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

Yuri Galletti<sup>1</sup>, Silvia Becagli<sup>2</sup>, Alcide di Sarra<sup>3</sup>, Margherita Gonnelli<sup>1</sup>, Elvira Pulido-Villena<sup>4</sup>, Damiano M. Sferlazzo<sup>3</sup>, Rita Traversi<sup>2</sup>, Stefano Vestri<sup>1</sup>, and Chiara Santinelli<sup>1</sup>

<sup>1</sup>CNR, Biophysics Institute, Pisa, Italy

<sup>2</sup>Department of Chemistry “Ugo Schiff”, University of Florence, Florence, Italy

<sup>3</sup>Laboratory for Observations and Measurements for the Environment and Climate (SSPT-PROTER-OEM), ENEA, Rome, Italy

<sup>4</sup>Institut Méditerranéen d’Océanologie, MIO – Marseille, Marseille, France

**Correspondence:** Yuri Galletti (yuri.galletti@pi.ibf.cnr.it)

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**Abstract.** Atmospheric fluxes of dissolved organic matter (DOM) were studied for the first time on the island of Lampedusa, a remote site in the central Mediterranean Sea (Med Sea), between 19 March 2015 and 1 April 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  $120.7 \text{ mmol DOC m}^{-2} \text{ yr}^{-1}$ . Over the entire time series, the average dissolved organic phosphorus (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 on 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 on the Med Sea than on the global ocean. Further, DOC fluxes from the atmosphere to the Med Sea can be up to 6 times larger than total river input. Longer time series combined with modeling 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 introduced to the atmosphere (Guerzoni and Chester, 1996). Industrial pollution can also originate from northern 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 are still very few data on the atmospheric deposition of dissolved organic carbon (DOC) to the surface ocean at both 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<sup>-1</sup> 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 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 more 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 the northwestern 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 on the island of Crete (Economou and Mihalopoulos, 2002). This study did not take into consideration dry deposition. None of the papers cited have studied atmospheric inputs at remote sites far away from possible pollution sources and/or large cities.

The main goals of this study are (1) to quantify total atmospheric deposition of DOC, dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP) on 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) and to estimate the impact of atmospheric deposition on the 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 Develop-

ment, on the island of Lampedusa, Italy (Fig. 1; <http://www.lampedusa.enea.it/>, last access: 14 November 2019).

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 and 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<sub>10</sub> (particulate matter with an aerodynamic equivalent diameter of less than 10 µm) amount and chemical composition analyses routinely performed on 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 every 15 d or immediately after strong rain or dust storm events between 19 March 2015 and 1 April 2017. Due to logistic constraints, nine sampling periods were longer than 20 d. 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, transferred to 250 mL polycarbonate bottles, and immediately frozen. Dry deposition was sampled by rinsing the collector with 250 mL of ultrapure Milli-Q water, which 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 prewashed 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 was 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<sub>2</sub>-



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

free ultrahigh-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  $\mu\text{M}$ ). The system blank was measured every day at the beginning and the end of analysis using low-carbon Milli-Q water ( $< 3 \mu\text{M C}$ ). Instrument accuracy was assessed every day by analyzing DOC consensus reference material (CRM), kindly provided by Dennis A. Hansell, with a nominal value of 41–44  $\mu\text{M}$  (batch 15, lot no. 07-15; Hansell, 2005). The average DOC concentration in the CRM measured in our laboratory during the period of the analysis was  $42.8 \pm 1.2$  ( $n = 15$ ).

## 2.4 DOP and DON analysis

Twenty-six out of 41 samples were analyzed for DON and DOP. The samples were collected between 19 March 2015 and 3 November 2016.

DON was estimated by subtracting the dissolved inorganic nitrogen (DIN) from the total dissolved N (TDN). DIN and TDN were analyzed by the conventional automated colorimetric procedure (CACP) according to Aminot and K  rouel (2007) with an estimated limit of detection of 0.02  $\mu\text{M}$ . 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  $\mu\text{M}$  and an analytical precision of 7 % at 0.1  $\mu\text{M}$ . Total dissolved P (TDP) was measured as SRP after UV digestion

(Armstrong et al., 1966). The photooxidation technique included a 2 h UV treatment in a Metrohm<sup>®</sup> 705 UV digester with a digestion efficiency of  $85 \pm 3$  %, assessed on a 1  $\mu\text{M}$  solution of  $\beta$ -glycerol-phosphate.

