acp-2019-192: Summertime surface PM1 aerosol composition and size by source region at the Lampedusa island in the central Mediterranean Sea, Mallet et al., 2019

Author response to reviewers (RC1, RC2), written by Marc D. Mallet on behalf of all authors. Reviewer comments are indicated in bold, author comments are indicated in normal text and sections taken from the manuscript are indicated in italics.

RC1.

The manuscript of Mallet et al. presents chemical composition and size distribution measurements conducted at the island of Lampedusa, Italy during a one-month period in the summer of 2013. It occurs that ammonium sulfate is the main contributor (63%) to the submicron non-refractory mass, followed by organics (33%). By performing Positive Matrix Factorization (PMF) analysis on the derived organic aerosol mass spectra it occurs that there are four factors contributing to the total organic aerosol, namely a hydrocarbon-like OA, a methanesulfonic acid-related OA, and two oxidized OA, a more oxidized and a less-oxidized one. The two secondary OOA factors contribute the most (more than 80%) to the total OA, but with having different origin. The more-oxidized was observed during easterly air masses from the eastern Mediterranean and central Europe while the less-oxidized during westerly winds from the western Mediterranean, the Atlantic Ocean and high altitudes over France and Spain from mistral winds. Finally, an attempt is made to investigate the aging of aerosols by comparing concurrent measurements at Lampedusa and Corsica, revealing a dependence on travel time between the two sites and an enhancement of organics (40%) and a significant increase in sulfate and ammonium (by a factor of 6 and 4, respectively) between Ersa (Corsica) and Lampedusa.

The paper is well written and easy to follow, though there are some issues and more thorough discussion should be made in specific sections. A very interesting point of the study is the study of the aging aerosol gradient and its dependence on the time travel of the air masses between Corsica and Lampedusa. Other than that the paper can be recommended for publication after addressing the issues listed below.

Authors: The authors would like to thank the reviewer for her/his time and helpful comments. The reviewer's main concerns were surrounding the lack of reported details surrounding the c-ToF-AMS measurements and data analysis and comparisons made between the cToF-AMS, SMPS and PILS measurements. We address these specific comments in the following section, "Specific comments:".

In addition to the changes outlined below, several other changes in the manuscript have been made (e.g. reference formatting, typos). The major change is that data presented in Table 1 and Supplementary Table S1 has now been combined and displayed in a new figure (Figure 8; see below). This figure summarises the PM_1 composition from all of the previous studies around the Mediterranean basin that have performed a PMF analysis. This new Figure makes it much easier to compare the results of our study to these previous studies by visualising the composition with pie charts pointing to the sampling location, rather than presenting the data in tables. Subsequent Figure and table numbers have been updated.

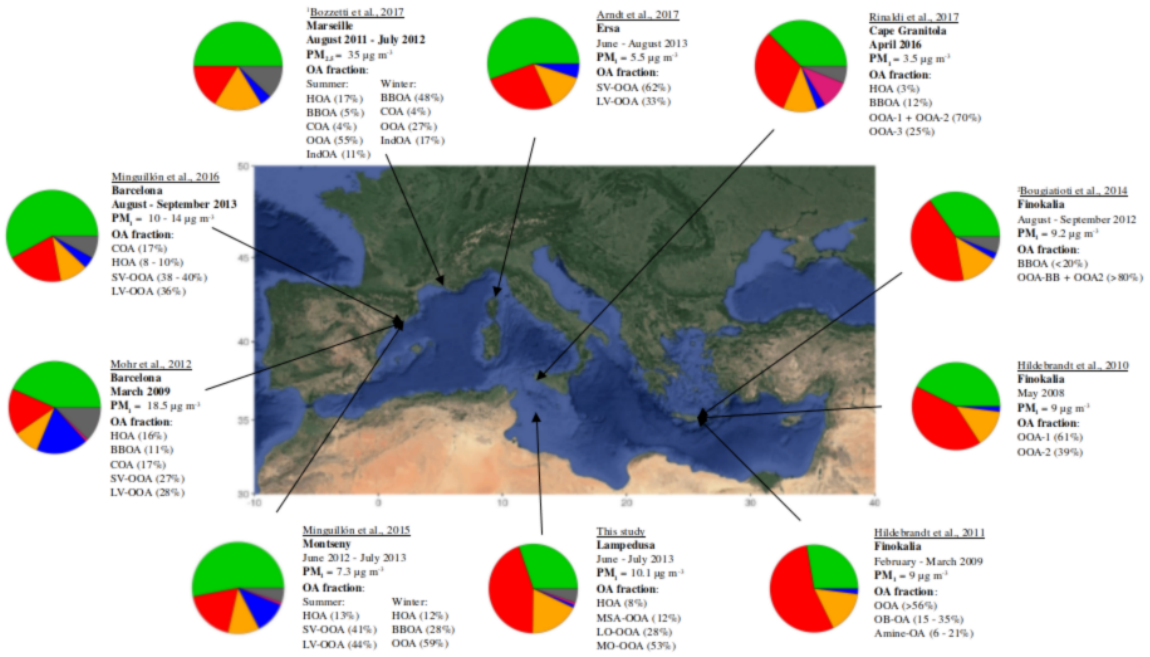

Figure 8 A summary of studies that have investigated NR-PM$_1$ composition (including PMF of OA) around the Mediterranean basin. Only studies that have investigated PMF-based OA source apportionment are reported. Pie charts display the average concentration during each study where green corresponds to organics, red to sulphates, orange to ammonium, blue to nitrate, pink to either chlorides or sea salt and black to elemental or black carbon. The OA fraction acronyms correspond to the following:HOA: Hydrocarbon-like Organic Aerosol, SV-OOA: Semi-volatile oxygenated Organic Aerosol, LV-OOA: Low-volatility oxygenated Organic Aerosol, BBOA: Biomass burning Organic Aerosol, COA: Cooking Organic Aerosol, OOA: Oxygenated Organic Aerosol, F4: "Factor -4" (unidentified PMF factor), IndOA: Industry-related Organic Aerosol, OB-OA: "Olive-branch Organic Aerosol. See Supplementary Tables S1 and S2 for further details about the sampling locations, instruments used and pie chart values. [1]This study collected on PM2.5 filters and nebulised into an HR-ToF-AMS. [2]Excludes fire-periods.

Specific comments:

1) More information about the c-ToF-AMS measurements and data analysis should be provided: - Response Factors and/or Relative Ionization Efficiencies of the different species. Was there a collection efficiency correction applied?? Was a constant CE used or a chemical composition dependent one e.g. Middlebrook et al. (2012)?

Also I would suggest creating a separate section after Section 2.2 as Quality control/Quality assurance of the measurements where I would include the comparisons between PM1 from chemical composition and SMPS, sulfate from c-ToF-AMS and PILS and the supporting measurements from the nanoMOUDI.

Authors: More detail has been given for the c-ToF-AMS measurements and data analysis in both sections 2.2 Instrumentation, measurements and data, and 2.3.1 Analysis of the cToF-AMS data. We did not include a separate QA/QC section but instead provided more detailed comments in the Experimental and Results section regarding the cToF-AMS measurements and comparisons between the SMPS and PILS.

With regards to the c-ToF-AMS ionization calibrations, relative ionization efficiencies and collection efficiencies, the following paragraph as been included in Section 2.2:

*"The ionization efficiency (IE) with respect to nitrate anions was calculated every 5-6 days using nebulised 350 nm mobility diameter ammonium nitrate particles (values varied between 1.42 * 10^{-7} and 1.53 * 10^{-7}). The relative IE (RIE) of ammonium was slightly higher than the default value and was 4.3 based on the mass spectrum of ammonium nitrate data from IE calibrations. The RIE of sulfate was determined by comparing the theoretical and the measured concentration of a solution of ammonium nitrate and ammonium sulfate and was determined to be the default value of 1.2. For the organic fraction, the default value of 1.4 was used. For each of the major species, a composition dependent collection efficiency was applied as proposed by Middlebrook et al., 2012 and was on average 0.549, very similar to the default value of 0.55."*

Further detail of the sea salt estimation has also been provided:

*"The PM1 sea salt concentration was estimated in the cTof-AMS by applying a scaling factor of 102 to the ion fragment (using the cumulative peak fitting analysis described in Muller et al., 2011) at 57.98 assigned to NaCl as proposed by Ovadnevaite et al., 2012. This scaling factor was determined by nebulising monodisperse 300 nm (mobility diameter) NaCl particles into the cToF-AMS and comparing the $NaCl^+$ signal to the total mass calculated using the number concentration from a CPC-3010. This calibration was done after the campaign but with similar tuning conditions. The sea salt-$SO4^{2-}$ (ss-$SO4^{2-}$) was calculated as 0.252 * 0.3 * [seasalt], where 0.252 is the mass ratio of $SO4^{2-}$ to Na^+ in sea salt and 0.3 is the mass ratio of Na^+ to sea salt (Ghahremaninezhad et al., 2016). Given these assumptions, the uncertainty in the seasalt concentrations are likely to be significantly higher than the typical 20%, although the total contribution of seasalt to the PM1 fraction was very small (0.30 µg m^{-3} ; <4 %)."*

2) On multiple occasions in the manuscript the term "agreement" is mentioned, but no actual metric is provided. For example, in L307 "reasonable agreement between the PM1 concentration calculated from composition measurements and the SMPS" is stated, but what does this translate to? Apart from the timeseries, no scatter plot is provided, no correlation coefficient, therefore how is this agreement defined? Same in L312.

Authors: The reviewer is correct that "agreement" is too loose of a term. The first instance when it is used:

"reasonable agreement between the PM1 concentration calculated from composition measurements and the SMPS..."

Now reads as:

"There was reasonable agreement (slope = 0.62; R^2 = 0.67) between the PM1 mass concentration calculated from composition measurements and the SMPS…"

The second instance of when it was used:

"For most of the campaign there was a good agreement between the PM_1 $SO_4$2+ and the TSP $SO_4$2+ concentration, with the exception of periods of high sea salt concentrations when the TSP SO 42+ were significantly higher (see Supplementary Figure S2)."

Now reads:

"During most of the campaign there was a reasonable agreement (slope = 1; R^2 = 0.6) between the PM1 SO_4^{2-} (c-ToF-AMS) and the TSP SO_4^{2-} (PILS) concentration, with the exception of periods of high sea salt concentrations when the TSP SO_4^{2-} were significantly higher (slope = 0.5; R^2 = 0.2 for TSP Cl- concentrations > 10 µg m^{-3}; see Supplementary Figure S2)."

Technical corrections:
L76 I would also add here the references of Bougiatioti et al. (2014) and Minguillon et al. (2015) as identifying biomass burning aerosol in the Mediterranean during summer

Authors: These references have been added. The sentence now reads :

"Furthermore, biomass burning aerosol has frequently been observed over the basin, in particular the dry season in summer when forest fires are more common (Bougiatioti et al., 2014; Minguillon et al., 2015; Pace et al., 2005)."

L126 change to "BBOA"

Authors: The incorrectly labelled "BBA" has been changed to "BBOA".

L140 secondary sites established (delete "were")

Authors: The incorrect use of "were" has been deleted. The sentence now reads:

"Numerous secondary sites established along the Mediterranean coasts in Spain, Italy and Corsica beyond the SOP-1a have also provided valuable knowledge of the atmospheric composition in the western and central Mediterranean regions (Chrit et al., 2017; Chrit et al., 2018; Becagli et al., 2017)."

L162 probably you mean Total Suspended Particulate (TSP)

Authors: "Total Suspected Particulate (TPS)" has been changed to "Total Suspended Particulate (TSP)".

L165 check font style

Authors: All fonts throughout the manuscript have now been made consistent.

L157-164 More information on the c-ToF-AMS measurements should be provided here

Authors: As detailed above, more details about the c-ToF-AMS measurements have been provided (IE, RIE, CE, seasalt scaling).

L299 Dry NR-PM1? There is nothing mentioned about using a dryer in the instrumentation section (2.2)

Authors: A nafion drier was used. The relative humidity at the AMS inlet was logged for ~ half of the campaign and was below 55%. This has been indicated in Section 2.2:

"A nafion drier was used, however the relative humidity at the inlet of the c-ToF-AMS was checked throughout the campaign and was always below 55%."

L307 Reasonable agreement meaning what? R2 of how much?

Authors: As described above, a slope and correlation coefficient for the PM1 from the cToF-AMS and SMPS has now been provided:

"There was reasonable agreement (slope = 0.62; R^2 = 0.67) between the PM1 mass concentration calculated from composition measurements and the SMPS…"

L312-314 Do you mean between c-ToF-AMS and PILS? If yes I would suggest to change and state the methods used, preferably also give a correlation coefficient

Authors: As described above, a slope and correlation coefficient has been provided. We have also indicated the instrument used (c-ToF-AMS and PILS):

"During most of the campaign there was a reasonable agreement (slope = 1; R^2 = 0.6) between the PM1 SO_4^{2-} (c-ToF-AMS) and the TSP SO_4^{2-} (PILS) concentration, with the exception of periods of high sea salt concentrations when the TSP SO_4^{2-} were significantly higher (slope = 0.5; R^2 = 0.2 for TSP Cl- concentrations > 10 μg m^{-3}; see Supplementary Figure S2)."

L340 low-volatility/ highly oxidized L340 Make title bold

Authors: This has been fixed. "typical of low-volatile/highly oxidized OOA" now reads as "typical of low-volatility/highly oxidized OOA".

L511-516 Night-time nucleation events have also been observed in the Eastern Mediterranean (Kalivitis et al. 2012)

Reference

Kalivitis, N., Stavroulas, I., Bougiatioti, A., Kouvarakis, G., Gagné, S., Manninen, H. E., Kulmala, M., and Mihalopoulos, N.: Night-time enhanced atmospheric ion concentrations in the marine boundary layer, Atmos. Chem. Phys., 12, 3627-3638, https://doi.org/10.5194/acp-12-3627-2012, 2012

Authors: This has now been included and referenced:

"Night-time NPF events have also been observed in the Eastern Mediterranean (Kalivitis et al., 2002)."

RC2

This study presents results on composition of fine PM fraction (approx. PM1) in Lampedusa, an island site in the southern central Mediterranean), by using a cToF-AMS. Results were obtained during the first CHARMEX Special Observation Period (SOP1) in summer 2013. Results were compared with similar studies performed in the Mediterranean region in different periods and specifically with those obtained at Ersa site, Corsica, during the sampling period. The novelty of this work lies in the fact that it is the first study of this type carried out on an island in the central Mediterranean. One of the main concerns of this study is the short duration of the sampling period (less than one month). This can affect its representativeness, the comparison with other studies and the interpretation of the results. However, results can be considered of interest in the framework of the CHARMEX SOP1.

Variations in PM1 composition are interpreted as a function of the origin of air masses. Higher concentrations of sulfate were obtained during transport from eastern Mediterranean, probably due to the impact of emissions from this region. A clear variation was also observed for the LO-OOA/MO-OOA ratios, with a higher contribution of the most oxidized aerosols with transport form the east.

Authors attempt to study the aging of aerosols during transport by comparing PM1 composition at Lampedusa and Ersa, when affected by the "same" air masses. Comparison was performed for the different clusters defined. This comparison was mainly focused on sulfate; differences were related to the accumulation of SO4 and the SO2 conversion (mainly related to the shipping emissions). A significant increase was obtained for sulfate concentrations during transport of air masses form the East. As shown in Figure 13, during transport from eastern Mediterranean, it seems that the Lampedusa site is affected by other air masses different to those impacting at Ersa. Thus, higher concentrations of sulfate at Lampedusa may be related to the impact of air masses from the East, that are not impacting at Ersa. Therefore, the proposed methodology has some limitations for estimating the aging under these scenarios.

The authors thank the reviewer for her/his time in reviewing the manuscript and their suggestions. Many of the reviewers comments were regarding small technical/grammatical errors which have been addressed (and described in more detail below). The reviewer has two larger concerns regarding the representativeness of the study period as well as the conflation of aging processes with the possible influence of different air masses

The reviewer's first concern is regarding the short duration (less than one month) of the field campaign, although she/he acknowledges the scope of the study within the broader framework of Charmex. Due to the scale and logistics of studies such as this one with extensive instrumentation, it is extremely difficult and expensive to perform longer-term measurements. Comparable studies which are summarised in this study (see updated Figure

8) are also of a similar length, with the exception of those on continental Europe that are more easily accessible. Furthermore, while we agree that the length of the campaign period is not enough to measure longer term climatology or seasonality, the link between the aerosol composition and size and the air mass back trajectory cluster analysis provides some detail about how the wider synotic conditions could influence the aerosol composition at Lampedusa. The authors do agree though that long term (multi-seasonal or multi-year) measurements at remote sites would be very valuable.

