Atmos. Chem. Phys. Discuss., 11, C15527–C15543, 2012
www.atmos-chem-phys-discuss.net/11/C15527/2012/

Atmospheric Chemistry and Physics Discussions

ACPD
11, C15527–C15543, 2012

Interactive Comment

Interactive comment on "Evidence for ships emissions in the Central Mediterranean Sea from aerosol chemical analyses at the island of Lampedusa" *by* S. Becagli et al.

S. Becagli et al.

silvia.becagli@unifi.it

Received and published: 20 February 2012

Answers to Reviewer 1

1. V and Ni are assumed as specific tracers for ship emissions. This assumption is not completely correct as V and Ni are tracers for any combustion process of heavy oils and not for ship emissions only. The V/Ni ratio could be specific marker for ship emissions but only in case the range of the ratio characteristic for ships emissions would be significantly different from that one for other heavy oil combustors.

We agree with the comment of the referee. In fact, we cannot distinguish different heavy oil combustion sources. However, our sampling site is far from sources of heavy

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

oil combustion other than ships, and backtrajectories suggest that airmasses with V high concentrations do not come from large power plants or other industries (refineries) in Sicily and in Southern Italy. Anyway, a possible long-range influence from far sources (i.e., refineries in Southern Sardinia) cannot be excluded. To be more general, we will rephrase the title and the text of the paper referring to heavy oil combustion sources, of which ships presumably play a large role. We believe that our results constitute an important contribution to the understanding of Mediterranean aerosols even if the specific ship source cannot be unequivocally identified.

2. Ni/Si and V/Si ratios are introduced to distinguish cases dominated by heavy oil combustion from those most influenced by Saharan dust. The authors considered enriched samples those with a ratio V/Si (or Ni/Si) 10 times higher than that one specific for crustal sources. But what is the value for the latter and what the reference for it? And more, what this factor of 10 represents? It appears this limit has been arbitrary fixed by the authors.

The Ni/V and V/Si ratios in the upper continental crust are 1.5x10-4 (black line in fig 1) and 3.1x 10-4, respectively. As reported in the caption of figure 1, these values are identified by Henderson and Henderson (2009). To improve clarity, we will add these values also to the text. A threshold 10 times higher than the typical value of the upper continental crust is commonly used in the literature to identify samples which are enriched in V with respect to the crustal composition (e. g., Chester et al., 2000; Adams et al., 1980). Samples showing an enrichment value <10 are generally supposed to indicate that a trace metal in the aerosol sample has a significant crustal source (usually called non-enriched element). In contrast, an enrichment >10 is assumed to indicate that a significant proportion of an element has a non-crustal source (anomalously enriched elements). It is well known that the need of a relatively high threshold to discriminate element enrichment with respect to the crust arises from the inhomogeneity of the crust composition. For instance, the same is not true in distinguishing sea salt and non-sea salt contribution of a certain marker, in which case the value of the sea

ACPD
11, C15527–C15543, 2012

water ratio is generally considered. We believe that the threshold values we use are robust for discriminating V enhancements which are not due to crustal contributions. A discussion of this aspect, with the justification of the selected thresholds, will be added to the paper.

3. Furthermore, Figure 1 shows that this criterion fails, as a not negligible number of cases with Si concentrations larger than 800 ng m-3 shows a Ni/Si ratio 10 times higher than that one characteristic for crustal sources.

Figure 1 shows that Ni is enriched also in some Saharan dust events (as suggested by the Si high concentration and confirmed by backtrajectories), as a consequence of mixing of particles produced by different sources. The occurrence of elevated Si amounts does not imply that dust is the only aerosol component. Conversely, it implies that dust is an important component. Other evidences of mixing are discussed at page 29924, line 21.

4. The authors assume that Si concentrations larger than 800 ng m-3 identify Saharan dust events. And again, where this limit value comes from?

