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~~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 ~~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 come ~~have~~ from a natural ~~origin, especially from~~ sea spray, and that Saharan dust can be an important carrier of organic substances, even ~~if~~though the load of DOC associated with dust is highly variable. Our estimates suggest that atmospheric input has ~~an~~a larger impact to the Med Sea ~~larger~~ than to the global ocean ~~and that~~. Further, DOC fluxes from the atmosphere to the Med Sea can be up to 6-fold larger than total river input. Longer time series, combined with ~~a~~ modelling ~~effort, are therefore mandatory in order to investigate~~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 ~~in~~of the ~~world~~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 ~~anthropic~~anthropogenic origin, are continuously exchanged between the ocean and the atmosphere, affecting biogeochemical cycles and the marine ecosystem. The Med Sea receives anthropogenic aerosols from the northern regions, which are characterized by the presence of important industrial sites, representing relevant sources of organic substances to the atmosphere (Guerzoni and Chester, 1996). Industrial pollution can also be originated from the North Africa as shown in the work by Rodríguez et al. (2011). In addition, the Sahara desert is an intermittent source of mineral dust, that can transport nutrients and organic carbon to the Basin (Goudie and Middleton, 2001; Prospero et al., 2005; Vincent et al., 2016). Atmospheric deposition of nutrients (N and P) strongly influences the marine biogeochemical cycles of the Med Sea, it has therefore received increased attention in the last 30

years (Migon et al., 1989; Herut et al., 2002; Ridame and Guieu, 2002; Markaki et al., 2003, 2010; Pulido-Villena et al., 2008; Izquierdo et al., 2012; Djaoudi et al., 2018). Compared to inorganic nutrients, there is still very few data on the atmospheric deposition of Dissolved Organic Carbon (DOC) to the surface ocean, both at the local and global ~~and local~~ scale. Organic carbon can be removed from the atmosphere ~~via both~~ through wet and dry deposition (Iavorivska et al., 2016). At the global scale, wet deposition transfers about 306-580 Tg DOC yr^{-1} to the surface of the Earth (Willey et al., 2000; Kanakidou et al., 2012). These values correspond to almost half of the DOC delivered to the oceans by rivers annually (IPCC, 2014). Atmospheric deposition of organic carbon can therefore affect regional C cycling~~, 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~~during a Saharan dust storm, suggesting a combination of heterogeneous reactions between organic matter and mineral dust in the troposphere. In the second study, ~~the~~a Saharan rain event coincided with a minimum in DOC input, suggesting ~~the presence of an aerosol poorly enriched in~~ 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 ~~performed~~carried out at the island of 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.

~~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.~~

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~~in the central Med Sea; (2) to investigate the contribution of natural and anthropogenic sources in atmospheric DOC; (3) to estimate the impact of atmospheric deposition on marine ecosystem.

2. Materials and methods

2.1 Sampling site

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

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~~(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~~It is flat and far from large islands or continental areas and from relevant pollutant sources. Precipitation shows a significant interannual variability and is concentrated in autumn and winter, with a maximum in October. Intense precipitation events, which are relatively infrequent, are generally associated with frontal passages and winds from the Northern sectors. Very dry conditions characterize late spring and summer. ~~-~~Although it is a remote marine environment, influences from ship traffic emissions (Becagli et al., 2012, 2017), volcanic aerosols (Sellitto et al., 2017), forest fires (Pace et al., 2005), and regional pollution (Pace et al., 2006)~~,~~ have been documented. ~~, 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} (particulate matter with aerodynamic equivalent diameter lower than 10 µm) amount and chemical composition analyses, routinely performed at Lampedusa, are used in this study.

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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~~of a 10 L ~~Polycarbonate~~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~~For wet deposition, the amount of water in the sampler was weighted ~~then it was collected in~~and transferred to 250 ml polycarbonate bottles and immediately frozen. ~~In case of dry~~Dry deposition~~,~~ was sampled by rinsing the ~~sampler was rinsed~~collector with 250 mL of ultrapure MilliQ water, ~~the sample~~that was ~~then collected in~~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.

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

~~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.~~

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2.3 DOC analysis

DOC analysis were carried ~~by~~out on a Shimadzu TOC-VCSN, equipped with a quartz combustion column filled with 1.2% Pt on alumina pillows of ~2 mm diameter. Samples were first acidified with 2N HCl and bubbled for 3 min with CO_2-free ultra-high purity air in order to remove the inorganic carbon. Replicate injections were performed until the analytical precision was lower than 1%. A five-point linear calibration curve was determined with standard solutions of potassium hydrogen phthalate in the same concentration range as the samples (40-400 µM). The system blank was measured every day at the beginning and the end of analyses using low-carbon Milli-Q water (<3 µM C). ~~The instrument functioning~~Instrument accuracy was assessed every day by ~~comparison of data with~~analyzing DOC Consensus Reference Material (CRM), kindly provided by Prof. D. Hansell~~. DOC~~, with a nominal value ~~was~~of 41-44 µM (batch 15 Lot #07-15~~), DOC~~) (Hansell, 2005). The average DOC concentration in the CRM measured in our laboratory during ~~value~~ the period of the analysis was 42.~~78~~8±1.2~~0~~ (n=15~~) (Hansell, 2005).~~).

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2.4 DOP and DON analysis

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

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

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

~~2.5~~2.5 DOC, DON and DOP fluxes

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

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

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

2.6 Ions and metals content in the deposition samples

~~The concentration of soluble~~Soluble ions metals ~~was~~were measured on ~~the~~ samples filtered on quartz filters. These filters have low ~~blanks level~~blank levels for metals and ions ~~respect to the determined concentration~~(Ca, Na, Al and Pb) both in the soluble and particulate fraction. ~~Just~~Immediately after filtration the ~~sample was~~samples were divided in two portions, used for measurements of ~~one for~~ ionic ~~content~~ and ~~the other for~~ metal content, ~~the latter was~~respectively. Samples for the determination of metal were spiked ~~by~~with 0.1 mL of sub-boiled distilled (s.b.) HNO_3 to preserve the metals in their soluble form.

Samples ~~was~~were keep ~~refrigerate~~refrigerated at +4°C until the analysis. Ions were determined ~~on the~~in solution by ion chromatography as reported in Becagli et al. (2011).

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

Metals ~~were determined~~ 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.~~6~~7 PM_{10} analysis

~~PM_{10} (particulate matter with aerodynamic equivalent diameter lower than 10 μm) is routinely~~PM_{10} is sampled on a daily basis at the island of Lampedusa (Becagli et al., 2013; Marconi et al., 2014; Calzolai et al., 2015) by using a low-volume dual-channel sequential sampler (HYDRA FAI Instruments) equipped with two PM_{10} sampling heads, operating at constant flow of 2.3 m^3/h in accord with the European rules for aerosol monitoring (UNI EN12341~~.~~). Aerosol is collected on 47 mm diameter Teflon filters (PALL Gelman) having 2 μm nominal porosity but certified to have 99% retention efficiency for 0.3 μm diameter particles. The PM10 mass was determined by weighting the Teflon filters ~~(47 mm diameter 2 μm nominal porosity)~~ before and after sampling with an analytical balance in controlled conditions of temperature (20±1 °C) and relative humidity (50±5%). The estimated error on PM_{10} mass is around 1% at 30 μg m^{-3} in the ~~applied~~routine sampling conditions. A quarter of each Teflon filter was extracted using MilliQ water (about 10 ml, accurately evaluated by weighing) in ultrasonic bath for 15 min, and the ionic content was determined by ion chromatography as for deposition samples (Becagli et al. 2011). Another quarter of the Teflon filter was used for the determination of metals in the atmospheric ~~particulate~~particles as ~~already~~ described for the deposition samples.

