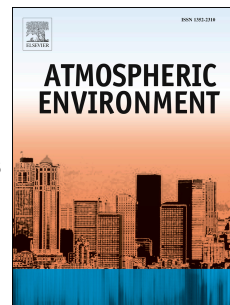


Accepted Manuscript

Source apportionment of PM10 in the Western Mediterranean based on observations from a cruise ship

C. Schembari, M.C. Bove, E. Cuccia, F. Cavalli, J. Hjorth, D. Massabò, S. Nava, R. Udisti, P. Prati



PII: S1352-2310(14)00708-0

DOI: [10.1016/j.atmosenv.2014.09.015](https://doi.org/10.1016/j.atmosenv.2014.09.015)

Reference: AEA 13247

To appear in: *Atmospheric Environment*

Received Date: 13 November 2013

Revised Date: 29 August 2014

Accepted Date: 5 September 2014

Please cite this article as: Schembari, C., Bove, M.C., Cuccia, E., Cavalli, F., Hjorth, J., Massabò, D., Nava, S., Udisti, R., Prati, P., Source apportionment of PM10 in the Western Mediterranean based on observations from a cruise ship, *Atmospheric Environment* (2014), doi: 10.1016/j.atmosenv.2014.09.015.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

1 **Source apportionment of PM₁₀ in the Western Mediterranean based on observations from a cruise**
2 **ship**

3
4 C. Schembari^{1,2}, M.C.Bove², E. Cuccia², F. Cavalli¹, J. Hjorth^{1*}, D. Massabò², S. Nava³, R. Udisti⁴, P.
5 Prati²,

6
7 *1: European Commission, JRC, Institute for Environment and Sustainability, I-21027, Ispra*
8 *(VA), Italy; 2: University of Genoa, Department of Physics and INFN, via Dodecaneso 33,*
9 *16146 Genova, Italy; 3: INFN, via Sansone 1, 50019, Sesto Fiorentino, Italy; 4: Analytical*
10 *Chemistry Section of the Dept. of Chemistry of the University of Florence, via della Lastruccia,*
11 *3-13, 50019 Sesto Fiorentino, Italy.*

12
13 **Abstract**

14 Two intensive PM₁₀ sampling campaigns were performed in the summers of 2009 and 2010 on the ship
15 Costa Pacifica during cruises in the Western Mediterranean. Samples, mainly collected on a hourly basis,
16 were analysed with different techniques (Particle Induced X-Ray Emission, PIXE; Energy Dispersive – X
17 Ray Fluorescence, ED-XRF; Ion Chromatography, IC; Thermo-optical analysis) to retrieve the PM₁₀
18 composition and its time pattern. The data were used for obtaining information about the sources of
19 aerosol, with a focus on ship emissions, through apportionment using chemical marker compounds,
20 correlation analysis and Positive Matrix Factorization (PMF) receptor modeling. For the campaign in
21 2010, 66% of the aerosol sulphate was found to be anthropogenic, only minor contributions of dust and
22 sea salt sulphate were observed while the biogenic contribution, estimated based on the measurements of
23 MSA, was found to be more important (26%), but influenced by large uncertainties. V and Ni were found
24 to be suitable tracers of ship emissions during the campaigns. Four sources of aerosol were resolved by
25 the PMF analysis; the source having the largest impact on PM₁₀, BC and sulphate was identified as a
26 mixed source, comprising emissions from ships. The correlations between sulphate and V and Ni showed
27 the influence of ship emissions on sulphate in marine air masses. For the leg Palma-Tunis. crossing a
28 main ship route, the correlations between aerosol sulphate and V and Ni were particularly strong ($r^2=0.9$
29 for both elements).

30
31 **KEY WORDS:** Mediterranean Sea, PM₁₀, source apportionment, ship emissions, Positive Matrix
32 Factorization.

33
34 * Corresponding author. Tel.: +39 332 789076; fax: +39 332 785837.

35 E-mail address: jens.hjorth@jrc.ec.europa.eu (J. Hjorth).

1. Introduction

The Western Mediterranean Basin is frequently exposed to high levels of air pollutants. This is due to both long range transport and local sources as well as the topography of the coasts and surrounding mountains that favours the development of combined sea breeze-upslope winds with stratifications of pollutants and subsidence over the coast and the sea during daytime in summer (Lelieveld and Dentener, 2000; Velchev, 2011). The area is influenced not only by long-range transport of continental aerosol from the north but also, due to its vicinity to North Africa, Saharan dust can frequently be observed during some periods (Kalivitis *et al.*, 2007), making the Mediterranean Sea an area heavily affected by aerosols.

Another important source of pollution is the intensive ship traffic. The main trace gases emitted from ships are sulphur dioxide and nitrogen oxides, both precursor gases to secondary pollutants. Ship emissions contribute significantly to air pollution in the Mediterranean Basin, particularly their emissions of SO_x: according to the study by Marmer *et al.* (2005), based on an inventory from 1990, 54% of the total sulphate aerosol column burden over the Mediterranean in summer originates from ship emissions. NO_x-emissions from ships are projected to increase in European waters and could be equal to land based sources by 2020, while for SO₂, a decrease in ship emissions are expected to take place in this period due to new legislation (Van Aardenne *et al.*, 2013).

Aerosol measurements and source studies over the basin are sparse and confined mostly to land sites. In particular, data on the contribution of ship emissions are still relatively scarce. Recent observations at the station on Lampedusa (Becagli *et al.*, 2011) produced a lower limit for the contribution of sulphate from ship emission to summer levels of PM₁₀, PM_{2.5} and PM₁ of 3.9%, 8% and 11% respectively. This was based on a direct measurement of the V concentration in PM and on the assumption of a minimum SO₄ to V ratio of 200.

In order to contribute to filling the gap of observations in the Mediterranean basin and to gain more insight into atmospheric dynamical and chemical mechanisms, the Joint Research Centre of the European Commission (JRC) performs ship borne measurements over the Mediterranean Sea. In the framework of a collaboration agreement between the JRC and Costa Crociere, measurements of air pollutants have been carried out since 2006 on cruise ships following a regular route in the Western Mediterranean from spring to autumn.

Two campaigns were carried out in 2009 and 2010 with the scope of carrying out a source apportionment analysis on the aerosol sampled along the route of the cruise ship. During the two campaigns in 2009 and 2010, in a joint experiment with the Department of Physics of the University of Genoa, a two-stage streaker sampler (Formenti *et al.*, 1996, and references therein) was installed on the ship. The elemental composition of the fine and coarse fraction of PM₁₀, separately collected by the streaker on an hourly basis, was measured by Ion Beam Analysis (i.e. by PIXE: Particle Induced X-Ray Emission) at the accelerator facility of INFN-Florence (Mandò, 2009; Lucarelli *et al.*, 2013). In addition, filter samples of PM₁₀ aerosol were collected and analyzed for soluble ions by Ion Chromatography and for organic and elemental carbon by a thermal optical transmittance (TOT) method. This dataset was

73 used for an investigation of the influence of ship emissions on the composition of aerosols over the sea
74 through a receptor model approach as well as analyses based on chemical marker compounds,
75 characterization of filter samples by calculation of back trajectories and on observed correlations between
76 the aerosol components.

77 78 **2. Material and Methods**

79 *2.1 Equipment for the long-term monitoring activity*

80 The monitoring station, placed in a cabin at the front of the top deck of the ship “*Costa Pacifica*”
81 permits to perform continuous measurements of NO_x, SO₂, O₃ and Black Carbon (technical details in
82 Schembari *et al.*, 2012). Black Carbon (BC) is measured by an Aethalometer (AE 21, 2 wavelengths,
83 Magee Scientific, USA). The Aethalometer and the corrections applied to the measurements were
84 discussed by Schembari *et al.* (2012).

85 Previous experiments (Sokolik and Toon, 1999) have shown that dust appreciably absorbs at
86 wavelengths below 600 nm. Thus, if the aerosol contains, in addition to BC, large amounts of dust, the
87 BC concentration values calculated at $\lambda = 370$ nm are expected to be enhanced with respect to those
88 deduced at $\lambda = 880$ nm, due to the presence of the UV-absorbing material. Based on observations of the
89 concentration ratio of BC ($\lambda=370$) to BC($\lambda=880$) during dust episodes, a ratio of 1.4 was fixed as
90 threshold to identify a dust episode. Also satellite image (<http://AQUA.nasa.gov>, <http://TERRA.nasa.gov>)
91 and dust surface concentrations maps from the on-line DREAM model (Dust Regional Atmospheric
92 Model, <http://www.bsc.es/projects/earthscience/DREAM>) were taken into account. BC measurements
93 that were found to be influenced by the presence of dust were not included in the analysis of the data.

94 *2.2 Equipment for the intensive monitoring campaigns*

95 In two periods, 24-31 August 2009 and 7-21 June 2010, intensive aerosol sampling campaigns were
96 carried out. The sampling strategy was based on a two-stage continuous streaker sampler. With the
97 streaker sampler (Formenti *et al.*, 1996), particles are separated at different stages: a pre-impactor
98 removes particles with aerodynamic diameter (D_{ae}) greater than 10 μm from the incoming air; a thin
99 Kapton foil, coated with APIEZON grease to prevent bouncing, collects particles with $2.5 \mu\text{m} < D_{ae} < 10$
100 μm and a Nucleopore polycarbonate filter intercepts all smaller particles. The two collecting plates are
101 paired on a cartridge, which rotates at constant speed (about 1,8° per hour), producing a circular
102 continuous deposition of particulate matter on both stages (the “streak”). The streaker sampler has been
103 appositely designed for PIXE analysis. The main limit of this instrument is the impossibility to weigh the
104 collected matter and therefore to measure directly the total concentration of fine and coarse PM10. A total
105 of three couples of streaker frames (one in 2009 and two in 2010) were sampled during the intensive
106 campaigns (one per week).

107 PIXE analysis of the streaker frames was performed at the HVEE 3 MV Tandatron accelerator,
108 installed at the LABEC (LABoratorio BENi Culturali) laboratory of INFN in Florence (Calzolari *et al.*,
109 2006; Lucarelli *et al.*, 2013). The streak is analyzed point by point, using a beam size that corresponds to
110 one hour of aerosol sampling. The Minimum Detection Limits (MDL), estimated for PIXE analysis at 1 σ

111 level, are $\sim 10 \text{ ng m}^{-3}$ for low-Z elements and $\sim 1 \text{ ng m}^{-3}$ for medium-high Z elements, while the
112 uncertainty of the elemental concentrations are determined as a sum of independent uncertainties on
113 standard sample thickness (5%), peak areas (from 2 to 20% or higher when concentrations approach
114 MDLs) and sampling parameters (of the order of a few percent).

115 From August 24 to 31, 2009 and June 7 to 14, 2010, PM10 samples were also collected on quartz
116 filters (47 mm diameter, flow rate $2.3 \text{ m}^3 \text{ h}^{-1}$) using Sven Leckel Ingenieurburo (<http://www.leckel.de/>)
117 sequential samplers placed on the top of the cabin where the monitoring station is, and nearby the
118 streaker sampler. This sampling was carried out on a variable time basis: the sampler was started 1 hour
119 after the departure from each harbor and stopped 1 hour before the arrival in the next port. Each leg was
120 then divided in periods of about 6 hours with one filter sampled per each period, this resulted in a variable
121 number of filters per leg and in a total of 15 filters. Samples were subsequently analyzed by ED-XRF
122 (Energy Dispersive – X Ray Fluorescence) at the Department of Physics of Genoa (Ariola *et al.*, 2006),
123 by a thermo-optical method with a SUNSET dual Optical Carbonaceous analyzer, to determine the OC-
124 EC (respectively, Organic and Elemental Carbon) concentrations following the EUSAAR-2 protocol
125 (Cavalli *et al.*, 2010). and by Ion Chromatography at the JRC (EMEP Laboratory). A comparison of PIXE
126 and ED-XRF results can be found in the Appendix (*electronic supplementary material*, Figure E1).

127 Main ions (Na^+ , Cl^- , Mg^{2+} , K^+ , Ca^{2+} , NO_3^- , NH_4^+ , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$) were analyzed by Ion
128 Chromatography (IC, Dionex DX 120 with electrochemical eluent suppression) with an uncertainty of \pm
129 10%, after extraction of the soluble species in an aliquot of 16 mm \varnothing in 20 ml 18.2 M Ω cm resistivity
130 water (Millipore mQ). IC and PIXE measurements are compared in the Appendix (Figure E2).

131 The MSA (methanesulfonic acid) concentrations for the 2010 sampling campaign were measured by
132 suppressed-conductivity, gradient elution, ion chromatography at the Dept. of Chemistry, University of
133 Florence (Udisti *et al.*, 2012).

134 In Table 1, the laboratory analyses performed after the 2009 and 2010 filter campaigns, are
135 summarized. In the analysis of the filters sampled in the 2009 campaign, positive organic
136 artifacts/contaminations on the quartz filters were found and the OC concentrations could not be
137 evaluated; therefore EC values only were retained.

138 The 2010 experimental set up was completed with an optical particle counter (GRIMM 1.108) to
139 measure the number of particles per unit volume and to estimate the mass concentration. The
140 reproducibility of the OPC in particle counting is $\pm 2\%$ (Putaud *et al.*, 2004).

141 Information about meteorological parameters (wind speed and direction, temperature, humidity with
142 10 min intervals from the meteorological station of the ship) and information about the ships position,
143 speed and sailing direction, were available. This information was used to identify situations where the
144 measurements might be influenced by emissions from Costa Pacifica: in all cases where the inlets of the
145 measurement station were downwind of the stack of the ship within an angle of ± 40 degrees the data
146 were discarded because of the risk of contamination from the stack.

147 During summer–autumn 2009 the route of the ship was Civitavecchia-Savona-Barcelona-Palma
148 de Mallorca-Tunis (La Golette)-Malta (Valletta)-Palermo-Civitavecchia. During the same seasons in 2010
149 the route was Civitavecchia-Savona-Barcelona-Palma de Mallorca-Tunis (La Golette)-Malta (Valletta)-
150 Catania-Civitavecchia (see Figure 1).

151 2.3 Calculation of aerosol composition

152 Concentration values of SO_4^{2-} , NH_4^+ and NO_3^- were directly retrieved from IC analysis, while all
153 the other aerosol components were obtained from the combination of analyzed species and conversion
154 factors: the *sea salt* component was calculated from the measured Na and Cl concentration values
155 (Seinfeld and Pandis, 1998), taking into account the seawater composition, the mineral *dust* component
156 was obtained by multiplication of nssCa^{2+} (nssCa^{2+} , non-sea-salt calcium, i.e. the amount of Ca in excess
157 of the contribution from sea salt) by 5.6, the value retrieved by Putaud *et al.* (2004) outside of Saharan
158 dust events, since the nssCa^{2+} concentration was found to be in the range of concentrations observed in
159 the absence of such dust events. Organic Matter (OM) was estimated as $\text{OM}=1.4 * \text{OC}$, applying the
160 conversion factor from Turpin and Lim, 2001.

161 The contributions of different sources to the sulphate content was estimated based on marker compounds
162 as described in the Appendix (Table E4).

163 2.4 Analysis by Positive Matrix Factorization.

164 Time series of elemental concentrations BC and PM10 (obtained by the OPC) collected during
165 the two cruises were treated by Positive Matrix Factorization (PMF) to identify and characterize the major
166 PM10 sources along the ship route. Most often, PMF, as in general all the receptor models, is used to
167 analyze data collected at a fixed site (the “receptor”) where concentration values of PM components and
168 of gaseous pollutants are modulated by meteorological conditions and source emission patterns. In the
169 case of a moving receptor (the ship), the concentrations of PM components and gaseous pollutants are
170 modulated also by the change in the coordinates. In spite of this additional complexity, PMF analysis has
171 previously been successfully applied to measurements performed from ships (Bhanuprasad *et al.*, 2008;
172 Moreno *et al.*, 2010).

