

Responses to the comments of Referee #2:

Comment 1: The paper by Dobashi et al. explores an important subject of secondary aerosol formation by nitrogen containing precursors over the open North Pacific. These types of studies are rare and difficult to come by and thus deserve to be published. The difficulty with the marine atmosphere research, especially in the Northern Hemisphere, is that it is often impacted by anthropogenic emissions via direct continental outflow or remnant terrestrial background. Multiple lines of evidence are, therefore, needed to rule out such impact and link atmospheric measurements to marine biological processes. The authors made a large effort in analyzing multiple tracers or species, but have not discussed the results in coherent and comprehensive manner. At the moment the paper is more like a measurement report without an in-depth analysis of underlying mechanisms or processes and often overselling correlation or similarity for a causal link. I encourage the authors to play devil's advocate and take an opposite side to assess if their argument can be falsified using same data. Therefore, a discussion where all evidence would be weighted pro and against is badly lacking. It may well be that the authors can compile compelling argument for their proposed link between nitrogen assisted secondary aerosol formation and nitrogen fixation in biologically active sea water, but a fair account should be given for the so called "null hypothesis" that observations were coincidental. It is also unclear how further studies should be geared in answering the remaining questions as a simple repetition will deliver same result.

Reply 1: We appreciate the referee's constructive and valuable comments. Taking fully account of the comments, we revised the manuscript to construct compelling arguments by showing additional data as below. Our major revisions include the following points:

(1) Discussion on possible effects of anthropogenic sources on the observed aerosols has been added by showing the data of elemental carbon (EC) concentration, as suggested by the referee.

(2) To make a compelling argument on the causal relationship between N₂-fixation rate (and Chl. *a*) in surface seawater and WSON concentrations, we have additionally shown and discussed the data of dissolved ON (DON) and dissolved inorganic nitrogen (DIN) in surface seawater in the revised manuscript.

(3) We added substantive discussion on the points raised by the referee mainly in section 6.

Our responses to the specific comments and details of the changes made to the manuscript are given below.

Comment 2: Abstract, line 22 "The result suggests..." (at best) and does not indicate, because the suggested link is only a proposition.

Reply 2: As the referee pointed out, the word “indicates” has been changed to ”suggests” in the revised manuscript (P.1, L.23).

Comment 3: Page 2, line 31. The manual operation of sampling clearly helped to avoid own ship emissions, but what about transcontinental/continental outflow pollution? Air mass trajectories suggest no contact with land, but they typically do not rule out entrainment of pollution from decoupled boundary layer or free troposphere. Were there any tracers like black carbon measured to rule out anthropogenic impact and confirm marine origin of the sampled air mass? Note that higher WSON concentration observed over ENP where trajectories originated close to the continental boundary.

Reply 3: Regarding possible influence of anthropogenic sources on the observed aerosols, the data of elemental carbon (EC) concentrations is additionally shown in Figure 5 as suggested by the referee. The EC concentrations in all the samples were below the lower detection limit ($\sim 0.1 \mu\text{gC m}^{-3}$) and did not show any statistically significant differences between WNP and ENP. This result suggests that effects of anthropogenic sources on the observed aerosols in ENP were likely small, which is consistent with the stable carbon isotope ratios shown in our study. We made additional statement on this point in the revised manuscript (P.7, L.6).

Comment 4: Page 2, line 37. Size segregated samples were collected every 48hours, but there were 51 fine and 9 coarse particles samples. More confusing are similar percentages of total samples collected. Please clarify why many coarse samples were missing in which case their percentage could not be as high.

Reply 4: First of all, we apologize for erroneous description of the number of sampling duration. As we initially aimed to focus on fine particles, the filters for the fine particle were exchanged every 12 or 24 hours, while those for the coarse particles were exchanged much less frequently (~ 96 hours, not 48 hours). That is why the numbers of samples collected are different between fine and coarse particles. The percentages indicate the number fraction of samples toward the total number after the data screening based on the

total sampling volume for each. Therefore, the percentages should be similar for filters of fine and coarse particles. In the revised manuscript, we have corrected the corresponding numbers of sampling time (P.2, L.30).

Comment 5: Page 3, line 23. Were SSW samples collected overboard with an acid cleaned bucket or using onboard plumbing system into acid cleaned bucket? In any case what was the approximate depth of SSW samples?

