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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Fluxes and sources of nutrients and trace metals atmospheric deposition in the northwestern Mediterranean" *by* Karine Desboeufs et al.

Anonymous Referee #1

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This study presents result on bulk deposition collected weekly for 3.5 years at a remote coastal site in NW Mediterranean. The study mainly focuses on deposition of nutrients and trace metals. Major sources of deposition are identified by applying a PMF model to the chemical database. A decrease on total deposition levels has been observed for the last years and it is related to the lower impact of Saharan dust events. It has been also evidenced the importance of the contribution of anthropogenic sources in the input of nutrients to the Mediterranean Sea. The topic is relevant and results are of scientific interest given the impact of atmospheric deposition on marine biomass.

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.

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 (NH3). Therefore the association of S with N may be related to the presence of ammonium sulfate (N from NH3) and not necessarily to the association between nitrate and sulfate. Actually, authors determined the concentrations of nitrate, NO2- 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.

Minor corrections

Page 2, L53. Delete "so": "...suggests so..." Page 3, L75. Replace "source" by

“sources”: “. . .PM concentrations and sources. . .” Page 3. L76. Please, avoid using “. . .”: “. . .on aerosols size distribution and precipitation patterns, among other factors.” Page 4, L122. A fraction of the particulates would be dissolved by adding HCl. 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,” 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. 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 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. 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.

Page 10, L250-253. Please, check this sentence. Page 10, L268. Please, replace “ta-

ble 1” by “Table 1”. Page 10, L274. “. . .is larger..” instead of “. . .are larger. . . 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. Page 12, L 317-319. Please, check this sentence, starting by “As mentioned by these authors. . .” and ending “. . . as pointed by . . .” 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? Figure 3 caption. Please, replace (g m-2 an-1) by (g m-2 yr-1) 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). 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. 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. Page 17. Figure 5 caption. Please, use Figure 5 instead of Fig.5. Page 17. Figure 5 caption. Please, indicate in the caption that the seasonal contributions (right) are normalized and that the dust events were excluded. Figure 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),. . . Page 20, L 507. Please, delete “..” after NH3. 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. Page 20, L516: “N:P ratios are” Page 21, L532. Please, check sentence; did you refer to emission inventories? 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.

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