173 PMF has been described in detail by its developers (Paatero and Tapper, 1994; Paatero, 1997)
174 and has been adopted in several studies for PM receptor modelling and for the assessment of particle
175 source contributions (e.g. Kim *et al.*, 2001; Liu *et al.*, 2003; Ramadan *et al.*, 2003; Qin *et al.*, 2006). In
176 this work, the PMF-2 version and the methodology described in Cuccia *et al.* (2010), were used. The
177 Polissar *et al.* (1998) procedure was used to assign measured data and associated uncertainties as the PMF
178 input data.

179 2.6 Calculation of back trajectories

180 Backtrajectories were calculated using the US NOAA Hysplit website
181 (<http://ready.arl.noaa.gov/HYSPLIT.php>), with GDAS meteorological data (1x1 degree horizontal
182 resolution, 23 vertical layers). For each filter, 5 days backtrajectories arriving at 50 m and at 500 m above
183 sea level were calculated for the positions where the filter sampling started and ended plus at the position

184 halfway through the sampling period. Based on these trajectories, samples were classified as ‘marine’ if
185 the air masses had been over the sea for at least the last 48 hours.

186

187 **3. Results and discussion**

188 *3.1 Meteorological conditions*

189 Weather conditions during the sampling campaigns were characterized by complex situations
190 with anti-cyclonic systems over the Western Mediterranean (see examples of synoptic maps in Figure E3
191 in the Appendix with *electronic supplementary material*). The anticyclonic system was less stable in 2010
192 than in 2009 with lower temperatures (22 °C vs. 27 °C average temperature) and stronger winds.

193 *3.2 Exclusion of non-representative data*

194 Between the 17th and 19th June a particular episode with a large increase in Al, Si, K, Ca, Fe, Ti,
195 BC concentration values (see *Figure E4 in the electronic supplementary material*), happened when the
196 ship was sailing from Tunis to Catania. Back-trajectories, computed with the NOAA Hysplit Model show
197 air masses starting near the African coast and passing on the Messina Strait, which may explain the large
198 increase of crustal and anthropogenic species during this period. This time period was not considered in
199 the PMF analysis (see below) because not being representative of the average PM composition.

200 *3.3 PM10 apportionment*

201 *3.3.1 Apportionment based on chemical marker compounds*

202 The chemical composition of the PM₁₀ samples collected during the cruise in 2010, calculated as
203 discussed in Chapter 2.3, is shown in Figure 2. Detailed information about measured concentrations are
204 given in the Appendix (Tables E1-E3).

205 It is seen that sulphate is generally the most abundant species (apart from samples with high
206 levels of sea salt), accounting for 38% and 44% of the measured components in 2009 and 2010,
207 respectively. Sulphur, which concentrations were well correlated with those of soluble sulphate measured
208 by Ion Chromatography Analysis ($R^2=0.8$ in 2009 and $R^2=0.9$ in 2010), was predominantly found in the
209 fine fraction (with S_{fine} being about 90% of total S) which thus appears to have its origin predominantly
210 from secondary formation in the atmosphere and combustion. The highest contributions of sulphate to
211 aerosol mass were found over the sea, where the average contribution by mass is 52%. Organic aerosol is
212 only a minor fraction but it should be noticed that filter sampling of organic aerosol can be subject to
213 severe artifacts (Turpin et al., 2000).

214 The results of the present study can be compared with another study performed along a route
215 across the Mediterranean from Barcelona to Istanbul during March and April, 2008 (Moreno et al., 2010).
216 The sea salt component seems to be similar while dust and Elementary and Organic Carbon components
217 are higher and the sulphate component is lower than our data. These differences may be related to
218 different meteorological conditions..

219 The total sulphate can be divided in specific components (sea salt sulphate; non sea salt sulphate:
220 crustal, biogenic, anthropogenic) and calculated using marker compounds as described in the Appendix

221 (Table E4); the results of such calculations for the 7-14 June 2010 cruise are reported in Figure 3. The
222 nss-sulphate of biogenic origin (i.e. from the oxidation of dimethylsulfide, DMS) was derived from the
223 measurements of MSA in the samples through the relation found by Bates *et al.* (1992), assuming an
224 average ambient temperature of 22 °C; which gives a value of 0.09 for the ratio, by mass, of MSA/SO₄,
225 where SO₄ here refers to sulphate formed by the oxidation of DMS. Assuming an uncertainty on the
226 average temperature of +/-4 °C, MSA/SO₄ is found to be in the range 0.03-0.15. This provides a best
227 estimate of sulphate of biogenic origin but it must be kept in mind that other factors than temperature
228 appear to influence the ratio between the MSA and sulphate yields by the oxidation of DMS (Castebrunet
229 *et al.*, 2009), and this adds an additional uncertainty to the estimate.

230 Observations made by Udisti *et al.* (unpublished data) at the site of Leghorn (Livorno, IT) are
231 congruent with the assumption of a ratio close to 0.1 between the yields of MSA and sulphate by the
232 atmospheric oxidation of DMS: It was found that for increasing MSA concentrations the MSA/SO₄ trend
233 approached a limit value of approximately 0.1. Assuming that biogenic emissions at the highest MSA
234 concentrations is the dominating source of sulphate, this could be taken as an estimate of the MSA/SO₄
235 ratio by the atmospheric oxidation of DMS at this site in the Western Mediterranean. The measurements
236 were carried out during the period March 2009 to March 2010.

237 The major contribution to SO₄ was from nssSO₄ of anthropogenic origin. The contribution from
238 crustal material, as estimated by this approach, is below 1%.

239 3.3.2 Correlations between S and other species, evidence of the impact of ship emissions

240 This analysis was performed on samples obtained outside of harbours as described in the
241 Appendix.

242 In the following, correlations with r exceeding 0.7 are denoted as 'strong'. When 'coarse' or
243 'fine' is not specified, the values refer to the sum of the two collecting plates in the streaker.

244 The PIXE correlation matrices for both years show strong and highly significant (p<0.005)
245 correlations of S_{coarse} with Na and Mg which clearly must be assigned to the contribution by sea-salt
246 which has relatively high contents of both Mg and S (12% and 8% of the Na content, respectively, CRC,
247 2000). In 2010 S_{coarse} was also strongly correlated to Si, Al and K_{coarse} which must be explained by the
248 contribution from mineral dust.

249 For what concerns the entire dataset, in neither of the two campaigns was S_{fine} found to be
250 strongly correlated to any other element. For what concerns the ionic species, nssSO₄ is found to be
251 strongly correlated to NH₄, which must be caused by a relevant contribution of ammonium sulphate to
252 nssSO₄. The correlations of MSA with the sulphur species are not significant so the correlation matrices
253 do not give clear evidence of a biogenic influence on these. It should be noted, that there are less data
254 points for the chemical species so it is more unlikely to observe statistically significant correlations than
255 in the PIXE data.

256 A fraction of the particulate matter directly emitted from a ship-engine consists of metal oxides,
257 originating from trace metal impurities in the fuel and lubricant oil; among these are V and Ni, that are

258 found to be typical constituents of ship emissions (Viana *et al.*, 2009 and references therein). These two
259 elements were predominantly found in the fine fraction and almost totally absent in the coarse fraction
260 sampled on the streaker during the two cruises. The V to Ni concentration ratio found in literature for
261 particles formed by heavy fuel oil combustion, lies typically in the range 2-5 (e.g. Becagli *et al.*, 2011;
262 Viana *et al.*, 2009; Mazzei *et al.*, 2008). The mean V to Ni concentration ratios measured along the
263 cruises were generally close to 3, apart from the legs Savona-Barcelona and Barcelona Palma in 2009,
264 where they were between 1 and 2. V and Ni were strongly correlated both years. Dust particles too
265 contain vanadium and nickel (Viana *et al.*, 2009; Moreno *et al.*, 2010); however they are mainly found in
266 the coarse fraction (Van Dingenen *et al.*, 2004) and as, moreover, the correlation with Si was very weak,
267 it was concluded that these elements were suitable tracers of anthropogenic emissions from combustion of
268 undistilled liquid fuels. This is in line with the observations made by Moreno *et al.* (2010).

269 V and Ni show significant correlations to BC and SO₂ in 2010 while these correlations were
270 much weaker in 2009.

271 For the year 2010, a sufficient number of filters (8) with 'marine' trajectories were available to
272 allow observing significant correlations. In this case the correlation between V, Ni and nssSO₄ is
273 stronger and the p-value is below 5%. NssSO₄ is also found to be strongly correlated with BC. The
274 positive correlations with SO₂ or NO_x are not found in this case while the correlation with BC remains,
275 This difference may be ascribed to a longer atmospheric lifetime of BC than of SO₂ and NO_x.

276 The square of the Pearson's correlation coefficient indicates how much of the observed variation
277 of a variable can be explained by the variation of another variable (assuming a linear dependence). Thus,
278 from the observed correlations of V and Ni with S it can be deduced that during the cruise in 2010, 24%
279 or 26% of the observed variations in the S-content of the aerosol samples could be explained by the
280 variation in V or Ni, respectively. For 2009 these correlations are not significant. For sea-trajectories
281 only, correlations of V and Ni with S are much stronger, with r^2 values of 0.5 for both of these
282 correlations; looking at the chemical measurements, variations in V and Ni explain 67% and 52% of the
283 variations of nssSO₄, respectively. Thus, as it may be expected, sea-trajectories show the strongest
284 evidence of the influence of ship emissions

285 In the leg Palma-Tunis, where the ship crosses a main naval route in the Mediterranean Basin, a
286 strong correlation between S_{fine}, V and Ni was found. Peak values of V, Ni and S_{fine} are found to be
287 coinciding also in other parts of the route of Costa Pacifica (Fig. E5 in the Appendix). These observations
288 support the notion that ship emissions are an important source of S_{fine} in parts of the route.

289 3.3.3 PMF analysis

290 The datasets used as input to PMF (one for the 2009 and one for the 2010 cruise), included the
291 most abundant elements obtained by PIXE analysis for the sea legs during both the 2009 and 2010 cruises
292 with a total of 273 hourly values for each species (hours when the ship was entering or stopping in the
293 harbours were excluded). The fine and coarse fraction of Na, Mg, Al, Si, Cl, K, Ca, Fe, V and Ni were
294 summed to get hourly concentration values in PM10 while only S was included in the PMF data set

295 divided in its fine (S_f) and coarse (S_c) fraction since the two time series turned out not to be correlated.
296 This is not surprising since S in the coarse fraction is expected to be dominated by $ssSO_4$ and mineral dust
297 while in the fine fraction S is likely to come from combustion sources and gas phase oxidation of SO_2 .
298 The two datasets were completed including the time series of hourly average BC concentration values
299 and PM10 mass concentration (from the OPC).

300 Four sources were resolved with both of the data sets, and labelled, according to their
301 characteristic tracers, as: *Sea Salt* (Na, Cl), *Combustion* (S_{fine} , V, Ni, BC), *Crustal* (Al, Si), *Not Identified*
302 (Figure 4 for the 2010 cruise and Figure E6 in the Appendix for the 2009 cruise):

303 Sea Salt: the Cl to Na concentration ratio is around 0.9 (average of 2009 and 2010 cruises),
304 which is smaller than the literature value of 1.8 (Seinfeld and Pandis, 1998). This can be due to Cl
305 evaporation in the atmosphere. It is well known that the Cl concentration can diminish through reactions
306 between the marine aerosol and nitric acid (Seinfeld and Pandis, 1998), sulphuric acid (Singh *et al.*, 1995)
307 and SO_2 (Sievering *et al.*, 1991); the very low Cl to Na value found in this study may be explained by the
308 low concentration of sea salt compared to acidic components of the aerosol. Most of S_c is found to be
309 associated with sea salt, however also S_{fine} and crustal elements, mainly during the 2009 cruise, are seen
310 in the profile.

311 Combustion: the V to Ni concentration ratio in the profile is the same for the two campaigns,
312 $\sim 2.9 \pm 0.4$, in agreement with the values reported in the literature as being typical of ship emissions, as
313 discussed above. This points to a strong contribution of ship emissions to this source which, however,
314 also has relevant contributions from elements that cannot be assigned to ship emissions (K, Ca, Fe). The
315 analysis does not allow distinguishing between secondary and primary sources of sulphate, however for
316 the case of ship emissions several studies have shown that sulphur is emitted predominantly as SO_2 ,
317 primary sulphate emissions are in the range 1-6% of the fuel sulphur content (Alfoldy *et al.*, 2013). The
318 source profile is rich in S with an S_f to V mass concentration ratio in the PMF profile of $(1.05 \pm$
319 $0.06) \times 10^2$, which corresponds to a sulphate to V concentration ratio of around 300. For comparison,
320 average sulphate to V mass ratios of 16 and 24 were found in particles emitted from ships at the harbour
321 of Rotterdam (Alfoldy *et al.*, 2013). Thus it appears that only a minor part of S_f may be assigned to
322 primary ship emissions of particles.

323 Crustal: The concentration ratios in the profile are partially different from the literature values of
324 average crustal abundance. In both of the years, the Si to Al ratio (2.3 for 2009, 1.7 for 2010) are similar,
325 but less than the average literature value (3.4, Mason, 1966); the Ca to Al ratio found in 2010 (1.1) is
326 higher than the reference value (0.44); this may be due to a contamination by aerosol of anthropogenic
327 origin or to the fact that mineral dust may well have a composition different from that of the crustal
328 average. In fact, it is known that the Si/Al ratio in aerosols is lower than the Mason value for rocks due to
329 the presence of clay minerals (Rahn, 1976).

330 Not Identified: the profile is characterized by relatively elevated concentrations of Na, Al, Si, S,
331 K, Ca, Fe and BC. It looks therefore as a combination of aged marine aerosol (high EV of Na and Mg,

332 low for Cl) and anthropogenic particulate matter. Probably this cannot be considered as a real source, but
333 rather as a residual sum of the different sources present in the area that the model does not manage to
334 distinguish.

335 The PM10 apportionment in each leg during the 2010 cruise is shown in Figure 5 while Figure 6
336 shows the average apportionment for single elements and BC. It turns out that *Combustion* contributes,
337 on average, to about 55% and 63%, respectively of PM10 and BC (Figures 6,7). It is worthwhile
338 repeating that this source most likely contains an important secondary component. *Sea salt* constitutes on
339 average 18% of PM10. The contribution of mineral dust is low, however it should be noted that this
340 contribution may be important under some conditions, e.g. during the episode from 17-19 June
341 The apportionment was not possible with the 2009 data since no information was available on PM10
342 concentration during that cruise, however the four factors extracted by PMF are reported in relative units
343 in Figure E6 in the electronic supplementary material for comparison.

344 3.3.4 Comparison of PMF and “chemical” apportionment

345 The PMF apportionment of sulphur (sum of fine and coarse fractions, S_f and S_c) can be compared
346 with the percentual contributions to total sulphate obtained by the IC analysis of the quartz filters sampled
347 from 7th to 14th June 2010 (one week only, as MSA was not measured in 2009). Results are given in
348 Table 2 for each leg and for the whole week. The two approaches show a good agreement for the sulphate
349 of marine origin while the PMF apportionment gives significantly higher contributions from the crustal
350 part than what is found by the chemical apportionment, where the contribution of mineral dust was
351 estimated as being negligible because of the low average content of sulphate in crustal material. This
352 discrepancy can be explained by the fact that the sulphur content of atmospheric mineral dust can be
353 strongly influenced by sulphate coatings, generated e.g. by in-cloud processes (Usher *et al.*, 2003). The S
354 fraction attributed by PMF to the *Combustion* source is comparable to the sum of the anthropogenic and
355 biogenic sulphate derived with the chemical analysis (~ 80 - 90%, for the first week of the 2010 cruise).
356 This is not surprising since the PMF data set could not include any tracer of biogenic sulphate production
357 and thus cannot resolve this specific contribution.

