

PAH volatilization following application of coal-tar-based pavement sealant

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ABSTRACT

Coal-tar-based pavement sealants, a major source of PAHs to urban water bodies, have recently been identified as a source of volatile PAHs to the atmosphere. We tracked the volatilization of PAHs for 1 year after application of a coal-tar-based pavement sealant by measuring gas-phase PAH concentrations above the pavement surface and solid-phase PAH concentrations in sealant scraped from the surface. Gas-phase concentrations at two heights (0.03 and 1.28 m) and wind speed were used to estimate volatilization flux. The sum of the concentrations of eight frequently detected PAHs (ΣPAH_8) in the 0.03-m sample 1.6 h after application ($297,000 \text{ ng m}^{-3}$) was about 5000 times greater than that previously reported for the same height above unsealed parking lots (66 ng m^{-3}). Flux at 1.6 h after application was estimated at $45,000 \mu\text{g m}^{-2} \text{ h}^{-1}$ and decreased rapidly during the 45 days after application to $160 \mu\text{g m}^{-2} \text{ h}^{-1}$. Loss of PAHs from the adhered sealant also was rapid, with about a 50% decrease in solid-phase ΣPAH_8 concentration over the 45 days after application. There was general agreement, given the uncertainties, in the estimated mass of ΣPAH_8 lost to the atmosphere on the basis of air sampling ($2\text{--}3 \text{ g m}^{-2}$) and adhered sealant sampling (6 g m^{-2}) during the first 16 days after application, translating to a loss to the atmosphere of one-quarter to one-half of the PAHs in the sealcoat product. Combining the estimated mass of ΣPAH_8 released to the atmosphere with a national-use estimate of coal-tar-based sealant suggests that PAH emissions from new coal-tar-based sealcoat applications each year ($\sim 1000 \text{ Mg}$) are larger than annual vehicle emissions of PAHs for the United States.

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1. Introduction

Coal-tar-based pavement sealant has been documented as an important source of polycyclic aromatic hydrocarbons (PAHs) in the urban environment (Mahler et al., 2005, 2010; Van Metre et al., 2009; Watts et al., 2010). Coal-tar sealant products contain extremely high concentrations of PAHs: the mean of the sum of the 16 U.S. Environmental Protection Agency Priority Pollutant PAH (ΣPAH_{16}) (<http://water.epa.gov/scitech/methods/cwa/pollutants.cfm>) was $70,000 \text{ mg kg}^{-1}$ for 12 products (Scoggins et al., 2009). Pavement sealant is the black, shiny substance sprayed or painted on the asphalt pavement of many parking lots, driveways, and even some playgrounds in an attempt to beautify and protect the underlying asphalt. Coal-tar-based pavement sealant (also known as sealcoat) is widely used in the central and eastern U. S. and, to

a lesser extent, in the western U. S., where use of asphalt-based sealant products is more common. An estimated 320 million liters (85 million gallons) of coal-tar-based sealant use annually in the United States has been reported (Scoggins et al., 2009).

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 traffic sources (Lee et al., 1995), and in regions where combustion of coal and wood are common (Liu et al., 2010). As early as 2005 it was hypothesized that volatilization from pavement with coal-tar-based sealants might be contributing PAHs to urban air (Motelay-Massei et al., 2005). A recent study reported PAH concentrations in air over sealed and unsealed parking lot pavement in Austin, Texas, USA, and PAH fluxes from that pavement (Van Metre et al., in press). Using measured air concentrations at two heights above seven sealed and three unsealed parking lots, Van Metre et al. (in press) estimated that the geometric mean flux

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of the sum of eight PAHs was about 60 times greater over sealed lots ($88 \mu\text{g m}^{-2} \text{h}^{-1}$) than over unsealed lots ($1.4 \mu\text{g m}^{-2} \text{h}^{-1}$). That study, however, did not address the question of emissions during and soon after sealcoat application or how the volatilization rate might change with time. The objective of this study was to determine how PAH concentrations in air and volatilization fluxes vary with time beginning soon after sealant application.

2. Methods

To evaluate PAH concentrations and fluxes from newly applied coal-tar-based pavement sealant, coal-tar-based pavement sealant was commercially applied to a $16 \times 16\text{-m}$ section of parking lot at the University of Texas J.J. Pickle Research Campus in Austin. The area sealed is relatively flat and is surrounded on three sides by asphalt pavement extending 25 m or more before encountering the nearest building (east side) or pavement edge and on the fourth side by a flat grassy area (see [Supplementary Data](#) for an aerial image of the site and photographs of sealant application and air samplers). Traffic frequency on the parking lot is not known, but is assumed to be relatively low on the basis of the location and observations made during sampling. Two coats of Tarconite (Neyra Industries, Inc., Cincinnati, Ohio), a refined coal-tar-emulsion pavement sealer, were applied on September 16, 2009, by a commercial applicator following industry norms. The Material Safety Data Sheet (MSDS) states that the product is <34% refined coal-tar by weight (see [Supplementary Data](#)). The first coat was applied from 2:05 to 2:10 pm and the second from 3:15 to 3:30 pm. The first sample was collected starting at 4:51 pm, when the surface was dry to the touch, and the samplers were run for 29 min. The sample time was centered at 95 min (1.6 h) after the end of application. The samplers were placed near the center of the sealed area normal to wind direction and 10 m downwind from the upwind edge. The second sample was collected the day after application from 2:42 to 3:42 pm. Subsequent samples were collected during the afternoon 5, 16, 45, 149, 232, 328, and 376 days after application. A replicate sample was collected on day 16. A sample of adhered sealant was collected for PAH analysis coincident with most air samples by scraping sealant from the surface.

