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Biogeosciences Discussions

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), close to the Sahara desert, between March 19th 2015 and April 1st 2017. The main goals of this work are: to quantify total atmospheric deposition of DOM in this area and to evaluate the impact of 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 allow to estimate 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 site mainly have natural origin, especially from sea spray and that Saharan dust can be an important carrier of organic substances, even if the load of DOC associated with dust is highly variable. Our estimates suggest that atmospheric input has an impact to the Med Sea larger than to the global ocean and that DOC fluxes from the atmosphere to the Med Sea can be up to 6-fold larger than river input. Longer time series, combined with a modelling effort, are therefore mandatory in order to investigate 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 in the world. It is very sensitive to natural variations in the atmosphere-ocean interactions (Mermex group, 2011). Organic matter and nutrients of natural and anthropic 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). 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 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; 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 global and local scale. Organic carbon can be removed from

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

the atmosphere via both 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 can therefore affect regional C cycling, radiative forcing, and human health (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 potential 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 in correspondence with a Saharan dust storm, suggesting a combination of heterogeneous reactions between organic matter and mineral dust in the troposphere. In the second study, the Saharan rain event coincided with a minimum in DOC input, suggesting the presence of an aerosol poorly enriched in organic matter (Djaoudi et al., 2018). These studies were conducted in coastal areas affected by human activities. Direct measurements of total OC (TOC) in rainwater were performed at the Crete Island (Eastern Mediterranean; 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 of 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/).

An interesting aspect of the Med Sea is related to Dissolved Organic Matter (DOM) stoichiometry. Mediterranean DOC and Dissolved Organic Nitrogen (DON) concentrations and their ratios are similar to those reported for the global ocean (Pujo-Pay et al., 2011; Santinelli, 2015). In the surface waters (0-100 m), C:N:P ratios show that Mediterranean DOM is depleted in Dissolved Organic phosphorous (DOP). The study of C:N:P ratio of DOM in atmospheric deposition is important in order to estimate the relative contribution of atmospheric DOM input to the inventory of the surface DOM pool and to understand the fate of the three elements in the water column.

This study reports the results of analyses on deposition collected at Lampedusa island (35.52°N, 12.63°E) located in central Med Sea. Lampedusa is located in an ideal position for the study of atmospheric DOC fluxes to the open Med Sea. The site is interesting, in particular, to investigate the mineral dust contribution (mean dust deposition=7.4 g $^{m-2}$ $year^{-1}$, Vincent et., 2016) to DOC deposition. Lampedusa is a flat island far from large islands or continental areas and from relevant pollutant sources. Although influences from ship traffic emissions (Becagli et al., 2012, 2017), volcanic

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

aerosols (Sellitto et al., 2017), forest fires (Pace et al., 2005), and regional pollution (Pace et al., 2006), have been documented, their contribution to the total aerosol load is small, and Lampedusa may be taken as representative for the remote marine environment of the central Med Sea. The importance of this study area is that previous work on DOC atmospheric deposition to the Med was essentially confined to the coastal areas, less representative of what is actually arriving to the open Med Sea. Measurements at Lampedusa provide additional important information on the deposition in the open Med Sea.

In addition to deposition, also measurements of PM_{10} amount and chemical composition, 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 by 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. In case of wet deposition, the amount of water in the sampler was weighted then it was collected in 250 ml polycarbonate bottles and immediately frozen. In case of dry deposition, the sampler was rinsed with 250 mL of ultrapure MilliQ water, the sample was then collected in 250 ml polycarbonate bottles and immediately frozen. A detailed description of sampling periods, deposition types, and collected volumes is reported in Table 1.

Samples for DOC, DON and DOP 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).

The concentration of soluble ions metals was measured on the samples filtered on quartz filters. These filters have low blanks level for metals and ions respect to the determined concentration both in the soluble and particulate fraction. Just after filtration the sample was divided in two portions, one for ionic content and the other for metal content, the latter was spiked by 0.1 mL of sub-boiled distilled (s.b.) HNO_3 to preserve the metals in their soluble form. Samples was keep refrigerate at +4°C until the analysis.

2.3 DOC analysis

DOC analysis were carried by 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). The instrument functioning was assessed every day by comparison of data with DOC Consensus Reference Material (CRM), kindly provided by Prof. D. Hansell. DOC nominal value was 41-44 μM (batch 15 Lot #07-15), DOC measured value was 42.78±1.20 (n=15) (Hansell, 2005).