The reviewer's second concern is regarding the comparisons between the sulphate concentrations measured concurrently at the Lampedusa and Ersa sites and the limitations of the methodology to estimate aging between the two sites. The reviewer is correct in that we do not know if there is an aging process (e.g. SO_2 -> SO_4^{2-}) between the two sites or if there are other air mass from the east that are impacting the sulphate concentrations. In order to address this concern, we have changed the title of the section from: *"3.6 Evidence of aging across the Mediterranean"* to *"3.6 Accumulation of sulphates across the Mediterranean"*. We have also changed instances when "growth" of sulphate to "accumulation" of sulphates which is more agnostics about the origin and mixing state of the sulphate aerosol. Lastly, we have changed the following sentence: *"It is expected that the accumulation of sulphate would increase as the total travel time increases due to the opportunity for SO2 conversion."* to: *"It is expected that the accumulation of sulphate would increase as the total travel time increases due to the opportunity for SO2 conversion or from the addition of sulphate from separate air masses which are not accounted for in the HYSPLIT model."*.

In addition to the Minor changes outlined below, several other changes in the manuscript have been made (e.g. reference formatting, typos). The major change is that data presented in Table 1 and Supplementary Table S1 has now been combined and displayed in a new figure (Figure 8; see below). This figure summarises the PM_1 composition from all of the previous studies around the Mediterranean basin that have performed a PMF analysis. This new Figure makes it much easier to compare the results of our study to these previous studies by visualising the composition with pie charts pointing to the sampling location, rather than presenting the data in tables. Subsequent Figure and table numbers have been updated.

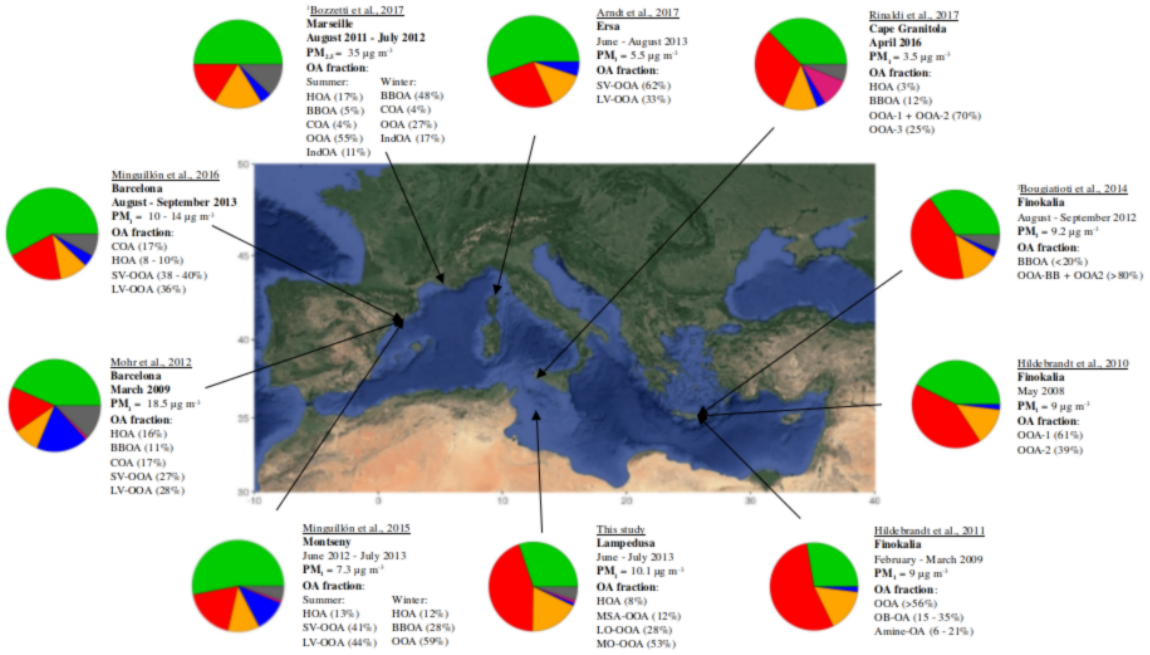

Figure 8 A summary of studies that have investigated NR-PM$_1$ composition (including PMF of OA) around the Mediterranean basin. Only studies that have investigated PMF-based OA source apportionment are reported. Pie charts display the average concentration during each study where green corresponds to organics, red to sulphates, orange to ammonium, blue to nitrate, pink to either chlorides or sea salt and black to elemental or black carbon. The OA fraction acronyms correspond to the following:HOA: Hydrocarbon-like Organic Aerosol, SV-OOA: Semi-volatile oxygenated Organic Aerosol, LV-OOA: Low-volatility oxygenated Organic Aerosol, BBOA: Biomass burning Organic Aerosol, COA: Cooking Organic Aerosol, OOA: Oxygenated Organic Aerosol, F4: "Factor -4" (unidentified PMF factor), IndOA: Industry-related Organic Aerosol, OB-OA: "Olive-branch Organic Aerosol. See Supplementary Tables S1 and S2 for further details about the sampling locations, instruments used and pie chart values. [1]This study collected on PM2.5 filters and nebulised into an HR-ToF-AMS. [2]Excludes fire-periods.

Minor changes

Line 99 (e.g. FLEXPART; (Stohl et al., 2005)

Authors: A closing bracket has been added - ”(e.g.FLEXPART; (Stohl et al., 2005)” now reads “(e.g. FLEXPART; (Stohl et al., 2005))”.

Line 108: (PMF; (Paatero, 1997;

Authors: A closing bracket has been added - “(PMF; (Paatero, 1997; Paatero and Tapper, 1994)” now reads “(PMF; (Paatero, 1997; Paatero and Tapper, 1994))”

Lines 144-146: is the first “detailed characterization” in the Central Mediterranean, at Lampedusa, or during the CHARMEX project?

Authors: It is the first detailed characterization of PM1 in the central remote Mediterranean in general. The sentence has been changed from:
“In this paper, we present the first detailed characterisation of PM1 in the central Mediterranean region from measurements of size-resolved chemical composition from the island site of Lampedusa during the ChArMex/ADRIMED SOP-1a.”

and now reads

"In this paper, we present the first detailed characterisation of PM1 in the central remote Mediterranean region, using measurements of size-resolved chemical composition on the island site of Lampedusa during the ChArMex/ADRIMED SOP-1a."

Line 162: Please, indicate the sampling flow

Authors: The sample flow of the TSP (16 lpm) has now been indicated.

Line 167: for major inorganic and organic. . .

Authors: This has been fixed. "Samples were analysed for major and organic anions..." now reads as "Samples were analysed for major inorganic and organic anions…"

Line 175: please indicate flow for MOUDI; did you use the same TSP inlet for all the instruments?

Authors: The flow rate for the MOUDI cascade impactor (10 lpm) has been provided. A TSP inlet was used for the MOUDI, PILS, c-ToF-AMS and SMPS which has now been explicitly stated in the respective descriptions of each inlet.

Line 177: which kind of filters did you use?

Authors: PTFE (2 μm pore size) and coated with high quality vacuum grease (Dekati DS-515) to avoid bouncing. This has now been indicated.

Line 179: Denjean et al. (2016)).

Authors: This has been fixed. "Denjean et al., (2016)) now reads as "Denjean et al., (2016)."

Line 214: by (Ovadnevaite et al., (2012).

Authors: This has been fixed. "...as proposed by (Ovadnevaite et al., 2012)" now reads as "...as proposed by Ovadnevaite et al., 2012."

Line 215: High uncertainty estimation of the sea salt

Authors: The high uncertainty estimated of the sea salt has been explained in more detail, although it was not quantified during the experiment. The section regarding the sea salt estimation now reads :

"The PM1 sea salt concentration was estimated in the cTof-AMS by applying a scaling factor of 102 to the ion fragment (using the cumulative peak fitting analysis) at 57.98 assigned to NaCl as proposed by Ovadnevaite et al., 2012. This scaling factor was determined by nebulising monodisperse 300 nm (mobility diameter) NaCl particles into the cToF-AMS and comparing the $NaCl^+$ signal to the total mass calculated using the number concentration from a CPC-3010. This calibration was done outside of the campaign but with similar tuning

*conditions. The sea salt-$SO4^{2-}$ (ss-$SO4^{2-}$) was calculated as 0.252 * 0.3 * [seasalt], where 0.252 is the mass ratio of $SO4^{2-}$ to Na^{+} in sea salt and 0.3 is the mass ratio of Na^{+} to sea salt (Ghahremaninezhad et al., 2016). Given these assumptions, the uncertainty in the seasalt concentrations are likely to be significantly higher than the typical 20%, although the total contribution of seasalt to the PM_1 fraction was very small (0.30 μg m^{-3} ; <4 %). Samples were analysed for major and organic anions"*

Line 299: please, specify the time period of the concentrations (hourly basis; 30 minute?)

Authors: the mean was calculated using the instrument time resolution of 3 minutes.

Lines 312, 313, 314, 565: SO42-

Authors: There were four instances when the sulphate anion was mistakenly written with a "+" instead of "-". These instances of SO_4^{2+} have been changed to SO_4^{2-}.

Line 314: (see Supplementary Figure S2).

Authors: This has been fixed. "(see Supplementary Figure S2." now reads as (see Supplementary Figure S2)."

Lines 319-322: this is estimation, more measurements, for a wider period are necessary for demonstrating this.

Authors: The reviewer is correct. The wording has been altered to keep it appropriate to the scope of the study.

"This indicates that, in these circumstances, the sea salt particles acted as a condensation sink for sulphate precursors. This has important implications for the radiative properties of these aerosols by altering the scattering properties and, potentially cloud condensation nuclei concentrations and composition."

Has been changed to:

"If these events are frequent, this could have important implications for the radiative properties of these aerosols by altering the scattering properties and, potentially cloud condensation nuclei concentrations and composition."

Lines 416-418: This comparison will depend on the sampling periods. This study was performed in summer, where high concentrations of sulfate are expected. The study by El Haddad et al (2013), also in summer, showed higher concentration of sulfate than OA

Authors: The following sentence has been removed:

"Furthermore, the contribution of ammonium sulphate was higher in this study than of all those undertaken in the eastern Mediterranean basin, highlighting the role contribution of sulphates across the Mediterranean."

This original sentence was based on the reported ammonium sulphate concentrations in this study and those from around the Mediterranean basin and was supposed to point out that those in this study were higher than *western* (not eastern as initially stated) Mediterranean. Although as the reviewer points out, making this comparison depends on the sampling periods which are not always in the same season. A more detailed study of local SO_2 sources near each of the sites would be beneficial.

Line 438. In figure 8: concentration of sulfate and ammonium seem higher during E – NE air masses; not north west as stated here; a similar pattern to that described for MO-OOA (Line 448).

Authors: The reviewer is correct. "north-westerley" has been changed to "north-easterly". Furthermore, Figure 8 is now Figure 9.

Line 450: Pattern of LO-OOA is similar to that of HOA Lines 463-466; Section 3.4. Figure 6. There is a clear difference between the ratio LO-OOA/MO-OOA during the eastern and western air masses; any comment on this?

Authors: Although the polar-plot pattern of LO-OOA is similar to that of HOA, the time series of the two factors were not well correlated ($R^2 = 0.30$).

The potential explanation for different contributions of LO-OOA and MO-OOA during the eastern and western air masses has now been reiterated at the end of the next paragraph:

"The higher contribution of MO-OOA compared with LO-OOA from eastern air masses, and vice-versa during western air masses, could be indicative of different OA sources prior to oxidation or due to different photochemical aging between the two directions."

More measurements, and likely using a higher resolution AMS, would be required to distinguish smaller differences in the MO-OOA and LO-OOA and their differing contributions from the east and west. It is possible that their courses are the same or similar, however they have been kept as separate factors due to their different diurnal and temporal trends and relation to different air masses.

Section 3.5. The measurements of size distribution are limited to the 14-600 nm fractions. The lower size is relatively high for studying the nucleation episodes. Moreover the different air humidity measured for the air clusters defined (sampling was at ambient conditions Line 469-472) may affect these measurements.

Authors: We now indicate that how statements regarding nucleation are constrained to observations > 14 nm. We also indicate that the humidity could shift the measured size distribution to larger sizes:

It should be noted that these size distributions are under ambient conditions without an inlet drier which could shift the size distribution to larger sizes if water is present. The ambient relative humidity for each air mass back trajectory cluster was: Eastern Mediterranean (53%), Central Europe (61%), Atlantic (74%), Western Mediterranean (70%), Mistral (low) (67%) and Mistral (high) (74%). Although the higher temperature inside the PEGASUS mobile laboratory could lower the relative humidity at the sampling point of the SMPS with respect to the ambient relative humidity, this was not measured or logged during the campaign.

Lines 485-487: Has the "nucleation mode ratio" been previously defined? Can you add a reference?

Authors: It has not been previously defined. We have, however, decided to remove this term and simply state it as "the ratio of the particle number concentration between 14 - 25 nm and 14 - 600 nm" or "the ratio of sub-25 nm and sub-600 nm particle number concentrations".

Line 501: Please, add a reference for shipping emissions

Authors: References have now been included for the statement regarding vanadium and nickel in shipping emissions (Healy et al., 2009; Isakson et al., 2001.):

Healy, R. M., O'Connor, I. P., Hellebust, S., Allanic, A., Sodeau, J. R., & Wenger, J. C.: Characterisation of single particles from in-port ship emissions. Atmospheric Environment, 43(40), 6408-6414, 2009.

Isakson, J., Persson, T. A., & Lindgren, E. S.: Identification and assessment of ship emissions and their effects in the harbour of Göteborg, Sweden. Atmospheric Environment, *35*(21), 3659-3666, 2001

Figure 6. caption: "less oxidized" (LO-OOA) . . .

Authors: The caption for Figure 6 has been changed from "..."less oxidised" (OOA)" to "..."less oxidised" (LO-OOA)".

Summertime surface PM_1 aerosol composition and size by source region at the Lampedusa island in the central Mediterranean Sea

Marc D. Mallet[1,2,3], Barbara D'Anna[2,4], Aurélie Même[2,*], Maria Chiara Bove[5,6], Federico Cassola[5,7], Giandomenico Pace[8], Karine Desboeufs[1], Claudia Di Biagio[1], Jean-Francois Doussin[1], Michel Maille[1], Dario Massabò[5], Jean Sciare[9], Pascal Zapf[1], Alcide Giorgio di Sarra[8] and Paola Formenti[1]

1. LISA, CNRS UMR7583, Université Paris Est Créteil (UPEC), Université de Paris ~~Diderot (UPD)~~, Institut Pierre Simon Laplace (IPSL), Créteil, France

2. IRCELYON, CNRS UMR 5652, Univ. Lyon1, Lyon, France

3. Centre National d'Etudes Spatiales (CNES), Toulouse, France

4. LCE, CNRS UMR 7376, Aix-Marseille Université, Marseille, France

5. Department of Physics & INFN, University of Genoa, Genoa, Italy

6. ARPAL Physical Agents and Air Pollution Sector, La Spezia, Italy

7. ARPAL CFMI-PC, Genoa, Italy (current affiliation)

8. Laboratory for Observations and Analyses of Earth and Climate, ENEA, Rome, Italy

9. The Cyprus Institute, Energy, Environment and Water Research Center, Nicosia, Cyprus

*now at Bruker

For submission to the ChArMex special issue in Atmos. Chem. Phys.

Abstract

Measurements of aerosol composition and size distributions were taken during the summer of 2013 at the remote island of Lampedusa in the southern central Mediterranean Sea. These measurements were part of the ChArMEx/ADRIMED (Chemistry and Aerosol Mediterranean Experiment/Aerosol Direct Radiative Forcing on the Mediterranean Climate) framework and took place during the Special Observation Period 1a (SOP-1a) from 11 June until 5 July 2013.

From compact time-of-flight aerosol mass spectrometer (cToF-AMS) measurements in the size range below 1 µm in aerodynamic diameter (PM_1), particles were predominately comprised of ammonium and sulphate. On average, ammonium sulphate contributed 63% to the non-refractory PM_1 mass, followed by organics (33%). The organic aerosol was generally very highly oxidised (f_{44} values were typically between 0.25 and 0.26). The contribution of ammonium

sulphate was generally higher than organic aerosol in comparison to measurements taken in the western Mediterranean but is consistent with studies undertaken in~~undertaken in~~ the eastern basin.

Source apportionment of organics using a statistical (positive matrix factorisation) model revealed four factors; a hydrocarbon-like organic aerosol (HOA), a methanesulfonic acid related oxygenated organic aerosol (MSA-OOA), a more oxidised oxygenated organic aerosol (MO-OOA) and a less oxidised oxygenated organic aerosol we label (LO-OOA). The MO-OOA was the dominant factor for most of the campaign (53% of the PM_1 OA mass). It was well correlated with SO_4^{2-}, highly oxidised, and generally more dominant during easterly air masses originating from the eastern Mediterranean and central Europe. The LO-OOA factor had a very similar composition to the MO-OOA factor, but was more prevalent during westerly winds with air masses originating from the Atlantic Ocean, the western Mediterranean, and in high altitudes over France and Spain from mistral winds. The MSA-OOA factor contributed an average 12% to the PM_1 OA and was more dominant during the mistral winds. The HOA, representing observed primary organic aerosol only contributed 8% of the average PM_1 OA during the campaign.

