Constraining the ship contribution to the aerosol of the central Mediterranean

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Abstract. Particulate matter with aerodynamic diameters lower than 10 µm, (PM10) 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 Strait of Sicily.

The PM10 samples were collected with 12 h time resolutions 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 Strait of Sicily, 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 air masses from the Strait of Sicily 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 a stable boundary layer. The V concentration was generally lower at Lampedusa than at Capo Granitola V, where it reached a peak value of 40 ng m⁻³.

Concentrations of rare earth elements (REEs), 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, air mass trajectories and ship routes allows us to unambiguously identify the large role of the ship source in the Strait of Sicily.

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 PM10. The estimated minimum ship emission contributions to PM10 were 2.0 µg m⁻³ at Lampedusa and 3.0 µg m⁻³ at Capo Granitola, corresponding with 11 and 8.6 % of PM10, 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 as well as secondary particles. Thus, ship emissions impact the greenhouse gas budget, (Stern, 2007), acid rain – through NO$_x$ and SO$_2$ oxidation products (Derwent et al., 2005), human health – through CO, hydrocarbons, particles (Lloyd’s Register Engineering Services, 1995; Corbett et al., 2007) and solar radiation budget through aerosol direct and indirect effects such as black carbon and sulfur containing particles (Devasthale et al., 2006; Lauer et al., 2007; Coakley Jr. and Walsh, 2002).

Heavy oil fuels used by ships contain varying transition metals. The aerosol emitted by ship engines is formed at high temperatures (> 800 °C) from V, Ni and Fe compounds (Sippula et al., 2009). The thermodynamics predict 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, or SECAs) have been implemented in several regions. Although the legislation is focussed on sulfur emissions, the overall health and environmental effects depend in a 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, 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 the quantification of ship contribution to the total aerosol amount difficult (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) respectively, i.e. 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 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 the unambiguous identification of the ship source and permits the constraint of 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 instruments deployed during the special observing period (1a) of ChArMEx, of the measurement strategy, meteorological conditions and main observations is given by Mallet et al., (2016).
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 ($35.5^\circ$ N, $12.6^\circ$ E), and at the Italian CNR (National Research Council) Research Centre at Capo Granitola ($36.6^\circ$ N, $12.6^\circ$ 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 plateau 45 m a.s.l on the northeastern 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 climatic parameters are carried out. Figure 1 shows the map of the central Mediterranean with the measurement stations.

PM$_{10}$ is routinely sampled on a daily basis at LMP (Becagli et al., 2013; Marconi et al., 2014; Calzolai et al., 2015) by using a low-volume dual-channel sequential sampler (HYDRA FAI Instruments) equipped with two PM$_{10}$ sampling heads, operating in accord with UNI EN12341. For the intensive ChArMEx campaign, samples were collected at 12 h resolution (08:00–20:00 and 20:00–08:00 LT–local time) from 1 June to 3 August 2013.

The two channels operated in parallel and were loaded with different types of filters: the first one with 47 mm diameter, 2 µm-nominal porosity Teflon filters, and the second one with 47 mm pre-fired, 2 µm-nominal porosity quartz filters. Ion chromatographic analysis of soluble ions, atomic emission spectroscopy for soluble metals and proton-induced X-ray emission (PIXE) for the total (soluble + insoluble) elemental composition were carried out on the Teflon filters. Elemental carbon (EC) and organic carbon (OC) were measured by analysing the quartz filters.

The sampling site at CGR is located at Torretta Granitola, a Research Center of the Italian National Research Council, in southwestern Sicily (12 km from Mazara del Vallo). The sampler was installed on the roof of one of the research centre buildings at about 20 m a.s.l., directly on the coastline, facing the Straight of Sicily.

At CGR PM$_{10}$ samples were collected at 12 h resolution (08:00–20:00 and 20:00–08:00 LT) with a TECORA Skypost sequential sampler on 47 mm pre-fired 2 µm-nominal porosity quartz filters, which were used to determine ions, metals, EC and OC on different fractions of the filter. Due to technical problems, some daytime (08:00–20:00 LT) samplings were lost at CGR.

