



Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Volatilization of polycyclic aromatic hydrocarbons from coal-tar-sealed pavement

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ARTICLE INFO

Article history:

Received 5 August 2011

Received in revised form 28 December 2011

Accepted 30 December 2011

Available online xxxxx

Keywords:

Air quality

Sealcoat

Pavement sealant

PAHs

Volatilization

ABSTRACT

Coal-tar-based pavement sealants, a major source of PAHs to urban water bodies, are a potential source of volatile PAHs to the atmosphere. An initial assessment of volatilization of PAHs from coal-tar-sealed pavement is presented here in which we measured summertime gas-phase PAH concentrations 0.03 m and 1.28 m above the pavement surface of seven sealed (six with coal-tar-based sealant and one with asphalt-based sealant) and three unsealed (two asphalt and one concrete) parking lots in central Texas. PAHs also were measured in parking lot dust. The geometric mean concentration of the sum of eight frequently detected PAHs (Σ PAH₈) in the 0.03-m samples above sealed lots (1320 ng m⁻³) during the hottest part of the day was 20 times greater than that above unsealed lots (66.5 ng m⁻³). The geometric mean concentration in the 1.28-m samples above sealed lots (138 ng m⁻³) was five times greater than above unsealed lots (26.0 ng m⁻³). Estimated PAH flux from the sealed lots was 60 times greater than that from unsealed lots (geometric means of 88 and 1.4 μ g m⁻² h⁻¹, respectively). Although the data set presented here is small, the much higher estimated fluxes from sealed pavement than from unsealed pavement indicate that coal-tar-based sealants are emitting PAHs to urban air at high rates compared to other paved surfaces.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely recognized as contaminants of concern in air and airborne particles (Simcik et al., 1997; European Commission, 2001; Bostrom et al., 2002; World Health Organization, 2002). Relatively high concentrations of PAHs in air occur in heavily industrialized urban areas (Simcik et al., 1997; Li et al., 2008), in proximity to PAH sources (Lee et al., 1995; Gallego et al., 2008), and in regions where combustion of coal and wood are common (Liu et al., 2010). The critical endpoint for health-risk evaluation for exposure to PAHs in air is the well-documented carcinogenicity of several PAHs (International Agency for Research on Cancer, 1985). Carcinogenicity has been demonstrated for coal tars and coal-tar-derived products, which contain high levels of PAHs, resulting from exposure by inhalation, ingestion, and direct contact (International Agency for Research on Cancer, 1985; Boffetta et al., 1997). Occupational exposure is, in most industries, by inhalation, and there is a substantial risk of lung, skin, or bladder cancer to workers in industries with “heavy exposure” to PAHs (e.g., coal gasification, coke production, roofing, and road paving) (Boffetta et al., 1997).

Air–soil exchange of semi-volatile organic compounds (SVOCs) has been the subject of research for several decades (Cousins and Mackay, 2001), with the quantification of fluxes of to the atmosphere as a common objective (e.g., Majewski et al., 1989; Harner et al., 2001; Gallego et al., 2008). Volatilization rate (flux) can be estimated using concentrations in air coupled with micrometeorological data (Kurt-Karakus et al., 2006; Scholtz and Bidleman, 2006). Most two- to five-ring PAHs are classified as semi-volatile and volatility decreases with increasing molecular weight (number of rings). The subcooled-liquid-phase vapor pressure, for example, for phenanthrene (PHE; three rings) is 113 mPa and for benzo[ghi]perylene (six rings) is 0.023 mPa (Mackay et al., 1992). Although PAHs in urban air have received considerable scientific attention (Simcik et al., 1997; Gigliotti et al., 2005; Motelay-Massei et al., 2005; Liu et al., 2007; Li et al., 2008), PAH fluxes from pavement to the atmosphere have not.

Coal-tar-based pavement sealants have been documented as an important source of PAH to the urban environment (Mahler et al., 2005, 2010; Van Metre et al., 2009; Watts et al., 2010). Pavement sealant (also known as sealcoat) is widely used on parking lots and driveways in the USA and Canada. Coal-tar-based products are used primarily in the central and eastern USA, and asphalt-based products are used primarily in the western USA. Sealant products are marketed as enhancing the appearance and extending the life

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of the asphalt pavement (e.g., <http://www.sealmaster.net/index.shtml>). One estimate puts annual use of coal-tar-based pavement sealant in the USA at 85 million gallons (320 million liters) (Scoggins et al., 2009). Coal-tar sealants contain extremely high concentrations of PAHs; the mean of the sum of the 16 US Environmental Protection Agency Priority Pollutant PAH (ΣPAH_{16}) was 70,000 mg kg⁻¹ for 12 products (Scoggins et al., 2009).

As early as 2005 it was reported that volatilization from pavement with coal-tar-based sealants might be contributing PAHs to urban air (Motelay-Massei et al., 2005). To date, only one published study has quantified gas-phase PAH concentrations near (although not directly above) sealed pavement, and fluxes were not evaluated (University of New Hampshire Stormwater Center, 2010). That study found that concentrations of PAHs in air 10 m from the edge of the sealed pavement were about 100 times higher than those near unsealed pavement 1 d after sealant application, but that concentrations dropped off rapidly, and by about 1 year after sealant application there was no significant difference in the concentrations.

