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Sources and mixing state of summertime background aerosol in the northwestern Mediterranean basin

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Abstract. An aerosol time-of-flight mass spectrometer (ATOFMS) was employed to provide real-time single particle mixing state and thereby source information for aerosols impacting the western Mediterranean basin during the ChArMEx-ADRIMED and SAF-MED campaigns in summer 2013. The ATOFMS measurements were made at a ground-based remote site on the northern tip

5 of Corsica Island. 27 distinct ATOFMS particle classes were identified and subsequently grouped into 8 general categories: EC-rich (elemental carbon), K-rich, Na-rich, Amines, OC-rich (organic carbon), V-rich, Fe-rich and Ca-rich. Mass concentrations were reconstructed for the ATOFMS particle classes and found to be in good agreement with other co-located quantitative measurements (PM_1, black carbon (BC), organic carbon, sulfate mass and ammonium mass). Total ATOFMS re-

10 constructed mass ($PM_{2.5}$) accounted for 70-90% of measured PM_{10} mass and was comprised of regionally transported fossil fuel (EC-rich) and biomass burning (K-rich) particles. The accumulation of these transported particles was favoured by repeated and extended periods of air mass stagnation over the western Mediterranean during the sampling campaigns. The single particle mass spectra proved to be valuable source markers, allowing the identification of fossil fuel and biomass burn-

15 ing combustion sources, and therefore highly complementary to quantitative measurements made

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by particle-into-liquid sampler ion chromatography (PILS-IC) and an aerosol chemical speciation monitor (ACSM), which have demonstrated that PM_1 and PM_{10} were comprised predominantly of sulfate, ammonium and OC. Good temporal agreement was observed between ATOFMS EC-rich and K-rich particle mass concentrations and combined mass concentrations of BC, sulfate, ammonium

20 and low volatility oxygenated organic aerosol (LV-OOA). This combined information suggests that combustion of fossil fuels and biomass produced primary EC- and OC-containing particles, which then accumulated ammonium, sulfate and alkylamines during regional transport. Three other sources were also identified: local biomass burning, marine and shipping. Local combustion particles (emitted in Corsica) contributed little to $PM_{2.5}$ particle number and mass concentrations but were easily

25 distinguished from regional combustion particles. Marine emissions comprised fresh and aged sea salt; the former detected mostly during one 5-day event during which it accounted for 50-80% of sea salt aerosol mass, while the latter detected throughout the sampling period. Dust was not efficiently detected by the ATOFMS, and support measurements showed that it was mainly in the $PM_{2.5-10}$ fraction. Shipping particles, identified using markers for heavy fuel oil combustion, were associated

30 with regional emissions, and represented only a small fraction of $PM_{2.5}$ particle number and mass concentration at the site.

1 Introduction

The atmosphere in the Mediterranean basin is strongly influenced by numerous and varied aerosol sources. Anthropogenic emissions from heavily industrialised parts of Southern Europe (e.g. Genoa

35 and Milan), the megacities of Istanbul and Cairo, a large range of smaller population centres disseminated all over the basin, as well as intense shipping activities render the Mediterranean basin one of the most impacted zones on the planet to air pollution (de la Paz et al., 2013; Karanasiou et al., 2014). Natural sources such as Saharan dust, sea-spray and frequent forest fires exert further considerable stress on regional air quality (Kanakidou et al., 2011). Transport of air pollution

40 from outside the Mediterranean region is one cause for increased concentrations of primary and secondary pollutants (Lelieveld et al., 2002). In the summertime upper troposphere, Asian monsoon outflow transports pollution across northern Africa and the Mediterranean (Scheeren et al., 2003). In the middle troposphere, westerly winds prevail, transporting polluted air masses from western Europe and North America (Marmer and Langmann, 2005). In the surface layer, land emissions from

45 south and central Europe are transported to the eastern Mediterranean by northerly winds (Sciare et al., 2003). The geography and regional meteorological processes in the western Mediterranean also favour the accumulation and ageing of polluted air masses (Gangoiti, 2001; Lelieveld et al., 2002; Millán et al., 2000, 2002; Millán and Salvador, 1997; Rodríguez et al., 2002; Salvador et al., 1999; Soriano et al., 2001). Arid conditions, combined with high solar radiation and photochemical

50 conversion rates significantly enhance air pollution mostly in the form of $PM_{2.5}$ and O_3. The high-

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est particulate matter (PM) concentrations are generally found in southern and eastern Europe and attributed to diverse emission sources such as industry, traffic, resuspended dust, shipping emissions and African dust intrusions (Karanasiou et al., 2007, 2009, 2011, 2014; Lelieveld et al., 2002; Querol et al., 2004; Rodríguez et al., 2007; Salameh et al., 2015). A number of studies have reported that

55 in rural environments in the Mediterranean, airborne PM and ammonium sulfate concentrations undergo a seasonal cycle characterised by a summer maximum (Bergametti et al., 1989; Kubilay and Saydam, 1995; Querol et al., 1998a, b; Rodríguez et al., 2002). This seasonal cycle has not been reported at rural sites in central and northern Europe, where high PM events are mostly recorded in winter during stagnant episodes caused by cold temperature inversions and low wind speed (Beek-

60 mann et al., 2015; Favez et al., 2007; Monn et al., 1995; Röösli et al., 2001; Turnbull and Harrison, 2000). Long term measurements at sites in the western and eastern Mediterranean basins by Querol et al. (2009) showed that mineral matter is the major component of PM_{10} (22-38%) in both areas, with relatively high proportions in $PM_{2.5}$ (8-14%), followed by sulfate, organic matter (OM), nitrate and ammonium. Most studies to date have documented Mediterranean aerosol properties in

65 the eastern basin or at coastal continent-based sites in the western basin, where they were subject to the proximity of considerable urban or industrial emissions. Land-based measurements of the background composition of western Mediterranean atmospheric aerosol is best investigated on the shore line of relatively industry-free, less urbanised islands and studies in such locations have thus far been limited. One of the central aims of the ChArMEx (Chemistry-Aerosol Mediterranean

70 Experiment; https://charmex.lsce.ipsl.fr) project is to make background aerosol observations in such islands as Corsica and the Balearic Islands. In addition, studies of the chemical composition of single aerosol particles in the Mediterranean are particularly scarce and are restricted to urban environments (Dall'Osto et al., 2013, 2016; Dall'Osto and Harrison, 2006; McGillicuddy, 2014). Single particle mass spectrometers, such as the aerosol time-of-flight mass spectrometer (ATOFMS), have proven

75 valuable in identifying and characterising a wide variety of particle sources; sea salt, mineral dust, vehicle exhaust, tyre wear, solid fuel combustion (coal, peat and wood), shipping and various industrial emissions (Beddows et al., 2004; Bhave et al., 2001, 2002; Dall'Osto et al., 2014; Giorio et al., 2012; Harrison et al., 2012; Healy et al., 2009, 2010, 2012; Liu et al., 2003; Spencer et al., 2008; Tao et al., 2011). Mixing state information – both internal and external – provided by mass spectrome-

80 ters has been used to determine the type of atmospheric processing particles have undergone (Gard et al., 1998), as well as their acidity and hygroscopicity (Denkenberger et al., 2007; Healy et al., 2015), properties which affect their ability to act as CCN (Furutani et al., 2008). Combination of ATOFMS and hygroscopicity tandem differential mobility analyser (HTDMA) data has shown that sea salt and particles containing amines and nitrate are hydrophilic, while the more organic carbon

85 (OC) particles contain the more hydrophobic they are (Herich et al., 2009; Wang et al., 2014). Fresh particles can be distinguished from aged ones by the presence of secondary inorganic species such as nitrate, sulfate and ammonium (Cahill et al., 2012; Healy et al., 2010; Liu et al., 2003; Pratt and

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Prather, 2009), which is also helpful in differentiating particles from local and transported sources (Healy et al., 2012). Single particle chemical speciation is therefore a useful tool, complementary to

90 characterising particle optical and physical properties (Moffet and Prather, 2009), for examining the effect aerosols have on air quality and climate. Measurements from the ATOFMS also provide useful information to validate mixing-state resolved models (Zhu et al., 2016). In air quality and climate models, mixing-state information is essential as this property strongly impacts aerosol composition, hygroscopicity, optical and CCN properties over urban areas (Zhu et al., 2016). An important

95 application of single-particle data is source apportionment of ambient aerosol. If a unique particle composition signature can be linked with a specific source, then number and mass concentration contributions can be estimated at a receptor site (Allen et al., 2000; Bein et al., 2006; Pratt and Prather, 2009; Qin et al., 2006; Reinard et al., 2007). Most chemical speciation measurements to date in the Mediterranean have focused on bulk aerosol, and while they provide quantitative data

100 they do not resolve the mixing states of ambient particles. As such, source identification and therefore apportionment – often one of the main goals of aerosol measurements – is limited with these techniques. In this context, an aerosol time-of-flight mass spectrometer (ATOFMS) was employed to provide real-time single particle mixing state and thereby source information for aerosols impacting the western Mediterranean basin during two ChArMEx special observation periods in summer 2013:

105 ADRIMED (Aerosol Direct Radiative Impact on the regional climate in the MEDiterranean region; Mallet et al., 2016) and SAF-MED (Secondary Aerosol Formation in the MEDiterranean).

2 Methodology

2.1 Sampling site and instrumentation

Measurements were performed at the atmospheric monitoring station in Ersa (coordinates: 42°58'09"N,

110 09°22'49"E), Cape Corsica, near the North tip of Corsica Island. This station is well positioned to investigate polluted air masses transported over the western Mediterranean basin from the highly industrialised regions of the Po Valley (Royer et al., 2010) and/or Marseille/Fos-Berre (El Haddad et al., 2011, 2013). The site was fully equipped for the measurement of aerosol chemical, physical and optical properties. This ground-based remote station is located at an altitude of 530 m above

115 sea level (asl) at the remote Cape Corsica Peninsula and has unobstructed views to the sea over ~270°(Lambert et al., 2011). The ADRIMED and SAF-MED field campaigns took place from 11th June to 5th July and from 12th July to 6th August 2013, respectively, during the Mediterranean dry season over the western and central Mediterranean basins. Some of the key instruments deployed during the campaigns are given in Table 1. A full list of instruments deployed during ADRIMED

120 can be found in the overview for this campaign by Mallet et al. (2016), while a summary of the main findings of the SAF-MED campaign is currently in preparation. The ATOFMS (TSI model 3800) was operated continuously from 12th June – 6th August, with a period of downtime from 12-18th July. A

detailed description of the ATOFMS can be found elsewhere (Gard et al., 1997). Briefly, it consists
of (i) an aerodynamic focussing lens (TSI AFL100) Su et al. (2004) that transmits particles in the
aerodynamic diameter (D_a) range 100-3000 nm, (ii) a particle sizing region, and (iii) a bipolar reflec-
tron time-offlight mass spectrometer. Single particles are desorbed/ionized using a pulsed Nd:YAG
laser (λ = 266 nm, ~1 mJ pulse^{-1}). Positive and negative ion mass spectra of individual aerosol par-
ticles are obtained, which enable identification of the chemical constituents. Gradual degradation in
the power of the sizing lasers during the campaign was observed and resulted in effective size ranges
of 300-3000 nm D_a for ADRIMED and 500-3000 nm D_a for SAF-MED.

