

We appreciate the referee's valuable comments on our work. Our responses to the specific comments and details of the changes made to the manuscript are given below.

Responses to the comments of Referee #1:

Comment 1: The authors convincingly show that regions R1 and R2 are not affected by terrestrial air masses; however, Figure 1 (right) shows that the 5-day back trajectories for R3 all recently had crossed the continent. How can it be convincingly stated that the increase in WSOC/Na⁺ and ozone can be attributed to aging and secondary production of aerosol from local marine organics rather than transport from other regions? Adding a vertical cross-section of the back trajectories in Figure 1 (right) might help to make this case.

Reply 1: We have now added a vertical cross-section of the back trajectories in Figure 1 as suggested. The air masses observed in R3 had been transported by low-level air flow from the Atlantic. In fact, they had passed over the Isthmus of Panama at higher altitudes as evident from the new figure, followed by descent to the sampling point in R3. This is consistent with the results from the isotopic analysis of WSOC, which suggest that the influence of land surface on the observed WSOC was insignificant.

In the revised manuscript, the following sentences have been added to the text and the caption of Figure 1:

(P.7, L.30–34) “It is noted that the observed aerosols in R3 had been transported by low-level air flow from the Atlantic, as indicated by the back trajectories in Figure 1. In fact, the trajectories had passed over the Isthmus of Panama at higher altitudes, followed by descent to the sampling point in R3 as seen in Figure 1, indicating less influence from the land surface. This is consistent with the results from the isotopic analysis of WSOC, which suggest that the influence of the land surface on the observed WSOC was insignificant.”

(Figure 1 caption) “A vertical cross-section of the back trajectories is shown in the right bottom panel.”

Comment 2: Similar to Point #1, the percentage exposures given in Figure 7 and discussed on Pg. 7, Lines 8-13, seem of little value to me as even a short exposure of a given air mass to the strong aerosol emissions sources in the terrestrial mixed layer would be enough to likely overcome marine influences over subsequent days. A better treatment of the air mass back trajectories including the past horizontal and vertical transport would be more

informative here. In addition, does the model provide any information about cloud processing or rainout over the transport period?

Reply 2: As shown in the vertical cross-section of the back trajectories added to Figure 1, the air masses had passed over the Isthmus of Panama at higher altitudes, suggesting that the influence of the land surface on the observed aerosols was likely insignificant. This is also clearly presented in Figure 7, which shows little exposure of the observed aerosols on the land surface and is consistent with the results from the isotopic analysis. The trajectory calculation shows that relative humidity (RH) in the air mass along the back trajectories was typically within the range of 60–80%, with a maximum of 95%. This indicates that cloud processing or rainout of aerosols was likely insignificant over the period of transport in our study.

Comment 3: Please add error bars to compositional traces in Figures 2, 4, 6, and 8 that reflect the uncertainty associated with each measurement.

Reply 3: Because adding error bars to the panels, particularly in Figures 4 and 8, reduces the clarity of the figures, we decided not to add them. Instead, we have added the uncertainty of each measurement including the blank subtraction in Table 1.

Comment 4: Non-normal observational distributions need to be treated more carefully than just a simple arithmetic mean and standard deviation. This is apparent from the large standard deviations reported for some species in Table 1 and the non-physical result of $90 \pm 25\%$ reported in the abstract and conclusions – the latter of which is particularly glaring. The authors should reassess the distribution of the data that go into the summary statistics and evaluate the appropriateness of geometric means and geometric standard deviations (if logarithmically distributed) or another functional form for reporting the data or, if there is not a good functional form, then median and percentile values should be reported.

Reply 4: Besides the mean values, we have added median and percentile values to Table 1.

Comment 5: The WSOC field blank concentrations are discussed on Page 3, Lines 30-31, but similar values for the speciated organic species and inorganic ion concentrations are not included. Please add these values to this paragraph. Is there any contamination associated with storing these samples in glass containers, which can leach inorganic cations? Also, please report the uncertainty associated with the ^{13}C and ^{15}N values in the subsequent paragraph on Page 4.

