AIR-SURFACE EXCHANGE OF POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN AREAS: INFLUENCE OF SEALED IMPERVIOUS SURFACES

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Introduction

Urban environments are characterized by numerous PAH sources (automobile traffic, industrial emissions, etc.). Among them, products used to construct or coat impervious surfaces could be sources of PAHs to urban air. One such product is parking lot "sealcoat", sprayed or painted on parking lots in an effort to enhance appearance and protect the underlying asphalt. And yet these "sealcoats" are widely used in North America and the two main applied sealants, e.g., coal tar and asphalt, are by-products of processes commonly associated with PAHs (conversion of coal into coke and refining of crude oil respectively). Recently, processes promoting volatilization into the urban atmosphere [1, 2] have been demonstrated, resulting in elevated concentrations of these mutagenic contaminants. To our knowledge, there has been no study measuring surface-air partition coefficients for PAHs directly in the field. Our novel air sampler, previously used to study the soil-air partitioning of pesticides [3], allows us to measure air concentrations of PAHs at or close to equilibrium with the surface by sampling the air very close to the surface and to measure the atmospheric concentration gradient by sampling the ambient air 1.5 m above the surface. It can provide useful information for modeling PAH fate in urban environments. The purpose of this paper is to investigate surface-air partitioning for PAHs in the field and the potential of sealed parking-lot surfaces as PAH sources to the urban environment.

Material and Methods

Sampling. High volume air and surface debris were collected above 5 surface types in Austin, Texas. Surfaces consisted of two currently used coal-tar sealed and asphalt-sealed parking lots (Austin downtown), and three other test plots (former airport) in the absence of any vehicle-related sources. The airport test surfaces were: coal-tar sealed, asphalt-sealed and unsealed asphalt. The field sampler[3] is a "hat-like" stainless steel dome standing 3 cm above the ground and connected to a high-volume air sampling pump (figure 1). The particle-phase compounds are trapped on a glass fibre filter (GFF) and the gas-phase compounds on a polyurethane foam (PUF) plug. Because it is close to the surface, the sampler collects PAHs in the stagnant layer of air just above the surface which is expected to be near air-surface equilibrium. The large diameter of the sampler results in a slow face velocity (2-5 cm s^{-1}) at the sampler perimeter. This allows more time to establish equilibrium. A high-volume air sampler was set up at 150 cm above ground level for measuring ambient air concentrations. Dust deposited on surfaces was sampled using hand-brushing and a vacuum-cleaner over an 80x80cm area. Samples (composites of three subsamples collected in a 15-m diameter circle) were placed in solvent-washed glass flasks fitted with aluminium foil-lined lids and kept frozen. They were then pulverized in an agate blender and sieved at 1 mm to eliminate debris and fragments. Density and organic carbon were measured for each sample.

Analysis. PUF and GFF samples were Soxhlet extracted for 24h with petroleum ether and concentrated to ~1mL under a gentle stream of clean, dry N_2. The dust samples were Soxhlet-extracted in a pre-washed (dichloromethane) cellulose thimble for 24 h with dichloromethane. The extracts underwent cleanup on an alumina:silicic acid column and PAHs were analyzed on a Hewlett-Packard 5890 gas chromatograph equipped with a mass selective detector (Model HP5970) using a DB5-MS (30 m x 0.25 mm i.d.; 0.25 µm film thickness) capillary column. Quantification was performed using the internal standard method, utilizing five deuterated PAHs (100 ng mL^{-1}) spiked into the cleaned up extracts.

Quality Control/Quality Assurance. For air, laboratory and field blanks consisted of pre-extracted PUFs extracted and analyzed as samples. Detection limits were 0.24-8.82 pg m^{-3}, depending on compound. Recoveries were 84-114%. Consequently, reported values were not recovery corrected but were blank corrected using the mean blank value. For dust samples, detection limits ranged from 0.04 to 0.4 ng kg^{-1}, depending on the PAH analyzed and recoveries were greater than 80% for all PAHs (certified reference material, SRM 1649). Instrument performance was estimated using quality control standards after every five samples run. Peaks were only integrated when the signal-to-noise ratio was ≥ 3.

