

Interactive comment on “Sources of reactive nitrogen in marine aerosol over the Northwest Pacific Ocean in spring” by Li Luo et al.

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Point by point reply

This paper presents a very interesting and important data set on Nr aerosol concentrations as well as the $\delta^{15}\text{N}$ of total N and NO_3^- in aerosols. The aerosols were collected on ship transects from China to the Northwest Pacific Ocean, and as such are presented as marine aerosols. This is a dataset that should be published and it is important work.

Reply: Thanks for reviewer’s appreciation of the merit of our work.

However, given the incredibly strong anthropogenic source strength of Nr in this region, I do not think these are representative of marine aerosols. Rather, this is a presentation

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of the impact of continental/ anthropogenic aerosols on the coastal/near shore marine environment. It is a subtle, but important distinction.

Reply: Thanks for the suggestion. We added statements clearly present that the marine aerosol sampled in ECSs was co-influenced by both sea salt and continental/anthropogenic aerosols (Section 3.1 Paragraph 3). But in the main text, we still use “marine aerosol”. “The much higher water-soluble nitrogen species in the ECSs marine aerosol (compared to that in the NWPO aerosol) indicates that continental/anthropogenic Nr strongly affected the marine aerosol. However, the amounts of sea-salt ions (such as Na⁺) in the ECSs aerosols sampled in both 2014 (123 ± 98 nmol m⁻³; Luo et al., 2016) and 2015 (151 ± 164 nmol m⁻³; Luo et al., unpublished data) were higher than those in land aerosol sampled during spring (23 ± 7.8 nmol m⁻³ in Beijing; Zhang et al., 2013), which implies that those aerosols sampled in the ECSs were also significantly influenced by sea salt. Thus, we define the aerosol collected by ship over the ECSs as marine aerosol.”

Section 2.2.5: The aerosol extracts do not contain salts, which is typically why SPE is used prior to FT-ICR MS analysis. It is not clear why this procedure was followed and some justification should be provided? It will lead to loss of organic carbon and organic nitrogen, indeed the % recoveries are < 50% and it does not seem appropriate. FT-ICR MS analysis using negative ion mode means it is not comparable to Altieri et al., or Wozniak et al. In those studies they analyzed samples in the positive ion mode. The negative ion mode would detect organonitrate compounds, whereas the amine and amino-acid compounds are detected in the positive ion mode. The listed elemental ratios based on positive ion mode analysis are not at all applicable in this work. Given the use of SPE and the negative ion mode analysis, the FT-ICRMS analysis needs to be removed from the manuscript, or interpreted in a completely different manner.

Reply: This comment is well taken. We removed all the text about the FT-ICRMS from the manuscript, and the conclusion is not altered.

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I agree with page 1 line 24-26 – the anthropogenic signal is so strong that there is no way these aerosols represent a background signal at all. The classification needs to be explained in more detail, and changed to something more appropriate. It seems impossible that aerosols classified as “background” could have such high concentrations of Nr. It is more likely that all of these aerosol samples are heavily influenced by anthropogenic pollution, with the signal declining as the polluted air is mixed with clean air off shore. Any local marine signal would be swamped by the large continental sources.

Reply: Agree with the reviewer. We defined the term “background” in Section 2.1 Paragraph 2 prior to Discussion. “Hereafter, we define background aerosol as aerosol not impacted by either dust or sea fog, rather than representing pristine conditions, the background is an environmental baseline collected within the study area during the investigation period.”

The similarity in 2014 and 2015 WSON concentrations is interesting given different chlorophyll fields. It is critical that some basic sampling information such as aerosol size is presented.

Reply: The sampling information has been added into the Section 2.1 Paragraph 1. “Total suspended particulate samples were collected using a high-volume sampler (TE-5170D; Tisch Environmental, Inc.) with Whatman[®]41 cellulose filters ...”

In addition, the authors need to provide information on field blanks and procedural blanks, especially for WSON and ammonium concentrations.

Reply: Descriptions of the blank were added into Section 2.2.1 to describe the field blanks and procedural blanks. “Eight filters of the same type as those used to collect samples were taken as blanks. All blank filters and aerosol samples were stored at –20 °C during the sampling periods and underwent the same extraction procedure. The NO₃⁻, NH₄⁺ and WSON content of the blank filters comprised less than 1%, 4% and 9%, respectively, of the average concentration of the corresponding N species in the

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aerosol samples.”

