Atmospheric deposition of organic matter at a remote site in the Central Mediterranean Sea: implications for marine ecosystem

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Abstract. Atmospheric fluxes of dissolved organic matter (DOM) were studied for the first time at the Island of Lampedusa, a remote site in the Central Mediterranean Sea (Med Sea), between March 19th 2015 and April 1st 2017. The main goals of this study were: to quantify total atmospheric deposition of DOM in this area and to evaluate the impact of Saharan dust deposition on DOM dynamics in the surface waters of the Mediterranean Sea. Our data show high variability in DOM deposition rates, without a clear seasonality, and a dissolved organic carbon (DOC) input from the atmosphere of 120.7 mmol DOC m^{-2} y^{-1}. Over the entire time-series, the average dissolved organic phosphorous (DOP) and dissolved organic nitrogen (DON) contributions to the total dissolved pools were 40% and 26%, respectively. The data on atmospheric elemental ratios also show that each deposition event is characterized by a specific elemental ratio, suggesting a high variability in DOM composition and the presence of multiple sources. This study indicates that the organic substances, transported by Saharan dust at Lampedusa, mainly come from a natural sea spray, and that Saharan dust can be an important carrier of organic substances, even though the load of DOC associated with dust is highly variable. Our estimates suggest that atmospheric input has a larger impact to the Med Sea than to the global ocean. Further, DOC fluxes from the atmosphere to the Med Sea can be up to 6-fold larger than total river input. Longer time series, combined with modelling would greatly improve our understanding of the response of DOM dynamics in the Med Sea to the change in aerosol deposition pattern due to the effect of climate change.

1. Introduction

The Mediterranean Sea (Med Sea) is the largest semi-enclosed basin and one of the most oligotrophic areas of the world's oceans. It is very sensitive to natural variations in the atmosphere-ocean interactions (Mermex group, 2011). Organic matter and nutrients of natural and anthropogenic origin, are continuously exchanged between the ocean and the atmosphere, affecting biogeochemical cycles and the marine ecosystem. The Med Sea receives anthropogenic aerosols from the northern regions, which are characterized by the presence of important industrial sites, representing relevant sources of organic substances to the atmosphere (Guerzoni and Chester, 1996). Industrial pollution can also be originated from the North Africa as shown in the work by Rodríguez et al. (2011). In addition, the Sahara desert is an intermittent source of mineral dust, that can transport nutrients and organic carbon to the Basin (Goudie and Middleton, 2001; Prospero et al., 2005; Vincent et al., 2016). Atmospheric deposition of nutrients (N and P) strongly influences the marine biogeochemical cycles of the Med Sea, it has therefore received increased attention in the last 30 years (Migon et al., 1989; Herut et al., 2002; Ridame and Guieu, 2002; Markaki et al., 2003, 2010; Pulido-Villena et al., 2008; Izquierdo et al., 2012; Djaoudi et al., 2018). Compared to inorganic nutrients, there is still very few data on the

atmospheric deposition of Dissolved Organic Carbon (DOC) to the surface ocean, both at the local and global scale. Organic carbon can be removed from the atmosphere through wet and dry deposition (Iavorivska et al., 2016). At the global scale, wet deposition transfers about 306-580 Tg DOC yr^{-1} to the surface of the Earth (Willey et al., 2000; Kanakidou et al., 2012). These values correspond to almost half of the DOC delivered to the oceans by rivers annually (IPCC, 2014). Atmospheric deposition of organic carbon can therefore affect regional C cycling (Yan and Kim, 2012; Decina et al., 2018). In addition, the expected increase in ocean stratification due to the global warming will enhance the impact of atmospheric inputs in the surface ecosystem (Kanakidou et al., 2012). The magnitude of atmospheric DOC inputs to open waters and the importance of its role in the carbon cycle highlight the need for a better and robust estimation of DOC deposition.

In the last years, a few studies have reported data on atmospheric deposition of DOC to the Med Sea. Total (dry + wet) atmospheric deposition was studied in North-Western Med Sea in 2006 (Pulido-Villena et al., 2008) and in 2015 (Djaoudi et al., 2018) with contrasting results. In the first study, the highest DOC flux was observed during a Saharan dust storm, suggesting a combination of heterogeneous reactions between organic matter and mineral dust in the troposphere. In the second study, a Saharan rain event coincided with a minimum in DOC input, suggesting little organic matter in aerosols (Djaoudi et al., 2018). These studies were conducted in coastal areas affected by human activities. Direct measurements of total OC (TOC) in rainwater were carried out at the island of Crete (Economou and Mihalopoulos, 2002). This study did not take into consideration dry deposition. None of the papers cited has studied atmospheric inputs in remote sites, far from possible pollution sources and/or large cities.

The main goals of this study are: (1) to quantify total atmospheric deposition of DOC, DON and DOP at the island of Lampedusa, representative of the remote marine environment in the central Med Sea; (2) to investigate the contribution of natural and anthropogenic sources in atmospheric DOC; (3) to estimate the impact of atmospheric deposition on marine ecosystem.

2. Materials and methods

2.1 Sampling site

Bulk atmospheric deposition (dry and wet) was collected at the Station for Climate Observations (35.52°N, 12.63°E), maintained by ENEA, the Italian National Agency for New Technologies, Energy and Sustainable Economic Development, on the island of Lampedusa, Italy (Fig. 1; http://www.lampedusa.enea.it/).

Lampedusa is located in an ideal position for the study of atmospheric DOC fluxes to the open Med Sea. It is flat and far from large islands or continental areas and from relevant pollutant sources. Precipitation shows a significant interannual variability and is concentrated in autumn and winter, with a maximum in October. Intense precipitation events, which are relatively infrequent, are generally associated with frontal passages and winds from the Northern sectors. Very dry conditions characterize late spring and summer. Although it is a remote marine environment, influences from ship traffic emissions (Becagli et al., 2012, 2017), volcanic aerosols (Sellitto et al., 2017), forest fires (Pace et al., 2005), and regional pollution (Pace et al., 2006) have been documented.

In addition to deposition, PM_{10} (particulate matter with aerodynamic equivalent diameter lower than 10 μm) amount and chemical composition analyses, routinely performed at Lampedusa, are used in this study.

2.2. Atmospheric deposition sampler

The sampler (Fig. 1) was positioned on the roof of the ENEA climatic station located on a 45 m a.s.l. plateau on the north-eastern coast of Lampedusa. A total of 41 samples were collected between March 19th 2015 and April 1st 2017, every 15 days or immediately after strong rain or dust storm events. Due to logistic constraints, 9 sampling periods were longer than 20 days. The deposition sampler is similar to those successfully employed in previous studies (Pulido-Villena et al., 2008; Markaki et al. 2010; De Vicente et al., 2012). It is composed of a 10 L polycarbonate bottle, with a polyethylene funnel attached on the top; a 20 μM mesh covers the funnel stem in order to prevent contamination by insects or organic debris. For wet deposition, the amount of water in the sampler was weighted and transferred to 250 ml polycarbonate bottles and immediately frozen. Dry deposition was sampled by rinsing the collector with 250 mL of ultrapure MilliQ water, that was transferred into 250 ml polycarbonate bottles and immediately frozen. A detailed description of sampling periods, deposition types, and collected volumes is reported in Table 1.

For DOC, DON and DOP analysis, samples were thawed and filtered through a sterile 0.2 μm Nylon filter pre-washed with 300 ml of ultrapure water to avoid any contamination. Filtered samples were frozen until the analysis. Before the analysis, samples were brought to room temperature (24 °C).

2.3 DOC analysis

DOC analysis were carried out on a Shimadzu TOC-VCSN, equipped with a quartz combustion column filled with 1.2% Pt on alumina pillows of ~2 mm diameter. Samples were first acidified with 2N HCl and bubbled for 3 min with CO_2-free ultra-high purity air in order to remove the inorganic carbon. Replicate injections were performed until the analytical precision was lower than 1%. A five-point linear calibration curve was determined with standard solutions of potassium hydrogen phthalate in the same concentration range as the samples (40-400 μM). The system blank was measured every day at the beginning and the end of analyses using low-carbon Milli-Q water (<3 μM C). Instrument accuracy was assessed every day by analyzing DOC Consensus Reference Material (CRM), kindly provided by Prof. D. Hansell, with a nominal value of 41-44 μM (batch 15 Lot #07-15) (Hansell, 2005). The average DOC concentration in the CRM measured in our laboratory during the period of the analysis was 42.8±1.2 (n=15).

2.4 DOP and DON analysis

Twenty-six out of 41 samples were analyzed for dissolved organic nitrogen (DON) and phosphorous (DOP). The samples were collected between March 19th 2015 and November 3rd 2016.

DON was estimated by subtracting the dissolved inorganic nitrogen (DIN) from the total dissolved N (TDN). DIN and TDN were analyzed by conventional automated colorimetric procedure (CACP) according to Aminot and Kerouel (2007) with an estimated limit of detection of 0.02 μM. TDN was analyzed after persulfate wet-oxidation (Pujo-Pay et al., 1997).

DOP concentrations were determined by subtracting the inorganic form (soluble reactive phosphorus, SRP) from the total dissolved P. SRP was measured spectrophotometrically after Murphy and Riley (1962) with a limit of detection of 0.02 μM and an analytical precision of 7% at 0.1 μM. Total dissolved P (TDP) was measured as SRP after UV digestion (Armstrong et al., 1966). The photoxidation technique included a 2 hours UV treatment in a Metrohm® 705 UV digester with a digestion efficiency of 85 ± 3 %, assessed on a 1 μM solution of β-glycerol-phosphate.

2.5 DOC, DON and DOP fluxes

DOC, DON and DOP fluxes were calculated using the following formula:

$$X_{Flux} = \frac{X \cdot V}{A \cdot d} \quad (1)$$

where X is the concentration measured in the sample (μM), V is the volume (L) of rain collected by the sampler or the volume of Milli-Q water (0.25 L) used to rinse the collector in case of dry deposition, A is the area of the funnel (0.1018 m^2), and d is the length of the sampling period expressed in days.

2.6 Ions and metals content in the deposition samples

Soluble ions metals were measured on samples filtered on quartz filters. These filters have low blank levels for metals and ions (Ca, Na, Al and Pb) both in the soluble and particulate fraction. Immediately after filtration the samples were divided in two portions, used for measurements of ionic and metal content, respectively. Samples for the determination of metal were spiked with 0.1 mL of sub-boiled distilled (s.b.) HNO_3 to preserve the metals in their soluble form. Samples were keep refrigerated at +4°C until the analysis. Ions were determined in solution by ion chromatography as reported in Becagli et al. (2011).

The particulate fraction of the deposition was extracted from the quartz filter through the solubilisation procedure reported in the EU EN14902 (2005) for aerosol samples. The extraction procedure was performed in a microwave oven at 220 °C by sub-boiling distilled HNO3 and 30% ultra-pure H_2O_2 for 25 minutes.

Metals in both soluble and particulate fractions were measured by means of an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Varian 720-ES) equipped with an ultrasonic nebulizer (U5000 ATC, Cetac Technologies Inc.). Daily calibration standards (internal standard: 1 ppm Ge) were used for quantification.