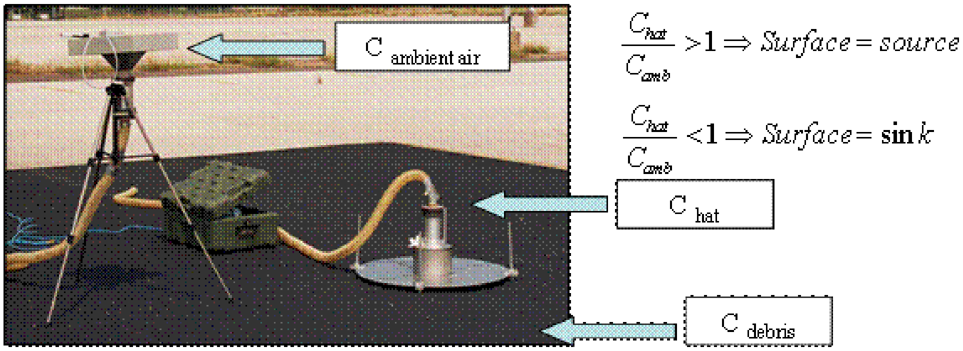

Figure 1: Photo of experimental design during sampling over asphalt-sealed surface at airport (note: unsealed asphalt surface has the lighter shading in the background).

Results and discussion.

PAH gradient between the ambient air and the air layer just above the surface.

PAH concentrations in ambient air (gaseous form only) had a mean of 37.8 and 29.4 ng m^{-3} in downtown Austin, and of 17.0 and 4.23 ng m^{-3} at the former airport, in summer and winter respectively. In summer 2004, SPAH concentrations in the air layer were: coal tar seal (417 ng m^{-3}) >> asphalt seal (49.6 ng m^{-3}) > unsealed asphalt (10.0 ng m^{-3}) at the former airport.Downtown, the currently-used surface showed very high concentrations in the air layer (833 ng m^{-3}). SPAH concentrations in the air layer (0-3 cm) were greater than the paired ambient air sample in all cases (except for the unsealed surface at the airport in summer). Thus, the ratios $C_{hat}/C_{ambient\ air}$ (figure 2) ranged from 0.75 (unsealed) to 24.3 (coal tar) in summer 2004 and from 3.25 (unsealed) to 54.4 (asphalt) in winter 2005. Ratios greater than 1 indicate flux from the surface to the air, the case for most samples collected here.When the ratios $C_{hat}/C_{ambient\ air}$ and the PAH concentrations in surface debris were compared for the various surfaces (figure 2), a strong correlation was found.

These values highlight 3 main results:

- The nature of surfaces plays a major role in the fate of PAHs in urban areas, especially in the revolatilization of organic contaminants to the atmosphere.

- Among the various surfaces, the high ratios for coal tar and asphalt sealants showed that these surfaces are a strong source of PAHs to air.

- The currently-used surfaces showed the highest ratios, highlighting the role of the automobile traffic in the PAH input to the impervious surfaces.