## 2.5 DOC, DON, and DOP fluxes

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

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

where  $X$  is the concentration measured in the sample ( $\mu\text{M}$ ),  $V$  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  $\text{m}^2$ ), and  $d$  is the length of the sampling period expressed in days.

## 2.6 Ion and metal content in the deposition samples

Soluble ions and metals were measured in samples filtered through quartz filters. These filters have low blank levels for metals and ions (Ca, Na, Al, and Pb) in both the soluble and particulate fraction. Immediately after filtration the samples were divided into two portions used for measurements of ionic and metal content, respectively. Samples for the determination of metal were spiked with 0.1 mL of subboiled distilled  $\text{HNO}_3$  to preserve the metals in their soluble form. Samples were kept refrigerated at  $+4^\circ\text{C}$  until the analysis. Ions were determined in solution by ion chromatography as reported in Becagli et al. (2011).

**Table 1.** Sampling period, type of deposition, and volume for the 41 samples collected on the island of Lampedusa.

Sample name	Sampling period			Deposition type	Volume collected (L)
	Start date (dd/mm/yyyy)	End date (dd/mm/yyyy)	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

The particulate fraction of the deposition was extracted from the quartz filter through the solubilization procedure reported in the EU EN14902 (2005) for aerosol samples. The extraction procedure was performed in a microwave oven at 220 °C by subboiling distilled HNO<sub>3</sub> and 30 % ultrapure H<sub>2</sub>O<sub>2</sub> for 25 min.

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<sub>10</sub> analysis

PM<sub>10</sub> is sampled on a daily basis on the island of Lampedusa (Becagli et al., 2013; Marconi et al., 2014; Calzolari et al., 2015) by using a low-volume dual-channel sequential sam-

pler (HYDRA FAI Instruments) equipped with two PM<sub>10</sub> sampling heads operating at a constant flow of 2.3 m<sup>3</sup> h<sup>-1</sup> in accord with the European rules for aerosol monitoring (UNI EN12341). Aerosol is collected in 47 mm diameter Teflon filters (Pall Gelman) with 2 µm nominal porosity but certified to have 99 % retention efficiency for 0.3 µm diameter particles. The PM<sub>10</sub> mass was determined by weighting the Teflon filters before and after sampling with an analytical balance in controlled temperature (20 ± 1 °C) and relative humidity (50 ± 5 %) conditions. The estimated PM<sub>10</sub> mass error is around 1 % at 30 µg m<sup>-3</sup> in the routine sampling conditions. A quarter of each Teflon filter was extracted using Milli-Q water (about 10 mL, accurately evaluated by weighing) in an 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 dissolved organic matter (DOM) sources, DOM concentrations were compared to concentrations of Al and Na and to the enrichment factor for Pb, EF(Pb), in the deposition samples as markers of crustal, sea spray, and anthropic sources, respectively.

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

$$EFX = \frac{\left(\frac{X}{Al}\right)_{\text{sample}}}{\left(\frac{X}{Al}\right)_{\text{crust}}}, \quad (2)$$

where  $(X/Al)_{\text{sample}}$  is the ratio between the metal  $X$  and Al concentrations in the sample, and  $(X/Al)_{\text{crust}}$  is the same ratio in the upper continental crust as reported in Henderson and Henderson (2009). By convention, elements with  $EF < 10$  are called “not enriched”, having a prevailing crustal source, whereas  $10 < EF < 100$  indicates a moderate enrichment, and  $EF > 100$  indicates 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<sup>-2</sup> d<sup>-1</sup>, with high variability. The overall sampling lasted for 746 d. The deposition was lower than 0.2 mmol DOC m<sup>-2</sup> d<sup>-1</sup> (Fig. 2 and Table 2) in half of the sampling days (52 %).

In 2015, the lowest deposition rates (< 0.1 mmol C m<sup>-2</sup> d<sup>-1</sup>) were measured in July (Lmp09), October (Lmp13), and November (Lmp15). The highest

deposition values (> 1.2 mmol C m<sup>-2</sup> d<sup>-1</sup>) 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<sup>-2</sup> d<sup>-1</sup>) 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 d of rain; data from <http://www.arpa.sicilia.it/> and <http://www.eurometeo.com/italian/climate>, last access: 10 June 2016).

