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Wind Effects on Passive Air Sampling of PAHs and PCBs

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Semipermeable membrane devices (SPMDs) are passive samplers designed by Huckins et al. (1990) for integrative sampling of the dissolved fractions of moderately lipophilic to highly lipophilic organic pollutants in water. Later on, SPMDs were successfully used to measure the vapor phase of organic pollutants in air by e.g. Petty et al. (1993) and Söderström and Bergqvist (2003). In a standard SPMD, passive sampling is achieved by physical absorption in a polyethylene tube, and diffusion through the tube resulting in dissolution in a lipid phase consisting of triolein (a neutral lipid found in most aquatic organisms). The sampling rate, R_S, is affected by the physicochemical properties of the sampled compound, the design of the sampler and the environmental conditions. In water, the uptake of compounds with log octanol-water partition coefficients (log K_{OW}) > 4.4 are generally controlled by the thin external layer of stagnant water (the boundary layer) at the membrane-water interface (Huckins et al. 1999; Vrana and Schuurmann 2002; Booij et al. 1998). The water flow/turbulence affects the thickness of the boundary layer, and thereby, the SPMD sampling of these compounds. Temperature and biofouling at the exterior of the membrane surface are environmental variables which also affect the R_S of SPMDs in water. Both temperature and wind-speeds are expected to affect the SPMD sampling in air as well, whereas the influence of biofouling is expected to be insignificant. The site effects of environmental variables can be reduced by using devices design to protect the SPMDs from e.g direct wind exposure as demonstrated by Ockenden et al. (2001).

Traditionally SPMDs have been calibrated prior to use and at a given temperature, as was made by e.g. Huckins et al. (1999). Pre-calibration of the R_S of SPMD has the disadvantage of being very time-consuming due to the many sampling conditions and the number of compounds that have to be tested. Furthermore, the field conditions can be difficult to replicate and maintain over extended periods, making it complicated to generate pre-calibrated R_S values that reflect the true air sampling situation. Huckins et al. (1993) suggested the use of performance reference compounds (PRCs) to calibrate the SPMD sampling *in situ* and thereby predict the true sampling rates. PRCs are compounds with moderate to high SPMD affinity which are not analytically interfering. They are added to the lipid phase of the SPMD prior to membrane enclosure and the theory states that the

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release rate of PRCs during sampling are related to the uptake rates of the compounds sampled by the SPMDs. In water, the theory of the PRC method has been confirmed by e.g. Booij et al. (1998). In air, Ockenden et al. (2001) found that the uptake and release of some PCBs were related.

This study tested whether the uptake of PAHs and PCBs, and the release of three PRCs, increased when SPMDs were exposed to high wind-speeds/turbulence (6 to 50 $m \cdot s^{-1}$) produced in an indoor, unheated and dark wind tunnel.

MATERIALS AND METHODS

A standard SPMDs, used for sampling, was a 91.4 cm long and 2.5 cm wide tube of low-density polyethylene (75-90 μm thickness, pore size ~10 Å) filled with 1 mL (0.915 g) of > 95 % pure triolein. Each sampler used in this study included two standard SPMDs mounted on separate steel spiders (steel rods attached to a 150 × 140 mm steel disc), which were horizontally positioned on top of each other inside a metal umbrella, designed to protect the SPMDs from direct particle deposition, sunlight, rain and air flow. Before and after sampling, SPMDs were stored in sealed solvent-cleaned tin cans at –18 °C. Four samplers were deployed in an indoor, unheated and dark wind tunnel located in a rural area of northern Sweden with no point sources of PAHs and PCBs (Figure 1). The air concentrations were therefore considered to be relatively constant at each site and during the sampling period. One sampler (C1) was also placed outside the wind tunnel in the building and another sampler (C2) was placed outside the building to control the sampling rates at the nearly still air in the building and at ambient air conditions, respectively (Figure 1). The wind tunnel had two compartments; one compartment (7.0 m) with a progressively decreasing cross-sectional area towards the outlet (from 1.9 to 0.6 m^2) causing different wind-speed/turbulence depending on the position in the compartment, and a second compartment (2.5 m) with a considerably smaller cross-sectional area (0.25 m^2) than the first, so the wind-speeds should be highest in this compartment (Figure 1). A fan located in the inlet of the larger compartment produced constant high air flow during the 18-day sampling period. The wind-speeds could not be measured at each sampling site due to high turbulence in the wind tunnel but the wind-speed in the inlet and the outlet of the wind tunnel was calculated to be 6 and 50 $m \cdot s^{-1}$, respectively. The average temperature during the 18-day sampling period, both inside and outside the building, was 15 °C.