2.2 ATOFMS Data Analysis

Over 1.2 million single particle mass spectra were generated by the ATOFMS during the sampling
period and clustered using the K-means algorithm (K=80), as described in detail elsewhere (Gross
et al., 2010; Healy et al., 2009, 2010). Clusters exhibiting very similar average mass spectra (in-
cluding those with the same major ions but varying relative signal intensities), comparable temporal
trends and size distributions were merged. The final merged clusters were then identified as particle
"classes"; 27 in total.

The particle class labelling scheme used herein is regularly used in the literature (Ault et al., 2010;
Dall'Osto and Harrison, 2006; Pratt and Prather, 2012; Spencer and Prather, 2006) and indicates
either the probable source (e.g. sea salt) or the dominant species in the positive ion mass spectra
(e.g. K, EC, Fe etc.), with the order of the ions indicating their relative mass spectral intensities. For
example, a particle class with high intensity mass spectral features for sodium and elemental carbon
is labelled *Na-EC*. In some cases this is followed by a secondary species detected in the negative
mass spectra (e.g. *K-NO$_X$*), which usually provides insight into the atmospheric ageing the particles
have undergone locally or during transport (Reinard et al., 2007).

Single-particle mass spectrometers such as the ATOFMS do not provide quantitative information
in the form of particle number or mass concentrations – rather the ATOFMS provides speciation in
particle counts classified by aerodynamic diameter. The transmission biases of the AFL, the number
of particles the system can size and ionise at any given time (data acquisition busy time), as well as
limited detection of particles <150 nm (determined by wavelength of sizing lasers and the amount
of scattered light) hinder full and accurate counting of particles over the entire ATOFMS size range
(100-3000 nm D_a). The desorption/ionisation laser used by the ATOFMS also complicates quan-
titative speciation. Shot-to-shot fluctuations in laser output power and variations in power density
(Gaussian) across the laser beam (Steele et al., 2005; Wenzel and Prather, 2004) create variance in
the amount of a particle that is desorbed and can also lead to variations in resultant mass spectral
peak height and area (Reinard and Johnston, 2008).

Given these limitations, in order to produce meaningful particle number and mass concentra-
tions for ATOFMS particle classes the total ATOFMS counts were scaled using quantitative particle

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counting instruments operated concurrently; an optical particle counter (OPC, TSI model 3300) and
160 a scanning mobility particle sizer (SMPS, TSI DMA model 3080 and CPC model 3010). Reconcil-
ing SMPS, OPS and ATOFMS data requires conversion of D_m (electrical mobility diameter; SMPS)
and D_o (optical diameter; OPC) measured with the SMPS and OPS into the corresponding ATOFMS
D_a (aerodynamic diameter), using the following relationship:

$$D_a = \frac{\rho_p D_{ve}}{\rho_0 \chi}$$

165 Where ρ_p is the particle density (discussed hereafter), D_{ve} is the volume equivalent diameter (op-
erationally equivalent to D_m or D_o), ρ_0 is standard density (1 g/cm^{-3}) and χ is the dynamic shape
factor (assumed to be 1, thus representing spherical shape). This is a simplified version of particle
diameter, morphology and density relationships that are covered in much greater detail elsewhere
(DeCarlo et al., 2004). No correction factors were used to merge the SMPS and OPS data; D_m and
170 D_o were both assumed to be equivalent to geometric diameter.

Knowledge of particle density is required for this conversion. This value can be estimated from
bulk mass concentration measurements made, for example, by an aerosol chemical speciation moni-
tor (ACSM) and an instrument which measures black carbon (BC), such as a multi-angle absorption
spectrometer (MAAP).

175 $$\textit{Average density} = \frac{m_{BC} + m_{org} + m_{Cl} + m_{SO_4} + m_{NO_3} + m_{NH_4}}{\frac{m_{BC}}{1.5} + \frac{m_{org}}{1.2} + \frac{m_{Cl}}{1.5} + \frac{m_{SO_4} + m_{NO_3} + m_{NH_4}}{1.5}}$$

2.3 Correlations

Reconstructed ATOFMS mass concentrations were then compared, using regression analysis and
the coefficient of determination, with those obtained by the TEOM (tapering element oscillating
microbalance; PM_{10} and PM_1 mass concentrations), PILS-IC (PM_{10} mass concentrations of SO_4^{2-},
180 NH_4^+, NO_3^-, K^+, Ca_2^+, Na^+, Mg^+, Cl^-, oxalate, methanesulfonate – MSA), MAAP (BC mass con-
centrations) and ACSM (PM_1 mass concentrations of SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, organic carbon).
Positive matrix factorisation (PMF) performed on the ACSM organic fragments produces factors
which correspond to a group of OA constituents with similar chemical composition and temporal
behaviour that are characteristic of different sources and/or atmospheric processes (Zhang et al.,
185 2011). Three factors were resolved; low-volatility oxygenated organic aerosol (LV-OOA, aged and
non-volatile), semi-volatile oxygenated organic aerosol (SV-OOA, less oxidised and aged than LV-
OOA) and hydrocarbon-like organic aerosol (HOA, representative of fossil fuel combustion). More
information on ACSM results and source apportionment are available in Michoud et al. (2016).

The coefficient of determination, as R^2, was used to evaluate the effectiveness of the ATOFMS
190 mass reconstruction. All R^2 values can be found in SI Table 1. This analysis was considered ap-
propriate as the objective of ATOFMS mass reconstruction was to produce mass concentrations as
similar as possible to other mass measurement techniques. R^2 values of <0.5, ~0.5-0.7 and >0.7 are

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typically considered indicative of weak, moderate and strong linear (positive or negative) relationships respectively.

3 Results and Discussion

3.1 Air mass back trajectories

Back trajectory analysis was performed using the HYSPLIT model (Revision 631, July 2014) (Draxler and Hess, 1998) to identify air masses influencing the sampling site. The HYSPLIT model was run using the PC Windows based software available online (http://www.ready.noaa.gov/HYSPLIT.php) and meteorological input from the Global Data Assimilation System (GDAS) archive. 120-hour back trajectories ending 500 m above ground level (AGL) at Ersa (Corsica) were calculated for each hour between 12th June and 7th August 2013 (total: 1344 trajectories). Five broad periods with different air mass regimes were identified in the period based on the ATOFMS, OPS, ACSM, PM_1 and PM_{10} temporal profiles. Separate cluster analyses were performed to classify the trajectories for each of these five campaign periods (Figure 1). A plot of total spatial variance as a function of the number of clusters was used to determine the number of clusters. The clustered HYSPLIT 120-hr back trajectories for each period were used to determine which air masses most influenced the ATOFMS measurements, and temporal profiles for particle numbers and mass concentrations have been labelled with these air mass origins (France, Mediterranean, Spain, North Atlantic, UK, Italy, eastern Europe).

Period 1 (12-20th June) was dominated by recirculating air masses over the Mediterranean Sea, Period 2 (20-26th June) by North Atlantic air masses, Period 3 (26th June-4th July) by trajectories passing largely over France, Period 4 (4-29th July) mostly by Mediterranean recirculations, and Period 5 (29th July-7th August) by Mediterranean recirculations and continental European air masses. The sampling site was therefore influenced by long-range North Atlantic marine emissions and European emissions which were subsequently recirculated over the Mediterranean Sea, with relatively infrequent input from the Sahara. Combined with a sampling period of 8 weeks, it is clear that the site was well placed to provide an insight into the composition of Mediterranean aerosol from diverse sources under a wide variety of meteorological conditions.

3.2 ATOFMS particle classes

Twenty-seven distinct ATOFMS particle classes were identified and subsequently grouped into 8 general "categories" for clarity based on the dominant marker ions; EC-rich (53% of total mass spectra), K-rich (32%), Na-rich (8%), Amines (4%), OC-rich (2%), V-rich (1%), Fe-rich (0.2%) and Ca-rich (0.2%). The contribution to total particle number and mass concentration of all particle classes can be found in Table 2.

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While the aerosol mixing state is varied, only a few particle classes represent the bulk of un-scaled particle numbers. The dominant classes are *EC-SO$_X$*, *K-SO$_X$* and *K-EC-Oxalate*. The Na-rich category is dominated by *Sea salt-aged* particles, the EC-rich category by *EC-SO$_X$* particles, the K-rich category by *K-SO$_X$* particles, the Amines category by *K-TMA* and *EC-TMA* particles, the
230 OC-containing category by *OC* particles and the V-rich category by *V* particles.

3.3 Mass Concentrations

Reconstructed ATOFMS mass concentrations were compared with those for PM$_{10}$, total PILS-IC species (PM$_{10}$) and PM$_1$ (total ACSM species + BC), shown in Figure 2. Reconstructed ATOFMS particulate mass accounted for 70-90% of PM$_{10}$ mass for most of the sampling period. Note that
235 ATOFMS particles account for relatively little of the PM$_{10}$ mass during periods when sea salt and dust are abundant, which is expected given the upper size limit (3 μm) of the instrument and the low detection efficiency for supermicron particles (Cahill et al., 2014). Total ATOFMS reconstructed mass concentrations were found to correlate well with total ACSM mass concentrations (R^2 =0.71), and moderately with mass concentrations of PILS-IC SO$_4^{2-}$ and NH$_4^+$ (R^2 =0.58, 0.44), the ACSM
240 factors LV-OOA (R^2 =0.59) and SV-OOA (R^2 =0.46), BC (R^2 =0.55) and PM$_1$ (R^2 =0.44).

ATOFMS reconstructed mass concentrations were dominated by EC-rich particles (52%), followed by K-rich (25%), Na-rich (12%), Amines (3%), OC-rich (3%), V-rich (3%), Ca-rich (1%) and Fe-rich (1%). The dominance of EC and K-rich ATOFMS particles does not suggest that PM$_{2.5}$ mass is comprised mostly of EC and K. These species are simply used as markers (and for naming
245 conventions) in ATOFMS analysis for fossil fuel and biomass combustion, while truly quantitative measurements by the PILS-IC and ACSM indicate that most of the PM$_{10}$ mass was comprised of organics (36%), sulfate (16%) and ammonium (10%). A detailed discussion follows in Section 3.4.1.

3.4 Particle Sources

Four general sources of ATOFMS PM$_{2.5}$ particles were identified during ADRIMED and SAF-MED,
250 namely regionally transported combustion, local biomass burning, marine, and shipping. Composition of the particle classes that may have originated from these sources, and comparison of their mass concentrations with other measurements is discussed in the following sections.

