



Characterization of
PM₁₀ sources in the
central
Mediterranean

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Characterization of PM₁₀ sources in the central Mediterranean

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Abstract

The Mediterranean Basin atmosphere is influenced by both strong natural and anthropogenic aerosol emissions, and is also subject to important climatic forcings. Several programs have addressed the study of the Mediterranean basin; nevertheless important pieces of information are still missing. In this framework, PM₁₀ samples were collected on a daily basis on the island of Lampedusa (35.5° N, 12.6° E, 45 m a.s.l.), which is far from continental pollution sources (the nearest coast, in Tunisia, is more than 100 km away). After mass gravimetric measurements, different portions of the samples were analyzed to determine the ionic content by Ion Chromatography (IC), the soluble metals by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), and the total (soluble + insoluble) elemental composition by Particle Induced X-ray Emission (PIXE). Data from years 2007 and 2008 are used in this study.

The Positive Matrix Factorization (PMF) model was applied to the 2 year long data set of PM₁₀ mass concentration and chemical composition to assess the aerosol sources affecting the Central Mediterranean basin. Seven sources were resolved: sea-salt, mineral dust, biogenic emissions, primary particulate ship emissions, secondary sulphate, secondary nitrate, and combustion emissions. Source contributions to the total PM₁₀ mass were estimated to be about 40 % for sea-salt, around 25 % for mineral dust, 10 % each for secondary nitrate and secondary sulphate, and 5 % each for primary particulate ship emissions, biogenic emissions, and combustion emissions. Large variations in absolute and relative contributions are found and appear to depend on the season and on transport episodes. In addition, the secondary sulphate due to ship emissions was estimated, and found to contribute by about one third to the total sulphate mass. Results for the sea-salt and mineral dust sources were compared with estimates of the same contributions obtained from independent approaches, leading to an estimate of the water content bound to the sea salt in the marine source.

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1 Introduction

Atmospheric aerosols are estimated to have negative effects on human health and to play a relevant role in climate, also affecting the hydrological cycle (IPCC). In this context, the Mediterranean Basin is a complex area, due to the strong influences from both natural and anthropogenic emissions, to the peculiar meteorology of the basin, and to conditions (high solar irradiation, summer temperature, humidity) favouring secondary aerosol formation processes (Pey et al., 2009; Im et al., 2012). Information on the aerosol sources and properties in the Mediterranean area is essential for the determination of the impacts on the health of the population living in the countries facing the Basin (among the world's most populated areas) and on the climate of the area. This is particularly important because future climate projections by IPCC consider the Mediterranean among the regions most sensitive to climate change (IPCC).

Owing to its importance, Mediterranean atmospheric aerosol and meteorology have been intensively studied (e.g., Salvador et al., 2014; Pey et al., 2013; Pace et al., 2006; Kopanakis et al., 2012; Dayan et al., 1989) and several international programs have focused on the assessment of chemistry and climate and their interactions, nevertheless important pieces of information are still missing. For instance, the source contribution and the forcing of short-lived species (both of them highly space and time variable) remain uncertain, and are not well taken into account in climate simulation.

Without aiming at a thorough review of the published information, it is worthy to recall that PM_{10} concentration is observed to increase from North-Western to South-Eastern Mediterranean due to increasing contributions from both natural and anthropogenic sources (Pey et al., 2013); the Western and Eastern Mediterranean basins have been observed to be characterized by different atmospheric dynamical and chemical processes (e.g., neutralization of secondary aerosol, Querol et al., 2009). The Mediterranean boundary layer has been observed to generally follow a clear annual behaviour, with minimum vertical extension during summer and maximum altitudes in winter (with an opposite trend with respect to the one commonly observed in continental areas)

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Additional samplings of PM₁₀ on quartz filters were performed in 2007, from 16 May to 15 August, using a low volume Tecora ECHO-PM sampler (2.3 m³ h⁻¹), with collection times ranging from 24 to 72 h, for a total of 24 samples.

2.2 Analyses

The mass of the collected PM₁₀ was obtained by gravimetric measurements of the Teflon filters before and after sampling. Before weighting, filters were conditioned for at least 24 h in an environmentally controlled room (35–45 % relative humidity, 25 °C).

Afterwards, every Teflon filter was cut into three portions: a quarter was analyzed for the ionic content by Ion Chromatography (IC), a second quarter for soluble metals by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES); the remaining half filter was analyzed for the total (soluble + insoluble) elemental composition by Particle Induced X-ray Emission (PIXE).

More in detail, the quarter of Teflon filter devoted to ion chromatography was extracted in about 10 mL (accurately weighted) of ultra-pure water (MilliQ water, resistivity > 18 MΩ) in ultrasonic bath for 15 min and analysed for the ionic content by using 3 Dionex ion chromatographs fed by an auto-sampler. Cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺), inorganic anions (F⁻, Cl⁻, NO₃⁻, SO₄²⁻), and some organic anions (methane-sulphonate – MSA, acetate, formate, glycolate, oxalate) were determined for each sample as reported in (Becagli et al., 2011). Detection limits (DLs) were in the range 0.08–0.16 ng m⁻³ and reproducibility was better than 5 %.

Another quarter was extracted in ultrasonic bath for 15 min with MilliQ water acidified at pH 1.5–2 with ultra-pure nitric acid obtained by sub-boiling distillation. This extract was used for the determination of the soluble part of selected metals (Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn) with an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Varian 720-ES) equipped with an ultrasonic nebulizer (U5000 AT+, Cetac Technologies Inc.). The value of pH was chosen because it is the lowest value found in rainwater (Li and Aneja, 1992) and therefore it leads to the determination

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Briefly, PMF is an advanced factor analysis technique (Paatero, 1997; Paatero and Hopke, 2003) that uses realistic error estimates to weigh data values and imposes non-negativity constraints in the computational process, which is based on a weighted least-squares approach. With more detail, PMF model may be written as $\mathbf{X} = \mathbf{G} \cdot \mathbf{F} + \mathbf{E}$, where \mathbf{X} is the $n \times m$ matrix of the m measured chemical species in n samples and \mathbf{G} and \mathbf{F} are factor matrices to be determined: \mathbf{G} is the $n \times p$ matrix of source contributions to the samples; \mathbf{F} is the $p \times m$ matrix of factor composition (source profiles); \mathbf{E} is the residual matrix.

