

Interactive comment on “Nitrogen speciation in various types of aerosol in spring over the northwestern Pacific Ocean” by L. Luo et al.

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Point by point reply

Anthropogenic activity is increasing nitrogen inputs to the oceans particularly downwind of fast growing economies such as in Asia and there is evidence that the deposition of this nitrogen to marine waters may be sufficient to cause a deleterious effect. This paper includes as noted later one very impressive illustration of this. This paper adds further information on deposition in this region and is therefore valuable although I would suggest it needs a few modifications before final publication.

Thanks for reviewer's appreciation of the merit of our story.

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One important general point that I think may need to be included in this paper is a discussion of the relationship between fog, aerosol and precipitation. There have now been several papers, at least some of which are referenced here, that illustrate that fogs are relatively regular occurrences in this region and may be important vectors of nitrogen deposition. This paper contributes further to this information. It is clear that fogs can contain high concentrations of many components and I think that has been known for many years from other settings such as the acid rain debate. However, although fogs can be sampled by aerosol collectors, or indeed by specialist fog samplers, I am not really sure if it is appropriate to compare aerosols collected under normal conditions and under fogs, since fog seem to me to be somewhere between rain and aerosol.

Thanks for this comment. We will add more descriptions into Introduction in Page 25586 Line 5 as below. “Fog is the intermediate stage between precipitation and aerosol. Fog forms by the activation of particulate with subsequent growth and incorporation of other gases and particles (Cape et al., 2011). Fog droplet is smaller in size when compares to rain drops, however, concentrations of water-soluble species in fog water were not necessarily to be higher or lower than that of precipitation (Sasakawa et al., 2002; Watanabe et al., 2006; Jung et al., 2013). Fogs can be sampled by specialist fog samplers; however, during aerosol sampling on the sea there is no way to avoid fog once sea fog forms. Fog chemistry was well studied previously on land and its impacts on terrestrial ecosystems were also highlighted (Chang et al., 2002; Lange et al., 2003). Moreover, researchers designed experiments to examine the aerosol chemistry for pre- and post- fog formation periods to explore the inland fog impact on aerosol chemistry (Biswas et al., 2008; Safai et al., 2009). Nevertheless, sea fog impact on aerosol, particularly, in the coastal and marginal seas of China has not yet been studied.”

Gas exchange processes between water (fog) droplets and aerosol particles may be different and hence if the observed differences in composition between fogs and other

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aerosols (e.g. 3.2, 3.3 Table 2) represent differences in sources, cycling or simply that they are different types of atmospheric particles. It is also not really clear to me how to convert concentrations to fluxes since conventional deposition velocities are not appropriate. This comment does not invalidate any of the information here, but just to caution that any comparison needs to be done carefully.

Reviewer is right. The chemistry of these aerosols we collected have altered by sea fog due to different addition, removal and cycling processes including gas exchange. Even aerosols with the same property may have changed into entirely different chemistry if aerosols have experienced different flow path with various temperature and humidity (formation history, as mentioned in Introduction), not mentioning after sea fog modification. We did not collect fog; yet, our aerosol collection was under influenced by fog (contamination). The aerosol was sampled by TSP, thus, the concentration unit is ng m^{-3} . We clearly knew that aerosol may act as a precursor for fog formation, but this does not necessarily mean all the aerosols we sampled were directly associated with fog. This is also why we can only defined our sample as “sea-fog modified aerosol”. As reviewer mentioned, the deposition rate of fog may differ from that of aerosol, yet, no technology so far to separate aerosol and fog droplet during aerosol sampling. Nevertheless, we observed distinctive chemistry for this type of aerosol either comparing with aerosols sampled during the same cruise or comparing with “non-foggy” aerosols collected in the ECS in previous study. Meanwhile, we believed the deposition of nitrogen species will be also changed by sea fog formation. As replied below, we will add more descriptions about the uncertainty of deposition velocity in our estimation, particularly, sea-fog modified aerosol deposition.

Page 25587 Line 8 Sampling only when “cruising”, presumably meaning the ship is moving forward, does not of itself guarantee clean sampling – it is about wind direction in relation to that ship’s moment.