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<sup>-2</sup> d<sup>-1</sup> from January to May (Lmp18 to Lmp23) and from June to August (Lmp27 to Lmp30). The highest DOC fluxes (> 0.8 mmol C m<sup>-2</sup> d<sup>-1</sup>) 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<sup>-2</sup> d<sup>-1</sup> from January to April (Lmp36 to Lmp41); these values are higher than those observed in the first 3 months of the previous year (Fig. 2 and Table 2).

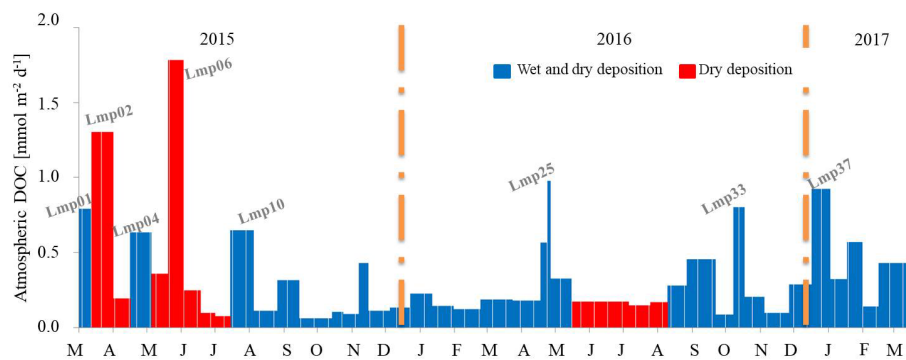
Atmospheric fluxes of DOC in wet deposition were correlated with monthly precipitation rates ( $r^2 = 0.47$ ,  $p < 0.05$ ,  $n = 12$ ). The precipitation rate ranged between 2.9 and 88.5 mm during the study period (2015–2017).

A mean daily deposition of 0.33 mmol C m<sup>-2</sup> d<sup>-1</sup> was calculated, taking into consideration the 2 years (from March 2015 to April 2017), corresponding to an annual DOC flux of 120.7 mmol C m<sup>-2</sup> yr<sup>-1</sup>.

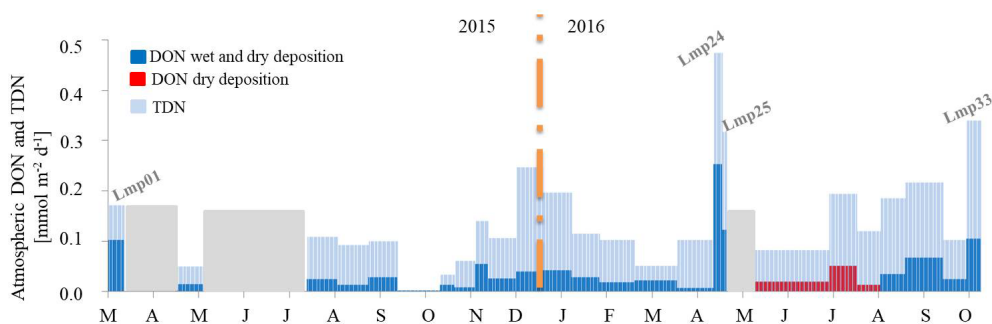
### 3.2 DON, TDN, DOP, and TDP atmospheric fluxes

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

Dissolved phosphorus fluxes ranged between 0 and  $2.7 \times 10^{-3}$  mmol DOP m<sup>-2</sup> d<sup>-1</sup> and between  $1 \times 10^{-4}$  and  $5 \times 10^{-3}$  mmol TDP m<sup>-2</sup> d<sup>-1</sup>, 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 four peaks in atmospheric DOP and TDP (Lmp04, Lmp10, Lmp31, and Lmp33) were re-



**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 refers to the length of the sampling period. Wet and dry deposition is indicated in blue; dry deposition is indicated in red.



**Figure 3.** Atmospheric DON and TDN deposition. Gray 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 refers to the length of the sampling period.

sponsible 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  $9 \times 10^{-5} \text{ mmol DOP m}^{-2} \text{ d}^{-1}$ , respectively; Table 2) despite high fluxes of DOC, DON, and TDP.

