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Comment

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

S. Rodríguez et al.

srodriguezg@aemet.es

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S. Rodríguez srodriguezg@aemet.es

We thank very much the comments raised by referee#2. They are really constructive and definitely contribute to improve the manuscript. These comments have been taken into account for preparing the revised version of the manuscript. Please, find below a reply to each comment.

Comment-1. The MCAR plots do show interesting and useful results. However, they are a bit of a blunt tool. They don't take into account the altitude of the trajectories (convective processes). They also include the emission magnitude of various sources

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regions. Thus it is possible for emissions from one source region could be allocated to another. Reply (C1):

A. Thanks for this comment. Information on the vertical component of the trajectories is not used for determining MCAR plots. In principle it is out of the scope in this version of the MCAR plots to use such information, but sure they will be considered in future versions of the MCAR plots analysis. In our modest opinion, the fact that the version of the MCAR algorithm used in this study allowed to identify potential sources of pollutants and the source regions of dust is of relevance. Sure that future version will use vertical component of trajectories.

B. Emission is not included or obtained as result in this analysis. MCAR (Median Concentrations at Receptor) plots represent the concentration (median or 50th concentration) of a given compound that is recorded at the receptor site (Izaña in this case) when air mass passed above each region defined in the 1x1 degree grid map. For example, Fig. 10A shows the median concentration of nitrate recorded at Izaña when air has passed by each 1x1 degree pixel of North Africa. The key issue is that the concentrations plotted in the MCAR plot are those recorded at the receptor site, and not concentrations in the ambient air of the source region (i.e. the philosophy is similar to that of the receptor modelling, such as positive matrix factorization, i.e. work with data recorded at the receptor site).

Specific Comments (address individual scientific questions/issues)

Comment-2. Page 3: The source of the AI data should be identified (i.e., which satellite?) Reply (C2): It is included in the caption of Figure 1 in the revised version of the manuscript.

Figure 1. Aerosol Index averaged for July and January 2008. Data recorded from Aura satellite with Ozone Monitor Instrument (OMI) and provided by Giovanni Analysis Tool of NASA.

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Comment-3. Page 4: The daytime upslope flow at Izaña is an important factor for aerosol collection only at night after January 2008. The consequence on sample representativeness of 24 hour sampling should be discussed. Reply (C3): we analysed this issue when starting to work with the data. The sampling was performed during a 24-h period from 2005 to 2007, whereas it was performed only at night during 2008. Because there are no significant dust sources in several kilometres around the observatory (which is surrounded by volcanic rock) change in the sampling duration does not affect to dust measurements (in fact dust components are not detected in the filter during non-dust events). We then focused on concentrations of particulate pollutants such as sulphate, nitrate and ammonium. Our analysis showed that the change in the sampling duration (and exclusion of sampling during daylight) did not produce a significant impact on the concentrations of particulate pollutants at Izaña (data of 2005 were not included in this analysis since only 6 month data are available for this year; July-Dec 2005). During both periods (2006-2007 and 2008), particulate pollutants ($\text{SO}_4=$, NO_3- and NH_4+) showed high concentrations during dust events and low concentrations during non dust events. This can be observed in the Figure 3 (of the original version of the manuscript). Moreover, we quantified how concentrations of $\text{SO}_4=$, NO_3- and NH_4+ changed after the sampling period. Table R1 (below) shows the mean concentrations of sulphate, nitrate and ammonium, and their ratio to aluminium. Values recorded during dust events and non dust events are segregated. Because absolute concentrations of the $\text{SO}_4=$, NO_3- and NH_4+ may change year-to-year due to a number of reasons (e.g. meteorology), the ratio of these compounds to Al should be used for comparison. Then, the impact of changing the sampling period was quantified by determining the ratio 2008 / 2006-2007 of the ratio of each compound to aluminium, e.g. $[(\text{SO}_4=/\text{Al})_{2008}/(\text{SO}_4=/\text{Al})_{2006-2007}]$, where a ratio equal to 1 means no change. During dust events (focus of this study), non significant change is observed in the ratios from 2006-2007 to 2008 (values within 0.94 and 1.06). The change in the ratios is within the analytical error range (10%, error already described in the original version of the manuscript). During non dust events (not subject to study here) a slight decrease is observed (Table

