (%)
Polycyclic aromatic hydrocarbons			
Acenaphtene	16.9 (13)	n.r.	-
Anthracene	186 (14)	96.0[a]	193
Benzo(a)pyrene	996 (10)	1140[a]	87
Fluorene	53.2 (7)	n.r.	-
Phenanthrene	1860 (16)	1920[a]	97
Organochlorine pesticides			
4,4’-DDE	201 (16)	261[a]	77
Dieldrin	88.2 (18)	88.0[b]	100
γ-HCH/lindane	< 13.2	4.1[b]	-
Organophosphorous pesticides			
Chlorpyrifos	266 (18)	279[c]	95
Diazinon	319 (9)	396[c]	81
Pyrethroids			
Cyfluthrin	3110 (9)	3730[c]	83
Cypermethrin	3700 (16)	4050[c]	91
Deltamethrin	43.8 (19)	n.r.	-
Permethrin	5070 (8)	4970[c]	102
PBDEs			
BDE 28	43.2 (17)	46.9[a]	92
BDE 47	512 (15)	497[a]	103
BDE 85	40.8 (16)	43.8[a]	93
BDE 99	827 (14)	892[a]	93
BDE 100	140 (21)	145[a]	96
BDE 119	< 13.2	< 0.2[d]	-
BDE 153	105 (20)	119[a]	88
BDE 154	68.6[e] (28)	83,5[a]	82
BDE 209	2740 (9)	2510[a]	109
PCBs			
PCB 28	16.1 (20)	13.4[a]	120
PCB 31	12.5 (15)	14.0[a]	89
PCB 52	18.0 (16)	21.8[a]	82
PCB 101	31.1 (20)	29.8[a]	104
PCB 105	11.2 (16)	13.2[a]	85
PCB 118	25.7 (17)	26.3[a]	98
PCB 138	28.5 (18)	27.6[a]	103
PCB 153	27.1 (18)	40.2[a]	68

Compound	**Measured concentration (RSD %)**	**Indicative, reference or certified concentration**	**Measured / indicative, reference or certified concentration (%)**
Phthalates			
BBP	98,000[f] (14)	93,000[g]	105
DBP	29,000 (9)	31,000[g]	94
DEHP	540,000[h] (14)	570,000[g]	95
DEP	8610[f] (15)	8240[c]	104
DiBP	6310 (20)	6000[g]	105
DiNP	178,000 (12)	182,000[c]	98
Synthetic musks			
Galaxolide	1,430 (16)	1,460[i]	98
Tonalide	1,700 (16)	1,650[i]	103
Other SVOCs			
Bisphenol-A	80,400[j] (19)	n.r.	-
Tributylphosphate	347 (14)	306[c]	113

n.r.: not reported

[a] Certified concentration

[b] Reference concentration

[c] Indicative concentration from Mercier et al. (2014)

[d] Information concentration

[e] n = 16

[f] n = 17

[g] Indicative concentration from Bergh et al. (2012)

[h] n = 15

[i] Indicative concentration from Peck et al. (2007)

[j] n = 13

References

Peck, A.M., Kucklick, J.R., Schantz, M.M. (2007) Synthetic musk fragrances in environmental Standard Reference Materials, *Anal. Bioanal. Chem.*, **387**, 2381–2388.

Bergh, C., Luongo, G., Wise, S., Ostman, C. (2012) Organophosphate and phthalate esters in standard reference material 2585 organic contaminants in house dust, *Anal. Bioanal. Chem.*, **402**, 51–59.

Mercier, F., Gilles, E., Saramito, G., Glorennec, P., Le Bot, B. (2014) A multi-residue method for the simultaneous analysis in indoor dust of several classes of semi-volatile organic compounds by pressurized liquid extraction and gas chromatography/tandem mass spectrometry, *J. Chromatogr. A*, **1336**, 101–111.

Table S3. Concentration distributions of the 48 SVOCs in home settled dust expressed with 95% confidence intervals (N = 3,581,991)

Compound	**Unit**	**%>LOD**	**%>LOQ**	**P5**	**P25**	**P50**	**P75**	**P95**	**GM**	**GSD**
Polycyclic aromatic hydrocarbons										
Acenaphthene	ng/g	68	37	< LOD	< LOD	< LOQ	18.6	30.4	-	-
				-	-	-	< LOQ - 30.0	21.3 - 523	-	
Anthracene	ng/g	92	71	< LOD	< LOQ	49.5	111	289	-	-
				-	-	36.5 - 73.1	75.9 - 174	172 - 7,175	-	
Benzo(a)pyrene	ng/g	99	98	19.0	32.6	100	285	637	103	3.9
				< LOD - 20.3	20.4 - 55.3	55.4 - 133	134 - 619	617 - 22,940	83.3 - 126	
Fluorene	ng/g	99	96	18.0	31.7	39.4	60.7	93.8	41.5	1.8
				< LOD - 21.3	24.0 - 33.3	34.1 - 48.8	51.5 - 72.0	72.3 - 526	37.3 - 46.2	
Phenanthrene	ng/g	100	100	130	177	281	630	1,625	355	2.4
				67.5 - 154	177 - 203	223 - 381	388 - 870	869 - 30,800	303 - 416	
Organochlorine pesticides										
Aldrin	ng/g	7	3	< LOD	< LOD	< LOD	< LOD	< LOQ	-	-
				-	-	-	-	-	-	
α-Endosulfan	ng/g	34	14	< LOD	< LOD	< LOD	< LOQ	29.0	-	-
				-	-	-	-	18.1 - 20,620	-	
4,4’-DDE	ng/g	69	52	< LOD	< LOD	5.3	8.1	78.8	-	-
				-	-	2.6 - 6.0	5.4 - 46.4	24.8 - 4,721	-	
Dieldrin	ng/g	53	24	< LOD	< LOD	< LOQ	< LOQ	51.0	-	-
				-	-	-	-	25.1 - 1,001	-	
Endrin	ng/g	0.5	0	< LOD	< LOD	< LOD	< LOD	< LOD	-	-
				-	-	-	-	-	-	
γ-HCH (lindane)	ng/g	94	66	< LOD	< LOQ	24.7	43.2	253	-	-
				-	-	15.9 - 28.6	26.2 - 86.4	77.9 – 11,250	-	
Oxadiazon	ng/g	53	31	< LOD	< LOD	< LOQ	19.6	48.9	-	-
				-	-	-	< LOQ - 47.2	23.4 - 640	-	
Organophosphorous pesticides										
Chlorpyrifos	ng/g	67	35	< LOD	< LOD	< LOQ	21.5	64.7	-	-
				-	-	-	< LOQ - 34	36.0 - 15,210	-	
Diazinon	ng/g	29	16	< LOD	< LOD	< LOD	< LOD	42.2	-	-
				-	-	-	-	26.3 - 276	-	
Dichlorvos	ng/g	0	0	-	-	-	-	-	-	-
				-	-	-	-	-	-	
Pyrethroids										
Cyfluthrin	ng/g	51	28	< LOD	< LOD	< LOQ	13.4	42.9	-	-
				-	-	-	< LOQ - 25.9	26.1 - 1,205	-	

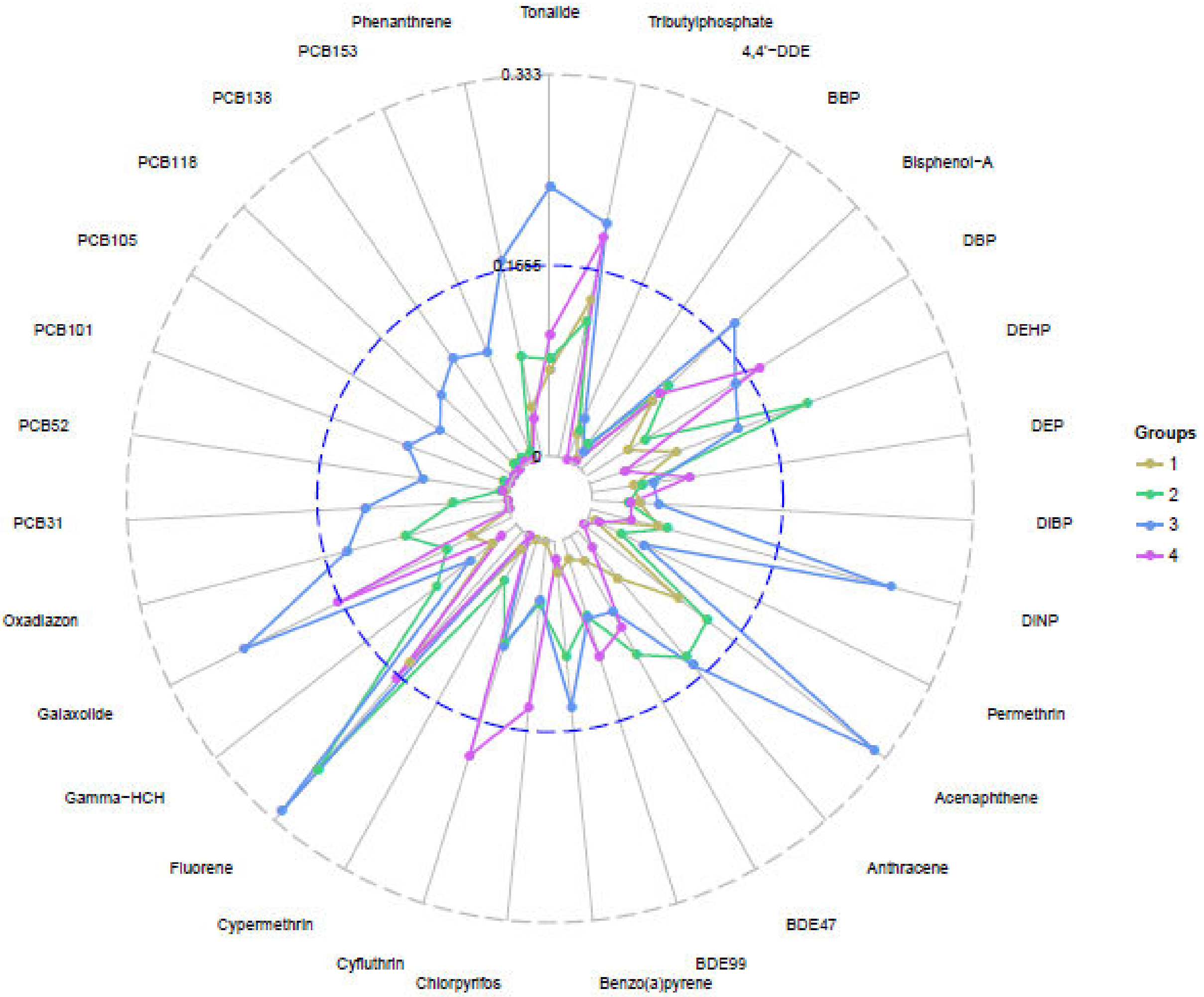
Compound	Unit	%>LOD	%>LOQ	P5	P25	P50	P75	P95	GM	GSD
Cypermethrin	ng/g	47	47	< LOD	< LOD	< LOD	358	3,954	-	-
				-	-	-	111 - 2,371	841 - 24,680	-	
Deltamethrin	ng/g	55	10	< LOD	< LOD	< LOQ	< LOQ	65.2	-	-
				-	-	-	-	< LOQ - 25,250	-	
Permethrin	µg/g	99	99	0.3	0.8	2.6	5.0	44.0	2.5	5.4
				< LOD - 0.4	0.4 - 1.1	1.1 - 3.3	3.4 - 14.3	20.9 - 1,643	1.7 - 3.8	
PBDEs										
BDE 28	ng/g	7	0	< LOD	< LOD	< LOD	< LOD	< LOQ	-	-
				-	-	-	-	-	-	
BDE 47	ng/g	86	54	< LOD	< LOQ	17.4	36.7	123	-	-
				-	-	< LOQ - 37.0	18.8 - 41.7	40.9 - 941	-	
BDE 85	ng/g	13	3	< LOD	< LOD	< LOD	< LOD	< LOQ	-	-
				-	-	-	-	-	-	
BDE 99	ng/g	90	62	< LOD	< LOQ	24.5	41.5	162	-	-
				-	-	< LOQ - 41.6	25.8 - 43.9	44.3 - 1,744	-	
BDE 100	ng/g	38	8	< LOD	< LOD	< LOD	< LOQ	29.8	-	-
				-	-	-	-	< LOQ - 432	-	
BDE 119	ng/g	1	0	< LOD	< LOD	< LOD	< LOD	< LOD	-	-
				-	-	-	-	-	-	
BDE 153	ng/g	20	3	< LOD	< LOD	< LOD	< LOD	< LOQ	-	-
				-	-	-	-	-	-	
BDE 154	ng/g	20	3	< LOD	< LOD	< LOD	< LOD	< LOQ	-	-
				-	-	-	-	-	-	
BDE 209	ng/g	98	88	< LOQ	421	757	1,822	184,600	1,569	9.4
				-	< LOQ - 576	412 - 4,082	852 - 137,300	3,855 - 238,200	489 - 5,033	
PCBs										
PCB 28	ng/g	45	25	< LOD	< LOD	< LOD	5.7	16.4	-	-
				-	-	-	< LOQ - 15.0	7.2 - 63.5	-	
PCB 31	ng/g	48	27	< LOD	< LOD	< LOD	5.3	23.2	-	-
				-	-	-	2.4 - 19	5.4 - 43	-	
PCB 52	ng/g	78	46	< LOD	< LOD	< LOQ	26.3	220	-	-
				-	-	-	6.8 - 219	30.1 - 2,101	-	
PCB 77	ng/g	22	18	< LOD	< LOD	< LOD	< LOD	8.9	-	-
				-	-	-	-	< LOD - 23.5	-	
PCB 101	ng/g	80	57	< LOD	< LOQ	7.7	75.2	425	-	-
				-	-	< LOQ - 17.6	13.8 - 399	81 - 3,644	-	
PCB 105	ng/g	54	36	< LOD	< LOD	< LOQ	21.2	182	-	-
				-	-	-	< LOQ - 173	24.2 - 1,288	-	

Compound	Unit	%>LOD	%>LOQ	P5	P25	P50	P75	P95	GM	GSD
PCB 118	ng/g	74	55	< LOD	< LOD	6.8	58.1	367	-	-
				-	-	< LOQ - 15.3	14.6 - 340	62.7 - 3,391	-	
PCB 126	ng/g	3	0	< LOD	< LOD	< LOD	< LOD	< LOD	-	-
				-	-	-	-	-	-	
PCB 138	ng/g	82	56	< LOD	< LOQ	6.3	54.4	385	-	-
				-	-	< LOQ - 11.5	11.1 - 330	62.2 - 2,519	-	
PCB 153	ng/g	79	56	< LOD	< LOQ	7.3	52.7	389	-	-
				-	-	< LOQ - 10.0	9.7 - 382	54.3 - 2,364	-	
Phthalates										
BBP	µg/g	100	100	2.1	5.4	10.6	28.7	439	15.5	5.0
				2.07 - 2.12	2.2 - 9.8	9.8 - 10.9	10.7 - 319	145 - 1,261	7.8 - 30.6	
DBP	µg/g	100	100	5.2	8.4	10.2	21.7	55.0	13.9	2.2
				2.3 - 5.4	5.6 - 9.6	9.6 - 19.1	18.8 - 29.9	28.4 - 158	11.3 - 17.0	
DEHP	µg/g	100	100	68.9	169	337	472	1,171	300	2.3
				63.6 - 74.3	80.9 - 271	257 - 341	340 – 1,030	765 - 6,156	221 - 408	
DEP	µg/g	98	72	< LOQ	< LOQ	3.2	5.3	27.8	-	-
				-	-	3.0 - 3.9	4.9 - 9.3	16.0 - 527	-	
DiBP	µg/g	100	100	6.3	12.9	17.0	37.4	177	25.3	2.8
				3.6 - 11.7	11.8 - 15.7	12.2 - 45.4	24.2 - 111	89.4 – 1,379	17.3 - 36.9	
DiNP	µg/g	100	100	32.0	57.6	143	377	907	160	2.8
				14.8 - 54.9	54.9 - 107	118 - 170	209 - 562	563 - 1,385	138 - 186	
Synthetic musks										
Galaxolide	ng/g	100	100	168	401	1,077	1,870	3,492	901	2.6
				< LOQ - 3,145	277 - 720	391 - 1,870	1,431 - 2,217	2,320 - 23,000	635 - 1,279	
Tonalide	ng/g	99	98	108	204	322	509	1,021	310	2.1
				< LOD - 133	131 - 233	232 - 405	419 - 533	630 - 2,490	268 - 358	
Other SVOCs										
Bisphenol-A	µg/g	100	98	1.5	3.3	4.2	5.9	13.9	4.4	1.9
				< LOQ - 2.1	2.0 - 3.5	3.5 - 5.0	5.0 - 9.4	11.1 - 31.3	3.9 - 5.0	
Tributylphosphate	ng/g	99	57	< LOQ	< LOQ	219	329	647	-	-
				-	-	< LOQ - 326	301 - 605	607 - 15,230	-	

LOD: limit of detection; LOQ: limit of quantification; P: Percentile; GM: geometric mean; GSD: standard deviation of the geometric mean (dimensionless);-: not applicable

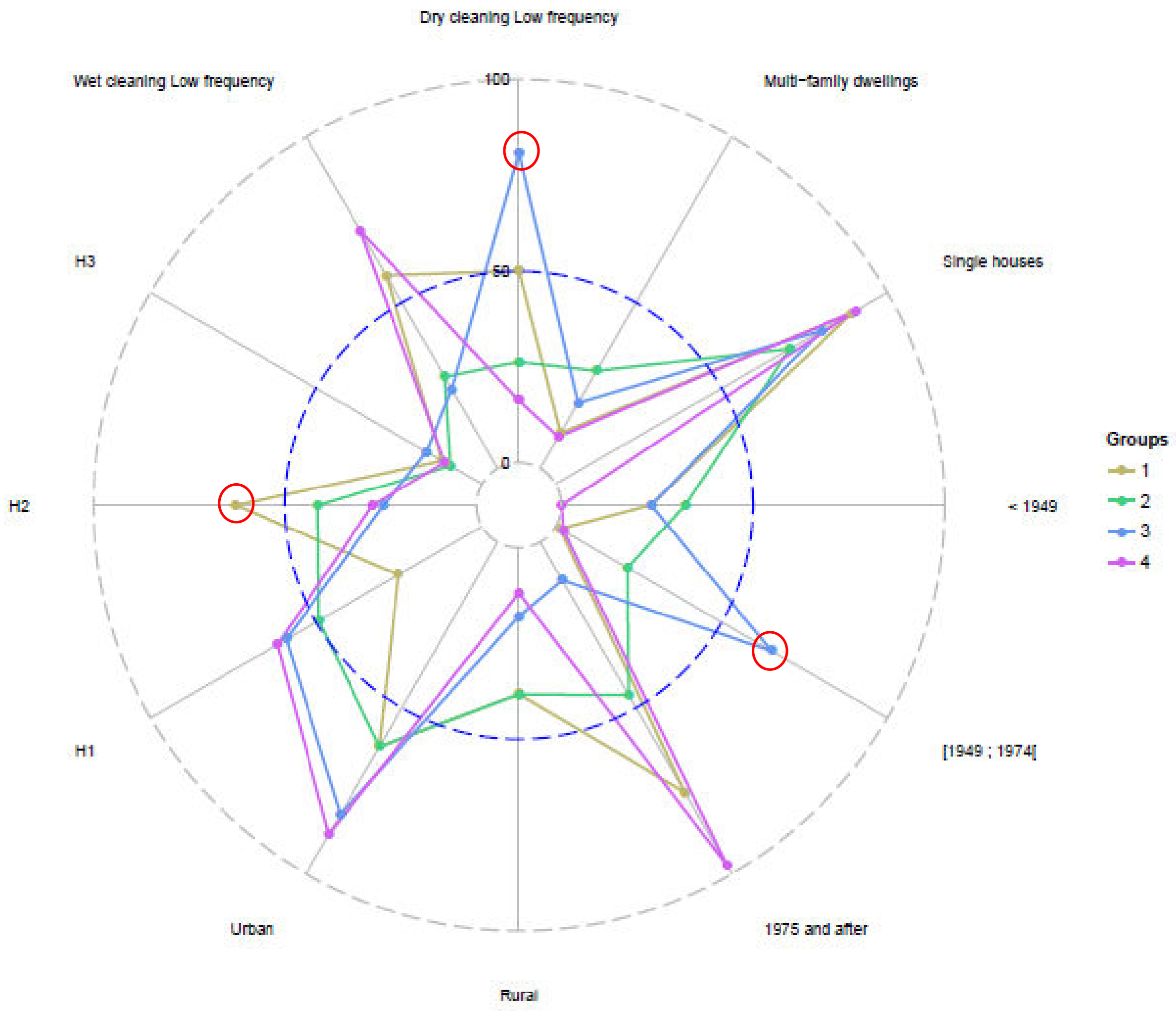
GM and GSD were calculated when at least 75% of data were above LOQ.

