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Interactive comment on "Sources and transformations of particle-bound polycyclic aromatic hydrocarbons in Mexico City" *by* L. C. Marr et al.

L. C. Marr et al.

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The authors thank the editor and referees for their reviews and thoughtful comments. The reviewers agree that the paper presents new and important information on the measurement of PAHs by three different methods. We have addressed the reviewers' concerns by adding new details to the discussion of PAH ratios and their relationship to gasoline- v. diesel-powered sources and a new section on uncertainty. The revised manuscript addresses all specific and technical comments, as described below. We have also responded to the editor's suggestion to quantify uncertainties.

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Reviewer 1

1) When explaining the observed PAH concentration patterns immediately after emission by the engine exhaust, the authors could also consider the additional possibility that semi-volatile PAHs may condense on existing particles.

In the first paragraph of the Results section, we added the sentence, **“As PAHs are semi-volatile, some of the particle-phase compounds may have been emitted originally as gases in hot exhaust and then may have condensed onto existing particles as the mixture cooled.”**

2) Given that particle diffusional losses to a sample line often limits the lower cutoff, and that the aerosol mass spectrometer was housed in a building located approximately 50 m from the experimental platform, the authors should estimate the extent of the losses of the AMS samples to the sampling line, using the length and diameter of the sample line, the sampling flow rate, and the PAH size distributions.

The reviewer inferred that we used a 50-m shared sampling line between instruments because the manuscript describes the Aerosol Mass Spectrometer (AMS) as being located 50 m from the other two methods. In fact, each instrument used its own sampling line, none of which was longer than 5.3 m, and maximum particle losses due to diffusion and bends in the line were calculated to be 6.5% for 30 nm particles and 0.7% for 1 μm particles (Salcedo et al., 2006). We have clarified the description of instrument location and sampling lines by adding the following explanation in the third paragraph of the Experimental section: **“Due to physical limitations of the site, a shared sampling line was not feasible, so long tubing with its potential for diffusional losses of particles was not a factor in this intercomparison. Although the three methods were located at different points on the rooftop, they were believed to be sampling from the same air mass, as verified by the simultaneous detection of short-term spikes in ambient concentrations by the two real-time instruments located at opposite ends of the building.”**

3) In large urban centers, vapor-phase naphthalene concentrations are an order of magnitude (or more) higher than those of the other vapor-phase PAHs, and generally represent over 90% of all 16 priority PAHs present in both phases. The authors observed a strong correlation between SPAH and naphthalene (Fig. 5) and suggested that it indicates that vehicles are a key source of particulate PAHs. This assertion is highly speculative. Could the high correlation occur because the PAS instrument is responding to naphthalene readily available on the surface of the (lube oil) particles where they are dissolved? This would explain the faster decay of the SPAH signal in the late morning, compared with the APAH signal, as naphthalene slowly desorbs from the particle as ambient temperature increases towards noon!*

The photoionization aerosol sensor (PAS) that measures SPAH is not sensitive to naphthalene because its solid-phase ionization energy is 6.4 eV, above the 6.0 eV provided by the instrument's lamp. To clarify the point in the manuscript, we added the sentence, **"Because the energy associated with the PAS' lamp (6.0 eV) is less than the ionization energy of solid-phase naphthalene (6.4 eV) (Seki, 1989), the instrument does not detect naphthalene,"** in the second paragraph of subsection "2.2 Aerosol photoionization."

To address the reviewer's second point, we added a paragraph at the end of the Discussion section: **"Another factor to be considered in these analyses is the semi-volatile nature of PAHs and their ability to repartition between gaseous and particulate forms (Allen et al., 1996). Some PAHs present on the surfaces of freshly emitted combustion particles may slowly desorb from the particles as ambient temperatures increase in the late morning. This phenomenon may contribute to the faster decay of the SPAH versus APAH* signal, if it involves PAHs that are detected by the PAS but not by the AMS, i.e. three-ring PAHs. Improved measurement techniques, especially at high time resolution for the smaller particle-phase PAHs, are needed to explore this hypothesis further."**

4) Interpretation of data obtained with such diverse sampling and analysis techniques

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presents a real challenge. Because the PAS analyzer signal is a measure of total PAH adsorbed on carbon particles, the results are necessarily not comparable with the other two techniques. At best, it appears to represent a lower limit of PAH concentrations. Given the current use of the PAS instrument in a variety of applications, it would be important to know how the PAS compares with the other two techniques used to measure total PAHs, on an absolute, not relative basis. The authors should consider adding such comparison data, perhaps in a Table 2.