In Section 2.2.3, please explain the recoveries of WSTN and TDN? How does n=6 if there were 44 and 39 aerosol samples analyzed?

Reply: The recoveries of WSTN and TDN represent the oxidation efficiency of prepared solution of N-containing organic and inorganic compounds standards (glycine, urea, ethylene diamine tetraacetic acid and ammonium sulfate) by using the alkaline potassium persulfate. The following sentences had been added into the Section 2.2.3. “To verify the WSTN and TDN oxidation efficiency, N-containing organic and inorganic compound standards (specifically, glycine, urea, ethylene diamine tetraacetic acid, and ammonium sulphate) were prepared in solution at a concentration of 800 μM -N for oxidation analysis. The recoveries of the N-containing compound standards under oxidation by alkaline potassium persulfate were within 95 ~ 105% (n = 6).”

What dry deposition velocities are used? There are large uncertainties associated with dry deposition velocities, which are size specific. If the aerosols are not size segregated, how can you apply a size-specific dry deposition velocity? These are going to be highly uncertain estimates and should be treated as such.

Reply: We agree. The dry deposition velocity varies by more than 3 orders of magnitude with particle size ranging from 0.1 to 100 μm (Hoppel et al., 2002). Thus, it is really hard to accurately estimate the N_r dry deposition by using TSP sample. In general, ammonium appears in submicron mode from 0.1 to 1 μm , with a small fraction residing in the coarser mode, by contrast, nitrate is distributed mainly in supermicron size ranging from 1 to 10 μm while WSON appears in a wide size spectrum. Thus, for any water-soluble nitrogen species, using a fixed deposition velocity to calculate the dry deposition might cause under- or over- estimation. In our observation, wind speed ranged from 0.8 to 18 m s^{-1} under wide RH ranging from 40 to 100%. Thus, it is not possible to provide variable dry deposition velocities for estimation N_r dry deposition under a wide range of environmental conditions; assumptions were made based on

existing knowledge. Here, deposition velocity of 2 cm s^{-1} was applied for nitrate, 0.1 cm s^{-1} for ammonium and 1.0 cm s^{-1} for WSON. We have detailed the issue of size and deposition velocity of nitrate, ammonium and WSON in our previous ACP paper (Luo et al.,2016). Following the reviewer's suggestion, the descriptions of deposition velocities of water-soluble nitrogen species were briefed in the Section 2.3. "The deposition velocities of water-soluble nitrogen species used herein were 2 cm s^{-1} for nitrate, 0.1 cm s^{-1} for ammonium, and 1.0 cm s^{-1} for WSON, which were consistent with our previous studies (Luo et al., 2016)."

Page 7 line 199-201: It's not clear what size the aerosols are, and so this comparison is difficult to understand. Regardless, these concentrations are incredibly high, and indicative of strong pollution sources.

Reply: Except the case for the Xi'an city, which was PM10, all other aerosols were collected comparably by TSP. We explicitly described the difference in the revised version in Section 3.1 Paragraph 2. (Details can be found in supplement)

If the authors want to claim that any of these aerosols are "background" aerosols, they need to find other background sites that have such high Nr concentrations.

Reply: Replied above.

Also, the data are very difficult to see on the log scale, it's a very large range of concentrations to present on one figure. This should be separated somehow.

Reply: Thanks for this suggestion. In this version, we added one more figure (i.e., y-axis is presented in liner scale) into supplementary material (Fig. S4). (Details can be found in supplement)

Page 7 line222, you can't tell the difference between 2014 and 2015 in the figures due to the log scale. A different way of presenting the data would help.

Reply: The y-axis now is in liner scale (attached). We also added descriptions of statistical significance ($p < 0.05$ for all cases) into figure 3 caption.(Details can be found

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in supplement)

I agree with the authors conclusion on page 8 paragraph 2 – the “background” aerosols should be re-labeled as it is very misleading.

Reply: We added the definition of “background” in Section 2.1 Paragraph 2.

Page 8 paragraph 3 – it is important to note that the surface seawater DON is the most likely source of primary WSON aerosols, but secondary WSON aerosols have many other sources, including e.g., surface ocean VOC emissions that go on to oxidize in the atmosphere and form secondary N-containing SOA.