358

359 4. Conclusions

360 The study has provided information about the sources of aerosol collected during the two
361 summer campaigns in the Western Mediterranean through apportionment using chemical marker
362 compounds, correlation analysis and PMF receptor modeling. A main scope of the analysis was to
363 quantify the contribution of ship emissions to sulphate in particles. Sulphate was found to account, in
364 average, for around 40% of the total particle mass in the two campaigns

365 The analysis based on chemical marker compounds showed for the year 2010 only minor
366 contributions of dust and sea salt to sulphate while the biogenic contribution, estimated based on the
367 measurements of MSA, was found to be more important (26%), but influenced by large uncertainties.

368 Most of the sulphate (66%) could not be explained by natural sources and was thus assigned to
369 anthropogenic influences.

370 V and Ni were found to be suitable tracers for emissions stemming from burning of heavy fuel
371 oil and they were found in a ratio typical of ship emissions. The correlations of V and Ni with sulphate
372 showed a strong influence of ship emissions on the leg Palma-Tunis, crossing a main ship route ($r^2=0.9$),
373 and similar impacts in other parts of the route. However, looking at the entire dataset and excluding local
374 plumes from nearby sources, the impact of ship emissions on sulphate according to this analysis was less
375 pronounced. Restricting the dataset to trajectories passing over the sea for the last 48 hours lead to a
376 considerable increase in the observed impact of ship emissions.

377 The hourly data set was analyzed by PMF and four sources were resolved with both the data
378 sets, and labelled, according to their characteristic tracers, as: *Sea Salt* (Na, Cl), *Combustion* (S_{fine} , V, Ni),
379 *Crustal* (Al, Si), *Not Identified*. '*Combustion*', which shows evidence of a contribution by ship emissions,
380 was found to contribute by 55%, 63% and 80% to PM10, BC and sulphate respectively.

381 Summarizing the results it can be concluded that ship emissions were found to be an important
382 source of aerosols in the Western Mediterranean, however their impacts show large spatial and temporal
383 variations.

384

385 **Acknowledgements**

386 Thanks are due to Costa Crociere and to the captain and crew of Costa Pacifica. The technical
387 assistance of V. Ariola of the Department of Physics of the University of Genoa, of Rosanna Passarella
388 and Kevin Douglas of JRC and of the whole staff of the INFN-LABEC laboratory in Florence has been
389 highly appreciated. This work has been partially supported by INFN under the grant for the NUMEN
390 experiment.

391

392 **References**

393

394 Alfoldy, B., J. Balzani Lööv, F. Lagler, J. Mellqvist, N. Berg, J. Beecken, H. Weststrate, J. Duyzer, L. Bencs, B. Horemans, F.
395 Cavalli, J.-P. Putaud, G. Janssens-Maenhout, A. Pinter Csordas, R. Van Grieken, A. Borowiak, J. Hjorth, 2013. Measurements of air
396 pollution emission factors for marine transportation, *Atmos. Meas. Tech. Discuss.*, 6 (7), 1777-1791,
397 <http://www.atmos-meas-tech.net/6/1777/2013/amt-6-1777-2013.html>

398

399 Ariola, V., D'Alessandro, A., Lucarelli, F., Marazzan, G., Mazzei, F., Nava, S., Garcia Orellana, I., Prati, P., Valli, G., Vecchi, R.,
400 Zucchiatti, A., 2006. Elemental characterization of PM10, PM2.5 and PM1 in the town of Genoa (Italy). *Chemosphere* 62, 226 –
401 232.

402

403 Bates T., Calhoun J., Wang Y., Quinn P., 1992. Variations in the methanesulphonate to sulphate molar ratio in submicrometer
404 marine aerosol particles over the south pacific ocean. *Journal of Geophysical research*, 97, 9859-9865.

405

406 Becagli, S., Sferlazzo, D. M., pace, G., di Sarra, A., Bommarito, C., Calzolari, G., Ghedini, C., Lucarelli, F., Meloni, D., Monteleone,
407 F., Severi, M., Traversi, R., Udisti, R. 2011. Evidence for ships emissions in the Central Mediterranean Sea from aerosol chemical
408 analyses at the Island of Lampedusa. *ACPD* 11, 29915-29947.

409

410 Bhanuprasad, S.G., Venkataraman, C., Bhushan, M., 2008. Positive matrix factor- ization and trajectory modelling for source
411 identification: a new look at Indian Ocean experiment tship observations. *Atmospheric Environment*, 42, 4836-4852.

412

413 Calzolari, G., Chiari, M., García Orellana, I., Lucarelli, F., Migliori, A., Nava, S., Taccetti, F., 2006. The new external beam facility
414 for environmental studies at the Tandatron accelerator of LABEC. *Nuclear Instruments and Methods B249* (1-2), 928-931.

415

416 Castebrunet, H., Martinerie, P., Genthon, C., Cosme, E, 2009. A three-dimensional model study of methanesulphonic acid to non
417 sea salt sulphate ratio at mid and high-southern latitudes, *Atmos. Chem. Phys.*, 9, 9449–9469, [www.atmos-chem-](http://www.atmos-chem-phys.net/9/9449/2009/)
418 [phys.net/9/9449/2009/](http://www.atmos-chem-phys.net/9/9449/2009/)

419

420 Cavalli, F., Viana, M., Yttri, K.E., Genberg, J.; Putaud, J.P, 2010. Towards a standardised thermal-optical protocol for measuring
421 atmospheric organic and elemental carbon: the EUSAAR protocol. *Atmospheric Measurement Techniques* 3, , 79-89.

422

423 Chiari, M., Lucarelli, F., Mazzei, F., Nava, S., Paperetti, L., Prati, P., Valli, G., Vecchi, R., 2005. Airborne particulate matter
424 characterization in an industrial district near Florence, by PIXE and PESA. *X ray Spectrometry* 34, 323 -329.

425

426 Cuccia, E., Bernardoni, V., MassabòD., Prati, P., Valli, G., Vecchi, R., 2010. An alternative way to determine the size distribution of
427 airborne particulate matter. *Atmospheric Environment* 44, 3304-3313.

428

429 CRC handbook of chemisrry and physics, 81st edition, 2000-2001, Editor D.R. Linde, CRC Press, 2000.

430

431 Formenti, P., Prati, P., Zucchiatti, A., Lucarelli, F., Mandò, P.A. , 1996. Aereosol study in the Genova area via a two stage streaker
432 and PIXE analysis. *Nuclear Instruments and Methods B113*, 359-362.

433

434 Kalivitis, N., Gerasopoulos, E., Vrekoussis, M., Kouvarakis, G., Kubilay, N., Hatzianastassiou, N., Vardavas, I., Mihalopoulos, N.,
435 2007. Dust transport over the eastern Mediterranean derived from Total Ozone Mapping Spectrometer, Aerosol Robotic Network,
436 and surface measurements. *J. Geophys. Res.* 112, D03202. doi:10.1029/2006JD007510.

437

- 438 Kim, E., Larson, T.V., Hopke, P.K., Slaughter, C., Sheppard, L.E., Claiborn, C., 2001. Source identification of PM_{2.5} in an arid
439 Northwest U.S. City by positive matrix factorization. *Atmospheric Research* 66, 291-305.
- 440
- 441 Lelieveld J., Berresheim H., Borrmann S., Crutzen P.J., Dentener F., Global air pollution crossroads over the Mediterranean.,
442 *Science* 298(5594), 794-799
- 443
- 444 Liu, W., Hopke, P.K., Han, Y.J., Yi, S.M, Holsen, T.M., Cybart, S., Kozlowski, K., Miligan, M., 2003. Application of receptor
445 modeling to atmospheric constituents at Potsdam and Stockton, NY. *Atmospheric Environment*, 37, 4997-5007.
- 446
- 447 Lucarelli, F., Calzolari, G., Chiari, M., Giannoni, M., Mochi, D., Nava, S., Carraresi, L., 2013. The upgraded external-beam
448 PIXE/PIGE set-up at LABEC for very fast measurements on aerosol samples, *Nucl. Instr. and Meth. in Phys. Res. B.*, doi:
449 <http://dx.doi.org/10.1016/j.nimb.2013.05.099>
- 450
- 451 Mandò, P.A., 2009, INFN-LABEC, Nuclear Techniques for Cultural Heritage and Environmental Applications. *Nuclear Physics*
452 *News*, 19, 5-12.
- 453
- 454 Marmer E., Langmann B., 2005. Impact of ship emissions on the Mediterranean summertime pollution and climate: a regional
455 model study., *Atmospheric Environment* 39, 4659-4669.
- 456
- 457 Mason, B. H., *Principles of Geochemistry*, Wiley, 1966
- 458
- 459 Mazzei, F., D'Alessandro, A., Lucarelli, F., Nava, S., Prati, P., Valli, G., Vecchi, R., 2008. Characterization of particulate matter
460 sources in an urban environment. *Science of Total Environment* 401, 81-89.
- 461
- 462 Moreno T., Perez N., Querol X., Amato F., Alastuey A., 2010. Physicochemical variations in atmospheric aerosol recorded at sea
463 onboard the Atlantic- Mediterranean 2008 Scholar Ship cruise., *Atmospheric Environment* 44, 2563-2576.
- 464
- 465 Moreno T., Pérez N., Querol X., Amato F., Alastuey A., Bhatia R., Spiro B., Hanvey M., Gibbons, W., 2010. Physicochemical
466 variations in atmospheric aerosols recorded at sea on board the Atlantic-Mediterranean 2008 Scholar Ship cruise (PartII): Natural
467 versus anthropogenic in fluences revealed by PM₁₀ trace element geochemistry, *Atmospheric Environment* 44, 2563-2576.
- 468
- 469 Nigam, A., Welch, W., Wayne Miller, J., and Cocher III, D. R., 2006. Effect of fuel sulphur content and control technology on PM
470 emission from ship's auxiliary engine. *Proc. Int. Aerosol Conf.*, St. Paul, USA, 10-15 September 2006, 1531-1532.
- 471
- 472 Paatero, P., Tapper, U., 1994. Positive Matrix Factorization: a non-negative factor model with optimal utilization of error estimates
473 of data values. *Environmetrics*, 5, 111-126.
- 474
- 475 Paatero, P., 1997. Least square formulation of robust nonnegative factor analysis. *Chemometrics and Intelligent Laboratory Systems*,
476 223-224.
- 477
- 478 Polissar, A., Hopke, P.K., Paatero, P., Malm, C., Sisler, J.F., 1998, Atmospheric aerosol over Alaska, 2. Elemental composition and
479 sources, *Journal of Geophysical Research*, 103, D15, 19,045-19,057.
- 480
- 481 Putaud, J.P., Van Dingenen, R., Dell'Acqua, A., Raes, F., Matta, E., Decesari, S., Facchini, M.C., Fuzzi, S., 2004. Size-segregated
482 aerosol mass closure and chemical composition in Monte Cimone (I) during MINATROC. *Atmospheric Chemistry and Physics*, 4,
483 889-902.
- 484

- 485 Qin, Y., Kim, E., Hopke, P. K., 2006. The concentrations and sources of PM_{2.5} in metropolitan New York City. *Atmospheric*
486 *Environment* 40, Supplement 2, 312-332.
- 487
- 488 Rahn, K. A., 1976. Silicon and aluminum in atmospheric aerosols: crust-air fractionation? *Atmospheric Environment* 10, 597-601.
- 489
- 490 Ramadan, Z., Song, X.H., Hopke, P.K., 2003. Identification of sources of Phoenix aerosol by positive matrix factorization. *Journal*
491 *of Air and Waste Management Association* 50, 1308-1320.
- 492
- 493 Schembari, C., Cavalli, F., Cuccia, E., Hjorth, J., Calzolari, G., Pérez, Pey, J., Prati, P., F. Raes, F., 2012. Impact of a European
494 directive on ship emissions on air quality in Mediterranean Harbours. *Atmospheric Environment* 61, 661-669.
- 495
- 496 Seinfeld, J.H., Pandis, S.N., *Atmospheric chemistry and physics*. John Wiley and Sons, 1998.
- 497
- 498 Sievering H, Boatman J, Galloway J, Keene W, Kim Y, Luria M, Ray J., 1991. Heterogeneous sulfur conversion in sea-salt aerosol
499 particles: the role of aerosol water content and size distribution. *Atmospheric Environment Part A General Topics* 25, 1479-1487.
- 500
- 501 Singh, H.B., 1995. *Composition, chemistry and climate of the atmosphere*. Van Nostrand Reinhold, New York.
- 502
- 503 Sokolik, I. N., Toon, O. B., 1999. Incorporation of mineralogical composition into models of the radiative properties of mineral
504 aerosol from UV to IR wavelengths, *J. Geophys. Res.*, 104, 9423-9444.
- 505
- 506 Turpin, B.J. and H.J. Lim, 2001. Species contributions to PM_{2.5} mass concentrations: Revisiting common assumptions for
507 estimating organic mass. *Aerosol Science and Technology* 35(1), 602-610.
- 508
- 509 Turpin, B. J., Saxena, P., Andrews, E., 2000. Measuring and simulating particulate organics in the atmosphere: problems and
510 prospects. *Atmospheric Environment* 34, 2983-3013.
- 511
- 512 Udisti, R., Dayan, U., Becagli, S., Busetto, M., Frosini, D., Legrand, M., Lucarelli, F., Preunkert, S., Severi, M., Traversi, R., Vitale,
513 V. 2012. Sea-spray aerosol in central Antarctica. Present atmospheric behavior and implications for paleoclimatic reconstructions.
514 *Atmospheric Environment* 52, 109-120, doi: 10.1016/j.atmosenv.2011.10.018.
- 515
- 516 Usher, C.R., Michel, A.E., Grassian, V.H., 2003. Reactions on Mineral Dust, *Chem. Rev.* 103, 4883-4939
- 517
- 518 Van Aardenne, J., A. Colette, B. Degraeuwe, P. Hammingh, M. Viana, I. de Vlieger, 2013. The impact of international shipping on
519 European air quality and climate forcing. EEA Technical Report no. 4.
- 520
- 521 Van Dingenen, R., F. Raes, J.-P. Putaud, U. Baltensperger, A. Charron, M.-C. Facchini, S. Decesari, S. Fuzzi, R. Gehrig, H.-C.
522 Hansson, R. M. Harrison, C. Haugline, A. M. Jones, P. Laj, G. Lorbeer, W., Maenhaut, W., Palmgren, F., Querol, X., Rodriguez, S.,
523 Schneider, J., ten Brink, H., Tunved, P., Torseth, K., Wehner, B., Weingartner, E., Wiedensohler, A., Wahlin, P., 2004. A
524 European aerosol phenomenology 1: physical characteristics of particulate matter at kerbside, urban, rural and background sites in
525 Europe, *Atmospheric Environment* 38, 2561-257.
- 526
- 527 Velchev, K., Cavalli F., Hjorth J., Vignati E., Dentener F., Raes F., 2011. Ozone over Western Mediterranean Sea-results from two
528 years of shipborne measurements., *Atmospheric Chemistry and Physics*, 11, 675-688.
- 529
- 530 Viana, M., Amato, F., Alastuey, A., Querol, X., 2009. Chemical Tracers of particulate emissions from commercial shipping.,
531 *Environmental science and technology* 43, 7472-7477.

