Responses to the comments of Referee #2:

We appreciate the referee's valuable comments on our work. Our responses to the specific comments are given below.

Comment 1: Carbon measurements are affected by uncertainties which are not reported here (missing information regarding uncertainties associated with blank values, and uncertainty provided for the sunset lab instrument). For that reason, caution should be taken when interpreting this dataset. More specifically: If based on a punch of 1.54cm2 for C analyses (please confirm since this information is not reported in the manuscript), using a typical air volume sampled of 900m3 and a total sampled filter area of 20x25=500cm2, then you should get about 2.77m3 of air sampled on the punch dedicated for EC and OC. This is quite low. Then results presented here for OC have been obtained from OC concentrations in the Sunset of 1–1.5 µgC for the lowest OC ambient concentrations (0.4-0.6µgC/m3) This is very close to the performance of the instrument. You mention in your manuscript (section 3.1, line 20) a detection limit below 2 ngC/m3 for EC which should correspond here to a value below 0.005µgC detected by the instrument. This is not realistic given the fact that the sunset lab instrument provides an accuracy of 0.1µgC. Taking this number (0.1µgC for EC) you have then a detection limit of EC in your samples of about 0.2-0.3µgC/m3. This value is too high and cannot serve in the manuscript to claim that samples were not affected by local contamination.

Reply 1**: First, we would like to point out that even if we take the number of 0.1 µgC for a filter punch of 1.54 cm^2 (with a volume of 2.77 m^3), the detection limit for EC is calculated to be about 0.02-0.03 µgC m^{-3}, not 0.2-0.3µgC m^{-3}. Under our operating conditions, 1σ of the instrument blank for EC is 0.05 µgC and the detection limit is calculated to be ~0.02 µgC m^{-3}. We did make a typographical error (2 ngC m^{-3} should be 20 ngC m^{-3}), which has been corrected in the revised manuscript. Nevertheless, the value of 20 ngC m^{-3} is still low, as it is similar to the concentrations reported for clean marine aerosols at Mace Head in the North Atlantic (Cooke et al., 1997). Additionally, the aerosol data with a total air volume < 800 m^3 were omitted in the original manuscript, because these aerosol samples might have been affected by local contamination in stagnant air. Indeed, these data correspond well with time-series of substantially high aerosol number concentrations measured by a water-based condensation particle counter (CPC) (Mochida et al., 2011), presumably caused by the ship's exhaust. After the data screening, we presented 32 samples out of the total 42 samples obtained in the present study. Together with the low concentration of EC and NO_3^- in the aerosol samples shown here, we believe that the collected aerosols presented in the manuscript were hardly affected by local ship emissions. According to**

the comment, we have added information about (1) the uncertainties associated with blank values, (2) the filter punch area, and (3) further details about the data screening, as described above, in the revised manuscript.

Comment 2: DEA measurements should also be affected by significant uncertainties which are missing here. Again, the scientific interpretation of DEA may suffer from these uncertainties. More specifically: DEA averaged concentrations of 0.2-0.5ng/m3 are reported in the paper (Table 2). Based on a punch of 1.54cm2 extracted in 10 ml, DEA detected by IC will be on average 0.05-0.15ppb. I am not sure that you can provide a realistic quantification of such low concentrations given the fact that IC calibration for such light organics is usually performed for concentrations above the ppb level. Without more information on IC protocols, I consider that uncertainties associated with DEA concentrations are too high to really bring a strong constrain on the formation mechanisms of organic nitrogen.

Reply 2**: In fact, for the separation and quantification of DEA^+, we used a filter cut of 21.2 cm^2 (much larger than that for the major ions) to extract samples in 5 mL (half of the volume used for the major ions) of Milli-Q water. This procedure enabled us to detect such low concentrations of DEA^+. We have added more information about this in the revised manuscript.**

Comment 3: End of the paragraph 2.3, you mention uncertainties associated with WSON and WION without giving more information. You can be more specific. WSTN may be significantly underestimated (11 & 43% conversion efficiency for the last N species reported in Table 1). This may lead to significant underestimation of WSON and significant overestimation of WION. Then, your interpretation of high levels of WION (which represents maybe the most significant contribution of this paper) should take into account these uncertainties. Unfortunately they are ignored in the conclusion (and abstract).