Even though Lampedusa is one of the most remote sites in the Mediterranean, PM_1 concentrations (10 ± 5 μg m^{-3}) were comparable to those observed in coastal cities and sites closer to continental Europe. Cleaner conditions corresponded to higher wind speeds. Nucleation and growth of new aerosol particles was observed during periods of northwesterly winds. From a climatology analysis from 1999 until 2012, these periods were much more prevalent during the measurement campaign than during the preceding 13 years. These results support previous findings that highlight the importance of different large-scale synoptic conditions in determining the regional and local aerosol composition and oxidation and also suggest that a non-polluted surface atmosphere over the Mediterranean is rare.

1. Introduction

The Mediterranean Sea is a unique marine environment, surrounded by mountain ranges and high coastal human populations from Africa, Europe, and Asia, and the two largest deserts in the world; Sahara Desert to the south and Arabian Desert to the East. It presents a diverse and dynamic atmospheric composition and is projected to undergo significant changes in the contribution of freshwater (Sanchez-Gomez et al., 2009), sea surface temperature and precipitation (Mariotti et al., 2015) over the coming decades. The burning of fossil fuels, including shipping pollution, in southern Europe and in large Mediterranean cities, as well as

natural sources of aerosol such as sea salt, forest fires and mineral dust provide a highly complex and dynamic mixture of organic and inorganic aerosol and aerosol precursors in this region (Lelieveld et al., 2002). Elevated aerosol loadings over the Mediterranean basin have been attributed to the long-range transport of continental anthropogenic aerosols (Perrone et al., 2013; Sciare et al., 2003; Sciare et al., 2008) and mineral dust transported from Africa (Querol et al., 2009b; Koçak et al., 2007). Boundary layer observations in the eastern Mediterranean have shown significant influence of long-range transported continental pollution from southern and central Europe (Sciare et al., 2003). Furthermore, biomass burning aerosol has frequently been observed over the basin, in particular the dry season in summer when forest fires are more common (Bougiatioti et al., 2014; Minguillon et al., 2015; Pace et al., 2005). Long-ranged plumes from Nnorth American fires have also been observed at high altitudes (Formenti et al., 2002; Ortiz-Amezcua et al., 2014; Brocchi et al., 2018; Ancellet et al., 2016).

Previous long-term observations of the chemical composition of aerosol in the Mediterranean have shown that PM_{10} (particulate mass with aerodynamic diameter less than 10 µm) is composed of secondary ammonium sulphate, primary and secondary organic aerosol from fossil fuels or biogenic origins, with contributions from natural aerosols from the Sahara Desert and sea spray (Bove et al., 2016; Koulouri et al., 2008; Schembari et al., 2014; Calzolai et al., 2015). Mineral and sea salt contributions are significantly less in $PM_{2.5}$ particle fraction (Querol et al., 2009a). Coarse mode particles contribute to the direct radiative effect over the Mediterranean (Perrone and Bergamo, 2011; Meloni et al., 2006) and can also act as condensation sinks for pollutants (Pikridas et al., 2012). Smaller (sub-micron) aerosol particles, while also contributing efficiently to the total aerosol optical depth in this region (Formenti et al., 2018), can also act as efficient cloud condensation nuclei and therefore have influence on cloud formation, lifetime and precipitation (Haywood and Boucher, 2000). Understanding the impact of different natural and anthropogenic sources on the regional composition of the atmosphere is therefore important in our understanding of the influences they have on the climate over the Mediterranean basin and surrounding regions. It is also now widely recognised that aerosols contribute to adverse health effects in humans (World Health Organization, 2016).

Consideration of both the local and regional meteorology are needed to characterise the sources and aging of aerosols (Petit et al., 2017). The National Oceanic and Atmospheric Administration's (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT; Stein et al., 2015) and other trajectory models (e.g. FLEXPART; (Stohl et al., 2005)) have become a widely-used resources in atmospheric studies to compute the backwards or forwards trajectories of air masses at any point on Earth. They can be useful for identifying the

possible origin of a particular episode associated with elevated concentrations of aerosols or gases. Combined with in-situ measurements over longer time periods, they provide a more holistic approach in understanding the link between local or region meteorology and atmospheric composition (Schmale et al., 2013; Tadros et al., 2018; Zhou et al., 2016). This is particularly useful for remote sites where local emissions are insignificant or infrequent.

Investigation of the aerosol physical and chemical properties can also help distinguish their respective sources. Positive matrix factorisation (PMF; (Paatero, 1997; Paatero and Tapper, 1994)) has proved to be a useful statistical tool in identifying aerosol sources or aging processes of organics. The source apportionment of $PM_{2.5}$ and PM_{10} over the Mediterranean, from PMF method, has been investigated in recent works and showed a large spatial variability in source contributions (Becagli et al., 2012; 2017; Calzolai et al., 2015; Amato et al., 2016; Diapouli et al., 2017). The PMF approach was also used to study the aerosol source and aging processes by utilising the complex nature of organic aerosol in the Mediterranean (e.g. Hildebrandt et al., 2010, 2011; Bougiatioti et al., 2014; Minguillón et al., 2016; Arndt et al., 2017; Michoud et al., 2017). This approach has become increasingly feasible with the recent widespread implementation of instruments capable of providing real-time, high time-and mass-resolved non-refractory aerosol composition, such as aerosol mass spectrometers (Ulbrich et al., 2009). PMF models have shown to successfully resolve the bulk-composition of sub-micron organic aerosol into the contributions from various primary sources (e.g. biomass burning, fossil fuel burning, cooking aerosol), but can also reveal the contributions and characteristics of secondary (SOA) organic aerosol (Zhang et al., 2011). Factors with similar mass spectra are consistently observed, albeit with different contributions at measuring sites all around the world. The most commonly observed primary organic aerosol factors are hydrocarbon-like OA (HOA), usually from fossil fuel burning as well as biomass burning (BBOA) while SOA can be usually separated into at least two factors, with low-volatility oxygenated OA (LV-OOA) and Semi-Volatile-OOA (SV-OOA) as common examples (Zhang et al., 2011; Crippa et al., 2014). Other types of OOA have also been observed, such as "Marine-OOA" (Schmale et al., 2013), although these are more difficult to resolve given the shift towards more uniform OA composition with aging.

The Chemistry-Aerosol Mediterranean Experiment (ChArMEx) collaborative research program, and the Aerosol Direct Radiative Impact on the regional climate in the MEDiterranean region (ADRIMED) project within, were undertaken to investigate the chemistry and climate interactions within the Mediterranean (Mallet et al., 2016). From 11 June until 5 July 2013, numerous experimental setups were deployed across the western and central Mediterranean in what is called the "Special Observation Period - 1a" (SOP-1a), including intensive airborne measurements (Denjean et al., 2016). Two super-sites were set-up at Ersa (at the northern tip

of Corsica Island, France) and at the Lampedusa Island (Italy), approximately 1000 km apart on a north-to-south axis in order to characterise surface aerosol chemical, physical and optical properties (Mallet et al., 2016). Numerous secondary sites ~~were~~ established along the Mediterranean coasts in Spain, Italy and Corsica beyond the SOP-1a have also provided valuable knowledge of the atmospheric composition in the western and central Mediterranean regions (Chrit et al., 2017; Chrit et al., 2018; Becagli et al., 2017).

In this paper, we present the first detailed characterisation of PM_1 in the central remote Mediterranean region, using ~~from~~ measurements of size-resolved chemical composition on ~~from~~ the island site of Lampedusa during the ChArMex/ADRIMED SOP-1a. We investigate the source apportionment of PM_1 by considering their chemical and microphysical properties along with ancillary PM_{10}, gaseous and meteorological data, air mass back trajectories as well as complimentary data collected at the Ersa site in Corsica.

2. Experimental

2.1 Sampling sites

Observations took place at the Roberto ~~Serao~~ Sarao station ~~(http://www.lampedusa.enea.it/)~~ on the island of Lampedusa (35°31'5''N, 12°37'51'' E, 20 m above sea level) from 11 June to 5 July 2013. Ancillary measurements for this study taken at Ersa at the northern tip of Cape Corsica (42°58'5'' N, 9°22'49'' E, 560 m above sea level), are also considered. The position of the stations is shown in Figure 1.

2.2 Instrumentation, measurements and data

Instruments at the Lampedusa super-site were housed in the PEGASUS (Portable Gas Field and Aerosol Sampling Unit) station, a portable observatory initiated by LISA, described in Mallet et al. (2016). Relevant to this study, a c-ToF-AMS (Aerodyne Inc., Billerica, USA), was used to measure the size-resolved composition of non-refractory particulate matter below 1 µm (NF-PM_1)(Drewnick et al., 2005). Data was collected with a 3-minute time resolution. The c-ToF-AMS was operated from a certified Total Suspended ~~Suspected~~ Particulate (TSP ~~TPS~~) sampling head (Rupprecht and Patashnick, Albany, NY, USA) followed by a cyclone impactor cutting off aerosol particles larger than 1 µm in aerodynamic diameter (using a flow rate of 16 lpm). A nafion drier was used, however the relative humidity at the inlet of the c-ToF-AMS was checked throughout the campaign and was always below 55%.

A particle-into-liquid sampler (Metrohm PILS; Orsini et al. (2003)) was installed on a TSP inlet and collected samples approximately every hour. Denuders to remove acid/base gases were not used. Samples were analysed for major inorganic and organic anions (F^-, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, $HCOO^-$, CH_3COO^-, $(COO^-)_2$) and cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) using Ion Chromatography (Metrohm, model 850 Professional IC) equipped with Metrosep A supp 7 pre-column and column for anions measurements and Metrosep C4-250 mm pre-column and column for cations measurements, and a 500 µL injection loop. The device was operated with a 1-hour time resolution.

A 13-stage rotating cascade impactor nanoMOUDI (Model 125B, Marple et al., 1991) was used to measure the size-segregated inorganic elemental composition. The nanoMoudi impactor, also operated from the TSP inlet, allows the separation of the particles in 13 size classes from 10 nm to 10 µm diameter with a backup stage. Each sample was collected for 3 days with a flow rate of 10 lpm to ensure enough material was collected on each impactor stage. ~~Filters~~ 47 mm diameter PTPE filters (2 µm pore size) were used and coated with high quality vacuum grease (Dekati DS-515) to avoid bouncing. They were then analysed using X-ray fluorescence (PW-2404 spectrometer by PANalytical™) for the particulate elemental concentrations for elements from Na to Pb as described in Denjean et al. (2016)).

A Scanning Mobility Particle Sizer (SMPS) measured the mobility number size distribution of aerosols every 3 minutes from 14.6 to 661.2 nm. diameter. The instrument is composed by an X-ray electrostatic classifier (TSI Inc., model 3080) and a differential Mobility Analyser (DMA; TSI Inc., model 3081), and a condensation particle counter (CPC; TSI Inc., model 3775) operated at 1.5/0.3 L min^{-1} aerosol/sheath flows. Data were corrected to take into account the particle electrical charging probabilities, the CPC counting efficiency, and diffusion losses. Each scan was recorded with a 5-minute time resolution. A drier was not used on the SMPS inlet and therefore the size distributions reported are for ambient conditions.

A GRIMM optical particle counter (OPC; GRIMM Inc., model 1.109) was used to measure the number size distribution over 31 size classes ranging from 0.26 µm up to 32 µm (nominal diameter range assuming the aerosol refractive index of latex spheres in the calibration protocol). The instrument was operated at a 6-second resolution and data were acquired as 3-minute averages.

The equivalent black carbon mass concentration (eBC) was determined by the measurement of light-attenuation at 880 nm performed by a spectral aethalometer (Magee Sci. model AE31)

operated at a 2-minute time resolution and equipped with a TSP particle inlet. As the evaluation of eBC is used as a qualitative tracer of pollution, the factory mass conversion factor of 16.6 m^2 g^{-1} was applied to the raw measurement of attenuation without further corrections.

The meteorological measurements (air pressure, temperature, relative humidity, wind direction and speed and precipitation) were collected by a Vaisala Milos 500 station with a sampling rate of 10 minutes. The wind sensor was installed on a 10-m meteorological tower, while the air temperature and humidity were measured at a height of 2 m.

2.3. Data analysis

2.3.1. Analysis of the cToF-AMS data

The cToF-AMS data set was processed using two different software analysis tools. The first makes use of the widely-used and standard Igor Pro package, Squirrel (version 1.57G). This software processes the raw data and analyzes the unit-mass resolution (UMR) output with a fragmentation table reported in Aiken et al. (2008). The second method uses a cumulative peak fitting analysis and residual analysis and allows the separation of multiple isobaric peaks not taken into account in the traditional analysis of unit mass resolution squirrel data treatment (Muller et al., 2011). Uncertainties in the major chemical species from the cToF-AMS are typically of the order of ±20% (Drewnick et al., 2005).

The ionization efficiency (IE) with respect to nitrate anions was calculated every 5-6 days using nebulised 350 nm mobility diameter ammonium nitrate particles (values varied between 1.42 * 10^{-7} and 1.53 * 10^{-7}). The relative IE (RIE) of ammonium was slightly higher than the default value- and was 4.3 based on the mass spectrum of ammonium nitrate data from IE calibrations. The RIE of sulfate was determined by comparing the theoretical and the measured concentration of a solution of ammonium nitrate and ammonium sulfate and was determined to be the default value of 1.2. For the organic fraction, the default value of 1.4 was used. For each of the major species, a composition dependent collection efficency was applied as proposed by Middlebrook et al., 2012 and was on average 0.549, very similar to the default value of 0.55.

The PM_1 sea salt concentration was estimated in the cTof-AMS by applying a scaling factor of 102 to the ion fragment (using the cumulative peak fitting analysis described in Muller et al.,

2011) at 57.98 assigned to NaCl as proposed by (Ovadnevaite et al., 2012). This scaling factor was determined by nebulising monodisperse 300 nm (mobility diameter) NaCl particles into the cToF-AMS and comparing the $NaCl^+$ signal to the total mass calculated using the number concentration from a CPC-3010. This calibration was done after the campaign but with similar tuning conditions. The sea salt-SO_4^{2-} (ss-SO_4^{2-}) was calculated as 0.252 * 0.3 * [seasalt], where 0.252 is the mass ratio of SO_4^{2-} to Na^+ in sea salt and 0.3 is the mass ratio of Na^+ to sea salt (Ghahremaninezhad et al., 2016). Given these assumptions, the uncertainty in the seasalt concentrations are likely to be significantly higher than the typical 20%, although the total contribution of seasalt to the PM1 fraction was very small (0.30 µg m^{-3}; <4 %).

Unconstrained positive matrix factorisation was performed on both the unit-mass-resolution spectra of organic aerosol as well as the peak-fitted peaks identified as organics using PMF2 v2.08D. This method requires both a matrix for both the organic signals as well as the errors associated with the organics. For the peak-fitted signals, errors for each mass were estimated as

$$\Delta I_I = \sqrt{(\alpha^2 t + (\beta + 1)}$$

Where I is the ion signal, ΔI is the absolute uncertainty in the ion signal, α and β are constants (1.2 and 0.001, respectively) and t is the instrumental sampling time in seconds (Drewnick et al., 2009; Allan et al., 2003). For both UMR and peak-fitted inputs, up to 8 factors were investigated by altering the seeds from 0 to 50 in increments of 1 and the fpeaks from -1 to 1 in increments of 0.1. Where I is the ion signal, ΔI is the absolute uncertainty in the ion signal, α and β are constants (1.2 and 0.001, respectively) and t is the instrumental sampling time in seconds. For both UMR and peak-fitted inputs, up to 8 factors were investigated by altering the seeds from 0 to 50 in increments of 1 and the fpeaks from -1 to 1 in increments of 0.1. This approach is explained in Ulbrich et al. (2009).

2.3.2. Air mass back-trajectory calculation and cluster analysis

In order to determine potential source regions for aerosols measured at Lampedusa during the SOP-1a, a series of cluster analyses were performed on HYSPLIT air-mass back-trajectories as per the following. Weekly GDAS1-analysis (Global Data Assimilation System; 1° resolution) trajectory files were downloaded from the Air Resources Laboratory (ARL) of the National Oceanic and Atmospheric Administration (NOAA) archive. 144-hour air-mass backwards trajectories were then calculated every hour over the measurement period with ending point at Lampedusa (height of 45 m) using HYSPLIT (Stein et al., 2015) from within the R-package, SplitR.