Input data were handled according to (Polissar et al., 1998): measured data were weighted with their overall analytical uncertainty increased by one third of the detection limit (DL); data below the DL were substituted with a value corresponding to DL/2, and a DL*5/6 uncertainty was associated to them. Missing data were handled filling the gaps with the geometric mean value calculated over the days with data and associating to them a 400 % uncertainty.

Mass concentration was put in the PMF analysis as an internal variable, with very high (400 %) uncertainty (Norris et al., 2009), as it is suggested when portions of the mass (not directly correlated with the other input variables) are not measured/available: in our case, no data on the carbonaceous fraction is available for the whole considered period. As additional test, PMF was also run with normalization of \mathbf{G} and \mathbf{F} matrices by multilinear regression analysis on the PM₁₀ gravimetric mass concentrations and gave comparable results for both contributions and profiles of the detected sources with respect to PMF runs performed with internal mass, thus assuring that mass data did not influence the profiles.

PMF was run with the algorithm PMF2 (Paatero, 1997) in the robust mode, in order to reduce the influence of outliers. Solutions with different numbers of factors were examined; rotational ambiguity was tested by analyzing multiple FPEAK rotations; several seeds were investigated and values of Q/Q_{exp} were examined (where Q is the weighted least-squares function to be minimized).

3 Results and discussion

3.1 PM₁₀ concentration

The PM₁₀ daily concentration is reported in Fig. 2: a great variability was observed, with values spanning one order of magnitude, as minima were found to be around 10 µg m⁻³ and several episodes reached more than 100 µg m⁻³.

The average PM₁₀ concentration for the whole period (2007–2008) was 32 ± 17 µg m⁻³ (median: 29 µg m⁻³, 25th percentile 21 µg m⁻³, 75th percentile 39 µg m⁻³); no relevant difference was observed between the two years 2007 and 2008, with mean PM₁₀ concentrations of 33 ± 15 µg m⁻³ and 32 ± 19 µg m⁻³, respectively. These values are similar to those measured in two different background/rural stations on the island of Crete, Greece (Kopanakis et al., 2012; Gerasopoulos et al., 2006) and in the range observed for urban background sites across Southern Europe (Karanasiou et al., 2014).

Despite the distance of the sampling site from pollution sources, concentrations exceeding the daily European Union's limit value (50 µg m⁻³) were registered in 24 days (out of 278 sampling days) in 2007, and in 32 (out of 284 sampling days) in 2008, i.e. for 10 % of the sampling period, being the highest concentrations due to Saharan dust events, as shown in (Marconi et al., 2014). The EU legal term of not exceeding the daily limit value of 50 µg m⁻³ for the percentile 90.4 of the annual values was not respected in 2008 (when percentile 90.4 was 52.5 µg m⁻³) and nearly reached in 2007 (when percentile 90.4 was 48.9 µg m⁻³).

3.2 PM₁₀ speciation

Average concentrations (and standard deviation) of the main measured elements/species for all the sampling period and in the different seasons are reported in Table 1. The determination of several elements by different techniques allowed performing a quality assurance analysis of data and studying the solubility of specific ele-

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ments (Becagli et al., 2012), by comparing results on the total content as obtained by PIXE and on the soluble content as obtained by IC or ICP-AES.

Sea-salt and mineral dust contributions were estimated assuming the average composition of seawater and Earth's soil (Mason, 1966). In particular, sea-salt concentration (i.e. [sea-salt]) was evaluated, for every day, according to the expression:

$$[\text{sea-salt}] = [\text{Cl}^-] + [\text{ssNa}^+] + [\text{ssCa}] + [\text{ssMg}] + [\text{ssK}] + [\text{ssSO}_4^{2-}]$$

where $[\text{Cl}^-]$ is the Cl concentration measured by IC and Na, Mg, K, Ca, and SO_4^{2-} contributions due to sea-salt ($[\text{ssNa}^+]$, $[\text{ssMg}]$, $[\text{ssK}]$, $[\text{ssCa}]$ and $[\text{ssSO}_4^{2-}]$) are estimated according to the following equations:

$$[\text{ssNa}^+] = [\text{Na}^+] - [\text{nssNa}^+] = [\text{Na}^+] - [\text{nssCa}] \cdot (\text{Na/Ca})_{\text{crust}} = [\text{Na}^+] - ([\text{Ca}] - [\text{ssCa}]) \cdot (\text{Na/Ca})_{\text{crust}}$$

$$[\text{ssCa}] = [\text{ssNa}^+] \cdot (\text{Ca/Na})_{\text{seawater}}$$

$$[\text{ssMg}] = [\text{ssNa}^+] \cdot (\text{Mg/Na})_{\text{seawater}}$$

$$[\text{ssK}] = [\text{ssNa}^+] \cdot (\text{K/Na})_{\text{seawater}}$$

$$[\text{ssSO}_4^{2-}] = [\text{ssNa}^+] \cdot (\text{SO}_4^{2-}/\text{Na})_{\text{seawater}}$$

where $[\text{Na}^+]$ and $[\text{Ca}]$ are the concentrations obtained respectively by IC and PIXE; $(\text{Na/Ca})_{\text{crust}}$ represents the mean Na/Ca ratio in the Earth crust, assumed to be 0.56 according to literature (Henderson and Henderson, 2009); $(\text{Ca/Na})_{\text{seawater}}$, $(\text{Mg/Na})_{\text{seawater}}$, $(\text{K/Na})_{\text{seawater}}$ and $(\text{SO}_4/\text{Na})_{\text{seawater}}$ are the mean elemental ratios in bulk seawater and are set to 0.038, 0.119, 0.037, and 0.253, respectively (Henderson and Henderson, 2009).

The contribution of mineral dust ([mineral dust]) was calculated as sum of the metal oxides for every day based on stoichiometric ratios (e.g., Nava et al., 2012):

$$[\text{mineral dust}] = 1.35[\text{nssNa}^+] + 1.66[\text{nssMg}] + 1.89[\text{Al}] + 2.14[\text{Si}] + 1.21[\text{nssK}] + 1.40[\text{nssCa}] + 1.67[\text{Ti}] + 1.43[\text{Fe}]$$

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data, strengthening the results of the analysis. Briefly, the analysis allowed the identification of 7 different sources which are identified as sea-salt, mineral dust, biogenic emission aerosol, secondary nitrate particles, secondary sulphate particles, primary particulate ship emissions, and combustion emission aerosol (see the following sections). All together, these sources reconstruct the measured gravimetric mass within 4 %. The six-factor solution was excluded, as it did not separate the secondary nitrate source from the combustion emission one; the eight-factor solution was also discarded, as it was identifying an unlikely source related primarily to Ca and Sr (44 and 21 % explained variations, respectively).