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

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121 **2.4 DOP and DON analysis**

122 Twenty-six samples out of the total 41 were analyzed for dissolved organic nitrogen (DON) and phosphorous (DOP).
123 The samples were collected between March 19th 2015 and November 3rd 2016.
124 DON was estimated by subtracting the dissolved inorganic nitrogen (DIN) from the total dissolved N (TDN). DIN and
125 TDN were analyzed by conventional, automated colorimetric procedure (CACP) according to Aminot and Kerouel
126 (2007) with an estimated limit of detection of 0.02 µM. TDN was analyzed after persulfate wet-oxidation (Pujo-Pay et
127 al., 1997).
128 DOP concentrations were determined by subtracting the inorganic form (soluble reactive phosphorus, SRP) from the
129 total dissolved P. SRP was measured spectrophotometrically after Murphy and Riley (1962) with a limit of detection of
130 0.02 µM and an analytical precision of 7% at 0.1 µM. TDP was measured as SRP after UV digestion (Armstrong et al.,
131 1966). The photoxidation technique included a 2 hours UV treatment in a Metrohm® 705 UV digester with a digestion
132 efficiency of 85 ± 3 %, assessed on a 1 µM solution of β-glycerol-phosphate.
133

134 **2.5 Ions and metals content in the deposition samples**

135 The concentration of soluble ions metals was measured on the samples filtered on quartz filters. These filters have low
136 blanks level for metals and ions respect to the determined concentration both in the soluble and particulate fraction. Just
137 after filtration the sample was divided in two portions, one for ionic content and the other for metal content, the latter
138 was spiked by 0.1 mL of sub-boiled distilled (s.b.) HNO_3 to preserve the metals in their soluble form.
139 Samples was keep refrigerate at +4°C until the analysis. Ions were determined on the solution by ion chromatography as
140 reported in Becagli et al. (2011).
141 The particulate fraction of the deposition was extracted from the quartz filter through the solubilisation procedure
142 reported in the EU EN14902 (2005) rule for aerosol samples. The extraction procedure was performed in a microwave
143 oven at 220°C for 25 min by sub-boiling distilled HNO3 and 30% ultra-pure H_2O_2.
144 Metals were determined in both soluble and particulate fractions by means of an Inductively Coupled Plasma Atomic
145 Emission Spectrometer (ICP-AES, Varian 720-ES) equipped with an ultrasonic nebulizer (U5000 ATC, Cetac
146 Technologies Inc.). Daily calibration standards (internal standard: 1 ppm Ge) were used for quantification.
147

148 **2.6 PM_{10} analysis**

149 PM_{10} (particulate matter with aerodynamic equivalent diameter lower than 10 µm) is routinely sampled on a daily basis
150 at the island of Lampedusa (Becagli et al., 2013; Marconi et al., 2014; Calzolai et al., 2015) by using a low-volume
151 dual-channel sequential sampler (HYDRA FAI Instruments) equipped with two PM_{10} sampling heads, operating in
152 accord with UNI EN12341. The PM_{10} mass was determined by weighting the Teflon filters (47 mm diameter 2 µm
153 nominal porosity) before and after sampling with an analytical balance in controlled conditions of temperature (20±1
154 °C) and relative humidity (50±5%). The estimated error on PM_{10} mass is around 1% at 30 µg m^{-3} in the applied
155 sampling conditions. A quarter of each Teflon filter was extracted using MilliQ water (about 10 ml, accurately
156 evaluated by weighing) in ultrasonic bath for 15 min, and the ionic content was determined by ion chromatography as
157 for deposition samples (Becagli et al. 2011). Another quarter of the Teflon filter was used for the determination of
158 metals in the atmospheric particulate as already described for the deposition samples.

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Preprint. Discussion started: 3 February 2020

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160 **2.7 Enrichment factor**

161 In order to obtain information on the DOM sources, DOM concentration is compared with concentration of Al, Na and
162 the enrichment factor of Pb (EF Pb) in the deposition as they are marker of crustal, sea spray and anthropic source
163 respectively.
164 The enrichment factor (EF) respect to crustal source for Pb, V and Ni are calculated by using Al as marker for crustal
165 aerosol. The following equation (Eq. 1) is used for EF calculation:

166 $$EF\ X=\frac{(\frac{X}{Al})sample}{(\frac{X}{Al})crust} \quad (1)$$

167

168 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
169 in the upper continental crust as reported in Henderson and Henderson (2009). By convention, element with EF<10 are
170 called "not enriched" having a prevailing crustal source, whereas 10<EF<100 indicate a moderate enrichment and
171 EF>100 indicate that the element (called "enriched") has a prevailing anthropogenic source (e.g. Lai et al., 2017).

