

**Sources and
transformations of
PAHs in Mexico City**

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Sources and transformations of particle-bound polycyclic aromatic hydrocarbons in Mexico City

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Abstract

Understanding sources, concentrations, and transformation of polycyclic aromatic hydrocarbons (PAHs) in the atmosphere is important because of their potent mutagenicity and carcinogenicity. The measurement of particle-bound PAHs by three different methods during the Mexico City Metropolitan Area field campaign in April 2003 presents a unique opportunity for characterization of these compounds and assessment of the methods. The three methods are (1) collection and analysis of bulk samples for time-integrated gas- and particle-phase speciation by gas chromatography/mass spectrometry; (2) aerosol photoionization for fast detection of PAHs on particles' surfaces; and (3) aerosol mass spectrometry for fast analysis of size and chemical composition. This research represents the first time aerosol mass spectrometry has been used to measure ambient PAH concentrations and the first time that fast, real-time methods have been used to quantify PAHs alongside traditional filter-based measurements in an extended field campaign. Speciated PAH measurements suggest that motor vehicles and garbage and wood burning are important sources in Mexico City. The diurnal concentration patterns captured by aerosol photoionization and aerosol mass spectrometry are generally consistent. Ambient concentrations typically peak at $\sim 110 \text{ ng m}^{-3}$ during the morning rush hour and rapidly decay due to changes in source activity patterns and dilution as the boundary layer rises, although surface-bound PAH concentrations decay faster. The more rapid decrease in surface versus bulk PAH concentrations during the late morning suggests that freshly emitted combustion-related particles are quickly coated by secondary aerosol material in Mexico City's atmosphere and may also be transformed by heterogeneous reactions.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of semi-volatile compounds formed as a byproduct of incomplete combustion and emitted by sources such as mo-

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tor vehicles, coal-fired power plants, wood fires, and cigarettes. Many PAHs are potent mutagens and carcinogens, and they account for the majority of mutagenic potency attributable to specific compounds in ambient particulate matter (Hannigan et al., 1998). The PAH benzo[a]pyrene has been directly linked to lung cancer through its selective formation of adducts along a tumor suppressor gene (Denissenko et al., 1996).

Transformations of PAHs on particles have the potential to affect the particles' toxicity through the formation of species that are more toxic, e.g. nitro-PAH (Sasaki et al., 1997), or less toxic. Heterogeneous reactions of PAHs (Bertram et al., 2001; Esteve et al., 2003, 2004) may serve as surrogates for heterogeneous chemistry of many types of organics; such reactions could change the particles' hydrophilicity and thus their potential to act as cloud condensation nuclei (Jones et al., 2004). A second mechanism of transformation is coating of freshly emitted particles by condensation of secondary aerosol components formed by gas-phase reactions. Through this type of transformation, PAHs that are initially present on the surface of particles may become less accessible for heterogeneous reactions and less bioavailable. PAHs are associated with black carbon, and coating of such particles has significant implications for radiative forcing and climate change (Chandra et al., 2004; Conant et al., 2003; Jacobson, 2001).

In the spring of 2003, a multinational team of over 100 atmospheric scientists from 30 Mexican, US, and European institutions conducted an intensive five-week field campaign in the Mexico City Metropolitan Area (MCMA) (de Foy et al., 2005). The overall goals of the effort were to contribute to the understanding of the air quality problem in Mexico City, through measurements and modeling, and also to serve as a model for the study of other megacities in the developing world. Recent studies of PAHs in Mexico City have reported concentrations there to be among the highest measured anywhere in the world. Median total particle-bound PAH concentrations along Mexico City's roadways range from 50 to 910 ng m⁻³, equivalent to smoking 0.4 cigarettes per hour or a lung cancer risk level of 2 × 10⁻⁵ for 10 h per week of exposure over 40 years (Marr et al., 2004; Velasco et al., 2004). The extremely high ambient concentrations in Mex-

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ico City provide a stronger signal for the analysis of diurnal patterns and comparison against concentrations of related pollutants. Comparison of PAH versus elemental carbon and active surface area concentrations in Mexico City suggests that surface PAH concentrations may diminish rapidly with particle aging (Marr et al., 2004). Because of the serious health effects of PAHs, it is important to understand their sources and loss processes under ambient conditions.

The measurement of particle-bound PAHs by three different methods – filters, aerosol photoionization, and aerosol mass spectrometry – during the five-week MCMA field campaign allows a more comprehensive characterization of these compounds in ambient air than has been possible in the past. Combined with measurements of numerous other species, including gas-phase PAHs, the data present a unique opportunity to characterize ambient concentrations, sources, and atmospheric processing of PAHs. This research represents the first time aerosol mass spectrometry has been used to measure ambient PAH concentrations and the first time that two fast, real-time methods have been used to quantify PAHs alongside traditional filter-based measurements in an extended field campaign. The objectives of this research are to (1) compare and contrast the three measurement methods, (2) describe the ambient concentrations and sources of PAHs in Mexico City, and (3) explain the differences in diurnal patterns observed in PAH versus other species concentrations.

2. Experimental

The measurements took place on the rooftop (12 m above ground level) of a three-story building at the Universidad Autónoma Metropolitana in Iztapalapa (UAM-I), approximately 10 km southeast of downtown Mexico City, whose elevation is 2240 m. The building houses the National Center for Environmental Research and Education, and the site is known by its Spanish acronym, CENICA. The site is located in a mixed-used medium-income neighborhood with light traffic. The nearest major roads are at least 1 km away.

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The five-week field campaign took place toward the end of the dry season during April 2003. It included Holy Week, which ended with Easter Sunday on 20 April. During the holiday week, many businesses closed and residents left on vacation. The average temperature during the field campaign was 21°C, with an average daily low of 15°C and high of 29°C. Winds were often northerly in the morning and southerly in the evening, with an average speed of 2 m s⁻¹. Rain occurred, usually briefly and in the afternoon and early evening, on 7, 8, 10, 12, 20, 22, 25, and 28 April.

Particle-bound PAHs were measured by three methods: (1) filter collection and analysis by gas chromatography/mass spectrometry (GC/MS), (2) aerosol photoionization, and (3) aerosol mass spectrometry. The “total” particulate PAH concentrations, defined in Table 1, measured by each method are referred to as FPAH, SPAH, and APAH, respectively. The filter sampler and photoionization aerosol sensor were located on opposite sides of an experimental platform, approximately 3 m apart and 4 m above the rooftop. The aerosol mass spectrometer was housed in a temperature-controlled storage building at the opposite end of the rooftop, approximately 50 m from the experimental platform.

