**Atmospheric
Chemistry
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Discussions

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Interactive comment on "Saharan dust aerosol over the central Mediterranean Sea: optical columnar measurements vs. aerosol load, chemical composition and marker solubility at ground level" *by* M. Marconi et al.

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Firstly I want to thanks Dr. Dulac for the constructive comments and detailed revision of the paper. Here below the detailed answer to each point.

"First, you might wish to remind that the Lampedusa station is a regional station of the WMO/GAW network."

This information will be added to the paper.

"Regarding the use of nssCa as a tracer for dust, I would like to emphasize that there is a rather high variability in crustal element ratio, as illustrated for instance by the early work of Bergametti et al. (1989) for Si/Al and Fe/Al ratios of dust aerosols in Corsica, depending on the source region of dust in Africa. This puts some uncertainty in using a single chemical tracer to identify desert dust events. In particular, loess deposits from southern Tunisia which are most probably an important source of dust over Lampedusa (see Fig. 5 in Prospero et al., 2002) seem particularly rich in calcite (e.g. Guieu et al., 2010). Avila et al. (2007) reports an average Al/Ca ratio of 0.65 and 0.53 for dust in red rains collected in NE Spain from source regions West and East of Greenwich meridian, respectively, which confirms this trend of higher Ca in long-range transported aerosols from the Great Eastern Erg region. Since you report having used back-trajectories to check that air masses with high nssCa events have an African origin, I wonder whether you could not use farther those air-mass trajectories to also check (i) a possible discrimination between the main dust source regions based on Si, Al, Fe and nssCa ratios, and (ii) the consistency of your single nssCa criteria depending on dust origins."

You are right, this is a very interesting topic, but our purpose is to identify Saharan dust events by nssCa, not quantifying their contribution or discriminate the dust source areas. Backward trajectory analysis is used to confirm the origin from Sahara instead of local resuspension. May be this is not clear in the text and few sentences will be added to clarify this concept. About the identification of the source area we have some preliminary analysis but the results are not clear to interpret, for a reliable identification we need to deep the analysis and it goes beyond the aims of the paper.

"By the way, information on which trajectories were used is presently missing in the methodology. Information on the OPC fitting procedure is also presently missing in the methods. You might also wish to confirm that the Grimm OPC was used with a TSP sampling head in order to capture large particles despite its low sampling flow (otherwise there is no hope to capture large particles). Regarding cascade impactor

samples, the information given in the material and methods section is very incomplete: how many samples, for what type of air mass...? For both the OPC and the cascade impactor, it would be worth reminding cut-off diameters. We also miss information on the daily filter sample set. I find that a table or a figure providing the number of available samples per month of the 6.5-yr sampling period would give a very useful idea of the data set. To finish regarding materials and methods, there is a need for further information regarding extraction methods: I note that the abstract only mentions extraction of the soluble fraction of dust at pH 1.5 in HNO3, whereas section 2 only describes a different method with HNO3+H2O2 using a microwave oven, when figure 6 finally presents results of 3 different extractions using HNO3 and a ultrasonic bath, HNO3-H2O2 and a microwave oven, and Milli-Q water and a ultrasonic bath."

More information, summarized below, will be added in the revised paper.

The Hybrid Single-Particle Lagragian Integrated Trajectory (HYSPLIT) modelling system (Draxler and Rolph, 2012) was used for the trajectory analysis.

Measurements with the Andersen 8-stage impactor were made with 3 days time resolution at a constant flow of 1.7 m3h-1 in the period 3 June-20 October, 2006. The cut-off sizes of the 8 stages are: 9, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7, 0.4 um.

The table 1 reporting the number of samples for each month and information on the additional measurements will be add to the paper.

Regarding the OPC measurements and data elaboration, a fitting procedure was implemented to parameterize the measured particle size distribution (PSD), then the modal parameters were obtained assuming that the particles are distributed as a multimode lognormal function. The procedure is based in the least square minimization of the difference between the experimental points and the fitting curve. The algorithm is able to find the peaks and the relative minimums of the volume size distributions and decide the number of modes to be used. For this purpose the 10-minutes average of the volume PSD was used.

A TSP sampling head and a low flow sampling rate of 1.2 L/min were used. The following information of the OPC sampling will be included in the text:

The particle size distribution was measured at the surface using an EnvironCheck Dust Monitor System manufactured by the GRIMM Aerosol Technik GmbH, that hosts an optical particle counter Model 107. It consists in an outdoor housing equipped with a total suspended particle (TSP) head, a volume controlled sampling (flow rate of 1.2 L/min), a dehumidification system, and temperature, relative humidity and pressure sensors. The OPC was deployed at Lampedusa from 28 April to June 2008 measuring the segregated size distribution in 31 diameter channels between 0.25 and 32 μm with 1 min time resolution. The cut-off diameters of the OPC channels are: 0.25, 0.28, 0.3, 0.35, 0.4, 0.45, 0.5, 0.58, 0.65, 0.7, 0.8, 1, 1.3, 1.6, 2.0, 2.5, 3, 3.5, 4, 5, 6.5, 7.5, 8.5, 10, 12.5, 15, 17.5, 20, 25, 30, 32 um.

