

## ***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.***

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1. The manuscript reports on chemical composition data of aerosols collected at the Italian island of Lampedusa, in the central Mediterranean. The island is influenced by marine air masses, dust aerosols, and ship emissions but also by biomass burning and industrial/urban emissions from northern African and Europe. I will not be long on my review as I substantially agree with Referee 1. The data analysis in the paper is meant to demonstrate the evidence and the importance of ship emissions based on correlation between V, Ni, and Si and their soluble parts, and SO<sub>4</sub>. However, these elements are not unique to ship emissions, beside, the evidence is not made that the

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enhanced ratios of V and Ni to Si should be attributed to ship emissions, and not, for example, to fuel emissions in Tunisia in the coastal region of the Gulf of Gabes, which, in springtime, should be mixed with low-level mineral dust during its northward transport to Europe.

We actually are not able to distinguish the source. However, in the selected events with high concentration of V, trajectories come from Tunisia only in a couple of cases. Thus, relatively near sources in Tunisia are expected to play a very minor role in the results. As discussed in the answers to reviewer 1, we will modify the title and the text to point out that our results provide information on heavy oil combustion emissions, and not only ships.

2. Incidentally, Si is considered as unique tracer of mineral dust but it is not, being also present in fly ash from high-temperature combustion. This is implicitly acknowledged by the authors which use Si for the studies of the bulk composition but Al and Fe when studying the size-segregated aerosol composition.

Si is the main component of the continental crust (66.6% as SiO<sub>2</sub>, 31.1% as Si in the upper continental crust) followed by Al (15.4% as Al<sub>2</sub>O<sub>3</sub>, 7.7% as Al in the upper continental crust) and Fe (5.4% as various oxides, 3.6% as Fe), as indicated by Handerson and Henderson (2009). For this reason Si is considered the best marker of crustal content, although it is not often reported in literature as a crustal marker because of the difficulties in its analytical determination. Si is measured with surface techniques like PIXE (Particle Induced X-Ray emission) on Teflon filter, as in our work (such a technique requires an accelerator of particles), or by X ray fluorescence. In the most commonly used ICP-AES on the extracted solution, the Si is not accurately determinable because the only way to solubilize the silica matrix is through HF, which forms volatile compounds of Silicon (SiF<sub>6</sub> and SiF<sub>4</sub>); in this way the other elements can be completely dissolved (even those linked to the silica matrix), but most of the Si is lost. Another limitation found in literature in using Si as crustal marker is the substrate for aerosol collection. Several authors use quartz filters (SiO<sub>2</sub>) that prevents

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the determination of the Si content in the atmospheric particulate (e.g. Nicolás et al., 2008).

In the samples collected on the 8-stage impactor only the soluble content in mild condition ( $\text{HNO}_3$ , pH 1.5) was determined by ICP AES (as stated in the methodological part of the paper, page 29921). The PIXE techniques is not applicable on these samples due to the non homogeneous deposition of particulate on the membranes. Details on this technique are reported in the papers by Calzolari et al. (2006) and Chiari et al. (2005), as reported in the manuscript. Thus, the use of different markers for the crustal components is mainly due to the availability of different measurement techniques on different filter types. We believe that Si would be the most appropriate dust marker, should it be available also on the multi-stage impactor. This aspect will be more clearly specified in the revised version.

About the importance of fly ash from high combustion processes as extra source for Si, one has to note that fly ash contains  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in addition to  $\text{SiO}_2$ , and is emitted in the atmosphere mainly from coal electric power plants (Gaffney and Marley, 2009). If the contribution of fly ash is high all these elements cannot be used as markers of crustal content. On the contrary, the contribution of fly ash to the  $\text{PM}_{10}$  is negligible (Gaffney and Marley, 2009) indeed all these elements are commonly used to identify the crustal component, and particularly in Mediterranean region (e.g. Remoundaki et al, 2011, Koçak et al.2007, Nicolás et al., 2008 ) where the general high dust content makes negligible the other sources of Si, Al, and Fe. Also the emission of Si from heavy oil combustions is 2-3 orders of magnitude lower than V (Agrawal et al., 2008). In the aerosol sample collected in Lampedusa V ranges from 0.2 to 30 ng m<sup>-3</sup>; the corresponding amount of Si from heavy oil combustion is 0.002-0.3 ng m<sup>-3</sup>. Since the Si content range from 10 to 12300 ng m<sup>-3</sup>, the contribution of Si from this source to the total Si is negligible also in samples not affected by high crustal content.