We have replaced the old Table 2, which listed measurement techniques, with new data that presents the total particle-phase measurements by each method during the overlapping measurement period: 27 and 29 April. The table also presents the ratio of total SPAH and APAH to FPAH. New text under the Results section and Discussion subsection "4.1 Method intercomparison" refers to the table:

"To facilitate interpretation of future studies using the PAS or AMS for measurement of PAHs, we compare total PAH concentrations determined by all three methods in Table 2. The totals shown for FPAH and APAH include all particle-phase PAHs detected by the filter and AMS methods, respectively. The table also shows ratios of SPAH and APAH to the more traditional FPAH. The ratio SPAH/FPAH falls in the range 0.5–1.0, except for one period on a weekday morning when the ratio is 1.7. The ratio APAH/FPAH ranges between 2.1–10, with the poorest agreement when PAH concentrations are low."

Information from the old Table 2 has been incorporated into the text under subsection "2.4 Additional measurements": **"Black carbon was measured at 4-min frequency by optical attenuation using an aethalometer (Magee Scientific AE-31, Berkeley, California)."**

5) The fact that the observations that the concentrations of CO and 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 appear to argue

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Discussion Paper

against a "build-up" of particles on weekends!

We removed the statement about buildup of particles during the week and modified the paragraph in subsection "4.1 Method intercomparison":

"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. The difference may not be significant, as the standard deviations of these averages are large and do in fact overlap. Concentrations of carbon monoxide (CO) and 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. Instead, sources of emissions that produce particles containing coated PAHs may be important on Friday and Saturday nights (Saturday and Sunday early mornings)."

6) The additional exploratory laboratory experiment findings with the photoionization aerosol sensor that its response dropped by a factor of ten when soot particles were coated with oleic acid (while the AMS response did not change) suggest that oil from fast cooking food preparations may also condense on the engine exhaust particles containing PAHs.

We now acknowledge in subsection "4.3 PAH transformations" that coating of particles may be due to condensation not only of secondary inorganic and organic aerosol but also of semi-volatile compounds emitted at high temperature, such as cooking oil. **"First, coating of PAH-containing particles by condensation of secondary inorganic or organic aerosol or of semi-volatile compounds that were emitted at high temperature, such as cooking oil, could shield the PAHs from detection by photoionization."**

7) Need to clarify whether the three instrument comparison campaign occurred during

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a 3-day intensive or a 5-week period. It is not clear from the text.

We added the sentence, **"The method intercomparison focuses on a three-day period, 27–30 April,"** to the third paragraph of the Experimental section. The third paragraph of the Results section reads, **"Figure 2 shows total particulate PAH concentrations measured by all three methods during the three days when they were operating simultaneously, 27–30 April."**

8) Clarify in the Abstract which species are referred to in "Ambient concentrations typically peak at 110 ng/m^3 *during the morning rush hour".*

The abstract now reads, **"Ambient concentrations of particle-phase PAHs typically peak at..."**

9) Stating LOD as less than a concentration (e.g. $<$*1 ng m*$^{-3}$*) is not common practice. Should specify the S/N ratio and the minimum concentration that the method can measure quantitatively.*