All the tree methods used for the extraction are described in section 2.2: extraction in water for IC measurements at lines 4-6 pag 21266 (used in figure 6 only for Mg, K and Ca determined by IC); HNO3 in ultrasonic bath at lines 10-12 pag 21266 (used for PM10 samples and impactor samples, red line in fig 6), and HNO3 - H2O2 in microwave oven at lines 26 and following pag 2166 (used only for multistage impactor fig 6 black line).

"I feel that a better contrast in the manuscript should be made between data from longterm monitoring and data from much more limited sampling periods. The latter should be better presented as illustrations or case studies, not yielding general conclusions. In addition those limited data sets could probably be better exploited if they are to be included in the paper."

We will improve this aspect of the paper.

"Indeed, information from cascade impactors and the OPC comes from a very limited sampling period compared to the total monitoring period, i.e. less than one particular summer or spring season, respectively, compared to 6.5 yr for long-term monitored

parameters. Such campaign results might well not be characteristic of the general situation unless you can argue the opposite. The use made of cascade impactors is the most questionable since it seems to me that you are deriving the size-segregated solubility of various elements using a single impactor sample. Since several samples are supposed to have been analysed from the summer sampling season, we would expect some synthetic information on the variability of the size distribution of the various elements. As above reported the cascade impactor campaign was performed in Lampedusa from 3rd June to 20th October 2006, but here we report the chemical composition in different conditions of solubilisation in the only crustal event recorded in this period showing nssCa> 483 ng m-3. Anyway a better characterization of the event will be reported in the paper. Regarding OPC data, it also seems that you are averaging data for all dust events of the 2-month sampling period to retrieve a single "average" dust size distribution, which seems rather questionable given the expected variability (for instance depending on the transport distance from source regions). Cannot you perform an inversion for every dust event during the campaign and check the variability? Can you compare the size distributions retrieved for those dust events to the size distribution of non-dust periods? To my knowledge, the Grimm OPC also derives PM1, PM2.5 and PM10 data, and I would expect at least some comparison to coincident PM10 data. As the referee pointed out it can be a non negligible variability of the dust aerosol distribution. In order to take into account the variability of the aerosol size distribution has been recomputed and the modal parameters and its standard deviation have been also determined. In this case, the multilognormal fit was carried out using 10-min averages of the measured PSD during all the dust events identified by the b) criterium (nssCa > 483 ngm-3). In addition, the same procedure has been used for the rest of cases named as "no dust". Then the modal parameters were averaged into a single size distribution for "dust" and "no dust" periods. Now, the table 3 reports the modal parameters for the dust and no dust periods found during the 2-months observations of the aerosol size distribution."

A brief discussion about the PSD variability will be added in the manuscript. The com-

parison of the PSD with non dust cases is also discussed in the same paragraph.

During the dust events, the 93%of particles are in the finest mode with a median diameter at 0.316 μm. A small fraction of the particles (1.17% of the total particles concentration) are larger than 1 μm. Conversely, the largest contribution to the total volume comes from the second mode (77.1 %) as shown in Table 3. However, large variability in the modal parameters is observed for the dust cases. The analysis of the standard deviation suggests that this variability is especially important for the particles within the third mode. The variation of the PSD modal parameters may be related with the different dust origin and transport mechanisms. In addition non-negligible day/night variability may arise due to the boundary layer diurnal evolution.

For the non-dust cases, the number of particles in the finest mode is larger than the observed for the dust cases and represents more than 98% of the total concentration. In addition a similar median diameter for the fine mode is observed for the dust and non-dust cases. Such particles are characteristic of anthropic sources (for instance combustion processes able to produce fine particles) or secondary processes (such as oxidation of SO2 and dimethylsulfide to sulphate and methanesulfonate). The chemical composition determined on 8 stage impactor confirms the presence of anthropic and secondary species in the first mode also in dust events. Conversely, significant differences appeared between the dust and non-dust cases for the second and third modes. The median diameters of both, second and third modes, are shifted to larger values for the non-dust cases. However a smaller fraction of the total particles concentration is larger than 1um and represents only the 0.84%. It should be pointed out that the small variability found in the volume of third mode and its large diameter may be related to the persistent influence of the marine aerosols in Lampedusa. Since no aerosol type discrimination is done for the non-dust cases, the marine aerosol contribution could have a significant effect in the retrieval of the averaged modal parameters. It might be especially relevant for the third mode resulting in a magnification of the averaged modal parameters. Furthermore the third mode is observed in more than 92% of the

dust cases and only in the 75% of the non dust cases.

The comparison between PM10 from gravimetric measurements ad OPC data was not performed because of the instrument do not provide the data of mass.

