Responses for referees

We thank the editor and reviewers for their valuable review of our manuscript "Fluxes and sources of nutrients and trace metals atmospheric deposition in the northwestern Mediterranean". Below are our detailed responses to their questions and comments. The reviewer's comments are in italic, the author's answers in plain text, quotes from the manuscript are in quotation marks. We provide with this document a revised version of the manuscript and a track version allowing to visualizing changes from the submitted manuscript.

Referee 1:

The conclusions are sound but, occasionally, the interpretations of the results are somewhat influenced by the limitations of the methodology. Thus, dry and wet deposition were not collected separately and, as stated by the authors, the method was not able to collect the gaseous deposition. Despite these limitations, authors very often extract conclusions based on the wet/dry deposition ratio. The wet deposition contribution was estimated from the registration of precipitation events occurring along the sample week. This is a good approximation but is subjected to errors that can affect the conclusions. Similarly, the section on "biogeochemical applications" is based on the interpretation of the variation of the N/P ratio. However, in the "Material and methods section", in the lines 145-146, it is stated that: "measured N fluxes in this study will be consider only representative of aerosols particles". Therefore, this should be taken into account in the discussion on N/P ratios.

The authors are aware to these limitations for data analysis, it's the reason why they mention these limitation or the method of estimation several times in the text, in particular when they discussed the data:

- For wet/dry deposition: P6 L169 "This method underestimates dry deposition, and provides a lower estimates of deposition dry event number vs total deposition event number"; P7 L211 "51% of the samples, i.e. 99 samples, sustained at least one event of precipitation during the week of sampling and are here referenced as wet deposition."; P12 L302 "Keeping in mind that dry deposition events can be underestimated by our method, the wet fluxes predominate the total deposition fluxes..".
- For N fluxes: P6 L156 "measured N fluxes in this study will be considered mainly representative of bulk deposition of aerosol particles and wet deposition of gaseous N."; P10 L264 "The case of N deposition is specific, since the N deposition flux corresponds mainly to total aerosol and wet gaseous deposition inputs in our samples."; P23 L573 "even if the N:P ratio from this study were obtained with comparable deposition collectors than previous literature (e.g. Markaki et al., 2010), it has to be kept in mind the deposition collectors were not optimized for gaseous N fluxes measurements, and the N:P ratio could be underestimated."

Moreover, the comparison between the data of this work and the previous data (chap. Seasonal Variability and Biogeochemical applications) shows that the distribution between dry and wet fluxes and N/P ratio are consistent with previous studies confirming the working assumptions are reliable.

As stated in the abstract and along the text (Page 17 L463-465), a good correlation was obtained between N and S fluxes. Authors concluded that this good correlation is due to a common origin associated to the inorganic secondary aerosol. It is true that frequently nitrate and sulfate are frequently associated in a common factor (I prefer to use the term factor instead of source when derived from receptor models) from PMF studies. This is usually attributed to the major secondary origin of these compounds. In the present study, N refers to both nitrate and ammonia (NH_3). Therefore the association of S with N may be related to the presence of ammonium sulfate (N from NH_3) and not necessarily to the association between nitrate and sulfate. Actually, authors determined the *concentrations of nitrate, NO_2- and ammonium separately. Nevertheless, due to possible artifacts on the preservation of N speciation, because of the time between collection and analyses, they preferred to express as total N (Lines 132-135). In my opinion the interpretation of the concentration values of NH4+ may help to interpret the cause of the correlation of S and N along the study period and to investigate the variation of the sources of N. (see also comment of referee 2)*

Thank you for drawing attention to this point. We agree with the referees. We removed the link with ammonium nitrate (in the abstract and in the text), and completed the discussion with a comparison with the literature on secondary aerosols in Med. As proposed by the referee 1, we paid attention to the N speciation along the study period. It appears that the highest NH_4^+ fluxes are correlated with highest Sexc fluxes, whereas that the highest NO_3 concentrations matched with the highest fluxes of Na. We added a figure in supplement and some precisions in the text about this new discussion to strengthen the conclusions: P21 L502 "In the case of the anthropogenic source factor, the good correlation obtained between N and Sexc supports a common origin which is probably associated to the inorganic secondary aerosol, i.e. ammonium sulfate. Indeed, the ammonium sulfate aerosols are currently observed in Corsica due to regional transport (Arndt et al., 2017) and generally in the Mediterranean remote sites (e.g. Calzolai et al., 2015). As stated previously, the using of N speciation is limited by the preservation conditions of our samples. However, we observed a concomitance between the highest deposited mass of NH4+ and Sexc, and of NO3- and Na (See supplement). It reinforces our conclusion on a partition between N as NH4+ mainly associated to ammonium sulfate for the anthropogenic factor, and N as NO3- present as NaNO3 for the marine factor. It is known that the deposition efficiency of particles in the coarse mode, as sea salts, is higher than the one of fine particles, as inorganic secondary aerosols. Our results suggest that the addition of nitrate on sea salt particles could be a key process in controlling the N atmospheric deposition fluxes to the Mediterranean surface waters. Recent works suggest that a large part of nitrogen associated to anthropogenic secondary aerosol could be soluble organic nitrogen (Violaki et al., 2015). Thus, the observed diversity in sources of deposited N could also mean a difference in N speciation in the fallout (inorganic vs organic)."

Page 2, L53. Delete "so": ". . .suggests so. . ." Page 3, L75. Replace "source" by "sources": ". . .PM concentrations and sources. . ." Done

Page 3. L76. Please, avoid using ". . .": ". . .on aerosols size distribution and precipitation patterns, among other factors." Done

Page 4, L122. A fraction of the particulates would be dissolved by adding HCl.

We agree but the methodology for size distribution measurements is not commented here since this part of work is not discussed in this paper. We added this information in the text p5 L130: "not discussed here".

Page 7,L217. I understand that you mean "Al" instead of "As". Please, replace ". . .is the cases of Si, Fe and As," by ". . .is the case of Si, Fe and Al,":

This sentence is about the sporadic feature of deposition fluxes, so it is really As, since as mentioned in the paper: "The most obvious case is for As which 23% of the total flux is obtained in only one week during June 2010 (0.1 mg m^{-2} $week^{-1}$).". It's also the case of Al but here only the elements with a biogeochemical interest are discussed.

Page 8, Figure 1. How do you identify the dust events? Did you use satellite images or dust model outputs? Please, indicated the sources or methods used.

The identification of dust events is supported by the methodology described in the session “3.4. The case of high deposition events”, so we added this reference in the caption of Figure 1 in order to clarify the information on dust events.

Page 8, L219-222. These high fluxes are coincident with rain and with a dust event. The combination of dust and rain seems to give to high deposition fluxes of dust related elements. Most of the dust events recorded seems to be coincident with rain precipitation. + Page 12. I agree that deposition of crustal elements is clearly controlled by the occurrence of dust events, but the concomitance with rain deposition highly influence the flux.

We agree on the fact that a combination between dust and rain favours high deposition fluxes, it is already mentioned in the text p10 L252: "The maximum of deposition during spring is explained by the concomitance of rainfall and high dust concentrations". However, we do not agree that the high fluxes are systematically coincident with rain and with a dust event: for example for the highest flux of Zn is a week when the rainfall is zero and without dust event. It's also the case for several peaks of deposition for Cu, Mn, Ni.

Page 9, L234 (and L256-L260). The seasonal pattern for N is not clear; it seems that it is due to a high deposition event at the end of 2010. The high N sample collected in November is a key event. This maximum concentration of N seems to be correlated to relatively high concentrations of Cu and K (not clear in Figure 1 and SI). Supporting meteo information could help to interpret its origin.

About the high N sample, the purpose of this study is not to evaluate precisely what is the origin of each event, but a general discussion on the background source apportionment of atmospheric fluxes. In this purpose, we need to exclude the outliers events issued from intense sporadic event. So, the proposed criterion in this study for selecting elemental deposition with a sporadic character of deposition is 25% of total flux occurred in 1 to 3 deposition events (See 3. Results and the explanation in the second paragraph). In this case, although a large flux is recorded in November 2010, this event represents only 9% of total flux in 2010 and 25% of total annual flux is reached by adding the 5 highest samples on the year. Even without this event, the average N flux in November is around 8 g/m2/month, i.e. in the same order of magnitude that the other months in winter. Thus, even without this event the N fluxes are higher in winter in comparison on the other months and hence the N pattern is not modified.

Page 9, L240-241. For most elements, it seems that the wet deposition is the predominant process in the October-April period; but the flux deposition in these periods is very low for most elements compared with spring and summer. As later explained in the text the highest deposition fluxes are recorded when the rain events are coincident with a dust event. However, I think that if you estimate the deposition occurring during dust events simultaneous with rain, these will explain a very high percentage of the total deposition flux for the dust related elements. I tried to do this calculation but I have not the information about dust events in the excel file from the SI. This would reflect the importance of the below cloud scavenging processes. I do not totally agree with sentence in L241. Dry deposition does not dominate total deposition for most elements in the period May-August; for most elements both processes seem to contribute in a similar proportion to bulk deposition in this period. Anyway, it should be clearly stated that the sampling methodology used does not permit to clearly distinguish dry from wet deposition.

A discussion on the contribution of dust events in coincidence with rain is already provided by the calculation on the contribution of highest wet dust events on the annual fluxes in the part "3.4. The case of high deposition events". This calculation shows that the dust wet deposition is not predominant on nutrients and certain metals fluxes, except for dust-related elements Fe, Si and Cr, Mn, Ni and V (p17 from L396). We agree with the interest of our results to show the importance of below cloud scavenging and we added a sentence for that p10 L254: "This emphasizes that the below-cloud scavenging of aerosol is the predominant process explaining atmospheric deposition of dust-related elements in this period.". Regarding the dry deposition, we disagree with the referee's comment. We noted the dry deposition is predominant in May, July and August in agreement with the results (Figure 2) which show that the wet deposition is typically inferior to 49% for all the elements for these months (in average = 36%), except for Si and Fe with a contribution of 60% in May.

Page 10, L250-253. Please, check this sentence. Done and modified: "For the elements mainly associated to dry deposition, i.e. Zn, P and Cr, Bergametti et al. (1989 and 1992) observed that the highest deposition was typically associated with the period of their highest aerosols concentrations in summer"

Page 10, L268. Please, replace "table 1" by "Table 1". Done

Page 10, L274. ". . .is larger.." instead of ". . .are larger. . : a "s" has been added to "Deviations" to make "are larger" agree

Page 12, L317-319. Please, check this sentence, starting by "As mentioned by these authors. . ." and ending ". . . as pointed by . . .": Done and modified: "As mentioned by Moulin et al. (1997) and Pey et al. (2013), this is probably due to the variation in large scale atmospheric circulation affecting dust atmospheric contents (lower values of the NAO indices during the last two decades)."

Page 12, Figure 3. There is a large difference between deposition rates measured in this study and previous data. The study by Vincent et al. 2016 shows similar results to these presented here. Do you have information about the time evolution of deposition fluxes in other areas in the Mediterranean basin? Are your values comparable with those recorded in other areas (in any)? Are there not data for the period 2002-2011 in proximal areas?

