**Atmospheric
Chemistry
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Discussions**

Interactive comment on **"Particulate polycyclic aromatic hydrocarbon spatial variability and aging in Mexico City"** *by* **D. A. Thornhill et al.**

D. A. Thornhill et al.

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Reply to Comments: Reviewer 1

The authors thank Dr. Baumgardner for his review and thoughtful comments. He writes, "The manuscript is well written, the analysis presented with clarity and no apparent loose ends are left dangling." The principal difficulty he has with the work is that the PAH measurements may be confounded by coating of the particles. He therefore requests a reanalysis of the data focusing only on periods of uncoated particles. We have addressed this concern by recalculating the statistics using a more limited subset of data that excludes coated particles. We set a criterion for uncoated particles based on the relationship between PAHs and effective black carbon (BC), described in greater detail in the reply to his first comment, below. As the reviewer suggested, this reanalysis resulted in much stronger correlations. The revised manuscript addresses

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all specific and technical comments, enumerated below.

1) The principal difficulty that I have with the conclusions and the analysis approach is...that the PPAH gets "buried" under a coating, presumably of secondary organics that condense on the primary particle. This seriously confuses the evaluation, compromises the measurements and greatly weakens subsequent conclusions based on these measurements. What I strongly recommend is that all of the correlations and statistics be computed only for those time periods when the EBC and the PPAH have the same trends. It is only speculation on my part at the moment, but I believe that there will be a much higher correlation between T0, T1, Pedregal and Pemex when this is done, although the correlation with Santa Ana and Tres Padres will remain low because they are seeing air that is already aged and has the PPAH coated.

The reviewer has an excellent point, and to begin to address it, we have first introduced a new abbreviation, SPAH, for particulate surface PAH, to refer to measurements from the photoionization detector. This change emphasizes that the method is limited to PAHs on surfaces of particles. As the reviewer suggests, we have recomputed statistics for only those periods when BC and SPAH have the same trends and have explained the analysis with new text in the Results section:

"Pollutant ratios can provide insight into sources of emissions, chemical transformations, and spatial and temporal variability in concentrations. Because of the measurement artifact associated with the photoemission method, i.e. that it does not detect PAHs that are buried under other aerosol components, we must screen out such measurements when calculating ratios. To do so, we assume that the ratio of total SPAHs to BC should be approximately constant. Based on the regression results shown in Figure 5, we examine the time series of (SPAH + 10) / BC, with SPAH in ng m^{-3} and BC in μg m^{-3}. Excluding the period corresponding to the most active photochemistry between 8:00–13:00 when primary combustion particles are most likely to be coated by secondary aerosol, the diurnal average is 13.6$\pm$0.6 μg ng^{-1}. The coefficient of variation is only 4.4%. Between 8:00–13:00, the value is significantly lower, ranging from

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7.2 to 10.2 μg ng^{-1}. We therefore apply the criterion (SPAH + 10) / BC > 11 μg ng^{-1} to identify data points representing uncoated particles."

The reanalysis produced much stronger correlations between SPAH and other pollutants, and we subsequently updated the regression statistics shown in Table 2 and the corresponding text in the Results section:

"Table 2 shows the slope and standard error of the least–squares linear regression and correlation coefficient (it^2) between SPAHs and carbon monoxide (CO), total nitrogen oxides (NO$_y$), and carbon dioxide (CO$_2$) measured by the AML. The table presents results calculated using all SPAH data and only uncoated SPAH data, screened using the criterion previously described. In most cases, except for Pico Tres Padres, focusing on fresh SPAH produces higher slopes and stronger correlations. Measurements at Pedregal took place over a weekend, so results from this site may not be representative.