3.4.1 Regionally Transported Combustion

Twelve ATOFMS particles classes were identified as originating from regionally transported com-
255 bustion, all found in the following 3 categories; EC-rich, K-rich and Amines. Average mass spectra for these particles classes are shown in Figure 3. All of the EC-rich classes were characterised by elemental carbon fragments ions $^{12,24,36\cdots}$C$^+$ in the positive mass spectra. *EC-SO$_X$* and *EC-Oxalate* did not contain detectable ^{39}K$^+$, indicating they most likely arise from fossil fuel combustion (oil burning or traffic). *EC-K*, *EC-K*-SO$_X$ and *EC-K*-Oxalate were characterised by a stronger signal

260   for $^{36}C_3^+$ relative to $^{39}K^+$; similar particles have previously been attributed to domestic coal com-
bustion (Healy et al., 2010), although other sources are certainly possible. *K-EC-NO$_X$*, *K-EC-SO$_X$*
and *K-EC-Oxalate* produced stronger signals for $^{39}K^+$ relative to $^{36}C_3^+$, a pattern usually associ-
ated with biomass burning particles. Sulfate ($^{97}HSO_4H^-$) dominated the SO$_X$ classes, but was also
present to a lesser extent in the other six EC-rich classes. Despite the average spectra for the EC-rich

265   classes showing large signals for sulfate and nitrate ($^{46}NO_2^-$, $^{62}NO_3^-$) most of the particles in these
classes produced no negative ion spectra or only weak negative ion signals. It is therefore not possi-
ble to definitively describe their anion mixing state; however certain conclusions can still be drawn
from their temporal profiles. Less nitrate, or weaker signals for these species, relative to sulfate was
expected given the high ambient temperatures; nitrate is usually mixed with EC in the form of am-

270   monium nitrate, which is more volatile than ammonium sulfate (Querol et al., 2009; Sciare et al.,
2008). A smaller signal for MSA, $^{95}(CH_3)SO_3^-$ (Neubauer et al., 1997), relative to sulfate was found
in the *K-EC-SO$_X$* class, indicating processing with marine emissions (Gaston et al., 2010). The ox-
alate classes are characterised by their signal at m/z -89, a marker for deprotonated oxalic acid (Yang
et al., 2009) and aged aerosol. Very small signals for ammonium ($^{18}NH_4^+$), not marked in the mass

275   spectra, were found in all classes with the exception of the *EC-Oxalate* class.

The positive ion mass spectra for *K-CN* and *K-SO$_X$* particles are exclusively dominated by $^{39}K^+$,
typical of biomass burning particles detected by ATOFMS (a.R. Lea-Langton et al., 2015; Pratt
et al., 2010; Qin and Prather, 2006; Silva et al., 1999). Sulfate ($^{97}HSO_4H^-$) dominates the negative
ion mass spectra of the *K-SO$_X$* particles, with additional signals for MSA ($^{95}(CH_3)SO_3^-$) and ox-

280   alate ($^{89}(COO)_2H^-$). $^{26}CN^-$, internally mixed carbon and nitrogen, probably in the form of nitrogen-
containing organic compounds (Silva et al., 1999), dominates the negative ion mass spectra of *K-CN*
particles. EC fragments were found in all K-rich negative ion mass spectra, indicating a biomass
combustion source.

Trimethylamine (TMA, $^{59}(CH_3)_3N^+$,) was the most abundant alkylamine marker ion in the three

285   Amine particle classes. Also present in all three classes was a marker ion for protonated dimethy-
lamine (DMA, $^{46}(CH_3)_2NH_2^+$). A comparison of ATOFMS datasets obtained in Cork, Paris, Zurich,
Dunkirk and Corsica (ADRIMED and SAFMED) found this ion only in the latter two datasets (Healy
et al., 2015). Ammonium ($^{18}NH_4^+$) was also found in all three Amine classes. The *K-TMA* class was
dominated by $^{39}K^+$, indicative of biomass burning, while *EC-TMA* particles produced $^{12,36}C_3^+$ sig-

290   nals, indicating fossil fuel combustion origins. *OC-TMA* particles are characterised by strong $^{39,41}K^+$,
OC ($^{27}C_2H_3^+$) and oxidised OC ($^{43}C_2H_3O^+$) signals, suggesting biomass burning sources and atmo-
spheric processing during transport to the site. Sulfate ($^{97}HSO_4H^-$) and nitrate ($^{46}NO_2^-$, $^{62}NO_3^-$,
$^{125}(NO_3)_2^-$) were found in the average negative mass spectra of *EC-TMA* and *OC-TMA*, however
only 0.3% and 18% of these particles actually produced negative mass spectra and *K-TMA* parti-

295   cles produced none. Alkylaminium sulfate particles have been shown to readily absorb water at low
relative humidities (<45%) (Chan and Chan, 2013; Hu et al., 2014), and particle-bound water has

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been shown to suppress negative ion formation in mass spectrometers (Neubauer et al., 1997, 1998). The proportion of Amine particles with negative mass spectra is low, in contrast to other particle classes which produced signals in up to 100% of their negative mass spectra (K-EC-SO_X, K-SO_X-
300   $Oxalate$). This suggests particle-bound water could have had a significant effect on negative ion formation for these particles. The average negative mass spectra should therefore not be considered as representative of every particle in these classes. Healy et al. (2015) previously assigned m/z -95 in amine-containing particles from this dataset to MSA. However, closer inspection of individual spectra suggests that at least some of the signal at -95 arises from miscalibrated negative ion mass spectra,
305   and is in fact associated with sulfate. Although m/z -95 cannot therefore be definitively assigned to MSA here, internal mixing of MSA and TMA is possible, as indicated by laboratory studies (Chen et al., 2015a). Furthermore, MSA was also measured in bulk PM_{10} during this campaign using the PILS-IC instrument, and is thus inevitably contained in a fraction of particles at this location. Temporal profiles for hourly summed particle numbers for the regionally transported combustion classes
310   are shown in Figure 4. There are three general temporal profiles; those of EC-SO_X, EC-K-SO_X, EC-K and EC-$Oxalate$, those of K-SO_X, K-EC-SO_X, K-CN and K-EC-$Oxalate$, and finally those containing TMA. The EC-rich particle classes dominated Period 1 and were considered markers for fossil fuel combustion because most of these did not contain detectable $^{39}K^+$. Their particle numbers remained relatively similar throughout the campaigns. For the first half of Period 1 regional air masses passed
315   over industrialised parts of France (Marseille) and Northern Italy (Po Valley) before reaching the site, while during the latter half of this period these air masses were then recirculated over the western Mediterranean (SI Figure 1 shows the air mass back trajectories calculated for this period using the HYSPLIT model).

    Particle numbers for all EC-rich and major K-rich classes decreased noticeably during Periods 2
320   and 5, which were influenced by synoptic scale air masses from the North Atlantic, effectively removing aerosol accumulated during the previous periods. On the other hand, K-rich particles, markers for biomass combustion, dominated Periods 3 and 4. Fires were detected by MODIS (Figure 5) over northern Italy, Ukraine and Russia throughout the sampling period and the site was heavily influenced by air masses passing over this region (Figure 1), which could explain the constant presence
325   of K-rich particles in the background aerosol. The increase in these particles during Period 3 may be explained by longer residence times of air masses over southern France and northern Italy relative to Period 1, and particle numbers then began to decrease when trajectories from the North Atlantic and UK arrived at the end of Period 3.

    A significant increase in fires was detected around the Black Sea from 10th July until the end of
330   the sampling period (Figure 5). The burning of wheat residuals has been previously documented in the eastern Mediterranean and contributed at least 30% of EC and OC measured during similar time periods between 2001-2006 (Sciare et al., 2008). For ~4 days during Period 4, air masses from over the Black Sea and eastern Europe influenced the site, followed by extensive stagnation and

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recirculation of that air over the western Mediterranean. These observations coincided with a further

335 increase in K-rich particle numbers relative to Period 3.

As shown in Figure 4, the three Amine particles classes, *K-TMA*, *EC-TMA* and *OC-TMA*, presented similar temporal profiles in Period 4 to those of major EC-rich and K-rich particles classes. Numbers of *K-TMA* and *EC-TMA* particles peaked during Period 4, while *K-TMA* particles dominated over *EC-TMA* particles during Period 3, as was the case for the major K-rich and EC-rich

340 classes. The dominant Amine class, *K-TMA*, correlated well with two major classes, *K-SO$_X$* and *K-EC-Oxalate*, particularly during Period 4 (R^2=0.76, 0.70 respectively). Partitioning of alkylamines from the gas phase to particles has been found to be enhanced during periods of high relative humidity or fog events, with uptake increasing with aerosol acidity Rehbein et al. (2011). No association between any of the Amine classes and local relative humidity was found in this case, suggesting that

345 this effect is not relevant close to the site but may have played a role close to the point of emission or during transport of the Amine particles to the site. It also provides further evidence that the Amine particles were not formed in the local environment.

To investigate how the dominant ATOFMS particle categories (EC and K-rich) compared with the dominant bulk PM$_{10}$ (excluding sea salt) species, hourly mass concentrations of PM$_{10}$, BC, ACSM

350 species (SO$_4^{2-}$, NH$_4^+$ and SVOOA) and reconstructed mass concentrations for ATOFMS EC-rich and K-rich particle categories (combined particle classes) were plotted (Figure 6). EC and K-rich mass concentrations have been stacked to compare their values with the contributions from BC, SV-OOA, LV-OOA, SO$_4^{2-}$ and NH$_4^+$ (also stacked). For the full sampling period reconstructed mass concentrations of all ATOFMS EC-rich particle classes correlated well with ACSM SO$_4^{2-}$ (R^2=0.61),

355 NH$_4^+$ (R^2=0.62) and the LV-OOA factor (R^2=0.59) mass concentrations (which accounted for the largest proportion of organics mass, 54%), OPS (for the channel 0.3-0.579 μm) number concentrations (R^2=0.69) and moderately with PM$_1$ (R^2=0.46) and BC (R^2=0.50) mass concentrations. Reconstructed mass concentrations for all K-rich classes (including local combustion) correlated with the same species but only moderately (R^2 ranged from 0.3-0.5). Individual particle classes did

360 not produce stronger correlations, suggesting that no single class was an important contributor of PM$_{2.5}$ composition.

The average mass spectra of ATOFMS EC and K-rich classes showed sulfate, nitrate, oxalate and MSA were present. From the PILS-IC and ACSM measurements it was clear that the dominant secondary inorganic ions were sulfate (19% of PM$_1$, 16% of PM$_{10}$) and ammonium (10% of PM$_1$,

365 10% of PM$_{10}$), with nitrate contributing relatively little to both PM$_1$ (4%) and PM$_{10}$ (4%) mass. K$^+$, oxalate and MSA contributed less again to PM$_{10}$ (0.4, 0.1 and 0.2% respectively). K$^+$ is readily ionised by the ATOFMS desorption/ionisation laser so its prevalence in ATOFMS particles is not necessarily representative of its mass concentration (Gross et al., 2000a).

The high level of agreement between mass concentrations of EC-rich+K-rich particles and BC+SV-

370 OOA+LVOOA+SO$_4^{2-}$+NH$_4^+$, shown in a scatter plot in Figure 6, suggests those particles were com-

prised to a considerable degree of LV-OOA, consistent with the ageing of the aerosol particles during regional transport, and SV-OOA, which suggests interaction with locally formed organic aerosol; details of organic aerosol formation and sources during the campaigns can be found in Michoud et al. (2016). However, no significant OC signals were found in any of the EC-rich or K-rich classes. Par-

375   ticles which did produce strong signals for OC ions contributed relatively little to total ATOFMS particle numbers. Similarly to ^{39}K$^+$, the ATOFMS favours ionisation of EC over OC (Ferge et al., 2006; Silva and Prather, 2000), which results in weak signals for OC in particles which also contain EC or K$^+$. This may account for the under-representation of organic aerosol in the ATOFMS measurements.