The value of 800 ng m-3 corresponds to the 72nd percentile of the Si concentration distribution. This threshold is not used as a single attribution criterion, but together with the trajectory analysis to support the identification of cases significantly influenced by dust (see page 29922, lines 15-18). The exact value of the threshold is not significant as far as cases with high crustal content are isolated. A more stringent limit could be the 75th percentile (corresponding to Si =925 ng m-3); 22 samples display values between 800 and 925 ng m-3. Previous studies carried out on the basis of aerosol optical depth measurements, show that dust is present at Lampedusa in about 26% of the days (Meloni et al., 2007). Although the dust occurrence at the surface may show a somewhat different behavior, we believe that the 75th percentile provides a good threshold. In any case, the Si amount is not used as a stringent method for dust identification, but to remove from the subsequent analyses cases in which dust is a

ACPD
11, C15527–C15543, 2012

major component. We believe that, although the choice of the threshold is somewhat arbitrary, the combined use of trajectories and Si content provides a robust criterion for the use made in the paper. We plan to clarify this aspect, use the 75th percentile, and expand the discussion of the possible markers for dust (as suggested also by reviewer 2) and the threshold selection.

5. The authors introduce also Vsol and Nisol as additional criteria to discriminate between crustal events and ship aerosol cases (lines 28-29) and set, in an arbitrary manner, a threshold of 6 ng m-3 for V sol claimed as a better tracer for antropic sources (line 25). In Table 1 they show a higher solubility for V and Ni in ship events than in pure Saharan dust events. This reviewer believes that in no case an extensive property, as Vsol, can be considered appropriate to discriminate different sources. For example, despite the lower solubility of V in natural aerosols, V concentrations larger than 6 ng m-3 can be reached during important dust events.

The values of 6 ng m-3 is not arbitrarily chosen. This value was derived from the experimental data. All the samples classified as enriched (i.e. Ni/Si >10 (Ni/Si)crust and V/Si>10 (V/Si)crust) displayed a concentration of Vsol > 8 ng m-3, and only in 6 cases 8 > Vsol > 6 ng m-3. This is stated at pag 29922 line 19-24 ("The measured concentrations of Vsol and Nisol for the non-enriched events are lower than for the enriched cases, and are below 8 and 2.6 ng m−3, respectively. Only 6 events (less than 5% of the dataset) are in the range 6–8 ng m−3 for V, and 2.3– 2.6 ng m−3 for Ni. The threshold of 6 ng m−3 (hereafter Vst) for Vsol is chosen to identify enriched samples on the basis of measurements of Vsol."). We plan to improve the discussion of this point, clarifying the criteria used to identify the threshold for Vsol.

We do not agree that V concentrations larger than 6 ng m-3 can be reached during important dust events. As shown by the simple calculation reported below, a dust event producing this amount of V would be exceptionally intense.

Since the V/Si ratio in the upper continental crust is 3.1x10-4, and about 40% of the

ACPD
11, C15527–C15543, 2012

Interactive Comment

total V is soluble in the crust, the Si concentration should be larger than 48000 ng m-3 to support a value of Vsol of 6 ng m-3. This is a huge amount of Si. The highest concentration of Si measured at Lampedusa is 12300 ng m-3. Although this value is very high (and is a single extremely intense event; as discussed above, the 75th percentile of the Si amount is 925 ng m-3; see also the following figure for the range of Si values), is by far smaller than that needed to obtain a value of Vsol = 6 ng m-3 due only to the crust contribution.

Furthermore, as shown in the figure 1 (attached to these comments), data from Lampedusa generally show that elevated values of Vsol correspond with low amounts of Si, and vice-versa. This behavior supports the conclusion that Vsol has a different source with respect to Si.

6. The ratio Vsol/Nisol for events classified as anthropogenic-influenced (on the basis the Vsol > 6 ng m-3) does not differ significantly from that obtained for events classified as crustal, 2.98 vs 2.54, respectively. This indicates that i) either the ratio is not specific for one or the other source and/or ii) aerosols comes, in fact, from different sources and they are not pure Saharan dust or ship events.

The referee is right, the two values are not very different (even if both significant at $p < 0.005$). As outlined in the text, similar values are found in the literature for ship and for crustal particles. The cases identified as affected by ships display a V/Ni ratio higher than that of crust and close to the literature value for ship emission, suggesting that heavy oil combustion contributes significantly. In any case, the discrimination between high and low ship contribution is not based on the slope of this correlation (i.e the V/Ni ratio) alone, but on a combination of factors (V/Ni ratio, V amount which is not attributable to dust, V and Ni solubility, trajectory analysis). These aspect will be clarified and the discussion improved.