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R1), in such a way that the ratio of the study pollutants ($\text{SO}_4=$, NO_3^- and NH_4^+) during 2008 are about 14 – 18% lower than that observed during 2006-2007. This should be considered for further studies on long term evolution of $\text{SO}_4=$, NO_3^- and NH_4^+ at Izaña during non-dust events (i.e. clean free troposphere conditions).

This finding is in agreement with the results of a previous study at Izaña. Rodríguez et al. (2009; Atmos. Chem. Phys., 9, 6319–6335, 2009) analysed the hourly averaged values of particle size distribution and PM10, and observed that no significant increases (with respect to the nocturnal background) in the concentrations of > 100 nm and PM10 particles occur during the daylight upslope winds at this site (increases of PM10 were of about $1 \mu\text{g}/\text{m}^3$). These low PM10 concentrations favoured the formation of nanoparticles.

As suggested by the referee, the effect of the change in the sampling period on the chemical composition of particles has been included in the revised version of the manuscript. The following text was added to the last paragraph of section 2.3 Chemical characterization: From 1st January 2008, sampling was only performed at night for avoiding upslope winds during daylight. We quantified what the impact of such change was on the chemical composition of particles. For this purpose, we determined the ratios $[(\text{SO}_4=/\text{Al})_{2008}/(\text{SO}_4=/\text{Al})_{2006-2007}]$, $[(\text{NO}_3^-/\text{Al})_{2008}/(\text{NO}_3^-/\text{Al})_{2006-2007}]$ and $[(\text{NH}_4^+/\text{Al})_{2008}/(\text{NH}_4^+/\text{Al})_{2006-2007}]$ during dust events and during non dust events. During dust events, no significant changes were observed in these ratios, which exhibited values of 1.06, 0.99 and 0.94, respectively. During non-dust events, these ratios showed values equal to 0.86, 0.82 and 0.86, respectively, which indicates a slight decrease in the concentrations of sulphate, nitrate and ammonium when avoiding daylight sampling. The fact that the decrease in the concentrations of sulphate, nitrate and ammonium is rather low when daily sampling is avoided is in agreement with previous studies; Rodríguez et al. (2009) observed that during upslope winds nanoparticles (< 10 nm diameter) exhibited important increases favoured by the low concentrations of PM10 in these ascending airflows. Because no significant sources of dust are present

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in several kilometres around the observatory (which is surrounded by volcanic rock and several cm size volcanic ashes, locally known as picón), change in sampling period did not affect to dust measurements.

Comment-4. Page 5: HF sample digestion of quartz filters will break down some or all of the filter matrix. Blank levels should be mentioned in the paper. Reply (C4): With the method filters are totally dissolved during acidic digestion. This method ensures the bulk digestion of dust, including silico aluminates. For this reason blank levels were subtracted from sample analysis. The following text has been added in the reviewed manuscript (2.3 Chemical characterization):

At least one blank laboratory filter and one blank field filter were analyzed for each analysis batch. Blank levels were subtracted from the bulk concentrations determined for each sample. Filters with very low blank concentrations (according to our analysis) were used: Schleicher & Schuell QF20 (2002-2006) and Munktell MK360 (2007-2008). The “filter + sample / blank filter” concentration ratio was within the range 10 -60 for Li, Rb, Ti, Fe, K, S and Cu, within the range 5 – 10 for Mn, Cu, Mg, Co, Mn, Ca, As, Al, Sr, V, P, Ce and La, within the range 2 -5 for V, Na, Pb, Bi, Th, Hf, Sb, and Pb, and within 1-2 for Ni, Cd, Cr, Cr, U, Sn, Ba, Zn, Ba and Zn. For analysis control, reference material NIST 1633b was added to a fraction of a blank filter to check the accuracy of the analysis of the acidic digestions: detection limit and accuracy were estimated in 0.4 ng/m³ and 2% for ICP-AES and 0.02 ng/m³ and 3% for ICP-MS. For ion chromatography and specific ion electrode, the detection limit and accuracy were 0.4 μg/m³ and 10% and 0.3 μg/m³ and 2%, respectively.