2.1. Time-integrated sampling and speciated analysis

To allow speciation of PAHs by GC/MS, time-averaged bulk samples were collected on 27–30 April. A high-volume (Hi-vol) air sampler equipped with a Teflon-impregnated glass fiber filter (20 cm × 25 cm) and two polyurethane foam plugs (PUFs) in series beneath the filter and without a size-selective inlet was used to collect semi-volatile and particle-associated PAHs at a flow rate of ~0.6 m³ min⁻¹. Gas-phase naphthalene and alkyl-naphthalenes were simultaneously collected on replicate Tenax-TA solid adsorbent cartridges at a flow rate of 200 cm³ min⁻¹. Samples were collected over four sampling intervals per 24-h period: 07:00–11:00, 11:00–16:00, 16:00–21:00, and an overnight sample from 21:00–07:00.

The filter and PUF samples were spiked with deuterated internal standards, Soxhlet extracted overnight in dichloromethane, fractionated by high performance liquid

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chromatography (HPLC) on a semipreparative Silica column, and the PAH-containing fractions were analyzed by GC/MS. The PUFs were spiked with phenanthrene-d₁₀, fluoranthene-d₁₀ and pyrene-d₁₀ prior to extraction and were analyzed by positive ion/chemical ionization GC/MS with selected ion monitoring (SIM) using a DB-17 column in an Agilent 5973 mass selective detector (MSD). Filters were spiked with pyrene-d₁₀, benzo[b]fluoranthene-d₁₂ and benzo[a]pyrene-d₁₂ prior to extraction and were analyzed by electron impact GC/MS-SIM using a DB-5MS column in a Hewlett Packard 5971A MSD. The Tenax samples were spiked with naphthalene-d₈ and 1-methylnaphthalene-d₁₀ prior to thermal desorption and EI GC/MS-SIM analysis as described previously (Reisen and Arey, 2005). Table 1 lists the particle-phase species identified.

2.2. Aerosol photoionization

The main advantages of aerosol photoionization are its sensitivity and ability to perform continuous, real-time measurements with a response time of less than 10 s. In this method, the aerosol sample is exposed to ultraviolet light from an excimer lamp at 207 nm, which causes PAHs on the surface of particles to photoemit electrons. An electric field removes the ejected electrons, and the positively charged particles are trapped on a filter, generating a current that is measured by an electrometer.

The photoelectric aerosol sensor (PAS 2000 CE, EcoChem Analytics, Texas, and Matter Engineering AG, Switzerland) reports results as total particle-bound PAHs. Because our experience suggests that the instrument is most sensitive to PAHs on the surfaces of particles and less sensitive to those buried under other aerosol compounds, we henceforth use “SPA” to refer to particle-bound surface PAHs detected by the photoionization sensor. “PAH” will continue to refer to the class of compounds more generally. The instrument is factory-calibrated for SPAH concentrations up to 1000 ng m⁻³, and it is expected to give a linear response up to 5000 ng m⁻³. The response is calibrated against filter-based analyses of PAHs, including species with molecular masses 202, 226, 228, 252, 276, and 300 (Hart et al., 1993; McDow et al., 1990). Previ-

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ous studies have shown a strong correlation between photoelectric charging and independently measured PAH concentrations for a variety of aerosols: oil burner exhaust, cigarette smoke, parking garage air, and ambient urban air in different cities (Siegmann and Siegmann, 2000). The sensor's response has also been reported to be linearly correlated ($r^2=0.82$) with bacterial genotoxicity (Wasserkort et al., 1996).

During this study, we cross-calibrated four photoionization sensors against the ensemble mean while sampling candle soot and ambient air at concentrations of 20–3000 ng m⁻³ for 5–30 min on four separate occasions. All instruments reported a concentration of zero with a zero-air filter applied. Correction factors ranged from 0.82 to 1.34 for the individual instruments.

2.3. Aerosol mass spectrometer

The Aerodyne Aerosol Mass Spectrometer (AMS) allows real-time, size and composition analysis of non-refractory submicron particles (Jayne et al., 2000; Jimenez et al., 2003). A summary of the main results from the AMS measurements during this field campaign is given by Salcedo et al. (2005a, b). A separate paper (Dzepina et al., 2005¹) describes in detail the algorithm for extracting particle-phase PAH concentrations from AMS spectra and its validation. Here, we report the total AMS PAH concentration (APAH), which represents the sum of the concentrations of PAHs between molecular weights of 202 and 300.

2.4. Additional measurements

Table 2 summarizes the measurements considered in this study. Black carbon and PAHs form during the same combustion processes. Their concentrations are correlated in ambient air, and are impacted by a variety of combustion sources, including traffic,

¹Dzepina, K., Salcedo, D., Marr, L. C., Arey, J., Worsnop, D. R., and Jimenez, J. L.: Detection of particle-phase polycyclic aromatic hydrocarbons (PAHs) in Mexico City using an Aerosol Mass Spectrometer, *Aerosol Sci. Technol.*, submitted, 2005.

cooking, and wood smoke (Marr et al., 2004; Schauer et al., 2003; Wallace, 2000; Watson and Chow, 2002; Zielinska et al., 2004). A meteorological station located on the experimental platform recorded temperature, humidity, pressure, and wind velocity every minute. The site was part of a routine air quality monitoring network and measured concentrations of criteria pollutants, including sulfur dioxide, carbon monoxide, ozone, nitrogen dioxide, and particulate matter.

3. Results

Figure 1 shows concentrations of selected PAHs (gas + particle phases) determined by GC/MS on Tuesday 29 April. These PAHs are shown because of their association with specific sources. Tunnel studies have shown that larger PAHs, in particular benzo[ghi]perylene and indeno[1,2,3-cd]pyrene, are emitted in gasoline-fueled vehicle exhaust (Marr et al., 1999; Miguel et al., 1998), while alkylated phenanthrenes are associated with diesel vehicles (Benner et al., 1989). Concentrations of benzo[ghi]perylene and methylphenanthrenes are highest in the morning, although the diurnal patterns of these two PAHs differ. Benzo[ghi]perylene concentrations are 36 times higher in the morning compared to the afternoon and evening, while methylphenanthrene concentrations are only 1–2 times higher in the morning. The potential causes for this difference are discussed in the next section.

