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Biogeosciences Discussions

Interactive comment on "Long-term atmospheric nutrient inputs to the Eastern Mediterranean: sources, solubility and comparison with riverine inputs" *by* M. Koçak et al.

Anonymous Referee #3

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Overall, this paper is a good paper. It reports fundamental data on atmospheric deposition of nutrient species to the eastern Mediterranean. Also the authors compared the atmospheric inputs with riverine inputs. It can be acceptable with moderate revision by carefully considering the following suggestions (particularly for the methodology) and corrections and clarifying my questions raised.

General:

1. **Title:**

I suggest removing "long term", and adding "from a long-term observation" after "Mediterranean"; or changing to "Long-term observation on atmospheric ——".

2. Site description and sample collection:

Please add the relevant description of general meteorology particularly in terms of precipitation and prevailing winds varying with seasons in the study region. The authors considered three seasons: transition (MAM), summer (JJAS), and winter (DJF) (see the first paragraph of page 5098). How about the Oct. and Nov.?

The Hi-vol TSP sampler was used in routine aerosol collection in this study. However, the authors also used the low-volume stacked filter unit (SFU) sampler and the substrate filter is polycarbonate membrane filter (Kocak et al., 2007c; AE). The SUF samples seem to be used for estimating the dry deposition velocity (DDV). To my knowledge, the kind of filter is not recommended by the USA's EPA for the PM mass concentration and ionic and metal measurements, but for the SEM studies. Teflon membrane filter is recommended. Kocak et al. (2007) reported the annual PM_{10} and $PM_{2.5}$ concentrations to be 36.4±27.8 and 9.7±5.9 $\mu g/m^3$, respectively. The fine mode aerosols only account for only 25% of the PM_{10}, rather unexpected. In my experience, polycarbonate is not a suitable substrate of aerosol collection.

3. Dissolution experiment and solubility:

Only 3 cm^2 of each filter sample was used for extraction with pure water (pH?). I wonder if such small size, i.e., less than 1/100 of each filer (3 of 500 cm^2) (20 cm × 25 cm) can be representative of a whole filter. In my experience, it is dangerous, likely resulting in high uncertainty. The authors may verify the homogeneity of the interested species in the filters once using such small size of filter. The extraction time is as long as 36 hours, which is much longer the time usually adopted, i.e, ∼1 hour, so that it is very difficult to compare the literature data. The authors must explain. Can the bacteria consume the extracted ammonium during the long extracting time? The instrument used for nitrate and ammonium determination is different from the common one, i.e, IC. Can it result in systematic error because of the different instruments?

When discussing the dissolution of aerosol nutrient species in pure water and seawater, the authors classified into three groups, which is different from those used for identifying the likely source regions, i.e., 7 (or 6) groups. I understand this is due to the rather small size of sample numbers used for seawater extraction. However, the authors may explain the reasons why certain tow groups can be combined together.

Moreover, the authors gave a simple factor for explaining the differences in SW/PW ratios of PO_4^{3-} and SiO_3^- concentrations, that is, inherent character (see the third paragraph of section 3.4) either of dust or anthropogenic aerosols. In fact, there are a number of factors affecting the dissolution of aerosol species, which can be found in the recently published special issue of Marine Chemistry.

The authors used the term "solubility" throughout the manuscript, but they did not report any solubility data particularly on P. First, they should make the operationally definition on the so-called "solubility" (sometimes it is called as "soluble percent"), otherwise it is very difficult to compare with literature data, especially because they adopted a much longer extracting time than that commonly applied.

