

# A pilot study to identify semi-volatile organic pollutants in residential house dust

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## ABSTRACT

Semi-volatile organic compounds (SVOCs), emitted from building materials and other sources in the indoor environments, are likely to be bound to particulates due to their relatively low vapour pressure. While toxic metals and biological pollutants in house dust have been investigated in several studies, little work has been done to detect SVOCs. In this paper, the preliminary results on the screening of SVOCs in house dust in selected six residential homes are presented. The dust particles (<150 µm) were solvent extracted and fractionated through an adsorption column. The fractions were analyzed using GC/MS in full scan electron impact mode. Each chromatogram was then carefully studied and the mass spectrum of each peak was compared to a standard MS library for their identification. Identified compounds included polyaromatic hydrocarbons, phthalates and long-chain alkyl benzenes. The presence of these chemicals can be attributed to the use of various building materials, consumer products and combustion products in homes.

## INDEX TERMS

Semi-volatile organic compounds; House dust; Polyaromatic hydrocarbons; Phthalates; Long-chain alkyl benzenes

## INTRODUCTION

The environmental health impact of indoor pollutants on humans has become an important area of study in the past two decades. Indoor environment is an important component in assessing overall exposure as people in general spend most of their time indoors. Studies in the United States in the early 1990s have shown that a typical resident spends 65–90% of his/her time inside the home, and this ratio is expected to be even higher for small children and the elderly (Lewis *et al.*, 1994).

House dust can contribute to human exposures in the indoor environment. Several studies have shown the presence of semi-volatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons (PAHs) and pesticides, as well as toxic metals and biological pollutants in house dust (Lewis *et al.*, 1994, 1999; Rudel *et al.*, 2001; Seifert *et al.*, 2000). Because of their relatively low vapour pressure, SVOCs are more likely to be bound to particulate phase in house dust rather than as free chemicals in the indoor air. Therefore dust could be an important exposure source for the SVOCs. Such exposure in small children is more significant as they spend more time playing on the floor, hence exposing to more dusts.

Dust is a complex matrix and difficult to analyse because of the large number of potential interferences. The primary objective of this pilot study is to develop a screening method for the measurement of organic compounds, mainly the SVOCs, in house dust and to identify the SVOCs from limited numbers of homes. Once the presence of a chemical is confirmed, specific analytical method can be developed for the quantitative analysis of chemicals of interest.

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## METHODS

House dusts collected in vacuum bags from six residential homes (coded A, B, C, D, G, and H) were sieved and the fine dust (<150 µm) collected through sieving was used in this study for the determination of chemicals in the house dust. Three grams of sieved fine dust (<150 µm) were placed in a centrifuge tube containing dry sodium sulphate for absorbing the moisture. The sample was extracted on a shaker for 1 hour, with 18 ml of solvent mixture of hexane and dichloromethane (DCM) (1:1). The solution was transferred from the tube after centrifugation to a 50-ml round flask. The extraction was repeated two more times and the combined extract was concentrated down to about 1 ml. The concentrated extraction solution was loaded to a pre-packed small silica gel column (Supelclean<sup>TM</sup> LC-Si SPE tubes, 1 g of silica gel) for clean up and fractionation. Fraction 1 and 2 were collected each with 5 ml of hexane, fractions 3 and 4 were collected each with 5 ml of hexane:DCM (7:3); fraction 5 and 6 were collected each with 5 ml of hexane:DCM (1:1). All eluates were concentrated under gentle nitrogen stream to about 0.4 ml. Ten micrograms of naphthalene-d<sub>8</sub> were added to the final solution as an internal standard prior to GC/MS analysis.

Samples were analysed in full scan electron impact (EI) mode over the mass range of  $m/z$  35–550 on an HP5890 gas chromatograph (GC) equipped with an HP5972 mass selective detector (MSD) (Hewlett-Packard, USA), and a DB-5 capillary column (30 m × 0.32 mm i.d. × 1.8 µm film thickness). The GC oven temperature program was set at an initial temperature of 40°C for 4 min, raised to 150°C at 10°C/min, and further increase to 290°C at 7°C/min and held for 25 min. Total analysis time was 60 min. The injector and the detector temperatures were 260 and 280°C, respectively. Column head pressure was 6 psi. One microlitre of the sample extract was injected in splitless mode.