2.~~7~~8 Enrichment factor

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

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

$$EF\ X = \frac{\left(\frac{X}{Al}\right)_{sample}}{\left(\frac{X}{Al}\right)_{crust}} \qquad (~~1~~2)$$

where $(X/Al)_{sample}$ is the ratio between the metal X and Al concentrations in the sample, and $(X/Al)_{crust}$ is the same ratio in the upper continental crust as reported in Henderson and Henderson (2009). By convention, element with EF<10 are

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called “not enriched” having a prevailing crustal source, whereas 10<EF<100 indicate a moderate enrichment and EF>100 indicate that the element ~~(called “~~(“enriched”) has a prevailing anthropogenic source (e.g. Lai et al., 2017).

3. Results

3.1 DOC atmospheric fluxes

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

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

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

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

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

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

3.2 DON and TDN, DOP and TDP atmospheric fluxes

~~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~~During most of the sampling period (93%), DON deposition was lower than 0.1 mmol m^{-2} d^{-1}. The main peaks were observed in March 2015 (Lmp01), in May (Lmp24 and Lmp25) and October 2016 (Lmp33) ~~in correspondence~~coinciding with high DOC deposition (Fig. 3 and Table 2).

~~DOP and Total dissolved~~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 ~~8·5~~$5 \cdot 10^{-5}$~~3~~ mmol TDP m^{-2} d^{-1}, respectively (Fig. 4 and Table 2). Between August 2015 and September 2016 (Lmp10-Lmp30) both DOP and TDP showed low fluxes. In 2015, atmospheric DOP and TDP showed the highest fluxes in May (Lmp04) and August (Lmp10). In 2016, the main peaks in DOP and TDP deposition were observed in October (Lmp31) and November (Lmp33). The 4 peaks in atmospheric DOP and TDP (Lmp04, Lmp10, Lmp31 and Lmp33) were responsible for 16% of total depositions ~~and were in correspondence~~coinciding 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~~DOP fluxes were very low (0 and $9 \cdot 10^{-5}$ mmol m^{-2} d^{-1}, respectively) (Table 2~~).),~~ despite high fluxes of DOC, DON and TDP.

~~Taking into consideration the entire sampling period (March 2015 – November 2016), the~~The overall mean DON and DOP daily deposition rates were 0.032 mmol N m^{-2} d^{-1} and $3.8 \cdot 10^{-4}$ mmol P m^{-2} d^{-1}, corresponding to ~~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~~during autumn (November 2015 and October 2016) and late spring (May 2016) depositions were very ~~poor~~low in P, compared to the other two elements.

3.4 The sources of atmospheric DOM

Previous works indicate that soluble fractions of V and Ni in aerosol samples are specific marker ~~of anthropic source at~~for anthropogenic sources for the area of Lampedusa (Becagli et al, 2012 and 2017~~), but in the considered~~). During this study, samples ~~they usually do~~did not show enrichment ~~factor higher than~~beyond 10, ~~therefore~~indicating that their source ~~in the deposition~~ is mainly from crustal ~~input.~~origin.

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

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

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Lmp02 (March-April 2015) is characterized by the second highest DOC deposition, ~~even if~~although no Saharan dust event occurred ~~in~~during this period (Fig. 6 and 7). The PM_{10} mean concentration was 29 µg m^{-3}~~, the~~ and average sea-salt aerosol value was 13.6 µg m^{-3} (Table 4~~),~~) with a 47% contribution to PM_{10}~~ of 47%.~~ This sample ~~is~~was 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;~~sampled during ~~this sampling period~~ a Saharan dust event, also ~~occurred~~showed high DOC input (Fig. 6), but the concentration of Al in the deposition was quite low (Fig. 7). The PM_{10} mean concentration was 26.4 μg m^{-3} and the average sea-salt in the aerosol was 8.8 μg m^{-3}, contributing by one third to the total particulate matter. As for Lmp03 the ratio Na/Al is quite high suggesting that sea spray ~~dominates~~ also dominated in this sample.

The mean PM_{10} concentration of Lmp06 (June 2015)**,** was 23.3 μg m^{-3}, with an average sea-salt aerosol concentration of 13.6 μg m^{-3} (Table 4). The average contribution of sea salt aerosol to the particulate matter concentration was 27%. The peculiar characteristic of this sample is the high concentration of soluble Al and low particulate Al in the deposition (Fig. 7). This feature is also observed in ~~the~~ samples Lmp10 and Lmp12, both presenting quite high concentration of DOC in July and September 2015.

Lmp25 (May 2016) was characterized by a mean PM_{10} concentration of 133.7 μg m^{-3} ~~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~~study 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~~further supporting the occurrence of an intense Saharan dust event. The ~~relevant~~ Saharan dust contribution for this sample is ~~well~~also revealed by the Al concentration (both soluble and particulate) ~~in the atmospheric deposition~~ (Fig. 7).

Lmp33 (October-November 2016) and Lmp34 (November 2016) ~~present a very~~are 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~~while Lmp34 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~~The fourth highest DOC deposition of the entire study period (Lmp37~~).~~) occurred in January 2017. Unfortunately no ancillary data was collected during this event.

4. Discussion

4.1 DOC input from the atmosphere

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

~~Our data allowed for the quantification of the~~The total DOC annual input from the atmosphere (120.7 mmol C m^{-2} y^{-1}~~);~~) found in this ~~value~~study, is very close to that measured at Cap Ferrat peninsula (Southern France) in 2006 (129 mmol C m^{-2} y^{-1}; Pulido-Villena et al., 2008) and in three lakes in the western Mediterranean basin (Southern Spain, 153.3 mmol C m^{-2} y^{-1} in 2005; De Vicente et al., 2012). This value is higher than ~~that reported for~~deposition in the north-western Med Sea ~~from February 2015 to July 2016,~~(59 mmol C m^{-2} y^{-1} at Frioul ~~island,~~Island in the Bay of 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 due to the different temporal and seasonal cycles of dry and wet deposition. In particular the marked differences between the~~se~~ 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

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seasonality. ~~If~~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) ~~together~~ accounted together for 43% of the annual DOC flux (52 mmol C m^{-2} y^{-1}). Depending on the origin and trajectories of the air masses, the atmosphere can carry significant amounts of DOC.

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

~~Moreover~~It is noteworthy that~~, 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~~leading role of atmosphere in the transport of ~~allocthonous~~allochthonous DOC to the Med Sea, as suggested recently by Santinelli et al. (2015) and Galletti et al. (2019).

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

~~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 DON flux (11.61 mmol N m^{-2} y^{-1}~~),~~) observed at Lampedusa~~,~~ was lower than that measured at Frioul Island (17.80 mmol N m^{-2} y^{-1}; Djaoudi et al., 2018). ~~Only~~In the ~~study by~~Eastern Med Sea, Markaki et al. (2010) ~~reports data on atmospheric DON fluxes and is focused on the Eastern Med Sea. These authors~~ reported ~~an~~a DON annual flux ~~(~~of 18.49 mmol N m^{-2} y^{-1}~~),~~ higher than that observed at Lampedusa. The comparison ~~among~~of our DOP deposition values (0.14 mmol P m^{-2} y^{-1}) ~~and~~with 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~~but lower than those obtained by Violaki et al. (2017) for both the West (1.16 mmol P m^{-2} y^{-1}) and East (0.90 mmol P m^{-2} y^{-1}) Med Sea. ~~Our values~~Results from our study are ~~instead~~

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very similar to those reported for the Eastern Med Sea in 2001 and 2002 (0.15 mmol P m^{-2} y^{-1}) (Markaki et al., 2010). Further, it is interesting to note that our DOP data are very similar to the TDP data reported for a coastal rural site in the NE Spain in 2002-2003 (0.10-0.14 mmol P m^{-2} y^{-1}, in 17 months of sampling; Izquierdo et al., 2012).