The PM$_{10}$ mass was determined by weighting the filters before and after sampling with an analytical balance in controlled conditions of temperature ($20 \pm 1 ^\circ$C) and relative humidity ($50 \pm 5 \%$). The estimated error on PM$_{10}$ mass is around $1 \%$ at $30 \mu g \ m^{-3}$ in the applied sampling conditions.

A quarter of each Teflon filter from LMP and a 1.5 cm$^2$ punch of the quartz filter from CGR were analysed by Ion Chromatography (IC) in the analytical conditions described in Marconi et al., (2014). The estimated uncertainty for IC measurements is $5 \%$ for all the considered ions.

Blank values were negligible with respect to the concentration in the samples for Teflon filters. Blank values for quartz filters were negligible for most of the analysed species. For some species characterized by high blank values, always lower than the 25th percentile value, they were subtracted from the measured concentrations.
Table 1. Sampling strategy and chemical measurements carried out on each filter for the two sites: Lampedusa (LMP) and Capo Granitola (CGR). The sampling time interval is at local time (LT).

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Filter</th>
<th>Sampling interval (LT)</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMP</td>
<td>Teflon</td>
<td>08:00-20:00 (daytime sample) 20:00-08:00 (nighttime sample)</td>
<td>– 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$_2$O$_2$ in microwave oven extract by ICP-AES (1/2 filter)</td>
</tr>
<tr>
<td></td>
<td>Quartz</td>
<td>08:00–20:00 (daytime sample) 20:00–08:00 (nighttime sample)</td>
<td>– EC / OC by thermo-optical analyser (1.5 cm × 1 cm punch)</td>
</tr>
<tr>
<td>CGR</td>
<td>Quartz</td>
<td>08:00–20:00 (daytime sample) 20:00–08:00 (nighttime sample)</td>
<td>– PM$_{10}$; – ions by IC (1.5 cm × 1 cm punch); – metals in HNO$_3$ pH 1.5 room temperature extract by ICP-AES (1.5 cm × 1 cm punch); – metals in HNO$_3$-H$_2$O$_2$ in microwave oven extract by ICP-AES (1.5 cm × 1 cm punch) – EC / OC by thermo-optical analyser (1.5 cm × 1 cm punch)</td>
</tr>
</tbody>
</table>

Another quarter of the Teflon filter from LMP and another 1.5 cm$^2$ punch of the quartz filter from CGR were extracted in an ultrasonic bath for 15 min with MilliQ water acidified at pH 1.5–2 with ultra pure HNO$_3$ obtained by sub-boiling distillation. This extract was used for the metal’s soluble part determination by means of an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Varian 720-ES) equipped with an ultrasonic nebulizer (U5000 AT+, Cetac Technologies Inc.). The pH chosen value is the 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, was used for the determination of metals by ICP-AES through the solubilisation procedure reported in the EU EN14902 (2005) rule, by concentrating sub-boiling distilled HNO$_3$ and 30% ultra pure H$_2$O$_2$ 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 the recovery at least 70% of the same elements measured by a 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 periods (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 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.

2.2 Atmospheric model and trajectory calculations

Numerical simulations with a non-hydrostatic mesoscale atmospheric model were used to characterize the meteorological conditions in the Strait of Sicily during the campaign and to support the interpretation of the experimental results. The Weather Research and Forecasting (WRF) model (Skamarock et al., 2008) outputs, provided by the Department of Physics of the University of Genoa, Italy, were used, covering the entire Mediterranean with a grid spacing of 10 km and hourly temporal resolution. Initial and boundary conditions to drive WRF simulations were obtained from the
Global Forecast System operational global model (Environmental Modeling Center, 2003) outputs (0.5 × 0.5 squared degrees). Some recent applications of the modelling chain are described in Mentaschi et al., (2015) and Cassola et al., (2016), where full details on the model configuration can also be found.

In particular, the WRF 3-D hourly meteorological fields were used to calculate backward trajectories with the NOAA HYbrid Single-Particle Lagrangian Integrated Trajectory Model (HYPLIT; Stein et al., 2015). The trajectories were used to assess the origin of the air masses impacting the monitoring sites and to support the source attribution suggested by the analysis of specific markers (see Sect. 3.2.2). The use of a high-resolution regional atmospheric model for trajectory calculations allows for a better representation of boundary layer properties and mesoscale phenomena such as land and sea breezes, which can have a relevant impact especially in complex topography coastal sites like CGR.