Deuterated acenaphthene, phenanthrene and pyrene were used as PRCs. When selecting the compounds used as PRCs, the environmental conditions at the sampling sites and the sampling time should to be considered to ensure that an acceptable range of PRC release occurs during the sampling. Generally, releases of the PRC amounts in the range of 20 - 80 % of the initial amount in the SPMDs are acceptable (Huckins et al. 2002a). In this study, the PRC amounts were measured before and after the sampling. The initial PRC amounts in the SPMD

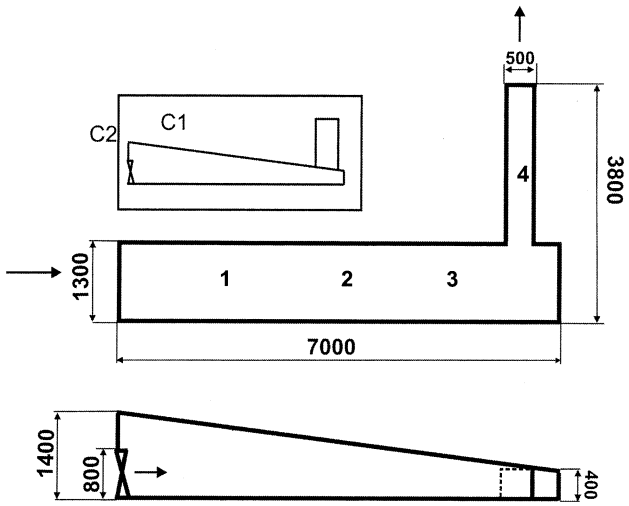

Figure 1. Experimental setup during the 21-day air sampling including two SPMD samplers used as controls of sampling rates outside the wind tunnel, C1, and outside the building, C2, a wind tunnel built in two compartments (1300 × 7000 mm and 500 × 2500 mm, respectively), an electrical fan (800 mm i.d.) mounted in the wall outside the building and in the inlet of the wind tunnel and five SPMD samplers inside the wind tunnel, denoted by numbers 1-5 in the figure. The wind-speed in the inlet (1400 × 1300 mm) and in the outlet (400 × 500 mm) of the wind tunnel was calculated to be 6 and 50 m· s^{-1}, respectively.

were measured by analysing an unexposed SPMD referred to as laboratory control (LC) according to the same procedures as the other SPMD.

The clean up and analytical methods used have been described in details previously by Söderström and Bergqvist (2003). In short, the membrane surface was cleaned in water and thereafter in n-hexane followed by hydrochloric acid (1 M). The organic pollutants were extracted by dialysis of the two SPMDs from one site together in a glass extraction column filled with cyclopentane: dichloromethane for 48 h, solvent exchange after 24 h. One mixture of the ^{13}C-PCBs PCB#28/47/52/101/105/118/138/153/156/180/194/209 and another mixture of ^{2}H-PAHs fluoranthene and benzo[g,h,i]perylene were added as internal standards of the clean up and the extracts were cleaned using a gel permeation chromatography (GPC) system that included a high resolution (HR)-GPC column followed by a mixed silica gel column including deactivated silica, potassium silicate and sodium sulfate. The sample volume was reduced by rotary evaporation, ^{2}H-labeled dibenzofuran was added as a recovery standard of the chemical analysis and each sample was transferred to a vial for GC/MS-analysis. The samples were analyzed, in two separate runs for the three PRC PAHs, 15 EPA PAHs (excluding fluorene, biphenyl, and four methylnaphthalenes plus one methyl phenanthrene and thereafter for the PCBs PCB #28/47/52/101/105/118/

128/138/141/153/156/180 by high-resolution gas chromatography /low-resolution mass spectrometry (HRGC/LRMS) operated in electron ionization mode monitoring selected ions.