2.7 PM_{10} analysis

PM_{10} is sampled on a daily basis at the island of Lampedusa (Becagli et al., 2013; Marconi et al., 2014; Calzolai et al., 2015) by using a low-volume dual-channel sequential sampler (HYDRA FAI Instruments) equipped with two PM_{10} sampling heads, operating at constant flow of 2.3 m^3/h in accord with the European rules for aerosol monitoring (UNI EN12341). Aerosol is collected on 47 mm diameter Teflon filters (PALL Gelman) having 2 μm nominal porosity but certified to have 99% retention efficiency for 0.3 μm diameter particles. The PM_{10} mass was determined by weighting the Teflon filters before and after sampling with an analytical balance in controlled conditions of temperature (20±1 °C) and relative humidity (50±5%). The estimated error on PM_{10} mass is around 1% at 30 μg m^{-3} in the routine sampling conditions. A quarter of each Teflon filter was extracted using MilliQ water (about 10 ml, accurately evaluated by weighing) in ultrasonic bath for 15 min, and the ionic content was determined by ion chromatography as for deposition samples (Becagli et al. 2011). Another quarter of the Teflon filter was used for the determination of metals in the atmospheric particles as described for the deposition samples.

2.8 Enrichment factor

In order to obtain information on DOM sources, DOM concentrations were compared to concentration of Al, Na and the enrichment factor for Pb, EF(Pb), in the deposition samples as markers of crustal, sea spray and anthropic source respectively.

The enrichment factor (EF) with respect to crustal sources of Pb, V and Ni were calculated by using Al as marker for crustal aerosol. The following equation (Eq. 1) is used for EF calculation:

$$EF\ X = \frac{(\frac{X}{Al})sample}{(\frac{X}{Al})crust} \quad (2)$$

where $(X/Al)_{sample}$ is the ratio between the metal X and Al concentrations in the sample, and $(X/Al)_{crust}$ is the same ratio in the upper continental crust as reported in Henderson and Henderson (2009). By convention, element with EF<10 are called "not enriched" having a prevailing crustal source, whereas 10<EF<100 indicate a moderate enrichment and EF>100 indicate that the element ("enriched") has a prevailing anthropogenic source (e.g. Lai et al., 2017).

3. Results

3.1 DOC atmospheric fluxes

Atmospheric fluxes of DOC ranged between 0.06 and 1.78 mmol C m^{-2} day^{-1}, with high variability. The overall sampling lasted for 746 days. The deposition was lower than 0.2 mmol DOC m^{-2} d^{-1} (Fig. 2 and Table 2) in half of the sampling days (52%).

In 2015, the lowest deposition rates (<0.1 C m^{-2} d^{-1}) were measured in July (Lmp09), October (Lmp13), and November (Lmp15). The highest deposition values (>1.2 mmol C m^{-2} d^{-1}) occurred between March and April (Lmp02), and in June (Lmp06), both periods were characterized by dry deposition (Fig.2 and Table 2). High DOC fluxes (>0.6 mmol C m^{-2} d^{-1}) were, however, also observed in March (Lmp01), May (Lmp04) and at the end of July (Lmp10), in correspondence with periods dominated by wet deposition. In 2015, the annual rainfall was 360 mm , slightly higher than the average annual rainfall for the island of Lampedusa (325 mm with 42 days of rain), (data from: http://www.arpa.sicilia.it/ and http://www.eurometeo.com/italian/climate).

In 2016, the DOC deposition rates were rather low and with less variability compared to the previous year. DOC fluxes ranged between 0.1 and 0.3 mmol C m^{-2} d^{-1} from January to May (Lmp18 to Lmp23), and from June to August (Lmp27 to Lmp30). The highest DOC fluxes (>0.8 mmol C m^{-2} d^{-1}) were observed in May (Lmp25) and between October and November (Lmp33; Fig. 2 and Table 2). In 2016, the annual rainfall was 378 mm (data from the local meteorological station of the Lampedusa Atmospheric Observatory).

In 2017, DOC fluxes ranged between 0.14 and 0.92 mmol C m^{-2} d^{-1}, from January to April (Lmp36 to Lmp41); these values are higher than those observed in the first three months of the previous year (Fig. 2 and Table 2).

Atmospheric fluxes of DOC in wet deposition were correlated with monthly precipitation rates (r^2=0.47, p<0.05, n=12). The precipitation rate ranged between 2.9 and 88.5 mm during the study period (2015-2017).

A mean daily deposition of 0.33 mmol C m^{-2} d^{-1} was calculated, taking into consideration the two years (from March 2015 to April 2017), corresponding to an annual DOC flux of 120.7 mmol C m^{-2} $year^{-1}$.

3.2 DON and TDN, DOP and TDP atmospheric fluxes

Dissolved Nitrogen fluxes ranged between $1.5 \cdot 10^{-3}$ and 0.25 mmol DON m^{-2} d^{-1} and between $1.6 \cdot 10^{-3}$ and 0.47 mmol TDN m^{-2} d^{-1}, respectively (Fig. 3 and Table 2). During most of the sampling period (93%), DON deposition was lower than 0.1 mmol m^{-2} d^{-1}. The main peaks were observed in March 2015 (Lmp01), in May (Lmp24 and Lmp25) and October 2016 (Lmp33) coinciding with high DOC deposition (Fig. 3 and Table 2).

Dissolved phosphorous fluxes ranged between 0 and $2.7 \cdot 10^{-3}$ mmol DOP m^{-2} d^{-1} and $1 \cdot 10^{-4}$ and $5 \cdot 10^{-3}$ mmol TDP m^{-2} d^{-1}, respectively (Fig. 4 and Table 2). Between August 2015 and September 2016 (Lmp10-Lmp30) both DOP and TDP showed low fluxes. In 2015, atmospheric DOP and TDP showed the highest fluxes in May (Lmp04) and August

(Lmp10). In 2016, the main peaks in DOP and TDP deposition were observed in October (Lmp31) and November (Lmp33). The 4 peaks in atmospheric DOP and TDP (Lmp04, Lmp10, Lmp31 and Lmp33) were responsible for 16% of total depositions coinciding with high DOC fluxes (Fig. 2). It is noteworthy that in March 2015 (Lmp01) and May 2016 (Lmp25), DOP fluxes were very low (0 and $9 \cdot 10^{-5}$ mmol m^{-2} d^{-1}, respectively) (Table 2), despite high fluxes of DOC, DON and TDP.

The overall mean DON and DOP daily deposition rates were 0.032 mmol N m^{-2} d^{-1} and $3.8 \cdot 10^{-4}$ mmol P m^{-2} d^{-1}, corresponding to annual fluxes of 11.61 mmol DON m^{-2} y^{-1} and 0.14 mmol DOP m^{-2} y^{-1}.

It should be noted that the these fluxes could be underestimated due to the missing samples in 2015 and 2016.

3.3 Elemental ratios in atmospheric DOM

DOC:DON:DOP ratios showed a marked variability (Fig. 5 and Table 3). DOC:DON molar ratios ranged between 2.2 (Lmp24, May 2016) and 45.9 (Lmp04, May 2015) (Fig. 5a). DOC:DOP molar ratios ranged between 244 (Lmp10, August 2015) and 11008 (Lmp25, May 2016) (Fig. 5b). DON:DOP ratio ranged between 9.2 (Lmp10, August 2015) and 1377 (Lmp25, May 2016) (Fig. 5c). No clear seasonal cycle was observed, even if during autumn (November 2015 and October 2016) and late spring (May 2016) depositions were very low in P, compared to the other two elements.

3.4 The sources of atmospheric DOM

Previous works indicate that soluble fractions of V and Ni in aerosol samples are specific marker for anthropogenic sources for the area of Lampedusa (Becagli et al, 2012 and 2017). During this study, samples did not show enrichment beyond 10, indicating that their source is mainly from crustal origin.

The DOC deposition was classified on the basis of the corresponding nssCa concentration in PM_{10}, (Following Marconi et al., 2014) (Fig. 6). Saharan dust events are identified as those with nssCa > 950 ng/m^3. DOC deposition, corresponding to average nssCa larger than the threshold (950 ng/mg^3), is highlighted in red. DOC deposition, corresponding to a Saharan dust event occurring in at least one day of the sampling period, is indicated in yellow (Fig. 6). A detailed description of the most interesting deposition events is given below.

The mean concentration of PM_{10} for Lmp01 (March 2015) was 50.1 μg m^{-3}**,** with an average dust value of 18.2 μg m^{-3} (Table 4). This sample is dominated by crustal input as revealed by the values of nssCa in the aerosol (1327.6 ng/m^3) and the Al concentration in the deposition (both soluble and particulate, Fig. 7). In this sample EF(Pb) indicates low contribution of anthropogenic sources. Na concentration in the deposition was 304 mg m^{-2} d^{-1} (Fig. 7).

Lmp02 (March-April 2015) is characterized by the second highest DOC deposition, although no Saharan dust event occurred during this period (Fig. 6 and 7). The PM_{10} mean concentration was 29 μg m^{-3} and average sea-salt aerosol value was 13.6 μg m^{-3} (Table 4) with a 47% contribution to PM_{10}. This sample was strongly affected by sea spray as indicated by the Na/Al ratio 60-fold higher than in Lmp01.

Lmp04 (May 2015), sampled during a Saharan dust event, also showed high DOC input (Fig. 6), but the concentration of Al in the deposition was quite low (Fig. 7). The PM_{10} mean concentration was 26.4 μg m^{-3} and the average sea-salt in the aerosol was 8.8 μg m^{-3}, contributing by one third to the total particulate matter. As for Lmp03 the ratio Na/Al is quite high suggesting that sea spray also dominated in this sample.

The mean PM_{10} concentration of Lmp06 (June 2015)**,** was 23.3 μg m^{-3}, with an average sea-salt aerosol concentration of 13.6 μg m^{-3} (Table 4). The average contribution of sea salt aerosol to the particulate matter concentration was 27%. The

peculiar characteristic of this sample is the high concentration of soluble Al and low particulate Al in the deposition (Fig. 7). This feature is also observed in samples Lmp10 and Lmp12, both presenting quite high concentration of DOC in July and September 2015.

Lmp25 (May 2016) was characterized by a mean PM_{10} concentration of 133.7 μg m^{-3} and with an average dust value of 42.5 μg m^{-3} (Table 4). This is the highest value of PM_{10} observed in the entire study and indicates the occurrence of a Saharan dust event. The average value of nssCa was 4815.1 ng/m^3, further supporting the occurrence of an intense Saharan dust event. The Saharan dust contribution for this sample is also revealed by the Al concentration (both soluble and particulate) (Fig. 7).

Lmp33 (October-November 2016) and Lmp34 (November 2016) are indicative of the two possible source of DOC, crustal and sea spray. Lmp33 shows higher DOC concentration than Lmp34. The former is characterized by very high Na concentration in the deposition, while Lmp34 is characterized by high crustal content (as reveled by the high concentration of Al, Fig. 7).