7. The method used to calculate back-trajectories is based on an oversimplifying assumption i.e. that wind follows a uniform and linear behavior both in terms of direction

and speed. An assumption that can be true only for a very limited space and time, if at all. Back-trajectories should be calculated using more robust tools, e.g. HYSPLIT.

We do not agree with this comment. Hysplit trajectories were used in a number of other studies we performed at Lampedusa, and it would have been easier to use this tool. However, there are implicit limitations in this type of trajectories, essentially related to the coarse resolution of the meteorological data and associated model, and to their use at very low altitude. NCEP reanalysis data used for the calculation of trajectories are available at 2.5° x 2.5° spatial resolution, 6 h temporal resolution, and 17 vertical levels; some improvement may be obtained by using higher spatial resolution datasets (i.e., ECMWF, although also this dataset has 6 h temporal resolution). As stated in the paper (lines 9-13 pag. 29925: “the use of relatively frequent wind measurements can be advantageous with respect to standard back-trajectories based on meteorological analyses, which have a broader spatial and temporal resolution, especially considering the goal of this trajectory analysis: the determination of the air mass paths in the maritime region surrounding Lampedusa.”) the data temporal resolution is very important for our application. Assuming a reasonable value of mean wind intensity of 6 m/s along the backtrajectory, an air particle covers about 260 km in 12 hours, which largely exceeds the area of interest, i.e. the surrounding of Lampedusa up to the southern part of the Strait of Sicily. The choice to calculate backtrajectories over 18 hours is a conservative choice, which allows to have an appropriate description in case of stagnant condition. The use of databases with 6 hour temporal resolution (both NCEP and ECMWF) implies that in most cases data from only 2 analyses would be used, probably temporally interpolating the original data. In any case, computing trajectories close to the surface is always problematic.

For supporting our point of view we used two different approaches.

1) We have made a comparison between the backtrajectories calculated by Hysplit (hereafter model backtrajectories, figure 2 plot on the left) using the NCEP data and our backtrajectories (hereafter calculated backtrajectories, figure 2 plot on the right)

ACPD
11, C15527–C15543, 2012

Interactive Comment

during the June/July 2008 event discussed in the manuscript (i.e., fig. 6 in the paper).

For simplicity in figure 2 we show the backtrajectories in a range of 180 km from Lampedusa. Although model and calculated backtrajectories present a general agreement, differences appears in correspondence of stagnant conditions (i.e., 22, 24 June and 3 July). As expected, the model has some difficulty in reproducing low wind conditions at the ground level, while measurements can better reproduce this situation typical of the summer time. This is an important point already evidenced in the paper (lines 3-5 pag. 29929) “Moreover, very low winds connected with stagnant conditions are not responsible for elevated values of Vsol, confirming that high Vsol values are not of local origin (i.e. from harbour activities).” The larger differences between the two approaches are observable on 4 and 7 of July, when a strong wind rotations occurred (see respectively the backtrajectories of 3-5 July and of 6-8 July). In addition, we would like to evidence that the model backtrajectories often at Lampedusa display a larger easterly component than retrievable from the measured wind.

2) A verification of the uncertainties associated with the Hysplit trajectories may be obtained by using clusters of trajectories arriving at slightly different end-points close to Lampedusa and slightly different times.

As an example, we have calculated the Hysplit “ensemble” trajectories for several cases studied in the paper. The ensemble trajectories are obtain by calculating 27 different trajectories from the selected starting location; each trajectory ensemble is calculated by offsetting the meteorological data by one grid point in the horizontal, and 0.01 sigma units in the vertical. As an example, we report here the results for July 4th, 5th (figure 3), and 7th (figure 4), 2008. The trajectory are calculated for the lowest model level. Trajectories ending at 12 UT and 18 UT are calculated for July 7.

