Dear Editor,

please find attached a revised version of the paper: Constraining the ship contribution to the aerosol of the Central Mediterranean. We have addressed all the questions raised by the reviewers, and I hope now it can be published on ACP.
I want to thank both reviewers for their constructive comments and suggestions. Please find bellow the detailed answers. All authors concur with the submission of the revised paper

Best regards,

Silvie Becagli

Answer to the reviewers' comments

Anonymous Reviewer #1

Dear Editor,
this manuscript presents an assessment of shipping contributions to PM10 aerosols in two locations in the Mediterranean Sea. It presents a very interesting integrated approach combining different tools such as analysis of the chemical composition of PM10, tracer analysis, back-trajectories and ship inventories and databases. Whereas certain of these tools are not novel and suffer from limitations (e.g., tracer methods), the combination of all of them provides very interesting results. Over all, the paper is of interest to the scientific community and merits publication after revision.

Specific comments are provided below:
- lines 110-113 would fit better in the Methods section

Figure 1 and the corresponding text were moved to the methods section as suggested.

- line 276: very good, it is very important that the authors highlight this kind of limitation.

- line 292: "smaller" should be "lower". In general, the English is correct but a review by a native speaker would be helpful.

The sentence was corrected. The paper was revised by a native English speaker.

- Figure 2: the nitrate contribution at LMP is surprisingly high, considering the thermal instability of this species. Can this be due to an artefact or high uncertainty of the measurements?

The nitrate concentrations measured in this campaign are in agreement with the long term measurements performed at Lampedusa (e.g., Calzolai et al., 2015) and with data from other remote sites in the western (Mallorca; e.g. Simo et al., 1991) and eastern Mediterranean (Finokalia; e.g. Mihalopoulos et al., 1997). The presence of artefacts in the nitrate sampling are documented in literature. These artefacts cause lower concentrations in the sample than in the atmosphere, in polluted regions due to NH4NO3 volatilization

deposited on the filter. We believe than in relatively clean conditions like those incurring in Lampedusa and Capo Granitola the impact of artefacts is small, and the derived values are reliable. These values also suggest that ship emissions may play a large role. A comment was added to the text.

- line 340: also, EC concentrations are much higher in CGR, supporting this interpretation (the dominance of anthropogenic sources of carbonaceous aerosols in CGR)

We agree with the reviewer (see also comment 11 of reviewer 2). The sentence was changed and the differences were discussed.

- Figure 4 is interesting but not so useful, it could be removed if the authors encounter space limitations

We agree with the reviewer; the discussion of the sea breeze is interesting, but not directly related with the paper main topic. We delete this part from the manuscript.

- line 402: about the representativeness of this kind of ratios: it should be stated that this ratio may have a large variability due to varying fuel composition and engine operating conditions

We agree with the reviewer. The sentence was modified.

- line 424: LCR=1-5, how specific are these values for the specific refinery in the Moreno et al study? Can they really be extrapolated to other refineries? What can the uncertainty be for other refineries? Please discuss

Section 3.1.2 was largely modified, also taking into account the different comments of the reviewers.
The discussion on the LCR variability was improved and new references to support the discussion were added. In particular, we have reported range of values for ship, refinery, and crustal components of the aerosols, also with reference to literature results.

- line 430: 24% of samples with LCR>1 and 8% >2, this is a very high contribution (32%), can the contribution from refineries be so high at LMP? From where? Or is this an example of the limitation mentioned above, the uncertainty of these LCR values when applied to other study areas? Please discuss

We have double checked the calculated LCR values. As correctly suggested by reviewer 2 (see his/her point 13), we did not take into account the uncertainty and the detection limit of La and Ce measurements. The instrumental detection limit on these determination was added in section 2.1. The very high values of LCR correspond with very low, in some cases below the detection limit, La and/or Ce concentrations. In these cases the uncertainty on LCR exceeds 100%. The elimination of these data points filters out most of the very high LCR values. We have thus redrawn Figure 5 (that becomes fig 4) accordingly, also indicating the range of values which are expected for the crustal component.

- Figure 6: again, the authors show only one point per type of dust, what is the uncertainty? The authors' results seem very conclusive with regard to their own samples, but it would still be useful

to see the potential variability in the other (refinery, UCC) types of dust. If no other data is available for this kind of sources, please mention as a limitation

The Lanthanoid content in Saharan dust measured in several aerosol size classes and from different areas of Sahara, as well for other compounds are reported in figure 6 (figure 5 in the revised version). The discussion on the variability of the composition was expanded (see also answer to the two previous comments).

- line 575: it is also possible that this is due to the larger aerosol dilution during transport towards LMP?

We agree with the reviewer. Dilution may be a cause of lower V concentration at LMP. A sentence on the possible role of dilution was added

- line 666: "two times higher than...", isn't this strongly dependent on fuel and engine operating conditions?

We agree. The sentence was changed accordingly.

- line 702: "component" should be "components"

The typo was corrected.

- line 703: the term "rough estimate" is more adequate than the "unambiguous identification" used in other parts of the text

In the text we use "rough estimation" referring to the quantitative estimation of the minimum contribution of ship aerosol (i.e., using the method of the minimum values reported in section 3.4). However, we believe that the combination of the different methods discussed in the paper leads to an unambiguous attribution of the measured aerosol to the ship source.

- line 722: "50%", again, this is very variable depending on engine conditions, meteorology (oxidation rate of SO2...), etc. Therefore this 20% difference can be expected

We agree. This is one of the reasons why we may estimate only the lower limit for sulfate contribution. The sentence was corrected.

- line 741: the higher % contributions obtained should not be considered a negative result, due to the potentially large variability of these contributions. It is correct to compare the order of magnitude with the previous literature, but the precision of the authors' method (and of other currently available methods) is not sufficient for them to carry out a detailed comparison of the results obtained. The results presented are quite positive, in my opinion.

We fully agree. The sentence is explaining possible reasons for the observed differences.

- line 781: should "as expected", be added at the start of the sentence?
We agree with the reviewer's comment, and added "as expected" at the beginning of the sentence.

Anonymous Reviewer #2

This is a nice work that attempts to provide some estimates of the contribution of ship emissions to the budget of specific chemical species as well as to PM10 in total. There is undoubtedly quite a large fraction of uncertainty into this, as the authors themselves admit and partly discuss, which is based not only on the methodological limitations but also on the short period of this study and the very specific spatial grid they are referring at. In this line, even though I recognize some weakness of the paper to provide substantial new concepts, ideas or methods (as required by ACP), I still see the importance of such local studies in a hot issue like ship emissions in the Mediterranean and support its appropriateness for publication in the CHARMEX SI. I am suggesting major revision mainly because I would like to urge the authors to reorganize the presentation of their results in a way that they show up better the important aspects coming out of it.

General comment:
As the authors mention in lines 704-706, the use of their results(they are referring to the V different ratios but this is transferred also to the rest of the analysis) is limited by the fact that they refer to specific meteorology, photochemistry, space and season. This is obvious and unavoidable, but still there should be some discrimination of what is indeed only of local interest and what could be somewhat generalized e.g. by using ranges of values, relations with the level of traffic, or better describing the sensitivity of those results and comparing them more detailed with existing literature (even their own previous work).

We only partly agree with the comments on the local nature of the study. Of course, the analysis refers to a specific region, meteorology, season, etc. However, we believe that the information we retrieve is sufficiently robust, and relevant on a larger scale than local, mainly because it is based on two sites with markedly different characteristics. In particular, the site of Lampedusa is relatively far from the main shipping route, and the observations there suggest that ship emissions impact the Mediterranean basin on a larger scale than local. We have however added some comments and references with the aim of placing the obtained results in a wider perspective.

Moreover, the structure of the paper, at some point, confused me by means that I was expecting a number of synergistic analyses to identify and discriminate ship emissions (e.g. the standard markers, then some improvement by rare earth elements, then further refinement via trajectories etc), while Figure 8 speaks for itself! The authors might like to start from Fig. 8 and then provide further poof or try to explain discrepancies e.g. between the two sites. My overall impression is that the paper started from V and after a loop of some necessary and some unnecessary steps it ends up again with V. I hope some of my more specific comments that follow will help authors make improvements to the manuscript.

We agree that links among the different parts of the analysis are lacking or have been poorly discussed. However, we believe that including these lacking links the logical structure of the paper is sound, and we did not change the overall structure of the paper in the revised version. We have explained in more detail the connections among the different analyses, and the way in which they affect data. Some parts were heavily reorganized (see e.g., section 3.1.2), and some non essential information was removed (e.g., figures 4). We believe that the presentation is now clearer, and thank the reviewer for this suggestion.

Specific comments:

1. The language is very clear to understand but it should definitely benefit from some native English speaker editing.

The paper was revised by a native English speaker.

2. The word "anthropic" is probably misused instead of "anthropogenic". This is not based on the frequency of use of the words in the relevant literature, but mainly on the meaning of "anthropic" which is more what is influenced by humans or taking place during human era, rather than what is generated by human activities. I see its use mainly in social sciences. In Greek they use the translation of the word anthropogenic and not anthropic to refer to sources or pollution (in any case they are both Greek words!).

We agree with the comment. We have checked the use of the terms "anthropic" and "anthropogenic" throughout the paper.

3. Part of the paragraph in lines 100-118 seem to fit better as introduction to section 2.1. That would also include Fig.1 and the description of the sites. I would suggest to keep in the introduction only the nice unfolding of the diachronically followed strategy.

Figure 1 and the text were moved to section 2.

4. In section 2.1 (lines 146-153) there is a great number of references to available measurement types at Lampedusa that seem irrelevant to the specific work. Only references contributing to the description of Lampedusa characteristics as a site should be included here.

The number of references was reduced as suggested.

5. In section 2.1 there is a lot of information about the techniques used in the two stations. Probably the authors would like to organize part of this info in a table, to help readers follow easier.

A table with the sampling strategy and measurements carried out on each filter was added.

6. Please add information on start-end times of the 12h sampling at the two sites. See e.g. line 172, what is meant by diurnal sampling?

The start and end sampling time was added in the text and in the table reporting the sampling strategy.

7. Section 2.3 (lines 228-232). Please check on Solomos et al. 2015 who are articulating improvements in resolving and forecasting the dispersion of smoke plumes, in their case, over particularly complex terrains (including BL and sea-breeze system particularities), by incorporating high-resolution (spatial and temporal) meteorology and satellite data. (Solomos S., V. Amiridis, P. Zanis, E. Gerasopoulos, F.I. Sofiou, T. Herekakis, J. Brioude, A. Stohl, R.A. Kahn, C. Kontoes, Smoke dispersion modeling over complex terrain using high resolution meteorological data and satellite observations – The FireHub platform, Atmospheric Environment, Volume 119, http://dx.doi.org/10.1016/j.atmosenv.2015.08.066.)

A comment and the reference were added in the discussion.

8. Section 3.1 (lines 276-278). Could you here quantify this low crustal elements contribution as a percentage? (see lines 295-296).

The percentage of crustal content with respect to the total PM10 concentration was added.

9. Section 3.1 (lines 283-284). A reference should be provided.

The sentence applies to Lampedusa (or remote marine sites). This is now specified in the text.

10. Section 3.1 (lines 286-288). Though I understand the meaning, this sentence should be rephrased.

We agree. The sentence was rearranged.