380   **3.4.2   Local biomass burning**

The sampling site on Corsica was chosen for its negligible local anthropogenic sources relative to the regional background. However, few local sources did influence the site, though these did not contribute significantly to particle number or mass concentrations. Local combustion events were detected in the form of *K-NO$_X$*, K-OCNOX, and *K-OC-SO$_X$* particles, and distinguished themselves

385   from the dominating regional aerosol by occurring mostly during Periods 1 and 2 over 5-7 hour events (Figure 7). The first event was observed on the 12th June from 13:00-18:00 UTC and its source as biomass burning (in the form of vegetation trimmings) was visually confirmed on the slopes northeast of the site.

The composition of these particles is consistent with this observation; K$^+$ is a common marker

390   for biomass combustion, which typically also produces organic aerosol (Pagels et al., 2013; Silva et al., 1999). Average mass spectra for local biomass burning particles are shown in Figure 8. Nitrate (^{46}NO$_2$$^-$, ^{62}NO$_3$$^-$) dominated the negative mass spectra of *K-NO$_X$* particles, but they also contained sulfate (^{97}HSO$_4$H$^-$), nitrogen-containing organic compounds (^{26}CN$^-$), EC (^{24,36,48}C$^-$) and oxygen (^{16}O$^-$). *K-OC-NO$_X$* and *K-OC-SO$_X$* are characterised by a large signal for ^{39}K$^+$ (confirmed by

395   the prominent signal for the ^{41}K$^+$ isotope, hydrocarbon fragments (^{27}C$_2$H$_3$$^+$, ^{29}C$_2H_5$$^+$, ^{51}C$_4H_3$$^+$, ^{63}C$_5H_3$$^+$) in the positive mode and strong signals for ^{43}C$_2$H$_3$O$^+$, a marker for oxidised organic aerosol (Silva and Prather, 2000). Sulfate was found in both OC-rich classes, but dominated the negative mass spectra of *K-OC-SO$_X$* particles. *K-OC-SO$_X$* particles also exhibited a small MSA (^{95}(CH)$_3$SO$_3$$^-$) signal, indicating at least some mixing with marine biogenic emissions prior to detec-

400   tion. Nitrate dominated the *K-OC-NO$_X$* class and was also present to a lesser extent in the *K-OC-SO$_X$* classes.

Garden waste biomass was frequently burned in the surrounding villages during June; such combustion was prohibited from July onwards which explains the lack of similar local events. No local wildfires or controlled agricultural burning was noted during the sampling period. Between 27th June

405   and 1st July, *K-NO$_X$*, *K-EC-NO$_X$* and possibly *K-OC-SO$_X$* were of regional biomass burning origin, because their temporality was noticeably different to the preceding short local events; this period

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was influenced by short-range air masses residing over southern France and northern Italy. Peak aerodynamic diameters for these particles were also larger during this period compared to previous local combustion events; 700-900 nm (D_a) versus 300-500 nm. This represents a significant amount

410 of growth through ageing, assuming these particles were of a similar size at their point of origin to those burned locally in Corsica. *K-NO$_X$* and *K-OC-SO$_X$* particles were also present throughout both campaigns, in low numbers outside of events, indicating persistent regional sources.

3.4.3 Sea Salt

ATOFMS sea salt particles were separated into two classes; fresh and aged. Their composition and

415 comparison with other sea salt measurements (e.g. Na and Cl mass concentrations from PILS-IC) are the subject of a detailed study of primary marine aerosols during ADRIMED (Claeys et al. 2016), so will only be discussed briefly here. Both sea salt classes are typical of those observed in other coastal/marine environments (Gard et al., 1998; Dall'Osto et al., 2004; Healy et al., 2010). Average mass spectra are shown in Figure 8. The positive modes for both fresh and aged particles are

420 similar and are characterised by sodium ions ($^{23}Na^+$, $^{46}Na_2^+$, $^{62}Na_2O^+$, $^{63}Na_2OH^+$ and $^{81,83}Na_2Cl^+$) and $^{39}K^+$. Fresh and aged sea salt particles were differentiated by their negative mass spectra, which showed peaks for $^{16}O^-$, $^{35,37}Cl^-$, nitrate ($^{46}NO_2^-$, $^{62}NO_3^-$) and $^{93,95}NaCl_2^-$ for fresh sea salt particles, while the signals for nitrate dominate the aged sea salt negative mode and sodium chloride adducts are virtually absent. The absence of NaCl ions and strong nitrate signals indicates extensive replace-

425 ment of Cl^- by NO_3^- (Gard et al., 1998), while the presence of nitrate in the negative mass spectra of the fresh sea salt particles suggests that these are not truly fresh but have also undergone some Cl replacement.

Temporal profiles for ATOFMS sea salt particle numbers, OPS number concentrations, PILS-IC sea salt aerosol (SSA, calculated using SSA=[Cl$^-$]+[Na+]×1.47; Bates et al., 2012) and ATOFMS

430 fresh sea salt mass concentrations are shown in Figure 9. The two ATOFMS sea salt classes presented noticeably different temporal profiles. Aged sea salt was present consistently in the background throughout both campaigns, while fresh sea salt was detected mostly during short periods (20-26th June, 30th July). This coincided with increases in OPS number concentrations in the 0.579-2.156 µm range and PILS-IC SSA. Correlation between ATOFMS fresh sea salt mass and SSA is

435 particularly strong (R^2=0.81) for the sea salt event during Period 2. Reconstructed mass concentrations for fresh sea salt particles accounted for 50-80% of SSA during the main event. This and a strong correlation between ATOFMS fresh sea salt mass concentrations and 0.579-2.156 µm particles (R^2=0.81) suggests a significant amount of fresh sea salt was in the PM$_{2.5}$ fraction; an estimated 30% of PM$_{10}$ SSA mass was accounted for by PM$_{2.5}$ ATOFMS fresh sea salt during the 5-day event

440 in Period 2.

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3.4.4 Mineral Dust

Three prominent mineral dust events were characterised by increases in Ca_2^+ mass concentrations and 2.156-8.032 μm particle number concentrations during 12-13th June, 17-19th June and 23-26th June (Figure 9). The third event coincided with the main sea salt event and was also distinguished by contributions of K^+. The 17-19th June event is likely related to a moderate African dust event that passed over Corsica, as shown by MSG\SEVIRI aerosol optical depth (SI Figure 2). The two other periods appear due to local dust. Two particle classes were identified as potential mineral dust by the ATOFMS; Fe and Ca. Average mass spectra are shown in Figure 8. Fe and Ca, along with Al and aluminosilicates are typical dust tracers which produce ions detectable by ATOFMS (Guazzotti et al., 2001; Silva et al., 2000; Sullivan et al., 2007).

K-rich dust is also a possibility. The Fe particles detected in Corsica were internally mixed with $^{39}K^+$, $^{23}Na^+$, $^{27}Al^+$, sulfate ($^{97}HSO_4H^-$) and nitrate, although only a weak signal for $^{27}Al^+$ and no aluminosilicate signals (e.g. $^{43}AlO^-$, $^{59}AlO_2^-$, $^{60}SiO_2^-$, $^{76}SiO_3^-$, $^{77}HSiO_3^-$, $^{103}AlSiO_3^-$) were found, which could also suggest industrial origins (Corbin et al., 2012; Dall'Osto et al., 2008; Zhang et al., 2009). Ca particles are dominated by $^{40}Ca^+$, with weaker signals for $^{56}CaO^+$ and $^{96}CaO_2^+$. 34% of all Ca particles produced positive EC ions, which suggests a vehicular traffic source (Gross et al., 2000b; Silva and Prather, 1997; Song et al., 2001) to and from the site and from a few local villages whose tourist population increases during the summer.

The Fe and Ca classes only contributed a small number of particles (0.2% each) relative to the total number ionised by the ATOFMS and no agreement between these potential dust particles and PILS-IC or OPS measurements was found. This indicates that mineral dust was not characterised well by the ATOFMS. Indeed, the dust particle mass-size distribution is mainly in the $>PM_{2.5}$ fraction, but submicron particles dominate the dust particle number size distribution (see Guieu et al., 2010)(Gomes et al., 1990) as confirmed by in situ and column-integrated particle size distribution measurements during the campaign (Denjean et al., 2016; Renard et al., 2016).

3.4.5 Shipping

Two V-rich particle classes (*V* and *EC-V*, 2% and 1% of ATOFMS mass respectively) were identified as originating from heavy fuel oil combustion; both contained $^{51}V^+$, $^{67}VO^+$, $^{56}Fe^+$, $^{58}Ni^+$ and sulfate ($^{97}HSO_4H^-$), which are typical markers for particles emitted by ships or oil refineries (Ault et al., 2009; Healy et al., 2009). A small signal for MSA ($^{95}(CH)_3SO_3^-$) was present in *EC-V* particles. Internally mixed sodium, potassium, calcium, vanadium, nickel and iron particles have also been observed in ship exhaust particles using off-line TEM-EDX and two-step laser mass spectrometry (L2MS) (Moldanová et al., 2009). Small signals for $^{39}K^+$ and $^{23}Na^+$ were found in the Corsica V-rich particles, but none for $^{40}Ca^+$. Heavy fuel oil combustion aerosols have a strong presence in the Mediterranean (Becagli et al., 2016; Pey et al., 2010; Querol et al., 2009). There are more than 15

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passenger ferry lanes incurring shipping traffic around the northern tip of the island; the closest pass is 16.5 km north and 12.5 km east of the site (Figure 10). Ferries travelling around the northern tip of Corsica Island, take approx. one hour to reach Bastia and between all five ferry companies ~50 sailings take place per week. Both V-rich classes displayed strong north-westerly and southwesterly

480   wind dependences (Figure 10), consistent with the distribution of most ferry lanes (Figure 10) V-rich particles were identified as aged regional emissions. Most freshly emitted shipping particles are typically less than 300 nm D_a (Healy et al., 2009). However, all shipping particles detected during this campaign had diameters larger than 300 nm D_a. Furthermore, it was unlikely that any fresh heavy oil combustion emissions were observed with the ATOFMS as the closest ferry lane is at least

485   12.5 km from the site. There are also no local power plants or refineries that could generate similar particles. *EC-V* and *V* particle numbers consistently featured a mode around 740 nm D_a indicating that the observed particles were aged to some degree.

3.5   Aged Particle Markers

As a substantial number of ionised ATOFMS particles produced low intensity signals in their neg-

490   ative ion mass spectra, or none at all, the average mass spectra are most representative of those species that ionised most efficiently i.e. nitrate and sulfate. Ions that usually produce relatively small signals, such as oxalate or MSA, were expected to be under-represented in the average mass spectra so an additional querying approach was taken to examine the mixing state of these species; particle numbers for classes found to contain these species are shown in Table 2. Oxalate ($^{89}(COO)_2H^-$) and

495   MSA ($^{95}(CH)_3SO_3^-$) ions were queried for peak height between 1 and 5000, to include all mass spectra containing these species. These particles were then clustered using the K-means algorithm to produce particle classes.