Cluster analyses were then performed on these calculated trajectories, using a trajectory clustering function within the R-package, OpenAir (Carslaw and Ropkins, 2012). Clustering was done using two different methods to calculate the similarity between different trajectories. The first uses the Euclidean distance between the latitude and longitude of each trajectory point (a total of 144 in this case, representing each hour prior to the arrival at the receptor site). The second uses the similarity of the angles of each trajectory from the origin. These two methods are described in Sirois and Bottenheim (1995). For each clustering method, the number of clusters was altered from two up to ten. Six clusters identified using the Euclidean-distance method were selected, producing a realistic separation of the air-mass backwards trajectories and distinct and physically meaningful differences in aerosol composition and size. An additional clustering analysis was also performed over 3 and 6 hour intervals and using 96-hour backwards trajectories and yielded similar results.

3. Results and Discussion

3.1. Analysis of local and synoptic meteorology

The analysis of the hourly resolved 144-h air mass backwards trajectories provides an indication of the origin of the air masses sampled at Lampedusa during the field campaign. Six distinct clusters are identified (Figure 2). Cluster 1, "Eastern Mediterranean", is representative of air masses that circulate around the eastern-central Mediterranean basin before arriving at the Lampedusa site (average altitude of 400 m). Cluster 2, "Central Europe" is representative of air masses arriving from central Europe (average altitude of 800 m). Cluster 3, "Atlantic" is representative of more marine-like air masses that predominately originate over the Atlantic Ocean, pass over the Strait of Gibraltar between Spain and Morocco, and cross the western Mediterranean basin (average altitude of 500 m). Cluster 4, 263 "Western Europe", cluster 5, "Mistral (low)", and cluster 6, "Mistral (high)", all have similar angular trajectories, but are distinguishable by their different wind speeds and altitudes (although the Euclidian method of cluster analysis only considers differences in horizontal distances). The two "Mistral" clusters typically originate over the northern Atlantic Ocean, travel over France at a high altitude before descending over the western Mediterranean and travelling with relatively higher wind speeds towards Lampedusa. The altitude of "Mistral –(high)" was, on average, higher than "Mistral (low)" (1400 m and 1000 m, respectively) and also coincided with higher wind speeds at Lampedusa (13 ms^{-1} and 9 ms^{-1}, respectively). In comparison, the trajectories of the "Western Europe" cluster spent much more time circulating at lower altitudes (700 m, on average) over the western Mediterranean basin and, to a certain extent, east of the Lampedusa site.

As a complement, the pressure, temperature, relative humidity, wind speed and direction time series recorded at the station are shown in Figure 3. Two main weather regimes are observed: the former characterized by intense (up to nearly 20 m s^{-1}) northwesterly winds, persisting for several days (10-13 June and 22-30 June) and cool temperatures, whereas the latter associated with low-gradient anticyclonic conditions and light winds from the east or southeast, also favouring warmer temperatures (14-21 June and 1-3 July). Temperatures were relatively stable over the sampling period, fluctuating between approximately 18.5 °C -and 28.2 °C. The relative humidity typically ranged from between 70% and 82% with very few and very brief episodes of drier air masses (relative humidity close to or below 50%). The wind speed and direction distributions during the campaign can be compared to the June-July climatology from 1999 to 2012 (Figure 4). During the sampling period of this study, the frequency of winds from the north-westerly sectors were nearly double the average when compared to normal conditions, approaching 40% with high winds speeds exceeding 10 m s^{-1} observed during more than 20% of the time.

Data of sea level pressure and 1000 mbar meridional wind component composite anomalies obtained from the National Center for Environmental Prediction (NCEP)/National Center for Atmospheric Research (NCAR) Reanalysis (Kalnay et al. 1996) indicate that this particular situation was induced by a "dipolar" pattern, characterized by positive pressure anomalies in the Western Mediterranean and negative ones in the eastern part of the basin (see Supplementary Figure S1). This produced a persisting, stronger than normal gradient over Southern Italy. As a consequence, surface dust episodes typically driven by strong south or southeasterly winds, associated to cyclonic systems moving along northern African coasts, were basically absent during the campaign.

3.2 Aerosol composition

The dry NR-PM_1 concentrations measured at Lampedusa by the cTof-AMS ranged from 1.9 to 33.~~4~~ 4 µg m^{-3}, with a mean of 10.2 µg m^{-3} over the sampling period. Sulphate contributed the most to the measured NR-PM_1 mass (41% ± 9% on average) followed by significant contributions from organics (31% ± 8%) and ammonium (17% ± 3%). The eBC, nitrate and sea salt (scaled from the NaCl component of m/z 58) contributed 6% (±4%), 1% (±0.4%) and 3% (±2%), respectively. Figure 5 shows the total PM_1 concentration (calculated as the sum of the individually measured species), with contribution from each of the species, as well as the calculated PM_1 mass concentration from the SMPS (assuming an average density based on the composition data). There was reasonable agreement (slope = 0.62; R^2 = 0.67) between the PM_1 mass concentration calculated from composition measurements and the SMPS, with

discrepancy observed during periods of high sulphate concentrations from the eastern Mediterranean.~~, likely~~ This could be due to a combination of a~~the~~ broader accumulation mode exceeding the upper size limits of the cToF-AMS inlet, differences in sampling line relative humidity, or unaccounted for variations in the collection efficiency. This figure also contains an indication of the air mass origin over the sampling period.

During~~For~~ most of the campaign there was a reasonable~~good~~ agreement (slope = 1; R^2 = 0.6) between the PM_1 SO_4^{2-} (c-ToF-AMS) and the TSP SO_4^{2-} (PILS) concentration, with the exception of periods of high sea salt concentrations when the TSP SO_4^{2-} were significantly higher (slope = 0.5; R^2 = 0.2 for TSP Cl- concentrations > 10 µg m^{-3}; see Supplementary Figure S2). Supporting measurements of the size-segregated composition from the cascade impactor corroborate this, indicating a higher contribution of elemental sulphur in the coarse mode during periods of higher sea salt (Supplementary Figure S3). These periods corresponded to~~with~~ the "Mistral" air masses, characterised by higher wind speeds and indicated the role of coarse ~~mode~~ sea salt particles in acting as a condensation sink for sulphate species. ~~This indicates that, in these circumstances, the sea salt particles acted as a condensation sink for sulphate precursors.~~ If these events are frequent, ~~T~~this could~~has~~ have important implications for the radiative properties of these aerosols by altering the scattering properties and, potentially cloud condensation nuclei concentrations and composition.

Figure 6 shows the organic mass, split according to different OA factors from the PMF of the OA peaks. From the unconstrained PMF of the UMR and peak-fitted organic mass spectra, the most meaningful solution was found from a 4-factor solution of the UMR analysis (see Supplementary Figures S4 and S5 for the mass reconstruction and time series' residuals). This has resulted in one factor resembling to a primary organic aerosol and three oxygenated organic aerosol (OOA) factors. Herein we label these factors HOA (hydrocarbon-like OA), MO-OOA (more oxidised OOA), LO-OOA (less oxidised OOA) and MSA-OOA (methanesulfonic acid-related OOA).

These factors were compared with ambient organic mass spectra listed in the AMS Spectral Database (Ulbrich et al., 2009). The spectra for the OOA factors (see Figure 7) were strongly correlated with each other (R > 0.97) and all three were similar to a "continental" OOA factor observed in a ship campaign in the Artic (Chang et al., 2011), as well as a low-volatility OOA factor identified in Paris (Crippa et al., 2013). Despite the similarities in their mass spectra, they exhibited different diurnal trends (Figure 7) and time series that were associated with different wind directions and air masses and were therefore not recombined into a single OOA factor.

The MO-OOA factor was the most dominant factor during the field campaign (~53% of the total OA mass) and was typical of low-volatility/highly oxidized OOA observed in many other studies, in the Mediterranean, with high contributions of m/z 44 (f_{44} = 0.31) (e.g. (Hildebrandt et al., 2010; Hildebrandt et al., 2011). This factor was the most prominent during air masses from the Eastern Mediterranean, central Europe and Atlantic (contributing to 71%, 58% and 55% to OA, respectively) and was strongly correlated with ammonium sulphate (R^2 = 0.68) over the whole campaign. It also had a distinct diurnal trend, with concentrations increasing during daylight hours, indicative of photochemical processing. The LO-OOA factor was slightly less oxygenated (f_{44} = 0.26) and exhibited a different time series (R^2 = 0.04), related to different air masses, than the MO-OOA. The less oxygenated OOA factor has also been associated with semi-volatile species and is often labelled as SV-OOA (Jimenez et al., 2009). Despite a distinct diurnal profile similar to previously reported SV-OOA factors (with a peak in the early morning), we refrain from labelling our LO-OOA this way because the mass spectrum was generally much more oxygenated and contained less f_{43} than typically reported SV-OOA (see Figure 9~~8~~).

The MSA-OOA factor contributed approximately 12% of the total OA during the campaign and is likely related to the biogenic emission and processing of dimethyl sulfide (DMS) from phytoplankton in the Mediterranean. This factor was also highly oxygenated (f_{44} = 0.20), but contains key peaks related to the fragmentation of MSA from the electron impact of the cToF-AMS. The most prominent of these peaks were m/z 96 ($CH_4SO_3^+$), 79 ($CH_3SO_2^+$), 78 ($CH_2SO_2^+$), 65 (HSO_2^+) and 45 (CHS^+). A similar factor was observed at Bird Island in the south Atlantic Ocean (Schmale et al., 2015), albeit without the contribution of significant m/z 44, suggesting a more aged or mixed aerosol during this campaign. A distinct diurnal pattern for the MSA-OOA was not observed.

While the MO-OOA, LO-OOA and MSA-OOA factors represent secondary organic aerosol and were the most dominant contribution of OA during the campaign (92% on average), a primary organic aerosol factor was observed and identified here as hydrocarbon-like OA (HOA). The mass spectrum of the HOA factor was characteristic of spectra observed in other studies, with prominent peaks at m/z 95, 91, 83, 81, 71, 69, 57, 55, 43 and 41. Although HOA is typically associated with emissions from incomplete combustion (Zhang et al., 2005), it was not well correlated with other expected tracers such as eBC, CO and NOx. This HOA was typically associated with south-westerly winds of low speed (<5 m s^{-1}; see Figure 10~~9~~) and peaked at approximately 6 am local time each morning. The poor correlation between the HOA factor and eBC could have been due to a variety of local sources with different HOA and eBC emission factors, a mixing of the PMF factor with some small peaks not associated with combustion processes or from regional HOA that has undergone some transport without significant

oxidation. The signal fraction of each m/z of the mass spectrum of the HOA factor however had strong correlations (0.69 < R < 0.89) with numerous hydrocarbon-like organic aerosol (HOA) factors from other studies (Hersey et al., 2011; Ulbrich et al., 2009; Ng et al., 2011; Lanz et al., 2007; Zhang et al., 2005).

3.3 Comparison with other observations around the Mediterranean

There are many factors that could influence the composition, the concentration, and oxidation level of different aerosol species over the Mediterranean. These include different aerosol sources which can follow different seasonal or yearly trends (e.g. biogenic emissions) as well as the existing aerosol load and the meteorological conditions that drive transport, dilution and aging processes. ~~Table 1 summarises the recent observations of NR-PM$_1$ composition from measurements in the remote Mediterranean.~~

The majority of previous studies of detailed PM$_1$ aerosol composition have been taken at coastal sites around the Mediterranean (Mohr et al., 2012; Minguillón et al., 2016; Minguillón et al., 2015; Haddad et al., 2013; Bozzetti et al., 2017) which could be expected to observe higher concentrations than at Lampedusa due to proximity to sources (e.g. traffic, fossil fuel use, heating, biomass burning, industrial activities). Aside from Lampedusa and the observations presented in this study, measurements at Finokalia and Cape Corsica could be considered the most remote sites where these measurements have been taken. Similar to the comparison of NR-PM1 measurements from Europe, North America and east Asia made by Zhang et al., 2007, Figure 8 summarises the recent observations of NR-PM$_1$ composition from measurements in and around the Mediterranean basin (see Supplementary Tables S1 and S2 for more details that are displayed in Figure 8).

The PM$_1$ mass loading observed at Lampedusa is comparable to most of these other studies performed at both remote marine sites and coastal sites in the Mediterranean ~~(see Supplementary Table S1 for a comparison with coastal urban sites)~~. With the exception of sites in the ~~E~~eastern Mediterranean, OA was the dominant NR-PM$_1$ constituent and summertime OA was generally considered mostly secondary, comprised of SV-OOA and LV-OOA with small contributions of HOA. For remote sites, the results are consistent with a predominance of OA in PM$_1$ fraction in summer. PMF analysis of Q-AMS measurements at the Finokalia remote site in the eastern Mediterranean in the summer of 2008 showed two OOA factors and a distinct lack of HOA (Hildebrandt et al., 2010). A more recent study during the late 2012 summer at Finokalia observed periods influenced by biomass burning, but otherwise also observed mostly oxygenated organic aerosol (Bougiatioti et al., 2014). Measurements undertaken in the western

Mediterranean at Cape Corse from 11 June until 6 August 2013, encompassed the sampling period of this study. For the period from 15 July until 5 August, PMF analysis showed 55%, 27% and 13% contributions of organic matter, sulphate and ammonium to non-refractory PM_1 (Michoud et al., 2017). Secondary oxygenated VOCs dominated the VOC spectrum during the campaign and were very well correlated with submicron organic aerosol. PMF analysis on the OA revealed a 3-factor solution where SV-OOA and LV-OOA were dominant, contributing by 44% and 53%, respectively, with a 4% HOA contribution. From the same measurements but reported over the extended period from 11 June 11 until 5 August 5, there was a higher LV-OOA contribution (62%)(Arndt et al., 2017) which is in agreement with our observations of MO-OOA at Lampedusa. The OA was mostly portioned into MO-OOA and LO-OOA (81%), indicative of well-aged or oxidised secondary organic aerosol from long-range transport of pollutants. ~~Furthermore, the contribution of ammonium sulphate was higher in this study than of all those undertaken in the eastern Mediterranean basin, highlighting the role contribution of sulphates across the Mediterranean.~~

Figure ~~8~~9 displays the behavior of the f_{44} and f_{43} fragments obtained during the field campaign. f_{44}, a proxy for OA oxidation (Jimenez et al., 2009), is calculated as the ratio of the mass at m/z 44 (mostly CO_2^+) to the total OA, while f_{43}, equal to the ratio of m/z 43 (mostly $C_2H_3O^+$) to the total OA, typically represents less aged OA. f_{44} was ~0.26 for the majority of the sampling period (Q1; 0.25, Q3: 0.27), while f_{43} was 0.036 (Q1: 0.028, Q3: 0.041). The campaign values are compared to values from the spectra for the four PMF factors and those observed in other field campaigns in the remote Mediterranean. The dotted lines (the so-called "Ng triangle"), encapsulate the f_{44} and f_{43} values of atmospheric OA from a vast number of studies (Ng et al., 2010), with the most aged OA in the top left corner and the most fresh in the bottom right. The high f_{44} values and the dominance of the highly oxygenated MO-OOA and LO-OOA factors show that the organic aerosol was extremely aged compared to other measurements.

3.4 Links to meteorology

The contribution of the major submicron chemical species and OA sources is further explained in the following by linking the measured and apportioned concentrations to the local meteorology (i.e., wind speed and wind direction) and to the air mass back trajectories to account for the long-range transport of aerosol as well as more distant sources. The bivariate polar plots of these PM_1 species and f_{44} as a function of wind speed and direction are shown -in Figure 10~~9~~.

Considering that the sampling site on Lampedusa is on the north east tip of the island, it is evident that the SO_4^{2-} and NH_4^+ were likely a result of north-ea~~we~~sterly marine air masses, in

agreement with previous results (e.g., Bove et al., 2016). Sea salt concentrations were highest during high north-westerly wind speeds. Higher concentrations of NO_3^-, HOA and some of the periods with elevated eBC concentrations were observed during low speed south-westerly winds, likely a result of the human settlements and activity on the island of Lampedusa (population of ~6000 located to the south west of the sampling site). Besides, the polar plot for eBC showed a patchier pattern, indicative of more local or point sources and the elevated signals were likely due to air masses passing over ship plumes. Although the mass spectra for the LO-OOA and MO-OOA factors were very similar, their bivariate polar plots indicate -different sources or photochemical processes. The MO-OOA was more prominent during north-easterly winds, indicating the most aged organics were influenced by air masses from the eastern Mediterranean, either from long-ranged transport or~~of~~ from circulation of closer pollution sources, while the LO-OOA was more dominant during northwesterly wind directions and air masses from over the western Mediterranean. Figure 1~~0~~ shows the average contribution of each species during different air mass periods (see Supplementary Table S2 for the mean concentrations and standard deviations).