The fourth highest DOC deposition of the entire study period (Lmp37) occurred in January 2017. Unfortunately no ancillary data was collected during this event.

4. Discussion

4.1 DOC input from the atmosphere

The relationship between monthly precipitation rates and DOC fluxes confirmed the importance of rain events in the Med Sea, (Djaoudi et al., 2018).

The total DOC annual input from the atmosphere (120.7 mmol C m^{-2} y^{-1}) found in this study, is very close to that measured at Cap Ferrat peninsula (Southern France) in 2006 (129 mmol C m^{-2} y^{-1}; Pulido-Villena et al., 2008) and in three lakes in the western Mediterranean basin (Southern Spain, 153.3 mmol C m^{-2} y^{-1} in 2005; De Vicente et al., 2012). This value is higher than deposition in the north-western Med Sea (59 mmol C m^{-2} y^{-1} at Frioul Island in the Bay of Marseille; Djaoudi et al., 2018). If the same sampling period is taken into consideration for both studies (from March 2015, the beginning of sampling in Lampedusa, to July 2016, the end of sampling at Frioul island), DOC input is 2-times higher at Lampedusa than at Frioul Island. This variability is probably due to the different temporal and seasonal cycles of dry and wet deposition. In particular the marked differences between the two sites could be influenced by the presence of a south-north decreasing gradient in the intensity of the mineral dust deposition as proposed by Vincent et al. (2016). Our data also show high variability in DOC deposition rates without a clear seasonality. While in 2015 and 2016 the highest deposition rates were between spring and autumn, in 2017 the highest deposition rates were in winter. In addition the two highest peaks observed in 2015 (Lmp02 and Lmp06, dry deposition) accounted together for 43% of the annual DOC flux (52 mmol C m^{-2} y^{-1}). Depending on the origin and trajectories of the air masses, the atmosphere can carry significant amounts of DOC.

Assuming that the annual DOC flux from this study (120.7 mmol C m^{-2} y^{-1}) is valid for the whole Med Sea (area=$2.5 \cdot 10^{12}$ m^2), we can estimate a total input of 3.64 Tg DOC y^{-1}. The global estimation for wet atmospheric DOC deposition is 306-580 Tg C y^{-1} and the input to the global ocean ranges between 90 and 246 Tg C y^{-1} (Willey et al., 2000; Kanakidou et al., 2012). The global dry deposition of organic carbon (OC) has been estimated to be 11 Tg C y^{-1}, (Jurado et al., 2008) leading to a total OC deposition to the oceans of 101-247 Tg C y^{-1}. The comparison of these

estimates indicates that the Med Sea, with an area equivalent to only 0.7% of the global oceans, receives from 1.5 to 4% of the global atmospheric input of DOC.

It is noteworthy that, our values are up to 6 times larger than the estimate of the total river input to the Med Sea (0.6-0.7 Tg DOC y^{-1}; Santinelli, 2015). These results confirm the leading role of atmosphere in the transport of allochthonous DOC to the Med Sea, as suggested recently by Santinelli et al. (2015) and Galletti et al. (2019).

A few episodes of Saharan outbreaks can strongly affect the annual dust flux, whereby a single outbreak can account for 40-80% of the flux (Guerzoni et al., 1997). The most intense dust deposition events in Lampedusa generally display higher values in spring (March-June) and in autumn (Vincent et al., 2016; Bergametti et al., 1989; Loye-Pilot and Martin, 1996; Avila et al., 1997; Ternon et al., 2010). In this study, we show that, although dust events can significantly contribute to the annual DOC fluxes, sea spray seems the dominant source of DOC in this area, in agreement with Mallet et al., 2019. The role of secondary organic aerosols as a source of organic matter in the Mediterranean Sea is well documented (Arndt et al., 2017; Michoud et al., 2017; Rinaldi et al., 2017) and could be relevant at Lampedusa. Finally, the correlation between monthly precipitation rates and DOC fluxes shows the importance of rain events as a source of DOC in the Med Sea, as proposed by Djaoudi et al. (2018).

4.2 Atmospheric DON, DOP input and elemental ratios

The annual DON flux (11.61 mmol N m^{-2} y^{-1}) observed at Lampedusa was lower than that measured at Frioul Island (17.80 mmol N m^{-2} y^{-1}; Djaoudi et al., 2018). In the Eastern Med Sea, Markaki et al. (2010) reported a DON annual flux of 18.49 mmol N m^{-2} y^{-1}, higher than that observed at Lampedusa. The comparison of our DOP deposition values (0.14 mmol P m^{-2} y^{-1}) with the few data reported in the literature shows that the fluxes at Lampedusa are markedly higher than those reported for the Western Med Sea (0.07 mmol P m^{-2} y^{-1}, Djaoudi et al., 2018; 0.03 mmol P m^{-2} y^{-1}, Migon and Sandroni, 1999), but lower than those obtained by Violaki et al. (2017) for both the West (1.16 mmol P m^{-2} y^{-1}) and East (0.90 mmol P m^{-2} y^{-1}) Med Sea. Results from our study are very similar to those reported for the Eastern Med Sea in 2001 and 2002 (0.15 mmol P m^{-2} y^{-1}) (Markaki et al., 2010). Further, it is interesting to note that our DOP data are very similar to the TDP data reported for a coastal rural site in the NE Spain in 2002-2003 (0.10-0.14 mmol P m^{-2} y^{-1}, in 17 months of sampling; Izquierdo et al., 2012).

Over the entire time-series, the average DOP and DON contributions to TDP and TDN were 40% and 26%, respectively. These data confirm that a significant fraction of the dissolved P and N in the atmospheric deposition was in the organic form. These values are similar to those observed in previous studies at Frioul Island (DOP 40%, DON 25%; Djaoudi et al., 2018), and in both the western and eastern Med Sea (DOP 38%; DON 32%; Markaki et al., 2010). The similarity among the depositions collected at the two sites (Lampedusa, Central Med Sea and Frioul, North-western Med Sea) suggests that the remote site of Lampedusa may be representative of DON and DOP deposition in the Med Sea, especially in the western basin.

The data on atmospheric elemental ratios show that each deposition event is characterized by a specific elemental ratio, suggesting a high variability in DOM composition and the presence of multiple sources. Djaoudi et al (2018) observed an average value of DOC:DON:DOP molar ratios of 1228:308:1 in atmospheric DOM, collected in the north-western Med Sea. In the surface Med Sea, DOC:DON:DOP ratios ranges between 1050:84:1 in the western basin to 1560:120:1 in the eastern basin (Pujo-Pay et al., 2011). The average values observed in our atmospheric deposition time-series (1909:292:1) indicate that atmospheric DOM is enriched in DOC and DON compared to marine DOM. This

observation is also valid comparing our values with those recently measured on marine samples collected at the MOOSE ANTARES offshore station (north-western Med Sea) (1227:100:1, Djaoudi et al., 2018).

All the analyzed samples, except few cases in summer 2016, are relative to dry+wet deposition (Table 1). Although the DON and DOP recorded during the dry period are generally on the low end side of the measured range (Table 2), no information on the role played by wet or dry deposition on DON and DOP input to the Med Sea can be drawn at this stage, due to the limited number of dry samples.

4.3 The contribution of Saharan dust to atmospheric fluxes of dissolved organic carbon

The input of Saharan dust can affect the chemistry of the Mediterranean aerosols and enrich the Med Sea with many elements (such as Co, Ni, trace metals). Very few studies are available on the interactions between organic carbon and Saharan dust, even though the organic material found in the troposphere is often associated with dust particles (Usher et al., 2003; Aymoz et al., 2004).

Our results show that Saharan dust events can represent a relevant, albeit intermittent, source of DOC to the central Med Sea. Focusing on the different peaks of DOC deposition, our results indicate that Lmp01, Lmp04 and Lmp25 are associated to a Saharan dust event and that aerosols were probably enriched with organic substances. We hypothesize that dust particles present in the aerosol adsorb organic molecules, facilitating their accumulation and transport (Usher et al., 2003). The role of Saharan dust in the transport of DOC is evident in Lmp25 (May 2016).

In addition Lmp01 (end of March 2015), Lmp04 (May 2015) and Lmp25 (May 2016) show a seasonality that could be linked to the transport of pollen attached to desert particles in the spring events, and this pollen would contribute to atmospheric DOC input in spring (end of March- May). Pollen originating in Morocco was detected in South Spain (Cabezudo et al., 1997) and various pollen types (Cannabis, Cupressus, Pinus, Platanus and Sambucus) were observed in Cordoba (South Spain) exclusively during dust African events (Cariñanos et al., 2004). This process would not occur in the other seasons (winter and autumn of no pollen production).

If all the Saharan dust deposition events (red and yellow in Fig. 6) are taken into account, an input of 49.58 mmol DOC m^{-2} to Lampedusa can be estimated, representing ~41% of the total DOC flux for the entire sampling period. The strong dust events (red in Fig. 6) lead a flux of 15.26 mmol DOC m^{-2}, representing 13% of the total flux. Each deposition event must be considered individually, as DOC content depends on the aerosol load (Formenti et al., 2003; Aymoz et al., 2004).

Wet deposition is the main driver of Saharan dust deposition to the Med Sea. However, dry deposition can be also important (Guerzoni et al., 1997) and its relative contribution strongly depends on meteorological conditions and local emission (Inomata et at., 2009). Some models have estimated that wet deposition represents up to 75-95% of total deposition (Iavorivska et al., 2016). While our results confirm the importance of wet deposition, it also stress the relevance of dry deposition (32% of the total deposition during the entire sampling period) that appears to be the main contributor of DOC and of other chemical species to the remote site of Lampedusa, as suggested by Morales-Baquero et al. (2013).

It is also evident that Saharan dust input is not always associated with high DOC input as seen in Lmp34, with high concentration of dust, but with low DOC concentration. Conversely, several samples (for example Lmp02, Lmp33 and Lmp37) characterized by high concentrations of DOC, do not show high crustal content. Indeed high DOC deposition events seems to be often associated to sea spray transport, (Lmp02, Lmp10, Lmp 12, Lmp 33 and Lmp 37; Fig. 6).

Similarly, samples Lmp01, Lmp04, Lmp10, Lmp12 and especially Lmp25, also show a large contribution of sea spray aerosol indicating a marine source for the DOC in these samples. This is a surprising result, because other studies (e.g., Pace et al., 2006) have shown that clean marine aerosol conditions are rare at Lampedusa.

Lmp23, Lmp27, Lmp32, Lmp35 and Lmp36 were not characterized by high DOC fluxes (Fig. 6), even if these sampling periods were characterized by at least one strong Saharan dust event (Fig. 6, in yellow). This observation supports the hypothesis that Saharan dust is not typically enriched with DOC, but it adsorbs organic molecules in the atmosphere, and depending on its route, can be enriched or not in DOC. The composition of sample Lmp34 further supports this hypothesis, with the third highest average nss Ca value (1092.2 ng/m^3), but with a DOC concentration (0.20 mmol m^{-2} d^{-1}) below the daily average flux of the entire sampling period (0.33 mmol m^{-2} d^{-1}) (Fig. 6, Tables 2 and 4).