The objective of this study was to determine if sealcoat is a source of PAHs to urban air. Here we present measurements of PAH concentrations in air directly above sealed and unsealed pavement, and use these measurements to estimate PAH volatilization fluxes from the pavement. The scope of the study is an initial assessment of 10 in-use parking lots in Austin, TX, and its northern suburban communities.

2. Materials and methods

Air above and dust from the surfaces of 10 parking lots in Austin and its northern suburban communities were sampled to determine concentrations of selected PAHs. The surfaces of seven of the parking lots were asphalt pavement with sealant [coal-tar-based sealant (six lots) or asphalt-based sealant (one lot) (determination on the basis of PAH analyses)], and three were unsealed asphalt pavement (two lots) or concrete pavement (one lot). The parking lots and surrounding land were relatively flat and all were in neighborhoods typical of recent urban development in the USA, i.e., composed mostly of single- and multi-family housing, shopping centers, and offices. Most of the parking lots were in areas developed during the past 10–15 years. Parking-lot size ranged from about 700 to 7000 m² (mean of 2600 m²).

The parking lot age and the age of the sealant are not known specifically. Property owners or managers were queried regarding both, but in some cases they did not respond or their recollections proved to be unreliable, as indicated by viewing the time series of aerial images available from Google Earth®. In most cases, evolving wear patterns in the sealant across multiple images made it relatively straightforward to tell when new sealant had been applied. Those images were used to bracket the dates of sealing of the lots to within about 6 months to 2 years (the time between images). One lot was recently sealed (5 months or less), but sealant age on the other six was much older, from about 3.6 to 8 or more years (Supplementary Data, Table S-1).

All parking lots were sampled once in August 2009 from about 2:30 to 4:30 pm, during what is generally the hottest part of the day, as an indication of likely daily summertime maximum concentrations and fluxes (hereinafter, “daytime” samples). Temperatures were measured by recording thermometer at the 1.28-m sampler height and mean temperature during sampling ranged from 36.5 to 43.3 °C. Four sealed lots and one unsealed lot also were sampled once in August 2009 from about 5:00 to 7:00 am, during what is generally the coolest part of the day (mean temperatures during sampling of 24.4–26.0 °C), as an indication of likely summertime daily minimum concentrations and fluxes (hereinafter, “nighttime” samples). Few cars were present on the lots during

sampling; 9 of the 10 lots were at churches with little weekday traffic. Equipment limitations prevented collection of duplicate samples, however, two of the lots were sampled twice, one 1 d and one 1 week following collection of the initial sample.

2.1. Sample collection

The sampling approach of Meijer et al. (2003) was used. Two high-volume air samplers were deployed simultaneously during each sampling period, one near the pavement surface (0.03 m) and one at 1.28 m above the pavement (Supplementary Data Fig. S-1). The near-surface sampler is a 1.3-m-diameter stainless steel disk positioned 0.03 m above the pavement surface and outfitted with a high-volume air pump. The 18-cm diameter air intake is located at the center of the disk facing the pavement so that only air in the 0–3 cm layer is sampled. Because the disk is near the pavement surface, it collects chemicals in the layer of air just above the surface with minimal disturbance (Meijer et al., 2003). At the sampling rate used, the velocity of air entering under the rim of the disk is slow (~ 0.026 m s⁻¹), but the residence time of air under the disk is short (~ 12 s), and the air entering under the outer rim is already in contact with the pavement surface. There is relatively little time for the air passing under the disk to interact with the surface, and the low velocity at the rim limits disturbance of the surface-air layer moving across the larger paved area, which is the air targeted for sampling. In a sense, then, the disk sampler is equivalent to a low-velocity, 3-cm-high (the height of the disk) by 4-m-long (the circumference of the disk) air-sampler intake positioned at the pavement surface. The second high-volume air sampler was mounted on a stand collecting air 1.28 m above the pavement surface with the intake facing upward, and was deployed about 3 m from the near-surface sampler normal to the direction of the wind. Both samplers contained a pre-cleaned glass fiber filter (GFF) mounted in front of two polyurethane foam (PUF) plugs in series; the GFF prevented particles from reaching the PUF. Air was drawn through the GFF/PUF media for 2 h at 0.19 and 0.27 m³ min⁻¹ for the 0.03-m and 1.28-m samplers, respectively. Air flow rate was monitored at 15-min intervals and adjusted if necessary to maintain a constant rate.

The PUF plugs were analyzed for gas-phase concentrations of PAHs. The GFFs (and associated particles) were not analyzed, and in most cases, the GFFs did not contain visible particles. During air sampling, wind speed and direction were recorded about every 10 min, and pavement surface temperature, barometric pressure, and air temperature under the surface sampler and at 1.28 m were recorded about every 30 min. Wind speed was monitored using an anemometer positioned 0.84 m above the pavement. Wind speed and air concentrations of PAHs were used to calculate PAH volatilization flux. Upwind fetch averaged 33 m but, because some lots were relatively small and irregularly shaped, was as short as 10 m. At the end of each sampling period, a dust sample was collected from the pavement surface, near where the air samples were taken, using an ASTM International approved vacuum for settled dust following methods described in Mahler et al. (2010). Dust samples were sieved (0.5 mm) to remove coarse material and the fine material was retained for chemical analysis.