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

It should be noted that 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 11 008 (Lmp25, May 2016; Fig. 5b). DON : DOP ratios 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) de-

positions 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 markers of anthropogenic sources for the area of Lampedusa (Becagli et al., 2012, 2017). During this study, samples did not show enrichment beyond 10, indicating that their source is mainly of crustal origin.

The DOC deposition was classified on the basis of the corresponding non-sea-salt (nss) Ca concentration in  $\text{PM}_{10}$  (following Marconi et al., 2014; Fig. 6). Saharan dust events are identified as those with  $\text{nss Ca} > 950 \text{ ng m}^{-3}$ . DOC deposition corresponding to an average  $\text{nss Ca}$  concentration larger than the threshold ( $950 \text{ ng m}^{-3}$ ) is highlighted in red. DOC deposition corresponding to a Saharan dust event occurring on at least 1 d 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  $\text{PM}_{10}$  for Lmp01 (March 2015) was  $50.1 \mu\text{g m}^{-3}$ , with an average dust value of  $18.2 \mu\text{g m}^{-3}$  (Table 4). This sample is dominated by crustal input as revealed by the values of  $\text{nss Ca}$  in the aerosol ( $1327.6 \text{ ng m}^{-3}$ )



**Table 2.** Atmospheric fluxes of DOC, DON, TDN, DOP, and TDP on the island of Lampedusa.

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

NA – not available.

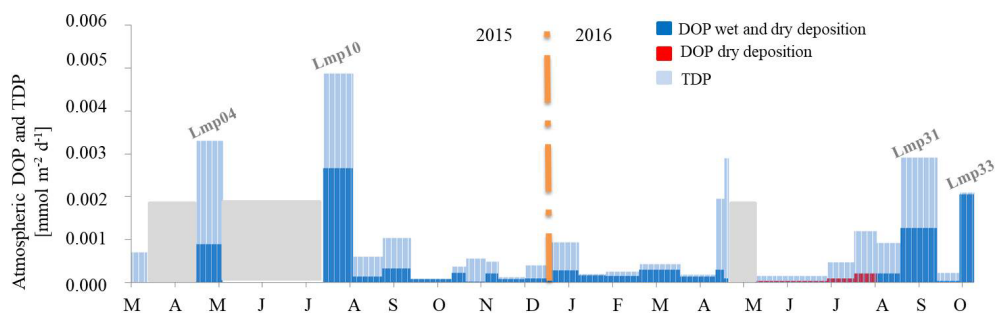
and the Al concentration in the deposition (both soluble and particulate; Fig. 7). In this sample EF(Pb) indicates a low contribution of anthropogenic sources. Na concentration in the deposition was 304 mg m<sup>-2</sup> d<sup>-1</sup> (Fig. 7).

Lmp02 (March–April 2015) is characterized by the second-highest DOC deposition, although no Saharan dust event occurred during this period (Figs. 6 and 7). The PM<sub>10</sub> mean concentration was 29 µg m<sup>-3</sup>, and the average sea-salt