Lastly, it is interesting to note that samples characterized by high values of DOC never present high EF(Pb). Samples presenting EF(Pb)>10 show very low DOC concentrations, indicating a small DOC contribution from anthropogenic aerosols at Lampedusa.

4.4 Implications for marine ecosystem

The measurements carried out at the Island of Lampedusa clearly show that the atmosphere is an important source of allocthonous DOC to the Central Med Sea. There is still little information on biological lability of atmospheric DOC; if it is biologically available, it can be used very quickly by marine prokaryotic heterotrophs and it can be channeled into the food web, whereas if it is mainly recalcitrant, it can accumulate and be transported by water masses circulation.

A conceptual exercise can be made in order to give an estimate of the implications of DOM deposition for marine ecosystem. According to D'Ortenzio et al. (2005), mixed layer depth (MLD) ranges between 15 and 30 m, close to the island of Lampedusa. Santinelli et al. (2012) observed an average mixed layer DOC concentration of 60 μM in the same area in September 1999, and estimated a bacterial carbon demand (BCD) of 0.32 μM C d^{-1} (assuming a bacterial growth efficiency of 15%), which represents the total amount of carbon needed to support the observed bacterial production. In September, the atmospheric DOC flux was 0.24 mmol C m^{-2} d^{-1} in 2015 and 0.38 C m^{-2} d^{-1} in 2016. Dividing the atmospheric deposition by the average MLD (22.5 m, D'Ortenzio et al. 2005), we estimate that the atmospheric input contributes to 0.011-0.017 μM DOC d^{-1} increase in the mixed layer. Assuming that the values of BCD observed in September 1999 (0.32 μM C d^{-1}) are valid also for September 2015 and 2016, and that all the DOC coming from the atmosphere is labile, it could satisfy 3-5% of the daily BCD. During summer the MLD varies between 10 and 15 m depth, with an average value of 12.5 m (D'Ortenzio et al. 2005). The DOC input from the atmosphere is expected to increase the DOC concentration in the mixed layer by 0.008-0.079 μM C d^{-1} from June to August 2015, and by 0.013-0.014 from June to August 2016, supplying 3-25% of the daily BCD, assuming similar DOC concentrations and bacterial activity as during September. Even if we are aware that these assumptions are hardly meet, in particular the estimate of DOC input to the whole Med Sea, based on the data collected in Lampedusa, we think that these calculations can give an idea of the relevant role that atmospheric input of DOC can have in sustaining heterotrophic prokaryotes productivity in the surface layer, particularly when the upper water column is strongly stratified.

The Mediterranean MLD seasonal variability is characterized by a basin scale deepening from November to February-March and an abrupt stratification in April, which is maintained throughout the summer and early autumn. Even if these estimates stress the potential role of atmospheric DOC in sustaining bacterial productivity in the surface ocean, a time

series of BCD, MLD and DOC concentrations in the surface layer, together with a network of stations for the quantification of atmospheric input of DOC in the different areas of the Med Sea, are mandatory in order to have an accurate estimate of the impact of DOC atmospheric on the functioning of marine ecosystem. It should be also noted that a fraction of atmospheric DOC could be recalcitrant, and through transport to depth, it could play a key role in carbon sequestration. The refractory nature of a part of atmospheric DOM has been proposed by Sánchez-Pérez et al. (2016), based on a 2-year time series data on Fluorescent DOM (FDOM) deposition in the North-western Med Sea (Barcelona coastal area, Spain). Their results show that atmospheric inputs induced changes in the quality of organic matter, increasing the proportion of FDOM substances in the DOM pool. Incubation experiments to investigate the biological lability of atmospheric DOC are also crucial to better understand the impact of atmospheric deposition on marine ecosystems.

Finally, the occurrence of Saharan dust events opens interesting considerations on their impact on the marine environment. Previous studies suggested that dust inputs can promote autotrophic production (Ridame and Guieu, 2002; Markaki et al., 2003). Instead Pulido-Villena et al. (2008) experimentally found that heterotrophic bacteria can reduce the amount of C exported to deeper waters, because a Saharan dust event would have induced the mineralization of 22-70% of bioavailable DOC, changing carbon sequestration.

4. Conclusions

Our data show that atmospheric input has a larger impact to the Med Sea than to the global ocean and DOC fluxes from the atmosphere to the Med Sea can be up to 6-fold larger than riverine input.

Organic substances transported by Saharan dust at Lampedusa are primarily of natural origin, in particular from sea spray. Saharan dust can be an important carrier of organic substances. However, the load of DOC associated with dust is highly variable and high DOC fluxes were observed also in absence of dust deposition events.

Atmospheric C:N:P molar ratios indicate that DOM is enriched in DOC and DON with respect to marine DOM and the contribution of atmospheric deposition to the marine DOM stoichiometry in the Med Sea could be relevant, in particular during stratified periods.

Further studies are needed to understand the link between atmospheric inputs and marine biogeochemistry. Data on stable carbon ($\delta^{13}C$) on atmospheric DOC would be crucial in order to gain information about its main sources. Incubation experiments should be carried out, both with aerosol rich or poor in DOC, in order to better understand how the microbial community can respond to dust input. Further studies are also needed to understand the link between aerosol origin and DOM concentration and quality, and to comprehend the potential link between DOC and the pollen during the spring. Lastly, longer time series combined with a modelling effort, would provide a solid base to assess the response of DOM dynamics in the Med Sea to changes in aerosol deposition pattern due to the effect of climate change.

Author contribution

YG and CS conceived of the study and the sampling design. YG, SB, DMS collected the samples. YG, MG, SB, RT, SV analyzed the samples. YG, CS, EPV, AdS analyzed the data and all authors assisted with data discussion and contributed to the revision and editing of the final manuscript. All authors are aware of and accept responsibility for this manuscript and have approved the final submitted manuscript.

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The authors declare that they have no conflict of interest.

The dataset generated for this study are available on request to the corresponding author.

References

Armstrong, F. A. J., Williams, P. M., and Strickland, J. H.: Photo-oxidation of organic matter in sea water by ultra-violet radiation, analytical and other applications, Nature, 211(5048), 481, https://doi.org/10.1038/211481a0, 1966.

Aminot, A., and Kérouel, R.: Dosage automatique des nutriments dans les eaux marines: méthodes en flux continu, Editions Quae, 2007.

Arndt, J., Sciare, J., Mallet, M., Roberts, G. C., Marchand, N., Sartelet, K., Sellegri, K., Dulac, F., Healy, R. M., and Wenger, J. C.: Sources and mixing state of summertime background aerosol in the north-western Mediterranean basin, Atmos. Chem. Phys., 17, 6975–7001, https://doi.org/10.5194/acp-17-6975-2017, 2017.

Aymoz, G., Jaffrezo, J. L., Jacob, V., Colomb, A., and George, C.: Evolution of organic and inorganic components of aerosol during a Saharan dust episode observed in the French Alps, Atmospheric Chemistry and Physics, 4(11/12), 2499-2512, https://doi.org/10.5194/acp-4-2499-2004, 2004.

Avila, A., Queralt-Mitjans, I., and Alarcón, M. : Mineralogical composition of African dust delivered by red rains over northeastern Spain. Journal of Geophysical Research: Atmospheres, 102(D18), 21977-21996, https://doi.org/10.1029/97JD00485, 1997.

Becagli, S., Ghedini, C., Peeters, S., Rottiers, A., Traversi, R., Udisti, R., Chiari, M., Jalba, A., Despiau, S., Dayan, U., and Temara, A.: MBAS (Methylene Blue Active Substances) and LAS (Linear Alkylbenzene Sulphonates) in Mediterranean coastal aerosols: sources and transport processes, Atmospheric environment, 45(37), 6788-6801, https://doi.org/10.1016/j.atmosenv.2011.04.041, 2011.

Becagli, S., Sferlazzo, D. M., Pace, G., di Sarra, A., Bommarito, C., Calzolai, G., Ghedini, C., Lucarelli, F, Meloni, D., Monteleone, F., Severi, M., Trasversi, R., and Udisti, R.: Evidence for heavy fuel oil combustion aerosols from chemical analyses at the island of Lampedusa: a possible large role of ships emissions in the Mediterranean, Atmospheric Chemistry and Physics, 12(7), 3479-3492, https://doi.org/10.5194/acp-12-3479-2012, 2012.

Becagli, S., Lazzara, L., Fani, F., Marchese, C., Traversi, R., Severi, M., di Sarra, A., Sferlazzo, D. M., Piacentino, S., Bommarito, C., Dayan, U., and Udisti, R.: Relationship between methanesulfonate (MS^-) in atmospheric particulate and remotely sensed phytoplankton activity in oligo-mesotrophic central Mediterranean Sea, Atmospheric Environment, 79, 681-688, https://doi.org/10.1016/j.atmosenv.2013.07.032, 2013.

Becagli, S., Anello, F., Bommarito, C., Cassola, F., Calzolai, G., Iorio, T. D., di Sarra, A., Gómez-Amo, J. -L., Lucarelli, F., Marconi, M., Meloni, D., Monteleone, F., Nava, S., Pace, G., Severi, M., Sferlazzo, D. M., Traversi, R., and Udisti, R.: Constraining the ship contribution to the aerosol of the central Mediterranean, Atmospheric Chemistry and Physics, 17(3), 2067-2084, https://doi.org/10.5194/acp-17-2067-2017, 2017.

Bergametti, G., Dutot, A. L., Buat-Menard, P., Losno, R., and Remoudaki, E.: Seasonal variability of the elemental composition of atmospheric aerosol particles over the northwestern Mediterranean, Tellus B, 41(3), 353-361, https://doi.org/10.1111/j.1600-0889.1989.tb00314.x, 1989.

Cabezudo, B., Recio, M., Sánchez-Laulhé, J., Trigo, M. D. M., Toro, F. J., and Polvorinos, F.: Atmospheric transportation of marihuana pollen from North Africa to the southwest of Europe. Atmospheric Environment, 31(20), 3323-3328, https://doi.org/10.1016/S1352-2310(97)00161-1, 1997.

Calzolai, G., Nava, S., Lucarelli, F., Chiari, M., Giannoni, M., Becagli, S., Trasversi, R., Marconi, M., Frosini, D., Severi, M., Udisti, R., di Sarra, A., Pace, G., Meloni, D., Bommarito, C., Monteleone, F., Anello, F., and Sferlazzo, D. M.: Characterization of PM 10 sources in the central Mediterranean, Atmospheric Chemistry and Physics, 15(24), 13939-13955, https://doi.org/10.5194/acp-15-13939-2015, 2015.

Cariñanos, P., Galan, C., Alcázar, P., and Domınguez, E.: Airborne pollen records response to climatic conditions in arid areas of the Iberian Peninsula, Environmental and Experimental Botany, 52(1), 11-22, https://doi.org/10.1016/j.envexpbot.2003.11.008, 2004.