Figure S1. Standardized SVOC median concentrations in each of the four groups of dwellings



The quantified concentrations are standardized and scaled between 0 and 1 to plot and compare the median values for the different ranges of concentrations, from a few ng/g to > 100 µg/g. To limit the influence of very high concentrations, the concentrations have been censored to twice the 95th percentile for each SVOC prior to the standardization.

Figure S2. Description of the four groups of dwellings according to the environment, building and floor cleaning frequencies (% of dwellings in each category for each group)



Red circles indicate the variables for which the dwellings in one group are in different proportions than in the three other groups. This difference is only significant for year of building construction (Chi-test; $P < 0.0001$).

Chapitre 3 : Contamination en COSV des particules en suspension dans les logements français

3.1 Matériel et méthodes

Les prélèvements de particules ont été réalisés en 2003-2005, dans le cadre de la campagne nationale « Logements » de l'Observatoire de la qualité de l'air intérieur (OQAI), dans un échantillon de 567 logements représentatifs du parc des résidences principales en France métropolitaine continentale (Kirchner et al., 2007). La localisation des 567 logements instrumentés est visualisée sur la Figure 5.

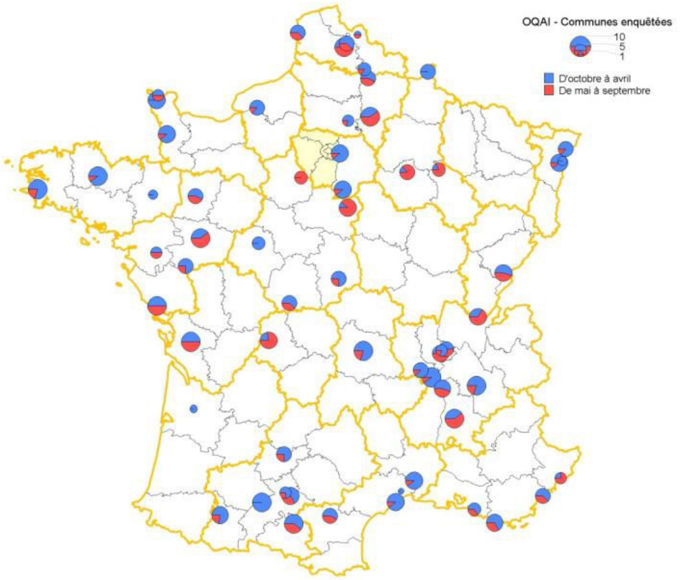


Figure 5 : Localisation géographique des 567 logements enquêtés dans le cadre de la campagne nationale « Logements » de l'Observatoire de la qualité de l'air intérieur

Les prélèvements ont été effectués avec un MiniPartisol (modèle 2100) durant une semaine complète dans le séjour des logements, pendant des périodes d'occupation prédéfinies, de 17h00 à 08h00 les jours de semaine et 24h/24 les samedis et dimanches. Avec un débit de prélèvement fixé à 1,8 L/min, le volume de prélèvement cible était de 13,3 m^3 pour une durée cumulée de 123 heures. Les filtres utilisés étaient des membranes Téflon de 37 mm de diamètre avec une bague support en PMP (polyméthylpentène) et une porosité de 2 µm. Les filtres ont été congelés immédiatement après pesée pour garantir leur conservation.

Afin de disposer d'une quantité de particules la plus importante possible, ce qui permet d'optimiser les limites de quantification, les filtres ayant collecté la fraction PM_{10} (particules de diamètre médian inférieur à 10 µm) ont été préférés aux filtres ayant collecté les $PM_{2,5}$ (particules de diamètre médian inférieur à 2,5 µm). Sur les 297 filtres valides, 285 étaient disponibles pour l'analyse des COSV.

Compte tenu des gammes de concentrations différentes attendues, chaque filtre a été découpé en quarts, préalablement à l'analyse. Le premier quart de filtre a été dédié à l'analyse des composés à l'état de traces, le deuxième à l'analyse des composés les plus fortement concentrés comme les phtalates, les HAP et les muscs. Les troisième et quatrième quarts étaient utilisés uniquement dans les cas où l'analyse sur un deux premiers quarts devait être reproduite. Les analyses ont été réalisées par thermodésorption associée à la chromatographie en phase gazeuse couplée à la spectrométrie de masse en tandem (TD-GC/MS/MS).

L'application des poids de sondage (i.e. l'inverse de la probabilité d'être tiré au sort lors de l'échantillonnage) à chacun des 285 logements a permis d'exprimer les concentrations mesurées à l'échelle du parc des résidences principales de France métropolitaine continentale. Compte tenu de l'analyse des filtres PM_{10} de 285 logements sur les 567 instrumentés, les poids de sondage ont dû être corrigés.

3.2 Résultats et discussion

Les résultats obtenus montrent que 35 des 66 COSV recherchés sont présents dans l'air d'au moins un logement sur deux. Les 13 HAP recherchés, 4 phtalates (BBP, DEHP, DiBP et DiNP) et le triclosan sont détectés dans plus de 95 % des logements. Quatre COSV n'ont jamais été détectés : cis-chlordane, heptachlore, BDE 119 et PCB 126. Les concentrations sont très hétérogènes et vont de quelques µg/m^3 pour le DEHP et le DiNP à quelques pg/m^3 pour les PCB, les PBDE, les alkylphénols et les pesticides organochlorés et organophosphorés.

La comparaison avec les données de la littérature montre que peu d'études ont documenté les concentrations en COSV dans l'air des logements en proportion de celles ayant renseigné les concentrations dans les poussières déposées au sol ou sur les surfaces. Encore moins d'études se sont intéressées spécifiquement aux COSV en phase particulaire dans l'air des logements. Cette comparaison ne fait pas apparaître de spécificités françaises en termes de composés en présence ou de concentrations mesurées.

Les exploitations détaillées sont présentées dans la publication soumise à *Atmospheric Environment*.

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 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 benzylbutyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP) and di-iso-nonyl phthalate (DiNP) and greater than 0.1 ng m^{-3} for triclosan, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-c,d)pyrene. 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 suspended particulate matter indoors also increases the exposure to SVOCs through inhalation.

Keywords: Indoor air quality, indoor environment, airborne particles, PM_{10}, particulate matter, endocrine disruptors

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.

1. Introduction

Semi-volatile organic compounds (SVOCs) refer to 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 established or suspected health effects and their widespread exposure through different environmental media and pathways (Hauser and Calafat, 2005; Hwang et al., 2008; Weschler and Nazaroff, 2008; Rudel and Perovich, 2009; Van der Veen and De Boer, 2012; Lehmann et al., 2015; Lyche et al., 2015).

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 suspended particulate matter 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 PM_{10} data 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). 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. 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. Damaged filters, equipment failure and lack of control in the 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 (EU, 2002). 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.

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 desorption (TD) 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., 2014). 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 were used instead of mass spectrometry 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, methoprotryne, oxadiazon, fenpropathrin, 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), di-isobutyl phthalate (DiBP), DiBP D_4, di-isononyl phthalate (DiNP), di-(2-methoxyethyl) phthalate (DMEP), dimethyl phthalate (DMP), di-n-octyl phthalate (DOP), 4-n-amylphenol, 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 D_{10}

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 (± 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 $^{13}C_{12}$, metolachlor D_6, chlorpyrifos D_{10} and trans-cypermethrin D_6, acetonitrile solution (100 mg L^{-1}) of trans-cyfluthrin D_6, cyclohexane solutions (10 mg L^{-1}) of chrysene D_{12}, pyrene D_{10}, galaxolide and tonalide, cyclohexane solution (100 mg L^{-1}) of BBP D_4 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 $^{13}C_{12}$-PBDE 47, 99 and 153, nonane/toluene (10%) solution (50 mg L^{-1}) of $^{13}C_{12}$-triclosan and toluene solution (50 mg L^{-1}) of tri-n-butylphosphate-d_{27} were purchased from Wellington Laboratories (Guelph, ON, Canada). Acetonitrile solution (100 mg L^{-1}) of bisphenol-A $^{13}C_{12}$ and isooctane solution (100 mg L^{-1}) of pentachlorobenzene $^{13}C_6$ 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 × 6 mm O.D. × 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 µL) 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 µL 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: thermal extraction and transfer into the GC system. In the first step, target compounds are thermally desorbed (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 TD-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 $^{13}C_{12}$, metolachlor D_6, pentachlorobenzene $^{13}C_6$, chlorpyrifos D_{10}, fenchlorphos, parathion D_{10}, trans-cyfluthrin D_6, trans-cypermethrin D_6, methoprotryne, fenpropathrin, tri-n-butylphosphate-d_{27}, chrysene D_{12}, pyrene D_{10}, $^{13}C_{12}$-PBDE 47, 99 and 153, BBP D_4, DiBP D_4, 4-n-amylphenol, bisphenol-A $^{13}C_{12}$ and $^{13}C_{12}$-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 TD-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 filter 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. This 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., submitted).

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 thirteen PAHs, DEHP, DiNP and triclosan were detected in more than 98% of the dwellings. DEHP was quantified in 100% of the dwellings. The other phthalates were also largely detected in airborne PM_{10}, except for the more volatile ones. DMP and DMEP were detected in 39% and 8% of the dwellings, respectively. BDE 47 and BDE 99 were the more concentrated PBDEs. Among PCBs, the tri- and tetra-congeners were detected less frequently 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 out of every two dwellings. Other than lindane, oxadiazon, 4,4’-DDT and 4,4’-DDE, the organochlorine and organophosphorous pesticides were detected in less than 20% of the dwellings. Four compounds were never detected, 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 concentrations were measured for the phthalates from several ng m^{-3} to maximum values greater than 1 µg m^{-3} for DEHP (2.3 µg m^{-3}) and DiNP (1.2 µg m^{-3}). 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}). Triclosan, permethrin, and the remaining PAHs stayed within an order of magnitude lower—i.e., medians of approximately 10–100 pg m^{-3}. The lowest PAH concentrations were observed for 3-ring congeners (anthracene and fluorene), and the highest were measured for 5- or 6-ring ones—namely, benzo(b)fluoranthene and benzo(g,h,i)perylene. Overall, the lowest concentrations were observed for BDE 47 > BDE 99 > 4,4'-DDT > PCBs.

The results from studies targeting particle-bound SVOCs in dwellings were considered for comparison, including the only other large French study, which involved 30 dwellings (Blanchard et al., 2014). 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 appear to be higher but remain on the same order of those measured during winter in Rome, Italy. The median PBDE concentrations are considerably lower in France than in North America, 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 $PM_{2.5}$ are lower than the medians measured in the present study. Regarding phthalates, the median concentrations are on the same order of magnitude as the ones measured elsewhere except for DiBP. Compared to Blanchard et al. (2014) 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 10 newly decorated apartments, with median concentrations of 1.9 and 1.3 µg 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 and are presented in Table 2b.

[Table 2b]

Regarding PBDEs, the maximum concentrations measured in France are comparable to those measured in the US by Batterman et al. (2009) and are even higher for BDE 85. If the overall PBDE concentrations are lower in the French housing stock than in the US, in some dwellings, concentrations as high as those in the US can be observed in airborne particles. With regard to phthalates, the DBP and DEP concentration ranges are on the same order of magnitude as in Norway and the US and lower than in China. 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 ranges of concentrations for trans- and cis-chlordane are rather high. 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. 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., 2015). 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 confirmed the major influence of smoking and the season in the particle-bound concentration of all SVOCs.

According to the results from the multiple comparisons, SVOCs can be categorized into four groups. Most of the SVOCs—i.e., 20 out of the 39 for which the statistical test could be 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, the other PAHs, 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 ± 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 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 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, warm summer temperatures increase window opening by the occupants and thus a more efficient dilution of SVOC concentrations originating from indoor sources.

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 SVOCs and PM_{10}

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 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 confirms that they have their own specific uses and sources indoors.

The median PM_{10} concentration measured in the French housing stock was 31 µg m^{-3}, and the 95th percentile was 182 µg 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 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 of 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 has been assessed simultaneously at a national level. These nationwide concentrations of SVOCs will enable an exposure assessment for the general population in France. This will include the assessment of exposure through the gas phase, which is currently being modeled from the particulate phase. The significant correlations observed among all major SVOCs and particulate matter imply that all sources of particles indoors may increase exposure to SVOCs through inhalation.

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LIST OF TABLES

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
Metolachor	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
Organophosphorous pesticides												
Chlorpyrifos	pg m^{-3}	41.8	10	83.5	3	< 41.8	< 41.8	< 41.8	< 41.8	< 83.5	NA	NA
Diazinon	pg m^{-3}	41.8	2	83.5	1	< 41.8	< 41.8	< 41.8	< 41.8	< 41.8	NA	NA

SVOC	Unit	LOD	% > LOD	LOQ	% > LOQ	P5	P25	P50	P75	P95	GM	GSD
Pyrethroids												
Permethrin	pg m^{-3}	20.9	76	41.8	54	< 20.9	< 41.8	55.9	162	1,836	NA	NA
PBDEs												
BDE 28	pg m^{-3}	0.4	22	1.0	9	< 0.4	< 0.4	< 0.4	< 0.4	1.9	NA	NA
BDE 47	pg m^{-3}	2.1	88	4.2	74	< 2.1	< 4.2	11.0	33.2	126	NA	NA
BDE 85	pg m^{-3}	4.2	1	8.4	1	< 4.2	< 4.2	< 4.2	< 4.2	< 4.2	NA	NA
BDE 99	pg m^{-3}	2.1	87	4.2	72	< 2.1	< 4.2	8.9	19.5	60.3	NA	NA
BDE 100	pg m^{-3}	2.1	47	4.2	26	< 2.1	< 2.1	< 2.1	4.3	13.6	NA	NA
BDE 119	pg m^{-3}	4.2	0	8.4	0	NA	NA	NA	NA	NA	NA	NA
BDE 153	pg m^{-3}	4.2	7	8.4	3	< 4.2	< 4.2	< 4.2	< 4.2	< 4.2	NA	NA
BDE 154	pg m^{-3}	4.2	3	8.4	1	< 4.2	< 4.2	< 4.2	< 4.2	< 4.2	NA	NA
PCBs												
PCB 28	pg m^{-3}	0.4	18	1.0	8	< 0.4	< 0.4	< 0.4	< 0.4	2.2	NA	NA
PCB 31	pg m^{-3}	0.4	23	1.0	11	< 0.4	< 0.4	< 0.4	< 0.4	2.2	NA	NA
PCB 52	pg m^{-3}	0.4	58	1.0	37	< 0.4	< 0.4	< 1.0	1.9	11.5	NA	NA
PCB 77	pg m^{-3}	0.4	11	1.0	6	< 0.4	< 0.4	< 0.4	< 0.4	1.5	NA	NA
PCB 101	pg m^{-3}	0.4	89	1.0	62	< 0.4	< 1.0	1.5	5.2	29.9	NA	NA
PCB 105	pg m^{-3}	0.4	61	1.0	43	< 0.4	< 0.4	< 1.0	2.6	18.5	NA	NA
PCB 118	pg m^{-3}	0.4	86	1.0	61	< 0.4	< 1.0	1.5	5.7	47.9	NA	NA
PCB 126	pg m^{-3}	1.0	0	2.1	0	NA	NA	NA	NA	NA	NA	NA
PCB 138	pg m^{-3}	0.4	89	1.0	65	< 0.4	< 1.0	2.3	8.4	53.6	NA	NA
PCB 153	pg m^{-3}	0.4	89	1.0	64	< 0.4	< 1.0	2.4	7.5	40.2	NA	NA
PCB 180	pg m^{-3}	0.4	77	1.0	53	< 0.4	< 1.0	1.3	4.4	25.1	NA	NA
Phthalates												
BBP	ng m^{-3}	0.17	98	0.42	85	< 0.42	0.6	1.6	5.3	31.9	2.0	5.0
DEHP	ng m^{-3}	1.7	100	4.2	100	9.1	22.3	46.2	110	389	52.6	3.3
DBP	ng m^{-3}	0.42	72	0.84	48	< 0.42	< 0.42	< 0.84	3.2	25.2	NA	NA
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

SVOC	Unit	LOD	% > LOD	LOQ	% > LOQ	P5	P25	P50	P75	P95	GM	GSD
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 m^3).

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

	Country		**France**	UK	Italy	US	Hong-K.	China	US	**Norway**	USA	China	**China**
	Size fraction		**PM_{10}**	TSP	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$/TSP	TSP	**PM_{10}**	TSP	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	**Dec. 2010 + June 2011**
	Estimate		**Median**	GM	AM	Median	Median	Median	Median	**AM**	Median	Median	**Median**
	n Dwellings		**n=30**	n=162	n=10	n=115	n=6	n=7	n=12	**n=2**	n=20	n=28[*]	**n=13**
	Unit	This study	**Blanchard et al., 2014**	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	**Zhang et al., 2014**
Anthracene	pg m^{-3}	12.6	**6**	50		5.7	10	80/190					
Benzo(a)anthracene	pg m^{-3}	44.4		60	208/50/36[#]	22	60	270/730					
Benzo(a)pyrene	pg m^{-3}	138	**65**	90	980/124/64[#]	52	100	600/970					
Benzo(b)fluoranthene	pg m^{-3}	306		180		3.6							
Benzo(g,h,i)perylene	pg m^{-3}	229		150	1,780/224/142[#]	170	170	1,200/1,560					
Benzo(k)fluoranthene	pg m^{-3}	64		110									
Chrysene	pg m^{-3}	75.9		140			100	520/1,050					
Dibenzo(a,h)anthracene	pg m^{-3}	21.6		30	170/28/18[#]	7.4	20	190/340					
Fluoranthene	pg m^{-3}	68.2	**22**	360		57	340	2,200/5,260					
Fluorene	pg m^{-3}	19.5		130			90	870/2,950					
Indeno(1,2,3-c,d)pyrene	pg m^{-3}	178		110	1,390/180/94[#]	150	180	1,150/1,500					
Phenanthrene	pg m^{-3}	54.1	**25**	340		58	470	2,880/10,200					
Pyrene	pg m^{-3}	53.9	**20**	290		69	290	980/3,400					
4,4'-DDT	pg m^{-3}	5.1											
Permethrin	pg m^{-3}	55.9											
BDE 47	pg m^{-3}	11	**7**				1.0	34.9/102	110				
BDE 99	pg m^{-3}	8.9	**8**				0.03	13.8/34.3	110				
PCB 101	pg m^{-3}	1.5											
PCB 118	pg m^{-3}	1.5											
PCB 138	pg m^{-3}	2.3											
PCB 153	pg m^{-3}	2.4											
PCB 180	pg m^{-3}	1.3											
BBP	ng m^{-3}	1.6	**2.4**							**5.5**	1.2		**0.138**
DEHP	ng m^{-3}	46.2	**41.5**							**13.5**	22.9	560*	**70**
DiBP	ng m^{-3}	0.861	**30.2**								33.9	720*	
DiNP	ng m^{-3}	7.9	**15.7**										
Triclosan	pg m^{-3}	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 (PM_{10}). 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**	US	China	Hong-Kong	**Norway**	USA	China	**China**	US
	Size fraction		**PM_{10}**	TSP	$PM_{2.5}$/TSP	$PM_{2.5}$	**PM_{10}**	TSP	TSP	**PM_{10}**	$PM_{2.5}$
	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**	June 1999- May 2000
	n Dwellings		**n=30**	n=12	n=7	n=6	**n=2**	n=20	n=28*	**n=13**	n=104
	Unit	This study	**Blanchard et al., 2014**	Batterman et al., 2009	Wang et al., 2014a	Wang et al., 2014a	**Rakkestad et al., 2007**	Tran and Kannan, 2015	Wang et al., 2014b	**Zhang et al., 2014**	Zhu and Jia, 2012
BDE 28	pg m^{-3}	nd - 13.5		nd - 25	nd - 45 / nd - 52	nd - 1.8					
BDE 85	pg m^{-3}	nd - 85.7		nd - 44	nd - 7.7 / nd - 10.2	nd - 2.1					
BDE 100	pg m^{-3}	nd - 308	**nd - 19**	nd - 370	0.5 - 57.9 / 1.8 - 141	nd - 22.1					
BDE 153	pg m^{-3}	nd - 107		nd - 110	nd - 20.6 / nd - 58.6	nd - 1.0					
BDE 154	pg m^{-3}	nd - 112		nd - 230	nd - 14.5 / nd - 192	nd - 0.6					
DBP	ng m^{-3}	nd - 138					**74 - 85**	0.9 - 451	nd - 4,920*	**7.3 - 1,466**	
DEP	ng m^{-3}	nd - 283						3.4 - 361		**0.08 - 7.4**	
DMP	ng m^{-3}	nd - 0.266						nq - 2.4	nd - 1,750*	**0.3 - 47.6**	
t-chlordane	pg m^{-3}	nd - 16.5									nd - 1,700
c-chlordane	pg m^{-3}	nd									nd - 670