A GC/MS total ion chromatogram of the PAH-containing HPLC fraction from a filter sample revealed a retene peak and also a large peak from a MW 306 species. Retene has been suggested as a marker for soft wood combustion (Ramdahl, 1983). The MW 306 species was subsequently identified to be 1,3,5-triphenylbenzene by matching its mass spectra and retention time on two different GC columns with those of an authentic standard. This compound has recently been suggested to be a potential marker for the burning of refuse, including plastics (Simoneit et al., 2005). In contrast to the other PAHs, which are all considered markers of vehicle exhaust, the 1,3,5-triphenylbenzene and retene concentrations are highest in the nighttime rather than morning or daytime

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samples.

Figure 2 shows total particulate PAH concentrations measured by all three methods during the three days when they were operating simultaneously, 27–30 April. Not all methods were operating during the entire interval. Filter measurements are not available for 28 April, and the AMS was not sampling continuously during this period.

In the figure, heavy solid and dotted lines show time-integrated averages corresponding to the filter sampling periods. To illustrate the fine temporal structure of PAH concentrations, the figure also shows 1-min SPAH in the background. Total (FPAH, SPAH, APAH) and modified (FPAH* and APAH*) results represent, respectively, all PAHs detected by each method and a modified total, intended to facilitate comparison against SPAH. The modified total is the sum of concentrations at molecular masses and mass-to-charge ratios (m/z) of 202, 226, 228, 252, 276, and 300, as shown in Table 1. It excludes signals at molecular masses and m/z 's of 216 and 240 that correspond to alky-PAHs, because the photoionization instrument's calibration does not account for such species. This modification also excludes benzofluorenes, but their contribution was at most 3% of the FPAH total.

The 1-min SPAH time series shows a strong diurnal pattern in ambient PAH concentrations, with concentrations generally starting to rise at ~05:00, peaking at ~08:00, and then dropping throughout the late morning. Peak concentrations often exceed 100 ng m^{-3} , and concentrations usually remain below 50 ng m^{-3} throughout the remainder of the day. However, on the first day shown in the figure, a Sunday, peak concentrations are about 50% lower compared to the other days.

Figure 3 shows the diurnal profiles (15-min averages) of SPAH and APAH* averaged over weekdays and weekends separately, excluding Maundy Thursday 17 April through Easter Sunday 20 April, when traffic and ambient pollutant concentrations were significantly lower than usual. The standard deviations of weekday SPAH and APAH* are ~2 and ~5 ng m^{-3} , respectively. We have isolated weekdays because motor vehicle activity, thought to be a major source of PAHs, is expected to differ significantly between weekdays and weekends (Marr et al., 2002). The temporal patterns of SPAH

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and APAH* are similar, with concentrations beginning to increase at 05:00, peaking at 08:00, and then falling off; but their absolute values differ during most hours of the day. On weekdays, SPAH is usually lower than APAH* by $\sim 20 \text{ ng m}^{-3}$, except during the peak period (06:30–08:30), when the two signals are comparable in magnitude. Linear, least-squares regression of the weekday diurnal profiles of APAH* against SPAH produces a slope of 0.86 ± 0.03 (standard deviation) and intercept of $21 \pm 1 \text{ ng m}^{-3}$ with $r^2 = 0.87$. An additional difference between the two is that APAH* does not seem to decay as fast as SPAH in the late morning.

The differences in weekday versus weekend concentrations are opposite for the two measurements of PAH concentration. Weekend SPAH concentrations are $\sim 30\%$ lower compared to weekday SPAH during the peak morning rush hour period, but weekend APAH* concentrations are up to two times higher compared to weekday APAH* between midnight and 11:00. Weekend APAH* is approximately twice as high as weekend SPAH, with a regression slope of 1.85 ± 0.09 , intercept of $21 \pm 3 \text{ ng m}^{-3}$, and $r^2 = 0.81$. Due to reduced emissions on weekends, we would expect PAH emissions and concentrations to be lower on weekends. The possible causes of this discrepancy will be discussed below.

SPAH is strongly correlated with both CO and naphthalene. Figure 4 shows 15-min averages of SPAH versus CO during the entire field campaign. The slope of the regression line, forced through zero, is $18.7 \pm 0.2 \text{ ng m}^{-3} \text{ ppm}^{-1}$, with $r^2 = 0.70$. Figure 5 shows SPAH versus all available naphthalene measurements ($n=24$), which are time-integrated over 4- to 10-h periods. For the relationship between SPAH and naphthalene, the slope is 0.024 ± 0.001 with $r^2 = 0.92$.

4. Discussion

4.1. Method intercomparison

The three PAH measurement techniques have complementary strengths. Collection of time-integrated samples with GC/MS analysis allows detailed, isomer-specific speciation and the ability to quantify both gas- and particle-phase concentrations. Aerosol photoionization is a sensitive and fast technique that detects total surface PAH concentrations. Aerosol mass spectrometry provides speciation by MW, size distributions, and measures of other aerosol components at 4-min resolution.

While the three methods generally report similar trends and the same order of magnitude for the concentrations, certain disparities may emphasize methodological limitations, transformation of PAHs, and/or uncertainties in calibration. Figures 2 and 3 show that APAH* is generally higher than SPAH, except during the morning rush hour between 06:30–08:30, when they are similar. The likely cause of lower SPAH values is the fact that the PAS responds only to surface-bound PAHs. The difference in mass loadings is also captured in the large intercept ($\sim 25 \text{ ng m}^{-3}$) of the correlation between APAH* and SPAH. As the particles are coated by condensation of the products of the active photochemistry in Mexico City (Shirley et al., 2005; Volkamer et al., 2005), the photoionization sensor becomes blind to the “buried” PAHs while the AMS, which fully vaporizes the non-refractory portion of the particles (Slowik et al., 2004), continues to detect them. This leads to higher PAH measurements with the AMS when aged particles dominate, i.e. during most of the day except the morning rush hour.

An intriguing observation is that while SPAH concentrations are higher on weekdays than on weekends, APAH* concentrations are actually higher on weekends, particularly between midnight and 11:00. A buildup of aged particles, containing coated PAHs, during the week and peaking on weekends may explain the observation. However, data are insufficient to confirm this hypothesis. Alternatively, sources of emissions that produce particles containing coated PAHs may be important on Friday and Saturday nights (Saturday and Sunday early mornings). Concentrations of carbon monoxide (CO) and

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black carbon (BC), indicators of gasoline and diesel engine activity, respectively, are not higher on Friday and Saturday nights and are not significantly different on weekends versus weekdays; so vehicle traffic does not appear to be the cause of higher APAH* on weekends.

