

Collection and Analysis of Samples for Polycyclic Aromatic Hydrocarbons in Dust and Other Solids Related to Sealed and Unsealed Pavement From 10 Cities Across the United States, 2005–07



Data Series 361

Cover: Collection of a dust sample from a sealed parking lot.

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By Peter C. Van Metre, Barbara J. Mahler, Jennifer T. Wilson, and
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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
Volume		
milliliter (mL)	0.034	ounce, fluid (fl. oz)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
Pressure		
kilopascal (kPa)	0.1450	pound per square inch (lb/ft ²)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Concentrations of semivolatile organic compounds and polycyclic aromatic hydrocarbons are given in micrograms per kilogram (µg/kg).

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Abstract

Parking lots and driveways are dominant features of the modern urban landscape, and in the United States, sealcoat is widely used on these surfaces. One of the most widely used types of sealcoat contains refined coal tar; coal-tar-based sealcoat products have a mean polycyclic aromatic hydrocarbon (PAH) concentration of about 5 percent. A previous study reported that parking lots in Austin, Texas, treated with coal-tar sealcoat were a major source of PAH compounds in streams. This report presents methods for and data from the analysis of concentrations of PAH compounds in dust from sealed and unsealed pavement from nine U.S. cities, and concentrations of PAH compounds in other related solid materials (sealcoat surface scrapings, nearby street dust, and nearby soil) from three of those same cities and a 10th city. Dust samples were collected by sweeping dust from areas of several square meters with a soft nylon brush into a dustpan. Some samples were from individual lots or driveways, and some samples consisted of approximately equal amounts of material from three lots. Samples were sieved to remove coarse sand and gravel and analyzed by gas chromatography/mass spectrometry. Concentrations of PAHs vary greatly among samples with total PAH (Σ PAH), the sum of 12 unsubstituted parent PAHs, ranging from nondetection for all 12 PAHs (several samples from Portland, Oregon, and Seattle, Washington; Σ PAH of less than 36,000 micrograms per kilogram) to 19,000,000 micrograms per kilogram for a sealcoat scraping sample (Milwaukee, Wisconsin). The largest PAH concentrations in dust are from a driveway sample from suburban Chicago, Illinois (Σ PAH of 9,600,000 micrograms per kilogram).

Introduction

Contamination of aquatic sediments by PAHs, which represent the largest class of suspected carcinogens (Björseth

and Ramdahl, 1985), has been increasing in urban areas during the last 20 to 40 years (Van Metre and others, 2000; Van Metre and Mahler, 2005). PAHs in the environment largely are a product of the incomplete combustion of petroleum, oil, coal, and wood (Edwards, 1983). Suspected sources in the urban environment include vehicles, home heating with fuel oil, wood, and coal, power plants (Sims and Overcash, 1983; Rogge and others, 1993), and parking lot sealants, also known as sealcoat (Mahler and others, 2005). In a study of PAHs in Austin, Tex., particles in simulated runoff from parking lots sealed with the coal-tar-based products had a mean total PAH concentration 65 times greater than that in particles from unsealed concrete and asphalt parking lots (Mahler and others, 2005). On the basis of comparison to stream suspended sediment concentrations, loads, and chemical assemblages, the study concluded that sealcoat was the major source of PAHs in the four watersheds studied. Data collected by the City of Austin indicated that coal-tar-based parking lot sealcoat contains about 5 percent PAH (50,000,000 micrograms per kilogram [$\mu\text{g}/\text{kg}$]) on average (City of Austin, 2005). Scoggins and others (2007) reported adverse biological effects in some streams receiving runoff from coal-tar sealed lots. From August 2005 through August 2007 the U.S. Geological Survey (USGS) collected samples of dust and other solids related to sealed and unsealed pavement in 10 U.S. cities to better understand occurrence and sources of polycyclic aromatic hydrocarbons (PAHs) in urban environments.