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

Bold highlights studies with the same size fraction sampled (PM_{10}). 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	
Benzo(k)fluoranthene	145	88	46	18	H+S > H+NS**> NH+S* NH+S > NH+NS*
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*

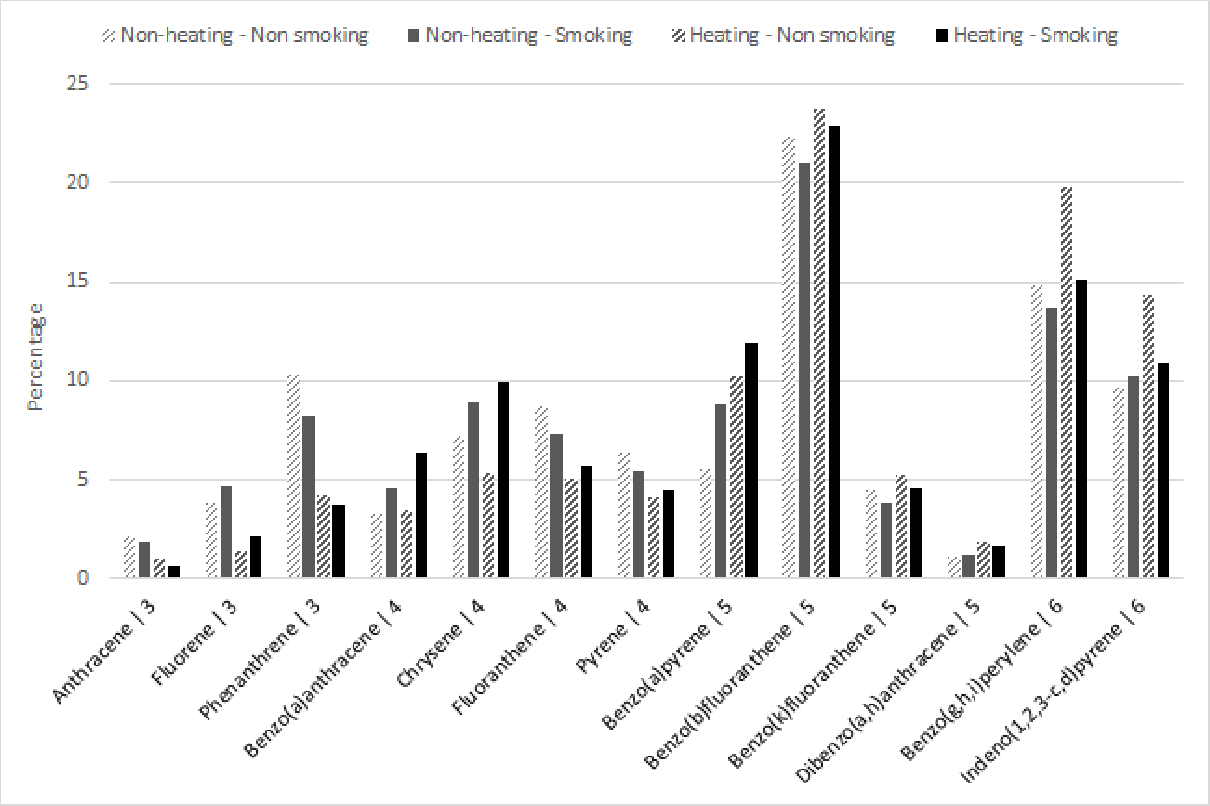
SVOCs influenced predominantly by smoking					
Fluorene	56	17	38	14	H/NH+S > H/NH+NS**
Phenanthrene	95	51	63	43	H/NH+S > NH+NS** H+S > H+NS***
Oxadiazon	< LOQ	< LOD	1.0	< LOD	H/NH+S > H/NH+NS***
Permethrin	90	78	124	53	NH+S > NH+NS*
BDE 47	45	12	23	4.8	H/NH+S > NH+NS*** H+S > H+NS*** > NH+NS*
BDE 99	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*
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.

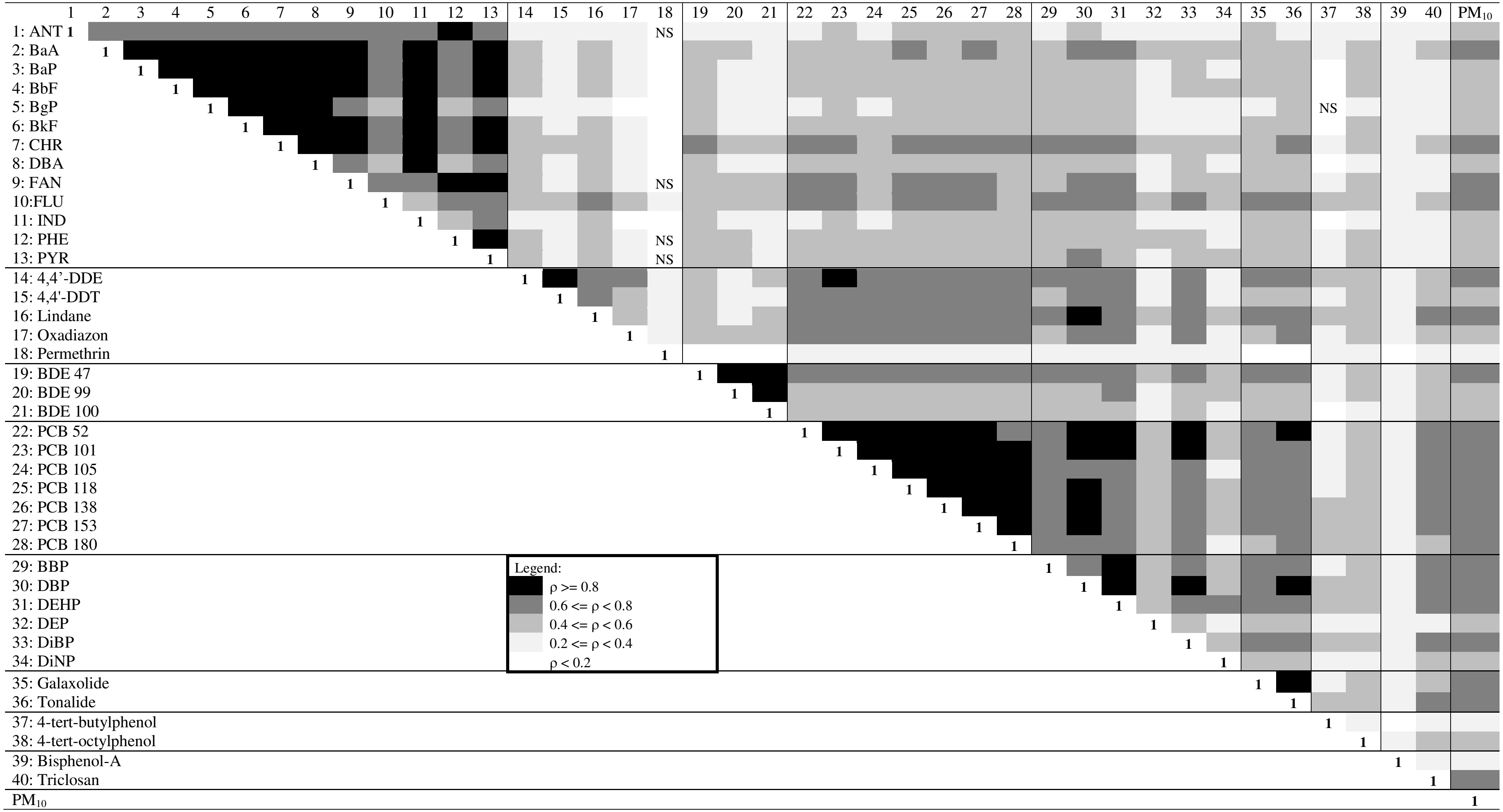
LIST OF FIGURES

Figure 1. Average relative contribution (%) of each PAH to the total concentrations of PAHs in PM_{10} 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 PM_{10} 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)

Chapitre 4 : Discussions

Les résultats des mesures d'un grand nombre de COSV en phase particulaire dans l'environnement domestique constituent un jeu de données unique pour caractériser les expositions et les risques pour la population française. La disponibilité de ces nouvelles données en France pointe la limite d'avoir, de fait, utilisé par défaut des données de la littérature pour choisir les COSV à analyser. Afin d'en évaluer les conséquences, une évaluation rétrospective de la hiérarchisation sanitaire conduite pour le choix des COSV à étudier a été réalisée. Ensuite, les concentrations des COSV quantifiés à la fois dans l'air et au sol ont été mises en perspective afin d'examiner dans quelle mesure les particules en suspension et les poussières déposées sont similaires en termes de concentrations et de mélanges de COSV en présence. Enfin, l'estimation des doses d'exposition aux COSV en phase particulaire à partir d'équations simples, de variables humaines d'exposition et des données de contamination a permis une première évaluation des contributions respectives de l'inhalation et de l'ingestion aux expositions domestiques des enfants et adultes à ces composés en phase particulaire dans le logement.

4.1 Évaluation rétrospective de la hiérarchisation sanitaire des COSV dans les logements français

Le choix des substances d'intérêt considérées ici a été fondé sur une hiérarchisation sanitaire initiale dont il est intéressant *a posteriori* d'évaluer la pertinence. Compte tenu du grand nombre de substances chimiques introduites dans l'environnement, le recours aux méthodes de hiérarchisation est fréquent pour classer celles-ci au regard du risque encouru qu'il soit environnemental ou sanitaire et prioriser les recherches et *in fine* les mesures de gestion à mettre en œuvre. Dans le champ de l'environnement intérieur, plusieurs approches ont été proposées dans différents contextes. La Commission européenne dans le cadre du projet INDEX (*Critical Appraisal of the Setting and Implementation of Indoor Exposure Limits in the EU*, 2002-2004) a mis en œuvre une démarche de hiérarchisation pour obtenir une liste restreinte de substances devant faire l'objet d'établissement de valeurs guides de qualité de l'air intérieur (VGAI) (Koistinen et al., 2010). En France, l'Anses procède de façon similaire pour identifier les substances pour lesquelles proposer des VGAI (Anses, 2007). Aux États-Unis, l'Agence pour la protection de l'environnement (US-EPA) a mis en place également une priorisation des polluants de l'air intérieur depuis le début des années 2000 (Johnson et al., 2002 ; Logue et al., 2011). En France, l'Observatoire de la qualité de l'air intérieur réalise également périodiquement une hiérarchisation sanitaire afin de définir les polluants nécessitant d'être mesurés dans le cadre des campagnes nationales de mesure (Mosqueron et Nedellec, 2002, 2005 ; Almeras, 2010). Ces hiérarchisations incluent également les polluants présents dans les poussières. Aux Pays-Bas, l'Agence de santé environnementale (RIVM) a hiérarchisé les substances qui pourraient entraîner des risques sanitaires via une exposition aux poussières domestiques (RIVM, 2007).

Ces approches sont basées sur le calcul d'indicateurs de risque renvoyant généralement à une démarche d'évaluation des risques sanitaires. Autrement dit, elles sont basées sur une mise en perspective des concentrations environnementales ou des doses d'exposition avec des valeurs toxicologiques de référence, combinant éventuellement des fréquences de détection et des catégories de danger (par exemple, les classifications cancérogènes de l'Organisation mondiale de la santé).

Une des limites fortes de ces méthodes tient au fait qu'en l'absence soit de données de toxicité, soit de résultats de mesures environnementales, une substance reste inclassable sans que pour autant le potentiel de risque pour la santé humaine n'ait été écarté. Ainsi, lors de la dernière classification de l'OQAI en 2010 (Almeras, 2010), sur les 1026 substances chimiques considérées, 667, soit 65 %, n'ont pas été classées du fait de données manquantes. Une telle proportion demeure problématique quand il s'agit de classer des substances pouvant avoir un effet sur la santé des populations. Une autre limite est liée à l'absence de données spécifiques au pays ou à la problématique considérée. L'utilisation par défaut de concentrations environnementales mesurées dans d'autres pays ou d'autres contextes peut biaiser les résultats. Par exemple, toujours dans la dernière hiérarchisation de l'OQAI, pour 23 % seulement des substances, les concentrations dans l'air intérieur sont issues d'études françaises ; 71 % des concentrations dans l'air intérieur proviennent d'études européennes et 5 % d'études hors Europe.

A partir des données de mesures obtenues ici, la hiérarchisation réalisée initialement a été évaluée au regard de ces deux limites évoquées.

4.1.1 Méthode

La méthode initiale de hiérarchisation des COSV (Bonvallot et al., 2010) est ciblée sur les COSV dans les poussières au sol exclusivement. Elle distingue les effets à seuil d'une part, des effets sans seuil d'autre part. Elle est basée, pour chaque COSV, sur le calcul d'un score pour chaque type d'effets tenant compte de la concentration médiane mesurée dans les poussières de logements et de la valeur toxicologique de référence (VTR) fondée sur l'effet critique, c'est à dire celui survenant pour les doses les plus faibles.

La concentration médiane est celle issue préférentiellement d'une étude française réalisée depuis moins de 10 ans. A défaut, une étude européenne est retenue, et *in fine* une étude d'un autre pays en l'absence de données européennes. En l'absence de concentration médiane, la moyenne arithmétique ou géométrique est utilisée. Lorsque la concentration médiane est inférieure à la limite de détection, le score du composé n'est pas calculé et il n'est pas inclus dans le classement. Compte tenu de la grande diversité des fractions de tamisage, ce paramètre n'a pas été un critère de sélection des études, malgré son influence indéniable discutée précédemment dans le Chapitre 1.

S'agissant des VTR, elles ont été recherchées dans les bases de données de référence (US-EPA, OEHHA, ATSDR, RIVM, Santé Canada). Dans le cas où plusieurs VTR étaient disponibles pour une exposition chronique par ingestion, la plus protectrice a été retenue. En l'absence de VTR, une valeur a été établie à partir des indicateurs toxicologiques publiés tels *Benchmark Dose*, *No Observed Adverse Effect Level* ou *Lowest Observed Adverse Effect Level*, auxquels des facteurs de sécurité ont été appliqués pour tenir compte notamment de la variabilité inter- et intra-espèce.

Les scores étaient alors calculés à partir du ratio de la concentration médiane par la VTR à seuil ou bien du produit de la concentration médiane par la VTR sans seuil. La liste initiale des COSV pour lesquels les scores ont été calculés a été établie sur la base des données publiées sur les COSV présents dans les poussières sédimentées dans les environnements intérieurs.

4.1.2 Résultats de la hiérarchisation initiale (2010)

Une liste de 156 substances a été considérée. Un score a pu être calculé pour 66 d'entre elles (42 %), dont 65 ayant des effets à seuil et 11 des effets sans seuil ; 10 substances appartiennent aux deux catégories. Il n'a pas été possible de prioriser 90 substances pour les raisons suivantes :

- 42 ne disposaient pas de concentration médiane issue de mesures déjà réalisées dans les poussières au sol (concentration médiane inférieure à la limite de détection), 17 d'entre elles n'ayant de toute façon pas d'indicateur toxicologique ;
- 8 n'avaient jamais fait l'objet de mesures dans les poussières ;
- 37 ne disposaient pas de VTR et aucun indicateur toxicologique n'a pu être construit ;
- 3 ne disposaient d'aucune mesure environnementale, ni de VTR ou d'indicateur toxicologique.

Les dix substances ayant les scores les plus élevés pour les effets à seuil et la classification des onze substances ayant des effets sans seuil sont présentées dans le Tableau 3.

Tableau 3 : Résultats de la classification initiale ayant conduit au choix des COSV d'intérêt

Classification des COSV ayant des effets critiques à seuil	**Classification des COSV ayant des effets critiques sans seuil**
1. le DEHP	1. le BDE 209
2. les paraffines chlorées C10-13	2. le DEHP
3. le dichlorvos	3. les HAP
4. les PCB	4. la dieldrine
5. le DiBP	5. le dichlorvos
6. la dieldrine	6. les PCB
7. le lindane	7. le lindane
8. les PFOS, perfluorooctane sulfonate	8. l'α-hexachlorocyclohexane (α-HCH)
9. le propoxur	9. le pentachlorophenol
10.le DBP	10.le folpet
	11.le 2,4,6-trichlorophénol

Deux tests de sensibilité portant sur l'utilisation de la concentration maximale mesurée au lieu de la médiane et l'inclusion de la fréquence de détection dans le calcul du score n'ont pas montré d'influence notable sur la classification finale.

4.1.3 Quelle hiérarchisation serait obtenue en se basant sur les concentrations mesurées dans les logements français ?

Au regard des données aujourd'hui disponibles, deux questions peuvent être posées :

A. les substances sont-elles aujourd'hui classées à l'identique au regard de la connaissance des concentrations dans les logements français (en réponse à l'impact sur l'utilisation de concentrations dans d'autres pays ou d'autres contextes) ?

B. peut-on classer des substances qui n'avaient pu l'être faute de données de contamination ? (en réponse à l'impact de la non-classification de substances du fait de données manquantes).

Les scores ont donc été recalculés en substituant les médianes utilisées initialement par celles présentées dans les Chapitre 2 et Chapitre 3.

Pour les effets à seuil, 27 composés sur 65 ont été concernés, tandis que pour les effets sans seuil, 7 substances sur 11 ont vu leur médiane évoluer. Les évolutions dans la classification sont présentées dans les Tableau 4 (effets à seuil) et Tableau 5 (effets sans seuil). Les COSV dont la concentration médiane dans les poussières au sol a été substituée sont sur fond gris. Les COSV indiqués en bleu sont ceux pour lesquels une évolution importante du score est notée, de plus ou moins 10 places dans le classement.

Pour les COSV ayant des effets à seuil, on observe un changement important dans la classification pour 8 substances, 5 en chute dans le classement et 3 ayant gagné des places. Le dichlorvos, qui n'a jamais été détecté, passe en dernière position du classement alors qu'il était troisième. Quatre autres pesticides, cyfluthrine, diazinon, oxadiazon et α-endosulfan, chutent dans le classement. Le dichlorvos, le diazinon, l'oxadiazon et l'α-endosulfan ont été interdits, ce qui peut expliquer la diminution de leurs concentrations par rapport aux données disponibles initialement. La rétrogradation de la cyfluthrine s'explique par l'absence d'études autres que celle de Leng et al. (2005) au moment de la hiérarchisation initiale. Or cette étude concerne un cas particulier où des mesures de pyréthrinoïdes ont été réalisées après un traitement insecticide, impliquant des concentrations élevées dans l'environnement intérieur.

