

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

Li Luo et al.

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Point by point reply

This manuscript describes ship-board measurements of marine aerosols collected during two cruises around the East China Sea and the northwestern Pacific Ocean in 2014 and 2015. In this manuscript, authors reported concentrations of water-soluble total nitrogen (WSTN), water-soluble organic nitrogen (WSON), nitrate (NO₃⁻) and ammonium (NH₄⁺), and values of $\delta^{15}\text{N}$ -WSTN and $\delta^{15}\text{N}$ -NO₃⁻ in aerosols as well as dissolved organic nitrogen (DON) and NO₃⁻ concentrations and $\delta^{15}\text{N}$ -DON and $\delta^{15}\text{N}$ -NO₃⁻ values in sea surface water, which provide good indications where future studies can understand possible sources of atmospheric WSON and air-sea exchange of N species. I

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believe that the contents, including data, of the manuscript should be eventually published because of scarcity of atmospheric WSON observation and its significance in biogeochemical N cycle.

Reply: Thanks for reviewer's appreciation of our data and the scientific significance.

I recommend publication of the manuscript after a major revision and the improvement of English.

Reply: We paid for editing service.

1. The title of this manuscript is “Sources of reactive nitrogen in marine aerosol over the Northwest Pacific Ocean in spring”; however, the authors mainly described the spatial distributions and concentrations of atmospheric reactive N species and potential sources of WSON. I recommend the authors to describe in their manuscript the sources of atmospheric inorganic N species, although they are relatively well-known compared to that of WSON.

Reply: Thanks for suggestion. We added more discussions of the sources of atmospheric inorganic N into Section 3.1 Paragraph 5. (Details can be found in supplement)

2. (Page 4, line 98-116) It is not clear that how many, what kind of aerosol samplers and filters were used during the cruises, and how avoided contamination from ship's exhaust. Was a impactor used to separate PM_{2.5} and PM₁₀? More detail information on sampling method should be described in the manuscript, although the authors referred to Luo et al. (2016).

Reply: Aerosol sampling information including the instrument model, company, aerosol type and sampling filter have been added into Section 2.1. No separation for PM_{2.5} and PM₁₀. Follow the reviewer's suggestion, the following explanation added into the Section 2.1. “ To avoid self-contamination from the research vessel, the TSP sampler was installed on the top of the tower at the ship head, and aerosols were sampled only during travel. More information about self-contamination from ship exhaust can

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be found in Luo et al. (2016).”

In general, a pre-combusted glass fiber or a quartz filter is used for determination of WSON. If the authors used the same method for aerosol sampling described in Luo et al. (2016), the authors should explain about the treatment of aerosol filter samples and field blank concentrations and blank correction, because Luo et al. (2016) used a Whatman 41 cellulose filter.

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 aerosol samples.”

For determination of DON in sea surface water, the authors mentioned that a 0.2 μm filter was used to remove particulate matters in sea surface water. Usually, a pre-combusted GF/F filter is used to remove particulate matter and minimize the influence of organic matter from the filters on DON concentration in seawater. Please update that what kind of filter was used for filtration of seawater sample. I am also wondering if any consensus reference material (CRM, e.g., deep Florida Strait water from Hansell lab, University of Miami) was used during DON measurement to check the accuracy of analysis.

Reply: The filter information has been added into the Section 2.1. The measured accuracy verified by our laboratory standard rather than other reference material, and the oxidation efficiency also has been added into the Section 2.2.3.(Details can be found in supplement)

(Page 6, line 188-Page 7, line 191) Dry deposition velocity. It is unclear if marine aerosols are segregated into PM_{2.5} and PM₁₀ during the aerosol sampling as men-

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tioned in question 2. Although size distributions of atmospheric N species can vary on meteorological conditions, it is known that, in the marine atmosphere, both atmospheric NH₄⁺ and WSON primarily exist on fine mode aerosols, whereas atmospheric NO₃⁻ is predominantly associated with coarse mode aerosols (e.g., Nakamura et al., 2006). I recommend the authors to describe more detail that what dry deposition velocity was used for each N species.

Reply: Thanks for the suggestion. The detail deposition velocity has been added into 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).”

4. (Page 8, line 228-232) The authors compared their NH₄⁺ and NO₃⁻ concentrations with those by Miyazaki et al. (2011) to explain why higher concentrations of inorganic N species were observed during the period of this study (spring). The authors mentioned that the study by Miyazaki et al. (2011) was carried out over the same regions. I doubt about it. The cruise by Miyazaki et al. (2011) was conducted from 44°N to 10°N along 155°E, which covers the subarctic to subtropical northwestern Pacific region. Although the study by Miyazaki et al. (2011) was carried out in summer, different sampling season is not the only reason why the authors observed high inorganic N species during their study period.