The highest concentrations of PM_1 were observed during "Eastern Mediterranean" and "Central Europe" air mass periods, when significant lifetime over the lower altitude marine environment and/or higher SO_2 emissions allowed the conversion and condensation of sulphate. These aged aerosols are corroborated by the high number concentrations within the accumulation mode during these periods relative to other periods, measured by the SMPS as well as the size-resolved sulphate composition, as discussed in the next section. In contrast to the "Eastern Mediterranean" and "Central Europe" air masses, sulphate concentrations were relatively low during the two "Mistral" air masses. This behavior has been found also in PM_{10}, with elevated values of sea salt aerosol and low non-sea salt sulphate during Mistral events (Becagli et al., 2017). The organic mass concentration was relatively uniform across the periods of different air mass origins, with the exception of the high Mistral winds which yielded OA concentrations approximately half the rest of the campaign and a higher contribution of MSA-OOA in comparison with other periods. The higher contribution of MO-OOA compared with LO-OOA from eastern air masses, and vice-versa during western air masses, could be indicative of different OA sources prior to oxidation or due to different photochemical aging between the two directions.

3.5 Aerosol size distributions

There are distinctions between the measured PM_1 size distributions during periods of different air mass origins (Figure 1~~2~~1). It should be noted that these size distributions are under ambient

conditions without an inlet drier which could shift the size distribution to larger sizes if water is present. The ambient relative humidity for each air mass back trajectory cluster was: Eastern Mediterranean (53%), Central Europe (61%), Atlantic (74%), Western Mediterranean (70%), Mistral (low) (67%) and Mistral (high) (74%). Although the higher temperature inside the PEGASUS mobile laboratory could lower the relative humidity at the sampling point of the SMPS with respect to the ambient relative humidity, this was not measured or logged during the campaign.

Consistent with the higher concentrations of sulphate and ammonium species, the "Eastern Mediterranean" and "Central Europe" had the most pronounced accumulation modes with respect to those from other clusters due to the presence of accumulation mode sulphate (see Supplementary Figure S6 for the size-resolved chemical composition). In contrast, the "Mistral (high)" air masses had very few particles in the accumulation mode and were mostly dominated by nucleation (> 14 nm observations only) and Aitken mode particles, in terms of number. There was only one period of "Mistral (high)" air masses, spanning 38 hours between 09:00 on 24 June until 23:00 on 25 June.

The most pronounced new particle formation (NPF) events and subsequent growth were observed during the two "Mistral" air masses, particularly between 25 and 27 June. Very high number concentrations in the nucleation mode were also observed in very brief periods during the Atlantic and, to an extent, the "Western Europe" air masses. There was a no trend (R^2 = 0.03) over the whole campaign between ~~the "nucleation mode ratio" (defined here as~~ the ratio of the particle~~s~~ number concentration between 14 ~~and~~ 25 nm and 14 ~~and~~ 600 nm~~)~~ and the fraction of $CH_3SO_2^+$ (a fragment of MSA, measured by the cToF-AMS) to total PM_1 organics (see Supplementary Figure S7. There was a weak positive trend during periods of the Mistral (high) air mass (R^2 = 0.39). No trends were observed between the ratio of sub-25 nm and sub-600 nm particle number concentrations~~nucleation mode ratio~~ and the occurrence of other cToF-AMS fragments such as amines that could be linked with biogenic gas-to-particle conversion. Furthermore, there was a weak negative trend between the ~~nucleation mode ratio~~ratio of sub-25 nm and sub-600 nm particle number concentrations and the calculated f_{44} (R^2 = 0.12). Without instrumentation to measure the concentration of clusters and smaller aerosols (<14 nm) in conjunction with organic vapours over a longer time period, it is difficult to isolate and conclude the origin of these nucleation particles in a general sense and we will limit our analysis to the most pronounced event during the campaign. Figure 1~~3~~2 shows the size distribution over this period as well as SO_2, eBC and $CH_3SO_2^+$, as well as the back trajectory ending at 04:00 UTC on 25 June at Lampedusa. This NPF event occurred during the night and therefore in the absence of photochemistry. There was no discernible increase in eBC or SO_2 during these events

and the 3-day cascade impactor sample from 25 until 28 June was characterized by the lowest concentrations of vanadium and nickel (released from heavy oil combustion events due to ship emissions) of the whole campaign. The air mass backwards trajectory during this event was characteristic of the "Mistral (high)" cluster. These are high altitude air masses descended over the Atlantic Ocean before having undergone a hydraulic jump over the southern France region and then a rapid descent over the western Mediterranean basin at high speed before arriving at the Lampedusa site. It is interesting to note that these air masses were anomalous for the typical June/July period at Lampedusa. Although the detected mass of $CH_3SO_2^+$ is likely due to the condensation of MSA on accumulation mode particles, and considering that the cTof-AMS collection efficiency below ~100 nm is poor, the increasing concentration of $CH_3SO_2^+$ did coincide with the nucleation events during this period, suggesting a possible nucleation and condensation of marine biogenic vapours. Different studies indicate that NPF events may be triggered by atmospheric mixing processes (Kulmala et al., 2004; Hellmuth, 2006; Lauros et al., 2007; Lauros et al., 2011) due to different phenomena like the enhancement of turbulence in elevated layers (Wehner et al., 2010), the break-up of the nocturnal inversion (Stratmann et al., 2003), or the turbulence associated with the nocturnal low-level jet (Siebert et al., 2007). Night-time NPF events have also been observed in the Eastern Mediterranean (Kalivitis et al., 2002).

Furthermore, the intrusion of descending mid-tropospheric air masses in the boundary layer (Pace et al., 2015) has been linked to the occurrence of NPF events and would be consistent with the absence of high concentrations of BC, SO_2, vanadium and nickel which could be expected from ship emissions (Healy et al., 2009; Isakson et al., 2001) in the boundary layer over the Mediterranean. Pace et al. (2006) have shown that clean marine aerosol conditions are rare at Lampedusa and generally associated with north-westerly progressively descending trajectories, in agreement with the findings of this study. The relative absence of pre-existing particles acting as a condensation sink favors NPF events as observed during the field campaign.

3.6 ~~Evidence of aging~~Accumulation of sulphates across the Mediterranean

In order to investigate the aging of aerosols across the north-south trajectory of European continental air masses, we compare the average NR-PM_1 composition measurements at Lampedusa to the concurrent measurements conducted at the Ersa site during summer 2013 (Michoud et al., 2016; Arndt et al., 2017). This is shown in Table 1~~2~~.

On average, the PM_1 non-refractory organic mass concentrations at both sites were similar with ~3 µg m^{-3}. NO_3^- concentrations were relatively small at both sites, but higher at Ersa (0.28 µg m^{-3}) than at Lampedusa (0.09 µg m^{-3}). Sulphate concentrations were a factor of 3.2 times higher at

Lampedusa (4.5 µg m^{-3}) than at Ersa (1.4 µg m^{-3}) while the ammonium concentrations were a factor of 2.7.

To investigate the possible accumulation of ammonium sulphate during the transport of air masses from Europe, the hourly air-mass back trajectories from Lampedusa were filtered so that only those that passed within ±1° latitude and longitude and within ±200 m altitude of the station height of Ersa (550 m) were selected. These thresholds were chosen arbitrarily since there is no clear distinction in horizontal or vertical distance from the site that would necessarily constitute a representative air mass. This resulted in a total of 192 hourly observations at the Ersa site over 32 unique air mass backward trajectory runs (see Figure 1~~3~~).

These trajectories were grouped mainly into the "Central Europe" cluster (n = 12). The median trajectory duration between the Ersa and Lampedusa sites was 53 hours, with a minimum of 33 hours and a maximum of 144 hours (corresponding to the total duration of the HYSPLIT model runs in this case). Those air masses grouped in the "Eastern Mediterranean" cluster had the longest duration time between the sites of 127 hours (while coincident with the Ersa site, these air masses still spent a significant amount of time over the eastern Mediterranean), followed by "Central Europe" (83 hours), "Western Europe" (45 hours) and then the "Mistral (low)" (38 hours). In general, between the two sites, there was a 40% enhancement in the organic mass concentration, but an increase in sulphate and ammonium by a factor of 6 and 4, respectively (Table 1~~2~~).

The accumulation of $(NH_4)_2SO_4$ between Ersa and Lampedusa appeared to be dependent on the travel time of the air mass, however different relationships were observed during different air mass clusters. The total sulphate concentration at Lampedusa minus the total sulphate concentration at Ersa for the same air mass and accounting for the travel time as a function of the travel time is shown in Figure 1~~5~~4.

There was a good positive correlation between the difference in sulphate concentrations between the two sites and the travel time for the "Central Europe" and "Eastern Mediterranean" air masses, while weak positive correlations were observed for the "Western Europe" and "Mistral (low)" clusters. It should be pointed out that the travel time was more than 110 hours for the "Eastern Mediterranean" air masses, while it was only between 33 and 58 hours for the other three air mass clusters. It is expected that the accumulation of sulphate would increase as the total travel time increases due to the opportunity for SO_2 conversion or from the addition of sulphate from separate air masses which are not accounted for in the HYSPLIT model. Although this relationship is somewhat demonstrated here, there are other factors that would influence the SO_4^{2-} accumulation. The sulphate concentrations presented

here are measured by an ACSM and cToF-AMS at the Ersa and Lampedusa sites, respectively. Both of these instruments have a 100% inlet efficiency between ~100 nm and 800 nm. The conversion of SO_2 to SO_4^{2-} via nucleation and condensation is dependent on the pre-existing aerosol size distribution and condensation sink. Therefore, the use of PM_1 composition can be misleading if the sulphate is condensing on coarse particles. This is demonstrated in Supplementary Figure S2 that shows the size-resolved mass distribution of sulphur and sodium collected every 3 days on multi-stage cascade impactor filters; the relative contribution of sulphur in the PM_1 is higher than that of PM_{10} in the absence of sodium (a tracer for sea salt). Furthermore, the concentrations of SO_4^{2-} measured by the PILS in the PM_{10} fraction and cToF-AMS in the PM_1 are approximately equal with low sea salt concentrations ($Na+ < 2\ \mu gm^{-3}$), but are nearly a factor of two higher with the PILS for higher sea salt concentrations (Supplementary Figure S3). Furthermore, the emission of SO_2, typically from ships in the Mediterranean, is not necessarily constant over time and is likely not uniformly spread over the basin and within the vertical column (e.g., Becagli et al. (2017)). This could possibly explain the discrepancy between the "accumulation~~growth~~ rate" of sulphate between the Eastern Mediterranean and Central European air mass origins. Moreover~~Furthermore~~, the sample size for this analysis is relatively small and potentially not representative of the general accumulation of SO_4^{2-} but nonetheless they highlight the magnitude of ~~growth~~accumulation under different air mass trajectories.

4. Concluding remarks

The measurements carried out at Lampedusa during the ChArMEx/ADRIMED SOP-1a field campaign has provided a unique insight into the surface layer aerosols in the remote Central Mediterranean. Air masses were influenced by transport from the eastern Mediterranean, central Europe, the western Europe, the Atlantic Ocean as well as western Europe. Air mass clustering has been performed to explain observed differences in the aerosol composition and size at Lampedusa.

Hourly PM_1 mass ranged from 1.9 to 33.4 $\mu g\ m^{-3}$, with an average of 10.2 $\mu g\ m^{-3}$. It was composed on average of 41% ± 9% sulphate, 31% ± 8% organics, 17% ± 3% ammonium, 6% ±4% black carbon, 1% ± 0.4% nitrate and 3% ± 2% sea salt. OA was highly oxidized (f_{44} ~0.26), and was apportioned to more oxidised oxygenated OA factor (MO-OOA, 53%), less oxidised OOA factor (LO-OOA, 28%), methanesulfonic acid OOA (MSA-OOA, 12%) and to hydrogen-like OA (HOA, 8%). The highest PM_1 mass loadings were observed for air masses from the Eastern Mediterranean and central Europe, mostly due to the accumulation of ammonium and

sulphate. Ancillary data from a remote site at the northern point of Cape Corsica in the Western Mediterranean showed increases of SO_4^{2-} concentrations between 2 and 12 µg m^{-3} when both sites (Corsica and Lampedusa) were connected. Apart from the dominance of ammonium sulphate on the PM_1 composition, the mass concentration and sources of OA have shown to be comparable to previous observations at European coastal and remote sites in the Mediterranean. The most pristine air masses, in terms of PM_1, were observed during periods with north-westerly winds which originated from the western Mediterranean or at high altitudes over the western European continent. Several nucleation and growth events, as well as large sea salt concentrations were observed during these pristine periods. The largest concentrations of PM_1 were observed from air masses from central Europe and those that had circulated over the eastern Mediterranean. In contrast to previous measurements of column-integrated aerosol optical properties (Pace et al., 2006; Meloni et al., 2006), we did not observe the presence of dust or biomass burning in the PM_1 range at the surface.

Our results also indicate a clear dichotomy of PM_1 aerosol composition from different source regions. Air masses from central Europe were characterised by a higher organic fraction than those from the eastern Mediterranean, which were enriched in sulphates. This difference could have potential implications on the optical properties and particularly the cloud condensation nuclei capabilities of those air masses. The relative occurrence of easterly air masses is not evident in the climatological wind roses, nor in a previous study by Pace et al. (2006) that took a climatological approach of the air mass back trajectories arriving at Lampedusa from 2001 - 2003. Nonetheless, a re-evaluation of the relative importance and occurrence of different air masses and aerosol properties should be undertaken.

Data availability. Open-access to the data used for this publication is provided to registered users following the data and publication policy of the ChArMEx program (http://mistrals.sedoo.fr/ChArMEx/ Data-Policy/ChArMEx_DataPolicy.pdf). Additional code used in the analysis of data can be obtained upon request from the corresponding or first author. Weekly GDAS1-analysis (Global Data Assimilation System; 1° resolution) trajectory files were downloaded from the Air Resources Laboratory (ARL) of the National Oceanic and Atmospheric Administration (NOAA) archive (ftp://arlftp.arlhq.noaa.gov/archives/gdas1/). 144-hour air-mass backwards trajectories were calculated using the R-package, SplitR (https://github.com/rich-iannone/SplitR). Cluster analyses were performed on these calculated trajectories, using the R-package, OpenAir (Carslaw and Ropkins, 2012); https://github.com/cran/openair). Spectra used for comparison of PMF OA factors from those observed in other studies can be found at http://cires.colorado.edu/jimenez-group/AMSsd/

Author contributions. PF, BD, KD, JFD, AGdS designed the experiment in Lampedusa, JS designed the experiment in Ersa, with contributions of co-workers. BD, AM, MCB, FC, GP, KD, CDB, JFD, MM, DM, JS, PZ, AGdS and PF performed the experiments. MDM, BD, AM, GP, KD, JS and PF analysed data and all authors contributed to data interpretation. MDM, BD, GP, KD and PF wrote the manuscript with contributions and/or comments from all co-authors.

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Figure 1 The Mediterranean basin. The two sites considered in this study, Lampedusa and Ersa, are indicated with white dots. Image is courtesy of Google Earth.

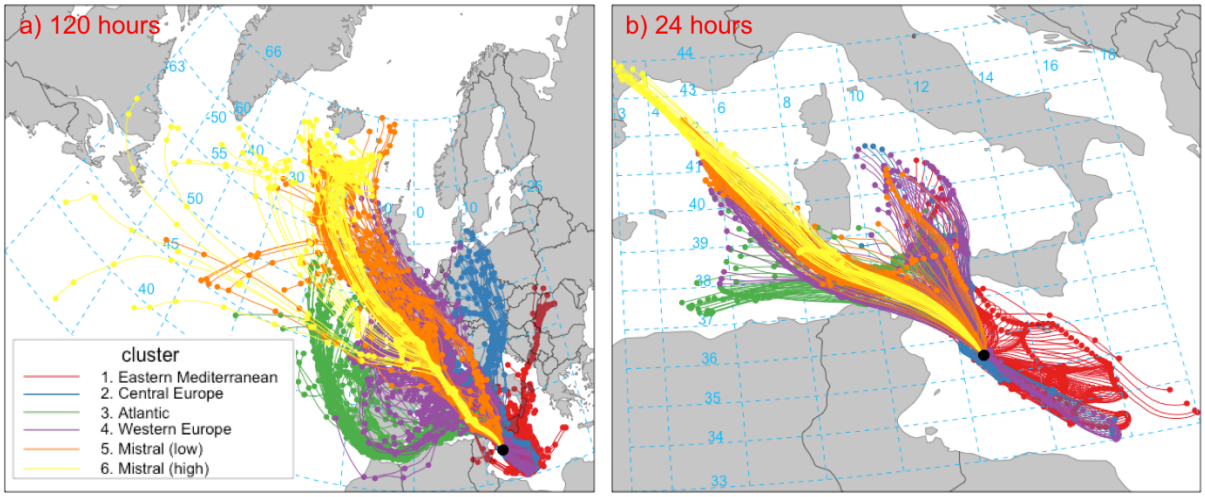


Figure 2 a) Hourly 144-hour (6 days) backwards trajectories from Lampedusa from 10 June 2013 until 5 July 2013, cut off at 120 hours (5 days). Colours represent the assigned cluster. B) The same as a) but cut off at 24-hour.