Also, the high temporal resolution of meteorological data (hourly instead of three- or six-hourly products typically available from global models) permits a better description of diurnal cycles and a more accurate trajectory computation without time interpolation between subsequent atmospheric fields (Solomos et al., 2015).

Specifically, 48 h-long back trajectories arriving at LMP and CGR were computed from a reference height of 10 m above the ground level, starting every six hours for the whole period of the campaign, from 10 June to 31 July 2013.

2.3 Ships/marine traffic

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

Three classes of ships defined by the AIS classification were considered: all the ships, the merchant ships (i.e. cargo and tanker) and the fishing vessels. Merchant and fishing vessels are the most frequent ships in the Straits of Sicily; 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 the aging of sea spray, mainly due to exchange reactions with anthropogenic H$_2$SO$_4$ and HNO$_3$, leading to the 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,

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

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 a 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 has been 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 northwesterly sector and often by subsiding air masses originating from the free troposphere (Jiang et al., 2003). Thus, elevated values of SSA and low concentrations of other compounds are generally found during mistral at Lampedusa.

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 data set, i.e. when measurements are available at both sites.

The largest PM$_{10}$ values were associated with elevated SSA during the mistral event at both sites. PM$_{10}$ is about two times larger at Capo Granitola than at Lampedusa. The PM$_{10}$ measured during the campaign at Lampedusa was significantly lower than its long-term average (31.5 µg m$^{-3}$; Marconi et al., 2014). No Saharan dust transport events occurred at low altitude in this period (e.g. Mailler et al., 2016), and the crustal aerosol contribution remained very low and almost constant at both sites (average < 1 µg m$^{-3}$ at LMP and around 3 µg m$^{-3}$ at CGR, corresponding to 4.6 and 8.2 % of the PM$_{10}$ at LMP and CGR respectively).

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 the 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 ($R^2 = 0.60$; $n = 59$; Fig. 3b), suggesting a strong influence of carbon species from primary sources, characterized by the simultaneous EC and OC emission. The influence from primary sources is apparent at EC > 0.4 µg m$^{-3}$. At LMP, on the contrary, OC was not correlated with EC (Fig. 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 Lim, 2001) at CGR, and of 2.1 (typical for remote sites characterized by the high impact of secondary sources, Turpin and Lim, 2001) at LMP to estimate the total organic aerosol amount from the OC measured values. Once we estimated OA with this method, the sum of the various species accounted for 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).
Table 2. Mean and standard deviation of PM$_{10}$ load and composition, and percentage with respect to PM$_{10}$ (in brackets) 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).

