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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Photochemical aging of organic and inorganic ambient aerosol from the Potential Aerosol Mass (PAM) reactor experiment in East Asia” *by* Eunha Kang et al.

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Authors Response to Reviewer 1

Reviewer 1 comments

Kang et al. present size- and chemically-resolved measurements of ambient aerosols from a Baengnyeong Island receptor site in South Korea. The measurements alternate sampling through a conventional inlet line and a PAM oxidation flow reactor to subject the ambient air to 5 days of simulated photochemical aging by OH radical. In general, passing ambient air through the reactor resulted in increased sulfate concentrations

from SO2 oxidation, and decreased organic and nitrate concentrations due to fragmentation/evaporation. The oxygen-to-carbon ratio of the organic aerosols increased from 0.6-0.8 to 1.0-1.2 depending on whether the air mass originated from China or the Korean Peninsula. Overall, I thought that the manuscript demonstrates a useful application of the flow reactor paired with particle instrumentation to examine effects of oxidative aging on the physical and chemical properties of ambient aerosols. There were a few sections that might benefit from further clarification or discussion. I would support publication in Atmospheric Chemistry and Physics after consideration of my comments below.

1. The authors never explain why the PAM reactor was only operated at a single OH exposure of 7*1011 molec cm-3 sec (5 days at [OH] = 1.5*106 cm-3). This condition should favor fragmentation reactions, resulting in the net decrease in organic concentrations that was observed. Why wasn’t the reactor also operated at lower OH exposures that might favor functionalization reactions, as has been done in other field studies that used the PAM reactor? (see, for example: Tkacik et al., 2014; Ortega et al., 2016; Palm et al., 2016). Presumably, this would have given more information about the precursors contributing to SOA formation. Because air masses had already been processed for ∼30- 60 hrs by the time they reach Baengnyeong Island (Fig. 8), I can see why it wouldn’t be necessary to survey as wide a range of conditions as the studies referenced above. But it isn’t clear to me why more reactor operating conditions were not studied (or, if they were studied, why the results weren’t presented).

[Response] Our experiment was done at Baengnyeong Island in 2011 as the first field measurement in Korea. The Baengnyeong island is located in the middle of the Yellow Sea without sizeable local sources, thus it is considered as an ideal place to monitor air masses transported from China or even from the Korean Peninsula. The Baengnyeong site was originally established as a background station to monitor Asian dust. The year-round AMS measurements at Baengnyeong Island (Choi et al., 2016) showed that the contribution from primary emission was very low even in clod season and OAs were mostly more oxidized compared to those of China or other urban sites such as New York or Mexico City. When meteorological conditions met, however, concentrations of aerosol and gaseous species are highly elevated in air masses directly transported from urban regions of nearby continents. Actually, we wished to capture these plumes. Considering the dynamic change of meteorological conditions in the study region, we designed the experiment as simple as possible and operated the PAM reactor with single OH exposure equivalent to $\sim$3-4 days of ambient aging. As you recommended, it would be perfect if the PAM would have been operated at low OH exposure. One of the reasons for high OH exposure was high humidity in summer. As mentioned above, we had planned to make measurement in spring. However, the experiment was delayed several times due to bad weather. As it takes 5 hours to get to the Island by ship, weather condition is critical for logistics. The biggest obstacle is severe fog as well as strong winds. Wind used to be strong in March-April and fog is the most frequent in May-June. July is a season for summer monsoon with heavy rains. That is how we had experiment in the middle of high summer, during which a strong typhoon passed across the center of the Yellow sea (8 August). It is not frequent for typhoon hit the center of the Yellow Sea. In the near future, PAM reactor will be operated with various OH exposure levels to observe the progress of SOA formation, growth and fragmentation in northeast Asia region.