11. Section 3.1 (lines 335-336, Fig. 3). I do not see this different behavior. At the same part of the plot which corresponds to lower values (see LMP axes) the behaviour seems similar – no specific correlation. So it is from a threshold and upwards that the influence of primary sources is shown on CGR. Please rearrange the interpretation.

We agree with the reviewer. Essentially, there are different concentration ranges at the two sites, and a correlation for moderate and elevated values at CGR. We have changed the sentence.

12. Section 3.1 (line 356, Fig. 4). On June 18 the diurnal cycle is opposite to what is described. (lines 359-362) This is not the case in all days … could the authors identify the sea breeze influenced days on the plot?

The discussion of the evolution linked to sea breeze and coastal circulation, and the different daily evolutions go beyond the main objective of the paper. Figure 4 was consequently deleted in the revised version.

13. Section 3.1.2 (lines 429-432). The percentage for LCR>1 at LMP seems large. How much is it biased by the fact that low La and Ce (especially Ce) values could produce arbitrary ratios? Please put a threshold to refine this analysis. Is this analysis with LCR used somehow to further constrain your statistical sample in the following parts? Or is it just to prove the appropriateness of V as a marker in this period? If so, what is the improvement brought in and how does it compare with the trajectories analysis?

We agree. The very high LCR values are discussed in the answer to reviewer 1 (see comment to line 430). The impact of the LCR values on the selected data was added, as well a discussion with respect to the trajectory analysis. The impact of LCR is shown in the following figures and in the dataset, and is discussed in the following parts of the paper. The cases with elevated values of LCR and possibly influenced by refineries have been highlighted also in figure 8 (figure 7 in the revised manuscript).

We understand the reviewer's point but the purpose of Figure 7 (figure 6 in the revised version) was just to give an overview of the results of the trajectory analysis and to show the air masses origin on a continental scale rather than a local one, as a consequence of the prevailing weather regimes observed during the campaign (e.g. the relatively high frequency of air masses coming from Central and Western Europe, especially in June 2013 due to the numerous Mistral episodes). In fact, Section 3.2.1 serves as an introduction to the more detailed analysis focused on the local aspects, which is discussed in the following Section 3.2.2. Furthermore, we cannot fully agree that contributions lower than 1% take up most of the scale in the plot, therefore we would rather keep Figure 7 (now figure 6) unchanged.

As the Reviewer correctly points out, the calculation of backtrajectories in the lowest layers and at short distances from the starting point may be affected by substantial uncertainties. However, this is particularly true when using coarse meteorological fields from global models (resolution of order of 50 km in space and three or six hours in time). In the present study outputs from a mesoscale model with relatively high spatial resolution (10 km and 35 vertical levels) and hourly temporal resolution are used to drive trajectory calculations. Though for some more specific applications and in particularly complex topography areas even higher resolutions would be required, we believe that for the purposes of our study the quality of meteorological fields is more than adequate. Indeed, our main focus is the description of transport within the marine boundary layer, which is reasonably well described using a 10-km grid spacing.

We agree with the reviewer that the limit ratio was determined arbitrarily.
In order to obtain a better estimate, we have tried to follow the reviewer's suggestion and have tried to fit different analytical curves to the data. However, we could not find a coherent fitting scheme for the different species, and ended up in choosing a simpler method. The limit ratio was calculated as the average of the observed values for V > 15 ng/m3.
This method allows to derive a quantitative estimate of the limit ratio, and to calculate its standard deviation.

Since we are determining a lower limit for the ship contribution to the total aerosol load, and a values of the ratio may still be decreasing for V around 15 ng/m^3, we used for each species a limit value which is equal to the average minus one standard deviation.

These limit values are somewhat different at Lampedusa and Capo Granitola, and are reported in figure 9 (now figure 8) and discussed in the text.

16. Section 3.4. I think this is the part that my general comment should be mostly taken into account. Highlight what is of general interest than only of local impact and use; elaborate further on comparisons (e.g. like in lines 741-746).

We have expanded the discussion at the end of section 3.4. See also the answer to reviewer 2 general comment.

Constraining the ship contribution to the aerosol of the Central Mediterranean

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Abstract

PM_{10} aerosol samples were collected during summer 2013 within the framework of the Chemistry and Aerosol Mediterranean Experiment (ChArMEx) at two sites located North (Capo Granitola) and South (Lampedusa Island), respectively, of the main Mediterranean shipping route in the Sicily Channel.

The PM_{10} samples were collected with 12 hour time resolution at both sites. Selected metals, main anions, cations, and elemental and organic carbon were determined.

The evolution of soluble V and Ni concentrations (typical markers of heavy fuel oil combustion) was related to meteorology and ship traffic intensity in the Sicily Channel, using a high resolution regional model for calculation of back trajectories. Elevated concentration of V and Ni at Capo Granitola and Lampedusa are found to correspond with airmasses from the Sicily Channel and coincidences between trajectories and positions of large ships; the vertical structure of the planetary boundary layer also appears to play a role, with high V values associated with strong inversions and stable boundary layer. The V concentration was generally lower at Lampedusa than at Capo Granitola, where it reached a peak value of 40 ng/m^3.

Concentrations of rare earth elements, La and Ce in particular, were used to identify possible contributions from refineries, whose emissions are also characterized by elevated V and Ni amounts; refinery emissions are expected to display high La/Ce and La/V ratios, due to the use of La in the fluid catalytic converter systems. In general, low La/Ce and La/V ratios were observed in the PM samples. The combination of the

analyses based on chemical markers, arimass trajectories, and ship routes allows to unambiguously identify the large role of the ship source in the Sicily Channel.

Based on the sampled aerosols, ratios of the main aerosol species arising from ship emission with respect to V were estimated with the aim of deriving a lower limit for the total ship contribution to PM_{10}. The estimated minimum ship emission contributions to PM_{10} was 2.0 $\mu g/m^3$ at Lampedusa, and 3.0 $\mu g/m^3$ at Capo Granitola, corresponding to 11% and 8.6% of PM_{10}, respectively.

1. Introduction

Ship emissions may significantly affect atmospheric concentrations of several important pollutants, especially in maritime and coastal areas (e.g. Endresen et al., 2003). Main emitted compounds are carbon dioxide (CO_2), nitrogen oxides (NO_x), sulfur dioxide (SO_2), carbon monoxide (CO), hydrocarbons, and primary and secondary particles. Thus, ship emissions impact the greenhouse gas budget (Stern, 2007), acid rain (through NO_x and SO_2 oxidation products; Derwent at al., 2005), human health (CO, hydrocarbons, particles; Lloyd's Register Engineering Services, 1995; Corbett et al., 2007) and solar radiation budget through aerosol direct and indirect effects (black carbon and sulfur containing particles; Devasthale et al., 2006; Lauer et al., 2007; Coakley and Walsh, 2002).

Heavy oil fuels used by ships contain varying transition metals. The aerosol emitted by ship engines is formed at high temperature (>800°C) from V, Ni, Fe compounds (Sippula et al., 2009). The thermodynamics predicts that the metals in these particles are mainly present as oxides. Sulfuric acid is found to form a liquid layer on the metal oxide ultrafine particles, leading to the metal partial dissolution, probably increasing the toxicity of the particles when inhaled.

In spite of the large amount of gas and particulate emitted by ships, maritime transport is relatively clean if calculated per kilogram of transported good. However, maritime transport has been increasing with respect to air and road transport (Micco and Pérez, 2001; Grewal and Haugstetter, 2007). In addition, emissions from other transport sectors are decreasing due to the implementation of advanced emission reduction technologies, and the relative impact of shipping emissions is increasing.

Regulations aiming at reducing emissions based on restrictions on the fuel sulfur content (sulfur emission control areas, SECAs) have been implemented in several regions. Although the legislation is focussed on sulfur emissions, the overall health and environmental effects depend in complex way on the physical and chemical properties of the emissions (WHO, 2013). Several studies have been carried out to determine the detailed chemical composition of shipping emissions (Agrawal et al., 2008a and b, Moldanová et al., 2009, Murphy et al., 2009, Lyyränen et al 1999, Cooper, 2003, Sippula et al. 2014); however, , the ships emissions are still poorly characterized with respect to on-road vehicles.

A large variety of anthropic sources (refineries, power plants, intense ship traffic, etc.) and natural emissions make the Mediterranean region one of the most polluted in the world (e.g., Kouvarakis et al., 2000; Marmer and Langmann, 2005). The multiplicity of Mediterranean sources (some of which with the same markers of ship aerosol) makes difficult the quantification of ship contribution to the total aerosol amount (e.g., Becagli et al., 2012).

The contribution of ships and harbour emissions to local air quality, with specific focus on atmospheric aerosol, has been investigated using models (Trozzi et al., 1995; Gariazzo et al., 2007; Eyring et al., 2005; Marmer et al., 2009), experimental analyses at high temporal resolution (Ault et al., 2010; Contini et al., 2011; Jonsson et al., 2011; Diesch et al., 2013; Donateo et al., 2014), receptor models based on the identification of chemical tracers associated with ship emissions (Viana et al., 2009; Pandolfi et al., 2011; Cesari et al., 2014), and integrated approaches with receptor and chemical transport models (Bove et al., 2014). Few studies exist in open sea (Becagli et al., 2012; Schembari et al., 2014; Bove et al., 2016).

In this context, studies performed at Mediterranean sites, where it is possible to distinguish ship emission from other sources of heavy fuel oil combustion, are important to investigate the current impact of the ship emissions on primary and secondary aerosols. This study contributes to the identification and characterization of the emissions from ships and the impact on the aerosol distribution in the central Mediterranean. The experiment was set up with the aim of unambiguously recognizing the ship source by a combination of methods.

2. Measurements and methods

In a previous study (Becagli et al., 2012) we used measurements of PM_{10} concentration and chemical composition carried out at Lampedusa to investigate the role of ship emissions in the central Mediterranean. Vanadium and Nickel were used as tracers of heavy fuel combustion together with trajectory analyses to assess the role of ship traffic. The ship source, however, could not be unequivocally separated from possible influences from refineries and power plants, which use similar fuels. In summer 2013 we addressed the same topic by implementing a specific strategy to target the aerosols due to ship emissions. PM_{10} samples were collected in parallel at Lampedusa (LMP) and at Capo Granitola (CGR), i.e., respectively South and North of the main shipping route through the Mediterranean, with the aim of isolating the ship source. The chemical analyses of the collected samples were complemented with measurements of Rare Earth Elements (REEs), trajectories and planetary boundary layer information from a high resolution regional model, and actual observations of ship traffic. The combination of these approaches allows to unambiguously identify the ship source, and permits to constrain its contribution to PM_{10} in the central Mediterranean.