The study of Vincent et al. (2016) is not limited to Corsica but is extended to the western basin (as mentioned in the text). In our knowledge, no data or study on dust concentration or deposition is available in the literature for this area. The other existing data are focused on eastern Mediterranean where a positive trend on AOD is observed between 2000 to now (Hsu et al., 2012, Solmon et al., 2015, Klingmüller et al, 2016). However, this increase of AOD is mainly explained by the soil using in Arabian Peninsula (decrease of soil moisture, increase of summer surface pressure..). The Arabian Peninsula, being not a source region for dust transported in Western Mediterranean, these results are not comparable with ours. In order to reinforce our conclusions, the discussion has been completed with conclusions of Evan et al. (2016) on the trend of dust emission in Sahara p 13 L340: "This trend could be also is related to the low dust activity period in Sahara during the 2000's in comparison to 1970-1990 proposed by Evan et al. (2016) from wind variability pattern."

Figure 3 caption. Please, replace (gm-2 an-1) by (g m-2 yr-1) Done

Page 15, L372. A similar Si/Al ratio (2.3, on average) was obtained for PM10 at different sites in Europe by Alastuey et el., 2016 (Atmos. Chem. Phys., 16(10), 6107–6129, doi:10.5194/acp-16-6107-2016, 2016). Reference added in the text

Page 16, L405-409.The heavy oil source may be contained in the anthropogenic source. The fact that the source was not identified does not necessarily imply that its contribution to deposition is not important.

It's possible that heavy oil source is integrated in the anthropogenic factor. However if this source had a large contribution in this factor, the Ni-V signature, typical of ship plumes should be dominant or at least equivalent to the signature of N and Sexc in link with secondary inorganic aerosol. Moreover, typical V/Ni ration in ship emissions are between 2.5 and 4.5 (Becagli et al., 2012), whereas the V/Ni ratio is higher than 8 in the anthropogenic factor confirming other sources of these elements. In order to support this conclusion, this argument has been added in the text p18 L441: "The heavy oil combustion signature could be contained in the anthropogenic factor. However, the typical V/Ni ratio of ship emissions are between 2.5 and 4.5 (Becagli et al., 2012), whereas this ratio is higher than 8 in the anthropogenic factor, suggesting that the ship plumes are dominant in this factor. Even if this source could be important for aerosol concentrations over the Mediterranean Sea (Becagli et al., 2017), it does not seem to be important for deposition in Corsica. "

Page 16, L420. These ratios are slightly different to those reported in page 15 for dust events, but, as stated, in the range of dust ratios.

The ratio reported in page 15 (now p17) correspond to the high dust deposition events, whereas in p16 (now p18) the ratio are for all the other samples. This result shows that there is a light difference of Si/Al ratio during dust event and in the background dust. But this difference is not significant in comparison to the range of Si/Al ratio in Saharan dust, so it's the reason why it's no discussed. However, the reference, Alastuey et al., 2016 (Atmos. Chem. Phys), has been added to show the consistence of Si/Al ratio with the ratio found in PM10 in various sites in Europe.

Page 17. Figure 5 caption. Please, use Figure 5 instead of Fig.5. Done

Page 17. Figure 5 caption. Please, indicate in the caption that the seasonal contributions (right) are normalized and that the dust events were excluded. Done

Page 18, L 471. This is a speculation. The difference could be related to many other factors; i.e. the size distribution of particles; the scavenging process (in-cloud, below cloud),. . .

We agree, it's an assumption and it's why we used "could mean" and not "mean". It's maybe a problem with our English but this sentence means that a difference in N speciation in the fallout could be a consequence of the observed difference in sources of deposited N, and not that it's the reason of the observed difference. This sentence has been modified for clarification: "Thus, the observed diversity in sources of deposited N could also mean a difference in N speciation in the fallout (inorganic vs organic)."

Page 20, L 507. Please, delete ".." after NH3. Done

Page 20, L513-514. Please, could you clarify why the interaction of dust with nitric acid is discarded? Is it because N is not present in the source profile of dust? In my opinion this is not enough to discard this reaction.

We agree with this comment, thank you. Indeed, during dust events, a link between dust and nitric acid could be during the high dust event. So, we modified the text to complete this conclusion: p17 L407: " However, a peak in N and P fluxes is systematically observed during high dust events, showing at the same time that intense dust deposition is also a source of these elements. The reactivity between dust and nitric acid previously observed in Mediterranean (e.g. Puteaud et al., 2004) could explain the link between dust fluxes and N fluxes." and p23 L559: "Our data suggest that the effect of mixing between dust and nitric acid did not commonly affect atmospheric dust deposited in Corsica, except maybe during certain high dust deposition."

Page 20, L516: "N:P ratios are" Done

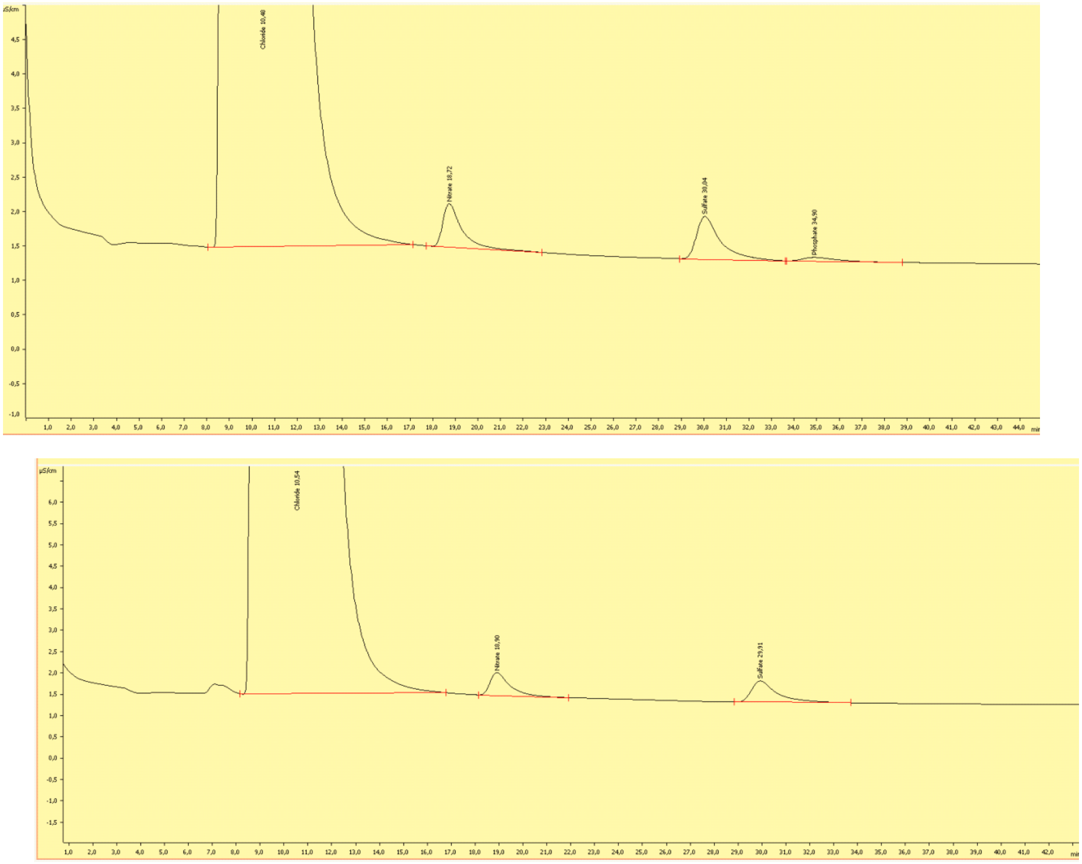
Page 21, L532. Please, check sentence; did you refer to emission inventories? Yes, modified

Please, unify the way to express ratios. Frequently, you use "/" : Si/Al, Mg/Al, Fe/Al, Mg/Na. . ., but you use ":" when talking about N:P. The choice to use ":" for N:P is because it's a molar ratio whereas "/" is used for the mass ratio.

Referee 2:

My main criticism is in the methodological part, I suggest the author to specify the aspects below reported in order to avoid the invalidation the whole data set. In the methodological part lines 133-135 the authors asses that NO_2 and NO_3 are determined by Ion chromatography, but they use HCl in the deposition collector, therefore I suppose that the chromatographic peak of Chloride is very high respect to those of NO_2 and NO_3, are the peaks well resolved? Are the peak of NO2 and NO3 on the tail of the peak of Cl? I suppose that the determination of these two ions is affected by high analytical error. I think the authors have to mention at least the reproducibility of this determination.

The chromatography program was optimised to prevent the effect of HCl on N determination. Various tests have made at different HCl concentrations to check that even for dry deposition (i.e. without dilution by rain) the peak of chloride didn't affect the results on N. An example of chromatograph is provided here to show the resolution between Cl and nitrate peak (Figures 1). Thus, the analytical error is not notably high.



Figures 1: chromatographs for samples of wet deposition (above) and of dry deposition (below)

Another analytical problem could be the high level of blank (22% for nutrient and 19 for metals, lines 135-136), which is the variability of blanks? Are the nutrient and metal concentrations in the sample significantly different from blank? A sentence on this is extremely important to validate the data set.

We realized from the referee's comments that the sentence in the manuscript about blank level was not clear. In order to complete the information about methodological conditions and to clarify the sentence, we changed it: "Field blank concentrations are significantly inferior to sample concentrations for all the studied elements. They represent in average from 1.4% ± 1.3% (Mn) to 12% ± 6% (Fe) of studied elements concentrations, with a maximum contribution of 19% for trace metals (V) and 22% for major nutrients (Fe)."

At lines 462-465 and in the abstract at line 31 the authors assess that the correlation between N (as total N, I suppose) and Sexc is due to the common origin and the presence of ammonium sulphate and ammonium nitrate. This is not true in my opinion for several reasons: -the correlation between N and S could indicate the presence of ammonium sulfate but not ammonium nitrate (in the latter compound there is not S) in marine environment nitrate react mainly with NaCl to give $NaNO_3$ *(as correctly assessed at lines 456-462) instead of with ammonia to give* NH_4NO_3 *(the latter reaction actually occurs in highly anthropized cities) -the correlation could indicate that the original atmospheric main N species could be NH4+ (but this is a pure hypothesis that has to be confirmed with other data). -the presence of ammonium sulfate in Mediterranean region is well documented, but sulphate and ammonia have not the same source; they met and react in the atmosphere. Please change the text in accord to these considerations.*

This comment is common with the referee 1, so please see previous response for referee #1.