We removed the old Table 2, which included limits of detection and now instead discuss them along with estimates of methodological uncertainties in the text. A new more complete discussion of uncertainties, presented in the last section of this document, is provided under subsection "4.1 Method intercomparison." Under subsection "2.3 Aerosol mass spectrometer," we added, **"The limit of detection, estimated as three times the standard deviation of the reported concentrations when the AMS was sampling ambient air through a filter, is 36 ng m**$^{-3}$ **for total APAH and 24 ng m**$^{-3}$ **for the modified total APAH*. Detection limits scale with the inverse of the square root of the averaging time, so over 15-min periods, these limits will be 19 and 12 ng m**$^{-3}$ **for APAH and APAH*, respectively. Uncertainties in the method due to systematic and random errors, described in greater detail in Dzepina et al. (2006), are +45% and -35% of the reported concentration."** Under subsection "2.2 Aerosol photoionization," we added, **"The manufacturer reports a limit of detection of 10 ng m 3."**

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10) Clarify what is "Maundy Thursday 17 April"

The word “Maundy,” a reference to the Christian religious calendar, has been removed from the text.

11) Figures 3 and 6 should specify the number of days represented by the data.

The description of Figure 3 in the Results section now reads, **“Figure 3 shows the diurnal profiles (15-min averages) of SPAH and APAH* averaged over weekdays (20 days) and weekends (8 days) separately, excluding Thursday 17 April through Easter Sunday 20 April, when traffic and ambient pollutant concentrations were significantly lower than usual.”** The first sentence of subsection “4.3 PAH transformations” was modified to read, **“Figure 6 shows diurnal cycles of SPAH, APAH*, CO, BC, hydrocarbon-like organic aerosol (HOA), and oxidized organic aerosol (OOA) averaged over 20 non-holiday weekdays.”**

12) Qualification. Benzo[ghi]perylene can be used as a marker of gasoline-powered vehicle activity, as it has the highest particle-phase 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).

The qualification **“particle-phase”** has been added to the text.

13) There are missing authors in the reference Miguel, A. H., Kirchsetter, T. W., and Harley, R. A.: On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles, Environ. Sci. Technol., 32, 450-455, 1998.

The omission of Hering, S. V. as a co-author of this paper was an oversight that has been corrected.

Reviewer 2

We thank this reviewer for his/her thoughtful comments and for bringing to our attention

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the Zielinska et al. 2004 paper which has additional information on PAH ratios found for “in-use” vehicle emissions and fuels. The reviewer had four specific, substantive comments which are repeated below with our responses and resulting revisions to our manuscript.

1) The authors conclude that the ratios of methylphenanthrene/phenanthrene reported for diesel emissions are always $>$1 and those for gasoline emissions $<$1 (page 12753). This is not entirely true. For example, the ratio $>$1 for newer gasoline vehicles has been reported (Zielinska et al., 2004). Conversely, the ratios $<$1 were observed for heavy-duty diesel vehicles (Fujita et al., 2006). Taking into account the large variations connected with state of the vehicle maintenance, vehicle age and mileage, fuel type and condition of lubricating oil, emission control technology, vehicle operating mode (cold start, hot stabilized), engine load, and ambient temperature, this ratio is not a very good indicator of the relative contribution of diesel-versus gasoline-vehicle emissions.

The reviewer is correct that our statement that the ratio of methylphenanthrenes/phenanthrene (Mphen/Phen) is always $<$1 for gasoline vehicles should be modified, since the Zielinska et al. 2004 paper has a ratio of 1.02 for the composite of 5 test gasoline vehicles (the ratio was 1.6 for 3 diesel vehicles). Single vehicles considered out of the “normal range” of particulate emissions included a “white smoker”, a “black smoker” and a “new technology” low-emitting vehicle which had Mphen/Phen ratios of 1.4, 0.6 and 1.3, respectively. However, additional data in the Zielinska et al. paper support our conclusion that the change in the ratio of methylphenanthrene/phenanthrene observed after the morning rush-hour likely is caused by a greater contribution from diesel emissions relative to gasoline emissions than during rush-hour.

