

Semipermeable membrane devices as passive samplers to determine polycyclic hydrocarbons (PAHs) in indoor environments

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Introduction

Most people spend the majority of their time indoors. Several studies have shown that concentrations of some air pollutants can be higher indoors than outdoors^{1,2}. Therefore, in order to evaluate risk to human health from exposure to air toxics, knowledge of contaminant levels and understanding of sources are important components in identifying high-risk populations.

Polycyclic aromatic hydrocarbons (PAHs) are formed by incomplete combustion of organic materials, and are widely distributed in the environment³. They are multi-ringed compounds and many of them are carcinogenic⁴. PAHs with three or four rings are mainly associated with the vapour phase whereas those with five and six ring PAHs are mainly bound to particles, and the partitioning mainly depends on the temperature⁵. Today, wood burning is considered to be the most important source of PAH emissions to air in Sweden, about 60% of total emissions, and mobile sources (traffic) contribute about 30%⁴. Thus, residential burning of wood may be a source of PAHs in indoor air. Cigarette smoking and cooking are other sources of PAHs to the indoor environment⁶.

Air concentrations of semi-volatile persistent organic compounds (POPs) such as PAHs are usually measured with an active (high volume) sampling technique. Active samplers are relatively expensive, in material and labour,

and they need electricity for their operation. Moreover, the pumps may be a problem when measuring in private residencies.

Semipermeable membrane devices (SPMDs) are diffusive samplers, with semiquantitative features, and can be used to measure the bioavailable (dissolved) fraction of POPs in water⁷, air⁸ and soil⁹, *i.e.* the fraction of a compound that is not absorbed on particles. They consist of a polyethylene film, containing triolein that has transient pores with a diameter of about 10Å, where lipophilic chemicals such as PAHs can permeate the thin wall of the tubing and partition into the lipid. The advantage of a diffusive sampling technique is that the samplers are simple to handle, need no electricity or heavy equipment, and a large number of samples can be deployed simultaneously. Since they have a long operating time, two to four weeks, the results can be used to determine time-integrated values. Moreover, the mechanism of uptake in the SPMD mimics accumulation through cell membranes into the lipids of an organism, and, hence, might mimic human uptake. In this paper we present estimates of indoor PAH levels using SPMDs in 16 single one-family houses. Nine of the households used wood burning as domestic heating, while seven used other heating systems (electrical or heating pumps).

Materials and Methods

Sampling area characteristics and experimental set-up. SPMDs were placed for two weeks in the living rooms of 16 volunteers in single one-family houses, in the same residential area, with (n=9) or without (n=7) wood burning appliances for domestic heating. The study was conducted in the small Swedish town Hagfors, which is situated in mid-Sweden, in the winter 2003. At two of the sites, the sampling was performed in duplicates. Moreover, blank SPMDs, field and lab blanks, were analysed in parallel with the samples. There was good agreement between the duplicates and only some minor residues of low-molecular weight PAHs were found in the blank samples.

SPMD design, analytical procedure and analysis. The SPMDs were purchased from ExposMeter AB (Umeå, Sweden) and were of standard performance (91.4 cm long and 2.5 cm wide tubes of low-density polyethylene filled with 1 mL of 95% pure triolein). The sampling procedure and analytical process are

explained in detail elsewhere⁸ and will be given here in brief. Before and after sampling the SPMDs were stored in sealed solvent-cleaned tin cans at -18°C . During sampling the SPMDs were mounted on a steel device, between rods attached to a steel disc (spider). The spider containing the SPMD was placed on a table in the living room and was retrieved after two weeks of exposure, placed in the can and transported to the lab.

The samples were thawed, washed in a solvent mixture and wiped dry with Kleenex tissue. The membranes were submerged in a solvent (95:5 (v:v) cyclopentane: dichloromethane) and extracted for two 24h periods. The two dialysis fractions were pooled, spiked with ^2H -PAH standards (Promochem, Kungsbacka, Sweden) as internal standards of the clean up. The excess solvent was evaporated and the samples were first cleaned on a high-resolution gel permeation chromatography system, and final enrichment was done on an open silica column system.

Analysis and detection were accomplished using high-resolution gas chromatography /low-resolution mass spectrometry (HRGC/LRMS). The MS instrument was a Fisons MD800 operating in electron impact (EI) mode using selected ion recording (SIR). The GC was a Fisons GC 8000 with a non-polar capillary column (60 m x 0.32 mm i.d., 0.25-mm film thickness) (J&W DB-5, Folsom, USA). The GC was programmed as follows: 90°C for 2 min, $8^{\circ}\text{C}/\text{min}$ to 240°C , $4^{\circ}\text{C}/\text{min}$ to 300°C and 300°C for 10 min. The most abundant ion of the native compounds and the ^2H -labeled PAH standards were monitored in the SIR mode. The compounds analysed were 28 PAHs and among these 16 EPA priority PAHs and eight methyl-PAHs.