5 During periods with PAH loadings below 30 ng m^{-3} , FPAH* and SPAH agree well, as shown in Fig. 1. During periods of elevated PAH loadings (07:00–11:00 on Sunday 27 April and 21:00–07:00 on 27–28 April), FPAH* is higher than SPAH, except during one period dominated by fresh emissions (07:00–11:00 Tuesday 29 April). Again, SPAH may be lower because it does not include PAHs on aged particles that have been
10 coated by secondary aerosol. During the period of fresh emissions when SPAH is higher, the PAHs captured on the filters are exposed to several hours of ambient air during the MCMA's most photochemically active period, i.e. weekday mornings; and the PAHs may be subject to reaction artifacts in the sampler. This type of degradation can reduce PAH concentrations by 50% (Schauer et al., 2003). The real-time SPAH and APAH measurements are much less susceptible to such artifacts.

15 In summary, while SPAH and APAH* agree at higher concentrations, SPAH is consistently lower than APAH* at lower loadings. In contrast, SPAH and FPAH* agree better at lower concentrations. The reasons for the disagreements are not fully known, and laboratory calibration experiments are needed to explore the differences further.

20 4.2. PAH sources

The limited number of samples and lack of precise information about Mexican source profiles in this study preclude a quantitative source apportionment. However, evidence suggests that motor vehicles are the major source of PAH emissions in Mexico City. Motor vehicles are responsible for 99% of CO emissions in the area (Secretaría del
25 Medio Ambiente, 2003), and PAH and CO concentrations are correlated, as shown in Fig. 4. The strong correlation between SPAH and naphthalene, shown in Fig. 5, also indicates that vehicles are a key source of particulate PAHs, if Mexico City follows the pattern of Southern California, where vehicles are responsible for 53% of naphthalene

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emissions (Lu et al., 2004).

These results provide insight into the diurnal patterns of gasoline- versus diesel-powered vehicles in the MCMA. Benzo[ghi]perylene can be used as a marker of gasoline-powered vehicle activity, as it has the highest emission factor of the 16 priority PAHs in light-duty vehicle exhaust but is not detected in heavy-duty diesel exhaust (Marr et al., 1999). During the 07:00–11:00 period, benzo[ghi]perylene accounts for 25% of the total particle-phase PAHs; and during the three remaining periods, it accounts for only 7–8% of the total. This result suggests that gasoline-powered vehicles are an especially significant source of PAHs during the morning rush hour.

On the other hand, methylphenanthrene can be used as an indicator of diesel exhaust (Westerholm et al., 1991). The relative contribution from diesel exhaust appears to increase during 11:00–16:00 relative to the earlier period, as reflected in methylphenanthrene levels that are of similar magnitude (Fig. 1) or increasing (27 April, data not shown), while concentrations of other PAHs except retene decrease significantly, presumably in response to a rising mixing height and reduced source activity.

The ratio of methylphenanthrenes/phenanthrene has been utilized in source apportionment studies to estimate the relative contributions of gasoline versus diesel emissions (Lim et al., 1999; Nielsen, 1996). Methylphenanthrenes/phenanthrene ratios of 1.5 for gas-phase emission measurements (Westerholm et al., 1991), and ranging from 1.7–8 for particle-phase emissions (Lim et al., 1999; Takada et al., 1990; Westerholm et al., 1991) have been reported for diesel vehicles, while for gasoline vehicles ratios of 0.2–0.7 have been reported (Takada et al., 1990; Westerholm et al., 1988). Although there are significant variations in reported ratios, and operating parameters such as the engine load are known to affect the ratio (Jensen and Hites, 1983), all the ratios reported for diesel emissions are >1 and those for gasoline emissions <1 . Figure 1 shows that the ratio of methylphenanthrenes/phenanthrene is <1 during the morning rush hour period and is >1 during the rest of the day. This observation is consistent with the dominant contribution of gasoline emissions to particle-phase PAH concentrations during the morning rush hour and with the increased importance of diesel emissions

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during the rest of the day.

Different diurnal traffic patterns of gasoline- and diesel-powered vehicles can explain these observations. In California, gasoline vehicle traffic peaks during the morning and evening rush hours (Marr et al., 2002). However, diesel vehicle traffic starts out slowly during the traditional morning rush hour and then peaks during the late morning and early afternoon. If this pattern were also true in the MCMA, then we would expect emissions from gasoline vehicles to be higher during the 07:00–11:00 period compared to the 11:00–16:00 period and the opposite effect for diesel vehicles. The observed PAH concentrations support this hypothesis. Additionally Fig. 6 shows that BC, which is associated with diesel exhaust, peaks 1–2 h later in the morning compared to CO, which is associated with gasoline exhaust.

The diurnal patterns of individual PAH masses, shown by Dzepina et al. (2005)¹, also suggest that activity patterns for gasoline versus diesel vehicles differ, with diesel vehicle traffic lagging the traditional early morning rush hour. The concentrations of lighter MW PAHs ($m/z=202$) peak one hour later and do not decrease as rapidly compared to concentrations of the heavier MW PAHs. Filter-based measurements of PAHs in a roadway tunnel have shown that gasoline vehicles have higher emission factors of the larger PAHs and that diesel vehicles have higher emission factors of the smaller PAHs (Marr et al., 1999). This fact, combined with diesel vehicle traffic that peaks after the morning rush hour, would produce the observed pattern.

The presence of triphenylbenzene and retene suggest that other sources also contribute to ambient PAHs in the MCMA. The high concentrations of triphenylbenzene at night are an indicator of garbage burning (Simoneit et al., 2005; Tong et al., 1984), a common nighttime activity in the MCMA. Concentrations of retene, a wood smoke marker (Ramdahl, 1983), are especially high on 27 April (not shown), when a forest fire burned for one hour on a nearby hill, Cerro de Estrella, starting at ~18:00.

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4.3. PAH transformations

Figure 6 shows average diurnal cycles of SPAH, APAH*, CO, BC, hydrocarbon-like organic aerosol (HOA), and oxidized organic aerosol (OOA) during non-holiday weekdays. HOA is an indicator of freshly emitted particles, which are likely to be primary combustion aerosols in Mexico City, while OOA is a highly oxygenated aerosol, which is likely to be secondary organic aerosols from the photooxidation of aromatics and other precursors (Zhang et al., 2005a, c). OOA may also be associated with biomass burning emissions during the latter part of the campaign. Note that the y-axes start at the background concentration of each pollutant, not at zero. While APAH*, SPAH, CO, BC, and HOA concentrations rise in concert starting at 06:00 each morning, SPAH falls off much more quickly and diverges from APAH*, CO, and BC at 09:00.