The chemicals and solvents used were analysed as a laboratory blank (LB) according to the same procedures as described above. The purity of the SPMDs and the contribution of the sampling procedures to the amounts found in the SPMDs were controlled by exposing one SPMD to air during deployment and retrieval of the samplers. This SPMD, referred to as the field control (FC), was analyzed as a single SPMD sample according to the same procedures as the other SPMDs. the total PAH amount found in the LB and the FC were equivalent to 1.5 and 17.3 %, respectively, of the lowest PAH amount found in the SPMDs whereas the PCB levels were below detection limit in both the LB and the FC. The low levels detected in the LC and the FC suggests that the sampling and analytical procedure made a minor effect on the results. The recoveries of the ^{13}C-PCBs were 80-130 %, 67-120 % of ^{2}H-fluoranthene and 57-95 % of ^{2}H-benzo[g,h,i]perylene and were compensated for.

RESULTS AND DISCUSSION

The total amount of PAHs (including five alkyl-PAHs) and PCBs, respectively, taken up by the SPMDs in the wind tunnel were more than double the amounts found in those placed outside the tunnel (C1) (Figure 2). Furthermore, slightly higher PAH and PCB amounts were found in the SPMDs exposed to ambient air (C2) compared to those exposed to the nearly still air inside the building (C1) (Figure 2). Thus, the uptakes of both PAHs and PCBs increased in the SPMDs exposed to the assumed highest wind-speeds/turbulence. This study showed a wind effect on the R_S indicated that the uptakes of PAHs and PCBs were controlled by the boundary layer at the membrane-air interface. These results are in agreement with those obtained in water by Booij et al. (1998) who observed that the R_S of PAHs and PCBs were three times higher under high flow compared to low flow conditions.

The different wind-speeds in the wind tunnel had a lower effect on the uptakes than expected, indicated that the wind-speeds inside the deployment devices were less variable than outside (Figure 2). Ockenden et al. (2001) measured the wind-speeds inside and outside devices with a similar design as we used and found considerably lower wind-speeds inside than outside them. The devices used in this study probably reduced the wind-speeds in a similar way and, consequently, similar uptakes of the both the PAHs and the PCBs were observed for the SPMDs deployed in the wind tunnel. Thus, a well-designed sampler can reduce the wind effect between sites (even when high wind-speeds occur during the sampling).

For the gas phase PAHs, the differences in the uptakes between the SPMDs inside and outside the wind tunnel increased with increasing log octanol-air partition coefficient (K_{OA}) (Figure 3). (K_{OA} values used in Figure 3 were estimated by $K_{OA} = (K_{OW} \cdot R \cdot T)\, H^{1}$ where T is the temperature, R is the gas constant and H is the