Over the entire time-series, the average DOP and DON contributions to TDP and TDN were 40% and 26%, respectively. These data confirm that a significant fraction of the dissolved P and N in the atmospheric deposition was in the organic form. These values are similar to those observed in previous studies at Frioul Island (DOP 40%, DON 25%; Djaoudi et al., 2018), and in both the western and eastern Med Sea (DOP 38%; DON 32%; Markaki et al., 2010). The similarity among the depositions collected at the two sites (Lampedusa, Central Med Sea and Frioul, North-western Med Sea) suggests that the remote site of Lampedusa may be representative of ~~what~~ DON and DOP deposition in the ~~Mediterranean~~Med Sea ~~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~~compared to marine DOM. This observation is also valid ~~when we compare~~comparing our values with those recently measured on marine samples collected at the MOOSE ANTARES offshore station (north-western Med Sea) (1227:100:1, Djaoudi et al., 2018).

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

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

The input of Saharan dust ~~has important effects on~~can affect 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~~studies are available on the interactions between organic carbon and Saharan dust, even ~~if~~though the organic material found in the troposphere is often associated with dust particles (Usher et al., 2003; Aymoz et al., 2004).

Our results show that Saharan dust events can represent a relevant, albeit intermittent, source of DOC to the central Med Sea. Focusing on the different peaks of DOC deposition, our results indicate that Lmp01, Lmp04 and Lmp25 are associated to a Saharan dust event and that ~~the aerosol, during its route to Lampedusa, was~~aerosols were probably enriched with organic substances. We hypothesize that ~~the~~ dust particles present in the aerosol ~~worked as condensation nuclei for~~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~~) 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~~).

~~-~~In addition Lmp01 (end of March 2015), Lmp04 (May 2015) and Lmp25 (May 2016) show a seasonality that could be linked to the transport of pollen attached to desert particles in the spring events, and this pollen would contribute to atmospheric DOC input in spring (end of March- May). Pollen originating in Morocco was detected in South Spain

(Cabezudo et al., 1997) and various pollen types (Cannabis, Cupressus, Pinus, Platanus and Sambucus) were observed in Cordoba (South Spain) exclusively during dust African events (Cariñanos et al., 2004). This process would not occur in the other seasons (winter and autumn of no pollen production).

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

Wet deposition ~~mainly controls~~is the ~~flux~~main driver of Saharan dust deposition to the Med Sea~~, but~~. However, dry deposition can be also important (Guerzoni et al., 1997) and its relative ~~importance~~contribution strongly depends on meteorological conditions and local emission (Inomata et at., 2009). Some models have estimated that wet deposition represents up to 75-95% of total deposition (Iavorivska et al., 2016). ~~Our data~~ While our results confirm the importance of wet deposition, ~~but similarly dry deposition~~it also ~~plays a crucial role. Our results stress~~stress the relevance of dry deposition (32% of the total deposition during the entire sampling period) that~~, in the remote site of Lampedusa,~~ appears to be the main contributor of DOC and of other chemical species~~,~~ to the remote site of Lampedusa, 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~~ seen in Lmp34, ~~that shows~~with high concentration of dust, ~~is not characterized by high~~ but with low DOC concentration~~ of DOC and~~. Conversely, several samples (for example Lmp02, Lmp33 and Lmp37) characterized by high ~~concentration~~concentrations of DOC, do not show high crustal content. Indeed high DOC deposition events seems to be often associated to sea spray transport, ~~for instance in samples~~ (Lmp02, Lmp10, Lmp 12, Lmp 33 and Lmp 37~~(~~; Fig. 6~~,~~). Similarly, samples Lmp01, Lmp04, Lmp10, Lmp12 and especially Lmp25, also show a large contribution of sea spray aerosol indicating a marine source for the DOC in ~~gray).~~these samples. This is a surprising result, because other studies (e.g., Pace et al., 2006) have shown that clean marine aerosol conditions are rare at Lampedusa.

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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~~one strong Saharan dust event (Fig. 6, in ~~orange~~,yellow). This observation supports the hypothesis that ~~dust from~~ Saharan ~~region~~dust is not typically enriched with DOC, but it ~~behaves as aggregation center of~~adsorbs organic molecules in the atmosphere, and depending on its route ~~it~~, can be enriched or not in DOC ~~during its route.~~. The composition of sample Lmp34 further supports this hypothesis~~. This sample shows~~, with the third highest average nss Ca value (1092.2 ng/m^3), ~~nevertheless~~but with a DOC ~~was very low~~concentration (0.20 mmol m^{-2} d^{-1}~~),~~) below the daily average flux of the entire sampling period (0.33 mmol m^{-2} d^{-1}) (Fig. 6, Tables 2 and 4).

~~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~~note that samples characterized by high values of DOC never present high EF(Pb~~) and the samples~~). Samples presenting EF(Pb)>10 ~~present~~show very low DOC ~~concentration, suggesting that anthropic~~

~~sources have~~concentrations, indicating a small ~~impact on DOC deposition~~DOC contribution from anthropogenic aerosols at Lampedusa.

4.4 Implications for marine ecosystem

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

Commento [CS4]: We believe that this sentence is important. Labile and biologically available is the same concept.

~~In~~ A conceptual exercise can be made in order to give an estimate of the ~~impact~~implications of ~~atmospheric DOC~~DOM deposition for marine ecosystem. According to ~~the surface waters we took into consideration a~~ D'Ortenzio et al. (2005), mixed layer depth (MLD) ~~ranging~~ranges 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 mixed layer 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~~. Dividing the atmospheric deposition by the average MLD (22.5 m~~)~~ ~~(~~, D'Ortenzio et al. 2005), we estimate that the atmospheric input ~~is expected to determine a~~contributes to 0.011-0.017 μM DOC d^{-1} increase in the mixed layer. Assuming that the values of BCD observed in September 1999 (0.32 μM C d^{-1}) are valid also for September 2015 and 2016, and that all the DOC coming from the atmosphere is labile, it could satisfy 3-5% of the daily BCD. ~~Instead in~~During summer the MLD ~~is~~varies between 10 and 15 m depth, with an average value of 12.5 m (D'Ortenzio et al. 2005). The DOC input from the atmosphere is expected to increase the DOC concentration in the mixed layer by 0.008-0.079 μM C d^{-1} from June to August 2015, and by 0.013-0.014 from June to August 2016. ~~, 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~~supplying 3-25% of the daily BCD. ~~These results highlight~~ assuming similar DOC concentrations and bacterial activity as during September. Even if we are aware that these assumptions are hardly meet, in particular the estimate of DOC input to the whole Med Sea, based on the data collected in Lampedusa, we think that these calculations can give an idea of the relevant role ~~of atmosphere~~ that atmospheric input of DOC can have in sustaining ~~the bacterial~~ heterotrophic prokaryotes productivity in the surface layer, particularly when the upper water column is strongly stratified.

The Mediterranean MLD seasonal variability is characterized by a basin scale deepening from November to February-March and an abrupt stratification in April, which is maintained throughout the summer and early autumn. Even if these ~~data~~estimates stress the potential role of atmospheric DOC in sustaining bacterial productivity in the surface ocean, a time series of BCD, MLD and DOC concentrations in the surface layer, together with a network of stations for the quantification of atmospheric input of DOC in the different areas of the Med Sea, are ~~crucial~~mandatory in order to have an accurate ~~estimation~~estimate of the ~~DOC atmospheric input~~ impact of DOC atmospheric on the functioning of marine ecosystem. It should be also noted that a fraction of atmospheric DOC could be recalcitrant, and ~~therefore could be~~

~~transported to~~through transport to depth, ~~playing~~it could play a key role in carbon sequestration ~~to depth~~. The refractory nature of a part of atmospheric ~~DOC~~ DOM ~~is hypothesized~~has been proposed by Sánchez-Pérez et al. (2016), ~~who collected~~based on 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.~~ the DOM pool. Incubation experiments to investigate the biological lability of atmospheric DOC are also crucial to better understand the impact of atmospheric deposition on marine ecosystems.