Trois COSV, le bisphénol A, le groupe des congénères tétra- des PBDE et le groupe des congénères hexa- des PBDE remontent respectivement de 22, 22 et 14 places dans le classement. Au regard des conclusions des mesures de bisphénol A dans les logements français, à savoir des concentrations plus élevées en comparaison de celles observées dans les autres pays, il est logique que ce composé remonte dans le classement. Les concentrations utilisées pour la hiérarchisation initiale étaient celles de Rudel et al. (2003), issues de mesures dans 120 maisons du Cape Cod, États-Unis, conduites entre juin 1999 et septembre 2001. S'agissant des PBDE, les concentrations utilisées dans la hiérarchisation initiale étaient celles issues de l'étude Greenpeace limitée à 8 logements français (Vicaire, 2009). Ce changement important de position dans le classement souligne la fragilité d'une hiérarchisation dès lors que des concentrations issues de mesures dans des échantillons restreints sont utilisées.

Pour les COSV ayant des effets sans seuil, la classification n'est globalement pas modifiée puisqu'un écart maximal de 6 places dans le classement est observé. Les quatre substances en tête de classement restent à la même position.

Enfin, quatre COSV qui n'étaient pas dans la liste des 66 hiérarchisés ont été mesurés et disposent donc de concentrations pouvant à présent être utilisées : l'aldrine, le chlorpyrifos, la cyperméthrine et la deltaméthrine. Les médianes étant cependant toutes inférieures aux limites de détection, l'inclusion de ces quatre COSV dans la liste hiérarchisée n'est pas permise.

Tableau 4 : Mise à jour de la hiérarchisation des COSV pour les effets à seuil

Composé	**Classement 2010***	**Classement 2015**	**Différence 2010/2015**
DEHP	1	1	=
paraffines chlorées, C10-13	2	2	=
dichlorvos	3	62	↓ 59
PCB	4	3	↑ 1
DiBP	5	8	↓ 3
dieldrine	6	13	↓ 7
lindane	7	7	=
PFOS	8	4	↑ 4
propoxur	9	5	↑ 4
DBP	10	10	=
Organoétains (DBT, TBT, TBT)	11	6	↑ 5
Penta-BDE	12	9	↑ 3
cyfluthrine	13	44	↓ 31
BBP	14	21	↓ 7
DiNP	15	12	↑ 3
diazinon	16	47	↓ 31
PFOA	17	15	↑ 2
pentachlorophénol	18	17	↑ 1
nonylphénol diéthoxylate	19	18	↑ 1
déchlorane	20	19	↑ 1
tetrabromobisphénol A	21	20	↑ 1
tonalide	22	31	↓ 9
BDE 209	23	14	↑ 9
nonylphénol monoéthoxylate	24	24	=
propylparabène	25	25	=
DOP	26	26	=
DEP	27	32	↓ 5
nonylphénol éthoxycarboxylate	28	27	↑ 1
folpet	29	28	↑ 1
perméthrine (cis)	30	23	↑ 7
fluoranthène	31	29	↑ 2
phénanthrène	32	37	↓ 5
Tetra-BDE	33	11	↑ 22
oxadiazon	34	49	↓ 15
pyrène	35	30	↑ 5
Hexa-BDE	36	22	↑ 14
α-endosulfan	37	48	↓ 11
bisphénol A	38	16	↑ 22
butylparabène	39	33	↑ 6
musk cétone	40	34	↑ 6
2,4,6-trichlorophénol	41	35	↑ 6
benzo(g,h,i)pérylène	42	36	↑ 6
dichlorure de di-n-octylétain	43	38	↑ 5

Composé	Classement 2010*	Classement 2015	Différence 2010/2015
α-hexachlorocyclohexane	44	39	↑ 5
éthyl-parathion	45	40	↑ 5
triclosan	46	41	↑ 5
octylphénol diéthoxylate	47	42	↑ 5
2,3,4,6-tetrachlorophénol	48	43	↑ 5
fluorène	49	52	↓ 3
2,4,5-trichlorophénol	50	45	↑ 5
anthracène	51	50	↑ 1
octylphénol monoéthoxylate	52	46	↑ 6
TBP	53	54	↓ 1
DMP	54	51	↑ 3
3,4,5-trichlorophénol	55	53	↑ 2
acénaphtène	56	58	↓ 2
2,3,4,5-tetrachlorophénol	57	56	↑ 1
galaxolide	58	55	↑ 3
2,3,5,6-tetrachlorophénol	59	57	↑ 2
éthyl et méthyl parabènes	60	59	↑ 1
2,4,6-tribromophénol	61	60	↑ 1
dioxines, furanes et PCB-DL	62	61	↑ 1

* « Classement 2010 » se réfère à la hiérarchisation publiée en 2010 (Bonvallot et al., 2010) intégrant des publications de données de concentrations jusqu'à mi-2009.

NB : Le tableau compte 62 lignes car les 3 organoétains sont traités ensemble, ainsi que l'éthyl- et le méthyl-parabènes. Les mélanges de paraffines chlorées, dioxines, furanes et PCB *dioxin-like* (PCB-DL) restent comptabilisés pour 1. On obtient bien un total de 65 substances hiérarchisées pour les effets critiques à seuil.

Tableau 5 : Mise à jour de la hiérarchisation des COSV pour les effets sans seuil

Composé	Classement 2010*	Classement 2015	Différence 2010/2015
BDE 209	1	1	=
DEHP	2	2	=
HAP	3	3	=
dieldrine	4	4	=
dichlorvos	5	6	↓ 1
PCB	6	8	↓ 2
lindane	7	7	=
α-hexachlorocyclohexane	8	9	↓ 1
pentachlorophénol	9	10	↓ 1
folpet	10	11	↓ 1
2,4,6-trichlorophénol	11	5	↑ 6

* « Classement 2010 » se réfère à la hiérarchisation publiée en 2010 (Bonvallot et al., 2010) intégrant des publications de données de concentrations jusqu'à mi-2009.

Une comparaison rigoureuse aurait nécessité que l'ensemble des substances priorisées aient été mesurées. Or du fait d'une seule méthode multirésidus utilisée, certains COSV n'ont pas pu être analysés. De plus, par définition, la priorisation visant à sélectionner les substances d'intérêt, toutes n'ont pas été retenues par la suite pour les mesures. Une autre limite de la comparaison tient aux données disponibles qui ne concernent que les concentrations mesurées dans les logements accueillant des enfants âgés de 6 mois à 6 ans et non pas le parc français de logements. Enfin, cette évaluation rétrospective n'a porté que sur le volet « concentration » et non pas sur la toxicité ; l'impact de la production de nouvelles VTR ou de la publication d'études récentes pouvant conduire à la modification de certaines d'entre elles n'a pas été évalué.

4.1.4 Conclusion sur la pertinence de la hiérarchisation des COSV

Sur la base des 156 COSV recensés et à la lumière des résultats de mesure obtenus, la hiérarchisation n'est pas fondamentalement remise en cause.

En revanche, la veille scientifique menée tout au long de la thèse a permis de mettre en évidence 108 nouvelles substances non considérées en 2010 et qui font aujourd'hui l'objet de mesures dans les poussières et l'air des environnements intérieurs. Afin d'identifier les COSV d'intérêt pour toute nouvelle étude qui devrait être conduite, il conviendrait de mettre à jour la hiérarchisation. Autrement dit, compte tenu de la production importante de connaissances sur le sujet des COSV, toute hiérarchisation doit être actualisée.

Les 108 COSV identifiés dans la littérature publiée ces dernières années sont listés dans le Tableau 6. Du fait de la toxicité des PBDE, ceux-ci ont peu à peu été retirés du marché européen et remplacés par d'autres retardateurs de flamme bromés (Covaci et al., 2011 ; Dodson et al., 2012) et des retardateurs de flamme organophosphorés (Van der Veen et De Boer, 2012). On peut également citer les siloxanes, composés chimiques formés par une chaîne linéaire ou cyclique d'atomes d'oxygène et de silicium, utilisés dans de nombreuses applications industrielles, ainsi que dans des produits de grande consommation, notamment les produits d'hygiène corporelle et les cosmétiques (Tran et Kannan, 2015a ; Tran et al., 2015b). Le décaméthylcyclopentasiloxane, ou D5, est également utilisé dans un procédé de nettoyage à sec alternatif à l'emploi du tétrachloroéthylène. Le benzotriazole, le benzothiazole et la benzophénone, et leurs dérivés, sont des agents anticorrosion, qui sont ajoutés dans les revêtements (peintures) et les plastiques. Certains sont suspectés d'être cancérogènes, mutagènes ou perturbateurs endocriniens (Wang et al., 2013a). La liste proposée au Tableau 6 devra être considérée pour des mesures à venir sur les COSV dans les environnements intérieurs.

Tableau 6 : Recensement des « nouveaux » COSV potentiellement présents dans les environnements intérieurs

Acronyme	**Nom du composé (en anglais)**	**N° CAS**
Bisphénols et dérivés (9)		
BPM	Bisphenol M	13595-25-0
BPB	Bisphenol B	77-40-7
BPF	Bisphenol F	620-92-8
BPP	Bisphenol P	2167-51-3
BPS	Bisphenol S	80-09-1
BPZ	Bisphenol Z	843-55-0
BPAP	Bisphenol AP	1571-75-1
BPAF	Bisphenol AF	1478-61-1
BADGE	Bisphenol A diglycidyl ether	1675-54-3
Phtalates et dérivés (11)		
DPHP	Di-propyl-heptylphthalate	53306-54-0
DIUP	Diisoundecylphthalate	26761-40-0
DCHP	Dicyclohexylphthalate	84-61-7
DIOP	Diisooctylphthalate	27554-26-3
DTDP	Ditridecylphthalate	119-06-2
DHPP	Di-n-heptylphthalate	3648-21-3
DiHP	Di-iso-heptylphthalate	71888-89-6
DUP	Di-undecylphthalate	3648-20-2
DAP	Diallyl-phthalate	131-17-9
DBzP	Butyl-octylphthalate	523-31-9
DiPrP	Dipropylphthalate	605-45-8

Acronyme	Nom du composé (en anglais)	N° CAS
Plastifiants non phtalates (7)		
DINCH	Diisononyl 1,2cyclohexanedicarboxylic acid	166412-78-8
DEHT	Di(2ethylhexyl) terephthalate	6422-86-2
DBA	Dibutyladipate	105-99-7
DiBA	Diisobutyl adipate	141-04-8
DEHA	Di (2-ethyl-1-hexyl) adipate	103-23-1
DBSb	Dibutyl sebacate	109-43-3
BEHSb	Bis (2-ethyl-1-hexyl) sebacate	122-62-3
Retardateurs de flamme bromés (37)		
BEH-TEBP (TBPH)	Bis(2-ethylhexyl) tetrabromo phthalate	26040-51-7
BTBPE	1,2-bis(2,4,6-tribromophenoxy)ethane	37853-59-1
DBDBE (BDBE-209)	Decabromodibenzyl ether	497107-13-8
DBDPE (BDPE-209)	Decabromodiphenyl ethane	84852-53-9
DBE-DBCH (TBECH)	4-(1,2-dibromoethyl)-1,2-dibromocyclohexane	3322-93-8
DBNPG	Dibromoneopentyl glycol	3296-90-0
DBP	2,4-dibromophenol	615-58-7
DBS	Dibromostyrene	31780-26-4
EBTEBPI	N,N′-ethylenebis(tetrabromophthalimide)	32588-76-4
EH-TBB	2-ethylhexyl 2,3,4,5-tetrabromobenzoate	183658-27-7
HBB	Hexabromobenzene	87-82-1
HBCYD	Hexabromocyclodecane	25495-98-1
HCTBPH	1,2,3,4,7,7-hexachloro-5-(2,3,4,5-tetrabromophenyl)-Bicyclo[2.2.1]hept-2-ene	34571-16-9
HEEHP-TEBP	2-(2-hydroxyethoxy)ethyl 2-hydroxypropyl 3,4,5,6-tetrabromophthalate	20566-35-2
PBB	Pentabromobenzene	608-90-2
PBB-Acr	Pentabromobenzyl acrylate	59447-55-1
PBBB	Pentabromobenzyl bromide	38521-51-6
PBBC	Pentabromobenzyl chloride	58495-09-3
PBEB	2,3,4,5,6-pentabromoethylbenzene	85-22-3
PBP	Pentabromophenol	608-71-9
PBP-AE	Pentabromophenol allyl ether	3555-11-1
PBT	2,3,4,5,6-pentabromotoluene	87-83-2

Acronyme	Nom du composé (en anglais)	N° CAS
TBCT	Tetrabromo-*o*-chlorotoluene	36569-21-6
TBBPA-BAE	Tetrabromobisphenol A bis(allyl) ether	25327-89-3
TBBPA-(B)DBPE	Tetrabromobisphenol A bis(2,3-dibromopropyl) ether	21850-44-2
TBBPA-BHEE	Tetrabromobisphenol A bis(2-hydroxyethyl) ether	4162-45-2
TBBPA-BME	Tetrabromobisphenol A bismethyl ether	37853-61-5
TBBPS	Tetrabromobisphenol S	39635-79-5
TBCO	1,2,5,6-tetrabromocyclooctane	3194-57-8
TBNPA	Tribromoneopentyl alcohol	1522-92-5
TBP-AE (ATE)	2,4,6-tribromophenyl allyl ether	3278-89-5
TBP-BAE (BATE)	2-bromoallyl 2,4,6-tribromophenyl ether	99717-56-3
TBP-DBPE (DPTE)	2,4,6-tribromophenyl 2,3-dibromopropyl ether	35109-60-5
TBX	1,2,4,5-tetrabromo-3,6-dimethylbenzene	23488-38-2
TDBP-TAZTO	1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-trione	52434-90-9
TTBP-TAZ	2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine	25713-60-4
OBTMPI (OBIND)	octabromo-1,3,3-trimethyl-1-phenylindane	155613-93-7
Retardateurs de flamme organophosphorés non-halogénés (11)		
BPA-BDPP (BADP)	Bisphenol A bis(diphenyl phosphate)	5945-33-5
DCP	Diphenyl cresyl phosphate	26444-49-5
DOPO	9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide	35948-25-5
DPEHP (EHDPP)	Diphenyl (2-ethylhexyl) phosphate	1241-94-7
PBDMPP	Tetrakis(2,6-dimethylphenyl)-m-phenylene biphosphate	139189-30-3
PBDPP (RDP)	Resorcinol bis(diphenyl phosphate)	57583-54-7
TEP	Triethyl phosphate	78-40-0
TIPPP	Tris(4-isopropylphenyl) phosphate	2502-15-0
TMPP (TCP)	Tricresyl phosphate	1330-78-5
TPP	Tri-n-propyl phosphate	513-08-6
TTBPP	Tris(4-t-butylphenyl)phosphate	78-33-1
Retardateurs de flamme organophosphorés halogénés (4)		
BCMP-BCEP	2,2-bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate) (V6)	38051-10-4
TDBPP	Tris (2,3 dibromopropyl) phosphate	126-72-7

Acronyme	Nom du composé (en anglais)	N° CAS
TDCPP	Tris(2,3-dichloropropyl) phosphate	78-43-3
TTBNPP	Tri[3-bromo-2,2-bis(bromomethyl)propyl]phosphate	19186-97-1
Siloxanes (16)		
D3 à D7	5 composés cycliques	D3 : 541-05-9 D4 : 556-67-2 D5 : 541-02-6 D6 : 540-97-6 D7 : 107-50-6
L4 à L14	11 composés linéaires	L3 : 107-51-7 L4 141-62-8 L5 : 141-63-9 L6 : 107-52-8
Benzotriazole, Benzothiazoles, Benzophénones (13)		
1-H-BTR	1-hydrogen-benzotriazole	95-14-7
1-OH-BTR	1- hydroxybenzotriazole	2592-95-2
TTR	Tolyltriazole	29385-43-1
5-Cl-BTR	5-chloro-1-hydrogenbenzotriazole	94-97-3
5,6-2Me-BTR	5,6-dimethyl-1-H-benzotriazole	4184-79-6
BTH	Benzothiazole	128366-28-9
2-OH-BTH	2-hydroxybenzothiazole	934-34-9
2-MeS-BTH	2-methylthio-benzothiazole	615-22-5
2-NH2-BTH	2-aminobenzothiazole	136-95-8
2-SCNMeS-BTH	2-thiocyanomethylthio-benzothiazole	64441-45-8
2-OH-4-MeO-BP	2-hydroxy-4-methoxy-benzophenone	131-57-7
22’-2OH-4-MeO-BP	2,2’-dihydroxy-4-methoxybenzophenone	131-53-3
22’44’-4OH-BP	2,2’,4,4’-tetrahydroxybenzophenone	131-55-5

Sources : (Nagorka et al., 2011 ; Dodson et al., 2012 ; Wang et al., 2013a ; Blanchard et al., 2014a ; Brown et al., 2014 ; Fromme et al., 2014 ; Takeuchi et al., 2014 ; Anses, 2015 ; Liagkouridis et al., 2015 ; Mizouchi et al., 2015 ; Sahlström et al., 2015 ; Tran et Kannan, 2015a ; Tran et al., 2015b)

4.2 Relations entre les COSV dans les particules en suspension et les poussières au sol

La répartition des COSV dans les différentes phases de l'environnement intérieur est déterminante en termes d'exposition. Une compréhension de cette répartition est indispensable dans un objectif de qualification des expositions (quelles voies sont concernées ou prépondérantes ?) et de quantification de celles-ci (quelles sont les doses absorbées ?). L'étude de cette répartition n'est cependant pas aisée. Expérimentalement, peu d'études ont intégré des mesures concomitantes dans l'air et les poussières déposées au sol. La revue documentaire réalisée au début de la thèse a permis d'identifier 41 publications combinant des mesures dans ces deux compartiments sur les 240 considérées d'intérêt, soit 17 %. Celles qui ont étudié quantitativement les relations entre les concentrations dans les deux médias n'ont pas toujours mis en évidence de corrélation significative. Cette observation peut s'expliquer par les choix métrologiques réalisés : mesure de la phase gazeuse uniquement, fraction de tamisage retenue, par exemple.

S'agissant de l'approche par modélisation, Weschler et Nazaroff (2010) rappellent qu'au cas par cas, pour une pièce donnée, il n'est pas possible de prédire la concentration dans l'air à partir de celle via les poussières déposées, et réciproquement, en l'état actuel des modèles et données disponibles. A l'échelle d'un échantillon de bâtiments, le calcul de la concentration médiane dans un média à partir de celle dans l'autre, pour un COSV donné, peut cependant donner une approximation correcte. L'impossibilité de modéliser précisément s'explique par le fait que les modèles sont très sensibles aux caractéristiques physico-chimiques des substances (Salthammer et Schripp, 2015) et que ces dernières ne sont pas établies de façon univoque, que ce soit expérimentalement ou par calcul. En outre, les caractéristiques physico-chimiques d'une substance peuvent varier significativement en fonction de la température, qui elle-même peut varier notablement au sein d'une pièce selon l'ensoleillement, l'ouverture des fenêtres, le fonctionnement du chauffage, etc. Enfin, les modèles proposés décrivent une répartition entre phases à l'équilibre, ce qui n'est pas toujours le cas. Des approches probabilistes se développent pour intégrer la variabilité des caractéristiques physico-chimiques (Salthammer et Schripp, 2015).

Les deux jeux de concentrations en COSV étudiés ont été examinés à la lueur de cette problématique de partition entre concentration dans l'air et concentration dans les poussières au sol, gardant à l'esprit la très forte limite de l'exercice résidant dans le fait que les concentrations n'ont pas été mesurées dans les mêmes logements, ni aux mêmes périodes (2003-2005 *versus* 2008-2009). Malgré cette limite, il est apparu intéressant d'examiner les similarités et différences de profils entre COSV en phase particulaire dans l'air et dans les poussières, en termes de substances en présence d'une part, et de concentrations d'autre part.