At the remaining sites (T1, Santa Ana, PEMEX, and T0), the strongest correlations and highest slopes tend to be observed at the more urbanized locations, T0 and T1. The different slopes are likely to be indicative of a different mix of sources at each site. Fresh SPAHs are reasonably well correlated with CO, with an R^2 of 0.72 to 0.93. The SPAH/CO slope is similar at T1, PEMEX, and T0 and an order of magnitude lower at Santa Ana. Fresh SPAHs are even more strongly correlated with NO$_y$; R^2 values range from 0.86 to 0.96 at the last four sites shown in Table 2. The SPAH/NO$_x$ and SPAH/CO$_2$ slopes are highest at T1 and T0, moderate at PEMEX, and lowest at Santa Ana. The regressions between PAHs and true NO$_x$ are not significantly different from those with NO$_y$, so henceforth, we will refer to the relationship as with NO$_x$. This notation will facilitate comparison with other studies, the majority of which use chemiluminescence and report results as NO$_x$."

Because screening the SPAH values constrains the usable data to specific hours of the day and because we are interested in the transport of all PAHs, whether coated or not, between sites, we did not recompute intersite correlation coefficients with the screened

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data. However, we did examine intersite correlation coefficients of BC, as a proxy for PAHs, and found similar results to those obtained with all SPAH data. We added the following sentence to the Results section:

"Correlations of BC between T0 and other sites were similar: –0.01 at Pico Tres Padres, 0.70 at T1, –0.06 at Santa Ana, 0.31 at PEMEX, and 0.95 at T0."

We also recalculated PAH v. AS and PAH v. BC regression lines shown in Fig. 5 using data representing uncoated particles only, which resulted in stronger correlations. Fig. 5 and text in the Results section have been modified appropriately. The reanalysis also resulted in slightly higher PAH/BC ratios, shown in Table 3, but the change did not affect the conclusions.

2) Effective BC –AETHALOMETERS DO NOT MEASURE BC – PLEASE CORRECT THIS.

In the Introduction, we added a paragraph that first refers to "light absorbing carbon" and then introduces the terms "black carbon" and "elemental carbon":

"Like PAHs, light absorbing carbon, also known as black carbon (BC) or elemental carbon depending on the measurement technique, originates from combustion sources (Bond and Bergstrom, 2006). BC is important because of its suspected toxicity, at least in the form of diesel exhaust particulate matter, and its role in radiative forcing. Coating of BC by condensation of non light–absorbing material changes throughout the day in Mexico City and alters the particles' optical properties, typically enhancing absorption (Baumgardner et al., 2007)."

We added the modifier "effective" to "black carbon" in the Abstract and the Methods section where we describe the measurement method:

"Effective black carbon (BC), operationally defined as the light–absorbing component of particles, was measured at 2–min intervals using an aethalometer (Magee Scientific AE–3) at a wavelength of 880 nm."

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The sentence emphasizes that the definition of black carbon is an operational one.

3) Likewise, the correlations between PPAH and BC, CO, NOx and CO2 should only be during periods when the trends are similar, up to the peak in the morning. In our measurements of CO and PPAH, we find very high correlations in the morning with the PPAH is fresh, as well as between EBC and PPAH and between light absorbing carbon (LAC), measured with the SP–2, and PPAH.

As the reviewer recommended, we reanalyzed the data during periods when PAHs are fresh and found much higher correlations between PAHs and BC, CO, NO_x, and CO_2. The slopes and R^2 values are reported in Table 2, along with the original statistics that considered all PAH data.

4) I recommend that in the methodology section the authors describe the problem of measuring PPAH with the PAS2000 and explain why they can only reliably evaluate the results when there is minimum chance that the PPAH is coated.

As the reviewer suggests, we also added an explanation to the Methods section and introduced a new abbreviation, SPAH, to refer to the surface PAH measurements from the PAS 2000:

"Our previous work has shown that the method is sensitive only to PAHs on the surfaces of particles and not those buried under other aerosol components (Marr et al., 2006), so measurements reported by the PAS are henceforth referred to as surface PAHs (SPAHs). In the Results section, we describe an approach for identifying measurements from the PAS that are not confounded by coating of the particles."

5) Finally, I would suggest that the reference to aging be removed from the title since there is not a clear line of arguments that link the results to aging, other than the coating of the PPAH – a process that has yet to be quantified and cannot be done in the present manuscript.

We changed the title to, "Spatial and Temporal Variability of Particulate Polycyclic Aro-

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matic Hydrocarbons in Mexico City."

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