532
533
534
535
536

Tables:

	24-31 August 2009	7-14 June 2010
PIXE (streaker)	X	X (also from 14 to 21 June)
Filters based sampling	PM1 & PM10	PM10
ED-XRF	X	
IC	X (PM10 only, no MSA)	X
TOT	EC	EC & OC

537

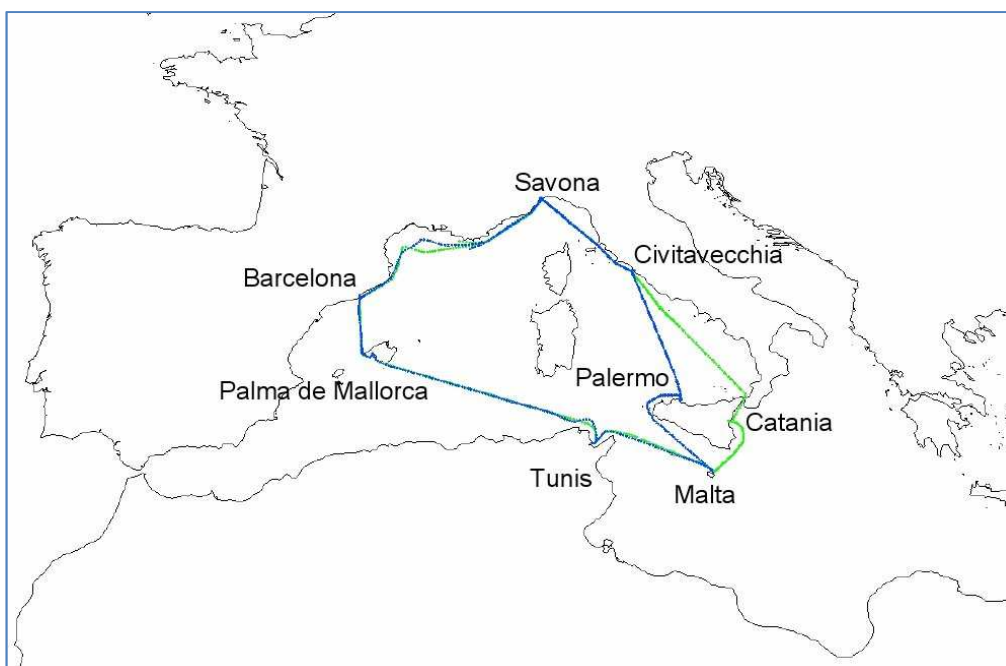
538 **Table 1:** Sampling and subsequent laboratory analyses performed during the 24-31 August 2009 and 7-14
539 June 2010 cruises. Data collected during the episode that occurred from 17 to 19 June has been excluded
540 in the PMF analysis.

541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561

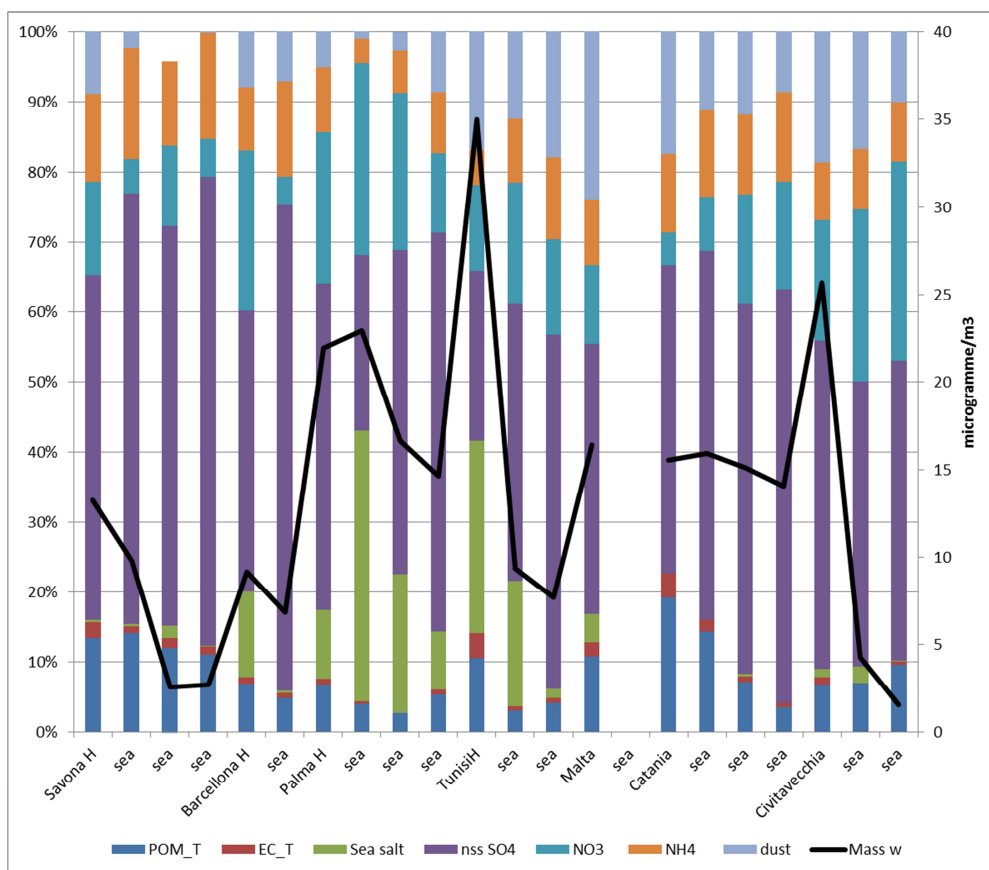
Leg	PMF				IC		
	Sea salt	Combustion	Soil	Not Id.	Sea salt	Anthrop.	Biog.
S-B	(3 ± 3)%	(89 ± 4)%	(2 ± 6)%	(5 ± 4)%	(3.7 ± 0.4)%	(49 ± 5)%	(47 ± 5)%
B-P	(12 ± 2)%	(82 ± 2)%	(2 ± 5)%	(3 ± 3)%	(3.2 ± 0.3)%	(85 ± 9)%	(11 ± 1)%
P-T	(19 ± 5)%	(69 ± 6)%	(3 ± 7)%	(9 ± 6)%	(18 ± 2)%	(63 ± 6)%	(19 ± 2)%
T-M	(9 ± 5)%	(79 ± 5)%	(1 ± 7)%	(10 ± 5)%	(8 ± 1)%	(71 ± 7)%	(21 ± 2)%
M-C	(1 ± 5)%	(96 ± 7)%	(2 ± 7)%	(1 ± 2)%			
C-C	(5 ± 2)%	(83 ± 2)%	(9 ± 5)%	(4 ± 3)%	(4.1 ± 0.4)%	(75 ± 6)%	(21 ± 2)%
C-S	(14 ± 5)%	(65 ± 5)%	(8 ± 7)%	(13 ± 6)%	(10 ± 1)%	(52 ± 5)%	(39 ± 4)%
Mean	(9 ± 3)%	(81 ± 4)%	(4 ± 6)%	(6 ± 4)%	(8 ± 1) %	66 ± 7	(26 ± 3)%

562
563 **Table 2:** Percent apportionment of total S (PMF) and total sulphate (IC) calculated in each leg of the first week
564 of the 2010 cruise. In the last row the mean values are given.
565

566 **Figures:**
567

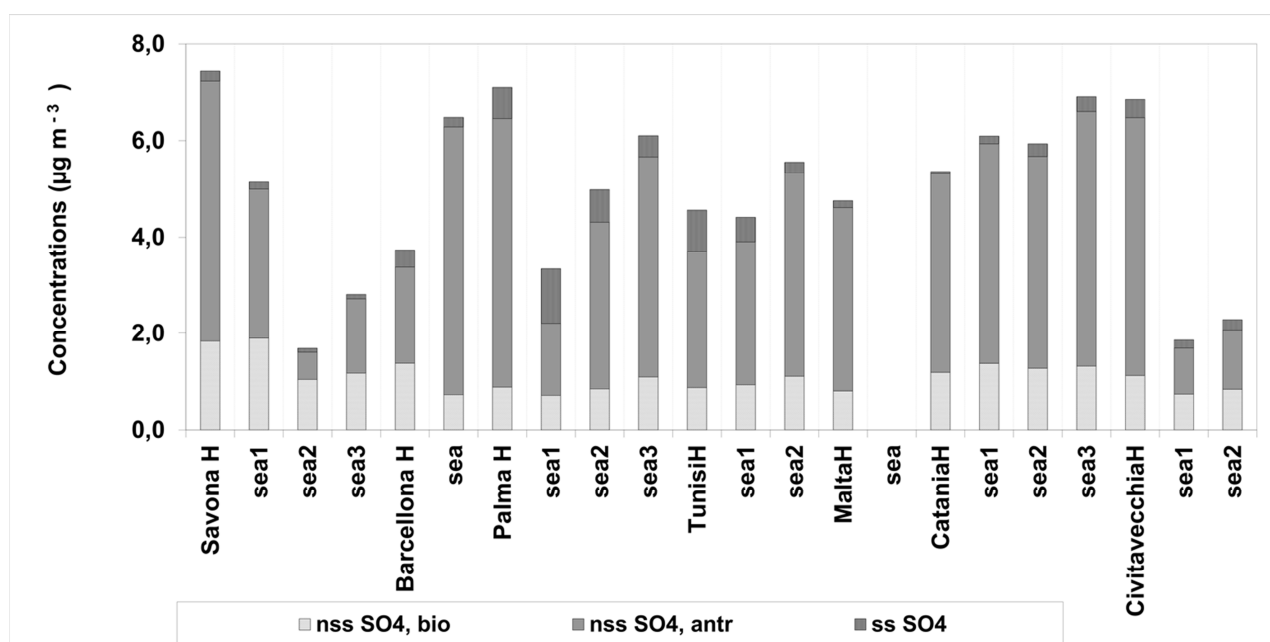


568 **Figure 1:** Route of Costa Pacifica during spring-summer-autumn 2009 (blue). During 2010 (green) the
569 ship followed the same route, with the only exception of the Sicilian harbour that was Catania instead of
570 Palermo.
571
572



573
 574 **Figure 2.** Chemical composition (% by mass) and concentrations of particles (Mass w) obtained by Ion
 575 Chromatography analysis during the sampling campaign in 2010. 'POM_T' and 'EC_T' are organic and
 576 elemental carbon concentrations calculated based on the thermo-optical (transmittance) measurements.

577
 578



579

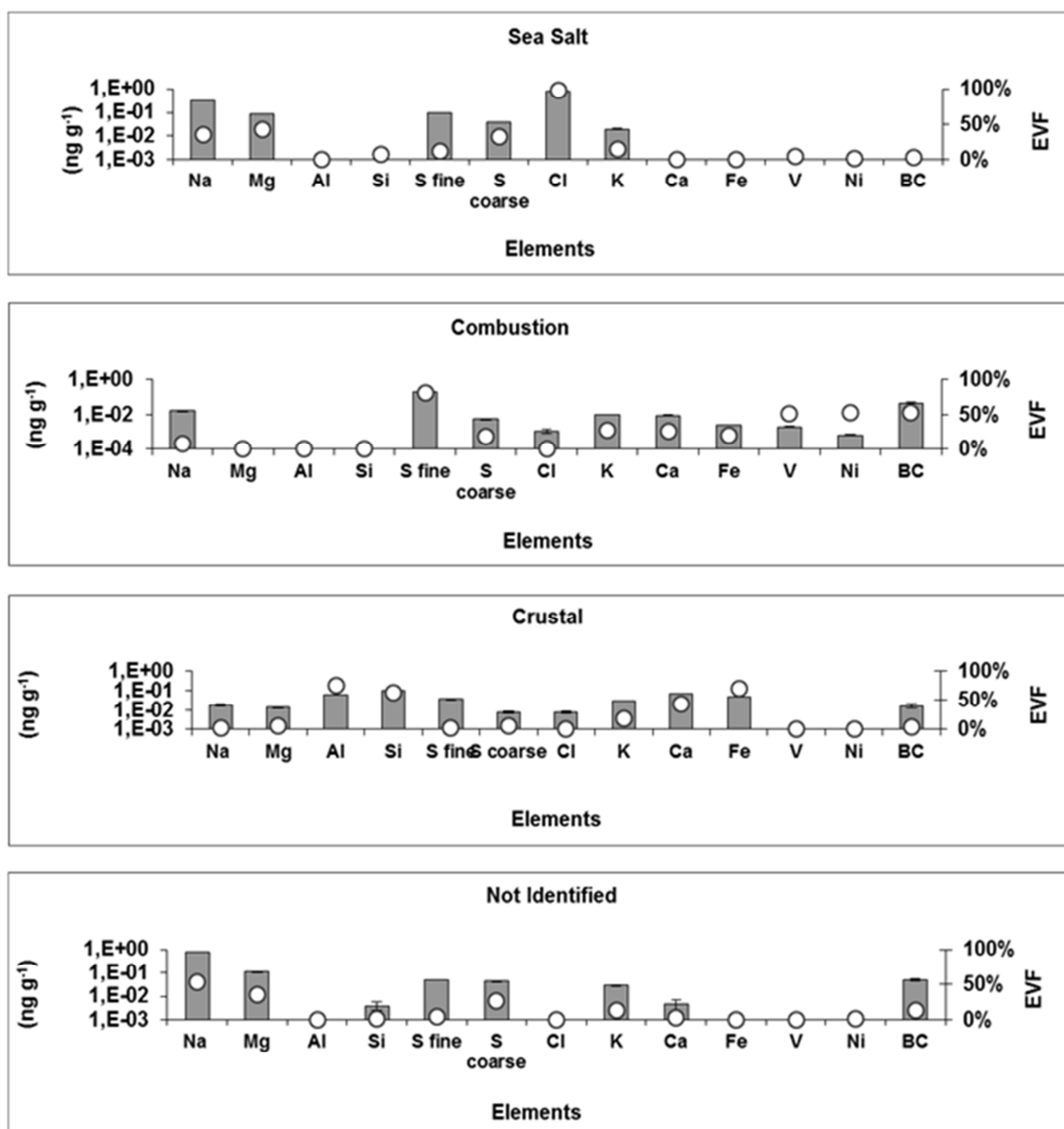
580

581

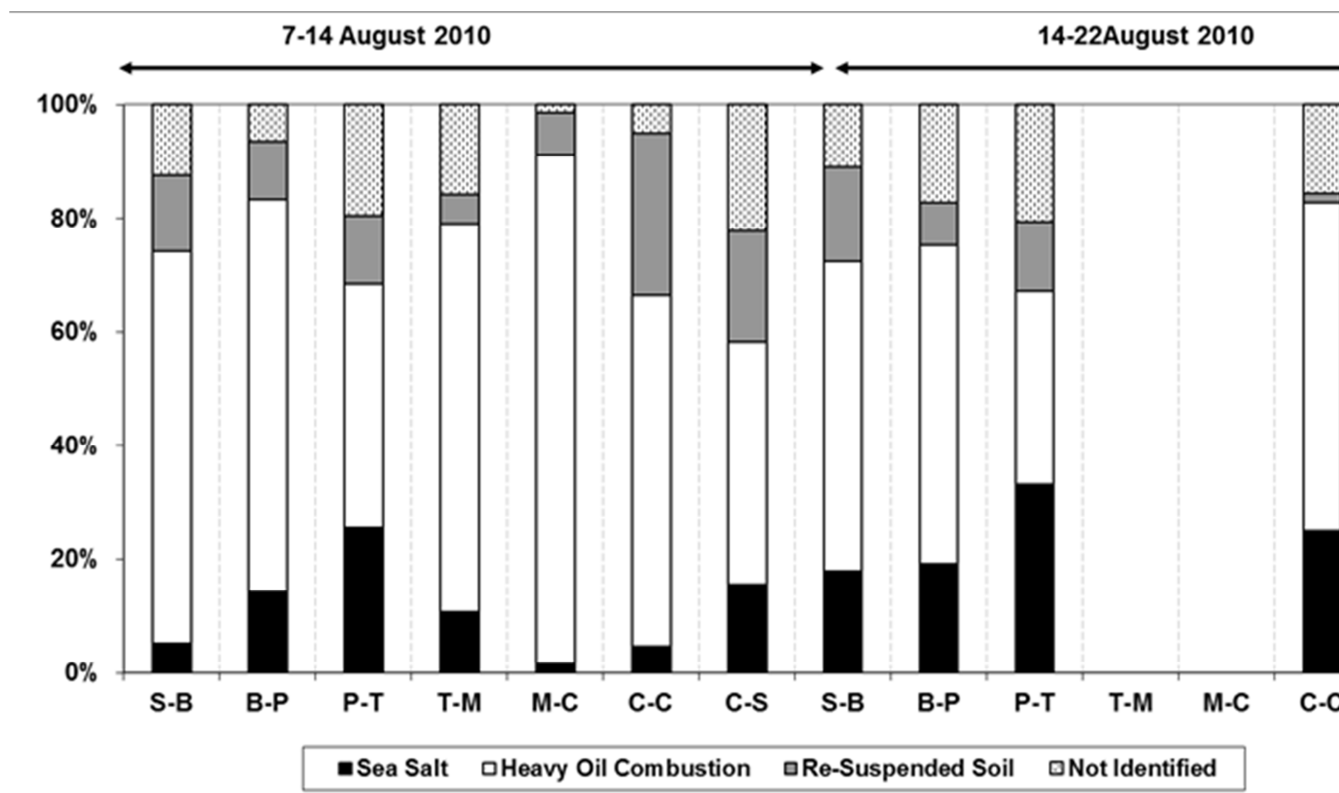
582

583

Figure 3: Contributions (sea salt sulphate; non sea salt sulphate: biogenic, anthropogenic) to the total SO_4^{2-} concentration, determined from chemical marker compounds as described in the text, for the 7-14 June 2010 cruise. The contribution from crustal material was found to be negligible.