***Reply 5:* SSW samples for the measurements of Chl.*a* and N₂-fixation rate were collected overboard with an acid cleaned bucket, where the depth of sampling was ~0 m. Meanwhile, seawater samples for DON (i.e., total DN (TDN) and DIN (Hashihama et al., 2009; 2015; Yasui-Tamura et al., 2020)), the data of which is newly added, were collected at 10-m depth using a conductivity-temperature-depth (CTD) system (Sea-Bird Electronics) equipped with acid-cleaned Niskin-X bottles (General Oceanics) (Hashihama et al., 2020). These descriptions have been added in the revised manuscript (P.3, L.2; P.4, L.2).**

Comment 6: Page 4, line 14. NH₄ and NO₃-N point to anthropogenic origin of nitrogen. NO₃ in coarse particles results from chloride depletion by HNO₃, while ammonia reduced ammonium ion is reacting with sulphate of whatever origin. Despite relatively low concentration of all inorganic species, their origin is pointing towards anthropogenic sources. It should also be noted that natural ammonia source over the oceans is almost negligible (unless the authors have evidence it is otherwise). I think that such discussion is essential, otherwise paper would look like a report instead of a scientific paper.

***Reply 6:* Regarding possible origin of NH₄⁺, Paulot et al. (2015) used global biogeochemical models with extensive ocean observational data to show that atmospheric NH_x (= NH₃ + NH₄⁺) fractions of oceanic origin were dominant (more than 70%) in the Equatorial Pacific (Figure 5 of Paulot et al. (2015)). The observed NH₄⁺ concentration levels in our study (ave. 40–50 ng m⁻³) agree well with those predicted by Paulot et al. in the same oceanic region (~20–60 ng m⁻³; Figure 5 of Paulot et al.). Furthermore, Paulot et al. (2015) suggested that the photolysis of DON either in seawater or in the atmosphere may be a possible source of NH₃ in this oceanic region. In fact, DON was dominant component of TDN in surface seawater, the longitudinal distribution of which was similar to that of WSON in our study (see Reply7), which implies this oceanic source of NH₃.**

A possible source of NO_3^- is not necessarily anthropogenic in the equatorial Pacific, while contribution of oceanic source in the open ocean cannot be ruled out. Several recent field studies suggested oceanic source of aerosol NO_3^- in the eastern equatorial Pacific with evidence of extremely low values of $\delta^{15}\text{N}$ of NO_3^- (e.g., lower than -5‰) (Kamezaki et al., 2019; Carter et al. 2021). In this oceanic region, alkyl nitrates are suggested to contribute to nitrate production, where relatively high concentrations of alkyl nitrates have been observed over the equatorial Pacific. Although we do not have measurement data of $\delta^{15}\text{N}$ of NO_3^- , we made additional discussions on the points of possible sources of NH_4^+ and NO_3^- in the revised manuscript (P.7, L.17–30).

Comment 7: Page 4, line 22. Is the similar longitudinal distribution of chlorophyll coincidental or causal? Similarity or regression cannot prove causal relationship unless more substantial support is provided and thoroughly discussed. One way to look at it is to use some specific anthropogenic pollution tracers showing no connection or opposite relationship with WSON and inorganic species.

***Reply 7:* To make convincing explanations on the causal relationship between Chl. *a* and WSON concentrations, we have added the data of DON and total DN (TDN) in surface seawater. As shown in the following Figure A, the longitudinal distribution of Chl.*a* concentrations was similar to those of N_2 -fixation rate, DON concentrations in surface seawater, and aerosol WSON concentrations. In particular, N_2 -fixation rate and DON concentrations in surface seawater showed a positive correlation with R^2 of 0.63, where DON was the dominant component ($>98\%$) of TDN during the cruise. Furthermore, no relationship was found between these parameters and EC concentrations as an anthropogenic tracer, where EC concentrations in all the samples were below the lower detection limit with no significant difference in the longitudinal distributions (revised Figure 5 as shown below). Together with the stable carbon isotope ratios of aerosols, overall results suggest the causal relationship between N_2 fixation rate and WSON in this study. These descriptions were added in the revised manuscript (P.6, L.22). Furthermore, sentences regarding this point have been revised in the abstract (P.1, L.23) and conclusion section (P.8, L.15).**