[Manuscript revision] Page 4 Line 100: Added the sentence: In previous studies, sulfate and organic aerosols were measured in Baengnyeong Island, showing the influence of pollution plumes transported from eastern China and the Korean Peninsula (Choi et al., 2016; Lee et al., 2015). Page 5 Line 113-122: This part was reworded as follows. The potential aerosol mass (PAM) reactor is a small flow-through aluminum cylinder equipped with long Hg lamps (model no. 82-9304-03, BHK Inc., 185 nm and 254 nm emission) to produce large amounts of OH and O3, creating a highly oxidizing environment. Detailed descriptions of the PAM reactors are given in previous publications (Kang et al., 2007; Kang et al., 2011b; Lambe et al. 2011). The OH exposure of PAM reactor was estimated against sulfur dioxide decay in the laboratory (Kang et al.,

2011b), giving 7 x 1011 molecules cm-3 s. It is equivalent to an integrated OH concentration over 4.6 days at a typical noon-time concentration of 1.5 x 106 molecules cm-3, which was lower by 25 % than was expected due to the external OH suppression. The OH suppression from VOCs and other OH-reactive gases were calculated using the oxidation chemistry model with 30 s-1 of external OH reactivity, representing rural areas. In the present study, therefore, we examined that the air masses reaching Baegnyeong Island were further oxidized during the effective aging time of 4.6 days.

2. What was the chloride concentration that was measured with the AMS? [Response] Chloride concentrations were very low, compared to other inorganic species such as nitrate, ammonium and sulfate. For instance, chloride concentration was less than 10 % of nitrate as shown in the figure below. That is why chlorine was not discussed in the text.

[Manuscript revision] The following is Figure 2b with chlorine.

3. P6, L143-L146: The authors state: "The difference in mass concentrations between the PAM aerosols and the ambient aerosols was in the range of $\sim$3–7 μg m-3 , indicating that photo-oxidation resulted either in the loss of pre-existing particles or in the formation of secondary aerosols." This statement seems to contradict the data presented in Table 1. For both the "organics-dominated" and "sulfate-dominated" episodes, the mean increase in mass from ambient to PAM-oxidized aerosols was +2.3 μg m-3 (14.0 to 16.3 and 24.3 to 26.6). Additionally, the net change in sulfate + nitrate+ ammonium + organics mass was -1.1 μg m-3 (8.0 to 6.9 and 11.2 to 10.1 μg m-3). So, how do the authors calculate that mass concentration increased by 3-7 μg m-3 following oxidation in the PAM reactor?

[Response] First of all, the mass difference of $\sim$3 – 7 μg m-3 was an error and should be -3 $\sim$ 7 μg m-3. Second, the mass concentration of -3$\sim$7 μg m-3 is the minimum and the maximum difference between ambient and PAM-processed aerosols calculated from hourly averaged concentrations that were converted from SMPS measurements for the entire experiment period. In Table 1, however, the mean mass concentrations are given for ambient and PAM processed air during each episode, of which difference was coincidently the same.

[Manuscript Revision] Page 6 Line 14: The error was corrected.

4. P8, L206: What is “non-linear oscillatory nucleation”?

[Response] In the previous laboratory experiment, Kang et al. (2011) examined the transient peaks of OA mass concentration at nuclei mode and smaller stable peaks at larger size range under high OH exposure. These transient peaks were supposed to be related to the non-linear oscillatory nucleation and growth of OA, which was referred by McGraw and Saunders (1984). An initial burst of particles followed by the oscillatory mode with a lower particle number density was explained by the competition between the rapid formation of nuclei mode clusters and the condensation onto new particle surfaces of condensable species. Our PAM reactor formed a large number of nuclei mode clusters by the rapid oxidation reaction.

[Manuscript revision] P9, line 207: The two references were given: McGraw & Saunders (1984) and Kang et al. (2011b). Also, the following sentence was added: It explains numerically the gas-to-particle conversion, considering competition in removal between the nucleation and growth of new particles for the condensable species.

5. P10, L235-L236: The authors state: “Thus, chemical transformation from low O:C to high O:C is more likely to explain the organic mass loss.” What is the change in temperature inside the reactor (with lamps on) relative to ambient temperature? How much of the decrease in organics can be explained by simple temperature-induced evaporation?