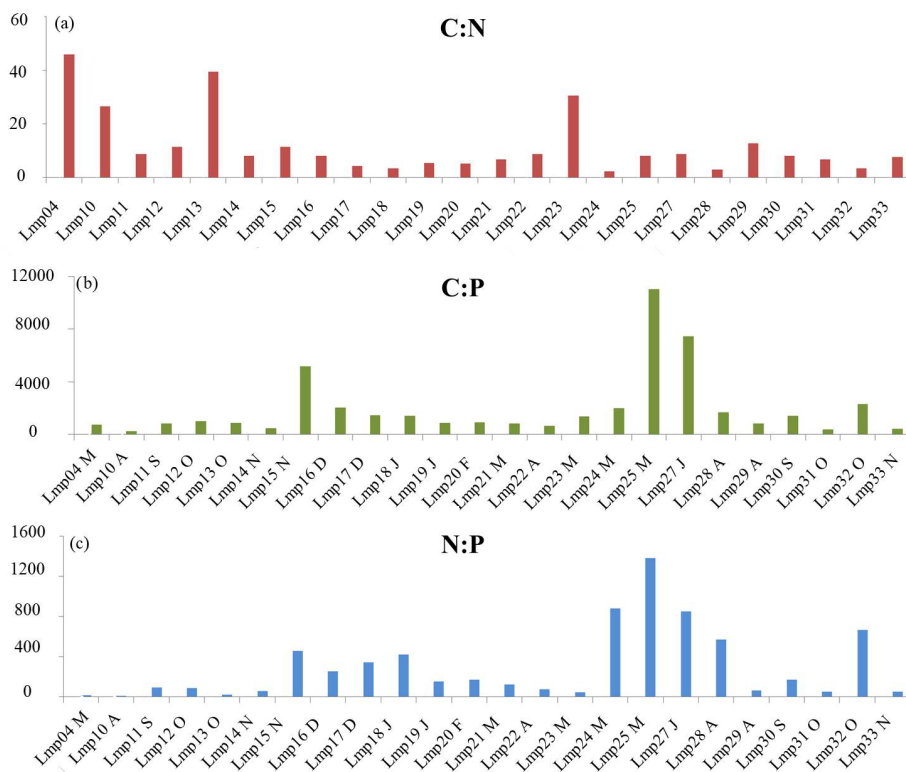
aerosol value was 13.6 µg m<sup>-3</sup> (Table 4) with a 47 % contribution to PM<sub>10</sub>. This sample was strongly affected by sea spray as indicated by the Na/Al ratio, which was 60 times higher than in Lmp01.

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<sub>10</sub> mean concentration was 26.4 µg m<sup>-3</sup>, and the average sea-





**Figure 4.** Atmospheric DOP and TDP deposition. Gray 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 refers to the length of the sampling period.



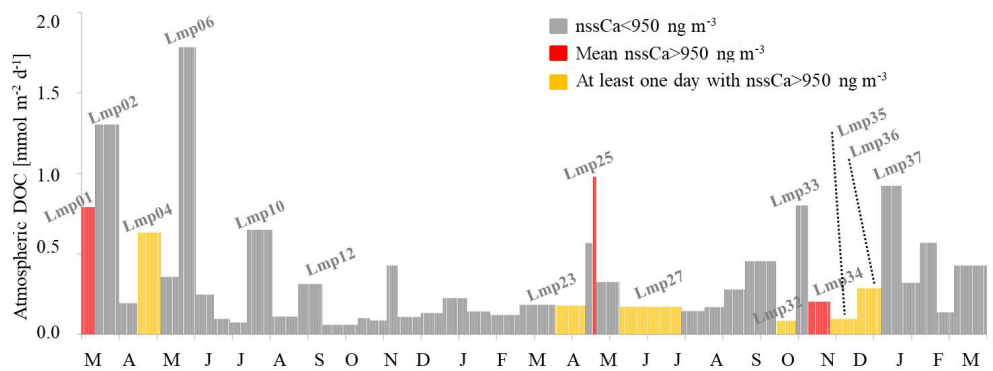
**Figure 5.** Temporal evolution of C : N (a), C : P (b), and N : P (c) ratios in atmospheric deposition samples. The sample name and the initials of each month (from March, Lmp04, to November, Lmp33) are reported on the x axis.

salt in the aerosol was  $8.8 \mu\text{g m}^{-3}$ , contributing 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  $\text{PM}_{10}$  concentration of Lmp06 (June 2015) was  $23.3 \mu\text{g m}^{-3}$ , with an average sea-salt aerosol concentration of  $13.6 \mu\text{g m}^{-3}$  (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 concentration of 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  $\text{PM}_{10}$  concentration of  $133.7 \mu\text{g m}^{-3}$  and an average dust value of  $42.5 \mu\text{g m}^{-3}$  (Table 4). This is the highest value of  $\text{PM}_{10}$  observed in the entire study and indicates the occurrence of a Saharan dust event. The average value of nss Ca was  $4815.1 \text{ ng m}^{-3}$ , 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).



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

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

Sample	Sampling date	C : N	C : P	N : P
Lmp01	28/03/2015	7.78	NA	NA
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	11 008.94	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

Lmp33 (October–November 2016) and Lmp34 (November 2016) are indicative of the two possible sources of DOC: crustal and sea spray. Lmp33 shows a higher DOC concentration than Lmp34. The former is characterized by a very high Na concentration in the deposition, while Lmp34 is characterized by high crustal content (as revealed 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 were 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).