3.5.1   Oxalate

The mixing states of particles containing oxalate as identified by single particle techniques is var-

500   ied, and indicates oxalate formation either in fog/cloud processing or photochemical oxidation of biogenic and anthropogenic VOCs. Oxalate has been found in biomass burning particles (Healy et al., 2010; Yang et al., 2009), mixed with industrial combustion particles containing Pb and Zn (Moffet et al., 2008)(Moffet et al., 2008a, 2008b), in aged sea salt (Yang et al., 2009) and in aged carbonaceous particles containing highly oxidised organics, non-oxygenated organics and amines

505   (Pratt et al., 2009; Qin et al., 2012). Oxalic acid has been found preferentially enriched on Asian mineral dust over carbonaceous particles (Sullivan and Prather, 2007), while Fitzgerald et al. (2015) characterised cloud processed African dust as rich in sulfate and oxalate.

In our study, oxalate was found in ~9600 particles, i.e. 0.8% of the total particles ionised. The mixing states derived from this query are similar to those produced from general clustering and

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510 are varied, suggesting that poor ionisation efficiency did not prevent oxalate from being detected in
certain types of particles.

From the querying approach it was apparent that K-rich particles produced more signals for ox-
alate than the more abundant carbonaceous particles. This could indicate preferential partitioning
to K-rich particles or more extensive oxidation of the OC in those particles versus EC-rich ones.

515 52% of the queried oxalate particles were dominated by $^{39}K^+$ and sulfate (~90% of all the queried
particles contained sulfate), supporting the identification of the *K-SO$_X$-Oxalate* class from the gen-
eral approach. Particles most similar to *K-NO$_X$* accounted for a further 33% and produced signals
for nitrate, EC, CN, CNO and sulfate. In contrast only 2% of queried oxalate particles produced
EC-rich positive mass spectra. Particles with typical dust tracers (Fe, Ca, Al, aluminosilicates) ac-

520 counted for 7% of the queried particles; this fraction applies to PM$_{2.5}$ but would certainly be larger
for PM$_{10}$. The remaining queried oxalate particles were classified as *aged sea salt* (3%), *OC* (2%), *V*
(0.7%) and *Cu-Pb* (0.4%). If the queried oxalate particle numbers were considered representative of
the whole ATOFMS dataset, then biomass burning emissions play a large role in the fate of particle
phase oxalate in the western Mediterranean.

525 The ATOFMS querying approach indicated a prevalence of oxalate mixed with K-rich particles,
however correlations between PILS-IC oxalate and K-rich mass were poor; better correlations were
found with EC-rich and K-rich mass concentrations combined (R^2=0.55), suggesting either that more
EC particles actually contained oxalate than was detected or another particle type transported in the
same air mass but which was not detected by the ATOFMS. Moderate correlations were also found

530 between oxalate and LV-OOA (R^2=0.54), WSOC (R^2=0.55) and BC (R^2=0.55) mass concentrations
(for the period 21st June-4th August); hourly mass concentrations for these species are shown in
Figure 11 (mean concentration of oxalate: 9.8 ng/m^3). Oxalic acid is often the single most abundant
water-soluble organic compound identified in ambient aerosols (Yu et al., 2005), which explains the
agreement between oxalate and WSOC mass concentrations. While the humidity was relatively high

535 (average of 70%) throughout the two campaigns, so too was the solar radiation, with few instances
of cloud or fog formation at the site. The association with SV-OOA also supports photochemical
oxidation as the dominant oxalate formation mechanism.

3.5.2 MSA

MSA is a well-established tracer for marine phytoplankton activity (Hallquist et al., 2009; Gaston
540 et al., 2010), formed from heterogeneous OH (daytime) and homogeneous NO$_3$ (nighttime) oxida-
tion of DMS, the enzymatic cleavage product of dimethylsulfoniopropionate (DMSP), a compound
produced by oceanic phytoplankton. It is therefore a good indicator of biogenic (marine) sulfate and
its presence in aerosols typically indicates that they have undergone some marine transport, rather
than being produced locally (Gaston et al., 2010). While MSA has been proposed to primarily con-
545 tribute to particle growth in the atmosphere (Kreidenweis et al., 1989; Wyslouzil et al., 1991a, b),

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there is evidence that MSA can also contribute to new particle formation (Dawson et al., 2012; Willis et al., 2016). Recently, Sellegri et al. (2016) showed that iodine-containing species are likely precursors to new particle formation in the Mediterranean; a query of the ATOFMS ADRIMED and SAF-MED dataset for iodine (m/z -127) only returned 34 particles containing this ion. Iodine is

550   rarely reported in ATOFMS studies and even then it is usually in low numbers of particles; Beddows et al. (2004) found ~3600 $PM_{2.5}$ ATOFMS particles containing iodine at a rural background site in the UK. Both MSA and sulfate influence particle hygroscopicity, meaning that the enhanced production of either of these species by anthropogenic particle types could have implications for subsequent cloud droplet formation in both marine and inland environments (Lee et al., 2010; O'Dowd et al.,

555   2004).

MSA was identified in 2700 particles (0.2% of total particles ionised). Sulfate was also found in all of these. The mixing states derived from the querying approach largely agrees with those from the general approach. Similar to oxalate, enhanced partitioning of MSA was observed for biomass combustion particles. Particles similar to the *K-SO$_X$*, *EC-K-SO$_X$* and *K-EC-SO$_X$* classes accounted

560   for 45%, 25% and 11% of the MSA queried particles. *EC-V, V* and *Cu-Pb* classes contributed 11%, 4% and 1% respectively.

The preference for partitioning to combustion particles is in contrast to findings from Riverside, California (Gaston et al., 2010) where only small fractions of carbonaceous ATOFMS particle types contained MSA, and Cork, Ireland (Healy et al., 2010), where only one ATOFMS particle class

565   of several carbonaceous classes identified was internally mixed with MSA. It has been suggested that accumulation of secondary species during transport over urban regions can potentially mask the detection of MSA by ATOFMS in carbonaceous particles (Pratt and Prather, 2009).

In addition, it has been demonstrated that the oxidation of biogenically emitted DMS to form MSA, can be catalysed by vanadium, which has also been shown to enhance the conversion of

570   anthropogenically produced SO_2 to sulfate (Ault et al., 2010). About 40% of OC-V-sulfate (residual fuel combustion primarily from ships) particles and 33% of aged sea salt particles in Riverside contained MSA. No MSA could be clearly identified in aged sea salt particles in Corsica; m/z -95 was only found in fresh sea salt particles and was likely a result of $NaCl_2$ as it was present in the typical isotopic ratio i.e. its signal was smaller than m/z -93. This is again in contrast to the study

575   in Cork harbour (Healy et al., 2010), where none of the V-rich shipping classes were associated with MSA. However, the authors note that the sampling site in Cork Harbour was very close to shipping berths, so most shipping particles detected were expected to be freshly emitted. *K-OC-SO$_X$* particles, identified with the general clustering approach, produced average mass spectra with MSA signals. This was not supported by the querying approach; no OC-rich particles were found to

580   contain MSA, or at least so few as to not resolve into their own clusters. No Amine particles were identified in the MSA query. As discussed earlier, the presence of MSA in TMA and other amine-containing particles is possible, as indicated by laboratory studies of particle formation and growth

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from reactions between MSA, TMA (or methylamine and DMA) and water (Chen et al., 2015a, b). Amines have been frequently observed in marine aerosol (Facchini et al., 2008; Gaston et al., 2010; Müller et al., 2009; Sorooshian et al., 2009), and particulate amine levels have been found to correlate with particulate MSA levels (Sorooshian et al., 2009). Facchini et al. (2008) observed that MSA, DMA, and diethylamine were the most abundant organic species detected in fine particles in the North Atlantic during periods of high biological activity.

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The remaining 3% of MSA queried particles was accounted for by particles containing dust tracers (Fe, Ca, Al). The Riverside study found that no MSA was found on submicron dust and only 3% of supermicron dust contained MSA (Gaston et al., 2010). The authors expected this since the dust they observed was locally produced, unlike MSA. In contrast, internally mixed OC, sea salt, sulfate, titanium (dust) and MSA formed particles $1 - 2$ μm in size at Mace Head during the EUCAARI project Dall'Osto et al. (2010) and were associated with a period of subtropical maritime air originating from the Azores high-pressure region. The number of dust particles identified with the MSA query in this work were statistically too few to consider submicron/supermicron ratios; from these previous studies it is not unusual to detect MSA on dust particles, however it is unlikely that they represent significant surfaces for MSA to condense onto as most of the MSA mass measured in the Mediterranean to date has been found in the submicron fraction. This observation is also echoed by Gaston et al. (2010); 67% of the submicron particles in Riverside contained MSA.

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In Riverside MSA-containing particles were also associated with fog processing markers $^{81}HSO_3^-$ and hydroxymethanesulfonate (HMS, $^{111}HOCH_2SO_3^-$), highlighting aqueous phase chemistry as an important pathway in MSA formation (Bardouki and Rosa, 2002), as well as the hygroscopic nature of MSA (Barnes et al., 2006). Other studies correlated HMS with relative humidity (RH) during stagnant fog events (Whiteaker and Prather, 2003), however in Riverside the HMS correlation with MSA suggested HMS formation was not due to local increases in RH; rather MSA-particles had undergone aqueous phase processing either in the marine environment or during subsequent transport. Unfortunately queries for m/z -81 and -111 did not return a statistically useful number of particles, and the summed signal for both of these groups was too low to produce a statistically useful time series.

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Hourly PILS-IC mass concentrations of MSA (average of 21 ng/m^3; lower than those measured in Paris; average of 122 ng/m^3; Crippa et al. (2013) compared to Mace Head, Ireland and Erdemli, Turkey) shown in Figure 12, did not correlate with any ATOFMS particle numbers or mass concentrations, or with any other measurements over the whole sampling period. However, some correlations were found for certain periods; from 7-15th July MSA mass agreed well with that of PILS-IC NO$_3^-$, while from 23rd July – 3rd August moderate correlations were found with PILS-IC NO$_3^-$ (R^2=0.53), SO$_4^{2-}$ (R^2=0.48) and NH$_4^+$ (R^2=0.54), and ACSM NO$_3^-$ (R^2=0.46). Increases in MSA mass coincided with sea salt events during Period 2 (Figure 12), although there were no good corre-

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lations with SSA concentration, suggesting MSA was not present on sea salt particles but formation

620 was enhanced by the influx of marine air masses.