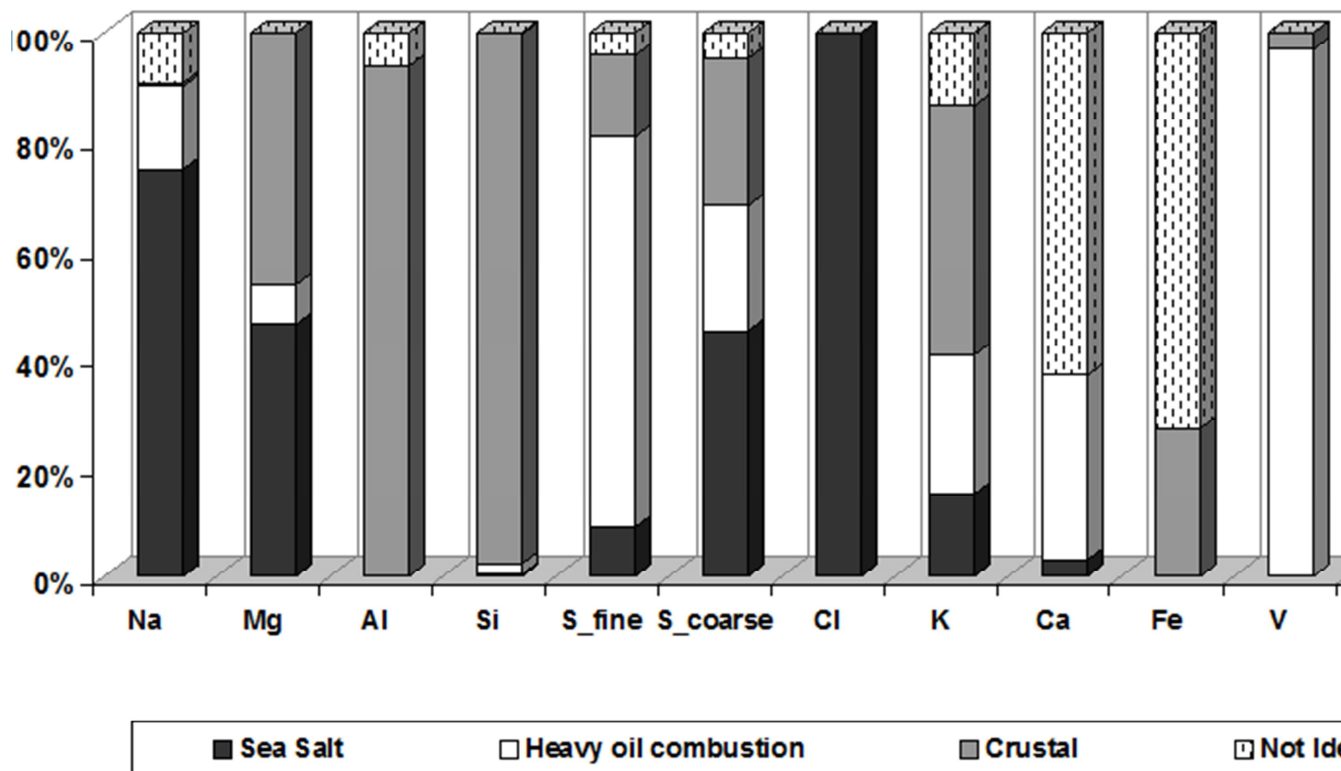


584
 585 **Figure 4:** PM_{10} source profiles (left axis) extracted by the PMF with the 2010 data set. On the right axis the
 586 Evaluation Factors (EV) given by PMF2 are shown for each element/compound (white circle). Data collected
 587 during the episode that occurred from 17 to 19 June has been excluded in the PMF analysis.
 588



589
590
591
592
593
594
595
596

Figure 5: Percentual contribution of the different sources to PM_{10} during the 2010 cruise in each sea leg. Data collected during the episode that occurred from 17 to 19 June has been excluded in the PMF analysis. In the last column the mean PM_{10} apportionment is given. Labels on X axis identify: S-B: Savona-Barcelona leg; B-P: Barcelona-Palma leg; P-T: Palma-Tunis leg; T-M: Tunis-Malta leg; M-C: Malta-Catania leg; C-C: Catania-Civitavecchia leg; C-S: Civitavecchia-Savona leg.

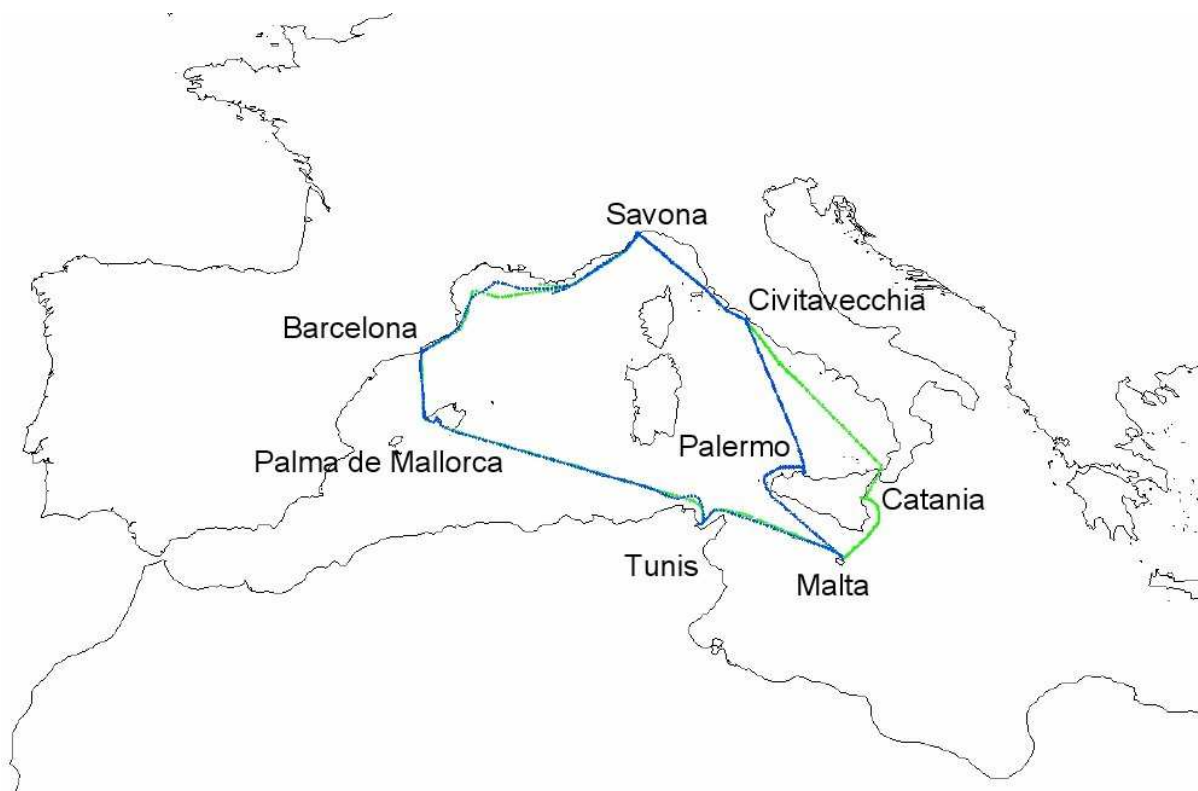


597
598
599
600

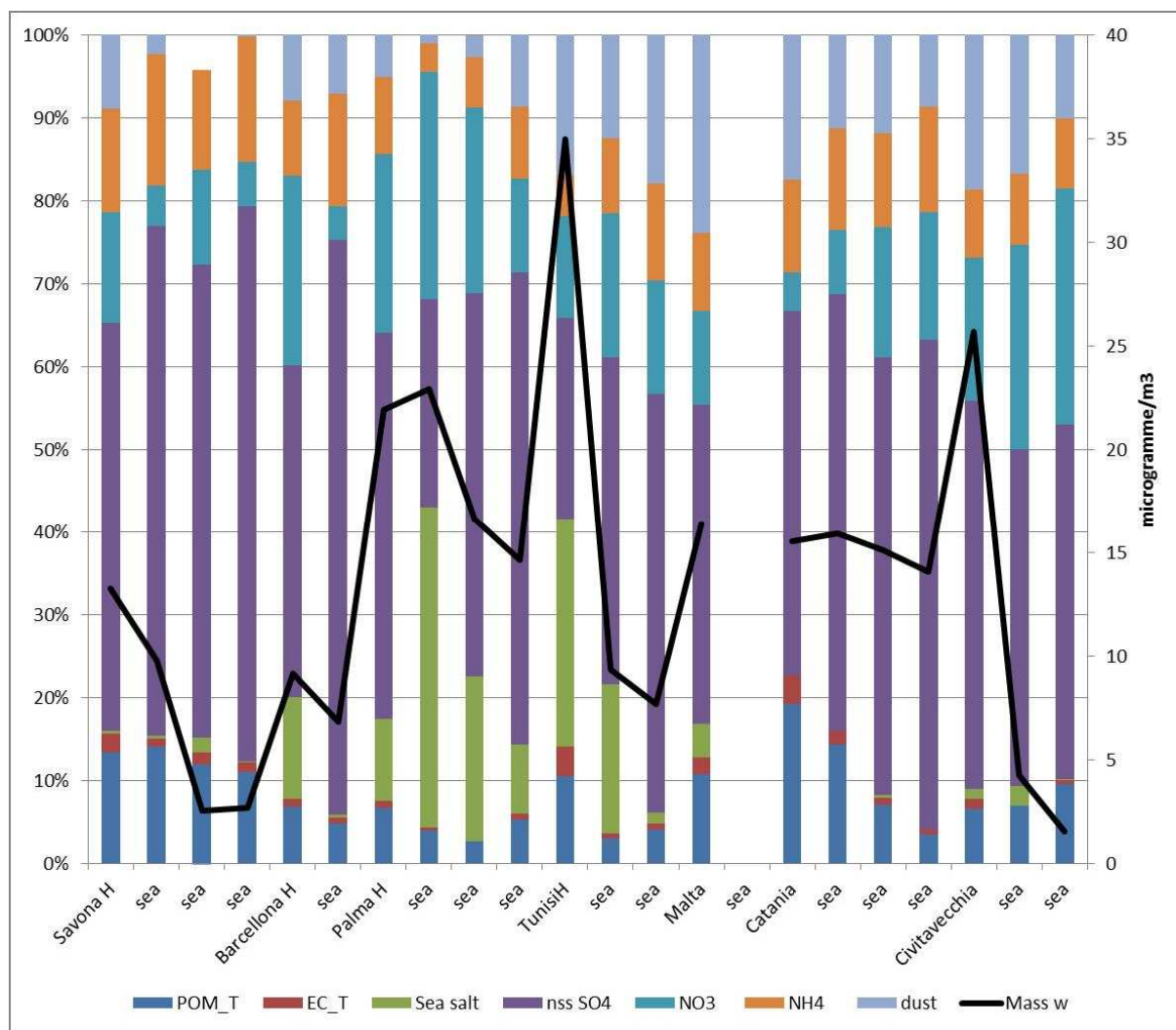
Figure 6: PMF mean apportionment of elemental and BC concentration values during the 2010 cruise.

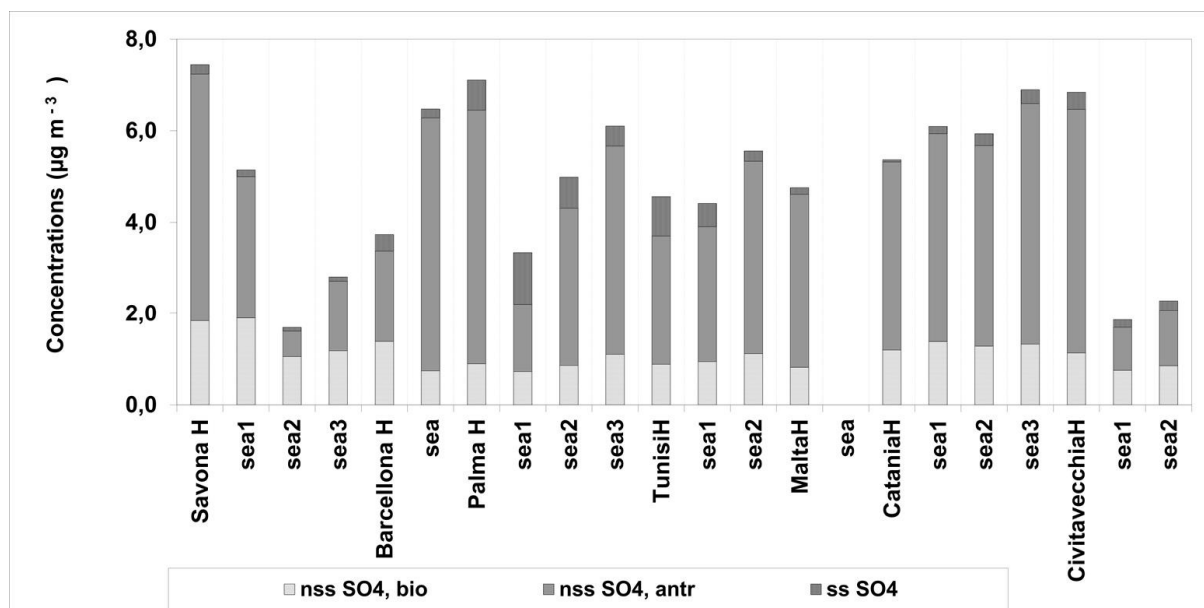
	24-31 August 2009	7-14 June 2010
PIXE (streaker)	X	X (also from 14 to 21 June)
Filter based sampling	PM1 & PM10	PM10
ED-XRF	X	
IC	X (PM10 only, no MSA)	X
TOT	EC	EC & OC