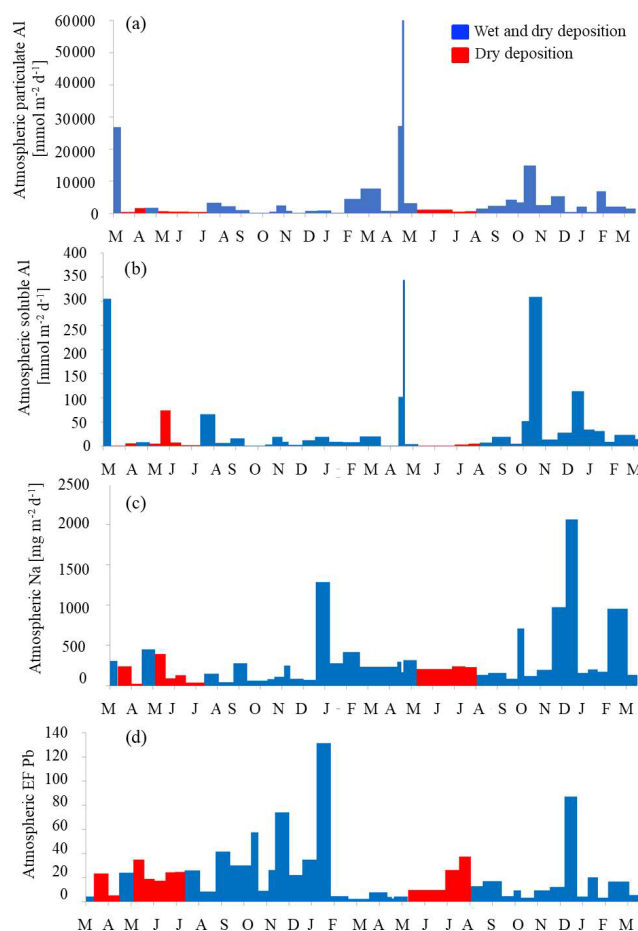
The total DOC annual input from the atmosphere ( $120.7 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ ) found in this study is very close to that measured at Cap Ferrat peninsula (southern France) in 2006 ( $129 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ ; Pulido-Villena et al., 2008) and in three lakes in the western Mediterranean basin (southern Spain,  $153.3 \text{ mmol C m}^{-2} \text{ yr}^{-1}$  in 2005; De Vicente et al., 2012). This value is higher than deposition in the northwestern Med Sea ( $59 \text{ mmol C m}^{-2} \text{ yr}^{-1}$  in the Frioul archipelago, 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 on Lampedusa, to July 2016, the end of sampling in the Frioul archipelago), DOC input is 2 times higher on Lampedusa than in the Frioul archipelago. 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 ( $52 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ ). Depending on the origin and trajec-

**Table 4.** The PM<sub>10</sub>, sea-salt aerosol, dust, and nss Ca mean values of the atmospheric total deposition.

Sample name	Mean PM <sub>10</sub> ( $\mu\text{g m}^{-3}$ )	Mean sea-salt aerosol ( $\mu\text{g m}^{-3}$ )	Mean dust ( $\mu\text{g m}^{-3}$ )	Mean nss Ca ( $\text{ng m}^{-3}$ )
Lmp01	50.1	13.0	18.2	1327.6
Lmp02	29.0	13.6	NA	62.2
Lmp03	28.1	9.8	NA	371.6
Lmp04	26.4	8.8	4	351.7
Lmp05	16.7	4.6	NA	87.3
Lmp06	23.1	6.1	NA	166.1
Lmp07	22.2	7.1	NA	139.3
Lmp08	26.5	5.4	NA	311.6
Lmp09	28.3	8.0	NA	188.2
Lmp10	29.1	5.2	3.4	492.7
Lmp11	NA	NA	NA	NA
Lmp12	NA	NA	NA	NA
Lmp13	NA	NA	NA	NA
Lmp14	NA	NA	NA	NA
Lmp15	NA	NA	NA	NA
Lmp16	NA	NA	NA	NA
Lmp17	NA	NA	NA	NA
Lmp18	NA	NA	NA	NA
Lmp19	NA	NA	NA	NA
Lmp20	NA	NA	NA	NA
Lmp21	NA	NA	NA	NA
Lmp22	NA	NA	NA	NA
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	NA	330.8
Lmp31	24.5	5.6	NA	286.2
Lmp32	32.9	8.7	NA	772.5
Lmp33	31.8	11.8	NA	344.2
Lmp34	35.3	7.8	NA	1092.2
Lmp35	22.3	7.5	0.4	394
Lmp36	35.8	12.3	4.6	661.5
Lmp37	NA	NA	NA	NA
Lmp38	NA	NA	NA	NA
Lmp39	NA	NA	NA	NA
Lmp40	NA	NA	NA	NA
Lmp41	NA	NA	NA	NA