4.2.1 Comparaison des substances en présence

Les mélanges des substances en présence en phase particulaire de l'air et dans les poussières au sol ont été examinés. Les classifications mises en œuvre pour le traitement des concentrations mesurées ont fait apparaître différentes typologies de logements selon leur contamination en COSV dans l'air ou dans les poussières. Concernant les COSV dans les poussières au sol, quatre groupes de logements se distinguent (cf. Chapitre 2). 41 % des logements apparaissent multipollués ; de nombreux COSV sont présents dans ces logements et en concentrations plus élevées que les médianes observées à l'échelle du parc global des logements accueillant des enfants de moins de 6 ans. 20 % de logements sont moyennement pollués et 15 % sont qualifiés de peu pollués, à savoir avec des concentrations en COSV inférieures à la limite de détection ou aux médianes observées dans le parc. Un dernier groupe représentant 24 % de logements correspond à ceux dans lesquels un COSV est en concentration très élevée par rapport aux autres logements (i.e. bien supérieure à la concentration médiane) ; il s'agit des logements ayant de fortes concentrations en BDE 209 et/ou en cyfluthrine.

S'agissant de la phase particulaire de l'air, l'étude des profils de contamination en COSV fait apparaître cinq groupes de logements : 29 % des logements apparaissent multipollués, à savoir présentant, pour 45 COSV, des concentrations toutes plus élevées que les médianes observées à l'échelle du parc des résidences principales ; 46 % des logements sont moyennement pollués et 25 % sont qualifiés de peu pollués, à savoir avec des concentrations inférieures à la limite de détection ou aux médianes observées pour 36 COSV. Au sein des logements multipollués, on distingue un groupe caractérisé par la présence en fortes concentrations des retardateurs de flamme bromés, représentant 3 % des logements. De même, au sein des logements moyennement pollués, certains (24 %) le sont par les HAP. Ces classifications attestent de l'hétérogénéité des mélanges de COSV en présence selon les logements. L'étude des similarités des mélanges de COSV dans les poussières au sol et en phase particulaire de l'air ne peut donc pas se faire pour tous les COSV considérés simultanément. Une approche par famille de COSV a été privilégiée.

Dans un premier temps, les fréquences de détection à l'échelle des parcs de logements de chaque COSV dans les poussières au sol et les particules en suspension ont été comparées pour les 48 composés mesurés dans les deux médias. La fréquence de détection dépend des performances analytiques des méthodes mises en œuvre. Néanmoins, cette comparaison fournit un éclairage sur la concomitance des COSV dans chaque média.

Cette comparaison est présentée sur la Figure 6. De façon générale, on observe une proximité des fréquences de détection dans les deux médias, pour un COSV donné. Cependant, pour 14 composés, soit un tiers de ceux considérés, un écart d'au moins 20 % des fréquences de détection est observé. Cet écart est toujours à la faveur d'une fréquence de détection plus élevée dans les poussières au sol.

Dans un second temps, les contributions relatives de chaque COSV dans la concentration totale de sa famille chimique, dans les poussières au sol et dans la phase particulaire de l'air respectivement, ont été déterminées. Autrement dit, les profils de contamination des poussières et de la phase particulaire de l'air par famille chimique ont été comparés. Ce type de mise en perspective a déjà été utilisé pour comparer les mélanges dans l'air intérieur et les poussières au sol (Fromme et al., 2004), dans les poussières de logements et les cheveux des occupants (Król et al., 2014), dans les poussières au sol à l'intérieur et à l'extérieur (Yu et al., 2012), dans l'air de différentes pièces du logement (Pei et al., 2013), dans les poussières au sol de différents environnements intérieurs : logements, écoles, bureaux, etc. (Kalachova et al., 2012 ; Tran et Kannan, 2015c), ou selon les saisons (Yu et al., 2012), selon différents modes de prélèvement : par aspirateur ou par lingette (Toms et al., 2009), selon la fraction de tamisage (Cunha et al., 2010) ou encore selon les pays (Dirtu et al., 2012 ; Wang et al., 2015).

Les données brutes des concentrations (145 échantillons de poussières et 285 échantillons de PM_{10}) ont été utilisées pour calculer les contributions respectives en pourcentage, par famille chimique et dans chaque logement. Pour chaque COSV, la moyenne des contributions dans l'ensemble des logements a été calculée pour chaque média. La comparaison des profils des mélanges de COSV par famille chimique est présentée sur la Figure 7.

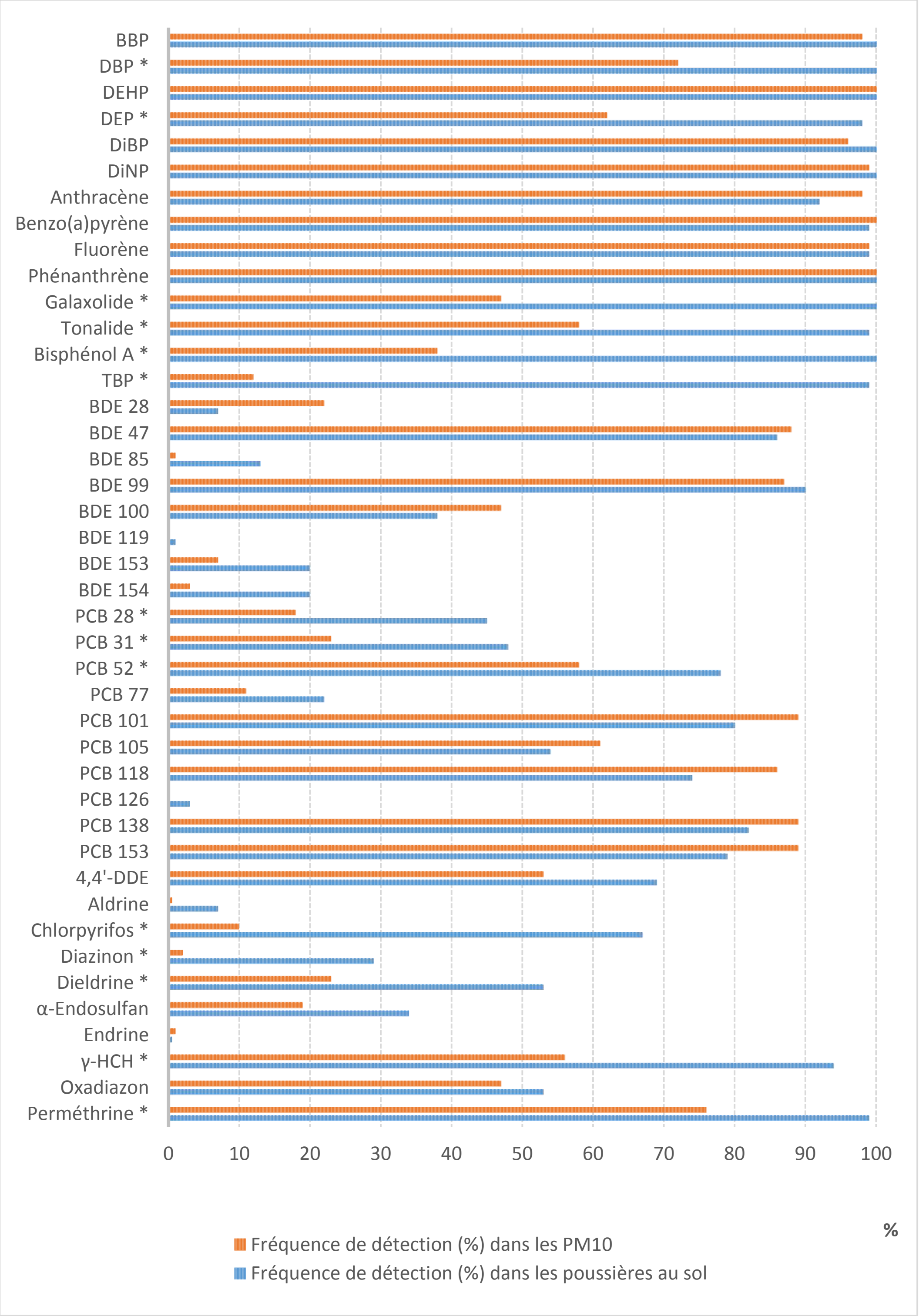


Figure 6 : Fréquences de détection dans les poussières déposées au sol et dans la phase particulaire de l'air (PM_{10}) pour les 42 COSV mesurés dans les deux médias

Note : Les COSV marqués d'une étoile sont ceux pour lesquels un écart d'au moins 20 % est observé entre la fréquence de détection dans les poussières au sol et celle dans la phase particulaire de l'air (PM_{10}).

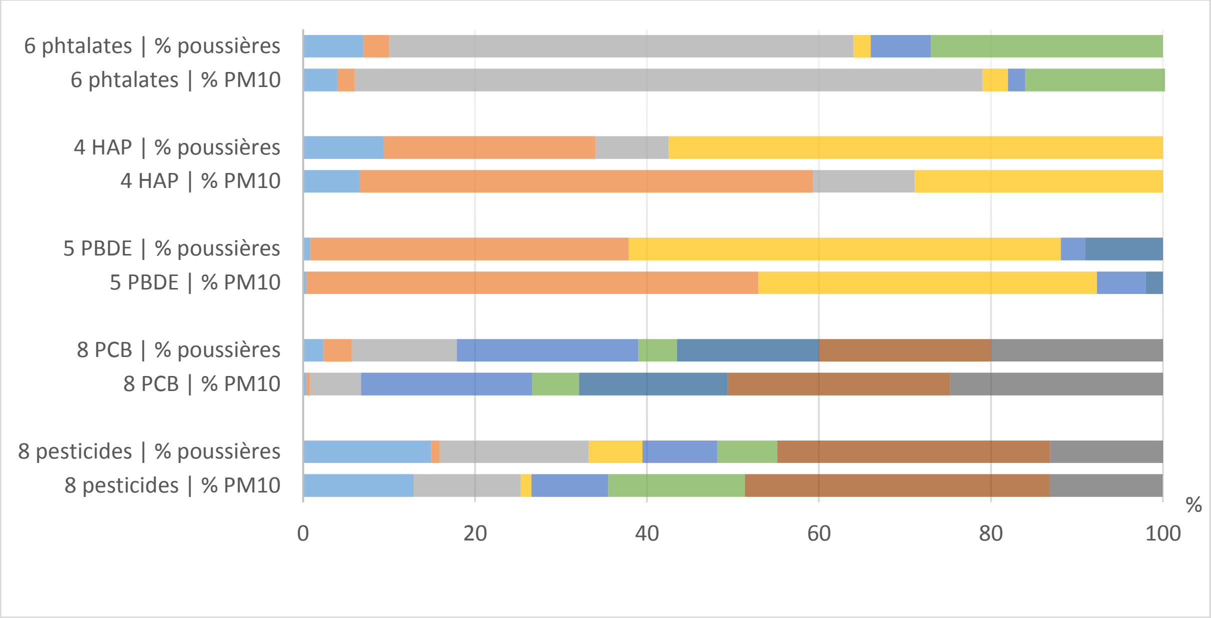


Figure 7 : Comparaison des mélanges de COSV dans les poussières au sol et dans la phase particulaire de l'air (PM_{10}) : contribution relative moyenne en % de chaque COSV dans son groupe chimique

Note : Les COSV quasiment jamais détectés dans les deux médias n'ont pas été considérés. Ainsi les substances prises en compte dans chaque groupe sont les suivantes, dans l'ordre des contributions de gauche à droite :

Phtalates : BBP, DBP, DEHP, DEP, DiBP et DiNP
HAP : anthracène, benzo(a)pyrène, fluorène et phénanthrène
PBDE : 28, 47, 99, 100 et 153. Les congénères 85, 119, 154 sont exclus.
PCB : 28, 31, 52, 101, 105, 118, 138 et 153. Les congénères 77 et 126 sont exclus.
Pesticides : 4,4'-DDE, aldrine, chlorpyrifos, diazinon, dieldrine, α-endosulfan, lindane et oxadiazon. L'endrine a été exclue. La perméthrine n'appartenant pas au groupe des pesticides organochlorés et organophosphorés n'a pas été considérée.

Cette mise en perspective des profils de contamination dans les poussières au sol et la phase particulaire de l'air montre des mélanges de COSV globalement relativement similaires. Quelques différences sont observées, à savoir une plus forte proportion de benzo(a)pyrène dans l'air par rapport aux poussières (53 % vs. 25 %) et la présence dans les poussières de plus fortes proportions de PCB 28 (2 % vs. 0,4 %) et de PCB 31 (3 % vs. 0,4 %), la contribution de ces congénères restant faible.

4.2.2 Comparaison des concentrations en COSV

Le second volet de la comparaison des poussières au sol et des particules en suspension en termes de contamination par les COSV porte sur la relation quantitative pouvant exister entre les concentrations dans chaque média.

La revue documentaire réalisée dans la première partie de ce travail et présentée au Chapitre 1 laisse penser qu'il existe une relation quantitative entre les concentrations des deux médias. La théorie relative à la répartition des COSV dans les différents compartiments de l'environnement intérieur le confirme également. En effet, selon les théories fondatrices de Pankow (1994) et Finizio et al. (1997), puis le modèle à l'équilibre défini par Weschler et Nazaroff (2008), les concentrations d'un COSV dans la phase gazeuse de l'air, la phase particulaire de l'air et les poussières déposées sont définies par les équations suivantes :

$$F = C_{\mathrm{g}} \times TSP \times K_{\mathrm{p}} \qquad \text{(Équation 1)}$$

$$C_{\mathrm{g}} = \frac{C_{\mathrm{d}}}{K_{\mathrm{d}}} \qquad \text{(Équation 2)}$$

Avec :

F : la concentration du composé en phase particulaire (µg/m^3)

C_g : la concentration du composé en phase gazeuse (µg/m^3)

TSP : la concentration totale des particules en suspension dans l'air (µg/m^3)

K_p : le coefficient de partage gaz/particules (m^3/µg)

C_d : la concentration dans les poussières déposées au sol (µg/µg)

K_d : le coefficient de partage gaz/poussières déposées (m^3/µg)

La combinaison des Équation 1 et Équation 2 conduit à l'Équation 3 qui établit la relation de proportionnalité entre la concentration en phase particulaire de l'air et celle dans les poussières déposées :

$$F = \frac{C_{\mathrm{d}} \times TSP \times K_{\mathrm{p}}}{K_{\mathrm{d}}} \qquad \text{(Équation 3)}$$

Les concentrations dans les poussières collectées dans les sacs d'aspirateur des foyers correspondent par définition à une intégration dans le temps et sont donc considérées comme étant à l'équilibre. Les mesures de COSV en phase particulaire ont été réalisées à partir de prélèvements de particules sur une durée de sept jours. Cette intégration longue permet de faire l'hypothèse que ces concentrations sont proches de celles à l'équilibre, et donc autorise l'emploi des Équations 1 à 3.

La Figure 8 présente le tracé des concentrations en phase particulaire exprimées en ng/g en fonction des concentrations dans les poussières déposées au sol en ng/g pour les 42 COSV mesurés dans les deux médias. Les concentrations étant mesurées dans des échantillons de logements différents, elles n'ont pu être appariées. Aussi, pour chaque COSV, les percentiles 25, 50 et 75 des concentrations en phase particulaire de l'air sont respectivement appariés aux percentiles 25, 50 et 75 des concentrations dans les poussières, pour les percentiles pouvant être calculés (42 COSV considérés initialement, mais *in fine* 16 paires de percentiles 25, 25 de percentiles 50 et 28 de percentiles 75). Afin de disposer de la même unité de comparaison, en masse de COSV par gramme de matière particulaire, les concentrations en phase particulaire sont calculées à partir de la concentration volumique ($\mu g_{COSV}/m^3$) et de la concentration en PM_{10} ($\mu g_{PM10}/m^3$) mesurée dans chacun des 285 logements.

La Figure 8 confirme l'existence d'une relation quantitative entre les concentrations des COSV en phase particulaire dans l'air et déposés sur le sol. Le fait que les points soient systématiquement au-dessus de la bissectrice suggère une tendance à l'enrichissement de la matière particulaire en suspension dans l'air en COSV par rapport à la poussière déposée au sol, et ce pour toutes les molécules. Cela pourrait s'expliquer par le fait que la fraction PM_{10} regroupe des particules de diamètre médian inférieur à 10 µm, alors que les poussières ont été tamisées à 100 µm. Comme les COSV sont associés à la fraction fine des particules (Cao et al., 2012), la sélection de cette fraction induira des concentrations toujours plus importantes que la prise en compte d'une fraction plus large en taille. Etant donné que tous les points se retrouvent à une distance équivalente de la bissectrice, cela suggère que cet effet d'enrichissement lié à la taille de particules est le même pour tous les COSV représentés et donc ne semble pas dépendre de la pression de vapeur ou de la masse molaire de ceux-ci.

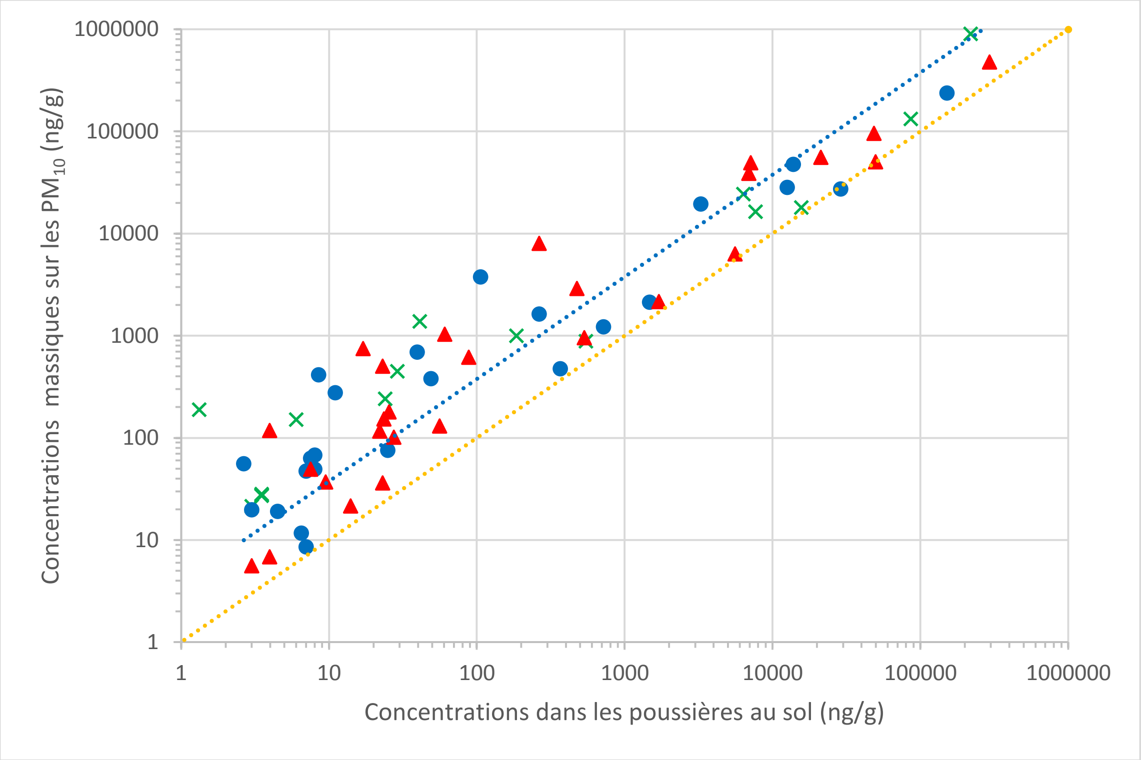


Figure 8 : Concentrations en COSV en phase particulaire de l'air en fonction des concentrations en COSV dans les poussières déposées au sol

Légende : Croix vertes : percentiles 25 ; points bleus : médianes ; triangles rouges : percentiles 75 ; pointillés orange : y=x ; pointillés bleus : courbe de tendance pour les points représentant les médianes

La difficulté de pouvoir prédire, à l'échelle d'un logement, la concentration en phase particulaire de l'air à partir de la concentration dans les poussières déposées à l'aide de l'Equation 3, tient notamment à l'incertitude des coefficients K_p et K_d. K_p peut être calculé à partir de la pression de vapeur saturante p_L^0 (Finizio et al., 1997) ou du coefficient de partage entre l'air et l'octanol, K_{oa} (Weschler et Nazaroff, 2010). K_d est dépendant du coefficient K_{oa} (Weschler et Nazaroff, 2010 ; Salthammer et Schripp, 2015). Le coefficient K_{oa} peut être calculé à partir du coefficient de partage entre l'octanol et l'eau (K_{ow}) et la constante de Henry (Shoeib et Harner, 2002). Au fait que ces variables ne disposent pas de valeurs univoques, s'ajoutent l'influence de la température qui n'est pas souvent prise en compte comme l'a montré un autre volet du projet ECOS-Habitat dédié à la modélisation (Wei et al., 2015a) et la non atteinte de l'équilibre de répartition entre phases.