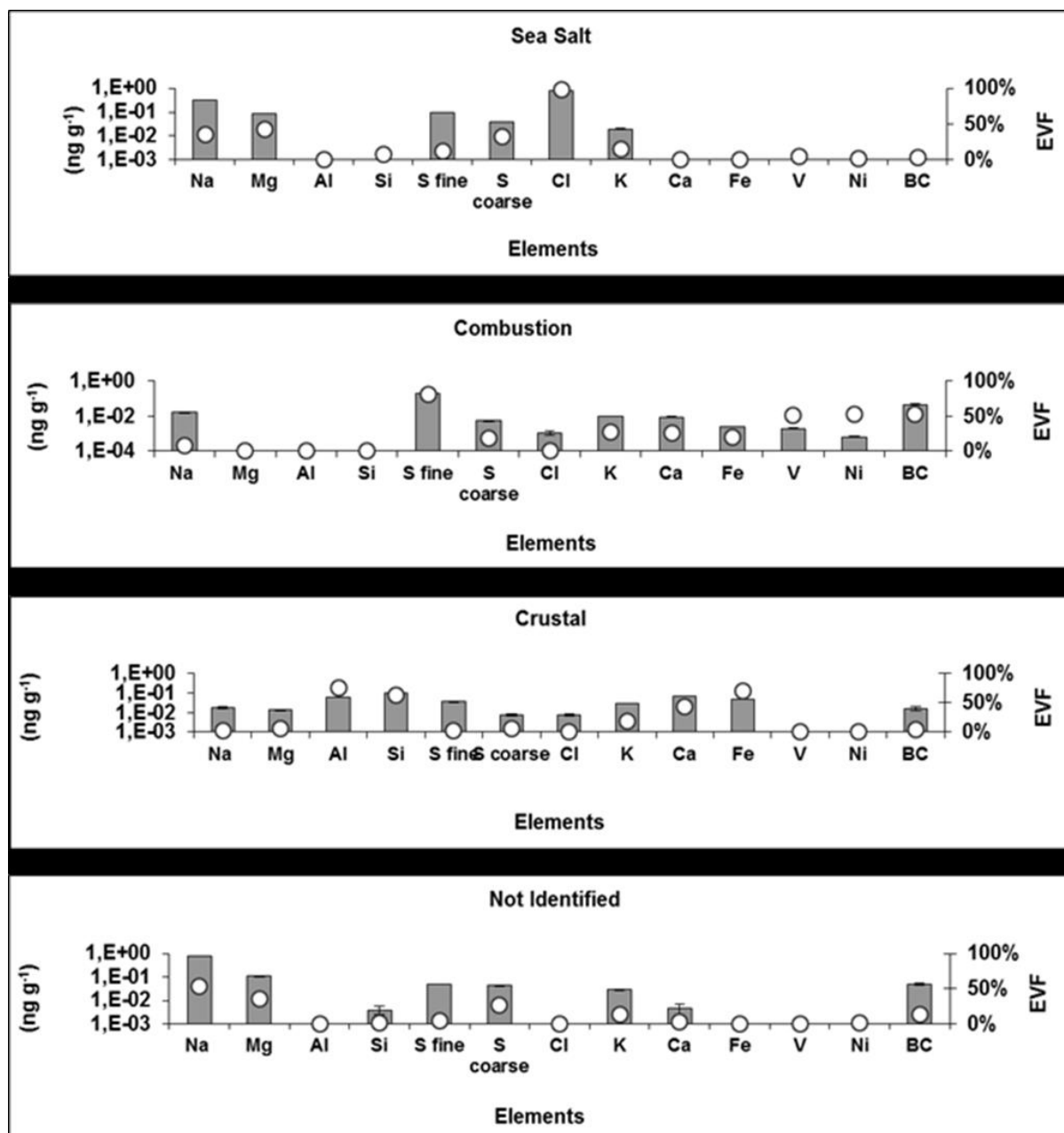
	PMF				IC		
Leg	Sea salt	Combustion	Soil	Not Id.	Sea salt	Anthrop.	Biog.
S-B	(3 ± 3)%	(89 ± 4)%	(2 ± 6)%	(5 ± 4)%	(3.7 ± 0.4)%	(49 ± 5)%	(47 ± 5)%
B-P	(12 ± 2)%	(82 ± 2)%	(2 ± 5)%	(3 ± 3)%	(3.2 ± 0.3)%	(85 ± 9)%	(11 ± 1)%
P-T	(19 ± 5)%	(69 ± 6)%	(3 ± 7)%	(9 ± 6)%	(18 ± 2)%	(63 ± 6)%	(19 ± 2)%
T-M	(9 ± 5)%	(79 ± 5)%	(1 ± 7)%	(10 ± 5)%	(8 ± 1)%	(71 ± 7)%	(21 ± 2)%
M-C	(1 ± 5)%	(96 ± 7)%	(2 ± 7)%	(1 ± 2)%			
C-C	(5 ± 2)%	(83 ± 2)%	(9 ± 5)%	(4 ± 3)%	(4.1 ± 0.4)%	(75 ± 6)%	(21 ± 2)%
C-S	(14 ± 5)%	(65 ± 5)%	(8 ± 7)%	(13 ± 6)%	(10 ± 1)%	(52 ± 5)%	(39 ± 4)%
Mean	(9 ± 3)%	(81 ± 4)%	(4 ± 6)%	(6 ± 4)%	(8 ± 1) %	66 ± 7	(26 ± 3)%

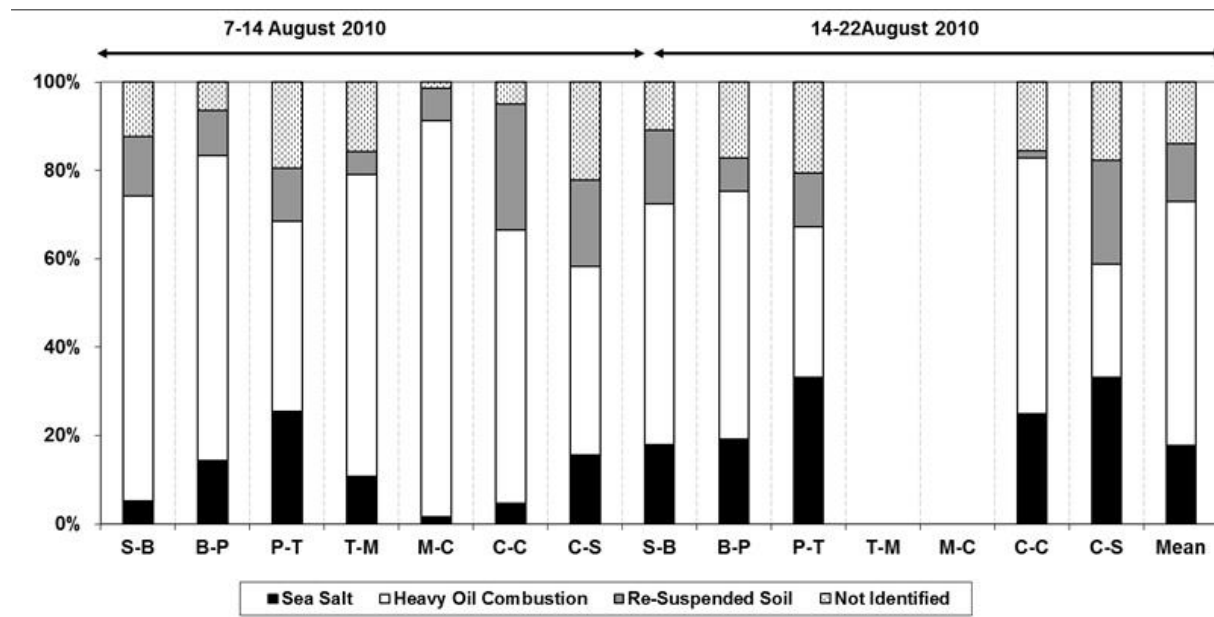


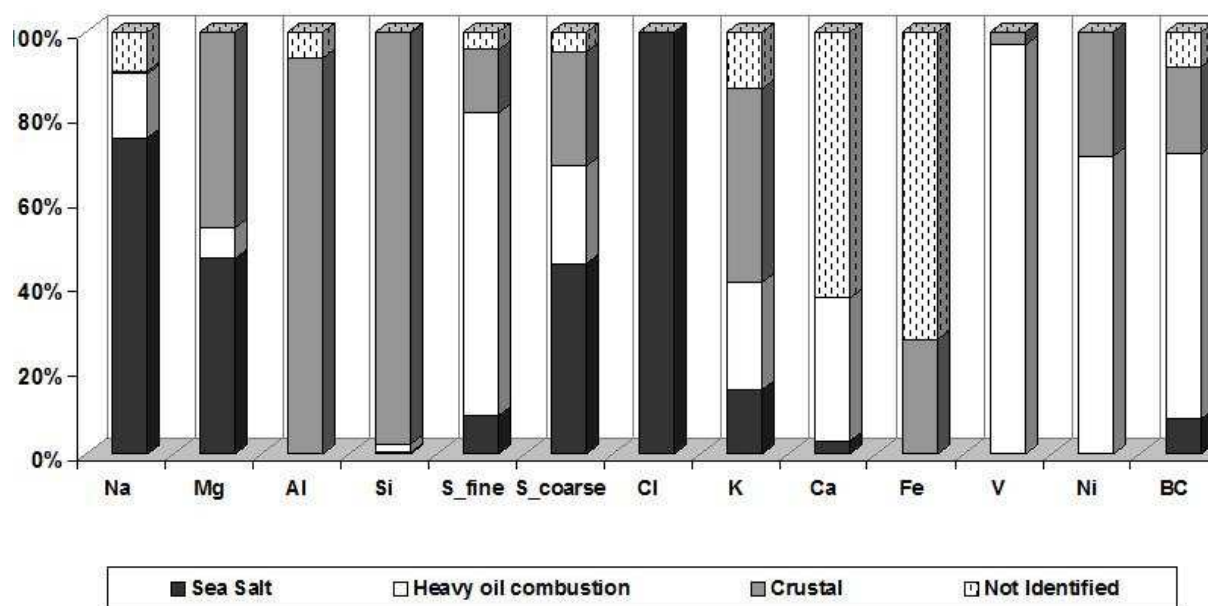
ACCEPTED MANUSCRIPT











Highlights:

- PM samples obtained with hourly resolution on a cruise ship were analysed
- Source apportionment by PMF with a moving receptor
- Sulphate apportionment based on chemical tracers (Na, Ca, MSA)
- Correlation analysis using V and Ni as tracers of ship emissions
- Ships have strong impact on sulphate concentrations in parts of the Mediterranean

Appendix

1
2
3

The following tables give detailed information about the concentrations measured during the two campaigns:

Sampling Campaign 24-31 August 2009			
(ng m⁻³)	PM10; SD	PM2.5; SD	MDL
Na	825; 614	171;146	20
Mg	173; 108	63;38	23
Al	248; 148	146;96	19
Si	690; 330	449; 216	17
S	3009; 1355	2825; 1345	18
Cl	706; 963	15; 18	18
K	264; 85	185; 86	19
Ca	416; 435	107; 149	23
Ti	16; 10	10; 5	8
V	14; 14	12; 14	5
Fe	174; 87	101; 50	2
Ni	7; 8	5; 7	1
Cu	2; 1	1; 1	1
Zn	11; 11	9; 10	1
Sampling Campaign 7-21 June 2010			
(ng m⁻³)	PM10; SD	PM2.5; SD	MDL
Na	1258; 706	461; 386	36
Mg	253; 161	86; 84	23
Al	258; 492	204; 473	19
Si	550; 1015	411; 974	16
S	1645; 976	1461; 961	17
Cl	1175; 1276	18; 16	18
K	226; 169	137; 164	18
Ca	333; 551	92; 132	27
Ti	8; 8	10; 17	9
V	19; 34	17; 29	8
Fe	117; 196	79; 175	2
Ni	7; 12	6; 10	1
Cu	2; 2	1; 3	1
Zn	13; 28	14; 42	1
Pb	2; 3	2; 5	2

4 **Table E1:** Averages and standard deviations of the elemental concentration values of PM10 and PM2.5 measured by streaker sampling and PIXE analysis separated for
 5 the 2009 and 2010 cruises. MDL is 'minimum detection limit'. Measurements of Pb are not available for 2009.

6
7
8
9
10
11

	BC	O₃	SO₂	NO_x
<i>24-31 August 2009</i>	<i>0.7 ± 0.4</i>	<i>41.4 ± 7.6</i>	<i>0.5 ± 0.3</i>	<i>1.0 ± 0.6</i>
<i>7-21 June 2010</i>	<i>0.5 ± 0.2</i>	<i>44.9 ± 5.6</i>	<i>0.3 ± 0.2</i>	<i>2.3 ± 1.2</i>

12
13 **Table E2.** BC ($\mu\text{g m}^{-3}$), O₃ (ppbv), SO₂ (ppbv) and NO_x (ppbv) concentration values (mean and standard deviation) measured along the ship route during the two
 14 intensive campaigns and obtained from 2006 to 2010 for the same months (June - August) and averaged on the "summer" period (JJA, June – July – August). SO₂ and
 15 NO_x measurements started in August 2009 only.

16
17
18
19
20
21
22
23
24
25
26

24-31 August 2009			
Compound	Max	Min	Mean \pm SD
NH ₄	4.0	0.5	2.3 \pm 0.1
NO ₃	3.5	0.4	1.4 \pm 0.1
SO ₄	13.6	2.8	8.6 \pm 0.3
EC	0.8	0.1	0.20 \pm 0.02
Sea Salt	10.9	0.9	3.1 \pm 0.2
Dust	16.5	0.6	3.8 \pm 0.4
7-14 June 2010			
Compound	Max	Min	Mean \pm SD
NH ₄	1.5	0.4	0.9 \pm 0.1
NO ₃	3.6	0.2	1.4 \pm 0.3
SO ₄	6.9	1.7	4.6 \pm 0.5
OM	1.6	0.3	0.6 \pm 0.1
EC	1.2	0.3	0.80 \pm 0.01
Sea Salt	11.7	0.5	2.7 \pm 0.8
Dust	2.0	0.1	0.8 \pm 0.2

27

28

29

30

31

32

33

Table E3: Chemical composition of the PM₁₀ samples collected along the sea legs on quartz filters between August. 24-31 2009 and June. 7-14 2010. Concentration values are given in $\mu\text{g m}^{-3}$. See text for the composition of Sea Salt and Dust. OM values are not available for the 2009 cruise.

Total SO₄	Sea salt SO ₄ (ssSO ₄)	$ssSO_4 = \left(\frac{SO_4}{Na} \right)_{seawater} * Na$		
	Not sea salt SO ₄ (nssSO ₄)	(Total SO ₄ – ssSO ₄)	Anthropogenic nssSO ₄ (nssSO _{4,antr})	$nssSO_{4,antr} = (nssSO_4 - nssSO_{4,bio} - nssSO_{4,cru})$
			Biogenic nssSO ₄ (nssSO _{4,bio}) (Bates et al. 1992)	$MSA/nssSO_{4,bio} \% = -1.5 * T^{0C} + 42.2$
			Dust nssSO ₄ (nssSO _{4,cru})	$nssSO_{4,cru} = \left(\frac{SO_4}{Ca} \right)_{cru} * nssCa$

34
35
36
37
38
39
40
41
42
43
44
45
46
47

Table E4: Relations used to calculate the different contributions to the total SO₄²⁻; sea salt sulphate and not sea salt sulphate, divided in: anthropogenic, biogenic and crustal. A value of 0.252 g/g was used for the ratio between sulphate and sodium in seawater (Seinfeld and Pandis, 1998). Based on the sulphur content in crustal material (Mason, 1966), the ratio between sulphate and Ca in dust was estimated to be 0.021 g/g. Applying this factor to the experimental data the estimated crustal contribution to nssSO₄ was found to be negligible (less than 1% on all filters).