Reply 3**: In the revised manuscript, an additional statement about the uncertainty associated with WSON and WION has been added to the text, as follows: (Section 2.3) "*This may lead to an underestimation of WSON and overestimation of WION if WSTN is associated with compounds that have nitrogen atoms adjacent to carbon atom.*" (Section 4, Conclusions) "*It should be noted that if organic compounds having nitrogen atoms adjacent to carbon atom in their molecular structure are present in the sampled aerosols, some components associated with WSON may not be determined quantitatively under our operating conditions. This may lead to an uncertainty of WSON being underestimated and thus, WION may be overestimated.*"**

We would like to mention that water-soluble organic nitrogen compounds that have

been found in marine aerosols (*e.g.*, amino acid, amine, amide, etc.) are mostly detected by our instrument. Thus, we believe that the uncertainty associated with the detection of compounds such as 4-pyrazole carboxylic acid and acetohydrazide (Table 1) appears to be insignificant.

Comment 4: The very high levels of nss-SO4 at the latitudes 40-44 (which is the focus region where high OC/ON are associated with marine biogenic emissions) is not discussed at all (volcanic eruption is proposed but for the lower latitudes). For that reason, very long range transport of anthropogenic SO2 is still hard to exclude here, bringing different lights to the "high" levels of organic nitrogen/carbon in this region.

***Reply 4*: At 40–44ºN, both nss-SO_4^{2-} and MSA showed high concentrations, with an average MSA/nss-SO_4^{2-} ratio of 0.021. This ratio is within the range (0.02–0.04) of those reported for clean marine air over the western North Pacific obtained by Nagao et al. (1999), who suggested that most nss-SO_4^{2-} transported to Hahajima (142.10ºE, 26.38ºN) in the summer originated from DMS oxidation, based on their long-term measurements of nss-SO_4^{2-} and MSA. Moreover, in the first paragraph, it is suggested that the aerosols sampled at 40–44ºN were largely influenced by oceanic emissions, based on the trajectory and the back-trajectory-weighted chlorophyll *a*. We believe that all of these results support significant influences of marine biological sources on aerosols in this oceanic region. Taking account of the comment, we have added the above explanation for high nss-SO_4^{2-} concentrations at 40–44ºN to the revised manuscript.**

Comment 5: Section 3.2. Based solely on day/night samples, it is claimed that local photochemistry had an insignificant effect on the temporal variation of TN (not ON?). You do not have sufficient data to claim such strong statement.

***Reply 5*: We agree that the statement was perhaps too strong. In the revised manuscript, we have changed the sentence, as follows: "*This result implies that the local time dependence on the temporal variations of ON was likely insignificant in the present study.*"**

Comment 6: Section 3.3. Russel et al. (2010) found primary WSOC in submicron aerosols. Based on the lack of correlation between your bulk WSOC and local Wind speed (or Na+) you conclude that the majority of your WSOC is secondary. Again, you do not have sufficient data to claim such strong statement. Submicron primary WSOC associated with sea salt is likely to have a lifetime of several days, and for that reason, can be disconnected from local supermicron sea salt emissions. Later in the paragraph you found a correlation of

0.37 between Na+ and WIOC and you conclude that your WIOC is originating from bubble-bursting. Although there is good reason to think that WIOC is mostly primary and associated with Na+, I am not sure that a r2 of 0.37 is enough to clearly state it. Again, you do not have sufficient data to claim such strong statement.