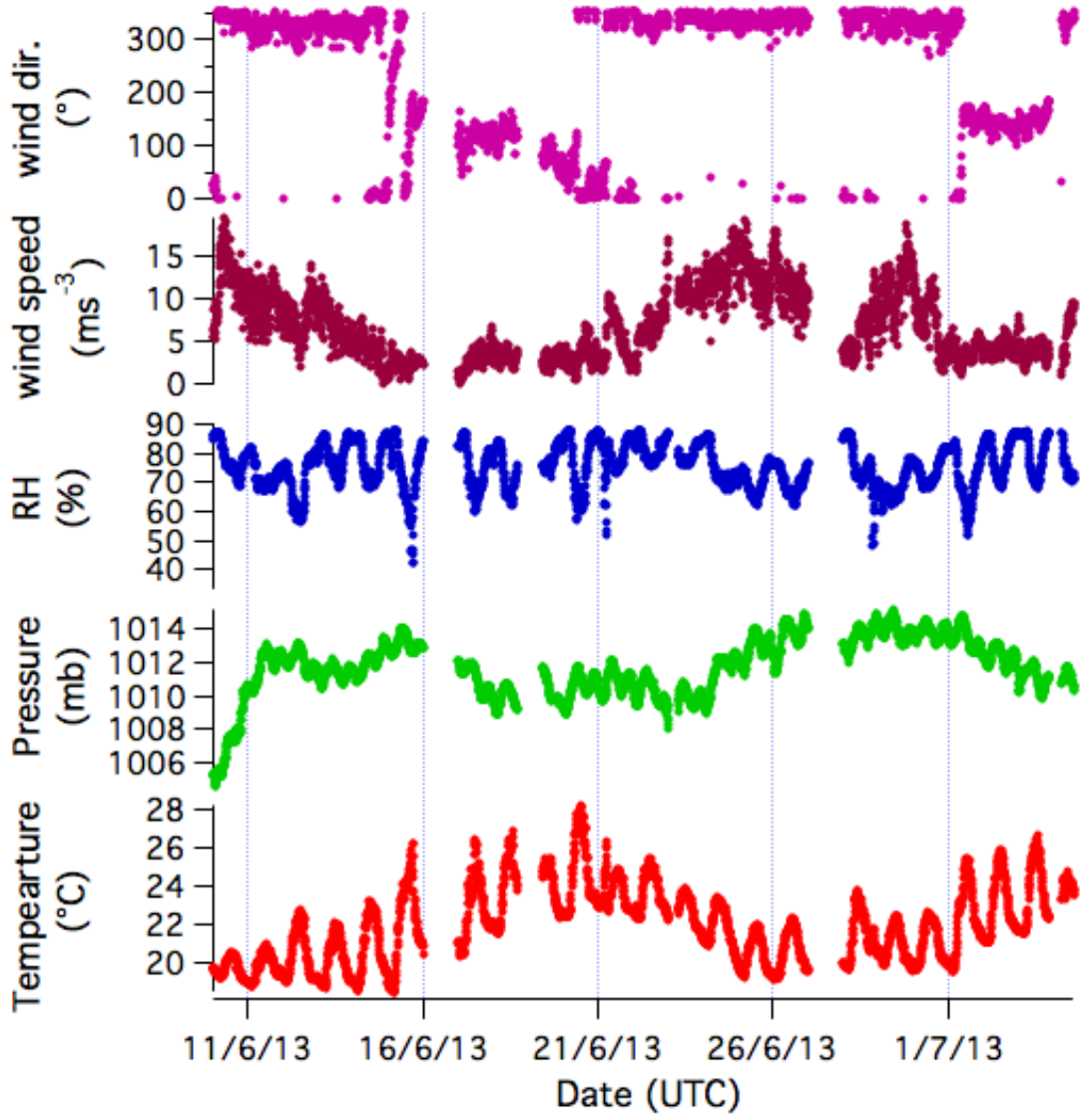


Figure 3 Meteorological conditions (wind direction and speed, relative humidity, pressure and temperature) measured at the Lampedusa site during SOP-1a.

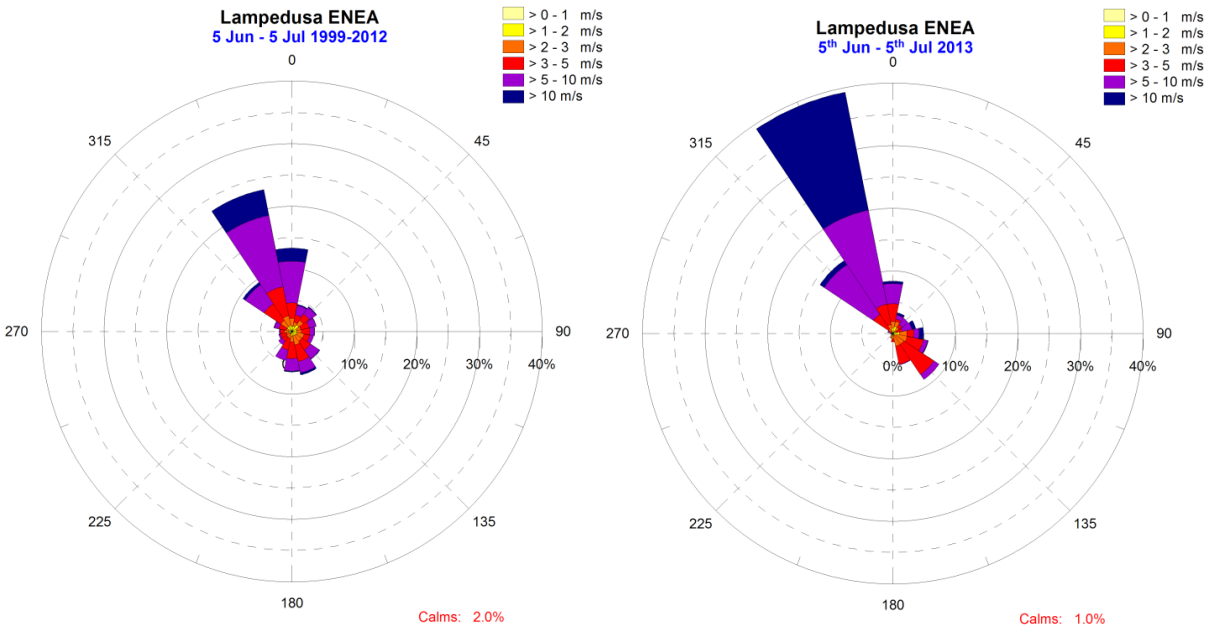


Figure 4 Wind speed and direction at Lampedusa during the period from 5 June until 5 July during the years from 1999 - 2012 (left) and during this campaign (right).

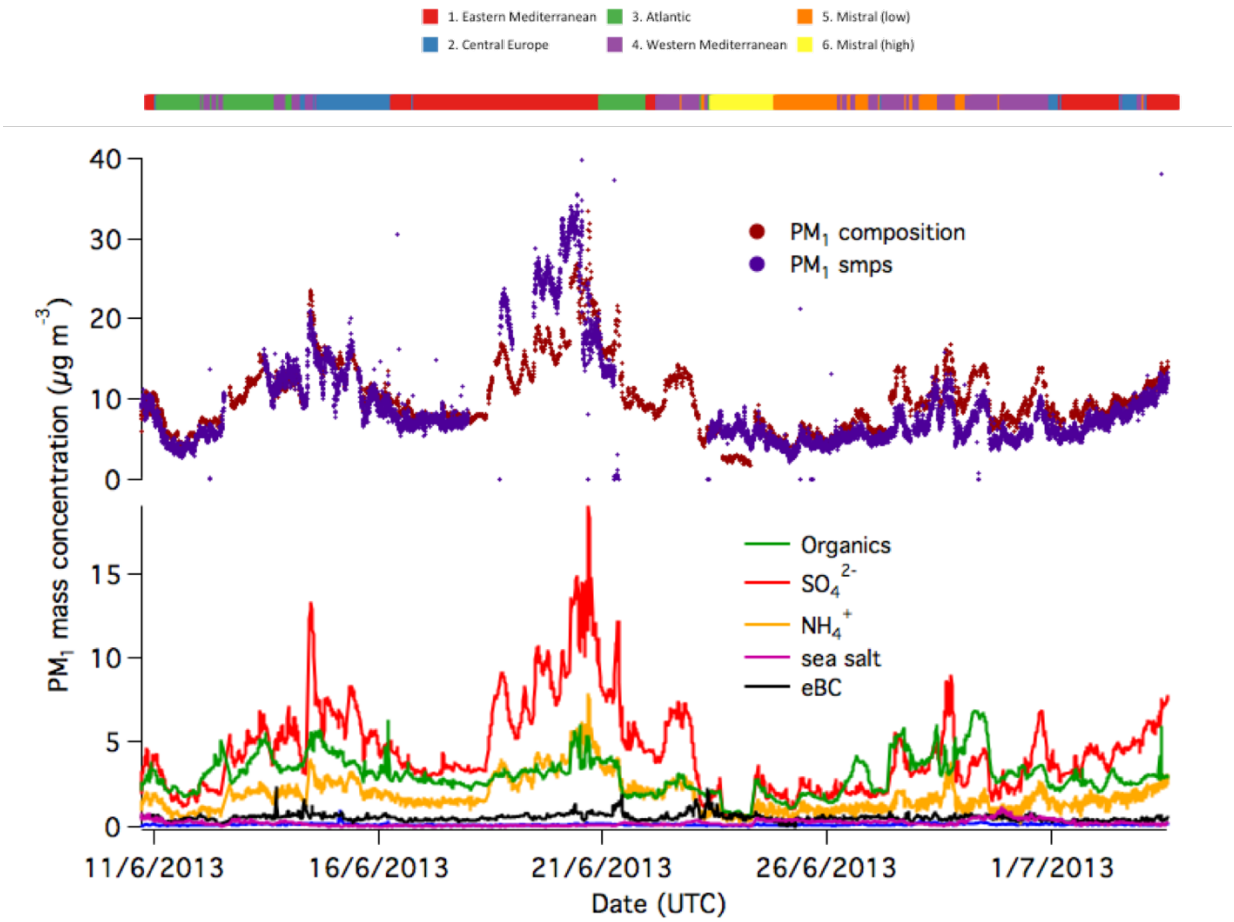
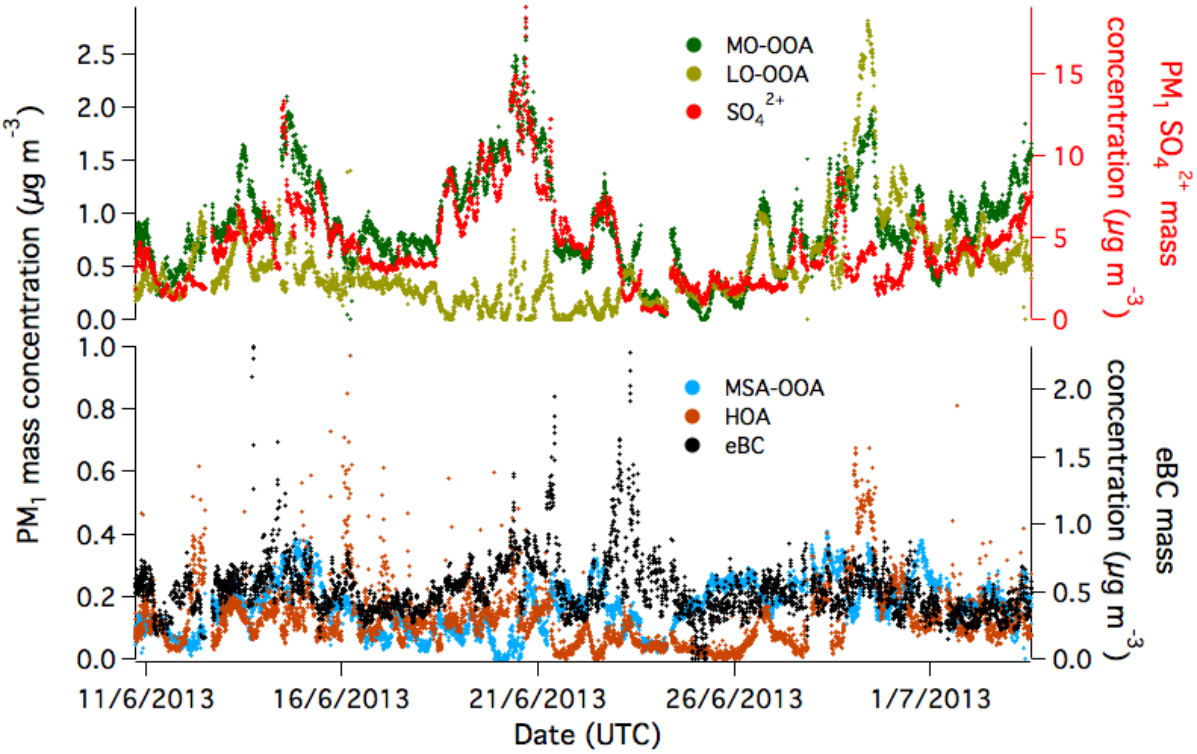


Figure 5 The time series of PM_1 mass concentration, coloured by the relative contribution from each species. The top bar is coloured according to the air mass origin.



989
990 *Figure 6 The time series of the PM_1 "more oxidised" OOA (MO-OOA), "less oxidised" (LO-OOA) and sulphate (top*
991 *panel) and methanesulfonic acid-related OOA (MSA-OOA), hydrocarbon-like OA (HOA) and eBC (bottom panel).*

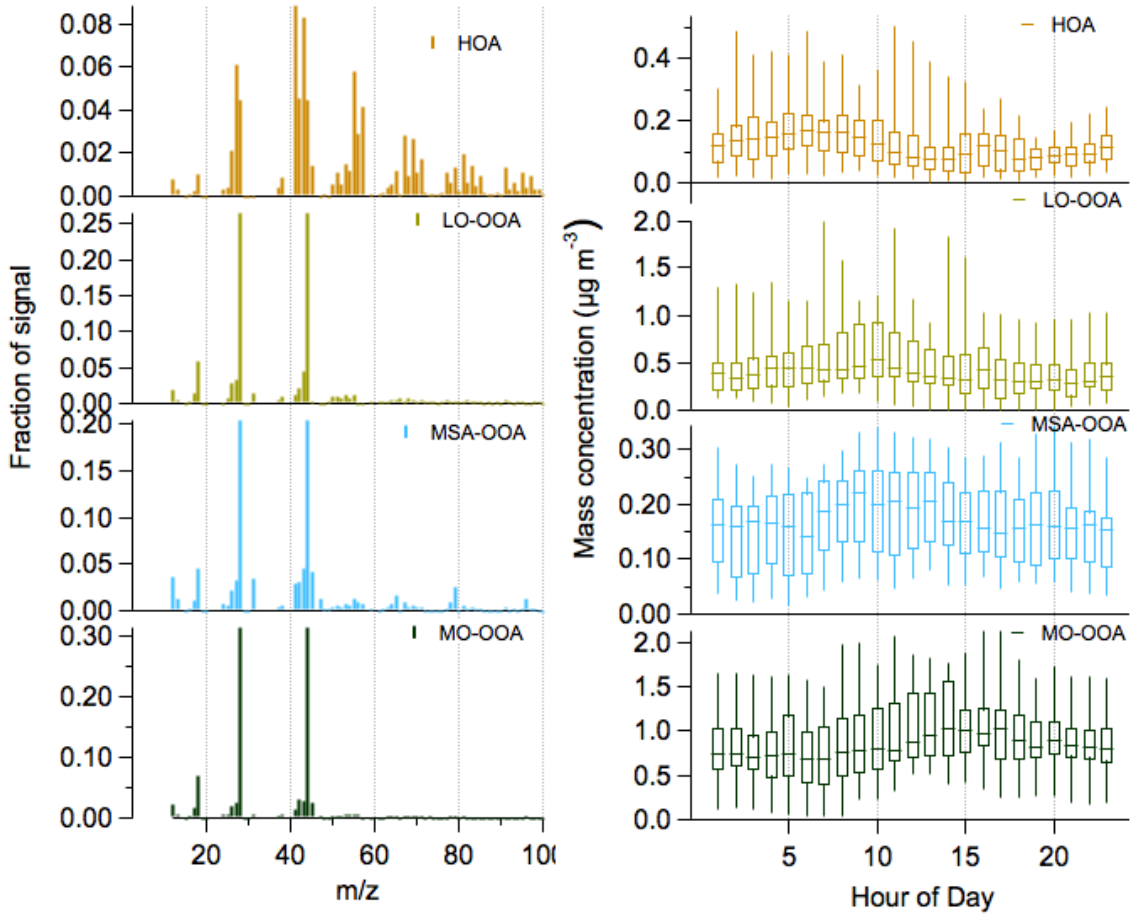
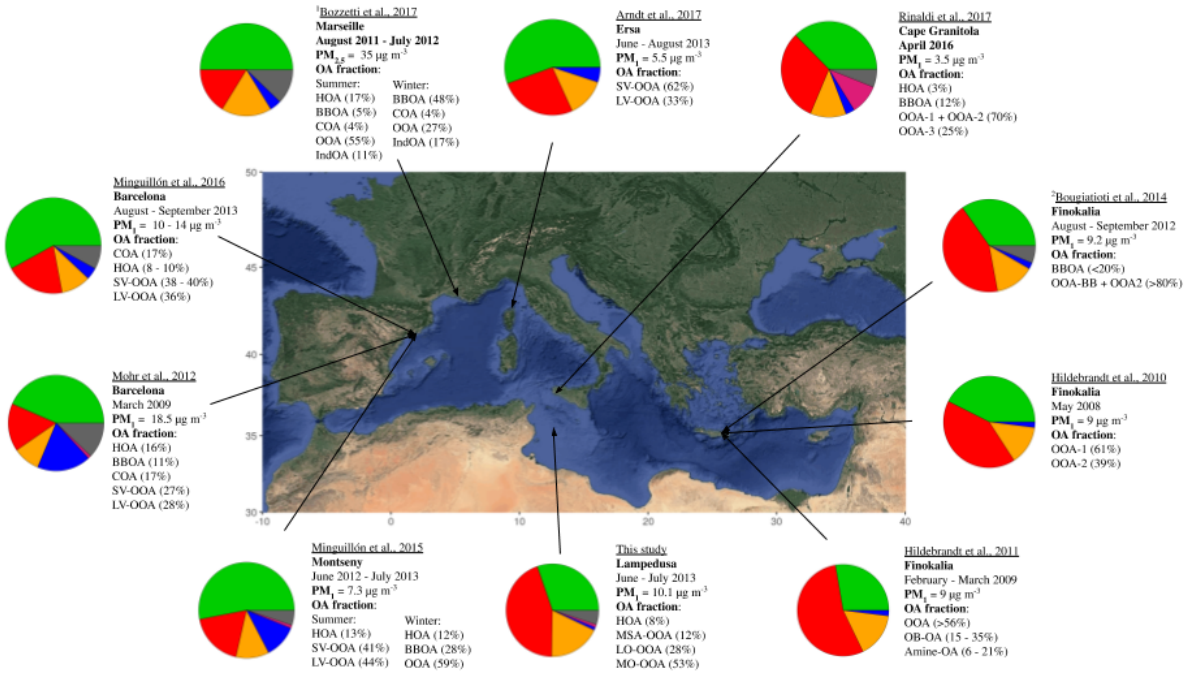