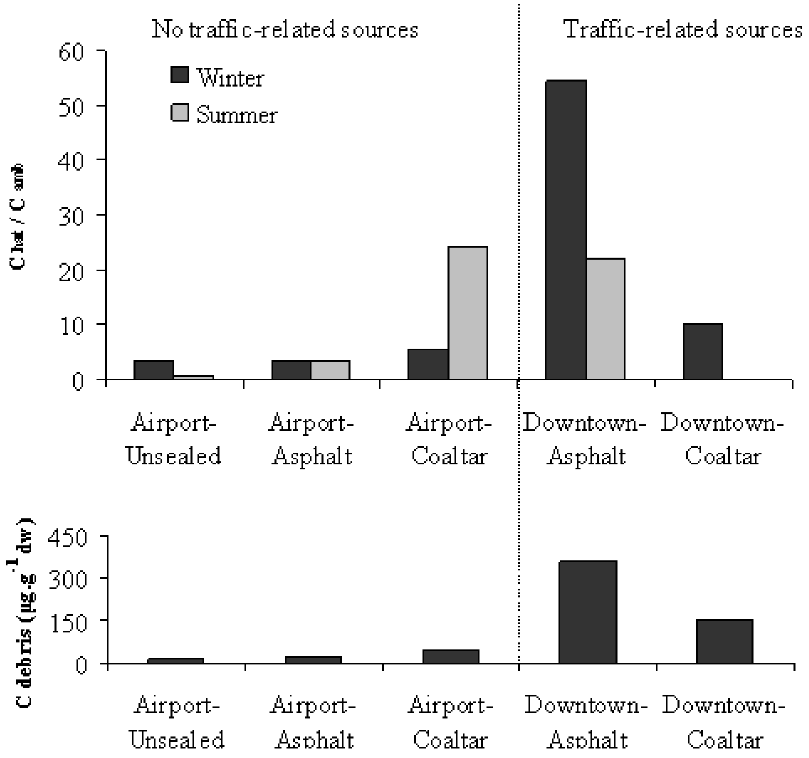

Figure 2: Ratios C_{hat} / $C_{ambient\ air}$ (top) and mean C_{debris} (µg.g^{-1}dw) (bottom) for Σ 8 PAHs.

Surface-air partitioning.

The air-surface exchange of gaseous chemical is a diffusive process, which can be described by a surface-air equilibrium partition coefficient K_{SA}. K_{SA} can be calculated as the concentration in the surface dust divided by the concentration in air. Meijer *et al.* (2003) showed that that the hat-sampler allowed sampling the air close to the equilibrium with soils. Using the same approach, a surface-air quotient Q_{SA} is calculated: $Q_{SA} = C_{debris}/C_{hat}$ (1)

where C_{debris} is the debris concentration (ng m^{-3}) and C_{hat} is the air concentration (ng m^{-3}) in the air layer above the impervious surface. The PAH concentration in debris is expressed on a volume basis (obtained by multiplying the dust concentration in ng g^{-1} dry weight by the density of the dry dust solids), so that K_{SA} and Q_{SA} are dimensionless.

Measured Q_{SA} were compared with octanol-air coefficient K_{OA} that is often used as a surrogate for environmental organic phases. K_{OA} values were calculated at the temperature of the sampling using temperature-dependent expressions [4, 5]. A linear relation was found between these two values for every surface. It is interesting for modelling purposes because K_{OA} is universal and can be measured directly whereas K_{SA} is surface-specific. These results confirmed the hypothesis developed by Hippelein and McLachlan [6], who determined a linear relationship between K_{SA} and K_{OA}, derived from the Karickhoff expression [7]: $K_{SA} = a\, \rho\, \Phi_{OC}\, K_{OA}$ (2)

where Φ_{OC} is the fraction organic carbon in a soil and ρ is the soil solids density (kg L^{-1}).

The predicted K_{SA} values (using equation 2) were plotted against the measured Q_{SA} values (figure 3). The agreement was good with slopes of the log-log relation near 1, confirming the utility of the model.

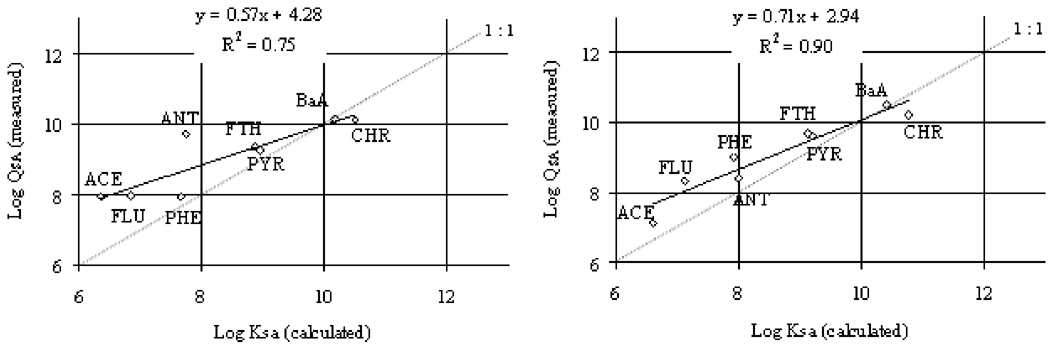

Figure 3: Predicted K_{SA} versus measured Q_{SA} for unsealed surface (left) and coal tar sealant (right)

Conclusion

In summary, a novel gradient sampling approach was successfully applied to several surfaces to investigate source strength of PAHs to ambient air. Surface debris was also analyzed. Large gradients in air were observed for asphalt and coal tar sealants, indicating the source strength of these surfaces. The field data was used to confirm the applicability of a KOA-based model of surface-air exchange that will be incorporated into a multimedia model of PAH fate in urban environments.

Acknowledgments

National Science and Engineering Research Council (NSERC) (Project STP-258056).

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