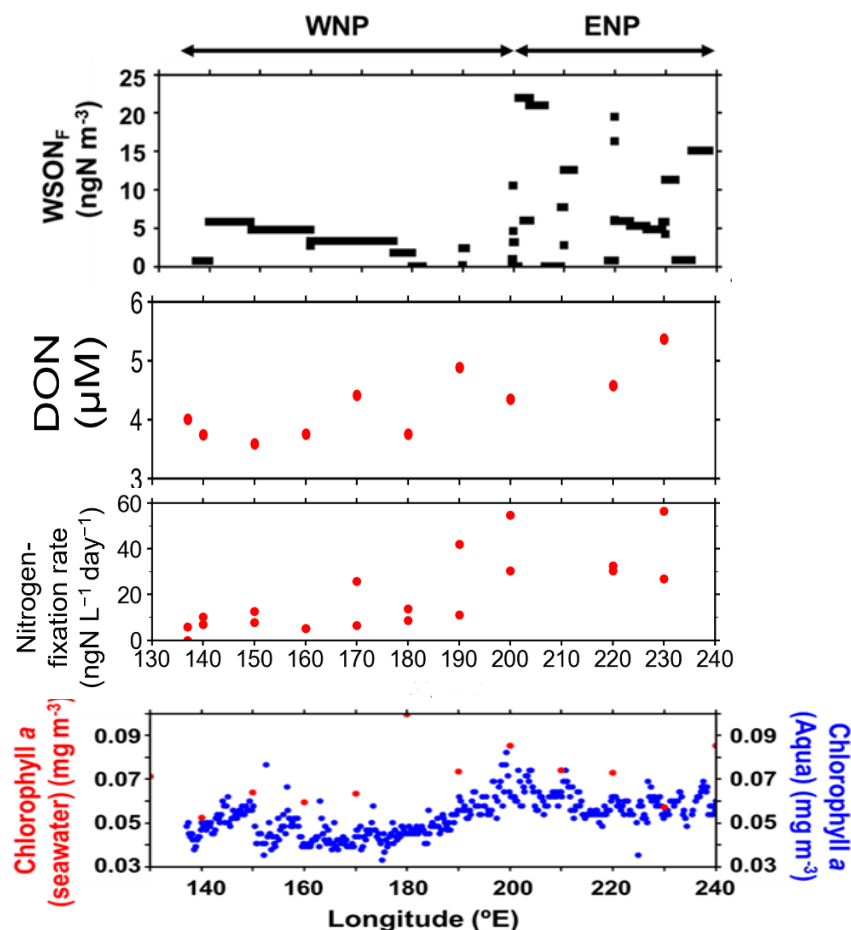
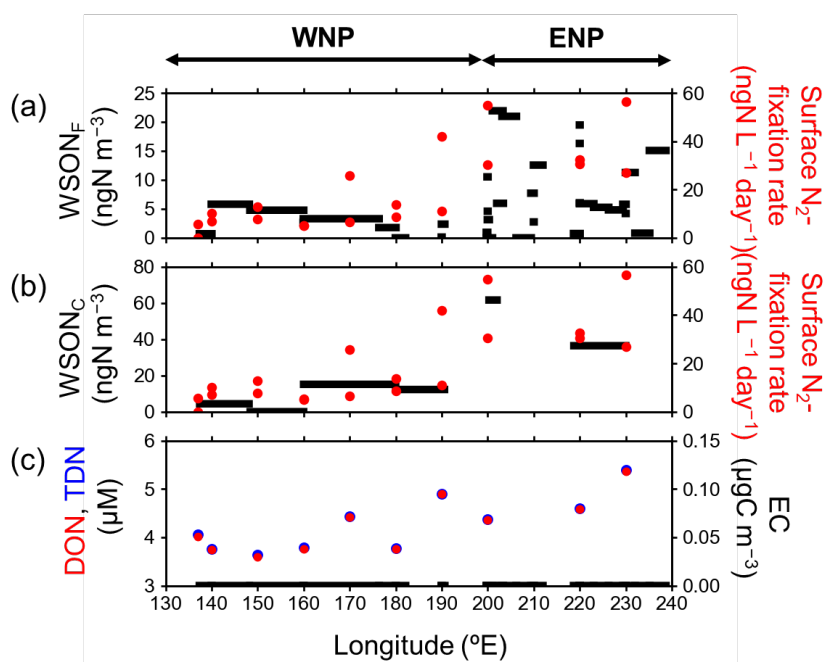


Figure A: Longitudinal distributions of $WSON_F$ and DON concentrations in aerosols and surface seawater, respectively, together with those of nitrogen-fixation rate and chlorophyll *a* concentrations.