Figure 7 The mass spectra for the 4 PMF factors (HOA: hydrocarbon-like organic aerosol, LO-OOA: less oxidised OOA, MO-OOA: more oxidised OOA, MSA-OOA: methanesulfonic acid-related OOA) retrieved from the PMF analysis of unit-mass resolution data.

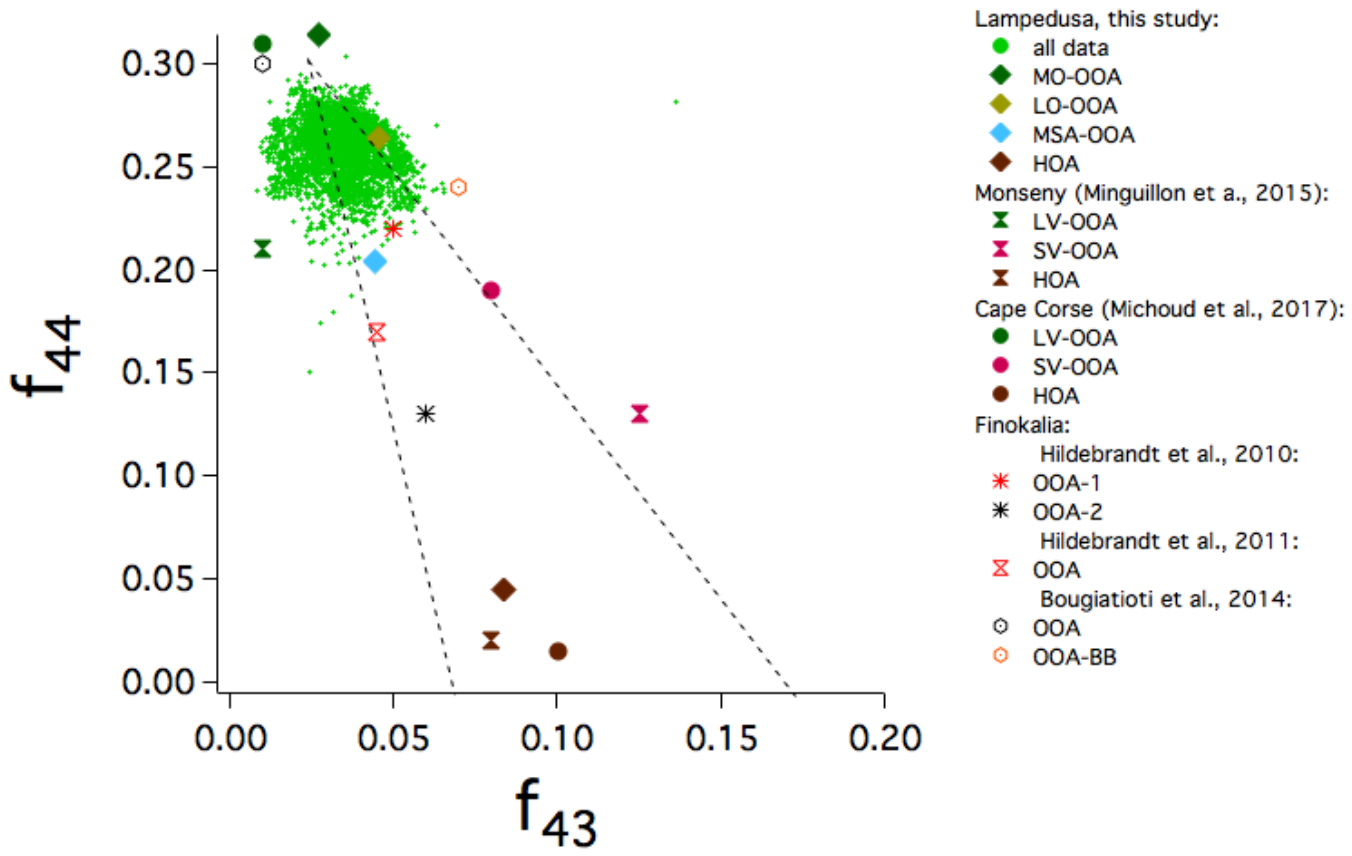


997 ~~*Table 1*~~ *Figure 8 A summary of studies that have investigated NR-PM$_1$ composition (including PMF of OA)* ~~*on islands*~~
998 *around*~~*within*~~ *the Mediterranean basin* ~~*and at coastal sites surrounding the basin*~~*. Only studies that have investigated*
999 *PMF-based OA source apportionment are reported. Pie charts display the average concentration during each study*
1000 *where green corresponds to organics, red to sulphates, orange to ammonium, blue to nitrate, pink to either chlorides*
1001 *or sea salt and black to elemental or black carbon. The OA fraction acronyms correspond to the following:*
1002 *HOA: Hydrocarbon-like Organic Aerosol, SV-OOA: Semi-volatile oxygenated Organic Aerosol, LV-OOA: Low-*
1003 *volatility oxygenated Organic Aerosol, BBOA: Biomass burning Organic Aerosol, COA: Cooking Organic Aerosol,*
1004 *OOA: Oxygenated Organic Aerosol, F4: "Factor -4" (unidentified PMF factor), IndOA: Industry-related Organic*
1005 *Aerosol, OB-OA: "Olive-branch Organic Aerosol. See Supplementary Tables S1 and S2 for further details about the*
1006 *sampling locations, instruments used and pie chart values.* ~~*PMF factors in bold indicate secondary organic aerosol.*~~
1007 ~~*After the results of this study, observations are ordered according to longitude (west to east).*~~ *[1]This study collected on*
1008 *PM2.5 filters and nebulised into an HR-ToF-AMS. [2]Excludes fire-periods.*

~~AUTHORS (YEAR)~~	~~LOCATION~~	~~PERIOD~~	~~INSTRUMENT~~	~~PM$_1$ MASS AND COMPOSITION~~	~~PMF FACTORS~~
~~**THIS STUDY**~~	~~Lampedusa (35°31'5"N, 12°37'51"E, 45 m a.s.l.)~~	~~10 June - 5 July 2013 (summer)~~	~~cToF-AMS~~	~~10.1 µg m^{-3} (OA: 30%, SO_4^{2-}: 44%, NH_4^+: 18%, NO_3^-: 1%, seasalt: 1%, eBC: 5%)~~	~~HOA (8%)~~ ~~**MSA-OOA (12%)**~~ ~~**LO-OOA (28%)**~~ ~~**MO-OOA (53%)**~~
~~**(MINGUILLÓN ET AL., 2015)**~~	~~Montseny (41°46'46"N, 02°21'19"E, 720 m a.s.l.)~~	~~June 2012 - July 2013~~	~~ACSM~~	~~Summer: 10.8 µg m^{-3} (OA: 60%, SO_4^{2-}: 20%, NH_4^+: %, NO_3^-: %, Winter: 6.3 µg m^{-3} (OA:, SO_4^{2-}: 8%, NH_4^{+}: %, NO_3^-: %,~~	~~Summer: HOA (13%) SV-OOA (41%) LV-OOA (44%) Winter: HOA (12%)~~

					BBOA (28%) **OOA (59%)**
(ARNDT ET AL., 2017)	Cape Corse (42°58'8.4"N, 9°22'48"E, 544 m a.s.l.)	11 June - 6 August 2013 (Summer)	Q-ACSM	5.5 μg m^{-3} (OA: 55%, SO_4^{2-}: 26, NH_4^+: 13%, NO_3^-: 5%)	**SV-OOA (62%)** **LV-OOA (33%)**
(MICHOUD ET AL., 2017)	Cape Corse (42°58'8.4"N, 9°22'48"E, 544 m a.s.l.)	July 15 - August 5 2013 (Summer)	Q-ACSM	6.8 μg m^{-3} (OA: 55%, SO_4^{2-}: 27%, NH_4^+: 13%, NO_3^-: 5%)	HOA (4%) **SV-OOA (44%)** **LV-OOA(53%)**
(RINALDI ET AL., 2017)	Cape Granitola (37°34'31.1"N, 12°39'34.2"E, 5 m a.s.l.)	April 2016 (Spring)	HR-ToF-AMS	3.5 μg m^{-3} (OA: 37%, SO_4^{2-}: 31%, NH_4^+: 12%, NO_3^-: 3%, seasalt: 10%, BC: 6%)	HOA (3%) BBOA (2%) **OOA-1 + OOA-2 (70%)** **OOA-3 (25%)**
HILDEBREANDT ET AL., 2010	Finokalia (35°20'N, 25°40'E, 150 m a.s.l.)	May 2008 (Spring)	Q-AMS	9 μg m^{-3} (OA: 28%, SO_4^{2-}: 55%, NH_4^+: 16%, NO_3^-: 2%)	OOA-1 (61%) OOA-2 (39%)
HILDEBRAND ET AL., 2011	Finokalia (35°20'N, 25°40'E, 150 m a.s.l.)	25 February - 26 March 2009 (late Winter)	Q-AMS	3.3 μg m^{-3} (OA: 43%, SO_4^{2-}: 42%, NH_4^+: 14%, NO_3^-: 2%)	**OOA (>56%)** OB-OA (15 – 35%) Amine-OA (6 – 21%)
BOUGIATIOTI ET AL., 2014	Finokalia (35°20'N, 25°40'E, 150 m a.s.l.)	August – September 2012	Q-ACSM	Fire events: OA: 46.5% , SO_4^{2-}: 29.2%, NH_4^+: 11.7%, NO_3^-: 3.2%, BC: 9.5% Nonfire periods: OA: 34.7% , SO_4^{2-}: 43%, NH_4^+: 13.7%, NO_3^-: 2.2%, BC: 6.1%	BBOA (<20%) **OOA1-BB + OOA2 (>80%)**

1009



1010

1011 *Figure 98 f_{43} (the ratio of m/z 43 to the total OA)* against f_{44} (ratio of m/z 44 to the total OA). The triangle is considered
1012 to encapsulate typical atmospheric values of OA according to Ng et al. (2010). The values for the various PMF factors
1013 from this study and other studies conducted in the remote Mediterranean are also displayed.

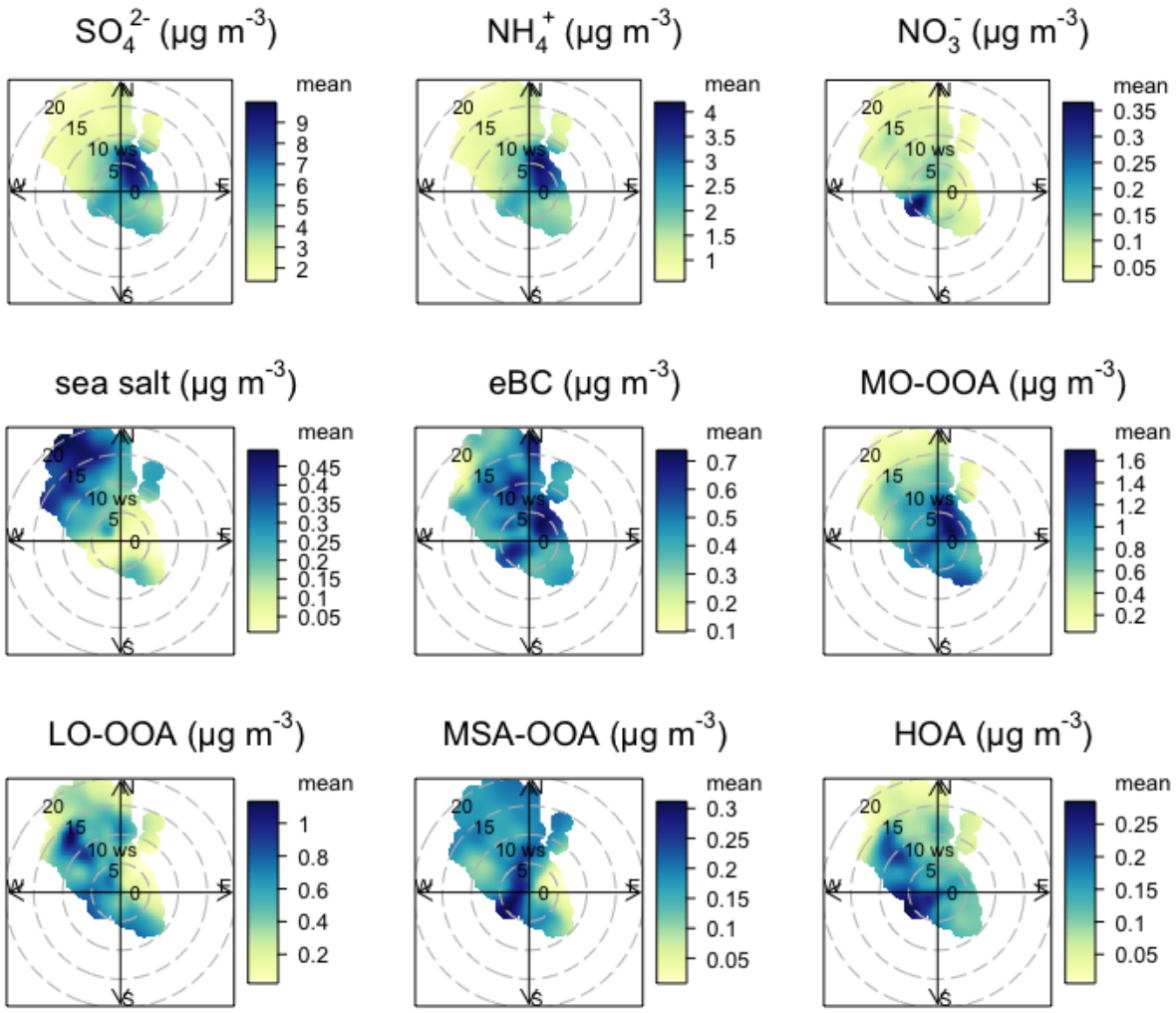


Figure 109 Bi-variate polar plots of mean concentrations of PM_1 species and f_{44} at Lampedusa. The angle represents the arrival wind direction, the radius represents the wind speed and the colours represent the mean concentrations for the respective wind directions and winds.