Fluxes and sources of nutrients and trace metals atmospheric deposition in the northwestern Mediterranean

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Abstract

Total atmospheric deposition was collected on a weekly basis over 3.5-yr (March 2008-October 2011) at a remote coastal site on the west coast of Corsica Island. Deposition time series of macro and micro-nutrient (N, P, Si, Fe), and trace metals (As, Cr, Cu, Mn, Ni, V, Zn) are investigated in terms of variability and source apportionment (from fluxes of proxies for aerosol sources (Al, Ti, Ca, Na, Mg, S, Sr, K, Pb)). The highest fluxes are recorded for Si, P, then Fe for nutrients, and for Zn and Mn for trace metals. For the majority of elements, data show some weeks with high episodic fluxes, except for N, Cr and V which present the lowest variability. Twelve intense mineral dust deposition events are identified during the sampling period. The contribution of these events to the fluxes of Fe and Si represents 52% and 57% of their total fluxes, respectively, confirming the important role of these sporadic dust events on the inputs of these elements in the Mediterranean. For N and P, the contribution of these intense dust deposition events is lower and reaches 10 and 15%, respectively. Out of these most intense events, positive matrix factorization (PMF) was applied to our total deposition database in order to identify the main sources of nutrients and trace metals deposited. Results show that P deposition is mainly associated to anthropogenic biomass burning inputs. For N deposition, inputs associated to marine sources (maybe associated to the reaction of anthropogenic N on NaCl particles) and anthropogenic sources are quasi-similar. A good correlation is obtained between N and S fluxes, supporting a common origin associated to the inorganic secondary aerosol, i.e. ammonium sulfate. For trace metals, their origin is very variable: with a large contribution of natural dust sources for Ni or Mn and on the contrary of anthropogenic sources for V and Zn.

1. Introduction

The Mediterranean Sea is a semi-enclosed basin situated at the interface between contrasted continental areas of three continents, namely southern Europe, northern Africa and the Middle East, which coastal areas are heavily populated. Thus, the Mediterranean basin continuously receives anthropogenic aerosols from industrial and domestic activities from all around the basin and other parts of Europe (Sciare et al., 2008; Becagli et al., 2012). In addition to deposition from this anthropogenic background, seasonal inputs from biomass burning occur mainly during dry summers (Chester et al., 1996; Guieu et al., 1997), and strong deposition pulses of mineral dust from the Sahara are superimposed (Guerzoni et al. 1999a), with some ‘extreme events’ with dust deposition fluxes as high as 22 g m^{-2} as recorded in 2004 (Bonnet and Guieu, 2006) on very short time scales of a few hours to a few days.

A number of key elements for marine biota are associated to those inputs. Thus, several authors showed that the atmospheric deposition of aerosols constitutes the main source of major nutrients, as N, P or Fe to the surface open waters of the Mediterranean Sea in the summer/autumn period when surface water stratification prevents inputs from deep water by vertical mixing (Guerzoni et al., 1999a; Bonnet and Guieu, 2006; Krom et al., 2010; Pulido-Villena et al., 2010; Richon et al., 2018a, Violaki et al., 2018). Besides the classical nutrients (N, P and Fe), the aerosols also carry trace metals (hereafter called TMs) such as Cr, Cu, Ni, Mn or Zn that are known to have a biological role, often as cofactors or part of cofactors in enzymes and as structural elements in proteins (Morel and Price, 2003). The recent study of Ridame et al. (2011) suggests that the trace metals released by Saharan dust could stimulate nitrogen fixation in summer in the Mediterranean Sea. This assumption is supported by the works of Tovar-Sanchez (2014) which show that the trace metals concentrations in surface microlayer of the Mediterranean Sea is correlated with the atmospheric deposition of mineral dust. However, it has been also suggested that the atmospheric deposition of particulate pollutants is responsible for the contamination of the Mediterranean waters in trace metals (Bethoux et al., 1990; Guerzoni et al., 1999b). Gallisai et al. (2014) also show negative effects of dust deposition on chlorophyll, coinciding with regions under a large influence of aerosols from European origin.

Thus, the partitioning/mixing between anthropogenic vs. natural atmospheric inputs is critical to estimate and predict the role of the atmospheric deposition on marine biosphere and associated services (Richon et al., 2018b). However in the Mediterranean Sea, the existing database on atmospheric fluxes of nutrients and trace metals remain quite limited. Most studies are focused on total deposition of dust and/or macro-nutrients as P and N (e.g. Markaki et al., 2010). This approach do not include the variety of nutrients and do not enable to distinguish the origin of nutrient-bearing particles. Moreover, the studies on trace metals deposition (Cd, Pb…) often show an influence of local sources (Guieu et al., 2010), limiting the reliability of these data. At the difference of atmospheric deposition, the source apportionment of suspended particles over the Mediterranean, from PMF method, has been highly investigated in recent works and showed a large spatial variability in source contributions (Becagli et al., 2012 and 2017; Calzolai et al., 2015; Amato et al., 2016; Diapouli et al., 2017). The signature of continental pollution sources was observed even in remote area, as central Mediterranean islands (Calzolai et al., 2015). Yet, PM concentrations and sources are probably different of sources of deposited particles which depends on aerosols size distribution and precipitation patterns, among other factors. Thus, in a context of anthropogenic changes, it is crucial to distinguish between anthropogenic vs natural atmospheric inputs of nutrients in order to assess how the evolution of chemical atmospheric forcing will modify the marine nutrient cycling.

Here we show a 3.5-yr long continuous series of total deposition fluxes of macro and micro-nutrient (N, P, Si, Fe), trace metals (As, Cr, Cu, Mn, Ni, V, Zn) and source tracers (Al, Ti, Ca, Na, Mg, S, Sr, K, Pb) at a remote coastal site in Corsica. Between March 2008 and October 2011, a monitoring station has been operated with a weekly sampling time step for total bulk deposition. In order to assess the contribution of sources in the fluxes of nutrients, a work on the source apportionment of various nutrients and TMs was carried out from these data (PMF method). A specific attention was also given on the different types of extreme atmospheric events which are relevant regarding the biogeochemistry in the Mediterranean Sea. They include Saharan events and intense summer storms that trigger the washout of the atmosphere over an altitude of several thousands of meters in a short time.

2. Material and methods

2.1. Sampling site and protocol

Total bulk deposition (i.e. dry + wet deposition) was sampled weekly from March 2008 to October 2011 using an open collector for nutrients and TMs analyses, except for N which the analyses started only from November 2009. Sampling was conducted at Cap Cuittone (42.44°N, 8.66°E, 190 m above sea level). The sampling site is on the Mediterranean coast of the National Corsica Park (Parc Naturel Régional de Corse) at 16 km to the SSE of Calvi, the main city in that part of the island which has no important industry (~5500 inhabitants), and about 3.5 km N of the village of Galeria (~350 inhabitants). Consequently, the data from this site could be considered representative of the open western Mediterranean Sea.

The sampler is a 120-mm diameter PTFE Teflon® funnel (collection aperture 0.0113 m^2) machined on a circular base with a thread adapted to 500 mL polypropylene (PP) Nalgene® bottle neck. The funnel stem is a long tapered stem in such a way that it soaks in the preloaded acid for limiting the evaporation of collected water. All the deposition sampling materials (Teflon®-PTFE capped funnels, 500 mL and 60 mL Nalgene® PP bottles, and 60 mL PP boxes with a screwing cap for bottle's corks) were thoroughly washed with hydrochloric acid at the ultra-clean laboratory of LISA following a protocol adapted for ultra-clean sampling (Heimburger et al., 2012). Before deployment, the sampling bottles are preloaded with 50 mL of hydrochloric acid (2%v/v) and weighed. Each funnel coupled to its bottle preloaded was deployed on the site at 2 m height. The position was controlled by a spirit level to ensure that the funnel aperture was horizontally leveled. Each week, before collection, the internal surface of the funnel was rinsed with 60 mL of 2%v/v ultrapure hydrochloric acid in ultrapure water, taking care to flush all the surface. The rinsing solution was collected in the sample bottle to be removed and replaced by a new 500 mL PP bottle for the next week. The funnel was replaced by a new one every 6 months. Field blanks were performed at the funnel installation and removal, but also from time to time by repeating twice the sampling procedure. One permanent staff of the Corsica National Park was carefully advised and performed sampling during all the monitoring period.

2.2. Chemical analyses

In the laboratory, total atmospheric deposition sampled bottles were weighted. The amount of rainwater collected in the funnel was deduced by subtracting added acid solution (i.e. 110 mL) to the sample total mass found in the bottle. Each sample was shaken and then 15 mL were immediately transferred into a PE sampling vial to measure the size distribution of the particulate phase (not discussed here). The rest of the sample was filtered before analysis with acid washed Nuclepore® polycarbonate filters (0.2-µm porosity). The filters were analysed by wavelength dispersive X-ray fluorescence (PW-2404 spectrometer by PANalytical™) for the particulate elemental concentrations for elements from Na to Pb, including macro (P) and micro-nutrient (Fe, Si), trace metals (As, Cr, Cu, Mn, Ni, V, Zn), and source tracers (Al, Ti, Ca, Na, Mg, S, Sr, K, Pb). Analyses of the filtered aqueous sample were performed by Inductively Coupled Plasma- Atomic Emission Spectrometry (ICP-AES, Spectro ARCOS Ametek®) coupled with a CETAC ultrasonic nebulizer for dissolved elemental concentrations of as many trace metals as possible (altogether 45 elements were analysed; Desboeufs et al., 2014). Due to the time between collection and analyses, the preservation of N speciation was not guaranteed and in consequence data are expressed as total N. The total dissolved inorganic N concentrations were obtained by adding NH_4^+ concentrations and NO_3^- and NO_2^- concentrations determined by ionic chromatography (Professional IC 850 by Metrohm®). Field blank concentrations are significantly inferior to sample concentrations for all the studied elements. They represent in average from 1.4% ± 1.3% (Mn) to 12% ± 6% (Fe) of studied elements concentrations, with a maximum contribution of 19% for trace metals (V) and 22% for major nutrients (Fe). Field blank concentrations are subtracted to samples concentrations collected in the same period.

The weekly elemental deposition fluxes were calculated from concentrations of all chemical species measured in dissolved and particulate samples by considering the sampler area and the total liquid volume (preloading + rinsing + rain). The total elemental deposition fluxes were estimated by adding particulate and dissolved fluxes except for N assumed totally acid-soluble. Atmospheric nitrogen exists in particulate phase but also as gaseous species (NO_X, HNO_3, NH_3). In our study, the used bulk collector has a design very close to the one of bulk collectors used during ADIOS project which are not optimized to collect gaseous nitrogen by dry deposition (Markaki et al., 2008). However, wet deposition including both washed-out particulate and gaseous nitrogen, measured N fluxes in this study will be considered mainly representative of bulk deposition of aerosol particles plus wet deposition of gaseous N.

2.3. Dry vs. wet deposition

The speciation between wet and dry deposition is a critical parameter to estimate the potential dissolved fluxes of nutrients. Precipitation (mm) was estimated on the site from the amount of water in the sample. The precipitation occurrences are in agreement with the rainfall records on Calvi airport which is distant by about 15 km. Since they are more representative of local rainfall, precipitation estimated from our samples were used for the attribution of deposition fluxes to wet vs. dry deposition. Wet deposition was considered when rainfall was larger than 1 mm during the sampling period. The threshold value of 1 mm integrates the uncertainties on the weighing of samples in order to ascertain that the rainfall was real. Samples which present no precipitation or rainfall lower than 1 mm, are considered as dry deposition. In consequence, dry deposition is assimilated to wet deposition when happening the same week as a precipitation event. This method underestimates dry deposition, and provides a lower estimates of deposition dry event number vs total deposition event number.