The PM_{10} samples were collected in summer 2013 as a contribution to the Chemistry and Aerosol Mediterranean Experiment (ChArMEx; http://charmex.lsce.ispl.fr). Lampedusa is one of the supersites of the ChArMEx experiment; a list of the
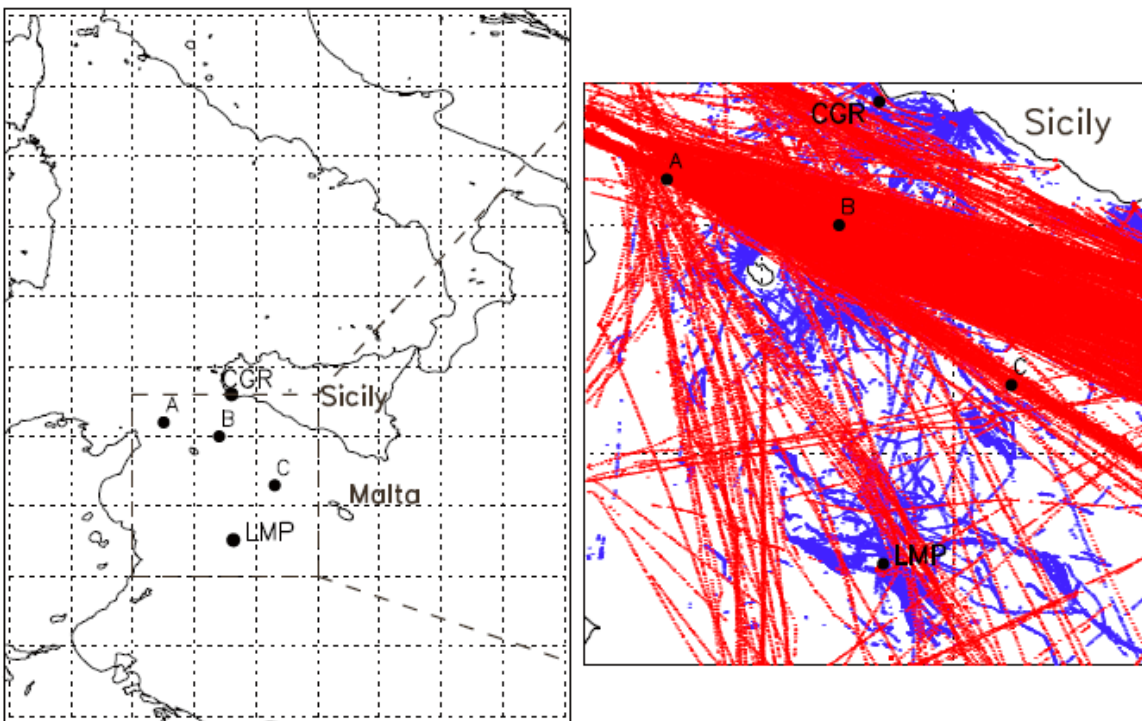
Figure 1. Map of the study area with the sites of Lampedusa (LMP) and Capo Granitola (CGR) (left panel). A, B, and C indicate the three sites selected to study the stability of the boundary layer in the Sicily Channel (see section 3.2.2). The ship routes in the study area during the first 10 days of June 2013 are displayed in the right panel. Red and blue dots show the routes of merchant and fishing vessels, respectively.

2.1. Aerosol sampling and chemical analyses

PM_{10} was sampled at two sites: at the Station for Climate Observations, maintained by ENEA (the Italian Agency for New Technologies, Energy, and Sustainable Economic Development) on the island of Lampedusa (35.5°N, 12.6°E), and at the Italian CNR (National Research Council) Research Centre at Capo Granitola (36.6°N, 12.6° E). Lampedusa is a small island in the Central Mediterranean sea, more than 100 km far from the nearest Tunisian coast. At the Station for Climate Observations, which is located on a 45 m a.s.l. plateau on the North-Eastern coast of Lampedusa, continuous observations of aerosol properties (di Sarra et al., 2011, 2015; Becagli et al., 2013; Marconi et al., 2014; Calzolai et al., 2015; Sellitto et al., 2017), aerosol radiative effects (e.g., Casasanta et al., 2011; di Sarra et al., 2011; Meloni et al., 2015), and other

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153 climatic parameters are carried out. Figure 1 shows the map of the central
154 Mediterranean with the measurement stations.
155 PM_{10} is routinely sampled on a daily basis at LMP (Becagli et al., 2013; Marconi et al.,
156 2014; Calzolai et al., 2015) by using a low volume dual channel sequential sampler
157 (HYDRA FAI Instruments) equipped with two PM_{10} sampling heads operating in accord
158 with UNI EN12341. For the intensive ChArMEx campaign, samples were collected at 12-
159 hour resolution (8:00-20:00 and 20:00-8:00 local time) from 1 June to 3 August, 2013.
160 The two channels operated in parallel and were loaded with different types of filters:
161 the first one with 47 mm diameter, 2 µm nominal porosity Teflon filters, and the second
162 one with 47 mm pre-fired, 2 µm nominal porosity, quartz filters. Ion chromatographic
163 analysis of soluble ions, atomic emission spectroscopy for soluble metals, and proton-
164 induced X-ray emission (PIXE) for the total (soluble+insoluble) elemental composition
165 were carried out on the Teflon filters. Elemental (EC) and organic carbon (OC) were
166 measured by analysing the quartz filters.
167 The sampling site at CGR is located at Torretta Granitola, a Research Center of the
168 Italian National Research Council, in South-Western Sicily (12 km from Mazara del
169 Vallo). The sampler was installed on the roof of one of the research centre buildings at
170 about 20 m a.s.l., directly on the coastline, facing the strait of Sicily.
171 At CGR PM_{10} samples were collected at 12 hour resolution (8:00-20:00 and 20:00-8:00
172 local time) with a TECORA Skypost sequential sampler on 47 mm pre-fired 2 µm
173 nominal porosity quartz filters, which were used to determine ions, metals, EC and OC
174 on different fractions of the filter. Due to technical problems, some daytime (8:00-
175 20:00) samplings were lost at CGR.
176 The PM_{10} mass was determined by weighting the filters before and after sampling with
177 an analytical balance in controlled conditions of temperature (20±1 °C) and relative
178 humidity (50±5 %). The estimated error on PM_{10} mass is around 1% at 30 $\mu g/m^3$ in the
179 applied sampling conditions.
180 A quarter of each Teflon filter from LMP and a 1.5 cm^2 punch of the quartz filter from
181 CGR were analysed by Ion Chromatography (IC) in the analytical conditions described
182 in Marconi et al. (2014). The estimated uncertainty for IC measurements is 5% for all
183 the considered ions.
184 Blank values were negligible with respect to the concentration in the samples for Teflon
185 filters. Blank values for quartz filters were negligible for most of the analyzed species.
186 For some species characterized by high blank values, always lower than the 25th
187 percentile value, they were subtracted from the measured concentrations.
188 Another quarter of the Teflon filter from LMP, and another 1.5 cm^2 punch of the quartz
189 filter from CGR were extracted in ultrasonic bath for 15 min with MilliQ water acidified
190 at pH 1.5–2 with ultrapure HNO_3 obtained by sub-boiling distillation. This extract was
191 used for the metals soluble part determination by means of an Inductively Coupled
192 Plasma Atomic Emission Spectrometer (ICP-AES, Varian 720-ES) equipped with an
193 ultrasonic nebulizer (U5000 AT+, Cetac Technologies Inc.). The pH chosen value is the
194 lowest found in rainwater (Li and Aneja, 1992) and leads to the determination of the

metals fraction available to biological organisms and, for some metals (e.g. V and Ni),
related to the anthropic source (Becagli et al., 2012).

The remaining half Teflon filter from Lampedusa another punch of the quartz filter from
CGR were used for the determination of metals by ICP-AES through the solubilisation
procedure reported in the EU EN14902 (2005) rule, by using concentrated sub-boiling
distilled HNO_3 and 30% ultrapure H_2O_2 in a microwave oven at 220°C for 25 min (P =
55 bar). This solubilisation procedure is not able to completely dissolve the silicate
species. However, this procedure allows to recover at least 70% of the same elements
measured by proton induced X ray emission technique also for elements with dominant
crustal source (unpublished data), due to the low crustal aerosol load in these sampling
period (e.g., Mailler et al., 2016). La and Ce presented very low concentrations in the
collected aerosol samples. Thus, particular attention was devoted to the minimization of
the La and Ce detection limit. In the used sampling and analytical conditions of LMP
samples the detection limits for La and Ce are 0.02 ng/m^3 and 0.08 ng/m^3, respectively,
and are about 4 times higher for the CGR samples, due to the smaller filter portion used
for the analysis.

The OC and EC measurements were carried out on a 1.5 cm^2 punch of the quartz filters
from Lampedusa and Capo Granitola by means of a Sunset thermo-optical
transmittance analyser, following the NIOSH protocol (Wu et al, 2016).

The overall aerosol sampling and analytical strategy for the two sites are reported in
table 1.

Table 1. Sampling strategy and chemical measurements carried out on each filter for
the two sites: Lampedusa (LMP) and Capo Granitola (CGR).

Sampling site	Filter	Sampling interval, local time.	Measurements
LMP	Teflon	8:00-20:00 (daytime sample)	• PM_{10}; • Ions by IC (1/4 of the filter); • metals in HNO_3 pH 1.5 room temperature extract by ICP-AES (1/4 of the filter); • metals in HNO_3-H_2O_2 in microwave oven extract by ICP-AES (1/2 filter)
		20:00-8:00 (nighttime sample)	
	Quartz	8:00-20:00 (daytime sample)	• EC/OC by thermo-optical analyser (1.5 cm x 1 cm punch)
		20:00-8:00 (nighttime	

		sample)	
CGR	Quartz	8:00-20:00 (daytime sample)	• PM$_{10}$; • Ions by IC (1.5 cm x 1 cm punch); • metals in HNO$_3$ pH 1.5 room temperature extract by ICP-AES (1.5 cm x 1 cm punch);
		20:00-8:00 (nighttime sample)	• metals in HNO$_3$-H$_2$O$_2$ in microwave oven extract by ICP-AES (1.5 cm x 1 cm punch) • EC/OC by thermo-optical analyser (1.5 cm x 1 cm punch)

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2.3. Atmospheric model and trajectory calculations

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224 Numerical simulations with a non-hydrostatic mesoscale atmospheric model were used
225 to characterize the meteorological conditions in the Sicily Channel during the campaign
226 and to support the interpretation of the experimental results. The Weather Research
227 and Forecasting (WRF) model (Skamarock et al., 2008) outputs, provided by the
228 Department of Physics of the University of Genoa, Italy, were used, covering the entire
229 Mediterranean with a grid spacing of 10 km and hourly temporal resolution. Initial and
230 boundary conditions to drive WRF simulations were obtained from the Global Forecast
231 System operational global model (Environmental Modeling Center, 2003) outputs
232 (0.5x0.5 squared degrees). Some recent applications of the modelling chain are
233 described in Mentaschi et al. (2015) and Cassola et al. (2016), where full details on the
234 model configuration can also be found.
235 In particular, the WRF 3-D hourly meteorological fields were used to calculate backward
236 trajectories with the NOAA HYbrid Single-Particle Lagrangian Integrated Trajectory
237 Model (HYSPLIT; Stein et al. 2015). The trajectories were used to assess the origin of
238 the air masses impacting the monitoring sites and to support the source attribution
239 suggested by the analysis of specific markers (see Section 3.2.2). The use of a high-
240 resolution regional atmospheric model for trajectory calculations allows a better
241 representation of boundary layer properties and mesoscale phenomena such as
242 land/sea breezes, which can have a relevant impact especially in complex topography
243 coastal sites like CGR.
244 Also, the high temporal resolution of meteorological data (hourly instead of three- or
245 six-hourly products typically available from global models) permits a better description
246 of diurnal cycles as well as a more accurate trajectory computation, without time
247 interpolation between subsequent atmospheric fields (Solomos et al., 2015).
248 Specifically, 48-h long back trajectories arriving at LMP and CGR were computed from a
249 reference height of 10 m above the ground level, starting every six hours for the whole
250 period of the campaign, from 10 June to 31 July, 2013.