There are two hypotheses that could most likely explain the faster decay of SPAH relative to other indicators of vehicle emissions. The timing of the decay in SPAH concentrations, i.e. during the hours of the most active photochemistry in Mexico City, suggests that a photochemical mechanism may be responsible. First, coating of PAH-containing particles by condensation of secondary inorganic or organic aerosol could shield the PAHs from detection by photoionization. Electron microscopy of individual particles collected during the field campaign indicates that extensive processing of soot particles, including condensation of sulfate, can occur within 30 min to several hours (Johnson et al., 2005). For PAHs to be detected by photoionization, electrons must be ejected from the molecules and must be able to escape from the surface of the particle. Coating of PAH-containing particles could reduce the SPAH signal by making it less likely for PAHs to be photoionized or for ejected electrons to escape the particle.

Previous experiments have shown that paraffin coatings of 30–60 nm completely inhibit the photoionization signal (Niessner et al., 1990). Sufficient ammonium nitrate and secondary organic aerosol (SOA) may be produced in Mexico City's atmosphere to coat primary particles and at least partially inhibit the detection of surface-bound PAHs by photoionization. The following analysis assumes that inorganic aerosol and

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SOA condense on preexisting particles, rather than homogeneously nucleate, which is consistent with observations (Dunn et al., 2004). During the late morning, OOA reaches $6 \mu\text{g m}^{-3}$ above its background value (Fig. 6). If we assume that OOA represents SOA and has a density of 1.1 g cm^{-3} (Bahreini et al., 2005), then the excess OOA is equivalent to a volume concentration of $6 \times 10^{-12} \text{ m}^3 \text{ m}^{-3}$. Divided over a maximum aerosol surface area of $1 \times 10^{-5} \text{ cm}^2 \text{ cm}^{-3}$ estimated from the AMS measurements, this amount of SOA can coat the particles to a thickness of 6 nm. Ammonium nitrate concentrations, which share a similar diurnal pattern to that of OOA, reach $12 \mu\text{g m}^{-3}$ above background in the late morning (Salcedo et al., 2005b) and can contribute an additional 7 nm of thickness to the coating. The density of inorganic aerosol is assumed to be 1.7 g cm^{-3} (Bahreini et al., 2005). The fractal nature of primary particles (DeCarlo et al., 2004; Slowik et al., 2004; Zhang et al., 2005b) and unknown division of surface area between primary and secondary aerosol contribute uncertainty to this estimate. Although the total calculated coating thickness of 13 nm is only an approximation, it is of the order of magnitude needed to suppress, at least partially, the photoionization signal.

Additionally, we have performed an exploratory laboratory experiment with the photoionization aerosol sensor and found that its response dropped by a factor of ten when soot particles were coated with oleic acid, while the AMS response did not change. The magnitude of surface coating and its relevance to ambient conditions were not characterized in this exploratory experiment.

The size distributions of individual PAH masses, presented by Dzepina et al. (2005)¹ also support the idea that particles containing PAHs are coated, or at least grow in size, throughout the day. Between 10:00 and 14:00, the mode of m/z 's 202 and 226 occurs at 300–400 nm. Later in the afternoon between 14:00 and 18:00, the size distributions broaden such that the peak extends beyond 600 nm. The shift to larger diameters, which is observed for all species in the city, is likely due to coagulation and condensation of secondary aerosol on preexisting particles (Dzepina et al., 2005¹).

The second hypothesis is that heterogeneous reactions of PAHs on the surfaces of

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particles may be responsible for the faster decay of SPAH versus other related pollutants. In the gas phase, the dominant loss process of PAHs during the daytime is reaction with the OH radical (Arey, 1998; Atkinson and Arey, 1994). In the particle phase, PAHs may undergo photolysis or reaction with oxidants such as OH, ozone, nitrogen oxides, and nitric acid; and the rate of reaction depends on the nature of the underlying particles and meteorological factors (Behymer and Hites, 1988; Calvert et al., 2002; Finlayson-Pitts and Pitts, 2000; Kamens et al., 1986, 1988, 1985). Recent laboratory experiments suggest that OH addition to pyrene and subsequent reactions can lead to its removal from particles, in the form of volatile products (Molina et al., 2004). A group of 11 PAHs adsorbed on graphite particles were found to have similar reactivities with OH (Esteve et al., 2004). As reaction with OH is the dominant loss process of gas-phase PAHs (Atkinson and Arey, 1994), we therefore investigate the heterogeneous reaction rate of OH with particle-phase PAHs to determine its role in the loss of PAHs in Mexico City. Heterogeneous oxidation by ozone may also be an important sink for PAHs (Donaldson et al., 2005), so the results presented here represent a lower limit of their reactive decay.

The analysis focuses on the period 09:00–10:00, when SPAH concentrations diverge from the others (Fig. 6). The predicted heterogeneous reaction rate R_{het} is

$$R_{\text{het}} = \frac{\omega\gamma}{4}A[\text{OH}] \quad (1)$$

where ω is the mean thermal velocity of OH (cm s^{-1}), γ is the heterogeneous reaction probability, A is the surface area concentration of PAHs ($\text{cm}^2 \text{cm}^{-3}$), and $[\text{OH}]$ is the OH concentration (molec cm^{-3}) (Bertram et al., 2001; Ravishankara, 1997). At 298 K, the mean thermal velocity of OH is $66\,100 \text{ cm s}^{-1}$. We assume a reaction probability of 0.5, which is consistent with experimental data for PAHs (Bertram et al., 2001).

At 09:00, the typical weekday SPAH concentration is 50 ng m^{-3} . Based on PAH speciation profiles during the morning hours, the average molecular mass of the mixture is 258 g mol^{-1} , so the corresponding surface PAH density is $1.2 \times 10^{14} \text{ molec m}^{-3}$. Assuming a molecular cross section of 1 nm^2 corresponding to benzo[a]pyrene (Karcher and

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Fordham, 1987), whose molecular mass is close to the average, we obtain a surface area PAH concentration of $1.2 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$. For comparison, this value is $\sim 10\%$ of the total surface area estimated from the AMS of $\sim 10^{-5} \text{ cm}^2 \text{ cm}^{-3}$ during 09:00–10:00. Given a typical OH concentration in Mexico City at 09:00 of $1.4 \times 10^6 \text{ molec cm}^{-3}$ (Shirley et al., 2005; Volkamer et al., 2005), the resulting R_{het} predicted by Eq. (1) is $14\,000 \text{ molec cm}^3 \text{ s}^{-1}$.