172

173 **3. Results**

174 **3.1 DOC atmospheric fluxes**

175 DOC atmospheric fluxes ranged between 0.06 and 1.78 mmol C m^{-2} day^{-1}, with a marked variability. The sampling
176 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
177 days (52%).
178 In 2015, the lowest deposition rates (<0.1 C m^{-2} d^{-1}) were measured in July (Lmp09), October (Lmp13), and November
179 (Lmp15). The highest ones (>1.2 mmol C m^{-2} d^{-1}) occurred between March and April (Lmp02), and in June (Lmp06),
180 both periods were characterized by dry deposition (Fig.2 and Table 2). High DOC fluxes (>0.6 mmol C m^{-2} d^{-1}) were
181 also observed in March (Lmp01), May (Lmp04) and at the end of July (Lmp10), in correspondence with periods
182 dominated by wet deposition. In 2015, the annual rainfall was 360 mm, slightly higher than the average annual rainfall
183 at the island of Lampedusa (325 mm with 42 days of rain), (data from: http://www.arpa.sicilia.it/ and
184 http://www.eurometeo.com/italian/climate).
185 In 2016, the DOC deposition rates were rather low and with a smaller variability compared to the previous year. DOC
186 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
187 (Lmp27 to Lmp30). The highest DOC fluxes (>0.8 mmol C m^{-2} d^{-1}) were observed in May (Lmp25) and between
188 October and November (Lmp33; Fig. 2 and Table 2).
189 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
190 values are higher than those observed in the first three months of the previous year (Fig. 2 and Table 2).
191 Atmospheric fluxes of DOC in the wet depositions were correlated with monthly precipitation rates (r^2=0.47, p<0.05,
192 n=12). The precipitation rate ranged between 2.9 and 88.5 mm.
193 A mean daily deposition of 0.33 mmol C m^{-2} d^{-1} was calculated, taking into consideration the two years (from March
194 2015 to April 2017), corresponding to an annual DOC flux of 120.7 mmol C m^{-2} $year^{-1}$.

195

196 **3.2 DON and TDN, DOP and TDP atmospheric fluxes**

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

DON and Total Dissolved Nitrogen (TDN) 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). In 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) in correspondence with high DOC deposition (Fig. 3 and Table 2).

DOP and Total dissolved phosphorous (TDP) fluxes ranged between 0 and $2.7 \cdot 10^{-3}$ mmol DOP m^{-2} d^{-1} and $1 \cdot 10^{-4}$ and $8 \cdot 10^{-5}$ 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 and were in correspondence with high DOC fluxes (Fig. 2). It is noteworthy that in March 2015 (Lmp01) and May 2016 (Lmp25), in correspondence with high fluxes of DOC, DON and TDP, DOP was very low (0 and $9 \cdot 10^{-5}$ mmol m^{-2} d^{-1}, respectively) (Table 2).

Taking into consideration the entire sampling period (March 2015 - November 2016), the 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 an 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 in the different periods (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 in autumn (November 2015 and October 2016) and late spring (May 2016) depositions were very poor 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 of anthropic source at Lampedusa (Becagli et al, 2012 and 2017), but in the considered samples they usually do not show enrichment factor higher than 10, therefore their source in the deposition is mainly from crustal input.

Besides, mean values of PM_{10}, sea salt aerosol, dust and non-sea-salt Ca (nss Ca) mean values in PM_{10} samples were calculated over the same intervals of the deposition measurements.

In Fig. 6 we reported the DOC deposition classified on the basis of the corresponding nssCa concentration in PM_{10}. Following Marconi et al. (2014), Saharan dust events are identified as those with nssCa > 950 ng/m^3. DOC deposition values corresponding to average nssCa larger than the threshold (950 ng/mg^3) are highlighted in red. DOC deposition corresponding to a Saharan dust event occurring in at least one day of the sampling period, are indicated in orange (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)

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

and the Al concentration in the deposition (both soluble and particulate, Fig. 7). In this sample EF(Pb) indicate the low contribution of the anthropic source. Na concentration in the deposition is 304 mg m^{-2} d^{-1} (Fig. 7).