2.4. Ships/marine traffic

Position and main characteristics of the ships travelling in the central Mediterranean were derived from the MarineTraffic database (http://www.marinetraffic.com/), which provides data with a high temporal resolution (about 3-5 minutes) by means of the Automatic Identification System (AIS).

Three classes of ships defined by the AIS classification were considered: all the ships, the merchant (i.e. cargo and tanker), and the fishing vessels. Merchant and fishing vessels are the most frequent ships in the Sicily Channel; merchant ships are expected to produce the highest impact due to their higher emissions (http://ec.europa.eu/environment/archives/air/pdf/chapter2_ship_emissions.pdf).

3. Results

3.1. PM$_{10}$ chemical composition at the two sites

The sea salt aerosol (SSA) component of PM$_{10}$ was estimated as the sum of Na$^+$, Mg^{2+}, Ca^{2+}, K$^+$, sulfate and chloride sea salt (ss) fractions. Details on the calculation of sea salt Na$^+$ and Ca^{2+}, and non-sea salt (nss) fractions are reported in Marconi et al. (2014). The Mg^{2+}, Ca^{2+}, K$^+$, and sulphate sea salt fractions were calculated from sea salt Na$^+$ (ssNa$^+$) by using the ratio of each component to Na$^+$ in bulk sea water: Mg^{2+}/Na$^+$ = 0.129, Ca^{2+}/Na$^+$ = 0.038, K$^+$/Na$^+$ = 0.036, SO$_4^{2-}$/Na$^+$ = 0.253 (Bowen, 1979). Chloride undergoes depletion processes during aging of sea spray, mainly due to exchange reactions with anthropogenic H$_2$SO$_4$ and HNO$_3$, leading to re-emission of gaseous HCl in the atmosphere. Thus, for chloride we use the measured chloride concentration instead of the one calculated from ssNa$^+$. Thus,

SSA = 1.46 *[ssNa$^+$] + [Cl$^-$].

The crustal component is calculated from Al, which represents 8.2% of the upper continental crust, UCC (Henderson and Henderson 2009). A previous study using an extensive data set at Lampedusa showed that the crustal content determined from the total Al was in very good agreement with calculations made from the sum of the metal oxides (Marconi et al., 2014). However, in this study we use measurements of the soluble Al concentration obtained by ICP-AES on the solution obtained with H$_2$O$_2$ and HNO$_3$ in microwave oven instead of the total Al content. Therefore, in this work we underestimate the crustal contribution by about 30% (unpublished results). However, it must be emphasized that the crustal aerosol contribution was very low throughout the measurement campaign.

Figure 2 shows the time series of the main PM$_{10}$ components at LMP and CGR. An intense Mistral event occurred from 22 June to 1 July. Mistral events are characterized

by strong winds from the north-westerly sector, and often by subsiding air masses originating from the free troposphere (Jiang et al., 2003). Thus, <mark>elevated values of SSA and low concentrations of other compounds are generally found during Mistral at Lampedusa</mark>.

Average concentrations of PM_{10} and of the different aerosol components for the whole measurement campaign and for the non-Mistral conditions are reported in Table 2. The averages were calculated over a homogeneous dataset, i.e., when measurements are available at both sites.

Table 2. Mean and standard deviation of PM_{10} load and composition, and percentage with respect to PM_{10} (in bracket) at Lampedusa and Capo Granitola. Mean, standard deviation and percentage are calculated on homogeneous data sets for both sites considering all the common sampling ("all data" columns) and excluding the mistral events ("Mistral excluded" columns).

	Lampedusa		Capo Granitola	
	All data	**Mistral excluded**	**All data**	**Mistral excluded**
PM_{10} ($\mu g/m^3$)	18.0±6.6	16.3±5.2	34.1±18.9	27.2±6.5
Sea Salt Aerosol ($\mu g/m^3$)	4.63±6.30 (25.7%)	2.33±3.21 (14.3%)	8.14±15.50 (23.9%)	2.12±6.51 (7.8%)
Crustal Aerosol ($\mu g/m^3$)	0.82±0.44 (4.6%)	0.90±0.43 (5.5%)	2.80±1.7 (8.2%)	3.02±1.75 (11.1%)
$nssSO_4^{2-}$ ($\mu g/m^3$)	3.95±2.28 (21.9%)	4.40±2.22 (27.0%)	6.78±3.08 (19.9%)	7.53±2.78 (27.7%)
NH_4^+ ($\mu g/m^3$)	0.98±0.56 (5.5%)	1.09±0.55 (6.7%)	1.48±0.94 (4.3%)	1.66±0.87 (6.1%)
NO_3^- ($\mu g/m^3$)	1.25±1.00 (7.0%)	1.02±0.02 (6.2%)	1.35±1.11 (4.0%)	1.01±0.82 (3.7%)
Organic aerosol ($\mu g/m^3$)	3.86±1.56 (21.4%)	4.04±1.59 (24.8%)	9.02±2.52 (26.5%)	9.53±2.29 (35.0%)
Elemental carbon ($\mu g/m^3$)	0.15±0.08 (0.8%)	0.15±0.08 (0.9%)	0.44±0.28 (1.3%)	0.51±0.26 (1.9%)
Unknown ($\mu g/m^3$)	2.52±3.26 (14.0%)	2.20±3.40 (13.5%)	4.11±7.78 (12.1%)	1.82±4.48 (6.7%)

310 The largest PM$_{10}$ values were associated with elevated SSA during the Mistral event at
311 both sites. PM$_{10}$ is about two times larger at Capo Granitola than at Lampedusa. The
312 PM$_{10}$ measured during the campaign at Lampedusa was significantly lower than its long-
313 term average (31.5 μg/m^3; Marconi et al., 2014). No Saharan dust transport events
314 occurred at low altitude in this period (e.g., Mailler et al., 2015), and the crustal aerosol
315 contribution remained very low and almost constant at both sites (average < 1 μg/m^3
316 at LMP and around 3 μg/m^3 at CGR corresponding to 4.6% and 8.2% of the PM$_{10}$ at
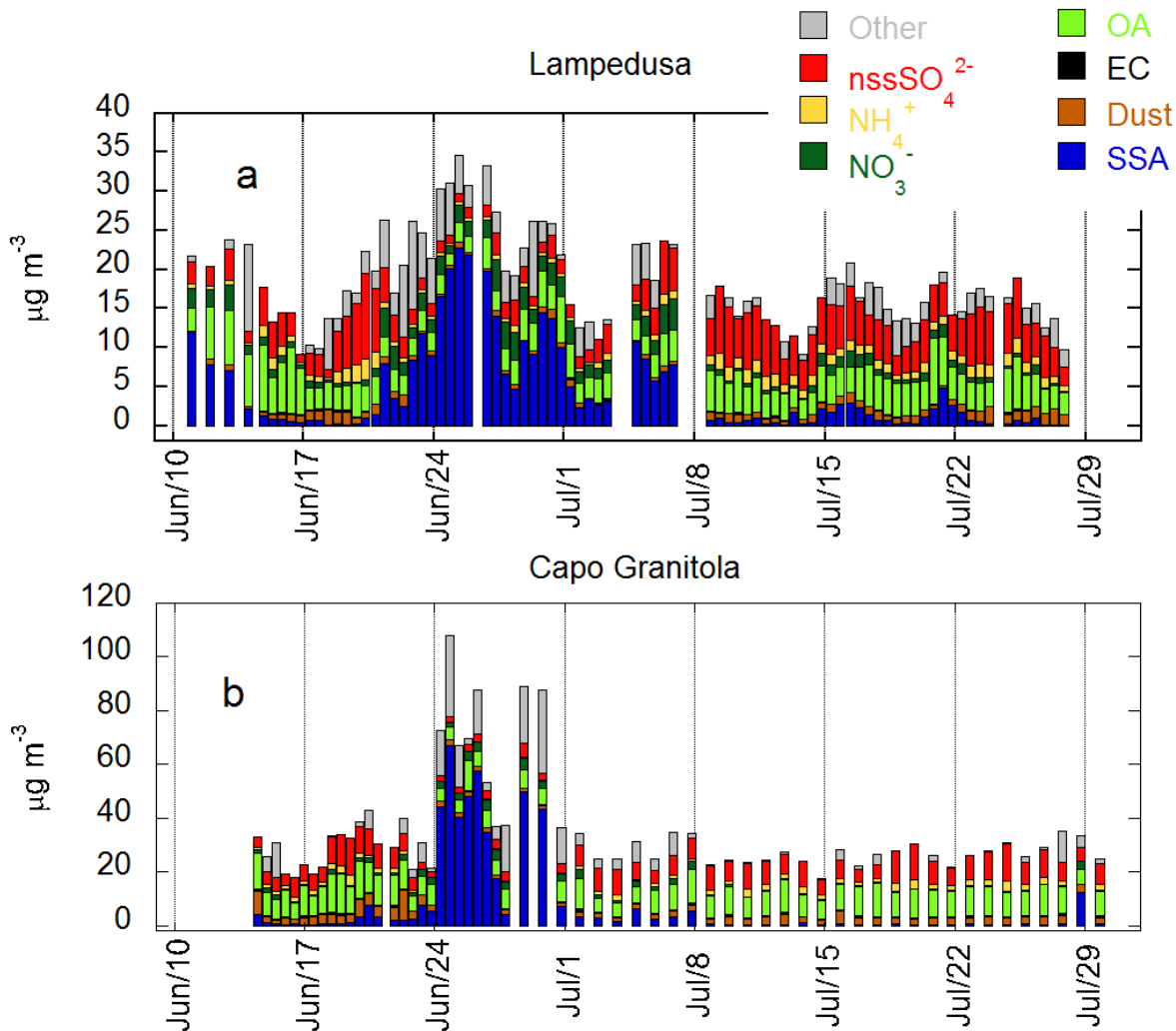317 LMP and CGR respectively).

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319
320 Figure 2. Time series of the main aerosol components at LMP (plot a) and CGR (plot b).
321 Note the different vertical scales of the graphs. OA stands for organic aerosol.
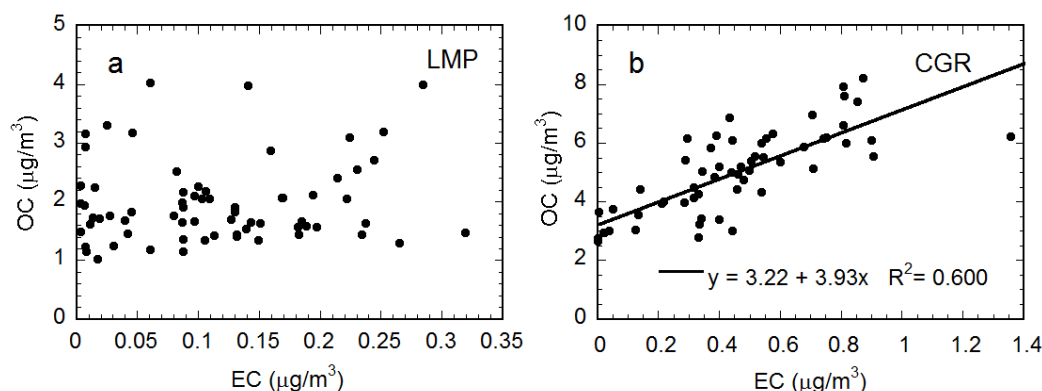322
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Figure 3. Scatter plot of OC vs. EC at LMP (plot a) and CGR (plot b). Note the different vertical scales.