D'Ortenzio, F., Iudicone, D., de Boyer Montegut, C., Testor, P., Antoine, D., Marullo, S., Santoleri, R., and Madec, G.: Seasonal variability of the mixed layer depth in the Mediterranean Sea as derived from in situ profiles, Geophysical Research Letters, 32(12), https://doi.org/10.1029/2005GL022463, 2005.

De Vicente, I., Ortega-Retuerta, E., Morales-Baquero, R., and Reche, I.: Contribution of dust inputs to dissolved organic carbon and water transparency in Mediterranean reservoirs, Biogeosciences 9, 5049-5060, https://doi.org/10.5194/bg-9-5049-2012, 2012.

Djaoudi, K., Van Wambeke, F., Barani, A., Hélias-Nunige, S., Sempéré, R., and Pulido-Villena, E.: Atmospheric fluxes of soluble organic C, N, and P to the Mediterranean Sea: Potential biogeochemical implications in the surface layer, Progress in Oceanography, 163, 59-69, https://doi.org/10.1016/j.pocean.2017.07.008, 2018.

Economou, C., and Mihalopoulos, N.: Formaldehyde in the rainwater in the eastern Mediterranean: occurrence, deposition and contribution to organic carbon budget, Atmospheric Environment 36(8), 1337-1347, https://doi.org/10.1016/S1352-2310(01)00555-6, 2002.

Formenti, P., Elbert, W., Maenhaut, W., Haywood, J., Osborne, S., and Andreae, M. O.: Inorganic and carbonaceous aerosols during the Southern African Regional Science Initiative (SAFARI 2000) experiment: Chemical characteristics, physical properties, and emission data for smoke from African biomass burning, Journal of Geophysical Research: Atmospheres, 108(D13), https://doi.org/10.1029/2002JD002408, 2003.

Galletti, Y., Gonnelli, M., Retelletti Brogi, S., Vestri, S., and Santinelli, C.: DOM dynamics in open waters of the Mediterranean Sea: New insights from optical properties, Deep Sea Research Part I: Oceanographic Research Papers, 144, 95-114, https://doi.org/10.1016/j.dsr.2019.01.007, 2019.

Goudie, A. S., and Middleton, N. J.: Saharan dust storms: nature and consequences, Earth-science reviews, 56(1-4), 179-204, https://doi.org/10.1016/S0012-8252(01)00067-8, 2001.

Guerzoni, S., and Chester, R. (Eds.): The impact of desert dust across the Mediterranean (Vol. 11), Springer Science & Business Media, Netherlands, 1996.

Guerzoni, S., Molinaroli, E., and Chester, R.: Saharan dust inputs to the western Mediterranean Sea: depositional patterns, geochemistry and sedimentological implications, Deep Sea Research Part II: Topical Studies in Oceanography, 44(3), 631-654, https://doi.org/10.1016/S0967-0645(96)00096-3, 1997.

Henderson, P., and Henderson, G.M. (Eds.): The Cambridge Handbook of Earth Science Data. University Press, Cambridge, 2009.

Hansell, D.A.: Dissolved organic carbon reference material program. Eos, Transactions American Geophysical Union 86(35), 318-318, https://doi.org/10.1029/2005EO350003, 2005.

Herut B., Collier R., and Krom M.D.: The role of dust in supplying nitrogen and phosphorus to the South East Mediterranean, Limnology and Oceanography, 47:870-878, https://doi.org/10.4319/lo.2002.47.3.0870, 2002.

Iavorivska, L., Boyer, E. W., and DeWalle, D. R.: Atmospheric deposition of organic carbon via precipitation, Atmospheric Environment, 146, 153-163, https://doi.org/10.1016/j.atmosenv.2016.06.006, 2016.

Inomata, Y., Igarashi, Y., Chiba, M., Shinoda, Y., and Takahashi, H.: Dry and wet deposition of water-insoluble dust and water-soluble chemical species during spring 2007 in Tsukuba, Japan, Atmospheric Environment, 43(29), 4503-4512, https://doi.org/10.1016/j.atmosenv.2009.06.048, 2009.

IPCC (Eds.): Climate change: mitigation of climate change, In: Edenhofer, O., Pichs-Madruga, R., Sokona, Y., Farahani, E., Kadner, S., Seyboth, K., Adler, A., Baum, I., Brunner, S., Eickemeier, P., Kriemann, B., Savolainen, J., Schlömer, S., von Stechow, C., Zwickel, T., and Minx, J. C., Contribution of working group III to the fifth assessment report of the intergovernmental panel on climate change, Cambridge University Press, Cambridge, 2014.

Izquierdo, R., Benítez-Nelson, C. R., Masqué, P., Castillo, S., Alastuey, A., and Àvila, A.: Atmospheric phosphorus deposition in a near-coastal rural site in the NE Iberian Peninsula and its role in marine productivity, Atmospheric environment, 49, 361-370, https://doi.org/10.1016/j.atmosenv.2011.11.007, 2012.

Jurado, E., Dachs, J., Duarte, C. M., and Simo, R.: Atmospheric deposition of organic and black carbon to the global oceans, Atmospheric Environment, 42(34), 7931-7939, https://doi.org/10.1016/j.atmosenv.2008.07.029, 2008.

Kanakidou, M., Duce, R. A., Prospero, J. M., Baker, A. R., Benitez-Nelson, C., Dentener, F. J., Hunter, K. A., Liss, P. S., Mahowald, N., Okin, G. S., Sarin, M., Tsigaridis, K., Uematsu, M., Zamora, L. M., and Zhu, T.: Atmospheric

fluxes of organic N and P to the global ocean, Global Biogeochemical Cycles 26(3), https://doi.org/10.1029/2011GB004277, 2012.
Lai, A. M., Shafer, M. M., Dibb, J. E., Polashenski, C. M., and Schauer, J. J.: Elements and inorganic ions as source tracers in recent Greenland snow, Atmospheric Environment, 164, 205–215, 2017.
Loÿe-Pilot, M. D., and Martin, J. M. (Eds.): Saharan dust input to the western Mediterranean: an eleven years record in Corsica, In The impact of desert dust across the Mediterranean (pp. 191-199), Springer, Dordrecht, 1996.
Marconi, M., Sferlazzo, D. M., Becagli, S., Bommarito, C., Calzolai, G., Chiari, M., di Sarra, A., Ghedini, C., Gómez-Amo, J. L., Lucarelli, F., Meloni, D., Monteleone, F., Nava, S., Pace, G., Piacentino, S., Rugi, F., Severi, M., Traversi, R., and Udisti, R.: Saharan dust aerosol over the central Mediterranean Sea: PM10 chemical composition and concentration versus optical columnar measurements, Atmos. Chem. Phys., 14, 2039–2054, https://doi.org/10.5194/acp-14-2039-2014, 2014.
Mallet, M. D., D'Anna, B., Même, A., Bove, M. C., Cassola, F., Pace, G., Desboeufs, K., Di Biagio, C., Doussin, J.-F., Maille, M., Massabò, D., Sciare, J., Zapf, P., di Sarra, A. G., and Formenti, P.: Summertime surface PM1 aerosol composition and size by source region at the Lampedusa island in the central Mediterranean Sea, Atmos. Chem. Phys., 19, 11123–11142, https://doi.org/10.5194/acp-19-11123-2019, 2019.
Markaki, Z., Oikonomou, K., Kocak, M., Kouvarakis, G., Chaniotaki, A., Kubilay, N., and Mihalopoulos, N.: Atmospheric deposition of inorganic phosphorus in the Levantine Basin, eastern Mediterranean: Spatial and temporal variability and its role in seawater productivity, Limnology and Oceanography, 48(4), 1557-1568, https://doi.org/10.4319/lo.2003.48.4.1557, 2003.
Markaki, Z., Loÿe-Pilot, M. D., Violaki, K., Benyahya, L., and Mihalopoulos, N.: Variability of atmospheric deposition of dissolved nitrogen and phosphorus in the Mediterranean and possible link to the anomalous seawater N/P ratio, Marine Chemistry, 120(1-4), 187-194, https://doi.org/10.1016/j.marchem.2008.10.005, 2010.
Mermex group (Eds.): White book of Mermex program, Progress in Oceanography, 91, 97-166, https://doi.org/10.1016/j.pocean.2011.02.003, 2011.
Michoud, V., Sciare, J., Sauvage, S., Dusanter, S., Léonardis, T.,Gros, V., Kalogridis, C., Zannoni, N., Féron, A., Petit, J.-E.,Crenn, V., Baisnée, D., Sarda-Estève, R., Bonnaire, N., Marchand,N., DeWitt, H. L., Pey, J., Colomb, A., Gheusi, F., Szidat, S., Stavroulas, I., Borbon, A., and Locoge, N.: Organic carbon at a remote site of the western Mediterranean Basin: sources and chemistry during the ChArMEx SOP2 field experiment, Atmos. Chem. Phys., 17, 8837–8865, https://doi.org/10.5194/acp-17-8837-2017, 2017.
Migon, C., Copin-Montegut, G., Elegant, L., and Morelli, J.: Atmospheric input of nutrients to the coastal Mediterranean area, Biogeochemical implications, Oceanologica acta. Paris, 12(2), 187-191, 1989.
Migon, C., and Sandroni, V.: Phosphorus in rainwater: Partitioning inputs and impact on the surface coastal ocean, Limnology and Oceanography, 44(4), 1160-1165, https://doi.org/10.4319/lo.1999.44.4.1160, 1999.
Morales-Baquero, R., Pulido-Villena, E., and Reche, I.: Chemical signature of Saharan dust on dry and wet atmospheric deposition in the south-western Mediterranean region, Tellus B: Chemical and Physical Meteorology, 65(1), 18720, https://doi.org/10.3402/tellusb.v65i0.18720, 2013.
Murphy, J., and Riley, J. P.: A modified single solution method for the determination of phosphate in natural water, Analytica chimica acta, 27, 31-36, https://doi.org/10.1016/S0003-2670(00)88444-5, 1962.
Pace, G., Meloni, D., and di Sarra, A.: Forest fire aerosol over the Mediterranean basin during summer 2003, Journal Geophys. Res., 110, D21202, https://doi.org/doi:10.1029/2005JD005986, 2005.
Pace, G., di Sarra, A., Meloni, D., Piacentino, S., and Chamard, P.: Optical properties of aerosols over the central Mediterranean, 1. Influence of transport and identification of different aerosol types, Atmos. Chem. Phys., 6, 697–713, 2006.
Prospero, J. M., Blades, E., Mathison, G., and Naidu, R.: Interhemispheric transport of viable fungi and bacteria from Africa to the Caribbean with soil dust, Aerobiologia, 21(1), 1-19, https://doi.org/10.1007/s10453-004-5872-7, 2005.
Pulido-Villena, E., Wagener, T., and Guieu, C.: Bacterial response to dust pulses in the western Mediterranean: Implications for carbon cycling in the oligotrophic ocean, Global Biogeochemical Cycles, 22(1), https://doi.org/10.1029/2007GB003091, 2008.
Pujo-Pay, M., Conan, P., and Raimbault, P.: Excretion of dissolved organic nitrogen by phytoplankton assessed by wet oxidation and 15N tracer procedures, Marine Ecology Progress Series, 153, 99-111, https://doi.org/10.3354/meps153099, 1997.
Pujo-Pay, M., Conan, P., Oriol, L., Cornet-Barthaux, V., Falco, C., Ghiglione, J. F., Goyet, C., Moutin T., and Prieur, L.: Integrated survey of elemental stoichiometry (C, N, P) from the western to eastern Mediterranean Sea, 2011.
Ridame, C., and Guieu, C.: Saharan input of phosphate to the oligotrophic water of the open western Mediterranean Sea, Limnology and Oceanography, 47(3), 856-869, https://doi.org/10.4319/lo.2002.47.3.0856, 2002.
Rinaldi, M., Gilardoni, S., Paglione, M., Sandrini, S., Decesari, S., Zanca, N., Marinoni, A., Cristofanelli, P., Bonasoni, P., and Ielpo, P.: Physico-chemical characterization of Mediterranean background aerosol at the Capogranitola