2.1. Sample collection

The sampling approach of [Meijer et al. \(2003\)](#) was used. Briefly, two high-volume air samplers were deployed simultaneously during each sampling period, one near the pavement surface (0.03 m) and one 1.28 m above the pavement. The near-surface sampler is a 1.3-m-diameter stainless-steel disk 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 ($\sim 0.026 \text{ m s}^{-1}$), but the residence time of air under the disk is short ($\sim 12 \text{ s}$), and the air entering under the outer rim already is 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 (referred to as the front and back PUFs); the GFF prevented particles from reaching the PUFs. PUFs and GFFs were pre-cleaned at the U.S. Geological Survey National Water Quality Laboratory (NWQL) in Denver, Colo. The 90-mm-diameter GFFs (type A/E, Pall Corp.) were cleaned by baking at $450 \text{ }^\circ\text{C}$, 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 them 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 $40 \text{ }^\circ\text{C}$ for at least 48 h and stored in 500-mL glass jars with Teflon[®]-lined lids.

To collect a sample, air was drawn through the GFF/PUF media in the 0.03-m and 1.28-m samplers at rates of 0.19 and $0.27 \text{ m}^3 \text{ min}^{-1}$, respectively. Sampling duration ranged from 29 min (the first sample) to 2 h. Air flow rate was monitored at 15-min, or shorter, intervals and adjusted if necessary to maintain a constant rate. Wind speed was monitored during air sampling using a recording anemometer positioned 0.60 m above the pavement surface near the samplers. Pavement surface temperature, barometric pressure, and air temperature under the surface sampler and at 1.28 m were recorded about every 10 min. Wind speed and air concentrations of PAHs were used to calculate volatilization rate (flux). Because of the small size of the sealed plot, upwind fetch was about 10 m over the sealed surface. Following collection, GFFs were re-wrapped in foil and bagged, and PUF plugs were replaced in their original glass jars. GFFs, PUF plugs, and samples of sealant scraped from the pavement were stored at $-15 \text{ }^\circ\text{C}$ pending analysis. The PUF plugs were analyzed for gas-phase concentrations of PAHs. The GFFs (and associated particles) were not analyzed, and visible particles were collected by the GFFs in only a few cases.

Total PAH losses (volatilization and degradation) from the adhered sealant were assessed by analyzing the product and samples of sealant scraped from the pavement surface coincident with each air sampling. For analysis of PAHs in the product, the product (obtained during application) was painted onto cleaned glass, dried indoors in the dark for 3 days, and scraped from the glass. Samples of adhered sealant were collected by scraping it from the pavement surface using a stainless-steel spatula. Care was taken during scraping to sample the adhered sealant layer without collecting the underlying asphalt.

2.2. Analytical

At the NWQL, the sealant samples (product and scrapings) 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) ([Zaugg et al., 2006](#)). Thirty-two PAH compounds were quantified ([Table 1](#)). For the analysis of air samples (air-method), top and bottom PUF plugs were extracted and analyzed together for most samples to provide complete collection of these PAH compounds ([Mendez et al., 2008](#); [You and Bidleman, 1984](#)). PUF plugs were fortified with the same surrogate compounds as sealant samples and extracted with 300 mL of 50% acetone in hexane for at least 12 h in a Soxhlet apparatus. Extracts from PUF (air) samples were processed through combined C-18/Florisil solid-phase extraction cleanup and 19 PAHs were quantified by GC/MS operated in combined full scan/selected-ion-monitoring mode for ([Table 1](#)) using procedures described in [Mendez et al. \(2008\)](#). Mass of PAH in the PUFs was converted to concentration (ng m^{-3}) using the volume of air

Table 1
Polycyclic aromatic hydrocarbon (PAH) compounds measured in air and sealant samples. Compounds are ordered by number of rings from naphthalene (2 rings) to coronene (7 rings); three of the last four compounds are polycyclic aromatic heterocyclic compounds (containing an N or S atom) and 9,10-anthraquinone is a PAH with 2 oxygen atoms substituted for hydrogen atoms on the center ring.