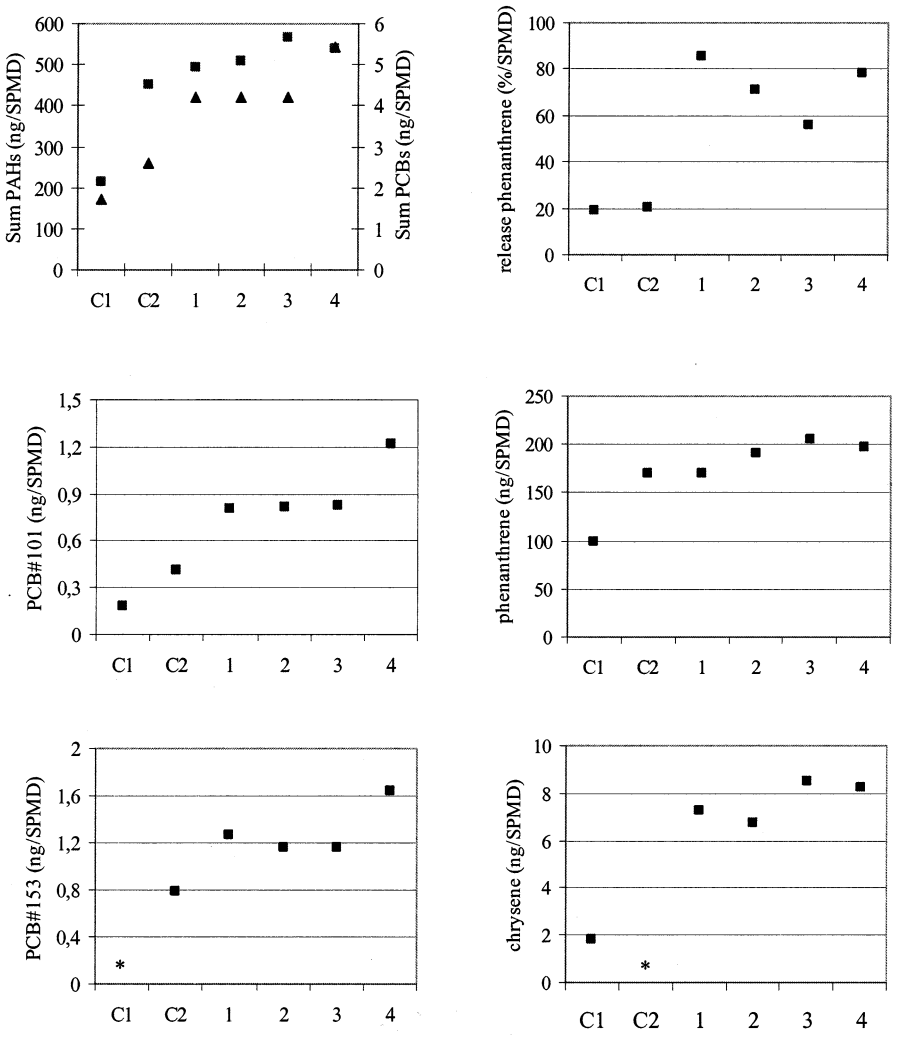

Figure 2. The amounts of 15 EPA PAHs, biphenyl plus five alkyl-PAHs and 12 PCBs, two individual PCBs and two individual PAHs taken up by SPMDs outside (C1, C2) and inside the wind tunnel (1-4) compared with the percentage amounts of 2H-phenanthrene released during the sampling. *not analysed due to interferences.

Henry's law constant. K_{OW} and H data were obtained from Mackay et al. (1992)). Thus, the effect of wind depended on the physicochemical properties of the gas phase PAHs sampled indicated that PAHs with higher log K_{OA} values were more restricted by the boundary layer. The high wind-speeds in the wind tunnel (by reducing the thickness of the boundary layer considerable) therefore had a higher influence on the R_S of the compounds with higher log K_{OA} values. These