Reply 5: We have added the field blank levels for the inorganic ions (Na^+ , Cl^- , Mg^{2+} , and MSA) and organic molecular tracers measured in this study, as follows:

(P.4, L.11–13) *“The MSA value of field blanks corresponded to less than ~12% of the concentrations of the ambient samples, whereas the blank values of Na^+ , Cl^- , and Mg^{2+} were less than 1% of the ambient concentrations.”*

(P.4, L.20–21) *“The values of a field blank were less than ~24% of the concentration of these molecular compounds in the ambient samples.”*

As the reviewer has pointed out, there was some contamination from the glass vials, particularly in the Na^+ concentration, as evident from the blank levels. However, the ambient concentrations of Na^+ in our samples were generally sufficiently high to neglect this contamination (<1%). The uncertainties associated with the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values have been added to Table 1.

Comment 6: I don't understand the value of Figure 6 and associated discussion on Pg. 6, Line 36 – Pg. 7, Line 7. Are the authors concluding that there is some sort of relationship between ^{13}C and ^{15}N ? The data do not seem to support this.

Reply 6: It was not our intention to discuss the linear relationship between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, but rather to show the ranges of the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values compared with those in seawater. In the revised manuscript, we have modified the sentences relevant to this point, both in the text and in the caption of Figure 6, as follows (P. 7, L.16–17):
“Figure 6 shows the ranges of the nitrogen isotope ratio of the water-soluble total nitrogen ($\delta^{15}\text{N}_{\text{WSTN}}$) and $\delta^{13}\text{C}_{\text{WSOC}}$ in the submicron aerosols for each oceanic region.”

Comment 7: On Page 4, Line 34, and throughout the text, a “correlation coefficient (r^2)” is reported, which is confusing and needs to be fixed. Typically, a correlation coefficient is denoted as “ r ” and a coefficient of determination is reported as “ R^2 ”. Which type of coefficient is being calculated and reported here?

Reply 7: Yes, a correlation coefficient is defined in our manuscript as “ r ” and a coefficient of determination as “ r^2 ”. This point has been clarified in the revised manuscript (P.5, L.1; P.8, L.33, 36).

Comment 8: The final line of the manuscript states that “This study provided direct evidence that the contribution of DOC was the dominant control on the submicron WSOC mass regardless of the oceanic areas over the study region.” Similar statements are elsewhere in the manuscript (e.g., Pg. 1, Ln. 30; Pg. 10, Ln. 5). While I agree that there is

indeed a compelling correlation between the concentrations of water-soluble sugars and the overall aerosol WSOC concentration and less compelling correlations with MSA and fatty acids, I do not think that this supports the strong assertion that DOC is the dominant control on submicron WSOC. This conclusion should be reworded to be more consistent with what is actually being demonstrated by this study – a “strong correlation”, not a “dominant control”.

Reply 8: As suggested, the final sentence in the conclusion section has been reworded as (P.11, L.12–14), “*This study provided direct evidence that the contribution of DOC was significantly correlated with the submicron WSOC mass across the study region regardless of the oceanic area.*” The other two sentences have been also modified as follows:

(P.1, L.31–34) “*The combined analysis of the $\delta^{13}\text{C}$ and monosaccharides, such as glucose and fructose, demonstrated that DOC concentration was closely correlated with the concentration levels of submicron WSOC across the study region regardless of the oceanic area. The result implies that DOC may characterize background organic aerosols in the MBL over the study region*”

(P.10, L.29–31) “*Nevertheless, the present study demonstrates that DOC is closely correlated with the submicron WSOC aerosol concentration and implies that it may characterize background OA in the MBL over the study region.*”

We appreciate the referee's valuable comments on our work. Our responses to the specific comments and some changes made in the manuscript are given below.

Responses to the comments of Referee #2:

Comment 1: Page 2, Line 22: Provide a reference for WSOC altering hygroscopicity.

***Reply 1:* Prather et al. (2013) has been added to the text as a reference (P.2, L.25).**

Comment 2: Page 4, Line 34; Page 8, Line 13: Report sample number when reporting correlations.

***Reply 2:* The number of samples has been provided in the revised manuscript (P.5, L.1; P.8, L.33).**

Comment 3: Figure 1 caption: what are the red traces in the right panel representative of? Clarify in caption, and thicken the red lines to allow for readers to see them more easily.