2.4. Positive Matrix Factorization (PMF)

Multivariate statistical methods, such as factor analysis, are widely used to identify source signatures and explore source–receptor relationships using the trace element compositions of atmospheric aerosols (e.g., Polissar et al., 2001, Calzolai et al., 2015) and precipitation (Keeler et al., 2006; Gratz et al., 2013). Since many sources emit characteristic relative amounts of certain trace elements, source–receptor techniques can be used with an understanding of these elemental signatures to identify the major sources influencing a given receptor site.

We applied EPA PMF v5.0 (Norris et al., 2014) to the matrices of tracers, nutrient and TMs total deposition measurements. PMF is a multivariate statistical technique that uses weighted least-squares factor analysis to decouple the matrix of observed values (X) into two matrices representing the factor scores (G) and factor loadings (F), as represented by the equation $X = GF + E$, where E is the residual matrix representing the difference between observed and predicted values (Paatero and Tapper, 1994; Paatero, 1997). Prior to applying PMF, we used the weekly deposition fluxes and we replaced fluxes reported as less than median detection limit (MDL) with the median value. The uncertainties for each samples correspond to the sum of uncertainties in sample collection (i.e. 10%) and analytical measurement (standard deviation of three replicate analysis for each sample). We included all valid samples, excluding the samples that we identified as extreme outliers, i.e. samples corresponding to dust events and high As deposition (12 samples) (see section extreme events). The deposition fluxes for 21 elements is used; i.e macro and micro-nutrient (N, P, Si, Fe) and TMs (As, Cr, Cu, Mn, Ni, V, Zn) and tracer elements (Al, Ti, Ca, Na, Mg, sea-salt S (Sss), Pb, K, and excess S (Sexc). The estimation of Sss fluxes is obtained from Na fluxes on the basis of typical seawater S/Na ratio (Henderson and Henderson, 2009) and Sexc fluxes in subtracting Sss to total S fluxes. Since S was used as sources tracers, the discrimination between ssS and excS enabled to have a best constrain on signature of sources. Elements with a signal-to-noise (S/N) ratio <5 were categorised as "weak" (i.e. As and N) and hence down-weighted so that the user-provided uncertainty was increased by a factor of three (Norris et al., 2014). The variability in the PMF solution was estimated using a block bootstrap technique, which calculates the stability of the model solution by randomly re-sampling blocks of the input dataset and computing the variability between model solutions. We applied 100 bootstrap runs to the PMF base run with the lowest Q value. We determined the final factor profiles based on our ability to identify all the factors, the robustness of Q values, the ability of the model to replicate measured results, and the bootstrap results.

3. Results and discussion

The 3.5-yr time-series of weekly fluxes (195 samples) for nutrients, TMs, major source tracer elements (Al, Na, S and K) and precipitation are presented in Figure 1. Corresponding time-series of other source tracer elements (Ti, Mg, Sr, Pb) are available in supplement with the total atmospheric fluxes data. The highest fluxes are recorded for Si, P then Fe for major nutrients and for Zn and Mn for trace metals. 51% of the samples, i.e. 99 samples, sustained at least one event of precipitation during the week of sampling and are here referenced as wet deposition. In our set of 195 samples, 21 presented a rainfall higher than 20 mm and the highest weekly rainfall recorded is 29 mm. However, no systematic link is observed between the biggest rain event and the nutrients or metals fluxes.

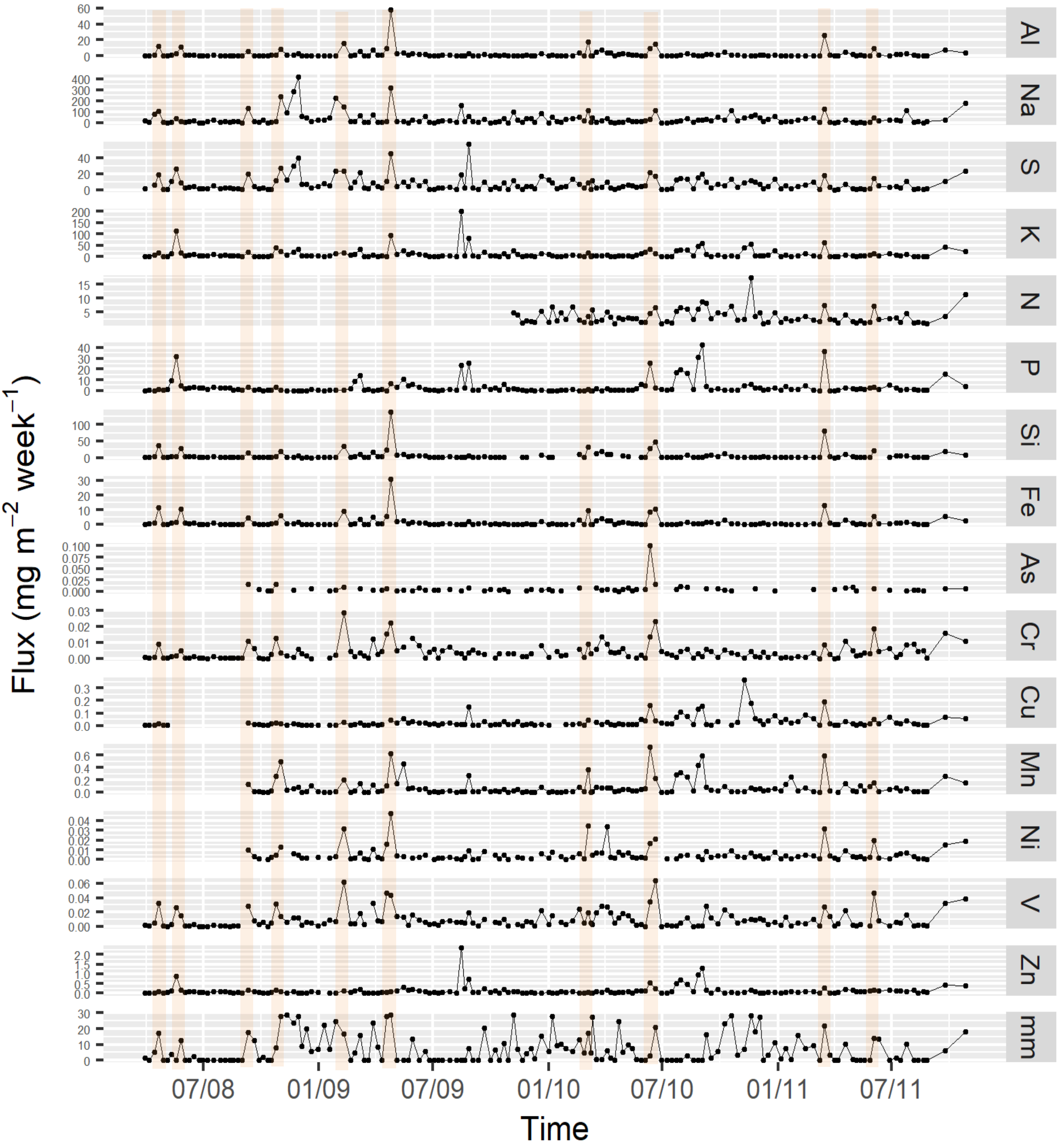


Figure 1: Temporal variability of bulk weekly fluxes from March 2008 to October 2011 for main markers, nutrients and trace metals, and rainfall on the same period. The 10 most intense dust event are displayed in the boxes in orange (see details in "The case of high deposition events")

The results emphasize large differences in timing of deposition fluxes between the studied elements. But for all the elements, data display some weeks with high episodic fluxes. Due to the sporadic character of specific events such as dust storms or forest fires giving rise to high deposition events, it is known that the fluxes of elements associated to these sources are often important on a short period. For example, for elements such as aluminium associated with dust events, a half or more of the annual deposition flux may occur in one event of a few days or even hours (Guieu et al., 2010), and high deposition events (>1 g m^{-2}) are responsible for the inter-annual variability of the Al deposition flux in the western Mediterranean basin (Löye-Pilot and Martin, 1996). As a consequence, the fluxes linked to these extreme events can dominate and hide the influence of more continuous emission sources. In our dataset, this is the cases of Si, Fe and As, for which 25% of total fluxes on 3.5 years is delivered by 1 to 3 weekly samples, whereas for the majority of nutrient and TMs, 25% of total fluxes are constituted from the 5 to 8 highest events. The most obvious case is for As which 23% of the total flux is obtained in only one week during June 2010 (0.1 mg m^{-2} $week^{-1}$). This event corresponds to one event of wet deposition of 7 mm, i.e. no particularly intense rain, and is concomitant with high fluxes for the other studied elements.

3.1. Seasonal variability

Monthly total and wet fluxes have been estimated to investigate the seasonal variability of the measured elements inputs over the northwestern Mediterranean (Figure 2). A large variability in the monthly deposition fluxes of all the elements is observed in agreement with the episodic pattern of weekly inputs. Nutrients deposition presents a clear seasonal pattern: P with the major deposition fluxes in summer, and N in winter, whereas the main fluxes are observed in spring for Fe, Si, Cr, Ni and V. For As, excluding June, which shows its highest monthly mean flux due to the intense event of June 2010, the maximum of fluxes are recorded at the end of summer and beginning of autumn. For Mn, no clear seasonality is observed. A monthly flux predominates in August and November for Zn and Cu, respectively, reaching at least twice the other monthly fluxes. For all the elements, the wet deposition predominates the total fluxes between October and April in agreement with the highest rainfall recording during this period, whereas dry deposition is the main way of input in May, July and August. Our results are in agreement with the seasonal pattern observed in the 1980's for Si and Fe deposition at Capo Cavallo, 8 km more North on the Corsican coast (Bergametti et al., 1989).

The maximum of deposition during spring is explained by the concomitance of rainfall and high dust concentrations, whereas Si and Fe atmospheric aerosols concentrations present their maximum in summer during the dry season. This emphasizes that the below-cloud scavenging of aerosol is the predominant process explaining atmospheric deposition of dust-related elements in this period. For the elements mainly associated to dry deposition, i.e. Zn, P and Cr, Bergametti et al. (1989 and 1992) observed that the highest deposition was typically associated with the period of their highest aerosols concentrations in summer. This is not the case for Cr in our results, which follows the Si and Fe behavior. At the difference of our Corsica site, no clear seasonal variability is observed for the deposition fluxes recorded at Cap Ferrat, 170 km more NNE on the French continental coast, a site affected by the anthropogenic influences from continental Europe (Pasqueron de Fommervault et al., 2015). That could be the case for Mn atmospheric fluxes on our site.

The case of N deposition is specific, since the N deposition flux corresponds mainly to total aerosol and wet gaseous deposition inputs in our samples. The general pattern for N with highest fluxes in winter could be linked to the thermal instability of the ammonium nitrate, which is the dominant form of N in aerosol particles associated to a decrease of rain events during the hot season, and to extremely typical intense nitrate episodes recorded from November to March in the western Mediterranean basin associated to maximum wet deposition (Querol et al., 2009). The highest N deposition flux is recorded in November 2010 (Figure 1), this event is associated with wet deposition and is coincident with a deposition peak for Cu and K.