2.2. Analytical

PUF plugs and GFFs were pre-cleaned at the US Geological Survey National Water Quality Laboratory (NWQL) in Denver, Colorado. The 90-mm-diameter GFFs (type A/E, Pall Corp.) were cleaned by baking at 450 °C, cooled in a desiccator for at least 2 h, weighed to the nearest 0.2 mg, wrapped in baked aluminum foil, and stored in resealable polyethylene bags. PUF plugs were cleaned by rinsing with tap and deionized water and then extracting for at least 12 h in

a Soxhlet apparatus with acetone followed by 50% acetone in hexane. The plugs were dried in a vacuum oven at 40 °C for at least 48 h and stored in pre-baked (450 °C for at least 2 h) 500-mL glass jars with Teflon[®]-lined lids.

Following field sample collection, GFFs were re-wrapped in foil and bagged, and PUF plugs were replaced in the glass jars. GFFs, PUF plugs, and pavement dust samples were stored at –15 °C pending analysis. At the NWQL, the dust samples were fortified with surrogate compounds (nitrobenzene-*d*₅, 2-fluorobiphenyl, and terphenyl-*d*₁₄), extracted by pressurized solvent extraction, and processed and analyzed by gas chromatography/mass spectrometry (GC/MS), as detailed in Zaugg et al. (2006). Top and bottom PUF plugs were extracted and analyzed together to provide complete collection of PAH (You and Bidleman, 1984; Mendez et al., 2008). PUF plugs were fortified with the same surrogate compounds as dust samples and extracted with 300 mL of 50% acetone in hexane for at least 12 h in a Soxhlet apparatus. Extracts from PUF samples were further processed, including through combined C-18/Florisil solid-phase extraction cleanup, and analyzed by GC/MS operated in combined full scan/selected-ion-monitoring mode for selected PAH using procedures described in Mendez et al. (2008) that included multi-level calibration and quantification relative to perdeuterated PAH injection internal standards. Mass of PAH in the PUFs was converted to concentration (ng m⁻³) on the basis of the volume of air sampled. Extract dilution was performed as necessary to ensure quantitative determination within the calibration range.

Laboratory blank and spike samples were included for quality control with each set of ~10 environmental samples (three sets total) and were prepared using two pre-cleaned PUF plugs for PUF samples and baked reagent sand for dust samples. Air-sampler equipment blanks for the 0.03-m and 1.28-m samplers produced no detections above the laboratory-blank censoring threshold (set at five times the laboratory blank levels). PAH recovery averaged 95 ± 14% (mean and standard deviation) from air-method spikes. Several PAHs were detected at low levels (maximum of 0.55 ng m⁻³ for benzo[*e*]pyrene) in the air-method laboratory blanks). However, carry-over contamination in the GC was not indicated because the blank was the first sample in the sample set to be analyzed (subsequent samples were analyzed from expected lowest to highest concentration). The four high molecular-weight PAHs detected in blanks (benzo[*e*]pyrene included) were not detected in the majority of environmental samples, indicating laboratory contamination of environmental samples likely did not occur. An important consideration in evaluating the potential effect of blank contamination on the interpretation of the environmental data is that concentrations and, therefore, estimated fluxes were dominated by the lower molecular weight 3- and 4-ring PAHs, particularly PHE, fluoranthene (FLU), and pyrene (PY). The highest concentration in a blank for PHE, FLU, or PY relative to the associated environmental samples was 5.3%, and most were less than 1% of the environmental concentration. We therefore conclude that blank contamination did not affect the interpretation of PAH concentrations or fluxes reported here.

Most PAHs were not detected or detected at very low concentrations in the dust method laboratory blanks; the highest detection was for dibenzo[*a,h*]anthracene at 0.00345 mg kg⁻¹. PAH recovery averaged 45 ± 8% from dust method spikes; the recoveries, although lower than obtained during method validation (Zaugg et al., 2006), were mostly within control limits set by the NWQL at three times F-pseudostigma of analyte recoveries from multi-year laboratory spikes. Surrogate recoveries indicate sample-specific procedural performance only, and were uniformly low for many dust samples compared with method-validation results (Zaugg et al., 2006), indicating some low bias in PAH concentrations for those dust samples. No surrogate or spike-sample recovery or blank-concentration corrections were applied to the sample data.

Some values were qualified with an “E” remark, indicating estimated, for one of several reasons, most commonly because the concentration was below the lowest calibration standard or was below the method’s applied reporting level set at least two times greater than the estimated method detection level (Zaugg et al., 2006; Mendez et al., 2008). Estimated concentrations were treated as detections for interpretations.