***Reply 3:* The red lines indicate the backward trajectory, which has now been mentioned in the caption of Figure 1 in the revised manuscript. The lines have been made bolder, as suggested.**

Comment 4: Page 5, Line 32: For the sake of comparison, it would be useful to provide info here about other archived datasets such as (for example) data collected in the Northeast Pacific Ocean showing both unimodal and bimodal characteristics for water soluble organic species: Maudlin, L. C., et al. (2015). Impact of wildfires on size resolved aerosol composition at a coastal California site, *Atmos. Environ.*, 119, 59-68, doi:10.1016/j.atmosenv.2015.08.039. Also, some discussion about the sources of the two modes in this study would be helpful for readers.

***Reply 4:* A statement on the comparison with Maudlin et al. has been added to the text. In addition, we have added a discussion on the possible sources of the two modes in this study. (P.5, L.34–P.6, L.7) “Bimodal size distributions of WSOC in marine aerosols were also observed in the western North Pacific (Miyazaki et al., 2010), whereas both unimodal and bimodal size distributions of water-soluble organic species were also reported in particles collected at a coastal site facing the Northeastern Pacific (Maudlin et al., 2015). The bimodal size observed in this study can be attributed to the difference in the formation processes of WSOC between the two size ranges. The two distinct size modes include (i) direct co-emissions associated with sea salt particles in both size ranges,**

(ii) aqueous-phase products in the submicron size range, and (iii) partitioning to the surface of coarse particles (i.e., sea salt) and/or heterogeneous reactions in the supermicron size range (Mochida et al., 2002). Although it is difficult to provide a clear explanation by this data set alone, the observed WSOC size distributions might be explained by some combination of these possible origins and processes. Here we focus on the submicron size of WSOC relevant to its isotope ratios and several chemical tracers.”

Comment 5: Page 6, Line 11: Have other studies also shown a link between organics and high Chl A? if so, I suggest a discussion of those other studies too and what their chief results were to enrich the discussion in this section of the paper. Some suggested studies to look up are: Facchini, M.C., et al. (2008). Important source of marine secondary organic aerosol from biogenic amines, Environ. Sci. Technol., 42, 9116e9121. <http://dx.doi.org/10.1021/es8018385>. Sorooshian, A., et al. (2009). On the link between ocean biota emissions, aerosol, and maritime clouds: airborne, ground, and satellite measurements off the coast of California, Global Biogeochem. Cycles, 23, GB4007, doi:10.1029/2009GB003464.

Reply 5: The following discussion has been added to the text: (P.6, L.26–30) *“Previous studies have shown a linkage between organics and high Chl a concentrations on timescales of months (O’Dowd et al., 2004; Sciare et al., 2009). However, Quinn et al. (2014) found no well-defined relationship between instantaneous Chl a in seawater and organic-mass enrichment in sea spray, suggesting no significant variability in the OC content of freshly emitted sea spray aerosol, despite significant variability in seawater Chl a levels. This point will be discussed in section 3.3.”*

Comment 6: Section 3.4: For the discussion about MSA and its lack of correlation with WSOC and Chl A, it may be useful here to bring up the point that other studies have observed that MSA may be enhanced in the presence of metals (mainly vanadium). Such catalytic effects that are speculated in past works may be at least one contributing factor as to why correlation is not observed between MSA and these other parameters: Gaston, C. J., et al (2010), Real-time detection and mixing state of methanesulfonate in single particles at an inland urban location during a phytoplankton bloom, Environ. Sci. Technol., 44(5), 1566–1572. Sorooshian, A., et al. (2015). Surface and airborne measurements of organosulfur and methanesulfonate over the western United States and coastal areas, J. Geophys. Res., 120, doi:10.1002/2015JD023822.

Reply 6: The observed increases in the MSA concentrations were most evident in R2, in which the possible influence of anthropogenic sources appeared to be very low.

