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Reply on RC2

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Author comment on "Long-range transport of anthropogenic air pollutants into the marine air: insight into fine particle transport and chloride depletion on sea salts" by Liang Xu et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-623-AC2, 2021

Anonymous Referee #2

General Response: We thank the Referee for your helpful comments. We have addressed all comments and provided point by point response below. The revised manuscript is presented in below Response.

This study investigates long-range transport of particles into the marine air and aging of sea salt particles. The authors investigated samples from research ship from the Eastern China seas (ECS) to the Northwestern Pacific Ocean (NWPO). They utilized transmission electron microscopy (TEM) to study the morphology and elemental composition of individual particles. They classified particles into different groups and found that S-rich organic matter and S-rich soot (anthropogenic aerosol, ~87%) dominated in the ECS, while sea salt particles were most abundant (~90%) in the NWPO. They further investigated aging of sea salt particles and classified them as fresh sea salt, partially aged and fully aged salt particles. They found higher number fraction of fully aged sea salt particles in the ECS site (86%) compared to the NWPO site (31%). The authors argue that significant Cl depletion of particles at the NWPO site and presence of minor fraction of anthropogenic aerosol, indicated anthropogenic gases transported to the site and responsible for the ageing of sea salt particles.

While the study is interesting, but several issues need to be addressed before it can be considered for publication.

Answer: We appreciated the Referee#2's comments which significantly improve the quality of the manuscript. We carefully answer them one by one as below. The modifications were highlighted in red in the revised manuscript.

Specific comments:

1. One of the main highlights of this study is that anthropogenic gases transported longer

distances compared to the anthropogenic aerosol. However, the results are not supported by any gas phase measurements. The authors should be carefully about some of the bold claims.

Answer: Indeed we do not have in-situ gas concentration data to discuss its transport. In order to solve the problem, we acquired satellite observation data to supplement our results (Figure S1).

2. The authors talk about primary and secondary aerosol, but their differentiation is not supported by any quantitative number. The authors should discuss about the O:C ratio. Also, particle classification sounds more subjective. The classification of different aging of salt particles is based on morphology and elemental composition. Perhaps a fixed criterion of elemental ratios would be useful to classify them along with morphologies.

Answer: I really appreciated the referee#2's comments. In my opinion, different instruments might have their own advantages to analyze aerosol particles. TEM/EDS is not good at quantifying the O and C because the carbonaceous substrate might affect its peak in the elemental spectra. In the individual particle analyses, integration of particle morphology and elemental composition can be an effective way to classify the particle type. We also want to make clear here about the data process. For the TEM analyses, we all manually classified the particles into different particle types based on their morphology and major compositions. The work is different from CCSEM and online instruments that can obtain compositions of large number of particles. Then they can process the semi-quantitative or quantitative data to classify particles even they could not concern the particle morphology. Therefore, I can say that these are different methodologies to identify particle types. It is hard to find a fixed ratio of elements to classify SSA aging degrees. For example, the elements in the center and periphery of a partially aged SSA are different (see Figure 5b). Here the best way is to combine elements and morphologies to identify SSA particles.

Although the classification of SSA particles was manual work, we distinguish the SSA aging degree following the rules in Section 3.4 to minimize the bias. The method was also applied in our previous paper (Chi et al., 2015, Sea salt aerosols as a reactive surface for inorganic and organic acidic gases in the Arctic troposphere, Atmospheric Chemistry and Physics).

3. The discussion of size dependent aging is not convincing. Some discussion is needed regarding possible Cl depletion of those particles by organics or sulfate? In general, do you see more organic coating for smaller particles?

Answer: Thanks. We try to improve the discussion part. In this study, we concerned the Cl-depletion of sea salts particles based on their elemental composition and morphology (Figure 4), although we did not analyze the organic species in aged particles. Here TEM images could not directly display possible organic coating for smaller SSA particles. But from the SSA aging reaction with organics, we could expect the possible organic coating. In addition, the previous literature used NanoSIMS to directly obtain the organic species mixed in aged sea salts (Chi et al., ACP, 2015). The literature also indicated that the organics should be prevalent in the aged particles.

If we clearly identify particle types (e.g., fresh, partially aged, and fully aged sea salt), we can obtain particle aging properties among different sizes. For individual particle analysis, particle number fractions among different size bins can be used to reflect properties of particle aging, as shown in Figure 8.

4. The authors talk about long-range transport, but discussion of air mass transport and ageing time are vague.

Answer: Based on the HYSPLIT backward trajectories, the air masses in the ECS samples were mainly from eastern China. Most of air masses in the NWPO samples originated from northwest, passing through Japan to sampling location. We added more description to discuss air mass transport.

