

Interactive comment on “Atmospheric Water-Soluble Organic Nitrogen (WSON) in the Eastern Mediterranean: Origin and Ramifications Regarding Marine Productivity” by Münevver Nehir and Mustafa Koçak

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Q1: There have been some recent reviews of WSON which the authors might reference (e.g. Cape et al., 2011 Atmos. Res 102,30-48) since they summaries much of the material and offer a somewhat wider perspectives and more recent information on the composition of WSON.

A1: Cape et al., 2011 was also used for defining the composition of WSON, including vehicle exhaust, cooking, algal blooms and degraded proteins (see lines 48,49, 50 and

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52).

Q2: There is also now a global model of WSON (Kanakidou et al., 2012 Global Biogeochem. Cycl.26, doi10.1029/2011GB004277) which has contributed to an updated global nitrogen cycle revising the Duce et al 2008 paper cited (Jickells et al., 2017 Global Biogeochem. Cycl.31, doi10.1029/2016GB005586).

A2: Jickells et al. 2017 was used to update change in reactive nitrogen and reactive anthropogenic organic nitrogen from mid 1800 to 2000s (see lines 68-70).

Q3: Line 60, while amines will neutralise acids, it is not obvious the rest of WSON will.

A3: The sentence was changed as follow 'Similar to ammonium, 'some' organic nitrogen species such as urea and amines have acid-neutralizing capacities (Ge et al., 2011)'. Urea was kept in the text since it shows slightly alkaline character. Furthermore, amino-acids such as Lysine, Histidine and Arginine exhibit alkaline character (see line 58).

Q4: Line 62 I don't think Twohy discusses WSON.

A4: Twohy et al. (2005) has mentioned about organo-nitrogen compounds. To quote Twohy et al. 'Our analysis indicates that organic species do not have to be mixed with inorganic particles to act as CCN, and that organo-nitrogen compounds nucleate cloud droplets in the Indian Ocean. If these particles are present in other polluted areas, they could contribute substantially to the global indirect aerosol effect' (conclusion page 3, 12th paragraph). Therefore, if these organo-nitrogen compounds nucleate cloud droplets, they would be water-soluble.

Q5: Line 80 and later on, there is really pretty clear Evidence that the Eastern Mediterranean is P limited. There is a vast body of work by Krom and colleagues that supports this (see most recently Pawley et al 2017Global Biogeochem.Cycl.31, 1010-1031 and the earlier summary in Krom et al 2010Prog. In Oceanography 85,236-244) and my reading of the Yücel 2017 paper does not actually contradict this view.

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A5: This issue was clarified as suggested (see lines from 76 to 87).

Q6: Line81-2 It is mentioned a little bit later on, but not here, that Mace et al have reported WSON from exactly the same site as the study here. This should be noted here and also in section 3.1.

A6: Reference was noted as advised (see lines 88-89 and 296-297).

Q7: Note also the reference list lacks dates and while in the text the authors refer to Mace et al a,b and c, these are not identified in the references by these letters.

A7: Correction was made considering Mace et al 2003a, b and c (see lines from 783 to 790).

Q8: Analytical Methods. In general the results seem to be of good quality, although there is no mention of how blanks were determined (i.e. what procedures were used to create blank samples for analysis), what standards were used in analysis and whether any certified reference materials were used.

A8: As stated before Operational blank filters for aerosol were processed in the same way as the collected samples with the exception that no air was passed through the filters. Information about blanks for rain was added to text: Operational blanks for rain samples were taken by using 100 mL of Milli-Q water after cleaning the HDPE buckets with phosphate free detergent, HCl (10 %) and Milli-Q water (see lines from 139 to 141).Details about standard, recovery analysis and quality assurance for WSTN was given in Materials and Methods section (see lines from 169 to 178).

Q9: I do not really understand what the sentence line163-4 about blanks being <10 % means, Is this true for all ions?

A9: Sentence was clarified by using 'for all' (see line 189-190)

Q10: On line163 20 ppb is ambiguous, is it as ppb nitrogen and Why not use molar units as elsewhere in the paper?

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A10: Molar unit was used as suggested (see line 179).

Q11: Section 2.4 discusses the quite well known challenges of estimating WSON and its relatively low precision as a derived quantity (see Cape et al for instance). The precision of WSON depends a lot on the Relative concentrations of the three components of the total nitrogen analysis, so it is not possible really to quote a single number. The authors discussion e.g. lines 170-174 and 175 (and lines 221-222) does not really explain what they actually estimate the precision to be. A11: Modification was made as suggested (see lines from 208 to 216).

Q12: The use of PMF (which I am no expert on) here seems to require provision of precision estimates, but I do not understand how the arbitrary thresholds used here (line 185-7) were arrived at or how sensitive these results are to these values.