"Regarding elemental solubility, I have the feeling that the section is presently too limited to the presentation of results. Added to the above remarks on methodology (description missing, size segregated solubility based on a single impactor sample), I find that this part of the paper is particularly weak. The relevant discussion is not complete and hardly accounts for an abundant literature on the topic: there are only 2 references cited (Fairlie et al., 2010, and Becagli et al., 2012) whereas many additional references are expected to be used. For instance, just taking some papers I have in mind, the important role on iron solubility of organic substances (in particular oxalate, see e.g. Saydam and Senyuva, 2002; Paris and Desboeufs, 2013) or of iron mineralogy (e.g. Journet et al. 2007) should be mentioned. The fact that Fe solubility increases with decreasing particle size (top of p.21279) has already been reported (e.g. Baker and Jickells, 2006) but does not seem to be a constant (Buck et al., 2010) and it has also probably much to do with the anthropogenic fraction of iron which is known to be more soluble than the crustal fraction (e.g. Baker et al., 2006) and possibly a forest fire fraction (Guieu et al., 2005). Avila et al. (2007) also addressed the problem of high variability in calcium solubility. Aluminium solubility is deeply discussed by Losno et al. (1993) and the role of acidic species by Losno et al. (1991). Etc. I would therefore recommend to skip the solubility part from the present paper and to submit it in another dedicated manuscript with additional work on cascade impactor samples, and serious consideration of the existing literature."

We agree that the presentation of the multi-stage impactor data may be improved. Also, we agree that a single sample may not be representative of a general behaviour. This will be stressed in the discussion. However, the analyses were preformed on 8 different stages, for 21 elements, and in 2 or 3 different solubility conditions. We believe that the derived results are useful to explain what we obtain on the solubility of PM10 samples.

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Besides, this study helps understanding if the soluble fraction or the total one of each marker is useful as marker of the Saharan dust . Finally, the study on the solubility in mild conditions is fundamental in order to understand the real amount of bioavailable metals. For these reasons we believe that it is worth including these data in the paper; we will however improve both presentation and discussion in the revised version.

"Finally, a few technical corrections: -p. 21265, line 27: you refer to the present section 2.1. By the way this sentence on extraction should rather be in section 2.2 where extraction is described.

-you have some misspelling in the references of Spanish authors: Rodriguez et al citations in the text omit the accentuated í that is used in the Ref. list; Gomes Amo in the text (p.21265) is Gómez-Amo in the references. -you might plot on figure 3 the limits used for dust events selection."

We will include these corrections in the revised paper.

Table 1. Number of PM10 samples collected in each month from June 2004 to December 2010.

	PM10 1 day every three sampling			PM10 daily resolution			PM 10 1 day every three sampling
	2004	2005	2006	2007	2008	2009	2010
	n	n	n	n	n	n	n
Jan		14*	9°	12	30	27	5
Feb		4*	6°	26	28	16	10
Mar		9*	8°	30	27	29	10
Apr		5*	10*	25	25**	25	11
May		9*	13*°	31	23**	30	11
Jun	4*	9*	10*°	30	29**	26	8
Jul	15*	9*	10*°	26	27	30	13
Aug	8*	9*	9°	30	21	31	11
Sep	8*	9*	1°	27	28	15	11
Oct	8*	9*	5°	17	27	-	9
Nov	8*	9*	8°	8	27	-	13
Dec	15*	10*	8°	30	22	-	2
TOT	66*	105	97	292	314	229	114
Year Sampling Coverage %	18	29	27	80	86	63	31

* PM1.0 and PM2.5 alternating sampling.
° also Andersen 8-stage impactor 3-day time resolution samplings (3rd June - 20th October 2006).
** also OPC measurements (28th April - 9th June 2008).

Fig. 1.

Table 3 will be Table 4: Aerosol size distributions and lognormal parameterization for dust and non-dust case (see text). Dv is the diameter characteristic of the mode, and σ is the standard deviation related to the lognormal curve. V (%) and N (%) are the percentage of particles belonging to the mode expressed as particle volume and number respectively.

dust	Dv (µm)	σ	V (%)	N (%)
Mode 1	0.316 ± 0.003	1.175 ±0.005	13 ± 7	93 ± 2
Mode 2	2.1 ± 0. 4	1.76 ±0.04	77 ± 10	7 ± 2
Mode 3	8 ± 3	1.12 ±0.13	14 ± 20	$(1.06 ± 1.08) \times 10^{-2}$
no dust	Dv (µm)	σ	V (%)	N (%)
Mode 1	0.3152 ± 0.005	1.166 ±0.003	16 ± 9	98.5 ± 0.7
Mode 2	2.9 ± 0.5	1.90 ±0.11	81 ± 11	1.5 ± 0.7
Mode 3	16 ± 3	1.007 ± 1	6.1 ± 1.5	$(1.29 ± 0.5) \times 10^{-3}$

Fig. 2.