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

Lmp04 (May 2015) shows a high value of DOC; during this sampling period a Saharan dust event occurred (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 g 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 dominates also 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 the samples Lmp10 and Lmp12 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} with a peak of 267.4 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 sampling period and indicates the occurrence of a Saharan dust event. The average value of nssCa in the sampling days was 4815.1 ng/m^3, with an incredible peak of 9207 ng/m^3, highlighting the occurrence of an intense Saharan dust event. The relevant Saharan dust contribution for this sample is well revealed by Al concentration (both soluble and particulate) in the atmospheric deposition (Fig. 7).

Lmp33 (October-November 2016) and Lmp34 (November 2016) present a very indicative pattern 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, conversely the second is characterized by high crustal content (as reveled by the high concentration of Al, Fig. 7).

Unfortunately PM_{10} data are not available for the fourth highest DOC deposition of the entire study period (Lmp37).

4. Discussion

4.1 DOC input from the atmosphere

The relationship between monthly precipitation rates and DOC fluxes confirmed the high efficiency in DOM atmospheric deposition of DOC via rain events in the Med Sea, as recently reported by Djaoudi et al. (2018).

Our data allowed for the quantification of the DOC annual input from the atmosphere (120.7 mmol C m^{-2} y^{-1}); this value 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 that reported for the north-western Med Sea from February 2015 to July 2016, at Frioul island, Marseille Bay (59 mmol C m^{-2} y^{-1}; 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

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

due to the different temporal and seasonal cycles of dry and wet deposition. In particular the marked differences between these 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. If 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) together accounted for 43% of the annual DOC flux (52 mmol C m^{-2} y^{-1}). Depending on the origin and trajectories of the air masses, 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 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 receives from 1.5 to 4% of the global atmospheric input of DOC, despite it covers only 0.7% of the global oceans area.

Moreover, if we consider the riverine DOC fluxes, 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 lead role of atmosphere in the transport of allocthonous DOC to the Med Sea, as suggested recently by Galletti et al. (2019).

Few episodes of Saharan outbreaks can strongly affect the annual dust flux, indeed 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 larger 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). Deposition data in this work reveal that dust events can contribute to the annual DOC fluxes but sea spray seems the dominant source of DOC in this area.

It should also be stressed that the DOC dynamics and its annual fluxes are not only influenced by dust deposition events. The wet deposition is also relevant, and the correlation between monthly precipitation rates and DOC fluxes confirms the high efficiency in DOC atmospheric deposition via rain events in the Med Sea, as recently proposed by Djaoudi et al. (2018).

4.2 Atmospheric DON, DOP input and elemental ratios

The DON annual 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). Only the study by Markaki et al. (2010) reports data on atmospheric DON fluxes and is focused on the Eastern Med Sea. These authors reported an annual flux (18.49 mmol N m^{-2} y^{-1}) higher than that observed at Lampedusa. The comparison among our values (0.14 mmol P m^{-2} y^{-1}) and the few DOP 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), whereas they are 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. Our values are instead 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).

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

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

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 what the Mediterranean area receives in terms of DON and DOP, 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 with respect to marine DOM. This observation is also valid when we compare 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).

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

The input of Saharan dust has important effects on the chemistry of the Mediterranean aerosols and its deposition can enrich the Med Sea with many elements (such as Co, Ni, trace metals). Very few data are available on the interactions between organic carbon and Saharan dust, even if 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 the aerosol, during its route to Lampedusa, was probably enriched with organic substances. We hypothesize that the dust particles present in the aerosol worked as condensation nuclei for 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) characterized by high DOC, when an intense intrusion of Saharan air masses was favored by one synoptic situation in which the role of the cyclonic circulation with a minimum depression was significant (www.meteogiornale.it).

If all the Saharan dust deposition events (red and orange in Fig. 6) are taken into account, the input of 49.58 mmol DOC m^{-2} to Lampedusa during the study period can be estimated, this value represents ~41% of the total flux for the entire sampling period. Instead, if only the strong dust events (red in Fig. 6) are taken into consideration a flux of 15.26 mmol DOC m^{-2} can be estimated, representing 13% of the total flux. Anyhow each deposition event must be considered individually, because it can be characterized by an enrichment of DOC or not depending on the aerosol load (Formenti et al., 2003; Aymoz et al., 2004).

Wet deposition mainly controls the flux of Saharan dust to the Med Sea, but dry deposition can be also important (Guerzoni et al., 1997) and its relative importance 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). Our data confirm the importance of wet deposition, but similarly dry deposition also plays a crucial role. Our results stress the relevance of dry deposition (32% of the total deposition during the entire sampling

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

period) that, in the remote site of Lampedusa, appears to be main contributor of DOC and of other chemical species, as suggested in the past by Morales-Baquero et al. (2013).

