

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

Anonymous Referee #1

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This manuscript explores the temporal and spatial variability of particulate PAH (PPAH) in Mexico City during 2003 and 2006 using measurements with a photoionization sensing (PAS) technique. Six sites in and around the center of Mexico City are sampled using a mobile unit during the month of March, 2006. The PPAH is compared with aerosol surface area (AS), black carbon estimated with measurements of the absorption coefficients and with CO, NO_x and CO₂. The authors conclude that PPAH has a large degree of spatial and temporal variability based on correlations between the five locations and the fixed T0 site. They also find low correlations between PPAH and AS as well as between PPAH and CO.

The manuscript is well written, the analysis presented with clarity and no apparent loose ends are left dangling. The principal difficulty that I have with the conclusions

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and the analysis approach is the same problem that Marr et al. (2006) had with their analysis of PPAH and that we had when we analyzed our results for the paper we wrote that also included PPAH measurements with the same technique (Baumgardner et al., 2007). Marr et al. had the advantage that they could compare the measurements from the photoionization detector with the AMS and GC-MS and with this comparison they conclude 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. The authors of this manuscript, after presenting the time series and various correlations, concede that the trends in the PPAH and very low correlations after the initial, early morning surge, are most likely due to the effect described by Marr et al. (2006). Considering the strong arguments of the earlier paper and given that many of the co-authors on the current manuscript are the same as in the Marr et al. paper, the authors could hardly argue otherwise. This being said, I am reluctant to give this paper a pass without asking for a moderate reanalysis and reorganization before it is accepted for ACP.

The PPAH measured with the PAS is clearly being biased by the coating after some period of time, dependent on the rate of production of whatever it is that is coating it and the processes that impact the rate of condensation; hence, the regression analysis and correlations that are based on all data points are a comparison of PPAH with and without the coating. The correlations between PPAH and AS shown in Fig. 4 show this distinctly where the afternoon slope shows very little PPAH with respect to the AS. What I strongly recommend is that all of the correlations and statistics be computed only for those time periods when the EBC (effective BC -AETHALOMETERS DO NOT MEASURE BC - PLEASE CORRECT THIS) and the PPAH have the same trends. All other periods should not be included in the comparisons as they don't represent an uncontaminated measure of the PPAH. 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.

Likewise, the correlations between PPAH and BC, CO, NO_x 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.

In summary, 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. Following this, the results can be presented with a greater degree of confidence in the fidelity of the measurements.

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.

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

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