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Atmospheric Chemistry and Physics 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 2

The authors thank the reviewer for his or her thoughtful comments. This reviewer agrees with the other reviewer that the manuscript is clearly written. We have addressed the reviewer's major concerns by conducting conducted a more detailed analysis of the role of meteorological conditions on the observations. We examined wind speed and direction and mixing depth in detail and added a new figure as a result. The revised manuscript addresses all specific and technical comments, as described below.

1) The paper, although clearly written, raises some important questions in its discussion section. Several of their receptor sites cannot be considered receptor sites at all

times because wind patterns in the metropolitan area are [not] very consistent, with well defined predominant direction, and vary with time of the day. The effect of atmospheric transport is mentioned, but no allusion is made to considering wind direction and speed in their calculations....I recommend the authors to include a more detailed analysis of the role of meteorological conditions, including wind direction and speed, inversion layer height, and stagnation, transport and photochemistry, in their data analysis. Doing so, I expect higher correlations between the different pollutants, over the different periods of the day when the trend of pollutants and meteorological conditions are similar.

To address the reviewer's concerns about meteorology, we have added new residence time analysis and concentration field analysis figures (Fig. 4) to the paper. The Methods section now explains:

"To evaluate transport to sites and identify source areas, we carried out residence time analysis and concentration field analysis (Ashbaugh et al., 1985; de Foy et al., 2007b; Seibert et al., 1994). Residence time analysis, calculated by summing back trajectories over a grid, produces a time exposure image of the back trajectories for a site, i.e. where the wind was coming from, over multiple hours. Concentration field analysis is the product of residence time analysis and pollutant concentrations at the receptor site each hour. The resulting concentration fields indicate the source areas or transport paths associated with high pollutant levels at a receptor site."

We added the text shown below to the Results section and added several references to these results in the Discussion section.

"Next, we examine transport within the basin. Figure 4 shows the residence time and BC concentration field analyses for T0 during 27–31 March, which were all Convection days, and T1 during 19–22 March, which were O_3–North and Cold Surge days. We chose to use BC as a proxy for PAHs because SPAHs can be diminished by coating of the aerosol, as described later in the text. In the residence time analysis, the mag-

ACPD
7, S8907–S8912, 2008

nitude in each grid cell represents the probability of a back trajectory passing through the cell relative to the total time interval of the trajectory. In the concentration field analysis, areas with high values are the result of back trajectories associated with high concentrations at the receptor site, whereas low values result from back trajectories associated with low concentrations. For both analyses, the values are normalized, with the maximum color value corresponding to the 90th percentile for that grid. The residence time analyses are plotted on a log scale, as they decrease rapidly away from the receptor site; and the concentration field analyses are plotted on a linear scale. While the residence time analysis shows that air parcels arriving at T0 are coming from all directions but less from the east, the concentration field analysis shows that high BC is associated with transport from the south, the center of the MCMA. For T1, the residence time analysis shows three preferred directions: northwest, east and south (gap flow). However, the concentration field analysis shows that high BC is not associated with transport from the gap flow, but rather with transport from the northeast, where the highway to the MCMA is located. The gap flow is strong and clean. For Pedregal, PEMEX, and Santa Ana, the residence time analyses agree with the wind transport episodes on those days; and the concentration field analyses all show that high BC is associated with transport from the central urban area of the MCMA. The results for Pico Tres Padres–transport from all directions and high BC associated with the urban area–are more uncertain because of the challenges in obtaining accurate trajectories on this hilltop site."

We also produced wind roses and polar graphs of concentrations as a function of wind direction, but these did not add more insight beyond what is shown in the residence time and concentration field analyses. Higher correlations were obtained when we isolated uncoated PAH data, described in the reply to the reviewer's second comment.

We investigated PAH concentrations as a function of mixing depth and while concentrations certainly peak while mixing depths are low, we found no day–to–day relationship between peak concentration and mixing depth. Given the ambiguity in inferring mixing

ACPD

7, S8907–S8912, 2008

depths (Shaw et al., 2007, ACPD, 7, 15025–15065) and the variability in PAH source strengths on a day–to–day basis, e.g. obviously lower concentrations on weekends, it is not surprising that a relationship is not apparent. During most of the daylight hours, surface PAH concentrations are very low and do not show enough day–to–day variability to allow elucidation of any relationship with afternoon mixing depths.

2) The authors of this paper suggested that particle coating with secondary aerosols may affect the reading of the PAS, which may be correct, but measurements done with the MS should not be affected by this process, and other phenomena should be presented to explain this decrease during photochemical periods. A better analysis of PAH and SOA interference may be achieved if data is analyzed in the early morning hours when photochemical activity is low, and primary sources are high.

As this reviewer and the other reviewer suggest, we reanalyzed the data only when photochemical activity is low and primary sources are high and obtained higher ratios of PAHs to other pollutants and stronger correlations. In fact, we used the ratio of PAH/BC to screen for periods when the particles are uncoated, as described in the reply to the other reviewer's first comment, added the new statistics to Table 2, and modified the explanatory text:

"Table 2 shows the slope and standard error of the least–squares linear regression and correlation coefficient (R^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.

ACPD
7, S8907–S8912, 2008

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."

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.

3) Finally, authors pointed that the correlation of PAHs with NOx, is likely due to diesel engines as sources of PAHs. Diesel engines are also high emitters of BC, which has been measured by aethalometer, and thus correlation between PAHs and BC should be high in source sites, and receptor sites with high impact of local sources.

We calculated PAH/BC ratios at each of the AML sites and now report these statistics in Table 2. We added the following text to the Results section:

"When all data are considered, SPAH/BC ratios are highest, approximately 10 ng 61549;g^{-1} at Pedregal, T1, and T0; and the correlations are strongest at these three sites and PEMEX. The correlations improve considerably for uncoated particles."

In light of the reviewer's comment, we also added the following paragraph to the Discussion:

"The ratios should be higher and correlations stronger in source areas and receptor

ACPD
7, S8907–S8912, 2008

sites with a large impact of local sources, and the results shown in Table 2 support this hypothesis. The highest ratios of SPAH to the four other pollutants and strongest correlations occur at T1 and T0. In MILAGRO, T1 is generally considered a receptor site, but concentration field analysis (Fig. 4) shows that it has strong local sources; and T0 is the closest site to the center of the MCMA. Values are intermediate at Pedregal and PEMEX, both of which are located toward the outskirts of the MCMA. Values are lowest at Pico Tres Padres and Santa Ana, the first of which can be thought of as a vertically downwind receptor site and the second of which is an outflow point of the MCMA basin."

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 15693, 2007.