<table>
<thead>
<tr>
<th></th>
<th>Lampedusa</th>
<th>Capo Granitola</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>All data</td>
<td>Mistral excluded</td>
</tr>
<tr>
<td>PM$_{10}$ (µg m$^{-3}$)</td>
<td>18.0 ± 6.6</td>
<td>16.3 ± 5.2</td>
</tr>
<tr>
<td>Sea Salt Aerosol (µg m$^{-3}$)</td>
<td>4.63 ± 6.30 (25.7 %)</td>
<td>2.33 ± 3.21 (14.3 %)</td>
</tr>
<tr>
<td></td>
<td>8.14 ± 15.50 (23.9 %)</td>
<td>2.12 ± 6.51 (7.8 %)</td>
</tr>
<tr>
<td>Crustal Aerosol (µg m$^{-3}$)</td>
<td>0.82 ± 0.44 (4.6 %)</td>
<td>0.90 ± 0.43 (5.5 %)</td>
</tr>
<tr>
<td></td>
<td>2.80 ± 1.7 (8.2 %)</td>
<td>3.02 ± 1.75 (11.1 %)</td>
</tr>
<tr>
<td>nssSO$_{4}^{2-}$ (µg m$^{-3}$)</td>
<td>3.95 ± 2.28 (21.9 %)</td>
<td>4.40 ± 2.22 (27.0 %)</td>
</tr>
<tr>
<td></td>
<td>6.78 ± 3.08 (19.9 %)</td>
<td>7.53 ± 2.78 (27.7 %)</td>
</tr>
<tr>
<td>NH$_{4}^{+}$ (µg m$^{-3}$)</td>
<td>0.98 ± 0.56 (5.5 %)</td>
<td>1.09 ± 0.55 (6.7 %)</td>
</tr>
<tr>
<td></td>
<td>1.48 ± 0.94 (4.3 %)</td>
<td>1.66 ± 0.87 (6.1 %)</td>
</tr>
<tr>
<td>NO$_{3}^{-}$ (µg m$^{-3}$)</td>
<td>1.25 ± 1.00 (7.0 %)</td>
<td>1.02 ± 0.02 (6.2 %)</td>
</tr>
<tr>
<td></td>
<td>1.35 ± 1.11 (4.0 %)</td>
<td>1.01 ± 0.82 (3.7 %)</td>
</tr>
<tr>
<td>Organic aerosol (µg m$^{-3}$)</td>
<td>3.86 ± 1.56 (21.4 %)</td>
<td>4.04 ± 1.59 (24.8 %)</td>
</tr>
<tr>
<td></td>
<td>9.02 ± 2.52 (26.5 %)</td>
<td>9.53 ± 2.29 (35.0 %)</td>
</tr>
<tr>
<td>Elemental carbon (µg m$^{-3}$)</td>
<td>0.15 ± 0.08 (0.8 %)</td>
<td>0.15 ± 0.08 (0.9 %)</td>
</tr>
<tr>
<td></td>
<td>0.44 ± 0.28 (1.3 %)</td>
<td>0.51 ± 0.26 (1.9 %)</td>
</tr>
<tr>
<td>Unknown (µg m$^{-3}$)</td>
<td>2.52 ± 3.26 (14.0 %)</td>
<td>2.20 ± 3.40 (13.5 %)</td>
</tr>
<tr>
<td></td>
<td>4.11 ± 7.78 (12.1 %)</td>
<td>1.82 ± 4.48 (6.7 %)</td>
</tr>
</tbody>
</table>

3.1.1 Ship emission markers: V and Ni

Several studies focused on the identification of shipping emission 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, b). The soluble fraction of these metals is even more representative for ship sources (Becagli et al., 2012).

Following Becagli et al., (2012), we used measurements of the V and Ni soluble fractions ($V_{\text{sol}}$ and $N_{\text{sol}}$, respectively). In the data set the $V_{\text{sol}}$ and $N_{\text{sol}}$ ratio with respect to Al was 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 $V_{\text{sol}}$ and $N_{\text{sol}}$.

Table 3. Correlation parameters between V and Ni at LMP and CGR calculated for all the samples, and for samples with V concentration higher than 6 ng m$^{-3}$.

<table>
<thead>
<tr>
<th></th>
<th>Slope ($\pm$ uncertainty)</th>
<th>$R^2$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All data</td>
<td>2.94 ± 0.03</td>
<td>0.986</td>
<td>124</td>
</tr>
<tr>
<td>$V_{\text{sol}} &gt; 6$ ng m$^{-3}$</td>
<td>2.99 ± 0.03</td>
<td>0.994</td>
<td>44</td>
</tr>
<tr>
<td>CGR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All data</td>
<td>2.82 ± 0.08</td>
<td>0.950</td>
<td>59</td>
</tr>
<tr>
<td>$V_{\text{sol}} &gt; 6$ ng m$^{-3}$</td>
<td>3.00 ± 0.05</td>
<td>0.989</td>
<td>34</td>
</tr>
</tbody>
</table>

The behaviour of V, Ni and their ratio are 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, 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, such as 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; and coincidences between the high-resolution back-trajectories and the position of different types of ships in the Strait of Sicily.

### 3.1.2 Rare earth elements

As discussed above, anthropogenic V and Ni originate from heavy oil combustion and may only be considered markers of the ship source 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, b; Du and Turner, 2015). This is because zeolitic fluidised-bed catalytic cracking (FCC) units enriched in La are used to crack long-chain olefins in crude oil to shorter-chain products (Bozlaker et al., 2013; Du and Turner, 2015; Kulkani et al., 2006; Moreno et al., 2008a, b).

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 are displayed in Fig. 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 detection limit. These cases may produce very large values of LCR which are not significant; and were removed from the time series.