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

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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~~riverine input.

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

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

~~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. Further studies are also needed to understand the link between aerosol origin and DOM concentration and quality, and to comprehend the potential link between DOC and the pollen during the spring. Lastly, longer time series ~~,~~ combined with a modelling effort, ~~are highly desirable in order~~would provide a solid base to assess the response of DOM dynamics in the Med Sea to ~~the change~~changes in aerosol deposition pattern due to the effect of climate change.

Author contribution

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

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The authors declare that they have no conflict of interest.

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

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

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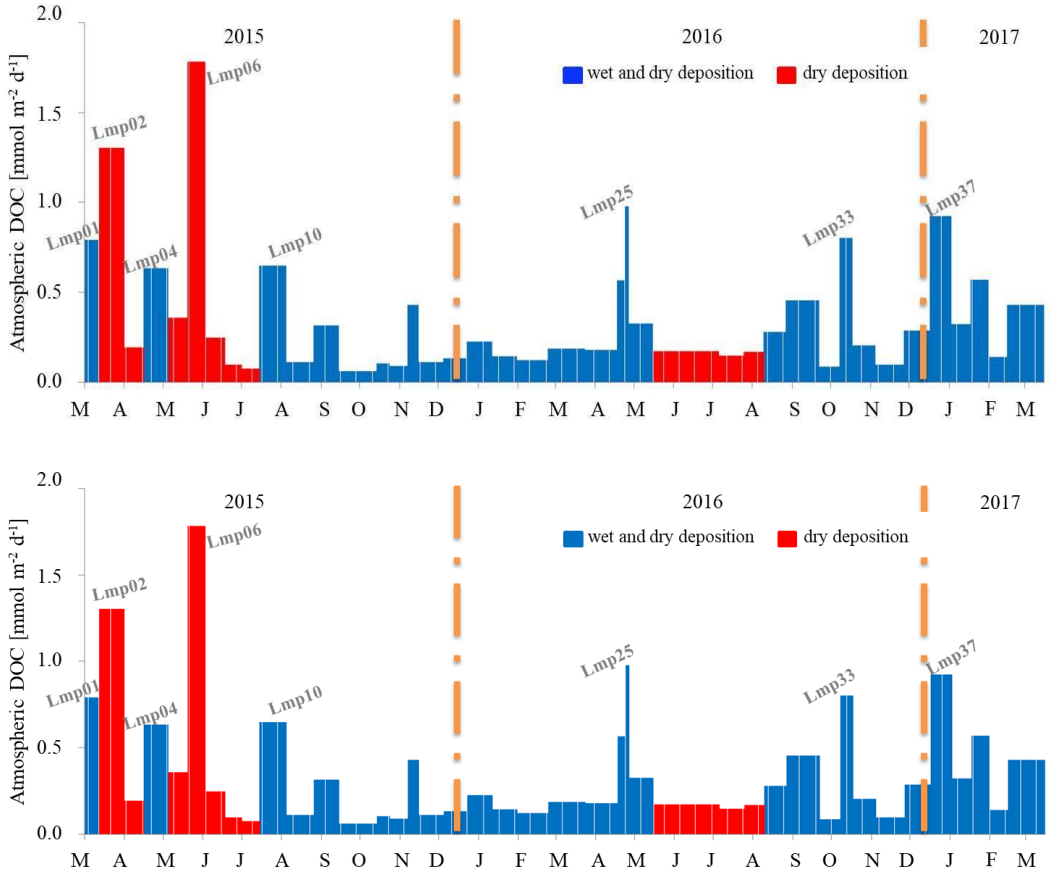

Figure 2: Atmospheric DOC fluxes during the study period. ~~The sign of~~ The month abbreviation and tick marks correspond to the ~~months is reported every 31 days~~end of the corresponding month. The width of the bar refer to the length of the sampling period. Wet and dry deposition is indicated in blue, dry deposition in red.

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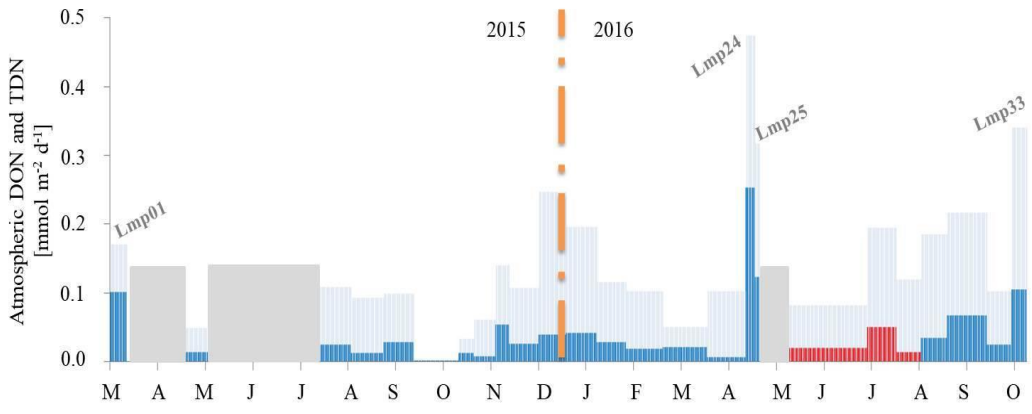

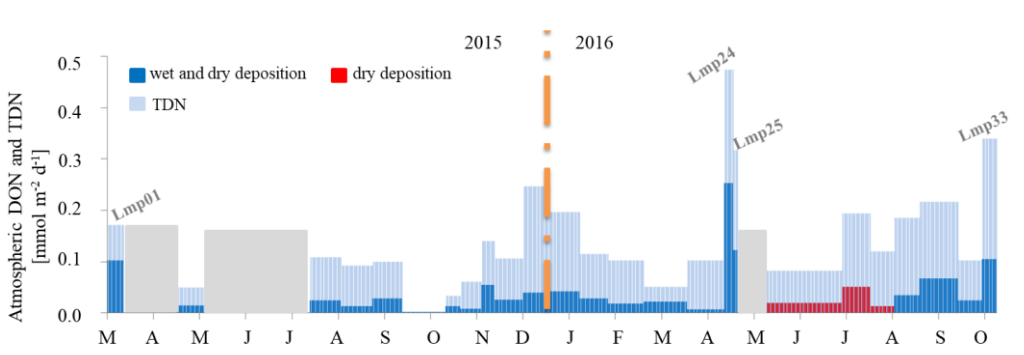

Figure 3. Atmospheric DON and TDN deposition ~~in blue (wet and dry deposition) and red (dry deposition), and TDN in cyan. No data are available in the grey~~Grey areas correspond to the periods with no data. The month abbreviation and tick marks correspond to the end of the corresponding month. The width of the bar refer to the length of the sampling period.

