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Interactive Comment

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

### Anonymous Referee #1

Received and published: 18 January 2006

General Comments This paper compares measurements of atmospheric PAH concentrations obtained by three different methods, including time-integrated filters, aerosol photoionization, and aerosol mass spectrometry. The study was carried out during what appears to be a 3-day intensive measurement period in Mexico City in late April 2003. The major objectives were to critically compare the different measurement approaches and methods, explaining the differences in PAH concentrations and patterns observed. The paper is well structured and presents new and important information on a class of highly toxic organic species.



#### **Specific Comments**

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.

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 50m 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.

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!

Interpretation of data obtained with such diverse sampling and analysis techniques 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.

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

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.

Technical Corrections (typing errors, clarifications, etc)

Need to clarify whether the three instrument comparison campaign occurred during a 3-day intensive or a 5-week period. It is not clear from the text.

Clarify in the Abstract which species are referred to in "Ambient concentrations typically peak at 110 ng/m3 during the morning rush hour".

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.

Clarify what is "Maundy Thursday 17 April"

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

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)".

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

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carbon from gasoline and diesel vehicles, Environ. Sci. Technol., 32, 450-455, 1998.

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