LCR at LMP and CGR was generally around the value expected for crustal aerosol (dashed grey area in Fig. 4); 10 samples from LMP and 2 samples from CGR show values of 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.

Moreno et al., (2008b) have shown that it is possible to identify aerosol from refineries based on the V-La-Ce-three-component plot. This type of plot is shown in Fig. 5 for the data from LMP and CGR. La and Ce were scaled in order to have the typical UCC composition in the centre of the plot.

The compositions of UCC (Henderson and Henderson, 2009), African desert dust (Castillo et al., 2008; Moreno et
al., 2006), FCC (Kulkarni et al., 2006), La-contaminated (refinery) Asian dust collected at Mauna Loa, Hawai’i (Olmez and Gordon, 1985), and PM$_{10}$ as well as PM$_{2.5}$ that were collected at Puertollano (Spain) in days possibly affected by refinery emissions (Moreno et al., 2008b) are also displayed in Fig. 5.

The data from CGR and LMP are grouped in a region with elevated values of V, and La and Ce generally lower than in refinery and dust cases.

Data from Puertollano shown in Fig. 5 are relative to days characterized by winds originating from sectors where refineries are located; however, these samples are affected by a mix of particles from several sources, including refineries. Aerosol samples from Spain affected by refineries, in most cases display larger LCR and LVR ratios than those found at LMP and CGR. The composition of all samples collected in this period at LMP is consistent with a large impact from ship emissions. Some cases at CGR may suggest the simultaneous occurrence of crustal and ship aerosols, or dominant crustal components (orange open dots in Fig. 5). Therefore, these cases display a relatively low V concentration and are mainly associated with the mistral event. A limited crustal contamination may possibly occur at CGR in these cases, due to resuspension due to the strong wind.

Cases with LCR > 1 (grey and pink open circles for CGR and LMP respectively) are highlighted in Fig. 5. The aerosol composition is consistent, however, with the ship source in these cases, suggesting that the impact of refineries is limited.

### 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 Sect. 2.3), are shown in an aggregated way in Fig. 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 (Fig. 6c and d), when areas with trajectory frequencies exceeding 10% are found farther to the north, up to the Gulf of Lion.

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 northwesterly winds (i.e. mistral episodes, see Sect. 3.1) over Sardinia and Strait of Sicily.

#### 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 backtrajectory pattern, the effective number of ships influencing the air mass, the stability of the boundary layer in the ship source region (i.e. the Strait of Sicily) and the REE to V ratios discussed in Sect. 3.1.2.

All back-trajectories arriving at LMP and CGR were considered and all trajectory-ship coincidences occurring within the last 36 hours before sampling were taken into account. It was assumed that the ship plume influenced the sampled air mass if:

- the trajectory passed within 15 km of the position of a ship;
- the corresponding air mass altitude was less than 500 m.

The total number of ships fulfilling these criteria was associated with each trajectory. The analysis was based on the available 1 h time resolution meteorological fields (a ship influencing a trajectory was counted once every hour).

To further explore the impact of different types of ships, the analysis was carried out considering the following three ship categories: all the ships, the merchant (i.e. cargo and tanker) and the fishing vessels.

The atmospheric stability is also expected to play a large role in modulating the ship impact (for an example of its influence on V amounts, see Becagli et al., 2012). A temper-
Figure 6. Trajectory frequency computed at each grid cell with starting points at LMP (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.

The temperature inversion (TI) index was calculated based on the 3-D atmospheric fields of the WRF model at three sites in the Strait of Sicily. The temperature inversions were used as a proxy to identify periods characterized by a stable boundary layer. The three sites, A (37.2°N, 11.5°E), B (37.0°N, 12.4°E) and C (36.3°N, 13.3°E) (Fig. 1) were selected in the regions of most frequent ship passage and crossing with the trajectories from LMP and CGR. The TI index was calculated as the difference between the temperature at the altitude of the maximum, T, and at the surface. A positive TI indicates an inversion and the TI value provides an indication of the inversion strength. Only positive values are considered in this analysis.