tories of the air masses, the atmosphere can carry significant amounts of DOC.

Assuming that the annual DOC flux from this study ( $120.7 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ ) is valid for the whole Med Sea (area =  $2.5 \times 10^{12} \text{ m}^2$ ), we can estimate a total input of  $3.64 \text{ Tg DOC yr}^{-1}$ . The global estimation for wet atmospheric DOC deposition is  $306\text{--}580 \text{ Tg C yr}^{-1}$ , and the input to the global ocean ranges between 90 and  $246 \text{ Tg C yr}^{-1}$  (Willey et al., 2000; Kanakidou et al., 2012). The global dry deposition of organic carbon (OC) has been estimated to be  $11 \text{ Tg C yr}^{-1}$  (Jurado et al., 2008), leading to a total OC deposition to the oceans of  $101\text{--}247 \text{ Tg C yr}^{-1}$ . The comparison of these estimates indicates that the Med Sea, with an area equivalent to only 0.7 % of the global oceans, receives 1.5 % to 4 % of the global atmospheric input of DOC.

**Figure 7.** Temporal dynamics of atmospheric particulate aluminum (a), soluble aluminum (b), soluble sodium (c), and the enrichment factor for lead (d). The month abbreviation and tick marks correspond to the end of the corresponding month. The width of the bar refers to the length of the sampling period.

It is noteworthy that our values are up to 6 times larger than the estimate of the total river input to the Med Sea ( $0.6\text{--}0.7 \text{ Tg DOC yr}^{-1}$ ; 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 on Lampedusa generally display higher values in spring (March–June) and in autumn (Vincent et al., 2016; Bergametti et al., 1989; Lojé-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 to be the dominant source of DOC in this area, which is 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 on 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 and DOP input and elemental ratios

The annual DON flux ( $11.61 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ ) observed on Lampedusa was lower than that measured in the Frioul archipelago ( $17.80 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ ; Djaoudi et al., 2018). In the eastern Med Sea, Markaki et al. (2010) reported an annual DON flux of  $18.49 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ , higher than that observed on Lampedusa. The comparison of our DOP deposition values ( $0.14 \text{ mmol P m}^{-2} \text{ yr}^{-1}$ ) with the few data reported in the literature shows that the fluxes on Lampedusa are markedly higher than those reported for the western Med Sea ( $0.07 \text{ mmol P m}^{-2} \text{ yr}^{-1}$ , Djaoudi et al., 2018;  $0.03 \text{ mmol P m}^{-2} \text{ yr}^{-1}$ , Migon and Sandroni, 1999) but lower than those obtained by Violaki et al. (2018) for both the western ( $1.16 \text{ mmol P m}^{-2} \text{ yr}^{-1}$ ) and eastern ( $0.90 \text{ mmol P m}^{-2} \text{ yr}^{-1}$ ) Med Sea. The results from our study are very similar to those reported for the eastern Med Sea in 2001 and 2002 ( $0.15 \text{ mmol P m}^{-2} \text{ yr}^{-1}$ ; Markaki et al., 2010). Further, it is interesting to note that our DOP data are very similar to the TDP data reported for a rural coastal site in NE Spain in 2002–2003 ( $0.10\text{--}0.14 \text{ mmol P m}^{-2} \text{ yr}^{-1}$  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 an organic form. These values are similar to those observed in previous studies in the Frioul archipelago (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, in the central Med Sea, and the Frioul archipelago, in the northwestern 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 northwestern Med Sea. In the surface Med Sea, the DOC:DON:DOP ratios range 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 at-

mospheric DOM is enriched in DOC and DON compared to marine DOM. This observation is also valid when comparing our values with those recently measured in marine samples collected at the MOOSE ANTARES offshore station (northwestern Med Sea; 1227:100:1; Djaoudi et al., 2018).

