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PAHs in Stockholm window films: Evaluation of the utility of window film content as indicator of PAHs in urban air

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ABSTRACT

The thin organic film that builds up on the exterior surface of windows has been proposed as a ubiquitously available passive sampler for semi-volatile organic contaminants (SOCs) in urban air. Readily available school windows were sampled in Stockholm city centre and suburban locations in both winter and summer season to evaluate the putative usefulness of this matrix for assessing the integrated load of urban air pollution by polycyclic aromatic hydrocarbons (PAHs). The window-area normalised concentrations indicated more PAH contamination in the winter than in the summer in both the city centre and suburban locations, with highest concentrations in the city centre in the winter ($\sum PAH_{43}$ 451–467 ng m^{-2}). However, normalising the PAH load to the amount of fatty window film, as measured by extractable organic matter (EOM), gave a more homogeneous picture with the EOM-normalised PAH load being inseparable both between summer and winter and between city centre and suburban locations.

To evaluate the possibility of quantitatively employing urban window films as a means to provide predicted environmental concentrations of PAHs in air (PEC_{air}), window film–air partition coefficients of PAHs were estimated using a set of coupled linear free energy relationships and physico-chemical properties of PAHs. Assuming dynamic equilibria between PAHs in air and dissolved in the window film, the obtained PEC_{air} from the window films were consistently overestimating the urban vapour-phase PAH concentrations by factors 4–135. This discrepancy is quantitatively consistent with a strong and overwhelming association with black carbon aerosol particles accumulated in the window film. For SOCs that have a lower tendency to associate with black carbon, bulk window film concentrations may work better than for PAHs to estimate their vapour-phase concentrations in urban air.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed during incomplete combustion of any organic material. This includes biomass burning (e.g., vegetation fires and woodfuel combustion) and fossil fuel combustion. Several of the PAH homologues are carcinogenic and/or mutagenic (IARC, 1983; Bostrom et al., 2002) and being ubiquitous, PAHs are part of the concern for air pollution. For instance, one study shows that in Austria, France and Switzerland human exposure to air pollution causes 6% of mortality as well as widespread respiratory illness (Kunzli et al., 2000). The effects of airborne PAHs on both human and environmental health have recently forced these pollutants to be regulated in the European Union (European Community, 2005). This in turn places heavy demand on efficient monitoring of these regulated pollutants.

Traditionally, the most common way of monitoring PAHs in air is with high-volume sampling systems. This method

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pumps a high volume of air through a filter and consecutive adsorbents. Particulate matter is collected by the filter and vapour-phase contaminants are collected by the adsorbent (Bidleman, 1988). While the use of high-volume samplers is relatively straightforward, their significant expense limits spatial and temporal coverage. A less expensive approach is to use passive samplers placed at locations of specific interest and left to equilibrate with the surrounding air (Bidleman, 1988; Gouin et al., 2005). This, however, is a more time consuming method and there may be some questions on how to estimate air concentrations from the amount of PAHs collected by the passive sampler (Bartkow et al., 2004; Gouin et al., 2005).

A possible alternative or complementary approach may be to use the thin organic film that forms on all impervious surfaces, such as windows, by condensation of air contaminants (Law and Diamond, 1998). The organic film on windows has been proposed as ubiquitously available passive samplers for inexpensive and easy monitoring of PAHs and other semi-volatile lipophilic air pollutants as airborne contaminants that adhere to the film can be collected and analysed (Diamond et al., 2000; Gingrich and Diamond, 2001; Rayne et al., 2005). Window films collected in urban Toronto (Canada) contained about 5% organic carbon (Lam et al., 2005) and nuclear magnetic resonance (NMR) spectroscopy showed that 35% was of carbohydrate, 35% aliphatic, 20% aromatic and 10% carbonyl structure (Lam et al., 2005; Simpson et al., 2006). This overall fatty composition makes it putatively suitable as a passive sampler for airborne lipophilic compounds.

