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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Transport of desert dust mixed with North African industrial pollutants in the subtropical Saharan Air Layer" *by* S. Rodríguez et al.

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We first want to thank the comments raised by Referee #1 about the PMF. We agree that the information provided about the application of PMF was not sufficient in the previous version of the manuscript. In the revised version of the ms we have added the information necessary to assess the rigorousness of the PMF analysis, including: a) minimum and maximum values of calculated mean signal-to-noise (S/N), percentage of data above the detection limit (%ADL), and relative errors for major and trace elements included in the PMF analysis; b) theoretical (degrees of freedom of the system) and

calculated values of the objective function Q; c) selection of the optimal number of sources; d) behaviour of the scales residuals; e) quality of the regression analysis of the factor scores from PMF (G matrix) to PM mass. Moreover, in this revised version of the ms, we have run again the PMF model by including phosphorus (P) in the data matrices. In the revised version of the manuscript, paragraphs 2.6 (Positive Matrix Factorization) and 3.4 (Positive Matrix Factorization modelling) were rewritten as follow:

2.6 Positive matrix factorization The identification of the chemical profile of the potential sources contributing to PM10 levels and composition was identified by analyzing the PM10 composition data set with the Positive Matrix Factorization model, version 2 (PMF2; Paatero, 1997). PMF model is a factor analytical tool that provides the chemical profile and contribution of the identified sources to each aerosol constituent (Paatero and Tapper 1994; Paatero 1997). The PMF model solves the matrix problem X= G$\times$F+E where X is the matrix of daily chemical speciated data while G and F are the unknown matrixes of factor scores (source contribution) and loading (source profile), respectively, and E is the matrix of residuals (difference between measured and calculated specie concentrations). The problem is solved by minimizing the objective function Q = E/S where S is the matrix of the uncertainty in each data value. The minimization of Q is based on the error-weighted least-squares method, thus the calculation of the matrix S is a crucial point so that the model gives the right weight to the input data and consequently the most reliable results. In the present study, the matrix S was calculated following the procedure described in Amato et al. (2009) and Escrig et al. (2009). With this method the uncertainties of the analytical procedures described in the section 2.3 are propagated jointly with the uncertainty related with the subtraction of the blank filters that are different filters from the sampled ones. The applied formula gives higher relative errors for small concentration data near the limit of detection. Once the uncertainties were calculated the number of species used within the PMF model was selected by looking at their signal-to-noise ratio (S/N) which provides a criterion to separate the species which retain a significant signal from the ones dominated by noise. Only species with S/N values higher than 2 were selected for

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the present study, thus weak species were not introduced in the model (Paatero and Hopke, 2003). Moreover, since S/N is sensitive to sporadic values much higher than the level of noise, the percentage of data above detection limit (%ADL) was used as complementary criterion for specie selection. The combination of both criteria allowed to select 21 species for the PMF2 analysis with averaged S/N, %ADL and relative error of major elements ranging respectively between 2.0, 32% and 85% for Cl- and 8.4, 70% and 14% for Ca. For trace elements S/N, %ADL and relative error between 2.0, 30% and 80% for Sb and 8.5, 70% and 14% for Ti, respectively, were calculated. In order to avoid bias in the results the data matrix was uncensored, i.e. negative or below detection limit values were included as such in the analysis without substituting them with below detection limit indicators (Paatero, 2007). Once the input data and errors matrices were prepared the PMF2 model was run in robust mode (Paatero, 1997) for source identification and apportionment. The optimal number of sources was selected by inspecting the variation of Q from PMF with varying number of sources (from 2 to 4) and by studying the physical meaningful of the calculated factors. Because Izaña is a remote site, the aerosol sampled at this observatory is aged and very well mixed. Consequently, only a limited number of sources can be expected from PMF analysis. In the present work a 3-factor solution was selected. The theoretical value of Q should be approximately equal to the number of degrees of freedom of the system [n $\times$ m – (p $\times$ (n – m)] (Paatero et al., 2002) where n, m and p are the number of samples, species and factors respectively. In our case the degrees of freedom were 3766 (k=2), 3591 (k=3), and 3416 (k=4) for i and j of 196 and 21 respectively, while the calculated Q were 5742 (k=2), 3818 (k=3), and 2901 (k=4). For k=4 the above condition was not satisfied being the Q calculated from the PMF smaller than the theoretical value of Q, i.e. the model simulated the data better than the errors allowed. Moreover, in the four-factor solution the additional factor did not have a meaningful chemical profile being loaded with almost all used species. One additional criteria used to evaluate the meaningfulness of the calculated sources was the inspection of the ratios between specific compounds pairs in the calculated chemical profiles. As shown in the following of this work with the