Identification of each peak was conducted by comparing the spectrum of the peak with Agilent NIST02 mass spectra library. A minimum of 80% of match was used for the identification, plus the judgement of the chemist on the interpretation of the mass spectrum. In some cases where the full structure could not be identified, characteristic fragment ions were used to identify the chemical class of which the chemical belong to. For example, instead of giving the full name of an aliphatic ester, a peak may be identified as ester only. The quantity of each peak represents was estimated by assuming equal response of each peaks to naphthalene-d<sub>8</sub> peak under total ion chromatogram (TIC).

## RESULTS

Our study has focused on screening and identification of organic chemicals in the dusts. The identified compounds are grouped into different chemical classes for the presentation of this paper. The amount of the five chemical classes, PAHs, long-chain alkyl benzenes (LCABs), aliphatic esters, phthalates, and carboxylic acids (CAs), are summarized in Table 1. The compounds that do not belong to these groups are not included in the table and not discussed in this paper. The analytical method used in this pilot study was not chemical class specific and the recoveries of chemicals were not determined in the method. Furthermore, the quantification was based on the assumption of equal response of all chemicals in the MS detector. Thus, the values given in Table 1 are not considered to be quantitative and should be used with caution.

PAHs were present in fractions 1–3 with the majority present in fraction 1. Dust from house A had the highest amount (290 µg/g fine dust) of PAHs, while smaller quantity of PAHs was also present in the dust from houses B (12 µg/g) and C (11 µg/g). The major PAHs identified in fraction 1 of the house A sample included fluoranthene, pyrene, phenanthrene, and benz[a]anthracene which together accounted for approximately 70% of the total PAH mass. Besides the major PAHs, some methyl-PAHs and dimethyl-PAHs were also found in this fraction. Fraction 3 of the same dust sample contained some semi-polar PAHs including 9,10-

anthracenedione, 11H-benzo[a]fluoren-11-one, and cyclopenta(def)phenanthrenone. These semi-polar PAHs were present in much lower but noticeable concentrations.

Phthalates were largely eluted in fractions 3 and 4. The concentrations of phthalates in the samples were in the range of 300–1200 µg/g dust sample with the highest concentration found in the dust from house G. One of the major phthalates detected in the samples was di-(2-ethylhexyl) phthalate (DEHP). Small quantity of DEHP and benzyl butyl phthalate (BBP) was also detected in the laboratory blank.

**Table 1** Groups of compounds found in each fractions from six houses (µg/g dust sample)

Fraction <sup>a</sup>	Group	Blank	A	B	C	D	G	H
1	PAHs	nd <sup>b</sup>	260	12	11	nd	nd	nd
	LCAB	nd	nd	nd	nd	nd	3	13
	Esters	nd	17	nd	Nd	18	nd	nd
2	PAHs	nd	14	nd	Nd	nd	nd	nd
	Esters	nd	33	63	43	50	53	19
3	PAHs	nd	15	nd	Nd	nd	nd	nd
	Phthalates	1	270	400	280	290	730	190
	Esters	nd	13	13	8	15	8	2
	CAs (C <sub>8</sub> –C <sub>18</sub> )	nd	3	8	Nd	230	nd	2
4	Phthalate	7	90	60	90	21	370	260
	Esters	nd	3	4	1	7	14	nd
	CAs (C <sub>8</sub> –C <sub>18</sub> )	nd	33	430	180	570	nd	330
	Phthalate	5	nd	nd	Nd	nd	87	80
5+6	Esters	nd	7	3	Nd	93	4	nd
	CAs (C <sub>8</sub> –C <sub>18</sub> )	nd	470	630	90	530	100	570
	Phthalate	13	360	460	370	310	1200	530
Sum	PAHs	nd	290	12	11	nd	nd	nd
	LCAB	nd	nd	nd	Nd	nd	3	13
	Phthalate	13	360	460	370	310	1200	530
	Esters	nd	73	83	52	180	80	21
	CAs (C <sub>8</sub> –C <sub>18</sub> )	nd	500	1100	270	1300	100	900

<sup>a</sup>Fraction: 1 and 2, hexane; 3 and 4, hexane:DCM (7:3), 5 and 6, hexane:DCM (1:1).