[Response] In our experimental setup, the PAM reactor was installed beside the window in the laboratory and ambient air was pulled through a Teflon tubing ($\sim$ 30 cm) from PM2.5 cyclone outside the laboratory. In the PAM reactor, the two UV lamps were

housed in Teflon tubing being purged by nitrogen gas. In the previous study by Ortega et al. (2016), UV lamps were housed in nitrogen-purged Teflon tubing. They reported about 2 °C higher inside the PAM reactor with full power-lighted UV lamps than the ambient air. Although we did not measure the temperature inside the PAM reactor, temperature increase was thought to be insignificant because the PAM reactors used in the two studies were the same kinds that were distributed by PennState. In a recent discussion (2016-10-17_PAM_Users_Mtg_Jimenez_Group_Final_v2.pdf) posted on PAM User’s meeting, however, about the 10 °C difference between PAM and ambient air caused the evaporation of NO3 up to 34 % and OA up to 25 %. Thus, we added more detailed information on the setup of PAM reactor and the relevant discussion as follows.

[Manuscript revision] P5, L114: “. . . equipped with long Hg lamps emitting 185 nm and 254 nm (model no. 82-9304-03, BHK Inc., USA) to produce large amounts of OH and O3, creating a highly oxidizing environment. The UV lamps were housed in Teflon sleeves being purged by nitrogen to prevent heat and O3 from building up. The results of Ortega et al. (2016) using the same PAM reactor as that used in the present study, demonstrated that temperate was increased by about 2 °C inside the PAM reactor and its effect on evaporation of OA or nitrate was insignificant.

6. P14, L343-L347: The authors state: “The nitrate loss is rather explicit in the PAM reactor because of efficient conversion of SO2 to sulfate, causing the aerosols to become acidic and causing particulate nitrate (HNO3(p)) to evaporate.” How much of the decrease in nitrate can be explained by simple temperature-induced evaporation from the lamps being turned on in the reactor?

[Response] As mentioned above, we did not measure the temperature inside the PAM reactor and thus, it is not plausible to quantitatively assess the loss of nitrate by temperature-induced evaporation. Based on the published results by Ortega et al. (2016) and a reported document (2016-10-17_PAM_Users_Mtg_Jimenez_Group_Final_v2.pdf), however, it is likely that the loss of nitrate by temperature-induced evaporation was insignificant in this study. These two studies imply that the increase in temperature would be no higher than 2 °C in our PAM reactor and nitrate was lost by 34 % at most when the increase in temperature was greater than 10 °C.

[Manuscript revision] P14, L344: The following sentence was added. As stated in section 2, the loss of nitrate by temperature-induced evaporation would be insignificant.

7. Table 1 and elsewhere: For the “organics-dominated” episode, the total mass of ambient sulfate + nitrate + ammonium + organics was 8.0 μg m-3 , whereas the mass calculated from the SMPS size distributions was 14.0 μg m-3 (assuming density of 1.2 μg m-3). Then, for the “sulfate-dominated” episode, the total mass of ambient sulfate + nitrate+ ammonium + organics was 11.2 μg m-3 compared to the mass of 24.3 μg m-3 calculated from SMPS. EC was typically $\sim$1 μg m-3 (Fig. 4). Thus, in both cases the aerosol mass measured by AMS was $\sim$50% of the mass calculated from SMPS. What collection efficiency was applied to the AMS data? Is it possible that a CE of 0.5 is approximately valid but was not applied? If not, a composition-dependent CE should be calculated and applied to the AMS mass concentrations that are presented. See, for example, Middlebrook et al., 2012.

[Response] Composition dependent CE is especially important when the particles are acidic or contain large amount of nitrate and when the OH exposure of PAM reactor is very high (Middlebrook et al., 2012; Ortega et al., 2016). In this study, the OH exposure was about 7 x 1011 molecules cm-3 s, for which the CE comes close to 0.5 (Ortega et al., 2016). In addition, the equivalent ratio of ([NH4]/(2x[SO4]+[NO3]) was 0.7$\sim$1.2 for ambient and PAM aerosol, respectively. According to Middlebrook et al. (2012), the CE would fall into the range of 0.45$\sim$0.5 if the equivalent ratio of the aerosol is between 0.7 and 1.2. The fraction of ammonium nitrate mass varied in the range of 0.01$\sim$0.22 in this study, for which the CE would stay constant near 0.5. While revising the manuscript, we were able to go over the collection efficiency of the AMS and composition dependent CE was applied to calculate AMS mass concentrations. As a

result, all AMS concentrations were modified in the revised manuscript. The composition dependent CE resulted in much better agreement between the mass measured by AMS and SMPS mass calculated with particle density of 1.2 g cm-3.