Commento [CS5]: Aggiungi nella legenda DON davanti a wet and dry.. and dry

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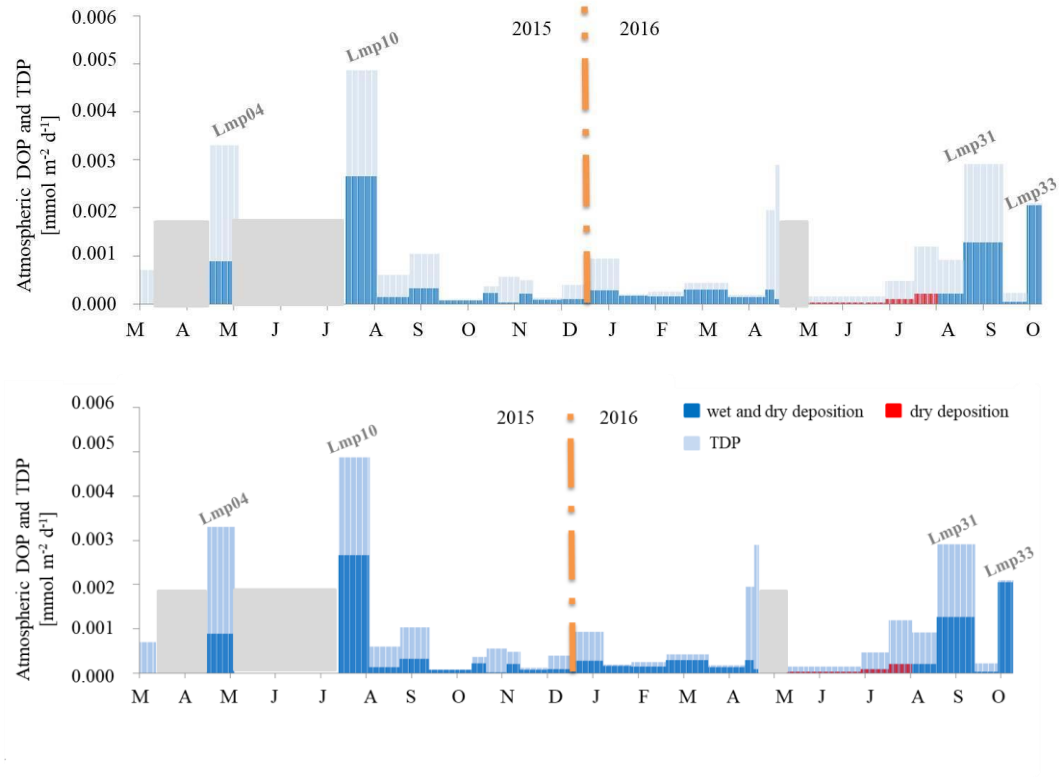

Figure 4. Atmospheric DOP and TDP deposition Grey areas correspond to the periods with no data. The month abbreviation and tick marks correspond to the end of the corresponding month. The width of the bar refer to the length of the sampling period. ~~Atmospheric DOP in blue (wet and dry deposition) and red (dry deposition), and TDP in cyan. No data are available in the grey areas.~~

Commento [CS6]: Aggiungi nella legenda DOP davanti a wet and dry.. and dry

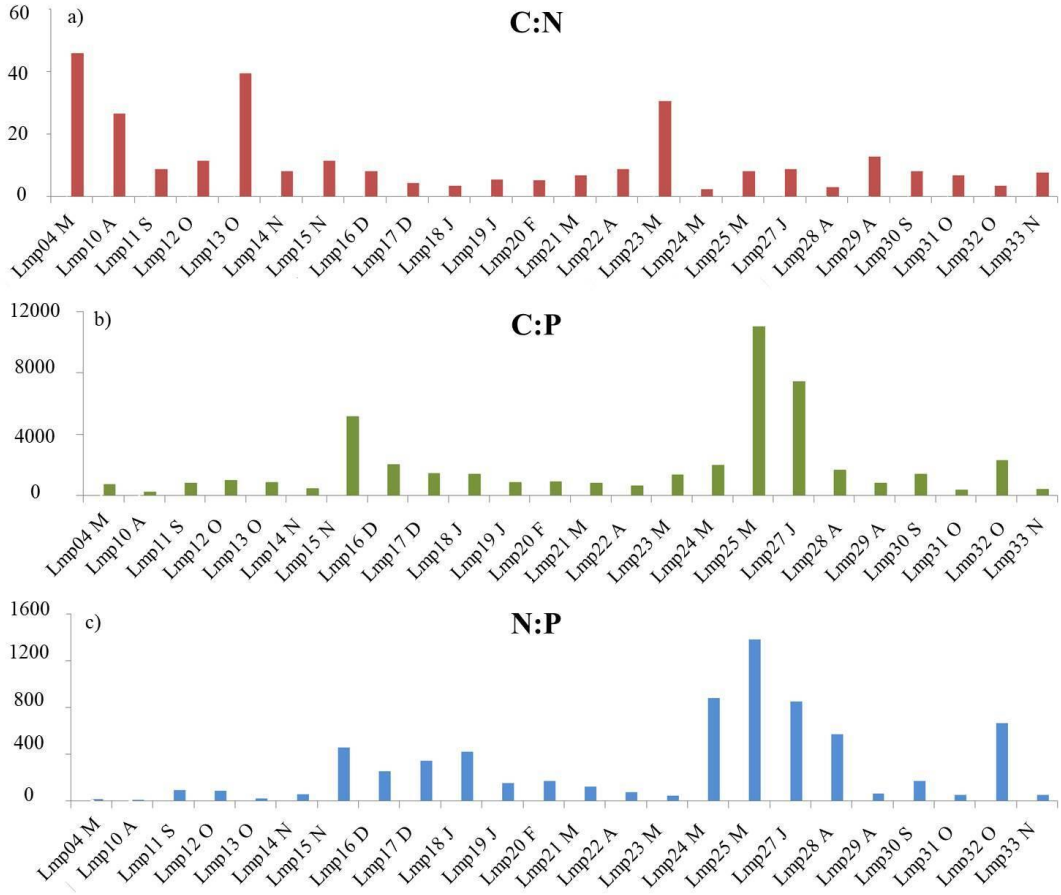

Figure 5. Temporal evolution of C:N (a), C:P (b) and N:P (c) ratios~~.~~ in atmospheric deposition samples. -Sample name and the ~~capital letter~~initials of ~~the~~each ~~corresponding~~ month ~~of the sampling~~ (from March, Lmp04, to November, Lmp33) are reported in the ~~horizontal~~ X-axis.

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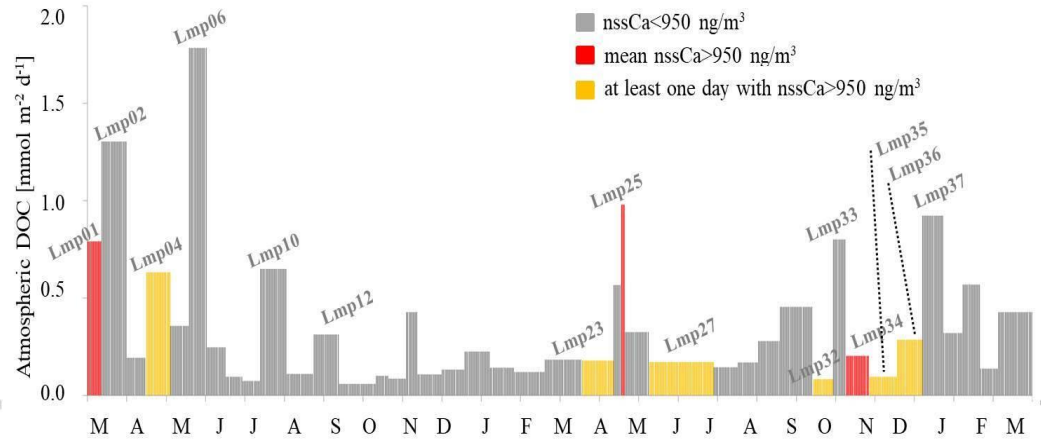

Figure 6. ~~**Intensity of**~~**Temporal dynamics in the dust deposition events during the sampling period color coded based on the contribution of non-sea salt Ca (nssCa~~~~) values.~~~~). . The month abbreviation and tick marks correspond to the end of the corresponding month. The width of the bar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