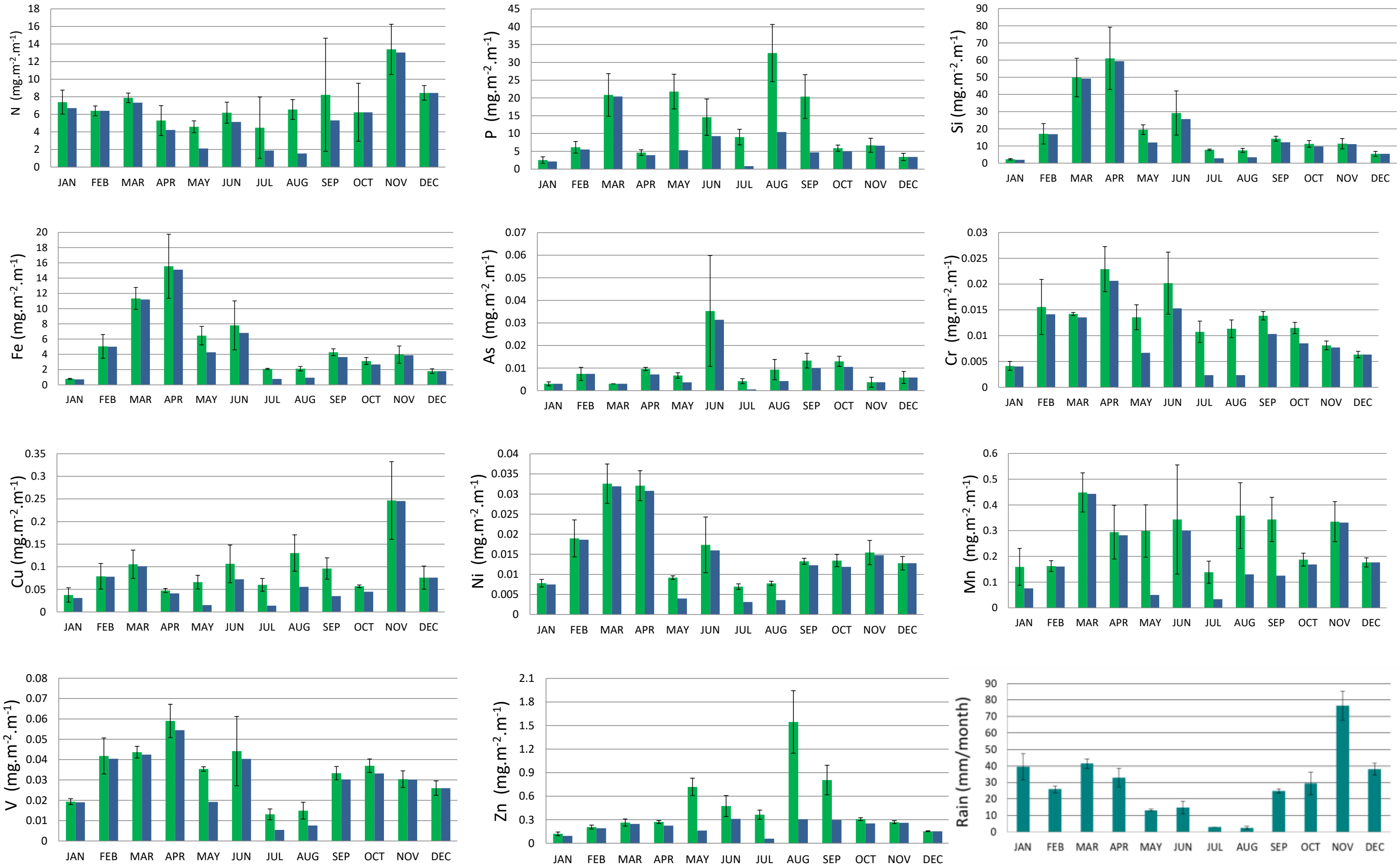


Figure 2: Temporal variation of monthly total (green bars) and wet (blue bars) deposition and precipitation during the sampling period March 2008–October 2011. Bars indicate standard deviations over the weekly values available over the period.

3.2. Inter-annual variability

The average annual total deposition fluxes for the major nutrients and trace metals during the 3.5 years of sampling are presented in Table 1. Among major nutrients, the most abundant nutrients in bulk deposition is Si followed by P and N which have fluxes in the same order of magnitude. The highest annual fluxes recorded for N in comparison to Fe is due to the sporadic pattern of Fe fluxes in comparison to N that shows more regular weekly fluxes. For trace metals, the highest annual fluxes are observed for Zn, Mn and Cu whereas the other trace metals have fluxes smaller by one order of magnitude. Except for Ni, the standard deviations on the mean fluxes are larger than 15%, and reach more than 50% for P, As and Cu, meaning a large inter-annual variability of their deposition, in agreement with the high recorded sporadic weekly fluxes for these elements. Our results are compared with other fluxes in Corsica (Table 1) as reported in the literature. Data show that for trace metals, the recorded values are in the same order of magnitude of previous measurements in Corsica. On the contrary, for the major elements as Fe, Si and N except for P, our deposition flux values are much lower than the previous ones obtained in Corsica (Table 1) and globally in the western Mediterranean (Bonnet et al., 2006; Pasqueron de Fommervault et al., 2015). A net decrease in N deposition is also observed between the 1990's and now in Europe (Waldner et al., 2014). The only element with highest deposition fluxes in comparison to the literature is P, suggesting an increase in atmospheric fluxes for this element. Keeping in mind that dry deposition events can be underestimated by our method, the wet fluxes predominate the total deposition fluxes (≥ 64%) for the majority of elements except for P and Zn, for which less than half of the total flux is associated to precipitation. This is in agreement with the seasonality of deposition of these elements which is high in summer when the contribution of dry deposition is the highest.

Table 1: Left part, annual total, wet and dry deposition fluxes (mg m^{-2} y^{-1}) of major nutrients and trace elements, and relative contribution (%) of wet periods on the total fluxes measured at Capo Cuittone, Corsica, between March 2008 and October 2011. Right part, annual deposition fluxes at various sites in Corsica available in the literature.

Element	**Total Flux**		***Wet Flux***	***Dry Flux***		**Capo Cavallo**[a]	**Pirio**[b]	**Ostrioni**[c]	**Bavella**[d]
	Average	Range	*Average*	*Average*	*% wet*	Fev. 1985 to Nov. 1987	Jan. 1995 to Mar. 1997	Jun. 2001 to May 2002	1984-1986
N	143 ±61	81-167	*107.6*	*19.9*	*84%*			355-377*	644-766
P	149 ±79	114-253	*73.3*	*75.4*	*49%*	24.2-40.1		43.2	
Fe	67 ±10	65-77	*56.2*	*10.5*	*84%*	395-406	118-156	1188	
Si	246 ±61	197-280	*206.7*	*39.3*	*84%*				
As	0.14 ±0.07	0.10-0.20	*0.10*	*0.06*	*64%*				
Cr	0.16 ±0.04	0.12-0.19	*0.11*	*0.05*	*69%*				
Cu	1.06 ±1.07	0.44-2.16	*0.72*	*0.33*	*68%*	2.3-3.7	0.7-1.4		
Mn	3.7 ±1.4	2.5-5.2	*2.15*	*1.20*	*64%*	12.5-15.2	6.3-6.5		
Ni	0.21 ±0.01	0.14-0.24	*0.16*	*0.03*	*84%*		0.4		
V	0.4 ±0.06	0.34-0.46	*0.33*	*0.07*	*83%*				
Zn	5.7 ±1.9	3.74-7.42	*2.51*	*3.20*	*44%*		4.2-6.1	6	

[a]: total bulk deposition from Bergametti et al. (1987 and 1992) and Remoudaki et al. (1991)
[b]: total bulk deposition from Ridame et al. (1999)
[c]: total bulk deposition from Guieu et al. (2010) and Markaki et al. (2010)
[d]: total wet deposition from Löye-Pilot et al. (1990)
** data obtained between jun. 2001 and May 2003*

3.3. Mineral dust deposition fluxes

The annual deposition fluxes of soil dust have been estimated from Al fluxes, considering an amount of Al of 7% (Guieu et al., 2010). The results show that the mean annual dust flux ranges from 1.39 to 1.94 g m^{-2} y^{-1}. Typically, 70% of the annual flux is related to 3 or 4 dust deposition events during the year, in agreement with the sporadic pattern of dust input over the year (Löye-Pilot et al., 1996). For example, a weekly maximum of 0.82 g m^{-2} w^{-1} is recorded during the last week of April 2009, representing 44% of the total flux for this year. It is well known that the intense dust events lead to a very high intra and inter-annual variability. Al deposition data recording in Corsica show a range of dust fluctuation for the period 1985-2002 in Corsica being to 4 to 28 g m^{-2} y^{-1} (Guieu et al., 2010), higher value being always associated with very intense events (>10 g m^{-2}). Our values between 2008 and 2011 are lower than the range previously measured between the 1980’s and early 2000’s, probably because no intense dust event (>1 g m^{-2}) has been recorded during the sampling period (Figure 3). This trend is consistent with the low annual deposition mass fluxes observed by Vincent et al. (2016) recorded in Corsica and more generally in the western Mediterranean between 2011 and 2013 (max 2.1 g m^{-2} yr^{-1}). This result is also coherent with the decreasing trend in PM_{10} concentrations over the Mediterranean region due to the decrease of dust contribution (Pey et al., 2013). As mentioned by Moulin et al. (1997) and Pey et al. (2013), this is probably due to the variation in large scale atmospheric circulation affecting dust atmospheric contents (lower values of the NAO indices during the last two decades). This trend could be also is related to the low dust activity period in Sahara during the 2000's in comparison to 1970-1990 proposed by Evan et al. (2016) from wind variability pattern. However, the kind of deposition collectors and the sampling sites being different, we cannot exclude effects of sampling conditions on the obtained results.