Comment-5. Page 5: A comparison of the two OC-EC techniques should be included since the analytical distinction between OC and EC is controversial and not necessarily consistent between techniques. Reply (C5): We agree this is important. From 2005 to 2007 total carbon was determined with a LECO analyser, whereas from 2007 and 2008 OC and EC analysis were performed with a SUNSET analyser. Sampler collected during 2007 were analysed with both techniques for intercomparison. Results are shown

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in Figure C5: $y = 0.9509x$, $R^2 = 0.9521$. Data obtained with the LECO are slightly lower (5%) than those obtained with the SUNSET analyser. The differences are enough low to guarantee an acceptable continuity in the times series.

The result of this intercomparison is described in the new version of the manuscript (2.3 Chemical characterization):

A set of 33 PM₁₀ samples collected during 2007 were analysed with the two techniques for inter-comparison; the good agreement found with the two techniques [OC + EC (SUNSET) = 0.951 \hat{A} total-carbon (LECO), $r_2 = 0.952$] guarantee a consistent continuity in the time series.

Comment-6. Page 6: The last paragraph of section 2.4 was not clear. In particular, I am not sure what is meant by process “2”. Reply (C6): This paragraph was reworded for avoiding confusing or obscure points. In the revised version it appears as follow: MCAR plots were determined for each aerosol compound analyzed in PM₁₀ (2005 – 2008). High concentrations of a given aerosol compound on a specific region of the MCAR plot is attributed to significant emission or formation rates of that aerosol specie in that area.

Comment-7. Page 8: Data from the publications of Savoie and Prospero could have been used to generate sulfate to Al and nitrate to Al ratios. Al concentrations can be estimated using the gravimetrically measured dust concentrations and the Al to dust ratio from bulk mineral composition. This approach would have produced values with larger uncertainties than direct measurements. Nevertheless, those values would likely have been useful for comparison purposes. However, any correlation between these pollutants and Al would have likely been because of coincident transport of aerosols from different sources in the same air mass. Reply (C7): This is a good suggestion. We have searched those articles. We did not found any one where the ratio of sulphate, nitrate or ammonium to dust was calculated. In many articles mean values of those components were provided during the study periods (which in most of cases in-

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clude dust and non-dust events). Only in a few cases the mean sulphate, nitrate or ammonium is provided only during dust periods. Following the suggestion of the referee we determined the mean sulphate, nitrate or ammonium ratio to Al (even if, as pointed by the referee, uncertainties may be large). We obtained ratios slightly lower than those we observed in Izaña. These results are discussed in the revised version of the manuscript as follow (section 3.1):

Unfortunately, no direct measurements of the sulphate, nitrate or ammonium ratios to aluminium were found in the literature to be compared with those we observed during dust events at Izaña. We then estimated those ratios at Barbados, assuming the mean content of Al in soil (6-8%; Prospero, 1999) and the sulphate, nitrate, ammonium and dust (gravimetrically determined) concentrations in TSP provided by Prospero, Savoie and collaborators (Savoie et al., 1992; Li-Jones and Prospero (1998). For mean contents of Al in soil within the range 8 – 6 %, sulphate, nitrate and ammonium ratios to Al within the range 0.23 – 0.31, 0.12 – 0.16 and 0.02 – 0.03 were found, respectively. Although this estimation may be subject to significant uncertainties, it is important to highlight that are close to those we observed at Izaña for TSP (Table 3). The fact that the ratios at Barbados are slightly lower than at Izaña, may be linked to the regional variability of the dust and pollutants mixings.

Savoie, D.L., Prospero, J.M., Oltmans, S.J., Graustein, W.C., Turekian, K.K., Merrill, J.T., Levy II, H.: Sources of nitrate and ozone in the marine boundary layer of the Tropical North Atlantic. *Journal of Geophysical Research* 97 (11), 575-589, 1992.