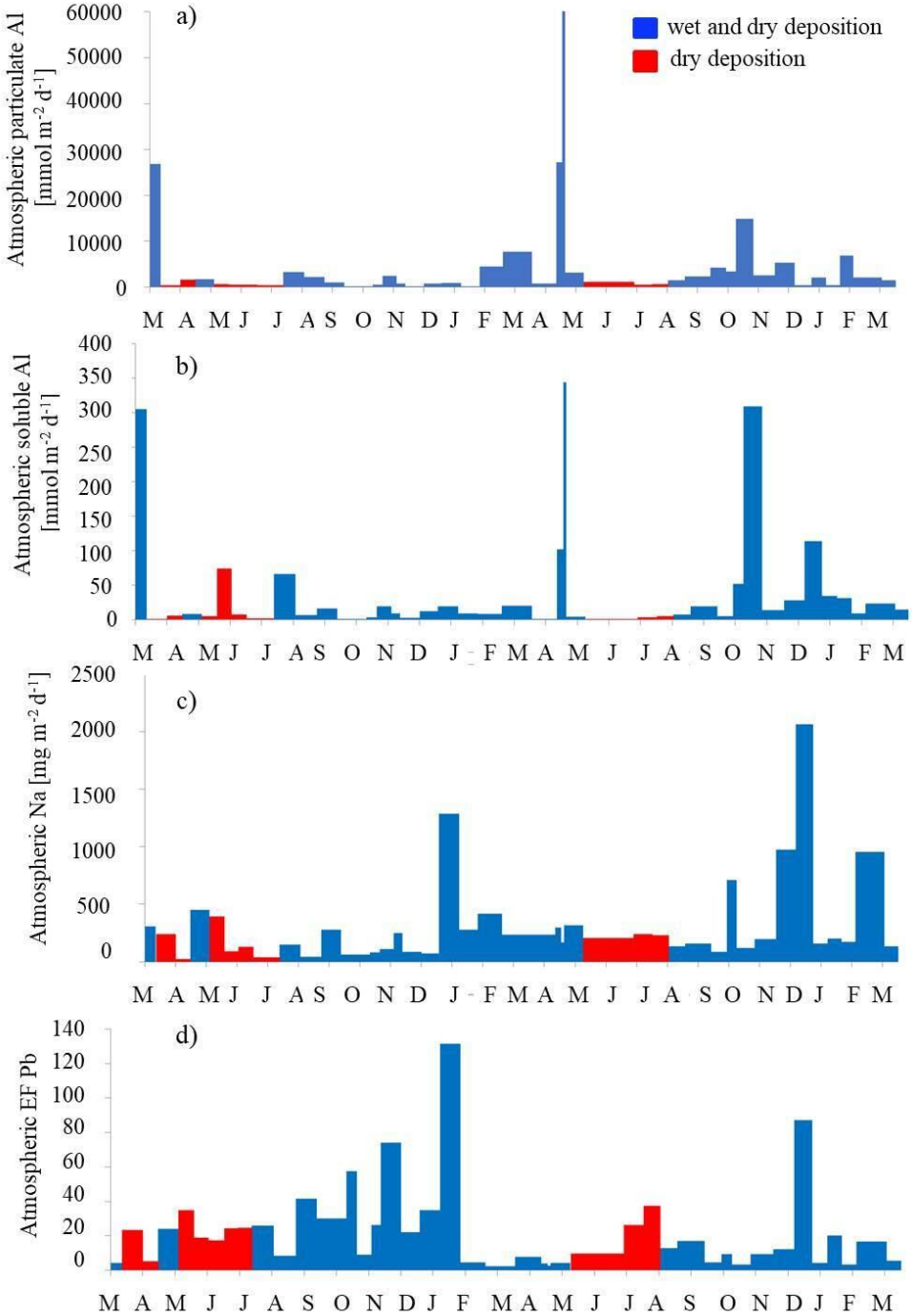

Figure 7. ~~Atmospheric~~Temporal dynamics of atmospheric particulate Aluminium (a), soluble Aluminium (b), soluble Sodium (c) and enrichment factor ~~of~~for Lead (d). . The month abbreviation and tick marks

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correspond to the end of the corresponding month. The width of the bar refer to the length of the sampling period.

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

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

742

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.

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

744

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

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

746

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

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

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

Reply to Editor

(EDITOR)

One of major conclusion of this manuscript is the organic species deposited in Lampedusa coming from natural sources (sea spray and dust), notably in summer. However, your discussion is supported by a too limited literature about OM sources in atmospheric aerosols in this area. One of the reviewers reminded you that you did not consider the potential role played by pollen.

(AUTHORS)

We thank the editor for this comment and we apologize for the missing references. In the revised manuscript, all the suggested paper about OM sources in atmospheric aerosols are cited and we stressed the potential role played by pollen. The following sentences were added in the discussion (paragraph 4.3): . "*The role of secondary organic aerosols as a source of organic matter in the Mediterranean Sea is well documented (Arndt et al., 2017; Michoud et al., 2017; Rinaldi et al., 2017) and could be relevant at Lampedusa."* and *"In addition Lmp01 (end of March 2015), Lmp04 (May 2015) and Lmp25 (May 2016) show a seasonality that could be linked to the transport of pollen attached to desert particles in the spring events, and this pollen would contribute to atmospheric DOC input in spring (end of March- May). Pollen originating in Morocco was detected in South Spain (Cabezudo et al., 1997) and various pollen types (Cannabis, Cupressus, Pinus, Platanus and Sambucus) were observed in Cordoba (South Spain) exclusively during dust African events (Cariñanos et al., 2004). This process would not occur in the other seasons (winter and autumn), when no pollen production occurs."* A sentence about the need of further studies was also added in the conclusions.

It is also surprising that your discussion does not take into account the presence of atmospheric secondary organic aerosols as a source of organic matter at Lampedusa in spring and summer (see Mallet et al., ACP, 2019) but generally in Med Sea (Arndt et al., 2017; Michoud et al., 2017; Rinaldi et al., 2017).

We thank the editor for this comment and we apologize for the inaccuracy. The following sentence was added in the discussion (paragraph 4.1): "*The role of secondary organic aerosols as a source of organic matter in the Mediterranean Sea is well documented (Arndt et al., 2017; Michoud et al., 2017; Rinaldi et al., 2017) and could be relevant at Lampedusa."*

Moreover, it is known that the regional pollution at Lampedusa is higher than presented in your manuscript (e.g. Pace et al. (2006) have shown that clean marine aerosol conditions are rare at

Lampedusa, contrary to your sentence p3L81) and a discussion on air masses trajectories is available in Mallet et al., 2019. So please add this information in your corrected version before publication.

In agreement with this comment, the sentence at P3 L81 was reworked as follows: *"Although the island of Lampedusa is a remote marine environment of the central Med Sea, 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".*

Reply to Referee 1

(REFEREE)

The manuscript addresses the atmospheric deposition of organic matter in the Mediterranean, for which there is little data available. It quantifies such deposition in the small island of Lampedusa in the Central Mediterranean, in terms of carbon, nitrogen and phosphorus. It also tries to untangle possible sources of such organic matter. In this aspect the manuscript is less conclusive as there is no good relationship to aerosol origin or type of deposition. The conclusion is that the OM is mainly coming from sea spray that the different air masses pick up and transport to wind up depositing. It could be in large part but really it is just a hypothesis that needs further exploration.

(AUTHORS)

We really thank the reviewer for his/her appreciation of our work.

We totally agree that regarding the possible sources of organic matter, we just reported some hypotheses. With the available data-set in fact we were just able to make an hypothesis about the main sources of DOM in the different sampling periods. The sampling periods cover a generally wide time interval, and the deposition data are the result of integrating deposition over air masses of different origin and with different aerosol characteristics and loads. This makes very difficult to find a correlation between aerosol origin and DOC input, since the different sources are mixed in our samples.

If we would have reduced the sampling periods, we would have had less variability in the sources, but in most of them we would have not had enough DOM to do all the analysis. Two weeks was therefore the best compromise we were able to find.