Agree. It is difficult indeed to avoid contamination from the vessel itself. Based on simultaneous one-second particle number concentration measurements made by Op-

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tical Particle Sizer (Tsi, US), we found ship plumes affect the TSP sampling occasionally during the cruising (data will be presented in a separate paper). We calculated the short-period plume contribution to the measured volume particle concentration of PM10 during each TSP sampling (self-contamination) and the contribution was less than 3%. According to this comment, we added above descriptions into sampling descriptions to let readers know the degree of self-contamination.

Page 25589 Line 9 it is probably worth adding a reference for sea water composition.

Chester, (1990) has been added.

RA calculation – this is really deriving the acidity from an ion balance calculation, which is OK but does ignore other ions such as bicarbonate which may be there at higher pH. It’s also not quite clear why a ratio rather than a cations-anions approach is preferable so I would suggest this approach needs bit of explanation and justification.

Thanks for this suggestion. Both approaches had been applied previously basing on the same concept of “imbalance of cations and anions”. The imbalance was basically caused by non-detected ions such as H^+ and HCO_3^- and CO_3^{2-} . Thus, both approaches are correct in terms of revealing the imbalance. However, when the amount of measured total ions distribute over a wide range (by a factor of 20 in our case), the ratio measure (the slope of the scatter plot of total anions vs. cations in ng m^{-3}) will be more effective to present the “relative” acidity. By contrast, the absolute value of imbalance (total cations – total anions) represents absolute acidity, which is applicable for a dataset with narrower range of ion concentration. In revision, we added one more reference (Kerminen et al., 2001) as well as explanations for the rationale of using RA.

Page 25589 Line 20 I assume the WSON error estimate is an average because it must be vary from sample to sample.

Thanks for this suggestion. The sentence is now “The standard errors propagated through WSON calculation vary from sample to sample (17% to 1500%). The average

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standard error is 116% when all samples are considered and is 81% when the extreme value is excluded.”

Section 2.3 It is important in any calculation of this type to emphasize the uncertainty in deposition velocities, particularly where wind speed and size distribution are not well known as here – a recent paper by Baker et al 2013 (DOI: 10.1002/gbc.20062) illustrates some of the difficulties in this.

This suggestion is well taken. In the version, we added discussions about uncertainties regarding wind speed changes and unknown grain size distribution. Baker et al. (2013) had been added in to Reference also.

Page 25592 Line 11 dust is highly variable as these authors know well, so 5 samples is a small basis for producing average values. The authors seem to be using 1000 ng/m³ as a threshold for dusty samples (see also the end of section 3.1) but I don't think this is stated.

In fact, we did not use a threshold value to define dust aerosol. The dashed line in Fig. 3 was just a reference line for background aerosol, which has concentrations significantly lower than other two types (See panel A with linear y-axis below). Actually, we provided CALIPSO Lidar Browse Images in Supplementary Information in the old version; yet, we missed to mention this criterion in the main text clearly. This is our mistake. In this version, we make a clearer CALIPSO images including satellite orbit trajectories into Figure S1 (see panel B below). The consistency between AI-defined dust aerosol and occurrence of dust and polluted dust defined by NASA will be presented in the newer version.

Page 25592 Line 15-20 the discussion of AI solubility here is difficult to follow partly because Fig3 does not contain an explicit AI solubility and also because of the earlier noted differently of really understanding their RA term.

Reviewer is correct. We should not mention solubility here in Section 3.1 (Aerosol

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type classification) and ask readers to “see below”. In this version, we added solubility estimate into Table 2 to help readers to follow our illustrations and discuss this issue latter in Section 3.3.1. rather than in Section 3.1.

Page 25594 Line 1-14 There are clearly several sources of Ca and K including seawater and dust but I suspect that beyond stating this, the authors could shorten this section and remove some vague speculation.

As suggested, we deleted the speculative part associated with fertilized soil and the spatial heterogeneity of seawater major ions.

Page 25594 Line 15-20 The tabulated data is in nM/m³ and yet figure 5 is in nequiv/m³ with no explanation. I would do everything in one unit and this affects the statements on ammonium/sulphate ion balances.