The major source of methyl-PAHs in emissions is likely to be unburned fuel, and the diesel fuels examined in the Zielinska et al. paper have at least an order of magnitude higher methylphenanthrene and dimethylnaphthalenes (μg/g) than the gasoline fuels (Zielinska et al., 2004). Naphthalene was the most abundant PAH in gasolines (Zielinska et al., 2004; Marr et al., 1999), while dimethylnaphthalene concentrations were greater than naphthalene in the diesel fuels. So an increase in diesel is likely to result in increased methylphenanthrenes and increased dimethylnaphthalenes. In part because of the large dilution resulting from the enhanced mixing height during the 11:00–16:00 time period, the ratios of methylphenanthrenes/phenanthrene and dimethylnaphthalene/naphthalene are more diagnostic for increased diesel emission contributions. In addition to naphthalene (discussed in our manuscript), we also measured methylnaphthalenes and dimethylnaphthalenes in Mexico City using Tenax TA sampling and we observed an increase in the ratio of dimethylnaphthalenes/naphthalene corresponding to the methylphenanthrene/phenanthrene increase, but we did not previously report this (because of our emphasis on particle-bound PAHs).

Although as the reviewer notes, many variables concerning the vehicles, including fuel and operating conditions may affect the ratio of methylphenanthrene/phenanthrene, we feel that at a single location, a change in the ratio most likely reflects a change in the on-road vehicle composition. As noted in the Discussion, the change in the ratio of gasoline/diesel vehicles is suggested not only by the changes in the ratios of methylphenanthrenes/phenanthrene and dimethylnaphthalenes/naphthalene but also by the later peak (1–2 h) in black carbon v. CO (see Fig. 6).

We cannot comment on the reported ratio of methylphenanthrenes/phenanthrene <1 for heavy duty diesel vehicles, because the quoted Fujita et al. 2006 manuscript has not yet been published.

2) Although the methylphenanthrene/phenanthrene ratio shown in Fig. 1 increases from <1 for the morning period (7:00–11:00) to >1 for the day period (11:00–16:00), it stays >1 for the evening (16:00–21:00) and close to 1 for the night (21:00–7:00) periods. If this ratio in an indicator of relative contribution of diesel- versus gasoline-vehicle emissions, it should presumably drop <1 for the evening rush hour traffic. How do the authors explain this inconsistency?

In contrast to the reviewer, we do not see an inconsistency in the fact that the methylphenanthrene/phenanthrene ratio does not return to <1 during the “evening rush hour” because the impact of fresh emissions will be less obvious at this time of day relative to the morning where a tight inversion layer exists and may, in fact, include a higher percentage of diesel traffic than in the morning. As we noted in the manuscript, we do not intend to imply a strict source apportionment, but rather to illustrate what emissions sources are likely present.

In response to Comments 1 and 2, we have now replaced the fourth paragraph in section “4.2 PAH Sources” with the following two paragraphs:

“The ratio of methylphenanthrenes to phenanthrene (Mphen/Phen) has been utilized in source apportionment studies to estimate the relative contributions of gasoline versus diesel emissions (Lim et al., 1999; Nielsen, 1996). For diesel vehicles, Mphen/Phen ratios of 1.5 for gas-phase emissions (Westerholm et al., 1991) and 1.4–8 for particle-phase emissions (Lim et al., 1999; Takada et al., 1990; Westerholm et al., 1991; Zielinska et al., 2004b) have been reported, while for gasoline vehicles, ratios of 0.2–0.7 (Takada et al., 1990; Westerholm et al., 1988) and most recently a ratio of approximately 1.0 for five in-use “normal particulate matter emitters” (Zielinska et al., 2004b), have been reported. While 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), in general ratios >1 have been reported from diesel emission sources.

The major source of methyl-PAHs in emissions is likely to be unburned fuel (Tancell et al., 1995; Williams et al., 1986), and methylphenanthrene and dimethylnaphthalene concentrations (μg g^{-1}) in diesel fuel are at least an order of magnitude higher than in gasoline (Zielinska et al., 2004b). While naphthalene is the most abundant PAH in gasoline (Marr et al., 1999; Zielinska et al., 2004b), dimethylnaphthalene concentrations are greater than naphthalene in diesel fuels. So an increase in the diesel contribution is likely to result in increased

emissions of methylphenanthrenes and dimethylnaphthalenes and an increase in the ratio of Mphen/Phen and dimethylnaphthalenes/naphthalene. Figure 1 shows that Mphen/Phen is $<$1 during the morning rush hour period and $>$1 during the rest of the day. In addition the dimethylnaphthalenes/naphthalene ratio shows a corresponding increase after the morning rush hour (dimethylnaphthalenes/naphthalene=0.09, 0.29, 0.09 and 0.15 corresponding to the morning, day, evening and night time periods in Fig. 1). These observations are 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 during the rest of the day.”

