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Understanding Semi-volatile Organic Compounds (SVOCs) in Indoor Dust

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Introduction

Indoor pollutant sources are ubiquitous. Volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) are among the broad classes of compounds found in the indoor environment through emissions and leaching from building materials, furnishings and human activities such as cooking, cleaning, use of consumer products etc. VOCs are organic chemicals with saturation vapour pressures greater than 10−2 kPa at 25°C, whereas SVOCs are those with saturation vapour pressures between 10^{-2} and 10^{-8} kPa at 25°C. ¹ The resulting air pollutants can be transported from sources to indoor air, surfaces, settled dust and airborne particles.

Human exposure to VOCs and SVOCs occurs by direct contacts through hand and other skin surfaces, ingestion through hand-to-mouth and diet activities, and inhalation of gases and airborne particles. SVOCs have relatively low vapour pressure and are easier to adhere to particles compared to VOCs. The interaction between SVOCs and indoor dust is complex due to the small size, the great surface area-to-volume ratio, surface settling and re-suspension of the dust particles. Chemicals in indoor dust particles is an important exposure source for humans. The exposure is revealed in the literature by correlations between the concentration of a pollutant in indoor dust and that in human body fluids and tissues. 2-5

The role of indoor dust as an exposure source has been gaining increased attention over the years. There are several literature reviews on the occurrence and levels of organic pollutants in house dust²⁻⁵ and they summarize broadly available information about the sources, concentration levels and the pollutant's relevance to human exposure. This editorial presents a summary of studies on per- and polyfluoroalkyl substances (PFAS), polychlorinated biphenyls (PCBs), and organophosphorus flame retardants (OPFRs) in settled dust in the indoor environment. This overview is not intended as a comprehensive review of these SVOCs in indoor dust studies. Rather, it serves as a brief discussion of the available information associated with the fate and transport mechanisms of these chemicals in indoor

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dust and highlights the need for experimental and empirical emission and mass transfer data for their source and exposure modelling.

Indoor Dust

In the EPA Exposure Factors Handbook Chapter 5, ⁶ indoor settled dust is defined as

Particles in building interiors that have settled onto objects, surfaces, floors and carpeting. These particles may include soil particles that have been tracked or blown into the indoor environment from outdoors, as well as organic matters.

Indoor dust is different in origin, properties and composition. Size distribution and properties of indoor dust vary widely dependent upon human activities and the indoor microenvironment, such as home, workplace, schools, childcare facilities, commercial buildings, etc. In field practice, indoor dust sampling should consider the age and location of the dust. For illustrative purposes, Table 1 lists properties of samples from two types of house dust (HD) measured and compared with reference material Arizona Test Dust (ATD) and Figure 1 shows the scanning electron microscope (SEM) images of these three dust types. As we can see, the particle size, shape, density and organic carbon content in the three types of dust are significantly different.

There are several scenarios of how dust settles on indoor surfaces: (1) dust without chemicals settled on a surface without a contaminated source; (2) dust without chemicals settled on a contaminated source surface; (3) dust with chemicals settled on a surface without a contaminated source; (4) dust with chemicals settled on a contaminated source surface. Indoor dust is a sink for indoor chemicals since it absorbs chemicals in the air. When the dust settles on a contaminated source surface, settled particles may interact with the surface materials through direct contact and pollutants can migrate to the dust and to the surface. Settled dust can consecutively re-suspend in the air. Indoor dust can also be generated by deterioration of indoor materials or consumer products. Thus, chemicals identified in dust particles reflect the types and levels of contamination in the indoor environment.

SVOCs in Indoor Dust

The SVOCs frequently reported in indoor dust are polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons, per- and polyfluoroalkyl substances (PFASs), flame retardants, phthalate, musks/fragrances and pesticides with concentrations between pg/g and a few mg/g of indoor dust. ² Due to space restriction, this editorial only focuses on the inadvertent generated PCBs (iPCBs), PFASs and organophosphate flame retardants (OPFRs) in indoor dust that have been studied in recent years in the laboratory of United States Environmental Protection Agency's Center for Environmental Measurement and Modeling.

Inadvertent generated PCBs

PCBs in the indoor environment have received significant attention by researchers for decades. The presence of legacy PCBs in indoor dust was determined worldwide by different

sampling methods. Their concentrations range from <1 to 890 μ g/g. ⁸ Although commercial PCB production was banned in 1979 in the USA, the presence of iPCBs has been associated with chemical production processes. For example, the most studied process leading to iPCB contamination is the production of diarylide yellow pigment and the resulting creation of PCB-11. Other iPCBs found in pigments and consumer products include PCB-28, PCB-52, PCB-77, as well as the nonachlorinated PCBs and PCB-209.⁹ Inadvertent PCBs have been detected in pigmented consumer products with concentrations up to parts per million. ¹⁰ Few studies reported concentrations of iPCBs in indoor dust. Recent studies have determined the concentrations of PCB-11 in indoor dust in the range of 0.5-0.9 ng/g, while concentrations of PCB-209 were much lower.¹¹ The role of iPCB-contaminated dust in human exposure has not yet been well characterized.