Reply: Thanks for the suggestion. We added description of secondary WSON aerosols into the Section 3.1 Paragraph 6. “However, the sources of marine aerosol WSON are complex mixture which composed of primary marine organic N and secondary N-containing organic aerosol. Biogenic organic material in SSW can be injected into the atmosphere to form an ice cloud via bubble bursting at the atmosphere-ocean interface (Wilson et al., 2015), this is probably the primary WSON aerosol source. Volatile organic compounds emitted from the surface ocean can react with NO_x and NH_x in the atmosphere to form secondary N-containing organic aerosol (Fischer et al., 2014; Liu et al., 2015). ”

Section 3.2 should be removed or reinterpreted given the focus on negative mode CHON compounds identified here.

Reply: The part of FT-ICRMS has been removed.

Page 9 section 3.3 second paragraph. There is a large difference in WSTN ₁₅N from 2014 to 2015 in these aerosols. This should be discussed. Figure 6 and discussion thereof: This is not a valid approach to understanding what is driving the ₁₅N of WSTN. A cross-plot of ₁₅N-NO₃⁻ vs ₁₅N-WSTON would provide more information on the influence of nitrate on the total N isotopic composition. Looking at figure 5, it looks like nitrate ₁₅N is a main control on the ₁₅N-WSTN. The lack of correlation between

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_15N WSTN and the relative concentration of NO₃⁻ is not useful. The relationship between the _15N RN and the relative concentrations of NH₄⁺ would be useful, but is not presented.

Reply: Thanks for the suggestions. The scatter plots of $\delta^{15}\text{N}$ -WSTN vs. $\delta^{15}\text{N}$ -NO₃⁻, $\delta^{15}\text{N}$ -WSTN vs. NO₃⁻, $\delta^{15}\text{N}$ -RN vs. NH₄⁺ and $\delta^{15}\text{N}$ -RN vs. NH₄⁺/RN have been added as Figure S7 and Figure S8 in the new version, and we redraw the Figure 5 and we rewrite the Section 3.2 Paragraph 1-3. (Details can be found in supplement)

Page 10 paragraph line 300, it is also a possibility that the aerosol WSON is secondary organic aerosol, which may have had its 15N altered by transport or chemical reactions. This is a very over-simplified approach to the interpretation of the 15N-WSON data.

Reply: We agree with the reviewer, however, there are limited studies of 15N about the marine aerosol WSON. The multiple sources of marine aerosol WSON and $\delta^{15}\text{N}$ -WSON fractionation during the processes of secondary N-containing organic aerosol formation are not clear to date. We discussed the possible causes to modulate $\delta^{15}\text{N}$ -WSON in the last paragraph in Section 3.2 and highlighted more studies in future are needed for the secondary marine N-containing organic aerosol, particularly from the 15N scope. “these high $\delta^{15}\text{N}$ -RN values may be attributable to $\delta^{15}\text{N}$ fractionation and 15N enrichment in the WSON during processes such as secondary N-containing organic aerosol formation by the reaction of NH_x or NO_x with organic aerosol (Fischer et al., 2014; Liu et al., 2015), complex atmospheric chemical reactions (i.e. the photolysis of organic nitrogen into ammonium; Paulot et al., 2015), aerosol WSON aging process, and in-cloud scavenging (Altieri et al., 2016). More studies are needed to explore nitrogen transformation processes, especially those focusing on secondary N-containing organic aerosol in the atmosphere from an isotopic perspective.”

Section 3.4 is too speculative given the limited information presented. Are the ammonium, nitrate, and WSON concentrations statistically different from 2014 to 2015 and between the three classifications? Is there a statistically significant relationship be-

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tween the $\delta^{15}\text{N}$ of DON in seawater or $\delta^{15}\text{N}$ NO_3^- in seawater and the $\delta^{15}\text{N}$ of TN, NO_3^- , or RN in the aerosols?

Reply: Thanks for the suggestion. The scatter plot of $\delta^{15}\text{N}$ -DON in SSW vs. $\delta^{15}\text{N}$ of aerosol NO_3^- , WSTN and RN in 2015 cruise are attached below. There were no significant relationship in scatter plots of the $\delta^{15}\text{N}$ -DON in SSW against the aerosol $\delta^{15}\text{N}$ - NO_3^- , RN and WSTN sampled correspondingly in time and space. According to the reviewer's suggestion, we rewrite the Section 3.3 Paragraph 2. (Details can be found in supplement)

Table 1. How are aerosol concentrations volume weighted? Is this a mass weighted average?

Reply: The volume weighted mean (C) calculated by the following equation: $C = \frac{\sum_{i=1}^n C_i V_i}{\sum_{i=1}^n V_i}$

where C_i is the concentration of water-soluble nitrogen species in aerosol, V_i is the sampling volume for an aerosol, n is the number of sample.