SSA accounted for about 26% and 24% of PM_{10} at LMP and CGR, respectively. The SSA contribution was about 14% of PM_{10} at LMP and 8% at CGR during the periods not influenced by the Mistral.   Non-sea salt SO_4^{2-} was the most abundant among the secondary inorganic species. Nitrate concentrations, although relatively high at both sites, are in agreement with the long term measurements performed at Lampedusa (e.g., Calzolai et al., 2015) and with data from other remote sites in the western (Mallorca; e.g. Simo et al., 1991) and eastern Mediterranean (Finokalia; e.g. Mihalopoulos et al., 1997). Organic aerosol (OA) was the most abundant component at CGR, where its mean concentration was > 9 μg/m^3 and represented 35% of PM_{10} in the days not characterized by Mistral. Elemental carbon and organic carbon show higher values at CGR than LMP. At CGR moderate and elevated values of OC and EC appear correlated (R^2=0.60; n =59; Figure 3b), suggesting a strong influence from carbon species primary sources, characterized by the simultaneous EC and OC emission. The influence from primary sources is apparent at EC > 0.4 ·g/m^3. At LMP, on the contrary, OC was not correlated with EC (figure 3a), indicating a strong impact of OC secondary and/or natural sources. This confirms that Lampedusa may be considered a background site in the central Mediterranean (see e.g., Artuso et al., 2009; Henne et al., 2010), and the observations there may be taken as representative for a relatively wide open sea region. Thus, we used a conversion factor of 1.8 (typical for urban background sites, Turpin and Lin, 2001) at CGR, and of 2.1 (typical for remote sites characterized by high impact of secondary sources, Turpin and Lin, 2001) at LMP to estimate the total organic aerosol amount from the OC measured values. Once estimated OA with this method, the sum of the various species accounted to more than 85% of the measured mass at

both sites. The unreconstructed mass could be due to an underestimation of OA from OC, or to the presence of bound water not removed by the desiccation procedure at 50% relative humidity (Tsyro, 2005; Canepari et al., 2013).

3.1.1. Ship emission markers: V and Ni

Several studies focussed on the identification of shipping emissions specific tracers (Viana et al., 2008; Becagli et al., 2012, Isakson et al., 2001, Hellebust et al., 2010). Vanadium and Nickel are generally considered the best markers for this source because, after sulfur, they are the main impurities in heavy fuel oil (Agrawal et al., 2008a and b). The soluble fraction of these metals is even more representative for the ship source (Becagli et al., 2012).

Following Becagli et al. (2012), we used measurements of the V and Ni soluble fractions (V_{sol} and Ni_{sol}, respectively). In the data set here considered the V_{sol} and Ni_{sol} ratio with respect to Al were always more than 10 times larger than for UCC, as expected for cases dominated by heavy oil combustions sources (ships, refineries, power plants, stainless steel production plants).

Table 3 reports slope, correlation coefficient, and number of samples of the linear correlation between V_{sol} and Ni_{sol}.

Table 3. Correlation parameters between V and Ni at LMP and CGR PM_{10} samples for all the samples and for samples with V concentration higher than 6 ng/m^3.

		Slope (± uncertainty)	R^2	n.
LMP	All data	2.94±0.03	0.986	124
	$V_{sol} > 6ng/m^3$	2.99±0.03	0.994	44
CGR	All data	2.82±0.08	0.950	59
	$V_{sol} > 6ng/m^3$	3.00±0.05	0.989	34

V_{sol} and Ni_{sol} are highly correlated, suggesting a common source. The obtained slope of the regression line (2.8-2.9, that increases to 3.0 for samples with V_{sol} >6 ng/m^3) is in the range of ratios typical for heavy fuel oil combustion sources. The same value was found at Lampedusa by Becagli et al. (2012), considering data from 2004 to 2008. The behaviour of V, Ni, and their ratio are then representative of heavy fuel oil combustion. It must be emphasized that the V/Ni ratio is expected to display a large variability due to varying fuel composition and engine operating conditions (Mazzei et al., 2008; Agrawal et al., 2008a and b, Viana et al. 2009; Pandolfi et al., 2011). It is however difficult to distinguish V and Ni originating from power plants, refineries, or ship

engines. Moreover, several refineries are present in Sicily (Siracusa, Gela, Milazzo) and in Sardinia (Cagliari) and may potentially influence the sampling sites.

A combination of methods is thus used in this study to unequivocally identify the ship source. The analysis is based on: additional chemical tracers, like the Rare Earth Elements, whose behaviour is specific for the refinery and the ship sources; high resolution back-trajectories, based on data from the high resolution regional model; information on the vertical mixing in the atmospheric boundary layer; coincidences between the high resolution back-trajectories and the position of different types of ships in the Sicily Channel.

3.1.2. Rare Earth elements

As discussed above, anthropogenic V and Ni originate from heavy oil combustion, and may be considered markers of the ship source only when other sources can be excluded. Few studies propose the use of lanthanoid elements (La to Lu) to distinguish refinery from ship emissions (Moreno et al., 2008a and b; Du and Turner, 2015; Kulkarni et al., 2006).

In particular, the ratio between the La and Ce concentrations (La/Ce ratio, hereafter LCR) and between La and V (hereafter LVR) can be used to identify specific sources. Shipping emissions are characterised by values of LCR between 0.6 and 0.8 and LVR < 0.1 (Moreno et al., 2008a, 2008b).

Crustal aerosols are characterized by LCR ranging from 0.4 to 0.6 and LVR usually in the range 0.2-0.3 (Moreno et al., 2008 a and b). LCR depends weakly on differences in dust source area and collected aerosol size fraction, contrarily to LVR, which reaches 0.9 for large (>10 μm) particles from specific areas of Sahara (e.g., Hoggar Massif; Handerson and Handerson, 2009; Moreno et al., 2006; Castillo et al, 2008).

Elevated values of LCR (from 1 to 13) are associated with emissions from refineries (Moreno et al., 2008a; Du and Turner, 2015). This is because zeolitic fluidised-bed catalytic cracking (FCC) unit enriched in La are used to crack long-chain olefins in crude oil to shorter-chain products (Bozlaker et al., 2016; Du and Turner 2015; Kulkani et al 2006; Moreno et al., 2008a, 2008b).

Mixing of aerosol from different sources may produce a large variability of LCR, with larger values corresponding to a stronger impact from refineries.

The time series of LCR and LVR at LMP and CGR is displayed in figure 4. The range of values expected for crustal aerosol is highlighted in the figure. Please, note that the uncertainty on LCR is very large when La and Ce concentrations are close to the measurement detection limit. These cases may produce very large values of LCR which are not significant; these cases were removed from the time series.

LCR at LMP and CGR was generally around the value expected for crustal aerosol (dashed grey area in figure 4); 10 samples from LMP and 2 samples from CGR show values LCR higher than 1. LCR is >1.5 in a single case, at LMP. .This suggests that the refineries impact is small in the collected samples.

435 Moreno et al. (2008b) have shown that it is possible to identify aerosol from refineries
436 based on V, La, Ce three-component plot. This type of plot is shown in figure 5 for the
437 data from LMP and CGR. La and Ce were scaled in order to have the typical UCC
438 composition in the centre of the plot.
439 The compositions of UCC (Henderson and Henderson, 2009), African desert dust
440 (Castillo et al., 2008; Moreno et al., 2006), FCC (Kulkarni et al., 2006), La-contaminated
441 (refinery) Asian dust collected at Mauna Loa, Hawai'i (Olmez and Gordon, 1985), and
442 PM_{10} and $PM_{2.5}$ collected at Puertollano (Spain) in days possibly affected by refinery
443 emissions (Moreno et al., 2008b) are also displayed in figure 5.
444 The data from CGR and LMP are grouped in a region with elevated values of V, and La
445 and Ce generally lower than for refinery and dust cases.
446 Data from Puertollano shown in figure 5 are relative to days characterized by winds
447 originating from sectors where refineries are located; however, these samples are
448 affected by a mix of particles from several sources, including refineries. Aerosol samples
449 from Spain affected in most cases display larger La to Ce and La to V ratios than those
450 found at LMP and CGR. The composition of all samples collected in this period at LMP is
451 consistent with a large impact from ship emissions. Some cases at CGR may suggest
452 the simultaneous occurrence of crustal and ship aerosols, or dominant crustal
453 component (orange open dots in figure 5). Therefore, these cases display a relatively
454 low V concentration and are mainly associated with the Mistral event. A limited crustal
455 contamination may possibly occur at CGR in these cases, due to resuspension due to
456 the strong wind.
457 Cases with LCR>1 (grey and pink open circle for CGR and LMP respectively) are
458 highlighted in figure 5. The aerosol composition is however consistent with the ship
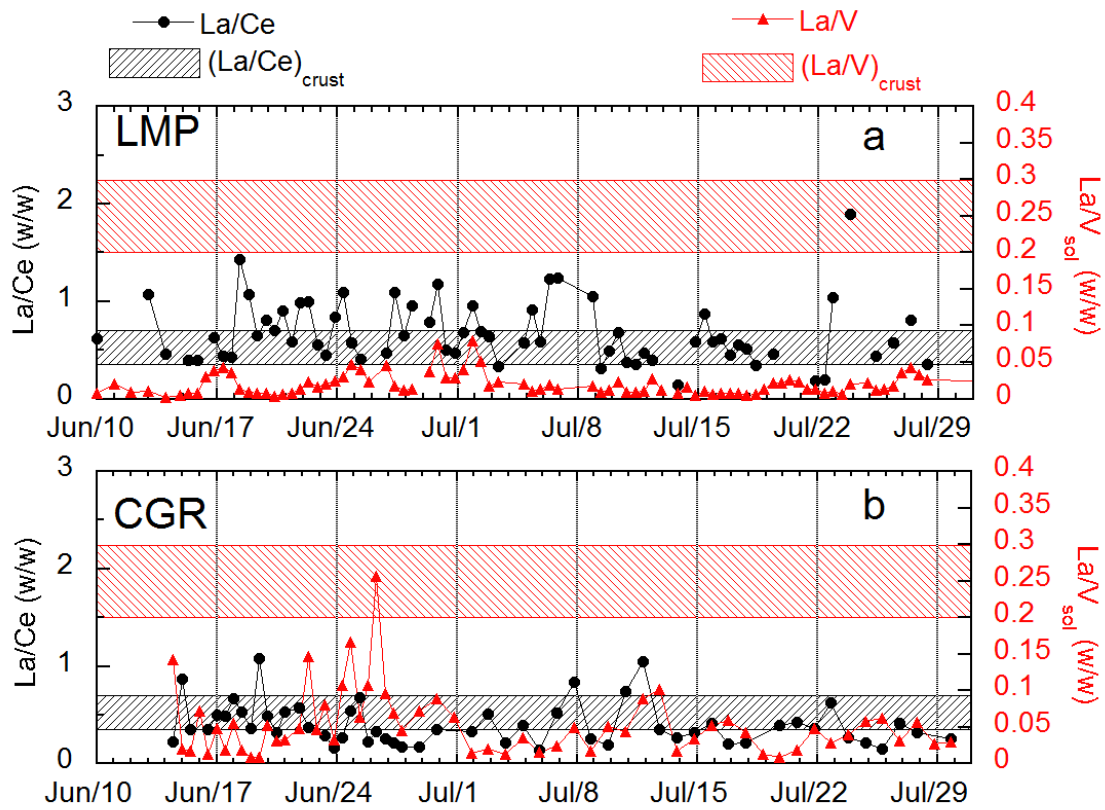459 source also in these cases, suggesting that the impact of refineries is limited.

