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

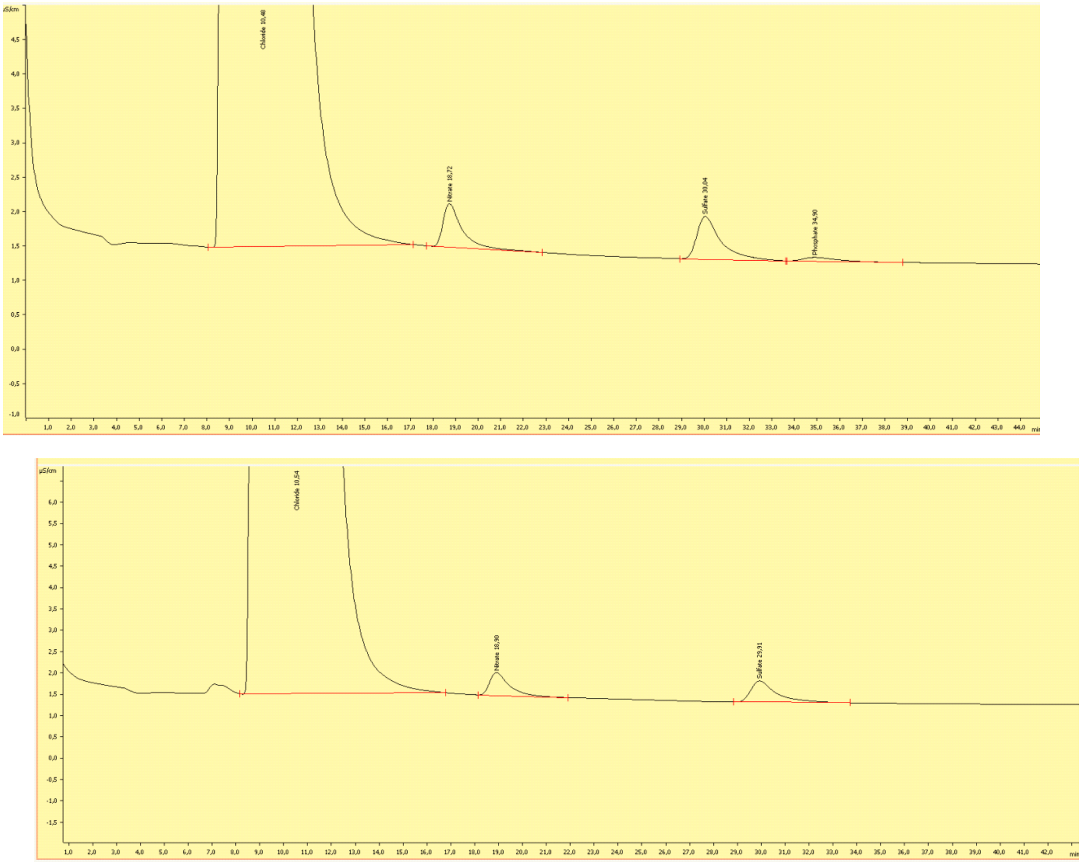
Page 21, L532. Please, check sentence; did you refer to emission inventories? Yes, modified

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.