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Interactive comment on "Atmospheric Water Soluble Organic Nitrogen (WSON) over marine environments: a global perspective" *by* K. Violaki et al.

Anonymous Referee #2

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General comments:

I believe this paper would benefit from major revisions, but because the topic and data are sound, I hope to support the publication of this paper in a later version assuming revisions are satisfactory. Currently, the study has a compelling introduction, easy to understand figures, and sound methods and data collection. Their data add helpful new information in key regions where WSON has not previously been measured. Additionally, the topic is important. Elucidating the marine sources of WSON will enable better interpretation of previously collected marine WSON data because it will provide a better understanding of the fraction of new atmospheric N inputs (as opposed to recycled inputs) into the ocean, which has implications on marine productivity.

However, the discussion and interpretation of the data require major revisions before I would want to fully endorse its acceptance into Biogeosciences. In particular, I have not seen the evidence to convince me from their data that productive marine waters are an important source WSON, which is one of the main points of the paper. One main concern is that the primary basis for the argument is correlation used to indicate causation, which is problematic, particularly because the potential for other WSON sources that affect interpretation of the proposed relationship was not discussed satisfactorily. Because they rely so heavily on correlations, it is additionally problematic that the authors base their arguments only on r2 and p values, and neglect to show the actual data. This practice makes it difficult for the reader to put the r2 value in context of possible outliers skewing the relationships. In order to better assess whether other aerosol sources could be producing a false association between WSON and marine productivity indices, I suggest including a more thorough discussion of other chemical tracers and potentially, better verification of sources from satellite data to the extent possible. Additionally, the discussion would benefit from a more thorough comparison with related findings from other studies.

Specific comments

The most important comments are regarding the marine WSON source hypothesis. At all 3 sites I find that the evidence provided for the marine WSON source hypothesis needs more support to be valid.

Tropical N. Atlantic: p. 11370, line 4: The two final statements in this section need more evidence: a) "Marine sources seem to control the fine mode WSON concentration levels, since significant correlation of WSON was found with ss-SO42- ($r2 = 0.6$, $p < 0.001$, $n = 15$)" and b) "The highest concentration of WSON was observed on 3 August (Fig. 4), when the air mass back trajectory had marine origin (Fig. 3b)."

For statement a), I remind the authors that correlation does not equal causation, so perhaps a better wording would be something like, "high ss-SO4 values were asso-

ciated with high WSON values (r2 =. . .)". But even if the wording is changed, I still don't think one can really say that marine sources control the fine mode WSON at this site based only on the WSON/ss-SO4 association. First, a correlation of 0.6 still typically incorporates a great deal of variability. Secondly, the sample size is relatively small (n=15). Thirdly, assessments based on correlation coefficients alone can sometimes lead to false associations due to outliers. For this third reason, the r2 values by themselves are not particularly useful for the reader. Therefore, if the authors want to discuss the association between WSON and ss-SO4, I suggest adding a new figure showing the actual data the correlation is based on. Finally, and most importantly, because correlation does not equal causation, it is important to show that other data sources were closely monitored to rule out other WSON sources on the days that had high WSON and high ss-SO4 in combination. Because WSON can be transported long distances, there needs to be more evidence to make a compelling case for a large marine WSON source, particularly their hypothesis seems to directly contradict others studies that found low total WSON on clean marine days , including in the same study region of the tropical North Atlantic (e.g., Lesworth et al., 2010; Zamora et al., 2011) (not to mention the author's own findings at Amsterdam Island, where WSON was low even though upwind Chl a concentrations were still relatively high).

For statement b), I would not call that trajectory "purely marine" because it goes right by the coast of Africa where dust storms routinely blow and where pollution from northern Africa and Europe frequently mix in. In fact, when I looked at the AOD, true color, and CALIPSO aerosol subtypes for that day, it seems that there was a great deal of dust in the atmosphere above the sample (see Figures 1-3 in the supplement attached), which may have impacted the results, as dust is known to carry WSON. To me, this casts strong doubt on whether this was truly an example of a "purely marine" day and so this argument should not be used to support the hypothesis of a marine WSON source. If this sample, which the authors said was the sample with the highest concentration of WSON, was removed from the WSON-ssSO4 plot because of the likely interference from high dust concentrations, what would the resulting r2 and p value be?

South Atlantic: p. 11371, l. 3: "When the ship crossed the episode- A area (Fig. 6), air masses had pure marine origin with extremely low BC levels . . .." First, there was no clear definition for how a sample was determined to be "pure marine," so it is important to define that in the methods section. As far as I can tell though, in the South Atlantic a "pure marine" sample was defined from a combination of back trajectories, BC concentrations, and DMS levels, and at the other two sites, "pure marine" was defined only back trajectories. At minimum, that inconsistency should be noted and discussed. However, for the following reasons, I don't think the authors really have the basis to define air masses "pure marine" based on their current criteria anyway, and I strongly suggest rewording the sections that contain this phrase. First, back trajectories alone are problematic because air masses are constantly mixing and the older the back trajectory, the more error there is. For example, at least one of the other days in the tropical North Atlantic that was defined as having a "pure marine" source from a back trajectory actually likely had another significant dust WSON source (see my point in the comment above). The BC criteria, meanwhile, were unspecified and unsubstantiated. Please quantitatively define what is meant in the sentence above by "extremely low BC levels" and also please define the cutoffs that constituted "pure marine" air. While using BC as a tracer is helpful, it must be used in combination with other components before calling an air mass "pure marine". For example, dust is known to occur in the Southern Hemisphere (e.g., Johnson et al., 2010, Gasso et al. 2010; Gaiero et al., 2013) and that cannot be accounted for from BC alone. If DMS concentrations were also used to determine "pure marine" samples, that method would also be flawed, because while high DMS concentrations do indicate that an air mass passed over productive marine DMS sources, they don't tell one what other sources of WSON might be in the air mass concurrently. The three following points below are related to this issue:

South Atlantic: p. 11371, l. 1: "The evaluation of biogenic activity as primary source of atmospheric organic nitrogenous compounds was based on DMS, since it is considered as an indicator of marine biological activity (Sciare et al., 1999)." As mentioned, while DMS can indicate biological activity, it cannot be used to assess whether biologi-

cal activity is the main source of WSON.

South Atlantic: p. 11371, l. 3: "When the ship crossed the episode- A area (Fig. 6), air masses had pure marine origin with extremely low BC levels and the measured WSON average concentration was 11.3 $\pm$ 3.3 nmol N m-3. These samples presented high average contribution of WSON to TDN (84 %), which indicates an important role of the marine biological activity in the biogeochemical cycle of organic nitrogen." Because the authors have not convincingly shown that there are no other sources of WSON in the air, I don't think they have the basis to claim that the WSON is from a marine source and not some other source.

South Atlantic: p. 11371, l. 8 and Table 1: "For the samples collected over the middle southern Atlantic atmosphere, which is considered as remote marine area, the average concentration of WSON was much lower (1.1 $\pm$ 1.2 nmol N m-3) corresponding to 43 % of TDN." I notice from Fig. 6 that in some parts of these remote regions where WSON is low, DMS concentrations were equally high (e.g., from Jan 23-25) as the DMS levels when WSON levels were high (in the 11.3 $\pm$ 3.3 nmol N m-3 range). This information casts doubt on the marine WSON source hypothesis. Can the authors look at satellite data from this time period to see if there were other recognizable WSON sources during the episode A period? I am also unclear about which days were binned into "S. Atlantic Ocean, High Chl a marine area" and "middle S. Atlantic, Marine remote" in Table 1 and the samples discussed in the above text from the paper. Please a) clearly define what days were in each period, b) indicate on Figure 5 where remote vs. non-remote days were located, and c) explain the criteria for this binning. Based on Fig. 5, much of the cruise took place in high Chl a regions, and so I am unsure why the authors separated out "High Chl a" and "remote" periods, and I also think the term "High Chl a" in Table 1 might be a bit misleading. An alternative wording could be "Highest Chl a period"? Regarding the binning, how did the authors deal with days with low WSON but high DMS days- were these days included or excluded, and why? For Fig. 5, (this is only a suggestion), it would be interesting to plot SeaWiFS Chl a along the track against

WSON, DMS, and BC; that might make it easier for the reader to understand why the authors binned the days as they did.

Amsterdam Island: p. 11372, l. 18: "Significant correlation was also found between coarse mode MS and coarse mode WSON (r2 = 0.9, p < 0.0001, N = 10) during summer period." Based on the detection limits (DL) listed in the methods, it seems that the DL for WSON should be greater than $\sim$0.64 nmol N/m3 (as $\sim$0.64 nmol N/m3 appears to be the DL for TDN). That excludes all but 2 of the coarse sample values during the summer period as best I can tell based on Fig. 8. Therefore I think any correlations with MS for these samples are probably not valid. Plus, in Figure 8, I only see 6 samples of coarse WSON during the austral summer. Perhaps the symbols are hidden and there are more samples than I can discern (in which case the authors should change Fig. 8 so that they are more visible), but either way please check consistency here as N=10 was listed in the text.

Amsterdam Island: p. 11372, l. 15: "The fine mode WSON was found to correlate significantly with fine mode MS- (r2 = 0.7, p < 0.01, N = 9) during austral summer, implying that probably part of WSON was produced secondary from biogenic marine precursors, following similar production mechanism with MSA." Please plot the data. Again, beware correlation and causation issues. Because of the small sample size, I would change "implying that probably part of WSON was produced secondary from biogenic marine precursors" to "implying that part of WSON might have been produced secondarily from biogenic marine precursors"

Amsterdam Island: Figure 10: what is the thin yellow line? Did all upwind air pass through the dotted box, or is that only typical? Why didn't the authors do back trajectories like with the other two sites in the Atlantic? Are the data shown in Fig. 10 averaged for all of January (if so, please state that)? There still seems to be relatively high chlorophyll a upwind, so the low WSON seems to conflict with the suggestion that local marine sources are a large or dominant source of WSON in the S. Atlantic.