2.3. Flux estimation

The transfer of any conservative entity (water vapor, heat, momentum, or chemical gases) from an evaporating surface to the atmosphere is governed primarily by the atmospheric turbulence generated by wind moving over that surface. These vertical fluxes (Q_z) can be expressed by a generalized flux gradient equation:

$$Q_z = -K_z(\partial c/\partial z) \quad (1)$$

where K_z is the transfer coefficient of eddy diffusivity, an unknown function of atmospheric turbulence and measurement height (z) that must be empirically determined, and $\partial c/\partial z$ is the gas-phase concentration gradient from the surface. By convention, the negative sign indicates movement away from the surface.

A wide variety of micrometeorologically based volatilization flux estimation methods are based on Eq. (1) (Majewski, 1999). These techniques have been developed by the agricultural meteorology and atmospheric science communities for estimating fluxes of momentum, heat, water vapor, CO₂, and NH₃, and have been successfully applied to the estimation of volatilization of pesticides (Majewski et al., 1990; Scholtz et al., 2002b; Kurt-Karakus et al., 2006). We estimated Q_z using the method described by Scholtz et al. (2002b) (hereinafter the Scholtz method). The Scholtz method is a dynamic advection–diffusion method that estimates volatilization fluxes for both daytime and nighttime and corrects for changing atmospheric stability (Scholtz et al., 2002b). It can use on-site meteorological measurements or those from a nearby climate station (on-site measurements were used here). This method also uses the physical/chemical properties of each of the measured PAH compounds, including their molecular diffusivities, to adjust the mass transfer coefficient (K). This method has been used successfully to simulate the soil–atmosphere exchange of select pesticides and to predict their concentrations in air above treated fields under variable meteorological conditions (Scholtz et al., 2002a).

As a check on the reasonableness of results from the Scholtz method, the Thornthwaite–Holzman equation (hereinafter the T–H method) (Thornthwaite and Holzman, 1939) also was used to estimate volatilization fluxes. The T–H method does not correct for changing atmospheric stability conditions (Majewski et al., 1989). Both methods rely on horizontal wind speed to estimate K_z (Eq. (1)). For the Scholtz method, mean wind speed in the boundary layer (taken here as 0–3 m) is needed and for the T–H method, wind speed at the heights where PAH concentration is measured is needed. Wind speed was measured at 0.84 m and an exponential wind profile above the pavement surface ($\bar{u} = 0$ at the surface) was assumed (Swinbank, 1964). This profile was used to estimate mean wind speed and wind speed at the air sampling heights. Details of the application of both methods are presented in Supplementary Data and parameters used to determine fluxes by the Scholtz method are given in Supplementary Data, Table S-1.

The accurate estimation of volatilization flux requires that certain field conditions are met. These include a spatially uniform surface area with the area surrounding the study plot of similar surface characteristics and spatially uniform surface–source strength. Both of these conditions require a minimum upwind–fetch to measurement–height ratio to ensure that the boundary layer has the same characteristic as the adjacent underlying

surface and that the fluxes are constant with height (Majewski, 1999). Because of the relatively short upwind fetch and complex urban terrain surrounding the parking lots, the field conditions ideal for volatilization flux measurements at each parking lot most likely were not met. Depending on the assumptions used and the measured wind speed, the necessary upwind fetch for the 1.28-m sampler is on the order of 50 m or more, greater than the fetch for some of the lots sampled (Supplementary Data, Table S-1). If the surrounding land surface is emitting PAHs at a lower rate than the parking lot, an upwind fetch shorter than ideal will result in a lower PAH concentration at 1.28 m than if the parking lot were larger, which in turn will result in a steeper air gradient and larger estimated fluxes. However, in the case of the sealed lots sampled here, the effect on PAH flux estimates of a larger-than-measured 1.28-m concentration is small, because the 0.03-m PAH concentrations are much larger than the 1.28-m concentrations (mean ratio of 11.4 ± 4.9) and the gradient is based on the difference between the two. Even if the actual PAH concentration in air at 1.28 m above the sealed lots were double that measured, it would reduce the estimated total PAH flux (Scholtz method) by an average of only 12%. Although total uncertainty of the flux estimates is not known, we think they provide a reasonable first estimate of flux from sealed pavement and of the relative differences in volatilization losses from sealed and unsealed pavement.

3. Results

3.1. PAH concentrations

Eight of the 19 PAHs measured were detected frequently ($\geq 68\%$) in the air samples: PHE, anthracene (AN), 4,5-methylphenanthrene (45MP), 1-methylphenanthrene (1MP), FLU, PY, chrysene (CHY), and benzo[b]fluoranthene (Bbf) (together, ΣPAH_8 ; non-detections treated as zeros) (Supplementary Data Table S-2). Detection rates for the other 11 PAH ranged from 0% (dibenzo[a,h]anthracene) to 50% (benzo[k]fluoranthene). Daytime ΣPAH_8 concentrations at both heights were significantly greater in air above sealed lots than above unsealed lots (Mann–Whitney test, p -values ≤ 0.026). The geometric mean ΣPAH_8 concentration for the daytime samples 0.03 m above sealed lots of 1320 ng m^{-3} (range of $322\text{--}4080 \text{ ng m}^{-3}$) was 20 times greater than the geometric mean for daytime samples 0.03 m above unsealed lots of 66.5 ng m^{-3} (range of $40.4\text{--}160 \text{ ng m}^{-3}$) (Fig. 1). The geometric mean ΣPAH_8 concentration in air 1.28 m above the sealed lots of 138 ng m^{-3} (range of $28.7\text{--}335 \text{ ng m}^{-3}$) was five times greater than that above unsealed lots (26.0 ng m^{-3} , range of $19.8\text{--}31.1 \text{ ng m}^{-3}$).