observatory (Sicily), EGU General Assembly Conference Abstracts, 23–28 April 2017, Vienna, Austria, 3161, 2017.
Rodríguez, S., Alastuey, A., Alonso-Pérez, S., Querol, X., Cuevas, E., Abreu-Afonso, J., Viana, M., Pérez, N., Pandolfi, M., De la Rosa, J.: Transport of desert dust mixed with North African industrial pollutants in the subtropical Saharan Air Layer, Atmospheric Chemistry & Physics, 11(13), http://dx.doi.org/10.5194/acp-11-6663-2011, 2011.
Sánchez-Pérez, E. D., Marín, I., Nunes, S., Fernández-González, L., Peters, F., Pujo-Pay, M., Conan, P., Marrasé, C.: Aerosol inputs affect the optical signatures of dissolved organic matter in NW Mediterranean coastal waters, Scientia Marina 80(4), 437-446, https://doi.org/10.3989/scimar.04318.20B, 2016.
Santinelli, C., Sempéré, R., Van Wambeke, F., Charriere, B., and Seritti, A.: Organic carbon dynamics in the Mediterranean Sea: An integrated study, Global Biogeochemical Cycles, 26(4), 2012.
Santinelli, C.: DOC in the Mediterranean Sea. In: Hansell D.A, Carlson C.A. (Eds.), Biogeochemestry of Marine Dissolved Organic Matter (Second edition), Academic Press, San Diego, pp. 579-608, https://doi.org/10.1016/B978-0-12-405940-5.00013-3, 2015.
Santinelli, C., Follett, C., Brogi, S. R., Xu, L., and Repeta, D.: Carbon isotope measurements reveal unexpected cycling of dissolved organic matter in the deep Mediterranean Sea, Marine Chemistry, 177, 267-277, https://doi.org/10.1016/j.marchem.2015.06.018, 2015.
Sellitto, P., Zanetel, C., di Sarra, A., Salerno, G., Tapparo, A., Meloni, D., Pace, G., Caltabiano, T., Briole, P., and Legras, B.: The impact of Mount Etna sulfur emissions on the atmospheric composition and aerosol properties in the central Mediterranean: a statistical analysis over the period 2000-2013 based on observations and Lagrangian modelling, Atmos. Environ., 148, 77-88, 2017.
Ternon, E., Guieu, C., Loÿe-Pilot, M. D., Leblond, N., Bosc, E., Gasser, B., Miquel, J. -C., and Martín, J.: The impact of Saharan dust on the particulate export in the water column of the North Western Mediterranean Sea, Biogeosciences, 7(3), 809-826, https://doi.org/10.5194/bg-7-809-2010, 2010.
Usher, C. R., Michel, A. E., and Grassian, V. H.: Reactions on mineral dust, Chemical Reviews, 103(12), 4883-4940, 2003.
Vincent, J., Laurent, B., Losno, R., Bon Nguyen, E., Roullet, P., Sauvage, S., Chevaillier, S., Coddeville, P., Ouboulmane, N., di Sarra, A. G., Tovar-Sánchez, A., Sferlazzo, D. M., Massanet, A., Triquet, S., Morales Baquero, R., Fornier, M., Coursier, C., Desboeufs, K., Dulac, F., and Bergametti, G.: Variability of mineral dust deposition in the western Mediterranean basin and south-east of France, Atmospheric Chemistry and Physics, 16(14), 8749-8766, https://doi.org/10.5194/acp-16-8749-2016, 2016.
Willey, J. D., Kieber, R. J., Eyman, M. S., and Avery, G. B.: Rainwater dissolved organic carbon: concentrations and global flux, Global Biogeochemical Cycles 14(1), 139-148, https://doi.org/10.1029/1999GB900036, 2000.

Figure 1: Sampling location (Lampedusa island 35.5° N, 12.6° E) and the total atmospheric deposition collector.

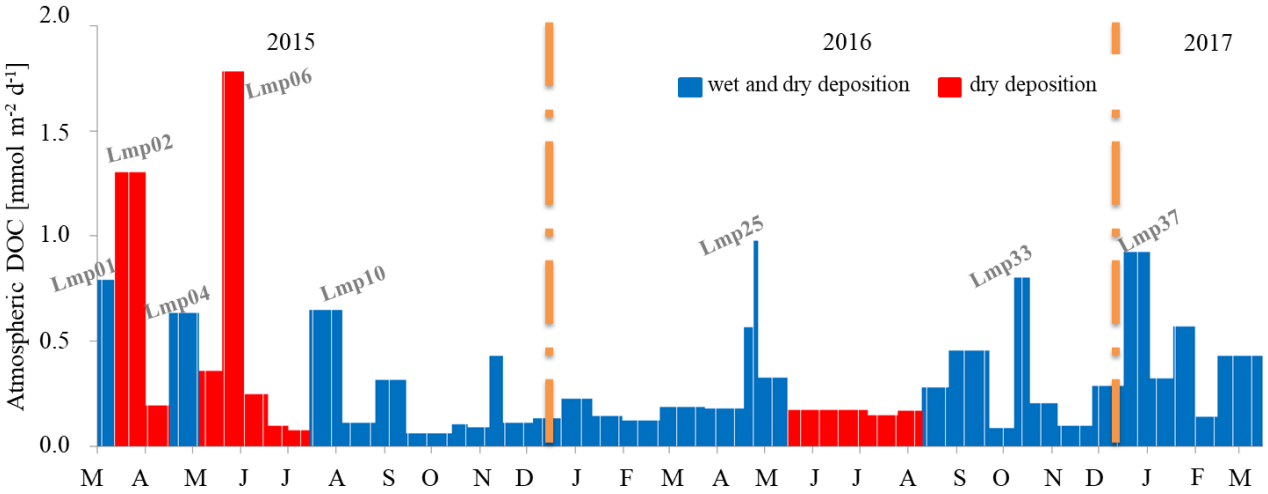


Figure 2: Atmospheric DOC fluxes during the study period. The month abbreviation and tick marks correspond to the end of the corresponding month. The width of the bar refer to the length of the sampling period. Wet and dry deposition is indicated in blue, dry deposition in red.

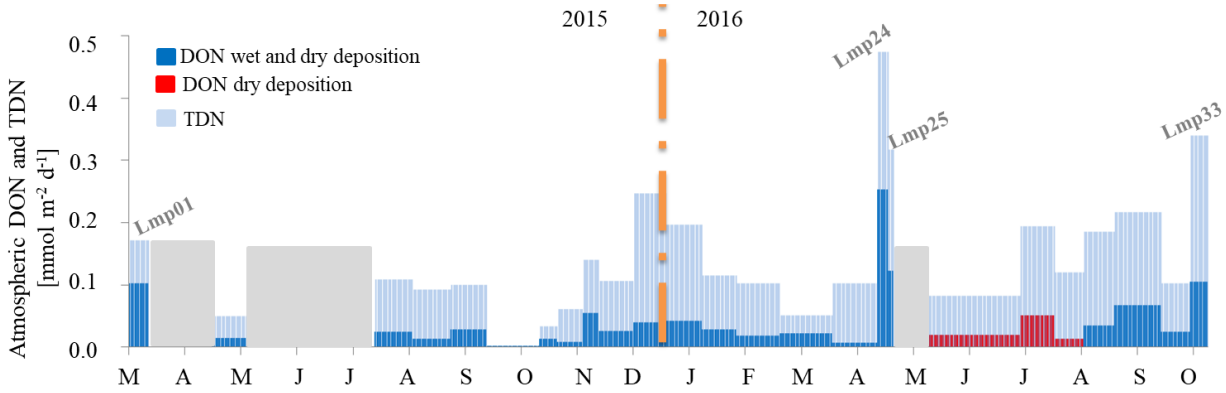
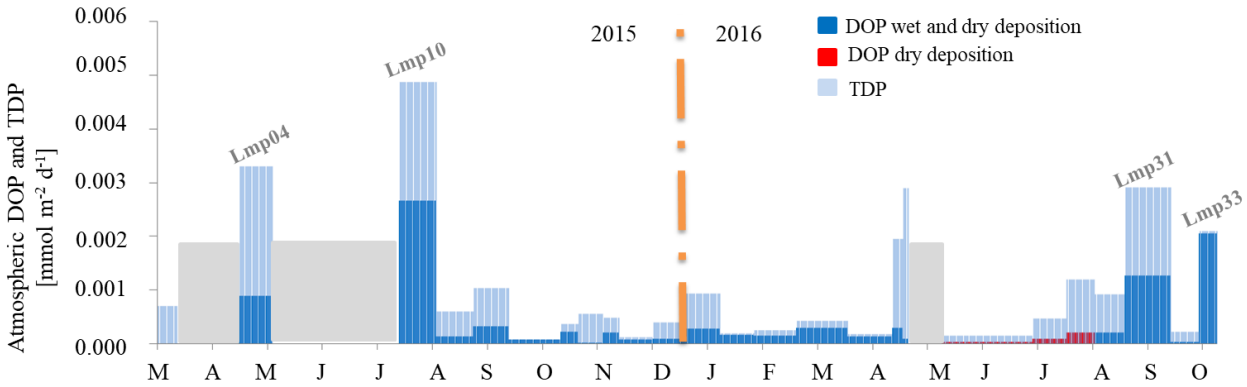


Figure 3. Atmospheric DON and TDN deposition. Grey areas correspond to the periods with no data. The month abbreviation and tick marks correspond to the end of the corresponding month. The width of the bar refer to the length of the sampling period.