Figure 7 summarizes the results of this analysis. It shows the time series of the number of the ships influencing the trajectories arriving at LMP and CGR, respectively, and the corresponding measured values of V. Samples which show a limited influence from ship emissions, determined on the basis of the La-Ce-V composition (see Sect. 3.1.2), are highlighted with arrows (orange arrows for samples with La-Ce-V ratios typical for crust; pink and gray for sample possibly influenced by refineries, i.e. with LCR > 1). Results are shown for the three classes of ships. The positive values of TI are also shown.

In general, there is a rather good correspondence between the cases classified as influenced by ships emissions and the number of ships encountered along the associated air mass trajectory at CGR. The correspondence is somewhat less evident at LMP. As discussed above, the V concentration ascribed to ships (data points without arrows in Fig. 7) is generally higher at CGR than at LMP. Part of this difference may be ascribed to the shorter distance between CGR and the main shipping route crossing the Strait of Sicily with respect to LMP, the consequent larger number of encountered ships and an aerosol dilution effect during transport from the sources to LMP.

Maxima of V attributed to ships occurred between 19 and 20 June at CGR (about 42 ng m⁻³) and on 21 June at LMP (36.1 ng m⁻³). Similar concentrations were measured at CGR also around 18–19 July, in conjunction with an in-
Figure 7. Time series of Vanadium concentration (black line with dots) and number of ships affecting the air masses sampled at CGR (upper panel) and LMP (lower panel). Green, red and blue lines indicate, respectively, the total number of ships and the number of merchant (i.e. cargo and tanker) and fishing vessels. The time evolution of the temperature inversion index ($dT$ in the figure) at three different locations in the Straight of Sicily is shown in the middle panel; brown, red and yellow curves show the behaviour at sites A–C (see text). The orange arrows identify samples classified as crustal, based on the La-Ce-V concentration; pink and gray arrows identify samples with LCR > 1, possibly influenced by refineries.

crease in the number of merchant vessels. The 18–21 June period is the only event with high V concentrations quasi simultaneously at both sites. This is due to the peculiar circulation patterns, with air mass trajectories from the marine sector south of Sicily to CGR, and from the Straight of Sicily to LMP, particularly on 18 and 19 June. The 19–21 June episode is the largest occurring at LMP, both for duration and V concentration. Especially at the beginning of the event, large values of V do not correspond with an increase of the number of ships along the air mass trajectories.

A possible explanation for this behaviour is provided by the temporal evolution of TI in the Straight of Sicily. The temperature inversion started to develop on 14 June and gradually increased in intensity until 22 June; the TI persistence and progressive increase in intensity provided suitable conditions for the ship plumes being trapped in the boundary layer, with a consequent build-up of the ship aerosol and V concentration. This process appears particularly efficient at CGR between 21 and 25 June.

A similar combined dependency on number of ships and TI appears also at LMP around 7 July. It is interesting to note that V from ships seems to depend more directly on the number of merchant ships (see, for example, the lack of V peaks on 17 June, 12 and 29 July at LMP, when the number of fishing vessels was high and the number of merchant ships was low) than on the total or the number of fishing ships.

Thus, the trajectory analysis, carried out in combination with the available information on the ship tracks, confirms that ship emissions are the main factors responsible for most of the moderate and elevated values of V measured at LMP and CGR during the campaign and in particular for those cases with LCR compatible with the ship source. This analysis also clearly suggests that the boundary layer structure plays a very important role in determining the impact produced by the emissions. This simplified approach confirms the importance of carefully characterizing the emission scenario and the meteorological conditions in studies on the ships’ emissions impact on air quality.

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 five years of data from Lampedusa (Becagl 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 8a and 8b shows nssSO$_4^{2-}$/V vs. V at LMP and CGR. At both sites, nssSO$_4^{2-}$/V decreases with 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 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 Fig. 8.

The nssSO$_4^{2-}$/V ratio may still be decreasing for V by around 15 ng m$^{-3}$ and we used a limit value equal to the average minus one standard deviation (solid red lines in Fig. 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 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.

NO$_x$ are among the main compounds emitted in the gas phase acting as aerosol precursors. The photochemistry of NO$_3$ 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, for example, Chen et al., 2005), and the NO$_x$ 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 8c and d show the NO$_3^{-}$/V ratio vs. 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 NO$_3$ lifetime is extremely low (1.8 h during the daytime and 6.5 h during the 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 the 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 four to six 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 vs. V at LMP and CGR. Similarly to sulfate and nitrate, OC/V de-
creases 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 Sect. 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 vs. V is less clear; in particular, several very low values of EC / V also appear 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 shipping, 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 also used to quantify the ship contribution at CGR.