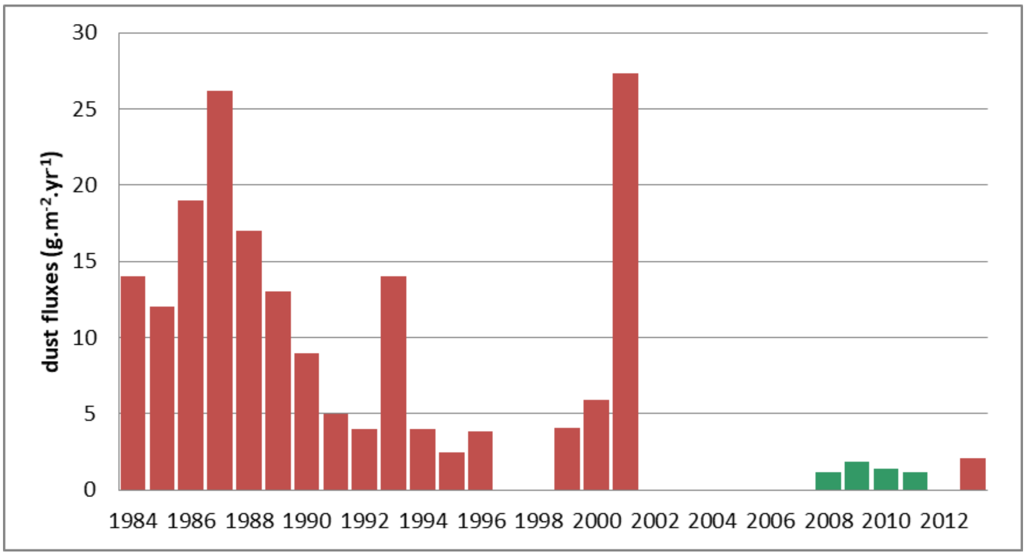
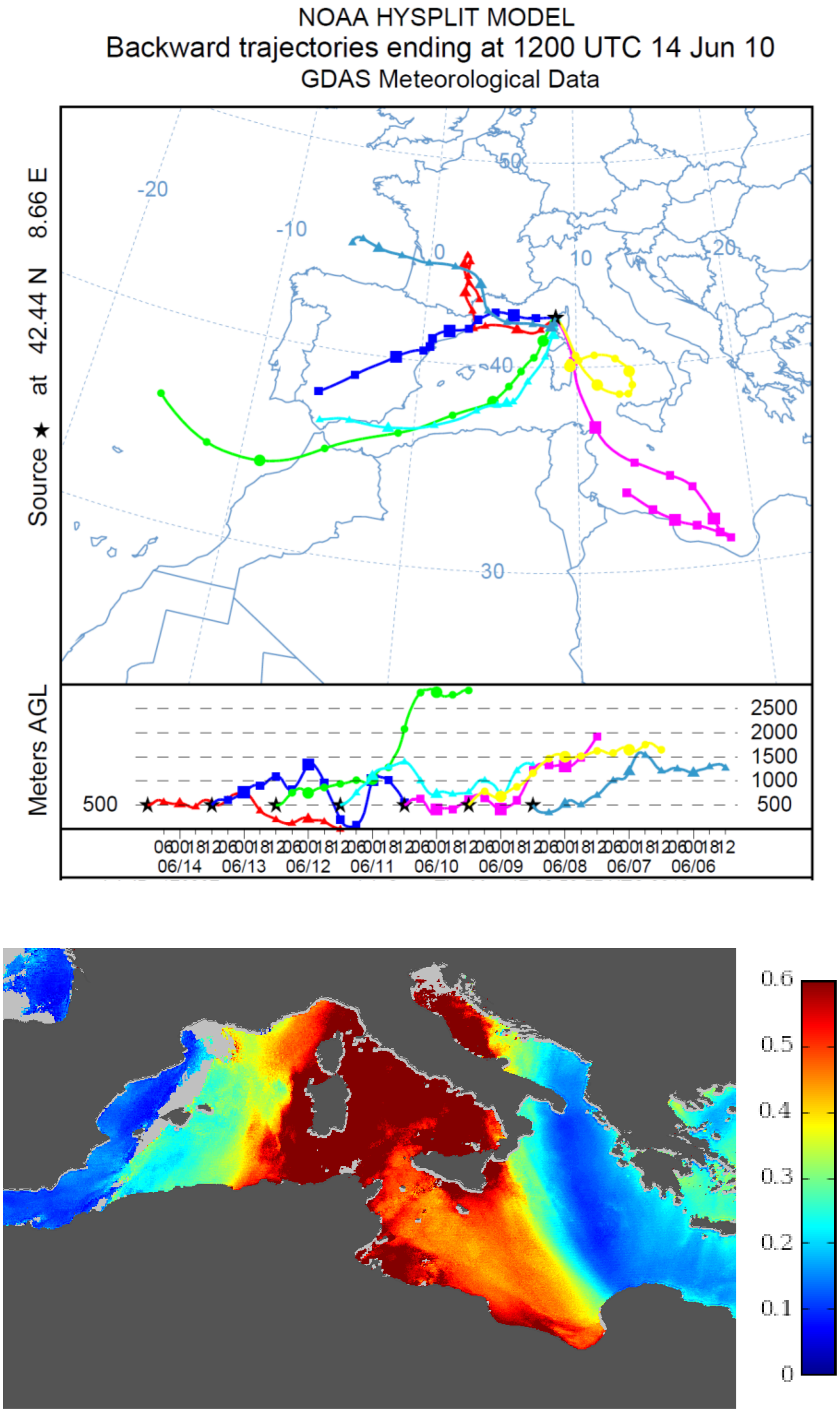


Figure 3: Time-series of dust fluxes (g m^{-2} an^{-1}) at various locations in Corsica issued from Löye-Pilot and Martin (1996) for years between 1984 and 1994, from Ridame et al. (1999) for 1995 and 1996, from Guieu et al. (2010) for 2001-2002, from Vincent et al. (2016) for 2013 (all in red) and from this work for 2008-2011 (in green).

3.4. The case of high deposition events

Over our sampling period (March 2008-October 2011), the average weekly dust deposition is 0.028 ± 0.07g m^{-2} w^{-1}. In order to identify the outlier dust events in the data set, we selected the samples with weekly fluxes higher than the last 95th percentile of data, i.e. the 5 % of highest values. Thus, weekly dust fluxes > 0.104 g m^{-2} w^{-1} are considered as the extreme dust events. From this threshold, 12 samples are isolated and correspond to 10 dust events (2 events concern two successive sampling periods in April 2009 and June 2010). All these events correspond to wet deposition periods (Figure 1). Observations of remote sensing data from MODIS or SEVIRI confirm that these events are due to intense Saharan dust plumes associated with clouds (not shown). Eight of these events happened in spring (between March and June), 1 in fall and 1 in winter, in agreement with the seasonal pattern of dust plumes over the western Mediterranean (Moulin et al., 1988) and in particular in Corsica (Bergametti et al., 1989; Salvador et al., 2014). The first week of one of the two dust events which fall in two sampling periods corresponds also with the high episode of As deposition (0.1 mg m^{-2} wk^{-1}) recorded in June 2010. This weekly As flux represents the annual flux measured in a remote environment like Scandinavia forest (0.1 mg m^{-2} yr^{-1} on average between 2002-2005; Hovmand et al., 2008). It is much larger than the weekly fluxes recorded in an urban environment as Venice where the reported fluxes range from 0.7 to 367 µg m^{-2} wk^{-1} between

2005-2010 (Morabito et al., 2014). The As/Al ratio (0.011) for this event shows a large enrichment in As (x16) in comparison to the average of other intense dust events (7.10^{-4}), which are in agreement with the crustal ratio (Mason and Moore, 1982). The identified sources of atmospheric particulate As are coal-fired industries, waste-incineration, oil refining, mining and fossil fuel combustion (Wai et al., 2016). In the given sample, an enrichment in comparison to the other intense dust events is also observed for P (x12), Sr (x9), Cu and Zn (x6) whereas no significant enrichment is observed during the second sampling week of the dust event. Besides dust and marine aerosol, the biomass burning and fossil fuel combustion are the main sources of anthropogenic Cu, P, Sr and Zn (Mahowald et al., 2008; Nava et al., 2015). Moreover, the particulate filter corresponding with this event was brown-grey, showing a probable mixing between dust and black carbon (not shown). During the As-rich deposition week, the back-trajectories show that the air masses came mainly from South in concomitance with a high dust intrusion in the western Mediterranean basin (Figure 4), no intense biomass burning event is recorded during this period on the pathways of back-trajectories. A mixing with dust and anthropogenic aerosol, rich in metals, over Mediterranean has been already observed (Dulac et al., 1987; Heimburger et al., 2016). Our observations suggest that either deposition from a likely local combustion source occurred during the week of the dust deposition event or the deposited dust was mixed with aerosols issued from combustion source along its transport over Africa or Mediterranean.



Figures 4: (a) Pathways of 3-day back-trajectories ending at 500 m at the sampling site at noon from NOAA HYSPLITT model for the week of As-rich event and (b) MSG/SEVIRI daily (daytime) mean aerosol optical depth oven Ocean for the 10th of June 2010 in agreement with the intrusion of an intense Saharan dust event during this week.

The dust flux associated to these most intense dust deposition events represents 56% of the total dust flux on the 3.5 years of recording. The contribution of dust events on the fluxes Fe and Si represents 52% and 57% of their total fluxes respectively. Our results confirm the important role of these sporadic dust events on the inputs of these elements. In agreement with previous observations, Si and Fe fluxes present also a good correlation with Al fluxes (R^2= 0.97 and 0.96, respectively) and mean mass ratios (Si/Al = 2.5 and Fe/Al = 0.57) are typical of Saharan dust (Formenti et al., 2008 and 2011) and of transported dust in European sites (Alastuey et al., 2016), supporting more generally the important role of dust deposition on Si and Fe.

For N and P, the contribution of the outlier dust events is lower and reaches 10 and 15% respectively, and even 11% for P if the As-dust mixed event is excluded. That means that other sources than soil dust dominate the fallouts of these species (Figure 1). However, a peak in N and P fluxes is systematically observed during high dust events, showing at the same time that intense dust deposition is also a source of these elements. The reactivity between dust and nitric acid previously observed in Mediterranean (e.g. Puteaud et al., 2004) could explain the link between dust fluxes and N fluxes. For trace metals, the high dust deposition events represent around 1/3 of total fluxes for Cr, Mn, Ni and V, whereas the contribution is low for As (10% without the intense event), Cu (16% and even 12% excluding As-dust mixed event) and Zn (9% and even 6% excluding As-dust mixed event). Keeping in mind that no high dust deposition event >1 g m^{-2} has been recorded during our 2008-2011 period of sampling, our data confirm that African dust wet deposition constitutes the major atmospheric source for Fe and Si to the northwestern Mediterranean and an important source for Cr, Mn, Ni and V (1/3 of their total fluxes).

3.5. Source apportionment and background deposition

In order to perform a source apportionment by the PMF method, we excluded the 12 samples corresponding to the high African dust deposition events in order to address background atmospheric deposition. We evaluated PMF solutions with two to six factors. Finally, a solution with 4 factors has been chosen since it is the optimum solution coupling a good agreement with our understanding of sources identification and the indicator of PMF optimization. The 4-factor solution was the most stable with a sharper decrease in the Q/Qexp trend and a constant global minimum Q value among 100 random runs. In terms of the stability of the PMF analysis, all factors of the 4-factor solution were reproduced in 100% of bootstrap runs, demonstrating that this solution was stable. No correlation between 4 factors has been observed, indicating that they represented distinct sources. The 4-factor solution enables to apportion the results between 4 sources: a dust factor (related to Si, Al, Ca, Fe and Ti), a marine aerosol factor (related to Na, Mg, Sr), an anthropogenic source factor (related to Cr, Pb, V, N, Sexc) and a biomass burning factor (related to K, P, Zn, Cu and Mn) (Figure 5). This source identification is based on the presence of tracer elements as well as on the ratio of the elements in the source profile. The source identification was also supported by the seasonal contributions of each source to the atmospheric fluxes shown in Fig. 5. The identification of factors was supported by the previous works on source apportionment of aerosol particles in the Mediterranean (Calzolai et al., 2015, Becagli et al., 2012 and 2017). However, even if the oil-combustion source (rich in Ni-V) has been typically observed in the central Mediterranean, no PMF solution (2- to 6-factor solutions) did enable us extracting a Ni-V factor, corresponding to a ship plume signature. The heavy oil combustion signature could be contained in the anthropogenic factor. However, the typical V/Ni ratio of ship emissions are between 2.5 and 4.5 (Becagli et al., 2012), whereas this ratio is higher than 8 in the anthropogenic factor, suggesting that the ship plumes are dominant in this factor. Even if this source could be important for aerosol concentrations over the Mediterranean Sea (Becagli et al., 2017), it does not seem to be important for deposition in Corsica. The marine factor is marked by Na, Sss, Mg and Sr, with at least 60% of their fluxes corresponding to this source. The elemental ratio obtained for this source (Mg/Na =0.13; K/Na =0.064; Ca/Na =0.070, Sr/Na =8.5×10^{-4}) are in agreement with the typical elemental ratio in seawater (Mg/Na =0.12; K/Na =0.037; Ca/Na =0.038; Sr/Na =7×10^{-4}; Bowen, 1979). It is known that sea salt aerosol concentrations are a function of surface wind speeds (O'Downd et al., 1993). The seasonal contribution of this source is consistent with a larger wind production in fall and winter, with a maximum of deposition in agreement with the maximum of rain in fall. Na represents on the total mass at least 15% for dust and biomass burning factors due to the high influence of marine environment on the Corsica Island. The factor identified as dust source, marked by Al, Fe, Si, Ti, is in agreement with the typical seasonal variation of dust deposition in Corsica with a maximum in spring and in fall (Bergametti et al., 1989). Moreover, the elemental ratios (Si/Al =2.7; Fe/Al = 0.72; Ti/Fe = 0.12) correspond to a Saharan dust signature (Si/Al between 2 and