Revised Figure 5: Longitudinal distributions of mass concentrations of (a) $WSON_F$ (black) and (b) $WSON_C$ (black), together with N_2 -fixation rate in the SSW samples (red solid circle), (c) DON (red solid circle) and TDN (blue solid circle) concentrations in surface seawater and aerosol EC concentrations (black) during the entire cruise.

Comment 8: Figure 3 is as useful as can be misleading as it contains only 17 of 51 fine aerosol samples and contains only 3 points with WSON >10ngN/m³. Most of the marine origin deltaC13 points (20-24 permille) probably belong to WNP region, so the highest value is of those 8 samples where WSON was >10ngN/m³. If those 8 points were eliminated, ENP and WNP regions become indistinguishable.

Reply 8: We do not intend to mention that ENP and WNP are different in terms of the isotopic characterization but intend to show that most of the aerosols were of marine origin observed during the entire cruise.

Comment 9: Figure 4. Absence of the correlation between MSA and WSON could be due to the temperature impact which favours SO₄ formation in subtropical latitudes instead of MSA. Have the authors looked at SO₄ to WSON correlation. If the source of sulphur and nitrogen species is biogenic, they should correlate to some extent, because 48hour sampling has a footprint of ~1000-1500km and biogenic processes overlap even if underlying mechanisms differ somewhat.

Reply 9: As the referee pointed out, dependence of temperature and/or OH levels in the subtropics on the relative yields of MSA to sulfate in the oxidation of DMS (e.g., Mungall et al., 2018) might partly result in the insignificant correlations between WSON and MSA. Scatter plots between sulfate and WSON are shown in Figure B below. For the fine particle, no relation was found between sulfate and WSON concentrations ($R^2 < 0.02$). This supports that the origin of the observed WSON aerosols differed from that of DMS or that the formation pathways of WSON were different from the oxidation processes of DMS within a timescale of 12-24 hours. On the other hand, sulfate and WSON concentrations in coarse particles showed some positive relationships, although the number of data is limited. This may reflect overlapping processes of biogenic sulfate and WSON on a timescale of several days of coarse-mode aerosol samplings, as the referee pointed out. In the revised manuscript, we made additional descriptions on these points (P.5, L.28).

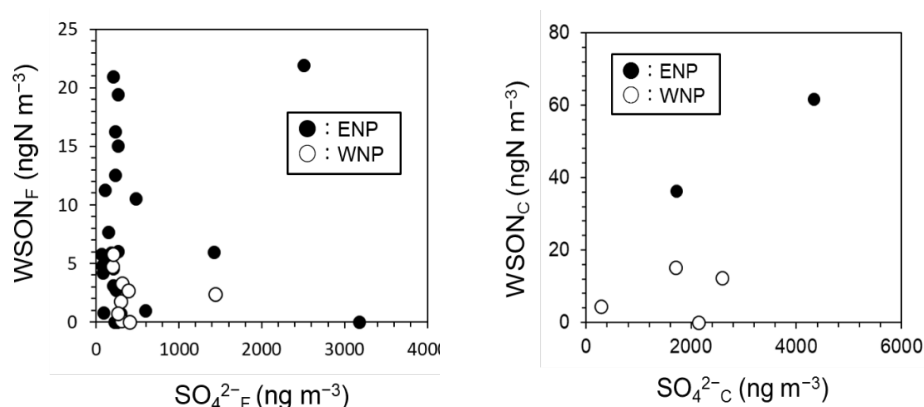


Figure B: Scatter plots between WSON and sulfate in fine (left) and coarse (right) particles.

Comment 10: Page 5, line 11. The authors correctly discuss primary versus secondary origin of WSON species, but secondary formation does not necessarily is of marine origin. The real challenge is to rule out anthropogenic sources of gaseous precursors leading to secondary WSON.

Reply 10: As described above, the EC concentrations in all the samples were below the lower detection limit, which did not show statistically significant differences between WNP and ENP. This suggests that contribution of anthropogenic sources on the observed aerosols in ENP were likely small, which is consistent with the stable carbon isotopic compositions in our study. Although we do not have measurement data of gas species, it is unlikely that only gas-phase precursors were of anthropogenic origin in spite that most of the observed aerosols were originated from ocean surface. Taking account of the referee's comment, additional statement on this point has been added to the text as follows.