***Reply 6*: In Miyazaki et al. (2010b), we reported no significant correlation between WSOC and Na^+ ($r^2 = 0.03$) in the submicrometer particles collected during a similar season in a similar region of the western North Pacific as that examined in the present study. In contrast, WSOC showed significant correlations with MSA and oxalic acid in the submicrometer range of those particles. These results support our conclusion that the majority of WSOC in our samples appears to be of secondary origin. Similarly, the r^2 between WIOC and Na^+ in the submicrometer range of those particles was much higher ($r^2 = 0.52$) than that for bulk aerosols, as we have already reported (Miyazaki et al., 2010b). This result supports that WIOC in the present study is mostly of primary origin. As we agree with the comment that the statement was perhaps too strong, the related sentences have been changed, as follows: (First paragraph of section 3.3) "*WSOC showed no significant correlation with Na^+ ($r^2 = 0.02$) or local wind speeds, supporting that the majority of WSOC appears to be derived from secondary production.*" (Second paragraph of section 3.3) "*WIOC in our samples showed a linear relation with Na^+ ($r^2 = 0.37$), as we observed the relation ($r^2 = 0.52$) in the submicrometer range of particles collected in a similar oceanic region (Miyazaki et al., 2010b). The result indicates that a bubble-bursting production mechanism could explain the major fraction of WIOC in the aerosols collected.*"**

Comment 7: Section 3.4. You use the isotopic information to confirm the biogenic source of OC. From the data shown in Figure 6, this is not convincing at all. A significant amount of samples have isotopic signatures closer to the continental signal (i.e. below -24); half of these samples showing MSA levels above 30ng/m3 (becoming 20ng/m3 in the text). In other words, it suggests anthropogenic influence for OC at the latitudes 40-44. It remains that samples with high isotopic ratio do show higher ON/OC for high MSA. However, later in the paragraph you claim that WSOC is secondary based on a correlation coefficient of 0.57 with MSA. Although there is good reason to think that WSOC is mostly secondary, I am not sure that a r2 of 0.57 is enough to clearly state it. What is the r2 value if you remove the 3 points of WSOC of high concentrations? (Isotopic signature of these 3 samples??). Again, you do not have conclusive correlation to claim such strong statement.

***Reply 7*:**

With regard to the criteria for the MSA levels, "20 ng m^{-3}" is correct. Accordingly, the number in Figure 6 has been corrected. The data points with the $\delta^{13}C$ values < −24‰

were obtained at 15-18°N and 30-35°N, which may include the influence of terrestrial sources, to some extent. However, the data obtained in these latitudinal regions do not significantly affect our conclusion. We applied $\delta^{13}C$ values of −22‰ to −21‰ for marine OC and −27‰ to −26‰ for terrestrial OC, which are found typically in the northern hemisphere. Following isotopic mass balance equations, our calculation indicates that marine sources contribute 88±12% of the aerosol carbon, on average. Even if we remove the data points for the three largest WSOC concentrations, the r^2 value for WSOC and MSA remains high (0.78). Additionally, WSOC showed significant correlations with MSA and oxalic acid in the submicrometer range of particles obtained in Miyazaki et al. (2010b), consistent with the majority of WSOC being a secondary product. For the three data points with the highest WSOC concentrations, $\delta^{13}C$ values are in the range of -20.7‰ to −22.3‰, which are similar to those of OC in seawater. Taking account of the comment, the last sentence of the paragraph has been revised, as follows: "*The result indicates an enrichment of nitrogen in organic aerosols in the oceanic region with high biological productivity and the preferential transfer of nitrogen-containing compounds from the sea surface to the marine atmosphere.*"

Comment 8: Section 3.5: You found here a positive correlation between WION and wind speed. Based on this result, you claim that WION is of primary origin. You state the same for WION/WIOC. From Figure 7a and 7b, I cannot see any clear correlation in these datasets. I do find no real connection between these datasets, in particular for the high latitudes(40-44N). For that reason, I cannot support the statements provided in the text regarding correlations with wind speed (which conclusion appears as one of the most significant of the paper). The end of the paragraph is confusing (you mention DMS as a gas precursor for ON). It is contradictory with the beginning (mechanisms of primary and secondary formation of WION remain elusive).