3. The seasonal evolution paragraph is largely based on hypothesis without proof. It would be good if the authors could provide with statistics on ship traffic frequency, its

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seasonality, and the distance of the ship route to Lampedusa. It must be said that the authors have not given themselves an easy task owing to the complexity of the aerosol population in that part of the Mediterranean.

We attempted to obtain more specific data on the ship traffic when preparing the manuscript. However, we could not find any reliable dataset for the extended time period of our measurements. Also, we are not aware of data or analyses on the seasonality of the ship traffic in the Mediterranean. Recent modeling studies which used different ship emission inventories assumed a constant source throughout the year (e.g., Marmer and Langmann, 2005; Jonson et al., 2009), explicitly because of lacking information. In fact, available reports (e.g., Verstreng et al., 2004; Cofala et al., 2007; REMPEC, 2008; Eurostat, 2009) do not provide information on the seasonal distribution of the ship traffic and emissions. A limited information is available only for selected regions (e.g., Tzannatos, 2010; ORTC, 2011).

Seasonal changes in the ship traffic appear to be primarily connected with touristic activities/passenger transport, and mainly interest specific coastal areas (e.g., the Ligurian sea, several routes in Greece, etc.). A seasonal change in the remote sensing detection of oil spills has been also reported (Ferraro et al., 2007), which is however attributed mainly to different sea and meteorological conditions leading to better detection conditions in summer. As a summary, ship traffic linked to tourist activities is expected to have a significant seasonal character, while other ships are expected to show a limited seasonal change. The emissions from the passenger ships are estimated to be small (Jonson et al., 2009), thus probably produce a limited effect on the seasonal distribution of the emissions.

The main path of the ship traffic in the Mediterranean follows Gibraltar-Sicily Channel-Suez, with other important routes reaching Barcelona, Trieste, Greece, and the Black Sea. Coastal traffic is important in several regions. These patterns are discussed in several studies. Maps can be found for example in REMPEC (2008; figures 4.1 and 4.2), and in Marmer and Langmann (2005, figure 1).

The main shipping route through the Sicily channel runs about 180 km North of Lampedusa.

The discussion of the seasonality of the ship traffic, its main routes, and the position of Lampedusa will be expanded in the paper.

4. I recommend the authors to strengthen their point by adding the forward trajectory analysis from the ship track points to identify episodes of advection to Lampedusa, and also use the full dataset to discriminate evidence of mixed and pure dust events.

We have tried to carry out an analysis similar to the one proposed by the reviewer already in the preparation of the paper. However, we could not find any reliable ship traffic database for the period of investigation. We agree that it would be preferable to identify single ship sources. It must be pointed out however that ship traffic occurring between through the Sicily channel is rather intense, and a diffuse emission region along the main traffic route is expected. Considering that our dataset is based on 24-h integrated samples, it may in any case not possible to identify single events.

Regarding the discrimination between dust and mixed events, the paper will be improved as follows:

- Improving the discussion on Si threshold in crustal events and select the heavy oil combustion enriched samples
- Reporting an additional figure (see answer to point 5 of reviewer 1) with the observed behavior of Si vs Vsol, and improving the discussion in order to point out the different sources of Si and V
- Clarifying role and criteria used to identify the used threshold on Vsol
- Improving the discussion and the description of the data selection methodology.

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 measure-

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ments from a crude oil tanker at sea, Environ. Sci. Technol., 42, 7098–7103.

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, and A. Stavarakaki (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  
C15549

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E. Yubero. (2008), Quantification of Saharan and local dust impact in an arid Mediterranean 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](http://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 (Greece), *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.

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

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