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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aerosol composition and source apportionment in the Mexico City Metropolitan Area with PIXE/PESA/STIM and multivariate analysis" *by* K. S. Johnson et al.

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Author Final Response Aerosol composition and source apportionment in the Mexico City Metropolitan Area with PIXE/PESA/STIM and multivariate analysis

The authors would like to thank the referee for many helpful comments and suggestions. In the following, we clarify several technical points in the work and answer questions raised in this review. Changes to the manuscript are noted.

1. Clarification of errors

– Mass calibrations were done with MicroMatter standards with 5% uncertainty. The error values provided in Sec. 4 refer to the fit of the PIXE spectrum by GUPIX. There

are two different spectral fit errors: a least squares fit error of the principal peak, and a statistical error which provides a reasonable lower limit alternative. For our data, the statistical error was used in PMF analysis. This information will be added to the text, and the statistical error values for PIXE elements will be added to Table 1. Errors for the abundant elements (S, Si, and K) were around 5% while most other elements ranged from 10% to 50%. This correction applies only to reporting errors within the text after re-examination of the spectrum fit information; the error values and PMF results remain unchanged.

2. "The finding that S may not be related to the Popocatepetl volcano emissions is in full agreement with the results published more recently by Miranda et al. (2005) ..."

– The reference will be added to Sec. 4.2 in the text.

3. "There is an assertion regarding the origin of soil-related particles (page 4007, line 10). The authors state that these particles are probably produced in the Rio Balsas region instead of the Texcoco Lake, as the work by Moya et al. (2004) tries to prove. In this regard, the results published by Vega et al. (2001) about the elemental characterization of soil particles with different origins in the MCMA may provide some help to solve this question."

– We had explored comparisons with Vega et al. (2001) that were initially not included in the discussion. Several comments will be added to the text in Sec. 4.4 to provide additional support for our conclusions. Overall we found that soil/dust particles during MCMA-2003 were similar in composition to paved roads, unpaved roads and/or tezontle soil, but less comparable to dry lake bed dust or agricultural soil. For example, element ratios calculated from PM2.5 average concentrations were: Fe/Si = 0.365 (compared with 0.231, 0.219, 0.345 for paved, unpaved roads, and tezontle soil, respectively), Ca/Si = 0.358 (0.295, 0.534, 0.363), Na/Si = 0.080 (0.008, 0.123, 0.041), and Al/Si = 0.296 (0.306, 0.288, 0.460). We note that Miranda et al. (2004) also found that soil-related particles collected from a southern MCMA site were similar in

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composition to paved/unpaved roads.

“Certainly, the authors have enough information to determine whether the elemental composition of the particles collected for this study is similar to the Texcoco Lake soils or not. Actually, this was attempted in the paper by Miranda et al. (2004) and they found the samples collected in downtown Mexico City have a composition similar to the Texcoco Lake soils. Moreover, the wind regimes were different during this study and those of Moya et al. and Miranda et al. Perhaps, some attention to these facts should be taken.”

–We did not observe the enrichment in Na, Cl, and Mg expected of dry lake bed dust, according to Vega et al. Although the lake bed dust also contained relatively high K, which was observed in our samples, the more likely source of K in our case was biomass burning emissions as discussed in Sec. 4.3. Since the CENICA location for MCMA-2003 was southeast of the downtown area, it may be expected that less similarity with the lake bed, toward the north, would have been observed in comparison to the study of Miranda et al. (2004) regarding the downtown site. In Sec. 4.4, we show that the wind direction after April 23rd, during a period of increasing soil element concentrations, comes predominantly from the southwest, rather than the north.

4. “The results in Fig. 1 correspond to contributions of the sources to the total mass measured with PIXE and PESA only, not to total mass measured with STIM. I think this should be explicitly written.”

– We will specify in Sec. 4 in the text that PMF analysis includes PIXE/PESA data.

5. “The information about H is confusing. In Table 1, there are results for H in the three stages; in Fig. 1, stage C does not present any contribution due to H and a very important factor containing H in stage A; Fig. 4 does not contain data for H (organic) in stage A and valid data in Stage C. The caption for Fig. 4 even explains the substrate was damaged for stage A. I suggest the authors to clarify this issue.”

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– A period of hydrogen data is missing for Stage A (sample no. 57-82) due to slight warping of the substrate during sampling that caused distortion of the PESA spectra. This was stated in the text (p. 4005, line 26-27). The remaining valid data points corrected for this missing interval were used to calculate the average, minimum and maximum concentration values for Stage A in Table 1. We will append H data in Fig. 4a in the revised manuscript to avoid confusion and will clarify this issue in the text.