Therefore, we believe that the effects of such a catalytic reaction on the increases in the MSA concentrations in R2 were likely insignificant in our data. In response to this important comment, we have added the following sentences to the discussion: (P.9, L.37–40) *“Gaston et al. (2010) suggested a possible catalytic role of vanadium in MSA formation. The observed increases in the MSA concentrations were most evident in R2, in which the impacts of anthropogenic sources appeared to be very low. Therefore, the effects of such a catalytic reaction on the increases in the MSA concentrations in R2 are likely insignificant.”*

Comment 7: Do the authors have any indication about how important cloud processing was during the research cruise in explaining any of the features in their WSOC data?

Reply 7: The back-trajectory calculation shows that relative humidity (RH) in the air mass along the back trajectories was typically within the range of 60–80%, with a maximum of 95%. This indicates that cloud processing or rainout of aerosols were likely insignificant over the period of transport in our study.

Comment 8: Figure 2: Was precipitation important in explaining any of the reductions in concentrations observed during the time period shown after the local maxima values observed?

Reply 8: We observed almost no precipitation during the observational period, particularly after 10 February when the reductions in WSOC concentrations were observed. Therefore, it is unlikely that the observed decrease in the concentrations could be explained by precipitation.

References

- Gaston, C. J., Pratt, K. A., Qin, X. Y., and Prather, K. A.: Real-time detection and mixing state of methanesulfonate in single particles at an inland urban location during a phytoplankton bloom, *Environ. Sci. Technol.*, 44(5), 1566–1572, 2010.
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- Miyazaki, Y., Kawamura, K., and Sawano, M.: Size distributions of organic nitrogen and carbon in remote marine aerosols: Evidence of marine biological origin based on their isotopic ratios, *Geophys. Res. Lett.*, 37, L06803, doi:10.1029/2010GL042483, 2010.
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on sea-salt particles, *J. Geophys. Res.*, 107(D17), 4325, doi:10.1029/2001JD001278, 2002.

O'Dowd, C., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J., and Putaud, J.-P.: Biogenically driven organic contribution to marine aerosol, *Nature*, 431, 676– 680, 2004.

Prather, K. A., Bertram, T. H., Grassian, V. H., Deane, G. B., Stokes, M. D., DeMott, P. J., Aluwihare, L. I., Palenik, B. P., Azam, F., Seinfeld, J. H., Moffet, R. C., Molina, M. J., Cappa, C. D., Geiger, F. M., Roberts, G. C., Russell, L. M., Ault, A. P., Baltrusaitis, J., Collins, D. B., Corrigan, C. E., Cuadra-Rodriguez, L. A., Ebben, C. J., Forestieri, S. D., Guasco, T. L., Hersey, S. P., Kim, M. J., Lambert, W. F., Modini, R. L., Mui, W., Pedler, B. E., Ruppel, M. J., Ryder, O. S., Schoepp, N. G., Sullivan, R. C., and Zhao, D.: Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol, *P. Natl. Acad. Sci. USA*, 110, 7550–7555, doi:10.1073/pnas.1300262110, 2013.

Quinn, P. K., Bates, T. S., Schulz, K. S., Coffman, D. J., Frossard, A. A., Russell, L. M., Keene, W. C., and Kieber, D. J.: Contribution of sea surface carbon pool to organic matter enrichment in sea spray aerosol, *Nat. Geosci.*, 7, 228–232, 2014.

Sciare, J., Favez, O., Sarda-Estève, R., Oikonomou, K., Cachier, H., and Kazan V.: Long-term observations of carbonaceous aerosols in the Austral Ocean atmosphere: Evidence of a biogenic marine organic source, *J. Geophys. Res.*, 114, D15302, doi:10.1029/2009JD011998, 2009.

We are grateful to Dr. Ceburnis for the valuable comments and references. Our responses to the comments and details of the changes made to the manuscript are given below.

Responses to the comments of Dr. Ceburnis:

Comment 1: I am somewhat confused over the terms “open oceans” and “coastal oceans”. By definition the ocean beyond a continental shelf should be considered an open ocean. The continental shelf in the reported region R3 does not extend beyond 100 km from the coast and the shelf sea occupied only a part of R3 region. In my opinion the difference between open ocean and coastal ocean in this study was in the abundance of chlorophyll in surface waters. However, chlorophyll rich waters can be found thousands of kilometres from the coast as in the North Atlantic & Arctic (O’Dowd et al., 2004; Yoon et al., 2007; Russell et al., 2010) or the Southern Ocean (Sciare et al., 2009). Is it not better referring to “high/rich” and “low/poor” chlorophyll regions?