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three-factor solution the values of the selected ratios in the calculated chemical profiles were very close to the corresponding ratios calculated starting from the ambient experimental data. Moreover, in the three-factor solution 90-100% of the scaled residuals were located between the optimal range -2 and +2 (Juntto and Paatero, 2004). Once the number of sources was selected the rotational ambiguity was handled by means of the Fpeak parameter (Paatero et al., 2005) by studying the variation in the Q values by varying Fpeak from -0.8 and +0.8. It was found that Q was minimized without rotations and an Fpeak of 0.0 was selected for the final PMF solution. After regression of the factor scores from PMF (G matrix) to PM mass the model was able to simulate 98% of measured PM mass with a coefficient of determination of 0.99.

3.4 Positive matrix factorization modelling The PMF2 model was used to identify the chemical profile of the sources that contribute to PM10 in the summer subtropical SAL. This was done for assessing the consistency of the above performed interpretations on the origin of the pollutants mixed with dust. Three potential sources affecting the levels and chemical composition of PM10 were identified (Figure 15): 1. Source 1 is traced by typical soil dust elements: Al, Ca, Fe, Mg, Mn, Ti, Rb, Sr, La and K. According to the model, this source accounts for 22.0 μg/m3 as averaged, i.e. 75% of bulk PM10. Moreover, it accounted for 22%, 16% and 96% of the measured concentrations of SO4=, NO3$-$ and Ca respectively as average during the whole study period. This source was also enriched in P and accounted for $\sim$60% of the mean concentration of this element. The Fe/Al, K/Al, Mg/Al, Ca/Al ratios in the chemical profile of this source were 0.53, 0.20, 0.16, 0.34, respectively in good agreement with the previously reported ratios calculated from the measured ambient concentrations of these elements (Table 3). 2. Source 2 shows a profile traced by SO4=, Ca, Na, Mg, V, Ni, As, Pb, P and NO3-. The concentration of NH4+ in the chemical profile of this source is almost negligible. The profile of the source includes SO4= and NO3$-$, present as Ca, Na and/or Mg (only for sulphate) salts, and potential industrial tracers, such as V, Ni, As, and Pb. The presence of species potentially affected by anthropogenic emissions (e.g. SO4=, Ni, As, Pb) with soil dust elements (e.g. Ca, Na) suggest that this sources is related with

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interaction between pollutants and dust. As average during the whole study period, this source accounted for 4.4 μg/m3 of PM10 (15% of bulk mass) and for 52%, 28%, 2% and 20% of SO4=, NO3−, Ca and P respectively. 3. Source 3 exhibits a chemical profile characterised by SO4=, NO3−, NH4+, Cl and P. This profile fits with that observed in the regions where emissions from the phosphate based fertilizer industry is present: Morocco, Eastern Algeria and Tunisia (Figures 8E, F and 10). This source accounts for the presence of ammonium-sulphate [(NH4)2SO4] and ammonium-nitrate [NH4NO3], even if the latter is expected to be present in very low concentrations. The ratios of these compounds in the chemical profile were 0.37 and 0.35 respectively, very close to the stoichiometric ratios for ammonium sulphate and nitrate (Chow et al., 1992). This source accounted for 2.3 μg/m3 of PM10 (8% of bulk mass) and 22%, 53%, 0% and 20% of sulphate, nitrate, Ca and P, respectively. In general, the contributions of the various sources obtained with PMF should be independented of one other if unrealistic rotations are not present in the solution. However, a certain degree of correlation between specific source pairs can be observed if physical and/or chemical atmospheric processes constraint such sources to be correlated (Kim and Hopke, 2008; Pandolfi et al., 2011). In our case the moderate to high correlation observed between the three profiles of sources, illustrated in Figures 15B-15D, evidence that the pollutants are very well mixed with dust. At remote sites such as Izaña, aerosols are aged and very well mixed, resulting in a relatively homogenous aerosol. This decreases the number of sources that may be properly identified by receptor modelling.

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