Organophosphorus flame retardants (OPFRs)

OPFRs, such as tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCPP), are additives to manufactured products to reduce flammability and serve as plasticizers but can leach and accumulate in dust on surfaces. Elevated OPFR concentrations in indoor dust have been reported by many researchers globally. For instance, thirteen organophosphate esters, including TCPP, TCEP and TDCPP, were measured in most of the house dust samples from 134 urban Canadian homes by Fan et al. ¹² Tajima et al. ¹³ measured the levels of ten OPFRs in indoor floor dust and upper surface dust from 128 Japanese dwellings of families with children in elementary school. The concentrations of TCPP, one of the main OPFRs in the dust, was reported to be < 0.56 to 621 μg/g and of TCEP to be < 0.65 to 92 μg/g. TCEP exceeded 50% detection rates in the upper surface dust with significant positive correlation $(P < 0.05)$ between the concentrations of TCPP in floor dust and upper surface dust $(n = 48)$. OPFRs were identified in dust from 497 homes and 151 daycare centres in Demark by Langer et al. 14 . The median mass fraction of TCEP from homes was 6.9 μg/g, and that of TCEP from the daycare centres was 16 μg/g, in addition to TCPP at 5.6 μg/g, and TDCPP at 7.1 μg/g. The maximum concentration was 1800 μg/g for TCEP and 350 μg/g for TCPP in daycare centres and 860 μg/g for TDCPP in homes. OPFRs in dust were also measured in building material markets, private cars, floor/carpet stores, offices, bedrooms and schools ^{15, 16} with the total concentration ranging from 5.9 to 4800 μg/g.

Per- and polyfluoroalkyl substances (PFASs)

PFASs have been detected in numerous consumer products 18-21 and are considered emerging contaminants by US EPA. ²⁰ Widespread use of PFAS and their ubiquitous presence in the environment caused continuous exposure to most people in the USA. Research shows that cumulative exposure to certain PFAS may lead to adverse health effects $20-22$ PFASs in indoor dust have been reported by a few studies internationally with a large variety in concentrations ranging from below the detection limit to hundreds of ng/g, or even μ g/g. 3, 23-29 PFASs that were frequently determined at high concentrations in dust are perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) and fluorotelomer alcohols (6:2 FTOH, 8:2 FTOH). ² The large difference between concentrations of PFASs in dust in different regions is associated with their presence in personal consumer products and the usage of household products or materials in addition to discrepancies of dust sampling

methods and locations. ^{4, 30} Some of the PFASs in indoor dust data up to 2017 have been summarized in the review by Lucattini et al^3 . Notably, more research has been conducted to address the presence of indoor dust and its implications to human exposure to PFAS in recent years. 23-29

For example, Winkens, et al. ²³ investigated 65 floor dust samples collected from children's bedrooms in Finland for 62 PFAS analytes. The dust samples were dominated by polyfluoroalkyl phosphoric acid esters (PAPs) and FTOHs while five perfluoroalkyl carboxylic acids (PFCAs) and PFOS were detected in more than half of the samples in addition to PFOA median concentration of 5.26 ng/g. Eighty-one indoor air samples and 29 indoor dust samples were collected from rooms of homes and hotels, textile shops and cinemas in Tianjin, China by Yao et al 24 with FTOHs being the predominant PFASs found in hotel dust (24.8 - 678 ng/g). In 2020, evaluated PFAS in indoor dust from 184 homes in North Carolina and 49 fire stations across the US and Canada were collected and analyzed by Hall et al 25. The data shows that FTOHs and di-polyfluoroalkyl phosphoric acid esters (diPAPs) were the most prevalent PFAS in both fire station and house dust samples, with the median in the range of approximately 100 ng/g dust or greater. In addition, PFAS detected in dust samples collected from childcare centres in USA, $^{26, 27}$ from cars, homes, offices and school classrooms in Ireland, ²⁸ and in working microenvironments (internet cafes, electronics shops, coffee shops, restaurants, etc.) in Greece²⁹ had a total PFAS concentrations ranging from several to thousands of ng/g.

Mass Transfer Mechanisms

While SVOCs in indoor dust have been identified as a major source of indoor contamination, understanding SVOC distribution and the transport mechanisms between chemicals, dust and surrounding environments will help characterize the exposure pathways.