<sup>b</sup>nd = not detected.

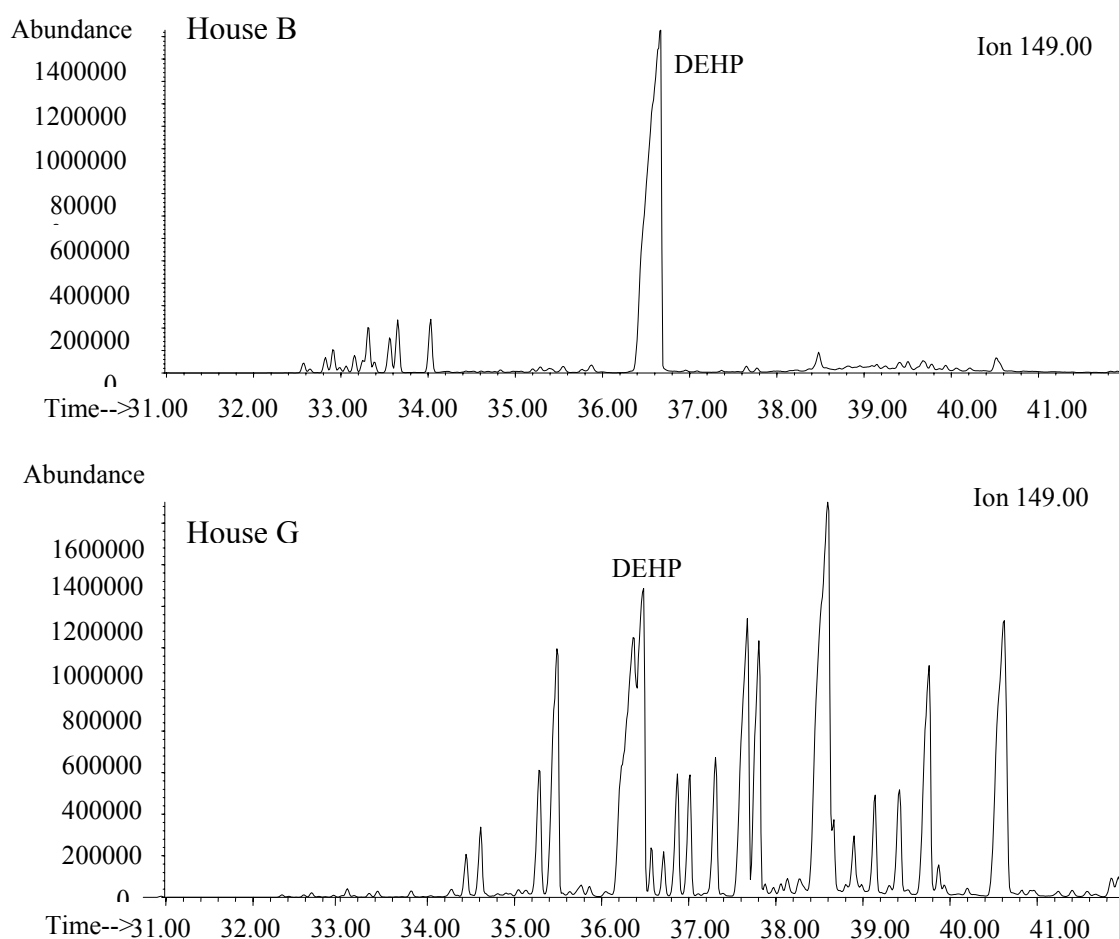
LCABs were found only in fraction 1 of dust samples from houses G and H. Because of the relatively low concentration of this class of chemicals (13 µg/g in dust from house H and 3 µg/g from house G), characteristic fragment ions of *m/z* 91, 105, and 119 were further used to map the LCAB profiles in the samples. An example of such profile is given in Figure 2. The length of the alkyl chain can be determined by the molecular ions that are usually present in the mass spectrum. LCABs isomers with four different molecular weight (MW) isomers were detected in the sample. They were MW = 232 (C<sub>17</sub>H<sub>28</sub>, C<sub>11</sub>-benzenes), MW = 246 (C<sub>18</sub>H<sub>30</sub>, C<sub>12</sub>-benzenes), MW = 260 (C<sub>19</sub>H<sub>32</sub>, C<sub>13</sub>-benzenes), and MW = 274 (C<sub>20</sub>H<sub>34</sub>, C<sub>14</sub>-benzenes).