Concentrations among PAHs had a wide range in any single sample, with PHE, FLU, and PY dominating and accounting for $91 \pm 6\%$ of ΣPAH_8 across all samples; these three PAHs were detected in all samples. Concentrations of higher molecular-weight PAHs were proportionally greater in samples from sealed lots than unsealed lots. The mean ratio of PHE + AN (three rings) to FLU + PY (four rings) was 0.83 ± 0.27 for samples from sealed lots and was 2.1 ± 0.52 for samples from unsealed lots, indicating a more pyrogenic (combustion) PAH signature (Hites et al., 1980) in the air above the sealed lots. Daytime concentrations of individual PAHs in near-surface samples were, on average, 2.8 times greater than nighttime concentrations for the same sites, but this ratio (daytime/nighttime) ranged widely (0.32–30).

Concentrations of PAHs in pavement dust followed patterns reported previously (Van Metre et al., 2009; Mahler et al., 2010), with concentrations from coal-tar-sealed lots (ΣPAH_8 range $1200\text{--}7100 \text{ mg kg}^{-1}$, ΣPAH_{16} range $1700\text{--}10,600 \text{ mg kg}^{-1}$) about 1000 times greater than concentrations in dust from unsealed lots (ΣPAH_8 range $0.47\text{--}6.3 \text{ mg kg}^{-1}$, ΣPAH_{16} range $0.60\text{--}9.2 \text{ mg kg}^{-1}$)

(Fig. 2; Supplementary Data Table S-3). The low laboratory surrogate recoveries (mean of 45%) indicate that the actual concentrations of PAHs in dust might be higher than reported. Relatively low PAH concentrations in the dust from one of the seven sealed lots sampled (ΣPAH_8 of 29 mg kg^{-1}) indicated that the sealant on that lot was an asphalt-based product. Total PAH concentrations (ΣPAH_{16}) in coal-tar products are about $70,000 \text{ mg kg}^{-1}$ and in asphalt products are about 50 mg kg^{-1} (Scoggins et al., 2009).

The age of sealant on the parking lots did not correlate to 0.03-m-air PAH concentration, dust PAH concentration, or PAH flux (Pearson correlation, all p -values >0.4). Mahler et al. (2005) reported a similar lack of relation between sealant age and PAH concentrations in pavement dust. The lack of a relation between air PAH concentrations and sealant age might be because sealant on the six coal-tar-sealed lots was relatively old ($\sim 3.6\text{--}8$ or more years; sealant on the asphalt-sealed lot was <5 months old), and the period of a rapid decrease in volatilization losses expected as the sealant dries and ages might have long since passed. For older sealed surfaces, large differences between PAH concentrations in the products applied may mask any remaining relation to sealant age, as PAH concentration varies widely among products (Scoggins et al., 2009). The lack of a relation between age of sealant and dust PAH concentrations might be because of the range of PAH concentrations in the products as well as variability in wear rates and the amount of dilution by soils and other low-PAH concentration materials.

Vertical air-concentration gradients were computed by dividing the difference in PAH concentrations by the vertical distance between sampling points (1.25 m). Gradients for individual PAH varied greatly within and between samples, largely as a function of the near-surface-sample concentration. All of the gradients measured (detection at both sampler heights) were positive upward (higher concentration nearer to the pavement), indicating volatilization. The largest gradients were for PHE, FLU, and PY in daytime samples from sealed lots, ranging, for example, from 74 to $1250 \text{ ng m}^{-3} \text{ m}^{-1}$ for PHE. In contrast, the daytime gradients for PHE from unsealed lots were $4.5\text{--}38 \text{ ng m}^{-3} \text{ m}^{-1}$. Daytime gradients for PHE, FLU, and PY were significantly greater above sealed lots than above unsealed lots (Mann–Whitney test, p -values ≤ 0.016). The ratio of daytime to nighttime gradients averaged $2.4 (\pm 1.6)$.

3.2. Fluxes

The Scholtz and the non-stability corrected T–H methods produced similar estimates of volatilization fluxes. The relative percent differences were about $\pm 10\%$ for three-ring PAH and trended to somewhat higher estimates for the T–H method relative to the Scholtz method for four- and five-ring PAH (generally 0–20% greater for T–H method with a maximum difference of 28% for BbF). Because the Scholtz method takes into account the molecular diffusivity of the PAHs, thereby adjusting for physical/chemical characteristics of each compound, and because we did not apply the atmospheric stability correction to the Thornthwaite–Holzman method (Majewski et al., 1989), the Scholtz method is likely to be more accurate, and further discussion of results is based on results from this method.