The aging time is hard to quantify due to the limitation of HYSPLIT. We roughly counted the transport time of the ECS samples is 24 to 48 hours.

Context: Indeed, the HYSPLIT backward trajectories show that the air masses in the ECS samples were mainly from eastern China (Figure 1).

Most of air masses in the NWPO samples originated from northwest, passing through Japan to sampling location within 48 hours.

5. What about the background ozone concentration at the sites? Aqueous sea salt particles, in presence of light and ozone can undergo rapid Cl2 formation via OH generation in the aqueous phase photochemistry of dissolved ozone.

Answer: Indeed, Cl_2 formation due to ozone in aqueous SSA particles under UV could lead to Cl-depletion. Unfortunately, we do not have in-situ background ozone concentration data to discuss its effect on SSA aging.

Here we obtain one ozone mapping in East Asia, the ozone concentration during our cruise did not show huge difference from satellite observation (see figure below). Therefore, we can conclude that ozone might be one of the factor causing Cl-depletion, but it should not be the major reason leading to huge difference in SSA aging degrees in different NWPO samples.

The image was downloaded from NASA Giovanni website,
http://giovanni.gsfc.nasa.gov/giovanni

We added one sentence to make explanation about the ozone in the manuscript.

6. The meteorological data is not discussed properly. Some of samples were collected at high RH conditions that may have aqueous sea salt particles, how that affect the aging of particles and transport of gases.

Answer: Thanks. This is an interesting point which we also concerned in this work. It is well known that the deliquescence relative humidity (DRH) of NaCl is near 75%, but its efflorescence relative humidity (ERH) is 44%. In our study, the sampling RH were higher than 40%, more than half of them were collected at RH above 60%. Thus, in the humid marine air, SSA particles could exist as aqueous droplets, at least their surfaces may be liquid-like due to the existence of hydrates (e.g., $MgCl_2$).

We added one paragraph to discuss comments in Question 5 and 6.

Context: Meteorological conditions also play an important role in SSA particles aging. The hygroscopic cycle of the pure SSA particles shows the deliquescence relative humidity (DRH) near 75% and its efflorescence relative humidity (ERH) near 44%. However, the natural SSA particles begin to take up water at 57% and form a liquid layer on particles due to various inorganic compounds (e.g., $MgSO_4$, $MgCl_2$, and $CaCl_2$) (Wise et al., 2009). In our study, the sampling RH values were higher than 40% and more than half of them were collected at RH above 60% (Table S1). Therefore, most SSA particles should exist as aqueous droplets during the particle hygroscopic cycle, or at least particle surfaces kept the aqueous phase due to the existence of various inorganic compounds (Wise et al., 2009). One previous study showed that Cl-depletion in the aqueous SSA particles due to

ozone under UV can produce Cl_2 (Oum et al., 1998). However, the averaged ozone concentration ranging from 42 to 46 ppb during our cruise did not exhibit large differences from the satellite observation in marine air (Figure S1c). Therefore, we conclude that ozone might be one factor causing Cl-depletion in aqueous SSA particles but should not be the major reason leading to the variations of SSA aging degree in different NWPO samples.

7. Samples from ECS to NWPO is very confusing. Please note the Fig.3 and Fig. 7 should have same notations. It seems like some of the samples that show higher aging of sea salt particles (samples 13, 14 and 15 in Fig 7). Are those same samples that also contain higher number fraction of anthropogenic particles?

Answer: Sorry for the confusion. Sample 15 should be classified into the ECS sample, but we mistakenly labeled it into the NWPO in Figure 7. This is the reason why Figure 3 and Figure 7 have different notations. We have corrected the error in Figure 7.

For Samples 13, 14, and 15, only Sample 15 contain higher fraction of anthropogenic particles. Because Sample 15 is closer to continent than other two samples. This also confirms our perspective that anthropogenic gases could be transported farther than aerosols in marine air.

8. The average number fraction of fully aged and partially aged sea salt particles seems ~45-50% from Fig. 7. Are there any bias for some of the high Cl depleted samples collected at the NWPO site?

Answer: In total, the fully aged and partially aged SSA particles accounted for 43% in the NWPO samples. The high resolution TEM images can obtain particle details, so it is no problem to identified different types of aged SSA. Due to the manual operation and labor work, we could not analyze large number of particles in the samples. As the reason, we randomly selected one area from center to periphery of the TEM grid which can fully cover the coarse and fine particles. We generally analyze all the particles in the area. The analyzed procedure can guarantee us to obtain enough particles and well represent all sized particles in the samples. We manually and carefully exam every single particle to minimize the bias.

Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2021-623/acp-2021-623-AC2-supplement.pdf