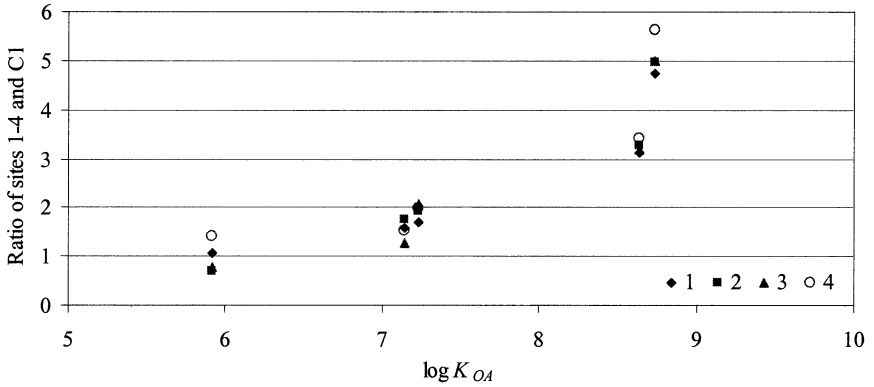

Figure 3. Ratio between the amounts of acenapthene (5.92), phenanthrene (7.14), anthracene (7.24), pyrene (8.64) and fluoranthene (8.74), respectively, taken up by the SPMDs inside (1-4) and outside (C1) the wind tunnel as a function of each compounds octanol-air partition coefficient (K_{OA}). K_{OA} estimated from $K_{OA} = (K_{OW} \cdot R \cdot T) \cdot H^{-1}$. K_{OW} and H values selected by Mackay et al. (1992).

correlations were not observed for the PAHs mainly bound to particles or for the PCBs.

After the 18 day-sampling period, the remaining amounts of ^{2}H-acenaphthene were below detection limit in all SPMDs due to its high exchange rate. The amounts of ^{2}H-phenanthrene and ^{2}H-pyrene released ranged between 18 and 78 % and 12 and 75 %, respectively, with generally higher releases of ^{2}H-phenanthrene compared to ^{2}H-pyrene indicating a negative correlation between the PRC amounts released and the log K_{OA} of the compounds. Thus, the amounts of ^{2}H-phenanthrene and ^{2}H-pyrene released after a three weeks field sampling would be in an acceptable range (20 to 80 % changes in the initial amounts) whereas the release of ^{2}H-acenaphthene would be too high (> 80 % of the initial amounts). However, in this study we wanted to investigate compounds that could be used as PRCs during both shorter and longer sampling times, rather than to select a narrow range of PRCs with a suitable rate of release for the sampling time we applied. The results found in this study agree with those found by Ockenden et al. (2001) who after a four month sampling campaign observed non-measurable releases of ^{13}C-labeled PCBs 138 and 180 due to their high K_{OA} values.

The precision of the PRC-^{2}H-pyrene data was low due to analytical interferences in the HRGC-LRMS analysis. These data were therefore excluded from further discussion. The amounts of the ^{2}H-phenanthrene released were up to four times higher from the SPMDs in the wind tunnel than from those outside the wind tunnel (Figure 2). In the wind tunnel, the amounts of ^{2}H-phenanthrene released from the SPMDs decreased significantly, progressing from sites one to three and increased again between sites three and four (Figure 2). Thus, the releases of ^{2}H-phenanthrene increased for the SPMDs exposed to the assumed highest wind-

speeds/turbulence indicated that also the release rates were controlled by the boundary layer at the membrane-air interface.

Both the uptakes and releases of the studied compounds were higher for the SPMDs in the wind tunnel compared to those outside the wind tunnel (C1) and thus, a wind effect on both the uptake and the release rates was found. Furthermore, the uptakes of PCBs and the releases of ^{2}H-phenanthrene varied similar between sites whereas the uptakes of PAHs differed somewhat from these patterns (Figure 2). Thus, the PRC data reflected the differences in uptakes between SPMDs, and the PRCs were able to predict the site effects of different wind conditions. These results are in agreement with those reported by Huckins et al. (2002b) who summarized the research results on the use of PRCs for *in situ* calibration of SPMD sampling in water, and found that PRC data can be used to predict the effects of environmental variables during sampling.

The releases of ^{2}H-phenanthrene were not able to fully reflect the uptakes of PAHs due to analytical interferences. This study also revealed problems with the precision of the PRC ^{2}H-pyrene caused by analytical interferences. Booij et al. (1998) used PRCs and found that they allowed the uptake kinetics of PAHs to be predicted, but with poor precision due to analytical interferences. Thus, when using PRCs to calibrate the SPMD sampling *in situ* robust analytical quality control should be used.

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