The further applied varying extracting time (1, 3, 6, and 36 hours) to examine the "pH" effect on the dissolution of Si and P. The difference between pure and sea water soluble P and Si concentrations is of course attributed to the pH effect. However, I really don't think this experiment can reflect the pH effect on the dissolution; it is a kinetic experiment. The authors must mention this experiment in the section methodology. They should describe how many samples were used for this experiment and how to do. Dissolved Si concentrations in pure water at 1, 3, and 6 hours were lower than that (those) in seawater at 36 hours. Their results of Si reveal that the refractory species such as Si would gradually dissolve, similar to Fe (Hsu et al., 2005; AE), which may be somewhat like the definition of "effective solubility" by Boyle et al. (2005; GBC). The pH is not so important for Si. The result of P also show the dissolved concentration was lower at 3 hours than that at 1 hour, similarly reflecting pH insignificant for P dissolution, at least for the currently applied leaching medium at nearly neural (pure water, $\sim$6) to basic (seawater, $\sim$8.1) condition. (I believe if they use acid rainwater with pH $\sim$3-4,

then they would clearly see the pH effect on Si and P.) If the authors attempted to examine the controlling factors of aerosol species dissolution, they may consider other aerosol acidic species, rather than Si and P themselves alone, which can be referred to Hsu et al. (2010a and b; JGR & MC). Also, the last second paragraph of section 3.4 is very unclear.

When the authors compared the seawater soluble and pure water soluble nutrient concentrations, they used the term "SW/PW (%) ratio", which may lead to misunderstanding, as the solubility or the solubility ratio (see P5100/L20), but they are not. It is the seawater soluble concentration relative to the pure water soluble concentration ratio; therefore I suggest just using "SW/PW soluble concentration ratio (SW/PW SCR)", and not using the percent (e.g., 80%) and using the digital figure (e.g., 0.80) (see P5100/L21).

4. Air mass trajectory clustering:

The authors employed air-mass trajectory analyses to identify the likely sources of atmospheric substances. They should give the rational why they choose the 1 km high (why not, for example, 100 m) to represent the mixed height, and even they ignored the two facts that their atmospheric particulate sampling was conducted on the ground level and the mixed layer particularly in winter may not often reach 1 km. Also, the precipitation chemistry is the whole air columnar integration of scavenged substances via in-cloud and below-cloud scavenging processes of raindrops. Even though the authors have analyzed the trajectories at three elevations (1, 2, and 3 km), they used only 1 km results to discuss the source regions, as given in section 3.3. They classified the trajectories into 7 types. However, as mentioned above, wet deposition is the columnar integration, and so I am wondering if replying on only 1 km trajectory results, they can accurately identify the source regions. Also to my understanding, the in-cloud scavenging may be similarly or even more important than the below-cloud scavenging in contribution particularly for wet deposition of ammonium and nitrate. Therefore, how to evaluate the trajectories within the elevations of raining clouds seems to be crucial for identifying the sources of wet deposition. Moreover, I am wondering whether snow would also be important for contributing wet deposition over the study region. If so, did the authors collect snow samples?

In addition, the authors may show the seven typical trajectories as classified, in a figure.

However, I suggest combining the clusters 1 and 2 just as a single cluster, as summarized in Table 3. Also I am not sure if the separation between clusters EU and NWT can be so clear, otherwise the authors may consider combining them.

5. Atmospheric and riverine deposition of nutrients:

The authors considered only the particulate ammonium and nitrate for the calculation of their dry deposition, ignoring the contribution of gaseous ammonia and nitric acid via dry deposition. Although the authors assumed the difference between the Whatman 41 cellulose filter and polycarbonate membrane filter is caused by the gaseous nitric acid and ammonia, the DDV of gases is different from particles. Usually the gaseous contributions are larger than the particulate contributions (Poor N. et al., 2001; AE). How to evaluate this uncertainty?