The purpose of this report is to present methods used to collect and analyze samples for PAH concentrations in parking lot dust, and to present the resulting data on concentrations of PAHs and selected other semivolatile organic compounds (SVOCs) in dust samples from sealed and unsealed parking lot surfaces in nine geographically diverse cities in the United States. Methods of collection and analyses of other parking-lot-related solid materials (surface scrapings, nearby street dusts, and nearby soils) are presented for three of the nine cities plus a 10th city (Milwaukee, Wis.) (fig. 1, table 1).



Figure 1. U.S. cities where samples of pavement dust or other pavement-related solids, or both, were collected.

Collection and Analysis of Samples

Cities included in this report are those where urban lake sediments were sampled by the National Water-Quality Assessment (NAWQA) Program of the USGS in 2004–07 (plus Austin, Tex., and Washington, D.C.). The design and methods for the NAWQA lakes study are presented in Van Metre and others (2004). Dust from sealed and unsealed pavement, scrapings from sealed pavement, and soil samples were collected from the watershed of one or more lakes in each city or in a suburb of the city (table 1). In five cities, a composite of dust samples from three sealed parking lots was collected; and in four of those five cities, a composite of dust samples from three unsealed parking lots also was collected. In four other cities, dust samples were collected from individual sealed parking lots; and in three of those four cities, dust samples also were collected from individual unsealed parking lots. In three cities, scrapings of sealed pavement were collected from individual sealed parking lots. The watershed of Lake in the Hills (suburban Chicago, Ill.) was sampled on two different occasions; samples of dust from the sealed driveways of two single-family homes, dust from roads adjacent to sealed and unsealed pavement, and soil from areas adjacent to sealed and unsealed pavement were collected in addition to samples of dust from individual sealed and unsealed parking lots (table 1).

Sample Collection Methods

Dust samples from driveways and parking lots were collected by USGS personnel by sweeping dust from areas of several square meters with a soft, clean, nylon brush into a clean plastic dustpan (fig. 2). Areas sampled generally were in drive lanes; areas with oil staining or heavy accumulations of sediment, such as near curbs, were avoided. Brushes and

dustpans were discarded after collection of each sample analyzed. For the composite samples, the same brush and dustpan were used to collect dust from three lots of the same surface type, composing a single composite sample; approximately equal amounts of dust were collected from each of the three lots. Dust samples from unsealed roads adjacent to sealed and unsealed parking lots or driveways (nearby street dusts) were composites of sweepings from as many as 10 areas of several square meters from about 5 to about 50 meters (m) from the edge of the sealcoated pavement and 1 m or more from the road curb. The roads were not sealed. Soil samples were collected from grass-covered medians or islands about 0.5 m from the edge of the curb at the edge of the parking lot (nearby soils). Soil samples were composites of three surface-soil plugs approximately 6 centimeters (cm) in diameter and 2 cm deep. Plugs were collected by pushing a clean polycarbonate jar into the soil. Soil sampling sites were selected where the curb would be expected to prevent runoff from the pavement from reaching the soil, although snow plowed from the pavement might have been piled on these areas in winter. Scraping samples were collected from the same areas as dust samples by gently scraping the sealcoated surface with a stainless steel spatula and sweeping the resulting flakes of sealcoat onto plain paper cards. Dust samples were sieved using a 0.5-millimeter stainless steel mesh to remove coarse sand, gravel, and debris; soil and scraping samples were not sieved. Dust, soil, and scraping samples were placed in clean glass jars and shipped chilled to the USGS National Water Quality Laboratory (NWQL) for analysis.

Analytical Methods

Samples were analyzed for PAHs using pressurized liquid extraction and gas chromatography/mass spectrometry (GC/MS) (Zaugg and others, 2006). Dust and scraping samples were prepared by extracting about 0.67 gram (g) dry



Figure 2. Collection of a dust sample from a sealed parking lot.