The ratio of the typical PAH concentration at 09:00 to R_{het} gives a characteristic lifetime of 2.3 h for heterogeneous reaction of OH with particulate PAHs. Given the uncertainty in reaction probability and other inputs to Eq. (1), we cannot rule out heterogeneous reactions as a mechanism for PAH loss. PAH reaction products, such as quinones, hydroxyl-PAHs, and nitro-PAHs were not found in the AMS signal (Dzepina et al., 2005¹), but at this point in its development, the AMS is not specific or sensitive enough to detect them at the very low expected concentrations. However, because APAH* does not also fall off at the same rate as SPAH at this time of day, coating of the particles is a more likely explanation for the rapid decay of SPAH.

5. Conclusions

Particulate PAH concentrations were measured by three different methods in Mexico City in April 2003: analysis of time-integrated filters, aerosol photoionization, and aerosol mass spectrometry. Speciated measurements suggest that motor vehicles are the predominant daytime source of PAHs and that wood and garbage burning are important nighttime sources. Particulate PAH concentrations are correlated with both CO and naphthalene. During the morning rush hour, total particulate PAH concentrations rise to a maximum of $\sim 110 \text{ ng m}^{-3}$ between 07:30–08:00 and then decrease throughout the remainder of the morning to $\sim 20 \text{ ng m}^{-3}$ in the afternoon. Overnight concentrations rise as high as 50 ng m^{-3} . The more rapid decrease in surface versus bulk PAH concentrations during the late morning suggests that freshly emitted combustion-related particles are quickly coated by secondary aerosol material in Mexico City's

atmosphere, and may also be transformed by heterogeneous reactions.

These results have important implications for public health and for climate. The diurnal pattern of ambient concentrations implies that exposure to PAHs will be much higher during the morning rush hour compared to the rest of the day. The rapid transformation of particle-phase PAHs during the morning suggests that the toxicity of fresh versus aged particles may differ. If PAHs are coated by other compounds, their bioavailability may decrease. Likewise, rapid coating of primary soot particles suggests that internally mixed particles containing black carbon cores will be prevalent in the outflow of Mexico City, which will lead to enhanced absorption of radiation and thus a larger perturbation of the regional radiation balance by these particles.

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Table 1. Particulate PAHs quantified by each method.

Species	M	GC/MS	PAS ^a	AMS ^b
Acephenanthrylene	202	FPAH ^c	SPAH	APAH*
Fluoranthene	202	FPAH*	SPAH	APAH*
Pyrene	202	FPAH*	SPAH	APAH*
1,2-Benzofluorene	216	FPAH		APAH
2,3-Benzofluorene	216	FPAH		APAH
1-Methylpyrene	216	FPAH		APAH
Methylated MW 216 species (4 isomers)	216	FPAH ^c		APAH
Benzo[ghi]fluoranthene	226	FPAH*	SPAH	APAH*
Cyclopenta[cd]pyrene	226	FPAH*	SPAH	APAH*
Benz[a]anthracene	228	FPAH*	SPAH	APAH*
Benzo[c]phenanthrene	228		SPAH	APAH*
Chrysene/triphenylene	228	FPAH*	SPAH	APAH*
Retene (1-methyl-7-isopropyl-phenanthrene)	234	FPAH		
Methylated MW 226 species (3 isomers)	240	FPAH ^c		APAH
Methylated MW 228 species (10 isomers)	242	FPAH ^c		APAH
Benzo[b+j+k]fluoranthenes	252	FPAH*	SPAH	APAH*
Benzo[a]pyrene	252	FPAH*	SPAH	APAH*
Benzo[e]pyrene	252	FPAH*	SPAH	APAH*
Perylene	252	FPAH ^c	SPAH	APAH*
Benzo[ghi]perylene	276	FPAH*	SPAH	APAH*
Indeno[1,2,3-cd]pyrene	276	FPAH*	SPAH	APAH*
Coronene	300	FPAH*	SPAH	APAH*
1,3,5-Triphenylbenzene	306	FPAH		

* These species are included in the modified FPAH* and APAH* totals which are intended for comparison to SPAH.

^a The PAS response, denoted SPAH here, has been calibrated against the sum of these PAHs. The signal is influenced by ionization potential and molecular size (Niessner, 1986).

^b The AMS response includes [M], [M-H], and [M-H₂] ions (see text and Dzepina et al., 2005¹, for details) but does not differentiate between isomers.

^c Identifications are based upon retention indices for these species. In all other cases, individual standards were available to determine retention times and mass spectra.

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Table 2. Particle- and gas-phase measurements at CENICA during April 2003.

Parameter	Method	Instrument	Frequency	Limit of detection
Speciated gas- and particle-phase PAHs	Filter, PUF, and Tenax collection and analysis	GC + Hewlett Packard 5971A MSD or Agilent 5973 MSD	4–10 h	$<1 \text{ ng m}^{-3}$, $<10 \text{ ng m}^{-3}$ for naphthalene
Particle-phase surface PAHs	Aerosol photoionization	EcoChem Analytics PAS 2000 CE	1 min	1 ng m^{-3}
Particle size and composition, including PAHs	Aerosol mass spectrometry	Aerodyne Aerosol Mass Spectrometer	4 min	18 ng m^{-3}
Black carbon	Optical attenuation	Magee Scientific AE-31	5 min	$0.1 \mu\text{g m}^{-3}$
Aerosol active surface area	Diffusion charging	EcoChem Analytics DC 2000 CE	1 min	$1 \text{ mm}^2 \text{ m}^{-3}$
Carbon monoxide	Infrared absorption	API 300A	1 h	0.04 ppm