4 Conclusions

As part of ChArMEx, two special observation periods on Corsica Island aimed to understand how the physical, chemical, optical properties and vertical distribution of aerosols affect the Mediterranean climate (ADRIMED), as well as develop a better understanding of the origins and particle proper-

625 ties of secondary organic aerosols (SAF-MED). Chemical composition is critical to achieving these aims. A single particle mass spectrometer (ATOFMS) provided detailed information on the mixing states and thereby sources of background aerosol in the western Mediterranean. Airmass trajectories and concurrent observations at the site were used to interpret ATOFMS observations. Overall, 27 distinct ATOFMS particle classes were identified from 1.2 million single particle mass spectra

630 and grouped into 8 general categories: EC, K-rich, Na-rich, Amines, OC-rich, V-rich, Fe-rich and Ca-rich. Mass concentrations were reconstructed for the ATOFMS particle classes and were in good agreement with other quantitative measurements (PM_1, ACSM species, BC). Total ATOFMS estimated mass ($PM_{2.5}$) accounted for 70-90% of PM_{10} mass, most of which was comprised of regionally transported aerosols containing fossil fuel combustion (EC-rich) particles, and K-rich particles

635 from biomass burning in northern Italy and the region surrounding the Black Sea, the accumulation of which was favoured by repeated and extended periods of air mass stagnation over the western Mediterranean. Amine-containing particles were also assigned to regionally transported combustion sources, both fossil fuel and biomass burning. Previous studies of aminecontaining particles found a strong dependence on relative humidity; this was not the case during these two campaigns,

640 suggesting these particles were not formed locally. Three other sources were also identified by the ATOFMS: local biomass burning, marine and shipping. Local biomass burning particles contributed little to $PM_{2.5}$ particle numbers and mass concentrations but were easily distinguished from regional combustion particles; no local sources of fossil fuel combustion were identified. Although the local emissions did not contribute significantly to particle number or mass concentrations the observa-

645 tions serve to highlight the ability of single particle measurements to distinguish between local and regional aerosol sources. Marine emissions comprised fresh and aged sea salt, the former detected mostly during one 5-day event and the latter detected throughout the sampling period. Mineral dust was not efficiently detected by the ATOFMS. Shipping particles, identified using markers for heavy fuel oil combustion, were identified as aged regional emissions which made only a small contribu-

650 tion to $PM_{2.5}$ particle numbers and mass concentrations. A query of the mixing states of oxalate, a photochemically aged aerosol marker, and MSA, a biogenic marine emissions marker showed that the majority of particles containing oxalate also contained K and sulfate, indicative of aged biomass burning emissions. MSA was also strongly associated with biomass burning particles and to a lesser

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extent with Shipping particles – probably related to transport time in the marine boundary layer.

655 Quantitative measurements by TEOM demonstrated that PM_1 particles accounted for most of PM_{10} mass concentrations over the whole sampling period. ACSM (PM_1) and PILS-IC (PM_{10}) sulfate and ammonium mass concentrations were very similar, indicating most of the mass of these species was in the PM_1 fraction. Accordingly, organics (36%), sulfate (16%) and ammonium (10%) constituted most of the PM_{10} mass. Mass concentrations of EC and K-rich particles were in good agreement

660 with those of ACSM sulfate, ammonium and the LV-OOA factor (which accounted for 54% of the organics), and BC. ATOFMS mass spectra provided valuable source markers, allowing the identification of fossil fuel and biomass burning combustion sources. Combined, this information shows these sources provided the primary particles, containing EC and OC, which then accumulated ammonium, sulfate and alkylamines during regional transport. The Mediterranean is a crossroad for air

665 masses transporting different types of aerosols from natural and anthropogenic origins. Identifying these sources and apportioning aerosol mass to them is a key component of future work to mitigate their effects on the Mediterranean climate.

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670 the manuscript with contributions from all co-authors.

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Table 1. List of instruments deployed at Cap Corsica during the ADRIMED and SAF-MED field campaigns. See text for instrument acronym details.

Parameter	Instrument	Make & Model	Temporal resolution	Institution
Particle number size distribution (10-500 nm, mobility diameter and 300 nm − 20 µm, optical diameter)	SMPS	TSI Instruments Ltd., DMA model 3080 and CPC model 3010	5 min (continuous)	CNRM GAME
	OPS	TSI Instruments Ltd., model 3300	5 min (continuous)	CNRM GAME
PM_{10} and PM_1 mass concentration	TEOM, TEOM-FDS		continuous	LSCE
Chemical composition and size distribution of non-refractory and refractory particles (100-3000 nm, vacuum aerodynamic diameter)	ATOFMS	TSI Instruments Ltd., model 3800-100	continuous	UCC
Chemical composition of non-refractory particles (30-1000 nm, vacuum aerodynamic diameter)	ACSM	Aerodyne Research Inc.	25 min (continuous)	LSCE
Black carbon (BC), $PM_{2.5}$	MAAP	Thermo-Scientific, model 5012	5 min (continuous)	LSCE
PM_{10} chemical composition (Na^+, Mg^+, Cl^-, Ca^{2+}, K^+, NH_4^+, NO_2^-, SO_4^{2-}, MSA, Oxalate)	PILS-IC		12/18 min (continuous)	LSCE
Pressure, temperature, relative humidity, solar radiation, rain, wind speed and direction	Weather station	Campbell Scientific, Model CR1000	5 min (continuous)	LSCE

Table 2. Detailed composition of ATOFMS dataset during ADRIMED and SAF-MED, by particle classes.

Category	Particle Class	No. of Particles	% of Total Ionised	% Particles with negative spectra	No. of Particles containing Oxalate	No. of Particles containing MSA	Assumed Density (g/cm³)	% of Total ATOFMS Mass	Unscaled Peak Aerodynamic Diameter (µm)
EC	EC-SOx	329555	28	3			1.4	22	0.74
	EC-Oxalate	15462	1	0.5			1.4	1	0.72
	EC-K	40666	3	16	222		1.4	4	0.76
	EC-K-SOx	13627	1	76		445	1.4	5	0.74
	EC-K-Oxalate	23399	2	0.3			1.4	1	0.74
	K-EC-NOx	1391	0.1	100			1.4	7	0.74
	K-EC-SOx	57553	5	100		191	1.4	4	0.85
	K-EC-Oxalate	161225	13	0.3			1.4	7	0.74
K-rich	K-CN	41740	3	35			1.8	17	0.76
	K-NOx	12078	1	100	3118		1.8	1	0.91
	K-SOx	296512	25	9		782	1.8	3	0.85
	K-SOx-Oxalate	28754	2	100	4988		1.8	2	0.97
	K-Aluminosilicate	3797	0.3	21	23		2	2	0.91
	K-Na	2500	0.2	14			2	1	0.79
Na-rich	Sea salt-fresh	26175	2	68			2.2	6	1.54
	Sea salt-aged	69566	6	59	270		2.2	3	1.81
	Na-EC	1415	0.1	100			2.2	3	0.59
Amines	K-TMA	25603	2	0			1.5	1	0.74
	TMA-EC	19688	2	0.3			1.5	1	0.78
	OC-TMA	3734	0.3	18			1.5	0.5	0.70
OC-rich	OC	13323	1	2	110		1.8	2	0.74
	K-OC-NOx	1368	0.1	100			1.8	0.2	0.66
	K-OC-SOx	7435	1	95			1.8	1	0.64
V-rich	V	9810	1	9	71	65	3.1	2	0.70
	EC-V	3827	0.3	43		198	3.1	1	0.69
Fe-rich	Fe	2199	0.2	71	215	37	3.6	0.5	0.88
Ca-rich	Ca	2400	0.2	82	352	14	2.6	1	1.08