P.7, L.6: *“It is possible to argue that anthropogenic sources might contribute to the observed WSTN including WSON and NH_4^+ as well as WSTN:WSOC ratios in aerosols shown above. Concentrations of EC as an anthropogenic tracer were below the lower detection limit ($\sim 0.1 \mu\text{gC m}^{-3}$) in all the aerosol samples, where they did not show any statistically significant differences between WNP and ENP (Figure 5). This result suggests that effects of anthropogenic sources on the observed aerosols in ENP were likely small. This is consistent with the stable carbon isotope analysis, which suggested that most of the observed aerosols were of marine origin, rather than terrestrial sources including anthropogenic origin. Although measurement data of gas species was not available in this study, it is unlikely that only gas-phase precursors were of anthropogenic origin in spite that most of the observed aerosols were originated from ocean surface.”*

Comment 11: Page 5, line 24. Why would N_2 fixation result primarily in inorganic dissolved nitrogen and not organic like amines?

Reply 11: In the original manuscript, we described that N_2 fixation results in not only NH_4^+ (inorganic DN) but also DON. Indeed, data obtained from Station ALOHA in the subtropical North Pacific has shown enrichment of N pools (i.e., NH_4^+ , NO_3^- , DON) within *Trichodesmium* blooms (Karl et al., 1992; Letelier and Karl, 1994). It has been shown that majority of the recently fixed N_2 is released directly as DON during the growth of *Trichodesmium*, primarily as dissolved free amino acids (Capone et al, 1994; Glibert and

Bronk, 1994). In fact, our data showed that DON was a dominant component of TDN (>98%) in surface seawater. In the revised manuscript, we revised the sentence on these points (P.5, L.40).

Comment 12: Page 6, line 18. Different ratio can arise from preferential production as well as from remnant anthropogenic source. Despite coming back to the same argument of anthropogenic origin I do not object authors argument about biogenic origin of WSON, but rather encourage the authors to look for more direct evidence in discounting anthropogenic origin.

***Reply 12:* As we mentioned above, the EC concentrations in all the samples were below the lower detection limit and did not show statistically significant differences between WNP and ENP. Together with the results of stable carbon isotope analysis, the overall results support that contribution of anthropogenic sources to the observed WSTN:WSOC ratio was likely small. We made additional description on this point, the statement of which is shown in Reply 10 above.**

Comment 13: Page 6, line 27. What about amines as a WSON species?

***Reply 13:* Aliphatic amines by gas-to-particle conversion are strong candidates for species of WSON observed in this study, as those amines of marine origin were observed in gas and aerosol phases in tropical/subtropical open oceans (e.g., Miyazaki et al., 2010; van Pinxteren et al., 2019). We have mentioned those amines in the revised manuscript as follows:**

P.7, L.32: “... Specifically, aliphatic amines by gas-to-particle conversion are one candidate for WSON species observed in this study, as those amines of marine origin were observed in gas and aerosol phases in tropical/subtropical open oceans (e.g., Miyazaki et al., 2010; van Pinxteren et al., 2019). Although the exact mechanism of the WSON formation is not apparent in this study, the current results of the shipboard measurements suggest that N_2 fixation in SSW could partly explain one of the missing sources of atmospheric WSON and ammonia indicated by previous modeling studies.”

Comment 14: Page 6, line 40. Discussion section is recommended to discuss all information presented in previous chapters and discussing them simultaneously in a comprehensive manner. I

encourage the authors of playing devil's advocate for their own advantage in taking critical view to their own data.

Reply 14: We added substantive discussion on the points above raised by the referee in section 6. We decided to add discussions within section 6, not in a new section, because some relevant statements have been already made in section 6 and it is more natural to add discussion in the same section to make a compelling argument. Along with the substantial addition of discussion, the title of section 6 has been changed to “Discussion on nitrogen fixation as a possible source of WSON in marine aerosols”

Others:

• With regard to the referee’s comment on further studies that should be geared in answering the remaining questions, we made additional statement as follows:

P.7, L.42: “...Further field studies are required to elucidate the effect of N_2 fixation in surface seawater on the emission of atmospheric reactive nitrogen in different oceanic regions. This includes, for example, simultaneous measurements of gas and particle phases of organic and inorganic nitrogen species together with measurements of biological and chemical parameters relevant to N_2 -fixing microorganisms in surface seawater by shipboard observations. Additional laboratory studies are needed to ...”

• Along with the addition of DON and TDN data in the revised manuscript, Fuminori Hashihama and Saori Yasui-Tamura, who measured those parameters in seawater, have been added as co-authors.

References:

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