In section 3.5.1 (**Here the statements are very confusing to readers**), the authors first mentioned they collected 20 sets of coarse and fine mode aerosol samples. (I really don't know the so called "stack" filter unit (impactor??) can accurately separate the coarse and fine size aerosols, except impactor and cyclone.) They then referred to Spokes et al. (2001) regarding to the approach of estimating the dry deposition velocity (DDV). So it seemed to that the authors followed Spokes et al. to estimate the dry deposition velocity. However, they further said they used 0.1 and 2 cm/sec for fine and coarse aerosols in their present study, respectively, according to Duce et al. (1991). Then they mentioned different, large ranges of dry deposition velocity were applied in literature. Next, they said they estimated the "logical" (see P5096/L26) dry deposition velocity of Si to be 1.59 cm/sec. In fact, the authors didn't describe how they estimated the dry deposition velocity, which can be referred to Hsu S.C. et al. (2009;

JGR), in the text. Also the values reported in Table 5 are not 0.1 and 2 cm/sec, as mentioned above. Please clarify the relevant statements.

The authors claimed the uncertainty in the estimation of dry deposition flux may be within a factor of two (P5097/L3), based on Duce et al. (1991). However, they referred to Migon et al. (2001) that the DDV of P ranged from 0.1 to 0.5 cm/sec (factor of 5) in the western Mediterranean, as identified of an anthropogenic origin. They further mentioned the DDVs of 1-2 and 0.1-0.6 (factor of 6) cm/sec have been applied for nitrate and ammonium in the Mediterranean. If considering the minimum value (0.1 cm/sec) reported in literatures and the one (1.56 or 2 cm/sec) used in the study for the DDV of P, the uncertainty of P dry deposition is as high as 20. Then I am not sure that the uncertainties can be within a factor of only 2. Therefore, the authors need to consider their own uncertainties, otherwise they must realize the situations considered by Duce.

The authors didn't compare their obtained atmospheric deposition in this study with previous studies conducted over the Mediterranean Sea. To date, many investigations on atmospheric deposition have been carried out for the Mediterranean Sea. They observed that the dry deposition of nitrate account for up to 83% of the nitrate total deposition. Also the total atmospheric deposition of nitrate (125 mmol/m^2/yr) is over three times of that (38 mmol/m^2/yr) of ammonium, which is considerably inconsistent with numerous literature results. The authors should explain. Once considering the contributions of gaseous ammonia through dry deposition, some conclusion would probably change, which the authors may be conservative.

In addition, the current subsection 3.5.2 needs to be reorganized. I strongly suggest adding a subsection "Riverine nutrient fluxes" between the current subsections 3.5.1 and 3.5.2; the latter subsection (current 3.5.2) moves as 3.5.3. Then the relevant discussion on the seasonality of atmospheric deposition and relative contributions between wet and dry deposition given in the current subsection 3.5.2 moves to the subsection 3.5.1. Then the results of riverine nutrient fluxes moves to the new subsection;

the comparison between atmospheric and riverine nutrient fluxes is kept, but as the subsection 3.5.3.

6. Conclusion:

Some conclusion given here is not so solid and/or obtained from this study. For instance, this study can not offer any evidence on active photochemical reaction in summer. In summer, high mixing height may result in low concentration of anthropogenic aerosols. Higher SW/PW ratios for P were found in European and Turkey than Southerly air flows; the authors attributed to higher anthropogenic nature. However when looking at the aerosol nitrate and ammonium concentrations, the former two air masses have comparable (even lower) ammonium and nitrate concentrations with the latter (see Table 3). The authors must rethink.

The statement "Solubility of Si was mainly constrained by the pH of the pure-water —– of the pure water" (see P5100/L24-26) is very confused. The authors seem to say the pH of pure water varying with each analyzed sample. Please clarify.

Specific:

Subsection 3.2.2: Too detailed.

Table 1: Just mention the sample numbers and time coverage in the text or the table caption. Please change P-PO_4^{-3} to PO_4^{3-}P and so on.

Table 2: The lower part of this table seems to be for P and Si; if so, please add the title. This table can be reorganized.

Table 3: please add the standard deviation for aerosol nutrient concentrations.

Table 4: the SW/PW (%) is easily misunderstood; please comments given above.

Table 5: The DDVs given here are different from those mentioned in the text.