The seven sources are described in the following sections. Profiles are reported in Fig. 3: the left y axis displays the fraction of the elemental mass concentration, reported in the graph as blue column, whereas the right y axis refers to the explained variation of each element, depicted as red squares (the contribution of one element in all the profiles sum up to one, when the variation of the element is completely reconstructed by the model). The evolution of the daily contribution of each identified source is shown in Fig. 4.

3.3.1 Sea-salt

Na⁺, Cl⁻, Mg, K and Br are the characterizing elements for this factor (Fig. 3, panel a); most of their mass concentration is explained by this source (explained variations: 64, 83, 48, 30, and 61 % respectively). Some SO₄²⁻ is also present. The elemental ratios are in good agreement with those measured in marine water, suggesting a common marine origin for the species characterizing this factor. More in detail, the source profile elemental ratios are reported in Table 2 together with the sea salt literature elemental ratio (Henderson and Henderson, 2009). Thus, this factor of the PMF is identified with the primary marine aerosol, sea salt aerosol.

The temporal evolution shows no clear seasonality, as it can be expected for this source, since the sampling site is located directly on the coast and sea-salt aerosol is known to be strongly related to wind intensity (Kishcha et al., 2011).

3.3.2 Mineral dust

Several crustal elements such as Al, Si, Ti, Mn, Fe, Sr, Ca, K and Mg characterize this factor (Fig. 3, panel b). This source reconstructs almost completely the mass concentration of some of these elements, such as Al, Si and Ti (more than 80 % of their signal).

Enrichment factors (EF) with respect to Al in this profile were calculated using the average Earth's soil composition reported by (Mason, 1966) and are reported in Table 3.

The values of these EFs, all close to 1 (with a moderate enrichment only for Ca and Sr which is usually associated with Ca in carbonates), strengthen the identification of this source as "mineral dust".

The temporal evolution of this factor shows no clear seasonality, being dominated by many narrow peaks. Sixty-hour backward trajectories ending at Lampedusa at 50 m.a.s.l. corresponding to the start, middle, and end time of the sampling interval were calculated for the peaks in PM₁₀ concentrations due to mineral dust larger than the 95th percentile (about 32 µg m⁻³), using the NOAA Air Resource Laboratory HYSPLIT transport model (Draxler and Rolph, 2012). The analysis showed that in about 86% of the cases at least one of the three trajectories associated to the sampling overpassed Northern Africa (see Fig. 5). This result should be read taking into account the uncertainties in the HYSPLIT trajectories due to the lack of meteorological measurements in the examined region, the low model horizontal resolution, and the possible rapid temporal variation of the air masses during the sampling interval. No relevant difference in the available crustal markers ratios was observed in correspondence of African dust transport episodes, suggesting a similar chemical composition for the Lampedusa soil and the African dust (limitedly to the measured elements), or a negligible impact of local dust. In fact, enrichments in Ca with respect to the average Earth's soil composition are reported for dust originating from different African areas, e.g. Western Sahara and Moroccan Atlas, due to the high content of minerals such as calcite and dolomite (Avila et al., 1997; Coz et al., 2009). An enhancement of Ca

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amounts for dust originating from the Algeria–Tunisia sector was shown by (Marconi et al., 2014).

The seasonality of African desert dust advection episodes in Lampedusa was discussed in a recent study (Marconi et al., 2014) based on a larger data-set (June 2004–December 2010), in which ground level aerosol concentrations are compared with aerosol optical depth measurements routinely performed at the Station for Climate Observations of Lampedusa, providing information on the dust content in the entire air column above the sampling site. African desert dust transports often occur above the boundary layer (mainly in summer); in fact, despite the strong seasonality observed for the aerosol optical depth, at the ground level no evident seasonal trend was observed for PM₁₀ or crustal markers, in agreement with the mineral dust temporal pattern obtained by PMF on the 2007–2008 data-set. In particular, as shown by (Marconi et al., 2014), while the aerosol optical depth and the frequency of occurrence of vertically integrated dust events peak in summer, a relative minimum of PM₁₀ concentration and its frequency of occurrence is found in the months of June–July.

3.3.3 Biogenic emissions

This factor is mainly characterized by MSA (Methanesulfonic Acid), and explains almost completely (87 %) its mass concentration. A small percentage (6 %) of the total mass of SO₄²⁻ is also accounted by this source, and constitutes however the prevalent absolute mass contribution to this factor.

MSA is used as a tracer for biogenic sulphur emissions (from phytoplankton processes), as it is solely produced by oxidation of dimethylsulfide (DMS). The evaluation of the nssSO₄²⁻ emitted by the biogenic source, (nss-SO₄²⁻)_{bio}, suffers by the variability of the (nss-SO₄²⁻)_{bio}/MSA emission ratio as this depends on the latitude, the NO_x levels and the temperature (Seinfeld and Pandis, 1998; Bates et al., 1992); this is especially true for the Mediterranean basin, where only a maximum value for such ratio has been estimated in previous studies (in Crete) (Mihalopoulos et al., 1997; Kouvarakis

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The $V_{\text{sol}}/Ni_{\text{sol}}$ ratio for this source is 3.40, in good agreement with the aforementioned literature data. Moreover, the interpretation of this factor as “primary ship emissions” is strengthened by the fact that the observed SO_4^{2-}/V_{sol} ratio (6.2 w/w ; as V has been found to have a 80 % solubility in ships exhausts, such value corresponds to a SO_4^{2-}/V ratio of 5.0) is of the same order of magnitude as the ones reported by (Agrawal et al., 2008) for the particulate matter freshly emitted from the main engine of an ocean going container vessel (SO_4^{2-}/V ranging from 8.9 to 11.9 depending on the engine operating conditions for the considered vessel). Much higher SO_4^{2-}/V values are reported when secondary aerosols (mainly SO_4^{2-}) are formed from the oxidation of the gaseous precursors (e.g., SO_2) (Becagli et al., 2012).

A clear seasonal evolution, with maxima during summer, is evident for this source; this is in agreement with the temporal evolution of ship emissions markers (Ni_{sol} , V_{sol} , $nssSO_4^{2-}$) observed by (Becagli et al., 2012) on a larger data set of samples collected at the same Lampedusa site (years 2004–2008). The authors explained the temporal evolution of these markers as due to three possible causes: (a) an increased photochemical activity in summer leading to a faster production of secondary aerosols, (b) a stronger stability of the marine boundary layer during summer, leading to an increase of their concentrations at the ground level, (c) prevalent winds from the Strait of Sicily (one of the main ship paths) during summer. Due to the primary origin of this factor, such seasonal behaviour appears to be more probably linked to the two latter phenomena.