Figure 1. It is not clear what "regional wind streamlines" are or where they came from. The blue on the background of the figure makes it difficult to see the symbols.

Reply: We enlarged streamlines and modified background color accordingly in Figure 1.

Figure 3. The caption says a is nitrate and b is ammonium, but they are labeled in the opposite manner.

Reply: Corrected.

Figure 4 should be removed.

Reply: Removed.

Figure 6. The caption says a is concentration and b is $\delta^{15}\text{N}$ but the plots are the

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opposite.

Reply: Corrected.

Abstract: Line 14 insert “of” between transport and anthropogenic, line 15 “continents may exert a profound impact”, line 16 should read “surface ocean” instead of “marine biogenic”,

Reply: Modified as suggested.

line 18 do the authors mean in the open ocean or do they mean in the atmosphere?,

Reply: Modified as suggested.

Line 26 are the concentrations statistically higher in 2014? If so this should be presented in the text.

Reply: We presented the statistical significance ($p < 0.05$ for all cases) between 2014 and 2015 in this version.

Introduction: Define SSW on first use.

Reply: Defined in the Introduction.

Page 3 paragraph 1 should clearly state that they are referring to primary WSON aerosols.

Reply: Thanks. Primary WSON aerosol has been clearly stated in the new version.

Page 8 second paragraph. It's not clear what is meant by “atmospheric diffusion”

Reply: “Atmospheric diffusion” has been changed into “atmospheric long-range transport”

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925-930, doi:10.1073/pnas.1516847113, 2016. Fischer, E. V., Jacob, D. J., Yantosca, R. M., Sulprizio, M. P., Millet, D. B., Mao, J., Paulot, F., Singh, H. B., Roiger, A., Ries, L., Talbot, R. W., Dzepina, K., and Pandey Deolal, S.: Atmospheric peroxyacetyl nitrate (PAN): a global budget and source attribution, *Atmospheric Chemistry and Physics*, 14, 2679-2698, doi:10.5194/acp-14-2679-2014, 2014. Hoppel, W., Frick, G., and Fitzgerald, J.: Surface source function for sea-salt aerosol and aerosol dry deposition to the ocean surface, *J. Geophys. Res.-Atmos.*, 107, AAC7.1–AAC7.17, doi:10.1029/2001JD002014, 2002. Liu Y, Liggio J, Staebler R, et al. Reactive uptake of ammonia to secondary organic aerosols: kinetics of organonitrogen formation[J]. *Atmospheric Chemistry & Physics*, 2015, 15(23):17449-17490. Luo, L., Yao, X. H., Gao, H. W., Hsu, S. C., Li, J. W., and Kao, S. J.: Nitrogen speciation in various types of aerosols in spring over the northwestern Pacific Ocean. *Atmospheric Chemistry and Physics*, 16, 325-341, doi:10.5194/acp-16-325-2016, 2016. Paulot, F., Jacob, D. J., Johnson, M. T., Bell, T. G., Baker, A. R., Keene, W. C., Lima, I. D., Doney, S. C., and Stock, C. A.: Global oceanic emission of ammonia: Constraints from seawater and atmospheric observations, *Global Biogeochemical Cycles*, 29, 1165-1178, doi:10.1002/2015gb005106, 2015. Wilson, T. W., Ladino, L. A., Alpert, P. A., Breckels, M. N., Brooks, I. M., Browse, J., Burrows, S. M., Carslaw, K. S., Huffman, J. A., Judd, C., Kalthau, W. P., Mason, R. H., McFiggans, G., Miller, L. A., Najera, J. J., Polishchuk, E., Rae, S., Schiller, C. L., Si, M., Temprado, J. V., Whale, T. F., Wong, J. P., Wurl, O., Yakobi-Hancock, J. D., Abbatt, J. P., Aller, J. Y., Bertram, A. K., Knopf, D. A., and Murray, B. J.: A marine biogenic source of atmospheric ice-nucleating particles, *Nature*, 525, 234-238, doi:10.1038/nature14986, 2015. Zhang, R., Jing, J., Tao, J., Hsu, S.-C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z.: Chemical characterization and source apportionment of PM_{2.5} in Beijing: seasonal perspective, *Atmos. Chem. Phys.*, 13, 7053–7074, doi:10.5194/acp-13-7053-2013, 2013.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2017-846/acp-2017-846-AC2->

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