Fluxes of the sum of the eight frequently detected PAHs ($Q_{z,8}$) ranged from $0.36 \mu\text{g m}^{-2} \text{ h}^{-1}$ from an unsealed lot during nighttime to $240 \mu\text{g m}^{-2} \text{ h}^{-1}$ from a sealed lot during daytime (Supplementary Data Table S-4). The geometric mean $Q_{z,8}$ from sealed lots during daytime ($88 \mu\text{g m}^{-2} \text{ h}^{-1}$, range $30\text{--}240 \mu\text{g m}^{-2} \text{ h}^{-1}$) was 60 times greater than from unsealed lots during daytime ($1.4 \mu\text{g m}^{-2} \text{ h}^{-1}$, range $0.57\text{--}8.4 \mu\text{g m}^{-2} \text{ h}^{-1}$) (Fig. 3). The geometric mean $Q_{z,8}$ from sealed lots during daytime was five times greater than from the sealed lots during nighttime ($17 \mu\text{g m}^{-2} \text{ h}^{-1}$, range

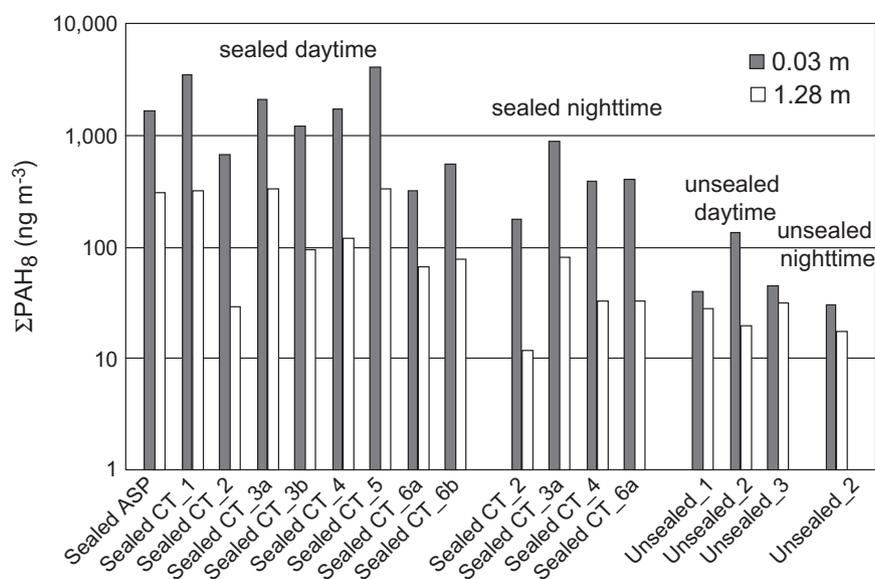


Fig. 1. Concentrations of ΣPAH_8 in air samples measured 0.03 m and 1.28 m above the pavement surface during the daytime (about 2:30–4:30 pm) and nighttime (about 5:00–7:00 am). CT in a sample name indicates coal-tar-based sealant and ASP indicates asphalt-based sealant.

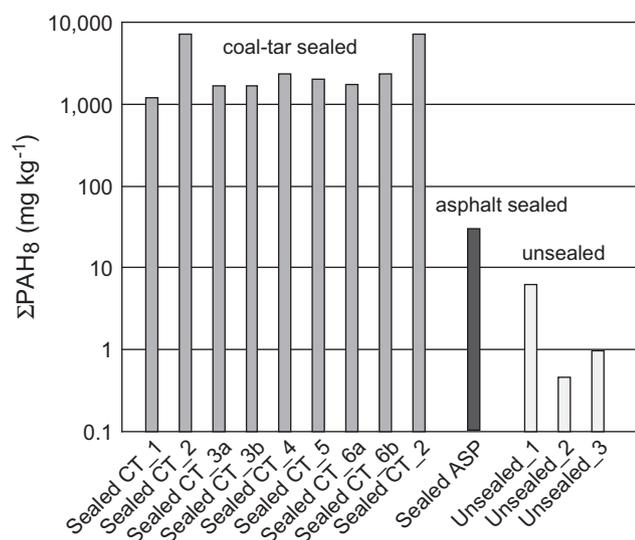


Fig. 2. Concentrations of ΣPAH_8 in dust samples from coal-tar sealed, asphalt sealed, and unsealed parking lots.

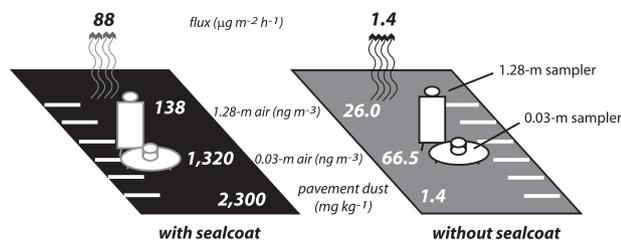


Fig. 3. Geometric mean daytime concentrations and fluxes of ΣPAH_8 for parking lots with and without pavement sealcoat.