A12: Appendix was added in order to clarify uncertainty estimates (see lines from 602 to 633). As it is well known, it is impossible to include negative values when one carries out multivariate statistics. Application of PMF without negative values, yielded worse slope than that of obtained by using threshold. For instance, the slope of the estimated WSON against measured WSON was 30 % less than unity. Furthermore, DISP error estimates showed that there were factor swaps and significant change in Q during DISP. In other words, PMF application without threshold exhibited that solutions were not robust.

Q13: Section 2.6 As I understand it PMF is a form of principal component analysis and hence is an appropriate tool for this kind of source apportionment. I would suggest the authors may be better putting an explanation of the principal of the method here and putting the highly technical discussion in to some sort of appendix, because I think many readers will not really be able to follow this section.

A13: We agree with the comment. Consequently, appendix was added into the text (see lines from 602 to 6633).

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Q14: Section 3.1 and 3.2 I Wonder if these sections could be shortened a bit given that the results are broadly in line with other work in this region.

A14: As can be seen from the Table 2, there are only two references in the region (Mace et al., 2003 and Violaki and Mihalopoulos, 2010). If one relies on these two references, the scientific discussion and comparison would be insufficient to enrich the findings/arguments about WSON. Thus, the 3.1 and 3.2 were preserved as is.

Q15: Line 304-307 I do not disagree with the interpretation here, but it is worth noting that this does carry the implicit assumption that land based sources dominate the emission of WSON.

A15: We agree with the comment. '(iii) small contributions from non-land based local emissions such as sea salt and algal blooms' was added as third reason.

Q16: Section 3.3. this section is very general and the issue is approached in a more quantitative manner in 3.5 and 3.6, so I wonder if the section could be shortened.

A16: We agree that more detail was given in 3.5 and 3.6, however, temporal variability (Section 3.3) includes both daily and seasonal variability and it is only one and a half page. It was kept as is.

Q17: Section 3.4 Mace et al suggested that the Saharan Dust was a major source of WSON at this site and they did this I think by a correlation between nssCa²⁺ and WSON. Here the association with dust seems to be weaker but the discussion does not really address this point, but simply notes there is an association with dust. This could be discussed further.

A17: Regarding Mace et al., 2003a this summary may be made. The obtained samples only covers dust period. Indeed, there was a strong correlation between nssCa²⁺ and WSON ($R^2 = 0.75$). On the other hand, there was also a strong correlation between nitrate and WSON ($R^2 = 0.69$) (Mace et al., 2003a, page 5-7, Table 3). Subsequently, even during the dust period (from March 22 to May 4) it seems that WSON was almost

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equally impacted by mineral dust (not sure only from Sahara, see below) and man-made nitrate. Moreover, I am not sure whether all dust events were originated from Sahara Desert. For example, Figure 2a (Mace et al., 2003a, page 5-3) shows that on 5 April 2000 the Erdemli site was under the influence of the Middle East (air masses arriving at 1000 and 900 hPa) and Sahara (air masses arriving at 700 and 500 hPa) Deserts at the same time. However, such an interpretation in the text would be impolite since the authors only considered Saharan Dust in spite of strong correlation between nitrate and WSON and air masses back trajectories.

Q18: Section 3.5 In Table 5 the WSON and other parameters are classified into 5 groups, but in the text here the discussion splits the data in to two. It would be easier for the reader if the manuscript discussion and the tables did one or other of these, rather than mix them up in this way.

A18: Modification in this section was made as advised (see lines from 472 to 478).

Q19: Section 3.6 As noted earlier I am no expert PMF. The striking thing for me from Figure 6 and the discussion, is that WSON does not resolve in any simple way in to any of the components identified, emphasizing the multiplicity of sources that it has, and this is particularly striking within such a large data set. I would also query the interpretation of what the associations mean (lines 469-474). The authors interpret the results in terms of formation mechanisms, but an alternative explanation might be emission sources.

A19: We agree with the suggestion. Therefore, Factors 1, 2 and 5 were respectively attributed to ammonium-bisulfate (regional emissions), nitrate (combustion) and soil re-suspension (see lines 515-518 and 522-524).

Q20: Section 3.7 As noted earlier the Eastern Mediterranean appears to be phosphorus limited. If this is the case then the addition of nitrogen will not necessarily stimulate any additional primary production, but rather contribute to the high N/P ratio (see earlier Krom and Pawley references) and so the hypothesis behind the calculation (line 500-

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509) is flawed and the conclusions about the impacts on new production are incorrect. Section 4. This is really a summary and not a conclusion and simply repeats the earlier material.

A20: Please see A5. The last paragraph of section 3.7 was removed from the text as suggested by Reviewer 2. We agree that the section 3.4 is not a conclusion. Thus, the summary was used instead of conclusion (see line 560).

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2017-601/acp-2017-601-AC1-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-601>, 2017.

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