3) It is difficult to draw general conclusions based on the one-day measurements, as shown in Fig.1.

As noted at the beginning of the subsection “4.2 PAH Sources” we do not claim to be able to do a quantitative source apportionment, but rather we seek to indicate the potential PAH sources in Mexico City. The second day for which we have a complete GC/MS speciation, April 27, shows the same trends with benzo[ghi]perylene highest in the morning and the methyphenanthrene/phenanthrene ratio increasing after the morning rush hour.

4) The authors also mention on page 12573, that “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 PAH in light-duty vehicle exhaust but it is not detected in heavy-duty diesel exhaust.” First, 16 priority PAH included some gas-phase PAH, such as naphthalene, that has certainly higher emission factor than benzo[ghi]perylene (if properly measured with filters followed by adsorbents). Next, although benzo[ghi]perylene is usually not present or present in very low concentrations in diesel vehicle emissions under warm conditions, its concentrations in the emissions from diesel vehicles running in lower temperatures are much higher (Zielinska et al., 2004). This is also true for coronene and indeno[1,2,3-cd]pyrene, the other two higher mw PAH that are usually associated

Full Screen / Esc
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Interactive Discussion
Discussion Paper

with gasoline vehicle emissions. In general, PAH emissions from diesel-powered vehicles are much more variable than from gasoline-powered vehicles."

The reviewer is correct that naphthalene has a higher emission factor than benzo[ghi]perylene. The Marr et al. (1999) study which we cited looked only at particle-bound PAHs. As also described in response to Reviewer 1's Comment 12, we have revised the sentence to add "particle-phase" as follows: **"Benzo[ghi]perylene can be used as a marker of gasoline-powered vehicle activity, as it has the highest particle-phase 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)."**

The Zielinska et al. 2004 paper notes that consistent with the earlier work we cited from Miguel et al. (1998) and Marr et al. (1999), "Gasoline vehicle exhaust contained higher proportions of particle, high-molecular-weight PAH (indeno[cd]pyrene, benzo[ghi]perylene, and coronene) as compared with diesel exhaust."

Therefore, in response to Comment 4, we have made two changes to the first paragraph under the Results section. We modified the third sentence to read, **"Studies of vehicle emissions have shown that larger PAHs, in particular benzo[ghi]perylene, indeno[1,2,3-cd]pyrene, and coronene are emitted in gasoline-fueled vehicle exhaust (Marr et al., 1999; Miguel et al., 1998; Zielinska et al., 2004b), while alkylated phenanthrenes are associated with diesel vehicles (Benner et al., 1989),"** and we changed the last sentence to, **"As seen in Fig. 1, the diurnal patterns of indeno[1,2,3-cd]pyrene and coronene are similar to that of benzo[ghi]perylene."**

We also modified the last sentence in the Fig. 1 caption: **"BghiP, IndPy and Cor are markers of gasoline vehicle exhaust, retene of soft wood combustion and TPBz of garbage burning."**

In light of the ambient temperatures in Mexico City during the study, the "cold" start increase in benzo[ghi]perylene from diesel vehicles tested at 30 °F is not likely to be an important factor.