Results and Discussion

PAH uptake on SPMDs. Most of the studied PAH components were found in all samples, including the cancerogenic benzo(a)pyrene (B(a)P, fluoranthene and indeno(1,2,3-*cd*)pyrene, indicating that they are contaminants in the vapour phase in indoor environments. Phenanthrene was the major compound and other abundant components were fluorine, naphthalene, and methylated phenanthrenes and naphthalenes. Figure 1 shows the sum of 15 EPA priority PAHs. Naphthalene is not included since steady-state concentrations may have been reached in the SPMDs during the 14 days of

exposure. The black bars represent the houses that used wood burning for domestic heating and the grey bars houses that utilized other heating systems. The five highest levels were found in houses that used wood burning. The uptakes were a factor of two to six higher in these places compared to the others that may represent background levels of PAH in the study area. The results indicate that the heating system may be a source of PAHs to the indoor air, although other sources such as cooking, or outdoor sources contributing to indoor pollutant levels, cannot be excluded.

The results may be compared with a study performed in the Bangkok region, Thailand where SPMDs were deployed to investigate variations in PAH concentrations at urban and rural/background sites⁸. In that study, the PAH uptakes were found to be about 20-50 ng *day⁻¹ in the rural/background areas and about 100-140 ng *day⁻¹ at the urban sampling sites. Thus, the background levels found in indoors air in our study was similar to the results found at background/rural sites in the Bangkok region. In three houses (#3, 4 and 8) (see Figure 1), the intermediate levels of PAHs were in the same range as in the urban sites of Bangkok, while at two houses (#2 and 7) the levels were even higher than that of the urban sites with dense traffic in the Thailand study.

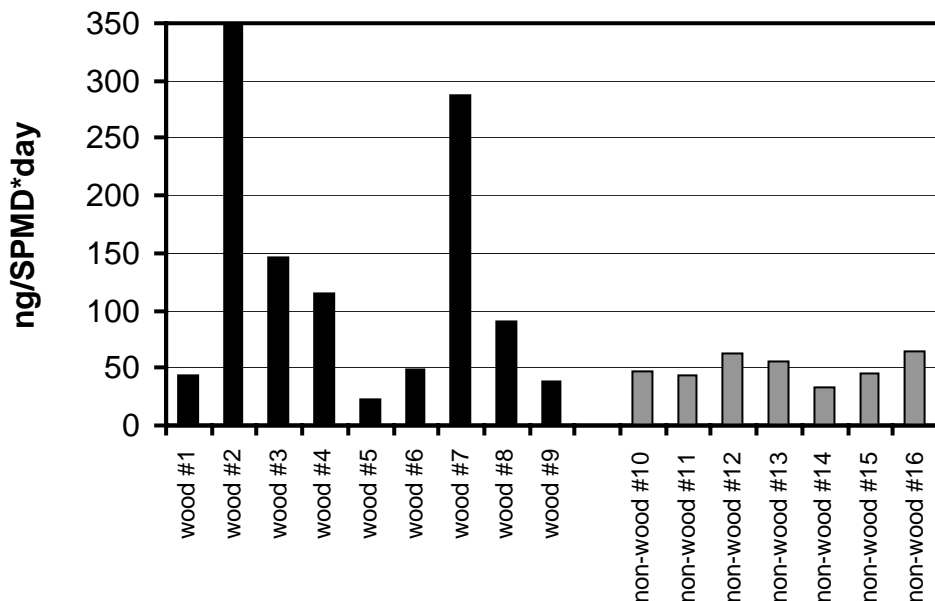


Figure 1. Amounts of PAHs (sum 15 EPA PAHs) in SPMDs exposed to air in single one-family houses with (black bars), or without (grey bars), wood burning as domestic heating.

When using SPMD the concentration increases by first-order kinetics. An important principle in SPMD sampling is the effort to be in the kinetic phase of uptake, where the uptake is linear. Assuming that equilibrium between the SPMD triolein and the environmental media is not approached, the formula for calculating the ambient air concentration can be simplified as:

$$C_{\text{air}} = C_{\text{SPMD}} / (R_{\text{air}} * t)$$

The C_{air} -value is the environmental concentration to be calculated and C_{SPMD} is the amount observed from the SPMD analysis, the R -value is the effective daily sampling rate for a specific compound and temperature expressed as m^3/day , and t is the time (days).

There are, to date, few R -value data for specific compounds and temperatures available in the literature. A study by Ockenden *et al.*, (1998)¹⁰ presented calibration data for SPMDs and some PCB congeners in air at two temperatures (4°C and 18°C). We used the mean PCB congener R -values at 18°C to estimate air concentrations of PAHs in our study. The concentration of PAHs found in the vapour phase in indoor air in this study corresponds to about 50 ng/m^3 for the houses not using wood burning as domestic heating, and the highest concentration obtained $\sim 450 \text{ ng/m}^3$ was found in a house with wood burning appliance. Phenanthrene, the most abundant compound found in this study, which is reported to be in the gas phase at approximately 95%⁵, can be an important marker compound for gas phase concentrations of PAHs. The highest concentrations of phenanthrene in this study (houses #2 and 7) were estimated at about 100 ng/m^3 . These levels of phenanthrene are similar to concentrations reported from the Chicago air, summer 1994, 66-98 ng/m^3 ⁵.

Retene has been suggested as a marker PAH for the burning of wood¹¹. However, this marker seems applicable only for emissions from the burning of soft wood¹². The emission profiles depends on the type of wood burned, but also on the efficiency of the wood stove. Retene was found in all samples indicating that it is present in indoor environments. The amounts were low

and ranged from 0.3-1.4 ng SPMD⁻¹ *day⁻¹. It cannot be clarified however, based on the data from this study, whether retene is a marker compound for wood combustion.

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