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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Latitudinal distributions of organic nitrogen and organic carbon in marine aerosols over the western North Pacific" *by* Y. Miyazaki et al.

Anonymous Referee #1

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This paper presents a new set of aerosol data collected in the Western North Pacific where the authors have already reported significant emissions of organic aerosols of a biogenic marine origin (Miyasaki et al., 2010a, 2010b). A focus is made here on organic nitrogen (watersoluble / water insoluble) and its comparison with organic carbon and tracers (MSA, DEA) on a latitudinal transect.

An attempt is made to investigate the formation mechanisms responsible for the observed concentrations of these marine organics. This paper is relatively clear in its presentation.

Although this paper presents a large set of chemical characterizations, most of the

conclusions drawn here are based on insufficient chemical information and scientific interpretation is often weak. Major comments are given below.

Major comments:

+ 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 1.54cm^2 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=500cm^2, 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.

+ 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 o 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.

+ 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).

+ 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.

+ 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.

+ 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 r^2 of 0.37 is enough to clearly state it. Again, you do not have sufficient data to claim such strong statement.

+ 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 r^2 of 0.57 is enough to clearly state it. What is the r^2 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.

+ 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 (40-44°N). 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).

Minor comments:

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

+ Introduction – line 19 / You can also add several references regardong the modelling 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).

+ 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”

+ Section Chemical analyses: - line 23, page 5, agreement between TC (sunset lab) and TC (Elemental analyzer). Please provide r^2, slope and intercept. - 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). - 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. You report for these 2 species uncertainties of 9 and 12%, respectively. But you WION uncertainties is then only 16%. Is it normal ?

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

+ 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”

+ Section 2.4, line 10 / “ended” instead of “started”

+ 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

+ Section 3.2, line 4, page 10: “acidic sulfates”. What do you mean exactly ? Later in this pragragh, please add “nss-“ before “SO42-“.

+ 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.

+ 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).

+ Rerecences: Some of them only contain 1 author et al. Please provide the full references.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 28721, 2010.