It is also evident by our data that Saharan dust input is not always associated with high DOC input, it cannot therefore be considered as the only process for DOC transport and deposition. For instance sample Lmp34, that shows high concentration of dust, is not characterized by high concentration of DOC and several samples (for example Lmp02, Lmp33 and Lmp37) characterized by high concentration of DOC, do not show high crustal content. Indeed high DOC deposition seems often associated to sea spray transport, for instance in samples Lmp02, Lmp10, Lmp 12, Lmp 33 and Lmp 37 (Fig. 6, in gray).

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 a strong Saharan dust event (Fig. 6, in orange). This observation supports the hypothesis that dust from Saharan region is not typically enriched with DOC, but it behaves as aggregation center of organic molecules in the atmosphere, and depending on its route it can be enriched or not in DOC during its route. Lmp34 further supports this hypothesis. This sample shows the third highest average nss Ca value (1092.2 ng/m^3), nevertheless DOC was very low (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).

However the data of atmospheric Na and soluble Al suggest a very high contribution of sea spray aerosol (the highest of the whole considered period) (Fig. 7). Therefore, for samples Lmp33 and Lmp37 the DOC source seems to be primary marine instead of crustal as for the samples Lmp01, Lmp04, Lmp10, Lmp12 and especially Lmp25.

Lastly, it is interesting to notice that samples characterized by high values of DOC never present high EF(Pb) and the samples presenting EF(Pb)>10 present very low DOC concentration, suggesting that anthropic sources have a small impact on DOC deposition 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. Very few information is available about the biological lability of atmospheric DOC: if labile, it can be used very quickly by the microbial loop, whereas if it is mainly recalcitrant, it can accumulate and be transported by water masses circulation.

In order to estimate the impact of atmospheric DOC deposition to the surface waters we took into consideration a mixed layer depth (MLD) ranging between 15 and 30 m, typical of the sea close to the island of Lampedusa in September, in according with the estimation reported by D'Ortenzio et al. (2005). Santinelli et al. (2012) observed an average DOC concentration of 60 μM in the same area in September 1999 (in the mixed layer), 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 them by the average MLD (22.5 m) (D'Ortenzio et al. 2005), we estimate that the atmospheric input is expected to determine a 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. Instead in summer the MLD is between 10 and 15 m, 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

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

June to August 2015, and by 0.013-0.014 from June to August 2016. Assuming that a BCD of 0.32 μM C d^{-1} is valid also for summer (three months) and that all the atmospheric DOC is labile, it could satisfy 3-25% of the daily BCD. These results highlight the relevant role of atmosphere input of DOC in sustaining the bacterial productivity in the surface layer, particularly when the 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 data 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 are crucial in order to have an accurate estimation of the DOC atmospheric input impact on the functioning of marine ecosystem. It should be also noted that a fraction of atmospheric DOC could be recalcitrant, and therefore could be transported to depth, playing a key role in carbon sequestration to depth. The refractory nature of a part of atmospheric DOC is hypothesized by Sánchez-Pérez et al. (2016), who collected a 2-year time series data on Fluorescent DOM (FDOM) deposition in the North-western Med Sea and studied the changes in the quality and quantity of marine DOM in the 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 DOM pool.

Lastly, as highlighted in the previous paragraphs, 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 river input.

This study indicates that the organic substances transported by Saharan dust at Lampedusa site mainly have natural origin, especially from sea spray and that Saharan dust can be an important carrier of organic substances. The load of DOC associated with dust is very 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 that the contribution of atmospheric deposition to the marine DOM stoichiometry in the Med Sea could be relevant, in particular during the stratification period.

For future studies, atmospheric and marine DOM molar ratios (C:N:P) could be measured over time in order to obtain information about changes in marine DOM pool. 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. Lastly, longer time series, combined with a modelling effort, are highly desirable in order to assess the response of DOM dynamics in the Med Sea to the change in aerosol deposition pattern due to the effect of climate change.

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

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.