The lack of a separate H/biomass burning factor in Stage C is explained by a strong correlation between H and soil elements; hydrogen could not be removed from the soil factor in PMF analysis. In Sec. 4.3 we report R2 = 0.58 correlation between soil in Stage C and organic H; this includes H in both Stages B and C. The correlation increases to R2=0.76 when only Stage C is considered and will be clarified in the text.

6. "I recommend the authors to improve the presentation of the results given in Figs. 2, 4 and 6 as the plots appear overloaded with data. In particular, data for Ni in Fig. 2 are too low as compared to those of SO2, while the results for all elements in Fig. 6 are virtually indistinguishable."

– Figures 2-4 are intended to illustrate the strong correlation among elements within various PMF factors to confirm and emphasize a common emissions source. The axis are clearly marked to enable reading the element concentrations; we will add a separate axis for Ni in Fig. 2 to improve the presentation. The individual time series of elements in Fig. 6 are nearly identical, making separate graphs unnecessary.

7. "The fact that Si (and therefore, soil derived particles) has higher concentrations in Stage C deserves especial attention, I think ... Is it possible to explain the high contribution of soil to the finest fraction with the existing information? Is it a new finding?"

– Soil/dust particles are typically most abundant in the coarse mode ($>$ 2.5 μm), and the fact that soil elements were found to comprise a large fraction of particle mass in Stage C (0.07-0.34 μm) was unexpected. Unfortunately we are not aware of previous measurements with comparable size resolution in Mexico City for comparison. It would

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be useful to follow-up with additional measurements and/or characterization of different size particles sampled from various dust/soil emissions sources. It is possible that the contribution of the soil component appears to be more prominent considering the loss of the volatile components during PIXE/PESA/STIM analysis and dominance of organic compounds during MCMA-2003 (Salcedo et al., 2006). While soil is a relatively minor component of total aerosol mass in the MCMA, its contribution becomes more important among the non-volatile fraction (Fig. 7).

8. "Somehow, I feel the comparison with other studies should be a little deeper."

– Comparisons with previous studies have been useful during our analysis, particularly for MCMA aerosol composition and speciation, the contribution and relative importance of various particulate emissions sources, and the role of sampling location on the different types of elements observed. Specifically, we show two instances when anthropogenic emissions came from the north (Sec. 4.2) in agreement with previous PIXE studies showing higher metal concentrations in the northern MCMA sites. An in-depth review of the previous measurements would only be possible by considering variability in meteorology, season, and a MCMA emissions inventory, which is beyond the scope of this paper. We note that an analysis of previous Mexico City aerosol studies from the point of view of the MCMA-2003 campaign has been done recently by Salcedo et al. (2006).

9. Minor Corrections

a.) The number of data points for PMF analysis were 130, 128, and 129 for Stages A, B, and C, respectively.

b.) Scanning Transmission Ion Microscopy (STIM) was used (Shutthanandan et al., 2002).

c.) Table 1 will be revised to include statistical error information; this error was used in PMF analysis.

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d.) The change has been made.

e.) While calculating an error estimate for the factorization is technically possible, its usefulness is not clear considering the fact that PMF accounts for measurement error and detection limits.

References

Miranda, J., Barrera, V. A., Espinosa, A. A., Galindo, O. S., Nunez-Orosco, A., Montesinos, R. C., Leal-Castro, A., and Meinguer, J.: PIXE analysis of atmospheric aerosols from three sites in Mexico City, Nucl. Instr. and Meth., B., 219-220, 157-160, 2004.

Miranda, J., Barrera, V. A., Espinosa, A. A., Galindo, O. S., and Meinguer, J.: PIXE analysis of atmospheric aerosols in Mexico City, X-Ray Spectrom., 34, 315-319, 2005.

Salcedo, D., Dzepina, K., Onasch, T. B., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Gaffney, J., Marley, N., Johnson, K. S., Zuberi, B., Molina, L. T., Molina, M. J., and Jimenez, J. L.: Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite, Atmos. Chem. Phys., 6, 925-946, 2006.

Shutthanandan, V., Thevuthasan, S., Disselkamp, R., Stroud, A., Cavanagh, A., Adams, E. M., Baer, D. R., Barrie, L. A., Cliff, S. S., Jimenez-Cruz, M., and Cahill, T. A.: Development of PIXE, PESA and transmission ion microscopy capability to measure aerosols by size and time, Nucl. Instr. and Meth.. B, 189, 284-288, 2002.

Vega, E., Mugica, V., Reyes, E., Sánchez, G., Chow, J. C., and Watson, J. G.: Chemical composition of fugitive dust emitters in Mexico City, Atmos. Environ., 35, 4033-4039, 2001.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 3997, 2006.