Compound	Measured in air	Measured in sealant	Abbreviations used in text and figures	In Σ PAH ₈	In Σ PAH ₁₆
Naphthalene		X			X
2-Ethyl naphthalene		X			
1,2-Dimethyl naphthalene		X			
1,6-Dimethyl naphthalene		X			
2,6-Dimethyl naphthalene		X			
2,3,6-Trimethyl naphthalene		X			
Acenaphthene		X			X
Acenaphthylene		X			X
Fluorene		X			X
1-methyl fluorene		X			
Phenanthrene	X	X	PHE	X	X
Anthracene	X	X	AN	X	X
4,5-methylene phenanthrene	X	X	45 MP	X	
2-methyl anthracene	X	X			
1-methylphenanthrene	X	X	1 MP	X	
Fluoranthene	X	X	FLU	X	X
Pyrene	X	X	PY	X	X
1-methylpyrene	X	X			
Benz[a]anthracene	X	X	BaA		X
Chrysene	X	X	CHY	X	X
Benzo[b]fluoranthene	X	X	BbF	X	X
Benzo[k]fluoranthene	X	X	BkF		X
Benzo[e]pyrene	X	X	BeP		
Benzo[a]pyrene	X	X	BaP		X
Perylene	X	X			
Benzo[ghi]perylene	X	X	BgP		X
Indeno[1,2,3-cd]pyrene	X	X	IP		X
Dibenzo[a,h]anthracene	X	X			X
Coronene	X				
9,10-anthraquinone		X			
Carbazole		X			
Phenanthridine		X			
Dibenzothiophene		X			

sampled. Extracts were diluted as necessary to ensure quantitative determination within the calibration range. 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 (Mendez et al., 2008; Zaugg et al., 2006). Estimated concentrations were treated as detections for interpretations.

For the three air samples expected to have the highest PAH concentrations (0.03-m samples collected soonest after sealant application), the front and back PUFs were analyzed separately to assess breakthrough. Relatively small PAH concentrations in the back PUFs (maximum of 2.5% of front PUF concentration) (Supplementary Data Table S-1) indicated that very little breakthrough occurred. For all other air samples, the front and back PUF were extracted and analyzed together.

Laboratory blank and spike samples were included for quality control with each set of about 10 environmental samples and were prepared using two pre-cleaned PUF plugs for PUF samples and baked reagent sand for sealant samples. PAH recovery averaged $99.7 \pm 8.1\%$ (mean and standard deviation) from air-method spikes (Supplementary Data Table S-1). Twelve PAHs, including all of the 5- and 6-ring, high-molecular weight PAHs [e.g., benzo[e]pyrene (BeP)], were detected in one of the air-method blank samples (with sample set 201006002), and several PAHs were detected in blanks from the other two sample sets (Supplementary Data Table S-1). The resulting concentrations in the blanks [using the median air sampling volume for the 0.03-m samples (20 m^{-3})] were below the reporting level of 1 ng m^{-3} in the environmental samples with the

exceptions of phenanthrene (PHE) and most of the high-molecular weight PAH in the blank associated with sample set 201006002. Carry-over contamination in the GC is 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 lack of detection of the high-molecular weight PAHs in 10 of 14 of the environmental samples in the same sample set further indicates that laboratory contamination of environmental samples during extraction and cleanup 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, in particular PHE, fluoranthene (FLU), and pyrene (PY). The highest concentration in a blank for PHE, FLU, or PY was 8.2% of the associated environmental sample (set 201006002), and most were less than 1% of the associated environmental sample concentration. We therefore conclude that blank contamination did not affect the interpretation of PAH concentrations or fluxes reported here.

PAH recovery from solid-phase method spikes averaged $83 \pm 12\%$ (Supplementary Data Table S-2). Concentrations of most PAHs detected in the solid-phase method blanks were very low relative to concentrations in the sealant samples; the highest detection in a blank was for FLU at 0.015 mg kg^{-1} , less than 0.0001% of the lowest environmental sample concentration of 2170 mg kg^{-1} . No spike or blank corrections were applied. The mass of sealant sample collected 16 d after application was very small (0.028 g), introducing large uncertainty into the analysis; the results therefore were not considered reliable and the data are not included in the analysis presented here.

2.3. Flux estimation

The transfer of any conservative entity (water vapor, heat, momentum, or chemical gas) from an evaporating surface to the atmosphere is governed primarily by the chemical characteristics of the entity (e.g., vapor pressure) and by the atmospheric turbulence generated by wind moving over that surface (Lumley and Panofsky, 1964; Rosenberg et al., 1983; Majewski, 1999). 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, CO_2 , NH_3 , and pesticides (Majewski et al., 1990; Scholtz et al., 2002a; Kurt-Karakus et al., 2006). We estimated vertical fluxes of PAHs 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 conditions and corrects for changing atmospheric stability conditions (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 selected 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 fluxes. Both methods rely on horizontal wind speed (u) to estimate K_z (Eq. (1)). For the Scholtz method, mean wind speed in the boundary layer (taken here as 0–3 m) is used; for the T–H method, wind speed at the heights where PAH concentration is measured (0.03 and 1.28 m) is used. Wind speed was measured at 0.60 m near the air samplers 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-3.