We now apply nM m⁻³ throughout entire paper except the part about ion stoichiometry, which is related to charge balance.

It is probably worth noting the importance of ammonia emissions in Asia which supply this neutralising ammonia.

As suggested, we added one sentence for the importance of ammonia emissions in Asia.

Page 25596 Line 15-20 rates of NO_x oxidation may also be important.

We added one reference and two sentences as below to discussion the lifetime and oxidation of NO_x. “The lifetime of NO_x in boundary layer is generally less than 2 days (Liang et al., 1998). Basing on our back trajectory analysis, the travel time of air mass from China inland to the marginal seas is long enough for oxidation of NO_x into HNO₃.”

Page 25596 Line 23 to Page 25597 Line 2 include references to explain the sources of the Jeju data and as noted before I am not really sure that it is simple to compare fog and aerosol in this way. They are obviously different but there are several possible

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explanations of why.

As indicated in Introduction, no data for aerosol collected on the sea or island during foggy day was reported so far. To compare with aerosols collected in non-foggy days is the only way and also meaningful. In fact, we proposed several possibilities for nitrogenous compound enrichment in the paragraph before the comparison (specifically on NH_4^+ and NO_3^-) among datasets. In this new version, we added more discussions about the possible causes and switched the two paragraphs to make the reading smooth.

Page 25597 Line 9-11. Without some knowledge of particle size I don't think you can say whether sulphuric or nitric acid is neutralized by ammonium, you simply have the ratio of ammonium to nitrate+2xsulphate on a molar basis.

Agree with reviewer. We delete the specific sentence and the deletion does not influence the paragraph integrity.

Page 25597 Line 20-30 Concentrations differences for WSON between aerosols and fog do not tell you about scavenging I think and the different WSON% of TN suggests different source regions to me.

According to this comments, we adjust the sentence to "Such high WSON concentration but low WSON% in TDN in sea fog modified aerosol may indicate the lower scavenging efficiency of WSON relative to other nitrogen species or its source region is different or both."

Section 3.3.3 As the authors show these aerosols are not at all "background" but quite contaminated so I would suggest changing the naming.

We added a few lines in Section 3.1, Aerosol type classification, to define the term "background". "Here in this paper, background aerosol stands for non-dusty and non-foggy aerosol in our classification. It is more like a baseline aerosol collected within the study area during the investigating period. Note that "background" may vary over

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space and time and it does not necessarily to be pristine."

The discussion of WSON sources in section 3.3.3 seems to assume there is one single source and to confuse the reader by arguing for no marine source (line 9) and a marine source (line 26). There are multiple sources of WSON (see for example Cape et al., 2011 review in atmospheric research).

We did not make a clear point. What we want to state is that we do not have "direct evidence (i.e., biological productivity data)" to support the natural WSON sourced from marine. Nevertheless, we have "indirect evidence", that is, the wind-driven sea spray. In the revision, we will clarify this part and add Cape et al., 2011 into References.

The discussion on Page 25600 Line 0-8 about sources of nitrate and ammonium from seawater I think is a bit confusing – it is very hard to see seawater as a significant source of nitrate and ammonium to aerosols, and I do not really understand the reasons for arguing for a source of ammonium and nitrate from photolysed marine DON.

We rewrote these two paragraphs to avoid confusing. In fact, we indicated that the seawater is impossible to be a source of aerosol nitrate and ammonium due to their low concentrations (a few tens to hundreds nM) in surface ocean. By contrast, DON concentration in the surface ocean is 1 to 2 orders of magnitude higher than ammonium and nitrate, thus, the surface ocean can act as a potential source of WSON. That is also why we emphasized the resemblance among these positive correlations of aerosol WSON, sea salt ions (Na^+ , Cl^- and Mg^{2+}) against wind speed. On the contrary, over a wide range of wind speed we observed relatively narrow concentration ranges of aerosol ammonium and nitrate. Since high wind speed implies vigorous exchange on the air-sea interface, during which both sea salt emission and scavenging were supposed to be high. Under efficient scavenging condition, to maintain a relatively uniform nitrate/ammonium concentration (quasi-static) some supply processes are need for compensation. Since the surface ocean is not a possible source for both ammonium and nitrate, therefore, we suggested that the alternative supplies might include

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deposition from the upper atmosphere and photochemical production. Nevertheless, we will reorganize these two paragraphs to clarify our arguments.