The mass transfer mechanisms that are responsible for SVOC transport from sources to dust include absorption, desorption, dust-air and dust-material partitioning, particle formation through abrasion, and migration via direct contact between SVOCs sources and dust. Those mass transfer processes are controlled by the physicochemical properties of SVOCs, such as vapour pressure (VP), octanol-air partitioning coefficient (K_{OA}) , dust-air equilibrium partition coefficient (K_{da}), dust diffusion coefficients (D_d), and dust-source material partition coefficient (K_{ds}). Vapour pressure and K_{OA} are properties of the chemical itself, whereas dK_{da} , D_d and K_{ds} also depend on properties of materials and dust. At the steady state, if K_{da} is known, unknown SVOC concentrations in the gas-phase can be calculated based on their measured concentrations in settled dust. These parameters can be applied to predict emissions and concentrations of SVOCs in air and dust for source and exposure models. The K_{da} , K_{ds} and D_d parameters are essential for the determination of dynamic process and further the inhalation, dermal and dust ingestion exposures.

Despite the fact that numerous studies are available in the literature to measure SVOC concentrations in indoor dust and examine correlations between contaminated dust and exposure, few studies have systematically looked into the mass transfer process between SVOCs from different sources and dust. The existing data has been mainly for phthalate

and brominated flame retardants with most of them being calculated by empirical equations using VP and K_{OA} . Table 2 summarizes experimentally determined K_{da} (K_{da} '), K_{ds} and D_d of PCB, OPFR, and PFAS available in the literature. As we can see, at present,

experimentally determined values of these parameters are scarce, especially for PFAS. There is a clear need for experimental investigation.

Methodology for Studying SVOC Dust Interaction

The direct measurement of emission, sorption and migration of SVOCs from consumer products and materials and settled dust is typically carried out using various environmental chambers (Table 3). The environmental conditions of those chambers, such as temperature, relative humidity, air exchange rate and air velocity, are often well controlled to avoid interferences. These chamber methods have been mainly used for measuring concentrations of SVOCs in the air and dust after the SVOC-dust interaction. Challenges for using these methods to obtain the K_{da} , K_{ds} and D_d parameters include but are not limited to (1) characteristics of the dust in terms of size, shape, surface area, porosity, morphology, density, etc; (2) the ability to maintain a constant SVOC concentration in dust; and (3) the ability to reach steady-state conditions in the testing system over a long period of experimental time. As a result, our knowledge of and ability to model the fate and transport of SVOCs to house dust remains limited and there is a clear need for consistent data to reduce the variability and uncertainty in the estimation of SVOC exposures via house dust. Appropriate design and modification for experimental investigation are in great demand.

Concluding Remarks

Chemical exposures via contaminated dust is unquestionable. Extensive research has been focused on investigating pollutant concentrations in dust or in the environment and biomarkers. An understanding of the fate and transport and exposure pathways of SVOCs in dust is the critical link between the two research areas. More studies are needed to generate sufficient information and data regarding fate and transport and exposure of chemicals in indoor dust by developing measurement methods, obtaining key parameters that control the dynamic mass transfer process and investigating the exposure pathways. This research will support scientific and public health institutions to understand the dust mode of exposure of SVOCs and inform public health protection measures.

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Figure 1.

SEM images for different dust, left - House Dust 2, middle - House Dust 6, right – Arizona Test Dust. The scale is 600 μ m. (Reproduced with permission from Liu and Folk⁷)

Table 1

Properties of the dust samples (Reproduced with permission from Liu and Folk⁷)

^a Arithmetic mean \pm standard deviation (SD) (n = 2); measured at room temperature by gravimetric method.

b Analyzed by Micromeritics Analytical Services.

 c^c Arithmetic mean \pm SD (n = 2); method: Brunauer-Emmett-Teller (BET) method with N₂.

 d Weighted mean value \pm SD (n = 2); method: light scattering (ISO 13320).

 e
Method: light scattering (ISO 13320).

f
Arithmetic mean \pm SD (n = 4); method: NIOSH 5040.

 g _{Estimate from the average of two separate dust samples.}

Table 2

Experimentally determined diffusion and partition coefficients of PCB, OPFR and PFAS from literature

8:2 FTOH 10:2

FTOH PFHxA

 a K_{da} is dimensionless, K_{da} can be converted to K_{da}', which is the dust-air partition coefficient in unit of m³/g, using $K'_{da} = K_{da} / (\rho \times 10^{-6})$. b. Average (n=3).

b.
Average (n = 3)

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Table 3

Methods for studying mass transfer between SVOCs and dust $\mathrm{^a}$

a. CLIMPAQ (Chamber for Laboratory Investigations of Materials, Pollution, and Air Quality); DEHP (di(2-ethylhexyl)phthalate); DnBP (di-nbutyl phthalate); PBDE (polybrominated diphenyl ether); HBCD (hexabromocyclododecane); DINP (di-isononyl phthalate); FLEC (Field and Laboratory Emission Cell); BEHTBP (bis(2-ethyl-1-hexyl) tetrabromophthalate); TBBPA (tetrabromobisphenol A); HBBZ (hexabromobenzene); BBzP (benzyl butyl phthalate); DEHA (bis(2-ethylhexyl) adipate); DINCH (1,2-cyclohexane dicarboxylic acid diisononyl ester); TCPS (tricresyl phosphate).