Since the film works as a passive sampler the vapour-phase concentration of prioritised semi-volatile contaminants such as PAH can in principle be estimated if the partition coefficient between the surface film and the surrounding air may be determined. The objective of this study was first to assess the spatial and seasonal variability in the PAH load on exterior windows in the urban environment. Second, we seek to use a set of coupled linear free energy relationships (LFER) and physico-chemical properties of PAHs to derive window film–air partition coefficients for PAHs. These parameters were then used in combination with film and urban air measurements to quantitatively evaluate the utility of the window films as passive samplers, from which the air concentration of urban PAHs could possibly be estimated.

2. Methods

2.1. Sampling of Stockholm window films

Windows without over-hang facing all points of the compass from a total of seven schools were sampled in the metropolitan Stockholm area. All samples from the same site were pooled, resulting in a wind-direction integrated sample from each school. Two schools were situated in Stockholm city centre (C) and five schools were situated in the southern suburbs (S) of Stockholm (Fig. 1). Sampling was performed in both winter and summer at the same locations. Window film accumulation time were several months for each sampling occasion. The sampling sites are further described in Table 1.

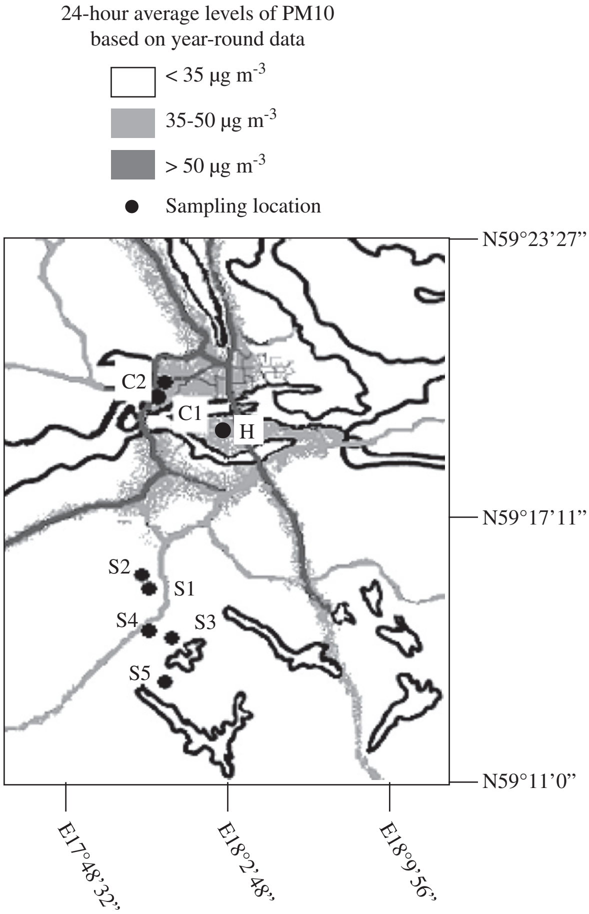

Fig. 1. Map of the relevant Stockholm area showing particulate matter (PM10) exposure (SLB Analys, 2007) and the window film sampling sites in city (C) and suburb (S). A reference high-volume sampling location (H) is also marked. Note that the highest PM10 levels ($>50\,\mu g\,m^{-3}$) are limited to a few highways as they pass through Stockholm city.

The window film sampling method was modified from Diamond et al. (2000). Briefly, low-lint paper tissues were pre-extracted in 2-propanol (Riedel-de Haen, Seelze, Germany) for 24 h using a Soxhlet extractor. Half the tissues were dried, covered in aluminium foil, in a fume hood; the other half was stored damp in glass jars. Sampling was performed by first wiping the window with pre-extracted dry paper tissues and then with an equal amount of damp (2-propanol) tissues. The samples were then stored in folded aluminium foil envelopes placed in ziploc plastic bags and held at $-18\,^{\circ}C$ until analysis.

2.2. Analysis of PAHs

The samples were Soxhlet extracted for 24 h with toluene (Fluka, Steinheim, Germany) using a Dean-Stark trap to remove any water. Five deuterated PAHs were thereafter added as internal standards to allow for