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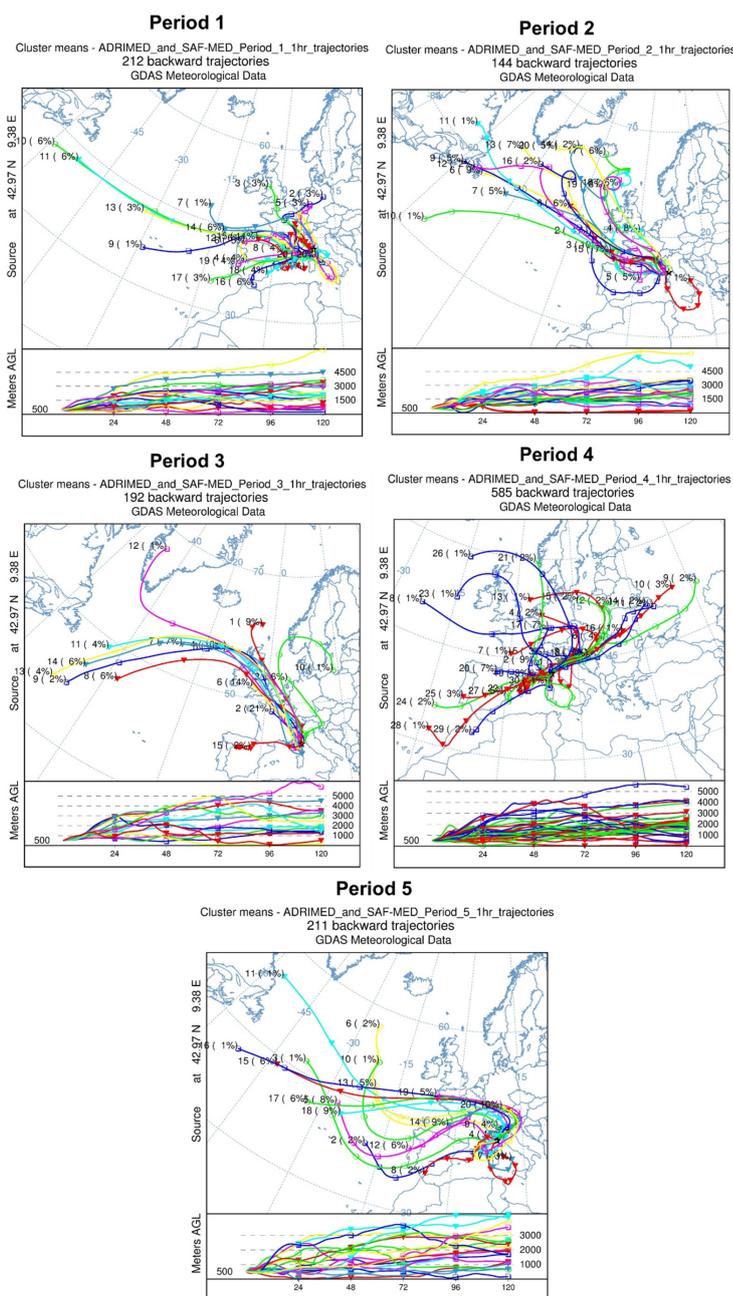and Physics
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Figure 1. Cluster analysis of 120-hour back trajectories calculated using the HYPLSIT model, ending at Cap Corse sampling site at 500 meters above ground level, every 1 hour, for the five periods identified during ADRIMED and SAF-MED.
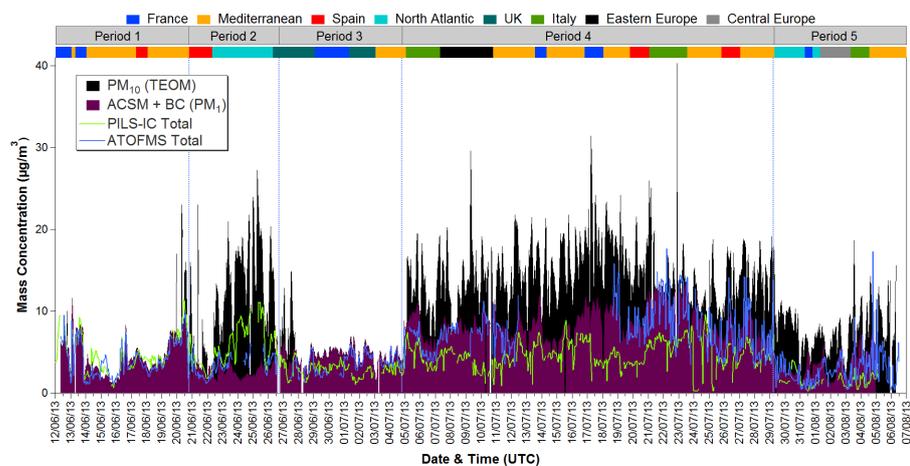
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Figure 2. Hourly mass concentrations of PM$_{10}$, total ACSM species + BC (PM$_1$), total PILS-IC species (PM$_{10}$) and total ionised ATOFMS particles during ADRIMED and SAF-MED.
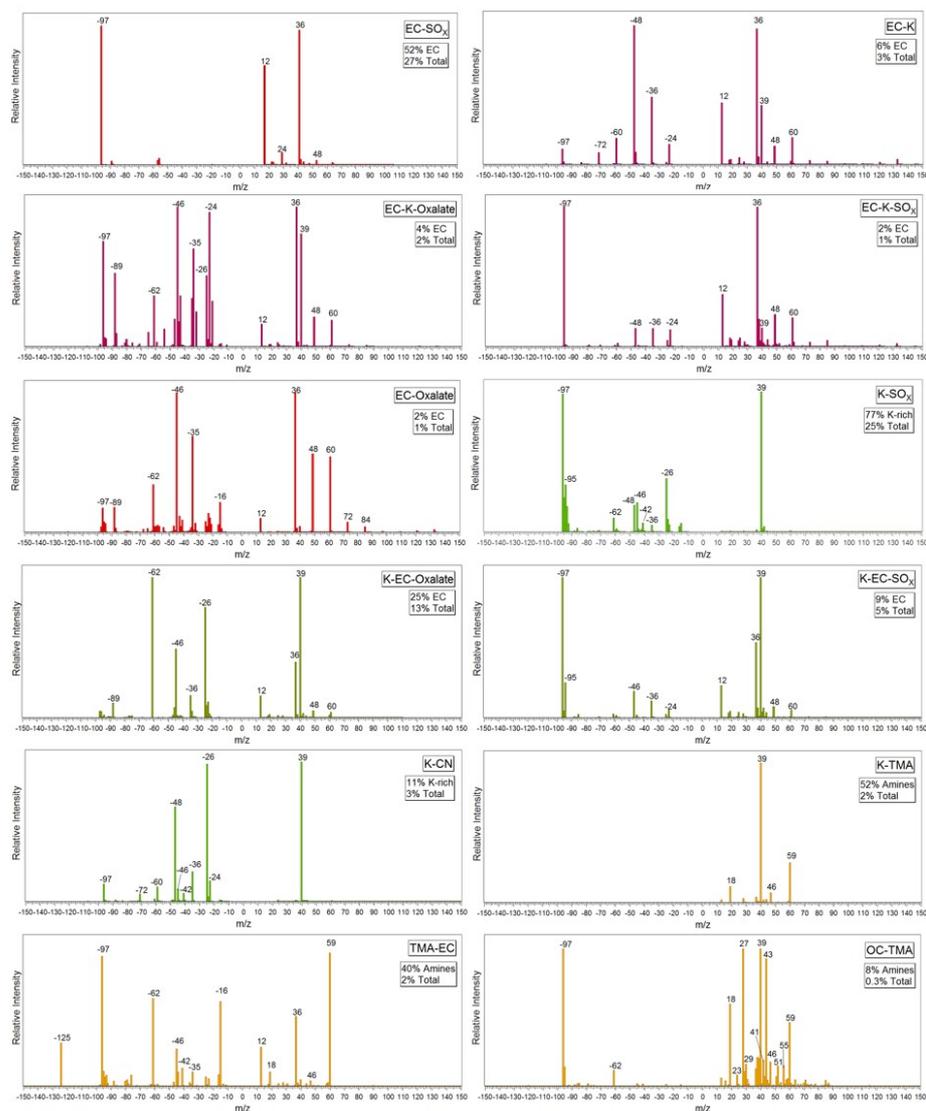
Figure 3. Average mass spectra of ATOFMS particle classes originating from regionally transported combustion sources during ADRIMED and SAF-MED. Percentages refer to fraction of ATOFMS category and total particle numbers.
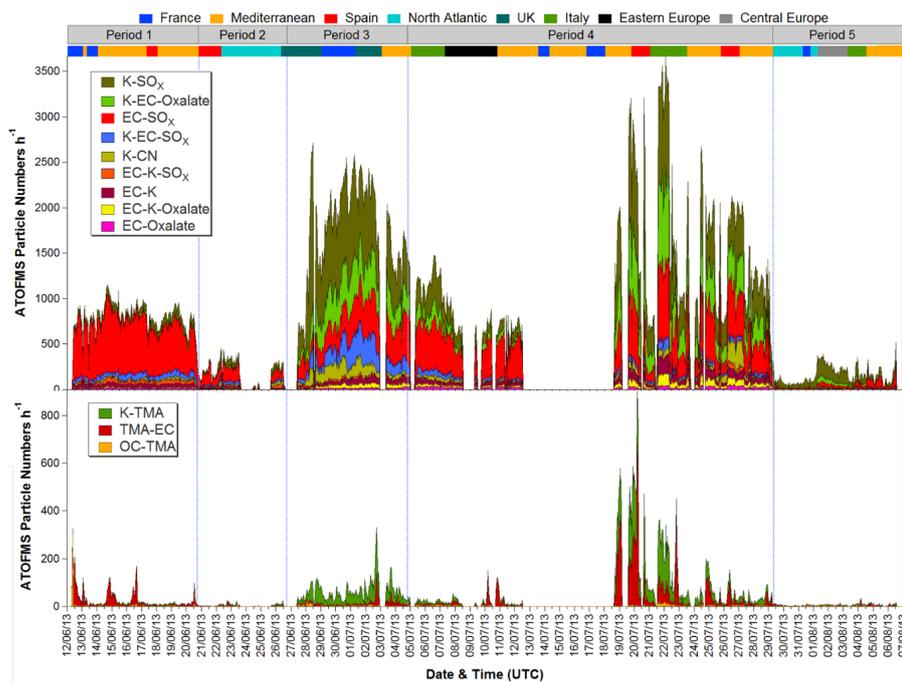
Figure 4. Time series (stacked) of hourly unscaled particle numbers for ATOFMS EC and major K-rich particle classes (top) and Amine classes (bottom) observed during ADRIMED and SAF-MED.

Figure 5. Locations of fires detected by the MODIS sensor on board the Terra and Aqua satellites over 10-day periods during ADRIMED and SAF-MED. Each red dot indicates a location where at least one fire was detected. (http://lance-modis.eosdis.nasa.gov/cgi-bin/imagery/firemaps.cgi)