$9.2\text{--}24 \mu\text{g m}^{-2} \text{h}^{-1}$). All differences were statistically significant (Mann–Whitney test, p -values ≤ 0.016).

PAH fluxes were comparable for the asphalt-sealed lot and the coal-tar-sealed lots, despite much lower PAH concentrations in dust from the asphalt-sealed lot relative to the six coal-tar-sealed

lots. The lack of a similar relation between dust and air concentrations above the different sealant types might be because the asphalt sealant was freshly applied (<5 months), whereas the coal-tar sealant was 3.6–8 or more years old. Higher volatilization rates soon after application are expected from either sealant product type (Gallego et al., 2008; University of New Hampshire Stormwater Center, 2010). The exact date of application of the asphalt-based sealant is not known, but field notes state that the coating was “fresh sealcoat” that was “soft and sticky to scrape”, suggesting application during the previous days to weeks.

4. Discussion

The results indicate that pavement treated with coal-tar-based sealant, and perhaps freshly applied asphalt sealant as well, is a much stronger source of PAHs to air than unsealed pavement, with about 60 times greater PAH flux (geometric mean estimated $Q_{Z,8}$). The sealant on the coal-tar-sealed parking lots sampled here was relatively old (3.6–8 or more years); an even larger difference in PAH fluxes would likely be measured for more recently sealed parking lots, because volatilization fluxes are expected to decrease over time after application. Does the high rate of volatilization of PAHs from sealed pavement mean that sealant is an important source of PAHs to urban air? This question can be evaluated in the context of PAH concentrations in air reported for other areas. PAH concentrations in air above sealed lots are high relative to concentrations in air reported in the literature for other urban and non-urban areas (Table 1). For example, concentrations of PHE in air 1.28 m above sealed lots were about four times higher than in air samples at urban/industrial sites in New Jersey, USA, and Toronto, Canada, and were comparable to those reported for Chicago, IL (Simcik et al., 1997), northern China (Liu et al., 2007), and London and Manchester, England (Halsall et al., 1993). The PHE concentrations are a little less than one-half the PHE concentrations in air in the industrial city of Guangzhou, China (Li et al., 2008), and less than one-tenth the concentration in the industrial city of Hangzhou, near Shanghai, China (Liu et al., 2001) (Table 1). Concentrations of PY above sealed lots exceeded those measured in urban air in other studies: they were 10–15 times higher than those measured for all of the cities listed in Table 1 except Guangzhou and Hangzhou, even though concentrations reported

Table 1
Concentrations of PAHs in air (ng m^{-3}) from various studies. Concentrations for this study are mean values for daytime samples only. Concentrations from (Motelay-Massei et al., 2005) and this study are for the gas-phase, and all other studies are the sum of gas- and particle-phases. PHE = phenanthrene, PY = pyrene, BaP = benzo[a]pyrene, nd = non-detect, sd = standard deviation.

Location	Setting/season	PHE		PY		BaP		Citation
		Mean	Range	Mean	Range	Mean	Range	
Jersey City, NJ, USA	Urban/industrial	15	(0.19–32)	2.1	(0.018–10)	0.19	(0.012–1.4)	Gigliotti et al. (2005)
Camden, NJ, USA	Urban/industrial	15	(0.66–98)	1.6	(0.062–4.6)	0.14	(0.027–0.90)	Gigliotti et al. (2005)
New Brunswick, NJ, USA	Suburban	8.4	(0.71–21)	0.85	(0.027–3.0)	0.1	(0–0.37)	Gigliotti et al. (2005)
Sandy Hook, NJ, USA	Coastal/rural	4.9	(0.078–16)	0.52	(0.008–2.7)	0.038	(0–0.23)	Gigliotti et al. (2005)
Alloway Creek, NJ, USA	Coastal/rural	3.5	(0.043–10)	0.4	(0.037–1.7)	0.032	(0.0017–0.12)	Gigliotti et al. (2005)
Pinelands, NJ, USA	Rural	2.3	(0.62–17)	0.21	(0.035–1.2)	0.031	(0.003–0.26)	Gigliotti et al. (2005)
Chicago, IL, USA	Urban/industrial	68	(8.6–250)	14	(1.8–100)	3.1	(1.9–32)	Simcik et al. (1997)
Lake Michigan, USA	Rural	10	(0.24–34)	1.8	(0.052–8.0)	0.18	(0.008–0.85)	Simcik et al. (1997)
Toronto, Canada	Urban	24.3		1.28		0.06		Motelay-Massei et al. (2005)
Toronto, Canada	Suburban	8.3		0.34		0.01		Motelay-Massei et al. (2005)
Ontario, Canada	Rural	4.63		0.19		<.005		Motelay-Massei et al. (2005)
London, England	Urban/summer	100.7		6.2		0.3		Halsall et al. (1993)
Manchester, England	Urban/summer	73.5		10.4		0.6		Halsall et al. (1993)
Northern China	Urban and rural	57	(4.1–215)	2.3	(nd–8.5)	nd		Liu et al. (2007)
Guangzhou, China	Urban/industrial	186	± 158 (sd)	20.6	± 18.6 (sd)	nd		Li et al. (2008)
Hangzhou, China	Urban	860	(98–2140)	210	(53–466)	114	(20–233)	Liu et al. (2001)
1.28-m air sealed lots	Suburban	78	(11–150)	30	(4.8–61)	<1	(<1–0.29)	This study
1.28-m air unsealed lots	Suburban	15	(11–20)	3.4	(2.9–4.2)	<1	(<1)	This study
0.03-m air sealed lots	Suburban	660	(120–1700)	300	(50–680)	1.27 ^a	(<1–2.9)	This study
0.03-m air unsealed lots	Suburban	36	(20–58)	13	(5.1–27)	<1	(<1–2.0)	This study