***Reply 1:* We agree. In the revised manuscript, we have used the term “high and low Chl *a* regions” to refer to R3 and R1/R2, respectively. (P. 1, L.18–22; P.5, L.18–19; P.10, L. 35–36)**

Comment 2: I suggest using the term “sea spray” when referring to primary marine particles as sea salt is only one component of sea spray (Section 3.1., line 31). Major sea salt ions should not be expected to correlate linearly with wind speed as there is a power law relationship between sea salt(spray) mass and wind speed, e.g. (Ovadnevaite et al., 2012), hence, moderate linear correlation observed. Cl depletion during certain periods was rightly attributed to acidifying species where sulfate (sulfuric acid) should have been dominant component contrary to nitrate (nitric acid) which significant presence could not be corroborated by stable carbon values (significant nitrate must be anthropogenic and consequently would have driven C13 to more depleted values). It is very likely that if sulfate was plotted against Cl/Na ratio an apparent anti-correlation was clearly revealed. Cl depletion by sulfuric acid is rarely implicated due to the ever-present nitrate, but in clean oceanic regions sulfuric acid must dominate the observed depletion.

Reply 2:* As suggested, the term “sea salt particles” has been replaced by “sea spray” in section 3.1 (P.4, L.31). In addition, we have added the following sentence to explain the moderate linear correlation between sea spray mass and local wind speed (P.5, L.1–3): “*This is consistent with the wind-driven production of primary marine aerosol particles, whereas the moderate linear correlation can be explained by a power law relationship between sea spray mass and local wind speed (e.g., Ovadnevaite et al.,

2012).”

Regarding the chloride depletion, the Cl^-/Na^+ ratio tended to decrease with increasing sulfate, whereas this is not apparent for nitrate. In the revised manuscript, the following sentence has been added: (P.5, L.29–30) *“In fact, the Cl^-/Na^+ ratio tended to decrease with increasing sulfate concentration (not shown in the figure), whereas this trend is not apparent for nitrate.”*

Comment 3: Despite anthropogenic sources contributed negligibly to the TC mass, its contribution cannot be totally discounted in the Northern Hemisphere and it would have resulted in slightly more negative stable carbon ratio of TC as it was measured (Section 3.5). Very small contribution of anthropogenic carbonaceous matter would not compromise the results of this study as the region was predominantly clean based on cumulative evidence from all the tracers. It is hard to discount small amount of anthropogenic tracers without concurrent BC measurements as the Shank et al. study was conducted during different season and meteorological conditions. Lastly, even small amount of BC is always accompanied by a small corresponding OC mass.

Reply 3: We did not intend to imply that the contribution of anthropogenic sources is negligible. Both the $\delta^{13}C$ and Lagrangian trajectory analysis indicated that marine-derived carbon accounted for the majority of submicron WSOC. These results contradict those of Shank et al. (2012), who suggested that there is little to no marine source of submicron OA to the atmosphere. Therefore we wish to emphasize that DOC substantially contributes to the submicron WSOC mass across the study region. In the revised manuscript, we have added/modified the following sentences taking into account the comment: (P. 10, L28–31) *“It is noted that the contribution of anthropogenic sources cannot be negligible although this is indicated by the isotopic analysis. Nevertheless, the present study demonstrates that DOC is closely correlated with submicron WSOC aerosols and implies that it may characterize background OA in the MBL over the study region.”*

We have also added the two references of Chesselet et al. (1981) and Ceburnis et al. (2011) to the Introduction section.

References

Ceburnis, D., Garbaras, A., Szidat, S., Rinaldi, M., Fahrni, S., Perron, N., Wacker, L., Leinert, S., Remeikis, V., Facchini, M. C., Prevot, A. S. H., Jennings, S. G., Ramonet, M., and O’Dowd, C. D.: Quantification of the carbonaceous matter origin in submicron marine aerosol by C-13 and C-14 isotope analysis, *Atmos. Chem. Phys.*, 11, 8593-8606,

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