4 and Ti/Fe between 0.1 and 0.15; Formenti et al., 2014), but also with the typical ratio found in PM10 in remote area in Mediterranean (Alastuey et al., 2016). The biomass burning/waste source is mainly characterized by Cu, K, P and Zn. K is commonly associated to waste/biomass burning or wood combustion (Dall'osto et al., 2013, Nava et al., 2015). The maximum of this source deposition in summer, in spite of a minimum of rain, corresponds with the intense forest fires observed in the Mediterranean region in this period, and which the extend impacts all the basin (Bossioli et al., 2016). Finally, Cr, Pb, V, Sexc and N are the characterizing elements found in the anthropogenic source. Even with >4-factor solutions, no profile distinguishing N, Sexc and metals is emphasized by PMF, suggesting a common source, at least geographically. Thus, the major contribution of N and Sexc in mixing with metals suggest that this source correspond with the secondary aerosols formed in air masses issued from combustion sources (traffic, industrial). The two sources of combustion identified by PMF, i.e. biomass burning and anthropogenic sources, have previously been observed in background aerosols in another remote site in Corsica (Arndt et al., 2017; Claeys et al. 2017).

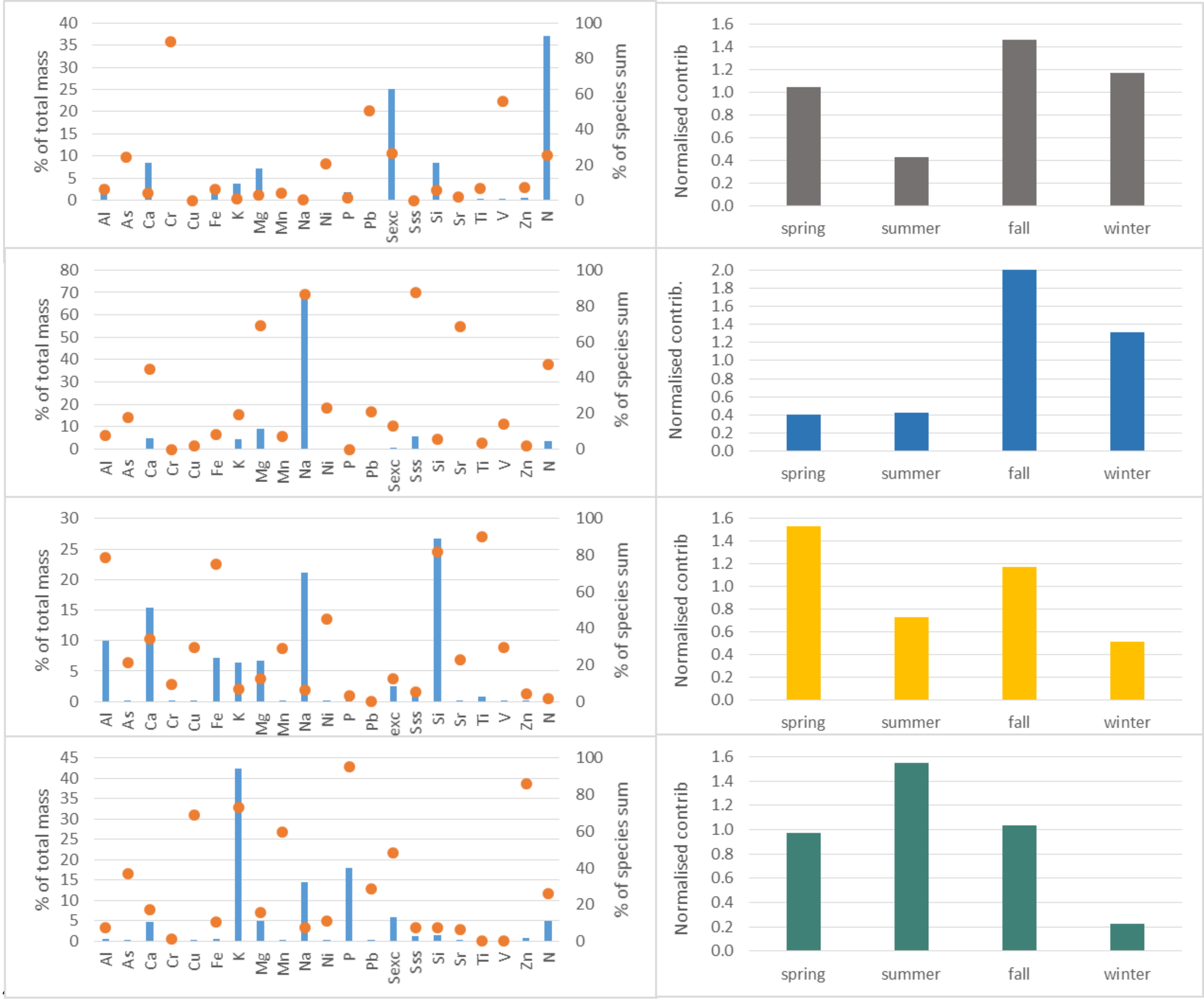


Figure 5: PMF-derived profiles of the four sources identified. From top to bottom: (a) anthropogenic, (b) marine, (c) dust and (d) biomass burning including fraction of total mass (blue columns) and fraction of elemental sum (orange circles) for the various elements (Left side). Normalized seasonal contributions of these four respective factores, excluding the 10 most intense dust events (Right side).

In Figure 6, we show the relative contribution from the identified sources to background deposition flux of nutrients and trace metals. The results show that the combustion sources (biomass burning or anthropogenic) predominates in the background inputs of major nutrients and TMs, except Fe and Si. Even for background deposition, the source apportionment of Fe and Si is quasi-similar to Al (correlation coefficient is close to 1 for the elemental fluxes even out of intense events and ratio Si/Al and Fe/Al are characteristics of mineral dust). These results suggest that even if the PMF apportionment source distributes the fluxes from the 4 sources, in all the cases, the fluxes of Fe and Si are associated to mineral dust sources, most probably Saharan dust.

Concerning major nutrients, P deposition is highly associated to biomass burning inputs out of the most intense dust deposition events. Considering that the dust deposition accounts for 15% of the total P deposition flux (incl. intense dust deposition events + background deposition), almost 85% of P inputs are associated to the deposition of biomass burning/waste/wood-related aerosol. This confirms the importance to consider the biomass combustion source to estimate the role of this element on the marine environment in the Mediterranean. For N deposition, the inputs associated to marine sources are quasi-similar to the inputs from combustion sources. Thus, almost 50% of N fluxes is explained by the marine source. Several works observed that the depletion of chloride (Cl) and the simultaneous occurrence of NO_3 in sea salt aerosol particles is due to the reaction between NaCl and HNO_3 when maritime and anthropogenic air masses are mixed, in Mediterranean environments (Sellegri et al., 2001; Bardouki et al., 2003; Pey et al., 2009) and in particular in Corsica (Claeys et al., 2017). The contribution of marine source to N deposition is probably due to the deposition of these processed sea-salt particles. In the case of the anthropogenic source factor, the good correlation obtained between N and Sexc supports a common origin which is probably associated to the inorganic secondary aerosol, i.e. ammonium sulfate. Indeed, the ammonium sulfate aerosols are currently observed in Corsica due to regional transport (Arndt et al., 2017) and generally in the Mediterranean remote sites (e.g. Calzolai et al., 2015). As stated previously, the using of N speciation is limited by the preservation conditions of our samples. However, we observed a concomitance between the highest deposited mass of NH_4^+ and Sexc, and of NO_3^- and Na (See supplement). It reinforces our conclusion on a partition between N as NH_4^+ mainly associated to ammonium sulfate for the anthropogenic factor, and N as NO_3^- present as $NaNO_3$ for the marine factor. It is known that the deposition efficiency of particles in the coarse mode, as sea salts, is higher than the one of fine particles, as inorganic secondary aerosols. Our results suggest that the addition of nitrate on sea salt particles could be a key process in controlling the N atmospheric deposition fluxes to the Mediterranean surface waters. Recent works suggest that a large part of nitrogen associated to anthropogenic secondary aerosol could be soluble organic nitrogen (Violaki et al., 2015). Thus, the observed diversity in sources of deposited N could also mean a difference in N speciation in the fallout (inorganic vs organic).

For trace metals, the marine source present the lowest contribution. The biomass burning/waste source is clearly predominant for Cu, Mn and Zn, whereas atmospheric fluxes of Cr and Ni are largely linked to the anthropogenic source. Fu et al. (2017) show that the Cr deposition in Cape Corsica, even during intense dust event is originated from an anthropogenic source, suggesting a contamination by a local source. Even if the Cape Corsica and our sites of deposition measurements are distant by about 100 km, both suggest that Cr deposition is controlled by an anthropogenic source. For Zn, Guieu et al. (2010) also showed a large contribution of non-dust source. Our work enables to support their conclusions and to identify a biomass combustion source rather than a fossil fuel or industrial origin. It appears that the deposition of Cu, Mn, Ni and V is influenced at least for 20% by dust deposition out of intense events. That means that for these trace metals, the natural dust inputs can represent up to 50% of annual fluxes.