La Figure 8 montrant une relation entre les concentrations en phase particulaire de l'air et dans les poussières déposées, l'Equation 3 a été testée sur le jeu de données à disposition. Les concentrations en phase particulaire F ont été calculées à partir des concentrations dans les poussières au sol C_d, puis comparées aux concentrations mesurées dans les PM_{10}.

Compte tenu des limites exposées précédemment, plusieurs valeurs des coefficients K_p et K_d sont retenues. Plus précisément, dans le cadre du volet dédié à la modélisation du projet ECOS-Habitat, les distributions des K_p et K_d ont été établies pour chacun des COSV étudiés, à partir des équations empiriques et des valeurs pour les variables qui les composent disponibles dans la littérature (Wei et al., 2015b). Les percentiles 25, 50 et 75 des K_p et K_d sont retenus respectivement pour chaque COSV considéré. Concernant la concentration en particules totales dans l'air intérieur (TSP), celle-ci n'a pas été mesurée dans les logements où les sacs d'aspirateur ont été prélevés. L'hypothèse est posée que cette concentration suit la même distribution que celle des PM_{10} dans les logements où les filtres PM_{10} ont été analysés pour la mesure des COSV. Trois percentiles de la distribution des concentrations en PM_{10} sont retenus pour les calculs : percentile 25 (22 $\mu g/m^3$), percentile 50 (31 $\mu g/m^3$) et percentile 75 (56 $\mu g/m^3$). Enfin, pour chaque COSV, la distribution des concentrations dans les poussières au sol mesurées dans les 145 logements a été introduite dans l'Equation 3.

Les COSV étudiés sont ceux mesurés dans les deux médias, à l'exception de ceux qui ne sont quasiment jamais détectés dans les deux milieux : aldrine, endrine, PCB 126 et BDE 119. Pour chacun des 38 COSV considérés, 3 919 concentrations en phase particulaire de l'air sont prédites. Les percentiles 25, 50 et 75 de ces distributions sont présentés dans le Tableau 7. Ils sont mis en perspective de ces mêmes percentiles pour les concentrations mesurées dans la fraction PM_{10}. Les concentrations prédites et mesurées inférieures à la limite de détection ont été substituées par 25 %, 50 % ou 75 % de la valeur de cette limite de sorte à ne pas perdre d'information. Les concentrations mesurées en fonction des concentrations modélisées sont représentées sur la Figure 9, pour chaque série de percentile.

Tableau 7 : Concentrations en phase particulaire de l'air prédites et mesurées pour 38 COSV (pg/m^3)

COSV	Percentiles 25		Percentiles 50		Percentiles 75	
	Concentration prédite	Concentration mesurée	Concentration prédite	Concentration mesurée	Concentration prédite	Concentration mesurée
Perméthrine	26,7	24,9	143	76,9	829	200
Oxadiazon	0,1	0,1	1,4	0,2	6,8	1,0
γ-HCH	4,1	1,0	11,0	2,5	31,8	5,8
α-Endosulfan	2,6	2,6	5,2	5,2	268	7,8
Dieldrine	1,0	1,0	1,1	2,1	12,5	3,1
Diazinon	10,4	10,4	20,9	20,9	1,5	31,3
Chlorpyrifos	10,4	10,4	3,6	20,9	15,4	31,3
4,4'-DDE	0,3	0,1	1,4	0,4	5,6	1,8
PCB 153	0,6	0,7	2,8	2,2	13,0	7,5
PCB 138	0,7	0,8	2,8	2,2	12,2	8,2
PCB 118	0,5	0,6	2,6	1,4	11,6	5,6
PCB 105	0,1	0,1	0,9	0,6	4,6	2,4
PCB 101	1,2	0,7	3,8	1,6	14,2	4,7
PCB 77	0,1	0,1	0,2	0,2	0,3	0,3
PCB 52	1,1	0,1	3,9	0,6	12,2	1,8
PCB 31	0,1	0,1	0,2	0,2	4,1	0,3
PCB 28	0,1	0,1	0,2	0,2	4,3	0,3
BDE 154	1,0	1,0	2,1	2,1	3,1	3,1
BDE 153	1,0	1,0	2,1	2,1	3,1	3,1
BDE 100	0,5	0,5	1,1	2,3	1,6	4,9
BDE 99	0,2	5,1	1,2	10,1	5,2	20,5
BDE 85	1,0	1,0	2,1	2,1	3,1	3,1
BDE 47	0,5	5,8	2,7	14,4	8,9	37,9
BDE 28	0,1	0,1	0,2	0,2	0,3	0,4
TBP	9,3	10,4	22,9	20,9	56,0	31,3
Bisphénol A	3,9	261	18,0	522	75,6	1553
Tonalide	4,8	2,6	11,7	15,2	29,0	37,5
Galaxolide	9,7	10,4	28,5	20,9	83,2	125
Phénanthrène	227	34,7	566	59,3	1564	104
Fluorène	41,9	13,3	92,3	20,3	207	43,8
Benzo(a)pyrène	24,7	35,9	210	144	1705	354
Anthracène	40,2	8,5	156	13,1	1674	20,8
DiNP	212	4361	683	8372	2411	18496
DiBP	1286	410	5460	842	20062	2439
DEP	867	209	2249	689	6327	2558
DEHP	859	22732	5713	53505	37496	114805
DBP	1036	433	2818	866	7722	2786
BBP	101	661	1049	1591	10343	4759

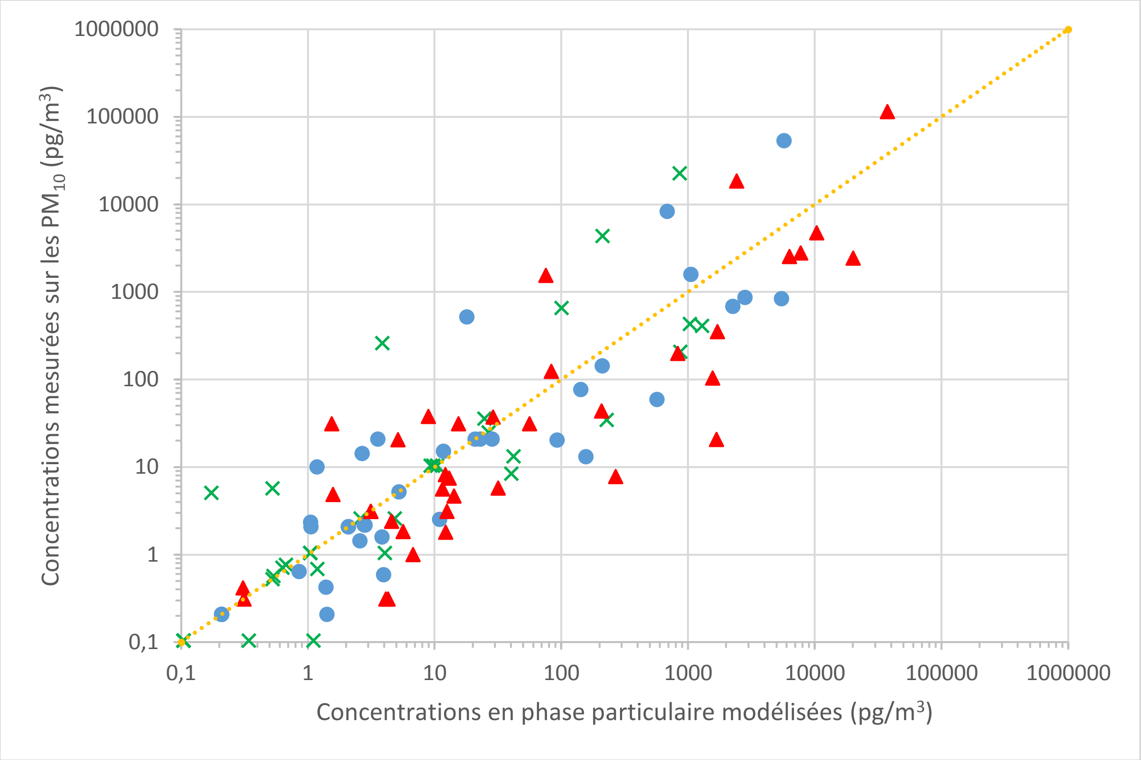


Figure 9 : Concentrations mesurées en phase particulaire de l'air en fonction des concentrations modélisées en phase particulaire dans l'air pour 38 COSV

Légende : Croix vertes : percentiles 25 ; points bleus : médianes ; triangles rouges : percentiles 75 ; pointillés orange : y=x

Compte tenu des limites soulignées du fait de concentrations mesurées dans des logements différents, de la non prise en compte de la température intérieure, de l'assimilation des concentrations en particules totales aux concentrations en PM_{10}, les concentrations prédites sont considérées cohérentes avec les concentrations mesurées même si certaines différences, parfois importantes, sont observées. Les concentrations modélisées ne sont pas systématiquement inférieures ou supérieures aux concentrations mesurées ; cela dépend des COSV considérés, y compris au sein d'une même famille chimique. Par exemple, les concentrations prédites en DiBP sont supérieures à celles mesurées, tandis qu'on observe l'inverse pour le DEHP. Un facteur 2 d'écart des concentrations est observé en moyenne sur les percentiles 25 et 50, tandis qu'un facteur 6 l'est sur les percentiles 75, lié notamment à un facteur 80 observé pour l'anthracène. La différence moyenne passe à un facteur 4 pour les percentiles 75 quand ce composé n'est pas considéré.

4.2.3 Conclusion de la comparaison des COSV en phase particulaire dans l'air et les poussières

Comme montré dans d'autres travaux, les concentrations en COSV dans les poussières déposées au sol sont liées aux concentrations en phase particulaire de l'air. Les poussières déposées sur les sols sont retrouvées dans l'air intérieur après remise en suspension, liée principalement aux activités des occupants. Idéalement, dans un contexte d'évaluation des expositions des populations, les concentrations doivent être mesurées dans les différents milieux. Mais la seule mesure dans les poussières déposées au sol tamisées à 100 µm, plus aisée qu'une mesure dans l'air, donne une indication du potentiel d'exposition par inhalation des COSV en phase particulaire. L'affinement des modèles, par exemple par la prise en compte de la température intérieure comme proposé dans le cadre du projet ECOS-Habitat, doit se poursuivre. La granulométrie des particules considérées, fraction de coupure dans l'air et fraction de tamisage dans les poussières au sol, a aussi une influence possible sur la modélisation qu'il conviendrait d'étudier.

4.3 Expositions aux COSV en phase particulaire : contributions relatives de l'inhalation et de l'ingestion

La connaissance de la contribution des voies d'exposition dans l'exposition globale à une substance est fondamentale afin d'envisager des actions de gestion ciblées sur les contributions prépondérantes. Les expositions aux COSV ayant été historiquement mises en évidence pour l'alimentation (phtalates dans les emballages alimentaires, dioxines et PCB dans les poissons, bisphénol A dans les biberons, boîtes de conserve ou bonbonnes d'eau), la question de la contribution de l'environnement intérieur, moins étudiée, est régulièrement posée. Elle varie *a priori* selon les populations et les COSV considérés. Pour l'environnement intérieur spécifiquement, la distinction des contributions respectives de l'inhalation et de l'ingestion est également utile.

Les contributions des voies d'exposition aux COSV particulaires dans le logement ont été examinées à partir des deux jeux de concentrations disponibles. Cette approche était exploratoire et n'avait pas pour objectif de calculer des doses d'exposition, ni d'être exhaustive des voies d'exposition. Aussi, seules l'inhalation des COSV particulaires en suspension dans l'air et l'ingestion des COSV présents dans les poussières déposées au sol ont été prises en compte. L'exposition par voie cutanée, qui fait l'objet de travaux très récents pour les COSV (Weschler et Nazaroff, 2012), n'a pas été considérée.

4.3.1 Méthode

La contribution de l'exposition par ingestion non intentionnelle de poussières ($CT_{\text{ingestion}}$) a été calculée à partir de l'Équation 4 suivante :

$$CT_{\text{ingestion}} = \frac{DJE_{\text{ingestion}}}{DJE_{\text{ingestion}} + DJE_{\text{inhalation-p}}} \qquad \text{(Équation 4)}$$

Où :

$DJE_{\text{ingestion}}$ est la dose journalière d'exposition par ingestion (µg/kg $_{\text{poids corporel}}$/jour)

$DJE_{\text{inhalation-p}}$ est la dose journalière d'exposition par inhalation des COSV sous forme particulaire (µg/kg $_{\text{poids corporel}}$/jour)

Les doses journalières d'exposition sont elles-mêmes définies par les Équation 5 et Équation 6 :

$$DJE_{\mathrm{ingestion}} = \frac{C_{\mathrm{d}} \times Q_{\mathrm{d}} \times t \times T_{\mathrm{ing}}}{P} \qquad \text{(Équation 5)}$$

$$DJE_{\mathrm{inhalation-p}} = \frac{F \times V \times t \times T_{\mathrm{inh}}}{P} \qquad \text{(Équation 6)}$$

Avec :

C_d : la concentration du composé dans les poussières déposées au sol (µg/g)

F : la concentration du composé en phase particulaire dans l'air (µg/m^3)

Q_d : la quantité de poussières ingérées non intentionnellement par jour (g/j)

V : le volume respiratoire journalier (m^3/j)

t : la fraction de temps quotidien passé dans le logement puisqu'on s'intéresse uniquement à cet environnement intérieur (-)

P : le poids corporel de la personne exposée (kg)

T_{ing} et T_{inh} : les taux d'absorption par ingestion et par inhalation respectivement (-)

En première approche, les taux d'absorption sont pris égaux à 100 % par défaut. L'Équation 4 se simplifie donc comme suit :

$$CT_{\mathrm{ingestion}} = \frac{C_{\mathrm{d}} \times Q_{\mathrm{d}}}{C_{\mathrm{d}} \times Q_{\mathrm{d}} + F \times V} \qquad \text{(Équation 7)}$$

Les calculs ont été réalisés à partir de l'Équation 7, considérant, pour cette approche exploratoire, deux groupes de population : un enfant âgé de 3 à 6 ans et un adulte. Dans le cadre de cette approche, il n'a pas été jugé nécessaire de conduire une modélisation pour plus de classes d'âge. De même, une modélisation probabiliste n'est pas apparue opportune. En revanche, afin de ne pas obtenir qu'une unique valeur mais d'encadrer les résultats, les calculs ont été réalisés considérant plusieurs valeurs pour chacun des paramètres entrant dans l'Équation 7.

Les percentiles 25, 50 et 95 des distributions des concentrations dans les poussières au sol et les particules en suspension ont été retenus. Le percentile 25 a été préféré au percentile 5 car ce dernier est inférieur à la limite de détection dans les deux milieux pour la majorité des COSV, ce qui pourrait conduire à des artefacts dans les calculs. Par ailleurs, les concentrations dans les poussières au sol et les particules en suspension étant associées, comme étudié dans le chapitre précédent, les situations combinant une faible concentration dans un milieu (p25) avec une très forte concentration dans l'autre (p95) n'ont pas été modélisées. Enfin, les concentrations mesurées inférieures à la limite de détection ont été substituées par 25 %, 50 % ou 95 % de la valeur de cette limite de sorte à ne pas perdre d'information et à pouvoir conduire les calculs pour l'ensemble des COSV. Les COSV qui ne sont quasiment jamais détectés dans les deux milieux, l'aldrine, l'endrine, le PCB 126 et le BDE 119, n'ont pas été considérés.

Concernant les variables humaines d'exposition, les choix réalisés par l'Anses en 2013 dans le cadre de l'évaluation des risques sanitaires du bisphénol A pour la santé humaine ont été considérés en premier lieu (Anses, 2013). Pour le volume respiratoire, les valeurs des percentiles 5, 50 et 95 des distributions établies par l'Anses ont été retenues, soit 10, 13 et 19 m^3 inhalé chaque jour par un enfant, et 11, 16 et 26 m^3 inhalé chaque jour par un adulte. En revanche, l'Anses n'a pas décidé de faire varier la quantité de poussières ingérées par jour et a utilisé une valeur moyenne pour chaque population. Ce paramètre pouvant jouer un rôle important, les recommandations de l'Institut de veille sanitaire (InVS) pour une évaluation déterministe des expositions ont été suivies (Dereumeaux et al., 2015) : une valeur médiane de quantité de poussières (intérieures et extérieures) ingérée quotidiennement par un enfant égale à 24 mg/j et un percentile 95 de 91 mg/j ont été retenus. La quantité de poussières ingérées quotidiennement par l'adulte fait l'objet de beaucoup moins d'études : deux sont recensées par l'US-EPA (2011) dont l'une qui n'a considéré que la quantité de terre extérieure ingérée (l'US-EPA propose une extrapolation pour inclure les poussières intérieures) et l'autre qui extrapole des données existantes pour l'enfant (US-EPA, 2011). L'US-EPA ne recommande *in fine* qu'une valeur médiane de 50 mg/j (US-EPA, 2011) pour l'adulte, l'InVS ne fait pas de recommandation et les publications ayant étudié la contribution relative des voies d'exposition aux COSV utilisent des valeurs très hétérogènes. Afin de ne pas baser les calculs sur l'unique valeur de 50 mg/j qui apparaît incohérente avec la médiane retenue pour un enfant et constatant que l'US-EPA et l'Anses proposent des quantités de poussières ingérées quotidiennement divisées par deux pour l'adulte par rapport à l'enfant, les valeurs utilisées pour l'adulte dans le contexte de cette approche exploratoire ont été prises égales à la moitié de celles retenues pour l'enfant, autrement dit une médiane et un percentile 95 respectivement égaux à 12 et 46 mg/j. A titre de comparaison, Wormuth et al. (2006) ont retenu une quantité de poussières ingérées par l'adulte dans le logement égale à 1 mg/j dans leur évaluation des expositions globales de la population européenne aux phtalates. Trudel et al. (2011) ont retenu une médiane égale à 2,6 mg/j de poussières intérieures ingérées par l'adulte pour l'évaluation des expositions globales des populations nord-américaine et européenne aux PBDE. Si l'on considère un temps quotidien médian passé dans son logement par la population française de 67 % (Zeghnoun et Dor, 2010), les quantités de poussières ingérées quotidiennement par l'adulte retenues ici prennent respectivement les valeurs de 8 et 31 mg/j si on ne considère que le temps passé dans le logement. Ces dernières valeurs n'apparaissent ni incohérentes, ni sous-estimées par rapport à celles retenues dans les évaluations de Wormuth et al. (2006) et (Trudel et al., 2011).

4.3.2 Résultats et discussion

Le Tableau 8 présente la part, en pourcentage, de l'exposition par ingestion de poussières de sol dans le logement dans l'exposition domestique aux COSV particulaires par inhalation et ingestion. Les proportions médianes des expositions par ingestion et par inhalation sont visualisées sur la Figure 10. Les résultats montrent une contribution toujours prépondérante de l'ingestion pour les situations médianes, que ce soit pour l'enfant ou l'adulte, à l'exception de quelques COSV. Pour l'α-endosulfan, le diazinon et le chlorpyrifos, les concentrations médianes dans les milieux sont inférieures à la limite de détection ; les calculs réalisés dépendent donc fortement de l'hypothèse posée pour substituer ces valeurs. Les contributions les plus faibles de l'exposition par ingestion sont observées pour le BDE 47 et le benzo(a)pyrène.