3.3.7 Combustion emissions

Several compounds, as K, Cu, NO_3^- , SO_4^{2-} and short carboxylic acids as Oxalates and Glycolates, whose signal is mostly explained by this source, characterize this factor. K and SO_4^{2-} are commonly associated with biomass burning, and short carboxylic acids have been recently associated with coal/waste/biomass burning (Wang et al., 2007). Enhancements of Cu in the aerosol produced by wood combustion have also been

reported by several studies (Dall'Osto et al., 2013). Therefore this factor has been interpreted as a generic combustion source, which includes biomass burning.

The temporal evolution (Fig. 4) of this factor shows no clear seasonality, even if important contributions during summer may be observed and may be linked to the more frequent occurrence of fires in the Mediterranean region. During spring and autumn the contributions from this source are generally low, while several high contribution days may be observed during winter. Figure 6 shows the combined evolution of the desert dust and combustion emissions contributions to PM_{10} , and some selected cases with air mass trajectories and satellite observations of active fires. Most of the winter cases characterized by elevated contributions of combustion sources display also a high contribution from the mineral dust source (see Fig. 6). The analysis of the backtrajectories shows that these days were mostly interested by African dust advection episodes. Several studies report that dust particles plumes from the Saharan area also export biomass-burning particles (Tesche et al., 2011; Rodriguez et al., 2011), mainly during the dry winter season. Further, small fires, often occurring in biomes as croplands, wooded savannas and tropical forests, are usually below the detection limit of the current generation of surface reflectance/thermal imagery instruments (Randerson et al., 2012). Therefore, winter contributions from this source are likely to be mainly due to small scale biomass burning activity in north Africa; nonetheless, some winter peaks of this source appear also connected with fires and/or biomass burning activity in Central-Eastern Europe (e.g., 13–15 March 2007, Fig. 6).

Summer peaks have been clearly connected by backtrajectory analysis to fires mainly in South Italy and Sicily, thus supporting the interpretation of this factor as a combustion source, with a main contribution from biomass burning.

3.3.8 Combustion emission source identification: additional data

As previously reported, additional data on the carbonaceous fractions in PM_{10} are available for limited periods in the years 2007–2008. In particular, 24 samplings of PM_{10} on quartz filters for EC / OC analysis were performed from 16 May to 15 August 2007 with

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integration times ranging from 24 to 72 h. The starting time of the sampling was set in the morning/early-afternoon (between 8 a.m. and 2 p.m. LT) due to manual filter change operations. In Fig. 7, the EC and OC contents are plotted together with the estimates of the contributions from the combustion emission source as obtained by PMF. EC and OC are produced in combustion processes of both fossil fuels and biomasses, while OC may have also a biogenic origin. Therefore, EC and, to a smaller extent, OC are good markers of combustion sources, while additional information from other chemical tracers (such as K, levoglucosan, glycolates or radiocarbon, Bernardoni et al., 2013) is needed for the assessment of the burnt fuel (biomass or fossil). As shown in Fig. 7, EC and OC are highly correlated with the combustion emission contribution estimated by the PMF, thus strengthening the attribution of the seventh PMF factor to a combustion source. Small discrepancies, as the one occurring at the beginning of July, may be attributed to episodic important contributions to EC and OC from heavy oil combustion, that is from the primary particulate ship emission source, also reported in Fig. 7.

3.4 PM₁₀ source apportionment

Figures 8 and 9 report the relative and absolute seasonal contributions of the seven identified sources (winter – December, January, February; spring – March, April, May; summer – June, July, August; fall – September, October, November). During all the seasons, natural sources (sea-salt, mineral dust, and biogenic emissions) give the largest contribution to PM₁₀, accounting for a minimum of 62 % in spring to a maximum of 76 % during fall. The maximum relative and absolute contribution of sea-salt is observed in winter, while relative contributions during the other seasons are comparable. This is consistent with a higher wind velocity during the winter months (7.4 vs. 5.6 ms⁻¹ in summer, 6.5 ms⁻¹ in spring, and 6.1 ms⁻¹ in fall during 2007 and 2008).

The mineral dust maximum relative contribution is found during fall (37 %), and is around 20 % in the other seasons. As expected, the maximum relative contribution of biogenic emissions is during summer, and is negligible in winter.

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Among the anthropogenic sources, primary particulate ship emissions and secondary sulphate display a clear and similar seasonality, with maxima in summer. No significant dependence on the season is observed for the relative contributions of secondary nitrate and combustion emissions. It is worth to note that the not explained mass is around 10 % across the seasons.

The annual average relative contributions are reported with their uncertainties in Fig. 10: the main contribution to aerosol comes from sea-salt, accounting for 40 % of the mass; the second contribution is from mineral dust (25 %). Taking into account also of the biogenic emissions, accounting for 4 % of the mass, the contribution of natural sources to the PM₁₀ in Lampedusa is estimated to be around 68 % on average. As concerns secondary nitrates and sulphates, they are estimated to contribute by 9 % and 11 % to the total PM₁₀, respectively. Finally, primary particulate ship emissions have been observed to give an average 4 % contribution, while 5 % of PM₁₀ was found to be due to combustion emissions. Uncertainties on the contributions were estimated propagating the uncertainties obtained by the PMF model on the **G** matrix.

In absolute terms, the following contributions were estimated: sea-salt, $12.9 \pm 1.1 \mu\text{g m}^{-3}$; mineral dust, $7.8 \pm 0.5 \mu\text{g m}^{-3}$; biogenic emissions, $1.1 \pm 0.2 \mu\text{g m}^{-3}$; secondary nitrate, $2.8 \pm 0.3 \mu\text{g m}^{-3}$; secondary sulphate, $3.4 \pm 0.4 \mu\text{g m}^{-3}$; primary particulate ship emissions, $1.2 \pm 0.2 \mu\text{g m}^{-3}$; combustion emissions, $1.5 \pm 0.3 \mu\text{g m}^{-3}$.