The accurate estimation of volatilization flux requires that certain field conditions be met. These include a spatially uniform surface area with similar surface characteristics across the area surrounding the study plot and a spatially uniform surface-source strength. Both of these conditions require a minimum upwind fetch to measurement height ratio to ensure that the boundary layer in which the flux is being determined has the same characteristics as the adjacent underlying surface and that the flux is constant with height (Majewski, 1999). Because of the relatively short upwind fetch (about 10 m), the field conditions ideal for volatility flux measurements 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. 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, 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 and the gradient is based on the difference between the two. Even if the actual PAH concentration in air at 1.28 m over the sealed lots were double that measured, it would reduce the estimated total PAH fluxes (Scholtz method) by only 2–4% in all samples except one collected during winter when concentrations at both heights were low; the change in that sample would be a 10% reduction. 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 fluxes with time after sealing.

3. Results

3.1. Concentrations

Detections and concentrations of the 19 PAHs measured in air samples varied greatly with time after application of the sealant. All 19 PAHs were detected in the 0.03-m sample 1.6 h after application and the total PAH concentration was $303,000 \text{ ng m}^{-3}$, whereas during the following winter (149 d after application) only six PAHs were detected in the 0.03-m sample and the total PAH concentration was 301 ng m^{-3} (Supplementary Data Table S-1). Eight of the 19 PAHs measured that were detected frequently ($\geq 68\%$) in a previous study (Van Metre et al., in press) also were detected frequently here ($\geq 65\%$): PHE, anthracene (AN), 4,5-methylphenanthrene (45 MP), 1-methylphenanthrene (1 MP), FLU, PY, chrysene (CHY), and benzo[*b*]fluoranthene (BbF). Detection rates for the other 11 PAHs ranged from 5% [dibenzo[*a,h*]anthracene, perylene, and indeno[1,2,3-*cd*]pyrene (IP)] to 70% (2-methylanthracene). For comparability with the previous study, we consider the same eight frequently detected PAHs as a total PAH here (ΣPAH_8 ; non-detections treated as zeros). The ΣPAH_8 accounted for 98–100% of the sum of all detected PAHs in all samples.

Concentrations of PAHs were very large initially and decreased rapidly in the 0.03-m samples (Fig. 1). The ΣPAH_8 concentration at 0.03 m decreased from $297,000 \text{ ng m}^{-3}$ 1.6 h after application to $96,800 \text{ ng m}^{-3}$ 24 h after application; by 16 days after application it was $33,300$ and $23,400 \text{ ng m}^{-3}$ (replicate samples on day 16, identified as 15.9 and 16.1 d after sealing on Fig. 1 and in Supplementary Data tables), about a 10-fold decrease relative to the 1.6 h sample. On the basis of this rapid decrease in concentrations over time, the 16-d period was deemed the “initial drying period” for the sealant. Concentrations in the 1.28-m samples were relatively large initially (5680 ng m^{-3}) and also decreased rapidly (Fig. 1).

Air samples collected during the first 5 months after sealing were dominated by the lower molecular weight, 3-ring PAH, with PHE and AN accounting for 74–85% of the ΣPAH_8 concentration in the 0.03-m samples. That percentage decreased to 47% in the 232-d sample and was 25 and 28% in samples collected 328 and 376 d after application, respectively. As the 3-ring fraction of ΣPAH_8 decreased, the 4- and 5-ring fraction increased: the sum of FLU, PY, CHY, and BbF increased from 11% of ΣPAH_8 in the 1.6-h sample to 70 and 66% 328 and 376 d after application, respectively. Similar shifts in PAH assemblages occurred in the 1.28-m samples (Supplementary Data Table S-1).