Evidently, small changes in the meteorological grid largely affect the trajectory path. The patterns retrieved from the surface observations are among those retrieved from Hysplit. However, the large spread in the model results does not allow a reasonable

ACPD
11, C15527–C15543, 2012

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

identification of the transport patterns. Moreover, time interpolation is also critical. The trajectory patterns show some change between 12 and 18 UT on July 7, 2008. The wind measured at Lampedusa on the same day suggest that south-westerly winds are occurring probably earlier than expected from the trajectories.

Summarizing, we believe that, in a site like Lampedusa where the local effects are minimal, using high resolution (10 minute wind) measurements of the wind provides much better detail on the dynamics, at least when trajectories are calculated for a limited duration, as it is our case. We will provide a more detailed explanation of these motivations in the text.

8. The authors, making use of the entire available database i.e. without any data filtering, study the relation between nss-sulphate and the Vsol and proposed a criterion to estimate the contribution of ship emissions to nss-sulphate concentrations at Lampedusa, i.e. minimum regression slope, SO4/Vsol = 200. The authors assume that that for the points lying on the curve y=200x, nss-SO4 and Vsol arise from the same source, i.e. ship emissions. The approach is however not valid. For example, those points could represent aerosol dominated by crustal components as both nss-SO4 and Vsol are also characteristic components of dust and neither nss-SO4 nor Vsol have been corrected for dust contribution.

Following the comment of the reviewer, figure 2 b was redrawn as shown in figure 5 by including the correction for the crustal contribution to Vsol, and by limiting the analysis to cases with Vsol > 6 ng m-3, i.e. the V and Ni enriched events in which the heavy oil combustion source plays an important role. Considering the SO4/Si ratio in the upper continental crust (6x10-3, Henderson and Henderson, 2009), we have estimated the sulphate contribution from dust, which is negligible: in the average it accounts for 0.2% with respect to the total nssSO4.

The red points in figure 5 are those obtained with this selection and after correction for crustal contribution. This selection and the correction for the crustal contribution to

ACPD

11, C15527–C15543, 2012

Interactive Comment

Vsol do not affect the derived minimum ratio. However, we believe that by including this correction, and by selecting cases in which the heavy oil combustion source is relevant, we may clarify the discussion.

Regarding the use of the SO4/Vsol minimum ratio, we do not expect to obtain a defined SO4/Vsol ratio (that does not probably exist even for a single source, due to the complex processes leading to SO4 formation); conversely, we look for a minimum ratio. Plot b of figure 2 clearly shows that no correlation exists between nssSO4 and V; the dashed line in the same figure represents the slope 200, not a correlation between the red points. From the figure and as stated in the text, we can only say that there are no samples with SO4/Vsol<200. We then use this minimum ratio to obtain a rough estimation of the minimum contribution of sulphate from the ship source (page 29931, lines 21-22), and not for a detailed quantification of the produced sulphur.

It must be considered that, once the dust cases have been taken into account, the addition of SO4 from sources other than heavy oil combustion would produce (as it appears from figure 2) an increase in SO4 without affecting Vsol. For instance, the ratio SO4/V in the upper continental crust is 19.2. Thus, we assume that the smallest SO4 to Vsol ratio may be ascribed to particles in which the contribution from heavy oil combustion is the dominant factor determining sulphate and Vsol amounts (it is likely that other aerosol components are present, which however are not expected in these cases to significantly contribute to the measured Vsol and SO4 amounts). It is still possible that we never have cases in which sulphates are mainly due to the heavy oil combustion source, i.e, also in the cases with SO4/Vsol =200 there are significant contributions from other sources. If this is the case, however, we would not expect a lower limit in the SO4 versus Vsol plot. The existence of a lower limit which is repeatable in several different cases led us to assume that in those cases heavy oil combustion is the dominant component in determining Vsol and SO4.

Beside, data from the special event (June-July 2008) from the 8 stage impactor (as reported in paper page 29931) case characterized by high heavy oil combustion contribution confirm that the minimum values we derive from bulk data is reasonable. As reported at page 29931, lines 11-13: "...During the special event of June/July 2008 the nssSO4 /V ratio values were all in the range 250–400, except for few spikes up to 1000, possibly due to the contribution from additional sources of SO4". In the following sentence we state: " A value of SO4/V in the same range (285) is derived for the finest particles stage (0.1–0.4 μm) of the impactor data...", which is an important additional information, since the 0.1–0.4 μm size fraction is expected to be largely influenced by the heavy oil source, and have a very limited dust content.