48 *Inter-comparison of compositional data*

49 In order to check the consistency of the data, the PM₁₀ elemental concentration obtained by PIXE were compared with the data obtained through
50 ED-XRF (only for the 2009 sampling campaign) and IC analysis of the quartz filters sampled during August 24-31 2009 and June 7-14, 2010. PM₁₀
51 elemental concentrations were obtained as the sum for each element of its concentration in the fine and coarse fraction sampled by the streaker. Hourly
52 concentration values provided by PIXE were averaged over the same time period of the sampling on quartz filters. The streaker performance (i.e. the cut-
53 point values) have been found in previous experiments (Chiari *et al.*, 2005; Mazzei *et al.*, 2006) not to be completely corresponding to the international
54 standards to collect PM_{2.5} and PM₁₀ so differences in the absolute values can be expected. However concentration values obtained by different methods
55 are expected to be correlated.

56 ED-XRF analysis: Quartz filters are characterized by a high Si content and this practically prevents the detection of light elements, in particular
57 from Na to Si. Moreover, medium energy X-Rays emitted from S to K, are subject to significant self-attenuation in the quartz matrix (Alessandri, 2011),
58 for this reason concentration values, obtained by ED-XRF analysis, were corrected by a multiplicative factor (S=1.7, Cl=1.7, K=1.5). In any case the
59 attenuation depends on the penetrating depth of aerosol particles inside the filter and cannot be exactly quantified: as a consequence, this effect may
60 significantly increase the uncertainties on the concentrations of these elements. Figure E2 (electronic supplementary material) shows the PIXE to ED-
61 XRF concentration ratios for elements detected with good statistics for the 2009 filters campaign.

62 Ion Chromatography (IC): The ratios between the concentrations of the elements in PM10 (PIXE vs. IC), are reported in Figure E3 (electronic
63 supplementary material) for the 2009 and 2010 filter campaigns. The overall picture shows a good correlation between PIXE and IC data ($R^2 \geq 0.7$, see
64 Figures E.3), with concentration ratios variable between 1.0 and 1.8. It should be noted, that PIXE analysis measures the total concentrations of the
65 elemental species while IC measures the soluble ionic fraction of that species: this may partially explain the higher values obtained by PIXE. OPC-
66 Gravimetric comparison: The mass concentration values (PM10) provided by the OPC were compared with the gravimetric PM10 concentration values
67 on the quartz filters sampled during the 2010 cruise. The two time series turned out to be correlated ($R^2 = 0.7$) with $PM10_{OPC} = 0.94 PM10_{grav}$. The
68 hourly PM10 values obtained by the OPC were therefore corrected and used to apportion the PM10 mass (see section PM10 apportionment).

69

70 *Correlation analysis*

71 For this analysis, filters and streaker samples showing evidence of plumes from close-by emissions from ship stacks were discarded because
72 otherwise the observed correlations might be strongly influenced by local peak values. The selection of filters to be discarded was done based on the
73 observation of concentration peaks of SO₂, as high sulphur emission rates are a characteristic feature of emissions from stacks on sea-going ships. Filters,

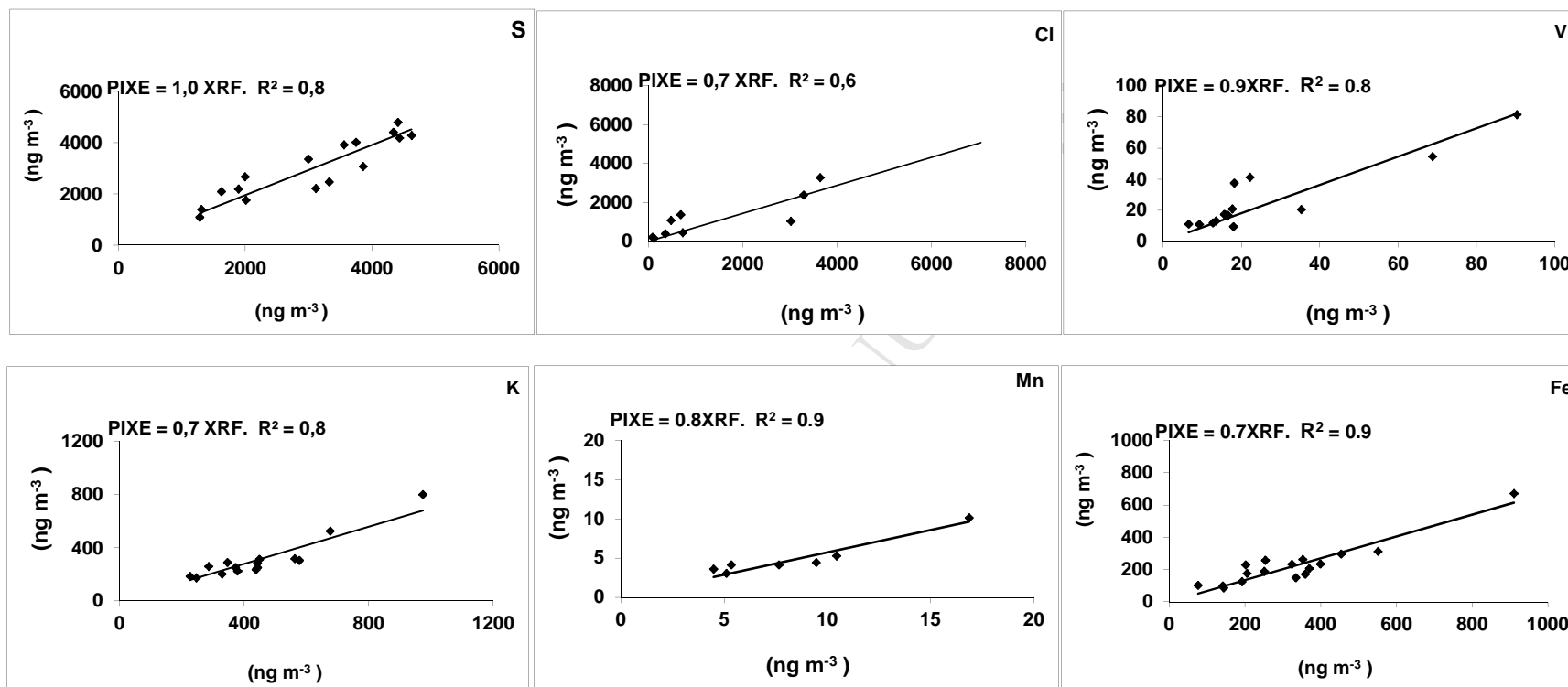
74 where the integrated SO₂ concentrations in peaks exceeded 10% of the total integrated SO₂ were discarded. ‘Peaks’ were defined as concentrations
75 exceeding 3 times the average. The resulting dataset, which is the basis of the following analysis, is in the following referred to as the ‘filtered data’.

76 The correlation matrices (Pearsons correlation coefficient) for the hourly elemental concentration values obtained by PIXE analysis of the
77 streaker samples and for the chemical species and elements in filter samples were calculated, for each of the two years. The same correlation coefficients
78 (r) were also calculated for samples with marine trajectories (see above) for the year 2010. Filters and streaker samples from harbours have not been
79 included. Also the p-value was calculated, the p-value is an estimate of the probability that the observed correlation is due to random variation of the
80 parameters. The continuous measurements of trace gases (10 minute resolution) and the PIXE measurements of elements sampled by the streaker (one
81 hour resolution) were integrated over the periods where the filters were sampled.

82

83

84

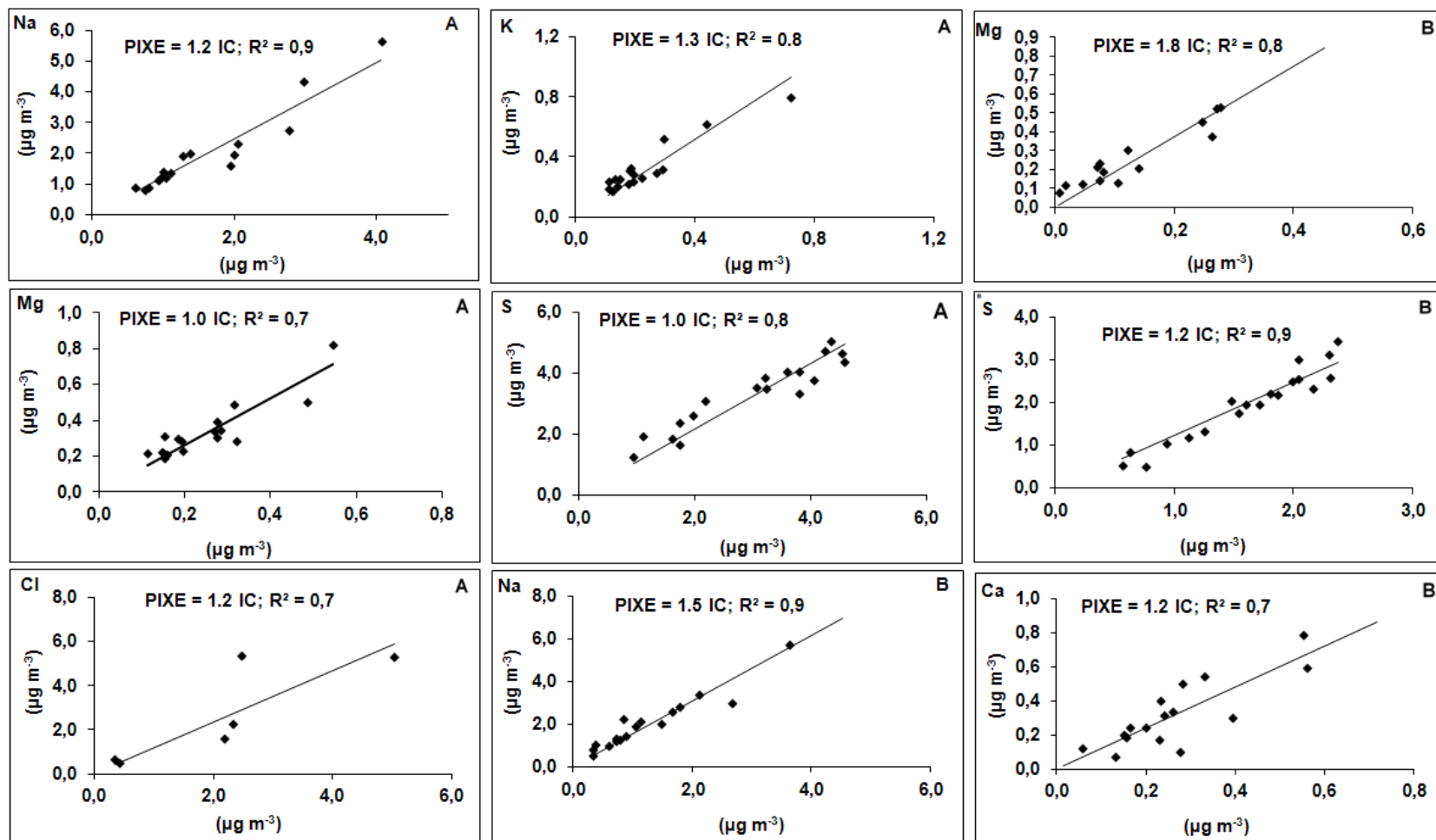


85

86 **Figure E.1:** Comparison between elemental concentration values determined by ED-XRF analysis of the quartz filters (x axis) during the 2009 cruise and the
 87 corresponding data obtained by the streaker + PIXE analysis (y axis).

88

89



90

91 **Figure E2:** Comparison between elemental concentration values determined by IC analysis of the quartz filters (x axis) during the 2009 (A) and 2010 (B) cruise
 92 and the corresponding data obtained by the streaker +PIXE analysis (y axis).

93

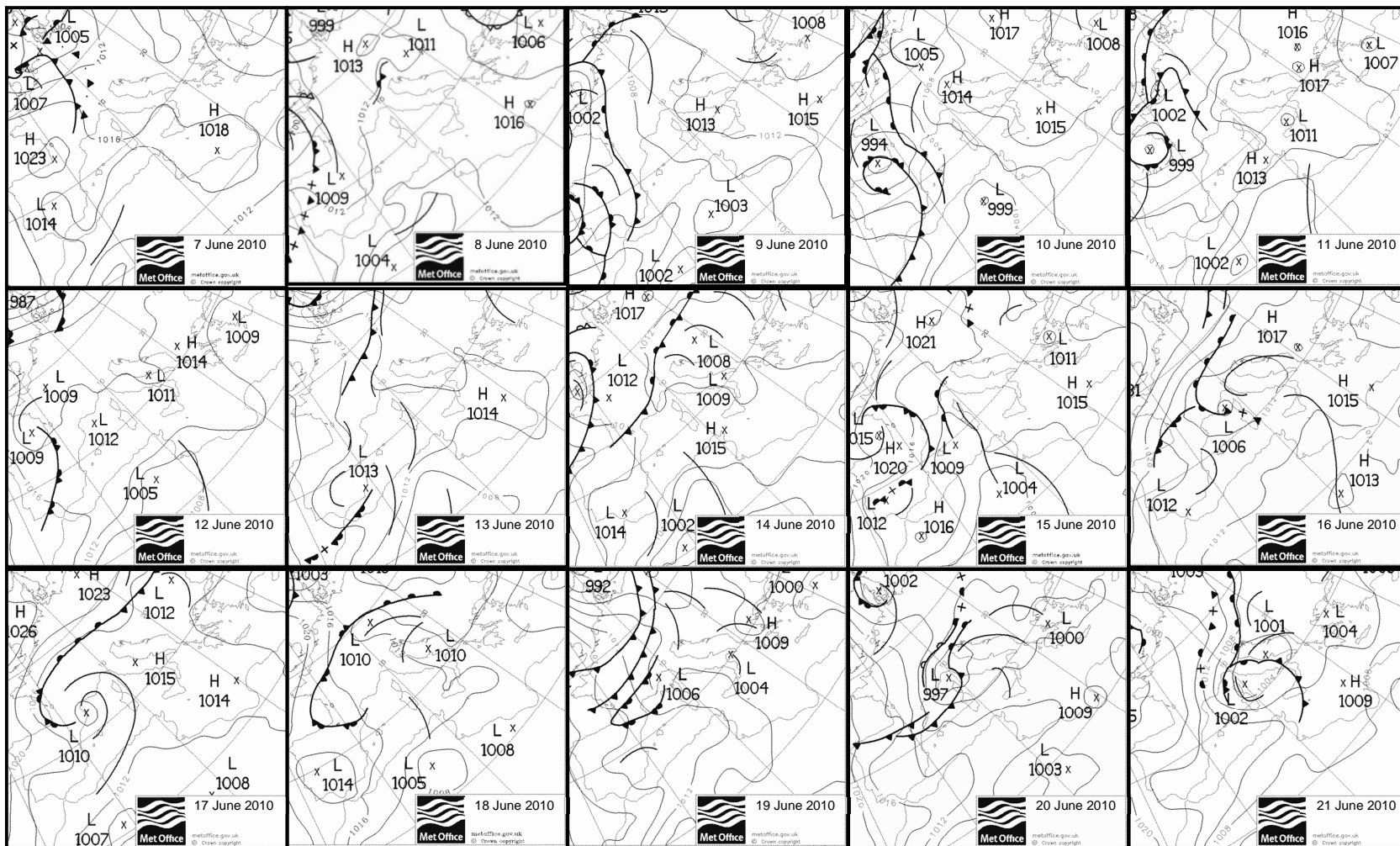
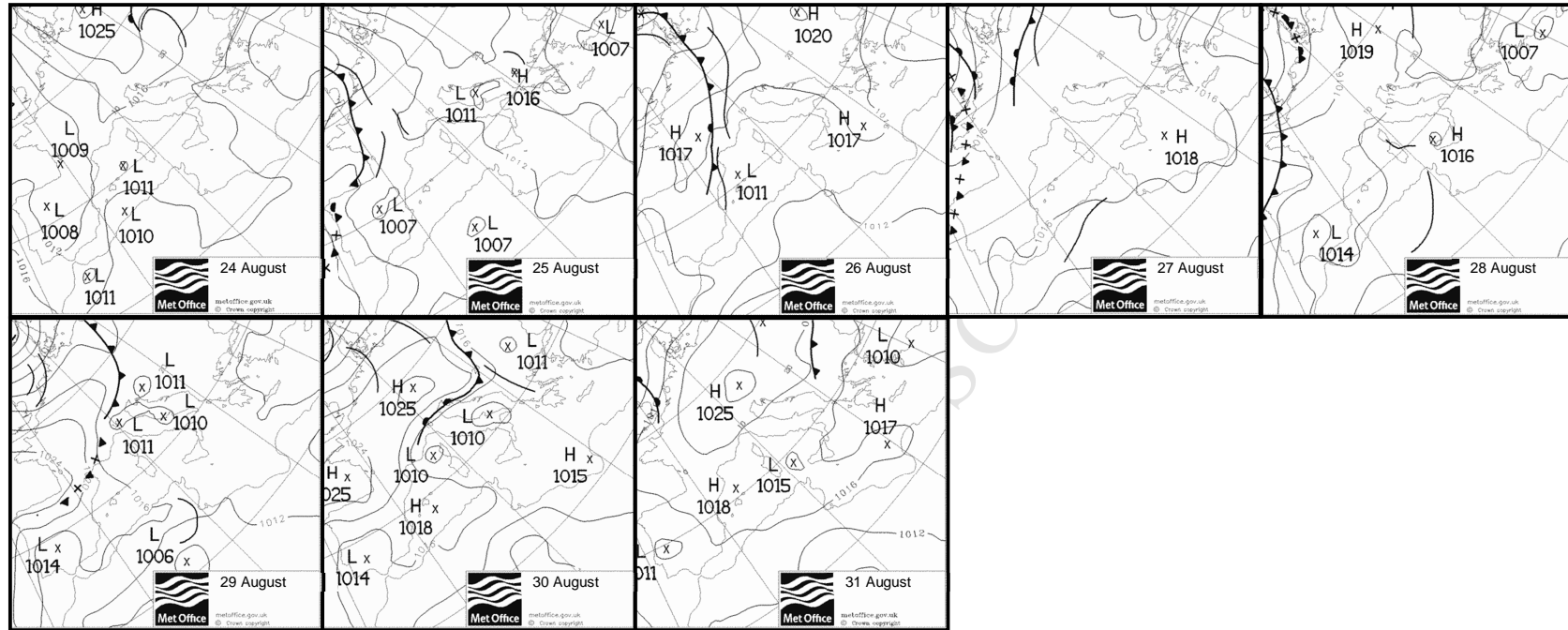