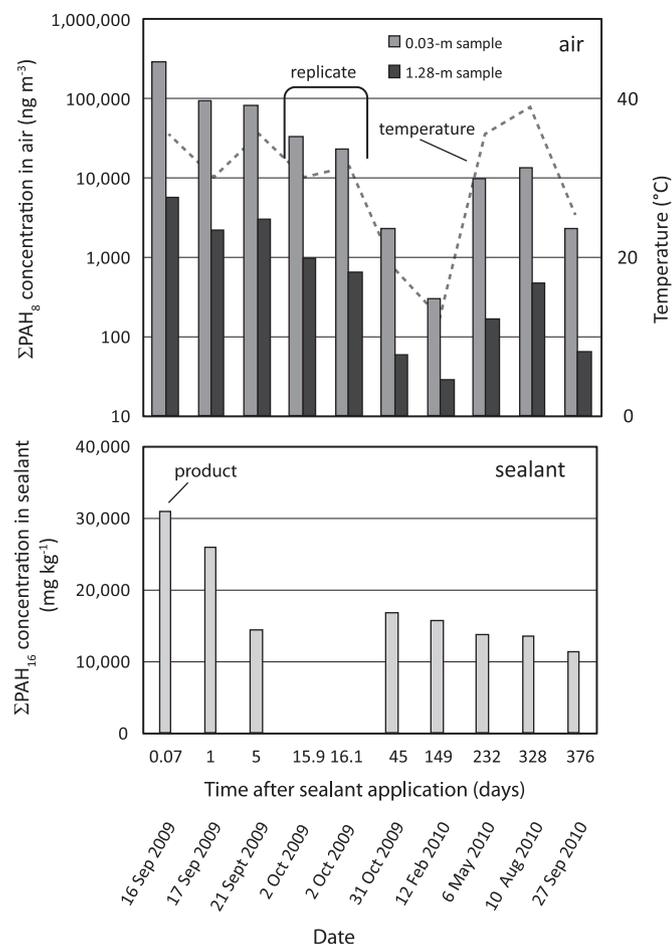


Fig. 1. Concentrations of PAHs in air (top) and sealant (bottom) at each sampling time after application. Temperature is shown (top graph) because of seasonal effect on air concentrations. Sealant samples (bottom graph) include the product (first bar) and adhered sealant scraped from the pavement. Sealant sample collected 16 days after application (2 Oct 2009) was not used because of quality-control issues. Note that the x-axis is categorical. ΣPAH_8 and ΣPAH_{16} are defined in the text and the PAHs in them are identified in Table 1.

Concentrations of PAHs in sealant samples decreased rapidly following application of the coal-tar-based sealant (Fig. 1; Supplementary Data Table S-2). The ΣPAH_{16} concentration in the fresh product was $30,900 \text{ mg kg}^{-1}$ and the ΣPAH_8 concentration was $25,900 \text{ mg kg}^{-1}$. The product analysis was done after 3 days of drying indoors, so an unknown amount of PAH was lost to volatilization prior to analysis. The ΣPAH_{16} concentration in the sealant sample 1 d after application was $25,800 \text{ mg kg}^{-1}$ and concentrations in sealant samples collected from 5 to 328 days ranged from $13,500$ to $16,700 \text{ mg kg}^{-1}$. At the end of the following summer (Sept. 27, 2010, and 376 days after sealing), the ΣPAH_{16} had decreased to $11,300 \text{ mg kg}^{-1}$, 37% of the original product concentration.

A weathering shift in PAH assemblage for the sealant samples occurred over the course of the study (Fig. 2), with a preferential loss of low molecular weight PAH, consistent with the decreasing proportion of 3-ring PAH over time in air concentrations. PHE in the sealant product was 26% of the sum of the 12 PAHs shown on Fig. 2, similar to the PHE fraction in the National Institute of Standards and Technology (NIST) coal-tar standard (27.5%) (NIST, 1992). This fraction progressively decreased in the solid-phase samples to 2.4% at 376 d as the fractions of higher molecular weight PAH progressively increased (Fig. 2).

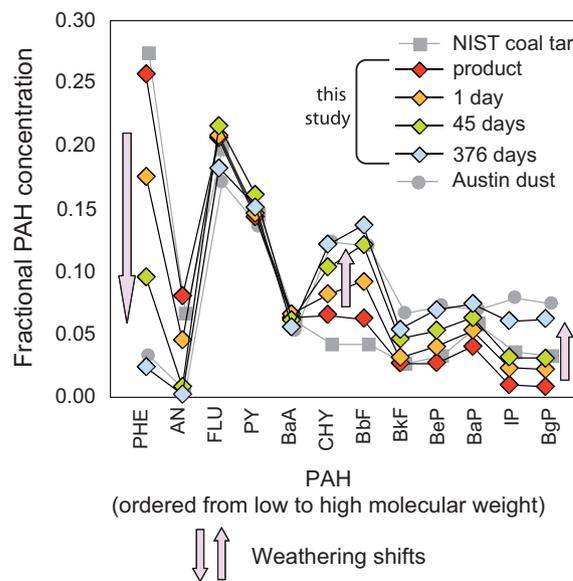


Fig. 2. Fractional PAH concentrations (concentration divided by the sum of the 12 PAHs shown) in selected sealant samples from this study in comparison to a PAH weathering pattern indicated by the NIST coal-tar standard (least weathered) and the mean profile in dust from sealed pavement in Austin (most weathered) (Van Metre and Mahler, 2010). PAH abbreviations are defined in Table 1. Directions of weathering shifts in proportional concentrations are indicated by the arrows.

3.2. Fluxes

The Scholtz and non-stability corrected T–H methods produced similar estimates of volatilization fluxes. The relative percent differences between the two methods were about $\pm 10\%$ for 3-ring PAH and trended to somewhat higher estimates for the T–H equation relative to the Scholtz method for 4- and 5-ring PAH (generally 0–20% greater for T–H with largest difference for BbF ranging from 9 to 27%). 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 T–H method (Majewski et al., 1989), results determined using the Scholtz method are likely to be more accurate, and further discussion is based on results from this method.

Fluxes of ΣPAH_8 ranged from $45,000 \mu\text{g m}^{-2} \text{ h}^{-1}$ in the sample collected 1.6 h after sealant application to $28 \mu\text{g m}^{-2} \text{ h}^{-1}$ 149 d after application and collected on February 12, 2010, when the air temperature was the lowest among all the sampling dates (Supplementary Data, Tables S-3 and S-4). In summer 2010 fluxes rebounded from the winter low to $830 \mu\text{g m}^{-2} \text{ h}^{-1}$ on August 10, 2010.