We added in the conclusions a sentence highlighting that in order to understand the link between aerosol origin and DOM concentration and quality further studies are necessary.

Also, I was surprised not to consider wind direction properties when analyzing deposited material. Lampedusa is a small island but I would not be surprised that when wind blows from directions other than

due East, and especially when it blows over the island from the West, substantial OM could be picked up from the island itself.

We thank the reviewer for this comment. At first, we took into consideration the air masses trajectories, but then we realized that there are some limitations in the use of wind direction to infer the aerosol sources.

Firstly, as above reported, the sampling periods cover a generally wide time interval, and the deposition data are the result of integrating deposition over air masses of different origin and with different aerosol characteristics and loads. Thus, in some cases information on the wind might suggest what are the dominant (if existing) wind conditions during a specific period; but due to possible differences in aerosol amounts and deposition, these conditions may not be representative of the integrated samples.

Secondly, the use of wind direction and speed identify the air mass origin (which is not what the reviewer is suggesting) may be problematic, since trajectories arriving to Lampedusa may take different paths depending on the synoptic conditions. A more elaborated approach would be required (e.g., trajectory reconstruction using wind, as in Becagli et al., 2012; or modeled backward trajectories based on meteorological analyses, as in Marconi et al., 2014). However, also in this case, the relatively long duration of the sampling interval and the variability of the deposition would prevent a robust attribution of the source regions.

Wind measurements conversely, as correctly suggested by the reviewer, might potentially provide useful information on the impact of local sources. The main local source area of anthropogenic particles is in the sectors between South and South-East of the sampling site; in this sectors there are the Lampedusa town, the power plant, the airport and the port. Previous studies have shown that wind from these directions is relatively infrequent, and the impact of these sectors is estimated to be negligible (see e.g., Artuso et al., 2009, with respect to atmospheric CO_2 measurements; Calzolai et al., 2015, with respect to PM10 measurements). This impact is expected to be even lower over samples integrated over are relatively large number of days.

Due to these reasons, we have preferred to associate the deposition samples' characteristics with those of PM10 samples collected daily and over the same time period. This allows to use aerosol properties measured in the same time intervals and influenced by the same sources to infer some overall conditions. Previous studies (e.g., Becagli et al., 2012, 2013, 2017; Marconi et al., 2014; Calzolai et al, 2016) have been dedicated at linking the PM10 measured composition with different aerosol sources.

A third aspect of the manuscript deals with estimating the local and Mediterranean basin-wide importance of such deposition estimates for the biogeochemical functioning of the Mediterranean. I like this part myself but I have to admit it is the least elaborated since it is based on assumptions that will be hardly met. For instance, calculations based on the extension to the whole Mediterranean of the measured

OM deposition at Lampedusa. Given it is so variable and without a clear reason, I would expect variability to increase when other locations are taken into account. Also, the lability of the deposited organic matter is an unknown, so the final role of the marine biota is also unknown. But anyhow, I like these exercises. Thus, to me the main value of the manuscript is to provide a much needed data series of OM deposition measurements.

We totally agree with the reviewer and we are aware that reporting the calculations based on the extension of our results to the entire Med Sea is a risk, because it is nor simple, nor appropriate, to assume that what is observed at one location is valid for the entire basin. However, we consider this as a first conceptual exercise that uses the new results from our study to give an estimate of the implications of DOM deposition for marine ecosystem, that needs to be supported by additional data.

To the best of the author's knowledge only one paper reports that a not-well quantified fraction of atmospheric DOM can be recalcitrant. Due to the lack of information, we decided to discuss implications taking into consideration both the possibilities: DOM is labile and DOM is recalcitrant. In the revised manuscript we will better stress the need for further investigations about the biological lability of DOM coming from the atmosphere

In order to better stress that these calculations are a conceptual exercise, we added the following sentences in the revised manuscript:

"A conceptual exercise can be made in order to give an estimate of the implications of DOM deposition for marine ecosystem."

"Even if we are aware that these assumptions are hardly meet, in particular the estimate of DOC input to the whole Med Sea, based on the data collected in Lampedusa, we think that these calculations can give an idea of the relevant role that atmospheric input of DOC can have in sustaining bacterial productivity in the surface layer, particularly when the upper water column is strongly stratified."

The methods are standard within the field and thus assure quality control. Maybe I am not clear whether monthly data were calculated and how or whether just sample data was provided always? or in what cases? That is, how where data treated when more than 1 sample per month was available? How was the data split when covering periods from two consecutive months?, etc.

We apologize for the inaccuracy. We did not calculate monthly data, we reported the sample data**.** In the figures 2, 3, 4, 6 and 7, the width of the bars refers to the duration of the sampling period (Table 1). This aspect will be clarified in the revised manuscript.

As a general rule, samples were collected every ~15 days, or immediately after strong rain or dust storm events. However, due to logistic problems the sampling period was longer than 20 days for 9 depositions (Table 1).

The DOC, DON and DOP fluxes, reported in the text and in the figures 2, 3, 4, 6 and 7 were calculated using the following formula:

$$X_{Flux} = X \cdot V / A \cdot d$$

where X is the concentration of DOC, DON or DOP measured in the sample and expressed in μM; V is the volume of rain collected by the sampler (expressed in L) or the volume of Milli-Q water used to wash the funnel walls in case of dry deposition (250 ml); A is the area of the funnel (0.1018 m^2), and d refers to the number of days of the sampling period. The DOC, DON and DOP fluxes are reported in the figures considering the flux corresponding to each sampling period. A paragraph with this explanation was added in the materials and methods section of the revised manuscript in order to clarify these calculations.

I understand that sample data is clearly reported in Fig. 5, but how were the rest treated is a bit mysterious, especially since bars have unequal width within and between figures.

The bars in the figure 5 corresponded to the C:N:P molar ratios (see Table 3), so they referred to a number, not a flux, and this is the reason why the width of the bars is always the same in figure 5, in contrast to fig. 2, 3, 4, 6 and 7, where the width of the bars is different since it refers to the length of sampling periods. We added the description of the bars in the caption.

In line 150 it is also important to know the flow rate of the low-volume sampler. Also, I guess that because of physical flow rate constraints a 1 μm filter could not be used. That would have been much more desirable since there tend to be organic rich particles at the very fine particle ranges, and they would have been missed, not a minor issue in this paper on OM. I would like the authors to comment on the choice of a 2 μm filter to collect particles.

The filters used in this study are those usually used for aerosol sampling, they have a nominal porosity of 2 μm, but they are certified for 99% efficiency for particles having 0.3 μm diameter.

The sampling flow is maintained constant at 2.3 m^3/h in order to maintain constant the sampling heads cut-off (10μm) as reported in the European rule UNI EN12341.

In order to clarify these concepts for a broad number of readers the text was changed as follows:

"PM10 (particulate matter with aerodynamic equivalent diameter lower than 10 μm) is routinely sampled on a daily basis at the island of Lampedusa (Becagli et al., 2013; Marconi et al., 2014; Calzolai et al., 2015) by using a low-volume dual-channel sequential sampler (HYDRA FAI Instruments) equipped with two PM10 sampling heads, operating at constant flow of 2.3 m3/h in accord with the European rules for aerosol monitoring (UNI EN12341). Aerosol is collected on 47 mm diameter Teflon filters (PALL Gelman) having 2 μm nominal porosity but certified to have 99% retention efficiency for 0.3 μm diameter particles. The PM10 mass was determined by weighting the Teflon

filters before and after sampling with an analytical balance in controlled conditions of temperature (20±1 °C) and relative humidity (50±5%).”

The manuscript is well structured and balanced. The title is informative of the contents. The language is proficient. Figures should be uniformed or clarified in aspects such as the x-axis but are otherwise well done. Other than that, I have no major concerns publishing the manuscript pretty much as it is.