Section 3.4 Others have done this kind of comparison of WSON and TN (e.g Jickells et al. DOI: 10.1098/rstb.2013.0115) and argue that it suggests most of the WSON is anthropogenic, do these authors have a different interpretation?

Follow the Figure 1 (rainwater only) in Jickells et al. (2013), we compiled global data including aerosol and rainwater and made comparisons in terms of WSON/TDN in Section 3.4. Jickells et al. stated that since nitrate and ammonium are mainly anthropogenic, the significantly positive correlation between WSON and TDN may imply WSON's anthropogenic origin. We agree with their interpretation for this positive trend. However, in old version Section 3.4, we did not mention the source of WSON. According to this question, we added sentences into this part of discussion to emphasize the anthropogenic source of WSON. We believe that anthropogenic WSON dominates in urban area and coastal/marginal seas where aerosol ammonium and nitrate concentrations are high; on the other hand, marine sourced WSON cannot be ignored in the open ocean where polluted components are relatively low such as our case of "background" aerosol in Section 3.3.3.

Note that the rain and aerosol data bases are different so the different %WSON may be sampling biases.

Thanks for reminding us. We added one sentence to remind readers that the sampling bias can be inherited in such comparison.

The list of references at the top of p25601 could probably go to the figure caption.

We re-checked the list and make sure all references go to the specific figure caption now.

P25602 the estimation that nitrogen deposition from the atmosphere exceeds river and offshore inputs is a startling illustration of the importance of these inputs in this region

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and might be highlighted. The comparison of impacts on productivity might best be made with "new" not total primary production rates.

Reviewer is right, it is better to compare with new production. However, no data about new production in the East China has been reported so far. Since primary production composed of upwelling-, atmospheric deposition-, riverine-induced plus recycled production. Such comparison is still meaningful.

Section 4 seems to be a summary not a conclusion.

We rewrote the Conclusion and the important of sea fog associated N deposition was highlighted. "We presented total dissolved nitrogen species including organic nitrogen in TSP sampled over the ECSs and NWPO during spring and the ECSs samples were collected in sea fog weather. Three types of aerosol, sea fog modified, dust and background aerosols, were classified. We found that sea fog formation significantly altered the aerosol chemistry resulting in the highest concentrations of all nitrogen species among three types of aerosol, accompanying with higher acidity and higher cation deficiency. On daily basis, the nitrogen supply from sea fog associated atmospheric deposition into the ECSs is around 6 times the nitrogen supply from the Yangtze River in spring (total amount of 3.1 Gg DIN d-1) and 2 times the supply from subsurface intrusion of Kuroshio (7.9 Gg NO₃- N d-1). Sea fog associated deposition and chemical processes require more attention and need to be considered in future aerosol monitoring especially in the marginal sea during the seasonal transition. In the open sea, the spring background aerosol ammonium and nitrate were 10 times higher than previous report for summer season indicating an anthropogenic influence and the importance of the seasonality of air mass source. The ammonium and nitrate varied in narrow ranges showing no correlation with wind speed, which may represent the degree of sea salt emission and scavenging. It is likely that nitrate and ammonium in the atmosphere above sea surface had reached a budget balance. Since the supply of nitrate and ammonium from surface ocean (bottom) is not possible, their source might come from upper boundary layer (top) or photochemical production. On the contrary,