637
638 **Figure 4. Atmospheric DOP and TDP deposition Grey areas correspond to the periods with no data. The month**
639 **abbreviation and tick marks correspond to the end of the corresponding month. The width of the bar**
640 **refer to the length of the sampling period.**
641

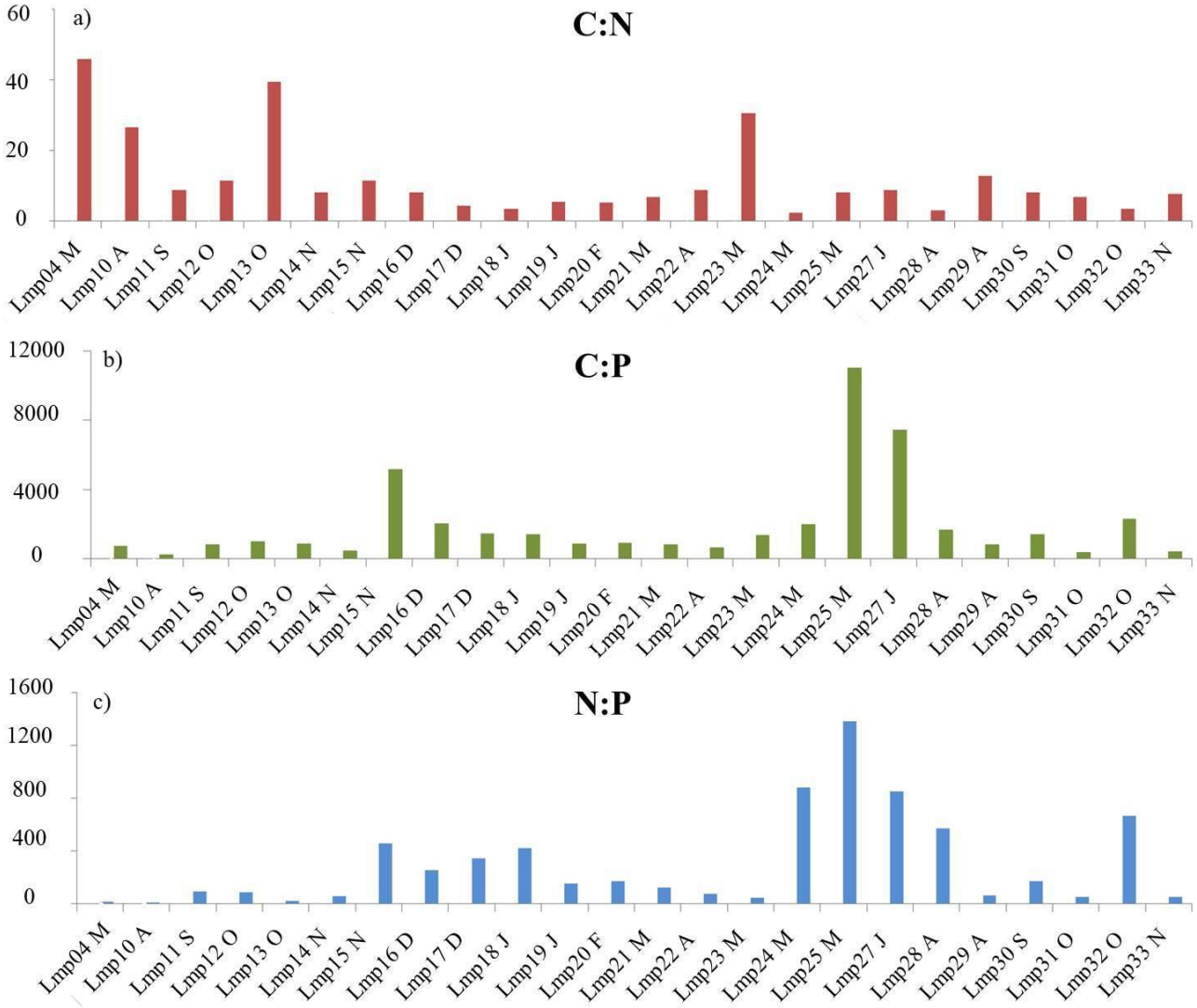


Figure 5. Temporal evolution of C:N (a), C:P (b) and N:P (c) ratios in atmospheric deposition samples. Sample name and the initials of each month (from March, Lmp04, to November, Lmp33) are reported in the X-axis.

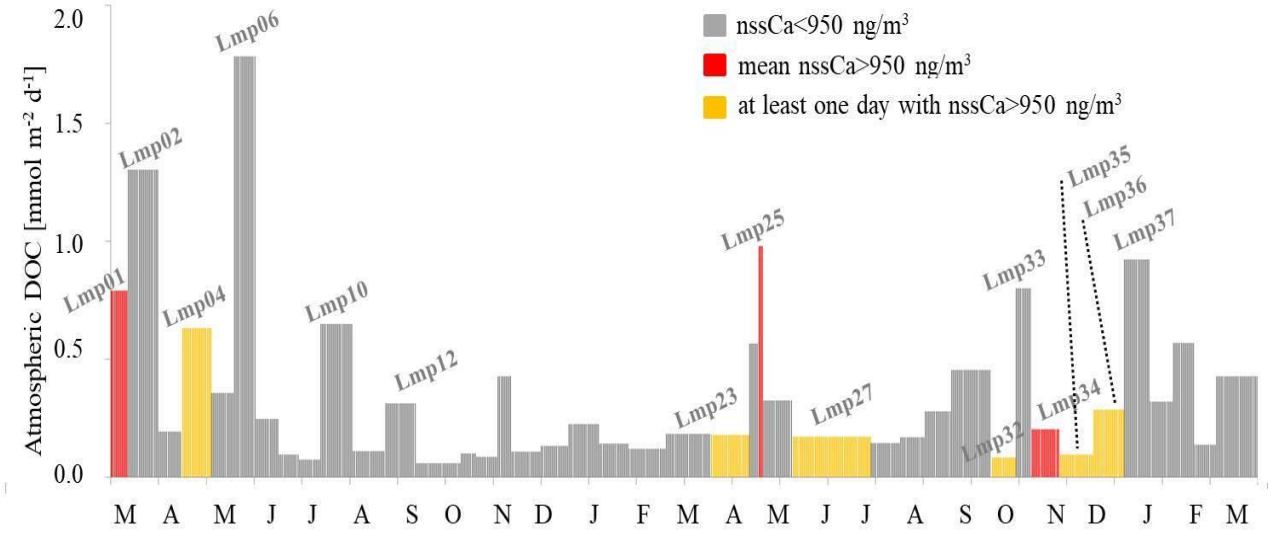


Figure 6. Temporal dynamics in the dust deposition events during the sampling period color coded based on the contribution of non-sea salt Ca (nssCa). The month abbreviation and tick marks correspond to the end of the corresponding month. The width of the bar refer to the length of the sampling period.

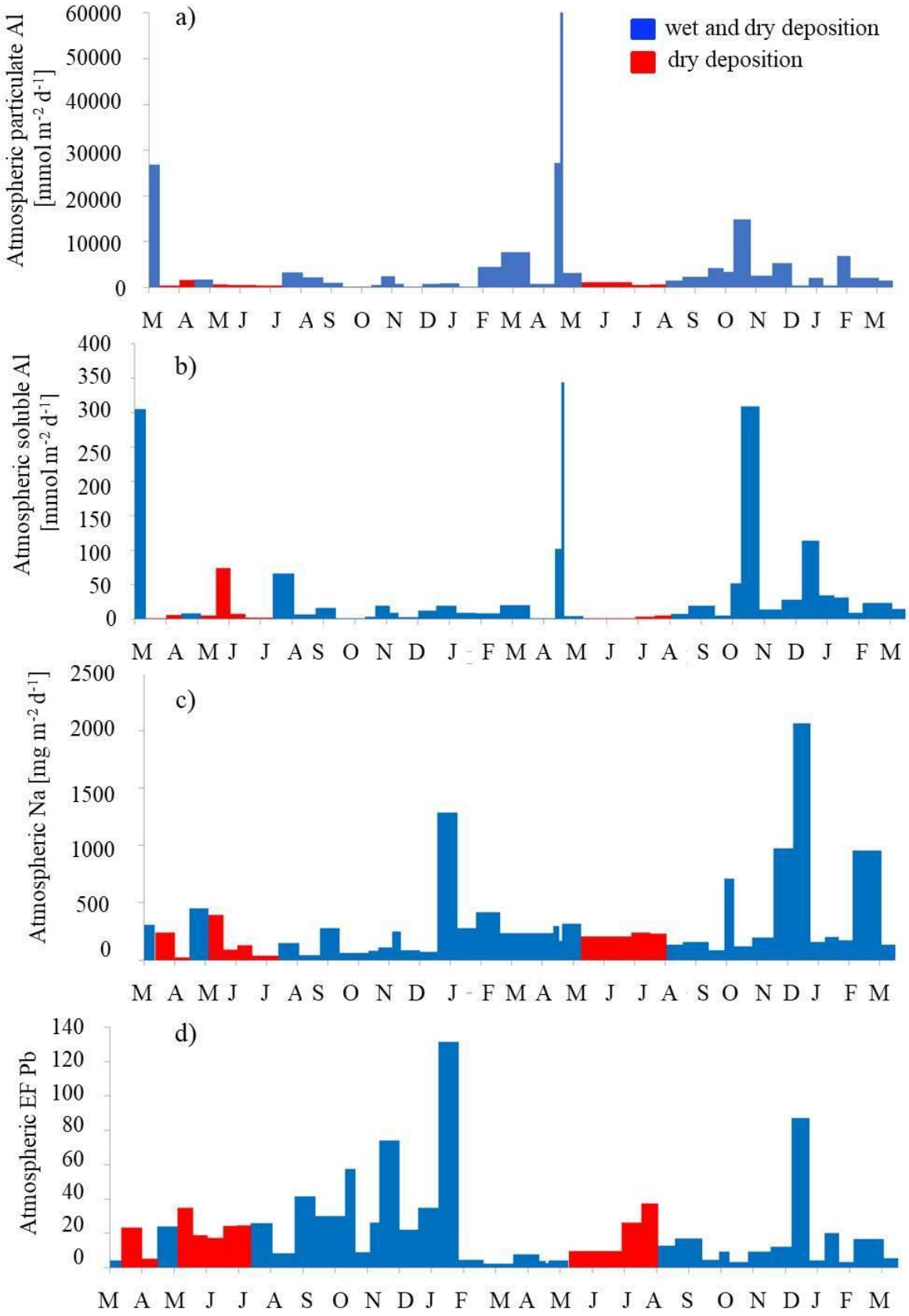


Figure 7. Temporal dynamics of atmospheric particulate Aluminium (a), soluble Aluminium (b), soluble Sodium (c) and enrichment factor for Lead (d). The month abbreviation and tick marks correspond to the end of the corresponding month. The width of the bar refer to the length of the sampling period.