### 3.4 Contribution of the ship aerosol to PM\(_{10}\)

With all the limitations described above, 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 species with respect to V and the minimum estimated contribution of ship emissions, for the average amount and for the maxima, of the total concentration of these species and of 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), suggests 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 amounts 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.

<table>
<thead>
<tr>
<th></th>
<th>nssSO(<em>{4}^{2-}) / V(</em>{\text{min}}) = 207</th>
<th>NO(<em>3^-) / V(</em>{\text{min}}) = 12.5</th>
<th>OA / V(_{\text{min}}) = 43.1</th>
<th>PM(_{10})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LMP</td>
<td>CGR</td>
<td>LMP</td>
<td>CGR</td>
</tr>
<tr>
<td>Average contribution</td>
<td>1.35 (34 %)</td>
<td>2.1 (31 %)</td>
<td>0.082 (4.5 %)</td>
<td>0.13 (9.0 %)</td>
</tr>
<tr>
<td></td>
<td>(µg m(^{-3}) %)</td>
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<td>(µg m(^{-3}) %)</td>
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<tr>
<td>Maximum contribution</td>
<td>7.5 (69 %)</td>
<td>8.8 (77 %)</td>
<td>0.45 (62 %)</td>
<td>0.53 (100 %)</td>
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<td>(µg m(^{-3}) %)</td>
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Table 4. Estimates of the average and maximum of the lower limit of nssSO\(_{4}^{2-}\), NO\(_3^-\), OA and PM\(_{10}\) from ships. Concentrations and percent with respect to the total amount of each species are reported. The maxima are derived by selecting cases with the largest ship impact (i.e. highest V concentration).
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 the ship contribution was 2.0 and 3.0 µg m$^{-3}$, corresponding to 11 and 8.6 % of PM$_{10}$ at LMP and CGR, respectively.

These percent contributions are higher than the annual average for the Mediterranean region estimated by Viana et al., (2014). It has to be considered that these authors used data from harbour or coastal sites, which are highly affected by other sources in addition to ships, and where gas-to-particle conversion is still at its initial phase. Moreover, the percentages reported in this study are relative to the summer season, when the ship contribution in the Mediterranean region is highest (Becagli et al., 2012).

The estimated lower limit for the ship contribution in cases with maximum ship impact was between 42 and 50 % of the total PM$_{10}$.

4 Summary and conclusions

In this study we have investigated the impact of the ship emissions to PM$_{10}$ on measurements made at two sites in the central Mediterranean. The main objectives of the study were to unambiguously identify the tracers of ship emissions in the sampled aerosol and to obtain a lower limit for the produced impact.

The PM$_{10}$ samples were collected in summer 2013, as a contribution to the Chemistry and Aerosol Mediterranean Experiment, in parallel at LMP and at CGR, respectively, south and north of the main shipping route through the Mediterranean.

The identification of aerosol originating from ships was based on an integrated analysis 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 is expected for heavy fuel oil combustion;
   - low amounts of La and Ce with respect to V and La/ Ce ratios similar to those in the UCC, which allowed the exclusion of 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 to the total amount of sulfate by at least 34 %, to the total amount of NO$_{3}^{-}$ by at least 5–9 %, and to the total amount of organic aerosol by at least 9–15 %. All these contributions correspond at least to 11 % of PM$_{10}$ at LMP (2.0 µg m$^{-3}$), and about 8.6 % of PM$_{10}$ at CGR (3.0 µg m$^{-3}$). In cases with largest ship impact, ships contributed up to about 12 µg 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 Mediterranean shipping 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.

5 Data availability

All the data presented in this paper are available upon request. Please contact the corresponding author (silvia.becagli@unifi.it).

Competing interests. The authors declare that they have no conflict of interest.

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References


Diesch, J.-M., Drewnick, F., Klimach, T., and Borrmann, S.: Investigation of gaseous and particulate emissions from various marine vessel types measured on the banks of the Elbe in Northern Ger-

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