3.4.1 Evaluation of the total contribution from ship emissions to PM₁₀ in Lampedusa

An estimate of the contribution of the shipping emissions to the secondary sulphate formation was performed following previous studies (Kim et al., 2008; Viana et al., 2009), based on the observed correlation between the daily contributions from the primary particulate ship emission source and those from the secondary sulphate source as assessed by PMF analysis. The contributions from these two sources are plotted one against the other in Fig. 11: the solid line represents the minimum amount of secondary sulphate that is expected to be associated to the observed primary particulate

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The mineral dust estimate from the PMF analysis is about 30% higher than the crustal content calculated as the metal oxides sum. It must be pointed out that no information on carbonates is available, and that the used analytical techniques are not sensitive to the Oxygen content, thus the estimated metal oxide mass is based on the assumption of an oxygen fraction according to the prevalent oxides of the crustal elements. Nevertheless, PMF may slightly overestimate the source contribution as a consequence of some profile interferences (Mazzei et al., 2008): in this case, the PMF retrieval associated a small amount of SO₄²⁻ and Cl⁻ to the crustal dust profile, probably due to their co-linearity in case of long-range transport episodes.

Coming to sea-salt, the stoichiometric approach gives an estimate of the average contribution of 8.3 μg m⁻³, to be compared with the PMF estimated contribution for the sea-salt source of 12.9 μg m⁻³. Since all the sea-salt elements are measured, this discrepancy is likely to be due to other compounds not visible with the applied analytical techniques, such as water or, to a lesser extent, organic compounds. In fact, although gravimetric measurements are performed in a controlled atmosphere (40% relative humidity, 25 °C), some water may endure and it is likely to be bound to hygroscopic aerosol components such as sea-salt; this is in agreement with recent studies that have shown water exists in ambient aerosol also at low relative humidity (Plinis et al., 2014; Engelhart et al., 2011). Therefore, taking into account for water, the PMF contribution from the sea-salt source may be possibly split in two contributions, namely “dry sea-salt” and “H₂O”, accounting for about 26 and 14% of the PM₁₀ mass in Lampedusa, respectively. This estimate lays in the 10 to 20% range reported in literature for unaccounted mass in Mediterranean background/rural sites (Koçak et al., 2007; Pey et al., 2009; Querol et al., 2009), which is generally attributed to water molecules of moisture.

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Table 1. Average concentrations (Av) and standard deviation (SD) of the main measured elements/species for all the sampling period and in the different seasons.

| n | Year 562 | | Winter (DJF) 136 | | Spring (MAM) 156 | | Summer (JJA) 142 | | Autumn (SON) 128 | |
|-------------------------------|-------------------|------|---------------------|------|---------------------|------|---------------------|------|---------------------|------|
| | ngm ⁻³ | | ngm ⁻³ | | ngm ⁻³ | | ngm ⁻³ | | ngm ⁻³ | |
| | Av | SD | Av | SD | Av | SD | Av | SD | Av | SD |
| Na | 3137 | 1996 | 3584 | 1972 | 3293 | 1937 | 2953 | 2108 | 2686 | 1860 |
| Mg | 374 | 187 | 377 | 171 | 405 | 201 | 345 | 190 | 367 | 177 |
| Al | 360 | 549 | 234 | 432 | 347 | 570 | 339 | 446 | 530 | 682 |
| Si | 896 | 1389 | 581 | 1106 | 889 | 1435 | 830 | 1097 | 1308 | 1756 |
| S | 1534 | 806 | 1051 | 387 | 1644 | 762 | 2098 | 904 | 1281 | 634 |
| Cl | 4708 | 3725 | 5727 | 3945 | 5263 | 3783 | 3592 | 3663 | 4212 | 3052 |
| K | 314 | 223 | 267 | 190 | 319 | 238 | 324 | 198 | 346 | 256 |
| Ca | 862 | 1120 | 694 | 916 | 922 | 1277 | 761 | 964 | 1077 | 1237 |
| Ti | 30 | 46 | 20 | 35 | 30 | 49 | 29 | 41 | 41 | 56 |
| V | 5.2 | 5.4 | 2.8 | 3.0 | 6.1 | 5.6 | 8.4 | 6.5 | 3.2 | 3.3 |
| Mn | 5.3 | 7.1 | 3.5 | 5.5 | 5.7 | 7.7 | 5.5 | 6.1 | 6.5 | 8.4 |
| Fe | 304 | 445 | 200 | 333 | 316 | 471 | 290 | 379 | 415 | 547 |
| Ni | 2.0 | 1.7 | 1.2 | 1.0 | 2.4 | 1.9 | 3.1 | 1.9 | 1.3 | 1.0 |
| Cu | 1.8 | 1.3 | 1.3 | 1.4 | 1.7 | 1.3 | 2.5 | 1.2 | 1.5 | 1.1 |
| Br | 15 | 11 | 20 | 13 | 15 | 10 | 13 | 11 | 12 | 9 |
| Sr | 7 | 8 | 6 | 5 | 8 | 10 | 6 | 7 | 7 | 8 |
| Na ⁺ | 3191 | 2191 | 3481 | 2230 | 3629 | 2352 | 2912 | 2211 | 2670 | 1751 |
| NH ₄ ⁺ | 673 | 452 | 477 | 313 | 757 | 481 | 954 | 441 | 463 | 340 |
| K ⁺ | 161 | 88 | 153 | 84 | 172 | 82 | 183 | 103 | 131 | 69 |
| Ca ²⁺ | 615 | 717 | 475 | 433 | 670 | 859 | 532 | 508 | 784 | 905 |
| Cl ⁻ | 4304 | 3743 | 5111 | 3807 | 4924 | 4019 | 3278 | 3646 | 3829 | 3072 |
| NO ₃ ⁻ | 2128 | 1148 | 1866 | 958 | 2434 | 1232 | 2283 | 1218 | 1861 | 1028 |
| SO ₄ ²⁻ | 3652 | 2074 | 2478 | 1110 | 4011 | 2059 | 4961 | 2276 | 3010 | 1674 |
| Ossal. | 144 | 85 | 101 | 58 | 151 | 83 | 194 | 80 | 126 | 88 |
| Glyc. | 6 | 5 | 5 | 4 | 8 | 6 | 7 | 6 | 6 | 4 |
| MSA | 22 | 23 | 4 | 4 | 22 | 19 | 46 | 25 | 14 | 14 |
| V _{sol} | 4.0 | 4.3 | 2.1 | 1.7 | 4.1 | 4.2 | 7.4 | 5.6 | 2.3 | 1.7 |
| Mn _{sol} | 3.1 | 3.9 | 1.9 | 3.9 | 3.3 | 4.2 | 3.4 | 3.0 | 3.9 | 4.2 |
| Ni _{sol} | 1.4 | 1.5 | 0.7 | 0.5 | 1.6 | 1.6 | 2.5 | 1.8 | 0.8 | 0.6 |
| Cu _{sol} | 1.2 | 1.1 | 0.7 | 1.1 | 1.3 | 1.3 | 1.8 | 0.9 | 0.9 | 0.8 |
| As _{sol} | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 |
| Pb _{sol} | 2.9 | 2.9 | 2.3 | 2.9 | 3.5 | 2.4 | 3.4 | 2.5 | 2.5 | 3.4 |
| Dust | 5765 | | 4021 | | 5774 | | 5327 | | 8093 | |
| SeaS. | 8335 | | 9626 | | 9554 | | 7013 | | 6946 | |