As with concentrations, fluxes soon after application were dominated by lower molecular weight PAH, with PHE accounting for 71–83% of ΣPAH_8 flux in samples collected from 1.6 h to 149 d after application. In the samples collected 328 and 376 d after application, this fraction was 25 and 28%, respectively. As the proportional contribution from PHE decreased, the proportional combined contribution from FLU and PY increased, accounting for 66 and 63% of ΣPAH_8 flux in the 328 and 376 d samples.

3.3. Total PAH losses to air

Total mass of ΣPAH_8 lost during the initial drying period of 16 days was estimated using two approaches: flux to the air, and loss from the solid-phase. For the first approach, a natural logarithmic (ln) regression equation was fit to the flux estimates for the samples

collected during the first 45 days after application, the resulting curve was adjusted for estimated diurnal variation in flux, and the adjusted curve was numerically integrated over the initial 16-d period (Fig. 3). Because of the timing of sampling (summer afternoon at approximate daily maximum air temperature), the regression equation likely represents the annual daily maximum flux. The ln-regression equation accounts for 95% of the variability in flux estimates ($r^2 = 0.95$) and is:

$$\Sigma\text{PAH}_8 \text{ flux} = -6,870 \cdot \ln(\text{time}) + 44,360 \quad (2)$$

where ΣPAH_8 flux is in $\mu\text{g m}^{-2} \text{h}^{-1}$, and time is in hours since the completion of application. The diurnal variation in flux was estimated using the geometric mean of the summertime daytime-to-nighttime ΣPAH_8 flux ratio (4.5 ± 2.9) reported for four coal-tar-sealed parking lots (Van Metre et al., in press). The diurnal variation was applied to the ln-regression-estimated flux using a sine function scaled to match the daytime:nighttime flux ratio and a 1-h time step. The mass of ΣPAH_8 emitted during the first 16 days after application estimated by this approach was 2.5 g m^{-2} . Uncertainty in this estimate includes uncertainty associated with measurement, flux estimation, and diurnal variation correction, most of which are not quantifiable here. We therefore conclude that total emissions likely are in the range of $2\text{--}3 \text{ g m}^{-2}$.

For the second approach, a logarithmic regression line was fit to the sealant product and scraping-sample PAH concentrations for the full year (a very similar regression results from fitting to the first 45 days after application) (Fig. 4), and the change in concentration was computed for the initial drying period of 16 days. Uncertainty associated with the resulting estimate stems in part from the fact that temperature is not constant throughout the year, so that losses are larger during the warmer months (i.e., 350–400 days following application, Fig. 4) than colder months (i.e., 100–200 days following application, Fig. 4). The resulting equation explains 87% of variation in concentrations ($r^2 = 0.87$):

$$\Sigma\text{PAH}_8 \text{ concentration} = -1,300 \cdot \ln(\text{time}) + 17,100 \quad (3)$$

where concentration is in mg kg^{-1} , and time is in days. The initial ΣPAH_8 concentration ($26,000 \text{ mg kg}^{-1}$) and the concentration at 16 days after application ($13,000 \text{ mg kg}^{-1}$) indicate a loss of roughly one-half of the PAH applied.

Estimating the mass of PAH lost from the sealant using the change in concentration over time requires an estimate of total mass of sealant applied per unit area. Standard application rates for coal-tar-emulsion sealants, assuming the application of two coats

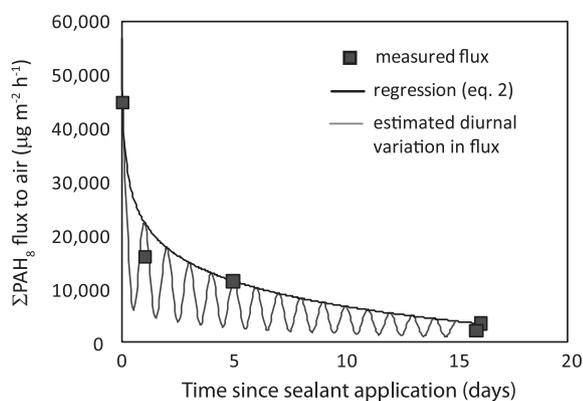


Fig. 3. Logarithmic regression model of flux of ΣPAH_8 to air during the first 16 days after sealant application (Eq. (2)). Estimation of the diurnal variation in flux was made using a sine function and daytime and nighttime measurements of flux previously reported for sealed pavement (Van Metre et al., in press).