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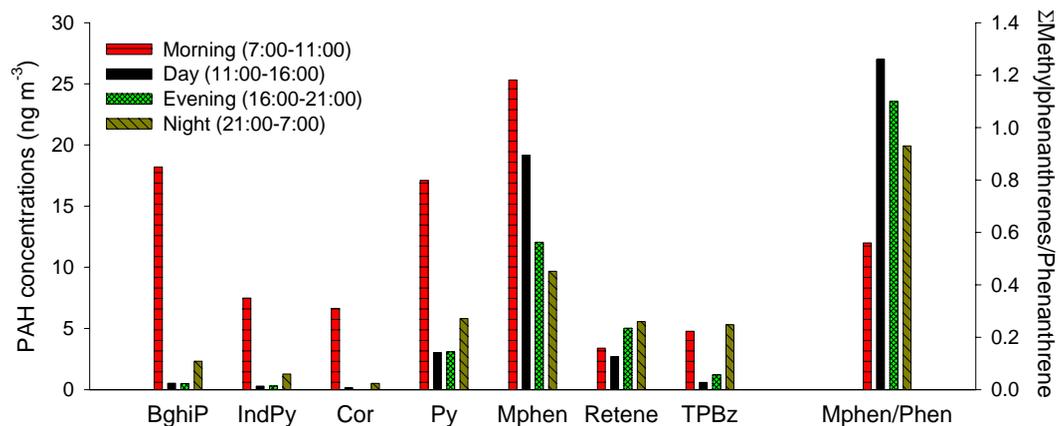


Fig. 1. Concentrations (gas + particle phases) of benzo[ghi]perylene (BghiP), indeno[1,2,3-cd]pyrene (IndPy), coronene (Cor), pyrene (Py), methylphenanthrenes (Mphen), retene (1-methyl-7-isopropylphenanthrene), and 1,3,5-triphenylbenzene (TPBz) on 29 April 2003. Also shown is the ratio Mphen/Phen, an indicator of the relative contribution of diesel versus gasoline vehicle exhaust. BghiP is a marker of gasoline vehicle exhaust, retene of soft wood combustion and TPBz of refuse burning.

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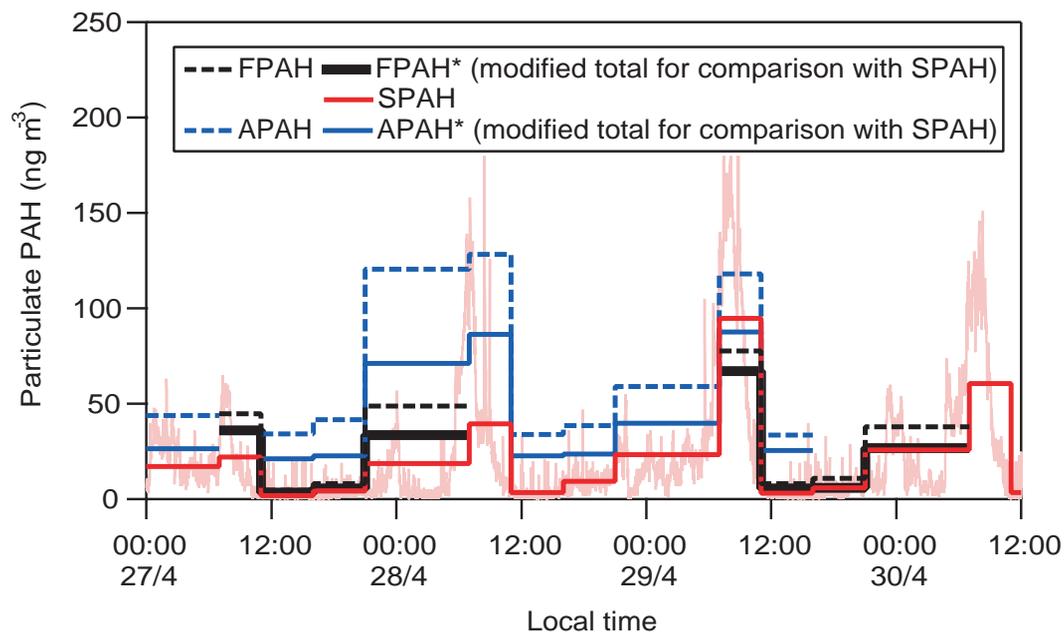


Fig. 2. Particulate PAH concentrations measured using filters (FPAH), photoionization (SPAH), and the AMS (APAH). The background time series shows 1-min SPAH.

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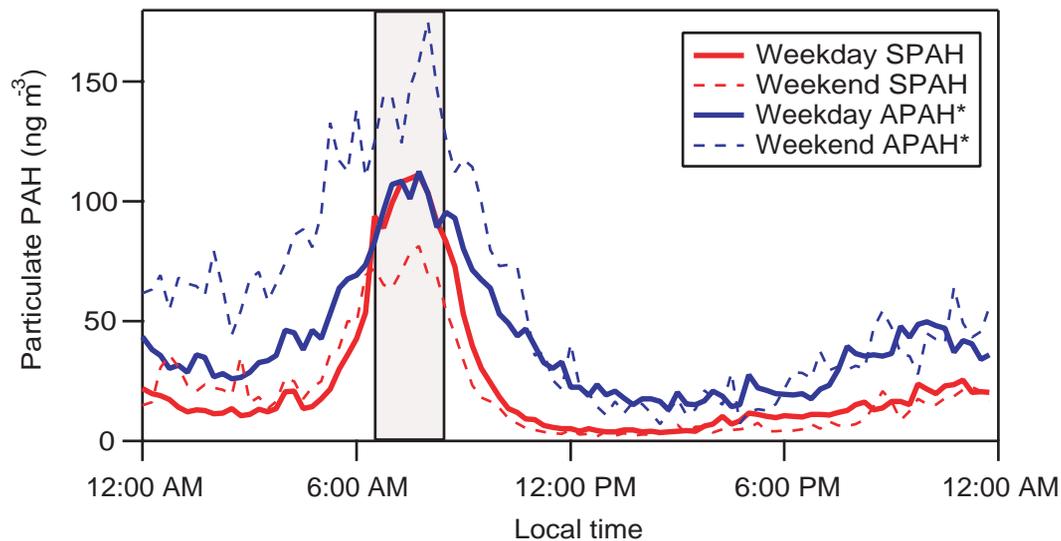