Reply: Agree. Since there were no more data of NH₄⁺ and NO₃⁻ in aerosol sampled on the same season and adjacent area, we can only compare with aerosol collected cover the western North Pacific Ocean. Base on the statistical significance (p < 0.05 for all cases), and we rewrite the Section 3.1 Paragraph 5 to discuss the variations of inorganic N in marine aerosol over the NWPO. (Details can be found in supplement)

5. (Page 8, line 233-242) The authors described that “Likely the source of WSON in background aerosol did not share the same source with NH₄⁺ and NO₃⁻” (line 234-235), as if DON in sea surface water is the only source of atmospheric WSON in

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the open ocean. What is the grounds for this? Because high atmospheric WSON and inorganic N species concentrations were observed in the East China Sea and inorganic N was also detected in the open ocean, the long range transport of anthropogenic WSON to the open ocean should be considered.

Reply: Thanks for suggestion. We agree with that DON in sea surface water is not the only source of atmospheric WSON in the open ocean and aerosol WSON collected in the NWPO also influenced by the anthropogenic emission. Thus, we rewrite this sentence to make it read clearly, and the anthropogenic WSON to the open ocean also added in Section 3.1 Paragraph 6.(Details can be found in supplement)

6. (Page 8, line 252-Page 9, line 263) The results of characteristics of CHON molecular compounds shows that 13%, 3% and 19% of marine aerosols collected in the East China Sea, northwestern Pacific Ocean during dust period and northwestern Pacific Ocean during non dust period, were derived from biological sources, respectively. Does this mean that 87%, 97%, and 81% of marine aerosols collected in the same regions were affected by anthropogenic sources? It seems like the contribution of biogenic sources to atmospheric WSON is still low in the open ocean. What is the contribution of biologically-derived atmospheric WSON in the other oceanic regions?

Reply: Part of FT-ICRMS has been removed, the conclusion is not altered.

7. (Page 11, line 331-Page 12, line 355) The authors described that atmospheric reactive N dry deposition flux can account for 14%-58% of the low $\delta^{15}\text{N-NO}_3^-$ in the northwestern Pacific Ocean during the spring. It is surprising to me that atmospheric reactive N deposition has a significant influence on $\delta^{15}\text{N-NO}_3^-$ values. My question is that dry deposition of atmospheric reactive N is strong enough to affect or change $\delta^{15}\text{N-NO}_3^-$ values below the thermocline in the northwestern Pacific Ocean? What is the depth of thermocline in the northwestern Pacific Ocean in the spring season? I recommend the authors to estimate the contribution of atmospheric reactive N dry deposition to primary production in their study area. I think most primary production

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in the East China Sea and northwestern Pacific Ocean is controlled by nutrients in seawater, which implies that main factor for controlling $\delta^{15}\text{N-NO}_3^-$ values in the ocean is marine N cycle.

Reply: Thanks for the suggestion. We rewrite the Section 3.3 Paragraph 2.(Details can be found in supplement)

1. (Page 5, line 136-137) How did the authors obtain the recovery efficiency (i.e.,95-105% (n = 6)) of WSTN and TDN?

Reply: The recoveries of WSTN and TDN are the oxidation efficiency of prepared solution of N-containing organic and inorganic compounds standards (glycine, urea, ethylene diamine tetraacetic acid and ammonium sulfate) by 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 $\mu\text{M-N}$ for oxidation analysis. The recoveries of the N-containing compound standards under oxidation by alkaline potassium persulfate were within 95 ~ 105% (n = 6)"

2. (Page 5, 155-156) The authors mentioned that the extraction efficiency on a carbon basis was on average $46\pm 24\%$ (n = 44). Does it mean that 64% of organic compounds in the extract was not identified?

Reply: This part has been removed.

3. (Page 6, line 159-163) The uncertainty of WSON estimated from propagating errors of WSTN, NO_3^- and NH_4^+ should be added.

Reply: The errors propagation has been added into the Section 2.3. "The standard errors propagated through the WSON calculation for the 2014 data can be found in Luo et al. (2016). For 2015, the standard errors propagated through WSON calculation varied from sample to sample from 7 to 210%; the average standard error of all samples

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was 33%.”

(Page 6, line 175) The authors mentioned that [NH₄⁺] in sea surface water typically less than 0.05 μmol L⁻¹. Is this a common condition in the East China Sea and the Northwestern Pacific Ocean during the sampling period (i.e., spring season)? Sea surface [NH₄⁺] can vary depending on sampling season and locations.

Reply: Reviewer is right. [NH₄⁺] in sea surface water varies depending on sampling season and locations. However, NH₄⁺ is much less than DON in this cruise agreeing with common sense for open oceans due to high bio-affinity of NH₄⁺. In this version, we eliminate “typically” in old statement to avoid confusion. The revised statement is “Since the average [NH₄⁺] in SSW at the selected sites during the 2015 cruise (12 sites and 23 samples) was 0.05 μM, which is much less than DON in μM level. . .”

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2017-846/acp-2017-846-AC3-supplement.zip>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-846>, 2017.