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461
462 Figure 4. Time series of LCR and LVR at a), Lampedusa, and b), Capo Granitola. The
463 horizontal red and grey shadow areas in each plot represent the ranges of values for
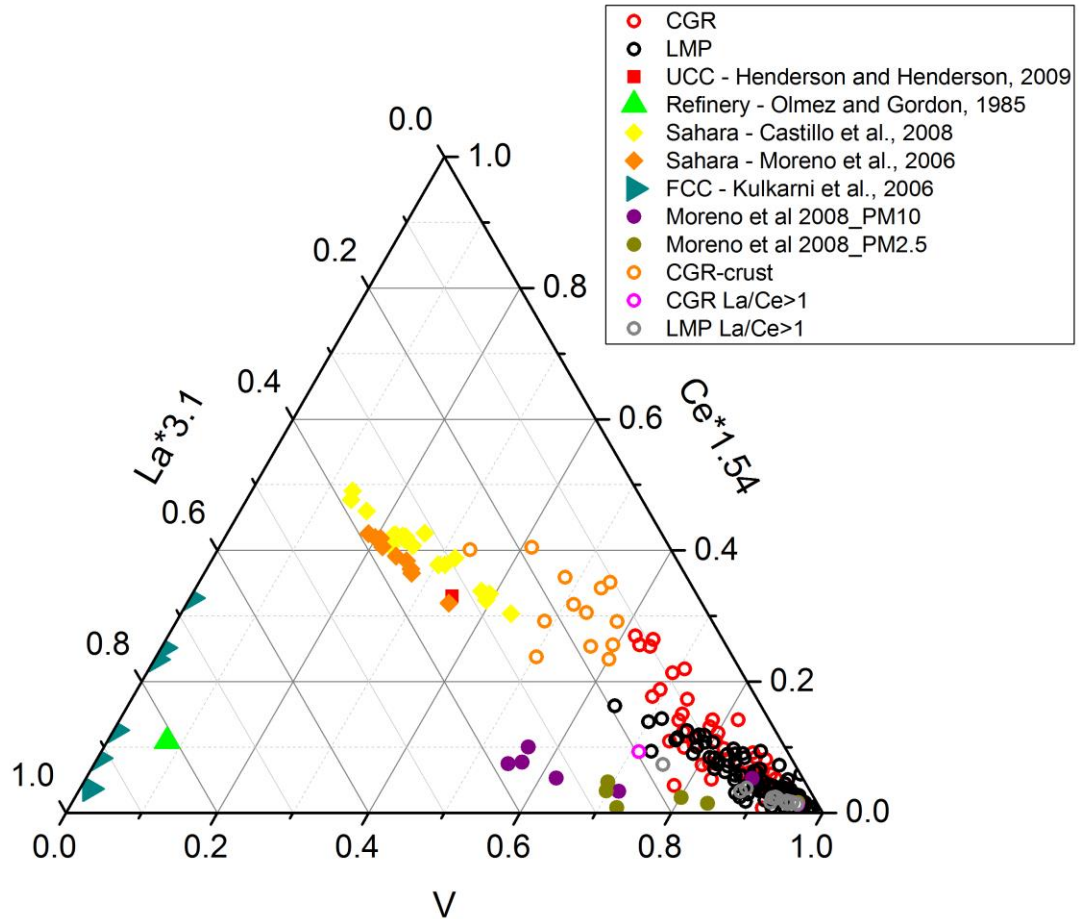464 upper continental crust LVR and LCR, respectively.
465

3.2. Trajectories and ship traffic

3.2.1 Origin of air masses during the campaign

All the trajectories arriving at LMP and CGR, calculated with the HYSPLIT model driven by WRF meteorological fields (see Section 2.3), are shown in an aggregated way in Figure 6, where the trajectory frequency at each point of the computing grid is shown for the whole period (upper panels) and for the 10 – 30 June interval (lower panels). The trajectory frequency pattern is elongated in the NW-SE direction at LMP, while it is distributed over a wider range of directions at CGR, despite a general prevalence of northerly sectors. The predominance of air masses coming from the northwest is particularly evident in June (lower panels); when areas with trajectory frequencies exceeding 10% are found farther to the north, up to the Gulf of Lion.

16

During the first part of the campaign (June 2013) the synoptic situation was characterized by a "dipolar" sea level pressure anomaly pattern, with positive anomalies in the western Mediterranean and negative ones in the eastern part of the basin (Denjean et al., 2016). This situation induced stronger and more frequent than usual north-westerly winds (i.e. Mistral episodes, see Section 3.1) over the Sardinia and Sicily Channels.
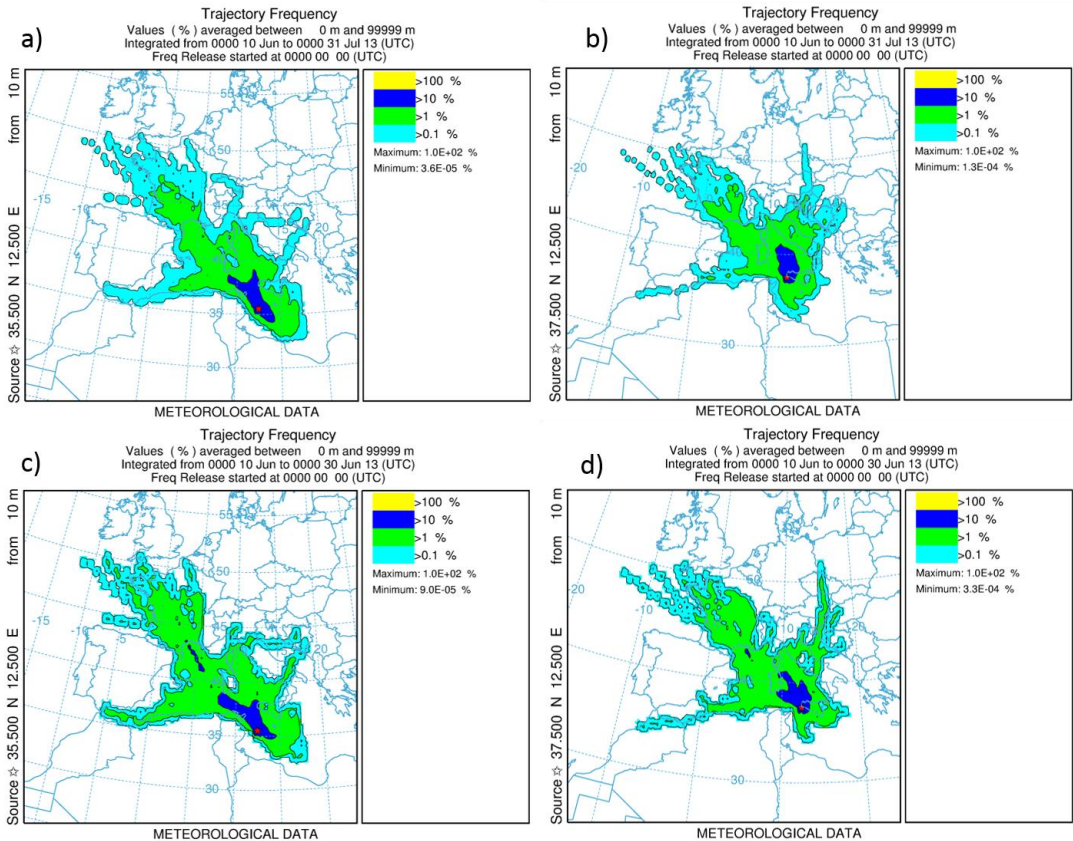

Figure 6. Trajectory frequency computed at each grid cell with starting points at LMP (panels a, c) and CGR (b, d). Upper panels show values averaged over the whole period of the campaign (10 June – 31 July 2013), while lower panels are relative to the 10-30 June interval.

3.2.2 Ship traffic

To further investigate the mechanisms determining the presence of ship emissions markers at the two sites we investigated the relationships among the amount of V, the back-trajectory pattern, the effective number of ships influencing the air mass, the stability of the boundary layer in the ship source region (i.e., the Sicily Channel), and the REE to V ratios discussed in section 3.1.2.

506 All back-trajectories arriving at LMP and CGR were considered and all trajectory-ship
507 coincidences occurring within the last 36 hours before sampling were taken into
508 account.
509 It was assumed that the ship plume influenced the sampled air mass if:
510   -   the trajectory passed within 15 km of the position of a ship
511   -   the corresponding air mass altitude was less than 500 m.
512 The total number of ships fulfilling these criteria was associated with each trajectory.
513 The analysis was based on the available 1-hour time resolution meteorological fields (a
514 ship influencing a trajectory was counted once every hour).
515 To further explore the impact of different types of ships, the analysis was carried out
516 considering the following three ship categories: all the ships, the merchant (i.e. cargo
517 and tanker), and the fishing vessels.
518 The atmospheric stability is also expected to play a large role in modulating the ship
519 impact (see e.g., its influence on V amounts, Becagli et al. 2012). A temperature
520 inversion, TI, index, was calculated based on the 3D atmospheric fields of the WRF
521 model at three sites in the Sicily Channel. The temperature inversions were used as a
522 proxy to identify periods characterized by a stable boundary layer. The three sites, A
523 (37.2°N, 11.5°E), B (37.0°N, 12.4°E), and C (36.3°N, 13.3°E) (figure 1) were selected
524 in the regions of most frequent ship passage and crossing with the trajectories from
525 LMP and CGR. The TI index was calculated as the difference between the temperature
526 at the altitude of the maximum T, and at the surface. A positive TI indicates an
527 inversion, and the TI value provides an indication of the inversion strength. Only
528 positive values are considered in this analysis.
529 Figure 7 summarizes the results of this analysis. It shows the time series of the number
530 of the ships influencing the trajectories arriving at LMP and CGR, respectively, and the
531 corresponding measured values of V. Samples which show a limited influence from ship
532 emissions, determined on the basis of the La-Ce-V composition (see section 3.1.2), are
533 highlighted with arrows (orange arrows for samples with La-Ce-V ratios typical for
534 crust; pink and gray for sample possibly influenced by refineries, i.e., with LCR>1).
535 Results are shown for the three classes of ships. The positive values of TI are also
536 shown.
537 In general, there is a rather good correspondence between the cases classified as
538 influenced by ships emissions and the number of ships encountered along the
539 associated air mass trajectory at CGR. The correspondence is somewhat less evident at
540 LMP. As discussed above, the V concentration ascribed to ships (data points without
541 arrows n figure 7) is generally higher at CGR than at LMP. Part of this difference may
542 be ascribed to the shorter distance between CGR and the main shipping route crossing
543 the Sicily Channel with respect to Lampedusa, the consequent larger number of
544 encountered ships, and an aerosol dilution effect during transport from the sources to
545 LMP.
546 Maxima of V attributed to ships occurred between 19 and 20 June at CGR (about 42
547 ng/m^3), and on 21 June at LMP (36.1 ng/m^3). Similar concentrations were measured at
548 CGR also around 18-19 July, in conjunction with an increase in the number of merchant

