Atmos. Chem. Phys. Discuss., 6, S1017–S1021, 2006
www.atmos-chem-phys-discuss.net/6/S1017/2006/

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.

Anonymous Referee #2

Received and published: 29 May 2006

This paper represents a further contribution to the characterization of fine particulate matter in the Mexico City Metropolitan Area (MCMA). This is achieved through the elemental analysis of the samples and the use of receptor models. It should be pointed out that this kind of studies has been performed as early as 1988 (Aldape et al., 1991), or 1989 (Vega et al.. 1997), 1993 and 1996 (Miranda et al., 1996; Miranda et al., 2000). A more recent paper was published by Aldape et al. (2005). In general, I believe this paper has a good scientific quality, although the authors must give more emphasis to the particular contributions offered by their work. Specifically, I could identify as major advances the following:

1. This study was carried out with a high resolution in size and time; not many works in the MCMA have been published in the past with these characteristics. 2. The application of a multivariate statistical model (PMF) that may reduce (or even eliminate) other misleading mathematical procedures or results found in other techniques as factor analysis. 3. The use of simultaneous ion beam analysis methods to obtain more information that was obtained with the single application of PIXE or XRF. 4. The addition of information acquired during the same time period to try to explain the behavior found for several elements (such as backward trajectories).

Nevertheless, it was also possible for me to find several points that require clarification or in-depth discussions. I can mention, for example:

1. The authors explain that one of the factors considered in their multivariate statistical method is the experimental uncertainty (page 4001, row 21). I hope there is not confusion between the terms “error” and “uncertainty.” Below, in section 4 (page 4003, row 10), the authors claim that the analytical errors are below 0.1 % for major elements. There is no mention to uncertainties, although they should be given, for example, in Table 1. The authors also explain that the calibration of the detection systems was attained with known elemental standards and refer the reader to the work by Shutthanandan et al. (2002). Unfortunately, in this reference I could find no clear explanation about the calibration standards used. Traditionally, with PIXE or XRF analysis, elemental standards such as MicroMatter thin films are used, which usually quote a 5% uncertainty in the elemental concentration. Therefore, I would not expect an uncertainty below this value. As the uncertainty seems to play a fundamental role not only in the measured elemental concentrations, but also in the PMF method itself, I believe it is necessary to justify thoroughly the quoted uncertainty. Otherwise, the authors must explain how the conclusions obtained with PMF will change with larger uncertainties. In case the authors refer properly to analytical errors, there should be mention to certified reference materials used to estimate the errors.

2. The finding that S may not be related to the Popocatepetl volcano emissions is in full

ACPD

6, S1017–S1021, 2006

agreement with the results published more recently by Miranda et al. (2005). Although this work does not provide the careful results obtained with backward trajectories, they found an episode related to winds coming from the North. Moreover, the correlation of S with other fuel tracers as V and Ni was observed in most of the papers dealing with elemental characterization of aerosols in the MCMA.

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. 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.

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.

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.

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

ACPD
6, S1017–S1021, 2006

EGU

are too low as compared to those of SO2, while the results for all elements in Fig. 6 are virtually indistinguishable.

7. The fact that Si (and therefore, soil derived particles) has higher concentrations in stage C deserves especial attention, I think. Usually, it is found that the most important contributions of soil-related sources in the MCMA correspond to the coarse fraction in PM10, because of the mechanical origin of these particles (although I am aware this study refers only to PM2.5). Is it possible to explain the high contribution of soil to the finest fraction with the existing information? Is it a new finding?

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

9. Other minor corrections are: a. It is useful to mention the number of valid data obtained in the analyses, and thus justify the application of PMF. b. Please, clarify if it was the method Scanning Transmission Ion Microscopy (STIM) used, or only Transmission Ion Microscopy (i.e., was the ion beam scanned on the sample?). c. Once the uncertainty aspect has been clearly explained, the presentation of data in Table 1 should be modified, writing only significant figures in agreement with the uncertainty. d. It is also advantageous to include standard deviations or type A uncertainties in the concentrations given in Table 1. e. Use the term “principal” instead of “principle” (page 4000, line 18; page 4001, line 20). f. Is it possible to give uncertainties in the contributions of the factors in Fig. 1?

References

Aldape, F., Flores M., J., Diaz, R.V., Miranda, J., Cahill, T.A., Morales, J.R.: Two year study of elemental concentrations of atmospheric aerosols in Mexico City, Int. J. PIXE, 1, 373-388, 1991.

Aldape, F., Flores M., J., Flores A., J., Retama-Hernandez, A., Rivera-Hernandez, O.: Elemental composition and source identification of PM2.5 particles collected in downtown Mexico City, Int. J. PIXE, 15, 263-270, 2005.

ACPD

6, S1017–S1021, 2006

Miranda, J., Andrade, E., Lopez-Suarez, A., Ledesma, R., Cahill, T.A., and Wakabayashi, P.H.: A receptor model for atmospheric aerosols from a southwestern site in Mexico City, Atmos. Environ., 30, 3471-3479, 1996.

Miranda, J., Crespo, I., Morales, M.A.: Absolute principal component analysis of atmospheric aerosols in Mexico City, Environ. Sci. & Poll. Res., 7, 14-18, 2000.

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., Meinguer, J.: PIXE analysis of atmospheric aerosols in Mexico City, X-Ray Spectrom., 34, 315-319, 2005.

Moya, M., Grutter, M., and Baez, A.: Diurnal variability of size-differentiated inorganic aerosols and their gas-phase precursors during January and February of 2003 near downtown Mexico City, Atmos. Environ, 38, 5651-5661, 2004.

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., García, I., Apam, D., Ruíz, M.E., Barbiaux, M., Application of a Chemical Mass Balance Receptor Model to Respirable Particulate Matter in Mexico City, J. Air & Waste Manage. Assoc. 47, 524-529, 1997.

Vega, E., Mugica, V., Reyes, E., Sanchez, G., Chow, J.C., Watson, J.G.: Chemical composition of fugitive dust emitters in Mexico City, Atmospheric Environment 35, 4033-4039, 2001.

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