***Reply 8*: At 10-40°N, the r^2 between WION and local wind speed (LWS) was 0.40, and that between WION/WIOC and LWS was 0.45. Because the term "correlation" does not seem to be suitable here, the sentence has been modified, as follows: "*The WION concentrations tended to increase with increasing local wind speed at 10–40°N.*" Similarly, the last sentences in the Conclusions have been revised, as follows: "*Both WION concentrations and WION/water-insoluble organic carbon (WIOC) ratios tended to increase with increasing local wind speeds, indicating that sea-to-air emissions of ON via sea spray contributes significantly to the marine organic aerosols over the study region.*" We have already mentioned in the text that the relation between WION and LWS at 40–44°N was less evident. Nevertheless, samples with high WION concentrations (> 150 ngN m^{-3}) and WION/WIOC (> 0.2) were indeed obtained at**

higher wind speeds (> 6 m s^{-1}). This means that, in addition to the possible primary production of WION, there may be another possibility that could partly explain the increase of WION at 40–44ºN. We discuss this point in the last two paragraphs of Section 3.5. We do not intend to say that DMS is a direct gas precursor for ON, but we do intend to mention that the secondary production process for ON, if it exists, might be similar to that for MSA from DMS. To avoid confusion, "DMS" in line 5 of page 14 and the phrase "remain elusive and" (last sentence in Section 3.5) have been deleted in the revised manuscript.

Minor comments:
Comment 9: Introduction – line 7 / You can also add the biogeochemical sulphur cycle (which is probably the most important biogenic contributor of marine CCN).

***Reply 9*: According to the comment, we have made an additional statement about the biogeochemical cycle of sulfur, as follows: "*The ocean is the largest source of natural reduced sulfur gas to the atmosphere, most of which is in the form of dimethylsulfide (DMS). DMS derived from phytoplankton is a biogenic precursor gas for sulfate (SO_4^{2-}) aerosols that alter the Earth's radiative forcing directly by scattering solar energy and indirectly by acting as cloud condensation nuclei (CCN).*"**

Comment 10: Introduction – line 19 / You can also add several references regarding the modeling of the global emissions of marine organics (Spracklen et al., GRL, 2008; Vignati et al., Atmospheric Environment, 2009; Myriokefalitakis et al., Advances in Meteorology, 2010).

***Reply 10*: All of the above references have been included the revised manuscript.**

Comment 11: Section Aerosol sampling / - Line 25-26. The ship track is not easy to understand from these 2 lines. Please re-phrase them - Provide briefly information on meteorological conditions (rain ?) - Line 30: "ending" instead of "starting"

***Reply 11*: The sentences have been modified, as follows: "*Aerosols were sampled during the R/V Hakuho-maru cruise (KH08-2) from Kushiro (42.98°N, 144.37°E) to Tokyo (35.65°N, 139.77°E), Japan, in the western North Pacific from 44°N to 10°N along 155°E, which covers the subarctic to subtropical region (Fig. 1). Aaerosol samplings were conducted between 24 August and 13 September 2008. The weather was mostly fine with very few rainfall events (< 6% of the total sampling time).*" Additionally, the word "starting" has been changed to "ending", as suggested.**

Comment 12: Section Chemical analyses:
line 23, page 5, agreement between TC (sunset lab) and TC (Elemental analyzer). Please provide r2, slope and intercept.

***Reply 12*: In the revised manuscript, the values of r^2, slope, and intercept have been provided.**

Comment 13: line 25, page 5, Quartz filters may show significant amount of blank values for Na, Mg, Ca. This will strongly affect the calculation of sea salts (and nss-SO4). Please provide more information on the IC results (including blank values).

***Reply 13*: According to the comment, the blank values for those ions have been provided in the revised manuscript.**

Comment 14: line 3, page 6, it is more straightforward to write WION = TN – WSTN, which species (TN and WSTN) have been directly determined by EA & TOC/TC analyzers.

***Reply 14*: We agree and the definition of WION has been rewritten, as suggested.**

Comment 15: You report for these 2 species uncertainties of 9 and 12%, respectively. But you WION uncertainties is then only 16%. Is it normal?