549 vessels. The 18-21 June period is the only event with high V concentrations quasi
550 simultaneously at both sites. This is due to the peculiar circulation patterns, with
551 airmass trajectories from the marine sector South of Sicily to CGR, and from the Sicily
552 channel to LMP, particularly on 18 and 19 June. The 19-21 June episode is the largest
553 occurring at LMP, both for duration and V concentration. Especially at the beginning of
554 the event, large values of V do not correspond with an increase of the number of ships
555 along the air mass trajectories.
556 A possible explanation for this behaviour is provided by the temporal evolution of TI in
557 the Sicily Channel. The temperature inversion started to develop on 14 June, and
558 gradually increased in intensity until 22 June; the TI persistence and progressive
559 increase in intensity provided suitable conditions for the ship plumes trapping in the
560 boundary layer, with a consequent build-up of the ship aerosol and V concentration.
561 This process appears particularly efficient at CGR between 21 and 25 June.
562 A similar combined dependency on number of ships and TI appears also at LMP around
563 7 July. It is interesting to note that V from ships seems to depend more directly on the
564 number of merchant ships (see, e.g., the lack of V peaks on 17 June, 12 and 29 July at
565 LMP, when the number of fishing vessels was high and the number of merchant ships
566 was low) than on the total or the fishing ships.
567 Thus, the trajectory analysis carried out in combination with the available information
568 on the ship tracks confirms that the ship emissions are the main responsible for most of
569 the moderate and elevated values of V measured at LMP and CGR during the campaign,
570 and in particular for those cases with La and Ce compatible with the ship source. This
571 analysis also clearly suggests that the boundary layer structure plays a very important
572 role in determining the impact produced by the emissions. This simplified approach
573 confirms the importance to carefully characterize the emission scenario and the
574 meteorological conditions in studies on the ships emissions impact on air quality.
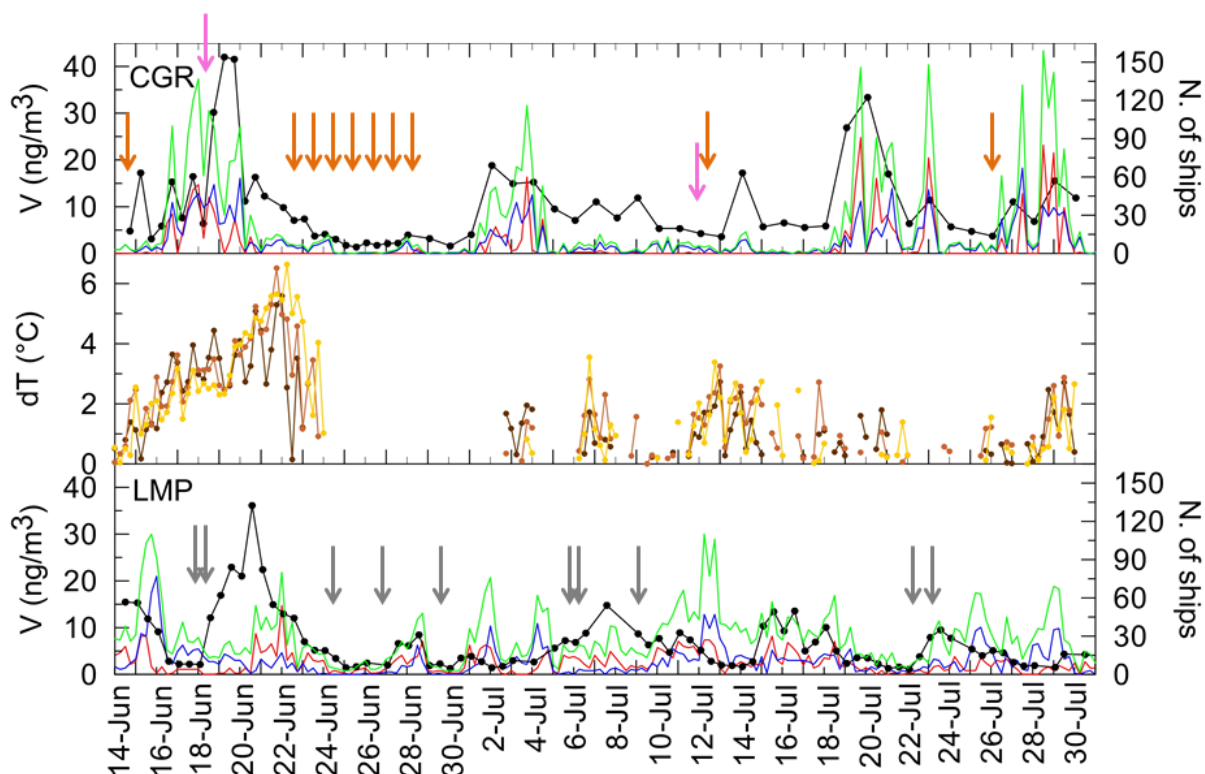575

3.3. Sulfate, nitrate, and organic carbon from ships

SO_2 is one of the main species emitted in the ship plume in the gas phase (Agrawal et al., 2008a, b). SO_2 is produced through oxidation of the S contained as impurity in heavy fuel oil, and is an aerosol precursor.

A previous study based on 5 years of data from Lampedusa (Becagli et al., 2012) has shown that the non-sea salt sulfate behaviour is not directly correlated with V and Ni

because several other SO_4^{2-} sources (anthropogenic, marine biogenic, crustal, volcanic) contribute to the non-sea salt sulfate in the Central Mediterranean Sea.

The same study suggested a lower limit of about 200 for the $nssSO_4^{2-}/V$ ratio for particles originating from heavy oil combustion at Lampedusa.

Figure 8 shows $nssSO_4^{2-}/V$ versus V at LMP and CGR. At both sites $nssSO_4^{2-}/V$ decreases for increasing V and reaches a lower limit at elevated values of V (> 15 ng/m^3). The analysis on REE, trajectories and ship traffic has shown that all samples with V > 15 ng/m^3 are strongly influenced by ships, and we assume that the ship emission is the dominant source of the sampled particles for these cases. This implies that in these cases virtually all sulfate originated from the ship source, and the observed lower limit for $nssSO_4^{2-}/V$ can be considered the lower limit for the sulfate to V ratio in the ship plume. Thus, to derive a lower limit for this ratio we calculate the mean and standard deviation of $nssSO_4^{2-}/V$ for V > 15 ng/m^3. The mean ratio and the mean ratio minus one standard deviation are shown in figure 8.

The $nssSO_4^{2-}$ to V ratio may still be decreasing for V around 15 ng/m^3, and we used a limit value equal to the average minus one standard deviation (dashed red lines in figure 8) to estimate the minimum expected contribution from ships to the total sulfate amount.

The calculated lower limit of the sulfate to V ratio at LMP is 207, in agreement with the values of 200 estimated by Becagli et al. (2012). The $nssSO_4^{2-}/V$ limit value at CGR, 323, is larger than at LMP. This difference is may be due to the contribution of other sulfate sources which may contribute to the $nssSO_4^{2-}$ even at high V concentration, and to the smaller distance from the ship source with respect to LMP. This result highlights the importance of remote sites like LMP to obtain information on the open Mediterranean.
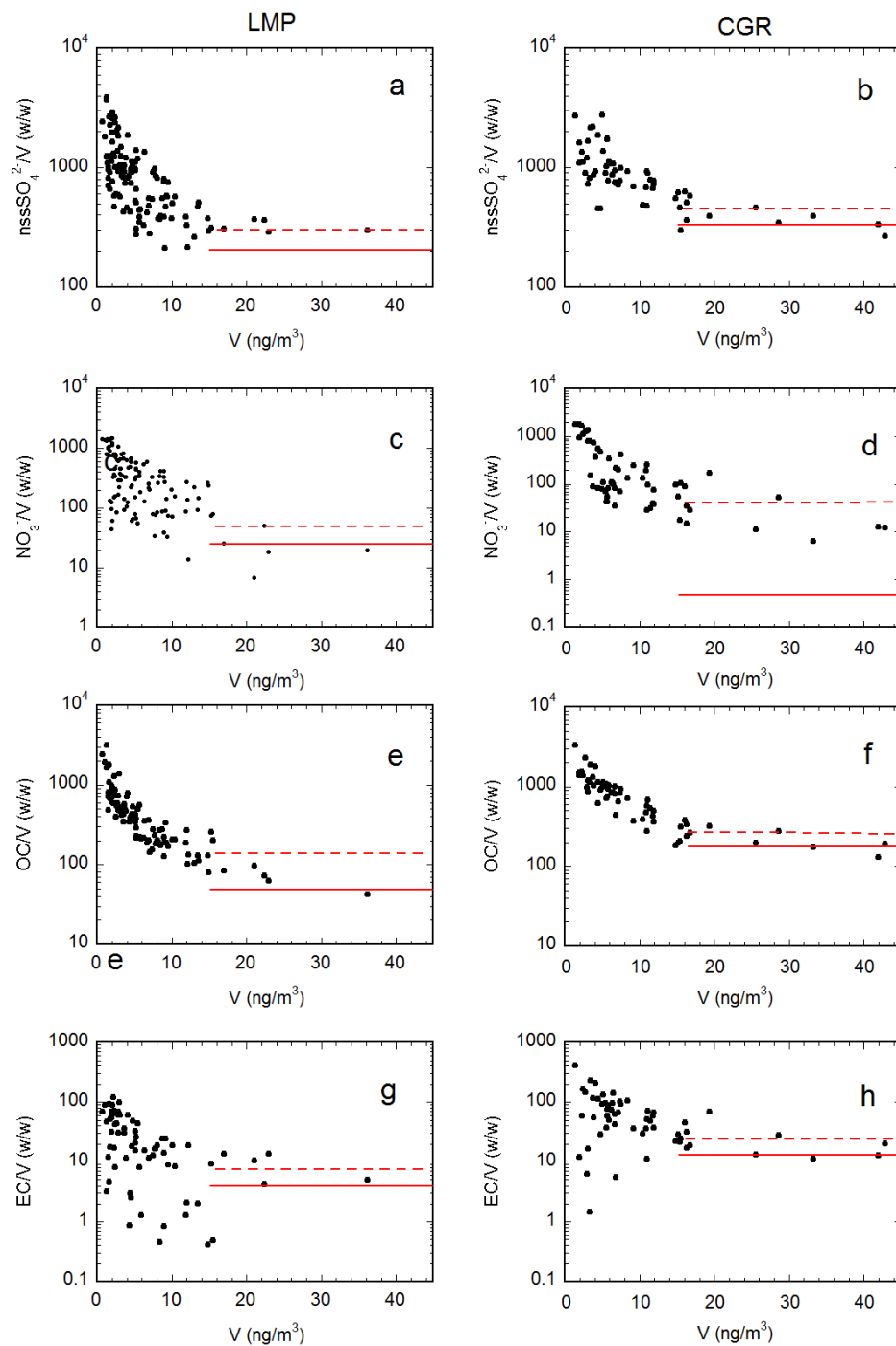
Figure 8. Scatter plots of $nssSO_4^{2-}/V$ (a and b), NO_3^-/V (c and d), OC/V (e and f) and EC/V (g and h) vs. V concentration at LMP (plots on the left) and CGR (plots on the right). The red lines in the plots represent the average (dashed line) and the average minus one standard deviation (solid line) calculated for samples with V>15 ng/m^3.