The previous aspects, and a discussion of the limitations of the method, will be added to the text to better support the obtained estimates. As stated above and in the paper, the method is used to derive a rough estimate of the minimum contribution of sulphate from heavy oil combustion. The data we found agree with those modeled by Marmer and Langmann (2005) for the same area.

9. Finally, even if a properly derived criterion involving V and/or Ni had been available among the many mentioned in the ms, then this criterion would have traced the contribution of all heavy oil combustion emissions including not only mobile, as concluded by the authors, but also fixed sources which are neglected in the whole paper. To be completely rigorous.

We agree with this comment. Consequently, as above stated, we will change the title in "Evidence for heavy oil combustion emissions in the Mediterranean Sea from aerosol chemical analyses at the island of Lampedusa", and will modify the text accordingly.

References not present in the manuscript

Adams, F.C., M. J. Van Craen, and P. J. Van Espen (1980), Enrichment of trace elements in remote aerosols, Environ. Sci. Technol., 14, 1002-1005.

Agrawal, H., W. A. Welch, J. W. Miller, and D. R. Cocker (2008), Emission measurements from a crude oil tanker at sea, Environ. Sci. Technol., 42, 7098–7103.

ACPD

11, C15527–C15543, 2012

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Chester, R., M. Nimmo, G.R. Fones, S. Keyse, and Z. Zhang (2000), Trace metal chemistry of particulate aerosols from the UK mainland coastal rim of the NE Irish sea, Atmos. Environ., 34. 949-958.

Cofala, J., M. Amann, C. Hayes, F. Wagner, Z. Klimont, M. Posch, W. Schopp, N. Tarrason, J. E. Jonson, C, Whall, an A. Stavrakaki (2007), Analysis of policy measures to reduce ship emissions in the context of the revision of national emission ceilings directive. International Institute for Applied Systems Analysis (IIASA), IIASA contract no. 06-107.

Eurostat (2009), Panorama of Transport, European Communities, Luxembourg.

Ferraro, G., Bernardini, A., David, M., Meyer-Roux, S., Muellenhoff, O., Perkovic, M., Carchi, D., Topouzelis, K., (2007). Towards an operational use of space imagery for oil pollution monitoring in the Mediterranean basin: a demonstration in the Adriatic Sea. Marine Pollution Bulletin 54, 403–422.

Gaffny J.S and Marley N.A. (2009), The impacts of combustion emission on air quality and climate – From coal to biofuels and beyond, Atmos. Environ., 43, 26-36.

Jonson, J.E., Tarrason, L., Klein, H., Vestreng, V., Cofala, J., Whall, C., (2009). Effects of ship emissions on European ground-level ozone in 2020. International Journal of Remote Sensing 30 (15-16), 4099-4110. Koçak, M., N. Mihalopoulos, N. Kubilay (2007), Contribution of natural source to high PM10 and PM2.5 events in the eastern Mediterranean, Atmos. Environ., 41, 3806-3818.

Meloni, D., A. di Sarra, G. Biavati, J. J. DeLuisi, F. Monteleone, G. Pace, S. Piacentino, and D. Sferlazzo (2007), Seasonal behavior of Saharan dust events at the Mediterranean island of Lampedusa in the period 1999–2005, Atmos. Environ., 41, 3041–3056 doi:10.1016/j.atmosenv.2006.12.001

Nicolás, J., M. Chiari, J. Crespo, I.G. Orellana, F. Lucarelli, S. Nava, C. Pastor, and E. Yubero. (2008), Quantification of Saharan and local dust impact in an arid Mediter-

ACPD

11, C15527–C15543, 2012

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

ranean area by the positive matrix factorization (PMF) technique, Atmos. Environ., 42, 8872-8882.