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https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

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596
597 **Figure 1: Lampedusa island (35.5° N, 12.6° E) and the deposition sampler.**

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

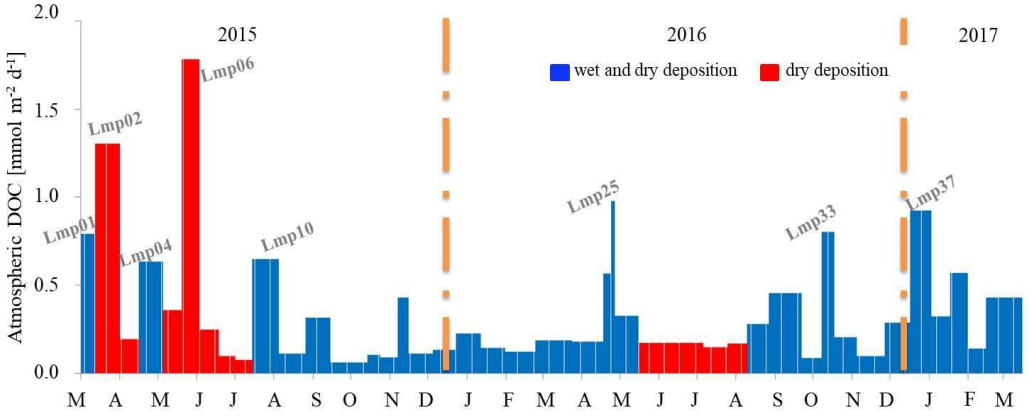

Figure 2: Atmospheric DOC fluxes during the study period. The sign of the months is reported every 31 days.

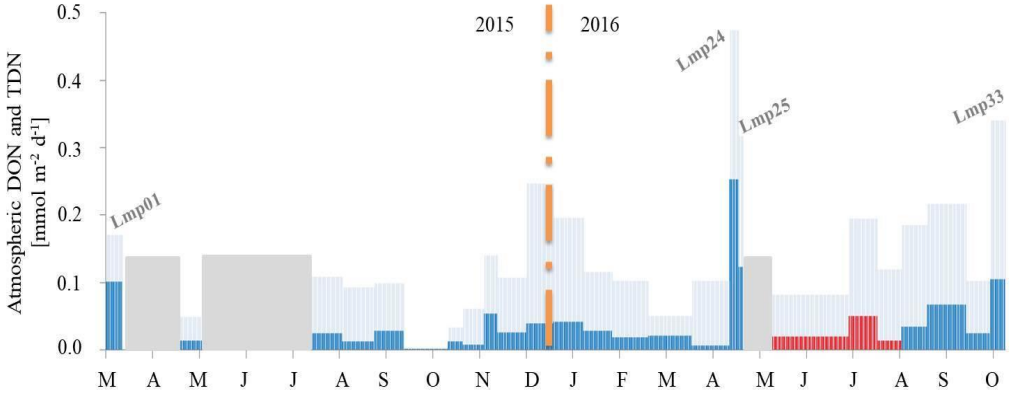

Figure 3. Atmospheric DON in blue (wet and dry deposition) and red (dry deposition), and TDN in cyan. No data are available in the grey areas.

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

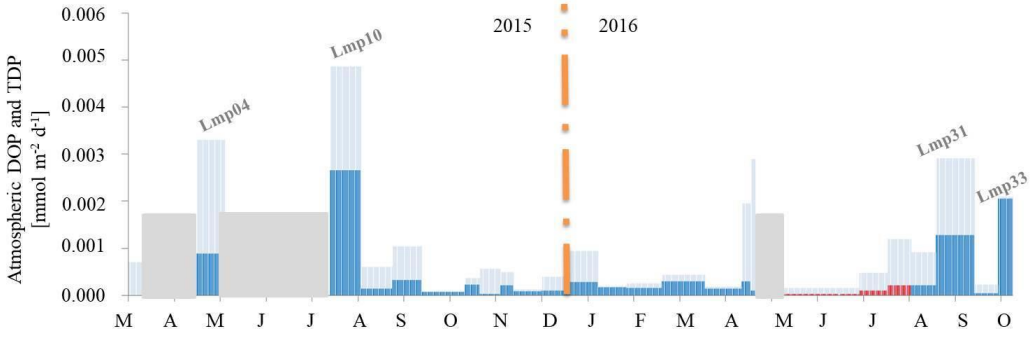

Figure 4. Atmospheric DOP in blue (wet and dry deposition) and red (dry deposition), and TDP in cyan. No data are available in the grey areas.