NOx are among the main compounds emitted in the gas phase acting as aerosol precursors. The photochemistry of NO_x leading to NO_3^- formation in the particulate phase is complex, especially in summer due to the presence of high amounts of OH radical (see e.g., Chen et al., 2005), and the NOx contribution to the particulate phase is not easy to be quantified.

Here we try to use the same approach used for sulfate for the determination of a lower limit for the NO_3^-/V ratio in the ship plume.

Figure 8 (plot c and d) shows the NO_3^-/V ratio versus V at the two sites. Similarly to sulfate, the average value of NO_3^-/V for V > 15 ng/m^3 is larger at CGR than at LMP. However, the standard deviation at CGR is significantly larger at CGR. The NOx concentration in the ship plume close to the source is larger than that of SO_2 and is strongly dependent on the engine operating conditions (Agrawal et al 2008b). The NOx lifetime is extremely low (1.8 hours during daytime and 6.5 hour during nighttime, Chen et al., 2005). However, the NO_3^-/V limit ratio values is low compared to the limit ratio for SO_4^{2-}. It has to be considered that NO_3^- takes part in other photochemical atmospheric reactions that lead to its removal. In addition, the presence of HNO_3 in gas phase not neutralized by NH_3 or by sea salt could explain the low NO_3^-/nssSO_4^{2-} ratio in the aerosol. Indeed, the NO_3^- concentration measured at LMP and CGR is 4-6 times lower than that of nssSO_4^{2-} (table 1). Low amounts of NO_3^- with respect to SO_4^{2-} from ship emissions are found in model simulations in Southern California (Dabdub, 2008). Indeed, Dabdub (2008) shows that the aerosol contribution from ship emissions is 0.05% for NO_3^-, and 44% for SO_4^{2-}.

Elemental and Organic Carbon are also present in the ship plume (Shah et al., 2004). In particular, OC constitutes about 15-25% and EC is generally lower than 1% of the PM sampled at the plume of main ship engine powered by heavy fuel oil (Agrawal et al., 2008b).

Figure 8 shows EC/V and OC/V versus V at LMP and CGR. Similarly to sulfate and nitrate, OC/V decreases with increasing V and reaches a minimum value for V > 15 ng/m^3 (43.1 and 179 at LMP and CGR, respectively) As discussed in section 3.1, other OC sources in addition to ships are present at CGR even at high values of V.

The pattern of the ratio EC/V versus V is less clear; in particular, several very low values of EC/V appear also at small values of V. This result is unexpected because V and EC are both markers of the primary ship aerosol, but the data here presented seem to suggest that non negligible EC contributions from other sources were present at CGR and that different fractionating effects acted during the transport. Also in this case the limit value is lower at LMP than at CGR.

Finally, as the limit ratios at CGR are likely affected by other sources than ship, we assume that the limit ratios obtained at Lampedusa for V>15 ng/m^3 are more representative of cases dominated by ship emissions during summer in a wide region. For this reason, the retrieved lower limits at LMP are used to quantify the ship contribution also at CGR.

3.4 Contribution of the ship aerosol to PM$_{10}$

With all the limitations above described, by using the lower limits for the ratios (nssSO$_4^{2-}$/V), (NO$_3^-$/V), and (OC/V) representative for ship aerosol it is possible to estimate the minimum contribution of nssSO$_4^{2-}$, NO$_3^-$ and OC emitted by ships to the total budget of these components, and also to the total PM$_{10}$ mass. It has to be noticed that the aerosol quantification obtained by this method is a rough estimate useful to constrain the ship aerosol contribution. In addition, due to possibly different meteorological conditions and photochemical activity, these values may vary spatially and seasonally.

The minimum ratio of each specie with respect to V, the minimum estimated contribution of ship emissions, for the average amount and for the maxima, to the total concentration of these species and to PM$_{10}$, are reported in Table 4. As previously discussed, the measured OC contribution is multiplied by 2.1 at LMP and by 1.8 at CGR to obtain the total organic aerosol contribution.

The estimated minimum concentration of non-sea-salt sulfate from ship emissions was 1.35 µg/m^3 on average during this campaign at LMP. This value is lower than in the previous study by Becagli et al. (2012) obtained over a longer period (2004-2008). The relative contribution to the total sulfate is however similar here and in Becagli et al. (2012), suggesting a similar role of nssSO$_4^{2-}$ from ship emissions to the total nssSO$_4^{2-}$ budget. The study by Becagli et al. (2012) covered an extended time period (2004-2008); the consistency with that study suggests that the results obtained during ChArMEx are not specific of summer 2013, but are representative for a wider temporal and spatial range.

At CGR the minimum ship contribution to sulfate, averaged over the same time period, is higher than at LMP (2.1 µg/m^3), but this higher value corresponds to a lower contribution to the total nssSO$_4^{2-}$, confirming that other nssSO$_4^{2-}$ sources are important at CGR.

Marmer and Langmann (2005) estimate that ship emissions contribute by 50% to the total amount of nssSO$_4^{2-}$ in the Mediterranean. This value is, as expected, larger than the estimated minimum contribution we derive (about 30%).

The estimated minimum contribution by ships to the total nssSO$_4^{2-}$ for cases with the largest ship impact (i.e. highest V concentration) is 69% and 77% at LMP and CGR, respectively.

Ships appear to contribute by small fractions to the total budget of NO$_3^-$. As previously mentioned, the NO$_3^-$ atmospheric chemistry is complex and the contribution of nitrate from ship emission could be highly variable, especially in the Mediterranean region where high amount of UV radiation and highly reactive radical species are present.

Organic aerosol from ships also contributes significantly to the total OA amount and to the total PM; in particular, at LMP virtually all the OA present in cases with maximum ship impact may be attributed to the ship source.

By summing these three contributions, it is possible to estimate the total aerosol mass due to ship emissions, and its contribution to the total mass of PM$_{10}$. The lower limit for

714 the ship contribution was 2.0 μg/m^3 and 3.0 μg/m^3, corresponding to 11% and 8.6% of
715 PM$_{10}$ at LMP and CGR, respectively.
716
717
718 **Table 4**. Estimates of the average and maximum of the lower limit of nssSO$_4^{2-}$, NO$_3^-$,
719 OA, and PM$_{10}$ from ships. Concentrations and percent with respect to the total amount
720 of each species are reported. The maxima are derived by selecting cases with the
721 largest ship impact (i.e. highest V concentration).
722

	nssSO$_4^{2-}$ (nssSO$_4^{2-}$/V)$_{min}$=207		NO$_3^-$ (NO$_3^-$/V)$_{min}$=12.5		OA (OC/V)$_{min}$=43.1		PM$_{10}$	
	LMP	CGR	LMP	CGR	LMP	CGR	LMP	CGR
Average contribution μg/m^3 (%)	1.35 (34%)	2.1 (31%)	0.082 (4.5%)	0.13 (9.0%)	0.59 (15%)	0.78 (8.7%)	2.0 (11%)	3.0 (8.6%)
Maximum contribution μg/m^3 (%)	7.5 (69%)	8.8 (77%)	0.45 (62%)	0.53 (100%)	3.3 (99%)	3.3 (22%)	11.2 (50%)	12.7 (42%)

723
724
725 These percent contributions are higher than the annual average for the Mediterranean
726 Region estimated by Viana et al. (2014). It has to be considered that these authors
727 used data from harbour or coastal sites, which are highly affected by other sources in
728 addition to ships, and where gas-to-particle conversion is still at its initial phase.
729 Moreover, the percentages reported in this study are relative to the summer season,
730 when the ship contribution in the Mediterranean region is highest (Becagli et al., 2012).
731 The estimated lower limit for the ship contribution in cases with maximum ship impact
732 was between 42% and 50% of the total PM$_{10}$.
733
734
Summary and conclusions
736
737 In this study we investigate the impact of the ship emissions to PM$_{10}$ on measurements
738 made at two sites in the central Mediterranean. The main objectives of the study were
739 to unambiguously identify the tracers of ship emissions in the sampled aerosol, and to
740 obtain a lower limit for the produced impact.
741 The PM$_{10}$ samples were collected in summer 2013, as a contribution to the Chemistry
742 and Aerosol Mediterranean Experiment, in parallel at Lampedusa and at Capo Granitola,
743 respectively South and North of the main shipping route through the Mediterranean.
744 The identification of aerosol originating from ships was based on an integrated analysis
745 combining chemical analyses, calculations of backward trajectories using a high

resolution regional model, and on tracking of ship traffic in the Mediterranean through the Automatic Identification System.

The main results of this study may be summarized as follows:

1. moderate and elevated values of V and Ni in the aerosol were unambiguously associated with the ship source; this attribution was based on:

   - the V to Ni ratio, which corresponds to what expected for heavy fuel oil combustion;

   - low amounts of La and Ce with respect to V, and La/Ce ratio similar to those in the UCC, which allowed to exclude power plants or refineries as sources significantly contributing to the observed aerosol;

   - coincidences between air mass trajectories and travelling ships;

2. in addition to travelling ships, also the planetary boundary layer vertical structure played an important role in determining the dispersion of aerosols from the ship source; temperature inversions appeared associated with elevated amounts of ship emissions tracers, suggesting that they favoured the build-up of aerosol concentration in the lowest atmospheric layers;

3. as expected, merchant ships (cargo and tankers) appeared to produce a larger impact on the measured aerosol than fishing vessels;

4. lower limits for the ratios $nssSO_4^{2-}/V$, NO_3^-/V, and OC/V, identifying the ship-dominated emission cases, were derived from the observations. The lower limits found at Lampedusa, which may be taken as a background site less affected by other types of anthropic emissions, are respectively 207, 12.5, and 44.1. These lower limits are expected to be season dependent;

5. by using these ratios, the lower limits to the contribution of the ship source to $nssSO_4^{2-}$, NO_3^-, OA, and to PM_{10} during the measurement campaign were estimated. Ship emissions contributed by at least 34% to the total amount of sulfate, by at least 5-9% to the total amount of NO_3^-, and by at least 9-15% to the total amount of organic aerosol. All these contributions correspond at least to 11% of PM_{10} at LMP (2.0 $\mu g/m^3$), and about 8.6% of PM_{10} at CGR (3.0 $\mu g/m^3$). In cases with largest ship impact, ships contributed up to about 12 $\mu g/m^3$ to PM_{10} in both sites, corresponding to 50% of PM_{10} at LMP and 42% at CGR;

6. Lampedusa is a small island in the southern sector of the central Mediterranean, relatively far from the main shipping Mediterranean route; thus, results at Lampedusa may be taken as representative of the impact of ships on the aerosol properties in a wide open sea area in the central Mediterranean during summer.

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