weight of sample (mean mass of 0.67 g, range 0.17 to 3.05 g) using pressurized liquid extraction at a pressure of 13,800 kilopascals twice, at temperatures of 120 and 200 degrees Celsius, with a mixture of water and isopropyl alcohol (50:50 and 20:80 for the two temperatures, respectively). Soil samples, which ranged in mass from 0.66 to 9.91 g, were extracted by the same method. Surrogate compounds were added to the sample prior to extraction to verify method recoveries. Following extraction, a buffer was added to the extract, and the compounds were isolated on a divinylbenzene-vinylpyrrolidone copolymer solid-phase extraction column. The adsorbed compounds were eluted with a dichloromethane/diethyl ether solution through sodium sulfate and Florisil solid-phase extraction columns. The extract was concentrated to approximately 0.5 milliliters (mL). An internal standard mixture was added to an aliquot of the extract, and the extract was analyzed by full scan on a Hewlett-Packard 5973 GC/MS system. Difficult sample matrixes were diluted before the full-scan analysis, and diluted surrogates were quantified as estimated concentrations in the samples. Compound identifications were based on comparison of gas chromatographic peak retention times and mass spectra to those of authentic standard compounds for the target compounds. A calibration curve was prepared for each compound from a set of calibration standards.

There were several changes in standard operation procedures for PAH analyses following USGS approval of method O-5506-06 in April 2006 (Zaugg and others, 2006), with full implementation of these procedures about January 1, 2007 (Michael Schroeder, U.S. Geological Survey, written commun., 2008). This change affected the analysis of samples collected in November 2006 and later (table 2). The list of PAH compounds analyzed prior to January 2007 was based on USGS method O-5505-03 (Olson and others, 2003) and beginning in January 2007 was based on USGS method O-5506-06 (Zaugg and others, 2006). Method O-5506-06 includes the same PAHs as method O-5505-03 plus additional compounds, such as phthalates. Prior to 2007, calibration standard solutions were prepared in ethyl acetate and, because sample extracts and standards should be prepared in the same solvents to ensure uniform chromatographic performance, the sample extracts were exchanged from dichloromethane-diethyl ether to ethyl acetate. Since January 2007, standard solutions were prepared in dichloromethane/diethyl ether, eliminating the need for the solvent exchange step. Final extract volumes changed from 10 mL, to 2 mL, to 0.5 mL currently (January 2008), to enable lower detection levels. In January 2007, the mass basis for calculating blank detections and reporting levels was lowered from 25 g to 10 g. The default reporting level (50 µg/kg) was not changed, but for samples of lower mass the reporting levels were adjusted in proportion to the mass relative to 10 g rather than 25 g. Finally, the analyte list prior to January 2007 was based on USGS method 2505 (Olson and others, 2003) and beginning in January 2007 was based on USGS method 5506. The schedule 5506 list contains the same PAH list as 2505, as well as additional compounds, such as phthalates.

Initial method detection level (MDL) for parent PAHs for a 25-g sample ranges from 7.7 (naphthalene) to 14.4 $\mu\text{g/kg}$ (dibenz[*a,h*]anthracene). Initial method reporting level (MRL) is 50 $\mu\text{g/kg}$ for all compounds reported (Zaugg and others, 2006). If less than 10 g was extracted, as was the case in this study, the reporting level was raised inversely proportional to the sample mass. The reporting level also could be raised because of background interferences. Reporting level for each sample was calculated on the basis of sample mass, volume of extract, and the MRL. Some concentrations are identified as estimated (E) on the basis of one or more of the following: quality-control (QC) data for the sample or batch of samples could not be brought into control guidelines, there were interference issues from the sample matrix, the peak was identified and quantified below the MRL, or the sample was diluted before analysis. Estimated values are detections but with lower or unknown precision.

Total PAH (ΣPAH) is defined here as the sum of concentrations of 12 parent PAHs (naphthalene, acenaphthylene, acenaphthene, 9H-fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*a*]pyrene, and dibenzo[*a,h*]anthracene). These are the same parent PAHs used for the consensus-based sediment quality guideline probable effect concentration (PEC), excluding 2-methylnaphthalene (Ingersoll and others, 2000) which was not quantified in this study. ΣPAH is listed two ways in table 2: computed with nondetections replaced by zero and computed using the reporting level for the nondetections. The latter are identified in table 2 as “less-than” (<) values if any individual PAHs were nondetections. For example, sample “DEK sealed composite” had nondetections for nine of the 12 PAHs in ΣPAH . The sum of the three detected compounds is 2,100 $\mu\text{g/kg}$, and the sum of the less-than values for each of the nine compounds that were not detected is 12,600 $\mu\text{g/kg}$; therefore, the actual value is assumed to be at least 2,100 $\mu\text{g/kg}$ and less than 15,000 $\mu\text{g/kg}$ —the sum of 2,100 and 12,600 rounded to two significant figures. The rounding convention followed was to round individual compound concentrations to three significant figures and round summations to two significant figures.