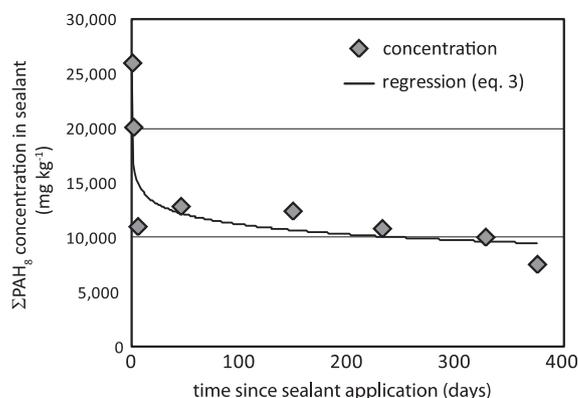


Fig. 4. Logarithmic regression model of ΣPAH_8 concentrations in the product (time zero) and sealant samples collected from the pavement surface during about 1 year after application (Eq. (3)).

of sealant as was done here, are 0.72 L m^{-2} (ASTM, 2003) and $0.6\text{--}0.8 \text{ L m}^{-2}$ (ASTM, 2004). Using the rate of 0.72 L m^{-2} , 53% volatiles reported in the MSDS for the Tarconite product used in this study (Supplementary Data; percent volatiles, determined by drying at 105°C (ASTM, 1998), is presumably mostly water, as the sealant is in a water emulsion, but might contain some PAHs), and a dry density of coal-tar-based sealant of 1.2 g cm^{-3} (Yang et al., 2010) results in 460 g m^{-2} dry sealant. Multiplying this amount of dry sealant by the difference between the initial and 16-day concentration of ΣPAH_8 ($13,000 \text{ mg kg}^{-1}$) yields an estimate of 6 g m^{-2} of ΣPAH_8 lost during the first 16 days of drying. This estimated loss is about 2 times that estimated on the basis of volatilization fluxes. The general agreement between the integrated total volatilization flux at 16 days ($2\text{--}3 \text{ g m}^{-2}$) and the total loss of PAHs from the adhered sealant (6 g m^{-2}) provides support for the magnitude of the estimated volatilization flux.

4. Discussion

The ΣPAH_8 concentration in the surface-air layer (0–0.03 m) 1.6 h after sealcoat was applied ($297,000 \text{ ng m}^{-3}$) was almost 5000 times greater than that recently reported over unsealed parking lots (66 ng m^{-3}) (Van Metre et al., in press). The estimated ΣPAH_8 flux to air from the newly sealcoated surface at 1.6 h ($45,000 \mu\text{g m}^{-2} \text{h}^{-1}$) was 32,000 times that estimated from unsealed parking lots ($1.4 \mu\text{g m}^{-2} \text{h}^{-1}$) (Van Metre et al., in press) and the flux at 16 days after application ($2800 \mu\text{g m}^{-2} \text{h}^{-1}$) was 2000 times that from unsealed parking lots. By 45 days after application, air concentrations and fluxes of PAHs over the test lot had decreased to within the same range as concentrations and fluxes measured over in-use parking lots with older sealant (Van Metre et al., in press), although the 45-d sample was collected during cooler weather than occurred during the sampling of the in-use parking lots. Comparison of the initial fluxes to air measured by this study with fluxes to air from parking lots with older sealant and comparison of initial and longer-term changes in PAH concentrations in sealant samples indicate that emissions during initial drying dominates total emissions. The mean summer daytime flux reported from parking lots with coal-tar-based sealant that was from about 3.6 to 8 y old was $88 \mu\text{g m}^{-2} \text{h}^{-1}$ (Van Metre et al., in press). That flux can be used to make a first-order estimate of total annual PAH loss from older sealant of about $0.1\text{--}0.2 \text{ g m}^{-2}$ [obtained by multiplying the flux by 1680 h (8 h a day for 7 months of the year), with 33% uncertainty], much less than the $2\text{--}3 \text{ g m}^{-2}$ loss estimated for this study during drying. On the basis

of Eq. (3), the decrease in PAH concentration (loss) during the first 16 days was $13,000 \text{ mg kg}^{-1}$, whereas the decrease from 16 to 365 days was only 4100 mg kg^{-1} . Thus the PAH loss during the initial drying period might be several times greater than the subsequent annual PAH loss. The rebound in flux with summer temperatures 1 year after application indicates that, once the initial release of PAHs to the air has occurred, flux likely is controlled by ambient air temperature.

Volatilization results in a shift over time in the PAH assemblage in the solid-phase samples (Fig. 2) and air samples. These shifts are consistent with the decrease in volatility of PAHs with increasing molecular weight. The subcooled-liquid phase vapor pressure, for example, for PHE is 113 mPa and for benzo[ghi]perylene (BgP) (6 rings) is 0.023 mPa (Mackay et al., 1992). Van Metre and Mahler (2010) presented a weathering pattern for coal-tar-based sealants that is similar to the weathering pattern on Fig. 2, and hypothesized that the cause of the weathering shift was differences in volatilization among the PAHs. That hypothesis is supported by the results of this study, which demonstrate that relative proportions of the lower molecular weight PAHs in solid-phase and air samples decrease during the months following application and relative proportion of the higher molecular weight PAHs increase.

