

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

Anonymous Referee #1

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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. 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 of the impact of continental/anthropogenic aerosols on the coastal/near shore marine environment. It is a subtle, but important distinction. The review is presented below as major and minor comments.

Major Comments: 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 pro-

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cedure 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-ICR MS analysis needs to be removed from the manuscript, or interpreted in a completely different manner. 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. 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. In addition, the authors need to provide information on field blanks and procedural blanks, especially for WSON and ammonium concentrations. 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? 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. Page 7 line 99-101: 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. If the authors want to claim that any of these aerosols are “background” aerosols, they

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need to find other background sites that have such high Nr concentrations. 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. It's not clear how the dust aerosols were identified as such and some explanation is required. Page 7 line122, 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. I agree with the authors conclusion on page 8 paragraph 2 – the “background” aerosols should be re-labeled as it is very misleading. 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. Section 3.2 should be removed or reinterpreted given the focus on negative mode CHON compounds identified here. Page 9 section 3.3 second paragraph. There is a large difference in WSTN $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ of WSTN. A cross-plot of $\delta^{15}\text{N}\text{-NO}_3^-$ vs $\delta^{15}\text{N}\text{-WSTON}$ would provide more information on the influence of nitrate on the total N isotopic composition. Looking at figure 5, it looks like nitrate $\delta^{15}\text{N}$ is a main control on the $\delta^{15}\text{N}\text{-WSTN}$. The lack of correlation between $\delta^{15}\text{N}$ WSTN and the relative concentration of NO_3^- is not useful. The relationship between the $\delta^{15}\text{N}$ RN and the relative concentrations of NH_4^+ would be useful, but is not presented. Page 10 paragraph line 300, it is also a possibility that the aerosol WSON is secondary organic aerosol, which may have had its $\delta^{15}\text{N}$ altered by transport or chemical reactions. This is a very over-simplified approach to the interpretation of the $\delta^{15}\text{N}\text{-WSON}$ data. 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 between the $\delta^{15}\text{N}$ of DON in seawater or $\delta^{15}\text{N}\text{NO}_3^-$ in seawater and the $\delta^{15}\text{N}$ of TN, NO_3^- , or RN in the aerosols? Minor Comments: Table 1. How are aerosol concentrations volume weighted? Is this a mass

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weighted average? 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. Figure 3. The caption says a is nitrate and b is ammonium, but they are labeled in the opposite manner. Figure 4 should be removed. Figure 7. The caption says a is concentration and b is $\delta^{15}\text{N}$ but the plots are the opposite. 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”, line 18 do the authors mean in the open ocean or do they mean in the atmosphere?, line 26 are the concentrations statistically higher in 2014? If so this should be presented in the text. Introduction: Define SSW on first use. Page 3 paragraph 1 should clearly state that they are referring to primary WSON aerosols. Page 8 second paragraph. It’s not clear what is meant by “atmospheric diffusion”

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