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Table 2. Elemental ratios for the sea-salt source.

| Ratio | Mg / Na ⁺ | SO ₄ / Na ⁺ | Cl ⁻ / Na ⁺ | K / Na ⁺ | Ca / Na ⁺ | Br / Na ⁺ |
|--------------------------------|----------------------|-----------------------------------|-----------------------------------|---------------------|----------------------|----------------------|
| PMF profile | 0.13 | 0.23 | 1.68 | 0.04 | 0.05 | 0.005 |
| Henderson and Henderson (2009) | 0.119 | 0.253 | 1.796 | 0.037 | 0.038 | 0.006 |

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[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)**Table 3.** Enrichment factors for the mineral dust source.

| EF(Mg) | EF(Si) | EF(K) | EF(Ca) | EF(Ti) | EF(Mn) | EF(Fe) | EF(Sr) |
|--------|--------|-------|--------|--------|--------|--------|--------|
| 0.90 | 0.83 | 0.92 | 2.81 | 1.21 | 0.79 | 1.05 | 1.72 |



Figure 1. Sampling site location.

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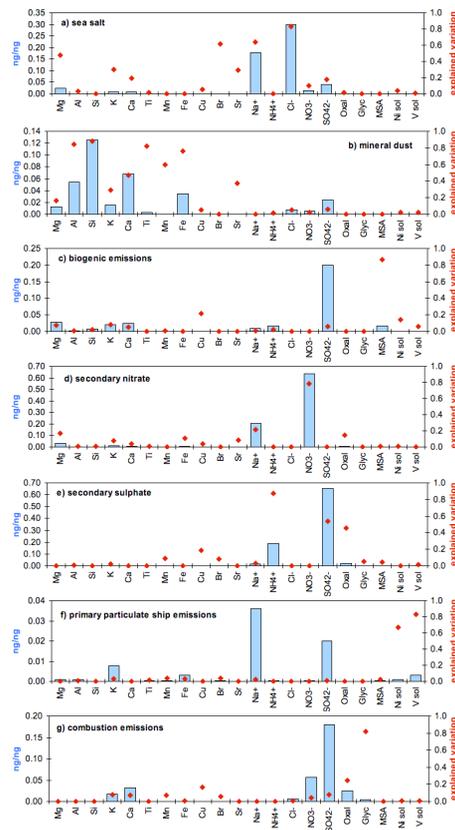


Figure 3. Profiles (fraction of the elemental mass concentration, blue columns) and explained variations (red squares, referring to the right y axis) of the identified PM₁₀ sources.

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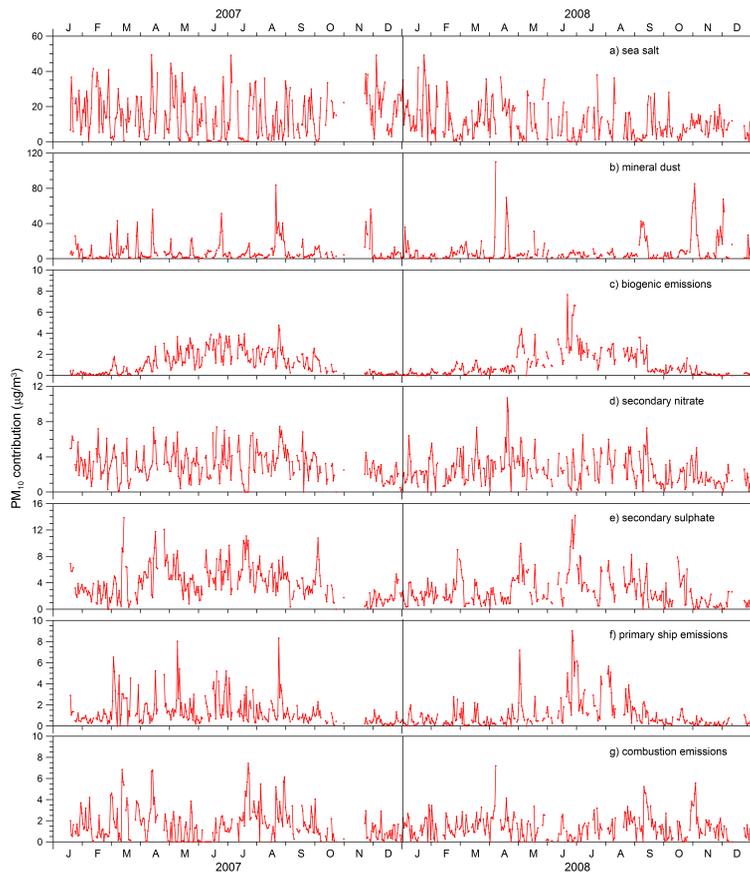


Figure 4. Temporal evolution of the PM₁₀ contributions from the identified sources.