ORTC (Observatoire Régional des Transports de la Corse) (2011), Les trafics passagers de la Corse au cours de la saison 2011. Available at www.ortc.info

Remoundaki, E., A. Bourliva, P. Kokkalis, R.E. Mamouri, A. Papayannis, T. Grigoratos, C. Samara, and M. Tsezos (2011), PM10 composition during an intense Saharan dust transport event over Athens (Geece), Sci. Total Environ., 409, 4361-4372.

REMPEC (Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea) (2008), Study of Maritime Traffic Flows in the Mediterranean Sea, Final Report, 2008. Available at http://www.mmla.org.mt

Tzannatos, E. (2010), Ship emissions and their externalities for Greece, Atmos. Environ., 44, 2194-2202.

Vestreng, V., M. Adams, and J. Goodwin (2004), Inventory Review 2004, Emission Data reported to CLRTAP and under the NEC Directive, EMEP/EEA Joint Review Report, EMEP/MSC-W Note 1/2004.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 29915, 2011.

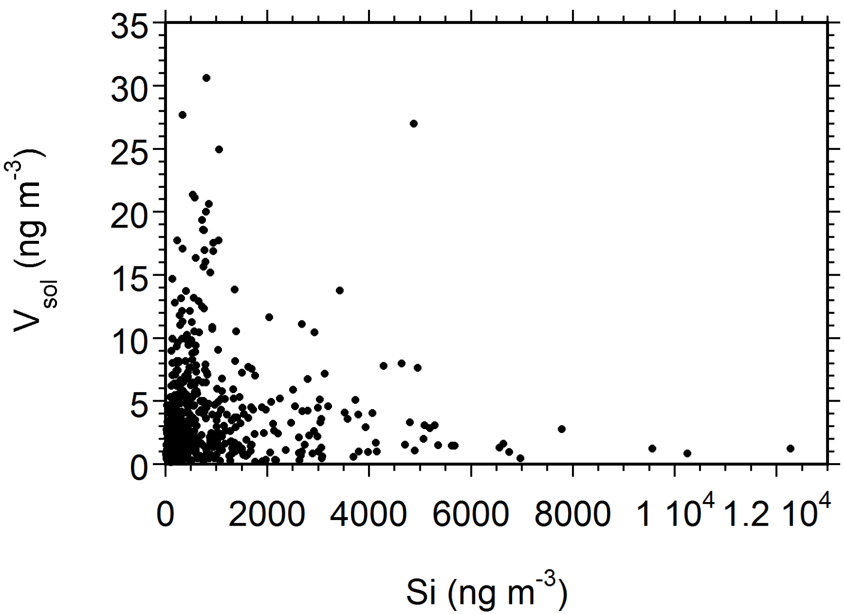

Fig. 1. Scatter plot Vsol vs. Si.