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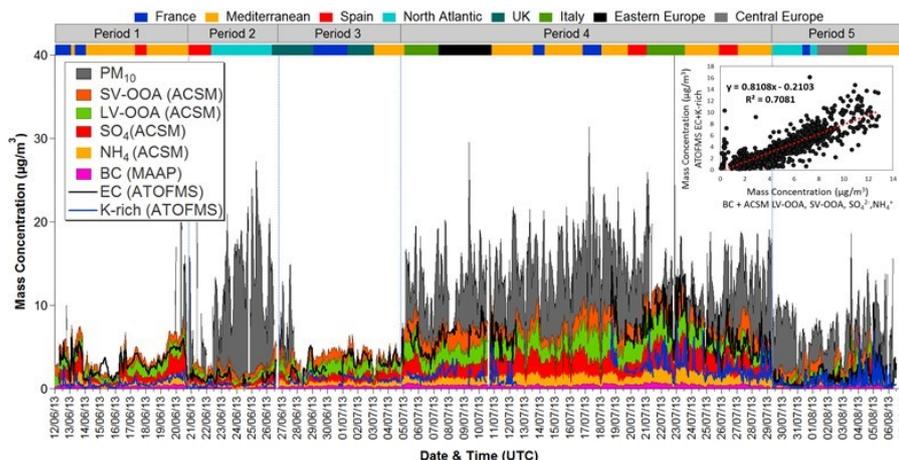
Figure 6. Hourly mass concentrations of PM_{10}, ACSM species (SO_4^{2-}, NH_4^+, organic aerosol factors SV-OOA and LV-OOA), BC and reconstructed ATOFMS EC and K-rich particles. BC and ACSM species profiles are stacked, as are both ATOFMS categories, but separately. This compares the ATOFMS mass concentrations with BC+ACSM species. Inset is a scatter plot of mass concentrations of ATOFMS EC-rich+K-rich particles compared with those for BC+SV-OOA+LV-OOA+SO_4^{2-}+NH_4^+.
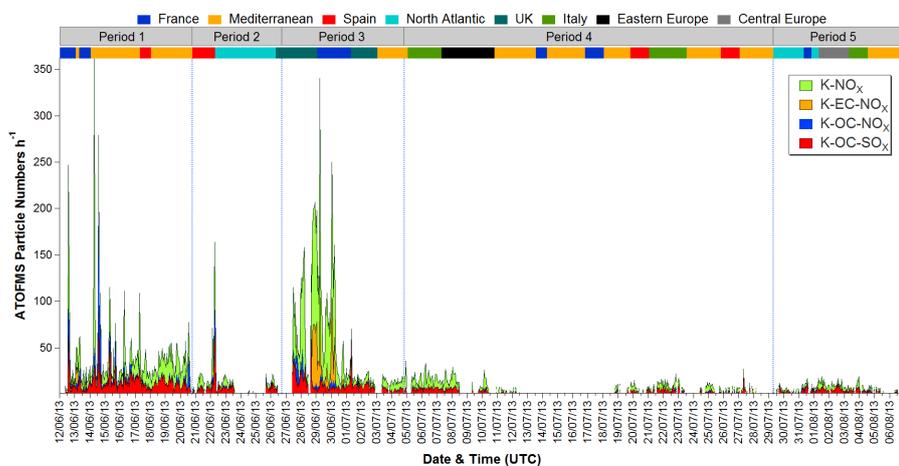
Figure 7. Time series of hourly unscaled particle numbers for ATOFMS particle classes associated with local biomass burning observed during ADRIMED and SAF-MED.
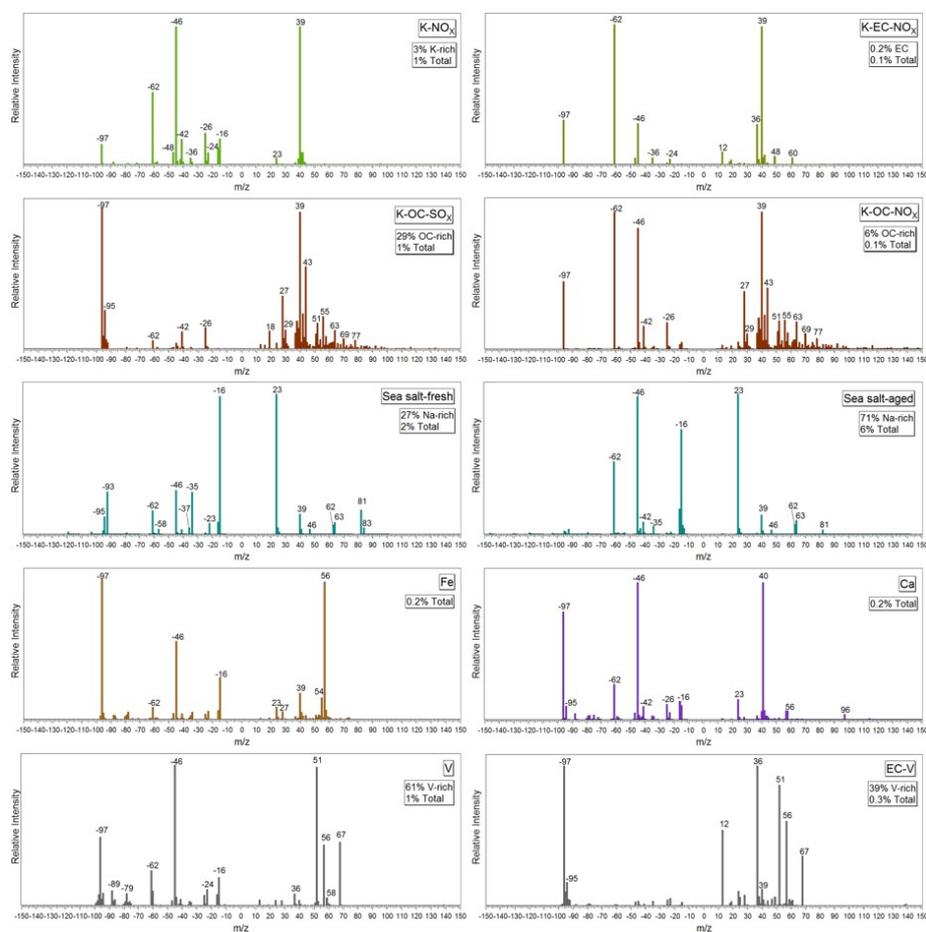
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Figure 8. Average mass spectra for ATOFMS particle classes from local biomass burning, marine, dust and shipping sources during ADRIMED and SAF-MED.
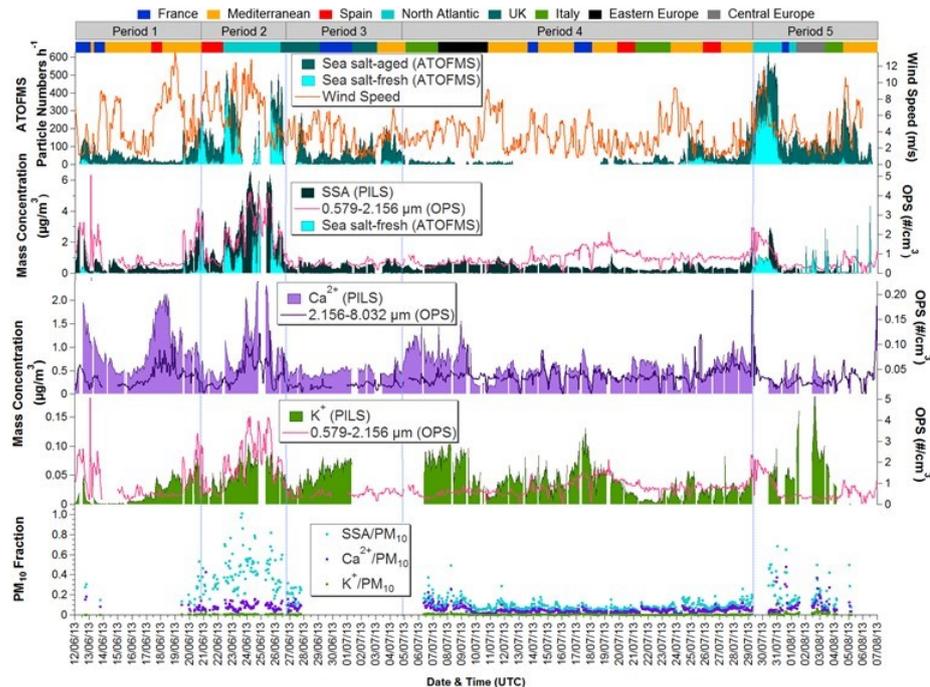
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Figure 9. Time series of hourly ATOFMS sea salt particle numbers, OPS number concentrations, PILS-IC SSA (sea salt aerosol), Ca^+, K^+ and ATOFMS fresh sea salt mass concentrations, and PM_{10} fractions observed during ADRIMED and SAF-MED.
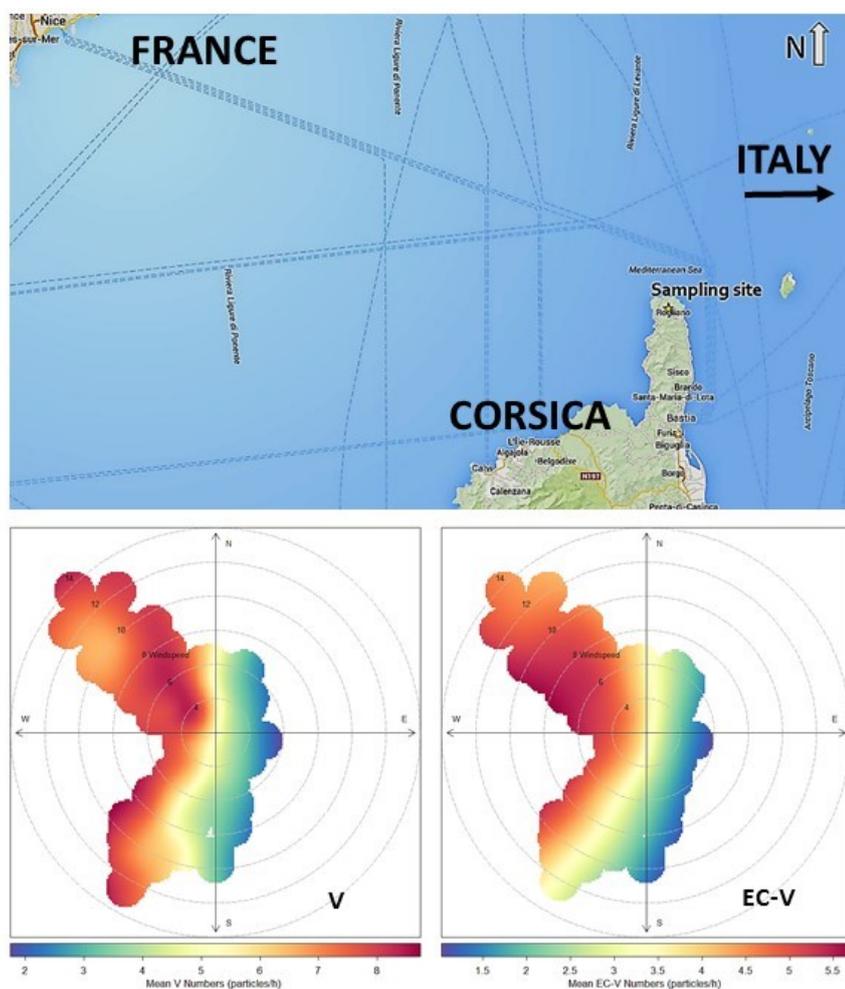
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Figure 10. Passenger ferry lanes around the sampling site on Corsica (top) and wind speed and direction dependences (bottom) for ATOFMS V-rich particles observed during ADRIMED and SAF-MED.
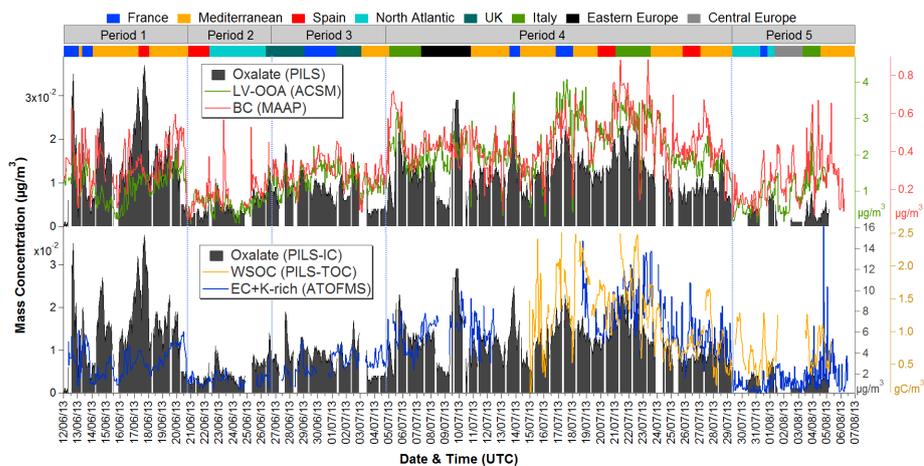
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Figure 11. Hourly mass concentrations of the ACSM factor SV-OOA, BC (black carbon), WSOC (water soluble organic carbon) and ATOFMS EC+K-rich particles during ADRIMED and SAF-MED.
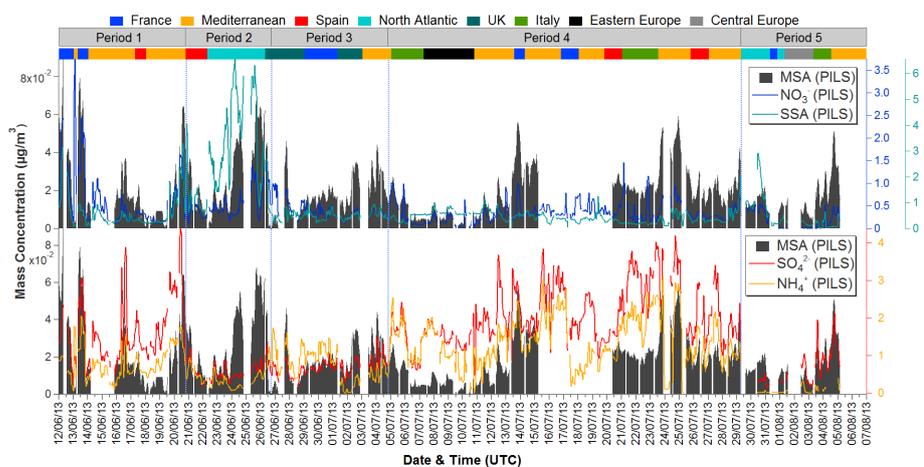

Figure 12. Hourly mass concentrations of PILS-IC species MSA (methanesulfonate), NO_3^-, SSA (sea salt aerosol), SO_4^{2-} and NH_4^+ during ADRIMED and SAF-MED.