The PAH losses to the atmosphere are larger than losses of PAHs from coal-tar-sealed pavement reported for other pathways. Over 16 days, estimated PAH losses were 6 g m^{-2} (sealant measurements) and $2\text{--}3 \text{ g m}^{-2}$ (air measurements). Given the uncertainty in these estimates and the potential for loss from the dried product by photolysis, we estimate that one-quarter to one-half of PAHs are lost to the atmosphere during the first 16 days following application. A study at the University of New Hampshire reported that an estimated 15% of PAH in sealant was lost to runoff during the 27 months following application (Watts et al., 2010). Other pathways that have been reported are tracking by vehicle tires (Scoggins et al., 2009) and feet (Mahler et al., 2010), transport by wind, and scraping by snow plows (University of New Hampshire Stormwater Center, 2010). The magnitude of transport by these pathways is not known, but they have been linked to contamination of soils adjacent to sealed pavement, dust from unsealed parking lots and streets (Van Metre et al., 2009; Watts et al., 2010; Yang et al., 2010), and to contamination of settled house dust in apartments near sealed lots (Mahler et al., 2010). Although the magnitude of PAH losses to air likely is greater than that of losses by these other pathways, some of the other pathways likely have more direct adverse effects on the environment. Runoff from sealed parking lots, for example, adversely affects aquatic life in urban streams (Scoggins et al., 2007) and is the largest contributor of PAHs to urban lakes (Van Metre and Mahler, 2010). Dust tracked indoors from coal-tar-sealed parking lots is incorporated into house dust, resulting in PAH concentrations in settled house dust that are 25 times greater than those in house dust in residences adjacent to pavement without coal-tar-base sealant (Mahler et al., 2010). Williams et al. (in press) reported that non-dietary ingestion of carcinogenic PAHs in settled house dust was 14 times greater for children living in residences adjacent to pavement with coal-tar-based sealcoat than for children living in residences adjacent to unsealed pavement, and was more than twice dietary ingestion of PAHs.

Concentrations of PAHs in air over recently sealed pavement are very large compared with concentrations reported in studies of air in urban and industrial regions of the United States (Simcik et al., 1997; Gigliotti et al., 2005), Canada (Motelay-Massei et al., 2005), and China (Liu et al., 2001, 2007) [summarized in (Van Metre et al., in press)]. For example, the PHE concentration at 1.28-m height 1.6 h after sealing (4330 ng m^{-3}) is 288 times higher than that measured in ambient air in Jersey City, NJ (USA), 64 times higher

than that measured in Chicago, Ill. (USA), and 5 times higher than that measured in Hangzhou, China (the highest concentration in ambient air we found in the literature). The PHE concentration at the same height 11 months after sealing (122 ng m^{-3}) was 8, 1.8, and 0.14 times that reported for Jersey City, Chicago, and Hangzhou, respectively, and is within the range of that measured at the same height over parking lots with coal-tar-based sealcoat 3.6 to more than 8 years old (Van Metre et al., in press).

The large PAH loss during initial drying estimated here raises the question of how important coal-tar-based sealcoat is as a source of PAHs to urban air. To make a first-order approximation of total PAHs emitted into the atmosphere each year from new application, the more conservative flux rate estimated here (2.5 g m^{-2}) was applied to a national estimate of coal-tar sealant use. At the recommended application rate of 0.72 L m^{-2} (ASTM, 2003), the estimated annual use of 320 million liters (Scoggins et al., 2009) will cover about 440 km^2 . Multiplying that area by 2.5 g m^{-2} yields an estimated total emission of about 1000 Mg (metric tons) of PAH₈ annually; if the estimated loss from the adhered sealant were used in this calculation (6 g m^{-2}), the total emission estimate would exceed 2000 Mg. Obviously, there are many uncertainties in this estimate, including measurement uncertainty, the assumption that all coal-tar-based sealant products volatilize PAHs equally, and the assumption that emissions in Austin are comparable to those in other settings. Air temperatures during sampling over the 16-d drying period were warm [$30\text{--}36 \text{ }^\circ\text{C}$ ($86\text{--}97 \text{ }^\circ\text{F}$)], thus, in northern climates the initial drying flux of PAHs might be lower or might extend over a longer time period. In addition to the temperature effect on volatilization, strong seasonality is expected for emissions because of the timing of sealant application: Application requires relatively warm weather, as it is recommended that the temperature of pavement and ambient air not be less than $7 \text{ }^\circ\text{C}$ ($45 \text{ }^\circ\text{F}$) during and for 12 h after application (ASTM, 2004).

The estimated emissions from application of coal-tar-based sealant ($\sim 1000 \text{ Mg}$ of PAH₈ annually) are larger than estimated PAH emissions from vehicles for the U.S. The estimated emissions of ΣPAH_{16} from motor vehicles in the U.S. for 2010 was 836 Mg, and they are dominated by naphthalene (Shen et al., 2011), which was not determined in this study. If only the six parent PAHs in common to the study by Shen et al. (2011) and this study are considered, the vehicle emissions were about 46 Mg for 2010, about 1/20th those estimated for newly applied coal-tar sealants. In spite of the uncertainty in estimated emissions, this study indicates that emissions from coal-tar-based sealcoat can be a large contributor to PAHs in urban air.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2012.01.036.

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