ACPD
11, C15527–C15543, 2012

Interactive Comment

ACPD
11, C15527–C15543, 2012

Interactive Comment

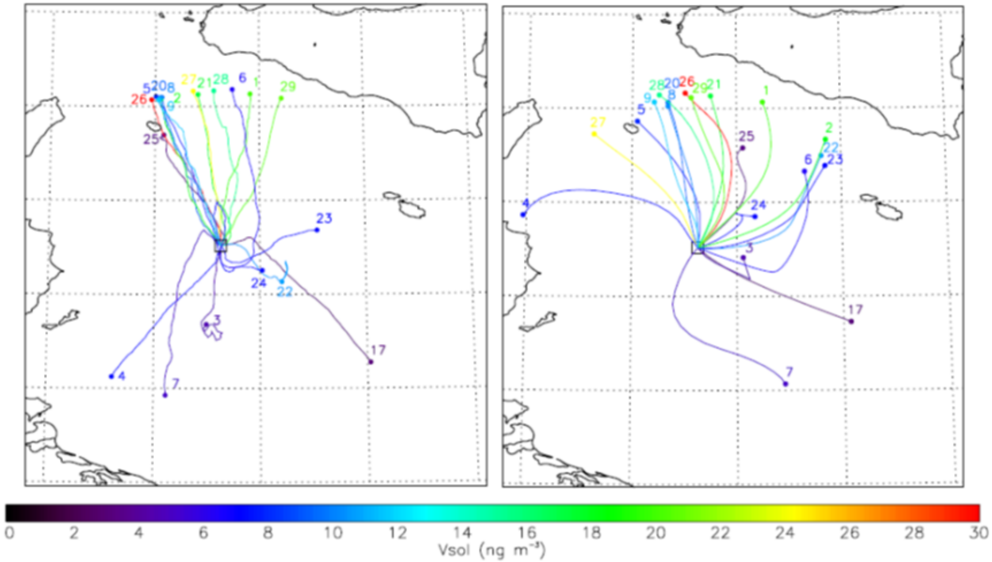

Fig. 2. Backtrajectories calculated by Hysplit (plot on the left) using the NCEP data and our backtrajectories (plot on the right) during the June/July 2008 event discussed in the manuscript (i.e., fig. 6 in

ACPD

11, C15527–C15543, 2012

Interactive Comment

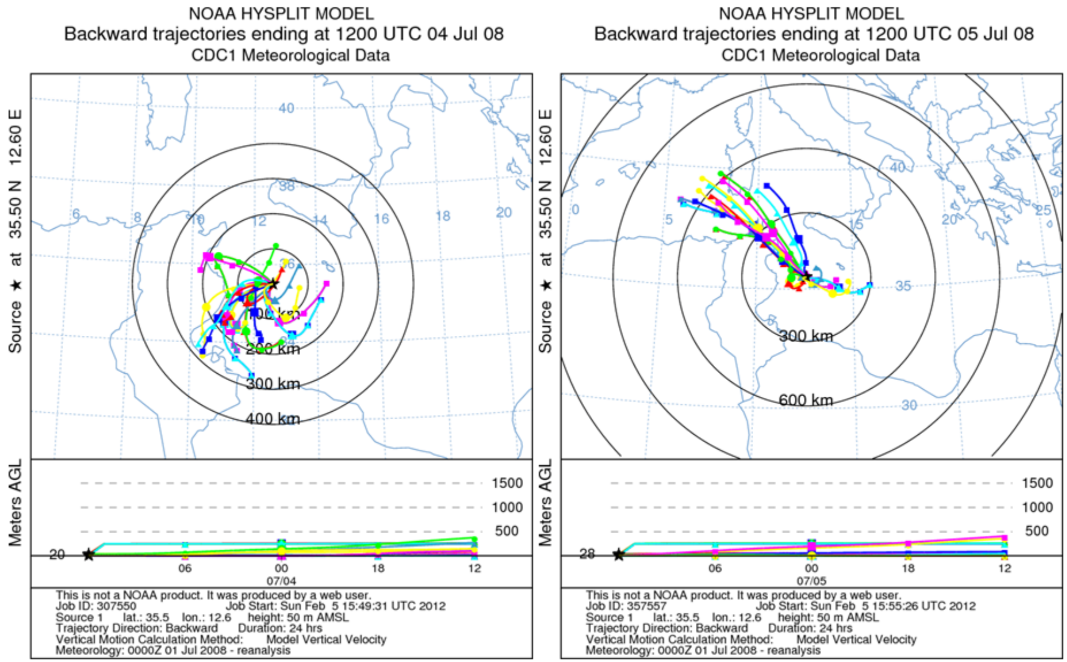

Fig. 3. Ensemble trajectories for July 4th (plot on the right) and 5th (plot on the left 2008. The trajectories are calculated for the lowest model level.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