Table 6: Please change P-PO_4^{-3} to PO_4^{3-}P and so on.

Figure 1: Specify the symbols (solid circle and diamonds) for atmospheric riverine sampling sites.

Minor corrections:

Page 5082

Line 19: N/P ratios in the atmospheric deposition (∼233) and riverine discharge (∼28) revealed that —

P5083

L4: half of the amount observed in the ultra- —-

L25: hypothesized

P5084

L12: that atmospheric input of inorganic nitrogen species is sufficient to the nitrogen requirement in —

L19: (dry and wet) deposition

P5085

L8: collected between January 1999 and December 2007.

L26: River water samples were collected once per month between — (*A question: the storm water may be missed, but they perhaps contribute the majorities of the annual amount.*).

P5086

L16: (18.2 MΩ) — *(PLEASE specify the pH of Milli-Q water.)*

P5087

L18: The annual river discharge ($Q_{annual)}$ is provided —- (*I am not sure my correction* *is right*)

P5088

L5-10: *Please rephrase the two sentences.*

P5090

L9-10: *These numbers in the parentheses is very unclear to me.*

L18: a dust event observed from 18 to 20 October 2002 —

L20: during this dust episode —-

L25: a large dust plume from the Middle —-

P5091:

L9-10: *These numbers in the parentheses is very unclear to me.*

L16: — Si_{diss} in rainwater —-

L20-23: *Rewrite this sentence.*

L26: *Add the unit after 1.1.*

P5092:

L7: the atmosphere

L16: Influence of airflows on nutrients

L17: By applying the cluster analysis, the —- ($n>3100$) at 1 km

L22: contributes

L26: , and representing

P5093

L2: trajectories, respectively.

L8: in aerosol and rain

L10: for the remaining air flow. —– Si_{diss} in aerosol (rain) —-

L11: than the remaining

L12: were mainly affected —

L18: air flows originated from

L19: found comparable.

L20: ammonium, the concentrations —

L25: for the remaining —

P5094

L5: difference in seawater and pure water solubilities of aerosol P (—-

L10: those in pure water.

P5095:

L4: compared to

L5: two times

L6: the remaining — local and/or regional —

L7: a different dissolution character —

L11: 36 hours housing the same

L12: Si concentrations measured at

L13: compared to values obtained at 1 h

L14: *the concentration for which species??* obtained at 1, 3, and 6 h were found —

L16-17: Please clarify this point, as commented above.

L18: less pronounced compared to Si.

L21: to pH, the observed

L26: Si_{diss}, there

L27: results obtained for

P5096

L3: $NaNO_3$,

L7: *Please specify the time when the 20 samples were collected, which may be related to the size distribution.*

L13: based on an assumption that —

L15: nutrient to the Eastern

L9: dry deposition contributions amounting

L17: for the studied rivers.

L22: for the remaining —

P5098

L9: the contribution from the

L15: those in the winter —

L16: higher fluvial discharge in the transitional period.

L20: in the transitional period and summer.

P5099

L11: 28, and in contrast,

L19: DIN, higher than those required by —

P5100

L4: inputs to the Northeastern —

L7: variability, up to an order of magnitude on the daily basis.

L9: are affected by —

L15: Higher aerosol nitrate and ammonium concentrations in the summer were due to the lack —

L22: the former air flows.

L24: character of crustal

P101

L1-2: be the main fresh water source over the study region with nutrient contributions more than 85% of the total riverine nutrient inputs.

L8: more than the amounts required by

L10: Atmospheric and total (?) molar Si/N ratio *(Please clarify here)*

Table 1 caption: NH4+ concentrations in aerosols — period between —

Please change WVM to VWM.

Table 3 caption: Mean aerosol nutrient concentrations and volume-weighted mean (VWM) concentrations of nutrients in rainwater, as a function of the categorized three-day air-mass back —

Table 5 caption: Summary of dry deposition velocities of the analyzed aerosol nutrients applied in the present study and the literature for —.

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