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Preprint. Discussion started: 3 February 2020

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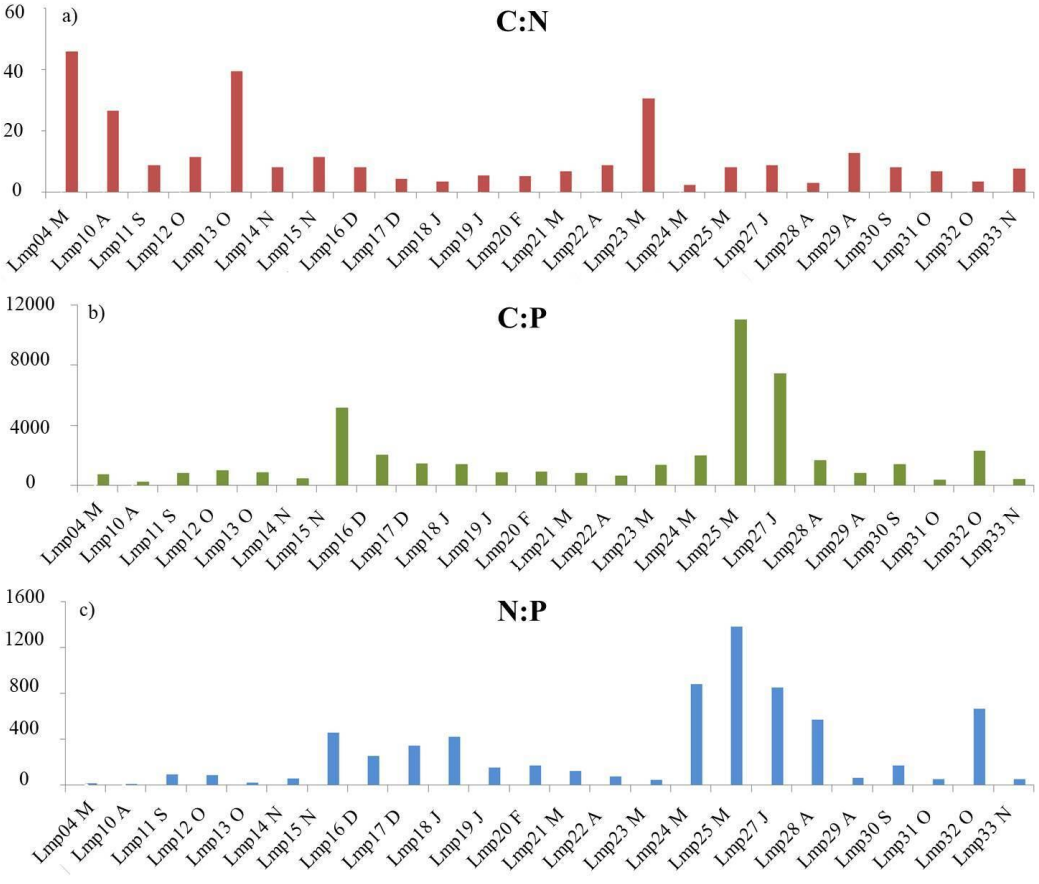

Figure 5. Temporal evolution of C:N (a), C:P (b) and N:P (c) ratios. Sample name and the capital letter of the corresponding month of the sampling (from March, Lmp04, to November, Lmp33) are reported in the horizontal axis.

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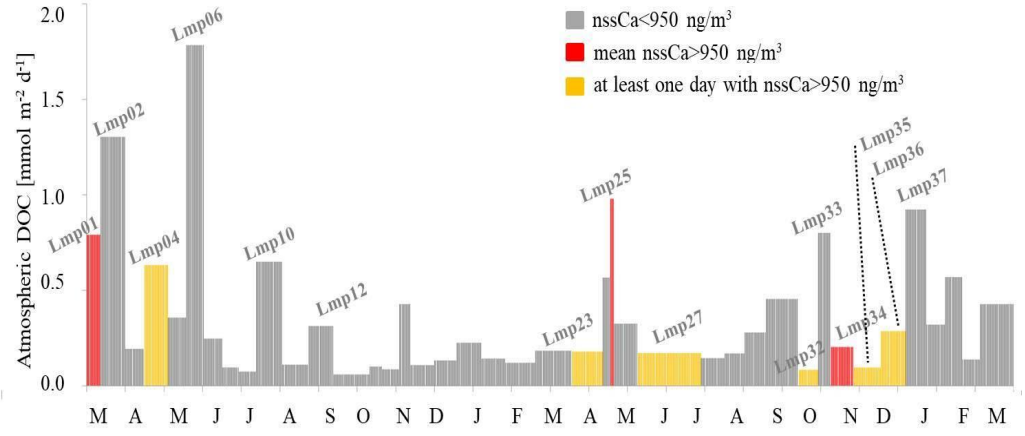
Preprint. Discussion started: 3 February 2020



612
613 **Figure 6. Intensity of dust deposition events during the sampling period based on non-sea salt Ca (nssCa) values.**
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Preprint. Discussion started: 3 February 2020