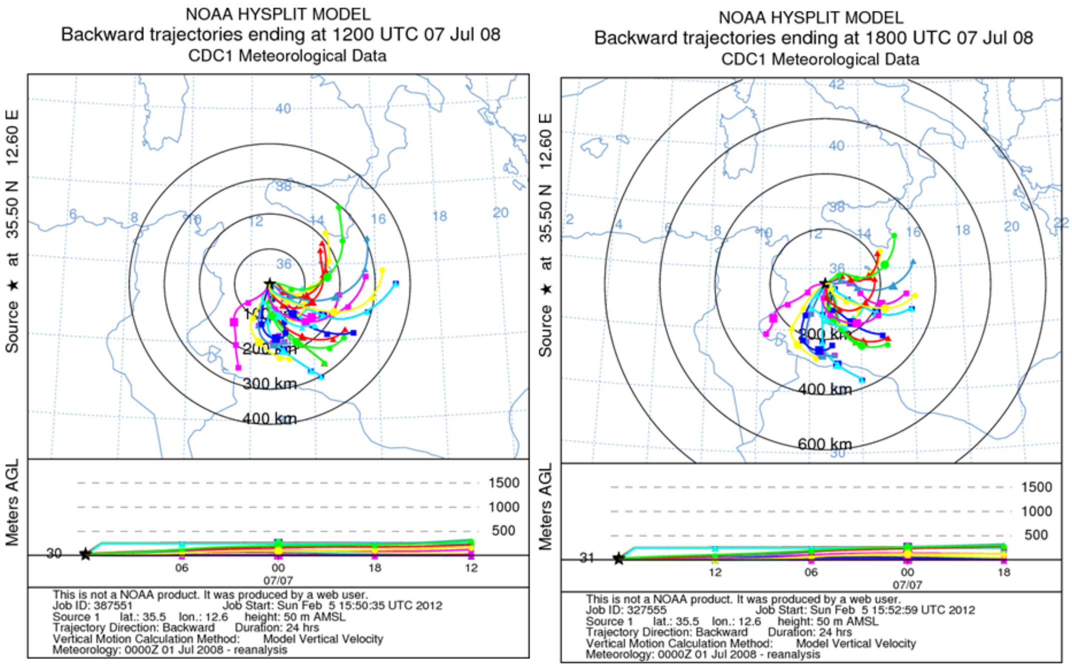

Fig. 4. Ensemble trajectories for July 7th 2008 ending at 12 UT (plot on the right) and 18 UT (plot on the left). The trajectories are calculated for the lowest model level.

ACPD
11, C15527–C15543, 2012

Interactive Comment

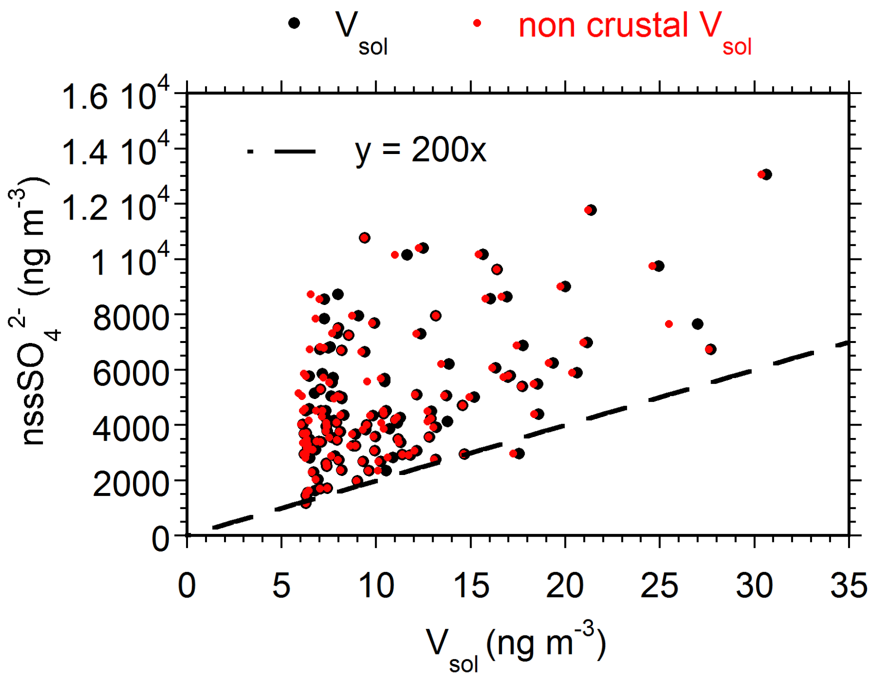

Fig. 5. Scatter plot nssSO4 vs. Vsol for Vsol>6 ng m-3. Dashed line in the plot b represents the ratio nssSO4/Vsol=200. The red points are obtained after correction for crustal contribution.

ACPD
11, C15527–C15543, 2012