655

Sample name	Sampling period			Deposition type	Volume collected [L]
	Start date	End date	Total days		
Lmp01	18/03/2015	28/03/2015	10	wet and dry	6
Lmp02	28/03/2015	17/04/2015	20	dry	0.26
Lmp03	17/04/2015	02/05/2015	16	dry	0.27
Lmp04	02/05/2015	21/05/2015	19	wet and dry	1.8
Lmp05	21/05/2015	05/06/2015	15	dry	0.28
Lmp06	05/06/2015	19/06/2015	15	dry	0.29
Lmp07	19/06/2015	04/07/2015	16	dry	0.26
Lmp08	04/07/2015	17/07/2015	14	dry	0.26
Lmp09	17/07/2015	31/07/2015	14	dry	0.27
Lmp10	31/07/2015	21/08/2015	20	wet and dry	9
Lmp11	21/08/2015	11/09/2015	22	wet and dry	2
Lmp12	11/09/2015	01/10/2015	20	wet and dry	5
Lmp13	01/10/2015	30/10/2015	29	wet and dry	0.5
Lmp14	30/10/2015	09/11/2015	11	wet and dry	2
Lmp15	09/11/2015	23/11/2015	14	wet and dry	0.6
Lmp16	23/11/2015	02/12/2015	9	wet and dry	1.2
Lmp17	02/12/2015	21/12/2015	19	wet and dry	1.9
Lmp18	21/12/2015	08/01/2016	18	wet and dry	1.8
Lmp19	08/01/2016	28/01/2016	20	wet and dry	6.1
Lmp20	28/01/2016	16/02/2016	19	wet and dry	2.7
Lmp21	16/02/2016	11/03/2016	26	wet and dry	2.1
Lmp22	11/03/2016	09/04/2016	28	wet and dry	7.1
Lmp23	09/04/2016	04/05/2016	26	wet and dry	0.3
Lmp24	04/05/2016	10/05/2016	6	wet and dry	2.3
Lmp25	10/05/2016	13/05/2016	3	wet and dry	1.9
Lmp26	13/05/2016	01/06/2016	19	wet and dry	0.7
Lmp27	01/06/2016	22/07/2016	50	dry	0.26
Lmp28	22/07/2016	10/08/2016	19	dry	0.24
Lmp29	10/08/2016	26/08/2016	16	dry	0.24
Lmp30	26/08/2016	12/09/2016	17	wet and dry	0.8
Lmp31	12/09/2016	08/10/2016	26	wet and dry	12
Lmp32	08/10/2016	24/10/2016	16	wet and dry	0.5
Lmp33	24/10/2016	03/11/2016	10	wet and dry	11
Lmp34	03/11/2016	21/11/2016	18	wet and dry	12
Lmp35	21/11/2016	13/12/2016	22	wet and dry	1.7
Lmp36	13/12/2016	02/01/2017	20	wet and dry	9.5
Lmp37	02/01/2017	19/01/2017	17	wet and dry	6.5
Lmp38	19/01/2017	03/02/2017	15	wet and dry	1.5
Lmp39	03/02/2017	17/02/2017	14	wet and dry	5
Lmp40	17/02/2017	03/03/2017	14	wet and dry	0.75

Lmp41	03/03/2017	01/04/2017	29	wet and dry	5.5

656 **Table 1. Sampling period, type of deposition and volume for the 41 samples collected at the Island of**
657 **Lampedusa.**

658

Sample name	DOC fluxes [mmol m^{-2} d^{-1}]	DON fluxes [mmol m^{-2} d^{-1}]	TDN fluxes [mmol m^{-2} d^{-1}]	DOP fluxes [mmol m^{-2} d^{-1}]	TDP fluxes [mmol m^{-2} d^{-1}]
Lmp01	0.80	0.10	0.17	0	$7 \cdot 10^{-4}$
Lmp02	1.30	n.a.	n.a.	n.a.	n.a.
Lmp03	0.19	n.a.	n.a.	n.a.	n.a.
Lmp04	0.63	0.01	0.05	$9 \cdot 10^{-4}$	$3 \cdot 10^{-3}$
Lmp05	0.36	n.a.	n.a.	n.a.	n.a.
Lmp06	1.78	n.a.	n.a.	n.a.	n.a.
Lmp07	0.25	n.a.	n.a.	n.a.	n.a.
Lmp08	0.10	n.a.	n.a.	n.a.	n.a.
Lmp09	0.07	n.a.	n.a.	n.a.	n.a.
Lmp10	0.65	0.02	0.11	$3 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
Lmp11	0.11	0.01	0.09	$1 \cdot 10^{-4}$	$6 \cdot 10^{-4}$
Lmp12	0.31	0.03	0.10	$3 \cdot 10^{-4}$	$1 \cdot 10^{-3}$
Lmp13	0.06	$1.5 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	$7 \cdot 10^{-5}$	$8 \cdot 10^{-5}$
Lmp14	0.10	0.01	0.03	$2 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Lmp15	0.09	$8 \cdot 10^{-3}$	0.06	$2 \cdot 10^{-5}$	$6 \cdot 10^{-4}$
Lmp16	0.43	0.05	0.14	$2 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
Lmp17	0.11	0.03	0.11	$7 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
Lmp18	0.13	0.04	0.25	$9 \cdot 10^{-5}$	$4 \cdot 10^{-4}$
Lmp19	0.23	0.04	0.20	$3 \cdot 10^{-4}$	$9 \cdot 10^{-4}$
Lmp20	0.14	0.03	0.12	$2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$
Lmp21	0.12	0.02	0.10	$2 \cdot 10^{-4}$	$3 \cdot 10^{-4}$
Lmp22	0.18	0.02	0.05	$3 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Lmp23	0.18	$6 \cdot 10^{-3}$	0.10	$1 \cdot 10^{-4}$	$2 \cdot 10^{-4}$
Lmp24	0.57	0.25	0.47	$3 \cdot 10^{-4}$	$2 \cdot 10^{-3}$
Lmp25	0.98	0.12	0.32	$9 \cdot 10^{-5}$	$3 \cdot 10^{-3}$
Lmp26	0.33	n.a.	n.a.	n.a.	n.a.
Lmp27	0.17	0.02	0.08	$2 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
Lmp28	0.14	0.05	0.19	$9 \cdot 10^{-5}$	$5 \cdot 10^{-4}$
Lmp29	0.17	0.01	0.12	$2 \cdot 10^{-4}$	$1 \cdot 10^{-3}$
Lmp30	0.28	0.04	0.18	$2 \cdot 10^{-4}$	$9 \cdot 10^{-4}$
Lmp31	0.45	0.07	0.22	$1 \cdot 10^{-3}$	$3 \cdot 10^{-3}$
Lmp32	0.08	0.02	0.10	$4 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
Lmp33	0.80	0.10	0.34	$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$
Lmp34	0.20	n.a.	n.a.	n.a.	n.a.
Lmp35	0.10	n.a.	n.a.	n.a.	n.a.
Lmp36	0.29	n.a.	n.a.	n.a.	n.a.
Lmp37	0.92	n.a.	n.a.	n.a.	n.a.
Lmp38	0.32	n.a.	n.a.	n.a.	n.a.
Lmp39	0.57	n.a.	n.a.	n.a.	n.a.
Lmp40	0.14	n.a.	n.a.	n.a.	n.a.
Lmp41	0.43	n.a.	n.a.	n.a.	n.a.

659 **Table 2. Atmospheric fluxes of DOC, DON, TDN, DOP and TDP at the Island of Lampedusa.**

660

Sample	Sampling date	C:N	C:P	N:P
Lmp01	28/03/2015	7.78	n.a.	n.a.
Lmp04	21/05/2015	45.87	715.08	15.59
Lmp10	21/08/2015	26.57	244.38	9.20
Lmp11	11/09/2015	8.67	807.94	93.15
Lmp12	01/10/2015	11.37	977.79	85.98
Lmp13	30/10/2015	39.44	864.07	21.91
Lmp14	09/11/2015	8.02	449.04	56.00
Lmp15	23/11/2015	11.26	5131.65	455.83
Lmp16	02/12/2015	7.97	2036.66	255.42
Lmp17	21/12/2015	4.24	1448.37	341.90
Lmp18	08/01/2016	3.34	1406.60	420.55
Lmp19	28/01/2016	5.38	832.69	154.79
Lmp20	16/02/2016	5.09	882.80	173.40
Lmp21	11/03/2016	6.63	812.40	122.55
Lmp22	09/04/2016	8.78	645.65	73.53
Lmp23	04/05/2016	30.48	1353.57	44.41
Lmp24	10/05/2016	2.24	1976.03	882.33
Lmp25	13/05/2016	7.99	11008.94	1377.41
Lmp27	22/07/2016	8.73	7405.29	848.62
Lmp28	10/08/2016	2.89	1641.49	568.76
Lmp29	26/08/2016	12.66	796.68	62.95
Lmp30	12/09/2016	8.06	1376.27	170.77
Lmp31	08/10/2016	6.74	356.03	52.84
Lmp32	24/10/2016	3.41	2275.72	666.53
Lmp33	03/11/2016	7.68	389.57	50.73

661 **Table 3. C:N:P molar ratios in atmospheric DOM.**

662

Sample name	Mean PM_{10} [$\mu g/m^3$]	Mean sea salt aerosol [$\mu g/m^3$]	Mean dust [$\mu g/m^3$]	Mean nssCa [ng/m^3]
Lmp01	50.1	13.0	18.2	1327.6
Lmp02	29.0	13.6	n.a.	62.2
Lmp03	28.1	9.8	n.a.	371.6
Lmp04	26.4	8.8	4	351.7
Lmp05	16.7	4.6	n.a.	87.3
Lmp06	23.1	6.1	n.a.	166.1
Lmp07	22.2	7.1	n.a.	139.3
Lmp08	26.5	5.4	n.a.	311.6
Lmp09	28.3	8.0	n.a.	188.2
Lmp10	29.1	5.2	3.4	492.7
Lmp11	n.a.	n.a.	n.a.	n.a.
Lmp12	n.a.	n.a.	n.a.	n.a.
Lmp13	n.a.	n.a.	n.a.	n.a.
Lmp14	n.a.	n.a.	n.a.	n.a.
Lmp15	n.a.	n.a.	n.a.	n.a.
Lmp16	n.a.	n.a.	n.a.	n.a.
Lmp17	n.a.	n.a.	n.a.	n.a.
Lmp18	n.a.	n.a.	n.a.	n.a.
Lmp19	n.a.	n.a.	n.a.	n.a.
Lmp20	n.a.	n.a.	n.a.	n.a.
Lmp21	n.a.	n.a.	n.a.	n.a.
Lmp22	n.a.	n.a.	n.a.	n.a.
Lmp23	39.5	18.3	3.8	488.1
Lmp24	30.7	18.7	1.2	154
Lmp25	133.7	15.5	42.5	4815.1
Lmp26	25.9	13.1	1.5	168.8
Lmp27	26.2	9.3	2.3	319.5
Lmp28	24.7	8.8	1.8	161.5
Lmp29	25	9.6	1.0	235.9
Lmp30	22.4	5.1	n.a.	330.8
Lmp31	24.5	5.6	n.a.	286.2
Lmp32	32.9	8.7	n.a.	772.5
Lmp33	31.8	11.8	n.a.	344.2
Lmp34	35.3	7.8	n.a.	1092.2
Lmp35	22.3	7.5	0.4	394
Lmp36	35.8	12.3	4.6	661.5
Lmp37	n.a.	n.a.	n.a.	n.a.
Lmp38	n.a.	n.a.	n.a.	n.a.
Lmp39	n.a.	n.a.	n.a.	n.a.
Lmp40	n.a.	n.a.	n.a.	n.a.

Lmp41	n.a.	n.a.	n.a.	n.a.

663 **Table 4. The PM_{10}, sea salt aerosol, dust and nssCa mean values of the atmospheric total deposition.**