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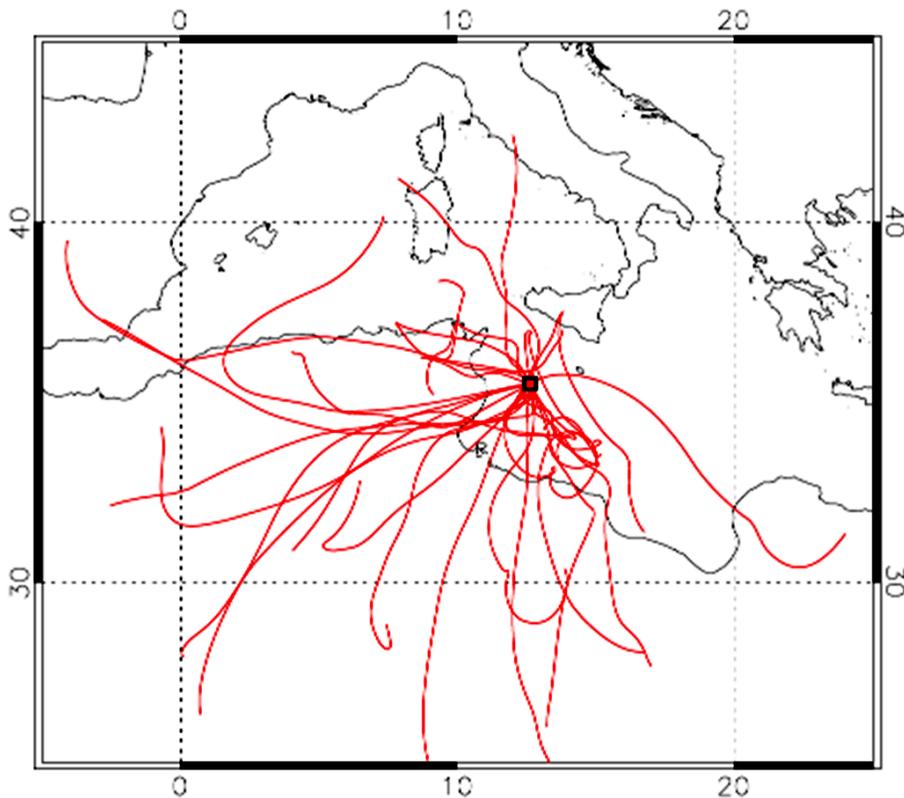


Figure 5. HYSPLIT backward trajectories ending at Lampedusa at 50 m a.s.l. corresponding to the peaks in the PM_{10} contributions due to mineral dust source (see text for the details).

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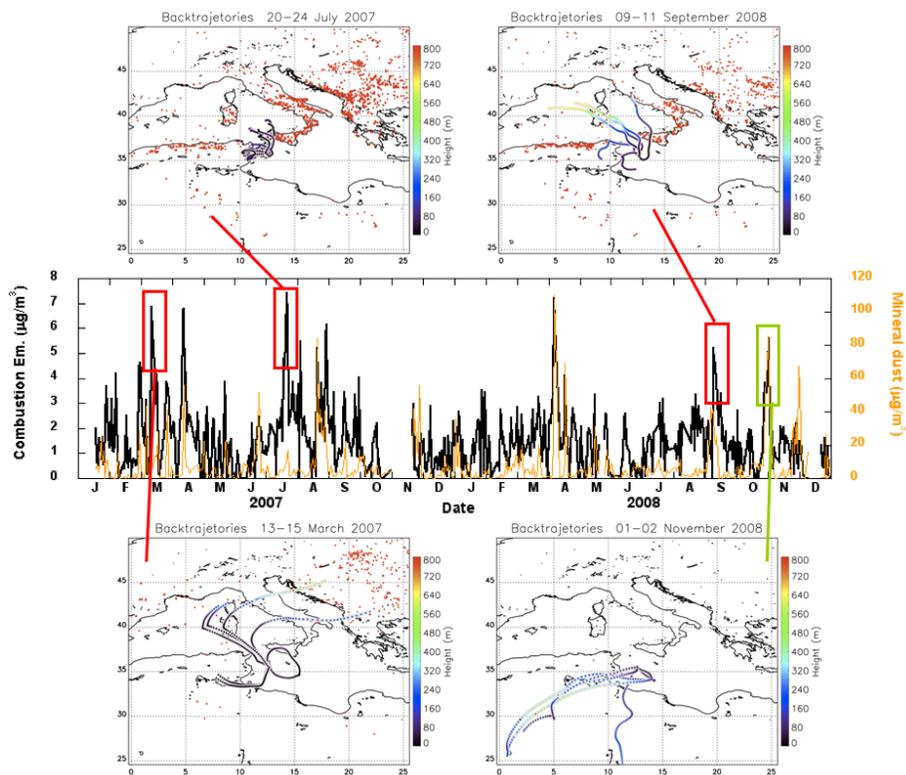


Figure 6. Temporal evolution of the “combustion emissions” and “mineral dust” sources; examples of trajectories from fires are evidenced in red, together with an example of advection from the Saharan region (green).

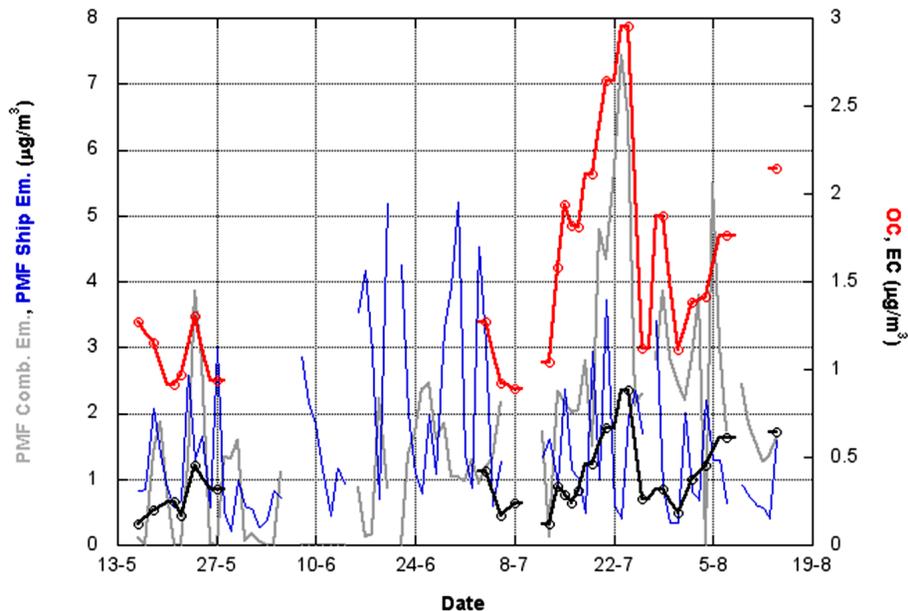


Figure 7. Comparison between EC and OC data and PMF estimates of the contributions of combustion emissions and primary particulate ship emissions in the period of EC / OC data availability. Results for EC and OC are reported with solid lines, black and red, respectively, referring to the secondary axis (empty rounds report the single sample result attributing it to the central sampling day).