Carboxylic acids (CAs) were detected in fractions 3–6 of all dust samples. Except for dust sample from house G, the concentrations of organic acids were the highest among all classes investigated. CAs are polar chemicals, they may have poor recoveries from sample

preparation and they also have poor peak shape under GC/MS operation conditions. Therefore, the underestimation of actual amount of CAs in the dust may have occurred.

## DISCUSSION

The extract was fractionated through a small silica gel column. The purposes of using the silica gel column were to clean up the samples prior to instrument analysis and to separate the chemical components in the extract so that a better separation result can be achieved on the GC chromatogram minimizing co-elution and interference problems of the complex mixtures of the extract. As indicated in Table 1, LCABs, which are non-polar in nature, eluted in fraction 1 only. That was followed by PAHs in fractions 1 and 2 with some semi-polar PAHs in fraction 3, while phthalates mainly eluted in fractions 3 and 4. CAs, which are the most polar chemicals among the chemical classes discussed in this paper, were spread from fraction 3 to fraction 6.



**Figure 1** Reconstructed ion chromatograms of  $m/z$  149 obtained from GC/MS of fraction 3 in house B dust (top) and fraction 3 in house G dust (bottom).

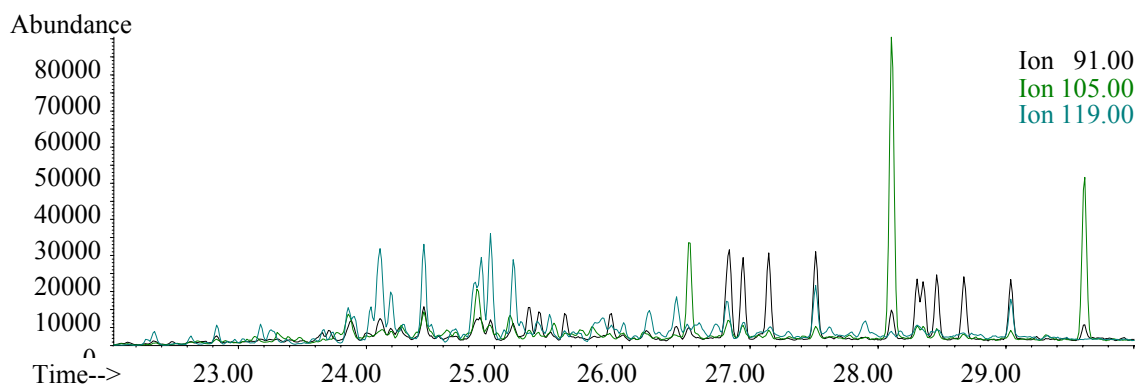
*PAHs*—Indoor PAHs can be generated through combustion, cooking and smoking. They can also be generated outdoors by vehicle emissions, which may be infiltrated into indoor

environment. A recent study has shown the presence of PAHs in fine dusts ( $<100\ \mu\text{m}$ ), in which the highest concentrations were found in dusts having size less than  $4\ \mu\text{m}$  (Lewis, 1999). This is probably due to the larger surface to mass ratio of smaller particulate. As the smaller particles are more likely to be carried into the respiratory system, PAHs associated with small particulate may have larger impact on human health.