^a Eight of nine detections, mean estimated using the Kaplan–Meier approach (Helsel, 2009).

here are for the gas phase only and concentrations reported by several of the other studies are for gas and particle phases combined.

Somewhat higher PAH concentrations above parking lots relative to concentrations reported in the literature might be the result of the close proximity of these samples to a source (pavement sealant). Of the studies listed in Table 1, two appear to have been from near street-level sources (Liu et al., 2001, 2007), two in parks or on rooftops in urban areas that are at least tens of meters from specific sources (Simcik et al., 1997; Li et al., 2008), and the others do not provide sufficient detail to know. The concentrations of PAHs in Chicago air have been characterized as very high (Cotham and Bidleman, 1995; Simcik et al., 1997; Gigliotti et al., 2005; Sun et al., 2006) and attributed, in decreasing order of importance, to coal combustion, natural gas combustion, coke ovens, and vehicle emissions (Simcik et al., 1999). In northern China, both urban and rural areas have high concentrations of PAHs primarily attributed to the wide-spread domestic burning of coal and biomass (Liu et al., 2007). However, the sites sampled in this study were all in suburban neighborhoods of Austin, a city with almost no heavy industry, and no coal-fired power plants or oil refineries. PAH concentrations 0.03 m above sealed lots were much higher than the concentrations reported for any of the studies listed in Table 1, with the exception of Hangzhou.

Comparison of PAH concentrations measured in this study to health-risk guidelines for PAHs provides additional context to the results. According to the World Health Organization (WHO), the concentrations of benzo[a]pyrene (BaP), as an indicator of the total PAH content, in air producing excess lifetime cancer risks of 1/10,000 and 1/100,000 are 1.2 and 0.12 ng m^{-3} (World Health Organization, 2002). This level of risk is based on analyses of risk for cancer from airborne mixtures of PAHs to which coke-oven workers are exposed and is for gas and particle phases combined. On the basis of the WHO analysis and available control strategies, a European Union (EU) panel proposed a guideline of 0.5 ng m^{-3} BaP (European Commission, 2001). Bostrom et al. (2002), proposed a guideline of 0.1 ng m^{-3} for BaP and 2.0 ng m^{-3} for FLU, because FLU has a carcinogenic potency about 20 times less than that of BaP. Some PAH concentrations measured in samples collected at 1.28 m in this study exceed one or more of these health-based guidelines. BaP was detected (although both values

were identified as estimated because they were below the method reporting level) in 2 of 9 daytime 1.28-m samples from sealed lots (0.16 and 0.29 ng m^{-3}) and was not detected in the three daytime 1.28-m samples from unsealed lots. These detections are below the BaP guidelines proposed by the WHO and EU and above the BaP guideline proposed by Bostrom et al. (2002). FLU was detected in all samples collected in this study. The geometric mean concentration of FLU in daytime 1.28-m samples from sealed lots was 48.1 ng m^{-3} (range 10.7–125 ng m^{-3}), 24 times the guideline proposed by Bostrom et al. (2002). The daytime 1.28-m sample concentration from unsealed lots (4.3 ng m^{-3} ; range 3.2–5.6 ng m^{-3}) was about twice the proposed guideline. Exposure could be limited, however, by the relatively short length of time spent on or near sealed pavement for most people and by presumably lower concentrations in air during cooler times of the year. These health risk guidelines are for total PAHs (gas and particle phases); higher molecular weight PAHs (including BaP, and, to somewhat lesser extent, FLU) occur predominantly in the particle phase (Simcik et al., 1999). In this study only the gas phase was measured, thus, concentrations of BaP and FLU reported here represent lower-limit estimates of total concentrations in air.

The data set presented here is small and leaves many questions unanswered, for example, what are air concentrations and volatilization rates during and immediately after sealant is applied, and how do they vary seasonally? Much higher estimated PAH fluxes from sealed pavement than from unsealed pavement, however, indicate that coal-tar-based sealants, and possibly recently-applied asphalt-based sealants, might be important sources of PAHs to urban air.

Acknowledgments

We thank Tom Harner, Environment Canada, for the generous loan of air sampling equipment and for advice on data interpretation. We thank Stewart Rounds and Alisa Mast, US Geological Survey, for their many helpful comments. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the US Government. We dedicate this paper to the memory of our friend and colleague Anne Motelay, University of Rouen, France.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemosphere.2011.12.072](https://doi.org/10.1016/j.chemosphere.2011.12.072).

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