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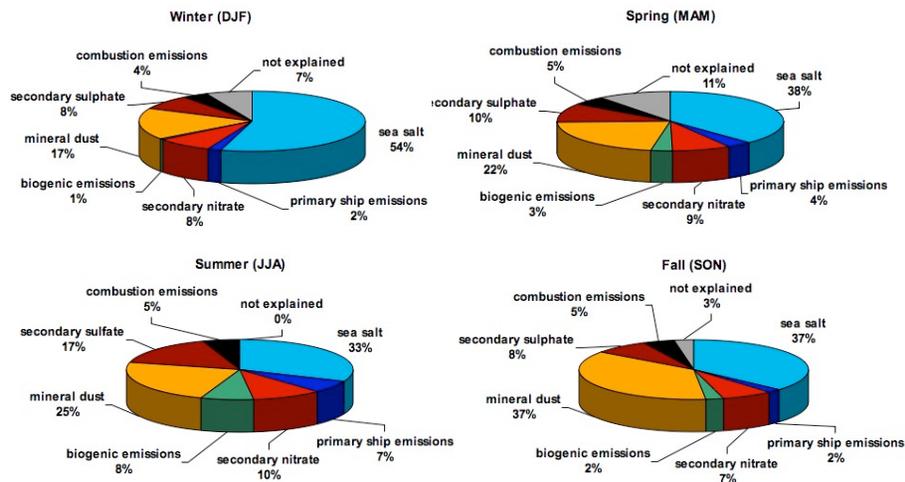


Figure 8. Seasonal relative contributions to PM₁₀ concentration (average over the years 2007–2008). Factors may sum to more than 100% due to number rounding.

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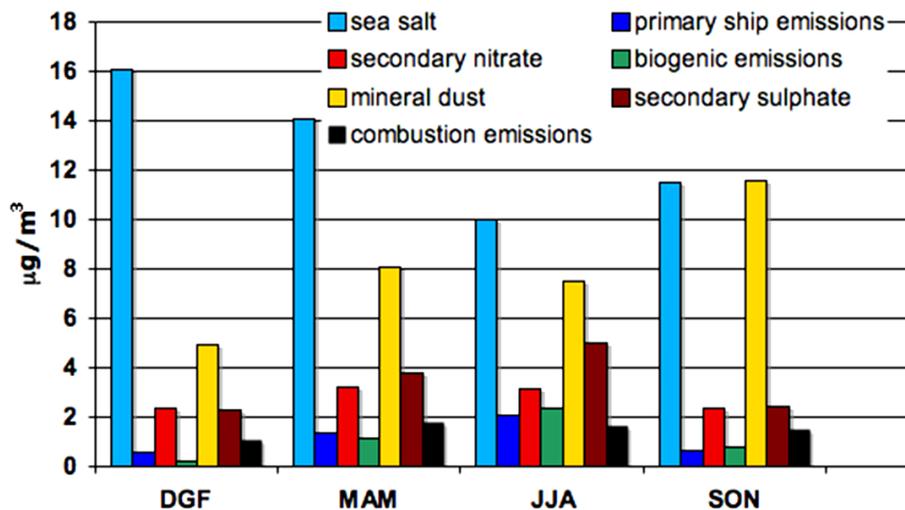


Figure 9. Seasonal absolute contributions to PM₁₀ concentration (average over the years 2007–2008).

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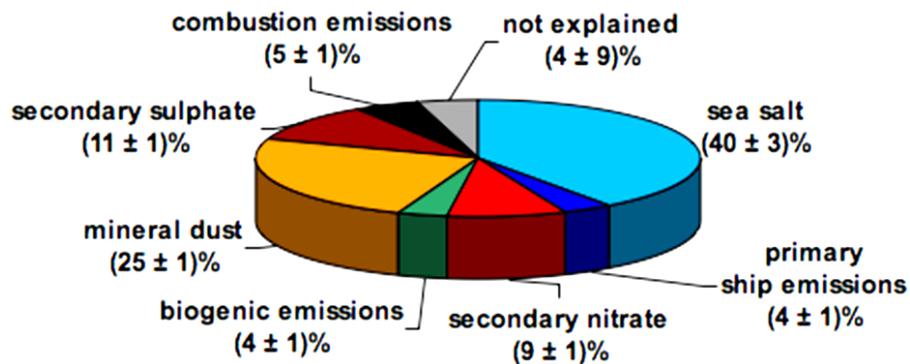


Figure 10. Relative annual contributions to the PM₁₀ concentration (average over the years 2007–2008).

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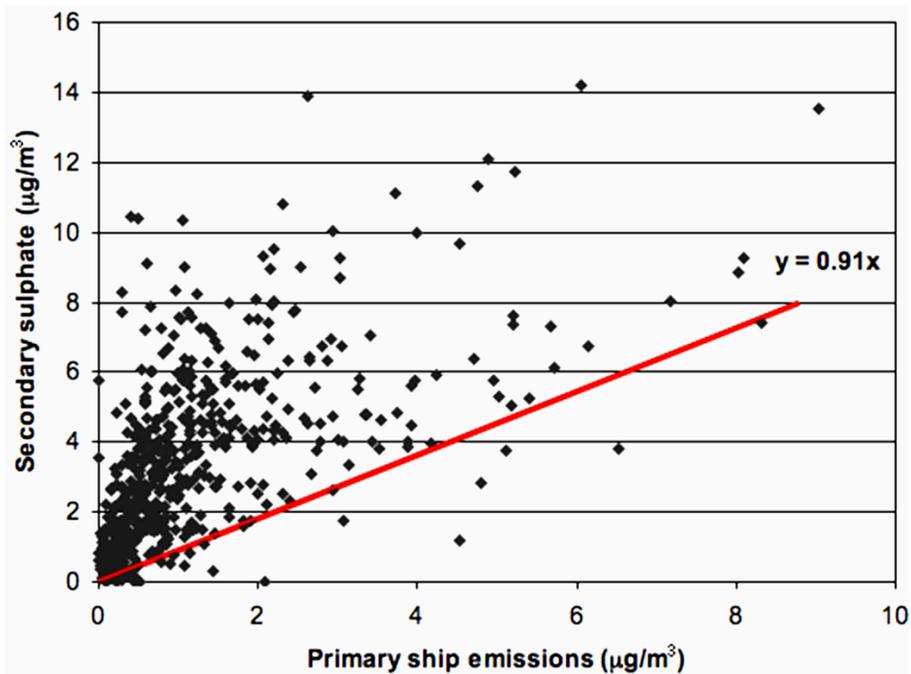


Figure 11. Correlation plot between the contributions from secondary sulphate and from primary particulate emitted by ships as obtained by the PMF analysis.

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