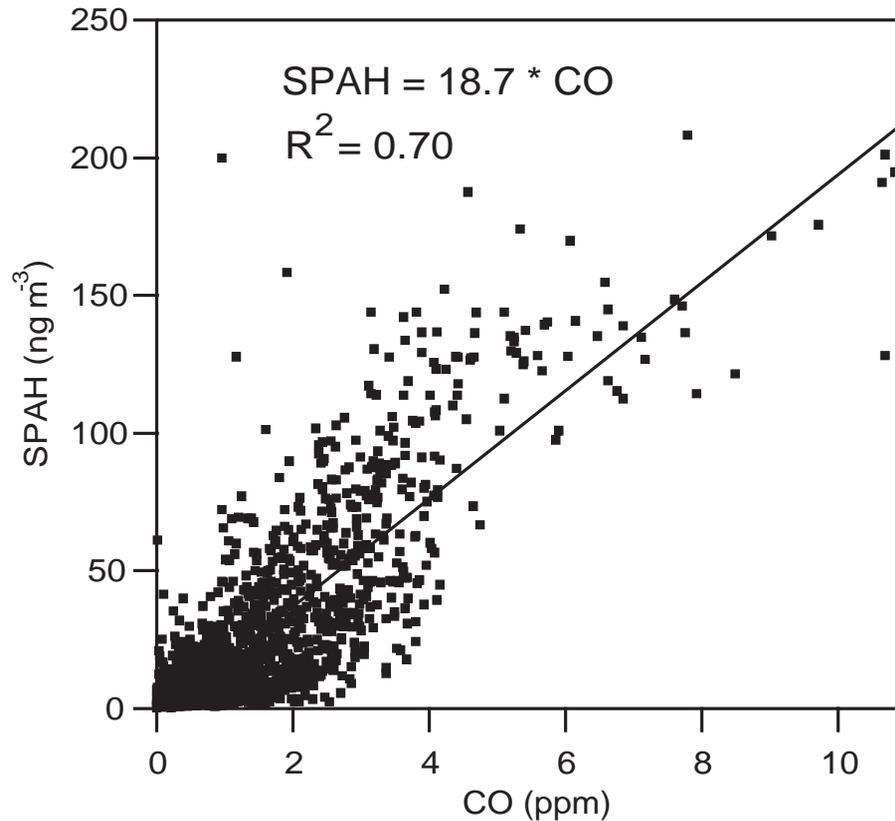
Fig. 3. Weekday, non-holiday diurnal cycles of SPAH and APAH*, excluding the holiday period, at 15-min resolution. The shaded area highlights the peak rush hour period between 06:30 and 08:30.

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**Fig. 4.** SPAH versus CO concentrations, 15-min averages.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

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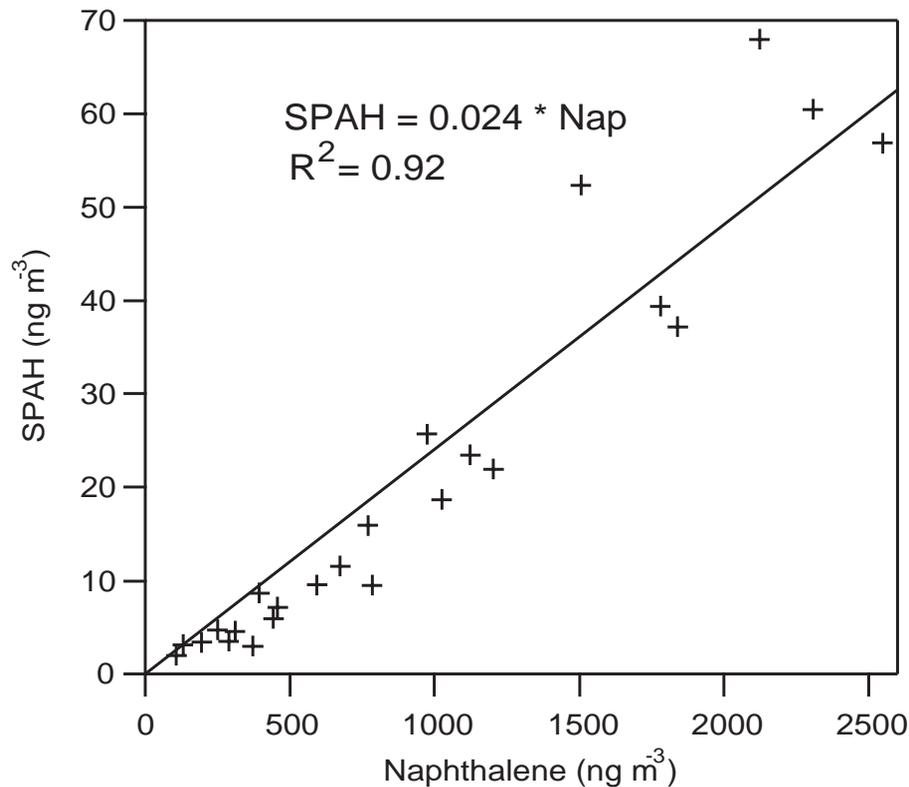


Fig. 5. SPAH versus naphthalene (gas-phase) concentrations.

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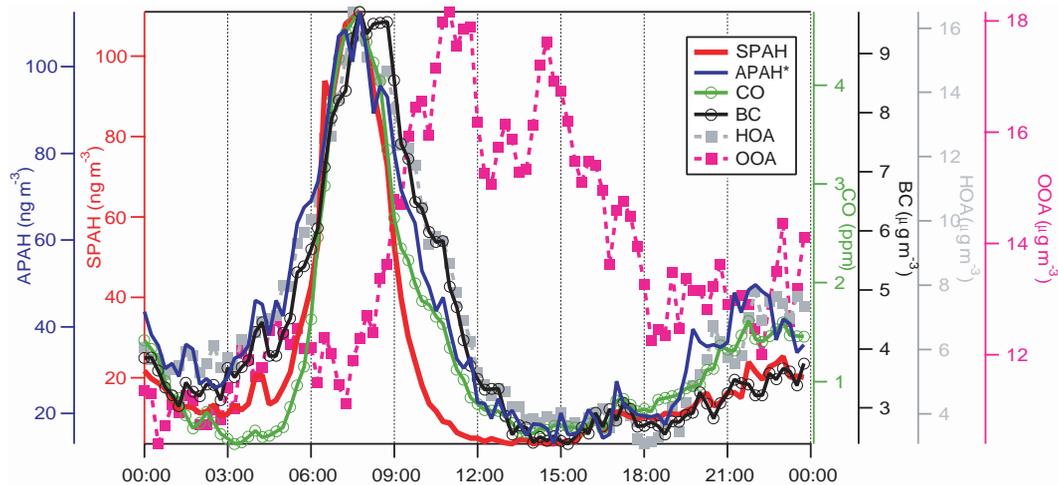


Fig. 6. Weekday, non-holiday diurnal cycles of SPAH, APAH*, CO, BC, HOA, and OOA, each on its own scale.

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