In addition to common PAHs found in the house dust samples screened, some methylated PAHs and semi-polar PAHs, which are not routinely monitored in most survey studies, were also detected. The knowledge on the levels of these methylated PAHs and semi-polar PAHs indoors and associated health risks of these PAHs is limited. Therefore, these PAHs should be considered to be included in future monitoring studies.

**Phthalates**—Phthalates were found in high concentrations ( $300\text{--}1200\ \mu\text{g/g}$ ) compared to the other groups of compounds. The concentrations are similar to the values reported of a recent study on the analysis of hormonally active agents in indoor air and dust (Rudel *et al.*, 2001), where phthalates were detected at high concentrations in all dust samples ( $0.3\text{--}524\ \mu\text{g/g}$ ) with the highest concentrations for DEHP ( $315\ \mu\text{g/g}$ ) and BBP ( $117\ \mu\text{g/g}$ ).

Although DEHP and BBP are the most commonly found phthalates in the indoor environment, the abundance of these two compounds compared to the other phthalates were quite different among the samples. An example of such different phthalate profile is clearly indicated in Figure 1. This can be attributed to the use of different consumer products in specific household. Phthalates are mostly used as plasticizers in plastics and in many consumer products, from nail polishing products and perfumes to tool handles. They have also been detected in adhesives, caulking, paint pigments (Gustafsson, 1992). Recent studies showed that the concentrations of phthalates in indoor air and dust were orders of magnitude higher than the typical concentrations of other compounds of environmental health concerns such as PAHs (Rudel *et al.*, 2001).



**Figure 2** Long-chain alkyl benzenes in the fraction 1 of house H.

**LCABs**—Long-chain alkyl benzenes (LCABs) are common process solvents for plasticizers in the manufacture of vinyl floor coverings. For example,  $\text{C}_{12}$ -benzene isomers have been detected in a library indoor air at concentration levels of between  $100$  and  $200\ \mu\text{g/m}^3$  (Gustafsson, 1992). Some other LCABs including  $\text{C}_{11}$ -benzene isomers,  $\text{C}_{12}$ -benzene isomers, and  $\text{C}_{13}$ -benzenes were also found to be emitted from vinyl tiles and other flooring materials with individual compound concentration up to  $80\ \mu\text{g/m}^3$  in small test chambers (Zhu *et al.*, 1999). Our study confirmed the presence of LCABs in house dust as well, which are probably originated from flooring materials used in homes.

**CAs**—Carboxylic acids were present in test samples in relatively high concentration. Although the presence of carboxylic acids is not likely to raise any health concern, it may

interfere with analysis of other compounds of interest, especially for the measurement of polar chemicals that elute in the same fractions as these acids.

## CONCLUSION AND IMPLICATIONS

This pilot study was conducted to screen fine house dust from six homes for the presence of organic chemicals. The results have shown that a number of SVOCs including PAHs, phthalates and LCABs were present in house dusts. More thorough analysis will be required in order to better characterize the organic compounds in house dusts and quantitatively determine the levels of such compounds. Identification of chemicals carried out in this study was however an essential first step.

House dust, especially those of smaller particulate size, may be re-suspended indoors when a disturbance, such as traffic or floor vacuuming, occurred. Inhalation and ingestion are the two major exposure routes to fine house dust. Such exposure may be more significant for small children who spend most time playing on the floor. Full characterization of house dust and detailed measurements of environmental pollutants are important to estimate the relative risks associated with exposure to dust indoors. Further studies in this direction are currently undertaken in our laboratories including measurements of selected environmental pollutants (PAHs, pesticides, and phthalates) in house dust from about 70 randomly selected homes in the city of Ottawa, Canada.

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