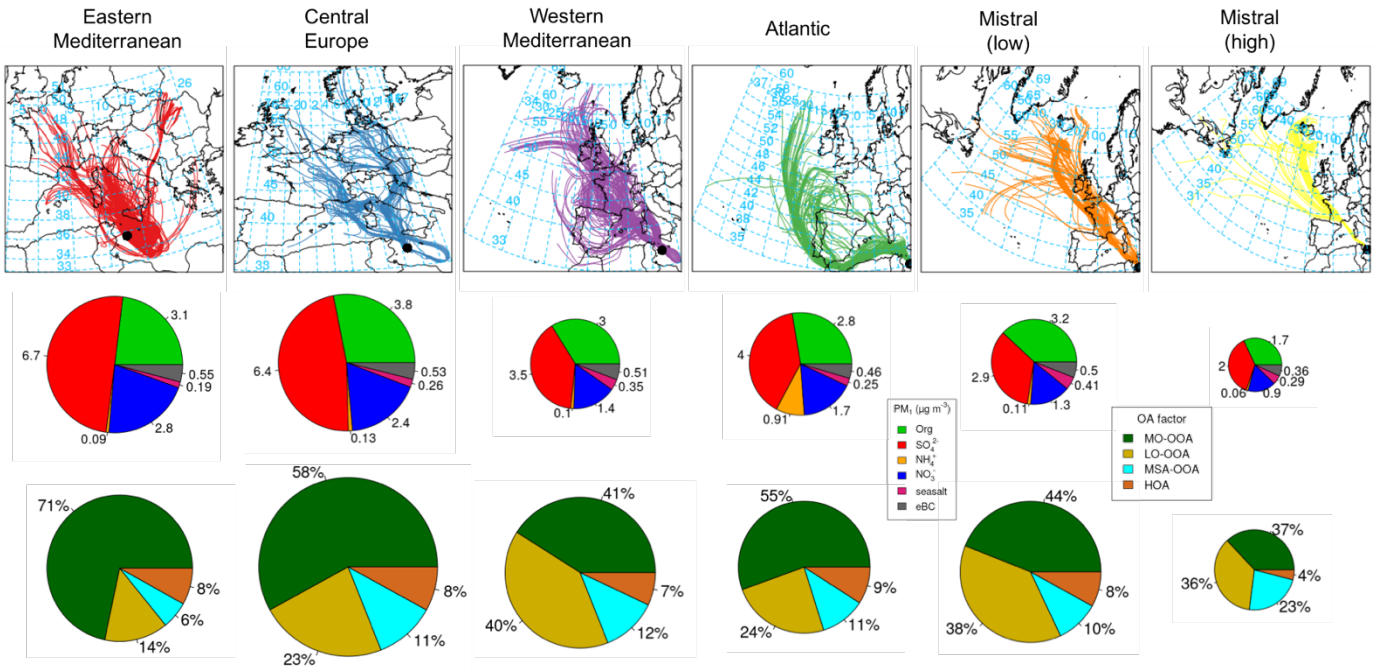


Figure 1~~0~~ top) 144 hour air mass back trajectories, assigned to each cluster; middle) the PM_1 composition for each air mass cluster and bottom) the contribution of OA factors for each air mass cluster. The diameter for the PM_1 composition pie graphs are proportional to the total PM_1 concentration for each air mass cluster period and the radius for the OA factor pie graphs is proportional to the total PM_1 organic concentration for each air mass cluster period.

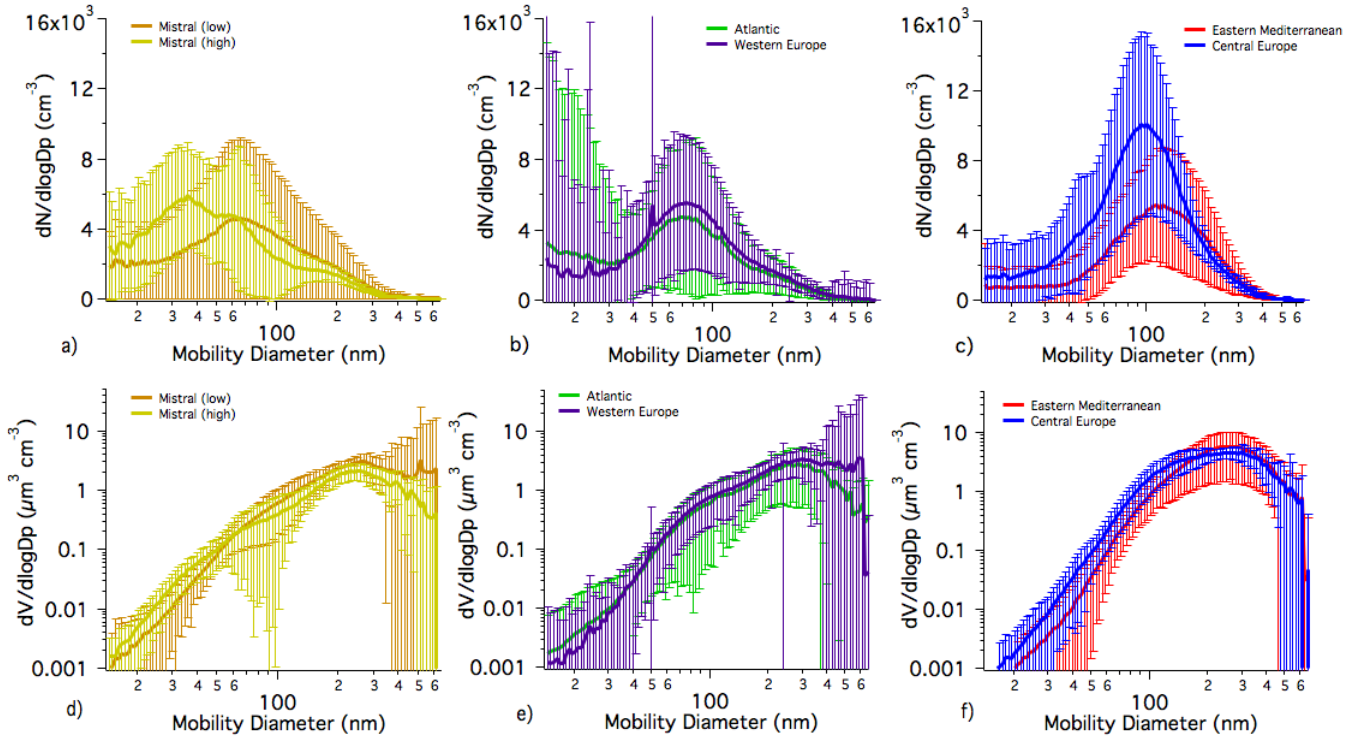


Figure 1~~1~~2 The number size distribution of PM_1 aerosol, coloured by averages for different air mass origin: a) Mistral (high) and Mistral (low); b) Atlantic and Western Europe; c) Eastern Mediterranean and Central Europe and the

volume size distribution of PM_1 aerosol, coloured by averages for different air mass origin: d) Mistral (high) and Mistral (low); e) Atlantic and Western Europe; f) Eastern Mediterranean and Central Europe.

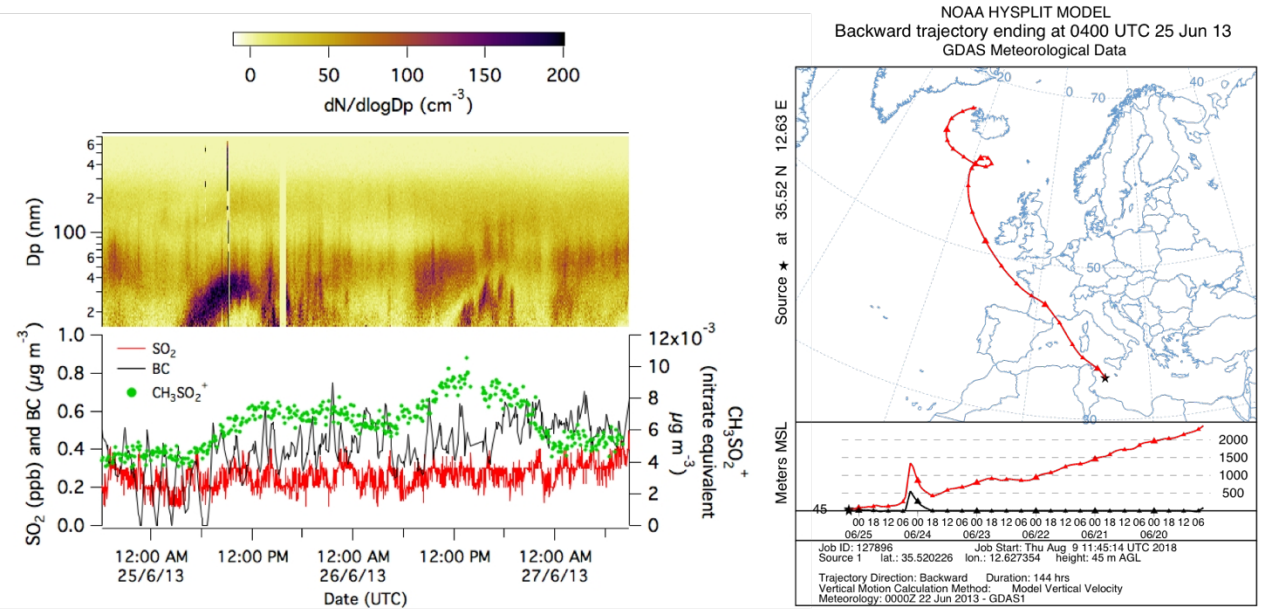


Figure 1~~3~~2 (left) The number size distribution during a new particle formation event on 25 June 2013 and the corresponding concentrations of SO_2, eBC and MSA fragment, $CH_3SO_2^+$, and (right) the HYSPLIT air mass backwards trajectory during the event.

Table 1~~2~~ Campaign average PM_1 concentration for the major aerosol species measured at the Ersa and Lampedusa sites during the SOP-1a period and for periods of coincident air mass backwards trajectories between Ersa and Lampedusa

SITE	SO_4^{2-}	ORGANIC	NH_4^+	NO_3^-
ERSA	1.4 ± 2.6	3.0 ± 1.1	0.7 ± 1	0.3 ± 0.1
LAMPEDUSA	4.5 ± 0.9	3.0 ± 1.6	1.9 ± 0.5	0.1 ± 0.2
ERSA (COINCIDENT WITH LAMPEDUSA)	0.9 ± 0.5	2.7 ± 1.1	0.5 ± 0.3	0.4 ± 0.3
LAMPEDUSA (COINCIDENT WITH ERSA)	5.3 ± 2.0	3.8 ± 0.8	2.0 ± 0.6	0.1 ± 0.1

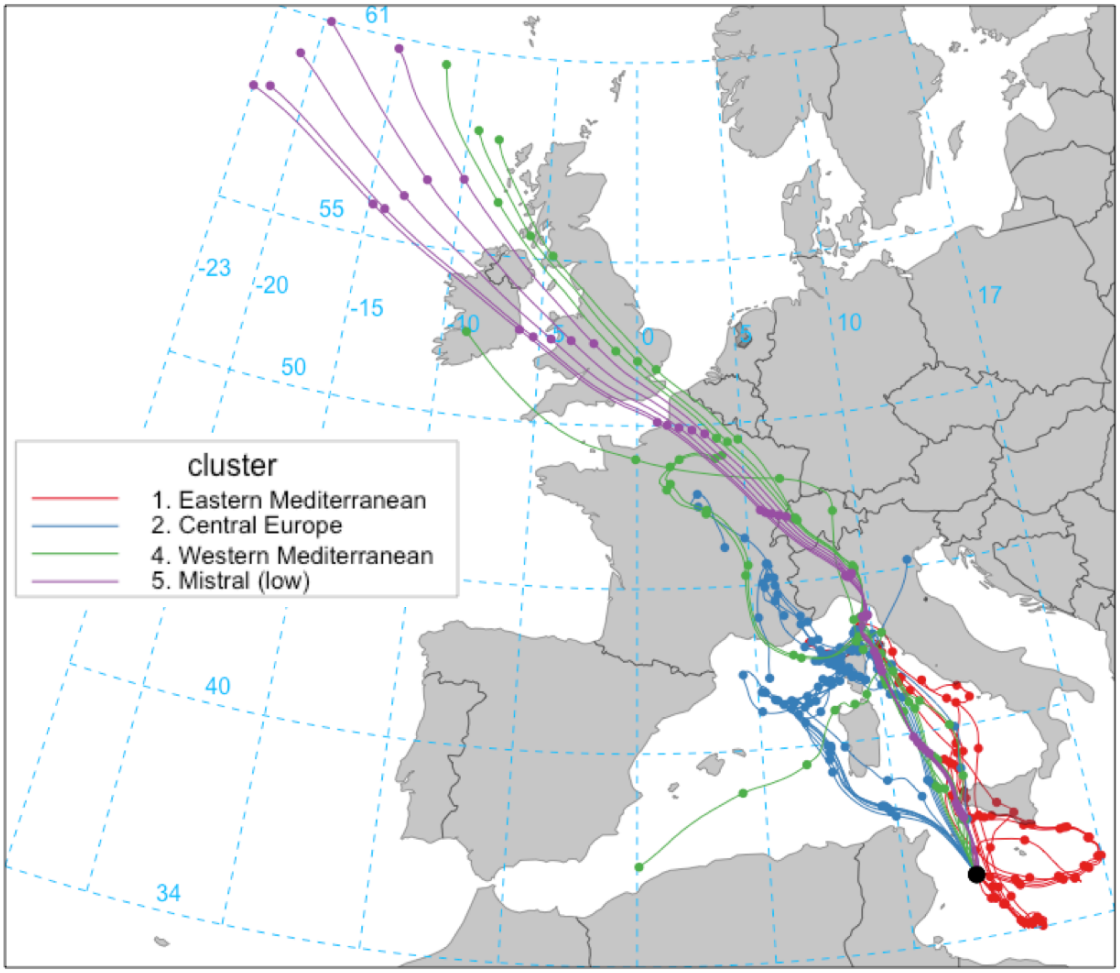


Figure 1~~4~~3 Hourly 120-hour (5 days) backwards trajectories from Lampedusa that passed within ±1° in latitude and longitude and ±200 m in altitude of the Ersa station. The colours represent the assigned cluster (performed on 144 hour trajectories).

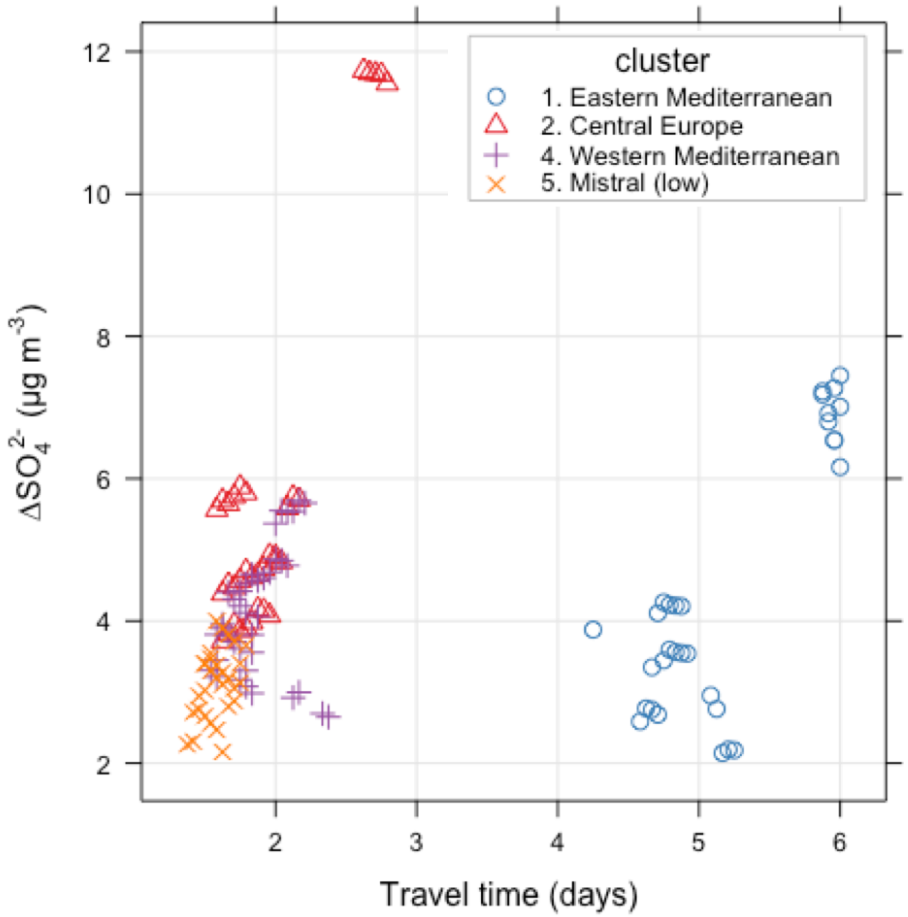


Figure 15 The difference in the PM_1 SO_4^{2-} mass concentration at Lampedusa and Ersa as a function of the travel time of the air masses from Ersa to Lampedusa. Colours represent the air mass origin cluster.