Tableau 8 : Contribution de l’exposition par ingestion de poussières de sol (%) dans l’exposition par inhalation et ingestion aux COSV particulaires dans le logement

	ENFANT			**ADULTE**		
COSV	**Min.**	**Situation médiane**	**Max.**	**Min.**	**Situation médiane**	**Max.**
Perméthrine	49	97	100	26	93	100
Oxadiazon	68	98	100	44	96	100
γ-HCH/lindane	49	95	100	26	88	100
α-Endosulfan	13	48	98	5	28	96
Dieldrine	35	87	100	16	73	99
Diazinon	7	19	97	3	9	94
Chlorpyrifos	7	41	98	3	22	96
4,4'-DDE	37	97	100	17	92	100
PCB 153	60	86	100	35	72	100
PCB 138	18	87	100	7	73	100
PCB 118	21	90	100	9	78	100
PCB 105	21	90	100	9	78	100
PCB 101	30	90	100	14	79	100
PCB 77	65	90	100	41	79	99
PCB 52	37	93	100	18	85	100
PCB 31	45	90	100	23	79	99
PCB 28	48	90	100	26	79	100
BDE 154	76	90	99	54	79	98
BDE 153	68	90	99	43	79	98
BDE 100	19	68	98	8	46	96
BDE 99	17	67	99	7	45	98
BDE 85	44	70	97	23	49	93
BDE 47	8	52	98	3	31	96
BDE 28	65	96	100	40	90	99
TBP	72	94	100	49	87	99
Bisphénol A	50	94	100	27	87	99
Tonalide	58	98	100	33	95	100
Galaxolide	56	98	100	32	96	100
Phénanthrène	57	89	100	32	77	99
Fluorène	24	78	98	10	59	97

COSV	ENFANT Min.	ENFANT Situation médiane	ENFANT Max.	ADULTE Min.	ADULTE Situation médiane	ADULTE Max.
Benzo(a)pyrène	9	58	98	3	36	96
Anthracène	54	87	100	30	74	99
DiNP	79	97	100	57	93	100
DiBP	63	98	100	39	96	100
DEP	29	90	100	13	78	100
DEHP	57	93	100	33	84	99
DBP	47	96	100	24	92	100
BBP	38	94	100	18	87	100

Note : Les « Min. » et « Max. » renvoient aux contributions minimale et maximale de l'exposition par ingestion issues des 42 calculs menés pour chaque COSV et chaque population. La situation médiane correspond au calcul réalisé avec les percentiles 50 des valeurs de tous les paramètres considérés.

Comme attendu, pour l'enfant comme pour l'adulte, les contributions minimales de l'exposition par ingestion sont calculées avec le volume respiratoire maximal (percentile 95), la concentration dans les particules en suspension maximale (percentile 95) et la quantité de poussières ingérées la plus faible (médiane). Cette contribution peut atteindre des valeurs faibles, égales par exemple à 3 % pour le BDE 47 et le benzo(a)pyrène.

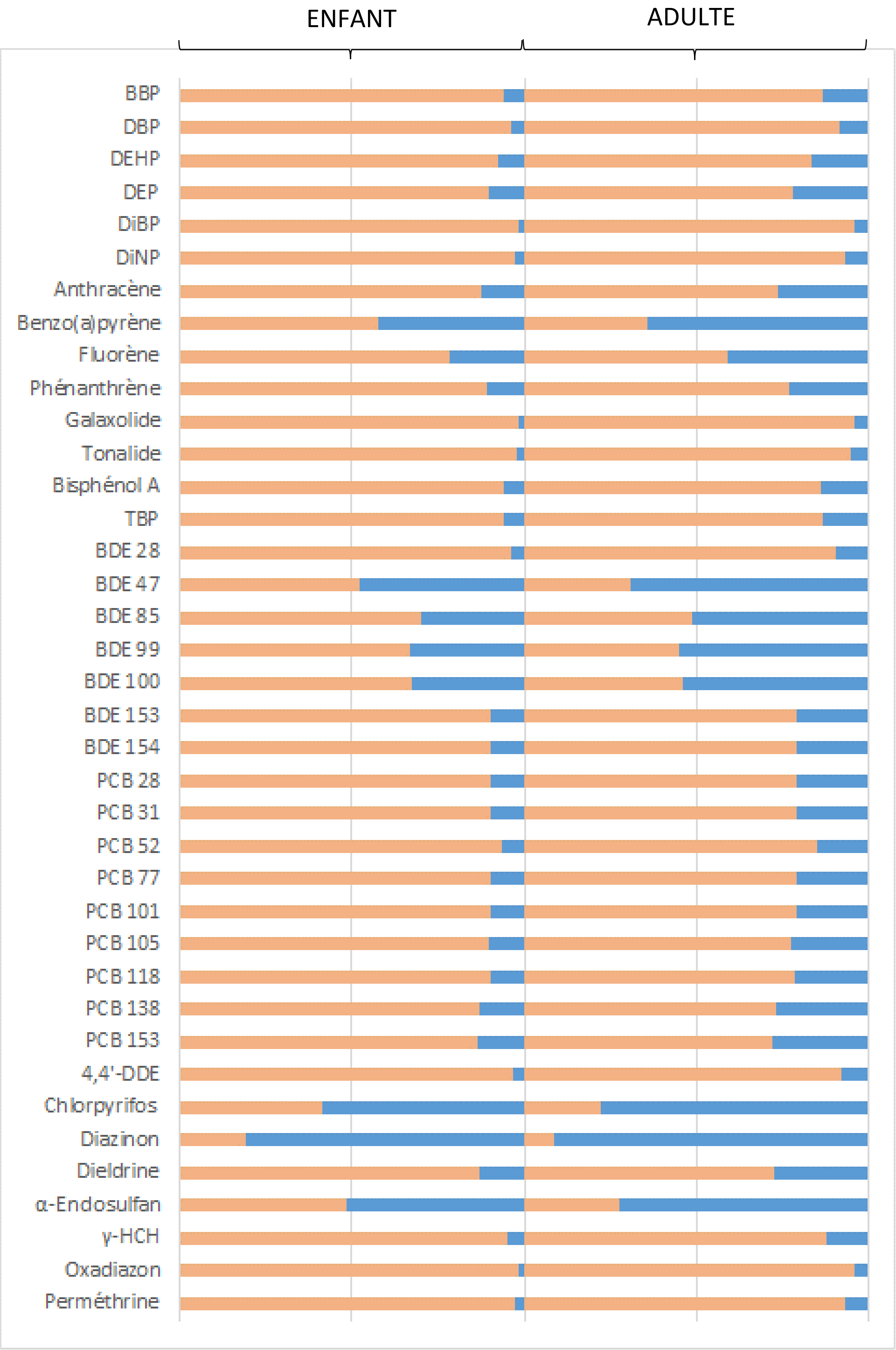


Figure 10 : Contributions respectives (%) de l'exposition par ingestion de poussières de sol (orange) et de l'exposition par inhalation (bleu) aux COSV particulaires dans le logement

Dans le cadre de cette approche exploratoire, les taux d'absorption ont été pris égaux à 100 % par défaut. Or les substances inhalées et ingérées n'atteignent pas toutes la circulation systémique. Pour l'ingestion, on parle notamment de biodisponibilité orale pour décrire la dose réellement absorbée par rapport à la dose externe ingérée (Denys et al., 2009). La biodisponibilité d'une substance intègre sa solubilisation par les fluides digestifs : la salive et les fluides du tractus gastro-intestinal (on parle de bioaccessibilité), son transport à travers la barrière gastro-intestinale et sa métabolisation avant transmission à la circulation systémique. Une évaluation plus juste des expositions nécessite donc de considérer précisément le taux d'absorption et peut inclure, pour l'ingestion, la prise en compte de la fraction bioaccessible pour laquelle il existe des données dans la littérature. Ces données concernent aujourd'hui principalement les métaux (Denys et al., 2009). La revue documentaire présentée au Chapitre 1 a souligné que la bioaccessibilité était peu étudiée pour les COSV dans les poussières intérieures et a confirmé son importance. Des valeurs de bioaccessibilité digestive, et dans quelques cas salivaire, sont disponibles pour 17 des 38 COSV considérés.

Le Tableau 9 présente la part en pourcentage de l'exposition par ingestion des poussières de sol dans le logement incluant la bioaccessibilité, facteur multiplicatif de la dose journalière d'exposition par ingestion. On observe une influence importante de ce paramètre, la contribution de l'ingestion des poussières pouvant ne plus être prépondérante pour certains COSV comme les PBDE et les phtalates, dans les situations médianes d'exposition. Ceci confirme l'importance de mieux prendre en compte ce facteur dans les évaluations des expositions aux COSV et aux substances chimiques de façon générale.

Tableau 9 : Contribution de l'exposition par ingestion de poussières de sol (%) dans l'exposition par inhalation et ingestion aux COSV particulaires dans le logement intégrant la bioaccessibilité

		ENFANT			**ADULTE**		
COSV	**Bioaccessibilité retenue**	**Min.**	**Situation médiane**	**Max.**	**Min.**	**Situation médiane**	**Max.**
Perméthrine	41 % (Ertl et Butte, 2012)	28	94	100	13	85	100
γ-HCH/lindane	51 % (Ertl et Butte, 2012)	33	90	100	15	79	100
PCB 153	44 % (Ertl et Butte, 2012)	40	74	100	19	53	99

COSV	Bioaccessibilité retenue	ENFANT Min.	ENFANT Situation médiane	ENFANT Max.	ADULTE Min.	ADULTE Situation médiane	ADULTE Max.
PCB 138	47 % (Ertl et Butte, 2012)	9	76	100	4	56	100
PCB 101	77 % (Ertl et Butte, 2012)	25	88	100	11	74	100
PCB 28	61 % (Ertl et Butte, 2012)	36	85	100	17	70	99
BDE 154	36 % (Yu et al., 2012)*	53	77	97	30	58	94
BDE 153	36 % (Yu et al., 2012)*	43	77	98	22	58	96
BDE 100	37 % (Yu et al., 2012)*	8	44	96	3	24	91
BDE 99	24 % (Yu et al., 2012)*	5	33	96	2	16	91
BDE 85	39 % (Yu et al., 2012)*	24	48	92	10	27	84
BDE 47	32 % (Yu et al., 2012)*	3	26	94	1	12	87
BDE 28	35 % (Yu et al., 2012)*	39	89	99	19	77	97
DiBP	13 % (Wang et al., 2013b)#	18	89	100	8	77	99
DEP		5	53	98	2	32	97
DEHP		15	62	96	6	40	92
BBP		7	68	100	3	46	99

* La série des valeurs de bioaccessibilité des poussières prélevées l'été a été retenue ; il s'agit des valeurs intermédiaires entre des valeurs plus fortes au printemps et plus faibles en hiver et automne.

Valeur la plus élevée retenue dans la fourchette proposée par Wang et al. (2,4 à 13 %)

4.3.3 Conclusion sur la contribution des voies d'exposition aux COSV particulaires dans le logement

Ces résultats ont une portée limitée du fait de la non prise en compte de l'inhalation de la phase gazeuse, ni de la contribution de l'exposition par voie alimentaire. Ils conduisent néanmoins à ne pas exclure la contribution potentiellement importante de l'ingestion de poussières déposées au sol à l'exposition intérieure aux COSV. Une contribution faible issue des calculs réalisés ici serait *a fortiori* encore plus minime après l'inclusion des autres contributions. Un tel résultat aurait alors conclu à la contribution mineure de l'exposition aux COSV dans les poussières au sol des logements ; ce travail exploratoire montre le contraire. Il rappelle également la nécessité d'acquérir des connaissances sur la bioaccessibilité des COSV en phase particulaire.

Chapitre 5 : Conclusion générale et perspectives

Deux jeux de données uniques relatives aux concentrations d'un grand nombre de COSV mesurés dans l'air en phase particulaire et dans les poussières déposées au sol ont été exploités en vue d'identifier les caractéristiques propres à chacun de ces milieux en termes de substances en présence et de niveaux de concentrations. L'originalité de ces données tient au fait qu'elles s'intéressent concomitamment à plusieurs familles chimiques de COSV, dans plusieurs milieux, et qu'elles permettent d'estimer les concentrations à l'échelle du parc français de logements.

Comparées aux données disponibles pour les logements des autres pays, les concentrations mesurées font notamment ressortir des spécificités françaises concernant deux COSV dans les poussières au sol : le DiBP et le bisphénol A. Ces deux composés pourront faire l'objet d'un focus spécifique dans les travaux d'évaluation des risques sanitaires pour la population française consécutifs à cette thèse.

La revue bibliographique a permis d'identifier les paramètres déterminants pour les expositions humaines aux COSV, comme le type de poussières collectées, leur taille, la variabilité spatio-temporelle des concentrations. Ces paramètres sont souvent passés sous silence ou ignorés dans la présentation de résultats. Dès lors que des comparaisons doivent être réalisées, il semble indispensable que ces paramètres soient pris en compte pour sélectionner des études comparables, ou *a minima* qu'ils soient rappelés. Un consensus est à rechercher pour la stratégie de prélèvement des poussières domestiques. La combinaison des approches environnementale et de biomonitoring humain pourrait fournir les éléments de réponse pour fonder ce consensus méthodologique.

La revue bibliographique a aussi mis en lumière un paramètre déterminant pour l'exposition humaine mais peu étudié pour les COSV, la bioaccessibilité. Des travaux expérimentaux sont à conduire pour corroborer et compléter les valeurs déjà proposées par certains auteurs et obtenir des valeurs pour les COSV n'ayant pas fait l'objet d'une évaluation de leur bioaccessibilité via les poussières comme les alkylphénols, les phénols, les composés perfluorés et les retardateurs de flamme organophosphorés.

De façon générale, pour plusieurs familles de COSV, les études menées jusqu'ici manquent de données relatives à certains aspects utiles à l’évaluation des expositions, comme l’influence de la sélection en taille des particules sur les concentrations en retardateurs de flamme organophosphorés ou en composés perfluorés. Les déterminants des concentrations en COSV sont peu étudiés et restent mal identifiés, entre autres du fait des nombreuses sources en présence qui ne peuvent pas toutes être inventoriées et qu'une utilisation brève d'un produit émettant des COSV suffit pour contaminer un espace pour plusieurs jours, semaines ou années. Ces lacunes représentent autant de futures pistes de recherche pour améliorer les connaissances sur l'exposition aux COSV dans les bâtiments.

La mise en perspective des concentrations mesurées dans les deux milieux, bien que délicate puisque correspondant à deux échantillons de logements, différents dans leur type (accueillant les enfants de 6 mois à 6 ans *versus* tout le parc de résidences de France métropolitaine) et investigués à des périodes séparées de plusieurs années, tend néanmoins à montrer qu’il existe une relation entre les particules déposées au sol et celles en suspension dans l’air. Les particules analysées correspondent à des fractions granulométriques différentes : tamisage à 100 µm des poussières de sol et coupure à 10 µm des particules prélevées dans l’air. La relation observée entre ces particules confirme que les COSV sont préférentiellement sur les particules les plus fines et que celles-ci sont plus présentes dans l’air que dans les poussières au sol. Les hypothèses de Weschler et Nazaroff ont été confortées, montrant qu’en tendance centrale, à l’échelle d’un large échantillon de pièces, les médianes des concentrations dans les particules en suspension peuvent être prédites par celles dans les poussières au sol, ou l’inverse, ce qui est utile dans un contexte d’évaluation des risques sanitaires pour une population. La phase gazeuse peut également être prédite, ce qui est intéressant à la lumière des recherches récentes qui montrent une exposition aux COSV en phase gazeuse par la voie cutanée. Pour une évaluation à l’échelle individuelle, des mesures semblent encore nécessaires pour qualifier l’exposition.

Enfin, tandis que les concentrations de nombreux COSV dans les logements français sont désormais connues, un nombre tout aussi important de « nouvelles substances » sont mesurées par d’autres équipes de recherche et détectées dans les bâtiments. Si les méthodes de hiérarchisation sont utiles pour repérer les COSV les plus problématiques nécessitant une action prioritaire, d’autres outils sont nécessaires pour identifier en amont les substances qui sont déjà présentes ou le seront demain dans les bâtiments. Un lien avec la réglementation européenne REACh relative aux substances chimiques est possiblement à trouver afin de pouvoir identifier les substances dont les usages pourraient conduire à des émissions dans les environnements intérieurs et nécessiter des mesures exploratoires. Ces mesures pourraient conforter les scénarios d’exposition modélisés en amont de la mise sur le marché et permettre le développement des connaissances sur les substances chimiques présentes dans l’environnement intérieur. Un champ de recherche très important reste donc ouvert.

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ANNEXES

Annexe 1 : Valorisations du travail de thèse

Articles scientifiques

Mandin C., Glorennec P., Ramalho O., Blanchard O., Bonvallot N., Wei W., Mercier F., Le Bot B. Semi-volatile organic compounds: key-issues regarding indoor exposure. Revue bibliographique soumise à *Environmental Science & Technology*

Mandin C., Mercier F., Lucas J-P., Ramalho O., Blanchard O., Bonvallot N., Raffy G., Gilles E., Glorennec P., Le Bot B. Semi-volatile organic compounds in home settled dust: A nationwide survey in France. Article soumis à *Indoor Air*

Mandin C., Mercier F., Ramalho O., Lucas J-P., Gilles E., Blanchard O., Bonvallot N., Glorennec P., Le Bot B. Semi-volatile organic compounds in the particulate phase in dwellings: A nationwide survey in France. Article soumis à *Atmospheric Environment*

Autre communication écrite

Bulletin de l'OQAI n°9 : Premier état de la contamination des logements français en composés organiques semi-volatils : pesticides, phtalates, retardateurs de flamme, etc. http://www/oqai.fr

Communications orales

Semi-volatile organic compounds (SVOCs) in home settled dust: a nationwide survey in France, Conférence internationale sur la santé environnementale, ISEE-ISES-ISIAQ, Bâle, 19-21 août 2013

ECOS-POUSS: a nationwide survey of semi-volatile organic compounds in home settled dust. Conférence internationale *Indoor Air* 2014, Hong-Kong, 5-11 juillet 2014

ECOS-PM: a nationwide survey of semi-volatile organic compounds in indoor air. Conférence internationale *Indoor Air*, Hong-Kong, 5-11 juillet 2014

Contamination des logements français en composés organiques semi-volatils et expositions associées. Les journées des jeunes chercheurs de l'Irset, Rennes, 16 décembre 2014

Nationwide estimates of semi-volatile organic compounds concentrations in settled dust and suspended particles in French homes. Conférence internationale *Healthy Buildings Europe*, Eindhoven, 18-20 mai 2015

Premier état de la contamination des logements français en composés organiques semi-volatils. Les Ateliers de l'OQAI, Paris, 11 juin 2015

Communications affichées

ECOS-POUSS: a nationwide survey of semi-volatile organic compounds in home settled dust. Conférence internationale Airmon, Marseille, 15-20 juin 2014

ECOS-PM. Expositions cumulées aux composés organiques semi-volatils dans l'habitat : contamination de l'air des logements en perturbateurs endocriniens. Les rencontres scientifiques de l'Anses, Paris, 28 novembre 2014

Environment and Health – Bridging South, North, East and West
Conference of ISEE, ISES and ISIAQ Basel, Switzerland, 19 – 23 August 2013
Abstract

Semi-volatile organic compounds in home settled dust: a nationwide survey in France

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Background. Semi-volatile organic compounds (SVOCs) are of concern due to their possible health effects and the widespread exposure through different environmental media and pathways. Among them, ingestion of settled dust in indoor environment is likely to be a non-negligible contributor to exposure, and especially for children due to their hand-to-mouth behavior. Indoor concentrations need to be further described to better characterize children exposure.

Aims. This study aims at determining the settled dust concentrations of around 50 SVOCs in a nationwide sample of French dwellings occupied by at least one child aged 6 months to 6 years.

Methods. Vacuum bags were collected in 300 dwellings on the occasion of a nationwide survey (2008-2009). Bags containing dust from other sources than indoor, not containing enough dust after sieving to <100 µm, or not properly stored during transport were discarded. 145 samples were finally analyzed. The samples were extracted by pressurized liquid extraction with dichloromethane, and then analyzed by gas chromatography coupled with mass spectrometry (GC/MS) or tandem mass spectrometry (GC/MS/MS).