Additional modifications

Numerous changes to the manuscript have been made to address uncertainties in the findings. We added quantitative statements about measurement uncertainty in the Methods section. For aerosol photoionization, **"Correction factors for the individual instruments ranged from 0.82 to 1.34. From our experience with the PAS in this and a previous field campaign (Marr et al., 2004), we estimate its uncertainty to be 20%."** For aerosol mass spectrometry, **"Uncertainties in the method due to systematic and random errors, described in greater detail in Dzepina et al. (2006), are +45% and -35% of the reported concentration."** FPAH analyses of particles by addition of deuterated internal standards, Soxhlet extraction, HPLC fractionation and GC/MS quantification has been utilized on the NIST standard reference material; and the major uncertainties have to do with the sampling. Under subsection "4.1 Methodological comparison," we expanded upon and further qualified the discussion of FPAH sampling uncertainties with the modified paragraphs:

"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 21:00–7:00 on 27–28 April), FPAH* is higher than SPAH, except during one period dominated by fresh emissions (7:00–11:00 Tuesday 29 April). Again, SPAH may be lower because it does not include PAHs on aged particles that have been coated by secondary aerosol. During the period of fresh emissions when SPAH is higher, the PAHs captured on 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% for 1–2 day sampling periods with 70–80 ppb ozone levels (Schauer et al., 2003). The susceptibility to artifactual degradation during FPAH sampling varies among individual PAH species (Arey, 1998; Sanderson and Farant, 2005), and

lower FPAH v. APAH values for certain PAHs have been found (Dzepina et al., 2006). The real-time SPAH and APAH measurements are much less susceptible to such artifacts. A second source of uncertainty in the FPAH measurements is volatilization of PAHs from particles captured on the filters. The amount of PAHs captured on PUFs is 15–70% of the total FPAH concentration.

In spite of considerable uncertainties, the three methods often report similar PAH concentrations; and disparities likely reflect methodological differences. 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. Due to sampling uncertainties, FPAH should be considered as a lower limit due to the potential for PAH degradation and volatilization during sampling. Likewise, SPAH represents a lower limit of total particle-phase concentrations; the method appears to be sensitive only to those PAHs that are present on particles' surfaces. Finally, uncertainty remains in APAH quantification due to the need to subtract the non-PAH organic background from the AMS signal. The reasons for the disparities are not fully known, and laboratory calibration experiments are needed to explore the differences further."

As suggested by the editor, we added error bars to the figures where possible and where they would not render the figure illegible. Figure 3 now shows error bars of one standard deviation on the weekday average SPAH and APAH* traces. The new figure caption is, **"Fig. 1. Non-holiday weekday and weekend diurnal cycles of SPAH and APAH* at 15-min resolution. The shaded area highlights the peak rush hour period between 06:30 and 08:30. Error bars of one standard deviation are shown at 1-h intervals for the weekday time series."** In the text under the Results section, we also added the sentence, **"Error bars in the figure show one standard deviation at 1-h intervals for the weekday time series,"** and in the next paragraph, **"Because weekend days are fewer, the standard deviations of the weekend time series, not shown for reasons of legibility, overlap between SPAH and APAH*."**

In subsection “4.1 Method intercomparison,” we now address the differences in SPAH and APAH* in light of the newly presented uncertainties, **“The differences exceed the methodological uncertainty bounds during 7 of the 11 overlapping periods in Fig. 2 and exceed one standard deviation in the diurnal averages between 03:00–05:00 and between 09:00–23:00 in Fig. 3.”** New text acknowledges that the conclusions about differences between SPAH and APAH* on weekends are weakened: **“The difference may not be significant, as the standard deviations of these averages are large and do in fact overlap.”**

Concentrations of FPAH, which had been reported in the *Atmospheric Chemistry and Physics Discussions* paper under standard conditions, have been adjusted for ambient conditions, thus matching the units of SPAH and APAH. Figures 1, 2, and 5 were adjusted accordingly.

Upon further consideration of the AMS results, we added four additional species to Table 1. These are described under subsection “2.3 Aerosol mass spectrometer”: **“We also report a modified total APAH (APAH*) to facilitate comparison against SPAH. The modified total includes only PAHs with molecular masses of 202, 226, 228, 252, 276, and 300, as shown in Table 1. It excludes signals at molecular masses of 216, 240, 242, 264, 266, and 290 that correspond to alky-PAHs and/or PAHs with partially saturated rings (such as, 11H-cyclopenta[ghi]perylene), because the photoionization instrument’s calibration does not account for such species.”**

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