Figure E3.a

94
95
96



97

98

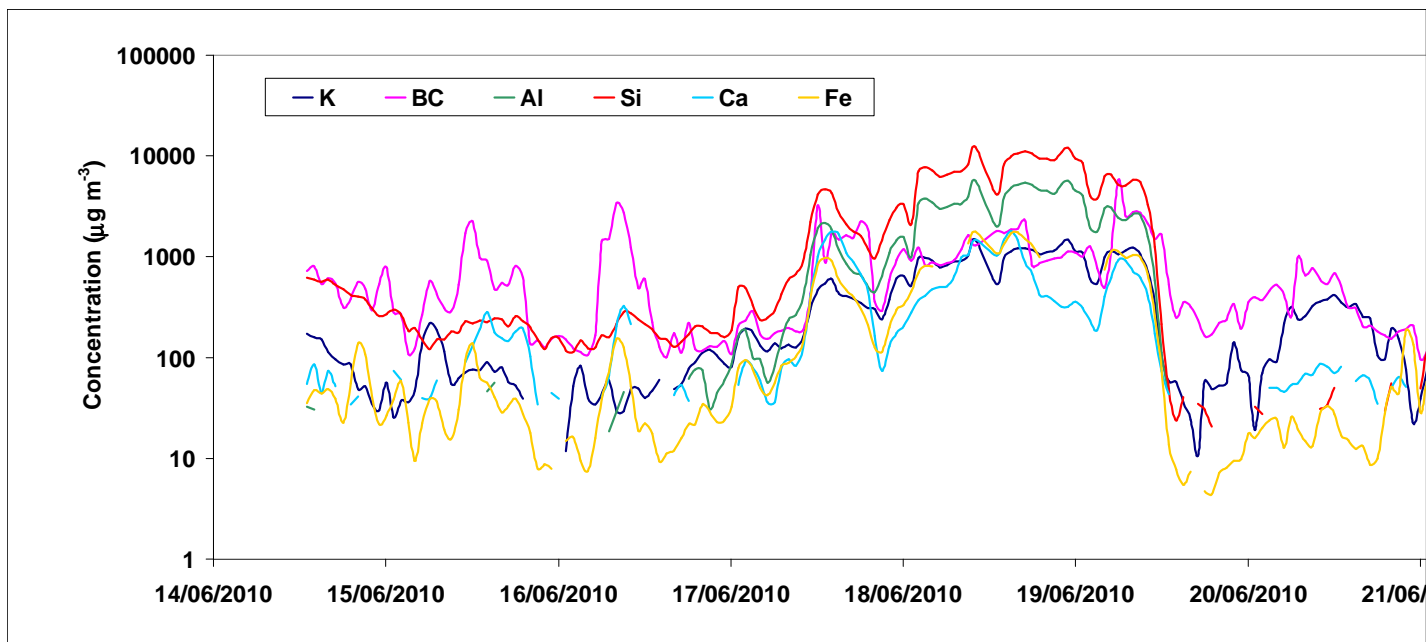
99

100

101

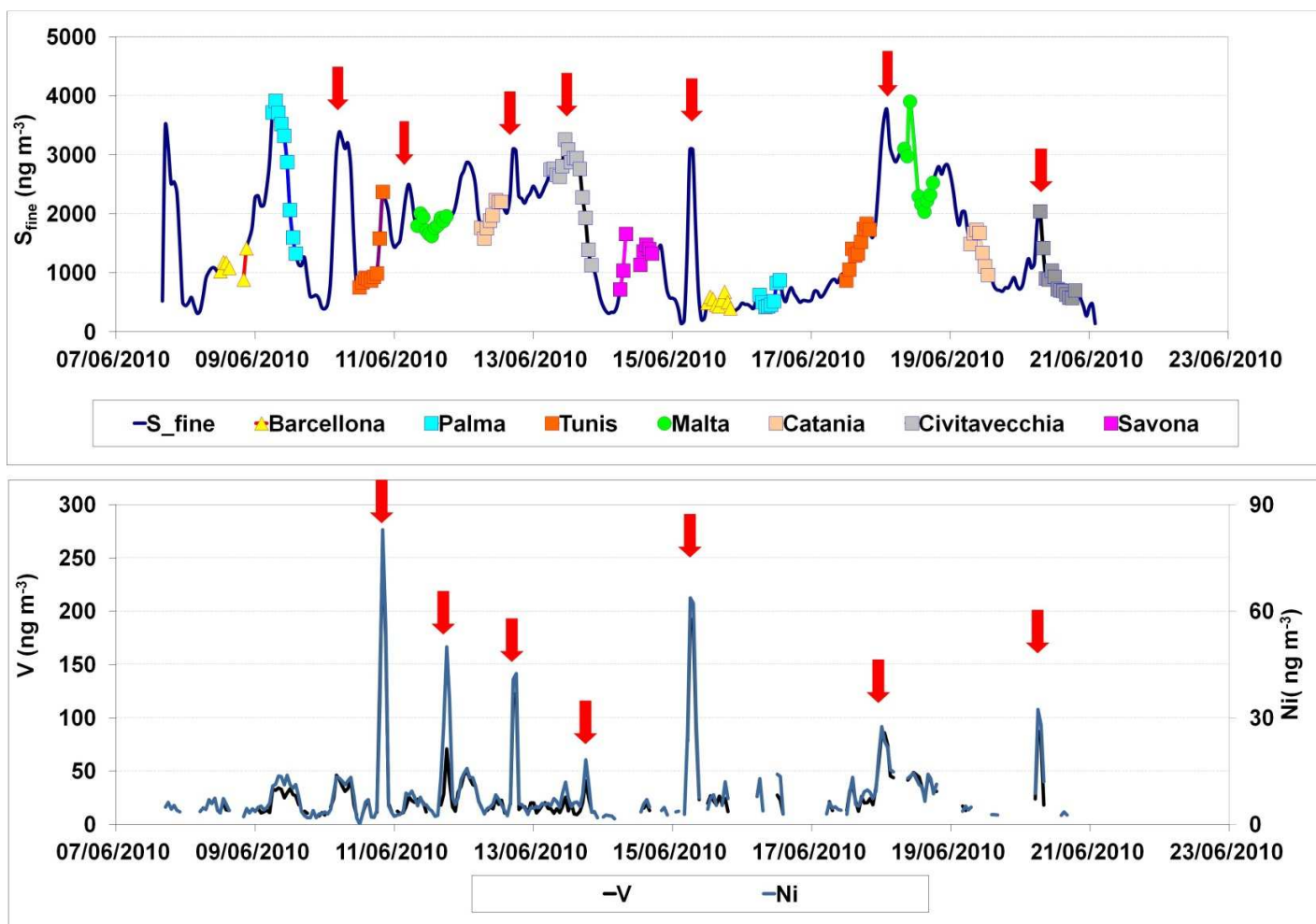
Figure E3.b

Figure E3: Synoptic maps of pressure field over Europe and North Atlantic at 00 UTC during the 2010 (a) and 2009 (b) cruise.



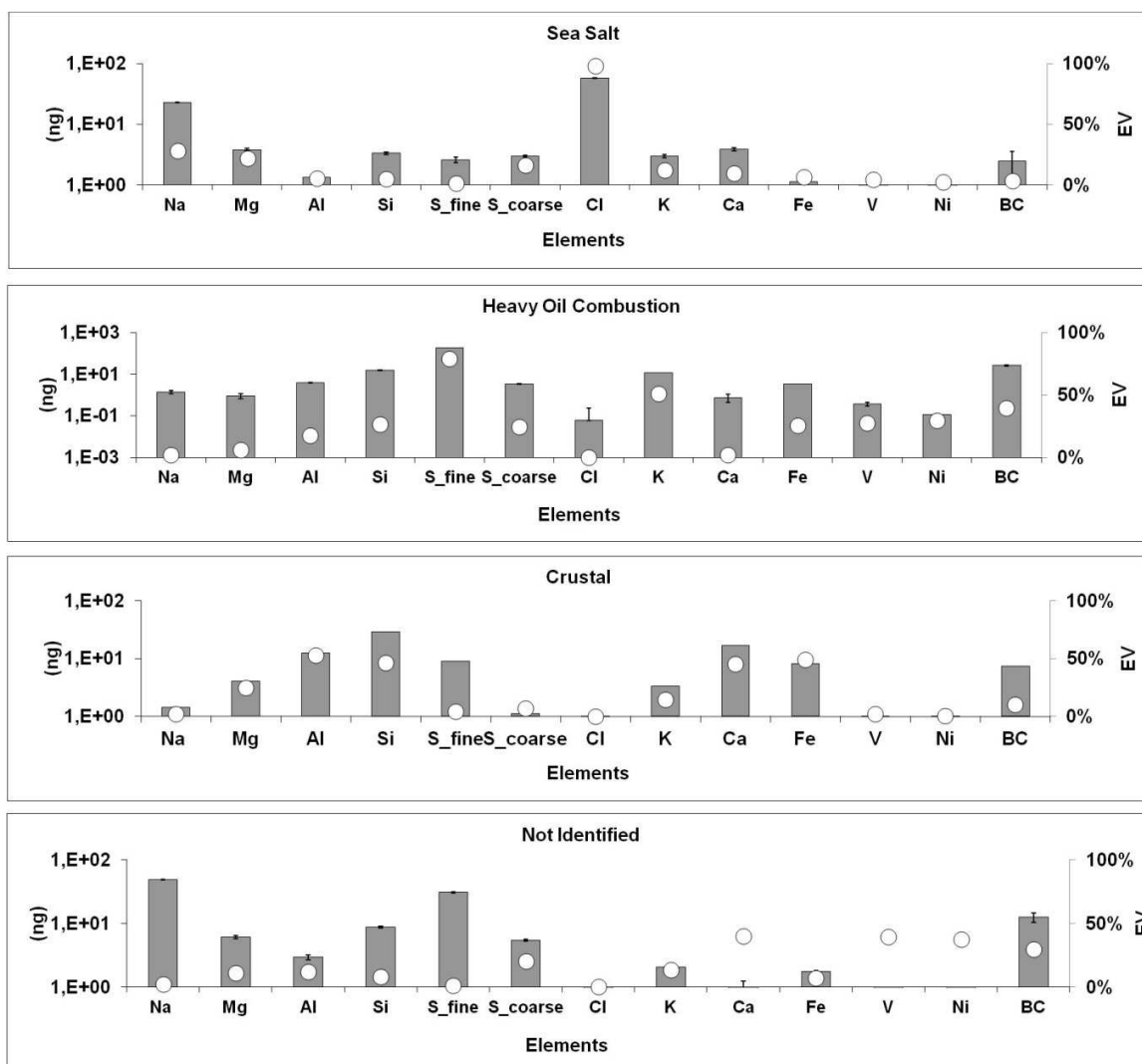
102
103
104
105
106
107

Figure E4: Time trends of elemental concentration values measured during the second week of the 2010 cruise: an episode characterized by high Al, Si, K, Ca, Fe and BC concentration values occurred between 18 and 19 June and was discarded in the PMF analysis



108
 109
 110
 111
 112
 113
 114

Figure E5: S_f , (top panel) V, Ni (bottom panel) concentration time trend during the 2010 cruise. Colored points highlight measurements in the harbours while red arrows marks correlated concentration peaks.



115
 116
 117 **Figure E6:** PM₁₀ source profiles (left axis) extracted by the PMF with the 2009 data set. On the right axis the
 118 Evaluation Factors (EV) for each element/compound are given (white circle)

119 *References:*

- 120 Assandri, L., 2011. Analisi tramite fluorescenza X del particolato atmosferico raccolto su filtri in teflon e fibra di quarzo. Master thesis in
121 Physics, University of Genoa.
- 122 Chiari, M., Lucarelli, F., Mazzei, F., Nava, S., Paperetti, L., Prati, P., Valli, G., Vecchi, R., 2005. Airborne particulate matter
123 characterization in an industrial district near Florence, by PIXE and PESA. X ray Spectrometry 34, 323 -329.
- 124
- 125 Mason, B. H., Principles of Geochemistry, Wiley, 1966
- 126
- 127 F. Mazzei, A. D'Alessandro, F. Lucarelli, F. Marengo, S. Nava, P. Prati, G. Valli, R. Vecchi, 2006. Elemental composition and
128 source apportionment of particulate matter near a steel plant in Genoa (Italy). Nuclear Instruments and Methods B 249, Issue 1-2,
129 548-551.
- 130
- 131 Seinfeld, J.H., Pandis, S.N., Atmospheric chemistry and physics. John Wiley and Sons, 1998.
- 132