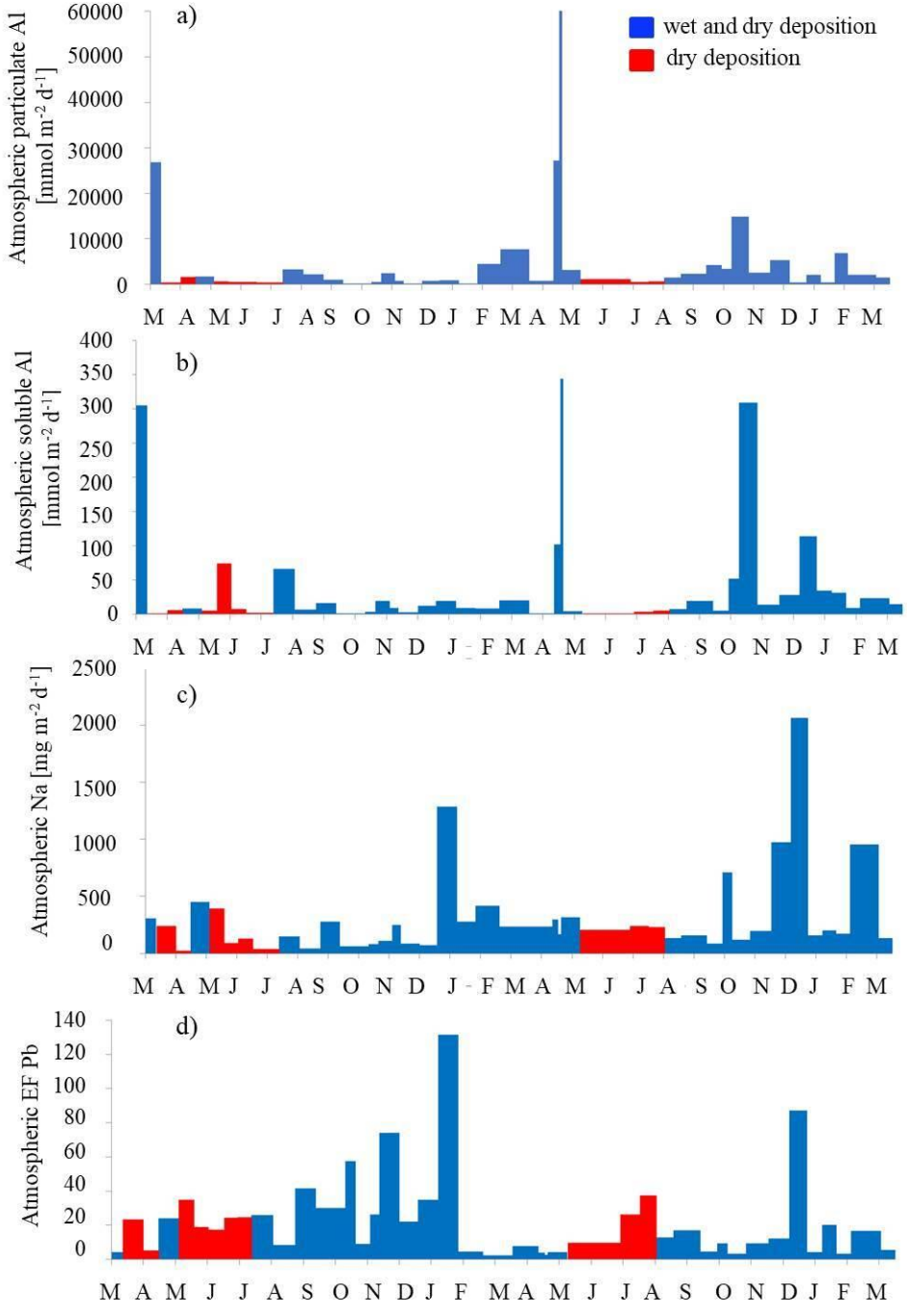

Figure 7. Atmospheric particulate Aluminium (a), soluble Aluminium (b), soluble Sodium (c) and enrichment factor of Lead (d).

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

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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

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

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

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Preprint. Discussion started: 3 February 2020

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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.

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

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

623

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

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

625

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

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.

https://doi.org/10.5194/bg-2020-14
Preprint. Discussion started: 3 February 2020

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

626 **Table 4. The PM_{10}, sea salt aerosol, dust and non-sea salt Ca (nss Ca) mean values of the atmospheric DOC**
627 **deposition.**