Quality-Control Results

Quality-control samples consist of laboratory QC samples and environmental QC samples. Laboratory QC for PAH analysis consisted of analysis of surrogate compounds in each environmental sample and analysis of spiked samples and blank samples concurrent with analysis of each set of environmental samples. Data reported here are from samples that were included in 11 different laboratory sample sets. The surrogate values for each sample (table 2) and spike values for each sample set (table 3) are reported in percent recovery. The method spike was 800 $\mu\text{g/kg}$ for all spikes listed in table 3, except for set numbers 200734010 and 200734011, which were spiked at 400 $\mu\text{g/kg}$. The acceptable range for spike recovery established by the NWQL is based on spike recover-

ies in past sample analyses and is recalculated periodically as more batches of samples are analyzed. Because USGS method 5506 is relatively new, acceptable ranges are based on analysis of 13 spike samples associated with 13 batches of samples (11 of which include samples reported here). The acceptable range is calculated as the median recovery plus or minus 3 times *f*-pseudosigma; *f*-pseudosigma is a measure of variance and is the interquartile range divided by 1.349 (Burkhardt and others, 2005). For the 18 unsubstituted parent PAHs analyzed (excluding perylene), only two of the spike samples for the 11 samples sets were out of range, both of them low. Median surrogate recoveries for all samples were 67 percent (2-fluorobiphenyl), 54 percent (nitrobenzene-*d*5), and 95 percent (*p*-terphenyl-*d*14) (table 2). Recoveries typically less than 100 percent were attributed to difficult sample matrices.

A concentration was detected in 28.3 percent of blank samples for the 18 parent PAH compounds, with the highest measured concentration in a blank at 27 $\mu\text{g/kg}$ for naphthalene (table 3; estimated value for sample set 200734107), which is below the MRL of 50 $\mu\text{g/kg}$. Frequent detections in blanks might be caused by cross-contamination of instruments resulting from the extremely high PAH concentrations in some of the parking lot dust and scraping samples. Blank concentrations were low or very low relative to reported sample concentrations in all sample sets. The highest percentage of a reported concentration accounted for by a blank detection was 4.1 percent for phenanthrene in sample set 2505R05362 (table 3) and environmental sample TNB4, solids near a storm drain on an unsealed parking lot (table 2). Eight other individual constituents had a blank detection that accounted for more than 1 percent of the environmental concentration, and the rest of the blank detections accounted for less than 1 percent of the environmental concentration. No blank corrections to environmental data were made.

For this study, two environmental duplicate samples for analysis of PAHs were collected. To obtain a duplicate sample, a single sample was collected using the same methods used for other samples. The dust was sieved and the dust or scraping sample was homogenized and split prior to extraction and analysis. The duplicates thus are designed to measure laboratory precision, not the repeatability of the field sample collection. The median relative percent difference (RPD) for all PAH compounds detected in both samples for NTR 4, a scraping sample, was 18.4 percent and the median RPD for detected PAH compounds in WTY 2, a dust sample from an unsealed lot, was 10.6 percent (table 3).

Concentrations of PAHs in Dust and Other Solids Related to Sealed and Unsealed Pavement

Concentration data for PAHs and selected other semi-volatile organic compounds are presented in table 2. Concentrations of PAHs vary greatly among samples, with ΣPAH

ranging from nondetection for all 12 PAHs (several samples from Portland, Ore., and Seattle, Wash.) to 19,000,000 µg/kg for a sealcoat scraping sample (Milwaukee, Wis.). The largest PAH concentrations in dust are from a driveway sample from suburban Chicago, Ill. (ΣPAH of 9,600,000 µg/kg).

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