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WSON revealed a similar pattern to sea salt ions (Na^+ , Mg^{2+} and Cl^-), of which concentrations increased as the wind speed increased. Such a similarity indicated that at least a portion of WSON should come from the surface ocean where DON emits with sea salt. The dust aerosols were significantly enriched in nitrate and ammonium, but not in WSON. Unless WSON-depletion processes had occurred, such disproportionate enrichment suggested that dust aerosols from high latitude and altitude may have less chance to contact WSON during the long range transport. Except background aerosols, the WSON to TDN ratios of sea fog modified and dust aerosols collected in the ECSs and NWPO fell within the pattern of global aerosols. Since nitrate and ammonium are mainly anthropogenic, the significantly positive correlation between WSON and TDN may imply WSON's anthropogenic origin. When TDN concentrations are low ($<100 \text{ nmol m}^{-3}$), the proportions of WSON in TDN are more diffusive indicating factors other than anthropogenic involved. The mean ratio of WSON to TDN in aerosols was only 1/2 of that for precipitation over the world. Such lower proportion of WSON in aerosol TDN suggested that aerosol is less capable of scavenging hydrophilic organic nitrogen when comparing with precipitation. Nevertheless, WSON occupies a significant portion in TDN for both aerosol and precipitation, thus, cannot be overlooked in the atmospheric nitrogen cycle.

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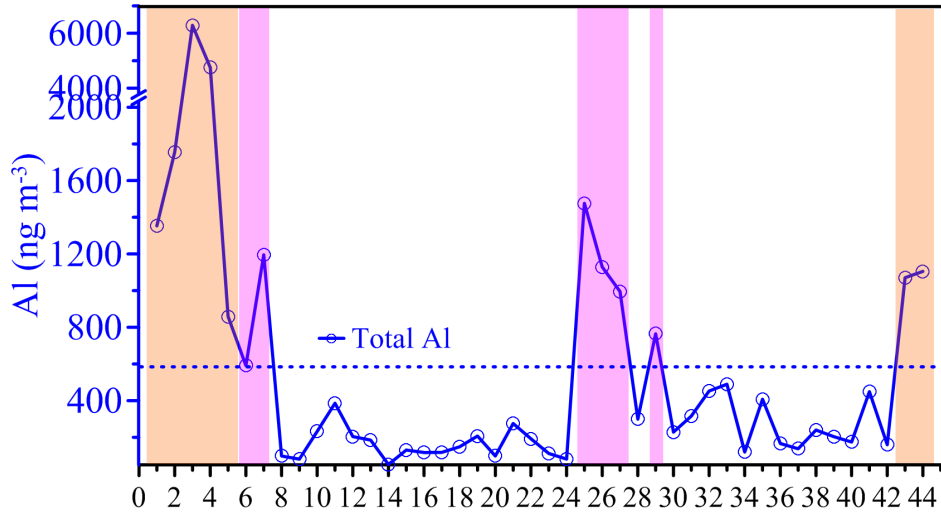


Fig. 1. Panel A Total Al concentration in collected TSP

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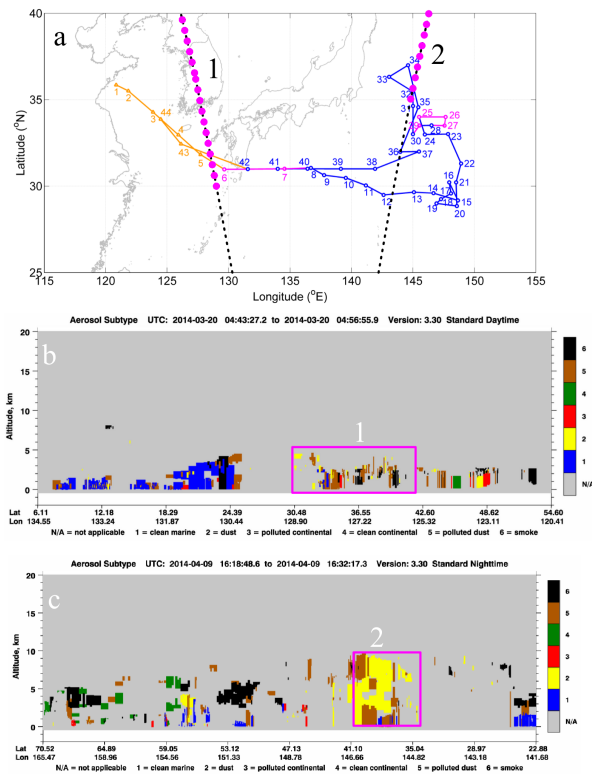


Fig. 2. Panel B The spatial coverage of CALIPSO images for dust and polluted dust (brown and yellow) during our cruise period

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