Prospero, J.M.. Long-term measurements of transport of African mineral dust to the southeast United States: Implications for the regional air quality. *Journal of Geophysical Research* 104, 15917-15927, 1999.

Comment-8. Page 8: If EC/OC data is not to be discussed in this paper, why was it mentioned at all? Reply (C8): the characterisation of carbonaceous species is out of the scope of this paper. We only included data of carbonaceous species in Table 4,

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just to provide a comprehensive view of the composition of the particles present within the Saharan Air Layer. Moreover, the relative contribution (%) of sulphate, nitrate and ammonium is affected by the relative contribution (%) of carbonaceous compounds. The interpretation of the OC data from Izaña is a trivial issue since many sources and processes may participate, including anthropogenic emissions, debris from soil or fragments of plants, among other. This will be subject of a further study which will include analysis of organic tracers.

Technical Corrections (typing errors, etc.)

Comment-9. Abstract: The first two sentences should be combined: Measurements of the chemical composition of particulate matter samples (TSP, PM10 and PM2.5) collected from 2002 to 2008 in the North Atlantic free troposphere at Izaña Global Atmospheric Watch (GAW) observatory (Tenerife, The Canary Islands) desert dust very frequently mixed with particulate pollutants in the Saharan Air Layer (SAL). Reply (C9): This has been done. Thanks for the suggestion.

Comment-10. Abstract: The country names should be reordered: Industrial emissions from Northern Algeria, Eastern Algeria, Tunisia, and the Atlantic coast of Morocco appear to be the most important source.... Reply (C10): Yes, we agree with the referee. The order suggested reflects the role or importance as source region of pollutants.

Comment-11. Table 4: Are the data presented as mass fraction (I think) or %? Reply (C11): Data are presented in absolute concentration ($\mu\text{g}/\text{m}^3$) and relative contribution (%). In order to avoid obscurities this sentence was added to the figure caption: Concentration of each aerosol compound is presented in absolute concentration ($\mu\text{g}/\text{m}^3$) and relative contribution (%).

Comment-12. General comment on English usage: I have great respect for those who write scholarly papers in English when English is not their first language. That said, the clarity and impact of this paper would be much improved if it were edited for English usage. Reply (C12): Thanks very much for this comment. The revised version of the

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manuscript has been reviewed and corrected by a native English speaker.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 8841, 2011.

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11, C5382–C5392, 2011

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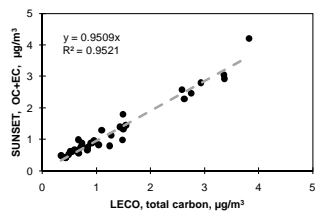


Figure C5

Fig. 1.

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Table R1. Mean concentration and ratio of several aerosol components during the period of 24-h sampling (2006–2007) and sampling only at night (2008).

		mean dust	mean Aluminium	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	SO ₄ ²⁻ / Al	NO ₃ ⁻ / Al	NH ₄ ⁺ / Al
		µg/m ³	µg/m ³	µg/m ³	µg/m ³	µg/m ³	ratio	ratio	ratio
24h sampling	2006-2007 dust events; aluminium: 1 µg/m ³	66.6	5.3	2.1	1.0	0.24	0.33	0.19	0.95
nocturnal sampling	2008 dust events; aluminium: 1 µg/m ³	50.5	4.8	1.7	0.6	0.13	0.42	0.33	0.86
		nocturnal / 24-h ratio:					1.06	0.93	0.94
24h sampling	2006-2007 non dust events; aluminium: 6.1 µg/m ³	0.56	0.040	0.30	0.10	0.062	0.56	2.29	1.37
nocturnal sampling	2008 non dust events; aluminium: 6.1 µg/m ³	0.52	0.0484	0.26	0.09	0.054	0.05	1.33	1.13
		nocturnal / 24-h ratio:					0.88	0.82	0.86

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Fig. 2.