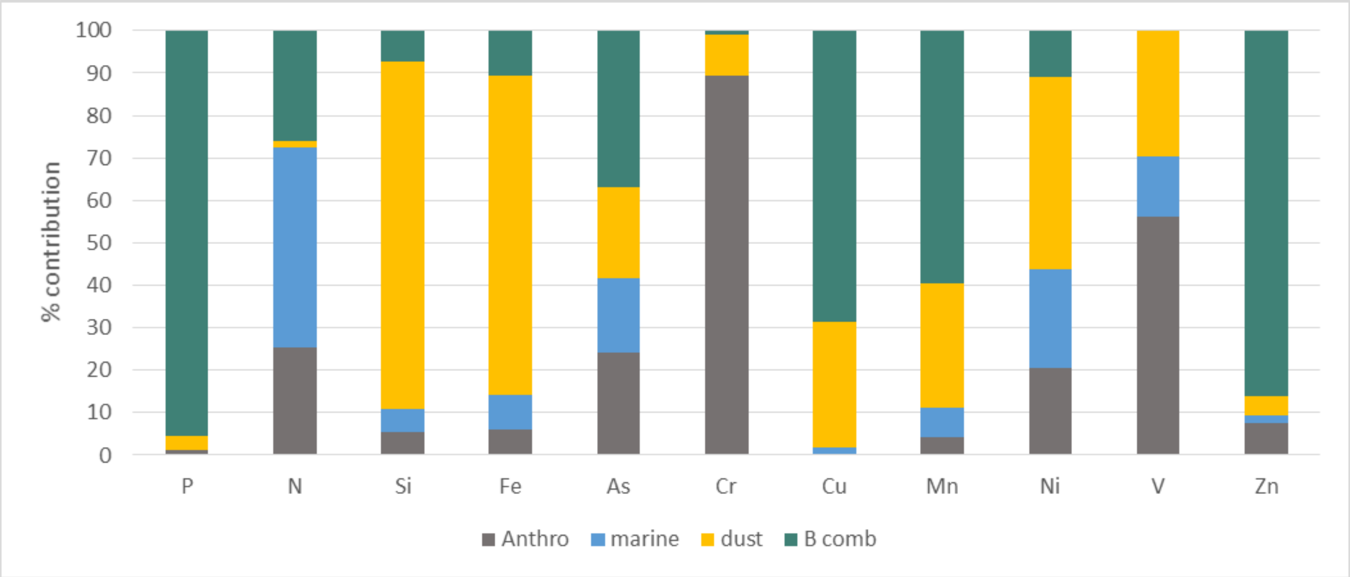


Fig. 6: Relative contribution of each of the 4 identified factors (Anthro= anthropogenic, marine, dust and B comb= biomass combustion) to the “background” mass fluxes of nutrients and TMs (i.e. excluding the 12 most intense African dust deposition samples out of 195 samples).

3.6. Biogeochemical implications

The typical N:P molar ratio in seawater required by marine phytoplankton corresponds to the Redfield ratio of 16. This ratio is generally higher in Mediterranean surface seawater, with values ranging from 20 to 100 on the basin (Ribera d’Alcala et al., 2003). The atmospheric input to the Mediterranean Sea displays a high N:P ratio for dissolved or soluble inorganic forms (Herut and Krom, 1996), which could be one possible reason of the high N:P ratio in Mediterranean deep sea waters (Markaki et al., 2010; Krom et al., 2010).

In our data set, the yearly deposition mass fluxes measured for N and P are quasi equivalent (0.14-0.15 g m^{-2} yr^{-1}; Table 1). However, weekly measurements show a very large variability in P fluxes, contrary to N. Hence, a large variability in the N:P molar ratio is observed in the atmospheric inputs at short time scales. A mean value of 35 is observed for the molar ratio but the weekly ratio ranges from 0.4 to 1220. The observed N enrichment in comparison to the Redfield ratio is in agreement with previous observations showing a preponderance of N relative to P in the atmospheric deposition over the Mediterranean Sea (Markaki et al., 2010). However, a detailed analysis shows that the atmospheric ratio is equal or higher than Redfield ratio only for 25% of samples, and higher than 160 only for 3 samples (4%). This value reaches 36% for the wet periods. The higher ratio observed in wet deposition could be linked to a wash-out effect of the gaseous N species (as NOx, NH_3) by rain (Ochoa-Hueso et al., 2011). The intense dust events present an average N:P ratio of 3.5, which is lower than previously reported for dust deposition (between 30 and 70; Morales-Baquero et al., 2013). However, this value is consistent with the typical N:P ratio in Saharan dust aerosols which is around to 2.5. The highest N:P ratio are generally due to the reactivity of dust aerosol with gaseous nitric acid to form nitrate on dust particles (Desboeufs et al., 2014). Our data suggest that the effect of mixing between dust and nitric acid did not commonly affect atmospheric dust deposited in Corsica, except maybe during certain high dust deposition. On the contrary, the mixing between sea salt and nitric acid identified with the source apportionment could be a source of N during the fall and winter period, when the biomass burning source is negligible. It appears also that the lowest N:P ratio values are mainly observed from May to September (Figure 7). During this period, the atmospheric deposition becomes the main sources of nutrients since the Mediterranean is highly stratified and the surface is depleted in nutrients. Thus, in these conditions, the atmospheric inputs will be deficient in N relative to phytoplankton requirements. Studies show that phytoplankton growth in western Mediterranean waters is usually limited by a lack of phosphate, rather than nitrate in summer (Lazzari et al., 2016; Richon et al., 2018a), even if phosphorus addition experiments have indicated also N limitation in this period (Tanaka et al., 2011). Our results suggest that the role of atmospheric aerosol input will be rather favorable in case of P-starvation of surface seawater. However, even if the N:P ratio from this study were obtained with comparable deposition collectors than previous literature (e.g. Markaki et al., 2010), it has to be kept in mind the deposition collectors were not optimized for gaseous N fluxes measurements, and the N:P ratio could be underestimated. The temporal evolution of marine N and P concentrations since 1985 has shown a high sensitivity to anthropogenic atmospheric deposition and they are expected to decline in the coming decades due to mitigation/control of pollutant emissions (Moon et al. 2016). Due to the high contribution of anthropogenic deposition sources on atmospheric P fluxes emphasized by our study, it is important to include precise anthropogenic P emissions inventories to estimate the impact of atmospheric deposition on carbon fluxes and phytoplankton biomass in the future.

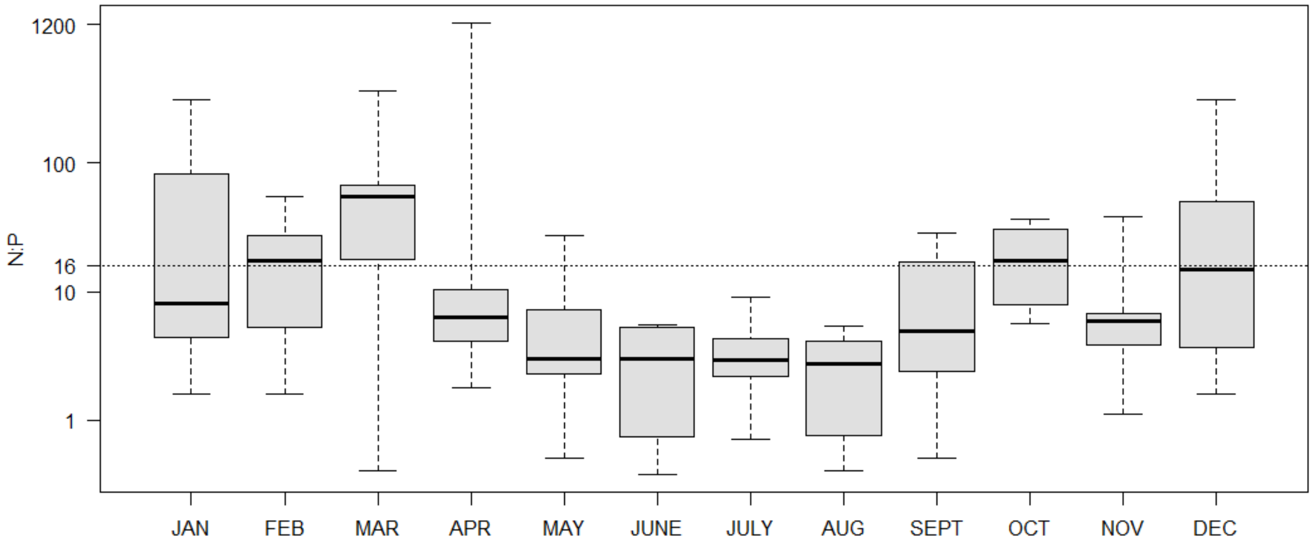


Figure 7: Box plots of monthly molar N:P ratio in deposition samples, showing the third quartile (Q3) and first quartile (Q1) range of the data and minimum and maximum of data. For the sake of comparison, The N:P scale is logarithmic and the Redfield ratio is displayed.

4. Conclusion

In a context of anthropogenic changes, in order to assess how the evolution of chemical atmospheric forcing will modify the marine nutrient cycling, it is crucial to distinguish between anthropogenic vs natural atmospheric inputs of nutrients to the oligotrophic Mediterranean surface waters. We monitored elemental atmospheric deposition on a weekly basis over 3.5-years (March 2008-October 2011) at a coastal site on the western coast of Corsica. The contribution of 4 different source types to the fallout of nutrients and trace metals was determined by statistical PMF method, namely desert dust, sea-salt, anthropogenic activities, and biomass combustion sources. The data show that Si and Fe fluxes are typically related to African dust deposition, with fluxes dominated by high dust deposition events. A typical Si/Al ratio of 2.5 is obtained whatever the samples. That shows that Al is a good proxy to estimate the Si fluxes in Mediterranean region since Si is often not measured when X-Ray fluorescence spectrometry is not available due its lost by HF digestion during the protocol of chemical analysis. Our results on the mineral dust fallout is of the same order of magnitude that of 2013 at another site in Corsica (Vincent et al., 2016) and confirm the fact that dust deposition has strongly decreased in Corsica in the recent years compared to the 1980's and 1990's, with no observed occurrence of a high dust deposition event larger than 1 g m^{-2} in 2008-2011 (this work) and 2013 (Vincent et al., 2016).

Atmospheric fluxes of Cu, Mn, Ni and V are also associated at least at 50% to mineral dust deposition, whereas half of atmospheric fluxes is issued either from biomass burning particles deposition (Cu and Mn), either from fossil fuel combustion (V), either both (Ni). The anthropogenic/combustion sources govern the atmospheric fluxes of major nutrient N and P, with a predominance of biomass combustion source for P and secondary aerosols for N. Dust deposition is contributing around 15% of deposited P at the yearly time scale. Confirming recent model results that desert dust is not dominant on atmospheric P fluxes (Richon et al., 2018b), our result show that these combustion sources need to be considered in P deposition modelling. Finally, Zn or Cr deposition is very largely associated to continuous combustion sources.

This work is a first tentative assessment of the origin of nutrients and trace metals deposited in the western Mediterranean. Of course, our study is not sufficient to apprehend the spatial variability of the influence of the identified source types over the basin. It needs to be supported by other studies of source apportionment on deposition samples in the region.

Aknowledgements:

The authors wish to warmly thank Pasquale Simeoni from Parc Naturel Régional de Corse who made possible the weekly samples collection and the maintenance of sampling site. This study received financial support from the French ANR through the project DUNE and from the MISTRALS programme funded by INSU, ADEME, CEA and Météo-France. This study contributes to WP5 on Atmospheric Deposition of the MISTRALS/ChArMEx project. The authors want to thank Rémi Losno for his involvement in the installation of deposition collectors, and the staff of the Parc Naturel Régional de Corse for assistance in sampling.

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