Other suggestions/comments (in no particular order) are listed as follows:

p. 11370, l. 11: “Two main episodes of phytoplankton blooms were encountered during the sampling period. These are clearly seen in Fig. 5, which depicts the chlorophyll a map derived from SeaWiFS satellite retrievals (http://disc.sci.gsfc.nasa.gov/giovanni) and referred to monthly average values (January 2007). The episode-A encountered by the ship over two days (30–31 January) and the episode-B began on 1 February and was followed until the end of the cruise.” First, I am unclear about why the authors differentiated between episodes in the first place. The first episode was said to occur from Jan. 30-31, and the next bloom started on Feb. 1 (the very next day), and went to the end of the cruise. So what is the scientific reason to differentiate between episodes a and b? On the map the bloom looks essentially contiguous, with the low point in chlorophyll a values present only because the ship went temporarily outside of the bloom. Also, wouldn’t February be a better month to average Chla over for Fig. 5 since that is when the blooms were, primarily? As an aside, when I tried to recreate Figure 5 from Giovanni (which is where the authors listed that they got the data), I got a slightly different looking picture with better data coverage (see Figure 4 in supplement attached). I wonder why this difference occurred? It could be possible that Giovanni altered something between when the authors downloaded the data and when I did? Either way, since now a version is available with better data coverage, perhaps the authors should use the more comprehensive data to overlay the cruise track instead? Or even better yet, they could obtain the values of satellite-derived chlorophyll a that coincide with the cruise track and plot those below Fig. 5. That would be a lot easier on the reader to interpret the location and strength of the blooms. Just a suggestion.

p. 11369, l. 14: “Almost 86% of WSON was found in the coarse mode atmospheric particles, denoting the important role of dust as a primary source of organic nitrogenous [compounds].” What evidence is there for dust being a primary rather than secondary source of WSON? Mace et al., 2003 presented the hypothesis that dust WSON might actually come mostly from adsorbed pollution, and this hypothesis has since been sup-

ported by subsequent studies (e.g., Zamora et al., 2011; Wang et al., 2013). Because the authors also mention that nss-SO4 was present, it seems possible that the WSON might have been from pollution mixed in with the dust rather than having dust itself be the primary source.

There were multiple other places in addition to the ones listed above where correlations were used to infer causation. I’d like to see more care being taken throughout the paper to reword these instances and to frame the interpretation with greater ambiguity. I also suggest adding figures plotting the data for any important correlations discussed in the paper.

While it appears that the methods for each study are sound, they are different for each of the sites. There were different collection filters (Teflon vs. quartz), collection methods (denuder vs. cascade impactor), desorption techniques (ultrasound vs. soft shaking), and pore size of extract filter (0.2 μm vs. 0.45 μm vs. unlisted for S. Atlantic (please do list this in the next version)). In the next version, please briefly discuss these differences and their potential impact on site intercomparison discussed in section 4.

p. 11369 line 15: “No correlation was found with inorganic nitrogen, indicating different sources.” No correlation with what? A dust tracer? Inorganic N? Any of the other tracer compounds? Please be more specific.

p. 11369: the information from the first paragraph would be clearer and easier for the reader to digest if organized in a Table.

p. 11371, second paragraph: This could also be better summarized in a table I think.

Technical corrections

Section 2.1.2, l. 13. a low volume aerosol sampler placed on [the] prow of the research vessel

p. 11365, l. 23:” Samples were stored at the ship in the freezer (4âŮęC) till the laboratory analysis.” Did the authors mean in the freezer -4 degrees, or in the refrigerator at

4 degrees?

Figure 1. The figure seems to indicate that Finokalia is a sampling site, which is a bit misleading. Perhaps better would be to distinguish between sites sampled in this study, and those discussed in context later by using different symbols and adding explanation of the symbols in the caption.

p. 11367 l. 13, please define LSCE

p. 11369 L. 4 and Table 1 caption, please define in the paper "D" and "Da" (aerosol diameter I presume), and make them consistent with each other throughout the paper.

Table 1 and Figures 2 and 4 captions, and throughout the text: I suggest changing North Atlantic to tropical North Atlantic. Or, samples were really only taken in the eastern part of the tropical N. Atlantic, being even more specific about the location.

Table 1: I find the titles of the columns to be confusing. Why are there 2 columns with the title "D(μm)"? I guess to show the cutoffs between "coarse" and "fine" mode fractions? But if that is the case, why is the "% to TDN" (which is also confusing wording to me but which I think means % contribution to TDN) less than 100% when coarse and fine are added together? Rewriting/ reorganizing these columns so that they are clearer would be helpful to the reader.

Fig. 6: is the Jan 21 sample taken over more than 24 hours (since the cruise started on the 19th?)

p. 11369 lines 12 and 14: did the authors mean to say, "organic nitrogenous compounds" in this sentence?

p. 11372. Methanesulfonate is defined (twice) as MS, but then the authors use MS- later. Please be consistent.

p. 11372, l. 10: "During austral summer increased concentrations of MS were observed that can be linked to a similar increase of marine productivity." Reference?

p. 11372, last paragraph: I think the authors can get rid of this paragraph as it does not add much to the main point.

References

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Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/11/C5053/2014/bgd-11-C5053-2014-supplement.pdf

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