We really thank the reviewer for his/her appreciation of our manuscript. We reworked the figures in order to uniform them and to eliminate any misunderstanding.

Reply to Referee 2

(REFEREE)

This paper presents a sound dataset concerning the dry and wet deposition fluxes of dissolved organic matter sampled for 2 years and a half at the island of Lampedusa (Italy). This site, in the central Mediterranean, is appropriately taken to represent the interaction atmosphere-sea surface in a remote marine environment. It is a well written paper which addresses a topic of interest: the role of DOM (and its components DON and DOP) deposition in the western Mediterranean. It explores the role of the frequent Saharan intrusions, a very interesting point since few studies have dealt with the interactions between organic carbon and Saharan dust. Finally, it specifically addresses the role of this atmospheric deposition for marine productivity.

The quantification of N and P atmospheric deposition to the Mediterranean has been previously addressed in many papers, the most relevant of them are adequately cited by the authors. However, I’d like to bring to the authors attention the work of Izquierdo et al. 2012 in Atmospheric Environment. Atmospheric phosphorus deposition in a near-coastal rural site in the NE Iberian Peninsula and its role in marine productivity, since it will provide more data for comparison, discussion and understanding of the role of African sources in marine biogeochemistry, and the relative contribution of dry and wet deposition.

The layout of the paper and data treatment are OK, and I have only a few suggestions, which I list below.

(AUTHORS)

We really thank the reviewer for his/her appreciation of our manuscript. In the revised version, all the comments and suggestions were taken into consideration. In the revised manuscript, the work of Izquierdo et al. (2012) was cited as suggested by the reviewer.

Introduction

Lines 34-35. Industrial pollution can also be originated from North Africa as has been shown in the work of Rodríguez et al (2011). Transport of desert dust mixed with North African industrial pollutants in the subtropical Saharan Air Layer. Atmospheric Chemistry and Physics 11, 6663–6685. I think it is worth considering.

In the introduction of the revised manuscript, we added this reference and a sentence about the possible contribution of pollution from North Africa: "Industrial pollution can also be originated from the North Africa as shown in the work by Rodríguez et al. (2011)."

Line 40. The work of Izquierdo et al 2012 could be included in this list of references, since it deals with how P dep influences the marine biogeochemical cycle in the western Med Sea.

In the introduction of the revised manuscript, we added this reference.

Line 45. This sentence should be revised as it is not true that atmospheric deposition affects radiative forcing and human health. Aerosols in the atmosphere do, but not deposition.

We agree with the reviewer that the sentence was not clear. In the revised manuscript, we changed it as follows: "*Atmospheric deposition of organic carbon can therefore affect regional C cycling (Yan and Kim, 2012; Decina et al., 2018).*"

Material and methods

I recommend to make some reorganization of the text, since some paragraphs in this section in fact correspond better to the Introduction. E.g. the paragraph dealing with the explanation of the Mediterranean seawater DOM stoichiometry compared to the world oceans (lines 70-75) should be moved to the Introduction.

We apologize for this inaccuracy, in the revised manuscript, this sentences was deleted.

Same thing with the paragraph justifying the appropriateness of Lampedusa as representing an unpolluted site in the central Med.

In agreement with this comment, in the revised manuscript the paragraph 2.1 was changed, reducing the excessive descriptive part.

Line 78. Revise the notation of units of mean dust deposition

OK.

Line 95. polycarbonate, not in capital letter Paragraph

OK.

104-108. Please list in this text the ions and metals analyzed

We listed the ions and metals in section 2.5 and we deleted this part since it is also reported at lines 135-140, as noted by the reviewer.

Line 105 and 136. blank levels, instead of blanks level

OK.

Lines 135-140. This has been already exposed in lines 104-108.

As above reported, we deleted the lines 104-108 and we added here the list of metals and ions.

Line 144. I see that the particulates retained in the filters (after wet and dry deposition filtration) was analysed. But the procedure of digestion and analysis is not reported. Same thing for particulates from the PM10 samples (line157). This should be described in the M&M.

In agreement with this comment, in the revised manuscript, the description of the procedure were added in the Material and Methods section.

Results

Line 202. Here there is an error, since the upper limit of TDP is 5*10 exp-3 (as deduced from Table 2).

We apologize for the inaccuracy. The mistake was corrected in the revised manuscript.

Line 244. Error in unit: 8.8 ug m-3

We apologize for the inaccuracy. The mistake was corrected in the revised manuscript.

Discussion

In this section I'd like a more in deep discussion of dry versus wet deposition and its relation to meteorology.

In agreement with this comment, in the revised manuscript, we added some information on dry versus wet deposition and its relation to meteorology. In particular, in the results we reported the annual rainfall during 2016 and in the description of the study area we added the following sentence: "*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.*" In the discussion (paragraph 4.2), we added the following sentence : "*All of the analyzed samples, except few cases in summer 2016, are relative to dry+wet conditions. Although the DON and DOP recorded during the dry samplings are generally on the low end side of the measured range (see Table 2), no information on the role played by wet and dry deposition processes may be drawn at this stage, due to the limited number of dry samples.*" Regarding DOC input, in the discussion (paragraph 4.1) we reported that "*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).*"

In the literature, the wet atmospheric deposition is considered the main pathway for the removal of organic carbon from the atmosphere. While our results that dry deposition is also important and we have reported a detailed discussion of this point in the paragraph 4.3: "Some models have estimated that wet deposition represents up to 75-95% of total deposition (Iavorivska et al., 2016). Our data While confirm the importance of wet deposition, it also stress the relevance of dry deposition (32% of the total deposition during the entire sampling period) that appears to be the main contributor of DOC and of other chemical species to the remote site of Lampedusa, as suggested by Morales-Baquero et al. (2013)."

High DOC deposition was recorded in Lmp25 (May 2016) and also in Lmp1 (end of March 2015) and Lmp 4 (May2015) coinciding with Saharan dust but low DOC was found in Saharan events during autumn and winter. In view of this clear seasonal differentiation, one could hypothesize that there is a role of pollen attached to desert particles in these spring events (end March-May) and this pollen would contribute DOC. This process would not occur in the other seasons (winter and autumn of no pollen production). This is a possible explanation that needs further attention. However, there are some reports

in the literature of joint pollen and dust transport: for example, Van Campo and Quet (1982) identified pollen types transported from North Africa to south France together with mineral desert dust, Franzen et al. 1994 documented the arrival of pollen from the Mediterranean to Fennoscandia during a dust event. Pollen originating in Morocco was detected South Spain (Cabezudo et al. 1997) and various pollen types (Cannabis, Cupressus, Pinus, Platanus and Sambucus) were observed in Cordoba (South Spain) exclusively during dust African events (Cariñanos et al. 2004).

We really thank the reviewer for this interesting suggestion. The contribution of pollen to atmospheric DOC in spring is an interesting hypothesis to test. In the revised manuscript, the following sentence was added in the discussion (paragraph 4.3): "*In addition Lmp01 (end of March 2015), Lmp04 (May 2015) and Lmp25 (May 2016) show a seasonality that could be linked to the transport of pollen attached to desert particles in the spring events, and this pollen would contribute to atmospheric DOC input in spring (end of March- May). Pollen originating in Morocco was detected in South Spain (Cabezudo et al., 1997) and various pollen types (Cannabis, Cupressus, Pinus, Platanus and Sambucus) were observed in Cordoba (South Spain) exclusively during dust African events (Cariñanos et al., 2004). This process would not occur in the other seasons (winter and autumn), when no pollen production occurs.*" A sentence about the need of further studies was added in the conclusions.

Figures In fig 2, 3 and 4, include a legend to indicate the color of wet and dry deposition.

In the revised manuscript, a legend was included in figures 2, 3 and 4.