Results. Phthalates (BBP, DBP, DEHP, DiBP, DiNP), bisphenol-A, galaxolide and phenanthrene were detected in 100% of dwellings. Median concentrations were respectively equal to 13.8; 13.0; 363; 28.9; 152; 4.5 µg/g of dust, 720 and 264 ng/g of dust. The maximum concentrations (above 1 mg/g of dust) were measured for four phthalates (DEHP, DiNP, DiBP, BBP) and permethrin. Some pesticides (aldrin, endrin, dichlorvos) and some polybrominated flame retardants (BDE-28,-85,-119 and -154) were detected in less than 10% of the dwellings.

Conclusion. This is the first study that provides SVOC concentrations in house dust in a large sample of French dwellings. These concentrations confirm the presence of many SVOCs. The data will now be used to assess children exposure.

Indoor Air 2014, Kong-Kong, 5-11 July 2014

Abstract

Topic C2: New chemical substances in buildings

ECOS-POUSS: A Nationwide Survey of Semi-Volatile Organic Compounds in Home Settled Dust

Corinne MANDIN[1,2,3,*], Fabien MERCIER[2,3,4], Jean-Paul LUCAS[1], Olivier RAMALHO[1], Olivier BLANCHARD[2,4], Nathalie BONVALLOT[2,4], Gaëlle RAFFY[2,3,4], Erwann GILLES[2,3,4], Philippe GLORENNEC[2,4], and Barbara Le BOT[2,3,4]

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Keywords: SVOC, dwelling, phthalate, PBDE, PCB

INTRODUCTION: Semi-volatile organic compounds (SVOCs) are of concern due to their established or suspected health effects and due to the widespread exposure through different environmental media and pathways. The objective of this study is to assess the indoor SVOC concentrations in home settled dust at a nationwide scale. Forty-eight SVOCs including phthalates, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pyrethroids, organochlorine and organophosphorous pesticides, synthetic musks, bisphenol-A and tributylphosphate, were selected after a health-based ranking and taking into account technical feasibility.

METHODS: Vacuum cleaner bags were collected during a nationwide survey carried out in dwellings where at least one child aged 6 months to 6 years lives (2008-2009). Bags containing dust from outside the dwelling, or not containing enough dust after sieving to <100 µm, or not properly stored during transport, were discarded. 145 dust samples were finally analyzed. SVOCs were extracted by pressurized liquid extraction with dichloromethane, and analyzed by gas chromatography / mass spectrometry (GC/MS) or tandem mass spectrometry (GC/MS/MS). The use of sampling weights enables to extrapolate the results to the national housing stock inhabited by children aged 6 months to 6 years.

RESULTS: 10 compounds were quantified in nearly (> 98%) all the dwellings (in brackets: median nationwide concentration in µg per g of dust): DEHP (341), DiNP (144), DiBP (17.1), BBP (10.8), DBP (10.3), bisphenol-A (4.29), DEP (3.27), permethrin (2.64), galaxolide (1.08), and BDE-209 (0.761). The highest concentrations (> 1 mg/g) were measured for DEHP, DiNP, DiBP, BBP, and permethrin.

CONCLUSIONS: The estimated nationwide home settled dust concentrations will enable an exposure assessment including also the indoor air contribution. In parallel, common modes of action are considered to derive toxicological indexes and to conduct a cumulative health risk assessment of indoor SVOC mixtures.

Indoor Air 2014, Kong-Kong, 5-11 July 2014

Abstract

Topic C2: New chemical substances in buildings

ECOS-PM: A Nationwide Survey of Semi-Volatile Organic Compounds in Indoor Air

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Keywords: SVOC, dwelling, airborne particles, PM_{10}, particulate matter

INTRODUCTION: Semi-volatile organic compounds (SVOCs) are of concern due to their established or suspected health effects and due to the widespread exposure through different environmental media and pathways. The objective of this study is to assess the indoor SVOC concentrations on airborne particles (PM_{10}) collected at a nationwide scale. Sixty-six SVOCs, including phthalates, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pyrethroids, organochlorine and organophosphorous pesticides, alkylphenols, synthetic musks, tributylphosphate and triclosan, were selected after a health-based ranking and taking into account technical feasibility.

METHODS: The samples (n = 300) were collected during a nationwide survey carried out by the French Observatory of indoor air quality (2003-2005) in a representative sample of the housing stock. The PM_{10} were collected in the living-room on polytetrafluoroethylene (PTFE) filters during 7 days (sampled volume: 14 m^3). The filters were stored at -18°C before analysis. SVOCs were analyzed by thermal desorption coupled with gas chromatography / tandem mass spectrometry (TD-GC/MS/MS).

RESULTS: Most of the PAHs, two phthalates (DiNP and DEHP), BDE-47 and BDE-99, and triclosan were quantified in more than 90% of the dwellings. Lindane, musks (galaxolide and tonalide), permethrin, bisphenol-A, and some PCBs were also commonly found. Pesticides such as atrazine, aldrin, endrin and chlordane were rarely detected. The use of sampling weights enables to extrapolate these results to the national housing stock.

CONCLUSIONS: This data, combined to other results from the ECOS-project, will be used to assess exposure to SVOCs in French homes and associated health effects. Relationships between concentrations, building characteristics and household activities will also be studied to identify SVOC determinants in indoor air.

Journée des jeunes chercheurs de l'Irset, 16 décembre 2014, Rennes

Résumé

Contamination des logements français en composés organiques semi-volatils et expositions associées

Nationwide Estimates of Semi-Volatile Organic Compounds Concentrations in settled dust and suspended particles in French Homes, and associated exposure

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Rattachement : Ecole doctorale Vie-Agro-Santé, Université de Rennes I. Équipe d'accueil : Inserm UMR 1085, Institut de recherche santé environnement travail (Irset) – LERES, Laboratoire d'Etude et recherche en environnement et santé, Rennes

Directeur : Prof Barbara Le Bot ; Co-directeur : Dr Philippe Glorennec

Semi-volatile organic compounds (SVOCs) are of concern due to their established or suspected health effects and due to the widespread exposure through different environmental media and pathways. The objective of this work is to assess the indoor concentrations in the domestic environment of a large group of SVOCs both in floor settled dust and on airborne particles, and to characterize the associated exposure.

Vacuum cleaner bags were collected during a nationwide survey carried out in French dwellings where at least one child aged 6 months to 6 years lives (2008-2009). After sieving at 100 µm, the dust samples were extracted by pressurized liquid extraction with dichloromethane, and analyzed by gas chromatography / mass spectrometry (GC/MS) or tandem mass spectrometry (GC/MS/MS). On the other hand, PM_{10} were sampled on Teflon filters over one week in the living-room during the nationwide survey carried out in a representative sample of the housing stock (2003-2005). SVOCs on filters were analyzed by thermal desorption coupled with gas chromatography / tandem mass spectrometry (TD-GC/MS/MS). The use of the dwelling sampling weights for both surveys made it possible to extrapolate the results at the nationwide scale.

In settled dust, 32 SVOCs out of 48 were detected in more than half of the dwellings. Similarly on PM_{10}, 41 SVOCs out of 66 were detected in more than half of the dwellings, confirming the ubiquity of SVOCs on particles, both airborne and settled, in the housing. The most concentrated compounds were phthalates, polycyclic aromatic hydrocarbons (PAHs), and bisphenol-A. In addition, permethrin, synthetic musks, and BDE-209 were among the most concentrated compounds in settled dust, and triclosan on PM_{10}. Overall, the SVOC concentrations appear to be in the same order of magnitude as in the other countries worldwide, except permethrin and bisphenol-A in settled dust which seem to be more concentrated in the French dwellings.

The last step will be a first overview of respective contributions of the different exposure pathways to the residential exposure, including inhalation and ingestion for young children and adults.

1ère conférence régionale *Healthy Buildings*, Eindhoven, 16-20 May 2015

Abstract

Nationwide estimates of semi-volatile organic compounds concentrations in settled dust and suspended particles in French homes

Corinne MANDIN[1,2,3,*], Fabien MERCIER[2,3,4], Jean-Paul LUCAS[1], Olivier RAMALHO[1], Olivier BLANCHARD[2,4], Nathalie BONVALLOT[2,4], Gaëlle RAFFY[2,3,4], Erwann GILLES[2,3,4], Philippe GLORENNEC[2,4], and Barbara Le BOT[2,3,4]

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INTRODUCTION: Semi-volatile organic compounds (SVOCs) are of concern due to their established or suspected health effects and due to the widespread exposure through different environmental media and pathways. The objective of this study was to assess the indoor concentrations in the domestic environment of a large group of SVOCs both in floor settled dust and on airborne particles.

METHODS: Vacuum cleaner bags were collected during a nationwide survey carried out in French dwellings where at least one child aged 6 months to 6 years lives (2008-2009). After sieving at 100 µm, the dust samples were extracted by pressurized liquid extraction with dichloromethane, and analyzed by gas chromatography / mass spectrometry (GC/MS) or tandem mass spectrometry (GC/MS/MS). On the other hand, PM_{10} were sampled on Teflon filters over one week in the living-room during the nationwide survey carried out in a representative sample of the housing stock (2003-2005). SVOCs on filters were analyzed by thermal desorption coupled with gas chromatography / tandem mass spectrometry (TD-GC/MS/MS). The use of the dwelling sampling weights made it possible to extrapolate the results at the nationwide scale.

RESULTS and DISCUSSION: In settled dust, 32 SVOCs out of 48 were detected in more than half of the dwellings. Similarly on PM_{10}, 41 SVOCs out of 66 were detected in more than half of the dwellings. The most concentrated compounds in both media were phthalates, polycyclic aromatic hydrocarbons (PAHs), and bisphenol-A. In addition, permethrin, synthetic musks, and BDE-209 were among the most concentrated compounds in settled dust, and triclosan on PM_{10}.

CONCLUSIONS: The concentrations of a wide range of SVOCs were measured in French dwellings for the first time. Overall they appeared to be in the same order of magnitude as in other countries, except permethrin and bisphenol-A in settled dust which seemed to be more concentrated.

Application: This data, combined to other results from the ECOS-project (see Glorennec et al., HB2015), will be used to assess exposure to SVOCs in French homes and associated health effects. Relationships between concentrations, building characteristics and household activities will also be studied to identify SVOC determinants in indoor air.

Keywords: SVOCs, settled dust, airborne particles, PM_{10}

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ECOS-POUSS: A Nationwide Survey of Semi-Volatile Organic Compounds in Home Settled Dust

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Context and objectives

- 90% time spent in indoor environments
- Many sources of SVOCs indoors (Mercier et al, 2011)
- Different routes of exposure (inhalation, ingestion, dermal contact)
- Neurotoxic and reprotoxic effects + cumulative effects

→ To determine indoor exposures to SVOCs in France: ECOS project
SVOCs in home settled dust: ECOS-POUSS

Target compounds chosen on the basis of:

- health-based ranking (Bonvallot et al, 2010)
- analytical feasibility: multiresidue method (Mercier F. PhD Thesis, 2009-2011)

48 compounds

→ 4 pyrethroids
→ 10 organophosphorous and organochlorine pesticides
→ 10 polychlorinated biphenyls (PCBs)
→ 6 phthalates
→ 9 polybrominated diphenyl ethers (PBDEs)
→ 2 synthetic musks
→ 5 polycyclic aromatic hydrocarbons (PAHs)
→ bisphenol-A
→ tributylphosphate

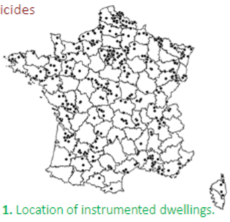

Figure 1. Location of instrumented dwellings.

Sampling

- Dwellings occupied by at least one **child aged 6 months to 6 years**: complex survey design (n=484; N=3,581,991) (Lucas et al, 2012)
- Dust collected from the **domestic vacuum cleaner bag** and stored at -18°C (conservation tests: Blanchard et al, 2014)

→ 145 vacuum cleaner bags

Analysis

- Samples sieved to **<100 µm**
- Samples extracted by pressurized liquid extraction with dichloromethane
- Analyzed by gas chromatography coupled with tandem mass spectrometry (**GC/MS/MS**) or mass spectrometry (**GC/MS**) for BDE-209 and BPA after derivatization (Mercier et al, 2014)

Results

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

The maximum concentrations are measured for four phthalates (DEHP, DiNP, DiBP, BBP) and permethrin.

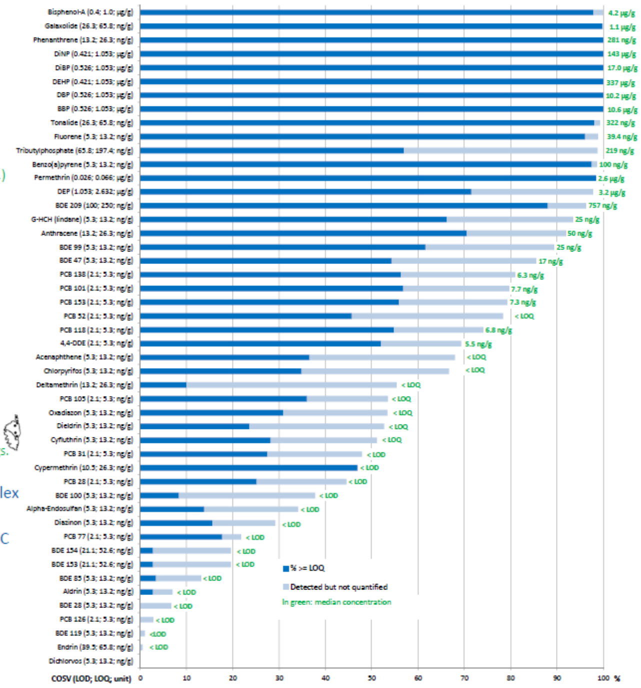

Figure 2. Frequency of detection (%; light blue), frequency of quantification (%; dark blue) and median concentrations (µg/g or ng/g; green labels) of the 48 SVOCs. France, 2008-2009, N = 3,581,991.

Next steps

Assessment of human exposure within ECOS Project in combination with measurements in indoor airborne PM and modeling of the gas phase

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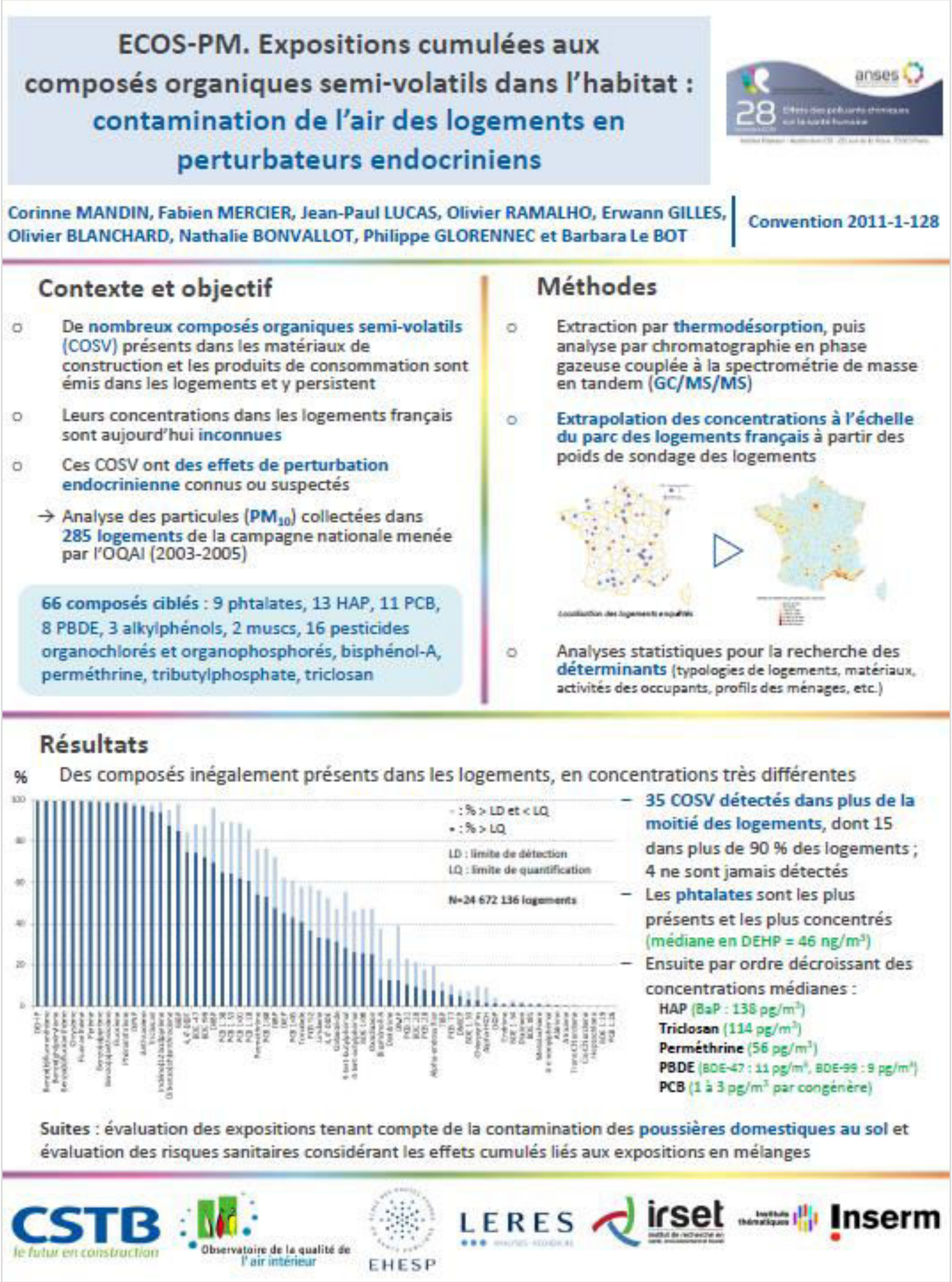

ECOS-PM. Expositions cumulées aux composés organiques semi-volatils dans l'habitat : contamination de l'air des logements en perturbateurs endocriniens

Corinne MANDIN, Fabien MERCIER, Jean-Paul LUCAS, Olivier RAMALHO, Erwann GILLES, Olivier BLANCHARD, Nathalie BONVALLOT, Philippe GLORENNEC et Barbara Le BOT

Convention 2011-1-128

Contexte et objectif

- De **nombreux composés organiques semi-volatils** (COSV) présents dans les matériaux de construction et les produits de consommation sont émis dans les logements et y persistent
- Leurs concentrations dans les logements français sont aujourd'hui **inconnues**
- Ces COSV ont **des effets de perturbation endocrinienne** connus ou suspectés

→ Analyse des particules (**PM$_{10}$**) collectées dans **285 logements** de la campagne nationale menée par l'OQAI (2003-2005)

66 composés ciblés : 9 phtalates, 13 HAP, 11 PCB, 8 PBDE, 3 alkylphénols, 2 muscs, 16 pesticides organochlorés et organophosphorés, bisphénol-A, perméthrine, tributylphosphate, triclosan

Méthodes

- Extraction par **thermodésorption**, puis analyse par chromatographie en phase gazeuse couplée à la spectrométrie de masse en tandem (**GC/MS/MS**)
- **Extrapolation des concentrations à l'échelle du parc des logements français** à partir des poids de sondage des logements

- Analyses statistiques pour la recherche des **déterminants** (typologies de logements, matériaux, activités des occupants, profils des ménages, etc.)

Résultats

Des composés inégalement présents dans les logements, en concentrations très différentes

- **35 COSV détectés dans plus de la moitié des logements**, dont 15 dans plus de 90 % des logements ; 4 ne sont jamais détectés
- Les **phtalates** sont les plus présents et les plus concentrés (médiane en DEHP = 46 ng/m^3)
- Ensuite par ordre décroissant des concentrations médianes :
  - **HAP** (BaP : 138 pg/m^3)
  - **Triclosan** (114 pg/m^3)
  - **Perméthrine** (56 pg/m^3)
  - **PBDE** (BDE-47 : 11 pg/m^3, BDE-99 : 9 pg/m^3)
  - **PCB** (1 à 3 pg/m^3 par congénère)

Suites : évaluation des expositions tenant compte de la contamination des **poussières domestiques au sol** et évaluation des risques sanitaires considérant les effets cumulés liés aux expositions en mélanges

Annexe 2 : Valorisations associées au projet ECOS-Habitat

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