All the analyzed samples except for a 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 of the measured range (Table 2), no information on the role played by wet or dry deposition in DON and DOP input to the Med Sea can be found 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, and 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 with 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 southern Spain (Cabezudo et al., 1997), and various pollen types (*Cannabis*, *Cupressus*, *Pinus*, *Platanus*, and *Sambucus*) were observed in Cordoba (southern Spain) exclusively during African dust events (Cariñanos et al., 2004). This process would not occur in the other seasons (winter and autumn, with no pollen production).

If all the Saharan dust deposition events (red and yellow in Fig. 6) are taken into account, an input of  $49.58 \text{ mmol DOC m}^{-2}$  to Lampedusa can be estimated, representing  $\sim 41$  % of the total DOC flux for the entire sampling period. The strong dust events (red in Fig. 6) lead to a flux of  $15.26 \text{ mmol DOC m}^{-2}$ , 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 also be important (Guerzoni et al., 1997), and its relative contribution strongly depends on meteorological conditions and local emission (Inomata et al., 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, they also stress the relevance of dry deposition (32 % of the total deposition during the entire sampling period), which 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 a high concentration of dust but with a 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 seem to be often associated with sea spray transport, (Lmp02, Lmp10, Lmp12, Lmp33, and Lmp37; 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 on 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 ( $1092.2 \text{ ng m}^{-3}$ ) but with a DOC concentration ( $0.20 \text{ mmol DOC m}^{-2} \text{ d}^{-1}$ ) below the daily average flux of the entire sampling period ( $0.33 \text{ mmol DOC m}^{-2} \text{ d}^{-1}$ ; 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) values. Samples presenting EF(Pb) > 10 show very low DOC concentrations, indicating a small DOC contribution from anthropogenic aerosols on Lampedusa.

#### 4.4 Implications for marine ecosystem

The measurements carried out on the island of Lampedusa clearly show that the atmosphere is an important source of allochthonous DOC for 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 mass circulation.

A conceptual exercise can be made in order to give an estimate of the implications of DOM deposition for the 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  $60 \mu\text{M}$  in the same area in September 1999 and estimated a bacterial carbon demand (BCD) of  $0.32 \mu\text{M C d}^{-1}$  (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  $0.24 \text{ mmol C m}^{-2} \text{ d}^{-1}$  in 2015 and  $0.38 \text{ mmol C m}^{-2} \text{ d}^{-1}$  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 a  $0.011$ – $0.017 \mu\text{M DOC d}^{-1}$  increase in the mixed layer. Assuming that the values of BCD observed in September 1999 ( $0.32 \mu\text{M C d}^{-1}$ ) are also valid 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  $0.008$ – $0.079 \mu\text{M C d}^{-1}$  from June to August 2015 and by  $0.013$ – $0.014 \mu\text{M C d}^{-1}$  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 met, in particular the estimate of DOC input to the whole Med Sea, based on the data collected on Lampedusa we think that these calculations can give an idea of the relevant role that the atmospheric input of DOC can play in sustaining heterotrophic prokaryote 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 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, is mandatory in order to have an accurate estimate of the impact of atmospheric DOC on the functioning of the marine ecosystem. It should also be 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 2-year time series data on fluorescent DOM (FDOM) deposition in the northwestern 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 understanding 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 have 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.

## 5 Conclusions

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

Organic substances transported by Saharan dust on 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 also observed in the 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 ( $\delta^{13}\text{C}$ ) in atmospheric DOC would be crucial in order to gain information about its main sources. Incubation experiments should be carried out with aerosol both rich and 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 pollen during the spring. Lastly, longer time series combined with a modeling 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.

**Data availability.** The dataset generated for this study is available on request from the corresponding author.

**Author contributions.** YG and CS conceived the study and the sampling design. YG, SB, and DMS collected the samples. YG, MG, SB, RT, and SV analyzed the samples. YG, CS, EPV, and 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 paper and have approved the final submitted manuscript.

**Competing interests.** The authors declare that they have no conflict of interest.

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