[Manuscript Revision] Page 5, line 112: For concentrations measured by AMS, composition dependent collection efficiency was applied by adopting the result of Middlebrook et al. (2012). Detailed descriptions of the HR-ToF-AMS and the sampling site can be found elsewhere (Lee et al., 2015).

8. Table 1 and elsewhere: The authors assume a density of 1.2 g cm-3 . I think it would be better to calculate an effective density directly from the AMS and SMPS size distributions that would be more applicable to the data. See, for example, DeCarlo et al., 2004.

[Response] We re-analyzed the AMS measurements with composition dependent collection efficiency. As a result, the AMS mass became much closer to SMPS mass that was calculated with the particle density of 1.2 g cm-3. Because the main mode of organics, sulfate and nitrate were found at the same size in their size distributions, the particles we observed were quite likely to be internally mixed. Thus, it wouldn’t be inappropriate to use the constant density and we would like to leave it as a further study. Actually, the estimation of species-specific density is beyond the scope of this study.

9. Figure 3: It is difficult to quantitatively interpret this figure. Instead of presenting this figure, please consider adding rows to Table 1: Mass (10-50 nm), Mass (50-200 nm), Mass (200- 400 nm) for all “ambient” and “PAM” columns during the organic and sulfate episodes.

[Response] The purpose of Figure 3 is to show the overall characteristic of the PAM measurement in the present study with an emphasis on the formation and loss of aerosol mass depending on particle size in a PAM reactor. As you recommended, Table 1 was revised with mass concentrations at the three size ranges for the organic and sulfate dominated episodes.

[Manuscript revision] In Table 1, the average concentrations of ambient and PAM aerosol mass were provided for the three separate size ranges of 10-50 nm, 50-200 nm, and 200-500 nm. Page 7 Line 179: Add the following sentence. The masses according to particle size are summarized for ambient and PAM processed aerosols in Table 1. For the two cases, aerosol masses increased in PAM reactor at nuclei (10-50 nm) and condensation (200-500 nm) mode. At size between 50 and 200 nm, however, the mass of PAM-processed aerosol was not evidently increased during sulfate-dominated episode and even decreased during organic-dominated episode. âĂČ

10. Figure 4: The authors mention PM10 mass measurements (P6, L131) but as far as I can tell do not present the results – please add time series here and discuss briefly in the text.

[Response] At Baegnyeong site, SO2, NO2, CO, O3, and PM10 have been measured by NIER. Unfortunately, the measurement data of PM10 mass are missing and thus, PM10 mass was removed in the revised manuscript as follows.

[Manuscript Revision] Page 6, Line 131: Ozone (O3), elemental carbon (EC), and organic carbon (OC) were simultaneously measured, along with meteorological parameters (Table 1).

11. Figure 5: Why/how is there organic signal at m/z = 32?

[Response] While O2 gives major signal to m/z 32, there is also the contribution from organics (CH4O) to the tail of peak in high resolution AMS. We checked and redefined the shape of all peaks when reprocessing AMS data with new collection efficiency. As a result, Figure 5 was remade.

[Manuscript revision] Figure 5 is replaced with a new one shown below.

12. Figure 6: The authors might consider smoothing some of the size distributions, especially for ammonium and Organics/Org43/Org44 during the sulfate episode. Also,

is there sufficient signal-to-noise to resolve chloride size distributions?

[Response] In Figure 6, the mass distributions of all species were redrawn using a smoothing function in AMS data processing program. As shown in Figure 2b, chloride concentration is too low to be resolved in size distribution. Thus, we did not include the chloride distribution in Figure 6.

[Manuscript revision] Figure 2b is remade with chloride signal, which is shown above. Figure 6 is redrawn, in which size distributions were smoothed.

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The references added to the revised manuscript are as follows.

McGraw and Saunders,: A condensation feedback mechanism for oscillatory nucleation and growth, Aerosol Science and Technology, 3(4), 367-380, 1984.

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The relevant table and figures are included in the file uploaded as a supplement.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2016-1133/acp-2016-1133-AC1-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2016-1133, 2017.