***Reply 15*: We calculated the uncertainty (precision) of WION (16%) by simply considering the propagating errors of TN (9%) and WSTN (12%). This calculation is correct. The accuracy for WION is discussed in Section 2.3.**

Comment 16: Section 2.3, line 16, page 6: “Table 1 summarizes the results” . . . of what ?

***Reply 16*: The sentence has been changed, as follows: “*Table 1 summarizes the results of the experiment.*”**

Comment 17: Section 2.4, line 4: “. . .every 1 hour along each of the 5-day backtrajectory” instead of “. . .every 1 hour the 5-day back trajectory each”

***Reply 17*: This has been revised, as suggested.**

Comment 18: Section 2.4, line 10 / “ended” instead of “started”

Reply 18**: This has been revised, as suggested.**

Comment 19: Section 3.1. The use of MSA as a tracer of biogenic emissions is confusing here and one might think that connection with chl-a is direct. One must keep in mind that DMS lifetime at these latitudes is typically of 1 day during the summer period. For that reason, enhancement of MSA cannot be really linked with in-situ chl-a measurements

Reply 19**: MSA was used as an indicator of secondary aerosols of marine biogenic origin in this study. In fact, the chlorophyll *a* data shown in Figure 2a are not from in-situ measurements, but from the satellite-derived average values taken from each position of the back trajectories (*i.e.*, they are not the values at the sampling points), as we stated in Section 2.4. The trajectory-weighted chlorophyll *a* data showed that the air masses corresponding to aerosol samples collected at 40–44ºN had passed over a higher chlorophyll *a* region, approximately 12-36 h before reaching the ship. This means that the time scale for the transport of air masses that were largely influenced by high biological activity upwind the sampling point is similar to that for the oxidation of DMS to MSA (~1 day). Thus, the enhanced MSA concentrations can be linked with the trajectory-weighted chlorophyll *a* at 40-44ºN, as shown in Figure 2. On the other hand, the trajectory-weighted chlorophyll *a* value was low in the subtropical region, although the MSA showed increased concentrations. This can be attributed to high marine bacteria activity rather than activities of phytoplankton in the subtropical regions (10-20ºN), which is indicated by the measured concentrations of cyanobacteria in surface seawater during the same cruise. We have added these statements in the revised manuscript.**

Comment 20: Section 3.2, line 4, page 10: "acidic sulfates". What do you mean exactly? Later in this paragraph, please add "nss-" before "SO42-".

Reply 20**: Acidic sulfates are sulfates that are available for reaction with gaseous amines. As suggested, "nss-" has been added before "SO_4^{2-}".**

Comment 21: Section 3.4, line 31, page 11: ". . . comparable to but higher". This is confusing. It is comparable or higher? I cannot be the 2 at the same time.

Reply 21**: In the revised manuscript, the sentences have been modified, as follows: "*The average ON/OC ratio was 0.19±0.11 during the study period, which is higher than the typical ON/OC ratios (0.06–0.11) reported for oceanic dissolved materials (Hansell and Carlson, 2002).*"**

Comment 22: Section 3.4: You compare your ON/OC obtained in the marine atmosphere with those reported in a boreal forest. I don't think that such comparison is really useful. You conclude higher ON/OC ratio in this study compared to others. What are these studies? (This ratio is lower than that reported by Miyasaki et al. (2010a), not higher).

***Reply 22*: We agree with the comment that the comparison with the ON/OC ratio at a forest site is not useful here. The description about the ratio at a forest site has been removed in the revised manuscript. Also the whole sentences have been modified to clarify the discussion, as follows: "*Miyazaki et al. (2010a) also reported higher ON/OC ratios (0.35–0.49) compared to those for the oceanic materials both in the submicrometer and supermicrometer size ranges of marine aerosols obtained farther north of our present study areas in the western North Pacific with high marine biological productivity. Based on the comparison with the typical ON/OC ratios in oceanic dissolved materials, the present results indicate an enrichment of organic nitrogen in the marine aerosol collected in the area studied.*"**

Comment 23: References: Some of them only contain 1 author et al. Please provide the full references.

***Reply 23*: In the revised manuscript, the full references have been provided.**